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# Theory of vibrational relaxation of polyatomic molecules in liquids

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A simple tractable theory of vibrational relaxation of polyatomic molecules in polyatomic solvents, which is also applicable to solid solutions, is presented. The theory takes as its starting point Fermi's golden rule, avoids additional assumptions such as the rotating wave or random phase approximations, and treats both the internal degrees of freedom of the relaxing molecule and the bath degrees of freedom in a fully quantum mechanical manner. The results yield intuitively understandable expressions for the relaxation rates. The treatment of the annihilation as well as the creation of all participating bosons allows the theory to go beyond earlier analyses which treated only cascade processes. New predicted features include temperature effects and asymmetry effects in the frequency dependence. The theory is constructed in a manner which facilitates the use of recent developments in the analysis of instantaneous normal modes of liquids. © 1994 American Institute of Physics.

## I. INTRODUCTION

Vibrational relaxation of polyatomic molecules in polyatomic solutions, liquid or solid, is of central importance to many problems in chemistry, physics, and biology. It is involved in thermal chemistry, shock-induced chemistry, electron transfer, photochemistry, photophysical processes such as excimer formation, and photobiological processes such as vision and photosynthesis.<sup>1-9</sup> The advent of picosecond tunable mid-infrared laser sources<sup>10</sup> is making it possible to study vibrational dynamics in a wide variety of systems. A large number of different molecules have been studied in liquids at room temperature. Vibrational relaxation of an initially excited mode<sup>10-16</sup> and the flow of vibrational energy into other modes<sup>17-22</sup> have been observed. Recently, the temperature dependencies of several polyatomic solute/solvent systems have been reported<sup>23,24</sup> and the first vibrational photon echoes in liquids and glasses<sup>24,25</sup> and the first Raman echoes in liquids<sup>26-28</sup> have been described. These experiments are beginning to reveal the great complexity of the dynamics associated with the mechanical degrees of freedom of polyatomic molecules in media that are themselves composed of polyatomic molecules.

Such experimental results have raised basic theoretical questions. Many years ago, the observation of an extremely long lifetime of vibrational excitation in liquid nitrogen<sup>29,30</sup> had already begun to raise fundamental questions regarding the precise manner in which relaxation in such a diatomic system occurs into the low frequency continuum bath modes. Recent observations show that in polyatomic systems at fixed temperature, the vibrational lifetime of a solute mode changes when the solvent is changed.<sup>11-13,31,32</sup> Furthermore, temperature-dependent measurements in these systems have displayed in one instance an "inverted" temperature dependence.<sup>23</sup> The vibrational lifetime actually becomes longer as the temperature is increased. Clearly, there is need for a theoretical description that can address issues such as

the solvent dependence of relaxation and the surprising inverted temperature dependence.

The phenomenon under investigation is, thus, the relaxation of an initially excited internal vibrational mode of a polyatomic molecule embedded in a polyatomic medium. The system could be a solute in a liquid or glassy solvent, or a guest molecule in a mixed molecular crystal. For convenience, we will use the terms solute and solvent in all cases. A high frequency vibration, lying well above the continuum of low frequency mechanical states of the system, is excited by a fast infrared pulse tuned to the 0→1 vibrational transition, or by Raman or stimulated Raman excitation. The initial excitation decays through pathways that involve the excitation of one or more vibrations of the solute or solvent, and one or more excitations of the low frequency continuum of the medium. In a mixed crystal sample, the low frequency continuum is composed of the well-defined acoustic and optical phonons of the crystal. In a liquid, the continuum is composed of the instantaneous normal modes<sup>33-37</sup> whose quanta will also be referred to as phonons in this paper. The requirement of energy conservation generally involves one or more of these phonons in the relaxation process since the probability that some combination of the discrete molecular vibrations of the solute and the solvent have a combined energy *exactly* equal to that of the originally excited mode is rather small. Anharmonic coupling among modes allows energy to flow from the initially excited mode into a combination of other modes. In the case of a cubic anharmonicity, relaxation occurs through the deexcitation of the initially excited vibration, the excitation of a solute or solvent vibration, and the excitation of a phonon. A quartic anharmonicity would correspond to a pathway involving, e.g., the deexcitation of the initial excitation along with the excitation of two vibrations, solute or solvent, and a phonon. The theory we develop in this paper provides relaxation rate expressions for arbitrary order processes through an easily understood expression and discusses in greater detail the cubic and quartic processes.

Important theoretical advances have been made in this field by a large number of workers.<sup>38-54</sup> However, despite the excellent foundation laid down by previous theoretical work, recent experimental work, particularly in polyatomic systems, requires new theoretical advances to describe vibrational relaxation. The goal of the present paper is to begin the construction of a comprehensive theory in this direction by focusing attention on some of the following specific questions:

(i) How can the semiclassical theory of Oxtoby and of Adelman *et al.*<sup>52,54</sup> be modified so that the bath is not classical, but is composed of quantum mechanical oscillations?

(ii) Does such modification give rise to a novel temperature dependence of the vibrational relaxation rate, particularly at low temperatures?

(iii) How is the relaxation rate changed if the rotating wave approximation (RWA), made by Nitzan and collaborators<sup>42-45</sup> in their fully quantum mechanical treatment, is not used? Are any important features of the relaxation phenomenon lost through the use of the RWA or does the convenience and ease of calculation it appears to provide make up for whatever physics it misses?

(iv) The diagrammatic expansion techniques of Califano *et al.*<sup>50,53</sup> produce expressions for the vibrational relaxation rates that appear to have little relation to intuitively expected results. Thus, if the relaxation of an oscillator of frequency  $\Omega$  occurs through the interaction of a discrete vibration of frequency  $\omega$  and a phonon band producing a continuous density of states  $\rho$ , the relaxation rate according to Califano *et al.* is of the form<sup>50,53</sup>

$$K_{\sigma} = (1 + n_{\omega} + n_{\Omega - \omega})\rho_{\Omega - \omega} + (n_{\omega} - n_{\Omega + \omega})\rho_{\Omega + \omega}, \quad (1.1)$$

where the  $n$ 's are Bose occupation factors, and where constant terms and frequency-dependent coupling strengths have been absorbed into the density of states  $\rho$ . What is the relation of expressions such as  $1 + n_{\omega} + n_{\Omega - \omega}$  to the product  $(1 + n_{\omega})(1 + n_{\Omega - \omega})$  which might be expected on intuitive grounds<sup>23</sup> and which would approximate the expression in Eq. (1.1) only for temperatures low enough to neglect the product  $n_{\omega}n_{\Omega - \omega}$ ? And what is the significance of a difference  $n_{\omega} - n_{\Omega + \omega}$  of occupation numbers in Eq. (1.1)?

(v) Is there anything in these theories which has the potential to produce the inverted temperature dependence observed in the experiments of Tokmakoff *et al.*?<sup>23</sup>

Vibrational relaxation cannot be said to be understood unless we know how to treat quantum mechanical baths, how to apply existing theory developed largely in the context of simple diatomic molecules to complex polyatomic molecules, how to go beyond technical approximations such as the rotating wave assumption, and fully understand their limitations and range of validity, and how to resolve the apparent contradiction between vibrational relaxation rates provided by different authors for the same systems.<sup>23,50,53</sup> The theory we present in this paper attempts to fill in these gaps and to provide answers to the questions posed above, making contact with, and employing features of, recent theoretical calculations of the density of instantaneous normal modes of liquids.<sup>33-37</sup>

This paper is laid out as follows: The basic theoretical development is presented in Sec. II following the level diagram relevant to typical experimental systems currently under investigation. With a Fermi golden rule as a point of departure, a correlation function expression for the relaxation rate is obtained in a form that makes particularly clear the separate contributions to the vibrational relaxation rate arising from the various vibrational manifolds participating in the process. A general expression is obtained which can be applied to polyatomic molecules in quantum reservoirs. In Sec. III, three specific cases are treated including those pertinent to cubic and quartic processes, and novel consequences of the theory are discussed. In Sec. IV, a comparison of our results is made with other work appearing in the literature. The relation of our theory to classical treatments is presented along with a clarification of the range of validity of assumptions such as the rotating wave approximation made in earlier treatments. A discussion forms Sec. V.

## II. GENERAL FORMULA FOR VIBRATIONAL RELAXATION RATE

As in most earlier calculations available in the literature, the present paper will focus on the calculation of the rate constant for *leaving* an initially populated vibrational state. The detailed kinetics of relaxation will be described in a subsequent publication. Of the various interactions responsible for the coupling between the initial vibrational state, other vibrational states of the solute or solvent, and the instantaneous normal modes of a liquid or the phonons of a crystal, the simplest nontrivial one is the so-called *cubic* term, in which the vibrational quantum of the initial state is annihilated, and a vibrational quantum of the solvent or solute is created along with a phonon. For such a cubic process to be responsible for the relaxation of a high frequency vibrational mode, i.e., one lying well above the continuum of low frequency modes, another vibrational mode of the system must have an energy close enough to the initial energy for conservation of energy to be made possible by a phonon within the limited range of the phonon bandwidth. The bandwidth is typically 100 to 200  $\text{cm}^{-1}$  for molecular liquids<sup>33-36</sup> and crystals.<sup>50,55</sup> Therefore, in many systems, *quartic* or higher order processes come into play. Figure 1 displays a prototypical set of energy levels and one particular pathway that could arise for vibrational relaxation induced by a quartic interaction. The initial vibration is annihilated (down arrow) and two vibrational modes (solute or solvent) and one phonon are created (up arrows). An example is provided by the system tungsten hexacarbonyl [ $\text{W}(\text{CO})_6$ ] in chloroform ( $\text{CHCl}_3$ ) solution, in which the asymmetric CO stretching mode at 1976  $\text{cm}^{-1}$  is likely to relax through a quartic (or higher order) interaction.<sup>23</sup> In  $\text{W}(\text{CO})_6$ , the highest frequency mode below the 1976  $\text{cm}^{-1}$  mode is at 580  $\text{cm}^{-1}$ .  $\text{CHCl}_3$  has a mode at 1250  $\text{cm}^{-1}$ . Therefore, relaxation cannot occur via a cubic interaction and requires a quartic process involving a combination of those two modes and a phonon of about 150  $\text{cm}^{-1}$ . In a related system of experimental interest,<sup>23</sup> viz.  $\text{W}(\text{CO})_6$  in carbon tetrachloride ( $\text{CCl}_4$ ) solution, the fact that the highest frequency  $\text{CCl}_4$  solvent mode is 780  $\text{cm}^{-1}$  prevents even a quartic process from causing relaxation, and at

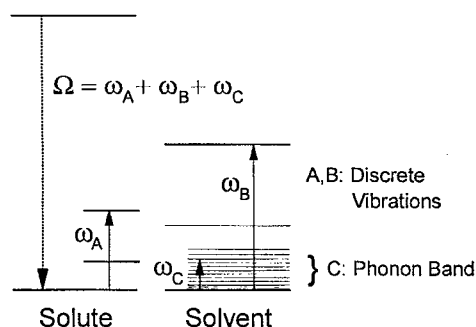


FIG. 1. A level diagram showing a typical configuration of interacting vibrations in a system of interest. The relaxing vibration of the solute has frequency  $\Omega$  which equals the sum of the frequency  $\omega_A$  of a discrete vibration of the solute, the frequency  $\omega_B$  of a discrete vibration of the solvent, and the frequency  $\omega_C$  of an appropriate phonon from the continuum provided by the solvent. Values characteristic of the system tungsten hexacarbonyl  $[\text{W}(\text{CO})_6]$  in chloroform ( $\text{CHCl}_3$ ) solution are  $\Omega = 1976 \text{ cm}^{-1}$  (this is the asymmetric CO stretching mode),  $\omega_A = 580 \text{ cm}^{-1}$  [this is the second-highest  $\text{W}(\text{CO})_6$  mode] and  $\omega_B = 1250 \text{ cm}^{-1}$  (this is a  $\text{CHCl}_3$  mode). The band phonon  $\omega_C$  required for energy conservation is about  $150 \text{ cm}^{-1}$ . Shown here is the usual cascade process. As explained in detail in the paper, this cascade process is only one of seven possible processes for this quartic configuration.

least a fifth order process is required. With the intention of describing all processes of this kind, we derive below expressions for the relaxation rate for arbitrary order and then discuss in greater detail third and fourth order processes as special cases.

We begin our analysis with the assumptions that the system-bath interaction is weak enough and the experimental probe times are long enough to justify making the standard weak-coupling and Markoffian approximations. The point of departure is then the Fermi golden rule for the relaxation rate  $K_\sigma$  of the level  $\sigma$ ,

$$K_\sigma = \frac{2\pi}{\hbar} \sum_{\sigma', r', r} |\langle \sigma, r | V_{SR} | \sigma', r' \rangle|^2 \delta(E_{\sigma, r} - E_{\sigma', r'}) \times \left( \frac{e^{-\beta E_r}}{Z_R} \right), \quad (2.1)$$

where  $\sigma$  and  $\sigma'$  denote the initial and final states of the relaxing system,  $r$  and  $r'$  denote those of the reservoir, i.e., of the rest of the degrees of freedom,  $V_{SR}$  is the system-reservoir interaction,  $Z_R$  is the reservoir partition function, and  $E_r$  is an eigenvalue of  $H_{0R}$  the reservoir part of the unperturbed Hamiltonian  $H_0$ . The complete Hamiltonian  $H$  of the system-reservoir complex is

$$H = H_0 + V_{SR} = H_{0S} + H_{0R} + V_{SR} \quad (2.2)$$

the eigenvalues of  $H_0$  being  $E_{\sigma, r} = E_\sigma + E_r$ , the sum of the respective eigenvalues of  $H_{0S}$  and of  $H_{0R}$ .

The standard technique of expressing the delta function in Eq. (2.1) in terms of the infinite time integral

$$\delta(E) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{iEz} dz \quad (2.3)$$

leads to

$$K_\sigma = (\hbar^2 Z_R)^{-1} \int_{-\infty}^{+\infty} \sum_r \langle \sigma, r | e^{-\beta H_{0R}} e^{-it(H_{0R} + H_{0S})/\hbar} \times V_{SR} e^{-it(H_{0R} + H_{0S})/\hbar} V_{SR} | \sigma, r \rangle dt. \quad (2.4)$$

We stress that Eq. (2.4) contains a thermal sum over the reservoir states  $r$ , but describes a *single* relaxing level  $\sigma$  of the system. While trivial, this is a definite difference between Eq. (2.4) and expressions usually written down in the literature.<sup>42,43,52</sup> Equation (2.4) is applicable to the usual experimental situation<sup>23</sup> in which the relaxing state  $\sigma$  is prepared initially via light excitation so as to have full, rather than thermal, population.

While the interaction  $V_{SR}$  can generally be of arbitrary form, it is most frequently of the product form  $V_{SR} = V_S V_R$ . For instance, if the reservoir and the relaxing system are both represented by oscillators, the natural expansion of the interaction potential about the potential minimum in a Taylor series,<sup>51</sup> followed by a retention of the lowest nonvanishing terms, would lead to the above product form with  $V_S$  and  $V_R$  both proportional to oscillator displacements. For the rest of the calculations, we will assume the product form. It is straightforward to generalize the results to the related case when the interaction is a sum of products. In the completely general case, one may always return to Eq. (2.4) as a point of departure.

Under the assumption of the product form in Eq. (2.4), one obtains

$$K_\sigma = (\hbar^2)^{-1} \int_{-\infty}^{+\infty} \langle V_R(t) V_R \rangle \left( \sum_{\sigma'} |\langle \sigma | V_S | \sigma' \rangle|^2 e^{it\Omega_{\sigma\sigma'}} \right) dt. \quad (2.5)$$

The vibrational relaxation rate is essentially the time integral of the product of the reservoir correlation function and a similar quantity characteristic of the relaxing system. We stress again that the results we derive are special to initial occupation of a single system state as is appropriate to the experimental situation we analyze. If the initial system state were thermal, Eq. (2.5) would be replaced simply by the time integral of the product of a system correlation function and a reservoir correlation function. This product form stems from two features: the assumed product form of the interaction and the use of the weak-coupling result with the consequent appearance of only the unperturbed Hamiltonian  $H_0$  in the exponential expressions describing the time dependence of the correlation function. In Eq. (2.5) and below, the notation used is

$$\langle A(t)B \rangle = (Z_R)^{-1} \text{Tr} e^{-\beta H_{0R}} e^{itH_{0R}/\hbar} A e^{-itH_{0R}/\hbar} B. \quad (2.6)$$

If a single energy difference  $\hbar\Omega$  (single final state energy of the states  $\sigma'$ ) is involved in the system transition, Eq. (2.5) reduces to

$$K_\sigma = U_\sigma \int_{-\infty}^{+\infty} e^{it\Omega_\sigma} \langle V_R(t) V_R \rangle dt, \quad (2.7)$$

where  $U_\sigma$  is given by  $(\hbar^2)^{-1} \sum_{\sigma'} |\langle \sigma | V_S | \sigma' \rangle|^2$ .

Equation (2.7) is simple, practical, and a direct consequence of the weak-coupling and product-form assumptions.

It describes the vibrational relaxation rate as being proportional to the square of the system interaction matrix element and to the Fourier component of the reservoir interaction correlation function evaluated at a frequency equal to the system transition frequency.

The calculation of the correlation function  $\langle V_R(t)V_R \rangle$  requires the explicit knowledge of the interaction  $V_R$ . A Taylor series expansion as in Eq. (3) of Velsko and Oxtoby<sup>51</sup> gives

$$V_R = \sum_{\alpha} \frac{\partial V_R}{\partial Q_{\alpha}} \bigg|_{\{Q=0\}} Q_{\alpha} + \frac{1}{2} \sum_{\alpha, \gamma} \frac{\partial^2 V_R}{\partial Q_{\alpha} \partial Q_{\gamma}} \bigg|_{\{Q=0\}} Q_{\alpha} Q_{\gamma} + \dots, \quad (2.8)$$

where the  $Q$ 's are normal mode or vibrational coordinates. It is thus of importance to evaluate Eq. (2.7) for cases in which the interaction consists of the product of the displacement operators of several oscillators. Of use in this evaluation is an easily derivable explicit expression for the correlation function of the displacement operator  $x_j$  of a harmonic oscillator of frequency  $\omega_j$ ,

$$\begin{aligned} \langle x_j(t)x_j \rangle &= (Z_R)^{-1} \text{Tr} e^{-\beta H_{0R}} e^{itH_{0R}/\hbar} x_j e^{-itH_{0R}/\hbar} x_j \\ &= \left( \frac{\hbar}{2M_j\omega_j} \right) [(1+n_{\omega_j})e^{-it\omega_j} + n_{\omega_j}e^{it\omega_j}]. \end{aligned} \quad (2.9)$$

Here  $M_j$  is the mass of the particle forming the harmonic oscillator, the boson occupation number  $n_E$  is given by

$$n_E = (e^{\hbar\beta E} - 1)^{-1}, \quad \beta = 1/kT, \quad (2.10)$$

$k$  is the Boltzmann constant, and  $T$  is the temperature. The derivation of Eq. (2.9) is straightforward and is therefore not detailed here. If the reservoir interaction is itself the product of  $N$  separate factors each proportional to one oscillator displacement, one obtains

$$\begin{aligned} \langle V_R(t)V_R \rangle &= \text{const} \prod_{j=1}^N \langle x_j(t)x_j \rangle \\ &= \sum_{\xi} C_{\xi} e^{-it\Omega_{\xi}} \left[ \prod_{j=1}^N (n_{\omega_j} + \epsilon_j^{\xi}) \right], \end{aligned} \quad (2.11)$$

where  $C_{\xi}$  is product of coupling constants involving factors such as  $\hbar/2M_j\omega_j$  and the appropriate  $x$  derivatives of  $V_R$ , the quantity  $\epsilon_j$  takes the values 1 or 0, where  $\xi$  denotes a particular distribution of these values over the  $N$  oscillators  $j$ , and where for any such distribution, the weighted algebraic sum of the frequencies of the oscillator is written as

$$\Omega_{\xi}^{\xi} = - \sum_{j=1}^N (-1)^{\epsilon_j^{\xi}} \omega_j. \quad (2.12)$$

Each of the distributions  $\xi$  corresponds to a particular process involving the annihilation (creation) of those vibrational quanta  $j$  for which  $\epsilon_j$  has the value 1 (0). The precise meaning of the  $\xi$  summation is

$$\sum_{\xi} = \sum_{\epsilon_1=0,1} \sum_{\epsilon_2=0,1} \dots \sum_{\epsilon_j=0,1} \dots \sum_{\epsilon_N=0,1}. \quad (2.13)$$

The vibrational relaxation rate as given by Eq. (2.7) is now immediately written down by carrying out the time integration

$$K_{\sigma} = \sum_{\xi} \delta(\Omega - \Omega_{\xi}^{\xi}) C_{\xi} \left[ \prod_{j=1}^N (n_{\omega_j} + \epsilon_j^{\xi}) \right]. \quad (2.14)$$

In most systems, a sum of some set of discrete vibrational energies does not equal the energy difference between the final and initial states. However, in any realistic situation, at least one oscillator provides a continuum density of states, making energy conservation possible. In a solid, such a continuous energy spectrum corresponds to a phonon band, and in a liquid, to what has been termed instantaneous normal modes.<sup>33-37</sup> Because the role the latter play is analogous to that of phonon modes in a crystal, we will use for their description the term liquid phonons, or simply phonons. We denote the continuous density of states of such an oscillator (band) by  $\rho_E$ , where  $E$  is the argument of the density of states function. We take our system to consist of one such oscillator band and  $N$  other discrete oscillators as in Eq. (2.11) and earlier in the above analysis. In some systems, energy conservation may require two or more phonons. While the present treatment can be extended to include such cases, we restrict the development here to the case of a single phonon. We rewrite Eq. (2.14) for the  $N+1$  oscillators, take the continuous band terms out of the product, carry out the summation of the delta functions over the continuous spectrum, and finally obtain

$$\begin{aligned} K_{\sigma} &= \sum_{\xi} C_{\xi} \left[ \prod_{j=1}^N (n_{\omega_j} + \epsilon_j^{\xi}) \right] \\ &\times [(1+n_{\Omega-\Omega_{\xi}^{\xi}})\rho_{\Omega-\Omega_{\xi}^{\xi}} + (n_{\Omega_{\xi}^{\xi}})\rho_{\Omega_{\xi}^{\xi}}]. \end{aligned} \quad (2.15)$$

Since no states exist at negative values of the argument of the density of states function, only one of the two terms in the second square bracket in Eq. (2.15) is nonvanishing for each distribution  $\xi$ . As stated above, each of the distributions corresponds to a separate process involving the creation or annihilation of quanta of the various interacting vibrations. If the discrete vibration frequency sum  $\Omega_{\xi}^{\xi}$  is less than the relaxation frequency  $\Omega$ , relaxation requires the creation of the band phonon, and the first of the two terms in the square bracket in Eq. (2.15) is nonzero. If, on the other hand, the discrete vibration frequency sum  $\Omega_{\xi}^{\xi}$  is larger than  $\Omega$ , relaxation requires the annihilation of the band phonon, the first of the two terms in the square bracket in Eq. (2.15) vanishes, and the second term is nonzero. The fact that the Bose distribution function satisfies

$$n_{-E} = -(1+n_E) \quad (2.16)$$

allows us to rewrite Eq. (2.15) in three other convenient forms. The first is

$$\begin{aligned} K_{\sigma} &= \sum_{\xi} C_{\xi} \left[ \prod_{j=1}^N (n_{\omega_j} + \epsilon_j^{\xi}) \right] \\ &\times (1+n_{\Omega-\Omega_{\xi}^{\xi}})(\rho_{\Omega-\Omega_{\xi}^{\xi}} - \rho_{\Omega_{\xi}^{\xi}}), \end{aligned} \quad (2.17)$$

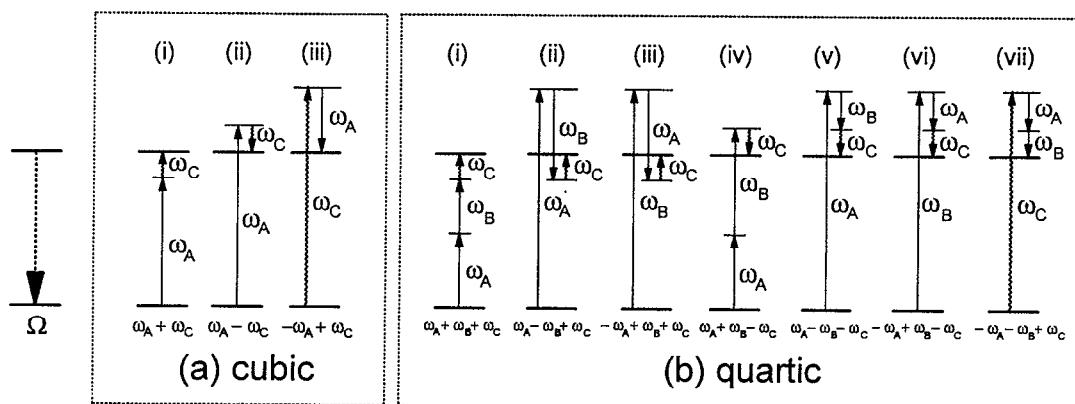


FIG. 2. Individual transitions involved in the (a) cubic and (b) quartic processes. The number of configurations (transitions)  $\xi$  involved is three for the cubic process, and seven for the quartic process as shown. The band phonon is represented by a wiggly line and has frequency  $\omega_C$ . The discrete vibration bosons are represented by solid lines and have frequencies  $\omega_A$  and  $\omega_B$ . The relaxing vibration has frequency  $\Omega$ . In (a), the first of the three transitions shown, viz. (i) is the usual cascade process treated in earlier theories. The transition shown as (ii) is present if  $\omega_A > \Omega$ . The transition (iii) is significant only if the band cutoff does not prevent the existence of continuous phonons at the large frequency  $\omega_C$  required. In (b) (i) represents again the usual cascade process, as in Fig. 1, and as treated in earlier theories. Transitions (ii) and (iii) are present if  $\Omega$  is smaller than one of the participating frequencies  $\omega_A$  or  $\omega_B$ . As in (ii) of (a), transitions (iv)–(vi) of (b) represent processes in which the continuous spectrum phonon is annihilated rather than created. Transition (vii) is analogous to (iii) of (a) in that it is significant only if the band cutoff does not prevent the existence of continuous phonons at the large frequency  $\omega_C$  required.

in which, once again, only one of the two density of state terms is nonvanishing for each distribution. The second form is

$$K_\sigma = \sum_{\xi} C_{\xi} \left[ \prod_{j=1}^N (n_{\omega_j} + \epsilon_j^{\xi}) \right] (\alpha_{\xi} + n_{|\Omega - \Omega_{\xi}|}) \rho_{|\Omega - \Omega_{\xi}|}, \quad (2.18)$$

in which the density of states is measured at the absolute value of the difference  $\Omega - \Omega_{\xi}$ , and the sign of the latter determines the value of  $\alpha_{\xi}$ ,

$$\alpha_{\xi} = 1, \text{ for } \Omega > \Omega_{\xi}^{\xi} \text{ and } \alpha_{\xi} = 0, \text{ for } \Omega < \Omega_{\xi}^{\xi}. \quad (2.19)$$

The third equivalent form uses the definition of the symbol  $m$  related to the occupation number  $n$  through

$$m_E = n_{|E|} = (e^{\hbar\beta E} - 1)^{-1}, \text{ if } E < 0, \\ m_E = n_E + 1 = (1 - e^{-\hbar\beta E})^{-1}, \text{ if } E > 0, \quad (2.20)$$

and is

$$K_\sigma = \sum_{\xi} C_{\xi} \left[ \prod_{j=1}^N (n_{\omega_j} + \epsilon_j^{\xi}) \right] m_{\Omega - \Omega_{\xi}^{\xi}} \rho_{|\Omega - \Omega_{\xi}^{\xi}|}. \quad (2.21)$$

Equation (2.15), along with its equivalent forms (2.17), (2.18), and (2.21), constitutes one of the central results of this paper. Each of those equations expresses the vibrational relaxation rate  $K_\sigma$  for leaving an initially occupied level  $\sigma$  of the relaxing molecule in terms of configurational sums of products of factors involving the Bose occupation numbers of individual oscillators participating in the relaxation process and the density of states of the continuous spectrum. The configurations consist of all possible realizations of the creation and annihilation of the participating bosons. It will be seen below that this feature of our theory, viz. the consid-

eration of all possible configurations, is one of the elements which sets it apart from earlier treatments in which only cascades were considered.

### III. APPLICATION OF THEORY TO CUBIC AND QUARTIC PROCESSES

We consider three particular examples corresponding to the case of the reservoir containing no discrete vibration ( $N=0$ ), one discrete vibration ( $N=1$ ), i.e., the cubic process, and two discrete vibrations ( $N=2$ ), i.e., the quartic process. In each case, we consider a system with a phonon band providing the continuous density of states. The first of these cases, although not very realistic, is mentioned for illustrative reasons. It corresponds to the reservoir consisting of no discrete vibration, but only a phonon band with a continuous density of states. The reservoir interaction operator is simply the oscillator displacement operator. The correlation function of the interaction is given essentially by the right-hand side of Eq. (2.9). In our general formula (2.18), there are no  $\omega$ 's and  $\Omega_{\xi}^{\xi}=0$ . Since no states exist at negative values of the argument of the density of states function, we have

$$K = C_{\Omega} (1 + n_{\Omega}) \rho_{\Omega}. \quad (3.1)$$

In Eq. (3.1) and the rest of the paper, we drop the label  $\sigma$  on  $K$ . Only creation (not annihilation) of the continuous band phonons is possible and the relaxation rate is proportional to the density of states at the value of the relaxing frequency.

Realistic examples are provided by the cubic and the quartic processes depicted in Fig. 2. We derive the relaxation rate for those cases below and discuss novel predictions of our calculations for these processes.

TABLE I. Cubic relaxation process parameters for Eq. (2.18)

$\epsilon^\xi$	$\alpha_\xi$	$\Omega_\xi^\xi$	Comments	Process in Fig. 2(a)
1	1	$+\omega$	$\Omega > \omega$	(i)
1	0	$+\omega$	$\Omega < \omega$	(ii)
0	1	$-\omega$		(iii)

### A. The cubic process

The reservoir in this case consists of one discrete vibration of frequency  $\omega$  in addition to the phonon band. Every elemental transition involves three ladder operators. The correlation function of the interaction is given by the product of two expressions such as that in the right-hand side of Eq. (2.9). The application of our general formula (2.18) proceeds as follows: There are two configurations  $\xi$  corresponding to the value of 1 and 0 assigned to  $\epsilon^\xi$ , respectively. The corresponding values of  $\Omega_\xi^\xi$  are  $+\omega$  and  $-\omega$ , respectively. Table I provides the necessary quantities for input into our general formula. Equation (2.18) then yields

$$K = n_\omega(1 + n_{\Omega+\omega})\rho_{\Omega+\omega}C_{\Omega+\omega} + (1 + n_\omega)(\alpha + n_{|\Omega-\omega|})\rho_{|\Omega-\omega|}C_{|\Omega-\omega|}, \quad (3.2)$$

where the quantity  $\alpha$  is given by the relative values of the relaxing frequency  $\Omega$  and the discrete vibration frequency  $\omega$ ,

$$\alpha = 1, \text{ if } \Omega > \omega \text{ and } \alpha = 0, \text{ if } \Omega < \omega. \quad (3.3)$$

The first term in Eq. (3.2) describes a usually improbable process in which the discrete vibrational quantum is annihilated rather than created, and the continuous phonon is created, its improbability stemming from the fact that the density of states required is at a rather high value of the argument—the phonon band often has a cutoff at frequency values far exceeded by the relaxing frequency. This process is depicted as (iii) in Fig. 2(a). The second term in Eq. (3.2) involves the creation of the discrete vibration quantum. If the frequency of the latter is smaller than the frequency of the relaxing vibration, the continuous band phonon is also created and the multiplying factor is  $1 + n_{\Omega-\omega}$ . We have then the cascade process depicted as (i) in Fig. 2(a). If, on the other hand, the frequency of the discrete vibration quantum exceeds the frequency of the relaxing vibration, the continuous band phonon is annihilated and the multiplying factor is  $n_{\omega-\Omega}$ . The situation is shown in (ii) of Fig. 2(a). In both (i) and (ii), the density of states factor has an argument which is the absolute value of the difference between the two frequencies.

### B. The quartic process

We now consider the reservoir to consist of two discrete vibrations of frequencies  $\omega_A$  and  $\omega_B$  in addition to the phonon band. These discrete vibrations could be of oscillators belonging either to the solute alone, to the solvent alone, or one to the solute and the other to the solvent. The application of our general formula (2.21) now proceeds as follows:

TABLE II. Quartic relaxation process parameters for Eq. (2.18).

$\epsilon_A^\xi$	$\epsilon_B^\xi$	$\alpha_\xi$	$\Omega_\xi^\xi$	Comments	Process in Fig. 2(b)
1	1	1	$\omega_A + \omega_B$	$\Omega > \omega_A + \omega_B$	(i)
1	0	1	$\omega_A - \omega_B$	$\Omega > \omega_A - \omega_B$	(ii)
0	1	1	$\omega_B - \omega_A$	$\Omega > \omega_B - \omega_A$	(iii)
1	1	0	$\omega_A + \omega_B$	$\Omega < \omega_A + \omega_B$	(iv)
1	0	0	$\omega_A - \omega_B$	$\Omega < \omega_A - \omega_B$	(v)
0	1	0	$\omega_B - \omega_A$	$\Omega < \omega_B - \omega_A$	(vi)
0	0	1	$-(\omega_A + \omega_B)$		(vii)

There are four configurations  $\xi$  corresponding to the various processes as shown in Table II. Our general formula then yields

$$K = [n_{\omega_A}n_{\omega_B}(1 + n_{\Omega+\omega_A+\omega_B})f_{\Omega+\omega_A+\omega_B} + (1 + n_{\omega_A})(1 + n_{\omega_B})m_{\Omega-(\omega_A+\omega_B)}f_{|\Omega-(\omega_A+\omega_B)|} + n_{\omega_A}(1 + n_{\omega_B})m_{\Omega-(\omega_B-\omega_A)}f_{|\Omega-(\omega_B-\omega_A)|} + (1 + n_{\omega_A})n_{\omega_B}m_{\Omega-(\omega_A-\omega_B)}f_{|\Omega-(\omega_A-\omega_B)|}], \quad (3.4a)$$

$$f_\nu = \rho_\nu C_\nu. \quad (3.4b)$$

In Eq. (3.4), we have used the general form (2.21) which contains the symbol  $m$  defined in Eq. (2.20). As in Eq. (3.2), the first term in Eq. (3.4) describes an usually improbable process involving annihilation rather than creation of quanta of both discrete vibrations [see (vii) in Fig. 2(b)]. The second term involves creation of the quanta of both discrete oscillators. In this case, if the sum of  $\omega_A$  and  $\omega_B$  is less than  $\Omega$ , the normal cascade situation occurs. This is depicted as (i) in Fig. 2(b) and is also the process shown in the illustrative Fig. 1. If, on the other hand, the sum of  $\omega_A$  and  $\omega_B$  exceeds  $\Omega$ , the second term in Eq. (3.4) describes the process shown in (iv) of Fig. 2(b). It involves the annihilation of the continuous spectrum phonon (represented by a wiggly line). The third and fourth terms describe the annihilation of a vibrational quantum of one of the two oscillators ( $A$  or  $B$ ) and the creation of a quantum of the other. The corresponding processes are, respectively, depicted in Fig. 2(b) as (ii) and (iii) in which the continuous band phonon is created, and (v) and (vi) in which it is annihilated. The reason there is no term involving the annihilation of the quanta of *all* the vibrations including the continuous spectrum phonon is simply that the initial state of our experiment consists of the relaxing oscillator already in an excited state. Generally, the number of processes  $\xi$  is given by  $2^{N+1} - 1$ . For the quartic process there are, thus, seven processes, while for the cubic process, there are three.

In all cases, the value of the factor  $f_\nu$ , which is the product of the density of states and the coupling constant, allows or forbids the processes and determines the strength of the allowed processes. While the Bose occupations are a strong source of the temperature dependence of relaxation, the factor  $f_\nu$  could, in principle, have a nontrivial temperature dependence particularly in liquids as shown elsewhere.<sup>23</sup>

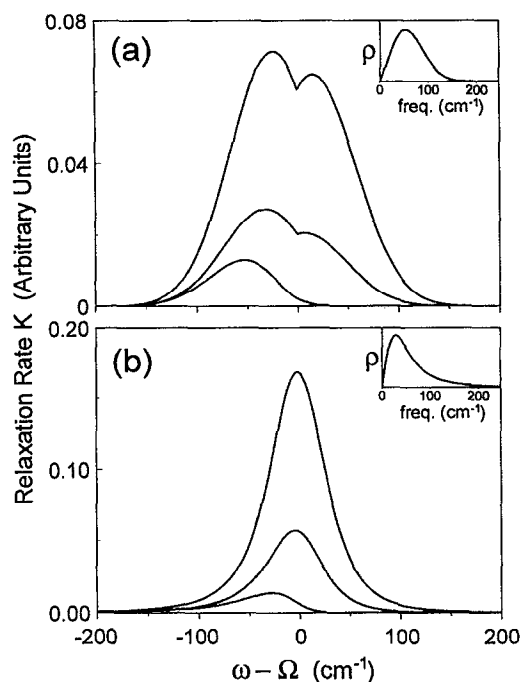


FIG. 3. Asymmetry effects arising in the frequency dependence of the relaxation rate as predicted by our theory. Plotted is the relaxation rate  $K$  arising in a cubic process as a function of the difference between the frequency  $\omega$  of a discrete vibrational oscillator participating in the relaxation and the frequency  $\Omega$  of the relaxing vibration. The density of states of the continuous band phonon, shown in the insets, has the form given in Eq. (3.5) in (a) and the form in Eq. (3.6) in (b). The coupling constant has been assumed independent of frequency for simplicity. The asymmetry in the relaxation rate is an explicit quantum effect.

### C. Novel predictions

There are a number of interesting consequences of expressions such as Eqs. (3.2) and (3.4), which we have derived above. To illustrate one of them, we consider the cubic process and investigate the dependence of the relaxation rate on the frequency  $\omega$  of the vibration involved in the relaxation pathway. An easily understood effect is that the relaxation rate rises in magnitude as  $\omega$  nears the value  $\Omega$  of the relaxing vibration. The quantum mechanics of the difference between emission and absorption of bosons (the possibility of spontaneous emission) results in a more interesting effect. If  $\omega$  is smaller than  $\Omega$  [see process (i) in Fig. 2(a)], relaxation involves the *creation* of the band phonon. Spontaneous emission is possible and the relaxation rate is therefore nonvanishing at absolute zero. If, however,  $\omega$  is larger than  $\Omega$ , only annihilation of the band phonon is possible [see process (ii) in Fig. 2(a)], there is no spontaneous process and the relaxation rate vanishes at absolute zero.

This asymmetry effect is displayed in Fig. 3, where we plot the relaxation rate  $K$  for a cubic process as a function of the difference  $\omega - \Omega$ . We have assumed two reasonable functional forms for the density of states and have ignored the frequency dependence of the coupling constant term  $C$ . The forms for the density of states are in qualitative accord with calculations of the instantaneous normal modes of liquids. In

Fig. 3(a), we take a Gaussian density of states biased to make it vanish at zero frequency

$$\rho_{\omega} = \text{const } \omega \exp \left[ -\frac{(\omega - \omega_0)^2}{(\Delta\omega)^2} \right]. \quad (3.5)$$

We have taken  $\omega_0 = 20 \text{ cm}^{-1}$  and  $\Delta\omega = 60 \text{ cm}^{-1}$ . The inset in Fig. 3(a) shows the density of states function. The asymmetry effect as well as the resonance effect on the vibrational relaxation rate are quite obvious. In Fig. 3(b), we take a form for the density of states that has been used previously<sup>57</sup> and represents theoretical calculations<sup>35</sup>

$$\rho_{\omega} = \text{const } \frac{\omega}{(B^2 - \omega^2)^2 + C^2 \omega^2}. \quad (3.6)$$

We have taken  $B = 50 \text{ cm}^{-1}$  and  $C = 100 \text{ cm}^{-1}$ . Both forms have their areas normalized to unity. The inset in Fig. 3(b) shows this form. The asymmetry and resonance effects are again clear. The maximum of the relaxation rate does not occur at the resonance position  $\omega = \Omega$  because of the values of the density of states factor. In Fig. 3(a), we see an additional interesting feature near resonance. The three curves in Figs. 3(a) and 3(b) correspond to three different temperatures. The lowest trace in each panel is for  $T = 10 \text{ K}$ , the middle trace is for  $T = 100 \text{ K}$ , and the top trace is for  $T = 300 \text{ K}$ . At the lowest temperature, essentially the entire curve in each panel is in the negative frequency range. This corresponds to  $\omega < \Omega$ , i.e., spontaneous emission of a phonon. At  $10 \text{ K}$ , only the low frequency part of the continuum of states will be populated. Relaxation of the initially populated vibration by absorption of a phonon ( $\omega > \Omega$ ) can only occur for  $\Omega \approx 0$ . As the temperature is increased, the occupation numbers of phonons throughout the continuum of states becomes significant. For  $\omega < \Omega$ , stimulated emission enhances the spontaneous emission. For  $\omega > \Omega$ , phonon absorption becomes increasingly likely. At sufficiently high temperature, stimulated emission overwhelms spontaneous emission and the relaxation rate of the initially excited vibration by processes with  $\omega < \Omega$  and  $\omega > \Omega$  approach each other (under the assumption of equal coupling constants).

The corresponding temperature dependence of the rate is displayed in Fig. 4. The density of states used corresponds to Fig. 3(b), i.e., to Eq. (3.6). Four different values of the difference  $\omega - \Omega$  are taken (a)  $-40$ ; (b)  $+40$ ; (c)  $-100$ ; and (d)  $+100 \text{ cm}^{-1}$ . The coupling constant  $C$  is taken to be the same for the four cases and to be temperature independent. For cases 4(a) and 4(c), spontaneous emission of the continuous band phonon is involved and the relaxing rate is therefore nonvanishing at  $T = 0 \text{ K}$ . This prediction of our theory is beyond the reach of classical theories. For cases 4(b) and 4(d), the band phonon is annihilated and the relaxation rate vanishes at absolute zero. Cases 4(a) and 4(b) are near resonance, while Figs. 4(c) and 4(d) are far from resonance. The magnitudes of the rate are appropriately larger for the former two. We see that the classically appropriate linear dependence on  $T$  is obtained as the temperature is increased.

The combined dependence of the vibrational relaxation rate on frequency and temperature is displayed in Fig. 5. The density of states form chosen is as given by Eq. (3.5) and thus corresponds to Fig. 3(a). The asymmetry effects dis-



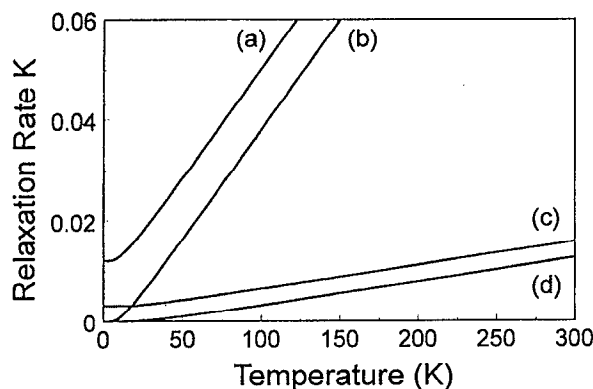


FIG. 4. The temperature dependence of the relaxation rate for the process represented in Fig. 3(b) for four different values of the difference  $\omega - \Omega$  (a)  $-40$ ; (b)  $+40$ ; (c)  $-100$ ; (d)  $+100$   $\text{cm}^{-1}$ . For cases (a) and (c), spontaneous emission of the continuous band phonon is involved and the relaxation rate does not vanish at  $T=0$  K. For cases (b) and (d), the band phonon is annihilated and the relaxation rate vanishes at  $T=0$  K. Cases (a) and (b) are near resonance, while (c) and (d) are far from resonance.

played in these plots are a direct consequence of quantum mechanics and would be absent in theories such as those in Refs. 52 and 54 which treat the bath classically.

#### IV. THE RELATION TO OTHER TREATMENTS

It is not our purpose in this section to carry out a comparative review of the entire literature on vibrational relaxation theory. Rather, we will touch upon only a few interesting questions and return to a comparative study of various treatments of vibrational relaxation including the present one in a future publication. Here we will address three specific issues: (a) the relation of our expressions with those obtained by Califano *et al.*<sup>50,53</sup> which appear to be quite different at the outset; (b) the differences brought about by the inclusion of the quantum mechanical nature of the reservoir in our treatment vis a vis the classical treatment of other authors such as Oxtoby and Adelman *et al.*,<sup>52,54</sup> and (c) the role of

the rotating wave approximation and the random phase approximation in the analysis of Nitzan and collaborators.<sup>42-45</sup>

##### A. Relation of our results to those of Califano *et al.*

Through the use of diagrammatic expansion techniques, Califano *et al.*<sup>50,53</sup> have obtained results that look considerably different from those obtained in our treatment. It is of importance to know what features of the theoretical derivation, if any, are responsible for the seeming discrepancy in the expressions. We restrict the comparison to the cubic process and write the form of Eq. (3.2) for the specific case when the relaxing frequency is larger than the discrete vibrational frequency participating in the relaxation process. The result that emerges from our present treatment is then

$$K = n_{\omega}(1 + n_{\Omega+\omega})\rho_{\Omega+\omega}C_{\Omega+\omega} + (1 + n_{\omega})(1 + n_{\Omega-\omega})\rho_{\Omega-\omega}C_{\Omega-\omega}. \quad (4.1)$$

The corresponding result of Califano *et al.*<sup>50,53</sup> can be written as

$$K = (n_{\omega} - n_{\Omega+\omega})\rho_{\Omega+\omega}D_{+} + (1 + n_{\omega} + n_{\Omega-\omega})\rho_{\Omega-\omega}D_{-}, \quad (4.2)$$

where the  $D$ 's are proportionality constants. While written in a form which facilitates comparison to Eq. (4.1), Eq. (4.2) is essentially identical to Eq. (16) of Ref. 53. Expressions similar to Eq. (4.2) have also been written down by Dlott and Fayer,<sup>1</sup> Chesnoy,<sup>58</sup> and by Nitzan *et al.*<sup>43</sup> The seeming disparity of Eqs. (4.1) and (4.2) presents a problem of reconciliation. The respective second terms appear at the outset to be equal to each other only under low temperature conditions which allow the neglect of the product of Bose factors, and the first terms seem to have little in common. Given that intuitive reasoning of the kind given in Ref. 23 seems not to yield expressions of the kind presented in Eq. (4.2), this comparison becomes important to resolve.

In order to understand the remarkably simple relation that exists between our result (4.1) and the Califano result (4.2), it is enough to write out the factor  $1 + n_{\omega} + n_{\Omega-\omega}$  explicitly in terms of the Bose distribution function and show that it is related to the product  $(1 + n_{\omega})(1 + n_{\Omega-\omega})$  appearing in Eq. (4.1) through

$$(1 + n_{\omega} + n_{\Omega-\omega}) = (1 - e^{-\hbar\beta\Omega})(1 + n_{\omega})(1 + n_{\Omega-\omega}). \quad (4.3)$$

When one also notices that the *same* proportionality constant relates the other two factors appearing in Eqs. (4.1) and (4.2), viz,  $n_{\omega}(1 + n_{\Omega+\omega})$  and  $n_{\omega} - n_{\Omega+\omega}$ ,

$$(n_{\omega} - n_{\Omega+\omega}) = (1 - e^{-\hbar\beta\Omega})n_{\omega}(1 + n_{\Omega+\omega}), \quad (4.4)$$

it is clear that the result of Califano *et al.*<sup>50,53</sup> and that obtained by us in the present paper, are completely equivalent to each other. The proportionality constants  $D_{\pm}$  of Califano *et al.* are given in terms of our  $C$ 's through

$$D_{\pm} = C_{\Omega\pm\omega}(n_{\Omega} + 1). \quad (4.5)$$

Deeper insight into this relation is provided by investigating the calculational methods employed. Our method is based on an evaluation of the Fourier transform of an expression such as  $\langle V_R(t)V_R \rangle$  in Eq. (2.7). There exists a general

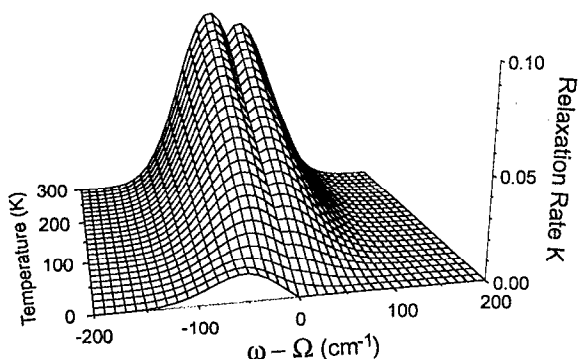


FIG. 5. A three-dimensional representation of the relaxation rate  $K$  as a function of the frequency difference  $\omega - \Omega$  and the temperature  $T$  corresponding to the cubic process described in Fig. 3 and in Eq. (3.3) of the text. The density of states function is assumed to be quasi-Gaussian as in Fig. 3(a).

relation between the Fourier transform of an equilibrium correlation function of two operators  $A(t)$  and  $B$  and that of either their commutators or their anticommutators. This relation has been known for a long time since the time of Kubo<sup>59</sup> and has been republished many times. The basic result is

$$\int_{-\infty}^{+\infty} e^{it\Omega} \langle A(t)B \rangle dt = e^{\hbar\beta\Omega} \int_{-\infty}^{+\infty} e^{it\Omega} \langle BA(t) \rangle dt. \quad (4.6)$$

It is obtained by considering a complex time (or inverse temperature) in the definition (2.6), making general physical assumptions which allow one to make an analytic continuation of the correlation function in the complex plane, specifically to replace  $t$  by  $t - i\hbar\beta$  in the left-hand side of Eq. (4.6), and performing cyclic permutations within the trace to obtain the right-hand side. Equation (4.6) allows one to relate the Fourier transform of  $\langle A(t)B \rangle$  to that of the correlation function of the commutator as well as the anticommutator of the corresponding operators. Thus, Eq. (4.6) leads directly to

$$\int_{-\infty}^{+\infty} e^{it\Omega} \langle A(t)B \rangle dt = (1 - e^{-\hbar\beta\Omega})^{-1} \times \int_{-\infty}^{+\infty} e^{it\Omega} \langle [A(t), B] \rangle dt, \quad (4.7)$$

$$\int_{-\infty}^{+\infty} e^{it\Omega} \langle A(t)B \rangle dt = (1 + e^{-\hbar\beta\Omega})^{-1} \times \int_{-\infty}^{+\infty} e^{it\Omega} \langle \{A(t), B\} \rangle dt. \quad (4.8)$$

The use of Eq. (4.7) allows one to write our primary relation (2.7) in the form of a commutator correlation function

$$\gamma_{\sigma} = U_{\sigma}(n_{\Omega} + 1) \int_{-\infty}^{+\infty} e^{it\Omega_{\sigma}} \langle [V_R(t), V_R] \rangle dt. \quad (4.9)$$

An inspection of the multiplicative factor in Eq. (4.9) makes clear the source of relation (4.5) between Eqs. (4.1) and (4.2). Results such as those of Califano *et al.* are obtained from the commutator correlation function, the differences such as  $n_{\omega} - n_{\Omega+\omega}$  being representative of the operator difference in a commutator.

## B. The relation to classical bath treatments such as those of Oxtoby

Oxtoby,<sup>52</sup> Adelman *et al.*,<sup>54</sup> and others have treated vibrational relaxation in the limit in which the reservoir may be approximated as being classical. The relationship of the theory of the present paper to such analyses is straightforward. Equation (4.8) derived above can be used to relate the correlation function of the bath operators to the correlation function of the anticommutators of the bath operators. The classical limit<sup>52,54</sup> replaces the anticommutator correlation by a classical correlation. The domain of validity of this replacement is thus the domain of validity of the treatments of Refs. 52 and 54. It is particularly clear that all processes involving spontaneous emission which we have described in equations such as Eq. (2.15) and in Fig. 2 are beyond the reach of the classical treatments. In particular, the disappearance of emis-

sion processes from the relaxation pathway at absolute zero, their quantitatively incorrect description at temperatures low with respect to  $\hbar\omega_A/k$  and  $\hbar\omega_B/k$  (and also with respect to  $\hbar\omega_C/k$ , although this restriction is less stringent), and the complete loss of the asymmetry effects in the frequency dependence depicted in Figs. 3–5 are among the casualties of the classical approximation. The classical treatments<sup>52,54</sup> become completely acceptable if used to address only observations at high enough temperatures.

## C. The relation to RWA and RPA treatment of Nitzan *et al.*

There are few existing quantum mechanical treatments of vibrational relaxation. Notable among them is that of Nitzan and Silbey<sup>43</sup> and Nitzan and Jortner.<sup>42</sup> These authors have given a thorough treatment of several issues. One of the differences between their treatment and ours is their use, in all cases, of the rotating wave approximation (RWA) and, in some cases, of the random phase approximation (RPA) to calculate the evolution. The random phase approximation as employed in Ref. 42 consists of the replacement of certain operators by their thermal averages. While an oversimplification, it gives results which differ little from those obtained via other methods such as cumulant expansions<sup>43</sup> when the expansion is truncated in the usual manner. The RPA is useful when a particular calculational procedure, the Heisenberg equation method, is employed because it introduces substantial simplifications into the evolution. However, as our treatment shows, it is not necessary to make the RPA. This is not meant to say that the approximations represented by the RPA are avoided in our treatment. They are instead incorporated in the *single* assumption of the validity of the Fermi golden rule rate. While the latter is by no means an exact consequence of the dynamics, the nature and extent of the assumptions involved is familiar. The fact that we do not have to make further approximations after the assumption of the validity of the Fermi golden rule is, therefore, a definite asset of our development.

The rotating wave approximation (RWA) is the other prominent ingredient of the treatment of Refs. 42–45. The basic idea, which consists of ignoring a large number of terms in the interaction Hamiltonian on the basis of near-resonance arguments, is a product of quantum optics investigations.<sup>60,61</sup> We will focus attention on a quartic process involving the deexcitation of the relaxing oscillator whose quantum is destroyed by  $a$ . The actual interaction Hamiltonian is  $a(b_A + b_A^{\dagger})(b_B + b_B^{\dagger})(b_C + b_C^{\dagger})$  along with its adjoint. This form is a direct consequence of expressing the interaction in terms of the Taylor expansion (2.8). The RWA of Refs. 42 and 43 employs the approximate replacement

$$a(b_A + b_A^{\dagger})(b_B + b_B^{\dagger})(b_C + b_C^{\dagger}) \approx ab_A^{\dagger}b_B^{\dagger}b_C^{\dagger} \quad (4.10)$$

as is clear from equations such as Eqs. (66) and (67) of Ref. 43 or Eq. (2.4) of Ref. 42. A glance at Fig. 2(b) in the present paper makes it clear that Eq. (4.10) immediately removes from consideration all six of the processes (ii)–(vii) in Fig. 2(b) and retains only the cascade process of (i) or of Fig. 1. The RWA employed by Nitzan and collaborators can never-

theless be a reasonable approximation when the cascade process is the only one that for various system reasons has high probability.

What is important to realize, however, is that the RWA is *not necessary* at the level of approximation employed. In quantum optics contexts, the RWA sometimes makes *exact solutions* possible as in the case of the Jaynes–Cummings model.<sup>62</sup> In those cases, it is worthwhile to employ the RWA. In treating our present system, whether via our methods or via the procedures employed by Nitzan *et al.*, there is no additional advantage to be gained by making the RWA. A very similar situation arises in the treatment<sup>63,64</sup> of the analysis of the relaxation of a ferromagnet model, as pointed out many years ago by one of the present authors.<sup>63</sup>

## V. DISCUSSION

The goal of the study in this paper has been to begin the construction of a simple and tractable theory of vibrational relaxation particularly geared to address polyatomic solutes in polyatomic solvents. The point of departure is the Fermi golden rule expression (2.1) along with the general Hamiltonian (2.2). Under the assumption of product interactions, Eqs. (2.5) and (2.7) are obtained as general consequences and, with the Taylor expansion expression (2.8) for the interaction, Eqs. (2.15), (2.17), (2.18), and (2.21) are obtained as explicit usable expressions for the vibrational relaxation rate. Specific instances for cubic and quartic processes are Eqs. (3.2) and (3.4), and the corresponding pictorial representation of the processes included in our theoretical description are in Fig. 2. Some interesting consequences are shown in Figs. 3–5.

We have refrained from making the RWA in our analysis and have thereby allowed for all combinations of possible processes. We have obtained intuitively understandable expressions for the vibrational relaxation rate and shown their equivalence to some of the earlier results such as those of Califano *et al.* which possess a strikingly different appearance. We have also commented on other earlier theories which have been developed under more restrictive assumptions.

One of the main advantages of our theory is the simplicity of approach—we do not employ complex diagrammatic expansions, uncertain RWAs, or uncontrollable RPAs. Rather, we use only straightforward exact manipulations starting from the Fermi golden rule. Our results thus inherit all the strengths and weaknesses (all reasonably well known and none hidden) of the Fermi golden rule. The possibility of treating annihilation as well as creation of ALL the participating bosons which emerges from our theory is also a definite advantage. All the earlier treatments appear to involve only the cascade process. Our results can be written down easily intuitively by using arguments of the kind described in Ref. 23. Our treatment is quantum mechanical—we do not treat classical baths and thereby miss any quantum effects. Our treatment does not merely treat discrete vibrations as in some earlier theories, but is realistic in its inclusion of continuous density of states. Such density of states factors obtained in modern treatments of liquids can be easily put into

our theory. Finally, our theory is particularly constructed to be useful to experiments on complex systems.

Although our formal theory does not require it, we have assumed implicitly that the coupling of the initially excited vibration to other vibrations (solute and solvent) is stronger than the coupling to phonon modes of the liquid or solid solvent. This is reflected in a “least number of phonons” depiction of the relaxation pathways. It means that an initially excited high frequency mode well above the low frequency continuum has been assumed to relax through pathways which employ a small number of other high frequency vibrations to match the initial energy to within that of one (or more) phonons from the continuum. Such pathways do not involve a large number of low frequency phonons. The assumption means that the system is taken to relax by the lowest order process consistent with energy conservation. However, if required, our general theory can handle any number of discrete vibrations and any number of continuum phonons.

Of the questions (i)–(v) raised in Sec. I, our treatment answers (i)–(iv) as discussed above. In its present form, it is able to address the inverted temperature dependence observed in Ref. 23 only by assuming that the liquid phonon density of states, and/or the coupling constants, have an appropriately strong temperature dependence in the opposite direction to that of the Bose occupation factors.<sup>23</sup> The normal tendency of the Bose occupation factors could then be overwhelmed and the rate would *decrease* with temperature. If the system is a mixed crystal, the continuum of low frequency states is the phonon spectrum of the crystal. The theory for a solute molecule in a liquid solution is identical except that the phonon spectrum of a crystal is replaced with the density of states of the low frequency instantaneous normal modes of the liquid. The real part of the INM spectrum corresponds to true oscillatory modes. Unlike the case in solids, the INM have an imaginary component which is related to the time evolution of the liquid structure. Although any mode in the real part of the spectrum is transitory, existing for only a short time period, these modes still provide a density of states from which energy can be removed and into which energy can be deposited. The density of states given by recent calculations<sup>33–37</sup> can provide an explicit input into our theory.

As in essentially all existing quantum mechanical theories of relaxation, we have calculated only the rate of *leaving* the initially excited vibration. Experiments have shown that in systems in which there is another mode with energy close to that of the initially excited mode, rapid equilibration of population can occur. For example, the IR active mode of W(CO)<sub>6</sub> at 1776 cm<sup>-1</sup> has a Raman active mode only 32 cm<sup>-1</sup> higher in energy. By performing IR pump/anti-Stokes Raman probe experiments,<sup>22</sup> it has been shown that these two modes exchange population rapidly (~1 ps). Equilibration occurs and then the two modes decay together with a lifetime of ~700 ps (in CCl<sub>4</sub> solution). The present theory does not describe population returning to the initially excited vibrational level following relaxation out of it. This return actually occurs and can have a profound impact on experimental observables. Two nearby levels can equalize their

populations on a very fast time scale by a cubic process. Subsequent relaxation on much slower time scales can require higher order processes. The equilibration of the two levels will reduce the population of the initially excited level to 0.5, not to 0. A biexponential decay can result in a population decay experiment. The rapid equilibration can also be a source of optical dephasing. In a photon echo experiment on vibrations in liquids,<sup>24</sup> the fast leaving rate from the initially excited state produces lifetime line broadening if the time for return of the population is comparable to, or longer than, the inverse of the frequency difference between the levels. Thus, population equilibration between a pair of levels will cause a pump-probe signal to decay to 0.5, but it can cause a photon echo signal to decay to 0. However, if the scattering out of, and into, the initially excited level is fast enough, motional narrowing of the line can occur. This could result in a complex temperature dependence in a photon echo decay experiment.

Following standard practice, we have considered all the participating oscillators in our system to be harmonic, the anharmonicity responsible for the relaxation stemming from the interactions among the oscillators. We believe that anharmonicity within the unperturbed oscillators themselves can be quite important in the theory of vibrational relaxation, particularly in the context of liquids. For this reason, we have begun calculations of the displacement autocorrelation function, and of the consequent characteristics of the vibrational relaxation rate, for anharmonic systems such as Morse oscillators. These matters, as well as the consequence of finite lifetime of the discrete modes, will be dealt with in a separate publication.

Another element missing from the present theory at this stage is the pathway that involves a molecule initially excited to  $n=1$  relaxing by being excited to  $n=2$ . For high frequency vibrations, such as the  $\sim 2000\text{ cm}^{-1}$  mode of tungsten hexacarbonyl, this process is insignificant even at room temperature. At room temperature,  $kT$  is of the order of  $200\text{ cm}^{-1}$ . Therefore, relaxing to a higher level is highly improbable. However, the lowest frequency modes of molecules can have energies on the order of  $200\text{ cm}^{-1}$ . In the case of such modes, relaxing to a higher level becomes probable. Extensions of our theories in these various directions will be treated in forthcoming publications.

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