

## NON-MARKOVIAN THEORY OF MOLECULAR RELAXATION. I. VIBRATIONAL RELAXATION AND DEPHASING IN CONDENSED PHASES

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The cumulant expansion is used to derive two formally different master equations for a two-level molecular system interacting with a bath, starting with the Liouville equation and using two different time ordering prescriptions. The two master equations reduce to the same form in the markovian limit for the bath (where its correlation time is much shorter than the relaxation process). In the non-markovian case, however, they are very different although they contain the same correlation functions of the bath. A detailed comparison is made between the predictions of the two approaches which enables us to understand their range of validity and limitations. We apply the formalism to the vibrational relaxation and dephasing of a molecular impurity in a solid matrix and obtain a closed expression for the vibrational line shape which goes smoothly from the markovian to the static limit (corresponding to homogeneous and inhomogeneous broadening, respectively). In contrast to the simple stochastic approaches we predict that the line shape in the non-markovian limit contains information regarding the interactions of each level separately with the bath. The difference between the interactions of the two levels with the bath (i.e., frequency modulation) causes a symmetrically broadened line. However, the fluctuations in the mean interaction energy of the two-level system with the bath, if correlated with the frequency modulation, result in an asymmetric line. The formalism has a direct impact for other related relaxation phenomena (dephasing and relaxation in liquids, exciton line shapes and intramolecular dephasing).

### 1. Introduction

Recent studies of vibrational relaxation and dephasing processes of molecules in condensed phases [1–28]<sup>‡</sup> (liquid or solid) are yielding useful information regarding the interactions and dynamical behavior of these systems. The rates of energy relaxation (“ $T_1$ ” type processes) may be extremely slow (up to seconds in some cases) since the fast molecular vibrations are not coupled efficiently to the low frequency bath modes [1]. The direct dissipation of molecular vibrational energy to the medium may thus not be the major mechanism for the energy relaxation and radiative, vibration to rotation, intermolecular energy transfer and other mechanisms may dominate.

Measurements of spectral line shapes of these impurities (by direct infrared absorption, ordinary Raman techniques, coherent Raman, etc.) contain a different

kind of information regarding dephasing (“ $T_2$ ” type) processes [6,7]. A proper dephasing process is any kind of interaction which results in the broadening of a spectral line, which does not arise from changes of population ( $T_1$  processes). Dephasing processes in condensed phases are often very fast (picoseconds or less) as they do not involve the transfer of large amounts of energy to the bath [6].

The various theoretical approaches used in the treatment of vibrational relaxation and line broadening may be classified as dynamical [9–19,21–25,27] or stochastic [7,8,20,26] in nature. The dynamical approaches are usually based on binary collision models [9,18,19] and thus do not include many body effects. Another dynamical approach which was applied to vibrational relaxation in solid matrices [28] is based on the formalism of multiphonon processes [12–14,17] which uses the solvable properties of a bath of harmonic oscillators. Usually the dynamical approaches were used for the calculation of molecular relaxation processes in the markovian (impact) limit; i.e., the typical

<sup>‡</sup> For reviews on impurities see refs. [28]; for a recent review on relaxation in liquids see ref. [29].

correlation time of the bath  $\tau_c$  is assumed to be very fast compared to the inverse perturbation  $\nu^{-1}$  exerted by the bath on the molecular system. In this case the relaxation of an isolated molecular level is exponential in time and the line shape is a lorentzian. The only information derived from the line shapes in this case is the linewidth  $\Gamma$  which is given by  $\nu^2 \tau_c$ . In practice, the interesting dynamics of the molecular processes occurs at short times where the typical time evolution is much more complicated than a simple exponential. This information is contained in the line wings which are therefore not lorentzian [30]. Thus, more dynamical information may be extracted from non-lorentzian line shapes when the markovian approximation for the bath does not hold, provided a suitable theory is available. The stochastic approach of Kubo [31] and Anderson and Weiss [32] is very useful for the analysis of line shapes as it avoids the markovian assumption and is valid for an arbitrary time scale of the bath relative to the molecular system. However, the properties of the bath are given in terms of stochastic parameters whose exact microscopic interpretation is fraught with difficulties. Moreover, in the simplest form of these theories, the predicted  $T_1$  processes correspond to an infinite temperature of the bath. This is a typical case in magnetic resonance, to which the formalism was originally developed [33] but this is not the case when dealing with high frequency ( $2000 \text{ cm}^{-1}$ ) molecular vibrations.

In this paper we present a dynamical theory for vibrational relaxation and dephasing in condensed phases without invoking the markovian assumption. We start with the Liouville equation using a general hamiltonian of a two level system interacting with a bath. Making use of the cumulant expansion [34], we derive reduced equations of motion (a master equation) for the density matrix for the system, which contain the information regarding the  $T_1$  and  $T_2$  processes. For that purpose we make use of two different ordering prescriptions in the cumulant expansion which result in two different types of master equations (local or non-local in time [34,35]). The two master equations are both exact in principle (provided the appropriate operators are evaluated to infinite order). They also yield identical results in the markovian limit. However, in general, when one evaluates the various operators in an approximate way and the markovian assumption does not hold, they predict a very different relaxation

behavior of the molecular system, and, consequently a different line shape. This arises since different statistical assumptions regarding the bath are *implicitly* made in both cases.

In section 2 we present briefly the basic formal expressions which are used in the derivation of our two master equations. In section 3 we derive the master equations for a general hamiltonian of a two-level molecular system interacting with a bath. We obtain the equations of motion for the reduced system density matrix and closed expressions for the line shape in terms of correlation functions of the bath. Section 4 contains an analysis and comparison of the line shapes derived from the two master equations. We consider several limiting behaviors and discuss the range of validity of both approaches. This is done without specifying explicitly the bath correlation functions. In section 5 we evaluate the bath correlation function for an impurity diatomic molecule embedded in a matrix and discuss the resulting line shapes. Although the specific application in section 5 is done for a vibrational relaxation in a solid matrix, the general formalism of section 4 is directly applicable to many other relaxation problems such as dephasing and relaxation in the liquid phase, intramolecular dephasing [36,37], molecular multiphoton processes [38,39] and exciton line shapes [40].

## 2. The COP and the POP Master equations

We consider a molecule interacting with a bath. The total hamiltonian is

$$H = H_S(Q_S) + H_R(Q_R) + H'(Q_S, Q_R), \quad (1)$$

where  $H_S(Q_S)$ ,  $H_R(Q_R)$  are the hamiltonians for our molecule and the bath with coordinates  $Q_S$  and  $Q_R$ , respectively, whereas  $H'$  is their interaction. We are interested in system operators (i.e., operators which depend only on  $Q_S$ ). For convenience, let us consider explicitly the system density matrix defined by tracing the total density matrix  $\rho$  (of the system + the bath) over the bath variables

$$\sigma \equiv T_{\text{bath}} \rho. \quad (2)$$

The basic formulation applies, however, to any set of system operators which have a closed commutator algebra with the hamiltonian.

The Liouville equation for  $\rho$  is

$$\dot{\rho} = -iL\rho \equiv -i[H, \rho], \quad (3)$$

where  $L(L_S, L_R, L')$  is the Liouville operator (commutator) corresponding to  $H(H_S, H_R, H')$ . We thus have, using eq. (1)

$$L = L_S(Q_S) + L_R(Q_R) + L'(Q_S, Q_R) = L_0 + L'. \quad (4)$$

Since there is some degree of arbitrariness in the partitioning (4) into  $L_0$  and  $L'$ , let us choose  $L'$  such that

$$\hat{T}_{\text{bath}} L'(Q_S, Q_R) \rho_{\text{bath}}^0 \equiv \langle L' \rangle = 0, \quad (5)$$

where  $\rho_{\text{bath}}^0$  is the equilibrium density matrix of the bath and  $\langle \rangle$  comes for bath averaged quantities. The condition (5) can be always achieved without loss of generality by including  $\langle L' \rangle$  in  $L_S$  and subtracting it from  $L'$ . We further assume that at time  $t = 0$  the system and bath are uncorrelated, i.e.

$$\rho(0) = \sigma(0) \rho_{\text{bath}}(0). \quad (6)$$

The cumulant expansion [31,32,34] is a very useful method for deriving the reduced equations of motion for  $\sigma$ . Using this expansion we write

$$\sigma(t) = U(t, 0) \sigma(0), \quad (7)$$

where

$$U(t, 0) = \exp_p \int_0^t d\tau K(\tau). \quad (8)$$

Here  $U$  is the Liouville time evolution operator. Since  $U$  and  $K$  are both system operators, the exponent in eq. (8) is not completely defined unless we specify a time ordering prescription. The subscript  $P$  in eq. (8) denotes the appropriate ordering prescription. The ability to choose the ordering prescription in many ways gives us a large degree of flexibility in the reduction scheme. Although the exact treatment of  $U$  is independent on the ordering prescription, once we evaluate  $K$  using some approximate method, the choice of the prescription becomes crucial. We shall consider here two different choices [33,35]:

(i) COP (chronological ordering prescription). This is a fully time ordered prescription and it appears naturally when the reduction is carried out using Fano-Zwanzig projection operators [30,41,42]. The resulting equations of motion are

$$\begin{aligned} d\sigma/dt = & -iL_S\sigma + \int_0^t d\tau \exp(-iL_S t) \langle R(t, \tau) \rangle \\ & \times \exp(iL_S \tau) \sigma(\tau). \end{aligned} \quad (9)$$

Using our choice of  $\langle L' \rangle = 0$  (eq. (5)) we have the following expression for  $R$ :

$$\begin{aligned} \langle R(t, \tau_1) \rangle = & \theta_2(t, \tau_1) + \sum_{n=2}^{\infty} \int_0^{\tau_1} d\tau_2 \dots \\ & \dots \int_0^{\tau_{n-1}} d\tau_n \theta_{n+1}(t, \tau_1, \tau_2, \dots, \tau_n), \end{aligned} \quad (10)$$

where:

$$\begin{aligned} \theta_1 = 0, \quad \theta_2 = m_2, \quad \theta_3 = m_3, \\ \theta_4 = m_4 - m_2(t, \tau_1) m_2(\tau_2, \tau_3), \quad \dots, \end{aligned} \quad (11)$$

and

$$\begin{aligned} m_n(\tau_1, \dots, \tau_n) = & (-i)^n \text{Tr}_{\text{bath}} \rho_{\text{b}}^0 \tilde{L}'(\tau_1) \tilde{L}'(\tau_2) \dots \tilde{L}'(\tau_n) \\ \equiv & (-i)^n \langle \tilde{L}'(\tau_1) \tilde{L}'(\tau_2) \dots \tilde{L}'(\tau_n) \rangle, \end{aligned} \quad (12)$$

and

$$\tilde{L}'(\tau) = \exp(iL_0 \tau) L' \exp(-iL_0 \tau). \quad (13)$$

To second order in the COP cumulant expansion, we set  $\theta_n = 0$  for  $n \geq 3$ , and we get:

$$d\sigma/dt = -iL_S\sigma - \int_0^t d\tau W(t-\tau) \sigma(\tau), \quad (14)$$

where

$$W(t-\tau) = \langle L'(t-\tau) \exp[-iL_S(t-\tau)] L'(0) \rangle \quad (14a)$$

and

$$L'(t) = \exp(iL_R t) L' \exp(-iL_R t). \quad (14b)$$

(ii) POP (partial ordering prescription). Here the reduced equations for  $\sigma$  assume the form:

$$d\sigma/dt = -iL_S\sigma + \exp(-iL_S t) \langle \Phi(t) \rangle \exp(iL_S t) \sigma, \quad (15)$$

where

$$\langle \Phi(t) \rangle = \sum_{n=1}^{\infty} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \dots \int_0^{\tau_{n-1}} d\tau_n \Phi_{n+1}(t, \tau_1, \dots, \tau_n), \quad (16)$$

and

$$\Phi_1 = 0,$$

$$\Phi_2 = m_2(t, \tau_1),$$

$$\Phi_3 = m_3(t, \tau_1, \tau_2),$$

$$\Phi_4(t, \tau_1, \tau_2, \tau_3) = m_4(t, \tau_1, \tau_2, \tau_3) - m_2(t, \tau_1) m_2(\tau_2, \tau_3) \quad (17)$$

$$- m_2(t, \tau_2) m_2(\tau_1, \tau_3) - m_2(t, \tau_3) m_2(\tau_1, \tau_2),$$

⋮

To second order POP cumulant expansion, we set  $\phi_n = 0$  for  $n \geq 3$  and we get

$$d\sigma/dt = -iL_S \sigma - \left( \int_0^t d\tau \Omega(t-\tau) \right) \sigma, \quad (18)$$

where

$$\Omega(t-\tau) = W(t-\tau) \exp[iL_S(t-\tau)]. \quad (18a)$$

Eqs. (14) and (18) are the basic expressions which will be used throughout the present work.

### 3. Application to the relaxation, dephasing and line shapes of impurity molecules in condensed phases

We consider an impurity diatomic molecule embedded in a dense medium (either liquid or a solid matrix). We further assume that our relaxation problem is fully specified in terms of two molecular levels hereafter denoted by  $|a\rangle$  (the ground state) and  $|b\rangle$  (an excited vibrational state). The most general hamiltonian for the molecule and the bath has thus the form (1) where

$$H_S(Q_S) = |a\rangle E_a \langle a| + |b\rangle E_b \langle b|, \quad (19a)$$

$$H'(Q_S, Q_R) = |b\rangle F(Q_R) \langle a| + |a\rangle F^\dagger(Q_R) \langle b| + |a\rangle G_a(Q_R) \langle a| + |b\rangle G_b(Q_R) \langle b|, \quad (19b)$$

and  $H_R(Q_R)$  is the bath hamiltonian. The bath operators  $F, F^\dagger, G_a, G_b$  are obtained by taking the appropriate system matrix elements of  $H'(Q_S, Q_R)$ . Hereafter we shall use a real representation so that  $F = F^\dagger$ . In this hamiltonian the  $F$  operator causes level attenuation ( $T_1$  processes) whereas  $G$  cause proper dephasing (broadening without relaxation). We shall now rearrange  $H'$  to the form:

$$H'(Q_S, Q_R) = F(Q_R) (|a\rangle \langle b| + |b\rangle \langle a|) + G_+(Q_R) (|a\rangle \langle a| + |b\rangle \langle b|) + G_-(Q_R) (|a\rangle \langle a| - |b\rangle \langle b|), \quad (20)$$

where

$$G_+ = \frac{1}{2}(G_a + G_b), \quad G_- = \frac{1}{2}(G_a - G_b). \quad (20a)$$

Here  $G_+$  represents the mean interaction of the two-level system with the bath, whereas  $G_-$  represents fluctuations of the two-level frequency,  $\omega_{ba} = E_b - E_a$ , due to the interaction with the bath. We note that  $G_+$  is a unit operator in the system subspace and is thus a pure bath operator. Formally we could thus include  $G_+$  in  $H_R$  and get  $G_+ = 0$  in eq. (20). This, however, may complicate  $H_R$  and make the explicit evaluation of the required correlation functions extremely difficult. In the impurity problem considered in section 6, for example,  $H_R$  is the harmonic lattice hamiltonian and it may be easily treated exactly.  $H_R + G_+$  is, however, no longer harmonic and the simplicity of the model is lost if  $G_+$  is incorporated in  $H_R$ . On the other hand, for a binary collision model it may be possible to include  $G_+$  in  $H_R$  with no major complication. The present formulation with the partitioning (20) thus enables us to adopt a zero order pure-bath hamiltonian ( $H_R$ ) which is treated exactly and treat  $G_+$  as well as  $G_-$  to any desired order.

After specifying the hamiltonian, we can now derive the master equations using the POP and COP. This is done in appendix A. The molecular density matrix  $\sigma$  has four components ( $\sigma_{aa}, \sigma_{bb}, \sigma_{ab}$  and  $\sigma_{ba}$ ) and thus the relaxation operators  $W$  and  $\Omega$  [eqs. (14) and (18)] are  $4 \times 4$  matrices. The resulting expressions for  $W$  and  $\Omega$  are given in terms of the two-time corre-

lation functions for the bath operators  $F$  and  $G$  defined as

$$\begin{aligned} \langle A(\tau) B(0) \rangle &\equiv \sum_{\alpha, \beta} \rho(\alpha) A_{\alpha\beta}(\tau) B_{\beta\alpha}(0) \\ &= \sum_{\alpha, \beta} \rho(\alpha) A_{\alpha\beta}(0) B_{\beta\alpha}(0) \exp(i\omega_{\alpha\beta}\tau), \end{aligned} \quad (21)$$

where  $A$  and  $B$  are two bath operators,  $\alpha$  and  $\beta$  are exact eigenstates of  $H_R$  and  $\omega_{\alpha\beta} = (E_\alpha - E_\beta)/\hbar$ .  $\rho(\alpha)$  is the equilibrium population of  $(\alpha)$ . We thus have, for the  $T_1$  part of  $W$ :

$$W_{bb,aa}(\tau) = -[e^{i\omega_{ab}\tau} \langle F(\tau) F(0) \rangle + \text{c.c.}], \quad (22a)$$

$$W_{aa,bb}(\tau) = -[e^{-i\omega_{ab}\tau} \langle F(\tau) F(0) \rangle + \text{c.c.}], \quad (22b)$$

$$W_{aa,aa}(\tau) = -W_{bb,aa}(\tau), \quad (22c)$$

$$W_{bb,bb}(\tau) = -W_{aa,bb}(\tau). \quad (22d)$$

The  $T_2$  part of  $W$  is:

$$\begin{aligned} W_{ab,ab}(\tau) &= 2e^{-i\omega_{ab}\tau} \{[\langle G_-(\tau) G_-(0) \rangle + \text{c.c.}] \\ &\quad + [\langle G_-(\tau) G_+(\tau) \rangle - \text{c.c.}] + [\langle F(\tau) F(0) \rangle + \text{c.c.}], \end{aligned} \quad (22e)$$

$$W_{ba,ba}(\tau) = W_{ab,ab}^*(\tau). \quad (22f)$$

Here  $\omega_{ab} = (E_a - E_b)/\hbar$ . All the other elements of  $W$  vanish. In the derivation of eq. (22), we have assumed that the  $F$  and  $G$  operators are uncorrelated, i.e.,  $\langle FG \rangle = \langle GF \rangle = 0$ . The  $\Omega$  matrix corresponding to the POP relaxation formalism may be now easily evaluated. Using eq. (18a), we have:

$$\Omega_{ab,ab}(\tau) = W_{ab,ab}(\tau) e^{i\omega_{ab}\tau}, \quad (23a)$$

$$\Omega_{ba,ba}(\tau) = W_{ba,ba}(\tau) e^{-i\omega_{ab}\tau}, \quad (23b)$$

$$\Omega_{ij,kl} = W_{ij,kl}, \quad \text{else.} \quad (23c)$$

We are now in a position to evaluate the absorption line shape for the system. The general expression for the absorption line shape is [43]:

$$I(\omega) \propto \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \mu(t) \mu(0) \rangle, \quad (24)$$

where  $\omega$  is the photon frequency,  $\mu$  is the system dipole operator and  $\langle \quad \rangle$  denotes a total trace over the

system and bath. Since typically in vibrational relaxation experiments  $\omega_{ba} \gg kT$  we have

$$\begin{aligned} \langle \mu(t) \mu(0) \rangle &= \langle \mu_{ab}(t) \mu_{ba}(0) \rangle \\ &= \langle \mu_{ab}(t) \rangle \mu_{ba}(0) = \sigma_{ba}(t) |\mu_{ab}(0)|^2, \end{aligned} \quad (25)$$

where we use the fact that  $\mu_{ba}(0)$  is independent on the bath and thus commutes with the trace over the bath. We thus have, using (24) and (25):

$$I(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \sigma_{ba}(t) = 2\text{Re} \int_0^{\infty} dt e^{i\omega t} \sigma_{ba}(t), \quad (26)$$

where  $\sigma_{ba}(t)$  is the solution of our reduced equations of motion [eqs. (14) or (18)] with the initial conditions  $\sigma_{ba}(0) = 1$ .

Making use of eqs. (14), (18), (22) and (23), we have, using the COP master equation,

$$\begin{aligned} \frac{d\sigma_{ba}(t)}{dt} &= -i\omega_{ba} \sigma_{ba}(t) - \int_0^t d\tau A(t-\tau) \\ &\quad \times \exp[-i\omega_{ba}(t-\tau)] \sigma_{ba}(\tau), \end{aligned} \quad (28a)$$

whereas, when using the POP master equation

$$\frac{d\sigma_{ba}(t)}{dt} = -i\omega_{ba} \sigma_{ba}(t) - \left( \int_0^t d\tau A(\tau) \right) \sigma_{ba}(t). \quad (28b)$$

Here

$$\begin{aligned} A(\tau) &= \Omega_{ba,ba}(\tau) \\ &= 2[\langle G_-(\tau) G_-(0) \rangle + \text{c.c.}] + 2[\langle G_-(\tau) G_+(\tau) \rangle - \text{c.c.}] \\ &\quad + e^{i\omega_{ba}\tau} [\langle F(\tau) F(0) \rangle + \text{c.c.}]. \end{aligned} \quad (29)$$

Eq. (28a) can be solved by a Laplace transformation. The general solution is then represented in the form

$$\sigma_{ba}^{\text{COP}}(t) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} dE e^{-iEt} \frac{1}{E - \omega_{ba} + iA(E)}, \quad (30)$$

where

$$A(E) = \int_0^{\infty} d\tau \exp[-i(E - \omega_{ba})\tau] A(\tau). \quad (30a)$$

Eq. (28b) can be solved directly

$$\sigma_{ba}^{\text{POP}}(t) = e^{-i\omega_{ba}t} \exp\left(-\int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 A(\tau_2)\right). \quad (31)$$

Substitution of eqs. (30) and (31) in eq. (26) results in our final expressions for the line shape:

$$I^{\text{COP}}(\omega) = 2\text{Im} \frac{1}{\omega - \omega_{ba} + i \int_0^\infty d\tau \exp[i(\omega - \omega_{ba})\tau] A(\tau)}, \quad (32)$$

and

$$I^{\text{POP}}(\omega) = 2 \text{Re} \int_0^\infty dt \exp[i(\omega - \omega_{ba})t] \times \exp\left(-\int_0^t d\tau (t-\tau) A(\tau)\right), \quad (33)$$

where we have used the relation:

$$\int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 A(\tau_2) = \int_0^t d\tau (t-\tau) A(\tau). \quad (34)$$

#### 4. General analysis of the line shapes

Eqs. (32) and (33) constitute our general expressions for the COP and POP line shapes. The two expressions are in principle identical provided we use the formulation of section 2 to make a complete (infinite order) cumulant expansion for  $A(t)$ , and in general  $A^{\text{COP}} \neq A^{\text{POP}}$ . However, when we use our second order expression for  $A(t)$  (eq. (29)), then eqs. (32) and (33) are no longer identical. Thus, although we are using the same information regarding the bath in both expressions (i.e.,  $A(\tau)$ ), we end up with a very different expression for the line shape. The reason is that by using the COP expression to second order, we assume  $\theta_n = 0$  for  $n \geq 3$  (eq. (11)), whereas when using the POP expression to second order, we assume  $\Phi_n = 0$  for  $n \geq 3$  (eq. (17)). Thus, by choosing the ordering in a truncated cumulant expansion, we are *implicitly* assuming different statistical properties of the bath.

In this section we shall compare and analyze the behavior of eqs. (32) and (33) under several limiting conditions.

#### 4.1. The markovian limit

Let us first consider the markovian (impact) limit. For that purpose we write

$$A(\tau) = v^2 \phi(\tau), \quad (35)$$

where  $\phi(0) = 1$ , and  $\phi(\tau)$  decays to zero with a characteristic time scale  $\tau_c$ .  $v$  is a measure of the interaction strength between the system and the bath, whereas  $\tau_c$  is its correlation time. In the markovian limit we assume  $v\tau_c \ll 1$ . Considering the POP line shape (33), we have

$$\exp\left(-\int_0^t (t-\tau) A(\tau) d\tau\right) \simeq \exp\left(-t \int_0^\infty A(\tau) d\tau\right). \quad (36)$$

Eq. (36) is valid on a coarse grained time scale  $v^{-1} \gg t \gg \tau_c$ . Substitution of (36) in (33) results in

$$I^{\text{POP}}(\omega) = 2 \text{Im} \frac{1}{\omega - \omega_{ba} + i \int_0^\infty d\tau A(\tau)}. \quad (37)$$

Turning now to the COP line shape, let us assume that since  $\tau_c$  is very short, then in the integral in eq. (32) we can write

$$\exp[i(\omega - \omega_{ba})t] \approx 1. \quad (38)$$

This assumes that for the relevant  $\omega$  range

$$(\omega - \omega_{ba})\tau_c \ll 1. \quad (39)$$

Substitution of (38) in (32) results in

$$I^{\text{COP}}(\omega) = I^{\text{POP}}(\omega) = 2 \text{Im} \frac{1}{\omega - \omega_{ba} + i \int_0^\infty d\tau A(\tau)}, \quad (40)$$

since  $|\int_0^\infty d\tau A(\tau)| \approx v^2\tau_c$ , then the relevant  $\omega - \omega_{ba}$  range is  $v^2\tau_c$ , thus condition (39) implies  $v^2\tau_c^2 \ll 1$ , which by assumption holds in the markovian limit. This provides a consistency check for our approximations.

In conclusion, we have shown that when  $v\tau_c \ll 1$ , the COP and POP line shapes are identical and assume a lorentzian form:

$$I(\omega) = \frac{\Gamma}{(\omega - \omega_{ba} - \Delta)^2 + \frac{1}{4}\Gamma^2}, \quad (41)$$

where

$$i\Delta + \frac{1}{2}\Gamma = \int_0^\infty d\tau A(\tau). \quad (42)$$

This result is expected, as in this limit, both reduced equations of motion (28a) and (28b) assume the form:

$$\dot{\sigma}_{ba} = -i(\omega_{ba} + \Delta) \sigma_{ba} - \frac{1}{2} \Gamma \sigma_{ba}. \quad (43)$$

#### 4.2. The line wings

The behavior on the line wings is determined by the short time behavior of  $A(\tau)$ . Thus the analysis of the line wings contains extremely valuable dynamical information regarding the system-bath interaction.

In general at very short times we have

$$\begin{aligned} & \exp\left(-\int_0^t d\tau A(\tau) d\tau (t-\tau)\right) \\ &= \exp\left(-A(0) \int_0^t d\tau (t-\tau)\right) = \exp\left[-\frac{1}{2} A(0) t^2\right]. \end{aligned} \quad (44)$$

Thus, the POP line shape (33) assumes a gaussian form:

$$I^{\text{POP}}(\omega) = \frac{1}{2} [2\pi/A(0)]^{1/2} \exp[-(\omega - \omega_{ba})^2 / 2A(0)]. \quad (45)$$

On the other hand, the COP line shape behaves in the wings as

$$I^{\text{COP}}(\omega) \simeq 2 \operatorname{Im} \frac{\int_0^\infty d\tau A(\tau) \exp[i(\omega - \omega_{ba})\tau]}{(\omega - \omega_{ba})^2}, \quad (46)$$

which need not be a gaussian, but rather depends on the form of  $A(\tau)$ .

#### 4.3. An example: exponential correlation function

For the sake of illustration, let us assume that the bath correlation function  $A(\tau)$  is exponential [31]:

$$A(\tau) = v^2 \exp(-\gamma\tau), \quad (47)$$

where  $\gamma = 1/\tau_c$ . Substitution of eq. (47) in eqs. (32) and (33) results in:

$$\begin{aligned} I^{\text{COP}}(\omega) &= \gamma v^2 / [(\omega - \omega_{ba} - v)^2 (\omega - \omega_{ba} + v)^2 \\ &+ \gamma^2 (\omega - \omega_{ba})^2], \end{aligned} \quad (48)$$

and

$$\begin{aligned} I^{\text{POP}}(\omega) &= 2 \operatorname{Re} \int_0^\infty d\tau \exp[i(\omega - \omega_{ba})\tau] \\ &\times \exp[-v^2 \gamma^{-2} (e^{-\gamma\tau} - 1 + \gamma\tau)]. \end{aligned} \quad (49)$$

Eq. (48) corresponds to the two-state jump model [31] and the line shape is changing from two distinct lines when  $v \gg \gamma$  to a single Lorentz line in the markovian (narrowing) limit ( $v \ll \gamma$ ). Eq. (49), on the other hand, corresponds to a system whose frequency undergoes a stationary gaussian process [31]. The line shape changes from a gaussian when  $v \gg \gamma$  to a narrow lorentzian in the other extreme.

This example demonstrates that the POP expression for the line shape which is a renormalized version of the COP takes care naturally for the effects of many perturbing levels and may thus be more suitable for relaxations in condensed phases.

#### 4.4. Asymmetry of the broadened line

From eqs. (32) and (33) it is clear that when  $A(\tau)$  is real, the line shape will be symmetric around  $\omega_{ba}$ , i.e.,

$$I(\omega_{ba} + \epsilon) = I(\omega_{ba} - \epsilon). \quad (50)$$

In this case we get

$$\begin{aligned} I^{\text{POP}}(\omega) &= 2 \int_0^\infty dt \cos(\omega - \omega_{ba}) t \\ &\times \exp\left(-\int_0^t d\tau (t-\tau) A(\tau)\right), \end{aligned} \quad (51)$$

and

$$I^{\text{COP}}(\omega) = \frac{\Gamma}{(\omega - \omega_{ba} - \Delta)^2 + \frac{1}{4} \Gamma^2}, \quad (52)$$

where

$$\Gamma(\omega - \omega_{ba}) = 2 \int_0^\infty d\tau A(\tau) \cos(\omega - \omega_{ba})\tau \quad (52a)$$

and

$$\Delta(\omega - \omega_{ba}) = \int_0^\infty d\tau \sin(\omega - \omega_{ba})\tau A(\tau). \quad (52b)$$

It is thus clear that when we adopt a classical treatment of the bath and consider  $F$  and  $G_{\pm}$  to be classical real functions of  $Q_R(t)$ , then the line shape will be symmetric.

#### 4.5. The role of $G_+$ and $G_-$

Let us consider now several limiting cases for  $G_+$  and  $G_-$ .

(i)  $G_- = 0$

In this case  $A(\tau) = 0$ , there will be no broadening of the line and it will be a  $\delta$  function of  $\omega$ . The reason for that is that  $G_-$  represents fluctuations in the two level frequency  $\omega_{ba}$ , whereas  $G_+$  represents fluctuations of the mean energy  $\bar{E}$  of the two level system  $\bar{E} = \frac{1}{2}(E_a + E_b)$ , due to the interactions with the bath. Fluctuations in  $\bar{E}$  alone cannot induce any broadening

(ii)  $\langle G_+ G_- \rangle = \langle G_- G_+ \rangle = 0$ , whereas  $G_- \neq 0$

This can happen if  $G_+ = 0$  or  $G_+$  is finite but *uncorrelated* with  $G_-$ . In this case  $A(\tau)$  (eq. (29)) is real and the line shape is symmetric (eq. (50)). We thus see that the asymmetry of the line within the second order cumulant expansion is caused by the correlations between the fluctuations in  $\bar{E}$  and in  $\omega_{ba}$ . Thus, although the fluctuations ( $G_+$ ) in  $\bar{E}$  cannot cause any broadening, they do modify the broadening caused by the fluctuation ( $G_-$ ) in  $\omega_{ba}$  and make the line asymmetric. Thus, analysis of line shapes in the non-markovian limit may give us information about the interaction of *each level* with the bath and not only about the difference in their interaction with the bath (i.e.,  $G_-$ ), as is implied by the simple stochastic approaches (7), (31).

(iii)  $G_+ = -G_-$

In this case  $G_a = 0$ , which implies that the bath is interacting only with the excited level. We thus have  $A(\tau) = 4 \langle G_-(-\tau) G_-(0) \rangle = \langle G_b(-\tau) G_b(0) \rangle$ . (53)

The COP line shape has an interesting symmetry in this case. Let us consider the line width functions  $\Gamma$ .

$$\begin{aligned} \Gamma(\omega - \omega_{ba}) &\equiv 2 \operatorname{Re} \int_0^{\infty} d\tau \exp[i(\omega - \omega_{ba})\tau] A(\tau) \\ &= 4 \operatorname{Re} \int_0^{\infty} d\tau \exp[i(\omega - \omega_{ba})\tau] \\ &\quad \times \{ \langle G_-(\tau) G_-(0) \rangle + \text{c.c.} \} + \{ \langle G_-(\tau) G_+(0) \rangle - \text{c.c.} \} \\ &\quad + 2 \operatorname{Re} \int_0^{\infty} d\tau e^{i\omega\tau} \{ \langle F(\tau) F(0) \rangle + \text{c.c.} \}. \end{aligned} \quad (54)$$

We can now make use of the general relations

$$A(-\tau) = A^*(\tau), \quad (55)$$

$$\operatorname{Re} \int_0^{\infty} d\tau e^{i\epsilon\tau} A(\tau) = \frac{1}{2} \int_{-\infty}^{\infty} d\tau e^{i\epsilon\tau} A(\tau) \quad (56)$$

and

$$\begin{aligned} &\int_{-\infty}^{\infty} d\epsilon e^{i\epsilon\tau} \langle A(\tau) B(0) \rangle \\ &= e^{-\beta\epsilon} \int_{-\infty}^{\infty} d\epsilon e^{i\epsilon\tau} \langle A(-\tau) B(0) \rangle, \end{aligned} \quad (57)$$

which states that it is  $\exp(-\beta\epsilon)$  times harder to take an energy  $\epsilon$  from the bath than to give it to the bath. (Here  $\beta = 1/kT$ .)

We further define

$$J_{\alpha\beta}(\epsilon) = 4 \int_{-\infty}^{\infty} d\tau e^{i\epsilon\tau} \langle G_{\alpha}(\tau) G_{\beta}(0) \rangle, \quad (58a)$$

where  $\alpha, \beta = +, -$

$$J_F(\epsilon) = 2 \int_{-\infty}^{\infty} d\tau e^{i\epsilon\tau} \langle F(\tau) F(0) \rangle. \quad (58b)$$

For  $\epsilon > 0$  we then have, making use of eqs. (54)–(58)

$$\begin{aligned} \Gamma(\epsilon) &= (1 + e^{-\beta\epsilon}) J_{--}(\epsilon) + J_{-+}(\epsilon) e^{-\beta\epsilon} \\ &\quad - J_{-+}(\epsilon) + J_F(\epsilon), \end{aligned} \quad (59)$$

$$\begin{aligned} \Gamma(-\epsilon) &= (1 + e^{-\beta\epsilon}) J_{--}(\epsilon) + J_{-+}(\epsilon) \\ &\quad - J_{-+}(\epsilon) e^{-\beta\epsilon} + J_F(\epsilon). \end{aligned} \quad (60)$$

When  $G_+ = -G_-$  we have  $J_{++} = J_{--} = J$ ,  $J_{+-} = J_{-+} = -J$ , and we get

$$\begin{aligned} \Gamma(-\epsilon) &= 2J e^{-\beta\epsilon} + J_F(\epsilon), \\ \Gamma(\epsilon) &= 2J + J_F(\epsilon). \end{aligned} \quad (61)$$

If we ignore  $J_F$  and consider only the  $T_2$  contribution to the width, we have the appealing relation

$$\Gamma(-\epsilon) = e^{-\beta\epsilon} \Gamma(\epsilon). \quad (62)$$

Thus, perturbations on the excited state result in an asymmetric level width function. Relation (62) does not hold, however, when  $G_a \neq 0$ . In fact, when  $G_+ = G_-$  ( $G_b = 0$ ), we get



$$\Gamma(\epsilon) = e^{-\beta\epsilon} \Gamma(-\epsilon). \quad (63)$$

This seems unreasonable at first sight as it implies larger line shape for smaller frequencies (i.e., giving energy to the bath is less likely than taking). However, let us consider the level shift due to the interaction with the bath.  $G_a$  tends to decrease  $\omega_{ba}$  whereas  $G_b$  tends to increase it. Thus  $G_a$  can favor the less likely absorption process, as the frequency of the two level system "dressed" by the bath becomes smaller than the original  $\omega_{ba}$ .

### 5. Vibrational line shape for a diatomic molecule in a solid matrix

We consider a diatomic impurity embedded in a rare gas matrix. We assume that  $T_1 \gg T_2$ ; i.e., the vibrational dephasing rate is much faster than the lifetime. This is the typical case in such experiments as the vibrational relaxation involves a very high order multiphonon or vibration rotation energy transfer which is usually extremely slow [1]. We thus consider in the interaction hamiltonian (20) only the  $G$  terms and ignore the contribution of  $F$  to the broadening. We further assume [12–15]:

$$\tilde{G}(\mathbf{Q}_R) = \sum_{j=1}^J a_j \exp(-\alpha_j x_j). \quad (64)$$

The tilde on  $G$  signifies that the thermal average  $\langle \tilde{G} \rangle \neq 0$ .  $G$  is given by

$$G = \tilde{G} - \langle \tilde{G} \rangle. \quad (64a)$$

Here,  $a_j$  are constant coefficients,  $\alpha_j$  denote the inverse range of the guest–lattice interaction potential while  $X_j$  is the separation between the  $j$ th (nearest neighbor) lattice atom and the center of mass of the impurity. We further define  $X_j = X_j^0 + x_j$ , where  $X_j^0$  is the equilibrium atom–impurity separation. We now expand  $x_j$  in terms of the (dimensionless) lattice normal modes

$$X_j = \sum_{\nu} q_{\nu} \beta_{\nu j}. \quad (65)$$

We thus have

$$\tilde{G}(\mathbf{q}) = \sum_j a_j \exp(-\alpha_j X_j^0) \exp\left(-\sum_{\nu} q_{\nu} \beta_{\nu j} \alpha_j\right). \quad (66)$$

Assuming that  $a_j$  and  $\alpha_j, \beta_j$  are independent on  $j$  and defining the phonon coupling parameters

$$\Delta_{\nu} = \beta_{\nu j} \alpha_j$$

we finally get

$$\tilde{G}(\mathbf{q}) = C \exp\left(-\sum_{\nu} \Delta_{\nu} q_{\nu}\right), \quad (67)$$

where

$$C \approx Z a \exp(-\alpha X_j^0), \quad (68)$$

$Z$  being the number of nearest neighbors to the impurity. The interaction parameters  $\Delta_{\nu}$  and  $C$  may depend on the state of the impurity ( $|a\rangle$  or  $|b\rangle$ ). We thus write:

$$\tilde{G}_{\alpha} = C_{\alpha} \exp\left(-\sum_{\nu} \Delta_{\nu\alpha} q_{\nu}\right), \quad (69)$$

where  $\alpha, \beta = +, -$ . Eq. (69) can be factorized in the form

$$\tilde{G}_{\alpha} = C_{\alpha} \prod_{\nu} G_{\alpha\nu}, \quad (70)$$

$$G_{\alpha\nu} = \exp(-\Delta_{\nu\alpha} q_{\nu}) \quad (70a)$$

which results in

$$\langle \tilde{G}_{\alpha}(t) \tilde{G}_{\beta}(0) \rangle = C_{\alpha} C_{\beta} \prod_{\nu} f_{\nu}^{\alpha\beta}(t), \quad (71)$$

$$f_{\nu}^{\alpha\beta}(t) = \langle G_{\alpha\nu}(t) G_{\beta\nu}(0) \rangle. \quad (71a)$$

The evaluation of the correlation function (71) is then reduced to the calculation of the single oscillator generating functions  $f_{\nu}^{\alpha\beta}(t)$  (eq. (71a)).

We now make use of the following thermal average for a harmonic oscillator [28,12–14,44]

$$\begin{aligned} \langle \exp[-\Delta_{\nu\alpha} q_{\nu}(t)] \exp[-\Delta_{\nu\beta} q_{\nu}(0)] \rangle \\ = \exp\left[\frac{1}{4}(2\bar{n}_{\nu} + 1)(\Delta_{\nu\alpha}^2 + \Delta_{\nu\beta}^2)\right] \\ \times \exp[\Delta_{\nu\alpha} \Delta_{\nu\beta} \langle q_{\nu}(t) q_{\nu}(0) \rangle], \end{aligned} \quad (72)$$

where

$$\langle q_{\nu}(t) q_{\nu}(0) \rangle = \frac{1}{2} [(\bar{n}_{\nu} + 1) e^{-i\omega_{\nu} t} + \bar{n}_{\nu} e^{i\omega_{\nu} t}], \quad (73)$$

$\omega_{\nu}$  is the frequency of the  $\nu$ th oscillator and  $\bar{n}_{\nu}$  is the mean occupation number of the  $\nu$ th mode

$$\bar{n}_{\nu} = [\exp(\hbar\omega_{\nu}/kT) - 1]^{-1}. \quad (74)$$

Using eqs. (70)–(72) and (64a) we get:

$$\begin{aligned} \langle G_\alpha(t) G_\beta(0) \rangle &= \langle \tilde{G}_\alpha(t) \tilde{G}_\beta(0) \rangle - \langle \tilde{G}_\alpha(0) \rangle \langle \tilde{G}_\beta(0) \rangle \\ &= C_\alpha C_\beta \exp(K^{\alpha\beta}) \{ \exp[K_1^{\alpha\beta}(t) + K_2^{\alpha\beta}(t)] - 1 \}, \end{aligned} \quad (75)$$

where

$$K_1^{\alpha\beta}(t) = \frac{1}{2} \int_0^\infty d\omega [\bar{n}(\omega) + 1] e^{-i\omega t} g(\omega) \Delta_\alpha(\omega) \Delta_\beta(\omega), \quad (75a)$$

$$K_2^{\alpha\beta}(t) = \frac{1}{2} \int_0^\infty d\omega \bar{n}(\omega) e^{i\omega t} g(\omega) \Delta_\alpha(\omega) \Delta_\beta(\omega), \quad (75b)$$

$$\begin{aligned} K^{\alpha\beta} &= K_1^{\alpha\beta}(0) + K_2^{\beta\alpha}(0) \\ &= \frac{1}{4} \int_0^\infty d\omega [2\bar{n}(\omega) + 1] g(\omega) [\Delta_\alpha(\omega)^2 + \Delta_\beta(\omega)^2], \end{aligned} \quad (75c)$$

where we have made the substitution

$$\begin{aligned} \sum_{\nu} &\rightarrow \int d\omega g(\omega), \\ \Delta_\nu, \bar{n}_\nu &\rightarrow \Delta(\omega), \bar{n}(\omega), \end{aligned} \quad (76)$$

$g(\omega)$  being the density of modes in the lattice.

Eq. (75) can be recast in the form:

$$\langle G_\alpha(t) G_\beta(0) \rangle = C_\alpha C_\beta \exp(K^{\alpha\beta}) [\exp(\phi_1^{\alpha\beta} - i\phi_2^{\alpha\beta}) - 1], \quad (77)$$

where  $\phi_1$  and  $\phi_2$  are real,

$$\begin{aligned} \phi_1^{\alpha\beta}(t) &= \frac{1}{2} \int_0^\infty d\omega g(\omega) [2\bar{n}(\omega) + 1] \\ &\quad \times \Delta_\alpha(\omega) \Delta_\beta(\omega) \cos \omega t, \end{aligned} \quad (77a)$$

$$\phi_2^{\alpha\beta}(t) = \frac{1}{2} \int_0^\infty d\omega g(\omega) \sin \omega t \Delta_\alpha(\omega) \Delta_\beta(\omega). \quad (77b)$$

Substitution of (77) in eq. (29) results in our final expression for  $A(\tau)$ :

$$\begin{aligned} A(\tau) &= 2[\langle G_-(\tau) G_-(0) \rangle + \text{c.c.}] + 2[\langle G_-(\tau) G_+(0) \rangle - \text{c.c.}] \\ &= 4C_-^2 \exp(K^{--}) \{ \exp[\phi_1^{--}(\tau)] \cos[\phi_2^{--}(\tau)] - 1 \} \\ &\quad - 4iC_+C_- \exp(K^{+-}) \exp[\phi_1^{+-}(\tau)] \sin[\phi_2^{+-}(\tau)] \\ &\equiv A_R(\tau) - iA_I(\tau). \end{aligned} \quad (78)$$

We shall now make use of eq. (33) for the evaluation of the POP line shape. As was discussed in detail in section 4 and demonstrated in the example for the exponential correlation function, we expect the POP expression to be more suitable for the stimulation of broadening by many degrees of freedom as it gives in second order a result which requires an infinite order cumulant expansion if we were to use the COP [35]. Our most general expression for the line shape is given by eq. (33), where  $A(\tau)$  is given by eq. (78). Let us consider now several limiting cases.

### 5.1. Special relations between $G_+$ and $G_-$

The imaginary part of  $A$  ( $A_I$  in eq. (78)) represents the *correlation* between the interactions  $G_+$  and  $G_-$  (or between the interactions of the two levels  $G_a$  and  $G_b$  with the bath). This correlation occurs when the same lattice modes perturb the two levels and in our expression (78), it amounts to a correlation between  $\Delta_+$  and  $\Delta_-$ . When  $\Delta_+$  and  $\Delta_-$  are uncorrelated,  $A_I$  vanishes and the line becomes symmetric (eq. (51)). Another possibility is that  $G_+(t)$  will be proportional to  $G_-(t)$  ( $G_+(t) = \eta G_-(t)$ ) where  $\eta$  is time independent. This implies that the same force is acting on both levels but with a different strength [20]. In this case we have

$$\begin{aligned} A(\tau) &= 4C_-^2 \exp(K^{--}) \{ \exp[\phi_1^{--}(\tau)] \cos[\phi_2^{--}(\tau)] - 1 \\ &\quad - i\eta \exp[\phi_1^{--}(\tau)] \sin \phi_2^{--}(\tau) \}. \end{aligned} \quad (79)$$

### 5.2. The markovian and static limits

In the markovian limit  $\nu\tau_c \ll 1$  and the line becomes a lorentzian (eq. (41)) with a width (fwhm)

$$\Gamma = 2 \int_0^\infty d\tau A_R(\tau), \quad (80)$$

where  $A_R(\tau)$  is defined in eq. (78). In the other extreme (static) when  $\nu\tau_c \gg 1$ , the line becomes a gaussian (eq. (45)) with a width (fwhm)

$$\gamma = 2[2A(0)/\ln 2]^{1/2}, \quad (81)$$

where

$$A(0) = 2C_-^2 \exp(2K^{--}). \quad (81a)$$

We thus have

$$\gamma = 4C_- (\ln 2)^{-1/2} \exp(K^{--}). \quad (82)$$

### 5.3. The linearized coupling

In order to obtain simple manageable expressions for the line shape, let us now use the linearized coupling

$$G_\alpha = C_\alpha \sum_\nu \Delta_{\nu\alpha} q_\nu, \quad (83)$$

which amounts to expansion of eq. (69) to first order in  $\Delta_{\nu\alpha}$ . In this case we have

$$\begin{aligned} \langle G_\alpha(t) G_\beta(0) \rangle &= C_\alpha C_\beta [K_1^{\alpha\beta}(t) + K_2^{\alpha\beta}(t)] \\ &= C_\alpha C_\beta [\phi_1^{\alpha\beta}(t) - i\phi_2^{\alpha\beta}(t)] \end{aligned} \quad (84)$$

and

$$A(\tau) = 4C_-^2 \phi_1^{--}(\tau) - 4iC_+ C_- \phi_2^{+-}(\tau) \equiv A_R - iA_I. \quad (85)$$

The line shape (eq. (33)) thus assumes the form:

$$I(\omega) = 2 \operatorname{Re} \int_0^\infty dt \exp[i(\omega - \omega_{ba})t] \exp[-B(t)], \quad (86)$$

where

$$\begin{aligned} B(t) &= 2 \int_0^t d\tau (t-\tau) \int_0^\infty d\omega g(\omega) \\ &\quad \times \{C_-^2 [2\bar{n}(\omega) + 1] (\Delta^-)^2 \cos \omega\tau \\ &\quad - iC_+ C_- \Delta^+(\omega) \Delta^-(\omega) \sin \omega\tau\}, \end{aligned} \quad (86a)$$

or, after performing the integration over  $t$

$$\begin{aligned} B(t) &= 2 \int_0^\infty d\omega g(\omega) \\ &\quad \times \{C_-^2 [2\bar{n}(\omega) + 1] (\Delta^-)^2 (1 - \cos \omega t) / \omega^2 \\ &\quad - iC_+ C_- \Delta^+ \Delta^- (\omega t - \sin \omega t) / \omega^2\}. \end{aligned} \quad (86b)$$

### 5.4. High temperature limit and Debye spectrum of the lattice

In the high temperature limit we have

$$\bar{n} = kT/\hbar\omega \gg 1, \quad (87)$$

and  $B(t)$  assumes the form:

$$B(t) = \int_0^\infty d\omega g(\omega) C_-^2 \Delta_-^2 \frac{8kT}{\hbar\omega} \frac{\sin^2(\omega t/2)}{\omega^2}. \quad (88)$$

We now assume a Debye spectrum for the solid

$$g(\omega) = 3\omega^2/\omega_D^2, \quad 0 < \omega < \omega_D. \quad (89)$$

We further assume that all modes contribute equally to the relaxation which amounts to

$$(\Delta_-)^2 = \Delta^2 \omega_D/\omega, \quad (90)$$

where  $\Delta$  is  $\omega$  independent. (The  $\omega_D/\omega$  term is introduced since  $\Delta$  scales as  $\omega^{-1/2}$ .)

Substitution of (89) and (90) in (88) results in

$$B(t) = \frac{12 C_-^2 \Delta^2 kT}{\omega_D^2} t \int_0^{\omega_D t/2} dx \frac{\sin^2 x}{x^2}. \quad (91)$$

In the markovian limit we can extend the integration in (91) to infinity which gives  $\pi/2$ . Thus the line shape then becomes the lorentzian (41) with a width

$$\Gamma = 12\pi C_-^2 \Delta^2 kT/\omega_D^2. \quad (92)$$

In the other (static) limit we have

$$B(t) \approx (12 C_-^2 \Delta^2 kT/2\omega_D) t^2,$$

and the line becomes a gaussian (45) where:

$$A(0) = 12 C_-^2 \Delta^2 kT/2\omega_D. \quad (93)$$

## 6. Low temperature limit and Debye spectrum of the lattice

In the low temperature limit ( $kT \ll \hbar\omega$ ) we have

$$\bar{n} = \exp(-\hbar\omega/kT). \quad (94)$$

Assuming that  $\Delta_+ \simeq \Delta_-$ ,  $C_+ = C_- = C$  and making use of eqs. (89) and (90) we get

$$A(t) = \frac{6 C^2 \Delta^2}{\omega_D^2} \int_0^{\omega_D} d\omega (1 + 2 e^{-\hbar\omega/kT}) \omega e^{-i\omega t}. \quad (95)$$

The temperature independent part of eq. (95) behaves asymptotically as  $t \rightarrow \infty$  as  $1/t$ . This is unphysical and reflects the fact that the impurity is not coupled equally well to all modes of the lattice as implied by eq. (90).

Inclusion of a different  $\Delta(\omega)$  inside the integration will make  $A(t)$  vanish much more rapidly with time as is physically expected. This, however, requires a further knowledge of  $\Delta(\omega)$ . For the sake of the temperature dependence of the line shape we shall, however, consider only the second terms in (95), thus we have in the markovian limit a lorentzian line shape with width:

$$\Gamma = \Gamma_0 + \frac{24 C^2 \Delta^2}{\omega_D^2} i \int_0^\infty dt \int_0^{\omega_D} d\omega \omega e^{-\hbar\omega/kT} e^{-i\omega t}, \quad (96)$$

$$\Gamma = \Gamma_0 + \frac{24 C^2 \Delta^2}{\omega_D^2} kT [1 - \exp(-\hbar\omega_D/kT)]. \quad (97)$$

In the static limit, we obtain:

$$B(t) \simeq A(0) t^2,$$

$$A(0) = 6 C^2 \Delta^2 \left\{ \frac{1}{2} + 2(kT/\omega_D)^2 [1 - \exp(-\hbar\omega_D/kT)] - 2(kT/\omega_D) \exp(-\hbar\omega_D/kT) \right\}. \quad (98)$$

### 7. Einstein lattice in the markovian limit

When we neglect the  $\omega$  dispersion of  $\Delta(\omega)$ ,  $\bar{n}(\omega)$ , we can use an Einstein model for the lattice; i.e., we put  $g(\omega) = \delta(\omega - \omega_0)$ . In this case, the markovian line width will be

$$\Gamma = 4 C^2 e^K \int_{-\infty}^{\infty} d\tau \exp[K_1(\tau) + K_2(\tau)], \quad (99)$$

where

$$K_1(\tau) = \frac{1}{2} [\bar{n}(\omega_0) + 1] \Delta^2 \exp(-i\omega_0\tau),$$

$$K_2(\tau) = \frac{1}{2} \bar{n}(\omega_0) \Delta^2 \exp(i\omega_0\tau),$$

$$K = \frac{1}{2} [2\bar{n}(\omega_0) + 1] \Delta^2. \quad (100)$$

We can now follow the analysis of Jortner [14] which was done for vibrational relaxation ( $T_1$ ) and expand the exponent in (99).

$$\Gamma = \frac{8\pi C^2 e^K}{\omega_0} \sum_{P=0}^{\infty} \frac{[\bar{n}(\bar{n}+1)(\Delta^2/2)^2]^P}{(P!)^2}. \quad (101)$$

Making use of the definition of a modified Bessel function [45]

$$I_0(Z) = \sum_{L=0}^{\infty} \frac{(Z/2)^{2L}}{(L!)^2} \quad (102)$$

we have

$$\Gamma = \frac{8\pi C^2 e^K}{\omega_0} I_0(\Delta^2 [\bar{n}(\bar{n}+1)]^{1/2}). \quad (103)$$

This result is valid for all temperatures. In the low temperature limit we can use the first two terms in eq. (101) and get

$$\Gamma = \frac{8\pi C^2}{\omega_0} \{1 + \Delta^2/2 + e^{-\hbar\omega/kT} [\Delta^2 + (\Delta^2/2)^2]\}. \quad (104)$$

In the high temperature limit, we can use the asymptotic expansion of  $I_0(Z)$

$$I_0(Z) \rightarrow (2\pi Z)^{-1/2} e^Z, \quad (105)$$

and we get:

$$\begin{aligned} \Gamma &= \frac{8\pi C^2 e^K}{\omega_0} \{2\pi\Delta^2 [\bar{n}(\bar{n}+1)]^{1/2}\}^{-1/2} \\ &\quad \times \exp\{\Delta^2 [\bar{n}(\bar{n}+1)]^{1/2}\} \\ &= \frac{8\pi C^2 \exp[(2kT/\hbar\omega + 1)\Delta^2/2]}{\omega_0} \\ &\quad \times (\hbar\omega/2\pi\Delta^2 kT)^{1/2} \exp(\Delta^2 kT/\hbar\omega). \end{aligned} \quad (106)$$

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### Appendix A: Evaluation of the relaxation matrix

Let us write a general matrix element in the  $Q_s$  space of the Liouville equation (3) where each matrix element is still a Liouville operator in  $Q_R$ :

$$\dot{\rho}_{ij}(Q_R) = -i \sum_{kl} L_{ij,kl}(Q_R) \rho_{kl}(Q_R), \quad (A.1)$$

where [20]

$$L_{ij,kl} \equiv H_{ik} \delta_{jl} - H_{jl}^* \delta_{ik}, \quad (A.2)$$

and  $H$  is the total hamiltonian [eqs. (1) and (19)]. Defining a four-component vector  $\rho = (\rho_{aa}, \rho_{bb}, \rho_{ab}, \rho_{ba})$  we have

$$\dot{\rho}_{aa} = -i\hat{F}(\mathcal{Q}_R)[\rho_{ab} - \rho_{ba}], \quad (\text{A.3})$$

$$\dot{\rho}_{bb} = -i\hat{F}(\mathcal{Q}_R)[\rho_{ba} - \rho_{ab}],$$

$$\dot{\rho}_{ab} = -i\omega_0 \rho_{ab} - i\hat{F}(\mathcal{Q}_R)[\rho_{aa} - \rho_{bb}] - 2i\hat{G}(\mathcal{Q}_R)\rho_{ab},$$

$$\dot{\rho}_{ba} = i\omega_0 \rho_{ba} - i\hat{F}(\mathcal{Q}_R)[\rho_{bb} - \rho_{aa}] - 2i\hat{G}(\mathcal{Q}_R)\rho_{ba},$$

where  $\hat{F}$  and  $\hat{G}$  are the tetradic operators corresponding to  $F$  and  $G$ ,

$$\hat{F} \equiv [F(|a\rangle\langle b| - |b\rangle\langle a|), \quad ], \quad (\text{A.4a})$$

$$\hat{G} \equiv [G_a(|a\rangle\langle a| + G_b|b\rangle\langle b|), \quad ], \quad (\text{A.4b})$$

and

$$\omega_0 = \omega_b - \omega_a. \quad (\text{A.5})$$

We thus have

$$d\rho/dt = -iL_0\rho - iL'\rho, \quad (\text{A.6})$$

$$L_0 = L_R + L_S, \quad (\text{A.7})$$

$$L' = \begin{pmatrix} 0 & 0 & \hat{F}_{aa,ab} & \hat{F}_{aa,ba} \\ 0 & 0 & \hat{F}_{bb,ab} & \hat{F}_{bb,ba} \\ \hat{F}_{ab,aa} & \hat{F}_{ab,bb} & \hat{G}_{ab,ab} & 0 \\ \hat{F}_{ba,aa} & \hat{F}_{ba,bb} & 0 & \hat{G}_{ba,ba} \end{pmatrix}, \quad (\text{A.8})$$

$$L_S = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & \omega_0 & 0 \\ 0 & 0 & 0 & -\omega_0 \end{pmatrix}, \quad (\text{A.9})$$

and  $L_R$  is the bath Liouvillian.

We are now in a position to evaluate the relaxation matrix  $W$ . Making use of eqs. (14a) and (A6)–(A9)

$$W_{bb,aa}(\tau) = \sum_{\alpha,\beta} P(\alpha) [e^{-i\omega_{ab}\tau} \langle L'(\tau)^{\beta\beta,\alpha\beta} L'(0)^{\alpha\beta,\alpha\alpha} \rangle + e^{i\omega_{ab}\tau} \langle L'(\tau)^{\beta\beta,\beta\alpha} L'(0)^{\beta\alpha,\alpha\alpha} \rangle], \quad (\text{A.10})$$

where

$$L'_{ab,cd}{}^{\alpha\beta,\gamma\delta} \equiv \langle \alpha\alpha, \beta\beta | L' | c\gamma, d\delta \rangle, \quad (\text{A.11})$$

$\alpha, \beta$  are bath states (eigenstates of  $H_R$ ) whereas  $P(\alpha)$  is the equilibrium distribution of bath states, and we are using here the double bracket tetradic notation [30].

Making use of the general relation holding for any Liouville operator [30]:

$$L'_{ab,cd} = -L'_{ba,dc}^*, \quad (\text{A.12})$$

we see that the second term in the square brackets is just the complex conjugate of the first. Thus we get from eqs. (A7)–(A10)

$$W_{bb,aa} = - \sum_{\alpha,\beta} P(\alpha) F_{ba}^{\beta\alpha}(\tau) F_{ba}^{*\beta\alpha}(0) e^{-i\omega_{ab}\tau} + \text{c.c.}, \quad (\text{A.13})$$

where

$$F_{ab}^{\alpha\beta} \equiv \langle b\beta | F(|a\rangle\langle b| + |b\rangle\langle a|) | a\alpha \rangle. \quad (\text{A.14})$$

Since

$$F_{ba}^{\beta\alpha}(\tau) = F^{\alpha\beta}(-\tau) \quad (\text{A.15})$$

thus we can write

$$W_{bb,aa}(\tau) = - [e^{-i\omega_{ab}\tau} \langle F(-\tau) F(0) \rangle + \text{c.c.}]. \quad (\text{A.16})$$

Similarly,

$$W_{aa,bb}(\tau) = - [e^{-i\omega_{ab}\tau} \langle F(\tau) F(0) \rangle + \text{c.c.}], \quad (\text{A.17})$$

where we define the two-time correlation functions of two bath operators as:

$$\begin{aligned} \langle A(\tau) B(0) \rangle &\equiv \sum_{\alpha,\beta} P(\alpha) A_{\alpha\beta}(\tau) B_{\beta\alpha}(0) \\ &= \sum_{\alpha,\beta} P(\alpha) A_{\alpha\beta} B_{\beta\alpha} e^{-i\omega_{\alpha\beta}\tau}. \end{aligned}$$

Similarly we have

$$W_{aa,aa}(\tau) = -W_{bb,aa}(\tau), \quad W_{bb,bb}(\tau) = W_{aa,bb}(\tau). \quad (\text{A.19})$$

We shall now turn to the evaluation of the  $T_2$  type terms:

$$\begin{aligned}
W_{ab,ab}(\tau) &= \sum_{\alpha,\beta} P(\alpha) \exp(-i\omega_{ab}\tau) \\
&\times \{ [L'(\tau)_{ab,ab}^{\beta\beta,\alpha\beta} L'(0)_{ab,ab}^{\alpha\beta,\alpha\alpha} + L'(\tau)_{ab,ab}^{\beta\beta,\beta\alpha} L'(0)_{ab,ab}^{\beta\alpha,\alpha\alpha}] \\
&+ [L'(\tau)_{ab,ab}^{\alpha\alpha,\alpha\beta} L'(0)_{ab,ab}^{\alpha\beta,\alpha\alpha} + L'(\tau)_{ab,ab}^{\alpha\alpha,\beta\alpha} L'(0)_{ab,ab}^{\beta\alpha,\alpha\alpha}] \\
&+ [L'(\tau)_{ab,aa}^{\alpha\alpha,\alpha\beta} L'(0)_{aa,ab}^{\alpha\beta,\alpha\alpha}] + [L'(\tau)_{ab,bb}^{\alpha\alpha,\beta\alpha} L'(0)_{bb,ab}^{\beta\alpha,\alpha\alpha}] \} \\
&\equiv W^I + W^{II} + W^{III}, \tag{A.20}
\end{aligned}$$

$$\begin{aligned}
W^I &= \sum_{\alpha,\beta} \exp(-i\omega_{ab}\tau) \\
&\times [G_b^{\alpha\beta*}(\tau) G_b^{\beta\alpha}(0) + G_a^{\beta\alpha}(\tau) G_a^{\beta\alpha}(0) \\
&- G_a^{\beta\alpha}(\tau) G_b^{\beta\alpha*}(0) - G_b^{\beta\alpha}(\tau) G_a^{\beta\alpha}(0)] P(\alpha) \\
&= \exp(-i\omega_{ab}\tau) [\langle G_a(\tau) G_a(0) \rangle + \langle G_b(-\tau) G_b(0) \rangle \\
&- \langle G_a(-\tau) G_b(0) \rangle - \langle G_b(\tau) G_a(0) \rangle], \tag{A.21}
\end{aligned}$$

$$W^{II} = \sum_{\alpha,\beta} P(\alpha) F_{ab}^{\alpha\beta*}(\tau) F_{ab}^{\beta\alpha}(0) = \langle F(-\tau) F(0) \rangle, \tag{A.22}$$

$$W^{III} = \sum_{\alpha,\beta} P(\alpha) F(\tau)_{ab}^{\alpha\beta} F(0)_{ba}^{\beta\alpha} = \langle F(\tau) F(0) \rangle. \tag{A.23}$$

We thus have:

$$\begin{aligned}
W_{ab,ab}(\tau) &= 2 \exp(-i\omega_{ab}\tau) \\
&\times \{ [\langle G_-(\tau) G_-(0) \rangle + \langle G_-(-\tau) G_-(0) \rangle] \\
&+ [\langle G_-(\tau) G_+(0) \rangle - \langle G_-(-\tau) G_+(0) \rangle] \} \\
&+ [\langle F(\tau) F(0) \rangle + \langle F(-\tau) F(0) \rangle], \tag{A.24}
\end{aligned}$$

where

$$G_+ \equiv \frac{1}{2} (G_a + G_b), \quad G_- \equiv \frac{1}{2} (G_a - G_b). \tag{A.25}$$

Similarly,

$$\begin{aligned}
W_{ba,ba}(\tau) &= 2 \exp(i\omega_{ab}\tau) \\
&\times \{ [\langle G_-(\tau) G_-(0) \rangle + \langle G_-(-\tau) G_-(0) \rangle] \\
&- [\langle G_-(\tau) G_+(0) \rangle - \langle G_-(-\tau) G_+(0) \rangle] \} \\
&+ [\langle F(\tau) F(0) \rangle + \langle F(-\tau) F(0) \rangle]. \tag{A.26}
\end{aligned}$$

Let us consider now the terms of the form  $W_{aa,ab}$ . These represent mixing of  $T_1$  and  $T_2$  and are expected to be very small as different pairs  $\alpha, \beta$  usually contribute to  $T_1$  and  $T_2$ . We thus assume that  $F$  and  $G$  are uncorrelated,

$$\langle F G_{\pm} \rangle = 0, \quad \langle G_{\pm} F \rangle = 0 \tag{A.27}$$

so that

$$W_{aa,ab} = W_{aa,ba} = W_{bb,ab} = W_{bb,ba} = 0,$$

$$W_{ab,aa} = W_{ba,aa} = W_{ab,bb} = W_{ba,bb} = 0. \tag{A.28}$$

Finally, we have to consider the off diagonal  $T_2$  type terms of the form  $W_{ab,ba}$

$$\begin{aligned}
W_{ab,ba} &= \sum_{\alpha,\beta} P(\alpha) [L'(\tau)_{ab,aa}^{\beta\beta,\beta\alpha} L'(0)_{aa,ba}^{\beta\alpha,\alpha\alpha} \\
&+ L'(\tau)_{ab,bb}^{\beta\beta,\alpha\beta} L'(0)_{bb,ba}^{\alpha\beta,\alpha\alpha}] \\
&= - \langle F(\tau) F(0) \rangle - \langle F(-\tau) F(0) \rangle, \tag{A.29}
\end{aligned}$$

and similarly,

$$W_{ba,ab} = W_{ab,ba}. \tag{A.30}$$

In practice, our molecular system contains more than two states (e.g., each vibrational level has many rotational states). Only the direct coupling between our two states of interest will contribute to the off diagonal  $T_2$  terms ( $W_{ab,ba}$  and  $W_{ba,ab}$ ), whereas coupling to all other states will contribute to the  $T_1$  ( $W_{aa,aa}$ ,  $W_{bb,bb}$ ) and the diagonal  $T_2$  ( $W_{ab,ab}$  and  $W_{ba,ba}$ ). We thus expect the contribution of  $\langle F(\tau) F(0) \rangle$  to the off diagonal  $T_2$  to be much smaller than the corresponding contribution to the diagonal  $T_2$  and  $T_1$ . We shall hereafter assume

$$W_{ab,ba} = W_{ba,ab} = 0. \tag{A.31}$$

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