

Optical Selection Studies of Radiationless Decay in an Isolated Large Molecule

ABRAHAM NITZAN AND JOSHUA JORTNER

Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel

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In this paper we present the results of a theoretical study of the nonradiative decay probability of a single vibronic level of a large isolated molecule. Utilizing Feynman's operator techniques, we were able to derive a theoretical expression of the dependence of the electronic relaxation rate on the excess vibrational energy in the excited electronic state for a "harmonic molecule" which is characterized by displaced potential surfaces. For a large effective electronic energy gap the nonradiative decay probability increases with increasing excess vibrational energy, while for a small energy gap the nonradiative decay in higher vibronic levels may be retarded. Our rough numerical calculations are found to be consistent with recent experimental data on optical selection studies in the isolated benzene molecule.

I. INTRODUCTION

Radiationless electronic relaxation processes in large molecules, which correspond to the statistical limit, can be handled by the "golden rule" rate expressions for the nonradiative decay. In earlier work¹⁻⁵ which provided a general understanding of the diverse phenomena related to the radiative (and nonradiative) decay of excited electronic states of large molecules, it has become fashionable to recast the nonradiative decay probability in terms of a product of the square of the nonadiabatic coupling, V , matrix element and the density of states, ρ , in the dissipative quasicontinuum. Such a factorization procedure is, of course, justified for a case of a dissipative continuum (i.e., for radiationless decomposition processes such as molecular predissociation and autoionization); however, in the case of nonradiative decay in a large molecule where the huge number of final states are characterized by widely varying coupling terms, the nature of the "coarse graining" procedure which will yield the properly averaged $\langle V^2\rho \rangle$ is by no means clear. Lin and Bersohn^{6,7} and Englman and Jortner⁸ have proposed that nonradiative decay processes in the statistical limit can be considered as intramolecular multiphonon processes in a large molecule. Adopting the formalism of the Mossbauer effect⁹ and the theory of optical line shapes and thermal ionization processes in solid state theory,¹⁰⁻¹⁴ it was demonstrated that the intramolecular nonradiative decay probability in the statistical limit does not have to be factored into a product $V^2\rho$ but rather expressed as a weighted density of states function (i.e., the density of states where each term is weighted by the appropriate coupling term). Such weighted density of states function can be handled as a limiting form of a generalized line shape function. Previous theoretical studies of an "isolated" molecule^{6-8,15} considered the nonradiative decay from a vibrationless level of an excited electronic state. When a molecule in an inert medium was handled,^{6-8,15} the nonradiative decay of a manifold of thermally averaged Boltzmann spread levels was considered.

A useful extension of the theory of multiphonon

processes in a large molecule will involve the understanding of optical selection studies in an isolated molecule. Electronic relaxation in different excited vibronic levels, corresponding to the same electronic configuration, can be experimentally studied by monitoring the fluorescence which results from narrow band optical excitation. Schlag and Von Weysenhoff¹⁶ have provided the first study of the fluorescence of β -naphthylamine at sufficiently low pressures so that the optically excited gas molecules decay on a time scale much shorter than the mean time between deactivating collisions. Assuming that the radiative width, i.e., the pure radiative lifetime, is constant, these experimental data demonstrate that the nonradiative decay probability reveals a roughly exponential dependence on the excess energy above the electronic origin of the lowest excited singlet state. For this system the nonradiative decay probability increases by about 2.5 orders of magnitude when the excess vibrational energy is varied by $12\,000\text{ cm}^{-1}$.¹⁷ Similar experiments involving optical selection studies of an "isolated" benzene molecule were performed by Parmenter, Selinger, and Ware¹⁸ and by Spears and Rice,¹⁹ where the excess of vibrational energy above the electronic origin of the lowest ${}^1B_{2u}$ excited singlet state was varied by 2500 cm^{-1} .²⁰ From a careful analysis of the experimental radiative decay times and quantum yields, it was concluded that the nonradiative decay probability exhibits a monotonous increase (by about a factor of 2) over this limited excess energy range.

We are aware of three recent theoretical studies concerning the interpretation of optical selection experiments in an isolated molecule. Fischer and Schlag²¹ have invoked the usual assumption of unimolecular reaction theory regarding the excess vibrational energy E_V to be randomly distributed over all internal degrees of freedom. This treatment, which is analogous to Englman and Jortner's⁸ weak coupling scheme at a finite temperature $kT = E_V$, is surveyed in Appendix I. It is our opinion that the Fischer-Schlag scheme is inadequate for the study of optical selection data because of the following reasons: (a) The basic assumption that the isolated molecule acts as "its own heat

bath" is not justified. (b) This "high temperature" treatment neglects the temperature dependence of the pre-exponential factor in the expression for the non-radiative transition probability. It was demonstrated by Lin⁶ and later by Freed and Jortner¹⁵ that this pre-exponential factor is proportional to terms of the form $\coth(\hbar\omega_k/2kT)$ (where ω_k is the frequency of a promoting mode) whereupon the Fischer-Schlag hypothesis will imply that nonradiative decay probability will involve an additional term of the form $\coth(\hbar\omega_k/2E_v)$ [which at large excess energy will reduce to $(2E_v/\hbar\omega_k)$]. This result seems to be in variance with the experimental data. (c) A rather serious approximation introduced in this treatment involves the assumption that the reduced displacements, Δ_j , of the equilibrium positions of each normal coordinate are small, i.e., $\Delta_j \ll 1$ for all j .

Brailsford and Chang²² have invoked the same approximations as previously applied by Englman and Jortner,⁸ neglecting the dependence of the non-radiative rate expression on the nuclear kinetic energy operator, neglecting frequency changes between the two electronic states, and assuming that the reduced displacements Δ_j are small. The last approximation leads to a nonradiative rate expression (valid up to Δ_j^2) which has the same functional dependence as the general thermally averaged transition probability, except that the thermally averaged occupation number of the j th vibrational mode has to be replaced by the number of quanta in this excited state vibrational mode, which is determined by the excitation process. This approximation, first derived by Lax¹³ for optical line shapes in solids, is valid for nonradiative decay processes in solid state theory and was applied in the study of thermal ionization processes in solids; however, it is not expected to be of general applicability for the study of nonradiative decay in large molecules.

Gelbart *et al.*²³ have utilized the analogy between the general expression for nonradiative decay probability in the statistical limit and the Boltzmann statistical expression for the total number of states for a grand canonical ensemble where the number of particles (i.e., phonons) is arbitrary but the energy is fixed. In view of the formal analogy with the Boltzmann statistical distribution, Gelbart *et al.*²³ were tempted to approximate the transition probability by the maximum term, using the method of Lagrange multipliers. This method is by no means quantitatively valid for the present physical situation since the phonon occupation number is relatively small. Another approximation invoked by Gelbart *et al.* in the derivation of their final expressions is qualitatively similar to that used by Brailsford and Chang,²² i.e., that the reduced displacements of the equilibrium positions of the normal coordinates are small relative to unity. This treatment is of interest as it provides insight concerning the qualitative features of the nonradiative rate constant and its dependence on

the excess vibrational energy, which can be recast in terms of a generalized energy gap form.

In view of current interest in optical selection studies in large isolated molecules, we have extended the formulation of radiationless transitions in an isolated molecule. We have been able to derive an exact expression for the dependence of the nonradiative decay probability on the excess vibrational energy in the excited state for a "harmonic molecule," characterized by displaced potential surfaces. The results demonstrate the conceptual value of the recent formulation of the theory of radiationless transitions in terms of multiphonon processes in large molecules. The present formulation is applicable both for electronic processes and some unimolecular photochemical rearrangement reactions in excited electronic states.

II. NONRADIATIVE DECAY FROM A SINGLE VIBRONIC LEVEL

In what follows we shall adopt the physical model system previously used by Englman, Freed, and Jortner,^{8,15} which is characterized by the following features:

(a) A two-electronic states system is considered. The higher electronic state $|s\rangle$ is characterized by the zero-order Born-Oppenheimer vibronic levels,

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

each of which is coupled (via the nonadiabatic intramolecular interaction term \hat{V}) to a manifold of zero-order vibronic levels

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

which correspond to a lower electronic configuration $|l\rangle$. Here \mathbf{r} represents electronic coordinates, while $\mathbf{Q}^{(s)}$ and $\mathbf{Q}^{(l)}$ correspond to the normal coordinates in the electronic states $|s\rangle$ and $|l\rangle$, respectively.

(b) The molecular vibrations are harmonic. The molecular vibrational wavefunctions are thus displayed as products of harmonic oscillator wavefunctions:

$$\begin{aligned} \chi_{si}(\mathbf{Q}^{(s)}) &= \prod_{\mu=1}^N X_{s\mu}(Q_{\mu}^{(s)}, v_{s\mu}), \\ \chi_{lj}(\mathbf{Q}^{(l)}) &= \prod_{\mu=1}^N X_{l\mu}(Q_{\mu}^{(l)}, v_{l\mu}), \end{aligned} \quad (\text{II.3})$$

where $v_{s\mu}$ and $v_{l\mu}$ represent the vibrational quantum numbers of the μ th normal mode in the two electronic states. This μ mode is characterized by the vibrational frequencies $\omega_{\mu}^{(s)}$ and $\omega_{\mu}^{(l)}$ and the effective masses $M_{\mu}^{(s)}$ and $M_{\mu}^{(l)}$. N represents the total number of normal modes.

(c) The normal modes and their frequencies are identical in the two electronic states except for the displacement in the origins of the normal coordinates, whereupon $\omega_{\mu}^{(s)} = \omega_{\mu}^{(l)} = \omega_{\mu}$ and $M_{\mu}^{(s)} = M_{\mu}^{(l)} = M_{\mu}$ for each $\mu = 1, \dots, N$. Let the equilibrium configurations

in the (zero-order) states $|s\rangle$ and $|l\rangle$ be characterized by $Q_\mu^{0(s)}$ and $Q_\mu^{0(l)}$ ($\mu=1, \dots, N$), respectively. The displacement of the origins of the potential surfaces is

$$\Delta Q_\mu = Q_\mu^{0(l)} - Q_\mu^{0(s)}. \quad (\text{II.4})$$

For large aromatic hydrocarbons where the molecular symmetry (of the isolated molecule) is practically unmodified between different low-lying electronically excited states, we expect that $\Delta Q_\mu \neq 0$ only for μ modes which correspond to totally symmetric vibrations.

(d) The electronic energy gap between the two electronic states $|s\rangle$ and $|l\rangle$ is sufficiently large so that the $\{|lj\rangle\}$ manifold acts as an effective dissipative quasicontinuum, whereupon the decay of each vibronic level $|si\rangle$ corresponds to the statistical limit.

(e) As usual, we shall assume that the states in the $|lj\rangle$ manifold do not carry oscillator strength from the ground electronic state $|00\rangle$. Provided that $|si\rangle$ involves only totally symmetric vibration, then in view of the propensity rules for nonradiative decay, $|lj\rangle$ has to contain a single nontotally symmetric promoting mode, whereupon the radiative transition $|00\rangle \rightarrow |lj\rangle$ is symmetry forbidden. Obviously, small Franck-Condon vibrational overlap $\langle 0|j\rangle$ factors [see (f)] and spin selection rules when $|lj\rangle$ corresponds to a triplet state are also helpful in this respect. We may thus assert that narrow band optical excitation leads initially to the population of a single (zero-order) vibronic component $|si\rangle$.

This initial state is characterized by the excess vibrational energy

$$E_V = \sum_\mu \hbar\omega_\mu v_{s\mu} \quad (\text{II.5})$$

above the pure electronic origin E_{s0} of the $|s\rangle$ electronic state.

(f) Interference effects between the resonances which originate from the coupling of each zero-order vibronic level $|si\rangle$ with the quasicontinuum $|lj\rangle$ are negligible. We are, of course, concerned with an isolated molecule at room temperature. Rotational fine structure should not worry us, and in view of angular momentum conservation laws each rotational sublevel will decay to its "own" quasicontinuum. The vibrational levels $|si\rangle$ which are accessible to direct optical excitation from the ground state to a nondegenerate electron excited state consist essentially of: (a) progressions of the totally symmetric modes (and their combination bands), (b) even number(s) of nontotally symmetric modes, (c) hot bands, and (d) sequential series resulting from excitation of the thermally populated ground state vibrational modes. It was usually assumed that all these zero-order vibronic states are well separated relative to their nonradiative width. However, in large molecules (temperature dependent) sequence congestion leads to excitation of very closely spaced levels $|si\rangle$. In this case symmetry arguments will be of con-

siderable assistance. The nonadiabatic coupling involves nuclear momentum operators $\partial/\partial Q_\kappa$ of nontotally symmetric promoting modes (which will be designated by κ and characterized by the symmetry Γ_κ). The direct products $\Gamma_s \otimes \Gamma_l \otimes \Gamma_\kappa$ and $\Gamma_i \otimes \Gamma_j \otimes \Gamma_\kappa$ must contain the totally symmetric representation of the molecular point group.^{6,7} The first direct product, which involves the symmetries of the electronic wavefunctions, just provides a recipe for the selection of the promoting modes. The second direct product, which involves the vibrational symmetries, implies²⁴ that the coupled states $|si\rangle$ and $|lj\rangle$ have the following characteristics: (a) They differ by one vibrational quantum number of the promoting mode; (b) they have the same occupation numbers of other nontotally symmetric vibrations²⁵; (c) only totally symmetric vibrational modes can be characterized by arbitrary vibrational occupation quantum numbers in the two coupled states. We may thus assert that each of a sequence members in the $|si\rangle$ manifold will be coupled to a different subset of the $|lj\rangle$ states, whereupon no interference effects in the nonradiative decay will be exhibited between members of the same sequence. On the other hand, members of a totally symmetric progression will be so widely spaced relative to their widths that although they decay to the same subject of $|lj\rangle$, no interference effects will be encountered.

The features of nonradiative decay of the $|si\rangle$ level can be experimentally monitored by observing the energy integrated photon counting rate $\dot{P}^{(si)}(t)$ and the quantum yield Y which in the statistical limit will be given by

$$\dot{P}^{(si)}(t) = \Gamma_{si} \exp\{-[(\Gamma_{si} + W_{si})/\hbar]t\}$$

and

$$Y^{(si)} = \Gamma_{si}(\Gamma_{si} + W_{si})^{-1},$$

where Γ_{si} is the radiative decay probability of the vibronic level $|si\rangle$, which in the case of a symmetry allowed transition (in view of vibrational sum rules) is independent of the particular vibronic state. In the case of vibronically induced transition, further complications arise and the dependence of Γ_{si} on the particular state has to be taken into account. In any case, from Eqs (II.6) and (II.7) the experimentalist can extract the nonradiative width W_{si} of the particular vibronic state. The purpose of this exercise is to provide a theoretical calculation of the nonradiative decay probability of a single vibronic level. In the statistical limit the single level nonradiative transition probability is related to the generalized line shape function

$$G^{(si)}(E) = \sum_j |\langle lj | \hat{V} | si \rangle|^2 \delta(E_{lj} - E_{si} - E) \quad (\text{II.6})$$

by

$$W_{si} = (2\pi/\hbar)G^{(si)}(0). \quad (\text{II.7})$$

Equation (II.6) differs from the thermally averaged

rate expressions for a molecule in an inert medium (or for the decay of the vibrationless level of an excited electronic state)⁸ as thermal averaging has now to be avoided. At this point we have to depart from previous work on multiphonon processes in large molecules, as the generating functions method introduces the thermal averaging procedure at the initial stage. Instead, we shall utilize Feynman's operator techniques²⁶ which are directly applicable for the evaluation of the single sum (II.6). Similar methods have been previously applied by Lax¹³ in the study of optical line shapes in solids and by Rickayzen²⁷ in the study of thermal ionization processes in semiconductors.

Making use of the integral representation of the delta function, Eq. (II.6) can be rewritten in the form

$$G^{si}(E) = (2\pi\hbar)^{-1} \int_{-\infty}^{\infty} \exp\left(-\frac{iEt}{\hbar}\right) L(t) dt, \quad (\text{II.8})$$

where the generating function $L(t)$ is given by

$$\begin{aligned} L(t) &= \sum_j \langle si | \hat{V} | lj \rangle \langle lj | \hat{V}^\dagger | si \rangle \\ &\quad \times \exp[i(E_{ij} - E_{si})(t/\hbar)] \\ &= \sum_j \langle si | \hat{V} \exp[iH_i(t/\hbar)] | lj \rangle \langle lj | \hat{V}^\dagger \\ &\quad \times \exp[-iH_s(t/\hbar)] | si \rangle. \end{aligned} \quad (\text{II.9})$$

The adiabatic Hamiltonians H_s and H_i for nuclear motion in the two electronic states are given in the form

$$H_s = \sum_\mu \left(-\frac{1}{2}\hbar\omega_\mu \frac{\partial^2}{\partial q_\mu^2} + \frac{1}{2}\hbar\omega_\mu q_\mu^2 \right) = \sum_{\mu=1}^N h_\mu, \quad (\text{II.10})$$

$$\begin{aligned} H_i &= \sum_\mu \left[-\frac{1}{2}\hbar\omega_\mu (\partial^2/\partial q_\mu^2) + \frac{1}{2}\hbar\omega_\mu (q_\mu + \Delta_\mu)^2 \right] - \Delta E \\ &= H_s + E_M - \Delta E + \sum_\mu \gamma_\mu q_\mu. \end{aligned} \quad (\text{II.11})$$

The dimensionless normal coordinates and displacements are defined by

$$q_\mu = (M_\mu\omega_\mu/\hbar)^{1/2} (Q_\mu - Q_\mu^{(s)}), \quad (\text{II.12})$$

$$\Delta_\mu = (M_\mu\omega_\mu/\hbar)^{1/2} \Delta Q_\mu^0. \quad (\text{II.13})$$

The linear coupling terms γ_μ (for each mode) are expressed in terms of the reduced displacements (II.13):

$$\gamma_\mu = \hbar\omega_\mu \Delta_\mu. \quad (\text{II.14})$$

Finally, ΔE corresponds to the electronic energy gap

$$\begin{aligned} \langle i | V_{si} \exp[iH_i(t/\hbar)] (V_{si}^\dagger)^\dagger \exp[-iH_s(t/\hbar)] | i \rangle &= J_\kappa(t) \prod_{\mu \neq \kappa} \langle X_{s\mu}(Q_\mu^{(s)}, v_{s\mu}) | \exp[i(h_\mu + \gamma_\mu q_\mu)(t/\hbar)] \\ &\quad \times \exp[-ih_\mu(t/\hbar)] | X_{s\mu}(Q_\mu^{(s)}, v_{s\mu}) \rangle \exp[i(E_M - \Delta E)(t/\hbar)], \end{aligned} \quad (\text{II.22})$$

where

$$\begin{aligned} J_\kappa(t) &= \langle X_{s\kappa}(Q_\kappa, v_{s\kappa}) | V_{si} \exp[i(h_\kappa + \gamma_\kappa q_\kappa)(t/\hbar)] (V_{si}^\dagger)^\dagger \exp[-ih_\kappa(t/\hbar)] | X_{s\kappa}(Q_\kappa, v_{s\kappa}) \rangle \\ &= \sum_{v_{i\kappa}''} \langle X_{s\kappa}(Q_\kappa, v_{s\kappa}) | V_{si} \exp[i(h_\kappa + \gamma_\kappa q_\kappa)(t/\hbar)] | X_{i\kappa}(Q_\kappa, v_{i\kappa}'') \rangle \langle X_{i\kappa}(Q_\kappa, v_{i\kappa}'') | (V_{si}^\dagger)^\dagger \\ &\quad \times \exp[-ih_\kappa(t/\hbar)] | X_{s\kappa}(Q_\kappa, v_{s\kappa}) \rangle \\ &= \sum_{v_{i\kappa}''} | \langle X_{s\kappa}(Q_\kappa, v_{s\kappa}) | V_{si} \exp[i(h_\kappa + \gamma_\kappa q_\kappa)(t/\hbar)] | X_{i\kappa}(Q_\kappa, v_{i\kappa}'') \rangle |^2 \exp[i\omega_\kappa(v_{i\kappa}'' - v_{s\kappa})t]. \end{aligned} \quad (\text{II.23})$$

between the vibrationless levels of the two electronic states,

$$\Delta E = E_{s0} - E_{i0}, \quad (\text{II.15})$$

while

$$E_M = \frac{1}{2} \sum_\mu \hbar\omega_\mu \Delta_\mu^2 \quad (\text{II.16})$$

represents the molecular nuclear relaxation energy (or half of the Stokes shift)⁸ due to the displacement of the potential surfaces.

The expression for the generating function can now be recast in terms of the operators

$$V_{si}(\mathbf{Q}) = \int d\mathbf{r} \phi_s(\mathbf{r}, \mathbf{Q}^{(s)}) \hat{V} \phi_i(\mathbf{r}, \mathbf{Q}^{(i)}), \quad (\text{II.17})$$

which can be expressed in terms of contribution from all the promoting modes

$$V_{si}(\mathbf{Q}) = \sum_{\kappa=1}^P V_{si}^\kappa, \quad (\text{II.18})$$

where

$$V_{si}^\kappa = C_{si}^\kappa (i\hbar/M_\kappa)^{1/2} (\partial/\partial Q_\kappa). \quad (\text{II.19})$$

The matrix elements C_{si}^κ were previously given by Freed and Jortner [Eqs. (II.18)-(II.20)].¹⁵ Equation (II.9) now takes the form

$$\begin{aligned} L(t) &= \sum_j \langle i | V_{si} \exp[iH_i(t/\hbar)] | j \rangle \langle j | V_{si}^\dagger \\ &\quad \times \exp[-iH_s(t/\hbar)] | i \rangle \\ &= \langle i | V_{si} \exp[iH_i(t/\hbar)] V_{si}^\dagger \exp[-iH_s(t/\hbar)] | i \rangle, \end{aligned} \quad (\text{II.20})$$

and making use of Eq. (II.18) we get

$$\begin{aligned} L(t) &= \sum_{\kappa=1}^P \langle i | V_{si}^\kappa \exp[iH_i(t/\hbar)] (V_{si}^\kappa)^\dagger \\ &\quad \times \exp[-iH_s(t/\hbar)] | i \rangle + \sum_{\substack{\kappa=1 \\ \kappa \neq \kappa'}}^P \sum_{\kappa'=1}^P \langle i | V_{si}^\kappa \\ &\quad \times \exp\left(iH_i \frac{t}{\hbar}\right) (V_{si}^{\kappa'})^\dagger \exp\left(-iH_s \frac{t}{\hbar}\right) | i \rangle. \end{aligned} \quad (\text{II.21})$$

The diagonal matrix elements in Eq. (II.21) can now be expressed by invoking two approximations: (a) the harmonic approximation for molecular vibrations; (b) the Condon approximation, whereupon the electronic integrals C_{si}^κ (Eq. II.19) are weakly dependent on the nuclear coordinates. Making use of Eqs. (II.3), (II.10), and (II.11), we get

This result can be considerably simplified assuming that for aromatic hydrocarbons $\Delta_\kappa = \gamma_\kappa = 0$ for all the promoting modes, whereupon utilizing the explicit form (II.19) of the coupling operators, Eq. (II.23) reduces to the simple form

$$J_\kappa(t) = |d(v_{s\kappa}, v_{s\kappa}+1)|^2 \exp(i\omega_\kappa t) + |d(v_{s\kappa}, v_{s\kappa}-1)|^2 \exp(-i\omega_\kappa t), \quad (\text{II.24})$$

where

$$d(v_{s\kappa}, v_{s\kappa}') = \langle X_{s\kappa}(Q_\kappa, v_{s\kappa}) | V_{s\kappa} | X_{s\kappa}(Q_\kappa, v_{s\kappa}') \rangle. \quad (\text{II.25})$$

The nonvanishing matrix elements (II.25) are

$$|d(v_{s\kappa}, v_{s\kappa}+1)|^2 = (|C_{s\kappa}|^2 \hbar \omega_\kappa / 4) (v_{s\kappa}+1) \quad (\text{II.26a})$$

and

$$|d(v_{s\kappa}, v_{s\kappa}-1)|^2 = (|C_{s\kappa}|^2 \hbar \omega_\kappa / 4) v_{s\kappa}. \quad (\text{II.26b})$$

The "mixed type" terms in Eq. (II.21) (i.e., $\kappa \neq \kappa'$) can be easily expressed in a similar manner, and again invoking the assumption that only nontotally symmetric modes act as promoting modes (i.e., $\Delta_\kappa = \gamma_\kappa = 0$), it can be demonstrated that the orthogonality property of the basis set $X_{i\kappa}$ immediately implies that these terms will vanish.

The generating function for the decay of a single vibronic level takes the form

$$\begin{aligned} L(t) &= \sum_{\kappa=1}^P J_\kappa(t) \left[\prod_{\mu \neq \kappa} g_\mu(t) \right] \exp\left(i(E_M - \Delta E) \frac{t}{\hbar}\right) \\ &= \sum_{\kappa=1}^P \left\{ |d(v_{s\kappa}, v_{s\kappa}+1)|^2 \exp\left(i(E_M + \hbar\omega_\kappa - \Delta E) \frac{t}{\hbar}\right) + |d(v_{s\kappa}, v_{s\kappa}-1)|^2 \exp\left(i(E_M - \hbar\omega_\kappa - \Delta E) \frac{t}{\hbar}\right) \right\} \prod_{\mu \neq \kappa} g_\mu(t), \end{aligned} \quad (\text{II.27})$$

where

$$g_\mu(t) = \langle X_{s\mu}(Q_\mu, v_{s\mu}) | \exp[i(h_\mu + \gamma_\mu q_\mu)(t/\hbar)] \exp[-ih_\mu(t/\hbar)] | X_{s\mu}(Q_\mu, v_{s\mu}) \rangle. \quad (\text{II.28})$$

The operators $\exp[i(h_\mu + \gamma_\mu q_\mu)(t/\hbar)] \exp[-ih_\mu t]$ which appear on the right-hand side of Eq. (II.28) will now be represented by making use of Feynman's theorem^{14,26}

$$\exp[-ih_\mu(t/\hbar)] \exp[i(h_\mu + \gamma_\mu q_\mu)(t/\hbar)] = T \exp\left[(i/\hbar) \left(\int_0^t \Delta h_\mu(t') dt' \right)\right], \quad (\text{II.29})$$

where

$$\Delta h_\mu(t') = \exp[-ih_\mu(t'/\hbar)] \Delta h_\mu \exp[+ih_\mu(t'/\hbar)] \quad (\text{II.30})$$

and

$$\Delta h_\mu = (h_\mu + \gamma_\mu q_\mu) - h_\mu = \gamma_\mu q_\mu, \quad (\text{II.31})$$

while T represents the chronological time-ordering operator. Thus, making use of (II.29), Eq. (II.28) can be recast in the form

$$g_\mu(t) = \langle X_{s\mu} | T \exp\left(i\omega_\mu \Delta_\mu \int_0^t q_\mu(t') dt'\right) | X_{s\mu} \rangle. \quad (\text{II.32})$$

Equations (II.27) and (II.32) involve a slight generalization of Lax's line shape formula¹³ adopted for nonradiative transitions in a large molecule. In solid state problems it is customary to assume¹⁴ that $\Delta_j \ll 1$ for all j and to expand the exponential in Eq. (II.32) in a power series in Δ_j retaining terms up to second order in Δ_j . As already pointed out, this procedure is unjustified in the case of nonradiative decay of a large molecule as it is common that $\Delta_j \sim 1$ for some j . It has been previously demonstrated by Rickayzen^{27,14} that the matrix elements $g_\mu(t)$ can be evaluated in a closed form without invoking any approximate expansion procedures. g_μ can be expressed in terms of "phonon" creation, a_μ^\dagger , and annihilation, a_μ , operators for the μ th vibrational mode by substituting

$$q_\mu = (1/\sqrt{2})(a_\mu + a_\mu^\dagger)$$

in Eq. (II.32). The time dependence of these operators in the Heisenberger presentation is simply $a_\mu(t') = a_\mu \exp(i\omega_\mu t')$ and $a_\mu^\dagger(t') = a_\mu^\dagger \exp(-i\omega_\mu t')$. Equation (II.32) now takes the form

$$\begin{aligned} g_\mu(t) &= \langle X_{s\mu} | T \exp\left(\frac{i\omega_\mu \Delta_\mu}{\sqrt{2}} \int_0^t dt' [a_\mu^\dagger(t') + a_\mu(t')]\right) | X_{s\mu} \rangle \\ &= \langle X_{s\mu} | T \exp\left(\frac{i\omega_\mu \Delta_\mu}{\sqrt{2}} \int_0^t dt' [a_\mu^\dagger \exp(-i\omega_\mu t') + a_\mu \exp(i\omega_\mu t')]\right) | X_{s\mu} \rangle \\ &= \langle X_{s\mu} | \exp(\lambda_\mu(t) a_\mu^\dagger) \exp\left(\frac{i\Delta_\mu \omega_\mu}{\sqrt{2}} \int_0^t \tilde{a}_\mu(t') \exp(i\omega_\mu t') dt'\right) | X_{s\mu} \rangle, \end{aligned} \quad (\text{II.33})$$

where

$$\lambda_\mu(t) = (\Delta_\mu/\sqrt{2})[1 - \exp(-i\omega_\mu t)] \quad (\text{II.34})$$

and

$$\tilde{a}_\mu(t') = \exp[-\lambda_\mu(t')a_\mu^\dagger]a_\mu \exp[\lambda_\mu(t')a_\mu^\dagger]. \quad (\text{II.35})$$

Making use of simple commutation relations,^{14,26} one gets

$$\tilde{a}_\mu(t') = a_\mu + \lambda_\mu(t'). \quad (\text{II.36})$$

From Eqs. (II.33), (II.35), and (II.36) we obtain

$$g_\mu(t) = \exp\{-i(t/\sqrt{2})\omega_\mu\Delta_\mu^2 + \frac{1}{2}\Delta_\mu^2[\exp(i\omega_\mu t) - 1]\} \langle X_{s\mu} | \exp[\lambda_\mu(t)a_\mu^\dagger] \exp[-\lambda_\mu^*(t)a_\mu] | X_{s\mu} \rangle. \quad (\text{II.37})$$

The diagonal matrix element in Eq. (II.37) is readily calculated by displaying the states $|X_{s\mu}\rangle$ in the c (number) representation

$$\begin{aligned} |X_{s\mu}\rangle &\equiv |v_{s\mu}\rangle = (v_{s\mu}!)^{-1/2} (a_\mu^\dagger)^{v_{s\mu}} |0\rangle, \\ \langle X_{s\mu} | &\equiv \langle v_{s\mu} | = (v_{s\mu}!)^{-1/2} \langle 0 | (a_\mu)^{v_{s\mu}}, \end{aligned} \quad (\text{II.38})$$

whereupon the diagonal matrix element in Eq. (II.37) takes the form

$$\langle X_{s\mu} | \exp[\lambda_\mu(t)a_\mu^\dagger] \exp[-\lambda_\mu^*(t)a_\mu] | X_{s\mu} \rangle = [1/(v_{s\mu}!)] \langle 0 | (a_\mu)^{v_{s\mu}} \exp[\lambda_\mu(t)a_\mu^\dagger] \exp[-\lambda_\mu^*(t)a_\mu] (a_\mu^\dagger)^{v_{s\mu}} | 0 \rangle. \quad (\text{II.39})$$

Utilizing the following operator relations,

$$\exp[-\lambda_\mu^*(t)a_\mu] | 0 \rangle = | 0 \rangle, \quad (\text{II.40a})$$

$$\langle 0 | \exp[\lambda_\mu(t)a_\mu^\dagger] = \langle 0 |, \quad (\text{II.40b})$$

$$\exp[-\lambda_\mu(t)a_\mu^\dagger] (a_\mu)^n \exp[\lambda_\mu(t)a_\mu^\dagger] = \{\exp[-\lambda_\mu(t)a_\mu^\dagger] a_\mu \exp[\lambda_\mu(t)a_\mu^\dagger]\}^n = [a_\mu + \lambda_\mu(t)]^n, \quad (\text{II.40c})$$

$$\exp[-\lambda_\mu^*(t)a_\mu] (a_\mu^\dagger)^n \exp[\lambda_\mu^*(t)a_\mu] = [a_\mu^\dagger - \lambda_\mu^*(t)]^n, \quad (\text{II.40d})$$

the matrix element (II.39) is recast in the form

$$\langle X_{s\mu} | \dots | X_{s\mu} \rangle = [1/(v_{s\mu}!)] \langle 0 | [a_\mu + \lambda_\mu(t)]^{v_{s\mu}} [a_\mu^\dagger - \lambda_\mu^*(t)]^{v_{s\mu}} | 0 \rangle. \quad (\text{II.41})$$

Binomial expansion of (II.41) and utilization of the relation

$$\langle 0 | (a_\mu)^{v_{s\mu}-r} (a_\mu^\dagger)^{v_{s\mu}-r} | 0 \rangle = (v_{s\mu}-r)! \quad (\text{II.42})$$

leads to the result

$$\langle X_{s\mu} | \exp[\lambda_\mu(t)a_\mu^\dagger] \exp[-\lambda_\mu^*(t)a_\mu] | X_{s\mu} \rangle = (v_{s\mu}!) \sum_{r=0}^{v_{s\mu}} \frac{(-1)^r |\lambda_\mu(t)|^{2r}}{(v_{s\mu}-r)!(r!)^2}. \quad (\text{II.43})$$

The nonradiative decay probability of a single vibronic level can now be expressed by invoking Eqs. (II.8), (II.27), (II.37), and (II.43):

$$W_{si} = (2\pi/\hbar) G^{si}(0)$$

$$\begin{aligned} &= \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt \exp\left(-i(\Delta E - E_M) \frac{t}{\hbar}\right) \left[\sum_{\kappa} d(v_{s\kappa}, v_{s\kappa}+1) \exp(i\omega_\kappa t) + \sum_{\kappa} d(v_{s\kappa}, v_{s\kappa}-1) \exp(-i\omega_\kappa t) \right] \\ &\quad \times \prod_{\mu \neq \kappa} \left\{ \exp\left[-\frac{1}{2}(it)\omega_\mu\Delta_\mu^2 + \frac{1}{2}\Delta_\mu^2[\exp(i\omega_\mu t) - 1]\right] (v_{s\mu}!) \sum_{r=0}^{\infty} \frac{(-1)^r |(\Delta_\mu/\sqrt{2})[1 - \exp(i\omega_\mu t)]|^{2r}}{(v_{s\mu}-r)!(r!)^2} \right\}. \end{aligned} \quad (\text{II.44})$$

Simple algebraic manipulations (and invoking our basic assumption that $\Delta_\kappa=0$ for $\kappa=1 \dots p$) lead to the final result

$$\begin{aligned} W_{si} &= \frac{1}{\hbar^2} \exp\left(-\frac{1}{2} \sum_{\mu} \Delta_\mu^2\right) \int_{-\infty}^{\infty} dt \left\{ \left[\sum_{\kappa} d(v_{s\kappa}, v_{s\kappa}+1) \exp\left(-i(\Delta E - \hbar\omega_\kappa) \frac{t}{\hbar}\right) + \sum_{\kappa} d(v_{s\kappa}, v_{s\kappa}-1) \right] \right. \\ &\quad \left. \times \exp\left(-i(\Delta E + \hbar\omega_\kappa) \frac{t}{\hbar}\right) \right\} \exp\left[\frac{1}{2} \sum_{\mu} \Delta_\mu^2 \exp(i\omega_\mu t)\right] \prod_{\mu \neq \kappa} (v_{s\mu}!) \sum_{r=0}^{v_{s\mu}} \left(-\Delta_\mu^2\right)^r \frac{[1 - \cos(\omega_\mu t)]^r}{(v_{s\mu}-r)!(r!)^2}. \end{aligned} \quad (\text{II.45})$$

From this result we conclude that

(a) Equation (II.45) represents the general expression for the nonradiative decay probability of a single vibronic level of a harmonic molecule characterized by displaced identical potential surfaces.

(b) The effective energy gap is modified by the frequency of the promoting mode(s) $\hbar\omega_\kappa$. The propensity rule¹⁵ for the promoting mode is satisfied for the decay of any single vibronic state.

(c) The nonradiative decay probability from the lowest vibronic component of the excited electronic state, whereupon $v_{s\mu}=0$ for all μ , is given from Eq. (II.45) in the form

$$W_{si} = \frac{1}{\hbar^2} \exp\left(-\frac{1}{2} \sum_{\mu} \Delta_{\mu}^2\right) \sum_{\kappa} \left\{ d(0_{\kappa}, 1_{\kappa}) \int_{-\infty}^{\infty} dt \exp\left[-i(\Delta E - \hbar\omega_{\kappa}) \frac{t}{\hbar}\right] \exp\left[\frac{1}{2} \sum_{\mu} \Delta_{\mu}^2 \exp(i\omega_{\mu}t)\right] \right\}, \quad (\text{II.46})$$

which just corresponds to the zero temperature case previously considered.^{8,15}

(d) The conventional thermally averaged nonradiative transition for a molecule in an inert medium which acts as a heat bath can be readily derived by taking

$$\langle W_s \rangle = \sum_{\mu} P_{(s\mu)} W_{s\mu}, \quad (\text{II.47})$$

where $P_{(s\mu)}$ are the Boltzmann weight factors

$$P_{(s\mu)} = \exp\left[-\beta(v_{s\mu} + \frac{1}{2})\omega_{\mu}\right] \prod_{\mu} 2 \sinh(\beta\omega_{\mu}/2), \\ \beta = (kT)^{-1}, \quad (\text{II.47}')$$

which leads (see Appendix II) to the Englman-Freed-Jortner^{8,15} expression

$$\langle W_s \rangle = \sum_{\kappa} \frac{|c_{s\kappa}|^2 \omega_{\kappa}}{4\hbar} \exp\left[-\frac{1}{2} \sum_{\mu} \Delta_{\mu}^2 (2\bar{v}_{\mu} + 1)\right] \int_{-\infty}^{\infty} dt \left\{ [\coth(\frac{1}{2}\beta\hbar\omega_{\kappa}) + 1] \exp\left(-i(\Delta E - \hbar\omega_{\kappa}) \frac{t}{\hbar}\right) \right. \\ \left. + [\coth(\frac{1}{2}\beta\hbar\omega_{\kappa}) - 1] \exp\left(-i(\Delta E + \hbar\omega_{\kappa}) \frac{t}{\hbar}\right) \right\} \exp\left[\sum_{\mu} (2\bar{v}_{\mu} + 1) \frac{1}{2} \Delta_{\mu}^2 \cos\omega_{\mu}t + i \sum_{\mu} \frac{1}{2} \Delta_{\mu}^2 \sin\omega_{\mu}t\right], \quad (\text{II.48})$$

where

$$\bar{v}_{\mu} = [\exp(\beta\hbar\omega_{\mu}) - 1]^{-1}. \quad (\text{II.48}')$$

(e) When $\Delta_{\mu} \ll 1$, the sum over r in Eq. (II.45) can be retained up to $r=1$ leading to Lax's equation¹³

$$W_{si} = \frac{1}{\hbar^2} \exp\left(-\frac{1}{2} \sum_{\mu} \Delta_{\mu}^2\right) \int_{-\infty}^{\infty} dt \left\{ \sum_{\kappa} d(v_{s\kappa}, v_{s\kappa} + 1) \exp[-i(\Delta E - \hbar\omega_{\kappa})(t/\hbar)] + \sum_{\kappa} d(v_{s\kappa}, v_{s\kappa} - 1) \right. \\ \left. \times \exp[-i(\Delta E + \hbar\omega_{\kappa})(t/\hbar)] \right\} \exp\left[\sum_{\mu} \frac{1}{2} (2v_{s\mu} + 1) \Delta_{\mu}^2 \cos\omega_{\mu}t + i \sum_{\mu} \frac{1}{2} \Delta_{\mu}^2 \sin\omega_{\mu}t\right]. \quad (\text{II.49})$$

This result is formally analogous to the expression for the thermally averaged nonradiative transition probability except that the occupation numbers $v_{s\mu}$ replace the thermally averaged occupation numbers which appear in the former treatment [see Eq. (II.48)]. Finally, it is worthwhile to note that retaining terms up to Δ_j^4 in the sum appearing on the right-hand side of Eq. (II.45) results in the expression previously derived by Brailsford and Chang.²²

(f) Our general expression (II.45) can be recast in a form which exhibits energy conservation in a way similar to Eq. (11) of Gelbart *et al.*²³ We shall consider the simple case when only a totally symmetric single mode α is optically excited, whereupon $v_{s\mu}=0$ for every $\mu \neq \alpha$. [See also section (g).] This situation corresponds to the case previously considered by Gelbart *et al.*²³ Replacing the term $(1 - \cos\omega_{\alpha}t)^r$ in Eq. (II.45) by

$$(1 - \cos\omega_{\alpha}t)^r = [2 \sin^2(\omega_{\alpha}t/2)]^r \\ = \left(-\frac{1}{2}\right)^r [\exp(i\omega_{\alpha}t/2) - \exp(-\frac{1}{2}i\omega_{\alpha}t)]^{2r} \\ = \sum_{p=0}^{2r} \frac{(2r)! (-1)^{2r-p}}{(2r-p)! p!} \exp[-i(r-p)\omega_{\alpha}t], \quad (\text{II.50})$$

we get

$$W_{si} = \frac{1}{4\hbar} \exp\left(-\frac{1}{2} \sum_{\mu} \Delta_{\mu}^2\right) \sum_{\kappa} |c_{s\kappa}|^2 \omega_{\kappa} v_{s\alpha}! \sum_{r=0}^{\mu_{s\alpha}} \left(+\frac{1}{2} \Delta_{\alpha}^2\right)^r [(v_{s\alpha} - r)! (r!)^2]^{-1} \sum_{p=0}^{2r} \frac{(2r)! (-1)^p}{(2r-p)! p!} \\ \times \int_{-\infty}^{\infty} dt \exp\left(-i[\Delta E_{\text{eff}} - (p-r)\hbar\omega_{\alpha}] \frac{t}{\hbar}\right) \exp\left[\frac{1}{2} \sum_{\mu} \Delta_{\mu}^2 \exp(i\omega_{\mu}t)\right],$$

where

$$\Delta E_{\text{eff}} = \Delta E - \hbar\omega_{\alpha}. \quad (\text{II.51})$$

Now taking

$$\exp\left[\frac{1}{2} \sum_{\mu} \Delta_{\mu}^2 \exp(i\omega_{\mu}t)\right] = \sum_{\{v_{\mu}\}} M(\{v_{\mu}\}) \exp\left[i \left(\sum_{\mu} v_{\mu} \omega_{\mu}\right) t\right], \quad (\text{II.52})$$

where

$$M(\{v_{\mu}\}) = \prod_{\mu} (1/v_{\mu}) \left(\frac{1}{2} \Delta_{\mu}^2\right)^{v_{\mu}} \quad (\text{II.52}')$$

and

$$\{v_{\mu}\} = \{v_1, v_2, \dots, v_N\}, \quad v_i = 1, 2, \dots, \infty, \quad i = 1 \dots N,$$

we can easily perform the integration over t to obtain

$$\begin{aligned} W_{s\alpha} &= (4\hbar)^{-1} \exp\left(-\frac{1}{2} \sum_{\mu} \Delta_{\mu}^2\right) \sum_{\kappa} |c_{s\kappa}|^2 \omega_{\kappa} \\ &\times v_{s\alpha}! \sum_{r=0}^{v_{s\alpha}} \left(\frac{1}{2} \Delta_{\alpha}^2\right)^r [(v_{s\alpha}-r)!(r!)^2]^{-1} \sum_{p=0}^{2r} \frac{(2r)!(-1)^p}{(2r-p)!p!} \\ &\times \sum_{\{v_{\mu}\}} \delta[(\Delta E_{\text{eff}}/\hbar) - (p-r)\omega_{\alpha} - \sum_{\mu} v_{\mu} \omega_{\mu}] M(\{v_{\mu}\}). \quad (\text{II.53}) \end{aligned}$$

It is obvious that for $\mu \neq \alpha$, v_{μ} can be identified with the occupation number $v_{i\mu}$ for the μ th oscillator in the final electronic state. For $\mu = \alpha$, let us define (for given r and p)

$$v_{i\alpha} = v_{s\alpha} - p + r - v_{\alpha} \quad (\text{II.54})$$

and

$$M_{rp}'(\{v_{i\mu}\}) = \prod_{\mu \neq \alpha} (1/v_{i\mu}) \left(\frac{1}{2} \Delta_{\mu}^2\right)^{v_{i\mu}} \otimes (v_{i\alpha} - v_{s\alpha} + p - r)^{-1} \left(\frac{1}{2} \Delta_{\alpha}^2\right)^{v_{i\alpha} - v_{s\alpha} + p - r}, \quad (\text{II.55})$$

so that finally we obtain

$$\begin{aligned} W_{s\alpha} &= (1/4\hbar) \exp\left(-\frac{1}{2} \sum_{\mu} \Delta_{\mu}^2\right) \sum_{\kappa} |c_{s\kappa}|^2 \omega_{\kappa} \\ &\times v_{s\alpha}! \sum_{r=0}^{v_{s\alpha}} \left(\frac{1}{2} \Delta_{\alpha}^2\right)^r [(v_{s\alpha}-r)!(r!)^2]^{-1} \sum_{p=0}^{2r} \frac{(2r)!(-1)^p}{(2r-p)!p!} \\ &\times \sum_{\{v_{i\mu}\}} M_{rp}'(\{v_{i\mu}\}) \delta[(\Delta E_{\text{eff}}/\hbar) - (v_{i\alpha} - v_{s\alpha})\omega_{\alpha} - \sum_{\mu \neq \alpha} v_{i\mu} \omega_{\mu}]. \quad (\text{II.56}) \end{aligned}$$

This is the general energy conservation law for the decay of a single (totally symmetric) vibronic state.

(g) The nonradiative decay probability for a single vibronic level depends on the occupation numbers of both the promoting modes ($v_{s\kappa}$, $\kappa = 1 \dots P$) and of the accepting modes ($v_{s\mu}$; $\mu \neq \kappa$, $\mu = 1 \dots N$) for which $\Delta_{\mu} \neq 0$. The dependence of $W_{s\alpha}$ on the occupation numbers $v_{s\kappa}$ of the promoting mode is expressed in terms of the $d(v_{s\kappa}, v_{s\kappa} \pm 1)$ terms [Eq. (II.26)]. Now, two different situations are of interest:

(g') The single vibronic level $|si\rangle$ which results from optical excitation from the vibrationless level of the ground electronic state, involves only totally symmetric modes in the excited electronic state. As the promoting modes are nontotally symmetric we expect that $v_{s\kappa} = 0$ for all κ , whereupon [invoking (II.26)]

$$\begin{aligned} W_{s\alpha} &= \exp\left(-\frac{1}{2} \sum_{\mu} \Delta_{\mu}^2\right) \sum_{\kappa} (|c_{s\kappa}|^2 \omega_{\kappa} / 4\hbar) \\ &\times \int_{-\infty}^{\infty} dt \exp\left(-i(\Delta E - \hbar\omega_{\kappa}) \frac{t}{\hbar}\right) \exp\left[\frac{1}{2} \sum_{\mu} \Delta_{\mu}^2 \exp(i\omega_{\mu}t)\right] \prod_{\mu} (v_{s\mu})! \sum_{r=0}^{v_{s\mu}} (-\Delta_{\mu}^2)^r \frac{(1 - \cos\omega_{\mu}t)^r}{(v_{s\mu} - r)!(r!)^2}. \quad (\text{II.57}) \end{aligned}$$

(g'') The single vibronic level $|si\rangle$ contains excited promoting modes. This situation may result from excitations of thermally excited vibrational levels of the ground electronic state. In this case we have

$$\begin{aligned} W_{s\alpha} &= \exp\left(-\frac{1}{2} \sum_{\mu} \Delta_{\mu}^2\right) \sum_{\kappa} (|c_{s\kappa}|^2 \omega_{\kappa} / 4\hbar) \int_{-\infty}^{\infty} dt \left[(v_{s\kappa} + 1) \exp\left(-i(\Delta E - \hbar\omega_{\kappa}) \frac{t}{\hbar}\right) \right. \\ &\left. + v_{s\kappa} \exp\left(-i(\Delta E + \hbar\omega_{\kappa}) \frac{t}{\hbar}\right) \right] \exp\left[\frac{1}{2} \sum_{\mu} \Delta_{\mu}^2 \exp(i\omega_{\mu}t)\right] \prod_{\mu} (v_{s\mu})! \sum_{r=0}^{v_{s\mu}} (-\Delta_{\mu}^2)^r \frac{(1 - \cos\omega_{\mu}t)^r}{(v_{s\mu} - r)!(r!)^2}. \quad (\text{II.58}) \end{aligned}$$

Now, when the electronic energy gap ΔE considerably exceeds the frequency of the promoting mode, we have

the simple relation

$$W_{si}(v_{sk} \neq 0)/W_{si}(v_{sk} = 0) \simeq \sum_k (2v_{sk} + 1).$$

In a large "isolated" molecule where sequence broadening is appreciable, we may expect that in certain spectral regions of the broadened "vibronic" bands corresponding to the totally symmetric vibration the promoting mode(s) will be optically excited. This effect will give rise to an oscillatory behavior of the energy dependence of the non-radiative decay probability, which will increase by a factor of ~ 3 in the region of the sequentially broadened vibronic bands where a promoting mode is optically excited. Very narrow band excitation sources (spectral width $\sim 1 \text{ cm}^{-1}$) are required to observe this effect.

III. A COMMENT ON THE STATISTICAL LIMIT

Up to this point we have implicitly assumed that the manifold $|lj\rangle$ acts as a statistical dissipative quasi-continuum. As the manifold $|lj\rangle$ is discrete, irreversibility of the nonradiative process is not inherent in the rate expression (II.6) or (II.7) for the isolated molecule. In fact, from the mathematical point of view, it is obvious that W_{si} diverges whenever energy conservation is ensued. The generalized delta functions in Eq. (II.6) provide just a means for bookkeeping. To provide a physically acceptable and numerically tractable expression for W_{si} we have to replace the delta functions in (II.6) by ordinary functions characterized by a finite width. This can be accomplished by the sum rule for the decay of a metastable state.²⁸ Equation (II.7) has to be replaced by the more general relation²⁸

$$W_{si} = (2/\hbar) \sum_j \{ | \langle lj | \hat{V} | si \rangle |^2 \gamma_{lj} / [(E_{si} - E_{lj})^2 + (\gamma_{lj})^2] \}, \quad (\text{III.1})$$

where γ_{lj} corresponds to the sum of the total widths (which include all radiative and all nonradiative contributions) of the initial $|si\rangle$ and of the final $|lj\rangle$ states. In the statistical limit the details of the dependence of the widths γ_{lj} are immaterial. We shall invoke the assumption that these widths are independent of the final state $|lj\rangle$, so that $(\frac{1}{2}\gamma_{lj}) = \langle \gamma \rangle$ for all $|lj\rangle$. A completely analogous treatment to that presented in Sec. II now leads a modified expression for the nonradiative transition probability where the integral in Eq. (II.45) contains an additional factor $\exp[-(\langle \gamma \rangle / \hbar) |t|]$ in the integrand. In particular, Eq. (II.57) which describes the excitation of a single vibronic level which consists of totally symmetric vibrational modes can now be recast in the form

$$W_{si} = \exp(-\frac{1}{2} \sum_{\mu} \Delta_{\mu}^2) \sum_k (|C_{st}^k|^2 \omega_k / 4\hbar) I_k, \quad (\text{III.2})$$

where

$$I_k = \int_{-\infty}^{\infty} dt \exp \left[-i \Delta E_{\text{eff}}^k \frac{t}{\hbar} - \langle \gamma \rangle \frac{|t|}{\hbar} \right] F(t) \quad (\text{III.3})$$

and

$$F(t) = \exp \left[\frac{1}{2} \sum_{\mu} \Delta_{\mu}^2 \exp(i\omega_{\mu} t) \right] \times \prod_{\mu} (v_{s\mu})! \sum_{r=0}^{v_{s\mu}} (-\Delta_{\mu}^2)^r \frac{(1 - \cos\omega_{\mu} t)^r}{(v_{s\mu} - r)! (r!)^2}, \quad (\text{III.4})$$

while $\Delta E_{\text{eff}}^k = \Delta E - \hbar\omega_k$ corresponds to the effective energy gap. In order to facilitate numerical calculations, this result will be considered in some detail. The function $F(t)$ [Eq. (III.3)] is a periodic function of t , being solely determined by $\sin\omega_{\mu} t$ and $\cos\omega_{\mu} t$, where the ω_{μ} 's correspond to the frequencies of the system. We can now reduce the infinite integration limits in (III.3) to finite limits by adopting Lax's procedure.¹³ Let $\tilde{\omega}_N$ be any common integer divider of every frequency ω_{μ} which appears in $F(t)$. (For computational purposes it will be advantageous to choose the largest normalizing frequency which we shall denote by ω_N .) Now setting $t = x/\omega_N$, we get $F(t) = F(x/\omega_N)$ which is a periodic function of the variable x , with a period of 2π . A straightforward extension of Lax's method leads to the result

$$I_k = \frac{2}{\omega_N} \text{Re} \sum_{n=0}^{\infty} \int_{2\pi n}^{2\pi(n+1)} \exp \left(-2\pi n i \frac{\Delta E_{\text{eff}}^k}{\hbar\omega_N} x - 2\pi n \frac{\langle \gamma \rangle}{\hbar\omega_N} x \right) F \left(\frac{x}{\omega_N} \right) dx \\ = \frac{2}{\omega_N} \text{Re} \left[1 - \exp \left(-2\pi i \frac{\Delta E_{\text{eff}}^k}{\hbar\omega_N} \right) \exp \left(-2\pi \frac{\langle \gamma \rangle}{\hbar\omega_N} \right) \right]^{-1} \\ \times \int_0^{2\pi} dx \exp \left(-\frac{i\Delta E_{\text{eff}}^k}{\hbar\omega_N} x - \frac{\langle \gamma \rangle}{\hbar\omega_N} x \right) F \left(\frac{x}{\omega_N} \right) \quad (\text{III.5})$$

Several comments should be made at this point:

(a) I_k expressed by Eq. (III.5) is independent of the choice of the common normalizing frequency $\tilde{\omega}_N$. We shall use the maximum frequency ω_N .

(b) If $E_{\text{eff}}^k/\hbar\omega_N$ is not an integer, then we expect that $I_k \rightarrow 0$ for $\langle \gamma \rangle/\hbar\omega_N \rightarrow 0$. This situation corresponds to the violation of energy conservation and will be encountered for a small molecule.

(c) Consider now the situation when energy conservation is ensued so that $\Delta E_{\text{eff}}^k/\hbar\omega_N$ is an integer while $\langle \gamma \rangle \ll \hbar\omega_N$. Under these circumstances Eq. (III.5) leads to

$$I_k(\gamma \ll \hbar\omega_N) = \frac{\hbar}{\pi \langle \gamma \rangle} \text{Re} \int_0^{2\pi} dx \times \exp \left(-\frac{i\Delta E_{\text{eff}}^k}{\hbar\omega_N} x \right) F \left(\frac{x}{\omega_N} \right), \quad (\text{III.6})$$

so that the nonradiative transition (III.6) probability under these circumstances is proportional to $\langle \gamma \rangle^{-1}$.

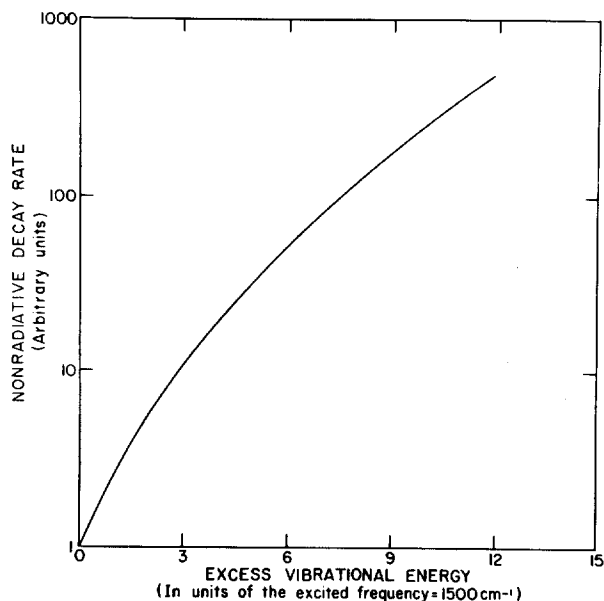


FIG. 1. Nonradiative decay rate as a function of the excess vibrational energy for a model molecule characterized by the accepting modes; $\omega_1=3000\text{ cm}^{-1}$; $\omega_2=1500\text{ cm}^{-1}$; $\Delta_1=0.8$; $\Delta_2=1.0$; $\Delta E_{\text{eff}}=30\,000\text{ cm}^{-1}$. ω_2 is taken to be the optically excited frequency.

This physical situation can be encountered in real life for the nonradiative decay of degenerate levels in a small molecule embedded in a medium. In what follows, we shall utilize this result (III.6) to provide a scheme for numerical calculations of the decay in a large molecule.

(d) In the statistical limit we expect that $\langle\gamma\rangle\gg\hbar\omega_N$ whereupon the following simplified result is obtained:

$$I_k(\gamma\gg\hbar\omega_N) = \frac{2}{\omega_N} \text{Re} \int_0^{2\pi} dx \times \exp\left(-\frac{i\Delta E_{\text{eff}}}{\hbar\omega_N} x\right) \exp\left(-\frac{\langle\gamma\rangle}{\hbar\omega_N} x\right) F\left(\frac{x}{\omega_N}\right). \quad (\text{III.7})$$

It was demonstrated by us²⁸ that the integral (III.7) is independent of $\langle\gamma\rangle$ over a wide region of this width provided that $\langle\gamma\rangle\ll\hbar\omega_N$, for all the molecular frequencies. The lower limit for $\langle\gamma\rangle$ corresponds to Bixon's condition⁵ for the statistical limit, while the upper limit is always realized in real life. Thus, for computational purposes in the statistical limit we should, in principle, utilize $I_k(\hbar\omega_N\gg\langle\gamma\rangle\gg\hbar\omega_N)$ which is given by (III.7).

IV. SOME NUMERICAL ESTIMATES

It is important to distinguish between the mathematical and the physical implications of the formalism derived herein for the semiquantitative estimates of the nonradiative decay probability of a single vibronic level of an isolated large molecule. In our approximate treatment the function F [see Eqs. (III.2)–(III.7)] contains very few frequencies which correspond to the totally symmetric vibrational modes. Furthermore, it

will be convenient for computational reasons to approximate these frequencies by rounded-off numbers so that ω_N will be as large as possible. The vibronic levels in the dissipative channel can be arranged in groups by taking the molecule frequencies to be integer multiples of the (large) normalizing frequency ω_N . Furthermore we shall assume that $\Delta E_{\text{eff}}/\hbar\omega_N$ is an integer. To calculate I_k we should note that: (a) The present procedure yields contributions to (III.7) from states which in real life are distributed over the energy region $\Delta E_{\text{eff}}\pm\hbar\omega_N$, while in fact the integral I_k should contain contributions from the energy region $\Delta E_{\text{eff}}\pm\langle\gamma\rangle$. (b) Grouping together the molecular vibrations corresponds to the case whereupon $\langle\gamma\rangle\ll\hbar\omega_N$. [See Eq. (III.6).] Thus a reasonable approximation for I_k in the statistical limit is

$$I_k \approx I_k(\langle\gamma\rangle\ll\hbar\omega_N)(\langle\gamma\rangle/\omega_N), \quad (\text{IV.1})$$

whereupon

$$I_k \approx (\pi\omega_N)^{-1} \int_0^{2\pi} dx \exp\left(-\frac{i\Delta E_{\text{eff}}}{\hbar\omega_N} x\right) F\left(\frac{x}{\omega_N}\right).$$

We have utilized this computational scheme for the evaluation of the nonradiative decay probability from single vibronic levels of the ${}^1B_{2u}$ state to the ${}^3B_{1u}$ state

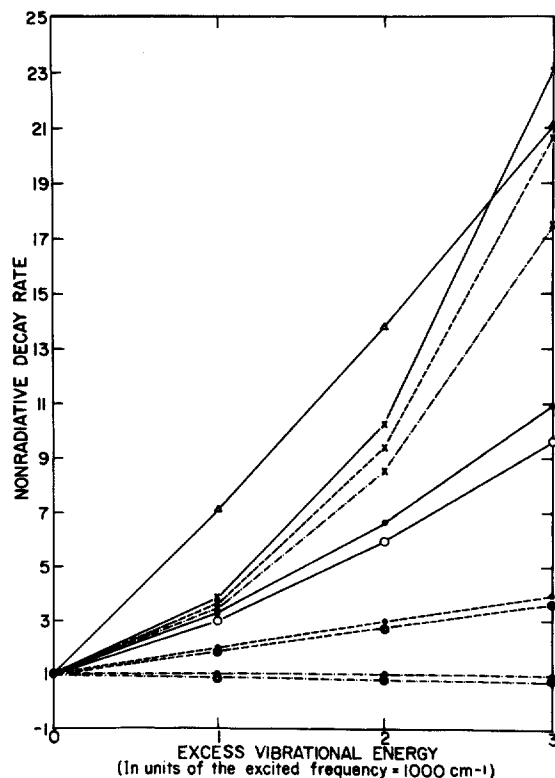


FIG. 2. Nonradiative decay rate as a function of the excess vibrational energy for a model molecule characterized by the accepting modes; $\omega_1=1000\text{ cm}^{-1}$; $\omega_2=3000\text{ cm}^{-1}$. ω_1 is taken to be the optically excited frequency. $-\cdot-\cdot-$, $\Delta E=6000\text{ cm}^{-1}$; $-\cdot-\cdot-$, $\Delta E=7000\text{ cm}^{-1}$; $-$, $\Delta E=8000\text{ cm}^{-1}$; \circ , $\Delta_1=0.24$, $\Delta_2=0.071$; Δ , $\Delta_1=0.24$, $\Delta_2=0.6$; \bullet , $\Delta_1=0.1$, $\Delta_2=0.071$; \times , $\Delta_1=0.9$, $\Delta_2=0.071$.

in the benzene molecule,^{18,19} assuming the validity of the statistical limit. The accepting modes are²⁹ $\hbar\omega$ (a_{1g} C stretching) ≈ 1000 cm^{-1} ; Δ (a_{1g} C stretching) = 0.24 and $\hbar\omega$ (a_{1g} H stretching) ≈ 3000 cm^{-1} ; Δ (a_{1g} H stretching) = 0.071, while $\Delta = 0$ for all the other modes. The electronic energy gap is $\Delta E = 8000$ cm^{-1} while the promoting mode corresponds to an a_{2g} H bending mode with $\hbar\omega_k = 1300$ cm^{-1} , so that $\Delta E_{\text{eff}} = 6700$ cm^{-1} . Model numerical calculations were performed utilizing Eqs. (III.2), (III.4), and (IV.2). The (rounded-off) effective energy gap was taken to be $\Delta E_{\text{eff}} = 10^3 n$ cm^{-1} ($n = 6-8$), so that the normalizing frequency was chosen to be $\hbar\omega_N = 1000$ cm^{-1} . Our theoretical results correspond to the nonradiative decay probability of the members of the totally symmetric progression built on the false electronic origin $6^1 1^0$, $6^1 1^1$, $6^1 1^2 \dots$ or of the members of the totally symmetric progression 1^0 , 1^1 , $1^2 \dots$. The present theoretical model results for the nonradiative decay of the level $6^1 1^n$ should be identical to the nonradiative decay probability of the level 1^n , as the $e_{2g}(6)$ vibration does not act as a promoting mode and $\Delta = 0$ for this nontotally symmetric vibration. The numerical results for a wide range of molecular parameters are presented in Figs. 1 and 2, while in Fig. 3 we display a more detailed comparison of the present calculations with the available experimental data,^{18,19} for the benzene molecule. From these results we conclude that:

(a) The experimental results of Selinger and Ware^{18a} and of Parmenter^{18b} are consistent with the general prediction of the present simple model (based on the displaced potentials picture) concerning the equal decay probabilities of the $6^1 1^n$ and of the 1^n levels. Thus Selinger and Ware report that the nonradiative decay times of the $6^1 1^0$ and the 1^0 vibronic levels differ by about 4%. The experimental data of Spears and Rice¹⁹ reveal somewhat larger deviation for the 1^0 level.

(b) From the theoretical results presented in Figs. 2 and 3 for the ${}^1B_{2u} \rightarrow {}^3B_{1u}$ transition in the benzene molecule, we realize that the best fit to the experimental data is obtained by the spectroscopic molecular parameters³⁰ and by an effective energy gap somewhere in the region 6000–7000 cm^{-1} . These conclusions concur with the available experimental data. A better theoretical fit to the experimental results could be accomplished by a slight variation of the Δ molecular parameters; however, we feel that in view of the simplified theoretical model, which neglects frequency changes, a better agreement will be fortuitous.

(c) The nonradiative decay probability of a single vibronic level is determined by the weighted density of states function, the weighting factor corresponds to the nonadiabatic coupling matrix elements $V_{si,lj}$. The latter terms decrease while the density of states, ρ , in the $|lj\rangle$ dissipative manifold increases with increasing the excess vibrational energy E_v . For relatively small effective energy gaps (see Fig. 2) the nonradiative decay probability decreases or remains constant with increasing E_v , indicating that the dominant effect is

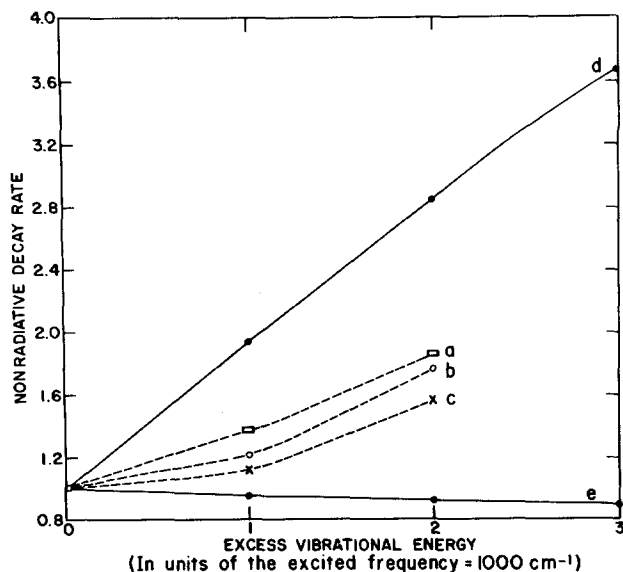


Fig. 3. Nonradiative decay rate vs excess vibrational energy for the ${}^1B_{2u} \rightarrow {}^3B_{1u}$ nonradiative transition of benzene: (a) Spears and Rice data¹⁹ for the decay of the $1^0 1^1 1^2$ levels; (b) Selinger and Ware data¹⁸ for the decay of the $6^1 1^0 6^1 1^1 6^1 1^2$ levels; (c) Spears and Rice data¹⁹ for the decay of the $6^1 1^0$ $6^1 1^1$ $6^1 1^2$ levels; (d) theoretical data with $\Delta E_{\text{eff}} = 7000$ cm^{-1} ; (e) theoretical data with $\Delta E_{\text{eff}} = 6000$ cm^{-1} .

that of decreasing $V_{si,lj}$. This situation corresponds to the verge of the statistical limit. On the other hand, for large effective energy gaps increase in ρ dominates so that the nonradiative decay probability (see again Fig. 2) increases with increasing E_v . For extremely large energy gaps the nonradiative decay probability exhibits an increasing exponential dependence on the excess vibrational energy. Thus the results presented in Fig. 1 for reasonable molecular parameters roughly reproduce the experimental features of the experimental results of Schlag and Von Weyssenhoff.¹⁶

V. DISCUSSION

In this paper we have provided a theoretical study of nonradiative decay of a single vibronic level of an isolated, large "harmonic molecule" which is characterized by identical displaced potential hypersurfaces. This model elucidates the gross features of optical selection studies in large isolated molecules. The effects of frequency changes between electronic states¹⁵ will lead to some qualitative modifications; however, the resulting theoretical expressions will be very cumbersome. It should be stressed that we have explicitly assumed that the initial vibronic level $|si\rangle$, which is accessible by optical excitation from the ground state, is only coupled to the $|lj\rangle$ dissipative continuum, while anharmonic coupling effects which may lead to intramolecular relaxation and energy redistribution within the $|s\rangle$ manifold in the isolated molecule were disregarded. Such approximation, which is consistent with the harmonic model, is justified for a medium-sized molecule like benzene, which was studied here in

some detail. However, in larger molecular systems intramolecular vibrational relaxation effects may be of considerable importance and deserve further study.

The most interesting conclusion emerging from the present study is that the nonradiative decay probability can either increase (for large energy gaps) or decrease (for a small energy gap) with increasing excess vibrational energy. The available experimental data correspond to the former case. It will be interesting to check experimentally the theoretical prediction concerning the decrease of the nonradiative decay probability in the higher vibronic components for medium sized molecules characterized by a small effective energy gap. Such a study has to be performed on a molecule embedded in a medium (which will provide the necessary line broadening effects in the $|lj\rangle$ manifold to make the decay statistical) and the molecule has to be characterized by a nonradiative decay probability which exceeds the (medium induced) vibrational relaxation probability within the $|si\rangle$ manifold. Singlet-triplet nonradiative decay processes in heterocyclic molecules or ketones might provide such a case.

Finally, we would like to point out that the general theoretical methods based on the Feynman operator technique applied herein for the study of the nonradiative decay probability are of wide generality and will find further use in other studies related to molecular processes. Similar methods can be applied for the study of the nature of the Condon approximation in the theory of electronic relaxation processes and of vibrational relaxation problems.

APPENDIX A. ANALYSIS OF THE SCHLAG-FISCHER SCHEME²¹

We present a survey of the treatment of Fischer and Schlag²¹ recast in terms of our notation and terminology. The basic assumption underlying this treatment is that the excess vibrational energy is effectively randomly redistributed among all the vibrational degrees of freedom. One can then define an effective temperature T_{eff} for which the molecule would have acquired the same excess vibrational energy, so that in the initial electron state

$$V_{s\mu} = [\exp(\beta\hbar\omega_{s\mu}) - 1]^{-1}; \quad \beta = (1/kT_{\text{eff}})$$

and the excess vibrational energy is given by (II.5), so that

$$E_V = \sum_{\mu} \hbar\omega_{s\mu} v_{s\mu} \approx \hbar\bar{\omega}\bar{v}L.$$

Here, L is the number of vibrational degrees of freedom and $\bar{\omega}$, \bar{v} are averaged values.

The unimolecular reaction theory scheme is used by Fischer and Schlag to obtain a result which is, as expected, identical to Englman, Freed, and Jortner's expression (II.48). We shall write it here in a slightly different form including the width of the states, for large energy gap (so that $\Delta E_{\text{eff}} = \Delta E$) and for a single

promoting mode

$$W = R \int_{-\infty}^{\infty} dt \exp[-i(\Delta E/\hbar)t + a(\bar{v}+1) \exp(i\bar{\omega}t) + a\bar{v} \times \exp(-i\bar{\omega}t) - (\langle\gamma\rangle/\hbar) |t|], \quad (\text{A1})$$

where

$$R = (|c_{st}|^2 \omega_{\kappa}/2\hbar) \coth(\hbar\omega_{\kappa}/2E_V) \times \exp[-a(2\bar{v}+1)] \quad (\text{A2})$$

and

$$a = L\frac{1}{2}\langle\Delta^2\rangle, \quad (\text{A3})$$

where $\langle\Delta^2\rangle$ is an average over Δ_{μ}^2 .

Now we expand

$$\begin{aligned} & \exp[a(\bar{v}+1) \exp(i\bar{\omega}t) + a\bar{v} \exp(-i\bar{\omega}t)] \\ &= \sum_{m=0}^{\infty} \sum_{P=0}^{\infty} (m!)^{-1} (P!)^{-1} [a(\bar{v}+1) \\ & \quad \times \exp(i\bar{\omega}t)]^m [a\bar{v} \exp(-i\bar{\omega}t)]^P \end{aligned} \quad (\text{A4})$$

and integrate over t , using

$$\int_{-\infty}^{\infty} e^{-iyx} e^{-b|x|} dx = \frac{2b}{y^2 + b^2} \quad (\text{A5})$$

to obtain

$$\begin{aligned} W &= \frac{R}{\bar{\omega}} \sum_{m=0}^{\infty} \sum_{P=0}^{\infty} \frac{[a(\bar{v}+1)]^m [a\bar{v}]^P}{m!P!} \\ & \quad \times \frac{2(\langle\gamma\rangle/\hbar\bar{\omega})}{[\epsilon - (m-P)]^2 + (\langle\gamma\rangle/\hbar\bar{\omega})^2}, \end{aligned} \quad (\text{A6})$$

where

$$\epsilon = \Delta E/\hbar\bar{\omega}.$$

As $\langle\gamma\rangle/\hbar\bar{\omega} \ll 1$, we replace the Lorentzian in Eq. (A4) by $\delta_{\Delta E/\hbar\bar{\omega}, m-P}$,³¹ to obtain

$$W = \frac{R}{\bar{\omega}} \sum_{P=0}^{\infty} \frac{a^{2P+\epsilon}}{P!(P+\epsilon)!} (\bar{v})^P (\bar{v}+1)^{P+\epsilon}. \quad (\text{A7})$$

Now, when the excess vibrational energy is small (i.e., $\bar{v} \ll 1$), the energy gap is large (i.e., $\epsilon \gg 1$) and the average origin shift is small ($a \sim 1$, i.e., $\Delta \ll 1$), we can neglect in Eq. (A6) all the terms with $P > 0$, so that

$$\begin{aligned} W &= (R/\bar{\omega}) (a^{\epsilon}/\epsilon!) (\bar{v}+1)^{\epsilon} \\ &= (R/\bar{\omega}) (a^{\epsilon}/\epsilon!) \exp(\epsilon\bar{v}), \end{aligned} \quad (\text{A8})$$

where we have used for $\bar{v} \ll 1$

$$(1+\bar{v})^{\epsilon} \sim 1 + \epsilon\bar{v} \sim \exp(\epsilon\bar{v}). \quad (\text{A9})$$

The final result is [substituting R from Eq. (A2)]

$$\begin{aligned} & (|c_{st}|^2 \omega_{\kappa}/2\hbar) \coth(\hbar\omega_{\kappa}/2E_V) \bar{\omega}^{-1} \\ & \quad \times \exp[-a(2\bar{v}+1) + \epsilon\bar{v}] (a^{\epsilon}/\epsilon!). \end{aligned} \quad (\text{A10})$$

Apart from the mathematical approximations introduced by Schlag and Fischer which we have just reviewed, we strongly feel that the basis assumption concerning the isolated molecule acting as "its own heat bath" is unjustified. Although intramolecular vibration relaxation may occur in large molecules due to anharmonic coupling, this process will not result in an effective Boltzmann distribution.

APPENDIX B. THE THERMAL AVERAGING PROCESS

We shall demonstrate that thermal averaging of Eq. (II.45) gives Eq. (II.48). We can, of course, average separately on each normal coordinate so that the κ part of Eq. (II.45) is averaged by taking $\bar{v}_\kappa = [\exp(\beta\omega_\kappa) - 1]^{-1}$ instead of $v_{s\kappa}$ in the expressions (II.26) for the d factors. The μ dependent part of Eq. (II.45) is averaged as follows: Instead of Eq. (II.43), we take

$$\begin{aligned} \langle s \rangle &\equiv \langle X_{s\mu} | \exp[\lambda_\mu(t)a_\mu^\dagger] \exp[-\lambda_\mu^*(t)a_\mu] | X_{s\mu} \rangle_T \\ &= [1 - \exp(-\beta\omega_\mu)] \sum_{v_{s\mu}=0}^{\infty} \exp(-v_{s\mu}\beta\omega_\mu) v_{s\mu}! \sum_{r=0}^{v_{s\mu}} \frac{(-1)^r |\lambda_\mu(t)|^{2r}}{(v_{s\mu}-r)!(r!)^2}. \end{aligned} \quad (\text{B1})$$

By substituting $P = v_{s\mu} - r$ and

$$\sum_{r=0}^{v_{s\mu}} \rightarrow \sum_{P=0}^{v_{s\mu}},$$

we get

$$\begin{aligned} \langle s \rangle &= [1 - \exp(-\beta\omega_\mu)] \sum_{v_{s\mu}=0}^{\infty} \sum_{P=0}^{v_{s\mu}} \frac{\exp(-v_{s\mu}\beta\omega_\mu) (v_{s\mu})! (-1)^{v_{s\mu}-P} |\lambda_\mu|^{2(v_{s\mu}-P)}}{P! [(v_{s\mu}-P)!]^2} \\ &= [1 - \exp(-\beta\omega_\mu)] \sum_{b=0}^{\infty} \sum_{P=0}^{\infty} \frac{\exp[-(b+P)\beta\omega_\mu] (b+P)! (-1)^b |\lambda_\mu|^{2b}}{P! (b!)^2} \\ &= [1 - \exp(-\beta\omega_\mu)] \sum_{b=0}^{\infty} \frac{(-1)^b |\lambda_\mu|^{2b}}{b!} \exp(-b\beta\omega_\mu) B \end{aligned} \quad (\text{B2})$$

where we have set

$$B = \sum_{P=0}^{\infty} \frac{\exp(-P\beta\omega_\mu) (b+P)!}{b! P!}. \quad (\text{B3})$$

By using the binomial theorem, it is easy to prove that

$$B = [1 - \exp(-\beta\omega_\mu)]^{-b-1}, \quad (\text{B4})$$

so that

$$\begin{aligned} \langle s \rangle &= \sum_{b=0}^{\infty} \left(\frac{1}{e^{\beta\omega_\mu} - 1} \right)^b \frac{(-1)^b (\lambda_\mu)^{2b}}{b!} \\ &= \sum_{b=0}^{\infty} (b!)^{-1} (-\bar{v}_\mu |\lambda|^2)^b \\ &= \exp[-|\lambda_\mu(t)|^2 \bar{v}_\mu] \\ &= \exp\left\{ \left(-\frac{1}{2}\Delta_\mu^2 2\bar{v}_\mu\right) + \frac{1}{2}\Delta_\mu^2 v_\mu [\exp(i\omega_\mu t) + \exp(-i\omega_\mu t)] \right\}. \end{aligned} \quad (\text{B5})$$

Taking (B5) to replace Eq. (II.43) and utilizing Eq. (II.26), we easily get Eq. (II.48) as the final result.

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Effect of Pressure on Molecular Motions of Bromobenzene and Toluene- d_3 in the Liquid State*

H. J. PARKHURST, JR., Y. LEE, AND J. JONAS†

Department of Chemistry, School of Chemical Sciences and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

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The pressure dependences of the proton spin-lattice relaxation times have been measured at 30°C in liquid bromobenzene and its mixtures with bromobenzene- d_5 up to 2.5 kbar, and in liquid toluene- d_3 and its mixtures with toluene- d_3 up to 4.5 kbar. The separation of the intramolecular and intermolecular contributions to proton dipolar relaxation allowed us to study the effect of pressure on reorientational and translational motions of the molecular liquids investigated. Activation volumes for the intramolecular and intermolecular T_1 ; and the rotational and translational correlation times were calculated. The data obtained indicate that the molecular shape seems to play a decisive role on the degree of coupling between the rotational and translational motions of these two model liquids. The effect of the difference in the dipole moments on this coupling seems to be less important.

INTRODUCTION

In an earlier study¹ in this laboratory the pressure dependences of the proton spin-lattice relaxation times in benzene and chlorobenzene in the liquid state have been measured. Since the separation of the intramolecular and intermolecular contributions to the dipolar relaxation was carried out the results were discussed in terms of pressure effects on rotational and translational motions and the degree of coupling between these. This earlier study left, however, one important question unanswered, namely what is the relative role of the molecular shape and the presence of dipole moment on the coupling between the rotational and translational motions.

In this study we attempted to provide some additional information on this question. For this purpose we measured the pressure dependences at 30°C of the proton spin-lattice relaxation in bromobenzene and its mixtures with bromobenzene- d_5 up to 2.5 kbar, and in toluene- d_3 and its mixtures with toluene- d_3 up to 4.5 kbar. The intramolecular and intermolecular contributions to proton dipolar relaxation rate were separated and their pressure dependence compared with that of viscosity and product of viscosity and density. The reason for choosing bromobenzene and toluene- d_3 was to find out whether the difference in their dipole moments will affect the degree of the coupling between the

rotational and translational motions in these two molecules, which are very similar in their shape. The results of this limited study indicated that the difference in the permanent dipole moments had no pronounced effect on the coupling. Activation parameters and theoretical correlation times were also calculated.

EXPERIMENTAL

The ¹H and ²D spin-lattice relaxation times were measured at 60 and 9.2 MHz, respectively, using a pulsed spectrometer previously described.² A 180°- τ -90° pulse sequence was used; the logarithm of the magnetization was plotted as a function of τ to obtain the relaxation times, T_1 to ($\pm 5\%$). A Varian model V-3800-1 high-resolution magnet system (air gap 3.8 in.) equipped with superstabilizer and shim coils was used for the measurements.

The pressure apparatus consisted of a Berylco-25 pressure bomb with temperature-controlling jacket through which ethylene glycol was circulated from a constant temperature bath. Carbon disulfide was used as a pressure-transmitting fluid in the bomb; a high-pressure separator was employed. The pressures were measured to ± 10 bar with a calibrated Heise-Bourdon pressure gauge, and the temperature next to the sample cell inside the bomb was continuously monitored ($\pm 0.2^\circ\text{C}$) with a copper-constantan thermocouple. The