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Effects of the potential barrier fluctuations in non-adiabatic long-distance electron transfer

Abstract Equations for the transition probability of non-adiabatic electron transfer are derived which take into account both the effect of reorganization of "non-symmetric" classical or quantum vibrational modes and the effects which are due to the dependence of the electron matrix element on the normal coordinates of "promoting" vibrational modes. Any number of vibrational modes with an arbitrary frequency spectrum are incorporated in a simple manner. The results are represented in a simple form convenient for the analysis of the dependence of the transition probability on the temperature, transfer distance, and driving force.

Keywords Non-adiabatic transitions · Promoting modes · Free energy relationships

Introduction

It is known that the effects of fluctuational preparation of the potential barrier for a tunneling particle may be of importance to charge transfer processes in condensed media. The physical meaning of this effect consists of the fact that the matrix element V_{DA} coupling the initial (at the donor site D) and final (at the acceptor site A) states of the tunneling particle may depend significantly on the coordinates q of the environmental vibrational modes [1, 2, 3, 4, 5, 6]. In view of the large number of works in this field, and in order to make the aim of the present paper clear, some points giving background on this topic are now presented.

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First, two different physical situations can be distinguished. The first one corresponds to the case where the tunneling particle interacts with the vibrational modes that undergo reorganization in the course of the transition (the so called "non-symmetric" modes). In the classical limit, the configuration of these nuclear modes at the top of the barrier separating the initial and final states along the optimum path is called the "transitional configuration". In the Condon approximation the transitional configuration coincides with the saddle point at the crossing of the diabatic free energy surfaces. The dependence of the electron matrix element on the coordinates of the non-symmetric vibrational modes may lead to a violation of the Condon approximation. This means that the electron matrix element participates in the competition for the transitional configuration. Non-Condon effects of this sort have been broadly investigated theoretically [1, 2, 3, 4, 5, 6] (see also [7] and references therein).

A second situation corresponds to the case where the tunneling particle interacts with the atoms whose equilibrium positions remain unchanged after the transition. Vibrational modes of this sort are called "promoting" [7]. In the absence of the above interaction, the promoting modes do not participate in the transition at all. However, if this interaction exists, these modes can significantly affect the transition probability, even in the absence of the non-Condon effects mentioned earlier.

Another situation of this type arises in particular when the tunneling is to some extent blocked by atoms of the molecular environment. A fluctuational shift of the atoms from their equilibrium positions then opens the "gate" for the transition. In this interpretation, the effect of these modes on the transition probability may be called "gating", as a particular case of a broader class of gating phenomena (which are out of the scope of the present paper). This situation is typical of the tunnel transfer of light atoms and defects in solids, and has been considered in detail with due account given to various effects in both low-temperature and classical limits [8, 9, 10] (for a general approach see [7]). A similar

effect has been discussed for biological processes of atom transfer [11, 12] and for electrochemical proton transfer in clathrates [13]. In fact, the same qualitative physical consequences also emerge for so-called distance-dependent tunneling [14].

The effect of the promoting modes on the transition probability has been mainly investigated for the transfer of atoms and atomic groups and is much less studied for electron transfer processes. The reason for this is that electron wave functions are much more delocalized and less sensitive to the fluctuations of the molecular environment. Therefore the effects under discussion may be insignificant in short-range electron transfer. The situation is different for long-distance electron transfer, where the overlaps of the electron wave functions occur at the tails of the electron densities, and even minor variations in the wave functions' decay can significantly affect the electron matrix element.

Electron transfer to long distances may occur in artificially organized molecular ensembles like adsorbed films and molecular layers [15, 16]. This is also a rather common phenomenon in biological macromolecules (see for example [17]). The preparation "of the favorable activation barrier for electron transfer through a well adjusted transient change of the intervening protein structure" is considered to be a possible mechanism for the acceleration of the reaction [18]. However, the change in the protein structure may also produce an effect on the barrier for the electron tunneling. It is assumed that electron transfer in such systems is facilitated by intermediate bridge groups. The participation of high- and low-lying molecular orbitals of these groups in the process is usually considered [7, 19, 20, 21, 22]. The only paper where the effect of promoting modes was discussed in relation to long-distance electron transfer in biological systems is [23], where some simple models of electron coupling with the protein "promoting" modes were considered (such as the exponential dependence of the electron matrix element on oscillator normal coordinates, neglecting the frequency dispersion). It was found in particular that this effect leads to a distortion of the shape of the rate constant versus driving force dependence, and a shift in its maximum. A similar effect was observed in our earlier work [24] on electron transfer in polar media. We refer the reader to [23] (and many references therein) for a detailed discussion of the relationship between the effects under investigation and other numerous theoretical works on non-Condon effects. The method used in [23] is rather complicated (although general) and requires considerable simplifying assumptions in some important models. At the same time another general approach exists [7], which allows for some approximations to be relaxed.

The goal of this paper is to elaborate rather general and simple equations for the description of the effect of promoting modes in long-distance electron transfer. They are convenient for both analytical and numerical calculations, and can serve as a framework for the treatment of experimental data. The treatment suggested is equally applicable to electron transfer processes in liquid and solid environments, as well as in biological macromolecules.

General relationships

A non-adiabatic electron transfer between a donor D and acceptor A mediated by bridge groups B is considered below. It is assumed that the electron orbitals of the bridge groups correspond to the superexchange situation. The electron transfer through dynamically populated intermediate states requires a different treatment and will be considered elsewhere.

The non-adiabatic character of the reaction implies that it is rather slow, so that the equilibrium distribution for all vibrational modes is maintained in the initial state. This means that both non-symmetric and promoting modes are considered on the same footing.

The transition probability for the non-adiabatic reaction may be written as follows [7]:

$$W_{DA} = \frac{1}{i\hbar k_B T} Z_i^{-1} \int_{c-i\infty}^{c+i\infty} d\theta \int dq\,dq'\, V_{DA}(q) V_{DA}(q') \rho_i$$
$$\times (q, q'; 1-\theta) \rho_f(q, q'; \theta) \qquad (1)$$

where $V_{DA}(q)$ is the effective electron matrix element (assumed to be a real quantity) coupling the donor and acceptor states, ρ_i and ρ_f are the vibrational density matrices calculated at the effective temperatures $T/(1-\theta)$ and T/θ, respectively, Z_i is the statistical sum of the initial state, the integration is performed over the dimensionless normal coordinates of vibrational modes q and over θ (along a contour parallel to imaginary axis).

The often-used Condon approximation means that the dependence of $V_{DA}(q)$ on the vibrational coordinates q is ignored. Our aim below is opposite. We want to estimate the effects arising from to the dependence of $V_{DA}(q)$ on some of the q-coordinates – on the coordinates of the "promoting" modes q_s.

A significant effect may be expected in the case of a strong q-dependence of $V_{DA}(q)$, such as of the type

$$V_{DA}(q_s) = V_{DA}^0 \exp\left[-B(q_s)\right] \qquad (2)$$

with a linear

$$B(q_s) = \frac{1}{2}\sum_k \gamma_k q_{sk} \qquad (3)$$

or a stronger dependence of the function $B(q_s)$ on q_s.

For the sake of definiteness we shall accept the exponential dependence of Eqs. 2 and 3 where the coupling constants γ_k may depend on the transfer distance R. In this model some further transformations may be performed exactly.

Introducing the new variables $(q+q')/2$ and $q-q'$ into Eq. 1 and integrating over $q-q'$ we obtain

$$W_{DA} = \frac{1}{i\hbar k_B T} Z_i^{-1} \int\limits_{c-i\infty}^{c+i\infty} d\theta \int dq V_{DA}^2(q)\Phi_i$$
$$\times (q; 1-\theta)\Phi_f(q;\theta)A(q) \qquad (4)$$

where $\Phi_i(q;1-\theta)$ and $\Phi_f(q;\theta)$ are the diagonal matrix elements of the density matrices (the quantum distribution functions) and $A(q)$ is a "width" arising after the integration over $q-q'$. For the model of harmonic vibrations with unchanged frequencies these have the form

$$\Phi_i(q,1-\theta) = \prod_k \left[\frac{1}{\pi}\tanh\frac{\hbar\omega_k(1-\theta)}{2k_B T}\right]^{1/2}$$
$$\times \exp\left[-(q_k - q_{k0i})^2 \tanh\frac{\hbar\omega_k(1-\theta)}{2k_B T}\right] \qquad (5)$$

$$\Phi_f(q,\theta) = \prod_k \left[\frac{1}{\pi}\tanh\frac{\hbar\omega_k\theta}{2k_B T}\right]^{1/2}$$
$$\times \exp\left[-(q_k - q_{k0f})^2 \tanh\frac{\hbar\omega_k\theta}{2k_B T}\right] \qquad (6)$$

$$A = \prod_k \frac{\sinh\frac{\hbar\omega_k}{2k_B T}}{\sinh\frac{\hbar\omega_k}{2k_B T} + \sinh\frac{\hbar\omega_k(1-2\theta)}{2k_B T}} \qquad (7)$$

where q_{k0i} and q_{k0f} are the equilibrium values of the normal coordinates of the "non-symmetric" modes, and those for the "promoting" modes are assumed to be zero, $q_{sk}^{0i} = q_{sk}^{0f} = 0$.

Equation 4 may be handled using various models and approximations. For example, rather general forms can be obtained in the high-temperature (classical) limit for the vibrational subsystem [7]. However, in order to be able to take into account possible quantum effects, we shall accept the model of harmonic vibrations below.

Model of harmonic vibrations

It will be assumed that the vibrational subsystem may be described as a set of harmonic oscillators of frequencies ω_{sk} (for "promoting" modes) and ω_l (for "non-symmetric" modes). The electron transfer results in the reorganization of the "non-symmetric" modes with reorganization energies E_{rl}. The total reorganization energy of the classical "non-symmetric" modes will be denoted as E_s.

In this model, the integration over vibrational coordinates is straightforward, with due account of Eqs. 2, 3, 5–7 resulting in

$$W_{DA} = \frac{1}{i\hbar k_B T}\left(V_{DA}^0\right)^2 \int\limits_{c-i\infty}^{c+i\infty} d\theta \exp\left[-H(\theta) - \beta\theta\Delta F\right] \qquad (8)$$

where $\beta = 1/k_B T$, and ΔF is the free energy of the transition (driving force),

$$H(\theta) = \beta\theta(1-\theta)E_s + \sum_l \frac{E_{rl}}{\left(\frac{1}{2}\hbar\omega_l\right)}\frac{\sinh\frac{\beta\hbar\omega_l(1-\theta)}{2}\sinh\frac{\beta\hbar\omega_l\theta}{2}}{\sinh\frac{\beta\hbar\omega_l}{2}}$$
$$- \frac{1}{4}\sum_k \gamma_k^2 \frac{\cosh\frac{\beta\hbar\omega_{sk}(1-\theta)}{2}\cosh\frac{\beta\hbar\omega_{sk}\theta}{2}}{\sinh\frac{\beta\hbar\omega_{sk}}{2}} \qquad (9)$$

and the summation is performed over all "promoting" (sk) and "non-symmetric"(l) modes.

Equations 8 and 9 differ from those of the ordinary electron transfer theory by the presence of the last term in Eq. 9, which is responsible for the modulation of the tunnel barrier, and are reduced to the latter at $\gamma_k = 0$. The effect of promoting modes results in an increase in the transition probability.

If the reorganization energy of the classical vibrational modes E_s is sufficiently large ($E_s >> k_B T$), the integral over θ may be calculated by the saddle point method, which gives

$$W_{DA} \approx \frac{\sqrt{2\pi}}{\hbar k_B T}\left(V_{DA}^0\right)^2\left[-\frac{d^2 H(\alpha)}{d\alpha^2}\right]^{-1/2}\exp\left[\alpha\frac{dH(\alpha)}{d\alpha} - H(\alpha)\right] \qquad (10)$$

where α is determined by Eq. 11:

$$\Delta F = -k_B T \frac{dH(\alpha)}{d\alpha} \qquad (11)$$

Equations 10 and 11 together with Eq. 9 for $H(\theta)$ ($\theta = \alpha$) give a parametric dependence of the transition probability on the driving force with the symmetry factor α playing the role of running variable [25]. Although these equations allow us to handle the systems with an arbitrary number of modes straightforwardly, a simple illustrative example will be considered below.

Effect of single promoting mode

In order to reveal the effect of the barrier fluctuations, one "promoting" bridge mode with frequency ω_s (and zero reorganization energy) is considered below, along with a set of classical environmental non-symmetric vibrational modes and one non-classical local mode with reorganization energies E_s and E_{rl} respectively. In the analysis of this effect, only its absolute value was usually estimated. The driving force dependence of the effect was first incorporated in [13] for the low-temperature hydrogen evolution from clathrates and in [23] for electron transfer. Below we shall illustrate this dependence in the model under consideration using the equations derived above. Equation 11 then takes the form

$$\Delta F = -(1-2\alpha)E_s - E_{rl}\frac{\sinh\frac{\beta\hbar\omega_l(1-2\alpha)}{2}}{\sinh\frac{\beta\hbar\omega_l}{2}}$$
$$- \frac{\gamma^2\hbar\omega_s}{8}\frac{\sinh\frac{\beta\hbar\omega_s(1-2\alpha)}{2}}{\sinh\frac{\beta\hbar\omega_s}{2}} \qquad (12)$$

In the absence of coupling with the promoting modes ($\gamma = 0$) and at $E_{rl} = 0$ this equation gives a known dependence of the symmetry factor on the driving force (Fig. 1)

$$\alpha = \frac{1}{2}\left(1 + \frac{\Delta F}{E_s}\right) \tag{13}$$
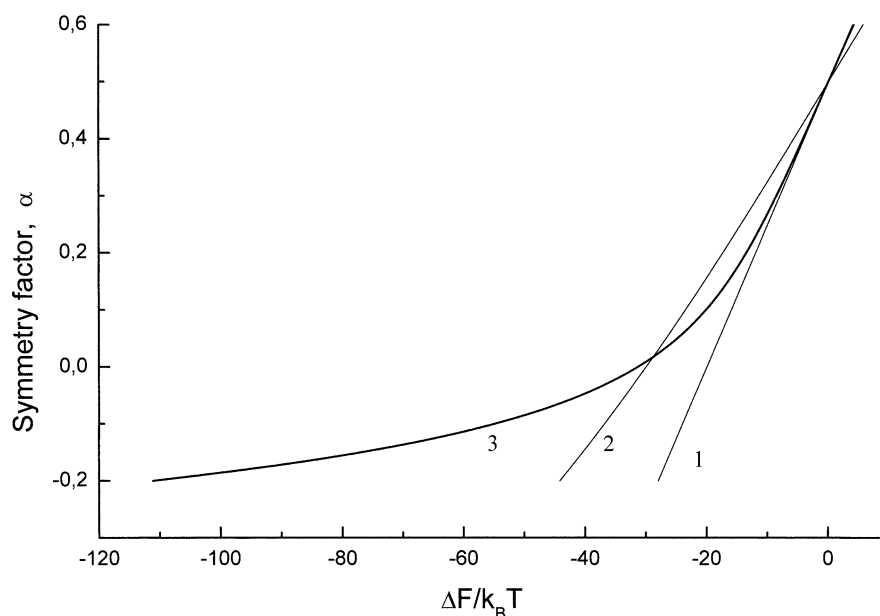
The effect of the barrier preparation is different depending on the vibrational frequency of the "promoting" mode. For low-frequency "promoting" modes ($\hbar\omega_s \ll k_B T$) its effect reduces to a shift in the reorganization energy

$$E_s \rightarrow E_s + \frac{\gamma^2 \hbar\omega_s}{8} \tag{14}$$

In view of the condition $\hbar\omega_s \ll k_B T$, this correction to E_s is usually small and the shape of the dependence of the transition probability on the driving force remains practically unchanged. However, the effect on the transition probability may still be considerable (Fig. 2) depending on the values of the coupling constant γ.

In the case of high-frequency "promoting" modes ($\hbar\omega_s \gg k_B T$), the dependence of α on ΔF is considerably modified in the region near $\alpha \approx 0$ (Fig. 1). This fact is also reflected in the dependence of $\log W_{DA}$ on ΔF, resulting in a shift of the maximum and a broadening of the curve (Fig. 3). In this respect the effect of the promoting mode is similar to that from high-frequency non-symmetric modes (see the second term in the right-hand side of Eq. 9). The difference is that the reorganization of the latter results in a decrease of the transition probability, whereas the fluctuations along the promoting mode lead to the increase in the transition probability (see curves 2 and 3 in Fig. 3).

Discussion and concluding remarks

The main new results of the present paper are Eqs. 9–11 for the transition probability of electron transfer, taking into account both the effect of reorganization of "non-symmetric" classical or quantum vibrational modes and the effect of preparation of the tunnel barrier due to the dependence of the electron matrix element on the normal coordinates of "promoting" vibrational modes. These equations obtained in the model of harmonic vibrations represent simple forms, which are convenient for the analysis of the dependence of the transition probability on the temperature, transfer distance, and driving force. The driving force dependence may be easily calculated with the use of standard programs available for PCs as a parametric plot of the type

$$W_{DA} = f(\alpha); \quad \Delta F = \varphi(\alpha) \tag{15}$$

with the symmetry factor α as running variable. It should be emphasized that any number of vibrational modes with arbitrary frequencies are incorporated in a simple manner (as a one-fold summation) without considerable increase in the computing time. This is an advantage over some other forms (see [23] for instance) where the incorporation of additional modes is performed by cumbersome calculations of the multiple sums of the products of several functions, or requires considerable simplifying approximations. The only restriction for the results obtained here is the assumption of sufficiently large reorganization energy for the classical vibrational modes (see inequality above Eq. 10). More generally, Eq. 4 may be used for calculations in other models and in other various limiting cases. We refer to a general approach in [7].

Fig. 1 The dependence of the symmetry factor α on the driving force. Curve 1: $E_s/k_B T = 20$, $E_1 = 0$, $\hbar\omega_1/2k_B T = 1$, $\hbar\omega_s/2k_B T = 5$, $\gamma = 0$; curve 2: 20, 10, 1, 5, 0; curve 3: 20, 0, 1, 5, 3

Fig. 2 The dependence of the transition probability on the driving force (low-frequency promoting mode; a weak dependence of the pre-exponential factor is ignored). Curve 1: $E_s/k_BT = 40$, $E_l = 0$, $\hbar\omega_l/2k_BT = 1$, $\hbar\omega_s/2k_BT = 0.1$, $\gamma = 0$; curve 2: 40, 0, 1, 0.1, 1; curve 3: 40, 0, 1, 0.1, 3
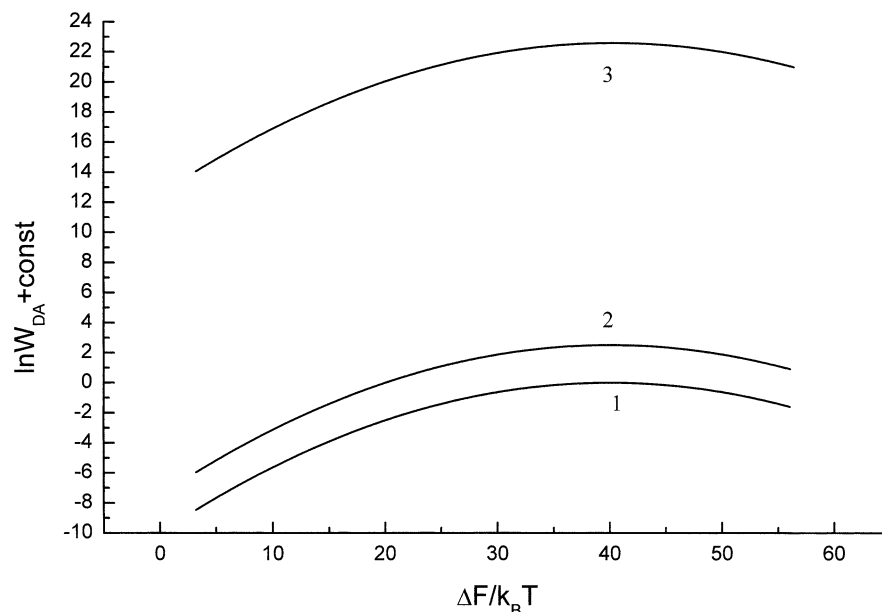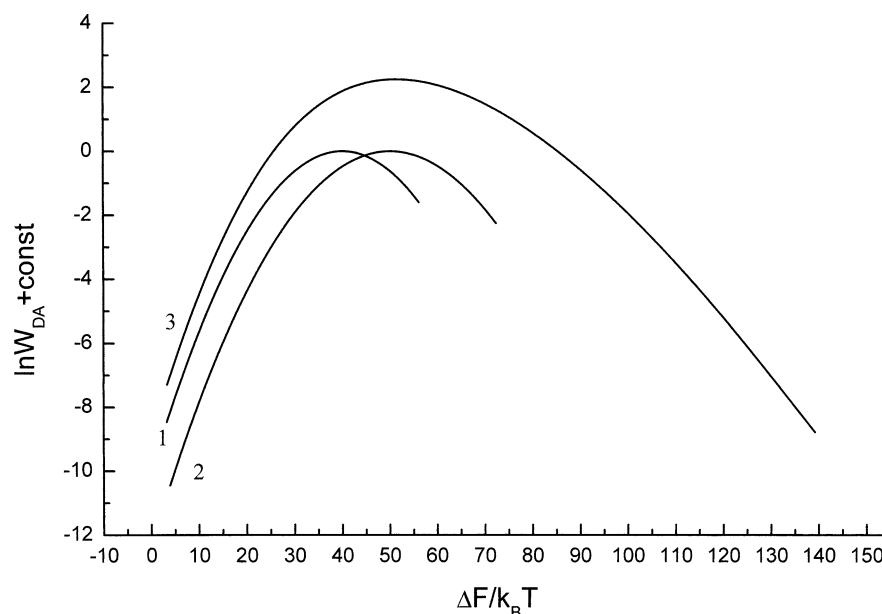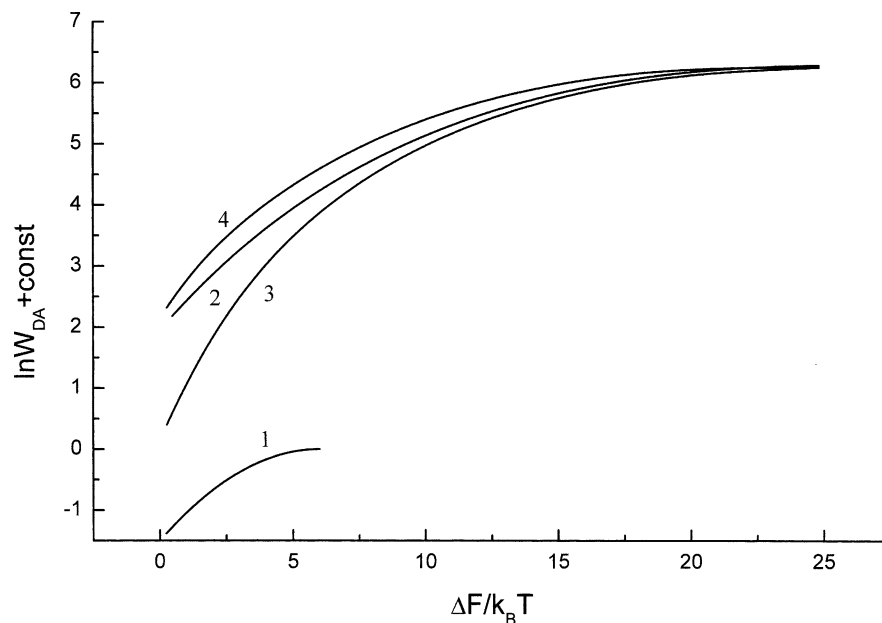

Fig. 3 The dependence of the transition probability on the driving force (high-frequency promoting mode). Curve 1: $E_s/k_BT = 40$, $E_l = 0$, $\hbar\omega_l/2k_BT = 1$, $\hbar\omega_s/2k_BT = 5$, $\gamma = 0$; curve 2: 40, 10, 1, 5, 0; curve 3: 40, 0, 1, 5, 3

The most direct effect of the barrier preparation is the increase in the transition probability, which depends on the coupling constants γ_k. Another one consists of the shift of the maximum in the log W_{DA} versus ΔF dependence and an increase in its width. It should be emphasized that the latter effect is due to the fact that the coupling of the electron tunneling with the fluctuations of the promoting modes allows for the dependence of the tunnel probability on the driving force of the transition, which is entirely absent in traditional electron transfer theory [26]. This could be a possible reason for some observed phenomena of electron transfer in biological systems. In particular, this may be of relevance to the reported data on the charge recombination from the primary quinone to the bacteriochlorophyll dimer of the reaction center from the photosynthetic purple bacterium *Rhodobacter sphaeroides* [27]. Various mutants were used to study the driving force dependence of the reaction rate constant at different temperatures. A slight increase of the reaction rate constant with a decrease in the temperature, and a considerable driving force dependence (with a practically absent inverted region) were observed. In order to fit the experimental data by the traditional Marcus theory, two different assumptions were invoked: either a strong temperature dependence of the environmental reorganization energy and coupling with an additional non-symmetric high-frequency mode, or temperature dependence of the reorganization energy

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Fig. 4 Temperature and driving force dependence of the transition probability. Curve 1: $E_s/k_BT = 6$, $E_1 = 0$, $\hbar\omega_1/2k_BT = 1$, $\hbar\omega_s/2k_BT = 3$, $\gamma = 0$, $T = 300$ K; curve 2: 6, 0, 1, 3, 5, 300 K; curve 3: 6, 0, 1, 3, 5, 150 K; curve 4: 6, 0,1, 3, 5, 150 K. $-\Delta F \rightarrow -\Delta F + 50$ meV. The last point on curve 1 corresponds to equality of the driving force and reorganization energy. The region on the right of this point is the inverted region (not shown)

and driving force (free energy of the transition) simultaneously.

It is worth noting that, in the traditional Marcus theory [26] with temperature independent parameters, the weak temperature dependence of the reaction rate constant would require small values of the reorganization energy. However, this would lead to a rather early onset of the inverted region with a rather small interval of the variation of the rate constant with the driving force (see curve 1 in Fig. 4). On the other hand, according to the results above, rather strong variation in the electron tunneling (if coupled with a high-frequency promoting mode) with the driving force reveals only slight temperature dependence (see curves 2 and 3 in Fig. 4). Moreover, the reaction rate constant is approximately independent of the free energy of the transition in a rather broad region where the driving force is larger than the reorganization energy, which may explain the failure to observe the inverted region in [27]. It should be emphasized that curves 2 and 3 in Fig. 4 were plotted with temperature independent parameters and they show normal temperature behavior of the reaction rate constant (a decrease with temperature). Therefore, the effect of the promoting mode alone cannot explain all of the tendencies observed experimentally. However, the assumption of a slight change of the parameters with temperature can improve the qualitative agreement. For example, a shift of the driving forces by 50 meV can alter the order of curves 2 and 3 in Fig. 4 (see curve 4) in accordance with the experimental observations.

It is worth emphasizing that all of the effects discussed here are due to the electron coupling with the promoting modes, unlike in most other works in the field (except those mentioned above), where non-Condon effects due to the electron coupling to non-symmetric modes were considered. The approach presented here is applicable to electron transfer processes in various systems, solid matrices, and liquid solutions, as well as biological macromolecules.

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