

Lasers

Introduction

LASER – Light Amplification by Stimulated Emission of Radiation

For stimulated emission to occur, medium must have some molecules in an excited state. But consider the thermal population of the excited state at room temperature if the wavelength of emission is 694 nm.

$$\frac{n_i}{N} = 6.2 \times 10^{-31}$$

No molecules of the medium are in the excited state. Therefore to create stimulated emission, a large number of molecules must be promoted to an excited state. The process of creating a large number of molecules in the excited state is called **population inversion**. Since excited state molecules are being continually stimulated to release a photon and drop to the ground state, a laser must have a way of keeping the excited state continually populated. Population inversion is created using a **flash lamp** or sometimes another laser.

Parts of a Laser

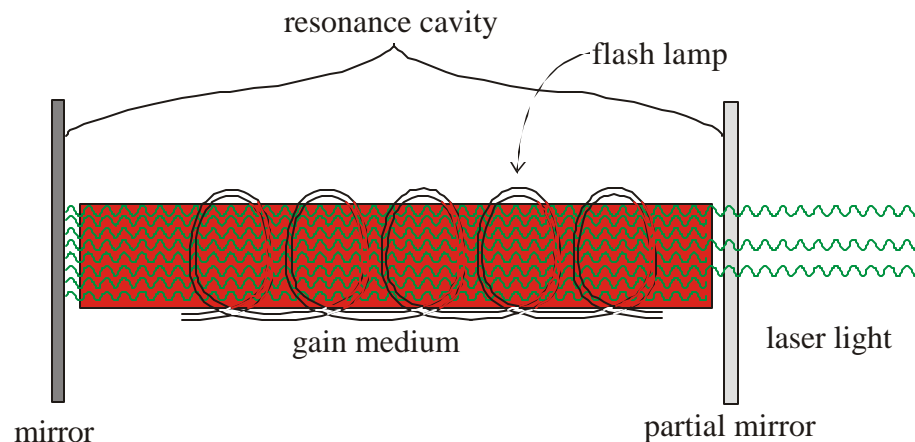
A laser has two main parts.

1.) **Gain medium**

- The medium that will be emitting the stimulated emission.

2.) **Resonance cavity**

- It is important to have a long gain medium to build intensity of light.
- Intensity of light is increased by being reflected back and forth through the gain medium.



Light comes out of resonance cavity via “leaking” through mirror.

Resonance Modes

Light emitted via spontaneous emission can have any direction.

Spontaneously emitted photons cause stimulated emission.

A stimulated emission photon has the same phase, frequency and direction as the photon that stimulated it.

Light with its photons having the same phase, frequency and direction is called **coherent light**.

Recall that electronic transitions have a finite linewidth. (Natural broadening, etc...)

However within the resonance cavity, the photons that do not have an integral number of wavelengths between mirrors destructively interfere with each other.

Only those photons with an integral number of wavelengths between the mirrors survive.

The wavelengths of light that transmit from the cavity are called **resonance modes**.

Surprise! Laser light is not really monochromatic, but ...

- For 694.4 nm light, the modes are 0.016 nm apart
- The number of modes is approximately 10 – 20; therefore, laser light is effectively monochromatic.

These resonance modes are one the reasons laser light is not infinitely coherent.

Two Operational Modes of Lasers

Continuous Wave Lasers (CW lasers)

Laser light is continuously emitted from resonance cavity.

Most applications of lasers use CW lasers.

- Raman spectroscopy
- Laser Pointer
- CD drive
- Construction levels
- Medical lasers
- Etching of semiconductor chips

Because gain medium is constantly being excited, the power of CW lasers is limited since the gain medium can overheat.

Pulsed Lasers

Laser light is emitted very briefly. 10 ms to 10 fs (that is 10^{-15} s!)

Applications of pulsed lasers include

- Cutting and welding of materials
- Studying transition state chemistry
- Studying nonlinear optics

Much more power can be delivered to a pulse.

- World record (2002): Petawatt laser at Lawrence Livermore National Laboratory.

$$1.25\text{PW} = \frac{600\text{J}}{500\text{fs}} = \frac{600\text{J}}{5 \times 10^{-13}\text{s}} = 1.25 \times 10^{15}\text{W}$$

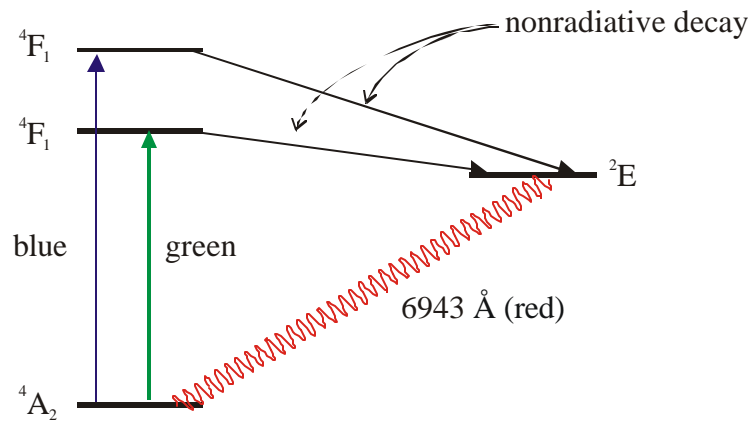
- Power capacity of electric utilities in United States: 0.7 PW
- Used for attempts to induce nuclear fusion.

Specific Lasers and Their Lasing Mechanisms

Ruby Laser

- Gain medium is Cr^{3+} ions in Al_2O_3 (garnet) matrix. $\approx 0.05\%$ by weight.

Energy levels of Cr^{3+} ions

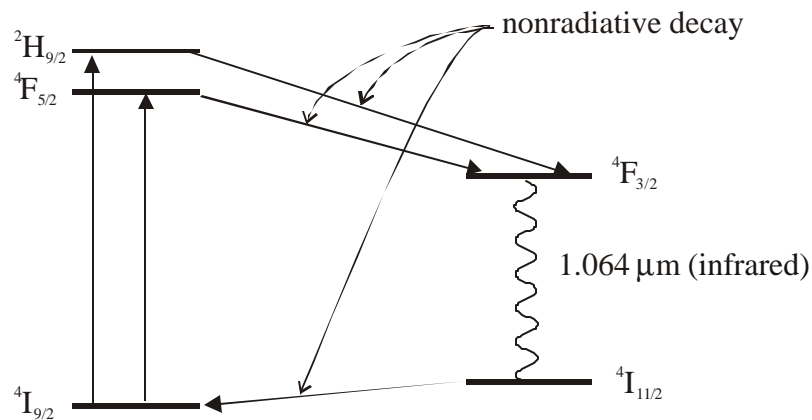


- The nonradiative decay must occur quickly before spontaneous emission.
- The spontaneous emission lifetime of 2E state is ≈ 2 msec (spin-forbidden transition).
- The ruby laser is an example of a **three-level system**.
 - Disadvantage of three level system is that the many ions in the ground state must be "optically pumped to excited state, i.e., population inversion is difficult to maintain.
 - As a consequence, the power (intensity) of the ruby laser is limited.
- Population inversion is created with Xenon flash lamp.

Nd: YAG Laser

- Gain medium is Nd^{3+} ions in $\text{Y}_3\text{Al}_5\text{O}_{12}$ (**Y**ttrium **A**luminum **G**arnet) matrix.

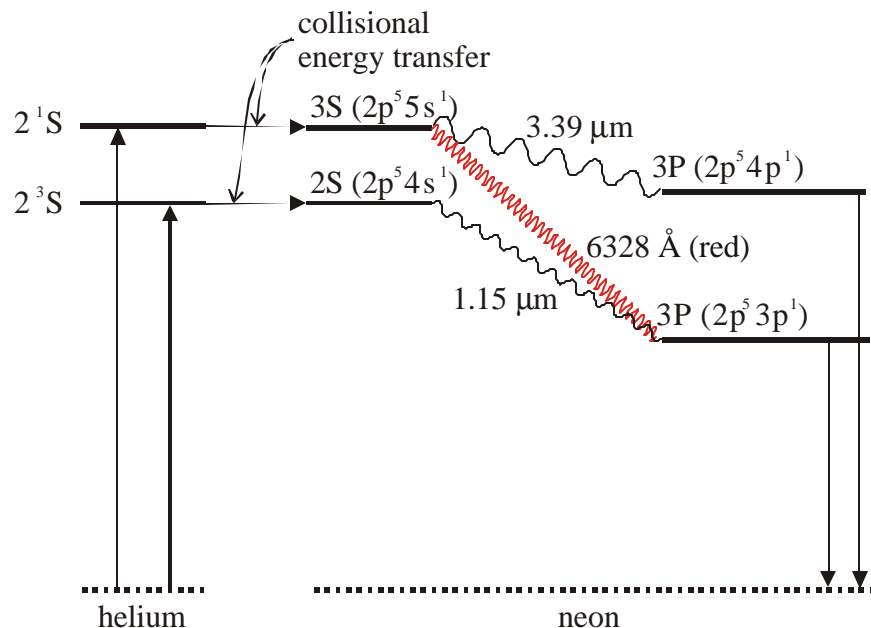
Energy levels of Nd^{3+} ions



- Example of a **four-level system**.
 - Population inversion for a four-level system is easier to maintain.
 - Thus, power of YAG laser can be much greater than three-level system.
- High thermal conductivity of YAG allows thermal energy to be dissipated quickly.
- Emission of light is in the infrared region.
- Light can be made green, by adding 'frequency doubling' crystal (potassium titanyl phosphate) in front of beam.

Helium-Neon (HeNe) Laser

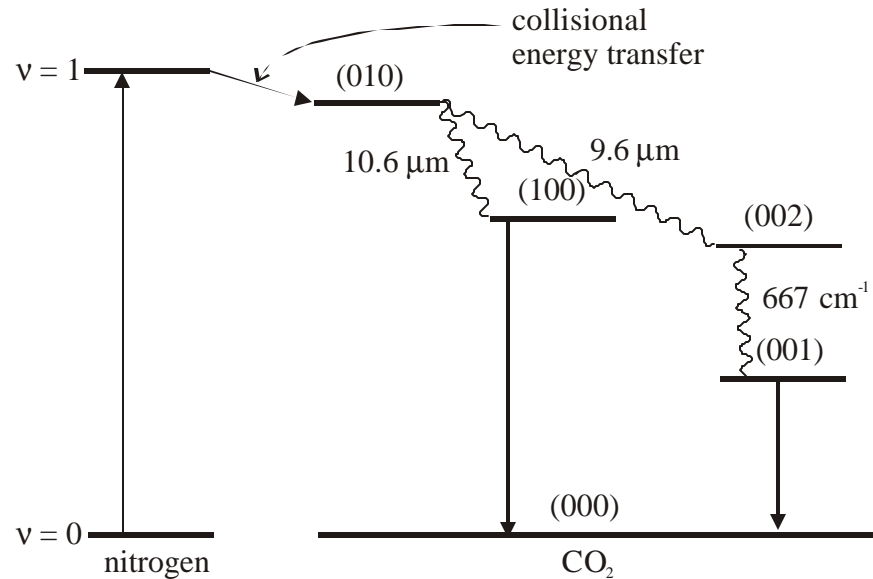
- Gain medium is neon gas
- Helium gas is necessary for collisional energy transfer and to inhibit collisions between neon atoms.



- Three lasing frequencies possible: 6328 Å, 1.15 μm , 3.39 μm
- The gain medium can flow since it is a gas.
- Flow allows gas to be cooled, thus the intensity of the laser can be increased.
- HeNe lasers are used barcode scanners.

CO₂ Laser

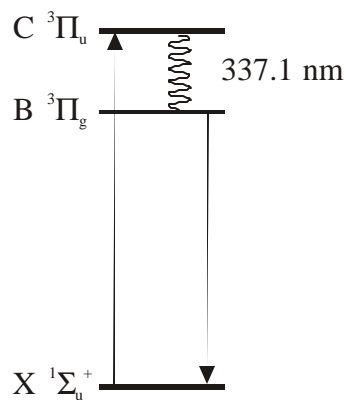
- Gain medium is carbon dioxide gas.
- Resonance cavity contains 5 times as much N₂ as CO₂.
- Population inversion occurs when vibrationally excited N₂ collides with CO₂ molecule and transfers energy.
- *Notation:* ($\#$, \dagger , \ddagger) \Rightarrow (sym $v = \#$, antisym $v = \dagger$, bending $v = \ddagger$).



- Three lasing frequencies possible: $10.6\ \mu\text{m}$, $9.6\ \mu\text{m}$ and $667\ \text{cm}^{-1}$
- CO₂ lasers are high intensity lasers used for metal cutting and welding.

Nitrogen Laser

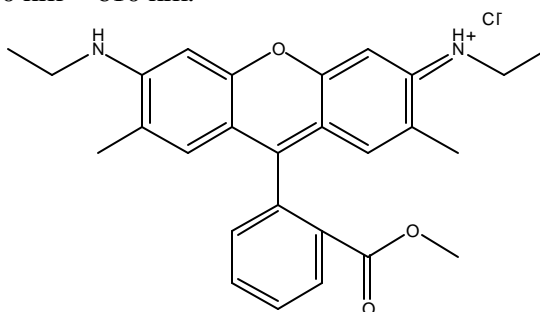
- Gain medium is N₂ gas.



- Since population inversion is difficult to maintain, the nitrogen laser is strictly a pulsed laser.
- Commonly used for spectroscopic applications.

Dye Lasers

- Gain medium is an organic dye such as Rhodamine-6G.
- Dye has a “broad spectrum”
 - Rhodamine-6G 570 nm – 610 nm.



- Dye is placed in solvent (often ethanol).
- Dye flows through chamber to allow cooling of gain medium.
- Another laser is used to create population inversion in the dye molecules. ($S_1 \rightarrow S_0$)
 - Examples include Nd-YAG, N_2 , Ar-ion, Kr-ion lasers.
- Laser is “tuned” with diffraction grating at the end of the resonance cavity.
- Other dyes can be used to create laser light from 400 nm to 1000 nm.

Applications of Lasers

Raman Spectroscopy

The use of laser light allows the Raman signals to be seen rather than being overwhelmed by the width of the incident beam.

The high intensity of laser light increases the intensity of the Raman signals, since Raman intensities are much, much lower than Rayleigh intensities.

Nonlinear Optics

We have previously stated that the dipole moment of a molecule in an electric field is proportional to the electric field, i.e.,

$$\mu = \mu_0 + \alpha E$$

where μ_0 is the permanent dipole moment, α is the polarizability of the molecule and E is the incident electric field.

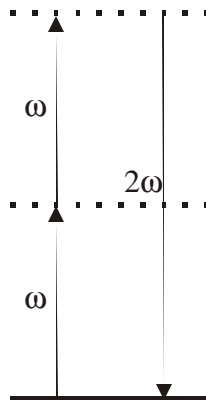
At high electric field intensities, nonlinear effects occur so that the linear relationship between the dipole moment and the electric field is no longer valid.

$$\mu = \mu_0 + \alpha E + \frac{1}{2}\beta E^2 + \frac{1}{6}\gamma E^3 + \dots$$

where β is the hyperpolarizability and γ is the second hyperpolarizability of the molecule.

Both β and γ are small so that at low electric field intensities, their contribution to the dipole moment of the molecule is negligibly small. As the electric field intensity increases, the effects of β and γ , etc ... become more important.

The hyperpolarizability β is the molecular property responsible for a process called frequency doubling or second harmonic generation.



Note: Two photons are absorbed into virtual electronic states and one photon with twice the incident frequency is emitted.

This process is also known as hyper-Rayleigh scattering.

Most common substance with high β is KH_2PO_4 (KDP)

Shining $10.6\ \mu\text{m}$ CO_2 laser through crystal creates $5.3\ \mu\text{m}$ laser light.

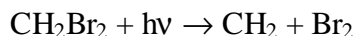
Green ($532\ \text{nm}$) laser pointers operate by doubling frequency of $1064\ \text{nm}$ laser output (diode laser).

Examining Transition States

Lasers can be made to create short pulses (to 10 fs)

Since these pulses are so short, they can be used to examine processes that occur very quickly like the formation of a transition state.

Consider the examining the dynamics of the photodissociation of methylene bromide.



We can determine the mode of dissociation using “**pump-probe**” femtosecond spectroscopy.

To use “pump-probe” spectroscopy on transition states, we need to use two laser pulses.

1. Pump pulse activates the reaction.
 - after the pump pulse hits the molecule, the electrons and nuclei start their rearrangement to the transition state.
 - even though the transition state is unstable, it does have a particular arrangement of electrons and nuclei and means it has its own potential energy surface with various vibrational levels.
2. Probe pulse analyses the structure of the transition state and length of time needed to make the transition state.
 - The time delay, τ , between the pump pulse and the probe pulse is varied to measure the formation time of the transition state and its lifetime.
 - As the absorption of the pulse increases, more of the molecules as have formed the transition state.
 - As the absorption of the pulse decreases, more of the molecules as have progressed past the transition state.
 - The frequency of the probe pulse is varied to find the structure of the transition state.
 - Since different transition states will absorb different frequency of light, we can discover, upon analysis, what the transition state may look like.

