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Theory of the interplay of luminescence and vibrational relaxation: A master-equation approach*

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A theory is developed to describe the interplay of vibrational relaxation and luminescence occurring simultaneously in a molecule, in terms of a master equation involving true sinks of probability. Specifically, the basic equation is the Montroll-Shuler equation augmented by the addition of sink terms which can be nonlinear as well as linear in the vibrational energy. These terms describe radiative and nonradiative decay and expressions for the former are derived explicitly in terms of Franck-Condon factors. Exact solutions in terms of known functions are obtained in the linear case for several physically motivated initial vibrational distributions, viz., δ-function, Boltzmann, Poisson, and Laguerre. Two perturbation schemes are developed to analyze the nonlinear case, one of which is useful for small nonlinearities and the other for arbitrarily large nonlinearities but for low temperatures. Illustrative applications of the theory include the exact calculation of time- and frequency-resolved emission spectra (linear decay calculation) and the perturbation analysis of quantum yields in the presence of strongly energy-dependent nonradiative transitions (nonlinear decay calculation).

I. INTRODUCTION

Optical absorption by a molecule results in its acquiring an electronic *and* a vibrational excitation, the latter due to the electron-phonon coupling. The ensuing deexcitation processes may or may not have comparable characteristic times. If they do not, they can be analyzed separately. If they do, they must be analyzed as a single complex process. A typical characteristic time for radiative emission (which causes electronic deexcitation) is 10^{-8} sec, whereas vibrational relaxation has generally been assumed to take less than 10^{-12} sec in the condensed phase. The four-orders-of-magnitude difference clearly justifies a decoupled description. Indeed the traditional theory[1] of luminescence deals only with the process of radiative emission and, in the analysis, takes the emitting state to be fully relaxed vibrationally. It has already been emphasized[2] that such a sequential picture of the combined process may not have universal applicability. Furthermore many observations of slow vibrational relaxation have been recently reported.[3] That systems exist in which luminescence and relaxation take place on comparable time scales is no longer under doubt. A theory of the combined process is therefore required.

Such a theory of simultaneous relaxation and luminescence should ideally consist of an exact calculation from the microscopics of the system. The complexity of the problem makes such a program impossible in practice and two types of theory naturally suggest themselves: microscopic analysis[4-6] involving plausible but uncontrollable[7] approximations, and exact analysis[8-10] based on macroscopic or semimicroscopic equations which are plausible but whose derivation from the microscopics may not be completely satisfactory. Both approaches are important and they complement each other. In this paper we develop the second approach.

In the context of pure vibrational relaxation, this semimicroscopic approach[11,12] is based on the master equation

$$\frac{dP_m}{dt}=\sum_n \gamma_{mn}P_n-\gamma_{nm}P_m\,, \tag{1.1}$$

wherein $P_m(t)$ is the probability that the mth vibrational site is occupied at a time t, and γ_{mn} is the transition rate from the nth to the mth state. The simplest extension of the traditional theory of luminescence to include relaxation effects is to substitute the relaxed probabilities $P_m(\infty)$ in the usual calculations by the time-dependent solutions $P_m(t)$ of Eq. (1.1). Such a program has been followed earlier.[8] The reverse effect viz. that of luminescence on relaxation is, however, neglected in such an analysis since Eq. (1.1) describes pure relaxation.

Luminescence involves the depletion of the excitation on the molecule and a natural way to describe its full interplay with relaxation is therefore to extend Eq. (1.1) to include a term describing the true decay of the probability. This term represents radiative emission from individual vibrational levels and should therefore be level dependent. One thus arrives at

$$\frac{dP_m}{dt}+\alpha_m P_m=\sum \gamma_{mn}P_n-\gamma_{nm}P_m\,, \tag{1.2}$$

which is the basis of the master equation theory of simultaneous luminescence and relaxation to be presented in this paper. The method of excitation and the molecular properties related to the electron-phonon coupling (such as Franck-Condon factors) determine the initial condition $P_m(0)$. A calculation from microscopic parameters yields the α's and the γ's. We then solve Eq. (1.2) for $P_m(t)$ and thus obtain the distribution of the excitation among the vibrational levels of the molecule at all times. Any quantity depending on the $P_m(t)$'s can then be calculated. For instance the quantum yield ϕ, the total fluorescence intensity $I(t)$ (also known as the differential photon rate) and the frequency-resolved intensity $I(\omega, t)$, are given by

$$\phi = \sum_m \int_0^\infty \alpha_m P_m(t)\, dt , \tag{1.3a}$$

$$I(t) = \sum_m \alpha_m P_m(t) , \tag{1.3b}$$

$$I(\omega, t) = \sum_m A_m(\omega) P_m(t) . \tag{1.3c}$$

An expression for $A_m(\omega)$ will be given in Sec. V. Generally the excitation on the molecule is depleted not only radiatively but also through other processes. These may be intermolecular as in the case of excitation transfer, or intramolecular as in the case of internal conversion and intersystem crossing. The transfer problem cannot be treated exactly in terms of Eq. (1.2), requires the solution of "interlocking" master equations (one for the relaxation and one for the transfer), and has been analyzed earlier by Kenkre.[13] In this paper we are concerned with *intra*molecular processes coexisting with relaxation, and, although our primary interest is in luminescence, some comments concerning nonradiative intramolecular decay will be found in Sec. V.

Previous work on this problem is due to Dexter,[2] Hizhnyakov and Tehver,[5] Fischer,[6] Lin,[8] Freed and collaborators[9] and the present authors.[10] Rubin and Shuler[12] analyzed the problem with level-independent luminescence decay rates. Related work[14] in unimolecular dissociation is due to Buff and Wilson, and Matthews *et al.*

This paper is organized as follows. We introduce the model and give expressions for the decay and transition rates in Sec. II. Exact solutions for the case of linear decay rates for several physically motivated initial distributions, viz. δ-function, Boltzmann, Poisson and Laguerre, are presented in Sec. III. Two separate approximation schemes for nonlinear decay rates are constructed in Sec. IV. Applications of the formalism are discussed in Sec. V where optical line shapes and fluorescence quantum yields are calculated.

II. THE MODEL

The basic model of the molecule used for luminescence calculations[1] consists of two electronic states and harmonic-oscillator vibrational states. If the electron-phonon coupling is linear in the molecule displacement (or, more generally, in the configuration coordinate), the "electronically excited" oscillator is merely displaced with respect to the "ground" oscillator. If the coupling is nonlinear, the frequency of the excited oscillator is different from that of the ground oscillator. Expressions for the decay rates α_m can be obtained within the Franck-Condon framework in a straightforward if tedious manner.[15] For linear coupling resulting in a Stokes shift $a^2\hbar\omega$, where ω is the (ground or excited) oscillator frequency, the decay rate is exactly linear in the energy.

$$\alpha_m = b + cm , \tag{2.1}$$

$$b = M[E_0^3 - \tfrac{3}{2}E_0^2\hbar\omega a^2 + \tfrac{3}{4}E_0\hbar^2\omega^2(a^4 + 2a^2) - \tfrac{1}{8}\hbar^3\omega^3(4a^2 + 6a^4 + a^6)] , \tag{2.2}$$

$$c = M(3E_0\hbar^2\omega^2 a^2 - \tfrac{3}{2}\hbar^3\omega^3 a^4) , \tag{2.3}$$

$$M = (4e^2/3\hbar^4 c^3)\,|\langle|\vec{r}|\rangle|^2 , \tag{2.4}$$

where E_0 and $\langle|\vec{r}|\rangle$ denote the zero-phonon energy difference and the pure electronic dipole matrix element between the excited and ground states, respectively. Quadratic and cubic terms appear in the case of nonlinear coupling characterized by a ground-oscillator frequency ω and excited oscillator frequency $\omega(1 - \Delta)$ and no Stokes shift:

$$\alpha_m = b_1 + c_1 m + d_1 m^2 + f_1 m^3 , \tag{2.5}$$

$$b_1 = M\left[E_0^3 - E_0^2\hbar\omega\frac{\Delta^2}{4(1-\Delta)} + E_0\hbar^2\omega^2\frac{\Delta^2(5\Delta^2 - 8\Delta + 8)}{(1-\Delta)^2} - \frac{\hbar^3\omega^3}{64}\frac{\Delta^2}{(1-\Delta)^3}(15\Delta^4 - 72\Delta^3 + 136\Delta^2 - 128\Delta + 64)\right] , \tag{2.6}$$

$$c_1 = M\left[E_0^2\hbar\omega\frac{\Delta(\Delta - 2)}{2(1-\Delta)} - E_0\hbar^2\omega^2\frac{\Delta^2(4 - \Delta^2)}{8(1-\Delta)^2} - \hbar^3\omega^3\frac{\Delta^2}{16(1-\Delta)^3}(\Delta^4 + 9\Delta^3 - 26\Delta^2 - 40\Delta + 32)\right] , \tag{2.7}$$

$$d_1 = M\left(-E_0\hbar^2\omega^2\frac{3\Delta^2(\Delta - 2)^2}{8(1-\Delta)^2} - \frac{3\hbar^3\omega^3\Delta^3(\Delta^3 - 12\Delta + 16)}{32(1-\Delta)^3}\right) , \tag{2.8}$$

$$f_1 = M\left(\hbar^3\omega^3\frac{5\Delta^3(\Delta - 2)^3}{16(1-\Delta)^3}\right) . \tag{2.9}$$

An important conclusion to be drawn from Eqs. (2.2)–(2.10) is that the linear expression for α_m is an exact consequence of the Franck-Condon principle when the electron-phonon coupling does not result in frequency changes and that in the general case α_m is given by a polynomial

$$\alpha_m = \sum_{r=0}^{3} b_r m^r . \tag{2.10}$$

The form of the relaxation rates γ_{mn} is determined by the interaction of the oscillator (molecule) with the heat bath which causes the relaxation. The Landau-Teller prescription[16] for these rates takes into account the harmonic-oscillator selection rules and the principle of detailed balance and can be shown to yield

$$\gamma_{mn} = k(m+1)\delta_{n,m+1} + ke^{-\beta} m \delta_{n+1,m} , \tag{2.11}$$

where k characterizes the molecule-bath interaction and β is the dimensionless inverse temperature $\hbar\omega/k_B T$, ω, k_B, and T being, respectively, the oscillator frequency, the Boltzmann constant, and the temperature. The density of states in a harmonic oscillator is constant, but that in a real molecule increases with increasing energy. To represent such an increasing density of states Kassel and also Buff and Wilson[14] considered a D-fold degenerate oscillator for which Eq. (2.11) is replaced by

$$\gamma_{mn} = k(m+1)\delta_{n,m+1} + k(m+D-1)e^{-\beta}\delta_{n+1,m} . \tag{2.12}$$

Substituting Eqs. (2.10) and (2.12) in (1.2) one has the extended Montroll-Shuler equation[10,13]

$$\frac{dP_m}{dt} + \alpha_m P_m = k\{(m+D-1)e^{-\beta}P_{m-1} + (m+1)P_{m+1} - [m + (m+D)e^{-\beta}]P_m\}, \tag{2.13}$$

which is the basic equation to be analyzed in this paper. The transformation

$$G(z) = \sum_{m=0}^{\infty} z^m P_m , \tag{2.14}$$

reduces (2.13) to

$$\frac{1}{ke^{-\beta}} \frac{\partial G}{\partial t} = D(z-1)G + [z^2 - z(e^{\beta}+1) + e^{\beta}] \frac{\partial G}{\partial z} - \frac{1}{ke^{-\beta}} \sum_r b_r \left(z \frac{\partial}{\partial z}\right)^r G . \tag{2.15}$$

Exact solutions of (2.15) and therefore of (2.13) can be obtained by generalizing the methods of Montroll and Shuler[11] if $b_r = 0$ for $r \geq 2$. If the latter condition is not met, approximate solutions must be sought. The two kinds of analysis are given respectively in Secs. III and IV.

III. LINEAR DECAY RATES: EXACT SOLUTION

For the linear decay case, exact solutions are possible. Setting $b_0 = b$, $b_1 = c$, and $b_r = 0$ for $r \geq 2$, Eq. (2.15) is solved by the method of characteristics,[17] to yield the following solution for G

$$\begin{aligned} G(z,t) = {} & e^{(-b+Dv')t}(\Gamma^+ - \Gamma^-)^D \\ & \times [(\Gamma^+ - z) + (z - \Gamma^-)e^{-vt})]^{-D} \\ & \times G_0\{[\Gamma^-(\Gamma^+ - z) + \Gamma^+(z - \Gamma^-)e^{-vt}] \\ & \times [(\Gamma^+ - z) + (z - \Gamma^-)e^{-vt}]^{-1}\}, \end{aligned} \tag{3.1}$$

where

$$\Gamma^{\pm} = \tfrac{1}{2}(e^{\beta} + 1 + \delta) \pm [\tfrac{1}{4}(e^{\beta} + 1 + \delta)^2 - e^{\beta}]^{1/2} ,$$

$$\delta = e^{\beta}c/k, \quad v = ke^{-\beta}(\Gamma^+ - \Gamma^-), \quad v' = ke^{-\beta}(\Gamma^- - 1) .$$

From Eq. (2.15) it can be seen that

$$G_0(z) \equiv G(z,0) = \sum_{m=0}^{\infty} z^m P_m(0) . \tag{3.2}$$

The time-dependent probabilities $P_m(t)$ can be obtained from Eq. (3.1) by expanding $G(z,t)$ in powers of z and setting $z = 1$ or equivalently as

$$P_m(t) = \lim_{z\to 0} \frac{1}{m!} \frac{\partial^m}{\partial z^m} G(z,t) . \tag{3.3}$$

The general nth factorial moment of the distribution is defined as

$$\begin{aligned} \langle m(m-1)\cdots(m-n+1)\rangle & = \sum m(m-1)\cdots(m-n+1)P_m(t) \\ & = \lim_{z\to 1} \frac{\partial^n}{\partial z^n} G(z,t) . \end{aligned} \tag{3.4}$$

The zeroth moment Q is the total probability, and the first moment $\langle n\rangle$ is proportional to the energy of the system. These quantities, defined as special cases of Eq. (3.4),

$$\begin{aligned} Q &= \lim_{z\to 1} G(z,t) , \\ \langle n\rangle &= \lim_{z\to 1} \frac{\partial}{\partial z} G(z,t) , \end{aligned} \tag{3.5}$$

are particularly useful because they are shown to be simply related to the fluorescence intensity and the quantum yield.

We shall now obtain from Eqs. (3.1) and (3.2), the explicit solutions for three initial distributions which are motivated by physical considerations.

A. δ-function distribution

The importance of this initial distribution stems from the fact that, by superposing solutions of appropriately weighted δ-function distributions, one can, in principle, solve the problem for any initial distribution. The generating function for a δ-function distribution at $m = l$, which represents the excitation being localized at l, is

$$G_0(z) = \sum_m \delta_{lm} z^m = z^l \,. \tag{3.6}$$

From Eqs. (3.1) and (3.6) we obtain

$$\begin{aligned} G(z, t) = {} & e^{(-b+Dv')t}(\Gamma^+ - \Gamma^-)^D \\ & \times \{[\Gamma^-(\Gamma^+ - z) + \Gamma^+(z - \Gamma^-)e^{-vt}]^l \\ & \times [(\Gamma^+ - z) + (z - \Gamma^-)e^{-vt}]^{-(l+D)}\} . \end{aligned} \tag{3.7}$$

Using the following expansion,[18a]

$$\begin{aligned} & (1 - y)^{a-c}(1 - y + sy)^{-a} = \sum_{n=0}^{\infty} y^n \frac{(c+n)!}{n!c!} F(-n; a; c; s) , \\ & |y|, |y(1 - s)| < 1 , \end{aligned} \tag{3.8}$$

and Eq. (3.7), we obtain the required (exact) solutions for $P_m(t)$:

$$\begin{aligned} P_m(t) = {} & g_m e^{(-b+Dv')t}(\Gamma^+ - \Gamma^-)^D e^{-l\beta} A_1'^{\,m+l} B_1'^{\,-(m+l+1)} \\ & \times F(-l, -m, D, s) , \end{aligned} \tag{3.9}$$

where F is the hypergeometric function and

$$A_1' = e^{\beta}(1 - e^{-vt}) , \quad B_1' = (\Gamma^+ - \Gamma^- e^{-vt}) ,$$

$$C_1' = (\Gamma^- - \Gamma^+ e^{-vt}) , \quad s = \left(1 - \frac{B_1' C_1'}{A_1'^2}\right) ,$$

$$g_m = (m + D - 1)! / m! \, (D - 1)!$$

From (3.9) or otherwise, the particular derived quantities, the total probability Q and the first moment $\langle n \rangle$, are shown to be

$$\begin{aligned} Q_l &= e^{(-b+Dv')t}(\Gamma^+ - \Gamma^-)^D \{[\Gamma^-(\Gamma^+ - 1) + \Gamma^+(1 - \Gamma^-)e^{-vt}]^l [(\Gamma^+ - 1) + (1 - \Gamma^-)e^{-vt}]^{-(l+D)}\} , \\ \langle n_l \rangle &= \{-l(\Gamma^- - \Gamma^+ e^{-vt})[\Gamma^-(\Gamma^+ - 1) + \Gamma^+(1 - \Gamma^-)e^{-vt}]^{-1} + (l + D)(1 - e^{-vt})[(\Gamma^+ - 1) + (1 - \Gamma^-)e^{-vt}]^{-1}\} Q_l . \end{aligned} \tag{3.10}$$

B. Boltzmann distribution

Excited-state distributions immediately following optical excitation have often been treated as having a Boltzmann form with a characteristic temperature that is different (in general) from the environment temperature and consistent with the initial energy. Examples may be found in the analysis of situations involving the fast intramolecular relaxation of large molecules in the gaseous phase due to anharmonic interactions followed by a slower collision-induced relaxation process. Such an analysis is justified if there does indeed exist a fast preliminary process leading to equilibration at a nonenvironment temperature. In any case initial Boltzmann distributions introduce considerable algebraic simplicity in the calculations and, by a suitable choice of the temperature, can be used to represent the actual distributions.

An initial Boltzmann distribution at a temperature $T_0 = \hbar\omega / k_B \beta_0$ is given by the expression

$$P_m(0) = g_m(1 - e^{-\beta_0})^D e^{-m\beta_0} . \tag{3.11}$$

Combining Eqs. (3.6), (3.7), and (3.11), we obtain

$$G_0(z) = (1 - e^{-\beta_0})^D (1 - z e^{-\beta_0})^{-D} , \tag{3.12a}$$

$$\begin{aligned} G(z, t) = {} & e^{(-bt+Dv't)}(\Gamma^+ - \Gamma^-)^D (1 - e^{-\beta_0})^D \\ & \times \{1 - e^{-\beta_0}[\Gamma^-(\Gamma^+ - z) + \Gamma^+(z - \Gamma^-)e^{-vt}] \\ & \times [(\Gamma^+ - z) + (z - \Gamma^-)e^{-vt}]^{-1}\}^{-D} \\ & \times [(\Gamma^+ - z) + (z - \Gamma^-)e^{-vt}]^{-D} . \end{aligned} \tag{3.12b}$$

Expanding $G(z, t)$ as a power series in z, we obtain

$$P_m(t) = g_m \, \mathfrak{A}(t) \exp[-m\beta(t)] , \tag{3.13a}$$

where

$$\begin{aligned} \mathfrak{A}(t) &= e^{-bt+Dv't}(\Gamma^+ - \Gamma^-)^D (1 - e^{-\beta_0})^D \\ & \quad \times [(\Gamma^+ - \Gamma^- e^{-vt}) - e^{\beta - \beta_0}(1 - e^{-vt})]^{-D} \\ &= e^{-bt+Dv't}[(1 - e^{-\beta_0})(1 - \Gamma^- e^{-\beta_0})^{-1}]^D \\ & \quad \times (1 - \Gamma^- e^{-\beta(t)})^D , \end{aligned} \tag{3.13b}$$

$$\beta(t) = \ln\left(\frac{\Gamma^+(1 - \Gamma^- e^{-\beta_0}) - \Gamma^-(1 - \Gamma^+ e^{-\beta_0})e^{-vt}}{(1 - \Gamma^- e^{-\beta_0}) - (1 - \Gamma^+ e^{-\beta_0})e^{-vt}}\right) . \tag{3.13c}$$

Note that the solution (3.13a) for the probabilities retains the form invariance under linear decay. This and other interesting properties of this distribution have been discussed earlier.[10a,b] This form invariance will be utilized in obtaining closed analytic expressions for quantities such as optical line shapes in Secs. IV and V. The moments in this case are given by

$$Q = \mathfrak{A}(t)(1 - e^{-\beta(t)})^{-D} , \tag{3.14a}$$

$$\langle n \rangle = D[\exp\beta(t) - 1]^{-1} Q . \tag{3.14b}$$

C. Poisson and Laguerre distributions

The Poisson and Laguerre polynomial distributions occur naturally in single oscillator radiative transitions. It is shown in Appendix A that, when under a uniform wide-band excitation an optical transition occurs from a Boltzmann ground-state distribution, the distribution in the excited state is given by a weighted Laguerre polynomial

$$\begin{aligned} P_m = {} & (1 - e^{-\beta}) \exp[-\tfrac{1}{2}a^2(1 - e^{-\beta}) - m\beta] \\ & L_m(-2a^2 \sinh^2(\beta/2)) . \end{aligned} \tag{3.15}$$

The zero-temperature limit of this expression yields the familiar Poisson distribution in the excited state:

$$P_m=(e^{-a^2/2}/m!)(\tfrac{1}{2}a^2)^m . \tag{3.16}$$

Hence, it is instructive to obtain solutions for both these initial distributions. Using the following expressions[18b] for the series expansion and the generating function of Laguerre polynomials,

$$L_n(y)=\sum_{k=0}^{n} {}^{n}c_k \frac{(-y)^k}{k!} \tag{3.17a}$$

$$\sum_n \alpha^n L_n(y)=(1-\alpha)^{-1}e^{y\alpha/(\alpha-1)} , \tag{3.17b}$$

we obtain, from Eqs. (3.15) and (3.16),

$$\Big[G_0(z)=\sum_m g_m z^m P_m(0)\Big]_{\text{Poisson}}$$

$$=e^{-a^2(1-z)/2}L_{D-1}(-\tfrac{1}{2}a^2 z) , \tag{3.18}$$

$$\Big[G_0(z)=\sum_m g_m z^m P_m(0)\Big]_{\text{Laguerre}}$$

$$=\frac{e^{-a^2/2}}{(D-1)!}\frac{\partial}{\partial z^{D-1}}\left\{\frac{z^{D-1}}{1-ze^{-\beta}}\exp\left[\frac{yze^{-\beta}}{ze^{-\beta}-1}\right]\right\} , \tag{3.19}$$

where

$$y=-2a^2\sinh^2(\beta/2) .$$

Explicit expressions for the P_m's can be obtained from Eqs. (3.18) and (3.19) for any given value of the degeneracy D. Here we restrict the analysis to the case $D=1$ for algebraic simplicity. Using (3.1) and (3.18), we obtain, for the Poisson distribution,

$$G(z,t)=B_2(t)(1-z\alpha_2)^{-1}\exp\{zy_2\alpha_2/(z\alpha_2-1)\} ,$$

$$P_m(t)=B_2(t)\alpha_2^m L_m(y_2) ,$$

where

$$B_2(t)=[D_2']^{-1}(\Gamma^+-\Gamma^-)\exp\{-bt+v't-\tfrac{1}{2}a^2B_2'[D_2']^{-1}\} ,$$

$$y_2=\tfrac{1}{2}a^2\{B_2'[D_2'^{-}]^{-1}-A_2'[C_2']^{-1}\} ,\quad \alpha_2=C_2'[D_2']^{-1} ,$$

$$A_2'=(\Gamma^+-1)e^{-vt}+(1-\Gamma^-) ,$$

$$B_2'=(\Gamma^+-1)\Gamma^-e^{-vt}+\Gamma^+(1-\Gamma^-) ,$$

$$C_2'=(1-e^{-vt}) ,\quad D_2'=(\Gamma^+-\Gamma^-e^{-vt}) . \tag{3.20}$$

Similarly, for the Laguerre polynomial distribution,

$$G(z,t)=B_3(t)(1-z\alpha_3)^{-1}\exp\{zy_3\alpha_3/(z\alpha_3-1)\} ,$$

$$P_m(t)=B_3(t)\alpha_3^m L_m(y_3) ,$$

where

$$B_3(t)=(\Gamma^+-\Gamma^-)[D_3']^{-1}(1-e^{-\beta})$$

$$\times\exp\{-bt+v't-a^2e^{-\beta/2}\sinh(\beta/2)+B_3'[D_3']^{-1}\} ,$$

$$y_3=A_3'[C_3']^{-1}+B_3'[D_3']^{-1} ,$$

$$\alpha_3=C_3'[D_3']^{-1} ,$$

$$A_3'=-2a^2\sinh^2(\beta/2)e^{-\beta}(\Gamma^+e^{-vt}-\Gamma^-) ,$$

$$B_3'=-2a^2\sinh^2(\beta/2)(1-e^{-vt}) ,$$

$$C_3'=(1-e^{-vt})+e^{-\beta}(\Gamma^+e^{-vt}-\Gamma^-) ,$$

$$D_3'=(\Gamma^+-\Gamma^-e^{-vt})-(1-e^{-vt}) . \tag{3.21}$$

Expressions (3.22) and (3.23) for the probabilities are useful in predicting line shapes for wide-band excitations. The zeroth and first moments for these distributions are obtained from Eqs. (3.20) and (3.21) to be

$$Q_{\text{Poisson}}=\frac{(\Gamma^+-\Gamma^-)}{D_2'-C_2'}\exp\left[-bt+v't-\frac{a^2}{2}\left(\frac{B_2'-A_2'}{D_2'-C_2'}\right)\right] ,$$

$$\langle n\rangle_{\text{Poisson}}\quad \frac{Q_{\text{Poisson}}}{(D_2'-C_2')}\left((1-e^{-vt})+\tfrac{1}{2}a^2\frac{(\Gamma^+-\Gamma^-)^2}{(D_2'-C_2')}e^{-vt}\right) , \tag{3.22}$$

$$Q_{\text{Laguerre}}=\frac{(\Gamma^+-\Gamma^-)(1-e^{-\beta})}{D_3'-C_3'}$$

$$\times\exp\bigg(-bt+v't$$

$$-\tfrac{1}{2}a^2e^{-\beta/2}\sinh(\beta/2)+\frac{A_3'+B_3'}{C_3'-D_3'}\bigg) ,$$

$$\langle n\rangle_{\text{Laguerre}}=Q_{\text{Laguerre}}\frac{C_3'D_3'-C_3'^2-B_3'C_3'-A_3'D_3'}{D_3'-C_3'} . \tag{3.23}$$

IV. NONLINEAR DECAY RATES: PERTURBATIVE APPROACHES

The assumption that the decay rates are linear in the vibrational energy is obviously not valid universally [see, for instance, Eq. (2.6)]. Nonlinear decay rates result in partial differential equations for the generating function $G(z,t)$ which cannot be solved exactly [see Eq. (2.16)]. We have therefore constructed two separate perturbative schemes. Both are based on the general development[19] wherein one observes the chain condition,

$$\mathcal{P}(t)=K(t-\tau)\mathcal{P}(\tau) ,\quad t\geq\tau , \tag{4.1}$$

satisfied by the probability vector $\mathcal{P}(t)$ (where K is the propagator) and develops the perturbation series

$$K(t)=K_0(t)+\int d\tau\, K_0(t-\tau)BK_0(\tau)+\cdots . \tag{4.2}$$

Here $P(t)$ and $K(t)$ satisfy the equations

$$\frac{dP}{dt}=(A+B)\mathcal{P} , \tag{4.3}$$

$$\frac{dK}{dt}=(A+B)K+I\delta(t) , \tag{4.4}$$

I being the identity, A and B being respectively, the exactly analyzable and the perturbation parts of the evolution matrix, and $K_0(t)$ being the solution of (4.4) for $B=0$.

The convergence (and therefore the usefulness) of the perturbation series (4.2) depends crucially on what part of the evolution matrix one chooses as the perturbation B. We identify two separate exactly soluble parts of the evolution matrix: (i) the linear-relaxation and linear-decay terms, and (ii) the "downward"-relaxation terms (which would constitute the entire relaxation matrix at $T=0$) accompanied by *all* other nonlinear decay terms. In case (i) we treat the nonlinear decay terms as the perturbation. This scheme works at all temperatures but is restricted to small nonlinearities.[20] Case (ii) provides a practically more useful scheme. In it we analyze the nonlinear terms exactly by solving a cascade problem and treat the "upward"-relaxation terms (which are reduced with respect to the "downward" terms by bias factors $e^{-\beta}$) as the perturbation. The greater usefulness of scheme (ii) stems from the fact that in several actual experimental situations there is considerable nonlinearity and $k_BT/\hbar\omega$ is much smaller than 1.

A. Perturbative-scheme (i)

In scheme (i) the matrix A, representing the exactly soluble unperturbed part of the full evolution, is given by

$$A=k\begin{pmatrix} -(e^{-\beta}+b) & 1 & 0 & \cdots \\ 1e^{-\beta} & -(1+2e^{-\beta}+b+c) & 2 & \cdots \\ 0 & 2e^{-\beta} & -(2+3e^{-\beta}+b+2c) & \cdots \\ \cdot & \cdot & \cdot & \\ \cdot & \cdot & \cdot & \\ \cdot & \cdot & \cdot & \cdots \end{pmatrix}. \tag{4.5}$$

The perturbation B is a diagonal matrix given by

$$B_{mn}=\left(\sum_{r=2} b_r m^r\right)\delta_{mn}\equiv B_m\delta_{m,n}\,, \tag{4.6}$$

and the propagator $K_0(t)$ is given by

$$K_0(t)=\begin{pmatrix} p_0^0 & p_0^1 & \cdots & p_0^m & \cdots \\ p_1^0 & p_1^1 & \cdots & & \cdots \\ p_m^0 & p_m^1 & \cdots & p_m^m & \cdots \\ \cdot & \cdot & & \cdot & \\ \cdot & \cdot & & \cdot & \\ \cdot & \cdot & & \cdot & \end{pmatrix}, \tag{4.7}$$

where $p_m^l(t)$ is the mth element of the solution of (4.3) with $B=0$, for the initial condition $p_n(0)=\delta_{l,n}$. These $p_m^l(t)$'s are explicitly given by (3.9) for all l and m. The probability with the first-order correction is

$$P_m(t)=p_m(t)+\int_0^t \sum_s \sum_r p_m^r(t-\tau)B_r p_r^s(\tau)P_s(0)\,d\tau\,, \tag{4.8}$$

where

$$p_m(t)=\sum p_m^l(t)P_l(0)\,. \tag{4.9}$$

As an application of this result consider the perturbation matrix B to represent quadratic decay terms

$$B_{mn}=-dn^2\delta_{m,n}\,. \tag{4.10}$$

For simplicity we consider an initial Boltzmann distribution at temperature $T_0=\hbar\omega/k_B\beta_0$. Substituting Eq. (4.9) in Eq. (4.8) we obtain

$$P_m(t)=p_m(t)-d\left[m_2 p_{m-2}(t)+m_1 p_{m-1}(t)+m_0 p_m(t)\right]. \tag{4.11}$$

The total probability Q and the first moment $\langle n\rangle$ are given, respectively, by

$$\begin{gathered} Q=Q_0[1-d\,m_3]\;, \\ \langle n\rangle=\langle n_0\rangle\,[1-dm_4]-dm_5Q_0\,. \end{gathered} \tag{4.12}$$

The details of the calculations and the functions M_1 to M_5 are given explicitly in Appendix B.

Instead of evaluating these corrections separately, we shall study the fluorescence intensity in a situation wherein there is a linearly increasing radiative rate cm and a nonradiative quadratic perturbation dm^2. Recalling the expressions for the time-resolved intensity from (1.3b) and denoting the exact and perturbed intensities by I_0 and I respectively, gives,

$$I(t)=I_0(t)-[bdm_3+cdm_5]Q_0-cdm_4\langle n_0\rangle. \tag{4.13}$$

The two intensities are plotted as functions of time in Fig. 1.

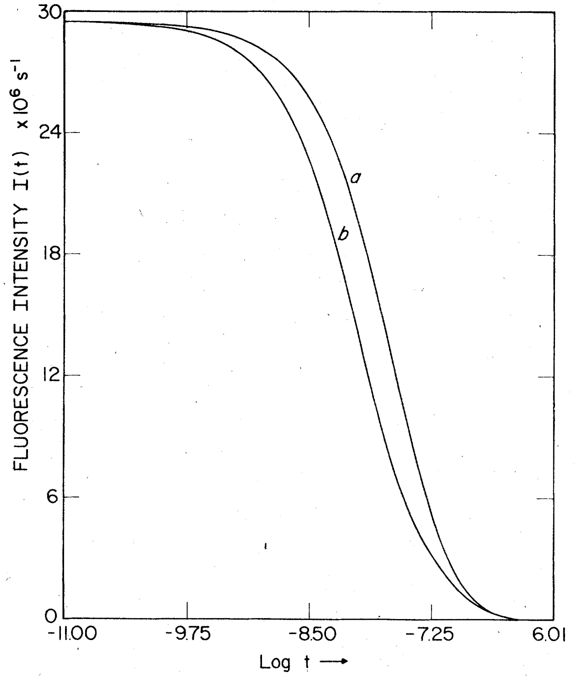

FIG. 1. Flourescence intensity for linear radiative decay (curve *a*); with additional quadratic nonradiative decay (curve *b*). Parameter values are $b=k=10^7$ sec^{-1}, $c=10^6$ sec^{-1}, $d=2.5\times10^4$ sec^{-1}, $D=1$.

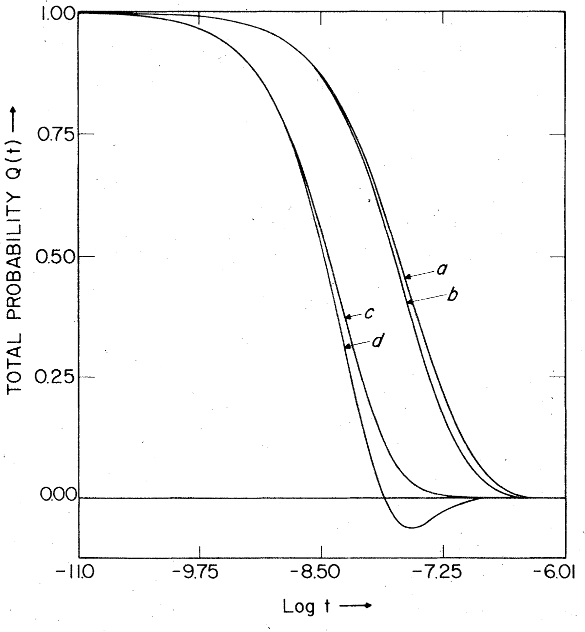

FIG. 2. Comparison of the solutions for the total probability: exact (curves *a, c*) and perturbative (curves *b, d*) results of scheme (i). Parameter values are $b=k=10^7$ sec^{-1}, $c'=c=10^6$ sec^{-1}, $D=1$ for curves *a, b* and $D=5$ for curves *c, d*.

As a check on the reliability of this perturbation scheme we use it in a case where the exact solution is known and can be compared with the solution given by the scheme. Thus for

$$B_{mn}=c'n\delta_{m,n}, \tag{4.14}$$

the scheme yields

$$\begin{aligned} P_m(t)&=p_m(t)+c'[\mathfrak{N}_1 p_{m-1}(t)+\mathfrak{N}_0 p_m(t)],\\ Q&=Q_0[1-c'D\mathfrak{N}_2],\\ \langle n\rangle&=\langle n_0\rangle[1-c'(D+1)\mathfrak{N}_2]-Q_0c'D\mathfrak{N}_3. \end{aligned} \tag{4.15}$$

As before, the functions $\mathfrak{N}_0$ to $\mathfrak{N}_3$ are given in Appendix B. A comparison of the exact and the perturbative solutions for Q is made in Fig. 2. Needless to say, the negativity of the probability is an unphysical characteristic and stems from the breakdown of the perturbation scheme for large times. Generally, the higher-order corrections extend the breakdown time. Note that the correction term is proportional to D. This causes the deviation from the exact solution to increase with the dimensionality of the oscillator: the larger the value of D, the shorter is the time for which the perturbative approach is valid. This can be seen in Fig. 2 where curves (c) and (d) have been plotted for $D=5$.

B. Perturbative-scheme (ii)

In scheme (ii) the unperturbed problem involves the solution of a cascade problem. Equation (2.14) yields, for the initial condition $p_m(0)=\delta_{m,n}$,

$$\begin{aligned} &\frac{1}{k}\frac{dp_m}{dt}+\left(m+\frac{\alpha_m}{k}\right)p_m=0, \quad m=n\\ &\frac{1}{k}\frac{dp_m}{dt}+\left(m+\frac{\alpha_m}{k}\right)p_m=(m+1)p_{m+1}, \quad m<n\\ &p_m=0, \quad m>n. \end{aligned} \tag{4.16}$$

The perturbation of the mth level is given by the *drain* term, $(m+D)e^{-\beta}p_m$, and the *feed* term, $(m+D-1)e^{-\beta}p_{m-1}$ which connect the mth level to the $(m+1)$th and $(m-1)$th level respectively. Hence the perturbation matrix has the form

$$B_{mn}=-(m+D)e^{-\beta}\delta_{mn}+(m+D-1)e^{-\beta}\delta_{m,n+1}. \tag{4.17}$$

The solution of Eq. (4.14) is obtained trivially through Laplace transforms or otherwise:

$$p_m^n(t)=\frac{n!}{m!}k^{n-m} \times\sum_{l=m}^{n}\left\{\prod_{\substack{j\neq l\\ m,n}}[k(j-l)+\alpha_j-\alpha_l]\right\}^{-1}e^{-(klt+\alpha_l t)}. \tag{4.18}$$

Obviously for $m>n$, $p_m^n(t)=0$. Hence the propagator is a matrix of the form

$$K_0(t)=\begin{pmatrix} p_0^0 & p_0^1 & p_0^2 & \cdots & p_0^r & \cdots \\ & p_1^2 & p_1^2 & \cdots & p_1^r & \cdots \\ & & p_2^2 & \cdots & p_2^r & \cdots \\ \text{zero} & & & \cdots & \cdot & \cdots \end{pmatrix}. \tag{4.19}$$

By inspection the probability at the mth level with the first-order correction is seen to be

$$P_m^n(t)=p_m^n(t)+ke^{-\beta}\int_0^t d\tau\left(\sum_{r=m}^{n+1} p_m^r(t-\tau)(r+D-1)p_{r-1}^n(\tau)-\sum_{r=m}^{n} p_m^r(t-\tau)(r+D)p_r^n(\tau)\right). \tag{4.20}$$

From Eq. (4.17), one can calculate all relevant quantities such as the differential photon count rate and the quantum yield. If α^R is the radiative part of the decay, the differential photon count rate is

$$I^n(t)=\sum_{m=0}^{n+1}\alpha_m^R p_m^n(t), \tag{4.21}$$

where the superscript n on $I(t)$ indicates that the excitation was initially on level n. The quantum yield to first order can be obtained as follows:

$$\begin{aligned}\Phi^n=\sum_{m=0}^{n+1}\alpha_m^R\int_0^\infty P_m^n(t)\,dt=&\sum_{m=0}^{n}\alpha_m^R\frac{n!}{m!}k^{n-m}\left\{\prod_{j=0}^{n-m}[k(n-j)+\alpha_{n-j}]\right\}^{-1}\\ &+ke^{-\beta}\left\{\sum_{m=0}^{n+1}\alpha_m^R\sum_{r=m}^{n+1}\frac{n!}{m!}(r+D-1)k^{n+1-m}\left[\prod_{j=0}^{r-m}k(r-j)+\alpha_{r-j}\right]^{-1}\left[\prod_{l=0}^{n-r+1}k(n-l)+\alpha_{n-l}\right]^{-1}\right.\\ &\left.-\sum_{m=0}^{n}\alpha_m^R\sum_{r=m}^{n}\frac{n!}{m!}(r+D)k^{n-m}\left[\prod_{j=0}^{r-m}k(r-j)+\alpha_{r-j}\right]^{-1}\left[\prod_{l=0}^{n-r}k(n-l)+\alpha_{n-l}\right]^{-1}\right\}.\end{aligned} \tag{4.22}$$

Despite its formidable appearance this expression is easily evaluated numerically. A similar expression including the quadratic correction is used in the next section to compute the quantum yield in the presence of radiationless transitions.

Finally, as in the case of scheme (i), we check the reliability of this scheme by comparing the solutions with the exact results of Sec. III. When α_m is linear, i.e.,

$$\alpha_m=b+cm, \tag{4.23}$$

one can obtain the solutions of Eq. (4.14) in terms of Bernoulli distributions. It is easy to see that the solutions $p_m(t)$'s are then

$$\begin{aligned}p_m^n(t)&=\lim_{z\to 0}\frac{1}{m!}\frac{\partial}{\partial z^m}\left\{e^{-bt}\left[e^{-(k+c)t}+z\frac{k}{k+c}\right.\right.\\ &\qquad\left.\left.\times(1-e^{-(k+c)t})\right]\right\}^n\\ &=e^{-bt}e^{-(k+c)mt}\left(\frac{k}{k+c}\right)^{n-m}(1-e^{-(k+c)t})^{n-m},\quad n\geq m,\\ p_m^n(t)&=0,\quad n<m.\end{aligned} \tag{4.24}$$

Using the solution (4.21) and Eq. (4.17) one can calculate the first-order correction to the probability explicitly. The total probability is then obtained by summing over the individual (corrected) probabilities and is compared with the exact solution in Eq. (3.10a). The comparison is shown in Fig. 3. The system is assumed to be excited initially at the tenth level, and the exact solution represented by Eq. (3.10) is shown as the solid curve. Since the exact probability is very insensitive to temperature and has nearly identical values for all three temperatures ($2\hbar\omega/k_B$, $\hbar\omega/k_B$, $\frac{2}{3}\hbar\omega/k_B$) we have chosen, only one curve has been drawn at $T=2\hbar\omega/k_B$. The perturbation solutions converge to the exact solution at low temperature but shown considerable deviation from it as the temperature increases.

V. APPLICATIONS

As illustrative applications of our theory, we present two calculations, one of which is exact and employs the results of Sec. III, the other being approximate and based on the perturbative development in Sec. IV.

A. Exact line-shape calculations

In earlier analyses of time-resolved emission and absorption line shapes, relaxation was decoupled from the emission process and the probabilities so obtained were used to compute the spectrum.[21a,b] Such a calculation is valid only if the emission or absorption process is level independent. In principle, Eq. (1.3c) can be used in conjunction with the results in Sec. III to predict the line shape for an *arbitrary* initial distribution. However, attention is here focused only on an initial Boltzmann distribution since it yields a usable result in a closed form.

The explicit form of Eq. (1.3c) is

$$I(\Omega,t)=C\sum_{n,m}|\langle n|m\rangle|^2[E_0+(m-n)\hbar\omega]^3 \times P_m(t)\delta(E_0+(m-n)\hbar\omega-\hbar\Omega)\,, \qquad (5.1)$$

where C is a constant of proportionality which includes the electronic matrix element and $|\langle n|m\rangle|^2$ are the Franck-Condon factors.

Using Eqs. (3.13a)–(3.13c), (A3a) and the following identity[18c]

$$\sum_{n=0}^{\infty}\frac{n!}{n+p!}L_n^p(x)L_n^p(y)z^n = [(1-z)^2xyz]^{-1/2}e^{-z(x+y)(1-z)^{-1}} \times I_p(2(xyz)^{1/2}(1-z)^{-1})\,, \qquad (5.2)$$

we obtain

$$I(\Omega,t)=C(\hbar\Omega)^3\mathcal{Q}(t)[1-e^{-\beta(t)}]^{-1} \times \exp(-\{p\beta(t)+a^2\coth[\beta(t)/2]\}/2) \times I_p(\tfrac{1}{2}a^2\,\mathrm{csch}[\beta(t)/2])\,, \qquad (5.3)$$

where $\Omega=E_0+ph\omega$ and I_p is the pth-order Bessel function with imaginary argument.

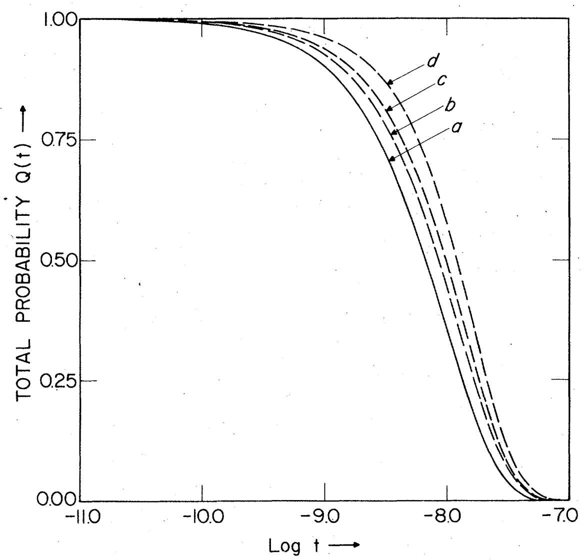

FIG. 3. Comparison of the solution for the total probability: exact (solid curve) and perturbative (dashed curves) results of scheme (ii). Parameter values are $b=5\times10^6$ sec^{-1}, $k=10^6$ sec^{-1}, $c=10^7$ sec^{-1}, $D=1$, $\beta=1.5$, 1, and 0.5 for curves b, c, and d, respectively.

The frequency-resolved spectra are plotted at different times in Fig. 4 in units of $\hbar\omega$. The spectra are initially broad but relax to those with narrow half-widths at later times. This is easily explained since at short times the temperature of the excited state is high and many of the upper levels are occupied. These have Franck-Condon factors to a broad range of levels in the ground state and hence the spectra are broad. At longer times the temperature drops down and only the lower levels of the excited state are populated to a nonnegligible extent. These levels have appreciable Franck-Condon factors only for a limited set of levels in the ground state and the spectra are consequently narrow.

An interesting feature of these spectra is that the position of the peak does not shift in time. This is directly connected to the observation made by Huang and Rhys[22a] and by Lax[22c] to the effect that spectral peaks from *time-independent* Boltzmann distributions do not shift with *temperature.* The connection arises from the following facts: (i) the point of departure of the analysis in Ref. 22 is the expression $e^{-p\beta/2}\,I_p(\frac{1}{2}a^2\,\mathrm{csch}(\beta/2))$ which also occurs in our Eq. (5.3) but with time-dependent β's; (ii) the maximization procedure required for the peak shifts with *temperature* on one hand,

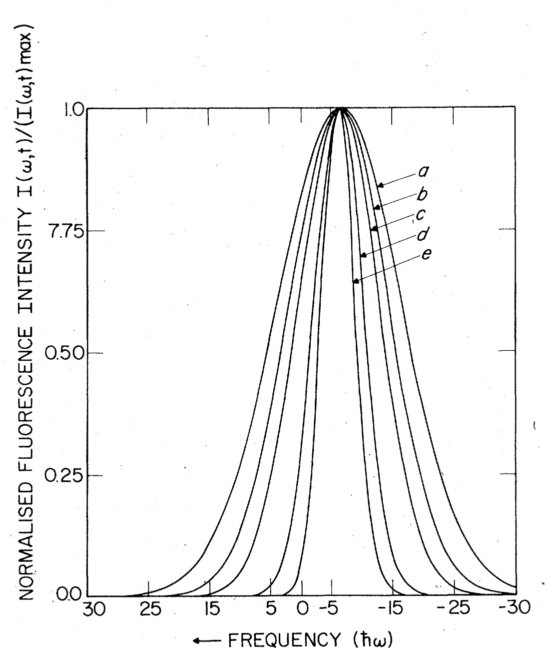

FIG. 4. Time and frequency resolved line shape. Parameter values are $k=10^9$ sec^{-1}, $b=10^8$ sec^{-1}, $c=10^7$ sec^{-1}, $\frac{1}{2}a^2=5\ \hbar\omega$, $\beta_0=\hbar\omega/k_BT_0=0.1$, $\beta=\hbar\omega/k_BT=1.5$. The curves a, b, c, d, and e are plotted at times 0.0 sec, 5×10^{-10} sec, 1×10^{-9} sec, 2.5×10^{-9} sec, and 5×10^{-9} sec respectively.

and with *time* on the other, are identical. The frequency p_0 at which the peak occurs is obtained by solving for the roots of the equation

$$\frac{\partial}{\partial p}\left[e^{-p\beta/2}I_p(z)\right] = e^{-p\beta/2}\left([-p+\ln(z/2)]I_p(z) - \sum_{m=1}^{\infty}\left(\tfrac{1}{2}z\right)^{2m+\nu}\frac{\psi(p+m+1)}{m!\,(m+p)!}\right)=0\,, \tag{5.4}$$

where $z=\frac{1}{2}a^2\operatorname{csch}(\beta/2)$ and ψ is the logarithmic derivative of a Γ function.[18d] Although the transcendental nature of this equation has prevented an explicit solution for p_0 in terms of $\beta(t)$, several conclusions have been drawn earlier[22] for limiting values of the parameter. Thus Huang and Rhys[22a] and Markham[22b] showed that for large values of the Stoke's shift parameter $\frac{1}{2}a^2$, the peak lies at $p_0=-\frac{1}{2}a^2$ for the case of high and low temperatures. Lax[22c] concluded from his analysis of the moments of the spectra that for large $\frac{1}{2}a^2$, the peak lies at $p_0=-\frac{1}{2}a^2$. Our own numerical calculation from Eq. (5.3) shows the same result for a wide range of intermediate values for temperature (ranging from 10 $\hbar\omega/k_B$ to 0.1 $\hbar\omega/k_B$) and for $\frac{1}{2}a^2$ (ranging from 10 to 1). These results are also in agreement with those of Dexter.[2]

Thus, although no formal proof exists, it seems that a probability evolution which is of the (time-dependent) Boltzmann form would yield no peak shift in time. If this is true, monitoring the peak shift in time would provide an experimental test of whether or not such a Boltzmannization does occur. This is more than an academic point because questions have been raised concerning the validity of several theoretical calculations particularly for radiationless transitions, which have assumed a rapid Boltzmannization.[23] It is to be pointed out, however, that this discussion is restricted to systems in which the frequency in the excited and ground states is nearly equal since a closed equation, like (5.3), is obtained only if the frequencies in the two states are identical.[24]

B. Fluorescence quantum yield in the presence of nonradiative processes

Experiments in aromatic and other large molecules have shown that the nonradiative decay processes such as internal conversion (IC) and intersystem crossing (ISC) are strongly level dependent.[25-27] Theoretical studies[28] carried out for various molecular models are in good agreement qualitatively and in reasonable agreement quantitatively with the experimental results. One of the predictions of these theories[27,28] is that the $S_1 \rightarrow S_0$ IC rate is more strongly level dependent than the ISC rate for large excitation energies. The exact form of the energy dependence varies from model to model but many of the results indicate IC rates that increase as fast as or faster than an exponential, beyond a critical energy. Such a rapid increase in the nonradiative decay rate has been observed in naphthalene[27] and has been interpreted to be mainly due to IC. Here we model such a decay rate and then predict the quantum yield as a function of initial excitation energy. Clearly, since the nonradiative decay is dominant over all the other rates, we will use the second perturbation scheme.

When several interacting modes are present in the molecule one may use the effective-frequency model developed by Freed and Heller.[9a,b] In this model the effective frequency ω_{eff} is proportional to the amount of energy removed per collision and hence is dependent on the collision partner. A more detailed analysis of this model will be found in Ref. 9a. We will assume for simplicity that we initially populate a single vibrational level whose energy is consistent with the excitation energy of the incoming photon. Our values for the model parameters are essentially those used to explain[9,26] vapor-phase data of naphthalene:

$$\omega=300\ \text{cm}^{-1}\ \text{(effective oscillator frequency)}$$

$$D=2\ \text{(oscillator degeneracy)}\,. \tag{5.5}$$

The radiative decay rate increases linearly with the energy. On the other hand, the nonradiative decay increases linearly with energy upto a certain critical energy and then increases exponentially. This critical energy has been chosen to be $25\hbar\omega$:

$$\begin{aligned}\alpha_m^R &= b+cm\\ \alpha_m^{NR} &= b'+c'm\,,\quad m\le 25\\ &= \alpha_{25}^{NR}\,e^{\lambda m}\,,\quad m>25\,.\end{aligned} \tag{5.6}$$

We choose $b=5\times10^6\ \text{sec}^{-1}$, $c=2.5\times10^5\ \text{sec}^{-1}$, $b'=5\times10^5\ \text{sec}^{-1}$, $c'=7.5\times10^5\ \text{sec}^{-1}$, and $\lambda=0.05$.

Extending Eqs. (4.22) to include quadratic corrections and using the parameter values in Eqs. (5.5) and (5.6), we have computed the quantum yield for various excitation energies for different values of k. The results are exhibited in Fig. 5. As can be seen for high excitation energies the yield increases as the relaxation rate k increases. This is because the excitation loses energy fast at higher pressures, populating levels with smaller nonradiative decay. The reverse happens at very low excitation energies. As k increases, the excitation gains energy, causing the quantum yield

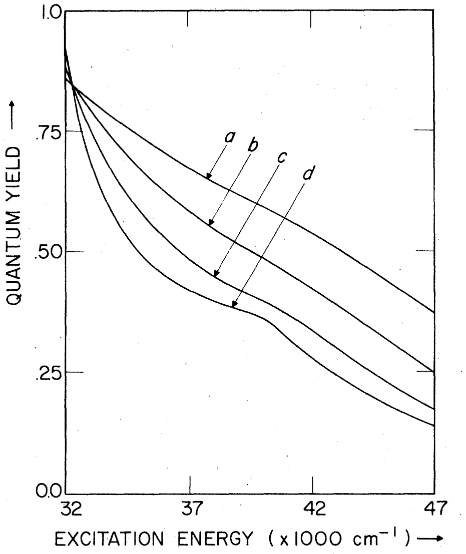

FIG. 5. Quantum yield as a function of the relaxation rate k (or equivalently, the pressure). For curves, a, b, c, and d, k equals 1×10^6 sec^{-1}, 1×10^7 sec^{-1}, 2.5×10^7 sec^{-1}, and 5×10^7 sec^{-1} respectively. See the text for other parameters.

to drop. This gives rise to the observed intersection of the yield curves. A similar effect has been observed in the fluorescence decay curves by Beddard *et al.*[26] For intermediate excitation energies one observes a sharp bend in the yield curve at low pressures. This bend corresponds to the critical excitation energy beyond which the radiationless decay increases exponentially. At higher pressures this bend is no longer pronounced and disappears altogether for very high pressures.

VI. CONCLUSION

We have presented above a master-equation theory of the interplay of vibrational relaxation with *intra*molecular decay processes, our primary interest being in radiative decay although we have also applied the techniques to situations involving nonradiative transitions. This development is closely related to the master-equation theory of the effects of relaxation on *inter*molecular excitation *transfer* constructed by Kenkre.[13] In fact, a formalism for describing the interplay of *all* three processes (relaxation, transfer, and luminescence) has been presented in Ref. 13 where it has also been shown how detailed techniques developed for the relaxation-luminescence problem (such as those described in the present paper) can be "borrowed" for the relaxation-transfer problem through the use of a certain transformation.[29] We also refer the reader to Ref. 13 for the discussion of the validity of such master-equation approaches. Here we only remark that among future problems to be tackled in this area, an important one is, in our opinion, that of working out the relation of these theories to the microscopic approaches of Nitzan and Jortner[4] and of Hizhnyakov and Tehver.[5] We indeed believe that the complexity of the field demands that the microscopic and the master-equation approaches be developed and used side by side.

Summarizing the primary results obtained in this paper, we note that (i) the exact solutions for the probabilities of individual vibrational levels are given in Eqs. (3.9), (3.13), (3.20), and (3.21) for the physically motivated initial distributions of the δ-function, Boltzmann, Poisson, and Laguerre forms, respectively; (ii) an illustrative application of these results may be found in the exact time-and-frequency-resolved spectrum exhibited in Eq. (5.3); (iii) the two perturbative schemes for nonlinear rates are represented by Eqs. (4.13) and (4.20), and Figs. 2, 3, and 5; (iv) the demonstrations that optical excitation from a Boltzmann ground (electronic)-state results in a Laguerre distribution in the excited state is in Appendix A and leads to Eq. (A6); and (v) the expressions for radiative decay rates calculated explicitly in terms of Franck-Condon factors are displayed in Eqs. (2.1)–(2.10).

Finally, we point out that the assumption that the Montroll-Shuler equation describes the actual details of the vibrational relaxation may be far fetched for certain real systems. The inapplicability of the equation may arise from at least three separate sources: (i) the actual relaxation rates may be nonlinear in the energy; (ii) the rates may be nonlocal in energy space, i.e. they may involve "multiphonon transitions" thus connecting level m to level n where $m \neq n \pm 1$; and (iii) the relaxation equation may be nonlinear in the probability itself.[30] From a formal viewpoint, consideration (iii), if present, is the most serious of the three as it might necessitate entirely new methods of solution. Our perturbation schemes can be quite effective for practical low-temperature computations in the presence of (i) and even of (ii), because in such situations only the "downward" rates are nonnegligible. This leads, as we have shown, to an exactly-soluble sequential or cascade problem no matter how large the nonlinearities. Further perturbation developments, which allow one to relax the restriction that the temperature be low, have been constructed by Seshadri and will be presented[31] in the context of an application to quantum yield calculations in the presence of radiationless transitions.

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APPENDIX A

We derive here the expression for the probability distribution in the electronic excited state for wide-band excitation from a Boltzmann ground state at a temperature $T = \hbar\omega_1/k_B\beta$. Using the transition rate given in Ref. 1, we have

$$P_m = (\text{const.}) M \sum_n E_{nm} |\langle n|m\rangle|^2 e^{-n\beta} , \tag{A1}$$

where E_{mn} is the energy of the transition given by $E_0 + \hbar(m\omega_2 - n\omega_1)$; ω_1 and ω_2 are the frequencies in the ground and excited state; E_0 is the energy of the $0 \to 0$ transition; M is the electronic part of the transition-matrix element defined in Eq. (2.4).

The sum in (A1) can be evaluated exactly when the excited- and ground-state oscillators involved in the transition have the same frequency, i.e., $\omega_1 = \omega_2 = \omega$. However for simplicity we treat E_{mn} as a constant. This approximation is justified if $E_0 \gg \hbar\omega$ as is usually the case. Then Eq. (A1) reduces to

$$P_m = (\text{const.}) M E_0 \sum_n |\langle n|m\rangle|^2 e^{-n\beta} . \tag{A2}$$

It can be shown that,[15] the Frank-Condon factor $|\langle m|n\rangle|^2$ is related to the associated Laguerre polynomials

$$\begin{aligned} |\langle m|n\rangle|^2 &= e^{-a^2/2} (m!/n!) [L_m^{n-m}(a^2/2)]^2 (\tfrac{1}{2}a^2)^{n-m}, \quad n \geq m \\ &= e^{-a^2/2} (n!/m!) [L_n^{m-n}(a^2/2)]^2 (\tfrac{1}{2}a^2)^{m-n}, \quad m \geq n . \end{aligned} \tag{A3a}$$

These are in turn related to the Charlier polynominals[18c] as

$$|\langle m|n\rangle|^2 = e^{-a^2/2} (\tfrac{1}{2}a^2)^{m+n} (m!n!)^{-1} C_m^2(n; \tfrac{1}{2}a^2) . \tag{A3b}$$

The Charlier polynomials can be obtained from the generating function

$$e^{-z}(1 - za^{-1})^n = \sum_{m=0}^{\infty} C_m(n;a) \frac{z^m}{m!} , \tag{A4a}$$

and obey the closure relation

$$\sum_{l=0}^{\infty} e^{-y} y^l (l!)^{-1} C_m(l,y) C_n(l,y) = n! y^{-n} \delta_{mn} . \tag{A4b}$$

The sum in Eq. (A2) can be performed using Eq. (A3b) by expanding the Charlier polynomials $C_m(l;y)$ in terms of $C_m(l; ye^{-\beta})$ using the generating function Eq. (A4a). A straightforward algebraic manipulation of Eq. (A4a) yields the following expansion:

$$C_m(l;y) = m! e^{-m\beta} \sum_{k=0}^{m} \frac{C_{m-k}(l; ye^{-\beta})}{(m-k!)k!} \left(\frac{e^{\beta}-1}{e^{\beta}}\right)^k . \tag{A5}$$

Substituting Eqs. (A3b), (A5) in (A2), using the closure relation (A4b) and normalizing we obtain

$$\begin{aligned} P_m = (1 - \overline{e}^{\beta}) \exp[-\tfrac{1}{2}a^2(1 - e^{-\beta}) - m\beta] \\ L_m(-2a^2 \sinh^2(\beta/2)) . \end{aligned} \tag{A6}$$

APPENDIX B

For initial Boltzmann distributions, when the linear decay term is treated as the perturbation, it can be easily seen from Eq. (4.9) that

$$P_m(t) = p_m(t) - c' \sum_{r,q} g_q \int_0^t p_m^r(t-\tau) r p_q^r(\tau) e^{-q\beta_0} d\tau , \tag{B1}$$

where the unperturbed solutions $p_m^n(t)$ are given by Eq. (3.9). Exploiting the form invariance of the Boltzmann distribution, Eq. (B1) can be cast in the form

$$P_m(t) = p_m(t) - c' g_m \left(\int_0^t \mathcal{A}(\tau) \frac{\partial [A'(t,\tau) e^{-m\beta'(t-\tau)}]}{\partial[-\beta(\tau)]} \right) d\tau , \tag{B2}$$

where the functions $\mathcal{A}(\tau)$ and $\beta(\tau)$ have been defined in Eqs. (3.13b) and (3.13c). $\mathcal{A}'(t,\tau)$ and $\beta'(t,\tau)$ are the functions $A(\tau)$ and $\beta(\tau)$ in which τ has been replaced by $(t-\tau)$ and β_0 is replaced by $\beta(\tau)$.

To evaluate (B2), we define the following quantities:

$$\begin{aligned} \overline{M}_1(t) &= \Gamma^+(1 - \Gamma^- e^{-\beta_0}) + \Gamma^-(\Gamma^+ e^{-\beta_0} - 1) e^{-vt} , \\ \overline{N}_1(t) &= (1 - \Gamma^- e^{-\beta_0}) + (\Gamma^+ e^{-\beta_0} - 1) e^{-vt} , \\ \overline{M}_2(t,\tau) &= \Gamma^+(1 - \Gamma^- e^{-\beta(\tau)}) + \Gamma^-(\Gamma^+ e^{-\beta(\tau)} - 1) e^{-v(t-\tau)} , \\ \overline{N}_2(t,\tau) &= (1 - \Gamma^- e^{-\beta(\tau)}) + (\Gamma^+ e^{-\beta(\tau)} - 1) e^{-v(t-\tau)} . \end{aligned} \tag{B3}$$

Substituting $\beta(\tau)$ in the equations for $\overline{M}_2(t,\tau)$ and $\overline{N}_2(t,\tau)$, we obtain

$$\begin{aligned} \overline{M}_2(t,\tau) &= (\Gamma^+ - \Gamma^-) \overline{M}_1(t)/\overline{M}_1(\tau) , \\ \overline{N}_2(t,\tau) &= (\Gamma^+ - \Gamma^-) \overline{N}_1(t)/\overline{M}_1(\tau) . \end{aligned} \tag{B4}$$

In this notation, we can write

$$\begin{aligned} \mathcal{A}'(t,\tau) &= s_1(t-\tau) [\overline{M}_2(t,\tau)]^{-D} , \\ \beta'(t,\tau) &= \ln[\overline{M}_2(t,\tau)/\overline{N}_2(t,\tau)] , \end{aligned} \tag{B5}$$

where

$$s_1(t-\tau) = (\Gamma^+ - \Gamma^-)^D e^{(-b+v'D)(t-\tau)} .$$

Substituting (B5) in (B3) and carrying out the differentiation, Eq. (B2) is seen to be

$$P_m(t)=p_m(t)-c'g_m\left(\int_0^t \mathcal{A}(\tau)s(t-\tau)\left\{m[\bar{N}_2(t,\tau)]^{m-1}[\bar{M}_2(t,\tau)]^{-(m+D)}\times\frac{\partial\bar{N}_2(t,\tau)}{\partial\beta(\tau)}-(D+m)[\bar{N}_2(t,\tau)]^{m}[\bar{M}_2(t,\tau)]^{-(m+D+1)}\frac{\partial\bar{M}_2(t,\tau)}{\partial\beta(\tau)}\right\}\right) . \tag{B6}$$

Using Eq. (B3), we find

$$[\bar{M}_2(t,\tau)]^{-1}\frac{\partial\bar{N}_2(t,\tau)}{\partial\beta(\tau)}=\bar{N}_1(\tau)[\Gamma^- -\Gamma^+e^{-v(t-\tau)}][(\Gamma^+-\Gamma^-)\bar{M}_1(t)]^{-1}$$

$$[\bar{M}_2(t,\tau)]^{-1}\frac{\partial\bar{M}_2(t,\tau)}{\partial\beta(\tau)}=e^{\beta}\bar{N}_1(\tau)[1-e^{-v(t-\tau)}][(\Gamma^+-\Gamma^-)\bar{M}_1(t)]^{-1} . \tag{B7}$$

Substituting (B7) into (B6) we obtain Eq. (4.14) where

$$\mathcal{N}_1(t)=(m+D-1)[\bar{M}_1(t)(\Gamma^+-\Gamma^-)]^{-1}[\Gamma^-\mathcal{S}_1-\Gamma^+\mathcal{S}_3e^{-vt}] ,$$

$$\mathcal{N}_0(t)=(m+D)[\bar{M}_1(t)(\Gamma^+-\Gamma^-)]^{-1}[\mathcal{S}_1-\mathcal{S}_3e^{-vt}] ,$$

$$\mathcal{S}_1(t)=\int_0^t \bar{N}_1(\tau)\,d\tau=(1-\Gamma^-e^{-\beta_0})t-(1-\Gamma^-e^{-\beta_0})(1-e^{-vt})v^{-1} ,$$

$$\mathcal{S}_2(t)=\int_0^t \bar{N}_1^2(\tau)\,d\tau=(1-\Gamma^-e^{-\beta_0})^2t+(1-\Gamma^+e^{-\beta_0})^2(1-e^{-2vt})(2v)^{-1}-2(1-\Gamma^-e^{-\beta_0})(1-\Gamma^+e^{-\beta_0})(1-e^{-vt})v^{-1} ,$$

$$\mathcal{S}_3(t)=\int_0^t \bar{N}_1(\tau)e^{v\tau}\,d\tau=(1-\Gamma^-e^{-\beta_0})(e^{vt}-1)v^{-1}-t(1-\Gamma^+e^{-\beta_0}) . \tag{B8}$$

The moments for the linear decay are given by the equations

$$Q(t)=Q_0+c'\int_0^t \mathcal{A}(\tau)\frac{\partial[\mathcal{A}'(t,\tau)(1-e^{-\beta(\tau)})^{-D}]}{\partial\beta(\tau)} ,$$

$$\langle n\rangle=\langle n^0\rangle+c'D\int_0^t \mathcal{A}(\tau)\times\frac{\partial[\mathcal{A}'(t,\tau)e^{-\beta'(\tau)}(1-e^{-\beta'(\tau)})^{-(D+1)}]}{\partial\beta(\tau)} . \tag{B9}$$

Using precisely the same algebraic techniques as before these can be shown to reduce to Eqs. (4.10). The functions N_2 and N_3 are given by

$$\begin{aligned}\mathcal{N}_2&=[(\Gamma^+-\Gamma^-)(\bar{M}_1(t)-\bar{N}_1(t))]^{-1}f_1(t) ,\\ \mathcal{N}_3&=[(\Gamma^+-\Gamma^-)(\bar{M}_1(t)-\bar{N}_1(t))]^{-1}f_2(t) ,\\ f_1&=(e^{\beta}-\Gamma^-)\mathcal{S}_1-(e^{\beta}-\Gamma^+)\mathcal{S}_3e^{-vt} ,\\ f_2&=\Gamma^+\mathcal{S}_3e^{-vt}-\mathcal{S}_1\Gamma^- .\end{aligned} \tag{B10}$$

The equations for the quadratic decay are more complicated as they involve second derivatives with respect to $\beta(\tau)$.

$$P_m(t)=p_m(t)-d\int_0^t \mathcal{A}(\tau)\frac{\partial^2}{\partial\beta(\tau)^2}[\mathcal{A}'(t)g_me^{-m\beta'(t)}]\,d\tau . \tag{B11}$$

This integration can be performed in the same manner as before yielding Eq. (4.11). The functions $\mathcal{M}_0$, $\mathcal{M}_1$, and $\mathcal{M}_2$ are given as

$$\mathcal{M}_0=(m+D)e^{\beta}[(\Gamma^+-\Gamma^-)\bar{M}_1(t)]^{-1}[e^{\beta}(D+m+1)\{[(\Gamma^+-\Gamma^-)\bar{M}_1(t)]^{-1}(\mathcal{S}_2-2\mathcal{S}_4e^{-vt}+\mathcal{S}_3e^{-2vt})\}+(\mathcal{S}_1-\mathcal{S}_3e^{-2vt})] ,$$

$$\mathcal{M}_1=(m+D-1)[(\Gamma^+-\Gamma^-)\bar{M}_1(t)]^{-1}[(\mathcal{S}_3\Gamma^+e^{-vt}-\mathcal{S}_1\Gamma^-)-\{2e^{\beta}[(\Gamma^+-\Gamma^-)\bar{M}_1(t)]^{-1}\times(m+D)[\mathcal{S}_2\Gamma^- -\mathcal{S}_4(\Gamma^++\Gamma^-)e^{-vt}+\mathcal{S}_5\Gamma^+e^{-2vt})\}] ,$$

$$\mathcal{M}_2=(m+D-1)(m+D-2)[(\Gamma^+-\Gamma^-)\bar{M}_1(t)]^{-2}(\mathcal{S}_5\Gamma^{+2}e^{-2vt}-2\mathcal{S}_4e^{\beta-vt}+\mathcal{S}_2\Gamma^{-2}) ,$$

$$\mathcal{S}_4=\int_0^t \bar{N}_1^2(\tau)e^{vt}\,d\tau=(1-\Gamma^-e^{-\beta_0})^2(e^{vt}-1)v^{-1}+(1-\Gamma^+e^{-\beta_0})^2(1-e^{-vt})v^{-1}-2(1-\Gamma^-e^{-\beta_0})(1-\Gamma^+e^{-\beta_0})t ,$$

$$\mathcal{S}_5=\int_0^t \bar{N}_1^2(\tau)e^{2v\tau}\,d\tau=(1-\Gamma^-e^{-\beta_0})^2(e^{2vt}-1)(2v)^{-1}+(1-\Gamma^+e^{-\beta_0})^2t-2(1-\Gamma^-e^{-\beta_0})(1-\Gamma^+e^{-\beta_0})(e^{vt}-1)v^{-1} . \tag{B12}$$

The moments for the quadratic decay are given by the equations

$$Q(t)=Q_0(t)-d\int_0^t \mathcal{A}(\tau)\frac{\partial^2}{\partial\beta(\tau)^2}[\mathcal{A}'(t)(1-e^{-\beta'(t)})^{-D}]\,d\tau,$$

$$\langle n\rangle=\langle n_0\rangle-dD\int_0^t \mathcal{A}(\tau)\times\frac{\partial^2}{\partial\beta(\tau)^2}[\mathcal{A}'(t)e^{-\beta'(t)}\times(1-e^{-\beta'(t)})^{-(D+1)}]\,d\tau. \tag{B13}$$

Simplifying as before, we obtain Eqs. (4.12), where

$$\begin{aligned}\mathfrak{M}_3&=Ds_2(t)[(D+1)s_2(t)f_3-f_1],\\ \mathfrak{M}_4&=(D+1)s_2(t)[(D+2)s_2(t)f_3-f_1],\\ \mathfrak{M}_5&=Ds_2(t)[2(D+1)s_2(t)f_4-f_2],\\ s_2(t)&=\{[\overline{M}_1(t)-\overline{N}_1(t)][\Gamma^+-\Gamma^-]\}^{-1},\\ f_3&=(e^\beta-\Gamma^-)^2\mathcal{S}_2+(e^\beta-\Gamma^+)^2\mathcal{S}_5e^{-2vt}\\ &\quad-2(e^\beta-\Gamma^-)(e^\beta-\Gamma^+)\mathcal{S}_4e^{-vt},\\ f_4&=-\Gamma^-(e^\beta-\Gamma^-)\mathcal{S}_2+e^{-\beta}(\Gamma^++\Gamma^--2)\mathcal{S}_4e^{\beta-vt}\\ &\quad-\Gamma^+(e^\beta-\Gamma^+)\mathcal{S}_5e^{-2vt}.\end{aligned} \tag{B14}$$

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