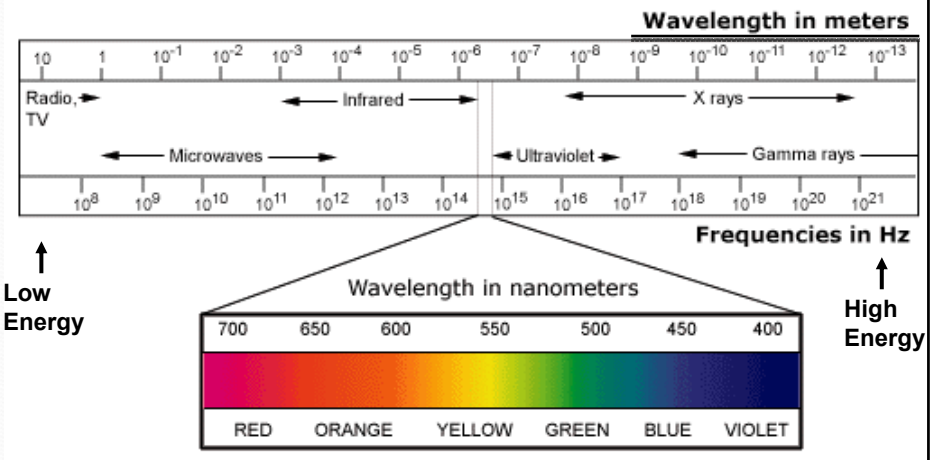
# Skoog – Chapter 6 Introduction to Spectrometric Methods

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

- Spectrometric method atomic
- molecular spectroscopy
- Interaction of electromagnetic radiation and matter
- Interaction between matter and other forms of energy
- Measurement of intensity of radiation by photoelectronic transducer or other electronic device

Electromagnetic radiation is classified into several types according to the frequency of its wave; these types include (in order of increasing frequency and decreasing wavelength): radio waves, microwaves, terahertz radiation, infrared radiation, visible light, ultraviolet radiation, X-rays and gamma rays. A small and somewhat variable window of frequencies is sensed by the eyes of various organisms; this is what we call the visible spectrum, or light.

| 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 |



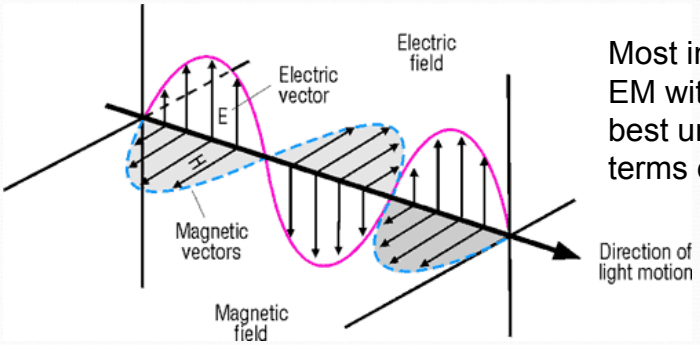

R O Y G B V

**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

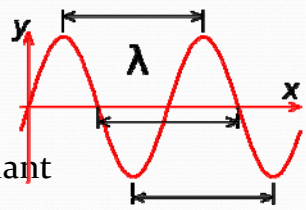
Sinusoidal wave model: wavelength, frequency, velocity and amplitude
Particle model: frequency of the wave is proportional to the particle's energy




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
Determined by source and remain invariant

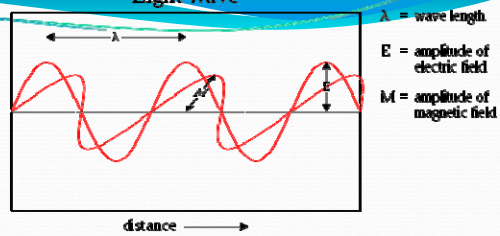
$\lambda_i$ = wavelength in medium i

$\eta_i$ = refractive index of medium i

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

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

## Light wave




Wave Equation

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

Where $y$ = magnitude of wavelength at time t

$A$ = amplitude of maximum value for y

$\omega$ = angular frequency = $2\pi\upsilon$

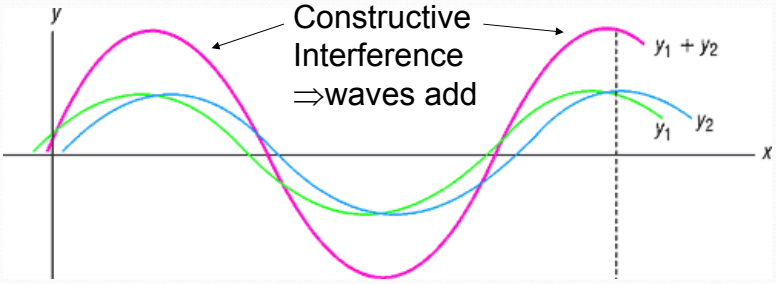
$\phi$ = phase angle

$t$ = time

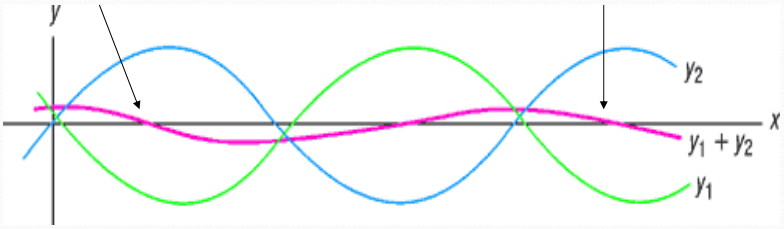
For a collection of waves the resulting position y at a given t can be calculated by

$$y = A_1 \sin(\omega_1 t + \phi_1) + A_2 \sin(\omega_2 t + \phi_2) + \ldots$$

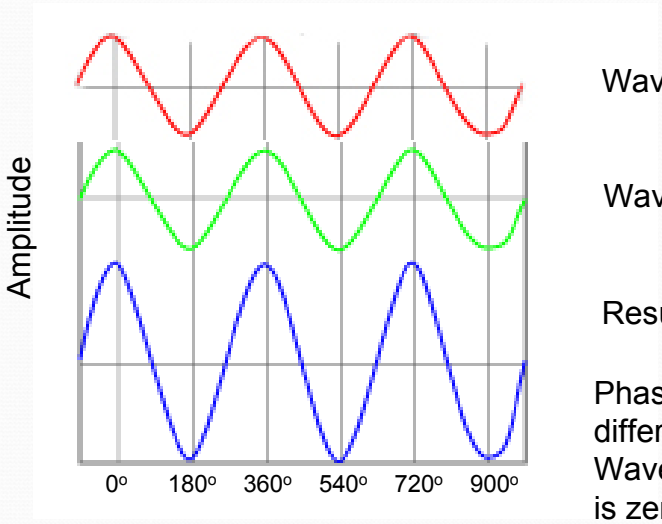
**Interference** - amplitude of the resulting wave depends on phase difference $\alpha_1 - \alpha_2$




Destructive Interference ⇒ waves cancel

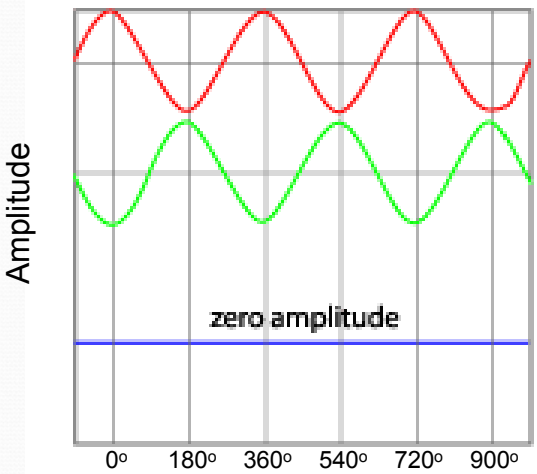



At $\alpha_1 - \alpha_2 = 0^o$ adding of waves gives Maximum Constructive Interference




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

## When $\alpha_1 - \alpha_2 = 180^o$ or $540^o$ adding of waves gives <u>Maximum Destructive Interference</u>




Wave 1

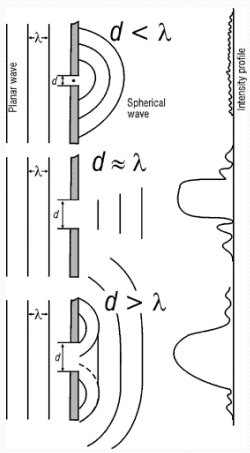
Wave 2

Resultant wave

Phase angle difference between Wave 1 & Wave 2 is $180^o$ ($\alpha_1 - \alpha_2 = 180^o$)

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

apparent bending of waves around small obstacles and the spreading out of waves past small openings.




Diffraction occurs with all waves, including sound waves, water w aves, and electromagnetic waves such as visible light, x-rays and radio waves.

The combination of diffraction effects & interference effects are important in spectroscopy for
1) diffraction gratings
2) slit width considerations

**Difference is a consequence of Interference**

interference is the addition (superposition) of two or more waves that results in a new wave pattern. Interference usually refers to the interaction of waves that are correlated or coherent with each other, either because they come from the same source or because they have the same or nearly the same frequency.

$\delta = \pm K \lambda$

$\delta$ is OE-OD

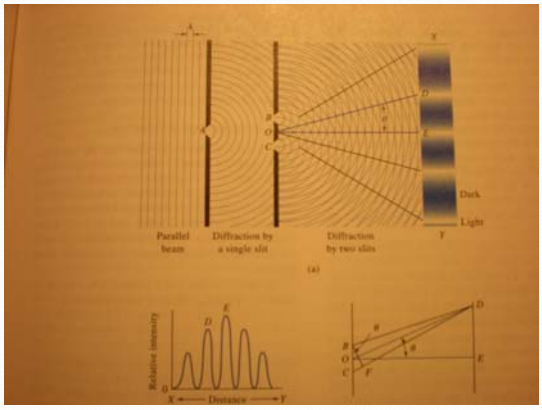
$\lambda$ is the wavelength of the light

Light band

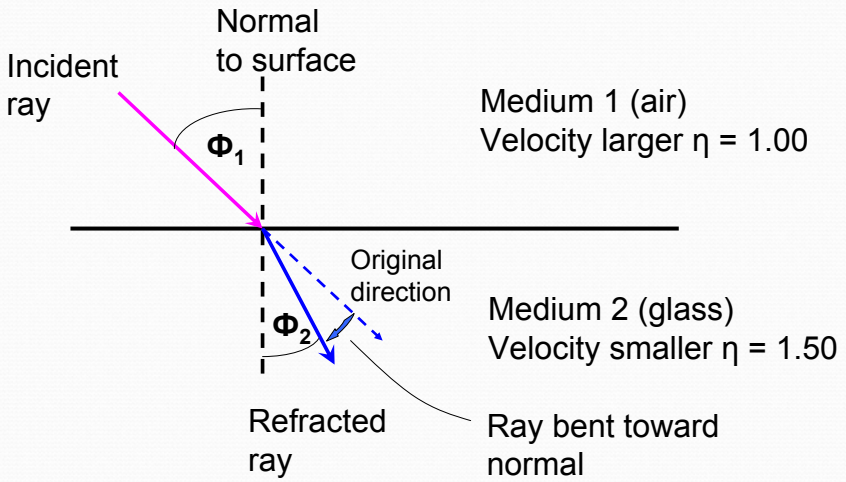
$\delta = \pm(2K+1)\lambda/2$

Maximum deconstructive

Dark band




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

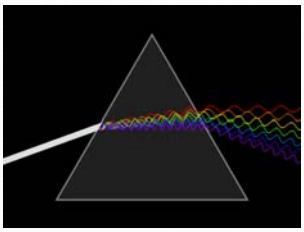


## Equation for Refraction (Snell)

$$\frac{\sin \Phi_1}{\sin \Phi_2} = \frac{v_1}{v_2} = \frac{\eta_2}{\eta_1} = \eta_2$$

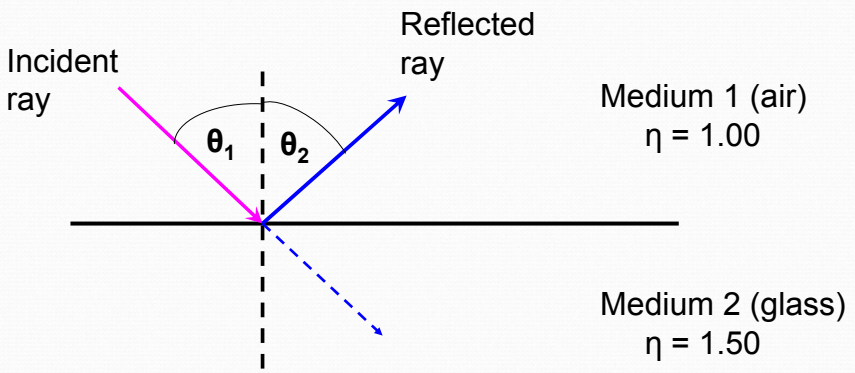
if medium 1 is air $\eta_1 = 1.0$

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 $\eta$ 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**.

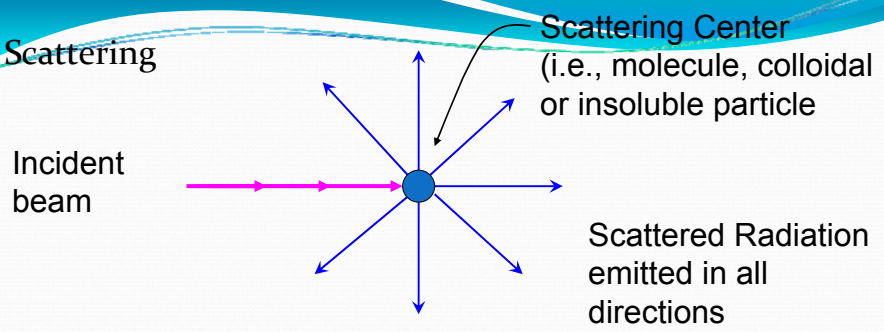
**Scattering** = EM interacts with matter and changes direction, usually without changing energy

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

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

scattering intensity → $I_s$

polarizability → $\alpha$

angle between incident beam & scattered beam → $\theta$

wavelength → $\lambda$

distance from scattering center to detector → $r$

incident beam intensity → $I_o$

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

Polarizability ($\alpha$) is 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 $\lambda$

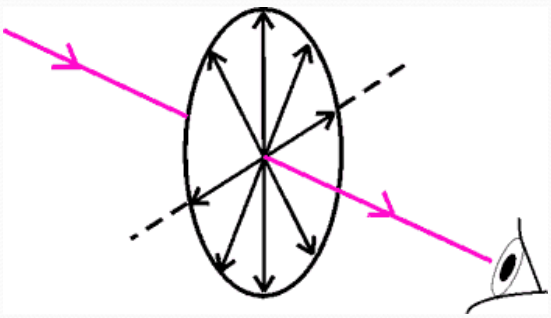
Applies in techniques like turbidimetry and nephelometry

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

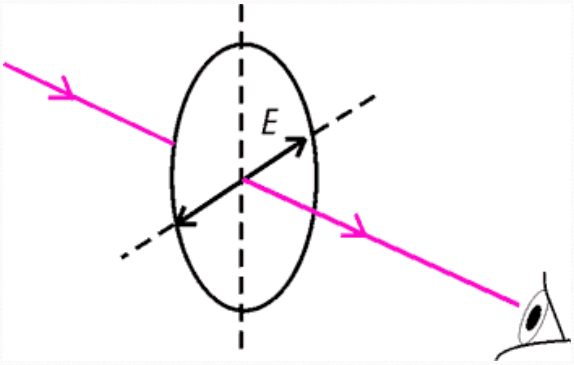
Forward scatter becomes greater than back scatter

**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

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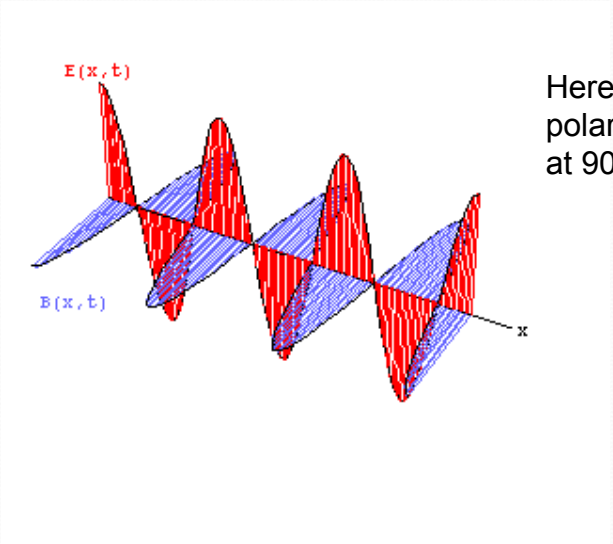
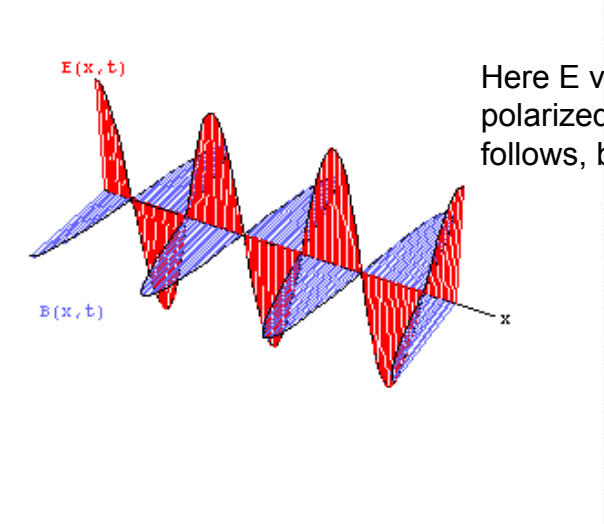



Here E vector is vertically polarized and H vector is at 90° in horizontal plane

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

EM radiation emitted or absorbed, a permanent energy transfer from emitting object or adsorbing media happens. EM need to be treated as discrete particles as photons or quanta.

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 Plank's constant (h)

$$\Delta E = h\nu = hc/\lambda$$

plank constant = $6.626 \times 10^{-34}$ j·s

This holds for absorption & emission of radiation

## Postulates of QM:

- 1. Atoms, ions and molecules exist in discrete energy states only
- $E_0$ = ground state
- $E_1$, $E_2$ , $E_3$ … = excited states
- Excitation can be electronic, vibrational or rotational
- Energy levels for atoms, ions or molecules different.
- Measuring energy levels gives means of identification – spectroscopy

- 2. When an atom, ion or molecule changes energy state, it absorbs or emits energy equal to the energy difference
- $\Delta E = E_1 - E_0$

- 3. The wavelength or frequency of radiation absorbed or emitted during a *transition* proportional to $\Delta E$
- $\Delta E = h \cdot \nu = h \cdot c/\lambda$

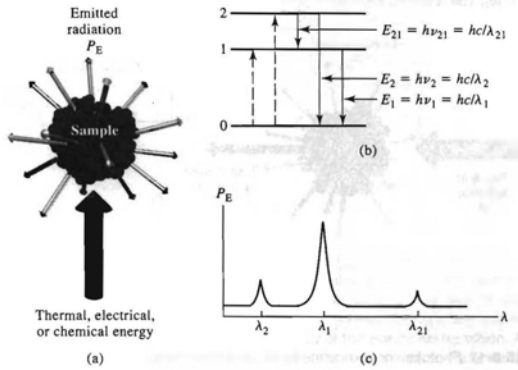



**FIGURE 6-15** Emission or chemiluminescence processes. In (a), the sample is excited by the application of thermal, electrical, or chemical energy. These processes do not involve radiant energy and are hence called nonradiative processes. In the energy level diagram (b), the dashed lines with upward-pointing arrows symbolize these nonradiative excitation processes, while the solid lines with downward-pointing arrows indicate that the analyte loses its energy by emission of a photon. In (c), the resulting spectrum is shown as a measurement of the radiant power emitted $P_E$ as a function of wavelength, $\lambda$.

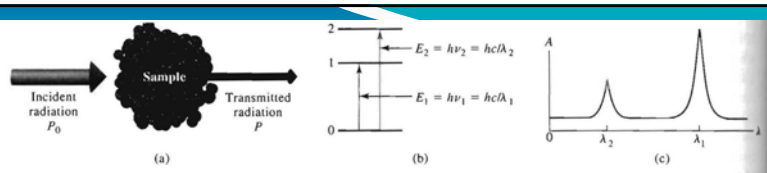



**FIGURE 6-16** Absorption methods. Radiation of incident radiant power $P_0$ can be absorbed by the analyte, resulting in a transmitted beam of lower radiant power $P$. For absorption to occur, the energy of the incident beam must correspond to one of the energy differences shown in (b). The resulting absorption spectrum is shown in (c).

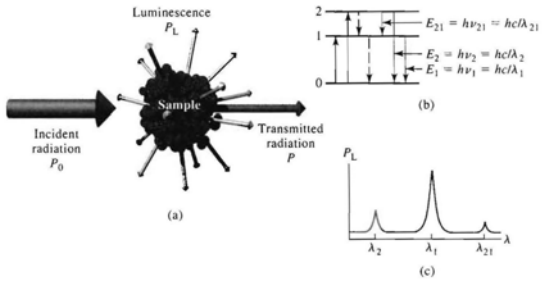



**FIGURE 6-17** Photoluminescence methods (fluorescence and phosphorescence). Fluorescence and phosphorescence result from absorption of electromagnetic radiation and then dissipation of the energy emission of radiation (a). In (b), the absorption can cause excitation of the analyte to state 1 or state 2. Once excited, the excess energy can be lost by emission of a photon (luminescence, shown as solid line) or by nonradiative processes (dashed lines). The emission occurs over all angles, and the wavelengths emitted (c) correspond to energy differences between levels. The major distinction between fluorescence and phosphorescence is the time scale of emission, with fluorescence being prompt and phosphorescence being delayed.

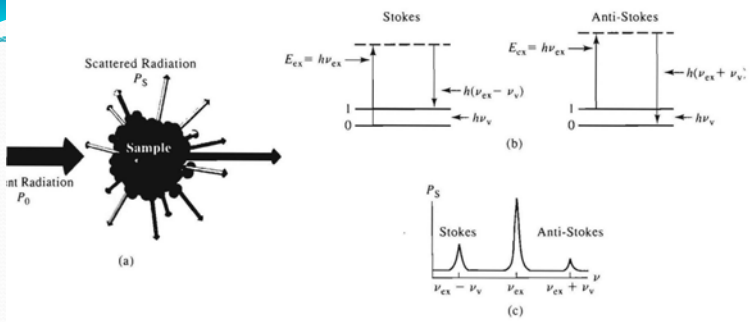
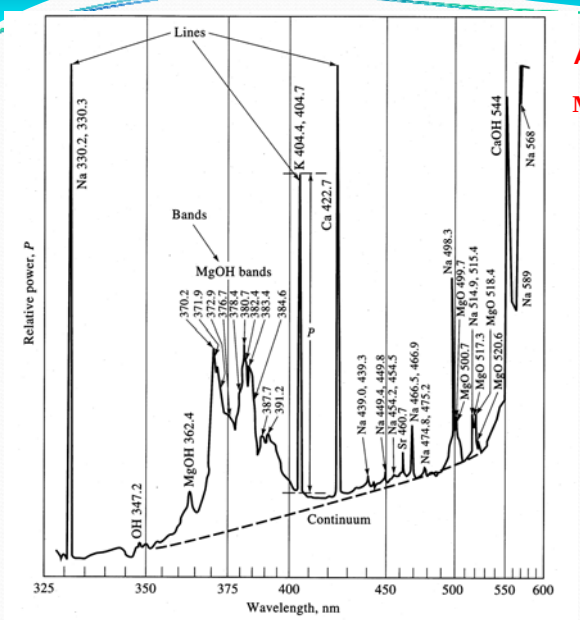



**FIGURE 6-18** Inelastic scattering in Raman spectroscopy. (a) As incident radiation of frequency $\nu_{ex}$ impinges on the sample, molecules of the sample are excited from one of their ground vibrational states to a higher so-called *virtual state*, indicated by the dashed level in (b). When the molecule relaxes, it may return to the first vibrational state as indicated and emit a photon of energy $E = h(\nu_{ex} - \nu_v)$ where $\nu_v$ is the frequency of the vibrational transition. Alternatively, if the molecule is in the first excited vibrational state, it may absorb a quantum of the incident radiation, be excited to the virtual state, and relax back to the ground vibrational state. This process produces an emitted photon of energy $E = h(\nu_{ex} + \nu_v)$. In both cases, the emitted radiation differs in frequency from the incident radiation by the vibrational frequency of the molecule $\nu_v$. (c) The spectrum resulting from the inelastically scattered radiation shows three peaks: one at $\nu_{ex} - \nu_v$ (Stokes), a second intense peak at $\nu_{ex}$ for radiation that is scattered without a frequency change, and a third (anti-Stokes) at $\nu_{ex} + \nu_v$. The intensities of the Stokes and anti-Stokes peaks give quantitative information, and the positions of the peaks give qualitative information about the sample molecule.

## Emission of radiation



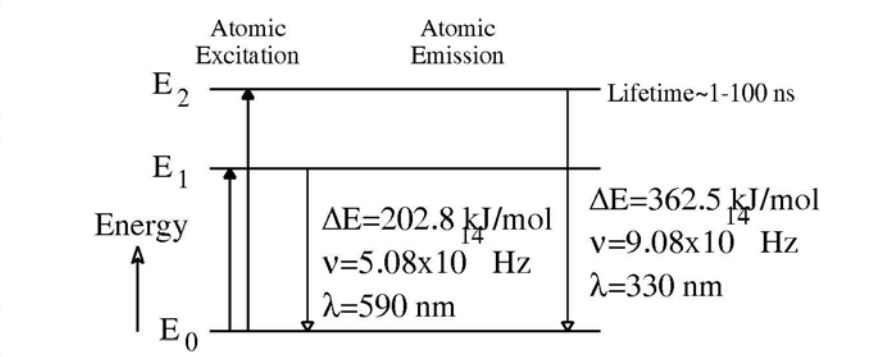

**Atom**: **line** emission spectra

**Molecule**:

vibrational and rotational transitions –
**band** emission spectra

Continuum Spectra:

# Line Spectra

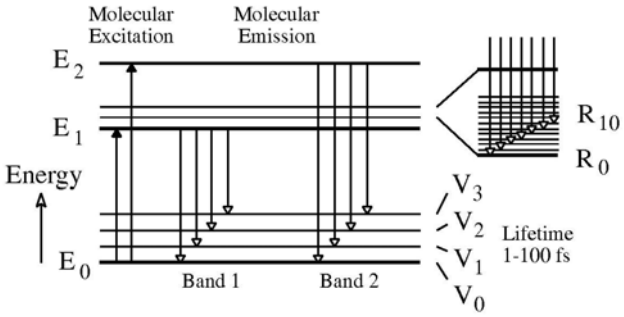



**line** emission spectra

Inner shell (core) electrons (1s←2p) - x-rays photons

Outer shell (valence) electrons (3d←4p) - UV/vis photons

# Band Spectra




vibrational and rotational transitions - **band** emission spectra

ΔE (Electronic) >100 MJ/mol (x-ray) to <100 kJ/mol (UV-vis)

ΔE (Vibrational) <1 to <100 kJ/mol (IR)

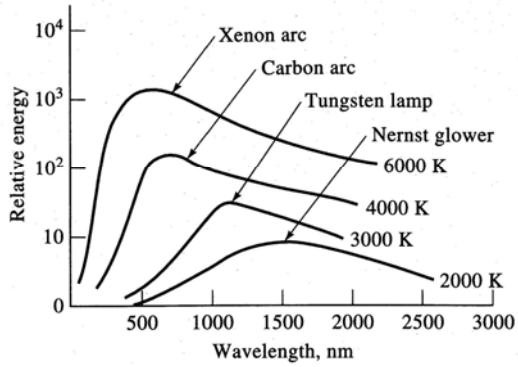
ΔE (Rotational) 10-100 J/mol (microwave)

Continuum Spectra:

Very broad band spectra in emission from solids

Produced by *blackbody* radiation - thermal excitation and relaxatio of many vibrational (and rotational) levels.

Blackbody Spectrum (Fig 6-18)

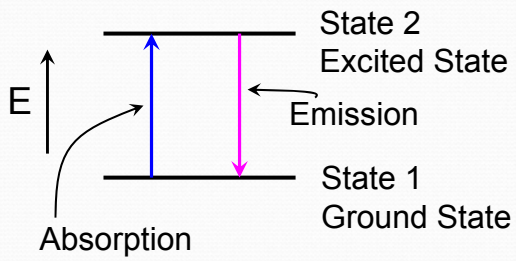



## Absorption and Emission

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

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

For UV-vis must consider:

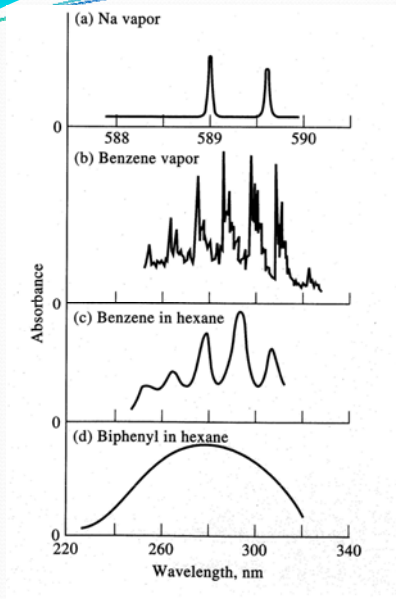
- electronic energy
- vibrational energy
- rotational energy

Ignore translational energy

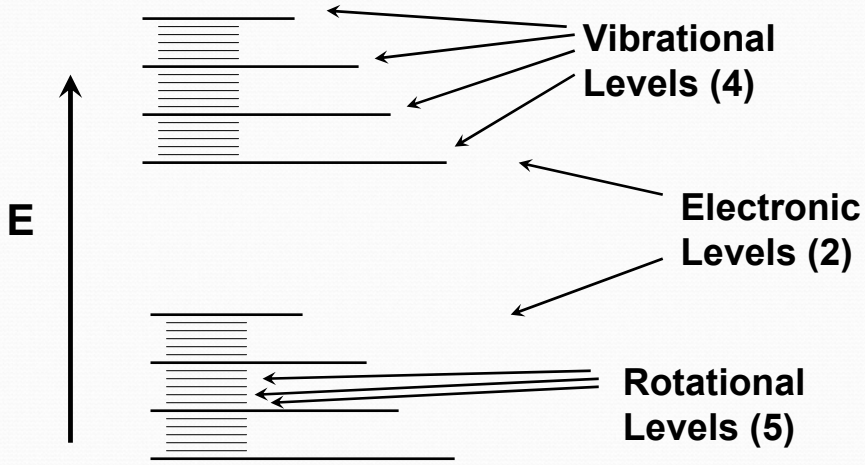
**Molecular Absorption** – more complex than atomic absorption because molecules have many more possible transitions

Absorption spectra affected by

| (1) number of atoms in molecule | (2) solvent molecules |
| --- | --- |
| more features | blurred features |




## Simplified Energy Level Diagram




For each electronic state - many vibrational states

For each vibrational state - many rotational states

→many features

- **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

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

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

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

Relaxation Processes:

Lifetime of excited state is short (fs→ms) - relaxational processes return excited species to ground state

Nonradiative relaxation

many small collisional relaxations

tiny temperature rise of surrounding species

Radiative relaxation (emission)

fluorescence (<$10^{-5}$ s) and phosphorescence (>$10^{-5}$ s)

Resonance fluorescence

produces emission at same energy/frequency/wavelength as absorption

common for atoms (no V or R levels)

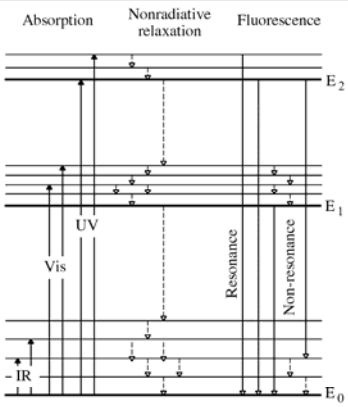
Non-resonance fluorescence

produces emission at lower energy (lower frequency/longer wavelength) than absorption (Stokes shift)

common in molecules - vibrational relaxation occurs before fluorescence

Phosphorescence

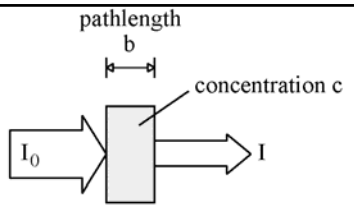
Produced by long-lived electronic state (up to hours)




Excitation methods:

(i) EM radiation
(ii) spark/discharge/arc
(iii) particle bombardment (electrons, ions... )
(iv) chemiluminescence (exothermic chemical reaction generates excited products)

# Quantitative Aspects of Absorption




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

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

Absorbance $A = -\log T$

$= -\log \frac{I}{I_0}$

$= \log \frac{I_0}{I}$

Examples:

T=1.00 (100 %T), A=0.00

T=0.10 (10 %T), A=1.00

T=0.001 (0.1 %T), A=3.00

# Quantitative Aspects of Absorption

Beer's Law:

Basis for absorbance spectrophotometry

$A \propto c$ and $A \propto b$

so $A \propto b \cdot c$

$A = a \cdot b \cdot c$

proportionality constant *absorptivity* - units of L/g·cm

If units of concentration are M (mol/L) then use *molar absorptivity* ε

$A = \varepsilon \cdot b \cdot c$

units of L/mol·cm

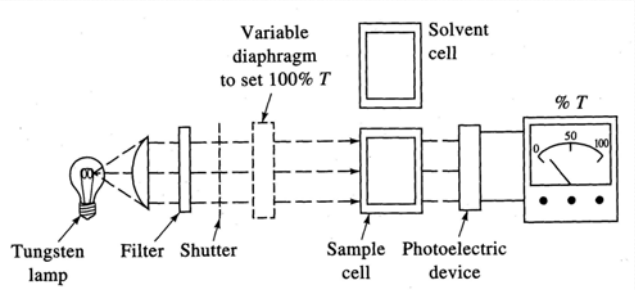
Phenomena used for optical measurements,

(1) Absorption (2) Emission (3) Luminescence (Fluorescence, Phosphorescence, Chemiluminescence (4)Scattering

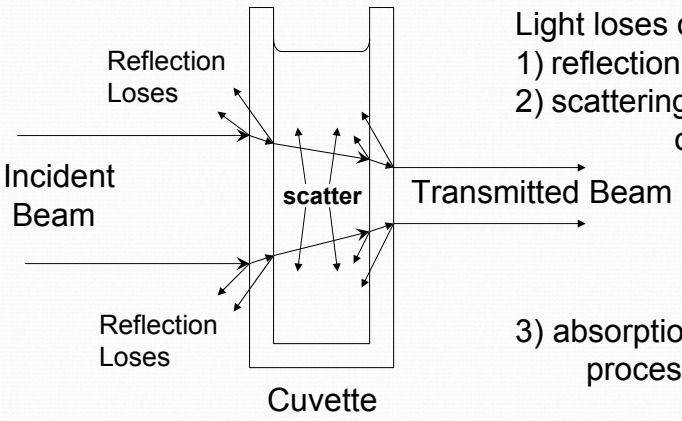
In all cases, response is proportional to concentration of analyte

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

# Homework 2

- 6-11
- 6-12
- 6-18
- 6-19