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Quantum Effects on the Rates of Electron-Transfer Reactions

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In this paper we compare the quantum-mechanical and classical theories of electron transfer in polar media, which involve large inner-shell reorganization energy. For symmetrical electron-transfer reactions, quantum corrections result from nuclear tunneling effects. These quantum effects increase the absolute value of the rate of the electron-transfer process for the $Co(NH_3)_6^{2+}$–$Co(NH_3)_6^{3+}$ exchange at room temperature by less than 1 order of magnitude.

Introduction

Nonadiabatic outer-sphere electron-transfer (ET) reactions in polar solvents can basically be characterized by the following three ingredients: (1) the electronic exchange matrix elements, corresponding to two-center one-electron exchange between the two ions, (2) the Marcus reorganization energy of the classical polar solvent, originating from the polarization fluctuations in the solvent outside the first coordination layer, and (3) the configurational changes in the bond lengths and the bond angles and the modification of the vibrational frequencies of the reactants and products in their first coordination layer.

The pioneering studies of Marcus[1] considered a classical description of the solvent fluctuations, which were subsequently handled in terms of a quantum-mechanical theory of solvent modes, developed by Levich and his school.[2] Marcus[1] had also advanced a classical description of inner-sphere reorganization effects. The classical approach is adequate provided that the thermal energy k_BT is high relative to the characteristic relevant vibrational energies. One expects that at room temperature k_BT is high relative to the vibrational energies associated with the fluctuations of the polar solvent. Accordingly, the Marcus approach is applicable to handle ET processes at room temperature, provided that the nuclear contribution is dominated by the reorganization of the exterior solvent. On the other hand, the characteristic frequencies associated with the ion-ligand motion are in the range $\hbar\omega_c$ = 250-500 cm^{-1}, so that the classical approximation will require some modifications at room temperature and is expected to be inapplicable at lower temperatures. The failure of the classical description for ET reactions, characterized by a substantial inner-sphere reorganization, is reflected in quantum effects on the reaction rates for ET. From the experimental point of view, such quantum effects[3-9] are manifested by the following phenomena: (A) absolute values of ET rates[7,8]—the ET rates cannot be accounted for in terms of the classical theory even at room temperature, as the contribution of the inner-shell reorganization has to be treated quantum mechanically; (B) isotope effects on ET rates—isotopic substitution in the first coordination layer is expected to result in a modification of the ET rate; (C) temperature-dependent activation energy[3]—as the contribution of the high-frequency modes in the first coordination layer is nonclassical, the ET process cannot be described in terms of a simple activated reaction; (D) deviations from the parabolic free-energy relationship[5]—the Marcus quadratic relation between the logarithm of the rate constant and the free energy of the reaction is expected to be violated for strongly exothermic reactions because of vibrational excitation of the high-frequency vibrational quantum modes of the participating molecules;[5b,c] and (E) temperature-independent low-temperature rate—under the unique circumstances when the role of solvent fluctuations is negligible and the effects of inner-shell reorganization dominate, the ET rate is finite and temperature independent in the temperature range where k_BT is low relative to the high-frequency vibrational energies.[6]

A quantum-mechanical treatment of nonadiabatic ET processes is available,[3-6] which provides a quantitative description of the effects of configurational changes in the solvent modes and in the high-frequency modes in the first coordination layer. From the theoretical point of view, quantum effects A-E can adequately be described in terms of nuclear tunneling effects on the ET processes. Such nuclear tunneling effects can be accounted for quantitatively in terms of Franck-Condon vibrational overlap integrals, which determine the nuclear contribution to the ET rate. Quantum effects A,[7,8] C,[3] D,[5] and E[6] have been explored from the theoretical point of view, while a quantitative description of effect B has not yet been provided. In this paper we present a discussion of quantum

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effects of nuclear tunneling on the absolute reaction rates of some ET processes in solution, which is complementary and supplementary to the work of Siders and Marcus.[8] We shall provide a detailed analysis of quantum effects on the $Co(NH_3)_6^{2+}$–$Co(NH_3)_6^{3+}$ and $Ru(NH_3)_6^{2+}$–$Ru(NH_3)_6^{3+}$ exchange reactions in aqueous solutions, which were investigated recently.[8] The quantum effect found by us for the rate of the $Co(NH_3)_6^{2+}$–$Co(NH_3)_6^{3+}$ exchange is in excellent agreement with the results of Siders and Marcus[8] for this reaction. In addition, we provide a set of model calculations for quantum effects on a symmetric ET process for a wide range of vibrational frequencies and inner-shell reorganization energies in an attempt to elucidate the role of quantum tunneling effects on ET processes at elevated room temperature. A further exploration of these nuclear tunneling phenomena is presented in the subsequent paper, which is devoted to the study of deuterium isotope effects on such reactions.

The cobalt hexaammine self-exchange reaction provides an excellent example for dramatic effects of large configurational changes in the first coordination layer. In a recent work from this laboratory,[9] we evaluated the Franck–Condon nuclear overlap G(Co) for the cobalt hexaammine self-exchange reaction, as well as the Franck–Condon nuclear overlap G(Ru) for the ruthenium hexaammine self-exchange reaction, obtaining $G(\mathrm{Co})/G(\mathrm{Ru}) \simeq 10^{-8}$ at 25 °C. This quantum-mechanical result was compared with the ratio of 10^{-5} obtained from the classical calculations of Stynes and Ibers.[10] Our previous conclusion that nuclear tunneling effects reduce the absolute rate of the cobalt hexaammine self-exchange reaction at 25 °C by ~3 orders of magnitude contradicts physical intuition. On the basis of general arguments, we expect that the quantum-mechanical rate should exceed the corresponding classical rate calculated with the same distortion parameters and frequency changes. While the quantum-mechanical result of our previous work[9] is accurate, the classical value for $G(\mathrm{Co})/G(\mathrm{Ru})$, quoted by us, was taken from the work of Stynes and Ibers.[10] This calculation is based on the use of the stretching force constant derived from normal mode analysis. The results of such an analysis depend on the assumed form of the force field and on the exact assignments of the spectral lines. In order to provide a proper comparison between the quantum-mechanical result with the classical result, one should adopt a consistent procedure which rests on the same basic model. This can be accomplished by performing the quantum calculations and by taking their classical limit. In what follows we shall attempt to provide a complete calculation of quantum effects on the rate constants for ET reactions. Detailed results will be presented for self-exchange reactions at room temperature.

Quantum-Mechanical Electron-Transfer Rates

The transition probability $W(R)$ for a nonadiabatic outer-sphere electron-transfer (ET) reaction between two ions separated by a distance R is given by[3,5,9]

$$W = (2\pi/\hbar)|V|^2 G(\Delta E, E_s, \{\Delta d_\kappa\}, \{\omega_\kappa'\}, \{\omega_\kappa''\}; T) \tag{1}$$

where V is the two-center one-electron exchange term between the two centers, whose evaluation was considered previously by us.[9] $G(\Delta E, E_s, \{\Delta d_\kappa\}, \{\omega_\kappa'\}, \{\omega_\kappa''\}; T)$ represents the thermally averaged vibrational overlap Franck–Condon factor, which incorporates the contributions of the solvent modes and the vibrations of the first coordination layer. The electronic and nuclear parameters that determine the Franck–Condon factor are the following: (1) The electronic energy gap, ΔE, between the initial and final electronic states. (2) The solvent reorganization energy,[1,2] E_s. According to Levich,[2] E_s is expressed in terms of the frequencies $\{\omega\}$, the reduced displacements $\{\Delta(\omega)\}$, and the density of states $(\rho(\omega))$ of the polar solvent modes

$$E_s = \int \mathrm{d}\omega\, \rho(\omega)[\Delta(\omega)^2/2]\hbar\omega \tag{2a}$$

which in the continuum limit reduces to the Marcus expression[1]

$$E_s = e^2\left(\frac{1}{n^2} - \frac{1}{D_s}\right)\left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{R}\right) \tag{2b}$$

(3) The parameters specifying the first coordination layer which involve the set, $\{\Delta d_\kappa\}$, of the equilibrium displacements in the first coordination layer and the vibrational frequencies $\{\omega_\kappa'\}$ and $\{\omega_\kappa''\}$ of the first coordination layer in the initial and in the final states, respectively. All of the electronic and nuclear terms appearing in eq 1 correspond to a fixed interionic separation R. In specifying the parameters which determine G, it was implicitly assumed that the thermal energy k_BT is sufficiently high to warrant a classical treatment of the solvent but is sufficiently low so that a quantum treatment of the first coordination layer is necessary. In what follows we shall consider explicitly the nuclear contribution to the ET rate. We shall rely heavily on our previous work, so that only essential results will be presented.

The thermally averaged Franck–Condon factor can be expressed in the form[3,6b,9]

$$G = (2\pi\hbar)^{-1}e^{-S_s}\int_{-\infty}^{\infty}\mathrm{d}t\, e^{-i\Delta E t/\hbar}[e^{f_s(t)} - 1]e^{f_c(t)} \tag{3}$$

where the solvent contribution is

$$f_s(t) = \int \mathrm{d}\omega\, \rho(\omega)(\Delta(\omega)^2/2)\{[n(\omega) + 1]e^{i\omega t} + n(\omega)e^{-i\omega t}\} \tag{4}$$

$$S_s = f_s(0) \tag{5}$$

while the contribution $f_c(t)$, from the first coordination layer, can be separated into a term due to equilibrium displacements and another term arising from frequency changes

$$f_c(t) = \Phi_c(t) + \phi_c(t) \tag{6}$$

$$\Phi_c(t) = -\sum_\kappa \frac{\omega_\kappa'\omega_\kappa''(\Delta d_\kappa)^2}{\omega_\kappa'' \coth \lambda_\kappa' + \omega_\kappa' \coth \mu_\kappa''} \tag{7}$$

$$\phi_c(t) = \sum_\kappa \ln\left\{\sinh(\hbar\omega_\kappa'/2k_BT)\left[\sinh^2(\lambda_\kappa' + \mu_\kappa'') + \frac{(\omega_\kappa' - \omega_\kappa'')^2}{4\omega_\kappa'\omega_\kappa''}\sinh 2\lambda_\kappa' \sinh 2\mu_\kappa''\right]^{-1/2}\right\} \tag{8}$$

where

$$\lambda_\kappa' = \tfrac{1}{2}(i\omega_\kappa' t + \hbar\omega_\kappa'/k_BT) \qquad \mu_\kappa'' = -\tfrac{1}{2}i\omega_\kappa'' t \tag{9}$$

and the sums in eq 7 and 8 are taken over all of the internal modes κ of both ions in the initial and final states. Finally, the change in the equilibrium configuration in the first coordination layer, originating from the totally symmetric vibrational mode, is conveniently given by

$$\Delta d_\kappa^2 = 6(\Delta r)^2 m/\hbar \qquad \text{for } \kappa \equiv a_{1g}$$
$$\Delta d_\kappa^2 = 0 \qquad \text{otherwise} \tag{10}$$

Δd_κ^2 being expressed in reciprocal frequency units. We

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[10] Stynes, H. C.; Ibers, J. A. *Inorg. Chem.* 1971, *10*, 2304.

shall present Δd_κ^2 in units of cm, so that $\omega_\kappa\,\Delta d_\kappa^2$ (where $\omega_\kappa \equiv \omega_\kappa'$ or ω_κ'' is given in cm^{-1} units) will be a dimensionless quantity.

The integral in eq 3 can be evaluated by the saddle-point method,[3,4,8,9] which results in

$$G = \hbar^{-1}\left[-2\pi\frac{\partial^2 F(t_0)}{\partial t^2}\right]^{-1/2}\exp[F(t_0)] \qquad (11)$$

where

$$F(t) = ti\,\Delta E/\hbar + f_c(t) + f_s(t) - S_s \qquad (12)$$

and the saddle point is determined by the condition

$$\partial F(t_0)/\partial t = 0 \qquad (13)$$

In general, the saddle-point equation has to be solved numerically. In the special case of symmetric ET reactions, when $\Delta E = 0$, one can find by inspection that

$$t_0 = i\hbar/2k_BT \qquad (14)$$

The final result for symmetric ET can be expressed in a cumbersome but manageable form

$$G = \hbar^{-1}(2\pi)^{-1/2}[-f_s^{II}(t_0) - \Phi_c^{II}(t_0) - \phi_c^{II}(t_0)]^{-1/2}\left(\prod_\kappa X_\kappa\right)\exp\left[-\frac{E_s}{4k_BT} - \sum_\kappa Y_\kappa\right] \qquad (15)$$

$$X_\kappa = \left[\frac{\sinh^2(\nu_\kappa' + \nu_\kappa'')}{\sinh 2\nu_\kappa' \sinh 2\nu_\kappa''} + \frac{(\omega_\kappa' - \omega_\kappa'')^2}{4\omega_\kappa'\omega_\kappa''}\right]^{-1} \qquad (16)$$

$$Y_\kappa = 2(\Delta d_\kappa)^2\omega_\kappa'\omega_\kappa''[\omega_\kappa' \coth \nu_\kappa'' + \omega_\kappa'' \coth \nu_\kappa']^{-1} \qquad (17)$$

$$\nu_\kappa' \equiv \hbar\omega_\kappa'/4k_BT \qquad \nu_\kappa'' = \hbar\omega_\kappa''/4k_BT \qquad (18)$$

$$\hbar^2\Phi_c^{II}\left(\frac{i\hbar}{2k_BT}\right) = -\sum_\kappa(\Delta d_\kappa\hbar\omega_\kappa'\omega_\kappa'')^2 \times \left[\frac{\omega_\kappa' \cosh \nu_\kappa' \operatorname{csch}^3 \nu_\kappa' + \omega_\kappa'' \cosh \nu_\kappa'' \operatorname{csch}^3 \nu_\kappa''}{(\omega_\kappa' \coth \nu_\kappa'' + \omega_\kappa'' \coth \nu_\kappa')^2} - \omega_\kappa'\omega_\kappa''\frac{(\operatorname{csch}^2 \nu_\kappa' - \operatorname{csch}^2 \nu_\kappa'')^2}{(\omega_\kappa' \coth \nu_\kappa'' + \omega_\kappa'' \coth \nu_\kappa')^3}\right] \qquad (19)$$

$$\hbar^2\Phi_c^{II}\left(\frac{i\hbar}{2k_BT}\right) = -\hbar^2\sum_\kappa\left[\frac{\omega_\kappa'^2}{\sinh^2 2\nu'} + \frac{\omega_\kappa''^2}{\sinh^2 2\nu_\kappa''} + \frac{1}{4}\frac{(\omega_\kappa'^2 \operatorname{sech}^2 \nu_\kappa' - \omega_\kappa''^2 \operatorname{sech}^2 \nu_\kappa'')^2}{(\omega_\kappa' \tanh \nu_\kappa' + \omega_\kappa'' \tanh \nu_\kappa'')^2} + \frac{1}{2}\frac{\omega_\kappa'^3 \sinh \nu_\kappa' \operatorname{sech}^3 \nu_\kappa' + \omega_\kappa''^3 \sinh \nu_\kappa'' \operatorname{sech}^3 \nu_\kappa''}{\omega_\kappa' \tanh \nu_\kappa' + \omega_\kappa'' \tanh \nu_\kappa''} + \frac{1}{4}\frac{(\omega_\kappa'^2 \operatorname{csch}^2 \nu_\kappa' - \omega_\kappa''^2 \operatorname{csch}^2 \nu_\kappa'')^2}{(\omega_\kappa' \coth \nu_\kappa' + \omega_\kappa'' \coth \nu_\kappa'')^2} - \frac{1}{2}\frac{\omega_\kappa'^3 \cosh \nu_\kappa' \operatorname{csch}^3 \nu_\kappa' + \omega_\kappa''^3 \cosh \nu_\kappa'' \operatorname{csch}^3 \nu_\kappa''}{\omega_\kappa' \coth \nu_\kappa' + \omega_\kappa'' \coth \nu_\kappa''}\right] \qquad (20)$$

$$\hbar^2 f_s^{II}(t_0) = -2E_sk_BT \qquad (21)$$

We note that the solvent contribution, which is treated classically, is incorporated into the E_s energy appearing in the exponential and in the f_s^{II} (eq 21) preexponential term. The contribution of the first layer appears in the exponential factors Y_κ (eq 17), which incorporate both distortions and frequency changes, in the preexponential factors X_κ (eq 16), which account for the frequency changes, and in the preexponential contributions Φ_c^{II} (eq 19) and ϕ_c^{II} (eq 20), which incorporate frequency changes.

The contribution of the Franck–Condon factor to the activation energy of the symmetrical ET reaction is

$$E_a = -\frac{\partial \ln G}{\partial(1/k_BT)} = \frac{E_s}{4} + \sum_\kappa\frac{(\Delta d_\kappa)^2\hbar\omega_\kappa'^2\omega_\kappa''^2(\operatorname{csch}^2 \nu_\kappa' + \operatorname{csch}^2 \nu_\kappa'')}{2(\omega_\kappa'' \coth \nu_\kappa' + \omega_\kappa' \coth \nu_\kappa'')^2} \qquad (22)$$

which consists of the "high-temperature" solvent contribution and the contribution of the intramolecular reorganization energy in the first coordination layer.

In order to assess the contribution of quantum effects on the ET rate, we consider the classical limit for the quantum modes. When $\nu_\kappa' \ll 1$ and $\nu_\kappa'' \ll 1$, the limiting form of the parameters in eq 16 and 17 is

$$X_\kappa^{(Cl)} = 2\omega_\kappa'\omega_\kappa''/(\omega_\kappa'^2 + \omega_\kappa''^2) \qquad (23)$$

$$Y_\kappa^{(Cl)} = (\Delta d_\kappa)^2\hbar\omega_\kappa'^2\omega_\kappa''^2/[2k_BT(\omega_\kappa''^2 + \omega_\kappa'^2)] \qquad (24)$$

At this stage it is useful also to introduce the inner-shell reorganization energy

$$E_c = \sum_\kappa\frac{2(\Delta d_\kappa)^2\hbar\omega_\kappa'^2\omega_\kappa''^2}{\omega_\kappa'^2 + \omega_\kappa''^2} = 4k_BT\sum_\kappa Y_\kappa \qquad (25)$$

It is possible to simplify the cumbersome relations if the frequency changes in the first coordination layer are small, so that

$$\left|\frac{\omega_\kappa' - \omega_\kappa''}{\omega_\kappa' + \omega_\kappa''}\right| \ll 1 \qquad (26)$$

Under these circumstances, we can introduce average frequencies $\bar\omega_\kappa'$ and $\bar\omega_\kappa''$ for the totally symmetric a_{1g} vibrations of the first coordination layer of the donor and the acceptor, respectively. These a_{1g} vibrations are accompanied by finite equilibrium displacements and contribute to the exponent in eq 15. Assuming that a single type of vibrational mode is totally symmetric, we set an average value

$$\omega = 2\bar\omega_\kappa'\bar\omega_\kappa''/(\bar\omega_\kappa' + \bar\omega_\kappa'') \qquad (27)$$

for this mode. For modest frequency changes, specified by condition 26, we obtain from eq 15

$$G = (2\pi)^{-1/2}[2E_sk_BT + E_c\hbar\omega \operatorname{csch} 2\nu]^{-1/2}\left(\prod_{\kappa=1}^{n} X_\kappa\right) \times \exp[-E_s/4k_BT - (E_c/\hbar\omega)\tanh \nu] \qquad (28)$$

where $\nu = \hbar\omega/4k_BT$ and X_κ is given by eq 16. In the high-temperature case we take $\nu \ll 1$, obtaining the classical result

$$G^{(Cl)} = (2\pi)^{-1/2}[2(E_s + E_c)k_BT]^{-1/2}\prod_\kappa X_\kappa^{(Cl)}\exp\left[-\frac{E_c + E_s}{4k_BT}\right] \qquad (29)$$

The quantum result, eq 28, constitutes a slight generalization of Holstein's formula[11] to include both solvent and quantum modes, while the classical result, eq 29, was presented by Marcus 25 yr ago.

Results and Discussion

Detailed numerical calculations were performed for the $Co(NH_3)_6^{2+}$–$Co(NH_3)_6^{3+}$ and $Ru(NH_3)_6^{2+}$–$Ru(NH_3)_6^{3+}$ exchange reactions using eq 15 and utilizing the structural and spectroscopic input data summarized in our previous

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[11] Holstein, T. *Ann. Phys. (N. Y.)* **1959**, *8*, 343.

work (Table I of ref 9). These calculations result in $G(\text{Co})/G(\text{Ru}) \simeq 10^{-8}$ at $T = 300$ K. On the other hand, a classical calculation based on eq 29 and 24 with the same input data results in $G(\text{Co})/G(\text{Ru}) \simeq 1.5 \times 10^{-9}$ at room temperature. The quantum contribution to the ruthenium hexaammine exchange reaction is negligibly small, so that the increase of the ratio of the Franck–Condon factors obtained from the complete calculation, relative to the classical result, reflects the role of quantum effects on the rate of the cobalt hexaammine symmetric exchange reaction. The nuclear tunneling quantum-type effect increases the transition probability of this symmetric ET process, which suffers large inner-shell reorganization, by a numerical factor of 7, i.e., by ~1 order of magnitude. This estimate of the quantum effect on the rate of the $\text{Co(NH}_3)_6^{2+}$–$\text{Co(NH}_3)^{3+}$ exchange is in excellent agreement with the quantum effect of 5 previously reported by Siders and Marcus[8] for this reaction rate.

Another interesting aspect of quantum effects on conventional symmetric ET rates concerns the temperature dependence of the activation energy. As is apparent from eq 22, the role of inner-shell reorganization will result in the increase of the activation energy with increasing temperature.[3,7] We have calculated the activation energy for the $\text{Co(NH}_3)_6^{2+}$–$\text{Co(NH}_3)_6^{3+}$ exchange reaction in solution. For this reaction the contribution of the solvent reorganization energy to E_a (eq 22) is $E_s/4 = 7.0$ kcal mol^{-1}, while the classical contribution of the first coordination layer (eq 25) amounts to $E_c/4 = 11.5$ kcal. Thus, the high-temperature limit for the activation energy amounts to 18.5 kcal mol^{-1}. The activation energy incorporating quantum effects in the first coordination layer is lower, varying in the range $E_a = 15.7$ kcal mol^{-1} at 273 K to $E_a = 16.6$ kcal mol^{-1} at 343 K. Nuclear tunneling effects result in the reduction of the apparent activation energy relative to the classical value.

To obtain an overview of the quantum effects on the reaction rate at room temperature, we have performed model calculations for a symmetric ET process characterized by a single vibrational mode which exhibits a configurational change, while all of the frequencies are not modified by the electron exchange. Utilizing eq 28 and 29 with $X_\kappa = X_\kappa^{(\text{Cl})} = 1$, we have calculated the ratio $G/G^{(\text{Cl})}$ for a series of values of the reduced displacement parameter $(\Delta d)^2$ (eq 10) and of the frequency, ω, of the displaced mode in the first coordination layer. From the results displayed in Figure 1, it is apparent that nuclear tunneling effects enhance the symmetric ET rate for high frequencies and for large configurational changes. For the $\text{Co(NH}_3)_6^{2+}$–$\text{Co(NH}_3)_6^{3+}$ exchange reaction, which is characterized by large inner-shell reorganization, i.e., $(\Delta d)^2 = 0.1$ cm and $\hbar\omega \simeq 400$ cm^{-1}, we estimate quantum effects to enhance the ET rate by ~1 order of magnitude. On the other hand, for the $\text{Ru(NH}_3)_6^{2+}$–$\text{Ru(NH}_3)_6^{3+}$ exchange, where inner-shell reorganization is exceedingly low, $(\Delta d)^2 \simeq 5 \times 10^{-3}$ cm and $\hbar\omega \simeq 400$ cm^{-1}, the quantum enhancement effect of the rate is only 10%.

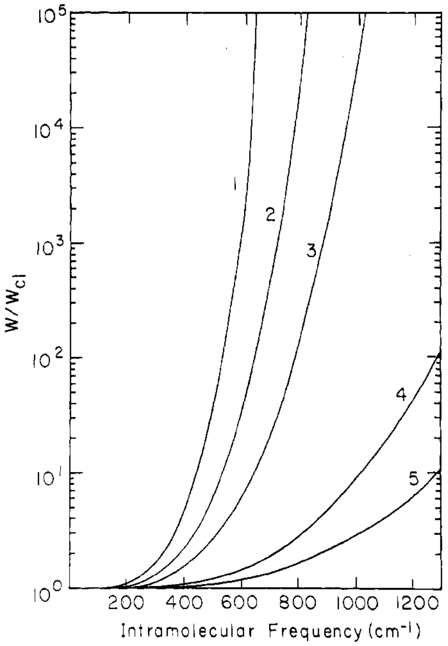

Figure 1. The ratio of the quantum-mechanical Franck–Condon factors to their high-temperature classical limit, W/W_{cl}, vs. intramolecular frequency in symmetric electron-exchange reactions at room temperatures ($k_BT = 200$ cm^{-1}). $(\Delta d)^2$ is as follows: 0.1, 0.05, 0.025, 0.005, and 0.0025 cm for curves 1–5, respectively.

The present analysis of quantum effects on ET rates was limited to symmetric reaction ($\Delta E = 0$) at room temperature. For symmetric ET the quantum contribution results in nuclear tunneling effects which enhance the rate. These nuclear tunneling effects survive even at room temperature. From the experimentalist's point of view, these room-temperature quantum effects are not very dramatic, as they can enhance the "normal" symmetric ET rate by less than 1 order of magnitude. Nevertheless, we feel that the quantitative elucidation of these quantum effects is of importance from the point of view of general methodology. Needless to say, quantum nuclear tunneling effects on ET will become more pronounced at low temperatures, as documented for some biological systems.[6] Furthermore, for strongly exothermic ET reactions, an additional quantum effect involving vibrational excitation of inner-shell vibrational modes will be exhibited, resulting in a considerable enhancement of the ET rates.[5]