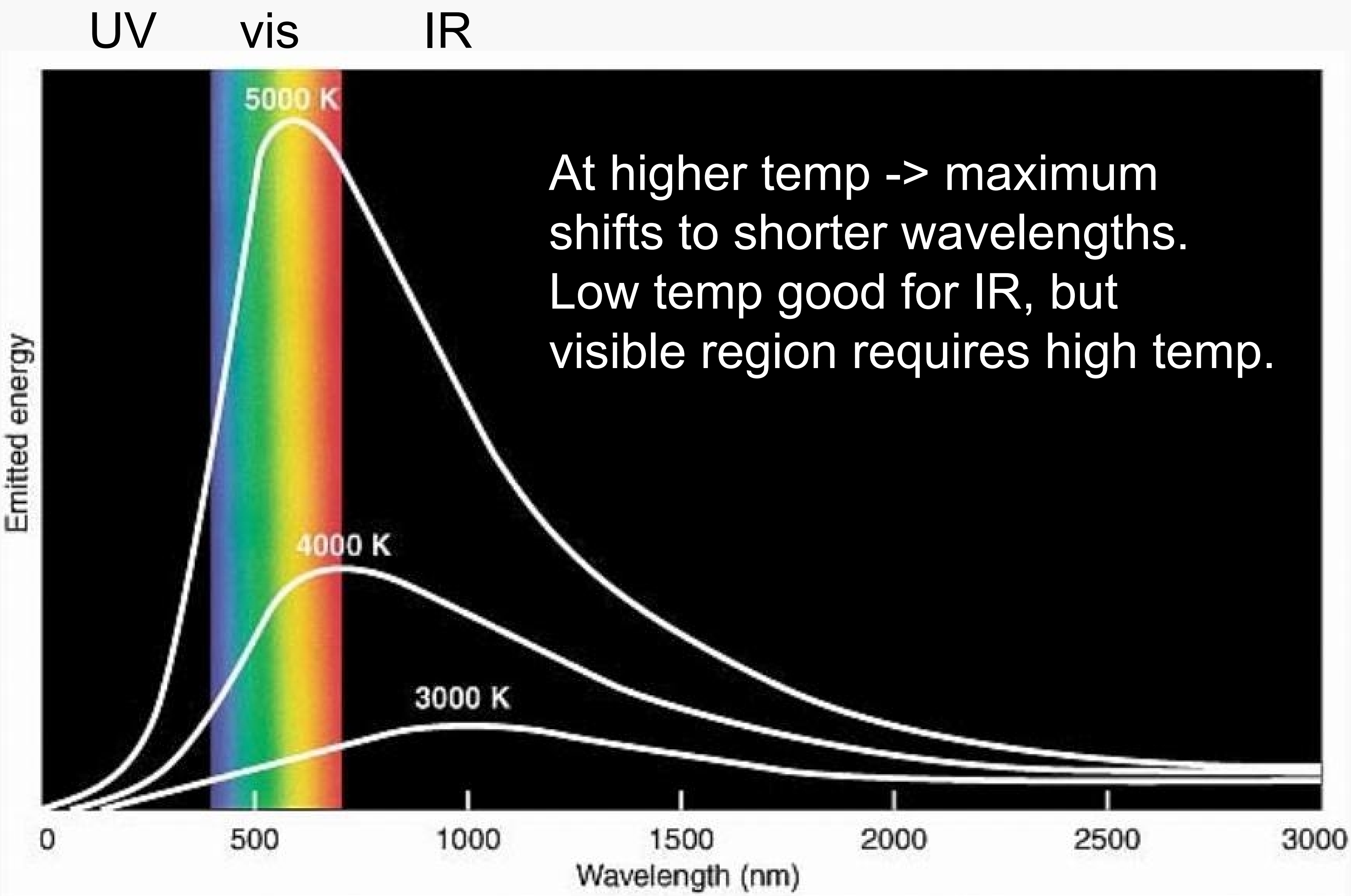
I) CONTINUUM SOURCES

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 ~ 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



IR Region thermal sources (Black Body) are:

a) Nernst Glower – fused mixture of ZrO_2, Y_2O_3, and ThO_2 normally operated at 1900 ^{o}C – better for shorter IR λ's (near IR)

b) Globar – silicon carbide normally operated at 1200 to 1400 ^{o}C – better at longer IR λ'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 ~3000 ^{o}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 ^{o}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

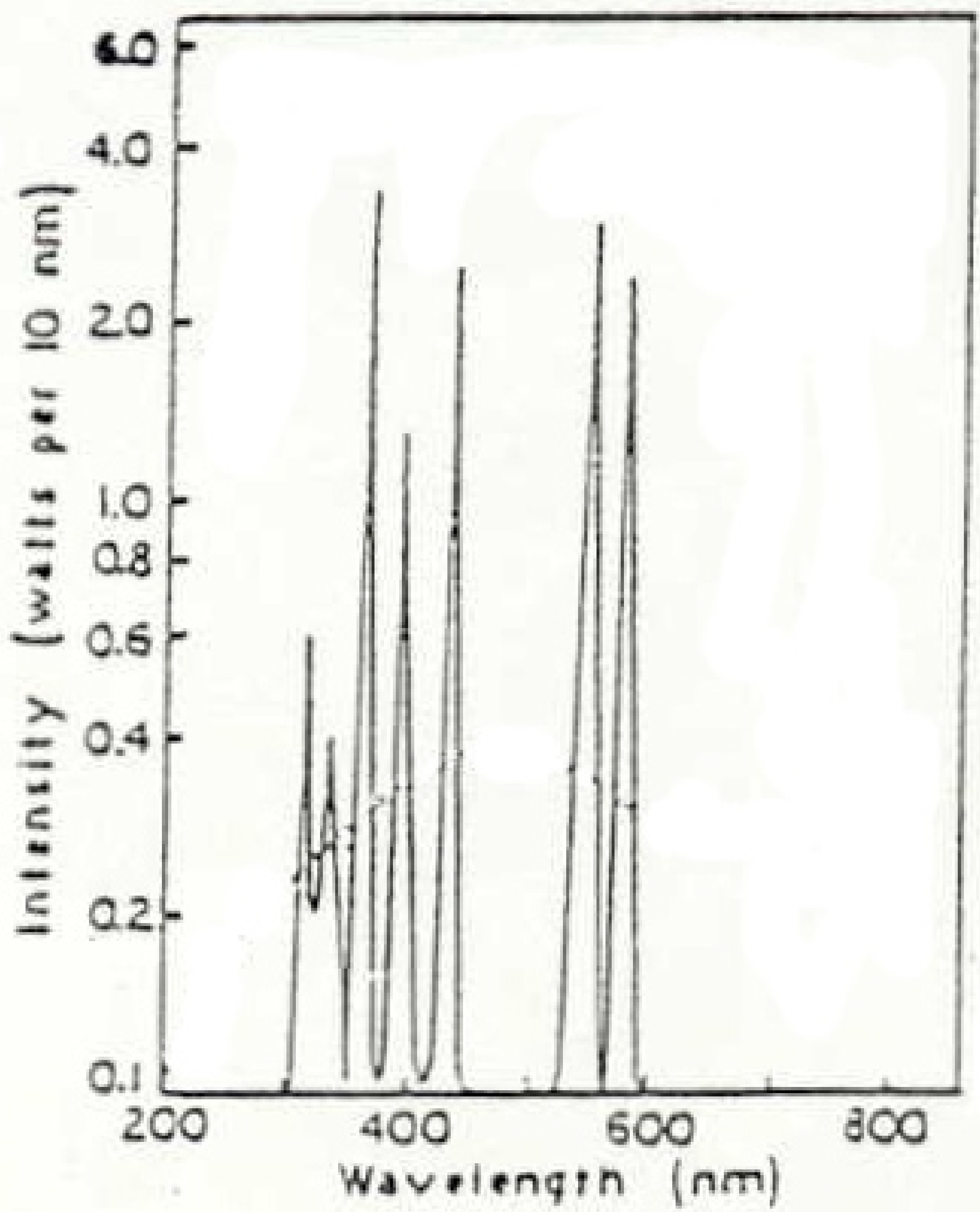
At high pressure → "smearing" of energy levels → spectrum approaches continuum

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) <u>Hydrogen Lamp</u>
- most common source for UV absorption measurements

H_2 emission is from 180 nm to 370 nm limited by jacket

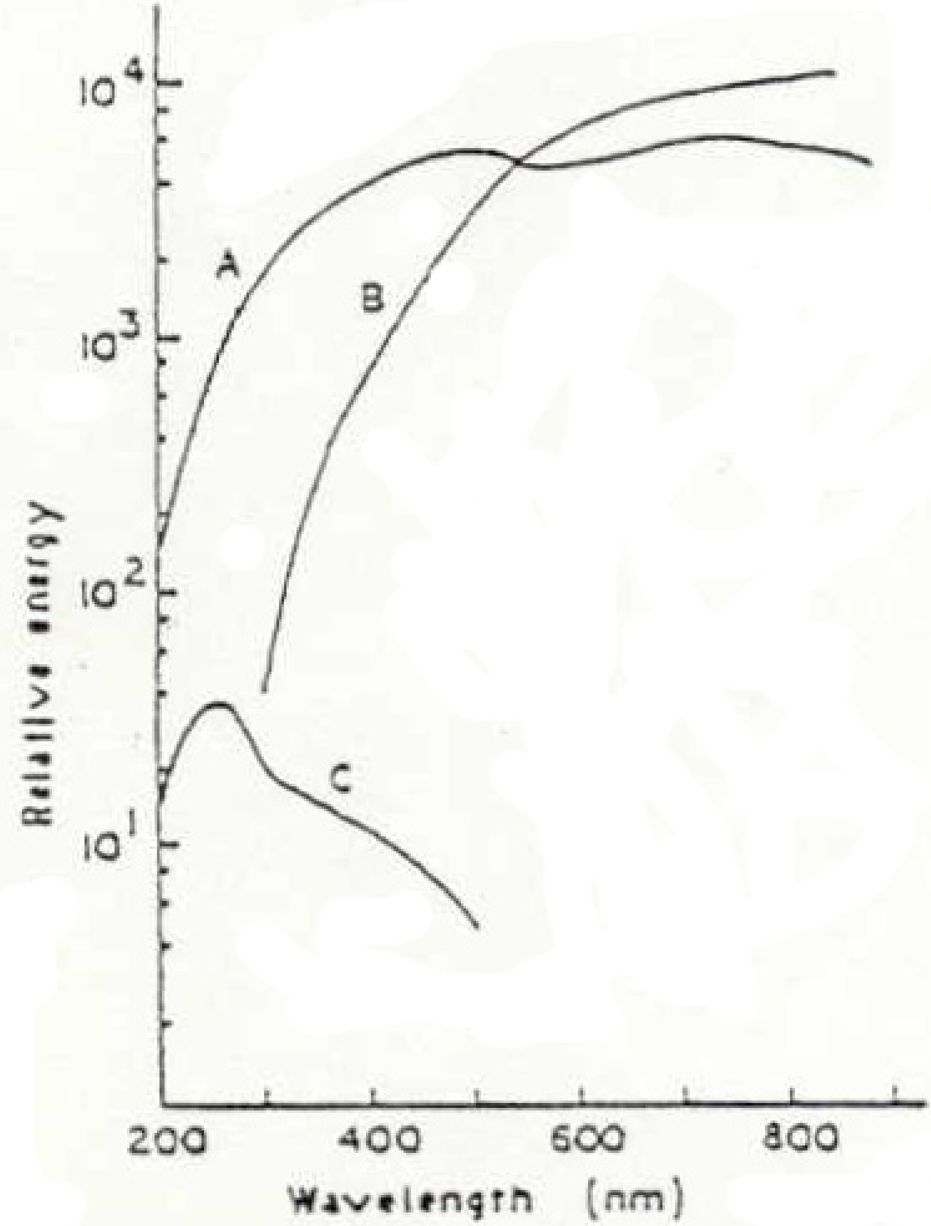
Line spectrum from →
100 watt Hydrogen Lamp at low pressure in Pyrex



b) <u>Deuterium Lamp</u> – same λ 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 → with quartz jacket

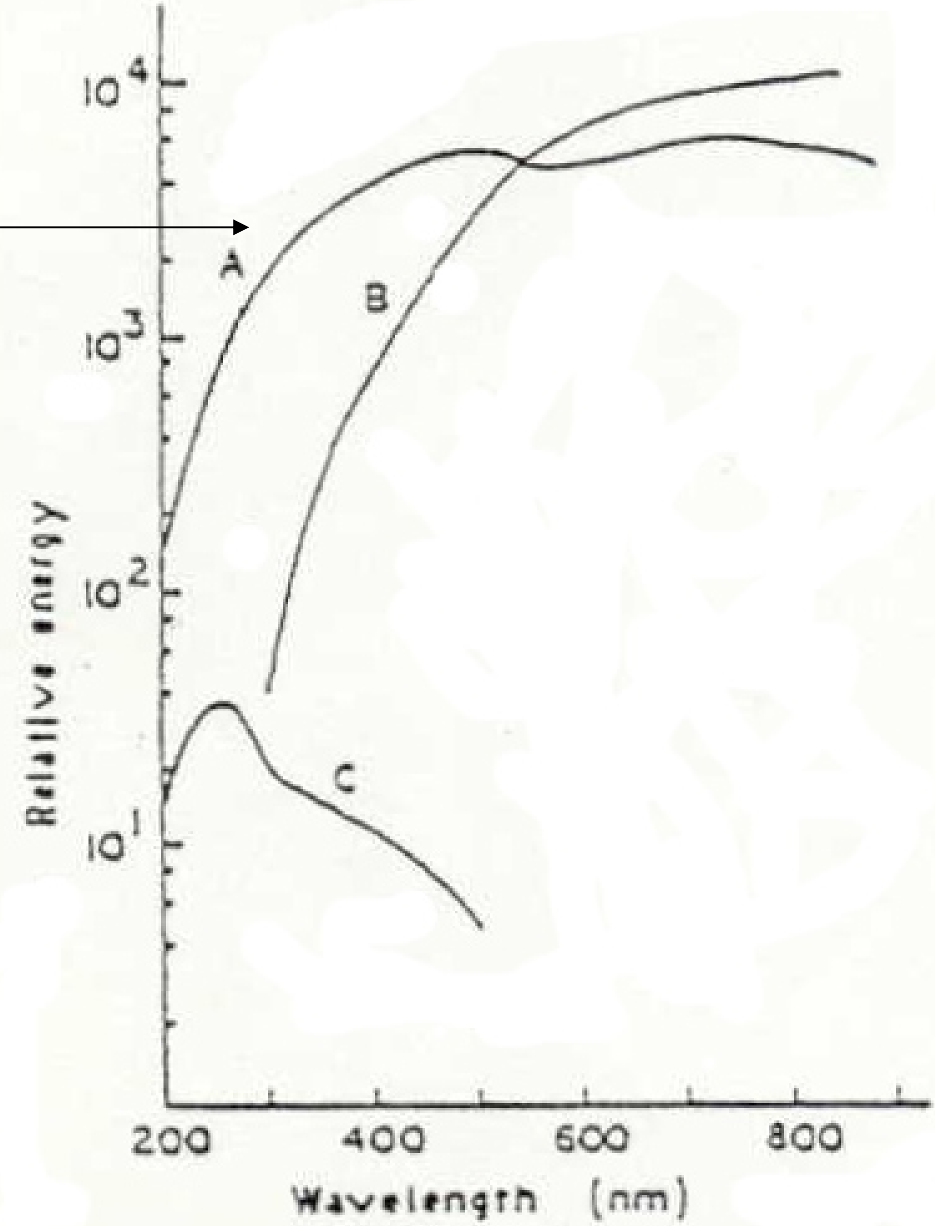


Relative output of various lamp
A-Xenon B-Tungsten C-Deuterium

For higher intensity

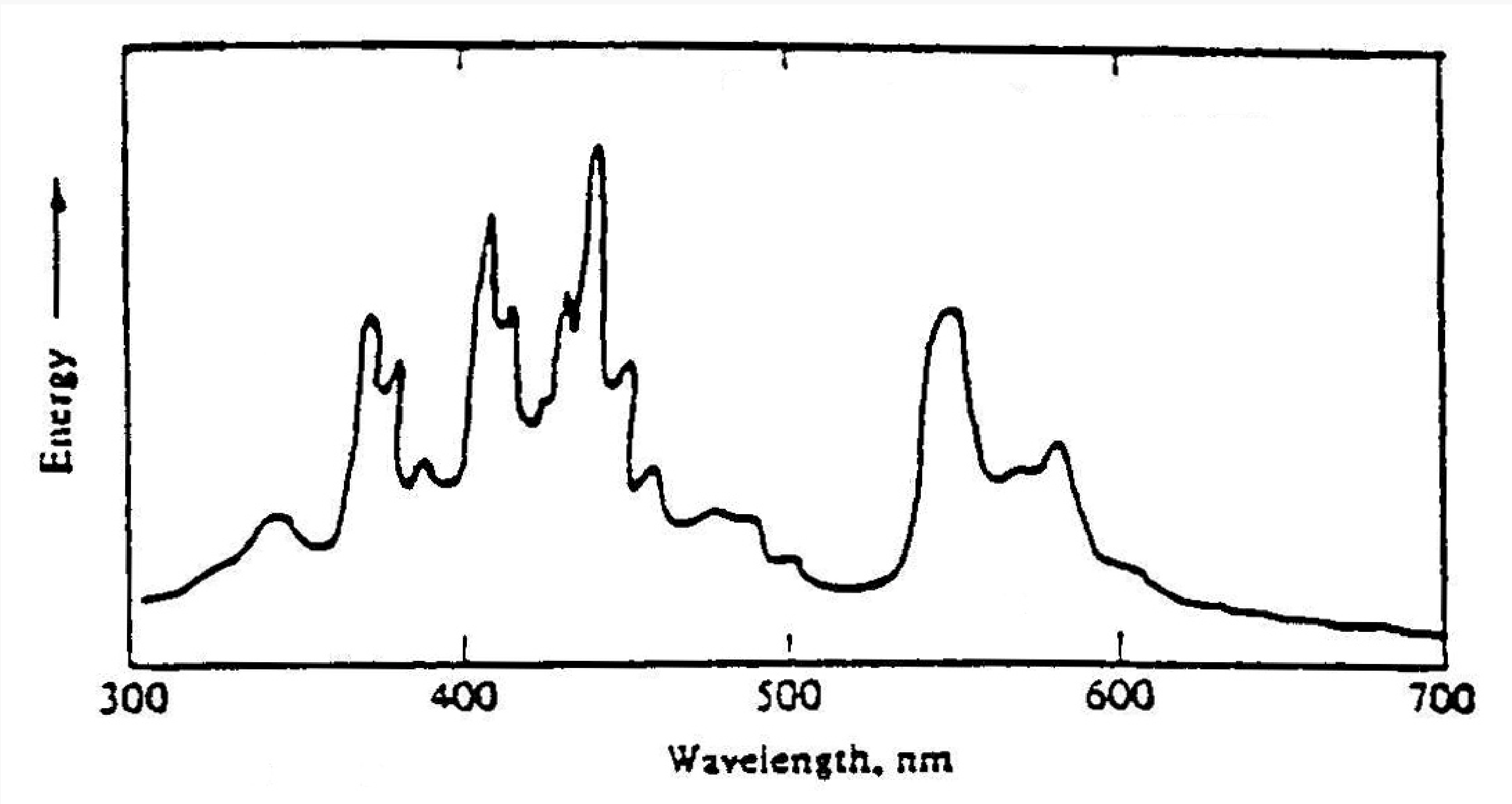
c) <u>Xenon Lamp</u> – Xe at high pressure (10-20 atm)

- 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_2 for UV and tungsten for visible region (switching mid scan)
- Sometimes use D_2 instead of H_2
- 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

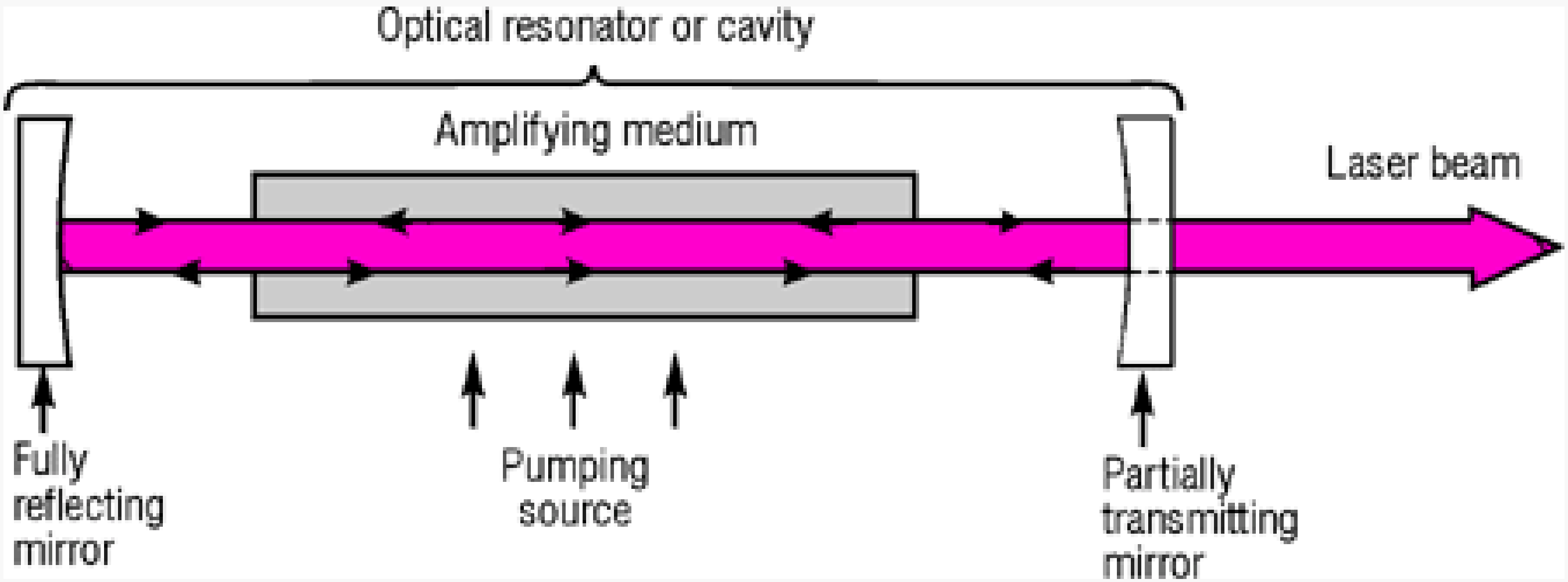
1) **<u>Gas (Vapor) Discharge Lamps</u>** at low pressure (i.e., few torr) – minimize collisional interaction so get line spectrum

   - most common are Hg and Na
   - often used for λ calibration
   - Hg pen lamp
   - fluorescent lights are another example
   - also used UV detectors for HPLC

2) **<u>Hollow Cathode Lamps (HCL)</u>** – for AA

3) **<u>Electrodeless Discharge Lamps (EDL)</u>** - AA

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



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

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

Wavelength Selection

Three main approaches:

1) Block off unwanted radiation – optical filters

2) Disperse radiation & select desired band – monochromator

3) Modulate wavelengths at different frequencies - interferometer

FILTERS

1) **Absorption** – colored glass, colored film, colored solutions – cheapest way