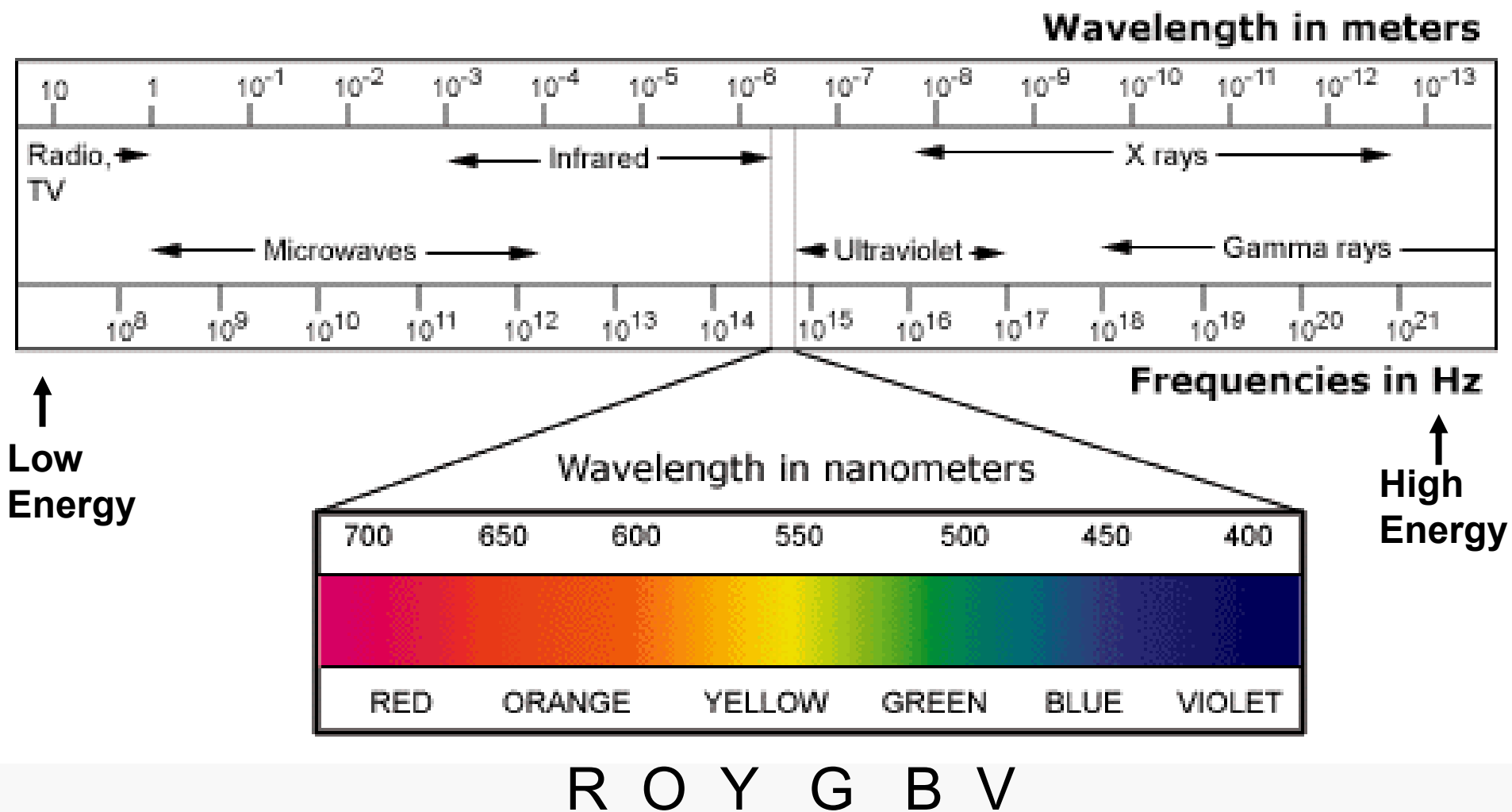


Skoog – Chapter 6

Intro to Spectrometric Methods

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

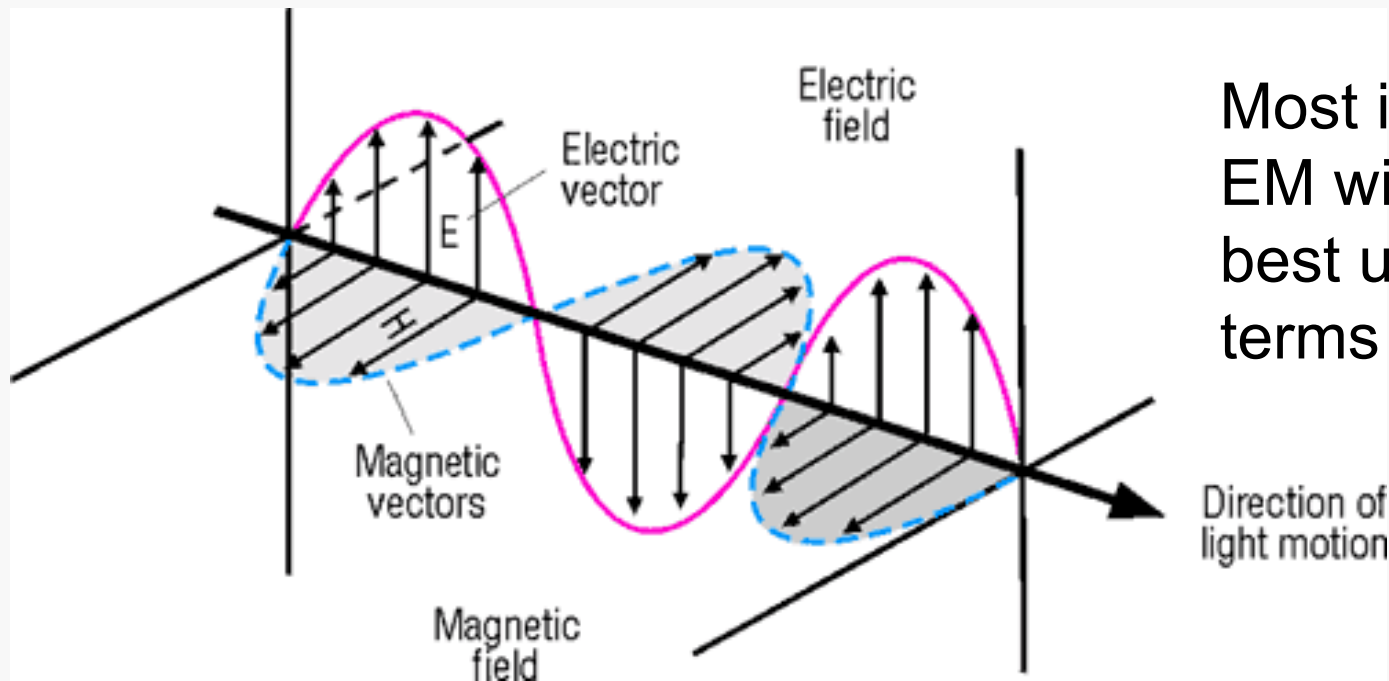
Spin States	Molecular Rotations	Molecular Vibrations	Outer Shell Electrons	Inner Shell Electrons	Nuclear Transitions
NMR EPR	Microwave Absorption Spectroscopy	Infrared Absorption Spectroscopy	UV-vis Absorption, Fluorescence	X-Ray Absorption, Fluorescence	Gamma Ray Spectroscopy



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 ν = frequency in cycles/s or Hz

λ_i = wavelength in medium i

η_i = refractive index of medium i

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

EM slows down in media other than vacuum because electric vector interacts with electric fields in the medium (matter) → 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

ω = angular frequency

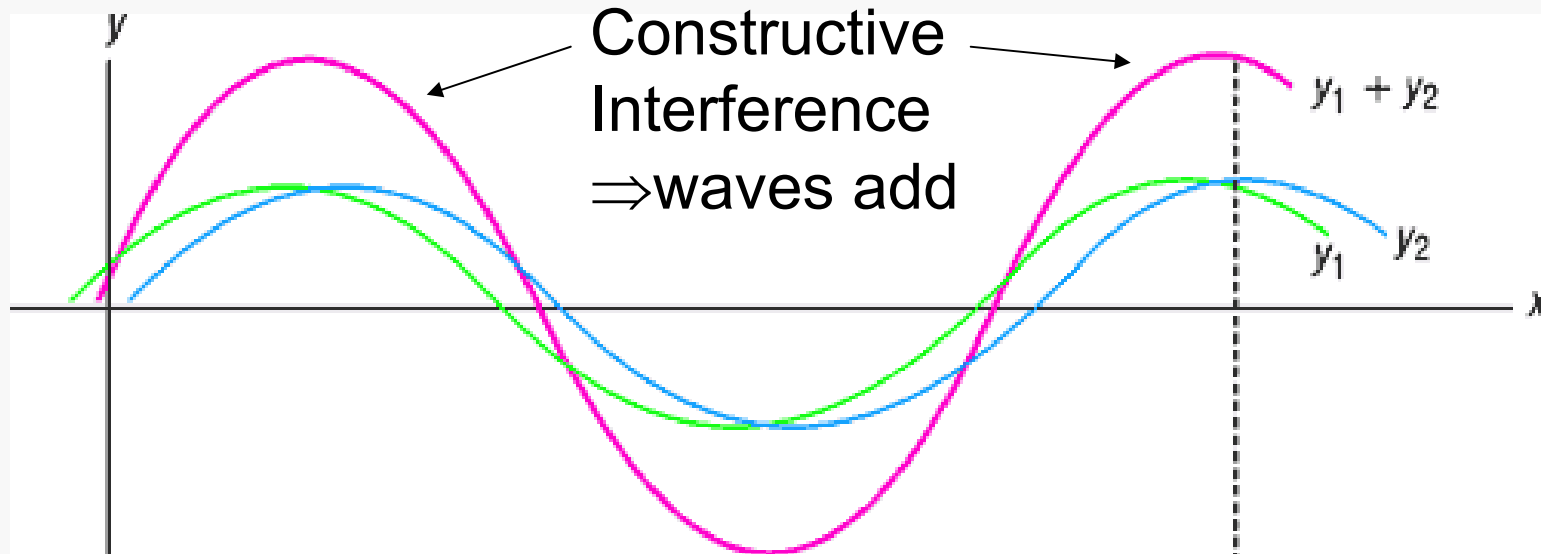
α = phase angle

t = time

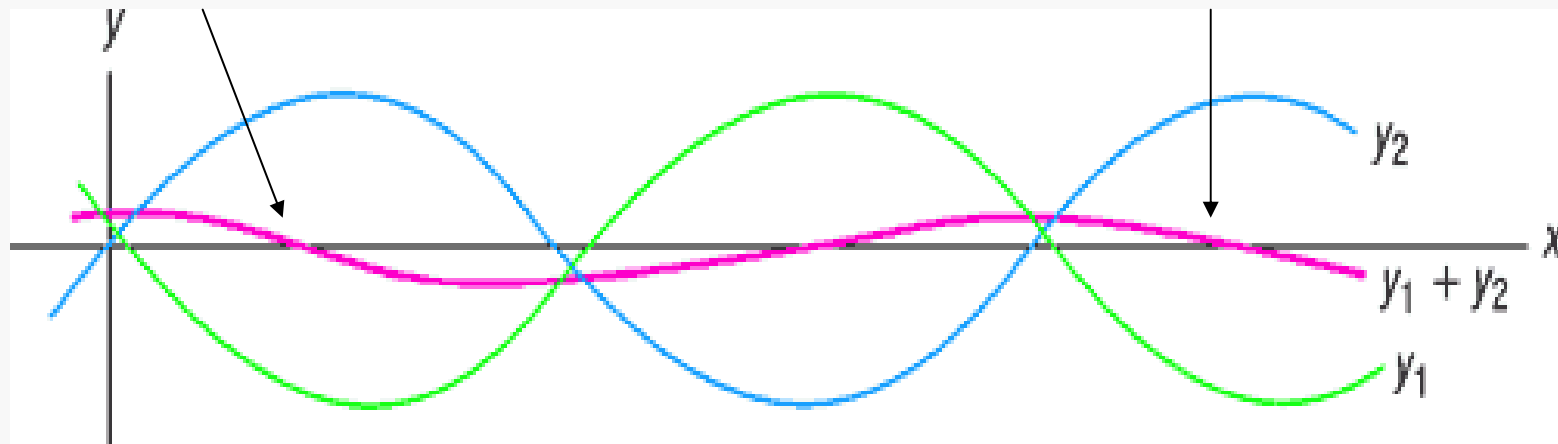
For a collection of waves the resulting position y at a given t can be calculated by

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

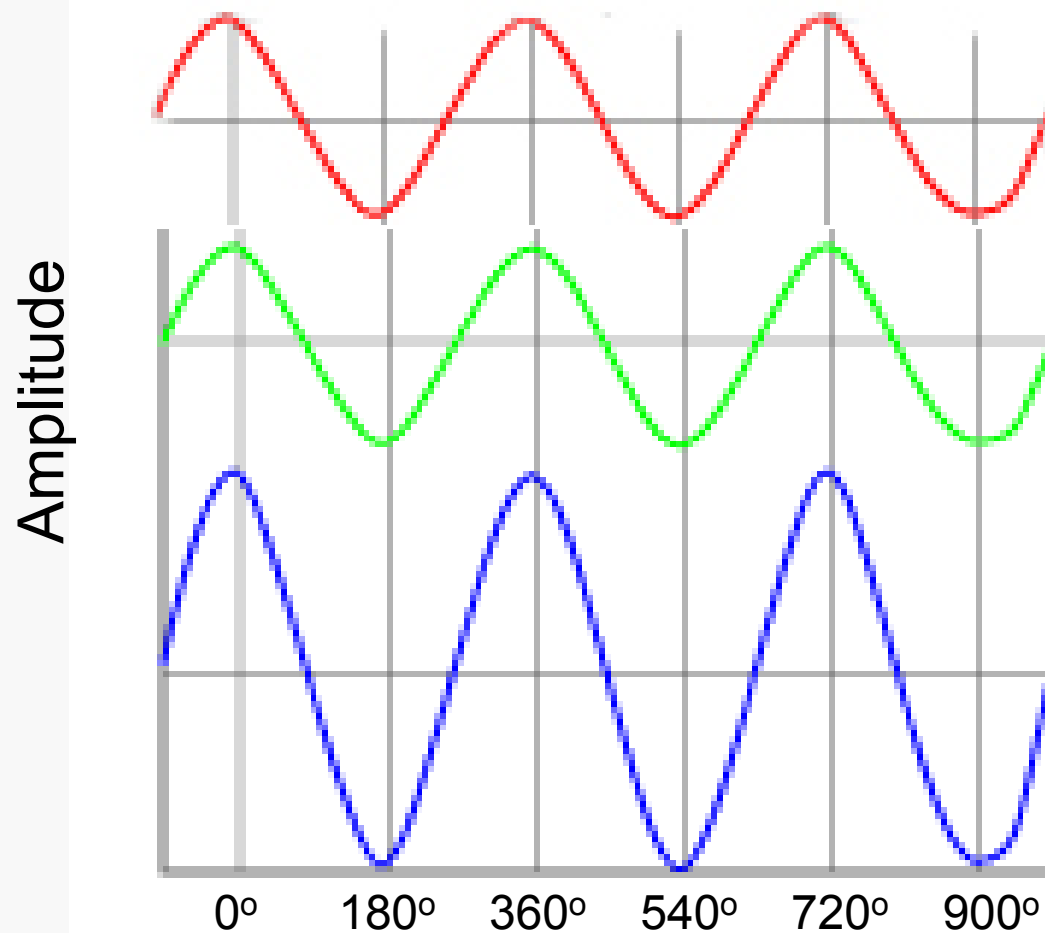
Interference - amplitude of the resulting wave depends on phase difference $\alpha_1 - \alpha_2$



Destructive Interference \Rightarrow waves cancel



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



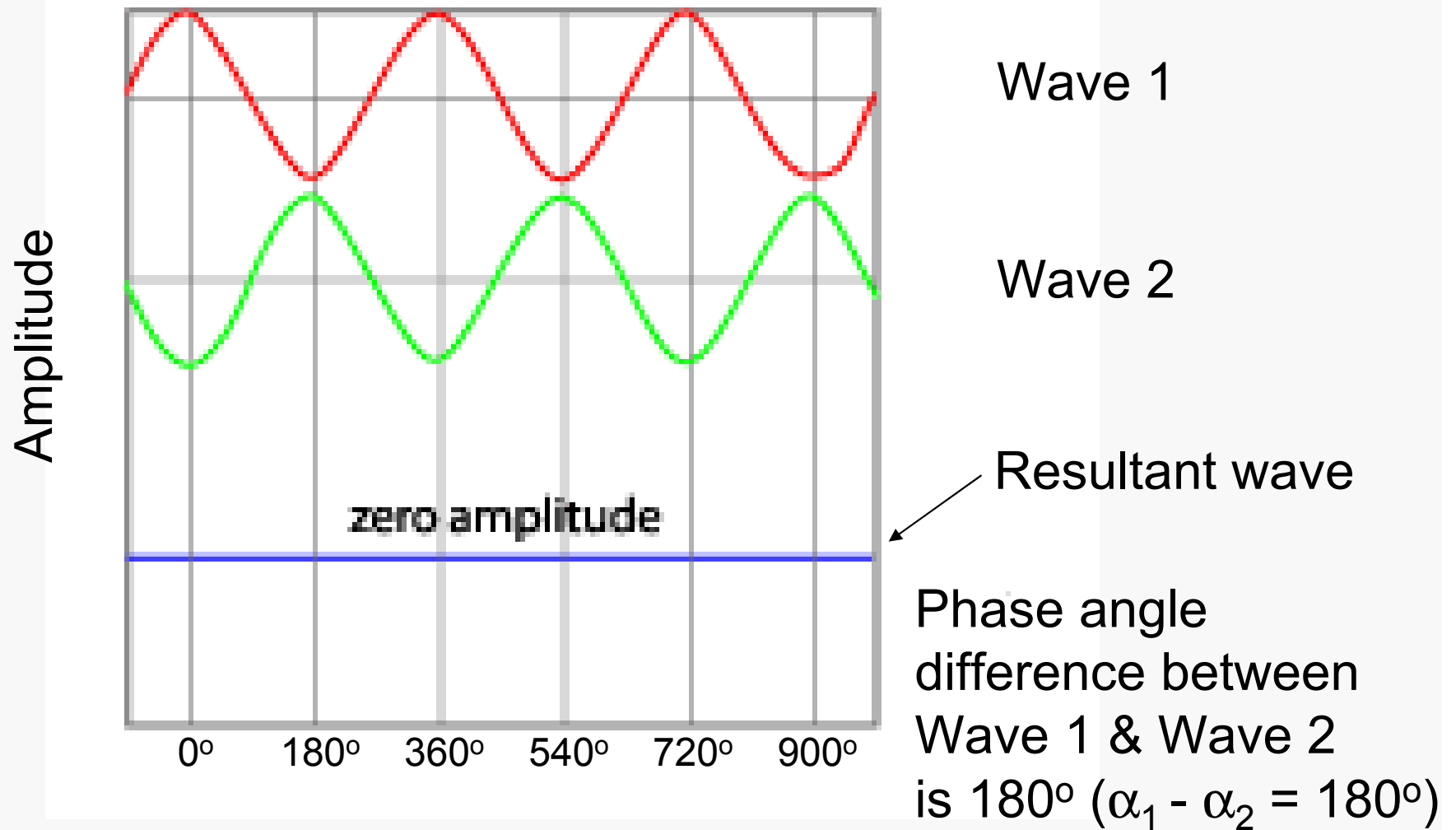
Wave 1

Wave 2

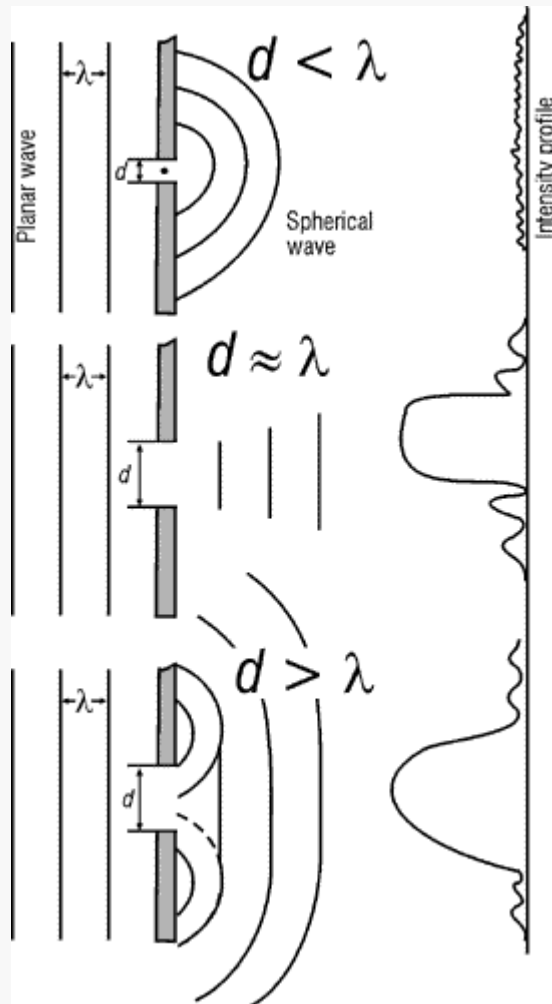
Resultant wave

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° adding of waves gives Maximum Destructive Interference



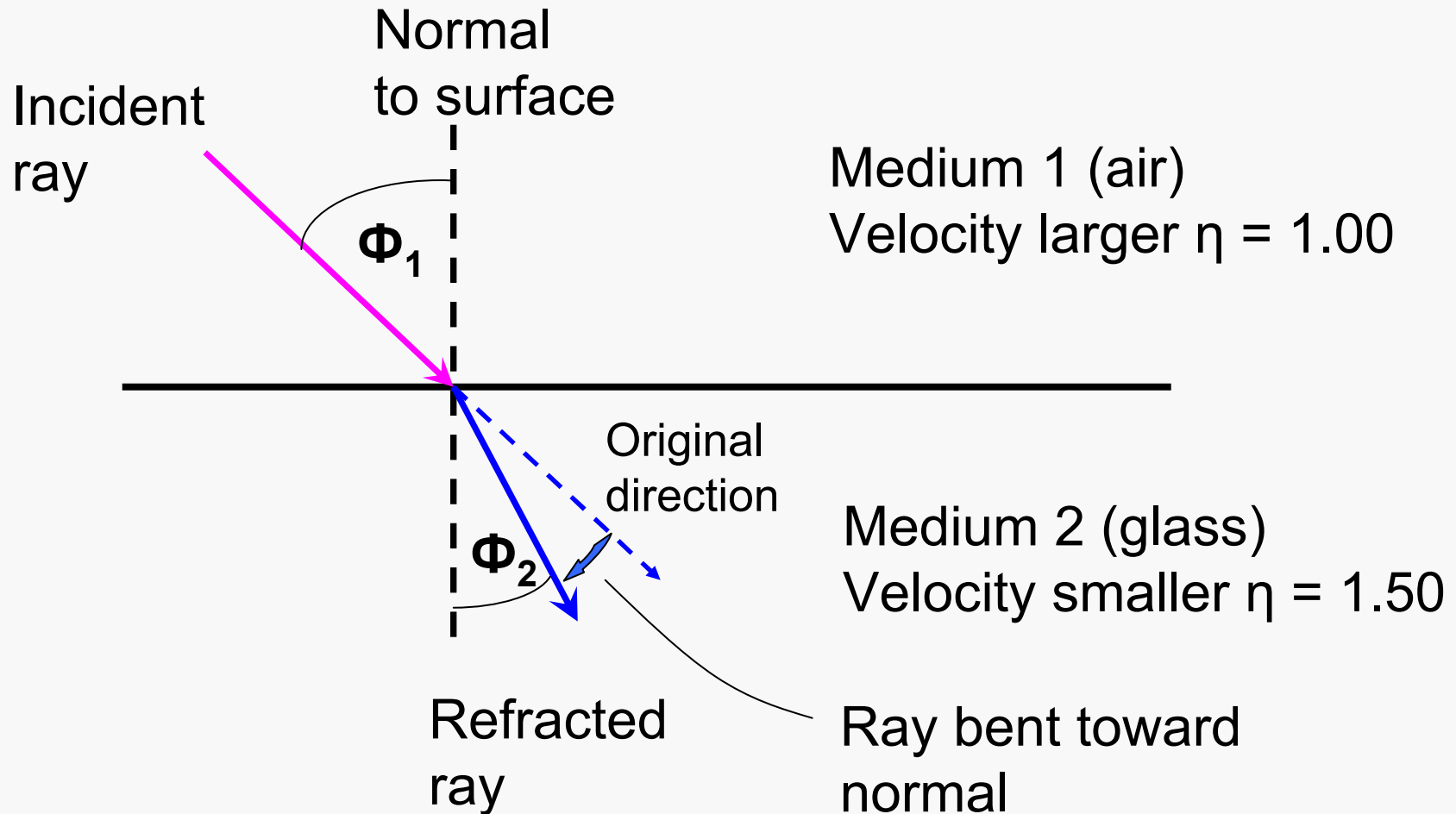
Diffraction = EM going past an edge or through a slit (2 edges) tends to spread



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



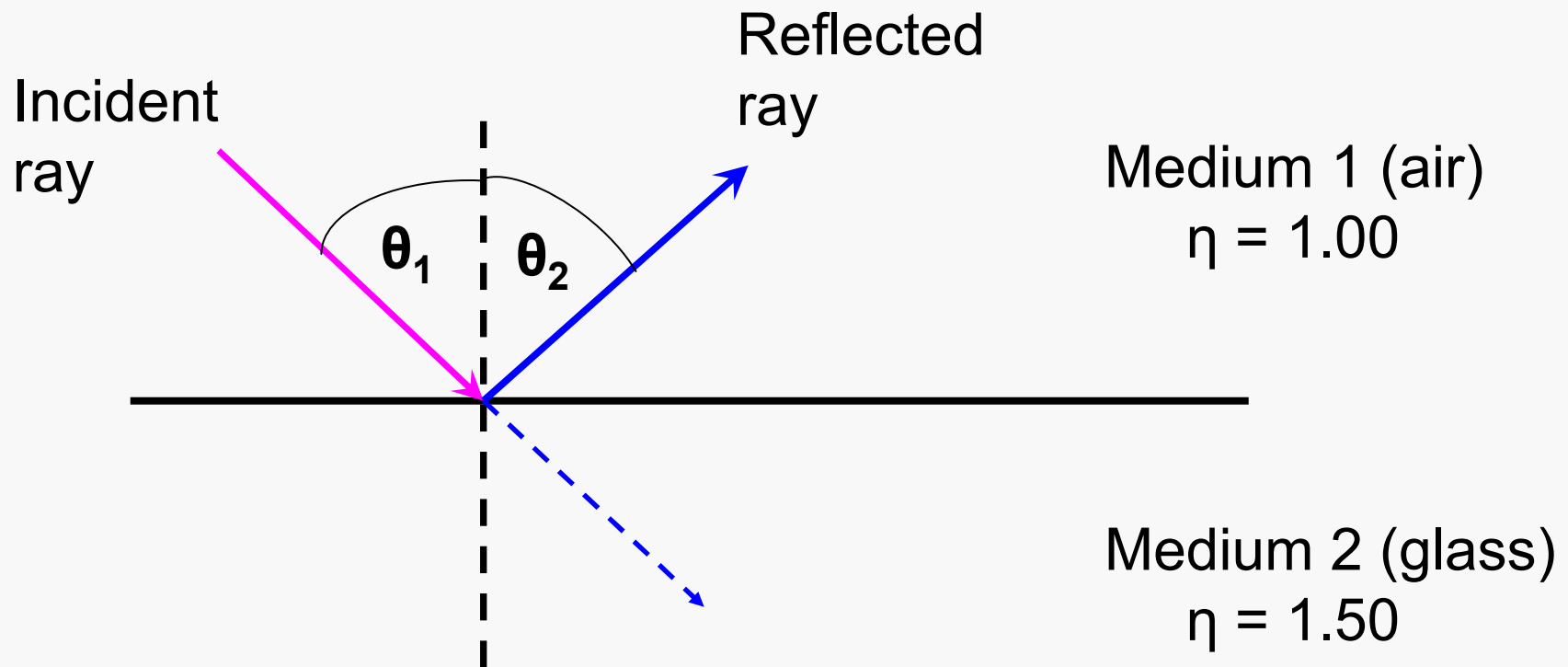
Equation for Refraction (Snell)

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

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

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

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**.

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

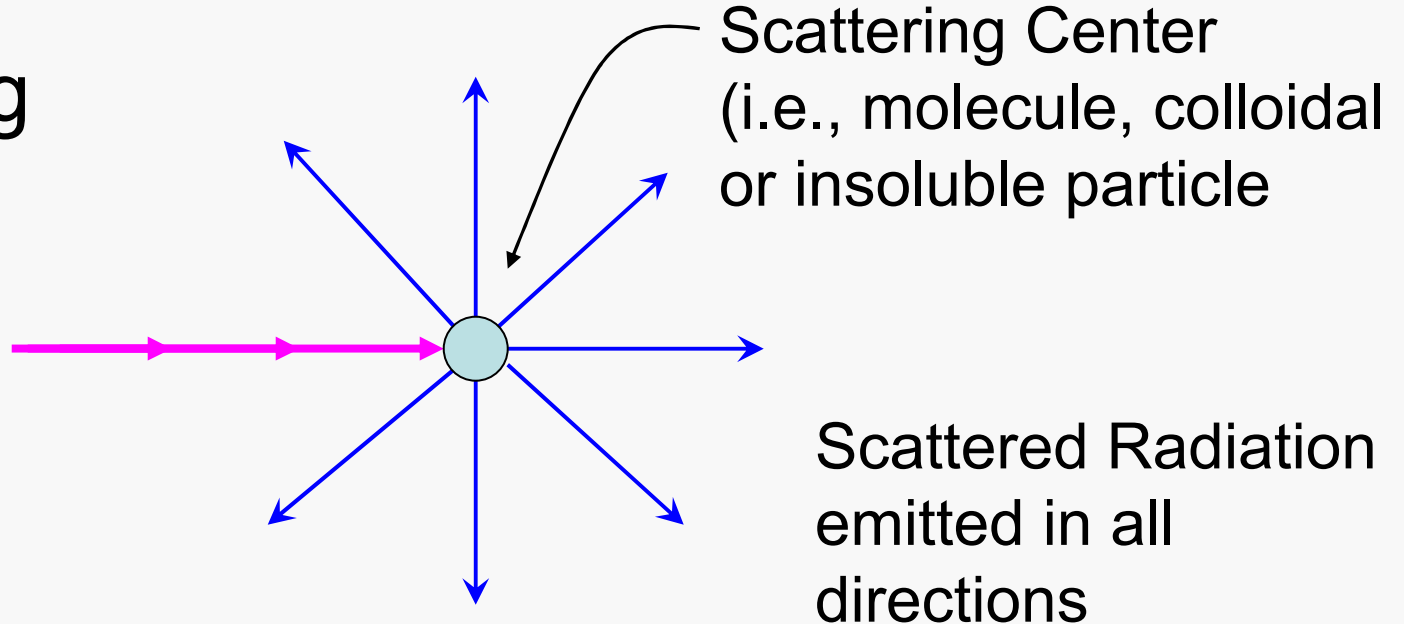
This can be described using both the wave or particle nature of light:

- 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



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

The diagram shows the Rayleigh Scattering equation with arrows pointing from descriptive labels to the corresponding terms in the formula:

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

Labels and their corresponding terms:

- scattering intensity → I_s
- wavelength → λ
- polarizability → α
- distance from scattering center to detector → r
- angle between incident beam & scattered beam → θ
- incident beam intensity → I_o

Notice the fourth power dependence on wavelength meaning short wavelengths are scattered more efficiently \Rightarrow 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 $< 10\% \lambda$ to 1.5λ

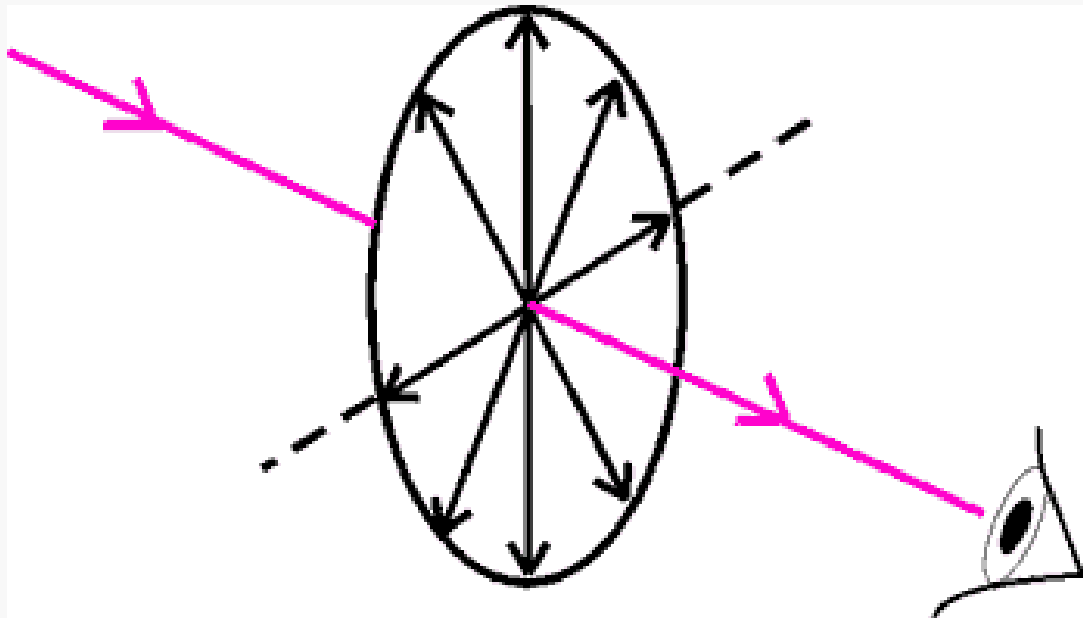
Applies in techniques like turbidimetry and nephelometry

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

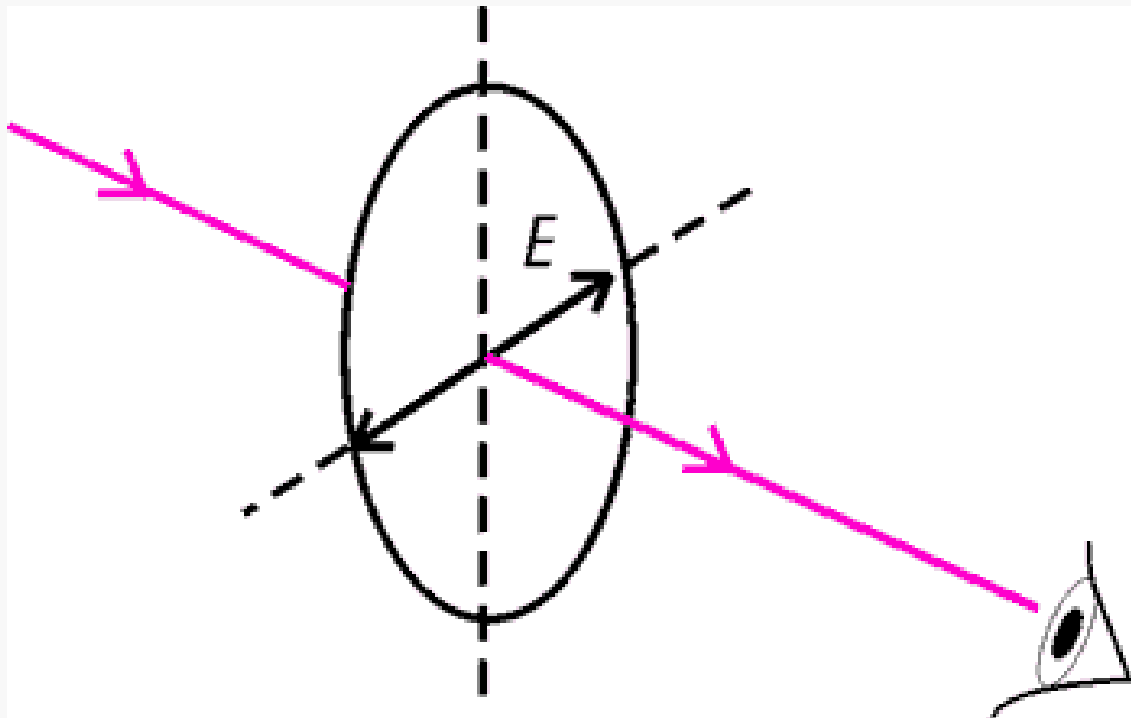
Forward scatter becomes greater than back scatter

Polarization

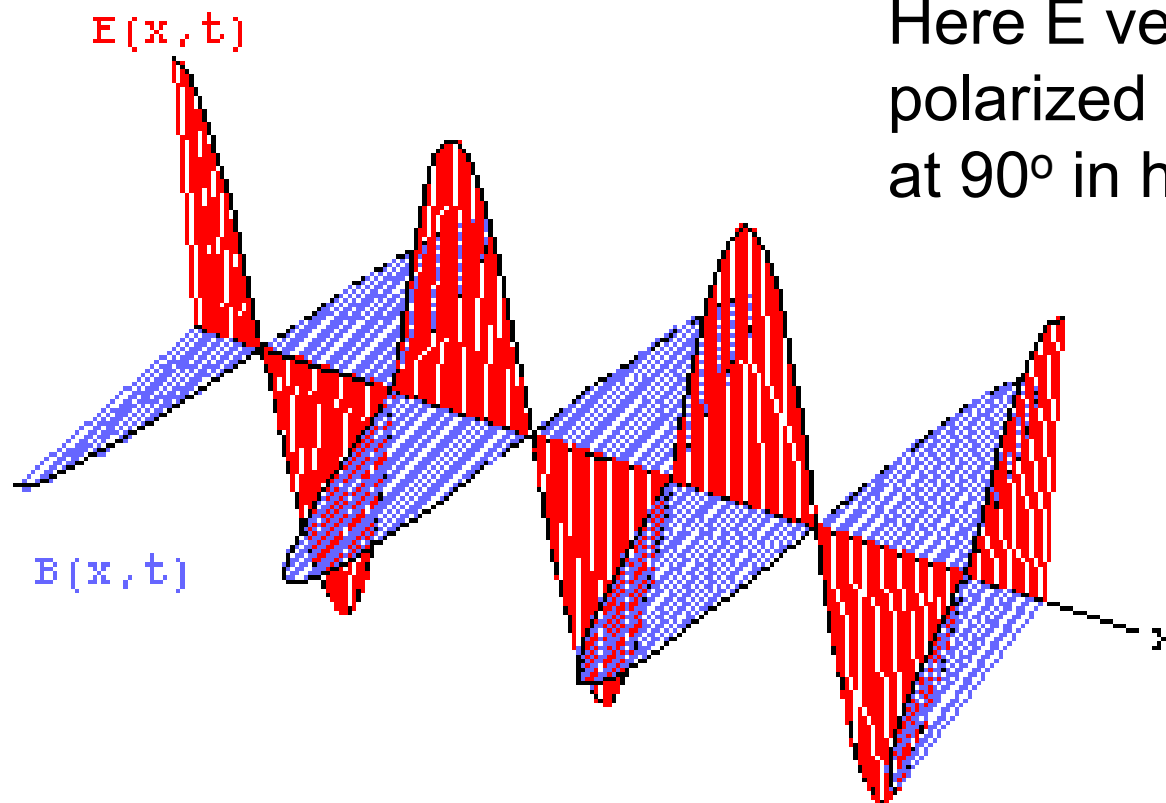
EM is said to be unpolarized if its electric vectors and magnetic vectors occur with equal amplitude in all direction



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

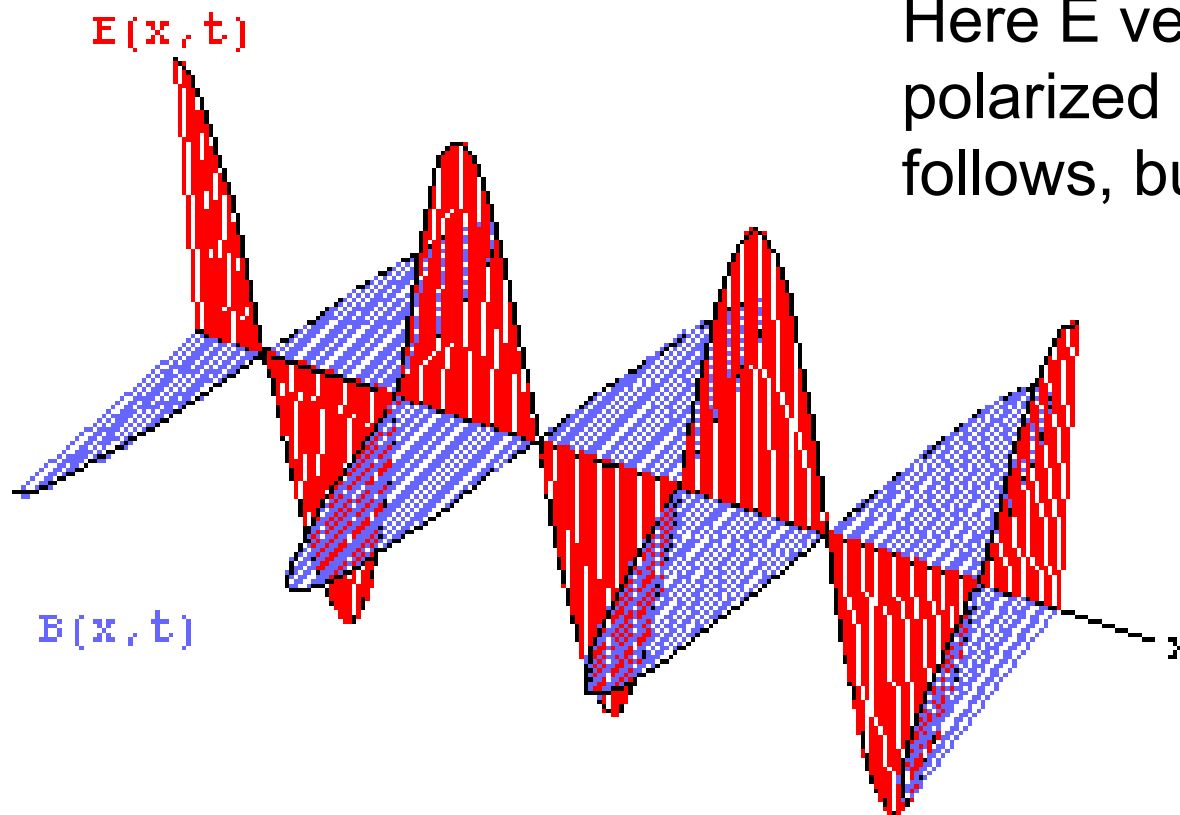


Linearly polarized light oscillates in one plane only as it moves through space



Here E vector is vertically polarized and H vector is at 90° 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

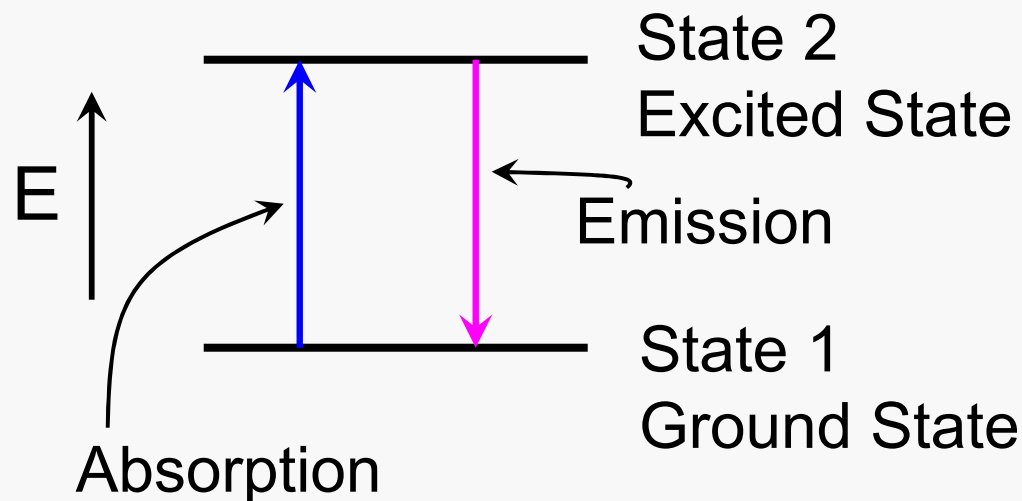
- Optical Rotatory Dispersion (ORD)
- Circular Dichroism (CD)
- Fluorescence Polarization

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 & ν is the frequency

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 Planck's constant (h)

$$\Delta E = h\nu$$

This holds for absorption & emission of radiation

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

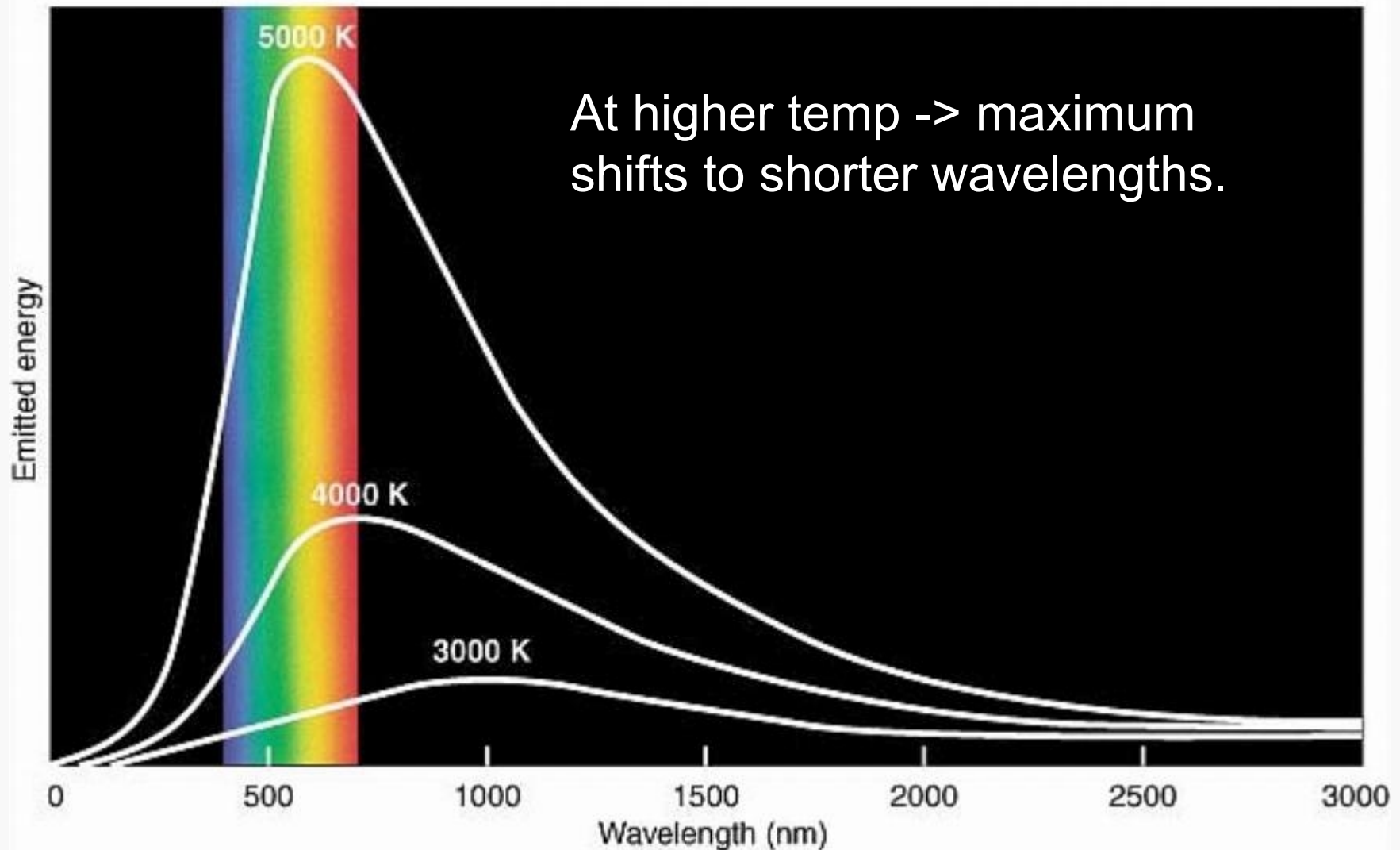
Peak at 285 nm from 3s to 5p = more E

UV-vis wavelengths promote outer shell electrons

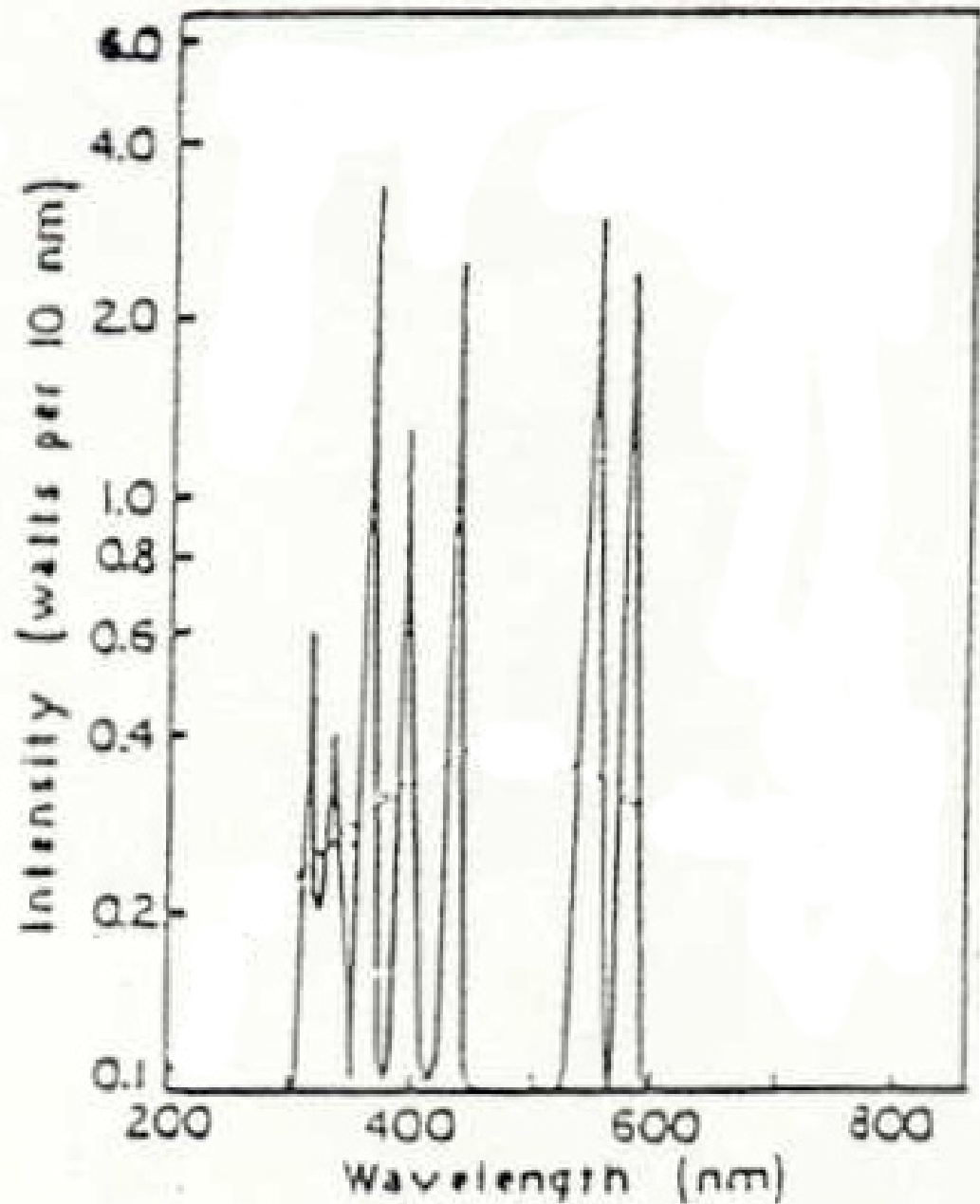
X-rays promote inner shell e^- = much more E

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

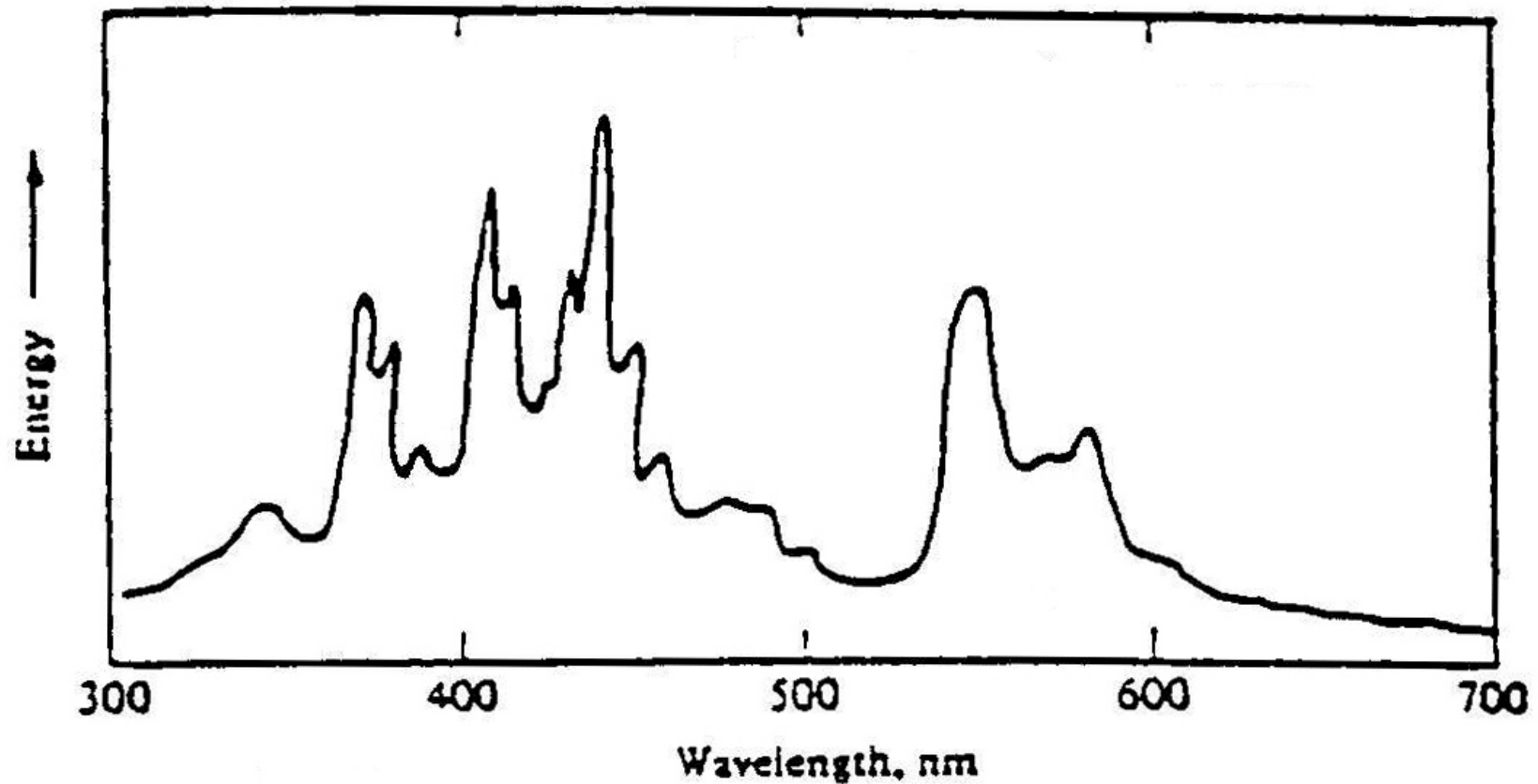
UV vis IR



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



High Pressure Mercury Spectrum – (e.g., 100 atm)



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

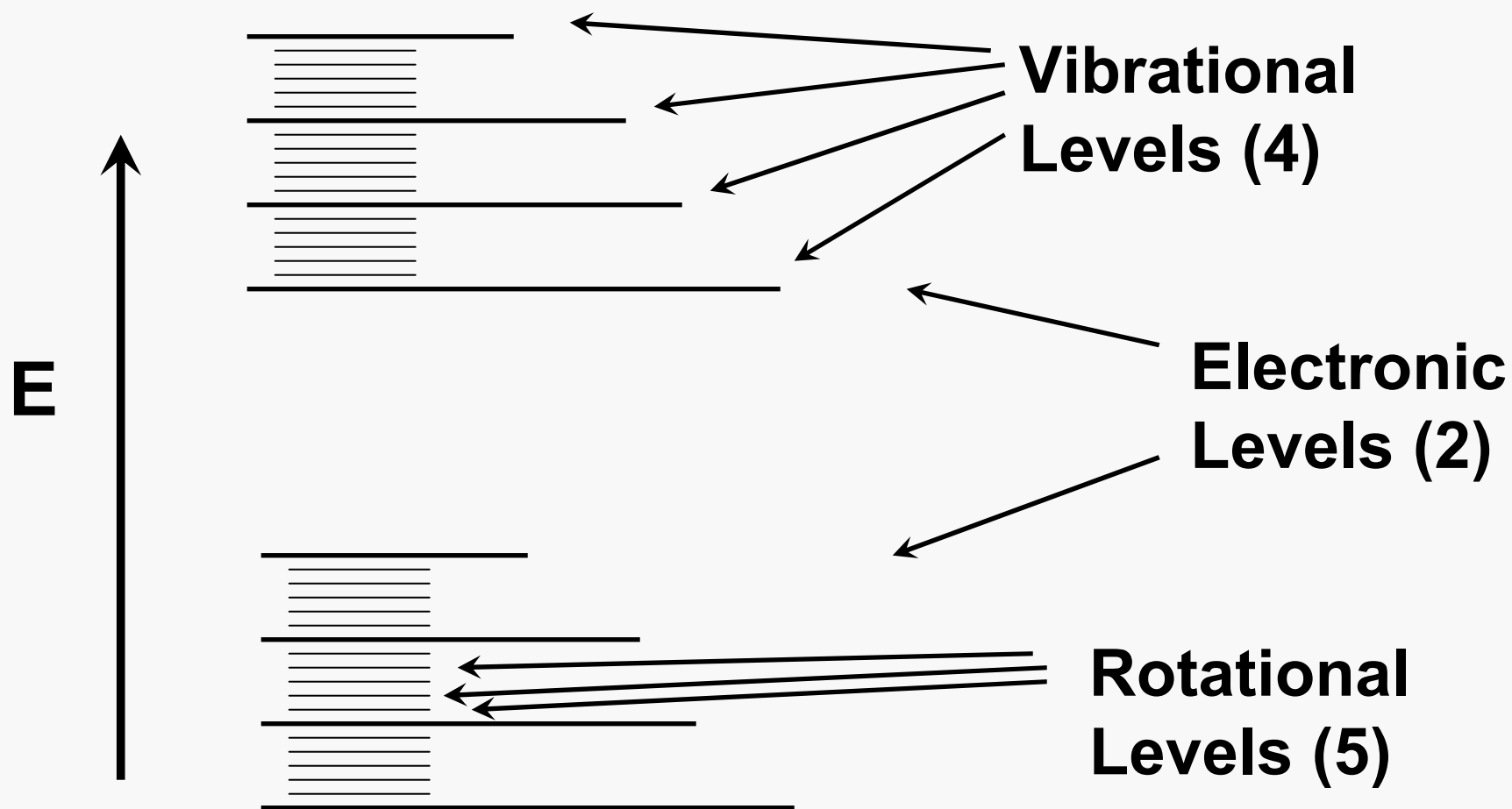
Electronic energy involves changes in energy levels of the outer electrons of a molecule

- 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 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

Quantitative Aspects of Absorption

Beer-Lambert Law (or Beer's Law)

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

Transmittance $\rightarrow T = \frac{I}{I_0}$

ϵ ← molar absorptivity
 C ← concentration
 b ← path length

$\%T = T \times 100$

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 ϵ 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

