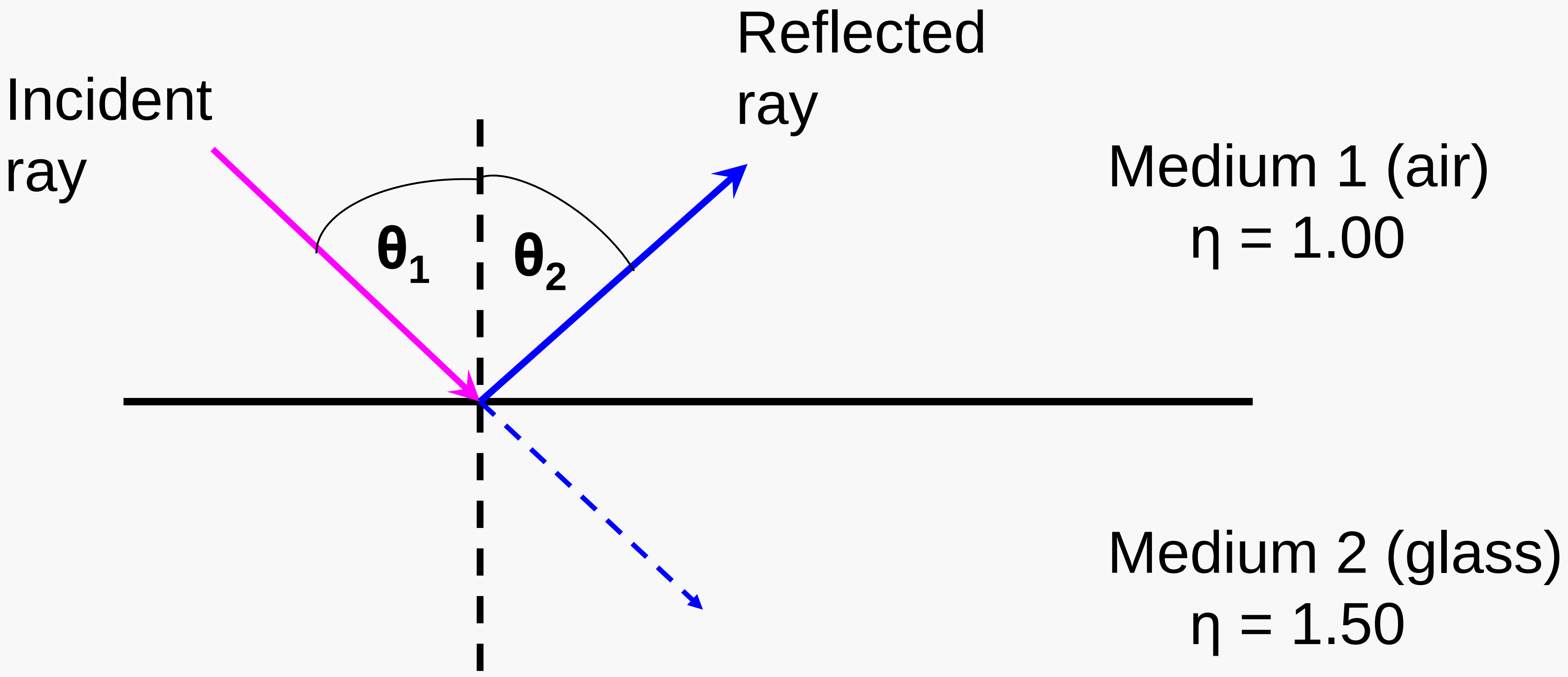
Reflection = EM strikes a boundary between two media differing in η and bounces back



Specular reflection = situation where angle of incidence (θ_i) equals angle of reflection (θ_r)

$$\text{Reflectance} = R = \frac{I_r}{I_i} = \frac{(\eta_2 - \eta_1)^2}{(\eta_2 + \eta_1)^2}$$

Where I_i and I_r = incident & reflected intensity

For radiation going from air ($\eta = 1.00$) to glass ($\eta = 1.50$) as shown in previous slide

$$R = 0.04 = 4\ \%$$

Many surfaces at 4 % each (i.e., many lenses) can cause serious light losses in a spectrometer. This generates **stray radiation** or **stray light**.

Homework

- Calculate the value from the previous slide (i.e. 4%) using the equation for R assuming light is traveling from air of η = 1.00 into glass of η = 1.70. Show your work and email your homework to David_Ryan@uml.edu in MS Word or Excel format by Friday.

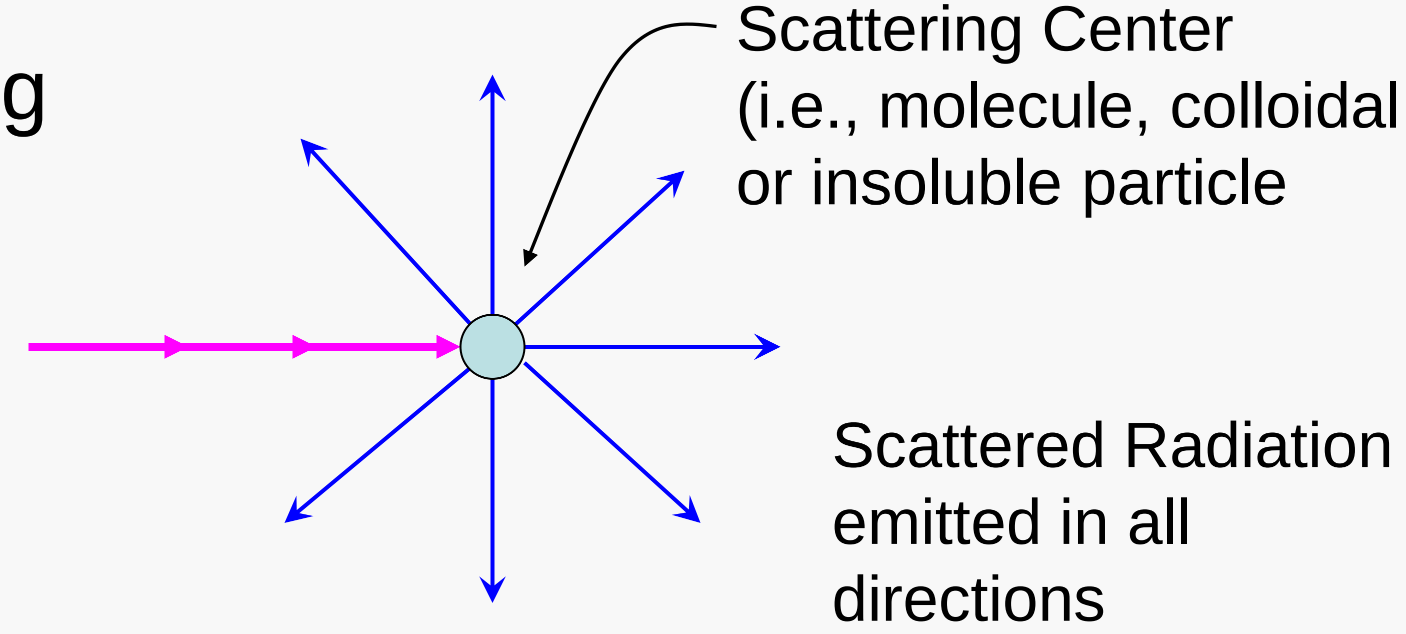
Scattering = EM interacts with matter and changes direction, usually without changing energy

This can be described using both the wave or particle nature of light:

1) Wave – EM induces oscillations in electrical charge of matter ⇒ resulting in oscillating dipoles which in turn radiate secondary waves in all directions = scattered radiation
2) Particle (or Quantum) – EM interacts with matter to form a virtual state (lifetime 10^{-14} s) which reemits in all directions.

Raman effect = when some molecules return to a different state ⇒ change in frequency

Scattering



Many types of scattering exist depending on several parameters characterizing the system, we will be concerned with:

Rayleigh Scattering, Large Particle Scattering and the Raman Effect (Raman Scattering or Raman Spectroscopy)

Rayleigh Scattering – scattering by particles whose longest dimension is < 5 % to 10 % of λ with no change in observed frequency

scattering intensity

polarizability

angle between incident beam & scattered beam

$$I_s = \frac{8\,\pi^4\,\alpha^2}{\lambda^4\,r^2}\,(1 + \cos^2\theta)\,I_o$$

wavelength

distance from scattering center to detector

incident beam intensity

Notice the fourth power dependence on wavelength meaning short wavelengths are scattered more efficiently ⇒ sky is blue

Polarizability (α) is measure of how well a given frequency induces a dipole in a substance

α Tends to be large for large molecules (e.g., proteins)

Large Particle Scattering – particle dimensions < 10 % λ to 1.5 λ

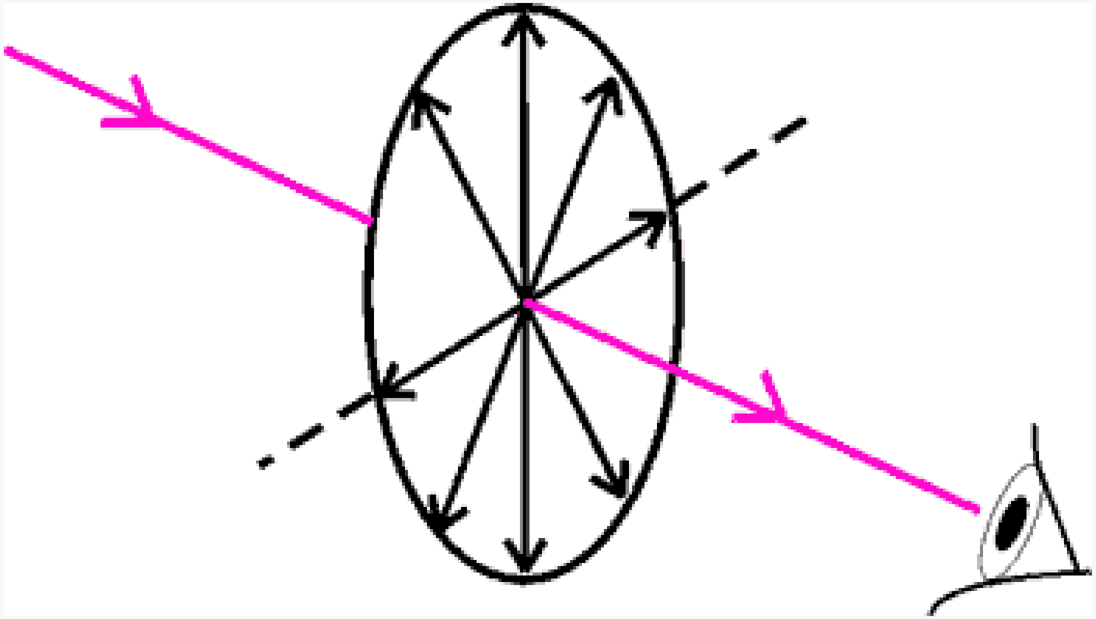
Applies in techniques like turbidimetry and nephelometry

Large particles do not act as a point source & give rise to various interference phenomena

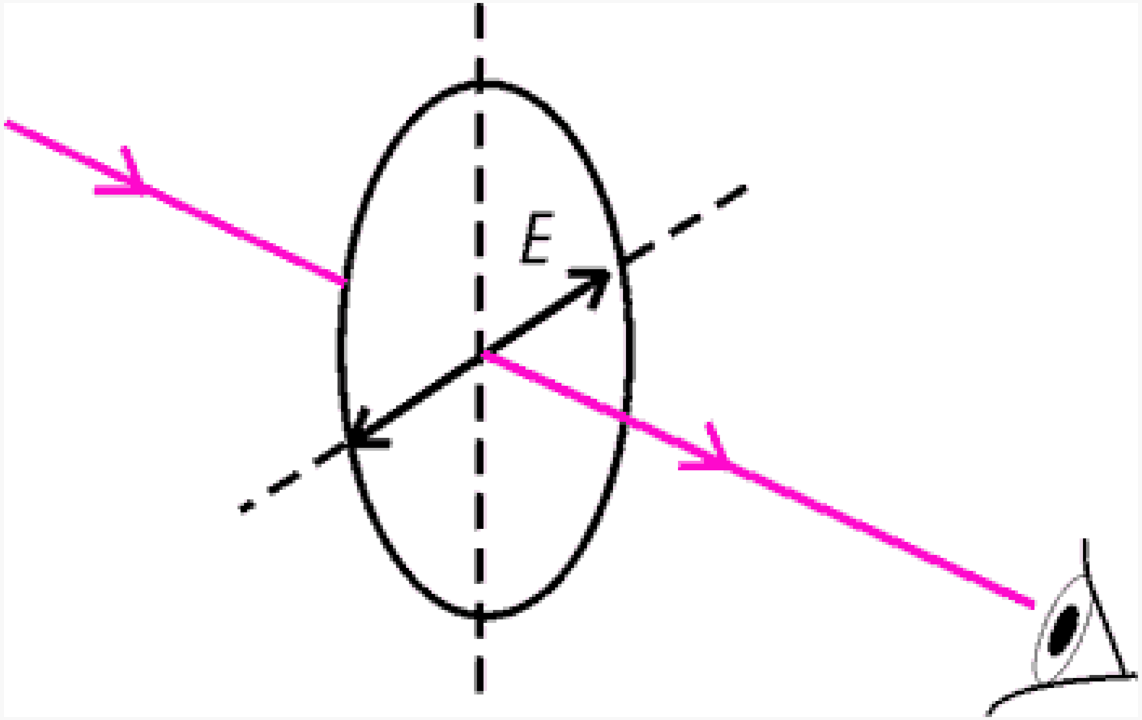
Forward scatter becomes greater than back scatter

Polarization

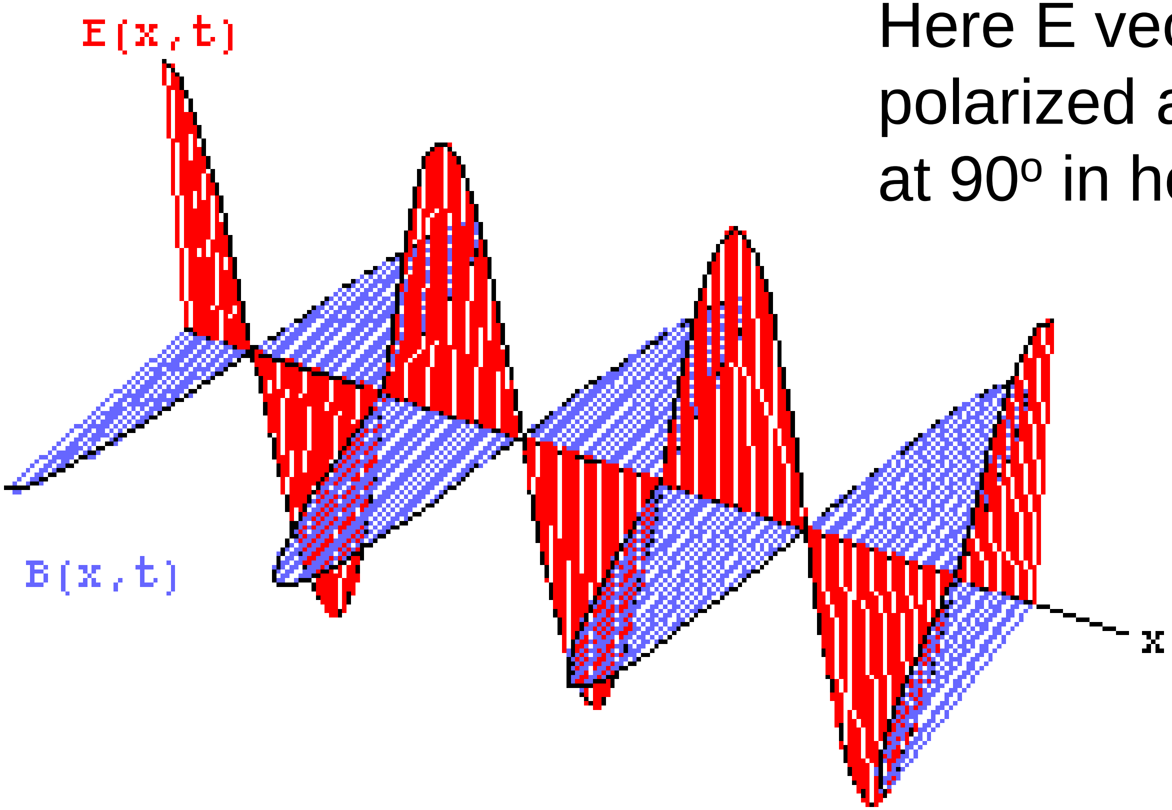
EM is said to be unpolarized if its electric vectors and magnetic vectors occur with equal amplitude in all direction



<u>Linearly polarized</u> light oscillates in one plane only as it moves through space

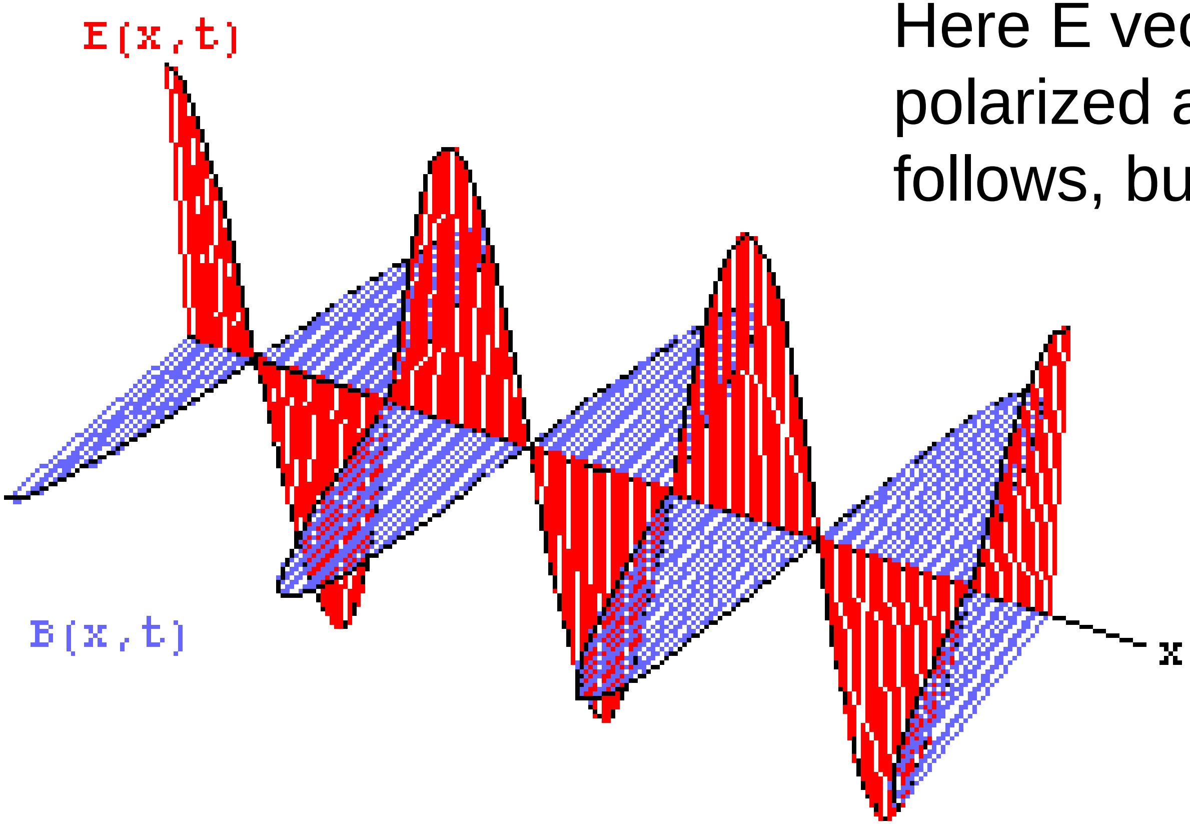


Linearly polarized light oscillates in one plane only as it moves through space



Here E vector is vertically polarized and H vector is at 90º in horizontal plane

Circularly polarized light rotates in either a left handed or right handed spiral as it moves through space



Here E vector is circularly polarized and H vector follows, but is offset by 90°

Combining equal beams where one is right circularly polarized and the other left, results in linearly polarized radiation

Polarization is particularly important for studying optically active materials using

- Optical Rotatory Dispersion (ORD)
- Circular Dichroism (CD)
- Fluorescence Polarization

In spectroscopy (EM interacts with matter), the energy of the transition (ΔE) must correspond to the energy of the light (EM) given by frequency (ν) and Plank's constant (h)

$$\Delta E = h\nu$$

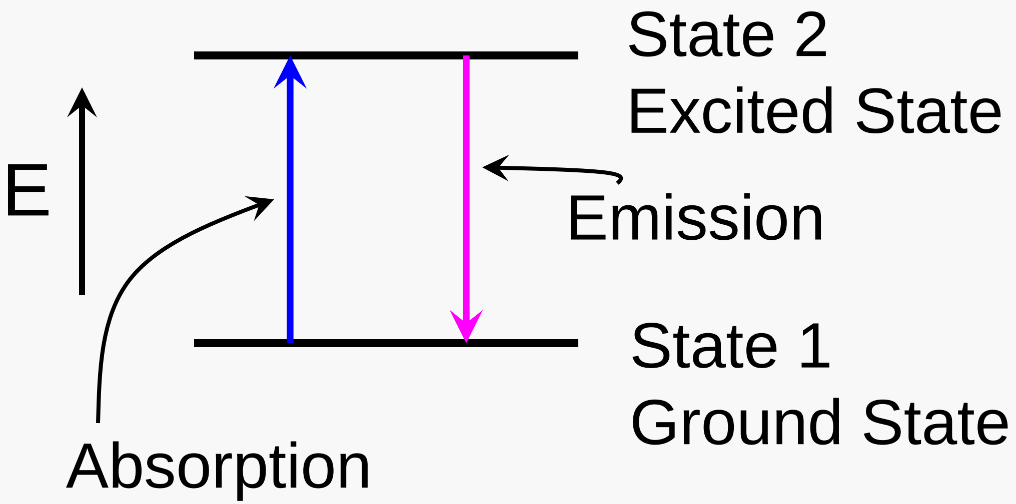
This holds for absorption & emission of radiation

Absorption and Emission

Two most interesting and most useful processes when EM interacts with matter

Atoms and molecules can exist in many possible energy states

Consider two states



State 2
Excited State

Emission

State 1
Ground State

E

Absorption

For absorption of EM

$$\Delta E = E_2 - E_1 = h\nu$$

Where E_1 & E_2 are energies of states & h is Planck's constant ν is the frequency

Atomic Absorption – atoms usually in gaseous state like mercury vapor generated in a flame absorb light & undergo electronic transition

Atomic spectra are simple line spectra because there are no bonds to vibrate or rotate around, just electrons to promote

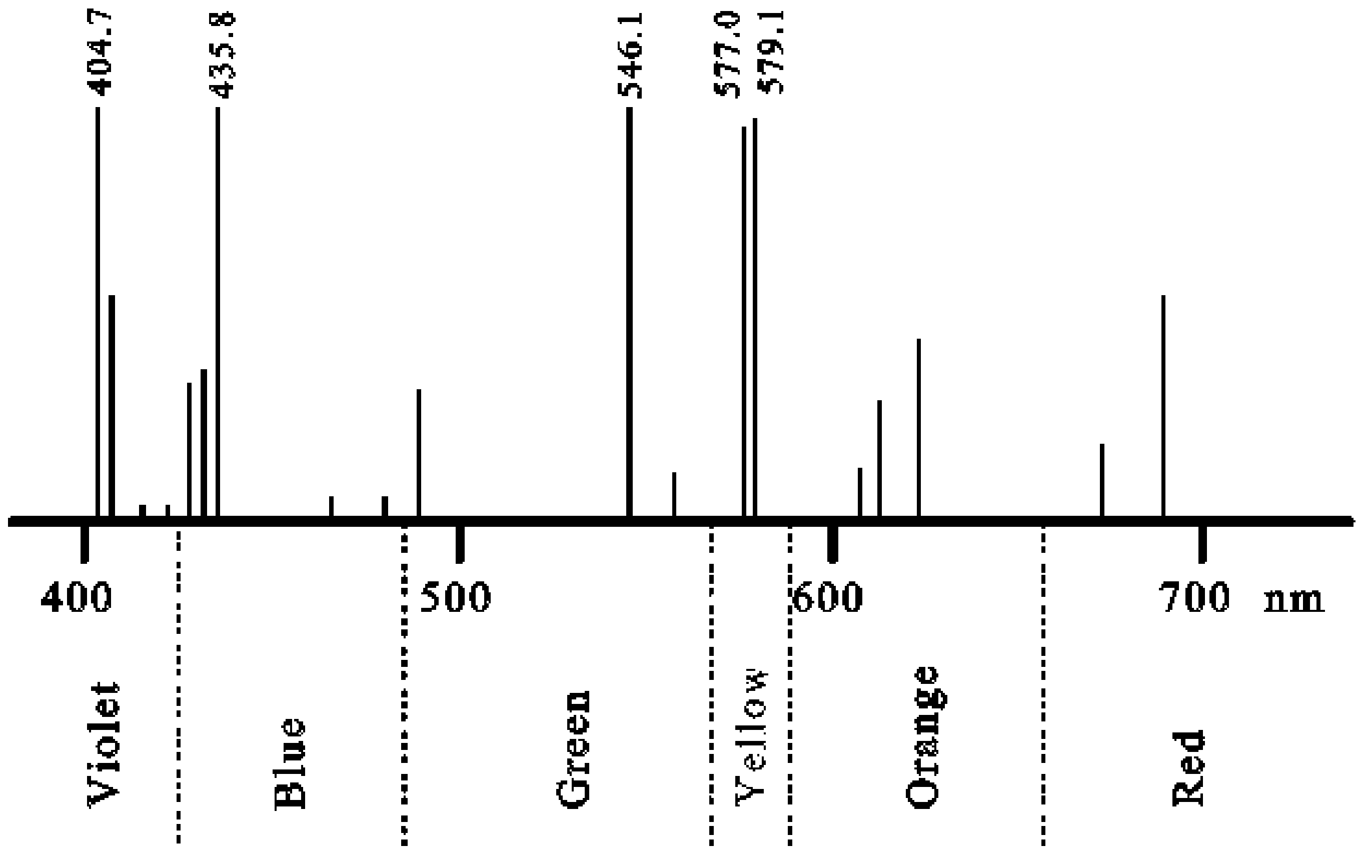
Example – Na vapor has 2 lines 589.0 nm & 589.6 nm which come from 3s electrons promoted to 2 possible 3p states of different E

Peak at 285 nm from 3s to 5p = more E

UV-vis wavelengths promote outer shell electrons

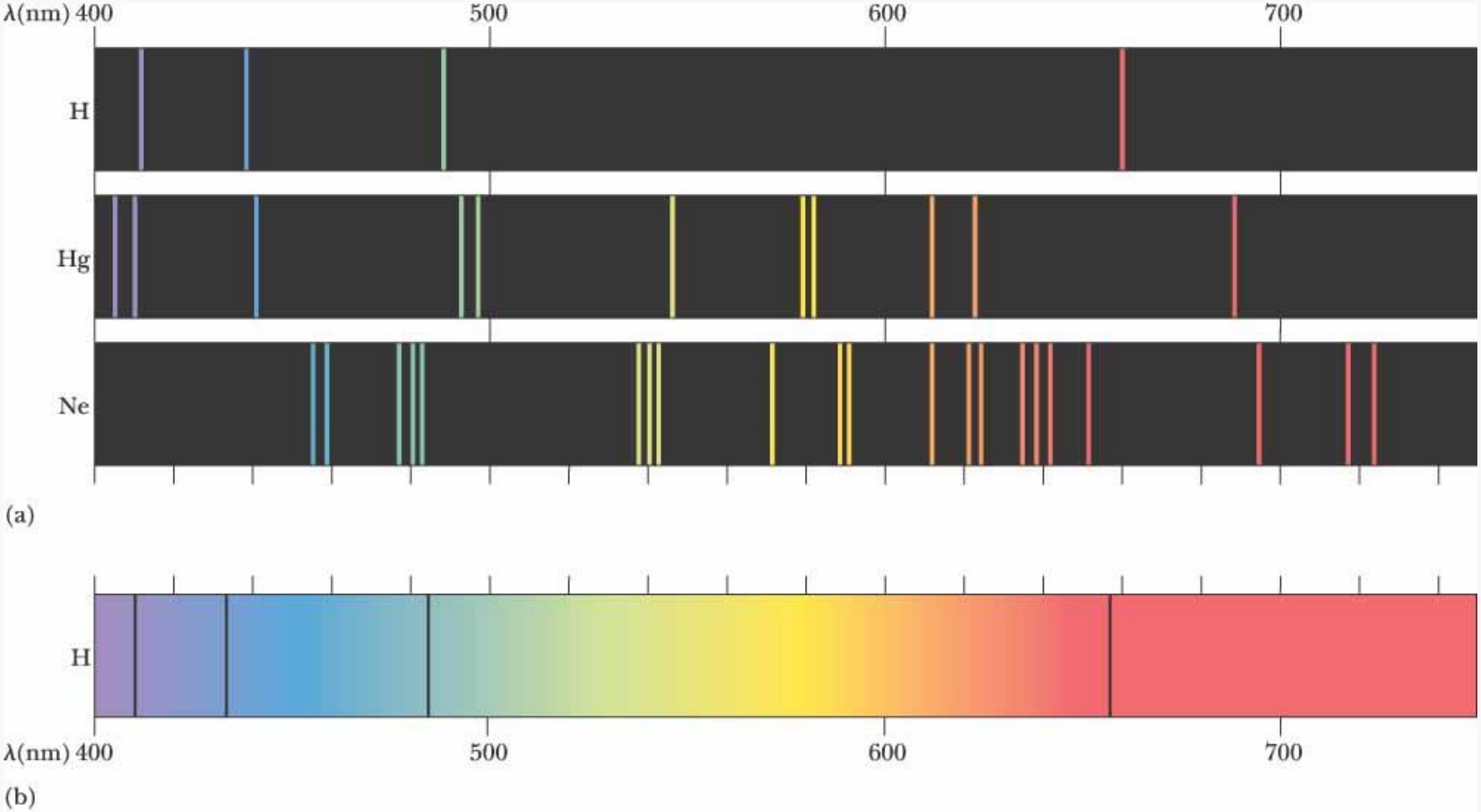
X-rays promote inner shell e^- = much more E

Atomic spectra are line spectra



Some prominent lines in the atomic spectrum of mercury (Hg)

Other atomic spectra – many lines per spectra, lines are very narrow



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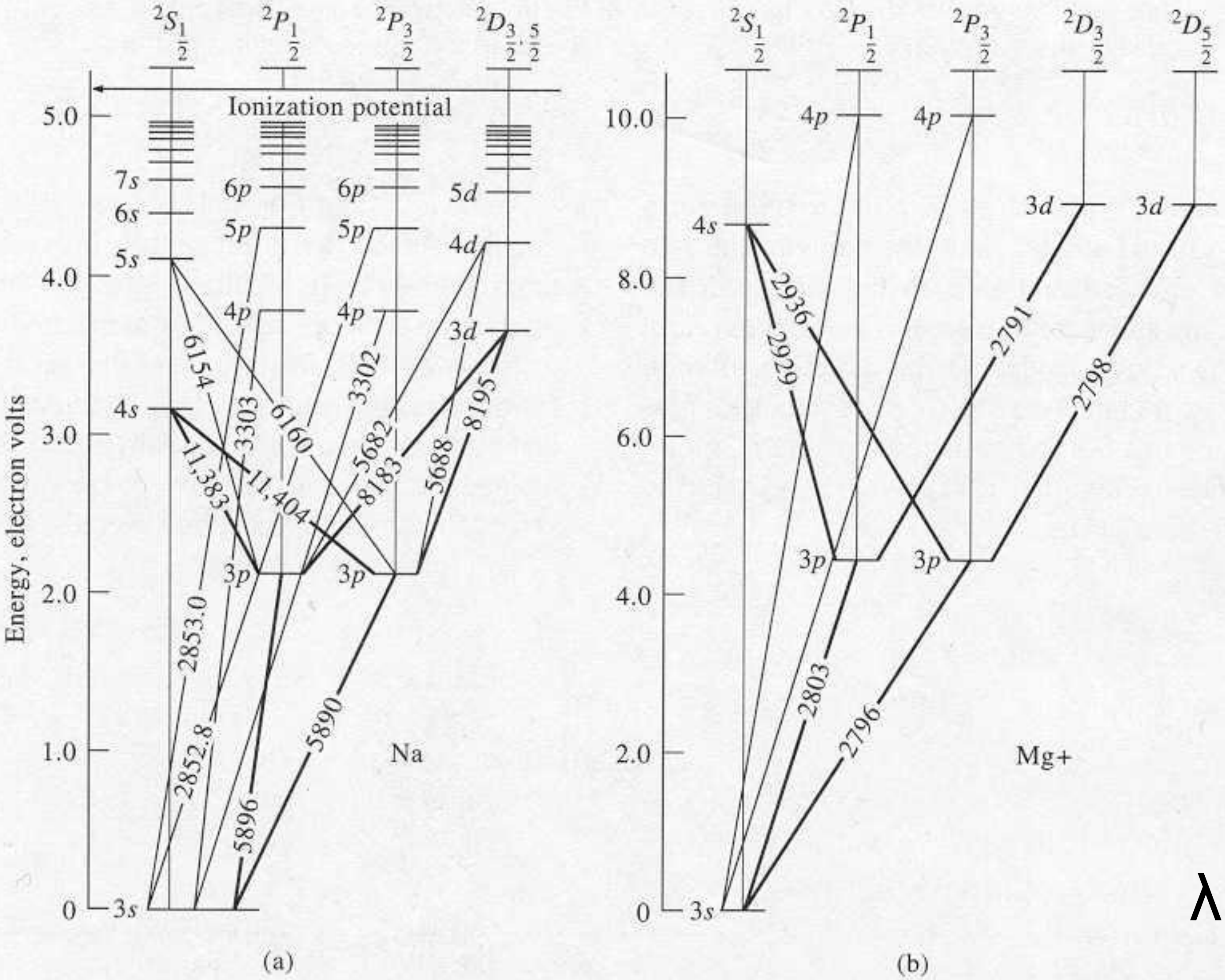
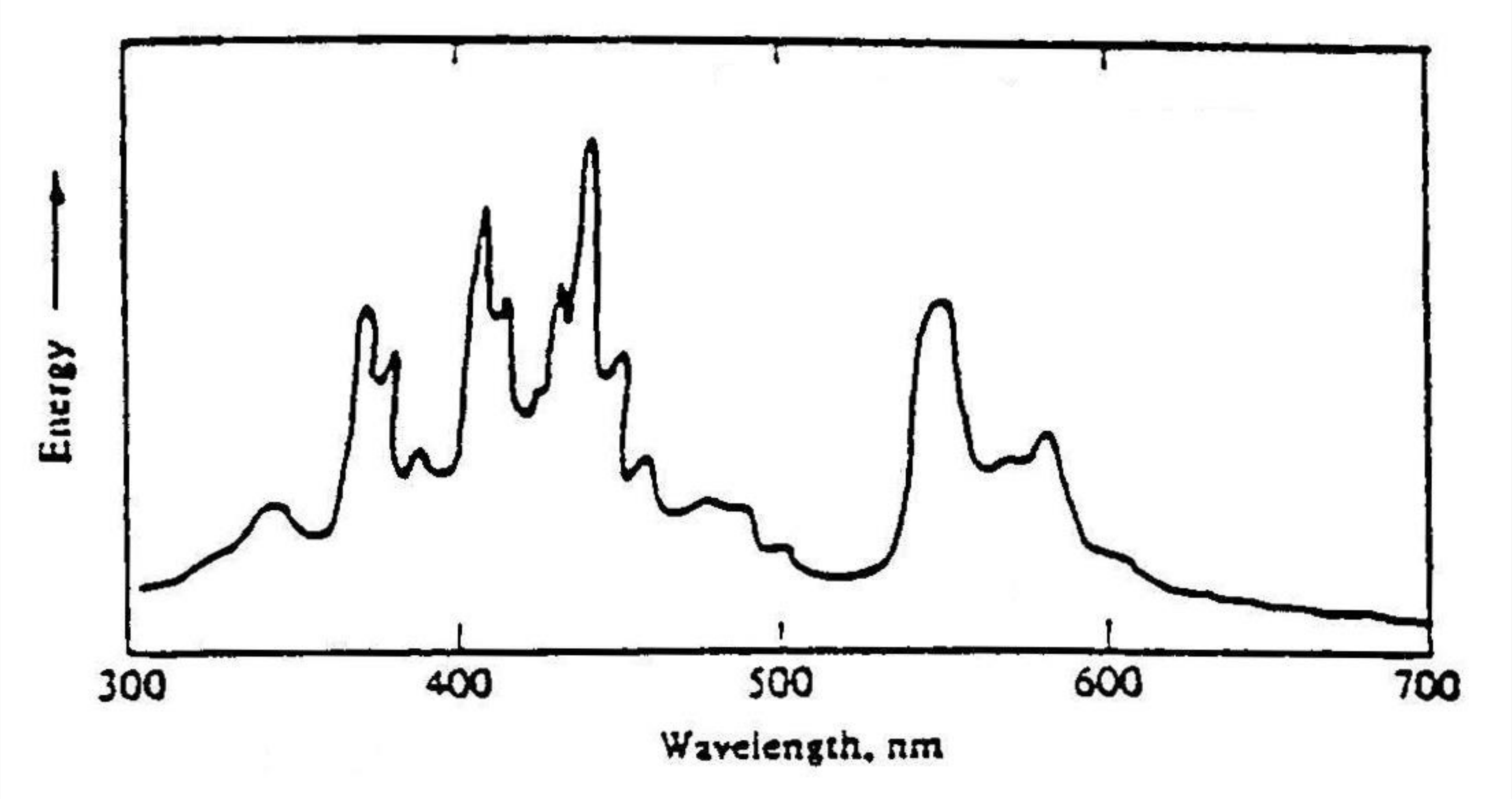


λ in Å

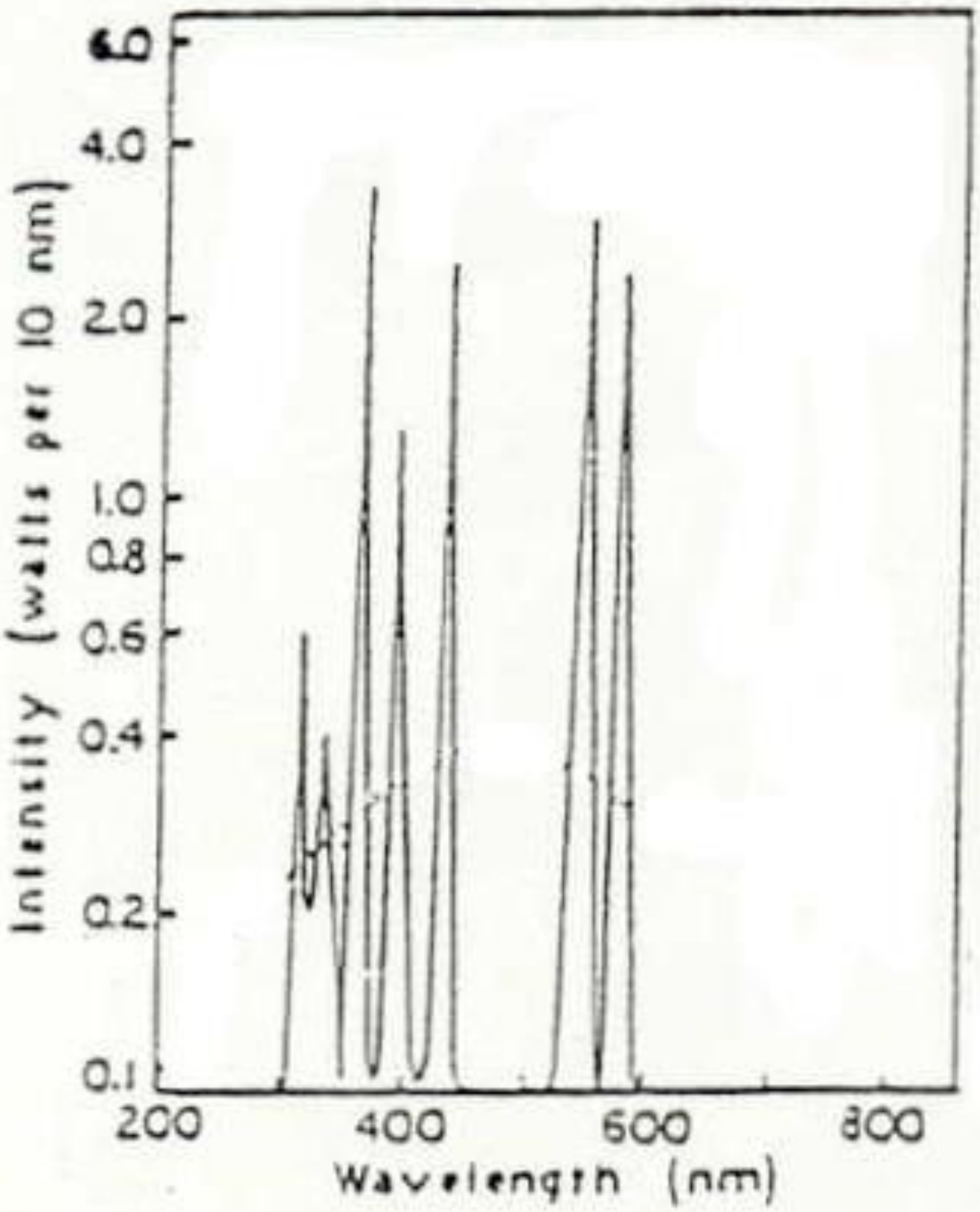
Figure 8-1 Energy level diagrams for (a) atomic sodium and (b) magnesium(I) ion. Note the similarity in pattern of lines but not in actual wavelengths.

Absorption & emission lines come from discrete transitions

<u>High Pressure Mercury Spectrum</u> – (e.g., 100 atm)



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



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)

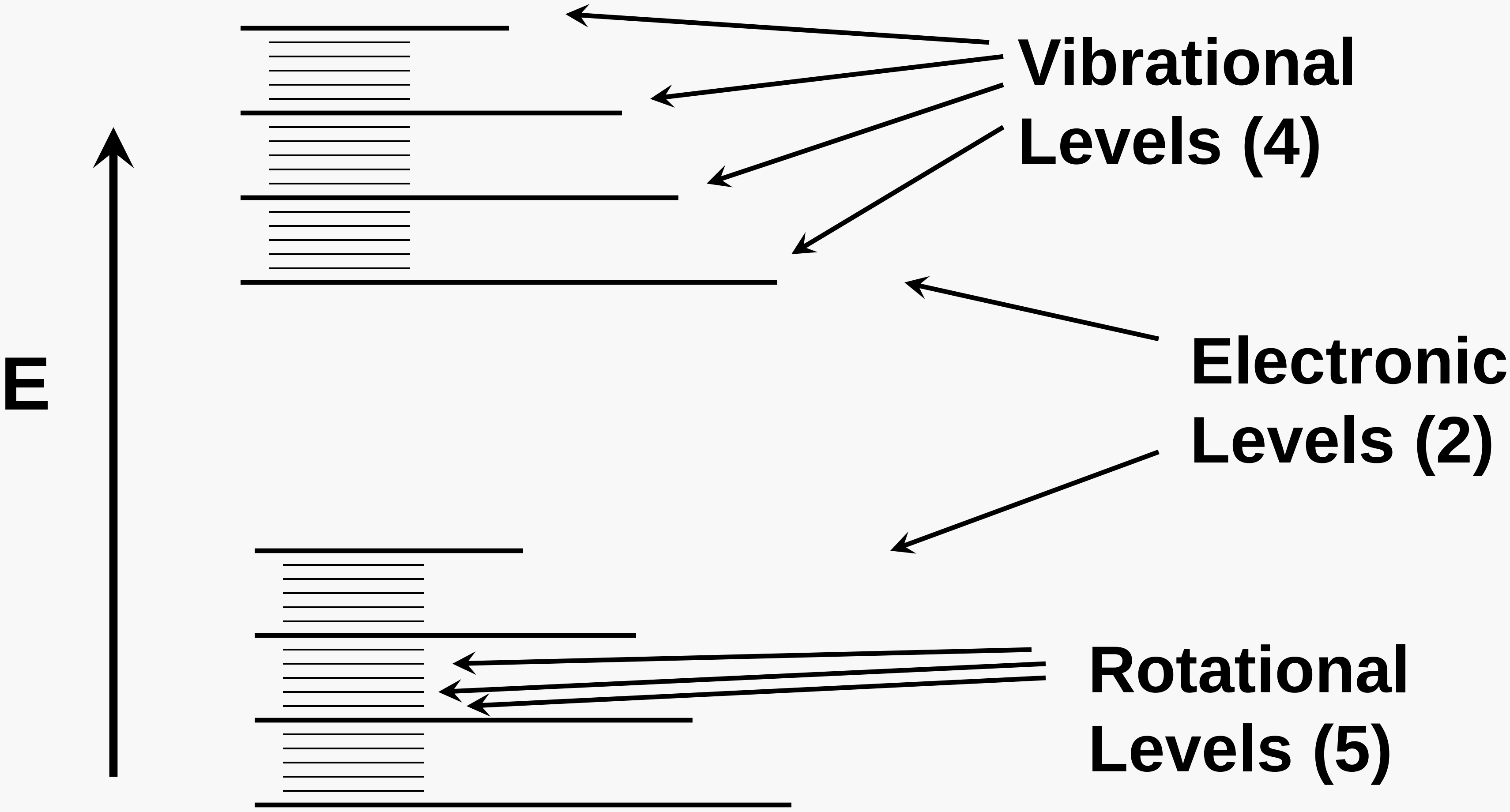
$$\Delta E = \Delta E_{elec.} + \Delta E_{vib.} + \Delta E_{rot.}$$

Energy change or transition for absorption

Largest energy

Smallest energy

Simplified Energy Level Diagram



E

Vibrational Levels (4)

Electronic Levels (2)

Rotational Levels (5)

In the IR region of the spectrum the radiation is not energetic enough to cause electronic transitions

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

Even less energetic radiation can be used i.e. microwaves and radio waves

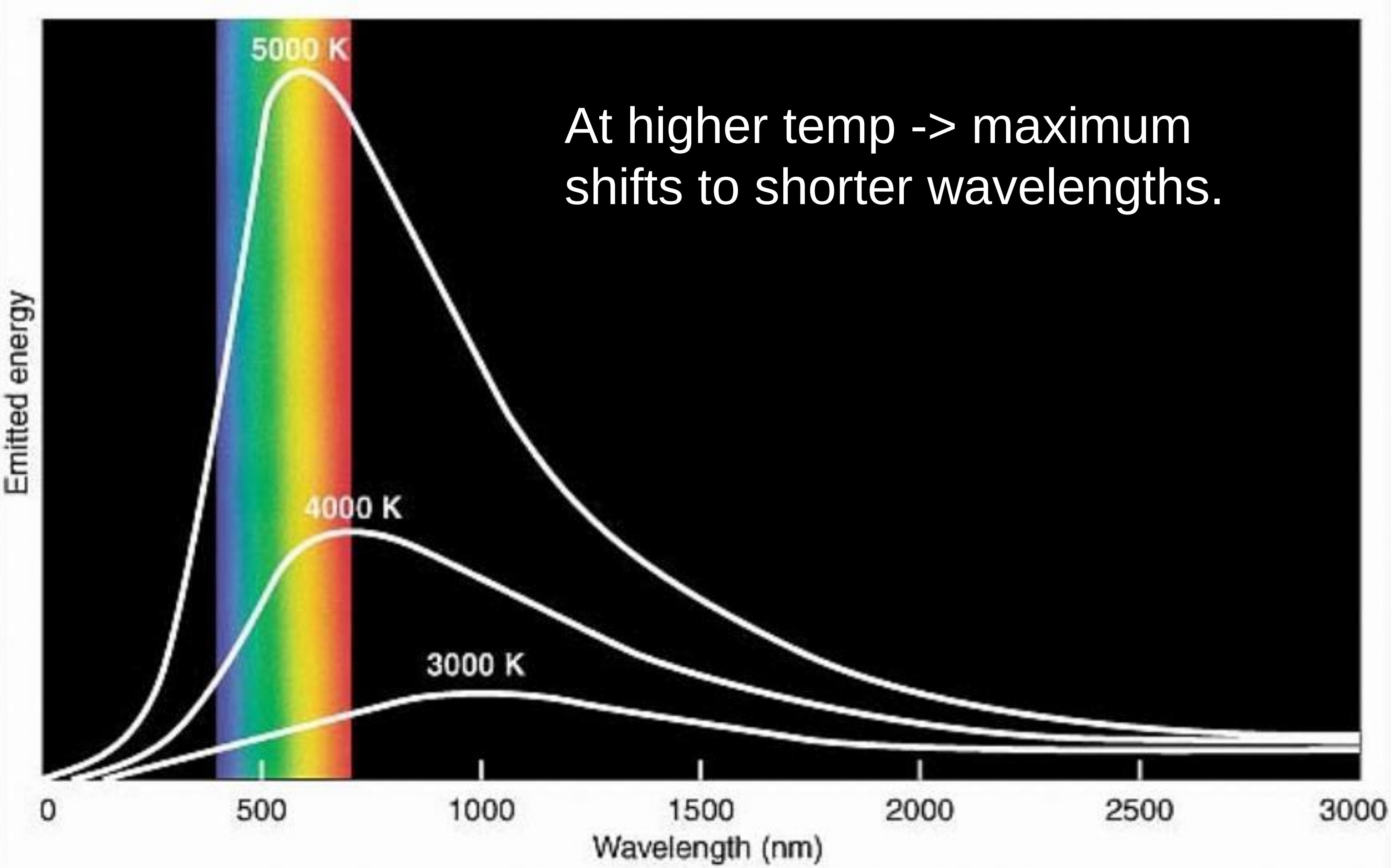
Place sample in magnetic field and can observe low energy transitions associated with changes in spin states e.g. NMR, EPR (ESR)

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 ΔE 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

Spectral Distribution Curves of a Tungsten (Black Body) Absorber/Emitter

UV vis IR



At higher temp -> maximum shifts to shorter wavelengths.

Quantitative Aspects of Absoption

Beer-Lambert Law (or Beer’s Law)

molar absorptivity

Absorbance

$$A = \log \frac{I_o}{I} = \varepsilon\ b\ C$$

concentration

path length

Transmittance

$$T = \frac{I}{I_o}$$

$$\%T = T \times 100$$

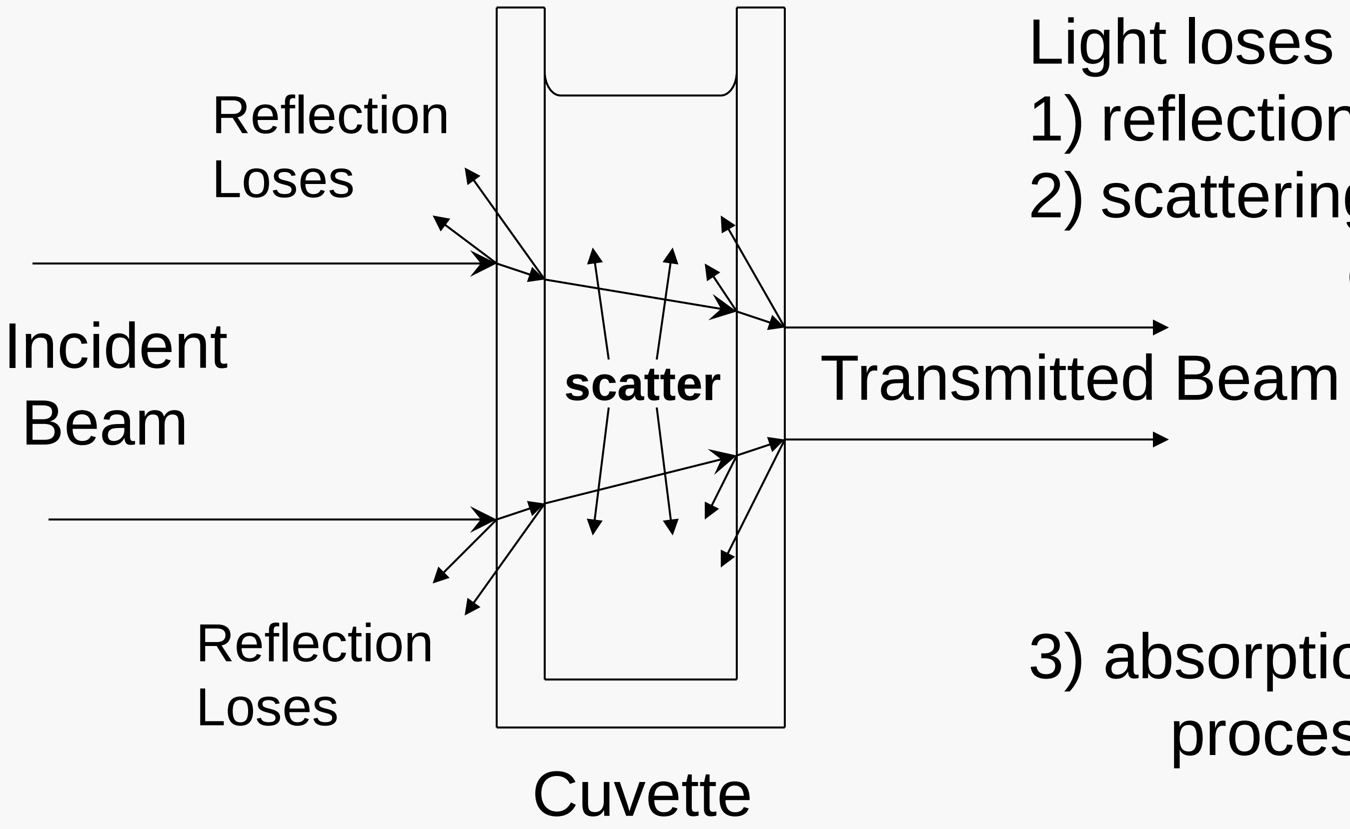
I_o = measured source intensity

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 ε is L/mol-cm
- To minimize the effect of light loses from reflection the procedure followed in UV-vis spectrophotometry is to measure I_o 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_o



Light loses occur due to:

1) reflection at boundaries
2) scattering by molecules or particles

3) absorption which is process of interest