

A rate constant expression for charge transfer through fluctuating bridges

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A rate constant expression for charge transfer reactions mediated by flexible bridges is presented as a series of terms of decreasing importance. The leading term corresponds to the static limit obtained from the Condon approximation. Corrections due to finite time fluctuations are evaluated explicitly, assuming a Gaussian shape of the coupling autocorrelation function and the Marcus model with a one-dimensional harmonic thermal bath. The use of this model for the interpretation of experimental data and the expected magnitudes of the fluctuation effects are discussed. © 2003 American Institute of Physics. [DOI: 10.1063/1.1601600]

I. INTRODUCTION

Theoretical interest in charge transfer (CT) processes has not diminished since the first theories^{1–3} were successfully tested.⁴ In fact, the increasing complexity of the systems considered and the greater breadth and accuracy of experiments have revealed a number of situations where the conventional approach does not fully account for the experimental observations, calling for improvement and generalization of the original theoretical models.^{5–7}

Most experimental work is focused on intramolecular charge transfer processes in donor–bridge–acceptor (*D–B–A*) systems, where the bridge is often a rigid spacer. More generally we can consider the “bridge” to be any medium between donor and acceptor (including solvent molecules, glasses, and flexible biomolecules such as DNA) that lowers the barrier for electron tunneling with respect to vacuum. The standard expression for the nonadiabatic thermal rate constant in such systems is often written as

$$k_{\text{CT}} = \frac{2\pi}{\hbar} |V|^2 \rho_{\text{FCT}}, \quad (1)$$

where V is the effective electronic coupling between D and A , and ρ_{FCT} is the density of states weighted by the Franck–Condon factor and thermally averaged. Equation (1) is derived in the nonadiabatic limit, assuming thermalized reactants. Two other assumptions, whose validity is sometimes questioned, are that (i) the coupling V does not depend on the nuclear coordinates (Condon approximation) and (ii) that states localized on the bridge are not thermally populated. The case opposite to that of assumption (ii) where transmis-

sion proceeds by thermally populating the bridge corresponds to the incoherent (hopping) mechanism, which has been extensively studied in the past few years both theoretically^{8–14} and experimentally.^{15–17} In this paper we focus on the tunneling regime where assumption (ii) holds and we examine the Condon approximation, and the consequences of its breakdown for the rate constant.

Several early papers discussed the validity of the Condon approximation, analyzing the theoretical consequences of its breakdown,^{18–20} but only in more recent years have both experimental and computational studies revealed the importance of the bridge dynamics on the CT rate. The simplest effect of bridge dynamics is the temperature dependence of the effective electronic coupling found for example by Davis *et al.* in a study of CT reactions mediated by polyvinylene bridges.²¹ In particular bridge conformations, the CT rate increases strongly, a phenomenon observed in several biological systems^{22–24} and sometimes referred to as *conformational gating*.^{25,26} The dynamical effects are seen when the bridge is a solvent molecule, as demonstrated in a series of papers by Zimmt and co-workers, who used specifically designed “C-clamp” *D–B–A* molecules.²⁷ Similarly, strong dynamic effects were observed by Castner *et al.*²⁸ in a CT reaction where the solvent also acts as an acceptor. Non-Condon effects have been also probed by other ultrafast measurements of electron transfer rates.²⁹

Since the CT rate depends on many factors, which cannot be easily separated, numerical simulations have often been used to quantify the effect of structural change in the bridge on the observed rate.^{30–38} In most of these calculations a classical molecular dynamics trajectory is generated and the *D–A* coupling is computed at given time intervals. For example, Nitzan and coworkers studied electron tunneling through water layers finding that several conformations lead to the formation of transient resonant states, which en-

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hance the tunneling rate.³² In most of these studies the analysis is performed in the limit of slow modulation where *dynamical* effects are ignored and a modified version of Eq. (1) can be used where V^2 is substituted by its time (or ensemble) average $\langle V^2 \rangle$,

$$k_{\text{CT}} \cong \frac{2\pi}{\hbar} \langle V^2 \rangle \rho_{\text{FCT}}. \quad (2)$$

Equation (2) captures the effect of structural averaging of the bridge conformation while it neglects the coupling between nuclear and electron dynamics. Balabin and Onuchic computed the time dependent D - A coupling, $V(t)$, for the photosynthetic reaction center, showing that the tunneling path changes in time influenced by the thermal structural changes of the protein.³³ They also introduced the *coherence parameter* $C = \langle V \rangle^2 / \langle V^2 \rangle$, which is close to unity when Condon approximation holds and close to zero when the coupling strongly depends on the bridge conformation. Troisi and Orlandi found a very low coherence parameter for the hole hopping between nonadjacent guanines in DNA, demonstrating that this process is ruled by conformational gating.³⁴ As we will see in Sec. III, the corrections to Eq. (2) due to dynamical effects are important only if the coherence parameter (which is not itself a dynamical quantity) is close to zero. Skourtis *et al.* computed the time evolution of the donor-acceptor coupling in azurin performing a fully time-dependent quantum-mechanical treatment of the electronic problem and making clear that quantum effects may be important for fluctuations at the same timescale as the electron transfer rate.³⁶ Cao investigated the opposite limit of fluctuations much slower than the electron dynamics (a limit not considered here) that leads to non exponential decay of the initial population.³⁹

Several papers have described quantum dynamical effects in electron transfer reaction.⁴⁰⁻⁴³ In particular Medvedev and Stuchebrukhov⁴⁴ have considered an electron transfer reaction coupled to a classical harmonic bath and obtained an expression for the rate in terms of the coupling autocorrelation function $\langle V(t)V(0) \rangle$. This quantity arises naturally in any quantum dynamics treatment⁴⁵ and can be evaluated numerically or analytically once a suitable model for the electronic-vibrational coupling is provided. This approach to rate calculations cannot be directly related to experimental measurements because the coupling autocorrelation function, in the context of CT processes, is not accessible experimentally and the connection to expressions valid in absence of coupling fluctuations [Eq. (1)] is not direct.

We show in this paper that it is possible to express the exact rate in the presence of fluctuating coupling as a series in which Eq. (2) is the leading term. The first corrective term to Eq. (2) quantifies the effect of finite time fluctuations [clarifying the validity of Eq. (2) as an approximation]. We first derive a hierarchical expression for the rate without assumptions on the nature of the bath or on the structure of the coupling autocorrelation function. Then we assume a classical harmonic thermal bath and classical bridge dynamics to get a more directly computable expression for the dynamical contribution to the rate. Using approximations akin to Mar-

cus' theory of electron transfer, we find a corrective term due to fluctuations that introduces only one additional parameter, intuitively related to the characteristic fluctuations time. Since our proposed expression introduces the effect of fluctuations as a correction to well-established formulas, it is particularly suitable for the analysis of experimental data when the possible importance of fluctuations is to be evaluated.

II. GENERAL CT RATE EXPRESSION IN THE PRESENCE OF A FLUCTUATING BRIDGE

Nuclear motions can be divided into two groups with regard to their effect on the electron transfer process.^{46,47} One group, which includes the donor and acceptor modes as well as some particular solvent motions (later indicated as $\{Q^{\text{DAS}}\}$), contains the modes along which the electronic energies of the initial and final states changes rapidly. This property has two implications. First, the electronic transition occurs only at a specific configuration (or regime of configurations) of these modes for which the initial and final electronic energies are nearly the same, i.e., where the corresponding potential energies cross. Second, since these modes couple energetically to the transition, their motion is important both to supply the needed electronic energy and to remove excess energy released during the transition. These modes are therefore referred to as *accepting modes*, a term used for such modes in the theory of molecular radiationless transition. An important consequence of the fact that the electronic transition is dominated by a particular regime of configurations along these modes is that the Condon approximation is applicable for these modes, i.e., the electronic coupling can be taken to be independent of their configuration, at the value corresponding to this local configuration regime.

A second group of nuclear motions includes the bridge modes (indicated as $\{Q^B\}$) and solvent motions that do not interact strongly with the donor and acceptor states. The energies of these latter states are only weakly dependent on the configuration of these modes, which is another way to say that the electron transfer is not limited to a local position along them. The electronic coupling can be strongly influenced by these modes,⁴⁸ but in this case the Condon approximation cannot be made. Because of their effect on the coupling these modes will be termed *inducing modes*.

The initial and final states can now be written as Born-Oppenheimer products,

$$\Psi_{Iv,a} = \psi_I(q, Q_{\text{DAS}}, Q_B) \Lambda_{Iv}^{\text{DAS}}(Q_{\text{DAS}}) \Lambda_a^B(Q_B), \quad (3a)$$

$$\Psi_{Fw,b} = \psi_F(q, Q_{\text{DAS}}, Q_B) \Lambda_{Fw}^{\text{DAS}}(Q_{\text{DAS}}) \Lambda_b^B(Q_B), \quad (3b)$$

where ψ and Λ represent the electronic and vibrational wave functions, respectively, q and Q are electronic and nuclear coordinates, and I and F denote the initial and final electronic states (only two states will be considered). In addition, v and w are indices of initial and final vibrational states on the DAS subsystem while a and b correspond to initial and final vibrational states on the B subsystem.

Our assumptions regarding these modes now imply a Hamiltonian of the form $H + V$ with

$$\begin{aligned}
 H &= \sum_{v,a} (E_{Iv} + E_a) |a\rangle |Iv\rangle \langle Iv| \langle a| \\
 &+ \sum_{w,a} (E_{Fw} + E_a) |a\rangle |Fw\rangle \langle Fw| \langle a| \\
 &= \sum_v E_{Iv} |Iv\rangle \langle Iv| \\
 &+ \sum_w E_{Fw} |Fw\rangle \langle Fw| + \sum_a E_a |a\rangle \langle a|, \quad (4)
 \end{aligned}$$

$$V = \sum_v \sum_w \sum_{ab} V_{Iv,Fwb} |a\rangle |Iv\rangle \langle Fw| \langle b| +, \quad (5)$$

and the probability of being in state $|a\rangle |Iv\rangle$, at a given temperature T , may be factorized as

$$P_{Iv,a}(T) = P_{Iv}(T) P_a(T). \quad (6)$$

The Golden Rule expression for a state to state transition in this system is

$$k_{Iv,a \rightarrow Fw,b} = \frac{2\pi}{\hbar} |\langle Iv,a | V | Fw,b \rangle|^2 \delta(E_{Iv} + E_a - E_{Fw} - E_b), \quad (7)$$

and the observed rate, resulting from summing over final states and thermal averaging over initial states, is

$$k = \sum_{v,a} P_{Iv} P_a \sum_{w,b} k_{Iv,a \rightarrow Fw,b}. \quad (8)$$

Writing the delta function in Eq. (7) as a Fourier transform, we get

$$\begin{aligned}
 k &= \frac{1}{\hbar^2} \sum_{v,a} P_{Iv} P_a \sum_{w,b} \int \langle Iv,a | V | Fw,b \rangle \\
 &\times \langle Fw,b | V | Iv,a \rangle e^{(i/\hbar)(E_a - E_b + E_{Iv} - E_{Fw})t} dt. \quad (9)
 \end{aligned}$$

The matrix elements in Eq. (9) may be written as

$$\langle Iv,a | V | Fw,b \rangle = \langle a | V_{Iv,Fw} | b \rangle, \quad (10)$$

i.e., after integrating over the coordinates $\{q\}$ and $\{Q_{\text{DAS}}\}$. For simplicity we assume that the matrix elements $V_{Iv,Fw}$ are real (that implies $V_{Iv,Fw} = V_{Fw,Iv}$). Equation (9) can be further manipulated to give

$$\begin{aligned}
 k &= \frac{1}{\hbar^2} \sum_{v,a} P_{Iv} P_a \sum_{Fw,b} \int \langle a | e^{(i/\hbar)Ht} V_{Iv,Fw} e^{-(i/\hbar)Ht} | b \rangle \\
 &\times \langle b | V_{Iv,Fw} | a \rangle e^{(i/\hbar)(E_{Iv} - E_{Fw})t} dt, \quad (11)
 \end{aligned}$$

$$\begin{aligned}
 k &= \frac{1}{\hbar^2} \sum_{v,a} P_{Iv} P_a \sum_{Fw,b} \int \langle a | V_{Iv,Fw}(t) | b \rangle \\
 &\times \langle b | V_{Iv,Fw} | a \rangle e^{(i/\hbar)(E_{Iv} - E_{Fw})t} dt, \quad (12)
 \end{aligned}$$

$$\begin{aligned}
 k &= \frac{1}{\hbar^2} \sum_v \sum_a P_{Iv} P_a \sum_{Fw} \int \langle a | V_{Iv,Fw}(t) V_{Iv,Fw} | a \rangle \\
 &\times e^{(i/\hbar)(E_{Iv} - E_{Fw})t} dt. \quad (13)
 \end{aligned}$$

We identify, in Eq. (13), the thermal over the bridge vibrational states $\sum_a P_a \langle a | O | a \rangle = \langle O \rangle_B$, so that we can write

$$\begin{aligned}
 k &= \frac{1}{\hbar^2} \sum_{Iv} P_{Iv} \sum_{Fw} \int \langle V_{Iv,Fw}(t) V_{Iv,Fw}(0) \rangle_B \\
 &\times e^{(i/\hbar)(E_{Iv} - E_{Fw})t} dt. \quad (14)
 \end{aligned}$$

We drop indexes I, F for now. We also use the Condon approximation for the $\{v, w\}$ states, which allows us to write

$$V_{vw}(t) V_{vw}(0) = V(t) V(0) S_{vw}, \quad (15a)$$

$$\langle V_{vw}(t) V_{vw}(0) \rangle_B = \langle V(t) V(0) \rangle_B S_{vw}, \quad (15b)$$

where S_{vw} are the Franck–Condon factors. We get

$$k = \frac{1}{\hbar^2} \sum_v P_v \sum_w \int \langle V(t) V(0) \rangle_B S_{vw} e^{(i/\hbar)(E_v - E_w)t} dt. \quad (16)$$

Finally we substitute the summation over the final states $\{w\}$ with an integral over the energy,

$$\begin{aligned}
 k &= \frac{1}{\hbar^2} \sum_v P_v \int \int \langle V(t) V(0) \rangle_B \rho_{\text{FC}v}(E) \\
 &\times e^{(i/\hbar)(E_v - E)t} dt dE, \quad (17)
 \end{aligned}$$

where the Franck–Condon weighted density of final states for initial vibronic state v , $\rho_{\text{FC}v}$, is defined as

$$\rho_{\text{FC}v}(E) = \sum_w S_{vw} \delta(E - E_w) \quad (18)$$

(note that this quantity is not temperature averaged and consequently it depends on v).

It is helpful, at this stage, to define the spectral density J as

$$J(E) = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} \langle V(t) V(0) \rangle_B e^{(i/\hbar)Et} dt. \quad (19)$$

This leads to the rate constant from any donor initial vibrational state v in the form,

$$k_v = \int_{-\infty}^{+\infty} J(E - E_v) \rho_{\text{FC}v}(E) dE. \quad (20)$$

Equation (20) will be used as a starting point for the derivation of approximate expressions in the next section. The main difference between this derivation and the others present in literature^{40,42,44} is in the separation of modes [Eq. (4)], which leads to a final expression containing the product of the spectral density, carrying information on the inducing-modes, and Franck–Condon weighted density of states, related only to the accepting modes. The combination of Eq. (20) and Eq. (17) gives a rate constant expression similar to the one presented in Ref. 44 [Eq. (1.2)], where the probability of energy exchange with the bridge vibrational modes is more evident. One difference between the two approaches is that Eq. (20) is not limited to classical accepting modes ($\hbar\omega_v/k_B T \ll 1$), but most of the following considerations can be readily cast in the formalism of Ref. 44.

III. SERIES EXPANSION OF THE RATE CONSTANT

The approximations that we will use to evaluate Eq. (20) are based on the qualitative knowledge about the functions $J_v(E)$ and $\rho_{\text{FC}v}(E)$. The correlation function $\langle V(t)V(0) \rangle_B$ has a maximum for $t=0$ and it reaches the constant value $\langle V \rangle^2$ for $|t|$ larger than a characteristic time τ_c . It is useful to decompose the coupling as

$$V(t) = \langle V \rangle + \delta V(t), \quad (21)$$

where $\langle \delta V(t) \rangle = 0$. Consequently, $J(E)$ can be decomposed as

$$J(E) = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \langle \delta V(t) \delta V(0) \rangle_B e^{(i/\hbar)Et} + \frac{2\pi}{\hbar} \langle V \rangle^2 \delta(E). \quad (22)$$

The first term has a maximum for $E=0$, it goes asymptotically to zero for $|E|$ larger than a typical width \hbar/τ_c . Such width for some of the systems mentioned in the introduction is about 200 cm^{-1} .^{22,28,34} In this range $\rho_{\text{FC}v}(E)$ is not expected to vary too much and the evaluation of the integral in Eq. (20) can be carried out after the Taylor's series expansion,

$$\rho_{\text{FC}v}(E) = \rho_{\text{FC}v}(E_v) + \rho'_{\text{FC}v}(E_v)(E - E_v) + \frac{1}{2}\rho''_{\text{FC}v}(E_v)(E - E_v)^2 + \dots \quad (23)$$

Using Eq. (23), Eq. (20) leads to a series of additional contributions to the rates,

$$k_v = k_v^{(0)} + k_v^{(1)} + k_v^{(2)} + \dots, \quad (24)$$

where the first three terms are

$$k_v^{(0)} = \rho_{\text{FC}v}(E_v) \int_{-\infty}^{+\infty} J(E) dE, \quad (25)$$

$$k_v^{(1)} = \rho'_{\text{FC}v}(E_v) \int_{-\infty}^{+\infty} E J(E) dE, \quad (26)$$

$$k_v^{(2)} = \frac{1}{3}\rho''_{\text{FC}v}(E_v) \int_{-\infty}^{+\infty} E^2 J(E) dE. \quad (27)$$

In general the n th contribution to the rate depends on the n -order moment of the spectral density and the n -order derivative of the density of states,

$$k_v^{(n)} = \frac{1}{n!} \left(\frac{d^n \rho_{\text{FC}v}}{dE^n} \right)_{E=E_v} \int_{-\infty}^{+\infty} E^n J(E) dE. \quad (28)$$

Note that the expansion does not contain further approximations with respect to Eq. (20). The qualitative argument we gave at the beginning simply suggests that the series converges rapidly. We will see that is possible to evaluate each term of the series for selected problems, showing that the series indeed is rapidly converging.

Using Eqs. (19) and (25) we can explicitly compute $k_v^{(0)}$,

$$k_v^{(0)} = \frac{2\pi}{\hbar} \langle V^2 \rangle \rho_{\text{FC}v}(E_v), \quad (29)$$

and, performing the average over the initial states v , we get

$$k^{(0)} = \sum_v P_v(T) k_v^{(0)} = \frac{2\pi}{\hbar} \langle V^2 \rangle \rho_{\text{FCT}}, \quad (30)$$

with ρ_{FCT} the thermally averaged Franck–Condon density of states,

$$\rho_{\text{FCT}} = \sum_v P_v(T) \rho_{\text{FC}v}(E_v). \quad (31)$$

This term corresponds to the static limit in which one averages the instantaneous rate expression over the distribution of static bridge configuration. The correction terms results from the bridge dynamics. We assume in the following that the ρ_{FCT} function can be evaluated using one of the expressions suggested in the literature.

The next step consists of calculating the corrections to Eq. (30) given by Eqs. (26) and (27). We assume for simplicity that the bridge dynamics is classical so that $\langle V(t)V(0) \rangle_B$ is an even function of time. Moreover, we take as a model for $\langle \delta V(t) \delta V(0) \rangle_B$ a Gaussian function with width τ_c . Although many other possibilities can be considered, the Gaussian shape is sufficiently general and was found consistent with recent computational results.^{22,34} The spectral density for this model correlation function is obtained from Eq. (22),

$$J(E) = \frac{2\pi}{\hbar} \left(\langle \delta V^2 \rangle \frac{\tau_c}{\sqrt{\pi\hbar}} \exp\left(-\frac{\tau_c^2(E)^2}{2\hbar^2}\right) + \langle V^2 \rangle \delta(E) \right). \quad (32)$$

It is important to point out that two levels of approximations have been introduced. The important results of Eqs. (24)–(30) rely only on the validity of the Golden Rule and on the modes separation introduced in Eq. (4). In contrast, Eq. (32) is valid only when the non-Condon effects arise primarily from of low frequency modes that can be treated classically (this should include torsions, which might show important non-Condon behavior). It is possible in principle to generalize the function $J(E)$, incorporating quantum effects,⁴⁹ so as to allow the study in the same theoretical framework of the contribution of high frequency inducing modes.

From Eq. (32) we can easily calculate the integrals in Eqs. (26) and (27). The first-order correction vanishes by symmetry, since $J(E)$ is even,

$$k_v^{(1)} = 0. \quad (33)$$

The second-order correction is

$$k_v^{(2)} = \frac{\pi}{\hbar} \langle \delta V^2 \rangle \frac{\hbar^2}{\tau_c^2} \rho''_{\text{FC}v}(E_v). \quad (34)$$

The unique parameter added to include the dynamical effect is the correlation time τ_c . For an extremely slow process [$\tau_c \rightarrow \infty, J(E) \rightarrow 2\pi\hbar \langle V^2 \rangle \delta(E)$], $k_v^{(0)}$ becomes the unique term contributing to the rate. With faster fluctuations $J(E)$ becomes broader and samples value of $\rho_{\text{FC}v}(E)$ at an energy different than $E=0$. Note however that the limit $\tau_c \rightarrow 0$ cannot be handled by the expansion in Eq. (23).

Next, the correction to the thermal rate is obtained by taking a thermal average over the initial states $\{v\}$ in Eq. (34). This leads to

$$k^{(2)} = \frac{\pi}{\hbar} \langle \delta V^2 \rangle \frac{\hbar^2}{\tau_c^2} \sum_v P_v(T) \rho_{\text{FC}v}''(E_v). \quad (35)$$

In the Appendix we show that the sum in Eq. (35) may be expressed by

$$\begin{aligned} \sum_v P_v(T) \rho_{\text{FC}v}''(E_v) &= \rho_{\text{FCT}}''(\Delta E^0) \\ &= \left(\frac{d^2 \rho_{\text{FCT}}(\Delta E)}{d\Delta E^2} \right)_{\Delta E = \Delta E^0}. \end{aligned} \quad (36)$$

ΔE is the energy difference between the vibrational ground state of the I and F states. ΔE^0 is the actual value of this energy gap for the system under investigation. Thus

$$k^{(2)} = \frac{\pi}{\hbar} \langle \delta V^2 \rangle \frac{\hbar^2}{\tau_c^2} \rho_{\text{FCT}}''(\Delta E^0). \quad (37)$$

It is now possible to express both $k^{(0)}$ and $k^{(2)}$, once a model expression for $\rho_{\text{FCT}}(\Delta E^0)$ is selected. General expressions have been widely discussed^{5,6} and they can be used to evaluate Eqs. (30) and (37). We will adopt here the simplest case, the classical expression derived by Marcus,

$$\rho_{\text{FCT}}(\Delta E^0) = \sqrt{\frac{1}{4\pi\lambda k_B T}} \exp\left(-\frac{(\lambda + \Delta E^0)^2}{4\lambda k_B T}\right), \quad (38)$$

where λ is the reorganization energy. Equations (30) and (37) then yield

$$k^{(0)} = \frac{\langle V^2 \rangle}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp\left(-\frac{(\lambda + \Delta E^0)^2}{4\lambda k_B T}\right), \quad (39)$$

$$k^{(2)} = k^{(0)} 2 \frac{\hbar^2}{\tau_c^2} \left[\frac{(\lambda + \Delta E^0)^2 - 2\lambda k_B T}{(4\lambda k_B T)^2} \right] \left(1 - \frac{\langle V \rangle^2}{\langle V^2 \rangle} \right). \quad (40)$$

To obtain Eq. (40) we have used the relation $\langle \delta V^2 \rangle = \langle V^2 \rangle - \langle V \rangle^2$.

The Marcus theory describes nonadiabatic electron transfer in terms of three parameters: the nonadiabatic coupling V and the parameters that determine the diabatic potential energy surfaces ($\lambda, \Delta E^0$). Equation (30) expresses the correction to the rate resulting from dynamical effects, in terms of two other parameters: the correlation time (τ_c) and the coherence parameter ($\langle V \rangle^2 / \langle V^2 \rangle$). In particular, the effect of fluctuations, as quantified by $k^{(2)}$, is negligible when the coherence parameter is close to 1, i.e., when Condon approximation holds, and reaches a maximum when the parameter is 0. The latter situation is found not only in extremely flexible systems, like the ones described in the Introduction, but also in the case of $\langle V \rangle = 0$, i.e., for processes forbidden by symmetry at the equilibrium nuclear configuration. The effect of the potential energy surface parameter on the corrective term $k^{(2)}$ is illustrated in Fig. 1. Note that $k^{(2)}$ is positive except for the small range of parameters where $-\lambda - (2\lambda k_B T)^{1/2} < \Delta E^0 < -\lambda + (2\lambda k_B T)^{1/2}$, i.e., in the limit between normal and inverted region. In any case the changes

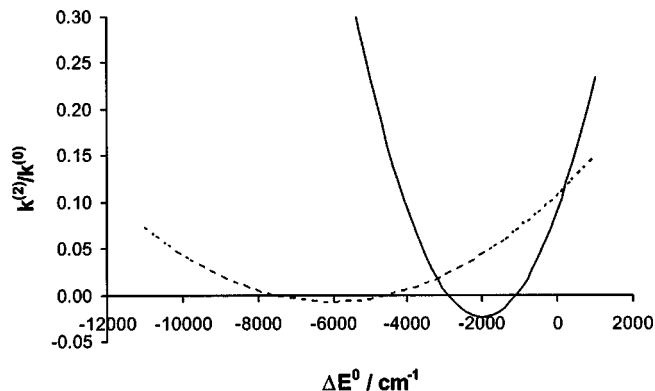


FIG. 1. Effect of the potential energy surface parameters on the ratio $k^{(2)}/k^{(0)}$ quantifying the relative importance of dynamical fluctuations on the rate constant. ΔE^0 is the energy difference between the ground vibrational states of the initial and final states. The graph is calculated according to Eq. 39 using $\hbar/\tau_c = 200 \text{ cm}^{-1}$, $T = 300 \text{ K}$, $\langle V \rangle = 0$, $\lambda = 2000 \text{ cm}^{-1}$ (solid line), $\lambda = 6000 \text{ cm}^{-1}$ (dashed line).

on k due to the correction $k^{(2)}$ are very small, in particular when displayed on the traditional logarithmic scale.

Equations (39) and (40) may be used to improve the fitting of experimental data or simply to estimate the contribution of fluctuations to the rate when the parameter τ_c can be computed or measured. For many systems of interest, characterized by a small coherence parameter, the correction $k^{(2)}$ is then expected to be significant ($k^{(2)}/k^{(0)} > 0.1$) and introduce anomalous temperature dependence to the rate constant. Figure 2 shows the temperature dependence of $k^{(2)}/k^{(0)}$ for a selected set of the other parameters. The relative contribution of $k^{(2)}$ is more important at lower temperatures. We note, however, that Eq. (40) cannot be used in the limit of $T \rightarrow 0$, since it is based on the assumption that the bridge motions are treatable classically. The temperature dependence of the rate constant is further complicated by the temperature dependence of λ and $\langle V(t)V(0) \rangle_B$ that has been neglected in Fig. 2.

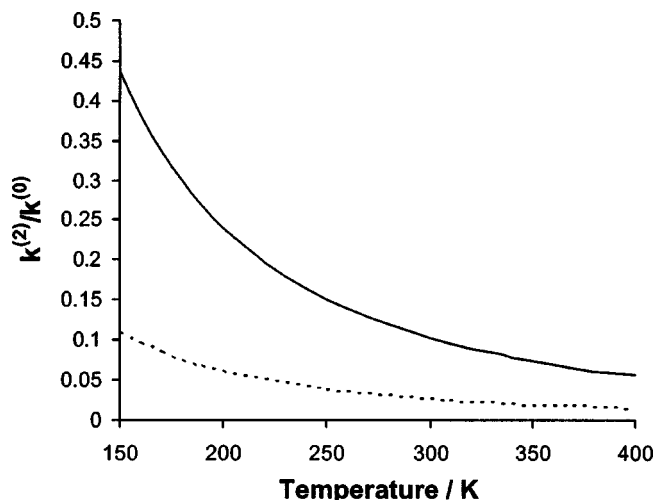


FIG. 2. Effect of the temperature on $k^{(2)}/k^{(0)}$. The graph is calculated according to Eq. (39) using $\langle V \rangle = 0$, $\lambda = 4000 \text{ cm}^{-1}$, $\Delta E^0 = 0 \text{ cm}^{-1}$, $\hbar/\tau_c = 200 \text{ cm}^{-1}$ (solid line), $\hbar/\tau_c = 100 \text{ cm}^{-1}$ (dashed line).

IV. CONCLUSION

The rate constant for electron transfer reaction through a fluctuating bridge has been expressed as a series of contributions of decreasing importance. The leading term, $k^{(0)}$, coincides with the classical expression except that the squared coupling is substituted by its average value, and is valid in the limit of slow fluctuations. The corrections due to finite time fluctuations have been expressed using a Gaussian model for the coupling autocorrelation function. The first nonzero correction to $k^{(0)}$ depends on the model used to describe the ρ_{FCT} function, and an expression derived from the Marcus theory for ρ_{FCT} was obtained. Within this model the correction $k^{(2)}$ was expressed in terms of two parameters, the correlation time and the coherence parameter, with a well defined physical meaning.

We noted that only the lowest order moments of the spectral density give a contribution to the rate, leading to an expression that is both simple and well-suited to the analysis of experimental data. In fact, the main difference with similar approaches based on the machinery of quantum dynamics, is that our final expressions do not contain the spectral density, a function hardly relatable to the experimental measures of CT rate. It is not generally possible, in fact, to measure CT rates for each individual energy, a limitation that prevents experimental access to the coupling autocorrelation function. Another advantage of this theoretical framework is that it can be readily extended to any model function of spectral density $J(E)$ or density of states $\rho_{\text{FCT}}(E)$.

The approach we proposed may be helpful for the quantitative understanding of the role of bridge fluctuations in charge transfer reactions, as it naturally leads to an expression valid in the static limit corrected by a fluctuation dependent term. This highly desirable separation allows an important improvement without hiding the structure of the conventional expressions, whose simplicity has encouraged their widespread use.

APPENDIX: PROOF OF EQ. (36)

We denote by ΔE the difference in energy between donor and acceptor ground vibrational states. It is easy to realize that the function $\rho_{\text{FCv}}(E)$ is in reality a function of $E - \Delta E$ so that Eq. (31) may be rewritten as

$$\rho_{\text{FCT}}(\Delta E) = \sum_v P_v(T) \rho_{\text{FCv}}(E_v - \Delta E). \quad (\text{A1})$$

Performing the second derivative respect to ΔE on both sides and taking the value at $\Delta E = \Delta E^0$ we get

$$\left(\frac{d^2 \rho_{\text{FCT}}(\Delta E)}{d\Delta E^2} \right)_{\Delta E = \Delta E^0} = \sum_i P_i(T) \left(\frac{d^2 \rho_{\text{FCv}}(E_v - \Delta E)}{d\Delta E^2} \right)_{\Delta E = \Delta E^0}. \quad (\text{A2})$$

But since

$$\left(\frac{d^2 f(x-y)}{dx^2} \right) = \left(\frac{d^2 f(x-y)}{dy^2} \right), \quad (\text{A3})$$

we have

$$\left(\frac{d^2 \rho_{\text{FCv}}(E_v - \Delta E)}{d\Delta E^2} \right)_{\Delta E = \Delta E^0} = \left(\frac{d^2 \rho_{\text{FCv}}(E - \Delta E^0)}{dE^2} \right)_{E = E_v}, \quad (\text{A4})$$

and then

$$\rho_{\text{FCT}}''(\Delta E^0) = \sum_v P_v(T) \rho_{\text{FCv}}''(E_v). \quad (\text{A5})$$

This expression was used to evaluate Eq. (37).

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