Intramolecular Nonradiative Transitions in the "Non-Condon" Scheme

ABRAHAM NITZAN AND JOSHUA JORTNER

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

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In this paper we consider the nonradiative intramolecular decay of a large molecule utilizing Born–Oppenheimer wavefunctions as a zero order basis, and bypassing the conventional Condon approximation for the calculation of the electronic coupling matrix matrix elements. The electronic adiabatic wavefunctions are expanded in terms of the Wigner–Brillouin perturbation series in the weak electronic–vibrational coupling limit. We have applied a generalized version of Feynman's operator calculus to derive general expressions for the nonradiative decay probability of a statistical harmonic molecule characterized by displaced potential surfaces. Numerical calculations were performed for the decay of the vibrationless excited electronic state in the "non-Condon" scheme. The numerical data for the decay rate in a two electronic level system in the weak electronic vibrational coupling limit exceed the results obtained invoking the Condon approximation by 2–3 orders of magnitude; the exact correction factor depends on the molecular parameters, and, in particular, is roughly proportional to the square of the (frequency normalized) electronic energy gap. Finally, the relevant off resonance coupling terms in the adiabatic representation are shown to be appreciably smaller than the near resonance coupling terms, demonstrating the superiority of the adiabatic basis over the crude adiabatic basis in describing electronic relaxation processes.

I. INTRODUCTION

The Condon approximation for radiative transitions in molecules and solids rests on the assumption that the electronic wavefunctions exhibit a weak dependence on the nuclear coordinates, whereupon the electric dipole matrix elements (connecting Born–Oppenheimer molecular states) can be factorized into separate electronic and nuclear parts.[1] This approximation is justified for strongly allowed optical transitions, while for symmetry forbidden transitions (to degenerate states) the inclusion of linear (and quadratic) terms in nuclear displacements provides the idealogical basis for the well known Herzberg–Teller scheme.[2] The Condon approximation has been extensively utilized in the theory of nonradiative processes in solids[3–5] and nonradiative transitions in large molecules.[6–10] The intramolecular coupling matrix elements between the zero order vibronic states $\varphi_s(\mathbf{r}, \mathbf{Q})\chi_{si}(\mathbf{Q})$ and $\varphi_l(\mathbf{r}, \mathbf{Q})\chi_{lj}(\mathbf{Q})$, in the adiabatic representation, are of the general form

$$V_{si,lj}^{A} = (\chi_{si}(\mathbf{Q}) \mid \langle \varphi_s(\mathbf{r}, \mathbf{Q}) \mid \partial/\partial \mathbf{Q} \mid \varphi_l(\mathbf{r}, \mathbf{Q}) \rangle \cdot (\partial/\partial \mathbf{Q}) \mid \chi_{lj}(\mathbf{Q}))$$
$$+ \tfrac{1}{2}(\chi_{si}(\mathbf{Q}) \mid \langle \varphi_s(\mathbf{r}, \mathbf{Q}) \mid (\partial/\partial \mathbf{Q}) \cdot (\partial/\partial \mathbf{Q}) \mid \varphi_l(\mathbf{r}, \mathbf{Q}) \rangle \mid \chi_{lj}(\mathbf{Q}))$$
$$= \left(\chi_{si}(\mathbf{Q}) \left| \frac{\langle \varphi_s(\mathbf{r}, \mathbf{Q}) \mid \partial U(\mathbf{r}, \mathbf{Q})/\partial \mathbf{Q} \mid \varphi_l(\mathbf{r}, \mathbf{Q}) \rangle}{E_s(\mathbf{Q}) - E_l(\mathbf{Q})} \cdot \frac{\partial}{\partial \mathbf{Q}} \right| \chi_{lj}(\mathbf{Q}) \right)$$
$$+ \tfrac{1}{2}(\chi_{si}(\mathbf{Q}) \mid \langle \varphi_s(\mathbf{r}, \mathbf{Q}) \mid (\partial/\partial \mathbf{Q}) \cdot (\partial/\partial \mathbf{Q}) \mid \varphi_l(\mathbf{r}, \mathbf{Q}) \rangle \mid \chi_{lj}(\mathbf{Q})), \quad \text{(I.1)}$$

where $\mathbf{r}$ are the electronic coordinates, $\mathbf{Q}$ represent the nuclear coordinates, $U(\mathbf{r}, \mathbf{Q})$ is the electrostatic molecular potential, while $E_s(\mathbf{Q})$ and $E_l(\mathbf{Q})$ correspond to the adiabatic potential energy surfaces which correspond to the two electronic states. Finally, ( ) and $\langle\ \rangle$ represent integrations over nuclear and electronic coordinates, respectively.

Following conventional trends[11,12] in the theory of nonradiative processes the following approximations are introduced at this point:

(a) The second contribution in Eq. (I.1) is discarded.

(b) The energy denominator $E_s(\mathbf{Q}) - E_l(\mathbf{Q})$ is assumed to be weakly dependent on the nuclear coordinates and is set to be equal to a constant (say, the electronic energy gap).

(c) The electronic matrix element $\langle \varphi_s \mid \partial U/\partial Q \mid \varphi_l \rangle$ is assumed to be a slowly varying function of the nuclear configuration.

Thus Eq. (I.1) is replaced by the approximate relation

$$V_{si,lj}^{A} \approx \frac{\langle \varphi_s(\mathbf{r}, \mathbf{Q}_0) \mid (\partial U/\partial \mathbf{Q}) \mid_{\mathbf{Q}_0} \varphi_l(\mathbf{r}, \mathbf{Q}_0) \rangle}{E_s(\mathbf{Q}_0) - E_l(\mathbf{Q}_0)} \cdot \left(\chi_{si}(\mathbf{Q}) \left| \frac{\partial}{\partial \mathbf{Q}} \right| \chi_{lj}(\mathbf{Q}) \right) \quad \text{(I.2)}$$

We should note that assumptions (b) and (c) provide necessary conditions for the validity of assumption (a), as each of the matrix elements in (I.1) does not separately involve an hermitian operator. Assumptions (b) and (c) constitute the Condon approximation for nonradiative transitions.

A number of recent publications[13,14] criticize assump-

tion (b). Sharf and Silbey[13] have originally pointed out that the dependence of the energy denominator on nuclear coordinates in Eq. (I.1) may lead to a serious underestimate of the intramolecular coupling matrix element calculated from (I.2), which is smaller by about one order of magnitude than the result obtained by utilizing the crude adiabatic functions as a zero order basis set. We note in passing that the choice of zero order basis set for describing a quantum relaxation process is arbitrary, as long as this basis is complete and a proper zero order Hamiltonian and perturbation operators are defined in a self-consistent manner. The crude adiabatic basis set has a serious drawback as the off resonance coupling terms with other electronic states are large, exceeding by about one order of magnitude the off resonance coupling terms in the adiabatic representations (see also Sec. V). Thus, only the adiabatic set is adequate for a proper description of the nonradiative decay in a two electronic level system, when the role of other off resonance excited states is disregarded. Nevertheless, Sharf and Silbey's criticism of the Condon approximation for the calculation of intramolecular coupling utilizing adiabatic wavefunctions is perfectly valid. In this context Siebrand[14] has applied a simple physical model to calculate the correction term to (I.2) arising from bypassing assumption (b), concluding that $V_{si,lj}^{A}$ is increased by a numerical factor of 2–3 (so that the theoretical nonradiative transition probability is increased by about one order of magnitude.[15] Also, Sharf and Silbey[16] have recently taken into account the Q dependence of the electronic integral. From an approximate calculation of the nonadiabatic coupling matrix element, Sharf and Silbey[15] concluded that the near resonance coupling term is of the same magnitude in the adiabatic and in the crude adiabatic schemes, while for off resonance states the crude adiabatic coupling exceeds the adiabatic coupling by 1–2 orders of magnitude. The validity of the Condon approximation for the calculation of nonradiative transition probabilities in solids was questioned by Kovarskii.[17] Utilizing Feynman's operator calculus[18] and taking the electronic–nuclear coupling term to be of first order in nuclear coordinates, the formalism of Lax[4] was extended to the non-Condon case. This treatment is limited to the case of impurity centers in solids, where the normalized (dimensionless) shifts of the origins of the potential surfaces, Δ_i, are appreciably smaller than unity and one can get away with discarding second order terms $O(\Delta_i^2)$ in the generating function.

In this paper we derive a general expression for the nonradiative intramolecular decay rate of a zero order Born–Oppenheimer molecular state without invoking the Condon approximation, in an attempt to resolve the following questions:

(1) What is the error introduced by the application of the Condon approximation for the calculation of nonradiative transition probabilities? In this context one has to consider both the nuclear dependence of the energy denominator and of the electronic wavefunction.

(2) How does the relation between the Condon approximation and the general result depend on the molecular parameters?

(3) To what extent does the present general treatment, which bypasses the Condon approximation, modify previous conclusions concerning the general features of molecular nonradiative transitions (i.e., the isotope effect,[6–9] the energy gap law,[7–9] and optical selection effects[19]), which were derived within the framework of the Condon approximation?

We shall apply a generalized version of the generating function method to recast an expression for the nonradiative transition probability without invoking the Condon approximation. Our treatment differs from the previous work of Kovarskii[17] as in the molecular case we cannot utilize expansions in the linear coupling parameters Δ_i, and our results are valid for $\Delta_i \sim 1$. The present extension of Kovarskii's procedure is in fact equivalent to Rickayzen's modification[5] of Lax's work[4] on radiative and nonradiative transitions in solids within the framework of the Condon approximation, which was also utilized recently by us for the study of optical selection in molecules.[19] In what follows we shall derive rather complicated general expressions for the nonradiative decay rate in a large (statistical) "harmonic" molecule characterized by displaced potential surfaces. Numerical calculations performed for the decay of a vibrationless molecule level (i.e., the zero temperature case for a molecule imbedded in an inert medium at zero temperature) demonstrate the nature of the serious deviations introduced by the Condon approximation and their dependence on the relevant molecular parameters. Finally, it is encouraging to discover that the general relations and correlations previously obtained in the theory of nonradiative molecular processes are not affected by bypassing the Condon approximation.

II. THE ADIABATIC ELECTRONIC FUNCTIONS

In this section we shall apply general perturbation theory[17] to obtain approximate adiabatic electronic functions as explicit functions of the nuclear coordinates. The conventional adiabatic electronic equation is

$$(T_r+U(\mathbf{r},\mathbf{Q}))\varphi(\mathbf{r},\mathbf{Q})=E(\mathbf{Q})\varphi(\mathbf{r},\mathbf{Q}), \quad \text{(II.1)}$$

where T_r is the electronic kinetic energy, and $\varphi(\mathbf{r},\mathbf{Q})$ is the electronic function, which depends parametrically on the nuclear coordinates $\mathbf{Q}$.[20] Applying perturbation theory we choose as a zero order Hamiltonian the electronic Hamiltonian at some constant nuclear configuration $\mathbf{Q}_0$,

$$H_0=T_r+U(\mathbf{r},\mathbf{Q}_0) \quad \text{(II.2)}$$

assuming that the perturbation may be taken to first order in the deviations $\mathbf{q}=\mathbf{Q}-\mathbf{Q}_0$ from this fixed configuration

$$V_c=U(\mathbf{r},\mathbf{Q})-U(\mathbf{r},\mathbf{Q}_0)\simeq\sum_\mu(\partial U/\partial Q_\mu)_0 q_\mu. \quad \text{(II.3)}$$

The validity of this approximation depends of course on the choice of the configuration $\mathbf{Q}_0$.

The zero order electronic functions will be denoted by $\varphi_n^0(\mathbf{r})$ or by $|n\rangle$ in Dirac's notation (n is the electronic quantum number), while the corresponding exact adiabatic functions will be denoted by $\varphi_n(\mathbf{r},\mathbf{q})$ (the nuclear coordinate being measured from the constant configuration $\mathbf{Q}_0$). Applying the Wigner–Brillouin perturbation expansion one gets[17]

$$\varphi_s(\mathbf{r},\mathbf{q})=\varphi_s^0(\mathbf{r})+\sum_n{}'\frac{\langle n\mid V_c\mid s\rangle\varphi_n^0(\mathbf{r})}{E_s(\mathbf{q})-E_n^0}$$
$$+\sum_m{}'\sum_n{}'\frac{\langle m\mid V_c\mid n\rangle\langle n\mid V_c\mid s\rangle}{[E_s(\mathbf{q})-E_n^0][E_s(\mathbf{q})-E_m^0]}\varphi_m^0(\mathbf{r})+\cdots$$
$$=\varphi_s^0(\mathbf{r})+\sum_n{}'\frac{\langle n\mid V_c\mid s\rangle}{E_s(\mathbf{q})-\tilde{E}_n(\mathbf{q})}\varphi_n^0(\mathbf{r})$$
$$+\sum_{m\neq n}{}'\sum_n{}'\frac{\langle m\mid V_c\mid n\rangle\langle n\mid V_c\mid s\rangle}{[E_s(\mathbf{q})-E_n^0][E_s(\mathbf{q})-\tilde{E}_m(\mathbf{q})]}\varphi_m^0(\mathbf{r})+\cdots, \quad \text{(II.4)}$$

where $E_n(\mathbf{q})$ is the exact electronic energy of the nth electronic state, E_n^0 is the corresponding zero order energy (which is an eigenvalue of H_0), while

$$\tilde{E}_n(\mathbf{q})=E_n^0+\langle n\mid V_c\mid n\rangle \quad \text{(II.5)}$$

is the energy in first order. The prime in these expressions denotes exclusion of the state s from the summation.

A condition for the validity of Eq. (II.4) is

$$\langle n\mid V_c\mid n\rangle/[E_s(\mathbf{q})-E_n^0]<1 \quad \text{(II.6)}$$

for every n. Now, if the constant energy E_n^0 exceeds the minimum value of $E_s(\mathbf{q})$, there may exist (and in the harmonic approximation we shall always encounter) a value of $\mathbf{q}$ for which $E_n^0=E_s(\mathbf{q})$. For such configuration $\mathbf{q}$ and near it, the approximate description (II.4) of the adiabatic function $\varphi_s(\mathbf{r},\mathbf{q})$ breaks down. We conclude that Eq. (II.4) provides a proper description of $\varphi(\mathbf{r},\mathbf{q})$ for $\mathbf{Q}$ values which are not far from $\mathbf{Q}_s$—the nuclear configuration for which E_s is minimum. Thus for a single electronic state it will be convenient to choose $\mathbf{Q}_0=\mathbf{Q}_s$. When two relevant electronic states are encountered, we must require for the sake of consistency that these electronic states will be characterized by small relative displacements of the origins of their potential surfaces. The present representation of the adiabatic wavefunctions is thus valid for the weak coupling limit,[8] $\boldsymbol{\Delta}\leq 1$. ($\boldsymbol{\Delta}$ denotes these reduced displacements). The fixed configuration $\mathbf{Q}_0$ is then chosen to be close to the minimum of both electronic surfaces.

We now approximate Eq. (II.4) by neglecting all the terms which include nondiagonal matrix elements of V_c with powers higher than unity, to get

$$\varphi_s(\mathbf{r},\mathbf{q})=\varphi_s^0(\mathbf{r})+\sum_n{}'\{\langle n\mid V_c\mid s\rangle/[E_s(\mathbf{q})-\tilde{E}_n(\mathbf{q})]\}\varphi_n^0(\mathbf{r}). \quad \text{(II.7)}$$

Strictly speaking we must add here a normalization factor, of the form

$$\{1+\sum_n{}'[|\langle n\mid V_c\mid s\rangle|^2/|E_s(\mathbf{q})-\tilde{E}_n(\mathbf{q})|^2]\}^{-1/2},$$

but in the following discussion this small correction term will be disregarded.

We shall now follow Kovarskii[17] by taking the following approximate relation for the energy denominators in (II.7):

$$E_s(\mathbf{q})-\tilde{E}_n(\mathbf{q})\simeq E_s^0-E_n^0-\sum_\mu\hbar\omega_\mu\boldsymbol{\Delta}_\mu^n q_\mu, \quad \text{(II.8)}$$

where Δ_μ^n is the (dimensionless) displacement of the projection on the μth vibrational mode of the potential surface of the nth electronic state relative to that of the sth electronic state; while $q_\mu=Q_\mu-Q_0{}^\mu=Q_\mu-Q_s{}^\mu$. E_s^0 and E_n^0 are the zero order electronic energies taken at $\mathbf{Q}_s$. Note that

$$E_M{}^n=\tfrac{1}{2}\sum_\mu\hbar\omega_\mu(\Delta_\mu{}^n)^2,$$

which represents half the Stoke's shift and which usually appears in this place, is contained in the definition of E_n^0. This is just the amount by which E_n^0 exceeds the minimum of the nth potential surface.

In all fairness we must confess that the approximate relation (II.8) seems to be somewhat doubtful. The expansion to first order in $\mathbf{q}$ is, of course, valid. The major difficulty pertains to the validity of the definition of the $\Delta_\mu{}^n$ terms, or, in other words, whether these terms can be identified with the displacements obtained experimentally from spectroscopical data. This identification is equivalent (for harmonic potential surfaces) to the approximation

$$E_s(\mathbf{q})-\tilde{E}_n(\mathbf{q})\simeq E_s(\mathbf{q})-E_n(\mathbf{q}). \quad \text{(II.9)}$$

In Appendix A we see that this approximation is valid provided that the two relevant electronic states (involved in the nonradiative process) are much closer to each other than any other electronic state. We conclude that in this case the relevant adiabatic electronic

functions are given [according to Eq. (II.7)] by

$$\varphi_s(\mathbf{r},\mathbf{q})=\varphi_s^0(\mathbf{r}) + \sum_n{}' \{\langle n \mid V_c \mid s\rangle/[E_s(\mathbf{q})-\tilde{E}_n(\mathbf{q})]\}\varphi_n^0(\mathbf{r}), \quad \text{(II.10)}$$

$$\varphi_l(\mathbf{r},\mathbf{q})=\varphi_l^0(\mathbf{r}) + \sum_n{}' \{\langle n \mid V_c \mid l\rangle/[E_l(\mathbf{q})-\tilde{E}_n(\mathbf{q})]\}\varphi_l^0(\mathbf{r}), \quad \text{(II.11)}$$

where the $\mathbf{q}$ dependence is given by Eqs. (II.3) and (II.8).[21]

III. THE GENERATING FUNCTION

In this section we display the nonradiative decay rate of an excited electronic state of a large molecule in terms of the corresponding generating function, without applying the Condon approximation.

The nonradiative decay rate in a large molecule is

$$W_{si}=(2\pi/\hbar)\sum_j \mid V_{si,lj}^A\mid^2\delta(E_{lj}-E_{si}), \quad \text{(III.1)}$$

where $\mid si\rangle$ denote the vibronic component i of the electronic state s, and W_{si} is its decay rate into the quasicontinuous manifold of the vibronic levels $\mid lj\rangle$ of a lower electronic state l.

The states $\mid lj\rangle$ and $\mid si\rangle$ are taken to be Born–Oppenheimer states: $\mid lj\rangle=\varphi_l(\mathbf{r},\ \mathbf{q})\chi_{lj}(\mathbf{q})$; $\mid si\rangle=\varphi_s(\mathbf{r},\mathbf{q})\chi_{si}(\mathbf{q})$, where $\mathbf{q}$ is the normalized nuclear coordinate measured from the minimum of the potential surface of the sth electronic state. In the harmonic approximation $\chi_{si}(\mathbf{q})$ is a product of harmonic oscillator wavefunctions centered around $\mathbf{q}=0$, while $\chi_{lj}(\mathbf{q})$ is a similar product of harmonic oscillator wavefunctions which are shifted in origin by a vector $\boldsymbol{\Delta}$. The matrix element in Eq. (III.1) is

$$V_{si,lj}^A=(\chi_{lj}(\mathbf{q}) \mid -\sum_\mu \hbar\omega_\mu\langle\varphi_l(\mathbf{r},\mathbf{q}) \mid \partial/\partial q_\mu \mid \varphi_s(\mathbf{r},\mathbf{q})\rangle(\partial/\partial q_\mu)-\tfrac{1}{2}\sum_\mu \hbar\omega_\mu\langle\varphi_l(\mathbf{r},\mathbf{q}) \mid \partial^2/\partial q_\mu^2 \mid \varphi_s(\mathbf{r},\mathbf{q})\rangle \mid \chi_{si}(\mathbf{q})). \quad \text{(III.2)}$$

Utilizing (II.10) and (II.11) we get for the matrix elements in the rhs of Eq. (III.2)

$$\langle\varphi_l(\mathbf{r},\mathbf{q}) \mid \partial/\partial q_\mu \mid \varphi_s(\mathbf{r},\mathbf{q})\rangle=\{\langle l \mid U_\mu \mid s\rangle/[E_s(\mathbf{q})-\tilde{E}_l(\mathbf{q})]\}+\sum_\alpha \langle l \mid U_\alpha \mid s\rangle q_\alpha(\partial/\partial q_\mu)[E_s(\mathbf{q})-\tilde{E}_l(\mathbf{q})]^{-1}, \quad \text{(III.3)}$$

$$\tfrac{1}{2}\langle\varphi_l(\mathbf{r},\mathbf{q}) \mid \partial^2/\partial q_\mu^2 \mid \varphi_s(\mathbf{r},\mathbf{q})\rangle=\langle l \mid U_\mu \mid s\rangle(\partial/\partial q_\mu)[E_s(\mathbf{q})-\tilde{E}_l(\mathbf{q})]^{-1}+\tfrac{1}{2}\sum_\alpha \langle l \mid U_\alpha \mid s\rangle q_\alpha(\partial^2/\partial q_\mu^2)[E_s(\mathbf{q})-\tilde{E}_l(\mathbf{q})]^{-1}, \quad \text{(III.4)}$$

where $U_\alpha=(\partial U/\partial Q_\alpha)_{Q_0}$. In these expressions we have neglected the terms which involve more than one nondiagonal matrix element of V_c. This assumption immediately implies that the $\mid n\rangle$ states in Eqs. (II.10) and (II.11) (where $n\neq s,\ l$) do not contribute to the matrix element in first order.

Inserting (III.3) and (III.4) into (III.2) we get

$$V_{si,lj}=-(\chi_{lj}(\mathbf{q}) \mid L_A \mid \chi_{si}(\mathbf{q})), \quad \text{(III.5)}$$

where

$$L_A=\sum_\mu \hbar\omega_\mu\left\{\left[\frac{\langle l \mid U_\mu \mid s\rangle}{E_s(\mathbf{q})-\tilde{E}_l(\mathbf{q})}+\sum_\alpha \langle l \mid U_\alpha \mid s\rangle q_\alpha\frac{\partial}{\partial q_\mu}[E_s(\mathbf{q})-\tilde{E}_l(\mathbf{q})]^{-1}\right]\frac{\partial}{\partial q_\mu} + \langle l \mid U_\mu \mid s\rangle\frac{\partial}{\partial q_\mu}[E_s(q)-\tilde{E}_l(\mathbf{q})]^{-1}+\tfrac{1}{2}\sum_\alpha \langle l \mid U_\alpha \mid s\rangle q_\alpha\frac{\partial^2}{\partial q_\mu^2}[E_s(\mathbf{q})-\tilde{E}_l(\mathbf{q})]^{-1}\right\}. \quad \text{(III.6)}$$

It will be convenient to rewrite Eq. (III.6), separating out the promoting modes, $\kappa=1\cdots P$, which are characterized by $\langle l \mid U_\kappa \mid s\rangle\neq 0$. For these modes we shall assume[9] that $\Delta_\kappa=0$. From Eq. (II.8) it is thus clear that the energy denominators in Eq. (III.6) do not contain coordinates of the promoting modes, whereupon the third term on the rhs of Eq. (III.6) will vanish. Equation (III.6) may be now recast in the form

$$L_A=\sum_\kappa \hbar\omega_\kappa\{\langle l \mid U_\kappa \mid s\rangle/[E_s(\mathbf{q})-\tilde{E}_l(\mathbf{q})]\}(\partial/\partial q_\kappa)+\sum_\mu \hbar\omega_\mu(\sum_\kappa \langle l \mid U_\kappa \mid s\rangle q_\kappa)(\partial/\partial q_\mu)[E_s(\mathbf{q})-\tilde{E}_l(\mathbf{q})]^{-1} + \tfrac{1}{2}\sum_\mu \hbar\omega_\mu(\sum_\kappa \langle l \mid U_\kappa \mid s\rangle q_\kappa)(\partial^2/\partial q_\mu^2)[E_s(\mathbf{q})-\tilde{E}_l(\mathbf{q})]^{-1}. \quad \text{(III.7)}$$

The following remarks are in order:

(a) Looking at the exact expression for L_A

$$L_A=\sum_\kappa \hbar\omega_\kappa\frac{\langle\varphi_l(\mathbf{r},\mathbf{q}) \mid \partial U(\mathbf{r},\mathbf{q})/\partial q_\kappa \mid \varphi_s(\mathbf{r},\mathbf{q})\rangle}{E_s(\mathbf{q})-E_l(\mathbf{q})}, \quad \text{(III.8)}$$

we notice that the first term in Eq. (III.7) is identical with what we obtain from Eq. (III.8) by replacing $\varphi_l(\mathbf{r}, \mathbf{q})$ and $\varphi_s(\mathbf{r}, \mathbf{q})$ by $\varphi_l^0(\mathbf{r})$ and $\varphi_s^0(\mathbf{r})$, respectively, by taking $U(\mathbf{r}, \mathbf{q})$ to first order in $\mathbf{q}$ and by making use of Eq. (II.9). Thus the first term in Eq. (III.7) includes the dependence of the energy denominator on the nuclear coordinates, disregarding the change of the electronic wavefunctions with nuclear displacement. The dependence of the electronic wavefunctions on the nuclear coordinates contributes to the second and third term in Eq. (III.7).

(b) Expression (III.7) for L_A contains also the second derivative of the electronic wavefunction with respect to the nuclear coordinates. This term has to be retained here to insure the Hermiticity of the perturbation operator in the non-Condon case.

It will be convenient to recast the perturbation operator in an alternative form. Let us define

$$[E_s(\mathbf{q})-\tilde{E}_l(\mathbf{q})]^{-1}=[E-\sum_\mu \gamma_\mu q_\mu]^{-1}\equiv\xi(\mathbf{q}), \quad \text{(III.9)}$$

where

$$E=E_s^0-E_l^0=\Delta E_{sl}-E_M, \quad \text{(III.10)}$$

$$E_M=\tfrac{1}{2}\sum_\mu \hbar\omega_\mu\Delta_\mu^2, \quad \text{(III.11)}$$

$$\gamma_\mu=\hbar\omega_\mu\Delta_\mu. \quad \text{(III.12)}$$

Δ_μ is the displacement of the lth potential surface relative to the sth potential surface, projected on the coordinate q_μ. ΔE_{sl} is the energy gap between the pure electronic origins of the s and l potential surfaces. We also define the momentum conjugate to q_μ:

$$P_\mu=-i(\partial/\partial q_\mu). \quad \text{(III.13)}$$

In terms of these quantities L_A will now take the form:

$$L_A=i\sum_\kappa \hbar\omega_\kappa\langle l \mid U_\kappa \mid s\rangle\xi(\mathbf{q})P_\kappa - \tfrac{1}{2}\sum_\kappa \langle l \mid U_\kappa \mid s\rangle q_\kappa \sum_\mu \hbar\omega_\mu[P_\mu^2, \xi(q)] \quad \text{(III.14)}$$

The generating function related to W_{si} is obtained[6,8,9] by taking the Fourier transform of the δ function in Eq. (III.1) and then introducing the energy exponential into the matrix elements, and finally replacing the energies by the corresponding (nuclear) Hamiltonians, so that

$$W_{si}=\frac{1}{\hbar^2}\int_{-\infty}^{\infty} dtL(t), \quad \text{(III.15)}$$

where

$$L(t)=\sum_j (\langle si \mid V_A \exp[iH_{\mathrm{BO}}(t/\hbar)] \mid lj\rangle)\times(\langle lj \mid V_A^\dagger \exp[-iH_{\mathrm{BO}}(t/\hbar)] \mid si\rangle) \quad \text{(III.16)}$$

H_{BO} is the Born–Oppenheimer Hamiltonian defined by its operation on the Born–Oppenheimer functions:

$$H_{\mathrm{BO}}(\chi(\mathbf{q})\varphi(\mathbf{r}, \mathbf{q}))=(T_r+U(\mathbf{r}, \mathbf{q}))\chi(\mathbf{q})\varphi(\mathbf{r}, \mathbf{q}) + \varphi(\mathbf{r}, \mathbf{q})T_q\chi(\mathbf{q}), \quad \text{(III.17)}$$

while V_A is the nonadiabatic perturbation operator whose matrix elements where defined above [Eq. (I.1)]. T_q here is the nuclear kinetic energy operator.

Utilizing Eqs. (III.5) and (III.14) we get

$$L(t)=\hbar^2\sum_j (\chi_{si} \mid \sum_\kappa \langle s \mid U_\kappa \mid l\rangle\{-i\omega_\kappa\xi(\mathbf{q})p_\kappa+\tfrac{1}{2}q_\kappa\sum_\mu \omega_\mu[p_\mu^2, \xi(\mathbf{q})]\} \exp[iH_{\mathrm{BO}}{}^l(t/\hbar)] \mid \chi_{lj}) \times(\chi_{lj} \mid \sum_\kappa \langle l \mid U_\kappa \mid s\rangle\{i\omega_\kappa\xi(\mathbf{q})p_\kappa-\tfrac{1}{2}q_\kappa\sum_\mu \omega_\mu[p_\mu^2, \xi(\mathbf{q})]\} \exp[-iH_{\mathrm{BO}}{}^s(t/\hbar)] \mid \chi_{si}). \quad \text{(III.18)}$$

In the derivation of (III.18) we have utilized the fact that p_κ is a Hermitian operator, while $[p_\mu^2, \xi(\mathbf{q})]$, which is the commutator of two Hermitian operators, is anti-Hermitian. $H_{\mathrm{BO}}{}^l$ and $H_{\mathrm{BO}}{}^s$ denote the nuclear Hamiltonians for the electronic states l and s, respectively.

Making use now of the closure relation:

$$\sum_j \mid \chi_{lj})(\chi_{lj} \mid =1, \quad \text{(III.19)}$$

we get the general result:

$$L(t)=\hbar^2\sum_\kappa\sum_{\kappa'}\langle s \mid U_\kappa \mid l\rangle\langle l \mid U_{\kappa'} \mid s\rangle\omega_\kappa\omega_{\kappa'}\{(\chi_{si} \mid \xi(\mathbf{q})p_\kappa \exp[iH_{\mathrm{BO}}{}^l(t/\hbar)]\xi(\mathbf{q})p_{\kappa'} \exp[-iH_{\mathrm{BO}}{}^s(t/\hbar)] \mid \chi_{si}) + \tfrac{1}{2}(\chi_{si} \mid \xi(\mathbf{q})p_\kappa \exp[iH_{\mathrm{BO}}{}^l(t/\hbar)]q_{\kappa'}\sum_\mu(\omega_\mu/\omega_{\kappa'})[p_\mu^2, \xi(q)] \exp[-iH_{\mathrm{BO}}{}^s(t/\hbar)] \mid \chi_{si}) + \tfrac{1}{2}(\chi_{si} \mid q_\kappa\sum_\mu(\omega_\mu/\omega_\kappa)[p_\mu^2, \xi(\mathbf{q})] \exp[iH_{\mathrm{BO}}{}^l(t/\hbar)]\xi(\mathbf{q})p_{\kappa'} \exp[-iH_{\mathrm{BO}}{}^s(t/\hbar)] \mid \chi_{si}) - \tfrac{1}{4}(\chi_{si} \mid q_\kappa\sum_\mu(\omega_\mu/\omega_\kappa)[p_\mu^2, \xi(\mathbf{q})] \exp[iH_{\mathrm{BO}}{}^l(t/\hbar)]q_{\kappa'}\sum_{\mu'}(\omega_{\mu'}/\omega_{\kappa'})[p_\mu^2, \xi(\mathbf{q})] \exp[-iH_{\mathrm{BO}}{}^s(t/\hbar)] \mid \chi_{si})\}. \quad \text{(III.20)}$$

It is easy to demonstrate that if $\Delta_\kappa=0$, the mixed terms where $\kappa\neq\kappa'$ will not contribute to $L(t)$. To prove this point we note that $[p_\kappa^2, \xi(\mathbf{q})]=0$ and also $(\chi \mid p_\kappa p_{\kappa'} \mid \chi)=(\chi \mid q_\kappa q_{\kappa'} \mid \chi)=(\chi \mid p_\kappa q_{\kappa'} \mid \chi)=0$ for any pair of promot-

ing modes $\kappa \neq \kappa'$. The expression for $L(t)$ will thus reduce to a single sum:

$$L(t) = \hbar^2 \sum_{\kappa} |\langle s | U_\kappa | l \rangle|^2 L^\kappa(t) \tag{III.21}$$

with

$$L^\kappa(t) = A_\kappa(t) + (i/2) B_\kappa(t) + (i/2) C_\kappa(t) - \tfrac{1}{4} D_\kappa(t), \tag{III.22}$$

where

$$A_\kappa(t) = \omega_\kappa^2 (\chi_{si} | \xi(\mathbf{q}) p_\kappa \exp[iH_{\mathrm{BO}}{}^l(t/\hbar)] \xi(\mathbf{q}) p_\kappa \exp[-iH_{\mathrm{BO}}{}^s(t/\hbar)] | \chi_{si}), \tag{III.23a}$$

$$B_\kappa(t) = \omega_\kappa (\chi_{si} | \xi(\mathbf{q}) p_\kappa \exp[iH_{\mathrm{BO}}{}^l(t/\hbar)] q_\kappa \sum_{\mu \neq \kappa} \omega_\mu [p_\mu^2, \xi(\mathbf{q})] \exp[-iH_{\mathrm{BO}}{}^s(t/\hbar)] | \chi_{si}), \tag{III.23b}$$

$$C_\kappa(t) = \omega_\kappa (\chi_{si} | q_\kappa \sum_{\mu \neq \kappa} \omega_\mu [p_\mu^2, \xi(\mathbf{q})] \exp[iH_{\mathrm{BO}}{}^l(t/\hbar)] \xi(\mathbf{q}) p_\kappa \exp[-iH_{\mathrm{BO}}{}^s(t/\hbar)] | \chi_{si}), \tag{III.23c}$$

$$D_\kappa(t) = (\chi_{si} | q_\kappa \sum_{\mu \neq \kappa} \omega_\mu [p_\mu^2, \xi(\mathbf{q})] \exp[iH_{\mathrm{BO}}{}^l(t/\hbar)] q_\kappa \sum_{\mu' \neq \kappa} \omega_{\mu'} [p_{\mu'}{}^2, \xi(\mathbf{q})] \exp[-iH_{\mathrm{BO}}{}^s(t/\hbar)] | \chi_{si}). \tag{III.23d}$$

The basic details concerning the evaluation of these matrix elements are presented in Appendix B, while the actual evaluation is given in the Appendixes C and D. The final results for the simplest case of the zero temperature limit (or for the decay of the zero vibrational level) take the form

$$A_\kappa(t) = -\tfrac{1}{8} \omega_\kappa^2 \exp\left(i \Delta E_\kappa \frac{t}{\hbar}\right) \int_0^\infty d\tau \int_0^\infty d\tau' [\bar{A}(\tau, \tau'; t) - \bar{A}(\tau, -\tau'; t) + \bar{A}(-\tau, -\tau'; t) - \bar{A}(-\tau, \tau'; t)], \tag{III.24}$$

$$\begin{aligned} C_\kappa(t) &= B_\kappa(t) \\ &= \tfrac{1}{8} i \omega_\kappa \exp\left(-i \Delta E_\kappa \frac{t}{\hbar}\right) \sum_\mu \left\{ \omega_\mu \int_0^\tau d\tau \int_0^{\tau'} d\tau' [\bar{B}^\mu(\tau, \tau'; t) - \bar{B}^\mu(\tau, -\tau'; t) + \bar{B}^\mu(-\tau, -\tau'; t) - \bar{B}^\mu(-\tau, \tau'; t)] \right\}, \end{aligned} \tag{III.25}$$

$$\begin{aligned} D_\kappa(t) = -\tfrac{1}{4} \exp\left(-i \frac{\Delta E_\kappa}{\hbar} t\right) \sum_\mu \sum_{\mu'} \Big\{ \omega_\mu \omega_{\mu'} \int_0^\infty d\tau \int_0^\infty d\tau' \\ \times [\bar{D}^{\mu\mu'}(\tau, \tau'; t) - \bar{D}^{\mu\mu'}(\tau, -\tau'; t) + \bar{D}^{\mu\mu'}(-\tau, -\tau'; t) - \bar{D}^{\mu\mu'}(-\tau, \tau'; t)] \Big\}, \end{aligned} \tag{III.26}$$

where

$$\Delta E_\kappa = \Delta E_{sl} - \hbar \omega_\kappa, \tag{III.27}$$

$$\bar{A}(\tau, \tau'; t) = \exp[-iE(\tau + \tau')] K(\tau, \tau'; t), \tag{III.28}$$

$$\bar{B}^\mu(\tau, \tau'; t) = (2i/\sqrt{2}) \exp[-iE(\tau + \tau')] \tau \gamma_\mu (\lambda_\mu + (i \gamma_\mu \tau'/\sqrt{2})) \exp(i \omega_\mu t) K(\tau, \tau'; t), \tag{III.29}$$

$$\bar{D}^{\mu\mu'}(\tau, \tau'; t) = 2 \exp[-iE(\tau + \tau')] \tau \gamma_\mu \tau' \gamma_{\mu'} \exp[i(\omega_\mu + \omega_{\mu'}) t] (\lambda_\mu + (i \gamma_\mu \tau/\sqrt{2})) (\lambda_{\mu'} + (i \gamma_{\mu'} \tau'/\sqrt{2})) K(\tau, \tau'; t), \tag{III.30}$$

and

$$K(\tau, \tau'; t) = \exp\left(\sum_\mu \{\tfrac{1}{2} \Delta_\mu^2 [\exp(i \omega_\mu t) - 1] - (\gamma_\mu^2/4)(\tau^2 + \tau'^2) - (i \gamma_\mu \lambda_\mu^*/\sqrt{2})(\tau + \tau') - [\gamma_\mu^2 \exp(i \omega_\mu t)/2] \tau \tau'\}\right). \tag{III.31}$$

In these equations $E = \Delta E_{s,l} - E_M$, where $E_M = \tfrac{1}{2} \sum_\mu \hbar \omega_\mu \Delta_\mu^2$; and $\lambda_\mu = (\Delta_\mu/\sqrt{2})[1 - \exp(-i \omega_\mu t)]$.

Equations (III.21), (III.22), and (III.24)–(III.31) summarize our result for the generating function $L(t)$.

IV. NONRADIATIVE DECAY RATE IN THE NON-CONDON CASE

We now turn to the task of transforming the generating function into an expression for the nonradiative decay rate:

$$\begin{aligned} W_{si} &= \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt L(t) \\ &= \sum_\kappa |\langle s | U_\kappa | l \rangle|^2 \int_{-\infty}^{\infty} L^\kappa(t) dt. \end{aligned} \tag{IV.1}$$

Our aim is thus to perform the integration over the t variable. This may be accomplished by utilizing the steepest descent method.[8,9] As we are interested here only in rough estimates, we shall apply a simpler scheme, assuming that we may replace all the molecular frequencies by a common average frequency. Invoking this assumption, we may perform the integration over t, using the relation[22]

$$\int_{-\infty}^{\infty} dt \exp\left[-i\Delta E_\kappa \frac{t}{\hbar} + \sum_\mu d_\mu \exp(i\omega_\mu t)\right] \cong \frac{2\pi}{\bar{\omega}} \frac{d^{(\Delta E_\kappa/\hbar\bar{\omega})}}{(\Delta E_\kappa/\hbar\bar{\omega})!}, \tag{IV.2}$$

where

$$d = \sum_\mu d_\mu. \tag{IV.3}$$

With this relation the t integration becomes straightforward, the final result for the nonradiative decay rate of the vibrationless level being

$$W_{s0} = \frac{|\langle s | \partial U/\partial q_\kappa | l \rangle|^2}{2\hbar\bar{\omega}} \exp(-g) \frac{2\pi}{\epsilon^2} \frac{g^{\epsilon_\kappa}}{\epsilon_\kappa!} \eta \tag{IV.4}$$

where

$$g = \tfrac{1}{2} \sum_\mu \Delta_\mu^2 \tag{IV.5a}$$

corresponds to the coupling strength, and

$$\epsilon_\kappa = \Delta E_\kappa/\hbar\bar{\omega} \cong \Delta E/\hbar\bar{\omega} - 1 = \epsilon - 1. \tag{IV.5b}$$

is the effective energy gap, corresponding to the electronic gap modified by the promoting mode.

The resulting expression, Eq. (IV.4), has just the form obtained in the Condon approximation multiplied by a "correction" factor η which is given by

$$\eta = \tfrac{1}{2}\epsilon^2 \int_0^\infty \int_0^\infty dx dx' \{\mathrm{Re}[A(x,x') - A(x,-x')] - 2g\,\mathrm{Im}[B(x,x') - B(x,-x')] - 2\epsilon_\kappa\,\mathrm{Re}[C(x,x') - C(x,-x')]$$
$$+ 2g^2\,\mathrm{Re}[L(x,x') - L(x,-x')] - 2g\,\mathrm{Re}[M(x,x') - M(x,-x')] + 2\epsilon_\kappa(\epsilon_\kappa - 1)\,\mathrm{Re}[N(x,x') - N(x,-x')]\}, \tag{IV.6}$$

where

$$A(x,x') = (F(x)F(x'))^{\epsilon_\kappa} G(x)G(x'), \tag{IV.7a}$$

$$B(x,x') = (F(x)F(x'))^{\epsilon_\kappa} G(x)G(x')x, \tag{IV.7b}$$

$$C(x,x') = (F(x)F(x'))^{\epsilon_\kappa - 1} G(x)G(x')[ix - xx'], \tag{IV.7c}$$

$$L(x,x') = (F(x)F(x'))^{\epsilon_\kappa} G(x)G(x')xx', \tag{IV.7d}$$

$$M(x,x') = (F(x)F(x'))^{\epsilon_\kappa - 1} G(x)G(x')[F(x) + F(x')]xx', \tag{IV.7e}$$

$$N(x,x') = (F(x)F(x'))^{\epsilon_\kappa - 1} G(x)G(x'), \tag{IV.7f}$$

$$F(x) = 1 + ix; \qquad G(x) = \exp(i\epsilon x - \tfrac{1}{2}gx^2). \tag{IV.7g}$$

The first term in Eq. (IV.6) [involving the A terms (IV.7a)] corresponds to A_κ in (III.23), the following two terms in (IV.6) corresponds to $B_\kappa = C_\kappa$ in (III.23), while the last three terms in (IV.6) correspond to the D_κ term in Eq. (III.23). Looking more closely at the origins of these different terms we notice that the A term corresponds to the contribution arising from the $\mathbf{q}$ dependence of the energy denominator alone [the first term in Eq. (III.6)], while the other five terms correspond to contributions in which the $\mathbf{q}$ dependence of the electronic wavefunctions and also the term involving second derivative of the electronic function were taken into account.

We see that the η factor is a sum of double integrals, each of which may be expressed as a product of two simple integrals. Thus η may be easily calculated numerically for various molecular parameters ϵ and g.

V. NUMERICAL CALCULATIONS

So far we have outlined the mathematical procedure for calculating nonradiative decay rates of excited states of a large molecule in the harmonic approximation. In principle we may utilize the procedure outlined herein for the calculation of the decay rate of any single initial vibronic level or of a thermally averaged manifold of vibronic levels. As we have seen, the zero temperature result is complicated enough so that we have limited our numerical calculations to the zero temperature (or the vibrationless initial level) case, further

approximated by taking a single average molecular frequency. We note that if this approximate calculation was our ultimate goal, we could have performed numerical integration of Eq. (III.6) in the $\mathbf{q}$ space taking $\chi_{si}(\mathbf{q})$ to be the ground vibrational state in the s electronic level, and choosing for $\chi_{lj}(\mathbf{q})$ the corresponding (energy conserving) vibrational state in the l electronic manifold. The present theoretical treatment is, of course, much more general.

Consider first the nonradiative decay originating from near resonance coupling in the two electronic levels system. In Table I we display the results of our calculations utilizing the adiabatic basis for the correction factor η for different molecular parameters ϵ and g. To gain some further insight into the nature of this term we decompose it into two contributions $\eta=\eta_A+\eta_B$, where η_A corresponds to the contribution due to the $\mathbf{q}$ dependence of the energy denominator alone, while η_B includes the contributions of the $\mathbf{q}$ dependence of the electronic wavefunctions and the second derivatives of these wavefunctions. These results lead to the following conclusions:

(1) The non-Condon result exceeds the result obtained in the Condon approximation by 2–3 orders of magnitude. This correction factor depends on the electronic energy gap, the molecular frequencies, and the coupling parameter g.

(2) The correction factor η increases with increasing the (frequency normalized) electronic energy gap ϵ approximately as ϵ^2 (note, however, that $\eta=k\epsilon^2$, where $k\neq 1$). It should be noted that this relation is by no means accurate, providing just a reasonable guess. It should also be noted that the correction factor depends on the coupling term g, increasing with increasing g values in the weak coupling limit.

(3) The difference between the Condon and the non-Condon results may not be attributed to the $\mathbf{q}$ dependence of the energy denominator alone as previously asserted.[13,14] We see that the contribution of the factor η_A is smaller than η_B. Thus one cannot get away with incorporating just the nuclear coordinates dependence of the energy gap, but must include the dependence of the adiabatic wavefunctions on these coordinates.

(4) In the previous works by Englman and Jortner[8] and Freed and Jortner[9] on the energy gap law, where the Condon approximation was applied, one gets for this single oscillator model in the weak coupling limit $W_{s0}\propto(1/\epsilon^2)(g^{\epsilon}\kappa/\epsilon_k!)$. For large energy gaps the approximate relation $\eta\propto\epsilon^2$ results in $W_{s0}\propto g^{\epsilon}\kappa/\epsilon_k!$, leading to a simplified version of the energy gap law for nonradiative decay in large molecules. Previous conclusions concerning the deuterium isotope effect do not depend on the form of the coupling matrix elements and will not be modified.

(5) The dependence of the correction factor on the electronic energy gap fit the qualitative suggestion of Sharf and Silbey.[13] However, the approximate relation $\eta=k\epsilon^2$ $(k\neq 1)$ and the dependence of the correction factor on the molecular coupling parameter g contradicts their conclusions.

(6) Previous work on optical selection studies[19] utilized the Condon approximation assuming that the electronic coupling matrix element is independent of the initial vibronic state. Utilizing the theoretical scheme outlined in the present work, one can calculate the changes of this coupling term between different initial vibronic states. Such calculations are rather cumbersome and were not yet attempted by us. However, earlier numerical computations[23] of the correction factor η_A using a simple harmonic model indicate that this non-Condon correction factor does not vary by more than 2% between different initial vibronic levels of the benzene lowest excited singlet state. Therefore our general conclusions concerning the theory of the optical selection problem are not modified.

TABLE I. Non-Condon correction to the nonadiabatic decay rate[a] in the weak coupling limit from the ground vibrational level of an excited electronic state.

ϵ	g	η_A	η_B	η	η/ϵ^2
8	0.25	11.0	78.4	89.4	1.40
8	0.50	11.5	89.1	100.6	1.57
8	1.00	12.7	118.9	131.6	2.06
10	0.25	13.9	129.7	143.6	1.44
10	0.50	14.3	143.4	157.7	1.58
10	1.00	15.4	178.2	193.6	1.94
12	0.50	17.2	211.5	228.7	1.59
12	1.00	18.3	252.0	270.3	1.88
1	0.50	1.2	−0.2	1.0	1.01
2	0.50	4.1	4.1	8.2	2.07
3	0.50	5.2	12.5	17.7	1.96
4	0.50	6.2	20.8	26.9	1.69
5	0.50	7.4	32.8	40.2	1.61
6	0.50	8.8	48.2	57.0	1.58
7	0.50	10.1	67.0	77.1	1.58
8	0.50	11.5	89.1	100.6	1.57
9	0.50	12.9	114.5	127.4	1.58
10	0.50	14.3	143.4	157.7	1.58
11	0.50	15.8	175.7	191.4	1.58
12	0.50	17.2	211.5	228.7	1.59

[a] The low ϵ values are significant only in the following context: (a) Specification of the square of the resonance coupling matrix element. (b) Nonradiative decay rate in a dense medium when the final $|lj\rangle$ states are broadened due to vibrational relaxation.

It is important to emphasize the difference in the magnitude of the adiabatic coupling terms in the near resonance (Table I) and in the off resonance case. In Table II we display numerical results for the relation η between the coupling matrix elements $|V^A_{si,lj}|^2$ calculated for off resonance coupling both in the Condon approximation and for the non-Condon case. Here $|si\rangle$ is taken as before to represent the vibrationless

TABLE II. Non-Condon correction to the square of the off resonance coupling matrix element $|\langle si|V^A|lj\rangle|^2$ between the ground vibrational level of the electronic state s and a lower vibrational level j, of the electronic state l.

ϵ	g	j	η_A	η_B	η	η/ϵ^2
8	0.5	0	1.0	2.5	3.5	0.06
8	0.5	1	1.3	3.6	4.9	0.08
8	0.5	2	1.7	5.3	7.0	0.11
9	0.5	0	1.0	2.6	3.6	0.05
10	0.5	0	1.0	2.7	3.7	0.04
8	0.25	0	1.0	2.4	3.4	0.05
8	1.00	0	1.1	2.6	3.7	0.06

level of the sth electronic state, while $|lj\rangle$ is now a lower vibrational level of the lth electronic manifold (taken to correspond to the ground or to the lower excited vibrational levels). These numerical results demonstrate that in this off resonance case the η correction factor is lower by about 2 orders of magnitude than in the resonance case, (i.e., $\eta\sim$1–10) provided that the adiabatic zero order basis is employed. This result is by no means surprising, being a direct consequence from our previous conclusion that for the resonance case $\eta\propto\epsilon^2$, combined with the observation that the off resonance coupling matrix elements just correspond to a near resonance coupling term calculated for a different electronic energy gap. We may thus conclude that the Condon approximation is not too bad for the calculation of off resonance coupling terms between lower vibrational states corresponding to different electronic configurations, and those off resonance coupling terms will be lower by about 2 orders of magnitude than the corresponding near resonance coupling terms.

A qualitative rationalization of these numerical results can be readily provided by noting that the Condon approximation involves essentially the application of the mean value theorem of integral calculus, taking out from the integral a function $F(q)$ which is assumed to be weakly dependent on nuclear coordinates, $F(\mathbf{q})\cong F(\mathbf{q}_0)$. This approximation will be justified provided that the function $f(q)$ retained in the integral (i.e., the product of the vibrational wavefunctions) is a smooth function of $\mathbf{q}$. However, if $f(\mathbf{q})$ oscillates widely, even small deviations of $F(\mathbf{q})$ from $F(\mathbf{q}_0)$ may appreciably modify the integral $\int F(\mathbf{q})f(\mathbf{q})d\mathbf{q}$.

VI. DISCUSSION

It will be useful to survey, at this point, the nature of the approximations involved in the derivation of the general equations for the nonradiative decay probability. These assumptions involve three different aspects: The approximate description of the electronic adiabatic wavefunctions; the calculation of the matrix elements of the nonadiabatic coupling V_A, and the features of the simplified molecular model. The expansion of the electronic wavefunctions up to the first order in the nondiagonal matrix elements of V_c [Eqs. (II.10) and (II.11)] rests on the following assumptions:

(a) The diagonal matrix elements of the scrambled zero order states $|n\rangle$ are smaller than the energy denominator.

(b) The weak electronic–vibrational coupling limit is considered.

(c) The relevant electronic states s and l are closer in energy relative to their separation from any other electronic state n.

Assumption (b) provides a necessary condition for the validity of assumption (a). It also allows us to use the expansion of the potential Eq. (II.3) up to first order in the nuclear displacements $\mathbf{q}$. Assumption (c) makes it possible to derive the coupling parameters Δ_i from experimental spectroscopic intensity distributions. By invoking this assumption we limit the validity of our theory to a two electronic state system. We should note, however, that assumption (c) provides a restriction on the physical interpretation of the coupling parameters Δ_i; nevertheless, it does not affect the validity of the general mathematical scheme presented herein. A two electronic state model system was conventionally applied in vibronic coupling theory and in previous studies of electronic relaxation[6–9]; however, in real life, the role of the other electronic states n may be of considerable importance. An interesting extension of the present work will involve a further study of these coupling parameters in a multielectronic level system. It should be stressed that our simplified theoretical model does not involve any other auxiliary restrictions concerning the molecular parameters (i.e., the magnitude of the electronic energy gap or the molecular frequencies) besides those mentioned above. In regard to the perturbation scheme employed herein, it is worthwhile noting, at this point, that the expansion (II.10)–(II.11) of the adiabatic wavefunctions employed herein, which rests on the Wigner–Brillouin perturbation expansion is more general than conventional perturbation expansions.

Concerning the evaluation of the matrix element of the nonadiabatic perturbation operator we assume that:

(d) Nondiagonal matrix elements of V_c are retained only to first order.

(e) As we focus attention on the weak coupling limit [see (c)], the contribution from the vicinity of the crossing of the potential surfaces is neglected by taking the principal part of the integrals (see Appendix B).

Concerning the molecular model we invoke the follow-

ing simplifying assumptions:

(f) The adiabatic potential surfaces are harmonic.

(g) The potential surfaces corresponding to the two electronic states are characterized by the same frequency, thus being identical except for a shift of their origins.

The present treatment is limited to the weak coupling limit which is adequate for the study of most cases of electronic relaxation processes in large molecules. The strong coupling limit which may be of considerable interest for the understanding of photochemical rearrangement reactions, may be also handled without invoking the Condon approximation, provided that we limit ourselves to a single oscillator. In cases when first order time dependent perturbation theory is still applicable one can perform numerical integrations in the $\mathbf{q}$ space utilizing the general $\mathbf{q}$ dependence of the electronic wavefunctions and potential surfaces, which was worked out by Kubo and Toyozawa.[3]

To conclude this discussion, we would like to point out that the Condon approximation is useless for quantitative estimates of nonradiative decay probability of a model system which mimic the features of large molecules, leading to results which will be too low by 2–3 orders of magnitude. This conclusion concurs with the recent numerical estimates of Burland and Robinson,[24] who found that the Condon approximation grossly underestimates the nonradiative decay of the $^3B_{1\mu}$ state of the benzene molecule. It should be, however, emphasized that this discrepancy just reflects the failure of the Condon approximation utilizing a proper adiabatic basis set and does not justify, in principle, the use of crude adiabatic functions. Our numerical data for the nonradiative decay in the weak coupling limit, utilizing the adiabatic basis, are within a numerical factor of 1–2 from the result which would be obtained adopting a truncated crude adiabatic basis set for a two level system and invoking the (unjustified) assumption that the adiabatic and the crude adiabatic potential surfaces are identical. Although the complete crude adiabatic basis set is adequate from the formal point of view,[25] one cannot get away with truncating this set and considering just a two electronic level system, as off resonance coupling terms with other electronic states in the crude adiabatic representation are large. As we have seen in the adiabatic case, the relevant off resonance terms are smaller by about one order of magnitude.

Any quantitative estimate of the nonradiative intramolecular decay rates (provided that the adiabatic potential surfaces are available) will have to bypass the Condon approximation. It is comforting to note that previous theoretical conclusions concerning the gross features of radiationless processes, such as the energy gap law and optical selection, which emphasize general relations and correlations rather than numerical estimates of the decay probabilities, are not modified by going beyond the Condon approximation.

APPENDIX A: THE q-DEPENDENCE OF THE ENERGY DENOMINATOR

The Wigner–Brillouin perturbation series for the electronic energy of a given electronic state may be summed using a similar method to that applied in Eq. (II.4) to get up to first order in nondiagonal matrix elements of V_c

$$E_s(\mathbf{q})=\tilde{E}_s(\mathbf{q})+\sum{}'\{|\langle n\mid V_c\mid s\rangle|^2/[E_s(\mathbf{q})-\tilde{E}_n(\mathbf{q})]\}. \tag{A1}$$

Suppose now that the state φ_l is close in energy to φ_s, so that the contribution of other states to $E_s(\mathbf{q})$ is relatively small, whereupon

$$E_s(\mathbf{q})=\tilde{E}_s(\mathbf{q})+|\langle l\mid V_c\mid s\rangle|^2/[E_s(\mathbf{q})-\tilde{E}_l(\mathbf{q})]. \tag{A2}$$

This is a second order equation for $E_s(\mathbf{q})$ whose solutions are

$$E_s(\mathbf{q})=\tfrac{1}{2}[\tilde{E}_s(\mathbf{q})+\tilde{E}_l(\mathbf{q})]\pm[\{\tfrac{1}{2}[\tilde{E}_s(\mathbf{q})-\tilde{E}_l(\mathbf{q})]\}^2+|\langle l\mid V_c\mid s\rangle|^2]^{1/2}. \tag{A3}$$

The second small (nondiagonal) term in the square root will be neglected. If φ_s is higher in energy than φ_l, the exact energy $E_s(\mathbf{q})$ will be higher than the zero order energy $\tilde{E}_s(\mathbf{q})$ so that we must choose the plus sign in Eq. (A3).[26] We get

$$E_s(\mathbf{q})-\tilde{E}_l(\mathbf{q})\simeq\tilde{E}_s(\mathbf{q})-\tilde{E}_l(\mathbf{q}). \tag{A4}$$

To calculate the vector

$$\boldsymbol{\gamma}^n=\langle n\mid(\partial U/\partial\mathbf{q})_0\mid n\rangle \tag{A5}$$

which is defined in terms of the elements $\gamma_\mu{}^n=\langle n\mid(\partial U/\partial q_\mu)_0\mid n\rangle$; $\mu=1\cdots N$, we make use of the relation

$$\begin{aligned}\langle n\mid(\partial U/\partial\mathbf{q})_0\mid n\rangle&=\langle\varphi_n(\mathbf{r},\mathbf{q})\mid\partial U(\mathbf{r},\mathbf{q})/\partial\mathbf{q}\mid\varphi_n(\mathbf{r},\mathbf{q})\rangle|_{q=0}\\&=\partial E_n(\mathbf{q})/\partial\mathbf{q}|_{q=0}\end{aligned} \tag{A6}$$

which is just the Hellmann–Feynman theorem applied to our case, and

$$E_n(\mathbf{q}) = E_n^0 - \tfrac{1}{2}\sum_\mu \hbar\omega_\mu(\Delta_\mu^n)^2 + \tfrac{1}{2}\sum_\mu \hbar\omega_\mu(q_\mu+\Delta_\mu^n)^2, \tag{A7}$$

where, as in the text, $\mathbf{q}$ and $\mathbf{\Delta}^n$ are measured from the equilibrium configuration of the state, s, and $E_n^0 = E_n(q=0)$. This yields

$$\tilde{E}_n(\mathbf{q}) = E_n^0 + \langle n \mid V_c \mid n\rangle = E_n^0 + [\partial E_n(\mathbf{q})/\partial \mathbf{q}]\,|_{q=0}\cdot\mathbf{q} = E_n^0 + \boldsymbol{\gamma}\cdot\mathbf{q} = E_n^0 + \sum_\mu \hbar\omega_\mu\Delta_\mu^n q_\mu \tag{A8}$$

so that for our molecular model

$$\begin{aligned}\tilde{E}_n(q) - \tilde{E}_m(\mathbf{q}) &= E_n^0 - E_m^0 + \sum_\mu \hbar\omega_\mu q_\mu(\Delta_\mu^n - \Delta_\mu^m)\\ &= E_n(\mathbf{q}) - E_m(\mathbf{q})\end{aligned} \tag{A9}$$

for any two electronic states, m and n.

Utilizing now Eq. (A4) we obtain

$$E_s(\mathbf{q}) - \tilde{E}_l(\mathbf{q}) \simeq \tilde{E}_s(\mathbf{q}) - \tilde{E}_l(\mathbf{q}) = E_s(\mathbf{q}) - E_l(\mathbf{q}) \tag{A10}$$

for the two relevant electronic states, s and l; moreover, the same remains true even if l is replaced by any other electronic state n:

$$\begin{aligned}E_s(\mathbf{q}) - \tilde{E}_n(\mathbf{q}) &= E_s(\mathbf{q}) - \tilde{E}_l(\mathbf{q}) + \tilde{E}_l(\mathbf{q}) - \tilde{E}_n(\mathbf{q}) \simeq E_s(\mathbf{q}) - E_l(\mathbf{q}) + E_l(\mathbf{q}) - E_n(\mathbf{q})\\ &= E_s(\mathbf{q}) - E_n(\mathbf{q})\end{aligned} \tag{A11}$$

which is what we wanted to assert.

APPENDIX B: OPERATOR AND COMMUTATION RELATIONS FOR THE EVALUATION OF THE GENERATING FUNCTION

Here we present the fundamental relations required for the evaluation of the matrix elements which appear in Eq. (III.24) for the generating function. First, we note that we have to perform integration in the $\mathbf{q}$ space, where the integrand contains terms of the form $\xi(\mathbf{q}) = (E - \sum_\mu \gamma_\mu q_\mu)^{-1}$. These terms diverge at many points in the $\mathbf{q}$ space, but as the integrand changes sign by passing through such a divergence point, it is reasonable to take the principal part of the integral as the relevant result. Bearing in mind that these divergence points correspond to the crossing of the electronic potential surfaces, we may conclude that in the weak coupling limit (which we have introduced already in Sec. II) the contributions from the crossing zone are negligible, so that the manner in which the integration is performed there is not in any way important.

We thus interpret $\xi(\mathbf{q})$ as $P[1/(E - \sum_\mu \gamma_\mu q_\mu)]$, where P denotes principal part. Now we utilize the following relations (for $\delta \to 0+$):

$$(b - i\delta)^{-1} = i\int_0^\infty \exp(-ibr)\,dr, \tag{B1}$$

$$Pb^{-1} = \mathrm{Re}(b - i\delta)^{-1} = \tfrac{1}{2}i\int_0^\infty (\exp(-ibr) - \exp(ibr))\,dr \tag{B2}$$

so that

$$\xi(\mathbf{q}) = P(E - \sum_\mu \gamma_\mu q_\mu)^{-1} = \tfrac{1}{2}i\int_0^\infty d\tau[G(\tau) - G(-\tau)] \tag{B3}$$

and also

$$[p_\mu^2, \xi(\mathbf{q})] = \tfrac{1}{2}i\int_0^\infty (F_\mu(\tau) - F_\mu(-\tau))\,d\tau, \tag{B4}$$

where

$$G(\tau) = \exp(-iE\tau + i\sum_\mu \gamma_\mu q_\mu \tau), \tag{B5}$$

$$F_\mu(\tau) = [p_\mu^2, G(\tau)] = \exp(-iE\tau)[p_\mu^2, \exp(i\gamma_\mu q_\mu \tau)]\exp(i\sum_{\mu'\neq\mu}\gamma_{\mu'}q_{\mu'}\tau). \tag{B6}$$

The matrix elements in Eqs. (III.24) are now most easily evaluated by making use of the creation and annihilation operator representation for the harmonic oscillator coordinates, in terms of which

$$q_\mu = (1/\sqrt{2})\,(a_\mu^\dagger + a_\mu),$$
$$p_\mu = (i/\sqrt{2})\,(a_\mu^\dagger - a_\mu), \tag{B7}$$

and by utilizing the relation (see Appendix C)

$$[p_\mu^2, \exp(i\gamma_\mu q_\mu \tau)] = (2i\gamma_\mu\tau/\sqrt{2})\,\exp(-\tfrac{1}{4}\gamma_\mu^2\tau^2)\,\exp[(i\gamma_\mu\tau/\sqrt{2})a_\mu^\dagger](a_\mu^\dagger - a_\mu)\,\exp[(i\gamma_\mu\tau/\sqrt{2})a_\mu]. \tag{B8}$$

We shall also make use of the following form of the vibrational Hamiltonian and wavefunctions:

$$\chi_{si} = \prod_\mu (v_{s\mu}!)^{-1/2}(a_\mu^\dagger)^{v_{s\mu}} \mid 0\rangle, \tag{B9}$$

$$H_{\mathrm{BO}}{}^s = \sum_{\mu=1}^{N}\left(-\tfrac{1}{2}\hbar\omega_\mu \frac{\partial^2}{\partial q_\mu{}^2} + \tfrac{1}{2}\hbar\omega_\mu q_\mu{}^2\right) = \sum_{\mu=1}^{N} h_\mu, \tag{B10}$$

$$H_{\mathrm{BO}}{}^l = \sum_{\mu=1}^{N}\left(-\tfrac{1}{2}\hbar\omega_\mu \frac{\partial^2}{\partial q_\mu{}^2} + \tfrac{1}{2}\hbar\omega_\mu (q_\mu+\Delta_\mu)^2\right) - \Delta E_{sl} = H_{\mathrm{BO}}{}^s - E + \sum_\mu \gamma_\mu q_\mu. \tag{B11}$$

Utilizing Feynman's techniques[18] it can be demonstrated[27] that

$$\exp[-ih_\mu(t/\hbar)]\exp[ih_\mu(t/\hbar)+i\gamma_\mu q_\mu(t/\hbar)] = \exp\{-\tfrac{1}{2}(it)\omega_\mu\Delta_\mu{}^2 + \tfrac{1}{2}\Delta_\mu{}^2[\exp(i\omega_\mu t)-1]\}\,\exp(\lambda_\mu a_\mu^\dagger)\,\exp(-\lambda_\mu{}^* a_\mu), \tag{B12}$$

where

$$\lambda_\mu = (\Delta_\mu/\sqrt{2})[1-\exp(-i\omega_\mu t)]. \tag{B13}$$

The following operator relations will also be required:

$$\exp(\alpha a)\mid 0\rangle = \mid 0\rangle,$$
$$\langle 0 \mid \exp(\alpha a^\dagger) = \langle 0 \mid, \tag{B14}$$
$$\exp(-\alpha a^\dagger)\,a^n\,\exp(\alpha a^\dagger) = (a+\alpha)^n,$$
$$\exp(-\alpha a)\,(a^\dagger)^n\,\exp(\alpha a) = (a^\dagger-\alpha)^n, \tag{B15}$$
$$\exp(-\alpha a^\dagger)\,\exp(a)\,\exp(\alpha a^\dagger) = \exp(a+\alpha),$$
$$\exp(-\alpha a)\,\exp(a^\dagger)\,\exp(\alpha a) = \exp(a^\dagger-\alpha), \tag{B16}$$
$$\exp(\hat{A}+\hat{B}) = \exp(\hat{A})\,\exp(\hat{B})\,\exp(-\tfrac{1}{2}[A,B]) \tag{B17}$$

for

$$[A,[A,B]] = [B,[A,B]] = 0.$$

Using these relations we may evaluate the desired matrix elements for any given vibrational state of the molecule. We may also get a thermal averaged result using the relation

$$\langle \exp(\hat{A})\rangle_T = \exp[\tfrac{1}{2}\langle \hat{A}^2\rangle_T], \tag{B18}$$

where $\hat{A}$ is an operator which is a linear combination of the coordinate and momentum operators of a harmonic oscillator, and $\langle\ \rangle_T$ denotes the thermal (Boltzmann) average.

APPENDIX C: PROOF OF THE RELATION (B8)

Into the commutator $[p^2, \exp(\alpha q)] \equiv R$ we insert [Eq. (B7)]

$$p = (i/\sqrt{2})\,(a^\dagger - a), \qquad q = (1/\sqrt{2})\,(a^\dagger + a),$$

to get

$$R = -\tfrac{1}{2}[\boldsymbol{((a^\dagger)^2 + a^2 - 2aa^\dagger)}, \exp\boldsymbol{((\alpha/\sqrt{2})\,(a^\dagger+a))}]. \tag{C1}$$

Utilizing Eq. (B16) we get

$$R = -\tfrac{1}{2}\exp(\tfrac{1}{4}\alpha^2)\{\boldsymbol{((a^\dagger)^2 + a^2 - 2aa^\dagger)}, \exp[(\alpha/\sqrt{2})a^\dagger]\exp[(\alpha/\sqrt{2})a]\}$$
$$= -\tfrac{1}{2}\exp(\tfrac{1}{4}\alpha^2)\,(R_1 + R_2 - 2R_3), \tag{C2}$$

where

$$R_1=[(a^\dagger)^2,\ \exp((\alpha/\sqrt{2})a^\dagger)\exp((\alpha/\sqrt{2})a)], \tag{C3}$$

$$R_2=[a^2,\ \exp((\alpha/\sqrt{2})a^\dagger)\exp((\alpha/\sqrt{2})a)], \tag{C4}$$

$$R_3=[aa^\dagger,\ \exp((\alpha/\sqrt{2})a^\dagger)\exp((\alpha/\sqrt{2})a)]. \tag{C5}$$

Making use of Eq. (B14) we obtain for these commutation relations the following results

$$R_1=\exp[(\alpha/\sqrt{2})a^\dagger]\exp[(\alpha/\sqrt{2})a][-(2/\sqrt{2})\alpha a^\dagger+\tfrac{1}{2}\alpha^2], \tag{C6}$$

$$R_2=\exp[(\alpha/\sqrt{2})a^\dagger]\exp[(\alpha/\sqrt{2})a][(2/\sqrt{2})\alpha a+\tfrac{1}{2}\alpha^2], \tag{C7}$$

$$R_3=\exp[(\alpha/\sqrt{2})a^\dagger]\exp[(\alpha/\sqrt{2})a][(\alpha/\sqrt{2})a^\dagger-(\alpha/\sqrt{2})a-\tfrac{1}{2}\alpha^2]. \tag{C8}$$

Inserting these equations into Eq. (C2) we obtain the final results (B8).

APPENDIX D: CALCULATIONS OF THE MATRIX ELEMENTS (III.24)

We shall present herein in detail the evaluation of the term $A_\kappa(t)$ Eq. (III.24a). The evaluation of the terms $B_\kappa(t)$, $C_\kappa(t)$ and $D_\kappa(t)$ Eqs. (III.24b)–(III.24d) is very much the same.

Into Eq. (III.24a) for $A_\kappa(t)$ we insert the expressions (B9) and (B10) for $H_{\mathrm{BO}}{}^s$ and $H_{\mathrm{BO}}{}^l$. Bearing in mind that $\xi(\mathbf{q})$ does not contain q_κ we may separate out the integral related to this promoting mode, obtaining

$$A_\kappa(t)=\omega_\kappa{}^2(x_{s\kappa}\mid p_\kappa\exp[ih_\kappa(t/\hbar)]p_\kappa\exp[-ih_\kappa(t/\hbar)]\mid x_{s\kappa})A_\kappa{}'(t), \tag{D1}$$

where

$$A_\kappa{}'(t)=(\chi_{si}{}'\mid\xi(\mathbf{q})\exp[iH_{\mathrm{BO}}{}^{l'}(t/\hbar)]\xi(\mathbf{q})\exp[-iH_{\mathrm{BO}}{}^{s'}(t/\hbar)]\mid\chi_{si}{}') \tag{D2}$$

in which the prime denotes exclusion of the κ mode, i.e.,

$$\chi_{si}{}'=\prod_{\mu\neq\kappa}x_{s\mu}(q_\mu)$$

$$H_{\mathrm{BO}}{}^{s'}=\sum_{\mu\neq\kappa}h_\mu,\qquad H_{\mathrm{BO}}{}^{l'}=H_{\mathrm{BO}}{}^{s'}-E+\sum_\mu\gamma_\mu q_\mu. \tag{D3}$$

Utilizing Eqs. (B3) and (B5) we may rewrite Eq. (D2) in the form

$$A_\kappa{}'(t)=(\tfrac{1}{2}i)^2\int_0^\infty d\tau\int_0^\infty d\tau'[A'(\tau,\tau';t)+A'(-\tau,-\tau';t)-A'(\tau,-\tau';t)-A'(-\tau,\tau';t)], \tag{D4}$$

where

$$A'(\tau,\tau';t)=(\chi_{si}{}'\mid\exp(i\sum_{\mu\neq\kappa}\gamma_\mu q_\mu\tau')\exp(iH_{\mathrm{BO}}{}^{l'}(t/\hbar))\exp(i\sum_{\mu\neq\kappa}\gamma_\mu q_\mu\tau)\exp(-iH_{\mathrm{BO}}{}^{s'}(t/\hbar))\mid\chi_{si}{}')\exp(-iE(\tau+\tau'))$$

$$=\exp[-iE(\tau+\tau'+(t/\hbar))]\prod_{\mu\neq\kappa}s_\mu \tag{D5}$$

with

$$s_\mu=(x_{s\mu}\mid\exp(i\gamma_\mu q_\mu\tau')\exp(ih_\mu(t/\hbar)+i\gamma_\mu q_\mu(t/\hbar))\exp(i\gamma_\mu q_\mu\tau)\exp(-ih_\mu(t/\hbar))\mid x_{s\mu})$$

$$=(x_{s\mu}\mid\exp(-ih_\mu(t/\hbar))\exp(i\gamma_\mu q_\mu\tau')\exp(ih_\mu(t/\hbar))\exp(-ih_\mu(t/\hbar))\exp(ih_\mu(t/\hbar)+i\gamma_\mu q_\mu(t/\hbar))\exp(i\gamma_\mu q_\mu\tau)\mid x_{s\mu}). \tag{D6}$$

Utilizing Eq. (B12) and also the transformation relation

$$\exp(-ih_\mu(t/\hbar))q_\mu\exp(ih_\mu(t/\hbar))=q_\mu(t)=\sqrt{2}^{-1}[a_\mu\exp(i\omega_\mu t)+a_\mu{}^\dagger\exp(-i\omega_\mu t)] \tag{D7}$$

we get

$$S_\mu=\exp\{-\tfrac{1}{2}(it)\omega_\mu\Delta_\mu{}^2+\tfrac{1}{2}\Delta_\mu{}^2[\exp(i\omega_\mu t)-1]\}$$

$$\times(x_{s\mu}\mid\exp\{(i\gamma_\mu\tau'/\sqrt{2})[a_\mu\exp(i\omega_\mu t)+a_\mu{}^\dagger\exp(-i\omega_\mu t)]\}\exp(\lambda_\mu a_\mu{}^\dagger)\exp(-\lambda_\mu{}^*a_\mu)\exp[(i\gamma_\mu\tau/\sqrt{2})(a_\mu{}^\dagger+a_\mu)]\mid x_{s\mu}) \tag{D8}$$

where

$$\mid x_{s\mu})=(v_{s\mu}!)^{-1/2}(a_\mu{}^\dagger)^{v_{s\mu}}\mid 0\rangle. \tag{D9}$$

For the simplest case where $v_{s\mu}=0$, we get, applying Eqs. (B14)–(B17) in a straightforward manner,

$$s_\mu=\exp\{-\tfrac{1}{2}(it)\omega_\mu\Delta_\mu^2+\tfrac{1}{2}\Delta_\mu^2[\exp(i\omega_\mu t-1)]-\tfrac{1}{4}\gamma_\mu^2(\tau^2+\tau'^2)-(i\gamma_\mu\lambda_\mu^*/\sqrt{2})(\tau+\tau')-\tfrac{1}{2}[\gamma_\mu^2\exp(i\omega_\mu t)]\tau\tau'\}. \quad \text{(D10)}$$

We still have to evaluate the integral over q_κ in Eq. (D1). This is

$$\begin{aligned} I_\kappa&=(x_{s\kappa}\mid\exp(-ih_\kappa(t/\hbar))p_\kappa\exp(ih_\kappa(t/\hbar))p_\kappa\mid x_{s\kappa})\\ &=-\tfrac{1}{2}(x_{s\kappa}\mid[a_\kappa^\dagger\exp(-i\omega_\kappa t)-a_\kappa\exp(i\omega_\kappa t)](a_\kappa^\dagger-a_\kappa)\mid x_{s\kappa}) \end{aligned} \quad \text{(D11)}$$

which, for the zero vibrational level, takes the form

$$I_\kappa=\tfrac{1}{2}\exp(i\omega_\kappa t). \quad \text{(D12)}$$

Utilizing now Eqs. (D1), (D4), (D5), (D10), and (D12), and redefining some functions as in Eqs. (III.29) and (III.32), we obtain after some elementary algebra Eq. (III.24) for $A_\kappa(t)$. The expressions (III.25) and (III.26) for $B_\kappa(t)=C_\kappa(t)$ and $D_\kappa(t)$ are obtained in a similar manner.

Evaluating similar expressions for a general vibrational state is also straightforward though somewhat more cumbersome. We may also derive the thermal averaged analog of $A_\kappa(t)$. To exhibit this possibility we apply Eq. (B16) to rewrite Eq. (D8) for s_μ in the form

$$\begin{aligned} s_\mu=\exp\{&-\tfrac{1}{2}(it)\omega_\mu\Delta_\mu^2+\tfrac{1}{2}\Delta_\mu^2[\exp(i\omega_\mu t)-1]\}\\ &\times\exp\{\tfrac{1}{2}\mid\lambda_\mu\mid^2-i(\gamma_\mu/2\sqrt{2})(\lambda_\mu+\lambda_\mu^*)(\tau+\tau')+\tfrac{1}{4}\gamma_\mu^2[\exp(-i\omega_\mu t)-\exp(i\omega_\mu t)\tau\tau']\}s_\mu'', \end{aligned} \quad \text{(D13)}$$

where

$$s_\mu''=(x_{s\mu}\mid\exp(y_\mu a_\mu-y_\mu^* a_\mu^\dagger)\mid x_{s\mu}) \quad \text{(D14)}$$

and

$$y_\mu=(i\gamma_\mu\tau'/\sqrt{2})\exp(i\omega_\mu t)+(i\gamma_\mu\tau/\sqrt{2})-\lambda_\mu^*. \quad \text{(D15)}$$

Replacing the matrix element s_μ'' by its thermal average and utilizing (B17), we get

$$\langle s_\mu''\rangle_T=\exp\{-\mid y_\mu\mid^2(\langle v_\mu\rangle_T+\tfrac{1}{2})\}. \quad \text{(D16)}$$

We also need the thermally averaged analog of I_κ, Eq. (D11). This is

$$\langle I_\kappa\rangle_T=\tfrac{1}{2}[(\langle v_\kappa\rangle_T+1)\exp(i\omega_\kappa t)+\langle v_\kappa\rangle_T\exp(-i\omega_\kappa t)]. \quad \text{(D17)}$$

Equations (D17), (D16), and (D13) may now be applied for obtaining the thermally averaged equivalents of Eq. (III.25).

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