

Master-equation theory of the effect of vibrational relaxation on intermolecular transfer of electronic excitation*

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A theory is developed to describe the effect of simultaneously occurring vibrational relaxation on intermolecular excitation transfer in the presence of radiative and nonradiative sinks. The basis is a master equation whose rates are combinations of the Förster-Dexter transfer rates and the Montroll-Shuler relaxation rates. Exact solutions are obtained for the probabilities of occupation of single vibrational levels as well as of site occupation, and for quantum yields and differential photon count rates. It is shown how phenomena exhibiting dependence of quantum yields or similar quantities on the wavelength of initial excitation can be quantitatively approached with the help of this analysis. The concept of time-dependent transfer rates is developed, and it is shown that at long times the transfer rate could tend to a value different from the thermalized Förster-Dexter rate. It is also shown how the relaxation process can result in an effective transfer rate (for singlets) whose dependence on the intermolecular distance R is other than R^{-6} .

I. INTRODUCTION

The study of the transfer of electronic excitation is of vital importance to diverse fields of research such as sensitized luminescence and photosynthesis, and many aspects of the process have been interpreted successfully in terms of the basic theory¹ of Förster and Dexter. However, one of its underlying assumptions being that vibrational relaxation is much faster than intermolecular (electronic) excitation transfer, the theory is inapplicable to situations wherein transfer times are comparable to relaxation times. Traditionally, extremely small values (10^{-12} sec or less) have been assigned to the latter in the condensed phase, and they have been believed to be smaller than transfer times by two orders of magnitude or more. If this extremely fast relaxation were a universal characteristic of condensed-phase systems, the above-mentioned inapplicability would hardly constitute a *practical* limitation of the theory. However, slow vibrational relaxation has been recently reported² in a number of systems in the solid and liquid phases. Indeed, some of these observations show that the process can be extremely slow, lasting for several seconds. There is now no doubt that situations exist wherein transfer times are small enough and relaxation times large enough for the two processes to compete and affect each other to appreciable extent. Furthermore, the advent of picosecond spectroscopy has brought processes taking 10^{-11} or 10^{-12} sec from the "infinitely fast" to the "accessible" category. As a consequence, excitation transfer may no longer be universally analyzed as decoupled from vibrational relaxation, and a theory of the single combined relaxation-transfer process is required.

Such a theory should ideally involve exact calculations from the exact microscopic equations of motion. However, the complexity of the problem makes this program impossible in practice and forces the use of alternative procedures. Thus one might attempt approximate solutions of the exact microscopic equations or obtain exact solutions from approximate *macroscopic* starting points such as master equations. In this paper we present a framework for the latter type of approach.

Several experiments associated directly or indirectly with the relaxation-transfer process have been reported. A qualitative explanation of Weber's red-edge effect³ and generally of observations⁴ of the dependence of transfer efficiency of the wavelength of the exciting light can be given in terms of preresolution transfer through rates dependent on the vibrational state. "Hot-transfer" observations have been reported in a variety of systems⁵ studied in the Soviet Union, and experiments of triplet transfer in liquids by Anderson *et al.*⁶ have also exhibited the interplay of relaxation and transfer.

Theoretical work aimed specifically at the relaxation-transfer problem has been primarily due to Hizhnyakov and Tehver,⁷ who have given an analysis of preresolution transfer based on the overlap of the absorption spectrum and the resonant secondary radiation spectrum of the molecules involved, and due to Dexter,⁸ who earlier emphasized that the sequential picture of relaxation occurring before transfer (or luminescence) does not have universal applicability, and analyzed the problem in the limit of no relaxation.

The basic quantity of interest in the present analysis is $P_m^M(t)$, the probability that the electronic excitation resides on site M and the system is in the m th vibrational state.⁹ In taking a master-

equation approach to the problem, we restrict ourselves to the description of quantities that do not require off-diagonal elements of the density matrix in the representation of "states $|M, m\rangle$ " and we tacitly assume that the probabilities follow a closed evolution equation having the master form

$$\frac{dP_m^M(t)}{dt} = \sum_{n, N} [\mathcal{R}_{mn}^{MN} P_n^N(t) - \mathcal{R}_{nm}^{NM} P_m^M(t)], \quad (1.1)$$

wherein the \mathcal{R} 's are the transition rates. It must not be forgotten that no rigorous and completely satisfactory derivation of a master equation has ever been given from the Schrödinger equation *under general conditions*, van Hove's work¹⁰ involving the diagonal singularity conditions, the initial random-phase assumption, and the " $\lambda^2 t$ limit" being perhaps the most satisfactory analysis available. It is therefore difficult, if at all possible, to assure oneself, from first principles, of the validity of such a starting point. However, it must also be emphasized that the Förster-Dexter theory¹ of intermolecular transfer decoupled from relaxation, and the Montroll-Shuler theory¹¹ of pure relaxation in a single molecule involving no transfer, are both based on a master-equation approach and have been successful at interpreting experiments. In fact, the basic evolution equations of these two theories are formally contained in (1.1). Thus, dropping the subscripts m and n and writing $\mathcal{R}^{MN} = F^{MN}$ reduces (1.1) to

$$\frac{dP_m^M(t)}{dt} = \sum_n [F^{MN} P_n^N(t) - F^{NM} P_m^M(t)], \quad (1.2)$$

the formal basis of the Förster-Dexter analysis, while dropping the superscripts M and N and writing $\mathcal{R}_{mn} = \gamma_{mn}$ reduces (1.1) to

$$\frac{dP_m(t)}{dt} = \sum_n [\gamma_{mn} P_n(t) - \gamma_{nm} P_m(t)], \quad (1.3)$$

which, when the Landau-Teller prescription¹² for the relaxation rates is incorporated into the γ 's, becomes the basic equation of the Montroll-Schuler analysis of pure relaxation.

To give Eq. (1.1) physical content, a specific form for \mathcal{R}_{mn}^{MN} must be chosen. Considering a dimer (a pair of molecules) for simplicity (see Fig. 1) note that the problem may be analyzed as the evolution of the system point on a phase space consisting of two quadrants (see Fig. 2). Each quadrant has the vibrational states of the "excited oscillator" of one site on one axis and those of the "ground oscillator" of the *other site* on the other axis. Relaxation corresponds to motion within the quadrants while transfer involves hops from one quadrant to the other. We now assume energy conservation during the transfer process, and this makes the transfer rates "horizontal"

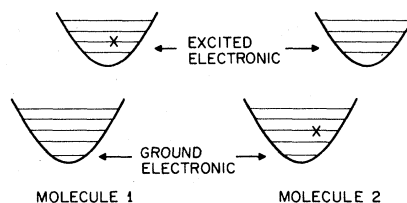


FIG. 1. Schematic representation of the dimer showing the "ground oscillator" and the "excited oscillator" of the two molecules, corresponding to the vibrational manifolds of the ground and excited electronic states. The crosses denote electrons and the figure shows molecule 1 as excited.

(see Fig. 2), since transfer from a point on one quadrant must take place to points on a line of slope -1 passing through the corresponding point on the other quadrant. This has been emphasized in Fig. 2 by showing these lines explicitly. We shall also neglect the internal dynamics on the lines.¹³ Finally, we assume that the relaxation rates do not depend on which site the electronic excitation occupies, meaning thereby that we believe the bath interaction (which causes relaxation) to be essentially independent of which molecule is under consideration. These physical assumptions result in

$$\mathcal{R}_{mn}^{MN} = \gamma_{mn} \delta_{M, N} + F_m^{MN} \delta_{m, n}, \quad (1.4)$$

which reduces (1.1) to

$$\begin{aligned} \frac{dP_m^M(t)}{dt} = & \sum_n [\gamma_{mn} P_n^M(t) - \gamma_{nm} P_m^M(t)] \\ & + \sum_N [F_m^{MN} P_n^N(t) - F_m^{NM} P_m^M(t)]. \end{aligned} \quad (1.5)$$

Equation (1.5), the basis of our analysis in this paper, describes the relaxation and the transfer parts of the combined process respectively, through the first and the second terms in its right-hand side.

II. TRANSFORMATION AND RESULTS FOR THE LIKE DIMER

The dimer problem involving *like* molecules is analyzed in this section. Thus M, N run over the values 1 and 2, and $F_m^{12} = F_m^{21} = F_m$. Equation (1.5)

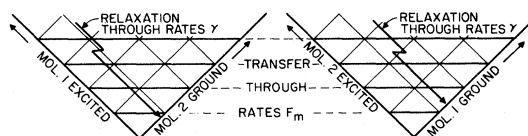


FIG. 2. Two-quadrant phase space of the dimer showing "horizontal," i.e., energy-conserving, transfer and intramolecular relaxation. See text for details.

reduces now to

$$\frac{dP_m^1(t)}{dt} = \sum_n [\gamma_{mn} P_n^1(t) - \gamma_{nm} P_m^1(t)] + F_m [P_m^2(t) - P_m^1(t)] \quad (2.1)$$

and a similar equation for $P_m^2(t)$. Basic to our analysis is the transformation

$$P_m^\pm(t) \equiv P_m^1(t) \pm P_m^2(t). \quad (2.2)$$

It results in

$$\frac{dP_m^+(t)}{dt} = \sum_n [\gamma_{mn} P_n^+(t) - \gamma_{nm} P_m^+(t)], \quad (2.3)$$

$$\frac{dP_m^-(t)}{dt} + 2F_m P_m^-(t) = \sum_n [\gamma_{mn} P_n^-(t) - \gamma_{nm} P_m^-(t)]. \quad (2.4)$$

These equations describe the decoupled evolutions of $P_m^+(t)$ and $P_m^-(t)$. Equation (2.3) is formally identical to (1.3) and can therefore be immediately solved if solutions to the corresponding pure relaxation problem are known. Equation (2.4) is formally identical to equations that have appeared in the work of Seshadri and the author¹⁴ in the context of luminescence competing with relaxation and in the earlier work of Matthews *et al.*¹⁵ and of Freed and Heller.¹⁶ The transformation (2.2) thus converts the relaxation-transfer problem into two *separate relaxation problems*: one with and the other without a true sink process.

Let us now use the Montroll-Shuler description^{11,12,14-17} for pure relaxation

$$\gamma_{mn} = k[(m+1)\delta_{n,m+1} + (m+D-1)e^{-\beta}\delta_{n,m-1}], \quad (2.5)$$

which arises from harmonic-oscillator selection rules, the assumed D -fold degeneracy of the oscillator,¹⁷ and the requirement of detailed balance. Here k characterizes the interaction with the bath and β is $\hbar\omega/k_B T$, the dimensionless inverse temperature, ω , k_B , and T being the oscillator frequency, the Boltzmann constant, and the temperature, respectively. The dependence of the transfer rates F_m on the vibrational energy label m can be obtained by computer calculations within the Franck-Condon framework. Such calculations have shown a monotonic increase with m which we shall model by the linear dependence

$$F_m = B + mC \quad (2.6)$$

for analytic tractability.

The relaxation-transfer problem as described by (2.1), with the substitutions (2.5) and (2.6), can be solved *exactly*. The first step is the solution of (2.3) and (2.4) with the help of techniques developed earlier for the pure relaxation¹¹ and the relaxation-with-sink¹⁴⁻¹⁶ problems; the second step is the reverse use of the transformation (2.2). The method of solution of (2.3) or (2.4) consists of solving the *first-order* partial differential equations for the Green's functions

$$G^\pm(z, t) \equiv \sum_m z^m P_m^\pm(t), \quad (2.7)$$

and it yields exact solutions for $P_m^\pm(t)$ for arbitrary initial conditions. The details are similar to the analysis presented in Refs. 11 and 14 and will not be given here. However, we shall treat a specific example which, while requiring relatively little algebraic detail, clarifies the physics of the situation. As stated above¹⁷ we have put $D=1$ in (2.5) for simplicity.

Let molecule 1 be initially excited electronically, the vibrational distribution being of a Boltzmann form at a nonenvironment temperature $T_0 = (\hbar\omega/k_B \beta_0)$. Thus,

$$P_m^1(0) = e^{-m\beta_0}(1 - e^{-\beta_0}), \quad (2.8)$$

$$P_m^2(0) = 0, \quad (2.9)$$

and the average vibrational energy of molecule 1, in units of $\hbar\omega$, is $(e^{\beta_0} - 1)^{-1}$. The transformation (2.2), when applied to (2.8) and (2.9), yields

$$P_m^\pm(0) = e^{-m\beta_0}(1 - e^{-\beta_0}). \quad (2.10)$$

With these initial conditions, the exact solution of (2.1) can be shown to be

$$\begin{aligned} P_m^{1,2}(t) = & \frac{1}{2} \{ e^{-m\beta'(t)} (1 - e^{-\beta'(t)}) \\ & \pm \frac{1}{2} \{ e^{-m\beta(t)} (1 - \Gamma^- e^{-\beta(t)}) (1 - e^{-\beta_0}) \\ & \times (1 - e^{-\beta_0} \Gamma^-)^{-1} \exp[-t[2B + k e^{-\beta}(1 - \Gamma^-)]] \} \} \end{aligned} \quad (2.11)$$

where the sum of the two curly brackets corresponds to $P_m^1(t)$, and the difference to $P_m^2(t)$, and where

$$\beta'(t) = \ln \left(\frac{e^\beta(1 - e^{-\beta_0}) - (1 - e^{\beta-\beta_0}) \exp[-tk(1 - e^{-\beta})]}{(1 - e^{-\beta_0}) - (1 - e^{\beta-\beta_0}) \exp[-tk(1 - e^{-\beta})]} \right), \quad (2.12)$$

$$\beta(t) = \ln \left(\frac{\Gamma^+(1 - e^{-\beta_0} \Gamma^-) - \Gamma^-(1 - e^{-\beta_0} \Gamma^+) \exp[-tke^{-\beta}(\Gamma^+ - \Gamma^-)]}{(1 - e^{-\beta_0} \Gamma^-) - (1 - e^{-\beta_0} \Gamma^+) \exp[-tke^{-\beta}(\Gamma^+ - \Gamma^-)]} \right), \quad (2.13)$$

$$\Gamma^\pm = \frac{1}{2}(e^\beta + 1 + \delta) \pm \left[\frac{1}{4}(e^\beta + 1 + \delta)^2 - e^\beta \right]^{1/2}, \quad (2.14)$$

with $\delta = 2Ce^\beta/k$. It might be useful to note that for $C=0$, signifying a transfer rate which is independent of the vibrational state, Γ^+ and Γ^- become respectively identical to e^β and 1, and (2.13) reduces to (2.12).

Equation (2.11) gives the probabilities of occupation of any vibrational state of either molecule for all times. It thus describes exactly, and in full detail, the relaxation-transfer process under the initial condition that the electronic excitation was placed entirely on molecule 1 in a Boltzmann distribution at a nonenvironment temperature. All information concerning the process present in the probabilities is thus available from (2.11)–(2.14). In particular, the simpler quantities $P^1(t)$ and $P^2(t)$, which denote the respective probabilities that molecule 1 and 2 are electronically excited, are obtained by summing (2.11) over the vibrational states:

$$P^1(t) = \frac{1}{2} \left[1 + \left(\frac{1 - e^{-\beta_0}}{1 - e^{-\beta(t)}} \right) \left(\frac{1 - \Gamma^- e^{-\beta(t)}}{1 - \Gamma^- e^{-\beta_0}} \right) \times \exp\{-t[2B + ke^{-\beta}(1 - \Gamma^-)]\} \right], \quad (2.15)$$

$$P^2(t) = \frac{1}{2} \left[1 - \left(\frac{1 - e^{-\beta_0}}{1 - e^{-\beta(t)}} \right) \left(\frac{1 - \Gamma^- e^{-\beta(t)}}{1 - \Gamma^- e^{-\beta_0}} \right) \times \exp\{-t[2B + ke^{-\beta}(1 - \Gamma^-)]\} \right], \quad (2.16)$$

where $\beta(t)$ and P^\pm are given by (2.13) and (2.14), respectively. Equations (2.15) and (2.16) should be compared with

$$P_{FD}^1(t) = \frac{1}{2}(1 + \exp\{-t[2B + 2C(e^\beta - 1)^{-1}]\}), \quad (2.17)$$

$$P_{FD}^2(t) = \frac{1}{2}(1 - \exp\{-t[2B + 2C(e^\beta - 1)^{-1}]\}), \quad (2.18)$$

which are the result of the Förster-Dexter (FD) theory,¹ wherein the relaxation process is assumed to be completed before transfer and the "thermalized" rate F^{th} is used:

$$F^{\text{th}} \equiv \sum_m F_m e^{-m\beta}(1 - e^{-\beta}) = B + C(e^\beta - 1)^{-1}. \quad (2.19)$$

III. TIME-DEPENDENT TRANSFER RATES

The comparison of our results (2.15) and (2.16) with the Förster-Dexter results (2.17) and (2.18) brings out several interesting points. To appreciate them consider the quantity $P^- = P^1 - P^2$. It can be shown¹⁸ that it obeys

$$\frac{dP^-(t)}{dt} + 2P^-(t)[B + C(e^{\beta(t)} - 1)^{-1}] = 0. \quad (3.1)$$

The corresponding quantity $P_{FD}^- \equiv P_{FD}^1 - P_{FD}^2$ in the Förster-Dexter theory obeys

$$\frac{dP_{FD}^-(t)}{dt} + 2P_{FD}^-(t)[B + C(e^\beta - 1)^{-1}] = 0. \quad (3.2)$$

Equations (2.20) and (2.21) may be considered consequences of a transfer process wherein the dynamics of the vibrational states is not described explicitly but the *transfer rates are taken to be generally time dependent*. Thus

$$\frac{dP^1(t)}{dt} = F(t)[P^2(t) - P^1(t)], \quad (3.3)$$

$$\frac{dP^2(t)}{dt} = F(t)[P^1(t) - P^2(t)] \quad (3.4)$$

reduce to the Förster-Dexter results (2.17), (2.18), and (3.2), when $F(t)$ is given by (2.19) and to our general results (2.15), (2.16), and (3.1) if $F(t)$ is given by

$$F(t) = B + C(e^{\beta(t)} - 1)^{-1}. \quad (3.5)$$

Observe the similarity of (3.5) and (2.19).

This time-dependent transfer rate $F(t)$ has the initial value $F(0) = B + C(e^{\beta_0} - 1)^{-1}$ corresponding to the initial vibrational distribution on molecule 1, and it changes in time as a consequence of the relaxation process. A striking result is that at large times the rate does not tend to the thermalized value F^{th} given by (2.19). Instead it tends to a smaller value

$$F(\infty) = B + C(e^{\beta(\infty)} - 1)^{-1} = B + C(\Gamma^+ - 1)^{-1}. \quad (3.6)$$

This behavior of the rate is intimately related to a result described in Ref. 14 wherein the temperature of an excited state tends at large times to a value below that of the environmental temperature. As will be explained in Sec. VII, this behavior of the transfer rate is expected to have general validity and not to be an artifact of the particular transition probabilities and master equations used in obtaining (3.6).

The transfer rate $F(t)$ has been plotted in Fig. 3, and the probability of the initially unexcited molecule in Fig. 4, as functions of time for several values of the initial temperature. If the latter is higher than the environmental temperature, the transfer rate is initially high, it slows down with time, crosses the value F^{th} and ends up being equal to (3.6) and therefore lower than the Förster-Dexter value. If the temperature of the initial distribution is low, the rate starts with a small value, rises to $F(\infty)$ and never reaches the FD value. The "depression" of $F(\infty)$ below F^{th} is, of course, independent of the initial distribution, and is small or large according as the ratio $C/ke^{-\beta}$ is small or large. The rate-depression phenomenon predicted above should not therefore be observable in the limit of very fast relaxation ($k \rightarrow \infty$) or of an m -independent $F_m(C \rightarrow 0)$.

It should be noted that whether the *average rate* of transfer is slower or faster than the FD rate

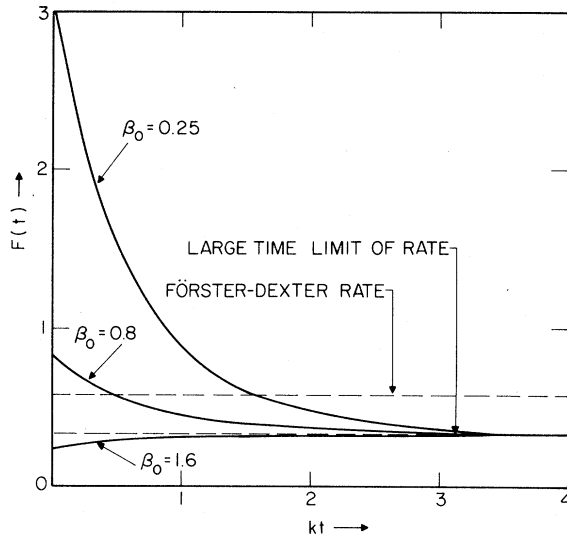


FIG. 3. Time-dependent transfer rate $F(t)$ as a function of time for several values of the initial temperature $T_0 = \hbar\omega/k_B\beta_0$ representing energy of initial excitation. Parameter values are arbitrary: $\beta=1$, $B=0$, $C=1$. The rate-depression phenomenon, i.e., the tendency of the rate $F(t)$ to the value $F(\infty)$ below the Förster-Dexter value F^{th} , is clearly seen.

F^{th} , will depend on the relative values of β_0 , β , and $C/ke^{-\beta}$. An initially high energy of excitation, measured by $\hbar\omega(e^{\beta_0} - 1)^{-1}$, does not guarantee faster transfer in spite of F_m being an increasing function of m . On the other hand, an initial excitation with a temperature below that of the envi-

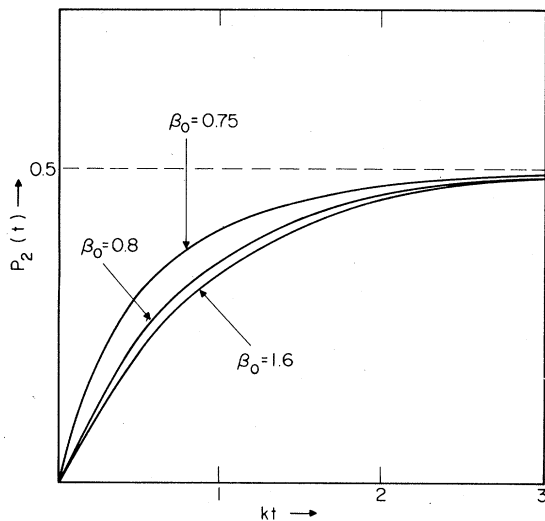


FIG. 4. Probability of the initially unexcited molecule as a function of time showing the dependence of transfer efficiency on the energy of initial excitation. Parameter values are the same as in Fig. 3.

ronment *does* guarantee transfer slower than the one given by the FD theory.

This analysis thus yields the explicit dependence of transfer efficiency on the initial energy of excitation. The case of low initial energy corresponds to Weber's observations³ of the red-edge effect. Excitation at long wavelengths, i.e., at the red edge of the spectrum, dumps a small amount of initial energy and, as has been *quantitatively* shown above, leads to less efficient transfer. In this discussion we have used initial distributions which have a Boltzmann form. This has been done for calculational convenience as it brings out the essential physics of the relaxation-transfer process.¹⁹ Excitation will generally result in a non-Boltzmann distribution, and the above simple form of the time-dependent transfer rate will be destroyed. However, the qualitative behavior of transfer described above will not change. For the forms of F_m and γ_{mn} used above, it is indeed possible to give exact solutions of $P^{1,2}(t)$ for *any* initial distribution.

IV. QUANTUM YIELDS AND LIGHT INTENSITIES

It has been shown above how the relaxation-transfer process may be studied in terms of exact analytical solutions for the probabilities. In a real system other processes involving a true decay of the probability coexist with relaxation and transfer and may compete with them. Examples of these are luminescence and nonradiative intramolecular transitions (such as intersystem-crossing and internal conversion). The competition of the latter with relaxation alone has been analyzed thoroughly by Freed and collaborators.¹⁶ The luminescence-relaxation problem has been treated by Seshadri and the author^{14,20} and the full details will be reported separately.²⁰ We now show how to analyze the combined relaxation-transfer-decay process where the decay may include both radiative and nonradiative channels, and how to obtain expressions for experimentally measurable quantities such as quantum yields and differential photon count rates.

To this end we extend Eq. (1.5) to include the decay processes by adding to its left-hand side the terms $\alpha_m P_m^M(t)$ and $\alpha'_m P_m^M(t)$. The first term represents radiative decay and, as has been shown elsewhere²¹ the assumption that it is linear in m ,

$$\alpha_m = b + mc, \quad (4.1)$$

is exact within the Franck-Condon framework provided the electron-phonon coupling does not involve nonlinear terms. The second term represents nonradiative decay. The assumption of linearity is poorer in its context, but following

Freed and Heller¹⁶ we shall use it in the present treatment, the reason being, as in the case of (2.6), analytical tractability. Thus,

$$\alpha'_m = b' + mc'. \quad (4.2)$$

The basic equation for the relaxation-transfer-decay process is then

$$\begin{aligned} \frac{dP_m^M}{dt} + (\alpha_m + \alpha'_m)P_m^M \\ = \sum_n (\gamma_{mn}P_n^M - \gamma_{nm}P_m^M) + \sum_N (F_m^{MN}P_N^M - F_m^{NM}P_m^M). \end{aligned} \quad (4.3)$$

Restricting the analysis to the dimer and making the transformation (2.2) we get

$$\frac{dP_m^+}{dt} + (\alpha_m + \alpha'_m)P_m^+ = \sum_n (\gamma_{mn}P_n^+ - \gamma_{nm}P_m^+), \quad (4.4)$$

$$\frac{dP_m^-}{dt} + (\alpha_m + \alpha'_m + 2F_m)P_m^- = \sum_n (\gamma_{mn}P_n^- - \gamma_{nm}P_m^-), \quad (4.5)$$

which are two decoupled equations both describing relaxation processes with true sinks. Since (2.6), (4.1), and (4.2) make the decay terms in (4.4) and (4.5) have the respective linear expressions $(b + b') + m(c + c')$ and $(b + b' + 2B) + m(c + c' + 2C)$, the same techniques used in the solution of (2.4) may be immediately applied to (4.4) and (4.5). One obtains, through (2.2), expressions for the probabilities $P_m^{1,2}(t)$ for all times corresponding to any given initial distribution. The solution of the relaxation-transfer-decay problem is thus complete within the above framework.

The experimentally accessible quantities $I(t)$, the differential photon count rate, and ϕ , the quantum yield of luminescence are, respectively, given by

$$I(t) = \sum_m \alpha_m P_m(t), \quad (4.6)$$

$$\phi = \left(\int_0^\infty dt I(t) \right) \left(\sum_m P_m(0) \right)^{-1}, \quad (4.7)$$

where we have not displayed the site labels on I , ϕ , and P_m . Equation (4.1) introduces a significant simplification in the computation of these quantities. The details of $P_m^{1,2}(t)$ are not needed, only the "zerth moment" $P^{1,2}(t)$ and the "first moment" $\sum_n n P_n^{1,2}(t) \equiv \langle n(t) \rangle^{1,2}$ being of interest:

$$I^{1,2}(t) = bP^{1,2}(t) + c\langle n(t) \rangle^{1,2}, \quad (4.8)$$

$$\begin{aligned} \phi^{1,2} = \left(b \int_0^\infty dt P^{1,2}(t) + c \int_0^\infty dt \langle n(t) \rangle^{1,2} \right) \\ \times \left(\sum_m P_m^1(0) + \sum_m P_m^2(0) \right)^{-1}. \end{aligned} \quad (4.9)$$

Note that the last factor in (4.9) contains the *total* initial probability that the dimer is excited. Expressions for $P^{1,2}(t)$ and $\langle n(t) \rangle^{1,2}$ can be computed exactly for arbitrary initial distributions. Defining $\langle n(t) \rangle^\pm \equiv \langle n(t) \rangle^1 \pm \langle n(t) \rangle^2$ and $P^\pm(t) \equiv P^1(t) \pm P^2(t)$, it is possible to write

$$\begin{aligned} \frac{d\langle n(t) \rangle^+}{dt} + \langle n(t) \rangle^+ [b + b' + c + c' + k(1 - e^{-\beta})] \\ = P^+(t) [ke^{-\beta} + \mathfrak{B}_r^+(t)], \end{aligned} \quad (4.10)$$

$$\begin{aligned} \frac{d\langle n(t) \rangle^-}{dt} + \langle n(t) \rangle^- \{b + b' + 2B + c + c' + 2C + k(1 - e^{-\beta})\} \\ = P^-(t) \{ke^{-\beta} + \mathfrak{B}_r^-(t)\}, \end{aligned} \quad (4.11)$$

$$\frac{dP^+(t)}{dt} + P^+(t) \{b + b'\} + \{c + c'\} \langle n(t) \rangle^+ = 0, \quad (4.12)$$

$$\frac{dP^-(t)}{dt} + P^-(t) \{b + b' + 2B\} + \{c + c' + 2C\} \langle n(t) \rangle^- = 0 \quad (4.13)$$

for a δ -function initial distribution of the probabilities: $P_m^1(0) = \delta_{m,r}$ and $P_m^2(0) = 0$. This represents initial excitation on molecule 1 in the *single vibrational state* r and these results can be used to calculate the required quantities for arbitrary initial distributions by using the principle of superposition. Information about the initially excited level r is contained only in the terms $\mathfrak{B}_r^\pm(t)$ of Eqs. (4.10) and (4.11). Explicit expressions for these terms are complicated, are completely analogous to those given in Eqs. (10) of Ref. 14(b) and will not be displayed here.

It is straightforward, if tedious, to develop explicit expressions for the differential photon count rate and the quantum yield for initial Boltzmann distributions. The procedure is described below.

The solution of (4.4) and (4.5) can be cast into the simple form

$$P(t) = \frac{1 + (1 - \Gamma^-)\chi(t)}{1 + (1 - \Gamma^-)\chi(0)} e^{-tg}, \quad (4.14)$$

where the "quasimoment"^{14b} $\chi(t)$ is given by

$$\chi(t) = (e^{\beta(t)} - 1)^{-1}. \quad (4.15)$$

The suffixes \pm have been omitted in (4.14), but we emphasize that Γ^- , $\chi(t)$, and g are different for $P^+(t)$ and $P^-(t)$. The substitution of $2B$ by $(b + b' + 2B)$ in (2.14) and (2.13) gives Γ^- and $\beta(t)$, respectively, for $P^-(t)$; and g is given by $[(b + b' + 2B) + ke^{-\beta}(1 - \Gamma^-)]$. The substitution of $2B$ by $(b + b')$ in those equations gives the respective values of Γ^- and $\beta(t)$ for $P^+(t)$; and g is given by dropping $2B$ from the expression corresponding to $P^-(t)$. The addition and subtraction of $P^+(t)$ and $P^-(t)$ then yields $P^1(t)$ and $P^2(t)$ through the transformation (2.2).

As a result of the invariance of the Boltzmann form,¹⁴ one can derive the following simple result for $\langle n(t) \rangle^\pm$:

$$\begin{aligned} \langle n(t) \rangle &= \chi(t)P(t) \\ &= \left[\frac{1}{1 + (1 - \Gamma^-)\chi(0)} \right] \chi(t)e^{-gt} \\ &\quad + \left[\frac{1 - \Gamma^-}{1 + (1 - \Gamma^-)\chi(0)} \right] \chi^2(t)e^{-gt}, \end{aligned} \quad (4.16)$$

where again the suffixes \pm on $\langle n(t) \rangle$, $P(t)$, $\chi(t)$, g , and Γ^- have not been displayed explicitly. The quantities $\chi^2(t)$ and $\chi(t)$ are connected through the differential equation

$$1 + \{1 - e^\beta - \delta\} \chi(t) - \frac{1}{ke^{-\beta}} \frac{d\chi(t)}{dt} = \delta \chi^2(t), \quad (4.17)$$

which has been derived in another context earlier.^{14b} The addition and subtraction of $\langle n(t) \rangle^+$ and $\langle n(t) \rangle^-$ gives $\langle n(t) \rangle^1$ and $\langle n(t) \rangle^2$, and the differential photon count rate and the quantum yield are then obtained from (4.8) and (4.9).

It may be useful to observe that while the calculation of the quantum yield ϕ involves the integrals $\int_0^\infty dt e^{-gt} \chi(t)$ and $\int_0^\infty dt e^{-gt} \chi^2(t)$, the latter can be expressed in the terms of the former through (4.17) as

$$\begin{aligned} \int_0^\infty dt e^{-gt} \chi^2(t) &= \left(\frac{1 + (1 - \Gamma^-)\chi(0)}{\delta g} + \chi(0) \frac{g - ke^{-\beta}(1 - \Gamma^-)}{\delta g} \right) \\ &\quad + g \left(\frac{1 - e^\beta - \delta}{\delta} - \frac{ge^\beta}{k\delta} \right), \end{aligned} \quad (4.18)$$

where

$$g = \int_0^\infty dt e^{-gt} \chi(t).$$

The evaluation of this integral g involves an infinite series as it is related to the Laplace transform of hyperbolic functions. A quick view of the dependence of the quantum yield on $\chi(0)$, which measures the initial energy of excitation, may be obtained by approximating $\chi(t)$ by an exponential leading to

$$g = \frac{\chi(0)}{g + \mu} + \frac{\mu \chi(\infty)}{g(g + \mu)}, \quad (4.19)$$

where μ is the rate constant in the assumed exponential decay of $\chi(t)$. Note in this context that $\chi(0)$ appearing in the + equations is the same as that appearing in the - equations.

V. GENERALIZATIONS

The analysis of the dimer of like molecules presented in Secs. II-IV will now be generalized in several different ways. In each of the following cases an additional term denoting a true sink

(radiative or nonradiative) may be added to the equations without changing the analysis in any essential way.

A. Generalization to a periodic array of many like molecules

Instead of (2.2) use the transformation

$$P_m^\xi(t) \equiv \sum_M P_m^M(t) e^{i\xi \cdot M}, \quad (5.1)$$

where M (as well as ξ) can be a three-dimensional vector and where the sum over M covers all the molecules in the array. Equation (5.1) when used in (1.5) yields

$$\frac{dP_m^\xi}{dt} + A_m^\xi P_m^\xi = \sum_n \{ \gamma_{mn} P_n^\xi - \gamma_{nm} P_m^\xi \}, \quad (5.2)$$

$$A_m^\xi = \sum_{(M-N)} e^{i\xi \cdot (M-N)} A_m^{MN}, \quad (5.3)$$

$$-A_m^{MN} = F_m^{MN} \text{ for } M \neq N \text{ and } A_m^{MM} = \sum_N F_m^{NM}. \quad (5.4)$$

Equation (5.2) which describes the evolution of the probability distribution (over the vibrational states m) of the " ξ th mode" of the transfer process, also presents a relaxation-with-decay problem already analyzed in the context of (2.4). Notice that the m dependence of the decay coefficient A_m^ξ is identical to that of F_m^M and techniques discussed in Secs. II-IV can therefore be trivially applied towards the solution of (5.2). Thus the initial information about $P_m^M(0)$ is translated into information about $P_m^\xi(0)$ through (5.1), Eq. (5.2) is solved as before, and (5.1) is used again to obtain the required probabilities $P_m^M(t)$ and any derived quantities.

B. Generalization to an arbitrary nonperiodic array of many like molecules

Here the transformation (5.1) is not useful because the absence of periodicity makes F^{MN} dependent on more than merely the difference $M-N$. Exact solutions of (1.5) can still be obtained in this case if solutions of the corresponding transfer problem are known. Required thus are the eigenvalues and eigenvectors of the matrix of A 's in

$$\frac{dP_m^M}{dt} + \sum_N A_m^{MN} P_m^N = \sum_n (\gamma_{mn} P_n^M - \gamma_{nm} P_m^M), \quad (5.5)$$

where the A 's are given by (5.4). Calling the eigenvalues A_m^ξ , Eq. (5.2) is again obtained although (5.3) does not hold. The analysis of the relaxation-transfer problem proceeds then as in Sec. VA. Of importance is the fact that the diagonalization of the matrix of A 's has nothing to do

with the vibrational manifold. Note here that in general the given transfer matrix must first be symmetrized by an appropriate transformation before attempting to find its eigenvalues and eigenfunctions.

A simple but important application of the generalization of this section is the analysis of the dimer of unlike molecules. The details of that analysis will be reported elsewhere.

C. Generalization to "nonhorizontal" transfer

By "nonhorizontal" transfer we mean that the transfer matrix F^{MN} is of the general nondiagonal form F_{mn}^{MN} in the vibrational states. This would correspond to (a) transfer processes wherein energy conservation does not hold on account of their being bath-assisted for instance, or to (b) the case where the internal dynamics on the "lines of slope 1" of Fig. 2 is *not* neglected, labels m, n being used also to denote points along those lines. For a dimer this means

$$\mathcal{R}_{mn}^{21} = \mathcal{R}_{mn}^{12} = F_{mn}, \quad \mathcal{R}_{mn}^{11} = \mathcal{R}_{mn}^{22} = \gamma_{mn}, \quad (5.6)$$

and it results in (2.3) for P_m^* with the matrix γ replaced by the matrix $(\gamma + F)$ and

$$\begin{aligned} \frac{dP_m^*}{dt} + \left(2 \sum_n F_{nm} \right) P_m^* \\ = \sum_n [(\gamma_{mn} - F_{mn}) P_n^* - (\gamma_{nm} - F_{nm}) P_m^*], \quad (5.7) \end{aligned}$$

for P_m^* . Comparing (5.7) to (2.4), one observes that F_m is replaced by $(\sum_n F_{nm})$ and γ_{mn} by $(\gamma_{mn} - F_{mn})$. The "nonhorizontal" part of transfer thus adds to the relaxation of the "+ mode" but subtracts from the relaxation of the "- mode". The generalization to an arbitrary nonperiodic array is obvious.

D. Generalization to coherent transfer

Much recent work²² has gone into extending the basic theory¹ of excitation transfer in order to incorporate coherent or wavelike transport. The author has shown²³ explicitly how the various theories can be reinterpreted in terms of non-Markoffian master equations. These replace the \mathcal{R} 's in a master equation such as (1.1) by memory-possessing rates making the equation nonlocal in time. Wavelike (coherent) behavior results in the early stages, and diffusive (incoherent) behavior in the later stages. The competition between such generalized transfer and relaxation may be described by

$$\begin{aligned} \frac{dP_m^{1,2}(t)}{dt} = \sum_n [\gamma_{mn} P_n^{1,2}(t) - \gamma_{nm} P_m^{1,2}(t)] \\ + \int_0^t dt' \mathcal{W}_m(t-t') [P_m^{2,1}(t') - P_m^{1,2}(t')], \quad (5.8) \end{aligned}$$

where we have considered a dimer of like molecules for simplicity, $\mathcal{W}_m(t)$ is related to F_m through

$$\int_0^\infty dt \mathcal{W}_m(t) = F_m, \quad (5.9)$$

and where we have not incorporated memory effects in the relaxation rates, although their inclusion is straightforward. The transformation (2.2) then results in

$$\begin{aligned} \tilde{P}_m^*(t) = \left(\epsilon + 2\tilde{\mathcal{W}}_m(\epsilon) + \sum_n \gamma_{nm} \right)^{-1} \\ \times \left(P_m^*(0) + \sum_n \gamma_{mn} \tilde{P}_n^*(\epsilon) \right), \quad (5.10) \end{aligned}$$

for the Laplace transform of $P_m^*(t)$, ϵ being the Laplace variable and tildes denoting transforms, and (2.3) for the evolution of $P_m^*(t)$. Whether or not (5.10) can be solved exactly will depend on the memory functions $\mathcal{W}_m(t)$.

VI. DISCUSSION OF THE ASSUMPTIONS

A. Use of master equations

As stated in Sec. I, despite important advances¹⁰ in the subject of nonequilibrium statistical mechanics, the exact domain of validity of master equations is still not understood well in general. It is thus possible that important physics is lost by the use of a master-equation approach in the present context. However, the virtue of such an approach is that it can be carried through without the use of uncontrollable approximations, and the results obtained are guaranteed to be consequences of the original equations and not the accidental outcome of an approximation. This is not so for any microscopic approach developed so far for the present problem. Furthermore, the previous success of the master-equation approach in the transfer problem alone¹ and in the relaxation problem alone¹¹ leads one to expect that it will be reasonably accurate for the transfer-relaxation problem.

We must also mention a shortcoming of the present approach which has nothing to do with its validity. Being concerned with probabilities, it is incapable, in the present form, of describing quantities requiring off-diagonal elements of the density matrix in the representation chosen. On account of this, as well as of the validity question, we shall attempt, in the near future, to relate this approach to a full density-matrix analysis.

B. Neglect of internal dynamics on "lines of slope-1"

These lines (see Fig. 2) are regions of constant energy in the dimer phase space. The internal dy-

namics on these lines represents probability flow among isoenergetic states which have the same molecule electronically excited, but have a different distribution of the vibrational quanta between the two molecules. The details of this internal motion of the system have been neglected in Sec. I for simplicity. This neglect is justified if there exists a physical process that leads to "mixing" or "equilibration" on each of the lines, and if it is considerably faster than both transfer and relaxation. The applicability of the present analysis would then be restricted to times larger than the characteristic times of the mixing process. This fast-mixing process would mean (see Fig. 2) that the two molecules are in communication with each other through means other than transfer, and it is perhaps related to the entropy-sharing process mentioned by Dexter and Fowler.²⁴

If the fast-mixing process is absent, our neglect of the internal dynamics should be considered as an "averaging" approximation. To drop this approximation, one must keep track, in greater detail, not only of the relaxation process but also of the transfer rates, since the latter are different from (and to) different points on those lines. However, the dependence is given by Franck-Condon factors. And the generalization of Sec. VC shows explicitly how to carry out the analysis for this general situation.

C. The form of the relaxation, transfer, and decay rates

The nearest-neighbor character of the relaxation rates and their peculiar dependence on the vibrational energy [see Eq. (2.5)] are consequences of harmonic-oscillator selection rules and an oscillator bath interaction that is linear in the oscillator displacement. The particular expression of Eq. (2.5) for the relaxation rate will not be valid if the bath-molecule interaction is nonlinear or if a harmonic oscillator is not a good representation of the molecule. This representation by a single oscillator involves a nontrivial assumption since a real molecule will have many modes. The Kassel-Buff-Wilson extension¹⁷ with the degeneracy D cannot cover the whole story in this context because the various modes of the molecule will have different energies. As in the analysis of Freed and Heller,¹⁶ we here consider an *effective* single oscillator or mode.

As mentioned in Secs. II and IV, the assumption of linearity in the vibrational energy does not have the same strength in the context of the transfer, radiative decay, and nonradiative intermolecular rates. In the third case it is not a good assumption, in the second it can be quite good (even totally valid), and in the first it is reasonable. We mention here that,

where necessary, the linearity assumption can be dropped and a perturbative scheme constructed to handle the problem. This scheme is entirely analogous to the one applied to the luminescence problem^{20,21(b)} and is based on Ref. 25.

Equation (1.4) assumes the transfer rates to be "horizontal," i.e., energy conserving. This is not an essential assumption. We have shown explicitly in Sec. V how bath-assisted transfer requiring "nonhorizontality," i.e., $F_{mn} \neq F_m \delta_{mn}$ can be handled within the framework of our analysis.

D. Use of initial Boltzmann distributions

We emphasize that when the various rates are given by Eqs. (2.5), (2.6), (4.1), and (4.2), we can give exact expressions for every quantity of interest for *arbitrary* initial conditions. Thus the probabilities can be shown to be certain combinations of hypergeometric functions when the initial excitation process causes a single vibrational state to be populated. And any general initial distribution can be analyzed as a superposition of these "initially localized" solutions. However, initial Boltzmann distributions introduce significant simplifications in the algebra and can be used to elucidate the physics of the situation. Thus high initial temperatures correspond to high initial energy and can therefore represent excitation at high frequencies. Our only object in using initial Boltzmann distributions has been to get at the essential physics with the minimum amount of algebra.

VII. CONCLUDING REMARKS

Several assumptions of various degrees of validity have gone into the analysis presented in this paper. However, they have all been made at one place (the starting point) in the analysis and have been followed by *exact* calculations. The assumptions have been discussed in the previous section, and it has been indicated *explicitly* how most of them can be relaxed within the framework of the analysis. The primary mathematical idea of the analysis is the trivial one of successive diagonalizations of the \mathcal{R} matrix, first of its transfer part and then of its relaxation part.²⁶ The first part is based on a transformation like (2.2) or (5.1) and results in a relaxation-decay problem for every mode, the decay containing transfer contributions. The relaxation-decay problem is then solved with the help of methods developed earlier.¹⁴

Before applying this theory to a specific system, values must be assigned to the various parameters. These are as follows: The relaxation rate k indicative of the strength of the bath interaction; the degeneracy D suitably chosen to mimic the real density of states; the frequency ω of the effective

oscillator; B and C in the transfer rate F_m , and b and c in the radiative decay rate α_m , all four of which can be calculated from Franck-Condon factors; and b' and c' in the nonradiative intramolecular decay rate α'_m .

What comes out of the present analysis is (i) a prescription for a quantitative attempt at the explanation of Weber's red-edge effect³ involving the dependence of transfer efficiency (specifically, of the quantum yield) on the wavelength of initial excitation; (ii) the concept of time-dependent transfer rates which is especially helpful in making quick calculations avoiding complicated algebra: thus, Eqs. (3.3) and (3.4) may be used with a simple dependence for $F(t)$ such as $F(t) = F(\infty) + [F(0) - F(\infty)]e^{-t/\tau}$; (iii) the rate-depression (or rate-enhancement) phenomenon whereby the long-time limit of the transfer rate is seen to be generally different from the thermalized Förster-Dexter value [see Eq. (3.6) and Fig. 3]; (iv) a natural mechanism that could be responsible for the observed deviation in some systems, of the dependence of the effective transfer rate on the intermolecular distance from the Förster-Dexter prediction of R^{-6} (for singlet transfer).

It should be noted that (iii) and (iv) do not require the particular linear forms for the rates used in our analysis. If the transfer rates from individual vibrational levels do increase with increasing vibrational energy, the result $F(\infty) < F^{\text{th}}$ is expected independently of the specific form for F_m . This is so because the higher vibrational states of the initially excited molecule will empty their excitation faster than the lower states (because F_m is larger at high m), leading to an effectively lower temperature and consequently a lower transfer rate.²⁷ By the same token, $F(\infty) > F^{\text{th}}$ will obtain if F_m decreases with increasing vibrational energy.²⁸ The rate depression or rate-enhancement effect is thus a general result. Slow relaxation has therefore two effects: the transfer rate $F(t)$ changes in time at a finite pace, and its

long-time value splits off from F^{th} . As has been mentioned in Sec. III the difference $F^{\text{th}} - F(\infty)$ is large or small according to the largeness or smallness of $C/ke^{-\beta}$. (See, however, footnote 28.)

The effective rate of transfer will obviously involve an average of $F(t)$ over an appropriate interval. The interval will depend on what property related to $F(t)$ is of interest and will be derived from the duration of some physical process (such as luminescence) used to probe $F(t)$. For simplicity let us consider the effective F as given by the following weighted average:

$$F_{\text{eff}} = \frac{\int_0^{\infty} dt e^{-t/\tau} F(t)}{\int_0^{\infty} dt e^{-t/\tau}}, \quad (7.1)$$

where τ may be a luminescence decay time. Equation (3.5) reduces (7.1) to

$$F_{\text{eff}} = B + (C/\tau) \int_0^{\infty} dt e^{-t/\tau} (e^{\beta(t)} - 1)^{-1}, \quad (7.2)$$

wherein F_{eff} is seen to depend on C in two ways: through the factor multiplying the integral and through $\beta(t)$. The latter dependence becomes clear on observing the presence of δ , which is proportional to C , in Eq. (2.13) for $\beta(t)$. The factor C is however dependent on the intermolecular distance R (just as B is) and goes as R^{-6} for singlet transfer by dipole-dipole interactions. It is clear therefore from (7.2) that F_{eff} will have an R dependence that is other than R^{-6} in general.²⁹ This result also is independent of the specifics used in the present analysis.

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- ¹⁸The demonstration is based on the observation that $P^-(t)$ is the "zereth moment" of the probability distribution $P^-(t)$, on Eq. (8a) of Ref. 14(b), and on the equality of $(e^{\beta(t)} - 1)^{-1}$ and the ratio of the first to the zeroth moment.
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- ²⁸It is important to realize that in a real system there are many modes and that it is possible that for some of them F_m increases while for others it decreases with increasing m . In such a case it is quite possible that the rate-depression or rate-enhancement effect is absent because of the cancellation of the contributions from the various modes.
- ²⁹In practice, this effect is expected to be observable only for very slow relaxation.