Effects of vibrational relaxation on molecular electronic transitions

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In this paper we explore the implications of the coupling between nonradiative electronic relaxation and vibrational relaxation in excited electronic states of large molecules. The physical model involved a two electronic level molecular system interacting with a harmonic medium via linear coupling terms in the molecular nuclear coordinates.Two models were advanced for the molecule–medium coupling which involve single phonon decay and alternatively double phonon (or rather phonon–vibron) decay. The functional form of our final results is independent of the specific model adopted for the vibrational relaxation. The molecular Hamiltonian and the intramolecular coupling were recast in terms of second quantization formalism where the nonadiabatic coupling operator was modified by a Franck Condon shift operator. The coupling between electronic and vibrational relaxation processes was formulated in terms of a generalized interaction picture, where the intramolecular coupling was treated to second order while the vibrational relaxation was handled to "infinite order" by the Wigner Weisskopf approximation as applied to the equations of motion for the nuclear operators for the normal molecular modes. The nonradiative decay rate of an excited electronic state was expressed in terms of a generalized time correlation function. We were able to demonstrate that our general expressions reduce to the (time independent) decay rate of a single vibronic level in the limit of slow vibrational relaxation and to a modified expression for the (time independent) decay rate of the thermally averaged electronic manifold in the limit of fast vibrational relaxation. In the general case of coupled electronic–vibrational relaxation the decay probability is time dependent. In the low temperature limit the nonradiative decay rate can be expressed in terms of a superposition of exponential functions.

I. INTRODUCTION

There has been extensive theoretical activity aimed towards the complete understanding of radiative and nonradiative decay processes of electronically excited molecular states.[1] Simultaneously, considerable progress has been accomplished in the description of vibrational relaxation of a molecule imbedded in a medium.[2–10] Several relaxation schemes, purely stochastic[2] or partially deterministic,[3–10] have been applied to handle the relaxation process of an oscillator or of a system of oscillators coupled to an infinite medium which acts as a heat bath, whereupon the relaxing system approaches thermal (Boltzmann) equilibrium from some initial (nonequilibrium) state.

The coupling between radiative and thermal relaxation process is of considerable interest. In this context one is usually interested in a system coupled to a thermal bath, which undergoes radiative excitation or decay. Such problems are frequently encountered for spin systems in NMR and ESR experiments[11–12] and for photon systems in laser and maser studies.[13–15] Most of the theoretical studies of these problems resulted in some form of a master equation for the density matrix of the system,[2,11–15] and much work has been performed to extract physical information from these equations. These methods are somewhat obscured by their generality, resulting in rather cumbersome theoretical expressions for the relaxation characteristics. For the grossly oversimplified model system involving harmonic oscillators some simpler solutions are available.[4–7] These physically transparent theoretical techniques involve a direct solution of the (linearized) Heisenberg equations of motion for the coordinate and momentum[4] (or alternatively for the creation and annihilation[5–7]) operators of the harmonic oscillators. This method, which was extensively used in the quantum theory of superfluidity and of superconductivity,[16] has been introduced by Senitzky[4] to handle the problem of a damped harmonic oscillator. Since then these theoretical techniques have been widely utilized in quantum optics,[6–7,14] and in solid state physics.[5,17–19] The same theoretical approach will be applied in the present work for the study of the effects of vibrational relaxation on nonradiative and radiative decay processes in polyatomic molecules.

The effects of vibrational relaxation on radiative and nonradiative processes in molecules and solids are usually disregarded,[1] whereupon theoretical and experimental studies focus attention on two limiting cases: (a) The isolated molecule limit[20–23] where the effects of externally induced vibrational relaxation are not considered. This physical situation corresponds to the decay of excited molecular states in the low pressure gas phase, where the duration between collisions considerably exceeds the relevant decay times. (b) The fast vibrational relaxation limit[24–26] where vibrational relaxation and excitation processes are fast on the time scale of electronic decay. This case, which is frequently encountered in the decay of electronically excited molecules in a dense medium or in "high pressure" gas phase, can be conveniently handled by considering the thermal average of the decay rates of well-defined initial vibronic levels of an isolated molecule. Thus, in

the common case of rapid vibrational relaxation the theoretical problem involves the calculation of the thermally averaged decay probability $\langle W\rangle_T$ of the form[24–26]

$$\langle W\rangle_T = \sum_i \exp(-\beta E_i) W_i [\sum_i \exp(-\beta E_i)]^{-1}, \quad \text{(I.1)}$$

where W_i is the decay rate for the ith vibronic level which is characterized by the energy E_i, the summation is taken over the entire single electronic manifold.

Our interest in the coupling between vibrational relaxation and nonradiative electronic relaxation has been motivated by several recent experimental studies, which can be summarized as follows:

(a) In the gas phase the total pressure may be easily varied, so that one can conveniently study a continuous transition from the isolated molecule case to the fast vibrational relaxation limit. Recently, several experimental studies have been published[27,28] focusing attention on the decay of electronically excited molecules under intermediate pressure conditions, where the pressure of a perturbing gas is sufficiently high to induce vibrational relaxation but still too low to establish thermal equilibrium of the excited state. Under these conditions the decay pattern of the excited state is not characterized by a single exponential, but rather includes a superposition of exponentials thus exhibiting a time dependent "lifetime". These results are interpreted in terms of the dependence of the nonradiative decay probability on the initial vibronic level, while in general the radiative decay rate (at least for symmetry allowed transitions) is practically independent of the initial vibrational population of the excited electronic state. Thus the nonexponential decay pattern monitors the time dependence of the population of the vibronic levels in the excited state.

(b) In dense media (i.e., liquids and solids) rapid vibrational relaxation (relative to the radiative and nonradiative decay rates) is usually taken for granted. This assumption which is entirely justified concerning radiative transitions (characterized by a radiative decay times $\geq 10^{-9}$ sec), has to be modified in the case of some ultrafast nonradiative decay processes exhibiting decay rates of the order of $\sim 10^{12}$–10^{11} sec^{-1}, which can exceed the vibrational relaxation rates of large molecules. A typical example in this category involves the lowest singlet state of the azulene molecule[29] where the sixth totally symmetric excited vibronic level is characterized by an electronic relaxation rate of 1.3×10^{11} sec^{-1}. Another interesting system is the first excited singlet state of the benzophenone molecule in solution[30] where the intersystem crossing rate of the lowest vibronic component is 2×10^{11} sec^{-1} while the decay rate of the $v=2$ vibronic state being 4×10^{10} sec^{-1}, thus the major decay pathway of the vibrationally excited state involves direct electronic relaxation, rather than vibrational relaxation to the electronic origin followed by intersystem crossing.

(c) In "isolated" small molecules the low density of the final molecular states cannot provide an effective intramolecular decay channel for electronic relaxation, and the radiative decay characteristics of these systems may exhibit the effects of intrastate coupling but not of electronic relaxation. When a small molecule is imbedded in an inert medium, efficient vibrational relaxation in the final vibronic manifold can result in a manifold of broadened levels, which provide a dissipative decay channel for the initially excited electronic state.[31] A proper treatment of the nonradiative decay of small molecules subjected to externally induced vibrational relaxations has to account explicitly for the latter effect.[32]

In this paper we present a theory for the nonradiative decay of an excited electronic state of a large molecule being simultaneously subjected to vibrational relaxation originating from an interaction with a dense medium, which will be represented herein by a phonon bath. A generalized interaction picture is utilized to represent the coupling between these two relaxation processes. Second order perturbation theory is applied for the description of the intramolecular electronic relaxation process, while vibrational relaxation is handled by the Wigner Weisskopf approximation applied to the Heisenberg equations of motion for the operators specifying the normal modes of the system.[6] This "infinite order" treatment of the vibrational relaxation process enabled us to explore different limiting cases for different relative rates of electronic and vibrational relaxation. We were able to demonstrate that our general expressions reduce to the decay of a single vibronic level (i.e., the isolated molecule case) in the limit of slow vibrational relaxation and to the decay of a thermally averaged initial vibronic manifold in the limit of fast vibrational relaxation. Some general, physically transparent theoretical expressions were derived for intermediate cases, exhibiting nonexponential decay resulting from the coupling of the two relaxation processes. These theoretical methods are general, being applicable for the coupling of vibrational relaxation both to radiative and nonradiative decay processes in excited electronic states of large molecules.

II. THE MODEL SYSTEM

We shall consider the nonradiative decay of an excited molecular state of a large molecule imbedded in a medium. It will be useful, at this stage, to present our approximations and assumptions concerning the following three major ingredients of the physical system: the medium, the molecule, and the features of the vibrational relaxation mechanism.

The medium is taken as a bath of phonons, whose frequencies, ω_ν, and their density of states, ρ, are taken

to be typical of the relevant solid matrices. Thus for solid rare gases the maximum frequency (corresponds roughly to the Debye frequency) is $\omega_\nu^{\max} \approx 60$–$80\ \mathrm{cm}^{-1}$ [33] while in solid hydrocarbons multiphonon transitions of impurity states lead to $\omega_\nu^{\max} \approx 200\ \mathrm{cm}^{-1}$.[34] The following approximations concerning the medium are invoked:

(a) The harmonic approximation for the medium vibrations is applied, whereupon anharmonic coupling between different medium modes is disregarded.

(b) The medium equilibrium nuclear coordinates and frequencies are identical in the initial and in the final electronic states of the impurity molecule.

(c) The medium is "inert" and does not modify the molecular energy levels or the intramolecular coupling[25] (which can occur via heavy atom effects on the spin orbit interaction). Furthermore, we shall disregard for the time being any coupling between the medium nuclear coordinates and the molecular electronic coordinates.

Thus the role of the medium is solely confined to supply a phonon bath for the dissipation of the vibrational energy of the molecule.

Focusing attention on the large molecule we invoke the following conventional simplifying assumptions which have been extensively utilized in previous work[1,20–25] on electronic relaxation:

(a) A two-electronic states system is considered. These electronic states $|s\rangle$ and $|l\rangle$ are characterized by the zero order Born–Oppenheimer vibronic levels:

$$|si\rangle \equiv |s\rangle\,|i\rangle = \phi_s(\mathbf{r}, \mathbf{Q}_s)\chi_{si}(\mathbf{Q}_s) \qquad \text{(II.1)}$$

for the upper electronic manifold and

$$|lj\rangle \equiv |l\rangle\,|j\rangle = \phi_l(\mathbf{r}, \mathbf{Q}_l)\chi_{lj}(\mathbf{Q}_l) \qquad \text{(II.2)}$$

which corresponds to the lower electronic configuration. ϕ and χ denote electronic and nuclear functions, respectively, $\mathbf{r}$ represents the electronic coordinates while $\mathbf{Q}_s$ and $\mathbf{Q}_l$ correspond to the normal coordinates of the states s and l, respectively.

(b) The molecular vibrations are assumed to be harmonic so that the nuclear functions may be displayed in the form

$$\chi_{si}(\mathbf{Q}_s, \{v_{s\mu}\}) = \prod_{\mu=1}^{N} X_{s\mu}(Q_{s\mu}, v_{s\mu}),$$

$$\chi_{lj}(\mathbf{Q}_l, \{v_{l\mu}\}) = \prod_{\mu=1}^{N} X_{l\mu}(Q_{l\mu}, v_{l\mu}), \qquad \text{(II.3)}$$

where $v_{s\mu}$ and $v_{l\mu}$ are the vibrational quantum numbers of the μth normal mode in the two electronic states. N represents the total number of normal modes.

(c) The normal modes and their frequencies ω_μ and effective masses M_μ are identical in the two electronic states. It will be useful to define the reduced dimensionless normal coordinates

$$q_{s\mu} = (\hbar/M_\mu\omega_\mu)^{-1/2}(Q_{s\mu} - Q_{s\mu}^0),$$

$$q_{l\mu} = (\hbar/M_\mu\omega_\mu)^{-1/2}(Q_{l\mu} - Q_{l\mu}^0). \qquad \text{(II.4)}$$

The only change in the normal coordinates between the two electronic states involves the displacements in the origins $Q_{s\mu}^0$ and $Q_{l\mu}^0$ of the normal coordinates

$$\Delta Q_\mu = Q_{l\mu}^0 - Q_{s\mu}^0 \qquad \text{(II.5)}$$

and the reduced displacement being given by

$$\Delta_\mu (\hbar/M_\mu\omega_\mu)^{-1/2}\Delta Q_\mu. \qquad \text{(II.6)}$$

When the molecular symmetry is practically unmodified between the two electronic states it may be assumed that $\Delta_\mu \neq 0$ only for totally symmetric modes. We note again that the displacements of origins, which represent the interaction between electronic and nuclear motions, are neglected for the time being for the medium modes, whereupon these modes do not supply final states for the electronic decay channel.

(d) We consider the statistical limit,[1] namely a large molecule with a large electronic energy gap, so that the $\{|lj\rangle\}$ manifold acts as an effective dissipative quasicontinuum for each of the vibronic levels $|si\rangle$. In a later work[32] we shall demonstrate that our results are also applicable for many cases involving the electronic relaxation of small molecules in solid matrices.

(e) We assume that the states in the $\{|lj\rangle\}$ manifold do not carry oscillator strength from the ground electronic state $|g0\rangle$. This assumption is usually justified on the basis of various symmetry arguments.[20,35] We may thus assert that narrow band short duration optical excitation lead initially to the population of a single (zero order) vibronic component $|si\rangle$.

(f) The intramolecular nonadiabatic coupling matrix elements for spin conserving transitions will be simplified by invoking a modified Condon approximation, being factorized into electronic and nuclear parts. This approximation is justified for radiative transitions. For nonradiative decay processes it is now well established that the conventional Condon approximation breaks down for near resonance coupling.[36] Several theoretical treatments, at different degrees of sophistication,[36] have established that in the weak electronic vibrational coupling limit (i.e., $\Delta_\mu \lesssim 1$ for all μ) the coupling matrix elements derived in the Condon approximation can be scaled by a numerical factor (consisting of the ratio of the modified electronic energy gap and the mean molecular frequency) to yield a reasonable approximation to the "exact" result. As we are interested in general relations this representation of the intramolecular nonadiabatic coupling in terms of a modified Condon approximation is quite adequate. Another way of justifying our procedure is to apply the crude adiabatic vibronic basis set as our zero order basis and the Herzberg Teller interaction as the intramolecular coupling.[37] This scheme, though weaker con-

ceptually than the adiabatic scheme is much easier from the point of view of mathematical manipulations.

(g) Interference effects between resonances which originate from the coupling of zero order vibronic level $|si\rangle$ with the quasicontinuum $\{|lj\rangle\}$ are assumed to be negligible, again from symmetry arguments.[30]

Concerning the medium–molecule interaction leading to the vibrational relaxation in the molecule, we utilize the following assumptions:

(a) The molecule–medium interaction involves only nuclear coordinates.

(b) The molecule–medium interaction will be considered to correspond to that of coupled harmonic oscillators. Low order coupling terms in molecular medium coordinates will be taken into account. These contributions correspond to the decay of a molecular vibration into one or into two medium phonons.

(c) Only those interaction terms which conserve energy to the lowest order are retained in the coupling Hamiltonian. This rotating wave (or resonant) approximation[38] corresponds to the replacement of a Hamiltonian of a system of linearly coupled oscillators displayed in second quantization representation

$$H=\sum_i \hbar\omega_i(a_i^+a_i+\tfrac{1}{2})+\sum_{i,j}\hbar G_{ij}(a_i^++a_i)\,(a_j^++a_j) \tag{II.7}$$

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

$$H=\sum_i \hbar\omega_i(a_i^+a_i+\tfrac{1}{2})+\sum_{i,j}\hbar G_{ij}(a_i^+a_j+a_ia_j^+). \tag{II.8}$$

The neglected operators of the form $a_i^+a_j^+$ and a_ia_j exhibit a time dependence which is determined by $\exp[\pm i(\omega_i+\omega_j)t]$ and undergo rapid oscillations, on the time scale of interest, whereupon their average contribution is small relative to that of the terms retained in (II.7).

Thus our model system involves a metastable electronic vibrational excited state of a large harmonic molecule interacting with a harmonic medium via linear coupling terms in the molecular and nuclear coordinates.

III. MODELS FOR VIBRATIONAL RELAXATION

In this section we shall focus attention on the problem of vibrational relaxation within a single electronic manifold. Several simple model Hamiltonians will be advanced to account for the medium induced vibrational relaxation of a single intramolecular vibrational mode; these will be specified as follows:

Case A: Single phonon decay. The molecular oscillator interacts with the phonon bath via linear interaction terms. Thus the intramolecular phonon decays into a single medium phonon.

Case B: Double phonon decay. The molecular oscillator interacts simultaneously with the low frequency medium phonon and with a high frequency medium phonon. The intramolecular vibration decays into two medium phonons.

Consider first the single phonon decay mechanism which, following the assumption of Sec. II, is characterized by the following Hamiltonian in second quantization representation

$$H=\hbar\omega(a^+a+\tfrac{1}{2})+\sum_\nu \hbar\omega_\nu(b_\nu^+b_\nu+\tfrac{1}{2})+\sum_\nu \hbar(G_\nu a^+b_\nu+G_\nu^* a b_\nu^+) \tag{III.1}$$

where a^+ and a are the creation and annihilation operators for the damped molecular vibration, b_ν^+ and b_ν represent the creation and annihilation operators for the bath νth vibrational mode, which is characterized by the frequency ω_ν, while G_ν corresponds to the coupling parameter of the molecular vibration with the νth medium phonon. Note that the rotating wave approximation has been applied to specify the coupling. Efficient vibrational relaxation in the model system (III.1) is expected to occur only provided that the frequency ω of the molecular oscillator overlaps the frequency spectrum $\{\omega_\nu\}$ of the bath frequencies. If this condition is not satisfied, the interaction term in Eq. (II.8) does not conserve energy. An attempt to describe the system under such conditions utilizing the Hamiltonian (III.1) will result in frequency renormalized stable discrete oscillator. In particular, if the oscillator's frequency is far from the frequency spectrum spanned by the medium modes with which it interacts, it provides a good approximation for the exact renormalized oscillator. We may thus conclude that in general the interaction term in Eq. (III.1) does not provide a proper description of the vibrational relaxation of high frequency molecular vibrations, although it may be useful for the relaxation of low frequency ($\omega\approx 100$–$200\ \mathrm{cm}^{-1}$) vibrational modes of large molecules.

Consider now mechanism (B) for vibrational relaxation which is applicable to a host matrix which consists of polyatomic molecules. In this case, the vibrational states of the medium consist of (low frequency) phonon states and of high frequency collective excitations, which originate from the intramolecular vibrations of the host molecules. These collective excitations of the polyatomic host matrix will henceforth be referred to as "vibrons". These high frequency medium modes cannot provide by themselves a vibrational relaxation channel for the guest molecule, as vibrational exciton band widths are rather narrow[39] ($\sim 10\ \mathrm{cm}^{-1}$) and the total number of these modes is rather low. The medium vibrons cannot be considered as an effective continuous decay channel for the intramolecular vibra-

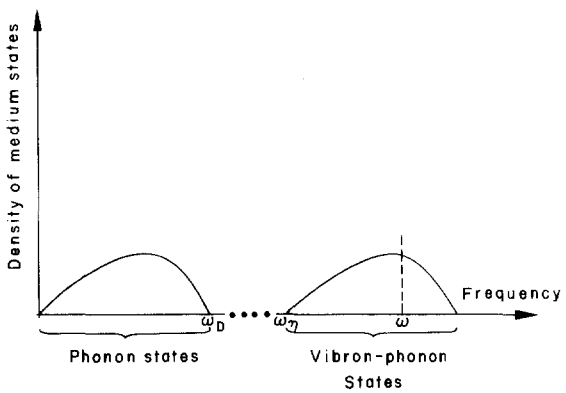

FIG. 1. Schematic density of states in a phonon–vibron system. ω_D is the Debye frequency of the phonons; ω_η is the vibron frequency. ω corresponds to the frequency of a guest molecule.

tion, but should be viewed rather as a degenerate single (or a small number of) vibrational state(s) of the medium. However, low frequency medium phonon states superimposed on a single medium vibron (Fig. 1) provide us with an acceptable dissipative continuum which overlaps the intramolecular vibrational frequency. Thus we assume that every vibrational mode of the decaying molecule is imbedded in a dense manifold of medium vibron–phonon states. This mechanism is physically similar to V–V energy transfer in the gas phase.[40] Let C_η^+ and C_η denote creation and annihilation operators for the ηth vibron, which is characterized by the frequency ω_η. A physically acceptable Hamiltonian, (based on the approximations outlined in Sec. II) is given by

$$H=\hbar\omega(a^+a+\tfrac{1}{2})+\sum_\nu \hbar\omega_\nu(b_\nu^+b_\nu+\tfrac{1}{2}) + \sum_\eta \hbar\omega_\eta(C_\eta^+C_\eta+\tfrac{1}{2}) + \sum_\nu\sum_\eta \hbar(G_{\nu\eta}a^+b_\nu C_\eta+G_{\nu\eta}^* a b_\nu^+ C_\eta^+), \quad \text{(III.2)}$$

where $G_{\nu\eta}$ are the appropriate coupling terms. It should be stressed at this point that the Hamiltonian (III.2) accounts for the dissipation of a single vibration of the guest molecule into two medium phonons. In polyatomic molecules other third order terms formally similar to the coupling in (III.2) may be of importance in describing intramolecular medium assisted energy redistribution. These contributions are of the form

$$\sum_\mu\sum_{\mu'}\sum_\nu \hbar(G_\nu^{\mu\mu'}a_\mu^+a_{\mu'}b_\nu+G_\nu^{\mu\mu'*}a_{\mu'}^+a_\mu b_\nu), \quad \text{(III.3)}$$

where conservation of energy is insured by the balance between the two intramolecular vibrations μ and μ' and the phonon mode i.e., $\omega_\mu-\omega_{\mu'}=\pm\omega_\nu$. We note, however, that the coupling terms (III.3) may be of importance for near degenerate intramolecular vibrations, however, they cannot in themselves lead to the thermalization of the vibrational modes of the guest molecule, as the total number of its vibrational quanta is unchanged. For the sake of mathematical simplification we shall neglect these terms in our treatment. Moreover, we shall invoke another rather serious approximation by assuming that every molecular oscillator relaxes independently, in other words, that the different molecular oscillators are not coupled via their interaction with the medium.

To conclude this section we note that high frequency vibrons are not provided by solid monoatomic matrices. To describe vibrational relaxation of high frequency molecular vibration in such matrix we should consider multiphonon processes including in the Hamiltonian terms up to high order in the medium coordinates, namely terms of the form $\sum_\nu \hbar[G_\nu^\mu a_\mu^+(b_\nu)^n+G_\nu^{\mu*}a_\mu(b_\nu^+)^n]$ with $n\sim10$, as the high molecular frequencies exceed by about an order of magnitude these of the medium phonons. Such contributions are expected to be extremely small, as may be deduced from the experimental observation that the vibrational relaxation of diatomic molecules in monoatomic solid matrices is extremely slow[3] and may proceed at a rate of $\sim$1–100 sec^{-1}.[41a] For polyatomic molecules in polyatomic matrices the vibrational relaxation may be greatly enhanced due to the effect of the phonon–vibron coupling. Recent experiments[41b] demonstrate that the vibrational relaxation rate in this case is $\sim10^{11}$–10^{12} sec^{-1}.

IV. CREATION AND ANNIHILATION OPERATORS REPRESENTATION OF MOLECULAR ELECTRONIC TRANSITIONS

It will be useful at this stage to formulate the theory of molecular electronic transitions in second quantization representation both for the vibrational modes and for the electronic states. As we consider here a two electronic states model, the representation of the electronic degrees of freedom in terms of creation and annihilation operators is rather trivial. We simply define a raising operator d^+ and a lowering operator d such that[42]

$$d^+|l\rangle=|s\rangle; \qquad d|s\rangle=|l\rangle, \qquad d^+|s\rangle=0 \qquad d|l\rangle=0, \quad \text{(IV.1)}$$

for all $\{|l\rangle\}$ so that these electronic operators are defined by their operation over the complete set of electronic functions.

The definition of raising and lowering operators in the nuclear space is somewhat more complicated. The difficulty arises from the differences between the potential surfaces in the two electronic states which yield a different set of vibrational wavefunctions for each electronic manifold. A cursory examination of the problem indicates that one has to define a different set of vibrational creation and annihilation operators for every vibronic manifold. The operators for a single electronic manifold are related to the operators of the second manifold by a well-defined transformation, not only in our simple model which is characterized by displaced

identical potential surfaces, but also in the more general case where the two potential surfaces differ also in the frequencies of the normal modes.[43]

This irritating ambiguity in the definition of the creation and annihilation operators for the nuclear wavefunctions may be overcome by a mathematical transformation which has become very popular in pseudopotential theory.[44] We replace the usual adiabatic basis set by an alternative basis, where the same vibrational set of functions corresponds to both electronic states. At the same time, the relevant interstate coupling operators are modified accordingly, so that the physically meaningful matrix elements are invariant.

It is easy to establish this transformation scheme for the present simplified molecular model system, where the vibrational wavefunctions (II.3) in the lth electronic state are just shifted in origin relative to those in the sth electronic manifold. Thus the single mode vibrational wavefunctions [defined by Eq. (II.3)] in the two electronic states are related by the simple transformation

$$X_{l\mu}(q_{l\mu};\, v_{l\mu}) = \exp(i\Delta_\mu p_{s\mu}) X_{s\mu}(q_{s\mu};\, v_{l\mu}), \quad \text{(IV.2)}$$

where $p_{s\mu}$ is the momentum operator conjugate to $q_{s\mu}$ while Δ_μ is defined by Eq. (II.6). The operator $\exp(i\Delta_\mu p_{s\mu})$ just performs the necessary shift of origin for the single mode nuclear wavefunctions in the two electronic states. Thus the total nuclear wavefunctions in the two electronic states are related by

$$\chi_{lj}(\mathbf{q}_l;\, \{v_j\}) = [\prod_\mu \exp(i\Delta_\mu p_\mu)]\chi_{sj}(\mathbf{q}_s;\, \{v_j\}). \quad \text{(IV.3)}$$

To demonstrate how this procedure works we have summarized in Appendix A the relatively simple relevant transformation for radiative processes. Utilizing the results derived in Appendix A, for any operator F which depends only on the electronic coordinates we have

$$(\langle \phi_l \chi_{lj}(\mathbf{q}_l;\, \{v_j\}) \mid F \mid \phi_s \chi_{si}(\mathbf{q}_s;\, \{v_i\})\rangle) = (\langle \phi_l \chi_{sj}(\mathbf{q}_s;\, \{v_j\}) \mid \hat{F} \mid \phi_s \chi_{si}(\mathbf{q}_s;\, \{v_i\})\rangle), \quad \text{(IV.4)}$$

where the transformed operator $\hat{F}$ takes the form

$$\hat{F} = \exp(-\tfrac{1}{4}\sum_\mu \Delta_\mu^2)[\langle s \mid F \mid l\rangle d^+ \times \prod_\mu \{\exp[(\Delta_\mu/\sqrt{2})\, a_\mu^+] \exp[-(\Delta_\mu/\sqrt{2})\, a_\mu]\} + \langle l \mid F \mid s\rangle d \prod_\mu \{\exp[-(\Delta_\mu/\sqrt{2})\, a_\mu^+] \exp[(\Delta_\mu/\sqrt{2})\, a_\mu]\}. \quad \text{(IV.5)}$$

$\langle\ \rangle$ and $(\ )$ represent integration over electronic and nuclear coordinates, respectively. This result is of interest for direct spin orbit coupling between the two electronic states.

Consider now the transformation of the nonadiabatic coupling between two electronic states. Invoking the modified Condon approximation[36c] and neglecting the second derivative of the electronic wavefunction with respect to nuclear coordinates, the (hermitian) approximate form of this operator is[45]

$$(H_v)_{si,lj} = \sum_\kappa C_{sl}{}^\kappa (\chi_{lj}(\mathbf{q}_l;\, \{v_j\}) \times \mid i(\partial/\partial q_\kappa) \mid \chi_{si}(\mathbf{q}_s;\, \{v_i\})), \quad \text{(IV.6)}$$

where

$$C_{sl}{}^\kappa = \hbar\omega_\kappa \langle \phi_l \mid i(\partial/\partial q_\kappa) \mid \phi_s\rangle\,|_{\mathbf{q}=0} \quad \text{(non-Condon correction)}. \quad \text{(IV.7)}$$

Utilizing Eq. (IV.3) we obtain the modified nonadiabatic operator in the form

$$V \equiv \hat{H}_v = \sum_\kappa C_{sl}{}^\kappa d[\prod_\mu \exp(ip_\mu \Delta_\mu)]p_\kappa + \text{h.c.} \quad \text{(IV.8a)}$$

or in a second quantization notation

$$V = \sum_\kappa C_{sl}{}^\kappa d\{\prod_\mu \exp[-(\Delta_\mu/\sqrt{2})\,(a_\mu^+ - a_\mu)] \times (i/\sqrt{2})\,(a_\kappa^+ - a_\kappa)\} + C_{sl}{}^{\kappa *} d^+\{\prod_\mu \exp[(\Delta_\mu/\sqrt{2})\,(a_\mu^+ - a_\mu)] \times (i/\sqrt{2})\,(a_\kappa^+ - a_\kappa)\}. \quad \text{(IV.8b)}$$

The effective coupling (IV.8) operator may be more conveniently handled if we replace the factors $-(1/\sqrt{2})\,(a_\kappa^+ - a_\kappa)$ by an exponential operator

$$\exp\{-[K_\kappa/\sqrt{2}](a_\kappa^+ - a_\kappa)\}$$

thus providing a more symmetrical form for the coupling operator. At the end of the evaluation of the coupling matrix element we shall take a derivative with respect to K_κ at $K_\kappa = 0$, so that

$$V = \sum_\kappa (\partial/\partial K_\kappa)\,(iC_{sl}{}^\kappa d\{\prod_\mu \exp[-(\Delta_\mu/\sqrt{2})\,(a_\mu^+ - a_\mu)] \times \exp[(K_\kappa/\sqrt{2})\,(a_\kappa^+ - a_\kappa)]\} + \text{h.c.}). \quad \text{(IV.9)}$$

The effective zero order molecular Hamiltonian H_0 whose eigenstates constitute our modified zero order basis will take in the second quantization representation on especially simple form:

$$H_0 = \Delta E d^+ d + \sum_\mu \hbar\omega_\mu (a_\mu^+ a_\mu + \tfrac{1}{2}); \qquad \Delta E = E_s - E_l, \quad \text{(IV.10)}$$

where the electronic energy is measured from the minimum potential surface of the lth electronic state. The sum in (IV.10) is taken over all the molecular vibrational modes.

We conclude this section with a remark concerning the significance of the operators $\exp(-[\Delta_\mu/\sqrt{2}](a_\mu^+ - a_\mu))$. This shift operator which has been used extensively in quantum optics as the generator of Glauber's coherent states,[46] may be called the Franck Condon operator as its matrix elements between eigenstates of the harmonic oscillator μ yield the appropriate Franck Condon

factors for the mode μ in the displaced potential surfaces model. The role of this operator in our scheme thus becomes apparent. It is not very difficult to generalize this operator for a more complex model where the electronic potential surfaces differ also in the frequencies of the different modes[43] but the mathematical handling of the matrix elements will then become rather cumbersome.

V. A GENERALIZED INTERACTION PICTURE FOR THE TRANSITION PROBABILITY

We shall formulate a relaxation scheme providing a proper description of the effects of vibrational relaxation on molecular electronic decay processes. One may consider different kinds of molecular processes and also different molecular dynamic observables. The processes of interest to us are radiative and nonradiative electronic transitions, the relevant observables related to these processes being:

(a) Radiative and nonradiative decay constants of the excited electronic state.

(b) Quantum yield for radiative emission from the excited electronic state.

(c) Optical line shapes for the absorption of radiation into the excited electronic state.

In this work we shall focus our attention on the problem of nonradiative decay probabilities (or lifetimes). A discussion of the optical lineshape problem has been also provided.[47] Here also one may distinguish between two experimental situations:

(a.1) The time evolution of the total occupation of the upper ($|s\rangle$) electronic manifold may be investigated by monitoring the fluorescence or phosphorescence originating from this electronic state.

(a.2) The time evolution of the occupation of a single vibronic level of the upper electronic manifold may be studied by monitoring the absorption of radiation by this vibronic level.

The experimental techniques of ultrafast spectroscopy developed by Rentzepis[48] provide direct information concerning both experimental problems. From the theoretical point of view the handling of the first problem is considerably easier, and we shall limit our treatment to the time evolution of the total occupation of a decaying electronic state. The general theoretical scheme developed herein will be applied for nonradiative spin conserving relaxation processes utilizing the nonadiabatic operator [Eq. (IV.9)]. It can be easily extended to handle intersystem crossing using spin–orbit coupling of the form (IV.4) and radiative decay processes using the modified dipole operator [given by Eq. (A10)]. The total Hamiltonian of the system is

$$H=H_0+H_L+V+H_{mL}. \tag{V.1}$$

The zero order molecular Hamiltonian H_0 is given by Eq. (IV.10)

$$H_0=\Delta E d^+d+\sum_\mu \hbar\omega_\mu a_\mu^+a_\mu. \tag{V.2}$$

The medium Hamiltonian describing the baths of phonons and vibrons as prescribed in Sec. II is

$$H_L=\sum_\nu \hbar\omega_\nu b_\nu^+b_\nu+\sum_\eta \hbar\omega_\eta C_\eta^+C_\eta. \tag{V.3}$$

The zero vibrational level in Eqs. (V.2) and (V.3) is defined as to include the vacuum state energies of the medium and of the molecular oscillators. The nonadiabatic perturbation Hamiltonian in (V.1) is given by Eqs. (IV.8) and (IV.9). Finally, for the molecule medium coupling we shall utilize two expressions as discussed in Sec. II:

$$H_{mL}=\sum_{\mu\nu}\hbar(G_\nu^\mu a_\mu^+b_\nu+G_\nu^{\mu*}a_\mu b_\nu^+) \tag{V.4}$$

for case A of single phonon decay, which is of limited applicability. Alternatively, we shall utilize the model Hamiltonian for double phonon decay (case B Sec. II)

$$H_{mL}=\sum_\mu\sum_\nu\sum_\eta\hbar(G_{\nu\eta}^\mu a_\mu^+b_\nu C_\eta+G_{\nu\eta}^{\mu*}a_\mu b_\nu^+C_\eta). \tag{V.5}$$

The zero order total Hamiltonian of the system is

$$H_0^t=H_0+H_L. \tag{V.6}$$

It will now be useful to define

$$\tilde{H}_0=H_0^++H_{mL} \tag{V.7}$$

so that

$$H=\tilde{H}_0+V. \tag{V.1'}$$

Let $|s, v_s, m_s\rangle$ denote the initial electronic (s) vibrational (v_s) and medium (m_s) state of the total system (accessible by optical excitation from the ground state). The probability, $P_s(t)$, for the molecule to remain in the initial electronic manifold s at time t is given by

$$P_s(t)=\sum_v\sum_m|(\langle s, v, m|\exp[-iH(t/\hbar)]|s, v_s, m_s\rangle)|^2, \tag{V.8}$$

where the summation is taken over all the molecular vibrational levels and the medium states. The decay rate W_s of the sth electronic manifold is given by

$$W_s=-dP_s/dt \tag{V.9}$$

which in general may be time dependent.

The evolution operator $U(t)=\exp(-iHt/\hbar)$ is given by

$$U(t)=U^0(t)\,U_I(t)=\exp(-i\tilde{H}_0t/\hbar)\,U_I(t), \tag{V.10}$$

where $U_I(t)$ is the evolution operator in the interaction representation given by

$$U_I(t)=T\exp\left(-i\int_0^t V_I(\tau)\,d\tau\right) \tag{V.10'}$$

which represents a time ordered expansion, T being the conventional time ordering operator, while

$$V_I(\tau)=\exp[i\tilde{H}_0(\tau/\hbar)]V\exp[-i\tilde{H}_0(\tau/\hbar)]. \tag{V.11}$$

Expansion of the evolution operator in a power series in the intramolecular interaction V yields the usual low order perturbation terms

$$U_I(t)=1-\frac{i}{\hbar}\int_0^t V_I(\tau)\,d\tau - \frac{1}{\hbar^2}\int_0^t d\tau\int_0^\tau d\tau' V_I(\tau)\,V_I(\tau'). \quad \text{(V.12)}$$

We note in passing that we have chosen to separate the Hamiltonian in Eq. (V.1) so that the truncation of the power series in Eq. (V.12) neglects the contribution of higher powers of V only, while no assumptions have been made concerning the magnitude of H_{mL}. The possibility of studying both limits of fast and of slow vibrational relaxation is thus open to us.

Inserting Eqs. (V.10) and (V.12) into Eq. (V.8) and bearing in mind that V does not couple an electronic state to itself, we obtain (up to second order in V)

$$\begin{aligned}P_s(t)=\sum_{v,m}\Bigg(&\Bigg(\langle s,v_s,m_s\mid\exp\left(i\tilde{H}_0\frac{t}{\hbar}\right)\mid s,v,m\rangle\Bigg)\times\Bigg(\langle s,v,m\mid\exp\left(-i\tilde{H}_0\frac{t}{\hbar}\right)\mid s,v_s,m_s\rangle\Bigg)\\&-\frac{1}{\hbar^2}\Bigg(\langle s,v_s,m_s\mid\left[\int_0^t d\tau\int_0^\tau d\tau'\exp\left(i\tilde{H}_0\frac{\tau'}{\hbar}\right)V^+\exp\left(-i\tilde{H}_0\frac{\tau'-\tau}{\hbar}\right)V^+\exp\left(-i\tilde{H}_0\frac{\tau}{\hbar}\right)\right]\\&\times\exp\left(i\tilde{H}_0\frac{t}{\hbar}\right)\mid s,v,m\rangle\Bigg)\Bigg(\langle s,v,m\mid\exp\left(-i\tilde{H}_0\frac{t}{\hbar}\right)\mid s,v_s,m_s\rangle\Bigg)\\&-\frac{1}{\hbar^2}\Bigg(\langle s,v_s,m_s\mid\exp\left(i\tilde{H}_0\frac{t}{\hbar}\right)\mid s,v,m\rangle\Bigg)\Bigg(\langle s,v,m\mid\exp\left(-i\tilde{H}_0\frac{t}{\hbar}\right)\\&\times\int_0^t d\tau\int_0^\tau d\tau'\exp\left(i\tilde{H}_0\frac{\tau}{\hbar}\right)V\exp\left(i\tilde{H}_0\frac{\tau'-\tau}{\hbar}\right)V\exp\left(-i\tilde{H}_0\frac{\tau'}{\hbar}\right)\mid s,v_s,m_s\rangle\Bigg)\Bigg).\end{aligned} \quad \text{(V.13)}$$

As $\tilde{H}_0$ does not couple different electronic states, we may replace in Eq. (V.13) $\mid s,v,m\rangle\langle s,v,m\mid$ by the sum over all electronic states which in the present two electronic state-system is just $\mid s,v,m\rangle\langle s,v,m\mid+\mid l,v,m\rangle\langle l,v,m\mid$. Applying the closure relation

$$\sum_{v,m}[\mid s,v,m\rangle\langle s,v,m\mid+\mid l,v,m\rangle\langle l,v,m\mid]=1 \quad \text{(V.14)}$$

we now obtain:

$$P_s(t)=1-\frac{2}{\hbar^2}\,\mathrm{Re}\int_0^t d\tau\int_0^\tau d\tau'\left(\langle s,v_s,m_s\mid\exp\left(i\tilde{H}_0\frac{\tau}{\hbar}\right)V\times\exp[i\tilde{H}_0(\tau'-\tau)/\hbar]V\exp\left(-i\tilde{H}_0\frac{\tau'}{\hbar}\right)\mid s,v_s,m_s\rangle\right). \quad \text{(V.15)}$$

The decay rate Eq. (V.9) is given by

$$W_s=\frac{2}{\hbar^2}\,\mathrm{Re}\int_0^\tau d\tau'(\langle s,v_s,m_s\mid\exp(i\tilde{H}_0\tau/\hbar)\,V\times\exp[i\tilde{H}_0(\tau'-\tau)/\hbar]V\exp(-i\tilde{H}_0\tau'/\hbar)\mid s,v_s,m_s\rangle). \quad \text{(V.16)}$$

The following comments are in order:

(a) The transition probability (V.16) is valid up to second order in V. The contributions of high order terms involving phonon assisted high order virtual transition between different v_s states are neglected.

(b) Our result is reduced to the well-known case of the radiationless decay in an isolated molecule, which was previously derived from the "golden rule" transition probability. Setting $H_{mL}=0$ in (V.16) than $\tilde{H}_0=H_0{}^t$ [Eqs. (V.6) and (V.7)] while $\mid s,v_s,m_s\rangle$ constitutes an eigenfunction of $H_0{}^t$. Equation (V.16) may be recast in the familiar form

$$\begin{aligned}W_s&=\frac{2}{\hbar^2}\,\mathrm{Re}\int_{-\tau}^0 d(\tau'-\tau)\,(\langle s,v_s\mid V\exp[iH_0{}^t(\tau'-\tau)/\hbar]V\exp[-iH_0{}^t(\tau'-\tau)/\hbar]\mid s,v_s\rangle)\\&=\frac{1}{\hbar^2}\int_{-\tau}^\tau dx(\langle s,v_s\mid V\exp(iH_0{}^tx/\hbar)\,V\exp(-iH_0{}^tx/\hbar)\mid s,v_s\rangle),\end{aligned} \quad \text{(V.17)}$$

where $x=\tau'-\tau$. Equation (V.17) is the identical to the result obtained in the isolated molecule limit by the generating function formalism,[25] except that in the latter case the integral extends from $-\infty$ to ∞. The exact mathe-

matical form is given by (V.17) while the more convenient formula containing unbounded integration (reflecting "exact" energy conservation) is obtained from (V.17) as for sufficiently long times, τ, the integral is independent of the $-\tau\cdots\tau$ integration interval. Equation (V.17) has also been utilized in the theory of radiationless transitions[49] with results similar to those obtained from the "golden rule" rate expression.

(c) While in the case of slow vibrational relaxation the operator (i.e., the autocorrelation function) in Eq. (V.17) depends on $x=\tau'-\tau$, the time correlation function for the case involving vibrational relaxation [Eq. (V.16)] is a more complicated function of both τ and τ'. This originated from the fact that the zero order wavefunctions are not eigenfunctions of $\tilde{H}_0$. However, it will be shown below that for fast vibrational relaxation the time correlation function becomes dependent again on $\tau'-\tau$ alone.

It will be useful at this stage to recast Eq. (V.16) in a slightly different form, separating out the electronic part of the matrix elements. Making use of Eq. (IV.8b) we obtain

$$W_s=\frac{2}{\hbar^2}\mathrm{Re}\int_0^t d\tau' \exp\left(-i(\tau'-\tau)\frac{\Delta E}{\hbar}\right)\Bigg(\langle v_s, m_s \mid \exp\left(i\tilde{H}_0'\frac{\tau}{\hbar}\right)\tilde{V}^+\exp\left(-i\tilde{H}_0\frac{\tau}{\hbar}\right)\times\exp\left(i\tilde{H}_0'\frac{\tau'}{\hbar}\right)\tilde{V}\exp\left(-i\tilde{H}_0'\frac{\tau'}{\hbar}\right)\mid v_s, m_s\rangle\Bigg), \quad \text{(V.18)}$$

where

$$\tilde{H}_0'=\sum_\mu \hbar\omega_\mu a_\mu^+ a_\mu+\sum_\nu \hbar\omega_\nu b_\nu^+ b_\nu+\sum_\eta \hbar\omega_\eta C_\eta^+ C_\eta+H_{mL} \quad \text{(V.19)}$$

$$\tilde{V}=\sum_\kappa C_{sl}{}^\kappa \prod_\mu \exp[(\Delta_\mu/\sqrt{2})(a_\mu^+-a_\mu)](i/\sqrt{2})(a_\kappa^+-a_\kappa) \quad \text{(V.20a)}$$

and

$$\tilde{V}^+=\sum_\kappa C_{sl}{}^{\kappa *}\prod_\mu \exp[-(\Delta_\mu/\sqrt{2})(a_\mu^+-a_\mu)](i/\sqrt{2})(a_\kappa^+-a_\kappa). \quad \text{(V.20b)}$$

W_s in Eq. (V.18) may thus be expressed as a Fourier transform of a generalized time correlation function

$$W_s=\frac{2}{\hbar^2}\mathrm{Re}\int_0^\tau d\tau \exp\left(-i(\tau'-\tau)\frac{\Delta E}{\hbar}\right)(v_s, m_s \mid \tilde{V}^+(\tau)V(\tau') \mid v_s, m_s), \quad \text{(V.21)}$$

where

$$\tilde{V}(t)=\exp\left(i\tilde{H}_0'\frac{t}{\hbar}\right)\tilde{V}\exp\left(-i\tilde{H}_0'\frac{t}{\hbar}\right). \quad \text{(V.22)}$$

Equation (V.21) and (V.22) provide us with the total decay probability of an electronic state, where the system has been "initially prepared" in the zero order state. It should, however, be borne in mind that while the initial vibronic state of the guest molecule is accessible by optical excitation, the medium is assumed to be initially, and to remain in thermal equilibrium. Thus, the matrix elements (V.21) over a single medium state should be replaced by a thermal average $\langle\ \rangle_T$ over the medium states. The final result for the decay rate is

$$W_s=\frac{2}{\hbar^2}\mathrm{Re}\int_0^\tau d\tau \exp\left(i(\tau-\tau')\frac{\Delta E}{\hbar}\right)G(\tau,\tau'), \quad \text{(V.23)}$$

where the generalized thermally averaged time correlation function is

$$G(\tau,\tau')=\langle v_s \mid V^+(\tau)V(\tau') \mid v_s\rangle_T. \quad \text{(V.24)}$$

To obtain an explicit expression for the correlation function we insert Eqs. (V.19) and (V.20) into Eq. (V.24), making the usual assumption that $\Delta_\kappa=0$ for every promoting mode κ.[24] This simplifying assumption is valid for symmetrical molecules in the common case where the promoting modes are nontotally symmetric. It is now easy to see that only terms diagonal in the promoting modes coordinates will contribute to the final result[20] whereupon the correlation function is expressed in the form

$$G(\tau,\tau')=\sum_\kappa \mid C_{sl}{}^\kappa\mid^2\langle J_\kappa\prod_{\mu\neq\kappa} g_\mu\rangle_T, \quad \text{(V.25)}$$

where g_μ and J_κ are single oscillator matrix elements,

$$g_\mu=(v_{s\mu} \mid \exp\{-(\Delta_\mu/\sqrt{2})[a_\mu^+(\tau)-a_\mu(\tau)]\}\exp\{(\Delta_\mu/\sqrt{2})[a_\mu^+(\tau')-a_\mu(\tau')]\} \mid v_{s\mu}) \quad \text{(V.26)}$$

$$J_\kappa=-(v_{s\kappa} \mid (1/\sqrt{2})[a_\kappa^+(\tau)-a_\kappa(\tau)](1/\sqrt{2})[a_\kappa^+(\tau')-a_\kappa(\tau')] \mid v_{s\kappa}). \quad \text{(V.27)}$$

We may save considerable effort by calculating matrix elements of the following form [see Eq. (IV.9)]

$$I_\mu = (v_{s\mu} \mid \exp\{-(\Delta_\mu/\sqrt{2})[a_\mu^+(\tau) - a_\mu(\tau)]\} \exp\{(K_\mu/\sqrt{2})[a_\mu^+(\tau') - a_\mu(\tau')]\} \mid v_{s\mu}) \tag{V.28}$$

so that the matrix elements (V.26) and (V.27) are expressed in terms of (V.28) via the relations

$$g_\mu = I_\mu(K_\mu = \Delta_\mu) \tag{V.29a}$$

$$J_\kappa = (\partial^2 I_\kappa/\partial^2\Delta_\kappa \partial^2 K_\kappa)_{\Delta_\kappa = K_\kappa = 0}. \tag{V.29b}$$

The time correlation function now takes the final form

$$G(\tau, \tau') = \sum_\kappa \mid C_{sl}{}^\kappa \mid^2 [(\partial^2/\partial\Delta_\kappa \partial K_\kappa) \langle \prod_\mu I_\mu \rangle_T]_{K_\mu = \Delta_\mu; \mu \neq \kappa; K_\kappa = \Delta_\kappa = 0} \tag{V.30}$$

Eqs. (V.23), (V.24) and (V.30) constitute our final result for the decay rate in coupled electronic–vibrational relaxation processes.

VI. COUPLED ELECTRONIC-VIBRATIONAL RELAXATION

To extract physical information from the formal expressions derived in Sec. V, we have to provide explicit solutions to the following two problems: (a) We have to evaluate the Heisenberg representation of the coupling operator $\tilde{V}$ [Eq. (V.20)] under a Hamiltonian $\tilde{H}_0'$ [Eq. (V.19)] which contains the molecular–medium interaction. (b) The thermally averaged matrix elements in Eq. (V.30) has to be evaluated as a function of the time variables τ and τ'.

The evaluation of the coupling operator (V.20) is reduced to the calculation of the Heisenberg representation of the creation and annihilation operators for the molecular vibrations [see Eqs. (V.28)–(V.30)]. The method adopted by us to handle this problem rests on the Wigner Weisskopf approximation.[50] This approach was introduced by Gordon Walker and Louisell[14] to treat the problem of a single oscillator interacting with a large number of atoms and was reformulated by Glauber[6] for the case of a single oscillator interacting with a heat bath, where the interaction Hamiltonian H_{mL} is given by Eq. (V.4). We shall use Glauber's results[6] for case A, while for case B [Eq. (V.5)] we have utilized a self consistent extension of the Wigner Weisskopf approximation, recently provided by us.[51]

We shall now present the general results for the Heisenberg representation of the operators corresponding to molecular harmonic oscillators, obtained within the framework of the Wigner Weisskopf approximation. These results provide a useful model for the study of vibrational relaxation in a dense medium. Two different models (referred to in Sec. II as case A and case B) will be discussed, in an attempt to get insight into the general features of the problem which are independent of the particular model Hamiltonian for the molecule–medium coupling. In deriving these results we have invoked the assumption (see Sec. II) that the relaxation processes of different molecular oscillators are independent and can be treated separately.

Consider first case A where the molecule–medium coupling is given by Eq. (V.4). For this model Hamiltonian Glauber[6] has derived the Heisenberg representation for the creation $a_\mu^+(t)$ and for the annihilation $a_\mu(t)$ operators in the form

$$a_\mu(t) = a_\mu(0)\, u_\mu(t) + \sum_\nu b_\nu(0)\, v_\nu{}^\mu(t), \tag{VI.1}$$

$$a_\mu^+(t) = a_\mu^+(0)\, u_\mu^*(t) + \sum_\nu b_\nu^+(0)\, v_\nu{}^{\mu *}(t), \tag{VI.2}$$

where $a_\mu(0) = a_\mu$ and $a_\mu^+(0) = a_\mu^+$. $u_\mu(t)$ and $v_\nu{}^\mu(t)$ are numerical functions of the time t. The explicit form of these functions is

$$u_\mu(t) = \exp\{-(\gamma_\mu + i\omega_\mu')t\}, \tag{VI.3}$$

$$v_\nu{}^\mu(t) = \{-iG_\nu{}^\mu/[\gamma_\mu + i(\omega_\mu' - \omega_\nu)]\}\{\exp(-i\omega_\nu t) - \exp[-(\gamma_\mu + i\omega_\mu')t]\}, \tag{VI.4}$$

where the modified frequencies are

$$\omega_\mu' = \omega_\mu + \delta\omega_\mu \tag{VI.5}$$

and where the level shift in Eq. (VI.5) and the level width [in Eqs. (VI.2) and (VI.3)] are defined by the relation

$$\delta\omega_\mu - i\gamma_\mu = \lim_{\delta \to 0^+} \sum_\nu [\mid G_\nu{}^\mu \mid^2/(\omega_\mu - \omega_\nu + i\delta)]. \tag{VI.6}$$

Replacing the sum over the medium modes in Eq. (VI.6) by an integral over the density of phonon states $\sum_\nu \to \int \rho(\omega_\nu)\, d\omega_\nu$ we have

$$\delta\omega_\mu = PP\int \mid G_\nu{}^\mu \mid^2 \rho(\omega_\nu')\, d\omega_\nu'/(\omega_\mu - \omega_\nu) \tag{VI.6'}$$

and

$$\gamma_\mu = \prod \mid G_\nu{}^\mu \mid^2 \rho_\nu \mid_{\omega_\mu = \omega_\nu}, \tag{VI.6''}$$

whereupon the level width due to vibrational relaxation is just given by the "golden rule" expression. Finally, it is important to mention the sum rule (normalization condition) for the functions (VI.3) and (VI.4) which for the present case reads[6]

$$\mid u_\mu(t) \mid^2 + \sum_\nu \mid v_\nu{}^\mu(t) \mid^2 = 1. \tag{VI.7}$$

Turning now our attention to the two phonon decay (case B) specified by the interaction (V.5), the harmonic oscillator operators in the Heisenberg representation have the form

$$a_\mu(t) = u_\mu(t)\, a_\mu + \sum_\nu \sum_\eta v_{\nu\eta}{}^\mu(t)\, b_\nu C_\eta \qquad \text{(VI.8)}$$

$$a_\mu{}^+(t) = u_\mu{}^*(t)\, a_\mu{}^+ + \sum_\nu \sum_\eta v_{\nu\eta}{}^{\mu *}(t)\, b_\nu{}^+ C_\eta{}^+. \qquad \text{(VI.9)}$$

In this case, we were able to show that[51]

$$u_\mu(t) = \exp[-(i\omega_\mu{}' + \gamma_\mu)t] \qquad \text{(VI.10)}$$

and

$$v_{\nu\eta}{}^\mu(t) = \{-iG_{\nu\eta}{}^\mu / [\gamma_\mu + i(\omega_\mu{}' - \omega_\nu - \omega_\eta)]\}$$
$$\times \{\exp[-i(\omega_\nu + \omega_\eta)t] - \exp[-(\gamma_\mu + i\omega_\mu{}')t]\}. \qquad \text{(VI.11)}$$

$\omega_\mu{}'$ is again given by Eq. (VI.5) while the level shift $\delta\omega_\mu$ and the level width γ_μ in Eqs. (VI.10) and (VI.11), are now given by the relation

$$\delta\omega_\mu - i\gamma_\mu = \lim_{\delta \to 0^+} \sum_\nu \sum_\eta \frac{|G_{\nu\eta}{}^\mu|^2 (\langle n_\nu \rangle_T + \langle n_\eta \rangle_T + 1)}{\omega_\mu - (\omega_\nu + \omega_\eta) + i\delta}. \qquad \text{(VI.12)}$$

The thermally averaged population $\langle n_i \rangle_T$ for the medium phonon mode i ($i = \eta$ or ν) is

$$\langle n_i \rangle_T = [\exp(\hbar\omega_\nu / kT) - 1]^{-1} \qquad \text{(VI.13)}$$

so that for case B we can replace the sum over the low frequency medium modes by an integral, retaining the sum over the vibrons:

$$\delta\omega_\mu = PP \sum_\eta \int d\omega_\nu \rho(\omega_\nu)$$
$$\times [|G_{\nu\eta}{}^\mu|^2 (\langle n_\nu \rangle_T + \langle n_\eta \rangle_T + 1)/(\omega_\mu - \omega_\eta - \omega_\nu)], \qquad \text{(VI.14a)}$$

$$\gamma_\mu = \pi \sum_\eta |G_{\nu\eta}{}^\mu|^2 (\langle n_\nu \rangle_T + \langle n_\eta \rangle_T + 1) \rho_\nu |_{\omega_\mu = \omega_\nu + \omega_\eta}. \qquad \text{(VI.14b)}$$

Finally, the normalization condition for the time dependent functions $u_\mu(t)$ and $v_{\nu\eta}{}^\mu(t)$ in Eqs. (VI.8) and (VI.9) is given for case B in the form

$$|u_\mu(t)|^2 + \sum_\nu \sum_\eta |v_{\nu\eta}{}^\mu(t)|^2 (\langle n_\nu \rangle_T + \langle n_\eta \rangle_T + 1) = 1. \qquad \text{(VI.15)}$$

We are thus provided with the necessary expressions for the Heisenberg representation of the harmonic oscillator creation and annihilation operators of the molecular vibrations for both case A [Eqs. (VI.1)–(VI.7)] and for case B [Eqs. (VI.8)–(VI.15)]. The following comments are in order:

(a) In both case A and case B the function $u_\mu(t)$ has the same functional form [Eqs. (VI.3) and (VI.10)].

(b) For both vibrational relaxation mechanisms we can specify the level width (or the vibrational relaxation rate) in terms of the "golden rule" rate expression [see Eqs. (VI.6) and (VI.14)]. As the present theory is phenomenological and no attempt is made to evaluate the molecule medium coupling terms, the final form of the electronic vibrational relaxation rates will be similar at a constant temperature.

(b) An interesting difference between the relaxation models A and B involves the temperature dependence of γ_μ. For single phonon decay (case A) γ_μ is temperature independent [Eq. (VI.6′)] as characteristic of a simple relaxation process. On the other hand for the double phonon decay (case B) γ_μ [Eq. (VI.14b)] exhibits a temperature dependence, which originates from the contribution of stimulated phonon decay processes.

(d) The general results are considerably simplified in the two limits:

(1) In the isolated molecule case $G_\nu{}^\mu = G_{\nu\eta}{}^\mu = \gamma_\mu = 0$ (for both cases A and B) and $u_\mu(t) = \exp(-i\omega_\mu t)$ while $v_\nu{}^\mu(t) = 0$. This leads just to the unperturbed harmonic oscillator, as expected. We shall refer to this limit where $\gamma_\mu \to 0$ or $\gamma_\mu t \ll 1$ for all times, t, of physical interest, as the slow vibrational relaxation limit.

(2) In the limit of rapid vibrational relaxation γ_μ is large, i.e., $\gamma_\mu t \gg 1$ for all times of physical interest. For the experimentally relevant time scale in this limit we have $a_\mu(t) = 0$ for both cases A and B while

$$v_\nu{}^\mu(t) = \{-iG_\nu{}^\mu / [\gamma_\mu + i(\omega_\mu{}' - \omega_\nu)]\} \exp(-i\omega_\nu t) \qquad \text{(VI.16)}$$

for case A, and

$$v_{\nu\eta}{}^\mu(t) = \{-iG_{\nu\eta}{}^\mu / [\gamma_\mu + i(\omega_\mu{}' - \omega_\nu - \omega_\eta)]\}$$
$$\times \exp[-i(\omega_\nu + \omega_\eta)t] \qquad \text{(VI.17)}$$

for case B. These two limits will be explored later.

(e) It should be borne in mind that case A is applicable for the relaxation of low frequency vibrational modes, while the relaxation of high frequency modes should be described in terms of case B.

As is common for many quantum chemical problems the time has come now to calculate the matrix elements which determine the time correlation function [Eqs. (V.14), (V.25), and (V.30)]. This problem reduces to the evaluation of the single oscillator matrix elements I_μ [Eq. (V.28)]. These terms are handled by introducing $a(t)$ and $a^+(t)$, [Eqs. (VI.1)–(VI.2) for case A or Eqs. (VI.8)–(VI.9) for case B] into Eq. (V.28) and applying the well-known commutation relations for the harmonic oscillator operators. In Appendix B we present the detailed calculation for the single phonon decay (case A) while in Appendix C we provide the details of the calculation for the more complicated case of double phonon decay (case B).

The final form of the thermally averaged product $\langle \prod_\mu I_\mu \rangle$ in Eq. (V.30) can be displayed in an identical form for both cases A and B, which is

$$\langle \prod_\mu I_\mu \rangle_T \simeq \prod_\mu \langle I_\mu \rangle_T = \prod_\mu A_\mu B_\mu D_\mu, \qquad \text{(VI.18)}$$

where

$$A_\mu = \exp\{-\tfrac{1}{4}(\Delta_\mu^2+K_\mu^2)+\tfrac{1}{2}K_\mu\Delta_\mu \exp[-\gamma_\mu(\tau-\tau')]\exp[-i\omega_\mu'(\tau-\tau')]\} \tag{VI.19}$$

$$B_\mu = (v_{s\mu})!\sum_{r=0}^{v_{s\mu}} \frac{(-1)^r}{(v_{s\mu}-r)!(r!)^2}[\tfrac{1}{2}\Delta_\mu^2\exp(-2\gamma_\mu\tau)+\tfrac{1}{2}K_\mu^2\exp(-2\gamma_\mu\tau')-\Delta_\mu K_\mu\exp[-\gamma_\mu(\tau+\tau')]\cos[\omega_\mu'(\tau-\tau')]]^r \tag{VI.20}$$

and

$$D_\mu = \exp(-\langle v_\mu\rangle_T\{\tfrac{1}{2}\Delta_\mu^2[1-\exp(-2\gamma_\mu\tau)]+\tfrac{1}{2}K_\mu^2[1-\exp(-2\gamma_\mu\tau')] - \Delta_\mu K_\mu\{\exp[-\gamma_\mu(\tau-\tau')]-\exp[-\gamma_\mu(\tau+\tau')]\}\cos[\omega_\mu'(\tau-\tau')]\}) \tag{VI.21}$$

while the final result for the time correlation function which is obtained by inserting Eqs. (VI.18)–(VI.21) into Eq. (V.30), takes the form

$$G(\tau,\tau') = \sum_\kappa |C_{sl}^\kappa|^2 \times \tfrac{1}{2}\{(\langle v_\kappa\rangle_T+1)\exp[-i\omega_\kappa'(\tau-\tau')-\gamma_\kappa(\tau-\tau')]+\langle v_\kappa\rangle_T\exp[i\omega_\kappa'(\tau-\tau')-\gamma_\kappa(\tau-\tau')]$$
$$+2(v_{s\kappa}-\langle v_\kappa\rangle_T)\exp[-\gamma_\kappa(\tau+\tau')]\cos[\omega_\kappa'(\tau-\tau')]\}\times\exp\{-\sum_\mu \tfrac{1}{2}\Delta_\mu^2+\sum_\mu \tfrac{1}{2}\Delta_\mu^2\exp[-i\omega_\mu'(\tau-\tau')-\gamma_\mu(\tau-\tau')]\}$$
$$\times\exp[-\sum_\mu \langle v_\mu\rangle_T(\tfrac{1}{2}\Delta_\mu^2[2-\exp(-2\gamma_\mu\tau)-\exp(-2\gamma_\mu\tau')]$$
$$-\Delta_\mu^2\{\exp[-\gamma_\mu(\tau-\tau')]-\exp[-\gamma_\mu(\tau+\tau')]\}\cos[\omega_\mu'(\tau-\tau')])]$$
$$\times\prod_\mu\left[(v_{s\mu})!\sum_{r=0}^{v_{s\mu}}\frac{(-1)^r}{(v_{s\mu}-r)!(r!)^2}\left(\frac{\Delta_\mu}{\sqrt{2}}\right)^{2r}\times\{\exp(-2\gamma_\mu\tau)+\exp(-2\gamma_\mu\tau')-2\exp[-\gamma_\mu(\tau+\tau')]\cos[\omega_\mu'(\tau-\tau')]\}^r\right]. \tag{VI.22}$$

It is worthwhile to bear in mind that γ in Eqs. (VI.18)–(VI.22) is defined by Eq. (VI.6′) for case A and by Eq. (VI.14b) for case B. The frequency shifts (VI.6′) and (VI.14a) may be neglected and ω_μ' may be replaced by ω_μ.

These results lead to the following conclusions:

(a) Equation (VI.22) together with Eq. (V.21) provide our final result for the nonradiative decay rate of a large molecule modified by vibrational (thermal) relaxation. The electronic transition is treated to second order while vibrational relaxation was handled to "infinite" order.

(b) Vibrational relaxation occurs both in the initial and in the final electronic levels system. Although the present treatment focuses attention on the nonradiative decay feature of a large "statistical" molecule, the results of the present study are applicable for the elucidation of the features of electronic relaxation of small molecules in a dense medium.[32] In the statistical limit vibrational relaxation in the final electronic manifold is of no importance while the nonradiative decay characteristics are just affected by vibrational relaxation in the initial electronic state. In the small molecule case vibrational relaxation in the final electronic manifold is crucial for providing a final dissipative channel for the electronic relaxation process.

(c) Our general equations for electronic vibrational relaxation in the limit of slow vibrational relaxation reduce to the result previously derived by us for the isolated molecule limit. In this case we have $\gamma_\mu=0$ so that Eqs. (VI.19)–(VI.21) reduce to the simple form

$$D_\mu = 1 \tag{VI.23}$$

$$B_\mu = (v_{s\mu})!\sum_{r=0}^{v_{s\mu}}\frac{(-1)^r}{(v_{s\mu}-r)!(r!)^2}\{\tfrac{1}{2}\Delta_\mu^2+\tfrac{1}{2}K_\mu^2-\Delta_\mu K_\mu\cos[\omega_\mu'(\tau-\tau')]\}^r \tag{VI.24}$$

$$A_\mu = \exp\{-\tfrac{1}{4}(\Delta_\mu^2+K_\mu^2)-\tfrac{1}{2}(K_\mu\Delta_\mu)\exp[-i\omega_\mu'(\tau-\tau')]\}. \tag{VI.25}$$

Inserting these results into Eq. (VI.18) and utilizing Eq. (V.30), the time correlation function takes the form

$$G(\tau,\tau') = G(\tau-\tau') = \exp(-\tfrac{1}{2}\sum_\mu \Delta_\mu^2)\sum_\kappa |C_{sl}^\kappa|^2(\{(v_{s\kappa}+1)\exp[-i\omega_\kappa'(\tau-\tau')]+v_{s\kappa}\exp[i\omega_\kappa'(\tau-\tau')]\}$$
$$\times\exp\{\sum_\mu \tfrac{1}{2}\Delta_\mu^2\exp[-i\omega_\mu'(\tau-\tau')]\})\times\prod_\mu\left((v_{s\mu})!\sum_{r=0}^{v_{s\mu}}\frac{(-1)^r\Delta_\mu^{2r}}{(v_{s\mu}-r)!(r!)^2}\{1-\cos[\omega_\mu'(\tau-\tau')]\}^r\right) \tag{VI.26}$$

which is just the generating function for the nonradiative decay of an initially excited $|s,\{v_\mu\}\rangle$ state.[20]

(d) Our general equations for electronic–vibrational relaxation in the fast vibrational relaxation limit reduce to a slightly modified form of the well-known result for the nonradiative decay of a (Boltzmann) thermally av-

eraged initial electronic state. In this limit we have for the relevant time scale $u_\mu(t)=0$, and relations (VI.16) or (VI.19) hold for cases A and B, respectively.

Focusing attention on case A we can utilize these relations in Eqs. (B9) and (B10) to get

$$\lambda_\mu(\tau,\tau')=0$$

$$\sigma_\nu{}^\mu(\tau,\tau')=[-iG_\nu{}^\mu/\gamma_\mu+i(\omega_\mu'-\omega_\nu)][\tfrac{1}{2}\Delta_\mu\exp(-i\omega_\nu\tau)-(K_\mu/\sqrt{2})\exp(-i\omega_\nu\tau')].$$

These relations in turn yield

$$A_\mu=\exp\{-\tfrac{1}{4}(\Delta_\mu{}^2+K_\mu{}^2)+\tfrac{1}{2}\Delta_\mu K_\mu\sum_\nu\{|G_\nu{}^\mu|^2/[\gamma_\mu{}^2+(\omega_\mu'-\omega_\nu)^2]\}\exp[i\omega_\nu(\tau-\tau')]\} \tag{VI.27}$$

$$B_\mu=1 \tag{VI.28}$$

$$D_\mu=\exp\left[-\sum_\nu\langle n_\nu\rangle_T\frac{|G_\nu{}^\mu|^2}{\gamma_\mu{}^2+(\omega_\mu'-\omega_\nu)^2}\left(\tfrac{1}{2}(\Delta_\mu{}^2+K_\mu{}^2)-\tfrac{1}{2}(\Delta_\mu K_\mu)\{\exp[-i\omega_\nu(\tau-\tau')]+\exp[i\omega_\nu(\tau-\tau')]\}\right)\right] \tag{VI.29}$$

Inserting these results into Eq. (VI.18) we obtain

$$\begin{aligned}\prod_\mu\langle I_\mu\rangle_T=\prod_\mu\Big[&\exp\Big(-\tfrac{1}{4}(\Delta_\mu{}^2+K_\mu{}^2)\{1+2\sum_\nu\langle n_\nu\rangle_T[|G_\nu{}^\mu|^2/(\gamma_\mu{}^2+(\omega_\mu'-\omega_\nu)^2)]\}\Big)\\&\times\exp\{\tfrac{1}{2}(\Delta_\mu K_\mu)\sum_\nu(\langle n_\nu\rangle_T+1)[|G_\nu{}^\mu|^2/(\gamma_\mu{}^2+(\omega_\mu'-\omega_\nu)^2)]\exp[-i\omega_\nu(\tau-\tau')]\\&+\tfrac{1}{2}(\Delta_\mu K_\mu)\sum_\nu\langle n_\nu\rangle_T[|G_\nu{}^\mu|^2/(\gamma_\mu{}^2+(\omega_\mu'-\omega_\nu)^2)]\exp[i\omega_\nu(\tau-\tau')]\}\Big].\end{aligned} \tag{VI.30}$$

To establish the correspondence between this result and previous results for the thermally averaged generating function[25] we may perform the summations over ν in Eq. (VI.30) by proceeding as follows; first we take $\langle n_\nu\rangle_T$ outside the summation at the point $\omega_\nu=\omega_\mu'$, secondly the summation is replaced by integration over the density of states and third we make use of the relation

$$\pi^{-1}\int d\omega_\nu[\gamma_\mu/\gamma_\mu{}^2+(\omega_\mu'-\omega_\nu)^2]\exp[i\omega_\nu(\tau-\tau')]=\exp[i\omega_\mu'(\tau-\tau')-\gamma_\mu|\tau-\tau'|]. \tag{VI.31}$$

As in our case $\tau\geq\tau'$ whereupon $|\tau-\tau'|=\tau-\tau'$ we get

$$\begin{aligned}\prod_\mu\langle I_\mu\rangle_T=\prod_\mu\Big(&\exp\{-\tfrac{1}{4}(\Delta_\mu{}^2+K_\mu{}^2)(2\langle v_\mu\rangle_T+1)\}\exp\{\tfrac{1}{2}\Delta_\mu K_\mu(\langle v_\mu\rangle_T+1)\exp[-i\omega_\mu'(\tau-\tau')-\gamma_\mu(\tau-\tau')]\}\\&+\{\tfrac{1}{2}\Delta_\mu K_\mu\langle v_\mu\rangle_T\exp[i\omega_\mu'(\tau-\tau')-\gamma_\mu(\tau-\tau')]\}\Big),\end{aligned} \tag{VI.32}$$

where we have put $\langle n_\nu\rangle_{T(\omega_\nu=\omega_\mu)}=\langle v_\mu\rangle_T$.

Thus the time correlation function takes the final form in the limit of rapid vibrational relaxation

$$\begin{aligned}G(\tau,\tau')=G(\tau-\tau')=&\exp[-\sum_\mu\tfrac{1}{2}\Delta_\mu{}^2(2\langle v_\mu\rangle_T+1)]\\&\times\tfrac{1}{2}\sum_\kappa|C_{sl}{}^\kappa|^2\{(\langle v_\kappa\rangle_T+1)\exp[-i\omega_\kappa'(\tau-\tau')-\gamma_\kappa(\tau-\tau')]+\langle v_\kappa\rangle_T\exp[i\omega_\kappa'(\tau-\tau')-\gamma_\kappa(\tau-\tau')]\}\\&\times\exp\{\tfrac{1}{2}\sum_\mu\Delta_\mu{}^2(\langle v_\mu\rangle_T+1)\exp[-i\omega_\mu'(\tau-\tau')-\gamma_\mu(\tau-\tau')]+\tfrac{1}{2}\sum_\mu\Delta_\mu{}^2\langle v_\mu\rangle_T\exp[i\omega_\mu'(\tau-\tau')-\gamma_\mu(\tau-\tau')]\}.\end{aligned} \tag{VI.33}$$

Equation (VI.33) was established for case A of vibrational relaxation. The same result can be derived for case B (where γ_μ is temperature dependent). Making use of Eq. (VI.17) we have for case B

$$\begin{aligned}\prod_\mu\langle I_\mu\rangle_T=\prod_\mu\Bigg\{&\exp\left[-\tfrac{1}{4}(\Delta_\mu{}^2+K_\mu{}^2)\left(1-2\sum_\nu\sum_\eta\frac{\langle n_\nu\rangle_T\langle n_\eta\rangle_T}{n_{\nu\eta}}\frac{|G_{\nu\eta}{}^\mu|^2n_{\nu\eta}}{\gamma_\mu{}^2+(\omega_\mu'-\omega_\nu-\omega_\eta)^2}\right)\right]\\&\times\exp\left[\tfrac{1}{2}(\Delta_\mu K_\mu)\sum_\nu\sum_\eta\left(\frac{\langle n_\nu\rangle_T\langle n_\eta\rangle_T}{n_{\nu\eta}}+1\right)\frac{|G_{\nu\eta}{}^\mu|^2n_{\nu\eta}}{\gamma_\mu{}^2+(\omega_\mu'-\omega_\nu-\omega_\eta)^2}\exp[-i(\omega_\nu+\omega_\eta)(\tau-\tau')]\right.\\&\left.+\tfrac{1}{2}(\Delta_\mu K_\mu)\sum_\nu\sum_\eta\frac{\langle n_\nu\rangle_T\langle n_\eta\rangle_T}{n_{\nu\eta}}\frac{|G_{\nu\eta}{}^\mu|^2n_{\nu\eta}}{\gamma_\mu{}^2+(\omega_\mu'-\omega_\nu-\omega_\eta)^2}\exp[i(\omega_\nu+\omega_\eta)(\tau-\tau')]\right]\Bigg\},\end{aligned} \tag{VI.34}$$

where $n_{\nu\eta}$ is defined by

$$n_{\nu\eta}=\langle n_\nu\rangle_T+\langle n_\eta\rangle_T+1. \tag{VI.35}$$

Utilizing Eq. (C11), taking the products $(\langle n_\nu\rangle_T\langle n_\eta\rangle_T/n_{\nu\eta})$ outside the summations in Eq. (VI.34) and making use of the definitions (VI.14b) we obtain again Eq. (VI.33) for the rapid vibrational relaxation limit.

The result obtained in the fast relaxation limit Eq. (VI.35) bears a close resemblance to the conventional form of the nonradiative decay probability of a thermally averaged initial electronic manifold.[24,25] Our result derived for the fast relaxation case exhibits a new feature as every frequency ω_μ is now replaced by $\omega_\mu'+i\gamma_\mu$. The uncertainty width of the frequency of each molecular mode is due to its interaction with the medium.

To elucidate the significance of this modification let us focus attention on the zero temperature limit of expression (VI.33).

$$G(\tau\tau')=\tfrac{1}{2}\sum_\kappa |\, C_{sl}{}^\kappa\,|^2 \exp[-i\omega_\kappa'(\tau-\tau')-\gamma_\kappa(\tau-\tau')]\exp\{-\tfrac{1}{2}\sum_\mu \Delta_\mu{}^2+\tfrac{1}{2}\sum_\mu \Delta_\mu{}^2\exp[-i\omega_\mu'(\tau-\tau')-\gamma_\mu(\tau-\tau')]\} \tag{VI.36}$$

which eventually leads to [using Eqs. (V.23) and (V.17)] the transition probability from the vibrationless level

$$W_{s0}=\frac{1}{\hbar^2}\sum_\kappa |\, C_{sl}{}^\kappa\,|^2 \exp(-\tfrac{1}{2}\sum_\mu \Delta_\mu{}^2)\ \mathrm{Re}\int_0^\tau d\tau' \exp\left[i(\tau-\tau')\frac{\Delta E}{\hbar}\right] G(\tau\tau')$$

$$=\frac{1}{2\hbar^2}\sum_\kappa |\, C_{sl}{}^\kappa\,|^2 \exp(-\tfrac{1}{2}\sum_\mu \Delta_\mu{}^2)\int_{-\tau}^{\tau} dx \exp\left(-ix\frac{\Delta E}{\hbar}\right)\exp(i\omega_\kappa'x-\gamma_\kappa\,|\,x\,|\,)$$

$$\times\exp[\tfrac{1}{2}\sum_\mu \Delta_\mu{}^2\exp(i\omega_\mu'x-\gamma_\mu\,|\,x\,|\,)]. \tag{VI.37}$$

Following conventional procedures we may replace the integration limits $-\tau\cdots\tau$ by $-\infty\cdots\infty$ (see also Sec. VII) Making now use of the expansion

$$\exp[\tfrac{1}{2}\sum_\mu \Delta_\mu{}^2\exp(i\omega_\mu'x-\gamma_\mu\,|\,x\,|\,)=\sum_{\{n\}}\exp[i(\sum_\mu n_\mu\omega_\mu')x-(\sum_\mu n_\mu\gamma_\mu)\,|\,x\,|\,]\prod_\mu[(\tfrac{1}{2}\Delta_\mu{}^2)^{n_\mu}/n_\mu!], \tag{VI.38}$$

we may evaluate the integral (VI.37) which yields

$$W_{s0}=\frac{1}{2\hbar^2}\sum_\kappa |\, C_{sl}{}^\kappa\,|^2\exp(-\tfrac{1}{2}\sum_\mu \Delta_\mu{}^2)$$

$$\times\sum_{\{n\}}[\gamma_\kappa+\sum_{\mu\neq\kappa} n_\mu\gamma_\mu/(\Delta E-\hbar\omega_\kappa-\hbar\sum_{\mu\neq\kappa} n_\mu\omega_\mu)^2+\tfrac{1}{4}(\gamma_\kappa+\sum_{\mu\neq\kappa} n_\mu\gamma_\mu)^2]\prod_\mu\frac{(\Delta_\mu{}^2/2)^{n_\mu}}{n_\mu!}. \tag{VI.39}$$

Noting that the factor

$$\exp(-\tfrac{1}{2}\sum_\mu \Delta_\mu{}^2)\prod_\mu[(\tfrac{1}{2}\Delta_\mu{}^2)^{n_\mu}/n_\mu!]$$

corresponds to the multimode Franck–Condon factor between the initial vibrationless level of the electronic state s and the level $\{n\}\equiv n_1, n_2, \cdots, n_\mu, \cdots$ of the electronic state l we see that Eq. (VI.39) corresponds to a modification of the conventional expression

$$W_{s0}=(2\pi/\hbar)\sum_{lj} |\, V_{s0,lj}\,|^2\delta(\Delta E-E_{lj});\qquad j\equiv\{n\}, \tag{VI.39'}$$

where the delta functions are replaced by Lorentzians. These Lorentzians are characterized by the widths (due to the vibrational relaxation) of the lj levels. We may note that the width of the level $j=\{n\}$ is the sum of the widths corresponding to the different modes, which, as expected, are proportional to their occupation numbers. The fact that γ_κ appears only with the coefficient $n_\kappa=1$ reflects the well known propensity rule that only the $\{lj\}$ states where the promoting mode is singly populated are coupled to the initial vibrationless level in the present model.

The modification of the transition probability in the fast vibrational relaxation limit [Eq. (VI.33)] is of limited significance in the statistical limit where it may be shown[32] that W_{so} does not depend on γ_μ and is given just by the former results of Jortner *et al.*[24,25] However this new result is of great importance in regarding nonradiative transitions in small molecules[32] imbedded in a medium. In this case the electronic relaxation is determined by the vibrational relaxation widths.

(e) Both in the slow relaxation limit (i.e., the isolated molecule case) and in the rapid relaxation limit the time correlation function depends just on $(\tau-\tau')$ [Eqs. (VI.33) and (VI.26)]. For experimentally relevant decay times, τ, the correlation function consists of a sharply peaked function for all τ, so that the transition probability in these two limits is independent of τ and the decay of the s electronic state is characterized by a single exponential.

(f) In the general case of coupled electronic vibrational relaxation the general form of the decay probability [Eq. (VI.22)] exhibits a simultaneous dependence on both τ and τ', and the nonradiative decay of the s state is nonexponential.

(g) The general expression, Eq. (VI.22), has been derived under the condition that the molecular oscillators are initially in a definite n state (by which we mean that the initial state is exactly defined by a given set of initial population numbers). Other initial conditions are also physically meaningful. Suppose that every molecular oscillator is initially obtained with a probability distribution corresponding to a Boltzmann distribution at some temperature T'. Then the function B_μ, Eq. (B14) [and the corresponding expression in Eq. (C2)] should be replaced by the appropriate thermal average, resulting in

$$\langle B_\mu\rangle_{T'} = \langle \exp[-\lambda_\mu^*(\tau,\tau')a_\mu^+]\exp[\lambda_\mu(\tau,\tau')a_\mu]\rangle_{T'}$$
$$= \exp[-|\lambda_\mu(\tau,\tau')|^2\langle n_\mu\rangle_{T'}] \tag{VI.40}$$

which should replace Eq. (VI.20) in the final result. The time correlation function $G(\tau,\tau')$ now takes the form [which should replace Eq. (VI.22)]

$$G(\tau,\tau') = \sum_\kappa |C_{sl}^\kappa|^2 \tfrac{1}{2}\{(\langle v_\kappa\rangle_T+1)\exp[-i\omega_\kappa'(\tau-\tau')-\gamma_\kappa(\tau-\tau')]$$
$$+\langle v_\kappa\rangle_T\exp[i\omega_\kappa'(\tau-\tau')-\gamma_\kappa(\tau-\tau')]+2(\langle v_\kappa\rangle_{T'}-\langle v_\kappa\rangle_T)\exp[-\gamma_\kappa(\tau+\tau')]\cos[\omega_\kappa'(\tau-\tau')]\}$$
$$\times\exp\{-\sum_\mu(2\langle v_\mu\rangle_T+1)\tfrac{1}{2}\Delta_\mu^2\}\exp\{\sum_\mu(\langle v_\mu\rangle_T+1)\tfrac{1}{2}\Delta_\mu^2\exp[-i\omega_\mu'(\tau-\tau')-\gamma_\mu(\tau-\tau')]$$
$$+\sum_\mu\langle v_\mu\rangle_T\tfrac{1}{2}\Delta_\mu^2\exp[i\omega_\mu'(\tau-\tau')-\gamma_\mu(\tau-\tau')]\}$$
$$\times\exp\{\sum_\mu(\langle v_\mu\rangle_T-\langle v_\mu\rangle_{T'})\tfrac{1}{2}\Delta_\mu^2[\exp(-2\gamma_\mu\tau)+\exp(-2\gamma_\mu\tau')-2\exp[-\gamma_\mu(\tau+\tau')]\cos[\omega_\mu'(\tau-\tau')]]\}. \tag{VI.41}$$

If $T'=T$ we obtain again the fast vibrational relaxation result.

(h) Another interesting case results when the initial state of the molecular vibrations is a Glauber coherent state. Such a distribution in the excited electronic state of a molecule may result from a broad band optical excitation of an electronically excited state of the molecule, provided that the potential surfaces corresponding to the ground and to the excited electronic states differ only by origin displacements. In this case, the initial state is taken to be a Glauber state $|\alpha\rangle=\exp(-\frac{1}{2}|\alpha|^2)\sum_n[\alpha^n/(n!)^{1/2}]|n\rangle$ instead of a n state. Eq. (B14) then yields

$$B_\mu = \langle\alpha_\mu|\exp(-\lambda_\mu^*(\tau,\tau')a_\mu^+)\exp(\lambda_\mu(\tau,\tau')a_\mu)|a_\mu\rangle$$
$$= \exp\{2i\alpha_\mu\,\mathrm{Im}[\lambda_\mu(\tau,\tau')]\}, \tag{VI.42}$$

(Im denotes imaginary part) which should replace Eq. (VI.20). We note that α_μ in Eq. (VI.38) is real, and is proportional to the origin displacement of the μth mode between the ground and the excited electronic states. The time correlation function $G(\tau,\tau')$ will be now given by

$$G(\tau,\tau') = \tfrac{1}{2}\sum_\kappa |c_{sl}^\kappa|^2\{(\langle v_\kappa\rangle_T+1)\exp[-i\omega_\kappa'(\tau-\tau')-\gamma_\kappa(\tau-\tau')]$$
$$+\langle v_\kappa\rangle_T\exp[i\omega_\kappa'(\tau-\tau')-\gamma_\kappa(\tau-\tau')]+2(\alpha_\kappa-\langle v_\kappa\rangle_T)\exp[-\gamma_\kappa(\tau+\tau')]\cos[\omega_\kappa'(\tau-\tau')]\}$$
$$\times\exp\{-\tfrac{1}{2}\sum_\mu\Delta_\mu^2+\tfrac{1}{2}\sum_\mu\Delta_\mu^2\exp[-i\omega_\mu'(\tau-\tau')-\gamma_\mu(\tau-\tau')\}$$
$$\times\exp\Big(-\sum_\mu\langle v_\mu\rangle_T\{\tfrac{1}{2}\Delta_\mu^2[2-\exp(-2\gamma_\mu\tau)-\exp(-2\gamma_\mu\tau')]$$
$$-\Delta_\mu^2\{\exp[-\gamma_\mu(\tau-\tau')]-\exp[-\gamma_\mu(\tau+\tau')]\}\cos[\omega_\mu'(\tau-\tau')]\}\Big)$$
$$\times\exp\{2i\sum_\mu(\Delta_\mu/\sqrt{2})\alpha_\mu[\exp(-\gamma_\mu\tau')\sin\omega_\mu'\tau'-\exp(-\gamma_\mu\tau)\sin\omega_\mu'\tau]\}. \tag{VI.43}$$

(i) The results obtained herein for the electronic vibrational relaxation features exhibit the same functional form for the two different models (cases A and B) for the molecule–medium coupling.

VII. THE LOW TEMPERATURE LIMIT

The general formula for electronic–vibrational relaxation derived in Sec. VI is rather cumbersome and direct physical information can be extracted from it only by numerical computations. This general result may be considerably simplified in the zero temperature limit, where, under certain conditions we shall be able to derive explicit expressions for the time dependent decay rate.

In the low temperature limit, we set $\langle v_\mu\rangle_T=0$ for every vibrational mode μ, and the vibrational relaxation width γ_μ is temperature independent [i.e., being given by (VI.14b) with $\langle n_\nu\rangle_T=\langle n_\eta\rangle_T=0$ for case B and by (VI.6′) for case A]. We shall also invoke a further simplifying assumption that only a single mode

(which corresponds to a nonpromoting mode) is initially vibrationally excited in the s electronic state. The rate of disappearance of the electronic state s with the initial molecular state being $|\, s, v_\alpha, \{0_\mu\}(\mu\neq\alpha)\,\rangle$, is now given from Eq. (VI.22)

$$G(\tau,\tau')=\tfrac{1}{2}\sum_\kappa |\, C_{sl}{}^\kappa\,|^2 \exp[-i\omega_\kappa'(\tau-\tau')-\gamma_\kappa(\tau-\tau')]$$
$$\times\exp\{-\tfrac{1}{2}\sum_\mu \Delta_\mu{}^2+\tfrac{1}{2}\sum_\mu \Delta_\mu{}^2$$
$$\times\exp[-i\omega_\mu'(\tau-\tau')-\gamma_\mu(\tau-\tau')]\}$$
$$\times(v_{s\alpha})!\sum_{r=0}^{v_{s\alpha}}\frac{(-1)^r}{(v_{s\alpha}-r)!(r!)^2}\left(\frac{\Delta_\mu}{\sqrt{2}}\right)^{2r}$$
$$\times\{\exp(-2\gamma_\mu\tau)+\exp(-2\gamma_\mu\tau')$$
$$-2\exp[-\gamma_\mu(\tau+\tau')]\cos[\omega_\mu'(\tau-\tau')]\}^r. \quad \text{(VII.1)}$$

Utilizing Eqs. (VI.22) with $\langle v_\mu\rangle_T=\langle v_\kappa\rangle_T=0$ for every μ and κ, the (time dependent) electronic decay rate may be displayed in the form

$$W_s(t)=\frac{1}{\hbar^2}\sum_\kappa |\, C_{sl}{}^\kappa\,|^2\exp(-\tfrac{1}{2}\sum_\mu \Delta_\mu{}^2)$$
$$\times(v_{s\alpha})!\sum_{r=0}^{v_{s\alpha}}\frac{(-1)^r\exp(-2\gamma_\alpha rt)}{(v_{s\alpha}-r)!(r!)^2}\left(\frac{\Delta_\alpha}{\sqrt{2}}\right)^{2r}L_r(t), \quad \text{(VII.2)}$$

where we have defined a set of auxiliary functions of an integer argument

$$L_r(t)=\mathrm{Re}\int_0^t dx$$
$$\times\exp\left[i(\Delta E-\hbar\omega_\kappa')\frac{x}{\hbar}-\gamma_\kappa x\right]f(x)(g(x))^r, \quad \text{(VII.3)}$$

which are determined by the following functions

$$f(x)=\exp\{\tfrac{1}{2}\sum_\mu \Delta_\mu{}^2\exp[-i\omega_\mu' x-\gamma_\mu x]\}, \quad \text{(VII.4a)}$$

$$g(x)=1+\exp(2\gamma_\alpha x)-2\exp(\gamma_\alpha x)\cos(\omega_\alpha' x). \quad \text{(VII.4b)}$$

For $r=0$ we obtain

$$L_0(t)=\mathrm{Re}\int_0^t dx f(x)\exp[i(\Delta E-\hbar\omega_\kappa')(x/\hbar)-\gamma_\kappa x]$$

which represents a slightly modified form of the integral encountered in calculating radiationless transition rate from the vibrationless level.[24,25] In this case it may be verified that $L_0(t)$ does not depend on t for experimentally significant times, so that as usual the upper limit of the integral is replaced by infinity.[52] We shall now invoke the additional assumption that $L_n(t)$ does not depend on t also for $n\neq 0$. We did not succeed to solve the integral (VII.7) analytically, and a numerical solution was provided. In order to reproduce the features of the nonradiative decay of a large molecule, we have performed numerical calculations on a model system consisting of a molecule characterized by 30 randomly chosen frequencies (in the range 500–3000 cm^{-1}). In order to mimic the decay characteristics in the statistical limit we have chosen the reduced displacements $\Delta_\mu\sim 1$. Numerical calculations performed by us on model systems have verified that the assumption that $L_r(t)$ is independent of t is valid in the statistical limit provided that the coupling is sufficiently strong (e.g., $\Delta_\mu\simeq 0.5-1.0$ for all μ), and for such times t for which

$$r\gamma_\alpha t\lesssim 1. \quad \text{(VII.5)}$$

We further note, however, that for $r\gamma_\alpha t>1$ only the term with $r=0$ will contribute significantly as the factor $\exp(-2\gamma_\alpha rt)$ in Eq. (VII.2) will suppress the $r>0$ contributions. We thus assert that in the statistical limit the upper integration limit in Eq. (VII.3) does not affect the final result. [For the term with $r=0$ this limit may be replaced by infinity according to Eq. (VII.5).] The time dependence of the nonradiative transition rate may be then recast in the physically transparent form

$$W_s(t)=\sum_{r=0}^{v_{s\alpha}}J_r\exp(-2\gamma_\alpha rt), \quad \text{(VII.6)}$$

where

$$J_r=\frac{2}{\hbar^2}\sum_\kappa |\, C_{sl}{}^\kappa\,|^2\exp(-\tfrac{1}{2}\sum_\mu \Delta_\mu{}^2)(v_{s\alpha})!$$
$$\times\frac{(-1)^r(\Delta_\alpha/\sqrt{2})^r}{(v_{s\alpha}-r)!(r!)^2}L_r. \quad \text{(VII.7)}$$

The rate of disappearance of the s electronic state initially excited to the $|\, s, v_\alpha, \{0_\mu\}_{(\mu\neq\alpha)}\,\rangle$ vibrational level, is in general time dependent (the decay being nonexponential and is given by Eqs. (VII.6) and (VII.7) for a large molecule in the low temperature limit. This time dependent decay rate [Eq. (VII.6)] is expressed as a superposition of contributions from the vibrationally excited levels, of the mode α through which the initially excited state can cascade downwards with the s electronic manifold.

It is instructive to notice that the analytical expressions (VII.6) and (VII.7) provide a proper description both of the slow relaxation and the fast relaxation limits. In these two cases the decay rate is time dependent. In the case of slow relaxation we can take $\gamma_\alpha t\ll 1$ whereupon we set all the exponentials involving γ_α in Eqs. (VII.3) and (VII.6) to be equal to unity, to obtain

$$W_s=\sum_{r=0}^{v_{\alpha s}}J_r$$

which is just the decay rate of the initially excited $|\, s, v_{s\alpha}, 0_{\mu\neq\alpha}\,\rangle$ level in the isolated molecule.[20] This result was derived for $t\ll\gamma_\alpha^{-1}$ where relation (VII.5) which provides a sufficient condition for the validity of Eq. (VII.6) does hold. Now, in the fast relaxation limit, we take $\gamma_\alpha t\gg 1$ and only the $r=0$ term contributes to the sum (VII.6). Thus the decay rate in this case reduces to $W_s=J_0$ which [see Eqs. (VII.3) and (VII.7)]

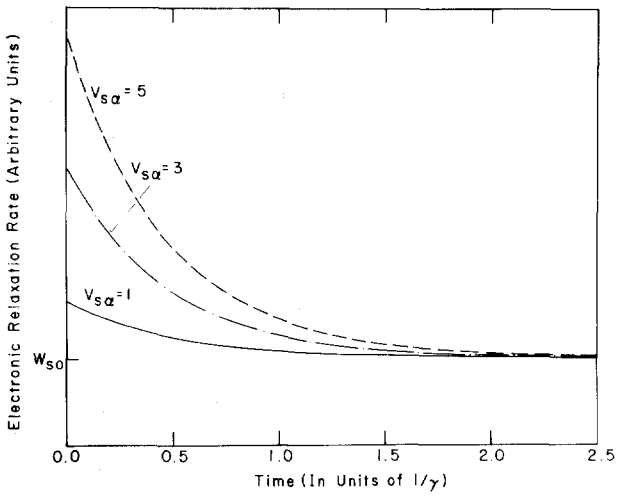

FIG. 2. Electronic relaxation rate as a function of time [Eq. (VII.6)], for a model molecule characterized by 30 randomly chosen frequencies (ω chosen between 500 cm^{-1} and 3000 cm^{-1}) and by origin shifts $\Delta_\mu=1$ for every vibrational mode. The electronic energy gap was taken as 12 000 cm^{-1}. The molecule is assumed to be initially in the excited vibronic state $|s, V_{s\alpha}, \{0_\mu\}_{\mu\neq\alpha}\rangle$. At long times the decay rate approaches W_{s0}, the decay rate of the vibrationless level of the sth electronic manifold.

is just the nonradiative decay rate from the vibrationless level of the s state. The validity of Eqs. (VII.6) and (VII.7) in the fast vibrational relaxation limit, (i.e., for $t\gg\gamma_\alpha^{-1}$) indicates that the validity range of these results considerably exceeds the time region determined by the sufficient condition (VII.5) in agreement with our general arguments. It is also worthwhile to notice that the decay rate from the vibrationless level of the s state (i.e., $v_{s\alpha}=0$) is independent of time.

To conclude this discussion we present in Fig. 2 typical results based on Eqs. (VII.6) and (VII.7) for the time dependence of electronic relaxation rate for a model system.

VIII. DISCUSSION

In this work, we have explored the implications of vibrational relaxation on electronic relaxation processes in large molecules in terms of a simplified model involving a "harmonic" two electronic levels molecular system interacting with a harmonic medium via one phonon or via two phonon (or rather phonon and vibron) coupling. We have limited ourselves to the study of electronic relaxation, and the role of radiative decay was disregarded. It is nevertheless expected that the total decay rate is $(1/\hbar)\Gamma=(1/\hbar)\Gamma_R+W_s(t)$, where Γ_R is the radiative width of any vibronic component in the s state. As we are interested here in ultrafast decay processes Γ_R can be neglected. Apart from the approximations inherent in this admittedly simplified treatment, no attempt was made to provide numerical estimates for the relevant molecule–medium coupling terms, but rather to explore general relations and correlations. A similar approach was adopted in the study of exciton phonon coupling and optical line broadening of exciton states in molecular crystals.[53] From the point of view of general methodology the molecule–phonon+vibron coupling (i.e., the two phonon decay) proposed herein provides in our opinion a reasonable physical picture for the vibrational relaxation processes of high frequency molecular vibration in a host medium which consists of polyatomic molecules. In this context we would like to comment that the present theory is applicable to nonradiative decay in dense media and cannot be used to handle electronic–vibrational relaxation processes in the gas phase, as collisional perturbations cannot be accounted for in terms of the coupling Hamiltonian [Eqs. (V.4) or (V.5)]. It is, however, important to bear in mind that the translational symmetry of the host matrix does not enter in our model, as we have specified the medium phonons in terms of their density of states. As the latter concept is also valid for disordered systems the present treatment is applicable for electronic–vibrational relaxation in solids, glasses and liquids.

We would like to mention two relevant problems in solid state physics which were handled by similar methods, either from the point of view of general methodology or in respect to the details of the calculations. In the classical work of Toyozawa[53] on the optical lineshapes of Wannier excitons the exciton lattice interaction and the exciton radiation coupling were simultaneously considered, the matter–radiation interaction being handled to second order while the exciton lattice coupling was treated to all orders in a manner similar to the present approach. Kreiger[17] has studied the scattering of slow neutrons by an harmonic oscillator which is subjected to vibrational relaxation and has utilized the Heizenberg representation of the coordinate and momentum operator for the damped harmonic oscillator provided by Senitzky,[4] to the treatment of Zemach and Glauber.[54] This method is similar to our approach to the vibrational relaxation problem.

To the best of our knowledge the present work provides the first comprehensive study of the coupling between nonradiative and vibrational relaxation processes. Several previous works in the field of electronic relaxation have direct bearing on the work. As it is well-known, early work on electronic relaxation referred to the problem of vibrational relaxation. Gouterman[55] considered the analogy between photon and phonon emission and considered the dissipation of electronic energy to lattice energy, disregarding the role of intrastate intramolecular relaxation. In the pioneering work of Robinson and Frosch[31d] vibrational relaxation in the final electronic manifold has been taken into account, without working out its full implications, so that the Robinson–Frosch formula corresponds to rare cases which are seldom encountered in real life.[32] It is also worthwhile to mention that in a recent publication Osherov and Medvedev[56] have pro-

vided a semiclassical theory which attempts to account for the influence of vibrational relaxation in the initial electronic manifold on the optical line shape of a model molecule characterized by one harmonic vibrational mode. Their theory essentially consists of replacing Eq. (I.1) by an equivalent expression in which W_i is averaged by a nonequilibrium time dependent density matrix. Besides the natural limitation of this semiclassical treatment (i.e., $kT \gg \hbar\omega$) the time dependence of the vibrational density matrix is taken to evolve only from vibrational relaxation, and other relaxation processes depleting the states are disregarded. Such approach may be suitable for the radiative transition problems. Moreover, vibrational relaxation in the final electronic manifold was disregarded in that work.[56]

The theoretical technique developed herein is quite general and may be readily applied to other intensity problems in the field of molecular physics:

(a) The occurrence of infrared emission originating from highly excited vibronic levels of the final electronic states involved in electronic relaxation has been predicted theoretically[57] and experimentally discovered.[58] The effect of infrared stimulated nonradiative decay of polyatomic molecules is of considerable interest. This effect will be trivial in the statistical limit, but for a medium sized molecule stimulated decay in the final electronic state will provide a novel interesting decay channel. The problem may be theoretically considered by replacing the phonon bath by a photon bath while the field–molecule coupling is again given by Eq. (V.4).

(b) The present theory is applicable to the nonradiative decay of small molecules in a dense medium[32] where vibrational relaxation in the final manifold provides the decay channel for electronic relaxation.

(c) The present scheme may be modified to include changes in the medium phonon states between the two electronic states, whereupon the role of vibrational relaxation of zero phonon lines can be studied.

(d) The present results are directly applicable for the study of vibrational relaxation (excluding electronic relaxation) effects on the optical line shapes.[47] There exists a formal analogy between the nonradiative transition probability and the optical line shape for a symmetry forbidden transition in the limit of zero frequency. We may utilize the Fourier transform of the autocorrelation function Eq. (VI.24), at energy $(\Delta E - E)$ to obtain the line shape of a symmetry forbidden transition at the photon energy E while for a symmetry allowed transition the contribution of the promoting modes in $G(\tau, \tau')$ has to be replaced by unity.[47]

From the point of view of the experimentalist the present work provides new information concerning nonexponential decay characteristics of a large molecule in a dense medium, which are of considerable interest for the understanding of ultrafast molecular decay processes. The beautiful experimental techniques of picosecond spectroscopy developed by Rentzepis,[48] provide for the time being just the half lifetime, while no information was as yet obtained (or claimed) concerning the detailed features of the decay characteristics. Further development of the experimental techniques will be of considerable interest.

APPENDIX A: TRANSFORMATION OF VIBRATIONAL WAVEFUNCTIONS AND TRANSITION OPERATOR FOR RADIATIVE PROCESSES

To demonstrate the transformation procedure of Sec. IV let us focus attention on the relatively simple case of radiative electronic matrix element. This is

$$\mu_{lj,si} = (\langle \phi_s \chi_{si}(\mathbf{q}_s, \mathbf{v}_i) \mid \mu \mid \phi_l \chi_{lj}(\mathbf{q}_l, \mathbf{v}_j) \rangle), \tag{A1}$$

where v_i and v_j are sets of vibrational quantum number characterizing the s and the l vibrational functions, respectively. $\langle\ \rangle$ denotes integration over electronic coordinates while $(\ )$ denotes integration over nuclear coordinates. μ represents the molecule–radiation field coupling operator.

Invoking the conventional Condon approximation one gets

$$\mu_{lj,si} = \langle s \mid \mu \mid l \rangle (\chi_{si}(\mathbf{q}_s, \mathbf{v}_i) \mid \chi_{lj}(\mathbf{q}_l, \mathbf{v}_j)). \tag{A2}$$

Now we utilize the transformation

$$\chi_{lj}(\mathbf{q}_l, \mathbf{v}_j) = \prod_\mu \exp(i\Delta_\mu p_\mu) \chi_{si}(\mathbf{q}_s, \mathbf{v}_j) \tag{A3}$$

to obtain

$$\mu_{lj,si} = \langle s \mid \mu \mid l \rangle (\chi_{si}(\mathbf{q}, v_i) \mid \prod_\mu \exp(-i\Delta_\mu p_\mu) \mid \chi_{sj}(\mathbf{q}, \mathbf{v}_j)). \tag{A4}$$

In what follows the s index for the nuclear coordinates and momenta will be omitted.

The operator for dipole allowed transition may thus be written

$$\hat{\mu} = M_{sl} d^+ \prod \exp(-i\Delta_\mu p_\mu) + \text{h.c.} \tag{A5}$$

with

$$M_{sl}=\langle s \mid \mu \mid l\rangle, \tag{A6}$$

where it is understood that this operator is to operate on a basis of functions where the same vibrational set of functions $\chi_s(\mathbf{q}, \mathbf{v})$ is attached to every electronic function. To obtain a complete second quantization notation we insert into Eq. (A5) the creation and annihilation operator representation of the momentum operator

$$p_\mu=(i/\sqrt{2})\,(a_\mu^+-a_\mu) \tag{A7}$$

and using the well-known identity

$$\exp(\hat{A}+\hat{B})=\exp(\hat{A})\,\exp(\hat{B})\,\exp(-\tfrac{1}{2}[\hat{A},\hat{B}]) \tag{A8a}$$

which holds provided that

$$[\hat{A},[\hat{A},\hat{B}]]=[\hat{B},[\hat{A},\hat{B}]]=0 \tag{A8b}$$

we obtain

$$\exp(i\Delta_\mu p_\mu)=\exp[-(\Delta_\mu/\sqrt{2})a_\mu^+]\exp[(\Delta_\mu/\sqrt{2})a_\mu]\exp(-\tfrac{1}{4}\Delta_\mu^2) \tag{A9}$$

so that

$$\hat{\mu}=M_{sl}\exp\Big(-\sum_\mu \tfrac{1}{4}\Delta_\mu^2\{d^+\prod_\mu \exp[(\Delta_\mu/\sqrt{2})a_\mu^+]\exp[-(\Delta_\mu/\sqrt{2})a_\mu]+d\prod_\mu \exp[-(\Delta_\mu/\sqrt{2})a_\mu^+]\exp[(\Delta_\mu/\sqrt{2})a_\mu]\}\Big) \tag{A10}$$

APPENDIX B: EVALUATION OF MATRIX ELEMENTS FOR THE ONE PHONON DECAY

In this and in the following appendices we shall make use of the following relations

$$[a_\mu(t),\, a_\mu^+(t)]=1 \tag{B1}$$

which implies

$$\exp[xa^+(t)+ya(t)]=\exp[xa^+(t)]\exp[ya(t)]\exp(\tfrac{1}{2}xy) \tag{B2}$$

and also

$$\exp[xa^+(t)]\exp[ya(t)]=\exp[ya(t)]\exp[xa^+(t)]\exp(-xy), \tag{B3}$$

$$\exp[-xa^+(t)][a(t)]^n\exp[xa^+(t)]=[a(t)+x]^n, \tag{B4}$$

$$\exp[-ya(t)][a^+(t)]^n\exp[ya(t)]=[a^+(t)-y]^n, \tag{B5}$$

where in all these relations the creation and annihilation operators are taken at the same time.

Utilizing Eq. (B2) we may rewrite Eq. (V.28) in the form

$$I_\mu=\exp(-\tfrac{1}{4}\Delta_\mu^2-\tfrac{1}{4}K_\mu^2)\,\langle v_{s\mu} \mid \exp[-(\Delta_\mu/\sqrt{2})a_\mu^+(\tau)]\exp[(\Delta_\mu/\sqrt{2})a_\mu(\tau)]$$
$$\times\exp[(K_\mu/\sqrt{2})a_\mu^+(\tau')]\exp[-(K_\mu/\sqrt{2})a_\mu(\tau')] \mid v_{s\mu}\rangle. \tag{B6}$$

Inserting now into this equation the expressions (VI.1) and (VI.2) for the time dependent damped creation and annihilation operators in the Glauber case,[6] and then utilizing Eq. (B3), we obtain

$$I_\mu=\exp\{-\tfrac{1}{4}\Delta_\mu^2-\tfrac{1}{4}K_\mu^2+\tfrac{1}{2}K_\mu\Delta_\mu[u_\mu^*(\tau')u_\mu(\tau)+\sum_\nu v_\nu^{\mu*}(\tau')v_\nu^\mu(\tau)]\}$$
$$\times\langle v_{s\mu} \mid \exp\{[(K_\mu/\sqrt{2})u_\mu^*(\tau')-(\Delta_\mu/\sqrt{2})u_\mu^*(\tau)]a_\mu^+\}$$
$$\times\exp\{[(\Delta_\mu/\sqrt{2})u_\mu(\tau)-(K_\mu/\sqrt{2})u_\mu(\tau')]a_\mu\}\exp\{\sum_\nu[(K_\mu/\sqrt{2})v_\nu^{\mu*}(\tau')-(\Delta_\mu/\sqrt{2})v_\nu^{\mu*}(\tau)]b_\nu^+\}$$
$$\times\exp\{\sum_\nu[(\Delta_\mu/\sqrt{2})v_\nu^\mu(\tau)-(K_\mu/\sqrt{2})v_\nu^\mu(\tau')]b_\nu\} \mid v_{s\mu}\rangle \tag{B7}$$

so that

$$\langle\prod_\mu I_\mu\rangle_T=\prod_\mu\{\exp\{-\tfrac{1}{4}\Delta_\mu^2-\tfrac{1}{4}K_\mu^2+\tfrac{1}{2}K_\mu\Delta_\mu[u_\mu^*(\tau')u_\mu(\tau)+\sum_\nu v_\nu^{\mu*}(\tau')v_\nu^\mu(\tau)]\}$$
$$\times\langle v_{s\mu} \mid \exp[-\lambda_\mu^*(\tau,\tau')a_\mu^+]\exp[\lambda_\mu(\tau,\tau')a_\mu] \mid v_{s\mu}\rangle\}\prod_\nu\langle\exp\{[-\sum_\mu\sigma_\nu^{\mu*}(\tau,\tau')]b_\nu^+\}\exp\{[\sum_\mu\sigma_\nu^\mu(\tau,\tau')]b_\nu\}\rangle_T, \tag{B8}$$

where

$$\lambda_\mu(\tau,\tau')=(\Delta_\mu/\sqrt{2})u_\mu(\tau)-(K_\mu/\sqrt{2})u_\mu(\tau') \tag{B9}$$

$$\sigma_\nu(\tau,\tau')=(\Delta_\mu/\sqrt{2})v_\nu^\mu(\tau)-(K_\mu/\sqrt{2})v_\nu^\mu(\tau'). \tag{B10}$$

If we evaluate the medium (thermal) part of Eq. (B8) we shall encounter cross terms of the type $\sigma_\nu\sigma_{\nu'}$ in which $\mu\neq\mu'$. The appearance of these terms is inconsistent with our assumption (stated in Sec. II) that the molecular oscillators are damped independently, or, in other words, that these oscillators are not coupled via their interaction with the medium. We shall, therefore, neglect these cross terms. This approximation is equivalent to the assumption

$$\langle\prod_\mu I_\mu\rangle_T=\prod_\mu\langle I_\mu\rangle_T \tag{B11}$$

as may easily be verified. This is just another way of stating the mutual independence of the molecular oscillators.

Equation (B8) will be thus replaced by

$$\prod_\mu\langle I_\mu\rangle_T=\prod_\mu(A_\mu B_\mu D_\mu), \tag{B12}$$

where

$$A_\mu=\exp\{-\tfrac{1}{4}\Delta_\mu{}^2-\tfrac{1}{4}K_\mu{}^2+\tfrac{1}{2}K_\mu\Delta_\mu[u_\mu{}^*(\tau')u_\mu(\tau)+\sum_\nu v_\nu{}^{\mu*}(\tau')v_\nu{}^\mu(\tau)]\} \tag{B13}$$

$$B_\mu=\langle v_{s\mu}\mid\exp[-\lambda_\mu(\tau,\tau')a_\mu{}^+]\exp[\lambda_\mu(\tau,\tau')a_\mu]\mid v_{s\mu}\rangle \tag{B14}$$

$$D_\mu=\prod_\nu C_\nu{}^\mu$$

with

$$C_\nu{}^\mu=\langle\exp[-\sigma_\nu{}^{\mu*}(\tau,\tau')b_\nu{}^+]\exp[\sigma_\nu{}^\mu(\tau,\tau')b_\nu]\rangle_T. \tag{B15}$$

The molecular matrix elements have been previously evaluated,[20] with the result

$$B_\mu=(v_{s\mu})!\sum_{r=0}^{v_{s\mu}}\frac{(-1)^r\mid\lambda_\mu\mid^{2r}}{(v_{s\mu}-r)!(r!)^2}. \tag{B16}$$

The medium thermally averaged matrix element is easily calculated using the well-known relation

$$\langle\exp(\hat{O})\rangle_T=\exp(\tfrac{1}{2}\langle\hat{O}^2\rangle_T), \tag{B17}$$

where $\hat{O}$ is an harmonic oscillator operator which is linear in the coordinate and momentum operators of the oscillator. We obtain

$$\begin{aligned}C_\nu{}^\mu&=\langle\exp(-\sigma_\nu{}^{\mu*}b_\nu{}^+)\exp(\sigma_\nu{}^\mu b_\nu)\rangle_T\\&=\langle\exp[\sigma_\nu{}^\mu b_\nu-\sigma_\nu{}^{\mu*}b_\nu{}^+]\rangle_T\exp(\tfrac{1}{2}\mid\sigma_\nu{}^\mu\mid^2)\\&=\exp(-\tfrac{1}{2}\mid\sigma_\nu{}^\mu\mid^2\langle 2b_\nu{}^+b_\nu+1\rangle_T)\exp(\tfrac{1}{2}\mid\sigma_\mu{}^\nu\mid^2)\\&=\exp(-\mid\sigma_\nu{}^\mu\mid^2\langle n_\nu\rangle_T).\end{aligned} \tag{B18}$$

The auxiliary functions appearing in Eqs. (B12)–(B15) are now evaluated by utilizing Eqs. (VI.3) and (VI.4):

$$u_\mu(\tau')u_\mu(\tau)=\exp[-\gamma_\mu(\tau+\tau')]\exp[-i\omega_\mu'(\tau-\tau')] \tag{B19}$$

$$\sum_\nu v_\nu{}^{\mu*}(\tau')v_\nu{}^\mu(\tau)=\{\exp[-\gamma_\mu(\tau-\tau')]-\exp[-\gamma_\mu(\tau+\tau')]\}\exp[-i\omega_\mu'(\tau-\tau')] \tag{B20}$$

$$\mid\lambda_\mu(\tau,\tau')\mid^2=(\Delta_\mu{}^2/2)\exp(-2\gamma_\mu\tau)+(K_\mu{}^2/2)\exp(-2\gamma_\mu\tau')-\Delta_\mu K_\mu\exp[-\gamma_\mu(\tau+\tau')]\cos[\omega_\mu'(\tau-\tau')] \tag{B21}$$

$$\begin{aligned}\sum_\nu\mid\sigma_\nu{}^\mu\mid^2\langle n_\nu\rangle_T&\simeq\langle v_\mu\rangle_T\sum_\nu\mid\sigma_\nu{}^\mu\mid^2\\&=\langle v_\mu\rangle_T(\tfrac{1}{2}\Delta_\mu{}^2[1-\exp(-2\gamma_\mu\tau)]+\tfrac{1}{2}K_\mu{}^2[1-\exp(-2\gamma_\mu\tau')]\\&\quad-\Delta_\mu K_\mu\{\exp[-\gamma_\mu(\tau-\tau')]-\exp[-\gamma_\mu(\tau+\tau')]\}\cos[\omega_\mu'(\tau-\tau')]).\end{aligned} \tag{B22}$$

The summations in Eqs. (B20) and (B22) are evaluated by transforming them into integration and assuming that these integrations over ω_ν may be extended from $-\infty$ to ∞. Utilizing Eqs. (B12)–(B22), Eqs. (VI.20)–(VI.23) are easily obtained.

APPENDIX C: EVALUATION OF MATRIX ELEMENTS IN THE TWO PHONON CASE

We present the evaluations of matrix elements analogous to those calculated in Appendix B, for the more general case described by Eqs. (VI.8)–(VI.11). Eq. (B1) and thus Eqs. (B2)–(B5) are valid also for this case. Thus starting from Eqs. (IV.28) we apply these relations to obtain again Eq. (B6). Applying now Eqs. (VI.8) and

(VI.9), Eq. (B6) may be recast in the more detailed form

$$I_\mu=\exp[-\tfrac{1}{4}\Delta_\mu^2-\tfrac{1}{4}K_\mu^2+\tfrac{1}{2}\Delta_\mu K_\mu u_\mu^*(\tau')u_\mu(\tau)]$$
$$\times\langle v_{s\mu}\mid\exp\{[(K_\mu/\sqrt{2})u_\mu^*(\tau')-(\Delta_\mu/\sqrt{2})u_\mu^*(\tau)]a_\mu^+\}\exp\{[(\Delta_\mu/\sqrt{2})u_\mu(\tau)-(K_\mu/\sqrt{2})u_\mu(\tau')]a_\mu\}$$
$$\times\exp[-(\Delta_\mu/\sqrt{2})\sum_\nu\sum_\eta v_{\nu\eta}{}^\mu{}^*(\tau)b_\nu{}^+C_\eta{}^+]\exp[(\Delta_\mu/\sqrt{2})\sum_\nu\sum_\eta v_{\nu\eta}{}^\mu(\tau)b_\nu C_\eta]$$
$$\times\exp[(K_\mu/\sqrt{2})\sum_\nu\sum_\eta v_{\nu\eta}{}^\mu{}^*(\tau')b_\nu{}^+C_\eta{}^+]\exp[-(K_\mu/\sqrt{2})\sum_\nu\sum_\eta v_{\nu\eta}{}^\mu(\tau')b_\nu C_\eta]\mid v_{s\mu}\rangle \quad (C1)$$

invoking the approximation introduced in Appendix B:

$$\langle\prod_\mu I_\mu\rangle_T=\prod_\mu\langle I_\mu\rangle_T$$

we may write

$$\langle I_\mu\rangle_T=\exp\{-\tfrac{1}{4}\Delta_\mu^2-\tfrac{1}{4}K_\mu^2+\tfrac{1}{2}K_\mu\Delta_\mu[u_\mu^*(\tau')u_\mu(\tau)+\sum_\nu\sum_\eta v_{\nu\eta}{}^\mu{}^*(\tau')v_{\nu\eta}{}^\mu(\tau)]\}$$
$$\times\langle v_{s\mu}\mid\exp[-\lambda_\mu^*(\tau,\tau')a_\mu^+]\exp[\lambda_\mu(\tau,\tau')a_\mu]\mid v_{s\mu}\rangle\prod_{\nu,\eta}\langle\exp[-\sigma_{\nu\eta}{}^\mu(\tau,\tau')b_\nu{}^+]\exp[\sigma_{\nu\eta}{}^\mu(\tau,\tau')b_\nu]\rangle_T. \quad (C2)$$

The new mathematical problem encountered here is that now one cannot apply relations of the type (B1)–(B5) for the two-phonon operators $b_\nu{}^+C_\eta{}^+$ and $b_\nu C_\eta$. This difficulty may be overcome by invoking the random phase approximation (RPA) utilized to obtain expressions (VI.8)–(VI.11).[51] Thus by the RPA we have

$$[b_\nu C_\eta,\ b_{\nu'}{}^+C_{\eta'}{}^+]=b_{\nu'}{}^+b_\nu\delta_{\eta\eta'}+C_{\eta'}{}^+C_\eta\delta_{\nu\nu'}+\delta_{\nu\nu'}\delta_{\eta\eta'}\simeq(\langle n_\nu\rangle_T+\langle n_\eta\rangle_T+1)\delta_{\nu\nu'}\delta_{\eta\eta'}. \quad (C3)$$

We notice that the operators $[1/(n_{\nu\eta})^{1/2}]b_\nu C_\eta[1/(n_{\nu\eta})^{1/2}]b_\nu{}^+C_\eta{}^+$, $n_{\nu\eta}=\langle n_\nu\rangle_T+\langle n_\eta\rangle_T+1$ behave in this approximation like simple (one phonon) creation and annihilation operators and thus fulfill Eqs. (B1)–(B5) {where $[1/(n_{\nu\eta})^{1/2}]b_\nu{}^+C_\eta{}^+$ replaces $a_\mu{}^+$ and $[1/(n_{\nu\eta})^{1/2}]b_\nu C_\eta$ replaces a_μ}. The medium part of Eq. (C2) may now be evaluated in a manner similar to that applied in Appendix B:

$$\text{Medium part}=\Big\langle\exp\Big(-\frac{\Delta_\mu}{\sqrt{2}}\sum_\nu\sum_\eta v_{\nu\eta}{}^\mu{}^*(\tau)(n_{\nu\eta})^{1/2}\frac{b_\nu{}^+C_\eta{}^+}{(n_{\nu\eta})^{1/2}}\Big)\exp\Big(\frac{\Delta_\mu}{\sqrt{2}}\sum_\nu\sum_\eta v_{\nu\eta}{}^\mu(\tau)(n_{\nu\eta})^{1/2}\frac{b_\nu C_\eta}{(n_{\nu\eta})^{1/2}}\Big)$$
$$\times\exp\Big(\frac{K_\mu}{\sqrt{2}}\sum_\nu\sum_\eta v_{\nu\eta}{}^\mu{}^*(\tau')(n_{\nu\eta})^{1/2}\frac{b_\nu{}^+C_\eta{}^+}{(n_{\nu\eta})^{1/2}}\Big)\exp\Big(-\frac{K_\mu}{\sqrt{2}}\sum_\nu\sum_\eta v_{\nu\eta}{}^\mu(\tau')(n_{\nu\eta})^{1/2}\frac{b_\nu C_\eta}{(n_{\nu\eta})^{1/2}}\Big)\Big\rangle_T$$
$$=\exp[\tfrac{1}{2}(\Delta_\mu K_\mu)\sum_\nu\sum_\eta v_{\nu\eta}{}^\mu(\tau)v_{\nu\eta}{}^\mu{}^*(\tau')n_{\nu\eta}]$$
$$\times\Big\langle\exp\Big(-\sigma_{\nu\eta}{}^\mu{}^*(\tau,\tau')\frac{b_\nu{}^+C_\eta{}^+}{(n_{\nu\eta})^{1/2}}\Big)\exp\Big(\sigma_{\nu\eta}{}^\mu(\tau,\tau')\frac{b_\nu C_\eta}{(n_{\nu\eta})^{1/2}}\Big)\Big\rangle_T$$
$$=\exp[\tfrac{1}{2}(\Delta_\mu K_\mu)\sum_\nu\sum_\eta v_{\nu\eta}{}^\mu(\tau)v_{\nu\eta}{}^\mu{}^*(\tau')n_{\nu\eta}]\exp\Big(-\sum_\nu\sum_\eta\mid\sigma_{\nu\eta}\mid^2\frac{\langle n_\nu\rangle_T\langle n_\eta\rangle_T}{n_{\nu\eta}}\Big), \quad (C4)$$

where

$$\sigma_{\nu\eta}{}^\mu(\tau,\tau')=(1/\sqrt{2})(n_{\nu\eta})^{1/2}[\Delta_\mu v_{\nu\eta}{}^\mu(\tau)-K_\mu v_{\nu\eta}{}^\mu(\tau')]. \quad (C5)$$

It must be stressed that the last equality in Eq. (C4) is by no means an exact mathematical result. It is obtained from Eq. (B18) using

$$\langle b_\nu{}^+b_\nu C_\eta{}^+C_\eta\rangle_T=\langle n_\nu\rangle_T\langle n_\eta\rangle_T. \quad (C6)$$

It should be noted that Eq. (B18) is not rigorously valid in our case, and that Eq. (C4) is really obtained using an approximation (consistent with previously invoked approximations) where we disregard terms of fourth order or higher, thus, in the molecular–medium coupling:

$$\langle\exp\{-\sigma_{\nu\eta}{}^\mu{}^*(\tau,\tau')[b_\nu{}^+C_\eta{}^+/(n_{\nu\eta})^{1/2}]\}\exp\{\sigma_{\nu\eta}{}^\mu(\tau,\tau')[b_\nu C_\eta/(n_{\nu\eta})^{1/2}]\}\rangle_T$$
$$=\langle\{1-\sigma_{\nu\eta}{}^\mu{}^*(\tau,\tau')[b_\nu{}^+C_\nu{}^+/(n_{\nu\eta})^{1/2}]+\cdots\}\{1+\sigma_{\nu\eta}{}^\mu(\tau,\tau')[b_\nu C_\eta/(n_{\nu\eta})^{1/2}]+\cdots\}\rangle_T$$
$$=1-\mid\sigma_{\nu\eta}{}^\mu(\tau,\tau')\mid^2(\langle n_\nu\rangle_T\langle n_\eta\rangle_T/n_{\nu\eta})+\cdots=\exp[-\mid\sigma_{\nu\eta}{}^\mu(\tau,\tau')\mid^2(\langle n_\nu\rangle_T\langle n_\eta\rangle_T/n_{\nu\eta})].$$

Equation (C4) and (C5) thus gives, to this approximation, the medium part of $\langle I_\mu \rangle_T$, while the molecular part will be identical to what has been obtained in Appendix B. The final result is thus

$$\prod_\mu \langle I_\mu \rangle_T = \prod_\mu \{A_\mu B_\mu D_\mu\}, \tag{C7}$$

where

$$A_\mu = \exp\{-\tfrac{1}{4}\Delta_\mu^2 - \tfrac{1}{4}K_\mu^2 + \tfrac{1}{2}K_\mu \Delta_\mu [u_\mu^*(\tau')u_\mu(\tau) + \sum_\nu \sum_\eta n_{\nu\eta} v_{\nu\eta}^{\mu *}(\tau') v_{\nu\eta}^{\mu}(\tau)]\} \tag{C8}$$

$$B_\mu = (v_{s\mu})! \sum_{r=0}^{v_{s\mu}} \frac{(-1)^r \mid \lambda_\mu(\tau, \tau') \mid^{2r}}{(v_{s\mu} - r)!(r!)^2} \tag{C9}$$

and finally

$$D_\mu = \exp[-\sum_{\nu\eta} \mid \sigma_{\nu\eta}^{\mu}(\tau, \tau') \mid^2 (\langle n_\nu \rangle_T \langle n_\eta \rangle_T / n_{\nu\eta})], \tag{C10}$$

where $\sigma_{\nu\eta}^{\mu}(\tau, \tau')$ is given by Eq. (C5) and where $\lambda_\mu(\tau, \tau')$ is given by Eq. (B9). Noting that

$$\frac{\langle n_\nu \rangle_T \langle n_\eta \rangle_T}{n_{\nu\eta}} = \frac{1}{\exp[\hbar(\omega_\nu + \omega_\eta)/kT] - 1} \tag{C11}$$

the analogy with the simple case result becomes apparent. The explicit forms of $u_\mu^*(\tau')u_\mu(\tau)$ and of $\mid \lambda_\mu(\tau, \tau') \mid^2$ will of course be identical to the previous expressions, Eqs. (B19) and (B21). The summation over the ν and η indices in order to obtain simple explicit forms for

$$\sum_\nu \sum_\eta n_{\nu\eta} v_{\nu\eta}^{\mu *}(\tau') v_{\nu\eta}^{\mu}(\tau)$$

and for

$$\sum_\nu \sum_\eta \mid \sigma_{\nu\eta}^{\mu}(\tau, \tau') \mid^2 \langle n_\nu \rangle_T \langle n_\eta \rangle_T / n_{\nu\eta}$$

is now more complicated as we should in principle convert this summation into a double integral over the phonon and vibron continua and then sum over as many such double continua as there are vibrons present. A considerable simplification will be obtained if we make two reasonable assumptions: (a) For a given molecular vibration, μ, there exists only a single vibron which is important for vibrational relaxation. (b) This vibron may be viewed as a single discrete state or, in other words, that the density of states in the vibron band may be approximated by a delta function. Invoking these assumptions the double sum is replaced by a single sum over phonon states, and the results for the above functions are again given by Eqs. (B20) and (B22) when now γ_μ is given by

$$\gamma_\mu = \pi \mid G_{\nu\eta}^{\mu} \mid^2 \rho_{\nu\eta} n_{\nu\eta} \mid_{\omega_\nu + \omega_\eta = \omega_\mu}. \tag{C12}$$

Note that if assumption (a) is not used, we shall obtain the same result with γ_μ given by a sum of expressions of the form (C12) over the relevant vibrons, so that the molecular oscillator decays into a number of continua, each consisting of the phonon continuum superimposed on a different vibron.

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