

Stochastic classical trajectory approach to relaxation phenomena. III. Comparison of trajectory results to quantum mechanical perturbation theory

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A simple model representing an impurity oscillator coupled anharmonically to a lattice is examined both by quantum mechanical perturbation theory and by stochastic classical trajectory simulations. Energy relaxation rates are computed as a function of temperature. Classical and quantum relaxation rates are found to agree well at high temperatures but, as expected, diverge drastically at low temperatures. If zero-point motion of the lattice is incorporated into the classical calculation, classical and quantum relaxation rates agree quite well for all temperatures, even for $T \rightarrow 0$. This suggests that the stochastic classical trajectory method can provide an accurate description of relaxation phenomena even at very low temperatures.

I. INTRODUCTION

The method of stochastic classical trajectories (SCT) has been shown in recent years to be a very useful tool for studying relaxation phenomena, energy transfer, transport properties, and configurational changes involving the interaction between a microscopic system of interest and a heat bath.¹⁻⁵ The importance of this method stems from its ability to incorporate known information about the microscopic subsystem and about the bath into a numerical framework which provides a complete nonperturbative solution for the dynamical behavior of the microscopic subsystem. The use of appropriately chosen noise and damping as forces affecting the microscopic system eliminates the need to perform large scale molecular dynamics calculations at the easily affordable cost of giving up what is usually irrelevant information.

While many SCT calculations are performed under conditions for which the classical limit may be taken for granted, an important class of relaxation and energy transfer phenomena are studied experimentally at low temperatures where the validity of SCT results is in doubt. For such systems, classical mechanical relaxation rates generally approach zero as the temperature approaches zero, whereas quantum mechanical rates remain finite in this limit. The following simple example illustrates the failure of classical mechanics in this regime.

Consider two anharmonically coupled linear oscillators, one of which is subjected to a friction force:

$$\begin{aligned}\ddot{x} + \omega_x^2 x &= A y^N, \\ \ddot{y} + \omega_y^2 y &= N A x y^{N-1} - \gamma \dot{y}.\end{aligned}\quad (\text{I. 1})$$

We will think of x as the "impurity" coordinate and y as the "bath" coordinate. If at $t=0$, $y=\dot{y}=0$, the x oscillator will never feel the presence of the y oscillator and will oscillate as if it is free; i. e., it will never relax. In fact a linear analysis of Eq. (I.1) shows that

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this solution is locally stable, i. e., if the bath oscillator y starts with a small but finite energy, the system will relax after some transient period to state where $y=\dot{y}=0$ and x oscillates unperturbed. This behavior of the classical system has no analog in the corresponding quantum system. The zero point motion of the y oscillator insures that the x - y coupling never vanishes completely even if y is initially in its lowest energy state. Indeed, the quantum mechanical relaxation rate of x may be calculated for small A using perturbation theory and the result is always finite for finite γ as shown below.

The example above suggests that a major correction to the classical trajectory approach will be obtained by including the zero-point motion in determining the initial conditions of all the oscillators in the system. This is indeed the course taken in most classical trajectory studies of gas-phase molecular processes.⁶

Having in mind the application of the SCT method to vibrational relaxation of impurity molecules imbedded in low temperature matrices, or to the dynamics of adsorbate molecules on cold surfaces, it will be useful to compare SCT results to quantum mechanical calculations in order to obtain a feeling for the applicability of the SCT method to such low-temperature phenomena.

II. THE MODEL

The model we use is derived from the Hamiltonian

$$H = \frac{P_x^2}{2m_x} + \frac{P_y^2}{2m_y} + \frac{1}{2}m_x\omega_x^2x^2 + \frac{1}{2}m_y\omega_y^2y^2 + V(x, y, P_x, P_y) \quad (\text{II. 1a})$$

with

$$V(x, y, P_x, P_y) = 2\lambda \operatorname{Re} \left[\left(\sqrt{\frac{m_y\omega_y}{2\hbar}} y + \frac{i}{\sqrt{2\hbar m_y\omega_y}} P_y \right)^N \times \left(\sqrt{\frac{m_x\omega_x}{2\hbar}} x - \frac{i}{\sqrt{2\hbar m_x\omega_x}} P_x \right) \right]. \quad (\text{II. 1b})$$

Here λ is a coupling parameter of energy dimensionality and Re denotes the real part. This choice of the Hamiltonian is suggested by the simple form it takes in

terms of the transformed coordinates

$$\begin{aligned} a_x &= \sqrt{\frac{m_x \omega_x}{2\hbar}} x - \frac{i}{\sqrt{2\hbar m_x \omega_x}} P_x, \\ a_x^\dagger &= \sqrt{\frac{m_x \omega_x}{2\hbar}} x + \frac{i}{\sqrt{2\hbar m_x \omega_x}} P_x, \end{aligned} \quad (\text{II. 2})$$

and similarly for a_y and a_y^\dagger . Under this transformation the Hamiltonian becomes

$$\begin{aligned} H &= \frac{1}{2} \hbar \omega_x (a_x^\dagger a_x + a_x a_x^\dagger) + \frac{1}{2} \hbar \omega_y (a_y^\dagger a_y + a_y a_y^\dagger) \\ &+ \lambda [a_x (a_y^\dagger)^N + a_x^\dagger a_y^N], \end{aligned} \quad (\text{II. 3})$$

where, of course, in classical mechanics $a_x^\dagger a_x + a_x a_x^\dagger = 2 \text{Re}(a_x^\dagger a_x)$, etc. In the equivalent quantum mechanical problem a_x^\dagger , a_x , a_x^\dagger , and a_y are the raising and lowering operators for the x and y oscillators.

The equations of motion in $x-P$ space take the form

$$\begin{aligned} \dot{x} &= \frac{P_x}{m_x} + \frac{2\lambda}{\sqrt{2\hbar m_x \omega_x}} \text{Im} \left[\left(\sqrt{\frac{m_y \omega_y}{2\hbar}} y + \sqrt{\frac{i}{2\hbar m_y \omega_y}} P_y \right)^N \right], \\ \dot{P}_x &= -m_x \omega_x^2 x - 2\lambda \sqrt{\frac{m_x \omega_x}{2\hbar}} \text{Re} \left[\left(\sqrt{\frac{m_y \omega_y}{2\hbar}} y + \sqrt{\frac{i}{2\hbar m_y \omega_y}} P_y \right)^N \right], \\ \dot{y} &= \frac{P_y}{m_y} - \frac{2N\lambda}{\sqrt{2\hbar m_y \omega_y}} \text{Im} \left[\left(\sqrt{m_y \omega_y 2\hbar} x + \sqrt{\frac{i}{2\hbar m_x \omega_x}} P_x \right)^{N-1} \right. \\ &\quad \times \left. \left(\sqrt{\frac{m_x \omega_x}{2\hbar}} x - \sqrt{\frac{i}{2\hbar m_x \omega_x}} P_x \right) \right] - \gamma y + R_1(t), \\ \dot{P}_y &= -m_y \omega_y^2 y - 2N\lambda \sqrt{m_y \omega_y 2\hbar} \text{Re} \left[\left(\sqrt{\frac{m_y \omega_y}{2\hbar}} y \right. \right. \\ &\quad \left. \left. + \sqrt{\frac{i}{2\hbar m_y \omega_y}} P_y \right)^{N-1} \left(\sqrt{\frac{m_x \omega_x}{2\hbar}} x - \sqrt{\frac{i}{2\hbar m_x \omega_x}} P_x \right) \right] - \gamma P_y + R_2(t), \end{aligned} \quad (\text{II. 4})$$

where to the terms derived from the Hamiltonian (II. 1) we have added friction and Gaussian white noise terms γ and $R_i(t)$ which act on the oscillator y . Our model thus corresponds to the physical picture in which x represents the system which is coupled to the thermal bath through the y mode. The specific form of damping taken in Eq. (II. 4) is chosen so that in the a , a^\dagger representation we get

$$\begin{aligned} \dot{a}_y &= \dots - \gamma a_y, \\ \dot{a}_y^\dagger &= \dots - \gamma a_y^\dagger, \end{aligned}$$

where we have written explicitly only the damping terms.

By exploiting the relationship between Langevin equations and Fokker-Planck equations,⁷ we can derive fluctuation-dissipation relations for R_1 and R_2 :

$$\langle R_1(0)R_1(t) \rangle = \frac{2kT\gamma}{m_y \omega_y^2} \delta(t), \quad (\text{II. 5})$$

$$\langle R_2(0)R_2(t) \rangle = 2kTm_y \gamma \delta(t), \quad (\text{II. 6})$$

and

$$\langle R_1(0)R_2(t) \rangle = \langle R_2(0)R_1(t) \rangle = 0. \quad (\text{II. 7})$$

Thus $R_1(t)$ and $R_2(t)$ are independent Gaussian delta-function correlated random functions.

The system (II. 4) can be readily integrated using the SCT method and the results compared to the quantum mechanical evolution which may be obtained in principle using the Hamiltonian (II. 3). This is done within perturbation theory in the next section.

III. QUANTUM MECHANICAL SOLUTION

Consider the following general Hamiltonian describing a harmonic oscillator coupled to a heat bath:

$$H = \frac{1}{2} \hbar \omega_x (a_x^\dagger a_x + a_x a_x^\dagger) + H_B + F a_x^\dagger + F^\dagger a_x, \quad (\text{III. 1})$$

where H_B is the bath Hamiltonian and where the last terms in Eq. (III. 1) describes the oscillator bath interaction. F is an operator in the bath subspace. Following a well known procedure⁸ we can derive a kinetic equation for the energy relaxation

$$\frac{dE}{dt} = -\Gamma [1 - \exp(-\beta \hbar \omega_x)] (E - E_{\text{eq}}), \quad (\text{III. 2})$$

where $\beta = (k_B T)^{-1}$ and where

$$E_{\text{eq}} = \frac{\hbar \omega}{\exp(\beta \hbar \omega) - 1} \quad (\text{III. 3})$$

and

$$\begin{aligned} \Gamma &= \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt \langle F(t)F^\dagger(0) \rangle \exp(i\omega_x t) \\ &= \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt \langle F(0)F^\dagger(t) \rangle \exp(-i\omega_x t). \end{aligned} \quad (\text{III. 4})$$

This result is obtained in the usual Markoffian, weak coupling limit. In our case [i.e., Eq. (II. 3)] F is λa_y^N so we obtain

$$\Gamma = \frac{\lambda^2}{\hbar^2} \int_{-\infty}^{\infty} dt \langle a_y^N [a_y^\dagger(t)]^N \rangle \exp(i\omega_x t). \quad (\text{III. 5})$$

The correlation function appearing in Eq. (III. 5) corresponds to the dynamics of the y oscillator coupled to the heat bath (but not to the x oscillator). It is given approximately by

$$\langle a_y^N [a_y^\dagger(t)]^N \rangle \approx \langle a_y^N (a_y^\dagger)^N \rangle \exp(i\omega_y t - N\gamma |t|). \quad (\text{III. 6})$$

Moreover, the equal time moment $\langle a_y^N (a_y^\dagger)^N \rangle$ may be obtained by using harmonic oscillator algebra

$$\langle a_y^N (a_y^\dagger)^N \rangle = N! \left[\frac{\exp(\beta \hbar \omega_y)}{\exp(\beta \hbar \omega_y) - 1} \right]^N. \quad (\text{III. 7})$$

Using Eqs. (III. 2), (III. 5), (III. 6), and (III. 7) we obtain finally

$$\frac{d(E - E_{\text{eq}})}{dt} = -k(T)(E - E_{\text{eq}}), \quad (\text{III. 8})$$

$$k(T) = \Gamma \left[1 - \exp(-\beta \hbar \omega_x) \right] = k(0) \frac{1 - \exp(-\beta \hbar \omega_x)}{[1 - \exp(-\beta \hbar \omega_y)]^N}, \quad (\text{III. 9})$$

$$k(0) = \frac{\lambda^2}{\hbar^2} N! \frac{2N\gamma}{(\omega_x - N\omega_y)^2 + (N\gamma)^2}. \quad (\text{III. 10})$$

We note in passing that in terms of the "classical" coupling coefficient $\bar{\lambda} = \lambda/(\hbar)^{(N+1)/2}$ the coupling (II. 1b) takes the (\hbar independent) form

$$V(x, y, P_x, P_y) = 2\lambda \operatorname{Re} \left[\left(\sqrt{\frac{m_y \omega_y}{2}} y + \frac{i P_y}{\sqrt{2m_y \omega_y}} \right)^N \right. \\ \left. \times \left(\sqrt{\frac{m_x \omega_x}{2}} x - \frac{i P_x}{\sqrt{2m_x \omega_x}} \right) \right] \quad (\text{III. 11})$$

and the rate (III. 10) becomes

$$k(0) = \bar{\lambda}^2 \hbar^{N-1} N! \frac{2N\gamma}{(\omega_x - \omega_y)^2 + (N\gamma)^2}. \quad (\text{III. 12})$$

Note that $k(0)$ is independent of \hbar for the harmonic case $N=1$ as expected, since classical and quantum mechanics agree for this case.

It should be noted that $k(T)$ [Eq. (III. 9)] depends on T (for a finite T) even for $N=1$. This is an artifact of the approximation (III. 6). In this approximation $\langle A_y[A_y^\dagger(t)] \rangle$ is taken to depend on the quantum thermal population of the oscillator ω_y [c.f. Eq. (III. 7)], whereas due to the presence of the friction γ , the result should depend on a range of frequencies of width γ about ω_y . A more rigorous treatment of Eq. (III. 5) for $N=1$ yields

$$\Gamma(N=1) = \frac{\lambda^2}{\hbar^2} \frac{e^{\beta\hbar\omega_x}}{e^{\beta\hbar\omega_x-1}} \frac{2\gamma}{(\omega_x - \omega_y)^2 + \gamma^2}, \quad (\text{III. 13})$$

so that $k(T) = k(0)$ for $N=1$. For $N>1$ the rigorous treatment becomes too involved to carry out and we shall use the approximation (III. 9).

Next we shall compare the quantum perturbation results Eqs. (III. 9) and (III. 10) for $N>1$ with SCT results based on Eqs. (II. 4) and (II. 5).

IV. STOCHASTIC TRAJECTORY RESULTS

A. Procedure

The stochastic classical trajectory equations (II. 4) were integrated numerically on a computer, using an integrator described elsewhere.⁹ The mass m_x and frequency ω_x were taken to be 20 amu and $4.5 \times 10^{13} \text{ s}^{-1}$, respectively, for all runs. The other parameters occurring in Eqs. (II. 4), m_y , ω_y , λ , and N , were varied from run to run, as discussed below. The temperature T was also varied via Eq. (II. 5). Typically, for each set of parameters, an average was taken over 20 trajectories with initial conditions selected at random from a canonical distribution at temperature T . The integration step length was taken to be $5 \times 10^{-16} \text{ s}$, and each trajectory was integrated for 80 000 time steps ($4 \times 10^{-11} \text{ s}$). Energy relaxation was monitored via the decay of the total energy of the two-particle system. An accurate value for the classical mechanical relaxation rate was obtained in this way, provided that the rate was relatively fast, i. e., $\gtrsim 10^8 \text{ s}^{-1}$.

B. Classical results

A comparison of stochastic classical trajectory relaxation rates with those obtained from the approximate quantum perturbation theory expression, Eqs. (III. 9) and (III. 10), are shown in Fig. 1. The classical rates approach zero at $T \rightarrow 0$, as discussed above, so agree-

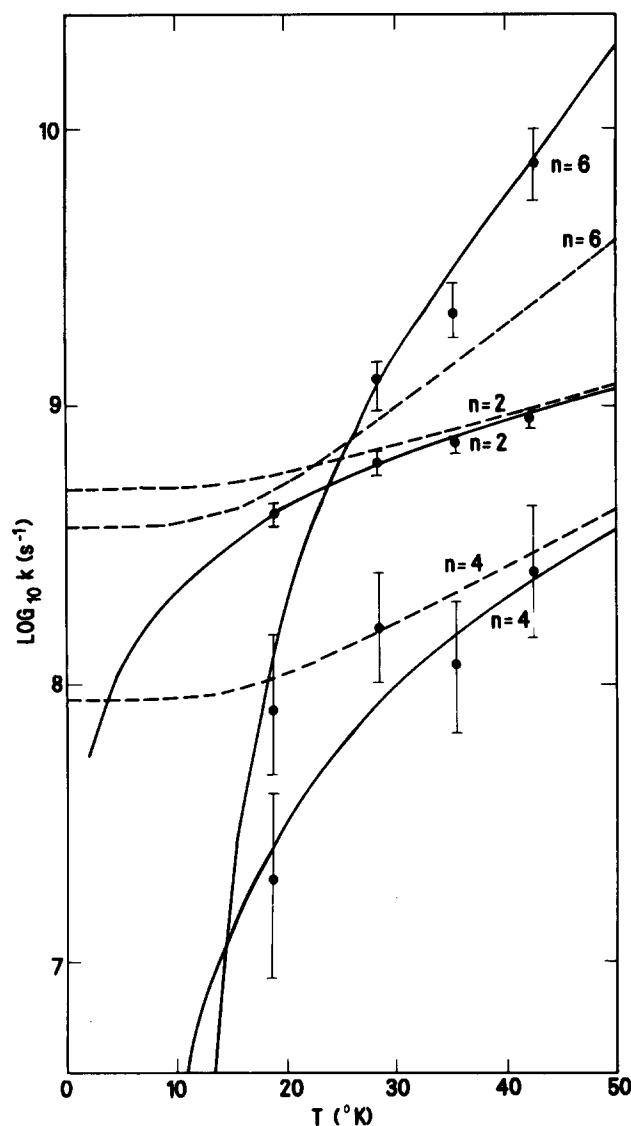


FIG. 1. Comparison of relaxation rate constants computed by quantum perturbation theory (dashed curves) and stochastic classical trajectories (points with error bars). Solid curves are drawn for eye only. Parameters are $m_x = 20$ amu, $m_y = 40$ amu, $\omega_x = 4.47 \times 10^{13} \text{ s}^{-1}$, $\omega_y = 7.45 \times 10^{12} \text{ s}^{-1}$, $\gamma = 3.5 \times 10^{11} \text{ s}^{-1}$.

ment with the quantum rates is poor at low temperatures. At temperatures large compared to $1/k_B$ times the zero-point energy of the bath oscillator (28 K), agreement between the quantum and classical rate becomes quite good. Note in particular that classical mechanics correctly describes the "resonance" effect. For the case shown in Fig. 1, $\omega_x/\omega_y = 6$. Quantum perturbation theory predicts that relaxation will be dominated by a six-phonon process; i. e., the $n=6$ term will be large. This effect is reproduced correctly by the classical calculation.

C. Quasiclassical results

As discussed previously, the failure of the classical mechanics at low temperature is due primarily to neglect of zero-point motion in the bath oscillators. We have carried out "quasiclassical" calculations in which

zero-point motion is introduced in the following approximate way. We note that the mean (canonical ensemble) energy of a classical oscillator is kT . The mean energy of a quantum (bath) oscillator at temperature T is

$$\langle E_{QM} \rangle = \hbar\omega_y \left[\frac{1}{2} + \frac{\exp(-\hbar\omega_y/kT)}{1 - \exp(-\hbar\omega_y/kT)} \right]. \quad (\text{IV. 1})$$

We thus define a "quasiclassical temperature" T_{QC} given by

$$T_{QC} = \frac{\hbar\omega_y}{k_B} \left[\frac{1}{2} + \frac{\exp(-\hbar\omega_y/k_B T)}{1 - \exp(-\hbar\omega_y/k_B T)} \right]. \quad (\text{IV. 2})$$

Our quasiclassical procedure for obtaining a relaxation rate corresponding to a temperature T is simply to run an ordinary classical simulation, but at the bath temperature T_{QC} rather than T . The mean energy of the bath oscillator will thereby be maintained at its cor-

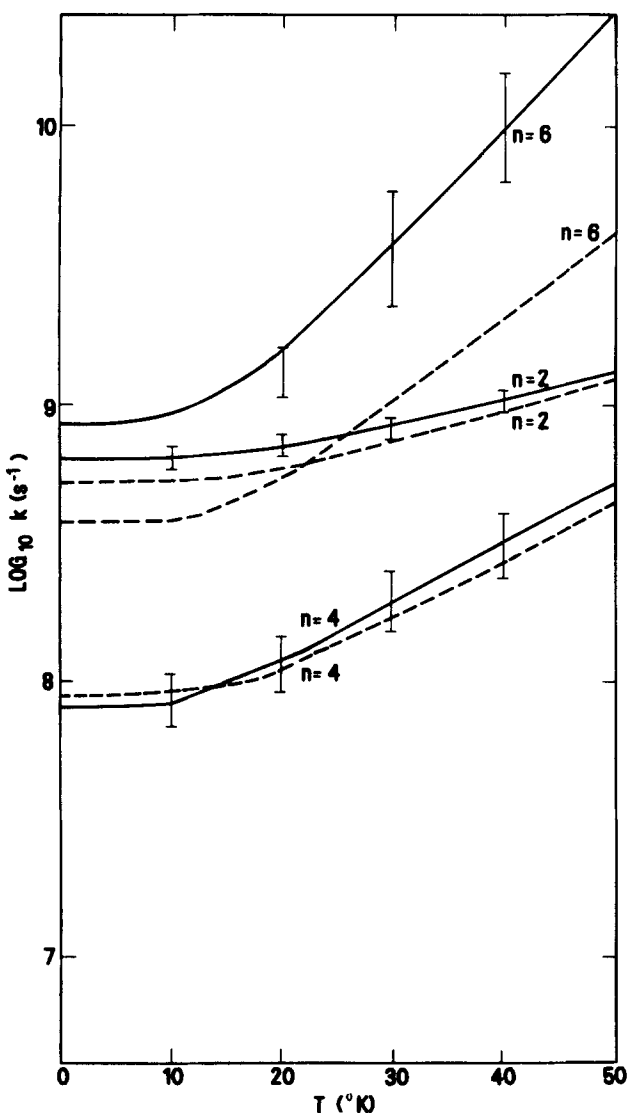


FIG. 2. Comparison of relaxation rate constants computed by quantum perturbation theory (dashed curves) with quasiclassical stochastic trajectory results (solid curves with error bars). Parameters are the same as for Fig. 1.

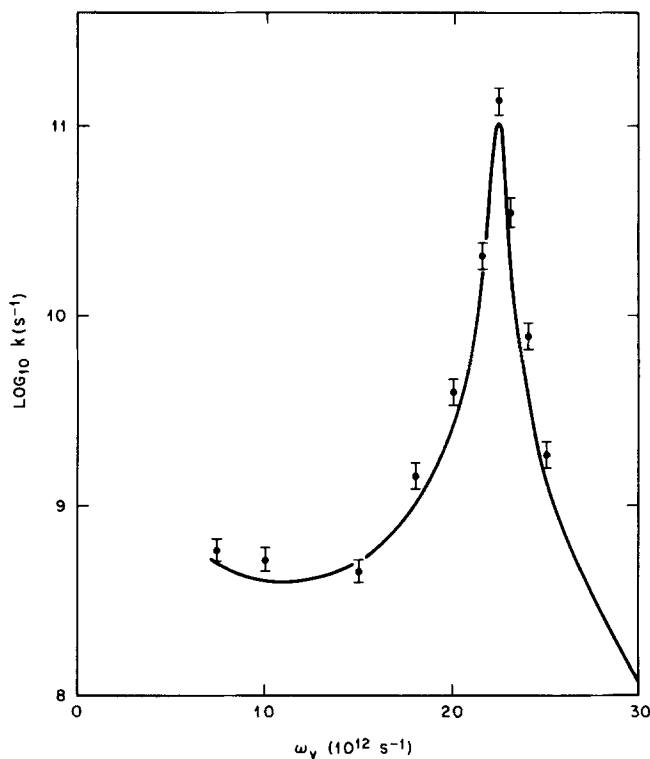


FIG. 3. Comparison of zero-temperature rate constants computed by quantum perturbation theory (solid curve) with quasiclassical stochastic trajectory results (points with error bars). Parameters are the same as for Fig. 1., with $n=2$ and ω_y varied.

rect quantum value. In Fig. 2 we compare the quasiclassical results with perturbation theory results for the same parameters employed for Fig. 1. Agreement is now good for the entire range of temperatures. The largest discrepancy is for the $n=6$ curves. This appears to be due, at least in large part, to the inadequacy of the perturbation theory expression, not to inaccuracy of the quasiclassical method. For lower coupling

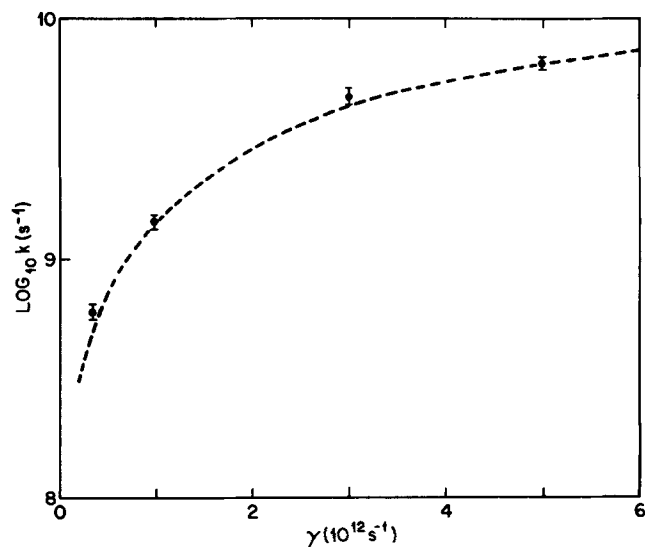


FIG. 4. Same as Fig. 3, but for variation of γ .

strengths λ for which perturbation theory is more accurate, agreement between the quantum and quasiclassical results becomes significantly better.

Agreement between the quantum perturbation expression and the quasiclassical simulations persists for wide variations of parameters. This is demonstrated in Figs. 3 and 4, which compare the zero-temperature energy relaxation rates computed by the two procedures as a function of ω_y and γ . Note in Fig. 3 the agreement in both the magnitude and width of the resonance at $\omega_y = \frac{1}{2}\omega_x$.

V. CONCLUSIONS

The SCT approach has become a valuable method for obtaining accurate descriptions of the dynamics of a variety of complex chemical processes.^{9,10} The method is nonperturbative, and is practical to apply even when many strongly coupled degrees of freedom must be described explicitly. To date, the method has been limited mainly to high temperatures. The present studies suggest that, if zero-point motion is incorpo-

rated properly, the SCT method can provide accurate descriptions of dynamical processes even at very low temperatures.

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