Physics of dye lasers

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The physical mechanisms important to the operation of tunable lasers utilizing organic dyes are discussed. The uniqueness of organic dyes as a tunable laser medium is reviewed by investigating the optical properties of two broadened energy levels. The complete energy level system is investigated and gain and efficiency are calculated. The wide variety of practical laser configurations possible for optically pumped dye lasere are examined. New topics of interest such as dye vapor lasers and short pulse generation are discussed.

CONTENTS

I. INTRODUCTION

A. Historical

Almost simultaneously with the invention of the laser, the question was asked whether a laser could be easily tuned over a broad range of frequencies. The organic dye laser has made the concept of a tunable laser a reality. Today, tunable organic dye lasers are available which cover the spectrum from the ultraviolet to the near infrared.

The first report of dye laser action was that of Sorokin and Lankard (1966) who observed laser emission from a solution of chloroaluminum pthalocyanine. Independently, Schäfer, Schmidt, and Volze (1966) obtained laser action in the infrared from a number of cyanine-type dyes. Dye laser action was also demonstrated independently by M. Spaeth and D. Bortfield (1966), and by B. I. Stepanov, A. N. Rubinov, and V. A. Mostovnikov (1967).

The uniqueness of these contributions was that they were the first reports of laser action from broad, diffuse energy bands rather than a set of discrete energy levels, typical of gas and rare earth lasers. The tunability of the dye laser is a consequence of the broadened electronic levels characteristic of organic dyes.

Another important advance was made by Soffer and McFarland (1967) who succeeded in spectrally narrowing and tuning a dye laser by replacing one of the resonator mirrors with a diffraction grating. This was the first demonstration that a laser could be efficiently tuned over a broad spectral range.

In a subsequent development, Sorokin and Lankard (1967) and also independently Schmidt and Schäfer (1967) replaced the high intensity laser pumping source with a flashlamp. Using a flashlamp system Snavely and Schäfer (1969) established the feasibility of a continuous dye laser. Their experiments showed that the widely held notion, that a cw dye laser was not possible because of metastable triplet state losses, was incorrect.

Finally, Peterson, Tuccio, and Snavely (1970) at Kodak Research Laboratories achieved the first continuous dye laser action using a focused argon laser as a pump. The cw dye laser with subsequent refinements has allowed the dye laser to realize its full potential as a useful tool for physics and chemistry.

B. Organic dyes

Organic dyes, according to commonly accepted terminology, are a class of colored substances which are useful for their ability to impart color to other substances. Presently, the definition is broadened to include organic compounds which have a strong absorption band somewhere from the ultraviolet to the near infrared. Organic compounds with this property contain an extended system of conjugated bonds (alternating single and double bonds). These compounds are much too complex for one to rigorously derive their absorption from quantum mechanics. However, chemists have used rather simple models to explain experimental observations for a given class of dyes Schäfer (1973). Nonradiative processes, so important to dye laser operation, are even more difficult to analyze quantitatively. A good discussion of radiationless processes is given by Becker (1969).

The energy levels of a typical organic dye are shown in Fig. 1. Each electronic level is a band composed of a continuum of vibrational and rotational levels. The lowest energy absorption is due to absorption from the electronic singlet ground state S_0 to the first excited singlet S_1. This strong absorption, usually in the visible region of the spectrum, is responsible for the useful property of dyes that they color other substances such as cloth, food, plastics, etc. In Fig. 2 we show the absorption spectrum of one of the more useful organic dyes rhodamine 6G. We see this absorption is about 50 nm wide. Also shown in Fig. 2 is the fluorescent emission from this dye. Not all dyes exhibit strong fluorescence, but the more useful laser dyes exhibit a near unity quantum efficiency. In a later section we will discuss in detail the nonradiative pathways which reduce fluorescent emission. Stimulated emission or laser action can occur over

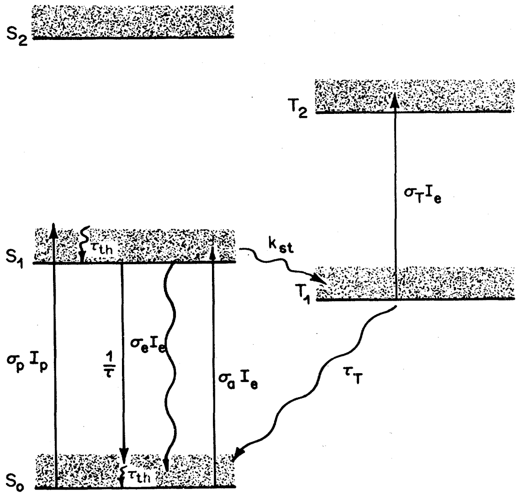

FIG. 1. Energy level diagram of a typical organic molecule.

the fluorescent band. Also shown in Fig. 2 is the triplet–triplet absorption. This absorption often overlaps the fluorescence band and can inhibit laser action.

Of the thousands of organic dyes available, only a few classes of dyes meet the stringent criteria for becoming useful laser dyes. The various classes of dyes and the region of the spectrum they cover are illustrated in Fig. 3.

C. Excited state reactions

The tuning range of a laser dye is often limited on the short wavelength side by an overlapping absorption. For example, there is considerable absorption at the peak of the rhodamine 6G fluorescence curve shown in Fig. 2. The degree of this overlap is determined by the Stokes shift of the fluorescence. In rhodamine 6G the tuning range is limited to the long wavelength side of the fluorescence spectrum (5600 Å–6500 Å).

In a more complex dye–solvent system it is possible to remove the effects of an overlapping self-absorption with an excited state chemical reaction. For example, the dye, 4-methyl-umbelliferone in an acidic solution undergoes a chemical reaction to form a species in the excited state which is unstable in the ground state (Shank *et al.*, 1970). The fluorescence of the excited species shifts 2000 Å away from the fluorescence of the unreacted molecule. Upon emission of a photon, the excited state species reverts back to the original unreacted molecule whose absorption does not overlap the emission. A tuning range of 1800 Å, from the near ultraviolet to the yellow, has been obtained from an acidic solution of 4-methyl-umbelliferone.

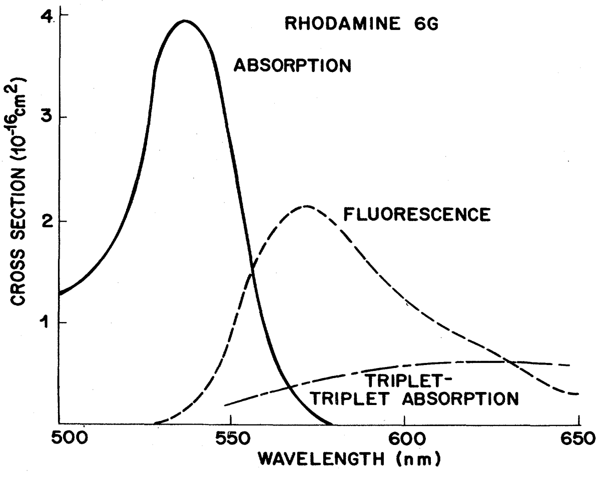

FIG. 2. Absorption, emission and triplet–triplet absorption cross sections for the dye Rhodamine 6G in methanol.

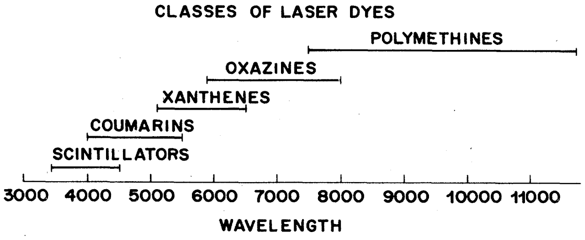

FIG. 3. Wavelength tunability ranges for various important classes of organic dyes.

D. Dye laser tunability and spectral condensation

Possibly the most interesting phenomenon associated with organic dye lasers from both the fundamental point of view, as well as practical usefulness, is the efficient spectral narrowing of dye laser oscillation when a frequency selective element is inserted into the optical cavity. A dye laser with a broad band optical cavity usually oscillates with a bandwidth of between 50 Å to 100 Å. With the insertion of frequency selective elements into the optical cavity, the bandwidth of oscillation can be reduced to a small fraction of an Angstrom without appreciable loss in power. Soffer and McFarland (1967) discovered this effect when they substituted a plane diffraction grating for one of the mirrors of a laser-pumped dye laser. Rotation of the grating resulted in tuning of the dye laser. In Fig. 4 we have illustrated how a plane diffraction grating supplies frequency selective feedback. Spontaneous emission from the dye laser medium is scattered off the dispersive grating at an angle dependent upon the wavelength. Only optical radiation at the desired wavelength of oscillation is returned to the cavity with low loss. The cavity Q is high only in the narrow region of the spectrum where the laser oscillates.

Homogeneous broadening of laser dyes is the physical mechanism which allows optical power to be efficiently channeled into a small oscillating bandwidth. To explore the meaning of homogeneous broadening as applied to dye lasers, let us consider the energy level diagram in Fig. 5. Normally a dye molecule is excited at some wavelength corresponding to the optical pump energy, and spontaneous and stimulated emission occur at a range of longer wavelengths according to the Franck–Condon principle. In Fig. 5 we show an energy level diagram in which molecules have been excited to the first singlet level S_1. Thermalization has taken place creating a dynamic equilibrium in which both the excited state and the ground state are separately in thermal equilibrium. The levels involved here are a continuum of rotational and vibrational states. Thermalization which results in a Boltzmann distribution of occupied levels has been achieved in both the excited and ground states.

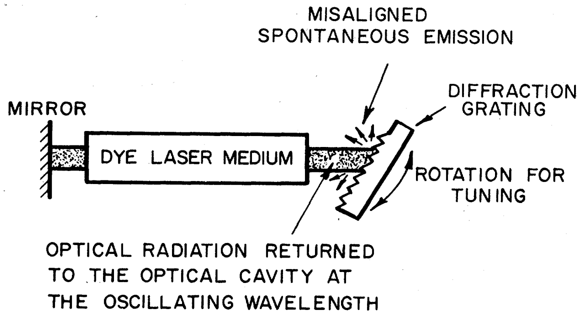

FIG. 4. Tuning of a dye laser with a diffraction grating.

Under lasing conditions with a broadband optical cavity, stimulated emission can take place from the bottom of the excited singlet state S_1 to any of the continuum of unoccupied vibrational and rotational levels in the ground state. After the emission of a photon, rapid thermalization takes place to the bottom of the ground state on a picosecond time scale, leaving the terminal level again unoccupied.

Now, suppose frequency selective feedback is placed in the optical cavity corresponding to the wavelength of a transition to level *a*. Laser emission could not take place, for example, to level *b* because the cavity Q would be too low for oscillation at that wavelength. The intensity of the optical field in the medium would be strongest at the oscillating wavelength corresponding to level *a*. Since the rate of stimulated emission is proportional to intensity, more molecules are caused to emit stimulated photons at the wavelength of the intense field. Because thermalization is so rapid, all molecules in the molecular system have an equal probability to emit to level *a*. As a result the emission to level *a* draws from the entire excited state population and spectral condensation is therefore very efficient.

II. OPTICAL PROPERTIES OF TWO BROADENED ENERGY LEVELS

In the previous section we pointed out that the electronic energy levels of an organic dye molecule are not sharply defined, but are rather a band of levels formed by smear of vibrational and rotational levels. In this section we will describe the optical properties of two such broadened electronic energy levels. For purposes of the discussion in this section we will confine our attention to the S_0 and S_1 levels, and for the present ignore the influence of other levels.

In Fig. 6 we have schematically drawn two energy levels which have a width $\Delta\nu$ and are spaced by an energy $h\nu_0$. We will consider the case where the levels are excited optically by pump photons of frequency ν_p. Emission from the levels will be observed at a frequency ν_e.

Upon excitation by a pumping photon, each level will be considered to be thermalized in a time very short compared to the radiative lifetime. Typically for organic dyes the thermalization time is expected to be on the order of picoseconds, while the radiative lifetime is in the nanosecond range.

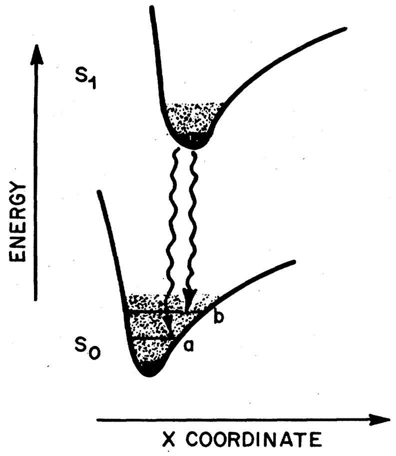

FIG. 5. An energy level diagram illustrating spectral condensation.

Measurements of the thermalization time have been performed by Ricard *et al.* (1972) for dye molecules in solution by investigating the risetime of stimulated emission on a picosecond time scale.

Let us now consider two levels which have been optically excited and are thermalized with populations N_0 and N_1. In each level the electrons will be distributed in energy, $\mathcal{E}$, according to a distribution function $\eta_i(\mathcal{E}_i)$. The level populations are then given by

$$N_i = \int \eta_i(\mathcal{E}_i)d\mathcal{E}. \qquad \text{(II.1)}$$

Under the condition of rapid thermalization the distribution functions can be approximated by a Boltzmann distribution given by

$$\eta_i(\mathcal{E}_i) = C_i g_i(\mathcal{E}_i)\exp(-\mathcal{E}_i/kT), \qquad \text{(II.2)}$$

where $g_i(\mathcal{E}_i)$ are the level degeneracies, and C_i is a normalizing factor.

The absorption coefficient for a simple system of two discrete levels is given by

$$k_\nu = -\frac{1}{I_\nu}\frac{dI_\nu}{dx} = \frac{h\nu n}{c}(B_{01}N_0 - B_{10}N_1), \qquad \text{(II.3)}$$

where I_ν is the intensity of radiation at frequency ν, n is the refractive index, and B_{01}, B_{10} are the Einstein coefficients

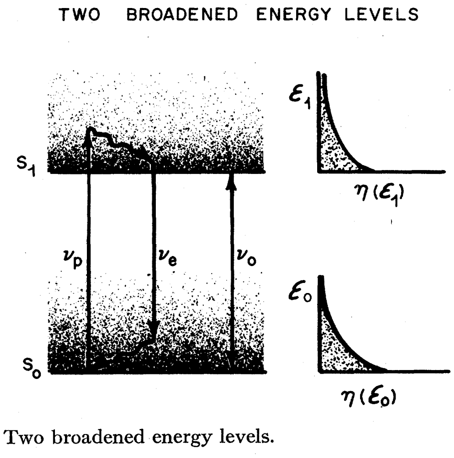

FIG. 6. Two broadened energy levels.

for stimulated emission and absorption. Such a system cannot exhibit negative loss or gain under steady state excitation. Laser action can only take place in more complex systems where it is possible to invert the population by some means and make $N_1 > N_0$. This is usually accomplished by utilizing additional energy levels as in the case of three or four level lasers. In the case of the broadened two level system, we will show how the width of the levels themselves will provide a means of achieving gain with optical excitation.

We can rewrite the absorption coefficient given by Eq. II.3 as an amplification or gain coefficient at a frequency, ν, for a system of two broadened levels as

$$\alpha(\nu) = [N_1\sigma_e(\nu) - N_0\sigma_a(\nu)], \tag{II.4}$$

where we have defined emission and absorption cross sections in terms of the Einstein coefficients as

$$\sigma_e(\nu) = (h\nu n/c)B_{10}(\nu), \tag{II.5a}$$

$$\sigma_a(\nu) = (h\nu n/c)B_{01}(\nu). \tag{II.5b}$$

The frequency dependent cross sections are defined in terms of the electron distribution functions (Stepanov, 1968) as

$$\sigma_e(\nu) = \int\sigma_e(\mathcal{E}_1,\nu)\eta(\mathcal{E}_1)d\mathcal{E}_1, \tag{II.6}$$

$$\sigma_a(\nu) = \int\sigma_a(\mathcal{E}_0,\nu)\eta(\mathcal{E}_0)d\mathcal{E}_0. \tag{II.7}$$

Equation (4) can be rewritten as

$$\alpha(\nu) = \sigma_e(\nu)[N_1 - (\sigma_a(\nu)/\sigma_e(\nu))N_0] \tag{II.8}$$

and the condition for amplification becomes

$$\frac{N_1}{N_0} > \frac{\sigma_a(\nu)}{\sigma_e(\nu)}. \tag{II.9}$$

To determine the ratio of the absorption and emission cross sections, let us assume $C_1 = C_0$ [Eq. (II.2)]. Equating up and down transitions we obtain

$$\sigma_e(\mathcal{E}_1,\nu)g_1(\mathcal{E}_1) = \sigma_a(\mathcal{E}_0,\nu)g_0(\mathcal{E}_0), \tag{II.10}$$

where

$$\mathcal{E}_1 = \mathcal{E}_0 + h(\nu - \nu_0). \quad \text{(see Fig. 6)} \tag{II.11}$$

Now using equations (II.2), (II.10), (II.11), (II.5), and (II.6), we obtain

$$\sigma_a(\nu)/\sigma_e(\nu) = \exp[-h(\nu_0 - \nu)/kT]. \tag{II.12}$$

Equation (II.12) with Eq. (II.9) gives the requirement for amplification in two broadened levels

$$N_0/N_1 > \exp[-h(\nu_0 - \nu)/kT]. \tag{II.13}$$

From the above it is clear that if $\nu \geq \nu_0$ the condition for gain is achieved only if there is a net population inversion between levels 0 and 1. However, more interestingly, for the case where $\nu < \nu_0$, amplification can occur even though there is no net population inversion. This is a very important distinction between a system of two discrete energy levels and a system of two broadened levels.

In order to determine the gain under conditions of optical pumping with a pump of intensity I_p, and frequency ν_p, we equate the absorption and emission of photons between the two broadened levels

$$N_0\sigma_a(\nu_p)I_p = N_1\left[\frac{1}{\tau} + \sigma_e(\nu_p)I_p\right] \tag{II.14}$$

and define

$$N = N_0 + N_1. \tag{II.15}$$

The quantity τ is the spontaneous emission lifetime. Solving the above for N_1 we get

$$\frac{N_1}{N} = \frac{1}{[1/\sigma_a(\nu_p)\tau Ip] + 1 + \exp[h(\nu_0 - \nu_p)/kT]}. \tag{II.16}$$

Clearly from (II.16) we observe that in order to obtain a large population in level 1, ν_p must be $> \nu_0$. Of course the width of the absorption band provides a limitation.

Now substituting (II.16) into (II.8) we obtain for the gain at a frequency ν

$$\alpha(\nu) = \sigma_e(\nu)N \times \left(\frac{1 + \exp[-h(\nu_0 - \nu)/kT]}{\{1/[\sigma_a(\nu_p)\tau I_p]\} + 1 + \exp[h(\nu_0 - \nu_p)/kT]} - \exp[-h(\nu_0 - \nu)/kT]\right). \tag{II.17}$$

In the two-level system described here it is possible to observe anti-Stokes fluorescence i.e., emission at wavelengths shorter than the pumping radiation. This comes about from the rapid thermalization of the bands. It is interesting to ask if it is possible to observe gain for wavelengths less than the pumping radiation. If we assume infinite pumping, Eq. (II.17) requires that

$$\exp[h(\nu - \nu_p)/kT] < 1 \tag{II.18}$$

in order to have gain. Thus, it is not possible to have anti-Stokes gain.

The width of the broadened levels, $\Delta\nu$, has a strong bearing on the size of the gain. For example if $h\Delta\nu \ll kT$, the system reduces to the equivalent of a two-level system and there is no gain.

From Eq. (II.17) we see that for the case of a very broad band (i.e., $h(\nu_p - \nu_0) \ll kT$)

$$\alpha(\nu) = \sigma_e(\nu)N \tag{II.19}$$

which is the limiting gain for a totally inverted system. Unfortunately, as $\Delta\nu$ is increased the cross section, $\sigma_e(\nu)$, is decreased. Dyes exhibiting the largest gains usually have energy bands with widths in the range 0.1 to 0.3 eV.

We should also point out that the width of energy bands is directly related to the spontaneous or natrual lifetime τ. According to Eq. II.17 the shorter τ becomes, the more intense the pumping radiation I_p must be to achieve gain. In fact for most dyes of interest for dye lasers (Parker, 1968)

$$1/\tau \approx 3 \times 10^{24}\sigma_{\max}$$

making τ typically in the nanosecond range.

III. DYE LASER GAIN AND EFFICIENCY

In the previous section we confined our discussion to an idealized model which considered only two levels. An actual dye molecule is considerably more complex. In this section we will endeavor to include the effects of triplet states, intersystem crossing, quenching processes, quantum efficiency and ground state reabsorption on laser action.

In Fig. 1 we have the complete energy level diagram and have illustrated all the processes which influence gain and population dynamics. The gain coefficient $\alpha(\nu)$ can be written as

$$\alpha(\nu) = \sigma_e N_1 - \sigma_a N_0 - \sigma_t N_t, \tag{III.1}$$

where σ_e and σ_a are the emission and absorption cross sections as before, and σ_t is the triplet absorption cross section. The first term is the stimulated emission term, while the second term represents a loss due to reabsorption from the ground state, and the third term is a loss due to excited state triplet absorption from $T_0 \rightarrow T_2$.

The optical pumping rate, $\sigma_p I_p$, is illustrated in the figure as molecules are excited from the ground state S_0 to the first excited singlet S_1. With more energetic pump photons it would also have been possible to excite the molecules into the higher lying singlet level S_2. In either case rapid thermalization takes place and all the molecules quickly find themselves near the bottom of the S_1 level in a matter of picoseconds or less. At this point a number of competing pathways are available for the molecules to lose excitation. The most desirable from the standpoint of dye lasers is of course stimulated emission, given by the rate $\sigma_a I_e$. Additionally, there is a radiative loss due to spontaneous emission with a rate $1/\tau$, where τ is the spontaneous emission lifetime.

The excited singlet state also decays by nonradiative processes with a rate k_{st} to the lowest triplet, and with a rate k_{ss} to the ground state singlet. It is convenient to define a quantum efficiency of fluorescence ϕ as the ratio of spontaneous emission to spontaneous emission plus nonradiative losses

$$\phi = 1/[1 + (k_{st} + k_{ss})\tau]. \tag{III.2}$$

This quantity is a measure of the probability that a molecule will emit a photon upon absorption of a photon. For most dyes of interest for dye lasers this quantity is near unity.

We can now incorporate all these processes into a set of rate equations which will describe the population dynamics of the system.

$$dN_1/dt = N_0(\sigma_p I_p + \sigma_a I_e) - N_1[\sigma_e I_e + (1/\tau\phi)], \tag{III.3}$$

$$dN_t/dt = N_1 k_{st} - (N_t/\tau_t), \tag{III.4}$$

$$N = N_1 + N_0 + N_t. \tag{III.5}$$

Equation III.3 is simply a balance of those processes that contribute to the population N_1, optical pumping and reabsorption from the ground state, and those processes through which excitation is lost: stimulated emission, spontaneous emission, nonradiative decay and intersystem crossing to the triplet. Equation (III.4) determines the triplet state population and Eq. (III.5) is a statement of conservation of molecules where N is the total population. Implicit in these equations is the assumption that we can neglect absorption of the dye laser radiation by molecules in the first excited singlet to higher excited singlet states (Leheny and Shah, 1975). Also we have assumed that the pump radiation is not absorbed by molecules in the triplet state. This is true for most laser dyes. In solving these equations we are going to neglect the spatial dependence of I_p and I_e. This is a good assumption for small gains and true for I_p in the case of transverse pumping. Tuccio and Strome (1972) have done a complete computer calculation for the cw dye laser including both transverse and longitudinal dependence of the pump and radiation fields.

Under conditions of steady state appropriate to a continuously operated dye laser

$$\frac{dN_0}{dt} = \frac{dN_1}{dt} = \frac{dN_t}{dt} = 0. \tag{III.6}$$

The triplet state population is then

$$N_t = k_{st}\tau_t N_1. \tag{III.7}$$

Using Eqs. (II.3), (II.4), and (II.5), we obtain the excited state population

$$N_1 = \frac{N(\beta_p I_p + \beta_a I_e)}{1 + \beta_e I_e + (1 + k_{st}\tau_t)(\beta_p I_p + \beta_a I_e)}, \tag{III.8}$$

where we have defined the quantities

$$\beta_p = \sigma_p \tau \phi \quad \text{and} \quad \beta_e = \sigma_e \tau \phi.$$

We can now solve for the gain using Eqs. (III.1), (III.7), (III.8), resulting in a final equation given by

$$\alpha = \alpha_0 - \xi \frac{I_e}{I_s} \Big/ \left(1 + \frac{I_e}{I_s}\right), \tag{III.9}$$

where α_0 is the small signal gain given by

$$\alpha_0 = \frac{N\beta_p I_p[(\sigma_e - k_{st}\tau_t\sigma_t) - \sigma_a]}{1 + \beta_p I_p(1 + k_{st}\tau_t)}, \tag{III.10}$$

and I_s is the saturation parameter which describes the reduction in gain as the intensity of the dye laser radiation is increased

$$I_s = \frac{1 + \beta_p(1 + k_{st}\tau_t)I_p}{\beta_e + \beta_a(1 + k_{st}\tau_t)}. \tag{III.11}$$

Note that the saturation intensity is dependent on the intensity of the pumping radiation. As I_p is increased, a greater dye laser intensity is required to saturate the gain. The quantity ξ given by

$$\xi = N k_{st}\tau_t\sigma_t \Big/ 1 + \frac{\sigma_e}{\sigma_a} + k_{st}\tau_t \tag{III.12}$$

is a loss parameter which describes an intensity-dependent loss $\xi(I_e/I_s)$ given in Eq. (III.9). The physical mechanism by which this loss arises depends on the reabsorption of dye laser radiation by ground state molecules which are raised

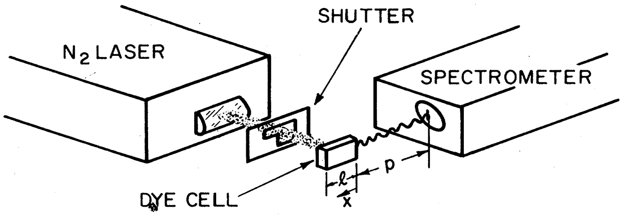

FIG. 7. Gain measurement apparatus.

to the excited singlet, intersystem cross to the triplet state and present a loss due to triplet state absorption. The quantity $\xi \rightarrow 0$ if the laser operates in a region of the spectrum where $\sigma_a \approx 0$, implying no ground state absorption. An interesting implication of this loss parameter is that it represents a mechanism whereby a laser amplifier can be self-limiting. For if

$$I_e/I_s > \alpha_0/\xi,$$

the gain given by Eq. (III.9) becomes a loss.

As with any laser, the power output of the dye laser is determined by mirror transmission, cavity losses, and gain. The condition of oscillation requires that the saturated gain equal the cavity losses.

$$\alpha_0 - \xi \frac{I_e}{I_s} \Big/ 1 + \frac{I_e}{I_s} = l + l_0, \tag{III.13}$$

where l is half the output mirror transmission, and l_0 is the residual cavity single pass loss of the cavity. This equation is strictly correct only for small gains. The output power is a maximum at some optimum value of the mirror transmission. The optimum output loss is

$$l_{\text{opt}} = [(l_0 + \xi)(\alpha_0 + \xi) - (l_0 + \xi)]^{\frac{1}{2}}, \tag{III.14}$$

and the maximum power output is given by

$$P_{\max} = h\nu_e A_e[(\alpha_0 + \xi)^{\frac{1}{2}} + (l_0 + \xi)^{\frac{1}{2}}]^2 I_s. \tag{III.15}$$

In the case where there are no triplet losses $\xi = 0$, and no residual losses $l_0 = 0$, and no ground state absorption $\sigma_a = 0$, a simple expression for the maximum output power is obtained

$$P_{\max} = h\nu_e \sigma_p I_p N, \tag{III.16}$$

and if we recognize that $\sigma_p I_p N$ is the number of absorbed pump photons we can calculate the power efficiency

$$\eta = \frac{P_{\max}}{P_{\text{abs}}} = \frac{\lambda_p}{\lambda_e}. \tag{III.17}$$

This is the ultimate efficiency that can be obtained from a dye laser with all the above loss mechanisms neglected. The deviation of this quantity from unity is simply the Stokes loss. For an actual device the other factors such as triplet losses, ground state reabsorption, and cavity losses serve to reduce the efficiency. Nonetheless, experimentally efficiencies as high as 50% have been reported (Sorokin *et al.*, 1967).

IV. GAIN SPECTROSCOPY

One of the fundamental quantities of importance for a laser medium is, of course, the optical gain. In this section we will discuss the measurement of gain in optically excited organic dyes. The measurement of gain, or gain spectroscopy, can provide unique information about the excited organic molecular systems not obtainable from either fluorescence or absorption spectroscopy.

Simple measurements of emission in highly excited systems with gain are difficult to interpret since emission is geometry dependent and not directly related to fundamental parameters. Under lasing conditions further complications are introduced by the coupling of molecular emission to optical cavity modes. Direct measurement of gain provides a fundamental quantity.

A useful and convenient method of measuring gain is based on measurements of amplified spontaneous emission. This technique was first demonstrated in high-gain pulsed metal vapor lasers by Silfvast and Deech (1970) and modified for pulsed dye lasers by Shank, Dienes, and Silfvast (1970). The experimental arrangement is shown in Fig. 7. The dye is pumped with 3371 Å light from a pulsed N_2 laser. The gain region is defined by the rectangular beam from the N_2 laser and focused with a cylindrical lens. The cell is divided into two sections so that the length of the pumped region may be varied from l to $l/2$ by blocking of the left half of the pumping beam with a shutter. After passing through a 250 μm pinhole, the amplified spontaneous emission from the pumped region enters a monochromator.

For a pinhole coaxial with a gain region and having an area less than or equal to the cross-sectional area of the gain region, the light intensity at wavelength λ entering the pinhole is given by

$$I_l(\lambda) = C \int_0^l \frac{\exp(\alpha_\lambda x)}{(p + x)^2}\, dx, \tag{IV.1}$$

where C is a constant for a given pumping intensity, α_λ is the intensity coefficient gain at wavelength λ, and p and x are defined in the figure. The quantity α_λ is assumed constant over the acceptance spectrum of the monochromator.

For $p \gg l$

$$I_l(\lambda) = C/\alpha_\lambda p^2[\exp(\alpha_\lambda l) - 1]. \tag{IV.2}$$

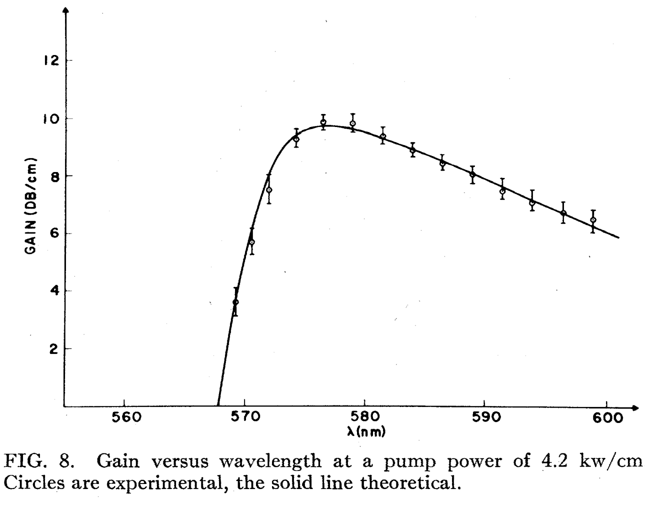

FIG. 8. Gain versus wavelength at a pump power of 4.2 kw/cm. Circles are experimental, the solid line theoretical.

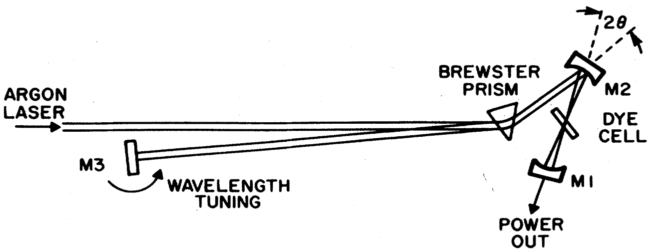

FIG. 9. cw dye laser optical cavity configuration.

Writing a similar equation for $I_{l/2}$ and combining we get

$$\alpha_\lambda = \frac{2}{l}\ln(I_l/I_{l/2} - 1).$$

Now by simply measuring the emission from a full and a half cell the gain can be readily calculated from the ratio.

In Fig. 8 we have plotted gain versus wavelength for the dye rhodamine 6G. The circles are experimental and the solid curve theoretical by using equation (III.1). The values of the parameters used for the curve are $N = 9.03 \times 10^{17}$ cm^{-3}, $- = 5.5 \times 10^{-9}$, and the values σ_a and σ_e were taken from Fig. 2. The fractional population density of the excited single population N_1/N was used as a free fitting parameter and was determined to be $N_1/N = 0.02$. Thus, gain spectroscopy appears to be a useful method of obtaining excited state population densities. The technique described here has been refined (Lingel *et al.*, 1973) and applied to the study of a number of organic dye systems (Dienes and Madden, 1973; Dienes *et al.*, 1973).

V. LASER CONFIGURATIONS

A wide variety of optical pumping and resonator schemes are possible for organic dye lasers. The ability one has to change concentration of the dye molecules allows a great deal of flexibility in adjusting the lasing solution to fit the spectral and spatial requirements of the pumping source. It is not the intent in this section to give a listing of practical dye laser configurations but rather to indicate the wide range of possibilities.

The high optical power densities achievable from laser sources make them ideal for optically pumping organic dyes. The laser pumped dye laser does have the disadvantage that an expensive and often inefficient laser pumping source is required. However, the spatial coherence of the laser source allows a more precise control over the optical pumping geometry than is possible from an incoherent flashlamp. For continuous dye laser operation, intensities in excess of 10^4 W/cm^2 are required. No incoherent lamp source exists which can achieve these intensities on a continuous basis. A laser source is ideal because a relatively low power laser beam (≈ 1 W) can be focused to easily achieve the required power density.

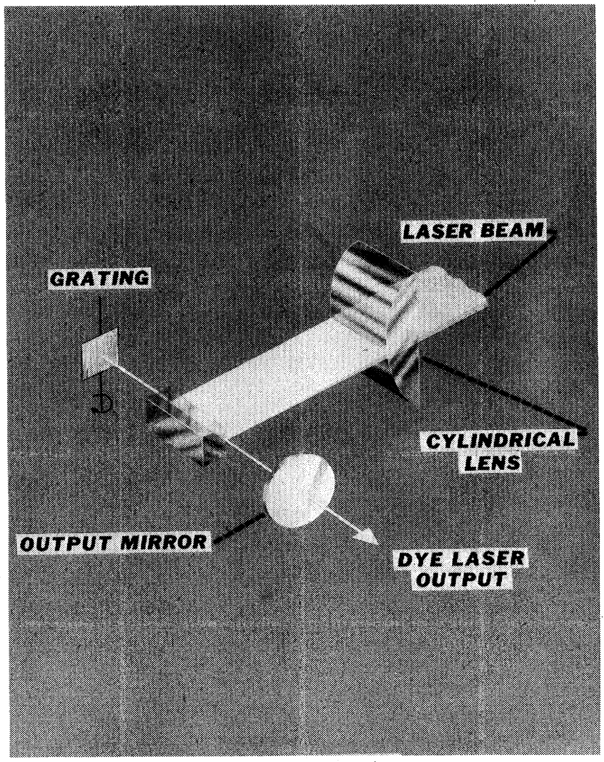

FIG. 10. Transversely excited dye laser pumped with a nitrogen laser.

A longitudinal pumping scheme typically used with cw dye lasers is shown in Fig. 9 (Kohn *et al.*, 1971). An argon ion laser is focused by mirror M_2 to a small spot ($\approx 20\mu$ diameter) in a dye cell. The dye is usually flowed through the cell to reduce thermal effects. As an alternative to a cell, the dye solution dan be pumped through a nozzle to form a high optical quality stream (Runge and Rosenberg 1972). Continuous dye lasers have been constructed with output powers of several watts, efficiency near 50%, and linewidths of less than 100 kHz.

Transverse optical pumping is achieved typically by using a cylindrical lens to focus a laser into a narrow stripe. The narrow stripe of radiation is then directed onto a dye cell and laser action takes place along the stripe transverse to the pumping radiation.

An example of transverse pumping is shown in Fig. 10. Here we show the rectangular beam from a nitrogen laser being focused by a cylindrical lens onto a cell containing organic dye. The laser cavity is formed by the mirror and grating.

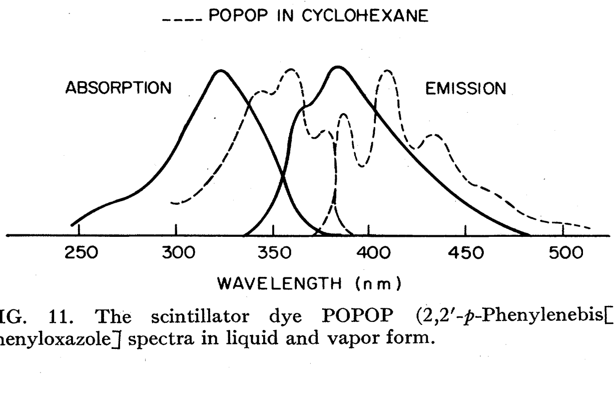

FIG. 11. The scintillator dye POPOP (2,2′-*p*-Phenylenebis[5-phenyloxazole] spectra in liquid and vapor form.

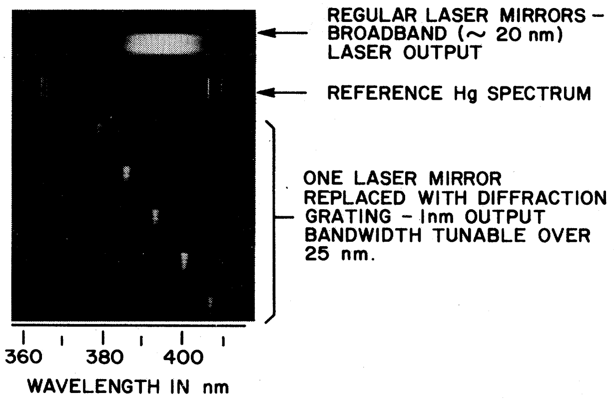

FIG. 12. The tuning range of the dye vapor laser POPOP with comparison of broadband and tunable operation.

The N_2 laser is a particularly useful pump for organic dyes. Myer *et al.* (1970) obtained laser action spanning the entire visible spectrum from 3600 Å to 7000 Å with several dyes using the single 3371 Å line as a pump. Hänsch (1972) has demonstrated that a transversely pumped dye laser can be made to emit in a 0.01 Å bandwidth with an etalon in the optical cavity. With the use of an additional passive etalon external to the cavity the bandwidth has been reduced to 7 MHz (Schäfer, 1973).

Flashlamps (Sorokin and Lankard, 1967) have found use as a pulsed dye laser pumping source owing to their relative simplicity, low cost, and high energies. Flashlamp-pumped dye lasers can be constructed which have an output energy of tens of joules. They have also been able to cover the entire visible spectrum from ultraviolet to infrared (Schäfer, 1973).

Recently a new type of "mirrorless dye laser" has been constructed by integrating a periodic structure within a gain medium (Kogelnik and Shank, 1971). One such device has been tuned over 600 Å (Shank *et al.*, 1971) with a linewidth less than 0.01 Å. Feedback is obtained by pumping the dye solution with fringes formed by the interference of two coherent beams. By pumping with two interfering coherent light beams, the gain and the refractive index of the laser medium are modulated. This spatial modulation provides a strong frequency selective coupling between oppositely traveling waves and introduces the feedback necessary for laser oscillation. Strongest coupling occurs when the wavelength of oscillation satisfies the Bragg condition. This requires the period of the spatial modulation equal to one-half the oscillating wavelength in the medium.

VI. DYE VAPOR LASERS

A number of workers have recently reported laser action in gaseous vapors of organic dyes (Borisevich *et al.*, 1973), (Steyer *et al.*, 1974), (Smith *et al.*, 1974). The vapors were formed by heating an evacuated cell containing the dye solid in an oven. In these experiments the dye vapor was pumped optically with a laser source.

Dyes in vapor form have a number of potential advantages over dyes dissolved in solvents. Most important, is the possibility of highly efficient operation using direct electrical excitation as is done in other gaseous laser systems. The problems of optical inhomogeneity, thermal distortion, and fluid flow associated with liquid dye lasers could also be alleviated.

The absorption and emission spectra of organic dyes in vapor form do not differ dramatically from liquid solutions. Typically the spectra of dye vapors are broadened and shifted to the blue by about 2000 cm^{-1} in comparison to solution spectra. Also the fine detail in the solution spectra appears to be washed out in the vapor phase. In Fig. **11** we have plotted the absorption and emission spectra of the organic dye vapor "POPOP" and the corresponding solution spectra.

One early concern with dye vapor lasers was whether they could be efficiently tuned. One might expect that without a solvent environment thermalization of the vibrational levels might be slow. On the contrary, it has recently been reported by Smith *et al.* (1974) that a dye laser using "POPOP" in the vapor phase can be tuned efficiently. In Fig. 12 we show the output spectra of a dye vapor laser in both broadband (~20 nm) and tunable narrowband operation. The tuning range is about 280 nm. Most interestingly the peak output power observed in the narrowband operation is 90% of the broadband power. This indicates that spectral condensation is nearly complete and that the levels are thermalized very quickly even though there is no solvent.

It appears that dye vapor lasers behave in most respects, in a similar manner to dye solution lasers. Providing that a means may be found to direct electrically excite dye vapors without decomposition of the organic molecules, organic vapors may become a useful and efficient source of tunable radiation.

VII. MODE-LOCKED DYE LASERS

Throughout the previous discussion in this paper we have emphasized the broad bandwidth dye lasers tunability. Another important feature of dye lasers is their ability to utilize this bandwidth to produce ultra-short optical pulses (Schäfer, 1973). Optical pulses with a time duration of less than a picosecond have been observed (Shank and Ippen, 1974). Since the frequency bandwidth required to produce a picosecond pulse is less than the large available bandwidth such pulses are also tunable.

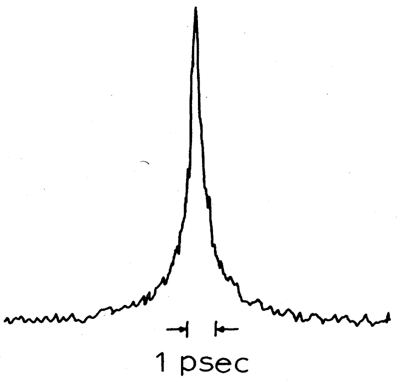

FIG. 13. Measured autocorrelation spectrum of a 0.3 picosecond pulse from a CW dye laser using second harmonic generation in KDP.

The technique of generating short pulses in lasers is called, "modelocking" (Smith *et al.*, 1974). The process of modelocking involves establishing a coherent phase relationship between several oscillating frequencies or modes in a laser cavity. This can be done by either active or passive means.

Using an acoustic modulator as an active modelocking element in a cw rodamine GG dye laser, pulses as short as 55 psec have been obtained (Dienes *et al.*, 1971). More dramatic results have been obtained using a saturably absorbing organic dye as a passive modelocking element. Both flashlamp (Bradley, 1971) pumped and cw dye lasers have been passively modelocked (Ippen *et al.*, 1972) to produce pulses in the picosecond range.

Optical pulses in the picosecond regime cannot be directly detected electronically. Ultrafast streak cameras (Bradley, 1971) or nonlinear optical techniques are required. In Fig. 13 we show an experimentally measured autocorrelation function of a 0.3 psec pulse from a passively modelocked dye laser using harmonic generation in KDP (Shank and Ippen, 1974).

VIII. CONCLUSION

The understanding and technology of dye lasers have shown great progress in the last few years. What remains to come are exciting applications in the areas of physics and chemistry. The narrow linewidth and tunability of the dye laser make it an ideal source for high resolution spectroscopy. Dye lasers show great promise in photoisotope separation and photo-iniated chemical reactions using frequency selective absorption. Many more applications appear on the horizon for this most unique and versatile laser medium.

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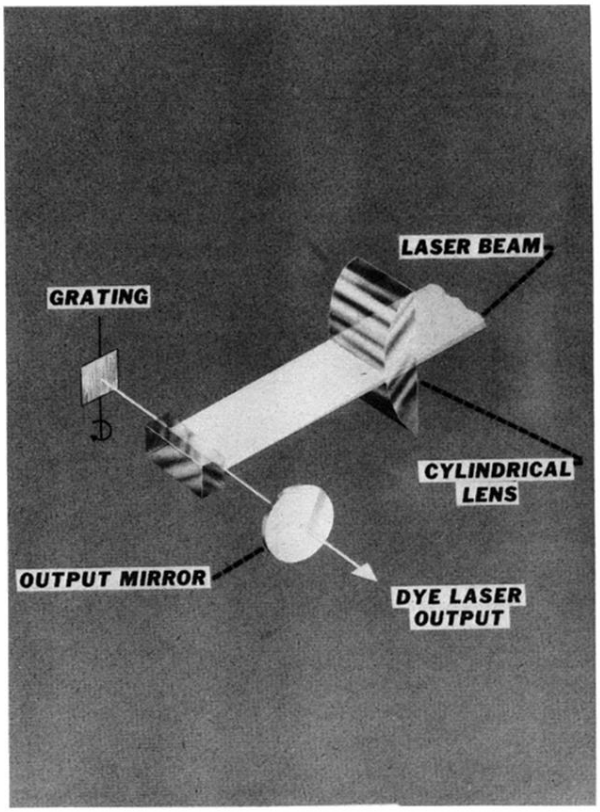

FIG. 10. Transversely excited dye laser pumped with a nitrogen laser.

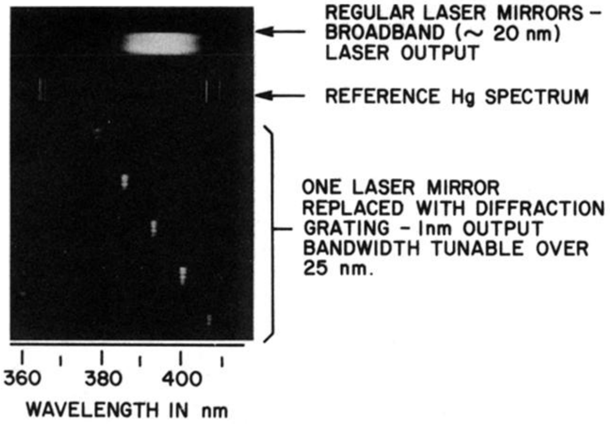

FIG. 12. The tuning range of the dye vapor laser POPOP with comparison of broadband and tunable operation.