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Interference effects on relaxation in three-level systems: Breakdown of the rate equation description

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The stochastic Liouville equation and exact quantum mechanical simulations have been used to test the validity of rate law predictions for the vibrational energy relaxation in a three-level system. The model system consists of a low lying ground state which is radiatively coupled to only one of three closely spaced excited states. All three excited states are strongly coupled to baths of known statistical properties (either Gaussian or Poisson). We follow the energy exchange between the excited states after the light is turned off. Two different types of bath correlation have been considered: (A) The couplings between the different levels are the same and (B) the couplings are uncorrelated with each other. We find that relaxation differs for these two cases, in contradiction to the prediction of the simple rate law description. We also present the first quantitative study of the interference between different pathways that can occur in such a three-level system. We find that the interference has a considerable effect on the decay of the middle level for the same bath (case A), even in the Markovian limit, while for independent baths (case B) interference becomes important only in the non-Markovian limit. These results are entirely different from the prediction of the conventional rate laws. We also discuss the effect of the excitation on the subsequent relaxation and the coherence transfer processes that lead to an oscillatory decay in the non-Markovian limit.

I. INTRODUCTION

Vibrational energy relaxation in liquids has been a subject of considerable interest in recent years.¹ Most experimental and theoretical work has concentrated on the study of small molecules (especially diatomics and triatomics) in simple, often cryogenic, solvents.² Under these circumstances, vibrational relaxation times range from microseconds to seconds, considerably longer than characteristic rotational and translational relaxation times. It suffices to decide which vibrational states take part in the relaxation, to assign rate constants for relaxation between these levels, and to attempt to fit the observed experimental data to these rate equations. The major theoretical question then is the extent to which the observations may be fitted by various models, such as the isolated binary collision model³ or a continuum hydrodynamic model.⁴

This paper is concerned with a different problem, namely the qualitatively different relaxation behavior that can occur when the vibrational decay rates occur on a picosecond time scale and thus are comparable to rotational and translational relaxation rates. The advent of picosecond spectroscopy⁵ has begun to open up this field by allowing the study of vibrational relaxation on a picosecond time scale. When there is no longer a time scale separation between vibrational and bath (rotational and translational) degrees of freedom, the rate equation description no longer is valid and new, non-Markovian effects begin to play a role. The relaxation of a molecule then depends not only on the state which

it is in but on its past history—the pathway through which it reached that state. In other words, memory effects begin to play a role.

These memory effects were demonstrated quite clearly by simulations⁶ of a two-level quantum system coupled strongly to a classical bath of known statistical properties. We have recently⁷ shown that the Stochastic Liouville equation approach developed by Kubo⁸ and others^{9,10} provides an exact theory in the case where the bath relaxation is Markovian. We demonstrated the agreement between simulation and theory and showed that for sufficiently fast vibrational relaxation (the non-Markovian limit) the process of excitation has a profound influence on the subsequent energy exchange between two vibrational levels coupled strongly by a stochastic bath.

In the present paper, we have generalized the above work to consider relaxation in a *three-level* system with emphasis on the results which are qualitatively different from those obtained previously in the two-level system. We have found several new results which are not adequately described by a Markovian, rate law approach. The first new feature that appears in a three-level system is that the stochastic forces that couple the different pairs of levels may differ. There can obviously be two limiting situations: all the stochastic forces can be the same due to the fact that they arise from interaction of the vibrational degrees of freedom with the same bath, or, in the other extreme, they can all be completely independent of each other, arising from uncorrelated baths. The rate law approach predicts that relaxation will be identical in both these situations. According to rate law, energy exchange between any pair of levels depends only on the stochastic force that couples them. Our results, however, indicate that

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this is not true.

A second interesting feature is the possibility of interference between different pathways of relaxation in a three-level system. If we denote the three levels by one, two, and three, then the direct relaxation pathway from one to three can interfere quantum mechanically with the indirect pathway passing through state two. In the specific case considered below (equal energy spacings, equal coupling strengths) rate law predicts that decay of level two is independent of the coupling between one and three. Our theoretical calculations show that this prediction of the rate law approach is incorrect.

Our analysis is based on the following time dependent Hamiltonian:

$$H(t) = H_0 + H_{\text{ext}}(t) + V(t), \quad (1.1)$$

where H_0 is the Hamiltonian of the vibrational degrees of freedom, $H_{\text{ext}}(t)$ is the interaction Hamiltonian between exciting light and the vibrating molecule, and $V(t)$ is the stochastic force. The explicit form of these terms will be given in the next section. For the stochastic force $V(t)$ we have assumed two different statistical properties: a two-state Poisson process in which the coupling matrix elements $V_{ij}(t)$ jump at random intervals between two possible values, and a Gaussian random process where the $V_{ij}(t)$ vary continuously with a Gaussian probability distribution. We have already shown in Ref. 7 that the stochastic Liouville equation (SLE) is exact in describing the relaxation for the Poisson bath, both in the Markovian and the non-Markovian domain. Therefore, in the present work, we have used the SLE to study the excitation-relaxation process in a Poisson bath. For the Gaussian bath, however, we have primarily used computer simulations since the SLE becomes too complicated due to the presence of an infinite number of bath modes of the stochastic diffusion operator. We have already seen⁷ that one needs at least six to eight of these bath modes in order to obtain reasonable results. This would lead, in the present case, to solving a rather large number of simultaneous equations, which is both tedious and expensive. We have, however, compared the simulation results with the SLE by including a limited number of bath modes and agreement is usually good and much superior to rate laws.

The organization of the paper is as follows. In Sec. II we describe the theoretical methods that have been used to study the relaxation. They include rate laws, simulation, and SLE. In Sec. III we present the results of our calculations and compare them with the rate law predictions. Section IV concludes with a brief discussion.

II. THEORY

The model system we have considered consists of a ground state $|g\rangle$ and three closely spaced excited states $|1\rangle$, $|2\rangle$, and $|3\rangle$. The energies of these levels in the isolated molecule are denoted by ϵ_g , ϵ_1 , ϵ_2 , and ϵ_3 , respectively; we take the energy difference $\epsilon_1 - \epsilon_g$ to be much larger than both $\epsilon_2 - \epsilon_1$ and $\epsilon_3 - \epsilon_2$ so that relaxation from the excited states to the ground state $|g\rangle$ is negli-

gible on the time scale of interest. For simplicity we assume that all the oscillator strength is carried from the ground state to the highest excited state $|3\rangle$ and that there is no radiative coupling between any two other states. The excited states may either be levels in the ground electronic manifold accessible by infrared radiation, or levels in an upper electronic manifold accessible by visible light.

For such a system the Hamiltonian has the form

$$H = H_0 + H_{\text{ext}}(t) + H_B + V, \quad (2.1)$$

where H_0 is the Hamiltonian for the vibrational degrees of freedom, $H_{\text{ext}}(t)$ is the interaction between the system and the electromagnetic radiation, H_B is the Hamiltonian for the bath (rotational and translational) degrees of freedom, and V is the interaction between the system and bath. In the interaction representation, the vibrational system evolves under the time dependent Hamiltonian

$$H(t) = H_0 + H_{\text{ext}}(t) + V(t), \quad (2.2)$$

where

$$V(t) = (|1\rangle\langle 2|) V_{12}(t) + (|2\rangle\langle 1|) V_{21}(t) \\ + (|1\rangle\langle 3|) V_{13}(t) + (|3\rangle\langle 1|) V_{31}(t) \\ + (|2\rangle\langle 3|) V_{23}(t) + (|3\rangle\langle 2|) V_{32}(t). \quad (2.3)$$

In writing Eq. (2.3) we have neglected the diagonal perturbations and kept only the off-diagonal terms. For $H_{\text{ext}}(t)$ we have made the well-known semiclassical approximation

$$H_{\text{ext}}(t) = F(t)(|3\rangle\langle g| + |g\rangle\langle 3|), \quad (2.4)$$

where

$$F(t) = A(t)H_r \cos \omega t. \quad (2.4a)$$

$A(t)$ gives the temporal shape of the exciting pulse, H_r is Rabi frequency, and ω is the radiation frequency. Two types of radiation pulses, square and Gaussian, have been used; they have been discussed in greater detail in Ref. 7.

For simplicity we have chosen $\epsilon_3 - \epsilon_2 = \epsilon_2 - \epsilon_1$; i.e., the excited states are equally spaced. We further chose $\epsilon_1 - \epsilon_g = 10(\epsilon_2 - \epsilon_1)$ for most of our simulations. The results are not very sensitive to this choice within a given range.

The stochastic coupling matrix elements $V_{ij}(t)$ are assumed to follow either a Gaussian or a Poisson stochastic process. The Poisson bath jumps between two states (which we call + and -) at an average rate $b/2$ and the probability that exactly one jump will occur in a time interval Δt is given by $(b/2) \exp(-b/2 \Delta t)$. We chose $V_{ij}^+ = V_{ji}^- = \pm V$. For the Gaussian bath, $V_{ij}(t)$ can be represented by its time correlation function

$$\langle V_{ij}(0) V_{ij}(t) \rangle = \langle V_{ij}^2(0) \rangle \exp(-bt) = V^2 \exp(-bt). \quad (2.5)$$

In our dimensionless units b , V , and t^{-1} are measured in units of ω_{12} (or ω_{23}) which is the frequency difference between excited states one and two (or between two and three).

A. Rate law

The rate equation description for the population changes in a three-level system can be obtained by solving the following system of differential equations:

$$\begin{aligned}\dot{N}_1 &= -(k_{12} + k_{13})N_1 + k_{21}N_2 + k_{31}N_3, \\ \dot{N}_2 &= -(k_{21} + k_{23})N_2 + k_{12}N_1 + k_{32}N_3, \\ \dot{N}_3 &= -(k_{32} + k_{31})N_3 + k_{13}N_1 + k_{23}N_2.\end{aligned}\quad (2.6)$$

If the energy levels one, two, and three are equally spaced, we have the following relations between the rate constants:

$$\begin{aligned}k_{12} &= k_{21} = k_{23} = k_{32} = K, \\ k_{13} &= k_{31} = K'.\end{aligned}\quad (2.7)$$

The populations $N_i(t)$ are then given by

$$\begin{aligned}N_1(t) - N_1(\infty) &= \frac{1}{2} [N_1(0) - N_3(0)] \exp[-(K + 2K')t] \\ &\quad - \frac{1}{2} [N_2(0) - N_2(\infty)] \exp(-3Kt),\end{aligned}\quad (2.8)$$

$$N_2(t) - N_2(\infty) = [N_2(0) - N_2(\infty)] \exp(-3Kt), \quad (2.9)$$

$$\begin{aligned}N_3(t) - N_3(\infty) &= \frac{1}{2} [N_3(0) - N_1(0)] \exp[-(K + 2K')t] \\ &\quad - \frac{1}{2} [N_2(0) - N_2(\infty)] \exp(-3Kt).\end{aligned}\quad (2.10)$$

The rate constants K and K' can be obtained in the weak coupling (or rapid modulation, i.e., Markov) limit, through time dependent perturbation theory which gives the following general expression¹ for the transition rate between any two levels i and j :

$$k_{ij} = \frac{2\hbar^{-2}}{1 + \exp(-\beta\hbar\omega_{ij})} \int_{-\infty}^{\infty} dt \exp(i\omega_{ij}t) \langle V_{ij}(t) V_{ji}(0) \rangle, \quad (2.11)$$

where the average is to be taken over the stochastic force, ω_{ij} is the frequency difference between levels i and j , and $\beta = (k_B T)^{-1}$. The stochastic force $V_{ij}(t)$, which couples levels i and j , can be either Gaussian or Poisson. For both these stochastic forces, the correlation function [taking $V_{ij}(t)$ to be Markov] is given by

$$\langle V_{ij}(t) V_{ji}(0) \rangle = \langle V_{ij}^2(0) \rangle \exp(-bt) = V^2 \exp(-bt). \quad (2.12)$$

Equation (2.11) gives the following expressions for rate constants (in the high temperature, or classical, approximation):

$$K = \frac{2V^2b}{1 + b^2}, \quad (2.13)$$

$$K' = \frac{2V^2b}{4 + b^2}. \quad (2.14)$$

We have used reduced units with $\omega_{12} = 1$.

In the Markov limit ($b \rightarrow \infty$, V fixed), the two rate constants K and K' become equal to each other and rate law predicts single exponential decay for all the levels. In the non-Markovian limit ($b \rightarrow 0$, V fixed), however, these are unequal and $K' \approx K/4$. Therefore, according to the rate law description, the channel $3 \rightarrow 2 \rightarrow 1$ should predominate in the non-Markovian limit.

The expressions (2.13) and (2.14) for the rate constants K and K' have some interesting properties. First, if we vary b (keeping V fixed), both K and K' go

through a maximum at values of b equal to one and two, respectively. In fact, this value of b is independent of V . In the Markovian limit, the rate constants vary as b^{-1} , whereas in the non-Markovian limit, they are proportional to b . Thus, b is analogous to the damping parameter of Kramer's theory.¹¹ Equation (2.9) predicts that interference between pathways has no effect on the decay of $C_2(t)$; i.e., the decay of level two does not depend on V_{13} . Moreover, rate law equations do not allow for the fact that the stochastic forces $V_{ij}(t)$ may be correlated with each other. As discussed in the Introduction, there are two limiting cases that can arise; all the stochastic forces $V_{ij}(t)$ that couple the three different levels can be the same (i.e., they arise from coupling of the system to the same bath), or they can be completely independent of each other. According to rate law, the decay of the levels should remain unchanged in going from the one extreme to the other. We have tested both these predictions by exact methods and the results will be discussed in the next section.

There has been considerable discussion¹¹ in the literature on the exact range of validity of rate laws. They are usually accepted to be valid in the Markovian limit. It is customary to discuss their validity in terms of dimensionless parameters ξ_{ij} and ζ , which are, in our notation,

$$\xi_{ij} = \frac{V}{|E_i - E_j|} = \frac{V}{|\omega_i - \omega_j|}, \quad \zeta = \frac{V}{b}. \quad (2.15)$$

The rate law description breaks down when ξ_{ij} and ζ become much larger than unity. It is this limit which we call the non-Markovian limit.

B. Simulation

We have carried out computer simulations only for the case of the Gaussian stochastic force. Since the simulation procedure has been discussed in detail in Refs. 6 and 7, we briefly mention here only those features which are new to the simulations presented in this paper.

At time $t = -T$ we place the system in the ground state of the molecular Hamiltonian. The subsequent time evolution of the total wave function is given by

$$|\psi(t)\rangle = \exp_0 \left[i \int_{-T}^t dt' H(t') \right] |g\rangle, \quad (2.16)$$

where \exp_0 indicates time ordering. If we are interested in the population of the i th level, we must project the total wave function $|\psi(t)\rangle$ onto $|i\rangle$. We define the population evolution function $P_i(t)$ for the i th level by

$$P_i(t) = \langle |i\rangle \langle \psi(t) |^2 \rangle, \quad i = g, 1, 2, 3, \quad (2.17)$$

where the outer brackets indicate ensemble averaging.

In order to monitor the time evolution of the population in the i th excited level after the excitation light is turned off at time $t = 0$, we introduce the normalized time correlation function $C_i(t)$ through

$$C_i(t) = \frac{P_i(t) - \frac{1}{3}[P_1(0) + P_2(0) + P_3(0)]}{P_i(0) - \frac{1}{3}[P_1(0) + P_2(0) + P_3(0)]}, \quad i = 1, 2, 3. \quad (2.18)$$

$C_i(t)$, defined in this way, decreases from one to zero

as t increases from zero to ∞ .

We write the ensemble average $P_i(t)$ as

$$P_i(t) = \frac{1}{N} \sum_{k=1}^N \left| \langle i | \exp_0 \left[i \int_{-\tau}^t dt' H^{(k)}(t') \right] | g \rangle \right|^2, \quad (2.19)$$

where N is the total number of runs in the simulation and $H^{(k)}(t)$ is the total Hamiltonian at time t for the k th run. To calculate the ensemble average, we have taken N very large, of the order of several thousands, to minimize the statistical error. The total Hamiltonian is approximated as piecewise constant, as discussed in Refs. 6 and 7.

C. Stochastic Liouville equation

The traditional methods of time dependent statistical mechanics (e.g., cumulant expansion, projection operator) are of little use when the perturbation is strong and the relaxation is non-Markovian. In Ref. 7 we have pointed out that even when the classical stochastic force $V(t)$ is Gaussian, cumulant expansion¹² leads to no simplification of the problem due to the fact that in the interaction representation $V(t)$ is a quantum mechanical operator which needs proper time ordering.^{13,14} The resulting expressions are useless for computational purposes.

In Ref. 7 we have also shown that one can use the stochastic Liouville equation (SLE) approach of Kubo^{2,3} to explain the results of the simulation quite successfully. For the two-level system (plus ground state) considered in that work, the agreement between the simulation and the SLE was found to be exact for the two-state Poisson bath. For the Gaussian bath, good agreement was obtained by including as few as six to eight of the infinite number of available bath states. In the following, we briefly review the SLE approach and then discuss a generalization to the case where the vibrational system is coupled to more than one random force.

We first consider case (A); i.e., the time dependent Hamiltonian $H(t)$ depends only on one random variable λ . In this case, one can easily derive the following equation of motion⁸ for the reduced density matrix:

$$\frac{d\sigma}{dt} = -i/\hbar [H, \sigma] + \Gamma_\lambda \sigma, \quad (2.20)$$

where σ and the stochastic diffusion operator Γ_λ are defined by the following equations:

$$\sigma(t) = \langle \rho(\lambda, \rho, t) \rangle = \int d\rho \rho P(\lambda, \rho, t), \quad (2.21)$$

$$\frac{\partial}{\partial t} W(\lambda, t) = \Gamma_\lambda W(\lambda, t), \quad (2.22)$$

where ρ , $P(\lambda, \rho, t)$ and $W(\lambda, t)$ are the total density matrix, the joint probability distribution of λ and ρ , and the singlet probability distribution for the random variable $\lambda(t)$, respectively. Equation (2.20) is Kubo's Stochastic Liouville equation.⁸ If one is interested in studying the relaxation behavior in the time domain, then the systematic method of treating the problem is to expand σ in eigenstates $|b_n\rangle$ of the diffusion operator Γ_λ

$$\sigma = \sum \sigma_n |b_n\rangle, \quad (2.23)$$

where $|b_n\rangle$'s can be obtained by solving the eigenvalue problem

$$\Gamma |b_n\rangle = E_n |b_n\rangle. \quad (2.24)$$

The operator Γ has a unique equilibrium state $|b_0\rangle$ defined by the equation

$$\Gamma |b_0\rangle = E_0 |b_0\rangle = 0. \quad (2.25)$$

Combining Eqs. (2.20) and (2.23), one finds

$$\begin{aligned} \frac{d\sigma_n}{dt} = & -iH_0^x \sigma_n - i \sum_{n'} \langle b_n | V(t) | b_{n'} \rangle \sigma_{n'} \\ & - iH_{\text{ext}}(t) \sigma_n + E_n \sigma_n. \end{aligned} \quad (2.26)$$

Equation (2.26) can be used to evaluate the dynamics of excitation-relaxation processes. To find the population relaxation from any level k we compute $\langle k | \sigma_0 | k \rangle$, whereas to find the phase relation between any two levels k and j , we need to compute $\langle k | \sigma_0 | j \rangle$. For the two state Poisson bath, Γ is the familiar 2×2 matrix with eigenvalues 0 and $-b$. In this case, Eq. (2.26) reduces to

$$\begin{aligned} \frac{d\sigma_n}{dt} = & -iH_0^x \sigma_n - iV \sum_{n'=0}^1 (\delta_{n+1,n'} + \delta_{n-1,n'}) (|1\rangle\langle 2| + |2\rangle\langle 1| \\ & + |2\rangle\langle 3| + |3\rangle\langle 2| + |3\rangle\langle 1| + |1\rangle\langle 3|)^x \sigma_{n'} \\ & - iH_{\text{ext}}^x \sigma_n - nb \sigma_n. \end{aligned} \quad (2.27)$$

$\delta_{n,m}$ is the usual Kronecker delta function.

For the Gaussian bath, the diffusion operator is a Fokker-Planck operator⁸

$$\Gamma = b \frac{\partial}{\partial \lambda} \left(V^2 \frac{\partial}{\partial \lambda} + \lambda \right), \quad (2.28)$$

with eigenfunctions⁷

$$|b_n\rangle = A_n \exp(-\lambda^2/2V^2) H_n(\lambda/\sqrt{2}V), \quad (2.29a)$$

$$\langle b_n | = H_n(\lambda/\sqrt{2}V). \quad (2.29b)$$

H_n is the Hermite polynomial of order n and the normalization constant A_n is given by⁷

$$A_n = (V2^n n! \sqrt{2\pi})^{-1}. \quad (2.30)$$

The eigenvalues are $-nb_n$ with n ranging from 0 to ∞ . In this case, Eq. (2.27) reduces to

$$\begin{aligned} \frac{d\sigma_n}{dt} = & -iH_0^x \sigma_n - iV \sum_{n'=0}^{\infty} 2^{n'} n^{-1/2} (\delta_{n',n+1} + 2n \delta_{n',n-1}) \otimes (|1\rangle\langle 2| \\ & + |2\rangle\langle 1| + |2\rangle\langle 3| + |3\rangle\langle 2| + |3\rangle\langle 1| + |1\rangle\langle 3|)^x \sigma_{n'} \\ & - iH_{\text{ext}}^x(t) \sigma_n - nb_n \sigma_n. \end{aligned}$$

The situation is a bit more complicated when the random forces which couple the different energy levels $|1\rangle$, $|2\rangle$, and $|3\rangle$ are independent of each other. In this case, the Stochastic Liouville equation can be easily shown to have the following form:

$$\frac{d\sigma}{dt} = -iH^x \sigma + \Gamma_1 \sigma + \Gamma_2 \sigma + \Gamma_3 \sigma, \quad (2.32)$$

where Γ_1 , Γ_2 , Γ_3 are the stochastic diffusion operators

for $V_{12}(=V_{21})$, $V_{23}(=V_{32})$, and $V_{31}(=V_{13})$, respectively. The Hamiltonian H is still given by Eq. (2.2) except that V_{ij} are now independent of each other.

The obvious next step is to expand σ in eigenfunctions of Γ_1 , Γ_2 , and Γ_3

$$\sigma = \sum_{l,m,n} \sigma_{lmn} |b_l^1\rangle |b_m^2\rangle |b_n^3\rangle, \quad (2.33)$$

where $|b_k^i\rangle$ denotes the k th bath state of the diffusion operator Γ_i . From Eqs. (2.32) and (2.33), we can derive the following equation of motion for the quantities σ_{lmn} :

$$\begin{aligned} \frac{d}{dt} \sigma_{lmn} = & -iH_{00}^x \sigma_{lmn} - i \sum_{l'=0}^1 \langle l | V_{12} | l' \rangle \langle 1 | \langle 2 | + | 2 \rangle \langle 1 | \rangle^x \sigma_{l'mn} - i \sum_{m'=0}^1 \langle m | V_{23} | m' \rangle \langle 2 | \langle 3 | + | 3 \rangle \langle 2 | \rangle^x \sigma_{lm'n} \\ & - i \sum_{n'=0}^1 \langle n | V_{13} | n' \rangle \langle 1 | \langle 3 | + | 3 \rangle \langle 1 | \rangle^x \sigma_{lmn'} - iH_{\text{ext}}^x(t) \sigma_{lmn} + E_l \sigma_{lmn} + E_m \sigma_{lmn} + E_n \sigma_{lmn}. \end{aligned} \quad (2.34)$$

The population of the i th energy level is now given by $\langle i | \sigma_{000} | i \rangle$ which is coupled through Eq. (2.34) to a large number of other matrix elements. For convenience, we write Eq. (2.34) in the following matrix form:

$$\dot{\sigma}(t) = \mathbf{A}(t) \sigma(t). \quad (2.35)$$

For the Poisson bath, the matrix $\mathbf{A}(t)$ is a complex symmetric matrix which is time dependent. Methods of solving this type of equation have been discussed in Ref. 7.

III. RESULTS

We present the results of our calculation in three subsections, each describing one basic new result.

A. Effects of correlations between matrix elements

It is a prediction of the rate law equations [Eqs. (2.8)–(2.10)] that the rate of population transfer between any two levels depends *only* on the stochastic forces which couple these two levels. In a multilevel system, like the one considered here, this implies that the rate of energy exchange between any two levels is invariant to a change in the statistical properties of the coupling between any other two levels. For instance, k_{12} should depend only on V_{12} and V_{21} , but not on V_{13} or V_{23} . An easy way to test this prediction is to consider the two different cases which we call (A) and (B). As mentioned before, for case (A) we assume the three stochastic forces which couple three pairs of levels to be the *same*, i.e., $V_{12}=V_{23}=V_{31}$. For case (B), these stochastic forces, although they have identical statistical properties, are completely independent of each other. If the rate law prediction holds, then the decay of population from any level i , described by the correlation function $C_i(t)$, should be the same for cases (A) and (B). As we show below, however, this is not true.

In our calculations, we have taken $V=0.5$ and have used two choices for b ; $b=2.0$ we refer to as the "Markovian model" and $b=0.2$ as the "Non-Markovian model." Of course the true Markov limit occurs only as $b \rightarrow \infty$ but even with this finite value of b the differences between the two models are quite striking. We find for the Markovian model ($b=2.0$) that the decay is faster for case (B) ("independent" baths) than that for case (A) ("same" bath). This difference is more pronounced for the Gaussian bath than for the Poisson bath. The

overall qualitative features are, however, much the same for cases (A) and (B); the decay of $C_i(t)$ is rapid and exponential and the effect of excitation is small. The decay of level two is much faster than that of levels one and three which is easily understandable from rate law descriptions. The results change qualitatively in the non-Markovian model ($b=0.2$) and cases (A) and (B) show different relaxation behaviors. For excitation pulses of time duration comparable with the bath correlation time, the decay is more oscillatory for case (A) than for case (B). This is especially true for the Poisson bath. For case (B), not only is the oscillation weaker but the decay is also somewhat faster. Figure 1 and 2 depict the decay behavior for Gaussian and Poisson baths, respectively. Figure 1, obtained from a simulation, is subject to statistical errors, while Fig. 2 is the exact solution of the stochastic Liouville equation.

For pulses of duration long compared to the bath correlation time, oscillation becomes weaker (Fig. 3). The decay for case (B) still remains faster than that for (A), by 20%–30%.

B. Interference between pathways

In our model system, the population of each level can relax through coupling to each of two other levels. Since the energy levels are equally spaced, the pathways for level one are essentially identical to those for level three, but those for two are different. According to the rate laws [Eq. (2.9)], decay of level two does not depend on the channel $3 \rightarrow 1$ (characterized by rate constant K'); i.e., $C_2(t)$ is independent of $V_{13}(t)$. In order to study this prediction, we have carried out a calculation by turning off the channel K' (which is equivalent to taking $V_{13}=0$) and compared the resulting relaxation with that, where both channels K and K' are open. The results are rather surprising and we describe them below. As before, we consider two cases (A) and (B) which stand for the same and the independent baths, respectively.

For case (A) (same bath) we find that the decay of level two changes considerably, even in the Markovian model, when channel K' is turned off; the resulting decay becomes faster. The relaxation of levels one and three becomes slower, as expected from rate laws. The faster decay of level two, when only channel $3 \rightarrow 2 \rightarrow 1$ is open and the slower decay when both $3 \rightarrow 2 \rightarrow 1$

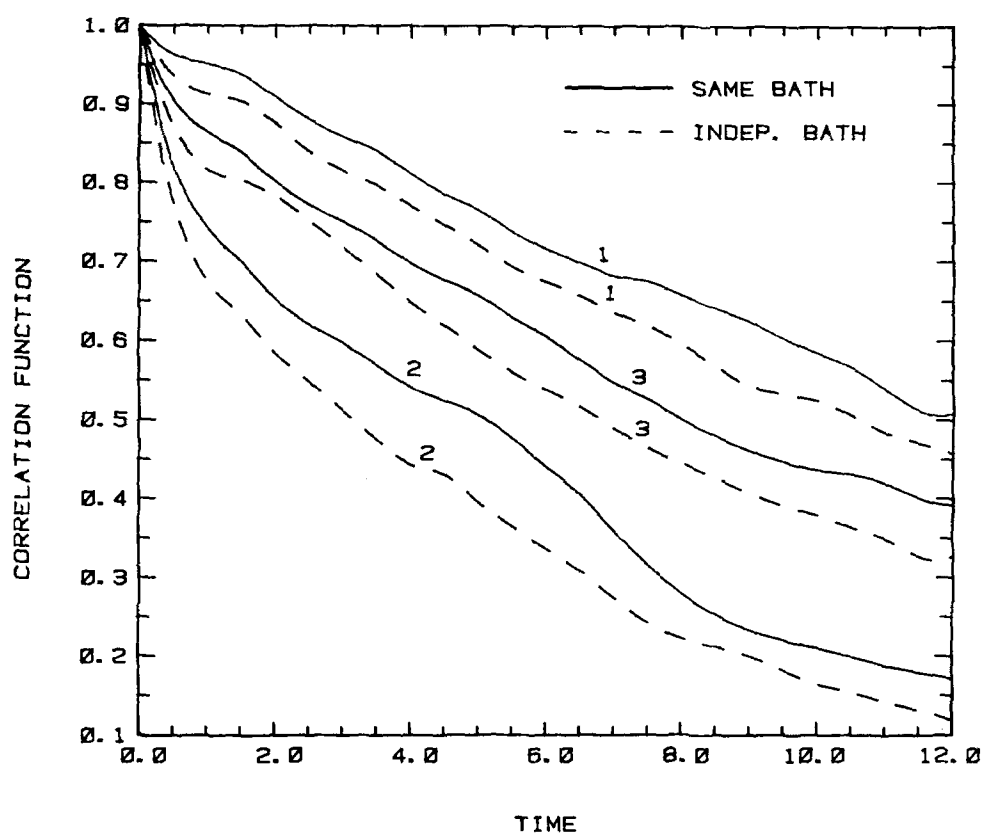


FIG. 1. Comparison of simulation results for Gaussian bath between same bath and independent bath. $T=3.0$, square pulse, $b=0.2$.

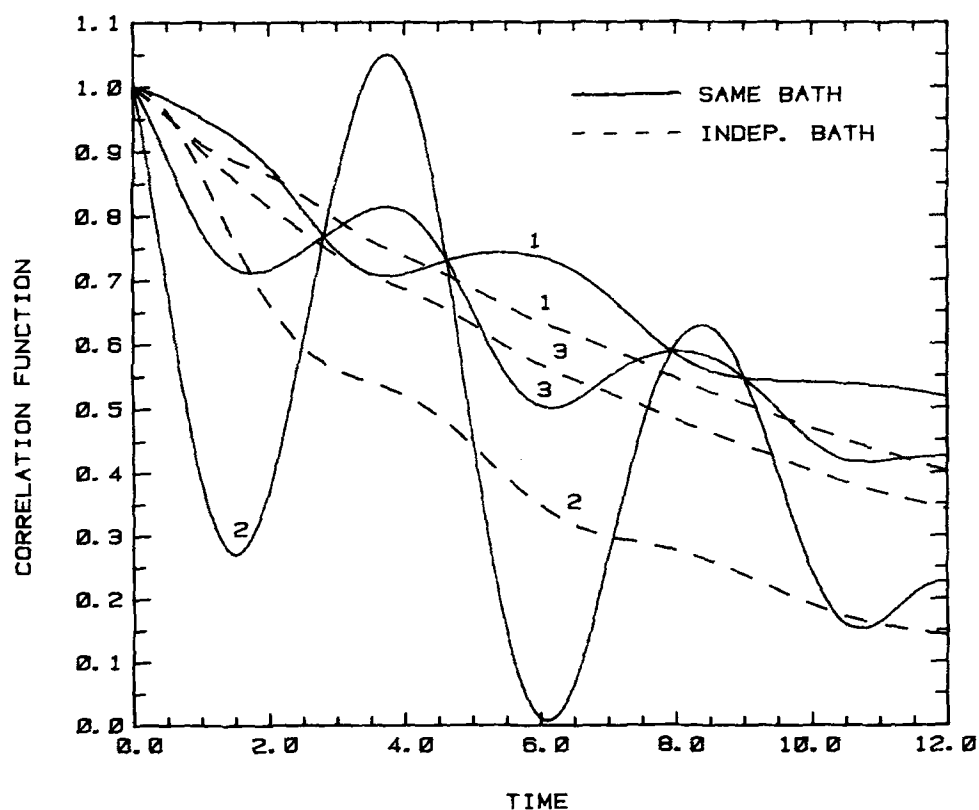


FIG. 2. Comparison of SLE results for Poisson bath between same bath and independent bath. $T=3.0$, square pulse, $b=0.2$.

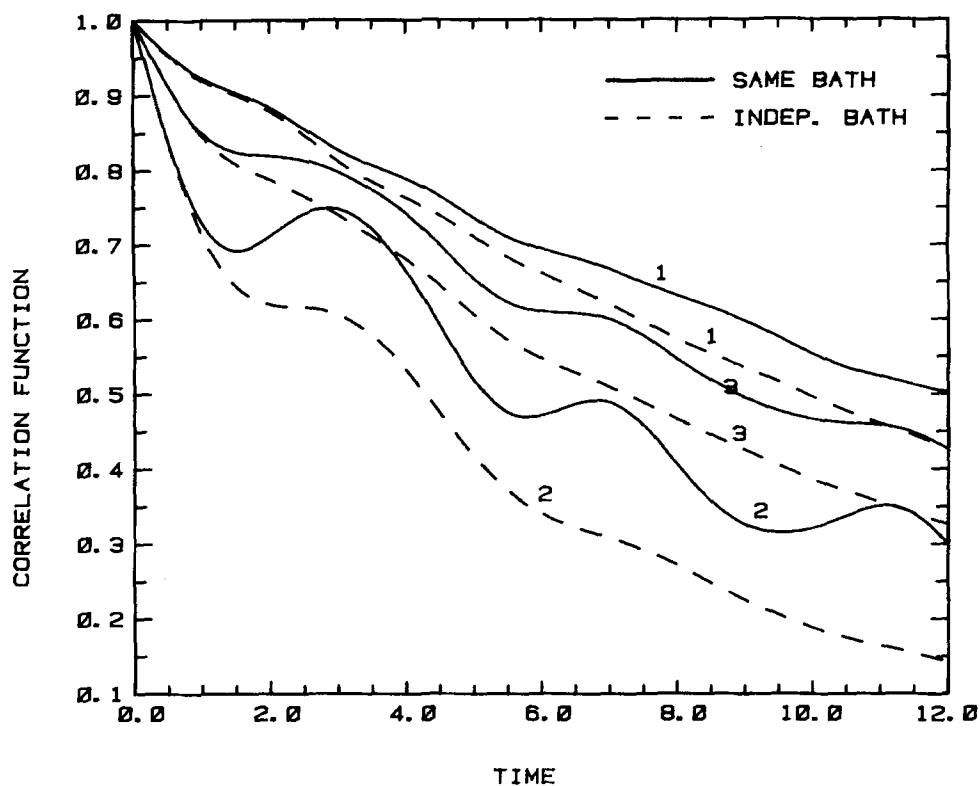


FIG. 3. Comparison of SLE results for Poisson bath with $T=10.0$, square pulse, $b=0.2$.

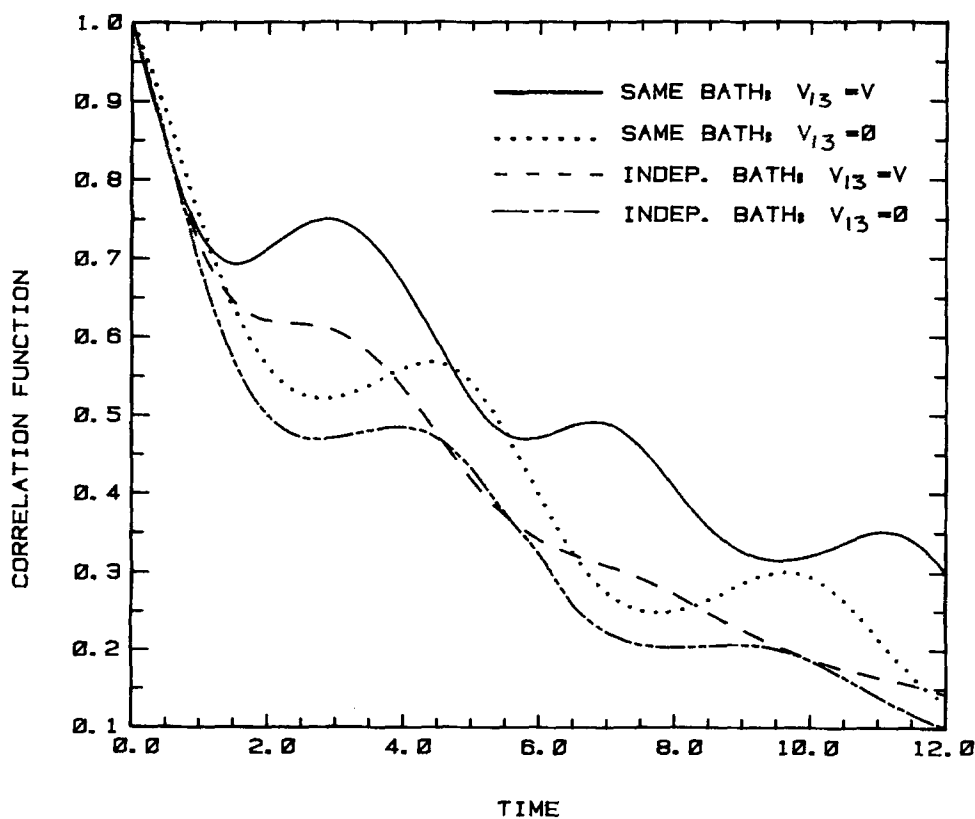


FIG. 4. Comparison of SLE results for $C_2(t)$ showing interference between pathways for Poisson bath, $T=10.0$, square pulse, $b=0.2$.

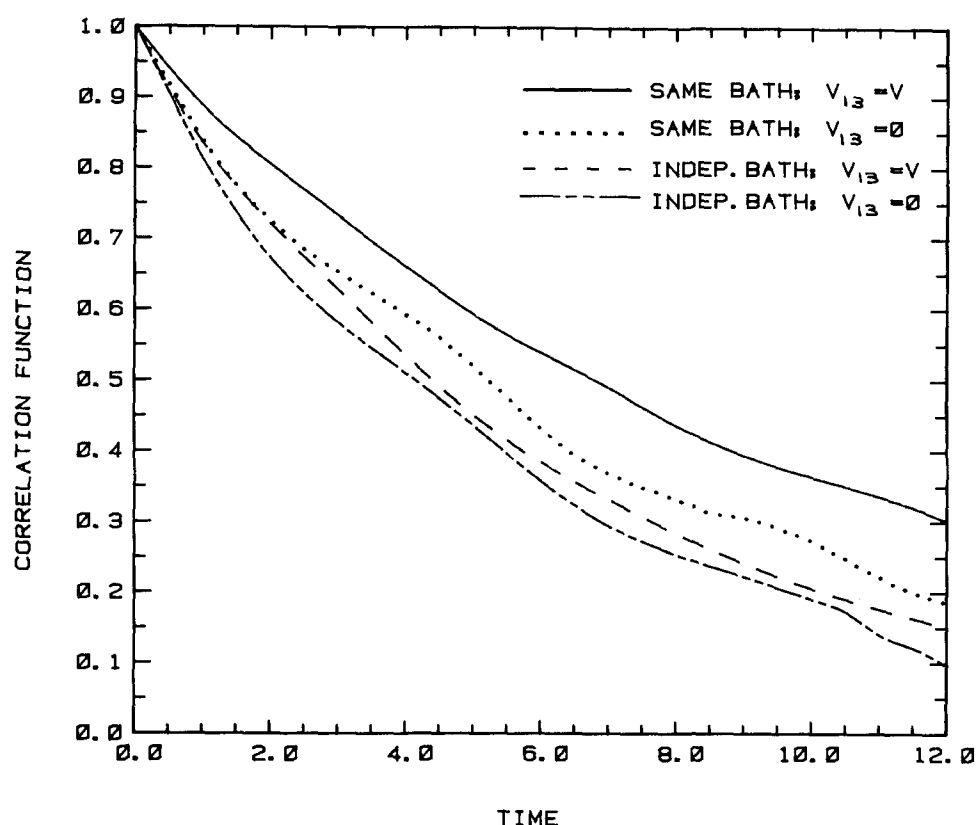


FIG. 5. Comparison of SLE results for $C_2(t)$ showing interference between pathways for Poisson bath. $T = 10.0$, Gaussian pulse, $b = 0.2$.

and $3 \rightarrow 1$ are open, clearly demonstrate that the two pathways interfere, in contradiction to the prediction of the rate laws.

For case (B) (independent baths), however, the decay of level two does *not* change significantly in the Markovian model. The relaxation of levels one and three behaves according to the rate laws. Thus, in this case, interference of pathways is absent and the rate law prediction holds.

In the non-Markovian model, the relaxation rate of level two changes both for cases (A) and (B) when channel K' turned off. The change is more pronounced for the same bath case than that for independent baths. Figures 4 and 5 compare the decay behavior of level two, for both same and independent bath, when $V_{13} = 0$ with the results when V_{13} is nonzero. As can be seen from the graphs, decay, on the average, is faster when channel K' is closed.

There are also some other interesting features that appear in the non-Markovian model. The decay of level three becomes faster at long times for the same bath when channel K' is turned off. This is clearly a reflection of the fact that level two decays at a faster rate which, in turn, influences the relaxation of level three. For the independent bath case, however, the decay of level three stays slower, in agreement with the rate law prediction.

C. Effect of excitation and coherence transfer

The effect of excitation on non-Markovian vibrational energy relaxation has been discussed in detail in Ref.

7. Our present study reveals essentially the same features; a short pulse gives rise to an oscillatory decay while a long Gaussian pulse makes the decay exponential, with a rate constant which is, however, very different from the prediction of weak coupling theory. One interesting new feature is that the decay of level two is more oscillatory than that of levels one and three. The oscillatory decay is a manifestation of the transfer of coherence¹⁵ that was initially established between levels g and three by the external field. For the Poisson bath, this coherence is propagated through the excited bath state σ_1 , as can easily be seen from the following equation of motion for the population of the three levels

$$\begin{aligned} \langle 1 | \dot{\sigma}_0 | 1 \rangle = & -iV \langle 3 | \sigma_1 | 1 \rangle + iV \langle 1 | \sigma_1 | 3 \rangle \\ & -iV \langle 2 | \sigma_1 | 1 \rangle + iV \langle 1 | \sigma_1 | 2 \rangle, \end{aligned} \quad (3.1)$$

$$\begin{aligned} \langle 2 | \dot{\sigma}_0 | 2 \rangle = & -iV \langle 3 | \sigma_1 | 2 \rangle + iV \langle 2 | \sigma_1 | 3 \rangle \\ & -iV \langle 1 | \sigma_1 | 3 \rangle + iV \langle 3 | \sigma_1 | 1 \rangle, \end{aligned} \quad (3.2)$$

$$\begin{aligned} \langle 3 | \dot{\sigma}_0 | 3 \rangle = & -iV \langle 2 | \sigma_1 | 3 \rangle + iV \langle 3 | \sigma_1 | 2 \rangle \\ & -iV \langle 1 | \sigma_1 | 3 \rangle + iV \langle 3 | \sigma_1 | 1 \rangle - iH_{\text{ext}}(t) [\langle g | \sigma_0 | 3 \rangle \\ & - \langle 3 | \sigma_0 | g \rangle]. \end{aligned} \quad (3.3)$$

Thus, the initial coherence established between levels three and g (manifested through $\langle 3 | \sigma_0 | g \rangle$ and $\langle g | \sigma_0 | 3 \rangle$), is transferred to other levels through the *excited* bath state.

It is also interesting to note that for short duration pulses, decay is much more oscillatory for case (A) (same bath) than that for case (B) (independent bath), as can be seen from Fig. 2. This implies that coherence

is more easily destroyed if the levels are coupled by independent baths, a result which is also expected intuitively.

IV. DISCUSSION

Two specific new results have come out of the present work on a model three level system coupled to a bath, (1) The population relaxation depends on the extended cross correlations between different matrix elements V_{ij} , an effect absent in the rate equation approach. (2) The relaxation of level two depends on the coupling between levels one and three, especially in the case when the V_{ij} 's are taken to be the same. In addition, this study reconfirms the results of our previous work⁷ by showing both the effect of excitation on relaxation and the role played by off-diagonal density matrix elements in non-Markovian relaxation.

What is the importance of the present results in interpreting experimental data? The first question that arises is the extent to which real systems are describable by the same or independent bath limit. While different matrix elements will certainly not be the same, there should, nevertheless, be strong correlations between them since they ultimately arise from the same intermolecular forces (whether they be short range repulsion, dipolar, or dispersion). To the extent to which these correlations exist, the same bath model should describe the real situation, and, as shown in our results, the deviations from rate equations should be correspondingly larger.

It is clear that in any relaxation taking place in tens of picoseconds or longer the new effects predicted here will be averaged out or small. But in the picosecond or subpicosecond region these effects may be observable. As a specific molecular example, consider the excitation of a particular C-H stretching normal mode in a hydrocarbon (such as the totally symmetric stretch). There are several nearby states to which this can relax: other nearby, C-H stretching modes, the overtone of the CH_2 deformation mode, and two molecule excitations where each molecule contains a single CH_2 deformation quantum. There may be interference between different relaxation pathways, as suggested by our theoretical results, which will affect the experimental observations.

We are not aware of any direct experimental proof of non-Markovian vibrational relaxation to date. One interesting picosecond spectroscopy study¹⁶ has shown a nonexponential population decay in ethanol, but the results could still be accounted for within a rate equation description by postulating an intermediate level leading to a relaxation given by a sum of exponentials. The non-Markovian effects we propose are subtle, but would be of considerable interest to observe experimentally.

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