

## An Introduction to Pulsed Dye Lasers

### Introduction

Light amplification by stimulated emission of radiation, that is--lasers, have become an important tool in chemistry. Lasers are ideal light sources for spectroscopy, chemical kinetics studies, and light scattering studies of molecular motion. High-powered lasers are finding use as light sources for photochemical synthesis, yielding products not available from other techniques. Dye lasers are an important class of lasers because they can be tuned to a range of wavelengths. The lasers you are probably familiar with, like He-Ne lasers, produce only fixed wavelengths and are therefore not good sources for spectroscopic studies. In this lab you will measure the absorption and fluorescence characteristics of several laser dyes and then set up a dye laser with the dyes and compare the laser emission characteristics.

### Theory

*Coherence* Laser light is unusual because it is coherent, intense, and formed in a narrowly divergent beam. The light is also monochromatic, that is, the laser produces a narrow range of wavelengths. Let us consider each of these characteristics. Figure 1 illustrates the difference between coherent and incoherent light sources. Incoherent light sources, such as light bulbs, produce many waves but the waves are out of step. Lasers produce light waves that are in step so that the electric and magnetic fields of the waves oscillate in phase with each other. This coherence increases the intensity of the light, in the following way. If the amplitude of a wave is "a," then the intensity of that one wave is  $a^2$ . The total intensity of an incoherent light source is just the sum of the intensity of all of the waves. For n waves the sum is  $na^2$ . In spatially coherent radiation the fields oscillate in phase so that the amplitudes add, giving a total amplitude of na. The total intensity is then the square of the total amplitude or  $n^2a^2$ . Thus, the increased intensity of laser light is caused by its coherence. Coherence is also responsible for the ease of forming beams of light, but the details are not necessary here. The monochromatic nature of the light is caused by the atomic or molecular transitions involved in the mechanism of laser action.

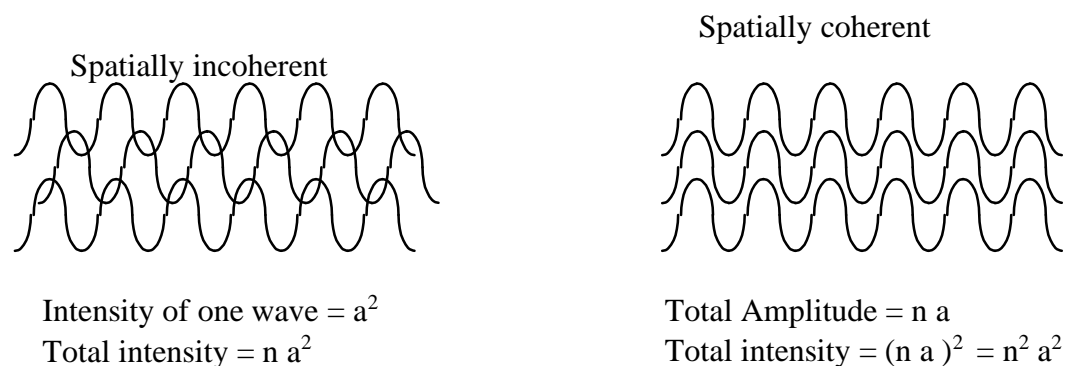


Figure 1. Coherent vs. incoherent radiation.

*Mechanism* In a laser the atoms or molecules of the medium are excited into excited states by energy from an electric discharge, flash lamps (like a high powered photographic flash), or another laser. The atoms or molecules then emit light while going back to their ground states. Three things are needed for laser emission: (1) a high probability of stimulated emission, (2) a population inversion, and (3) a resonant cavity. Figure 2 compares spontaneous and stimulated emission. After an atom or molecule absorbs light, it is left in an excited state. This state may lose energy by emitting a photon or it may lose energy through collisions with other atoms or molecules in the form of heat. In all that follows, we will assume that this latter pathway of loss of energy as heat is not important. When an atom or molecule emits a photon it returns to its lower energy state. In the *absence* of any other light source, this photon emission is a random event with a certain probability, and is called spontaneous emission. Spontaneous emission is familiar to chemists because it is the process responsible for fluorescence and phosphorescence.

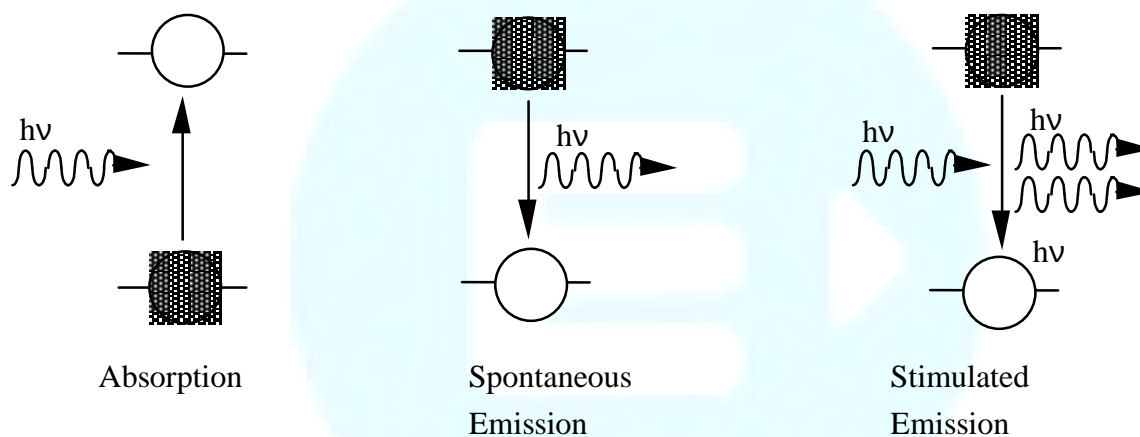
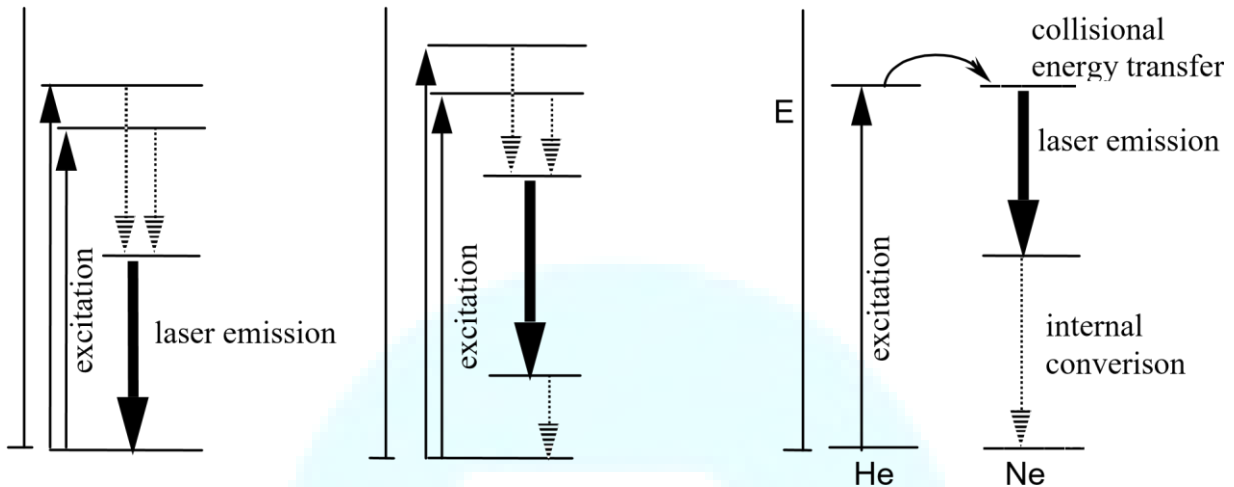


Figure 2. Spontaneous vs. Stimulated emission.

However, if light at the frequency of the transition is present, an excited state may be stimulated to emit a photon. Picture that if an oscillating electric field of just the right frequency passes an excited atom, that the atom is jostled about and therefore finds it easier to emit its energy. Therefore, if one photon is present at the start, after emission a new photon is present along with the original. This process is called stimulated emission. One important characteristic of stimulated emission is that the two photons are synchronized by the process; that is, they are coherent. For laser action the probability of stimulated emission must be greater than that for spontaneous emission.

The second requirement for laser emission is a population inversion. Under normal circumstances, there are more atoms or molecules in low energy states than in high energy states. In a population inversion the opposite is true. Different types of lasers create this population inversion in several ways. The ruby laser operates by a "two level system" as shown in Figure 3. The energy diagram includes the ground state for the  $\text{Cr}^{3+}$  ion and several excited states. The

population inversion is created when an intense flash of light excites  $\text{Cr}^{3+}$  ions from their ground states into a variety of excited states. These excited states rapidly lose energy to produce ions in the lowest energy excited state by a process called internal conversion. In internal conversion the excess energy is lost as heat. The lowest energy excited state in ruby has an unusually long lifetime, i.e. low probability for spontaneous emission. Therefore, as the higher excited states depopulate many ions are caught in this lowest excited state, creating a population inversion with



the ground state. Stimulated emission can then start a cascade of emission back to the ground state. This concerted cascade results in an intense burst of light and results in laser emission.

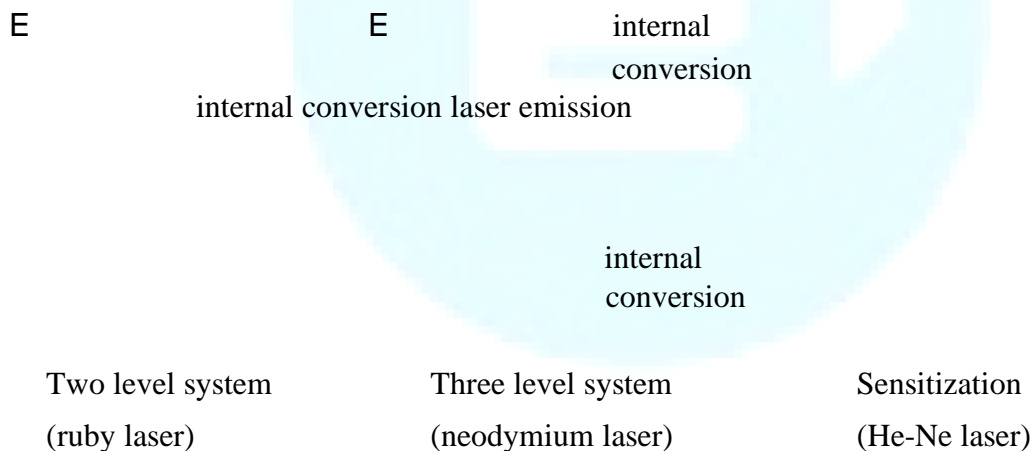


Figure 3. Mechanisms for establishing a population inversion. The dashed arrows indicate loss of energy in the form of heat.

The common neodymium laser and the two lasers used in this lab, the nitrogen laser and the dye laser, operate on a "three level system". In this case laser emission occurs to another excited state and not the ground state. The common red He-Ne laser operates by exciting He atoms that then transfer their energy during collisions into an excited state of the Ne atom (Figure 3). Laser emission is then created from a three level system in the Ne atom. This process is called sensitization, where the excited He atoms are the sanitizers.

The last requirement for laser action is a resonant cavity. In a dye laser, the dye solution is held in a cuvet. Two mirrors are placed on either side of the cuvet to make a cavity (see Figure 6). When the dye fluoresces, after a short pulse of exciting light, some of the fluorescent light bounces off the mirrors back into the cuvet. The reflected light can then bring about stimulated emission. If the stimulated emission is intense enough laser emission will result, as molecules rapidly drop back into their ground states. Each time a beam of light passes through the excited dye solution it "gains" intensity through spontaneous emission. Sometimes one pass is sufficient, sometimes several passes are necessary to build enough intensity to produce enough stimulated emission for laser action. The "gain" of the system is therefore an important parameter. Two important factors that influence the gain are the upper state lifetime and any competing processes that depopulate the upper state without emission of a photon (nonradiative processes). It is best to maximize the former and minimize the later. Only certain dyes have long enough excited state lifetimes. The proper choice of solvent and dye concentrations can help to minimize competing processes. The optical layout can also influence the gain of the dye laser. You might wonder, however, if the dye cell is surrounded by mirrors, how does the light get out? One of the mirrors is made partially reflective so that most of the light escapes from the cavity.

*Dye Lasers* The energy diagram for the typical molecule is shown in Figure 4. The ground states of most molecules are singlets, so that absorption of light produces excited singlet states. Spontaneous emission then results in fluorescence. However, it is possible through a process called intersystem crossing for molecules to switch into their excited triplet states. Spontaneous emission from a triplet state occurs very slowly, by comparison with fluorescent transitions, and is called phosphorescence.

Molecular fluorescence is responsible for dye laser emission. The wavelength of laser emission is limited by the range of fluorescence wavelengths. To choose a dye, we then pick a dye with its fluorescence emission spectrum near the desired laser wavelength. We must also choose a dye with a long lived first excited singlet state, so that a population inversion is easy to build up.

The dye should also be easily excited by available light sources. Figure 4 shows that the fluorescence spectrum is shifted to the red (longer wavelengths) from the absorbance spectrum of the dye. This means that the exciting light should be bluer than the desired laser emission wavelength. Xenon lamps are commonly used to excite, or "pump", dye lasers. In this lab we will use a pulsed nitrogen laser to excite our dye. The wavelength of emission of a nitrogen laser is between 337.04 and 337.14 nm, in the ultraviolet. Therefore, a molecular absorption band for the dye must occur at 337 nm. Because the pulse width of the nitrogen laser is a few nanoseconds, the output from our dye laser will also be on the order of nanoseconds. (Xenon lamps can be used as excitation sources to produce continuous wave, (CW), emission rather than pulsed output).

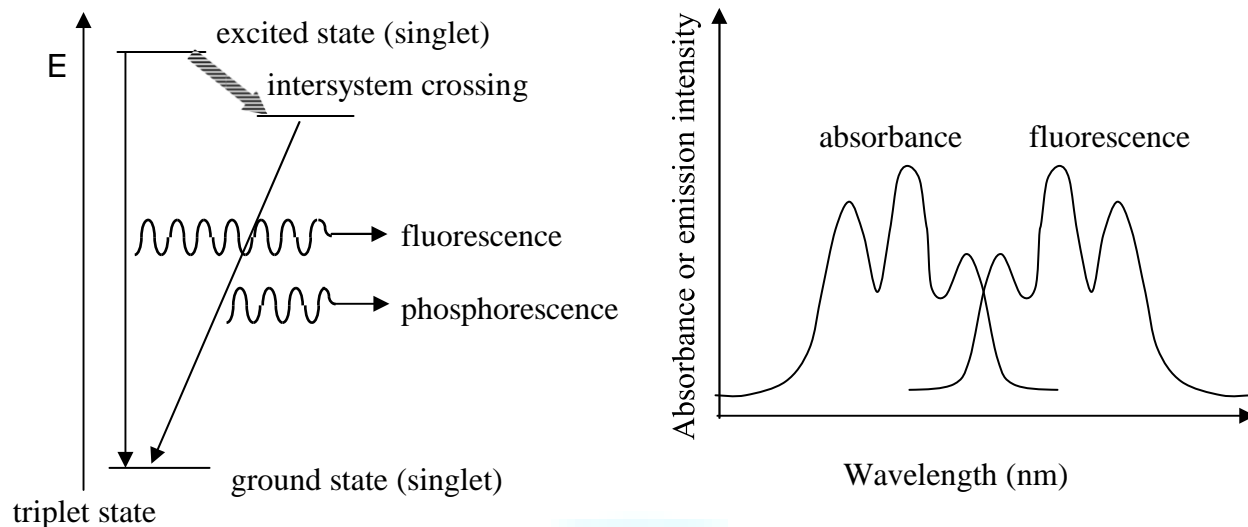


Figure 4. Molecular transitions and spectra

Intersystem crossing is a competing process with dye laser emission. Intersystem crossing is more efficient in the presence of heavy atoms (e.g. heavy halogens) or species with unpaired electrons (e.g. O<sub>2</sub>). Therefore, solvents like methanol are preferred to halogenated solvents like CCl<sub>4</sub>. Laser gain can be improved by degassing to remove O<sub>2</sub>.

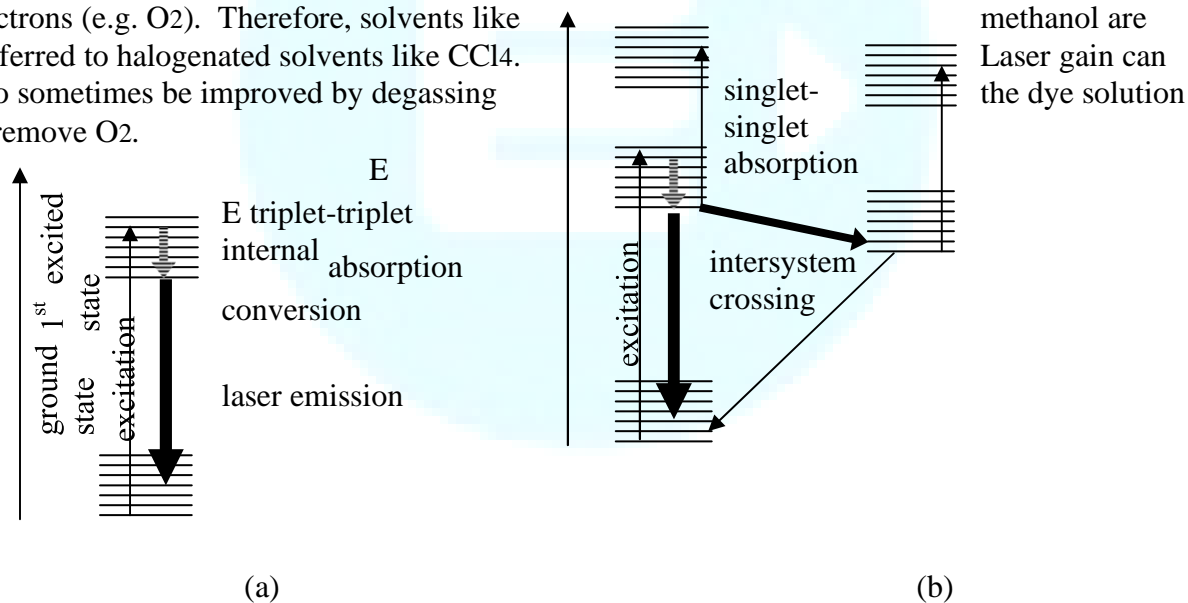


Figure 5. (a) Mechanism for dye laser action. (b) Energy loss mechanisms that compete with laser action.

The mechanism for dye laser emission is shown in Figure 5. Dye molecules are excited into excited singlet states by the pump light source. Internal conversion rapidly occurs resulting in all of the molecules dropping into the first vibrational level of the lowest excited state. There are still more molecules in the first vibrational level of the ground electronic state compared to the

lowest excited state, but a population inversion does exist with respect to higher vibrational levels of the ground state. Stimulated emission inside the laser cavity then results, with conversion of excited electronic states into vibrationally excited ground state molecules. Because many final vibrationally excited levels are available the laser emission can be tuned over narrow ranges.

To maximize the gain of the laser, competing processes should be improbable. The effects of intersystem crossing have been discussed above and should be minimized. In addition, singlet-singlet and triplet-triplet absorption from excited states decrease the pump light intensity and, therefore, are also an energy loss mechanism in the cavity (see Figure 5).

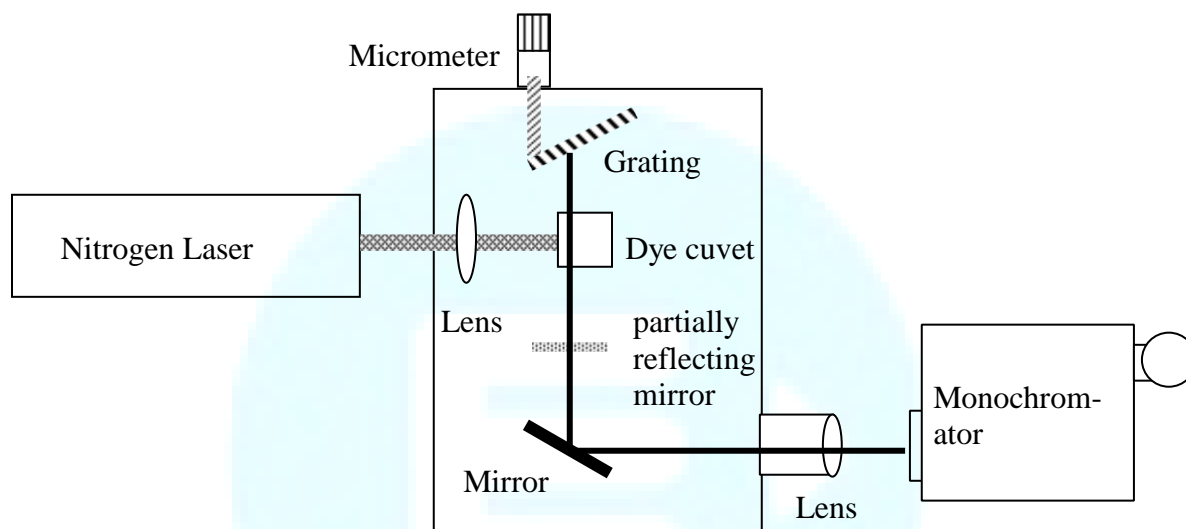


Figure 6. Dye Laser optics with emission wavelength determination using a monochromator.

The optical layout of a wavelength tunable dye laser is shown in Figure 6. The output of a N<sub>2</sub> laser is focussed using a quartz lens or front surface mirrors into a thin horizontal line upon the front of a quartz cuvet. The concentration of the dye is adjusted so that all of the exciting light is absorbed within a few millimeters of the front window of the cuvet. Fluorescence from this narrow area is then reflected back into the cell by a partially reflecting mirror and the grating, leading to laser emission. The beam leaves the cavity through the partially reflecting mirror. A second mirror directs the beam out of the dye laser. The wavelength of the laser is set by adjusting the grating with a micrometer. The grating is set to reflect the wavelength of interest back through the dye cuvet.

## Experimental Methods

Fluorescence Spectra The spectrum of fluorescence emission of a compound is determined using a spectrofluorimeter. A diagram is shown in Figure 7. The excitation wavelength is set to maximize the fluorescence intensity of the dye. The emission monochromator is then scanned to

determine the fluorescence spectrum. The result is displayed on a strip chart recorder as intensity (in arbitrary units),  $I_f$ , versus wavelength (see Figure 4). Even though the fluorescence emission is in all directions, the fluorescence is sampled at a 90 degree angle to the excitation light beam to minimize the amount of excitation light that reaches the emission monochromator. A xenon arc lamp is necessary to provide high intensity excitation throughout the visible and UV range.

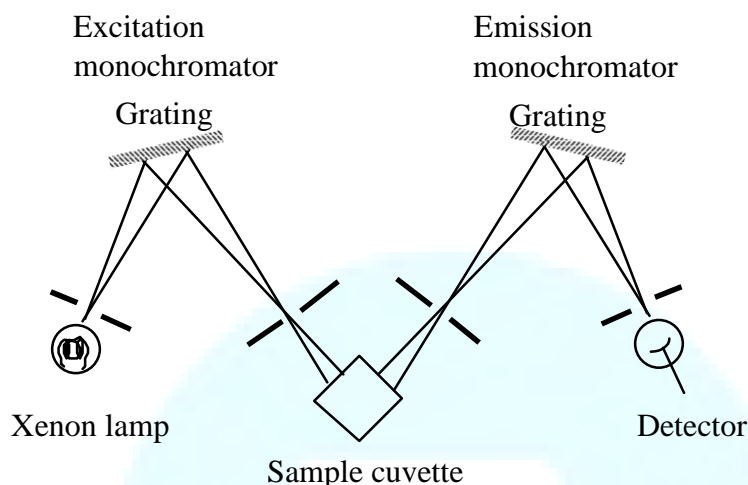
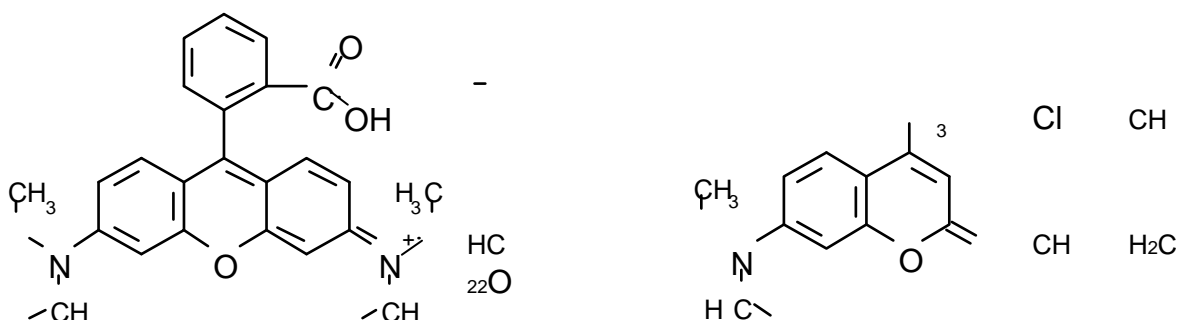


Figure 7. Fluorescence Spectrophotometer

**Absorbance Spectra** The theory of absorbance spectroscopy should be familiar to the student. The importance of absorbance spectroscopy for our present study is that an absorbance spectrum shows the relationship between the absorption band that is being pumped by the nitrogen laser at 337nm and the fluorescence band that gives rise to laser emission. In many cases the absorption band that is pumped is not the lowest excited state. For laser emission to occur, the pumped absorption must depopulate through internal conversion to the lowest excited state, from which the laser emission will occur. The fluorescence efficiency will depend on which excited state is being pumped.

### Procedure

**Overview** You will determine the absorbance and fluorescence spectrum for the dyes rhodamine B and coumarin 1. Their structures are shown below.



Rhodamine B

7-diethylamino-4-methylcoumarin (coumarin 1)

Each dye will then be used as the active medium in a nitrogen laser pumped dye laser. You will measure the wavelength of laser emission and the bandwidth of the laser line. In the absence of any wavelength tuning elements (i.e. a grating in place of the fully reflecting mirror), the wavelength of laser emission will correspond to the maximum of the gain curve (Figure 8). The gain is the ratio of photons leaving the dye cell divided by the photons entering the dye cell. Stimulated emission causes the gain to be greater than one. Absorption decreases the gain.

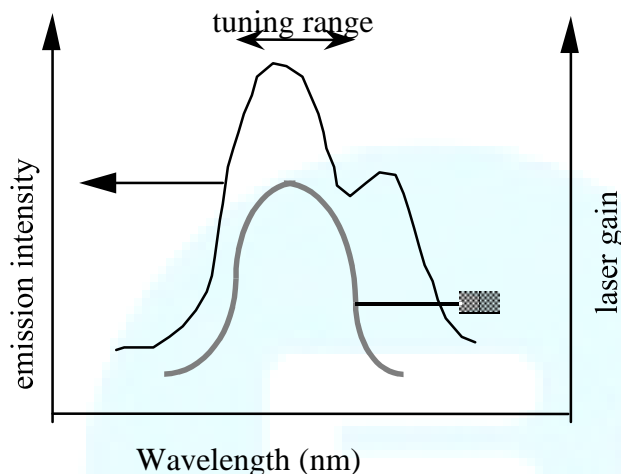


Figure 8. Laser gain curve and tuning range.

UV/Vis and Fluorescence Characterization Make up  $1 \times 10^{-3}$  M solutions of rhodamine B and coumarin 1 in ethanol for the dye laser. This concentration is much too high for absorption or fluorescence studies. Dilute each dye to  $1 \times 10^{-5}$  M in ethanol. Obtain the UV/Vis absorption spectrum and fluorescence spectrum of both dyes. Since the transitions are broad, wide slit settings and fast scan times are sufficient. You can use the nitrogen laser wavelength for fluorescence excitation.

Laser Emission Characterization Fill a dye laser cuvet with  $1 \times 10^{-3}$  M rhodamine B solution. Place the cuvet in the dye laser head, but temporarily leave the cell compartment cover off to observe the fluorescence. Turn on the nitrogen laser and observe the fluorescence of the dye. Replace the compartment cover. Adjust the micrometer if necessary for laser action. The approximate wavelength of laser emission can be read from the micrometer.

Align the 1/4 meter monochromator so that the laser beam falls on the entrance slit. Attach the photomultiplier cable to an oscilloscope. Adjust the photomultiplier voltage to observe the light pulses on the oscilloscope; 200V should be sufficient. If in later stages the output voltage should become greater than about 1V, turn down the high voltage. Adjust the wavelength control on the monochromator to maximize the observed pulse height. This is the wavelength of maximum laser emission,  $\lambda_{\text{max}}$ . To determine the laser line width, adjust the monochromator to give pulses



of one half the maximum value; record this point both above and below the laser wavelength maximum. The difference between the two half height values is the full width at half maximum, fwhh.

Adjust the micrometer to a new wavelength and observe any changes in  $\lambda_{\max}$  and the fwhh. Then, measure the  $\lambda_{\max}$  and fwhh for coumarin 1, in an analogous fashion for two settings of the micrometer.

### Discussion

(1) Compare the spatial dispersion of fluorescence (observed from above with the cell compartment cover off) with that of laser emission.

#### For each dye:

(2) Qualitatively compare the dye laser  $\lambda_{\max}$  values with the wavelength of maximum fluorescence. Qualitatively compare the fwhh of the laser emission with the range of fluorescence wavelengths. Include any general observations in comparison of the two dyes.

(3) Using a rough hand drawing, draw the normal absorbance spectrum of the dye and its fluorescence spectrum on the same axis. Are any transitions missing in either spectra? Identify the absorbance band that is pumped by the nitrogen laser by labeling the nitrogen laser wavelength on your hand drawing.

(4) Converting wavelengths to  $\text{cm}^{-1}$ , draw an energy level diagram, to scale, showing the ground state and at least three of the detected excited states (they will all be singlet states) with appropriate vibrational manifolds (range of vibrational energies). Show, also, your two excited state to ground state laser transitions with arrows and label with a transition arrow the excited state level that is pumped by the nitrogen laser. Your diagram should be similar to Figure 5. To help you draw the diagram, fill in the following table for each dye. Use the approximate full range of each absorption or fluorescence band, and not the fwhh. For the laser emission use the fwhh values.

Transition	Start of emission or absorption		End of emission or absorption band	
	$\lambda$	$\text{cm}^{-1}$	$\lambda$	$\text{cm}^{-1}$
first excited state				
second excited state if present				
third excited state if present				
fluorescence				
laser emission (setting one)				

laser emission (setting two)				
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HINT: Here is an analogy that might help in constructing the energy level diagrams. The wavelengths measured from your spectra are like point-to-point distances in map drawing. If the distance from Waterville to Bangor is 60 miles, the map that you draw of Maine should show that distance between the two cities. However, the distance between Waterville and Bangor doesn't tell you whether Waterville is in southern or northern Maine. The absolute position of Waterville in the state is really not necessary, however, if you only travel between the two cities. Similarly, we can't determine the absolute energy of the ground state of our dyes. However, we can determine the *difference* in energy (analogous to the point-to-point distance) between the ground state and each excited state. It is this energy difference, relative to the ground state, that is plotted in Figure 5. Now, how can you determine how large the cities are? If you start from Waterville and drive to Bangor, you reach the southern city limit in 58 miles. If you continue driving, you reach the northern city limit after a total of 62 miles traveled, Figure 9. Therefore, Bangor has a diameter of roughly  $62-58=4$  miles, which would correspond to its fwhh. The Starting and Ending wavelengths in the table above are of similar value in determining the energy spread, that is, the range of accessible vibrational energy levels, in the ground and excited states of your molecule.

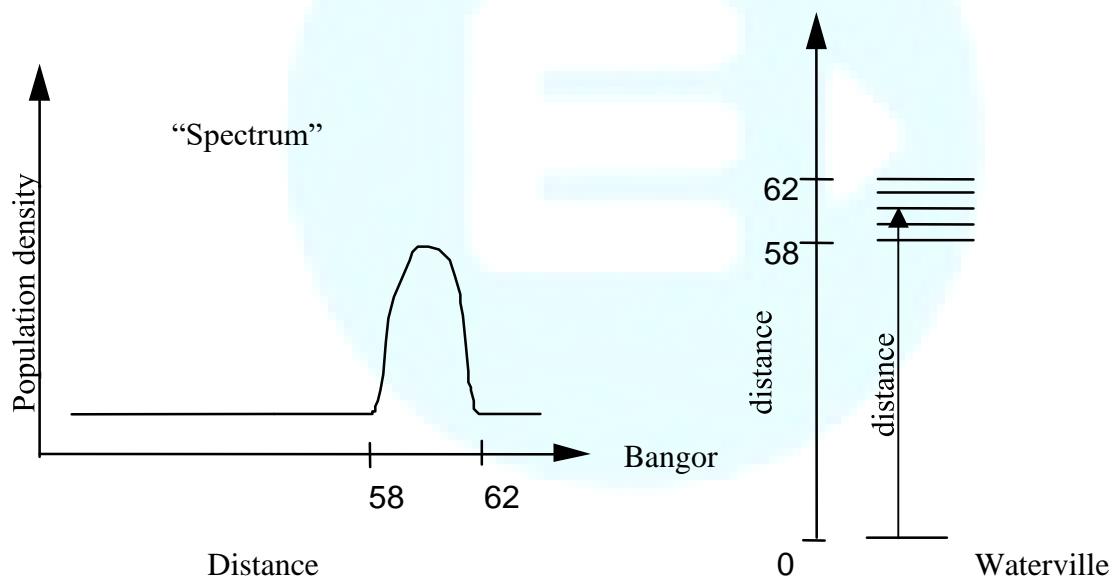


Figure 9. The distance from Waterville to Bangor's southern boundary is 58 mi and to the northern boundary is 62 mi.