Application of Reaction Path Smoluchowski Equation Formalism to the Photoisomerization of *Trans*-Stilbene

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The reaction path Smoluchowski equation approach developed in a recent work to calculate the rate constant for a diffusive multidimensional barrier crossing process is extended to incorporate the configuration-dependent diffusion matrix. The resulting formalism is then applied to the investigation of stilbene photoisomerization dynamics. Adapting a model two-dimensional potential and a model diffusion matrix proposed by Agmon and Kosloff [*J. Phys. Chem.*, **91** (1987) 1988], we derive an eigenvalue equlation for the relaxation rate constant of the stilbene photoisomerization. This eigenvalue equation is solved numerically by using the finite element method. The advantages and limitations of the present method are discussed.

Introduction

The photoisomerization of *trans*-stilbene (see Figure 1) provides a useful model system for the investigation of reaction dynamics occurring in condensed phases[1-5]. The electronically excited *trans*-stilbene adiabatically crosses to the twisted form, that is often called the phantom state, through the thermally activated internal rotation, and this twisted stilbene rapidly decays to the ground electronic state by internal conversion, which subsequently relaxes to either the *cis* or *trans* isomer. Among these processes, the passage over barrier from the *trans* form to the phantom state is the rate determining step in the photoisomerization of *trans*-stilbene. This barrier crossing process, involving an internal rotation of the bulky phenyl group, experiences the frictional drag of solvent. To explain the dependence of the photoisomerization rate on solvent viscosity, Kramers's theory of chemical reaction[6] has been often used[1-5]. Considering the one-dimensional dynamics along the reaction coordinate, Kramers derived an expression for the rate of reaction involving the crossing of a potential energy barrier under the thermal noise from the surrounding medium. According to his theory, the reaction rate is inversely proportional to the solvent viscosity. But it has been found that this simple Kramers's theory prediction is not obeyed in many systems. In the case of stilbene photoisomerization, for example, a fractional viscosity dependence was observed[1,2],

$$k = \frac{Z}{\eta^a} \exp(-V_b/k_B T) \qquad (1.1)$$

here Z, η and V_b are preexponential factor, solvent viscosity and barrier height, respectively. And a is typically between zero and unity. Possible factors that may result in the deviation from Kramers's theory are non-Markovian effects[1,5,7,8], complicated interrelation between the microscopic friction and macroscopic viscosity[2], solvent variations of barrier heights[9-11], and the multidimensional nature of the reaction system[12], etc. Using a two-dimensional model potential, Agmon and Kosloff[13] recently investigated the photoisomerization dynamics of *trans*-stilbene and ascribed the fractional

dependence on solvent viscosity to the multidimensionality of potential energy surface. Their methodology relied on the direct numerical solution of the time-dependent Smoluchowski equation.

Recently we have derived a theory for multidimensional barrier crossing processes occurring in highly viscous media[14]. The theory was based on a sophisticatedly constructed reaction path Smoluchowski equation, and has several advantages over previous theories. For example, the theory can deal with the effects of frictional anisotropy and reaction path curvature. The theory is also applicable to reaction involving low potential energy barrier. However, the theory was developed for a restrictive case involving constant diffusion matrix. In the present work, we extend the theory to incorporate the effect of configuration dependency of the diffusion matrix. We then apply the proposed theory to the investigation of the stilbene photoisomerization dynamics.

This paper is arranged as follows. In Sec. II, we describe the model potential and diffusion matrix used in the present work. In Sec. III, we summarize the reaction path Smoluchowski equation approach[14], and extend the formalism to derive an eigenvalue equation for the relaxation rate constant for the isomerization reaction of stilbene which involves a configuration dependent diffusion matrix. The numerical procedure used to solve the eigenvalue equation is then detailed in Sec. IV. Finally, we present the computational results and discuss the advantages and limitations of the present approach in Sec. V.

Model Potential and Diffusion Matrix

Agmon and Kosloff[13] proposed several model two-dimensional potential energy surfaces for *trans*-stilbene photoisomerization. Of which the one used in the present work has the following form:

$$V(\theta, \phi) = V_\theta(\theta, \phi) + V_\phi(\phi) \qquad (2.1)$$

where

$$V_\theta(\theta, \phi) = V_\theta(\theta, 0)(1 + \alpha\cos^2\phi)/(1 + \alpha) \qquad (2.2)$$

$$V_\theta(\theta, 0) = Q_\theta[3\cos(2\theta) - 6\cos(4\theta) + \cos(6\theta) - 4\cos(\theta)]/8 \qquad (2.3)$$

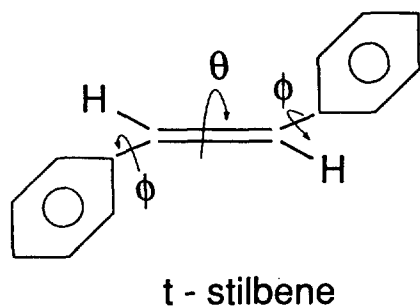$$V_\phi(\phi) = -3Q_\phi\cos(2\phi)/8. \qquad (2.4)$$

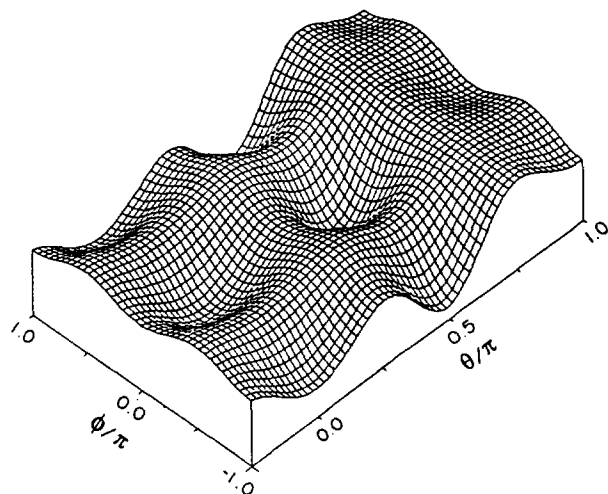**Figure 1.** The structure of *trans*-stilbene.

Figure 2. Model potential energy surface for the isomerization of excited *trans*-stilbene.

Here θ is the rotational angle around the double bond (see Figure 1). This is the reaction coordinate. ϕ is the rotational angle of carbon-phenyl bond. Q_θ, Q_ϕ, and α are positive parameters. The potential profile along the reaction coordinate θ with $\phi=0$ has a well for the *trans* configuration ($\theta=0$) and a deeper well in the perpendicular configuration ($\theta= \pm \pi/2$). The potential energy barrier between the two wells is located at $\theta=0.26\ \pi$, and its height is 1.15 Q_θ relative to the bottom of the *trans* well. The potential V_ϕ provides a potential energy valley along the reaction coordinate. The steepness of this potential energy valley is modulated by the factor $(1+\alpha\cos^2\phi)/(1+\alpha)$ in $V_\theta(\theta, \phi)$. The valley has the most gentle slope at the saddle point ($\theta=0.26\ \pi$) for $\alpha>0$, as can be seen in Figure 2.

We assume that the diffusion matrix is given by

$$D_{\theta\theta}(\phi)=D\ f(\phi)^{-1};\ \ D_{\phi\phi}=D;\ \ D_{\theta\phi}=D_{\phi\theta}=0. \qquad (2.5)$$

The diffusion coefficient D, associated with the carbon-phenyl bond rotation, is assumed to be independent of the solvent viscosity η and the coordinates (θ, ϕ), while the diffusion along the reaction coordinate θ depends on the solvent viscosity and the orientation of the phenyl ring through the function $f(\phi)$ given by

$$f(\phi)=\gamma_1(1+\gamma_2)^{-1}(1+\gamma_2\cos^2\phi)\eta \qquad (2.6)$$

where γ_1 and γ_2 are positive parameters. Accordingly, the diffusion coefficient for the reaction coordinate motion increases by a factor of $(1+\gamma_2)$ as ϕ varies to $\pi/2$.

Theory

Dynamics of reactions occurring in solution is influenced by the solvent friction. While the path of a gas-phase reaction on the potential energy surface (PES) is governed by the inertial anisotropy and PES characteristics, the path of a solution-phase reaction may also be altered by the frictional anisotropy. For reactions occurring in highly viscous medium, however, the inertal effects on the reaction dynamics are negligible. In such high friction regime, it is the forces due to friction and forces derived from the PES (rigorously speaking, the mean free energy surface) which determine the perferred path of reaction, and the stochastic motion of the reaction system on the PES can be described by the Smoluchowski equation[15,16]:

$$\frac{\partial W}{\partial t}=\sum_{i=1}^{F}\sum_{j=1}^{F}\left[\frac{\partial}{\partial x_i}D_{ij}\frac{\partial}{\partial x_j}+\beta\frac{\partial}{\partial x_i}D_{ij}\left(\frac{\partial V}{\partial x_j}\right)\right]W \qquad (3.1)$$

Here F is the degrees of freedom that needs to be considered for describing the reaction dynamics. $W(\{x_i\},\ t)$ is the probability density that the system has the configuration represented by $\{x_i\}$ at time t. (D_{ij}) is the diffusion matrix and $V(\{x_i\})$ is the potential energy. $\beta=1/k_BT$ with the Boltzmann constant k_B and the absolute temperature T.

As the reaction dynamics of gas-phase reactions is described more conveniently in a mass-weighted coordinate system which renders the inertial tensor isotropic, introducing a friction-weighted coordinate system simplifies the description of solution-phase reaction dynamics. In a coordinate system in which the friction tensor is isotropic, the reaction path is determined only by the PES characteristics. Based on this idea, we recently developed a rate theory for solution phase reactions[14]. When the diffusion matrix (D_{ij}) in Eq. (3.1) is diagonal and independent of position, the friction matrix (ξ_{ij}), related to the diffusion matrix (D_{ij}) by the relation

$$(\xi_{ij})=k_BT(D_{ij})^{-1} \qquad (3.2)$$

is also diagonal; *i.e.*, $\xi_{ij}=\xi_i\delta_{ij}$. In such a case the friction-weighted coordinates are defined simply by

$$\bar{x}_i=\xi_i^{1/2}x_i, \qquad (3.3)$$

and in the friction-weighted coordinate system the Smoluchowski equation, Eq. (3.1), reduces to

$$\frac{\partial W}{\partial t}=\sum_{i=1}^{F}k_BT\frac{\partial^2 W}{\partial \bar{x}_i^2}+\sum_{i=1}^{F}\frac{\partial}{\partial \bar{x}_i}\left(W\frac{\partial V}{\partial \bar{x}_i}\right) \qquad (3.4)$$

We then define the diffusional reaction coordinate (DRC), corresponding to the intrinsic reaction coordinate (IRC) for gas-phase reaction[17], by the steepest descent path from the saddle point. As the IRC is the path followed by the gas-phase reaction system, starting from the saddle point and allowed to move with infinitely slow velocity to either of the reactant and product potential wells, DRC is the path followed by the reaction system in the high friction regime. The DRC concept will be useful unless the true reaction path bypasses the saddle point completely, as the IRC for gas-phase reactions is useful only in a corresponding situation.

For a system with F degrees of freedom, we have shown explicitly in Ref. 14 how to calculate the DRC and F-1 normal

coordinates that describe vibrations orthogonal to the reaction path. In terms of these coordinates, the Smoluchowski equation given by Eq. (3.4) was transformed into a reaction path Smoluchowski equation (RPSE). The RPSE involves one special degree of freedom, *i.e.*, the DRC which is the slowest variable unless the potential energy barrier is too low, and F-1 harmonic modes which are the fast variables unless the frictional anisotropy or the potential energy characteristics are abnormal. This suggests approximations which formally eliminate the transverse degrees of freedom and thus yield a reduced equation of motion for only the DRC. This reduction enables one to save computing time enormously. Here we briefly review the main features of the derivation to make the present paper relatively self-contained.

In friction-weighted coordinate system $\{\bar{x}_i\}$, the DRC, defined by the arc length s along a curve $(\{\bar{x}_i^*(s)\})$, is determined by solving a system of differential equations,

$$\frac{d\bar{x}_i^*}{ds} = \nu \left(\frac{\partial V}{\partial \bar{x}_i}\right)_* \bigg/ \left[\sum_{j=1}^{F}\left(\frac{\partial V}{\partial \bar{x}_j}\right)_*^2\right]^{1/2} \quad (i=1, 2, \cdots, F), \qquad (3.5)$$

where the asterisk notation on the derivatives denotes evaluation at $(\{\vec{x}_i^*(s)\})$ and $\nu = \pm 1$ depending on whether s lies before or after the saddle point $s=0$. The nonreactive transverse coordinates, q_k $(k=1, 2, \cdots, F-1)$, at each point on the reaction path are determined by diagonalizing the projected force constant matrix[18] K^p,

$$K^p = (1-P) \cdot K \cdot (1-P), \qquad (3.6)$$

where $K = (K_{ij}) = (\partial^2 V/\partial \bar{x}_i \partial \bar{x}_j)_*$, 1 is the unit maxtrix, and P is the projector whose element is

$$P_{ij} = \left(\frac{d\bar{x}_i^*}{ds}\right)\left(\frac{d\bar{x}_j^*}{ds}\right) \qquad (3.7)$$

The diagonalization yields $F-1$ nonzero eigenvalues, Λ_k $(k=1, 2, \cdots, F-1)$, and corresponding orthonormal eigenvectors, $(\{L_{ik}(s)\})$ $(k=1, 2\cdots, F-1)$. The nonreactive normal coordinates, q_k's are then given by $q_k = \sum_i d_i L_{ik}$ where d_i is the displacement vector $d_i = \bar{x}_i - \bar{x}_i^*$. Constructing the reaction path coordinate system, $\{q_1, q_2, \cdots, q_{F-1}, q_F \equiv s\}$ in this way, we can transform the Smoluchowski equation (3.4) into the reaction path Smoluchowski equation (RPSE),

$$\frac{\partial W}{\partial t} = k_B T F_2 W + F_1 W + W(F_2 V) \qquad (3.8)$$

where F_1 and F_2 are complicated differential operators and their explicit forms have been listed in Ref. 14. Since the DRC is a minimum energy path[17], we can approximate the potential along the reaction path as follows:

$$V(\{q_k\}) \cong V_o(s) + \sum_{k=1}^{F-1} \Lambda_k q_k^2/2, \qquad (3.9)$$

First setting the probability density function $W(\{q_k\}, t)$ as

$$W(\{q_k\}, t) = W_{eq}(\{q_k\})Z(s)e^{-\lambda t}, \qquad (3.10)$$

where W_{eq} is the equilibrium distribution function,

$$W_{eq}(\{q_k\}) = \exp\left[-\beta V_0(s) - \sum_k' \beta\Lambda_k(s)q_k^2/2\right], \qquad (3.11)$$

and then averaging over the nonreactive coordinates, one can reduce the RPSE, Eq. (3.8), to an eigenvalue equation

for the relaxation rate constant λ:

$$Z'' - \left\{\beta V_0' + \sum_1' \frac{\Lambda_1'}{2\Lambda_1} + \left[1 + \sum_k' \frac{B_{kF}^2}{\beta\Lambda_k}\right]^{-1}\left[\sum_1'\left(\frac{B_{1F}^2\Lambda_1'}{\beta\Lambda_1^2}\right.\right.\right.$$
$$\left.\left.\left. - \frac{2B_{1F}B_{1F}'}{\beta\Lambda_1}\right)\right]\right\}Z' + \lambda\beta\left[1 + \sum_k' \frac{B_{kF}^2}{\beta\Lambda_k}\right]^{-1}Z = 0 \qquad (3.12)$$

The lowest nonzero eigenvalue for this eigenvalue equation can be identified with the relaxation rate constant unless the potential energy barrier is too low[14].

For the stillbene photoisomerization dynamics the diffusion matrix, given by Eq. (2.5), is diagonal but depends on the configuration, so that the above procedure (hereafter, referred as Case I) to obtain the relaxation rate constant λ should be generalized and a more complicated coordinate transformation is necessitated. For simplicity, hereafter, the derivation will be presented specifically for the model two-dimensional system devised for the *trans*-stilbene photoisomerization.

The friction matrix, related to the diffusion matrix by Eq. (3.2), may be derived from the Rayleigh dissipation funtion F[19,20];

$$\xi_{ij} = \frac{\partial^2 F}{\partial \dot{x}_i \partial \dot{x}_j} \qquad (3.13)$$

For the model diffusion matrix given by Eq. (2.5), we have

$$F = (\xi_1 \dot{x}_1^2 + \xi_2 \dot{x}_2^2)/2 \qquad (3.14)$$

with $x_1 = \theta$, $x_2 = \phi$, $\xi_2 = k_B T/D = \zeta$, and $\xi_1 = \zeta f(x_2)$.

We then transform the natural Cartesian-like coordinates (x_1, x_2) into generalized friction-weighted coordinates $(\bar{x}_1, \bar{x}_2)$ according to

$$\bar{x}_1 = (\xi_1^\ddagger)^{1/2} x_1, \qquad (3.15)$$

$$\bar{x}_2 \equiv \xi_2^{1/2} \int_{x_2^\ddagger}^{x_2} dx_2' \, \Delta^{-1/2}(x_2') \qquad (3.16)$$

Here $\xi_1^\ddagger$ is the value of ξ_1 at the saddle point $(x_1^\ddagger, x_2^\ddagger)$ [*i.e.*, $\xi_1^\ddagger = \zeta f(x_2=0)$], and $\Delta(x_2)$ measures the variation of the friction coefficient ξ_1 along x_2:

$$\Delta(x_2) = \xi_1(x_2)/\xi_1^\ddagger \qquad (3.17)$$

In this $(\bar{x}_1, \bar{x}_2)$ coordinate system, the Rayleigh dissipation funcion reduced to the form

$$F = \frac{\Delta}{2}(\dot{x}_1^2 + \dot{x}_2^2) \qquad (3.18)$$

so that $\bar{\xi}_{ij} = \Delta \delta_{ij}$. That is, in the friction-weighted coordinate system, the friction matrix becomes *locally* isotropic. Hence, as explained above, the preferred reaction path is again determined only by the potential energy surface. We can then use the same procedure as described above for Case I to find the DRC s, the nonreactive normal coordinate q, and the freqency associated with the q motion. We may also approximate the potential energy surface along the reaction path by

$$V(s, q) \cong V_o(s) + \Lambda q^2/2 \qquad (3.19)$$

With the relations,

$$\frac{\partial}{\partial x_1}=\frac{\partial \bar{x}_1}{\partial \bar{x}_1}\frac{\partial}{\partial x_1}=(\xi_1^{\ddagger})^{1/2}\frac{\partial}{\partial \bar{x}_1} \qquad (3.20)$$

$$\frac{\partial}{\partial x_2}=\frac{\partial \bar{x}_2}{\partial x_2}\frac{\partial}{\partial \bar{x}_2}=(\xi_2)^{1/2}\Delta^{-1/2}\frac{\partial}{\partial \bar{x}_2} \qquad (3.21)$$

the Smoluchowski equation, Eq. (3.1), is transformed into the form

$$\frac{\partial W}{\partial t}=\frac{1}{\Delta}\Big[\sum_{i=1}^{2}k_BT\frac{\partial^2 W}{\partial \bar{x}_i^2}+\sum_{i=1}^{2}\frac{\partial}{\partial \bar{x}_i}\Big(W\frac{\partial V}{\partial \bar{x}_i}\Big)\Big]$$
$$+\Big[k_BT\Delta^{-1/2}\frac{\partial \Delta^{-1/2}}{\partial \bar{x}_2}\frac{\partial W}{\partial \bar{x}_2}+\Delta^{-1/2}\frac{\partial \Delta^{-1/2}}{\partial \bar{x}_2}\frac{\partial V}{\partial \bar{x}_2}W\Big] \qquad (3.22)$$

Then using the relation between the friction-weighted coordinates and the reaction path coordinates[14],

$$\frac{\partial q_k}{\partial \bar{x}_i}=L_{ik}-L_{iF}\frac{\chi_k}{1+\chi_F} \qquad (3.23)$$

we transform Eq. (3.22) to the RPSE

$$\frac{\partial W}{\partial t}=k_BT\ F_2W+F_1W+W(F_2V)+k_BT\Delta^{-1/2}F_3W+\Delta^{-1/2}WF_3V \qquad (3.24)$$

Here F_1, and F_2 have the same expressions as for Case I[14], and F_3 is the new differential operator arising from the coordinate dependence of the friction matrix:

$$F_3=\sum_{i=1}^{2}\Big[\frac{\partial \Delta^{-1/2}}{\partial q_i}\frac{\partial}{\partial q_i}-\frac{\chi_i}{1+\chi_F}\Big(\frac{\partial \Delta^{-1/2}}{\partial s}\frac{\partial}{\partial q_i}+\frac{\partial \Delta^{-1/2}}{\partial q_i}\frac{\partial}{\partial s}\Big)\Big]$$
$$+\sum_{i=1}^{2}\sum_{j=1}^{2}\frac{\chi_i\chi_j}{(1+\chi_F)^2}\frac{\partial \Delta^{-1/2}}{\partial q_i}\frac{\partial}{\partial q_j} \qquad (3.25)$$

Again we assume that the probability density function $W(s, q, t)$ have the following form,

$$W(s, q, t)=W_{eq}(s, q)Z(s)e^{-\lambda t} \qquad (3.26)$$

Where W_{eq} is the equilibrium distribution function,

$$W_{eq}(s, q)=\exp\Big[-\beta V_o(s)-\frac{1}{2}\beta\Lambda(s)q^2\Big] \qquad (3.27)$$

Substituting Eq. (3.26) into Eq. (3.24), we obtain

$$-\lambda Z=\frac{1}{\Delta}\Big\{\frac{1}{\beta(1+\chi_F)^2}Z''-\Big[\frac{1}{(1+\chi_F)^2}(V_0'+\frac{1}{2}\Lambda'q^2)$$
$$-\frac{\chi_q}{(1+\chi_F)^2}\Lambda q+\frac{1}{\beta(1+\chi_F)^3}\frac{\partial \chi_F}{\partial s}-\frac{\chi_q}{\beta(1+\chi_F)^3}B_{qF}\Big]Z'\Big\}$$
$$+\frac{1}{\beta\Delta^{1/2}}\Big[\frac{1}{(1+\chi_F)^2}\frac{\partial \Delta^{-1/2}}{\partial s}-\frac{\chi_q}{(1+\chi_F)^2}\frac{\partial \Delta^{-1/2}}{\partial q}\Big]Z' \qquad (3.28)$$

where prime denotes the differentiation with respect to s.

For the given model potential for the stilbene photoisomerization, $\chi_q=\chi_F=0$ because the reaction path is straight, and $(\partial \Delta^{-1/2}/\partial s)=0$ because Δ is a function of q only [i.e., $\Delta=\Delta(q)$]. Hence Eq. (3.28) reduces to

$$-\lambda Z=\frac{1}{\Delta}\Big\{\frac{1}{\beta}Z''-(V_0'+\frac{1}{2}\Lambda'q^2)Z'\Big\} \qquad (3.29)$$

We then multiply Eq. (3.29) by $|J|\exp(-\beta\Lambda q^2/2)$, where the metric $|J|$ is

$$|J|=\Big|\frac{\partial(x_1, x_2)}{\partial(s, q)}\Big|=\Big|\frac{\partial(x_1, x_2)}{\partial(\bar{x}_1, \bar{x}_2)}\Big|\ \Big|\frac{\partial(\bar{x}_1, \bar{x}_2)}{\partial(s, q)}\Big|$$

$$=(\xi_1^{\ddagger}\xi_2)^{-1/2}\Delta^{1/2}(1+\chi_F)=(\xi_1^{\ddagger}\xi_2)^{-1/2}\Delta^{1/2} \qquad (3.30)$$

and integrate the resulting equation over q. The result is

$$Z''-\beta\Big\{V_0'+\frac{A}{2B}\Lambda'\Big\}Z'+\lambda\beta\frac{C}{B}Z=0 \qquad (3.31)$$

Here, A, B and C are

$$A=\int_{-\infty}^{\infty}dq\Delta^{-1/2}q^2\exp(-\beta\Lambda q^2/2) \qquad (3.32)$$

$$B=\int_{-\infty}^{\infty}dq\Delta^{-1/2}\exp(-\beta\Lambda q^2/2) \qquad (3.33)$$

$$C=\int_{-\infty}^{\infty}dq\Delta^{1/2}\exp(-\beta\Lambda q^2/2) \qquad (3.34)$$

$V_o(s)$ is given by

$$V_o(s)=V(s, 0)=Q_\theta[3\cos(2\gamma s)-6\cos(4\gamma s)$$
$$+\cos(6\gamma s)-4\cos(\gamma s)]/8-3Q_\phi/8, \qquad (3.35)$$

where $\gamma=(\xi_1^{\ddagger})^{-1/2}$. $\Lambda(s)$ is given by

$$\Lambda(s)=\Big(\frac{\partial^2 V}{\partial \bar{x}_2^2}\Big)_{x_2=0}=\Big[\xi_2^{-1}\Delta^{1/2}\Big(\Delta^{1/2}\frac{\partial^2 V}{\partial x_2^2}+\frac{\partial \Delta^{1/2}}{\partial x_2}\frac{\partial V}{\partial x_2}\Big)\Big]_{x_2=0} \qquad (3.36)$$

For the given model diffusion matrix, $\xi_1^{\ddagger}$ and Δ are given by

$$\xi_1^{\ddagger}=\xi_1(0)=\gamma_1\eta\zeta \qquad (3.37)$$

$$\Delta(x_2)=[1+\gamma_2\cos^2(x_2)]/(1+\gamma_2) \qquad (3.38)$$

We can set $x_2^{\ddagger}=0$ because the choice of origin is not important. Since $(\partial V/\partial x_2)_{x_2=0}=0$, $(\partial^2 V/\partial x_2^2)_{x_2=0}=-2\alpha V_\theta(s, 0)/(\alpha+1)+3Q_q/2$ and $\Delta(0)=1$, we obtain

$$\Lambda(s)=-V_\theta(s, 0)\frac{2\alpha}{\xi_2(\alpha+1)}+\frac{3Q_q}{2\xi_2} \qquad (3.39)$$

In order to obtain A, B and C, we approximate $\Delta^{-1/2}$ and $\Delta^{1/2}$ up to q^2 order.

$$[\Delta(q)]^{-1/2}=\Big\{1+\gamma_2\cos^2\Big[\xi_2^{-1/2}\int_0^q dx\sqrt{(1+\gamma_2\cos^2 x)/(1+\gamma_2)}\Big]\Big\}^{-1/2}$$
$$\cong 1+\frac{\gamma_2}{2(1+\gamma_2)\xi_2}q^2 \qquad (3.40)$$

$$[\Delta(q)]^{1/2}\cong 1-\frac{\gamma_2}{2(1+\gamma_2)\xi_2}q^2 \qquad (3.41)$$

By substituting Eq. (3.40) and Eq. (3.41) into Eqs. (3.32)-(3.34) and integrating over q, we obtain the following expressions for A, B and C:

$$A=\Big[\frac{1}{\beta\Lambda}+\frac{\gamma_2}{2(1+\gamma_2)\xi_2}\frac{3}{(\beta\Lambda)^2}\Big]\Big(\frac{2\pi}{\beta\Lambda}\Big)^{1/2} \qquad (3.42)$$

$$B=\Big[1+\frac{\gamma_2}{2(1+\gamma_2)\xi_2}\frac{1}{\beta\Lambda}\Big]\Big(\frac{2\pi}{\beta\Lambda}\Big)^{1/2} \qquad (3.43)$$

$$C=\Big[1-\frac{\gamma_2}{2(1+\gamma_2)\xi_2}\frac{1}{\beta\Lambda}\Big]\Big(\frac{2\pi}{\beta\Lambda}\Big)^{1/2} \qquad (3.44)$$

Thus we finally obtain the following eigenvalue equation for the relaxation rate constant λ:

$$Z''-\beta\Big\{V_0'+\Big[\frac{1}{2\beta\Lambda}+\frac{\gamma_2}{2(1+\gamma_2)\xi_2}\frac{1}{(\beta\Lambda)^2}\Big]\Lambda'\Big\}Z'$$

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$$+\lambda\beta\left\{1-\frac{\gamma_2}{(1+\gamma_2)\xi_2}\frac{1}{\beta\Lambda}+\frac{\gamma_2^2}{2[(1+\gamma_2)\xi_2\beta\Lambda]^2}\right\}Z=0 \quad (3.45)$$

This equation cannot be solved analytically. In the next section we detail the numerical procedure to solve this equation.

Conputational Procedure

We solve Eq. (3.45) numerically by the finite element method (FEM)[21,22] which is a very efficient algorithm for solving the eigenvalue problem. Here we briefly describe the main scheme to solve the Sturm-Liouville equation,

$$[P(s)Z'(s)]'+\lambda R(s)Z(s)=0 \quad (4.1)$$

(1) Put Eq. (4.1) into variational form as follows

$$\delta I=\delta\int_a^b ds\{P(s)[Z'(s)]^2-\lambda R(s)[Z(s)]^2\}=0 \quad (4.2)$$

(2) Discretize a full integral range into n small intervals separated by a distance l with $s_1=a$ and $s_{n+1}=b$. The interval $[s_k, s_{k+1}]$ is called kth finite element. The integral above can be considered as $\delta I=\sum_{k=1}^{k}\delta I_k$ with I_k being the integral over the kth element.

(3) In each element, $Z(s)$ is assumed as $Z(s)=Z^k(y)=(1-y)\varphi^k+y\varphi^{k+1}$, where y is the local normalized coordinate with $s=s_k+yl$ and φ^k's are yet undetermined values at nodal points. With the assumed linear interpolation function I_k is directly integrated in each element. Summing the resulting I_k's we obtain I which is a function of φ^k's, $I=I(\varphi^1, \varphi^2, \cdots, \varphi^{n+1})$. By variational principle, φ^k's are determined by solving the following simultaneous equations.

$$\frac{\partial I}{\partial\varphi^k}=0, \quad (k=1, 2,\cdots, n+1) \quad (4.3)$$

(4) Because of periodic boundary condition, $\varphi^{n+1}=\varphi^1$, Eq. (4.3) can be represented in the matrix form, $PX=\lambda RX$. Here X is an $n\times1$ column matrix, $(\varphi^1, \varphi^2,\cdots,\varphi^{n-1}, \varphi^n)^T$, and P and R are $n\times n$ matrices.

Here p^i and r^i_{jk} are given by

$$p^i=\frac{1}{l}\int_0^1 dyP[a+(i-1)l+y] \quad (i=1, 2,\cdots, n+1) \quad (4.4)$$

$$r^i_{jk}=l\int_0^1 dyR[a+(i-1)l+y]\phi_j\phi_k, \quad (i=1, 2,\cdots, n+1)$$

$$(j, k=1, 2) \quad (4.5)$$

$$\phi_1=1-y, \quad \phi_2=y, \quad (4.6)$$

(5) Solving this matrix eigenvalue equation, we get eigenvalues λ_i $(i=0, 1,\cdots, n)$. This eigenvalue problem is solved using standard numerical procedures available in IMSL[23].

Of the eigenvalues $\{\lambda_i\}$, the zero eigenvalue λ_0 corresponds to the stationary solution, and unless the barrier height is too small, the lowest nonzero eigenvalue λ_1 is well separated from the other eigenvalues and can be identified with the relaxation rate constant for the barrier crossing reaction, *i.e.*, $\lambda_1=k_f+k_r$, where k_f and k_r are forward and backward reaction rate constant, respectively[24].

Result and Discussion

To test the efficiency and accuracy of the algorithm detailed in the previous section, we calculated the eigenvalues for a harmonic oscillator and for a model two-dimensional potential used by Larson and Kostin[25]. We find that setting the value of n equal to 100 yields numerical eigenvalues that are in good agreement with the analytical ones for the harmonic oscillator case and with the numerical ones for the Larson and Kostin potential up to fifth eigenvalue. Because only the lowest nonzero eigenvalue is important, this accuracy is sufficient for the present work.

As can be seen in Figures 3 and 4, the relaxation time, which is the inverse of the relaxation rate constant λ_1, is almost proportional to the solvent viscosity for the potential parameters employed. This is the behavior predicted by the simple Kramers's rate expression. Figure 5 displays the effect of varying the parameter γ_2 in Eq. (2.6). As the parameter γ_2 is increased, the reactive flux away from the DRC (*i.e.*, at larger ϕ angles) experiences smaller frictional retardation. Accordingly, as the solvent viscosity increases, contribution from this *off-DRC flux* will increase. This may result
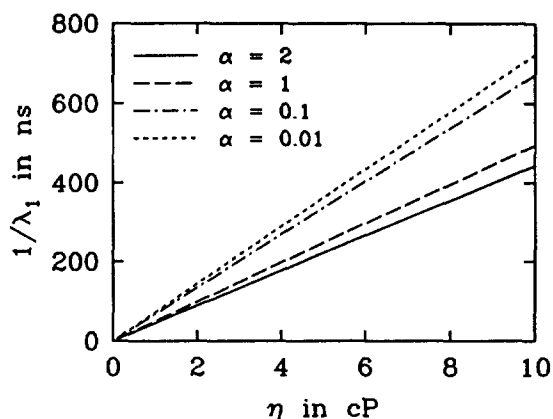
$$P=\begin{bmatrix} p^n+p^1 & -p^1 & 0 & \cdot & \cdot & \cdot & 0 & -p^n \\ -p^1 & p^1+p^2 & -p^2 & 0 & & & & 0 \\ 0 & -p^2 & p^2+p^3 & -p^3 & & & & \cdot \\ \cdot & & & \cdot & & & & \cdot \\ \cdot & & & & \cdot & & & \cdot \\ \cdot & & & & & \cdot & & 0 \\ 0 & & & & -p^{n-2} & p^{n-2}+p^{n-1} & p^{n-1} \\ -p^n & 0 & \cdot & \cdot & \cdot & 0 & -p^{n-1} & p^{n-1}+p^n \end{bmatrix}$$

$$R=\begin{bmatrix} r^n_{22}+r^1_{11} & r^1_{12} & 0 & \cdot & \cdot & \cdot & 0 & r^1_{12} \\ r^1_{12} & r^1_{22}+r^2_{11} & r^2_{12} & 0 & & & & 0 \\ 0 & & & & & & & \cdot \\ \cdot & & & & & & & \cdot \\ \cdot & & & & & & & \cdot \\ \cdot & & & & & & & \cdot \\ 0 & & & & & r^{n-2}_{12} & r^{n-2}_{22}+r^{n-1}_{11} & r^{n-1}_{12} \\ r^n_{12} & 0 & \cdot & \cdot & 0 & 0 & r^{n-1}_{12} & r^{n-1}_{22}+r^n_{11} \end{bmatrix}$$

Reaction Path Smoluchowski Equation Formalism

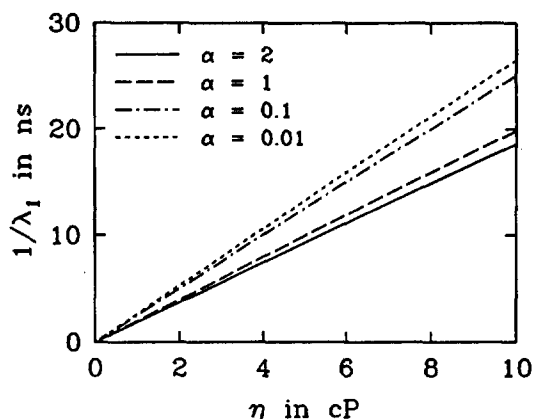*Bull. Korean Chem. Soc., Vol. 12, No. 6, 1991* 697

Figure 3. Dependence of relaxation time on the solvent viscosity. Values of the potential and friction parameters used are $Q_\theta = Q_\phi = 5$ $k_B T$, $D = 10$ ns^{-1}, $\gamma_1 = 2$ cP^{-1}, and $\gamma_2 = 0$.
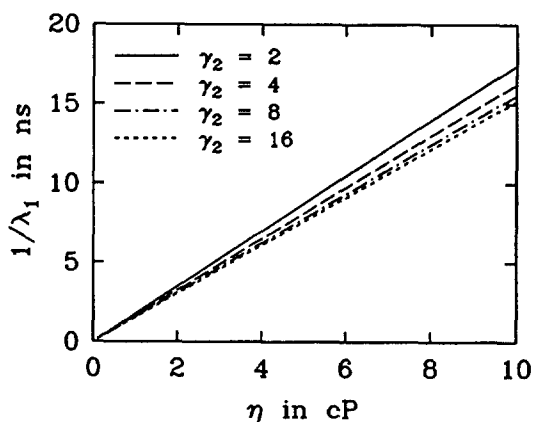

Figure 4. Dependence of relaxation time on the solvent viscosity. Values of the potential and friction parameters used are $Q_\theta = Q_\phi = 2.5$ $k_B T$, $D = 10$ ns^{-1}, $\gamma_1 = 2$ cP^{-1}, and $\gamma_2 = 0$.

Figure 5. Effects of ϕ-dependence of diffusion coefficient. Values of model parameters used are $Q_\theta = 2.5$ $k_B T$, $Q_\phi = 1.0$ $k_B T$, $\alpha = 0.0$, $D = 10$ ns^{-1}, and $\gamma_1 = 2$ cP^{-1}

in the deviation from the simple Kramers's prediction. However, inclusion of the ϕ-dependence of diffusion coefficient by varying the parameter γ_2 does not change the situation as can be seen from Figure 5. Thus, the results of the present calculation does not support the conjecture of Agmon and Kosloff[13] that the fractional viscosity dependence of
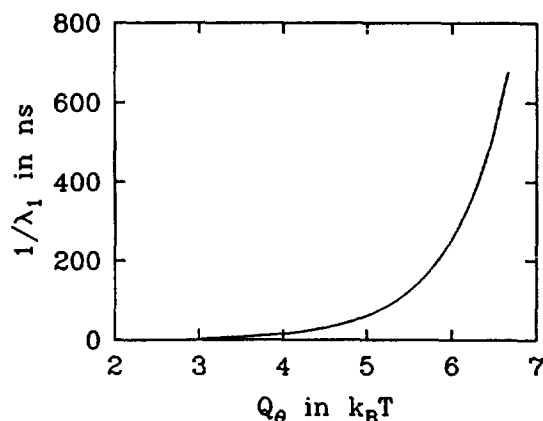

Figure 6. Variation of the relaxation time with the height of potential energy barrier. Values of model parameters used are $Q_\phi = 5.0$ $k_B T$, $\alpha = 0.1$, $D = 10$ ns^{-1}, $\gamma_1 = 2$ cP^{-1}, $\gamma_2 = 4$, and $\eta = 1$ cP.
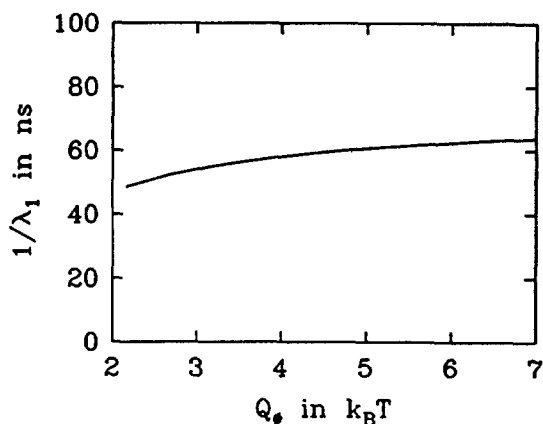

Figure 7. Variation of the relaxation time with the width of potential energy valley. Values of model parameters used are $Q_\theta = 5.0$ $k_B T$, $\alpha = 0.1$, $D = 10$ ns^{-1}, $\gamma_1 = 2$ cP^{-1}, $\gamma_2 = 4$, and $\eta = 1$ cP.

trans-stilbene photoisomerization is due to the multidimensional nature of the reaction system. However, we cannot dismiss the possibility that failure to observe the fractional viscosity dependence of rate constant may be due partly to the limitations of the present formalism. In the present theory, the potential energy valley along the nonreactive transverse coordinate has been approximated to be parabolic and the frequency of the transverse well has been assumed to be large so that the probability density function retains the equilibrium distribution along the transverse coordinate. Therefore the dynamic effects associated with the transverse coordniate motion, which can be the major factor for the deviation from the Kramers's theory, are considered only to a limited extent.

To investigate the effect of the potential energy surface characteristics, we also calculate the relaxation rate constant with varying parameters Q_θ, Q_ϕ, and α. Note that increasing the value of Q_θ increases the height of the potential energy barrier, while increasing the value of Q_ϕ narrows the potential energy valley along the reaction path. The parameter α modulates the steepness of the potential energy valley. As expected, the relaxation time increases exponentially with the increase in the barrier height; see Figure 6. On the other
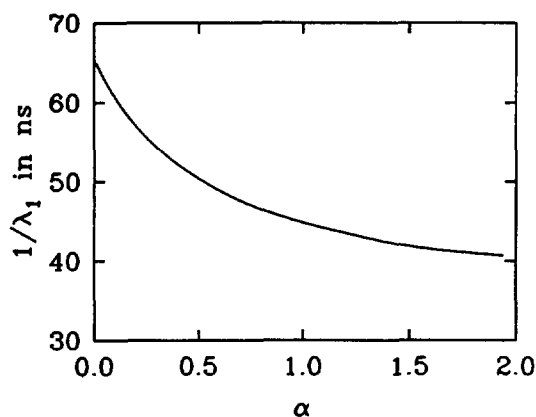
Figure 8. Variation of the relaxation time with the potential parameter α. Values of model parameters used are $Q_\theta = Q_\phi = 5.0$ k_BT, $D = 10$ ns^{-1}, $\gamma_1 = 2$ cP^{-1}, $\gamma_2 = 4$, and $\eta = 1$ cP.

hand, the relaxation time varies mildly with Q_ϕ and α; see Figures 7 and 8.

To conclude, the main advantage of the present method is that calculating the relaxation rate constant is far less time consuming when compared to the direct numerical method of Agmon and Kosloff[13]. Nevertheless, by computing the one dimensional eigenvalue equation, we can incorporate several major dynamic effects arising in multidimensional system to some extant. But application of the present method to the system having a potential energy surface that are too anharmonic along the nonreactive normal coordinates appears to be less satisfactory.

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