

Bridge mediated two-electron transfer reactions: On the influence of intersite Coulomb interactions

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Donor-acceptor two-electron transfer (TET) mediated by a linear molecular bridge is described theoretically. The particular case is considered where the TET takes place in the presence of a strong electronic intersite coupling within the bridge and against the background of fast vibrational relaxation processes. For such a situation the coarse-grained description of bridge-assisted electron transfer in molecular systems can be utilized [Petrov *et al.*, *J. Phys. Chem. B* **106**, 3092 (2002)]. In the present case it leads to kinetic equations and rate expression for TET reactions. Our recent treatment of completely nonadiabatic TET reactions [Petrov *et al.*, *J. Chem. Phys.* **120**, 4441 (2004)] including a reduction to single-exponential kinetics (with overall transfer rate K_{TET}) is generalized here to the case of strong intrabridge coupling and the presence of intersite Coulomb interactions. The dependence of K_{TET} on the bridge length which is determined by a separate stepwise and concerted contribution is discussed in detail. It is found that the intersite Coulomb interaction favors the TET if the donor and the acceptor are uncharged in their completely reduced states (with two excess electrons present). © 2004 American Institute of Physics. [DOI: 10.1063/1.1780165]

I. INTRODUCTION

Bridge-mediated electron transfer (ET) processes are of basic importance for numerous oxidation-reduction reactions in molecular systems discussed in chemical¹⁻³ or biological research.⁴⁻¹⁰ The most detailed understanding reached so far is related to the mechanisms of ET reactions with the participation of a single electron. For instance, it is a well established fact that single-electron transfer (SET) between donor (D) and acceptor (A) redox centers linked by a molecular bridge (B) takes place via the multistep sequential and the unistep superexchange pathway.¹¹⁻¹⁵ At room temperature, the first pathway is more effective for long bridges, while the second one dominates ET in short bridges. This conclusion is supported by experimental results on SET through proteins^{15,16} and the DNA.^{13,14,17} In the case of a molecular wire the superexchange and the sequential ET mechanisms are responsible for the formation of an interelectrode current (see, for instance, Refs. 9, 18, and 19).

Less is known on the respective mechanisms of bridge-assisted ET if two or more electrons are involved. A first move has been made in our recent theory on distant two-electron transfer (TET).²⁰⁻²³ It generalizes earlier results on D - A TET in polar solvents²⁴⁻²⁶ as well as between active centers of enzymes.²⁷⁻³¹ The generalization concerns a detailed account for the bridge states $|B_m\rangle \equiv |D(e)B_1B_2 \cdots B_m(e) \cdots B_NA\rangle$ and $|\tilde{B}_n\rangle \equiv |DB_1B_2 \cdots B_n(e) \cdots B_NA(e)\rangle$ (note, that “ e ” indicates the position of the excess electrons among the D and the A units as well as among the N different B units). Together with the intermediate state $|I\rangle \equiv |D(e)B_1B_2 \cdots B_NA(e)\rangle$ the bridge states are the prerequisites for the sequential and the

superexchange mechanisms resulting in the formation of the stepwise and the concerted routes of *nonadiabatic* TET. This TET proceeds between the donor state $|D\rangle \equiv |D(2e)B_1B_2 \cdots B_NA\rangle$ and the acceptor state $|A\rangle \equiv |DB_1B_2 \cdots B_NA(2e)\rangle$ both with two excess electrons localized. It could be shown that the stepwise mechanism includes two single-electron transitions, namely, $|D\rangle \rightleftharpoons |B_1\rangle \rightleftharpoons |B_2\rangle \rightleftharpoons \cdots \rightleftharpoons |B_N\rangle \rightleftharpoons |I\rangle$ and $|I\rangle \rightleftharpoons |\tilde{B}_1\rangle \rightleftharpoons |\tilde{B}_2\rangle \rightleftharpoons \cdots \rightleftharpoons |\tilde{B}_N\rangle \rightleftharpoons |A\rangle$. Each transition comprises a multistep single-electron sequential and a unistep single-electron superexchange pathway. Note that these transitions appear at a small intersite electronic coupling, so that just the localized DBA states define the D - A regime of the TET. The concerted mechanism takes place via a specific unistep two-electron superexchange pathway $|D\rangle \rightleftharpoons |A\rangle$, comprising the intermediate states $|B_1\rangle, |B_2\rangle, \dots, |B_N\rangle, |\tilde{B}_1\rangle, |\tilde{B}_2\rangle, \dots, |\tilde{B}_N\rangle$, and $|I\rangle$.

It is the goal of the present studies to consider TET for the case of a strong intersite electronic coupling within the bridge where a description becomes necessary using electronic states which extend over the whole bridge. These extended states are supposed to couple weakly to the D and to the A . Therefore, the ET between the bridge and the $D(A)$ unit is of the nonadiabatic type while the ET along the bridge proceeds as a coherent process. When carrying out numerical calculations we will concentrate on a typical type of reaction where the overall TET time $\tau_{\text{TET}} = K_{\text{TET}}^{-1}$ (K_{TET} denotes the respective overall D - A TET rate) is much larger than $\tau_{\text{rel}}^{(\mu)}$ and $\tau_{\text{rel}}^{(M)}$. Here, the $\tau_{\text{rel}}^{(\mu)}$ determines the vibrational relaxation time within the μ th extended electronic bridge state, and the $\tau_{\text{rel}}^{(M)}$ are the relaxation times within the localized D ,

I , and A states ($M=D,I,A$). Since the inequality

$$\tau_{\text{TET}} \gg \tau_{\text{rel}}^{(M)}, \tau_{\text{rel}}^{(\mu)} \quad (1)$$

holds, the D - A TET process proceeds against the background of fast vibrational relaxation. At the same time, relaxation processes between different extended bridge states may be faster or slower than the D - A TET reaction itself.

Conditions like that given in Eq. (1) have already been used to analyze D - A SET.³² In particular, the bridge-length dependence of the overall transfer rate has been computed. It could be demonstrated that the dependence for the case of extended bridge states completely differs from that where the SET within the bridge takes place between localized states and, thus, is also of the nonadiabatic type. This difference is mainly caused by two mechanisms: the thermal activated coherent ET through the bridge and the complete coherent superexchange ET. Consequently, a similar problem is typical for TET reactions. Here, one has to find out which mechanism becomes responsible for the stepwise and the concerted routes, if the bridge-internal transfer couplings become large. Additionally, one has to clarify the influence of intersite Coulomb interactions on the efficiency of bridge mediated TET.

In order to answer the mentioned questions the paper is organized as follows: In the following section the model used for the description of bridge-mediated TET is introduced and the basic kinetic equations together with respective rate constants are derived. Section III demonstrates the reduction of the multiexponential TET kinetics to a single-exponential D - A TET reaction as well as the derivation of the related overall transfer rate K_{TET} . In Sec. IV results are presented which relate to the formation of stepwise and concerted TET routes if the transitions between the extended bridge states are either fast or slow. The paper ends with some concluding remarks in Sec. V.

II. MODEL AND THEORY

A. Hamiltonian of the DBA system

Let us consider a DBA system with a regular linear bridge of N units. The bridge has the D and A units at its terminal sites $m=1$ and $m=N$, respectively. To remain sufficiently simple we employ a tight binding model where single-electron transitions are described by the transfer couplings between neighboring sites of electron localization. However, in the case of TET the coupling of the $D(A)$ center to the terminal site $m=1(N)$ depends on the number of excess electrons present at the $D(A)$. According to the notation given in introductory part, single-electron transitions $|D\rangle \rightarrow |B_1\rangle$, ($|B_N\rangle \rightarrow |I\rangle$), and $|I\rangle \rightarrow |\tilde{B}_1\rangle$, ($|\tilde{B}_N\rangle \rightarrow |A\rangle$) are defined via the couplings $V_{D1}(V_{AN})$ and $V'_{D1}(V'_{AN})$. Since a regular bridge is considered intrabridge transitions $|B_m\rangle \rightarrow |B_{m\pm 1}\rangle$ and $|\tilde{B}_n\rangle \rightarrow |\tilde{B}_{n\pm 1}\rangle$ can be characterized by the single quantity V_B (for details see Ref. 22 as well as Fig. 1).

To obtain the DBA Hamiltonian H defined by extended bridge states we may follow the scheme already used in Ref. 32 to describe SET processes. In the case of TET, however,

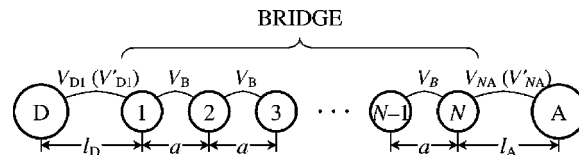


FIG. 1. Linear DBA system with a regular bridge connecting the donor and the acceptor redox centers. The quantities l_D , a , and l_A denote the distances between the different units. (The single-electron couplings V_{D1} , V_{NA} , V'_{D1} , V'_{NA} , and V_B are discussed in the text.)

the complete basis of electronic states has to comprise the localized electronic DBA states $|D\rangle$, $|I\rangle$, $|A\rangle$ as well as the two types of extended DBA states, namely,

$$|\beta_\mu\rangle = \sum_{m=1}^N u_\mu(m) |B_m\rangle, \quad |\tilde{\beta}_\mu\rangle = \sum_{n=1}^N \tilde{u}_\mu(n) |\tilde{B}_n\rangle. \quad (2)$$

Here, the quantities $u_\mu(m)$ and $\tilde{u}_\mu(n)$ are the transformation coefficients from the localized bridge states $|B_m\rangle$ and $|\tilde{B}_n\rangle$ to the extended bridging states $|\beta_\mu\rangle$ and $|\tilde{\beta}_\mu\rangle$, respectively. In what follows we will use the phrase “bridging states” instead of “bridge states” to underline the fact that the TET is mediated by two different types of these states as introduced in Eq. (2).

According to the mentioned transformation the TET DBA Hamiltonian can be separated into four different terms,

$$H = H_e + H_{l-b} + H_{e-v} + H_v. \quad (3)$$

The first part includes all considered electronic states and reads

$$H_e = \sum_M E_M |M\rangle \langle M| + \sum_{\mu=1}^N [\epsilon_\mu |\beta_\mu\rangle \langle \beta_\mu| + \tilde{\epsilon}_\mu |\tilde{\beta}_\mu\rangle \langle \tilde{\beta}_\mu|], \quad (4)$$

with E_M ($M=D,I,A$) and ϵ_μ ($\tilde{\epsilon}_\mu$) denoting the energies of the localized and the extended DBA states $|M\rangle$ and $|\beta_\mu\rangle$ ($|\tilde{\beta}_\mu\rangle$), respectively. (Note that the “tilde” describes those bridging states where already one excess electron is located at A .) The second term of Eq. (3) takes the form

$$H_{l-b} = \sum_{\mu=1}^N [V_{D\mu} |D\rangle \langle \beta_\mu| + V_{A\mu} |I\rangle \langle \beta_\mu| + V'_{D\mu} |I\rangle \langle \tilde{\beta}_\mu| + V'_{A\mu} |A\rangle \langle \tilde{\beta}_\mu| + \text{H.c.}]. \quad (5)$$

This Hamiltonian defines the interaction between the localized and the extended DBA states with the couplings

$$V_{D\mu} = V_{D1} u_\mu(1), \quad V_{\mu A} = V_{NA} u_\mu(N), \\ V'_{D\mu} = V'_{D1} \tilde{u}_\mu(1), \quad V'_{\mu A} = V'_{NA} \tilde{u}_\mu(N). \quad (6)$$

The interaction of the electronic DBA states with the vibrational reservoir (thermal bath) is given by the third term of Eq. (3),

$$\begin{aligned}
H_{e-v} = & -\frac{1}{2} \sum_M \sum_j \hbar \omega_j Q_j^{(M)} Q_j |M\rangle \langle M| \\
& + \sum_{\mu, \mu'=1}^N \sum_j \hbar \omega_j [g_j(\mu, \mu') Q_j |\beta_\mu\rangle \langle \beta_{\mu'}| \\
& + \tilde{g}_j(\mu, \mu') Q_j |\tilde{\beta}_\mu\rangle \langle \tilde{\beta}_{\mu'}|, \quad (7)
\end{aligned}$$

where $\hbar \omega_j Q_j^{(M)} Q_j$ and $\hbar \omega_j g_j(\mu, \mu') Q_j$ [$\hbar \omega_j \tilde{g}_j(\mu, \mu') Q_j$] are the couplings of the localized and extended *DBA* states to the *j*th vibrational mode of frequency ω_j , respectively. The second type of coupling constants read

$$g_j(\mu, \mu') = -\frac{1}{2} \sum_{m=1}^N u_\mu^*(m) u_{\mu'}(m) Q^{(m)}. \quad (8)$$

The $Q_j^{(M)}$ are the dimensionless equilibrium positions related to the *j*th vibrational normal mode Q_j . The expression for $\tilde{g}_j(\mu, \mu')$ is obtained from Eq. (8) by replacing the $u_\mu(m)$ by the $\tilde{u}_\mu(m)$. In Eq. (7) off-diagonal contributions with respect to μ and μ' are responsible for relaxational transitions between different extended bridging states. The fourth term on the right-hand side of Eq. (3), H_v , is the vibrational Hamiltonian.

B. Kinetic equations and rate constants

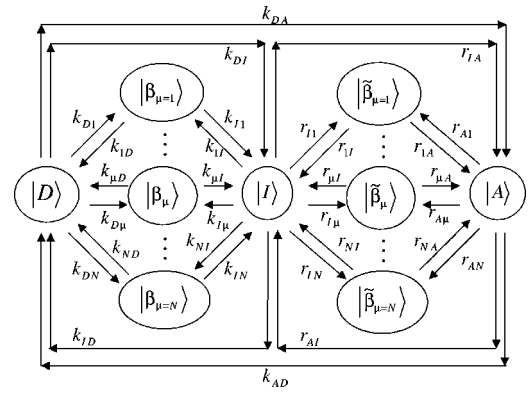
Since fast vibrational relaxation within each electronic state has been assumed [cf. inequality (1)], the vibrational coordinates instantaneously reach an equilibrium state within every step of the TET process. Therefore, concentrating on the time domain $t \gg \tau_{\text{rel}}^{(M)}$, $\tau_{\text{rel}}^{(\mu)}$ we may carry out a coarse-grained description of the TET process. Then, it suffices to only use the total electronic state populations $P_M(t) = \langle M | \text{tr}_{\text{vib}} \rho(t) | M \rangle$ referring to every state $|M\rangle = |D\rangle, |I\rangle, |A\rangle, |\beta_\mu\rangle$, and $|\tilde{\beta}_\mu\rangle$ involved in the TET. It has been explained in detail in our foregoing papers^{11,21,22,32} how to derive from the generalized master equation for the density operator $\rho(t)$ kinetics equations for the level populations $P_M(t)$. When compared with the procedure applied to SET the derivation of the TET kinetic equations has to account for the presence of two types of extended bridging states, $|\beta_\mu\rangle$ and $|\tilde{\beta}_\mu\rangle$, as well as for the presence of the intermediate state $|I\rangle$. Otherwise, the calculations are identical with those in Refs. 22 and 32. We omit any details of the derivation and present the basic set of kinetic equations ($M, M' = D, I, A, \beta_\mu, \tilde{\beta}_\mu$):

$$\dot{P}_M(t) = -q_M P_M(t) + \sum_{M' \neq M} q_{M'M} P_{M'}(t). \quad (9)$$

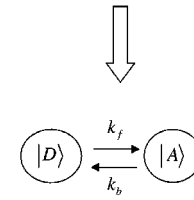
Here, the $q_M = \sum_{M' \neq M} q_{MM'}$ are the escape rates related to the states $|M\rangle$ while the

$$q_{MM'} = \frac{2\pi}{\hbar} |T_{MM'}|^2 (\text{FC})_{MM'} \quad (10)$$

are the rate constants characterizing the transition from the *M*th to the *M'*th electronic *DBA* state. The rate constants read in detail ($\mu, \mu' = 1, 2, \dots, N$)



(a) Multi-exponential kinetics



(b) Single-exponential kinetics

FIG. 2. Kinetic scheme of the TET reaction with the participation of extended bridging states $|\beta_\mu\rangle$ and $|\tilde{\beta}_\mu\rangle$ (a). For a small population of the bridging states as well as of the intermediate state the kinetics is reduced to the transition between the localized *D* state, $|D\rangle$, and the localized *A* state, $|A\rangle$ (b).

$$\begin{aligned}
q_{\beta_\mu \beta_{\mu'}} & \equiv k_{\mu\mu'}, & q_{\beta_{\mu'} \beta_\mu} & = k_{\mu\mu'} e^{-(\epsilon_\mu - \epsilon_{\mu'})/k_B T}, \\
q_{\tilde{\beta}_\mu \tilde{\beta}_{\mu'}} & \equiv r_{\mu\mu'}, & q_{\tilde{\beta}_{\mu'} \tilde{\beta}_\mu} & = r_{\mu\mu'} e^{-(\tilde{\epsilon}_\mu - \tilde{\epsilon}_{\mu'})/k_B T}, \\
q_{MM'} & \equiv k_{MM'}, & q_{M'M} & = k_{MM'} e^{-(E_M - E_{M'})/k_B T}, \\
q_{\beta_\mu M} & \equiv k_{\mu M}, & q_{M \beta_\mu} & = k_{\mu M} e^{-(\epsilon_\mu - E_M)/k_B T}, \\
q_{\tilde{\beta}_\mu M} & \equiv r_{\mu M}, & q_{M \tilde{\beta}_\mu} & = r_{\mu M} e^{-(\tilde{\epsilon}_\mu - E_M)/k_B T}.
\end{aligned} \quad (11)$$

The given set completely determines the kinetics of the TET process in the *DBA* system.

There are two types of rate constants. One defines charge transfer between the *DBA* states [cf. the scheme (a) of Fig. 2]. The other type, $k_{\mu\mu'}$ and $r_{\mu\mu'}$ (not contained in Fig. 2) is responsible for relaxation processes among the extended bridging states. As discussed below the population distribution in the bridge states caused by these processes forms specific channels for thermally activated TET. Since we will only consider the limiting cases of fast and slow relaxations among extended bridging states, there is no need to further specify the $k_{\mu\mu'}$ and the $r_{\mu\mu'}$ (cf. the discussion in Ref. 32).

As shown in Eq. (10) each rate constant is defined by two factors, the square of the coupling between the actual electronic states, $|T_{MM'}|^2$, and the Franck-Condon factor $(\text{FC})_{MM'}$. For the transitions between the localized and the extended *DBA* states the electronic couplings are given by $T_{D\mu} = V_{D\mu}$, $T_{I\mu} = V_{A\mu}$ and $\tilde{T}_{I\mu} = V'_{D\mu}$, $\tilde{T}_{A\mu} = V'_{A\mu}$. Superexchange coupling is described by the following expressions:

$$|T_{DI}|^2 = \frac{|V_{D1}V_{AN}|^2|V_B|^{2(N-1)}}{\prod_{\mu=1}^N(\epsilon_{\mu}-E_D)(\epsilon_{\mu}-E_I)}, \quad (12)$$

$$|T_{IA}|^2 = \frac{|V'_{D1}V'_{AN}|^2|V_B|^{2(N-1)}}{\prod_{\mu=1}^N(\tilde{\epsilon}_{\mu}-E_I)(\tilde{\epsilon}_{\mu}-E_A)}, \quad (13)$$

and (note $\Delta E_{ID}=E_I-E_D$, $\Delta E_{IA}=E_I-E_A$)

$$|T_{DA}|^2 = \frac{|V_{D1}V_{AN}V'_{D1}V'_{AN}|^2}{\Delta E_{ID}\Delta E_{IA}} \times \frac{|V_B|^{4(N-1)}}{\prod_{\mu=1}^N(\epsilon_{\mu}-E_D)(\epsilon_{\mu}-E_A)(\tilde{\epsilon}_{\mu}-E_D)(\tilde{\epsilon}_{\mu}-E_A)}. \quad (14)$$

The first two equations define the superexchange single-electron couplings between pairs of respective localized *DBA* states $|D\rangle$, $|I\rangle$, and $|A\rangle$ while the latter equation specifies the superexchange two-electron coupling between the $|D\rangle$ and $|A\rangle$ states.

Concrete expressions for the Franck-Condon factors strongly depend on the spectral properties of the vibrational reservoir.³³⁻³⁵ For our numerical computations we shall utilize the well-known Jortner expression^{8,36} which works in a wide temperature region to zero temperature and which reads

$$\begin{aligned} (\text{FC})_{MM'} &= \frac{1}{\hbar\omega_{MM'}} \exp[-S_{MN} \coth(\hbar\omega_{MM'}/2k_B T)] \\ &\times \{ [1+n(\omega_{MM'})]/n(\omega_{MM'}) \}^{\nu_{MM'}/2} \\ &\times I_{|\nu_{MM'}|} \{ 2S_{MM'} \sqrt{n(\omega_{MM'})[1+n(\omega_{MM'})]} \}. \end{aligned} \quad (15)$$

Here, we introduced $\nu_{MM'} \equiv \Delta E_{MM'}/\hbar\omega_{MM'}$. Note the correspondence $\Delta E_{MM'}=E_M-E_{M'}$ for $M, M'=D, I, A$ as well as $\Delta E_{\mu D(I)}=\epsilon_{\mu}-E_{D(I)}$ and $\Delta E_{\mu A}=\tilde{\epsilon}_{\mu}-E_A$, $S_{MM'} \equiv \lambda_{MM'}/\hbar\omega_{MM'}$ ($\lambda_{MM'}$ is the reorganization energy of the $M \rightarrow M'$ electron transfer reaction). Furthermore, $n(\omega) = [\exp(\hbar\omega/k_B T) - 1]^{-1}$ denotes the Bose distribution and $I_{\nu}(z)$ stands for the modified Bessel function.

III. D-A REGIME OF TET

As already explained in Refs. 15 and 32 for SET and in Refs. 22 and 23 for TET the multiexponential kinetics of bridge-mediated charge transfer is reduced to single-exponential *D-A* kinetics (with a single overall transfer rate), if and only if the population of the bridging *DBA* states and, additionally, of the intermediate state $|I\rangle$ in the case of TET becomes less than 10^{-2} . Such a small population offers a simple way to derive the overall transfer rate by using the steady-state approximation.²³ By the way, this approximation has been used earlier for the derivation of the overall transfer rate in the case of a direct *D-A* TET where in contrast to bridge-mediated TET only the state $|D(e)A(e)\rangle$ mediates the TET reaction.²⁴

In the present case the energy of the intermediate state, E_I , is positioned above the energies of the donor and acceptor states, E_D and E_A , respectively. Therefore, a small population of the state $|I\rangle$ occurs if

$$\exp[-(E_{D(A)}-E_I)/k_B T] \ll 1, \quad (16)$$

while a small population of the bridging states $|\beta_{\mu}\rangle$ and $|\tilde{\beta}_{\mu}\rangle$ is present if

$$\begin{aligned} \exp[-(\epsilon_{\mu}-E_{D(A)})/k_B T] &\ll 1, \\ \exp[-(\tilde{\epsilon}_{\mu}-E_{D(A)})/k_B T] &\ll 1. \end{aligned} \quad (17)$$

Keeping in mind these inequalities we can set $\dot{P}_M(t)=0$ in Eq. (9) for all $M=I, \beta_{\mu}, \tilde{\beta}_{\mu}$ ($\mu=1, 2, \dots, N$). It brings us to the solution

$$\begin{aligned} P_D(t) &\approx k_b/K_{\text{TET}} + (k_f/K_{\text{TET}})e^{-K_{\text{TET}}t}, \\ P_A(t) &\approx (k_f/K_{\text{TET}})(1 - e^{-K_{\text{TET}}t}), \\ P_I(t) &\approx 0, \quad P_{\beta_{\mu}}(t) \approx 0, \quad P_{\tilde{\beta}_{\mu}}(t) \approx 0, \end{aligned} \quad (18)$$

which shows that on the coarse-grained time scale the TET process represents a *D-A* TET reaction with a single overall transfer rate

$$K_{\text{TET}} = k_f + k_b. \quad (19)$$

The forward (k_f) and the backward (k_b) components of the rate describe direct transitions between the *D* and the *A* units [cf. scheme (b) of Fig. 2]. Each component is determined by a contribution following from stepwise and concerted TET:

$$k_{f(b)} = k_{f(b)}^{(\text{step})} + k_{f(b)}^{(\text{conc})}, \quad (20)$$

where

$$\begin{aligned} k_f^{(\text{step})} &= \frac{K_{DI}K_{IA}}{K_{ID}+K_{IA}}, \quad k_f^{(\text{conc})} = k_{DA}, \\ k_b^{(\text{step})} &= \frac{K_{AI}K_{ID}}{K_{ID}+K_{IA}}, \quad k_b^{(\text{conc})} = k_{AD}. \end{aligned} \quad (21)$$

While the concerted contribution is determined by a *two-electron* unistep superexchange transition between the *D* and the *A* units [cf. Eqs. (10), (11), and (14)] the stepwise contribution includes two *single-electron* transitions between the same centers, each with its own transfer rate. For instance, in the case of the forward reaction, the first transition $|D\rangle \rightarrow |I\rangle$ and the second one $|I\rangle \rightarrow |A\rangle$ are characterized by the transfer rates K_{DI} and K_{IA} , respectively. These SET rates (as well as the backward rates) read in more detail

$$\begin{aligned} K_{DI(IA)} &= k_{DI(IA)} + k_{DI(IA)}^{(\text{act})}, \\ K_{AI(ID)} &= k_{AI(ID)} + k_{AI(ID)}^{(\text{act})}. \end{aligned} \quad (22)$$

The expressions indicate that the rates are given as the sum of a single-electron superexchange contribution [cf. Eqs. (10)–(13)] and a thermal activated contribution. The latter quantity strongly depends on the relation between the rate constants $k_{\mu M}$ ($r_{\mu M}$) responsible for the ET and the rate constants $k_{\mu\mu'}$ ($r_{\mu\mu'}$) describing relaxation among the bridging states $|\beta_{\mu}\rangle$ and $|\beta_{\mu'}\rangle$. For the sake of clarity we will consider TET for the case where the characteristic time of intrabridge relaxation, τ_B , is much smaller or much larger than τ_{TET} . For both cases, it is possible to derive an expression for the thermal activated rate without noting the concrete form of $k_{\mu\mu'}$ and $r_{\mu\mu'}$.

Slow intrabridge relaxation, $\tau_B \gg \tau_{\text{TET}}$. In such a case the transfer rates $k_{\mu\mu'}$ and $r_{\mu\mu'}$ can be ignored within the basic kinetic equations, Eq. (9). Noting the small minor population of the bridging states as well as of the intermediate state the solution, Eqs. (18) and (19)–(21), is obtained, where the thermal activated components of the effective transfer rates (22) take the following form:

$$\begin{aligned} k_{DI(ID)}^{(act)} &= \sum_{\mu=1}^N \frac{k_{D(I)\mu} k_{\mu I(D)}}{k_{\mu D} + k_{\mu I}}, \\ k_{IA(AI)}^{(act)} &= \sum_{\mu=1}^N \frac{r_{I(A)\mu} r_{\mu A(I)}}{r_{\mu A} + r_{\mu I}}. \end{aligned} \quad (23)$$

Fast intrabridge relaxation, $\tau_B \ll \tau_{\text{TET}}$. A similar case has already been studied for D - A SET transfer in Ref. 32, and we will proceed here in the same way. Since fast relaxation among the extended bridging states has been assumed a (quasi)equilibrium of the populations $P_{\beta_\mu}(t)$ [$P_{\tilde{\beta}_\mu}(t)$] is achieved at every step of the TET reaction so that

$$P_{\beta_\mu}(t) = W_B(\epsilon_\mu) P_B(t), \quad P_{\tilde{\beta}_\mu}(t) = W_B(\tilde{\epsilon}_\mu) \tilde{P}_B(t), \quad (24)$$

where $P_B(t) = \sum_{\mu} P_{\beta_\mu}(t)$ and $\tilde{P}_B(t) = \sum_{\mu} P_{\tilde{\beta}_\mu}(t)$ are the integral populations of the extended electronic states. Moreover, we introduced the statistical weights of the extended bridging states,

$$W_B(\epsilon_\mu) = Z_B^{-1} e^{-\epsilon_\mu/k_B T} \left(Z_B = \sum_{\mu=1}^N e^{-\epsilon_\mu/k_B T} \right), \quad (25)$$

and

$$W_B(\tilde{\epsilon}_\mu) = \tilde{Z}_B^{-1} e^{-\tilde{\epsilon}_\mu/k_B T} \left(\tilde{Z}_B = \sum_{\mu=1}^N e^{-\tilde{\epsilon}_\mu/k_B T} \right). \quad (26)$$

Using the Eqs. (24) we obtain

$$\begin{aligned} k_{DI(IA)}^{(act)} &= \frac{K_{D(I)B} K_{BI(D)}}{K_{BD} + K_{BI}}, \\ k_{IA(AI)}^{(act)} &= \frac{\tilde{K}_{I(A)B} \tilde{K}_{BA(I)}}{\tilde{K}_{BA} + \tilde{K}_{BI}}, \end{aligned} \quad (27)$$

where the transfer rates

$$\begin{aligned} K_{D(I)B} &= \sum_{\mu=1}^N k_{D(I)\mu}, \quad K_{BD(I)} = \sum_{\mu=1}^N W_B(\epsilon_\mu) k_{\mu D(I)}, \\ \tilde{K}_{I(A)B} &= \sum_{\mu=1}^N r_{I(A)\mu}, \quad \tilde{K}_{BI(A)} = \sum_{\mu=1}^N W_B(\tilde{\epsilon}_\mu) r_{\mu I(A)} \end{aligned} \quad (28)$$

describe transitions between the localized DBA states and the extended bridging DBA states.

IV. RESULTS AND DISCUSSION

The expressions (19)–(28) determining the overall D - A TET rate K_{TET} have to be considered as the main result of the present paper. K_{TET} is given by two contributions originated by the stepwise TET as well as by the unistep concerted TET. To demonstrate the importance of both contribu-

tions for the overall D - A TET we will consider TET through a regular bridge. If not any additional interaction between the bridge units except the off-diagonal site-site interaction $V_{mm\pm 1} \equiv V_B$ is present, the energies of the extended bridging states, Eq. (2), are given by

$$\begin{aligned} \epsilon_\mu^{(reg)} &= E_B - 2|V_B| \cos \left[\frac{\pi\mu}{N+1} \right], \\ \tilde{\epsilon}_\mu^{(reg)} &= \tilde{E}_B - 2|V_B| \cos \left[\frac{\pi\mu}{N+1} \right], \end{aligned} \quad (29)$$

where $E_B \equiv E_1 = E_2 = \dots = E_N$ and $\tilde{E}_B \equiv \tilde{E}_1 = \tilde{E}_2 = \dots = \tilde{E}_N$ denote the identical energies of the localized bridging states in the DBA system with a regular bridge. However, resulting from the Coulomb interaction between sites of electron localization the actual energies ϵ_μ and $\tilde{\epsilon}_\mu$ differ from those given in Eq. (29) and have to be calculated numerically.

Next, let us consider the bridge-length dependence of K_{TET} . It can be derived analytically if the energetic shifts ΔE_m and $\Delta \tilde{E}_m$ caused by the mentioned Coulomb interaction do not strongly alternate the reference site energies E_B and \tilde{E}_B . Such a shift may appear, for example, if the bridge and the surrounding medium are both consist of nonpolar units while the D and the A redox centers are screened by polar groups (for more details see Refs. 21–23). In the zero-order approximation with respect to the intersite Coulomb interaction (i.e., for $E_m \approx E_B$) the energies ϵ_μ of the extended bridging states $|\beta_\mu\rangle$ are given by Eqs. (29). Let $t_{\mu\mu'} = \sum_m u_\mu^{(reg)}(m) u_{\mu'}^{(reg)}(m) \Delta E_m$ be the off-diagonal contribution caused by the energetic irregularity. If the inequality

$$|t_{\mu\mu'}| \ll |\epsilon_\mu^{(reg)} - \epsilon_{\mu'}^{(reg)}| \quad (30)$$

is will satisfied for each $\mu' \neq \mu$ then in the first approximation with respect to the energetic perturbation one derives

$$\epsilon_\mu \approx \epsilon_\mu^{(reg)} + \Delta \epsilon_\mu \left(\Delta \epsilon_\mu = \sum_m [u_\mu^{(reg)}(m)]^2 \Delta E_m \right), \quad (31)$$

where the transformation coefficients referring to a regular bridge

$$u_\mu^{(reg)}(m) = \tilde{u}_\mu^{(reg)}(m) = \sqrt{\frac{2}{N+1}} \sin \left[\frac{\pi\mu m}{N+1} \right] \quad (32)$$

are real quantities. Substituting Eqs. (31) and (32) into Eqs. (12) and (13) we obtain the corrections of the superexchange couplings originated by the intrasite Coulomb interaction [see the Appendix, Eqs. (A7)–(A12)]. This allows us to denote the single-electron superexchange transfer rates, Eq. (10), as

$$k_{ID(IA)} = k_{ID(IA)}^{(0)} e^{-\alpha_{ID(IA)}(N-1)} e^{\Theta_{ID(IA)}(N)}. \quad (33)$$

The quantities

$$k_{ID}^{(0)} = \frac{2\pi}{\hbar} \frac{|V_{D1} V_{AN}|^2}{\Delta \mathcal{E}_I \Delta \mathcal{E}_D} (\text{FC})_{ID} \quad (34)$$

and

$$k_{IA}^{(0)} = \frac{2\pi}{\hbar} \frac{|V'_{D1} V'_{AN}|^2}{\Delta \tilde{\mathcal{E}}_I \Delta \tilde{\mathcal{E}}_A} (\text{FC})_{IA} \quad (35)$$

can be interpreted as rates of a *DBA* system with a single unit in the bridge (note the definitions $\Delta \mathcal{E}_M/|V_B| \equiv (E_B - E_M)/2|V_B| + \sqrt{[(E_B - E_M)/2|V_B|]^2 - 1}$ and $\Delta \tilde{\mathcal{E}}_M/|V_B| \equiv (\tilde{E}_B - E_M)/2|V_B| + \sqrt{[(\tilde{E}_B - E_M)/2|V_B|]^2 - 1}$). Analogously, by using the Eqs. (10), (14) and (A7), (A10) (A12) we may derive the expression for the two-electron superexchange transfer rate:

$$k_{DA} = k_{DA}^{(0)} e^{-\alpha_{DA}(N-1)} e^{\Theta_{DA}(N)}, \quad (36)$$

$$k_{DA}^{(0)} = \frac{2\pi}{\hbar} \frac{|V_{D1} V_{AN} V'_{D1} V'_{AN}|^2}{\Delta \mathcal{E}_D \Delta \mathcal{E}_A \Delta \tilde{\mathcal{E}}_D \Delta \tilde{\mathcal{E}}_A \Delta E_{ID} \Delta E_{IA}} (\text{FC})_{DA}. \quad (37)$$

The dominant dependence of the rates, Eqs. (33) and (36), on the number of bridge units *N* is given by the first exponential function including the decay parameters

$$\alpha_{ID} = \Lambda(E_I) + \Lambda(E_D), \quad \alpha_{IA} = \tilde{\Lambda}(E_I) + \tilde{\Lambda}(E_A), \quad (38)$$

and

$$\alpha_{DA} = \Lambda(E_D) + \Lambda(E_A) + \tilde{\Lambda}(E_D) + \tilde{\Lambda}(E_A). \quad (39)$$

These parameters determine the decrease of the respective single- and two-electron superexchange transition rates in a regular bridge. Corrections following from the intersite Coulomb interaction are located in the Franck-Condon factors (FC)_{ID} and (FC)_{IA} (via the driving forces $\Delta E_{ID} = E_I - E_D$ and $\Delta E_{IA} = E_I - E_A$). However, a more pronounced influence enters via the second exponential functions in the rates, Eqs. (33) and (36) [the respective exponents $\Theta_{ID}(N)$, $\Theta_{IA}(N)$, and $\Theta_{DA}(N)$ can be found in the Appendix, Eqs. (A11) and (A12)].

To illustrate the relations derived so far we will discuss in the following a self-exchange TET oxidation-reduction reaction. For such a reaction, the *D* and the *A* redox-centers are identical and, consequently, $K_{ID} = K_{IA}$, $K_{DI} = K_{AI} = \exp(-\Delta E_{ID}/k_B T) K_{ID}$, $k_{DA} = k_{AD}$. Using the Eqs. (19)–(22) we obtain

$$K_{\text{TET}} = e^{-\Delta E_{ID}/k_B T} K_{ID} + 2k_{DA}. \quad (40)$$

The first term on the right-hand side defines the thermally activated stepwise process whereas the second term is responsible for concerted TET. In turn, along with a single-electron superexchange term the transfer rate K_{ID} , Eq. (22), contains an additional activation term, so that the stepwise TET route includes two types of thermal activation. One type is related to the population of the intermediate state (with gap ΔE_{ID}) and the other to the population of the bridging states $|\beta_\mu\rangle$ (and $|\tilde{\beta}_\mu\rangle$).

Note that the concrete expression for the single-electron transfer rate K_{ID} strongly depends on the relaxation (fast or slow) among the extended bridging states [cf. Eqs. (23) and (27)]. However, there exists an important type of thermal activated TET where the concrete relation between the char-

acteristic times τ_B and τ_{TET} is of minor importance. Such a type is met if the intrabridge coupling $|V_B|$ exceeds the thermal energy $k_B T$ so that inequality

$$e^{-(\epsilon_2 - \epsilon_1)/k_B T} = e^{-(\tilde{\epsilon}_2 - \tilde{\epsilon}_1)/k_B T} \ll 1 \quad (41)$$

is satisfied during the *D-A* TET process. [At room temperature, the validity of condition (41) is already guaranteed at $|V_B| > 0.1$ eV.] Condition (41) indicates that only the lowest lying extended bridging states $|\beta_1\rangle$ and $|\tilde{\beta}_1\rangle$ give the main contribution to the stepwise TET rate. Keeping in mind this fact it is possible to represent K_{TET} , Eq. (40), as the sum of three terms,

$$K_{\text{TET}} = k^{(ba)} + k^{(as)} + 2k_{DA}. \quad (42)$$

The first term,

$$k^{(ba)} = e^{-(\epsilon_1 - E_D)/k_B T} \frac{k_{1I} k_{1D}}{k_{1I} + k_{1D}}, \quad (43)$$

corresponds to activated SET through the extended bridging states $|\beta_1\rangle$ and $|\tilde{\beta}_1\rangle$. The second term in Eq. (42),

$$k^{(as)} = k_{DI} = e^{-\Delta E_{ID}/k_B T} k_{ID}, \quad (44)$$

follows from an additional type of a thermal activated *D-A* TET. It takes place through the intermediate state $|I\rangle$ and includes a unistep superexchange single-electron *D-A* hopping with the participation of virtual bridge states $\{|\beta_\mu\rangle\}$. The third term, $2k_{DA}$, is associated with a unistep two-electron superexchange hopping between the same centers. Note that because the gap $\epsilon_1 - E_D$ exceeds the gap ΔE_{ID} then at low temperature a superexchange component $k^{(as)}$ of the stepwise transfer rate $K^{(step)} = k^{(ba)} + k^{(as)}$ becomes more effective than its pure activation component $k^{(ba)}$. In turn, the concerted transfer rate k_{DA} is not disappeared even at zero temperature and thus at low temperature it can exceed even the $k^{(ba)}$.

To study bridge-length dependence of K_{TET} at different value of intersite Coulomb interaction we have to introduce into Eq. (42) concrete expressions for all transfer rates. The superexchange transfer rates are given by the Eqs. (33) and (36) at $V_{1D} = V'_{NA}$ and $V'_{1D} = V_{NA}$. Moreover, in line with the general definition (10) we have

$$k_{1D} = \frac{2\pi}{\hbar} |V_{1D}|^2 [u_1^{(reg)}(1)]^2 (\text{FC})_{1D}, \quad (45)$$

$$k_{1I} = \frac{2\pi}{\hbar} |V_{NA}|^2 [u_1^{(reg)}(N)]^2 (\text{FC})_{1I}.$$

(Noting the weak perturbation of the bridge levels we use the $[u_\mu^{(reg)}(m)]^2$ instead of the exact quantities $u_\mu^2(m)$.) In all expressions for the rate constants the Franck-Condon factors are assumed to be given by Eq. (15). The intersite Coulomb interaction enters the rate constants via the energy gaps $\Delta E_{MM'} = E_M - E_{M'} = (E_M^{(0)} - E_{M'}^{(0)}) + (\Delta E_M - \Delta E_{M'})$ and $\epsilon_\mu - E_M = (\epsilon_\mu^{(reg)} - E_M^{(0)}) + \Delta \epsilon_{\mu M}$ where ΔE_M ($M = D, I, A, B_m, \tilde{B}_n$) is the shift of $E_M^{(0)}$ caused by the intersite Coulomb interaction. To have a concrete expressions for $\Delta \epsilon_{\mu M}$ we use the expressions for $\Delta E_M = \epsilon_M^{(Coul)}$ derived earlier in Ref. 23 to obtain the perturbation of the localized

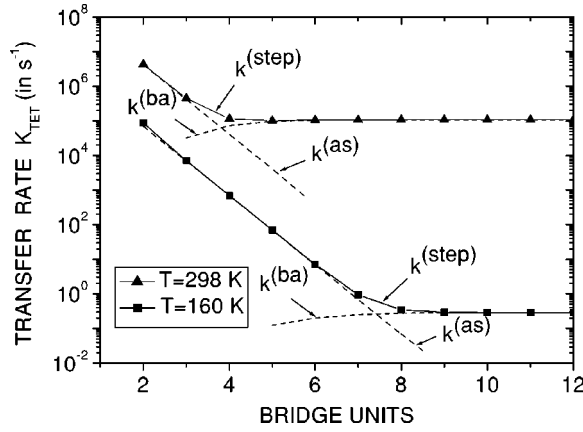


FIG. 3. Bridge-length dependence of the overall D - A TET rate $K_{\text{TET}} = K^{(\text{step})} + K^{(\text{conc})}$ at two different temperatures. The main contribution follows from the stepwise mechanism which includes $k^{(ba)}$ following from a thermal activated ET and $k^{(as)}$ originated by a thermal activated single-electron superexchange mechanism (both are shown by dashed lines). All curves are calculated for a self-exchange TET reaction in using the parameters $\Delta E_D = 0.75$ eV, $\Delta E_I = \Delta \tilde{E}_I = 0.65$ eV, $\Delta E_{DA} = 0$, $\lambda_{D1} = \lambda_{M1} = \lambda_{I1} = \lambda_{NA} = 0.6$ eV, $\lambda_{D1} = \lambda_{IA} = 0.7$ eV, $\omega_0 = 600$ cm^{-1} , $U = 0$, $V_{D1} = V_{NA} = V_{D1} = V_{NA}' = 0.04$ eV, $V_B = 0.20$ eV.

DBA states. For the self-exchange D - A TET reaction under consideration and for the case where the identical D and A units are displaced from the respective terminal bridge units by the distances $l_D = l_A = a$ (cf. Fig. 1) we may derive [compare Eqs. (A13)–(A15) of Ref. 23]

$$\Delta E_D = \Delta E_A = 0, \quad \Delta E_I = U/(N+1), \quad (46)$$

$$\Delta E_m = 2U/(N+1) - U/m - 2U/[N - (m-1)], \quad (47)$$

$$\Delta \tilde{E}_n = 2U/(N+1) - 2U/n - U/[N - (n-1)]. \quad (48)$$

The quantity $U = q_1^2/4\pi\epsilon a > 0$ gives the intersite Coulomb interaction with charges $q_1 \equiv q[D(e)] = q[A(e)] = -q[B_m(e)] > 0$ separated by a distance a and positioned in a medium with permittivity ϵ .

Let us first discuss the rates $K^{(\text{step})} = k^{(ba)} + k^{(as)}$ and $K^{(\text{conc})} = 2k_{DA}$ for a DBA system with a regular bridge and in the absence of the intersite Coulomb interaction. Figure 3 shows the relative contribution of two thermal activated components of the stepwise transfer rate $K^{(\text{step})}$. (Here and below we consider a bridge with $N \geq 2$ units where the ET across the bridge is also involved in the formation of TET.) It is clearly seen that the thermal activated superexchange component $k^{(as)}$ dominates at low temperatures. At room temperature and for a short bridges with $N = 2, 3$ units it is larger than the thermal activated component $k^{(ba)}$. It becomes comparable with $k^{(ba)}$ if $N = 4$ and can be ignored if $N > 4$. At $T = 160$ K, a thermal activated single-electron superexchange mechanism gives the main contribution for longer bridges with $N = 2 - 6$ units. This behavior follows from the fact that energy gap

$$\epsilon_1 - E_D = \epsilon_1^{(\text{reg})} - E_D^{(0)} = E_B - E_D^{(0)} - 2|V_B| \cos \pi/(N+1) \quad (49)$$

exceeds the gap ΔE_{ID} . Since the energy gap $\epsilon_1^{(\text{reg})} - E_D^{(0)}$ reduces to $E_B - E_D^{(0)} - 2|V_B|$ if the bridge length increases, at the fixed temperature one finds an increase of $k^{(ba)}$ if the

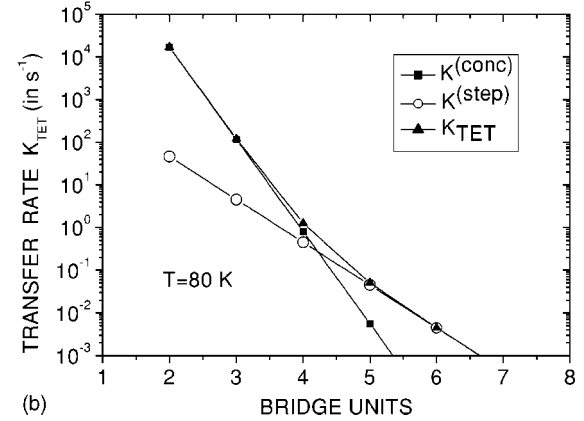
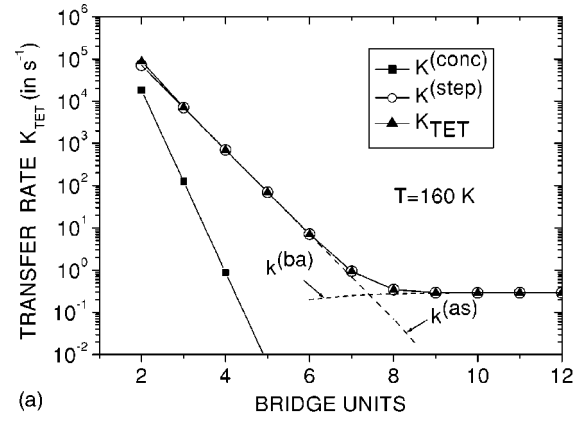


FIG. 4. Bridge-length dependence of the overall D - A TET rate $K_{\text{TET}} = K^{(\text{step})} + K^{(\text{conc})}$ at low temperatures. (a) the rate $K^{(\text{step})}$ exceeds $K^{(\text{conc})}$; (b) the concerted TET route dominates the overall rate ($N = 2, 3$), it is comparable to the stepwise route ($N = 4$) and it becomes unimportant ($N > 4$) (the calculations have been done with the same parameters as in Fig. 3).

bridge length increases. In contrast, the thermal activated single-electron superexchange rate $k^{(as)}$ decreases exponentially with increasing N . As far as $K^{(\text{conc})} = 2k_{DA}$ is completely determined by the pure superexchange (two-electron) mechanism, its relative contribution to K_{TET} increases if temperature decreases (at $T = 0$ K, K_{TET} is completely determined by the concerted rate). It can be seen from Fig. 4 that at low temperatures the bridge-length dependence of the overall D - A TET is determined by a competition between the thermal activated superexchange component of $K^{(\text{step})}$ and the rate $K^{(\text{conc})}$ originated by concerted TET. At $T = 160$ K, the stepwise TET route remains efficient at any bridge length [Fig. 4(a)] while at $T = 80$ K [Fig. 4(b)] the concerted route is more important for a short bridge with $N = 2, 3$ units. If $N = 4$ the stepwise and concerted rates approximately coincide. But at $N \geq 5$ the stepwise route starts to dominate.

The intersite Coulomb interaction influences the D - A TET reaction via an alteration of the energy gaps $\Delta E_{MM'}$ and $\epsilon_\mu - E_M$. For a self-exchange reaction, these gaps read [cf. Eqs. (46)–(48) and (A3)]

$$\Delta E_{ID} = \Delta E_{IA} = \Delta E_{ID}^{(0)} + U/(N+1), \quad \Delta E_{DA} = \Delta E_{DA}^{(0)}, \quad (50)$$

$$\Delta \epsilon_{\mu D(A)} = \Delta \tilde{\epsilon}_{\mu D(A)} = [2U/(N+1)][1 - 3f_\mu(N)], \quad (51)$$

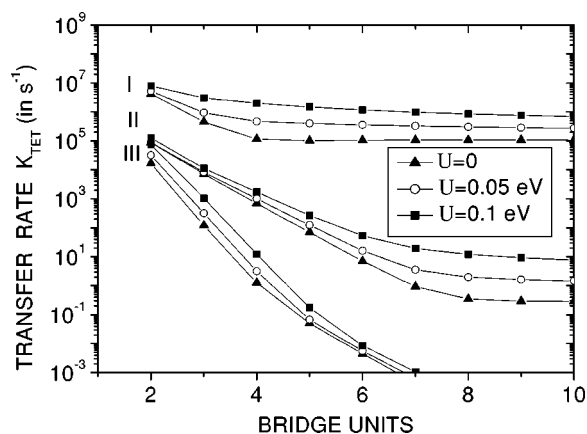


FIG. 5. Enhancement of the efficiency of the D - A TET reaction caused by the presence of intersite Coulomb interactions (the case $T=298$ K, 160 K, and 80 K corresponds to the curves I, II, and III, respectively; the calculations have been done with the same parameters as in Fig. 3).

$$\Delta \epsilon_{\mu I} = \Delta \tilde{\epsilon}_{\mu I} = [U/(N+1)][1 - 6f_{\mu}(N)], \quad (52)$$

where we have introduced the function

$$f_{\mu}(N) = \sum_{m=1}^N \frac{1}{m} \sin^2 \frac{m\mu}{N+1}. \quad (53)$$

A detailed inspection of the given formulas shows that independently of the number of bridge units N the shift $\Delta \epsilon_{\mu M}$ ($M=D, I, A$) due to the Coulomb interaction is negative. Accordingly, all energy gaps $\epsilon_{\mu} - E_M$ between the extended bridging states and the localized states are reduced, which can be also seen in Fig. 5. Actually, at room temperature where the stepwise rate dominates the D - A TET, the rate K_{TET} is determined by two thermal activated single-electron components, namely, $k^{(ba)}$ and $k^{(as)}$. The thermal activated rate $k^{(ba)}$ dominates at $N > 4$. At each particular value of U its behavior completely follows Eq. (43) where the energy gap, Eq. (49), now reads

$$\epsilon_1 - E_D = \epsilon_1^{(reg)} - E_D^{(0)} + \Delta \epsilon_{1D}. \quad (54)$$

The thermal activated superexchange rate $k^{(as)}$ includes the intersite Coulomb interaction by two different factors. One defines the thermal activation across the energy gap ΔE_{ID} [cf. Eqs. (44) and (50)], while the other factor Θ_{ID} introduces the correction to the single-electron superexchange coupling [cf. Eqs. (33), (44), and (A11)]. The complex competition between both mechanisms let $k^{(as)}$ increase with increasing U at each fixed N . As a result, the decrease of the rate with increasing N is slowed down, which is clearly seen for both temperatures, $T=298$ K, and $T=160$ K. [Note that at $T=160$ K, $k^{(as)}$ exceeds $k^{(ba)}$ up to $N=6$, while at $T=296$ K this is only the case up to $N=3$. To realize this see also Fig. 4(a).] At a given set of parameters and at a low temperature of about 100 K, the concerted mechanism of D - A TET starts to exceed the stepwise one (for short bridges with $N=2-4$ units). The corresponding rate k_{DA} includes the effect of the intersite Coulomb interaction only via the quantity Θ_{DA} which is responsible for the change of the two-electron superexchange coupling [cf. Eqs. (36) and (A12)]. Θ_{DA} is negative at any N and thus the Coulomb

interaction leads to a weaker decrease of $K^{(conc)} = 2k_{DA}$. It follows from Fig. 5 that at $T=80$ K the rate $K^{(conc)}$ exceeds $K^{(step)} \approx k^{(as)}$ for a bridge with $N < 5$ units [compare also with Fig. 4(b)].

V. CONCLUSION

The present paper focuses on TET reactions in donor-bridge-acceptor (DBA) systems which are characterized by extended bridging states. It has been demonstrated that the complex multiexponential kinetics of the TET process in a DBA system can be reduced to a much more simpler D - A TET, described by a single overall transfer rate K_{TET} . This rate contains a contribution from the *stepwise* and from the *concerted* transfer mechanism [cf. Eqs. (19) and (20)]. The whole description is based on the fundamental supposition that the TET proceeds against the background of fast vibrational relaxations within the electronic levels involved in the transfer process. Since the characteristic time τ_{rel} of vibrational relaxation in molecular system is of the order of 10^{-12} s to 10^{-10} s (Refs. 37 and 38) the use of a single TET rate K_{TET} is justified if it does not exceed $10^{10}/\text{s}$.

It has been demonstrated that two mechanisms contribute to the formation of the stepwise TET route. The first contribution is given by a thermal activated mechanism, which includes two single-electron steps with the participation of the extended bridging states and the local intermediate state $|I\rangle$ (with one excess electron at the D and one already at the A). During the first step one of the two excess electrons originally located at the D (in the case of forward ET reaction) is transferred through the extended bridging states $|\beta_{\mu}\rangle$ without any dissipation, i.e., in a coherent way. This thermal activated coherent process leads to the formation of the intermediate state $|I\rangle$. Therefore, the first step can be understood as a bridge-assisted oxidation-reduction reaction $|D\rangle \rightarrow |I\rangle$. The second step is similar to the first one. The second excess electron leaves the D via thermal activation into the somewhat different extended bridging states $|\tilde{\beta}_{\mu}\rangle$. In conclusion, the second step corresponds to the oxidation-reduction reaction $|I\rangle \rightarrow |A\rangle$.

The two steps described so far also exist as a unistep superexchange transition between the D and the A . However, it is important to note that this process is accompanied by a thermal activated superexchange transition $|D\rangle \rightarrow |I\rangle$. This observation follows from the fact that the energy E_I is positioned far above the energy E_D . Therefore, the second mechanism contributing to the stepwise TET route can be understood as a thermal activated superexchange stepwise mechanism.

The two mentioned steps of forward (and backward) D - A TET form a complete thermal activated stepwise reaction $|D\rangle \rightleftharpoons |I\rangle \rightleftharpoons |A\rangle$. In the case of a self-exchange reaction, the simplest rate expressions related to both stepwise mechanisms are given in Eqs. (42)–(44), including different activation energies $\epsilon_1 - E_D$ and ΔE_{ID} . Generally, the kinetics of the D - A TET stepwise mechanism is characterized by transfer rates K_{DI} and K_{ID} (corresponding to the forward transition $|D\rangle \rightarrow |I\rangle$ and the respective backward transition $|I\rangle \rightarrow |D\rangle$) as well as by the rates K_{IA} and K_{AI} [referring to

$|I\rangle \rightarrow |A\rangle$ and the reverse $|A\rangle \rightarrow |I\rangle$ process, cf. Eq. (22)]. If the bridging states are populated according to a thermal activation the respective thermal activated coherent ET pathways along the bridge are described by the rates $k_{DI}^{(act)}$ and $k_{ID}^{(act)}$ as well as $k_{AI}^{(act)}$ and $k_{IA}^{(act)}$. If the bridging states are involved in unistep superexchange transitions between the D and the A the related rates are given by rates k_{DI} , k_{ID} and k_{AI} , k_{IA} . Analytic expressions for all SET rates are presented in the Eqs. (23), (27), and (33).

It is important to underline that these superexchange mechanisms are different from conventional bridge-assisted SET. In the latter case the superexchange contribution to the overall transfer rate connects the initial and final states of the ET and thus exists even at zero temperature. In the present case, however, the single-electron superexchange component of each stepwise process has to be thermally activated. This behavior follows from the fact that the stepwise TET route does not take place between the initial and final states of the reaction (the state $|D\rangle$ and $|A\rangle$, respectively), but only between the *intermediate* state $|I\rangle$ and either the initial or the final TET state. Therefore, the superexchange rate $k_{D(A)I} = \exp[-\Delta E_{ID(A)}/k_B T] k_{ID(A)}$ vanishes at zero temperature.

The TET mechanism changes strongly if the intermediate state $|I\rangle$ is involved in a superexchange transition. This is the case if $|I\rangle$ forms (along with the bridge states $|\beta_\mu\rangle$ and $|\bar{\beta}_\mu\rangle$) a specific two-electron superexchange coupling just between the initial and the final states of the TET reaction. Since these states are characterized by the presence of both excess electrons either at the D or the A , this two-electron superexchange becomes responsible for the concerted TET mechanism. Note that due to the fact that $E_D \geq E_A$, the respective transfer rate, Eq. (36), does not vanish at $T=0$ K, and thus at low temperatures the concerted superexchange mechanism of TET mainly contributes to K_{TET} [cf. Figs. 4(b) and Fig. 5, in particular the set of curves III].

How important the influence of a Coulomb interaction may be on long-range D - A ET has already been noted earlier for the D - A SET in Ref. 39 as well as for a nonadiabatic D - A TET in Ref. 15. In the present paper we have shown that the Coulomb interaction between sites of excess electron localization in the DBA system reduces the energy gaps between the extended and the localized states. At a fixed number of bridge units it enhances the efficiency of the stepwise and the concerted mechanisms of D - A TET (cf. Fig. 5). Note that this result follows from the used model, where we set $q[D(2e)] = q[A(2e)] = q(B_m) = 0$. This means that within the redox centers D and A the charge of the two excess electrons is entirely compensated, i.e., the completely reduced states are neutral. If an excess electron leaves the D or the A , the respective unit is positively charged while the particular bridge unit B_m becomes negatively charged, $q[B_m(e)] < 0$. This results in an attractive force between the redox centers as well as the single reduced bridge unit and, consequently, in a lowering of the respective energy gaps. However, the behavior may become quite different if for the same type of bridge (with $q(B_m) = 0$, $q[B_m(e)] < 0$) the completely reduced units are negatively charged ($q[D(2e)] = q[A(2e)] = q^- < 0$) so that $q[D(e)] = q[A(e)] = 0$. Now, an attractive force between the redox center and the reduced

bridge unit is absent and there will be no change of the related energy gaps. Finally, we assume $q[D(2e)] = q[A(2e)] = q^- < 0$, and $q[D(e)] = q[A(e)] = q^- < 0$. Now, an additional repulsion appears between the respective center and the reduced bridge unit if an excess electron leaves the redox center. This repulsion increases the energy gaps and, thus, suppresses the D - A TET reaction. All these conclusions refer to the nonadiabatic type of a D - A TET reaction. If an excess electron, however, is strongly delocalized in the bridge, the Coulomb effects as discussed in the present paper need a reformulation. This is due to the fact that the thermal activated motion of an excess electron along the bridge mainly proceeds in a coherent way (see the discussion in Refs. 40, 43–45). In the case of a TET reaction it corresponds to the thermal activated single-electron coherent pathways in the common stepwise route.⁴⁶ A more detailed discussion of all noted cases will be given elsewhere.

Finally, we will point to the difference between bridge-assisted nonadiabatic D - A TET studied earlier in Refs. 21–23 and the presently discussed case where the charge motion is mediated by extended bridging states. First we have to mention that both types of TET reactions contain a contribution from a stepwise and from a concerted TET. And, in both cases the concerted contribution is originated by a two-electron superexchange coupling between the D and the A units (via the bridge states and the particular intermediate states denoted as $|I\rangle$). The only difference arises from the different types of bridging states (localized or delocalized states).

Let us turn to the case where the bridging states are populated by a single excess electron. Now, the ET from the D to the A occurs in different ways, although the bridge population within the D - A regime of the TET reaction remains small (less than 10^{-2}). In the case of nonadiabatic TET, an inelastic (incoherent) sequential charge motion determines the D - A TET process. Electron hopping takes place between neighboring sites of excess electron localization (including the D , the A as well as all bridge units). Another type of electron motion takes place when the bridge is characterized by delocalized states. In this case, only the release of an electron from the D or A into the bridge (and vice versa) defines the inelastic step of the ET. The electron motion through the bridge is completely coherent. This fact results in a different dependence of the stepwise transfer rate on the bridge length (dependence on the number N of bridge units). For nonadiabatic TET through a nonbiased regular bridge one obtains $K^{(step)} \sim [1 + \xi(N-1)]^{-1}$.¹⁵ In the case of adiabatic transfer through the bridge the length dependence (for a self-exchange reaction) follows as $K^{(step)} \sim \exp\{-(E_B - E_D^{(0)} - 2|V_B| \cos[\pi/(N+1)]/k_B T)\}$ [cf. Eqs. (43) and (49)]. These two fundamentally different types of bridge-length dependencies represent a well suited tool to specify the type of bridge-assisted D - A TET once respective experimental data are available.

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APPENDIX: DETERMINATION OF THE SUPEREXCHANGE TRANSFER COUPLINGS

Using relation, Eq. (31), we may denote the identity

$$\prod_{\mu=1}^N (\epsilon_{\mu} - E_M) = \prod_{\mu=1}^N (\epsilon_{\mu}^{(reg)} - E_M^{(0)}) e^{S(E_M)}, \quad (A1)$$

where for each localized *DBA* state $|M\rangle = |D\rangle, |I\rangle, |A\rangle$ the quantity

$$S(E_M) = \sum_{\mu=1}^N \ln[1 + \Delta\epsilon_{\mu M} / (\epsilon_{\mu}^{(reg)} - E_M^{(0)})] \quad (A2)$$

is defined via the energy shifts

$$\Delta\epsilon_{\mu M} = (\epsilon_{\mu} - E_M) - (\epsilon_{\mu}^{(reg)} - E_M^{(0)}) \quad (A3)$$

of the energy gaps between the μ th extended *DBA* states and the *M*th localized *DBA* states. Each shift is the result of the intersite Coulomb interaction within the *DBA* system. If $|\epsilon_{\mu M} / (\epsilon_{\mu}^{(reg)} - E_M^{(0)})| \ll 1$, the quantity (A2) can be denoted in a somewhat simpler form

$$S(E_M) = \sum_{\mu=1}^N \Delta\epsilon_{\mu M} / (\epsilon_{\mu}^{(reg)} - E_M^{(0)}). \quad (A4)$$

Introducing the superexchange decay parameter^{40–42}

$$\Lambda(E) = \ln\{(E_B - E)/2|V_B| + \sqrt{[(E_B - E)/2|V_B|]^2 - 1}\} \quad (A5)$$

we arrive at the relation (V_B is a real quantity)

$$\frac{(-1)^{N+1} V_B^N}{\prod_{\mu=1}^N (\epsilon_{\mu}^{(reg)} - E)} = \frac{\sinh \Lambda(E)}{\sinh[(N+1)\Lambda(E)]}, \quad (A6)$$

which allows us to represent Eqs. (12)–(14) in the form

$$|T_{MM'}| = |T_{MM'}^{(reg)}|^2 e^{\Theta_{MM'}}. \quad (A7)$$

The quantities $|T_{MM'}^{(reg)}|^2$ are the square of the single-electron superexchange couplings ($M=D, M'=I$ or $M=I, M'=A$) and the two-electron superexchange couplings ($M=D, M'=A$) for the case of regular bridge. The concrete expressions for all quantities are

$$|T_{DI}^{(reg)}|^2 = \frac{|V_{D1} V_{AN}|^2}{|V_B|^2} \frac{\sinh \Lambda(E_D)}{\sinh[(N+1)\Lambda(E_D)]} \times \frac{\sinh \Lambda(E_I)}{\sinh[(N+1)\Lambda(E_I)]}, \quad (A8)$$

$$|T_{IA}^{(reg)}|^2 = \frac{|V'_{D1} V'_{AN}|^2}{|V_B|^2} \frac{\sinh \tilde{\Lambda}(E_I)}{\sinh[(N+1)\tilde{\Lambda}(E_I)]} \times \frac{\sinh \tilde{\Lambda}(E_A)}{\sinh[(N+1)\tilde{\Lambda}(E_A)]}, \quad (A9)$$

and

$$|T_{DA}^{(reg)}|^2 = \frac{|V_{D1} V_{AN} V'_{D1} V'_{AN}|^2}{|V_B|^4 \Delta E_{ID} \Delta E_{IA}} \times \frac{\sinh \Lambda(E_D)}{\sinh[(N+1)\Lambda(E_D)]} \frac{\sinh \Lambda(E_A)}{\sinh[(N+1)\Lambda(E_A)]} \times \frac{\sinh \tilde{\Lambda}(E_D)}{\sinh[(N+1)\tilde{\Lambda}(E_D)]} \frac{\sinh \tilde{\Lambda}(E_A)}{\sinh[(N+1)\tilde{\Lambda}(E_A)]}. \quad (A10)$$

The quantity $\tilde{S}(E_M)$ is given by Eq. (A2) where $\Delta\epsilon_{\mu M}$ and E_B are replaced by $\Delta\tilde{\epsilon}_{\mu M} = (\tilde{\epsilon}_{\mu} - E_M) - (\tilde{\epsilon}_{\mu}^{(reg)} - E_M^{(0)})$ and \tilde{E}_B , respectively. Analogously, the superexchange decay parameter $\tilde{\Lambda}(E)$ is given by Eq. (A5) where E_B is replaced by the \tilde{E}_B . If $\exp[-\Lambda(E_M)] \ll 1$ the expression $\sinh \Lambda(E_M) / \sinh[(N+1)\Lambda(E_M)]$ reduces to $\exp[-\Lambda(E_M)N]$ and, thus, the superexchange transfer rates can be given as in Eqs. (33)–(36).

The quantities $\Theta_{MM'}$ have to be considered as correction factors whose precise form is given by the following formulas:

$$\Theta_{ID} = -[S(E_I) + S(E_D)], \quad \Theta_{IA} = -[\tilde{S}(E_I) + \tilde{S}(E_A)], \quad (A11)$$

$$\Theta_{DA} = -[S(E_D) + S(E_A) + \tilde{S}(E_D) + \tilde{S}(E_A)]. \quad (A12)$$

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