

Theory – The total energy of a molecule can be broken down into several types of energy

For UV-vis must consider:

electronic energy

vibrational energy

rotational energy

Ignore translational energy

**Molecular Absorption** – more complex than atomic absorption because molecules have many more possible transitions

Electronic energy involves changes in energy levels of the outer electrons of a molecule

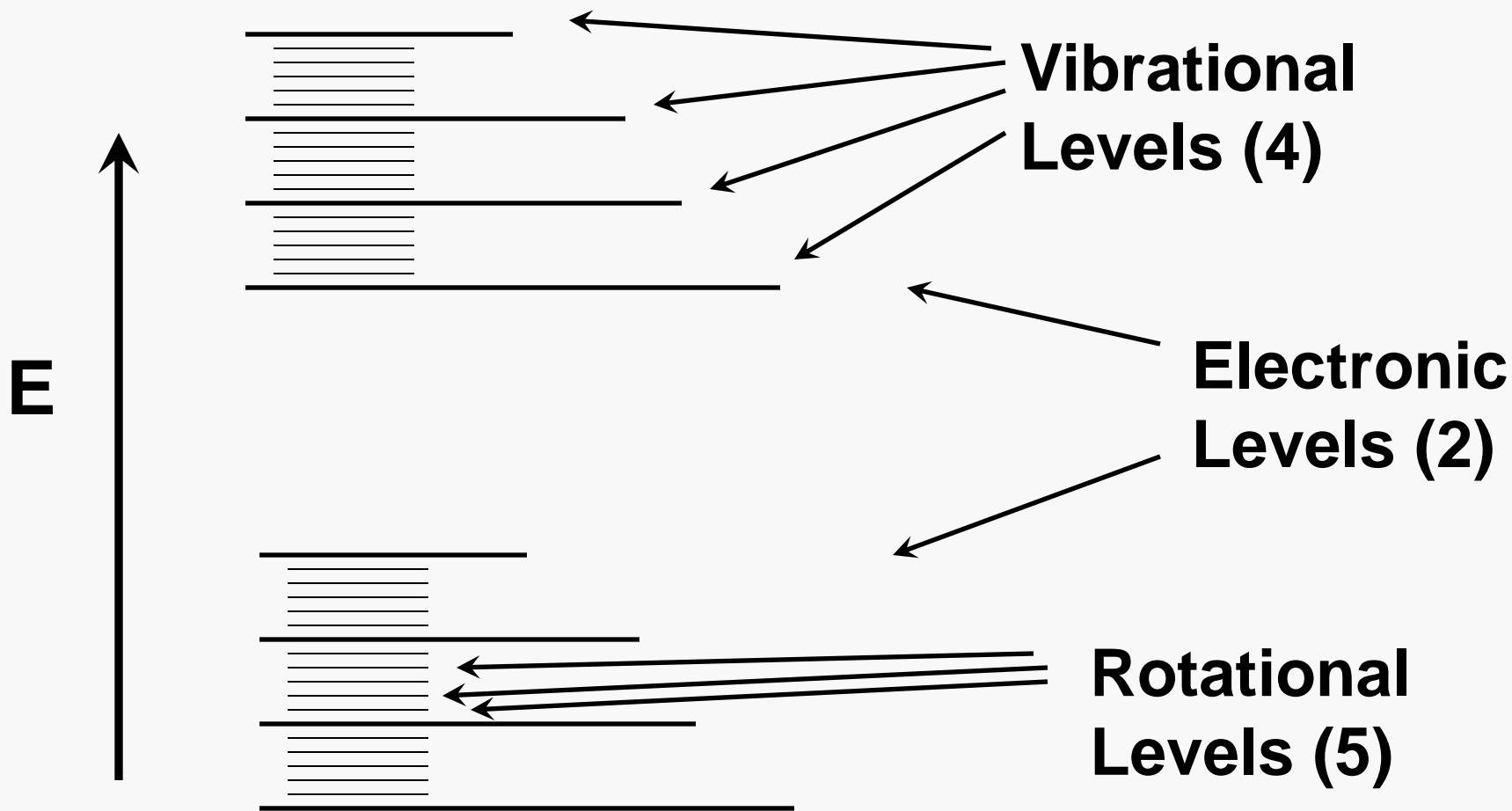
- these changes correspond to the energy of the ultraviolet-visible radiation

- these changes are quantized (i.e. discrete levels exist corresponding to quanta of light)

$$\Delta E = \Delta E_{\text{elec.}} + \Delta E_{\text{vib.}} + \Delta E_{\text{rot.}}$$

Energy change or transition for absorption      Largest energy      Smallest energy

# Simplified Energy Level Diagram



Once the excited state is formed, it will eventually “relax” or go back down to the ground state either by:

- 1) Nonradiative relaxation = no light (heat)
- 2) Emission = light emitted that is characteristic of the transition
  - 1) Large  $\Delta E$  then more energetic radiation i.e. shorter wavelength UV, x-ray, etc.
  - 2) Greater or lesser intensity depending on the number of atoms or molecules involved in the transition
  - 3) Also a probability factor

# Quantitative Aspects of Absorption

## Beer-Lambert Law (or Beer's Law)

Absorbance  $\rightarrow A = \log \frac{I_0}{I} = \epsilon b C$

Transmittance  $\rightarrow T = \frac{I}{I_0}$        $\%T = T \times 100$

molar absorptivity  
concentration  
path length

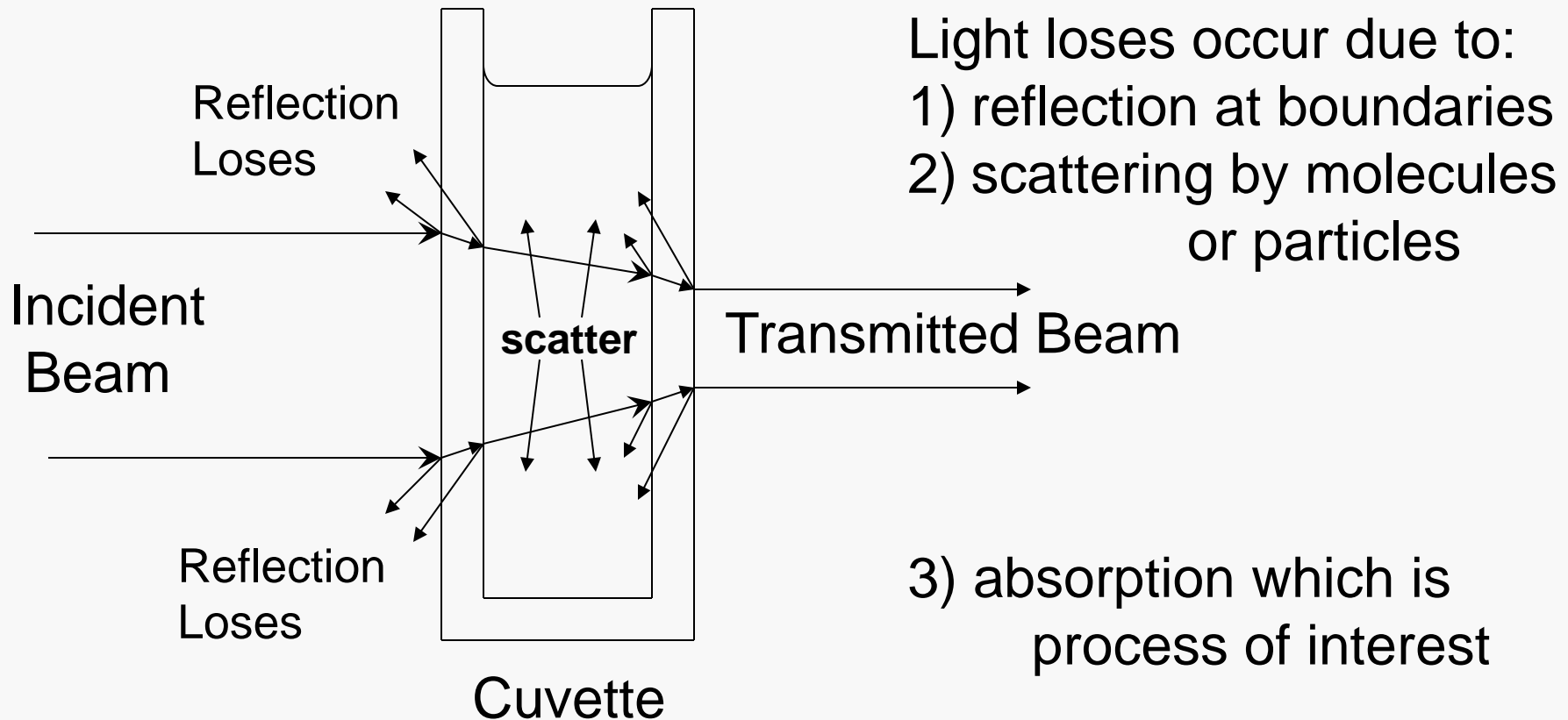
$I_0$  = measured source intensity

$I$  = measured intensity after absorption

Intensity change does not change absorbance

- Absorbance & Transmittance are unitless
- If  $C$  is mol/L &  $b$  is in cm then  $\epsilon$  is L/mol-cm
- To minimize the effect of light losses from reflection the procedure followed in UV-vis spectrophotometry is to measure  $I_0$  with a reference blank of pure solvent in the light path & then measure  $I$  under the same conditions – cuvettes should be optically matched if using 2 & clean, free of scratches, lint, fingerprints, etc.

Effects other than absorption that reduce source intensity (i.e., scattering, reflection) may also be measured as absorbance and must be accounted for when measuring  $I$  &  $I_0$



# Components of Optical Instruments

- General Design of Optical Instruments
- Sources of Radiation
- Wavelength Selectors
- Sample Containers
- Radiation Transducers (Detectors)
- Signal Processors and Readouts
- Fiber Optics



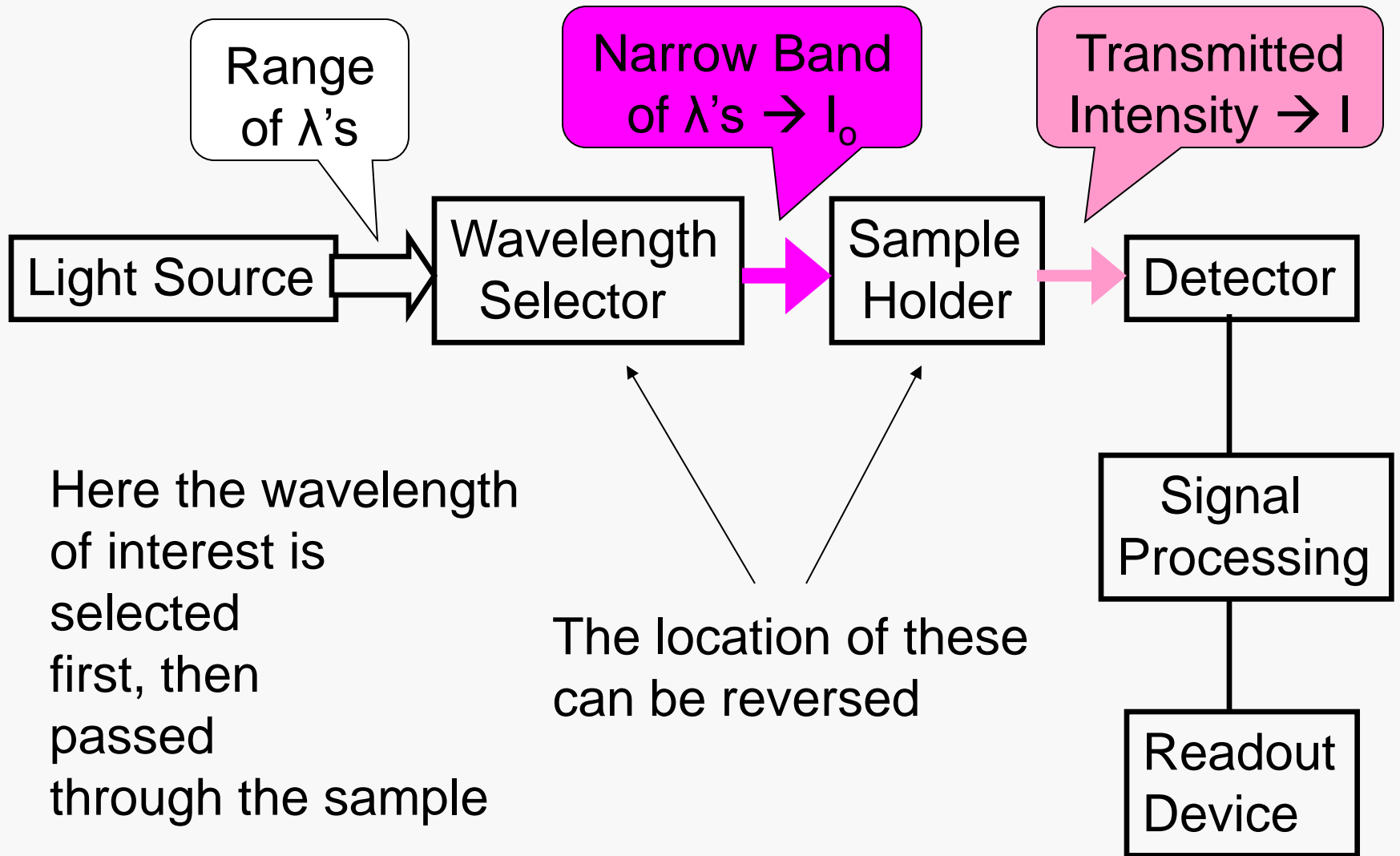
# Ultraviolet – Visible – Infrared Instrumentation

- Focus our attention on measurements in the UV-vis region of the EM spectrum
- Good instrumentation available
- Very widely used techniques
- Longstanding and proven methods
- IR instrumentation will be considered from time to time particularly when there are similarities to UV-vis

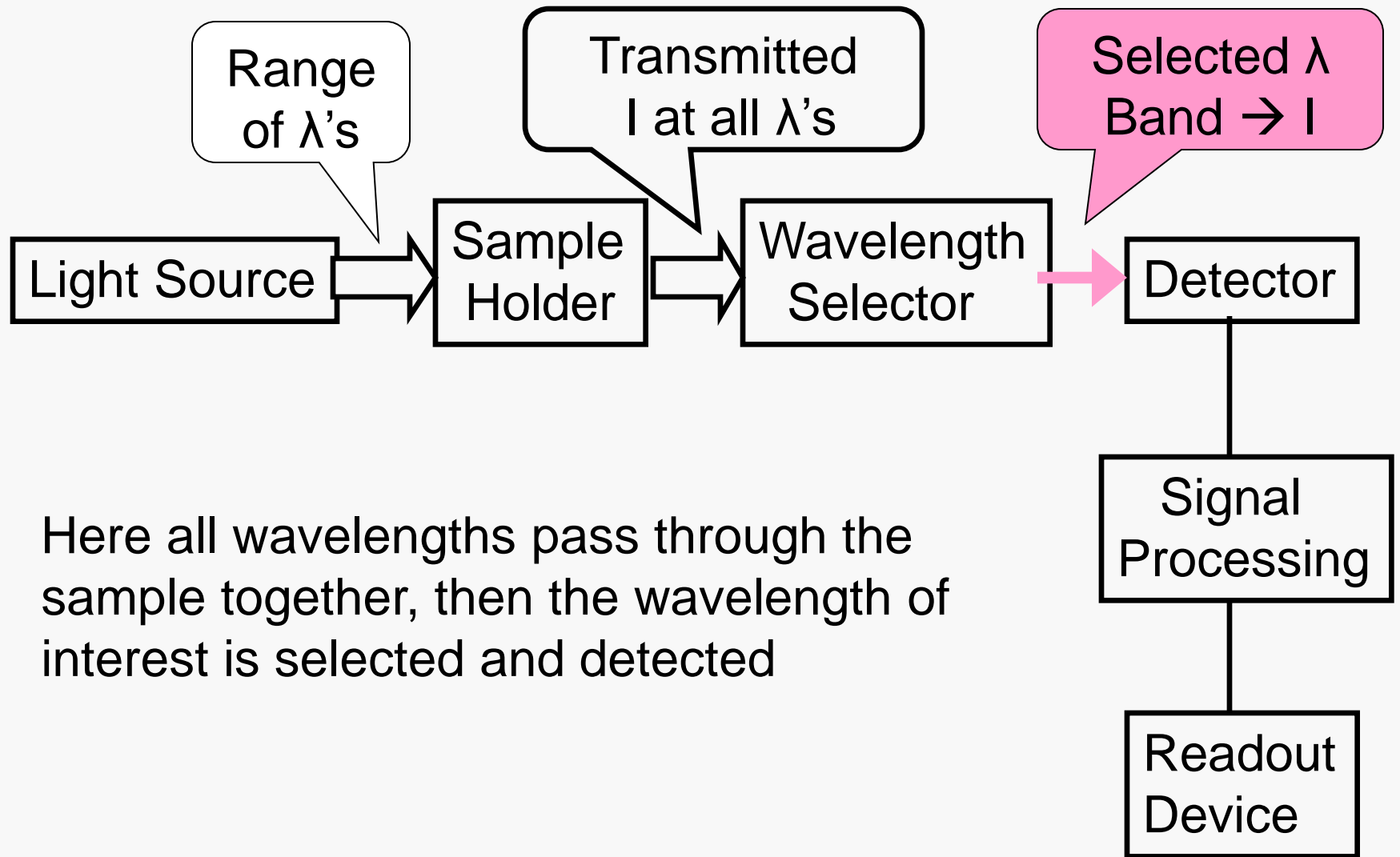
## Absorption measurements require:

- 1) source of radiation
- 2) device for dispersing radiation into component wavelengths
- 3) a means of putting sample into the optical path, i.e., cell
- 4) Detector to convert the EM to an electrical signal
- 5) readout device or circuitry, i.e., meter, computer, recorder, integrator, etc.

# Block diagram of instrument for absorption



# Block diagram of instrument for absorption

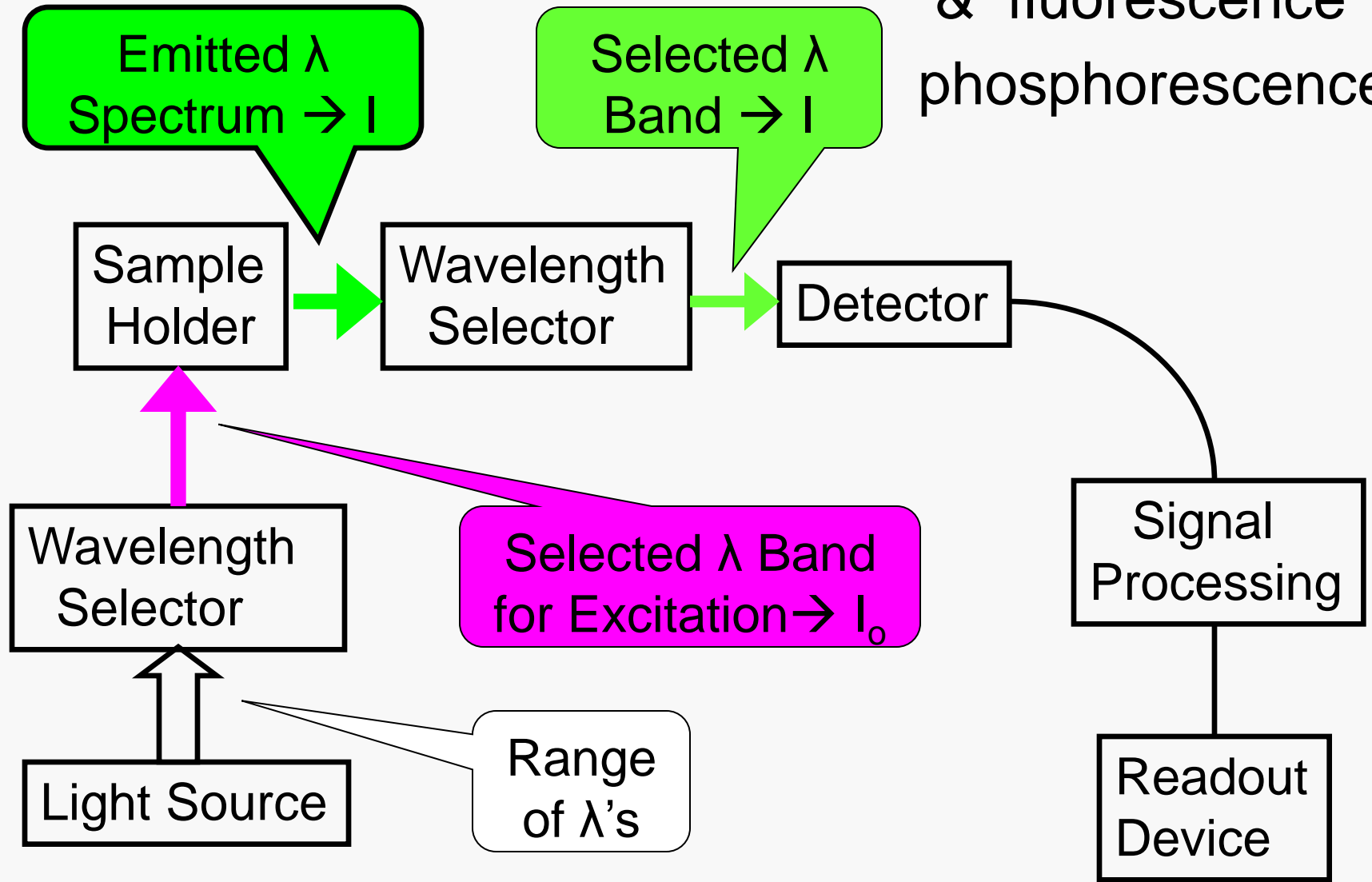


Here all wavelengths pass through the sample together, then the wavelength of interest is selected and detected

## Emission measurements require:

- 1) means of exciting emission i.e., way of populating upper energy level which spontaneously emits
- 2) device for dispersing radiation into component wavelengths
- 3) a means of putting sample into the optical path, i.e., cell
- 4) Detector to convert the EM to an electrical signal
- 5) readout device or circuitry, i.e., meter, computer, recorder, integrator, etc.

Block diagram of instrument for emission i.e.,  
& fluorescence phosphorescence



The requirements for the various components used in different instruments change with the type of spectroscopy as well as for different kinds of measurements within a type of spectroscopy

We will consider the components separately then combine them to make the overall instrument

And finally look at the measurements with regard to theory and practice

## **Sources** – important characteristics

- 1) Spectral distribution i.e., intensity vs.  $\lambda$   
(continuum vs. line sources)
- 2) Intensity
- 3) Stability – short term fluctuations  
(noise), long term drift
- 4) Cost
- 5) Lifetime
- 6) Geometry – match to dispersion device



# I) CONTINUUM SOURCES

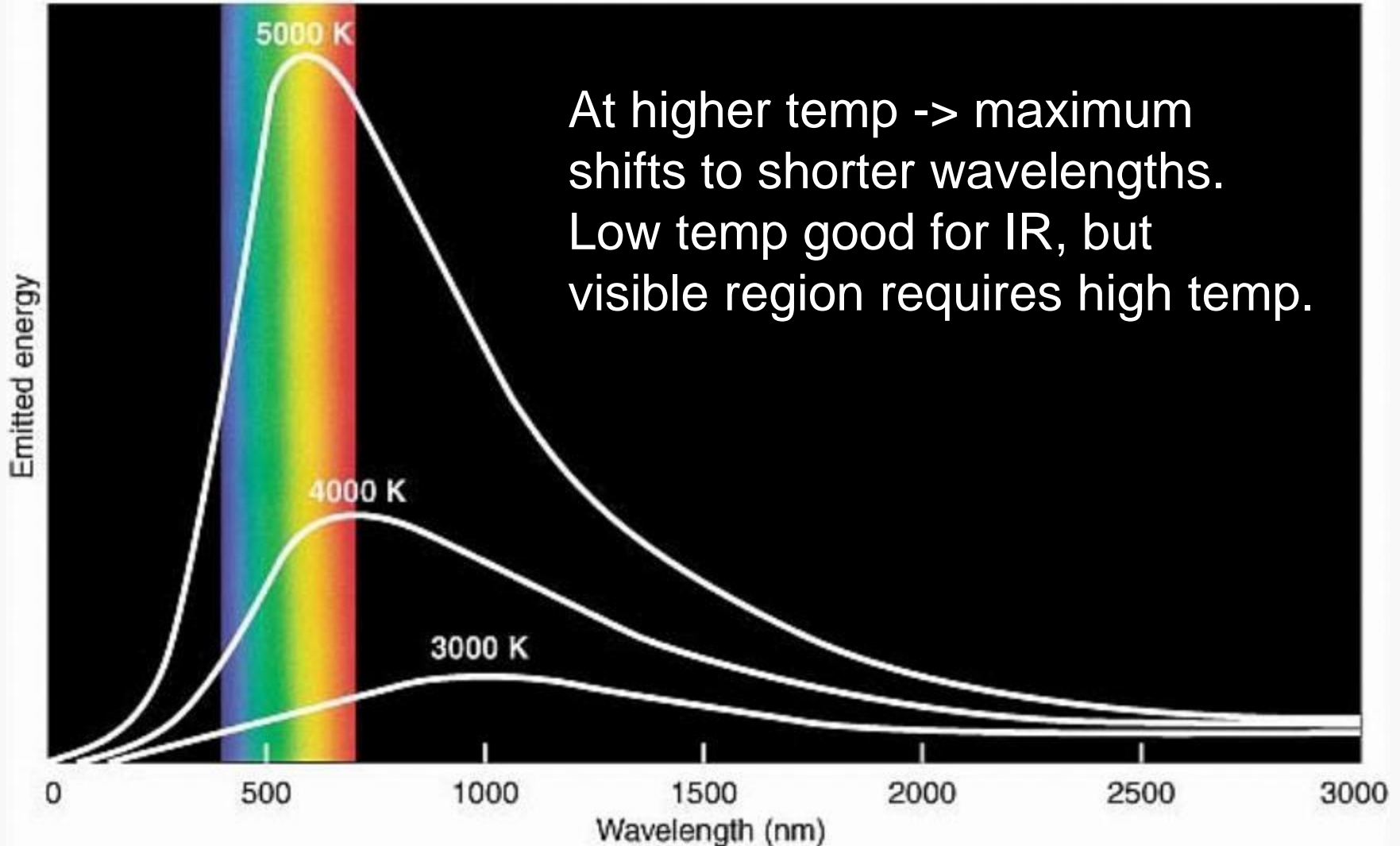
- 1) Thermal radiation (incandescence) – heated solid emits radiation close to the theoretical “Black Body” radiation i.e., perfect emitter, perfect absorber

## Behavior of Black Body

- Total power  $\sim T^4$  therefore need constant temperature for stability when using incandescent sources
- Spectral distribution follows Planck’s radiation law

# Spectral Distribution Curves of a Tungsten (Black Body) Lamp

UV      vis      IR



**IR Region** thermal sources (Black Body) are:

- a) Nernst Glower – fused mixture of  $\text{ZrO}_2$ ,  $\text{Y}_2\text{O}_3$ , and  $\text{ThO}_2$  normally operated at  $1900\text{ }^\circ\text{C}$  – better for shorter IR  $\lambda$ 's (near IR)
- b) Globar – silicon carbide normally operated at  $1200$  to  $1400\text{ }^\circ\text{C}$  – better at longer IR  $\lambda$ 's (doesn't approach Black Body)
- c) Incandescent Wire – e.g., nichrome wire – cheapest way

- All operated at relatively low temperature.
- Good for IR and give some visible emission.
- Operated in air so will burn up if temp goes too high

## Advantages

- Nernst Glower – low power consumption, operates in air, long lifetime
- Globar – more stable than Nernst Glower, requires more power & must be cooled. Long lifetime, but resistance changes with use

## Visible Region sources are:

- a) Glass enclosed Tungsten (W) filament - normally operated at  $\sim 3000$  °K with inert atmosphere to prevent oxidation. Useful from 350 nm to 2000 nm, below 350 nm glass envelope absorbs & emission weak
- b) Tungsten-Halogen lamps - can be operated as high as 3500 °K. More intense (high flux). Function of halogen is to form volatile tungsten-halide which redeposits W on filament, i.e., keeps filament from burning out. Requires quartz envelope to withstand high temps (which also transmits down to shorter wavelengths). Fingerprints are a problem – also car headlights

**2) Gas Discharge Lamps** – two electrodes with a current between them in a gas filled tube. Excitation results from electrons moving through gas. Electrons collide with gas → excitation → emission

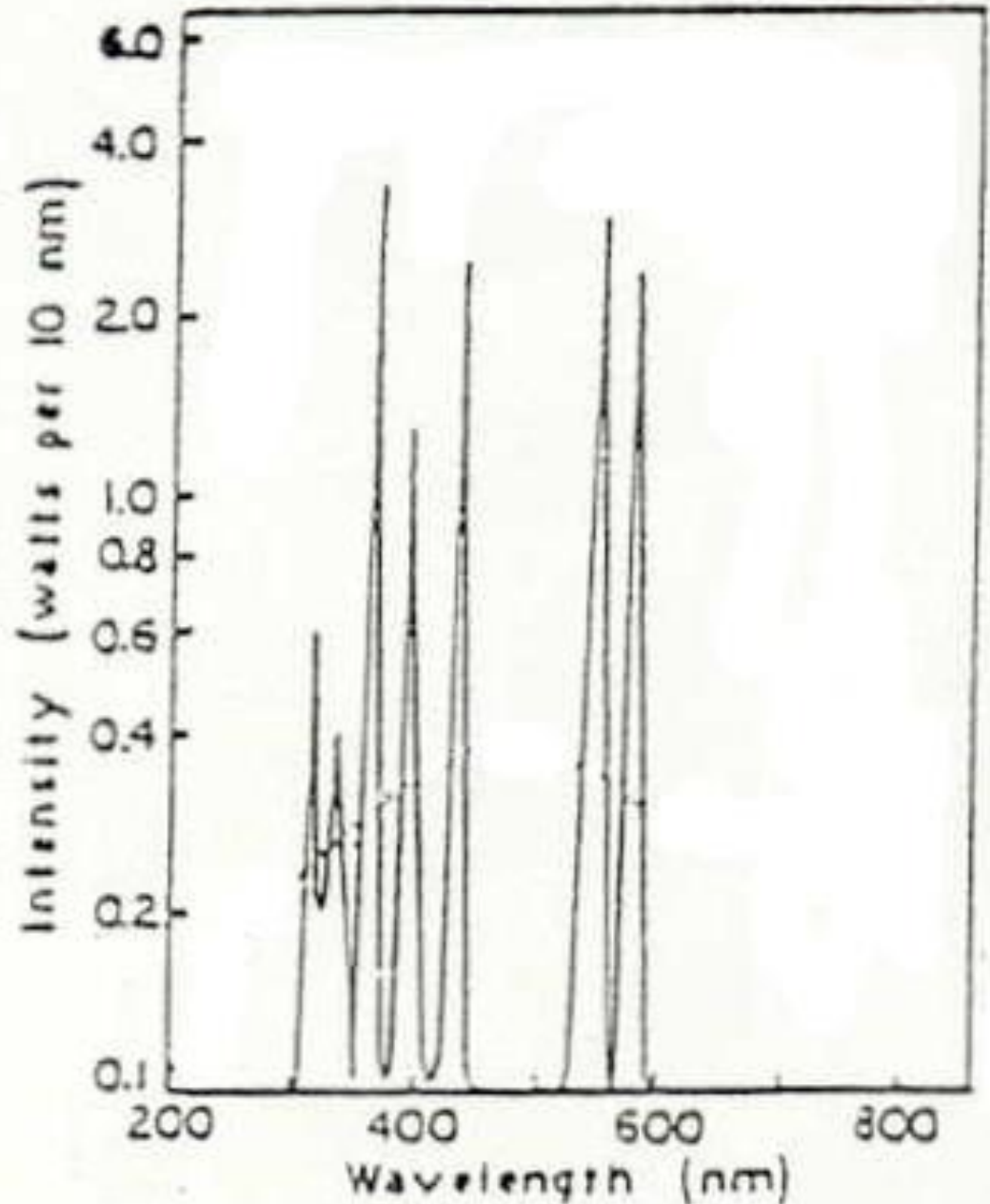
At high pressure → “smearing” of energy levels → spectrum approaches continuum

The higher the pressure, the greater the probability that any given molecule or atom will be perturbed by its neighbor at the moment of emission.

a) Hydrogen Lamp  
- most common  
source for UV  
absorption  
measurements

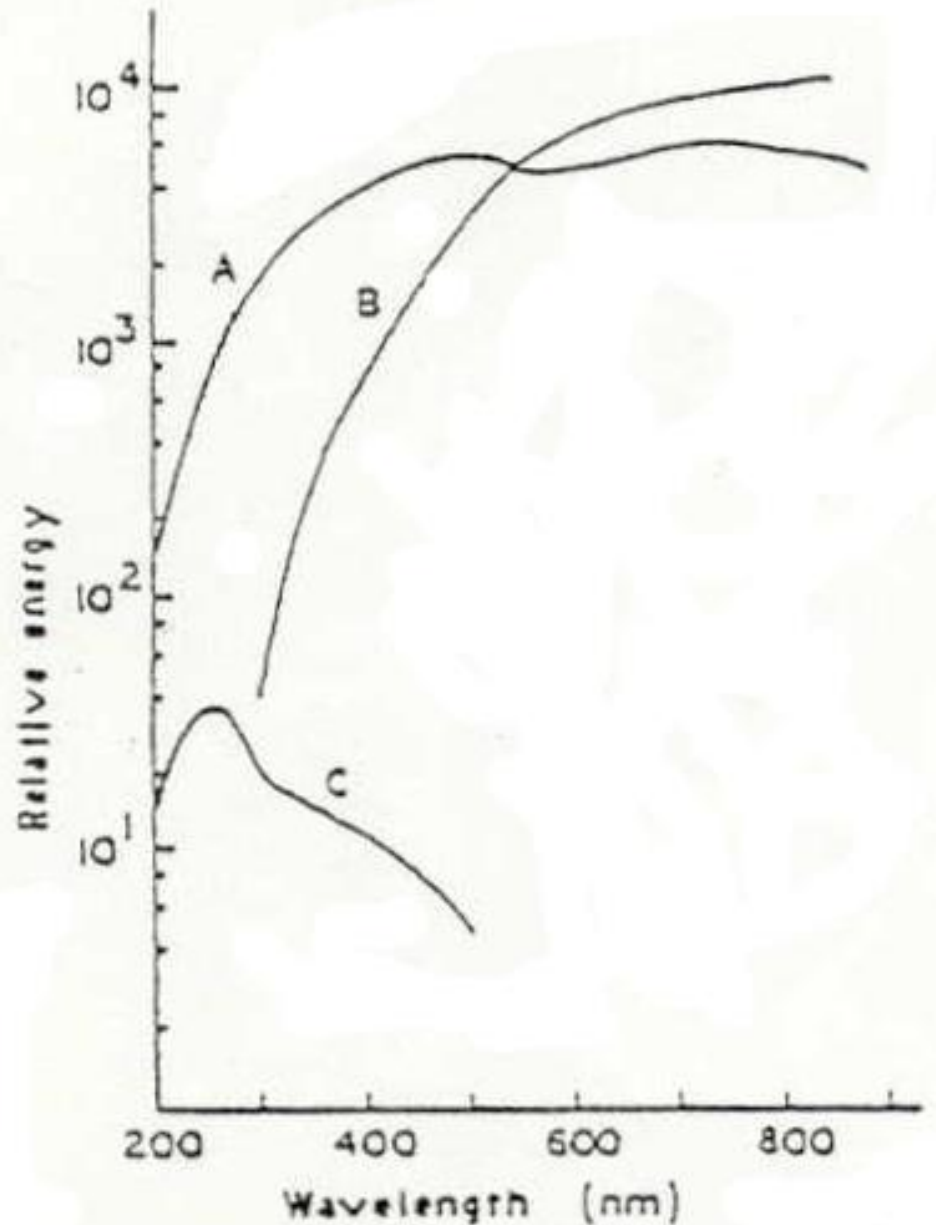
H<sub>2</sub> emission is from  
180 nm to 370 nm  
limited by jacket

Line spectrum from →  
100 watt Hydrogen  
Lamp at low pressure in  
Pyrex



b) Deuterium  
Lamp – same  $\lambda$   
distribution as  
 $H_2$  but with  
higher intensity  
(3 to 5 times) -  
 $D_2$  is a heavier  
molecule & moves  
slower so there is  
less loss of energy  
by collisions

High pressure  $D_2 \rightarrow$   
with quartz jacket



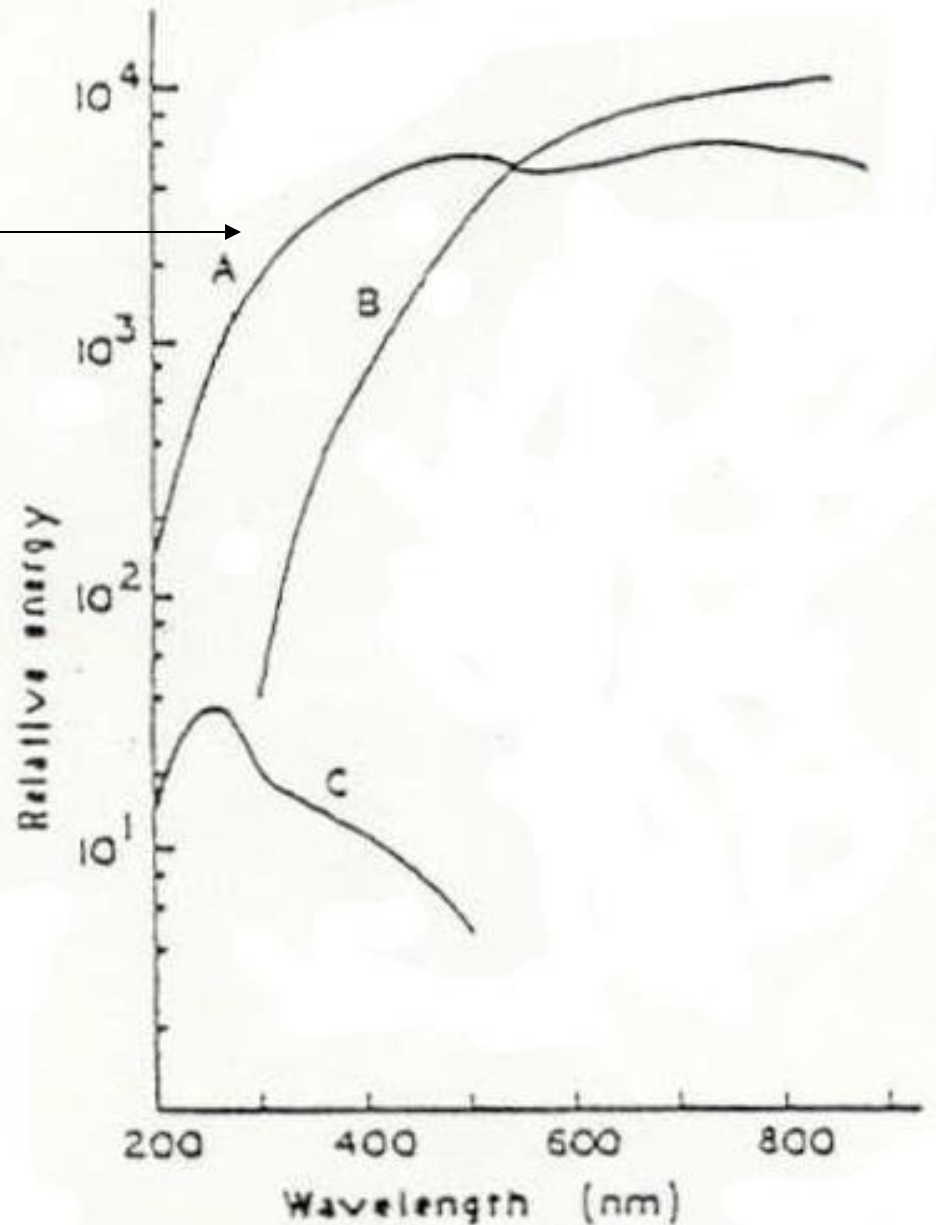
Relative output of various lamp  
A - Xenon B - Tungsten C - Deuterium



For higher intensity

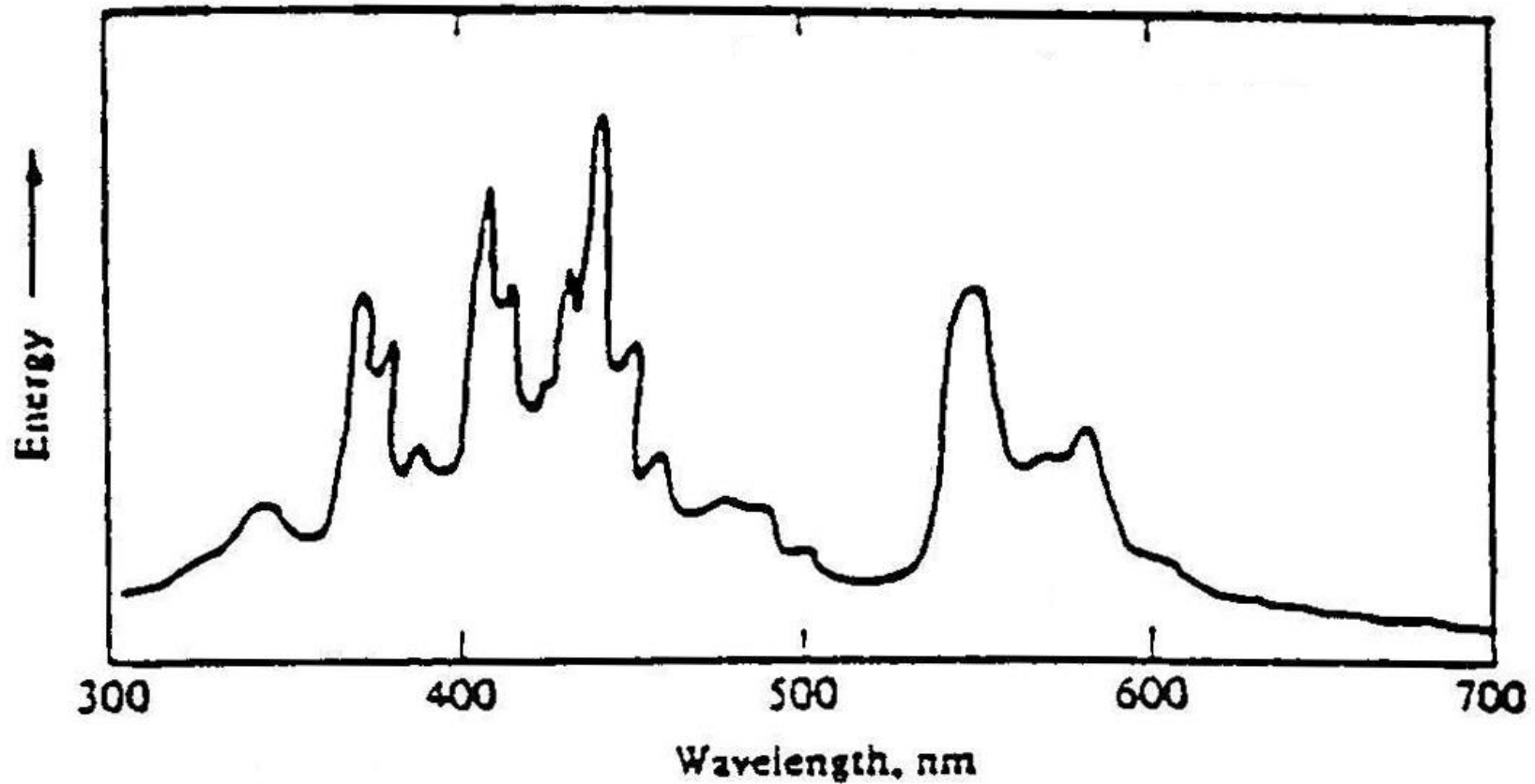
c) Xenon Lamp – Xe  
at high pressure  
(10-20 atm)

- high pressure needed to get lots of collisions for broadening leading to continuum
- short life relatively
- arc wander (stabilize)
- need jolt to start
- output = f(time)



Relative output of various lamp  
A - Xenon B - Tungsten C - Deuterium

d) High Pressure Mercury Lamp – can't completely eliminate bands associated with particular electronic transitions even at very high pressures (e.g., 100 atm)

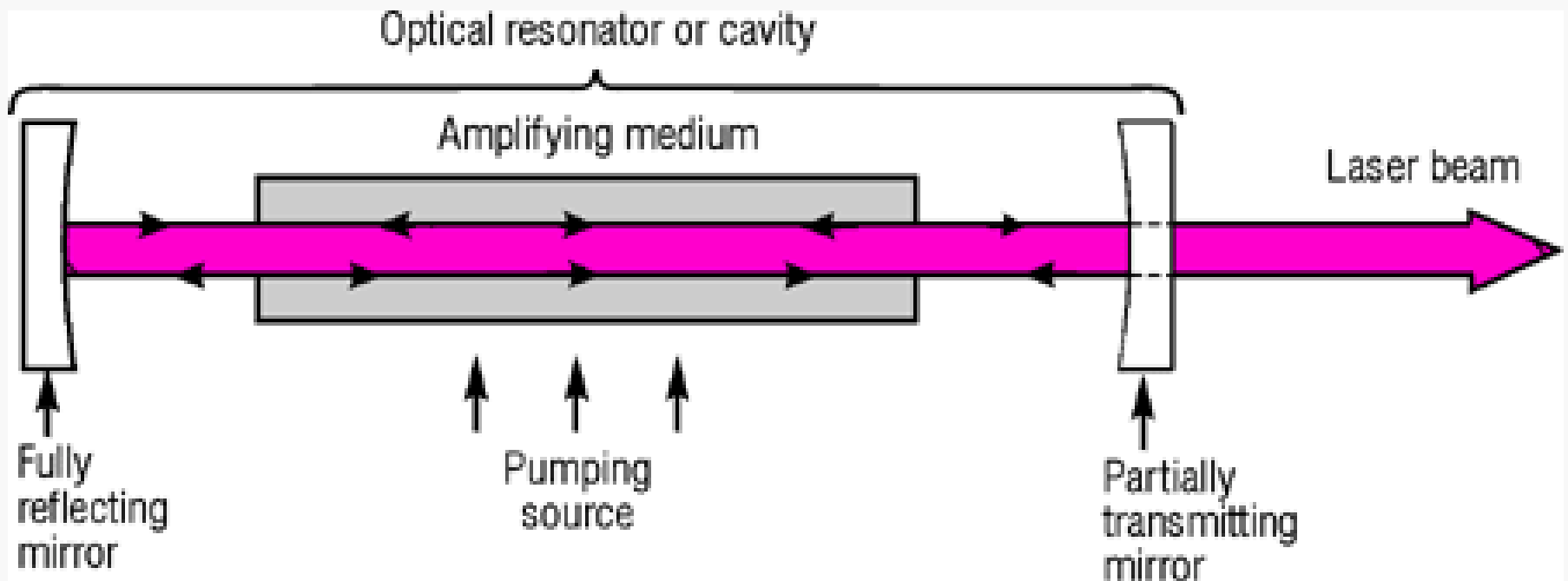


- For UV-vis absorption spectrophotometry usually use H<sub>2</sub> for UV and tungsten for visible region (switching mid scan)
- Sometimes use D<sub>2</sub> instead of H<sub>2</sub>
- For fluorescence spectrophotometry use xenon arc lamp in scanning instruments
- Can use He below 200 nm
- Hg at low pressure is used in fixed wavelength (non scanning) fluorometers
- Can use mixture of Hg and Xe

## II) LINE SOURCES

- 1) **Gas (Vapor) Discharge Lamps** at low pressure (i.e., few torr) – minimize collisional interaction so get line spectrum
  - most common are Hg and Na
  - often used for  $\lambda$  calibration
  - Hg pen lamp
  - fluorescent lights are another example
  - also used UV detectors for HPLC
- 2) **Hollow Cathode Lamps (HCL)** – for AA
- 3) **Electrodeless Discharge Lamps (EDL)** - AA

4) **Lasers (Light Amplification by Stimulated Emission of Radiation)** – start with material that will exhibit stimulated emission and populate upper states typically using another light source



Stimulated Emission – photon strikes excited state causing it to emit a burst of photons

Pumping source used to populate upper states can be flashlamp, another laser or electrical

Often use prism to select pumping wavelength

Advantages of lasers

1) Intense

2) Monochromatic – very narrow band

3) Coherent – all radiation at same phase angle

4) Directional – full intensity emitted as beam

## Limitations of lasers

- 1) High cost in many cases
- 2) Wavelength range is somewhat limited
- 3) Many operate in pulsed mode – some are continuous wave (CW)

Pulsed mode lasers are not always problematic as light sources, can use pulse frequency with gated detection

# Types of Lasers:

## 1) Solid State Lasers

a) Ruby laser –  $\text{Al}_2\text{O}_3 + \text{Cr(III)}$  - 694.3 nm pumped with Xe arc flashlamp – pulsed (can be continuous)

b) Nd/YAG laser – yttrium aluminum garnet + Nd - 1064 nm

## 2) Gas Lasers

a) Neutral atom – He-Ne – 632.8 nm continuous

b) Ion lasers –  $\text{Ar}^+$  or  $\text{Kr}^+$  514.5 nm



c) Molecular lasers – CO<sub>2</sub> (10,000 nm = 1000 cm<sup>-1</sup>) or N<sub>2</sub> (337.1 nm) pulsed

d) Eximer lasers – inert gas + fluorine creates eximers ArF<sup>+</sup> (193 nm), KrF<sup>+</sup> (248 nm), XeF<sup>+</sup> (351) pulsed

**3) Dye Lasers** – tunable over 20 – 50 nm many dyes available for wide range of λ's

**4) Semiconductor Diode Lasers** – wide range of λ's available, continuous