Numerical simulation of rate constants for a two degree of freedom system in the weak collision limit

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(Received 3 October 1986; accepted 24 December 1986)

In two recent papers, we examined the role of intramolecular vibrational relaxation (IVR) in determining the rate for energy activation in polyatomic molecules for both strong[1] and weak collision[2] models. In each study, we compared theoretical predictions with the result of numerical calculations for a quartic bistable coordinate coupled nonlinearly to a Morse oscillator[1] and linearly to a harmonic oscillator.[2] We found that in each case the rate constant was sensitive to the degree of coupling between the reaction coordinate and the nonreactive degree of freedom. For weakly coupled systems, the numerical results agree with the predictions of one-dimensional theories which assume that the rate for *energy transfer between modes is slow* compared to the rate for energy activation in the reaction coordinate. For strongly coupled systems, multidimensional theories which assume that the rate for *energy transfer between modes is fast* compared to the rate for energy activation in the reaction coordinate must be used. In this Note, we present numerical simulation data for the rate of barrier crossing in a two degree of freedom Markovian system.

Rate constants were calculated using the absorbing boundary version of the reactive flux.[3] The dynamics is described by the Langevin equation where the friction tensor is taken to be isotropic. We use the potential studied by DeLeon and Berne[4]:

$$V(x,y) = 4y^2(y^2-1)e^{-z\lambda x} + 10(1-e^{-\lambda x})^2 + 1, \qquad (1)$$

where y, a quartic bistable coordinate, is nonlinearly coupled to x, a Morse oscillator, for nonzero z. All calculations use a temperature $\beta^{-1} = 0.1$, and the units of mass and barrier frequency defined by Eq. (1). The equations of motion were integrated using the velocity version of the Verlet algorithm[5] on an FPS-164 attached processor.

Our simulation data are displayed in Fig. 1. The various theoretical predictions are described below for energy activation in a single well.[6]

(1) The *one-dimensional theory* approximates the friction on the bistable reaction coordinate as γ, the diagonal element of the mass weighted isotropic friction tensor. The rate constant is given approximately by

$$k_{1D} = \beta Q \gamma e^{-\beta Q}, \qquad (2)$$

where βQ is the barrier height along the reaction coordinate, i.e., the difference in energy between the saddle point and the well minima.

(2) The *first order two-dimensional theory* consists of the asymptotic result accurate to first order in the friction[8]

$$k_{\text{low}} = (\beta Q)^2 \gamma e^{-\beta Q}. \qquad (3)$$

(3) The *corrected two-dimensional theory* with first order corrections to Eq. (3) in the friction[9]

$$k_{\text{corr}}/k_{\text{TST}} = z(1 + a_2 z^{1/3})^{-1}, \qquad (4)$$

where $z = k_{\text{low}}/k_{\text{TST}}$, $a_2 = 1.372$, and k_{TST} is the transition state theory rate constant.[10]

The total rate constant k for all friction is approximately[11]

$$k^{-1} \simeq k_{ED}^{-1} + k_{\text{SD}}^{-1}, \qquad (5)$$

where k_{ED} is the energy activation rate constant given by Eq. (2), (3), or (4), respectively, and k_{SD} is the Kramers rate constant for saddle crossing.[7]

Figure 1(a) displays the results for the uncoupled system. As expected, the one-dimensional theory of Eq. (2)

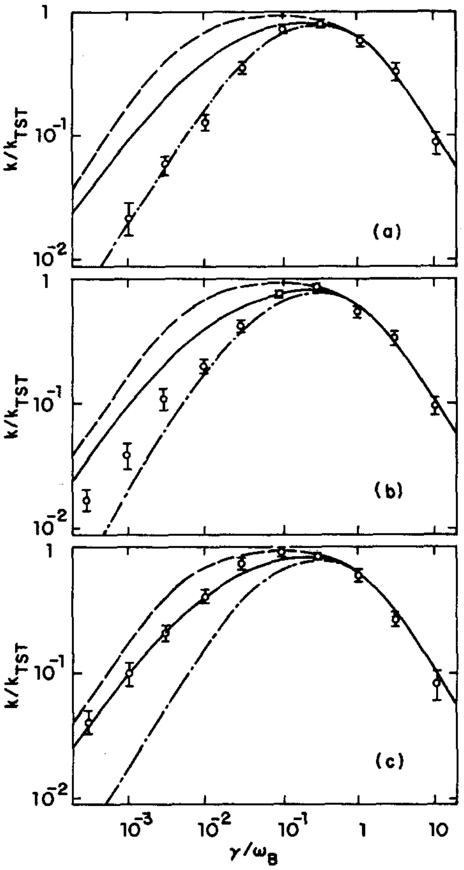

FIG. 1. A log–log plot of the rate constant as a function of friction. The dots are simulation results with error bars indicating 95% confidence intervals (Ref. 14). The dash–dotted line is the one-dimensional theory [Eqs. (2) and (5)], the dashed line is the first order two-dimensional theory [Eqs. (3) and (5)], and the solid line is the two-dimensional theory with first order corrections [Eqs. (4) and (5)]. (a) No coupling between modes ($\lambda = 1.0$ and $z = 0.0$). (b) Intermediate coupling between modes ($\lambda = 2.8$ and $z = 1.0$). (c) Strong coupling between modes ($\lambda = 1.95$ and $z = 2.3$).

0021-9606/87/074296-02$02.10

accurately predicts the numerical data.

Figure 1(c) shows the results for the strongly coupled system. The two-dimensional theory of Eq. (4) shows excellent agreement. There is rapid IVR and the assumption of fast equipartitioning between modes implicit in Eqs. (3) and (4) is met. In particular, Eq. (4) shows good agreement with the exact RRKM solution.[9] Note that even for small frictions ($\gamma/\omega_B < 10^{-3}$), Eq. (3), which does not include $\gamma^{1/3}$ corrections, shows large deviations and higher order terms in the friction are important.[12] For a greater number of degrees of freedom differences are even larger.

The coupling for the system corresponding to Fig. 1(b) is intermediate to that of Figs. 1(a) and 1(c). As expected, the simulation results fall between those of the weakly coupled and strongly coupled systems.

Two comments should be made in relation to our previous study.[2] First, our data are consistent with the eigenvalue analysis which places the transition from two-dimensional energy activation to overdamped behavior at higher friction.[13] Second, the Appendix of Ref. 2 contains a discussion of possible mechanisms acting in the weak collision model, absent in the strong collision model, which may increase diffusion in irregular regions of phase space or increase the measure of phase space accessible to reactive trajectories. Comparison of Fig. 1 with the corresponding results in Fig. 1 of Ref. 1 for the BGK model provides no evidence of increased diffusion. Further studies at higher temperatures would allow more definitive comments on the differences in dimensionality dependence of weak and strong collision models.

This work was supported by a grant from the National Science Foundation.

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[6] For application to the double well problem, one multiplies by 1/2 since once the particle is activated it will oscillate freely many times before being deactivated with equal probability in either well.

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[12] Energy activation rate constants for multidimensional systems differing from Eqs. (3) and (4), in the choice of the energy threshold for activation, have been proposed; see A. Nitzan, J. Chem. Phys. **82**, 1614 (1985). Our simulation data confirm that the threshold used in Eqs. (3) and (4) is the correct one.

[13] For the case of isotropic friction discussed here, the eigenvalue analysis of Ref. 2 reduces to that previously presented by Hänggi; see the second citation of Ref. 10 and Ref. 14.

[14] The procedure for calculation of error bars is described in the Appendix of J. E. Straub, M. Borkovec, and B. J. Berne, J. Chem. Phys. **84**, 1788 (1986).

ERRATA

Erratum: The theory of the Fe^{2+}–Fe^{3+} electron exchange in water [J. Chem. Phys. 76, 1490 (1982)]

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We correct an error in our work which does not affect the conclusions. A factor of $\frac{1}{2}$ is missing from the second and third terms of Eq. (C3) and the error is propagated through several following equations.[1] The corrected equations read

$$G(e_1,e_2) = \tfrac{1}{2}Q(A,A)e_1^2 + \tfrac{1}{2}e_1Q(A,B)e_2 + \tfrac{1}{2}e_2Q(B,A)e_1 + \tfrac{1}{2}Q(B,B)e_2^2, \tag{C3}$$

$$G(e_1,e_2) = e_1e_2Q(A,B) + \tfrac{1}{2}(e_1^2 + e_2^2)Q(A,A), \tag{C4}$$

$$\Delta G(e_1,e_2) \equiv G[\tfrac{1}{2}(e_1+e_2),\tfrac{1}{2}(e_1+e_2)] - G(e_1,e_2) = (e_1-e_2)^2[Q(A,B) - Q(A,A)]/4, \tag{C5}$$

$$\Delta G_{\rm os} = \Delta G(e_1,e_2)^{\rm eq} - \Delta G(e_1,e_2)^{\rm opt} = (e_1-e_2)^2[Q(A,B)^{\rm eq} - Q(A,B)^{\rm opt} - Q(A,A)^{\rm eq} + Q(A,A)^{\rm opt}]/4. \tag{C6}$$

In effect the error changed the definition of $Q(A,B)$ by a factor of $\frac{1}{2}$ in such a way that the earlier Eq. (C8) does lead to the correct expression for $\Delta G_{\rm os}$ within the assumed simple model, but it is better to conserve the relation $Q(r,r') \rightarrow Q(r,r)$ as $r \rightarrow r'$. $\Delta G_{\rm os}$ is the medium reorganization contribution to the activation energy for electron exchange; it is one quarter of the "reorganization energy" associated with the vertical excitation from the initial to the final state.[2] The formulation of $\Delta G_{\rm os}$ as $\Delta G(e_1,e_2)^{\rm eq} - \Delta G(e_1,e_2)^{\rm opt}$ will