1 of 1

ANL/CHM/PP--80246

30246
J. Chem. Phys.

**A General Stochastic Liouville Theory
for Sequential and Superexchange Electron-Transfer Reactions
Involving Three Marcus Potential Surfaces**

Jau Tang

Chemistry Division, Argonne National Laboratory

Argonne, IL 60439

The submitted manuscript has been authored
by a contractor of the U. S. Government
under contract No. W-31-109-ENG-38.
Accordingly, the U. S. Government retains a
nonexclusive, royalty-free license to publish
or reproduce the published form of this
contribution, or allow others to do so, for
U. S. Government purposes.

MASTER

3B
1980-1981

Abstract

A general theory for nonadiabatic electron-transfer reactions at high temperature involving three Marcus parabolic potential surfaces is presented. The theory can be applied to a three-component system with a donor, a bridging intermediate and an acceptor as well as to a system with charge separation from a photo-excited state followed by charge recombination to a third or ground state. Using the nonperturbative stochastic Liouville approach, analytical expressions are derived for the superexchange and the sequential electron-transfer rate constants covering all three conditions: the "nondegenerate", the "degenerate" and the "quasi-degenerate" regimes.

1. Introduction

Since the pioneering study of electron-transfer reactions by Marcus,¹ most of the theoretical treatments have mainly focused on a donor-acceptor system involving two Marcus surfaces. There are some recent attempts²⁻¹⁰ to extend the theory to a three-component system involving an extra intermediate state. For the "nondegenerate" condition, it has been shown that one can use an effective superexchange coupling based on the second-order perturbation theory. For the "degenerate" or the "quasi-degenerate" condition where the second-order perturbation theory is inadequate, the problems were first investigated by Mukamel et al.^{5,6} They have applied the Padé approximation to include higher order terms of perturbation series. Except the Padé approximation, their approach is very general in regard to solvent dynamics. In another simpler approach by Tang et al.,⁷⁻¹⁰ the nonperturbative stochastic Liouville approach of Zusman¹¹ is used. In this approach, the solvent motion is assumed to be overdamped and follows the classical description of Smoluchowski diffusion. In the more recent work,⁹ analytical rate expressions for both the superexchange and the sequential processes were derived, assuming the "nondegenerate" condition with the direct free energy gap much larger than the electronic couplings. The analytical results bridge the nonadiabatic and the solvent-controlled adiabatic regimes. In another recent work,¹⁰ the "degenerate" regime was considered where the direct free energy gap vanishes and all three Marcus surfaces cross at one point. As an extension to our previous reports, we will treat in this work in an unified manner all three regimes covering the "nondegenerate", the "degenerate" and the more complicate "quasi-degenerate" conditions for three Marcus surfaces.

2. The stochastic Liouville theory

In this work we shall consider electron-transfer reactions involving three Marcus parabolic surfaces. It can be a three-component system involving a donor, an intermediate, and an acceptor, represented by $|1\rangle$, $|2\rangle$, and $|3\rangle$, respectively. The theory can also apply to a system with charge separation from a photo-excited state $|1\rangle$ to a charge-separated state $|2\rangle$ followed by charge recombination to a third state $|3\rangle$. The charge-recombined state $|3\rangle$ could be a ground state or a metastable state having a different displacement in the reaction coordinate with respect to the initial photo-excited state. For the three-component system considered here, we shall assume a large separation between the donor and the acceptor, thus, there is no direct electronic coupling between them. They can influence each other in a superexchange manner through the intermediate state with the coupling to the donor (V_{12}) and to the acceptor (V_{23}). As illustrated in Fig. 1, a Marcus free-energy parabola $U_k(x)$ is assigned to each component in the reaction coordinate

$$\begin{aligned}U_1(x) &= \frac{\lambda}{2}x^2 \\U_2(x) &= \frac{\lambda}{2}(x-x_2)^2 - E_{g(12)} \\U_3(x) &= \frac{\lambda}{2}(x-x_3)^2 - E_{g(13)},\end{aligned}\tag{1}$$

where λ is the force constant. $E_{g(ij)}$ is the free-energy gap defined as the energy separation between the bottoms of the j -th and the i -th parabolas. The bottom of these three parabolas are assumed at x_1 , x_2 , and x_3 , where $x_1 = 0$, x_2 and $x_3 > 0$. The reorganization energy $E_{r(i)}$ can be related to these displacements x_i and x_j by

$$E_{r(i)} = \frac{\lambda}{2}(x_i - x_j)^2 . \quad (2)$$

As in the previous work, we shall assume here that the first and the third parabolas cross at $x = 0$, thus $E_{r(13)} = E_{g(13)}$. The stochastic Liouville equation of Zusman¹¹ can be generalized to a three-component system which can be expressed in the following Laplace transform with the variable s

$$\begin{aligned} s \hat{\rho}_{11} - \rho_{11}(0) &= i \frac{V_{12}}{\hbar} (\hat{\rho}_{12} - \hat{\rho}_{21}) + L_1 \hat{\rho}_{11} \\ s \hat{\rho}_{22} &= -i \frac{V_{12}}{\hbar} (\hat{\rho}_{12} - \hat{\rho}_{21}) + i \frac{V_{23}}{\hbar} (\hat{\rho}_{23} - \hat{\rho}_{32}) + L_2 \hat{\rho}_{22} \\ s \hat{\rho}_{33} &= -i \frac{V_{23}}{\hbar} (\hat{\rho}_{23} - \hat{\rho}_{32}) + L_3 \hat{\rho}_{33} \\ s \hat{\rho}_{12} &= -i \frac{U_{12}}{\hbar} \hat{\rho}_{12} + i \frac{V_{12}}{\hbar} (\hat{\rho}_{11} - \hat{\rho}_{22}) + i \frac{V_{23}}{\hbar} \hat{\rho}_{13} + L_{12} \hat{\rho}_{12} \\ s \hat{\rho}_{23} &= -i \frac{U_{23}}{\hbar} \hat{\rho}_{23} + i \frac{V_{23}}{\hbar} (\hat{\rho}_{22} - \hat{\rho}_{33}) - i \frac{V_{12}}{\hbar} \hat{\rho}_{13} + L_{23} \hat{\rho}_{23} \\ s \hat{\rho}_{13} &= -i \frac{U_{13}}{\hbar} \hat{\rho}_{13} - i \frac{V_{12}}{\hbar} \hat{\rho}_{23} + i \frac{V_{23}}{\hbar} \hat{\rho}_{12} + L_{13} \hat{\rho}_{13} \\ \hat{\rho}_{21} &= \hat{\rho}_{12}^* \\ \hat{\rho}_{32} &= \hat{\rho}_{23}^* \\ \hat{\rho}_{31} &= \hat{\rho}_{13}^* , \end{aligned} \quad (3)$$

V_{13} vanishes because the donor and the acceptor are assumed to be separated by a great distance.

Here $U_{ij}(x)$ is defined as $U_i(x) - U_j(x)$. The Smoluchowski diffusion operator L_i is defined by

$$L_i = \frac{1}{\tau_L} [1 + (x - x_i) \frac{\partial}{\partial x}] + \frac{k_B T}{\lambda \tau_L} \frac{\partial^2}{\partial x^2} \quad (4)$$

where τ_L , known as the longitudinal relaxation time, is a constant in time for a Debye solvent. The diffusion operator L_{ij} involved in the $\hat{\rho}_{12}$, $\hat{\rho}_{23}$, and $\hat{\rho}_{13}$ can be neglected because of fast oscillation of these off-diagonal density-matrix elements.^{11,12} The subset of eq. (3) involving these off-diagonal elements can be expressed by

$$\begin{pmatrix} s + \frac{i}{\hbar} U_{12}(x) & 0 & -\frac{i}{\hbar} V_{23} \\ 0 & s + \frac{i}{\hbar} U_{23}(x) & \frac{i}{\hbar} V_{12} \\ -\frac{i}{\hbar} V_{23} & \frac{i}{\hbar} V_{12} & s + \frac{i}{\hbar} U_{13}(x) \end{pmatrix} \begin{pmatrix} \hat{\rho}_{12} \\ \hat{\rho}_{23} \\ \hat{\rho}_{13} \end{pmatrix} = \begin{pmatrix} \frac{i}{\hbar} V_{12} (\hat{\rho}_{11} - \hat{\rho}_{22}) \\ \frac{i}{\hbar} V_{23} (\hat{\rho}_{22} - \hat{\rho}_{33}) \\ 0 \end{pmatrix} \quad (5)$$

One can solve $\hat{\rho}_{12}$ and $\hat{\rho}_{23}$ from eq. (5) and one has

$$\begin{aligned} \hat{\rho}_{12} &= i \frac{V_{12}}{\hbar} \frac{(\hat{\rho}_{11} - \hat{\rho}_{22}) \left[(s + i \frac{U_{13}}{\hbar})(s + i \frac{U_{23}}{\hbar}) + \frac{V_{12}^2}{\hbar^2} \right] + (\hat{\rho}_{22} - \hat{\rho}_{33}) \frac{V_{23}^2}{\hbar^2}}{\text{Det}(s)} \\ \hat{\rho}_{23} &= i \frac{V_{23}}{\hbar} \frac{(\hat{\rho}_{22} - \hat{\rho}_{33}) \left[(s + i \frac{U_{13}}{\hbar})(s + i \frac{U_{12}}{\hbar}) + \frac{V_{23}^2}{\hbar^2} \right] + (\hat{\rho}_{11} - \hat{\rho}_{22}) \frac{V_{12}^2}{\hbar^2}}{\text{Det}(s)}, \end{aligned} \quad (6)$$

where $\text{Det}(s)$, the determinant of the matrix in eq. (5), can be given by

$$\text{Det}(s) = (s+i\frac{U_{12}}{\hbar})(s+i\frac{U_{23}}{\hbar})(s+i\frac{U_{13}}{\hbar}) + \frac{V_{12}^2}{\hbar^2}(s+i\frac{U_{12}}{\hbar}) + \frac{V_{23}^2}{\hbar^2}(s+i\frac{U_{23}}{\hbar}) . \quad (7)$$

From eq. (1) one can show that

$$\begin{aligned} U_{12}(x) &= \frac{x}{\xi_{12}} - \Delta E \\ U_{23}(x) &= \frac{x}{\xi_{23}} + \Delta E \\ U_{13}(x) &= \frac{x}{\xi_{13}} , \end{aligned} \quad (8)$$

where $1/\xi_{ij}$ is related to the difference in the slope of two adiabatic surfaces $U_i(x)$ and $U_j(x)$ at their crossing point, and

$$\begin{aligned} \xi_{12} &= \frac{1}{\sqrt{2\lambda E_{r(12)}}} \\ \xi_{23} &= \frac{1}{\sqrt{2\lambda E_{r(23)}}} , \quad \text{if } x_3 > x_2 \\ &= \frac{-1}{\sqrt{2\lambda E_{r(23)}}} , \quad \text{if } x_3 < x_2 \\ \xi_{13} &= \frac{1}{\sqrt{2\lambda E_{r(13)}}} \end{aligned} \quad (9)$$

$$\Delta E \equiv U_{21}(x=0) = E_{r(12)} - E_{g(12)} .$$

The direct free-energy gap ΔE is defined as the free-energy difference between $U_2(x)$ and $U_1(x)$ at $x = 0$. The roots for the determinant $\text{Det}(s)$ in eq. (7) is a cubic polynomial equation of s which can be solved analytically. Using eq. (8), one can express $\text{Det}(s)$ as

$$\begin{aligned} \text{Det}(s) = & (s + \frac{i}{\hbar} \frac{x}{\xi_{13}}) [s + \frac{i}{\hbar} (\frac{x}{\xi_{12}} - \Delta E)] [s + \frac{i}{\hbar} (\frac{x}{\xi_{23}} + \Delta E)] \\ & + \frac{V_{12}^2}{\hbar^2} [s + \frac{i}{\hbar} (\frac{x}{\xi_{12}} - \Delta E)] + \frac{V_{23}^2}{\hbar^2} [s + \frac{i}{\hbar} (\frac{x}{\xi_{23}} + \Delta E)] . \end{aligned} \quad (10)$$

As demonstrated by our previous work,^{9-10,13} the k -th root of $\text{Det}(s)$ can be solved approximated by assuming a form with $s \approx -i(x - x_{ck})/\hbar\xi_k$, and then determining ξ_k and x_{ck} by their substitution in $\text{Det}(s)$ while retaining the lowest order terms of x in the expansion. Explicit solutions of $\text{Det}(s)$ will be discussed later.

As one can seen from eq. (6), both $\hat{\rho}_{12}$ and $\hat{\rho}_{23}$ are represented by a ratio of two polynomial functions of s , i.e., $F_{12}(s)/\text{Det}(s)$ and $F_{23}(s)/\text{Det}(s)$, respectively. By expanding them about their poles, or equivalently the roots of $\text{Det}(s)$, one has

$$\begin{aligned} \hat{\rho}_{12} &= i \frac{V_{12}}{\hbar} \sum_{k=1}^3 [A_k(\hat{\rho}_{11} - \hat{\rho}_{22}) + B_k(\hat{\rho}_{22} - \hat{\rho}_{33})] \frac{1}{s - s_k} \\ \hat{\rho}_{23} &= i \frac{V_{23}}{\hbar} \sum_{k=1}^3 [C_k(\hat{\rho}_{11} - \hat{\rho}_{22}) + D_k(\hat{\rho}_{22} - \hat{\rho}_{33})] \frac{1}{s - s_k} \end{aligned} \quad (11)$$

where

$$\begin{aligned}
A_k &= \frac{1}{F_k} \lim_{x \rightarrow x_{ck}} \left[(s_k + \frac{i}{\hbar} U_{13}(x)) (s_k + \frac{i}{\hbar} U_{23}(x)) + \frac{V_{12}^2}{\hbar^2} \right] \\
B_k &= \frac{V_{23}^2}{\hbar^2 F_k} \\
C_k &= \frac{V_{12}^2}{\hbar^2 F_k} \\
D_k &= \lim_{x \rightarrow x_{ck}} \left[(s_k + \frac{i}{\hbar} U_{13}(x)) (s_k + \frac{i}{\hbar} U_{12}(x)) + \frac{V_{23}^2}{\hbar^2} \right] \\
F_k &= \lim_{x \rightarrow x_{ck}} \text{Det}'(s_k) = \frac{1}{\hbar^2} (V_{12}^2 + V_{23}^2 + \Delta E^2) - \frac{x_{ck}^2}{\hbar^2} \left(\frac{1}{\xi_{12}\xi_{13}} + \frac{1}{\xi_{12}\xi_{23}} + \frac{1}{\xi_{13}\xi_{23}} \right) - \frac{x_{ck}\Delta E}{\hbar^2} \left(\frac{1}{\xi_{12}} - \frac{1}{\xi_{23}} \right),
\end{aligned} \tag{12}$$

where $\text{Det}'(s)$ in the above equation is defined as the first derivative of $\text{Det}(s)$.

With help of eqs. (11) and (12), one can substitute these off-diagonal elements $\hat{\rho}_{12}$ and $\hat{\rho}_{23}$ in the first three equations of eq. (3). These equations describe evolution of the diagonal elements $\hat{\rho}_{11}$, $\hat{\rho}_{22}$ and $\hat{\rho}_{33}$, i.e., the population in $|1\rangle$, $|2\rangle$, and $|3\rangle$, and they are given by

$$\begin{aligned}
s\hat{\rho}_{11} - \rho_{11}(0) &= - \frac{V_{12}^2}{\hbar^2} \sum_{k=1}^3 [A_k(\hat{\rho}_{11} - \hat{\rho}_{22}) + B_k(\hat{\rho}_{22} - \hat{\rho}_{33})] \frac{2s}{s^2 + (x - x_{ck})^2 / \hbar^2 \xi_k^2} + L_1 \hat{\rho}_{11} \\
s\hat{\rho}_{22} &= \frac{V_{12}^2}{\hbar^2} \sum_{k=1}^3 [A_k(\hat{\rho}_{11} - \hat{\rho}_{22}) + B_k(\hat{\rho}_{22} - \hat{\rho}_{33})] \frac{2s}{s^2 + (x - x_{ck})^2 / \hbar^2 \xi_k^2} \\
&\quad - \frac{V_{23}^2}{\hbar^2} \sum_{k=1}^3 [C_k(\hat{\rho}_{11} - \hat{\rho}_{22}) + D_k(\hat{\rho}_{22} - \hat{\rho}_{33})] \frac{2s}{s^2 + (x - x_{ck})^2 / \hbar^2 \xi_k^2} + L_2 \hat{\rho}_{22} \\
s\hat{\rho}_{33} &= \frac{V_{23}^2}{\hbar^2} \sum_{k=1}^3 [C_k(\hat{\rho}_{11} - \hat{\rho}_{22}) + D_k(\hat{\rho}_{22} - \hat{\rho}_{33})] \frac{2s}{s^2 + (x - x_{ck})^2 / \hbar^2 \xi_k^2} + L_3 \hat{\rho}_{33}.
\end{aligned} \tag{13}$$

With the approximation of $2s/(s^2 + (x-x_{ck})^2/\hbar^2\xi_k^2)$ by a δ -function $2\pi\hbar |\xi_k| \delta(x-x_{ck})$, eq. (13) can be reduced to

$$\begin{aligned}
 s\hat{\rho}_{11} - \rho_{11}(0) &= -\frac{2\pi}{\hbar}V_{12}^2 \sum_{k=1}^3 [A_k(\hat{\rho}_{11}-\hat{\rho}_{22}) + B_k(\hat{\rho}_{22}-\hat{\rho}_{33})] |\xi_k| \delta(x-x_{ck}) + L_1\hat{\rho}_{11} \\
 s\hat{\rho}_{22} &= \frac{2\pi}{\hbar}V_{12}^2 \sum_{k=1}^3 [A_k(\hat{\rho}_{11}-\hat{\rho}_{22}) + B_k(\hat{\rho}_{22}-\hat{\rho}_{33})] |\xi_k| \delta(x-x_{ck}) \\
 &\quad - \frac{2\pi}{\hbar}V_{23}^2 \sum_{k=1}^3 [C_k(\hat{\rho}_{11}-\hat{\rho}_{22}) + D_k(\hat{\rho}_{22}-\hat{\rho}_{33})] |\xi_k| \delta(x-x_{ck}) + L_2\hat{\rho}_{22} \\
 s\hat{\rho}_{33} &= \frac{2\pi}{\hbar}V_{23}^2 \sum_{k=1}^3 [C_k(\hat{\rho}_{11}-\hat{\rho}_{22}) + D_k(\hat{\rho}_{22}-\hat{\rho}_{33})] |\xi_k| \delta(x-x_{ck}) + L_3\hat{\rho}_{33} .
 \end{aligned} \tag{14}$$

The above equation indicates that transitions occur most efficiently at the effective crossing points x_{ck} ($k = 1, 2$ and 3).

One can solve eq. (14) using the Green's function method.¹² The Green's functions $G_1(x, x'; t)$, $G_2(x, x'; t)$ and $G_3(x, x'; t)$ for the Smoluchowski diffusion equation on a parabolic surface are well known and they are given by¹²⁻¹⁵

$$\begin{aligned}
 G_1(x, x'; t) &= \sqrt{\frac{\lambda_1}{2\pi k_B T (1-e^{-2\psi_{1L}})}} \exp\left\{-\frac{\lambda_1[x-x'e^{-\psi_{1L}}]^2}{2k_B T(1-e^{-2\psi_{1L}})}\right\} \\
 G_2(x, x'; t) &= \sqrt{\frac{\lambda}{2\pi k_B T (1-e^{-2\psi_{1L}})}} \exp\left\{-\frac{\lambda[x-x_2-(x'-x_2)e^{-\psi_{1L}}]^2}{2k_B T(1-e^{-2\psi_{1L}})}\right\} \\
 G_3(x, x'; t) &= \sqrt{\frac{\lambda}{2\pi k_B T (1-e^{-2\psi_{1L}})}} \exp\left\{-\frac{\lambda[x-x_3-(x'-x_3)e^{-\psi_{1L}}]^2}{2k_B T(1-e^{-2\psi_{1L}})}\right\} .
 \end{aligned} \tag{15}$$

At $t = 0$ $G_k(x, x'; 0)$ is 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

$$\begin{aligned}\rho_{11,eq}(x) &= \sqrt{\frac{\lambda}{2\pi k_B T}} e^{-\frac{\lambda x^2}{2k_B T}} \\ \rho_{22,eq}(x) &= \sqrt{\frac{\lambda}{2\pi k_B T}} e^{-\frac{\lambda(x-x_2)^2}{2k_B T}} \\ \rho_{33,eq}(x) &= \sqrt{\frac{\lambda}{2\pi k_B T}} e^{-\frac{\lambda(x-x_3)^2}{2k_B T}}.\end{aligned}\tag{16}$$

The Laplace transform of the Green's function can be shown to satisfy the following Smoluchowski equation¹²

$$(s - L_k) \hat{G}_k(x, x') = \delta(x-x'), \quad k = 1, 2, 3.\tag{17}$$

With the Green's function method, eq. (14) can be solved in terms of the Green's function

$$\begin{aligned}\hat{\rho}_{11}(x) &= \frac{1}{s} \rho_{11,eq}(x) - \frac{2\pi}{\hbar} V_{12}^2 \sum_{k=1}^3 |\xi_k| [A_k(\hat{\rho}_{11}(x_{ck}) - \hat{\rho}_{22}(x_{ck})) + B_k(\hat{\rho}_{22}(x_{ck}) - \hat{\rho}_{33}(x_{ck}))] \hat{G}_1(x, x_{ck}) \\ s\hat{\rho}_{22}(x) &= \frac{2\pi}{\hbar} V_{12}^2 \sum_{k=1}^3 |\xi_k| [A_k(\hat{\rho}_{11}(x_{ck}) - \hat{\rho}_{22}(x_{ck})) + B_k(\hat{\rho}_{22}(x_{ck}) - \hat{\rho}_{33}(x_{ck}))] \hat{G}_2(x, x_{ck}) \\ &\quad - \frac{2\pi}{\hbar} V_{23}^2 \sum_{k=1}^3 |\xi_k| [C_k(\hat{\rho}_{11}(x_{ck}) - \hat{\rho}_{22}(x_{ck})) + D_k(\hat{\rho}_{22}(x_{ck}) - \hat{\rho}_{33}(x_{ck}))] \hat{G}_2(x, x_{ck}) \\ s\hat{\rho}_{33}(x) &= \frac{2\pi}{\hbar} V_{23}^2 \sum_{k=1}^3 |\xi_k| [C_k(\hat{\rho}_{11}(x_{ck}) - \hat{\rho}_{22}(x_{ck})) + D_k(\hat{\rho}_{22}(x_{ck}) - \hat{\rho}_{33}(x_{ck}))] \hat{G}_3(x, x_{ck}).\end{aligned}\tag{18}$$

We can now define $\hat{\sigma}_1(s)$, $\hat{\sigma}_2(s)$ and $\hat{\sigma}_3(s)$ as the overall populations on each surface, i.e., $\int dx \hat{\rho}_{kk}(x)$ (for $k=1, 2, 3$). By integration of $\hat{\rho}_{kk}(x)$ in eq. (18) over x , one can obtain

$$\begin{aligned}
s\hat{\sigma}_1(s) - 1 &= -\frac{2\pi}{\hbar}V_{12}^2 \sum_{k=1}^3 |\xi_k| [A_k(\hat{\rho}_{11}(x_{ck}) - \hat{\rho}_{22}(x_{ck})) + B_k(\hat{\rho}_{22}(x_{ck}) - \hat{\rho}_{33}(x_{ck}))] \\
s\hat{\sigma}_2(s) &= \frac{2\pi}{\hbar}V_{12}^2 \sum_{k=1}^3 |\xi_k| [A_k(\hat{\rho}_{11}(x_{ck}) - \hat{\rho}_{22}(x_{ck})) + B_k(\hat{\rho}_{22}(x_{ck}) - \hat{\rho}_{33}(x_{ck}))] \\
&\quad - \frac{2\pi}{\hbar}V_{23}^2 \sum_{k=1}^3 |\xi_k| [C_k(\hat{\rho}_{11}(x_{ck}) - \hat{\rho}_{22}(x_{ck})) + D_k(\hat{\rho}_{22}(x_{ck}) - \hat{\rho}_{33}(x_{ck}))] \\
s\hat{\sigma}_3(s) &= \frac{2\pi}{\hbar}V_{23}^2 \sum_{k=1}^3 |\xi_k| [C_k(\hat{\rho}_{11}(x_{ck}) - \hat{\rho}_{22}(x_{ck})) + D_k(\hat{\rho}_{22}(x_{ck}) - \hat{\rho}_{33}(x_{ck}))].
\end{aligned} \tag{19}$$

For a nonadiabatic process, $G_k(x, x')$ can be approximated by $\rho_{kk,eq}(x)/s$.¹² With this approximation of $G_k(x, x')$ and eq. (18), $\hat{\rho}_{kk}(x)$ can be evaluated at the crossing point x_{ck} . It can be shown from eqs. (18) and (19) that $\hat{\rho}_{kk}(x_{ck}) = \rho_{kk,eq}(x_{ck})\hat{\sigma}_k(s)$. If one replaces $\hat{\rho}_{kk}(x_{ck})$ in eq. (19) with $\rho_{kk,eq}(x_{ck})\hat{\sigma}_k(s)$, one may transform eq. (19) into the following kinetic equation involving only $\hat{\sigma}_k(s)$

$$\begin{aligned}
s\hat{\sigma}_1(s) - 1 &= -(k_{12} + k_{13})\hat{\sigma}_1(s) + k_{21}\hat{\sigma}_2(s) + k_{31}\hat{\sigma}_3(s) \\
s\hat{\sigma}_2(s) &= k_{12}\hat{\sigma}_1(s) - (k_{21} + k_{23})\hat{\sigma}_2(s) + k_{32}\hat{\sigma}_3(s) \\
s\hat{\sigma}_3(s) &= k_{13}\hat{\sigma}_1(s) + k_{23}\hat{\sigma}_2(s) - (k_{31} + k_{32})\hat{\sigma}_3(s).
\end{aligned} \tag{20}$$

The kinetic equation derived above describes nonadiabatic transitions among the $|1\rangle$, $|2\rangle$, and $|3\rangle$. The sequential transition rate constants k_{12} , k_{21} , k_{23} , k_{32} and the superexchange rate constants k_{13} , k_{31} are given by

$$\begin{aligned}
 k_{12} &= \frac{2\pi}{\hbar} \sum_{k=1}^3 (V_{12}^2 A_k - V_{23}^2 C_k) |\xi_k| \rho_{11,eq}(x_{ck}) \\
 k_{23} &= \frac{2\pi}{\hbar} \sum_{k=1}^3 V_{23}^2 (D_k - C_k) |\xi_k| \rho_{22,eq}(x_{ck}) \\
 k_{13} &= \frac{2\pi}{\hbar} \sum_{k=1}^3 V_{23}^2 C_k |\xi_k| \rho_{11,eq}(x_{ck}) \\
 k_{21} &= \frac{2\pi}{\hbar} \sum_{k=1}^3 V_{12}^2 (A_k - B_k) |\xi_k| \rho_{22,eq}(x_{ck}) \\
 k_{32} &= \frac{2\pi}{\hbar} \sum_{k=1}^3 (V_{23}^2 D_k - V_{12}^2 B_k) |\xi_k| \rho_{33,eq}(x_{ck}) \\
 k_{31} &= \frac{2\pi}{\hbar} \sum_{k=1}^3 V_{12}^2 B_k |\xi_k| \rho_{33,eq}(x_{ck}) .
 \end{aligned} \tag{21}$$

By substitution of A_k , B_k , C_k and D_k as defined earlier from eq. (12), these rate constants in eq. (21) can be expressed as

$$\begin{aligned}
k_{12} &= \frac{2\pi}{\hbar} \sum_{k=1}^3 \frac{V_{12}^2 [V_{12}^2 - V_{23}^2 - \frac{x_{ck}}{\xi_{13}} (\frac{x_{ck}}{\xi_{23}} + \Delta E)] |\xi_k| \rho_{11,eq}(x_{ck})}{V_{12}^2 + V_{23}^2 + \Delta E^2 - x_{ck}^2 (\frac{1}{\xi_{12}\xi_{23}} + \frac{1}{\xi_{12}\xi_{13}} + \frac{1}{\xi_{23}\xi_{13}}) - x_{ck} \Delta E (\frac{1}{\xi_{12}} - \frac{1}{\xi_{23}})} \\
k_{23} &= \frac{2\pi}{\hbar} \sum_{k=1}^3 \frac{V_{23}^2 [V_{23}^2 - V_{12}^2 - \frac{x_{ck}}{\xi_{13}} (\frac{x_{ck}}{\xi_{12}} - \Delta E)] |\xi_k| \rho_{22,eq}(x_{ck})}{V_{12}^2 + V_{23}^2 + \Delta E^2 - x_{ck}^2 (\frac{1}{\xi_{12}\xi_{23}} + \frac{1}{\xi_{12}\xi_{13}} + \frac{1}{\xi_{23}\xi_{13}}) - x_{ck} \Delta E (\frac{1}{\xi_{12}} - \frac{1}{\xi_{23}})} \\
k_{13} &= \frac{2\pi}{\hbar} \sum_{k=1}^3 \frac{V_{12}^2 V_{23}^2 |\xi_k| \rho_{11,eq}(x_{ck})}{V_{12}^2 + V_{23}^2 + \Delta E^2 - x_{ck}^2 (\frac{1}{\xi_{12}\xi_{23}} + \frac{1}{\xi_{12}\xi_{13}} + \frac{1}{\xi_{23}\xi_{13}}) - x_{ck} \Delta E (\frac{1}{\xi_{12}} - \frac{1}{\xi_{23}})} \\
k_{21} &= \frac{2\pi}{\hbar} \sum_{k=1}^3 \frac{V_{12}^2 [V_{12}^2 - V_{23}^2 - \frac{x_{ck}}{\xi_{13}} (\frac{x_{ck}}{\xi_{23}} + \Delta E)] |\xi_k| \rho_{22,eq}(x_{ck})}{V_{12}^2 + V_{23}^2 + \Delta E^2 - x_{ck}^2 (\frac{1}{\xi_{12}\xi_{23}} + \frac{1}{\xi_{12}\xi_{13}} + \frac{1}{\xi_{23}\xi_{13}}) - x_{ck} \Delta E (\frac{1}{\xi_{12}} - \frac{1}{\xi_{23}})} \\
k_{32} &= \frac{2\pi}{\hbar} \sum_{k=1}^3 \frac{V_{23}^2 [V_{23}^2 - V_{12}^2 - \frac{x_{ck}}{\xi_{13}} (\frac{x_{ck}}{\xi_{12}} - \Delta E)] |\xi_k| \rho_{33,eq}(x_{ck})}{V_{12}^2 + V_{23}^2 + \Delta E^2 - x_{ck}^2 (\frac{1}{\xi_{12}\xi_{23}} + \frac{1}{\xi_{12}\xi_{13}} + \frac{1}{\xi_{23}\xi_{13}}) - x_{ck} \Delta E (\frac{1}{\xi_{12}} - \frac{1}{\xi_{23}})} \\
k_{31} &= \frac{2\pi}{\hbar} \sum_{k=1}^3 \frac{V_{12}^2 V_{23}^2 |\xi_k| \rho_{33,eq}(x_{ck})}{V_{12}^2 + V_{23}^2 + \Delta E^2 - x_{ck}^2 (\frac{1}{\xi_{12}\xi_{23}} + \frac{1}{\xi_{12}\xi_{13}} + \frac{1}{\xi_{23}\xi_{13}}) - x_{ck} \Delta E (\frac{1}{\xi_{12}} - \frac{1}{\xi_{23}})}
\end{aligned} \tag{22}$$

Here the Boltzmann distribution $\rho_{kk,eq}(x_{ck})$ at the effective crossing point x_{ck} on the k -th surface is given by $(\lambda/2\pi k_B T)^{1/2} \exp(-\lambda(x_{ck} - x_k)^2/2k_B T)$ as defined in eq. (16). It can be shown that the forward and the backward transition rate constants, k_{ji} and k_{ij} in eq. (22) satisfy the detailed balance principle, i.e., $k_{21} = k_{12} \exp(-E_{k(12)}/k_B T)$ and $k_{32} = k_{23} \exp(-E_{k(23)}/k_B T)$, and $k_{31} = k_{13} \exp(-E_{k(13)}/k_B T)$.

We have derived in eq. (22) a very general expression for the sequential and the superexchange electron-transfer rate constants covering the "degenerate" regime with $\Delta E = 0$, the "quasi-degenerate" regime with $\Delta E \sim V$, and the "non-degenerate" regime with $\Delta E \gg V$. Now we need to express x_{ck} and ξ_k in terms of physical parameters such as the free energy gap ($E_{g(0)}$), the reorganization energy ($E_{r(0)}$), and the electronic couplings (V_{12} and V_{23}). By assuming $s_k = -i(a_k x + b_k)/\hbar$, $a_k = 1/\xi_k$ and $b_k = -x_{ck}/\xi_k$, the coefficients of the first order term in x and the constant term in the expansion of $\text{Det}(s)$ from eq. (10) are given by

$$b_k^3 - b_k(\Delta E^2 + V_{12}^2 + V_{23}^2) + \Delta E(V_{23}^2 - V_{12}^2) = 0$$

$$a_k = \frac{\frac{b_k^2 - b_k \Delta E - V_{12}^2}{\xi_{12}} + \frac{b_k^2 + b_k \Delta E - V_{23}^2}{\xi_{23}} + \frac{b_k^2 - \Delta E^2}{\xi_{13}}}{b_k^2 - \Delta E^2 - V_{12}^2 - V_{23}^2} \quad (23)$$

Roots for any cubic equation of b_k can be solved analytically, although they generally have a very complicate expression. We shall consider in the following a few cases which can be easily solved.

For the non-degenerate case with $\Delta E^2 \gg V_{12}^2 + V_{23}^2$, one has

$$\begin{aligned} x_{c1} &= \xi_1 \Delta E, \quad \xi_1 = \xi_{12} \\ x_{c2} &= -\xi_2 \Delta E, \quad \xi_2 = \xi_{23} \\ x_{c3} &= 0, \quad \xi_3 = \xi_{13} \end{aligned} \quad (24)$$

Here x_{ck} 's are simply the crossing point of Marcus surfaces $U_1(x)$, $U_2(x)$ and $U_3(x)$. With x_{ck} and ξ_k from eq. (24), the nonadiabatic electron-transfer rate constants in eq. (22) can be reduced to

$$\begin{aligned}
k_{12} &= \frac{2\pi}{\hbar} V_{12}^2 [\xi_{12} \rho_{11,eq}(\xi_{12} \Delta E) \\
&\quad + \frac{V_{12}^2 - V_{23}^2}{V_{12}^2 + V_{23}^2 - \frac{\xi_{23}}{\xi_{13}} (1 + \frac{\xi_{12}}{\xi_{23}}) \Delta E^2} |\xi_{23}| \rho_{11,eq}(-\xi_{23} \Delta E) + \frac{V_{12}^2 - V_{23}^2}{\Delta E^2} \xi_{13} \rho_{11,eq}(0)] \\
k_{23} &= \frac{2\pi}{\hbar} V_{23}^2 [|\xi_{23}| \rho_{22,eq}(-\xi_{23} \Delta E) \\
&\quad + \frac{V_{23}^2 - V_{12}^2}{V_{12}^2 + V_{23}^2 - \frac{\xi_{12}}{\xi_{13}} (1 + \frac{\xi_{12}}{\xi_{23}}) \Delta E^2} \xi_{12} \rho_{22,eq}(\xi_{12} \Delta E) + \frac{V_{23}^2 - V_{12}^2}{\Delta E^2} \xi_{13} \rho_{22,eq}(0)] \\
k_{13} &= \frac{2\pi}{\hbar} (\frac{V_{12} V_{23}}{\Delta E})^2 [\xi_{13} \rho_{11,eq}(0) \\
&\quad + \frac{\xi_{12} \rho_{11,eq}(\xi_{12} \Delta E)}{V_{12}^2 + V_{23}^2 - \frac{\xi_{12}}{\xi_{13}} (1 + \frac{\xi_{12}}{\xi_{23}}) \Delta E^2} + \frac{|\xi_{23}| \rho_{11,eq}(-\xi_{23} \Delta E)}{V_{12}^2 + V_{23}^2 - \frac{\xi_{23}}{\xi_{13}} (1 + \frac{\xi_{23}}{\xi_{12}}) \Delta E^2}] .
\end{aligned} \tag{25}$$

The last two terms in the expressions for k_{12} and k_{23} are from the higher-order contributions. They have a small effective coupling strength and are generally negligible. However, they can be important if the first term has an extreme high barrier ($\frac{1}{2} \lambda \xi_{12}^2 \Delta E^2 \gg k_B T$). The last term in k_{12} corresponds to a transition at x_{c3} . It is proportional to $\rho_{11,eq}(0)$ and is an activationless process. This is the same reason why the superexchange process can be important here because it is proportional to $\rho_{11,eq}(0)$ and is activationless, even though the effective coupling strength is of second-order.

For the degenerate case with $\Delta E = 0$, one can also obtain a simple solution for the three

roots for eq. (23) as given by

$$\begin{aligned}
 x_{c1} &= 0, \quad \frac{1}{\xi_1} = \frac{\frac{V_{12}^2}{\xi_{12}} + \frac{V_{23}^2}{\xi_{23}}}{V_{12}^2 + V_{23}^2} \\
 x_{c2} &= -\xi_2 \sqrt{V_{12}^2 + V_{23}^2}, \quad \frac{1}{\xi_2} = \frac{1}{2} \left[\frac{1}{\xi_{13}} + \frac{1}{V_{12}^2 + V_{23}^2} \left(\frac{V_{23}^2}{\xi_{12}} + \frac{V_{12}^2}{\xi_{23}} \right) \right] \\
 x_{c3} &= \xi_3 \sqrt{V_{12}^2 + V_{23}^2}, \quad \frac{1}{\xi_3} = \frac{1}{2} \left[\frac{1}{\xi_{13}} + \frac{1}{V_{12}^2 + V_{23}^2} \left(\frac{V_{23}^2}{\xi_{12}} + \frac{V_{12}^2}{\xi_{23}} \right) \right].
 \end{aligned} \tag{26}$$

With x_{ck} and ξ_k from the above equation and eq. (22), one can show

$$\begin{aligned}
k_{12} &= \frac{2\pi}{\hbar} \frac{V_{12}^4}{V_{12}^2 + V_{23}^2} \{ (V_{12}^2 - V_{23}^2) |\xi_1| \rho_{11,eq}(0) \\
&\quad + \frac{[V_{12}^2 - V_{23}^2 - (V_{12}^2 + V_{23}^2) \frac{\xi_2^2}{\xi_{13}\xi_{23}}] |\xi_2| [\rho_{11,eq}(-\xi_2 \sqrt{V_{12}^2 + V_{23}^2}) + \rho_{11,eq}(\xi_2 \sqrt{V_{12}^2 + V_{23}^2})]}{1 - \xi_2^2 (\frac{1}{\xi_{12}\xi_{23}} + \frac{1}{\xi_{23}\xi_{13}} + \frac{1}{\xi_{12}\xi_{23}})} \} \\
k_{23} &= \frac{2\pi}{\hbar} \frac{V_{23}^2}{V_{12}^2 + V_{23}^2} \{ (V_{23}^2 - V_{12}^2) |\xi_1| \rho_{22,eq}(0) \\
&\quad + \frac{[V_{23}^2 - V_{12}^2 - (V_{12}^2 + V_{23}^2) \frac{\xi_2^2}{\xi_{13}\xi_{12}}] |\xi_2| [\rho_{22,eq}(-\xi_2 \sqrt{V_{12}^2 + V_{23}^2}) + \rho_{22,eq}(\xi_2 \sqrt{V_{12}^2 + V_{23}^2})]}{1 - \xi_2^2 (\frac{1}{\xi_{12}\xi_{23}} + \frac{1}{\xi_{23}\xi_{13}} + \frac{1}{\xi_{12}\xi_{23}})} \} \\
k_{13} &= \frac{2\pi}{\hbar} \frac{V_{12}^2 V_{23}^2}{V_{12}^2 + V_{23}^2} \{ |\xi_1| \rho_{11,eq}(0) \\
&\quad + \frac{|\xi_2| [\rho_{11,eq}(-\xi_2 \sqrt{V_{12}^2 + V_{23}^2}) + \rho_{11,eq}(\xi_2 \sqrt{V_{12}^2 + V_{23}^2})]}{1 - \xi_2^2 (\frac{1}{\xi_{12}\xi_{23}} + \frac{1}{\xi_{23}\xi_{13}} + \frac{1}{\xi_{12}\xi_{23}})} \}
\end{aligned} \tag{27}$$

These two special cases have been investigated in our previous treatments in which $x_3 > x_2$ was assumed.^{9,10}

For the quasi-degenerate regime, we shall assume $\Delta E^2 (V_{23}^2 - V_{12}^2)^2 \ll (\Delta E^2 + V_{23}^2 + V_{12}^2)^3$ so that the last term in the cubic equation of b_k can be neglected. The roots of eq. (23) can then have a simple and manageable form. With this assumption, one has

$$\begin{aligned}
\frac{1}{\xi_1} &= \frac{1}{\Delta E^2 + V_{12}^2 + V_{23}^2} \left[\frac{\Delta E^2}{\xi_{13}} + \frac{V_{12}^2}{\xi_{12}} + \frac{V_{23}^2}{\xi_{23}} \right] \\
x_{01} &= 0 \\
\frac{1}{\xi_2} &= \frac{1}{2(\Delta E^2 + V_{12}^2 + V_{23}^2)} \left[\frac{\Delta E^2 + V_{23}^2}{\xi_{12}} + \frac{\Delta E^2 + V_{12}^2}{\xi_{23}} + \frac{V_{12}^2 + V_{23}^2}{\xi_{13}} + \left(\frac{1}{\xi_{23}} - \frac{1}{\xi_{12}} \right) \Delta E \sqrt{\Delta E^2 + V_{12}^2 + V_{23}^2} \right] \\
x_{02} &= \xi_2 \sqrt{\Delta E^2 + V_{12}^2 + V_{23}^2} \\
\frac{1}{\xi_3} &= \frac{1}{2(\Delta E^2 + V_{12}^2 + V_{23}^2)} \left[\frac{\Delta E^2 + V_{23}^2}{\xi_{12}} + \frac{\Delta E^2 + V_{12}^2}{\xi_{23}} + \frac{V_{12}^2 + V_{23}^2}{\xi_{13}} - \left(\frac{1}{\xi_{23}} - \frac{1}{\xi_{12}} \right) \Delta E \sqrt{\Delta E^2 + V_{12}^2 + V_{23}^2} \right] \\
x_{03} &= -\xi_3 \sqrt{\Delta E^2 + V_{12}^2 + V_{23}^2} .
\end{aligned} \tag{28}$$

One can obtain explicit rate expressions for the sequential and the superexchange electron-transfer reactions by substitution of x_{α} and ξ_k from eq. (28) into eq. (22). Because of their fairly lengthy expression, only the superexchange rate constant is explicitly given in the following

$$\begin{aligned}
k_{13} &= \frac{2\pi}{\hbar} \frac{V_{12}^2 V_{23}^2}{V_{12}^2 + V_{23}^2 + \Delta E^2} \left(|\xi_1| \rho_{11,eq}(0) \right. \\
&\quad + \frac{|\xi_2| \rho_{11,eq} [\xi_2 \sqrt{V_{12}^2 + V_{23}^2 + \Delta E^2}]}{(V_{12}^2 + V_{23}^2 + \Delta E^2) [1 - \xi_2^2 (\frac{1}{\xi_{12}\xi_{13}} + \frac{1}{\xi_{12}\xi_{23}} + \frac{1}{\xi_{23}\xi_{13}})] - \Delta E \sqrt{\Delta E^2 + V_{12}^2 + V_{23}^2} (\frac{\xi_2}{\xi_{12}} - \frac{\xi_2}{\xi_{23}})} \\
&\quad \left. + \frac{|\xi_3| \rho_{11,eq} [-\xi_3 \sqrt{V_{12}^2 + V_{23}^2 + \Delta E^2}]}{(V_{12}^2 + V_{23}^2 + \Delta E^2) [1 - \xi_3^2 (\frac{1}{\xi_{12}\xi_{13}} + \frac{1}{\xi_{12}\xi_{23}} + \frac{1}{\xi_{23}\xi_{13}})] - \Delta E \sqrt{\Delta E^2 + V_{12}^2 + V_{23}^2} (\frac{\xi_3}{\xi_{12}} - \frac{\xi_3}{\xi_{23}})} \right) \tag{29}
\end{aligned}$$

The first term represents an activationless process, whereas the second term can be slightly activated or highly activated depending on the sizes of ΔE , ξ_{ij} (related to the reorganization energy), V_{12} , V_{23} and temperature. The activationless term can also be expressed as

$$k_{13, \text{activationless}} = \frac{2\pi}{\hbar} \frac{1}{\sqrt{4\pi k_B T E_{r(13)}}} \frac{V_{12}^2 V_{23}^2}{|\Delta E^2 + V_{12}^2 \sqrt{\frac{E_{r(12)}}{E_{r(13)}}} \pm V_{23}^2 \sqrt{\frac{E_{r(23)}}{E_{r(13)}}}|}, \quad (30)$$

where "+" is used for $x_3 > x_2$, "-" for $x_3 < x_2$ as shown from eq. (9). As ΔE sweeps pass 0, the rate constant exhibits a "resonance" behavior. For a general condition of V_{12} and V_{23} , the cubic equation of b_k in eq. (23) can be solved¹⁶ and the roots are given by

$$b_1 = \mu + v, \quad b_{2,3} = -\frac{\mu+v}{2} \pm i\frac{\mu-v}{2}\sqrt{3}$$

$$P = -(\Delta E^2 + V_{12}^2 + V_{23}^2)$$

$$Q = (V_{23}^2 - V_{12}^2)\Delta E$$

$$\mu = \left[-\frac{Q}{2} + \sqrt{\frac{P^3}{27} + \frac{Q^2}{4}} \right]^{1/3} \quad (29)$$

$$v = \left[-\frac{Q}{2} - \sqrt{\frac{P^3}{27} + \frac{Q^2}{4}} \right]^{1/3}.$$

The procedure of treatment for this general condition of V_{12} and V_{23} is similar and straightforward. By simply substituting x_{ck} and ξ_k ($a_k = 1/\xi_k$ and $b_k = -x_k/\xi_k$) in eq. (22), one can obtain an explicit but very complicate rate expression.

3. Conclusions

We have applied the stochastic Liouville equation of Zusman to investigate the nonadiabatic electron-transfer reactions involving three Marcus parabolic surfaces such as in a three-component system with a donor, a distant acceptor and a bridging intermediate, or to a system with charge separation from an photo-excited state followed by charge recombination to a third or ground state. In this work, the Green's function method is employed to derive an analytical rate expression for the superexchange and the sequential electron-transfer reactions. All three regimes covering the "nondegenerate" ($\Delta E^2 \gg V_{12}^2 + V_{23}^2$), the "degenerate" ($\Delta E = 0$), and the "quasi-degenerate" ($\Delta E^2 \sim V_{12}^2 + V_{23}^2$) conditions are treated in an unified manner. Only in the "nondegenerate" regime, the second-order perturbation theory for the effective superexchange coupling is valid. If the direct free energy gap ΔE is smaller or comparable to the electronic couplings (V_{12} and V_{23}), "resonance" phenomena due to energy-level crossing can happen as ΔE sweeps pass 0. In this treatment, only the nonadiabatic reactions were considered. In our derivation the adiabatic term $f_k(x, x')$ in the approximation of $G_k(x, x')$ by $\rho_{kk,eq}(x)/s + f_k(x, x')$ was neglected. By keeping it, one can derive a full rate expression in terms of the adiabaticity factor. This has been demonstrated in our previous work⁹ considering only the simple "nondegenerate" case with a large ΔE . For the "degenerate" and the "quasi-degenerate" regimes and the effects of a more general solvent dynamics with a non-Debye solvent,¹⁷⁻¹⁹ however, the treatment is more complicate and requires further efforts.

Acknowledgement

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract W-31-109-Eng-38.

Figure Captions

Fig. 1. Schematic representation of three Marcus free-energy parabolas in the reaction coordinate for the donor (U_1), the intermediate (U_2), and the acceptor (U_3) in a three-component system. $E_{g(12)}$ and $E_{g(13)}$ are the corresponding free-energy gaps, ΔE is the direct free energy gap.

References

- ¹ R. A. Marcus, J. Chem. Phys. **24**, 966 (1956); **24**, 979 (1956).
- ² R. A. Marcus, Chem. Phys. Lett. **133**, 471 (1987).
- ³ M. Bixon and J. Jortner, J. Phys. Chem. **92**, 7148 (1988).
- ⁴ J. S. Joseph, W. Bruno and W. Bialek, J. Phys. Chem. **95**, 6242 (1991).
- ⁵ Y. Hu and S. Mukamel, J. Chem. Phys. **91**, 6973 (1989).
- ⁶ Y. Hu and S. Mukamel *Perspectives in Photosynthesis*, edited by J. Jortner and B. Pullman (Kluwer Academic Publishers, The Netherlands, 1989).
- ⁷ J. Tang, Z. Wang, and J. R. Norris, J. Chem. Phys. (in press).
- ⁸ J. Tang and J. R. Norris, Chem. Phys. (in press).
- ⁹ J. Tang, J. Chem. Phys. (submitted).
- ¹⁰ J. Tang, J. Chem. Phys. (submitted).
- ¹¹ L. D. Zusman, Chem. Phys. **49**, 295 (1980).
- ¹² I. Rips and J. Jortner, J. Chem. Phys. **87**, 6513 (1987).
- ¹³ J. Tang, J. Chem. Phys. (submitted).
- ¹⁴ T. Fonseca, J. Chem. Phys. **91**, 2869 (1989).
- ¹⁵ R. K. Pathria, *Statistical Mechanics*, (Pergamon Press, Oxford, 1972).
- ¹⁶ G. A. Korn and T. M. Korn, *Mathematical Handbook for Scientists and Engineers* (McGraw-Hill, New York, 1961).
- ¹⁷ G. van der Zwang and J. T. Hynes, J. Chem. Phys. **76**, 2993 (1982); J. Phys. Chem. **89**, 4181 (1985).
- ¹⁸ M. Sparpaglione and S. Mukamel, J. Chem. Phys. **88**, 3263 (1988).

¹⁹ Y. J. Yan, M. Sparpaglione, and S. Mukamel, *J. Phys. Chem.* **92**, 4842 (1988).

DATE

FILMED

4 / 4 / 94
tb / tr

END