ASPECTS OF PICOSECOND SPECTROSCOPIC STUDIES

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ABSTRACT

Two novel experiments have been designed to determine spectroscopic parameters and distinguish radiationless energy transfer mechanisms using the properties of mode-locked lasers. A unique experiment to determine fine and hyperfine energy level splittings was designed using the quantum beat fluorescence technique with synchronous excitation by a mode-locked laser. An intermolecular energy transfer process was employed in an experiment which was designed to evaluate the energy rates for internal conversion and vibrational relaxation in the picosecond domain.

Towards the implementation of the designed experiments a mode-locked c.w. dye laser was designed and constructed. The operational characteristics of the laser were determined and the laser's ability to perform the designed experiments was evaluated. The laser, as designed, required further modification to perform the spectroscopic experiment; however, the laser was able to perform the energy transfer experiment and gave indications that vibrational relaxation is a much faster process than internal conversion, even when both processes occur in the picosecond time domain.

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CHAPTER 1

Introduction

A. Developments in Short Time Interval Experimentation

Scientific research has taken great strides with the developement of instruments which extend our vision into unexplored regions about which we could only theorize. Research into the domain of the very small in size has jumped forward with the developement of X-ray devices and electron microscopes. Spectroscopy took a leap forward in the developement of very narrow bandwidth, with the developement of the high spectral density and narrow bandwidth light source **called** the laser.

With the developement of mode-locking of lasers in 1964 (1) the frontier of very fast event measurements has been opened. S.L. Shapiro refered to the mode locked c.w. dye laser as a "super measuring tool" in his book (2) on picosecond techniques and applications. Prior to this developement the measurement of very fast events was essentially limited by the high frequency cutoff of semiconductors and stray capacitances in electronic circuitry. Q-switched lasers will operate in the nanosecond domain but are limited by the laser cavity

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round trip time. With the advent of mode-locked organic dye lasers, pulses as short as three hundred femtoseconds have been used in experiments studying very fast processes (3). Processes with characteristic times as small as one picosecond can be studied directly and even faster events can be studied after deconvolution of the effect of the pulse width from the signal being studied.

B. Scope Of This Thesis

The scope of this report is to detail the developement of an experimental study in a heuristic form, from its conception, through the instrument developement stage and ending with data acquisition. This study is not intended to be a theoretical study of either the experimental apparatus or the processes which are proposed to study. The theoretical discussions which are included are intended to shed light on decisions made in the design of the experiments.

C. Outline Of The Following Chapters

Chapter two includes the description of two types of experiments which offer the opportunity to determine new information in a unique way. Through examination of the processes involved the practicality of the experiment is considered and the demands on the

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experimental apparatus are evaluated.

The purpose of chapter three is to give background information about mode-locking, which is required for the design of the light source and provide an explanation of the design options which were chosen.

Chapter four deals with the development of the experimental apparatus. The problems incurred during the developement of the equipment **are** included as well as a discussion of outstanding problems of the system.

The fifth chapter covers the characterization of the laser systems discussed in chapters three and four. This chapter also includes a discussion of diagnostic equipment which would have been useful for a more definite characterization of the system.

Chapter six is a collection of preliminary results which are included as proof of the system's operational ability and a discussion of the project as a whole.

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CHAPTER 2

Backround for proposed experiments

A. Time Correlated Fluorescence

a. Precursor Information

In the pursuit of determining fine and hyperfine energy splittings of states in isolated atoms and molecules, new techniques are being employed to measure previously unmeasureable energy separation. The determination of the fine splitting of the nD levels of sodium (n=4,5,6,...) is an example of a study which has taken stepwise advances with the application of new techniques.

The determination of fine splitting intervals of the nD levels of sodium prior to the development of the laser was accomplished by interferometry (4) as in the work of K.W.Meissner et.al.(5). Intervals were todetermined for n equal three to six with an accuracy of plus or minus fifty megahertz.

With the development of the tunable, high spectral density light sources (lasers) it became possible to produce a detectable signal from two photon absorption (6). Through the use of counter propagating beams it is possible to greatly reduce the doppler width of the transition being studied (7-10) and by this

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technique the precision of the fine structure intervals for n equals four to six were redetermined with an increase in accuracy by up to a factor of thirteen, to plus or minus three megahertz.

The next developement in the study of the nD states was the application of quantum beat spectroscopic techniques. C.Fabre, S.Haroche and their coworkers employed a quantum beating phenomenum to measure the fine structure intervals for n equals nine to sixteen. The accuracy of their determinations varied from one and one half megahertz to five hundred kilohertz. Further studies of the states with n equals seven and eight were precluded by the bandwidth of the detection apparatus.

Quantum beat laser spectroscopy has also been sucessfully applied to other atoms and molecules (11-13) to determine zeeman splittings and hyperfine structure splittings.

To describe the principles of quantum beat spectroscopy a three level system as depicted in figure 2.1 shall be used but it should be kept in mind that the description is expandable to systems with more than three levels.

If the energy interval E₂₃ between states two and three is within the the bandwidth of the device used to excite them and transitions from states two and three are both allowed, excitation of this system will cause

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the system to be in an excited state which is a coherent superposition of states two and three. During the decay to the ground state the fluorescent intensity will decay exponentially, modulated by the frequency E_{23}/\hbar . Mathematically the fluorescent intensity has the form

$$I(t) = I_0 \exp[-\lambda t] [1 - A\cos(E_{23}t/\hbar)]$$
 (2.1)

and appears as in figure 2.2. The convolution theorem (14) indicates that by taking the fourier transform of the fluorescent intensity a function is produced which is the convolution of a lorentzian function, of width 1, and delta functions loacted at frequencies of zero and plus and minus E_{23} /h. Therefore by recording the fluorescent intensity as a function of time it is, in principle, possible to determine the energy E_{23} . The above approach is well illustrated in the work of Paisner and Haroche (11).

Prior to the developement of laser techniques and high speed electronics, quantum beat experiments were being performed by researchers such as Corney and Series (15), and Dodd et.al. (16) using resonance lamps and electro-optic modulators. They noticed that the modulation of the fluorescence of a cadmium sample went through a maximum while the modulation frequency of the

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exciting light was changed. If it is assumed that the quantum beating phenomenom is occuring, as we would expect, the fluorescent signal from their sample should be the convolution of the input intensity with the fluorescence signal from a single pulse excitation, or in mathematical form

$$I(t) = \int F(\tau) I(t-\tau) d\tau \qquad (2.2)$$

where F(t) is the fluorescent responce function I(t) is the exciting light intensity

The exciting light intensity can be approximated by a modulation function of the form

$$I(t) = I(0) \{1 - Asin(\omega, t)\}$$
 (2.3).

The observed results of this experiment are most easily understood by considering the fluorescence intensity in the frequency domain. Transforming the temporal intensity into the frequency domain produces an intensity which is the product of two functions, one being Lorentzian functions at v equals 0, ω and $-\omega$ and the other being delta functions at v equals 0, ω_1 and $-\omega_1$. It is clear that as ω equals ω_1 the modulation of the signal at ω will be at its maximum. These experiments were limited



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by the inability of the modulator to function at frequencies above 462 KHz. and maintain a modulation depth of at least one percent.

b. Experimental Proposal

It was proposed to construct a device to perform energy interval determinations. The technique used was a modification of the quantum beat technique employed by Series and Dodd. The modification was to replace the exciting light, which they modulated by five percent, by a pulsed laser whose greater intensity and modulation would increase the experiment's signal to noise ratio.

The description of a pulsed laser as a modulated light source is slightly misleading in that the laser source corresponds to an overmodulated system, that is, it cannot be represented by the input modulation function in equation (2.3). If however the pulse width is small compared to the pulse period, equation (2.2) can be rewriten by approximating the input intensity as a comb function which simplifies the integral to a summation of the form

 $I(t;\tau) = I_{\bullet} \sum_{i} (\exp(-\lambda(t-i\tau)) [1-A\cos(\omega(t-i\tau))]) \cdot (2.4)$

In order to produce a pulse repetition rate

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which is fast enough to extend the quantum beat experiments using single pulse techniques (11-13, 17, 18), it is necessary to have pulse separations which are comparable to the round trip time 2L/C of typical laser cavities or about five nanoseconds.

Assuming a pulsed laser with the above characteristics could be built or bought, computer modeling of the experiment was performed. The ripple on the fluorescent intensity signal given in equation 2.2 was calculated for a number of values of λ , A, ω and tau. Plots of the ripple and intensity as a function of tau were generated to investigate the factors affecting the narrowness of the peak in the signal's ripple. The model function was modified to include two beat frequencies and the beat frequency separation was varied to investigate the resolving power of this hypothetical experiment. Typical results of the experimental simulation are given in figure (2.3). The vertical lines in the intensity versus pulse period plot represent the maximum and minimum in the fluorescent intensity for a given pulse period tau. The ripple was calculated by dividing the difference between the maximum and minimum signal by the average signal.

From the computer modeling it was determined that peaks disappeared when the lifetime of the states approach the beat period. In such cases the natural line

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-1-1--

width of the lines would overlap and render the lines inherently inseperable because of the immutability of the natural linewidth. While the resolving power of the experiment is, as would be expected, dependent upon the lifetime of the states being studied, even in a case of an unusually short lifetime of fifty nanoseconds, peaks separated by four percent of their frequency were easily resolved.

B. Stimulate and Probe Technique of Lifetime Determination

(Ground State Recovery)

a. Precursor Information

The nomenclature for describing the energy levels in large molecules involves dividing the states of the molecule into manifolds according to the potentials with which they are related and to the multiplicity of the states. This is a natural consequence of the separation of the systems eigenfunctions into nuclear and electronic factors which is referred to as the Born Oppenheimer approximation. The lowest manifold is usually refer to as the ground state and is denoted by a subscript 0. All other manifolds are given a subscript which represents an ordering of manifolds in increasing energy with the same multiplicity. For instance, a manifold of singlet states with only one other singlet manifold between it and the ground state is called the second singlet manifold and is abreviated S_2 . Similarly, the lowest triplet manifold is denoted T_1 . A pictorial representation of this nomenclature is included in figure 2.4.

Decay mechanisms can be classified by a number of their characteristics. A pictorial summary of these classifications is also given in figure 2.4. The most obvious characteristics of a decay are its lifetime and whether it emits light as part of its decay. Long lived decays are refered to as phosphorescence and correspond on the microscopic scale to nonallowed transitions between states of differing multiplicity, i.e. triplet-singlet transitions. Phosphorescent decays usually have lifetimes of 1E-4 seconds or longer. Shorter lived decays are referred to as fluorescent and have lifetimes of the order of 1E-8 seconds. The microscopic interpretation of fluorescence is that it is generated by allowed transitions between states of the same multiplicity, i.e. singlet-singlet transitions. Both of the above types of mechanisms involve the emission of electromagnetic radiation and are hence referred to as radiative relaxations.

Another class of decay mechanisms are those which do not involve electromagnetic radiation and are called radiationless processes. This group can be further subdivided into groups depending on the manifolds between

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which the relaxation occurs. Decay mechanisms which cause a change of energy level within a single manifold of states are called vibrational relaxation. Transitions which occur between manifolds of differing multiplicity are referred to as intersystem crossing. Internal conversion is when the molecule moves from one manifold to another without changing its multiplicity.

A number of decay mechanisms are possible through interaction with neighbouring molecules and are referred to as intermolecular energy transfer. Of particular interest to this work is the dipole-dipole energy transfer mechanism. The molecule which loses energy is called the donor and the molecule which gains energy is refered to as the acceptor. The energy transfer reaction can be represented as

D*+A--D+A*

where

A and D are the acceptor and donor in any state A^{*} and D^{*} are the same molecules in states of higher energy than A and D

The energy level diagram for this process is given in figure 2.5. The energy is coupled between the molecules by the electromagnetic field but does not involve the emission of a photon. The range of this interaction can be of the order of tens of nanometers. This process was first observed by Cario and Franck in 1922 in a mixture of mercury and thallium vapours (19). Review papers of this process have been writen by numerous workers (20-22) including Forster (23) and, most recently, Kellog (24).

In the study of nonradiative decay processes it is useful to examine very fast processes in order to reduce the complicating effects of competing processes which are slower. Such studies have been attempted for a number of multi-benzene ring molecules (25-30) where the nonradiative decay is dominent, occurs in the picosecond domain and is hypothesized to be caused by a torsional effect on the benzene rings. Because motion of the rings is involved, one would expect to see some effect of the environment in which the molecule exists, most probably through the solvent's viscosity. Experiments have been performed on a number of these molecules whose structural representation is given in figure 2.6. Theoretical studies of the three ring tri-phenyl-methane dyes have been carried out by Forster (31) who predicted a lifetime with a viscosity dependence varying like $n^{2/3}$. The lifetimes of these dyes fall in a range from subpicosecond up to about 100 picoseconds in very viscose solvents. As a consequence, the experiments are very difficult and the interpretation of the results are not

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Molecule

| Ethyl Violet | $X = Y = Z = N(C_2H_5)_2$ |
|-----------------|--|
| Crystal Violet | $X = Y = Z = N(CH_3)_2$ |
| Malachite Green | X =Y= N (C H ₃) ₂ , Z=H |

Figure 2.6

Structural Diagram of Some Molecules With Very Fast Relaxation as clear cut as might be hoped for. The fact that, given the time scales on which these events proceed, it is not clear what processes should be dominant among those which occur in large polyatomic molecules was pointed out by Madge (27) in a paper on the tri-phenyl-methane dye crystal violet.

The group of Ippen et.al., with a resolution of .05 ps., observed the recovery of the ground state absorption of malachite green in a number of solvents (32). They decided the functional form of the the decay they observed could best be described by a biexponential decay. They attributed this biexponential recovery to a fast internal conversion $(S_1 \rightarrow S_0)$ followed by a slower relaxation back to a thermal distribution in the ground state. In a further study of tri-phenyl-methane dyes (33) Schneider and Wirth used the ($S_2 - S_1$) absorption as a monitor of the S population. By observing the slower of the two lifetimes observed by Ippen, they inferred the internal conversion process must be slower than the vibrational relaxation. Schneider and Wirth did not appear to include in their interpretation any contribution to their observed signal from $(S_2 - S_0)$ transitions of molecules which were still isoenergetic with S, states after internal conversion.

More recently, a letter was writen by Hirsch (34) in which he reported his observations of biexponential

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time dependance of the luminance of malachite green. This experiment should produce knowledge of the S₁ population, however only the slower time constant which he observed corresponds to those times observed by others and he suggests no models by which to explain his data.

Even if the interpretation of the experiments leaves room for doubt, the recognition that the interpretation of Ippen could be checked if some way was devised to monitor the S_1 population was correct.

Mechanisms using contact interactions are limited by diffusion, which in high viscosity solvents is very slow. As a result of this intersystem crossing rate enhancement techniques such as the heavy atom solvent method are too slow to be effective. What is required is some interaction which is fairly long range. One such mechanism is dipole-dipole intermolecular energy transfer.

The rate constant for dipole-dipole intermolecular energy transfer (35) is given by the expression

 $k = (1/\tau) (R_0/R)^6 (2.5)$

where

$$\begin{split} &R_0 = (9000 \ln (10) \kappa^2 n \ / 128 n^5 N \) \int f_D(\nu) \varepsilon_A(\nu) \ d\nu / \nu^4 \ (2.5a) \\ &\tau = \text{mean lifetime of the donor} \\ &n = \text{quantum yield of the donor without transfer} \\ &\kappa^2 = \text{an orientation factor} \end{split}$$

(=.656 for random orientation)

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n = the refractive index of the medium

N = Avagadro's number

 $f_{D}(v)$ = fluorescence spectral distribution

in units of light quanta and normalized to unity

 $\boldsymbol{\epsilon}_{A}$ (v)=molar decadic extinction coefficient

v = frequency in units of inverse centimeters

The recovery of the system has the function form:

 $f(t) = \exp\{-t/\tau - 2\gamma(t/\tau)\frac{1}{2}\}$

where $\gamma = C/C_0$ and $C_0 = 3000/2\eta^{3/2} NR_0^{3/2}$

The theory on which this relation is based assumes that the acceptor donor separation remains constant over the duration of the interaction. The application of the theory of dipole-dipole interactions will require an evaluation of the motion of molecules due to diffusion over the duration of the interaction to ensure that the approximations used in the theory have been fulfilled.

Experimentally, the application of this theory

to explain phenomenon of very short duration has been sucessful in studies of rhodamine 6G and malachite green by Rehm (36) and Porter (37) with time resolutions of 20 ps. and 10 ps. respectively. This energy exchange process has also been studied as a technique to increase the excitation efficiency in optical pumping of dye lasers (38-41).

b. Experimental Proposal

It was proposed to construct an instrument which is capable of determining lifetimes in the tens of picoseconds range. It was further proposed that the device be used in an experiment utilizing intermolecular energy transfer as a means of labeling the S1 manifold population in Malachite Green.

The proposed acceptor molecules are members of the carbocynine dye family which were chosen because of their high molar absorption coefficient, typically 2.5E5 /M.cm., and the fact that their absorption band could be matched to the fluorescence spectrum of Malachite Green.

By restricting the lower limit of the lifetimes for which the system is designed, the device's light source can operate with pulse widths greater than those attained by researchers whose aim is to produce short pulses. This allows the use of the equipment without the more expensive diagnostic devices used by researchers who work at the extremes of the capabilities of mode-locked dye laser equipement.

A computer simulation of the experiment was performed assuming gaussian laser pulses and exponential recovery of the ground state population. The results of the simulation indicated that the effects of non-zero pulse width are less than five percent for pulse widths less than one fourth of the lifetime.

Over the period for which this experiment's feasibility was considered, the value of R was determined with three levels of approximation. The first approximation was that the frequency, over the fluorescence and absorption profiles is constant, as suggested by Forster (23), and the fluorescence and absorption functions can be represented by Gaussian functions of appropriate height and width. In this approximation the integral in equation (2.5a) can be evaluated analytically. As a second approximation absorption spectra for malachite green and DTDCB were recorded on a Cary 14 spectrophotometer and the mirror symetry of absorption and fluorescence, as noted in the related tri-phenyl-methane dye crystal violet (29), was used to approximate the fluorescence spectrum of malachite green. In this case the integral has to be evaluated numerically and hence the frequency need not be considered a constant over the range of the

-23-

integrand. In a third approximation a fluorimeter using a half meter Jarrell Ash monochrometer and the 98160B, S-20 response photomultiplier was used to record the fluorescent spectrum of malachite green. Since the fluorescence is in the red part of the spectrum, where the fluorimeter's efficiency varies rapidly, an Electro Optics Associates calibrated light source was used to compensate for the changing efficiency of the device. Evaluation of R_0 by all three levels of approximation gave values of approximately three nanometers, which implies that the concentration required to reduce the lifetime by fifty percent is about 1E-2 M.

For the purpose of producing a conservative estimate of the distance traveled by the molecule, by diffusion over the duration of the decay, a one nanosecond duration and a solvent viscosity of fifteen Poise were assumed. The average distance traveled under these conditions was approximately .03 nanometers which is less then R_0 by a factor of one hundred and hence the restriction of the applicability of Forster's energy transfer theory to interactions in high viscosity solvents and involving characteristic times of a nanosecond or shorter is fulfilled.

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CHAPTER 3

Design Considerations for the Light Source

A. Requirements for Proposed Experiments

The proposed experiments require a pulsed light source whose repetition rate can be varied and is in the 250 megahertz range. The pulse width must be small compared to the duration of the events they are used to measure which may extend to the tens of picoseconds range. It is important that the light source be tunable such that it is not necessary to depend on chance coincidence of transition and light frequencies.

The organic dye laser would fulfill the requirements for tunability and also for an intense light source. Frequencies of hundreds of megahertz are in the range of laser cavity mode separations and pulses of width 10 picoseconds and shorter will require a substantial portion of the available gain profile of a dye laser. These conditions of bandwidth limited operation of a laser describe a condition called mode-locked operation.

B. Methods of Mode-Locking

A laser is a positive feedback optical frequency oscillator. The frequencies for which the feedback is

-25-
positive are determined by the laser cavity resonance modes with slight shifts due to the gain medium in the cavity. These frequencies have the form

r

The frequencies at which the laser will oscillate are determined by the feedback and the ability of the gain medium to compensate for cavity losses.

Ordinarily a laser will oscillate on a number of modes of the cavity. Under most circumstances the oscillation of each mode will be independant of the other oscillating modes and the phase relationships between the oscillating modes are randomized by the di's. If a nonlinear medium is added to the cavity a large number of new resonant frequencies will be created from the sums of odd numbers of modes of the laser without the nonlinear material. These frequencies will differ from the cavity fundamental modes, iC/2L, by sums and differences of odd numbers of the di's. The relatively large density of modes in the vicinity of the frequencies

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wi allows interactions to decrease the di's to zero, leaving an evenly spaced set of cavity modes with fixed phase relationships because the di's are not present. Calculation of the intensity in this case gives interference terms which are time dependent with frequencies which are harmonics of C/2*L and which do not cancel on average.

In practical systems the phase relationships are appropriate for pulse production of periodicity 2*L/C. The pulse width in any system is limited by the bandwidth of the device used to produce them. In this system the pulse width is limited by the bandwidth of the laser's gain.

Understanding mode-locking on an experimental level requires an understanding of the temporal behavior of the processes which occur in a mode-locked laser. Explanations of mode-locking in the time domain do not lend themselves to the same degree of abstraction as frequency domain explanations and therefore are appropriate to only specific systems. There are currently two popular dye laser mode-locking schemes in common usage. They are refered to as passive, saturable absorption mode-locking and synchronous pump mode-locking.

The synchronous pumping scheme (42, 43) produces a periodic modulation in the laser's gain by pumping the dyè with a laser which is itself mode-locked. If the dye

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laser's cavity is matched, to a high degree of accuracy (44), to the length of the pump laser by an integral ratio such that gain only occurs at times approximately when the mode-locked dye laser pulse is in the laser medium the dye laser pulse will be amplified. Energy arriving at the amplifier at other times will experience only losses, hence only a single pulse will oscillate in the cavity. In synchronous pumping the nonlinear mixing is between the gain and the cavity modes. This technique allows the user to mode-lock a dye laser by mode-locking a laser in which the process is easier to accomplish.

Passive mode-locking by saturable absorption is accomplished by including in the laser cavity, a material which will absorb low intensity light pulses more than high intensity light pulses. Given infinite temporal resolution, the examination of a dye laser's output would reveal the output to be a collection of randomly spaced pulses with a random distribution of intensities (45, 46). The pulse widths would be approximately the inverse of the laser's oscillating bandwidth. To produce mode-locking by passive saturable absorption a material which has a limited ability to absorb light is included inside the laser cavity. The transfer function for a saturable absorber appears as in figure 3.1. At low

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Figure 3.1 Transfer Function of a Saturable Absorber

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and attenuates the input intensity by a constant factor; however, as the input intensity increases, the output intensity asymptotically approaches the input intensity minus a constant which is the limiting energy which can be absorbed by the absorbing material. As the collection of pulses, discussed earlier, circulates in the laser cavity, those pulses of low intensity will have a larger fraction of their energy absorbed than does an intense pulse, as illustrated in figure 3.1. After successive passes through the absorber the laser's energy will be concentrated in a single pulse.

In a real mode-locked dye laser system, the previous description has to be made somewhat more complicated to include effects due to the finite recovery time of the saturable absorber. This recovery time will allow low intensity pulses to be unattenuated by the absorber if they follow closely behind an intense pulse. Fortuitously, because of the high stimulated emission cross section of laser dyes (42), the gain of the amplifier in a dye laser can be swept out by the leading, intense pulse and hence the trailing pulses will not be amplified by the same amount as the intense pulse. This also leads to the compresion of the laser's energy into a single pulse.

Further discussions of laser mode-locking in general (47) and details of mode-locking of dye lasers

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specifically (45) are available in a number of review articles.

C. Options and Their Merits

A number of optical pumping sources are available for dye laser operation. Nitrogen lasers operating at 337.1 nm. with pulse lengths from five to fifteen nanoseconds can provide intense pulses in the megawatt range. Flashlamp pumping of dye lasers produces less intense pulses than nitrogen laser pumping does; however, their longer duration of approximately one microsecond allows their energy per pulse to be much higher than with other pump sources. To produce continuous operation of the dye laser an argon ion laser is commonly used because of its high c.w. power.

Reports of mode-locking of dye lasers pumped by these three techniques have appeared in the scientific literature (48-50). In the context of this report, all three methods have advantages and disadvantages for their application to this project.

The nitrogen laser pumped system has the advantage that experience gained using pulsed nitrogen laser systems prior to this work could be employed and most of the parts of such a system were already present in the laboratory. The flashlamp pumped system has economy as its main advantage in that flashlamps are much less expensive than nitrogen or argon ion lasers. Using a c.w. dye laser has the advantage of pulse to pulse reproducibility of pulse width and intensity.

The disadvantages involved with the use of a nitrogen laser pumped system are a lack of pulse to pulse reproducability, restriction to short cavities because of of the short duration for which gain is available and incompletely established mode-locking. The longer pumping times associated with flashlamp pumping allows the use of longer cavities; however, the intensity of the mode-locked pulses varies rapidly and pulse measurement techniques are required. The use of the argon ion laser pump scheme has the disadvantage that the author had no experience with such systems; however, the scientific literature implies that mode-locking is as simple as adding dye until mode-locking occurs (51).

The synchronous pumping technique has the advantage of higher intensity output due to the absence of the absorber and, in the case of having two separate dye cells, six glass surfaces. To implement a sync-pumped system requires rigid control of the dye laser cavity length to within ten microns and a very expensive acousto-optic loss modulator and its associated radio frequency driver.

The advantages of passive mode-locking are the ability to provide continuous variation of the cavity

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length and the simplicity of the design if a mixed amplifier/ absorber is used.

It was decided to construct a passively mode-locked, argon ion laser pumped dye laser system. More over it was decided to attempt passive mode-locked operation using the composite amplifier/ absorber dye technique which had been previously employed by Ippen (51) and Scavennec (52) with slightly different laser configurations and more lately by Diels (53) in a laser configuration using a Spectra Physics model 375 dye laser as was used in this work. As an alternate plan, a separated dye scheme was considered which used an absorber dye cell in which one surface was the output mirror as suggested by a theoretical analysis by Bradley (54) and as employed sucessfully by a number of researchers (55, 56) including Peterson in the first c.w. dye laser (57).

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CHAPTER 4

Experimental Apparatus

Spectrometers, whether those used for classical spectroscopy or laser spectroscopy, can be divided into four conceptual parts. These parts will be denoted as the light source, the sample, the detection and recording apparatus and, connecting the previous parts, the beam manipulating optics.

The requirements for the light source has been detailed in the previous chapter.

The sample preparation procedure and sample cell requires the purification and containment of high temperature, corrosive, gaseous samples and temperature controled, dissolved samples in high viscosity solvents.

The detection and recording apparatus must be able to support very fast measurement of the laser intensity for diagnostics of the light source. The **able** detectors should be to produce signals under conditions of very low light levels, such as low intensity fluorescence, or very low signal to noise. Detector responses will be primarily at or near the laser wavelength; however, extended red response is necessary for measurement of the DOTCI fluorescence profile.

The only significant, non-trivial requirement

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for the beam steering optics is to be able to focus large diameter, off axis beams with a minimum of spherical aberrations and pointing error.

A. Detectors

Over the course of this research a number of light detectors were required. Since almost all of these devices had to be constructed from components, a description of the detectors will follow. Electrical and working diagrams are included in appendix A.

a. Photodiodes

Two additional types of photodiodes were used and they were built into a number of different circuits depending on the application. The photodiodes were Hewlett-Fackard 4220 diodes and United Detector Technology PIN-5D diodes. The H-P 4220 devices were used in both fast and slow detectors while the PIN-5D diodes were used only in slow devices as is dictated by their large active area.

The two fast detectors which were built were H-P 4220 diodes mounted in a capacitance matched housing (58). The devices were constructed to drive a 50 ohm input impedance oscilloscope using General Radio GR874 connectors. The current limiting resistor was reduced to 1 kilohm and the detector was generally run with one hundred to one hundred thirty volts bias voltage. Both

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detectors were tested using a ten picosecond rise time diode laser and both had rise times of approximately 150 ps. One of the diodes was also tested to ensure that the reduction of the limiting resistor to 1. Kilohm did not reduce the speed of the devices.

The H-P 4220 diode was also built into a device in which high speed was unnecessary. Electrically this device is a photoconductive arrangement used to drive a unit gain voltage follower. The amplifier used was an eight pin dual inline package (DIP) form of the 741 operational amplifier powered by a plus and minus 9. volt battery power supply. A 14 pin DIP socket was used to mount all the components in order to provide a compact, easily maintained light detecting assembly. Since this device was constructed to provide a reference signal to a lock-in amplifier it was not necessary to include an offset control for the 741 op amp.

Two light detectors were constructed using PIN-5D photodiodes. Both devices operated in a photoconductive mode and were used to drive voltage followers. In order to use these devices with a log ratio amplifier it was necessary to include offset controls on the voltage followers and one device had variable gain to allow rough matching of signal strengths by electronic means. 741 operational amplifiers were used for the voltage followers. One of the devices had a gain of 1 and the

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other had a gain of 3,10,100 or 1000 as selected with a rotary switch. Both of these detectors were equiped with offset correction circuitry.

b. Photomultipliers

During this research three different photomultipliers were used. They were RCA 1P28, EMI 9635QA and EMI 9816QB tubes.

The 9635QA was used with a PAR model 182 commercial housing and dynode chain consisting of a 13 times 100 Kilohm voltage divider with a 150 volt zener diode used to stabilize the cathode-first dynode potential difference. This device was used for detecting slowly varying light levels and hence its slow response was not a limiting problem.

The 1P28 tube was built into a non-commercial housing (see appendix A) and dynode chain consisting of a 10 times 100 Kilohm voltage divider with the last three resistors in the divider each connected in parallel with a .01 uf. capacitor to maintain the linearity of the tube's gain under pulsed load conditions. This device, although it has lower gain than the 96350A, which was used in the initial stages of this work, has a faster response and for this reason was used for those applications which called for reasonably fast detection but involved signals smaller than could be detected with

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a photodiode.

The EMI 98160B photomultiplier was mounted in a PAR model 182 housing which was modified to accept the longer tube. The dynode chain was a 14 times 100 Kilohm voltage divider with the last three dynodes capacitively decoupled as was described for the 1P28. This decoupling was included in order that the device could be used in unrelated studies using fast pulsing light sources and was not necessary in these studies. This tube was used to detect low level light signals that were beyond the range of S-5 and Bialkali photocathodes but not beyond the 98160B's S-20 response.

The housings mentioned were either modified or specifically designed to be attached to a heat pipe oven designed for one of the experiments using this system.

c. Other detection

In addition to the non-commercial devices used, a Coherent Radiation model 212 radiometer was used. This device covers the range of powers from 1 nw. to 300 mw. using a solar cell. The response of this detector is quite slow and as such was only useful to detect average powers. It was the only calibrated detector used for this report.

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B. The Light Source

a. The pump laser

A crude estimate based on guesses of conversion efficiencies indicated that the pump laser would need to have of the order of watts of output power. By buying a ten watt laser which was upgradeable to fifteen watts it was hoped that the experiments would have sufficient light intensities to be practical. In order to increase the versatility of the ion laser it was decided to buy an extended cavity version of the laser so that it would be useful in intra-cavity experiments and, with the addition of an etalon, in experiments calling for single mode output. The pump laser decided on was a Spectra-Physics Model 170 Argon Ion Laser.

The Model 170 laser required one major maintenance procedure which a factory trained technician's experience was necessary to prescribe. Experience would have precluded the need for the service call. The manifestations of the problem were a gradual deterioration of the laser's output power of about 75% over a one day period. Adjustment of the rear mirror caused the output to rise sharply followed by deterioration of the intensity with a time constant of less than one second. Alignment of the laser at low power followed by increasing the plasma current caused the laser power to increase to a point where considerable transverse mode structure appeared

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and the output power dropped. This condition stabilized and the output power continued to increase until maximum plasma current was reached. These symptoms are characteristic of dirty optics; however, conventional cleaning techniques were ineffective. Cleaning procedures used on the Brewster's angle windows were application of the solvents acetone, iso-propanol and methanol, a lens cleaning solution sold by Kodak, a common laboratory detergent named Alcanox and a ten percent solution of hydrofluoric acid. The mild abrasives jeweler's rouge and tin oxide were also employed. With repeated cleaning of the brewster's angle windows the laser's output power increased to its previous level and the other symptoms disappeared. The most effective cleaning procedure was found to be the use of an Alcanox and tin oxide mixture followed by distilled water to remove the Alcanox, followed by reagent grade acetone to remove the water. All solutions were applied on lens paper held in a hemostat. The application of the detergent, abrasive mixture was accompanied by vigorous rubbing of the window with a force of one to three Newtons.

b. The dye laser

It was decided to employ commercial systems for the dye laser, wherever possible. This was the first c.w. dye laser used in this research group and in order

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to limit the number of sources of error it was decided to buy the expertise associated with dye laser mechanical design. Tward this end a Spectra-Physics Model 375 Jet Stream Dye Laser was purchased. The laser cavity is basically an astigmatically compensated folded cavity as described by H. Kogelnik (59) and drawn schematically in figure 4.1.

The folding and end mirror, M2 and M3, were coated with a multilayer dielectric to provide high reflectivity over the gain profile of the dye for which they were designed, namely rhodamine 6G. Mirror M4 was coated for high reflectance of the argon ion laser wavelengths. Etalon El was a wedged interference filter which causes the devices transmission maximum to be a function of the position of the optical axis along the wedge. This allowed the angle of the etalon to be fixed at Brewster's angle for minimum losses while tuning is accomplished by translating the wedge with respect to the optical axis. Etalon E2* is an optional .11 mm. solid etalon which could be used to narrow the laser's linewidth from .5nm. to .05 nm.. Tuning this etalon was accomplished by tilting the etalon's holder with respect to the optical axis. Mirror Ml was the output reflector for which broad band dielectric mirrors with reflectivities of 88%, 95%, and 98% were used. In this configuration there were a minimum number of adjustments necessary.



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Figure 4.1 Optical Schematic of the Dye Laser Fine tuning of the pump beam positioning in the jet stream could be accomplished easily in preparation for the replacement of the output mirror with a more complex device.

An alternate output assembly was constructed to allow the use of separate amplifier and absorber dye solutions. The working drawings for the lens positioning device and the dye cell output coupler are included in appendix B. The use of two lenses allowed the laser cavity to have a smaller beam waist in the dye cell than was possible with a single lens. The two lens system also had the advantage that a wide range of beam diameters at the waist could be provided by adjusting the inter-lens spacing.

The output assembly was mounted on one of two platforms, depending on whether changing the cavity length was important. One platform was an air bearing translation stage (see appendix B) which allowed smooth translation over a one meter range. The other platform was held securely to the optical table by two one and one half inch steel rods.

c. Design problems and modifications

A number of modifications were made to the laser system to overcome problems which were not forseen

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because they represent design flaws in commercial products. The majority of these problems are associated with the model 170 ion laser as would be expected because of its higher level of complexity than the other components.

The model 170 laser, when operating ideally, will start after a fifteen second delay period during which the cathode warms up. The only way to start the laser if the initial starting procedure fails is to turn the laser off, allow it to cool and reinitiate the starting procedure. The argon ion laser used in this research developed the inability to start with the first starting sequance and eventually would only start after five or six attempts to initiate lasing. In order to decrease the wear on the cathode from repeated heating and cooling, a manual override was built into the laser exciter. The start pulse was generated by firing a silicon controled rectifier whose gate was connected to a thermal time delay relay. By adding a normally closed switch in series with the anode of the SCR, starting pulses could be manually initiated without turning off the laser. The procedure is to open the switch at the SCR's anode, allow enough time to charge the capacitor in the circuit and close the switch which will short circuit the capacitor through the SCR and thus initiate a start pulse. The charging of the capacitor procedes

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with a time constant of about one second and therefore the switch should be held open for about five seconds.

Another problem is associated with the pressure sensing circuitry in the argon laser. The laser has a built in pressure monitoring circuit which only allows repressurization of the laser tube when the pressure falls below some threshold value. This circuit functioned erratically and only while the arc discharge was running. Since introduction of fresh argon into the tube was most often accompanied by termination of the arc discharge, even when the fill threshold circuitry did work, the restart procedure had to be performed a number of times to pressurize the laser to an approprate level. This problem was circumvented by installing a normally open switch in parallel with the switch contacts in relay K401 on the fill threshold circuit board. Closure of this switch simulated the action of the fill threshold circuitry under low pressure conditions, which allowed pressurization of the tube under any condition as long as the laser power supply was on.

When a low water pressure condition occured, replacing the system's water filter would solve the problem for a period of months. However at one time the water pressure became a problem which was intermittent and did not go away with replacement of the water filter. It was determined that the problem caused by a decrease

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in the laboratory's water pressure by about thirty percent for approximately one second. It was decided to reduce the threshold of the water pressure interlock on the assumption that an ongoing low pressure condition would cause the water temperature interlock to protect the system and a drastic decrease in the water pressure would still be covered by the water pressure interlock. To further limit the possibility of damage due to a prolonged low pressure condition, a pressure gauge was installed at the power supply's water input to allow manual inspection of the condition of the water supply. It was never necessary to turn the laser off manually because of water pressure problems. The fact that this problem did not exist for the first three years of the laser's operation seems to indicate a decrease in the average water pressure supplied to the laboratory. Figure 4.2 is a schematic diagram of the dye circulation system. The components below and to the left of the dashed line are standard Spectra Physics model 376 dye circulator parts supplied with the dye laser. the other components were added to promote mode-locked operation for the reasons stated in the remainder of this section.

An unforseen problem associated with the dye laser was the inability to mode-lock the laser if the amplifier dye solution temperature rose above twenty six degrees celsius. The elevated temperature probably

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terminated mode-locking through a decrease in the viscosity of the ethylene glycol solvent which causes degradation of the optical quality of the jet stream (60, 61). The dye circulator has built in water cooling and in an attempt to improve its efficiency the water supply line was separated from the argon laser water supply. When that proved insufficient a water jacket was constructed using quarter inch copper tubing inside a forty centimeter long piece of half inch copper tubing with water flowing between the tubes. The water jacket was capable of lowering the dye solution's temperature below fifteen degrees celsius where lasing was again stopped, presumably because of an increase in viscosity causing low jet stream velocity. With the addition of a metering valve the water flow could be adjusted to maintain a dye temperature of approximately room temperature.

The Spectra-Physics model 375 dye laser was found to be very sensitive to vibrations and disturbances in its jet stream. For this reason efforts were made to decouple vibrations from the dye circulator to the dye laser and to remove air bubbles in the amplifier dye solution. The dye solution return line was arranged such that the dye return tube was not continuous. This prevented the vibration of the circulator motor from being transmitted up the return line to the laser. To

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prevent surface wave effects on the jet stream, the point at which the jet stream strikes the dye catcher was extended from approximately ten centimeters to thirty centimeters from the active volume of the amplifier. The angle of incidence of the jet stream with the dye catcher was kept as close to glancing as possible.

A single device was constructed to perform both acoustic filtering and the removal of air bubbles from the dye solution. A schematic diagram of this device is that portion of figure 4.2 labled as a shock cushion. The acoustic filtering was accomplished using an air pressure head which allowed small variations in the circulator pump rate to be absorbed by compression of the air. Air bubble removal was accomplished by providing a horizontal tube in which the dye solution flows downward. Air bubbles flowed upward relative to the solution under the influence of gravity. By making the horizontal cross sectional area as large as possible the dye flow velocity was minimized, allowing the maximum number of air bubbles to have an upward velocity relative to the device. These bubbles rose to the top of the device and were removed from the dye flow. The two functions discussed above are incorporated into the same device by allowing the top of the column to be pressurized with air when the system is started.

The introduction of the filter-bubble remover

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causes the pressure at the jet stream to slowly increase or decrease when the system was started or stopped. At low pressures the jet stream sputtered dye which was wasteful of dye and increased the risk of droplets of dye striking the mirror surfaces. To avoid this problem a bypass valve was installed around the filtering device to allow maintenance of high pressure for as long as possible.

d. Outstanding Problems

There are still a number of outstanding problems for which experience in using the system has indicated possible solutions.

The evaluation of the laser tube pressure is still a major problem at this time. The pressure is determined by measuring the potential difference from the cathode to the anode while the plasma current is at its maximum rated current. Unfortunately, even when the laser was new, connection of the system's panel meter to the pressure sensing circuitry caused transient signals in the circuitry to be produced. These transients were capable of terminating the arc discharge which was required for determination of the pressure. An additional panel meter permenently connected to the pressure sensor would eliminate the need to generate transients to

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measure the pressure. Protective circuitry would have to be included to prevent damage to the meter from the start pulse transient and the initial high voltage supplied by the start boost circuitry. Another way to avoid this problem may be to monitor one of the catenode discharges. This scheme has the advantage that the catenode discharges can be generated even when an arc discharge cannot. This would allow pressure readings when the arc discharge will not run, which are not possible in the current configuration. By comparing the catenode voltages with the pressure readings from the time a tube is new it may be possible to calibrate the catenode voltage in terms of the tube pressure. Care should be taken to evaluate the effects of the main plasma current on the catenode discharge since it introduces electrons or ions into the catenode discharge regions. A measurement of the catenode discharge potential with no main discharge current can be made by disconecting the start pulse circuitry as described earlier in this chapter.

There exists an outstanding problem of a 360 Hz. ripple of approximately five percent on the argon laser's output. The ripple is phase locked to the line voltage and has been attributed to some problem in the full wave three phase bridge rectifier used in the high current power supply in the laser exciter. The ripple exists

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throughout the exciter, most notably on the low voltage power supply which supplies all the control circuitry. Attempts were made to eliminate the ripple by replacing the full wave bridge involved however this had no effect. The filtering in the low voltage power supply was increased in an attempt to at least eliminate the ripple in the control circuitry. The filter capacitors were increased from 100 uf. to 2,000 uf. but had no effect on the ripple. It may be interesting to note that the higher capacitance is actually the value given for the circuit in the schematic diagrams. Since the problem has remained insoluble to date even with the aid of factory trained technicians, it was decided to attempt to circumvent the manifestions of the problem rather than seek a solution.

C. The Time Correlated Fluorescence Spectrometer

a. Sample Cell Considerations

The decision to use sodium as a sample required consideration of the sample cell's construction. Because sodium has a melting point of approximately one hundred degrees Celsius it is necessary for the sample cell to be heated to at least that value to have any significant vapour pressure. When using a heated cell which has to have windows, a problem of condensation of the sample on the windows usually occurs. Because the windows are exposed, they are the most difficult part of the cell to insulate and hence will be the coldest part of the cell. Experimentation is possible with a simple heated tube; however, it is necessary to frequently heat the windows to reevaporate the sample which has condensed on the windows. Added complications arise when working with sodium in that the windows are attacked by sodium and will eventually become opaque. Achieving temperature stability in this system is a major problem, especially when the windows are frequently being reheated.

There is a heated cell which has an indefinite life without heating the windows called a heat pipe oven. The operational mechanism was originally used to function as an efficient means to transfer heat (62); however, it has a number of properties which make it useful in sample cell design (63). The operative processes involved in the heat pipe oven are a cycle of evapo**ration**., diffusion, condensation and capillary action. The sample cell is a tube which is lined with a fine mesh and is heated at the center and cooled at the ends where the windows are located. The sample is initially placed in the center of the cell which is then sealed and evacuated to remove as much as possible of any volatile inpurities

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in the cell. The cell is then filled with an inert gas to' approximately the pressure of the sample at which the experiments are to be run. When the oven is heated the sample is evaporated and proceeds under the influence of diffusion to the cooler regions of the cell where it condenses on the mesh. The liquid will travel through the mesh by capillary action to the center of the cell where it is reevaporated and the process starts over again. The outward flow of metal atoms functions as a diffusion pump, forcing the inert buffer gas out of the center of the cell and hence the center of the cell will be pure sample vapour at approximately the same pressure as the buffer gas. Under these conditions, changes in the power supplied to the heater causes changes in the volume of the sample region rather than changes in the sample temperature. Estimates of the temperature required to start heat pipe action can be found in references such as the book edited by A.N. Nesmeianov (64).

Two heat pipe ovens were constructed with the second ovens design taking into account that which was learned from construction of the first oven. The working drawings for the second heat pipe oven are included in appendix C. The center of the oven was heated by a 144 watt heating tape driven by a variable transformer. Chromel Alumel thermocouples were installed under the heating tape to allow monitoring of the cell temperature.

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The heated part of the cell was insulated with asbestos tape. Inside the oven three layers of sixty mesh stainless steel screen were used to allow transport of the liquid sample and a 12 mm. strip of .005 inch thick phosphor bronze was used to hold the screen in the side arm against the cell wall to ensure maximum free aperture for detection of fluorescence. The windows were water cooled and to prevent light from the laser being scattered by the windows and detected with the fluorescence, a pair of aluminum rods with a quarter inch hole through their centers were inserted into the oven to function as apertures. Care was taken to ensure that all gas flow passages were not obstructed in order to allow rapid evacuation of the cell and provide paths for equalization of the pressure in the cell when the system is running. The sample cell was connected to a large vessel which was designed to reduce the effects of heating the cell on the cell pressure, and to allow small changes of the cell pressure to be made with only limited chance of plating the sample on the windows. The second oven built included mounting devices for the oven itself and provisions for mounting a photomultiplier housing to the side arm.

b. Electronic Detection ApparatusFigure 4.3 is a schematic diagram of the

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experimental apparatus used for this experiment. The output from the photodiode (PD) was used to trigger a Philips PM 3410/3419A/3419B sampling oscilloscope whose vertical input was taken from a 1P28 photomultiplier (PMT). The oscilloscope was used with the X deflection either externally controlled or manually controlled by a potentiometer adjustment. By controling the X (time) axis it was possible to sample the fluorescence intensity at set time delays with respect to the laser excitation pulses.

The conditions under which this experiment was run lead to weak fluorescence signals, therefore for a set X deflection the Y output of the oscilloscope was a series of pulses with an average rate proportional to the fluorescence intensity. By varying the X deflection of the display the shape of the fluorescence intensity was evaluated. A General Radio 1191 counter was used to measure the pulse rates.

The detection apparatus was originally intended for much more intense signals which would have allowed the use of a computer data gathering system. The X deflection of the oscilloscope was controlled externally by a digital to analogue converter while an analogue to digital converter measured the Y output for a given X deflection. An algorithm to take data in this fashion was written and encoded on a PDP-11 system called a

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MINC-11 with an RT-11 operating system. Testing of the program indicated that if an appropriate input could be found, it could be automatically be recorded. The computer system involved could have been used in low fluorescence conditions but would have involved buying or building a frequency to voltage converter.

D. The Lifetime Determination Apparatus

a. Optical Arrangement

The lifetime measuring technique employed was to saturate a transition with a laser pulse and observe, with a delayed second pulse, how the absorption recovers. This was accomplished by the optical apparatus depicted in figure 4.4. The beam splitter used was an uncoated one inch diameter by one half inch thick optical flat positioned at forty five degrees to the beam which produced three beams with intensity ratios of 1:1:10. The device, constructed of the translation stages and reflector, is a Michelson interferometer which produces two parallel but not colinear beams. A short focal length camera lens was used for L_1 because the short focal length produced a small focused spot and camera lenses are designed to avoid spherical aberrations which would deform the focused spot. A camera lens was also chosen to enable



Cab

the expanding probe beam to be refocused to a spot at the spatial filter. The lens position was chosen such that an image of excited dye volume at the pinhole was the same size as the pinhole. Mirrors M_1 and M_2 were not required but were included to ease alignment of the device.

b. Sample Cell Preparation

In an effort to optimize the lifetime which was to be measured with respect to the measuring apparatus, the sample dye was dissolved in a high viscosity solvent, namely glycerin. To avoid the thermal Schlierin effects seen by other workers (33) a flowing dye system was used.

The use of glycerin as a solvent created air bubbles in the sample solution. The techniques used to solve this problem for the amplifier dye are not applicable because the two order of magnitude increase in the solvent viscosity renders the air bubbles' gravity induced velocity relative to the dye effectively zero. Preparing the sample by placing it in an evacuated bell jar for a day decreased the problem; however, when the sample was circulated using gear pumps any air bubbles trapped in the system were finely subdivided by the pump and remained in the system from then on. A nonagitating circulating system was devised which not only allowed circulation without generating small bubbles but also allowed the sample to be pumped on by a vacuum pump when circulation was not required. A schematic diagram of the circulating system is included in figure 4.5 along with its operating conditions.

The sample solutions were prepared by adding solvent to the dye and mixing using the stirring function of a Precision Scientific constant temperature controller. Magnetic stirring devices were found to be ineffective in that they mixed only the volume which was swept out by the stirring bar. A propeller or fan'type stirring device was found to be most effective. The dyes were generally found to require one to two days to dissolve to the point that crystals were not visible in a microscope. Heating the solutions reduced the time required to dissolve the dyes; however, at elevated temperatures dye degradation was observed when using DOTCI.

c. Electronic Detection Apparatus

The probe beam intensity was converted into a voltage by the adjustable gain photodiode assembly. A frequency reference of the saturating beam's chopping frequency was created, by a helium-neon laser which was chopped and detected by a slow HP 4220 photodiode assembly when light choppers without internal reference

-52-.


| Operation | Valve Positions | | | | |
|----------------------------|-----------------|---|----|---|-----------|
| | 1 | 2 | 3. | 4 | |
| Fill Reservoir | 0 | С | 0 | С | 0=0pen |
| Degas Sampl <mark>e</mark> | 0 | С | C | С | C = Close |
| Circulate Sample | С | 0 | С | 0 | |

Figure 4.5 Sample Handling System For High Viscosity Sample Solutions

C = Closed

signals were used. Light chopping frequencies up to one kilohertz were used in an attempt to overcome the instability of the laser's output which had large frequencies up to about 200 hertz.

It was intended that a PAR lockin amplifier be used to detect the variation in the signal which was synchronous with the reference frequency. It was found that residual air bubbles in the sample solution cause either decreases in the signal by deflecting the probe beam or increases in the signal intensity due to scatter of the saturating beam into the probe beam. These changes in signal were sufficiently large to overload the lock-in amplifier and prevent further measurements for a few time constants of the amplifier while the system recovered. To reduce this problem an input filter was constructed with a capacitor, for A.C. coupling, followed by a symetric voltage clamp and a limitimg resistor. Germanium diodes were used in the voltage clamp which implies that voltages greater than 200 millivolts or less than -200 millivolts will be dissipated in the limiting resistor. This prevented overloading of the lock-in and only a short time was required for the system to recover from a bubble.

For a given probe beam delay the pen on a strip chart recorder was lowered to record several seconds of the detected signal before the pen was raised and the

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probe beam delay was manually changed. This process was repeated such that the detected signal was recorded over the full range of allowed delays. Generally measurements were made every 4.23 picoseconds of probe beam delay which coresponded to .025 inches of displacement of a translation stage in the Michelson interferometer. Laser Setup and Characterization

A. Laser Setup

a. Mixed Amplifier Absorber Dye Scheme

In this chapter the operation of the laser system shall be discussed for all configurations used. Although the first configuration described was unsucessful at producing mode-locked operation it shall be included for the sake of completeness because it did play an important role in the design of the final laser system.

Amplifier/ absorber dye solutions were created by mixing two solutions of known concentration of absorber and amplifier dyes. The dye solution containing a high concentration of the absorber had an amplifier dye concentration which was equal to that in the second dye solution, which had no absorber dye in it initially. This procedure allowed the amplifier dye concentration to be kept constant while mixing the two solutions. The absorber dye concentration increased from zero to a value determined by the total amount of the concentrated absorber solution which could be added to the amplifier dye solution.

Using the procedure described above, a number of amplifier dye concentrations were used in the laser

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cavity with the standard optics supplied by the manufacturer. No mode-locking was observed under these conditions. The output mirror was changed from an 88% reflecting optic to a 95% and later a 98% reflecting mirror. This was done on the assumption that by decreasing the ratio of the cavity's linear losses (not intensity dependent) to its nonlinear losses the contrast ratio between intense and weak pulses will increase more rapidly with each pass through the cavity. The dye mixing procedure was repeated using the 95% and 98% output couplers in the laser cavity and also failed to produce mode-locking. It was later determined that the approach of increasing the cavity's Q was correct in that another group (53), using a Spectra-Physics Model 375 dye laser, found that they could only produce mode-locking by this scheme if they used the highest possible reflectances for the output reflector and even with that reflector it was necessary to move the mirror transverse to the optical axis until they found a region of anomalously high reflectivity before mode-locking would occur.

b. Separated Amplifier and Absorber Dye Scheme The first step in producing mode-locking using
separate dye cells is to optimize the positioning of the pump laser beam at the jet stream. This can be readily
done by running the dye laser with an output mirror

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rather than the dye cell/ output mirror assembly and optimizing the dye laser's output power.

The following steps will require an aperture in the laser cavity to function as a screen for viewing the affects of the lens assembly. The hole for the optical axis should be sufficiently large that it does not intercept any laser light in the beam. The aperture in this work was mounted with double sided tape to the output plate of the model 375 dye laser structure. This mounting position produced a screen to output mirror distance of not less than 15 cm.

When the aperture is in place the output mirror should be replaced with the dye cell/ output mirror assembly, and the assembly aligned by establishing lasing without any additional focussing optics in the cavity.

It should now be possible to install the lens assembly into the cavity and produce a symmetrical image on the screen by positioning the assembly by hand. If a symmetrical image cannot be produced the output mirror assembly can be rotated about its horizontal axis to give a symmetrical image. If large rotations are required to produce a symmetrical image then the height of the lens assembly should be adjusted. With some practice it is possible to translate the lens assembly along the optical axis while maintaining the symmetrical image on the screen. As the lens assembly is translated between

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the extremes of its travel the image on the screen will decrease in size until it disappears into the aperture and then increase in size again. If this longitudinal translation is repeated a number of times the lens assembly will probably, at the point where the image size is a minimum, be at a point appropriate for laser action and a flash of laser light will occur. It was usually possible to stop translating the lenses and have laser action persist. By iteratively adjusting the translation stage under the lens assembly and the two rotations of the output coupler it should be possible to produce mode-locking. There are three general classes of measurements which can be used to monitor the developement of mode-locking.

The most straight forward technique of monitoring the development of mode-locking is to use fast detection of the laser intensity and monitor the pulse itself. In this work a sampling oscilloscope with a 300 ps. risetime was used and therefore the description shall be with respect to that type of detection. If the oscilloscope is not adjusted to trigger on the signal, increases in the fuzziness of the display will accompany improvements in the mode-locking of the laser. If the oscilloscope is triggering on the signal the display will consist of a periodic waveform whose period is the laser cavities round trip time divided by some integer. As mode-locking

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improves the integral number of periods per cavity round trip time will decrease to one from four or five. When there were only one or two pulses per round trip time it was possible to adjust the laser cavity such that a discontinuous change in the sharpness occured. This change is illustrated by the oscillographs in figure 5.1 which shows mode-locked pulses detected using a Philips sampling oscilloscope whose output was displayed on a Tektronix oscilloscope and recorded with an oscilloscope camera. Figure 5.1a shows a partially mode-locked output whereas figure 5.1b is of an output which, to the ability of the detection apparatus, is fully mode-locked. Figure 5.1c is a photograph of the detection of mode locked pulses which deteriorated into partial mode-locking while the picture was being taken. This bimodal operation has been observer by others using mode-locked c.w. dye lasers using the same dyes (65). Note the decrease in the peak and average intensities as it will be mentioned later.

A second class of measurement which displays effects which have been correlated to mode-locking is measurement of the average intensity on a time scale of one microsecond. As the laser approaches mode-locked operation the intensity will increase and there will be a noise component with a period of approximately one microsecond and a magnitude of approximately 30% of the

-70-

Figure 5.1

Oscillographs of Two Modes of Operation of the Mode-Locked Laser

- a. Long Pulse Operation
- b. Short Pulse Operation
- c. Oscillograph Made During a Change of Operating Modes







signal. When complete mode-locking occurs there is a discontinuous increase in the intensity of about 15% and the noise decreases in magnitude to 5% of the signal and has a characteristic time of about 5 microseconds. The stepping of the average intensity occurs at the same time as the output pulses convert from partial to complete mode-locking. When it is not possible to monitor the laser's intensity with a high speed detector, monitoring the average intensity can give a fair idea of the operational status of the laser.

Mode-locked lasers have a larger oscillating bandwidth than the same lasers in a non-mode-locked condition. This leads to a third type of measurement by which the laser's status can be monitored. By passing a beam of diverging laser light through a Fabry-Perot etalon and onto a screen a pattern made up of a number of concentric rings will appear, given an appropriate choice of etalon. The width of the rings will be determined by the finesse and free spectral range of the etalon and the bandwidth of the laser. Given an appropriate choice of etalon parameters the width of the etalon fringes will be proportional to the laser's bandwidth. When mode locking occurs an increase in the laser's oscillating bandwidth should cause the etalon fringes to become thicker. In this work a one mm. air spaced etalon with a finesse of 45 was used. This choice

-72-

of etalon parameters produces a free spectral range of 150 gigahertz and an instrumental bandwidth of about 3.25 gigahertz. The laser's bandwidth is much larger than the etalon's instrumental bandwidth and therefore will be the dominant factor determining the ,ring width. The free spectral range of the etalon is greater than the laser bandwidth which implies that adjacent rings will not overlap. The ring patterns observed in this work changed from Having a finesse of ten to a finesse of three, as shown in figure 5.2. The change in ring pattern occured simultaneously with the changes in the average intensity and the narrowing of the laser pulses. Short of using a fast real time image processing system, this feature of mode-locked lasers is not as useful as the previously described techniques; however, it is a more direct evidence of mode-locking than the information gained from monitoring the average intensity.

B. Characterization of the Laser

This laser system was tested under conditions of varying dye concentrations of amplifier dyes (Rhodamine 6G, Rhodamine B, binary mixtures of the Rhodamines 6G and B and binary mixtures of Rhodamine B and Fluorescein Disodium Salts) and absorber dyes (DODCI and binary mixtures of DODCI and Malachite Green). All dyes used

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Figure 5.2

Etalon Rings Produced With Dye Laser Output

a. Laser in Non-Mode-Locked Condition

b. Laser in Mode-Locked Condition



in the laser were laser grade except for the Malachite Green which was purified before use. The dye laser's cavity length was varied and adjustments were made to the output lens system such that the beam waist in the absorber was varied.

Measurement of the laser light's wavelength was performed using a 1.5 meter Bausch and Lomb spectrograph which was calibrated using neon and iron emission lines produced by a hollow cathode discharge lamp. Evaluation of the spectrogram was accomplished with a traveling microscope digitizer and a computer program which did a rigorous weighted least squares calculation of arbitrary order and calculated the standard deviation of the wavelenght in a rigorous way. The standard deviations calculated using this program were approximately .01 nm.. In the interest of speeding up the calibration proceedure, visual comparisons of the laser's wavelength to the calibration spectra were made using the 1.5 meter Bausch and Lomb spectrograph and a 35 mm. SLR camera equiped with extender rings. In the spectral region in which the laser operated, the density of calibration lines allowed accuracies of approximately .2 nm. with a worst possible error of 1 nm. where calibration lines have their maximum separation.

For both single dye solutions used as amplifying media a dye concentration of 1E-3 molar in ethylene

-75-

glycol was found to be optimum in terms of ease of mode-locking. Binary amplifier dye concentrations were found not to allow mode-locking. The wavelength region overwhich mode-locking would occur was not dependent on the amplifier dye concentration but could be shifted to longer wavelengths by increasing the concentration of the saturable absorber dye. It was found that saturable absorber dye concentrations in the range of 4E-5 M. to 1E-4 M. were effective at mode-locking the dye laser. Addition of Malachite Green, which is reputed to enhance mode-locked operation above threshold (66), was found to inhibit mode-locking at all concentrations up to and including that suggested by Ippen (67). It is possible that the reason mode-locked operation was not promoted by the extra absorber is that the cavity's linear losses were so high that the inclusion of additional losses prevented oscillation. the assumption that the losses in this cavity were higher than the losses in cavities used by other workers can be substantiated by the fact that the four watt pump laser threshold is significantly higher than the thresholds of less than one watt common in most mode-locked c.w. dye laser cavities (55, 68).

The mode-locked laser pulse was initially observed using a Philips sampling oscilloscope which had a rise time of three hundred picoseconds and was the limiting factor in the detection apparatus. Once operation

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of the laser had been optimized it was possible to use a Tektronix R7704/7T11/7S11/S2 sampling oscilloscope which has a faster response but has more inherent noise in its detector and a higher triggering threshold. The detection apparatus using the Tektronix oscilloscope was limited by the photodiode risetime of approximately 150 ps. With this apparatus pulse substructure was observed. An example of an oscilloscope trace of a pulse is given in figure 5.3. The two peaks in each pulse are separated by approximately 350 ps. which corresponds to light traveling 10.5 cm. in air. The pulse substructure was independ nt of the laser's alignment, the choice of detectors the position of the detector and the length and type of wire used to connect the detector to the oscilloscope. It was noted that the optical path from the jet stream to the end mirror and back to the jet stream was 10 cm. It was suggested by Ippen (67) that "double pulsing" would be a problem in a laser with a configuration like the one used in this work, as opposed to those configurations with centrally located amplifier dye cells. A possible explanation for this composite pulse structure involves the recovery of the gain and absorption in the laser. The first pulse sweeps out the gain in the amplifier and proceeds to the end mirror and back to the amplifier. Before the first pulse passes through the amplifier a second pulse sweeps out that

-77-

Figure 5.3

Oscillograph of Mode-locked Laser Pulses

a. Average Intensity

b. Pulse intensity



gain which has recovered after the first pulse. Hence the first pulse is not amplified on its second pass through the amplifier. It is clear that repeating this argument one would conclude that the laser's output should be a large pulse followed by a string of less intense pulses. The saturable absorber however, will discriminate against pulses that follow the large pulse at times which are long compared to the absorber's recovery time of about 300 picoseconds. Hence only one trailing pulse is seen.

For the shortest possible cavity length of approximately 60 cm. mode-locked operation was produced between 568. nm. and 578. nm.. Dilution of the DODCI caused the region over which mode-locking occurred to shift to longer wavelengths while maintaining roughly the same extent (7.5 nm.).

Extending the length of the laser cavity shifted the mode-locking region to longer wavelengths to the extent that it was possible to mode-lock the laser at wavelengths up to 620 nm. when the cavity was lengthened to 100 cm. The cavity length was changed over small distances while in mode-locked operation during which the frequency of oscillation did not change by more than a small part of its bandwidth, as determined by monitoring the bandwidth with an etalon, and the mode-locked condition did not terminate in any way inconsistent with

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operation while not moving. A summary of the wavelengths for which mode-locking was possible is given in figure 5.4 along with other mode-locked c.w. dye laser systems.

Changing the amplifier dye concentration did not have a noticeable effect on the range of mode-locking. The amplifier dye was changed to rhodamine B and mode-locking required the removal of the diverging lens, L2. The mode-locked rhodamine B/DCDCI laser produced mode-locked pulses at wavelengths between 599 and 609 nm. with a 60 cm. laser cavity length. Composite amplifier dye solutions using rhodamine 6C and rhodamine B as well as Rhodamine B and Flucrescien Disodium Salts were used in an unsucessful attempt to produce mode-locking between the mode-locking regions of the separate amplifiers.

Throughout these measurements the pulse width of the mode-locked pulses remained below the detection limited pulse width of the detection apparatus used. Pulse width determinations were attempted using dimethyl-POPOP in benzene as a medium for two photon fluorescence. The laser's intensity was insufficent to produce detectable fluorescence. A lower limit for the pulse width was established by assuming the pulses were bandwidth limited. This assumption implies the relation $\Delta t = .441/\Delta v$. Using the interferometer data mentioned in section 5.A.b the bandwidth was estimated as 1.7

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wavenumbers and hence the lower limit for the laser pulses was 8.5 picoseconds.

The average intensity of the mode-locked rhodamine 6G/DODCI laser output was approximately two milliwatts and varied by only twenty five percent regardless of the wavelength or cavity length. When rhodamine B was used as the amplifier dye the mode-locked laser had an average intensity which varied from 2.5 milliwatts to 5. milliwatts with alignment of the laser. Assuming the output is a pair of bandwidth limited pulses, these average powers correspond to peak powers of the order of one watt.

The independence of the average power from the cavity length may indicate a possible explanation of the operating wavelength's dependence on the cavity length. For longer cavity lengths the energy per pulse must be higher such that the average power remains constant. This would lead to an increase in the production of the photoisomer of DODCI which is involved in mode-locking the laser (79). The increased concentration of the photoisomer, which has its absorption red shifted with respect to the normal isomer, may be leading to a shift of the operating point to longer wavelengths.

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CHAPTER 6

Results of Application Experiments

A. Preliminary results of Time Correlated Fluorescence Studies

Studies were attempted using sodium dimer because it provided a large number of excited states for which laser excitation was possible and it has hyperfine structure due to its nuclear spin of 3/2.

The sodium used was standard laboratory reagent grade sodium stored in a liquid paraffin bath as supplied by the BDH Chemical Company. For the preliminary experiments an intense emission at approximately 580nm. was excited.

Analogue detection of the intensity of the fluorescence was found to be impractical with the apparatus used because of low signal levels. When the sampling oscilloscope was used in the "normal" (non-smoothed) mode the display was a collection of pulses of essentially the same magnitude, indicating that the signal was primarily composed of single photon events. Using the GR-1191 counter to detect the rate at which the sampling oscilloscope detected a signal, an average pulse frequency of the order of a hundred pulses per second was measured using a ten second gate to make

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the measurement. The sample cell was cooled to room temperature and the count rate droped to of the order of one pulse per second, indicating that laser scatter from surfaces in the sample cell were not a significant factor in the detected signal. With the sample cell at its operating temperature and the laser excitation blocked count rates of about the same as those for a cold sample cell were detected, indicating that the photomultiplier's dark current was probably responsible for the small backround measurement.

An example of the type of results produced by the experimental apparatus described here are given in table 6.1. Since the possible, trivial explainations of the observed signal have been eliminated, we may ascribe the modulation of the signal to modulation of the fluorescence intensity. It should be noted that a ripple in the fluorescence signal would be expected even if no quantum beat modulation occured. The magnitude of the inherent modulation in this experiment depends on the length of the exponential decay compared to the pulse period of the exciting light. Clearly, if the fluorescence lifetime is short with respect to the pulse period, there will be a significant decrease in the fluorescence between excitation pulses which will appear as a ripple in the detected signal. Conversely, if the lifetime is long with respect to the pulse period, little

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Table 6.1

Typical Output of the Quantum Beat Experiment.

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| Approximate Cavity Length (cm.) | Intensities (in counts) | | Ripple | Time required for These measurements | |
|---------------------------------------|-------------------------|--------------------|----------------------------|---|--------|
| | Average | Maximum | Minimum | | |
| 68. | 122.8 <u>+</u> 3.0 | 155.0 <u>+</u> 4.8 | 94 . 3 <u>+</u> 1.2 | •49 <u>+</u> •05 | 3 min. |
| 69. | 126.3 <u>+</u> 3.3 | 148.5 <u>+</u> 5.6 | 106.9 <u>+</u> 0.9 | •33 <u>+</u> •05 | 2 min. |

Experiment terminated when mode-locking stopped.

change in the fluorescence intensity will occur between the excitation pulses and the ripple in the signal will be small. In the mathematical modeling of this experiment the inherent ripple expected, for even the short lifetime of 100 ns., was less than five percent at the pulse period used. For these reasons the existence of a quantum beat signal can be inferred and the beat frequency can be said to be in the 200 MHz. region. The exact value of the level splittings responsible for the beats will require further experimentation to evaluate.

The continuation of this experiment was not practical at the time the data was taken because the determination of the intensity, for a given delay with respect to the excitation, required approximately one minute of reliable laser operation. Even a crude measurement of the intensity's ripple requires measurements at at least two time delays. A minimal sampling of the ripple versus cavity length relation required a duration over which reliable operation of the laser was improbable. Recovery of mode-locked operation involved adjustment of the laser cavity and as a consequence of that, a loss of knowledge as to whether the laser wavelength was appropriate for exciting the states of interest.

Reinitiation of this experiment will require a number of improvements of the apparatus including improvements in intensity, stability and calibration.

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Increasing the laser system's output power would allow the data acquisition rate to be increased, possibly to the point where the experiment could be performed in a time for which reliable operation can be assured. The most straight forward solution to this problem is the construction of a dye laser amplifier (71) or redesign of the laser cavity as suggested by Johnston (72); however, it may also be useful to consider the possibility of lowering the cavity losses by using quality laser optics instead of surplus industrial optics.

It may be possible to increase the duration of stable operation such that an experiment can be completed before adjustments are required to the laser cavity. Improvements to the acoustic filtering and the bubble removal would seem to be reasonable starting points for increasing the laser's stability.

Continuation of this experiment would require the assignment of the spectra in order to correctly determine the quantum numbers associated with the specific transitions which are studied. This is a difficult but not impossible task which is made much easier if the spectra is displayed with its ordinate being a linear function of wavelength or frequency, such that patterns can be recognized. This would require, at least, computer processing of the spectra to linearize the effects of the type of tuning used in the laser and

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to detect and eliminate the effects of mode hopping.

B. Results of Lifetime Determination Experiments The Malachite green used in this experiment was obtained as a biological stain from BDH Chemicals Limited. Thin layer chromatography (commonly refered to as TLC) was used to examine the dye and the dyestock was found to contain an impurity which was removed when the dye crystals were washed in ethyl acetate.

The DOTCI was obtained as laser grade dye from the Exciton Chemical Company and the DTDCB was obtained from the Pierce Chemical Company. TLC of these carbocyanine dyes indicated that no impurity was present.

Lifetimes of the S₁ manifold were measured and variations due to differences in temperature were compensated for by calculating a correction factor which adjusted the lifetimes to that which would be expected at twenty celsius. By employing the viscosity versus temperature data for glycerin, tabulated in the CRC Handbook of Physics and Chemistry, and assuming the lifetime has a viscosity dependence of the viscosity to the two thirds power, as predicted by the Forster model (31) and observed by Ippen (32), Yu (25) and others, it is possible to predict the lifetime which would be measured at some temperature if the lifetime is known at some other temperature.

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An example of the type of data produced by this apparatus is given in figure 6.1. It should be noted that the time axis of the chart recorder's output represents the passage of time during the experiment and does not have a one to one relationship with the delay time between the arrival of light pulses at the sample. The method by which this data was acquired was previously described in subsection 4:D:c.

The results of the processing of a number of experimental runs are summarized in table 6.2. Clearly the duration of the depleted absorption was decreased with the addition of acceptor molecules into the sample. The decrease of the lifetimes was approximately that which was expected from the calculation of the rate constant using the theoretical considerations discussed earlier. The association of this decrease with dipole-dipole energy transfer is therefore not excluded, but is only one of a number of possible explanation of the observed affect. It is possible, even if improbable, that both DOTCI and DTDCB both have very short (and approximately equal) lifetimes which were the actual source of the lifetimes which were measured. This explanation is considered improbable in that it requires the lifetimes of both of the acceptor dyes to be anomalously short in comparison to the lifetimes of others of the related carbo-cyanine dyes which have

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| 5×10 ⁻⁴ M | | averages |
|---|---|---------------|
| Malachite Green | 58±3 61±3 62±7 57±2 | 59 ±2 |
| Malachite Green + 10 ⁻³ M. DTDCB | $\begin{array}{c} 45 \pm 2 \\ 43 \pm 2 \\ 48 \pm 2 \\ 45 \pm 1 \end{array}$ | 45 <u>+</u> 1 |
| Malachite Green + 10 ⁻³ M. DOTCI | 43±2 | 43 ±2 |

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lifetimes in the nanosecond domain (73). A lifetime experiment, using the apparatus described in this work, with a sample consisting of acceptor molecules without any donor molecules would indicate definitively if the lifetimes observed were direct acceptor lifetime observations. Further conformation of the processes involved can be accomplished by further lifetime determinations using different acceptor concentrations. For small values of the factor γ . (=C/C₀) the lifetime is a quadratic function of C and a number of lifetimes recorded for differing concentrations of the acceptor will allow the concentration dependence to be compared with that predicted by theoretical considerations.

The current interpretation of the change in lifetimes as being induced by dipole-dipole energy exchange leads to the conclusion that the population of the S manifold of Malachite Green is persistent throughout the recovery of the ground state absorption. This indicates that the internal conversion rate must be slower than the vibrational relaxation rate, as was suggested by Schneider, Wirth and Dorr. It also indicates that the low quantum yield data which lead Ippen and Shank to assume that the faster rate was the internal conversion rate was misleading.

The apparatus used in this experiment was functional up to the time when this research was

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discontinued due to failure of the argon ion laser's plasma tube. There are, however, a number of improvements which would be worth consideration if this type of experiment were to be reinitiated.

The precision with which the tranmission was determined could be greatly increased if the fluctuations in the detected signal, caused by sources other than sample absorption, could be reduced. The major sources of spurious fluctuations were minute air bubbles in the sample dye and the fluctuations of the mode-locked laser's output power, which is probably caused by variation of the jet stream's geometry.

An increase in the output power of the laser system would ease the restriction on the spot size to which the two beams have to be focused. Larger focussed spots in the sample dye cell would decrease the effects of the air bubbles in the sample because their size relative to the spot size would decrease. The larger spot size would also promote beam alignment in the sample cell, which was a trial and error process at the time of the last system failure.

Automation of the translation stages used in the interferometer would allow automatic data collection to greater accuracy because convergence criteria could be used to control the dwell time of each delay.

When this work was discontinued it had been

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determined that acceptor absorption by the 2E-3 M. DOTCI was not going to prevent the measurement of a lifetime as did 2E-3 M. DTDCB.

Further exploitation of the apparatus built for this thesis can be suggested by the reviews of ultra fast processes (2, 74-77) and articles such as that by Greene (73).

C. Discussion and Conclusions

This study was undertaken with the primary objective being to develope an apparatus capable of producing and employing light pulses with pulse widths in the picosecond domain, for spectroscopic and energy transfer process studies. This objective has been sucessfully acomplished. This concluding chapter briefly highlights the results of this work.

The first steps into a new field of research have been completed. The problems associated with starting up a new apparatus have been solved. Those aspects of the research in which practical improvements could be made were isolated and possible corrective actions were considered.

The c.w. mode-locked dye laser system which was designed and constructed for this work performed \mathcal{L} satisfactorily in an energy transfer process experiment

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and gave indications that, with improvements in the laser's stability and output power, it would function satisfactorily for guantum beat spectroscopic experiments. The problems which restrict the use of the laser in quantum beat experiments were not ascribed to mechanisms which are inherent in the system and would render then insoluble. Techniques have been suggested which would serve as a starting point for investigations to overcome the difficulties.

At the time of this writing the laser system was inoperative due to catastrophic failure of the argon ion laser. The high cost of recovering the system is a characteristic of the finances associated with this type of research.

The laser spectrometer described in this work is a reasonable project to reinitiate if a concerted effort is made to enter the field of short interval experimentation, with all the finances and allocation of manpower it requires. If at least one person with experience in dealing with some of the problems outlined in the previous chapters is associated with such a project it is possible that the system could be made to function as an efficient, competitive tool in the field of short interval experimentation.

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Appendix A.

Drawings And Schematics For Detectors

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a. The Photomultiplier Housing



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This housing was designed with concern for the light tightness of the device. This design turned out to be more expensive than necessary in that the large number of light traps added machining operations which increased the cost. The same light tight effect could have been accomplished by using a metal cylinder with light tight caps and a side port, with provisions for mounting, welded to the cylinder. b. The Detectors





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Appendix B.

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Drawings And Schematics For Laser System

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a. The Translation Stage









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PARTS NO. 1 AND 2



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In practice the us**able** length of the translation stage was less than a meter. The air bearings had a tendency to create vibrations unless the translation stage was used with weights attached to load down the bearings. The steel rods tended to rust over a period of **mo**nths, requiring cleaning with steel wool. For a second generation translation stage a number of useful modifications could be made.

Ey shortening the translation stage to 75 cm., replacing the three quarter inch rods with one inch rods and eliminating the central support, the stage would be easier to use. In this new configuration it would be possible to replace the air saddle bearings with air bushings which would eliminate the vibration problem. It would be advisable to replace the steel rods with stainless steel because of the corrosive atmosphere in the laboratory.

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b. The Lens Mounting Device







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The lens mount table was found to be difficult to use in that precise adjustment of the lens holder was difficult, due to friction between the table and the lens holder and due to the coarseness of the adjustment screw controling longitudinal motion. It was found that the table could be replaced with a commercial translation stage which gave better over the longitudinal translation. 11

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c. The Dye Cell / Output Reflector







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The Dye cell / Output Reflector was constructed with all its fabricated parts made from brass. The choice of material was made solely on the basis of ease of machining. It was later determined the another factor should have been taken into account. When two bearing surfaces are of similar hardness they will tend to gall at the same rate. As a consequence of this roughening of the bearing surfaces the device will tend to seize or at least become difficult to operate. When materials of dissimillar hardness are used only the softer material will gall and there will remain one smooth surface which will maintain smooth operation.

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d. The Electrical Schematics for

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the Model 270 Exciter

The schematic on the previous page includes a solenoid (J1001) and a reference to switch S106. These devices can be ignored as they were not included with the laser. The schematic for the light control circuitry does not describe the circuitry in the light control section of the exciter and can only be used as an indication of the design philosophy used in the light control circuits.

The fill threshold circuitry can be defaulted by shorting pin 18 to pin 20 of the Fill Control circuit board. The start sequence can be initiated after tube warmup by installing a switch on the electrical control circuit board to open the circuit above CR213 to allow capacitor C209 to charge before the switch is closed again. Appendix C.

The Heat Pipe Oven





1 VACUUM TIGHT CAN

-VOLUME APPROXIMATELY 1 LITER -ACCESS THROUGH A 🖁 O SEAL STRAIGHT THREAD SWAGELOK CONNECTOR

> HEAT PIPE OVEN PRESSURE BALLAST

Appendix D.

Raw Data from Lifetime Experiments

| Date: | Absorber | [A] | Т | Lifetimes (ps.) | |
|---|--|--|--|--|--|
| | | (M.) | (C.) | as measured | corrected to 20. C. |
| 15-0CT-79 15-0CT-79 15-0CT-79 23-0CT-79 27-JAN-80 10-FEB-80 10-FEB-80 9-MAR-80 9-MAR-80 | none none none DTDCE DTDCB DTDCB DTDCB DTDCB DTDCB | 1 E - 3 1 E - 3 | 21.0 21.0 21.0 21.0 18.2 18.5 18.2 18.2 18.2 18.1 | $56 + 3 \\ 59 + 3 \\ 50 + 3 \\ 60 + 7 \\ 55 + 2 \\ 47 + 2 \\ 45 + 2 \\ 50 + 2 \\ 47 + 1 \\ 46 + 2 \\ $ | $58 \cdot \pm 3 \cdot 61 \cdot \pm 3 \cdot 62 \cdot \pm 7 \cdot 57 \cdot \pm 2 \cdot 45 \cdot \pm 2 \cdot 43 \cdot \pm 1 \cdot 43 \cdot \pm 3 \cdot \pm 4 $ |

All lifetimes were measured using a Malachite Green concentration of 5E-4 M. with glycerin used as the solvent.

- ** References **
- L.E. Hargrove, R.L. Fork and M.A. Pollack Applied Physics Letters 5 (1964) 4
- 2. S.L. Shapiro (editor) <u>Topics in Applied Physics</u> : <u>V.18 Ultrashort</u> <u>Light Pulses.</u> Springer-Verlag
- 3. E.P. Ippen, C.V. Shank and R.L. Woerner Chemical Physics Letters 46 (1977) 20
- 4. K.W. Meissner The Journal of the Optical Society of America 31 (1941) 405
- 5. K.W. Meissner, L.G. Mundie and P. Stelson Physical Review 74 (1948) 932 Physical Review 75 (1949) 891
- D. Pritchard, J. Apt and T.W. Ducas Physical Review Letters 32 (1974) 641
- 7. T.W. Hansch, K.C. Harvey, G. Meisel and A.L. Schawlow Optics Communications 11 (1974) 50
- 8. M.D. Levenson and M.M. Salour Physics Letters 48A (1974) 331
- 9. F. Biraben, B. Cagnac and G. Grynberg Physics Letters 48A (1974) 459
- 10. F. Biraben, B. Cagnac and G. Grynberg Physical Review Letters 32 (1974) 643
- 11. S. Haroche, J.A. Paisner and A.L. Schawlow Physical Review Letters 30 (1974) 948
- 12. W. Gornik, D. Kaiser, W. Lange and H.H. Schulz Optics Communications 6 (1972) 327
- 13. R. Wallenstein, J.A. Paisner and A.L. Schawlow Physical Review Letters 32 (1974) 1333

- 14. G. Arfken <u>Mathematical Methods for Physicists :</u> <u>second edition</u> Academic Press, 1970
- 15. A. Corney and G.W. Series Proceedings of the Physical Society 83 (1964) 213
- 16. J.N. Dodd, W.N. Fox, G.W. Series and M.J. Taylor Proceedings of the Physical Society 74 (1959) 789
- 17. C. Fabre, M. Gross and S. Haroche Optics Communications 13 (1975) 393
- S. Haroche, M. Gross and M.P. Silverman Physical Review Letters 33 (1974) 1063
- 19. Cario and Franck
 Z. Physik 17 (1923) 202
- 20. R. Livingston The Journal of Physical Chemistry 61 (1957) 860
- 21. J. Lavorel The Journal of Physical Chemistry 61 (1957) 864
- 22. G.W. Robinson and R.P. Frosch The Journal of Chemical Physics 38 (1963) 1187
- 23. Th. Forster Discussions of the Faraday Society 27 (1959) 7
- 24. R.E. Kellogg The Journal of Luminescence 1,2 (1970) 435
- 25. C.J. Mastrangelo and H.W. Offen Chemical Physics Letters 46 (9177) 588
- 26. W. Yu, F. Pellegrino, M. Grant and R.R. Alfano The Journal of Chemical Physics 67 (1977) 1766
- 27. D. Magde and M.W. Windsor Chemical Physics Letters 24 (1974) 144
- 28. D.A. Cremers and M.W. Windsor Chemical Physics Letters 71 (1980) 27

- 29. G.N. Lewis, T.T. Magel and D. Lipkin The Journal of the American Chemical Society 54 (1942) 1774
- 30. J.M. Grzybowski, S.E. Sugamori, D.F. Williams and R.W. Yip Chemical Physics Letters 55 (1979) 455
- 31. Th. Forster and G. Hoffman Z. Physik Chem. NF 75 (1971) 63
- 32. E.P. Ippen, C.V. Shank and A. Bergman Chemical Physics Letters 38 (1976) 387
- 33. P. Wirth, S. Schneider and F. Dorr Optics Communications 20 (1977) 155
- 34. M.D. Hirsch and H. Mahr Chemical Physics Letters 60 (1979) 299
- 35. G. Porter and C.J. Tredwell Chemical Physics Letters 56 (1978) 278
- 36. D. Rehm and K.B. Eisenthal Chemical Physics Letters 9 (1971) 387
- 37. G. Porter and C.J. Tredwell Chemical Physics Letters 56 (1978) 278
- 38. S.A. Ahmed, J.S. Gergely and D. Infante The Journal of Chemical Physics 51 (1974) 1584
- 39. S. Speiser and R. Katraro Optics Communications 27 (1978) 287
- 40. C. Lin and A. Dienes The Journal of Applied Physics 44 (1973) 5050
- 41. C.E. Moeller, C.M. Verber and A.H. Adelman Applied Physics Letters 18 (1971) 278
- 42. C.K. Chan Spectra-Physics Laser Technical Bulletin No. 8 February 1978
- 43. C.K. Chan and S.O. Sari Applied Physics Letters 25 (1974) 403
- 44. A. Scavennec Optics Communications 17 (1976) 14
- 45. D.J. Bradley The Journal of Physical Chemistry 82 (1978) 2259
- 45. D.J. Bradley and G.H.C. New Proceedings of the IEEE 52 (1974) 313
- 47. P.W. Smith Proceedings of the IEEE 58 (1970) 1342
- 48. R.J. von Gutfeld Applied Physics Letters 18 (1971) 481
- 49. D.J. Bradley and F. O'Neill Opto-Electronics 1 (1959) 69
- 50. F. O'Neill Optics Communications 6,(1972) 360
- 51. C.V. Shank and E.P. Ippen Applied Physics Letters 24 (1974) 373
- 52. A. Scavennec and N.S. Nahman IEEE Journal of Quantum Electronics QE-10 (1974) 95
- 53. J.-C. Diels, E. Van Stryland and G. Benedict Optics Communications 25 (1978) 93
- 54. D.J. Bradley, G.H.C. New and S.J. Caughey Optics Communications 2 (1970) 41
- 55. E.G. Arthurs, D.J. Bradley, P.N. Puntambekar, I.S. Ruddock and T.J. Glynn
- 55. F. O'Neill Optics Communications 5 (1972) 350
- 57. O.G. Peterson, S.A. Tuccio and B.B. Snavely Applied Physics Letters 17 (1970) 245

* *

- 58. G.H. McCall The Review of Scientific Instruments 43 (1972) 865
- 59. H.W. Kogelnik, E.P. Ippen, A. Dienes and C.V. Shank IEEE Journal of Quantum Electronics QE-8 (1972) 724
- 60. P.K. Runge and R. Rosenberg IEEE Journal of Quantum Electronics QE-8 (1972) 910
- 61. O. Teschke, J.R. Whinnery and A. Dienes IEFE Journal of Quantum Electronics QE-12 (1976) 513
- 62. G.M. Grover, T.P. Cotter and G.F. Erickson The Journal of Applied Physics 35 (1964) 1990
- 63. C.R. Vidal and J. Cooper The Journal of Applied Physics 40 (1969) 3370
- 64. A.N. Nesmeianov (editor) <u>Vapour Pressure of the Elements</u> pp.128 Elsevier, New York
- 65. E.P. Ippen, C.V. Shank and A. Dienes Applied Physics Letters 21 (1972) 348
- 66. E.P. Ippen and C.V. Shank Applied Physics Letters 27 (1975) 488
- 67. E.P. Ippen private communications
- 58. J.P. Letouzey and S.O. Sari Applied Physics Letters 23 (1973) 311
- 69. A. Dienes, E.P. Ippen and C.V. Shank Applied Physics Letters 19 (1971) 258
- 70. D.J. Kuizenga Applied Physics Letters 19 (1971) 260

- 71. R.S. Adrian, E.G. Arthurs, D.J. Bradley A.G. Roddie and J.R. Taylor Optics Communications 12 (1974) 140
- 72. W.D. Johnston and P.K. Runge IEEE journal of Quantum Electronics QE-8 (1972) 724
- 73. C.J. Tredwell and C.M. Keary Chemical Physics 43 (1979) 307
- 74. P.M. Rentzepis Science 169 (1970) 239
- 75. W. Kaiser and A. Laubereau Pure and Applied Chemistry V:50 pp. 1231-1238 Pergaman Press Ltd., 1978
- 76. K.B. Eisenthal Accounts of Chemical Research 8 (1975) 118
- 77. E.P. Ippen and C.V. Shank Physics Today May (1978) 41
- 78. B.I. Green, R.M. Hochstrasser and R.B. Weisman The Journal of Chemical Physics 70 (1979) 1247
- 79. E.G. Arthurs, D.J. Bradley and A.G. Roddie Optics Communications 8 (1973) 118 Chemical Physics Letters 22 (1973) 230

- 58. G.H. McCall The Review of Scientific Instruments 43 (1972) 865
- 59. H.W. Kogelnik, E.P. Ippen, A. Dienes and C.V. Shank IEEE Journal of Quantum Electronics QE-8 (1972) 724
- 60. P.K. Runge and R. Rosenberg IEEE Journal of Quantum Electronics QE-8 (1972) 910
- 61. O. Teschke, J.R. Whinnery and A. Dienes IEEE Journal of Quantum Electronics QE-12 (1976) 513
- 62. G.M. Grover, T.P. Cotter and G.F. Erickson The Journal of Applied Physics 35 (1964) 1990
- 63. C.R. Vidal and J. Cooper The Journal of Applied Physics 40 (1969) 3370
- 64. A.N. Nesmeianov (editor) <u>Vapour Pressure of the Elements</u> pp.128 Elsevier, New York
- 65. E.P. Ippen, C.V. Shank and A. Dienes Applied Physics Letters 21 (1972) 348
- 66. E.P. Ippen and C.V. Shank Applied Physics Letters 27 (1975) 488
- 67. E.P. Ippen private communications
- 58. J.P. Letouzey and S.O. Sari Applied Physics Letters 23 (1973) 311
- 69. A. Dienes, E.P. Ippen and C.V. Shank Applied Physics Letters 19 (1971) 258
- 70. D.J. Kuizenga Applied Physics Letters 19 (1971) 260

- 71. R.S. Adrian, E.G. Arthurs, D.J. Bradley A.G. Roddie and J.R. Taylor Optics Communications 12 (1974) 140
- 72. W.D. Johnston and P.K. Runge IEEE journal of Quantum Electronics QE-8 (1972) 724
- 73. C.J. Tredwell and C.M. Keary Chemical Physics 43 (1979) 307
- 74. P.M. Rentzepis Science 169 (1970) 239
- 75. W. Kaiser and A. Laubereau Pure and Applied Chemistry V:50 pp. 1231-1238 Pergaman Press Ltd., 1978
- 76. K.B. Eisenthal Accounts of Chemical Research 8 (1975) 118
- 77. E.P. Ippen and C.V. Shank Physics Today May (1978) 41
- 78. B.I. Green, R.M. Hochstrasser and R.B. Weisman The Journal of Chemical Physics 70 (1979) 1247
- 79. E.G. Arthurs, D.J. Bradley and A.G. Roddie Optics Communications 8 (1973) 118 Chemical Physics Letters 22 (1973) 230