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Time-Dependent Effective Rates for Molecular Processes

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The concept of time-dependent effective rates for molecular processes such as luminescence, introduced in our earlier work, is developed further by obtaining two new results. One is the explicit evaluation of those rates for four initial conditions corresponding to experimentally relevant methods of excitation of the molecule. The other is a proof that the limiting values of those rates for long times or for infinitely fast relaxation are independent of the initial condition. The latter result extends the validity of the "rate depression effect" (whereby the long time limit of the effective rate is different from its thermalized value) to arbitrary initial conditions.

I. Introduction

Several master-equation treatments of the effect of vibrational relaxation on other molecular processes have appeared recently in the literature. The effect on nonradiative intramolecular processes such as intersystem crossing has been analyzed by Freed, Heller, and Fung [1, 2], that on luminescence by the present authors [3–5] and that on intermolecular excitation transfer by Kenkre [6]. The concept of effective rates (e.g. for luminescence or transfer) that are time-dependent, arises naturally in our treatment of the subject, as has been explicitly shown in [6], where it has been discussed in the context of the general transport problem. An unexpected result of our earlier analyses is that these time-dependent effective rates tend, at long times, to limiting values that are *different* from their thermalized values [3–6]. Since this result had been obtained only for the particular initial condition of a Boltzmann distribution among the vibrational states of the molecule, the question of whether it possesses greater generality was open. This paper settles that question. We show that the result is indeed independent of the initial condition and also display the explicit time dependence of these experimentally relevant rates for several other initial conditions of physical interest.

In Sect. II we exhibit the model used [1–6] for such analyses, define two effective rates of experimental interest, and show how to evaluate them for the model for arbitrary initial conditions. In Sect. III we display the explicit rate expressions for four types of initial excitation of the molecule and write down their limiting values. In Sect. IV we prove that they are independent of the nature of the initial distribution. A discussion is given in Sect. V.

II. The Model and the Rates

The recently used [1–6] model for the description of vibrational relaxation occurring simultaneously with other molecular processes regards the molecular excited state as a D-fold degenerate harmonic oscillator. The D-fold degeneracy provides a rapidly increasing density of states which represents the features of a polyatomic molecule. If this oscillator is assumed to be interacting linearly with a heat bath the pure relaxation equation is a generalized Montroll-Shuler equation [7–9]. When intramolecular decay of excitation, corresponding e.g. to luminescence, is incorpo-

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rated by adding sink-like terms α_m to that equation, it takes the form [1–5, 9]

$$\frac{\partial P_m}{\partial t}+\alpha_m P_m = k[(m+D-1)e^{-\beta}P_{m-1} + (m+1)P_{m+1} - \{m+e^{-\beta}(m+D)\}P_m] \tag{2.1}$$

In this equation P_m is the probability of occupation of the m^{th} vibrational state, k is a relaxation parameter denoting the strength of the molecule-bath interaction and $\beta=\hbar\omega/k_B T$ where ω is the oscillator frequency, k_B and $2\pi\hbar$ are the Boltzmann and Planck's constant respectively and T is the temperature. We shall assume that α_m is linear in m, i.e., $\alpha_m=b+cm$. This allows one to solve (2.1) exactly. This assumption is reasonable [5] for purely radiative decay, to which we shall restrict our attention for the present. For a detailed discussion of the assumptions underlying (2.1) see Refs. [5] and [6].

Depending on the experimental quantity being studied one can define two average rates for the decay problem. One of them refers to the rate of decay of the total probability Q. We call this rate $K_p(t)$. It is defined as

$$K_p(t) = -\frac{1}{Q}\cdot\frac{dQ}{dt} \tag{2.2}$$

and from (2.1), it is obtained as

$$K_p(t) = b + c\langle n\rangle/Q \tag{2.3}$$

where $\langle n\rangle$ is the first moment of the probabilities. The other rate of experimental interest is the usual fluorescence decay rate $K_I(t)$ defined as the negative logarithmic derivative of the fluorescence intensity $I(t)$. Since the latter is defined as

$$I(t)=\sum_m \alpha_m P_m(t) = bQ + c\langle n\rangle \tag{2.4}$$

it is given by

$$K_I(t) = b + c\left[\frac{b\langle n\rangle + c\langle n^2\rangle}{bQ+c\langle n\rangle}\right] \tag{2.5}$$

where $\langle n^2\rangle$ is the second moment. Hence, in order to compute $K_p(t)$, we need to know only Q and $\langle n\rangle$ whereas to compute $K_I(t)$ we also need to know $\langle n^2\rangle$.

A solution of (2.1) with α_m given by the linear expression above has been obtained by the generating function technique [1–5, 8]. Defining the generating function as

$$G(z,t) = \sum_{m=0}^{\infty} z^m P_m(t) \tag{2.6}$$

we obtain from (2.1)

$$\frac{1}{ke^{-\beta}}\frac{\partial G}{\partial t} = G\left\{D(z-1)+\frac{be^{\beta}}{k}\right\} + \frac{\partial G}{\partial z}\left\{z^2 - z\left(1+e^{\beta}+\frac{ce^{\beta}}{k}\right)+e^{\beta}\right\}. \tag{2.7}$$

The general solution obtained by the method of characteristics [10] is given by

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

where

$$\Gamma^{\pm} = (1/2)(e^{\beta}+1+\delta) \pm [(1/4)(e^{\beta}+1+\delta)^2 - e^{\beta}]^{1/2},$$
$$\delta = e^{\beta}c/k, \quad v = ke^{-\beta}(\Gamma^+ - \Gamma^-), \quad v' = ke^{-\beta}(\Gamma^- - 1). \tag{2.8}$$

The function $G_0(z)$, defined as

$$G_0(z) \equiv G(z,0) = \sum_{m=0}^{\infty} z^m P_m(0) \tag{2.9}$$

completely characterizes the initial distribution. We had earlier obtained [5] explicit solutions for the $P_m(t)$'s for several initial distributions. Here since we are interested only in the effective decay rates, we concentrate on the moments. The general n^{th} factorial moment can be defined as [8]

$$\begin{aligned}&\langle m\cdot(m-1)\dots(m-n+1)\rangle \\ &= \sum_{m=0}^{\infty}(m)(m-1)\dots(m-n+1)P_m \\ &= \lim_{z\to 1}\frac{\partial^n G(z,t)}{\partial z^n}.\end{aligned} \tag{2.10}$$

The moments Q, $\langle n\rangle$ and $\langle n^2\rangle$ are then obtained as

$$Q = \lim_{z\to 1} G(z,t) \tag{2.11a}$$

$$\langle n\rangle = \lim_{z\to 1} z\frac{\partial G(z,t)}{\partial z} \tag{2.11b}$$

$$\langle n^2\rangle = \lim_{z\to 1} z\frac{\partial}{\partial z}\left(z\frac{\partial G}{\partial z}\right) = \lim_{z\to 1} z^2\frac{\partial G}{\partial z^2} + \lim_{z\to 1} z\frac{\partial G}{\partial z} \tag{2.11c}$$

Equations (2.8) and (2.10) allow us to compute the moments for any initial distribution. Utilizing the expressions (2.4) and (2.5) for the effective rates and substituting (2.11) one obtains the effective rates. Explicit expressions for a δ-function, Boltzmann, Poisson and Laguerre initial distributions are given below.

III. Explicit Expressions

The significance of the four initial conditions to be used in the analysis below will be discussed in Sect. IV.

i) δ-Function Distribution

The generating function for this case for which $P_m(0)=\delta_{l,m}$ is

$$G(z,t)=e^{(-b+Dv')t}(\Gamma^+-\Gamma^-)^D\{[\Gamma^-(\Gamma^+-z)+\Gamma^+(z-\Gamma^-)e^{-vt}]^l\cdot[(\Gamma^+-z)+(z-\Gamma^-)e^{-vt}]^{-(l+D)}. \quad (3.1)$$

Here l represents the vibrational state which is initially excited. Substituting (3.1) in (2.11), we obtain

$$Q_l=e^{(-b+Dv')t}(\Gamma^+-\Gamma^-)^D\{[\Gamma^-(\Gamma^+-1)+\Gamma^+(1-\Gamma^-)e^{-vt}]^l[(\Gamma^+-1)+(1-\Gamma^-)e^{-vt}]^{-(l+D)}\}, \quad (3.2\text{a})$$

$$\langle n_l\rangle=\{-l(\Gamma^--\Gamma^+e^{-vt})[\Gamma^-(\Gamma^+-1)+\Gamma^+(1-\Gamma^-)e^{-vt}]^{-1}+(l+D)(1-e^{-vt})[(\Gamma^+-1)+(1-\Gamma^-)e^{-vt}]^{-1}\}Q_l. \quad (3.2\text{b})$$

$$\langle n_l^2\rangle=[l(l-1)\{-\Gamma^-+\Gamma^+e^{-vt}\}^2\cdot\{\Gamma^-(\Gamma^+-1)+\Gamma^+(1-\Gamma^-)e^{-vt}\}^{-2}+2l(l+D)\{\Gamma^-(\Gamma^+-1)+\Gamma^+(1-\Gamma^-)e^{-vt}\}^{-1}\{(\Gamma^+-1)+(1-\Gamma^-)e^{-vt}\}^{-1}\{-\Gamma^-+\Gamma^+e^{-vt}\}\{1-e^{-vt}\}+(l+D)(l+D-1)\{(\Gamma^+-1)+(1-\Gamma^-)e^{-vt}\}^{-2}\cdot\{1-e^{-vt}\}^2]Q_l+\langle n_l\rangle \quad (3.2\text{c})$$

Utilizing these expressions for the moment and (2.4), we obtain

$$K_p(t)=b+c[l(-\Gamma^-+\Gamma^+e^{-vt})\{\Gamma^-(\Gamma^+-1)+\Gamma^+(1-\Gamma^-)e^{-vt}\}^{-1}+(l+D)(1-e^{-vt})\cdot\{(\Gamma^+-1)+(1-\Gamma^-)e^{-vt}\}^{-1}] \quad (3.3)$$

The limiting values of this rate are as follows.

$$\lim_{t\to 0}K_p(t)=b+cl \quad (3.4\text{a})$$

$$\lim_{k\to 0}K_p(t)=b+cl \quad (3.4\text{b})$$

$$\lim_{t\to\infty}K_p(t)=b+\frac{cD}{(\Gamma^+-1)}, \quad (3.4\text{c})$$

$$\lim_{k\to\infty}K_p(t)=b+\frac{cD}{(e^\beta-1)}. \quad (3.4\text{d})$$

Needless to say, as the limit $t\to 0$ is taken in (3.4a), k does not tend to ∞ so that $kt\to 0$ is assured. Similar statements apply to all the other limits also.

Let us examine the fluorescence decay rate $K_I(t)$. $K_I(t)$ has a more complicated time dependence compared to $K_p(t)$ because of the occurrence of the second moment $\langle n^2\rangle$. An explicit expression can be obtained by substituting (3.2a, b, c) in (2.5). Instead of giving the full expression which is rather unwieldy we display only its limiting values. The limiting value of $K_I(t)$ as $t\to 0$ is the same as that as $k\to 0$ and contains nothing unexpected. The other limits ($t\to\infty$ and $k\to\infty$) are different and follow the same pattern as the one for $K_p(t)$. Noting that

$$\lim_{t\to\infty}\frac{\langle n^2\rangle}{Q}=\frac{D(D+1)}{(\Gamma^+-1)^2}+\frac{D}{(\Gamma^+-1)}$$
$$\lim_{k\to\infty}\frac{\langle n^2\rangle}{Q}=\frac{D(D+1)}{(e^\beta-1)^2}+\frac{D}{(e^\beta-1)} \quad (3.5)$$

we obtain

$$\lim_{t\to\infty}K_I(t)=b+\frac{cD}{(\Gamma^+-1)}+c^2\frac{\Gamma^+}{(\Gamma^+-1)}\frac{D}{(b(\Gamma^+-1)+cD)} \quad (3.6\text{a})$$

$$\lim_{k\to\infty}K_I(t)=b+\frac{cD}{(e^\beta-1)}+c^2\frac{e^\beta}{(e^\beta-1)}\frac{D}{(b(e^\beta-1)+cD)} \quad (3.6\text{b})$$

It can be seen by comparing (3.4c) and (3.6a) and (3.4d) and (3.6b) that

$$\lim_{k\to\infty}K(t)=\lim_{k\to\infty}\lim_{t\to\infty}K(t)$$

where $K(t)$ is either $K_p(t)$ or $K_I(t)$. That this is a general property of the limiting values of these rates and that it is independent of the nature of the initial distribution, will be seen in Sect. 4.

ii) Boltzmann Distribution

In an earlier paper [4], we had discussed the time evolution of a quasi-moment $\mathscr{X}(t)$ for an initial Boltzmann distribution which is defined as

$$\mathscr{X}(t)=\langle n\rangle/Q. \quad (3.7)$$

Comparing (2.4) and (3.7), it is clear that $\mathscr{X}(t)$ has the same time dependence as $K_p(t)$ barring a constant additive factor. In the following, we discuss the rates in greater detail.

For an initial Boltzmann distribution [5] at a temperature $T_0 = \hbar\omega/k_B\beta_0$

$$P_m(0) = (1-e^{-\beta_0})e^{-m\beta_0} \tag{3.8}$$

$$\begin{aligned} G(z,t) &= e^{(-bt+Dv't)}(\Gamma^+-\Gamma^-)^D(1-e^{-\beta_0})^D \\ &\cdot\{1-e^{-\beta_0}[\Gamma^-(\Gamma^+-z)+\Gamma^+(z-\Gamma^-)e^{-vt}] \\ &\cdot[(\Gamma^+-z)+(z-\Gamma^-)e^{-vt}]^{-1}\}^{-D} \\ &\cdot[(\Gamma^+-z)+(z-\Gamma^-)e^{-vt}]^{-D}. \end{aligned} \tag{3.9}$$

Using (2.11) and (3.9), the moments are given by

$$Q = \mathscr{A}(t)(1-e^{-\beta(t)})^{-D}, \tag{3.10a}$$

$$\langle n\rangle = D[\exp\beta(t)-1]^{-1}Q. \tag{3.10b}$$

$$\langle n^2\rangle = D(D+1)[e^{\beta(t)}-1]^{-2}Q + D[e^{\beta(t)}-1]^{-1}Q \tag{3.10c}$$

where

$$\begin{aligned} \mathscr{A}(t) &= e^{-bt+Dv't}(\Gamma^+-\Gamma^-)^D(1-e^{-\beta_0})^D \\ &\cdot[(\Gamma^+-\Gamma^-e^{-vt})-e^{\beta-\beta_0}(1-e^{-vt})]^{-D} \\ &= e^{-bt+Dv't}[(1-e^{-\beta_0})(1-\Gamma^-e^{-\beta_0})^{-1}]^D \\ &\cdot(1-\Gamma^-e^{-\beta(t)})^D, \end{aligned} \tag{3.11a}$$

$$\beta(t) = \ln\left(\frac{\Gamma^+(1-\Gamma^-e^{-\beta_0})-\Gamma^-(1-\Gamma^+e^{-\beta_0})e^{-vt}}{(1-\Gamma^-e^{-\beta_0})-(1-\Gamma^+e^{-\beta_0})e^{-vt}}\right) \tag{3.11b}$$

Substituting (3.10) in (2.4) and (2.5), we obtain

$$K_p(t) = b + cD[e^{\beta(t)}-1]^{-1}, \tag{3.12a}$$

$$K_I(t) = b + cD[e^{\beta(t)}-1]^{-1} + \frac{c^2e^{\beta(t)}D}{(e^{\beta(t)}-1)[b(e^{\beta(t)}-1)+cD]} \tag{3.12b}$$

The limits of $\beta(t)$ as $t\to\infty$, $k\to\infty$ are

$$\lim_{t\to\infty}\beta(t) = \ln\Gamma^+ \tag{3.13a}$$

$$\lim_{k\to\infty}\beta(t) = \beta. \tag{3.13b}$$

Thus

$$\lim_{t\to\infty}K_p(t) = b + \frac{cD}{(\Gamma^+-1)} \tag{3.14a}$$

$$\lim_{k\to\infty}K_p(t) = b + \frac{cD}{(e^\beta-1)} \tag{3.14b}$$

$$\lim_{t\to\infty}K_I(t) = b + \frac{cD}{(\Gamma^+-1)} + c^2\frac{\Gamma^+}{(\Gamma^+-1)}\frac{D}{(b(\Gamma^+-1)+CD)} \tag{3.14c}$$

$$\lim_{k\to\infty}K_I(t) = b + \frac{cD}{(e^\beta-1)} + c^2\frac{e^\beta}{(e^\beta-1)}\frac{D}{(b(e^\beta-1)+CD)}. \tag{3.14d}$$

Note from a comparison of (3.4) and (3.6) on one hand and (3.14) on the other that the various limiting values for the δ-function distribution are the same as those for the Boltzmann distribution. That this is a general property of all initial distributions will be proven later.

iii) Poisson Distribution

For simplicity we shall set the degeneracy $D=1$ for both Poisson and Laguerre distributions. In this case [5]

$$P_m(0) = \left(\frac{e^{-a^2/2}}{m!}\right)(a^2/2)^m \tag{3.15}$$

and

$$G(z,t) = B_2(t)(1-z\alpha_2)^{-1}\exp\{zy_2\alpha_2/(z\alpha_2-1)\}, \tag{3.16}$$

where

$$B_2(t) = [D_2']^{-1}(\Gamma^+-\Gamma^-)$$

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

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

$$\alpha_2 = C_2'[D_2']^{-1},$$

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

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

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

Using the moments obtained by substituting (3.16) in (2.11) the explicit expressions for the rates are seen to be

$$K_p(t) = b + \frac{c\alpha_2}{(1-\alpha_2)^2}(1-\alpha_2-y_2) \tag{3.17a}$$

$$K_I(t) = b + c\frac{\alpha_2(1-\alpha_2-y_2)}{(1-\alpha_2)^2} + \frac{c^2\alpha_2}{(1-\alpha_2)^3}(1-\alpha_2-y_2-\alpha_2y_2) \tag{3.17b}$$

Noting that

$$\lim_{t\to\infty}y_2 = \lim_{k\to\infty}y_2 = 0$$

$$\lim_{t\to\infty}\alpha_2 = \frac{1}{\Gamma^+}; \quad \lim_{k\to\infty}\alpha_2 = e^{-\beta} \tag{3.18}$$

we find that the rates have the same limiting values as in the case of the previous distributions given by (3.14).

iv) Laguerre Distribution

In this case

$$P_m(0)=(1-e^{-\beta})\exp[-\tfrac{1}{2}a^2(1-e^{-\beta})-m\beta] \cdot L_m(-2a^2\sinh^2\beta/2)) \tag{3.19}$$

and

$$G(z,t)=B_3(t)(1-z\alpha_3)^{-1}\exp\{zy_3\alpha_3/(z\alpha_3-1)\}, \tag{3.20}$$

where

$$B_3(t)=(\Gamma^+-\Gamma^-)[D'_3]^{-1}(1-e^{-\beta}) \cdot\exp\{-bt+v't-a^2e^{-\beta/2}\sinh(\beta/2)+B'_3[D'_3]^{-1}\},$$

$$y_3=A'_3[C'_3]^{-1}+B'_3[D'_3]^{-1},$$

$$\alpha_3=C'_3[D'_3]^{-1},$$

$$A'_3=-2a^2\sinh^2(\beta/2)e^{-\beta}(\Gamma^+e^{-vt}-\Gamma^-),$$

$$B'_3=-2a^2\sinh^2(\beta/2)(1-e^{-vt}),$$

$$C'_3=(1-e^{-vt})+e^{-\beta}(\Gamma^+e^{-vt}-\Gamma^-),$$

$$D'_3=(\Gamma^+-\Gamma^-e^{-vt})-(1-e^{-vt}).$$

It can be shown from (3.20) that

$$K_p(t)=b+cy_4 \tag{3.21a}$$

$$K_I(t)=b+cy_4+\frac{c^2}{b+cy_4}\left[\frac{D'_3+C'_3}{D'_3-C'_3}y_4-\frac{C'^2_3}{(D'_3-C'_3)^2}\right] \tag{3.21b}$$

where

$$y_4=\frac{C'_3D'_3-C'^2_3-A'_3D'_3-B'_3C'_3}{(D'_3-C'_3)^2}.$$

Once again noting that

$$\lim_{t\to\infty} y_4=\frac{1}{(\Gamma^+-1)},\quad \lim_{t\to\infty} C'_3=\frac{(\Gamma^+-1)}{\Gamma^+},\quad \lim_{t\to\infty} D'_3=(\Gamma^+-1) \tag{3.22a}$$

$$\lim_{k\to\infty} y_4=\frac{1}{(e^\beta-1)},\quad \lim_{k\to\infty} C'_3=\frac{(e^\beta-1)}{e^\beta},\quad \lim_{k\to\infty} D'_3=(e^\beta-1), \tag{3.22b}$$

we recover the usual limiting values for K_p and K_I given in (3.14).

IV. Result for Arbitrary Initial Distribution

So far we have considered specific distributions and derived the limiting values from their generating functions. Consider now an *arbitrary* initial distribution characterized by $P_l(0)$, with $l=0, 1\ldots\infty$. The generating function for such a distribution is obtained by a linear superposition of the δ-function generating function $G_l(z,t)$

$$G(z,t)=\sum_{l=0} P_l(0)\,G_l(z,t) \tag{4.1}$$

the ratio of the n^{th} moment to the zeroth moment of this distribution is given by

$$\frac{\langle l(l-1)\ldots(l-n+1)\rangle}{Q(t)}=\frac{\lim\limits_{z\to1}\frac{\partial^n}{\partial z^n}\sum\limits_{l=0}^{\infty}P_l(0)\,G_l(z,t)}{\lim\limits_{z\to1}\sum\limits_{l=0}^{\infty}P_l(0)\,G_l(z,t)}. \tag{4.2}$$

As can be seen from (3.1), we can factor out the purely time-dependent part $f(t)$ of $G_l(z,t)$ as shown below

$$G_l(z,t)=f(t)\,\hat{G}_l(z,t) \tag{4.3a}$$

$$f(t)=e^{-(b+Dv')t}(\Gamma^+-\Gamma^-)^D \tag{4.3b}$$

$$\hat{G}_l(z,t)=\{\Gamma^-(\Gamma^+-z)+\Gamma^+(z-\Gamma^-)e^{-vt}\}^l \cdot\{(\Gamma^+-z)+(z-\Gamma^-)e^{-vt}\}^{-(l+D)}. \tag{4.3c}$$

Hence

$$\frac{\langle l(l-1)\ldots(l-n+1)\rangle}{Q}=\frac{\lim\limits_{z\to1}\frac{\partial^n}{\partial z^n}\sum\limits_{l=0}^{\infty}P_l(0)\,\hat{G}_l(z,t)}{\lim\limits_{z\to1}\sum\limits_{l=0}^{\infty}P_l(0)\,\hat{G}_l(z,t)}. \tag{4.4}$$

The long-time limit of this ratio can be obtained by first letting $t\to\infty$ and then taking the derivatives $w\cdot r\cdot t$ z. We note that

$$\lim_{t\to\infty}\hat{G}_l(z,t)=\Gamma^{-l}\cdot\frac{1}{(\Gamma^+-z)^D} \tag{4.5}$$

and is independent of l. This gives

$$\lim_{t\to\infty}\frac{\langle l(l-1)\ldots(l-n+1)\rangle}{Q}$$

$$=\frac{\lim\limits_{z\to 1}\Gamma^{-l}\dfrac{\partial^n}{\partial z^n}(\Gamma^+-z)^{-D}\cdot\sum\limits_{l=0}^{\infty}P_l(0)}{\lim\limits_{z\to 1}\Gamma^{-l}\dfrac{1}{(\Gamma^+-z)^D}\sum\limits_{l=0}^{\infty}P_l(0)}$$

$$=\frac{D(D+1)\dots(D+n-1)}{(\Gamma^+-1)^n}. \tag{4.6}$$

In particular, the ratios of the first and second moments to the zeroth moment are always

$$\lim_{t\to\infty}\langle n\rangle/Q=D/(\Gamma^+-1)$$

$$\lim_{t\to\infty}\frac{\langle n^2\rangle}{Q}=\lim_{t\to\infty}\frac{\langle n\cdot n-1\rangle}{Q}+\frac{\langle n\rangle}{Q}$$

$$=\frac{D\cdot(D+1)}{(\Gamma^+-1)^2}+\frac{D}{(\Gamma^+-1)}. \tag{4.7}$$

It is easy to prove in an exactly analogous fashion that

$$\lim_{k\to\infty}\frac{\langle l(l-1)\dots(l-n+1)\rangle}{Q}=\frac{D(D+1)\dots(D+n-1)}{(e^\beta-1)^n} \tag{4.8a}$$

$$\lim_{k\to\infty}\langle n\rangle/Q=\frac{D}{(e^\beta-1)} \tag{4.8b}$$

$$\lim_{k\to\infty}\langle n^2\rangle/Q=\frac{D(D+1)}{(e^\beta-1)^2}+\frac{D}{(e^\beta-1)}. \tag{4.8c}$$

Substitution of these results in (2.4) and (2.5) establishes the general result that K_p and K_I have the limiting values given by (3.14) independent of the nature of the initial condition.

Also, comparing (4.6) and (4.8a) one obtains the result

$$\lim_{k\to\infty}\frac{\langle l(l-1)\dots l-n+1\rangle}{Q}$$

$$\equiv\lim_{k\to\infty}\lim_{t\to\infty}\frac{\langle l(l-1)\dots(l-n+1)\rangle}{Q} \tag{4.9}$$

An application of this result to expressions for the rates K_p and K_I yields

$$\lim_{k\to\infty}K_p(t)=\lim_{k\to\infty}\lim_{t\to\infty}K_p(t) \tag{4.10a}$$

$$\lim_{k\to\infty}K_I(t)=\lim_{k\to\infty}\lim_{t\to\infty}K_I(t). \tag{4.10b}$$

It should be borne in mind, however, that the converse is not true, i.e.,

$$\lim_{t\to\infty}K(t)\neq\lim_{t\to\infty}\lim_{k\to\infty}K(t) \tag{4.11}$$

where $K(t)$ is either $K_p(t)$ or $K_I(t)$.

V. Discussion

The new results of this paper are (i) the explicit expressions for the time-dependent effective rates for the four initial distributions of physical interest, (ii) the limiting values of these rates for long times and for infinitely fast relaxation, and (iii) the proof that these values and therefore the "rate depression effect" are independent of the initial distribution. Equations (3.3), (3.12), (3.17) and (3.21) constitute result (i). Equations (3.4), (3.6) and (3.14) provide result (ii), and result (iii) is the content of Sect. IV.

The physical significance of the four initial distributions we have chosen is as follows. If the oscillator is (molecule) in the ground electronic state at zero temperature, broad band excitation by light is easily shown to result in a Poisson distribution in the vibrational manifold of the excited electronic state. If the ground electronic state occupation has a Boltzmann form at a non-zero temperature, the Franck-Condon factors lead, on broad band excitation, to the Laguerre distribution in the excited state. With the help of lasers, selection of particular vibrational levels in the excited electronic state is possible. This corresponds to the δ-function distribution. Furthermore, the latter can be used through the principle of superposition for any initial distribution. Finally the Boltzmann distribution provides algebraic simplicity for the present model and also represents situations involving the formation of quasi-equilibrium states [11]. Details of the demonstration that the Poisson and Laguerre distributions are realized in the corresponding cases will be found in [5], particularly in its Appendix A.

We emphasize that what was called the "rate depression effect" (see Fig. 3 of Ref. 6) is a general consequence of finite relaxation times ($k\neq 0$) and of the level-dependence of the decay rates $\alpha_m(c\neq 0)$. In the light of the contents of this paper, the result is seen to be independent of the initial distribution. It is trivial to obtain the thermalized expressions for the two effective rates by performing the required averages over the Boltzmann distribution:

$$K_p^{\text{thermal}}=b+\frac{cD}{(e^\beta-1)} \tag{5.1}$$

$$K_p^{\text{thermal}}=b+\frac{cD}{(e^\beta-1)}+c^2\frac{e^\beta}{(e^\beta-1)}\cdot\frac{D}{(e^\beta-1)+cD} \tag{5.2}$$

Comparison of (5.1) with (3.14a) and (3.14b) and of (5.2) with (3.14c) and (3.14d) shows that the thermalized values of the rates equal their infinitely fast relaxation limits but are different from their long time limits. In fact, if $c>0$, it follows that $\Gamma^+>e^\beta$

which results in the long-time limits being *smaller* than the thermalized values. As none of the arguments presented above is altered by the substitution of linear radiative rates by linear non-radiative ones, it is instructive to compare our results with those of [1–2]. In [1,2] it is concluded from the stochastic analysis of singlet-triplet intersystem crossing that the fast relaxation (high pressure) limit is the same as the long-time limit. Their model is the same as ours. Their conclusion, however, differs from ours. In particular the first factor in (3.32) of [2] is given as $\lambda + \frac{D\mu}{(J-1)}$. The quantities λ, μ, J, and v in their notation correspond respectively to our b, c, e^{β} and k. Therefore their (3.32) is valid only for the infinite relaxation case. For the long-time but finite relaxation case, J will have to be replaced by

$$J'' = 1/2\left(J+1+\frac{\mu J}{v}\right)+\sqrt{1/4(J+1+\mu J/v)^2-J}.$$

Also, (3.37) of Ref. [2] implies that the two limits of the effective rates are identical, which, as we have seen, is at variance with our demonstration. Our analysis is also of interest to the case treated in [12] wherein the emission rate at infinitely long time has been set equal to the thermal rate given by (5.1) (see Eq. (3.1) of Ref. 12).

The explicit evaluation of the rates and the demonstration of the generality of the rate depression effect are given in the present paper in the context of decay processes such as luminescence. However, these results make an obvious contribution to the transfer problem discussed earlier. The details are straightforward and will not be given here.

Finally, we wish to point out that systems with decay rates α_m varying linearly with vibrational energy are known [13]. Although the harmonic-oscillator model for the molecule used here may not necessarily be applicable in detail to these systems, it may be feasible to detect the rate depression phenomenon in them at least in a qualitative sense.

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