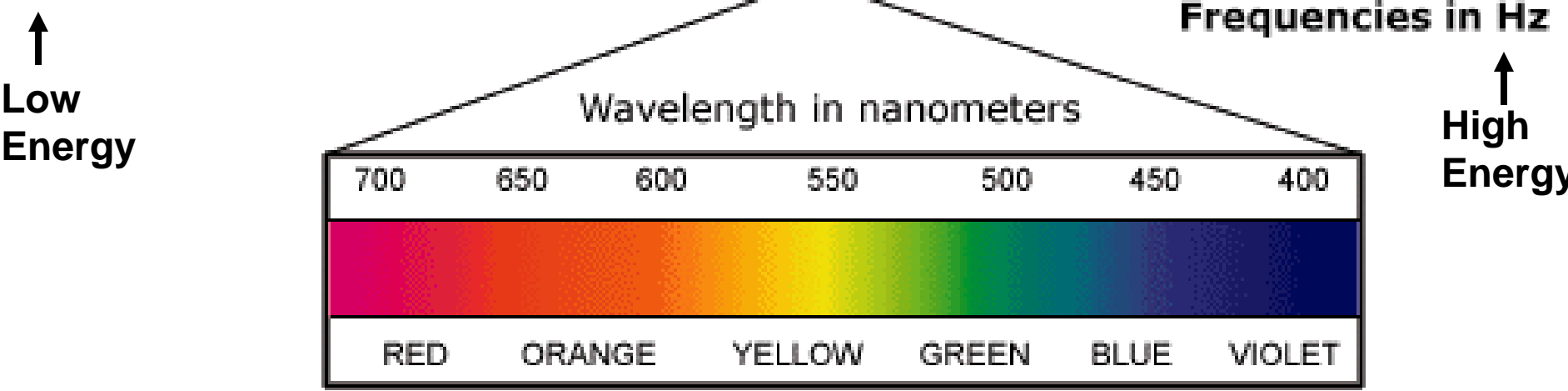
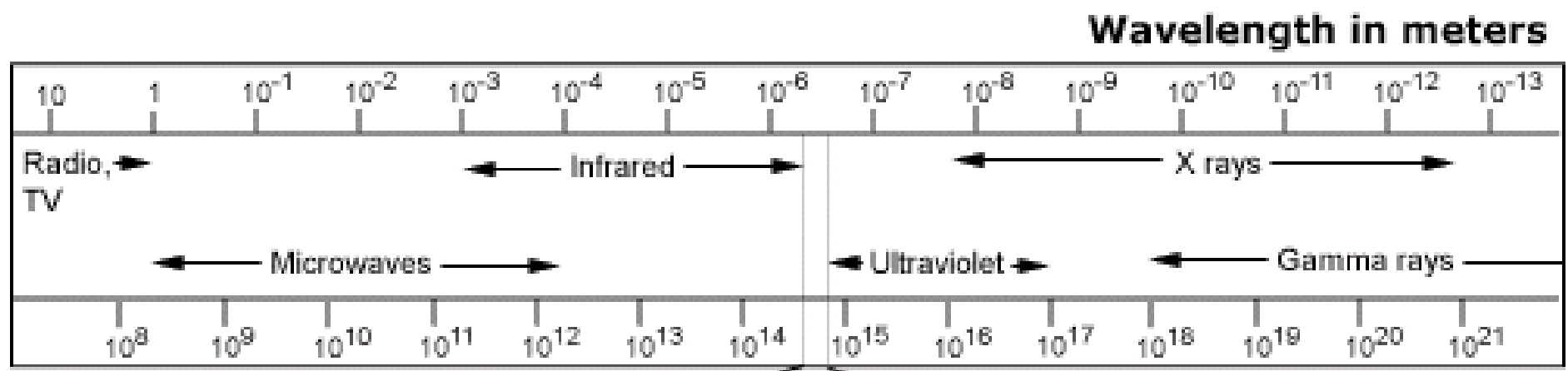


# Introduction to Spectrometric Methods

- General Properties of Electromagnetic Radiation (EM)
- Wave Properties of EM
- Quantum-Mechanical Properties of EM
- Quantitative Aspects of Spectrochemical Measurements

Spin States	Molecular Rotations	Molecular Vibrations	Outer Shell Electrons	Inner Shell Electrons	Nuclear Transitions
NMR EPR	Microwave Absorption Spectroscopy	Infrared Absorption Spectroscopy	UV-vis Absorption, Fluorescence	X-Ray Absorption, Fluorescence	Gamma Ray Spectroscopy

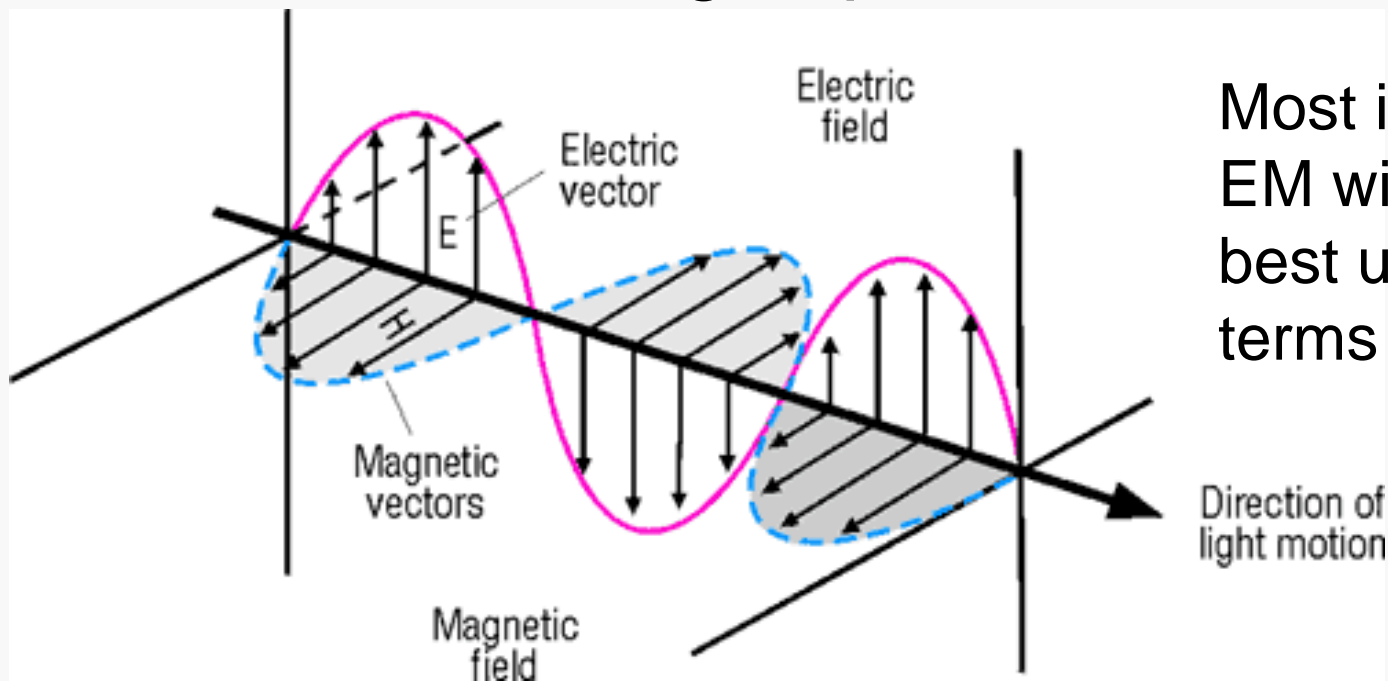


R O Y G B V

**Spectroscopy** = methods based on the interaction of electromagnetic radiation (EM) and matter

**Electromagnetic Radiation** = form of energy with both wave and particle properties

EM moves through space as a wave



Most interactions of EM with matter are best understood in terms of electric vector

# Relationship between various wave properties

$$\nu \lambda_i = \frac{C}{\eta_i}$$

Where  $\nu$  = frequency in cycles/s or Hz

$\lambda_i$  = wavelength in medium  $i$

$\eta_i$  = refractive index of medium  $i$

$C$  = speed of light in vacuum ( $2.99 \times 10^{10}$  cm/s)

EM slows down in media other than vacuum because electric vector interacts with electric fields in the medium (matter)  $\rightarrow$  this effect is greatest in solids & liquids, in gases (air) velocity similar to vacuum

# Wave Equation

$$y = A \sin (\omega t + \alpha)$$

Where  $A$  = amplitude

$\omega$  = angular frequency

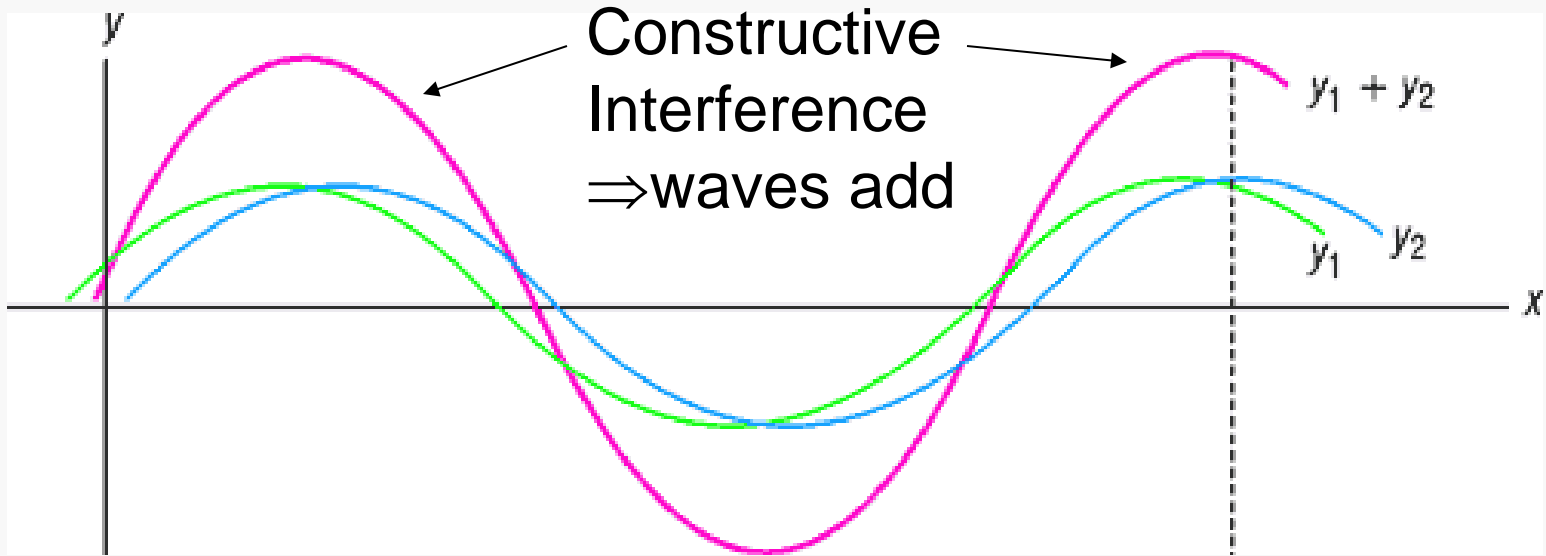
$\alpha$  = phase angle

$t$  = time

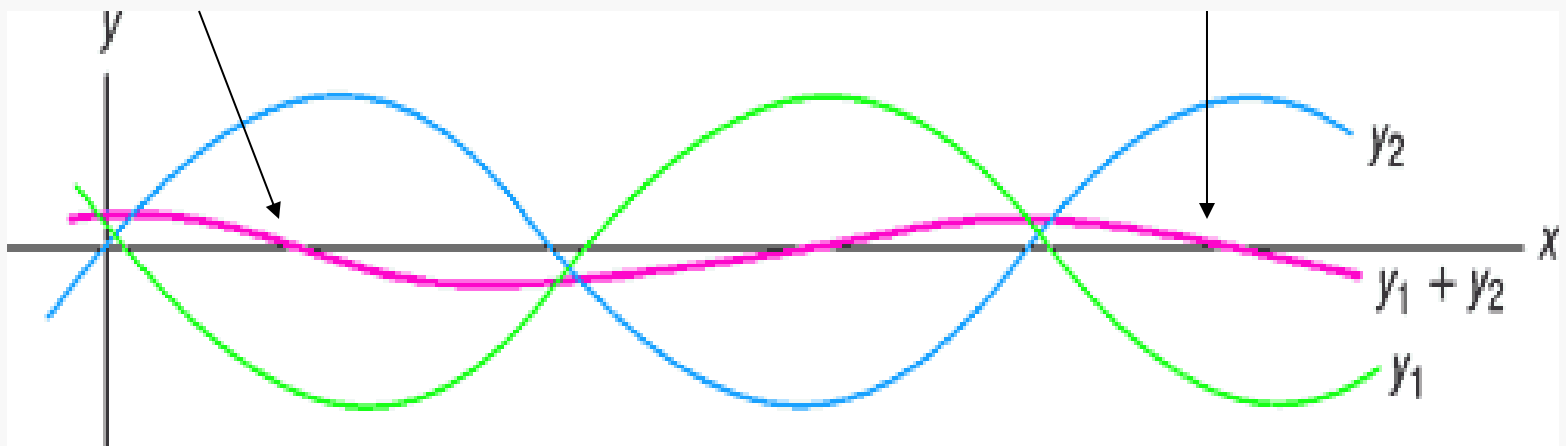
For a collection of waves the resulting position  $y$  at a given  $t$  can be calculated by

$$y = A_1 \sin (\omega_1 t + \alpha_1) + A_2 \sin (\omega_2 t + \alpha_2) + \dots$$

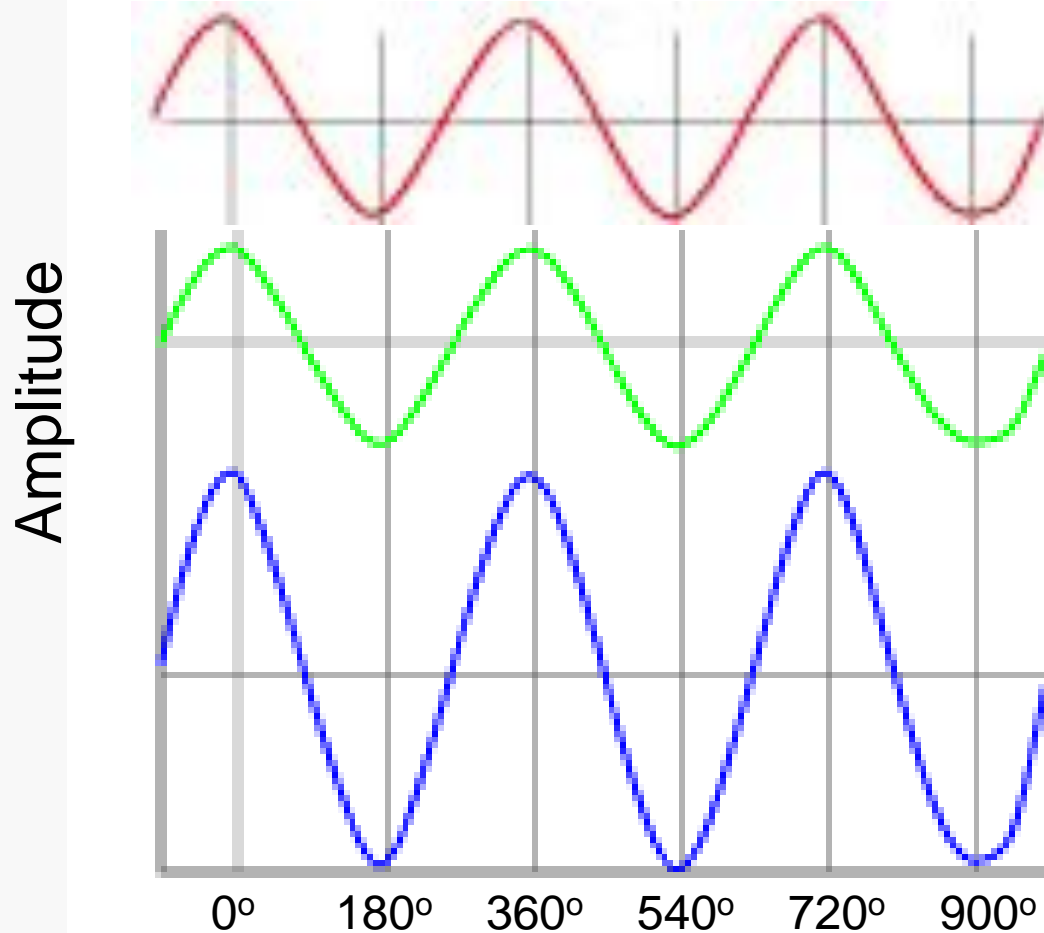
**Interference** - amplitude of the resulting wave depends on phase difference  $\alpha_1 - \alpha_2$



Destructive Interference  $\Rightarrow$  waves cancel



At  $\alpha_1 - \alpha_2 = 0^\circ$  adding of waves gives  
Maximum Constructive Interference



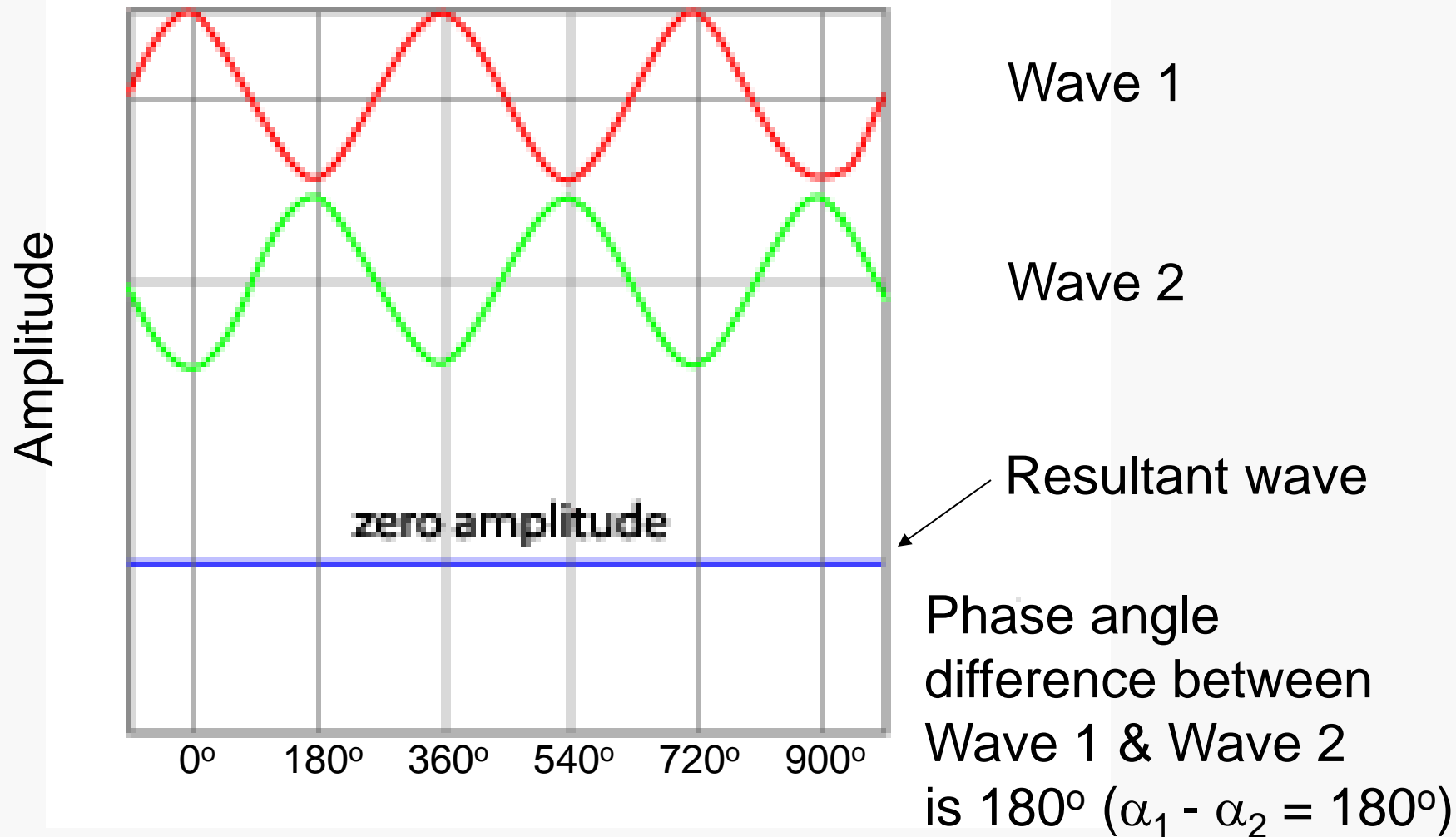
Wave 1

Wave 2

Resultant wave

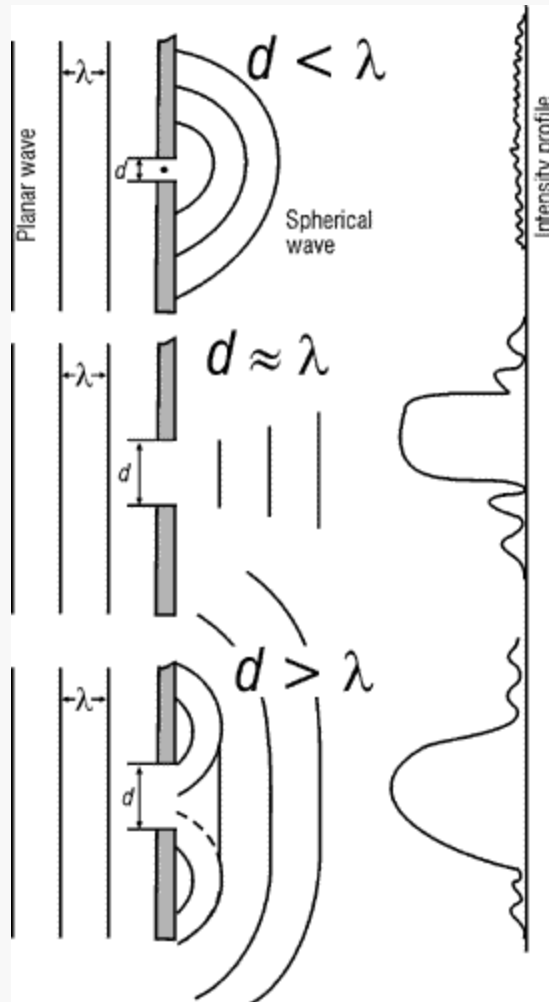
Phase angle  
difference between  
Wave 1 & Wave 2  
is zero  $\alpha_1 - \alpha_2 = 0^\circ$

When  $\alpha_1 - \alpha_2 = 180^\circ$  or  $540^\circ$  adding of waves gives Maximum Destructive Interference





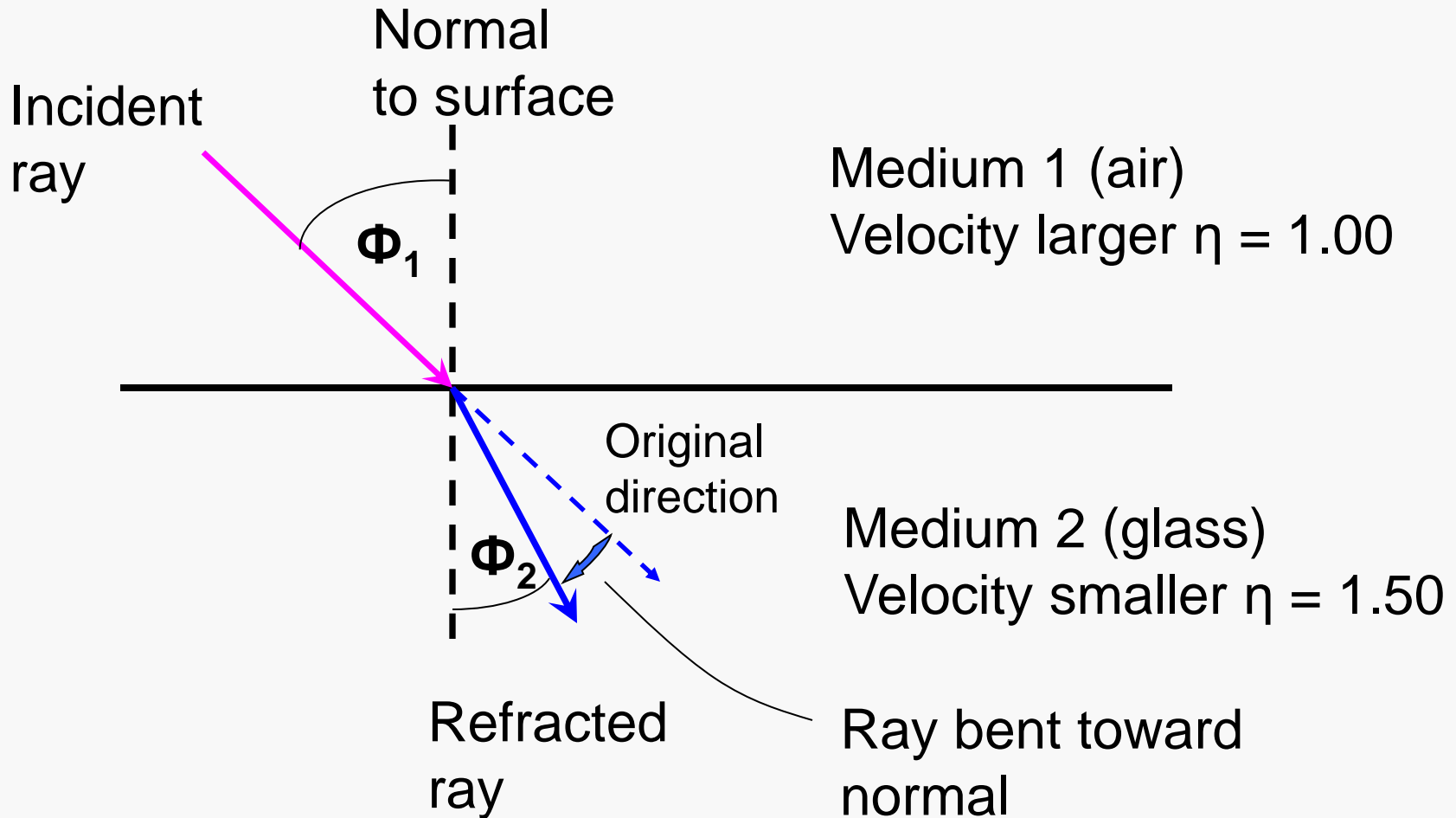
Diffraction = EM going past an edge or through a slit (2 edges) tends to spread



The combination of diffraction effects & interference effects are important in spectroscopy for

- 1) diffraction gratings
- 2) slit width considerations

**Refraction** = change in velocity of EM as it goes from one medium to another



## Equation for Refraction (Snell)

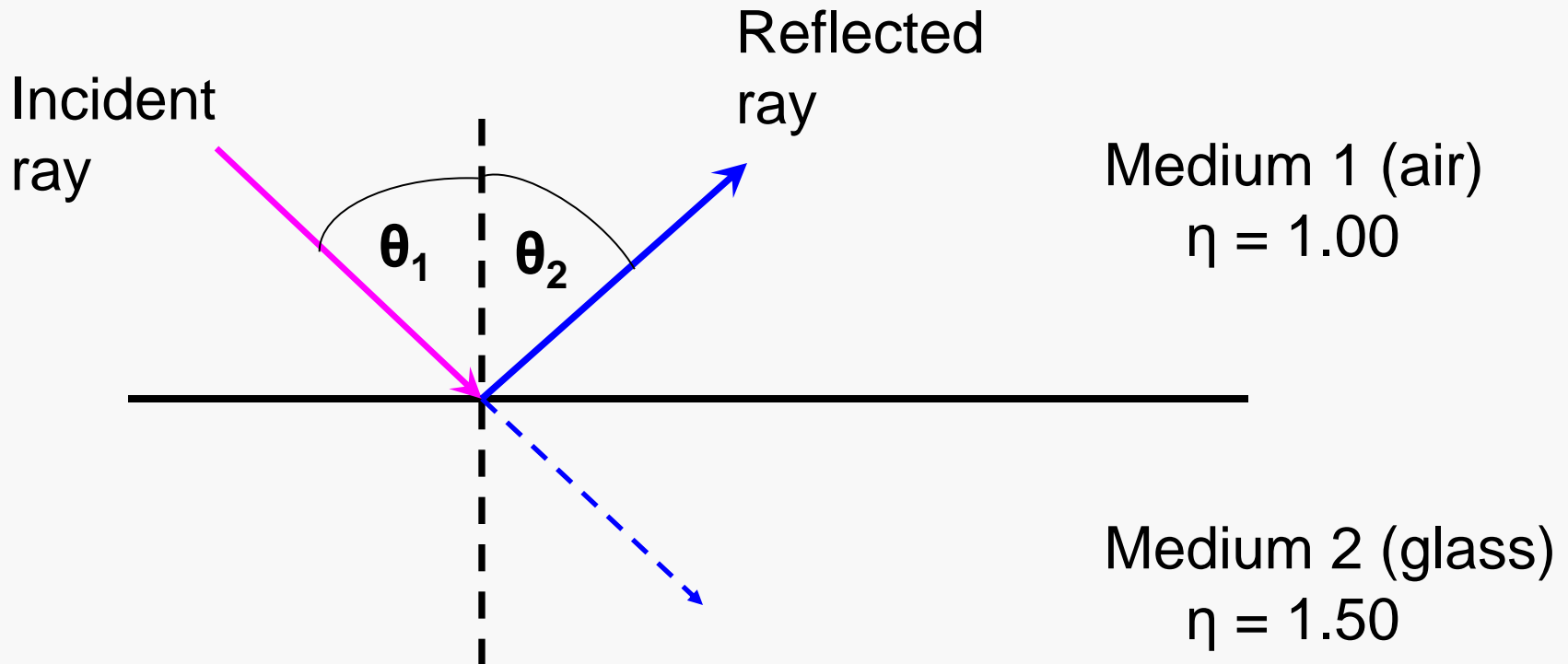
$$\frac{\sin \Phi_1}{\sin \Phi_2} = \frac{v_1}{v_2} = \frac{\eta_2}{\eta_1} = \eta_2 \quad \begin{array}{l} \text{if medium 1} \\ \text{is air } \eta_1 = 1.0 \end{array}$$

Magnitude of the direction change (i.e., size of the angle depends on velocity (shown in equation as  $v$ ) this is how a prism works

Direction of bending depends on relative values of  $\eta$  for each medium. Going from low  $\eta$  to higher, the ray bends toward the normal. Going from higher  $\eta$  to lower the ray bends away from the normal.



**Reflection** = EM strikes a boundary between two media differing in  $\eta$  and bounces back



Specular reflection = situation where angle of incidence ( $\theta_i$ ) equals angle of reflection ( $\theta_r$ )

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

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  $\eta = 1.00$  into glass of  $\eta = 1.70$ . Show your work and email your homework to [David\\_Ryan@uml.edu](mailto: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:

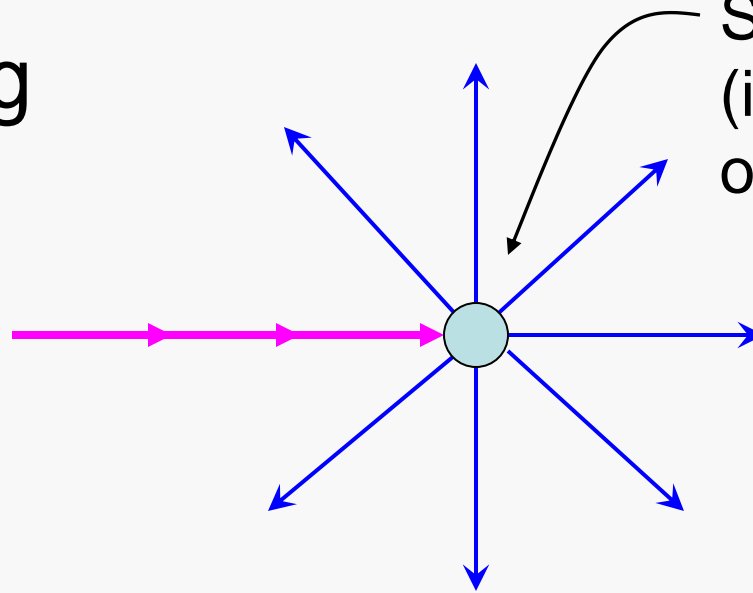
- 1) Wave – EM induces oscillations in electrical charge of matter  $\Rightarrow$  resulting in oscillating dipoles which in turn radiate secondary waves in all directions = scattered radiation
- 2) Particle (or Quantum) – EM interacts with matter to form a virtual state (lifetime  $10^{-14}$  s) which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

Raman effect = when some molecules return to a different state  $\Rightarrow$  change in frequency



# Scattering

Incident  
beam



Scattering Center  
(i.e., molecule, colloidal  
or insoluble particle)

Scattered Radiation  
emitted in all  
directions

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  $\lambda$  with no change in observed frequency

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

scattering intensity  $I_s$

wavelength  $\lambda$

distance from scattering center to detector  $r$

polarizability  $\alpha$

angle between incident beam & scattered beam  $\theta$

incident beam intensity  $I_o$

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

Polarizability ( $\alpha$ ) is a measure of how well a given frequency induces a dipole in a substance

$\alpha$  Tends to be large for large molecules (e.g., proteins)

Large Particle Scattering – particle dimensions  $< 10\% \lambda$  to  $1.5 \lambda$

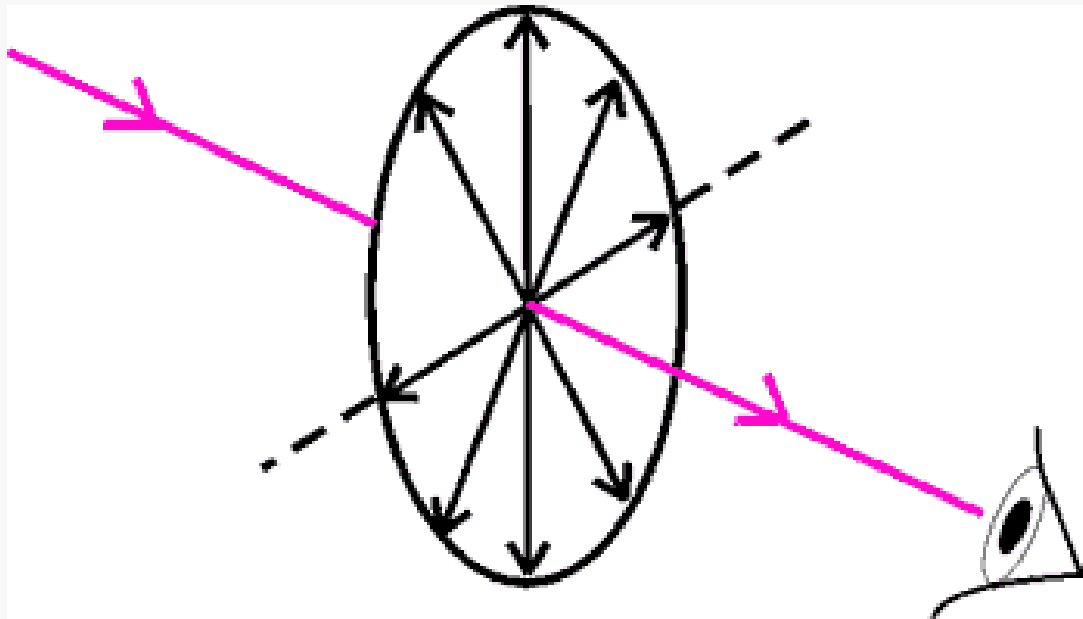
Applies in techniques like turbidimetry and nephelometry

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

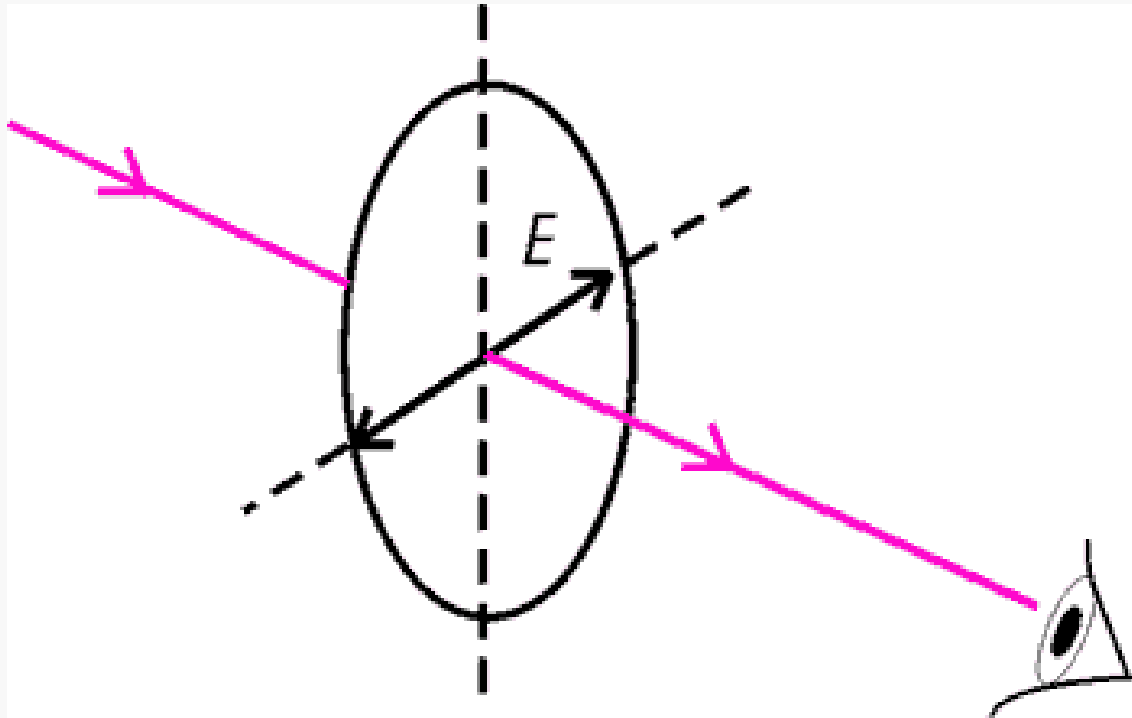
Forward scatter becomes greater than back scatter

# Polarization

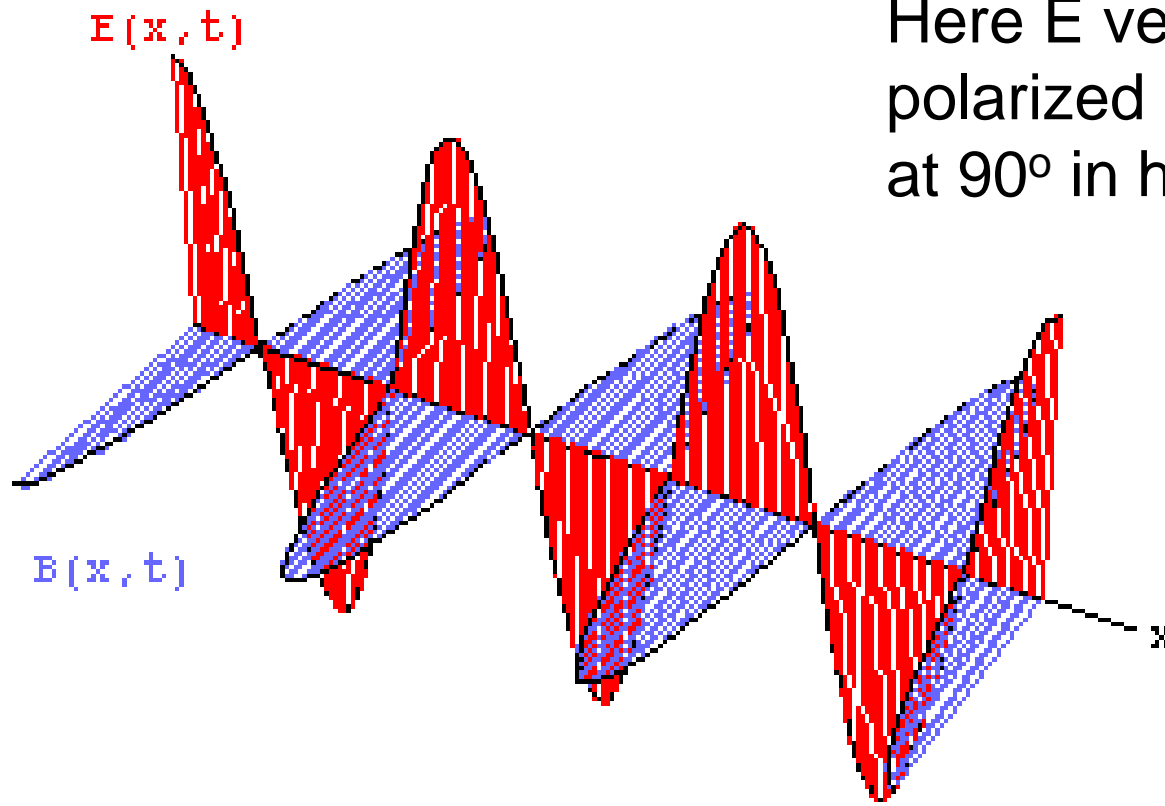
EM is said to be unpolarized if its electric vectors and magnetic vectors occur with equal amplitude in all direction



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

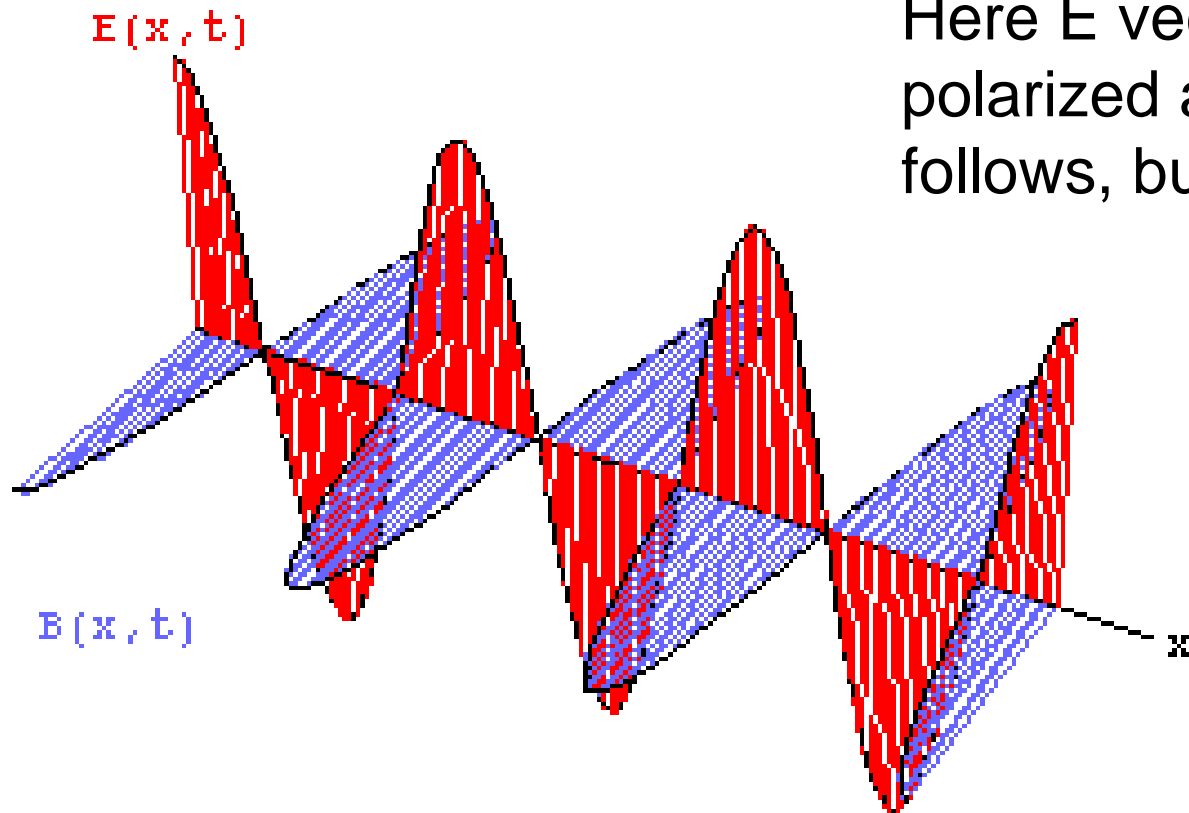


Linearly polarized light oscillates in one plane only as it moves through space



Here E vector is vertically polarized and H vector is at  $90^\circ$  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  $90^\circ$

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 ( $\Delta E$ ) must correspond to the energy of the light (EM) given by frequency ( $\nu$ ) and Planck's constant ( $h$ )

$$\Delta E = h\nu$$

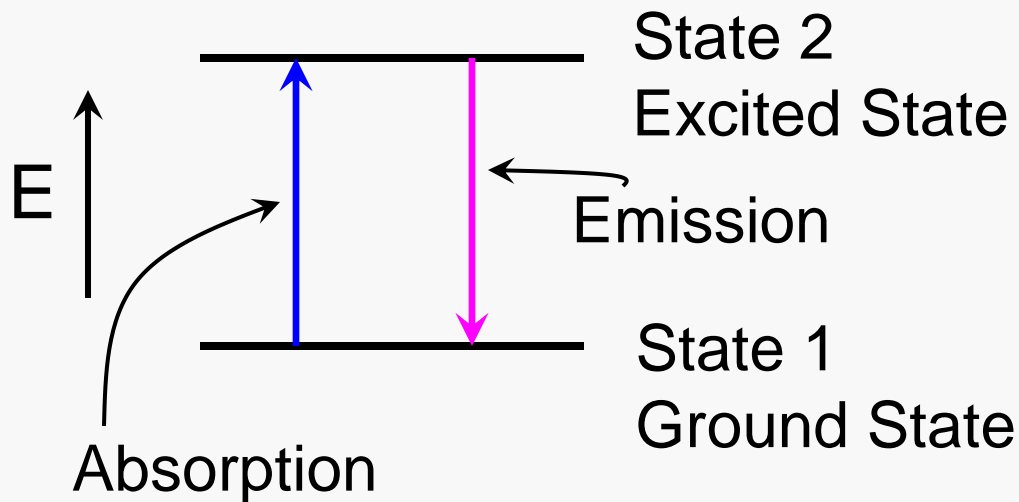
This holds for absorption & emission of radiation

# 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



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  
 $\nu$  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

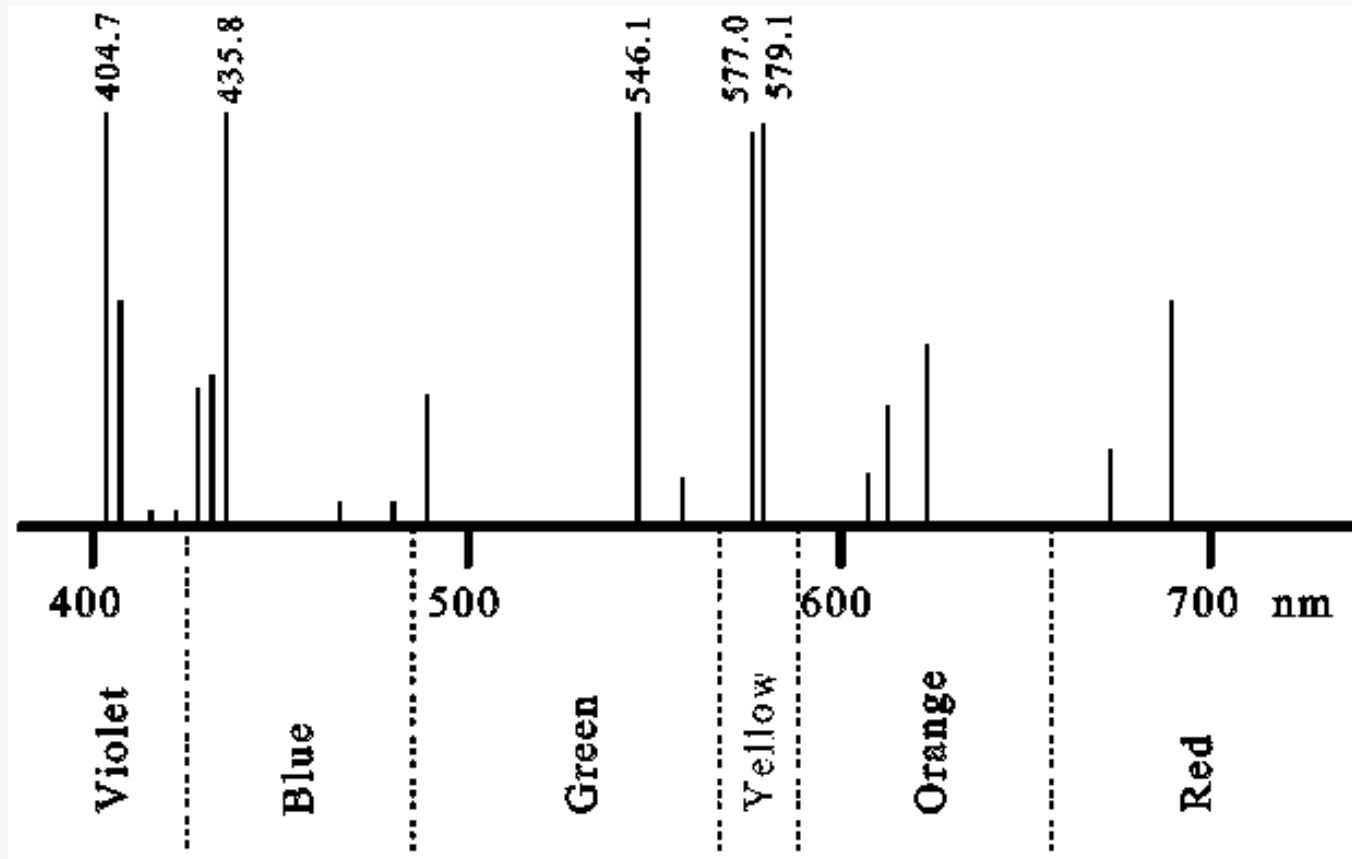
Example – Na vapor has 2 lines 589.0 nm & 589.6 nm which come from 3s electrons promoted to 2 possible 3p states of different E

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

UV-vis wavelengths promote outer shell electrons

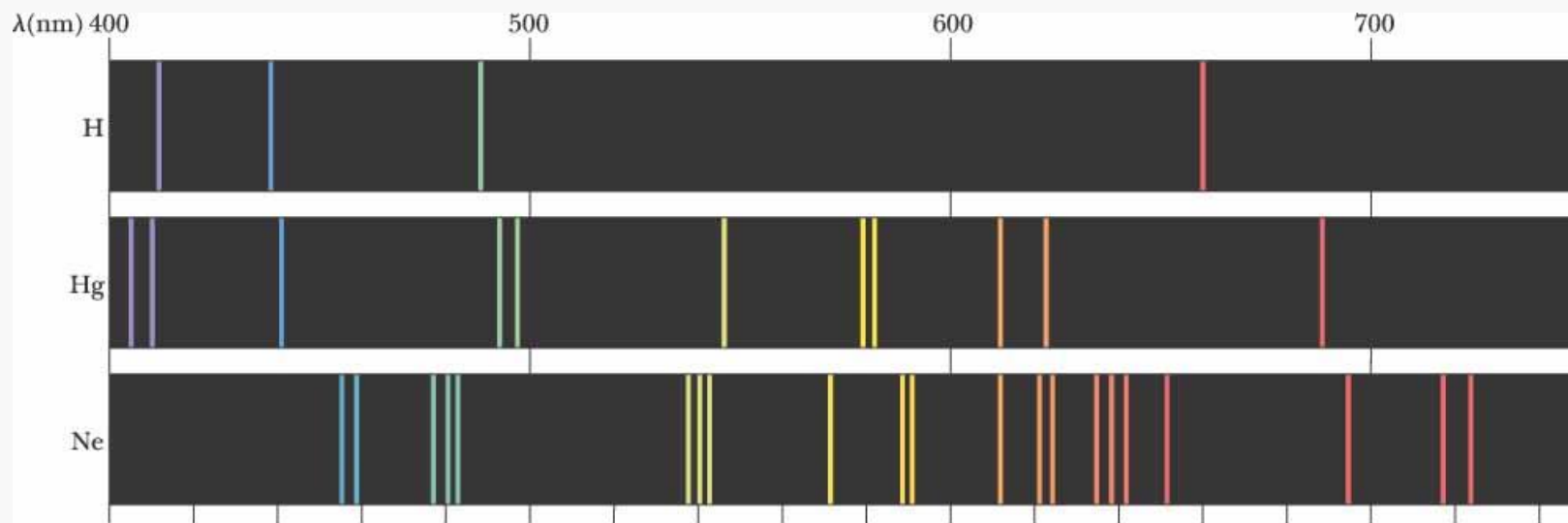
X-rays promote inner shell  $e^-$  = much more E

# Atomic spectra are line spectra

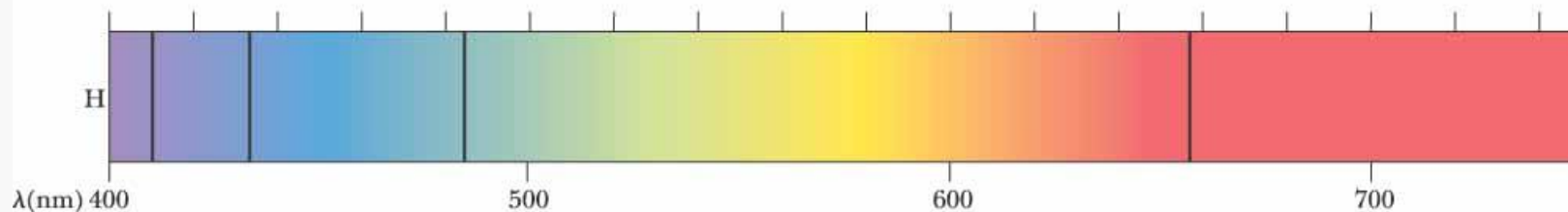


Some prominent lines in the atomic spectrum of mercury (Hg)

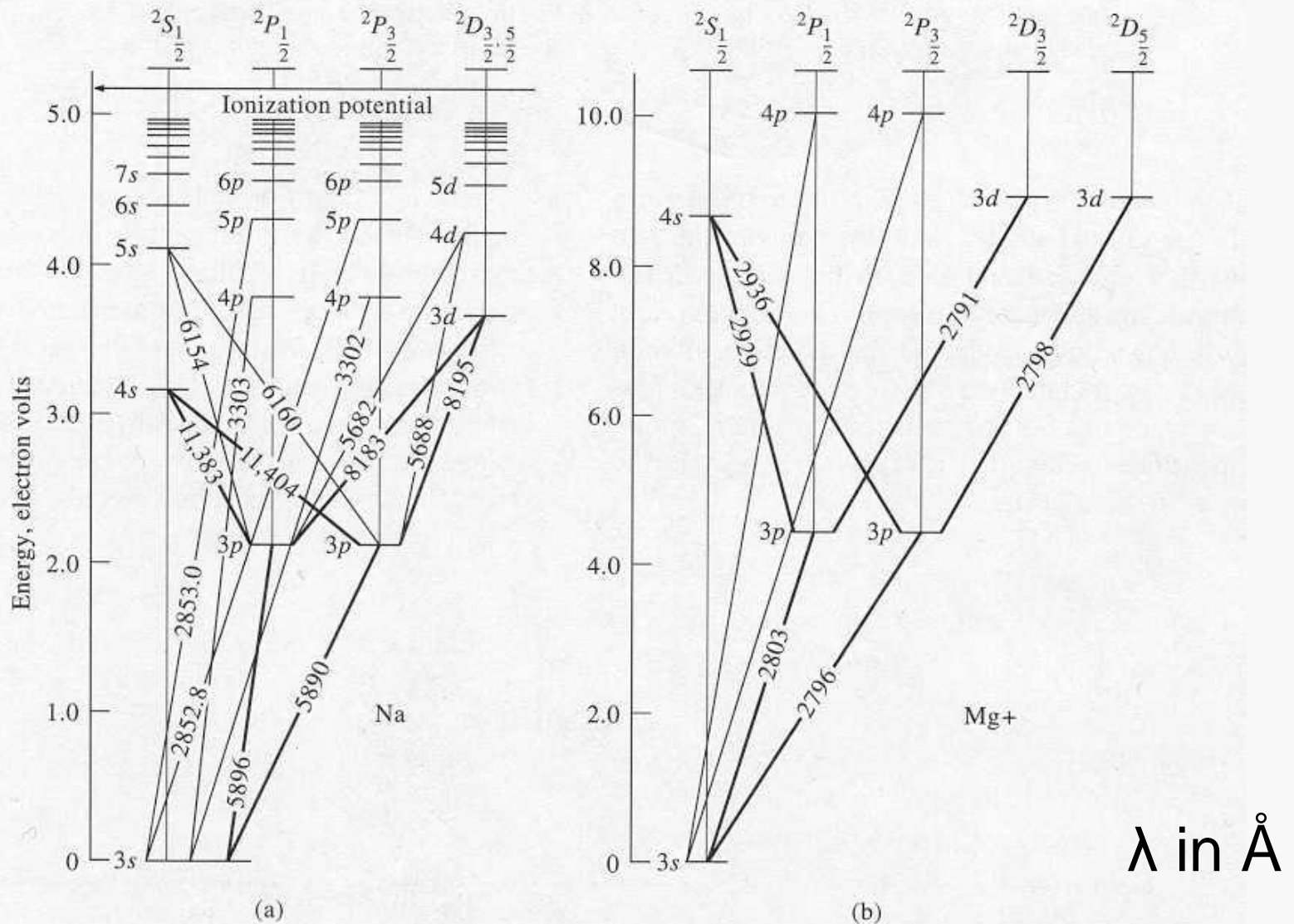
# Other atomic spectra – many lines per spectra, lines are very narrow



(a)



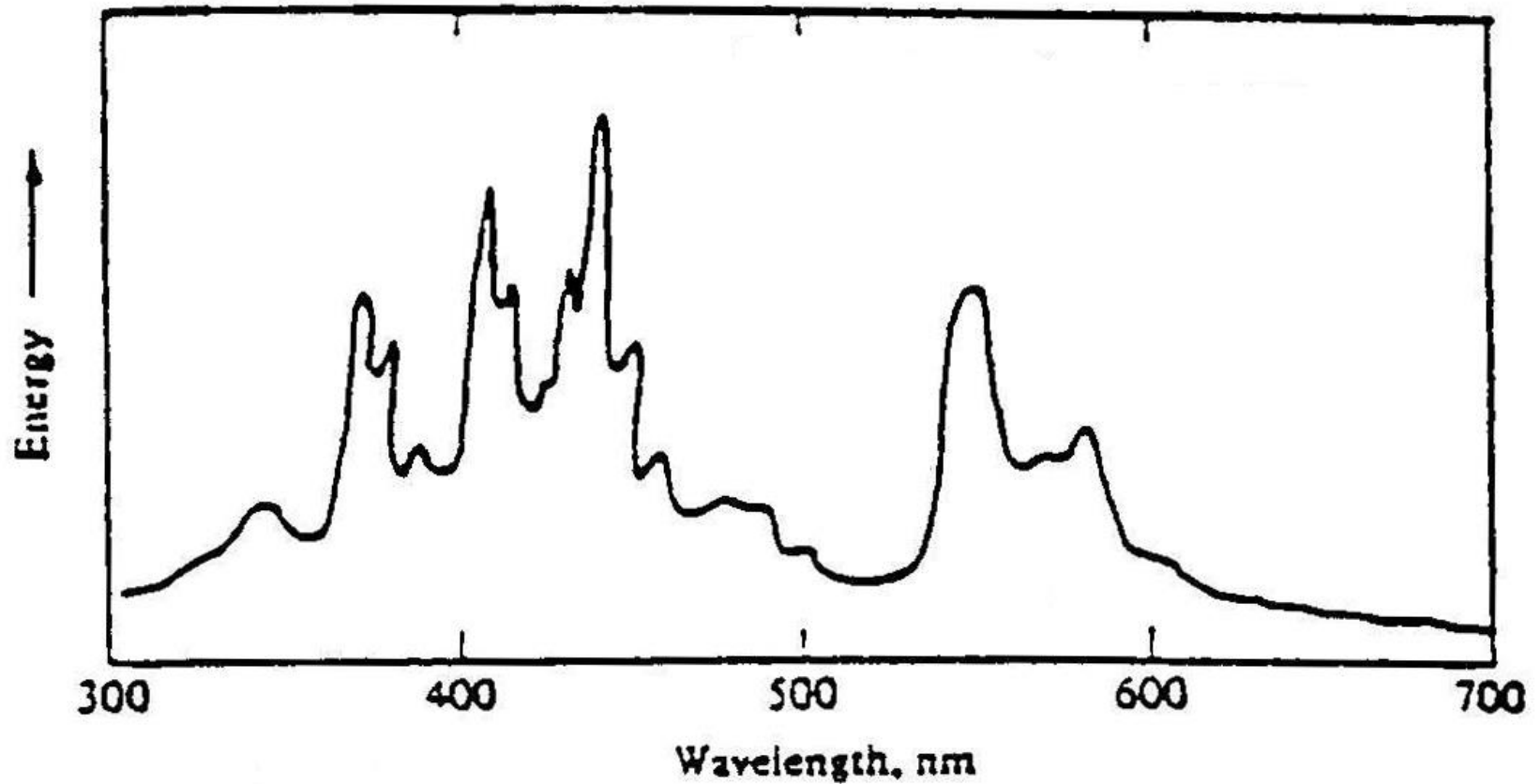
(b)



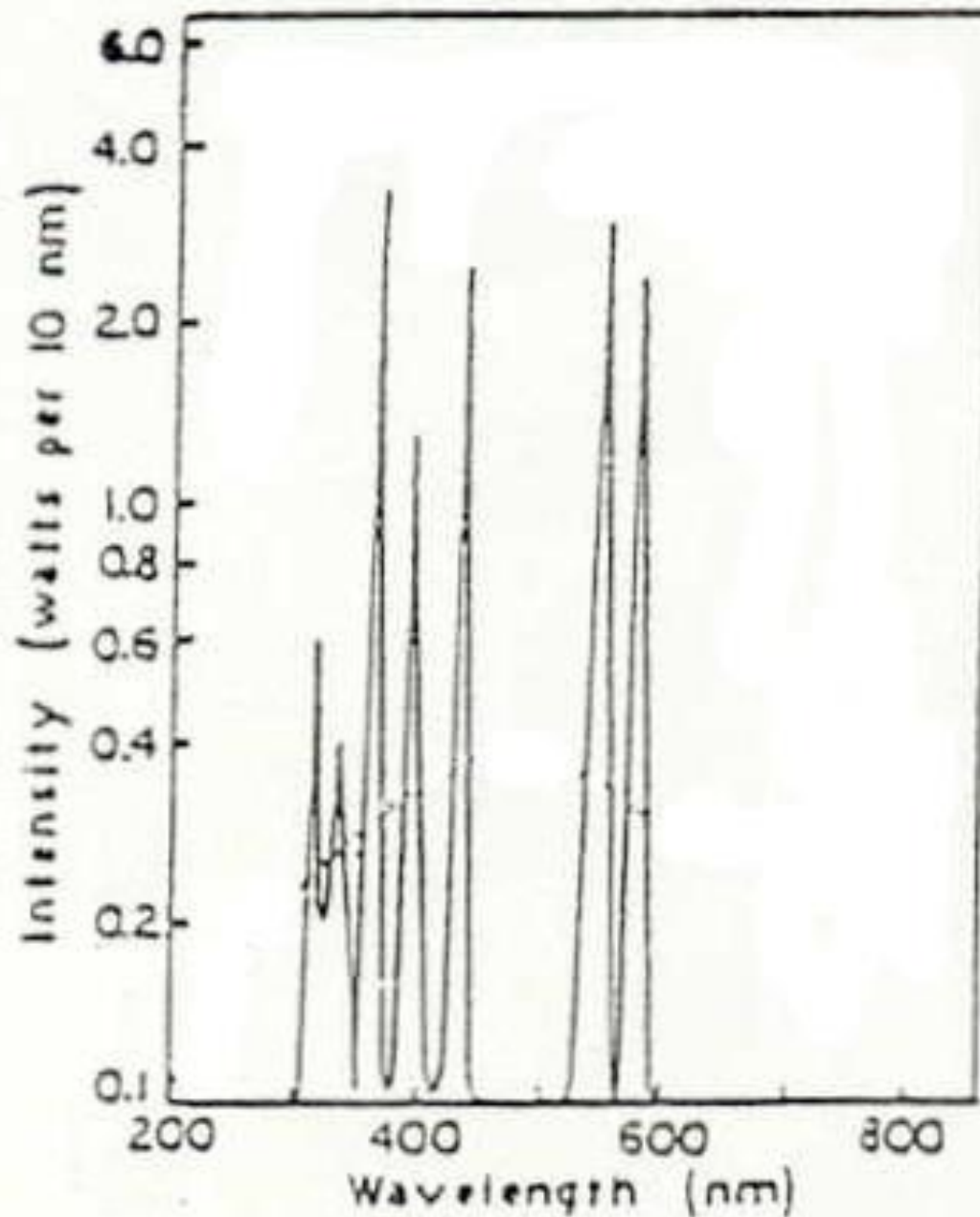
**Figure 8-1** Energy level diagrams for (a) atomic sodium and (b) magnesium(I) ion. Note the similarity in pattern of lines but not in actual wavelengths.

Absorption & emission lines come from discrete transitions

# High Pressure Mercury Spectrum – (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

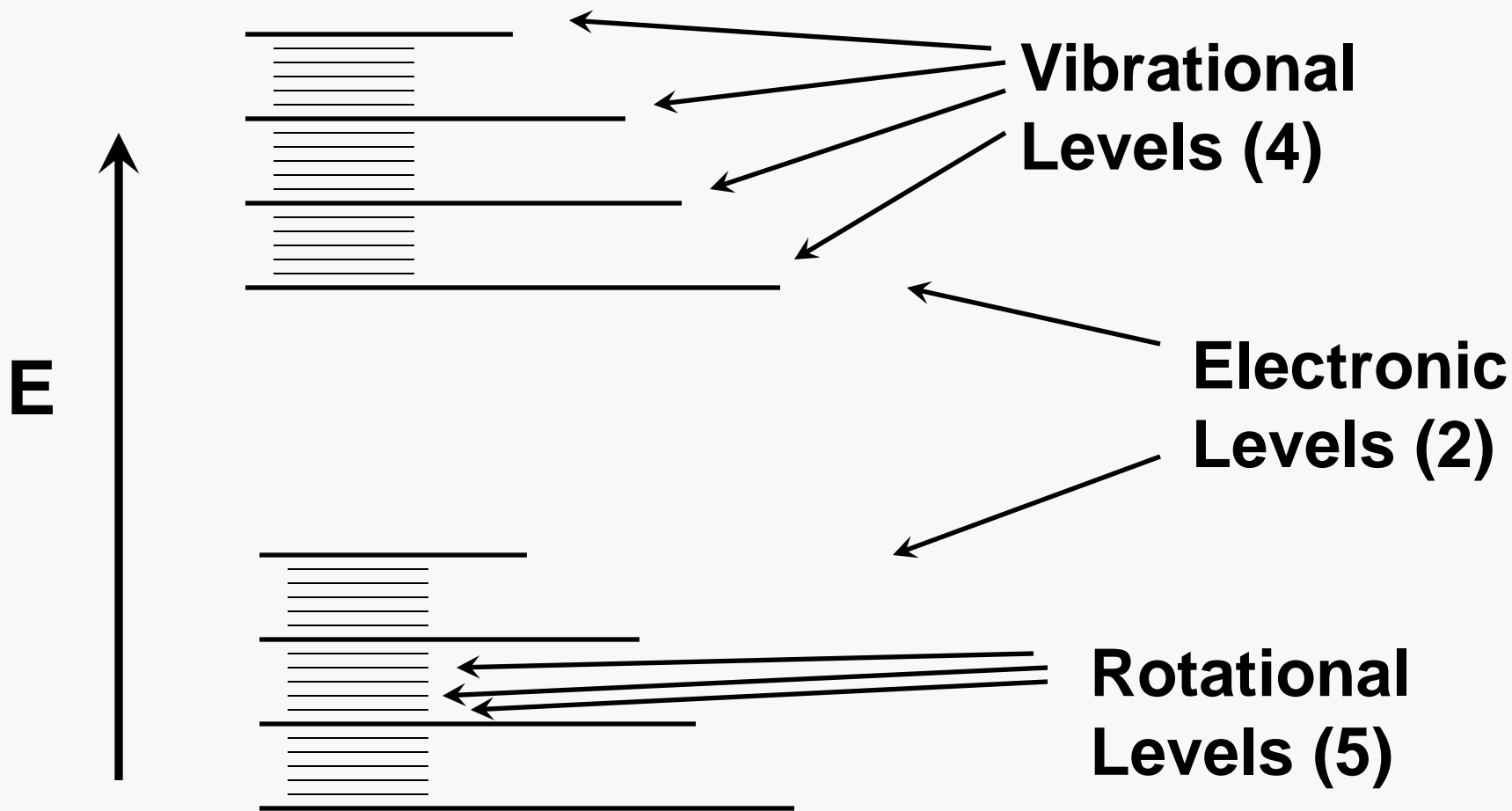
- these changes correspond to the energy of the ultraviolet-visible radiation

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

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

Energy change or transition for absorption      Largest energy      Smallest energy

# Simplified Energy Level Diagram



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

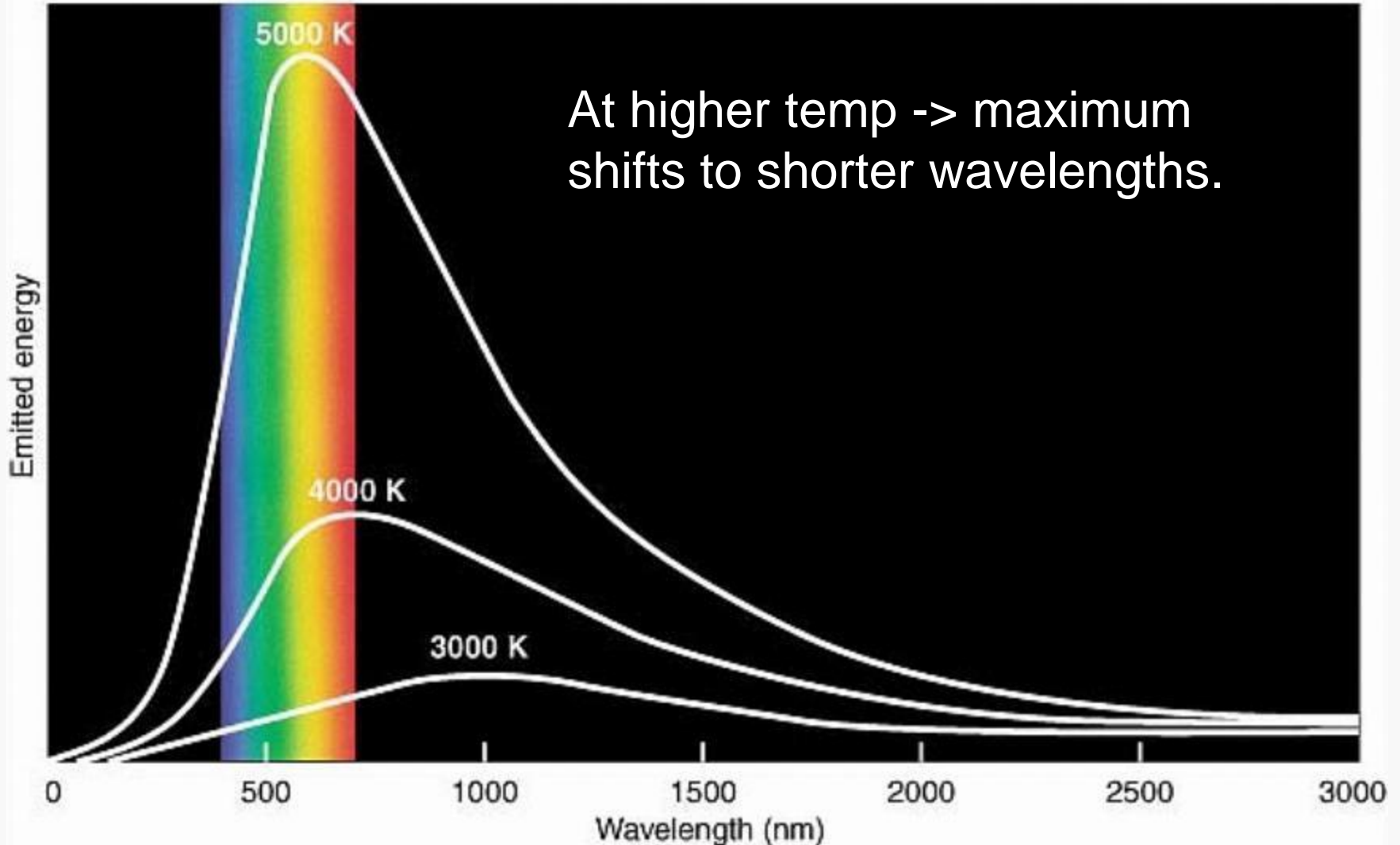
Place sample in magnetic field and can observe low energy transitions associated with changes in spin states e.g. NMR, EPR (ESR)

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  $\Delta E$  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

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

UV      vis      IR



# 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  $I$  &  $I_0$

