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Vibrational relaxation of a molecule in a dense medium

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In this paper we consider some features of vibrational relaxation of a guest molecule in a host matrix. The model system involves a harmonic molecule interacting with a harmonic medium. The molecule-medium coupling was handled by the rotating wave approximation considering linear terms in the intramolecular displacements and high terms in the medium displacements. Three specific models for the molecule-medium coupling were considered, which involve single phonon decay, vibron–phonon decay and multiphonon decay. Within the framework of the random phase approximation the Heisenberg equations of motion for the system could be expressed in terms of a unified scheme which is valid for both single phonon and multiphonon processes. Explicit solutions were derived utilizing the Wigner–Weisskopf approximation. This generalized formalism was applied for the study of the time evolution of the distribution, the cooling and the heating processes of the oscillator by a thermal field and for the coupling between vibrational relaxation and infra-red emission.

1. INTRODUCTION

This paper is concerned with the problem of vibrational relaxation of a vibrationally excited or electronically and vibrationally excited molecule in a dense medium. Non equilibrium vibrational distributions in ground or in excited electronic states can be prepared by several methods : (*a*) infra-red excitation in the ground state [1], (*b*) Raman scattering resulting in a vibrationally excited ground state [2], (*c*) Optical excitation to electronically-vibrationally excited states [3], (*d*) Electronic relaxation from an electronically excited state of a large molecule to highly excited vibrational levels of a lower electronic configuration [4], (*e*) Electronic energy transfer from the host matrix or from an excited donor atom to electronically-vibrationally excited states of an acceptor molecule [5]. To date, several experimental spectroscopic methods have been applied for the study of vibrational relaxation, which involve spontaneous Raman anti-Stokes scattering [2], time resolved absorption [4 (*b*)], time resolved emission [6], and the recently developed techniques of picosecond spectroscopy [7, 8], all of which are applicable to monitor molecular vibrational relaxation in a dense medium.

To describe the features of vibrational relaxation of a guest molecule in a host matrix we shall adopt the simplest possible picture involving a harmonic molecule interacting with a harmonic medium, which is represented in terms of a phonon bath. The molecule-medium coupling will be recast in any order in respect to the medium displacements.

The problem under consideration is closely related to vibrational relaxation of a localized vibration in a crystal due to anharmonic interactions, which was previously handled utilizing perturbation theory [9]. For the general problem of the quantum behaviour of a harmonic oscillator subjected to linear coupling with a ' loss mechanism ' one can directly solve the Heisenberg equations of motion for the coordinate and momentum [10] (or for the creation and annihilation operators [11, 12]) of the oscillator. This approach was introduced by Senitzky [10] and has since then been extensively utilized in quantum electronics, in particular, in relation to the problems of the dynamics of coherent quantum states [12] and noise in lasers [13]. Similar techniques were applied in solid state theory for the study of neutron scattering [14] and anharmonic phonon relaxation [11].

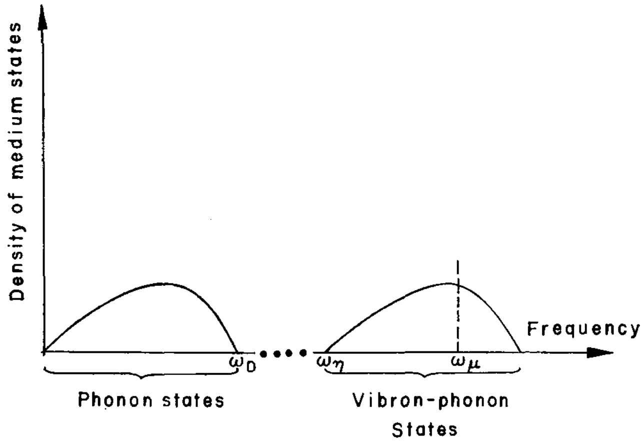
In the present study the effect of the molecular oscillator on the medium is considered as a small perturbation, but the effect of the medium on the oscillator is handled to ' infinite order ' within the framework of the Wigner–Weisskopf approximation [15], as applied to the Heisenberg equations of motion for the operators of the molecular normal modes. We were able to demonstrate that within the framework of the random phase approximation (RPA) the features of the vibrational relaxation for a general molecule-medium interaction can be described in terms of a unified set of equations of motion, and we were able to provide a general solution for these equations. Our general approach will be then applied for the study of several specific cases which were previously handled [10–14, 16] only by the use of special models (i.e. linear or anharmonic coupling) for the molecule-medium interactions.

2. Model system

We consider a harmonic polyatomic molecule where each mode is specified by the creation operator a_μ^+, the annihilation operator a_μ and the frequency ω_μ. The molecular vibrational hamiltonian is thus

$$H_{\mathrm{m}}=\sum_{\mu} \hbar\omega_\mu a_\mu^+ a_\mu. \tag{2.1}$$

The medium is described in terms of a set of harmonic oscillators, each of which is characterized by the frequency ω_ν and by the creation and annihilation operators



Schematic density of states in a phonon–vibron system. ω_D is the Debye frequency of the phonons ; $\omega\eta$ is the vibron frequency. $\omega\mu$ corresponds to an intramolecular frequency of a guest molecule.

b_ν^+ and b_ν. The density of states of the medium frequencies (figure) will be denoted by $\rho_\nu = \rho(\omega_\nu)$. Thus the zero order medium hamiltonian is

$$H_{\rm L} = \sum_\nu \hbar\omega_\nu b_\nu^+ b_\nu. \tag{2.1 a}$$

The total hamiltonian of the system is

$$H = H_{\rm m} + H_{\rm L} + H_{\rm mL}, \tag{2.2}$$

where $H_{\rm mL}$ denotes the molecule-medium coupling.

At this stage we shall invoke the following simplifying assumptions :

(*a*) Each molecular oscillator decays into its own phonon bath, whereupon the molecular vibrations are not coupled to each other via their interaction with the medium.

(*b*) The molecule-medium coupling is linear in the molecular displacements. Interaction terms of the form

$$\left(\sum_\nu a_\mu a_{\mu'}\, b_\nu + h\,.\,c\right)$$

which lead to medium assisted intramolecular energy redistribution, will be disregarded.

Thus the mathematical formulation of the problem is reduced to a single harmonic oscillator (characterized by the creation and annihilation operators a^+ and a, respectively, and by the frequency ω) interacting with the phonon bath. The Hamiltonian for this system is

$$H = \hbar\omega a^+ a + \sum_\nu \hbar\omega_\nu b_\nu^+ b_\nu + H_{\rm mL} \tag{2.2 a}$$

(*c*) The interaction term $H_{\rm mL}$ will be recast in terms of the rotating wave (or resonant) approximation [17]. The rotating wave approximation corresponds to the replacement of the hamiltonian for a system of linearily coupled oscillators

$$H = \sum_i \hbar\omega_i(a_i^+ a_i + \tfrac{1}{2}) + \sum_i \hbar G_{ij}(a_i^+ + a_i)(a_j^+ + a_j) \tag{2.3}$$

(where a_i^+ and a_i now represent the creation and the annihilation operators of the ith oscillator characterized by the frequency ω_i, while G_{ij} are the coupling constants), by the approximate hamiltonian

$$H = \sum_i \hbar\omega_i(a_i^+ a_i + \tfrac{1}{2}) + \sum_{ij} \hbar G_{ij}(a_i^+ a_j + a_i a_j^+). \tag{2.3 a}$$

Thus terms of the form $a_i^+ a_j^+$ and $a_i a_j$ are neglected. The argument [17 (*a*, *b*)] justifying this approximation is as follows : the free time evolution of the terms neglected in (2.3) is

$$\left.\begin{aligned} a_i a_j &\propto \exp\,[-i(\omega_i + \omega_j)t], \\ a_i^+ a_j^+ &\propto \exp\,[i(\omega_i + \omega_j)t] \end{aligned}\right\} \tag{2.3 b}$$

while the operators of the form $a_i a_j^+$ retained in (2.3 *a*) exhibit the time evolution

$$a_i a_j^+ \propto \exp\,[-i(\omega_i - \omega_j)t]. \tag{2.3 c}$$

When the coupling terms G_{ij} are sufficiently small, transitions will take place on a time scale which is long relative to the rapid oscillators of the terms (2.3 *b*). These neglected terms undergo many oscillations on the time scale of interest, whereupon their average value is expected to be small, as compared to the average value of the slowly varying terms (2.3 *c*). Thus the high frequency off resonance terms are neglected retaining only the near resonance low frequency contribution. Detailed numerical calculations [17 (*c*)] have demonstrated that the rotating wave approximation is adequate provided that $G_{ij}/\omega_i \sim G_{ij}/\omega_j \lesssim 0{\cdot}5$. In the case of vibrational relaxation this condition is always satisfied.

Up to this point we have been concerned with linearily coupled linear oscillators (equation (2.3)). In what follows we shall adopt the rotating wave approximation in the general sense, assuming that under the conditions of sufficiently weak coupling one can neglect high frequency terms which will average out on the time scale of interest.

Three simple model hamiltonians will be advanced to account for the medium induced vibrational relaxation of a single vibrational mode :

Case A : Single phonon decay. The molecular oscillator interacts with the medium via linear terms in the medium displacements, so that the interaction term is

$$H_{\mathrm{mL}} = \sum_{\nu} \hbar (C_\nu a^+ b_\nu + G_\nu{}^* a b_\nu{}^+), \qquad (2.4\,a)$$

where G_ν is the coupling parameter with the νth phonon mode. This interaction hamiltonian was extensively studied by Glauber and others [12, 16]. The interaction (2.4 *a*) is adequate provided that the molecular frequency ω overlaps the frequency spectrum of the oscillator, i.e. $\rho(\omega) \neq 0$. If this condition is violated, this interaction term does not conserve energy. For the relaxation of molecular frequencies ($\omega \sim 100$–3000 cm^{-1}) in a monoatomic lattice ($\omega_\nu{}^{\max} \sim 100$ cm^{-1}) the single phonon decay model is usually inadequate.

Case B : Double phonon decay. We consider vibrational relaxation in a host matrix consisting of polyatomic molecules. The vibrational states of the medium involve a continuous spectrum of low frequency phonon states and ' isolated ' high frequency intramolecular vibrations which form narrow vibrational ' exciton ' bands (see figure). These high frequency medium modes, which will be referred to as ' vibrons ', cannot be considered as an effective decay channel for intramolecular vibrations. However, low frequency medium phonons superimposed on a single medium vibron may provide us with a legitimate dissipative continuum which overlaps the intramolecular vibrational frequency. The interaction hamiltonian is now

$$H_{\mathrm{mL}} = \hbar \sum_{\nu} \sum_{\eta} (G_{\nu\eta} a^+ b_\nu c_\eta + G_{\nu\eta}{}^* a b_\nu{}^+ c_\nu{}^+), \qquad (2.4\,b)$$

where c^+ and c represent the vibron creation and annihilation operators, and $G_{\nu\eta}$ corresponds to the two phonon coupling term.

Case C : Multiphonon decay. The general form of the interaction within the framework of the rotating wave approximation can be expressed in terms of a multiphonon (i.e. *n* phonon) decay process.

$$H_{\mathrm{mL}}=a^{+}\sum_{\substack{\nu_1,\nu_2,\ldots\nu_n\\ \nu_1\neq\nu_2\neq\ldots\nu_n}}\hbar G_{\nu_1\nu_2}\ldots b_{\nu_1}b_{\nu_2}\ldots b_{\nu_n}$$

$$+a\sum_{\substack{\nu_1,\nu_2\ldots\nu_n\\ \nu_1\neq\nu_2\neq\ldots\nu_n}}\hbar G_{\nu_1\nu_2}\ldots b_{\nu_1}{}^{+}b_{\nu_2}{}^{+}\ldots b_{\nu_n}{}^{+}. \qquad (2.4\,c)$$

We have disregarded in equation (2.4 *c*) the terms which involve two or more equal indices in the medium phonon modes. This approximation is entirely justified as the number of these neglected terms in a continuous phonon spectrum is relatively small. It should be noted that from the formal point of view, case B is just a special example of case C. We have made a distinction as cases B and C correspond to different physical situations.

To complete the exposition of the model system two further simplifying assumptions will be introduced :

(*d*) The medium states do not change appreciably during the relaxation process. The thermally averaged occupation numbers of the phonon or vibron modes

$$\langle n_\nu\rangle_{\mathrm{T}}=[\exp(\beta\hbar\omega_\nu)-1]^{-1} \qquad (2.5\,a)$$

and

$$\langle n_\eta\rangle_{\mathrm{T}}=[\exp(\beta\hbar\omega_\eta)-1]^{-1}, \qquad (2.5\,b)$$

where $\langle\ \rangle_{\mathrm{T}}$ denotes thermal average and $\beta=(k_BT)^{-1}$, provide a good approximation for the medium states throughout the relaxation process.

(*e*) The random phase approximation (RPA) [18] will be utilized to simplify the equations of motion. As we have assumed (see (*d*)) that the medium states are not appreciably affected by the relaxation process we shall replace the products of the medium boson creation and annihilation operators by the appropriate ensemble thermal averages. This approximation neglects the contribution of innumerable terms corresponding to off diagonal elements which are randomly out of phase with one another. The RPA method involves a generalized self consistent field procedure [18] which incorporates the effect of the average oscillatory field of the medium particles. Applying the RPA to the problem at hand we replace the products of boson creation and annihilation operators by the appropriate thermal averages, so that

$$b_{\nu'}b_\nu{}^{+}\xrightarrow{\mathrm{RPA}}\delta_{\nu\nu'}(\langle n_\nu\rangle_{\mathrm{T}}+1), \qquad (2.6\,a)$$

$$c_{\eta'}c_\eta{}^{+}\xrightarrow{\mathrm{RPA}}\delta_{\eta\eta'}(\langle n_\eta\rangle_{\mathrm{T}}+1) \qquad (2.6\,b)$$

and

$$b_\nu{}^{+}b_{\nu'}\xrightarrow{\mathrm{RPA}}\delta_{\nu\nu'}\langle n_\nu\rangle_{\mathrm{T}}, \qquad (2.7\,a)$$

$$c_\eta{}^{+}c_{\eta'}\xrightarrow{\mathrm{RPA}}\delta_{\eta\eta'}\langle n_\eta\rangle_{\mathrm{T}}. \qquad (2.7\,b)$$

3. THE RELAXATION PROCESS

3.1. *Equations of Motion*

The equations of motion of the creation and annihilation operators (in the Heisenberg representation) for the three relaxation models outlined in § 2 can be written in a straightforward manner.

3.1.1. *Single phonon decay*

$$\dot{a}=(i/\hbar)[H, a]=-i\omega a-i\sum_{\nu} G_{\nu}b_{\nu}, \tag{3.1}$$

$$\dot{b}_{\nu}=(i/\hbar)[H, b_{\nu}]=-i\omega_{\nu}b_{\nu}-iG_{\nu}^{*}a. \tag{3.2}$$

3.1.2. *Two phonon decay*

$$\dot{a}=-i\omega a-i\sum_{\nu,\eta} G_{\nu\eta}b_{\nu}c_{\eta}, \tag{3.3}$$

$$\dot{b}_{\nu}=-i\omega_{\nu}b_{\nu}-i\sum_{\eta} G_{\nu\eta}^{*}ac_{\eta}^{+}, \tag{3.4}$$

$$\dot{c}_{\eta}=-i\omega_{\eta}c_{\eta}-i\sum_{\nu} G_{\nu\eta}^{*}ab_{\nu}^{+} \tag{3.5}$$

We shall also require the time evolution of the product of the medium operators

$$\begin{aligned}\frac{d}{dt}(b_{\nu}c_{\eta})&=(i/\hbar)[H, b_{\nu}c_{\eta}]=(i/\hbar)\{[H, b_{\nu}]c_{\eta}-b_{\nu}[c_{\eta}, H]\}\\&=\dot{b}_{\nu}c_{\eta}+b_{\nu}\dot{c}_{\eta}=-i\omega_{\nu}b_{\nu}c_{\eta}-i\sum_{\eta'} G_{\nu\eta'}^{*}ac_{\eta'}^{+}c_{\eta}-i\omega_{\eta}b_{\nu}c_{\eta}-i\sum_{\nu'} G_{\nu'\eta}^{*}ab_{\nu}b_{\nu'}\end{aligned} \tag{3.6}$$

Invoking now the RPA and utilizing equations (2.6) and (2.7) we get

$$\frac{d}{dt}(b_{\nu}c_{\eta})=-i(\omega_{\nu}+\omega_{\eta})b_{\nu}c_{\eta}-iG_{\nu\eta}^{*}(\langle n_{\nu}\rangle_{\mathrm{T}}+\langle n_{\eta}\rangle+1)a. \tag{3.7}$$

3.1.3. *Multiple decay*

The hamiltonian is now

$$H=\hbar\omega a^{+}a+\sum_{\nu}\hbar\omega_{\nu}b_{\nu}^{+}b_{\nu}+\sum_{\{\nu\}}\hbar\left[G\{\nu\}a^{+}\prod_{\nu}b_{\nu}+G^{*}\{\nu\}a\prod_{\nu}b_{\nu}^{+}\right], \tag{3.8}$$

where we denote phonon sets by $\{\nu\}=1, 2 \dots N$. The relevant equations of motion are

$$\dot{a}=-i\omega a-i\sum_{\{\nu\}} G\{\nu\}\Pi b_{\nu}, \tag{3.9}$$

$$\dot{b}_{\nu'}=(i/\hbar)[H, b_{\nu'}]=-i\omega_{\nu'}b_{\nu'}-i\sum_{\{\nu-1\}} G^{*}\{\nu\}a\prod_{\nu\neq\nu'} b_{\nu}^{+} \tag{3.10}$$

and

$$\frac{d}{dt}\left(\prod_{\nu}b_{\nu}\right)=\sum_{\nu'} b_{1}b_{2}\dots\dot{b}_{\nu'}b_{\nu'+1}\dots b_{N}, \tag{3.11}$$

where we denote $\{\nu\}=\{\nu-1\}\nu'$.

Utilizing equations (3.8), (3.10) and (3.11) we have

$$\begin{aligned}\frac{d}{dt}\left(\prod_{\nu}b_{\nu}\right)=-i\left(\sum_{\nu}\omega_{\nu}\right)\prod_{\nu}b_{\nu}-i\Bigg(\sum_{\nu'}b_{1}b_{2}\dots b_{\nu'-1}\\\times\left[\sum_{\{\nu-1\}}G^{*}\{\nu\}\prod_{\nu\neq\nu'}b_{\nu}^{+}\right]b_{\nu'+1}\dots b_{N}\Bigg)a.\end{aligned} \tag{3.12}$$

Invoking again the random phase approximation (equations (2.6) and (2.7)) we get

$$\frac{d}{dt}\left(\prod_{\nu} b_{\nu}\right) = -i\left(\sum_{\nu}\omega_{\nu}\right)\prod_{\nu} b_{\nu} - i\left[\sum_{\nu'}\langle n_1\rangle\langle n_2\rangle \right.$$
$$\left. \ldots \langle n_{\nu'-1}\rangle[\langle n_{\nu'+1}\rangle+1]\ldots[\langle n_N\rangle+1]G\{{}^*\nu\}\right]a, \tag{3.13}$$

where the index T in $\langle\ \rangle_{\mathrm{T}}$ has been omitted.

From equations (3.1)–(3.8) we conclude that the three different cases for vibrational relaxation considered herein can be described by the following unified hamiltonian :

$$H = \hbar\omega a^+ a + \sum_{\nu} \hbar\omega_{\nu} b_{\nu}^+ b_{\nu} + \sum_{\boldsymbol{\nu}} (G_{\boldsymbol{\nu}} B_{\boldsymbol{\nu}} a^+ + G_{\boldsymbol{\nu}}^* B_{\boldsymbol{\nu}}^+ a) \tag{3.14}$$

and by the following set of linear equations of motion in the Heisenberg representation

$$\dot{a} = -i\omega a - i\sum_{\boldsymbol{\nu}} G_{\boldsymbol{\nu}} B_{\boldsymbol{\nu}}, \tag{3.15 a}$$

$$\dot{B}_{\boldsymbol{\nu}} = -i\omega_{\boldsymbol{\nu}} B_{\boldsymbol{\nu}} - i n_{\boldsymbol{\nu}} G_{\boldsymbol{\nu}}^* a, \tag{3.15 b}$$

where the number $n_{\boldsymbol{\nu}}$ is

$$n_{\boldsymbol{\nu}} = \langle [B_{\boldsymbol{\nu}}, B_{\boldsymbol{\nu}}^+]\rangle_{\mathrm{T}}. \tag{3.16}$$

Thus, for case A, $B_{\boldsymbol{\nu}} = b_{\nu}$, $G_{\boldsymbol{\nu}} = G_{\nu}$, $\omega_{\boldsymbol{\nu}} = \omega_{\nu}$ and $n_{\boldsymbol{\nu}} = 1$; for case B, $B_{\nu} = b_{\nu} c_{\eta}$, $G_{\boldsymbol{\nu}} = G_{\nu\eta}$, $\omega_{\boldsymbol{\nu}} = \omega_{\nu} + \omega_{\eta}$ and $n_{\boldsymbol{\nu}} = \langle n_{\nu}\rangle + \langle n_{\eta}\rangle + 1$; while for case C, $B_{\boldsymbol{\nu}} = \prod_{\nu} b_{\nu}$, $G_{\boldsymbol{\nu}} = G\{\nu\}$, $\omega_{\boldsymbol{\nu}} = \sum_{\nu}\omega_{\nu}$ and $n_{\boldsymbol{\nu}} = \sum_{\nu'} \langle n_1\rangle\langle n_2\rangle \ldots \langle n_{\nu'-1}\rangle(\langle n_{\nu'+1}\rangle + 1) \ldots (\langle n_N\rangle + 1)$. We can now proceed to consider the solutions for these unified equations of motion without referring to the specific models. The decay characteristics for the three interaction models considered by us will have the same functional form.

3.2. *Solutions of the equations of motion*

The set of the equations (3.15) has been studied by Gordon *et al.* [17(*a*)] in their treatment of quantum statistics of masers and attenuators. We shall provide a slight generalization of their solution. The essence of the treatment [17 (*a*)] is that equation (3.15) involves only commuting operators. Thus, for the purpose of the mathematical manipulations these operators may be handled as simple *c* functions. Defining the Laplace transforms

$$\left.\begin{aligned} a(s) &= \int_0^{\infty} \exp(-st) a(t)\, dt, \\ B_{\boldsymbol{\nu}}(s) &= \int_0^{\infty} \exp(-st) B_{\boldsymbol{\nu}}(t)\, dt \end{aligned}\right\} \tag{3.17}$$

we have

$$\left.\begin{aligned}&\int \exp(-st)\dot{a}(t)\,dt = sa(s)-a,\\&\int \exp(-st)\dot{B}_\nu(t)\,dt = sB_\nu(s)-B_\nu,\end{aligned}\right\} \tag{3.18}$$

where $a=a(0)$ and $B_\nu=B_\nu(0)$ are the corresponding Schrodinger operators. Equation (3.15) now yield

$$sa(s)-a=-i\omega a(s)-i\sum_\nu G_\nu B_\nu(s), \tag{3.19}$$

$$sB_\nu(s)-B_\nu=-i\omega_\nu B_\nu(s)-iG_\nu{}^*n_\nu a(s). \tag{3.20}$$

From equation (3.20) we obtain

$$iG_\nu B_\nu(s)=i\frac{G_\nu B_\nu}{s+i\omega_\nu}+\frac{|G_\nu|^2n_\nu}{s+i\omega_\nu}a(s). \tag{3.21}$$

Inserting this result into equation (3.19) we get

$$a(s)\left[s+i\omega+\sum_\nu\frac{|G_\nu|^2n_\nu}{s+i\omega_\nu}\right]=a-i\sum_\nu\frac{G_\nu B_\nu}{s+i\omega_\nu} \tag{3.22}$$

which may be recast in a more transparent form

$$a(s)=u(s)a+\sum_\nu v_\nu(s)B_\nu, \tag{3.23}$$

where

$$u(s)=\frac{1}{s+i\omega+\sum_\nu\dfrac{|G_\nu|^2n_\nu}{s+i\omega_\nu}} \tag{3.24}$$

and

$$v_\nu(s)=\frac{-iG_\nu}{(s+i\omega_\nu)\left[s+i\omega+\sum_\nu\dfrac{|G_\nu|^2n_\nu}{s+i\omega_\nu}\right]}. \tag{3.25}$$

Taking now the inverse Laplace transforms we may write equation (3.23) in the form

$$a(t)=u(t)a+\sum_\nu v_\nu(t)B_\nu \tag{2.26}$$

with the functions $u(t)$ and $v_\nu(t)$ being given by

$$u(t)=\frac{1}{2\pi i}\int_{-\infty+i\epsilon}^{\infty+i\epsilon}dy\exp(iyt)\frac{1}{y+\omega-\sum_\nu\dfrac{|G_\nu|^2n_\nu}{y+\omega_\nu}} \tag{3.27}$$

and

$$v_\nu(t)=\frac{1}{2\pi i}\int_{-\infty+i\epsilon}^{\infty+i\epsilon}dy\exp(iyt)\frac{G_\nu}{(y+\omega_\nu)\left[y+\omega-\sum_\nu\dfrac{|G_\nu|^2n_\nu}{y+\omega_\nu}\right]} \tag{3.28}$$

and where we have defined $s = iy$. At this point Gordon Walker and Luisell apply a somewhat oversimplified procedure in order to evaluate transforms (3.27) and (3.28). The rigorous mathematical procedure which has been provided by Goldberger and Watson [19], yields the following results

$$u(t) = \exp\left[-i\omega' t - \gamma t\right], \tag{3.29}$$

$$v_\nu(t) = \frac{-iG_\nu}{i(\omega' - \omega_\nu) - \gamma}\left[\exp(-i\omega_\nu t) - \exp(-i\omega' t - \gamma t)\right], \tag{3.30}$$

where the modified oscillator frequency is

$$\omega' = \omega + \delta\omega. \tag{3.31}$$

In equations (3.29)–(3.31) we have defined the level shift $\delta\omega$ and the level width γ by the relation

$$\delta\omega - i\gamma = \lim_{\eta \to 0^+} \sum_\nu \frac{|G_\nu|^2 n_\nu}{\omega - \omega_\nu + i\eta} \tag{3.32}$$

so that

$$\delta\omega = PP \sum_\nu \frac{|G_\nu|^2 n_\nu}{\omega - \omega_\nu}, \tag{3.33}$$

$$\gamma = \Pi \sum_\nu |G_\nu|^2 n_\nu \delta(\omega - \omega_\nu). \tag{3.34}$$

To conclude this formal discussion it is important to mention the normalization condition (sum rule) for the functions $u(t)$, equation (3.29), and $v(t)$, equation (3.30),

$$|u(t)|^2 + \sum_\nu |v_\nu(t)|^2 n_\nu = 1 \tag{3.35}$$

which insures (within the framework of the random phase approximation) that the commutation rule $[a(t), a^+(t)] = 1$ holds at every instant t. To demonstrate this point we make use of equation (3.27) to get

$$\begin{aligned}[a(t), a^+(t)] &= \Big[ua + \sum_\nu v_\nu B_\nu,\ u^* a^+ + \sum_\nu v_\nu^* B_\nu^+\Big] \\ &\overset{\text{RPA}}{=} |u|^2 + \sum_{\nu,\nu'} v_\nu v_{\nu'}^* [B_\nu, B_{\nu'}] = |u|^2 + \sum_\nu |v_\nu|^2 \langle [B_\nu, B_\nu^+] \rangle_{\mathrm{T}}.\end{aligned} \tag{3.36}$$

Utilization of equation (3.16) yields

$$[a(t), a(t)^+] = |u|^2 + \sum_\nu |v_\nu(t)|^2 n_\nu = 1. \tag{3.37}$$

Equations (3.26), (3.29) and (3.30) specify the general functional form of the vibrational relaxation without referring to specific models for the molecule-medium interaction. It should, however, be born in mind that the specific form of the level shift (3.33) and of the level width (3.34) are different for single and for multiphonon decay. In particular we should note that for a single phonon decay γ is temperature independent, and exhibits temperature dependence for the case of multiphonon decay.

4. Some applications for vibrational relaxation

We have just demonstrated that externally induced vibrational relaxation via single and multiphonon processes can be incorporated within the framework of a unified theoretical scheme (see equations (3.14), (3.15), (3.26), (3.29) and (3.30)). It will be useful to apply this generalized formalism to derive some features of vibrational relaxation which were previously handled by the application of specific models for the molecule-medium coupling.

4.1. *The time evolution of the population*

Let $\rho(0)=\rho_{\text{osc}}\rho_B$ be the initial density operator of the system, where ρ_{osc} is the initial density operator of the oscillator and ρ_B is the initial density operator for the thermal bath (or phonon field). The average population $n(t)$, of the oscillator at time t may be computed from the general expression

$$n(t)=\operatorname{Tr}\{a^+(t)a(t)\rho(0)\}. \tag{4.1}$$

The initial density operator will be diagonal in the population number representation under the following conditions : (*a*) The oscillator is initially in a pure $|n\rangle$ state and the medium is in thermal equilibrium. (*b*) Both the oscillator and the medium are initially in a thermal (Boltzmann) distribution. Provided that either condition (*a*) or (*b*) is satisfied we have

$$n(t)=\operatorname{Tr}\{|u(t)|^2a^+a\rho\}+\operatorname{Tr}\left\{\left(\sum_\nu |v_\nu(t)|^2B_\nu{}^+B_\nu\right)\rho\right\}. \tag{4.2}$$

In equations (4.1) and (4.2) Tr represents the trace over the oscillator and the bath states. A partial trace over bath states taken for the first term in equation (4.2) gives $\operatorname{Tr}_B\rho_B=1$, and a partial trace over the oscillator states taken for the second term in (4.2) yields $\operatorname{Tr}_{\text{osc}}\rho_{\text{osc}}=1$. Thus we get

$$\begin{aligned} n(t)&=\operatorname{Tr}_{\text{osc}}\{a^+a\rho_{\text{osc}}\}|u(t)|^2+\operatorname{Tr}_B\left\{\left(\sum_\nu |v_\nu(t)|^2B_\nu{}^+B_\nu\right)\rho_B\right\}\\ &=|u(t)|^2n(0)+\sum_\nu |v_\nu(t)|^2\langle B_\nu{}^+B_\nu\rangle_{\text{T}}, \end{aligned} \tag{4.3}$$

where $n(0)$ is the initial population of the oscillator. Consider now the second term in the r.h.s. of equation (4.3). For a thermal bath $\langle B_\nu{}^+B_\nu\rangle_{\text{T}}$ is just a thermal average, yielding $\langle n_\nu\rangle_{\text{T}}$ in case A, $\langle n_\nu\rangle_{\text{T}}\langle n_\eta\rangle_{\text{T}}$ in case B and $\prod_\nu \langle n_\nu\rangle_{\text{T}}$ in case C. It may be easily verified that for every one of the three relaxation models considered by us we have

$$\frac{\langle B_\nu{}^+B_\nu\rangle_{\text{T}}}{\langle[B_\nu,B_\nu{}^+]\rangle_{\text{T}}}=\frac{\prod_\nu\langle n_\nu\rangle_{\text{T}}}{n_\nu}=\frac{1}{\exp(\hbar\omega_\nu/k_BT)-1} \tag{4.4}$$

This is trivially true for cases A and B and may be proved by induction in the general case C. Now, as the function $v_\nu(t)$ (as a function of ν) is sharply peaked at $\omega_\nu=\omega$ we may write

$$\sum_{\nu} |v_\nu(t)|^2 n_\nu \frac{\langle B_\nu{}^+ B_\nu\rangle_{\mathrm{T}}}{n_\nu} \cong \left[\exp\left(\frac{\hbar\omega}{k_B T}\right)-1\right]^{-1} \times \sum_{\nu} |v_\nu(t)|^2 n_\nu = \langle n\rangle_{\mathrm{T}}(1-|u(t)|^2) \tag{4.5}$$

in which $\langle n\rangle_{\mathrm{T}}$ is the thermally averaged population of the oscillator. Utilizing this result, equation (4.3) finally yields

$$n(t)=|u(t)|^2 n(0)+(1-|u(t)|^2)\langle n\rangle_{\mathrm{T}} \tag{4.6}$$

with

$$|u(t)|^2=\exp(-2\gamma t). \tag{4.6 a}$$

Equation (4.6) implies that the time evolution of the population of the oscillator (which is characterized by a diagonal initial density operator) involves two contributions : an exponential decay of the initial state characterized by a decay time 2γ, and a built up of the thermal distribution of states. This result was previously obtained only for single phonon coupling [12, 16].

It is also interesting to note that the non-radiative decay of the average distribution initially being at the nth level is determined by the rate 2γ rather than by the width of the nth states, which is just $2n\gamma$. This feature originates from the fact that the interaction of the oscillator with a thermal bath results both in excitation and deactivation processes, providing the non-radiative analogue of the well known harmonic oscillator paradox [16], which will be briefly discussed in § 5.

4.2. *A description of a cooling process*

We shall now consider the decay of the oscillator from an initially excited vibrational level, which may be prepared by optical excitation from a lower electronic state. Let $|m\rangle = 1/\sqrt{m!}(a^+)^m|0\rangle$ be the initial state of the oscillator and let the phonon field be at zero temperature, so that its state may be described by the product $\prod_{\nu} |0_\nu\rangle$. The state at time t has the form

$$\begin{aligned}\psi(t)&=\exp[-iH(t/\hbar)]\psi(0)=\exp[-iH(\hbar/t)]\frac{1}{\sqrt{m!}}(a^+)^m \left|0, \prod_{\nu} 0_\nu\right\rangle \\ &=\frac{1}{\sqrt{m!}}\exp[-iH(t/\hbar)](a^+)^m \exp[iH(t/\hbar)]\left|0, \prod_{\nu} 0\right\rangle_\nu.\end{aligned} \tag{4.7}$$

The last step in (4.7) is legitimate provided that virtual processes are neglected so that we set

$$\exp[iH(t/\hbar)]\left|0, \prod_{\nu} 0_\nu\right\rangle = \left|0, \prod_{\nu} 0_\nu\right\rangle. \tag{4.8}$$

Thus we have

$$\psi(t)=\frac{1}{\sqrt{m!}}(a^+(t))^m\left|0, \prod_{\nu} 0_\nu\right\rangle. \tag{4.9}$$

We are interested in the probability $p(m, n, t)$ to find the oscillator in some state $|n\rangle$ at time t, which is given by

$$p(m, n\,;\ t)=\sum_{\{n_\nu\}}\left|\left\langle n, \prod_\nu n_\nu|\psi(t)\right\rangle\right|^2=\langle\psi(t)|n\rangle\langle n|\psi(t)\rangle, \tag{4.10}$$

where $\sum_{\{n_\nu\}}$ represents a sum over all final bath states. Inserting equation (4.9) into equations (4.10) we get

$$p(m, n\,;\ t)=\frac{1}{m!}\left\langle 0\,;\ \prod_\nu 0_\nu|a(t)^m|n\right\rangle\left\langle n|(a^+(t))^m|0\,;\ \prod_\nu 0_\nu\right\rangle. \tag{4.11}$$

Utilizing now equation (3.26) we obtain

$$(a(t))^m=\sum_{k=0}^{m}\frac{m!}{k!(m-k)!}(u(t))^{m-k}a^{m-k}\left(\sum_\nu v_\nu(t)B_\nu\right)^k \tag{4.12}$$

which leads to

$$\begin{aligned}p(m, n\,;\ t)&=\sum_{k=0}^{m}\frac{m!}{(k!)^2[(m-k)!]^2}\langle 0|a^{m-k}|n\rangle\langle n|(a^+)^{m-k}|0\rangle\\&\quad(|u(t)|^2)^{m-k}\times\left\langle\prod_\nu 0_\nu\left|\left(\sum_\nu v_\nu(t)B_\nu\right)^k\left(\sum_\nu v_\nu^*(t)B_\nu^+\right)\right|\prod_\nu 0_\nu\right\rangle\\&=\frac{m!}{[(m-n)!]^2n!}(|u(t)|^2)^n\left\langle\prod_\nu 0_\nu\left|\left(\sum_\nu v_\nu(t)B_\nu\right)^{m-n}\right.\right.\\&\qquad\qquad\left.\left.\times\left(\sum_\nu v_\nu^*(t)B_\nu^+\right)^{m-n}\right|\prod_\nu 0_\nu\right\rangle.\end{aligned} \tag{4.13}$$

To evaluate the bath matrix elements we make use of the following relations :

$$\sum_\nu v_\nu(t)B_\nu=a(t)-u(t)a, \tag{4.14}$$

$$[a(t), a^+(t)]=[a, a^+]=1, \tag{4.15 a}$$

$$[a(t), a^+]=u(t)\,;\ [a, a^+(t)]=u^*(t) \tag{4.15 b}$$

to obtain

$$\left[\sum_\nu v_\nu(t)B_\nu, \sum_\nu v_\nu^*(t)B_\nu^+\right]=1-|u(t)|^2. \tag{4.16}$$

Making use of the relation we may recast the bath matrix element in the following form :

$$\begin{aligned}&\left\langle\prod_\nu 0_\nu\left|\left(\sum_\nu v_\nu(t)B_\nu\right)^{m-n}\left(\sum_\nu v_\nu^*(t)B_\nu^+\right)^{m-n}\right|\prod_\nu 0_\nu\right\rangle\\&\qquad=(m-n)!(1-|u(t)|^2)^{m-n}\end{aligned} \tag{4.17}$$

so that we finally obtain

$$p(m, n\,;\ t)=\frac{m!}{(m-n)!n!}(|u(t)|^2)^n(1-|u(t)|^2)^{m-n}$$

with

$$|u(t)|^2=\exp(-2\gamma t). \tag{4.18}$$

An alternative derivation of this result utilizing coherent state representation is given in Appendix A.

Finally, we note at the risk of triviality that equation (4.18) is meaningful only provided that $n<m$. Also note that

$$\sum_{n=0}^{m} p(m, n\,;\ t)=(|u(t)|^2+1-|u(t)|^2)^m=1 \tag{4.19}$$

which provides a good consistency check.

From equation (4.18) we assert that (*a*) the decay of the initial m state is exponential, characterized by the decay time $2m\gamma$; (*b*) the decay of the lower levels is non-exponential, characterized by superposition of a decay component having the lifetime $2n\gamma$ and a built -up term $[1-\exp(-2\gamma t)]^{m-n}$; (*c*) the population of the oscillator levels is given by a Bernoulli distribution. These results confirm a simple kinetic analysis [9] and were previously obtained quantum mechanically for the special case of two phonon decay. Our results demonstrate that the general muliphonon interaction handled by the RWA and the RPA approximations result in the conventional kinetic decay scheme [9].

4.3. *A description of a heating process by a thermal field*

From the point of view of general methodology it is interesting to consider the evolution of the population of different states of the oscillator, initially located in the ground $|0\rangle$ state. This treatment will elucidate the details of the rate of vibrational excitation of the oscillator by the medium. We start with the oscillator in the ground level $|0\rangle$ and the field in thermal equilibrium at a temperature T. The bath states can be represented as a superposition of Glauber's coherent states $|\beta_\nu\rangle$. We shall thus make use of the Glauber's P representation [20] of the density matrix for a chaotic phonon field

$$\rho_B=\prod_\nu \frac{1}{\pi\langle n_\nu\rangle}\int d^2\beta_\nu \exp\left(-\frac{|\beta_\nu|^2}{\langle n_\nu\rangle}\right)|\beta_\nu\rangle\langle\beta_\nu|, \tag{4.20}$$

where

$$|\beta_\nu\rangle=\exp(-\tfrac{1}{2}|\beta_\nu|^2)\sum_{n_\nu}\frac{\beta_\nu{}^n}{\sqrt{n!}}|n\rangle \tag{4.20 a}$$

so that the initial density operator for the oscillator-field system is

$$\rho(0)=\rho_B(0)\rho_{\text{osc}}(0)=\prod_\nu \frac{1}{\pi\langle n_\nu\rangle}\int d^2\beta_\nu \times\left[\exp\left(-\frac{|\beta_\nu|^2}{\langle n_\nu\rangle}\right)|\beta_\nu\rangle\langle\beta_\nu|\right]|0\rangle\langle 0|. \tag{4.21}$$

At time t we have [12]

$$\left.\begin{aligned} |0\rangle &\to \Big|\sum_{\nu} v_\nu(t)\beta_\nu\Big\rangle, \\ |\beta_\nu\rangle &\to \Big|\sum_{\nu} y_{\nu\nu'}(t)\beta_{\nu'}\Big\rangle \end{aligned}\right\} \tag{4.22}$$

Inserting equations (4.22) into equations (4.21) and taking the trace over the field states, we obtain the reduced density matrix for the oscillator in the form

$$\rho_{\text{osc}}(t) = \int d^2\beta_\nu \prod_\nu \frac{1}{\pi\langle n_\nu\rangle} \exp\left(-\frac{|\beta_\nu|^2}{\langle n_\nu\rangle}\right) \times \Big|\sum_\nu \beta_\nu v_\nu(t)\Big\rangle\Big\langle\sum_\nu v_\nu(t)\beta_\nu\Big|. \tag{4.23}$$

The probability to observe the oscillator in the n state $|m\rangle$ at the time t is

$$P_m(t) = \langle m|\rho_{\text{osc}}(t)|m\rangle = \prod_\nu \frac{1}{\pi\langle n_\nu\rangle} \int d^2\beta_\nu \exp\left(-\frac{|\beta_\nu|^2}{\langle n_\nu\rangle}\right) \times \left|\Big\langle m\Big|\sum_\nu \beta_\nu v_\nu(t)\Big\rangle\right|^2 = \int d^2\xi\, |\langle m|\xi\rangle|^2 F(\xi, t), \tag{4.24}$$

where

$$F(\xi, t) = \int \delta^{(2)}\left(\xi - \sum_\nu v_\nu(t)\beta_\nu\right) \prod_\nu \frac{1}{\pi\langle n_\nu\rangle} \exp\left[-\frac{|\beta_\nu|^2}{\langle n_\nu\rangle}\right] d^2\beta_\nu \tag{4.25}$$

in which

$$\delta^{(2)}(z) = \delta(\text{Re } Z)\delta(\text{Im } Z)$$

The function $F(\xi, t)$ may be evaluated explicitly to give [12]

$$F(\xi, t) = \frac{1}{\pi \sum_\nu \langle n_\nu\rangle |v_\nu(t)|^2} \exp\left[-\frac{|\xi|^2}{\sum_\nu \langle n_\nu\rangle |v_\nu(t)|^2}\right] \tag{4.26}$$

so that equation (4.24) yields

$$P_m(t) = \frac{1}{\pi \sum_\nu \langle n_\nu\rangle |v_\nu(t)|^2} \frac{1}{m!} \int d^2\xi\, |\xi|^{2m} \exp(-|\xi|^2) \times \exp\left[-\frac{|\xi|^2}{\sum_\nu \langle n_\nu\rangle |v_\nu(t)|^2}\right] \tag{4.27}$$

which on evaluating the integral, results in

$$P_m(t) = \frac{1}{1+B}\left(\frac{B}{B+1}\right), \tag{4.28}$$

where

$$B=\sum_{\nu}\langle n_\nu\rangle_{\mathrm{T}}|v_\nu(t)|^2\simeq\langle n\rangle_{\mathrm{T}}(1-|u(t)|^2)=\langle n\rangle_{\mathrm{T}}(1-\exp(-2\gamma t)). \tag{4.29}$$

Equations (4.28 and 4.29) provide us with the time dependence of the population of the oscillator initially located in the ground state. As $t\to\infty(u(t)\to 0)$ the equation (4.28) goes over to the known equilibrium form of the diagonal matrix elements of ρ_{osc} in the n-representation. It is also easy to show that the non-diagonal matrix elements vanish in this limit, thus exhibiting the diagonal nature of the oscillator's density operator in the n representation at thermal equilibrium.

4.4. *Heating by a coherent field*

If the external field may be described as a multimode coherent (Glauber) field we have instead of equation (4.20)

$$\rho_B=\prod_{\nu}|\beta_\nu\rangle\langle\beta_\nu|, \tag{4.30}$$

where β_ν is given by equation (4.20 *a*).

We start again from the ground state $|0\rangle$ of the oscillator and consider its time evolution. A procedure identical to that utilized in the thermal case leads now to

$$\rho_{\mathrm{osc}}(t)=\left|\sum_{\nu}\beta_\nu v_\nu(t)\right\rangle\left\langle\sum_{\nu}v_\nu(t)\beta_\nu\right| \tag{4.31}$$

so that the oscillator is excited into a coherent state of increasing amplitude. The probability for finding the oscillator at the mth level at time t is now given by the usual Poisson distribution

$$P_m(t)=\frac{|\delta|^{2m}}{m!}\exp[-|\delta|^2]\,;\quad \delta=\sum_{\nu}v_\nu(t)\beta_\nu. \tag{4.32}$$

This result is of little interest for phonon assisted excitation, however, it may be of considerable interest for the study of infra-red induced vibrational excitation.

5. VIBRATIONAL RELAXATION AND INFRA-RED EMISSION

Up to this point we have considered non-radiative vibrational relaxation (and thermal excitation) of a harmonic molecule disregarding the interaction of the system with the radiation field. When the vibrational mode of the oscillator is infra-red active, photon absorption and emission can take place simultaneously with thermal vibrational relaxation and excitation process. This problem is of interest because of several reasons : (*a*) The simultaneous interaction of the molecular oscillator with the radiation field and with the phonon bath provides a simple example for the decay of a metastable state into two continua, which was popular in the theory of electronic relaxation. (*b*) The simplified physical system of a harmonic oscillator, which consists of an equidistant spectrum raises some interesting problems concerning the features of the radiative decay. The radiative decay width of the nth state is proportional to n, while for large n the correspondence principle implies that this width should be independent of n. This harmonic oscillator paradox was discussed by Weisskopf and Wigner [15] (for a special case $n=2$) and by Zeldovich *et al.* [16].

It is easy to incorporate the effects of the radiative interactions on the decaying oscillator. The total hamiltonian of the system subjected both to vibrational relaxation and radiative decay is taken as

$$H=\hbar\omega a^{+}a+\sum_{\nu}\hbar\omega_{\nu}b_{\nu}^{+}b_{\nu}+\sum_{\mathbf{v}}\hbar(G_{\mathbf{v}}B_{\mathbf{v}}a^{+}+G_{\mathbf{v}}^{*}B_{\nu}^{+}a)+\sum_{\lambda}\hbar\omega_{\lambda}f_{\lambda}^{+}f_{\lambda} \\ +\sum_{\lambda}\hbar(g_{\lambda}f_{\lambda}^{+}a+g_{\lambda}^{*}f_{\lambda}a^{+}), \tag{5.1}$$

where the photon field is characterized by the creation operators f_{λ}^{+} and the annihilation operators f_{λ} and by the frequencies ω_{λ} (the index $\boldsymbol{\lambda}$ specifies the energy and the polarization of a photon). g_{λ} represents the coupling between the oscillator and the λth radiation field mode. In the model hamiltonian (5.1) we have neglected the coupling between the radiation field and the medium phonons. This coupling will result in a parallel decay channel for the harmonic oscillator. This problem is soluble within the framework of the Wigner–Weisskopf approximation [15], however, the solution is rather cumbersome and does not contribute to the problem at hand.

Following the procedure outlined in § 2 the equations of motion for the operators of the harmonic oscillator and of the two fields take the simple form

$$\dot{a}=-i\omega a-i\sum_{\mathbf{v}}G_{\mathbf{v}}B_{\mathbf{v}}-i\sum_{\lambda}g_{\lambda}f_{\lambda}, \tag{5.2 a}$$

$$\dot{B}_{\mathbf{v}}=-i\omega_{\mathbf{v}}B_{\mathbf{v}}-in_{\mathbf{v}}G_{\mathbf{v}}^{*}a, \tag{5.2 b}$$

$$\dot{f}_{\lambda}=-i\omega_{\lambda}f_{\lambda}-ig_{\lambda}^{*}a. \tag{5.2 c}$$

The solution for the harmonic oscillator operators takes the form

$$a(t)=u(t)a+\sum_{\mathbf{v}}v_{\mathbf{v}}(t)B_{\mathbf{v}}+\sum_{\lambda}w_{\lambda}(t)f_{\lambda}, \tag{5.3}$$

where the functions in (5.3) are (see Appendix B)

$$u(t)=\exp(-i\tilde{\omega}t-\tilde{\gamma}t), \tag{5.4 a}$$

$$v_{\mathbf{v}}(t)=\frac{-iG_{\mathbf{v}}}{i(\omega'-\omega_{\mathbf{v}})-\tilde{\gamma}}[\exp(-i\omega_{\mathbf{v}}t)-\exp(-i\omega't-\tilde{\gamma}t)], \tag{5.4 b}$$

$$W_{\lambda}(t)=\frac{-ig_{\lambda}}{i(\omega'-\omega_{\lambda})-\tilde{\gamma}}[\exp(-i\omega_{\lambda}t)-\exp(-i\omega't-\tilde{\gamma}t)]. \tag{5.4 c}$$

The frequency

$$\tilde{\omega}=\omega+\delta\tilde{\omega} \tag{5.5}$$

is now modified in terms of the level shift

$$\delta\tilde{\omega}=PP\sum_{\mathbf{v}}\frac{|G_{\mathbf{v}}|^{2}n_{\mathbf{v}}}{\omega-\omega_{\mathbf{v}}+i\eta}+PP\sum_{\lambda}\frac{|g_{\lambda}|^{2}}{\omega-\omega_{\lambda}+i\eta} \tag{5.6}$$

while the total width $\tilde{\gamma}$ is

$$\tilde{\gamma}=\gamma+\gamma_{\mathrm{IR}} \tag{5.7}$$

where the vibrational relaxation width γ is given by equation (3.34) while the radiative width is

$$\gamma_{\mathrm{IR}}=\pi \sum_{\lambda} |g_{\lambda}|^2\delta(\omega-\omega_{\lambda}). \tag{5.8}$$

Equations (5.3)–(5.8) describe the parallel non-radiative and radiative decay of the oscillator into two independent continua whereupon the total width is just given as the sum of the independent contributions from two decay channels.

It is straightforward matter to generalize the results of § 2 to incorporate the effects of radiative decay. Some of the pertinent results can be summarized as follows :

(*a*) Consider a harmonic oscillator initially at the state $|n\rangle$ interacting with a phonon bath and with a photon field both in thermal equilibrium at a temperature T. The decay of the average population is immediately obtained from equation (4.6) in the form

$$n(t)=n \exp\left[-2(\gamma+\gamma_{\mathrm{IR}})t\right]+(1-\exp\left[-2(\gamma+\gamma_{\mathrm{IR}})t\right])\langle n\rangle_{\mathrm{T}}. \tag{5.9}$$

(*b*) Consider the decay of an initially prepared state $|n, \prod_{\nu} 0_{\nu}, \prod_{\lambda} 0_{\gamma}\rangle$ where the phonon bath is at $T=0$ while all the occupation numbers of the photon field are $n_{\lambda}=0$. The probability for finding the oscillator in the m state $(m<n)$ at a time t is immediately obtained from equation (4.18).

$$P(m, n\,;\; t)=\frac{m!}{(m-n)!n!}\exp(-2n\tilde{\gamma}t)[1-\exp(-2n\tilde{\gamma}t)]^{m-n}. \tag{5.10}$$

(*c*) The optical line shape for absorption at $T=0$ is :

$$L(E)\propto -\operatorname{Im}\langle 0_{\mu}, 0_{\nu}, 1_{\lambda}|V_{\mathrm{T}}G(E)V_{\mathrm{r}}|0_{\mu}, 0_{\nu}, 1_{\lambda}\rangle,$$

where $G(E)$ is the Green's function for the system and V_{r} represents the radiative interaction. Linear response theory yields

$$L(E)\propto -\operatorname{Im}\left[i\int_{0}^{\infty} \exp(iEt)\langle 0|a(0)a^{+}(t)|0\rangle\, dt\right]. \tag{5.11}$$

Utilizing equations (3.26) and (3.29) we get

$$L(E)\propto \frac{\tilde{\gamma}}{(E-\omega)^2+\tilde{\gamma}^2}. \tag{5.12}$$

Thus the general optical line shape is lorentzian being determined by the total width $\tilde{\gamma}$. This result provides an alternative route for resolving the harmonic oscillator paradox as consecutive absorption occurs for all equidistant levels.

(*d*) The optical line shape for emission may be obtained by considering the oscillator in an initial state $|n\rangle$, given the radiation field and the medium phonon bath in a vacuum state. The observable of interest is now the population $n_\lambda(t)$ of a radiation field mode $\boldsymbol{\lambda}$ at time t. This is given by

$$n_\lambda(t) = \left\langle n, \prod_\nu 0_\nu, \prod_\lambda 0_\lambda | f_\lambda^+(t) f_\lambda(t) | n, \prod_\nu 0_\nu, \prod_\lambda 0_\lambda \right\rangle. \tag{5.13}$$

It may be asserted (see Appendix B) that $f_\lambda(t)$ is given in our model by

$$f_\lambda(t) = W_\lambda a + \sum_{\lambda'} X_{\lambda\lambda'} f_{\lambda'} + \sum_\nu Y_{\lambda\nu} b_\nu, \tag{5.14}$$

where W_λ is given by equation (5.4 c) and where $X_{\lambda\lambda'}$ and $Y_{\lambda\nu}$ are some other functions of t. Inserting this expression for $f_\lambda(t)$ into equation (5.13) and utilizing equation (5.4 c) we obtain

$$n_\lambda(t) = n|W_\gamma|^2 = n \frac{|g_\lambda|^2}{(\omega' - \omega_\lambda)^2 + \tilde{\gamma}^2} [1 + \exp(-2\tilde{\gamma}t) - 2\exp(-\tilde{\gamma}t)\cos((\omega' - \omega_\lambda)t)]. \tag{5.15}$$

The line shape for emission $L(E) = \rho_\lambda n_\lambda(t)$ (where ρ_λ is the density of states in the photon field) takes the form

$$L(E) = \frac{1}{\pi} n \frac{\gamma_{\rm IR}}{(\omega' - \omega_\lambda)^2 + \tilde{\gamma}^2} [1 - \exp(-2\tilde{\gamma}t) - 2\exp(-\tilde{\gamma}t) \times \cos[(\omega' - \omega_\lambda)t]] \tag{5.16}$$

which for sufficiently long times exhibits again the lorentzian lineshape (5.12)

6. DISCUSSION

In this paper we have advanced a unified approach for the study of vibrational relaxation in a dense medium. When the rotating wave and the random phase approximations are invoked, both single phonon and multiphonon vibrational relaxation processes can be incorporated within the same scheme. The disadvantages of the present approach are :

(a) The harmonic approximation is used both for the molecule and the medium.

(b) The coupling terms G_ν are introduced as parameters of the theory so that no attempt is made to calculate numerically the generalized level width γ (equation (3.34)) which determines the features of the vibrational relaxation.

(c) No attempt was made to consider medium induced intramolecular energy redistribution.

From the experimental point of view vibrational relaxation times vary from ~ 1 sec for a diatomic molecule ($^3\Sigma_u$ state of N_2) in low temperature rare gas solids [5], to ~ 1 nsec for the ground electronic state of some polyatomic molecules (liquid benzene at $T \approx 300$ K) [21] and to ~ 6 psec for excited electronic states of large molecules (Rhodamine 6G) in a polyatomic solvent [6]. Obviously, vibrational relaxation of a high frequency molecular vibration in a monoatomic solid involves a high order multiphonon process where the corresponding coupling G_ν

terms are very small. When vibrational relaxation in a polyatomic dense host medium takes place the participation of the medium vibrons reduces the order of the multiphonon process leading to an efficient pathway for the relaxation process. The role of the medium vibrons will be also crucial for vibrational relaxation in an excited electronic state of a pure molecular crystal or in a one component liquid or glass where near resonance intermolecular electronic energy transfer leading to a vibrationally excited ground state molecule may occur.

The vibron–phonon relaxation mechanism may also partially account for some features of intramolecular energy redistribution involving the interaction terms $(a_\mu{}^+ a_{\mu'} b_\nu + \text{h.c.})$. In this case the μ'th intramolecular vibration may be viewed as a vibron, with the following restrictions :

(*a*) First, it must be assumed (as is usually the case) that these molecular vibrations are in thermal equilibrium. (*b*) Second, we have to limit ourselves to the relaxation of a single μ molecular vibration while the transient population of the μ' vibrational modes are not taken into account. Thus all the μ' molecular vibrations and the lattice modes are taken as a common heat bath for the relaxation of a single molecular mode. This point of view is useful when a single molecular vibrational mode is initially excited (optically in the ground or in the electronically excited state) and we can monitor the decay of this mode. This approach may be also of interest in the study of energy redistribution in organic photochemical processes.

Finally, we would like to point out that the theoretical scheme developed herein was recently applied by us for the study of the coupling between electronic relaxation and vibrational relaxation in excited electronic states of large molecules [22].

APPENDIX A : TREATMENT OF THE COOLING PROCESS BY THE APPLICATION OF COHERENT STATE REPRESENTATION

A considerable simplification of the formulation of the cooling process (§ 4.2) may be achieved by utilizing Glauber's coherent state representation. To demonstrate this possibility we shall formulate the cooling processes in this representation, where for the sake of simplicity, only case (*a*) will be considered.

The important feature of the coherent states, from our point of view, is that given the oscillator and the bath modes initially in coherent states $|\alpha\rangle$ and $|\beta_\nu\rangle$, these states evolve under the hamiltonian equation (2.3 *a*) to give the coherent states $|\alpha\rangle$ and $|\beta_\nu\rangle$ [12], where the (complex) amplitudes $\alpha(t)$ and $\beta_\nu(t)$ are determined by a set of equations analogous to the set (3.1, 2)

$$\left.\begin{aligned} \dot{\alpha}(t) &= -i\omega\alpha(t) - i\sum_\nu G_\nu\beta_\nu(t), \\ \dot{\beta}_\nu(t) &= -i\omega_\nu\beta_\nu(t) - iG_\nu{}^*\alpha(t), \end{aligned}\right\} \tag{A 1}$$

whose solution is given by (in analogy to the solution (3.26)).

$$\left.\begin{aligned} \alpha(t) &= u(t)\alpha + \sum_\nu v_\nu(t)\beta_\nu, \\ \beta_\nu(t) &= v_\nu(t)\alpha + \sum_{\nu'} y_{\nu\nu'}(t)\beta_{\nu'} \end{aligned}\right\} \tag{A 2}$$

where $u(t)$ and $v_\nu(t)$ are given by equations (3.27)–(3.28). With these relations at hand we start with the density matrix at time $t=0$ with the oscillator at the state $|m\rangle$ and the medium at $T=0$

$$\rho(0)=\left|\, m\rangle \left(\prod_\nu |0_\nu\rangle\langle 0_\nu|\right) \langle m \,\right| = \frac{1}{\pi^2}\int\int d^2\alpha d^2\gamma \langle\alpha|m\rangle \times \langle m|\gamma\rangle |\alpha\rangle\langle\gamma| \left(\prod_\nu |0_\nu\rangle\langle 0_\nu|\right). \qquad \text{(A 3)}$$

The density matrix at time t may be simply obtained by replacing $|\alpha\rangle$ by $|\alpha(t)\rangle=|\alpha u(t)\rangle$ (as $\beta_\nu=0$) and $|0_\nu\rangle=|\beta_\nu\rangle$ by $|\beta_\nu(t)\rangle=|\alpha v_\nu(t)\rangle$ so that the density matrix at time t takes the form

$$\rho(t)=\frac{1}{\pi^2}\int\int d^2\alpha d^2\gamma \langle\alpha|m\rangle\langle m|\gamma\rangle |\alpha u(t)\rangle\langle\gamma u(t)| \prod_\nu |\alpha v_\nu(t)\rangle\langle\gamma v_\nu(t)|. \qquad \text{(A 4)}$$

Taking the trace over the medium states we obtain the reduced density matrix for the oscillator

$$\rho_{\text{osc}}(t)=\frac{1}{\pi^2}\int\int d^2\alpha d^2\gamma \langle\alpha|m\rangle\langle m|\gamma\rangle \left(\prod_\nu \langle\gamma v_\nu(t)|\alpha v_\nu(t)\rangle\right) \times |\alpha u(t)\rangle\langle\gamma u(t)|. \qquad \text{(A 5)}$$

The probability to find the oscillator at time t in the state $|n\rangle$ is

$$\langle m|\rho|m\rangle = P(m,n\,;\,t)=\frac{1}{\pi^2}\int\int d^2\alpha d^2\gamma \langle\alpha|m\rangle\langle m|\gamma\rangle \times \langle n|\alpha u(t)\rangle\langle\beta u(t)|n\rangle \prod_\nu (\langle\beta v_\nu(t)|\alpha v_\nu(t)\rangle) \qquad \text{(A 6)}$$

making use now of the following relations for the scalar products between coherent states and between a coherent and a n-state

$$\langle\alpha|\beta\rangle=\exp\{\alpha^*\beta-\tfrac{1}{2}|\alpha|^2-\tfrac{1}{2}|\beta|^2\}, \qquad \text{(A 7)}$$

$$\langle\alpha|n\rangle=\exp(-\tfrac{1}{2}|\alpha|^2)\frac{\alpha^n}{n!}. \qquad \text{(A 8)}$$

Equation (A 6) may be recast in the form

$$\langle m|\rho|m\rangle=\frac{1}{n!m!\pi^2}\int\int d^2\alpha d^2\gamma \left\{\exp[-\tfrac{1}{2}|\alpha|^2(1+|u|^2) -\tfrac{1}{2}|\beta|^2(1+|u|^2)](\alpha^*)^m\gamma^m(\alpha u)^n(\beta^* u^*)^n \exp\left[\sum_\nu \gamma^*\alpha|v_\nu|^2 -\tfrac{1}{2}|\alpha|^2|v_\nu|^2-\tfrac{1}{2}|\gamma|^2|v_\nu|^2\right]\right\}. \qquad \text{(A 9)}$$

Inserting the relation equation (3.35)) $\sum_\nu |v_\nu(t)|^2=1-|u(t)|^2$ we obtain

$$P(m, n\,;\ t)=\frac{|u|^2}{n!m!\pi^2}\int d^2\alpha d^2\gamma \exp\left[-|\alpha|^2-|\gamma|^2 + \gamma^*\alpha(1-|u|^2)\right](\alpha^*)^m\alpha^n\beta^m(\beta^*)^n \qquad \text{(A 10)}$$

expanding now

$$\exp(\beta^*\alpha(1-|u|^2)=\sum_{l=0}^{\infty}\frac{1}{l!}(\beta^*)^l\alpha^l(1-|u|^2)^l \qquad \text{(A 11)}$$

and making use of the relation

$$\int d^2\alpha \exp(-|\alpha|^2)(\alpha^*)^m\alpha^{n+i}=m!\pi\delta_{m,\,n+l} \qquad \text{(A 12)}$$

we readily obtain

$$P(m, n\,;\ t)=\frac{m!}{n!(m-n)!}|u|^2(1-|u|^2)^{m-n} \qquad \text{(A 13)}$$

which is equivalent to equation (4.18).

APPENDIX B: SOLUTION OF EQUATION (5.2)

Starting from the set of coupled differential equations, equation (5.2) and following closely the procedure outlined by equations (3.17)–(3.28) we easily obtain

$$a(s)=u(s)a+\sum_{\nu}v_\nu(s)B_\nu+\sum_{\lambda}w_\lambda(s)f_\lambda, \qquad \text{(B 1)}$$

where

$$u(s)=\left[s+i\omega+\sum_{\nu}\frac{|G_\nu|^2n_\nu}{s+i\omega_\nu}+\sum_{\lambda}\frac{|g_\lambda|^2}{s+i\omega_\lambda}\right]^{-1}, \qquad \text{(B 2 \textit{a})}$$

$$v_\nu(s)=-iG_\nu\left[(s+i\omega_\nu)\left(s+i\omega+\sum_{\nu}\frac{|G_\nu|^2n_\nu}{s+i\omega_\nu}+\sum_{\lambda}\frac{|g_\lambda|^2}{s+i\omega_\lambda}\right)\right]^{-1}, \qquad \text{(B 2 \textit{b})}$$

$$W_\lambda(s)=-ig_\lambda\left[(s+i\omega_\lambda)\left(s+i\omega+\sum_{\nu}\frac{|G_\nu|^2n_\nu}{s+i\omega_\nu}+\sum_{\lambda}\frac{|g_\lambda|^2}{s+i\omega_\lambda}\right)\right]^{-1} \qquad \text{(B 2 \textit{c})}$$

so that, taking the inverse Laplace transform, equations (5.3)–(5.4) are obtained. We note that inserting equation (B 1) into the Laplace transform of equation (5.2 *c*)

$$f_\lambda(s)=\frac{1}{s+i\omega_\lambda}f_\lambda-\frac{ig_\nu}{s+i\omega_\lambda}a(s) \qquad \text{(B 3)}$$

we obtain

$$\begin{aligned} f_\lambda(s)&=\frac{1}{s+i\omega_\lambda}f_\lambda-\frac{ig_\lambda{}^*}{s+i\omega_\lambda}\left[u(s)a+\sum_{\nu}v_\nu(s)b_\nu+\sum_{\lambda'}W_{\lambda'}(s)f_\lambda\right]\\ &=\frac{ig_\lambda{}^*}{s+i\omega_\lambda}u(s)a+\sum_{\lambda'}X_{\lambda\lambda'}(s)f_\lambda+\sum_{\nu}Y_{\lambda\nu}(s)b_\nu \end{aligned} \qquad \text{(B 4)}$$

which, taking the inverse transform, leads to equation (5.14) where W_λ is given by equation (5.4 *c*). (Note that g_λ is replaced by g_κ^* which has no consequences for the results equations (5.15) and (5.16)).

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