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**Continuous wave energy transfer dye lasers in the near infrared  
spectral region: Theory, modeling, simulation, performance**

**Panoutsopoulos, Basilios, Ph.D.**

**City University of New York, 1991**

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**CONTINUOUS WAVE ENERGY TRANSFER DYE LASERS  
IN THE NEAR INFRARED SPECTRAL REGION  
Theory - Modeling - Simulation - Performance**

by

**Basilios Panoutsopoulos**

A dissertation submitted to the Graduate Faculty in Engineering  
in partial fulfillment of the requirements for the degree of Doctor of Philosophy,  
The City University of New York

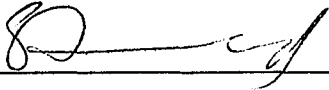
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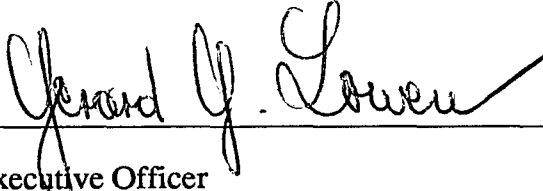
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**ABSTRACT****CONTINUOUS WAVE ENERGY TRANSFER DYE LASERS IN THE NEAR  
INFRARED SPECTRAL REGION****Theory - Modeling - Simulation - Performance**

by

**Basilios Panoutsopoulos**

Adviser: Professor Samir Ahmed

Energy transfer processes in dye mixture lasers in which optical excitation energy is absorbed by one dye (the donor) and transferred to a second dye (the acceptor) in which laser action takes place, have been extensively studied to improve the efficiency and broaden the attainable spectral range of pulsed dye lasers. In this work, we developed a theoretical simulation model which predicts the attainable gain spectrum of cw laser pumped energy transfer dye lasers (ETDL) as function of donor and acceptor concentrations, their spectral parameters, energy transfer parameters, laser cavity and pump power and excitation wavelength. The model takes into account contributions due to both radiative and non radiative energy transfer.

Numerical simulation results applied the model to different dyes. The model predicts that there are a number of useful dye candidates pairs that would benefit from the ETDL approach in terms of reduced power and attainable spectral range. Analysis of the relevant gain parameters of cw ETDLs, together with results for a representative and practically useful Donor - Acceptor pair, is presented. Thus, for instance, the model predicts that the

blue-green argon ion laser may be used to excite infrared lasing dyes such as Nile Blue 690, which normally require separate red krypton ion laser for excitation.

These predictions were confirmed by experimental results where we were able to achieve the first reported operation of a cw energy transfer dye laser. In this work we used the argon ion laser to excite an ETDL with Rhodamine 610 as donor and Nile Blue 690 as acceptor to demonstrate laser action in the near infrared, with operational parameters very close to those predicted by our theoretical simulation model. It is believed that the results obtained in this work open up a new and practically useful avenue for CW laser operation with improved spectral capabilities and reduced pump requirement.

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## **1 Introduction and Background**

### **1.1 Development of Single Dye and Energy Transfer Dye Mixture Lasers**

#### **Development of Single Dye Lasers:**

The efficient luminescence exhibited by many organic compounds make their use as laser materials attractive and this possibility was considered early in laser research. Initial experiments produced disappointing results. Beginning 1967 the production of coherent, visible radiation by fluorescent organic dyes in solution has been demonstrated; the device based upon this phenomenon is called dye laser.

The organic dye laser belongs to the family of liquid lasers and must be distinguished from the inorganic liquid laser based upon the fluorescence of rare earth ions in liquid solvents, a device that is similar to many respects to the solid state laser. The properties of the inorganic liquid laser have been extensively reviewed, [1-3].

The earliest published suggestions that organic materials could be used as active media seen to be those of Brock et al., [4], and Rautian and Sobelmann, [5], who proposed in 1961 that triplet state phosphorescence could serve as the basis for an organic laser. In 1964 Stockman et al., [6], discussed a laser process based upon a singlet state fluorescence, and Stockman, [7], described early results in the experimental effort to realize a dye laser using the dye perylene excited by a fast powerful flashlamp.

The first report of stimulated emission from an organic dye solution excited by a laser was first reported by Sorokin and Lankard [8] who observed laser emission from a solution of chloroaluminum phtalocyanine, and subsequently by Schafer, Schmidh, and Volze [9] who obtained laser action from a number of cyanine type dyes. Dye laser

action was also demonstrated independently by Spaeth and Bortfield [10], and Stepanov, Rabinov and Mostovnikov [11]. 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 consequence of the broadened electronic levels characteristics of organic dyes. Soffer and McFarland [12] succeeded in spectrally narrowing band tuning a dye laser by replacing one of the resonators with a diffraction grating. This was the first demonstration that a laser could be efficiently tuned over a broad spectral range. Sorokin and Lankard [13], and Schmidt and Schafer [14] replaced the high intensity laser pumping source with a flashlamp excitation, very fast and of high intensity, established the feasibility of a continuous dye laser. These people showed experimentally that the widely held notion, that a cw laser was not possible because of metastable triplet state losses, was incorrect.

Development in the continuous dye laser over the past two decades have made it unique among existing lasers. The first system was reported by Peterson, Tuccio, and Snavely [15] at Kodak Research Laboratories. It had a 55 mW output with a fixed bandwidth of about 3 n.m. 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 in many applications.

Typical applications include areas such as fundamental physics, spectroscopy techniques, industrial applications, medicine, military, large scale laser isotope separation, and laser radar as well as light detection and ranging (lidar). In particular, the techniques of fluorescence and saturation spectroscopy have permitted precision spectral measurements to be made in atomic sodium [16], and atomic hydrogen [17], and accurate

trace analysis of sodium in the laboratory [18], and the atmosphere [19]. Laser spectroscopy is described in Walther, [20] and high resolution laser spectroscopy in Shimoda, [21]. Applications of laser for ultrafast light pulses in Shapiro, [22], applications of lasers in physical chemistry and biophysics in Jousset-Dubien, [23], and in medicine and biology by Wolbarsht, [24]. Dye lasers offer to researchers both pulsed and continuous wave operation that is tunable from the near-UV to the near-IR. The wavelength range have been extended to the UV spectral region using harmonic and sum frequency generation, Blit et al. [25], and in IR utilizing mixing in  $\text{LiNbO}_3$ , Pine [26]. Such versatility emerges from the large choice of molecular dye species available coupled with a wide variety of excitation sources. This unique flexibility furnishes many economic and engineering design advantages. Emission at any particular wavelength is achieved by simply changing the dye, which offer significant savings in capital and operating cost, although complicating the design of the dye laser itself.

#### **Development of Energy Transfer Dye Mixture Lasers:**

Energy transfer in binary dye laser mixtures was first investigated by Lin et al., [27,28], Ahmed at al., [29], Kenney-Wallace and al., [30], C. E. Moeller and al., [31], in pulse lasers. This process can provide ways of extending the wavelength regions in which lasing is achieved by using a mixture of dyes. It was shown that energy transfer from donor will usually decrease the threshold pump intensity needed for direct excitation of the acceptor lasing dye. This way became possible to excite dyes that can not be excited directly from the pumping source. Excitation of a dye laser through energy transfer processes is very efficient for the improvement of dye laser efficiency and the extension of their tuning range. This ability of a higher energy dye (donor) to transfer

energy to a lower energy dye (acceptor) in order to maximize energy coupling into the lasing medium is efficient to extend to which the fluorescence spectrum of the higher energy dye overlaps the absorption spectrum of the lower energy lasing dye. Therefore energy transfer dye lasers have become the subject of intense study, but only a few mixture systems (donor - acceptor pairs) have been reported to have efficient transfer for dye operation, [32]. Coumarin dyes can not be used as efficient donor in Coumarin - Xanthene dye mixtures, [33], since a strong triplet - triplet absorption of Coumarin overlaps the fluorescence region of Xanthene dyes. However, the detriment effect due to T-T absorption of the donor dye can be removed from the dye mixture systems under short pulse pumping. Urisu and Kajiyama, [34], observed gain enhancement in N<sub>2</sub> laser pumped Coumarin 30 - Rhodamine 6G mixtures relative to a solution containing Rhodamine 6G alone. Improvement of laser peak power has been reported for a mixture of Coumarin 1 - Uranine, [35], too.

Continuous wave dye laser emission in the near infrared region has been reported where a krypton ion laser served as pump source, [36]. The generation of broadly tunable, narrow linewidth, high power radiation in the near infrared is important for a number of scientific applications. The infrared radiation may be utilized as a spectroscopic source or in laser - matter interactions that require a high power, wavelength tunable light source. Frequency doubling of the near infrared radiation leads to a tunable source of high spectral brightness in the near ultraviolet and visible blue, [32]. Also difference frequency experiments can be performed which involve mixing tunable mid infrared radiation with a fixed frequency laser source to generate tunable mid infrared radiation, [37,38]. Lasing properties of several near-IR dyes are reported by Pierce and Birge, [39].

## 1.2 Thesis Statement

The concept of energy transfer in laser dye mixtures has been studied to improve the efficiency and broaden the spectral range of pulsed dye lasers. In this work we develop a theoretical model to predict the gain spectrum of a cw laser pumped energy transfer dye laser (ETDL) as function of acceptor and donor concentrations, their absorption and emission spectra, pump power and wavelength, and dimensions of the active region. The model predicts that there are a number of candidate dye pairs which would benefit from such an approach, in terms of reduced pump requirements and increased attainable spectral range. It also shows that the use of the argon ion laser, which is a convenient and widely used pump source, may be practically extended through the use of energy transfer processes to a number of dyes which would otherwise require excitation at longer wavelengths from a krypton ion laser. These predictions are confirmed by experiments in which argon laser excitation, which cannot normally be used to excite Nile Blue, is used to excite a mixture of Rhodamine 610 (donor) and Nile Blue 690 (acceptor) to demonstrate laser action in the near infrared.

### **1.3 Thesis Organization**

In Chapter One we provide a general background on the development of single dye lasers and dye mixture lasers. In these lines we present the historical development along with typical characteristics and applications. The thesis statement and organization are included here.

In Chapter Two we discuss the optical properties of organic dyes. The optical properties of organic dyes form the basis for the operation of dye lasers.

In Chapter Three we examine the energy transfer processes in dye mixtures and we develop the concept of energy transfer efficiency. We continue examining the fluorescence of single dyes and dye mixtures.

In Chapter Four we develop a complete model of a cw energy transfer dye mixture laser. The model is based on the rate equations approach and uses some necessary and practically valid approximations to derive a simple and useful expression of the dye gain spectrum as function of donor and acceptor concentration, their spectral characteristics, energy transfer parameters, laser cavity dimensions and pump power and wavelength.

In Chapter Five we present simulation and experimental results from an operating cw ETDL consisting from a pair of two well known and commonly used dyes, Rhodamine 610 as donor and Nile Blue 690 as acceptor. From a comparison of the theoretical and experimental results we see that there is a small difference, peak shift between the predicted and experimental results. This difference may be due to inherent assumptions of the model, lower pump power, and experimental errors.

In Chapter Six we present conclusions of our work. These conclusions form the basis for design better cw ETDs. Finally we discuss topics that need further research or improvement for more efficient cw ETDs.

## 1.4 References

1. Lempicki, A. and H. Samelson. *Organic Laser Systems*. Lasers. A. K. Ed., Vol. 1, pp. 181-252, 1966.
2. Heller, A. *Liquid Lasers Design of Neodymium Based Inorganic Ionic Systems*. J. Mol. Spectry., Vol. 28, pp. 101-117, Sept. 1968.
3. Heller, A. *Liquid Lasers Fluorescence Absorption and Energy Transfer of Rare Earth Ions Solutions in Selenium Oxychloride*. J. Mol. Spectry., pp. 208-232, Oct. 1968.
4. Brock, E. G., P. Czavinsky, E. Hormats, H. C. Nedderman, D. Stirpe, and F. Unterleitner. *Coherent Stimulated Emission from Molecular Crystals*. J. Chem. Phys., Vol. 35, pp. 759-760, Aug. 1961.
5. Rautian, S. E. and I. I. Sobelman. *Remarks on Negative Absorption*. Opt. Spectry., Vol. 10, pp. 65-66, Jan. 1961.
6. Stockman, D. L., W. R. Mallory and K. F. Tittel. *Stimulated Emission in Aromatic Organic Compounds*. Proc. IEEE (Correspondence), vol. 52, pp. 318-319, March 1964.
7. Stockman, D.L. *Stimulated Emission Considerations in Fluorescent Organic Molecules*. Proceedings of the 1964 ONR Conf. on Organic Lasers, Defence Documentation Center for Scientific and Technical Information. Cameron Station, Alexandria, Va.
8. Sorokin, P. P. and J. R. Lankard. *Stimulated Emission Observed from an Organic Dye, Chloro-aluminum Phthalocyanine*. IBM J. Res. and Dev., Vol. 10, pp. 162-163, March 1966.
9. Schafer, F. P., W. Schmidt, and J. Volze. *Organic Dye Solution Laser*. Appl. Phys. Letters, Vol. 9 (8), pp. 306-309, October 1966.
10. Spaeth, M. and D. Bortfield. Appl. Phys. Lett., Vol. 5, p. 179, 1966.
11. Stepanov, B. I., A. N. Rubinov, and V. A. Mostovnikov. JETP Lett., Vol. 5, p. 117, 1966.
12. Soffer, B. H. and B. B. McFarland. *Continuously Tunable, Narrow-Band Organic Dye Lasers*. Appl. Phys. Lett., Vol. 10 (10), p. 266, 1967.
13. Sorokin, P. P. and J. R. Lankard. *Flashlamp Excitation of Organic Dye Lasers*. IBM J. Res. Dev., Vol. 11, p. 148, 1967.
14. Schmit, W. and F. P. Schafer. *Blitzlampengepumpte Farbstofflaser*. Z. Naturfosch, 22a, p. 1563, 1967.
15. Peterson, O. G., S. A. Tuccio, and B. B. Snavely. *CW Operation of an Organic Dye*

*Solution Laser*. Appl. Phys. Lett., Vol. 17 (6), p. 245, 1970.

16. Hansch, T. W., I. S. Shahin, and A. L. Schawlow. *High Resolution Saturation Spectroscopy of the Sodium D Lines with a Pulsed Tunable Dye Laser*. Phys. Rev. Lett., Vol. 27, pp. 707-710, Sept. 1971.

17. Hansch, T. W., I. S. Shahin, and A. L. Schawlow. *Optical Resolution of the Lamp Shift in Atomic Hydrogen by Laser Saturation Spectroscopy*. Nature, Phys. Sci., Vol. 235, pp. 63-65, Jan. 1972.

18. Kuhl, J. and G Marowsky. *Narrow Band Dye Laser as a Light Source for Fluorescence Analysis in the Subnanogram Range*. Opt. Comun., Vol. 4, pp. 125-128, Oct. 1971.

19. Gibson, A. J. *Flashlamp - pumped Dye Laser for Resonance Scattering Studies of the Upper Atmosphere*. J. Sci. Instrum. (J. Phys. E), Ser. 2, Vol. 2, pp. 802-806, Sept. 1969.

20. Walther, H. (Ed.). *Laser Spectroscopy*. Topics in Applied Physics, Vol. 2, Berlin: Springer Verlag, 1976.

21. Shimoda, K. (Ed.). *High Resolution Laser Spectroscopy*. Topics in Applied Physics, Vol. 13, Berlin: Springer Verlag, 1976.

22. Shapiro, S. I. (Ed.). *Ultrafast Light Pulses*. Topics in Applied Physics, Vol. 18, Berlin: Springer Verlag, 1977.

23. Jousset-Dubien, J. (Ed.). *Lasers in Physical Chemistry and Biophysics*. Amsterdam: Elsevier, 1975.

24. Wolbarsht, M. L. (Ed.). *Laser Applications in Medicine and Biology*. New York: Plenum Press, 1971.

25. Blit, S., E. G. Weaver, T. A. Rabson, F. K. Tittel. *Continuous Wave UV Radiation Tunable from 285 to 400 nm by Harmonic and Sum Frequency Generation*. Appl. Opt., Vol. 17, pp. 721-723. 1978.

26. Pine, A. S. *Doppler-limited Molecular Spectroscopy by Difference Frequency Mixing*. J. Opt. Soc. Am. Vol. 64, pp. 1683-1690. 1974.

27. Lin, C. and A. Dienes. *Direct Measurement of Radiationless internal Conversion Rate from Second Excited Singlet to the First Excited Singlet State of Laser Dye Molecules*. Opt. Commun. Vol. 9, p. 21, 1973.

28. Lin, Chinlon and A. Dienes. *Study of Excitation Transfer in Laser Dye Mixtures by Direct Measurements of Fluorescence Lifetime*. J. App. Phys., 44, 5050-5052, 1973.

29. Ahmed, S. A., J. S. Gergerly, and D. Infante. *Energy Transfer Organic Dye Mixture Lasers*. J. Chem. Phys. Vol. 61, p. 1584, 1974.

30. Kenney-Wallace, G. A., J. H. Flint, S. C. Wallace. *Resonance Energy Transfer Between Lasing Dyes in Micellar Media.* Chem. Phys. Lett. Vol. 32, p. 71, 1975.
31. Moeller, C. E., C. M. Verber, and A. H. Adelman. *Laser Pumping by Excitation Transfer in Dye Mixtures.* App. Phys. Lett., Vol. 18, pp.278-280. 1971.
32. Hamadini, S. M, and G. Magyar. Opt. Commun., Vol. 4, p. 310, 1971.
33. Pavlopoulos, T. G. Opt. Commun., Vol. 24, p. 172, 1978.
34. Urisu, T. And K. Kajiyama. *Concentration Dependence of the Gain Spectrum in Energy Transfer Dye Mixtures.* J. Appl. Phys., Vol. 47, p. 3563, 1976.
35. Muto, Shinzo and Chiaki Ito. *Characteristics of Coumarin 1-Uranine Energy Transfer Dye Laser.* Jpn. J. Appl. Phys. Vol. 20, p. 1591, 1981.
36. Romnek, K. M., O. Hildebrand and E. Gobel. *High Power CW Dye Laser Emission in the Near IR from 685 nm to 965 nm.* Opt. Commun., Vol. 21, pp. 16-19. 1977.
37. Dewey, C. F. Jr. and L. O. Hocker. Appl. Phys. Letters, Vol. 18, p. 58, 1971.
38. Meltzer, D. W. And L. S. Goldberg. Opt. Commun., Vol. 5, p. 209, 1972.
39. Pierce, B. M., and R. R. Birge. *Lasing Properties of Several Near-IR Dyes for a Nitrogen Laser Pumped Dye Laser with an Optical Amplifier.* IEEE, J. Quant. Electr., Vol. QE-18, p. 1164, 1982.

## 2 Organic Dyes and Dye Lasers

### 2.1 Introduction

The development of dye lasers has been intimately tied to the systematic search for organic dye structures and dye media in which stimulated emission is observed. An array of photochemical properties such as absorptivity, emission yield, Stokes shift, and triplet formation influence threshold and peak power lasing characteristics. The tailoring of dyes must also contend with variables having to do with photochemical reactions which degrade dye and produce competitively absorbing products, thus influencing dye service life as well as other parameters. The advent of powerful laser or flashlamp pump sources and the needs for high output and repetition rate requires photostable dyes than ever before. The photostability of dyestuffs interest many technologies. These include not only dye laser applications but also new systems for information and computer technology (imaging, photoconductivity, and molecular electronics). Advances in these important areas will depend significantly on the development of robust, reliable dye media in which operation can be substantially prolonged.

In this chapter we present the basic structure of a dye. We relate its physical properties of interest with its operation as a laser medium. The physical characteristics of a dye are used in the next chapters to determine the energy transfer between two appropriately selected dyes, and predict the behaviour of a cw ETDL.

## 2.2 Optical Properties of Organic Dyes and Dye Lasers

The class of organic molecules which absorb strongly and fluoresce intensely are called Dyes. The electronic energy level structure of such molecules primarily arises from two valence electrons and consist of singlet ( $S_0, S_1, S_2, \dots$ ) and triplet ( $T_1, T_2, \dots$ ) levels. In the singlet states the spin of the two electrons are antiparallel, while in the triplet states are parallel. In general, spin-flip transitions ( $S \rightarrow T$  or  $T \rightarrow S$ ) are optically much less probable than  $S \rightarrow S$  or  $T \rightarrow T$  transitions. The absorption and emission spectra of these molecules are fairly broad and continuous due to the substructure of vibrational and rotational levels. Fig. 1-2 is a schematic representation of transitions and energy level structure associated with an organic dye laser.

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. 2-2.

Laser action for such a dye medium involves excitation ( $S_0 \rightarrow S_1$ ) through intense optical pumping which is accomplished through a flashlamp or another laser, followed by rapid ( $\sim 10^{-12}$  s) internal conversion to the lowest vibrational-rotational level of the  $S_1$  electronic state. This leads to population inversion and subsequent laser emission between this low-lying  $S_1$  level and a high vibrational level of the  $S_0$  ground electronic state.

Although the emission spectral width for these dyes can be quite extensive (typically 20-50 nm FWHM), the range of wavelengths over which laser action can occur is appreciably less. Laser oscillation on the short wavelength side of the emission profile is prevented by singlet absorption ( $S_0 \rightarrow S_1$ ) while on the long-wavelength side it is the drop

in probability of the emission that restricts the range of wavelengths available for laser action. Fig. 2-3 shows the portion of the wavelength range useful for laser action. The dye has to be circulated through some form of heat exchanger to avoid the development of thermal (and thereby refractive index) inhomogeneities. A filter is often used to reduce the scattering loss from bubbles.

### Physics of Dye Lasers:

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, [1]. We shall examine the optical properties of two such broadened electronic energy levels. At the first approach we shall consider the ground state level  $S_0$  and the first excited level  $S_1$ , and we shall ignore the influence of the other levels.

In Fig. 2-4 we have schematically drawn two energy levels which have a width  $\Delta v$  and are spaced by an energy difference  $h\nu_0$ . The dye molecule is excited optically by pump photons of frequency  $\nu_p$ . Light emission will be observed at frequency  $\nu_e$ .

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 of the order of nanoseconds. Measurements of the thermalization time have been performed by Ricard, Lowdermilk, and Ducing, [2], for dye molecules in solution by investigated the rise time of stimulated emission on a picosecond time scale.

Let us now consider two levels which has been optically excited and are thermalized

with populations  $N_0$  and  $N_1$ , [3]. In each level the electrons will be distributed in energy,  $E$ , according to the distribution function  $\eta_i(E_i)$ . Then the level populations are:

$$N_i = \int \eta_i(E_i) dE \quad 2-1$$

Under the conditions of rapid thermalization the distribution functions can be approximated by a Boltzmann distribution:

$$\eta_i(E_i) = C_i g_i(E_i) \exp\left\{-\frac{E_i}{kT}\right\} \quad 2-2$$

where:  $C_i$  is a normalizing factor,

$g_i(E_i)$  is the level degeneracy.

The absorption coefficient for a simple two discrete level system is:

$$\begin{aligned} k_\nu &= -\frac{1}{I_\nu} \frac{dI_\nu}{dz} \\ &= \frac{h\nu n}{c} \{B_{01}N_0 - B_{10}N_1\} \end{aligned} \quad 2-3$$

where:  $I_\nu$  is the intensity of radiation at frequency  $\nu$ ,

$n$  is the refractive index of the dye,

$B_{01}$  is the Einstein absorption coefficient,

$B_{10}$  is the Einstein emission coefficient.

Such a system can not 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, such that  $N_1 > N_0$ , [4]. This is usually accomplished by utilizing additional energy levels as in the case of three or four level system. 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 write the absorption coefficient, Eq. 2-3, as an amplification or gain coefficient at a frequency,  $\nu$ , for a system of two broadened levels as, [5]:

$$\alpha(\nu) = N_1\sigma_e(\nu) - N_0\sigma_a(\nu) \quad 2-4$$

where: 
$$\sigma_e(\nu) = \left\{ \frac{h\nu n}{c} \right\} B_{10}(\nu)$$

the emission cross section, and

$$\sigma_a(\nu) = \left\{ \frac{h\nu n}{c} \right\} B_{01}(\nu)$$

the absorption cross section.

The frequency dependent cross sections are defined in terms of the electron distribution functions, Stepanov and Rabinov [3], as:

$$\sigma_e(\nu) = \int \sigma_e(E_1, \nu) \eta(E_1) dE_1 \quad 2-5$$

$$\sigma_a(\nu) = \int \sigma_a(E_0, \nu) \eta(E_0) dE_0 \quad 2-6$$

Then the gain equation, Eq. 2-4, can be rewritten as:

$$\alpha(\nu) = \sigma_e(\nu) \left\{ N_1 - \frac{\sigma_a(\nu) N_0}{\sigma_e(\nu)} \right\} \quad 2-7$$

and the condition for amplification becomes:

$$\frac{N_1}{N_0} > \frac{\sigma_a(\nu)}{\sigma_e(\nu)} \quad 2-8$$

To determine the ratio of the absorption and emission cross sections, let us assume  $C_1=C_2$ . Equating up and down transitions we obtain:

$$\sigma_e(E_1, \nu)g_1(E) = \sigma_a(E_0, \nu)g_0(E_0) \quad 2-9$$

where:  $E_1 = E_0 + h\{\nu - \nu_0\}$

Using the above equations, we can finally write the expression of the absorption over emission cross section as:

$$\frac{\sigma_a(\nu)}{\sigma_e(\nu)} = \exp\frac{-h\{\nu_0 - \nu\}}{kT} \quad 2-10$$

Substituting Eq 2-10 to Eq. 2-9 we get the requirement for amplification in two broadened levels system:

$$\frac{N_1}{N_0} > \exp\frac{-h(\nu_0 - \nu)}{kT} \quad 2-11$$

From the above it is clear that if  $\nu > \nu_0$  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 not 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 pump of intensity  $I_p$ , and frequency  $\nu_p$ , we equate the absorption and emission of photons between the two broadened levels,

$$N_0\sigma_a(\nu_p)I_p = N_1\left\{\frac{1}{\tau} + \sigma_e(\nu_p)I_p\right\} \quad 2-12$$

where:  $\tau$  is the spontaneous emission lifetime.

The total concentration,  $N$ , is:

$$N = N_0 + N_1 \quad 2-13$$

where:  $N_0$  is the population on the ground state,

$N_1$  is the concentration on the excited state.

Solving for the excited population,  $N_1$ , we get:

$$N_1 = \frac{N}{\frac{1}{\sigma_a(\nu_p)\tau_p} + 1 + \exp\frac{h\{\nu_0 - \nu_p\}}{kT}} \quad 2-14$$

We observe that in order to obtain a large population in level 1, the condition  $\nu_p > \nu_0$  must be satisfied.

We obtain the total gain at a frequency  $\nu$  by substituting Eq. 2-14 into Eq. 2-7:

$$\alpha(\nu) = \sigma_e(\nu)N \left\{ \frac{1 + \exp\frac{-h\{\nu_0 - \nu\}}{kT}}{\frac{1}{\sigma_a(\nu_p)\tau_p} + 1 + \exp\frac{h\{\nu_0 - \nu_p\}}{kT}} - \exp\frac{-h\{\nu_0 - \nu\}}{kT} \right\} \quad 2-15$$

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

For the case of very broad band  $h(\nu_p - \nu_0) \ll kT$ , the gain equation reduces to:

$$\alpha(\nu) = \sigma_e(\nu)N \quad 2-16$$

This is the limiting gain for the 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 in the range of 0.1 to 0.3 eV. The width of energy bands is directly related to the spontaneous or natural lifetime,  $\tau$ .

According to Eq. 2-15 the shortest  $\tau$  becomes, the more intense the pumping radiation  $I_p$  must be to achieve gain. For most dyes of interest  $1/\tau = 3 \times 10^{24} \sigma_{\max}$  making  $\tau$  typically in the nanosecond range, Parker [6].

**A Typical Organic Dye: Rhodamine 6G:**

Rhodamine 6G is a well known and extensively studied dye. It is perhaps the most widely used dye in dye lasers. It converts efficiently pump light to emitting light and this is the main reason there is an extensive literature of available data. In Table 2-1 we list the various cross sections and in Table 2-2 we list the intraband decay lifetimes for this dye.

TABLE 2-1

## Cross Sections for Rhodamine 6G

$$\lambda_p = 530nm, \quad \lambda_e = 580nm$$

Ground-state pump' s absorption cross section:

$$\sigma_{S_1 \leftarrow S_0}(\omega_p) = 3.8 \times 10^{-16} \text{ cm}^2$$

Ground-state laser' s absorption cross section:

$$\sigma_{S_1 \leftarrow S_0}(\omega_e) = 1.0 \times 10^{-19} \text{ cm}^2$$

Excited-state laser' s emission cross section:

$$\sigma_{S_0 \leftarrow S_1}(\omega_e) = 1.2 \times 10^{-16} \text{ cm}^2$$

Excited-state pump' s absorption cross section:

$$\sigma_{S_2 \leftarrow S_1}(\omega_p) = 4.0 \times 10^{-17} \text{ cm}^2$$

Excited-state laser' s absorption cross section:

$$\sigma_{S_2 \leftarrow S_1}(\omega_e) = 1.0 \times 10^{-17} \text{ cm}^2$$

Triplet-state pump' s absorption cross section:

$$\sigma_{T_2 \leftarrow S_1}(\omega_p) = 1.0 \times 10^{-17} \text{ cm}^2$$

Triplet-state laser' s absorption cross section:

$$\sigma_{S_2 \leftarrow S_1}(\omega_e) = 1.0 \times 10^{-17} \text{ cm}^2$$

TABLE 2-2

## Intraband Decay Lifetimes for Rhodamine 6G

$$|S_1\rangle \rightarrow |S_0\rangle : T_{S_0 \leftarrow S_1} = T_1 = 3.7 \times 10^{-9} \text{ sec}$$

$$|S_2\rangle \rightarrow |S_1\rangle : T_{S_1 \leftarrow S_2} \approx 0 (\text{fast!})$$

$$|S_1\rangle \rightarrow |T_1\rangle : T_{T_1 \leftarrow S_1} = 5.0 \times 10^{-8} \text{ sec}$$

$$|T_2\rangle \rightarrow |T_1\rangle : T_{T_1 \leftarrow T_2} \approx 0 (\text{fast})$$

$$|T_1\rangle \rightarrow |S_0\rangle : T_{S_0 \leftarrow T_1} = 5.0 \times 10^{-8} \text{ sec}$$

## Structure of an Organic Dye Molecule Energy Diagram and Transitions

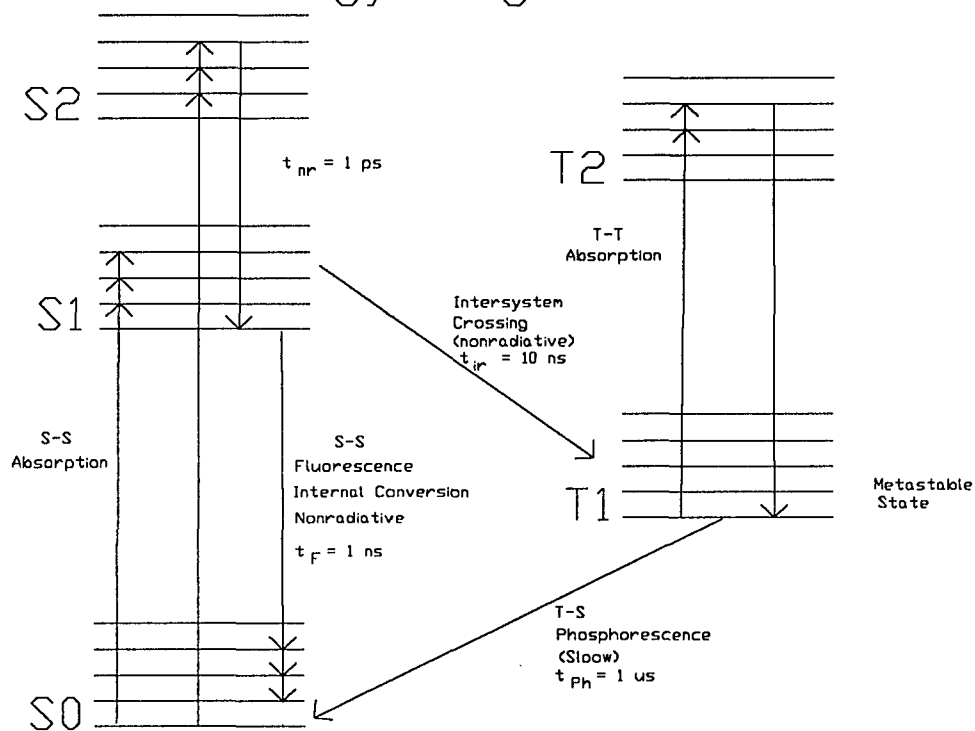


Figure 2-1. Schematic representation of energy level structure and transitions relevant to laser action associated with an organic dye.

## Classes of Laser Organic Dyes Wavelength Tunability Range

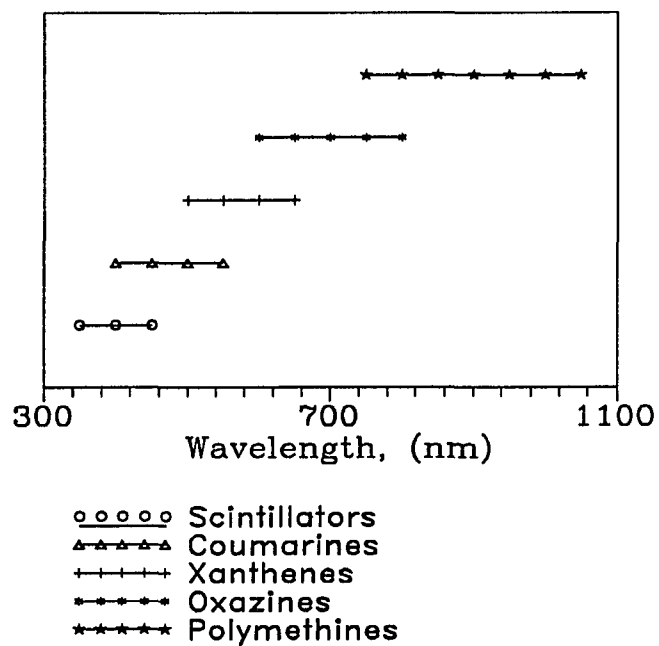


Figure 2-2. Various classes of dyes useful for laser operation, with the respective operational range.

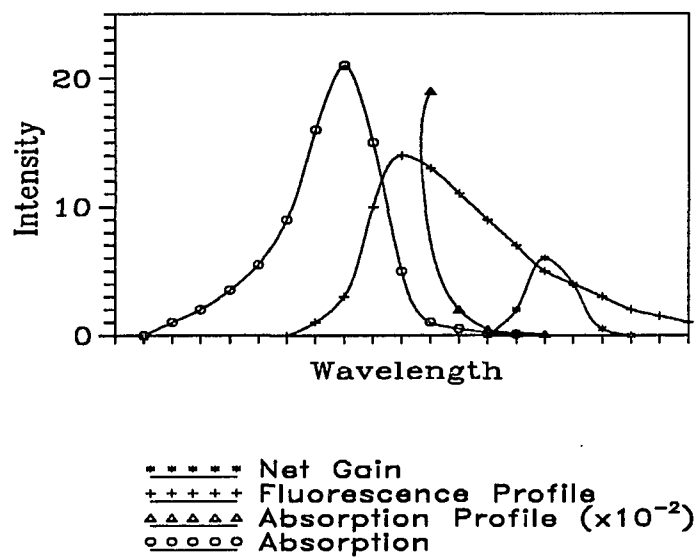


Figure 2-3. Portion of the wavelength range of a dye useful for laser action. Lasing may occur only in the range under the net gain curve.

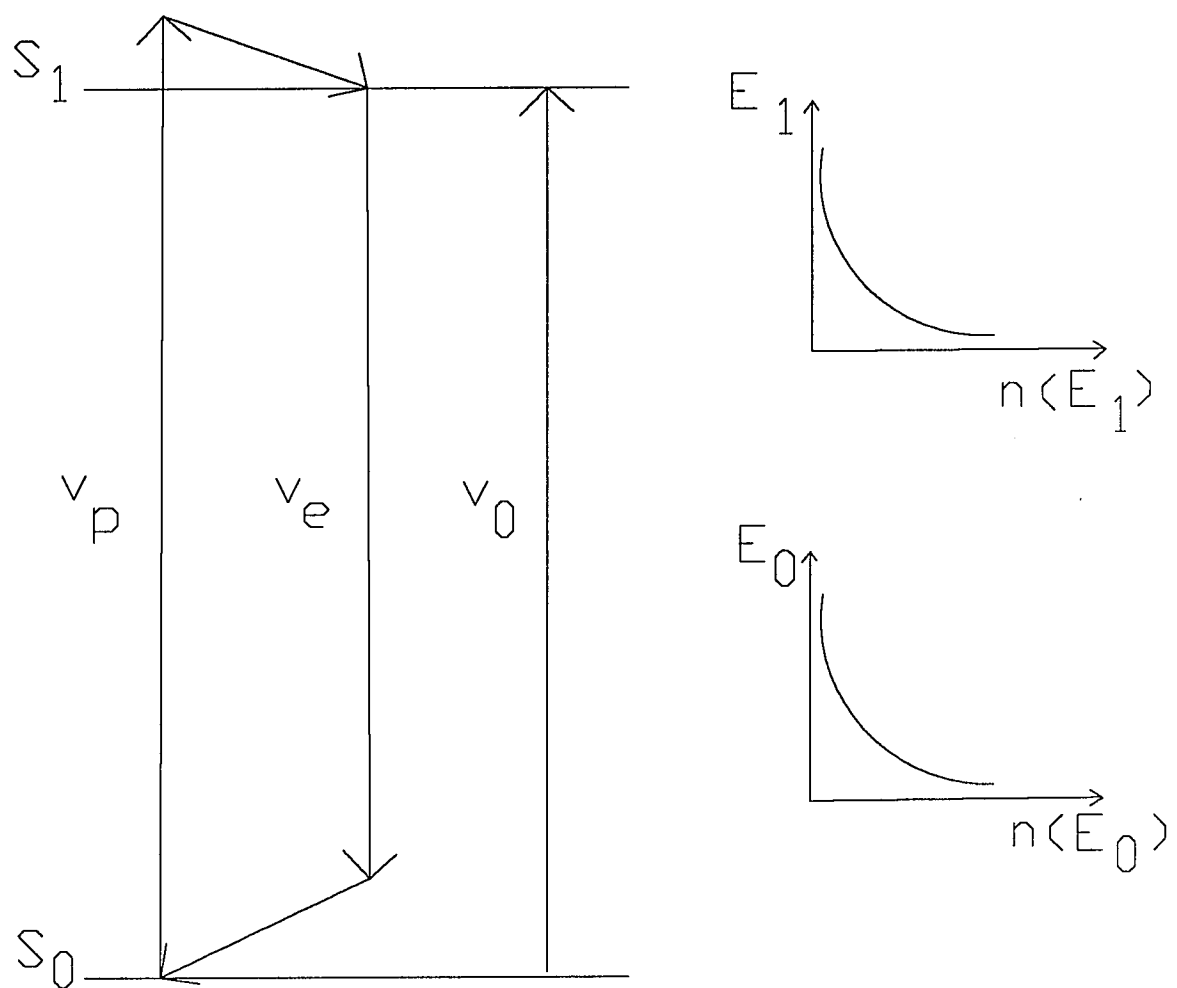


Figure 2-4. Schematic representation of a two energy level system.

## 2.3 References

1. Bass, M., T. F. Deutsch, and M. J. Weber. *Dye Lasers*, in *Lasers*, Vol. 3, A. K. Levine and A. J. DeMaria, (Eds.), New York: Marcel Dekker, pp. 274-278, 1971.
2. Ricard, D., W. H. Lowdermilk, and J. Ducing. *Chem. Phys. Lett.*, Vol. 16, p. 617, 1972.
3. Stepanov, B. I. and A. N. Rubinov. *Lasers Based on Solutions of Organic Dyes*. *Sov. Phys. Uspeci*, Vol. 11, p. 304, 1968.
4. Shank, C. V. *Physics of Dye Lasers*. *Rev. Mod. Phys.*, Vol. 47, No. 3, p. 649, July 1975.
5. Peterson, O. G., J. P. Webb, W. C. McColgin, and J. H. Eberly. *Organic Dye Laser Threshold*. *J. App. Phys.*, Vol. 42. p. 1917, 1971.
6. Parker, C. A. *Photoluminescence of Solutions*. Amsterdam: Elsevier Publ. Co., 1968.

### **3 Energy Transfer Processes and Fluorescence in Dye Mixtures**

#### **3.1 Energy Transfer Processes in Dye Mixtures**

##### **3.2.1 Energy Transfer Mechanisms in a Dye Mixture**

The subject of energy transfer between unlike molecules in solution has received considerable theoretical attention [1-3]. Energy transfer in laser dye mixture has been utilized to achieve better dye laser performance. The main mechanisms that have been proposed for such an energy transfer are:

- a) Radiative transfer, and
- b) Non-radiative transfer:
  - i) resonance transfer due to long range dipole - dipole interaction, and
  - ii) diffusion controlled collisional transfer.

In mechanism (a) we have absorption of donor emission by an acceptor; mechanisms (b) are non radiative and the excitation transfer takes place before the excited donor emits, in contrast to mechanism (a). These mechanisms contribute to the donor fluorescence quenching and enhance the acceptor fluorescence yield. Theory and experiment have shown that these various mechanisms involved may be distinguished by simply measuring the donor fluorescence lifetime as a function of acceptor concentration. For example, if the donor lifetime is little affected by the concentrations of the acceptor molecules, then mechanism (a) can be considered the dominant one.

### 3.2.2 Radiative Transfer

The radiative transfer is a two step process. During the first phase a molecule emits a photon; during the second phase another molecule absorbs the radiation, i.e.:



As there is no direct interaction between the donor, D, and the acceptor, A, molecules, the donor decay time is not affected by the process or by the concentration of acceptor molecules. For this case, the efficiency of transfer is governed by the amount of overlap between the fluorescence spectrum of the donor and the absorption spectrum of the acceptor, and by the values of molar extinction coefficient of the absorption spectrum of the acceptor. Thus as the concentration of the acceptor is increased, the fluorescence yield of the donor is decreased but the fluorescence decay time of the donor remains unaffected.

Understandably, viscosity is unimportant. Since the probability for radiative transfer falls off with distance, R, as  $R^{-2}$ , the transfer distance can be very large, often being limited only by the physical size of the container.

The radiative process has been nicknamed "trivial" because it is easy to conceive and explain, not because it is unimportant.

Singlet - singlet radiative transfer is due to the absorption of a fraction  $\alpha_r$  of the excited donor,  $D_1$ , fluorescence photons of concentration [D], by the acceptor, A, of concentration [A]. In general, at any given wavelength,  $\lambda$ , the fraction  $\alpha_r(\lambda)$  of the excited donor,  $D_1$ , fluorescence photons absorbed by the acceptor is given by Birks, [4], as:

$$\alpha_r(\lambda) = F_{0D}(\lambda) \{1 - \exp\{-2.3[A]D E_A(\lambda)\}\} \quad 3-3$$

where:  $F_{0D}(\lambda)$  is the normalized spectrum of the donor normalized to unit area over the wavelength scale,

$[A]$  is the molar concentration of the acceptor, Mole/Litre

$D$  is the specimen thickness,

$E_a(\lambda)$  is the absorption spectrum of the acceptor.

Integrating equation (3) over all wavelengths we get:

$$\alpha_r = \int_0^{\infty} F_{0D}(\lambda) \{1 - \exp\{-2.3[A]D E_A(\lambda)\}\} d\lambda \quad 3-4$$

or equivalently:

$$\alpha_r = 1 - \int_0^{\infty} F_{0D}(\lambda) \exp\{-2.3[A]D E_A(\lambda)\} d\lambda \quad 3-5$$

Unlike the frequently used approximate expression for  $\alpha_r$  [4], which is based on the assumption that  $2.3D[A]E_A \ll 1$ , Eq. (5) gives the exact expression of  $\alpha_r$ . This permits us to evaluate with accuracy the value of  $\alpha_r$  at any given acceptor concentration,  $[A]$ .

The quantum efficiency,  $f_r$ , of radiative transfer acting alone, is, [4]:

$$f_r = \alpha_r \phi_{0D} \quad 3-6$$

where:  $\phi_{0D}$  is the quantum yield of the donor in the absence of acceptor.

In the presence of non radiative transfer, the quantum efficiency of radiative energy transfer,  $f_r$ , is given by, [4]:

$$f_r = (1 - f_{nr}) \alpha_r \phi_{0D} \quad 3-7$$

where:  $f_{nr}$  is the non radiative transfer efficiency.

### 3.2.3 Non-Radiative Transfer

The non radiative transfer is an one step process involving the simultaneous de-excitation of the donor and the excitation of the acceptor. Since there must be an interaction between the donor and acceptor, the donor yield and decay time are both affected by the presence of acceptors.

The interaction between donor and acceptor is composed principally of a Coulomb and an exchange interaction. The Coulomb term, which is the long range term, can be represented by a multipole expansion, the first term of which is the dipole - dipole term, the second the dipole quadruple, and so on. If the optical transitions are allowed, the dipole - dipole term predominates; the higher terms and the exchange term can be neglected, Foster [5,6].

In liquids the effects of diffusion and possibly excitation migration must be considered in addition to that of resonance transfer, Brown et al. [7]. The effect of diffusion on energy transfer by a dipole - dipole interaction was first treated by Kurskii and Selivanenko [8]. The approach of Antonov - Romanovski and Galanin [9] for rigid solutions was expanded to include liquids by Kilin et al. [10] and Agrest et al. [11]. The Foster formulation was modified to include Brownian translational motion by Bagdasaryan and Muler [12]. Their mathematical solution is limited to steady state excitation, so that no variation in donor decay rate with acceptor concentrations could be indicated. A quantitative description of the decrease in donor decay time as a function of the diffusion coefficient  $D$  has been presented by Yokota and Tanimoto [13], Steinberg and Katchalski [14], and Birks and Leite [15]. When the diffusion coefficient,  $D$ , is very large and transfer is diffusion controlled, the probability of energy transfer is proportional to  $D$ . When the diffusion coefficient,  $D$ , is small and the long range dipole dipole

interaction is dominant, the transfer probability of energy transfer varies as  $D^{3/4}$ . The above ideas have been expanded to include molecular displacements during the lifetime of the excited state by Mikhelashvili [16].

We define the mean diffusion length,  $r$ , in a liquid as, Birks and Leite [17]:

$$r = (2D\tau_{0D})^{1/2} \quad 3-8$$

where:  $\tau_{0D}$  is the fluorescence decay time of the donor in the absence of acceptor,

and

$$D = D_D + D_A \quad 3-9$$

where:  $D_D$  the diffusion coefficient of the donor,

$D_A$  the diffusion coefficient of the acceptor.

Based on the above definition, the studies of energy transfer can be divided into three regimens:

1. A diffusion controlled or Stern Volmer region where  $r > R_0$ ,
2. An intermediate region where  $r \sim R_0$ ,
3. An inductive resonance or Foster region where  $r < R_0$ .

The appropriate determination of the radiationless transfer efficiency,  $f_{nr}$ , depends on the appropriate selection of the kinetics responsible for radiationless transfer [18,19]. To avoid complications and uncertainties in the processes of selecting the most appropriate kinetics, and given the fact that the erroneous selection of the kinetics will result in a significant error in the non radiative efficiency values, we use a general expression for the radiationless transfer efficiency,  $f_{nr}$ . In this expression  $f_{nr}$  does not rely on selection criteria, and is intended to apply over the whole range of diffusion and resonance energy transfer parameters which are expected to apply in quenching experiments, [19].

$$f_{nr} = 1 - \frac{K_0}{K} + \frac{K_0}{K^{3/2}} \pi^{1/2} A \exp[A^2/K] [1 - \text{erf}(A/K^{1/2})] \quad 3-10$$

where:

$$K = K_0 + 4\pi D R_{eff} \tilde{N} [A]$$

$$A = 4\pi^{1/2} D^{1/2} R_{eff}^2 \tilde{N} [A]$$

$$K_0 = 1/\tau_{0D}$$

$$R_{eff} = r_{AD} + 0.724 \left[ \frac{r_0^6 K_0}{D} \right]^{1/4}$$

$$D = D_D + D_A$$

$$\tilde{N} = \frac{N}{1000}$$

where:  $\tau_{0D}$  is the fluorescence decay time of the donor in the absence of acceptor,

$R_{eff}$  is the distance of closest approach of donor and acceptor,

$D$  is the total diffusion coefficient,

$D_D$  is the diffusion coefficient of the donor,

$D_A$  is the diffusion coefficient of the acceptor

$N$  is Avogadro's number

$r_0$  is the critical distance at which one half of the donor molecules decay by energy transfer and one half by radiative and non-radiative depopulation rates,

$r_{AD}$  is the distance of closest approach between donor and acceptor.

### 3.3.4 Transfer Efficiency

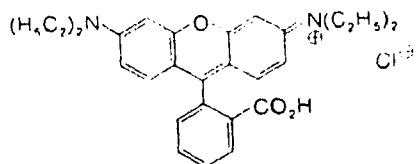
The total transfer efficiency,  $f$ , of energy transfer from a donor dye to an acceptor

dye, is defined as the sum of the radiative, Eq. 3-7, and non radiative, Eq. 3-10, energies transfer efficiencies, that is:

$$f \equiv f_{nr} + f_r \quad 3-11$$

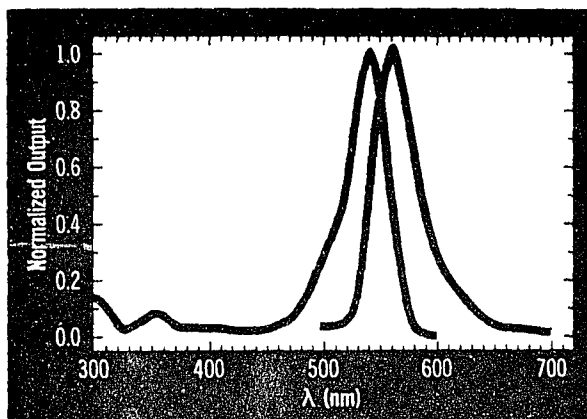
The transfer efficiency for a dye mixture of consisting of Rhodamine 610 Perchlorate as donor and Nile Blue 690 Perchlorate as acceptor, has been calculated and used for the gain evaluation later in this work. Fig. 3-1 shows typical data for Rhodamine 610, and Fig. 3-2 for Nile Blue 690. The results of the energy transfer evaluation are shown in Fig. 3-3. We see that the total transfer efficiency is increased linearly for low concentrations and reaches saturation as the concentration is increased.

## Rhodamine B

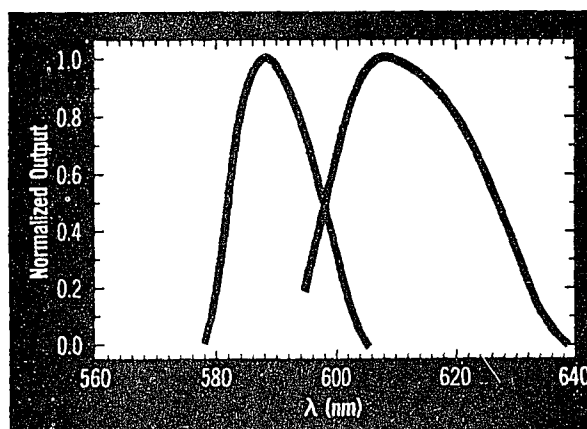


CAS No.: 81-88-9  
Synonym: Rhodamine 610

Lasing  $\lambda_{max}$  609 (N<sub>2</sub>)  
588 (YAG)  
MW 479.02



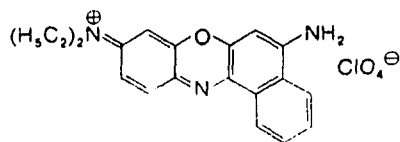
- Absorption max: 545 nm  
 $\epsilon_{max} = 1.06 \times 10^5 \text{ L mole}^{-1} \text{ cm}^{-1}$   
 $\epsilon_{545} = 7.2 \times 10^4 \text{ L mole}^{-1} \text{ cm}^{-1}$   
 $\epsilon_{515} = 4 \times 10^3 \text{ L mole}^{-1} \text{ cm}^{-1}$
- Fluorescence max: 565 nm  
 Solvent: Methanol  
 Uncorrected



- Laser Output**
- Nd:YAG Pump  
 Solvent: Methanol  
 Conc. (molar):  $3 \times 10^{-4}$   
 $\lambda_{exc} = 588 \text{ nm}$ ; range = 578-605 nm
  - Nitrogen Pump  
 Solvent: Methanol  
 Conc. (molar):  $4.6 \times 10^{-3}$   
 $\lambda_{max} = 609 \text{ nm}$ ; range = 595-639 nm

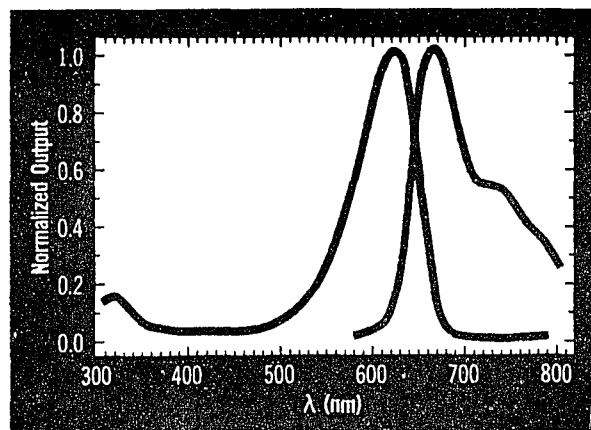
Figure 3-1 Typical data characteristics of Rhodamine 610, [21].

# Nile Blue A Perchlorate

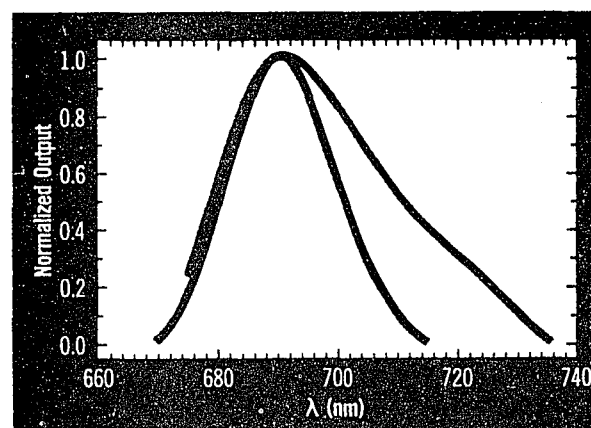


CAS No.: 53340-16-2  
 Synonym: Nile Blue 690 Perchlorate  
 Quantum yield (in EtOH) 0.23

Lasing  $\lambda_{max}$  693 (N<sub>2</sub>)  
 690 (YAG)  
 MW 417.85



— Absorption max: 627 nm  
 $\epsilon_{max} = 7.68 \times 10^4 \text{ L mole}^{-1} \text{ cm}^{-1}$   
 $\epsilon_{532} = 1.07 \times 10^4 \text{ L mole}^{-1} \text{ cm}^{-1}$   
 $\epsilon_{337} = 8.5 \times 10^3 \text{ L mole}^{-1} \text{ cm}^{-1}$   
 — Fluorescence max: 660 nm  
 Solvent: Methanol  
 Corrected



**Laser Output**  
 — Nd:YAG Pump  
 Solvent: Methanol  
 Conc. (molar):  $2 \times 10^{-4}$   
 $\lambda_{max} = 690 \text{ nm}$ ; range = 678-733 nm  
 — Nitrogen Pump  
 Solvent: Methanol  
 Conc. (molar):  $4 \times 10^{-4}$   
 $\lambda_{max} = 693 \text{ nm}$ ; range = 675-718 nm

Figure 3-2 Typical data characteristics of Nile Blue 690, [21].

Energy Transfer Efficiency  
in a Dye Mixture  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser

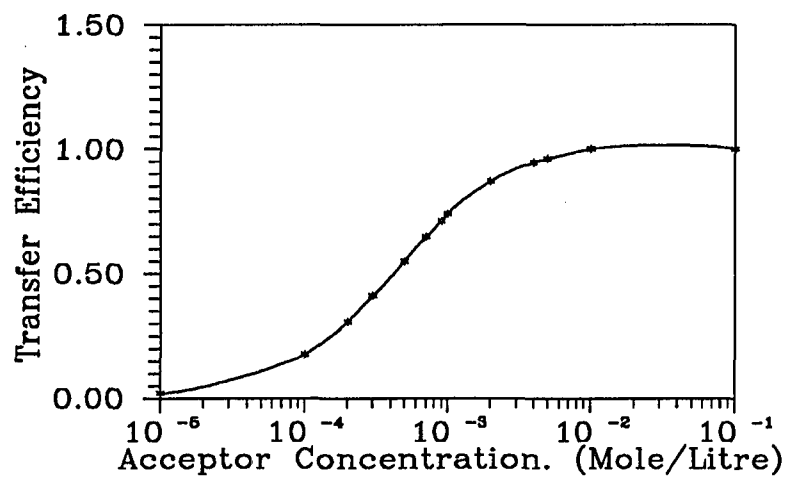


Figure 3-3. Energy transfer efficiency in a dye mixture.

### 3.2 Fluorescence a Dye Mixture

In this section we develop expressions for the fluorescence of donor and acceptor in a dye mixture, [4,20]. The fluorescence of the donor is due to the direct excitation of a pump source, but that of the acceptor is due to the direct excitation of the pumping source, if any, and contribution of both the radiative and non-radiative energy transfer processes.

#### Donor Fluorescence:

The fluorescence intensity of a solution containing a single dye only, the donor, is:

$$F_{0D} = I_0 \{1 - \exp\{-2.3E_D(\lambda_p) [D]d\}\} \phi_{0D} \quad 3 - 12$$

where:  $I_0$  is the intensity of the exciting light,  
 $E_d$  is the decadic extinction coefficient of the donor,  
 $[D]$  is the donor molar concentration,  
 $d$  is the specimen thickness,  
 $\lambda_p$  is the pumping source wavelength,  
 $\phi_{0D}$  is the quantum yield of the donor alone.

Similar expression holds for the fluorescence of the acceptor alone.

The above equation can be written in the more convenient form:

$$F_{0D} = Q_1 \Phi_{0D} \quad 3 - 13$$

where:  $Q_1 \equiv I_0 \{1 - \exp[-2.3E_d \lambda_p [D]d]\}$

is the fluorescence decay time of the donor in the absence of acceptor,

### Fluorescence of the donor in the presence of acceptor:

The fluorescence intensity of a solution containing donor in the presence of acceptor is given by:

$$F_D = I_0 \{1 - \exp\{-2.3E_D(\lambda_p)[D]d - 2.3E_A(\lambda_p)[A]d\}\} \left\{ \frac{E_D(\lambda_p)[D]}{E_D(\lambda_p)[D] + E_A(\lambda_p)[A]} \right\} \{(1 - f_{nr})\phi_{0D} - f_r\} \quad 3-14$$

where:  $f_r = (1 - f_{nr})\alpha_r\phi_{0D}$

The above equation can be written as:

$$F_D = I_0 \{1 - \exp\{-2.3E_D(\lambda_p)[D]d - 2.3E_A(\lambda_p)[A]d\}\} \left\{ \frac{E_D(\lambda_p)[D]}{E_D(\lambda_p)[D] + E_A(\lambda_p)[A]} \right\} \{1 - f_{nr}\} \{1 - \alpha_r\} \phi_{0D} \quad 3-15$$

which can be written in the more convenient form:

$$F_D = Q_2 \left\{ \frac{E_D(\lambda_p)[D]}{E_D(\lambda_p)[D] + E_A(\lambda_p)[A]} \right\} \{1 - f_{nr}\} \{1 - \alpha_r\} \phi_{0D} \quad 3-16$$

where:

$$Q_2 = I_0 \{1 - \exp\{-2.3E_D(\lambda_p)[D]d - 2.3E_A(\lambda_p)[A]d\}\}$$

Physically the term  $E_D(\lambda_p)[D]/\{E_D(\lambda_p)[D] + E_A(\lambda_p)[A]\}$  measures the part of the incident light which is absorbed by the donor molecules. The term  $(1 - f_{nr})$  gives the fraction of the excited donor molecules in nonradiative manner, that is, it represents the radiative part.

Dividing Eq. 3-16 by Eq. 3-12, we get,

$$F_D = F_{0D} \left\{ \frac{Q_2}{Q_1} \right\} \{1 - f_{nr}\} \{1 - \alpha_r\} \left\{ \frac{E_D(\lambda_p)[D]}{E_D(\lambda_p)[D] + E_A(\lambda_p)[A]} \right\} \quad 3-17$$

where:

$$\frac{Q_2}{Q_1} \equiv \frac{1 - \exp\{-2.3E_D(\lambda_p)[D]d - 2.3E_A(\lambda_p)[A]d\}}{1 - \exp[2.3E_D(\lambda_p)[D]d]}$$

### Acceptor Fluorescence:

The fluorescence intensity of the acceptor in a solution containing a mixture of two dyes, both donor and acceptor, when illuminated at a wavelength of donor and acceptor excitation is the result of:

1. Direct absorption of the incident light by the acceptor,
2. Absorption of the fluorescence of the donor, i.e. radiative transfer, and
3. Non radiative energy transfer from the donor.

The expression for the acceptor fluorescence is:

$$\begin{aligned} F_A = & Q_2 \left\{ \frac{E_D(\lambda_p)[D]}{E_D(\lambda_p)[D] + E_A(\lambda_p)[A]} \right\} f_{nr} \Phi_{0A} \\ & + Q_2 \left\{ \frac{E_A(\lambda_p)[A]}{E_D(\lambda_p)[D] + E_A(\lambda_p)[A]d} \right\} \Phi_{0A} \\ & + Q_2 \left\{ \frac{E_D(\lambda_p)[D]}{E_D(\lambda_p)[D] + E_A(\lambda_p)[A]} \right\} f_r \Phi_{0A} \end{aligned} \quad 3-18$$

where:  $E_D$  is the decadic extinction coefficient of the donor,  
 $E_A$  is the decadic extinction coefficient of the acceptor,  
 $[D]$  is the donor molar concentration,  
 $[A]$  is the acceptor concentration.

The above equation can be written in the more convenient form:

$$F_A = \left\{ \frac{E_D(\lambda_p)[D][f_{nr} + f_r] + E_A(\lambda_p)[A]}{E_D(\lambda_p)[D] + E_A(\lambda_p)[A]} \right\} Q_2 \phi_{0A} \quad 3-19$$

multiplying the denominator and nominator by  $Q_1 \phi_{0D}$ , we get,

$$F_A = F_{0D} \left\{ \frac{E_D(\lambda_p)[D][f_{nr} + f_r] + E_A(\lambda_p)[A]}{E_D(\lambda_p)[D] + E_A(\lambda_p)[A]} \right\} \left\{ \frac{Q_2}{Q_1} \right\} \left\{ \frac{\phi_{0A}}{\phi_{0D}} \right\} \quad 3-20$$

The total fluorescence of a dye mixture containing a donor and an acceptor dye is the sum of the individual fluorescences, that is:

$$F = F_D + F_A \quad 3-21$$

Figure 3-4 shows the absorption and fluorescence spectra of Rhodamine 610 and Nile Blue 690. The figure shows clearly the overlap of the Rhodamine 610 fluorescence (donor) with the Nile Blue 610 absorption (acceptor).

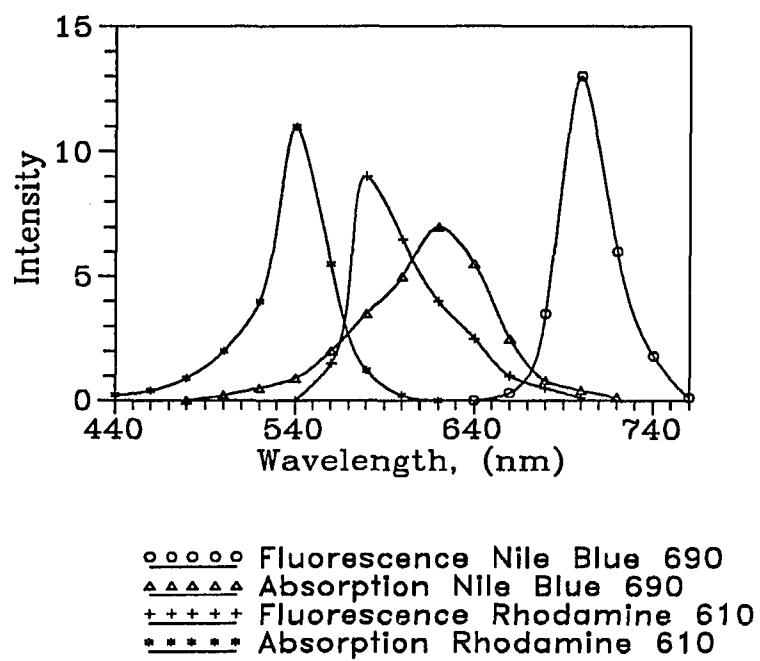


Figure 3-4. Typical absorption and fluorescence spectra of Rhodamine 610 (donor) and Nile Blue 690 (acceptor).

### 3.3 References

1. Foster, Th. *Transfer Mechanisms of Electronic Excitation*. Discuss. Faraday Soc., Vol. 27, p. 1, 1959.
2. Foster, Th. *Zwischenmolekulare Energiewanderung und Fluoreszenz*. Ann. Physik., Vol 2, p. 55, 1948.
3. Gosele, U., M. Hauser, U. K. A. Klein, and R. Frey. *Diffusion and Long Range Energy Transfer*. Chem. Phys. Lett., Vol. 34, P. 519, 1975.
4. Birks, J. B. *Photophysics of Aromatic Molecules*. New York: John Wiley and Sons, 1970.
5. Foster. Th., Z. Naturforsch. Vol. 4a, p. 321 1949.
6. Foster, Th., Angew. Chemie, Vol. 81, p.364; Internat. Ed. Vol. 8, p. 333, 1969.
7. Brown, F. H., M. Furst, and H. Kallmann. *Light and High Induced Energy Transfer in Liquid and Rigid Organic Scintillators*. Discuss. Faraday Soc., Vol. 27, p. 43, 1959.
8. Kurskii, Y. A., and A. S. Selivanenko. Opt. Spectrosc. (USSR), Vol. 8, p. 340, 1960.
9. Antonov-Romanovski, V. V. and M. D. Galanin. Opt. Spektrosk., Vol. 3, p. 389, 1957.
10. Kilin, S. F., M. S. Mikhrlashvili, and I. M. Rozman. *On the Transfer of Electronic Excitation Energy in Liquid Solutions*. Opt. Spectrosc. (USSR), Vol. 16, p. 576, 1964.
11. Agrest, M. M., S. F. Kilin, M. M. Rikenglaz, and I. M. Rozman. *Transfer of Electronic Excitation Energy in Liquid Solution*. Opt. Spectrosc. (USSR), Vol. 27, p. 514, 1969.
12. Bagdasaryan, K. S., and A. L. Muler. *Quantitative Verification of the Theory of Resonance Energy Transfer with Brownian Motion Taken into Account*. Opt. Spectrosc. (USSR), Vol. 18, p. 558, 1965.
13. Yokota, M. and O. Tanimoto. *Phonon Assisted Energy Transfer Between Trivalent Rare Earth Ions*. J. Phys. Soc. Jap., Vol. 32, p. 1577, 1967.
14. Steinberk, I. Z., and E. Katchalski. *Theoretical Analysis of the Role of Diffusion in Chemical Reactions, Fluorescence Quenching and Non Radiative Energy Transfer*. J. Chem. Phys., Vol. 48, p. 2404, 1968.
15. Birks, J. B., and M. S. C. P. Leite. *Energy Transfer in Organic Systems. IX. Effects of Diffusion on Transfer Efficiency*. J. Phys. B, Vol. 3, p. 513, 1970.
16. Mikhelashvili, M. S. *Transfer of Electronic Excitation Energy in a Liquid*. Opt.

Spectrosc. (USSR), Vol. 30, p. 141, 1971.

17. Birks, J. B., and Georgious, S., *Energy Transfer in Organic Systems*. V. J. Phys. B, (Proc. Phys. Soc.), Ser. 2, Vol. 1., pp. 266-273, 1968.

18. Sebastain, P. J., and K. Sathianandan. *Donor Concentration Dependence of the Emission Peak in Rhodamine 6G - Rhodamine B Energy Transfer Dye Laser*. Opt. Comm., Vol. 35, p. 113, 1980.

19. Ali, M. A., S. A. Ahmed, and A. S. Chokhavatia, *Examination of a Generalized Model for Radiationless Energy Transfer in Dyes*. J. Chem. Phys., Vol. 91, pp. 2892-2897, 1989.

20. Lakowicz, Joseph R. *Principles of Fluorescence Spectrometry*. New York: Plenum Press, 1986.

21. Kodak. *Optical Products*. Eastman Kodak Company, New York 14650.

## **4 Theory and Modeling of a Continuous Wave Energy Transfer Dye Laser**

### **4.1 Introduction**

In this work we develop a theoretical model to predict the gain spectrum of a cw laser pumped energy transfer dye laser (ETDL) as function of acceptor and donor concentrations, their absorption and emission spectra, pump power and wavelength, and dimensions of the active region. The model predicts that there are a number of candidate dye pairs which would benefit from such an approach, in terms of reduced pump requirements and increased attainable spectral range. It also shows that the use of the argon ion laser, which is a convenient and widely used pump source, may be practically extended through the use of energy transfer processes to a number of dyes which would otherwise require excitation at longer wavelengths from a krypton ion laser. These predictions are confirmed by experiments in which argon laser excitation, which cannot normally be used to excite Nile Blue, is used to excite a mixture of Rhodamine 610 (donor) and Nile Blue 690 (acceptor) to demonstrate laser action in the near infrared.

## 4.2 Theory and Development of an Analytical Model

### 4.2.1 Rate Equations

In the present section, we are using the rate equations which govern the rate at which populations of various levels change under the action of a continuous wave laser pump, in the presence of laser radiation, for a given two dye mixture solution with specified characteristics for each dye. The rate equation approach provides a convenient means of studying the time dependence of atomic population of various levels under the presence of radiation at frequencies corresponding to different transitions of the atoms. It also gives the steady state population difference between the actual levels involved in the laser transition and allows one to study whether an inversion of the population is achievable in a transition and, if so, what would be the minimum pumping rate required to maintain a steady population inversion for continuous wave operation of the laser. In addition allows the derivation of an expression for the dye mixture gain in terms of readily available dye and kinetics terms.

We shall model the two dye mixture laser using the rate equations approach, Statz and de Mars [1], and Dunsmuir [2]. In our model of the two dye, donor - acceptor, mixture laser system we shall include the population excitation due to the cw laser source, the energy transfer due to the non radiative decay process, the energy transfer due radiative decay process, the triplet-triplet losses and shall not include the induced emission rate [3]. The rate equations of donor and acceptor laser dye mixture at threshold, a set of two coupled equations, take the form:

For the singlet state:

The rate equations of donor and acceptor laser dye mixture at threshold are given by:

a) the donor equation is:

$$\frac{dN_{1D}}{dt} = \frac{\sigma_{aD}(\lambda_p) I_p(r, z) N_{0D}}{h \nu_p} - \frac{N_{1D}}{\tau_{0D}} - k_{nr} N_{1D} N_{0A} \quad 4-1$$

where:  $N_{1D}$  is the population of the donor in the excited state,  $\text{cm}^{-3}$ ,

$\sigma_{aD}(\lambda_p)$  is the absorption cross section of the donor at the pumping wavelength,  $\text{cm}^2$ ,

$\lambda_p$  is the wavelength of the pumping beam,  $\text{cm}$

$I_p(r, z)$  is the power flux of the pumping beam,  $\text{W}/\text{cm}^2$ ,

$N_{0D}$  is the population of the donor at the ground state,  $\text{cm}^{-3}$ ,

$h$  is Planck's constant,

$\nu_p$  is the frequency of the pumping beam,  $\text{s}^{-1}$ ,

$N_{1D}$  is the population of the acceptor at the excited state,  $\text{cm}^{-3}$ ,

$\tau_{0D}$  is the lifetime of the donor at the excited singlet state,  $\text{s}$ ,

$k_{nr}$  is the rate constant for the energy transfer due to a non radiative process,  $\text{cm}^3/\text{s}$ ,

$N_{0A}$  is the population of the acceptor at the ground state,  $\text{cm}^{-3}$ .

The term to the left hand side represents the rate of change of the excited donor population as function of time. On the right hand side, the first term represents the absorption of the pump light energy, the second term represents depopulation of the excited state by spontaneous emission, and the third term represents the energy transfer from donor to acceptor due a non radiative process. When the population is in equilibrium the first term is balanced by the second and third terms. The term  $h \nu_p$

represents the quantum energy of a photon at the frequency  $\nu_p$ .

b) the acceptor equation is:

$$\frac{dN_{1A}}{dt} = \frac{\sigma_{aA}(\lambda_p)I_p(r,z)N_{0A}}{h\nu_p} - \frac{N_{1A}}{\tau_{0A}} + k_{nr}N_{1D}N_{0A} + k_rN_{1D} \quad 4-2$$

where:  $N_{1A}$  is the population of the acceptor in the excited state,  $\text{cm}^{-3}$ ,

$\sigma_{aA}(\lambda_p)$  is the absorption cross section of the acceptor at the pumping wavelength,  $\text{cm}^2$ ,

$\lambda_p$  is the wavelength of the pumping beam,  $\text{cm}$

$I_p(r,z)$  is the power flux of the pumping beam,  $\text{W}/\text{cm}^2$ ,

$N_{0A}$  is the population of the acceptor at the ground state,  $\text{cm}^{-3}$ ,

$h$  is Planck's constant,

$\nu_p$  is the frequency of the pumping beam,  $\text{s}^{-1}$ ,

$N_{1A}$  is the population of the acceptor at the excited state,  $\text{cm}^{-3}$ ,

$\tau_{0A}$  is the lifetime of the acceptor at the excited singlet state,  $\text{s}$ ,

$k_{nr}$  is the rate constant for the energy transfer due to a non radiative process,  $\text{cm}^3/\text{s}$ ,

$N_{1D}$  is the population of the donor at the excited state,  $\text{cm}^{-3}$ ,

$k_r$  is the rate constant for the energy transfer due to the radiative process,  $\text{s}^{-1}$ .

The term on the left hand side represents the rate of change of the excited acceptor population as function of time. On the right hand side, the first term represents the absorption of the pump light energy, the second term represents depopulation of the excited state by spontaneous emission, the third term represents the energy transfer from donor to acceptor due to a non radiative process, and the fourth term represents

the energy transfer from donor to acceptor due to the radiative process. When the population is in equilibrium the first, third, and fourth terms are balanced by the second term. The term  $h\nu_p$  represents the quantum energy of a photon at the frequency  $\nu_p$ . The singlet state equations include energy transfer processes and nonradiative decay processes, but do not include [3] the induced emission rate.

For the triplet state:

The population dynamics of the triplet state is described by the triplet state rate equations.

a) the donor equation:

$$\frac{dN_{1D}}{dt} = N_{1D}k_{s1D} - \frac{N_{1D}}{\tau_{1D}} \quad 4-3$$

where:  $N_{1D}$  is the population of the excited donor molecules in the triplet state,  $\text{cm}^{-3}$ ,

$k_{s1D}$  is the probability per unit time that an excited donor singlet molecule will make the transition to the triplet state,  $\text{s}^{-1}$ ,

$\tau_{1D}$  is the triplet lifetime of a donor molecule, s,

$N_{1D}$  is the population of the excited donor molecules in the singlet state,  $\text{cm}^{-3}$ .

b) the acceptor equation:

$$\frac{dN_{1A}}{dt} = N_{1A}k_{s1A} - \frac{N_{1A}}{\tau_{1A}} \quad 4-4$$

where:  $N_{1A}$  is the population of the excited acceptor molecules in the triplet state,  $\text{cm}^{-3}$ ,

$k_{s1A}$  is the probability per unit time that an excited acceptor singlet molecule

will make the transition to the singlet state,  $s^{-1}$ ,

$\tau_{tA}$  is the triplet life time of the acceptor molecule, s,

$N_{1A}$  is the population of the excited donor molecules in the singlet state,  
 $cm^{-3}$ .

## 4.2.2 Population Densities of Ground and Excited State Dye Molecules

The molecules are considered to be in either the ground state, or the first excited state, or the triplet state. The principle of conservation of matter requires conservation of molecules, so that for the donor molecules:

$$N_D = N_{1D} + N_{0D} + N_{1D} \quad 4-5$$

where:  $N_D$  is the population of the donor molecules,  $\text{cm}^{-3}$ ,

$N_{1D}$  is the population of the excited donor molecules,  $\text{cm}^{-3}$ ,

$N_{0D}$  is the population of the ground state molecules,  $\text{cm}^{-3}$ ,

$N_{1D}$  is the population of the triplet state molecules,  $\text{cm}^{-3}$ .

and, for the acceptor molecules:

$$N_A = N_{1A} + N_{0A} + N_{1A} \quad 4-6$$

where:  $N_A$  is the population of the donor molecules,  $\text{cm}^{-3}$ ,

$N_{1A}$  is the population of the excited donor molecules,  $\text{cm}^{-3}$ ,

$N_{0A}$  is the population of the ground state molecules,  $\text{cm}^{-3}$ ,

$N_{1A}$  is the population of the triplet state molecules,  $\text{cm}^{-3}$ .

The population concentration of either donor or acceptor is determined from the concentration of the dye as:

$$N = A[N]C \quad 4-7$$

where:  $N$  is the population concentration of either the acceptor or donor molecules,  $\text{cm}^{-3}$ ,

A is Avogadro's number,  $6.023 \times 10^{23}$  Molecules/Mole,

[N] is the concentration of either the acceptor or donor, Mole/Litre,

C is a conversion factor from *litre* to  $cm^3$ , equal to  $1.0 \times 10^{-3}$  Litre/ $cm^3$ .

### 4.2.3 Absorption of Light by a Dye Mixture Medium

Beer - Lambert law states that if a monochromatic light beam of intensity  $I(0)$  is incident normally on a specimen of thickness  $d$ , containing  $N$  molecules of the absorbing species per unit volume, the intensity of the light is attenuating according to the equation:

$$\begin{aligned} I(z) &= I(0)e^{-\sigma(\lambda)Nz} \\ &= I(0)e^{-\mu z} \quad 0 < z < d \end{aligned} \quad 4-8$$

where:  $I(z)$  is the light beam intensity at distance  $z$ ,  $W/cm^2$ ,  
 $I(0)$  is the light beam intensity at the surface of the absorbing medium,  $W/cm^2$   
 $\sigma(\lambda)$  is the molecular absorption cross section at wavelength  $\lambda$ ,  $cm^2$ ,  
 $N$  is the concentration of molecules in the absorbing medium,  $cm^{-3}$ ,  
 $\mu$  is the absorption coefficient,  $cm^{-1}$ ,  
 $z$  the distance in the direction of the beam propagation,  $cm$

Beers - Lambert law is expressed usually in the form:

$$I(z) = I(0)10^{-\epsilon(\lambda)[M]z} \quad 0 < z < d \quad 4-9$$

where:  $\epsilon$  is the decadic molar extinction coefficient,  $Liter\ Mole^{-1}\ cm^{-1}$   
 $[M]$  is the molar concentration of the absorbing species,  $Mole/Liter$

In the case of a two component mixture the total absorption at a given wavelength will be the sum of the absorbances of the two component, then Beer - Lambert law takes the form:

$$I(z) = I(0)e^{-\{\sigma_{aA}(\lambda)[N_A] + \sigma_{aD}(\lambda)[N_D]\}z}$$

$$= I(0)10^{-\{\epsilon_A(\lambda)[N_A] + \epsilon_D(\lambda)[N_D]\}z} \quad 0 < z < d \quad 4-10$$

where:  $\epsilon_A(\lambda)$  is the decadic molar extinction coefficient of the acceptor at wavelength  $\lambda$ , Liter Mole<sup>-1</sup> cm<sup>-1</sup>

$[N_A]$  is the molar concentration of the absorbing species of the acceptor, Mole/Liter

$\epsilon_D(\lambda)$  is the decadic molar extinction coefficient of the donor at wavelength  $\lambda$ , Liter Mole<sup>-1</sup> cm<sup>-1</sup>

$[N_D]$  is the molar concentration of the absorbing species of the donor, Mole/Liter

A relationship between the decadic extinction coefficient,  $\epsilon$ , and the molecular absorption cross section,  $\sigma$ , can be found by writing Eq. 4-8 and Eq. 4-9 in the form:

$$\log \frac{I_0}{I} = \epsilon[M]d$$

$$\ln \frac{I_0}{I} = \mu d = \sigma N d$$

and comparing, we get:

$$\sigma = 3.82 \times 10^{-21} \epsilon$$

A simplification can be made in the case the absorbance of the acceptor is much

less than the of the absorbance of the donor at the pumping wavelength, then Eq. 4-10 takes the simpler form:

$$I(z) = I(0)10^{-\epsilon_D(\lambda)N_D z} \quad 0 < z < d \quad 4-11$$

#### 4.2.4 Pumping Laser Beam Characteristics

The laser pumped cw dye laser geometry in which our model is based on is the customary longitudinal arrangement used in almost all cw dye lasers, [4,5]. The active region of the laser is assumed to have length  $d$  in the  $z$  direction with both pump and laser beams having their waists at the entrance surface,  $z=0$ . Assuming that the pump beam and laser beam propagate in the fundamental Gaussian mode, the radial intensity distribution of the pump irradiance,  $I_p(r,z)$ , can be written for the case in which the pump is not absorbed as, [6]:

$$I_p(r,z) = \left[ \frac{4P_p(0)}{b_p h c} \right] \left[ \frac{W_{p0}}{W_p} \right]^2 \exp[-2r^2/W_p^2] \quad 4-12$$

with:

$$W_p^2 = \frac{\lambda_p b_p}{2\pi} \left[ 1 + \frac{4z^2}{b_p^2 p} \right]$$

$$W_{p0}^2 = \frac{b_p \lambda_p}{2\pi}$$

where:  $b_p$  is the confocal parameter of the pump beam, cm,

$P_p(0)$  is the incident pump power, Watt,

$z$  is the distance along the beam axis, cm,

$W_p$  is the beam radius at any point  $z$ , cm,

$W_{(p0)}$  is the beam radius at the point  $z=0$ , cm,

$r$  is the radial distance from the cavity axis, cm,

$h$  is Planck's constant,

$c$  is the velocity of light in free space, cm/s.

The above equation does not express accurately the pump irradiance in the laser cavity, however, since the absorption necessary to produce population inversion, and hence gain has been ignored. Thus, modified Eq. 4-12 to include absorption, using Beer's - Albert's law, yields:

$$I_p(r, z) = \left[ \frac{4P_p(0)}{b_p h c} \right] \left[ \frac{\exp[-2r^2/W_p^2]}{1 + 4z^2/b_p^2} \right] \exp[-N_0 \sigma_a(\lambda_p) z] \quad 4-13$$

where:  $N_0$  is the concentration of the ground state molecules,  $\text{cm}^{-3}$ ,  
 $\sigma_a(\lambda_p)$  is the singlet state absorption cross section,  $\text{cm}^2$ .

It is important to note that an accurate description of the dye laser would include transverse as well as longitudinal dependence of the variables. To solve the complete non linear problem including this additional complication would be a formidable task. A much simpler problem, however has been considered by Pike [7]. For the case when the active region is confined to within a distance less than the confocal parameter of the beam waist, i.e. the Gaussian beams can be considered to be of constant diameter.

The laser and pumping beam geometries in the vicinity of the active region are shown in detail in Figure 4-1. The active region of the laser is assumed to have length  $d$  in the  $z$  direction with both pump and laser beams having their waists at the entrance surface,  $z=0$ . The waist diameters of pump and laser beams are assumed to be  $2W_{p0}$  and  $2W_{l0}$  respectively. For generality it is assumed that the pump and laser beams also have different confocal parameters  $b_p$  and  $b_l$ .

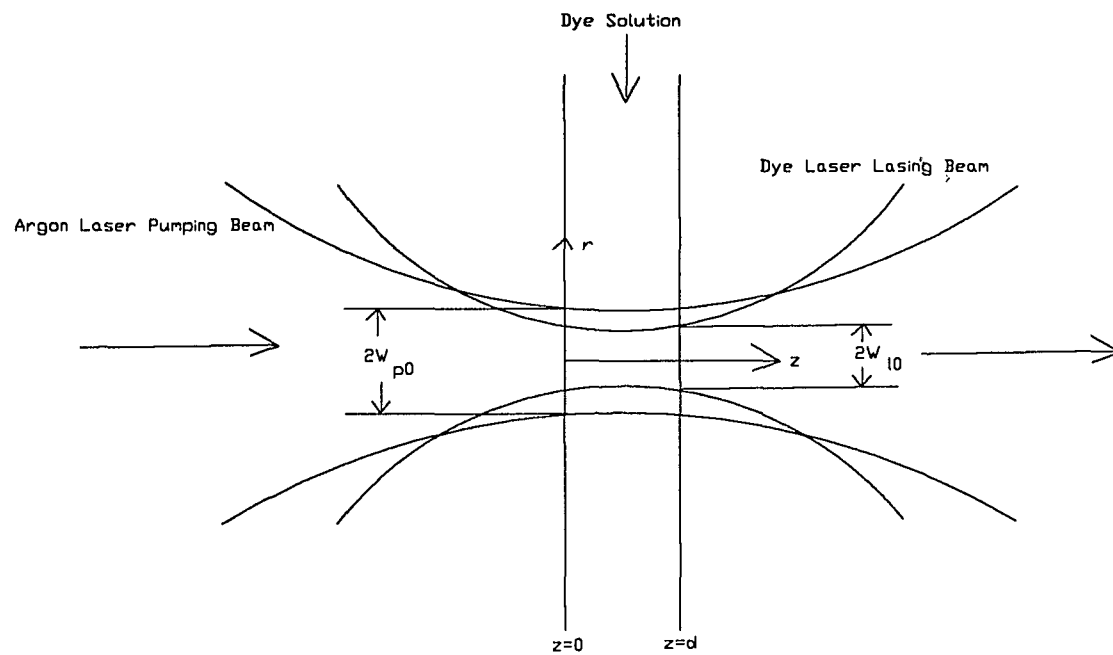


Figure 4-1. Large scale representation of the active region of a cw dye laser.

### 4.2.5 Population of Excited States

Under steady state conditions of continuous constant excitation, the concentration of molecules in the singlet excited state is in equilibrium with the ground state concentration, i.e.:

$$\frac{dN_{1D}}{dt} = 0, \quad 4-14$$

and

$$\frac{dN_{1A}}{dt} = 0; \quad 4-15$$

then, the rate equations, Eq. 4-1 and 4-2, take the form:

$$0 = \frac{\sigma_{ad}(\lambda_p)I_p(r, z)N_{0D}}{h\nu_p} - \frac{N_{1D}}{\tau_{0D}} - k_{nr}N_{1D}N_{0A} \quad 4-16$$

$$0 = \frac{\sigma_{aA}(\lambda_p)I_p(r, z)N_{0A}}{h\nu_p} - \frac{N_{1A}}{\tau_{0A}} + k_{nr}N_{1D}N_{0A} + k_rN_{1D} \quad 4-17$$

Solving the first equation, Eq. 4-16, we get the population concentration in the excited state of the donor:

$$N_{1D}(\cdot) = \frac{\sigma_{ad}(\lambda_p)I_p(r, z)N_{0D}}{\left\{ k_{nr}N_{0A} + \frac{1}{\tau_{0D}} \right\} h\nu_p} \quad 4-18$$

Defining [7]:

$$\tau_D = k_{nr}N_{0A} + \frac{1}{\tau_{0D}} \quad 4-19$$

we can rewrite Eq. 4-18 as:

$$N_{1D}(\cdot) = \frac{\sigma_{aD}(\lambda_p) I_p(r, z) N_{0D}}{h\nu} \tau_D \quad 4-20$$

Solving the second equation, Eq. 4-17, we get the population concentration of the excited state of the acceptor:

$$N_{1A} = \tau_{0A} \left\{ \frac{\sigma_{aA}(\lambda_p) I_p(r, z) N_{0A}}{h\nu_p} + k_{nr} N_{1D} N_{0A} + k_r N_{1D} \right\} \quad 4-21$$

We rewrite the above equation in a more convenient form:

$$N_{1A} = \tau_{0A} N_{1D}(r, z) \{k_{nr} N_{0A} + \tau_{0D}^{-1} - \tau_{0D}^{-1} + k_r\} + \frac{\tau_{0A} I_p(r, z) \sigma_{aA}(\lambda_p) N_{0A}}{h\nu_p} \quad 4-22$$

Upon substitution of  $k_r = \alpha_r k_{fd}$ ,  $\phi_{0d} = k_{fd} \tau_{0d}$ , and Eq. 4-19, we obtain:

$$N_{1A} = \tau_{0A} N_{1D} \left\{ \frac{1}{\tau_D} - \frac{1}{\tau_{0D}} + \alpha_r \frac{\phi_{0D}}{\tau_{0D}} \right\} + \frac{\tau_{0A} I_p(r, z) \sigma_{aA}(\lambda_p) N_{0A}}{h\nu_p} \quad 4-23$$

Substituting Eq. 3-7 into the above and after some algebraic simplifications, we get:

$$N_{1A} = \frac{\tau_{0A} N_{1D}}{\tau_D} \{ \alpha_r \phi_{0D} (1 - f_{nr}) + f_{nr} \} + \frac{\tau_{0A} I_p(r, z) \sigma_{aA}(\lambda_p) N_{0A}}{h\nu_p} \quad 4-24$$

Finally, upon substitution of Eqs. 3-7, 3-9 and 4-20 into the above we obtain:

$$N_{1A} = \tau_{0A} \frac{I_p(r, z)}{h\nu_p} [\sigma_{aD}(\lambda_p) N_{0D} f + \sigma_{aA}(\lambda_p) N_{0A}] \quad 4-25$$

Eq. 4-20 and Eq. 4-25, represent the population concentration of the excited acceptor and donor molecules as function of the concentration and the characteristics of the system and the donor and acceptor dyes.

This equation can be simplified if the absorption cross section of the acceptor at the pumping wavelength is much smaller than the one of the donor, then we can write:

$$N_{1A} = \tau_{0A} \frac{I_p(r, z)}{h\nu_p} \{\sigma_{aD}(\lambda_p) N_{0D}\} \quad 4-26$$

Under the steady state conditions of the continuous, constant excitation, the concentration of molecules in the triplet state is in equilibrium with the singlet state concentration. Then the triplet rate equations take the form:

a) the donor equation:

$$N_{1D} = k_{stD} \tau_{tD} N_{1D} \quad 4-27$$

b) the acceptor equation:

$$N_{1A} = k_{stA} \tau_{tA} N_{1A} \quad 4-28$$

### 4.2.6 Dye Gain Coefficient and Laser System Gain

For a transversely pumped dye laser jet the building of the output laser beam,  $I_e$ , along the cell axis,  $z$ , is, [8]:

$$\begin{aligned} \frac{dI_e}{dz} = & N_{1A}\sigma_{eA}(\lambda_e)I_e - N_{0A}\sigma_{aA}(\lambda_e)I_e - N_{0D}\sigma_{aD}(\lambda_e)I_e \\ & - N_{1A}\sigma_{atA}(\lambda_e)I_e - N_{1D}\sigma_{atD}(\lambda_e) - A(\lambda_e)I_e \end{aligned} \quad 4-29$$

where:  $A(\lambda_e)$  denotes the optical losses in the cavity which depend on the emitting wavelength, but do not depend on the molecular concentrations,  $\text{cm}^{-1}$ .

The right term represents the rate of change of the buildup up of the light as function of distance in the cavity, the first right term represents the buildup of light, the rest of the terms on the right represent the losses due to absorption by the donor and acceptor molecules.

If the optical losses in the cavity are due to the mirrors only, then these losses can be expressed as:

$$A(\lambda) = -\frac{1}{2d} \ln[R_1(\lambda)R_2(\lambda)] \quad 4-30$$

where:  $R_1, R_2$  are the reflection coefficients of the mirrors, and  $d$  is the active length of the medium.

The reflection coefficients are functions of wavelength.

The growth of irradiance in a laser medium as a result of amplification by the active medium can be expressed as:

$$\frac{dI_e}{dz} = GI_e \quad 4-31$$

We define the system's gain as, [8]:

$$G = \frac{1}{I_e} \frac{dI_e}{dz} \quad 4-32$$

Substituting Eq. 4-29 into Eq. 4-32, we obtain:

$$\begin{aligned} G(N_A, N_D, \lambda_e) = & N_{1A} \sigma_{eA}(\lambda_e) - N_{0A} \sigma_{aA}(\lambda_e) - N_{0D} \sigma_{aD}(\lambda_e) \\ & - N_{1tA} \sigma_{atA}(\lambda_e) - N_{1tD} \sigma_{atD}(\lambda_e) - A(\lambda_e) \end{aligned} \quad 4-33$$

The gain coefficient per unit length of the dye mixture is defined as:

$$\begin{aligned} g(N_A, N_D, \lambda_e) = & N_{1A} \sigma_{eA}(\lambda_e) - N_{0A} \sigma_{aA}(\lambda_e) - N_{0D} \sigma_{aD}(\lambda_e) \\ & - N_{1tA} \sigma_{atA}(\lambda_e) - N_{1tD} \sigma_{atD}(\lambda_e) \end{aligned} \quad 4-34$$

To develop a gain equation which can be used to predict the gain of cw ETDL, the following two assumptions will be made:

- the absorption of the donor molecules in the triplet state is negligibly small in the fluorescence spectrum region of the acceptor molecule, as it is the practical case; the absorption of the donor molecules in the triplet state will only be considered;
- a small fraction of the available donor molecules are in the first state of the donor; then  $N_{0D} \approx N_D$ .

Taking into account the first assumption, as it is the practical case, then the fifth term can be neglected; thus the above equation takes the simplified form:

$$g(N_A, N_D, \lambda_e) = N_{1A} \sigma_{eA}(\lambda_e) - N_{0A} \sigma_{aA}(\lambda_e) - N_{0D} \sigma_{aD}(\lambda_e) - N_{1tA} \sigma_{atA}(\lambda_e) \quad 4-35$$

But at the triplet excited population of the acceptor at the steady state is

$$N_{1tA} = k_{st} \tau_t N_{1A} \quad 4-36$$

and conservation of molecules requires that

$$N_A = N_{0A} + N_{1A} + N_{1tA} \quad 4-37$$

Substituting Eq. 4-36 into Eq. 4-37 we get the ground state population of the acceptor.

$$N_{0A} = N_A - N_{1A} - k_{st}\tau_t N_{1A} \quad 4-38$$

Substituting Eq. 4-38 into Eq. 4-35 we get:

$$\begin{aligned} g(N_A, N_D, \lambda_e) = & N_{1A} \{ \sigma_{eA}(\lambda_e) + \sigma_{aA}(\lambda_e) \\ & - k_{st}\tau_t(\lambda_e) [\sigma_{aA}(\lambda_e) - \sigma_{atA}(\lambda_e)] \} \\ & - N_A \sigma_{aA}(\lambda_e) \end{aligned} \quad 4-39$$

We define as the effective cross section of the acceptor the terms in the curved brackets, so:

$$\sigma_{eff} \equiv \sigma_{eA}(\lambda_e) + \sigma_{aA}(\lambda_e) - k_{st}\tau_t[\sigma_{aA}(\lambda_e) - \sigma_{atA}(\lambda_e)] \quad 4-40$$

The gain coefficient equation of a dye mixture takes the form:

$$g(N_A, N_D, \lambda_e) = N_{1A} \sigma_{eff}(\lambda_e) - N_A \sigma_{aA}(\lambda_e) - N_{0D} \sigma_{aD}(\lambda_e) \quad 4-41$$

Finally, taking into account the second assumption  $N_{0D} \approx N_D$ , the above equation takes the form:

$$g(N_A, N_D, \lambda_e) = N_{1A} \sigma_{eff}(\lambda_e) - N_A \sigma_{aA}(\lambda_e) - N_D \sigma_{aD}(\lambda_e) \quad 4-42$$

This last equation shows clearly that the gain of the dye mixture depends on the concentration of both donor and acceptor, in addition to wavelength dependence because the absorption and emission cross section of donor and acceptor are wavelength dependent. The best optimum will be found, according to our model, if all these dependances have been taken into account. In our work this and for a specific wavelength, the maximum gain is found as function of acceptor and donor concen-

trations; then the same process is repeated for another wavelength and the maximum gain is obtained as function of both concentrations. A triad of wavelength, acceptor concentration, and donor concentration gives the maximum gain of a dye mixture for a given laser system.

### 4.3 Analytical Model of a Continuous Wave Energy Transfer Dye Laser

An analytical model is now developed, taking into account all previous results found in previous sections.

The total light energy that is absorbed in the laser jet of thickness  $d$ , taking into account both donor and acceptor absorption, is:

$$\begin{aligned} \int I_p(z) dz &= \int_0^d I(0) e^{-\{\sigma_{aA}(\lambda)[N_A] + \sigma_{aD}(\lambda)[N_D]\}z} dz \\ &= \int_0^d I(0) 10^{-\{\epsilon_A(\lambda)[N_A] + \epsilon_D(\lambda)[N_D]\}z} dz \quad 0 < z < d \quad 4-43 \end{aligned}$$

The excited donor population, at the steady state, is:

$$N_{1D}(\cdot) = \frac{\sigma_{aD}(\lambda_p) I_p(r, z) N_{0D}}{h\nu} \tau_D \quad 4-44$$

The excited acceptor population, at the steady state, is:

$$N_{1A}(\cdot) = \tau_{0A} \frac{I_p(r, z)}{h\nu_p} [\sigma_{aD}(\lambda_p) N_{0D} f + \sigma_{aA}(\lambda_p) N_{0A}] \quad 4-45$$

The equation of the dye mixture gain per unit length is:

$$g(N_A, N_D, \lambda_e) = N_{1A} \sigma_{eff} - N_A \sigma_{aA}(\lambda_e) - N_D \sigma_{aD}(\lambda_e) \quad 4-46$$

Substituting Eq. 4-43, and Eq. 4-45, into Eq. 4-46, we can rewrite the gain equation in terms of the parameters of the system.

$$\begin{aligned} g(N_A, N_D, \lambda_e) &= \sigma_{eff}(\lambda_e) \{ \tau_{0A} [\sigma_{aD}(\lambda_p) N_{0D} f + \sigma_{aA}(\lambda_p) N_{0A}] \\ &\quad \left[ \frac{4P_p(0)}{b_p h c} \right] \left[ \frac{\exp(-2r^2/W_p^2)}{1 + (4z^2/b_p^2)} \right] \exp[-\{N_D \sigma_{aD}(\lambda_p) + \sigma_{aA}(\lambda_p) N_{0A}\}z] \} \\ &\quad - N_A \sigma_{aA}(\lambda_e) - N_D \sigma_{aD}(\lambda_e) \quad 4-47 \end{aligned}$$

Finally, following the approach developed by Pike [4], the on axis,  $r=0$ , single pass gain,  $g_0$ , can be written as:

$$g_0(N_A, N_D, \lambda_e) = \sigma_{eff}(\lambda_e) \{ [\tau_{0A} \sigma_{ad}(\lambda_p) f + N_{0A} \sigma_{aA}(\lambda_p)] \int_0^d \left[ \frac{4P_p(0)}{b_p h c} \right] \left[ \frac{\exp[-N_D \sigma_{ad}(\lambda_p) - N_{0A} \sigma_{aA}(\lambda_p)] z}{1 + (4z^2/b_p^2)} \right] dz \} - N_A \sigma_{aA}(\lambda_e) d - N_D \sigma_{ad}(\lambda_e) d \quad 4-48$$

Furthermore, if it is assumed that  $d \ll b_p$  ( a good assumption for a practical cw laser system [4-6,8] ), the above equation can be cast in the simpler form:

$$g_0(N_A, N_D, \lambda_e) = \sigma_{eff}(\lambda_e) \{ \tau_{0A} 4P_p(0) \left[ \frac{\sigma_{ad}(\lambda_p) N_D f + \sigma_{aA}(\lambda_p) N_{0A}}{\sigma_{ad}(\lambda_p) N_D + \sigma_{aA}(\lambda_p) N_{0A}} \right] \left[ \frac{1 - \exp[-N_D \sigma_{ad}(\lambda_p) d - N_{0A} \sigma_{ad}(\lambda_p) d]}{b_p h c} \right] \} - N_A \sigma_{aA}(\lambda_e) d - N_D \sigma_{ad}(\lambda_e) d \quad 4-49$$

Taking into account that  $N_{0A} = N_A - N_{1A} - N_{iA}$  the above equation takes the final form:

$$g_0(N_A, N_D, \lambda_e) = \sigma_{eff}(\lambda_e) \{ \tau_{0A} 4P_p(0) \left[ \frac{\sigma_{ad}(\lambda_p) N_D f + \sigma_{aA}(\lambda_p) N_{0A}}{\sigma_{ad}(\lambda_p) N_D + \sigma_{aA}(\lambda_p) N_{0A}} \right] \left[ \frac{1 - \exp[-N_D \sigma_{ad}(\lambda_p) d - [N_A - N_{1A} - N_{iA}] \sigma_{ad}(\lambda_p) d]}{b_p h c} \right] \} - N_A \sigma_{aA}(\lambda_e) d - N_D \sigma_{ad}(\lambda_e) d \quad 4-50$$

Comparing Eq. 46 and Eq. 50, we get the excited acceptor population concentration as:

$$N_{1A} = \tau_{0A} 4P_p(0) \left[ \frac{\sigma_{aD}(\lambda_p)N_D f + \sigma_{aA}(\lambda_p)N_{0A}}{\sigma_{aD}(\lambda_p)N_D + \sigma_{aA}(\lambda_p)N_{0A}} \right] \left[ \frac{1 - \exp[-N_D \sigma_{aD}(\lambda_p)d - [N_A - N_{1A} - N_{1A}] \sigma_{aD}(\lambda_p)d]}{b_p h c} \right] \quad 4-51$$

Eq. 50 gives the on axis gain of a dye mixture as function of the dyes concentration, their spectra characteristics, the transfer efficiency between donor and acceptor, and the pumping beam characteristics. This is a useful expression of the dye mixture gain because its simplicity and availability of the required data, [9]. This expression will be used for a series of computer simulations that will provide the optimum operating conditions for the ETDL.

## 4.4 References

1. Statz, H. and G. de Mars. *Transients and Oscillations in Masers*. Quantum Electronics. C. H. Townes (Ed.), New York: Columbia University Press, pp. 530-537, 1960.
2. Dunsmuir R. *Theory of Relaxation Oscillations in Optical Masers*. J. Electron Control., Vol. 10, pp. 453-458, 1961.
3. Urisu, Tsuneo and Kenji Kajiyama. *Concentration Dependence of the Gain Spectrum in Energy-Transfer Dye Mixtures*. J. Appl. Phys., Vol. 47, No 8, pp. 3563-3565, 1976.
4. Teschke, O., Andrew Dines, and John R. Whinnery. *Theory and Operation of High-Power CW and Long-Pulse Dye Lasers*. IEEE J. Quantum Electronics, QE-12, 383-395 (1976).
5. Snavely, B. B. *Continuous Wave Dye Lasers*, in *Dye Lasers*, F. P. Schafer, Ed. New York: Springer-Verlag, 91-120, 1973.
6. Svelto, Orazio. *Principles of Lasers*. Third Edition, New York: Plenum Press, (English Translation), 1989.
7. Pike, H. A., Unpublished Thesis, Univ. of Rochester, Rochester, N Y. 1971.
8. Peterson, O. G., J. P. Webb, W. C. McColgin and J. H. Eberly. *Organic Dye Laser Threshold*. J. Appl. Phys. Letters, Vol. 42, p. 1917, 1971.
9. Ali, M., B. Panoutsopoulos, and S. A. Ahmed. *On the Feasibility of Generating CW Argon Pumped Energy Transfer Dye Laser Emission in the Near IR Spectral Region*. App. Opt. Vol. 30, No 3, p. 312, 1991.

## 5 Simulation and Experiments of a Continuous Wave Energy Transfer Dye Laser

### 5.1 Numerical Simulation

Simulation calculations were carried out to simulate a cw ETDL with a solution of the a mixture consisting of Rhodamine 610 Perchlorate as donor and Nile Blue 690 Perchlorate as acceptor in Ethylene Glycol. The parameters used in the calculations to obtain the on axis single pass gain, were those of typical argon laser pumped cw dye lasers [1-4]. Specifically we assumed the following:

- a cw argon laser, capable of delivering 7 W at 514.5 nm as the pump source;
- a 0.025 cm length of active region for dye laser,  $d$  [5];
- a 20  $\mu\text{m}$  pump beam radius  $W_{p0}$  [1,5];
- $k_{sIA} \tau_{IA} \approx 1$  for Nile Blue 690 in Ethylene Glycol, which is a typical value for dye lasers [1-6];
- since, there appears to be no data in the literature on the triplet state of Nile Blue A Perchlorate, a value of  $0.1 \times 10^{-16} \text{ cm}^2$  was assumed for the triplet state absorption cross section at the wavelength of peak fluorescence ( $\lambda = 680 \text{ nm}$ ). The value assumed was based on comparison of known singlet and triplet absorption cross section in Rhodamine 690, and the known singlet absorption cross section for Nile Blue 690;
- spectral data (singlet state absorption and singlet state stimulation emission cross sections) on the donor and acceptor in ethylene glycol used in our calculations were taken from References [1,6-8];
- data required for the calculation of the total transfer efficiency,  $f$ , (Eq. 3-11), were based on the parameters of the two dyes and References [1,8-12].

The mathematical computer software package "Mathematica" was used for numerical evaluation of the dye gain expression as function of the acceptor and donor concentration for a number of emitting wavelengths. Part of the calculations were repeated using the software package "MathCAD". The results obtained with both software packages were found in agreement. The donor and acceptor concentration, range of interest was selected as:  $10^{-5}$  Mole/Litre to 1 Mole/Litre, and the lasing wavelength in the range of 650 to 750 nm.

Fig. 5-1 shows the self absorption and stimulation emission cross section of Nile Blue 690 Perchlorate values used in the numerical calculations.

Table 5-1 shows typical values of the parameters for donor (Rhodamine 610 Perchlorate) and acceptor (Nile Blue 690 Perchlorate) dyes used for the numerical calculation of the dye mixture gain.

Table 5-2 shows typical values of the solvent parameters, (Ethylene Glycol) used in the numerical calculations.

Table 5-3 shows typical values of the laser system, of the pump power and wavelength and the expecting lasing wavelength.

Table 5-4 shows the value of typical physical constants used in the simulation calculations.

Table 5-5 shows part of the numerical simulation results for the gain at a lasing wavelength of 700 nm, and a typical values of donor and acceptor concentrations.

Table 5-6 shows part of the numerical simulation results for the gain as function of wavelength for typical pairs of donor and acceptor concentration.

Stimulated Emission and Self Absorption  
of Nile Blue in a Dye Mixture  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser

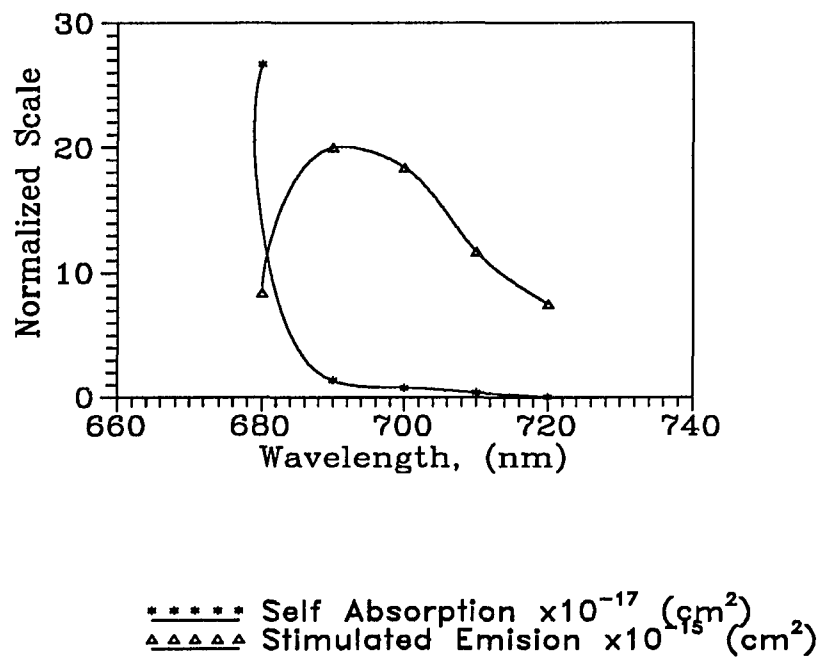


Figure 5-1. Self absorption and stimulated emission for Nile Blue Perchlorate 690.

TABLE 5-1 Laser Dyes Parameters	
Dyes:	Donor: Rhodamine B Perchlorate Acceptor: Nile Blue A Perchlorate
Donor: Rhodamine B Perchlorate	
Parameters:	
$\sigma_{Da}(\lambda_p) = 1.0 \times 10^{-18} \text{ cm}^2$	
$\tau_D = 8.0 \times 10^{-9} \text{ s}$	
$N_D =$ in the range of 1 to $1 \times 10^{-5}$ Moles/Litre	
Acceptor: Nile Blue A Perchlorate	
Parameters:	
$\sigma_{Aa}(\lambda_p) = 1.15 \times 10^{-17} \text{ cm}^2$	
$\sigma_{Ae}(\lambda_e) = 2.0 \times 10^{-16} \text{ cm}^2$	
$\sigma_{Aa}(\lambda_e) = 5.0 \times 10^{-18} \text{ cm}^2$	
$\tau_A = 1.0 \times 10^{-9} \text{ s}$	
$N_A =$ in the range of 1 to $1 \times 10^{-5}$ Moles/Litre	

TABLE 5-2  
Solvent Parameters

Solvent: Ethylene Glycol

*Characteristics:* Ethylene Glycol is a colorless, odorless liquid with a bittersweet taste. It is very hygroscopic.

*General Properties:*

Molecular weight	62.07
Freezing point, (C)	-13
Boiling point, (C)	197.3
Flash point, (C)	110
Minimum ignition temperature, (C)	410
Density, (g/cm <sup>3</sup> )	1.11
Refractive index	1.43
Viscosity, (cPoise)	26.09
Dielectric constant	37.7
Ionization potential, (eV)	10.49
Solubility	water, alcohol

*Optical Properties:*

Wavelength, (nm)	210	220	230	240	250	260	280
Transmission, (%)	20	35	40	60	75	90	98

Table 5-3 Laser System Parameters	
Cavity jet stream thickness:	0.25 mm
Pumping Power, $P_p$	= 7 W
Pumping Power (Main Line), $\lambda_p$	=514.5 nm
Emitting Wavelength, $\lambda_e$	=710 nm

Table 5-4 Physical Constants
Avogadro's: $A = 6.023 \times 10^{23}$ molecules/Mole
Planck's: $h = 6.63 \times 10^{-34}$ J.s
Speed of Light in Vacuum: $c = 3 \times 10^{10}$ cm/s

TABLE 5-5  
Calculation of Gain  
( $\lambda_e=700$  nm)

		[D] Moles/Litre						
[A] Moles/Litre	f	0	1x10 <sup>-5</sup>	1x10 <sup>-4</sup>	1x10 <sup>-3</sup>	1x10 <sup>-2</sup>	1x10 <sup>-1</sup>	1.0
1.0x10 <sup>-5</sup>	0.02	0.00010	0.00029	0.00187	0.0086	0.0098	0.00978	0.0097
1.0x10 <sup>-4</sup>	0.18	0.00091	0.00262	0.01659	0.0769	0.0869	0.08690	0.0868
5.0x10 <sup>-4</sup>	0.55	0.00182	0.00659	0.04570	0.2148	0.2444	0.24316	0.2430
1.0x10 <sup>-3</sup>	0.74	-0.0027	0.02965	0.05014	0.2545	0.2910	0.28941	0.2893
5.0x10 <sup>-3</sup>	0.96	-0.2017	-0.1987	-0.1741	-0.067	-0.049	-0.0504	-0.050
1.0x10 <sup>-2</sup>	1.0	-0.6586	-0.6576	-0.6491	-0.612	-0.603	-0.6039	-0.603

TABLE 5-6			
Dye Mixture Gain as Function of Wavelength			
$(\lambda_e = 700 \text{ nm})$			
Emitting Wavelength (nm)	[A]= $10^{-3}$ [D]= $10^{-3}$	[A]= $10^{-3}$ [D]= $10^{-2}$	[A]= $10^{-4}$ [D]= $10^{-3}$
680	0.114717	0.132453	0.033056
690	0.221555	0.263318	0.811373
700	0.254551	0.291013	0.076949
710	0.166328	0.188411	0.478213
720	0.125804	0.138364	0.030318

### 5.1.1 Gain of Dye Mixture as Function of Donor Concentration

The effect of the donor concentration on the dye mixture gain is examined next. Numerical solutions were carried using the exact expression of Eq. 4-48. Fig. 5-2 to 5-6 show the dependence of the on axis single pass gain,  $g_0$ , on the donor concentration for five wavelengths, 680, 690, 700, 710, 720 nm, and for three values of acceptor concentration,  $10^{-3}$ ,  $10^{-4}$ ,  $10^{-5}$  Mole/Litre. The results exhibit a linear dependence of the on axis gain on donor concentrations at low concentration reaching saturation at high donor concentration. Maximum gain is observed around 700 nm and for donor and acceptor concentrations of  $10^{-2}$  and  $10^{-3}$  Mole/Litre respectively.

These calculations were repeated again, with, however, the approximate expression of Eq. 4-50 replacing the exact expression of Eq. 4-48. As expected, essentially the same results were obtained. This indicates that the simpler expression of Eq. 4-50 represents a reasonable and practically useful approximation.

Simulation Results:  
Gain of Dye Mixture at 680 nm  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser

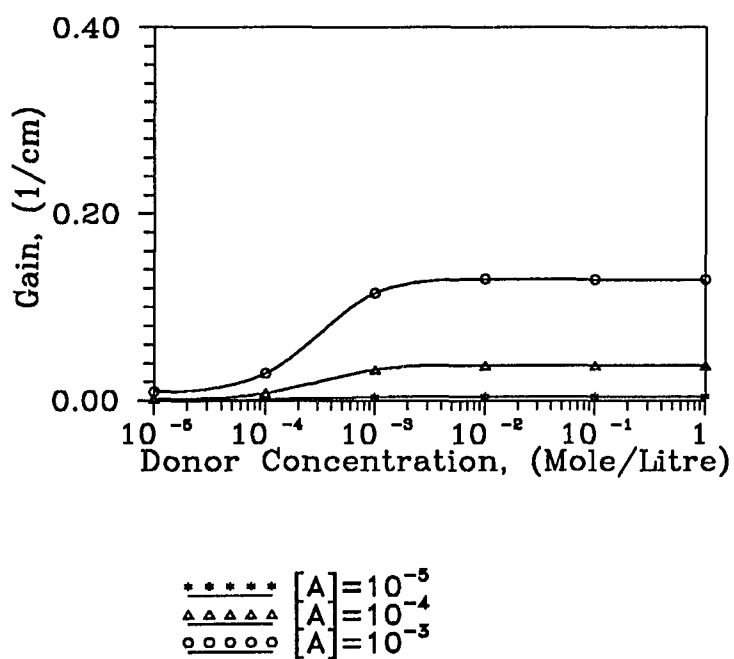


Figure 5-2. Gain of a dye mixture as function of donor concentration at 680 nm.

Simulation Results:  
Gain of Dye Mixture at 690 nm  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser

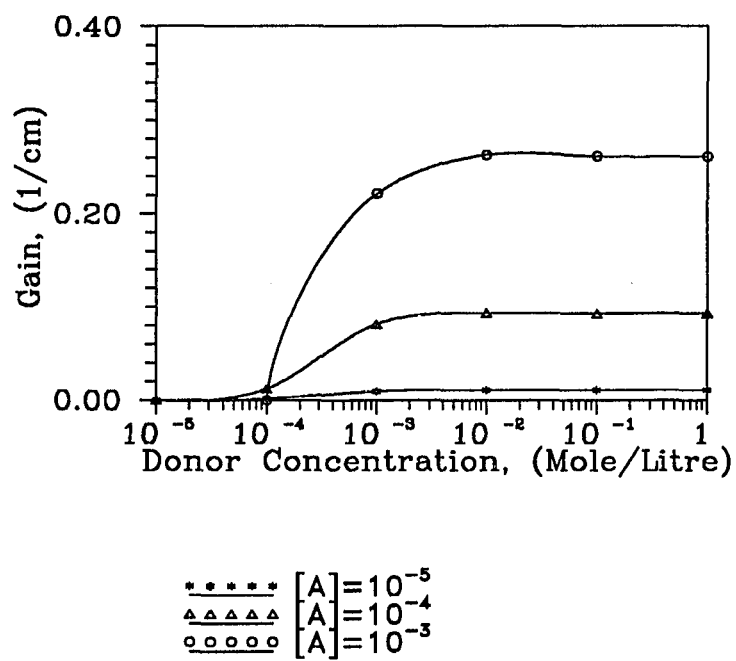
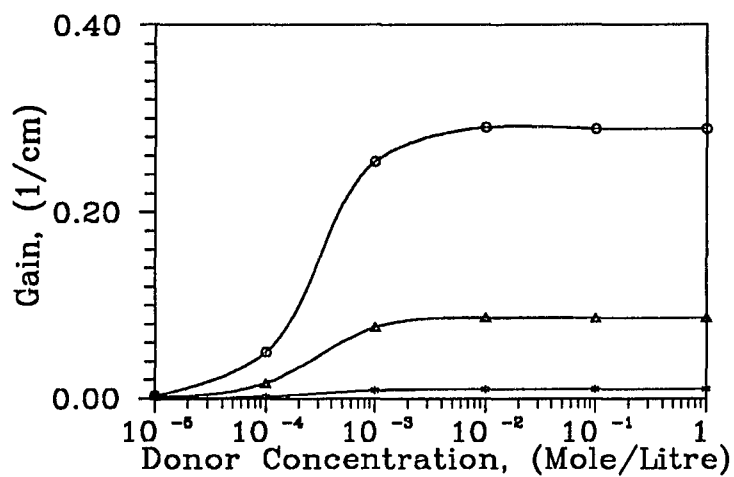


Figure 5-3. Gain of a dye mixture as function of donor concentration at 690 nm.

Simulation Results:  
Gain of Dye Mixture at 700 nm  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



\* \* \* \* \* [A] = 10<sup>-5</sup>  
△ △ △ △ △ [A] = 10<sup>-4</sup>  
○ ○ ○ ○ ○ [A] = 10<sup>-3</sup>

Figure 5-4. Gain of a dye mixture as function of donor concentration at 700 nm.

Simulation Results:  
Gain of Dye Mixture at 710 nm  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser

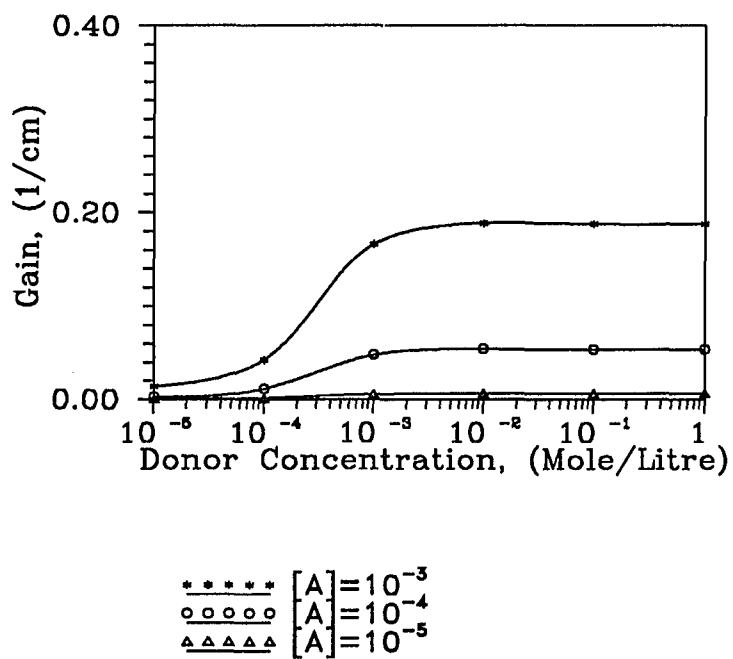


Figure 5-5. Gain of a dye mixture as function of donor concentration at 710 nm.

Simulation Results:  
Gain of Dye Mixture at 720 nm  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser

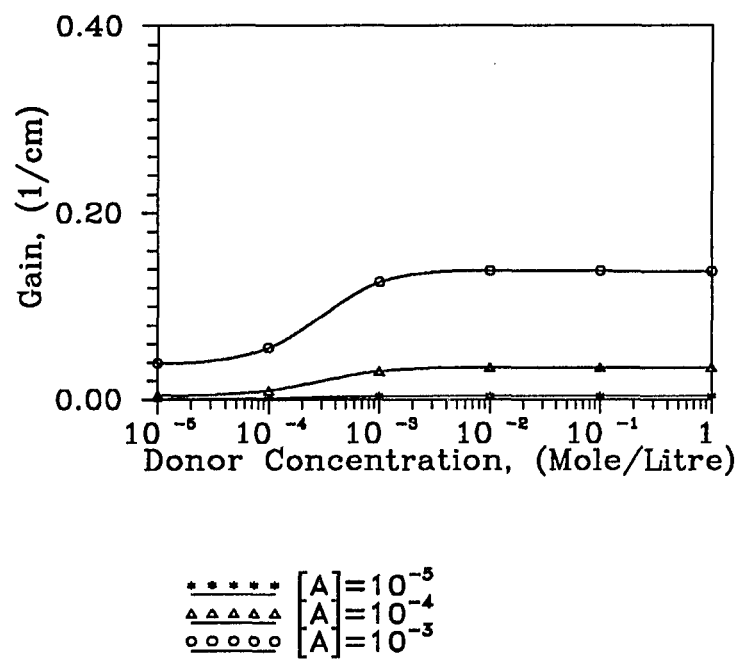


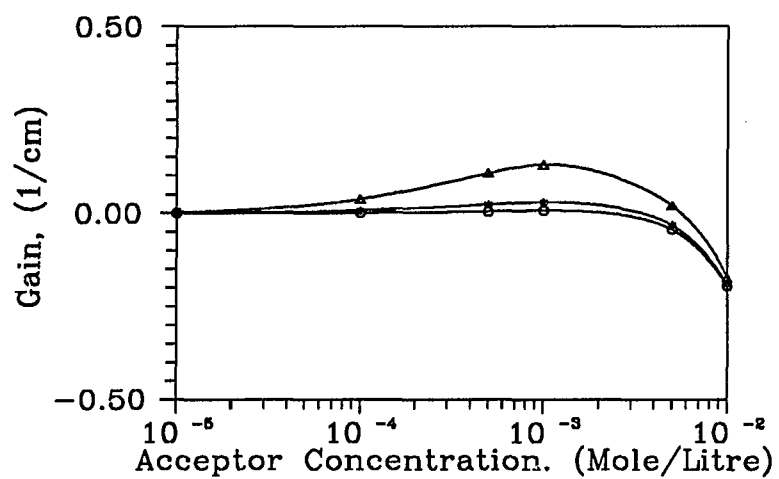
Figure 5-6. Gain of a dye mixture as function of donor concentration at 720 nm.

### 5.1.2 Gain of Dye Mixture as Function of Acceptor Concentration

In this section we examine the effect of acceptor concentration on the dye mixture gain. Numerical simulations were carried out using the exact expression 4-48. Fig. 5-7 to Fig. 5-11 show the dependence of the on axis single pass gain,  $g_0$ , on the acceptor concentration for five wavelengths, 680, 690, 700, 710, 720 nm, and for three values of acceptor concentration,  $10^{-3}$ ,  $10^{-4}$ ,  $10^{-5}$  Mole/Litre. The results show a clear peak of the dye mixture gain as function of acceptor concentration. Comparison of the results in Figures 5-7 to 5-11, shows that maximum gain occurs around 700 nm and for approximate concentrations of  $10^{-2}$  and  $10^{-3}$  Mole/Litre of donor and acceptor, respectively.

These calculations were repeated again, with, however, the approximate expression of Eq. 4-50 replacing the exact expression of Eq. 4-48. As expected, essentially the same results were obtained. This indicates that the simpler expression of Eq. 4-50 represents a reasonable and practically useful approximation.

Simulation Results:  
Gain of Dye Mixture at 680 nm  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



\*\*\*\*\* [D] = 10<sup>-4</sup>  
△△△△△ [D] = 10<sup>-2</sup>  
○○○○○ [D] = 10<sup>-0</sup>

Figure 5-7. Gain as function of acceptor concentration at 680 nm.

Simulation Results:  
Gain of Dye Mixture at 690 nm  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser

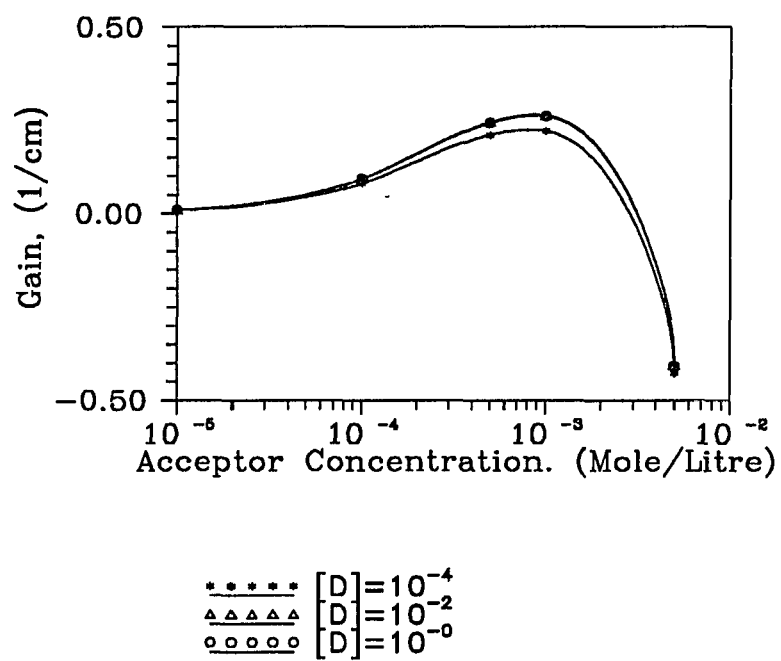


Figure 5-8. Gain as function of acceptor concentration at 690 nm.

Simulation Results:  
Gain of Dye Mixture at 700 nm  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser

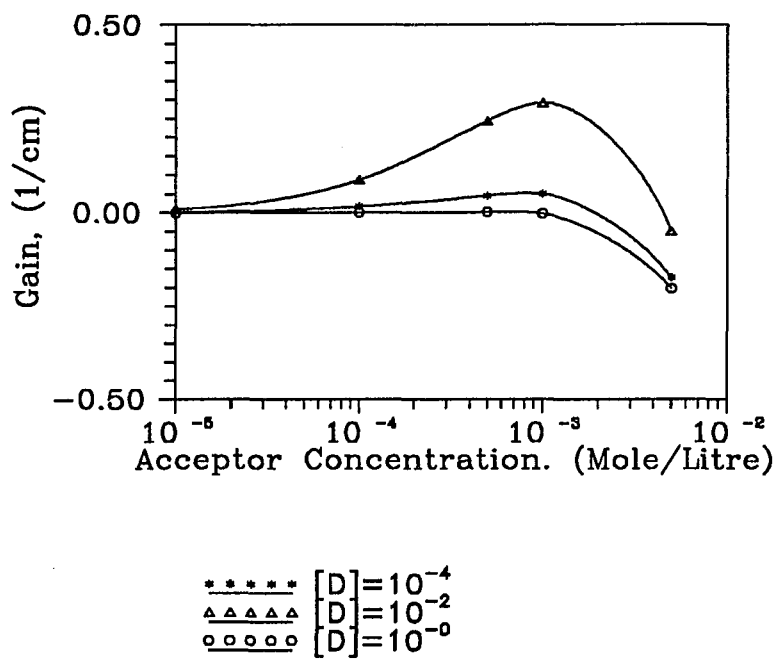


Figure 5-9. Gain as function of acceptor concentration at 700 nm.

Simulation Results:  
Gain of Dye Mixture at 710 nm  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser

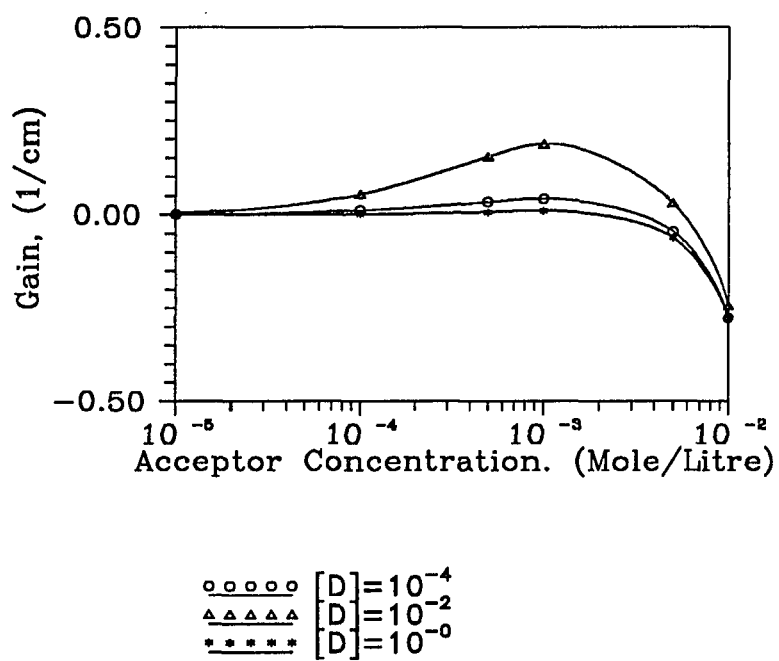
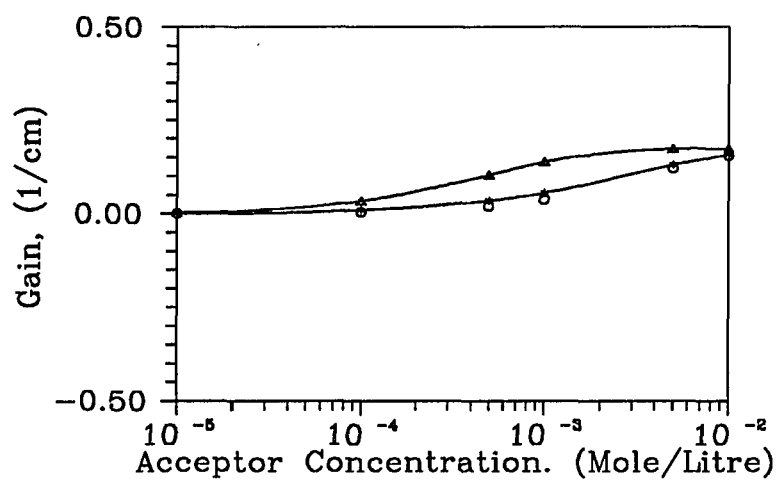


Figure 5-10. Gain as function of acceptor concentration at 710 nm.

Simulation Results:  
Gain of Dye Mixture at 720 nm  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



\*\*\*\*\*)  $[D] = 10^{-4}$   
\*\*\*\*\*  $[D] = 10^{-2}$   
\*\*\*\*\*  $[D] = 10^{-0}$

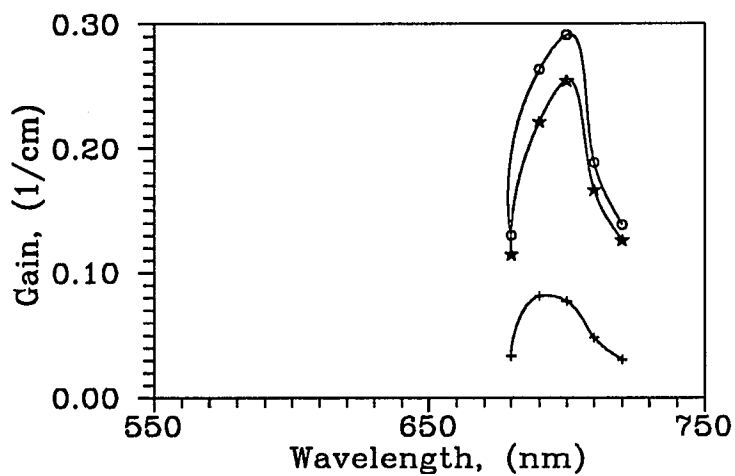
Figure 5-11. Gain as function of acceptor concentration at 720 nm.

### 5.1.3 Gain of Dye Mixture as Function of Wavelength

The wavelength dependence of the dye mixture gain gives valuable information for the attainable range and optimum operating wavelength of a cw ETDL. Fig. 5-12 shows the wavelength dependence of the on axis single pass gain,  $g_0$ , for a given pair of donor and acceptor concentrations. The results exhibit a clear peak around 700 nm, the expected value of lasing. The results indicate that for a given donor concentration,  $[D]$ , and acceptor concentration,  $[A]$ , there is an optimum value of lasing wavelength,  $\lambda_e$  which corresponds to a maximum value of the dye mixture gain. It can also be seen that the gain of Nile Blue A 690 Perchlorate in the binary solution is higher than that in the neat solution. We note that lasing will occur at this optimum triad of values of donor and acceptor concentrations and emitting wavelength if the assumed values for the triplet state data are correct.

These calculations were repeated again, with, however, the approximate expression of Eq. 4-50 replacing the exact expression of Eq. 4-48. As expected, essentially the same results were obtained. This indicates that the simpler expression of Eq. 4-50 represents a reasonable and practically useful approximation.

Simulation Results:  
 Gain of Dye Mixture  
 Donor: Rhodamine B  
 Acceptor: Nile Blue  
 Solvent: Ethylene Glycol  
 Pump Source: Argon Ion Laser



*****	[D] = 10 <sup>-3</sup>	[A] = 10 <sup>-3</sup>
ooooo	[D] = 10 <sup>-2</sup>	[A] = 10 <sup>-3</sup>
+++++	[D] = 10 <sup>-3</sup>	[A] = 10 <sup>-4</sup>

Figure 5-12. Gain as function of wavelength for different donor and acceptor concentrations.

## 5.2 Experimental Results

A series of experiments were performed in order to verify the validity of the model. We measured the fluorescence of both donor and acceptor alone, and dye mixtures with a variety of donor and acceptor concentrations in the range of 550 to 750 nm. The previous simulation and experimental results were used as a guide for the design and successful operation of the first cw ETDL.

The first phase of experiments consisted of measuring the fluorescence of the donor and acceptor alone as well as a series of pair of dyes mixtures with a variety of donor and acceptor concentrations for the same donor and acceptor. Several pair of dyes were selected in order to examine attainable spectral range, fluorescence output, and energy transfer efficiency. Based on these results, and selection criteria for choice of dyes for different spectral output requirements we selected Rhodamine 610 Perchlorate as donor and Nile Blue 690 Perchlorate as acceptor.

The second phase of experiments consisted on design and realization of a cw ETDL. The results of phase one showed that the selected pair of donor - acceptor was promising of laser action. The donor efficiently absorbed the pumped energy from the argon ion laser, energy was transferred from donor to acceptor efficiently, and the fluorescence of the mixture was greater than that of the acceptor alone in the lasing range of interest. The simulation results determined the optimum triplet of donor and acceptor concentrations and lasing wavelength. Having the above as guide we designed and successfully operated the first continuous wave energy transfer dye laser in the near infrared spectral region using an argon laser as pumping source.

### 5.2.1 Fluorescence Measurements of Single and Mixture Dyes

In this section we describe the fluorescence measurement experiments of the donor and acceptor alone, and dye mixtures. The experimental setup used for fluorescence measurements is shown in Fig. 5-13.

The Coherent model CR-999 argon ion laser was used as the pump source. This laser gives maximum output power 4W. The sample dye cell had dimensions 1x1x2 cm approximately. The cell was pumped with approximately 30 mW argon green power which was monitored and kept constant using a power meter. A Jarrel Ash 82-020 spectrometer was used to monitor the fluorescence intensity distribution of the samples from the plastic cell. The fluorescence radiation was collected with an appropriate set up consisting of a series of two lenses, into the input slot of the spectrometer. A greater amount of the collected fluorescence increases the reading sensitivity of the phase lock in amplifier. To avoid error due to different cell material, we used the same cell for all experiments. The spectrometer was equipped with a photomultiplier, RCA 6217, which was converting the light output into a corresponding voltage. Because the wide range of wavelength measurements we found necessary to use a calibration curve for correction of the results. The numerical results in arbitrary scale were provided by a lock in amplifier which was fed with the outputs of photomultiplier and a beam chopper.

Fig. 5-14 shows the calibration curve of the photomultiplier RCA 6217. Its sensitivity is decreasing, almost linearly, as function of wavelength and for the range of 550 to 750 nm. Because the previous range is the range of interest, the use of the calibration curve was necessary for correction of the readings.

Fig. 5-15 to Fig. 5-18 present the fluorescence results of the donor alone, Rhodamine 610, and for the range of 550 to 650 nm. As pump source we used the argon ion laser described before. To perform the series of experiments we used the setup described before. Ethylene Glycol was used as solvent. From the experimental data we see that the fluorescence of the donor alone is function of wavelength and dye concentration. We observe that there is a dyad of values, dye concentration and wavelength, that presents a clear peak fluorescence intensity. The peak value as function of both the emitting wavelength and dye concentration occurs at 590 nm and  $2 \times 10^{-4}$  Mole/Litre.

Fig. 5-15 to Fig. 5-18 present the fluorescence results of the acceptor alone, Nile Blue 690, and for the range of 650 to 750 nm. As pump source we used an argon ion laser. To perform the series of experiments we used the setup described before. As solvent we used Ethylene Glycol. From the experimental data we concluded that the fluorescence of the donor alone is function of wavelength and dye concentration. There is a dyad of values, dye concentration and wavelength, that presents a clear peak fluorescence intensity. The concentration of the dye has a small effect on the fluorescence intensity compared with the donor dye. This is mainly due to the fact the acceptor's absorption band does not coincide well with the pumping source emitting source. The peak value as function of both the emitting wavelength and dye concentration was found to occur at 680 nm and  $2 \times 10^{-3}$  Mole/Litre.

Fig. 5-19 to Fig. 5-22 present the fluorescence intensity of many pairs of donor and acceptor dye concentrations, Rhodamine 610 and Nile Blue 690 respectively, for the range of 550 to 750 nm. As pump source we used an argon ion laser. To perform the series of experiments we used the setup described before. As solvent we used

Ethylene Glycol. We were able to do the following useful conclusions based on the experimental results:

- the fluorescence intensity of the donor and acceptor pair of mixtures depend strongly on the triad of donor concentration, acceptor concentration and the emitting wavelength.
- comparison of the donor fluorescence alone in the mixture shows that the donor fluorescence intensity in dye mixture is less than that of the donor alone, for the same donor concentration.
- comparison of the acceptor fluorescence alone in the mixture shows that the acceptor fluorescence intensity in the mixture is much greater than that of the acceptor alone, for the same acceptor concentration.

It is obvious from the last two statements that the acceptor, Nile Blue 690, was benefited from a such mixture because it presents an increase of its fluorescence intensity. At the same time the intensity of the donor has been decreased showing transfer of energy from donor to acceptor. The results show a promising dye mixture for lasing in the acceptor fluorescence range, near infrared, while pumping in the donor absorption range, in the blue - green range. Using this method of energy transfer we can succeed to lase dyes from a given pump source that otherwise would be impossible.

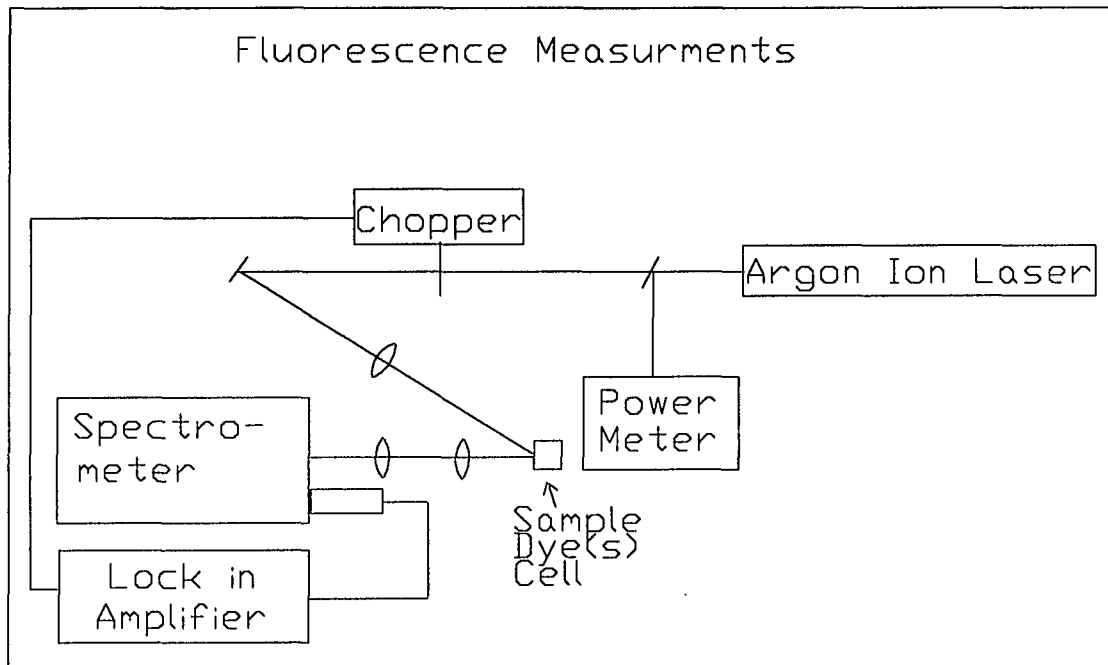


Figure 4-13. Experimental setup for fluorescence measurements.

Relative Calibration Curve for  
Jarrel Ash Spectrometer 82-020  
and Photomultiplier RCA-6217

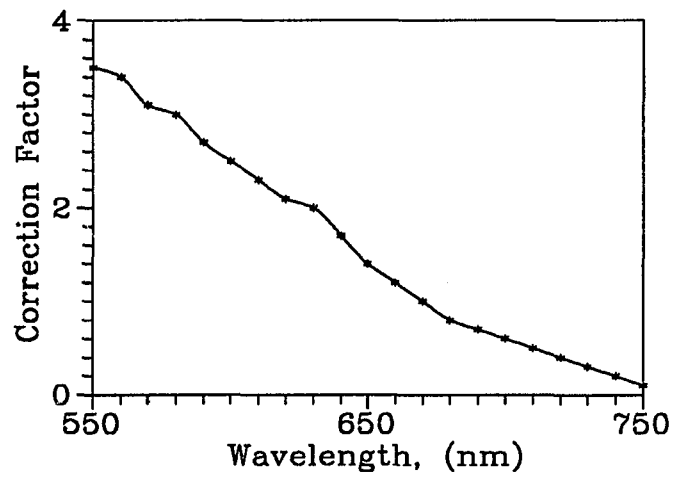
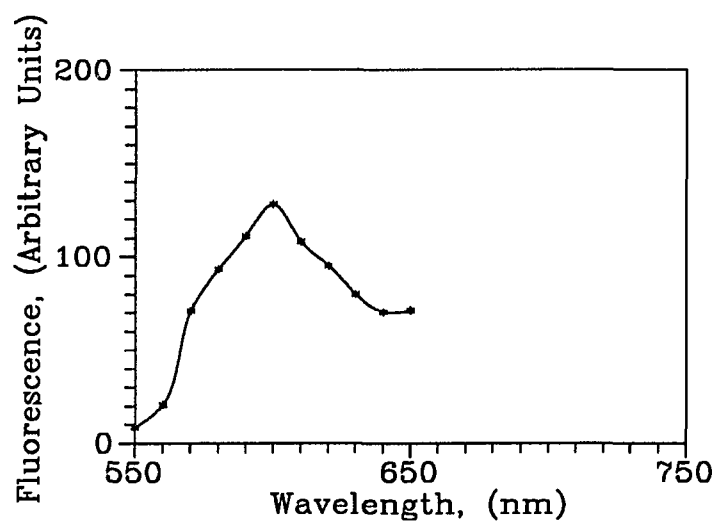


Figure 4-14. Calibration curve for the spectrometer used.

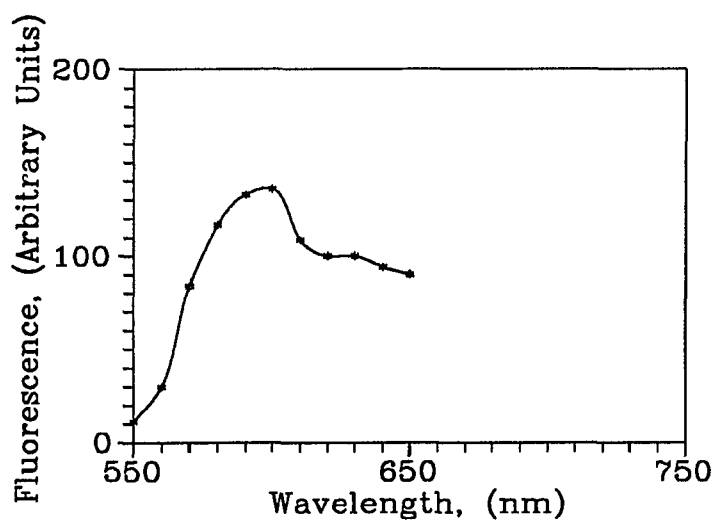
Experimental Results:  
Fluorescence of Single Dye  
Dye: Rhodamine B  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



\*\*\*\*\*  $2 \times 10^{-2}$  Mole/Litre

Figure 4-15. Fluorescence of donor alone.

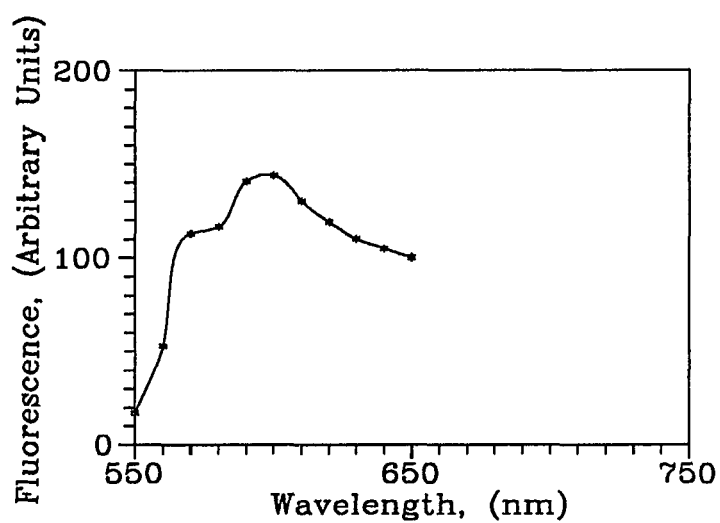
Experimental Results:  
Fluorescence of Single Dye  
Dye: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



\*\*\*\*\*  $2 \times 10^{-3}$  Mole/Litre

Figure 4-16. Fluorescence of donor alone.

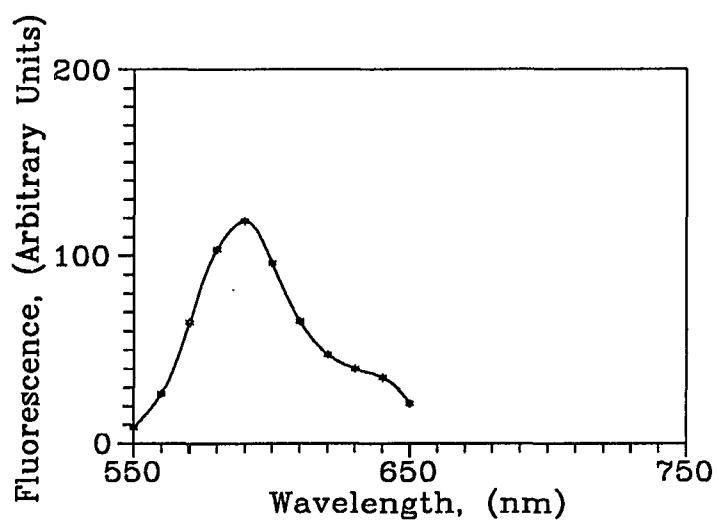
Experimental Results:  
Fluorescence of Single Dye  
Dye: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



.....  $2 \times 10^{-4}$  Mole/Litre

Figure 4-17. Fluorescence of donor alone.

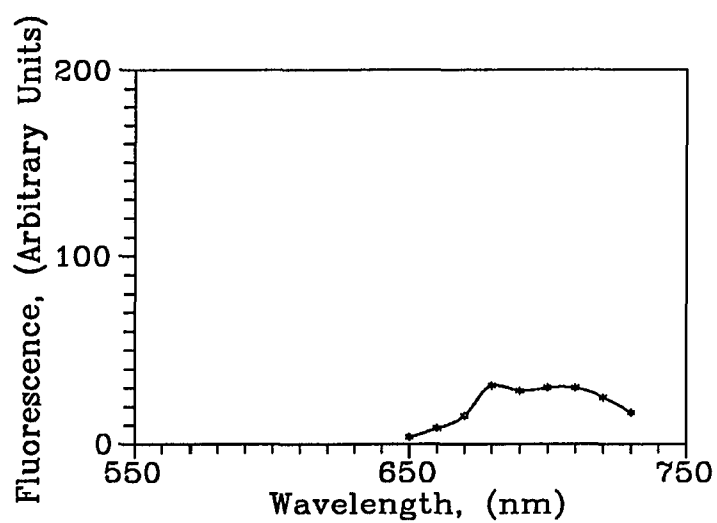
Experimental Results:  
Fluorescence of Single Dye  
Dye: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



\*\*\*\*\*  $2 \times 10^{-5}$  Mole/Litre

Figure 4-18. Fluorescence of donor alone.

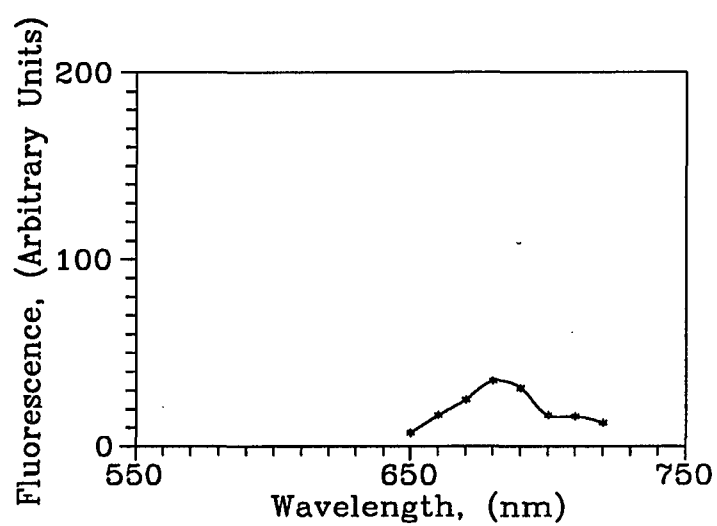
Experimental Results:  
Fluorescence of Single Dye  
Dye: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



.....  $2 \times 10^{-2}$  Mole/Litre

Figure 4-19. Fluorescence of acceptor alone.

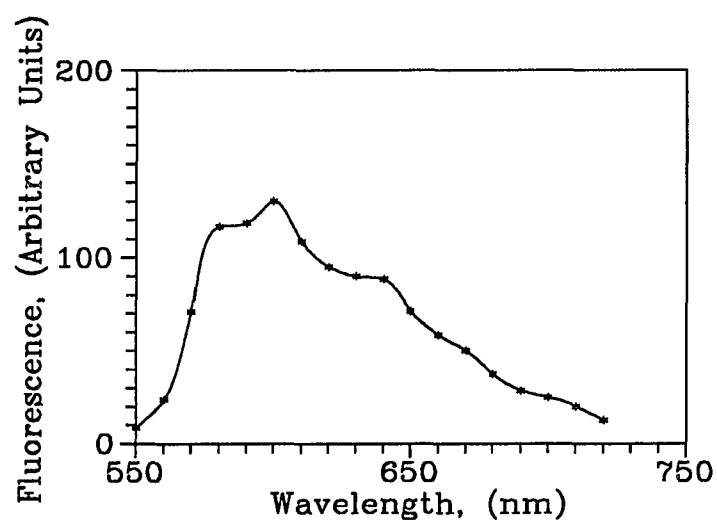
Experimental Results:  
Fluorescence of Single Dye  
Dye: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



\*\*\*\*\*  $2 \times 10^{-3}$  Mole/Litre

Figure 4-20. Fluorescence of acceptor alone.

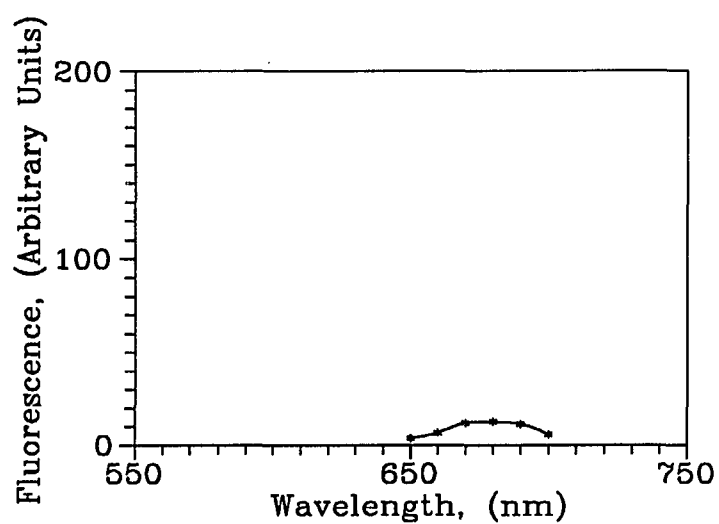
Experimental Results:  
Fluorescence of Single Dye  
Dye: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



.....  $2 \times 10^{-4}$  Mole/Litre

Figure 4-21. Florescence of acceptor alone.

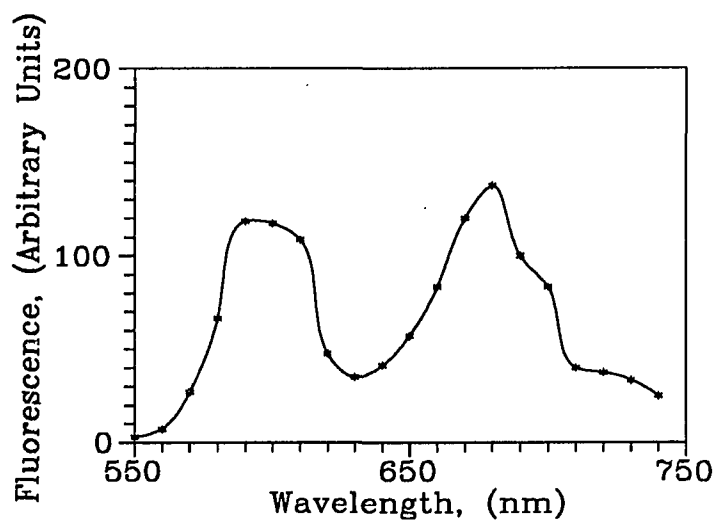
Experimental Results:  
Fluorescence of Single Dye  
Dye: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



.....  $2 \times 10^{-5}$  Mole/Litre

Figure 4-22. Florescence of acceptor alone.

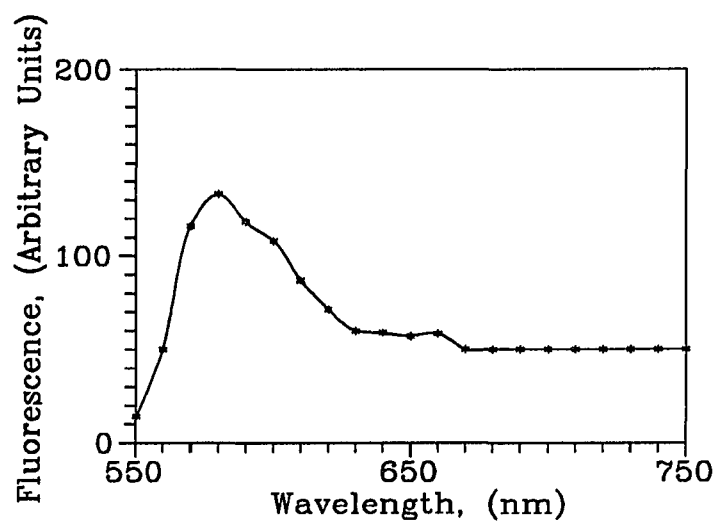
Experimental Results:  
Fluorescence of a Single Dye  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



\*\*\*\*\*  $[D]=10^{-2}$  Mole/Litre  
 $[A]=10^{-2}$  Mole/Litre

Figure 4-23. Fluorescence of dye mixture.

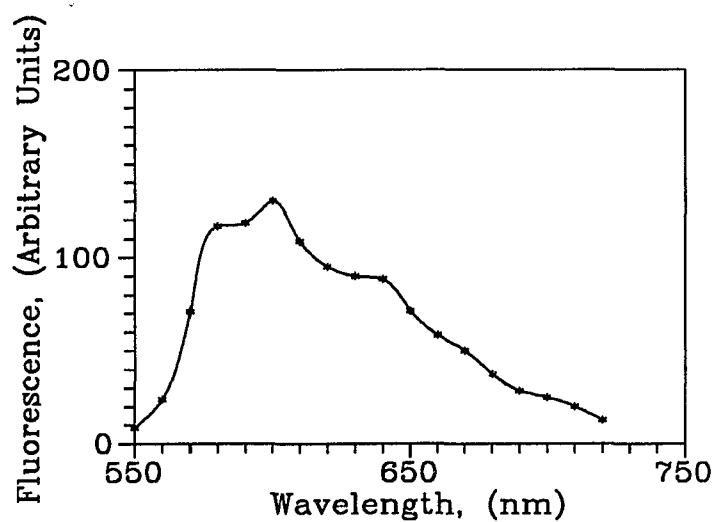
Experimental Results:  
Fluorescence of a Single Dye  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



\*\*\*\*\* [D] =  $10^{-2}$  Mole/Litre  
          [A] =  $10^{-3}$  Mole/Litre

Figure 4-24. Fluorescence of dye mixture.

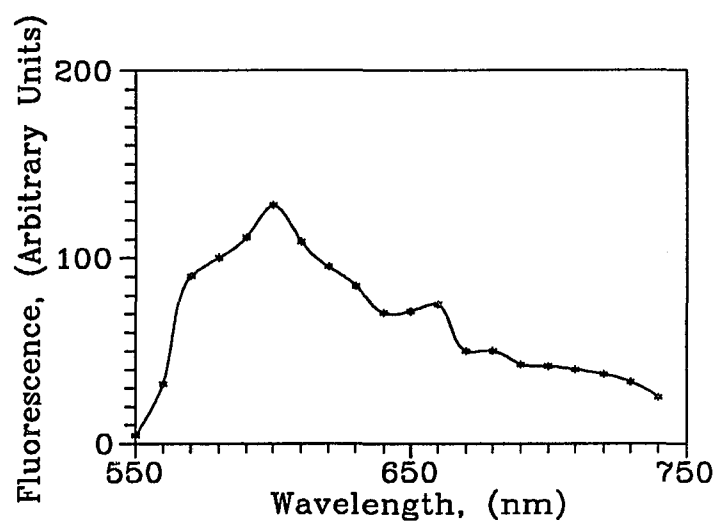
Experimental Results:  
Fluorescence of Dye Mixture  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



\*\*\*\*\*  $[D]=10^{-2}$  Mole/Litre  
 $[A]=10^{-4}$  Mole/Litre

Figure 4-25. Fluorescence of dye mixture.

Experimental Results:  
Fluorescence of Dye Mixture  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



.....  $[D]=10^{-2}$  Mole/Litre  
 $[A]=10^{-5}$  Mole/Litre

Figure 4-26. Florescence of dye mixture.

Experimental Results:  
Fluorescence of Dye Mixture  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser

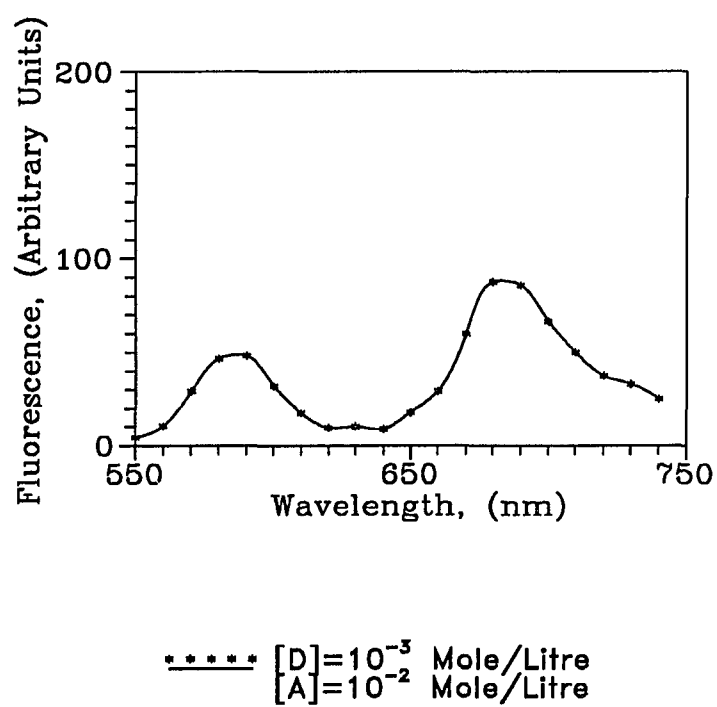
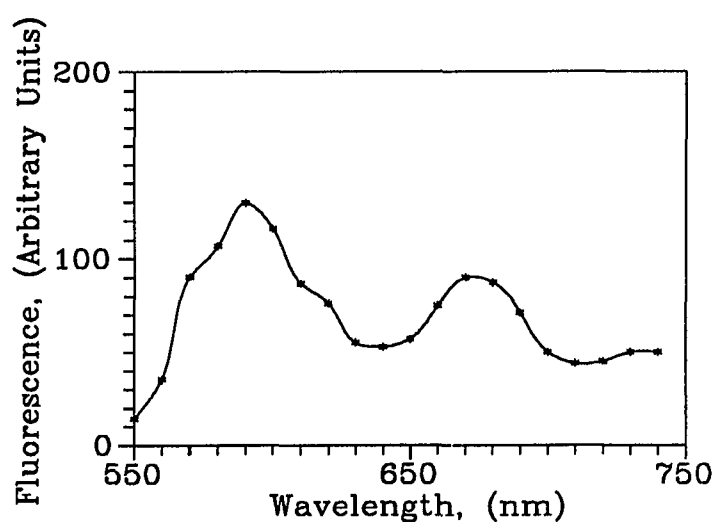


Figure 4-27. Florescence of dye mixture.

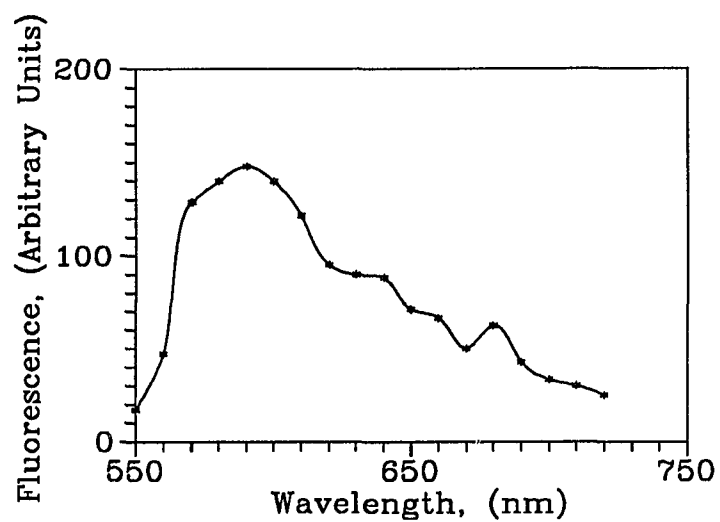
Experimental Results:  
Fluorescence of Dye Mixture  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



\*\*\*\*\*  $[D]=10^{-3}$  Mole/Litre  
 $[A]=10^{-3}$  Mole/Litre

Figure 4-28. Fluorescence of dye mixture.

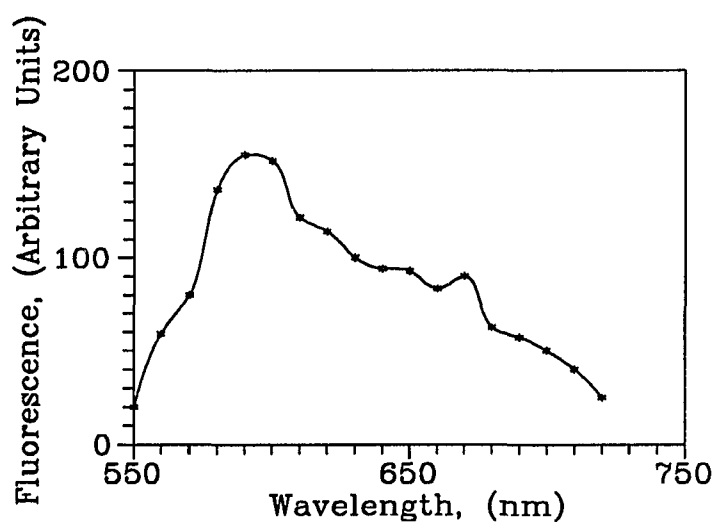
Experimental Results:  
Fluorescence of Dye Mixture  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



\*\*\*\*\*  $[D]=10^{-3}$  Mole/Litre  
 $[A]=10^{-4}$  Mole/Litre

Figure 4-29. Florescence of dye mixture.

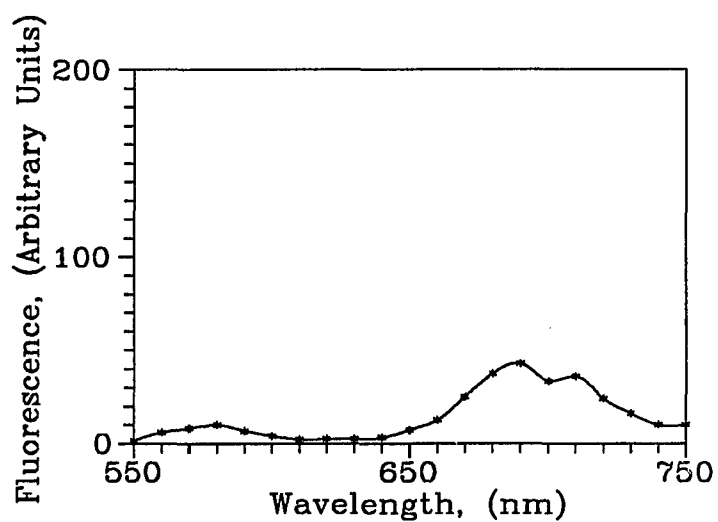
Experimental Results:  
Fluorescence of Dye Mixture  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



\*\*\*\*\*  $[D]=10^{-5}$  Mole/Litre  
 $[A]=10^{-5}$  Mole/Litre

Figure 4-30. Fluorescence of dye mixture.

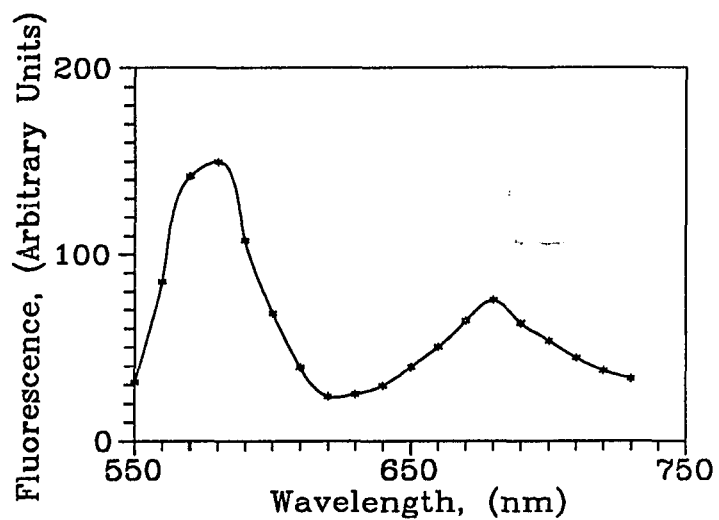
Experimental Results:  
Fluorescence of Dye Mixture  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



\*\*\*\*\*  $[D]=10^{-4}$  Mole/Litre  
 $[A]=10^{-2}$  Mole/Litre

Figure 4-31. Fluorescence of dye mixture.

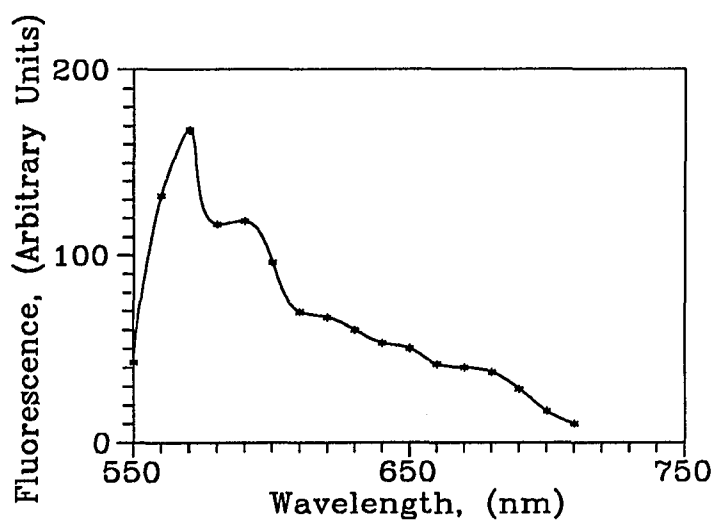
Experimental Results:  
Fluorescence of Dye Mixture  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



\*\*\*\*\*  $[D]=10^{-4}$  Mole/Litre  
 $[A]=10^{-3}$  Mole/Litre

Figure 4-32. Fluorescence of dye mixture.

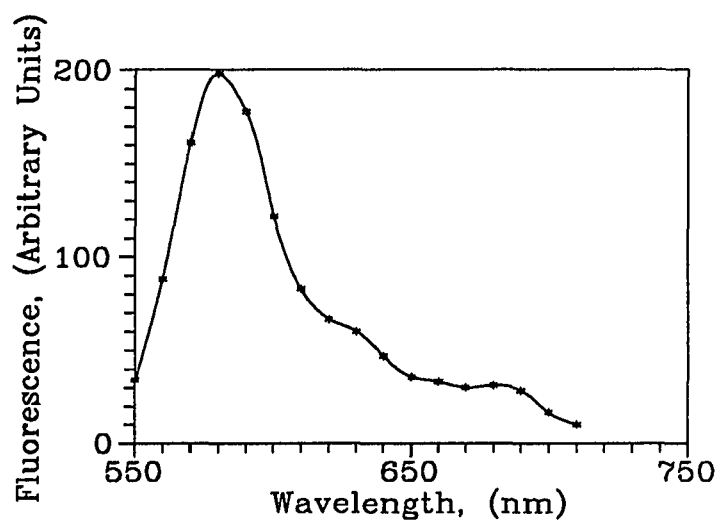
Experimental Results:  
Fluorescence of Dye Mixture  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



\*\*\*\*\*  $[D]=10^{-4}$  Mole/Litre  
 $[A]=10^{-4}$  Mole/Litre

Figure 4-33. Fluorescence of dye mixture.

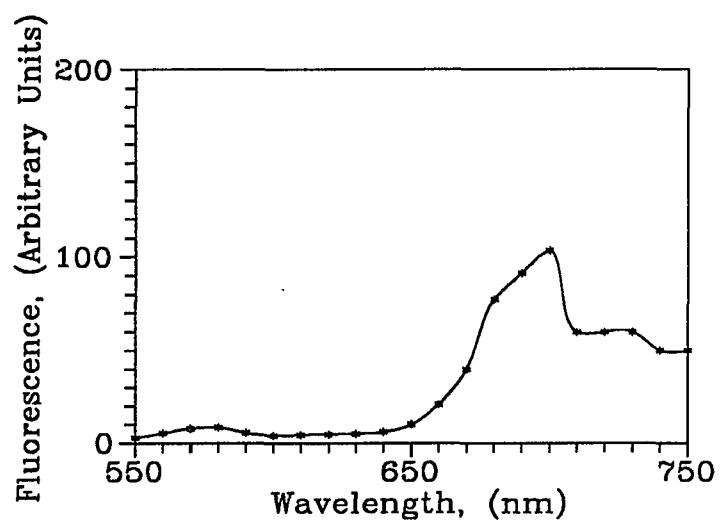
Experimental Results:  
Fluorescence of Dye Mixture  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



\*\*\*\*\*  $[D]=10^{-4}$  Mole/Litre  
 $[A]=10^{-5}$  Mole/Litre

Figure 4-34. Fluorescence of dye mixture.

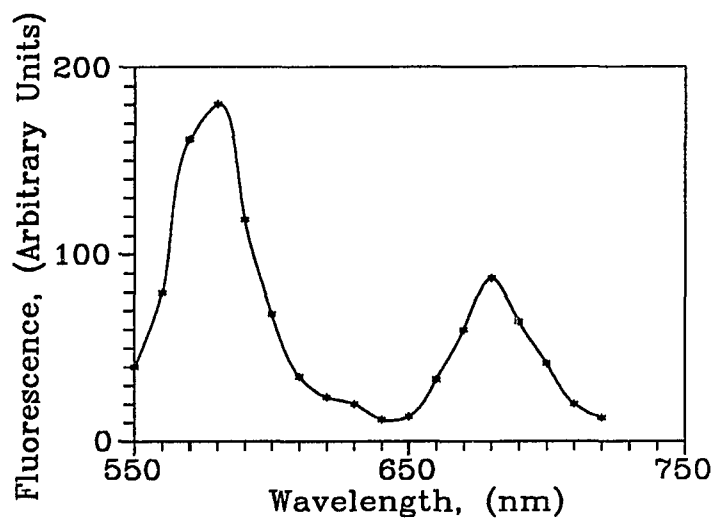
Experimental Results:  
Fluorescence of Dye Mixture  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



\*\*\*\*\*  $[D]=10^{-5}$  Mole/Litre  
 $[A]=10^{-2}$  Mole/Litre

Figure 4-35. Fluorescence of dye mixture.

Experimental Results:  
Fluorescence of Dye Mixture  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



\*\*\*\*\*  $[D]=10^{-5}$  Mole/Litre  
 $[A]=10^{-3}$  Mole/Litre

Figure 4-36. Fluorescence of dye mixture.

Experimental Results:  
Fluorescence of Dye Mixture  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser

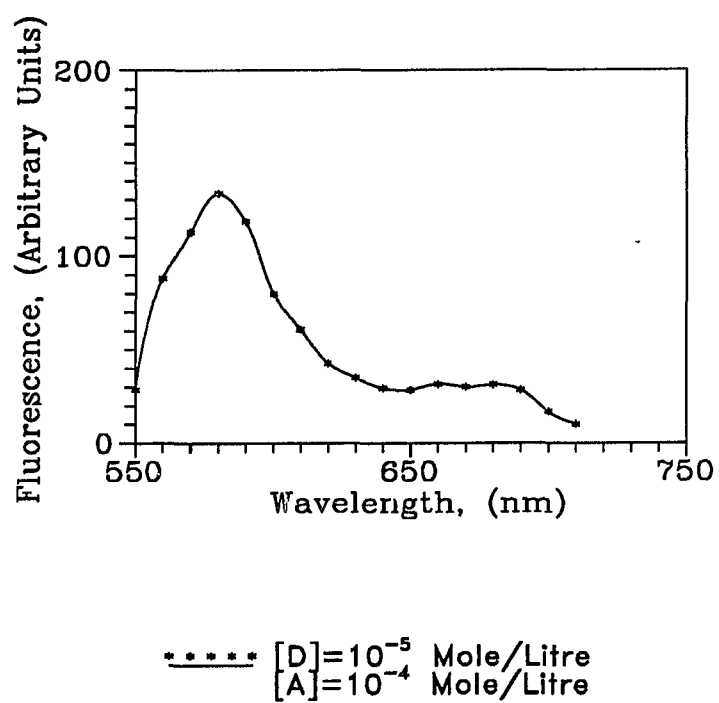
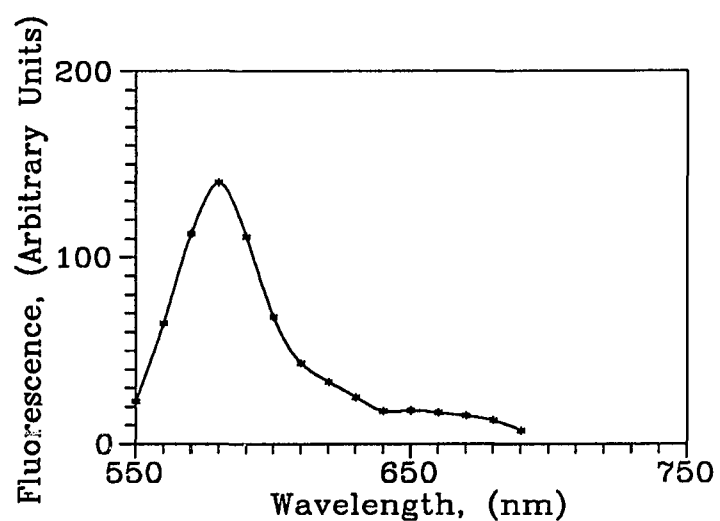


Figure 4-37. Fluorescence of dye mixture.

Experimental Results:  
Fluorescence of Dye Mixture  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



..... [D] =  $10^{-5}$  Mole/Litre  
[A] =  $10^{-5}$  Mole/Litre

Figure 4-38. Fluorescence of dye mixture.

### **5.2.2 Realization of a CW Energy Transfer Dye Laser**

The final and conclusive part of this work was the realization of the proposed scheme for a cw ETDL. To realize a cw ETDL we took into account our simulation and experimental results for the optimum operational conditions of the cw ETDL. We successfully demonstrated the operation of a cw ETDL for first time, [13]. The experimental setup used is shown in Fig 4-39

The pump source was an argon ion laser, Coherent model Innova 70. This laser is designed for a broad range of applications requiring reliable continuous wave laser light in the blue and green regions of the visible spectrum. The system uses an exceptionally stable resonator and the metal ceramic tube design which makes it an ideal tool for use in research and industry. The laser head and power supply are separate units. This argon ion laser is capable of delivering a maximum output power of 4 W in the blue-green region. All available power was used to pump the dye laser mixture.

The dye laser, model CR 590, was used for a mixture operation with Rhodamine 610 Perchlorate as donor, and Nile Blue 690 Perchlorate as acceptor. The dye mixture was flowing continuously and cooled using the pump and water cooling system provided with the dye laser by Coherent. The dye laser system, CR 599-01, consist of a dye laser head and a utility module. The optical schematic for the dye laser cavity is given in Fig. 4-40. All components are mounted to a 2" diameter Invar rod for stability. The basic configuration is an astigmatic three mirror cavity. The pump beam is focused on the dye in a direction not collinear with the laser mode by broadband reflecting mirror. The jet stream which is inserted at Brewster angle

compensates for the astigmatism introduced by the use of the of axis mirror. The jet stream is normally 1/4 mm thick, 1-1/2 mm wide and flows at 7 m/s. The TEM<sub>00</sub> mode of the dye laser is similar in appearance to that of a gas laser. The laser head consists of a 2" solid bar of low thermal expansion Invar which acts as an optical bench for the components of the dye laser. The Invar rod is convenient for mounting intracavity accessories such as etalons for single frequency operation. There are orthogonal position and angular controls for the pump beam focusing mirror, jet stream, and cavity reflectors. To operate the dye laser in the near infrared, we found necessary to change the cavity mirrors.

A Jarrel Ash 82-020 spectrometer was used to monitor the output fluorescence and lasing wavelength. The spectrometer used for measuring the wavelength of the fluorescence beam was equipped with an RCA 6217 photomultiplier which was converting the light output into a corresponding voltage. The numerical results were provided by a lock in amplifier which was fed with the outputs of photomultiplier and a beam chopper.

The following method was used to obtain lasing from the dye mixture:

- The donor and acceptor concentrations were increasing continuously, up to the expected values of  $5 \times 10^{-3}$  and  $10^{-3}$  Mole/Litre respectively.
- For every pair of donor and acceptor concentrations the laser cavity was aligned and tuned peak for maximum on axis fluorescence at the expecting lasing wavelength. Eventually laser action at 714 nm was successfully obtained at  $5 \times 10^{-3}$  and  $10^{-3}$  Mole/Litre donor and acceptor concentrations. The first experimental result are tabulated in Table 5-7, [14].

Fig. 4-41 shows the simulation results of dye mixture gain for donor and acceptor

concentrations of  $5 \times 10^{-3}$  and  $10^{-3}$  Mole/Litre, respectively. The maximum gain occurs at 700 nm.

Fig. 4-42 shows the on axis fluorescence of dye mixture gain for donor and acceptor concentrations of  $5 \times 10^{-3}$  and  $10^{-3}$  Mole/Litre, respectively, just before the generation of laser radiation.

Fig. 4-43 presents the distribution of lasing output power as function of wavelength. The maximum output occurs at 714 nm.

For comparison, Figure 4-44 presents the laser output as function of wavelength as well as the numerical simulation results for the dye mixture gain, the experimentally measured on axis fluorescence intensity, for the same donor (Rhodamine 610 Perchlorate) and acceptor (Nile Blue 690 Perchlorate) concentrations of  $5 \times 10^{-3}$  and  $10^{-3}$  Mole/Litre, respectively. On the same Figure, the fluorescence of the single dye solutions for both donor and acceptor, and for the same concentrations as that of the mixture, are shown. We notice that the donor fluorescence in the mixture is less than that of the single donor, while the acceptor fluorescence in the mixture has been increased dramatically compared to that of the single acceptor.

To perform the series of experiments we used the setup described before. As solvent we used Ethylene Glycol. Comparison of the results shows a successful modeling as we were able to predict accurately the donor and acceptor concentrations and lasing wavelength for the selected pair of dyes. The acceptor, Nile Blue 690, was able to lase in the near infrared in a dye mixture, while getting energy from the donor which was pumped by a argon ion laser. The successful operation was based in the principle of energy transfer in dye mixtures.

<b>TABLE 5-7</b> <b>Experimental Results of a Continuous Wave Energy Transfer Dye Laser</b>
Donor: Rhodamine 610 Perchlorate, $5 \times 10^{-3}$ Mole/Litre
Acceptor: Nile Blue 610 Perchlorate, $10^{-3}$ Mole/Litre
Solvent: Ethylene Glycol
Input Source: Argon Ion Laser, 4 W
Maximum Output Power: 20 mW
Wavelength at Maximum Output Power: 714 nm

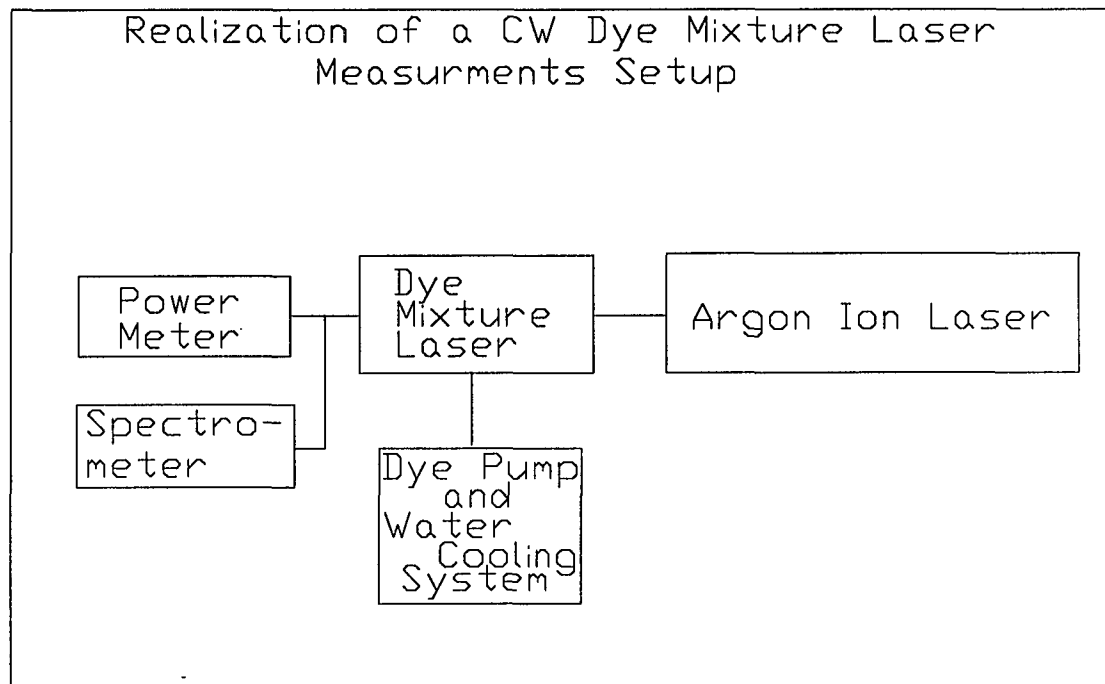


Figure 5-39. Experimental setup for the realization of a cw ETDL and measurements.

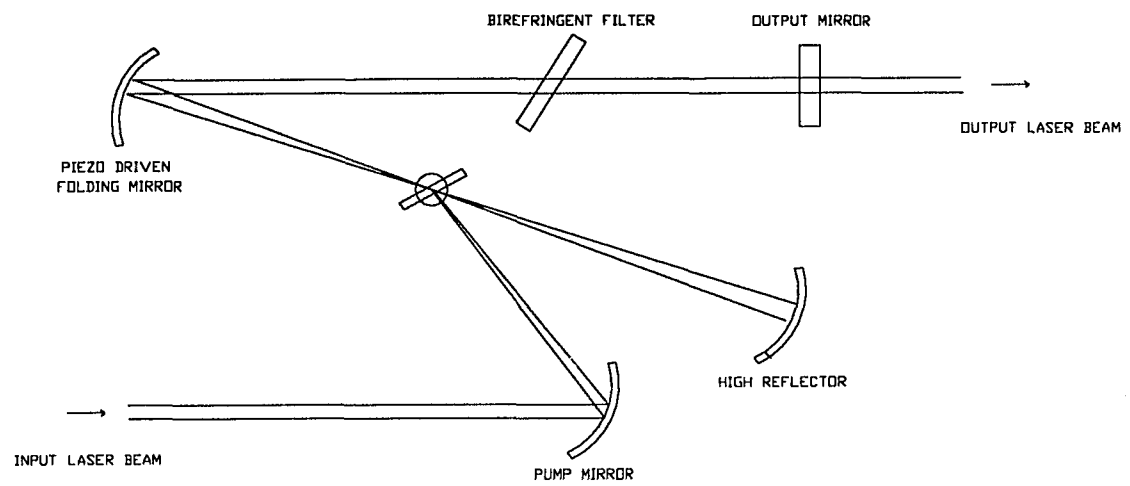
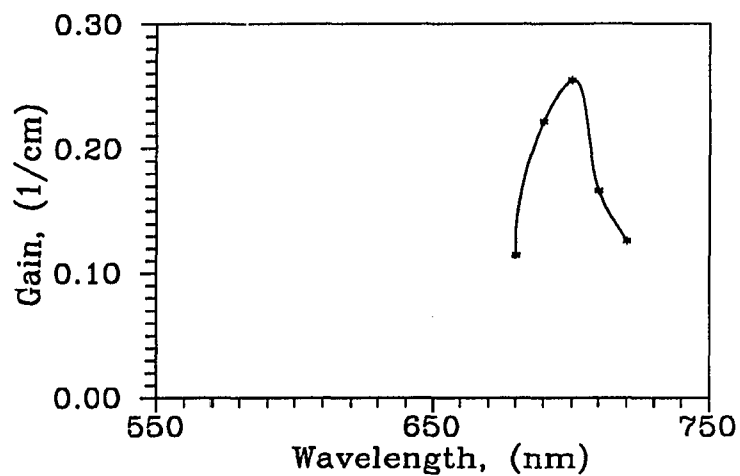


Figure 5-40. Optical schematic of the dye laser cavity.

Simulation Results:  
Gain of Dye Mixture  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



\*\*\*\*\*  $[D]=5 \times 10^{-3}$  (Mole/Litre)  
 $[A]=1 \times 10^{-3}$  (Mole/Litre)

Figure 5-41. Dye mixture gain for the operational cw ETDL.

Fluorescence of Dye Mixture:  
Donor: [Rhodamine B] =  $10^{-3}$  (Mole/Litre)  
Acceptor: [Nile Blue] =  $10^{-3}$  (Mole/Litre)  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser

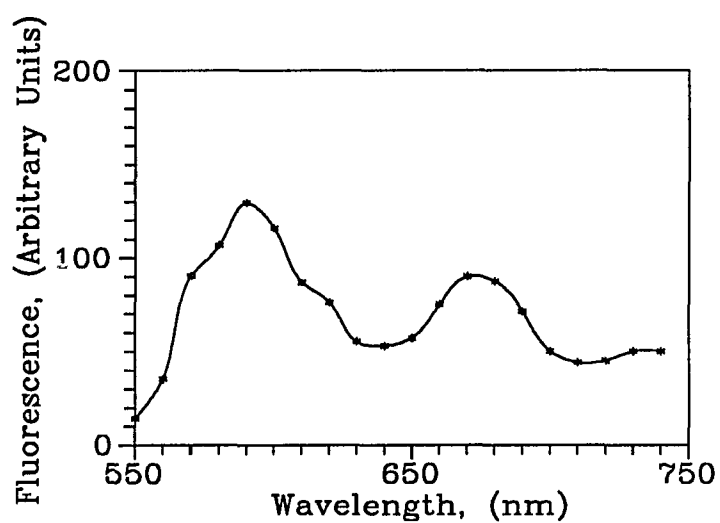
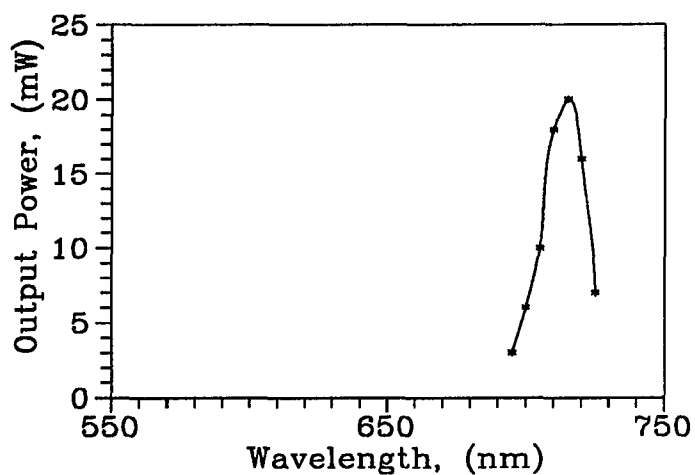


Figure 5-42. Dye mixture fluorescence for the operational cw ETDL.

Experimental Results:  
Output Power as Function of Wavelength  
for a Dye Mixture  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser



\*\*\*\*\*  $[D]=5 \times 10^{-3}$  Mole/Litre  
 $[A]=1 \times 10^{-3}$  Mole/Litre

Figure 5-43. Dye mixture laser output power for the operational cw ETDL.

Comparison of Simulation,  
and Experimental Results:  
Donor: Rhodamine B  
Acceptor: Nile Blue  
Solvent: Ethylene Glycol  
Pump Source: Argon Ion Laser  
[D]= $5 \times 10^{-3}$  Mol/Lit, [A]= $10^{-3}$  Mol/Lit

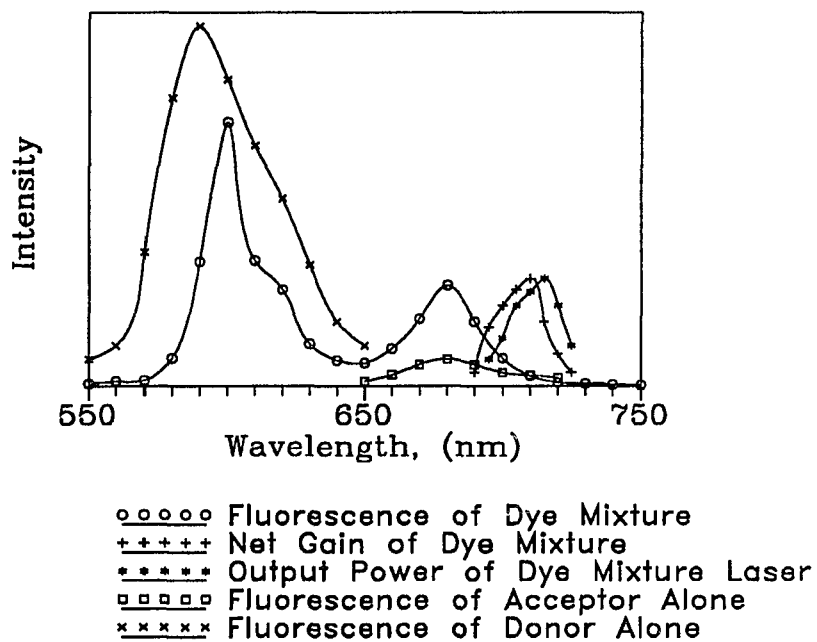


Figure 5-44. Comparison of simulation and experimental results.

### 5.3 References

1. Urisu, Tsuneo and Kenji Kajiyama. *Concentration Dependence of the Gain Spectrum in Energy-Transfer Dye Mixtures*. J. Appl. Phys., Vol. 47, No 8, pp. 3563-3565, 1976.
2. Shammai, Speiser and Reuven. *Computer Simulation of an Energy Transfer Dye Laser*. Optics Comm., 27, 287-291, 1978.
3. Dienes, A., and M. Madden. *Study of Excitation Transfer in Dye Mixtures by Measurements of Gain Spectra*. J. App. Phys., 44, 4161-4164, 1973.
4. Snavely, B. B., *Continuous Wave Dye Lasers in Dye Lasers, (Topics in Applied Physics)* Schafer, F. P. (Ed.), Berlin: Springer-Verlag, 1973.
5. Teschke, O., Andrew Dines, and John R. Whinnery. *Theory and Operation of High-Power CW and Long-Pulse Dye Lasers*. IEEE J. Quantum Electronics, QE-12, 383-395 (1976).
6. Peterson, O. G., J. P. Webb, W. C. McColgin and J. H. Eberly. *Organic Dye Laser Threshold*. J. Appl. Phys. Letters, Vol. 42, p. 1917, 1971.
7. Lin, Chinlon and A. Dienes. *Study of Excitation Transfer in Laser Dye Mixtures by Direct Measurements of Fluorescence Lifetime*. J. App. Phys., 44, 5050-5052, 1973.
8. Sebastain P. J., and K. Sathianandan. *Donor Concentration Dependence of the Emission Peak in Rhodamine 6G - Rhodamine B Energy Transfer Dye Laser*. Optics Comm., 35, pp. 113-114, 1980.
9. Lu, P. Y., Z. X. Yu, R. R. Alfano and J. I. Gersten. *Picosecond Studies of Energy Transfer of Donor and Acceptor Dye Molecules in Solution. II. A Concentration Dependence*. Physical Review A, Vol. 26, p. 3610, 1982.
10. Lu, P. Y., Z. X. Yu, R. R. Alfano and J. I. Gersten. *Picosecond Studies of Energy Transfer of Donor and Acceptor Dye Molecules in Solution. II. A Concentration Dependence*. Physical Review A, Vol. 27, p. 2100, 1983.
11. Sebastain P. J., and K. Sathianandan. *Energy Transfer Rhodamine 6G - Safranin T Dye laser*. Optics Comm., 32, pp. 422-424, 1980.
12. Birks, J. B., And M. S. C. P. Leite. *Energy Transfer in Organic Systems. IX. Effects of Diffusion on Transfer Efficiency*. J. Phys. B, Vol. 3, p. 513, 1970.
13. Ahmed, S. A., B. Panoutsopoulos, and M. Ali. *Theory, Simulation, and Performance of a cw Energy Transfer Dye Laser*. Submitted in Laser '91 LASERION, International Laser Symposium, Munchen, Germany, June 1991.
14. Panoutsopoulos, B., M. Ali and S. A. Ahmed. *Realization of a Continuous Wave*

*Energy Transfer Dye Mixture Laser in the Near Infrared.* Submitted in Optics Letters.

## 6 Conclusion and Further Work

The basic objective of this work was to develop a theoretical model that will predict the behaviour of cw energy transfer dye mixture lasers. Based on the theoretical model developed, we examined the effects of energy transfer parameters, donor and acceptor concentration, spectra characteristics, laser geometry, and pump source power and wavelength. To select an appropriate pair of dyes, we performed a detailed analysis of many dye pairs and selected two well known dyes, Rhodamine 610 as donor and Nile Blue 690 as acceptor. Following a detailed analysis of the factors affecting the dye gain performance, an ETDL was theoretically modeled using the above pair of dyes, and with numerical simulation we determined the optimum pair of donor and acceptor concentrations and the wavelength for which the dye gain is maximum, with an argon ion laser excitation source. The simulation predicted the operational viability of the system.

The energy transfer approach was used to overcome the limitation of argon ion laser pumped dyes to lase in the near infrared and to extend their applications and versatility. The krypton ion laser is the required pumping source of dyes that lase in the near infrared which is expensive and inefficient compared with the argon ion laser. In the energy transfer approach, two dyes are diluted in the solvent. The dyes are selected such that the donor be able to absorb energy from the pump source and fluorescence in the absorption region of the acceptor, while the acceptor absorbs the energy transferred by the donor, and lases in its fluorescence range. The optimum concentration of the dyes and the lasing wavelength are determined from the numerical simulation.

In conclusion, we have presented a theoretical model which predicts the dependence of the gain spectrum of cw laser pumped energy transfer laser (ETDL) on acceptor and

donor concentrations, as well as energy transfer parameters. Analysis of the relevant gain parameters was also presented. The method developed can be used to govern the performance of cw ETDL by changing one or more of the relevant gain parameters which are contained in the gain equation.

Future application of the model is expected to show that there are many candidate dye pairs which would benefit from such an approach in terms of reduced pump power and increased attainable spectral range. It is expected also to show that the use of the argon ion laser, which is a convenient and widely used pump source, may be practically extended through the use of energy transfer processes to the cw excitation of dyes which would otherwise require excitation at longer wavelengths from a krypton ion laser.

## 7 Bibliography - References

### Bibliography:

Bass, M., T. F. Deutsch, and M. J. Weber. *Dye Lasers*, in *Lasers*, Vol. 3, A. K. Levine and A. J. DeMaria, (Eds.), New York: Marcel Dekker, pp. 274-278, 1971.

Berlman, B. Isadore. *Energy Transfer Parameters of Aromatic Compounds*. New York: Academic Press, 1973.

Bernheim, R. A. *Optical Pumping: An Introduction*. New York: W. A. Benjamin, Inc., 1965.

Birks, John B. *Photophysics of Aromatic Molecules*. London: Wiley-Interscience, 1970.

Brackmann, Ulrich. *Lambdachrome Laser Dyes*. Acton, MA 01720.

Charschan, S. S. (Ed.) *Lasers in Industry*. New York: Van Nostrand Reinhold Company, 1972.

COHERENT. *Innova 70 Series Gas Laser*. 3210 Porter Drive, Palo Alto, CA 94304.

COHERENT. *Model CR-599 Dye Laser*. 3210 Porter Drive, Palo Alto, CA 94304.

Duarte, J. F. and Lloyd W. Hillman (Eds). *Dye Laser Principles - with Applications*. Boston: Academic Press, Inc., 1990.

Exciton. *Laser Dye Catalog*. Exciton Inc. 1989.

Kodak. *Optical Products*. Eastman Kodak Company, New York 14650.

Jarrel Ash Division / Fisher Scientific Co. *Instruction Manual - Spectrometer Model 82000 series*. MA, 02154.

Jodon Engineering Associates, Inc. *Optical Power Meter 450B*. Ann Arbor, Michigan 48103.

Joussot-Dubien, J. (Ed.). *Lasers in Physical Chemistry and Biophysics*. Amsterdam: Elsevier, 1975.

Lakowicz, Joseph R. *Principles of Fluorescence Spectrometry*. New York: Plenum Press, 1986.

Parker, C. A. *Photoluminescence of Solutions*. Amsterdam; Elsevier Publ. Co., 1968.

Princeton Applied Research Co. *Instruction Manual - Precision Lock-in Amplifier, Model HR-8*. Princeton, NJ 08540.

Schafer, F. P. (Ed.). *Dye Lasers. (Topics in Applied Physics)* Berlin: Spinger-Verlag, 1973.

Stamford Research Systems, Inc. *Optical Chopper, Model SR 540*. Sunnyvale, CA 94089.

Statz, H. And G. de Mars. *Transients and Oscillations in Masers*. Quantum Electronics. C. H. Townes (Ed.), New York: Columbia University Press, pp. 530-537, 1960.

Svelto, Orazio. *Principles of Lasers*. Third Edition, New York: Plenum Press, (English Translation), 1989.

Tarasov, L. V. *Lasers Physics*. Moscow: Mir Publishers. (English Translation), 1983.

Wells, C. H. J. *Introduction to Molecular Photochemistry*. London: Chapman and Hall, 1972.

Wolbarsht, M. L. (Ed.). *Laser Applications in Medicine and Biology*. New York: Plenum Press, 1971.

**References:**

Agrest, M. M., S. F. Kilin, M. M. Rikenglaz, and I. M. Rozman. *Transfer of Electronic Excitation Energy in Liquid Solution*. Opt. Spectrosc. (USSR), Vol. 27, p. 514, 1969.

Ahmed, S. A., J. S. Gergerly, and D. Infante. *Energy Transfer Organic Dye Mixture Lasers*. J. Chem. Phys. Vol. 61, p. 1584, 1974.

Ali, M. A., S. A. Ahmed, and A. S. Chokhavatia, *Examination of a Generalized Model for Radiationless Energy Transfer in Dyes*. J. Chem. Phys., Vol. 91, pp. 2892-2897, 1989.

Ali, M., B. Panoutsopoulos, and S. A. Ahmed. *On the Feasibility of Generating CW Argon Pumped Energy Transfer Dye Laser Emission in the Near IR Spectral Region*. App. Opt. Vol. 30, No 3, p. 312, 1991.

Antonov-Romanovski, V. V. and M. D. Galanin. Opt. Spektrosk., Vol. 3, p. 389, 1957.

Bagdasaryan, K. S., and A. L. Muler. *Quantitative Verification of the Theory of Resonance Energy Transfer with Brownian Motion Taken into Account*. Opt. Spectrosc. (USSR), Vol. 18, p. 558, 1965.

Birks, J.B., and Georgious, S., *Energy Transfer in Organic Systems*. V. J. Phys. B, Proc. Phys. Soc., Ser. 2, Vol. 1., pp. 266-273, 1968.

Birks, J. B., and M. S. C. P. Leite. *Energy Transfer in Organic Systems. IX. Effects of Diffusion on Transfer Efficiency*. J. Phys. B, Vol. 3, p. 513, 1970.

Blit, S., E. G. Weaver, T. A. Rabson, F. K. Tittel. *Continuous Wave UV Radiation Tunable from 285 to 400 nm by Harmonic and Sum Frequency Generation*. Appl. Opt., Vol. 17, pp. 721-723. 1978.

Brock, E. G., P. Czavinsky, E. Hormats, H. C. Nedderman, D. Stirpe, and F. Unterleitner. *Coherent Stimulated Emission from Molecular Crystals*. J. Chem. Phys., Vol. 35, pp. 759-760, Aug. 1961.

Brown, F. H., M. Furst, and H. Kallmann. *Light and High Induced Energy Transfer in Liquid and Rigid Organic Scintillators*. Discuss. Faraday Soc., Vol. 27, p. 43, 1959.

Dewey, C. F. Jr. and L. O. Hocker. Appl. Phys. Letters, Vol. 18, p. 58, 1971.

Dienes, A., and M. Madden. *Study of Excitation Transfer in Dye Mixtures by Measurements of Gain Spectra*. J. App. Phys., 44, 4161-4164 1973.

Dunsmuir R. *Theory of Relaxation Oscillations in Optical Masers*. J. Electron Control., Vol. 10, pp. 453-458, 1961.

Foster, Th. *Zwischenmolekulare Energiewanderung und Fluoreszenz*. Ann. Physik., Vol 2, p. 55, 1948.

- Foster, T., Z. Naturforsch. Vol. 4a, p. 321 1949.
- Foster, Th. *Transfer Mechanisms of Electronic Excitation*. Discuss. Faraday Soc., Vol. 27, p. 1, 1959.
- Gibson, A. J. *Flashlamp - pumped Dye Laser for Resonance Scattering Studies of the Upper Atmosphere*. J. Sci. Instrum. J. Phys. E, Ser. 2, Vol. 2, pp. 802-806, Sept. 1969.
- Gosele, U., M. Hauser, U. K. A. Klein, and R. Frey. *Diffusion and Long Range Energy Transfer*. Chem. Phys. Lett., Vol. 34, P. 519, 1975.
- Hamadini, S. M, and G. Magyar. Opt. Commun., Vol. 4, p. 310, 1971.
- Hansch, T. W., I. S. Shahin, and A. L. Schawlow. *High Resolution Saturation Spectroscopy of the Sodium D Lines with a Pulsed Tunable Dye Laser*. Phys. Rev. Lett., Vol. 27, pp. 707-710, Sept. 1971.
- Hansch, T. W., I. S. Shahin, and A. L. Schawlow. *Optical Resolution of the Lamp Shift in Atomic Hydrogen by Laser Saturation Spectroscopy*. Nature, Phys. Sci., Vol. 235, pp. 63-65, Jan. 1972.
- Heller, A. *Liquid Lasers Design of Neodymium Based Inorganic Ionic Systems*. J. Mol. Spectry., Vol. 28, pp. 101-117, Sept. 1968.
- Heller, A. *Liquid Lasers Fluorescence Absorption and Energy Transfer of Rare Earth Ions Solutions in Selenium Oxychloride*. J. Mol. Spectry., pp. 208-232, Oct. 1968.
- Kenney-Wallace, G. A., J. H. Flint, S. C. Wallace. *Resonance Energy Transfer Between Lasing Dyes in Micellar Media*. Chem. Phys. Lett. Vol. 32, p. 71, 1975.
- Kilin, S. F., M. S. Mikhrlashvili, and I. M. Rozman. *On the Transfer of Electronic Excitation Energy in Liquid Solutions*. Opt. Spectrosc. (USSR), Vol. 16, p. 576, 1964.
- Kuhl, J. and G Marowsky. *Narrow Band Dye Laser as a Light Source for Fluorescence Analysis in the Subnanogram Range*. Opt. Comun., Vol. 4, pp. 125-128, Oct. 1971.
- Kurskii, Y. A., and A. S. Selivanenko. Opt. Spectrosc. (USSR), Vol. 8, p. 340, 1960.
- Lempicki, A. and H. Samelson. *Organic Laser Systems*. Lasers. A. K. Ed., Vol. 1, pp. 181-252, 1966.
- Lin, C. and A. Dienes. *Direct Measurement of Radiationless internal Conversion Rate from Second Excited Singlet to the First Excited Singlet State of Laser Dye Molecules*. Opt. Commun. Vol. 9, p. 21, 1973.
- Lin, Chinlon and A. Dienes. *Study of Excitation Transfer in Laser Dye Mixtures by Direct Measurements of Fluorescence Lifetime*. J. App. Phys., 44, 5050-5052 1973.

Lu, P. Y., Z. X. Yu, R. R. Alfano and J. I. Gersten. *Picosecond Studies of Energy Transfer of Donor and Acceptor Molecules in Solution. II. A Concentration Dependence*. Physical Review A, Vol. 27, p.2100, 1983.

Meltzer, D. W. And L. S. Goldberg. Opt. Commun., Vol. 5, p. 209, 1972.

Mikhelashvili, M. S. *Transfer of Electronic Excitation Energy in a Liquid*. Opt. Spectrosc. (USSR), Vol. 30, p. 141, 1971.

Moeller, C. E., C. M. Verber, and A. H. Adelman. *Laser Pumping by Excitation Transfer in Dye Mixtures*. App. Phys. Lett., Vol. 18, pp.278-280. 1971.

Muto, Shinzo and Chiaki Ito. *Characteristics of Coumarin 1-Uranine Energy Transfer Dye Laser*. Jpn. J. Appl. Phys. Vol. 20, p. 1591, 1981.

Panoutsopoulos, B., M. Ali and S. A. Ahmed. *Realization of a Continuous Wave Energy Transfer Dye Mixture Laser in the Near Infrared*. Submitted in Optics Letters.

Pavlopoulos, T. G. Opt. Commun., Vol. 24, p. 172, 1978.

Peterson, O. G., S. A. Tuccio, and B. B. Snavely. *CW Operation of an Organic Dye Solution Laser*. Appl. Phys. Lett., Vol. 17 (6), p. 245, 1970.

Peterson, O. G., J. P. Webb, W. C. McColgin, and J. H. Eberly. *Organic Dye Laser Threshold*. J. App. Phys., Vol. 42. p. 1917, 1971.

Pierce, B. M., and R. R. Birge. *Lasing Properties of Several Near-IR Dyes for a Nitrogen Laser Pumped Dye Laser with an Optical Amplifier*. IEEE, J. Quant. Electr., Vol. QE-18, p. 1164, 1982.

Pike, H. A., Unpublished Thesis, Univ. of Rochester, Rochester, N Y. 1971.

Pine, A. S. *Doppler-limited Molecular Spectroscopy by Difference Frequency Mixing*. J. Opt. Soc. Am. Vol. 64, pp. 1683-1690. 1974.

Rautian, S. E. and I. I. Sobelman. *Remarks on Negative Absorption*. Opt. Spectry., Vol. 10, pp. 65-66, Jan. 1961.

Ricard, D., W. H. Lowdermilk, and J. Ducing. Chem. Phys. Lett., Vol. 16, p. 617, 1972.

Romnek, K. M., O. Hildebrand and E. Gobel. *High Power CW Dye Laser Emission in the Near IR from 685 nm to 965 nm.* Opt. Commun., Vol. 21, pp. 16-19. 1977.

Schafer, F. P., W. Schmidt, and J. Volze. *Organic Dye Solution Laser*. Appl. Phys. Letters, Vol. 9 (8), pp. 306-309, October 1966.

Schmit, W. and F. P. Schafer. *Blitzlampengepumpte Farbstofflaser*. Z. Naturfosch, 22a, p. 1563, 1967.

Sebastain, P. J., and K. Sathianandan. *Donor Concentration Dependence of the Emission Peak in Rhodamine 6G - Rhodamine B Energy Transfer Dye Laser*. Opt. Comm., Vol. 35, p. 113, 1980.

Sebastain P. J., and K. Sathianandan. *Energy Transfer Rhodamine 6G - Safranin T Dye laser*. Optics Comm., 32, pp. 422-424, 1980.

Shammai, Speiser and Reuven. *Computer Simulation of an Energy Transfer Dye Laser*. Optics Comm., 27, 287-291, 1978.

Shank, C. V. *Physics of Dye Lasers*. Rev. Mod. Phys., Vol. 47, No. 3, p. 649, July 1975.

Shapiro, S. I. (Ed.). *Ultrafast Light Pulses*. Topics in Applied Physics, Vol. 18, Berlin: Springer Verlag, 1977.

Shimoda, K. (Ed.). *High Resolution Laser Spectroscopy*. Topics in Applied Physics, Vol. 13, Berlin: Springer Verlag, 1976.

Snively, B. B. *Continuous Wave Dye Lasers*, in *Dye Lasers*, F. P. Schafer, Ed. New York: Springer-Verlag, 91-120, 1973.

Sorokin, P. P. and J. R. Lankard. *Stimulated Emission Observed from an Organic Dye, Chloro-aluminum Phthalocyanine*. IBM J. Res. and Dev., Vol. 10, pp. 162-163, March 1966.

Soffer, B. H. and B. B. McFarland. *Continuously Tunable, Narrow-Band Organic Dye Lasers*. Appl. Phys. Lett., Vol. 10 (10), p. 266, 1967.

Sorokin, P. P. and J. R. Lankard. *Flashlamp Excitation of Organic Dye Lasers*. IBM J. Res. Dev., Vol. 11, p. 148, 1967.

Spaeth, M. and D. Bortfield. Appl. Phys. Lett., Vol. 5, p. 179, 1966.

Steinberk, I. Z., and E. Katchalski. *Theoretical Analysis of the Role of Diffusion in Chemical Reactions, Fluorescence Quenching and Non Radiative Energy Transfer*. J. Chem. Phys., Vol. 48, p. 2404, 1968.

Stepanov, B. I., A. N. Rubinov, and V. A. Mostovnikov. JETP Lett., Vol. 5, p. 117, 1966.

Stepanov, B. I. and A. N. Rubinov. *Lasers Based on Solutions of Organic Dyes*. Sov. Phys. Uspechi, Vol. 11, p. 304, 1968.

Stockman, D. L., W. R. Mallory and K. F. Tittel. *Stimulated Emission in Aromatic Organic Compounds*. Proc. IEEE (Correspondence), vol. 52, pp. 318-319, March 1964.

Stockman, D.L. *Stimulated Emission Considerations in Fluorescent Organic Molecules*. Proceedings of the 1964 ONR Conf. on Organic Lasers, Defence Documentation Center for Scientific and Technical Information. Cameron Station, Alexandria, Va.

Teschke, O., Andrew Dines, and John R. Whinnery. *Theory and Operation of High-Power CW and Long-Pulse Dye Lasers*. IEEE J. Quantum Electronics, QE-12, 383-395, 1976.

Urisu, T. And K. Kajiyama. *Concentration Dependence of the Gain Spectrum in Energy Transfer Dye Mixtures*. J. Appl. Phys., Vol. 47, p. 3563, 1976.

Walther, H. (Ed.). *Laser Spectroscopy*. Topics in Applied Physics, Vol. 2, Berlin: Springer Verlag, 1976.

Yokota, M. and O. Tanimoto. *Phonon Assisted Energy Transfer Between Trivalent Rare Earth Ions*. J. Phys. Soc. Jap., Vol. 32, p. 1577, 1967.