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APPROXIMATE ANALYTIC SOLUTIONS FOR THE OPTICAL PUMPING OF FLUORESCENT DYES

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16. Abstract

A general technique for solving a system of rate equations describing the interaction of an electromagnetic field and a molecular system is presented. The method is used to obtain approximate time-dependent solutions for the upper-level population of fluorescent dyes in the presence of a pump field.

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Introduction

Dye lasers offer spectroscopists tunable and coherent radiation from 336 to 1176 nanometers (nm). Tunability is achieved by manipulating dye concentrations, solvents, and resonator losses. Laser-pumped pulsed dye lasers are especially useful for time-resolved spectroscopy because the laser pulses have the same shape as the pump pulses above threshold. However, pulses produced by these lasers are not always as energetic as might be required. In general, the stringent requirements on spectral purity limit the pulse energies to a few hundred microjoules.

A possible remedy to the low pulse energies of such systems is regenerative or multipass amplification using flashlamp-exited amplifiers [1], [2], and [3]. The theoretical understanding of such an amplifier is based on a knowledge of the time-dependence of the amplifier inversion. Because of the order of magnitude variance in flashlamp rise times and triplet-state deactivation rates, triplet-state accumulation must be treated as a variable. Sorokin et al. [4] have

produced computer solutions to the rate equations for short-pulse laser pumping. Schäfer and Schmidt [5] have given analog computer plots for the excited singlet-state population in the limit of very long triplet lifetimes. Moreover, Keller [6] has examined the effects of triplet states on the efficiency of a dye laser using computer solutions and neglecting the depletion of the ground-state population due to pumping. He also provides steady-state solutions for the number of photons in the laser cavity.

This paper develops a technique for solving coupled-rate equations to a high degree of accuracy. The method is applied to the inversion in a flashlamp-pumped dye solution. A three-level approximation is used to describe the dye-field interaction.

Dye-Pumping Mechanisms

A large molecule, such as a typical dye, has many normal vibrations that are coupled to electronic states. Transitions between such states are broadened by collisional and electrostatic perturbations with the solvent molecules. Moreover, each vibronic sublevel of an electronic state has rotational fine-structure; however, this is smeared out by the rapid rate of collisions (10^{12} collisions/s).

The pump radiation in this system corresponds to an electronic transition from the ground vibronic level to an excited vibronic level. This leads to a nonequilibrium Frank-Condon state. Furthermore, the transition is between

singlet states and is strongly allowed (1 in figure 1). The state, S_1, quickly thermalizes (10^{-12} s) because of solvent collisions. At this stage, a molecule may either fluoresce to the lowest electronic state (2 in figure 1) by Frank-Condon selection rules or make a nonradiative "intersystem crossing" to a lower triplet state at a rate, k_{ST}. This is detrimental to laser action in three ways: (1) it competes with fluorescence; (2) it creates optical losses by placing molecules in triplet level T_1, which can make triplet-triplet transitions ($T_1 \rightarrow T_2$ in figure 1); and (3) it depletes the ground-state population and therefore the number of molecules in the fluorescence cycle because of the long lifetime of T_1. Phosphorescence from T_1 to the ground vibronic manifold is spin-forbidden and may trap molecules for times ranging from milliseconds to seconds. However, the use of paramagnetic collision partners in the solution (O_2 for example) that induce a strong spin-orbit coupling can decrease the triplet lifetime through radiationless deactivation. In addition to the previously mentioned processes, singlet-singlet absorption ($S_1 \rightarrow S_2$ in figure 1) may take place and cause additional optical losses. These are not as significant as triplet-triplet losses because of the relatively small population of S_1.

Using this description for the interaction, the system can be modeled with rate equations and phenomenological decay rates. If the thermalization rates are approximated within each singlet manifold as being instantaneous, the system may be described by three levels: S_0, S_1, and T_1. In the absence of stimulated

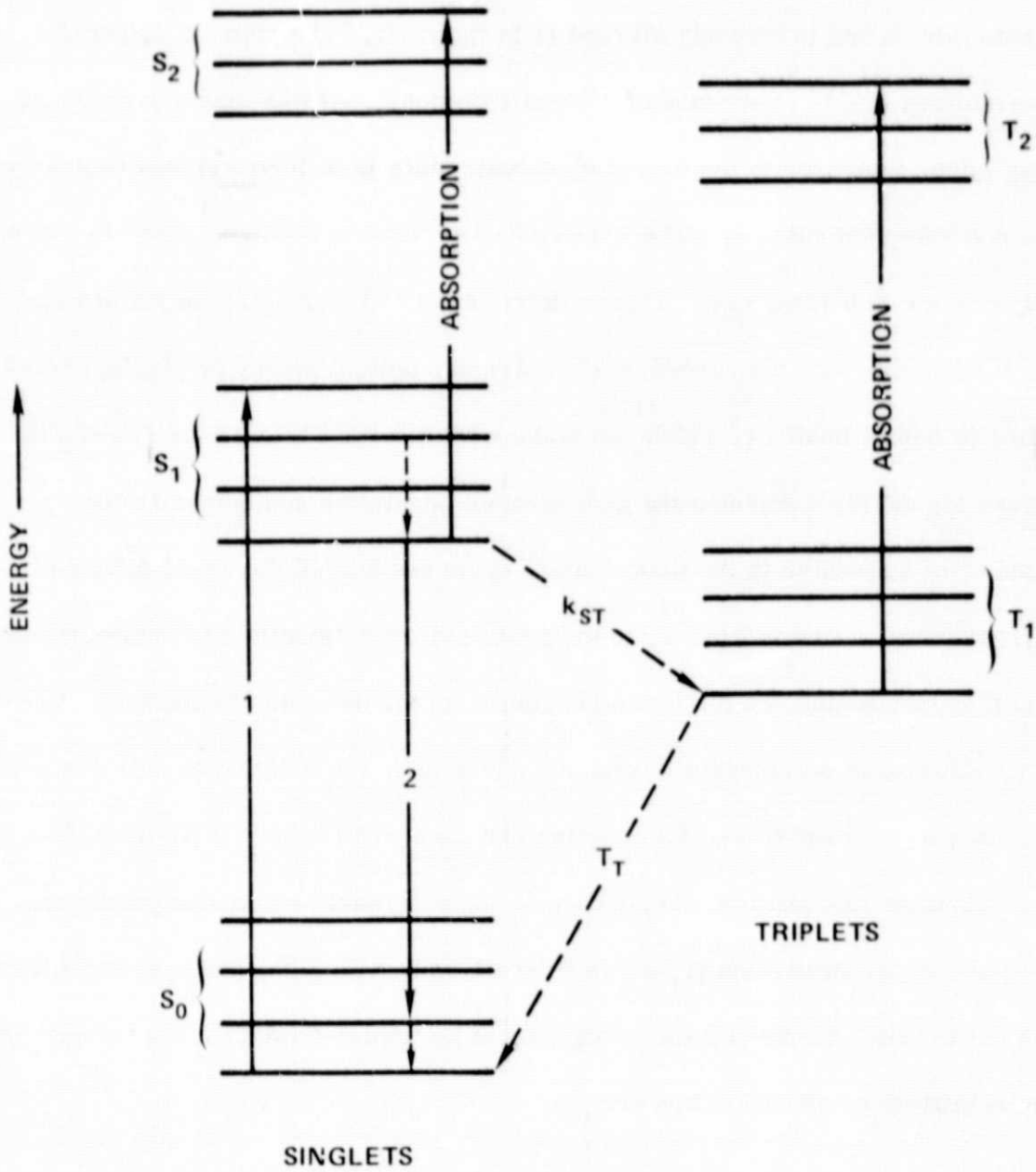

Figure 1. Energy level representation of a dye molecule. Lines 1 and 2 denote excitation and fluorescence, respectively. Dashed lines indicate non-radiative transitions, and solid lines indicate radiative transitions. Intersystem crossing is described by a rate, k_{ST}, and the lifetime of the triplet state by T_T.

emission, the populations of the levels obey the following differential equations:

$$\frac{dN}{dt} 1 = -\gamma N_1 + N_0 W(t) \tag{1a}$$

$$\frac{dN}{dt} T = k_{ST} N_1 - N_T / T_T \tag{1b}$$

$$\frac{dN}{dt} 0 = N_1 / T_s + N_T / T_T - N_0 W(t) \tag{1c}$$

where

N_1, N_T, N_0 = the populations of S_1, T_1, and S_0, respectively

T_s = the fluorescence lifetime of S_1

T_T = the total lifetime of T_1

k_{ST} = the intersystem crossing rate between S_1 and T_1

$W(t)$ = the time-dependent pumping rate given by:

$$W(t) = \frac{\lambda^3 g(\lambda)}{8\pi h c T_s} I(t, \lambda) \tag{2}$$

where $I(t, \lambda)$ is the flashlamp intensity as a function of time, and $g(\lambda)$ is some line-shape function of the pump wavelength, λ,

$$\gamma = (k_{ST} + 1/T_s) \tag{3}$$

For a typical dye, such as Rhodamine 6G, the fluorescence lifetime of S_1 is about 5×10^{-9} s, and the intersystem crossing rate is on the order of $5 \times 10^{7} s^{-1}$.

Solving the Rate Equations

The rate equations given in equation 1 may be rewritten as a single matrix equation:

$$\begin{bmatrix} \dot{N}_1 \\ \dot{N}_T \\ \dot{N}_0 \end{bmatrix} = \begin{bmatrix} -\gamma & 0 & W(t) \\ k_{ST} & -1/T_T & 0 \\ 1/T_s & 1/T_T & -W(t) \end{bmatrix} \begin{bmatrix} N_1 \\ N_T \\ N_0 \end{bmatrix} \tag{4}$$

which may be abbreviated by:

$$\dot{\overrightarrow{N(t)}} = \overleftrightarrow{M(t)} \times \overrightarrow{N(t)} \tag{5}$$

Equation 5 is a matrix equation with the matrizant solution given by:

$$\overrightarrow{N(t)} = \mathrm{EXP}\left[\int \overleftrightarrow{M(t)dt} \right] \overrightarrow{N(0)} \tag{6}$$

where $\overrightarrow{N(0)} = \begin{vmatrix} 0 \\ 0 \\ N_0 \end{vmatrix}$ is the initial population vector.

Because $\overleftrightarrow{M(t)}$ is not in diagonal form, we can expand the exponential matrix operator as a power series. This yields:

$$\mathrm{EXP}\left[\int \overleftrightarrow{M(t)}dt\right] = \overleftrightarrow{I} + \int_0^t \overleftrightarrow{M(t_1)}dt_1 + 1/2 \int_0^t\int_0^t \overleftrightarrow{M(t_2)}\overleftrightarrow{M(t_3)}dt_2dt_3 + \ldots \tag{7}$$

For the particular matrix of concern,

$$\int \overleftrightarrow{M(t)}dt = \begin{vmatrix} -\gamma t & 0 & Z(t) \\ k_{ST}t & -t/T_T & 0 \\ t/T_s & t/T_T & -Z(t) \end{vmatrix} \tag{8}$$

where

$$Z(t) = \int W(t)dt \tag{9}$$

This formulation can be used to approximate the ground-state population, $N_0(t)$, to an arbitrary degree of accuracy. The ground state is chosen for two reasons: (1) it is the least sensitive to the magnitude of its own first derivative, and (2) it is a function of both $N_1(t)$ and $N_T(t)$. The approach to solving for $N_1(t)$ is based on solving the first-order differential equation (1a) using an approximation for $N_0(t)$ derived from the expansion given by equation 7. Designating

the order of the $N_0(t)$ approximation by a superscript,

$$^{0}N_0(t) = N_0 \tag{10}$$

$$^{1}N_0(t) = N_0[1 - Z(t)] \tag{11}$$

$$^{2}N_0(t) = N_0\ [1 - Z(t)(1 - t/T_s - Z(t)] \tag{12}$$

Similarly, for $N_T(t)$

$$^{0}N_T(t) = {}^{1}N_T(t) = 0 \tag{13}$$

$$^{2}N_T(t) = N_0 k_{ST}[tZ(t)] \tag{14}$$

The first-order expression for $N_0(t)$ can be used to solve equation 1a for $N_1(t)$. Examining equation 1a, we see that it has the standard solution:

$$N_1(t) = EXP(-\gamma t)\ \left[\int EXP(\gamma t)\,{}^{i}N_0(t)W(t)dt + C\right] \tag{15}$$

where C is chosen so that $N_1(0) = 0$. Substituting equation 11 into equation 15 gives:

$$N_1(t) = N_0 EXP(-\gamma t)\ \left[\int EXP(\gamma t)\left[1 - Z(t)\right]W(t)dt + C\right] \tag{16}$$

This expression accounts for the depletion of the S_0 population but assumes that all molecules entering T_1 remain there.

Finite Triplet Lifetime

The accumulation of molecules in T_1 combined with a relatively small value for T_T can result in a sizable return rate to the ground level. Using the expansion (equation 7), we arrived at a value for $N_T(t)$ given in equation 13. The triplet contribution to $N_0(t)$ appears in equation 1c as $N_T(t)/T_T$. Substituting equation 14, the contribution to $N_0(t)$ by this rate can be estimated by the term:

$$\frac{N_0 k_{ST}}{T_T} \int tZ(t)dt \tag{17}$$

Equation 17 can be used to modify either equation 11 or equation 12 before using them to solve equation 1a. The modified term is given by:

$$^1N_0(t) = N_0\left[1 - Z(t) + k_{ST}/T_T \int tZ(t)dt\right] \tag{18}$$

Linearly Rising Flashlamp

This section examines the approximations derived for the case of a pump source with a constant slope, which has the form:

$$I(t, \lambda) = mt \tag{19}$$

Equation 19 results in:

$$Z(t) = B(\lambda)mt^2/2 \tag{20}$$

Substituting equation 20 into equation 16 and integrating yields for the population of S_1:

$$N_1(t) = N_0 B(\lambda) m/\gamma \left[t - 1/\gamma - B(\lambda) m V(t)/2 + EXP(-\gamma t) \left[1/\gamma - 3B(\lambda) m/\gamma^3 \right] \right] \tag{21}$$

where

$$V(t) = \left(t^3 - 3t^2/\gamma + 6t/\gamma^2 - 6/\gamma^3 \right) \tag{22}$$

Expression 22 can be modified to account for molecules that make the transition from T_1 to S_0 by adding the term:

$$N_0 B(\lambda)^2 m^2 k_{ST} R(t)/T_T \gamma \tag{23}$$

where

$$R(t) = \left[t^5 - 5t^4/\gamma + 20t^3/\gamma^2 - 60t^2/\gamma^3 + 120t/\gamma^4 - 120/\gamma^5 + EXP(-\gamma t)/\gamma^5 \right] \tag{24}$$

Expression 21 modified by equation 23 is plotted for various parameters in figures 2 through 4. Figure 2 shows the effect of varying the pump slope. Because a relatively long T_T was chosen, flashlamps that rise quickly produce higher peak populations but are short-lived since most of the molecules become trapped in T_1. However, for smaller pump slopes, the triplet return rate is in better competition with pumping. This permits the population to be maintained for longer periods at lower levels.

Figures 3 and 4 show that k_{ST} and T_T play complementary roles. The duration of inversion is strongly dependent on both rates. As figure 4 indicates,

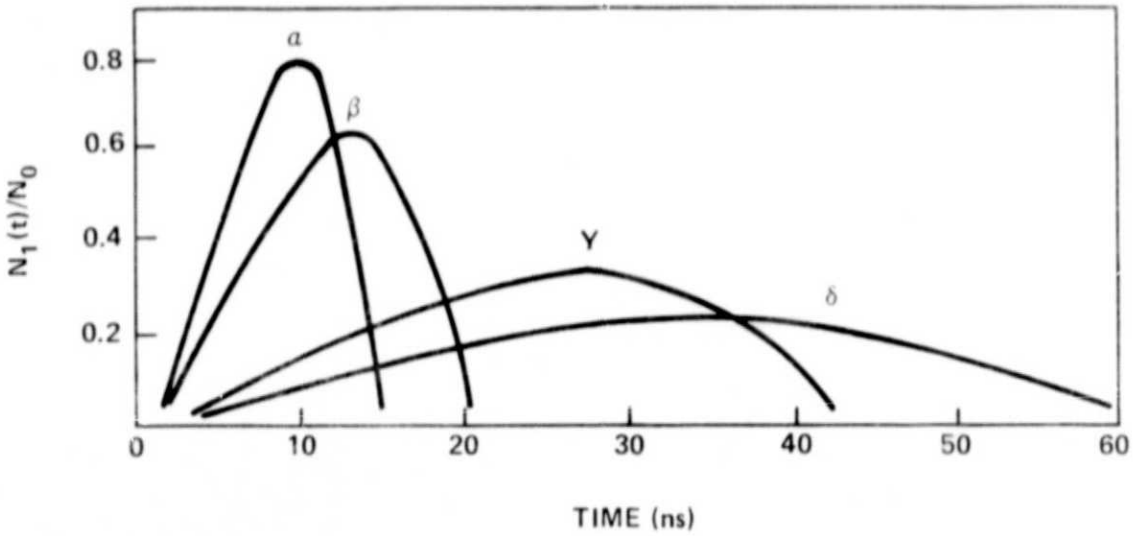

Figure 2. Relative population densities of S_1 as a function of time for various flashlamp slopes. The slopes (m) are given in watts-cm^{-2}-s^{-1}: α: 5×10^{11}, β: 3×10^{11}, γ: 7×10^{10}, δ: 5×10^{10}. The relevant constants are: $k_{ST} = 2 \times 10^{7} s^{-1}$, $T_s = 5 \times 10^{-9}$ s, and $T_T = 1 \times 10^{-6}$ s.

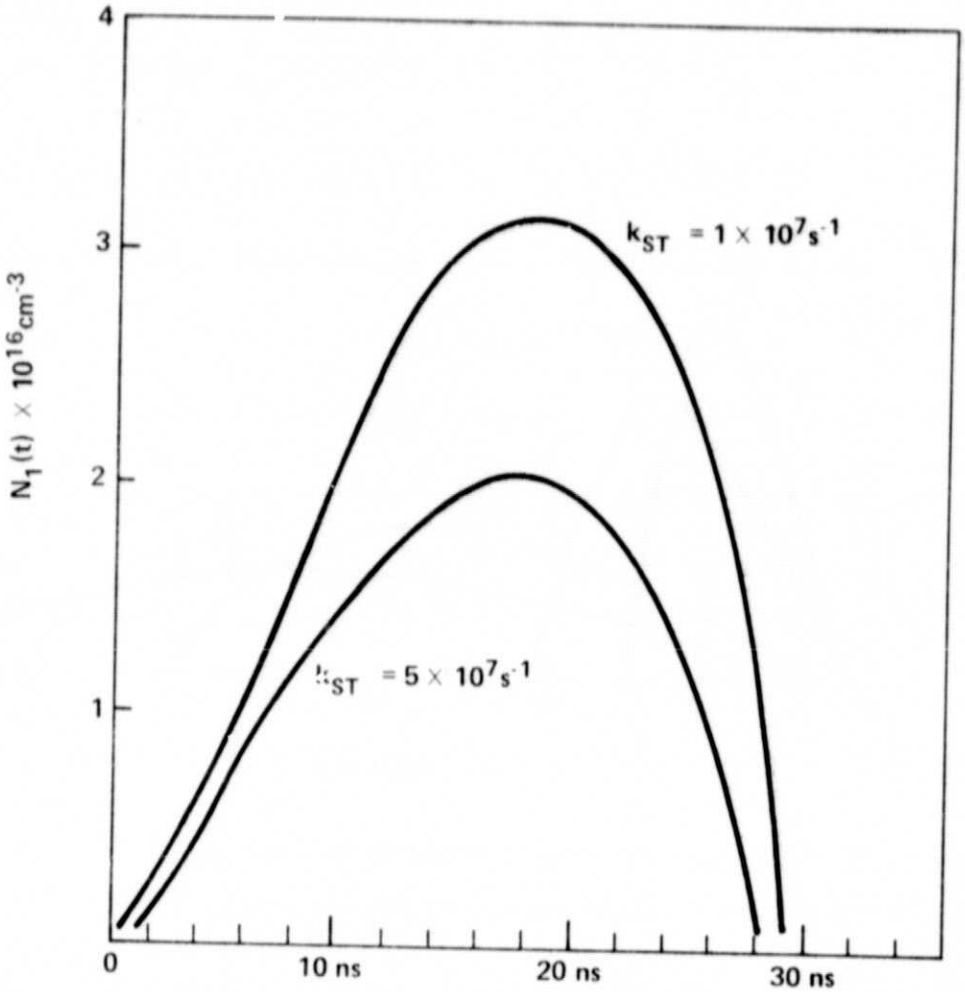

Figure 3. Population density of S_1 as a function of time for two values of the intersystem crossing rate k_{ST}. The relevant constants are: $m = 3 \times 10^{11}$, $T_S = 5 \times 10^{-9}$s, and $T_T = 1 \times 10^{-6}$s.

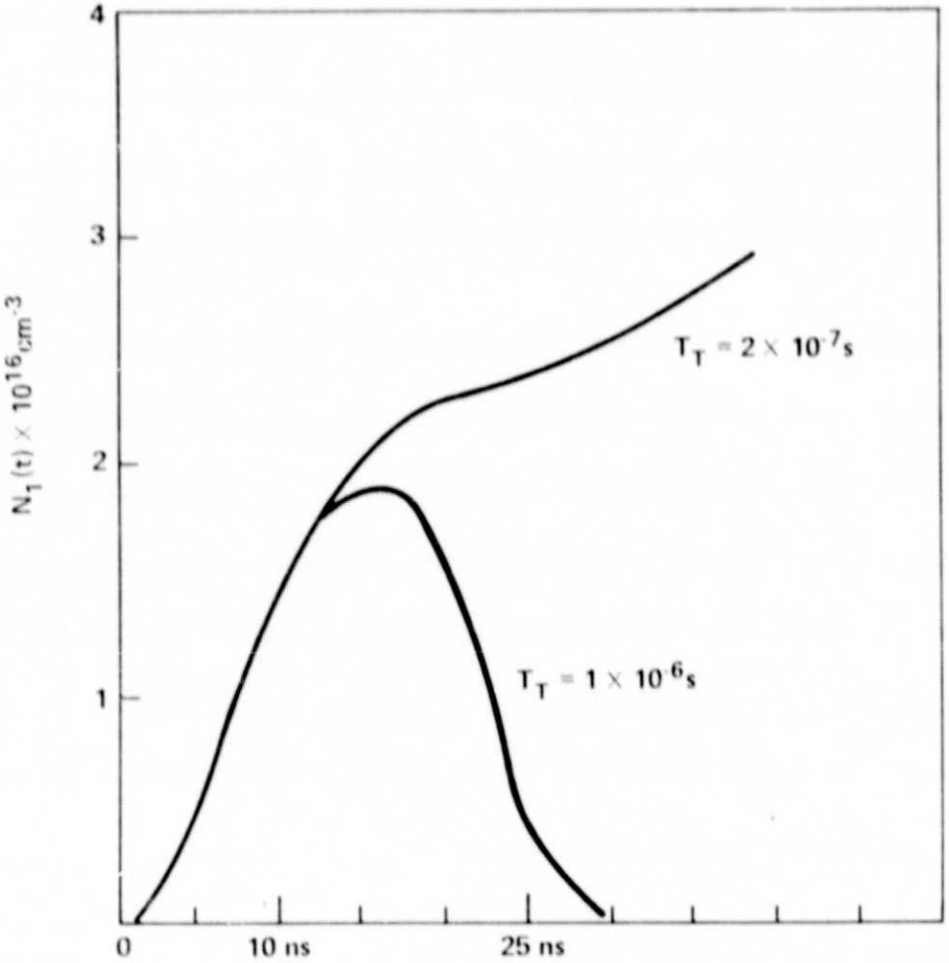

Figure 4. Population density of S_1 as a function of time for two values of the triplet lifetime, T_T. The relevant constants are: $m = 3 \times 10^{11}$, $T_S = 5 \times 10^{-9} s$, and $k_{ST} = 5 \times 10^{-7} s^{-1}$.

for T_T values that are short ($\approx k_{ST}^{-1}$), we can achieve a nondamped inversion. Depending on the resonator losses, such a situation could result in continuous-wave laser operation. In actual practice, the shortening of T_T is accomplished by using some quenching agent. However, most quenching agents are not specific for triplet states and therefore also increase k_{ST}. On the basis of how this affects each rate, a net enhancement may or may not be achieved.

The analytic approximations given exhibit all the coarse features of the population of S_1 as a function of time. The plots given agree well with respect to both peak population density and time-dependence when compared to computer solutions. For comparison of the two solutions, the reader should consult References 4 through 6. The results given can be readily used to estimate the single-pass gain as a function of time for a particular dye. Moreover, the same technique can be used in conjunction with a fourth rate equation for the cavity-photons to examine transient laser action.

Conclusions

This paper describes how the use of a matrix expansion can lead to analytic approximate solutions for a component of a set of rate equations. The application of this approach to the optical pumping of dyes illustrates the validity of the resulting expressions. All the important features concerning the dye problem can be found in the first-order solutions given. More subtle effects leading to

detailed structure can be found by including higher order terms in the matrix expansion.

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