

## Quantum-mechanical theory of the organic-dye laser

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We develop a fully quantum-mechanical theory for the organic-dye-solution laser, obtain density-matrix equations of motion for the single-mode radiation-density operator and the matter-density operator, and solve and investigate the steady-state case. We generalize the usual Born-Markoff approximation master equation for two matter states to include four matter states, each one of which interacts with the laser radiation field. This allows us to treat exactly the organic-dye molecular triplet-state levels which participate in the laser operation in an essential way. For experimentally realizable conditions the steady-state solution contains features which are qualitatively different from nondye lasers. These effects are directly attributable to intensity-dependent triplet-state radiation absorption losses. At threshold the diagonal matrix elements of the radiation photon distribution ( $R_n$ ) can be a decreasing function of the photon number  $n$  with an inflection point rather than the usual truncated Gaussian. This necessitates redefinition of threshold. For pumping just above threshold there may be both a maximum and a minimum in  $R_n$  rather than just a maximum as in usual laser theories. We also specify the effect of triplets on the narrowing of  $R_n$  for pumping above threshold and the subsequent widening of  $R_n$  for pumping well above threshold. Many of our results require photon-counting experiments for verification. Also, our equations are easily reducible to a semiclassical theory, where our treatment of the triplets variables is an improvement over the usual rate equations.

### I. INTRODUCTION

A great deal of laser-theory research was carried out during the early years of the laser. By 1968 the fundamentals of laser theories, from energy-balance approaches to fully quantum-mechanical approaches, had been carried out. The fully quantum-mechanical approaches had been carried out using three essentially equivalent methods<sup>1</sup>: Langevin equations for the laser-system operators,<sup>1-3</sup> Fokker-Planck equations for the distribution function of macroscopic laser variables,<sup>1-4</sup> and density-operator equations of motion<sup>2,3,5-7</sup> had been developed and applied to the various existing types of lasers.

The organic-dye laser, however, entered the picture somewhat late relative to other developments in the laser field. Organic-dye laser operation was not reported until 1966,<sup>8</sup> and then output was in pulses only. It was not until<sup>9</sup> 1970 that continuous-wave organic-dye lasers were obtained. Because of their wide-range tunability, organic-dye lasers have been of great interest to experimentalists ever since their inception. However, there has not been a concomitant theoretical interest. Most theories have been rate-equations approaches based on energy-balance considerations, although semiclassical theories have been considered.<sup>10,11</sup> Such theories describe many laser phenomena very well. However, in order to investigate detailed properties of the radiation, such as photon statistics and radiation intensity fluctuations, it is necessary to include radiation fluctuations.

If the organic-dye laser were qualitatively the

same as other lasers, radiation fluctuations could be included simply by directly applying one of the previously developed quantum-mechanical theories.<sup>1-7</sup> However, because of the presence of "triplet-state losses," which was one of the primary stumbling blocks preventing successful dye laser operation for so long, there are differences in the development of a complete organic-dye laser theory. In particular, whereas in most laser systems the laser radiation interacts with two matter-energy levels, for the organic-dye laser the laser radiation interacts directly with four matter levels. Two "singlet"-state levels are analogous to the usual laser two-state system, which is predominantly emissive. In addition, there are two triplet levels which are populated by a decay from the upper singlet level and are predominantly absorptive. The laser radiation loss associated with the triplets, then, is intensity dependent in two ways. The first is because of its direct absorptive interaction with the laser radiation, and the second is because of the dependence of the triplet state population on the singlet-state population (which is responsible for the laser radiation emission). The presence and nature of these triplet-state losses make the dye laser different from other lasers. Hence we have redeveloped the laser theoretical formalism to apply to the organic-dye laser.

In particular, we extend an approach previously used by one of us for lasers in which two states interact with the laser radiation<sup>7,12</sup> to include four states, so that the theory is applicable to the organic-dye laser. The theory is a microscopic quantum-statistical approach which starts with the Liouville equation for the density operator of the

laser system. This reduces to the Born-Markoff approximation master equation if, as for the organic-dye laser, the ratio of an interaction time to the relaxation time of the system is much smaller than 1.

We obtain equations of motion for the organic-dye laser which can be the starting point for a complete theoretical study of the organic-dye laser. In this paper we solve the equations for the steady-state radiation distribution.

Because of the algebraic complexity of the solution we first consider two reduced versions of the exact solution for  $R_n$ . In one we neglect the triplets, which gives the "usual" (singlet-state) solution in which two states interact with the laser field. In the other we neglect terms which are small for pumping not too far above threshold. Finally, we present the results of a computer study of the exact solution. We have found that the triplets may be specified by two parameters,  $\alpha$  and  $\beta$ . The dimensionless parameter  $\alpha$  is a product of ratios of dye-molecule parameters. Its value ranges between 0 and 1 for laser operation, with larger values of  $\alpha$  meaning increased triplet presence.  $\beta$  is the fraction of excited triplet states which deexcite and return to the lower triplet state. For experimentally obtainable values of  $\alpha$  (apparently, little is known about  $\beta$ ), there are features of the radiation density matrix which are qualitatively different from that of nondye lasers. First, there may be a maximum *and* a minimum in  $R_n$  rather than just a maximum. Second, the old definition of threshold is inadequate, and we find that at threshold  $R_n$  may be a decreasing function of  $n$  with an inflection point rather than the usual truncated Gaussian. We also present quantitative features of  $R_n$  which depend on organic-dye parameters.

In Sec. II we discuss the role of the organic-dye molecule in the lasing process in terms of a typical energy-level diagram. Since the role of the triplets is so important and yet is often treated incompletely in the literature, we discuss the triplet-state losses in detail. Section III contains a discussion of our organic-dye laser model and Hamiltonian. In Sec. IV we present the organic-dye laser equations after a brief discussion of our theoretical approach, and in Sec. V we solve for and discuss the steady-state solution. Appendix I contains details of the formal derivation of the organic-dye laser equations presented in Sec. IV.

## II. ORGANIC-DYE-SOLUTION LASER

We shall give several references for the organic-dye laser below. The most complete single reference is the book edited by Schaefer.<sup>13</sup>

### A. Laser operation

The role of the organic dye in the laser process can be understood in terms of the energy-level diagram pictured in Fig. 1 for a typical organic dye. The energy levels pictured are actually singlet- ( $S_0$  and  $S_1$ ) and triplet-state ( $T_1$  and  $T_2$ ) bands of rotational and vibrational levels associated with each electronic level. Singlet denotes the usual two-electron antisymmetric (spin-zero) state and triplet the two-electron symmetric (spin-one) state. In the diagram the vibrational (rotational) levels are represented by the longer (shorter) horizontal lines. The small separation between adjacent levels of the same band combined with their widths results in a "continuum" of possible radiation emission wavelengths. The fluorescence emission spectrum, which we explain in the next paragraph, is an example of this.

When the dye molecules are at thermal equilibrium, their energies are given by a Boltzmann distribution at the bottom of the  $S_0$  electronic level. At room temperature most of the molecules are within  $200 \text{ cm}^{-1}$  of the bottom of  $S_0$ . To obtain fluorescence an external source pumps some of the dye molecules to levels of the  $S_1$  band. After being excited to a state in the  $S_1$  band, the dye molecule decays nonradiatively to the bottom of the  $S_1$  band. This relaxation time is fast enough ( $\sim 10^{-11} - 10^{-12}$  sec) relative to the radiative lifetime ( $\nu_{S_1, u}^{-1} \cong 5 \times 10^{-9}$  sec) that the dye molecules "thermalize" at the bottom of the  $S_1$  level. Then, in the absence of external radiation, spontaneous emission takes place from near the bottom of the  $S_1$  level to the  $S_0$  level. Next, for most laser dyes there is a fast nonradiative relaxation ( $\nu_{S_1, l} \cong 10^{11} - 10^{12} \text{ sec}^{-1}$ ) back to the bottom of the  $S_0$  level, where the pumping cycle can start again.

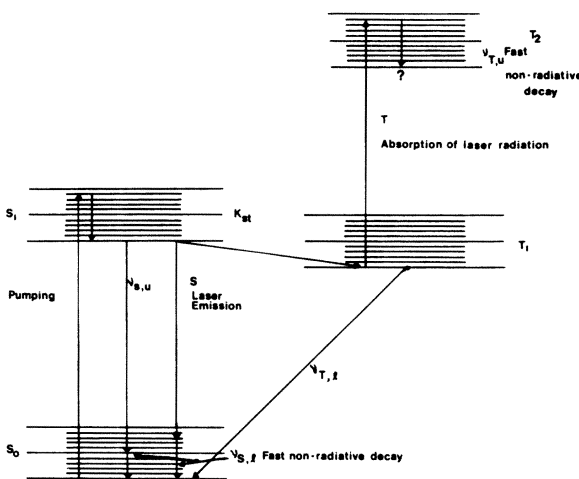


FIG. 1. Energy-level diagram for a typical organic-dye molecule.

The laser emission process associated with the singlets is the same as fluorescence, except for the added presence of external radiation, which causes stimulated emission. If the lasing process were adequately described in terms of the singlet bands alone the usual four-state laser theory (in which two states interact with the radiation) would be appropriate (levels 1-4 in Fig. 2) and we would expect no qualitatively new features for the organic-dye laser. However, the usual four-state laser description is inadequate because of the triplet states.

The lower triplet band  $T_1$  generally has energy levels lower than the lowest  $S_1$  levels, and some of the dye molecules decay nonradiatively from near the bottom of  $S_1$  to the  $T_1$  band. This process is denoted by  $K_{ST}$ , the singlet-to-triplet crossover rate. The decay to the triplet level causes losses in two ways, which we collectively term "triplet-state losses." One loss is the depletion of the upper singlet population available for lasing. The other loss is an absorption of laser radiation in a transition to an upper triplet band ( $T_2$ ). A fast nonradiative decay from the upper triplet level to nearby vibrational and rotational states prevents reemission of laser radiation.

In order to get continuous operation the triplet-state losses are reduced by the addition of "triplet-state quenching agents" to the organic-dye solution. This reduces the lower triplet-state lifetime ( $\nu_{T,l}^{-1}$ ) from approximately  $10^{-3}$  to approximately  $10^{-7}$  sec (for the dye Rhodamine 6G). This shorter triplet-state lifetime is of the order of magnitude required to reduce the triplet losses enough to get continuous operation.<sup>14</sup> Thus the triplet losses are still an important loss mechanism in the operation of a continuous-wave dye laser. This means that an adequate model for the organic-dye laser requires the inclusion of six states, four of which

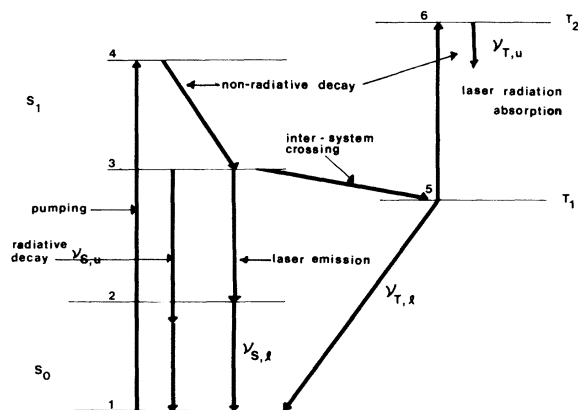


FIG. 2. Organic-dye laser as a six-state system.

interact with the laser radiation. This is pictured in Fig. 2. The bottom of the  $S_0$  level is the ground state and the top of  $S_1$  is the upper pump level. The bottom of the  $S_1$  level (state 3) is a single level with width  $\nu_{S,u}$  (the  $u$  refers to upper), the bottom of the  $T_1$  level (state 5) is a single level with width  $\nu_{T,l}$  (the  $l$  refers to lower), the top of the  $S_0$  level (state 2) is a level with width  $\nu_{S,l}$ , and the top of the  $T_2$  level (state 6) is a level with width  $\nu_{T,u}$ . These four levels are directly involved in the laser transition process. Between the singlet levels there is dominantly stimulated *emission*, whereas between the triplet levels there is dominantly stimulated *absorption*. The triplet absorptive loss is intensity dependent, since it depends on the laser radiation intensity. Also, since the population of the upper lasing level (at the bottom of  $S_1$ ) is also dependent on the intensity, there is a further, though indirect, dependence of the triplet loss on radiation intensity. There also are singlet-state losses which may be associated with additional singlet states. However, we have found that their inclusion has no qualitative effects on the laser radiation, so we do not treat them explicitly in this paper.

#### B. Triplet losses

In the energy balance approaches of most previous organic-dye laser papers,<sup>9,10,13-26</sup> the triplets have been included in various approximations. In this paper we treat the triplets exactly, since as our results show the behavior of the statistical properties of the radiation distribution are sensitive to the details of the organic-dye molecules.

We noted above that the decay rate of the lower triplet level ( $\nu_{T,l}$ ) had to be increased in order to obtain continuous operation. A minimum condition on  $\nu_{T,l}$  necessary for laser operation has been given before<sup>19</sup> (a more exact expression, including radiation losses, can be found in Ref. 38) and depends on other dye-molecule parameters. In terms of our notation this condition is

$$\alpha \equiv TK_{ST}/S\nu_{T,l} < 1,$$

where  $T$  is the triplet stimulated absorption rate,  $S$  is the singlet stimulated emission rate, and  $K_{ST}$  is the intersystem crossing rate. Physically this says that the ratio of the stimulated singlet emission to stimulated triplet absorption rates must be greater than the ratio of the "creation" to the decay rates of the lower triplet level. The parameter  $\alpha$  partially expresses the extent to which triplet losses are important in the operation of a dye laser. For small values of  $\alpha$ , triplet losses are relatively small. For larger  $\alpha$  the triplet losses are more important. For instance [see Eq. (5.22)],

the minimum pumping needed to obtain laser oscillation (threshold) increases as  $\alpha$  increases. For  $\alpha = 1$ , the triplet losses balance the singlet emission, and no amount of pumping will give laser oscillation. Hence for  $\alpha > 1$  the triplet losses dominate and continuous operation cannot take place. We show below that the parameter  $\alpha$  arises naturally in the fully quantum-mechanical theory. Furthermore, we shall show that new qualitative features of the dye laser may be parametrized in terms of  $\alpha$ . However, there is another parameter important for specifying the qualitative features of the organic-dye laser radiation, which we describe in the next paragraph.

In describing the role the triplet states play in the lasing process we have not specified what happens after the triplet absorption and subsequent fast nonradiative decay to near the bottom of the upper triplet band ( $T_2$ ). The literature does not provide definite information about what happens next. Presumably, in many cases there is a further decay and the molecule returns to the lower triplet level, where it can once again act as a radiation absorber. However, there are mechanisms by which a dye molecule in the upper triplet state can "decay," as far as the laser radiation field is concerned. For instance, organic-dye molecules in their more excited states are more likely to interact with their surroundings, which would remove the molecule from the triplet levels. Also, there are other singlet bands above  $S_1$  which may be situated so that intersystem crossing would take place from  $T_2$  back to the singlet band. In this case also, the upper triplet would not be returned directly to the  $T_1$  level. In any case, a molecule in the upper triplet level may decay to levels other

than the lower triplet level, which leads us to specify the fraction of the dye molecules which, once excited from the lower triplet band to the upper triplet band, return to the lower triplet band. The most detailed treatments in the literature make an approximation<sup>13</sup> which is equivalent to assuming *all* of the excited triplets return to the lower triplet level. We have found it important to include a "fractional return parameter" ( $\beta$ ) which specifies what fraction of excited triplet states return to the lower triplet band. In this paper we present the results for the two possible extremes, all returned ( $\beta = 1$ ) and none returned ( $\beta = 0$ ). When all the excited triplets are returned to the lower triplet level, the steady-state solution for the radiation distribution  $R_n$  is qualitatively the same as for other lasers. However, when none are returned,  $R_n$  exhibits features which are unique to the dye laser. It is conceivable that using our results experimental values of  $\beta$  could be obtained which would increase the apparently small amount known about what happens to a dye molecule once in an excited triplet-state electronic band.

Table I is a summary which we have obtained from the literature<sup>13-37</sup> of data for the commonly used laser dye Rhodamine 6G. The data in Table I correspond to parameters used in our theoretical development, so we have made conversions from the data given in the literature to data listed in the table.<sup>38</sup> In many cases, we have made the conversion by reducing our microscopic equations and comparing our notation with the rate equations used in the literature. Details of the conversions, as well as a much more complete table including more information on Rhodamine 6G and other laser dyes, are to be found in Ref. 38.

TABLE I. Rhodamine 6G organic-dye-molecule laser parameters. The data presented here form a condensed version of a table (itself a composite of information collected from Refs. 15-37) which appears in Ref. 38.

Definition	Symbol	Range
Upper singlet-state lifetime	$\nu_{S_1,u}^{-1}$	$(4.8-7.4) \times 10^{-9}$ sec
Lower triplet-state lifetime	$\nu_{T_1,l}^{-1}$	$1.0 \times 10^{-3}-2.5 \times 10^{-7}$ sec
Intersystem crossing rate	$K_{ST}$	$(0.30-2.8) \times 10^7$ sec <sup>-1</sup>
Singlet molecular emission rate	$S$	$1.0-15.0$ sec <sup>-1</sup>
Triplet molecular absorption rate	$T$	$0.11-14.0$ sec <sup>-1</sup>
Radiation decay rate	$\nu_R$	$2.0 \times 10^5-1.0 \times 10^7$ sec <sup>-1</sup>
Lower singlet decay rate	$\nu_{S,l}$	$(0.1-1.0) \times 10^{12}$ sec <sup>-1</sup>
Upper singlet decay rate	$\nu_{T,u}$	$(0.1-1.0) \times 10^{12}$ sec <sup>-1</sup>
Singlet ratio of interaction time to relaxation time	$\Lambda_S$	0.025-0.04
Triplet ratio of interaction time to relaxation time	$\Lambda_T$	0.01-0.03
Triplet parameter	$\alpha = (T/S) K_{ST}/\nu_{T,l}$	$0.001 \lesssim \alpha$
Fractional return parameter	$\beta$	No data given

### III. ORGANIC-DYE LASER MODEL AND HAMILTONIAN

Our model for the organic-dye laser is pictured in Fig. 3. Lines connecting different elements of the system represent interactions between them. The principal components are the radiation and matter parts of the system. We have included several radiation modes in the model since, although we treat only the single-mode case here, we intend to extend our treatment to the multimode case. The matter systems are the organic-dye molecules, which are excited by the external pump.

The significant difference between usual laser models and the dye laser model is the existence of the triplet states. In the diagram we represent the singlet and triplet states separately, even though they are associated with a single molecule, since they participate in the lasing process in essentially different ways. Also, by separating the singlets and triplets we can show explicitly in the model diagram that singlets are pumped externally, whereas triplets are pumped by a decay from the singlets. This is signified in the diagram by the arrow pointing from the pump to the singlets and from the singlets to the triplets.

The decay of the triplet and singlet molecular levels, mentioned above, is included by means of the matter reservoir. The dissipation of the laser radiation (owing to interaction with the laser cavity mirrors, scattering in the lasing medium, etc.) is included by means of the radiation reservoir.

The possibility of including the center-of-mass motion of the dye molecules is represented in the diagram by the box enclosing the singlet- and triplet-state boxes. The organic-dye solution's flow through the cavity has a negligible effect on the dye laser radiation distribution; thus we shall neglect center-of-mass motion in this paper. If the dye solution flow is such that its residence time in the laser beam is smaller than the lifetime of the low-

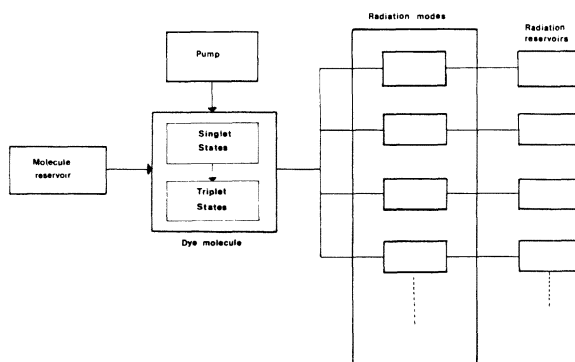


FIG. 3. Organic-dye laser model.

er triplet level, then this flow could, in effect, act as a triplet-state quencher. Thus although the value of  $\nu_{T,i}$  would be affected, center-of-mass motion would not need to be included explicitly in this instance. However, a proper treatment of the vapor-phase organic-dye laser may require explicit treatment of center-of-mass motion.

The system Hamiltonian, which contains terms corresponding to each part of the laser model described above, as well as to the interactions between the various parts of the system, is

$$H = H_R + H_M + V_{R-M} + H_{R-\text{res}} + V_{R-\text{res}} + H_{M-\text{res}} + V_{M-\text{res}}, \quad (3.1)$$

where  $H_R$  is the radiation Hamiltonian,  $H_M$  the molecule Hamiltonian,  $H_{R-\text{res}}$  the radiation-reservoir Hamiltonian, and  $H_{M-\text{res}}$  the molecule-reservoir Hamiltonian.  $V_{R-M}$  is the radiation-molecule interaction,  $V_{R-\text{res}}$  the radiation-radiation reservoir interaction, and  $V_{M-\text{res}}$  the molecule-molecule reservoir interaction Hamiltonians.

The radiation field Hamiltonian expressed in terms of normal modes is

$$H_R = \sum_{\vec{k}} \sum_{\alpha} \hbar \Omega_{\vec{k}} (a_{\vec{k},\alpha}^{\dagger} a_{\vec{k},\alpha} + \frac{1}{2}), \quad (3.2)$$

where the sum  $\vec{k}$  is over all cavity modes and the sum over  $\alpha$  corresponds to possible polarizations. The symbol  $\Omega_{\vec{k}}$  is the frequency corresponding to the mode of the wave vector  $\vec{k}$ ,  $\hbar = h/2\pi$  (Planck's constant)/ $2\pi$ , and  $a_{\vec{k},\alpha}^{\dagger}$  and  $a_{\vec{k},\alpha}$  are the usual creation and annihilation operators with commutation relations

$$\begin{aligned} [a_{\vec{k},\alpha}, a_{\vec{k}',\alpha'}^{\dagger}] &= \delta_{\vec{k}\vec{k}'} \delta_{\alpha\alpha'}, \\ [a_{\vec{k},\alpha}, a_{\vec{k}',\alpha'}] &= 0, \\ [a_{\vec{k},\alpha}^{\dagger}, a_{\vec{k}',\alpha'}^{\dagger}] &= 0. \end{aligned}$$

In this paper we treat only the single-mode case (this is equivalent to assuming that a tuning device makes the losses infinite for all modes but one), and use the single-mode radiation Hamiltonian

$$H_R = \hbar \Omega (a^{\dagger} a + \frac{1}{2}). \quad (3.3)$$

The polarization index has been suppressed for simplicity.

The matter-energy-level Hamiltonian for lasers is usually written in terms of the Pauli spin operators (or combinations of them),<sup>2-7</sup> since there is a formal analogy between the two matter states interacting with the laser radiation and the up and down spin states. However, since for the organic-dye laser four states interact with the laser radiation, the Hamiltonian of the dye molecular levels is in the second quantized form. As indicated previously, the singlet- and triplet-state Hamiltonians

are specified separately,

$$H_S = \sum_{\sigma} \sum_i s_{\sigma,i}^{\dagger} s_{\sigma,i} \epsilon_i, \quad (3.4)$$

$$H_T = \sum_{\sigma} \sum_j t_{\sigma,j}^{\dagger} t_{\sigma,j} \epsilon_j. \quad (3.5)$$

The sum over  $\sigma$  is the sum over all dye molecules participating in the lasing process. The sums over  $i$  and  $j$  are over the singlet and triplet states, respectively,  $\epsilon_i$  and  $\epsilon_j$  are the energies of the  $i$ th and  $j$ th levels, respectively, and  $s_{\sigma,i}^{\dagger}$ ,  $s_{\sigma,i}$  and  $t_{\sigma,j}^{\dagger}$ ,  $t_{\sigma,j}$  are the singlet and triplet creation and annihilation operators, respectively, which have the anticommutation relations

$$\begin{aligned} \{s_{\sigma,i}^{\dagger}, s_{\sigma,j}\} &= \delta_{ij}, \quad \{t_{\sigma,i}^{\dagger}, t_{\sigma,j}\} = \delta_{ij}, \\ \{s_{\sigma,i}^{\dagger}, s_{\sigma,j}^{\dagger}\} &= \{s_{\sigma,i}, s_{\sigma,j}\} = \{t_{\sigma,i}^{\dagger}, t_{\sigma,j}^{\dagger}\} = \{t_{\sigma,i}, t_{\sigma,j}\} = 0, \\ \{s_{\sigma,i}^{\dagger}, t_{\sigma,j}^{\dagger}\} &= \{s_{\sigma,i}^{\dagger}, t_{\sigma,j}\} = \{s_{\sigma,i}, t_{\sigma,j}^{\dagger}\} = \{s_{\sigma,i}, t_{\sigma,j}\} = 0. \end{aligned} \quad (3.6)$$

Since individual dye molecules are "distinguishable" from one another, all commutators of operators associated with different molecules are zero. For example,  $[s_{\beta,i}, s_{\sigma,j}^{\dagger}] = 0$  for  $\sigma \neq \beta$ .

The radiation-matter interaction Hamiltonian ( $V_{R-M} \equiv V_{R-S} + V_{R-T}$ ) is the well-known  $\vec{J} \cdot \vec{A}$  matter-radiation interaction in the dipole approximation (valid since the wavelength of optical radiation is much larger than the distance of the electron from the molecule center of mass).  $V_{R-S}$  is the radiation-singlet interaction Hamiltonian and  $V_{R-T}$  is the radiation-triplet interaction Hamiltonian.

The expression for  $V_{R-S}$  is

$$V_{R-S} = i \sum_{\sigma} \sum_{i,j} \sum_k \gamma_{\sigma ijk} (s_{\sigma,i}^{\dagger} s_{\sigma,j} a_k^{\dagger} + s_{\sigma,j}^{\dagger} s_{\sigma,i} a_k), \quad (3.7)$$

for  $\epsilon_j > \epsilon_i$  and where  $\gamma_{\sigma ijk} = [4\pi e^2 (\epsilon_j - \epsilon_i)^2 / \hbar \Omega_k V]^{1/2} \times (\vec{\epsilon} \cdot \vec{x}) \Gamma(x)$ . The expression for  $V_{R-T}$  is

$$V_{R-T} = i \sum_{\sigma} \sum_{i,m} \sum_k \gamma_{\sigma imk} (t_{\sigma,i}^{\dagger} t_{\sigma,m} a_k^{\dagger} + t_{\sigma,m}^{\dagger} t_{\sigma,i} a_k), \quad (3.8)$$

for  $\epsilon_i > \epsilon_m$  and where  $\gamma_{\sigma imk} = [4\pi e^2 (\epsilon_m - \epsilon_i)^2 / \hbar \Omega_k V]^{1/2} \times (x_{im}) \Gamma(x)$ ,  $m$  is the mass of the electron,  $x_{im}$  is the appropriate dipole matrix element,  $e$  is the charge on an electron,  $V$  is the laser cavity volume, and  $\Gamma(x)$  is the spatial cavity eigenfunction. To prevent double counting the sums over matter states are restricted to the case where the energy of the second index is greater than that of the first. For single-mode operation we drop the sum over  $k$ .

The two terms in the interaction Hamiltonians represent first (from left- to right-hand sides) a decrease in molecular energy level accompanied

by the emission of a photon, and second an increase in molecular energy level accompanied by the absorption of a photon. We have left out terms which correspond to the lowering of the molecular energy level accompanied by the absorption of a photon and the raising of the molecular energy level accompanied by the emission of a photon. This is often referred to as the rotating-wave approximation.

It is unnecessary to explicitly treat the reservoir Hamiltonians and their corresponding interaction Hamiltonians, since we are interested only in the effects of the reservoirs (pumping and decay). The Appendix has a discussion of formal elimination of explicit consideration of reservoir variables.

The next step in the development of an organic-dye laser theory is to use the above physical model and Hamiltonian to derive equations of motion for organic-dye molecules and laser radiation variables. The physical differences between the organic-dye laser and other lasers have been included in the model and Hamiltonian already discussed above. The derivation of organic-dye laser equations of motion are formally analogous to previous laser theories, although one obtains two "extra" equations corresponding to the triplet-state levels. Therefore in Sec. IV we discuss our theoretical approach in general terms and then present and explain the organic-dye laser equations of motion.

#### IV. ORGANIC-DYE LASER EQUATIONS

The starting point for our theoretical approach is the quantum Liouville equation for the density operator  $\hat{\rho}(t)$  of a system,

$$\frac{d\hat{\rho}(t)}{dt} = \frac{i}{\hbar} [H, \hat{\rho}(t)], \quad (4.1)$$

where  $H$  is the Hamiltonian of the system. We write the Hamiltonian in the form  $H = H_0 + \lambda V$ , where  $\lambda$  is a dimensionless parameter. The first Born approximation master equation in the Markoff approximation is

$$\frac{d\hat{\rho}(t)}{dt} + \frac{i}{\hbar} [H_0, \hat{\rho}(t)] = -\lambda^2 \int_0^{\infty} d\tau [V, [V(\tau), \hat{\rho}]], \quad (4.2)$$

where  $V(\tau) = e^{iH_0\tau/\hbar} V e^{-iH_0\tau/\hbar}$ . This equation has been used for gas laser theories<sup>5,7</sup> and has been discussed in general elsewhere.<sup>39</sup> Briefly, such a master equation is valid if there exists an interaction time ( $t_{\text{int}}$ ) which is much smaller than a relaxation time ( $t_{\text{rel}}$ ) of the system,  $t_{\text{int}}/t_{\text{rel}} \ll 1$ . For the organic-dye laser this ratio in our notation is  $\Lambda_S = SN/\nu_{S,i}$  for the singlet-radiation interaction and  $\Lambda_T = TN/\nu_{T,u}$  for the triplet-radia-

tion interaction, where  $N$  is the number of organic-dye molecules participating in lasing,  $S$  is the singlet stimulated emission rate,  $T$  is the triplet stimulated absorption rate,  $\nu_{s,l}$  is the lower singlet decay rate, and  $\nu_{t,u}$  is the upper triplet decay rate. The range of values we have calculated for  $\Lambda_S$  and  $\Lambda_T$  for continuous-wave operation using the dye Rhodamine 6G (see Table I) confirms the validity of the Born-Markoff master equation (4.2).

One of us<sup>7</sup> has shown that the first Born approximation treatment of the radiation-matter interaction is sufficient to describe the laser photon statistics if matter-radiation correlations are retained by requiring that the radiation-matter density matrix not be factorizable into the product of a radiation density matrix times a matter density matrix. We treat the radiation-matter interaction, as well as the various reservoir-laser-system interactions, in the Born-Markoff approximation. Then, after eliminating the reservoirs by tracing over a complete set of reservoir variables, we obtain equations of motion for the single-molecule-radiation density operator  $\hat{D}(1, t)$  and the radiation density operator  $\hat{R}(t)$  (see Appendix).

We treat the radiation variables of the equations of motion for  $\hat{D}(1, t)$  and  $\hat{R}(t)$  in the number representation, since for the Born approximation master equation the diagonal matrix is coupled only to diagonal, and not to off-diagonal, matrix elements. The resulting equations for the radiation density matrix,  $R_n = \langle n|R|n \rangle$ , and the diagonal single-particle radiation density matrix,  $D_n^i(t) \equiv \langle n|\langle j|D(1, t)|j\rangle|n \rangle$  [where  $n$  is the photon number,  $j$  is the  $j$ th molecular state, and we have left out the single-particle index (1) for convenience], are

$$\begin{aligned} \frac{dR_n(t)}{dt} = & -\nu_R [nR_n - (n+1)R_{n+1}] \\ & -SN[(n+1)(D_n^{S,u} - D_{n+1}^{S,l}) + n(D_n^{S,l} - D_{n+1}^{S,u})] \\ & -TN[(n+1)(D_n^{T,u} - D_{n+1}^{T,l}) + n(D_n^{T,l} - D_{n+1}^{T,u})], \end{aligned} \quad (4.3)$$

$$\begin{aligned} \frac{dD_n^{S,u}(t)}{dt} = & -(\nu_{S,u} + K_{ST})D_n^{S,u} + R_n(t)\nu_e \\ & -S(n+1)(D_n^{S,u} - D_{n+1}^{S,l}), \end{aligned} \quad (4.4)$$

$$\frac{dD_n^{S,l}(t)}{dt} = -\nu_{s,l}D_n^{S,l} - S_n(D_n^{S,l} - D_{n+1}^{S,u})(n+1), \quad (4.5)$$

$$\frac{dD_n^{T,u}(t)}{dt} = -\nu_{t,u}D_n^{T,u} - T(D_n^{T,u} - D_{n+1}^{T,l})(n+1), \quad (4.6)$$

$$\begin{aligned} \frac{dD_n^{T,l}(t)}{dt} = & K_{ST}D_n^{S,u} + \beta\nu_{t,u}D_{n-1}^{T,u} - \nu_{t,l}D_n^{T,l} \\ & -nT(D_n^{T,l} - D_{n-1}^{T,u}). \end{aligned} \quad (4.7)$$

These are the fundamental equations for our quantum-mechanical theory of the organic-dye laser, and are the starting point for further theoretical work. In the above equations the dye-molecule states are labeled doubly, first according to whether they are singlet ( $S$ ) or triplet ( $T$ ), and second according to whether they are upper ( $u$ ) or lower ( $l$ ). Also,  $\beta$  is defined as the fractional return of excited triplets and  $\nu_e$  as the molecular excitation rate (via the external pump).

In Eq. (4.3) for  $R_n$  the first two terms on the right-hand side represent radiation decay due to the radiation reservoir. The third term represents stimulated and spontaneous emission of molecules in the single state, the fourth term represents stimulated absorption of molecules in the ground singlet state, and the fifth and sixth terms are the corresponding terms for molecules in the triplet state.

Thus it is apparent that  $S$  and  $T$  may be identified as singlet and triplet stimulated emission (absorption) rates. The contributions of emission and absorption to the population levels is also evident in the equations for the single-particle radiation density matrices. For instance, in Eq. (4.4) for the upper singlet level, the term  $-S(n+1)D_n^{S,u}$  represents the loss of population due to spontaneous and stimulated emission in transitions to the lower lasing level. The term  $+S(n+1)D_{n+1}^{S,l}$  corresponds to an increase in population of the upper lasing level owing to reabsorption of laser radiation from the lower lasing level. Also, the molecule reservoirs induce the different decay rates of the appropriate molecular levels. For instance, in Eq. (4.5) for the lower singlet level the term  $-\nu_{s,l}D_n^{S,l}$  is the decay of the lower lasing level. Similar terms appear in the other molecular-level equations.

As we have mentioned earlier, the lower triplet level is also pumped, although not in the usual manner, since the triplet population stems from crossover from the upper singlet level. Accordingly, the pump term in Eq. (4.7) equals the unfactorized "population" probability of the upper singlet state times the crossover rate ( $K_{ST}D_n^{S,u}$ ). Note that Eq. (4.7) also includes the triplet return terms  $\beta\nu_{t,u}D_{n-1}^{T,u}$ , where the parameter  $\beta$  specifies the fractional return ( $0 \leq \beta \leq 1$ ).

## V. STEADY-STATE DISTRIBUTION

The organic-dye laser equations (4.3)–(4.7) can be used for a study of various features of possible

laser operation. The existence of the continuous wave single-mode organic-dye laser makes the steady-state solution a physically reasonable and logical case to consider first. It is conventional at this point to adiabatically eliminate the matter variables and write a time-dependent equation for  $R_n$ . However, this is unnecessary for the steady state. We shall discuss this further in a future paper which includes the physically realizable case in which adiabatic elimination of the molecular-state populations is inappropriate. The rest of this paper includes the solution and investigation of  $R_n$  in the steady state. In Sec. V A we obtain the steady-state solution. Secs. V B and V C contain an investigation of the solution in simplified forms, first with the triplet states omitted and then with the relatively small singlet absorption and triplet emission terms omitted. In Sec. V B we investigate the exact solution.

#### A. Steady-state solution

Since we are interested in the radiation density matrix  $R_n$ , we break all terms such as  $D_n^{S,i}$  into

$$n \left[ \nu_R + SN \left( \eta_n^{S,i} - \frac{R_{n-1}}{R_n} \eta_{n-1}^{S,u} \right) + TN \left( \eta_n^{T,i} - \frac{R_{n-1}}{R_n} \eta_{n-1}^{T,u} \right) \right] \\ = (n+1) \left[ \nu_R \frac{R_{n+1}}{R_n} + SN \left( \frac{R_{n+1}}{R_n} \eta_{n+1}^{S,i} - \eta_n^{S,u} \right) + TN \left( \frac{R_{n+1}}{R_n} \eta_{n+1}^{T,i} - \eta_n^{T,u} \right) \right]. \quad (5.2)$$

The square-bracket term which multiplies  $n+1$  on the right-hand side of Eq. (5.2) contains all couplings between the  $n$  and  $n+1$  photon states, i.e., terms representing increases from  $n$  to  $n+1$  photons and decreases from  $n+1$  to  $n$  photons. In the steady state the sum of all such terms must be zero.

The same argument holds for the left-hand side of Eq. (5.2), which contains couplings between the  $n$  and  $n-1$  photon states, so that the coefficient of  $n$  is also equal to zero. This occurs because the  $\vec{J} \cdot \vec{A}$  interaction allows only single-photon processes to take place. Setting the coefficient of  $n+1$  equal to zero gives the following recursion relation between  $R_{n+1}$  and  $R_n$ :

$$R_{n+1} = \frac{S\eta_n^{S,u} + T\eta_n^{T,u}}{S\eta_{n+1}^{S,i} + T\eta_{n+1}^{T,i} + \nu_R/N} R_n. \quad (5.3)$$

The formal solution to Eq. (5.3) is

$$R_{n+1} = \pi_{p=0}^n G(p) R_0, \quad (5.4)$$

where

$$G(p) \equiv \frac{S\eta_p^{S,u} + T\eta_p^{T,u}}{S\eta_{p+1}^{S,i} + T\eta_{p+1}^{T,i} + \nu_R/N}, \quad (5.5)$$

and where  $p$  is an integer,  $\pi_{p=0}^n$  is the product of terms from  $p=0$  to  $p=n$ , and the solutions for the

products of two terms  $D_n^{S,i} = \eta_n^{S,i}(t) R_n(t)$ . This exact expression is just the conditional probability relation that the probability of  $n$  photons and the  $i$ th molecular state equals the probability of  $n$  photons times the probability of the  $i$ th molecular state, given that there are  $n$  photons. The  $\eta_n^{S,u}(t)$  contains the radiation-matter correlations.

Letting the time derivative equal zero, the solutions of Eqs. (4.4)–(4.7) for the  $\eta_n^{S,u}$  are

$$\eta_n^{S,u} = \nu_e \left( \nu_{S,u} + K_{ST} + \frac{2S(n+1)}{1+2S(n+1)/\nu_{S,i}} \right)^{-1}, \quad (5.1a)$$

$$\eta_{n+1}^{S,i} = \frac{2S(n+1)}{\nu_{S,i} + 2S(n+1)} \eta_n^{S,u}, \quad (5.1b)$$

$$\eta_n^{T,u} = \frac{2T(n+1)}{\nu_{T,u} + 2T(n+1)} \eta_{(n+1)}^{T,i}, \quad (5.1c)$$

$$\eta_n^{T,i} = K_{ST} \left( \nu_{T,i} + \frac{2nT(1-\beta)}{1+2nT/\nu_{T,u}} \right)^{-1} \eta_n^{S,u}. \quad (5.1d)$$

Next, we obtain the steady-state solution to Eq. (4.3) for  $R_n$  by setting the time derivative equal to zero and rearranging the terms to give

$\eta$ 's in Eqs. (5.1) are to be used.

Equation (5.4) is complicated, and its thorough investigation requires a computer study. However, in order to gain a better understanding of the workings of Eq. (5.4) we first investigate it in two simplified forms.

#### B. Singlet-state case (triplets excluded)

Leaving out the triplets greatly simplifies things, since terms and equations associated with the triplets are left off. The resulting steady-state solution for  $R_n$  is

$$R_{n+1} = S\eta_n^{S,u} \left[ S\eta_n^{S,u} \left( \frac{2S(n+1)}{\nu_{S,i} + 2S(n+1)} \right) + \frac{\nu_R}{N} \right]^{-1} R_n \\ \equiv g(n) R_n, \quad (5.6)$$

where

$$\eta_n^{S,u} = \nu_e \left( \nu_{S,u} + \frac{2S(n+1)}{1+2S(n+1)/\nu_{S,i}} \right)^{-1}. \quad (5.7)$$

The formal solution is

$$R_{n+1} = \prod_{p=0}^n g(p) R_0.$$

With a change in notation this expression is identi-



cal to the usual solution for a four-level gas laser (in which two levels interact with the laser radiation) with stationary atoms.<sup>7,12</sup> This is as we might expect, since eliminating the triplets reduces our model to the usual four-level model.

We next investigate the properties of the singlet state  $R_n$  by using Eqs. (5.6) and (5.7), and then find the threshold number of pumped molecules necessary for laser operation ( $N_{th}$ , hereafter referred to as the threshold value of pumping), find the maximum in  $R_n$ , and investigate the narrowing of  $R_n$  for pumping above threshold (i.e., for  $N > N_{th}$ ).

First, the threshold value of pumping ( $N_{th}$ ) is obtained by setting the numerator equal to the denominator for  $n=0$  in Eq. (5.6) [i.e., let  $g(0)=1$ ]. To a good approximation the result is

$$N_{th} = \nu_R / S. \quad (5.8)$$

This says that the threshold number of molecules is given by the ratio of the photon decay rate to a stimulated emission rate.

Possible extrema in  $R_n$  are found by setting the numerator equal to the denominator in Eq. (5.7) [i.e.,  $g(n)=1$ ].<sup>7</sup> There is only one root, which is a maximum

$$n_{max} \cong (\nu_{s,u} / 2S)(N / N_{th} - 1). \quad (5.9)$$

Notice that for threshold pumping ( $N \cong N_{th}$ ) the maximum is zero, which points out that the above definition of threshold is identical to the condition that the maximum in  $R_n$  be at  $n=0$ . For pumping below threshold, Eq. (5.9) gives a negative value for  $n_{max}$ , which is unphysical, i.e., there is no maximum. For pumping above threshold the maximum is for a positive value of  $n$  which depends on the upper singlet decay rate ( $\nu_{s,u}$ ), the stimulated emission rate ( $S$ ), and the pumping ( $N$ ).

We can understand the behavior of  $R_n$  and the meaning of the definitions of  $N_{th}$  and  $n_{max}$  in more detail by considering the formal recursion relation solution, Eq. (5.6). Since  $R_n$  is a product of a succession of  $g(p)$  [i.e.,  $R_n = g(n)g(n-1) \cdots g(0)R_0$ ] the behavior of  $g(p)$  determines the behavior  $R_n$ . We consider approximate expressions for  $g(n)$  in two limits. For small  $n$  ( $2Sn \ll \nu_{s,i}$ ),

$$g(n) \cong \left( \frac{N_{th}}{N} + \frac{2}{\nu_{s,u}} \frac{\nu_R n}{N} \right)^{-1}, \quad (5.10)$$

and for large  $n$  ( $2Sn \gg \nu_{s,i}$ ),

$$g(n) \cong \left( 1 + \frac{\nu_R}{N} \frac{\nu_{s,i}}{S\nu_{s,u}} \right)^{-1}. \quad (5.11)$$

By comparing the above two expressions one might suppose (and detailed analysis confirms) that this  $g(n)$  is a decreasing function of  $n$  [see Eq. (5.10)], which approaches a constant less than 1 for large

enough ( $n$ ) [see Eq. (5.11)]. The qualitative behavior of  $R_n$ , however, depends on the value of the external pump ( $N$ ). If  $N < N_{th}$ , then  $g(0)$  is less than 1, as are all other  $g(n)$ . Then since  $R_n$  is a product of a succession of  $g(n)$ ,  $R_n$  is a monotonically decreasing function of  $n$ , which means it has a "thermal" behavior [see Fig. 4(a)]. If  $N = N_{th}$ , then  $g(0) = 1$ , but  $g(n) < 1$  for  $n > 0$ . In this case there is a maximum in  $R_n$  at  $n=0$ , and  $R_n$  is monotonically decreasing for  $n > 0$  [see Fig. 4(b)]. If  $N > N_{th}$ , then  $g(0) > 1$  and  $R_n$  is an increasing function of  $n$  for  $n < n_{max}$ , where  $n_{max}$  is defined as  $g(n_{max}) = 1$ . For  $n > n_{max}$   $g(n)$  is less than 1 and  $R_n$  becomes a decreasing function of  $n$ . Hence  $R_n$  has peaked (or "nonthermal") behavior [see Figs. 4(c) and 4(d)].

To complete the study of  $R_n$  we discuss the "narrowing" of  $R_n$  as the laser is pumped above threshold. This requires a calculation of  $\langle n \rangle$  and  $\langle n^2 \rangle$  from Eq. (5.6), where  $\langle n \rangle$  is defined as  $\bar{n}$ , since "narrowing" is usually discussed in terms of the normalized peakedness  $\langle n \rangle / \sigma^2 \equiv \langle n \rangle / (\langle n^2 \rangle - \langle n \rangle^2)$ . To do this generally is difficult, since near and just above threshold the equation for each moment is related to higher moments and no simple solution is possible. It is easier to plot  $R_n$  using a computer and measure the width ( $\sigma^2$ ) directly from the computer output. Then, since to a good approximation for pumping well above threshold  $n_{max} \cong \langle n \rangle$ , one can calculate  $\langle n \rangle / \sigma^2$  for different values of  $N$ . We have done this and find that for pumping not too far above threshold  $R_n$  behaves in the same way as for general laser systems. That is, at threshold  $R_n$  is approximated by a truncated Gaussian ( $n_{max} = 0$ ) (see Fig. 4). As the laser is pumped above threshold the maximum moves to the right-hand side along the positive  $n$  axis and  $R_n$  narrows and becomes Poisson-like (i.e.,  $n_{max} / \sigma^2$  increases with  $N$ ). However, we have found that for pumping far enough above threshold  $R_n$  widens again.

For pumping far above threshold, the moments of  $R_n$  can be calculated, since (for  $2Sn \gg \nu_{s,i}$ ) the equation for  $R_n$  reduces to

$$\begin{aligned} \frac{dR_n}{dt} = & -2\nu_R [nR_n - (n+1)R_{n+1}] \\ & - 2NS \frac{\nu_e}{\nu_{s,i}} [(n+1)(R_n - R_{n+1}) + n(R_n - R_{n-1})], \end{aligned} \quad (5.12)$$

and equations for the moments uncouple, which gives

$$\langle n \rangle = (N / \nu_R) (\nu_e / \nu_{s,i}) S, \quad (5.13)$$

$$\langle n^2 \rangle = 2\langle n \rangle^2 + \frac{1}{2}\langle n \rangle \cong 2\langle n \rangle^2. \quad (5.14)$$

Using these results we see that in the limit of

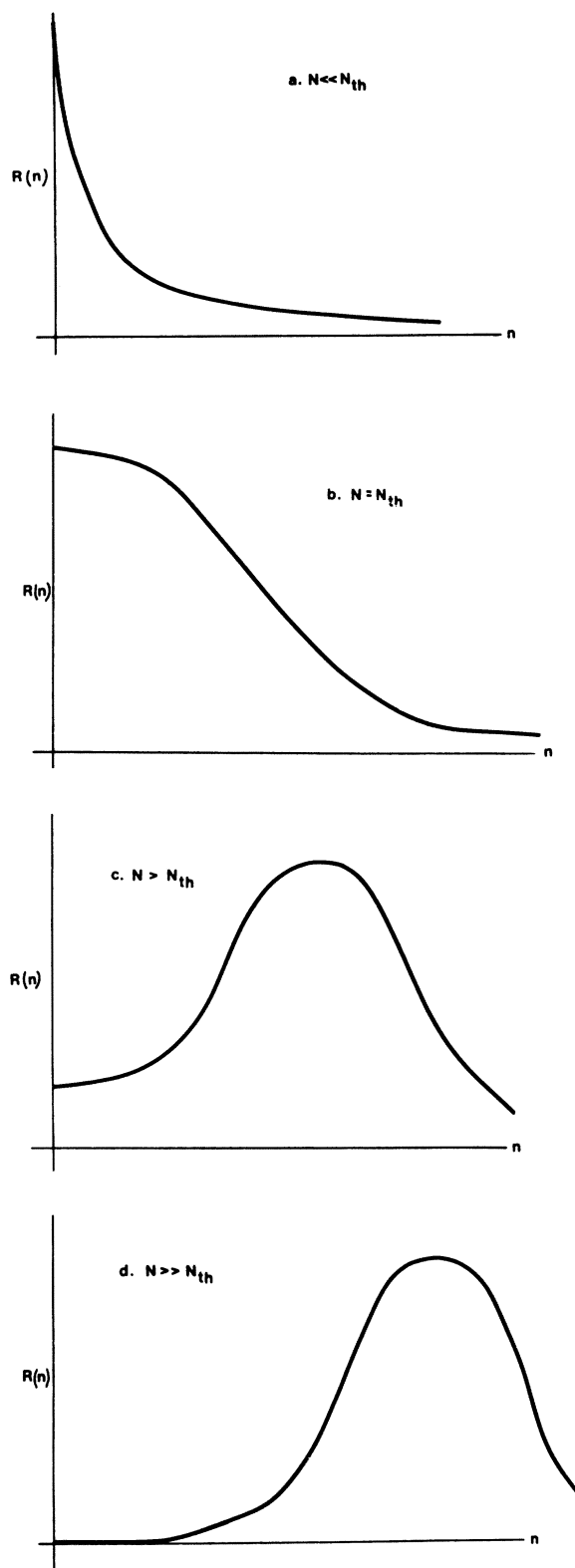


FIG. 4. Typical plot of the radiation distribution vs photon number for different pump values.

large pumping  $\langle n \rangle / \sigma^2 \rightarrow \langle n \rangle^{-1} \sim N^{-1}$ , which means that  $R_n$  widens as the pump is increased.

If the pumping is too large, the condition for the validity of the Born-Markoff master equation is violated. However, the widening of  $R_n$  occurs within the range of validity. An order-of-magnitude calculation shows that the pumping necessary to observe this widening effect for a single-mode continuous-wave dye laser is of the order of tens of watts, which is near or beyond present limits.<sup>40</sup> However, larger pump sources will very likely be available in the near future.

### C. Approximate solution (triplets included)

We can obtain a qualitative understanding of the dye laser solution, Eq. (5.4) (including triplets), if we neglect the second term in the numerator and the first term in the denominator, which correspond to the relatively insignificant processes (true for pumping not too far above threshold) of triplet-state emission and singlet-state absorption. Thus, keeping only the three dominant terms in Eq. (5.4) which correspond to singlet emission, triplet absorption, and radiation losses, and making appropriate approximations, the expression for  $R_{n+1}$  is

$$R_{n+1} \cong \frac{\eta_n^{S,u} R_n}{\alpha \eta_n^{S,u} [1 + (2T/\nu_{T,i})(n+1)(1-\beta)]^{-1} + \nu_R/NS}, \quad (5.15a)$$

whose formal solution is

$$R_n = \prod_{p=0}^{n-1} g(p) R_0,$$

where

$$g(p) = \frac{\eta_p^{S,u}}{\alpha \eta_p^{S,u} [1 + 2T(p+1)(1-\beta)/\nu_{T,i}] + \nu_R/NS}. \quad (5.15b)$$

The term on the left-hand side in the denominator of  $g(p)$  corresponds to the triplet-state absorption. The  $\alpha$  in this term shows its appropriateness as a measure of the strength of the triplet-state effect.

Just as in the case of the singlet solution discussed above, we can understand features of  $R_n$  by considering  $g(n)$ . The presence of the triplets in the denominator of  $g(n)$  [Eq. (5.15b)] is the added complication. It is convenient to consider two separate cases, one for which the upper triplet return is unity ( $\beta = 1$ ) and one for which there is no upper triplet return ( $\beta = 0$ ).

When  $\beta = 1$ ,  $g(n)$  simplifies to

$$g(n)_{\beta=1} = \frac{\eta_n^{S,u}}{\alpha \eta_n^{S,u} + \nu_R/NS}. \quad (5.16)$$

In this case the expression for  $g(n)$  in the limit of small  $n$  ( $2S \ll \nu_{s,i}$ ) is

$$g(n)_{\beta=1} \cong \frac{1}{\alpha + \nu_R \nu_{s,u} / NS \nu_e + 2\nu_R n / N \nu_e}, \quad (5.17)$$

and in the limit of large  $n$  ( $2Sn \gg \nu_{s,i}$ ),

$$g(n)_{\beta=1} \cong \frac{1}{\alpha + \nu_R \nu_{s,i} / NS \nu_{s,u}}. \quad (5.18)$$

A comparison with the singlet state  $g(n)$  under the same conditions [see Eqs. (5.10) and (5.11)] shows that its functional form is identical to  $g(n)_{\beta=1}$ . Thus although there are quantitative differences between the singlet state  $R_n$  and the organic-dye laser  $R_n$  for  $\beta=1$ , there are no qualitative differences. Thus the triplet state  $R_n$  for  $\beta=1$  has the same features as those pictured in Fig. 4 for a typical laser.

When  $\beta=0$ ,  $g(n)$  is

$$g(n)_{\beta=0} = \frac{\eta_n^{S,u}}{\alpha \eta_n^{S,u} [1 + (2T/\nu_{T,i})(n+1)]^{-1} + \nu_R / NS}. \quad (5.19)$$

Owing to the  $n+1$  in the triplet term in the denominator,  $g(n)_{\beta=0}$  has a functional dependence on  $n$  different from the singlet  $g(n)$ , and different from  $g(n)_{\beta=1}$ . Notice that this different dependence of  $g(n)$  on  $n$  is retained for any  $\beta$  less than 1. We present the two extremes of the  $\beta=0$  and  $\beta=1$  cases to simplify the discussion.

#### D. Exact solution

Owing to the algebraically complicated nature of the exact solution, many of the results of this section are in a graphical form taken from computer output. The equations we do present are only approximate, and for simplicity we have set  $\beta=0$  in them. Our discussion of the organic-dye laser radiation distribution, as for the singlet-state radiation distribution, is in terms of the extrema of  $R_n$ , the threshold value of pumping ( $N_{th}$ ), and the narrowing and widening of  $R_n$  for pumping above threshold ( $N > N_{th}$ ).

##### 1. Radiation distribution extrema

We obtain the extrema in the radiation distribution by setting  $R_{n+1} = R_n$  in Eq. (5.4) and solving for  $n$ . That is,

$$G(n) = \frac{S\eta_n^{S,u} + T\eta_n^{T,u}}{S\eta_{n+1}^{S,i} + T\eta_{n+1}^{T,i} + \nu_R/N} = 1. \quad (5.20)$$

After making an approximation accurate to  $\sim 10^{-7}$  we obtain a *quadratic* equation. Leaving out some small terms, the expression for the extrema in the photon distribution is

$$n_{\text{extrema}} = \frac{N\nu_e}{4\nu_R} - \frac{(\nu_{s,u} + K_{ST})}{4S} - \frac{\nu_{T,i}}{4} \pm \frac{1}{4} \left[ \left( \frac{N\nu_e}{\nu_R} - \frac{(\nu_{s,u} + K_{ST})}{S} + \frac{\nu_{T,i}}{T} \right)^2 - \frac{N4\nu_e K_{ST}}{\nu_R S} \right]^{1/2}. \quad (5.21)$$

The new result is that unlike the gas laser for which there is only one extremum in  $R_n$  (a maximum) there are two extrema, one a maximum (corresponding to the plus sign) and one a minimum (corresponding to the minus sign). Depending on dye-molecule parameters the minimum may or may not be physical—that is, it may or may not have a positive  $n$  value. Typical plots of the radiation distribution as a function of  $n$ , for different values of  $\alpha$ , above threshold, are given in Fig. 5. For small values of  $\alpha$  there is only a maximum in the region of positive photon number. However, above a critical value of  $\alpha$  (see below), both the maximum and minimum may appear.

The behavior of the maximum [see Eq. (5.21)] of the radiation distribution as a function of laser parameters is typical of lasers. As the external pump ( $N$ ) is turned up the maximum in the photon distribution also increases. Increasing the singlet stimulated emission rate ( $S$ ) increases the value

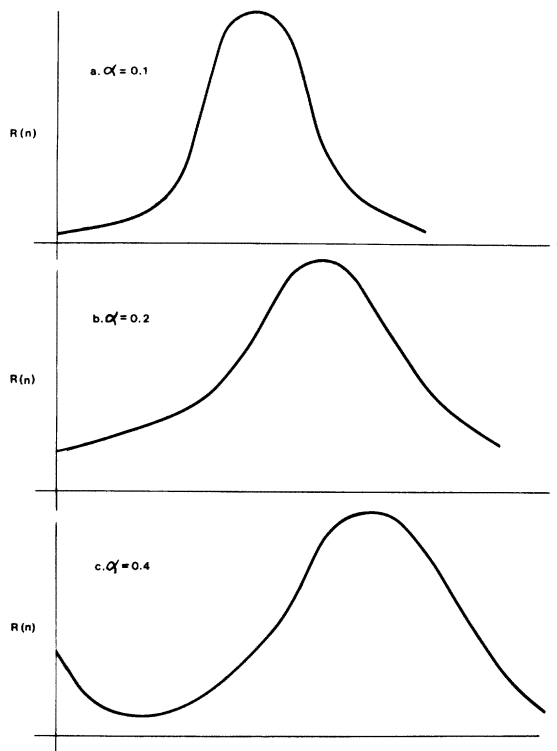


FIG. 5. Radiation distribution vs photon number for different values of  $\alpha$  (pumping fixed above threshold).

of  $n_{\max}$ . This is not surprising, since the pumping and singlet emission processes contribute to the photon population. On the other hand, increasing the photon loss parameter and/or the singlet decay rate decreases the maximum. Also, increasing the triplet absorption rate ( $T$ ) and decreasing the lower triplet decay rate ( $\nu_{T,i}$ ), both of which increase triplet-state absorptive losses, decreases  $n_{\max}$ . Finally, the effect of increasing the singlet-to-triplet crossover rate ( $K_{ST}$ ) (i.e., increasing the triplet losses) is to decrease the maximum in  $R_n$ . The surprising feature is the minimum in the distribution.

We can understand the minimum  $R_n$  in terms of the  $G(n)$  in the recursion relation (5.4). As we have already pointed out, when there is only a maximum in the distribution it arises from  $G(0)$  being greater than 1 and  $G(n)$  being a decreasing function of  $n$ . Owing to the triplet terms, however,  $G(n)$  can be an increasing function  $n$  for some values of  $n$ . With reference to Eq. (5.4), the presence of the triplet term in the denominator of  $G(n)$  may cause  $G(n)$  to be less than 1 for small  $n$ . That is, for  $\alpha$  large enough (and for values experimentally realizable) and  $n$  small enough,  $g(n)$  is less than 1 and  $R_n$  is a decreasing function of  $n$ . However, since the triplet absorption term decreases as a function of  $n$  owing to both  $n_n^{S,u}$  and its "own" triplet denominator,  $1 + 2Tn/\nu_T$ , it decreases faster as a function of  $n$  than the singlet emission term. Thus for large enough  $n$   $g(n)$  may again take on values greater than 1 and  $R_n$  once again become an increasing function of  $n$ . For large enough  $n$  the triplet absorption term becomes negligible and the decrease in the singlet emission term becomes dominant, and  $R_n$  again decreases. If  $\alpha$  is not large enough the effect of the triplets is not enough to cause a minimum and the radiation distribution is typical, as pictured in Fig. 5(a). But for  $\alpha$  large enough (but not too large to prevent laser operation) a plot of  $R_n$  may look like that pictured in Fig. 5(c). In Sec. VD2 we shall find that the existence of two extrema requires a redefinition of threshold.

### 2. Laser threshold

We found that the usual definition of threshold [the value of  $N$  obtained from  $G(0) = 1$ ] is equivalent to the condition that there be an extremum (in that case a maximum) in the radiation distribution at  $n = 0$ . Applying this definition to Eq. (5.20) for the organic-dye laser, the result, which we refer to as  $N_{\text{thold}}$ , is

$$N_{\text{thold}} \cong \nu_R(\nu_{S,u} + K_{ST})/\nu_e S(1 - \alpha). \quad (5.22)$$

The factor  $(1 - \alpha)^{-1}$  shows the increase in laser

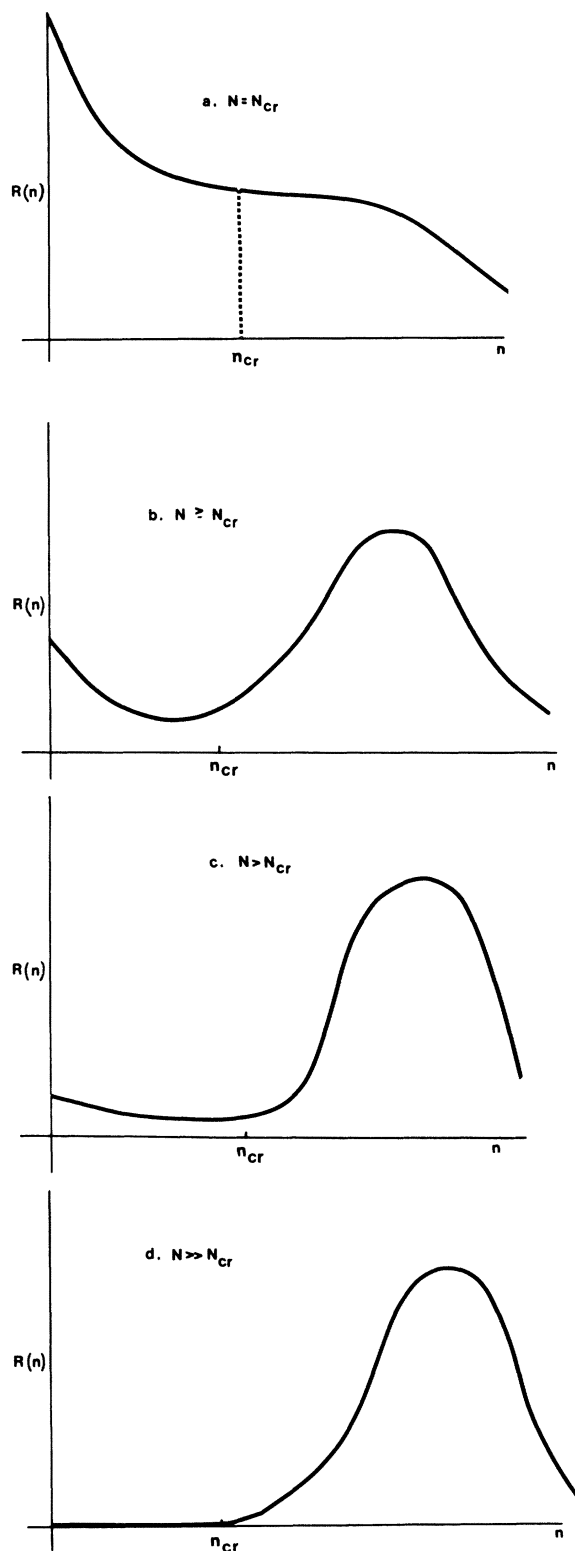


FIG. 6. For organic dye laser (with  $\alpha$  large enough and  $\beta$  small enough), radiation distribution vs photon number for different pumping values.

threshold owing to the triplets. However, we have changed the subscript to "thold," since this expression is incorrect in cases for which both the maximum and minimum occur in the radiation distribution.

This can be seen by examining plots of  $R_n$  vs  $n$ , for different values of pumping, in which both extrema appear. For small pumping  $R(n)$  is qualitatively the same as that for typical lasers, pictured in Fig. 4(a). However, for some larger value of pumping,  $R_n$  has the shape pictured in Fig. 6(a), which has neither a maximum nor minimum, but rather an inflection point. We call the value of pumping for which this takes place  $N_{cr}$ , and the value of photon number  $n$  corresponding to the inflection  $n_{cr}$ .  $N_{cr}$  is found by setting the expression in square brackets in Eq. (5.21) equal to zero and solving for  $N$ .  $n_{cr}$  is found by substituting  $N_{cr}$  into Eq. (5.21).

For  $N$  larger than  $N_{cr}$ , the maximum in  $R(n)$  is to the right-hand side of  $n_{cr}$  and the minimum is to the left-hand side [Figs. 6(b) and 6(c)]. The larger the pumping, the further to the left-hand (right-hand) side of  $n_{cr}$  the minimum (maximum) is. For pumping large enough the minimum is far enough to the left-hand side of  $n_{cr}$  that it disappears (i.e., occurs for negative photon number  $n$ , which, of course, is nonphysical). Thus the old definition of threshold is incorrect in such cases, since there is no value of pumping for which the maximum in  $R(n)$  is at  $n=0$ . In fact, since the old definition of threshold gives the value of  $N$  for which an extremum appears in  $R(n)$  at  $n=0$ , and since, as we just showed, when there are two extrema in  $R(n)$  the maximum occurs for positive values of  $n$ , the old definition corresponds to the value of pumping for which the minimum occurs at  $n=0$ . Thus we need a new definition of threshold for the organic-dye laser. In order to see what this definition should be, consider the algebraic behavior of  $R(n)$  for positive and negative  $n$ , even though for negative  $n$  there is no physical meaning. If the triplet state effect is small enough (small enough  $\alpha$  and large enough  $\beta$ ) the inflection point occurs for negative  $n$ . As pumping ( $N$ ) is increased, the maximum moves to the right-hand side until it reaches  $n=0$ , at which point the laser has reached threshold and the old definition of threshold is correct. As triplet-state effects are increased (by, for example, increasing  $\alpha$ ), the inflection point ( $n_{cr}$ ) moves to the right-hand side, eventually occurring at  $n=0$ , and for further increases in triplet-state losses, occurring at  $n>0$  (see Fig. 8).

Thus it is apparent that for  $n_{cr} < 0$ , the old definition of threshold is correct, whereas for  $n_{cr} > 0$  threshold must be redefined. If for this latter

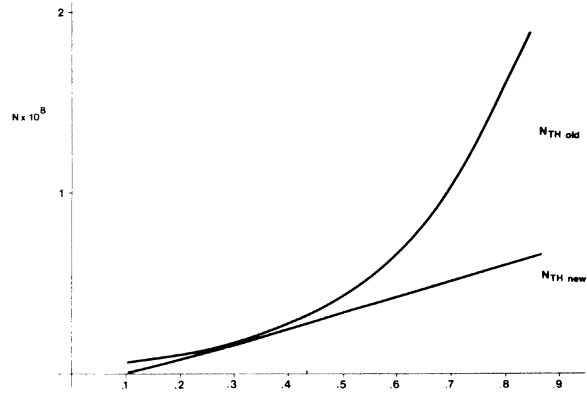


FIG. 7. Plot of  $N_{thold}$  and  $N_{thnew}$  vs  $\alpha$ .

case we call  $N_{cr}$  threshold, then the definition is consistent at  $n_{cr}=0$  where the old and new definitions must agree. Thus the new definition of threshold is

$$N_{th} = N_{thold}, \quad n_{cr} \leq 0, \quad (5.23)$$

$$N_{th} = N_{cr}, \quad n_{cr} \geq 0. \quad (5.24)$$

Figure 7, showing typical plots of  $N_{thold}$  and  $N_{thnew}$  as a function of  $\alpha$ , shows that the differences between them become larger as  $\alpha$  increases. On the  $\alpha$  axis we have labelled  $\alpha_{cr}$ , the critical value of  $\alpha$ . For  $\alpha$  greater than  $\alpha_{cr}$  there are two extrema in  $R(n)$  and the threshold is given by  $N_{cr}$ . For  $\alpha$  less than  $\alpha_{cr}$  there is only a maximum in  $R(n)$  and threshold is  $N_{thold}$ .  $\alpha_{cr}$  is determined by the condition that  $N_{cr} = N_{thold}$ , which means that  $n_{cr} = 0$ . Imposing this condition gives, to good approximation (and letting  $\beta=0$ ),

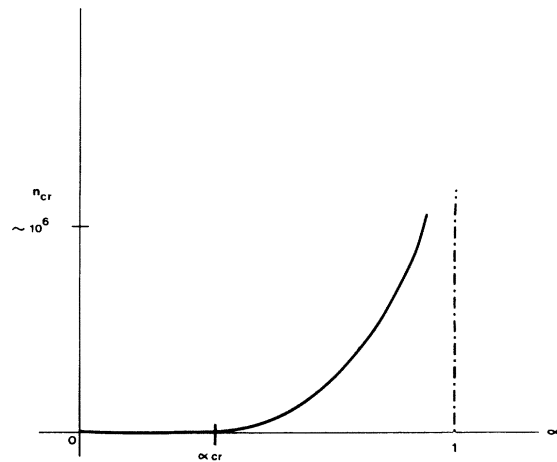


FIG. 8. Value of  $n_{cr}$  at dye laser threshold, as a function of  $\alpha$ .

$$\alpha_{cr} \cong \left( \frac{K_{ST}}{\nu_{S,u} + K_{ST}} \right)^{1/2} - \frac{K_{ST}}{2(\nu_{S,u} + K_{ST})}. \quad (5.25)$$

Experimental variations in  $\alpha$  would be most easily carried out by variations in the three parameters  $T$ ,  $S$ , and  $\nu_T$ , and we may regard  $K_{ST}$  and  $\nu_{S,u}$  as fixed. This means that expression (5.25) is, in effect, an expression specifying a critical  $\alpha$ . For typical parameters for the dye Rhodamine 6G,  $\alpha_{cr} \cong 0.27$ , which is well within the range of experimentally realizable values for  $\alpha$ .

In Sec. VD3 we give an account of the narrowing and widening of  $R_n$  as  $N$  is increased above threshold. Although there are no features unique to the organic-dye laser the triplets do have an effect on the narrowing and widening of  $R_n$ .

### 3. Narrowing and widening above threshold

In order to investigate the narrowing and widening for pumping above threshold we have found the maximum and variance ( $\sigma^2$ ) of  $R_n$ . As before, we characterize the radiation distribution as approximately Gaussian in photon number near threshold, where  $n_{max}/\sigma^2 \ll 1$ . As the laser is pumped above threshold, the radiation distribution usually narrows and approaches a Poisson distribution, which means  $n_{max}/\sigma^2 \rightarrow 1$ . Thus a plot of  $n_{max}/\sigma^2$  vs pumping looks qualitatively like curve a in Fig. 9, where  $(N/N_{th})$  is the ratio of actual pumping to threshold pumping. Also,  $n_{max}/\sigma^2$  begins to decrease again for large enough pumping, which is depicted in curve b. The presence of the triplets affects the dependence of  $n_{max}/\sigma^2$  on  $N/N_{th}$  in three different ways.

First, since for dye lasers at threshold,  $n_{cr}$  ( $\cong n_{max}$ ) has increased value for increased  $\alpha$ , plots of  $n_{max}/\sigma^2$  have positive y intercepts which increase

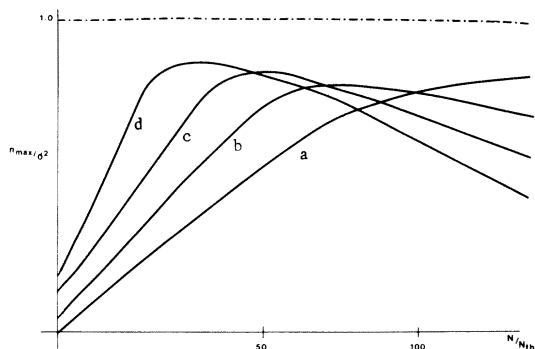


FIG. 9. Normalized radiation distribution parameter ( $n_{max}/\sigma^2$ ) as a function of pumping above threshold ( $N/N_{th}$ ) for different values of the triplet loss parameter ( $\alpha$ ). Curve a,  $\alpha=0.1$ ; b,  $\alpha=0.5$ ; c,  $\alpha=0.8$ ; d,  $\alpha=0.9$ .

with  $\alpha$ , rather than the zero y intercepts of typical lasers. The second difference is based on our finding that the plot of  $n_{max}/\sigma^2$  vs  $N/N_{th}$  is approximately a straight line just above threshold. For the organic-dye laser the slopes of these straight lines increase with increasing  $\alpha$  (see Fig. 10 for a typical plot of the slope vs  $\alpha$ ). This increase indicates that the triplet presence causes narrowing of  $R_n$ . Finally, the maximum of  $n_{max}/\sigma^2$  occurs for smaller values of  $N/N_{th}$ , for correspondingly larger values of  $\alpha$ . Thus the widening in  $R_n$  for pumping far above threshold occurs for smaller values of pumping relative to threshold and may be easier to observe experimentally in the presence of triplets than without them.

## VI. CONCLUSION

We have shown how the values of the organic-dye-molecule parameters (in particular  $\alpha$  and  $\beta$ ) affect the laser threshold behavior, the functional form of the photon distribution  $R_n$ , and the narrowing (and widening) of  $R_n$  for pumping above threshold. As present, little is known about values of  $\beta$ . However,  $\alpha [\equiv (T/S)K_{ST}/\nu_{T,I}]$  can be varied experimentally to almost any value desired (see Table I) in one of two ways. First, since both  $S$  and  $T$  have different dependences on laser wavelength,  $\alpha$  can be varied simply by tuning the laser to different wavelengths. Second, since the lower triplet decay rate ( $\nu_{T,I}$ ) is increased (decreased) by the addition (reduction) of quenching agents,  $\alpha$  may be varied by varying the amount of quenching agent used (unfortunately  $K_{ST}$  may also change with the concentration).

Initial experimental work could be done to search for the effects we have discussed. Thus one could,

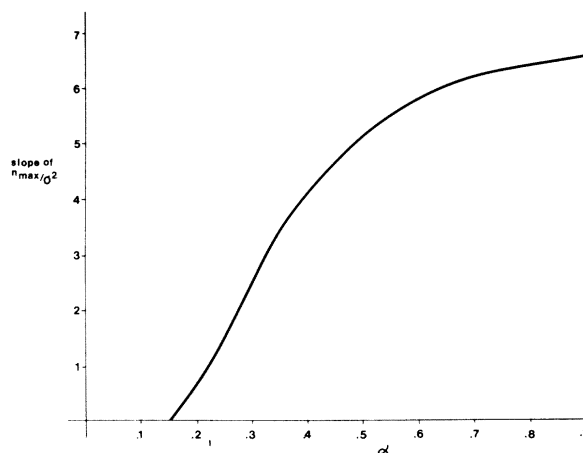


FIG. 10. Slope of ( $n_{max}/\sigma^2$  vs pump) vs  $\alpha$  (pumping just above threshold).

for example, perform the following experiments: A photon counting experiment could be done to search for a minimum in  $R_n$ . In addition to varying  $\alpha$ , the external pump can be varied to see if the minimum moves to smaller photon numbers. By operating the laser at threshold the unique behavior of the dye laser at threshold could be investigated. Similarly, the value of threshold, as a function of triplet parameters, could be checked. By means of photon counting experiments the slope of  $n_{\max}/\sigma^2$  just above threshold (for different values of  $\alpha$ ), the maximum in  $n_{\max}/\sigma^2$  just above threshold, and the narrowing of  $R_n$  well above threshold could be checked. Once these effects have been verified for a particular dye, the study of such effects in other dyes could be used as a tool to obtain information about organic-dye-molecule parameters in other dyes.

In the future we plan to treat the multimode and high-power cases, mode locking, the vapor-phase dye laser, phase and amplitude fluctuations, and various time-dependence phenomena.

#### APPENDIX

This appendix contains some of the more salient details of the derivation of the equations of motion, (4.3)–(4.7), using the Born-Markoff approximation master equation.

The Liouville equation of motion for the density operator  $P(t)$  of the entire organic-dye laser system includes terms associated with the reservoirs. We can write it in the following way:

$$\frac{dP(t)}{dt} = \frac{-i}{\hbar} [H_{\text{res}} + H_S + V_{\text{res},S}, P(t)]. \quad (\text{A1})$$

$$\begin{aligned} \frac{dD(N,t)}{dt} = & \frac{-i}{\hbar} [H_R + H_M(N), D(N,t)] + K_M D(N,t) + K_R D(N,t) \\ & + \text{Tr}_{\text{res}} \int_0^\infty d\tau \{V_{RT}, [V_{RT}(-\tau), D(N,t)d_{\text{res}}(t)]\} + \text{Tr}_{\text{res}} \int_0^\infty d\tau \{V_{RS}, [V_{RS}(-\tau), D(N,t)d_{\text{res}}(t)]\}, \end{aligned} \quad (\text{A4})$$

where

$$V_{RT}(-\tau) = e^{i(H_M+H_R)\tau/\hbar} e^{i(K_N+K_R)\tau} V_{RT} e^{-i\tau(H_M+H_R)/\hbar} \quad (\text{A5})$$

and

$$V_{RS}(-\tau) = e^{i(H_M+H_R)\tau/\hbar} e^{i(K_M+K_R)\tau} V_{RS} e^{-i\tau(H_M+H_R)/\hbar}. \quad (\text{A6})$$

In the above we have left out negligible terms associated with multiple-molecule effects. In order to obtain an equation for the single-molecule-radiation-density operator  $D(1,t)$ , we sum the above equation over  $N-1$  of the particles. Neglecting

$H_{\text{res}}$  includes all reservoir Hamiltonians,  $H_S$  is the system (radiation and molecules) Hamiltonian, and  $V_{\text{res},S}$  contains the reservoir system interaction Hamiltonians. Since the details of the reservoirs are of no interest here we eliminate explicit consideration of them. First we assume that the density operator for the entire system may be factorized into a product of reservoir and nonreservoir density operators,

$$P(t) = D(N,t)d_{\text{res}}(t), \quad (\text{A2})$$

where  $D(N,t)$  is the density matrix for the radiation and  $N$  dye molecules and  $d_{\text{res}}(t)$  is a product of the density operators associated with the reservoirs of the system. Substituting Eq. (A2) into Eq. (A1) and taking the trace over reservoir variables, we obtain

$$\begin{aligned} \frac{dD(N,t)}{dt} = & \frac{-i}{\hbar} [H_R + R_S, D(N,t)] \\ & - i \text{Tr}_{\text{res}} [V_{R-M}, D(N,t)d_{\text{res}}(t)] \\ & + K_R D(N,t) + K_M D(N,t), \end{aligned} \quad (\text{A3})$$

where  $H_R$  is Eq. (3.3),  $H_M$  is Eqs. (3.4) and (3.5), and  $V_{R-M}$  is Eqs. (3.7) and (3.8).  $K_R$  and  $K_M$  are linear time-independent operators which specify the effects of radiation and matter reservoirs on  $D(N,t)$ . We treat the reservoirs in such a fashion that the Hermiticity, positive definiteness, and normalization of the dye molecule and radiation density matrices are preserved.

When we carry out a Born-Markoff treatment of the radiation dye-molecule interaction in Eq. (A3) the result is

small terms associated with the two-molecule density operator and the radiation reservoir we obtain

$$\begin{aligned} \frac{dD(1,t)}{dt} = & \frac{-i}{\hbar} [H_R + H_M(1), D(1,t)] + K_M D(1,t) \\ & + \text{Tr}_{\text{res}} \int_0^\infty d\tau \{V_{RT}, [V_{RT}(-\tau), D(1,\tau)d_{\text{res}}]\} \\ & + \text{Tr}_{\text{res}} \int_0^\infty d\tau \{V_{RS}, [V_{RS}(-\tau), D(1,\tau), d_{\text{res}}]\}. \end{aligned} \quad (\text{A7})$$

Tracing over all molecule variables in Eq. (A4) gives the equation for the radiation density opera-

tor  $R(t)$ ,

$$\begin{aligned} \frac{dR(t)}{dt} = & \frac{-i}{\hbar} [H_R, R(t)] + K_R R(t) \int_0^\infty d\tau \\ & + N \text{Tr}_{\text{res}} \text{Tr}_1 \int_0^\infty d\tau \{ V_{RT}, [V_{RT}(-\tau), D(1, t) d_{\text{res}}] \} \\ & + \{ V_{RS}, [V_{RS}(-\tau), D(1, t) d_{\text{res}}] \}. \end{aligned} \quad (\text{A8})$$

The effect of the reservoirs on the radiation-matter interaction Hamiltonian appears in the exponent  $e^{+(K_M + K_R)\tau}$  in  $V(-\tau)$  [Eqs. (A5) and (A6)]. This exponent propagates the time dependence due to the reservoir interactions of the interaction Hamiltonian operators. The net effect is to add a decay to the time dependence of the radiation and molecule operators.<sup>3</sup> For instance, in the Heisenberg representation the "free" time dependence of the operator associated with the  $j$ th molecular level is  $s_j(t) = s_j e^{-i\omega_j t}$ , where  $\omega_j$  is the frequency as-

sociated with the energy of the  $j$ th level. The effect of a molecule reservoir on time dependence of  $s_j$  is to add on a decay time associated with the  $j$ th level,

$$\text{Tr}_{\text{matter res}} [s_j(t) s_j^\dagger(0)] = \langle s_j(t) s_j^\dagger(0) \rangle = s_j s_j^\dagger e^{-i\omega_j t} e^{-\nu_j t}, \quad (\text{A9})$$

where  $\nu_j$  is the decay rate of the  $j$ th level caused by the reservoir. Values for  $\nu_j$  and other reservoir parameters are phenomenological and not calculated from first principles.

When we write the interaction Hamiltonians explicitly, and include the effects of tracing over the reservoirs in the interaction terms in Eqs. (A7) and (A8), we can then, after rearranging terms, do the time integration. The resulting terms for the radiation-singlet interaction (the terms for the radiation-triplet interaction are the same, except for a change to triplet notation) are

$$\begin{aligned} \text{Tr}_{\text{res}} \int_0^\infty d\tau \{ V_{RS}, [V_{RS}(-t), D(1, t) d_{\text{res}}] \} = & - \sum_{ij} \frac{\gamma_{ij}^2 (\nu_i + \nu_j + \nu_R) \{ s_j^\dagger s_i a^\dagger + s_i^\dagger s_j a, [s_j^\dagger s_i a^\dagger + s_i^\dagger s_j a, D(1, t)] \}}{(\Omega - \omega_{ij})^2 + (\nu_i + \nu_j + \nu_R)^2} \\ & - \sum_{ij} \frac{i\gamma_{ij}^2 (\Omega - \omega_{ij}) \{ s_j^\dagger s_i a^\dagger + s_i^\dagger s_j a, [s_j^\dagger s_i a^\dagger - s_i^\dagger s_j a, D(1, t)] \}}{(\Omega - \omega_{ij})^2 + (\nu_i + \nu_j + \nu_R)^2}, \end{aligned} \quad (\text{A10})$$

where  $\omega_{ij} \equiv (\epsilon_i - \epsilon_j)/\hbar$ ,  $\nu_i$  and  $\nu_j$  are the decay rates associated with the  $i$ th and  $j$ th molecular levels, and  $\nu_R$  is the decay rate of the laser radiation. The second (imaginary) term on the right-hand side represents an energy shift which is important in some problems. It does not contribute when the laser is at resonance (i.e., when the mode frequency  $\Omega$  equals the molecular transition frequency  $\omega_{ij}$ ). (Purely for convenience we have assumed resonance in this paper.) Equations (A7) and (A8) then are

$$\begin{aligned} \frac{dD(1, t)}{dt} = & \frac{-i}{\hbar} [H_R + H_M, D(1, t)] + K_M D(1, t) \\ & - S\xi D(1, t) - T\Upsilon D(1, t), \end{aligned} \quad (\text{A11})$$

$$\begin{aligned} \frac{dR(t)}{dt} = & \frac{-i}{\hbar} [H_R, R(t)] + K_R R(t) \\ & - \text{Tr}_{\text{molecule}} N(S\xi + T\Upsilon) D(1, t), \end{aligned} \quad (\text{A12})$$

where

$$\begin{aligned} S = & \gamma_{ij}^2 / (\nu_i + \nu_j + \nu_R), \quad T \equiv \gamma_{im}^2 / (\nu_i + \nu_m + \nu_R), \\ \xi D(1, t) = & \{ s_j^\dagger s_i a^\dagger + s_i^\dagger s_j, [s_i^\dagger s_i a^\dagger + s_i^\dagger s_j a, D(1, t)] \}, \end{aligned}$$

and

$$\Upsilon D(1, t) \equiv \{ t_m^\dagger t_i a^\dagger + t_i^\dagger t_m a, [t_m^\dagger t_i a^\dagger + t_i^\dagger t_m a, D(1, t)] \}.$$

When we take (A11) and (A12) in the number rep-

resentation in the radiation variables and molecular energy-level representation, we obtain the organic-dye laser equations of motion, (4.3)–(4.7).

In these equations we have already included the reservoir kernels explicitly. For the radiation reservoir we have taken a simple-harmonic-oscillator zero-temperature reservoir. Including a finite-temperature reservoir is easily accomplished, and would have negligible effect on the results. The reservoirs also induce the different decay rates for the appropriate molecular levels. The reservoirs are responsible for the molecular excitation rate  $\nu_e$ , the pumping of (or decay from the upper singlet state to) the lower triplet level, and the fractional return of the upper triplet to lower triplet states.

The simplest way to completely specify  $\nu_e$  is to impose the normalization condition that the sum of the probabilities that the organic-dye lasing levels are occupied is 1 (i.e.,  $D_n^{S,u} + D_n^{S,l} + D_n^{T,u} + D_n^{T,l} = D_n$ ). This condition is physically reasonable, at least in the steady state. Our normalization condition stems from the fast rotational and vibrational relaxation rates. Imposing this condition results in the expression

$$\nu_e = \frac{\nu_{S,u} + K_{ST}}{(1 + K_{ST}/\nu_{T,l})}, \quad (\text{A13})$$

which depends solely on the decay constants of the molecule.



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