Optical Selection Studies of Radiationless Decay in an Isolated Large Molecule. II. Role of Frequency Changes

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In this paper we provide an extension of the theoretical study of nonradiative decay of a single vibronic level of a large molecule. We have derived theoretical expressions for the dependence of the electronic relaxation rate on the excess vibrational energy in the excited electronic state of a "harmonic molecule" which is characterized by displaced and frequency modified potential surfaces. The simple case of displaced potential surfaces was handled by relating the potential surfaces via a simple displacement operator. To handle frequency changes in optical selection we have applied Feynman's operator techniques to disentangle exponential operators which involve nonlinear terms. The role of frequency changes in optical selection experiments was elucidated.

I. INTRODUCTION

Radiationless transitions from a single initial vibronic level of an isolated[1] molecule have been of considerable current experimental and theoretical interest.[2–6] Recent work[7–9] has applied the formalism of multiphonon processes in solids,[10,11] utilizing Kubo's generating function method,[10c] for the calculation of the radiationless decay of a Boltzmann-averaged manifold of initial states, assuming rapid vibrational relaxation relative to the electronic relaxation rate. This scheme also handles the decay of the vibrationless level of an isolated molecule, which corresponds to the zero temperature case.[8,9] The treatment of the decay of a single initial vibronic level[12] is straightforward in principle, but is so tedious that serious approximations were introduced by several workers[2–4] in order to get manageable results. In a recent work[5] we applied Feynman's operator calculus[11,13] to derive a general expression for the radiationless decay rate of a single initial vibronic level in a large molecule. This theory of optical selection rests on the following simplifying assumptions:

(a) A two electronic state system is applicable.
(b) The molecular vibrations are harmonic.
(c) The decay of each vibronic level $|si\rangle$ corresponds to the statistical limit.
(d) The quasicontinuous manifold $|lj\rangle$ does not carry oscillator strength from the ground electronic state $|00\rangle$.[14]
(e) Interference effect between resonances which result from a second order coupling between different zero order vibronic levels $|si\rangle$, caused by their interaction with the same quasicontinuum, may be neglected.
(f) The normal modes are identical in the two electronic states.
(g) The frequencies are identical in the two electronic states, so that a given vibrational mode is just displaced between the two electronic states.

Conditions (a), (c), (d) and (e) are frequently encountered in a real life situation. The harmonic approximation (b) is serious, and may lead to an underestimate of the nonradiative decay probability. Restrictions (f) and (g) correspond to the expansion of the change in the potential surfaces $\Delta E(Q)=E_s(Q)-E_l(Q)$ between the two electronic states up to first order in nuclear displacements.

In this work we have extended the operator calculus technique so that we have been able to derive a general theoretical expression for the decay of a single vibronic state in a two electronic level system, which involves frequency changes. Cross second order terms in $\Delta E(Q)$ are still neglected [Restriction (f)]. We have developed a scheme in which we can evaluate in principle the nonradiative transition rate to any order in the relative frequency changes. The first order expressions have been worked out in a closed form which can be used for numerical computations.

In Sec. II of this work we derive the results for a constant frequency model by an alternative and more transparent method. This simple physical situation involves just linear terms in nuclear displacement, and we shall show that in this case Feynman's operator calculus is not required. When quadratic terms are involved, we cannot get away with the simple technique of Sec. II. In Sec. III we demonstrate the application of Feynman's operator method to the nonlinear case and these results are applied in Sec. IV for the problem of optical selection in a system of displaced potential surfaces characterised by different frequencies. In what follows we shall adopt the notation introduced in Paper I.

Glossary of Symbols

s	Initial electronic state
l	Final electronic state
$\|si\rangle$, $\|lj\rangle$	Vibronic levels
$\|00\rangle$	Ground state
W_{si}	Nonradiative decay rate of the level $\|si\rangle$

$L(t)$	The generating function [Eq. (2.2)]
$L^{\kappa}(t)$	The κ mode contribution of the generating function [Eq. (4.2)]
H_s, H_l	Nuclear Hamiltonians for the s and l electronic states
Q_μ	The μth normal coordinate
q_μ	Dimensionless normal coordinate
$V_{sl}(Q)$	Perturbation operator in the nuclear space [Eq. (2.3)]
C_{sl}^{κ}	Electronic matrix element (for a definition see Ref. 9)
P	Number of promoting modes
μ	General mode index
κ	Promoting mode index
ω_μ	Frequency of the mode μ
M_μ	Mass of the mode μ
Δ_μ	Relative (dimensionless) displacement of the origin of the μ the mode between the two potential surfaces
$X_{s\mu}$	Single mode vibrational function (for the mode μ in the electronic state s)
$v_{s\mu}$	Population of the mode μ in the electronic state s
$\langle v_\mu \rangle_T$	Averaged (thermal) population of the mode μ [Eq. (2.25)]
h_s^{μ}	Hamiltonian of the mode μ in the electronic state s
p_μ	Momentum (dimensionless) of the mode μ
$a_\mu^{\dagger}$, a_μ	Creation and annihilation operators for the mode μ
ΔE	Electronic energy gap $(E_s - E_l)$
η_μ	Frequency change
ξ_μ	Relative frequency change [Eq. (4.9)]
$d(v_1, v_2)$	Promoting mode matrix element [Eq. (2.6)]

II. RADIATIONLESS TRANSITIONS FROM A SINGLE VIBRONIC LEVEL IN THE CONSTANT FREQUENCY MODEL

In this section we shall provide an alternative derivation of the nonradiative decay rate of a single vibronic level in a two-electronic-level system characterized by displaced identical potential surfaces. For this physical situation the two potential surfaces can be related by a simple displacement operator. Our starting point is the expression for the nonradiative transition probability:

$$W_{si} = \frac{1}{\hbar^2}\int_{-\infty}^{\infty} L(t)\,dt, \tag{2.1}$$

where $L(t)$ is the generating function,

$$L(t) = \langle i \mid V_{sl}(\mathbf{Q}) \exp[iH_l(t/\hbar)] V_{sl}^{\dagger}(\mathbf{Q}) \times \exp[-iH_s(t/\hbar)] \mid i\rangle. \tag{2.2}$$

Using the explicit form for the perturbation matrix

$$V_{sl}(\mathbf{Q}) = \sum_{\kappa=1}^{P} C_{sl}^{\kappa}\left(\frac{i\hbar}{M_\kappa^{1/2}}\right)\frac{\partial}{\partial Q_\kappa} \equiv \sum_{\kappa=1}^{P} V_{sl}^{\kappa}, \tag{2.3}$$

we get

$$L(t) = \sum_{\kappa=1}^{P} \langle i \mid V_{sl}^{\kappa} \exp\left(iH_l\frac{t}{\hbar}\right)(V_{sl}^{\kappa})^{\dagger} \exp\left(-iH_s\frac{t}{\hbar}\right) \mid i\rangle + \sum_{\substack{\kappa=1 \\ \kappa\neq\kappa'}}^{P}\sum_{\kappa'=1}^{P} \langle i \mid V_{sl}^{\kappa} \exp\left(iH_l\frac{t}{\hbar}\right)(V_{sl}^{\kappa'})^{\dagger} \exp\left(-iH_s\frac{t}{\hbar}\right) \mid i\rangle. \tag{2.4}$$

The second term may be neglected if $\Delta_\kappa = 0$ for every promoting mode,[5] whereupon

$$L(t) = \exp\left(-i\Delta E\frac{t}{\hbar}\right)\sum_{\kappa=1}^{P} J_\kappa(t) \prod_{\mu\neq\kappa} g_\mu(t), \tag{2.5}$$

where

$$J_\kappa(t) = \langle X_{s\kappa}(Q_\kappa, v_{s\kappa}) \mid V_{sl}^{\kappa} \exp[ih_s^{\kappa}(t/\hbar)] V_{sl}^{\kappa\dagger} \exp[-ih_s^{\kappa}(t/\hbar)] \mid X_{s\kappa}(Q_\kappa, v_{s\kappa})\rangle$$
$$= \mid d(v_{s\kappa}, v_{s\kappa}+1)\mid^2 \exp(i\omega_\kappa t) + \mid d(v_{s\kappa}, v_{s\kappa}-1)\mid^2 \exp(-i\omega_\kappa t), \tag{2.6a}$$

$$\mid d(v_{s\kappa}, v_{s\kappa}+1)\mid^2 = \tfrac{1}{4}\mid C_{sl}^{\kappa}\mid^2 \hbar\omega_\kappa (v_{s\kappa}+1), \tag{2.6b}$$

$$\mid d(v_{s\kappa}, v_{s\kappa}-1)\mid^2 = \tfrac{1}{4}\mid C_{sl}^{\kappa}\mid^2 \hbar\omega_\kappa v_{s\kappa}, \tag{2.6c}$$

and

$$g_\mu(t) = \langle X_{s\mu}(q_\mu, v_{s\mu}) \mid \exp[i(h_s^{\mu} + \hbar\omega_\mu\Delta_\mu q_\mu + \tfrac{1}{2}\hbar\omega_\mu\Delta_\mu^2)(t/\hbar)] \exp[-ih_s^{\mu}(t/\hbar)] \mid X_{s\mu}(q_\mu, v_{s\mu})\rangle. \tag{2.7}$$

We note here that we have changed the definition of $g_\mu(t)$ relative to that in Paper I [Paper I, Eq. (II.28)] so that

$$\prod_{\mu\neq\kappa} g_\mu(t)$$

includes in it the nuclear relaxation energy E_M.

The relevant nuclear Hamiltonians in Eq. (2.17) are

$$h_s^{\mu} = -\tfrac{1}{2}\hbar\omega_\mu(\partial^2/\partial q_\mu^2) + \tfrac{1}{2}\hbar\omega_\mu q_\mu^2, \tag{2.8}$$

$$h_s^{\mu} + \hbar\omega_\mu\Delta_\mu + \tfrac{1}{2}\hbar\omega_\mu\Delta_\mu^2 = \tfrac{1}{2}\hbar\omega_\mu[\partial^2/\partial(q_\mu+\Delta_\mu)^2] + \tfrac{1}{2}\hbar\omega_\mu(q_\mu+\Delta_\mu)^2. \tag{2.9}$$

These Hamiltonians may be related by the simple transformation

$$h_s^{\mu}+\hbar\omega_\mu\Delta_\mu+\tfrac{1}{2}\hbar\omega_\mu\Delta_\mu^2=\exp(ip_\mu\Delta_\mu)\,h_s^{\mu}\exp(-ip_\mu\Delta_\mu), \tag{2.10}$$

in which p_μ is the (dimensionless) momentum conjugate to q_μ. This transformation also holds for any function of h_s^{μ}, so that

$$\begin{aligned} g_\mu(t)&=\langle X_{s\mu}(q_\mu, v_{s\mu}) \mid \exp(ip_\mu\Delta_\mu)\,\exp[ih_s^{\mu}(t/\hbar)]\exp(-ip_\mu\Delta_\mu)\exp[-ih_s^{\mu}(t/\hbar)] \mid X_{s\mu}(q_\mu, v_{s\mu})\rangle \\ &=\langle X_{s\mu}(q_\mu, v_{s\mu}) \mid \exp[i\Delta_\mu p_\mu(0)]\exp[-i\Delta_\mu p_\mu(t)] \mid X_{s\mu}(q_\mu, v_{s\mu})\rangle. \end{aligned} \tag{2.11}$$

Making now the following substitutions:

$$p_\mu(0)=(i/\sqrt{2})\,(a_\mu^{\dagger}-a_\mu), \tag{2.12}$$

$$p_\mu(t)=(i/\sqrt{2})[a_\mu^{\dagger}\exp(i\omega_\mu t)-a_\mu\exp(-i\omega_\mu t)], \tag{2.13}$$

$$\mid X_{s\mu}(q_\mu, v_{s\mu})\rangle=[1/v_{s\mu}!)^{1/2}](a_\mu^{\dagger})^{v_{s\mu}}\mid 0\rangle, \tag{2.14}$$

Eq. (2.11) takes the form

$$g_\mu(t)=(1/v_{s\mu}!)\,\langle 0\mid (a_\mu)^{v_{s\mu}}\exp[-(\Delta_\mu/\sqrt{2})\,(a_\mu^{\dagger}-a_\mu)]\exp\{(\Delta_\mu/\sqrt{2})[a_\mu^{\dagger}\exp(i\omega_\mu t)-a_\mu\exp(-i\omega_\mu t)]\}\,(a_\mu^{\dagger})^{v_{s\mu}}\mid 0\rangle. \tag{2.15}$$

This matrix element may be evaluated by utilizing the following operator relations:

$$\exp(xa^{\dagger}+ya)=\exp(xa^{\dagger})\,\exp(ya)\,\exp(\tfrac{1}{2}xy), \tag{2.16}$$

$$\exp(xa^{\dagger})\,\exp(ya)=\exp(ya)\,\exp(xa^{\dagger})\,\exp(-xy), \tag{2.16'}$$

$$\exp(-xa^{\dagger})\,a^n\exp(xa^{\dagger})=(a+x)^n, \tag{2.16''}$$

$$\exp(-ya)\,(a^{\dagger})^n\exp(ya^{\dagger})=(a^{\dagger}-y)^n. \tag{2.16'''}$$

Using these relations Eq. (2.15) may be recast in the form

$$g_\mu(t)=v_{s\mu}!\sum_{r=0}^{v_{s\mu}}\frac{(-1)^r\mid\lambda_\mu(t)\mid^{2r}}{(v_{s\mu}-r)\,!(r!)^2}\exp\{\tfrac{1}{2}\Delta_\mu^2[\exp(i\omega_\mu t)-1]\}, \tag{2.17}$$

where

$$\lambda_\mu(t)=(\Delta_\mu/\sqrt{2})[1-\exp(-i\omega_\mu t)]. \tag{2.18}$$

Making use of Eqs. (2.1), (2.5), (2.17) and (2.18) we get, after some algebra,

$$\begin{aligned} W_{si}=\frac{1}{\hbar^2}\exp(-\tfrac{1}{2}\sum_\mu\Delta_\mu^2)\int_{-\infty}^{\infty}dt\Bigg\{\Bigg[\sum_\kappa d(v_{s\kappa}, v_{s\kappa}+1)\exp\left(-i(\Delta E-\hbar\omega_\kappa)\frac{t}{\hbar}\right) \\ +\sum_\kappa d(v_{s\kappa}, v_{s\kappa}-1)\exp\left(-i(\Delta E+\hbar\omega_\kappa)\frac{t}{\hbar}\right)\Bigg]\exp[\tfrac{1}{2}\sum_\mu\Delta_\mu^2\exp(i\omega_\mu t)]\prod_{\mu\neq\kappa}v_{s\mu}\sum_{r=0}^{v_{s\mu}}(-\Delta_\mu^2)^r\frac{[1-\cos(\omega_\mu t)]^r}{(v_{s\mu}-r)\,!(r!)^2}\Bigg\}. \end{aligned} \tag{2.19}$$

This result for the decay of a single level was previously derived by us [I, Eq. (II.45)].

The case of rapid vibrational relaxation in a medium may also be handled in a simple manner. In this case we must thermally average the rate W_{si} [Eq. (2.19)]. The thermal average equivalent of Eq. (2.15) is

$$\langle g_\mu(t)\rangle_T=\langle\exp[-(\Delta_\mu/\sqrt{2})\,(a_\mu^{\dagger}-a_\mu)]\exp\{(\Delta_\mu/\sqrt{2})[a_\mu^{\dagger}\exp(i\omega_\mu t)-a_\mu\exp(-i\omega_\mu t)]\}\rangle_T, \tag{2.20}$$

where

$$\langle\hat{A}_\mu\rangle_T=T_r[\exp(-\beta h_\mu)\hat{A}_\mu], \qquad \beta=(k_BT)^{-1}. \tag{2.21}$$

As the operators in the two exponents in Eq. (2.20) commute with their commutator we may rewrite Eq. (2.20) in the form:

$$\langle g_\mu(t)\rangle_T=\exp\{\tfrac{1}{4}\Delta_\mu^2[\exp(i\omega_\mu t)-\exp(-i\omega_\mu t)]\}\,\langle\exp[\lambda_\mu(t)\,a_\mu-\lambda_\mu^*(t)\,a_\mu^{\dagger}]\rangle_T. \tag{2.22}$$

Using now the well known relation[10]

$$\langle\exp(\hat{A})\rangle_T=\exp(\tfrac{1}{2}\langle A^2\rangle_T), \tag{2.23}$$

where A is a linear combination of harmonic oscillator coordinate and momentum, we get

$$\begin{aligned} \langle g_\mu(t)\rangle_T&=\exp\{(\Delta_\mu^2/4)[\exp(i\omega_\mu t)-\exp(-i\omega_\mu t)]\}\,\exp\{\tfrac{1}{2}\langle[\lambda_\mu(t)\,a_\mu-\lambda_\mu^*(t)\,a_\mu^{\dagger}]^2\rangle_T\} \\ &=\exp\{\tfrac{1}{4}\Delta_\mu^2[\exp(i\omega_\mu t)-\exp(-i\omega_\mu t)]\}\,\exp[-\tfrac{1}{2}\mid\lambda_\mu(t)\mid^2(2\langle v_\mu\rangle_T+1)], \end{aligned} \tag{2.24}$$

in which

$$\langle v_\mu\rangle_T=[\exp(\beta\hbar\omega_\mu)-1]^{-1}. \tag{2.25}$$

Utilizing now Eqs. (2.1), (2.5), (2.6), (2.18) and (2.25) we get $[v_{s\kappa}$ in (2.6) is averaged to give $\langle v_\kappa\rangle_T]$:

$$\langle W_s\rangle_T=\sum_\kappa \frac{|C_{sl}|^2\omega_\kappa}{4\hbar}\exp[-\tfrac{1}{2}\sum_\mu \Delta_\mu^2(2\langle v_\mu\rangle_T+1)]\int_{-\infty}^{\infty}dt\left\{\left[[\coth(\tfrac{1}{2}\beta\hbar\omega_\kappa)+1]\exp\left(-i(\Delta E-\hbar\omega_\kappa)\frac{t}{\hbar}\right)\right.\right.$$

$$\left.\left.+[\coth(\tfrac{1}{2}\beta\hbar\omega_\kappa)-1]\exp\left(-i(\Delta E+\hbar\omega_\kappa)\frac{t}{\hbar}\right)\right]\exp[\sum_\mu \tfrac{1}{2}\Delta_\mu^2(\langle v_\mu\rangle_T+1)\ \exp(i\omega_\mu t)+\sum_\mu \tfrac{1}{2}\Delta_\mu^2\langle v_\mu\rangle_T\exp(-i\omega_\mu t)]\right\}.$$

This is the result for the decay rate of a thermally averaged vibronic manifold, and is identical to the expression previously given by Freed and Jortner.[9] Thus we have derived all our previous results in a concise and physically transparent manner.

III. FEYNMAN'S DISENTANGLING PROCEDURE FOR THE NONLINEAR CASE

In Paper I we have utilized Feynman's method to disentangle exponential operator of the form

$$\exp[it(Fa^\dagger a+Ma^\dagger+Na)],$$

where F, M, and N are numerical factors.

We shall now extend the same method to disentangle exponential operators with nonlinear terms:

$$K=\exp(it\{Fa^\dagger a+Ma^\dagger+Na+G[(a^\dagger)^2+a^2]\}), \tag{3.1}$$

where G is another numerical factor.

Feynman's theorem[13] is

$$\mathfrak{T}\exp\left(\int_0^t A(\tau)\,d\tau\right)\exp\left(\int_0^t B(\tau)\,d\tau\right)$$

$$=\exp\left(\int_0^t A(\tau)\,d\tau\right)\mathfrak{T}\exp\left(\int_0^t \tilde{B}(\tau)\,d\tau\right), \tag{3.2}$$

where the operator $A(\tau)$ commutes with $A(\tau')$ for $\tau\neq\tau'$,

$$\tilde{B}(\tau)=\exp\left(-\int_0^\tau A(\tau')\,d\tau'\right)B(\tau)\exp\left(\int_0^\tau A(\tau')\,d\tau'\right), \tag{3.3}$$

and $\mathfrak{T}$ is the time ordering operator defined by Feynman.[13] We now use the following operator relations:

$$\exp(-\mu a^\dagger a)(a^\dagger)^n\exp(\mu a^\dagger a)=(a^\dagger)^n\exp(-\mu n), \tag{3.4a}$$

$$\exp(-\mu a^\dagger a)a^n\exp(\mu a^\dagger a)=a^n\exp(\mu n), \tag{3.4b}$$

$$\exp(-\mu a^n)(a^\dagger)^m\exp(\mu a^n)=(a^\dagger-n\mu a^{n-1})^m, \tag{3.4c}$$

$$\exp[-\mu(a^\dagger)^n]a^m\exp[\mu(a^\dagger)^n]=[a+n\mu(a^\dagger)^{n-1}]^m \tag{3.4d}$$

together with Feynman's theorem (3.2) to disentangle K. The first step is simple and corresponds to the usual transformation into the interaction representation:

$$K=\exp(itFa^\dagger a)\mathfrak{T}\exp\left(i\int_0^t[M\exp(-iF\tau)a^\dagger+N\exp(iF\tau)a+G\exp(-2iF\tau)(a^\dagger)^2+G\exp(2iF\tau)a^2]d\tau\right). \tag{3.5}$$

In the next step we disentangle the $(a^\dagger)^2$ term. To achieve this goal we have to replace each a by

$$\tilde{a}=a+2iG\left(\int_0^\tau d\tau'\exp(-2iF\tau')\right)a^\dagger$$

$$=a+(G/F)[1-\exp(-2iF\tau)]a^\dagger \tag{3.6}$$

according to Eq. (3.4d). Note that the change is of first order in G/F. The result is

$$K=\exp(itFa^\dagger a)\exp[(G/2F)\tilde{\eta}_2(t)(a^\dagger)^2]\times\exp[-(G^2/F)t-(G^2/F^2)\tilde{\eta}_2^*(t)]\times\mathfrak{T}\exp\left(i\int_0^t d\tau\{-(2G^2/F)\tilde{\eta}_2^*(\tau)a^\dagger a+[M\exp(-iF\tau)+N\tilde{\eta}_2(\tau)\exp(iF\tau)(G/F)]a^\dagger+N\exp(iF\tau)a+G\exp(2iF\tau)(G/F)^2[\tilde{\eta}_2(\tau)]^2(a^\dagger)^2+G\exp(2iF\tau)a^2\}\right), \tag{3.7}$$

where

$$\tilde{\eta}_2(\tau)=1-\exp(-2iF\tau) \tag{3.8}$$

The time ordered part of the right hand side of Eq. (3.7) is similar in structure to the operator K itself, given in Eq. (3.1). That means that we may repeatedly disentangle this expression along the lines described above. Every cycle generates terms of higher order in G/F. This procedure may be continued to any desired order.

The final step will be to disentangle the $a^\dagger$ term,

retaining within the time ordered part of (3.7) only the operators a and a^2. The time ordering operator may be omitted at this stage. The result is

$$K=Q_1Q_2, \tag{3.9}$$

with[15]

$$Q_1=\exp[-i(G^2/F)t-(G^2/2F^2)\bar{\eta}_2^*(t)+\delta(t)+\cdots], \tag{3.10}$$

$$\delta(t)=i\int_0^t d\tau[N\gamma(t)\exp(iFt)+G\gamma(t)^2\exp(2iFt)], \tag{3.11}$$

$$\gamma(t)=(M/F)\bar{\eta}_1(t)+(NG/F^2)\exp(-iFt)[\bar{\eta}_1(t)]^2+\cdots, \tag{3.12}$$

$$\bar{\eta}_1(t)=1-\exp(-iFt), \tag{3.13}$$

$$\begin{aligned}Q_2=\exp[it(F+\cdots)a^\dagger a]&\times\exp\{[(G/2F)\bar{\eta}_2(t)+\cdots](a^\dagger)^2\}\\&\times\exp(\{(M/F)\bar{\eta}_1(t)+(NG/F^2)\\&\times\exp(-iFt)[\bar{\eta}_1^*(t)]^2+\cdots\}a^\dagger)\\&\times\exp(\{-(N/F)\bar{\eta}_1^*(t)+(GM/F^2)[\bar{\eta}_1^*(t)]^2+\cdots\}a)\\&\times\exp[-(G/2F)\bar{\eta}_2^*(t)a^2].\end{aligned} \tag{3.14}$$

IV. RADIATIONLESS TRANSITIONS FROM A SINGLE VIBRONIC LEVEL WITH FREQUENCY CHANGES

We now turn to the task of generalizing the result (2.19) to the case where the potential surfaces of the two electronic states differ not only in their origins but also in the frequencies of the normal modes.

Our starting point will again be Eq. (2.1). Expression (2.5) for $L(t)$ is still correct provided that $\Delta_\kappa=0$ as the second term on the rhs of Eq. (2.4) vanishes because of symmetry restrictions.[9] Equations (2.6) for the d terms and Eq. (2.7) for $g_\mu(t)$ should of course be modified. In order to perform this extension we start from the nonvanishing part of Eq. (2.4)

$$L(t)=\sum_{\kappa=1}^{P}L^\kappa(t), \tag{4.1}$$

$$\begin{aligned}L^\kappa(t)=\langle i\mid V_{sl}{}^\kappa\exp[iH_l(t/\hbar)]V_{sl}{}^{\kappa\dagger}&\\\times\exp[-iH_s(t/\hbar)]\mid i\rangle.&\end{aligned} \tag{4.2}$$

For $V_{sl}{}^\kappa$ it is easy to get

$$V_{sl}{}^\kappa=C_{sl}{}^\kappa(i\hbar/M_\kappa{}^{1/2})(\partial/\partial Q_\kappa)=-C_{sl}{}^\kappa(\hbar\omega_\kappa)^{1/2}p_\kappa, \tag{4.3}$$

where

$$p_\kappa=-i(\partial/\partial q_\kappa)=(i/\sqrt{2})(a_\kappa{}^\dagger-a_\kappa). \tag{4.3'}$$

The Hamiltonian H_s is

$$H_s=\sum_\mu h_s{}^\mu=-\sum_\mu(\hbar^2/2M_\mu)(\partial^2/\partial Q_\mu)+\tfrac{1}{2}M_\mu{}^2\omega_\mu Q_\mu{}^2. \tag{4.4}$$

For H_l we may write

$$H_l=-\Delta E+\sum_\mu h_l{}^\mu, \tag{4.5}$$

where ΔE is the electronic energy gap and $h_l{}^\mu$ is to be obtained from $h_s{}^\mu$ by shifting the origin and changing the frequency. First we make the transformation $\omega_\mu\rightarrow\omega_\mu+\eta_\mu$ to get

$$\tilde{h}_l{}^\mu=-(\hbar^2/2M_\mu)(\partial^2/\partial Q_\mu{}^2)+[1+(\eta_\mu/\omega_\mu)]^2\tfrac{1}{2}(M_\mu\omega_\mu{}^2)Q_\mu{}^2. \tag{4.6}$$

Transforming now into dimensionless coordinates by the substitution

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

the expressions for $h_s{}^\mu$ and $\tilde{h}_l{}^\mu$ become

$$h_s{}^\mu=-\tfrac{1}{2}\hbar\omega_\mu(\partial^2/\partial q_\mu{}^2)+\tfrac{1}{2}\hbar\omega_\mu q_\mu{}^2, \tag{4.7}$$

$$\begin{aligned}\tilde{h}_l{}^\mu&=-\tfrac{1}{2}\hbar\omega_\mu(\partial^2/\partial q_\mu{}^2)+[1+(\eta_\mu/\omega_\mu)]^2\tfrac{1}{2}\hbar\omega_\mu q_\mu{}^2\\&=\tfrac{1}{2}\hbar\omega_\mu(\partial^2/\partial q_\mu{}^2)+\tfrac{1}{2}\hbar\omega_\mu(1+\xi_\mu)q_\mu{}^2,\end{aligned} \tag{4.8}$$

where

$$\xi_\mu=(2\eta_\mu/\omega_\mu)+(\eta_\mu{}^2/\omega_\mu{}^2). \tag{4.9}$$

$h_l{}^\mu$ may now be written in the form [analogous to Eq. (2.10)]

$$h_l{}^\mu=\exp(ip_\mu\Delta_\mu)\tilde{h}_l{}^\mu\exp(-ip_\mu\Delta_\mu), \tag{4.10}$$

so that, in terms of creation and annihilation operators, we get

$$h_s{}^\mu=\hbar\omega_\mu a_\mu{}^\dagger a_\mu, \tag{4.11}$$

$$\begin{aligned}h_l{}^\mu=\exp(ip_\mu\Delta_\mu)\{&\hbar\omega_\mu(1+\tfrac{1}{2}\xi_\mu)a_\mu{}^\dagger a_\mu\\&+\tfrac{1}{4}\hbar\omega_\mu\xi_\mu[(a_\mu{}^\dagger)^2+a_\mu{}^2+1]\}\exp(-ip_\mu\Delta_\mu),\end{aligned} \tag{4.12}$$

with p_μ given by (4.3a). In Eqs. (4.11) and (4.12) we have neglected a constant factor $\frac{1}{2}\hbar\omega_\mu$ which is going to be cancelled anyway after substituting in Eq. (4.2).

Making use of Eqs. (4.12), (4.11), (4.5), (4.4), (4.3), and (4.2), we get

$$\begin{aligned}L^\kappa(t)=\hbar\omega_\kappa\mid C_{sl}{}^\kappa\mid^2\exp[-i\Delta E(t/\hbar)]&\\\times\exp[(i/4)\sum_\mu\omega_\mu\xi_\mu t]J_\kappa'(t)\prod_{\mu\neq\kappa}g_\mu'(t),&\end{aligned} \tag{4.13}$$

where $J_\kappa'(t)$ and $g_\mu'(t)$ represent a generalized version of the J_κ and the g_μ terms of Sec. II, and are given by

$$\begin{aligned}J_\kappa'(t)=\langle v_{s\kappa}\mid p_\kappa\exp(it\{&\omega_\kappa(1+\tfrac{1}{2}\xi_\kappa)a_\kappa{}^\dagger a_\kappa\\&+\tfrac{1}{4}\omega_\kappa\xi_\kappa[(a_\kappa{}^\dagger)^2+a_\kappa{}^2]\})p_\kappa\exp(-it\omega_\kappa a_\kappa{}^\dagger a_\kappa)\mid v_{s\kappa}\rangle\end{aligned} \tag{4.14}$$

and

$$g_\mu'(t)=\langle v_{s\mu}\mid \exp(ip_\mu\Delta_\mu)\,\exp\{it\{\omega_\mu(1+\tfrac{1}{2}\xi_\mu)a_\mu^\dagger a_\mu +\tfrac{1}{4}\omega_\mu\xi_\mu[(a_\mu^\dagger)^2+a_\mu^2]\}\}\exp(-ip_\mu\Delta_\mu) \times\exp(-it\omega_\mu a_\mu^\dagger a_\mu)\mid v_{s\mu}\rangle, \quad (4.15)$$

where

$$\mid v_{s\mu}\rangle=(v_{s\mu}!)^{-1/2}(a_\mu^\dagger)^{v_{s\mu}}\mid 0\rangle. \quad (4.16)$$

Our aim now is to recast expressions (4.14) and (4.15) in a computable form. We begin with the expression for $g_\mu'(t)$ and rewrite it in the form

$$g_\mu'(t)=\exp\{it\omega_\mu[(1+\xi_\mu)(\Delta_\mu^2/2)-v_{s\mu}]\} \times\langle v_{s\mu}\mid \exp\{it\{\omega_\mu(1+\tfrac{1}{2}\xi_\mu)a_\mu^\dagger a_\mu +(\Delta_\mu/\sqrt{2})\omega_\mu(1+\xi_\mu)(a_\mu^\dagger+a_\mu) +\tfrac{1}{4}\omega_\mu\xi_\mu[(a_\mu^\dagger)^2+a_\mu^2]\}\}\mid v_{s\mu}\rangle \quad (4.17)$$

It is straightforward now to utilize (3.1), (3.9), and (3.11), with

$$F_\mu=\omega_\mu(1+\tfrac{1}{2}\xi_\mu), \qquad G_\mu=\tfrac{1}{4}\omega_\mu\xi_\mu,$$
$$M_\mu(=N_\mu)=\omega_\mu(1+\xi_\mu)(\Delta_\mu/\sqrt{2}) \quad (4.18)$$

to get

$$g_\mu'(t)=U_\mu(t)\,V_\mu^{v_{s\mu},v_{s\mu}}(t)\,\exp[it\omega_\mu(\xi_\mu v_{s\mu}/2)], \quad (4.19)$$

where $U_\mu(t)=Q_1(t)\exp[it\omega_\mu(1+\xi_\mu)(\Delta_\mu^2/2)]$ [$Q_1(t)$ is given by Eq. (3.10) with F, M, and G defined by Eq. (4.18)] is a function which does not depend on $v_{s\mu}$, and

$$V_\mu^{v_{s\mu},v_{s\mu}}(t)=\langle v_{s\mu}\mid \exp[\lambda_2^\mu(t)(a_\mu^\dagger)^2] \times\exp\{[\lambda_1^\mu(t)+\lambda_3^\mu(t)]a_\mu^\dagger\}\exp\{[-\lambda_1^{\mu*}(t)+\lambda_3^\mu(t)] \times\exp(iF_\mu t)a_\mu\}\exp[-\lambda_2^{\mu*}(t)a_\mu^2]\mid v_{s\mu}\rangle, \quad (4.20)$$

$$\lambda_1^\mu(t)=(M_\mu/F_\mu)[1-\exp(-iF_\mu t)],$$
$$\lambda_2^\mu(t)=(G_\mu/2F_\mu)[1-\exp(-2iF_\mu t)],$$
$$\lambda_3^\mu(t)=(M_\mu G_\mu/F_\mu^2)[\bar{\eta}_1^{\mu*}(t)]^2\exp(-iF_\mu t). \quad (4.21)$$

With the J_κ' term we shall deal in a similar manner, noting that the p_κ terms yield four different matrix elements. The result is

$$J_\kappa'(t)=R_\kappa(t)\,\exp[it\omega_\kappa(\xi_\kappa v_{s\kappa}/2)]\Lambda_\kappa(t), \quad (4.22)$$

where $R_\kappa(t)=Q_1(t)$, with F and G given by Eq. (4.18) and with $M=0$, is again a function which is independent on the initial occupation numbers $v_{s\kappa}$, and

$$\Lambda_\kappa(t)=v_{s\kappa}\exp[-it\omega_\kappa(1+\tfrac{1}{2}\xi_\kappa)]S_\kappa^{v_{s\kappa}-1,v_{s\kappa}-1}(t) +(v_{s\kappa}+1)\exp[it\omega_\kappa(1+\tfrac{1}{2}\xi_\kappa)]S_\kappa^{v_{s\kappa}+1,v_{s\kappa}+1}(t) +[v_{s\kappa}(v_{s\kappa}+1)]^{1/2}\{\exp[it\omega_\kappa(1+\tfrac{1}{2}\xi_\kappa)]S_\kappa^{v_{s\kappa}+1,v_{s\kappa}-1} +\exp[-it\omega_\kappa(1+\tfrac{1}{2}\xi_\kappa)]S_\kappa^{v_{s\kappa}-1,v_{s\kappa}+1}(t)\}, \quad (4.23)$$

with

$$S_\kappa^{v_1v_2}(t)=\langle v_1\mid \exp[\lambda_2^\kappa(t)(a_\kappa^\dagger)^2]\exp[-\lambda_2^{\kappa*}(t)a_\kappa^2]\mid v_2\rangle. \quad (4.24)$$

This is a special form of v_κ [Eq. (4.20)] corresponding to $\lambda_1=\lambda_3=0$.

Inserting Eq. (4.20) and (4.22) into Eq. (4.13), we get the following expression for $L^\kappa(t)$:

$$L^\kappa(t)=\hbar\omega_\kappa\mid C_{sl}^\kappa\mid^2\exp[-i\Delta E(t/\hbar)] \times\exp[(i/4)\sum_\mu\omega_\mu\xi_\mu t]R_\kappa(t)[\prod_{\mu\neq\kappa}U_\mu(t)] \times\exp[(i/2)\sum_\mu\omega_\mu\xi_\mu v_{s\mu}t]\Lambda_\kappa(t)[\prod_{\mu\neq\kappa}V_\mu^{v_{s\mu},v_{s\mu}}(t)]. \quad (4.25)$$

The functions R_κ and U_μ can be expressed to any desired order in ξ. We note that if we use the expressions for R_κ and U_μ up to the first order we get an extension of Freed and Jortner's first order result[9] for the case $v_{s\kappa}>0$. However, this first order result is open to criticism. An examination of the functions $R_\kappa(t)$ and $U_\mu(t)$ reveals that their structure is essentially of the following form:

$$\exp[O(\xi)\exp(i\omega t)+O(\xi^2)\exp(2i\omega t)]. \quad (4.26)$$

In an attempt to simplify their general result, Freed and Jortner[9] neglected the higher order terms in the exponent. This function is yet to be Fourier-transformed, which means that this approximation is not justified (Appendix A). So we cannot get away by taking $R_\kappa(t)$ and $U_\mu(t)$ in low order for the calculation of the component $L^\kappa(t)$ of the generating function. This difficulty may be overcome by substituting for the term $R_\kappa(t)$ and $U_\mu(t)$ an alternative form which is valid to any order, while the matrix elements S and V are retained to first order in ξ. To this end we note that $v_{s\mu}=0$ (for every μ), $L^\kappa(t)$ must be given by the exact result of Jortner and Freed,[9] which we denote by D^κ:

$$D^\kappa=\mid C_{sl}^\kappa\mid^2\exp[-i\Delta E(t/\hbar)]\bar{f}_\kappa(t)\prod_{\mu\neq\kappa}f_\mu(t), \quad (4.27a)$$

where

$$f_\mu(t)=A_\mu\exp\left(-\frac{(1+\eta_\mu/\omega_\mu)^{-1}\Delta_\mu^2\{1-\exp[i(\omega_\mu+\eta_\mu)t]\}}{(2+\eta_\mu/\omega_\mu)(1+\eta_\mu/\omega_\mu)^{-1}-(\eta_\mu/\omega_\mu)(1+\eta_\mu/\omega_\mu)^{-1}\exp[i(\omega_\mu+\eta_\mu)t]}\right), \quad (4.27b)$$

$$\bar{f}_\kappa(t)=\tfrac{1}{2}(1+\eta_\kappa/\omega_\kappa)^{1/2}\hbar(\omega_\kappa+\eta_\kappa)A_\kappa\exp[i(\omega_\kappa+\eta_\kappa)t]\left(1+\frac{(\eta_\kappa/\omega_\kappa)^2}{4(1+\eta_\kappa/\omega_\kappa)}\{1-\exp[2i(\omega_\kappa+\eta_\kappa)t]\}\right), \quad (4.27c)$$

and where

$$A_\mu=\exp(-\tfrac{1}{2}i\eta_\mu t)\left[(1+\eta_\mu/\omega_\mu)^{-1}+\left(\frac{1}{2}\frac{\eta_\mu/\omega_\mu}{1+\eta_\mu/\omega_\mu}\right)^2\{1-\exp[2i(\omega_\mu+\eta_\mu)t]\}\right]^{-1/2}. \tag{4.27d}$$

That means that $L^\kappa(t)$ may be recast in the form

$$L^\kappa(t)=D^\kappa\{\exp[it\omega_\kappa(1+\tfrac{1}{2}\xi_\kappa)]S_\kappa^{1,1}(t)\}^{-1}\exp(\tfrac{1}{2}i\sum_\mu\omega_\mu\xi_\mu v_{s\mu}t)\Lambda_\kappa\prod_{\mu\neq\kappa}V_\mu^{v_{s\mu},v_{s\mu}}(t). \tag{4.28}$$

A simpler expression may be obtained for the common case in which $v_{s\kappa}=0$ for every promoting mode. Then Eq. (4.28) will be reduced to

$$L^\kappa(t)\,(v_{s\kappa}=0)=D^\kappa\exp(\tfrac{1}{2}i\sum_\mu\omega_\mu\xi_\mu v_{s\mu}t)\prod_{\mu\neq\kappa}V_\mu^{v_{s\mu},v_{s\mu}}(t). \tag{4.29}$$

The last step is to evaluate the matrix elements V_μ and S_κ. These matrix elements are of the general form

$$Z^{v,u}(\alpha;\beta;\gamma;\delta)=(u!v!)^{-1/2}\langle 0\mid a^v\exp[\alpha(a^\dagger)^2]\exp(\beta a^\dagger)\exp(\gamma a)\exp(\delta a^2)(a^\dagger)^u\mid 0\rangle, \tag{4.30}$$

in terms of which we have

$$V_\mu^{v_1,v_2}(t)=Z^{v_1,v_2}[\lambda_2{}^\mu(t);\lambda_1{}^\mu(t)+\lambda_3{}^\mu(t);-\lambda_1{}^{\mu*}(t)+\lambda_3{}^\mu(t)\exp(iF_\mu t);-\lambda_2{}^{\mu*}(t)], \tag{4.31}$$

$$S_\kappa^{v_1,v_2}(t)=Z^{v_1,v_2}[\lambda_2{}^\kappa(t);0;0;-\lambda_2{}^\kappa(t)]. \tag{4.32}$$

For Z we get (Appendix B)

$$Z^{u,v}(\alpha;\beta;\gamma;\delta)=(u!v!)^{1/2}\sum_{s=0}^{\min\{v-r,u-q\}}\sum_{q=0,2\cdots u-1,u}\sum_{r=0,2\cdots v-1,v}2^{(r/2)+(q/2)}\frac{d(r)d(q)}{r!q!s!(v-r-s)!(u-q-s)!}\times\alpha^{(1/2)r}\beta^{v-r-s}\gamma^{u-q-s}\delta^{(1/2)q}, \tag{4.33}$$

where

$$d(2n)=1\times3\times5\times\cdots\times(2n-1). \tag{4.34}$$

Equations (2.1), (4.1), (4.23), (4.27), (4.28), (4.31), (4.32), and (4.33) summarize our derivation of a computable form of the nonradiative decay rate in the nonlinear case. Equation (2.1) now gives the decay rate of the level $\mid si\rangle$, where $L(t)$ is given by Eq. (4.1) as a sum over the contributions of all the promoting modes. This contribution $L^\kappa(t)$ is given by Eq. (4.28) in terms of Freed and Jortner's[9] zero temperature result, Eqs. (4.27a)–(4.27d), and the auxilliary functions $\Delta_\kappa(t)$ Eq. (4.32), $S_\kappa^{v_1,v_2}(t)$ [Eq. (4.32)] and $V_\mu^{v_1,v_2}(t)$ [Eq. (4.31)]. In these functions the relevant matrix element $Z^{u,v}$ is given by Eqs. (4.33) and (4.34). The integration over t may now be performed numerically using the procedure described in Paper I.

V. DISCUSSION

In this paper we have provided a theoretical treatment of the nonradiative decay of a single excited vibronic level of a large "statistical" molecule, using a two electronic state model characterized by displaced and frequency-modified harmonic potential surfaces. All the previous treatments of the related problem concerning the decay of a Boltzmann averaged manifold, which consider changes in the molecular frequencies between the two electronic states, resulted in complicated approximate expressions. These complications arise from the fact that the coupling between electronic states is taken to contain second order terms in the nuclear displacements [Eqs. (4.8) and (4.10)], while if only origin shifts are taken into account, the coupling contains only first order terms in these displacements. We are aware of three previous works in which attempts have been made to include frequency changes in molecular nonradiative transitions theory. Freed and Jortner[9] have derived the exact result for the zero temperature case, which we have also used in the present paper [Eq. (4.27)]. Their attempt to simplify this exact result by expanding to the first order in small parameters is, however, open to criticism. We have demonstrated above that this expansion of the exponent of the generating function in powers of $\xi e^{i\omega t}$, where ξ is small, is illegitimate, as higher powers of $e^{i\omega t}$ may substantially contribute to the Fourier-transformed final result for the transition probability. [See the discussion concerning Eq. (4.26) and Appendix A.] An earlier attempt by Lin and by Lin and Bersohn[7] to include frequency changes in their treatment of the thermally averaged decay probability is also incomplete for the same reasons. Another treatment by Fischer[16] is unjustified due to other reasons. This author included frequency changes by taking the nuclear Hamiltonian in a particular electronic state n to be of the form

$$\sum_\mu\hbar\omega_\mu{}^n a_\mu{}^\dagger a_\mu+\sum_\mu g_\mu{}^n\hbar\omega_\mu{}^n(a_\mu{}^\dagger+a_\mu), \tag{5.1}$$

where $\omega_\mu{}^n$ is the frequency of the μth normal mode in the electronic state n, and $g_\mu{}^n$ is related to the origin shift of the potential surfaces of this electronic state. However, the author has disregarded the change in the creation and annihilation operators themselves due to the frequency changes. In fact, the creation and annihilation operators for a harmonic oscillator are defined by

$$a=(M\omega/2\hbar)^{1/2}[q+(ip/M\omega)], \tag{5.2}$$

$$a^\dagger=(M\omega/2\hbar)^{1/2}[q-(ip/M\omega)], \tag{5.3}$$

where q and p are the coordinate and momentum of the oscillator, so that if $a'^\dagger$ and a' are the corresponding creation and annihilation operators for an oscillator of the same mass and a different frequency ω', the following relations hold[17]

$$\begin{aligned} a'&=\mathcal{E}_1 a^\dagger+\mathcal{E}_2 a,\\ a'^\dagger&=\mathcal{E}_1 a+\mathcal{E}_2 a^\dagger, \end{aligned} \tag{5.4}$$

where

$$\mathcal{E}_1=\tfrac{1}{2}[(\omega'/\omega)^{1/2}-(\omega/\omega')^{1/2}],$$

$$\mathcal{E}_2=\tfrac{1}{2}[(\omega'/\omega)^{1/2}+(\omega/\omega')^{1/2}].$$

Fischer's relatively simple result is thus an outcome of an approximate treatment.

In the present paper we have also utilized an expansion of the generating function in powers of $\xi\exp(i\omega t)$ but this expansion is performed on that part of the generating function which even in its lowest order form contains contributions of higher powers of $\exp(i\omega t)$ [Eq. (4.33)], so that it is sensible to expect that in this case the expansion will not cause a serious error.

In order to get some insight into the nature of our final result it will be useful to inquire what properties which were obtained for the simplified constant frequency model are conserved in our more general case. For the simple model without frequency changes (see Sec. II) we have found that:

(1) The generating function can be recast as a product of separate contributions from different vibrational modes. In particular, we may factorize the contribution of the promoting mode from that of the accepting modes.

(2) The generating function consists of two terms, one which is proportional to $v_{s\kappa}$ while the other behaves like $v_{s\kappa}+1$. This leads in a case of a large energy gap to the relation[5]

$$W_{si}(v_{s\kappa}\neq 0)/W_{si}(v_{s\kappa}=0)\simeq\sum_\kappa(2v_{s\kappa}+1),$$

indicating the enhancement of the nonradiative decay of vibronic levels which contain promoting mode(s).

(3) The simple result, Eq. (2.19), demonstrates the propensity rule for the promoting mode, namely that it must gain or lose one quantum of vibrational excitation in the electronic transition.

(4) The simple result Eq. (11.19) yields (via numerical calculations)[5] an exponential increase of the decay rate as a function of initial excess vibrational energy in the statistical limit, and a varying behavior in the small electronic energy gap case.

Turning now to our theoretical result for optical selection studies including frequency changes, the following remarks may be made:

(a) The generating function may still be factorized into independent contributions of normal modes. This factorization holds as long as we do not introduce mixed second order terms into the coupling, which will then lead to different normal modes in the two electronic states.

(b) The effective energy gap is now modified by an additional term of the form $\frac{1}{2}\sum_\mu\omega_\mu\xi_\mu v_{s\mu}$ (including the term which corresponds to the promoting mode).

(c) The generating function contains now four additive terms [see Eq. (4.23)], but for $v_{s\kappa}=0$ we shall get only one term as in the simple case.

(d) The terms which appear in $\Lambda_\kappa(t)$ [Eq. (4.23)] still contain the promoting mode frequency in a way which leads in the simple case to the propensity rules for this mode. However, in the present case the energy gap is modified by the term $\frac{1}{2}\omega_\kappa\xi_\kappa v_{s\kappa}$ [see (b)], and also by terms appearing in S_κ.

(e) Conclusion (2) for the simple case will not hold as the dependence of the result on $v_{s\kappa}$ is now very complicated.

(f) If the promoting mode does not change its frequency, we shall regain all our previous conclusion which concerned it (propensity rules and dependence on $v_{s\kappa}$).

(g) When all the frequencies are set equal in the two electronic states the new general result (Sec. V) reduces to the simple case, Eq. (2.19), providing a good consistency check.

(h) It is plausible that the numerical results for optical selection including both origin shifts and frequency changes will not modify qualitatively our previous conclusions.[5] This suggestion rests on the fact that qualitative considerations which involve the effects of the density of states and of the Franck–Condon factors will not change. So we will expect that the decay rate in the statistical limit will increase in higher initial levels and will exhibit varying behavior in case of small electronic energy gap. To obtain quantitative results one must, of course, perform the numerical calculation as prescribed above. This is a straightforward but cumbersome task.

APPENDIX A: A COMMENT ON THE CONVERGENCE PROBLEMS

Suppose, for example, that E/ω is an even integer and we want to compare

$$\int_{-\infty}^{\infty}dt\exp[-iEt+\xi\exp(i\omega t)]$$

and

$$\int_{-\infty}^{\infty} dt \exp[-iEt+\xi^2 \exp(2i\omega t)].$$

Expanding the integrand in the form

$$\exp[\xi \exp(i\omega t)]=\sum_{n=0}^{\infty}\frac{\xi^n}{n!}\exp(in\omega t), \qquad (A1)$$

it is easy to get

$$\int_{-\infty}^{\infty} dt \exp[-iEt+\xi \exp(i\omega t)]=2\pi\sum_{n=0}^{\infty}\frac{\xi^n}{n!}\delta(E-n\omega). \qquad (A2)$$

In the statistical limit it may be shown that $\delta(E-n\omega)$ may be replaced by $\delta_{E,n\omega}$, so that we get $2\pi[(\xi)^{E/\omega}/(E/\omega)!]$. In the same way we get

$$\int_{-\infty}^{\infty} dt \exp[-iEt+\xi^2 \exp(2i\omega t)]=2\pi\frac{(\xi^2)^{E/2\omega}}{(E/2\omega)!}, \qquad (A3)$$

which is greater than the first result for every ξ. Of course higher order terms may vanish. If $E/k\omega$ is not an integer, the kth order term will not contribute. That means that the sequence will converge even if the lower contributions will not diminish regularly.

APPENDIX B: EVALUATION OF MATRIX ELEMENTS

Starting from

$$Z=(u!v!)^{-1/2}\langle 0 \mid a^v \exp[\alpha(a^\dagger)^2] \times\exp(\beta a^\dagger)\exp(\gamma a)\exp(\delta a^2)(a^\dagger)^u \mid 0\rangle \qquad (B1)$$

and using Eqs. (3.4c) and (3.4d), we get

$$Z=(u!v!)^{-1/2}\langle 0 \mid (a+2\alpha a^\dagger+\beta)^v(a^\dagger+2\delta a+\gamma)^u \mid 0\rangle. \qquad (B2)$$

It is easier to evaluate the generating function of this matrix element

$$\begin{aligned}\tilde{Z}&=(u!v!)^{-1/2}\langle 0 \mid \exp[\rho(a+2\alpha a^\dagger+\beta)] \times\exp[\sigma(a^\dagger+2\delta a+\gamma)] \mid 0\rangle \\ &=(u!v!)^{-1/2}\exp(\alpha\rho^2)\exp(\beta\rho)\exp(\rho\sigma) \times\exp(\gamma\sigma)\exp(\delta\sigma^2) \qquad (B3)\end{aligned}$$

In terms of $\tilde{Z}$ we have

$$Z=(\partial^{v+u}\tilde{Z}/\partial\rho^v\partial\sigma^u)\mid_{\rho=\sigma=0}. \qquad (B4)$$

In performing the derivatives we make use of the relation

$$\begin{aligned}\partial^n/\partial X^n \exp(\alpha X^2)\mid_{x=0}&=0 \qquad \text{if } n \text{ is odd} \\ &=1\times3\times5\times\cdots\times(n-1)(2\alpha)^{n/2} \\ &\qquad \text{if } n \text{ is even.} \qquad (B5)\end{aligned}$$

Using this, Eq. (4.33) is reached after some algebra.

[1] More generally, we mean the case in which the radiationless transition rate is much faster than the vibrational relaxation in the initial manifold. Such a case may be encountered also in solution. [See A. Nitzan, J. Jortner, and P. M. Rentzepis, Chem. Phys. Letters **8**, 445 (1971)].

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[14] We adopt here the usual two-letter symbol for the vibronic states. The first letter labels the electronic state and the second represents the corresponding vibrational level. s and L will denote the initial and final electronic states, respectively, while i and j will denote the corresponding vibrational levels.

[15] In Eqs. (3.10)–(3.14), F is a zero order term and should be replaced by $F\{1+O[(G/F)^2]+\cdots\}$.

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