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On the theory of nonadiabatic bridge–mediated electron transfer

Influence of structural and energetic disorder

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Abstract. Effects of structural and energetic disorder on nonadiabatic electron transfer (ET) reactions are discussed theoretically. To account for the sequential as well as the superexchange mechanism of ET our recent approach is used presented in J. Phys. Chem. A **105**, 10176 (2001). The overall charge motion is characterized by the numerical solution of rate equations for the electronic state populations and an averaging with respect to the disorder configurations. Introducing a single effective transfer rate which can be deduced from the experiment the dependence of this rate is discussed on the geometry of the ET system as well as on the disorder model. The theory is applied to donor–acceptor complexes connected by oligomers of the amino acid proline. In particular, a pronounced dependence is found of the effective transfer rate on disorder with respect to the reorganization energy.

PACS. 34.10.+x General theories and models of atomic and molecular collisions and interactions (including statistical theories, transition state, stochastic and trajectory models, etc.) – 34.30.+h Intramolecular energy transfer; intramolecular dynamics; dynamics of van der Waals molecules – 31.70.Hq Time-dependent phenomena: excitation and relaxation processes, and reaction rates

1 Introduction

It is a ubiquitous observation that any electron transfer (ET) reaction in molecular donor–acceptor (DA) complexes is influenced by effects of structural disorder [1,2]. Disorder may alternate the ET through the bridging (B) units interconnecting the D and the A as well as through a change of the ET parameters in the D and A unit itself. Numerous studies addressed this problem (see, *e.g.* [1] for a recent overview). The influence of structural disorder on a simple model DBA–complex has been investigated in [3]. Related studies for molecular wires may be found in [4,5]. Proteins as well as the DNA have been considered in [6] and [7], respectively.

Typically all these descriptions are based on fluctuating parameters, like the site energies and the inter–site couplings which are not derived from a microscopic model. Such a more involved attempt becomes possible if one combines MD simulations with quantum chemical calculations of the various electronic energies and tunneling matrix elements (see, for example, Refs. [8,9]). Although such a treatment is of large methodological interest it often suffices to introduce normal distributions for the respective ET parameters.

In the present paper we will follow this last mentioned approach but we will not only deal with so–called diagonal and off–diagonal disorder, *i.e.* disorder with respect to the various site energies of the transferred electron (diabatic energies) and the inter–site couplings, respectively. Instead, disorder with respect to the electron–vibrational coupling is considered, too. Moreover our studies are focused on nonadiabatic bridge mediated ET. If the site energies of the bridge are far away from the D and A level (some eV above) the ET may be characterized by two different mechanisms. One leads to a direct (coherent) charge motion from the D to the A and is known as the superexchange ET. The other one describes sequential (nonadiabatic) ET from one site of the system to the neighboring sites. In order to achieve a uniform description with rate expressions accounting for both mentioned mechanisms we follow our earlier work [10–13].

These our studies are based on a microscopic model which uses a separation of the electronic states of the ET system into (localized) diabatic D, B and A levels. All these levels are augmented to potential energy surfaces (PES) which may comprise intramolecular as well as solvent vibrations. Then, electron–vibrational states introduced in this manner are used to define the electron–vibrational density matrix and to derive respective equations of motion. Provided that the vibrational dynamics

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are fast compared to the characteristic time of the overall ET reaction the description can be reduced to rate equations governing the diabatic (electronic site) populations. However, as a byproduct the correct rates for the elementary hopping and superexchange transitions are obtained. A proper classification of these mechanisms follows from a perturbational expansion of the rates with respect to the inter–site coupling. Since (at least in principal) the diabatic states are many–electron states and the PES include all vibrational coordinates, Coulombic effects among electrons as well as solvent polarizations may be accounted for.

In references [10,11] we could also demonstrate that for small integral bridge populations the complicated bridge–mediated ET reduces to single–exponential kinetics with a transfer rate which is the sum of the overall sequential and superexchange rate. As a general result a distinct change of the overall ET rate with an increasing number of bridge units has been obtained. It indicates the transition from a region where the superexchange mechanism of ET dominates to a region governed by sequential transfer processes.

The approach was successfully applied to explain the measurements of reference [14] on DBA–systems with the bridge units formed by the amino acid proline. It is the aim of the present paper to extend the mentioned description of ET by incorporating the influence of static disorder.

Since the rate equations which describe the ET reaction in a given disorder configuration of the DBA–system are linear we may solve them numerically in computing the *eigenvalues* and *eigenvectors* of the rate matrix. Both types of quantities determine the complete time–dependence of the electronic state populations. Therefore, we may characterize the disorder–averaged ET if we repeatedly calculate the rate matrix *eigenvalues* and *eigenvectors* for every disorder configuration, and, afterwards, introduce the respective configuration average (*cf.*, *e.g.* [15]). Additionally, single overall (effective) transfer rates are introduced to carry out a comparison with experimentally deduced bridge–length dependent rates. As already done in [10,11,13] we apply our theory to ET reactions through a polyproline chain and relate the results to the measured data of [14]. However, it is not the intention of this paper to improve the fit of the measured rates of [14]. Rather we demonstrate the influence of disorder on an ET model with parameters deduced from a concrete experiment.

The paper is organized as follows. In the subsequent section we shortly comment on the used ET model and on the way how to compute disorder averaged electron populations and ET rates. In Section 3 concrete rate expressions are introduced and the results of our numerical simulations are explained in detail. The paper ends with some concluding remarks in Section 4.

2 Electron transfer kinetics

To arrive at rate equations including microscopically founded rate expressions we start with the Hamiltonian of the DBA–system. It is written in the standard form following from an expansion with respect to the local (diabatic) electronic states φ_m of the D, the A, and all B units

$$H_{\mathrm{DBA}} = \sum_{m,n} \Big(\delta_{m,n} H_m(q) + (1-\delta_{m,n}) V_{mn}(q) \Big) \times \mid \varphi_m \rangle \langle \varphi_n \mid . \quad (1)$$

Here, the indices m and n pass through the N bridging units and the D–site ($m = 0$) as well as the A–site ($m = N + 1$). The meaning of the φ_m depends on the type of ET. If an excess electron is moving through the system the φ_m describe the lowest state of the D, B and A part if this additional electron is added. If ET is initiated by an optical excitation of the D the state φ_0 may correspond to the first excited state of the D (but modified due to the embedding in the ET system). But in any case all the φ_m have to be considered as many–electron states (which as already underlined will be not computed in the present paper). The concrete form of the interstate couplings V_{mn} depends on the chosen way to introduce the diabatic states, but in any case, the V_{mn} have to be consider as a many–electron matrix elements. The vibrational Hamiltonian H_m include respective potential energy surfaces PES $U_m(q)$ defined *versus* a certain set $q = \{q_\xi\}$ of vibrational coordinates. In the most general case those might be intramolecular as well as solvent coordinates. As discussed at length in [10] the q can be reduced to intramolecular vibrations if a nonpolar solvent is considered. However, the latter acts as a heat bath for the intramolecular vibrations and cause their fast vibrational relaxation. The equilibrium value $U_m^{(0)}$ of the PES will be identified with the site energy E_m (possibly, the zero–point energy of all vibrations is included).

Once started with the ET–Hamiltonian, equation (1), nonadiabatic ET reactions mediated by a network of B units can be characterized by the following kinetic equations for the electronic site populations (*cf.* [10,11])

$$\frac{\partial}{\partial t} P_m = -\sum_n K_{mn} P_n. \quad (2)$$

The quantities $K_{mm} = \sum_{l \neq m} k_{m \to l}$ and $K_{mn} = -k_{n \to m}$ (for $m \neq n$) are determined by the transition rates $k_{m \to n}$ for the transition from site m to site n. (Since the concrete form of all rates is less important for the following we postpone the presentation of respective expressions to Sect. 3.) The set of kinetic equation (2) guarantees the conservation of probability ($\sum_m P_m = 1$) and has to be completed by the initial condition (usually taken as a complete D population $P_m(0) = \delta_{m,0}$).

2.1 Consideration of disorder

All quantities entering the ET Hamiltonian can be subject to fluctuations caused by structural and energetic disorder. Let us characterize such fluctuations by a set of parameters y which enters the Hamiltonian, equation (1) and

which describes a specific energetic and structural configuration in the DBA complex. A very basic choice would be the identification of these parameters with the Cartesian coordinates describing the spatial arrangement of the D the A and all bridging units. From this, in principle, would follow the concrete form of the ET Hamiltonian, equation (1). A more indirect choice for the set y is the use of the site energies, the transfer integrals and the electron–vibrational couplings defining H_{DBA}, equation (1). (If the transfer proceeds in the high–temperature limit the description of the electron–vibrational coupling can be reduced to the use of the various reorganization energies.) We will proceed by identifying the set y with the site energies, the transfer integrals and the reorganization energies. (By the way, this approach is unavoidable for larger systems since electronic structure calculations generating the disorder of the ET–parameters from structural disorder cannot be repeated, say 10^4 times to achieve good statistics.)

The need to compute disorder averages is caused by the experimental standard techniques to characterize ET like the measuring of the fluorescence decay or the absorbance change of one of the DBA–system parts (*cf.* [1]). All the data are ensemble measures and are directly related to the ensemble (disorder) average of the respective electronic state populations. In order to compute such averaged populations the parameter set y will be additionally labeled by r counting all complexes contained in the sample volume V. Then, the particular state population $P_m(t)$ related to site m differs for different ET systems and we write $P_m(t; y_r)$. The measured value follows as the ensemble (configuration) average $\langle P_m(t)\rangle = \sum_{r\in V} P_m(t; y_r)/n_{\mathrm{DBA}}V$ (n_{DBA} is the volume density of the DBA complexes in the probe).

There are different ways to account for disorder when discussing dynamic phenomena in molecular systems. A direct consideration would be the simulation of the dynamics for every member of the disordered ensemble followed by the ensemble average of the dynamics. (Of course such a direct numerical averaging can be avoided if disorder averaged dynamic equations can be derived.) If the solution of the dynamic equations can be constructed directly, it only remains to introduce the ensemble average with respect to this solution. This is the way we will follow in the present paper. It becomes possible since the rate equations taken to simulate the ET reaction are linear and, consequently, can be formally solved *via* the *eigenvalues* and *eigenvectors* of the rate matrix. This approach is not new and has been extensively used in, for example, discussing excitation energy dynamics in polymeric chains [15].

Once the *eigenvalues* $\kappa(\alpha)$ and *eigenvectors* $e_m(\alpha)$ of the rate matrix K_{mn} have been determined the solution of equation (2) reads as

$$P_m(t) = \sum_{\alpha} c(\alpha)\mathrm{e}_m(\alpha)\mathrm{e}^{-\kappa(\alpha)t}. \tag{3}$$

According to the dimension of K_{mn} the index α runs from 0 to $N+1$. The $\kappa(\alpha)$ are assumed to be ordered with increasing magnitude starting with $\kappa(0) = 0$. Furthermore, we proceed from the assumption that the *eigenvectors* $e_m(\alpha)$ are normalized. The set of arbitrary prefactors $c(\alpha)$ has to be determined by the initial condition for equation (2). Noting that the rate vanishes for $\alpha = 0$ it follows

$$P_m(t) = P_m(\infty) + \sum_{\alpha>0} c(\alpha)\mathrm{e}_m(\alpha)\mathrm{e}^{-\kappa(\alpha)t}, \tag{4}$$

where the $P_m(\infty) = c(0)e_m(0)$ determine the asymptotic value of the population at site m.

Every *eigenvalue* and every component of the respective *eigenvector* as well as the prefactor $c(\alpha)$ depend on the parameter set y characterizing the disorder. Therefore, we can introduce the disorder averaging of the populations according to

$$\langle P_m(t)\rangle = \langle P_m(\infty)\rangle + \frac{1}{Vn_{\mathrm{DBA}}}\sum_{r\in V}\sum_{\alpha>0} c(\alpha; y_r)\mathrm{e}_m(\alpha; y_r)\mathrm{e}^{-\kappa(\alpha;y_r)t}. \tag{5}$$

The notation makes obvious that the averaging can be carried out for every time–dependent part of the population independently. This may become of some advantage if the $\kappa(\alpha)$ differ strongly and one is interested in the long–time behavior only. Then, in equation (5) the complete summation with respect to α may be restricted to the interesting subset.

2.2 Effective transfer rate

Equation (5) demonstrates that the redistribution of electron population described by the $\langle P_m(t)\rangle$ does not follow a multi–exponential law. Nevertheless, it is of some advantage when, for example, studying the dependence of the ET on the DBA geometry (*e.g.* on the length of the bridge in the case of a linear DBA complex), to fit the population by a single–exponential law with an effective ET rate $k_{\mathrm{ET}}^{(\mathrm{eff})}$. Concentrating on the decay of the D population, we choose the following *ansatz*

$$\langle P_D(t)\rangle = \langle P_D(\infty)\rangle + (1 - \langle P_D(\infty)\rangle)\exp\left(-k_{\mathrm{ET}}^{(\mathrm{eff})}t\right). \tag{6}$$

The right–hand side coincides with the correct time–dependence of the disorder averaged D–population for $t = 0$ and $t = \infty$, but interpolates it in between by a simple exponential time–dependence. Therefore, it is just the definition of $k_{\mathrm{ET}}^{(\mathrm{eff})}$. The inverse of $k_{\mathrm{ET}}^{(\mathrm{eff})}$ can be easily obtained by a time–integral

$$\frac{1}{k_{\mathrm{ET}}^{(\mathrm{eff})}} = \int_0^{\infty} \mathrm{d}t\, \frac{\langle P_D(t)\rangle - \langle P_D(\infty)\rangle}{1 - \langle P_D(\infty)\rangle}. \tag{7}$$

The use of this mean (effective) transfer rate corresponds to the well–known approach in the theory of reaction kinetics where a complex transition process is described by

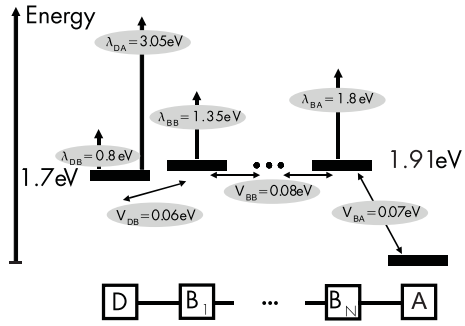


Fig. 1. Energy level scheme for the regular reference D–polyproline–A system according to reference [10]. The thick bars stand for the electronic site energies E_m ($m = D, B_1, ...B_N, A$). The energy gap $\Delta E_{\rm DB}$ between the D and every molecule of the polyproline bridge amounts to 0.21 eV, and for the gap between the D and the A we have $\Delta E_{\rm DA} = 1.7$ eV. All site energies of the bridge units are identical (for the regular system). Respective values for the transfer integrals and reorganization energies are indicated in the graph. The model system studied in parallel to the D–polyproline–A system mainly deviates by assuming identical parameters for the D and the A (vanishing driving force $\Delta E_{\rm DA}$, and $V_{\rm DB} = V_{\rm BA} = 0.06$ eV as well as $\lambda_{\rm DB} = \lambda_{\rm BA} = 0.8$ eV).

a single mean first–passage time (see, for example [16,17]). In a similar way a mean relaxation time of electron transfer processes in regular and stochastic fields can be introduced [18].

If we insert equation (5) into equation (7) it follows

$$k_{\rm ET}^{\rm (eff)} = \frac{\sum\limits_{p\in V}\sum\limits_{\beta>0} c(\beta;y_p)e_D(\beta;y_p)}{\sum\limits_{r\in V}\sum\limits_{\alpha>0} c(\alpha;y_r)e_D(\alpha;y_r)/\kappa(\alpha;y_r)}. \qquad (8)$$

It is obvious that these quantities have to be distinguished from the simply averaged rate $\langle k_{\rm ET}\rangle = \sum_{r\in V}\kappa(1;y_r)/Vn_{\rm DBA}$, where $\kappa(1;y_r)$ characterizes the slowest part of the ET for the given disorder configuration.

3 Numerical results

In the following we will concentrate on a linear arrangement of the D, the N bridge units, and the A (*cf.* Fig. 1) as it is given by the D–polyproline–A system studied experimentally in [14]. The DBA complex is formed by two metal compounds with Ru(II) as the D and Co(III) as the A as well as an oligomer of the aminoacid proline. The whole structure reads $[\{(\mathrm{bpy})_2\mathrm{Ru(II)L}\}\text{-}(\mathrm{Pro})_n\mathrm{Co(III)(NH_3)_5}]^{3+}$. It has been discussed at length in references [10,11] that this system nicely demonstrates the transition of the ET from the superexchange mechanism to the sequential one when enlarging the bridge.

Although no comments have been given in [14] on the possible influence of disorder we will use this system here to demonstrate the importance of energetic disorder when discussing ET reactions. The system attracts particular interest since it shows the transition from superexchange to sequential ET. And, an additional advantage is that the ET proceeds in the high–temperature limit. Since the two ET regimes are dominated by different sets of ET parameters we expect a different influence of disorder effects. The obtained behavior in the experimentally studied D–polyproline–A is confronted by the ET in a fictitious system (model system) where the D and the A couple with identical parameters to the bridge and where the driving force $\Delta E_{\rm DA}$ vanishes (all parameters can be found in the caption to Fig. 1).

As it was shown in [10,11] the ET in D–polyproline–A is of the nonadiabatic type and takes place in a region where quantum effects of the nuclear motion are absent (high–temperature limit). Therefore, one type of rate–expressions entering K_{mn} in equation (2) describes sequential ET between neighboring sites

$$k_{m\to n}^{\rm (seq)} = \frac{2\pi}{\hbar}|V_{mn}|^2\mathcal{D}_{mn}(\Delta E_{mn}). \qquad (9)$$

The quantity $\mathcal{D}_{mn}$ is the (combined Franck–Condon weighted and thermally averaged) density of states and $\Delta E_{mn} = E_m - E_n$ denotes the driving force for the transition from site m to site n. In the high–temperature limit $\mathcal{D}_{mn}$ becomes of the Marcus–type and reads

$$\mathcal{D}_{mn}(\Delta E_{mn}) = \frac{1}{\sqrt{4\pi\lambda_{mn}k_{\rm B}T}} \times \exp\left\{-\frac{(\Delta E_{mn}-\lambda_{mn})^2}{4\lambda_{mn}k_{\rm B}T}\right\}. \qquad (10)$$

The reorganization energy λ_{mn} may be written as

$$\lambda_{mn} = \frac{1}{2}\sum_{\xi}\omega_\xi^2\left(q_\xi^{(m)} - q_\xi^{(n)}\right)^2 \qquad (11)$$

provided that the ET couples to (mass–weighted) normal–mode coordinates whose frequencies ω_ξ do not change with the change of the electronic diabatic state level φ_m ($q_\xi^{(m)}$ and $q_\xi^{(n)}$ denote respective equilibrium positions).

Besides the rates of sequential transfer which couple the D with the first proline molecule in the B, the A with the last one, and neighboring prolines within the B, there is a direct coupling between D and the A *via* the superexchange mechanism of ET. The respective rate expression reads

$$k_{\rm D\to A}^{\rm (super)} = \frac{2\pi}{\hbar}|T_{\rm DA}|^2\mathcal{D}_{\rm DA}(\Delta E_{\rm DA}) \qquad (12)$$

where $\mathcal{D}_{\rm DA}$ is given by equation (10) (including the reorganization energy $\lambda_{\rm DA}$) and the superexchange coupling matrix element follows as (*cf.*, *e.g.*, [10,11])

$$T_{\rm DA} = \frac{V_{\rm D,1}V_{1,2}...V_{N-1,N}V_{N,\rm A}}{\sqrt{\Delta E_{1\rm D}\Delta E_{1\rm A}\Delta E_{2\rm D}\Delta E_{2\rm A}...\Delta E_{N\rm D}\Delta E_{N\rm A}}}. \qquad (13)$$

The various driving forces $\Delta E_{m\rm D}$ and $\Delta E_{m\rm A}$ are the result of an additional approximation replacing the

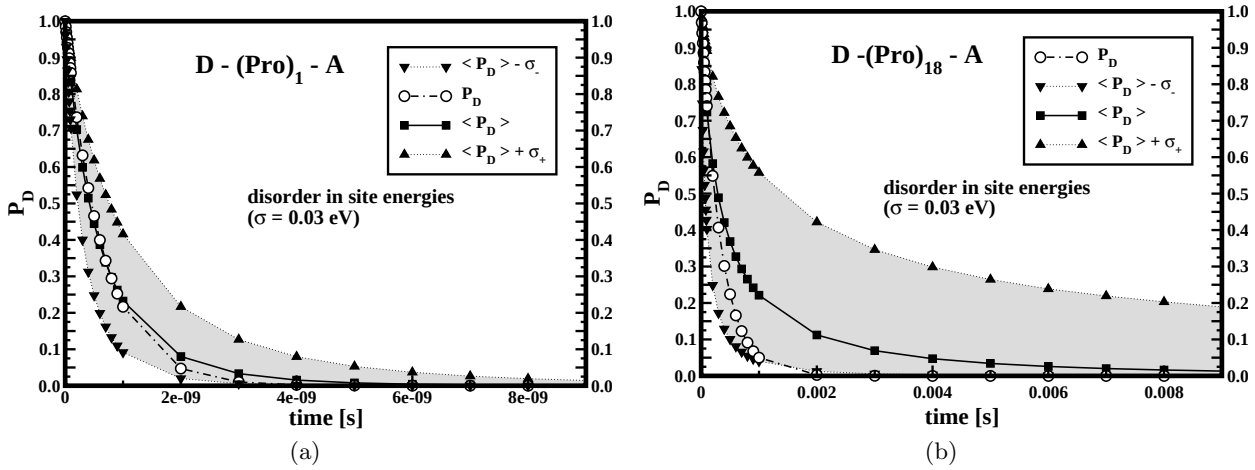


Fig. 2. Time–dependence of the donor population for the case of diagonal disorder in the D–polyproline–A system. (a) Bridge with a single proline molecule, (b) bridge with 18 proline molecules (for further parameters see inset and Fig. 1). The configuration averaged population $\langle P_D \rangle$, the population of the ordered reference system P_D, and the upwards and downwards mean deviations are shown.

correct electron–vibrational spectra by single energy differences (for more details see [10]). Furthermore, the Frank–Condon factors accompanying the coupling matrix elements have been also removed. Finally, we note that all rates obey the detailed balance law

$$k_{n\to m} = \exp\left[-\frac{\Delta E_{mn}}{k_{\mathrm{B}}T}\right] k_{m\to n}. \tag{14}$$

3.1 Description of disorder

As already stated the easiest approach to account for disorder would be the assumption that every parameter entering the rate formulas of the preceding section may fluctuate according to a Gaussian distribution around the ensemble average. Since nonadiabtic ET in the high–temperature limit is considered the fluctuating parameters comprise the site energies E_m, the inter–site coupling energies V_{mn} and the reorganization energies λ_{mn}. The (static) fluctuations of the reorganization energies may look somewhat unusual. But equation (11) indicates that these fluctuations are caused by structural fluctuations too, namely by those leading to an alteration of all quantities describing the coupling of the transferred electron to the nuclear motion.

3.2 Influence of disorder on the time dependence of the populations

In order to illustrate the disorder influence on the time dependence of the ET the donor population is singled out imagining an experiment where the decay of this population is directly measured *e.g. via* fluorescence decay or change of absorbance of the D. Besides plotting the ensemble average $\langle P_D \rangle$ of the donor population the standard deviation will be indicated at every time step, too. Since a quantity is considered which decays nearly exponentially it is necessary to distinguish between the upper ($\Delta P_D^{(+)}(t) \equiv \sigma_+(t)$) and the lower ($\Delta P_D^{(-)}(t) \equiv \sigma_-(t)$) standard deviations. They are defined as

$$\Delta P_D^{(\pm)}(t) \equiv \sigma_\pm(t) = \left\{ \frac{1}{V n_{\mathrm{DBA}}^{(\pm)}} \sum_r \left(P_D^{(\pm)}(t; y_r) - \langle P_D(t) \rangle \right)^2 \right\}^{\frac{1}{2}}, \tag{15}$$

where the summation concerns all those subsystems where the actual population either deviates upwards ($P_D^{(+)}(t; y_r)$) or downwards ($P_D^{(-)}(t; y_r)$) from the mean value ($n_{\mathrm{DBA}}^{(\pm)}$ denotes the respective volume densities). To get an impression of the scattering of the donor population within the ensemble besides $\langle P_D \rangle$ we also draw $\langle P_D \rangle + \Delta P_D^{(+)}$ and $\langle P_D \rangle - \Delta P_D^{(-)}$. The respective stripes around $\langle P_D \rangle$ (*cf.* Figs. 2 to 5) show the region where the majority of D populations decays. The result P_D for the regular (without disorder) D–polyproline–A system or regular model system is given as a reference. Both quantities follow from using the ensemble averages of all ET parameters involved.

Let us start with the case where all couplings and reorganization energies are fixed and only fluctuations of the site energies are allowed. Figures 2 to 5 show the results for the D–polyproline–A system as well as for the model system. A general observation would be that disorder favors a slower decrease of the D population at long times than the regular case predicts. This behavior is independent of the concrete system and the extension of the bridge.

DBA complexes bridged by one to three proline molecules are dominated by the superexchange ET (Figs. 2a and 4a). The transfer of an electron along a proline chain with more than three units can be chiefly attributed to the hopping mechanism (see Figs. 2b and 4b). As it has to be expected the proline system will barely

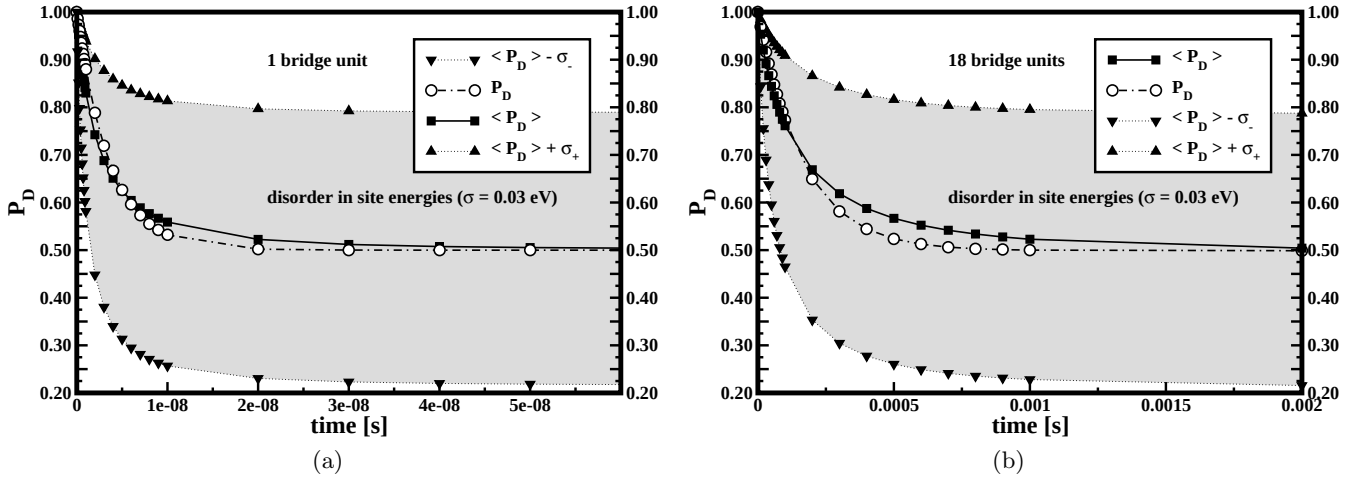


Fig. 3. Time–dependence of the donor population for the case of diagonal disorder in the DBA model system. (a) Bridge with a single unit, (b) bridge with 18 units (for further parameters see inset and Fig. 1). The configuration averaged population $\langle P_D \rangle$, the population of the ordered reference system P_D, and the upwards and downwards mean deviations are shown.

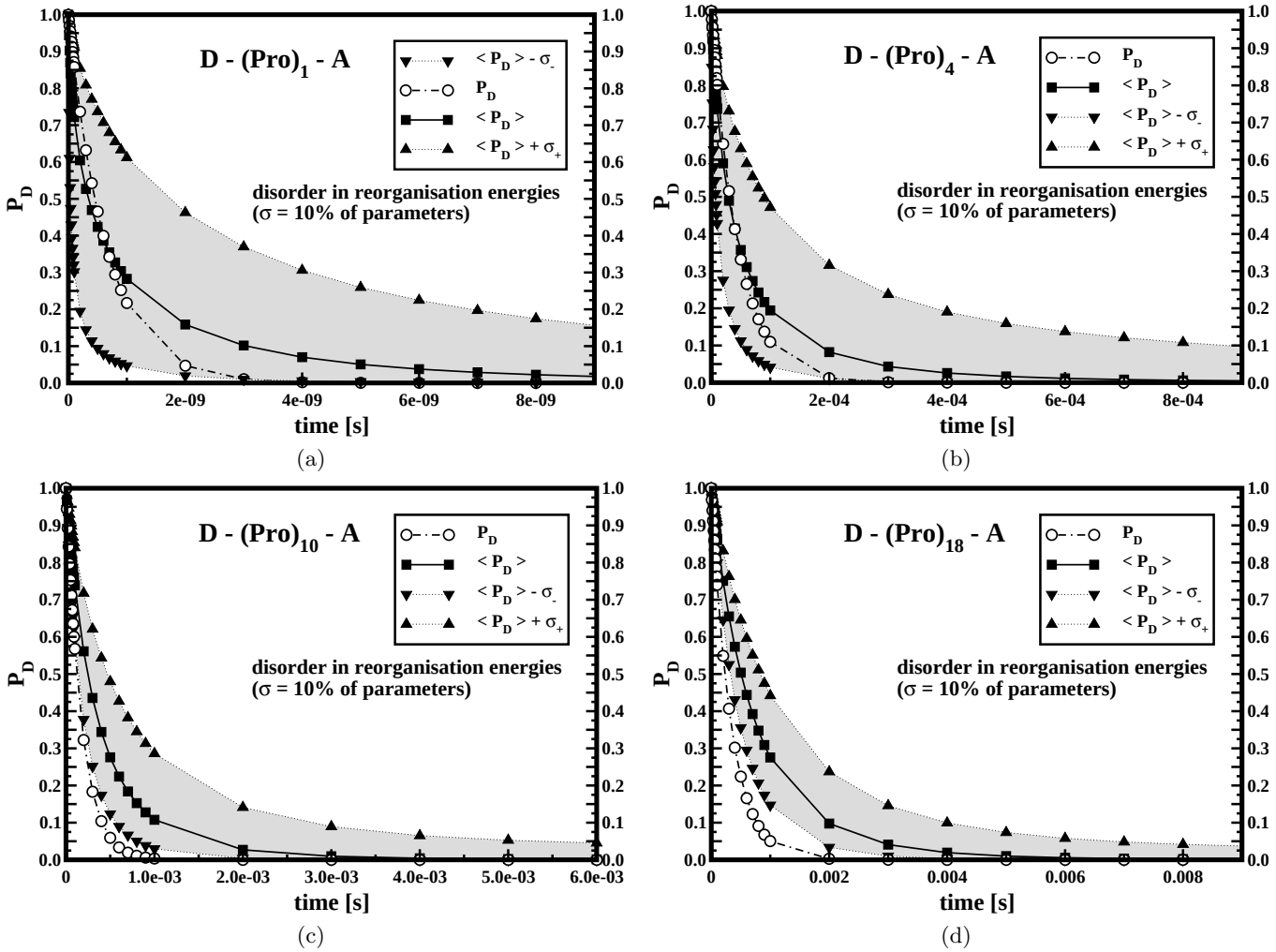


Fig. 4. Time–dependence of the donor population for the case of disorder with respect to the reorganization energies in the D–polyproline–A system. (a) Bridge with a single proline molecule, (b) bridge with four proline molecules, (c) bridge with 10 proline molecules, (d) bridge with 18 proline molecules (for further parameters see inset and Fig. 1). The configuration averaged population $\langle P_D \rangle$, the population of the ordered reference system P_D, and the upwards and downwards mean deviations are shown.

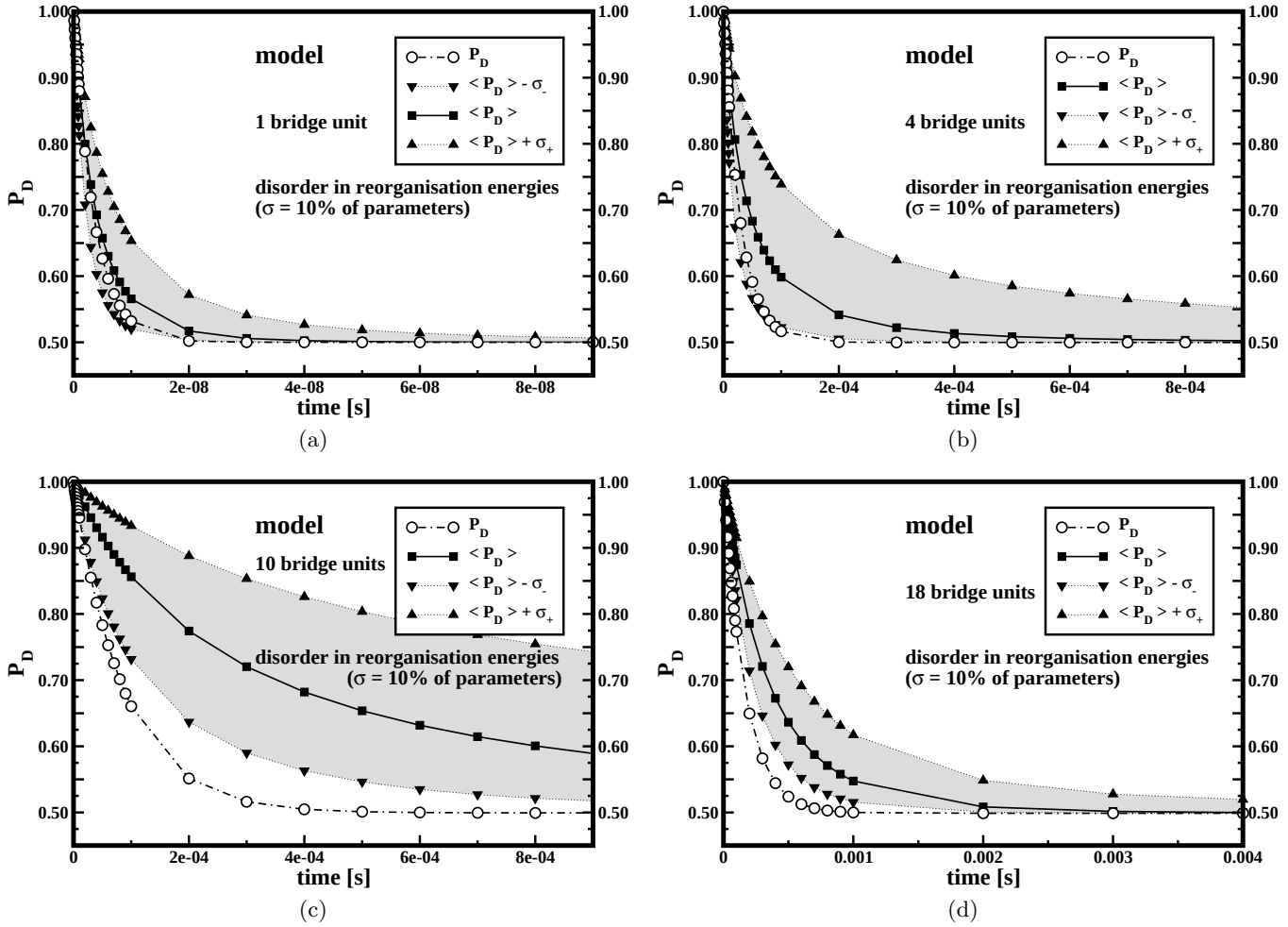
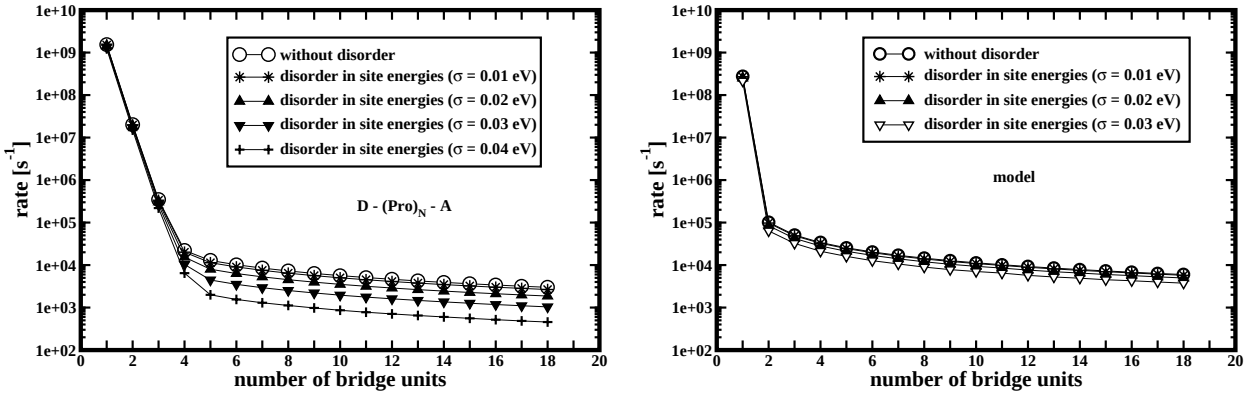


Fig. 5. Time–dependence of the donor population for the case of disorder with respect to the reorganization energies in the DBA model system. (a) Bridge with a single unit, (b) bridge part with four units, (c) bridge with 10 units, (d) bridge with 18 units (for further parameters see inset and Fig. 1). The configuration averaged population $\langle P_D \rangle$, the population of the ordered reference system P_D, and the upwards and downwards mean deviations are shown.

be influenced by disorder for those bridge lengths where the superexchange contributes the most to the ET process (Fig. 2a). ET through longer proline chains is dominated by the sequential ET and shows a stronger dependence on disorder. In contrast to the polyproline system, the main contribution in the model system comes from the sequential transfer for any number of bridge molecules (*cf.* Figs. 3 and 5). Regarding the dependence on the number of bridge units, the ET in the superexchange–dominated proline systems will be faster by one or two orders of magnitude compared to that in the model system. For a larger number of bridge molecules the situation will change and the electron transport in the proline system will lag behind that of its model counterpart. For all the examples studied so far $\langle P_D(t) \rangle$ and $P_D(t)$ cross each other at times that vary between $1/\kappa(1)$ and $1/3\kappa(1)$ given for the rigid system. The greater the disorder the slower does the occupation of the donor site decline after the crossing point, and most prominently so for long–range ET (compare graphs in Fig. 2).

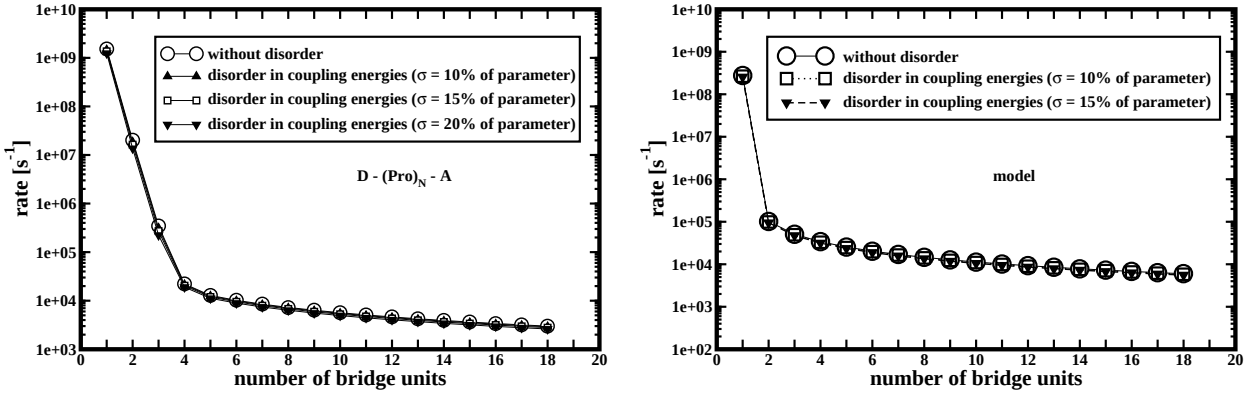
The site-energy gap of $\Delta E_{\mathrm{DA}} = 1.7$ eV in polyproline causes the donor to be depopulated virtually entirely. Due to the missing driving force ($\Delta E_{\mathrm{DA}} = 0$ eV) in the model system it results $P_D(\infty) = 0.5$. Furthermore, apart from the timescales, there is no principal difference in how the P_D– and $\langle P_D \rangle$-curves of the model systems run for the case with a single bridge (see Fig. 3a) and the case with 18 bridge units (Fig. 3b). This has to be expected since all chain lengths are dominated by the hopping mechanism.

Interestingly there is only a minor influence of fluctuating inter–site couplings on the ET (we do not give concrete data here but refer to Fig. 7 explained in the following section). Therefore we will turn to an investigation of the influence of fluctuating reorganization energies. Figures 4 and 5 show a sequence of diagrams for DBA complexes with a single, with four, ten, and eighteen proline molecules whose every reorganization energies have been generated by normal distributions with standard deviations of 10% of the respective mean value (*cf.* Fig. 1). For all numbers of bridge units the run of the curves



(a) (b)

Fig. 6. Bridge–length dependence of the effective transfer rate, equation (8) for the case of diagonal disorder (with standard deviation σ). (a) D–polyproline–A system, (b) DBA model system (for the used parameters see inset and Fig. 1).



(a) (b)

Fig. 7. Bridge–length dependence of the effective transfer rate, equation (8), for the case of off–diagonal disorder (with standard deviation σ). (a) D–polyproline–A system, (b) DBA model system (for the used parameters see inset and Fig. 1).

related to the disorder (ensemble) average are distinct from that of the regular system. This behavior is valid for the D–polyproline–A system as well as the model system. Such an influence of disorder with respect to the electron–vibration coupling has also to be expected when discussing the effective transfer rates defined in equation (8). This will be the subject of the following section.

3.3 Disorder effects on the length dependence of the effective transfer rate

The dependence of the effective transfer rate $k_{\mathrm{ET}}^{(\mathrm{eff})}$, equation (8) on the extension of the bridge is shown in Figures 6 to 8. As in the ordered DBA–system the effective rate changes in its bridge–length dependence if the the number of bridge units reaches four (D–polyproline–A system, *cf.* Figs. 6a to 8a) or two (model system, *cf.* Figs. 6b to 8b), indicating the transition from the superexchange dominated ET to sequential ET. However, for any number of bridge units $k_{\mathrm{ET}}^{(\mathrm{eff})}$ is smaller than the rate of the respective rigid system. This is synonymous to a slower asymptotic population redistribution from the D to the A.

Concentrating first on fluctuations of the site energies (see Fig. 6) the influence of disorder on the proline systems is stronger than that on the model system. And following from the disorder influence on the time–dependence of the populations (*cf.* Figs. 2 and 3) the effective rate decreases when increasing the strength of site–energy fluctuations. In contrast to this behavior the influence of disorder in the coupling energies is negligible as can be seen from Figures 7. Only a very slight affection by disorder appears in the superexchange–dominated regions of the D–polyproline–A system.

Finally, Figures 8 display the bridge–length dependence of the effective ET rate as influenced by disorder with respect to the reorganization energies. Both types of studied systems are notably affected by disorder in the reorganization energies. The ideal D–polyproline–A reference system shows a kink at the transition point where superexchange–dominated ET reactions are replaced by those dominated by hopping transitions (see top of Fig. 8 and also [10,11]). In contrast, the disordered curves run rather smoothly. Since such a smooth transition for the

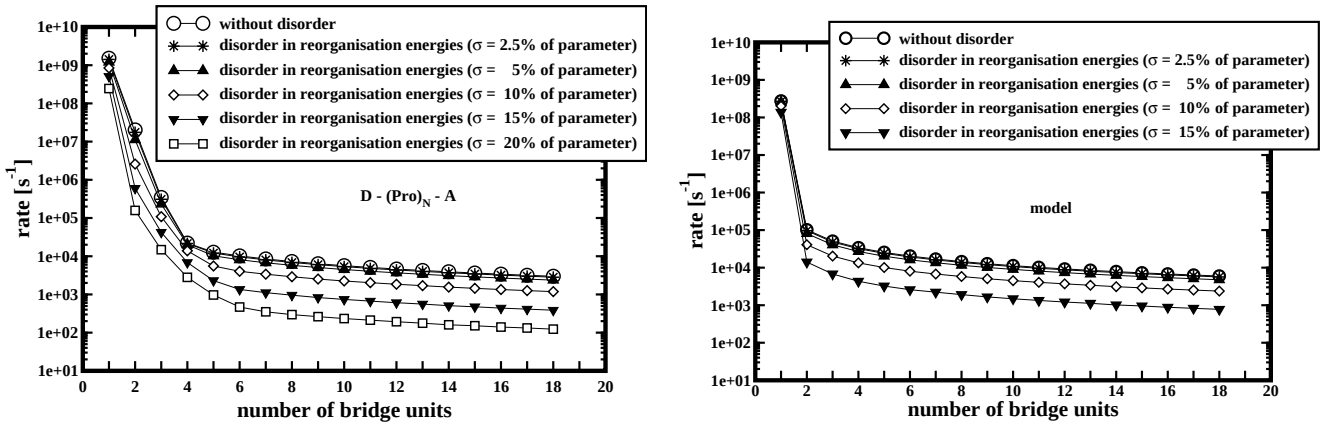


Fig. 8. Bridge–length dependence of the effective transfer rate, equation (8) for the case of disorder with respect to the reorganization energies (with standard deviation σ). (a) D–polyproline–A system, (b) DBA model system (for the used parameters see inset and Fig. 1).

length–dependence of the rate has been observed in the experiment [14] the present incorporation of disorder improves the calculation published in the foregoing papers [10,11].

All effects of disorder for small bridges (left from the kink) have to be attributed to the reorganization energy λ_{DA}, which is directly related to the dominating superexchange mechanism. As soon as the bridge is enlarged to reach the hopping dominated transfer, the relevance of disorder effects is swapped between the reorganization parameters. Disorder in λ_{DA} does not contribute to a reduction in the effective transfer rate, but fluctuations in all other reorganization energies do.

Figure 8b also includes a kink at two bridge units. This is due to the missing bridge parameters at one bridge unit, which disallows a direct comparison with systems that include more than one bridge unit. Therefore, a smoothing by disorder cannot be expected.

4 Conclusions

The influence of energetic disorder on nonadiabatic ET reactions in donor bridge acceptor systems has been discussed theoretically. The approach is based on rate equations for the electronic state populations which account for the superexchange type of ET reaction as well as the sequential type. The solution of the rate equations has been achieved in determining the *eigenvalues* and *eigenvectors* of the rate matrix. The remaining configuration (disorder) averaging has been carried out with respect to the resulting multi–exponential form of the electronic state populations. Since the high–temperature limit of nonadiabatic ET has been considered structural disorder could be mapped on fluctuating site–energies, inter–site couplings and reorganization energies. The incorporation of the latter quantities is in contrast to other studies on the influence of disorder on ET reactions.

Numerical calculations have been presented for the D–polyproline–A system $[\{(\mathrm{bpy})_2\mathrm{Ru(II)L}\}^{\cdot}(\mathrm{Pro})_n\,\mathrm{Co(III)(NH_3)_5}]^{3+}$ with a varying number of proline bridge molecules as studied experimentally in [14] and theoretically (without the account of disorder) in [10,11]. The results are confronted with those of a fictitious model system with vanishing driving force between the donor and the acceptor and similar coupling of both to the terminal units of the proline chain.

A single effective transfer rate has been introduced to study the influence of disorder on the bridge–length dependence of the ET rate. This effective rate is different from a simple configuration averaged rate and properly reflects the time–asymptotics of the ET reaction. It shows a remarkable dependence on (statically) fluctuating reorganization energies, especially for the D–polyproline–A system. Furthermore, the effective rate in its dependence on the bridge length is characterized by a smooth transition from the region where the superexchange mechanisms of ET dominates to the region governed by sequential transition processes. This behavior coincides much better with the observations than that offered within a theory neglecting any influence of disorder.

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