On the coupling between vibrational relaxation and molecular electronic transitions†

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Vibrational relaxation of a harmonic molecule in contact with its surrounding medium is studied, and its effect on the electronic relaxation rate in such molecules is examined. Results of earlier works which considered harmonic phonon models for the medium are extended to the case of a general thermal bath. The formal expression for the vibrational relaxation rate is modified but the general form of the final results for the electronic and vibrational time evolution is shown to remain intact.

1. INTRODUCTION

The coupling between electronic and vibrational relaxation processes in molecular systems has become a subject of much experimental and theoretical concern [1–6]. Effects of this coupling are negligible when either one of these processes is much faster than the other. Thus electronic relaxation is usually studied in the isolated molecule [7] limit (where the decay rate of a single vibronic level is considered) or in the fast vibrational relaxation limit [8] (where this decay rate is averaged over a Boltzmann distribution of vibrational levels). When both electronic and vibrational relaxations occur on the same time scale, they can no longer be considered separately and a theory which describes the evolution of the system under both relaxation processes should be provided. Experimentally this situation occurs in gas phase studies of radiative or radiationless electronic transitions under intermediate pressure conditions, or in dense-phase studies of fast electronic relaxation processes. (By ‘ fast ’ we mean rates comparable to vibrational relaxation rates in dense phases, i.e., 10^{11}–10^{12} sec^{-1} for large molecules.)

Theoretical studies of this problem have been recently published by several workers [2–6]. In particular Lin [4] and also Heller and Freed [5] have considered stochastic models in which transition probabilities between the different vibronic levels are taken as input data, thus providing a kinetic scheme from which the time evolution of observables (like fluorescence intensity) and quantum yields may be calculated. On the other hand, Nitzan and Jortner [7] have provided a quantum mechanical theory in which electronic transition rates and lineshapes are calculated from a given model Hamiltonian. In this theory the

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vibrational relaxation is introduced via a coupling between the molecular vibrations and a bath of harmonic oscillators. In this form the theory is limited to describing electronic–vibrational relaxation of a molecule imbedded in a dense medium which may be modelled as a phonon bath.

In this note we extend the Nitzan–Jortner theory to account for processes occurring in a general medium. We show that the assumption that the medium may be represented by a phonon bath may be relaxed without altering the forms of the expressions obtained for the vibrational and the electronic relaxation processes. The results obtained in NJ1[6a] and in NJ2[6b] are thus shown to be valid in any medium (within the framework of the models described in these papers).

2. Review of previous results

The model applied by Nitzan and Jortner [6] is characterized by the following assumptions :

(a) Assumptions concerning the medium :
  (i) The medium is represented by a harmonic phonon bath.
  (ii) The medium states are not modified by the electronic transition in the impurity molecule.
  (iii) The medium does not modify the molecular energy levels and the intramolecular coupling (or the molecule–radiation field coupling).

(b) Assumptions concerning the molecule :
  (i) A two electronic state system is sufficient for describing the electronic transition.
  (ii) Only one electronic state is initially populated. (This will be the ground state when absorption lineshape is considered or the initially excited state when radiationless transition rates are calculated.)
  (iii) Harmonic molecular vibrations.
  (iv) The normal modes and their frequencies are identical in the two electronic states. Potential surfaces are displaced in the electronic transitions.
  (v) The molecule is large and corresponds to the statistical limit. (The case of small molecule can be described within the present model in the fast vibrational relaxation limit.)
  (vi) Interference effects (which arise when vibronic states in the initial electronic manifold are effectively coupled to the same final states) are neglected.
  (vii) The condon approximation or its modification is invoked in calculating the vibronic coupling.

(c) Assumptions concerning the molecule medium interaction :
  (i) The molecule medium interaction is taken to be the lowest-order product of molecule and medium coordinates which is capable of inducing an energy conserving transition.
  (ii) The molecule medium interaction is simplified by invoking the rotating wave approximation.

(iii) Interference effects (which arise when two vibrational modes are coupled to the same medium modes) are disregarded.

Within the framework of this model the electronic transition rate takes the form

$$W_S = \frac{2}{\hbar^2} \mathrm{Re} \int_0^\tau d\tau \exp\left[i(\tau - \tau')\frac{\Delta E}{\hbar}\right] G(\tau, \tau'),\qquad (1)$$

where ΔE is the electronic energy gap and where the time correlation function $G(\tau, \tau')$ is given by

$$G(\tau, \tau') = \sum_\kappa |C_{sl}{}^\kappa|^2 \langle J_\kappa \prod_{\mu \neq \kappa} g_\mu \rangle_\mathrm{T}.\qquad (2)$$

Here $C_{sl}{}^\kappa$ are electronic matrix elements between the two electronic states s and l, $\langle \ \rangle_\mathrm{T}$ denotes thermal average over medium states and g_μ and J_κ are single oscillator matrix elements given in terms of the matrix element

$$I_\mu = \langle m_{s_\mu}| \exp\{-(\Delta_\mu/\sqrt{2})[a_\mu{}^\dagger(\tau) - a_\mu(\tau)]\} \exp\{(K_\mu/\sqrt{2})$$
$$\times [a_\mu{}^\dagger(\tau') - a_\mu(\tau')]\}|m_{s_\mu}\rangle,\qquad (3)$$

by

$$\left.\begin{array}{l} g_\mu = I_\mu(K_\mu = \Delta_\mu), \\[2mm] J_\kappa = (\partial^2 I_\kappa/\partial\Delta_\kappa\partial K_\kappa) \quad \Delta_\kappa = K_\kappa = 0. \end{array}\right\}\qquad (4)$$

in which m_{s_μ} is the initial population of the molecular vibrational mode μ in the initial electronic state s. $a_\mu{}^\dagger$ and a_μ are creation and annihilation operators for the mode μ and Δ_μ denotes the reduced origin displacement of this mode. κ is the index of the promoting modes of the particular electronic transition. It is assumed that $\Delta_\kappa = 0$. Finally, for any nuclear operator A ($A = a_\mu, a_\mu{}^\dagger$), $A(t)$ stands for the time dependent operator

$$A(t) = \exp\left(iH\frac{t}{\hbar}\right) A \exp\left(-H\frac{t}{\hbar}\right),\qquad (5)$$

where

$$H = \sum_\mu \hbar\omega_\mu a_\mu{}^\dagger a_\mu + \sum_\nu \hbar\omega_\nu b_\nu{}^\dagger b_\nu + H_\mathrm{int},\qquad (6)$$

in which $b_\nu{}^\dagger$ and b_ν are creation and annihilation operators for the νth medium mode, ω_μ and ω_ν are frequencies of the molecular and medium phonons, respectively, and H_int is the molecule medium interaction which induces the vibrational relaxation. Its general form is

$$H_\mathrm{int} = \sum_\mu \sum_\nu \hbar(G_\nu{}^\mu a_\mu{}^\dagger B_\nu + G_\nu{}^{\mu*} a_\mu B_\nu)^\dagger,\qquad (7)$$

where ν is a vector which corresponds to a group of medium phonons $\nu_1, \nu_2, \ldots,$ $G_\nu{}^\mu$ are coupling terms, and B_ν are products of medium operators

$$B_\nu = b_{\nu_1} b_{\nu_2}\cdots.\qquad (8)$$

The matrix elements g_μ and J_κ may be calculated once expressions for $a_\mu^\dagger(\tau)$ and $a_\mu(\tau)$ are available. Obtaining such expressions is equivalent to solving the vibrational relaxation problem. For a molecule imbedded in a dense medium this was done in NJ1, resulting in

$$a_\mu(t) = u_\mu(t)a_\mu + \sum_\nu v_\nu{}^\mu(t)B_\nu, \tag{9}$$

where the functions $u_\mu(t)$ and $v_\nu{}^\mu(t)$ are given by

$$u_\mu(t) = \exp\left[-i\omega_\mu't - \gamma_\mu t\right] \tag{10}$$

$$v_\nu{}^\mu(t) = \frac{-iG_\nu{}^\mu}{i(\omega_\mu' - \omega_\nu) - \gamma_\mu}\left[\exp\left(-i\omega_\nu t\right) - \exp\left(-i\omega_\mu't - \gamma_\mu t\right)\right], \tag{11}$$

in which

$$\omega_\mu' = \omega_\mu + \delta\omega_\mu, \tag{12}$$

$$\delta\omega_\mu = PP\sum_\nu \frac{|G_\nu{}^\mu|^2 n_\nu}{\omega_\mu - \omega_\nu}, \tag{13}$$

$$\gamma_\mu = \prod\sum_\nu |G_\nu{}^\mu|^2 n_\nu \delta(\omega_\mu - \omega_\nu), \tag{14}$$

$$n_\nu = \langle[B_\nu \cdot B_\nu^\dagger]\rangle_T, \tag{15}$$

and finally

$$\omega_\nu = \sum_i \omega_{\nu_i} \tag{16}$$

Equations (2)–(4) and (9)–(11) can now be utilized to yield the final result for the correlation function $G(\tau, \tau')$ [NJ2 equation (VI.22)]

$$G(\tau, \tau') = \sum_\kappa |C_{sl}{}^\kappa|^2 \times \tfrac{1}{2}\{(\langle m_\kappa\rangle_T + 1)\exp\left[-i\omega_\kappa'(\tau - \tau') - \gamma_\kappa(\tau - \tau')\right]$$

$$+ \langle m_\kappa\rangle_T \exp\left[i\omega_\kappa'(\tau - \tau') - \gamma_\kappa(\tau - \tau')\right] + 2(m_{s\kappa} - \langle m_\kappa\rangle_T)$$

$$\times \exp\left[-\gamma_\kappa(\tau + \tau')\right]\cos\left[\omega_\kappa'(\tau - \tau')\right]\} \times \exp\left\{-\sum_\mu \tfrac{1}{2}\Delta_\mu{}^2\right.$$

$$+ \sum_\mu \tfrac{1}{2}\Delta_\mu{}^2 \exp\left[-i\omega_\mu'(\tau - \tau') - \gamma_\mu(\tau - \tau')\right]\}$$

$$\times \exp\left[-\sum_\mu \langle m_\mu\rangle_T(\tfrac{1}{2}\Delta_\mu{}^2[2 - \exp\left(-2\gamma_\mu\tau\right) - \exp\left(-2\gamma_\mu\tau'\right)]\right.$$

$$- \Delta_\mu{}^2\{\exp\left[-\gamma_\mu(\tau - \tau')\right] - \exp\left[-\gamma_\mu(\tau + \tau')\right]\}\cos\left[\omega_\mu'(\tau - \tau')\right])]$$

$$\times \prod_\mu\left[(m_{s\mu})!\sum_{r=0}^{m_{s\mu}} \frac{(-1)^r}{(m_{s\mu}-r)!(r!)^2}\left(\frac{\Delta_\mu}{\sqrt{2}}\right)^{2r} \times \{\exp\left(-2\gamma_\mu\tau\right)\right.$$

$$\left.+ \exp\left(-2\gamma_\mu\tau'\right) - 2\exp\left[-\gamma_\mu(\tau + \tau')\right]\cos\left[\omega_\mu'(\tau - \tau')\right]\}^r\right], \tag{17}$$

which together with equation (1) provides a convenient departure point for calculating the electronic transition rate as a function of molecular spectroscopical parameters $(\Delta_\mu, \omega_\mu', m_{s\mu})$ and vibrational relaxation rates (γ_μ).

3. Vibrational relaxation in a general medium

Equations (1)–(5) do not depend on the particular model for the medium. In what follows we repeat the calculation which leads to equations (9)–(16) for a general medium†, retaining however, assumptions (*a* ii), (*a* iii), (*c* ii) and (*c* iii). The medium Hamiltonian will now be represented by its spectral resolution.

$$H_{\text{medium}} = \sum_{\alpha} \sum_{\epsilon} \hbar\epsilon |\alpha, \epsilon\rangle \langle \epsilon, \alpha|, \tag{18}$$

where $|\alpha, \epsilon\rangle$ denotes an energy eigenstate of the medium : ϵ is the total medium energy (in frequency units) while α stands for other quantum numbers apart from energy which are necessary to characterize the medium eigenstates. We assume that the whole system (molecule + medium) is confined in a macroscopic finite box so that the medium energy states are discrete and normalizable

$$\langle \alpha' \epsilon' | \alpha\epsilon \rangle = \delta_{\alpha \alpha'} \delta_{\epsilon\epsilon'}. \tag{19}$$

According to assumption (*c* iii) the vibrational modes of the molecule can be considered separately in the vibrational relaxation process. The molecular Hamiltonian will be thus taken simply as that of a single harmonic oscillator

$$H_{\text{molecule}} = \hbar\omega_\mu a_\mu{}^\dagger a_\mu, \tag{20}$$

where, as before, $a_\mu{}^\dagger$ and a_μ are boson creation and annihilation operators. Finally the molecule medium operator is assumed to take the form

$$H_{\text{int}} = \sum_{E} \hbar(G_E{}^\mu a_\mu{}^\dagger B_E + G_E{}^{\mu*} a_\mu B_E{}^\dagger), \tag{21}$$

where $G_{E\mu}$ is a coupling parameter and where $B_E{}^\dagger$ and B_E are operators which add to or takes from the medium an amount of energy E. The general form of these operators is

$$B_E{}^\dagger = \sum_{\alpha'} \sum_{\alpha} \sum_{\epsilon} F(\epsilon) |\alpha', \epsilon + E\rangle \langle \epsilon, \alpha|, \tag{22}$$

$$B_E = \sum_{\alpha'} \sum_{\alpha} \sum_{\epsilon} F^*(\epsilon) |\alpha, \epsilon\rangle \langle \epsilon + E, \alpha'|, \tag{23}$$

where $F(\epsilon)$ is a function of the energy ϵ. In writing the form (21) for the molecule–medium interaction we assume that this interaction is of the form of a product between a coordinate of the molecular oscillator and some function of the medium coordinates. This function is then expanded in terms of the medium energy eigenstates, and finally we retain only terms which are capable of conserving energy (according to assumption (*c* ii)).

The following analysis is closely related to the analysis in NJ1 which leads to equations (9)–(16). The equations of motions for the operators α_μ and B_E are obtained from the general Heizenberg equation

$$A = \frac{i}{\hbar} [H, A], \tag{24}$$

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† A different but equivalent treatment of vibrational relaxation of a harmonic oscillator in a general medium has been recently provided by Nitzan and Silbey [9]. The present approach, however, is more readily applicable when the effect on electronic transitions is considered.

in which A is a_μ or B_E and

$$H = H_{\text{molecule}} + H_{\text{medium}} + H_{\text{int}}.$$ (25)

This leads to

$$\dot{a} = -i\omega a - i\sum_E G_E B_E,$$ (26 a)

$$\dot{B}_E = -iEB_E - ia\sum_{E'} G_{E'}{}^*[B_E, B_{E'}{}^\dagger],$$ (26 b)

where the index μ has been supressed as we deal here only with a single molecular vibration. We now linearize equation (26 b) by replacing the medium operator $[B_E, B_{E'}{}^\dagger]$ by its thermal average

$$[B_E, B_{E'}{}^\dagger] = n_E \delta_{EE'},$$ (27 a)

where

$$n_E = \langle [B_E, E_{E'}{}^\dagger] \rangle_T.$$ (27 b)

This is a random phase approximation on the medium which amounts to the assumption that processes in the medium are fast relative to the molecular vibrational relaxation. The linearized system of equations

$$\left.\begin{aligned} \dot{a} &= -i\omega a - i\sum_E G_E B_E \\ \dot{B}_E &= -iEB_E - iG_E{}^* n_E a \end{aligned}\right\}$$ (28)

is now identical in form to (NJ1–3.15) and is solved in the same way to yield

$$\left.\begin{aligned} a(t) &= u(t)a + \sum_E v_E(t)B_E, \\ a^\dagger(t) &= u^*(t)a^\dagger + \sum_E v_E{}^*(t)B_E{}^\dagger, \end{aligned}\right\}$$ (29)

where

$$u(t) = \exp\left[-i\omega't - \gamma t\right],$$ (30)

$$v_E(t) = \frac{iG_E}{i(E-\omega')+\gamma}\left[\exp\left(-iEt\right) - \exp\left(-i\omega't - \gamma t\right)\right],$$ (31)

$$\omega' = \omega + \delta\omega,$$ (32)

$$\delta\omega = PP\sum_E \frac{|G_E|^2 n_E}{\omega - E},$$ (33)

$$\gamma = \pi\sum_E |G_E|^2 n_E \delta(\omega - E).$$ (34)

Equations (29)–(34) are analogous to equations (9)–(14). In addition the commutation relation $[a(t), a^\dagger(t)] = 1$ leads to

$$|u(t)|^2 + \sum_E |v_E(t)|^2 n_E = 1,$$ (35)

which is analogous to (NJ1-3.37). Equations (29)–(35) provide a formal solution to the problem of vibrational relaxation of a harmonic oscillator in a general medium.

4. Time Evolution of the Population

Although the results (39)–(35) are highly formal and contain the unknown functions G_E and n_E, they may be used to obtain results for the time evolution of different observables of the vibrational relaxation process. In order to demonstrate this application we consider the time evolution of the population of the molecular oscillator. This is given by (NJ1-4.3) :

$$m(t) = |u(t)|^2 m(0) + \sum_E |v_E(t)|^2 \langle B_E{}^\dagger B_E \rangle_\mathrm{T}, \tag{36}$$

where $m(t)$ is the population of the molecular oscillator at time t. Utilizing equation (27 b), the second term in the right-hand side of equation (36) may be recast in the form

$$\sum_E |v_E(t)|^2 n_E M(E, T) \tag{37}$$

where

$$M(E, T) = \frac{\langle B_E{}^\dagger, B_E \rangle_\mathrm{T}}{\langle [B_E, B_E{}^\dagger] \rangle_\mathrm{T}}. \tag{38}$$

$|V_E(t)|^2$ as a function of E is, according to equation (31), sharply peaked around $E = \omega'$ (as the relation γ/ω' is of the order $\sim 10^{-3}$). Therefore, we can approximate the expression (37) by taking the function $M(E, T)$ outside the sum at the point $E = \omega'$. This enables us to apply the sum rule (35) and finally leads to

$$m(t) \simeq |u(t)|^2 m(0) + (1 - |u(t)|^2) M(\omega', T). \tag{39}$$

To obtain an explicit form for the function $M(E, T)$ defined by equation (38) we utilize equations (22), (23) and (19) to obtain

$$B_E{}^\dagger B_E = \sum_\alpha \sum_{\alpha'} \sum_\epsilon |F(\epsilon)|^2 g(\epsilon) |\alpha, \epsilon + E\rangle \langle \epsilon + E, \alpha'|, \tag{40 a}$$

$$B_E B_E{}^\dagger = \sum_\alpha \sum_{\alpha'} \sum_\epsilon |F(\epsilon)|^2 g(\epsilon + E) |\alpha, \epsilon\rangle \langle \epsilon \alpha'|, \tag{40 b}$$

where

$$g(\epsilon) = \sum_\alpha \langle \alpha, \epsilon | \epsilon, \alpha \rangle \tag{41}$$

is the degeneracy of the energy level ϵ of the medium. Taking thermal (Boltzmann) average of equations (40 a) and (40 b) over the medium states, using again equation (19), we arrive at

$$\langle B_E{}^\dagger B_E \rangle_\mathrm{T} = \sum_\epsilon \exp[-\beta(\epsilon + E)] g(\epsilon) g(\epsilon + E) |F(\epsilon)|^2, \tag{42}$$

and

$$\langle B_E B_E{}^\dagger \rangle_\mathrm{T} = \sum_\epsilon \exp(-\beta \epsilon) g(\epsilon) g(\epsilon + E) |F(\epsilon)|^2$$

$$= \langle B_E{}^\dagger B_E \rangle_\mathrm{T} \exp(\beta E), \tag{43}$$

where

$$\beta = \frac{1}{k_B T}.$$ (44)

Equations (38) and (42)–(43) now yield

$$M(E, T) = \left(\frac{\langle B_E B_E^\dagger \rangle_T}{\langle B_E^\dagger B_E \rangle_T} - 1 \right)^{1}$$

$$= [\exp(\beta E) - 1]^{1}.$$ (45)

Utilizing equations (30), (39) and (45) we finally obtain

$$m(t) \cong \exp(-2\gamma t)m(0) + [1 - \exp(-2\gamma t)][\exp(\beta\omega') - 1]^{-1},$$ (46)

which is the usually accepted expression for thermal relaxation of vibrational population of a harmonic oscillator. The result (46) enables us to identify the quantity γ, defined formally by equation (14), with the experimentally observable vibrational relaxation rate.

5. Calculation of the electronic transition rate

Our aim is to show that our present approach which leads to the results (29)–(34) instead of the results (9)–(14) obtained for a harmonic medium, yields the same final expression for the correlation function $G(\tau, \tau')$ as expression (17) which was obtained in NJ2. To this end we note that all we have to prove is that the result [NJ2, (VI.18)–(VI.21)] for the thermally averaged matrix element $\langle I_\mu \rangle_T$ (equation (3)) is conserved in our present approach. The following derivation is similar to that presented in Appendix C of NJ2†, but differs from it as we cannot utilize boson algebra for the medium operators.

Starting from equation (3) we use the fact that the equal time operators $a_\mu^\dagger(\tau)$, $a_\mu(\tau)$ commute like boson operators to obtain

$$I_\mu = \langle m_{s\mu}| \exp\left[-\frac{\Delta_\mu}{\sqrt{2}} a_\mu^\dagger(\tau) \right] \exp\left[\frac{\Delta_\mu}{\sqrt{2}} a_\mu(\tau) \right] \exp\left[\frac{K_\mu}{\sqrt{2}} a_\mu^\dagger(\tau') \right]$$

$$\times \exp\left[-\frac{K_\mu}{\sqrt{2}} a_\mu(\tau') \right] |m_{s\mu}\rangle \exp\left[-\tfrac{1}{4}(\Delta_\mu^2 + K_\mu^2) \right].$$ (47)

Inserting equation (9), this expression for I_μ is recast in the form

$$I_\mu = S_\mu \tilde{P}_\mu,$$ (48)

where

$$S_\mu = \exp\left[-\tfrac{1}{4}(\Delta_\mu^2 + K_\mu^2) \right] \langle m_{s\mu}| \exp\left(-\frac{\Delta_\mu}{\sqrt{2}} u_\mu^*(\tau) a_\mu^\dagger \right)$$

$$\times \exp\left(\frac{\Delta_\mu}{\sqrt{2}} u_\mu(\tau) a_\mu \right) \exp\left(\frac{K_\mu}{\sqrt{2}} u_\mu^*(\tau') a_\mu^\dagger \right) \exp\left(-\frac{K_\mu}{\sqrt{2}} u_\mu(\tau') a_\mu \right) |m_{s\mu}\rangle$$ (49)

† Note that equation (NJ2–C2) is in error. It should read

$$\langle I_\mu \rangle_T = \exp\{ -\tfrac{1}{4}\Delta_\mu^2 + \tfrac{1}{4}K_\mu^2 + \tfrac{1}{2}K_\mu\Delta_\mu u_\mu^*(\tau')u_\mu(\tau) \} \times \text{medium part}$$

$$\times \langle v_{s\mu}| \exp[-\lambda_\mu^*(\tau, \tau') a_\mu^\dagger] \exp[\lambda_\mu(\tau, \tau') a_\mu] |v_{s\mu}\rangle$$

where the medium part is given in (NJ2–C4).

is the molecular matrix element and where $\hat{P}_\mu$ is a medium operator which takes the form

$$\hat{P}_\mu = \exp\left[-\frac{\Delta_\mu}{2}\sum_E v_E{}^{\mu*}(\tau)B_E{}^\dagger\right]\exp\left[\frac{\Delta_\mu}{\sqrt{2}}\sum_E v_E{}^\mu(\tau)B_E\right]$$

$$\times\exp\left[\frac{K_\mu}{\sqrt{2}}\sum_E v_E{}^{\mu*}(\tau')B_E{}^\dagger\right]\exp\left[-\frac{K_\mu}{\sqrt{2}}\sum_E v_E{}^\mu(\tau')B_E\right]. \quad (50)$$

The thermally averaged quantity $\langle I_\mu\rangle_T$ is obtained from equation (48) by replacing the operator $\hat{P}_\mu$ by its thermal average $\langle\hat{P}_\mu\rangle_T$. It is obvious that this term, $\langle\hat{P}_\mu\rangle_T$, contains all the difference between the present approach and the treatment in NJ2. It is thus sufficient to consider this term only. In evaluating $\langle P_\mu\rangle_T$ the following approximations, concerning commutation relations of the operators B_E and $B_E{}^\dagger$ are invoked :

(*a*) $[B_E, B_E{}^\dagger]$ will be approximated by equation (27 *a*) in consistency with the RPA which leads to equation (28).

(*b*) $[B_E{}^\dagger, B_E{}^\dagger]$ and $[B_E, B_E]$ are taken to be zero. From the definitions (22)–(23) it is easy to see that these commutators are given by

$$[B_E{}^\dagger, B_E{}^\dagger] = \sum_\alpha\sum_{\alpha'}\sum_\epsilon F(\epsilon)[F(\epsilon+E')g(\epsilon+E')-F(\epsilon+E)g(\epsilon+E)]$$

$$\times|\alpha, \epsilon+E+E'\rangle\langle\epsilon, \alpha'| \quad (51)$$

(and $[B_E, B_E]$ by the complex conjugate). Also due to the highly peaked nature of $v_E{}^\mu$, these commutators appear only between such operators for which $E-E'$ is of order γ_μ (~ 1 cm^{-1}). Taking the commutator (51) as zero amounts to assuming a weak dependence of the function $F(\epsilon)G(\epsilon)$ on ϵ, such that

$$\left(\frac{d[F(\epsilon)g(\epsilon)]}{d\epsilon}\right)_{\epsilon=\omega'_\mu}\gamma_\mu \ll 1. \quad (52)$$

With these approximations the operators $B_E/\sqrt{n_E}$ and $B_E{}^\dagger/\sqrt{n_E}$ commute like boson operators. This can be utilized to recast equation (50) in the form (see e.g. NJ2 equations (B1–B5))

$$P_\mu = \exp\left[\frac{K_\mu\Delta_\mu}{2}\sum_E v_E{}^\mu(\tau)v_E{}^{\mu*}(\tau')n_E\right]\exp\left[\tfrac{1}{2}\sum_E|\sigma_E{}^\mu(\tau,\tau')|^2 n_E\right]$$

$$\times\exp\left[\sum_E\sigma_E{}^\mu(\tau,\tau')B_E-\sum_E\sigma_E{}^{\mu*}(\tau,\tau')B_E{}^\dagger\right], \quad (53)$$

where

$$\sigma_E(\tau,\tau') = \frac{\Delta_\mu}{\sqrt{2}}v_E{}^\mu(\tau)-\frac{K_\mu}{\sqrt{2}}v_E{}^\mu(\tau'). \quad (54)$$

In taking the thermal average of equation (53) we further approximate it by taking the lowest-order term in a cumulant expansion

$$\langle\exp[\sum_E\sigma_E{}^\mu B_E-\sum_E\sigma_E{}^{\mu*}B_E{}^\dagger]\rangle_T \cong \exp\{\tfrac{1}{2}\langle[\sum_E(\sigma_E{}^\mu B_E-\sigma_E{}^{\mu*}B_E{}^\dagger)]^2\rangle_T\}$$

$$= \exp\{-\tfrac{1}{2}\sum_E|_E{}^\mu|^2[\langle B_E B_E{}^\dagger\rangle_T+\langle B_E{}^\dagger B_E\rangle_T]\}$$

$$\cong \exp\{-\tfrac{1}{2}\sum_E|\sigma_E{}^\mu|^2 n_E(2M(E,T)+1)\}, \quad (55)$$

where $M(E, T)$ is given by equation (45). As $|\sigma_E{}^\mu|^2$ is sharply peaked around $E = \omega_\mu{}'$ we can take the factor $2M + 1$ outside the summation and replace it by $2\langle m_\mu \rangle_T + 1$ where $\langle m_\mu \rangle_T = [\exp(\beta \hbar \omega_\mu) - 1]^{-1}$ is the thermal population of the mode μ.

Equations (53)–(55) then lead to

$$\langle P \rangle_T = \exp\left\{ \frac{K_\mu \Delta_\mu}{2} \sum_E v_E{}^\mu v_E{}^{\mu *}(\tau') n_E \right\} \exp\left\{ - \langle m_\mu \rangle_T \sum_E |\sigma_E{}^\mu(\tau, \tau')|^2 n_E \right\}. \quad (56)$$

At the same time the molecular matrix element, equation (49), can be evaluated as described in NJ2, to yield

$$S_\mu = \exp\left[-\tfrac{1}{4}(\Delta_\mu{}^2 + K_\mu{}^2) + \frac{\Delta_\mu K_\mu}{2} u_\mu{}^*(\tau') u_\mu(\tau) \right]$$

$$\times (v_{s\mu})! \sum_{r=0}^{m_{s\mu}} \frac{(-1)^r |\lambda_\mu(\tau, \tau')|^{2r}}{(m_{s\mu} - r)!(r!)^2}, \quad (57)$$

with

$$\lambda_\mu(\tau, \tau') = \frac{\Delta_\mu}{\sqrt{2}} u_\mu(\tau) - \frac{K_\mu}{\sqrt{2}} u_\mu(\tau'). \quad (58)$$

Equations (54) and (56)–(58) are easily seen to be equivalent to equations (C8)–(C10) of NJ2. The summations over E in equation (56) are easily evaluated as described in equations (NJ2: B20, B22), to yield again the result (17). It should be stressed that the approximations invoked in the present treatment are completely equivalent to those made in NJ2 (Appendix C). Within these approximations we have thus established that the results obtained in NJ2 are independent of the particular nature of the thermal bath.

6. CONCLUSION

This paper contains two main results. First we derived formal expressions for vibrational relaxation of a harmonic oscillator interacting with a general medium (equations (29–35), (46)). Secondly we showed that the expression for electronic relaxation rate of a molecule imbedded in such a general medium retains the form obtained earlier for the simpler harmonic medium model. This result (equation (17)) is thus shown to be valid not only for molecules imbedded in an inert solid matrix but for impurity molecules in gas phase systems as well.

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