Chapter 10: Lasers

One of the most important tools in scientific measurement and the development of technology in general is the **laser**. The word "laser" is an acronym for Light Amplification by Stimulated Emission Radiation. What a laser does is use a spectroscopic transition to amplify the intensity of a light source by stimulating emission from the upper state of the transition. In order to do this, the system must have a population inversion.

Fractional Population of Quantum States

A molecule will exist in a quantum state with an energy determined by that quantum state. For a sample containing a large number of molecules, several quantum states will be available, and the molecules will be distributed among them. If the sample is thermalized[1], the distribution will follow the Maxwell-Boltzmann distribution law.

Maxwell-Boltzmann Distribution Law

According to the **Maxwell-Botlzmann distribution** law, the fraction of the number of molecules in the sample that are in a specific quantum state will be given by

$$\frac{N_i}{N_{tot}} \propto d_i e^{-\frac{E_i}{kT}}$$

where N_i/N_{tot} is the fraction of the total number of molecules in the i^{th} quantum state which has energy E_i relative to the lowest energy the molecule can attain. If the fraction of molecules in each quantum state is added, the result must be unity.

$$\sum_i \frac{N_i}{N_{tot}} = 1$$

Partition Functions

To ensure this, a **partition function** is introduced to normalize the distribution.

$$q = \sum_i d_i e^{-\frac{E_i}{kT}}$$

[1] The word "Thermalized" means that all of the molecules in the sample are in "thermal contact" with one another (typically due to a large frequency of collisions with other molecules in the sample) so that there is an equilibrium established for the exchange of energy between molecules in the sample.

And so

$$\frac{N_i}{N_{tot}} = \frac{d_i e^{-\frac{E_i}{kT}}}{q}$$

The partition function, which is a function of temperature as well as the physical properties of the molecules under consideration, can be expressed as a product of partition functions for each type of motion available in the molecule. If electronic, vibrational and rotational energy levels only are considered, the partition function can be expressed as

$$q_{tot} = q_{elec}q_{vib}q_{rot}$$

When considering each type of motion, it is important to consider both the energy levels and the degeneracies of states. As was seen in the case of rotational motion (Chapter IV), at low energies, the degeneracy part of the expression dominates, but at higher energies, the exponential part of the function takes over. If the energy E_i is very large (relative to kT) then there will be essentially no population in the i^{th} level. This is the case, in general, for electronic excitation; the energy level is so high in nergy relative to kT that there are essentially no molecules in excited electronic state *except at extraordinarily high temperatures*. In this case, where the energy is very large relative to kT

$$\begin{aligned} q &= d_1 e^{-\frac{0}{kT}} + \sum_{i\neq 1} d_i e^{-\frac{E_i}{kT}} \\ &\approx d_1 \cdot 1 + \sum_{i\neq 1} d_i e^{-\infty} \\ &= d_1 + \sum_{i\neq 1} d_i \cdot 0 \\ &= d_1 \end{aligned}$$

Naturally, q will become larger for motions will small energy level differences (such as rotational motion) where the word "small" is always considered relative to kT.

Based on the above equations and the degeneracies and energy level expressions for the harmonic oscillator (for q_{vib}) and the rigid rotor (for q_{rot}) the following approximate expressions can be used to estimate partition functions for each type of motion.

	Expression	Approx. Exp.	Magnitude Estimate
q_{elec}	$q = \sum_i d_i e^{-\frac{E_i}{kT}}$	d_1	1
q_{vib}	$q = \sum_v d_v e^{-\frac{hc\omega_e(v+1/2)}{kT}}$	$(1-\exp\{-\omega_e hc/kT\}\}^{-1}$	1-10

q_{rot}	$q = \sum_J (2J+1) e^{-\frac{hcBJ(J+1)_i}{kT}}$	kT/B	100-1000

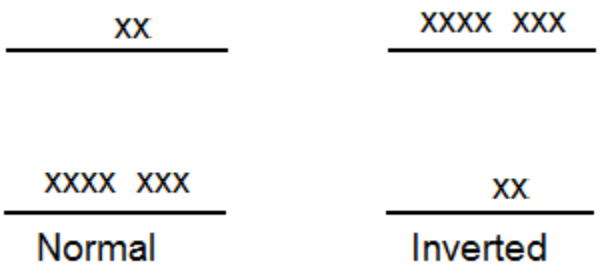
Rotational and Vibrational Temperatures

The above discussion suggests that the temperature of a system can be determined by measuring the populations of individual quantum states. This can be done using spectroscopic intensity data. A line or band in spectrum will be more intense if there are a larger number of molecules in the originating state of the transition. (This is essentially Beer's Law that says that spectral intensity is proportional to concentration.)

Sometimes these analyses will yields results that are not consistent between different types of motion within the molecule. For example, analysis of the vibrational intensity distribution may yield a temperature that is different than the analysis of the rotational intensity distribution. For this reason, scientists often refer to the "**vibrational temperature**" or the "**rotational temperature**" of a sample. These are non-equilibrium situations and are usually dependent on the dynamics of how a molecule was formed within a sample. Some pathways may leave an excess of energy in vibrational modes whereas other may lead to rotationally hot product molecules due to an excess of energy in rotational motion. Typically after a large number of collisions which energy may be transferred from one molecule to another, these temperatures will equilibrate and the Maxwell-Boltzmann distribution law will describe all fractional populations irrespective of the type(s) of motion that dominate(s) an energy level.

Population Inversion

In the case where all available energy levels are singly degenerate, the **Maxwell-Boltzmann distribution** law suggests that fractional population should decrease with increasing energy. In some cases, the non-equilibrium distribution of molecules through the available quantum states becomes inverted. Again, this situation can be created by the specific dynamics of how a system is prepared. In the case that a population inversion can be created, a laser can be made that uses the sample of molecules with this inverted population as a gain medium to create the laser light output.



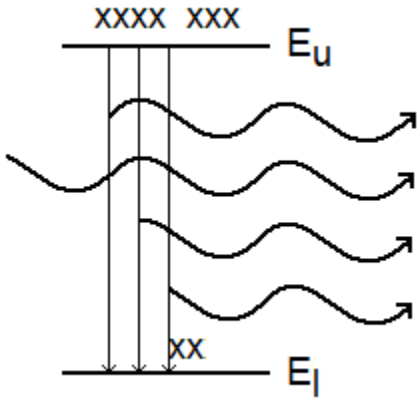
Theoretically, any system in which a **population inversion** can be induced can be used as a gain medium for a laser.

Types of Lasers

There are many different types of lasers built on many different principles and techniques of creating population inversions. A population inversion can be induced in a system through the fast absorption of light, a chemical reaction that creates a non-equilibrium distribution of molecules, "zapping" a system with electrons, or many other ways. We will consider several of them in this section.

Two-level laser

The simplest type of laser is a two-level laser, although many argue that a true two-level laser cannot exist[2]. None the less, it is instructive to consider a simplified system with only two levels, in which a population inversion has been introduced. Once the population inversion has been achieved, light of a frequency that matches the resonance between the two levels is passed through the sample. This can "tickle" a molecule into dropping to the lower level by giving off a photon. If this happens, the stimulated emission will be coherent (in phase and of the same frequency) as the stimulating photon. If many molecules are stimulated to emit, the gain will be substantial and a strong beam of coherent, monochromatic light will be produced.



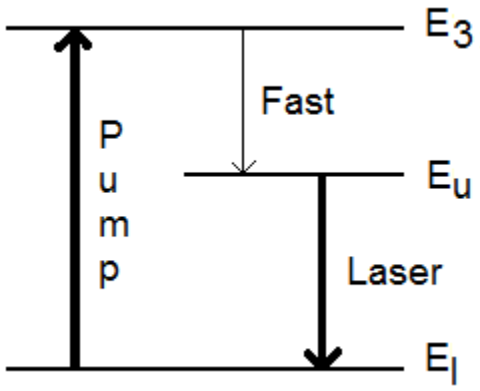
Naturally as laser output is achieved, the upper-level population will deplete and that of the lower level will grow. When a Maxwell-Boltzmann distribution is established, laser output will cease. So in order to keep the laser operating, the upper state must be repopulated or the lower state must be depopulated. The nature of the laser is defined by the manner in which these population/depopulation events occur. The manner in which the light is manipulated can also define the nature of the laser and how it operates.

[2] Others argue that excimer lasers and dye lasers are two-level lasers. The difference depends on what is considered a "level".

Three-level lasers

There are several examples of three-level lasers. In these systems, a third level is introduced in order to either populate the upper level of the laser transition or depopulate the lower level. This difference defines two types of three-level laser systems.

In the case that the third level (E_1) lies above the upper level of the laser transition (E_u), the following schematic energy level diagram will result.

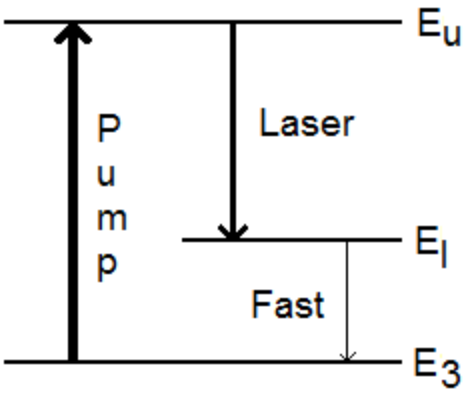


In this system, The level E_3 is populated by the absorption of light (which is what is depicted in the diagram above) or some other method. The transition between E_1 and E_u is much faster than the transition between E_u and the lower level of the laser transition, E_l. As such E_u will be populated quickly and a population inversion will be established. As this laser operates, E_u will be depopulated, so a fresh supply of molecules in this level must be provided by the pump source cycling molecules out of E_l and back to E_3.

An example of this type of three-level laser is the ruby laser[3], in which the gain medium is a ruby crystal. The pump exciting molecules from E_l to E_3 is provided by a flash lamp. Since the flash lamp is pulsed, this system produces pulsed laser output. The wavelength of the ruby laser output is 694.3 nm. The helium-neon (HeNe) laser (Microwave Determination of Average Electron Energy and Density in He–Ne Discharges, 1964) is another example of this type of laser. The HeNe laser is a continuous wave laser (meaning it is not pulsed like the ruby laser) that produces red light at 632.8 nm.

A second type of three-level laser is one on which the third level (E_3) lies below the lower level (E_l) of the laser transition. In this system, the upper level of the laser transition is populated either by a chemical or electrical pump or by a chemical reaction. The lower level is depopulated by a fast transition (or a chemical reaction). Since this depopulation happens faster than the population of E_l through the laser transition, a population inversion is maintained easily.

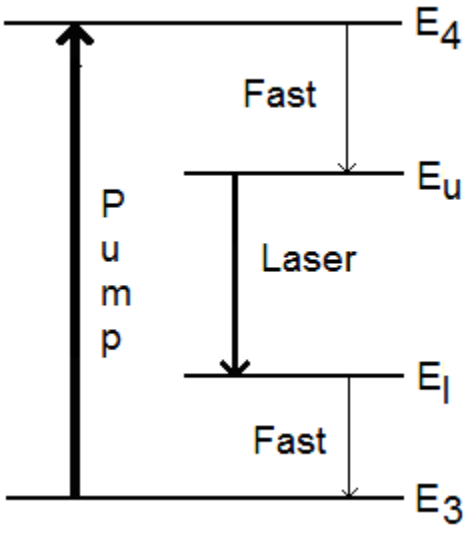
[3] There are actually two levels in a ruby laser that act as E_3. For a complete description, see (Maiman, 1960)



An example of this type of laser is the chemical laser in which the upper level of the laser transition is populated through a chemical reaction which creates vibrationally excited molecules (Spencer, Jacobs, Mirels, & Gross, 1969) (Kasper & Pimentel, 1965) (Hinchen, 1973). Such lasers typically produce output in the infrared.

Four-level lasers

A four-level laser incorporates elements of both types of three-level lasers by having an energy level above the upper level of the laser transition that rapidly populates E_u and one below the lower state of the laser transition that rapidly depopulates the lower level, E_l.



Briefly, a pump (usually supplied by a flash lamp) excites molecules from E_3 to E_4. A fast transition from E_4 to E_u populates the upper state of the laser transition. A fast transition from E_l to E_3 then depopulates the lower level of the laser transition, maintaining a population inversion between E_u and E_l until E_4 is no longer able to populate E_u.

The Nd:YAG (Geusic, Marcos, & Van Uitert, 1964) (neodymium YAG) laser is an example of a four level laser. In this laser, neodymium (III) ions entrained in a yttrium

aluminum garnet crystal provide the four energy levels. The laser produces a polarized pulsed output at 1064 nm.

Q-switching

One of the important devices that makes a Nd:YAG laser (and many others) is a **Q-switch**. A Q-switch is a polarized filter that changes direction fo polarization when an electrical potential is applied to it. In one orientation, the switch blocks laser output light (preventing stimulated emission amplification) and in the other orientation, it allows for this light to pass.

The Q-switch is used to limit laser gain (which would deplete the upper level of the laser transition) until an optimal population inversion is achieved. The Q-switch is then "opened" and laser output is generated until the population inversion is relaxed. The timing is critical and must be tuned for each laser (and usually re-optimized several times a day while the laser is in operation, as changes in temperature can change the characteristics of the YAG crystal dramatically.

Examples of laser systems

There are many types of laser commonly used in science today. The range of applications of lasers in science and technology is extremely broad, ranging from household applications (such as television remote controls) to manufacturing applications (such as laser cutting and welding, or laser lithography used in the manufacture of microelectronics), to medicine (including specific procedures such as laser eye surgery) to basic fundamental science. The specific needs of a particular job determine which laser is best for the job.

N_2 laser

A nitrogen laser is a **continuous wave** laser that provides ultraviolet output at 337 nm, but can be tuned to several wavelengths near its strongest output line. The laser gain transition is the 0-0 band in the B-X transition of N_2. The upper state is populated by subjecting the gas to an electrical discharge. Applications of the N_2 laser is pumping of dye lasers (described in section B.4.d), diagnostics of air samples and laser desorption techniques.

Excimer Lasers

An excimer laser is one in which the upper state of the transition is a **metastable state** of a molecule, and the lower state is dissociative. Because the lower state is not bound, molecules that land in that state after emitting a photon immediately dissociate, allowing for no buildup of population in the lower level of the laser transition. As such, any population in the upper state implies a population inversion.

The upper (metastable) state is populated by a pulsed electrical discharge through a gas containing the precursors of the excimer molecules. Since these precursors (usually involving

HCl or HF gas) are particularly caustic (to say nothing of how reactive the soup of radicals and ions produced by the electrical discharge are!) these laser require a very high level of maintenance. However, because of the simplicity of the energy level scheme, these lasers are very easy to tune to provide strong laser output. These lasers are used in a number of applications including the pumping of dye lasers and laser eye surgery. The pulses that emanate from these laser have a time on the order of a few nanoseconds.

The output wavelength of an excimer laser is determined by the particular excimer formed in the discharge. The most commonly used excimer lasers are XeCl (308 nm) and ArF (193 nm.) The following table shows several common excimers and their output wavelengths.

Excimer	Wavelength (nm)
ArF	193
KrCl	222
KrF	248
XeCl	308
XeF	351

Rare Gas Ion Lasers

Another important class of lasers is the **rare gas ion laser**. In this laser, the gain medium is provided by an ion of a noble as (such as Ar^{+}). The gas is ionized by means of an electrical discharge. These lasers typically have several wavelengths which can be selected for the output. These lasers are used widely as pump lasers for dye lasers and also in Laserium light shows.

Tunable Dye Lasers

Tunable dye lasers are a very flexible type of laser as they provide selectable output wavelengths. Many of them can be scanned through a set of wavelengths which can be very useful in a number of applications (such as laser spectroscopy.) The gain medium in a dye laser is provided by a strong fluorescent dye dissolved in a liquid solvent (such as methanol.) The range of output wavelengths is determined by the specific dye. Commercially available dyes are available that span the entire visible spectrum. Ring dye lasers are capable of very high resolution (narrow wavelength or frequency range.)

Pulse Amplification

Pulse amplification is a technique used to increase the output power of a laser. In this technique, a seed beam is passed through a dye cell and is crossed by a pulsed pump beam which excites the dye, providing another stage of gain for the seed beam. Most dye lasers have at least one stage of pulse amplification in them to achieve suitable power for the specific application.

Frequency Doubling

Another useful technique that extends the wavelength output range of laser is **frequency doubling**. In this technique, laser output is focused on a special crystal (such a beta-Barium Borate or BBO) which has nonlinear optical properties that allow it to fuse two photons of frequency ν into one photon with frequency 2ν. Frequency doubling is not a terrifically efficient process and usually comes at a significant price to output intensity. However, the benefit of frequency doubling a tunable dye laser output is that one can extend the tunable range of laser output into the ultraviolet.

Ultrafast Lasers

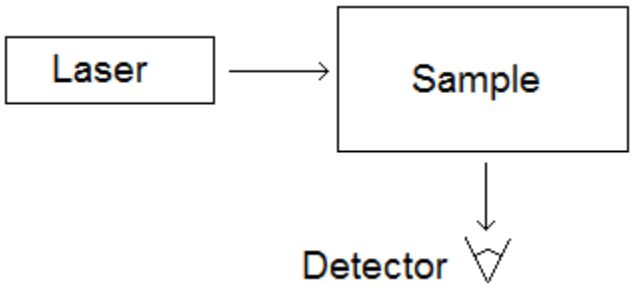
A fairly recent development in technology is the development of **ultrafast lasers**. This class of device delivers laser output in very short (on the order of femtoseconds) pulses of laser output. On this time scale, it is possible to take snapshots of chemical reaction intermediates since the laser pulse time is comparable to the lifetime of a chemical intermediate. These lasers, however, have very brad spectral output due to the **Heisenberg uncertainty principle** precluding simultaneously small uncertainties in time and wavelength.

Laser Spectroscopy

Typical **spectroscopy** experiments require four elements: 1) a light source, 2) a sample, 3, a monochrometer and 4) a detector. In laser methods, a laser can serve as both a light source and a monochrometer. It can also serve as just one of those two, or be used in a totally different way such that it serves as neither!

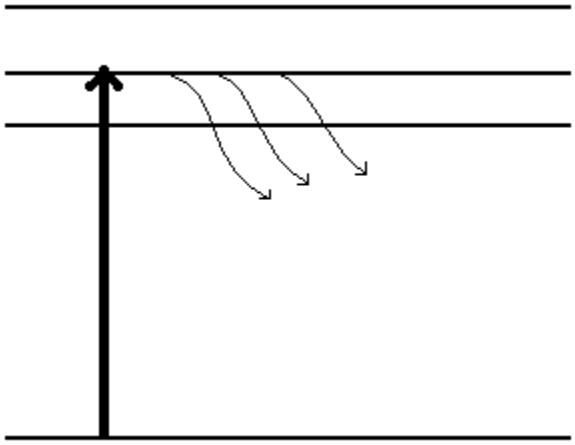
Total Fluorescence

In a **total fluorescence** experiment, the laser is used as both the light source as well as the monochrometer. The data obtained is similar to that obtained in a regular absorption spectroscopy experiment.



The laser used in this kind of experiment would typically be a tunable dye laser that will be scanned through a range of wavelengths in order to map the absorption spectrum of the sample. The detector must be placed at an angle to the incident laser beam in order to minimize direct exposure to the laser light, which will swamp the signal (and probably ruin the detector!)

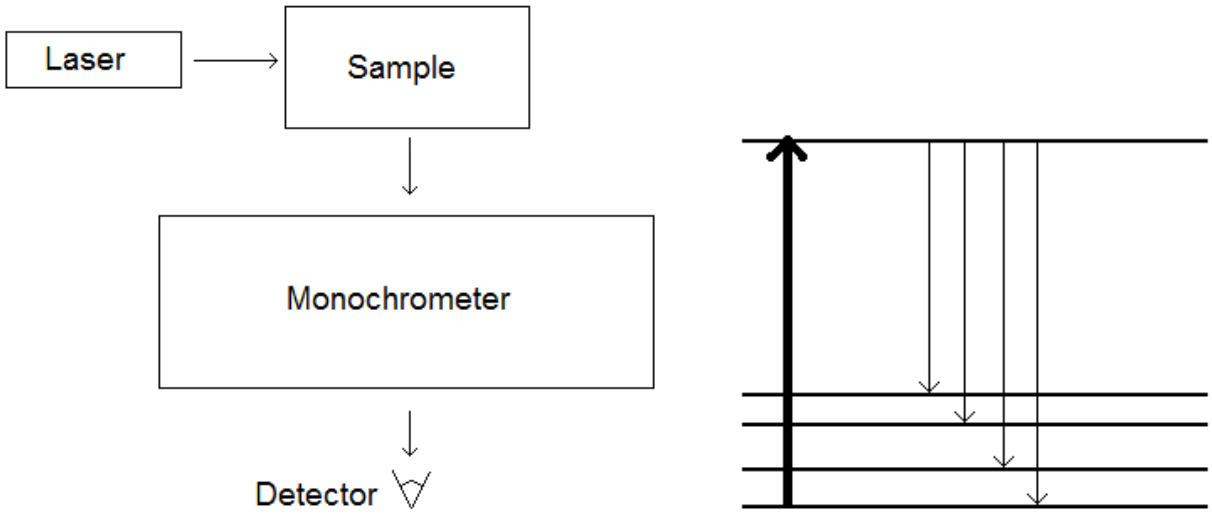
What is detected is actually photons produced in the fluorescence of the sample, which is increased whenever the laser frequency coincides with a resonance frequency.



Monitoring fluorescence intensity as a function of excitation laser wavelength produces an absorption spectrum of the molecule. By and large, the total fluorescence method yields information about the upper state of a transition since scanning the tunable laser maps the energy levels in the upper state.

Dispersed Fluorescence

In a **dispersed fluorescence** spectrum, The wavelength of the excitation laser is fixed and the fluorescence is collected by a monochrometer and separated into its wavelength components.



By separating the fluorescence into its wavelength components, the lower level energy levels are mapped. As such, this experiment is similar to an emission spectrum, but has the advantage of

having only a single upper level quantum state. This type of experiment yields information about the lower level of the transition.

Molecular Beam Spectroscopy (A Sub-Doppler Method)

Laser excitation (total fluorescence) spectroscopy and dispersed fluorescence spectroscopy have resolution that is limited by the instrumentation and the natural **Doppler width** of the lines in the spectrum (caused by the motion of molecules in the gas phase, which can be parallel, antiparallel or at some angle to the direction of the laser beam propagation.) A number of techniques exist that allow for sub-Doppler resolution (resolution that is better than the **Doppler limit** would otherwise allow.

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Vocabulary and Concepts

Problems

1. A dye laser produces pulses of 15.0 mJ at a wavelength of 564 nm. How many photons are being produced per pulse?

2. In the above problem, consider the optical gain medium occupying a volume of 1.00 mL. What is the minimum concentration (in mol/L) of chromophores needed to produce pulses of 15.0 mJ at 564 nm?

3. Consider a two-level system, in which the difference in energy is 1.0 eV. If both levels are singly degenerate, calculate the fractional population of each level at 10 K, 100 K, and 1000 K.