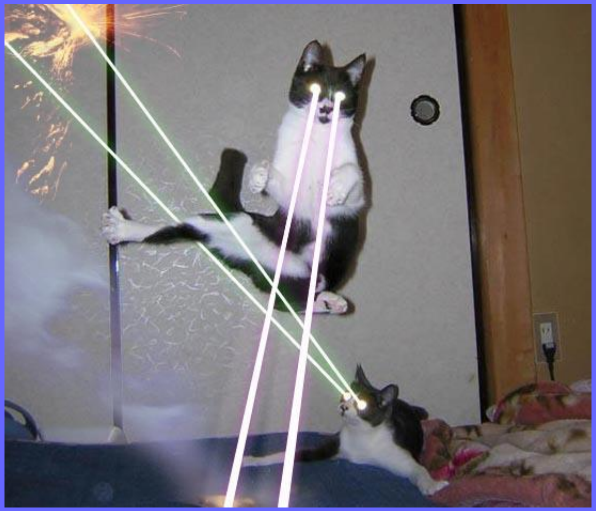
Chemistry 4631

Instrumental Analysis

Lecture 11



Components of Optical Instruments

UV to IR

Basic components of spectroscopic instruments:

- stable source of radiant energy
- transparent container to hold sample
- device to isolate selected region of the spectrum for measurement
- detector to convert radiant energy to a signal
- signal processor and readout

Components of Optical Instruments

Some components of optical instruments use Lasers.

And some Lasers are based on semiconductor technology.

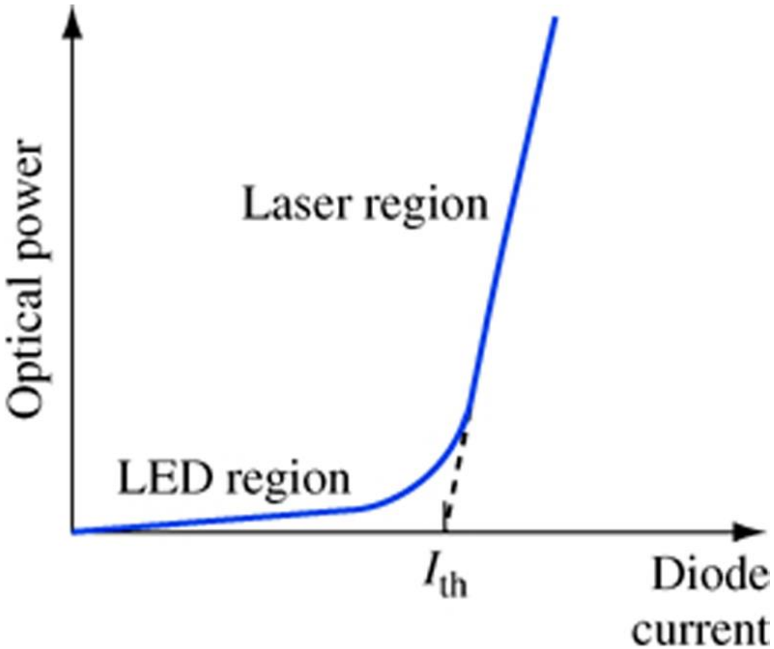
Line Sources are LASERS.

Components of Optical Instruments

Laser

Light Amplification by Stimulated Emission of Radiation

- **High Intensities**
- **Narrow Bandwidths**
- **Coherent Outputs**



Components of Optical Instruments

Applications

- **CD/DVD Readers**
- **Fiber Optics**
- ***Spectroscopy Sources***
- **Material Processing**
- **Photochemistry**

Laser Sources in UV, vis, and IR

Used for

- **high resolution spectroscopy**
- **kinetic studies**
- **routine analysis**

Components of Optical Instruments

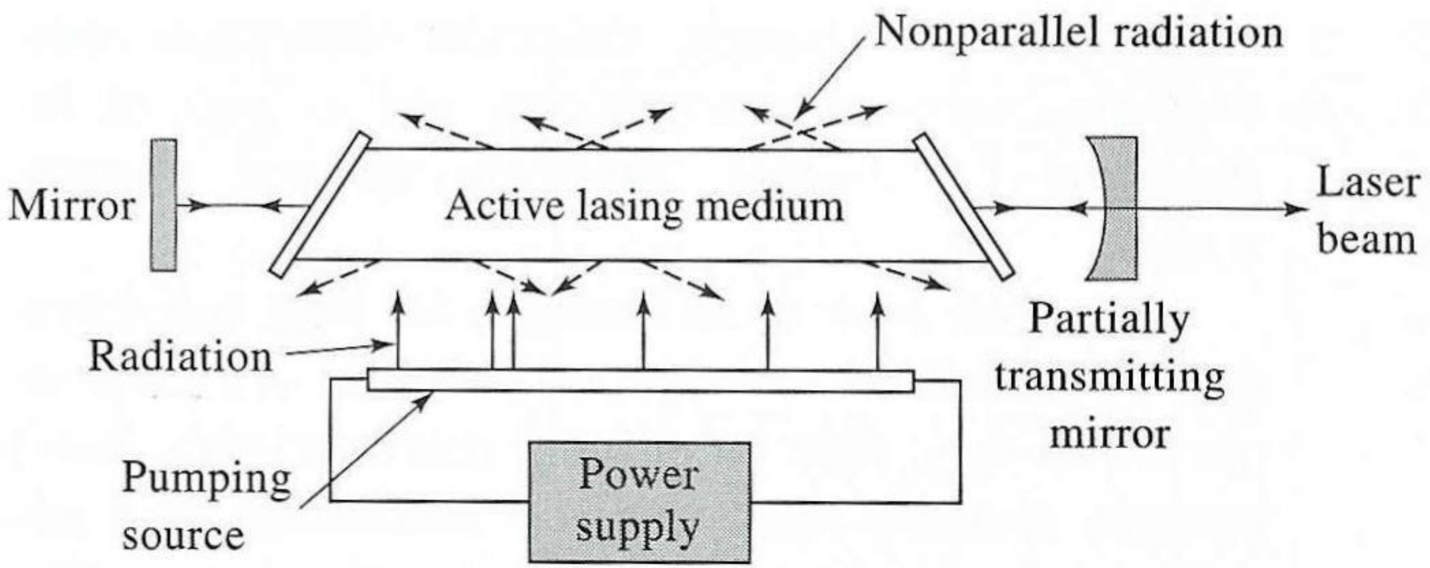
Background

In 1917 Einstein predicted that:

- under certain circumstances a photon incident upon a material can generate a second photon of
  - **Exactly the same energy (frequency)**
  - **Phase**
  - **Polarization**
  - **Direction of propagation**
- **In other word, a coherent beam resulted.**

Components of Optical Instruments

Laser



Nonparallel radiation dissipates out the top and bottom of the medium and parallel or coherent radiation is left.

Components of Optical Instruments

Laser Sources

Lasing Medium:

solid crystal (ruby)

semiconductor (gallium arsenide)

solution (organic dye)

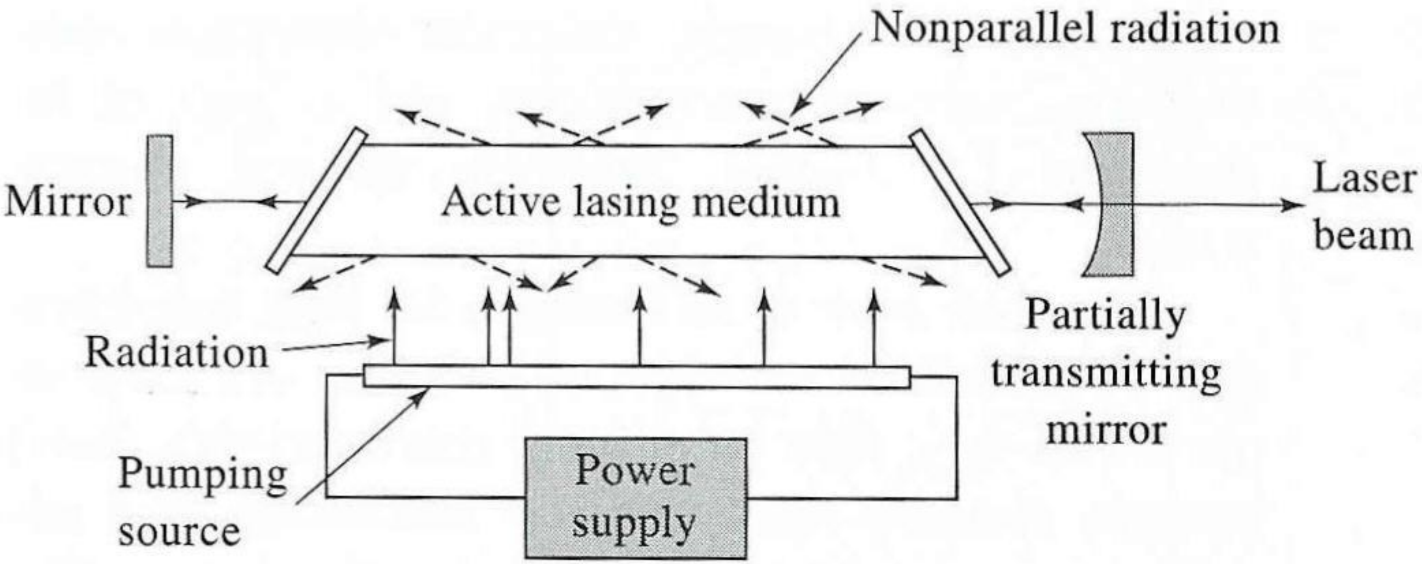
gas (argon or krypton)

Components of Optical Instruments

Lasing Medium – must be activated or "pumped" using radiation from an external source.

This can be a few photons of the correct energy to trigger a cascade of photons of the same energy. Or could be an electrical discharge into a gas.

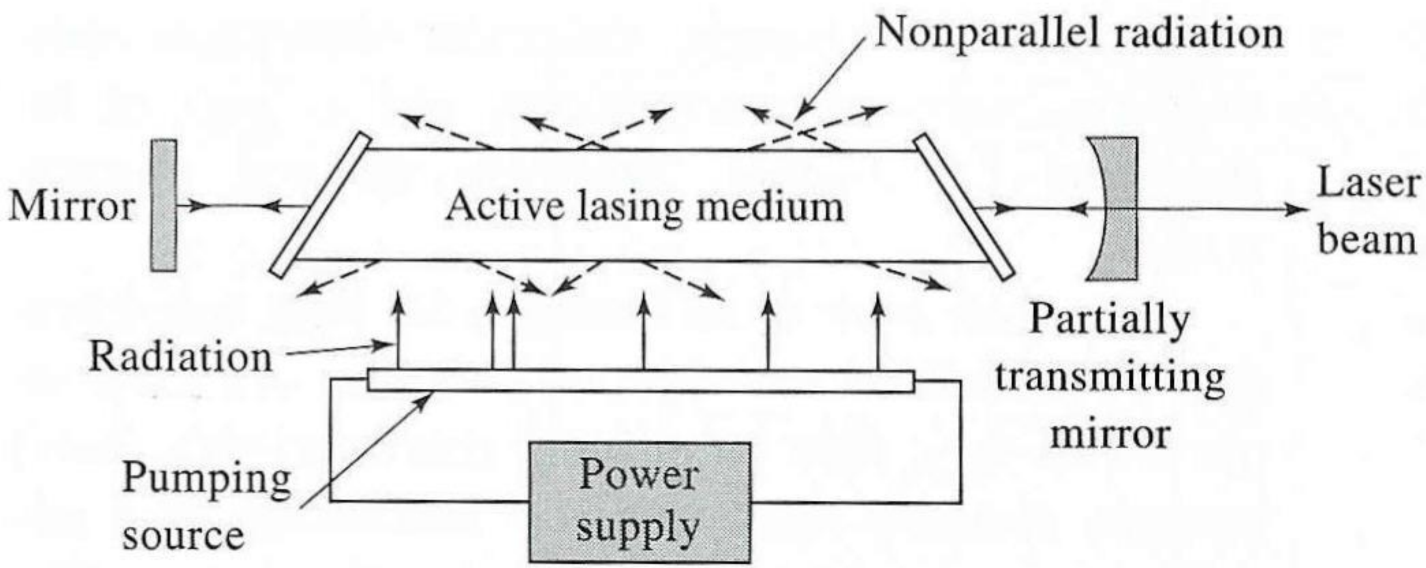
Components of Optical Instruments



Components of Optical Instruments

Once the cascade begins the laser functions as a resonator, passing the radiation back and forth through the medium using mirrors. This generates even more photons – "amplification".

Components of Optical Instruments



Components of Optical Instruments

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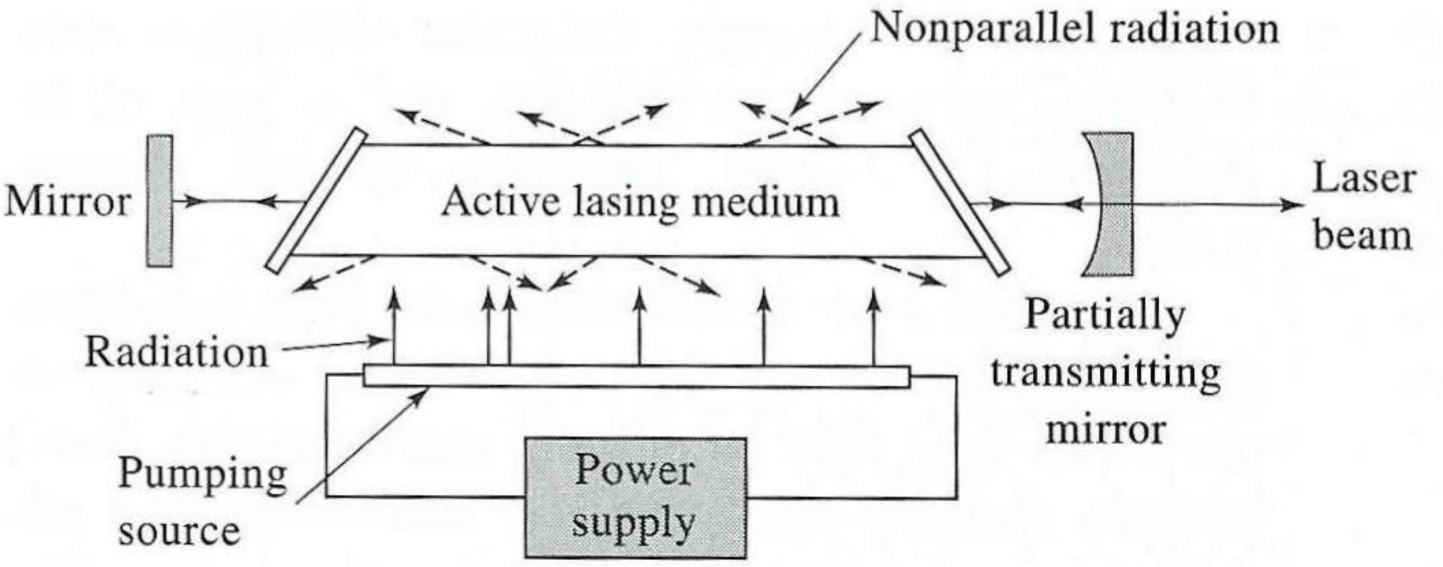
Components of Optical Instruments



Components of Optical Instruments

Laser

Processes include:

- **pumping**
- **spontaneous emission (fluorescence)**
- **stimulated emission**
- **adsorption**
- **population inversion**

Components of Optical Instruments

Pumping

Lasing Medium – must be activated or "pumped" using radiation from an external source.

This can be a few photons of the correct energy to trigger a cascade of photons of the same energy. Or could be an electrical discharge into a gas.

Components of Optical Instruments

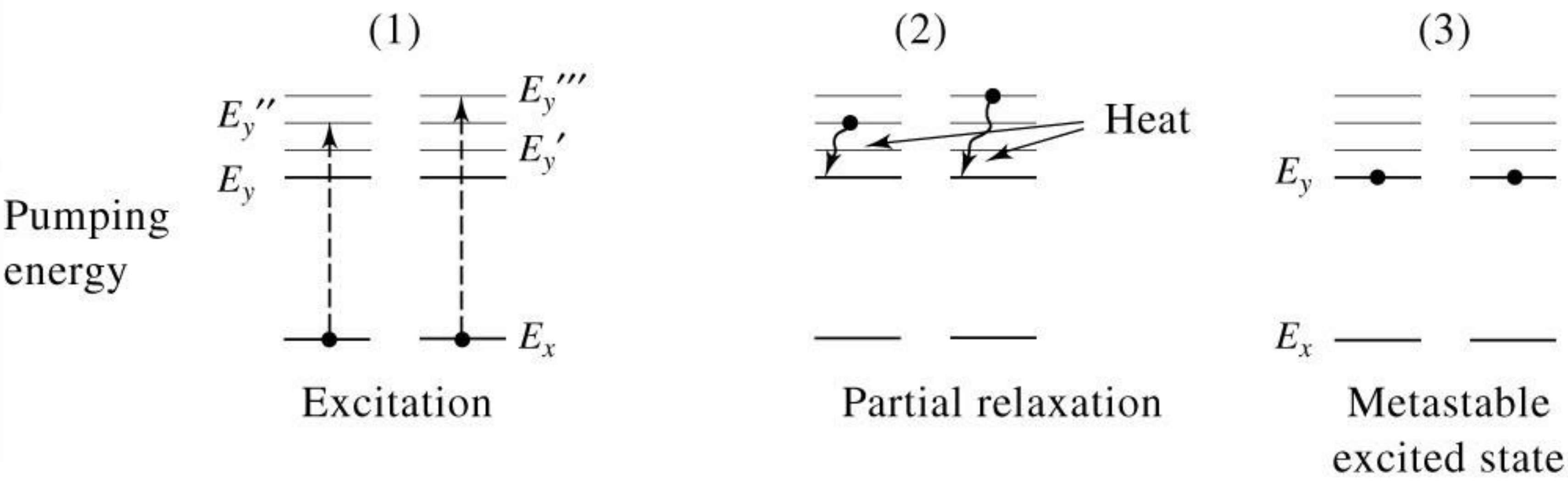
Pumping

Occurs when the medium is excited by external radiation or electricity.

This action populates higher electronic or vibrational energy levels of the active medium. Relaxation occurs through vibrations to the lowest excited level.

Components of Optical Instruments

Pumping



(a) Pumping (excitation by electrical, radiant, or chemical energy)

Components of Optical Instruments

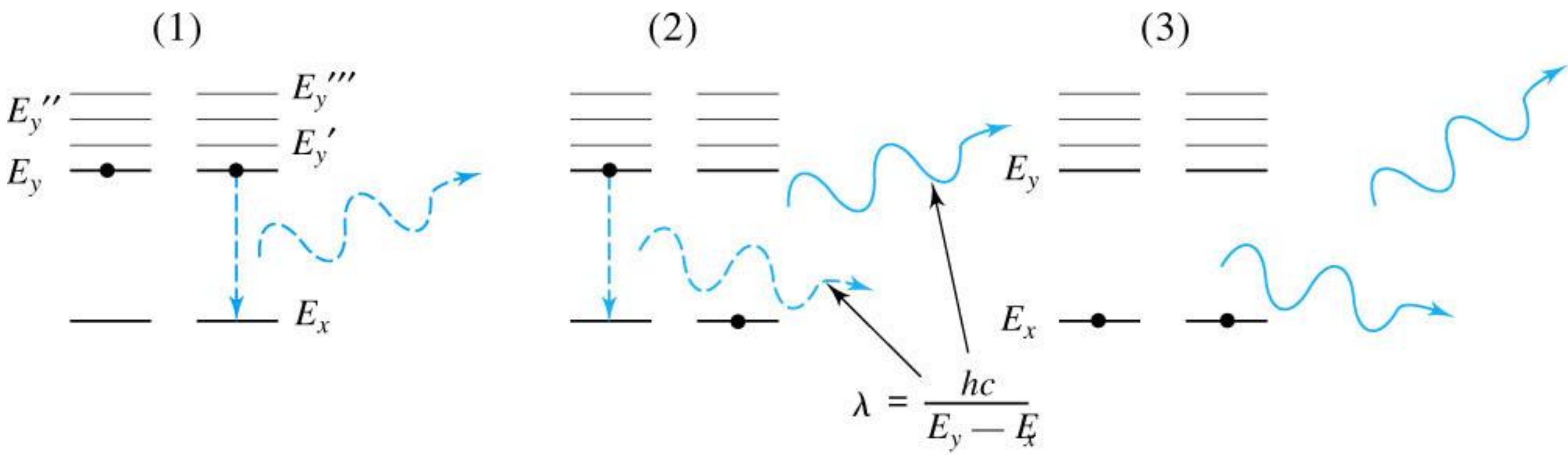
Spontaneous emission

The excess energy in the higher levels is lost by emission of radiation returning to ground state.

This type of emission is <u>incoherent</u> since it is a random process with species differing in direction and phase of emission.

Components of Optical Instruments

Spontaneous emission



(b) Spontaneous emission

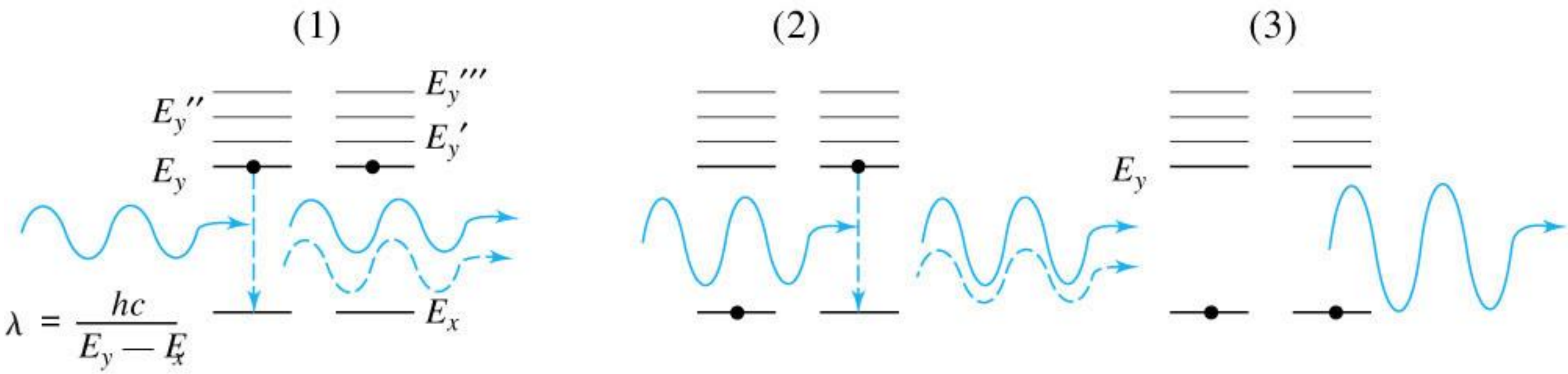
Components of Optical Instruments

Stimulated emission

Excited species are struck by photons with the same energy as that of the spontaneous emission energy. Causes immediate relaxation to ground state. This type of emission is coherent since the photons travel in phase and the same direction.

Components of Optical Instruments

Stimulated emission



(c) Stimulated emission

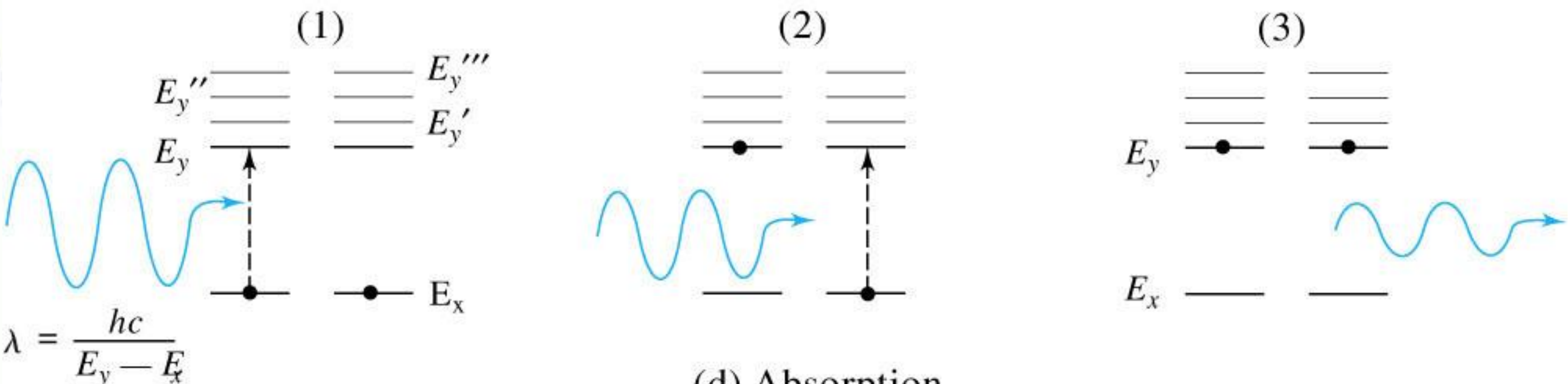
Components of Optical Instruments

Absorption

Process that competes with stimulated emission. Two photons of same energy are absorbed to produce a metastable excited state.

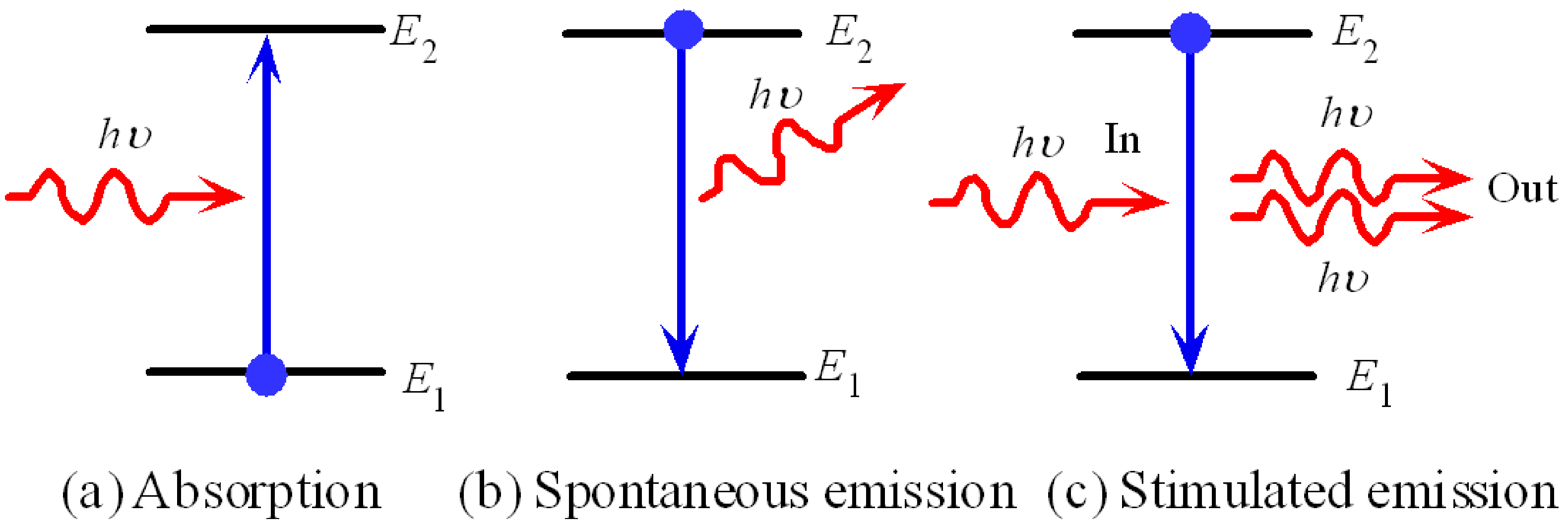
Components of Optical Instruments

Absorption



(d) Absorption

Components of Optical Instruments



Absorption, spontaneous (random photon) emission and stimulated emission.

Components of Optical Instruments

In a system, all three mechanisms occur.

However the stimulated emission is very sluggish compared to the spontaneous emission.

We need to have a much stimulated emission as possible for lasing action.

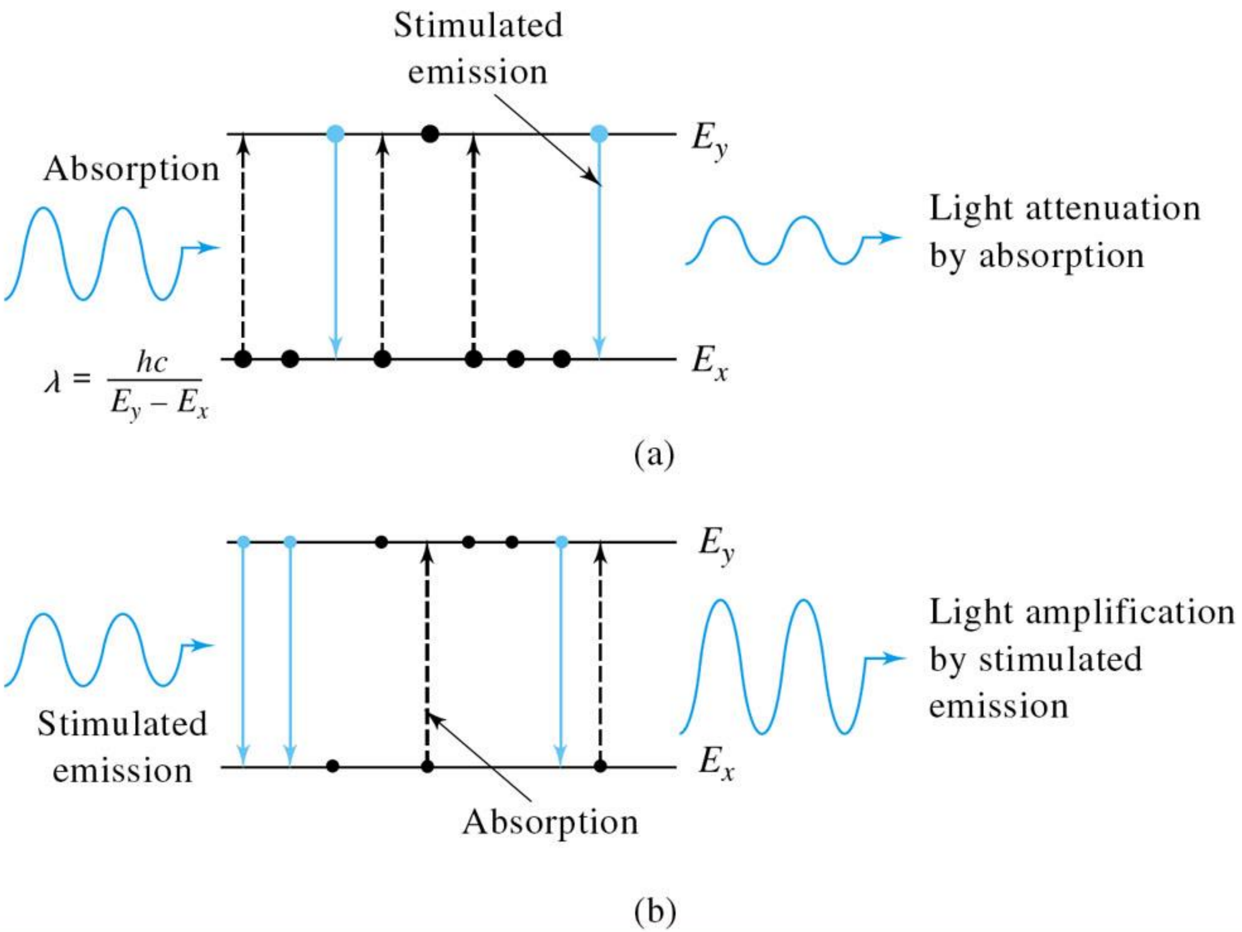
How?

Components of Optical Instruments

For Light Amplification to occur the number of photons produced by stimulated emission must exceed the number lost by absorption.

Stimulated emission > Absorption

Components of Optical Instruments



Components of Optical Instruments

Stimulated emission > Absorption

This can only occur when the number of particles in the higher energy state exceeds the number in the lower.

This process is known as <u>population inversion</u>.

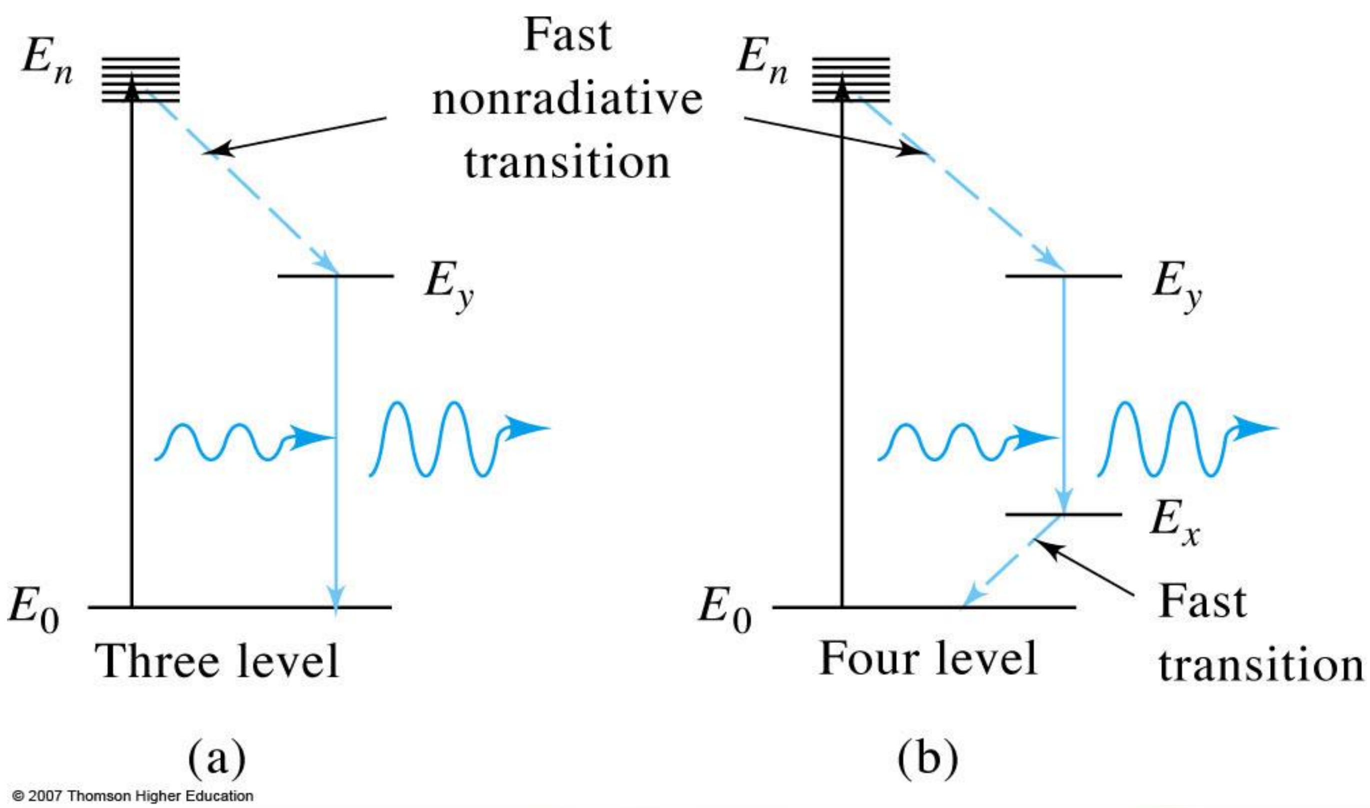
(created by pumping)

Components of Optical Instruments

- It is not possible to achieve population inversion with a 2-state system.
- In 2-state system, the best we can get is $N_1 = N_2$.
- To create population inversion, a 3-state system is required.
- The system is pumped with radiation of energy E_{31} then atoms in state 3 relax to state 2 non-radiatively.
- The electrons from E_2 will now jump to E_1 to give out radiation.

Components of Optical Instruments

3- and 4- level laser systems



Components of Optical Instruments

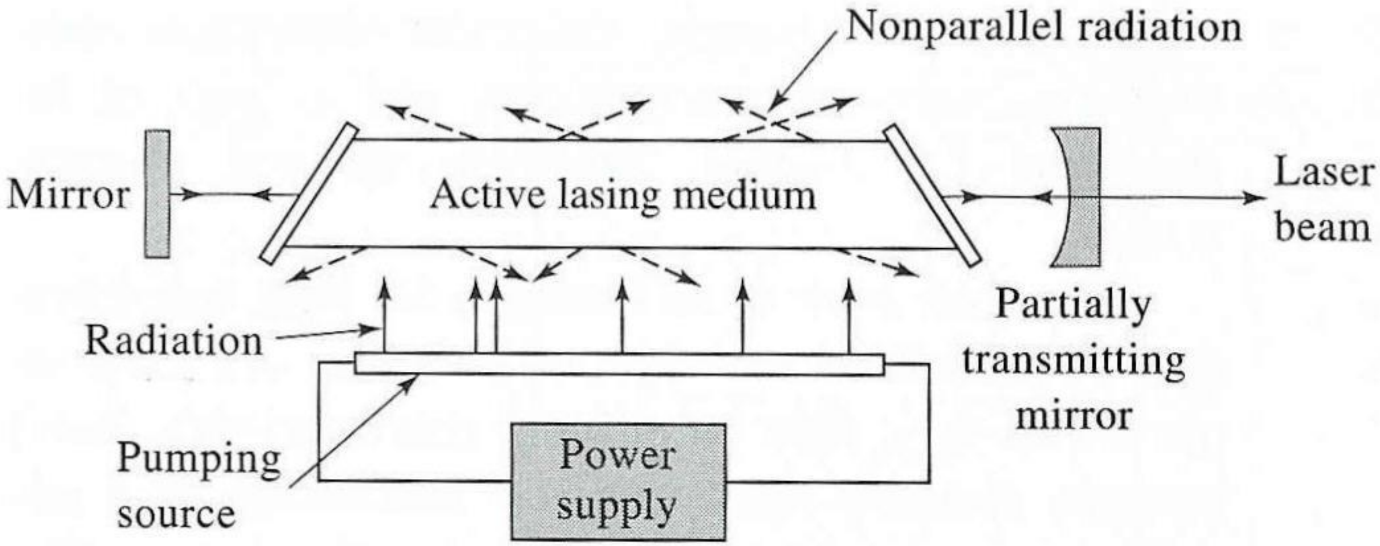
Optical Feedback

The probability of photon producing a stimulated emission event can be increased by reflecting back through the medium several times.

A device is normally fashioned in such a way that the 2 ends are made highly reflective.

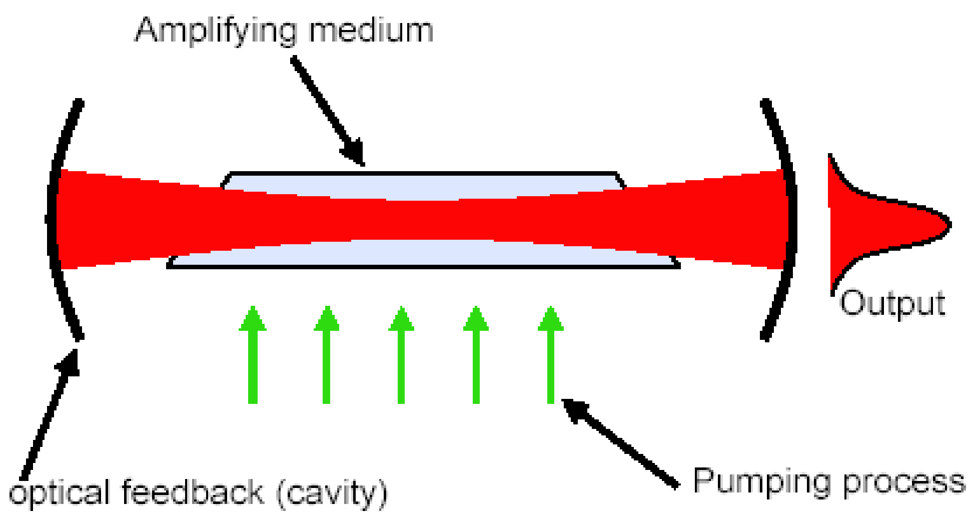
This is called an oscillator cavity or *Fabry Perot* cavity.

Components of Optical Instruments



Components of Optical Instruments

- Pumping process prepares amplifying medium in suitable state
- Optical power increases on each pass through amplifying medium
- If gain exceeds loss, device will oscillate, generating a coherent output



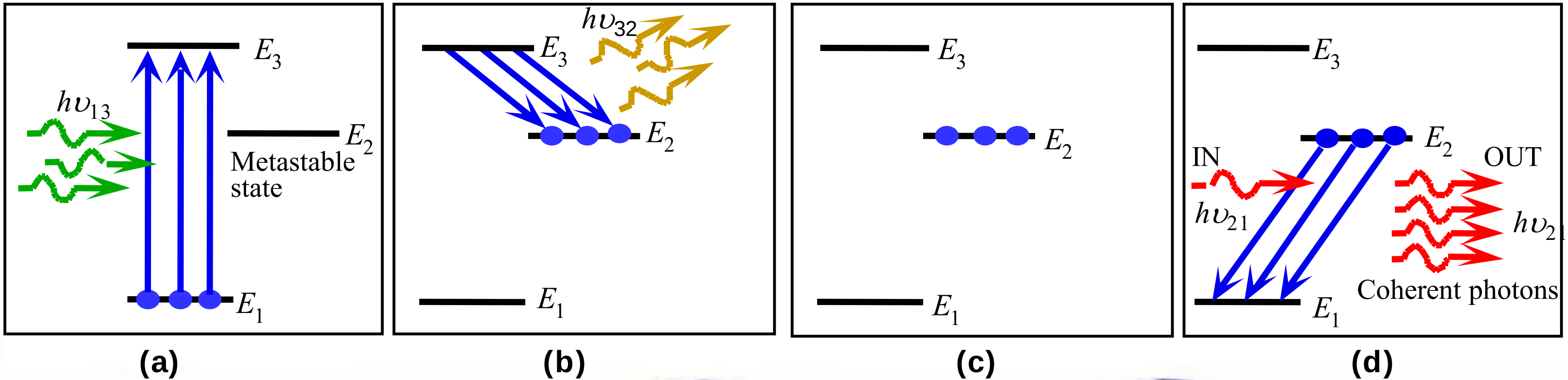
Components of Optical Instruments

Once the cascade begins the laser functions as a resonator, passing the radiation back and forth through the medium using mirrors. This generates even more photons – "amplification".

Components of Optical Instruments

Recap

Excite atoms from E1 to E3.
Exciting atoms from E1 to E3 → optical pumping
Atoms from E3 decays rapidly to E2 emitting hv32
If E2 is a long lived state, atoms from E2 will not decay to E1 rapidly
Condition where there are a lot of atoms in E2 → population inversion.



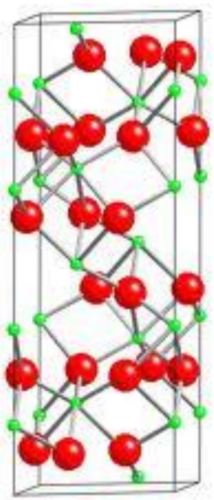
Components of Optical Instruments

Solid State

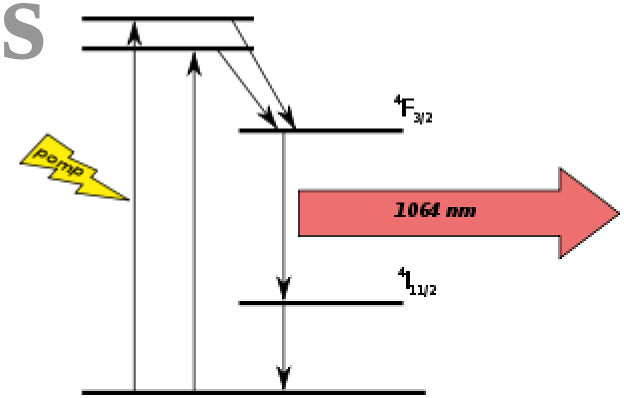
Ruby Laser – one of the first lasers, made up of Al_2O_3 with 0.05% Cr(III) in the Al (III) lattice. The Cr(III) is the active lasing material.

λ = 694.3 nm (has a deep red color)

Al – green
O - red



Components of Optical Instruments



Solid State

Nd:YAG Laser – most widely used. (4-level)
Lasing medium is made up of neodymium ion in a crystal of yttrium aluminum garnet ($Y_3Al_2(AlO_4)_3$, or $Y_3Al_5O_{12}$).
Very high radiant power output at 1064 nm and frequency doubled to give intense line at 532 nm.

Components of Optical Instruments

Gas Lasers

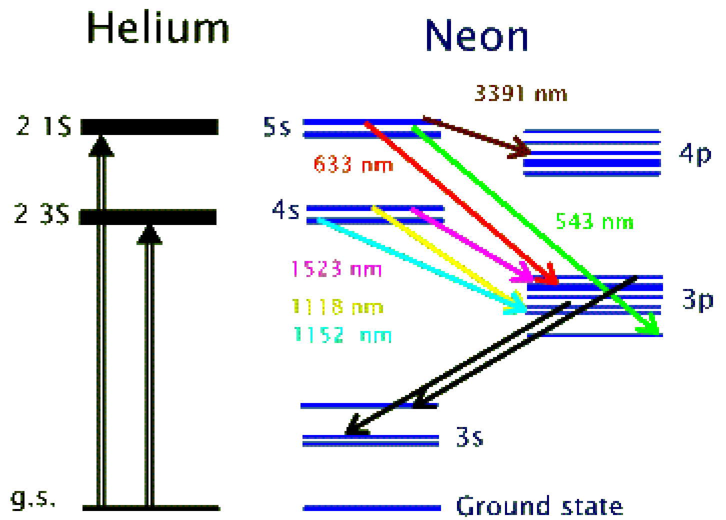
Four types

- **neutral atom lasers (He/Ne)(most common)**
- **ion lasers with active species (Ar^+ or Kr^+)**
- **molecular lasers (CO_2 or N_2)**
- **eximer lasers (gas mixtures)**

Components of Optical Instruments

Gas Lasers

- neutral atom lasers (He/Ne)(most common)
  - Low cost and maintenance, reliable, low power consumption, 632.8 nm



  - the two excited states of helium, 3S and 1S, get populated as a result of electromagnetic pumping. Both of these states are metastable and do not allow de-excitations via radiative transitions. Instead, the helium atoms give off their energy to neon atoms through collisional excitation. In this way the 4s and 5s levels in neon get populated.

Components of Optical Instruments

Gas Lasers

- ion lasers with active species (Ar^+ or Kr^+)
  - Ar^+ 514.4 and 488.0 nm lines of high intensity
  - 4-level device
  - Argon ions formed by electrical discharge
  - Go from ground state (3 principle quantum #) to 4p states, lasing occurs when relax to 4s state
  - Very high intensity – used for Raman

Components of Optical Instruments

Gas Lasers

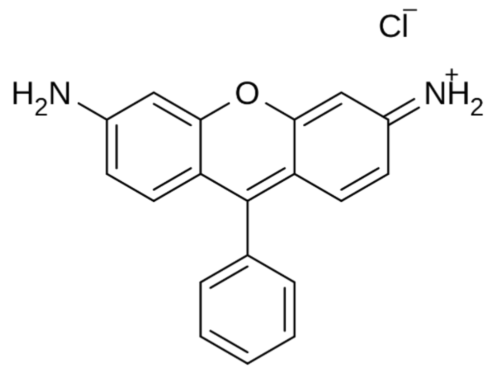
- **molecular lasers (CO_2 or N_2)**
  - **CO_2 used in IR 10.6 μm**
- **eximer lasers (gas mixtures)**

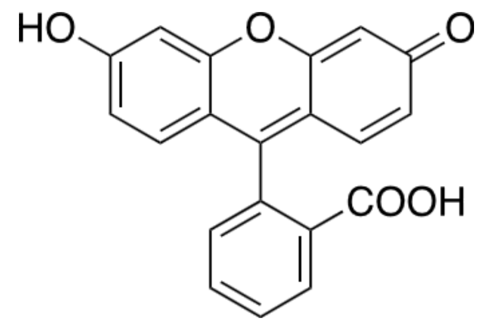
Components of Optical Instruments

Dye Lasers

- **Continuously tunable over a 20 - 50 nm range.** (wider range of λ's)
- **Bandwidth ~ 0.01 nm.**
- **Active material is an organic dye that fluoresces in the UV, vis, or IR region.**

Components of Optical Instruments

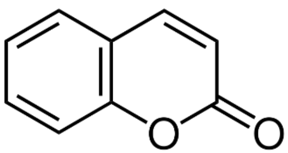


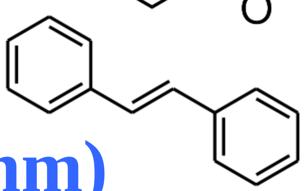


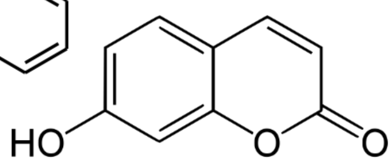
Dye Lasers

Examples:

- rhodamine 6G, can be tuned from 635 nm (orangish-red) to 560 nm (greenish-yellow)
- fluorescein (green, 530–560 nm)
- coumarin (blue 490–620 nm)
- stilbene (violet 410–480 nm),
- umbelliferone (blue, 450–470 nm)







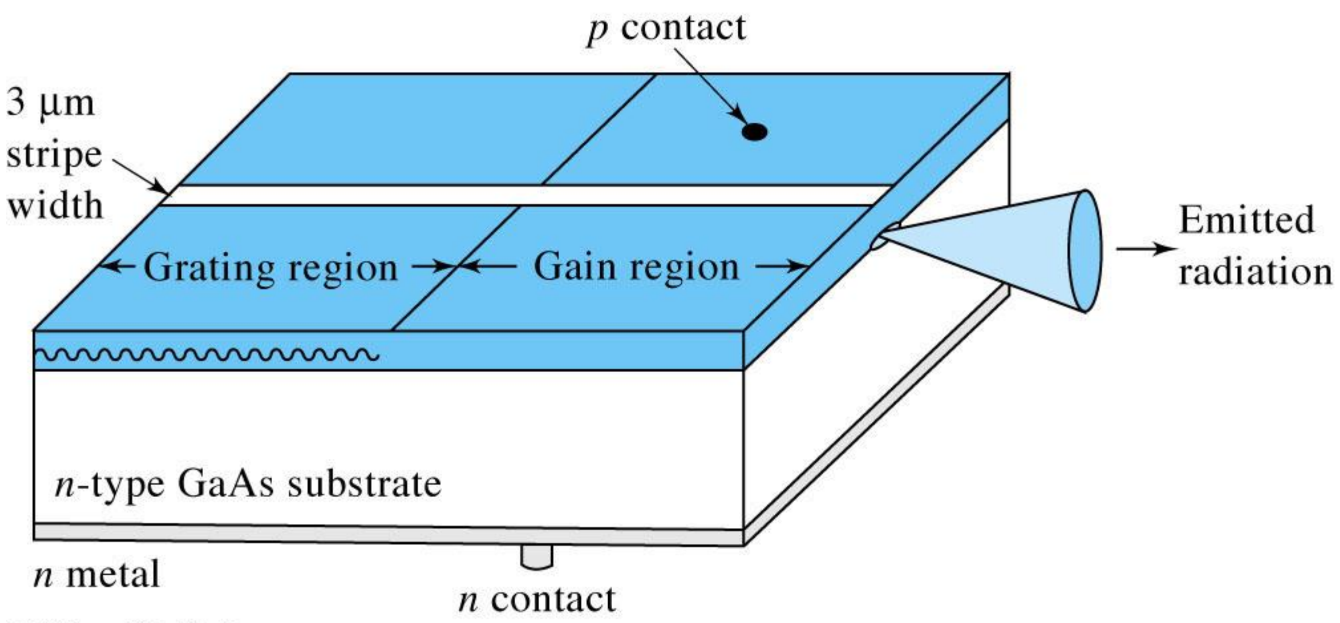
Components of Optical Instruments

Semiconductor Diode Lasers

Apply a voltage across a semiconductor diode in the forward direction to excite electrons into the conduction band creating hole-electron pairs. When the electrons relax into the valence band energy is released equal to the band-gap energy. $E_g = h\nu$

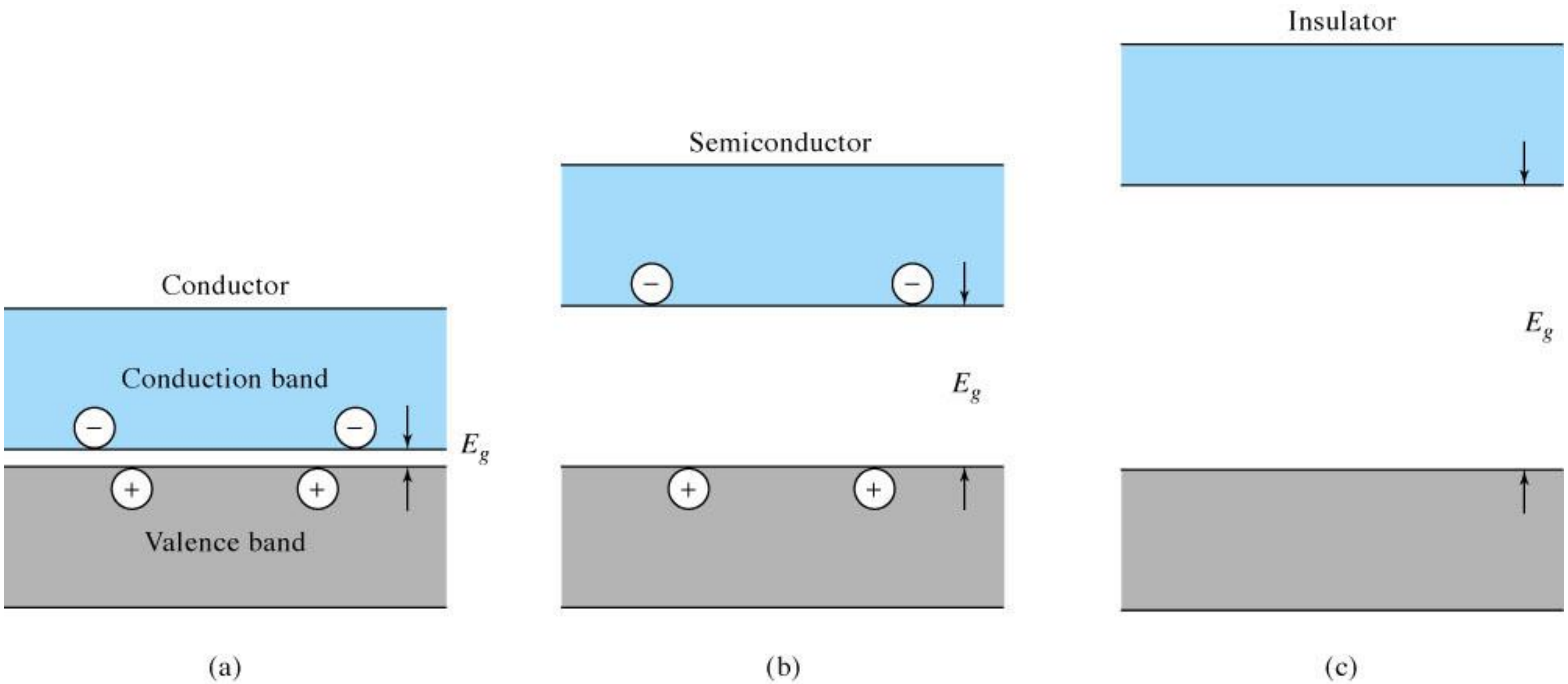
Components of Optical Instruments

Semiconductor Diode Lasers



Components of Optical Instruments

Semiconductor Diode Lasers



Assignment