JOURNAL OF CHEMICAL PHYSICS VOLUME 120, NUMBER 9 1 MARCH 2004

Bridge mediated two-electron transfer reactions: Analysis of stepwise and concerted pathways

E. G. Petrov
Bogolyubov Institute for Theoretical Physics, National Academy of Sciences of Ukraine, UA-03143 Kiev, Ukraine

V. May
Institüt für Physik, Humboldt Universität zu Berlin, D-12489, Berlin, Germany

(Received 26 September 2003; accepted 4 December 2003)

A theory of nonadiabatic donor (D)–acceptor (A) two-electron transfer (TET) mediated by a single regular bridge (B) is developed. The presence of different intermediate two-electron states connecting the reactant state $D^{--}BA$ with the product state DBA^{--} results in complex multiexponential kinetics. The conditions are discussed at which a reduction to two-exponential as well as single-exponential kinetics becomes possible. For the latter case the rate K_{TET} is calculated, which describes the bridge-mediated reaction as an effective two-electron D–A transfer. In the limit of small populations of the intermediate TET states D^-B^-A, $DB^{--}A$, D^-BA^-, and DB^-A^-, K_{TET} is obtained as a sum of the rates $K_{\mathrm{TET}}^{(\mathrm{step})}$ and $K_{\mathrm{TET}}^{(\mathrm{sup})}$. The first rate describes stepwise TET originated by transitions of a single electron. It starts at $D^{--}BA$ and reaches DBA^{--} via the intermediate state D^-BA^-. These transitions cover contributions from sequential as well as superexchange reactions all including reduced bridge states. In contrast, a specific two-electron superexchange mechanism from $D^{--}BA$ to DBA^{--} defines $K_{\mathrm{TET}}^{(\mathrm{sup})}$. An analytic dependence of $K_{\mathrm{TET}}^{(\mathrm{step})}$ and $K_{\mathrm{TET}}^{(\mathrm{sup})}$ on the number of bridging units is presented and different regimes of D–A TET are studied. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1644535]

I. INTRODUCTION

Two-electron transfer (TET) processes and processes which incorporate even more electrons are common for enzyme regulated reactions in biological systems. For example, multielectron transfer could be clearly attributed to different enzyme complex mediated oxidation-reduction reactions. TET reduction process have been reported for different types of reductases,[1,2] oxidases,[3–5] and hydrogenases.[6–8] All these reactions involve numerous intermediate states[1,3,9–11] and proceed in a much more complex way as single-electron transfer (SET) processes. Protein film voltametry represents an experimental technique which enables direct observation of such electron transfer reactions.[12,13]

In biological systems, SET, TET, and higher multielectron reactions incorporate charge motion along specific structures like peptide chains and DNA strands as well as complete redox chains. In the various types of fumarate reductases, for example, the redox chains are given either by the chain of hemes or by Fe–S clusters.[2] Such structures form molecular bridges and mediate the electron transfer across large spatial distances. To account for the influence of molecular bridges on electron transfer reactions represents a long-standing task of theoretical chemical physics. We consider it as a particular challenge to formulate a theory of bridge-mediated multielectron transfer reactions.[14–17]

In recent studies on nonadiabatic bridge-mediated SET[18–20] the derivation of kinetic equations could be demonstrated as well as rate constants which account for different transfer mechanisms (sequential and superexchange SET). As a particular result conditions could be specified for which the overall SET rate follows by additive contributions from the sequential and the superexchange SET mechanism.[20]

Turning back to TET reactions, it has to be considered as a continuous problem to correctly characterize the different mechanisms contributing to the observed overall processes. At present, there are some basic results on the description of TET in polar liquids where the transfer directly proceeds.[21,22] Current theoretical studies on TET reactions in biological systems concentrate on electronic structure calculations of, e.g., the active centers of enzymes and their dependency on the position of the transferred electrons[4,7] or on possible TET pathways.[14,15] To estimate the rate constants characterizing the TET process, so far phenomenological versions of the Marcus theory[16] have been used. In particular, the matrix element responsible for the concerted two-electron hopping transition has been introduced as a phenomenological parameter.[17] Such treatments of TET reactions indicates the need for a theory, which is founded on nonequilibrium quantum statistics and, in this way, gives a correct description of the concerted as well as stepwise TET pathways mediated by the molecular bridge.

In the following we will present such a theoretical description of nonadiabatic long-range TET reactions. The reaction to be investigated starts with two electrons located at the donor (D). Both are transferred through a chain of bridging molecules (B), and thereafter they are captured at the acceptor (A). The whole course of the reaction will be covered by a description which generalizes earlier approaches derived for the study of nonadiabatic D–A SET (for an overview see, e.g., Refs. 23–29 and the textbooks[30–33]). It is just the nonadiabatic character of the transfer process which enables us to utilize a coarse-grained approach and to simplify the necessary rate equations considerably.[18,20,34]

The paper is organized as follows: In the next section we set up a model for the TET process covering all two-electron configurations of the DBA system. This is continued by the description of a particular density matrix approach which enables us to derive rate equations and respective rate constants for the nonadiabatic TET. The latter include expressions originated by the sequential and the superexchange electron transfer mechanism. A reduction of the TET kinetics to two-exponential and single-exponential ones is carried out in Sec. III. The conditions to be fulfilled to have this simplified behavior are specified. Section IV is devoted to an analysis of the bridge-length dependence of the stepwise and the concerted part of the overall D–A TET rate. A detailed discussion of those mechanisms originating the bridge-assisted D–A TET is given in the concluding Sec. V. Computational details are displaced to the Appendix.

II. COARSE-GRAINED DESCRIPTION OF TET

As it is well-known nonadiabatic SET takes place across different sites of electron localization. Due to the weak intersite electronic coupling the transfer proceeds against the background of considerably faster intrasite relaxation processes, and the whole mechanism is known as the sequential SET. If the SET occurs between a D and A center connected by a molecular bridge long-range superexchange D–A SET may represent an alternative charge transfer mechanism.[18–20] Since for both mentioned mechanisms the characteristic time scale Δt of the overall electron motion exceeds the characteristic time $\tau_{\rm rel}$ of intrasite relaxation the SET kinetics can be described by a simplified set of coarse-grained rate equations (see Refs. 18 and 20). The sequential and superexchange mechanisms enter via respective rate expressions. We must expect similar conditions for nonadiabatic TET reactions if the characteristic transfer time, $\tau_{\rm TET}$, substantially exceeds $\tau_{\rm rel}$. Therefore, the inequality

$$\tau_{\rm rel} \ll \tau_{\rm TET} \tag{1}$$

represent the precondition to employ a coarse-grained description of TET processes on a time scale $\Delta t \gg \tau_{\rm rel}$.

A. Basic model

Theoretical studies on TET processes in a DA complex dissolved in a polar liquid are based on the use of three distinct two-electron configurations. The TET starts at the initial configuration, $|D^{--}A\rangle$, with the two electrons at the D site. It is followed by the intermediate configuration, $|D^{-}A^{-}\rangle$, and the TET ends at the final configuration, $|DA^{--}\rangle$, with the two electrons located at the A site.[21,22] This course of TET directly corresponds to the stepwise mechanism $D^{--}A \rightleftarrows D^{-}A^{-} \rightleftarrows DA^{--}$, which has to be confronted with the concerted TET, $D^{--}A \rightleftarrows DA^{--}$. Thus, the intermediate electronic configuration $D^{-}A^{-}$ is of basic importance for the TET process between the contacting redox centers.

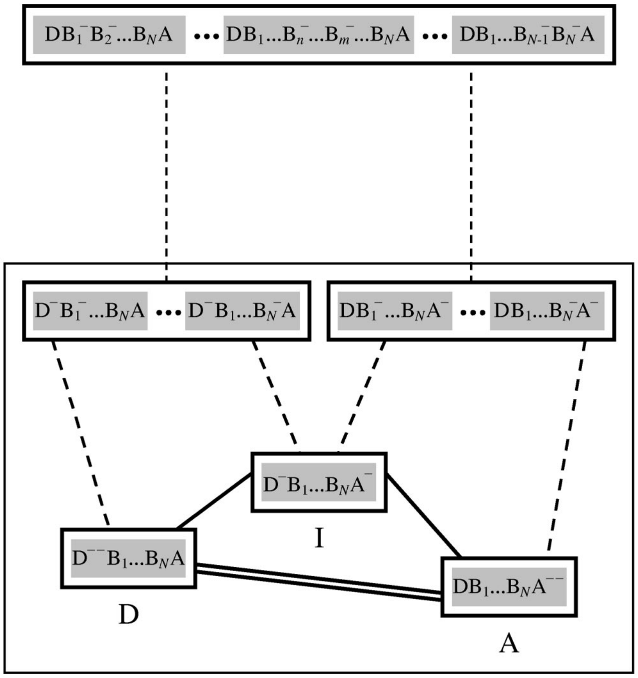

FIG. 1. Pathway scheme of bridge-assisted TET reactions. Thick dashed lines indicate the sequential single-electron pathways. Sole and double solid lines display single-electron and two-electron superexchange pathways, respectively. The thin dashed lines correspond to the pathways via twofold reduced bridging states.

In the present paper, we consider a generalization of this TET model to the case of long-range TET mediated by a bridge of N units connecting the D and the A. According to a possible large number of bridge units the number of accessible two-electron configurations become also large (cf. Fig. 1). Let us start with those states in which the bridge has not been reduced. To these types of states belongs the initial state of the TET reaction

$$|D\rangle \equiv |D^{--}B_1B_2\cdots B_m\cdots B_NA\rangle, \tag{2}$$

the intermediate state

$$|I\rangle \equiv |D^{-}B_1B_2\cdots B_m\cdots B_NA^{-}\rangle, \tag{3}$$

and the final state of the reaction

$$|A\rangle \equiv |DB_1B_2\cdots B_m\cdots B_NA^{--}\rangle. \tag{4}$$

Furthermore there exist two categories of states including a singly reduced bridge,

$$|B_m\rangle \equiv |D^{-}B_1B_2\cdots B_m^{-}\cdots B_NA\rangle, \tag{5}$$

and

$$|\tilde{B}_n\rangle \equiv |DB_1B_2\cdots B_n^{-}\cdots B_NA^{-}\rangle. \tag{6}$$

Every category has to be subdivided into N different states. If both transferred electrons in the bridge, we arrive at the manifold of N^2 doubly reduced bridge states (note that a double occupation of a single bridge unit is not forbidden),

$$|B_{mn}\rangle \equiv |D^{-}B_1B_2\cdots B_m^{-}\cdots B_n^{-}\cdots B_NA\rangle. \tag{7}$$

The possible TET routes are depicted in Fig. 1. Below, however, we will exclusively restrict our studies to TET processes where doubly reduced bridge states do not take part. In particular, this would be the case for TET through short bridges where the Coulomb repulsion between the transferred electrons strongly increases the energetic position of the states $|B_{nm}\rangle$ relative to all other TET states (see also the discussion in Ref. 35).

Resulting from this restriction, the mechanisms of TET named *stepwise* TET from now on can be characterized as follows (see Fig. 1). It consists of two sequential SET routes each related to a single-electron hopping transitions between nearest neighbor bridge units. The first type of a sequential SET route, i.e., the sequence of reactions: $D^{--}B_1 \cdots B_N A \rightleftarrows D^- B_1^- \cdots B_N A \rightleftarrows D^- B_1 B_2^- \cdots B_N A \rightleftarrows \cdots D^- B_1 \cdots B_N^- A \rightleftarrows D^- B_1 \cdots B_N A^-$, represents an electron transfer from the initial state $|D\rangle$ to the intermediate state $|I\rangle$. Then, the second type of sequential SET let move the second electron from the D to the A: $D^- B_1 \cdots B_N A^- \rightleftarrows D B_1^- \cdots B_N A^- \rightleftarrows D B_1 B_2^- \cdots B_N A^- \rightleftarrows \cdots D B_1 \cdots B_N^- A^- \rightleftarrows DBA^{--}$. In the scheme of state Eqs. (2)–(6) the overall TET is completed by the transition from the intermediate state $|I\rangle$ to the final state $|A\rangle$.

Apparently, the transitions $|D\rangle \rightarrow |I\rangle$ and $|I\rangle \rightarrow |A\rangle$ can also proceed directly via the (single-electron) superexchange mechanisms (full lines in Fig. 1). It will be the particular aim of the following derivations to present an approach which accounts for stepwise TET as well as includes all possible superexchange mechanism. Beside the described superexchange we have also to expect the so-called *concerted* TET leading directly from state $|D\rangle$ to state $|A\rangle$ (double solid line in Fig. 1).

In order to derive rate equations which incorporate the different types of TET pathways, in a first step, we have to set up a respective Hamiltonian. We abbreviate all two-electron states, Eqs. (2)–(6), by $|M\rangle$ $(M = D, B_m, I, \tilde{B}_n, A)$ and get TET Hamiltonian as

$$H_{\mathrm{TET}} = H_0 + V, \tag{8}$$

with the zero-order part

$$H_0 = \sum_M H_M |M\rangle\langle M|, \tag{9}$$

where the H_M denote the vibrational Hamiltonian which belong to the states $|M\rangle$. The couplings (transfer integrals) H_{MN} between the different two-electron states are included in the interaction Hamiltonian,

$$V = \sum_{M,N} (1 - \delta_{M,N}) H_{MN} |M\rangle\langle N|. \tag{10}$$

However, only those H_{MN} are included for which the state $|M\rangle$ and $|N\rangle$ can be translated into one another by a single-electron exchange.

Let us introduce the eigenstates and energies of the Hamiltonian H_M as $|M\nu_M\rangle$ and $E(M,\nu_M)$, respectively, where ν_M denotes the quantum number of the vibrational state belonging to the electronic state $|M\rangle$. In the case that all vibrational quantum numbers of the electronic state $|M\rangle$ are zero we will denote the respective energy by E_M. If an energetic bias is present we assume $\Delta = E_m - E_{m+1} = \tilde{E}_n - \tilde{E}_{n+1}$ and may write (for a regular bridge)

$$E_m = E_B - (m-1)\Delta, \quad \tilde{E}_n = \tilde{E}_B - (n-1)\Delta. \tag{11}$$

(There is a variety of reasons for Δ. Its presence may result from externally applied as well as internal intermembrane electric fields acting along the bridge. However, the bias can also be introduced by slightly changing the chemical structure of the bridge units or of the groups surrounding the bridge.) Moreover, non-Condon effects are neglected and the coupling matrix elements are approximated by

$$V_{M\nu_M\, N\nu'_N} = \mathcal{M}_{MN} \langle \nu_M | \nu'_N \rangle, \tag{12}$$

where $\langle \nu_M | \nu'_N \rangle$ denotes the vibrational overlap integral. The transfer matrix elements $\mathcal{M}_{MN} = \langle M | \hat{V}_{\mathrm{tr}} | N \rangle$ characterize the transitions between the electronic states $|M\rangle$ and $|N\rangle$, Eqs. (2)–(6) of the whole DBA system. We shall specify these matrix elements utilizing the tight binding model where the transfer operator $\hat{V}_{\mathrm{tr}}$ describes the single-electron transitions. It allows to express $\mathcal{M}_{MN}$ via the couplings $V_{\lambda\lambda'}$ between the molecular orbitals related to the neighboring bridge sites. For instance, if $|M\rangle = |D\rangle$ and $|N\rangle = |B_1\rangle$, then $\mathcal{M}_{DB_1} = V_{D1}$, and if $|M\rangle = |I\rangle$ and $|N\rangle = |\tilde{B}_1\rangle$, then $\mathcal{M}_{I\tilde{B}_1} = V'_{D1}$. Analogously, one obtains $\mathcal{M}_{IB_N} = V_{AN}$ and $\mathcal{M}_{A\tilde{B}_N} = V'_{AN}$. In the case of a regular bridge we set for all sites in the bridge $\mathcal{M}_{B_m\, B_{m\pm 1}} = \mathcal{M}_{\tilde{B}_n\, \tilde{B}_{n\pm 1}} = V_{mm\pm 1} \equiv V_B$.

All bridge-assisted electron transfer processes caused by the single-electron couplings, are depicted in Fig. 2. The presence of two single-electron stepwise pathways can be clearly identified. The direct couplings T_{DI} and T_{IA} are the result of a superexchange mechanism [cf. the Appendix C, Eqs. (C1) and (C2)]. The energetic position of all considered TET states are represented in Fig. 3.

B. Derivation of kinetic equations

Our considerations on TET reactions will be based on the fact that inequality (1) is fulfilled. The related fast vibrational relaxation within every electronic state of the TET results in electron vibrational level broadening[18] and dephasing.[36–38] Here, we denote the broadening of the energy level $E(M,\nu_M)$ by $\Gamma(M,\nu_M)$.

It has been discussed at length in Ref. 18 how to compute the electron vibrational dynamics in a case characterized by Eq. (1). In a first step one has to set up equations of motion for the electron vibrational density matrix,

$$\rho_{M\nu_M, N\nu'_N}(t) = \langle M\nu_M | \rho(t) | N\nu'_N \rangle, \tag{13}$$

where $\rho(t)$ is the related reduced density operator. The influence of an additional heat bath causing fast vibrational relaxation has been taken into consideration by energy relaxation and dephasing rates. Next, one changes to a time region which is large compared to the fast vibrational relaxation processes (coarse-graining approximation). This change is

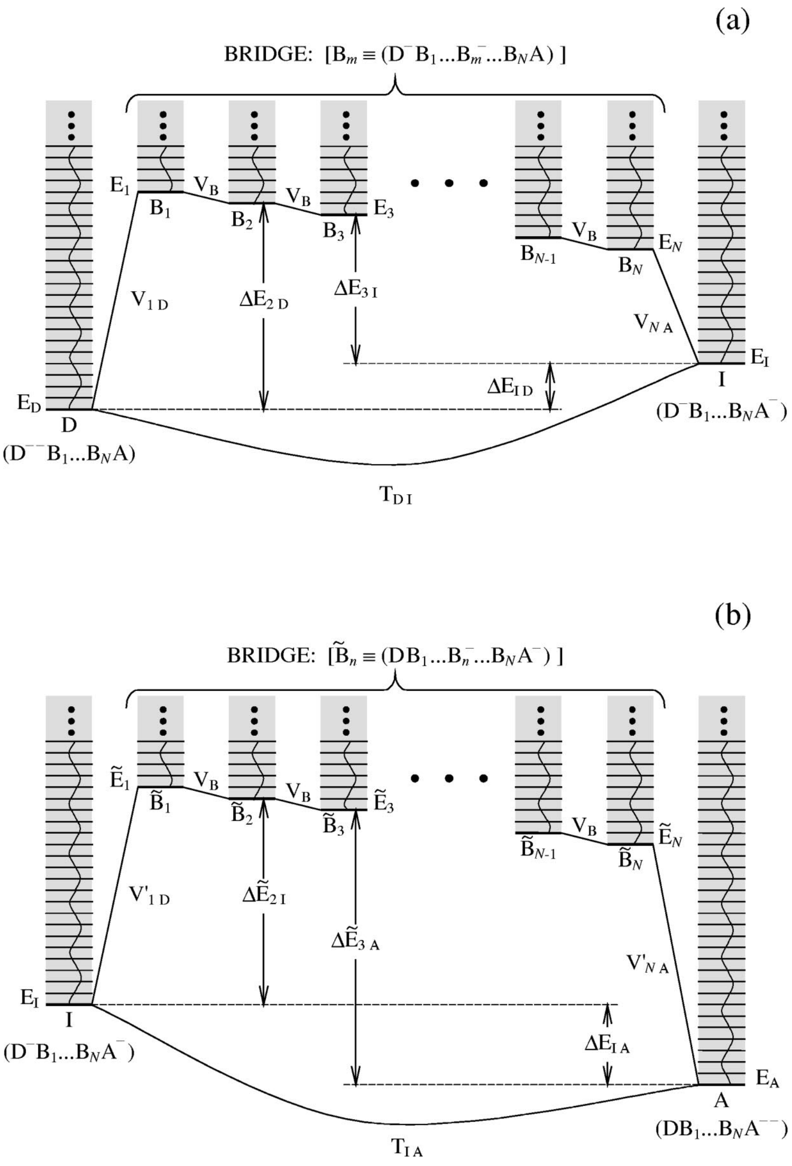

FIG. 2. Energetic scheme of the *DBA* states participating in the TET. The single-electron transitions along the first, $(D^{--}BA)\rightleftarrows(D^-B_1^-A)\rightleftarrows\cdots(D^-B_N^-A)\rightleftarrows(D^-BA^-)$, and the second, $(D^-BA^-)\rightleftarrows(DB_1^-A^-)\rightleftarrows\cdots(DB_N^-A^-)\rightleftarrows(DBA^{--})$, stepwise pathways are shown [panels (a) and (b), respectively]. Wavy lines indicate the fast relaxation within the various electronic state.

achieved in reducing the exact density matrix equations to the following approximate versions valid for the diagonal density matrix elements:

$$\frac{\partial}{\partial t}\rho_{M\nu_M,M\nu_M}(t)=\frac{i}{\hbar}\langle M\nu_M|[V,\rho(t)]_-|M\nu_M\rangle, \tag{14}$$

and the off-diagonal density matrix elements (note in particular $M\neq N$)

$$\rho_{M\nu_M,N\nu'_N}(t)=\frac{\langle M\nu_M|[V,\rho(t)]_-|N\nu'_N\rangle}{\Delta\varepsilon(M\nu_M,N\nu'_N)}. \tag{15}$$

The reduced set of equations of motion assumes that the time dependence of the diagonal density matrix elements is exclusively determined by the coupling to other TET states whereas relaxation processes do not contribute (they are just finished at every time step). In contrast the time derivative has been removed in the equation of motion for the off-diagonal density matrix elements. This approximation results in a determination of the time dependence mainly by the dephasing rates and is justified by the rapidness of the dephasing. The related dephasing rates enter the equation via $\Delta\varepsilon(M\nu_M,N\nu'_N)=E(M,\nu_M)-E(N,\nu'_N)-i(\Gamma(M,\nu_M)+\Gamma(N,\nu'_N))$.

Equations (14) and (15) will be used to derive rate equations for the electronic state populations

$$P_M(t)=\sum_{\nu_m}P_{M\nu_M}(t)=\sum_{\nu_m}\rho_{M\nu_M,M\nu_M}(t), \tag{16}$$

where the transition rates are obtained as expansions with respect to the transfer integrals V_{MN}. In order to derive the related perturbation theory we first introduce the projector

$$\mathcal{P}A=\sum_{\nu_m}A_{M\nu_M,M\nu_M}|M\nu_M\rangle\langle M\nu_M|, \tag{17}$$

and the orthogonal complement $\mathcal{Q}=1-\mathcal{P}$. The latter projects any operator A defined in the electron vibrational state space on the part which has only off-diagonal matrix elements. A projection on the part of A including only diagonal matrix elements with respect to the states $|M\nu_M\rangle$ is

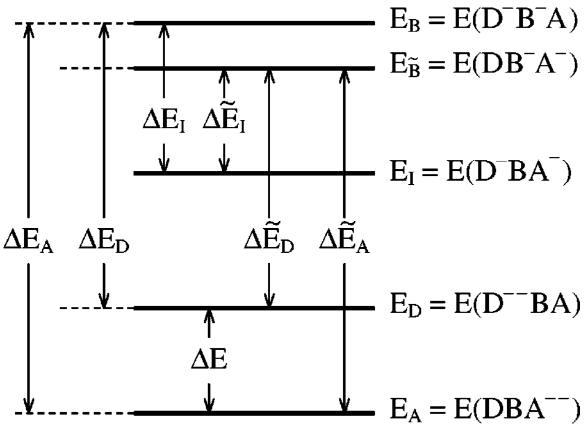

FIG. 3. Energetic positions $E_M \equiv E(M,0_M)$ of the states involved in the TET together with respective energy gaps.

achieved by $\mathcal{P}$. Furthermore, we change from the matrix notation, Eqs. (14) and (15), to the operator notation

$$\frac{\partial}{\partial t}\mathcal{P}\rho(t) = -i\mathcal{P}L_V\mathcal{Q}\rho(t) \tag{18}$$

and

$$\mathcal{Q}\rho(t)(t) = -i\mathcal{Q}RL_V(\mathcal{P}\rho(t)+\mathcal{Q}\rho(t)). \tag{19}$$

Note the introduction of $L_V = (1/\hbar)[V,\dots]_-$. It allows to replace $L_V\rho(t)$ by $L_V\mathcal{Q}\rho(t)$ in the first equation. The resolvent superoperator $R = \int_0^\infty d\tau S_0(\tau)$ could be introduced in the second equation since it generates an expression as in Eq. (15) when changing to matrix elements. The newly defined time-propagation superoperator S_0 is determined by the zero-order Liouvillian $L_0 = (1/\hbar)[H_0,\dots]_-$ as well as by a part describing dissipation.

To get the required rate equations, in a next step, we have to derive a master equation for the diagonal part $\mathcal{P}\rho$ of the density operator. This is easily achieved by formally solving Eq. (19) as

$$\mathcal{Q}\rho(t) = -i(1+i\mathcal{Q}RL_V)\mathcal{P}\rho(t) \tag{20}$$

and inserting the result into Eq. (18). It follows

$$\frac{\partial}{\partial t}\mathcal{P}\rho(t) = -\mathcal{R}\mathcal{P}\rho(t). \tag{21}$$

Here $\mathcal{R}$ denotes the superoperator which describes any type of TET. Its expansion with respect to the transfer coupling (10),

$$\mathcal{R} = \mathcal{R}_2 + \mathcal{R}_4 + \mathcal{R}_6 + \cdots \tag{22}$$

enables one to arrange the different TET processes in a proper order. The various terms of the expansion can be written as

$$\begin{aligned}\mathcal{R}_{2k} = {} & -(-i)^{2k}\int_0^\infty d\tau_{2k-1}\int_0^\infty d\tau_{2k-2}\cdots\int_0^\infty d\tau_1 \\ & \times \mathcal{P}L_V\mathcal{Q}S_0(\tau_{2k-1})L_V\mathcal{Q}S_0(\tau_{2k-2}) \\ & \times L_V\cdots\mathcal{Q}S_0(\tau_1)L_V,\end{aligned} \tag{23}$$

but in any case they only contain an even number of interactions.

Taking the matrix elements of Eq. (21) we obtain for the electron vibrational state populations

$$\begin{aligned}\frac{\partial}{\partial t}P_{M\nu_M}(t) = {} & -\sum_{N,\nu'_N}\langle M,\nu_M|(\mathcal{R}|N\nu'_N\rangle\langle N\nu'_N|)|M\nu_M\rangle \\ & \times P_{N\nu'_N}(t).\end{aligned} \tag{24}$$

According to the coarse graining approximation there is vibrational equilibrium established at every electronic state and at every time $t \gg \tau_{\mathrm{rel}}$. Therefore, we can assume the following thermal equilibrium relation to be fulfilled:

$$P_{M\nu_M}(t)/P_{M\nu'_M}(t) = \exp\{-[E(M,\nu_M)-E(M\nu'_M)]/k_BT\}. \tag{25}$$

Changing to the total TET state population, Eq. (16), we may set (see, e.g., Refs. 18 and 34)

$$P_{M\nu_M}(t) = W(E(M,\nu_M))P_M(t), \tag{26}$$

where

$$W(E(M,\nu_M)) = Z_M^{-1}\exp[-E(M,\nu_M)/k_BT],$$

$$Z_M^{-1} = \sum_{\nu_M}\exp[-E(M,\nu_M)/k_BT], \tag{27}$$

is the statistical weight of the electron-vibrational state $|M\nu_M\rangle$. Noting Eq. (26) we obtain from Eq. (24) the set of balancelike equations,

$$\dot{P}_M(t) = -\sum_N \mathcal{K}_{MN}P_N(t), \tag{28}$$

with

$$\begin{aligned}\mathcal{K}_{MN} = {} & \sum_{\nu_M}\sum_{\nu'_N} W(E(N,\nu'_N))\times\langle M\nu_M|(\mathcal{R}|N\nu'_N\rangle \\ & \times\langle N\nu'_N|)|M\nu_M\rangle.\end{aligned} \tag{29}$$

Now, noting the fact that the symbols M and N indicate electronic states (2)–(6) related to the whole DBA system we obtain (see Appendix A) the set of coupled rate equations (A8)–(A16) with respective sequential and superexchange rate constants.

III. OVERALL TET RATES

The concrete form of the balancelike equations (28), as given by the set of rate equations, Eqs. (A8)–(A16), reflects the rather complicated kinetics of the TET process, also shown in scheme (a) of Fig. 4. Generally, such kinetics has a multiexponential character for each of the $2N+3$ state populations $P_M(t)$ $(M = D,I,A,B_1,\dots B_N,\tilde{B}_1,\dots\tilde{B}_N)$,

$$P_M(t) = P_M(\infty) + \sum_{r=1}^{2N+2} B_M^{(r)}\exp(-K_rt). \tag{30}$$

The steady-state populations, $P_M(\infty) = \lim_{s\to 0}(sF_M(s))$, as well as the overall transfer rates K_r can be deduced from the

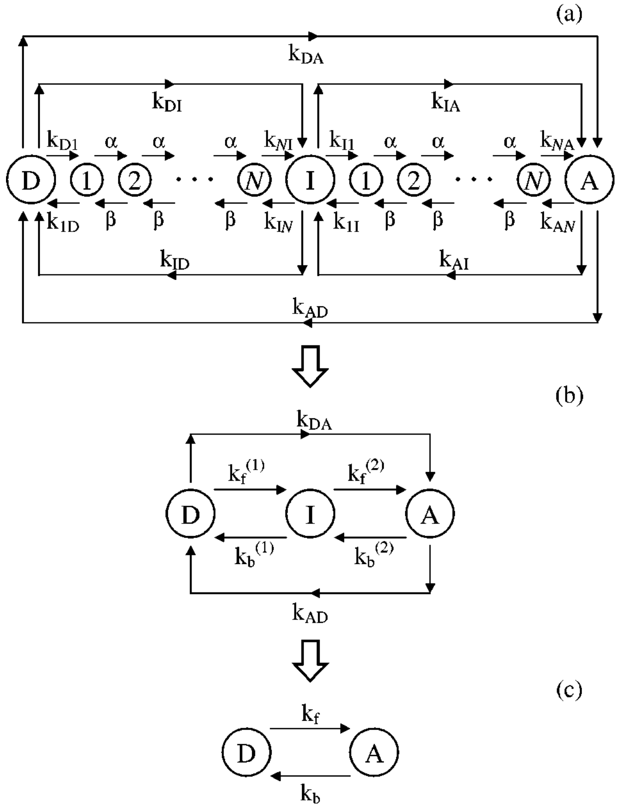

FIG. 4. Complete kinetic scheme of the bridge-assisted TET process [part (a)]. For a small bridge-state population the kinetics is reduced to the transitions between the three electronic states, $|D\rangle$, $|I\rangle$, and $|A\rangle$ [the related transfer rates are also shown, part (b)]. If the population of the intermediate state $|I\rangle$ becomes also small the three-state kinetics reduce to $D-A$ TET kinetics with an effective single forward and single backward rate only [part (c)].

exact solution of the set (A8)–(A16) for all Laplace-transformed populations $F_M(s)$ (the solution is given in Appendix B). In most cases a numerical computation of the overall transfer rates becomes necessary. However, further analytical considerations are possible whenever the intermediate states become less populated. (This has been discussed at length for SET which is reduced to a single-exponential $D-A$ SET kinetics.[20]) Therefore, we will concentrate on the description of such a simple overall time behavior. A two-exponential TET process will be described in the following section whereas single-exponential behavior is discussed in the section afterwards.

A. Two-exponential TET kinetics

According to the general solution, Eq. (30), of the rate equations (A8)–(A16), two-exponential TET kinetics requires the existence of two rates which are much smaller than all other ones. Let these rates be K_1 and K_2. Then, the exact solution (30) reduces to

$$P_M(t) \simeq P_M(\infty) + B_M^{(1)} e^{-K_1 t} + B_M^{(2)} e^{-K_2 t}, \tag{31}$$

which, of course, is only valid in a time domain $t \gg K_3^{-1}, K_4^{-1}, \ldots, K_{2N+2}^{-1}$.

If the total bridge state population $P_B(t)$ remains small during the TET reaction the solution (31) describes TET only between the electronic states $|D\rangle$, $|I\rangle$, and $|A\rangle$. Just the inequality

$$P_B(t) = \sum_{m=1}^{N} (P_m(t) + P_{\tilde{m}}(t)) \ll 1 \tag{32}$$

represents a necessary and sufficient condition for the reduction of the multiexponential TET kinetics to a two-exponential process. If $t \to \infty$ the inequality (32) can be rewritten as

$$\lim_{s\to 0} sF_B(s) = \sum_{m=1}^{N} (\lim_{s\to 0} sF_m(s) + \lim_{s\to 0} sF_{\tilde{m}}(s)) \ll 1. \tag{33}$$

This relation has to be considered as a necessary condition for the appearance of two-exponential kinetics (see also Ref. 18). Since all the Laplace-transformed populations $F_M(s)$ have a rather complicated form this is also valid for the inequality (33).

To get analytical expressions for the two smallest transfer rates K_1 and K_2 we shall start from the exact Eqs. (B10) which, however, only determine the Laplace-transformed populations of the DBA states $|D\rangle$, $|I\rangle$, and $|A\rangle$ [the bridge populations are given by Eqs. (B1) and (B2)]. If this reduced set of rate equations is transformed back into the time domain we get the following three kinetic equations [see the scheme (b) of Fig. 4]:

$$\begin{aligned}
\dot{P}_D(t) &= -(k_f^{(1)} + k_{DA}) P_D(t) + k_b^{(1)} P_I(t) + k_{AD} P_A(t), \\
\dot{P}_I(t) &= -(k_f^{(2)} + k_b^{(1)}) P_I(t) + k_f^{(1)} P_D(t) + k_b^{(2)} P_A(t), \\
\dot{P}_A(t) &= -(k_b^{(2)} + k_{AD}) P_A(t) + k_f^{(2)} P_I(t) + k_{DA} P_2(t).
\end{aligned} \tag{34}$$

The rates introduced here have to be identified with Laplace-transformed expressions as introduced in the Appendix B, Eq. (B10),

$$\begin{aligned}
&k_f^{(1)} + k_{DA} = R_{DD}(0), \quad k_f^{(2)} + k_b^{(1)} = R_{II}(0), \\
&k_b^{(2)} + k_{AD} = R_{AA}(0), \quad k_f^{(1)} = R_{ID}(0), \\
&k_b^{(1)} = R_{DI}(0), \quad k_f^{(2)} = R_{AI}(0), \quad k_b^{(2)} = R_{IA}(0).
\end{aligned} \tag{35}$$

Using the Eqs. (B3), (B4)–(B6), and (B11) as well as the recursion formula (B7) we may identify the rates of the Eqs. (34) with basic rate expressions of sequential and superexchange transitions

$$\begin{aligned}
&k_f^{(1)} = k_{DI}^{(\mathrm{seq})} + k_{DI}^{(\mathrm{sup})}, \quad k_b^{(1)} = k_{ID}^{(\mathrm{seq})} + k_{ID}^{(\mathrm{sup})}, \\
&k_{DI}^{(\mathrm{seq})} = k_{D1} k_{NI} \alpha^{N-1} / D_1, \quad k_{DI}^{(\mathrm{sup})} = k_{DI}, \\
&k_{ID}^{(\mathrm{seq})} = k_{1D} k_{IN} \beta^{N-1} / D_1, \quad k_{ID}^{(\mathrm{sup})} = k_{ID}
\end{aligned} \tag{36}$$

and

$$\begin{aligned}
&k_f^{(2)} = k_{IA}^{(\mathrm{seq})} + k_{IA}^{(\mathrm{sup})}, \quad k_b^{(2)} = k_{AI}^{(\mathrm{seq})} + k_{AI}^{(\mathrm{sup})}, \\
&k_{IA}^{(\mathrm{seq})} = k_{I1} k_{NA} \alpha^{N-1} / D_2, \quad k_{IA}^{(\mathrm{sup})} = k_{IA}, \\
&k_{AI}^{(\mathrm{seq})} = k_{1I} k_{AN} \beta^{N-1} / D_2, \quad k_{AI}^{(\mathrm{sup})} = k_{AI},
\end{aligned} \tag{37}$$

where

$$\begin{aligned} D_1 &\equiv k_{NI}\alpha^{N-1}+k_{1D}\beta^{N-1}+k_{1D}k_{NI}D(N-2),\\ D_2 &\equiv k_{NA}\alpha^{N-1}+k_{1I}\beta^{N-1}+k_{1I}k_{NA}D(N-2). \end{aligned} \tag{38}$$

The main bridge length dependence of rates of transfer is originated by the function

$$D(M)\equiv D(s=0;M)=\alpha^M\frac{1-\gamma^{M+1}}{1-\gamma}, \tag{39}$$

where

$$\gamma\equiv\beta/\alpha=\exp(-\Delta/k_BT)\leqslant 1 \tag{40}$$

denotes the ratio of the backward and the forward site-to-site rate constants. In Eq. (40) Δ is the intersite energy bias [introduced in Eq. (11)]. The transfer rates (36) and (37) define two overall TET rates,

$$\begin{aligned} K_1&=\tfrac{1}{2}[a_1+d_1+\sqrt{(a_1-d_1)^2+4a_2d_2}],\\ K_2&=\tfrac{1}{2}[a_1+d_1-\sqrt{(a_1-d_1)^2+4a_2d_2}], \end{aligned} \tag{41}$$

where we have introduced the following abbreviations:

$$\begin{aligned} a_1&\equiv k_f^{(2)}+k_b^{(2)}+k_{AD}, \quad a_2\equiv k_{DA}-k_f^{(2)},\\ d_1&\equiv k_f^{(1)}+k_b^{(1)}+k_{DA}, \quad d_2\equiv k_{AD}-k_b^{(1)}. \end{aligned} \tag{42}$$

Having determined the two overall TET rates we may present the other quantities entering the Eqs. (31) for the time-dependent populations. They read

$$\begin{aligned} P_D(\infty)&=\frac{a_1k_b^{(1)}+d_2k_f^{(2)}}{K_1K_2},\\ P_I(\infty)&=\frac{K_1K_2-(a_1+a_2)k_b^{(1)}-(d_1+d_2)k_f^{(2)}}{K_1K_2},\\ P_A(\infty)&=\frac{d_1k_f^{(2)}+a_2k_b^{(1)}}{K_1K_2} \end{aligned} \tag{43}$$

as well as ($j=1,2$)

$$\begin{aligned} B_D^{(j)}&=(-1)^{j+1}\frac{(a_1-K_j)(k_b^{(1)}-K_j)+d_2k_f^{(2)}}{K_j(K_1-K_2)},\\ B_I^{(j)}&=(-1)^j\left[\frac{(a_1-K_j)(k_b^{(1)}-K_j)}{K_j(K_1-K_2)}\right.\\ &\qquad\left.+\frac{a_2(k_b^{(1)}-K_j)+k_f^{(2)}(d_1+d_2-K_j)}{K_j(K_1-K_2)}\right],\\ B_A^{(j)}&=(-1)^{j+1}\frac{k_f^{(2)}(d_1-K_j)+a_2(k_b^{(1)}-K_j)}{K_j(K_1-K_2)}. \end{aligned} \tag{44}$$

At this point of our discussion let us formulate the conditions for which the exact solution, Eqs. (B10) becomes identical with that of the kinetic equations (34). Therefore, we have to consider the quantities $R_{MN}(s)$ which have been introduced when considering the Laplace-transformed rate equations (cf. Appendix B). We expand the $R_{MN}(s)$ with respect to s and assume that the approximations $s+R_{MM}(s)\approx s+R_{MM}(0)+sR'_{MM}(0)\approx s+R_{MM}(0)$ as well as $R_{MN}(s)\approx R_{MN}(0)+sR'_{MN}(0)\approx R_{MN}(0)$ are fulfilled for both roots $s=-K_1$ and $s=-K_2$ [$M,N=D,I,A$; $R'_{MN}(0)\equiv(dR_{MN}(s)/ds)_{s=0}$]. Then, one can see that the multistate DBA system shows a two-exponential TET kinetics, Eq. (31) only if

$$|R'_{MN}(0)|\ll|\delta_{M,N}-K_j^{-1}R_{MN}(0)| \quad (j=1,2). \tag{45}$$

A comparison of this inequality with the condition, Eq. (33), for a small steady bridge population indicates their complete correspondence.

B. Single-exponential *D–A* TET kinetics

So far we arrived at a description of bridge-assisted TET where the two forward ($k_f^{(1)},k_f^{(2)}$) and two backward ($k_b^{(1)},k_b^{(2)}$) transfer rates contain additive contributions from the single-electron sequential and the single-electron superexchange mechanisms. Remember that this additivity is a direct consequence of the small population of all bridging states. This two-exponential TET corresponds to an effective three-state system. If the intermediate state $|I\rangle$ carries a pronounced population the overall transfer rates K_1 and K_2 (note that $K_1>K_2$) contain a mixture of rate expressions caused by the single-electron stepwise and the two-electron superexchange (concerted) mechanism. The situation changes substantially when

$$K_1\gg K_2, \tag{46}$$

which indicates that the TET process, Eq. (31), is determined by two strongly separated kinetic phases, a fast and a slow one with the characteristic times $\tau_1=K_1^{-1}$ and $\tau_2=K_2^{-1}$, respectively. If $t\ll\tau_2$ we have $\exp(-K_2t)\simeq 1$, and, thus, the fast phase is defined by the time-dependent factor $\exp(-K_1t)$ for all three populations, $P_D(t)$, $P_I(t)$, and $P_A(t)$. The first phase of the TET is finished for $t\gg\tau_1$, but $t\ll\tau_2$. As a result, a redistribution of the initial populations $P_M(0)=\delta_{M,D}$ took place, and for $\tau_2\gg t\gg\tau_1$ the transient populations, $P_M(t\gg\tau_1)\equiv P_M(+0)$, have been formed. They are easily derived from Eq. (31) at $\exp(-K_1t)=0$ and $\exp(-K_2t)=1$.

Below we present concrete expressions for the overall transfer rates K_1 and K_2 as well as for the (intermediate) populations $P_M(+0)$, bearing in mind that the energy E_I exceeds the energies E_D and E_A (cf. Fig. 3). For such a condition, the following inequality is satisfied:

$$k_b^{(1)},k_f^{(2)}\gg k_f^{(1)},k_b^{(2)},k_{DA},k_{AD}. \tag{47}$$

Note that in line with Eq. (41) the inequality (46) is reduced to

$$(a_1+d_1)^2\gg 4(a_1d_1-a_2d_2). \tag{48}$$

Therefore, the following approximate expression for the overall transfer rates can be presented

$$K_1\approx a_1+d_1, \quad K_2\approx\frac{a_1d_1-a_2d_2}{a_1+d_1}. \tag{49}$$

According to the inequalities (47) this can be rewritten as

$$\begin{aligned} K_1&\approx k_b^{(1)}+k_f^{(2)},\\ K_2&\approx\frac{k_f^{(1)}k_f^{(2)}+k_b^{(2)}k_b^{(1)}}{k_b^{(1)}+k_f^{(2)}}+k_{DA}+k_{AD}, \end{aligned} \tag{50}$$

and the transient populations take the following form:

$$\begin{aligned} &P_D(+0)=1-(k_f^{(1)}+k_{DA})/(k_b^{(1)}+k_f^{(2)}),\\ &P_I(+0)=k_f^{(1)}/(k_b^{(1)}+k_f^{(2)}),\\ &P_A(+0)=k_b^{(2)}/(k_b^{(1)}+k_f^{(2)}). \end{aligned} \tag{51}$$

From these expressions it is seen that the ratio $P_I(+0)/P_A(+0)$ is determined by the ratio of the stepwise and the concerted rate constants, $k_f^{(1)}/k_{DA}$. Note that $P_I(+0)$ gives the maximal value possible for the population of the intermediate state I (cf. Fig. 4). But inequality (47) tells us also that $P_I(+0)\ll 1$, i.e., the population of state I remains very small at any time t,

$$P_I(t)\ll 1. \tag{52}$$

This inequality indicates that at $t\gg K_1^{-1}$ the two-exponential kinetics (31) is reduced to a single-exponential one,

$$\begin{aligned} &P_D(t)\simeq P_D(\infty)+(1-P_D(\infty))e^{-K_{\mathrm{TET}}t},\\ &P_A(t)\simeq P_A(\infty)(1-e^{-K_{\mathrm{TET}}t}). \end{aligned} \tag{53}$$

This kinetics describes a $D-A$ TET with an overall transfer rate $K_2=K_{\mathrm{TET}}$. The latter can be represented as the sum of a stepwise and a concerted contribution,

$$K_{\mathrm{TET}}=\tau_{\mathrm{TET}}^{-1}=K_{\mathrm{TET}}^{(\mathrm{step})}+K_{\mathrm{TET}}^{(\mathrm{conc})}. \tag{54}$$

Since $K_{\mathrm{TET}}=k_f+k_b$ contains a forward and a backward part [cf. scheme (c) in Fig. 4], $K_{\mathrm{TET}}^{(\mathrm{step})}$ and $K_{\mathrm{TET}}^{(\mathrm{conc})}$ separate correspondingly. We have

$$\begin{aligned} &K_{\mathrm{TET}}^{(\mathrm{step})}=K_{\mathrm{step}}^{(f)}+K_{\mathrm{step}}^{(b)},\\ &K_{\mathrm{step}}^{(f)}=\frac{k_f^{(1)}k_f^{(2)}}{k_b^{(1)}+k_f^{(2)}},\quad K_{\mathrm{step}}^{(\mathrm{b})}=\frac{k_b^{(2)}k_b^{(1)}}{k_b^{(1)}+k_f^{(2)}}, \end{aligned} \tag{55}$$

and

$$\begin{aligned} &K_{\mathrm{TET}}^{(\mathrm{conc})}=K_{\mathrm{conc}}^{(f)}+K_{\mathrm{conc}}^{(b)},\\ &K_{\mathrm{conc}}^{(f)}=k_{DA},\quad K_{\mathrm{conc}}^{(b)}=k_{AD}. \end{aligned} \tag{56}$$

IV. DISCUSSION OF RESULTS

We consider the derivation of the overall TET rates and the description of the conditions at which a multiexponential TET is reduced to a two-exponential as well as a single-exponential TET as the main result of the present studies. Additionally, it could be shown in which way the overall transfer rates are expressed by the sequential and the superexchange rate constants.

When considering distant electron transfer it is of interest to describe the dependence of rate expressions on the number of bridge units. Concentrating on the (single-exponential) $D-A$ TET this dependence is contained in the stepwise and concerted components of the overall transfer rate (54). First let us consider the stepwise channel of the $D-A$ TET. The stepwise transfer rates (36) and (37) contain contributions from the single-electron sequential and single-electron superexchange transfer rates between the $|D\rangle$ and the $|I\rangle$ as well as between the $|I\rangle$ and the $|A\rangle$ electronic states of a whole DBA system. Using the definitions (38) and (39) one can rewrite the sequential contribution as

$$\begin{aligned} &k_{DI(IA)}^{(\mathrm{seq})}=\frac{k_{f0}^{(1(2)\mathrm{seq})}}{1+\xi_{1(2)}R(N)},\\ &k_{ID(AI)}^{(\mathrm{seq})}=\frac{k_{b0}^{(1(2)\mathrm{seq})}[1-(1-\gamma)R(N)]}{1+\xi_{1(2)}R(N)}. \end{aligned} \tag{57}$$

It follows from Eq. (57) that the N dependence of the sequential mechanism of SET is concentrated in the factor

$$R(N)=(1-\gamma^{N-1})/(1-\gamma), \tag{58}$$

provided that $\gamma\neq 0$ and that the sequential decay parameters ξ_1 and ξ_2 are not too small.

The quantities

$$k_{f0}^{(1\ \mathrm{seq})}=\frac{k_{D1}k_{NI}}{k_{NI}+k_{1D}},\quad k_{b0}^{(1\ \mathrm{seq})}=\frac{k_{IN}k_{1D}}{k_{NI}+k_{1D}}, \tag{59}$$

and

$$k_{f0}^{(2\ \mathrm{seq})}=\frac{k_{I1}k_{NA}}{k_{NA}+k_{1I}},\quad k_{b0}^{(2\ \mathrm{seq})}=\frac{k_{AN}k_{1I}}{k_{NA}+k_{1I}} \tag{60}$$

define rates of sequential transfer through a bridge with a single unit. The related decay parameters read

$$\xi_1=\frac{k_{1D}(k_{NI}-\alpha(1-\gamma))}{\alpha(k_{NI}+k_{1D})} \tag{61}$$

and

$$\xi_2=\frac{k_{1I}(k_{NA}-\alpha(1-\gamma))}{\alpha(k_{NA}+k_{1I})}. \tag{62}$$

Note that due to a single-electron character of sequential pathway the rate constants in Eqs. (59)–(62) are identical to the hopping rate constants between the nearest sites of electron localization. Therefore, e.g., the rate $k_{D1}(k_{I1})$ characterizes the hopping of an electron from the state with two electrons (single electron) at the D to the adjacent wire unit while the rate $k_{AN}(k_{IN})$ characterizes the similar process with respect to the A.

To derive the single-electron superexchange contribution to the stepwise transfer rates (36) and (37) one has to specify the superexchange rate constants $k_{DI(ID)}$ and $k_{IA(AI)}$. These rate constants are defined in Appendix A, Eq. (A7), and are proportional to the square of the superexchange couplings $|T_{DI}|^2$ and $|T_{IA}|^2$, respectively. Here, we restrict ourself to the consideration of a small intersite bridge bias Δ, where the effective transfer couplings are given by Eqs. (C21) and (C23), Appendix C. A small change in the notation leads to the following expressions:

$$k_{DI(ID)}^{(\mathrm{sup})}=k_{f0}^{(1(2)\ \mathrm{sup})}e^{-\zeta_1(N-1)} \tag{63}$$

and

$$k_{IA(AI)}^{(\mathrm{sup})}=k_{b0}^{(1(2)\ \mathrm{sup})}e^{-\zeta_2(N-1)}. \tag{64}$$

Here, the rate $k_{DI}^{(\mathrm{sup})}(k_{AI}^{(\mathrm{sup})})$ characterizes the distant coherent transfer of an electron from the state with two electrons at the $D(A)$ to the state with one electron at the $A(D)$. The rate $k_{ID}^{(\mathrm{sup})}(k_{IA}^{(\mathrm{sup})})$ describes the reverse process. [Compare the definition of DBA electronic states (2)–(4) and the scheme (a) of Fig. 4.] The superexchange decay parameters

$$\zeta_1=-2\ln\left[\frac{|V_B|}{(\Delta E_D\Delta E_I)^{1/2}}\right] \tag{65}$$

and

$$\zeta_2=-2\ln\left[\frac{|V_B|}{(\Delta\tilde{E}_A\Delta\tilde{E}_I)^{1/2}}\right] \tag{66}$$

are mainly responsible for the distant dependence of the superexchange rate. Note that in the presence of an energetic bias in the bridge an additional N dependence also appears in the quantities

$$k_{f0}^{(1(2)\ \mathrm{sup})}=\frac{2\pi}{\hbar}\,\frac{|V_{D1}V_{NA}|^2}{\Delta E_D\Delta E_I}(FC)_{DI(ID)} \tag{67}$$

and

$$k_{b0}^{(1(2)\ \mathrm{sup})}=\frac{2\pi}{\hbar}\,\frac{|V'_{D1}V'_{NA}|^2}{\Delta\tilde{E}_A\Delta\tilde{E}_I}(FC)_{IA(AI)}\,. \tag{68}$$

The N dependence is located in the Franck–Condon factors through the driving forces ΔE_{ID} and ΔE_{IA} [cf. Eqs. (C10) and (C11)] characterizing the corresponding single-electron reaction.

Two couples of decay parameters, (ζ_1,ξ_1) and (ζ_2,ξ_2), characterize the efficiency of the first and the second single-electron bridge-mediated stepwise pathway, respectively. At the same time, the efficiency of the concerted pathway is defined by the two-electron superexchange rate constants k_{DA} and k_{AD} [compare Eq. (56)]. Introducing the two-electron superexchange decay parameter as

$$\zeta=-2\ln\left[\frac{|V_B|^2}{(\Delta E_D\Delta E_A\Delta\tilde{E}_D\Delta\tilde{E}_A)^{1/2}}\right] \tag{69}$$

and utilizing Eq. (C25), a respective simplified notation of each concerted rate can be given,

$$k_{DA(AD)}=k_{DA(AD)}^{(0)}e^{-\zeta(N-1)}. \tag{70}$$

Here, the rate $k_{DA}(k_{AD})$ characterizes the distant coherent transfer of two electrons from the state with two electrons at the $D(A)$ to the state without extra electrons at the $A(D)$. Such a process is possible owing to a virtual electronic configuration D^-BA^- corresponding to the state with one electron at the D center and one electron at the A center.

In the case of a bridge with an energy bias the factor

$$k_{DA(AD)}^{(0)}=\frac{2\pi}{\hbar}\,\frac{|V_{D1}V_{NA}V'_{D1}V'_{NA}|^2}{\Delta E_D\Delta E_A\Delta\tilde{E}_D\Delta\tilde{E}_A\Delta E_{ID}\Delta E_{IA}}\times(\mathrm{FC})_{DA(AD)} \tag{71}$$

includes an additional N dependence originated by the energy gaps ΔE_{ID} and ΔE_{IA} as well as by the Franck–Condon factor [through the driving force ΔE_{DA} of the TET reaction, cf. Eq. (C12)].

In order to demonstrate the bridge-length dependence of the rate we take Jortner's form[39] for all rate constants. Let ω_{MN} be the single characteristic frequency accompanying the $M\rightarrow N$ electronic transition and λ_{MN} be the corresponding reorganization energy. Then Jortner's form of the rate constant (A7) can be written as (see also Refs. 18, 25, 30, 31, and 33)

$$k_{MN}=\frac{2\pi}{\hbar}\,\frac{|V_{MN}|^2}{\hbar\omega_{MN}}\Phi_{\nu_{MN}}, \tag{72}$$

where we have introduced

$$\Phi_{\nu_{MN}}=\exp\left[-S_{MN}\coth\frac{\hbar\omega_{MN}}{k_BT}\right]\left(\frac{1+n(\omega_{MN})}{n(\omega_{MN})}\right)^{\nu_{MN}/2}\times I_{|\nu_{MN}|}(2S_{MN}[n(\omega_{MN})(1+n(\omega_{MN}))]^{1/2}). \tag{73}$$

The expression contains the modified Bessel function $I_\nu(z)$, the Bose distribution function $n(\omega)=[\exp(\hbar\omega/k_BT)-1]^{-1}$, and we have set $S_{MN}\equiv\lambda_{MN}/\hbar\omega_{MN}$, $\nu_{MN}\equiv\Delta E_{MN}/\hbar\omega_{MN}$.

First let us discuss the reduction of the multiexponential TET kinetics to the two-exponential one. In line with the theory proposed, such a reduction is only possible at a small integral bridge population, which is completely justified by the results of Fig. 5. Moreover, the derived analytic results on the two-exponential kinetics [cf. Eqs. (31), (41)–(44)] coincide completely [cf. Fig. 5(a)] with those obtained by a numerical solution of the basic set of Eqs. (A8)–(A16) provided that (32) is fulfilled during the TET process. Note that the bridge population evolve in time as well [cf. the numerical results depicted in Fig. 5(b)]. But due to the small population of each bridging state this kinetics is well separated from the kinetics of the populations $P_D(t)$, $P_I(t)$, and $P_A(t)$.

If in the course of the TET process the bridging states $|B_m\rangle$, Eq. (5), and $|\tilde{B}_n\rangle$, Eq. (6), as well as the intermediate state $|I\rangle$, Eq. (3), have a small population, then the TET is reduced to a single-exponential $D-A$ TET. This statement is supported by the results shown in Fig. 6. Again, despite the fact that both types of bridge populations, $P_m(t)$ and $P_{\tilde{n}}(t)$ [denoted in Fig. 6(b) by the numerals 1 and 2, respectively], as well as the intermediate state population $P_I(t)$ show a time dependence according to their respective transfer rates the basic populations $P_D(t)$ and $P_A(t)$ display a single-exponential kinetics (53) with overall $D-A$ TET rate (54).

Figures 7–10 show the $D-A$ TET rate in dependency on the number N of bridging units. Special attention is put on the temperature dependence since it determines the contribution by the thermally activated stepwise transfer mechanism. Figure 7(a) demonstrates that the stepwise contribution to the overall transfer rate K_{TET}, Eq. (54) exceeds the concerted one, so that $K_{\mathrm{TET}}\approx K_{\mathrm{TET}}^{(\mathrm{step})}$. Indeed, the analysis of the inter-state transfer rates (36) and (37) indicates that at a given set of parameters [specifying the elementary rate constants (72)] the inequality, $k_f^{(2)}\gg k_b^{(1)}$ [cf. Fig. 7(b)], is fulfilled, and thus the stepwise transfer rate, Eq. (55) follows as

$$K_{\mathrm{TET}}^{(\mathrm{step})}\approx k_b^{(1)}\exp(-\Delta E_{ID}/k_BT). \tag{74}$$

This expression indicates that the limiting step of the stepwise TET process is related to a single-electron $|D\rangle\rightarrow|I\rangle$ transition. Note that a noticeable contribution in this thermally activated transition is given by the superexchange (at

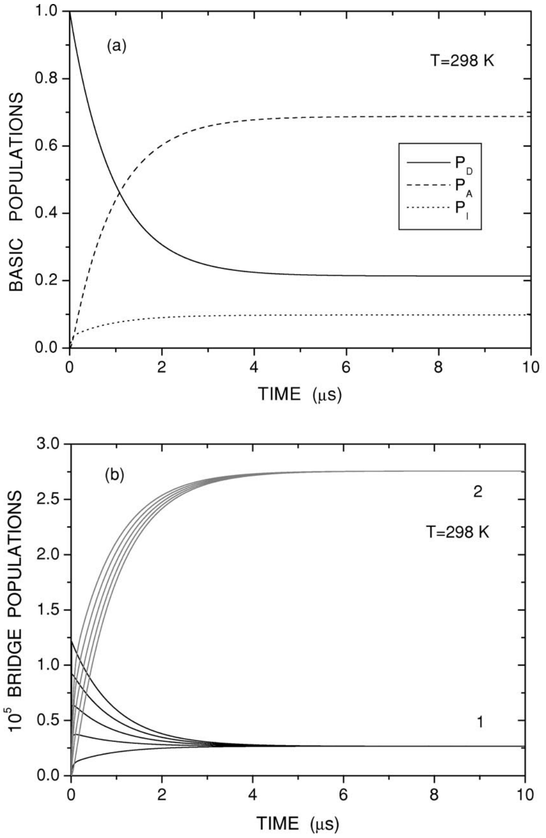

FIG. 5. TET kinetics in a bridge with five units, without energy bias and for a small population $P_m(t)$ and $P_{\tilde{m}}(t)$ of the two types of bridge states. Analytic results for the populations $P_D(t)$, $P_I(t)$, and $P_A(t)$ according to Eqs. (31), (41)–(44) and the numerical solution of the set of Eqs. (A8)–(A16) completely agree [part (a)]. The bridge populations related to the first (1) and the second type of bridge states (2) show their own kinetics [panel (b)]. The calculations are based on the Eqs. (54)–(73) and by choosing the following parameters: $\Delta E_D=0.29$ eV, $\Delta E_I=0.27$ eV, $\Delta\tilde{E}_I=0.21$ eV, $\Delta\tilde{E}_A=0.26$ eV, $\Delta E=0.03$ eV; $\lambda_{1D}=\lambda_{NI}=\lambda_{DI}=0.6$ eV, $\lambda_{I1}=\lambda_{NA}=\lambda_{IA}=0.4$ eV, $\lambda_{DA}=0.8$ eV, $\lambda_{m\,m\pm1}\equiv\lambda_B=0.8$ eV; $\omega_{MN}=\omega_0=100$ cm^{-}; $V_{D1}=V_{NA}=V'_{D1}=V'_{NA}=0.03$ eV, $V_B=0.04$ eV.

$N=1-4$) and the sequential (at $N>4$) single-electron pathway [compare the N dependence of both contributions plotted in Fig. 7(b)]. At lower temperatures the contribution of the concerted mechanism increases [compare Fig. 7(a) with Fig. 8(a) and Fig. 8(b)]. For instance, at $T=150$ K [Fig. 8(a)] the concerted mechanism dominates the TET at $N=1-2$ while at $T=100$ K the same mechanism works effectively up to $N=4$ [Fig. 8(b)]. In contrast to the stepwise mechanism the concerted mechanism works also at small temperatures down to $T=0$. Note that the stepwise pathway also includes a superexchange (single-electron) contribution. But due to the thermally activated origin of the stepwise rate, Eq. (74), the superexchange single-electron contribution can only work at the presence of thermal activation. This fact reflects the specificity of the $D-A$ TET process. (However, in the case of single-electron $D-A$ transfer the superexchange channel contributes down to $T=0$.) Therefore, in the case of $D-A$ TET the contribution of the concerted mechanism increases at decreasing temperature.

It follows from the comparison of Fig. 7(b) with Fig. 9 that the contribution of the single-electron superexchange channel to the interstate transfer rates (characterizing the stepwise pathway) strongly increases at decreasing temperature. This means that at low temperatures even the stepwise pathway is used since it covers single-electron superexchange channels (which however have to be thermally activated in contrast with the two-electron superexchange channel).

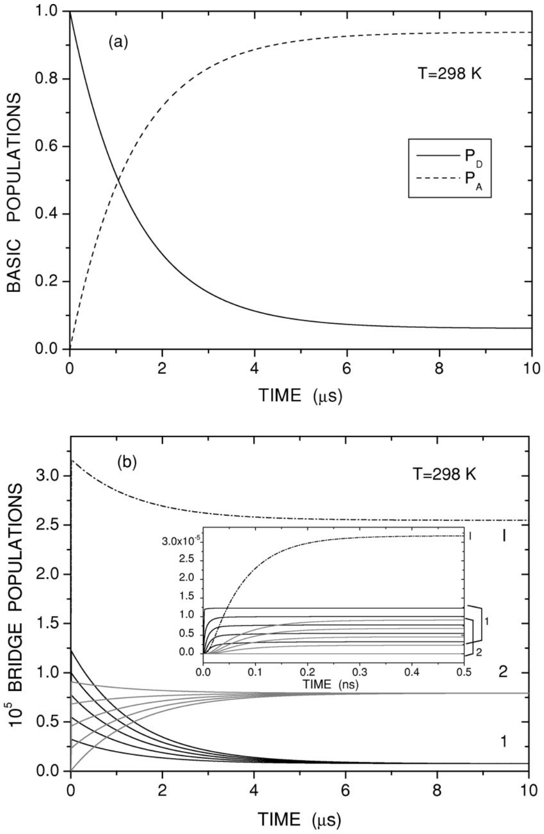

FIG. 6. $D-A$ kinetics of a TET reaction in a bridge with five units, without energy bias and for a small bridge state population and a small population of the intermediate state. Analytic results [cf. Eqs. (53) and (54)–(56)] and the numerical solution of the set of Eqs. (A8)–(A16) completely agree [part (a)]. The bridge populations related to the first (1) and the second type of bridge states (2) as well as the population of the intermediate state I show their own kinetics [panel (b)]. The calculations are based on the $\Delta E_D=0.29$ eV, $\Delta E_I=0.09$ eV, $\Delta\tilde{E}_I=0.03$ eV, $\Delta\tilde{E}_A=0.3$ eV, $\Delta E=0.07$ eV. All other parameters are identical to those used for Fig. 5.

Figure 10 displays the influence of the energy bias Δ on the concerted and the stepwise bridge-assisted superexchange contribution to the overall $D-A$ TET. At low temperatures under consideration just the single-electron and the two-electron superexchange channels determine the thermally activated stepwise and the concerted pathway of the electron transfer, respectively. It is seen that at $N=1-4$ the concerted contribution exceeds the stepwise one, while at $N>4$ the distance dependence of the K_{TET} is determined by the stepwise mechanism of the $D-A$ TET. This means that at low temperatures the main contribution to the $D-A$ TET stems from the single-electron and the two-electron superexchange mechanisms (stepwise and concerted pathways, respectively). Figure 10 also shows that a change of Δ generally affects the stepwise transfer rate. This follows from the fact that at $N>4$ for which K_{TET} is given by Eq. (74), the

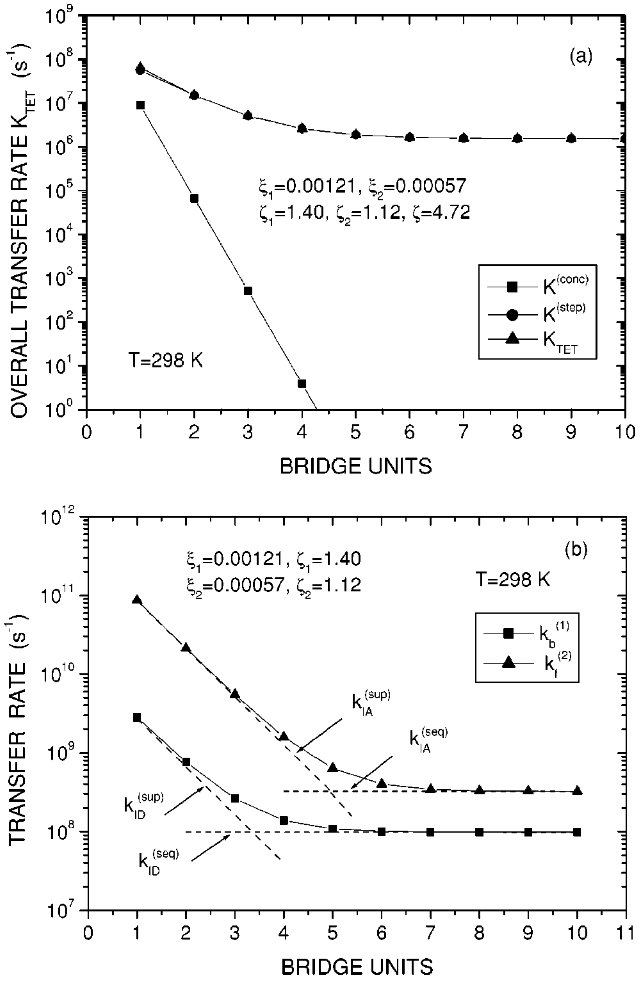

FIG. 7. Bridge length dependence of the overall $D-A$ TET transfer rate K_{TET} (at room temperature) as well as its stepwise ($K_{\mathrm{TET}}^{(\mathrm{step})}$) and concerted ($K_{\mathrm{TET}}^{(\mathrm{conc})}$) components [part (a)]. The different contributions to the stepwise transfer rate $K_{\mathrm{TET}}^{(\mathrm{step})}$ (single-electron transfer channels, superexchange channel—up to $N\sim 3-4$ bridge units—and the sequential transfer channel at $N>4$) are shown in part (b). The calculations are based on the Eqs. (54)–(73) and by choosing the following parameters: $\Delta E_D=0.20$ eV, $\Delta E_I=0.10$ eV, $\Delta\tilde{E}_I=0.05$ eV, $\Delta E=0.15$ eV; $\lambda_{1D}=\lambda_{NI}=\lambda_{1I}=1.2$ eV, $\lambda_{DI}=0.8$ eV, $\lambda_{NA}=1.4$ eV, $\lambda_{IA}=0.5$ eV, $\lambda_{DA}=0.2$ eV, $\lambda_{m\,m\pm 1}\equiv\lambda_B=0.5$ eV; $\omega_{MN}=\omega_0=800\ \mathrm{cm}^{-}$; $V_{D1}=V_{NA}=V'_{D1}=V'_{NA}=0.02$ eV, $V_B=0.07$ eV.

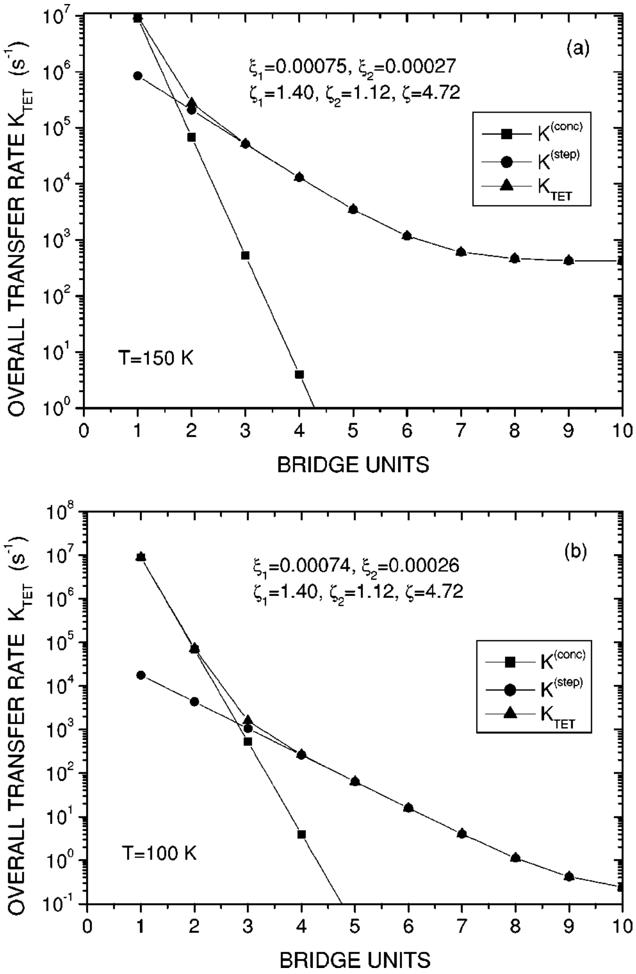

FIG. 8. Bridge length dependence of the overall $D-A$ TET transfer rate K_{TET} as well as its stepwise ($K_{\mathrm{TET}}^{(\mathrm{step})}$) and concerted ($K_{\mathrm{TET}}^{(\mathrm{conc})}$) components at different temperatures (other parameters like those of Fig. 7). Part (a) $T=150$ K, part (b) $T=100$ K.

main dependence of K_{TET} on Δ is concentrated at ΔE_{ID}, Eq. (C10) rather than in the rate constant $k_b^{(1)}$, Eq. (36). This circumstance indicates directly that the stepwise $D-A$ TET process is originated by a thermally activated mechanism.

V. CONCLUSION

The present paper has been devoted to the study of nonadiabatic two-electron transfer (TET) in a donator (D) acceptor (A) complex mediated by a molecular bridge. Focusing on nonadiabatic reactions the intersite electron transitions take place on a time scale $\Delta t\gg\tau_{\mathrm{rel}}$, where τ_{rel} characterizes the time of intrasite vibrational relaxation. Therefore, the whole analysis can be based on the coarse-grained kinetic equations (A8)–(A16), valid for $t\gg\tau_{\mathrm{rel}}$.

An analysis of the exact solution based on the Laplace-transformed state populations allowed to formulate the conditions, Eqs. (33) and (45), for which the multiexponential kinetics of the TET process, Eq. (30), is reduced to a two-exponential kinetics, Eq. (31). The respective two overall transfer rates K_1 and K_2 are given in Eq. (41). It has been demonstrated that such a reduction becomes possible if the

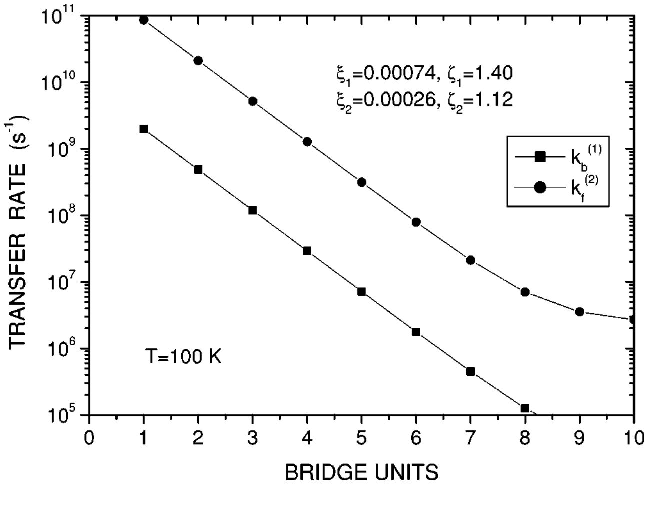

FIG. 9. Bridge length dependence of the fastest interstate transfer rates $k_b^{(1)}$ and $k_f^{(2)}$ characterizing the transitions from the intermediate state I in the three-state DBA system [see scheme (b) in Fig. 4]. The calculations have been done with the same parameters as in Fig. 7.

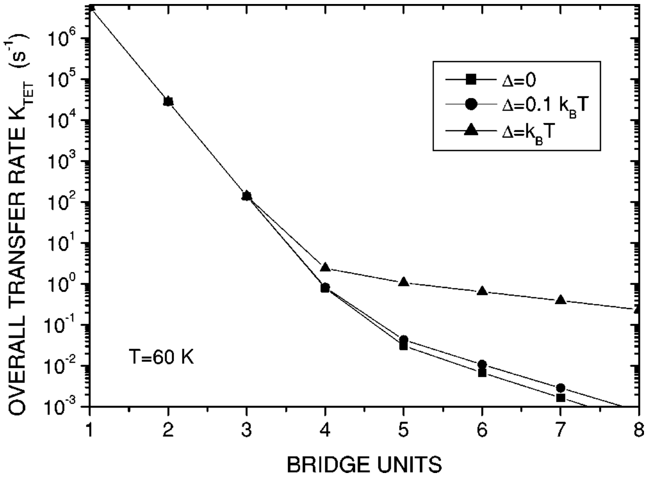

FIG. 10. Low temperature bridge length dependence of the overall $D-A$ TET rate K_{TET} at different values of the bridge internal energy bias Δ. The calculations have been done with the same parameters as in Fig. 7.

integral population of the bridging states remains small (less then 10^{-2}) during the whole TET process.

If, additionally, the population of the intermediate state $|I\rangle$, Eq. (3) (with one electron at the D and one at the A), remains also small, then the two-exponential kinetics turns to a single-exponential one [cf. Eq. (53)] characterized by a single overall $D-A$ TET transfer rate K_{TET}. Certain conditions have been derived [cf. Eqs. (45) and (46)] at which the transfer rate K_{TET} can be given by a sum of the stepwise and the concerted transfer rates, Eq. (54).

Within the model of a regular bridge, we have presented analytic expressions for both mentioned transfer rates, Eqs. (55) and (56) as well as Eqs. (57)–(70). The stepwise transfer rate characterizes the single-electron pathways of $D-A$ TET. It contains two contributions related to the sequential and superexchange mechanism of bridge-assisted single-electron transfer between the state $|D\rangle$ (both electrons at the D) and the state $|I\rangle$ (one electron at the D and another electron at the A) as well as single-electron transfer between the state $|I\rangle$ and the state $|A\rangle$ (both electrons at the A).

Since the single-electron pathways follow from thermal activation the stepwise contributions to K_{TET} are strongly suppressed with decreasing temperature. In contrast, the concerted transfer rate, which is originated by a specific two-electron superexchange coupling (between the state with two electrons at the D and the state with two electrons at the A), can act at low temperatures down to $T=0$. Therefore, the contribution of the concerted mechanism to the $D-A$ TET increases with decreasing temperature.

The model of a regular bridge has been used to derive analytical results on the N dependence of the stepwise as well as concerted contributions to the overall $D-A$ TET rate. The Coulomb interaction between the transferred electrons located within the bridge as well as at the D and A induces a shift of the site energies. This may also happen for the bridge-site reorganization energies $\lambda_{m\,m\pm1}$ which can differ from λ_B. (In the case of a single-electron $D-A$ transfer this problem has been already discussed in, e.g., Ref. 40.) If, however, among all possible bridging states only those with a single electron in the bridge are involved in the TET process the general form of the nonadiabatic rate constants (72) [see also the more general expression (A7)] does not change. [In particular, the square of the superexchange couplings are further defined by Eqs. (C1)–(C3).] Only the energy gaps, Eqs. (C4)–(C12) as well as the reorganization energies have to be modified. In the present paper, however, we assumed a strong screening of the D and A redox centers by surrounding polar groups (as it is often the case in enzymes). Therefore, any Coulomb interaction of the transferred electrons with these centers could be neglected. Studying TET in a bridge with an energy bias a deviation from the standard exponential law $\sim\exp[-\zeta(N-1)]$ characterizing the decrease of the superexchange rate with the number of bridge units N has been obtained. This deviation could be explained by the change of the energy gap for every bridging unit.

The key result of the present paper is the specification of the stepwise and concerted contributions to the overall transfer rate which characterizes the nonadiabatic $D-A$ TET process mediated by a molecular bridge. This has been done in the framework of a tight binding model where the electronic energies and intersite couplings enter as phenomenological parameters. Such a model allowed us to derive the analytic dependence of both contributions on the bridge length (number of bridging units N). Note that the examination of the bridge-length dependence of the overall transfer rate is the most direct way to specify the stepwise and concerted electron transfer routes in a concrete system. However, even for a SET process such an experimental examination has been done only recently (see discussion in Refs. 19 and 20). Therefore, a detailed test of bridge-length effects on nonadiabatic TET reactions by comparing with experimental data has to be postponed to the future. Another way to distinguish the stepwise and concerted routes is an examination of the pH dependence of the overall transfer rate characterizing the TET reactions in enzymes. Recently, we used this way to analyze the reduction of micothione reductase by NADPH.[41] It has been shown that such a reduction takes place along the concerted route. Probably, further progress in the theoretical description of bridge-assisted TET could be achieved with the combination of semiphenomenological analytic expressions (containing the precise bridge-length dependence of transfer rates) and quantum-chemical estimations of electronic energies and of the various (site-to-site and superexchange) electronic couplings. (In the case of SET, just such methods allowed to specify single-electron pathways between redox-centers of number protein macromolecules.[26–29])

ACKNOWLEDGMENTS

This work is supported in part by the Fund of Fundamental Research of NASU and the Volkswagen-Stiftung, Germany (priority area *Intra- and Intermolecular Electron Transfer*).

APPENDIX A: DERIVATION OF KINETIC EQUATIONS

The concrete form of the kinetic equations follows from Eq. (28) if the expansion (22) is introduced into Eq. (29).

The first term $\mathcal{R}_2$ of this expansion corresponds to the standard (second-order) Born approximation. It leads to rate constants which describe the sequential pathway of TET. Higher-order terms result in superexchange single-electron and two-electron rate constants. A similar result has been presented earlier in Ref. 18 for the derivation of SET rate equations. Therefore, we do not repeat details of the derivation. We only present the superexchange couplings for the transitions between the two-electron states $|D\rangle$ and $|I\rangle$, $|I\rangle$ and $|A\rangle$, as well as $|D\rangle$ and $|A\rangle$. Moreover, we will only consider pure electronic energy gaps ΔE_{MN} (in Fig. 3 these gaps are shown for a bridge without energy bias).

Let $|M\rangle$ be the donor state $|D\rangle$. Then, the Born approximation of the quantities $\mathcal{K}_{DN}$, Eq. (29) follows from the general expression (29) as

$$\mathcal{K}_{DN}=\mathcal{K}_{DN}^{(\mathrm{Born})}=\delta_{N,D}k_{D1}-\delta_{N,1}k_{1D}. \tag{A1}$$

Here, $k_{D1}=k_{1D}\exp[-(E_1-E_D)/k_BT]$ and

$$k_{1D}=\frac{2\pi}{\hbar}\sum_{\nu_D}\sum_{\nu_1}|V_{1\nu_1\,D\nu_D}|^2\times W(E(1,\nu_1))L(E(1,\nu_1)-E(D,\nu_D)). \tag{A2}$$

The quantity $L(x)$ denotes the Lorentzian-type broadening of the δ function. Employing the Condon approximation, Eq. (12), and following the approach given in Ref. 18 we can write the rate constant k_{1D} in the standard form:

$$k_{1D}=\frac{2\pi}{\hbar}|V_{1D}|^2\ \ (\mathrm{FC})_{1D}. \tag{A3}$$

Here, $(\mathrm{FC})_{1D}$ is the Franck–Condon factor for the $1\rightarrow D$ electron transition. In the considered case of nonadiabatic electron transfer any rate constant characterizing electron hopping between adjacent sites has a similar form.

Higher-order expansion terms in Eq. (22) result in two effects, the renormalization of those rate constants derived in the Born approximation and the appearance of superexchange rate constants. In the case of nonadiabatic electron transfer the rate renormalization is of less importance and will be neglected. The superexchange contributions, if related to the D, are of the single-electron type (rate constants k_{DI} and k_{ID}) and of the two-electron (concerted) type (rate constants k_{DA} and k_{AD}). Therefore we get

$$\mathcal{K}_{DN}=\mathcal{K}_{DN}^{(\mathrm{Born})}+\mathcal{K}_{DN}^{(\mathrm{sup}\ 1)}+\mathcal{K}_{DN}^{(\mathrm{sup}\ 2)}, \tag{A4}$$

where the first term is given by Eq. (A1) while

$$\mathcal{K}_{DN}^{(\mathrm{sup}\ 1)}=\delta_{N,D}k_{DI}-\delta_{N,I}k_{ID} \tag{A5}$$

and

$$\mathcal{K}_{DN}^{(\mathrm{sup}\ 2)}=\delta_{N,D}k_{DA}-\delta_{N,I}k_{AD}. \tag{A6}$$

In Eqs. (A5) and (A6), the superexchange rate constants take the form

$$k_{MN}=\frac{2\pi}{\hbar}|T_{MN}|^2(\mathrm{FC})_{MN}, \tag{A7}$$

where expressions of the square of single-electron and two-electron superexchange couplings defining the $D-A$ TET are given in Appendix C.

Substituting Eqs. (A4)–(A6) in Eq. (28) we get

$$\dot{P}_D(t)=-(q_D+k_{DA})P_D(t)+k_{1D}P_1(t)+k_{ID}P_I(t)+k_{AD}P_A(t), \tag{A8}$$

$$\dot{P}_1(t)=-q_1P_1(t)+k_{D1}P_D(t)+\beta P_2(t), \tag{A9}$$

$$\dot{P}_m(t)=-qP_m(t)+\alpha P_{m-1}(t)+\beta P_{m+1}(t), \tag{A10}$$

$$\dot{P}_N(t)=-q_NP_N(t)+k_{IN}P_I(t)+\alpha P_{N-1}(t), \tag{A11}$$

$$\dot{P}_I(t)=-(q_I^{(1)}+q_I^{(2)})P_I(t)+k_{NI}P_N(t)+k_{DI}P_D(t)+k_{1I}\tilde{P}_1(t)+k_{AI}P_A(t), \tag{A12}$$

$$\dot{P}_{\tilde{1}}(t)=-\tilde{q}_1P_{\tilde{1}}(t)+k_{I1}P_I(t)+\beta P_{\tilde{2}}(t), \tag{A13}$$

$$\dot{P}_{\tilde{n}}(t)=-qP_{\tilde{n}}(t)+\alpha P_{\tilde{n}-\tilde{1}}(t)+\beta P_{\tilde{n}+\tilde{1}}(t), \tag{A14}$$

$$\dot{P}_{\tilde{N}}(t)=-\tilde{q}_NP_{\tilde{N}}(t)+k_{AN}P_A(t)+\alpha P_{\tilde{N}-\tilde{1}}(t), \tag{A15}$$

$$\dot{P}_A(t)=-(q_A+k_{AD})P_A(t)+k_{NA}P_{\tilde{N}}(t)+k_{IA}P_I(t)+k_{DA}P_D(t). \tag{A16}$$

Note that in the Eqs. (A10) and (A14), m,n run over $2,3,\ldots,N-1$. Furthermore, we used the abbreviation $m\equiv B_m$, and $\tilde{n}\equiv\tilde{B}_n$ so that we can identify $P_m(t)$ with $P_{B_m}(t)$ and $P_{\tilde{n}}(t)$ with $P_{\tilde{B}_n}(t)$.

The Eqs. (A8)–(A16) have to be complemented by the following abbreviations for the different rate expressions:

$$\begin{gathered}q_D\equiv k_{D1}+k_{DI},\quad q_1\equiv k_{1D}+\alpha,\quad q_N\equiv k_{NI}+\beta,\\ \tilde{q}_1\equiv k_{1I}+\alpha,\quad \tilde{q}_N\equiv k_{NA}+\beta,\quad q_A\equiv k_{AN}+k_{AI},\\ q_I^{(1)}\equiv k_{IN}+k_{ID},\quad q_I^{(2)}\equiv k_{I1}+k_{IA},\quad q\equiv\alpha+\beta.\end{gathered} \tag{A17}$$

Here $\alpha\equiv k_{mm+1}$ and $\beta\equiv k_{m+1m}$ $(m=1,2,\ldots,N-1)$, are the rates characterizing the forward and backward jumps of a single-electron between neighboring bridge units.

APPENDIX B: EXACT SOLUTION OF THE LAPLACE TRANSFORMED SET OF RATE EQUATIONS

The solution of the Eqs. (A8)–(A16) can be constructed by changing to the Laplace transform $F_M(s)=\int_0^\infty\exp(-st)P_M(t)\,dt$ of all electronic populations.

Noting the initial condition $P_M(0)=\delta_{M,D}$ the solution of the Laplace-transformed rate equations (A9)–(A11) and (A13)–(A15) governing the bridge populations P_m and $P_{\tilde{n}}$ are obtained as

$$F_m(s)=\frac{1}{D_1(s)}[k_{D1}\alpha^{m-1}C_N(m)F_D(s)+k_{IN}\beta^{N-m}C_1(m)F_I(s)] \tag{B1}$$

and as

$$F_{\tilde{n}}(s)=\frac{1}{D_2(s)}[k_{I1}\alpha^{n-1}\tilde{C}_N(n)F_I(s)+k_{AN}\beta^{N-n}\tilde{C}_1(n)F_A(s)]. \tag{B2}$$

The following abbreviations have been introduced:

$$\begin{aligned} D_1(s)=&\,sD(s;N-1)+[s(k_{1D}+k_{NI})+\beta k_{1D}+\alpha k_{NI}\\ &+k_{1D}k_{NI}]D(s;N-2)-\alpha\beta(k_{1D}+k_{NI})\\ &\times D(s;N-3), \end{aligned} \tag{B3}$$

$$\begin{aligned} D_2(s)=&\,sD(s;N-1)+[s(k_{1I}+k_{NA})+\beta k_{1I}+\alpha k_{NA}\\ &+k_{1I}k_{NA}]D(s;N-2)-\alpha\beta(k_{1I}+k_{NA})\\ &\times D(s;N-3) \end{aligned} \tag{B4}$$

as well as

$$\begin{aligned} &C_N(m)=(k_{NI}-\alpha)D(s;N-m-1)+D(s;N-m),\\ &C_1(m)=(k_{1D}-\beta)D(s;m-2)+D(s;m-1), \end{aligned} \tag{B5}$$

and

$$\begin{aligned} &\tilde{C}_N(n)=(k_{NA}-\alpha)D(s;N-n-1)+D(s;N-n),\\ &\tilde{C}_1(n)=(k_{1I}-\beta)D(s;n-2)+D(s;n-1). \end{aligned} \tag{B6}$$

In the Eqs. (B3)–(B6), we introduced a new function $D(s;M)$, which obeys the recursion relation

$$D(s;M)=(s+\alpha+\beta)D(s;M-1)-\alpha\beta D(s;M). \tag{B7}$$

It follows

$$D(s;M)=(\alpha\beta)^{M/2}\frac{\sinh[\Lambda(s)(M+1)]}{\sinh\Lambda(s)}, \tag{B8}$$

where

$$\exp\Lambda(s)=(s+\alpha+\beta)/(2\alpha\beta)^{1/2}. \tag{B9}$$

Introducing the expressions (B1) and (B2) into the Eqs. (A8), (A12), and (A16) results in three coupled equations for the Laplace-transformed population of the states $|D\rangle$, $|I\rangle$, and $|A\rangle$. The equations read

$$\begin{aligned} &(s-R_{DD}(s))F_D(s)-R_{DI}(s)F_I(s)-k_{AD}F_A(s)=1,\\ &R_{ID}(s)F_D(s)-(s-R_{II}(s))F_I(s)+R_{IA}(s)F_A(s)=0,\\ &k_{DA}F_D(s)+R_{AI}(s)F_I(s)-(s-R_{AA}(s))F_A(s)=0, \end{aligned} \tag{B10}$$

with the abbreviations

$$\begin{aligned} &R_{DD}(s)=\frac{k_{1D}k_{D1}C_N(1)}{D_1(s)},\quad R_{DI}(s)=\frac{k_{1D}k_{IN}\beta^{N-1}}{D_1(s)},\\ &R_{ID}(s)=\frac{k_{NI}k_{D1}\alpha^{N-1}}{D_1(s)},\quad R_{AA}(s)=\frac{k_{NA}k_{AN}\tilde{C}_1(N)}{D_2(s)},\\ &R_{AI}(s)=\frac{k_{NA}k_{I1}\alpha^{N-1}}{D_2(s)},\quad R_{IA}(s)=\frac{k_{1I}k_{AN}\beta^{N-1}}{D_2(s)},\\ &R_{II}(s)=(k_{IN}-k_{ID})-\frac{k_{NI}k_{IN}C_1(N)}{D_1(s)}+(k_{I1}-k_{IA})\\ &\qquad-\frac{k_{1I}k_{I1}\tilde{C}_N(1)}{D_2(s)}. \end{aligned} \tag{B11}$$

Then, by solving the Eqs. (B10), expressions for the Laplace transform of P_D, P_I, and P_D are obtained as

$$\begin{aligned} &F_D(s)=\frac{1}{\mathrm{Det}(s)}[(s-R_{II}(s))(s-R_{AA}(s))\\ &\qquad-R_{IA}(s)R_{AI}(s)],\\ &F_I(s)=\frac{1}{\mathrm{Det}(s)}[R_{ID}(s)(s-R_{AA}(s))+R_{IA}(s)k_{DA}],\\ &F_A(s)=\frac{1}{\mathrm{Det}(s)}[k_{DA}(s-R_{II}(s))+R_{ID}(s)R_{AI}(s)], \end{aligned} \tag{B12}$$

where we introduced

$$\begin{aligned} \mathrm{Det}(s)=&\,(s-R_{DD}(s))(s-R_{II}(s))(s-R_{AA}(s))\\ &-[R_{IA}(s)R_{AI}(s)(s-R_{DD}(s))+R_{DI}(s)R_{ID}(s)\\ &\times(s-R_{AA}(s))+k_{AD}k_{DA}(s-R_{II}(s))]\\ &-R_{DI}(s)R_{IA}(s)k_{DA}-R_{AI}(s)R_{ID}(s)k_{AD}]. \end{aligned} \tag{B13}$$

Laplace-transformed bridge populations, $F_m(s)$ and $F_{\tilde{n}}(s)$, are expressed by those of the donor, acceptor, and intermediate state population [$F_D(s)$, $F_I(s)$, and $F_A(s)$, respectively].

The exact solution for all Laplace-transformed populations $F_M(s)$ $[M=D,I,A,1,\ldots,N,\tilde{1},\ldots,\tilde{N}]$, Eqs. (B1), (B2), and (B12) permits a description of the TET kinetics within all time domains (provided that $t\gg\tau_{\mathrm{rel}}$). Solving $\mathrm{Det}(s)=0$ (at least numerically) one obtains $2N+2$ nonzero roots $s_1,s_2,\ldots,s_{2N+2}$ which determine the transfer rates according to $K_1=-s_1$, $K_2=-s_2$, $\ldots$, $K_{2N+2}=-s_{2N+2}$. Therefore, state populations follow as Eq. (30).

APPENDIX C: SUPEREXCHANGE COUPLINGS AT *D–A* TET

Next we present the square of the superexchange couplings characterizing the distant single-electron ($|D\rangle\rightleftarrows|I\rangle$ and $|I\rangle\rightleftarrows|A\rangle$) and the distant two-electron ($|D\rangle\rightleftarrows|A\rangle$) transfer. Their precise form follows from the specification of the transfer matrix elements $\mathcal{K}_{MN}$, Eq. (29). It yields

$$|T_{DI}|^2=\frac{|V_{D1}V_B^{N-1}V_{NA}|^2}{\Pi_{m=1}^N\Delta E_{mD}\Delta E_{mI}}, \tag{C1}$$

$$|T_{IA}|^2=\frac{|V'_{D1}V_B^{N-1}V'_{NA}|^2}{\Pi_{m=1}^N\Delta\tilde{E}_{mI}\Delta\tilde{E}_{mA}}, \tag{C2}$$

and

$$\begin{aligned} |T_{DA}|^2=&\frac{|V_{D1}V_B^{N-1}V_{NA}|^2}{\Pi_{m=1}^N\Delta E_{mD}\Delta E_{mA}\Delta E_{ID}}\\ &\times\frac{|V'_{D1}V_B^{N-1}V'_{NA}|^2}{\Pi_{m=1}^N\Delta\tilde{E}_{mD}\Delta\tilde{E}_{mA}\Delta E_{IA}}. \end{aligned} \tag{C3}$$

The gaps in the Eqs. (C1)–(C3) are defined as the energy differences between the corresponding electron vibrational states but taken at the vibrational ground state. If an energy bias in the bridge is absent, a part of the energy gaps is represented in Fig. 3. From this we may conclude that $\Delta E_{mD}=\Delta E_D$, $\Delta E_{mI}=\Delta E_I$, $\Delta E_{mA}=\Delta E_A$, $\Delta\tilde{E}_{mD}=\Delta\tilde{E}_D$, $\Delta\tilde{E}_{mI}=\Delta\tilde{E}_I$, $\Delta\tilde{E}_{mA}=\Delta\tilde{E}_A$.

If a bridge with an energy bias mediates the D–A TET, the energy gaps take a more complicated form. For instance, if the energy gaps $\Delta E_{1D}=\Delta E_D$, $\Delta E_{NI}=\Delta E_I$, $\Delta\tilde{E}_{1I}=\Delta\tilde{E}_I$, and $\Delta\tilde{E}_{NA}=\Delta\tilde{E}_A$ are fixed while the electronic energies of the interior bridge units change in line with Eq. (11), one has to take

$$\Delta E_{mD}=\Delta E_D-(m-1)\Delta, \tag{C4}$$

$$\Delta\tilde{E}_{mD}=\Delta\tilde{E}_D-(m-1)\Delta-(N-1)\Delta, \tag{C5}$$

$$\Delta E_{mI}=\Delta E_I+(N-m)\Delta, \tag{C6}$$

$$\Delta\tilde{E}_{nI}=\Delta\tilde{E}_I-(n-1)\Delta, \tag{C7}$$

$$\Delta E_{nA}=\Delta E_A+(N-n)\Delta+(N-1)\Delta, \tag{C8}$$

$$\Delta\tilde{E}_{nA}=\Delta\tilde{E}_A+(N-n)\Delta, \tag{C9}$$

and

$$\Delta E_{ID}=(\Delta E_D-\Delta E_I)-(N-1)\Delta, \tag{C10}$$

$$\Delta E_{IA}=(\Delta E_A-\Delta E_I)+(N-1)\Delta, \tag{C11}$$

$$\Delta E_{DA}=\Delta E+2(N-1)\Delta. \tag{C12}$$

The relations (C4)–(C11) allow to derive an analytical dependence of the superexchange rate constants on the number of bridging units N (see below).

Using Eq. (C1) and Eq. (C2) one can represent the square of the two-electron coupling (C3) as

$$|T_{DA}|^2=\frac{|\tilde{T}_{DI}\tilde{T}_{IA}|^2}{\Delta E_{ID}\Delta E_{IA}}. \tag{C13}$$

Here we have introduced

$$|\tilde{T}_{DI}|^2=|T_{DI}|^2\prod_{m=1}^{N}(\Delta E_{mI}/\Delta E_{mA}),$$
$$|\tilde{T}_{IA}|^2=|T_{IA}|^2\prod_{m=1}^{N}(\Delta\tilde{E}_{mI}/\Delta\tilde{E}_{mD}). \tag{C14}$$

If an energetic bias is not present in the bridge the latter quantities simplify to give

$$|\tilde{T}_{DI}|^2=|T_{DI}|^2(\Delta E_I/\Delta E_A)^N,$$
$$|\tilde{T}_{IA}|^2=|T_{IA}|^2(\Delta\tilde{E}_I/\Delta\tilde{E}_D)^N. \tag{C15}$$

It follows from the definition of the electronic states (see also Fig. 3) that $\Delta\tilde{E}_D=\Delta E_{ID}+\Delta\tilde{E}_I$, $\Delta E_A=\Delta E_{IA}+\Delta E_I$, and thus if $\Delta E_{ID}\ll\Delta\tilde{E}_I$ and $\Delta E_{IA}\ll\Delta E_I$, we may identify

$$|T_{DA}|^2=\frac{|T_{DI}T_{IA}|^2}{\Delta E_{ID}\Delta E_{IA}}, \tag{C16}$$

where now

$$|T_{DI}|^2=\frac{|V_{D1}V_{NA}|^2}{\Delta E_D\Delta E_I}\left(\frac{V_B}{\Delta E_D\Delta E_I}\right)^{N-1}, \tag{C17}$$

$$|T_{IA}|^2=\frac{|V'_{D1}V'_{NA}|^2}{\Delta\tilde{E}_I\Delta\tilde{E}_A}\left(\frac{V_B}{\Delta\tilde{E}_I\Delta\tilde{E}_A}\right)^{N-1}. \tag{C18}$$

[Note that the same expressions follow from the general form (C14) if the energy difference between the electronic states $|D\rangle$, $|I\rangle$ and $|A\rangle$ is small, so that $\Delta E_{mI}\approx\Delta E_{mA}$ and $\Delta\tilde{E}_{mI}\approx\Delta\tilde{E}_{mD}$.] Equation (C16) reflects the fact that the two-electron superexchange through a bridge of N units results from two single-electron D–A superexchange pathways associated with the couplings T_{DI} and T_{IA}. In other words, the two-electron superexchange is originated by repeated single-electron superexchange transitions.

In the case of a regular bridge and at a small intersite energy bias Δ the basic expressions (C1)–(C3) can be transformed into a more appealing form. Therefore, we rewrite the denominators of the expressions (C1)–(C3) by utilizing the relations (C4)–(C11). Let us start with the specification of the product $\Pi_{m=1}^{N}\Delta E_{mD}$. According to the identity

$$\prod_{m=1}^{N}\Delta E_{mD}=(\Delta E_D)^N\prod_{m=1}^{N}[1-(m-1)(\Delta/\Delta E_D)]$$
$$=(\Delta E_D)^N\exp\left\{\sum_{m=1}^{N}\ln[1-(m-1)\times(\Delta/\Delta E_D)]\right\} \tag{C19}$$

and by noting the limit of a small intersite energy bias $(N-1)\Delta\ll\Delta E_D$, one can expand $\ln[1-(m-1)(\Delta/\Delta E_D)]$ with respect to $(m-1)(\Delta/\Delta E_D)$. The lowest order contribution gives

$$\prod_{m=1}^{N}\Delta E_{mD}=(\Delta E_D)^N e^{-(1/2)(\Delta/\Delta E_D)N(N-1)}. \tag{C20}$$

In the same way one can specify the approximate form of the product $\Pi_{m=1}^{N}\Delta E_{mI}$. Therefore, in accordance with Eq. (C1) one may derive

$$|T_{DI}|^2\approx\frac{|V_{D1}V_{NA}|^2}{\Delta E_D\Delta E_I}e^{-\zeta_1(N-1)}e^{-\zeta_{DI}N(N-1)}. \tag{C21}$$

Here the superexchange decay parameter ζ_1 is defined by Eq. (65). We have also introduced an additional parameter

$$\zeta_{DI}=\frac{1}{2}\left(\frac{\Delta}{\Delta E_I}-\frac{\Delta}{\Delta E_D}\right)>0 \tag{C22}$$

which modifies the N dependence of the superexchange coupling. Analogously, by using the approximate form of the product $\Pi_{m=1}^{N}\Delta\tilde{E}_{mI}\Delta\tilde{E}_{mA}$ one can represent Eq. (C2) as

$$|T_{IA}|^2\approx\frac{|V'_{D1}V'_{NA}|^2}{\Delta\tilde{E}_I\Delta\tilde{E}_A}e^{-\zeta_2(N-1)}e^{\zeta_{IA}N(N-1)}. \tag{C23}$$

Here, the superexchange decay parameter ζ_2 is defined by Eq. (66) while

$$\zeta_{IA}=\frac{1}{2}\left(\frac{\Delta}{\Delta\tilde{E}_I}-\frac{\Delta}{\Delta\tilde{E}_A}\right)>0. \tag{C24}$$

Note that due to the inequalities $\Delta E_I < \Delta E_D$ and $\Delta \tilde{E}_I < \Delta \tilde{E}_A$ (cf. Fig. 3) the correction parameters ζ_{DI} and ζ_{IA} become positive. Therefore, a different influence of the energy bias Δ exist on the factors $|T_{DI}|^2$ and $|T_{IA}|^2$.

Taking the same approximations the two-electron coupling reads

$$|T_{DA}|^2 \approx \frac{|V_{D1}V_{NA}V'_{D1}V'_{NA}|^2}{\Delta E_D \Delta E_A \Delta \tilde{E}_D \Delta \tilde{E}_A \Delta E_{ID} \Delta E_{IA}} \times e^{-\zeta(N-1)} e^{\zeta_{DA} N(N-1)}, \tag{C25}$$

where the two-electron superexchange decay parameter ζ is given by Eq. (69), and

$$\zeta_{DA} = \frac{1}{2}\left[\left(\frac{\Delta}{\Delta E_D} + 3\,\frac{\Delta}{\Delta \tilde{E}_D}\right) - \left(\frac{\Delta}{\Delta \tilde{E}_A} + 3\,\frac{\Delta}{\Delta E_A}\right)\right]. \tag{C26}$$

The Eqs. (C21), (C23), and (C25) allow to analyze the corrections to the distance dependence of the superexchange transfer rates when a small intrabridge energy bias Δ is present.

[1] M. P. Patel and J. S. Blanchard, Biochemistry **40**, 5119 (2001).

[2] L. J. C. Jeuken, A. K. Jones, S. K. Chapmen, G. Cecchini, and F. A. Armstrong, J. Am. Chem. Soc. **124**, 5702 (2002).

[3] J. H. Kim, M. G. Ryan, H. Knaut, and R. Hille, J. Biol. Chem. **271**, 6771 (1996).

[4] M. Pavlov, Per E. M. Siegbahn, M. R. A. Blomberg, and R. H. Crabtree, J. Am. Chem. Soc. **120**, 548 (1998).

[5] S. Iwata, C. Ostermeier, B. Ludwig, and H. Michel, Nature (London) **376**, 660 (1995).

[6] J. W. Peters, W. N. Lanziltta, B. J. Lemon, and L. C. Seefeld, Science **282**, 1853 (1998).

[7] Per E. M. Siegbahn and R. H. Crabtree, J. Am. Chem. Soc. **119**, 3103 (1997).

[8] H. Dobbek, V. Svetlitchnyi, L. Gremer, R. Huber, and O. Meyer, Science **293**, 1281 (2001).

[9] R. Huber, P. Hof, R. O. Duarte, J. J. G. Moura, M.-Y. Liu, J. LeGall, R. Hille, M. M. Archer, and M. J. Romao, Proc. Natl. Acad. Sci. U.S.A. **93**, 8846 (1996).

[10] A. Kohen and J. P. Klinman, Acc. Chem. Res. **31**, 397 (1998).

[11] S. M. Kanzok, R. H. Schirmer, I. Türbachova, R. Iozeff, and K. Becker, J. Biol. Chem. **275**, 40180 (2000).

[12] A. Niemz, J. Imbriglio, and V. M. Rotello, J. Am. Chem. Soc. **119**, 887 (1997).

[13] F. A. Armstrong, H. A. Heering, and J. Hirst, Chem. Soc. Rev. **26**, 169 (1997).

[14] P. K. Agarwal, S. P. Webb, and S. Hammes-Schiefer, J. Am. Chem. Soc. **122**, 4803 (2000).

[15] S. P. Webb, P. K. Agarwal, and S. Hammes-Schiefer, J. Phys. Chem. B **104**, 8884 (2000).

[16] R. Marcus, Annu. Rev. Phys. Chem. **15**, 155 (1964); Angew. Chem. **105**, 101 (1993).

[17] I.-S. H. Lee, E. H. Jeoung, and M. M. Kreevoy, J. Am. Chem. Soc. **119**, 2722 (1997).

[18] E. G. Petrov and V. May, J. Phys. Chem. A **105**, 10176 (2001); E. G. Petrov, Ye. V. Shevchenko, V. I. Teslenko, and V. May, J. Chem. Phys. **115**, 7107 (2001).

[19] M. Bixon and J. Jortner, Chem. Phys. **281**, 393 (2002).

[20] E. G. Petrov, Ye. V. Shevchenko, and V. May, Chem. Phys. **288**, 269 (2003).

[21] L. D. Zusman and D. N. Beratan, J. Chem. Phys. **105**, 165 (1996); J. Phys. Chem. A **101**, 4136 (1997); J. Chem. Phys. **110**, 10468 (1999).

[22] T. Bandyopadhyay, A. Okada, and M. Tachiya, J. Chem. Phys. **110**, 9630 (1999).

[23] K. V. Mikkelsen and M. A. Ratner, Chem. Rev. **87**, 113 (1987).

[24] M. D. Newton, Chem. Rev. **91**, 767 (1991).

[25] R. A. Marcus and N. Sutin, Biochim. Biophys. Acta **811**, 265 (1985).

[26] D. N. Beratan, J. N. Onuchic, and H. B. Gray, in *Metal Ions in Biological Systems*, edited by H. Sigel and A. Sigel (Dekker, New York, 1991), Vol. 27, pp. 97–127.

[27] B. H. Gray and J. R. Winkler, Annu. Rev. Biochem. **65**, 537 (1996).

[28] J. Jortner and M. Bixon (eds.), Adv. Chem. Phys. **106, 107** (1999) (series eds. I. Prigogine and S. A. Rice).

[29] O. Farver and I. Pecht, Adv. Chem. Phys. **107**, 555 (1999).

[30] D. DeVault, *Quantum-Mechanical Tunneling in Biological Systems*, 2nd ed. (Cambridge University Press, London, 1984).

[31] E. G. Petrov, *Physics of Charge Transfer in Biosystems* (Naukowa Dumka, Kiev, 1984) (in Russian).

[32] A. M. Kuznetsov, J. Ulstrup, and T. Sov, *Electron Transfer in Chemistry and Biology: An Introduction to the Theory* (Wiley, New York, 1998).

[33] V. May and O. Kühn, *Charge and Energy Transfer Dynamics in Molecular Systems* (Wiley-VCH, Berlin, 1999).

[34] A. A. Demidenko and E. G. Petrov, Theor. Math. Phys. **49**, 928 (1982).

[35] E. G. Petrov and P. Hänggi, Phys. Rev. Lett. **86**, 2862 (2001); E. G. Petrov, V. May, and P. Hänggi, Chem. Phys. **281**, 211 (2002).

[36] D. Segal, A. Nitzan, W. B. Davis, M. R. Wasielewski, and M. A. Ratner, J. Phys. Chem. B **104**, 3817 (2000).

[37] D. Segal and A. Nitzan, Chem. Phys. **281**, 235 (2002).

[38] V. May, Phys. Rev. B **66**, 245411 (2002).

[39] J. Jortner, J. Chem. Phys. **64**, 4860 (1976).

[40] G. S. M. Tong, I. V. Kurnikov, and D. N. Beratan, J. Phys. Chem. B **106**, 2381 (2002).

[41] E. G. Petrov, V. I. Teslenko, and V. May, Phys. Rev. E **68**, 061916 (2003).