Stiffness Effects in Multidimensional Diffusive Barrier Crossing

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The model of Agmon and Kosloff for two-dimensional diffusive barrier crossing is extended. We demonstrate how an increase in stiffness of the potential perpendicular to the reaction coordinate leads to viscosity dependent rates which are closer to the one-dimensional Kramers result. The range over which the dynamics are truly two dimensional is characterized by a fractional viscosity dependence of reaction rates and viscosity dependent activation energies. It is a transition region between Kramers behaviors observed in the two extreme limits. A simple kinetic approximation rationalizes these observations as arising from two competing pathways. It shows surprisingly good agreement with the full calculation.

1. Introduction

In the last decade the Kramers [1] model of diffusive barrier crossing has been revived and extended as part of an effort to understand molecular chemical transformations in solution. Some of the review articles published in the last few years are listed below [2–6]. Until recently much of the theoretical research focused on non-Markovian (memory) effects and frequency dependent friction [2–8]. In this approach other degrees of freedom are usually represented as a harmonic bath. It seems that presently attention is directed towards the understanding of truly multidimensional barrier crossing phenomena [9–13].

Advances in theory are motivated by parallel progress in experiment, especially in the study of photochemical isomerization following ultrafast laser excitation [14]. One model system that has been extensively studied is the isomerization of stilbene, both in solution and pressurized gasses [14–23]. Focusing on the high friction limit, it is often found [15–17] that the dependence of the isomerization rate coefficient, \( k \), on the solvent’s macroscopic (shear) viscosity, \( \eta \), is weaker than predicted by the Kramers theory [1]: Instead of an inverse viscosity dependence, one has

\[
k = \frac{b}{\eta^a}, \quad 0 < a \leq 1
\]

with constant \( a \) and \( b \). A similar viscosity dependence is also observed in ligand binding to myoglobin [24].

The above deviation from Kramers’ prediction can be explained in several ways: (i) Non-Markovian theories [2, 5, 7, 8] can predict slower than \( 1/\eta \) viscosity dependence, though often with non-realistic potential parameters [15, 17, 20a]. (ii) Macroscopic viscosity may be a poor approximation to the microscopic friction. Indeed, better agreement with experiments showing the fractional viscosity dependence, Eq. (1), can sometimes be obtained [16] using the conventional Kramers theory with microscopic friction assumed proportional to the rotational diffusion lifetime. (iii) Potentials may vary systematically with solvent composition [18, 19]. (iv) Multidimensional effects may be dominant [10–13]. While we concentrate below on multidimensional effects, this by no means implies that we believe other effects listed above to be unimportant in explaining the experimental results.

To our knowledge, Agmon and Kosloff [11] were the first to consider the explicit solution for diffusion barrier crossing dynamics in more than one degree of freedom, with anisotropic diffusion and a potential more general than a channel connecting reactants and products [10]. Their model was motivated by earlier work on hemeprotein dynamics [9] and by the experimental observation [15] that, while trans-stilbene shows a fractional viscosity dependence \( (a < 1) \), its stiff counterpart (trans-“stiff” stilbene, see Fig. 1) conforms to Kramers kinetics \( (a = 1) \). The evident difference between these two molecules is that “stiff” stilbene has only one active degree of freedom in its isomerization process (rotation around the double-bond, dihedral angle \( \theta \)), whereas stilbene has an additional rotational motion available (around the phenyl-carbon bond, dihedral angle \( \phi \)). The effect of the perpendicular degree of freedom, \( \phi \), is manifested in two ways. First, the barrier for \( \theta \)-isomerization is expected to decrease as the phenyl rings are rotated out of planarity, due to a decrease of \( \pi \)-orbital coupling. Such an effect still awaits verification by quantum chemistry calculations [25]. Second, the diffusion tensor in these two coordinates is expected to be anisotropic: The phenyl ring rotation displaces much less solvent than the isomerization...
motion and is therefore less sensitive to macroscopic viscosity. In addition, the $\theta$-motion might be less viscosity sensitive when the phenyl rings cut through the solvent with their narrow side i.e., the diffusion coefficient in $\theta$ decreases as the phenyl rings are rotated out of plane [26]. This last effect has not yet been incorporated in the model.

![Chemical structures of stilbene and biindanylidene](image)

**Fig. 1**

Chemical structure of stilbene and biindanylidene ("stiff"-stilbene)

By solving numerically the time-dependent Smoluchowski equation in two dimensions for a potential surface and diffusion tensor with the above mentioned properties, it was shown [11] that viscosity dependences of the form [1] arise. However, it was never explicitly demonstrated that the kinetics become more Kramers-like as the potential along the perpendicular coordinate $\phi$ becomes stiffer as, for example, one expects for "stiff"-stilbene. In the present contribution, we extend the results of Ref. [11] by adding to the potential surface a parabola in $\phi$ and investigating the viscosity dependence as a function of its stiffness. The investigation involves a wide range of viscosity and temperature. A deeper investigation of two dimensional models is timely, especially because in the last year or so several experimental results have been interpreted with the aid of similar ideas [20b–22].

2. Theoretical Procedures

We investigate below a simple extension of the Agmon-Kosloff hypothetical stilbene potential [11], namely

$$V(\theta, \phi) = V_0(\theta, \phi) + V_\phi(\theta, \phi) + \beta \phi^2$$  \hspace{1cm} (2)

with the functions $V_0$ and $V_\phi$ given in Ref. [11]

$$V_0(\theta, \phi) = Q_0[3\cos(2\theta) - 6\cos(4\theta) + \cos(6\theta)
- 4\cos(\theta)[1 + x\cos^2(\phi)]/[8(x + 1)]$$ \hspace{1cm} (3a)

$$V_\phi(\theta, \phi) = Q_\phi[3\cos(2\phi) - 4\cos(4\phi) + \cos(6\phi)]/8$$ \hspace{1cm} (3b)

with $Q_0 = 3$ and $Q_\phi = 2$ energy units (these units were chosen such that the barrier resembles that of stilbene in alkanes, ca. 14.7 kJ/mol) and $x = 4$. For $\beta = 0$ the potential in Eq. (2) reduces exactly to that of Ref. [11]. Increasing values of $\beta$ mimic increasing stiffness of the phenyl ring rotation ($\phi$-coordinate). Experimentally, such increased stiffness can be obtained by a series of aliphatic rings of decreasing size e.g., 7–5 membered rings [16b, 22]. We stress that the stiffness parameters, $\beta$, never modifies the energy profile along the one-dimensional projection of the reaction coordinate ($\phi = 0$). A comparison of a "normal" ($\beta = 0$) and "stiff" ($\beta > 0$) potential is shown in Fig. 2. The initial trans configuration with in-plane phenyl rings is at the origin of the coordinates ($\theta = 0, \phi = 0$) while the final "perpendicular" conformation is at $\theta = \pi/2$ and $\phi = 0$.

The diffusion tensor, $D$, is assumed diagonal and the diagonal elements are denoted by $D_{\theta\theta}$ and $D_{\phi\phi}$. As in Ref. [11], we assume that

$$D_{\phi\phi} = \text{const} = 1$$ \hspace{1cm} (4)

in units of radian$^2$/time, while $D_{\theta\theta}$ varies. This represents an extreme idealization of a situation where the smaller amplitude motion of the phenyl ring is less sensitive to solvent viscosity compared with the larger amplitude isomerization. The rate coefficients are considered a function of $D_{\theta\theta}^{-1}$, which is assumed proportional to the macroscopic viscosity, $\eta$. In relation to interpretations [16] stressing the role of deviations from the Stokes-Einstein hydrodynamic relation, we note that here the reaction coordinate $\theta$ strictly conforms to such a relation, while the assumed (large) deviations from classical hydrodynamics are only in the perpendicular coordinate, $\phi$.

![Potential surface](image)

**Fig. 2**

Effect of the stiffness parameters, $\beta$, on the potential surface, Eqs. (2) and (3). Equipotential contour spacings are 1 and 2 energy unit for $\beta = 0$ and 10, respectively.
The dynamics on the potential surface are assumed [11] to obey the Smoluchowski (diffusion-in-a-potential-field) equation

$$\delta p(\theta, \phi, t)/\delta t = V \cdot D \cdot \left( \mathbf{V} + \mathbf{V}^2(\theta, \phi)/k_B T \right) p(\theta, \phi, t)$$  \hspace{1cm} (5)

for the time evolution of the probability density distribution, $p(\theta, \phi, t)$, in the two dimensional space $(\theta, \phi)$. In Eq. (5), $T$ is the absolute temperature and $k_B$ is Boltzmann’s constant. The initial distribution is a delta function at the origin of the coordinates,

$$p(\theta, \phi, 0) = \delta(\theta) \delta(\phi).$$  \hspace{1cm} (6)

This differs from the initial distribution in Ref. [11], which was like a Gaussian centered at the origin. This difference, however, persists only for the first few time steps during which the initial distribution thermalizes in the reactant’s well. As long as the isomerization barriers are high, the barrier crossing process evolves on a considerably slower time scale.

A detailed description of the computational procedures is given in Ref. [11], where the spatial operator was evaluated by a fast Fourier transform (FFT) routine, and time evolution obtained by Chebyshev propagation. The Chebyshev expansion [27] allows us to take comparably large time steps. Unfortunately, the FFT algorithm may be tricky to implement, and does not easily handle delta function distributions or complicated boundary conditions. In the present calculation we have replaced the FFT procedure by a Master operator. This amounts to discretizing the $(\theta, \phi)$ plane and assigning transition probabilities among nearest-

Fig 3
Effect of stiffness on the density distribution, $p(\theta, \phi, t)$, propagated on the potential surfaces of Fig. 2. Logarithmic contours for $\beta = 10/100$, $n = 1, 2, \ldots$. 
neighboring points along $\theta$ or $\phi$ (no diagonal transitions are allowed) in such a way that Eq. (5) becomes a Master equation with detailed balancing. While additional details may be found in Refs. [9, 28, 29], we stress that implementing fine-differencing in space via a prescription in which detailed-balancing is rigorously obeyed, ensures that as $t \to \infty$ we obtain the exact equilibrium distribution namely, $\exp[-V(\theta, \phi)/k_B T]$ properly normalized. The Master operator is one line of computer code, compared with the large software package needed to implement the FFT routine.

To obtain the reaction rate, we first integrate the density distribution, $p(\theta, \phi, t)$, over the reactants' region to obtain the reactants’ “survival probability”, $S(t)$. This quantity is denoted by $Q(t)$ in Ref. [11]. The reactants' region is assumed to be separated from the products’ region by the ridge line on the potential surface. For a potential with the simple shape shown in Fig. 2, these ridges are straight lines parallel to $\phi$, at $\theta \approx \pm 0.26 \pi$. Next, we fit $S(t)$ to the solution of a 2-state kinetic scheme, reactants $\Rightarrow$ products, which is

$$S(t) = S_{\infty} + (1 - S_{\infty}) \exp(-t/\tau)$$

$$\tau^{-1} = k_1 + k_r, \quad S_{\infty} = k_r \tau.$$  \hspace{1cm} (7a)

Here $k_r$ is the forward (reactants $\to$ products) rate coefficient, while $k_1$ is a similar quantity for the reverse direction. The ultimate equilibrium survival probability, $S_{\infty}$, can be calculated analytically from the potential as the integral of $\exp[-V(\theta, \phi)/k_B T]$ over the reactants' region divided by its integral over the whole space. With the knowledge of $S_{\infty}$, we fit our $S(t)$ data to Eq. (7a) to determine $\tau$ and then evaluate (say) the forward rate coefficient as $k_r = (1 - S_{\infty})/\tau$. This procedure differs from that of Ref. [11], which used both $S_{\infty}$ and $\tau$ as fitting parameters.

3. Results

We have propagated the Smoluchowski equation (5), starting from a delta-function initial distribution, for several values of $D_{\infty}$ ($D_{\infty} = 1$ rad$^2$/time) and three values of the stiffness parameter, $\beta$, in the potential function of Eq. (2). The probability density was subsequently integrated and analyzed via Eq. (7) to yield rate coefficients. These calculations were carried out on a Convex computer with single precision accuracy and a grid of $64 \times 32$. This grid represents the rectangle $-\pi \leq \theta \leq \pi, -\pi/2 \leq \phi \leq \pi/2$, with periodic boundary conditions at its edges. Propagations on a doubled grid ($128 \times 64$) yielded rate coefficients that differed by 5% at most. In several cases, we have propagated to extremely long times so that the final distribution was very close to the equilibrium density. We verified in these cases that the analytic values of $S_{\infty}$.

Table 1

Parameters used in the propagation of Eq. (5) on a 64 × 32 grid and parameters obtained from the kinetic analysis via Eq. (7). $D_{\infty} = 1$ rad$^2$/time, $n_0, \Delta t$ and $n$ are number of Bessel coefficients, time step and total number of time steps, cf. Ref. [11]. Note the general agreement of $k_r$ for $\beta = 0$ and $k_r T = 0.6$ with data in Table 1, runs 1 and 2, of Ref. [11].

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are reproduced to 3–4 digit accuracy. Propagation parameters and rate coefficients obtained are collected in Table 1.

Fig. 3 compares the time dependence of the probability density, $p(\theta, \phi, t)$, for two values of $\beta$. When $D_{66} = 0.1$ and $\beta = 0$, a considerable fraction of the flux bypasses the $\phi = 0$ barrier and proceeds via the "indirect" route that combines isomerization ($\theta$-motion) with phenyl ring rotation ($\phi$-motion). This agrees with the results in Fig. 4 of Ref. [11]. As $\beta$ increases, the indirect route becomes higher in energy (see Fig. 2), so most of the flux flows via the direct barrier crossing route, and the reaction becomes more "one-dimensional".

Fig. 4 shows a typical kinetic analysis by the two-state kinetic model, Eq. (7). We usually exclude from the analysis the first few time steps, during which the initial distribution reaches quasi-equilibrium in the reactants’ well, and very long times for which the difference $S(t) - S_{\infty}$ becomes smaller than the numerical accuracy of our calculation. Occasionally, we found that the decay of $S(t) - S_{\infty}$ was not well represented by a single exponential over the whole time range. In these cases we used the initial decade of the decay in the analysis.

Fig. 5 shows the forward rate coefficient, $k_\theta$, obtained from the above kinetic analysis, as a function of viscosity, $\eta \propto D_{66}^{-1}$. Over the anisotropy range in the diffusion tensor considered in Ref. [11], namely $0.1 \leq D_{66}/D_{00} \leq 10$, we obtain straight lines on a log-log scale (Fig. 5). The slope of these lines yields the parameter $a$. The parameters $a$ and $b$ of Eq. (1) are collected in Table 2. For $\beta = 0$, we find $a = 0.60$, in excellent agreement with Ref. [11]. As $\beta$ is increased, the indirect path becomes less probable (see Fig. 3) and $a$ increases smoothly to unity. This qualitatively agrees with the experimental observation for stilbenes, whose behavior becomes more Kramers-like when the phenyl ring rotation is restricted e.g., in "stiff" stilbene [15,16]. As the dynamics become more one-dimensional, the magnitude of the rate coefficients decrease due to the elimination of alternate pathways. We note that experimental rate coefficients for stiffened stilbene derivatives are typically larger than for the unbridged molecule [22]. Within the present model, this is not a consequence of reduced dimensionality. It could be attributed [16] to a decrease in the one-dimensional barrier height, perhaps due to electronic interactions with the bridging atoms.

Fig. 6a Viscosity dependence over an extended range. Full curves are interpolation by 4th order polynomials. Dotted line is a fit to the high viscosity end of the $\beta = 0$ data, showing the convergence to a Kramers behavior in this limit. Data from Table 1

Fig. 6b A different representation of the data in Fig. 6a, showing the viscosity dependence of the rate coefficient times the viscosity. Full curves are the fractional viscosity fit (Fig. 5) utilizing the parameters from Table 2

In Fig. 6 we have considerably extended the anisotropy range. A propagation for the largest anisotropy value $D_{66}/D_{00} = 1000$, required some 100 hrs of Convex time. The results show that, for the present model, the power law behavior depicted by Eq. (1) actually represents a transition region between the two asymptotic limits of large and small anisotropy. In both of these limits one has a Kramers 1/$\eta$ behavior, though with a different prefactor. This agrees with Eq. (16) of Ref. [11]. The reason why the dynamics become effectively one dimensional in these two limits is physically clear: For large $D_{00}$ the density has no time to develop in the orthogonal,

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Table 2

<table>
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<td>$b$</td>
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\( \phi \) direction. The dynamics then represents direct over the barrier evolution of a “frozen” (in \( \phi \)) initial distribution. In the opposite limit of small \( D_{\infty} \) the initial density rapidly equilibrates in the perpendicular direction. Therefore, it retains its shape and diminishes in amplitude, as an increasing fraction of the population in the reactants’ region crosses the ridgeline into the products’ region. The rate of this process is governed by the magnitude of \( D_{\infty} \) at various \( \phi \) values. Since we have assumed that \( D_{\infty} \) scales as \( 1/\eta \) for all values of \( \phi \), we regain the Kramers behavior in this limit too. Most of the photoisomerization experiments [14—22] have not explored such huge viscosity variations in the diffusive regime.

![Graph showing viscosity dependence at a higher temperature](image)

**Fig. 7**

Viscosity dependence at a higher temperature. Lines are a fit to Eq. (1)

Returning to more moderate variations in anisotropy, we have investigated temperature effects on the observed fractional viscosity behavior, Eq. (1). Fig. 7 shows the viscosity dependence of the reaction rate for a higher temperature, again for the three values of the stiffness parameter, \( \beta \). As expected, increasing temperature results in increasing reactivity and decreasing selectivity, as depicted by the increase in the slope, \( a \). The increase in \( a \) is more prominent for smaller \( a \) values. Since increasing \( T \) is equivalent to a scaling-down of the potential surface, it leads to a decrease in the variation of the barrier height along the perpendicular coordinate and hence to a more Kramers-like behavior [11].

![Graph showing temperature dependence of the reaction rate coefficient](image)

**Fig. 8**

Temperature dependence of the reaction rate coefficient. Lines are a fit to the Arrhenius expression, \( \ln k_f = -E_A/k_B T + \text{const.} \). The two numbers next to each line denote the values of \( D_{\infty} \) and \( E_A \), respectively

In Ref. [19b] the photoisomerization of trans-stilbene was studied as a function of temperature in isoviscous alcohols. A dependence of the activation energy, \( E_A \), on viscosity was interpreted as a failure of the fractional viscosity behavior, Eq. (1). It is more appropriate to interpret the observed behavior as a temperature dependence of \( a \). In Fig. 8 we have rearranged the data of Figs. 6 and 7 to yield Arrhenius plots at different \( D_{\infty} \) values. To these we have added data \( k_B T = 0.4 \). For large \( D_{\infty} \) (small viscosity) the activation energy is large, since the majority of the reactive flux proceeds directly over the relatively large barrier pertaining to the \( \theta \) motion at \( \phi = 0 \). For small \( D_{\infty} \), much of the flux goes via the indirect path which involves lower isomerization barriers, resulting in a considerably smaller activation energy. This behavior is in qualitative agreement with the experimental data shown in Fig. 3 of Ref. [19b].

The effect of stiffness on the viscosity dependence of the activation energy is shown in Fig. 9. As observed above (see Figs. 5 and 7), the variation of \( a \) with \( T \) diminishes as, with increasing stiffness, \( a \) → 1. Indeed we find (Fig. 9) that for \( \beta = 1 \) the variations in \( E_A \) with viscosity are smaller than for \( \beta = 0 \). One might say that such variations [19b] are an indication of truly multidimensional dynamics. It is therefore expected that “stiff”-stilbene will show a viscosity independent \( E_A \).

**Table 3**

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<th>C</th>
<th>D</th>
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\(^a\) Energies relative to the origin of the coordinates.
\(^b\) \( \theta \) and \( \phi \) values in units of radian/\( \text{rad} \).
\(^c\) \( f_{\theta \theta} \) and \( f_{\phi \phi} \) in units of energy/radian².

### 4. A Kinetic Model

In order to qualitatively understand the physics behind the effects demonstrated in Figs. 5—7, it is instructive to construct a simple kinetic model. We apply the model to the case where \( \beta = 0 \). The model involves four states, A, B, C, and D, corresponding to the four distinct wells in the potential surface of Fig. 2. The coordinates (\( \theta, \phi \)), energies and force-constants (\( f_{\theta \theta}, f_{\phi \phi} \)) of the four states, as evaluated from the potential surface, Eqs. (2)–(3), are collected in Table 3. Between the four states one has transitions according to the following kinetic scheme

\[
\begin{align*}
B & \xrightarrow{k_1} C \\
\text{A} & \xrightarrow{k_1} \text{D}
\end{align*}
\]
In this scheme state A represents the initial state, A and B are the reactants while C and D are the products. This corresponds most closely to the dividing surface employed in our full calculation, with an absorbing boundary condition at the product states (C and D). There are two paths leading from initial state to products: The direct path with \( k_{\text{dir}} \equiv k_1 \) and the indirect path, involving the intermediate state B.

The effective rate coefficient for the indirect path, \( k_{\text{ind}} \), is evaluated under steady-state conditions, assuming \( \frac{d[B]}{dt} = 0 \). This gives

\[
k_{\text{ind}} = \frac{k_1 k_2}{k_3 + k_{-2}}.
\]  

(9)

The overall forward rate coefficient for the conversion of A to products (C \( \cup \) D) is

\[
k_i = k_{\text{dir}} + k_{\text{ind}}.
\]  

(10)

Since \( k_3 \) and \( k_{-2} \) will be proportional to \( D_{\eta \eta} \), hence to \( 1/\eta \), while \( k_1 \) and \( k_{-1} \) will be proportional to \( D_{\phi \phi} \) and are hence constants, the overall viscosity dependence has the form

\[
k_i = \frac{a}{1 + b \eta} + \frac{c}{\eta},
\]  

(11)

with \( a, b \) and \( c \) constants. This form indeed shows a \( 1/\eta \) behavior in the two extreme limits of \( \eta \to 0 \) and \( \eta \to \infty \) (cf. Eq. (16) in Ref. [11]), with a transition region in between.

To evaluate \( k_i \) from Eqs. (9) and (10), we need to know the rate coefficients for the various steps in the reaction scheme, Eq. (8). We estimate these from the one-dimensional Kramers expression [1] which, in the diffusive regime for parabolic well and barrier, becomes [13]

\[
2 \pi k_B T k_i = (-f_{\phi}^o f_{\phi}^o f_{\eta}^o f_{\eta}^o)^{1/2} D_{\eta \eta} \exp[-\Delta V''/k_B T].
\]  

(12)

Here \( f_{\phi}^o \) and \( f_{\eta}^o \) are the force-constants at the reactants’ well and the barrier, respectively. Both are evaluated along some one dimensional coordinate, \( \phi = \theta \) or \( \phi \) in the present case. In other words, the potential near the reactants (\( \phi = \theta \)) and transition state (\( \phi^t \)) is approximated (up to a constant) as \( \frac{1}{2} f_{\phi}^o (\theta - \phi)^2 \) and \( \frac{1}{2} f_{\eta}^o (\eta - \phi^t)^2 \), respectively. \( \Delta V'' = V'(\phi^t) \)

\( V'(\phi^t) \) is the classical barrier height along \( \phi \). \( f_{\phi}^o \) and \( f_{\eta}^o \) are the corresponding well and barrier force-constants along the direction \( \phi \) perpendicular to \( \phi \). Using the data in Tables 3 and 4, one can evaluate the rate coefficients \( k_i \) for \( i = 1, 2, -2 \) and 3, to be used in Eq. (9). These coefficients were multiplied by a statistical factor of 2, to account for the fact that each well in Fig. 2 leads to two equivalent wells, and collected in Table 5.

Table 5
Rate parameters for the reaction scheme in Eq. (8)

<table>
<thead>
<tr>
<th>Rate coefficient</th>
<th>Transition</th>
<th>( k_1/D_{\phi \phi} )</th>
<th>( k_2/D_{\phi \phi} )</th>
<th>( k_{-2}/D_{\eta \eta} )</th>
<th>( k_3/D_{\phi \phi} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnitude</td>
<td></td>
<td>0.0846</td>
<td>0.326</td>
<td>0.808</td>
<td>0.812</td>
</tr>
</tbody>
</table>

Fig. 10
Viscosity dependence of the reaction rate coefficient as calculated from the kinetic model, Eqs. (9) and (10). The overall rate coefficient (full curve) is the sum of the contributions from the direct and indirect pathways (dashed curves). Circles denote results from exact propagation, Table 4.

The outcome of the kinetic approximation is shown in Fig. 10. While the direct rate coefficient is a straight line on a log-log plot, the indirect rate coefficient is constant at small viscosities and Kramers-like at large viscosities, see Eq. (11). When these two curves intersect, they give rise to the full curve, which shows the above mentioned transition between the two asymptotic limits. In simple chemical language, increasing viscosity induces a change of mechanism, from a direct to an indirect pathway. As the stiffness, \( \beta \), is increased, the direct pathway dominates: The curve for \( k_{\text{dir}} \) drops until eventually is does not intersect the \( k_{\text{dir}} \) curve at all. Hence as \( \beta \to \infty \) we get that \( k_{\text{dir}} \to k_{\text{dir}} \), with a pure Kramers behavior over the whole viscosity range.

5. Conclusion
We have extended the two dimensional diffusive barrier crossing model of Agmon and Kosloff [11] in several directions, with the following conclusions:

(a) Over an extended anisotropy range in the diffusion tensor, the rate coefficient shows a Kramers-like behavior in the two extreme limits with a transition region, which can be described by a fractional viscosity dependence, Eq. (1).
(b) As the stiffness of the potential in the perpendicular coordinate is increased, the transition region decreases until the dynamics become Kramers-like over the whole anisotropy range.

(c) In the regime where two dimensional dynamics is important, the power $a$ in Eq. (1) increases with temperature. This is manifested by an Arrhenius activation energy which varies with anisotropy. As the stiffness of the potential increases, this temperature effect diminishes.

(d) A simple kinetic scheme, employing four states with transition rates evaluated from the two dimensional potential surface by the one-dimensional Kramers expression, produces a qualitatively good agreement with the exact solution of the two-dimensional Smoluchowski equation. Within this framework, the observed behavior is a consequence of a viscosity dependent change in mechanism.

It is interesting to note that, for anisotropy, $D_{\perp \parallel}/D_{\parallel \parallel}$, which is proportional to the macroscopic viscosity, all of the above conclusions are borne out by photochemical isomerization experiments:

(a) Experimental rate coefficients conform to fractional viscosity dependences over a limited viscosity range [15 - 17].

(b) "Stiff"-stilbene shows a 1/η viscosity dependence, as opposed to stilbene which shows the fractional viscosity dependence [15,16].

(c) Stilbene has a viscosity dependent activation energy for its isomerization, the larger the viscosity the smaller the activation energy [19b].

(d) Isomerization of substituted stilbenes can be interpreted [22] with the aid of kinetic schemes which are similar to Eq. (8).

Although this qualitative agreement between model and experiment does not necessarily imply that the model is the correct description of experiment, it will be interesting to check its predictions experimentally. For example, one could check whether the activation energy for isomerization of "stiff" stilbene is viscosity independent. It would also be interesting to initiate measurements at extremely high viscosities in an effort to determine the asymptotic form of the viscosity dependence.

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References
