

Stochastic theory of combined radiative and nonradiative transport

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(Received 11 July 1997; accepted 12 September 1997)

A stochastic theory of combined radiative and nonradiative transport is presented. The stochastic approach is physically clear and versatile, allowing the consideration of the combined effect of radiative and nonradiative transport, carried out here for the first time. The stochastic approach is formulated for delta-pulse excitation and for the photostationary state. General equations for the intensity, polarization, and anisotropy decays are derived. © 1997 American Institute of Physics. [S0021-9606(97)52347-6]

I. INTRODUCTION

Radiative transfer, i.e., the transfer of energy mediated by real (as opposed to virtual) photons, is a common process of energy transport in astrophysics, plasmas, and in atomic and molecular luminescence. It plays an important role in solar concentrators, discharge and fluorescent lamps, scintillation counters, and lasers.

For the purposes of this work, molecular radiative transfer is defined as the emission of a photon by an electronically excited molecule, with subsequent absorption by a ground state molecule. In assemblies of like molecules, one elementary process of radiative transfer leads to another, until one of two things happens: (a) the excitation energy is irreversibly lost through a nonradiative path (internal conversion, intersystem crossing, quenching,...) or, (b) the photon escapes from the sample. This repeated radiative transfer is called either radiative transport or radiation trapping. Its importance depends on many factors: extent of spectral overlap between absorption and emission, absorption strength, fluorescence quantum yield, concentration, cell size and shape, excitation and detection geometries, etc. It is particularly important in solutions of highly fluorescent compounds with a good absorption–emission spectral overlap, whether concentrated or in large volumes. When present, radiative transport affects the measured fluorescence decays and spectra, as well as the fluorescence polarization. These observables are then a function of the excitation and emission wavelengths, concentration, and excitation and detection geometries.

A stochastic theory of radiative transport allowing the calculation of all observables from known parameters was recently presented.^{1,2} Such an approach is here refined and extended to cases where nonradiative transport operates in parallel with radiative transport.

The stochastic approach is formulated in Sec. II A for delta-pulse excitation, the principal results being the decay laws, Eqs. (15) and (17). It is next shown that these decay laws become single exponential for long times. The photostationary state is then briefly discussed in Sec. II B. The anisotropy of fluorescence is discussed in Sec. II C, the effect of radiative transport being contrasted to that of nonradiative transport. The main results in this section are Eqs. (32) and (33). In Sec. III, the combined effect of radiative and nonradiative transport is discussed. General equations for the po-

larization and anisotropy decays are derived [Eqs. (38) and (39)]. The main results are summarized in Sec. IV.

II. STOCHASTIC APPROACH

A. Formulation and delta-pulse response

Consider a homogeneous distribution of ground state molecules in a given enclosure (e.g., a fluorescence cell). Let there be the absorption of a photon at $t=0$, according to a given (normalized) spatial distribution $P_1(\mathbf{r})$. The excited molecule generated at time $t=0$ will relax to the ground state, with a rate constant Γ , Γ being the reciprocal molecular lifetime,

$$\Gamma = k_r + k_{nr} = \frac{1}{\tau_0}, \quad (1)$$

where k_r and k_{nr} are the radiative and nonradiative decay constants, respectively.

As a consequence of the decay, there is a probability $p_b(\lambda, t)$ that, between t and $t+dt$, a photon with wavelength λ will hit the enclosure's boundary at a given point \mathbf{r}_b , and will thus leave the sample (neglecting reflection). This probability can be written as

$$p_b(\lambda, t) = \sum_{n=1}^{\infty} p_{bn}(\lambda, t), \quad (2)$$

where $p_{bn}(\lambda, t)$ is the probability that a photon with wavelength λ will cross the boundary at point \mathbf{r}_b between t and $t+dt$, after exactly n absorption–emission events. This probability can in turn be written as

$$p_{bn}(\lambda, t) = f_{bn}(\lambda) g_n(t), \quad (3)$$

where $f_{bn}(\lambda)$ is the probability that a photon with wavelength λ will hit the boundary at point \mathbf{r}_b (thus leaving the sample), after exactly n absorption–emission events; and $g_n(t)$ is the probability that an n th generation molecule will emit a photon between t and $t+dt$, given that it will emit one. Assuming that the photon propagation time is negligible, this probability (normalized density function) is given by¹

$$g_n(t) = \Gamma \frac{(\Gamma t)^{n-1}}{(n-1)!} e^{-\Gamma t}. \quad (4)$$

The probability $f_{bn}(\lambda)$ is

$$f_{bn}(\lambda) = \frac{1}{4\pi} \Phi_0 F(\lambda) \int_V [1 - \alpha_b(\mathbf{r}, \lambda)] P_n(\mathbf{r}) d\mathbf{r}, \quad (5)$$

where the integration goes over the whole volume V of the enclosure, Φ_0 is the fluorescence quantum yield, the absorption probability $\alpha_b(\mathbf{r}, \lambda)$ is given by

$$\alpha_b(\mathbf{r}, \lambda) = \int_0^{|\mathbf{r}_b - \mathbf{r}|} k(\lambda) \exp[-k(\lambda)x] dx, \quad (6)$$

where $k(\lambda)$ is the optical density of the medium at the wavelength λ , and $P_n(\mathbf{r})$, probability that an n th generation photon will be emitted at \mathbf{r} , is

$$P_n(\mathbf{r}) = \int_V \int_V \dots \int_V f(\mathbf{r}, \mathbf{r}_{n-1}) \Phi_0 f(\mathbf{r}_{n-1}, \mathbf{r}_{n-2}) \dots \times \Phi_0 f(\mathbf{r}_2, \mathbf{r}_1) P_1(\mathbf{r}_1) d\mathbf{r}_{n-1} d\mathbf{r}_{n-2} \dots d\mathbf{r}_1, \quad (7)$$

with $f(\mathbf{r}, \mathbf{r}')$, probability of absorption at \mathbf{r} for emission at \mathbf{r}' , given by

$$f(\mathbf{r}, \mathbf{r}') = \int_0^\infty F(\lambda) k(\lambda) \frac{1}{4\pi |\mathbf{r} - \mathbf{r}'|^2} \times \exp[-k(\lambda)|\mathbf{r} - \mathbf{r}'|] d\lambda, \quad (8)$$

where $F(\lambda)$ is the normalized emission spectrum.

Equation (7) can be written as a recurrence relation,

$$P_{n+1}(\mathbf{r}) = \Phi_0 \int_V f(\mathbf{r}, \mathbf{r}_n) P_n(\mathbf{r}_n) d\mathbf{r}_n. \quad (9)$$

From it, one obtains the spatial distribution function $p_n(\mathbf{r})$ of the n th generation excited molecules,

$$p_n(\mathbf{r}) = \frac{P_n(\mathbf{r})}{\int_V P_n(\mathbf{r}) d\mathbf{r}} = \frac{\int_V f(\mathbf{r}, \mathbf{r}_{n-1}) p_{n-1}(\mathbf{r}_{n-1}) d\mathbf{r}_{n-1}}{\int_V \int_V f(\mathbf{r}, \mathbf{r}_{n-1}) p_{n-1}(\mathbf{r}_{n-1}) d\mathbf{r}_{n-1} d\mathbf{r}} = \frac{\alpha_{n-1}(\mathbf{r})}{\bar{\alpha}_{n-1}}, \quad (10)$$

where $\alpha_{n-1}(\mathbf{r})$ is the probability that a photon emitted according to the $(n-1)$ th generation spatial distribution will be absorbed at \mathbf{r} , and $\bar{\alpha}_{n-1}$ is the probability that a photon emitted according to the $(n-1)$ th generation spatial distribution will be absorbed somewhere within the enclosure. The spatial distributions given by Eq. (10) converge to a stationary distribution for large n . The equation for the stationary distribution of excited molecules, $p_s(\mathbf{r})$, is obtained from Eq. (10) by taking the limit $n \rightarrow \infty$ on both sides.

The normalized (i.e., scaled to one for $t=0$) decay law is

$$\begin{aligned} \rho_b(\lambda, t) &= \frac{p_b(\lambda, t)}{p_b(\lambda, 0)} \\ &= e^{-\Gamma t} \sum_{n=1}^{\infty} \frac{\int_V [1 - \alpha_b(\mathbf{r}, \lambda)] P_n^0(\mathbf{r}) d\mathbf{r} (k_r t)^{n-1}}{\int_V [1 - \alpha_b(\mathbf{r}, \lambda)] P_1^0(\mathbf{r}) d\mathbf{r} (n-1)!}, \end{aligned} \quad (11)$$

where $P_i^0(\mathbf{r})$ stands for $P_i(\mathbf{r})$ when $\Phi_0 = 1$. Using Eq. (10),

$$\begin{aligned} \rho_b(\lambda, t) &= e^{-\Gamma t} \sum_{n=1}^{\infty} \left(\frac{1 - \alpha_{bn}(\lambda)}{1 - \alpha_{b1}(\lambda)} \right) \\ &\quad \times \left(\frac{\int_V P_n^0(\mathbf{r}) d\mathbf{r}}{\int_V P_1^0(\mathbf{r}) d\mathbf{r}} \right) \frac{(k_r t)^{n-1}}{(n-1)!}, \end{aligned} \quad (12)$$

where

$$\alpha_{bi}(\lambda) = \int_V \alpha_b(\mathbf{r}, \lambda) p_i(\mathbf{r}) d\mathbf{r}. \quad (13)$$

Taking into account Eqs. (9) and (10) and the definition of $\bar{\alpha}_i$ [see Eq. (10)], one has

$$\frac{\int_V P_n^0(\mathbf{r}) d\mathbf{r}}{\int_V P_1^0(\mathbf{r}) d\mathbf{r}} = \prod_{i=1}^{n-1} \bar{\alpha}_i, \quad (14)$$

and Eq. (12) becomes,

$$\rho_b(\lambda, t) = e^{-\Gamma t} \sum_{n=1}^{\infty} \left(\frac{1 - \alpha_{bn}(\lambda)}{1 - \alpha_{b1}(\lambda)} \right) \left(\prod_{i=1}^{n-1} \bar{\alpha}_i \right) \frac{(k_r t)^{n-1}}{(n-1)!}. \quad (15)$$

The emission integrated over wavelengths and space directions is

$$\begin{aligned} \rho(t) &= e^{-\Gamma t} \sum_{n=1}^{\infty} \frac{\int_V P_n^0(\mathbf{r}) d\mathbf{r} - \int_V \int_V f(\mathbf{r}, \mathbf{r}') P_n^0(\mathbf{r}) d\mathbf{r} d\mathbf{r}'}{\int_V P_1^0(\mathbf{r}) d\mathbf{r} - \int_V \int_V f(\mathbf{r}, \mathbf{r}') P_1^0(\mathbf{r}) d\mathbf{r} d\mathbf{r}'} \\ &\quad \times \frac{(k_r t)^{n-1}}{(n-1)!} \\ &= e^{-\Gamma t} \sum_{n=1}^{\infty} \frac{1 - \bar{\alpha}_n}{1 - \bar{\alpha}_1} \frac{\int_V P_n^0(\mathbf{r}) d\mathbf{r} (k_r t)^{n-1}}{\int_V P_1^0(\mathbf{r}) d\mathbf{r} (n-1)!}. \end{aligned} \quad (16)$$

Using again Eq. (14), Eq. (16) becomes

$$\rho(t) = e^{-\Gamma t} \sum_{n=1}^{\infty} \left(\frac{1 - \bar{\alpha}_n}{1 - \bar{\alpha}_1} \right) \left(\prod_{i=1}^{n-1} \bar{\alpha}_i \right) \frac{(k_r t)^{n-1}}{(n-1)!}. \quad (17)$$

Knowing that a stationary distribution is reached for the higher generations ($\bar{\alpha}_n \rightarrow \bar{\alpha}_s$), one gets from Eq. (17),

$$\begin{aligned} \rho(t) &= e^{-\Gamma t} \sum_{n=1}^{\infty} \left(\frac{1 - \bar{\alpha}_n}{1 - \bar{\alpha}_1} \right) \left(\prod_{i=1}^{n-1} \bar{\alpha}_i \right) \frac{(k_r t)^{n-1}}{(n-1)!} \\ &\cong e^{-\Gamma t} \sum_{n=1}^m \left(\frac{1 - \bar{\alpha}_n}{1 - \bar{\alpha}_1} \right) \left(\prod_{i=1}^{n-1} \bar{\alpha}_i \right) \frac{(k_r t)^{n-1}}{(n-1)!} + e^{-\Gamma t} \\ &\quad \times \sum_{n=m+1}^{\infty} \left(\frac{1 - \bar{\alpha}_s}{1 - \bar{\alpha}_1} \right) \left(\prod_{i=1}^m \bar{\alpha}_i \right) \bar{\alpha}_s^{n-m-1} \frac{(k_r t)^{n-1}}{(n-1)!} \\ &= e^{-\Gamma t} \sum_{n=1}^m \left(\frac{1 - \bar{\alpha}_n}{1 - \bar{\alpha}_1} \right) \left(\prod_{i=1}^{n-1} \bar{\alpha}_i \right) \frac{(k_r t)^{n-1}}{(n-1)!} \\ &\quad + e^{-\Gamma t} \left(\frac{1 - \bar{\alpha}_s}{1 - \bar{\alpha}_1} \right) \left(\prod_{i=1}^m \bar{\alpha}_i \right) \sum_{n=m+1}^{\infty} \frac{(k_r \bar{\alpha}_s t)^{n-1}}{(n-1)!} \end{aligned}$$

$$\begin{aligned}
&= e^{-\Gamma t} \left[\sum_{n=1}^m \left(\frac{1-\bar{\alpha}_n}{1-\bar{\alpha}_1} \right) \left(\prod_{i=1}^{n-1} \bar{\alpha}_i \right) \frac{(k_r t)^{n-1}}{(n-1)!} \right. \\
&\quad \left. - \left(\frac{1-\bar{\alpha}_s}{1-\bar{\alpha}_1} \right) \left(\prod_{i=1}^m \frac{\bar{\alpha}_i}{\bar{\alpha}_s} \right) \sum_{n=1}^m \frac{(k_r \bar{\alpha}_s t)^{n-1}}{(n-1)!} \right] \\
&\quad + \left(\frac{1-\bar{\alpha}_s}{1-\bar{\alpha}_1} \right) \left(\prod_{i=1}^m \frac{\bar{\alpha}_i}{\bar{\alpha}_s} \right) e^{(k_r \bar{\alpha}_s - \Gamma)t}, \quad (18)
\end{aligned}$$

showing that a long time exponential, with lifetime

$$\tau_s = \frac{\tau_0}{1 - \bar{\alpha}_s \Phi_0}, \quad (19)$$

is asymptotically attained. The approximation made in Eq. (18) is of course the better, the higher m . A similar approximation holds for Eq. (15). The usefulness of this approach has been demonstrated.³ It is interesting to note that Eqs. (15) and (17) are formally identical to the decay law derived before from a kinetic scheme considering only macroscopic populations.⁴

B. Continuous excitation (photostationary state)

For nonsaturating excitation conditions, one may also obtain the steady-state intensities from Eqs. (15) and (17),

$$\frac{I_b(\lambda)}{I_{0b}} = F(\lambda) \sum_{n=1}^{\infty} [1 - \alpha_{bn}(\lambda)] \left(\prod_{i=1}^{n-1} \bar{\alpha}_i \right) \Phi_0^{n-1}, \quad (20)$$

$$\frac{I_b}{I_{0b}} = \frac{\Phi_b}{\Phi_0} = \sum_{n=1}^{\infty} (1 - \bar{\alpha}_{bn}) \left(\prod_{i=1}^{n-1} \bar{\alpha}_i \right) \Phi_0^{n-1}, \quad (21)$$

$$\begin{aligned}
\frac{I}{I_0} = \frac{\Phi}{\Phi_0} &= \sum_{n=1}^{\infty} (1 - \bar{\alpha}_n) \left(\prod_{i=1}^{n-1} \bar{\alpha}_i \right) \Phi_0^{n-1} \\
&= (1 - \bar{\alpha}_1) + (1 - \bar{\alpha}_2) \Phi_0 \bar{\alpha}_1 + \dots \quad (22)
\end{aligned}$$

The meaning of the equations is apparent from the expansion explicitly shown for Eq. (22). Equations (20)–(22) can be converted into finite sums by means of approximations similar to those carried out for Eq. (17).

C. Fluorescence anisotropy

It is well known that nonradiative transport decreases the ensemble fluorescence anisotropy. For a pair of randomly oriented and nonrotating molecules, and for the Förster dipolar mechanism, Galanin calculated in 1950⁵ that the acceptor fluorescence anisotropy is only 4% of that of the donor. This result was later shown to be in fact the zero-time value of the indirectly excited molecule anisotropy.⁶ In any event, neglect of the contribution of indirectly excited molecules to the ensemble anisotropy is a good and frequent approximation in nonradiative transport studies, where theoretical efforts concentrate on the calculation of the survival probability of the directly excited molecules. This calculation is difficult on account of the possibility of return of the excitation. Nevertheless, good approximations,⁷ experimentally tested,^{8,9} are available.

The situation with radiative transport is, in a sense, the opposite of that with nonradiative transport. In fact, and owing to its long-ranged nature, the return of excitation has negligible probability. On the other hand, the contribution of indirectly excited molecules to the overall anisotropy is considerable, and cannot be neglected: The radiative mechanism has a higher orientational selectivity than the nonradiative one.¹⁰

For the purposes of computing the effect of radiative transport on fluorescence anisotropy, we consider only results for directions contained in the horizontal plane (including the usual front-face and right-angle geometries), for which the anisotropy of fluorescence takes the highest value. We further suppose that molecular rotational motion is negligible during the lifetime and that the exciting photons carry vertical polarization.

We start with the calculation of the depolarization due to the radiative transfer of the electronic excitation energy. To conform with usage, we write r_0 (fundamental anisotropy) for the anisotropy of first generation molecules, implying that $r_1 = r_0$. The anisotropy of second generation molecules, indirectly excited by reabsorption, will be

$$r_2 = \beta r_0, \quad (23)$$

where β is the depolarization factor ($\beta < 1$). As mentioned, the probability of return of the excitation to the original molecule is negligible, and therefore the anisotropy of fluorescence of molecules belonging to the n th generation is obtained by repeated application of Eq. (23),

$$r_n = \beta^{n-1} r_0 \quad (n = 1, 2, \dots). \quad (24)$$

A quantum electrodynamical calculation of the depolarization factor β , by Andrews and Juzeliūnas,¹⁰ gave $\beta = 0.28$ (an identical value is obtained from classical electrodynamics¹). This value may be compared to that of the nonradiative dipole–dipole transfer mechanism, which is^{5,6,10} $\beta = 0.04$. The polarization retained after one transfer is thus seven times greater for the radiative case, precluding, as mentioned, the common approximation in nonradiative transport of neglecting the contribution of higher order generations.

For excitation with vertically polarized light, the definition of anisotropy is

$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)}, \quad (25)$$

where the parallel and perpendicular intensities are measured for a direction at right angle with the excitation, and contained in the horizontal plane. The denominator of Eq. (25) is usually proportional to the intensity emitted in all directions. An alternative measure of linear polarization is the polarization p , appropriate for light beams,

$$p(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + I_{\perp}(t)}, \quad (26)$$

where the denominator is the intensity emitted in the direction of measurement. In most fluorescence experiments, anisotropy is a more useful parameter than polarization, be-

cause the denominator is proportional to the intensity decay and simpler expressions result. When several incoherent sources are present (e.g., a mixture of fluorescent compounds), both polarization and anisotropy can be expressed as a sum of contributions, the weight of each being the fraction of the intensity emitted in all directions (anisotropy), or the fraction of the intensity emitted in the direction of measurement (polarization).

When radiative transport is present, the denominator of Eq. (25) is no longer proportional to the intensity decay. In fact, the symmetry of the emitting ensemble is lowered, and a complicated positional pattern of polarizations emerges. Both anisotropy and polarization become local quantities (i.e., relative to the measurement point \mathbf{r}_b). From the experimental point of view, Eq. (25) can still be used. But from the theoretical one, information is limited to the decay at a given boundary point, Eqs. (15) or (17), which is proportional to $I_{\parallel}(t) + I_{\perp}(t)$ and not to $I_{\parallel}(t) + 2I_{\perp}(t)$ (both measured at \mathbf{r}_b). Polarization, as given by Eq. (26), is therefore of more direct meaning. Nevertheless, given that anisotropy is the parameter used in the absence of radiative transport, it is important to obtain a generalized, albeit local anisotropy, that will reduce to the usual result in the limiting situation of negligible radiative transport. To do so, one takes into account the relation between the local anisotropy and local polarization,

$$p = \frac{3r}{2+r}, \quad (27)$$

or

$$r = \frac{2p}{3-p}. \quad (28)$$

The total polarization is first obtained,

$$p_b(\lambda, t) = \sum_{n=1}^{\infty} a_{bn}(\lambda, t) p_n, \quad (29)$$

where p_n is the polarization of the n th generation. From Eqs. (24) and (27),

$$p_n = \frac{3\beta^{n-1}r_0}{2 + \beta^{n-1}r_0}. \quad (30)$$

The fractional contribution $a_{bn}(\lambda, t)$ is

$$a_{bn}(\lambda, t) = \frac{I_{bn}(\lambda, t)}{I_b(\lambda, t)} = \frac{[1 - \alpha_{bn}(\lambda)] \left(\prod_{i=1}^{n-1} \bar{\alpha}_i \right) \frac{(k_r t)^{n-1}}{(n-1)!}}{\sum_{n=1}^{\infty} [1 - \alpha_{bn}(\lambda)] \left(\prod_{i=1}^{n-1} \bar{\alpha}_i \right) \frac{(k_r t)^{n-1}}{(n-1)!}}. \quad (31)$$

The polarization is therefore

$$p_b(\lambda, t)$$

$$= \frac{\sum_{n=1}^{\infty} [1 - \alpha_{bn}(\lambda)] \left(\prod_{i=1}^{n-1} \bar{\alpha}_i \right) \frac{(k_r t)^{n-1}}{(n-1)!} \frac{3\beta^{n-1}r_0}{2 + \beta^{n-1}r_0}}{\sum_{n=1}^{\infty} [1 - \alpha_{bn}(\lambda)] \left(\prod_{i=1}^{n-1} \bar{\alpha}_i \right) \frac{(k_r t)^{n-1}}{(n-1)!}}. \quad (32)$$

Finally, the anisotropy is received from Eq. (28),

$$r_b(\lambda, t) = \frac{\sum_{n=1}^{\infty} [1 - \alpha_{bn}(\lambda)] \left(\prod_{i=1}^{n-1} \bar{\alpha}_i \right) \left(\frac{1}{2 + \beta^{n-1}r_0} \right) \frac{(k_r \beta t)^{n-1}}{(n-1)!}}{\sum_{n=1}^{\infty} [1 - \alpha_{bn}(\lambda)] \left(\prod_{i=1}^{n-1} \bar{\alpha}_i \right) \left(\frac{1}{2 + \beta^{n-1}r_0} \right) \frac{(k_r t)^{n-1}}{(n-1)!}}. \quad (33)$$

By a reasoning similar to that of Eq. (17), it may be shown that for long times the anisotropy becomes

$$r_b(\lambda, t) \cong r_0 \exp[-\bar{\alpha}_s(1-\beta)k_r t]. \quad (34)$$

Similarly, the polarization will be

$$p_b(\lambda, t) \cong \frac{3}{2} r_0 \exp[-\bar{\alpha}_s(1-\beta)k_r t]. \quad (35)$$

It should be stressed that the reabsorption probabilities of Eqs. (32)–(33) must be computed with an absorption probability whose orientational dependence is that of a radiating electric dipole, and not that of an isotropic emitter, because it is now assumed that molecular rotation is frozen during the lifetime. However, the results are expected not to greatly differ.

III. COMBINED RADIATIVE AND NONRADIATIVE TRANSPORT

A. Importance of nonradiative transport

The contribution of nonradiative energy transport has been completely neglected up to now. Nonradiative transport will be present whenever the average distance between molecules is smaller or of the order of the Förster radius for self-transfer. Because some of the parameters that favor radiative transport, like high absorption–emission spectral overlap and high molecular radiative constant, also favor nonradiative transport by the dipole–dipole mechanism, the Förster radius for self-transfer tends to be significant. It is therefore important to discuss the effect of nonradiative transport on the macroscopic observables like the fluorescence intensity decay, quantum yield, and anisotropy decay.

In a system where both mechanisms are operative, and neglecting coherence, the excitation will perform a series of short range hops by the nonradiative mechanism, alternating with long distance jumps by the radiative one. What conclusions can be drawn from this picture? First, it is well known that the ensemble decay law is unaffected by pure nonradiative transport.¹¹ In this way, each series of short hops will not change the decay probability of that subensemble. Second, because the hops are performed locally, the excitation spread during the lifetime does not exceed a few Förster

radii, and cannot change significantly the spatial distribution of the generations considered in the radiative model. Another consequence of the nonradiative hops is the efficient randomization of the orientation of the emitting dipole. In this way, and depending on the importance of the nonradiative mechanism, the assumption of isotropic emission may be appropriate even in cases where molecular rotation is insignificant during the excited state lifetime. All these considerations lead to the conclusion that nonradiative transport leaves the decay law practically unchanged.

B. Fluorescence anisotropy

As regards the anisotropy decay, the contribution of nonradiative transport may be quite important. Invoking again the model of a series of short hops alternating with long jumps, a strong depolarization is expected for each series of hops. Nonradiative transport will therefore contribute to the anisotropy decay. When significant, it may even be the dominant mechanism. It is thus of interest to obtain an expression for the combined effect of radiative and nonradiative transport. To do so, we try to modify the anisotropy decay for pure radiative transport, Eq. (33). Following the n th radiative step, an $(n+1)$ th generation molecule is excited (at a certain time t_{n+1}). Owing to the nonradiative hops, there is a probability $G(t-t_{n+1})$ that the excitation will remain in that molecule. If the next radiative jump ($n+1 \rightarrow n+2$) occurs from the initially excited molecule, one may still apply the depolarization equation (23). If, on the other hand, the radiative jump originates from an indirectly excited molecule by the nonradiative mechanism, total depolarization is expected. In this way, the emission probability for polarized emission will be, for each radiative step, $g_1(t)G(t)$, where $g_1(t)$ is given by Eq. (4) and $G(t)$ is the probability that the excitation is in the directly excited molecule, when nonradiative transport is operative. The function $G(t)$ is given by several theoretical treatments.⁷ In this way, the probability of emission of polarized radiation by an n th generation molecule will be

$$g'_n(t) = \underbrace{g_1 G \otimes g_1 G \otimes \dots \otimes g_1 G}_{n \times} \quad (36)$$

while the population of that generation will continue to be proportional to $g_n(t)$. Hence, Eq. (24) is replaced by

$$r_n(t) = \beta^{n-1} r_0 \frac{g'_n(t)}{g_n(t)}, \quad (37)$$

and Eqs. (32) and (33) by

$$p_b(\lambda, t) = \frac{\sum_{n=1}^{\infty} [1 - \alpha_{bn}(\lambda)] \left(\prod_{i=1}^{n-1} \bar{\alpha}_i \right) \left(\frac{3(\beta\Phi_0)^{n-1} r_0 g'_n(t)}{2 + \frac{g'_n(t)}{g_n(t)} \beta^{n-1} r_0} \right)}{\sum_{n=1}^{\infty} [1 - \alpha_{bn}(\lambda)] \left(\prod_{i=1}^{n-1} \bar{\alpha}_i \right) \Phi_0^{n-1} g_n(t)}, \quad (38)$$

$$r_b(\lambda, t) = r_0 \frac{\sum_{n=1}^{\infty} [1 - \alpha_{bn}(\lambda)] \left(\prod_{i=1}^{n-1} \bar{\alpha}_i \right) \left(\frac{(\beta\Phi_0)^{n-1} g'_n(t)}{2 + \frac{g'_n(t)}{g_n(t)} \beta^{n-1} r_0} \right)}{\sum_{n=1}^{\infty} [1 - \alpha_{bn}(\lambda)] \left(\prod_{i=1}^{n-1} \bar{\alpha}_i \right) \left(\frac{\Phi_0^{n-1} g_n(t)}{2 + \frac{g'_n(t)}{g_n(t)} \beta^{n-1} r_0} \right)}. \quad (39)$$

It must be remarked that the above considerations and formulas are not completely general. A unified treatment of the problem of combined radiative and nonradiative transport that includes the continuous variation from the r^{-6} interaction to the r^{-2} interaction^{10,12} is wanting. We considered only the combined effect of the (extreme cases of) radiative and nonradiative (dipole-dipole) processes. This is nevertheless expected to be valid for most situations.

IV. CONCLUSIONS

A stochastic theory of combined radiative and nonradiative transport has been presented. This approach is physically clear and versatile, allowing the consideration of the combined effect of radiative and nonradiative transport, carried out here for the first time.

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