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**Theory for Electron-Transfer Reactions
Involving Two Marcus Surfaces with a Different Force Constant**

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Abstract

Theory for electron-transfer reactions at high temperature involving two Marcus parabolic surfaces with a different force constant is presented. The dynamic solvent effects are also considered using the stochastic Liouville equation, assuming an overdamped Debye solvent. An analytical expression for the adiabatic/nonadiabatic electron-transfer rate constant is derived.

1. Introduction

Since the pioneering work of Marcus,¹ most theoretical treatments of electron-transfer reactions have assumed that the Marcus free energy surfaces for the reactant and the product have the same force constant. As pointed out by Marcus,¹ this assumption becomes invalid if saturation of the solvent polarization occurs. This situation can happen for a polar solvent with a dipole moment μ in a strong electric field (E) such that $\mu E/k_B T \geq 1$. In this case, the Langevin function for the induced polarization is in the saturation regime and is no longer a linear function of $\mu E/k_B T$.² The problem for such a system with two free energy surfaces characterized by a different force constant has been considered by Marcus.³ He suggested that the system can be treated in an approximated manner by using an average force constant $\lambda_{\text{eff}} = 2 \lambda_1 \lambda_2 / (\lambda_1 + \lambda_2)$, where λ_1 and λ_2 are the force constants for each individual parabolic potential. More recently, Kakitani and Mataga⁴ have examined the same problem considering the initial neutral state of the reactant and the final ionic state having a different force constant. They have applied the approximation of Hopfield⁵ by introducing the electron insertion spectrum and the electron removal spectrum so that the electron transfer rate is proportional to the integrated overlap of these two spectra. This idea was originated much earlier by Förster⁶ and Dexter⁷ in their energy-transfer study in which the energy-transfer rate is assumed to be proportional to the convolution of the emission band of the sensitizer and the absorption band of the activator. However, as pointed out later by Soules and Duke,⁸ this approximation is valid only if there is no correlation between the interactions of the solvent bath with the reactant state and with the product state. They have shown that, because of the long-range nature of the interactions, the couplings of the bath to two electronic states are highly correlated. Thus, the approach of

Kakitani and Mataga may be questionable.

A stochastic Liouville approach based on the hybrid Bloch-Smoluchowski equation was proposed by Zusman⁹ to describe the electron-transfer reactions in a medium with a large friction at high temperature. It has been shown by Garg et al.¹⁰ that the Zusman equation can be derived from a more fundamental theory based on the "spin-boson" model in which the bath was treated quantum mechanically. The "spin-boson" model¹⁰⁻¹⁶ can be shown¹⁶ to be equivalent to the formalism of Soules and Duke⁸ in their study of energy transfer. For an overdamped solvent, the Bloch-Fokker-Planck equation derived by Garg et al.¹⁰ can be reduced to the Bloch-Smoluchowski equation of Zusman. In this work, we will use this approach to investigate electron-transfer reactions involving two parabolic surfaces with a different force constant. By applying the stochastic Liouville equation of Zusman, an analytical expression for the rate constant is derived. In addition, the dynamic solvent effects will also be considered, assuming an overdamped Debye solvent at high temperature.

2. The stochastic Liouville theory and analytical results

Let us consider a system involving two Marcus potential surfaces with a different force constant. As shown in Fig. 1, the reactant state $|1\rangle$ and the product state $|2\rangle$ can be assigned a Marcus free-energy parabola in the reaction coordinate as given by

$$U_1(x) = \frac{\lambda_1}{2} x^2 \quad (1)$$

$$U_2(x) = \frac{\lambda_2}{2} (x - x_0)^2 - E_g ,$$

where λ_1 and λ_2 are the force constants; E_g is the free-energy gap between the bottoms of the second parabola and the first one. The bottom of the first parabola $U_1(x)$ is assumed at 0 and the second one $U_2(x)$ at x_0 . The Zusman equation⁹ can be expressed in the Laplace transform with the variable s

$$\begin{aligned} s \hat{\rho}_{11} - \rho_{11}(0) &= i \frac{V_{12}}{\hbar} (\hat{\rho}_{12} - \hat{\rho}_{21}) + L_1 \hat{\rho}_{11} \\ s \hat{\rho}_{22} &= -i \frac{V_{12}}{\hbar} (\hat{\rho}_{12} - \hat{\rho}_{21}) + L_2 \hat{\rho}_{22} \\ s \hat{\rho}_{12} &= -i \frac{U_{12}}{\hbar} \hat{\rho}_{12} + i \frac{V_{12}}{\hbar} (\hat{\rho}_{11} - \hat{\rho}_{22}) + L_{12} \hat{\rho}_{12} \\ \hat{\rho}_{21} &= \hat{\rho}_{12}^* , \end{aligned} \quad (2)$$

where $U_{12}(x)$ is defined as $U_1(x) - U_2(x)$. The initial density matrix at the reactant state $|1\rangle$, $\rho_{11}(0)$, is assumed at thermal equilibrium. The Smoluchowski diffusion operators L_1 , L_2 and L_{12} are given by

$$\begin{aligned}
L_1 &= \frac{1}{\tau_{L1}} \left[1 + x \frac{\partial}{\partial x} \right] + \frac{k_B T}{\lambda_1 \tau_{L1}} \frac{\partial^2}{\partial x^2} \\
L_2 &= \frac{1}{\tau_{L2}} \left[1 + (x - x_0) \frac{\partial}{\partial x} \right] + \frac{k_B T}{\lambda_2 \tau_{L2}} \frac{\partial^2}{\partial x^2} \\
L_{12} &= \frac{1}{2} (L_1 + L_2) ,
\end{aligned} \tag{3}$$

where τ_{Lk} , the longitudinal relaxation time on the k-th surface, is a constant in time for a Debye solvent.

As argued by Zusman⁹ the evolution of the off-diagonal elements $\hat{\rho}_{12}$ and $\hat{\rho}_{21}$ involves fast oscillation and the diffusion operator L_{12} can be neglected here. One can solve for $\hat{\rho}_{12}$ and $\hat{\rho}_{21}$ in terms of $\hat{\rho}_{11}$ and $\hat{\rho}_{22}$. Eq. (2) can then be reduced to

$$\begin{aligned}
s \hat{\rho}_{11} - \rho_{11}(0) &\approx - \frac{2s}{\hbar^2 s^2 + U_{12}^2} V_{12}^2 (\hat{\rho}_{11} - \hat{\rho}_{22}) + L_1 \hat{\rho}_{11} \\
s \hat{\rho}_{22} &\approx \frac{2s}{\hbar^2 s^2 + U_{12}^2} V_{12}^2 (\hat{\rho}_{11} - \hat{\rho}_{22}) + L_2 \hat{\rho}_{22} ,
\end{aligned} \tag{4}$$

One may notice that $2s/(\hbar^2 s^2 + U_{12}(x)^2)$ in the above equation can be approximated by a δ -function $2\pi\delta(U_{12}(x))/\hbar$ which is important only around the points where $U_{12}(x)$ vanishes. Two roots, x_{c1} and x_{c2} , can be found for the quadratic equation of $U_{12}(x) = \frac{1}{2}\lambda_1 x^2 - \frac{1}{2}\lambda_2 (x - x_0)^2 + E_t = 0$ and they are given by

$$\begin{aligned}
x_{c1} &= \frac{\lambda_2 x_0}{\lambda_2 - \lambda_1} - \sqrt{\frac{\lambda_1 \lambda_2 x_0^2 + 2E_g(\lambda_2 - \lambda_1)}{(\lambda_2 - \lambda_1)^2}} \\
x_{c2} &= \frac{\lambda_2 x_0}{\lambda_2 - \lambda_1} + \sqrt{\frac{\lambda_1 \lambda_2 x_0^2 + 2E_g(\lambda_2 - \lambda_1)}{(\lambda_2 - \lambda_1)^2}} .
\end{aligned} \tag{5}$$

If $\lambda_1 \lambda_2 x_0^2 + 2E_g(\lambda_2 - \lambda_1) \geq 0$, these two roots are real numbers and represent the physical crossing points of two surfaces $U_1(x)$ and $U_2(x)$. Because the transition is dominant at the crossing points, $2s/(\hbar^2 s^2 + U_{12}(x)^2)$ in eq. (4) can be approximated by expansion around x_{c1} and x_{c2} . One has

$$\begin{aligned}
s \hat{\rho}_{11} - \rho_{11}(0) &\approx - \left[\frac{2s}{\hbar^2 s^2 + \frac{1}{\xi_1^2} (x - x_{c1})^2} + \frac{2s}{\hbar^2 s^2 + \frac{1}{\xi_2^2} (x - x_{c2})^2} \right] V_{12}^2 (\hat{\rho}_{11} - \hat{\rho}_{22}) + L_1 \hat{\rho}_{11} \\
s \hat{\rho}_{22} &\approx \left[\frac{2s}{\hbar^2 s^2 + \frac{1}{\xi_1^2} (x - x_{c1})^2} + \frac{2s}{\hbar^2 s^2 + \frac{1}{\xi_2^2} (x - x_{c2})^2} \right] V_{12}^2 (\hat{\rho}_{11} - \hat{\rho}_{22}) + L_2 \hat{\rho}_{22} .
\end{aligned} \tag{6}$$

The factors $1/\xi_1$ and $1/\xi_2$ are the difference in the slope of two potential surfaces at the crossing points, i.e., $|U_{12}'(x_{c1})|$ and $|U_{12}'(x_{c2})|$, respectively. They are found to be identical as given by

$$\frac{1}{\xi} = \sqrt{\lambda_1 \lambda_2 x_0^2 + 2E_g(\lambda_2 - \lambda_1)} . \tag{7}$$

By using the approximation of $2s/(\hbar^2 s^2 + (x - x_{ck})^2/\xi^2)$ by a δ -function $2\pi\xi\delta(x - x_{ck})/\hbar$, eq. (6) can

be reduced to

$$\begin{aligned} s \hat{\rho}_{11} - \rho_{11}(0) &= - \frac{2\pi}{\hbar} V_{12}^2 \xi [\delta(x-x_{c1}) + \delta(x-x_{c2})] (\hat{\rho}_{11} - \hat{\rho}_{22}) + L_1 \hat{\rho}_{11} \\ s \hat{\rho}_{22} &= \frac{2\pi}{\hbar} V_{12}^2 \xi [\delta(x-x_{c1}) + \delta(x-x_{c2})] (\hat{\rho}_{11} - \hat{\rho}_{22}) + L_2 \hat{\rho}_{22} . \end{aligned} \quad (8)$$

The above equation can be solved by the Green's function method.¹⁷⁻¹⁹ The Green's functions $G_1(x, x'; t)$ and $G_2(x, x'; t)$ for the Smoluchowski diffusion equation on a parabolic surface are well known and they are given by¹⁷⁻²⁰

$$\begin{aligned} G_1(x, x'; t) &= \sqrt{\frac{\lambda_1}{2\pi k_B T (1 - e^{-2\gamma\tau_{11}})}} \exp\left\{-\frac{\lambda_1[x-x'e^{-\gamma\tau_{11}}]^2}{2k_B T(1 - e^{-2\gamma\tau_{11}})}\right\} \\ G_2(x, x'; t) &= \sqrt{\frac{\lambda_2}{2\pi k_B T (1 - e^{-2\gamma\tau_{12}})}} \exp\left\{-\frac{\lambda_2[x-x_0-(x'-x_0)e^{-\gamma\tau_{12}}]^2}{2k_B T(1 - e^{-2\gamma\tau_{12}})}\right\} . \end{aligned} \quad (9)$$

At $t = 0$ both $G_1(x, x'; 0)$ and $G_2(x, x'; 0)$ are given by $\delta(x-x')$. As time approaches infinity, $G_k(x, x'; \infty)$ is given by the Boltzmann distribution $\rho_{kk,eq}(x)$ as

$$\begin{aligned} \rho_{11,eq}(x) &= \sqrt{\frac{\lambda_1}{2\pi k_B T}} e^{-\frac{\lambda_1 x^2}{2k_B T}} \\ \rho_{22,eq}(x) &= \sqrt{\frac{\lambda_2}{2\pi k_B T}} e^{-\frac{\lambda_2(x-x_0)^2}{2k_B T}} . \end{aligned} \quad (10)$$

The Laplace transform of the Green's function satisfies the following equation

$$(s - L_k) \hat{G}_k(x, x') = \delta(x - x'), \quad k = 1, 2. \quad (11)$$

With the Green's function method, one can show from eq. (8)

$$\begin{aligned} \hat{\rho}_{11}(x) &= \frac{1}{s} \rho_{11,eq}(x) - \frac{2\pi}{\hbar} V_{12}^2 \xi \hat{G}_1(x, x_{c1}) (\hat{\rho}_{11}(x_{c1}) - \hat{\rho}_{22}(x_{c1})) \\ &\quad - \frac{2\pi}{\hbar} V_{12}^2 \xi \hat{G}_1(x, x_{c2}) (\hat{\rho}_{11}(x_{c2}) - \hat{\rho}_{22}(x_{c2})) \\ \hat{\rho}_{22}(x) &= \frac{2\pi}{\hbar} V_{12}^2 \xi \hat{G}_2(x, x_{c1}) (\hat{\rho}_{11}(x_{c1}) - \hat{\rho}_{22}(x_{c1})) \\ &\quad + \frac{2\pi}{\hbar} V_{12}^2 \xi \hat{G}_2(x, x_{c2}) (\hat{\rho}_{11}(x_{c2}) - \hat{\rho}_{22}(x_{c2})). \end{aligned} \quad (12)$$

The overall populations $\hat{\sigma}_1(s)$ and $\hat{\sigma}_2(s)$ on each surface, defined as $\int dx \hat{\rho}_{kk}(x)$ (for $k=1, 2$), can be obtained by integrating $\hat{\rho}_{kk}(x)$ in eq. (12) over x , and they are given by

$$\begin{aligned} s\hat{\sigma}_1(s) - 1 &= - \frac{2\pi}{\hbar} V_{12}^2 \xi (\hat{\rho}_{11}(x_{c1}) - \hat{\rho}_{22}(x_{c1})) - \frac{2\pi}{\hbar} V_{12}^2 \xi (\hat{\rho}_{11}(x_{c2}) - \hat{\rho}_{22}(x_{c2})) \\ s\hat{\sigma}_2(s) &= \frac{2\pi}{\hbar} V_{12}^2 \xi (\hat{\rho}_{11}(x_{c1}) - \hat{\rho}_{22}(x_{c1})) + \frac{2\pi}{\hbar} V_{12}^2 \xi (\hat{\rho}_{11}(x_{c2}) - \hat{\rho}_{22}(x_{c2})). \end{aligned} \quad (13)$$

One can show that $G_k(x, x')$ can be approximated by $\rho_{kk,eq}(x)/s + f_k(x, x')$.¹⁷ With the help of this relation and eq. (12), one can evaluate $\hat{\rho}_{kk}(x)$ at x_{c1} and x_{c2} , the crossing points. One has

$$\begin{aligned}
\hat{\rho}_{11}(x_{c1}) - \hat{\rho}_{22}(x_{c1}) &= \frac{\rho_{11,eq}(x_{c1}) \hat{\sigma}_1(s) - \rho_{22,eq}(x_{c1}) \hat{\sigma}_2(s)}{1 + \frac{2\pi}{\hbar} V_{12}^2 \xi[f_1(x_{c1}, x_{c1}) + f_2(x_{c1}, x_{c1})]} \\
\hat{\rho}_{11}(x_{c2}) - \hat{\rho}_{22}(x_{c2}) &= \frac{\rho_{11,eq}(x_{c2}) \hat{\sigma}_1(s) - \rho_{22,eq}(x_{c2}) \hat{\sigma}_2(s)}{1 + \frac{2\pi}{\hbar} V_{12}^2 \xi[f_1(x_{c2}, x_{c2}) + f_2(x_{c2}, x_{c2})]} .
\end{aligned} \tag{14}$$

In deriving the above relation, we have assumed that the crossing points are generally far apart except the special case with $\lambda_1 \lambda_2 x_0^2 + 2E_g(\lambda_1 - \lambda_2) = 0$. Thus, the cross terms such as $f_1(x_{c1}, x_{c2})$ and $f_2(x_{c2}, x_{c1})$ are negligible comparing to $f_1(x_{c1}, x_{c1}) + f_2(x_{c1}, x_{c1})$ and $f_1(x_{c2}, x_{c2}) + f_2(x_{c2}, x_{c2})$.

With help from eqs. (13) and (14), one can derive the following kinetic equation involving only $\hat{\sigma}_k(s)$

$$\begin{pmatrix} s + k_{12} & -k_{21} \\ -k_{12} & s + k_{21} \end{pmatrix} \begin{pmatrix} \hat{\sigma}_1(s) \\ \hat{\sigma}_2(s) \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \tag{15}$$

where

$$\begin{aligned}
k_{12} = \frac{2\pi}{\hbar} V_{12}^2 \xi \left[\frac{\rho_{11,eq}(x_{c1})}{1 + \frac{2\pi}{\hbar} V_{12}^2 \xi [f_1(x_{c1}, x_{c1}) + f_2(x_{c1}, x_{c1})]} \right. \\
\left. + \frac{\rho_{11,eq}(x_{c2})}{1 + \frac{2\pi}{\hbar} V_{12}^2 \xi [f_1(x_{c2}, x_{c2}) + f_2(x_{c2}, x_{c2})]} \right] \\
k_{21} = \frac{2\pi}{\hbar} V_{12}^2 \xi \left[\frac{\rho_{22,eq}(x_{c1})}{1 + \frac{2\pi}{\hbar} V_{12}^2 \xi [f_1(x_{c1}, x_{c1}) + f_2(x_{c1}, x_{c1})]} \right. \\
\left. + \frac{\rho_{22,eq}(x_{c2})}{1 + \frac{2\pi}{\hbar} V_{12}^2 \xi [f_1(x_{c2}, x_{c2}) + f_2(x_{c2}, x_{c2})]} \right] .
\end{aligned} \tag{16}$$

The adiabaticity factor $f_k(x_c, x_c)$ on the k -th surface can be approximated¹⁷ by $\int [G_k(x_c, x_c; t) - \rho_{kk,eq}(x_c)] dt$ as given by

$$\begin{aligned}
f_1(x_c, x_c) &= \sqrt{\frac{\lambda_1}{2\pi k_B T}} e^{-\frac{\lambda_1 x_c^2}{2k_B T}} \left[\int_0^\infty dt \frac{1}{\sqrt{1 - \Delta_1^2(t)}} \exp\left(\frac{\lambda_1 x_c^2}{k_B T} \frac{\Delta_1(t)}{1 + \Delta_1(t)} \right) - 1 \right] \\
f_2(x_c, x_c) &= \sqrt{\frac{\lambda_2}{2\pi k_B T}} e^{-\frac{\lambda_2 (x_c - x_0)^2}{2k_B T}} \left[\int_0^\infty dt \frac{1}{\sqrt{1 - \Delta_2^2(t)}} \exp\left(\frac{\lambda_2 (x_c - x_0)^2}{k_B T} \frac{\Delta_2(t)}{1 + \Delta_2(t)} \right) - 1 \right] ,
\end{aligned} \tag{17}$$

where $\Delta_1(t) = \exp(-t/\tau_{L1})$ and $\Delta_2(t) = \exp(-t/\tau_{L2})$ for a Debye solvent. For a non-Debye solvent, the expression for $\Delta_k(t)$ is more complicate and has been widely studied.^{18,21,23} The electron-transfer rate expression derived in eq. (16) contains adiabaticity factors which bridge the nonadiabatic and the solvent-controlled adiabatic regimes. These factors can be evaluated using eq. (17) and have been discussed with great details by Rips and Jortner.¹⁷ For nonadiabatic

processes, the denominator in eq. (16) containing adiabaticity factors can be replaced by one.

3. Discussion and conclusions

We have derived in eq. (16) an analytical rate expression for electron-transfer reactions. By substitution of x_{c1} and x_{c2} from eq. (5), ξ from eq. (7), $\rho_{11,eq}(x_c)$ and $\rho_{22,eq}(x_c)$ from eq. (10) into eq. (16), one can express the rate constant in terms of the free-energy gap E_g , the reorganization energy E_{r1} ($1/2\lambda_1 x_0^2$) and E_{r2} ($1/2\lambda_2 x_0^2$). Because the force constant for each Marcus parabola can be different, E_{r1} and E_{r2} may not be equal. The rate constant in the nonadiabatic regime can be given by

$$k_{12} = \frac{2\pi}{\hbar} V_{12}^2 \frac{1}{\sqrt{4\pi E_{r1} k_B T (1 + \frac{E_g}{E_{r1}} - \frac{E_g}{E_{r2}})}} \exp\left\{-\frac{(E_{r2} - E_g)^2}{k_B T [E_{r2} + \sqrt{E_{r1} E_{r2} + E_g(E_{r2} - E_{r1})}]^2}\right\} \\ + \frac{2\pi}{\hbar} V_{12}^2 \frac{1}{\sqrt{4\pi E_{r1} k_B T (1 + \frac{E_g}{E_{r1}} - \frac{E_g}{E_{r2}})}} \exp\left\{-\frac{(E_{r2} - E_g)^2}{k_B T [E_{r2} - \sqrt{E_{r1} E_{r2} + E_g(E_{r2} - E_{r1})}]^2}\right\}. \quad (18)$$

If x_{c1} and x_{c2} are of the same order of magnitude, both terms in eq. (18) are comparable and the rate expression is a sum of two quasi-gaussian profiles. By defining $E_r = (E_{r1} + E_{r2})/2$, $\Delta E_r = E_{r1} - E_{r2}$ and assuming $\Delta E_r/E_r$ is very small, i.e., $E_{r1} \approx E_{r2}$, one can show that the second term in eq. (18) involves a highly activated process with $\exp(-1/2\lambda_1 x_{c2}^2/k_B T)$ and is much smaller than $\exp(-1/2\lambda_1 x_{c1}^2/k_B T)$ of the first term. Thus, only the first term representing crossing at x_{c1} is important. Eq. (18) can be reduced to the lowest order expansion of $\Delta E_r/E_r$ as

$$k_{12} = \frac{2\pi}{\hbar} V_{12}^2 \frac{1}{\sqrt{4\pi E_r k_B T [1 + \frac{\Delta E_r}{E_r} (\frac{1}{2} - \frac{E_s}{E_r})]}} \exp\left\{ - \frac{(E_r - E_s - \frac{\Delta E_r}{2})^2}{2E_r k_B T [1 - \frac{\Delta E_r}{4E_r} (1 + \frac{E_s}{E_r})]} \right\} . \quad (19)$$

From the rate expression in eq. (19) one can observe the asymmetry between the normal and the inverted regions. If $E_{r2} > E_{r1}$, the inverted region (E_s larger than E_{r2}) has a larger radius of curvature and is broader; however, if $E_{r2} < E_{r1}$, the inverted region has a smaller radius of curvature and is thus sharper. If $E_{r2} = E_{r1} = E_r$ and $\Delta E_r = 0$, eq. (19) can be easily reduced to the well-known symmetric Marcus rate expression.

In conclusion, we have applied the stochastic Liouville equation of Zusman to investigate the electron-transfer reactions at high temperature for a two-component system involving a different force constant. The dynamic solvent effects can be treated using the Green's function method for the hybrid Bloch-Smoluchowski equation, assuming an overdamped Debye solvent. We have derived an analytical expression for the electron-transfer rate, covering both the nonadiabatic and the solvent-controlled adiabatic regimes. The effects of high-frequency intramolecular vibrational modes were not considered here because of the intrinsic high temperature approximation in the Zusman's approach. These effects can be considered which are now under investigation using the spin-boson model.

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Figure Captions

Fig. 1. Schematic representation of two Marcus free-energy surfaces in the reaction coordinate. The parabolic potential profiles for the reactant state (U_1) and the product state (U_2) are assumed to have a different force constant. E_g is the free-energy gap; $x_{c,1}$ and $x_{c,2}$ are the crossing points of two surfaces; 0 and x_0 are the positions in the reaction coordinate for the bottoms of U_1 and U_2 .

References

- ¹ R. A. Marcus, J. Chem. Phys. **24**, 966 (1956); **24**, 979 (1956).
- ² C. J. F. Böttcher, *Theory of Electric Polarization*, Vol. 1, (Elsevier Scientific Publishing, Amsterdam, 1973)
- ³ R. A. Marcus, J. Chem. Phys. **43**, 679 (1965).
- ⁴ T. Kakitani and N. Mataga, Chem. Phys. **93**, 381 (1985).
- ⁵ J. J. Hopfield, Proc. Natl. Acad. Sci. USA **71**, 3640 (1974).
- ⁶ T. Förster, Naturwiss. **33**, 166 (1946); Ann. Physik, **2**, 55 (1948); Z. Naturforsch. **417**, 321 (1949).
- ⁷ D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).
- ⁸ T. F. Soules and C. B. Duke, Phys. Rev. B **3**, 262 (1971).
- ⁹ L. D. Zusman, Chem. Phys. **49**, 295 (1980).
- ¹⁰ A. Garg, J. N. Onnuchic, and V. Ambegaokar, J. Chem. Phys. **83**, 4491 (1985).
- ¹¹ A. J. Leggett, S. Chakravarty, A. T. Dorsey, M. P. A. Fisher, A. Garg, and W. Zwerger, Rev. Mod. Phys. **59**, 1 (1985).
- ¹² J. N. Onuchic, D. N. Beratan and J. J. Hopfield, J. Phys. Chem. **90**, 3707 (1986).
- ¹³ I. Rips and J. Jortner, J. Chem. Phys. **87**, 2090 (1987).
- ¹⁴ S. Chakravarty and A. J. Leggett, Phys. Rev. Lett. **52**, 5 (1984).
- ¹⁵ D. Xu and K. Schulten, *The Photosynthetic Bacterial Reaction Center II*, edited by J. Breton and A. Vermeglio, (Plenum Press, New York, 1992).
- ¹⁶ J. Tang, J. Chem. Phys. **98**, 6263 (1993)
- ¹⁷ I. Rips and J. Jortner, J. Chem. Phys. **87**, 6513 (1987).

- ¹⁸ T. Fonseca, J. Chem. Phys. **91**, 2869 (1989).
- ¹⁹ J. Tang, J. Chem. Phys. (submitted).
- ²⁰ R. K. Pathria, *Statistical Mechanics*, (Pergamon Press, Oxford, 1972).
- ²¹ G. van der Zwang and J. T. Hynes, J. Chem. Phys. **76**, 2993 (1982); J. Phys. Chem. **89**, 4181 (1985).
- ²² M. Sparpaglione and S. Mukamel, J. Chem. Phys. **88**, 3263 (1988).
- ²³ Y. J. Yan, M. Sparpaglione, and S. Mukamel, J. Phys. Chem. **92**, 4842 (1988).

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