

# *Ch. 6: Introduction to Spectroscopic methods*

## *Spectroscopy:*

A branch of science that studies the interaction between EM radiation and matter.

## *Spectrometry and Spectrometric methods :*

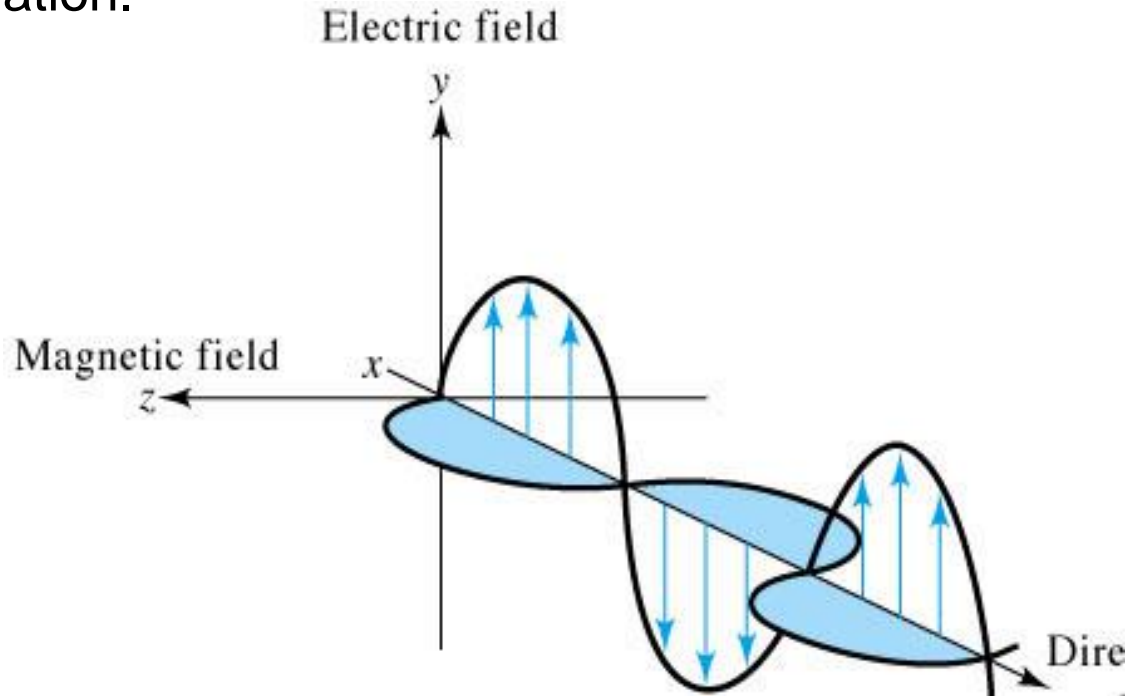
Measurement of the intensity of radiation with a photoelectric transducer or other types of electronic device.

# What is Electromagnetic Radiation?

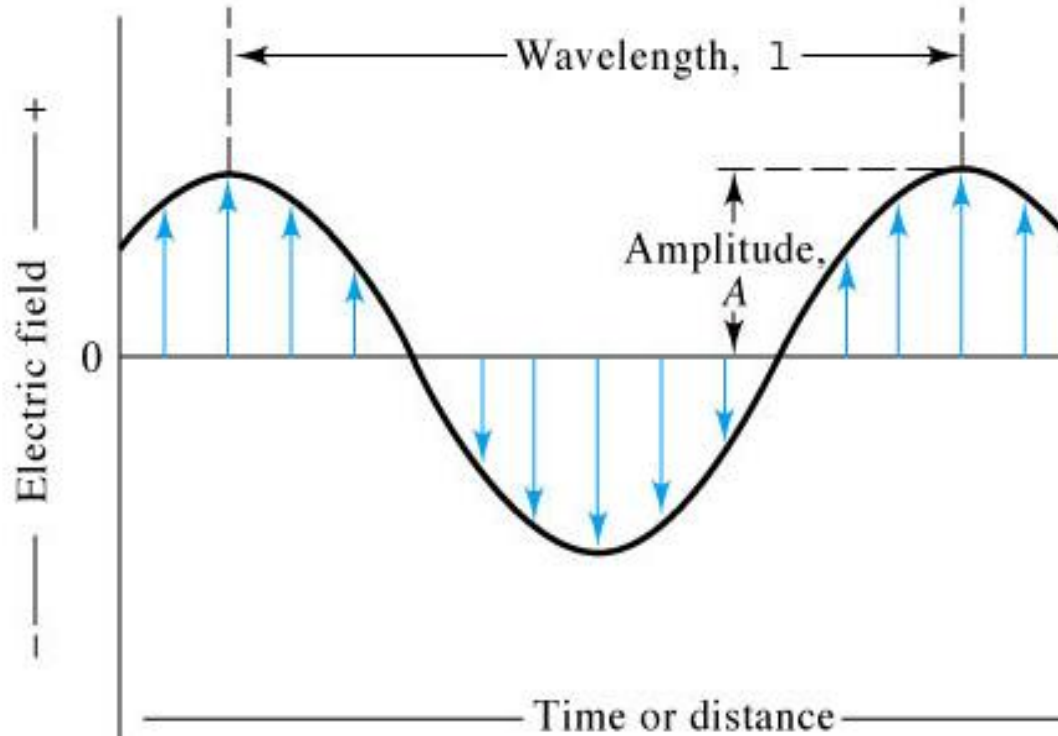
- EMR is a form of energy that has both Wave and Particle Properties.
- Many of the properties of electromagnetic radiation are conveniently described by means of a classical sinusoidal wave model, which embodies such parameters as wavelength, frequency, velocity, and amplitude.
- In contrast to other wave phenomena, such as sound, electromagnetic radiation *requires no supporting medium* for its transmission and thus passes readily a vacuum.

# EMR as a Wave

For many purposes, electromagnetic radiation is conveniently represented as electric and magnetic field that undergo in-phase, sinusoidal oscillations at right angles to each other and to the direction of propagation.

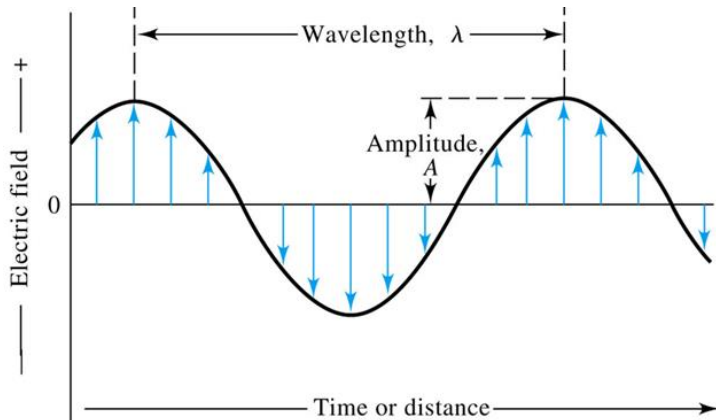


**Figure-6.1(a)** Representation of a single ray of plane-polarized electromagnetic radiation. The term plane polarized implies that all oscillations of either the electric or the magnetic fields lie within a single plane.



**Figure -6.1(b)** is a two –dimensional representation of the electric vector component of the ray in 6(a).

# Properties of electromagnetic radiation



(b)

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○ **Period (p)** – the time required for one cycle to pass a fixed point in space.

○ **Frequency (V)** – the number of cycles which pass a fixed point in space per second.  
 $=1/p$

- **Amplitude (A)** – The maximum length of the electric vector in the wave (Maximum height of a wave).
- **Wavelength (λ)** – The distance between two identical adjacent points in a wave (usually maxima or minima).
- **Wavenumber (1/λ)** - The number of waves per cm in units of  $\text{cm}^{-1}$ .

Velocity of propagation =  $v_i = \nu \cdot \lambda_i$

Speed of light = Frequency x Wavelength

- **Frequency** of a beam of radiation is determined by the source and **invariant**
- **Velocity** of radiation depends upon the **composition of the medium** through which it passes.

For electromagnetic waves the Speed ( $c$ ) *in vacuum* is a *Constant*

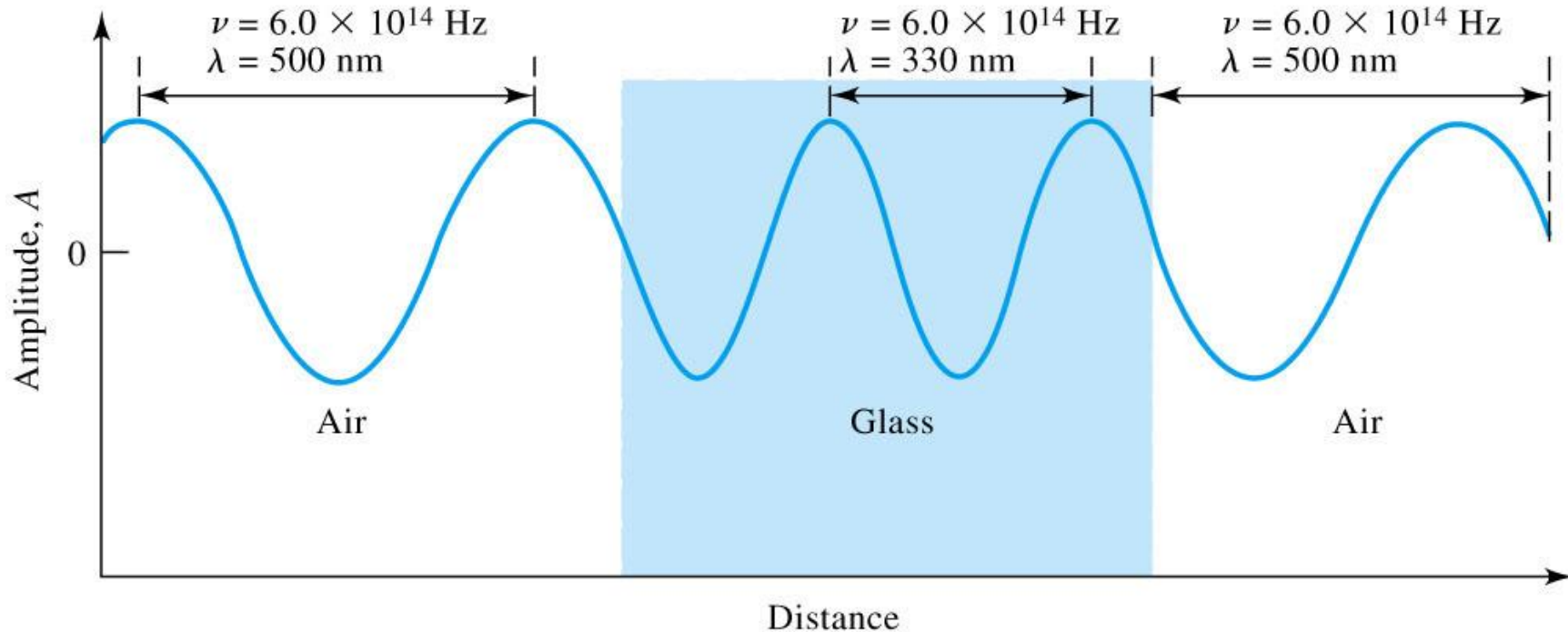
Speed of light in vacuum =  $c = 2.99792 \times 10^8 \text{ m/s} = c = \nu \cdot \lambda$

Speed of light in air = only 0.03% less than the one in vacuum.

Therefore for either air or vacuum;  $c = 3.00 \times 10^8 \text{ m/s}$

In any medium containing matter, propagation of radiation is slowed by the interaction between the electromagnetic field of the radiation and the bound electrons in the matter. Since the radiant frequency is invariant and fixed by the source, the wavelength must decrease as radiation passes from a vacuum to another medium.

# Effect of the Medium on a Light Wave



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- Frequency remains the same.
- Velocity and Wavelength change.

- This constant speed means a direct, Inverse Relationship Between Wavelength and Frequency

$$\nu \propto 1/\lambda$$

The relationship between frequency  $\nu$  of light and energy  $E$ ,

**Planck's Equation:**  $E = h\nu$  ;

Where

$h = \text{Planck's constant}$

$$= 6.6 \times 10^{-27} \text{ erg.sec} = 6.6 \times 10^{-34} \text{ joule.sec}$$

In vacuum, velocity of light  $\rightarrow c = \nu\lambda = 3 \times 10^{10} \text{ cm/s}$  which gives,

$$\nu = c/\lambda$$

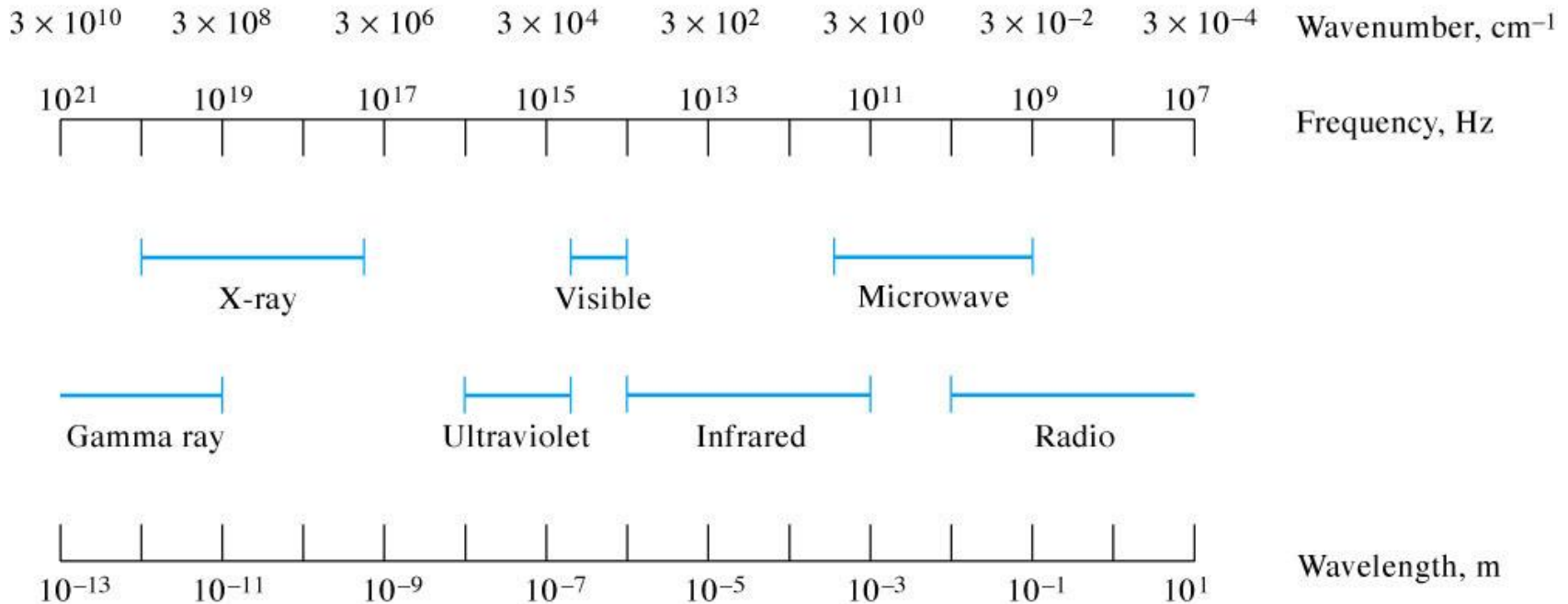
$$E = h(c/\lambda) = hc\nu \quad (\text{where, } \nu = 1/\lambda = \text{wavenumber})$$

Energy directly proportional to wavenumber



# The Electromagnetic Spectrum

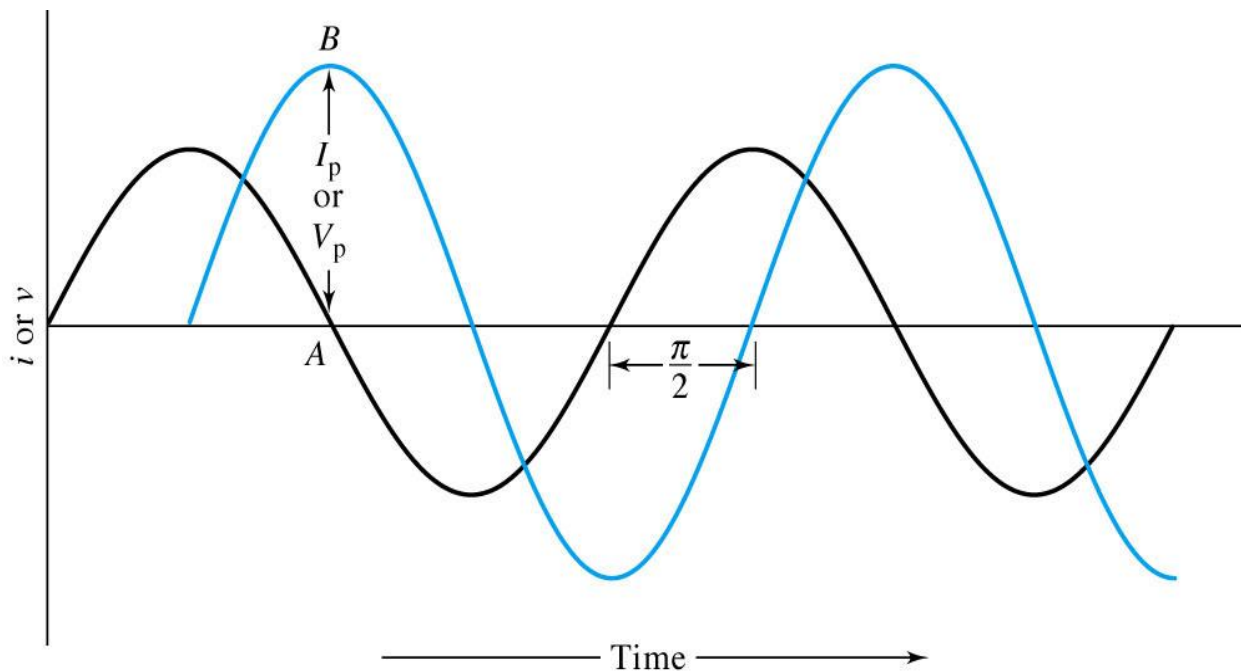
- The Higher the Frequency the Shorter the Wavelength
- The Longer the Wavelength, Lower the Frequency.



**TABLE 6-1** Common Spectroscopic Methods Based on Electromagnetic Radiation

Type of Spectroscopy	Usual Wavelength Range*	Usual Wavenumber Range, $\text{cm}^{-1}$	Type of Quantum Transition
Gamma-ray emission	0.005–1.4 Å	—	Nuclear
X-ray absorption, emission, fluorescence, and diffraction	0.1–100 Å	—	Inner electron
Vacuum ultraviolet absorption	10–180 nm	$1 \times 10^6$ to $5 \times 10^4$	Bonding electrons
Ultraviolet-visible absorption, emission, and fluorescence	180–780 nm	$5 \times 10^4$ to $1.3 \times 10^4$	Bonding electrons
Infrared absorption and Raman scattering	0.78–300 $\mu\text{m}$	$1.3 \times 10^4$ to $3.3 \times 10^1$	Rotation/vibration of molecules
Microwave absorption	0.75–375 mm	13–0.03	Rotation of molecules
Electron spin resonance	3 cm	0.33	Spin of electrons in a magnetic field
Nuclear magnetic resonance	0.6–10 m	$1.7 \times 10^{-2}$ to $1 \times 10^3$	Spin of nuclei in a magnetic field

# Mathematical Description of a Wave

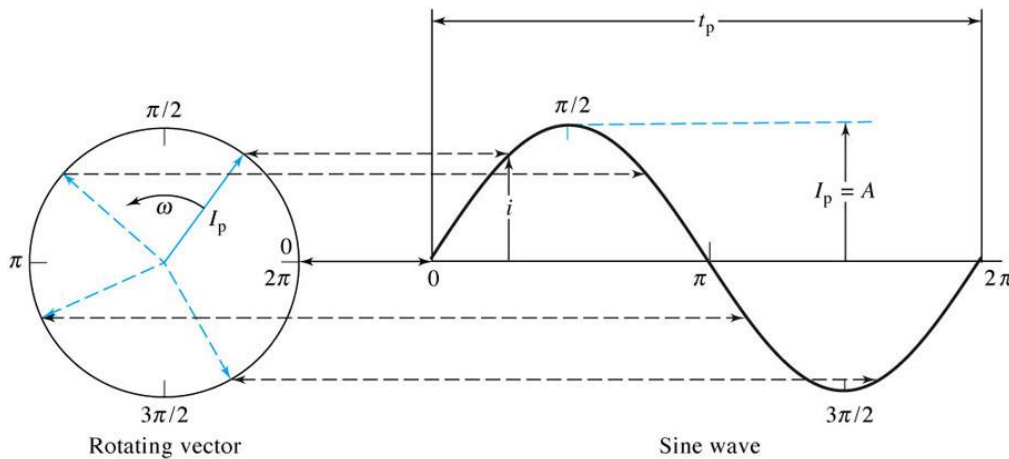


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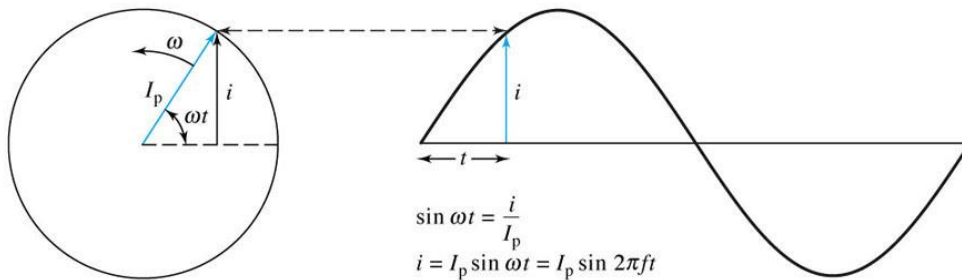
Sine waves with different amplitudes and with a phase different of 90 degree

# Mathematical Description of a Wave

A wave can be described by an equation for a sine wave



(a)



(b)

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

$Y$  = magnitude of the electric field at time  $t$ ,

$A$  = Amplitude

$\phi$  = phase angle

$\omega$  = angular velocity

$$\omega = 2\pi\nu = \frac{2\pi\nu}{\lambda}$$

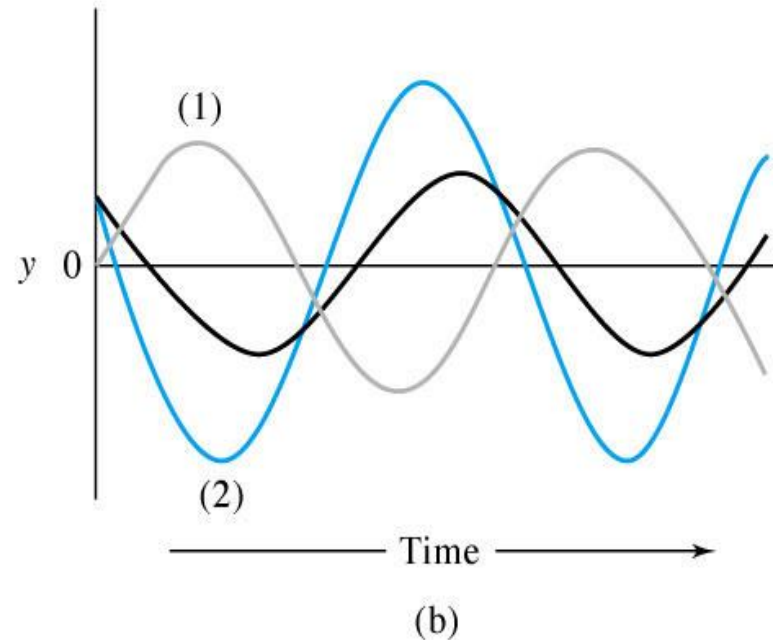
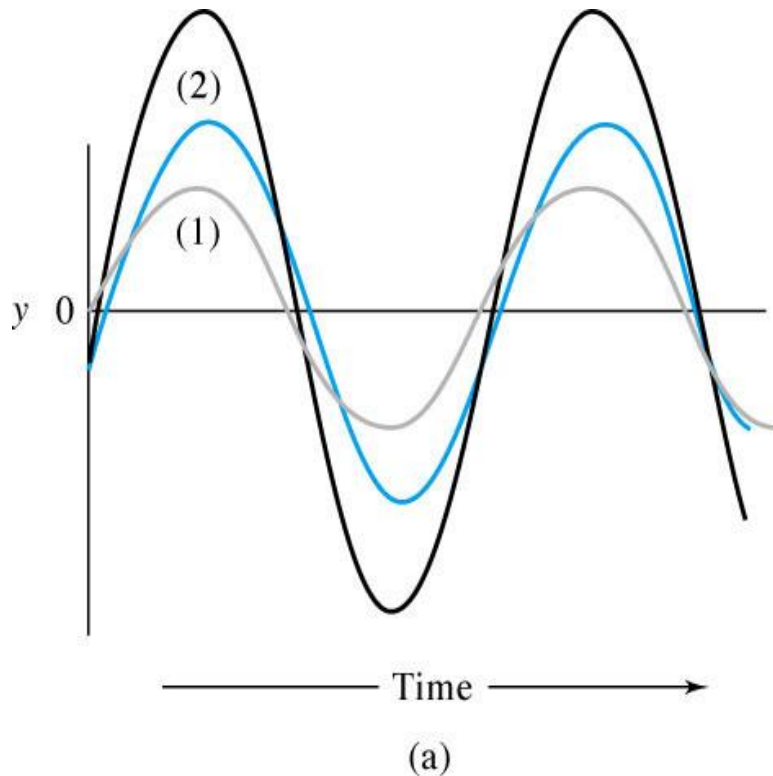
The angular velocity is related to the frequency of the radiation

$$Y = A \sin(2\pi\nu t + \phi)$$

# Superposition of Waves

□ If two plane-polarized waves overlap in space, the resulting electromagnetic disturbance is the **algebraic sum of the two waves**.

$$Y = A_1 \sin(2\pi\nu_1 t + \phi_1) + A_2 \sin(2\pi\nu_2 t + \phi_2) + \dots$$

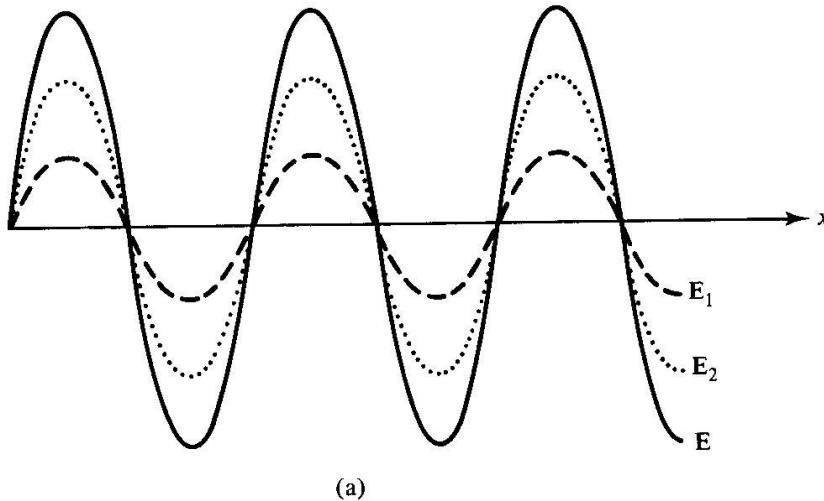


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Superposition of sinusoidal wave: (a)  $A_1 < A_2$ ,  $(\Phi_1 - \Phi_2) = 20^\circ$ ,  $\nu_1 = \nu_2$ ;  
(b)  $A_1 < A_2$ ,  $(\Phi_1 - \Phi_2) = 200^\circ$ ,  $\nu_1 = \nu_2$

# Optical Interference

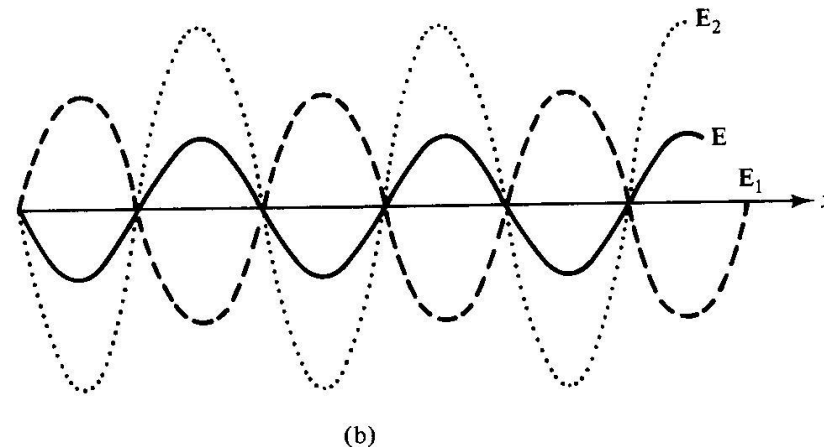
**Optical Interference:** The interaction of two or more light waves yielding an irradiance that is not equal to the sum of the irradiances.



## -Constructive Interference

- 1) Have identical frequency
- 2)  $\phi_2 - \phi_1 = \delta = \pm m2\pi$

*$\phi_2 - \phi_1 = 0$ , or 360 deg or integer multiple of 360 deg.*



## - Destructive Interference

- 1) Have identical frequency
- 2)  $\phi_2 - \phi_1 = \delta = (2m+1)\pi$

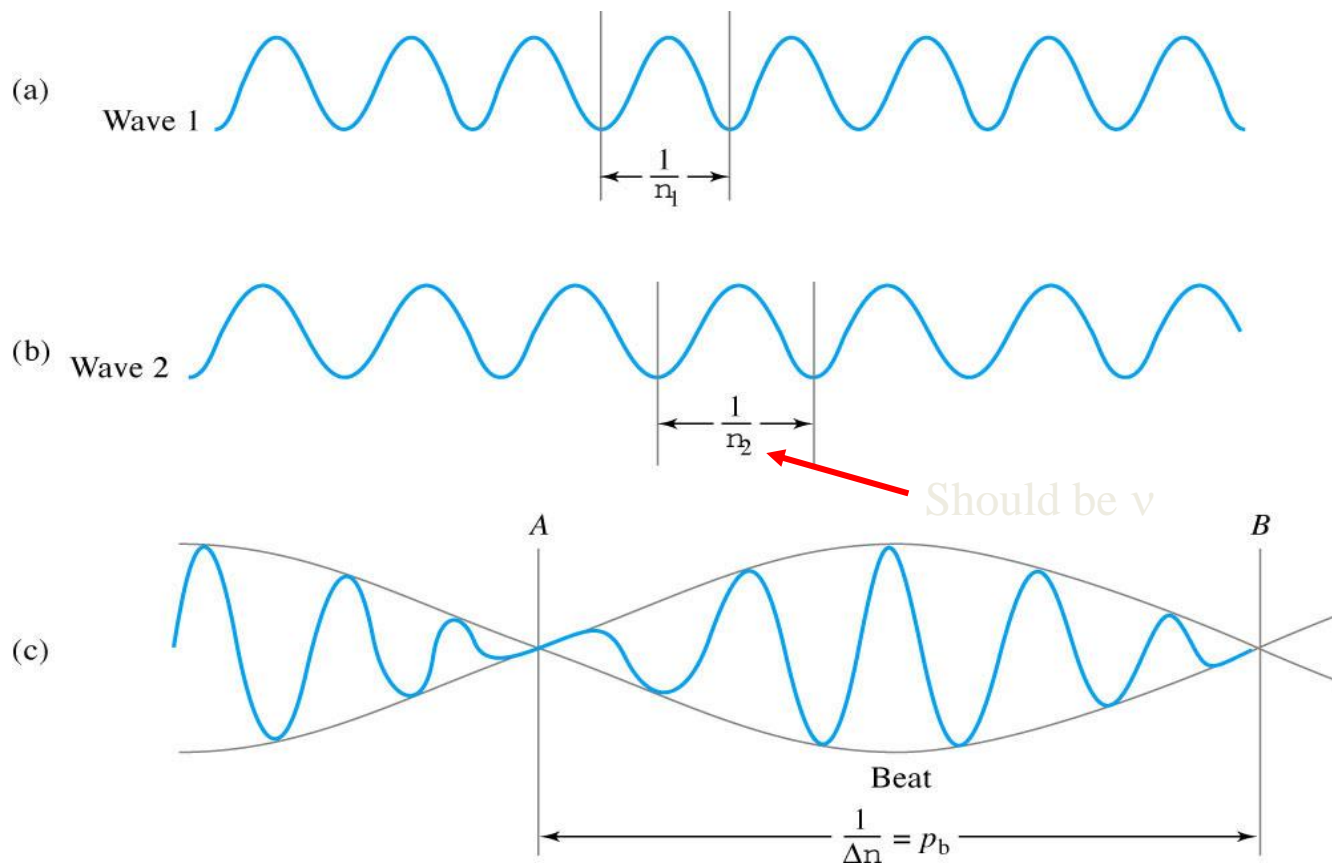
*$\phi_2 - \phi_1 = 180$  deg or 180 + integer multiple of 360 deg.*

Figure 3-4 – Ingle and Crouch,

# Periodicity or Beat

- ✓ Superposition of two sinusoidal wave of different frequencies but identical amplitudes.
- ✓ The resultant wave is no longer sinusoidal but exhibit a periodicity
- ✓ (a) wave1 period=  $1/\nu_1$ ,  
(b) wave2 period=  $1/\nu_2$     $\nu_2 = 1.25 \nu_1$ ;   (c) combined wave pattern result:  $1/\Delta\nu$

$$\Delta\nu = |\nu_1 - \nu_2|$$



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An important aspect of superposition is that:

➤ a complex waveform can be broken down into simple components by a mathematical operation called the *Fourier transformation*.

➤ *Jean Fourier (1768-1830)* demonstrated that, any periodic function, regardless of complexity, can be described by a sum of simple sine or cosine terms.

➤ of the original signal. The Fourier transform decomposes a function of time (a *signal*) into the frequencies that make it up.

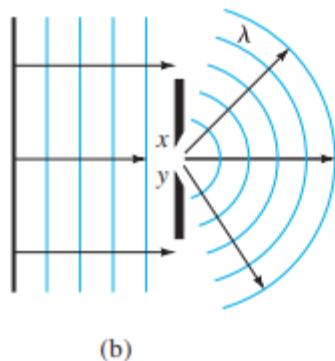
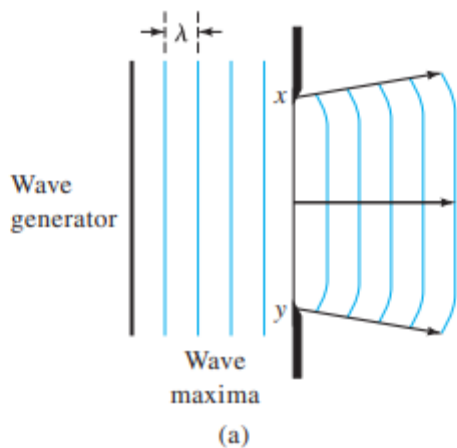
The Fourier transform is called the *frequency domain representation*

➤ *FT is a tedious and time consuming when done by hand. Efficient computer programs are necessary.*



# Diffraction:

➤ The Bending of Light as It Passes Through an Aperture or Around a Small Object



➤ Diffraction is a consequence of interference

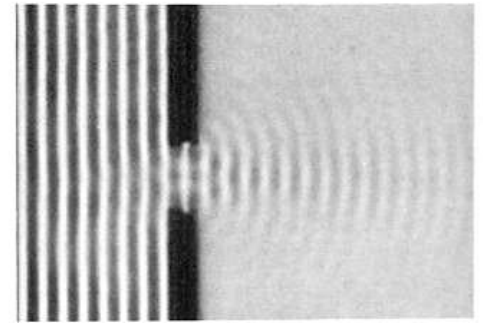
➤ not only observed for EMR but also for mechanical or acoustical waves

- For example, diffraction is easily demonstrated in the laboratory by mechanically generating waves of constant frequency in a tank of water and observing the wave crests before and after they pass through a rectangular opening, or slit

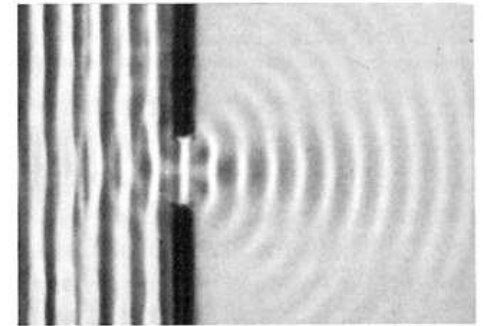
**FIGURE 6-7** Propagation of waves through a slit: (a)  $xy \gg \lambda$ ; (b)  $xy = \lambda$ .

# Diffraction of Waves in a Liquid

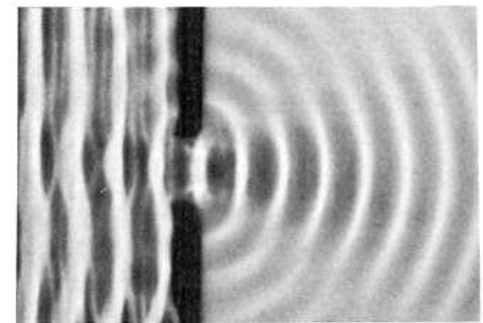
- Diffraction increases as **aperture size**  $\rightarrow \lambda$
- When the slit is wide relative to the wavelength (a), diffraction is slight and difficult to detect.
- when the wavelength and the slit opening are of the same order of magnitude diffraction becomes more pronounced. Here, the slit behaves as a new source from which waves radiate in a series of nearly  $180^\circ$  arcs. The direction of the wave front appears to bend as a consequence of passing the two edges of the slit



(a)



(b)

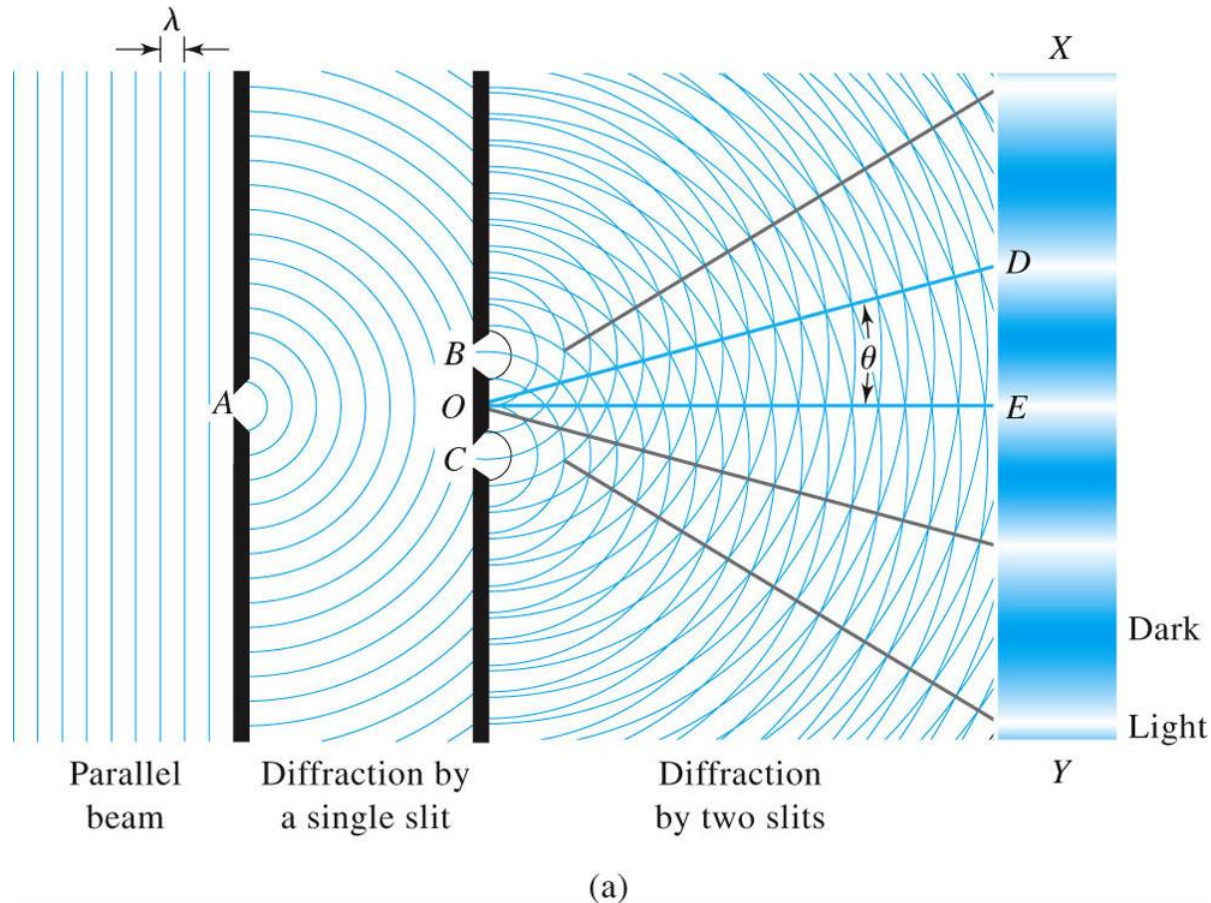


(c)

**FIGURE 10.2** Diffraction through an aperture with varying  $\lambda$  as seen in a ripple tank. (Photo courtesy PSSC Physics, D. C. Heath, Boston, 1960.)

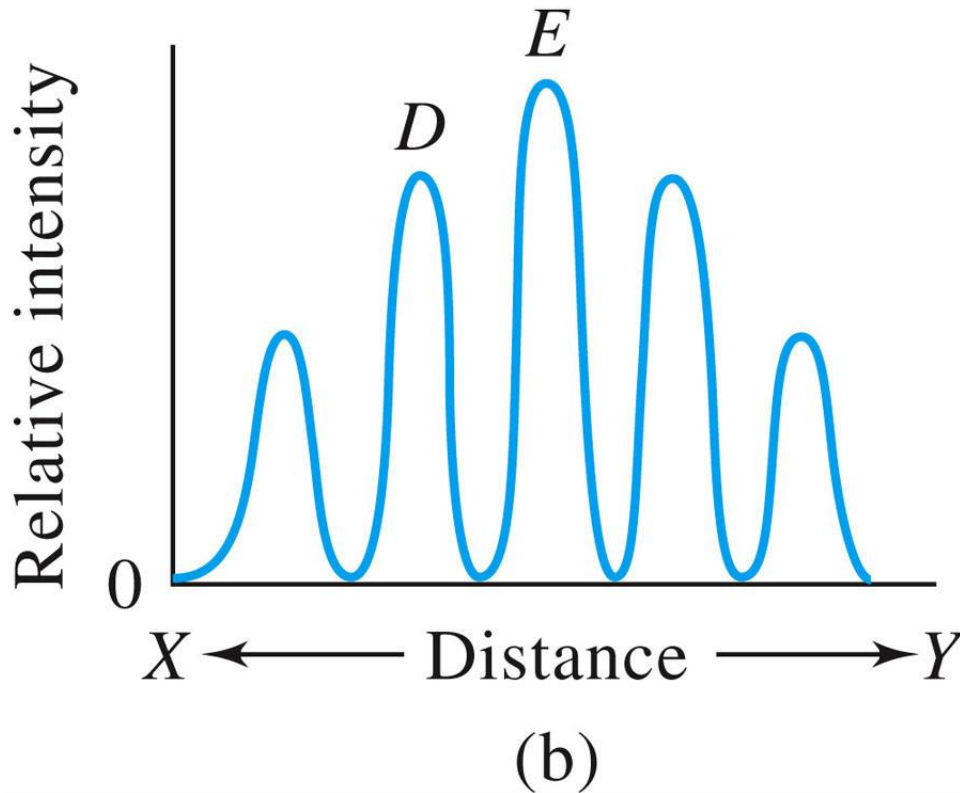
# Diffraction Pattern From Multiple Slits

- If the radiation is monochromatic, a series of dark and light images is observed.



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# Diffraction Pattern From Multiple Slits



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<https://app.jove.com/v/10424/interference-diffraction-single-and-double-slit-experiments>

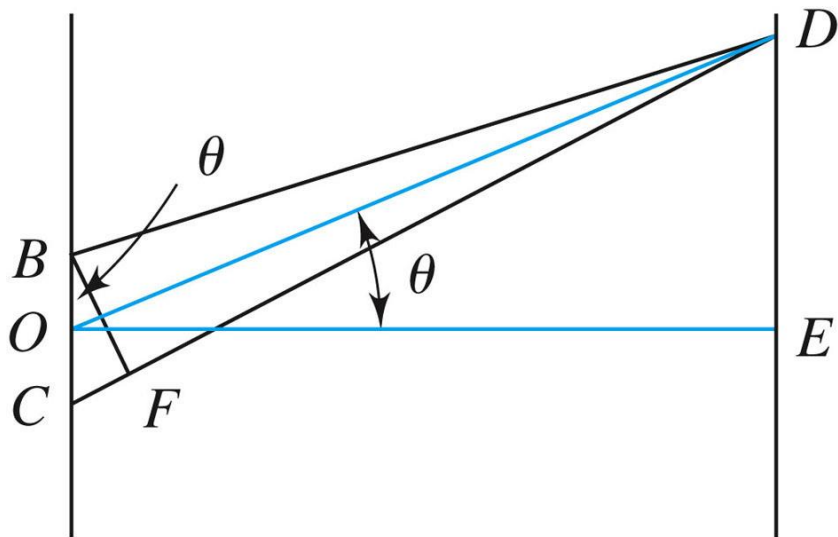
If slit width  $\rightarrow \lambda$

The band intensities decrease only gradually with increasing distances from the central band.

If slit width  $> \lambda$

The decrease is much more pronounced

# Diffraction Pattern From Multiple Slits



(c)

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The conditions for maximum constructive interference can be derived.  $\theta$ =diffraction angle  
 BD and CD are the light paths from the slits B and C to the point D.

**Assumption:**  $OE \gg BC$

then,  $BD \parallel OD \parallel CD$

$BF \perp CD$  and forms BCF triangle

And  $BCF \approx DOE$

Angle CBF =  $\theta$ =diffraction angle

$$CF = BC \sin \theta = n\lambda$$

$$DE = OD \sin \theta \rightarrow \sin \theta = DE / OD$$

$$\underline{BC \cdot DE = n\lambda}$$

$$OD = OE$$

Example 6.1.  $OE = 2.0 \text{ m}$ ,  $BC = 0.3 \text{ mm}$ ,  $n = 4$

$\lambda = ?$  If  $DE = 15.4 \text{ mm}$

$$\frac{0.3 \text{ mm} \times 15.4 \text{ mm}}{2.0 \text{ m} \times 1000 \text{ mm/m}} = 4 \times \lambda$$

$$\lambda = 5.78 \times 10^{-4} \text{ mm} \quad 578 \text{ nm}$$

# Coherent Radiation

**Coherency:** When two waves have an initial phase difference of zero or constant for a long time, they are considered coherent.

Conditions for coherency of two sources of radiation are:

1. They must have identical frequencies and
2. The phase relationships between the two remains constant with time

Incoherency test: Illuminate the slits with W-lamp-  
result is ;

- disappearance of the dark and light patterns
- more or less uniform illumination of the screen

This behaviour is the consequence of the incoherent character of W-lamp.

# Incoherent sources

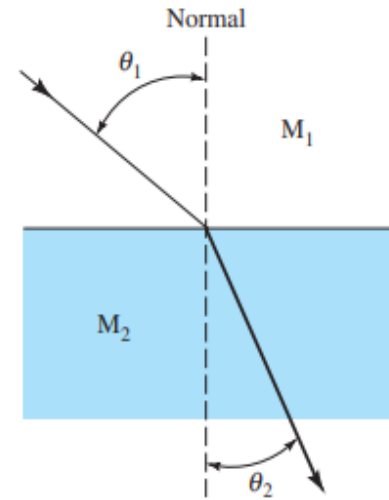
- Light is emitted by individual atoms or molecules
- resulting beam is the summation of countless individual events
- phase differences are variable
- constructive and destructive interferences occur randomly
- average of the emissions are observed as an illumination

# Coherent sources

- optical lasers, rf oscillators, microwave sources.

## 6B-7 Transmission of Radiation: The Refractive Index

- Experimental observations show that the rate radiation propagates through a transparent substance is less than its velocity in a vacuum and depends on the kinds and concentrations of atoms, ions, or molecules in the medium
- Each medium has a characteristic “index of refraction” that is defined as the ratio between the speed of light in vacuum and the speed of light in the medium.
- Light travels more slowly in a medium with a high index of refraction and more quickly in a medium with a low index of refraction.



**FIGURE 6-10** Refraction of light in passing from a less dense medium  $M_1$  into a more dense medium  $M_2$ , where its velocity is lower.

$$\eta = \frac{c}{v_i}$$

$c$  is the speed of light in vacuum in (m/s),  
 $v$  is the speed of light in the medium in (m/s).



- ♠ The refractive index of most liquids lies between 1.3 and 1.8
- ♠ it is 1.3 to 2.5 or higher for solids.

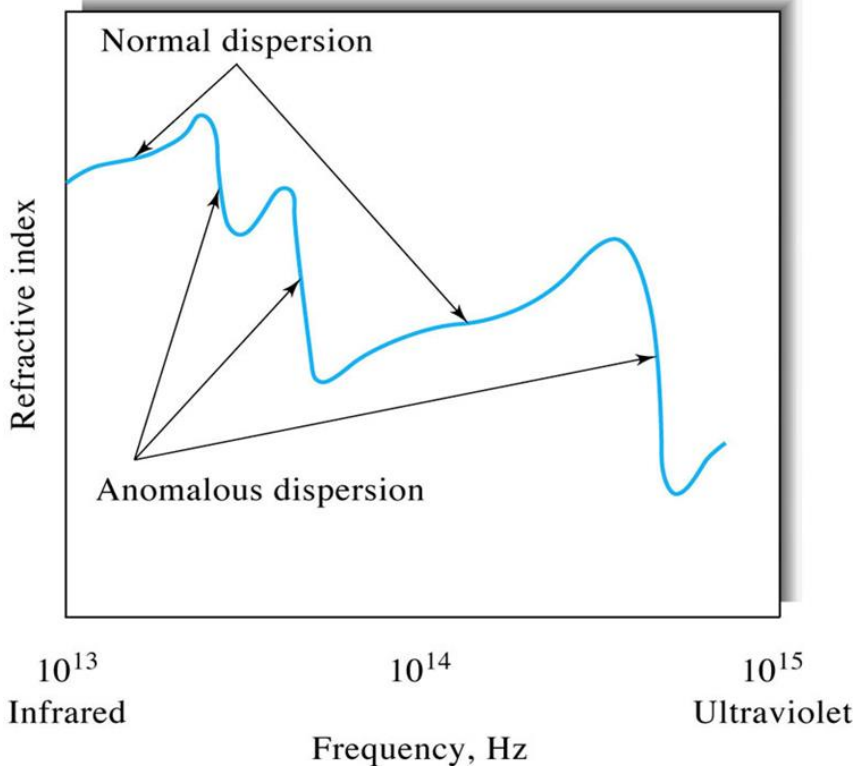
**TABLE 4.1 Approximate Indices of Refraction of Various Substances\***

Air	1.000 29
Ice	1.31
Water	1.333
Ethyl alcohol (C <sub>2</sub> H <sub>5</sub> OH)	1.36
Fused quartz (SiO <sub>2</sub> )	1.4584
Carbon tetrachloride (CCl <sub>4</sub> )	1.46
Turpentine	1.472
Benzene (C <sub>6</sub> H <sub>6</sub> )	1.501
Plexiglass	1.51
Crown glass	1.52
Sodium chloride (NaCl)	1.544
Light flint glass	1.58
Polystyrene	1.59
Carbon disulfide (CS <sub>2</sub> )	1.628
Dense flint glass	1.66
Lanthanum flint glass	1.80
Zircon (ZrO <sub>2</sub> ·SiO <sub>2</sub> )	1.923
Fabulite (SrTiO <sub>3</sub> )	2.409
Diamond (C)	2.417
Rutile (TiO <sub>2</sub> )	2.907
Gallium phosphide	3.50

\*Values vary with physical conditions—purity, pressure, etc. These correspond to a wavelength of 589 nm

# Dispersion and Prisms

- Since the velocity of radiation in matter is wavelength dependent and since  $c$  in Equation 6-11 is independent of wavelength, the refractive index of a substance must also change with wavelength
- The variation in refractive index of a substance with wavelength or frequency is called **Dispersion**



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$$\eta = \frac{c}{v_i}$$

**Normal Dispersion:**

A region where gradual increase in  $\eta$  wrt increase in frequency.

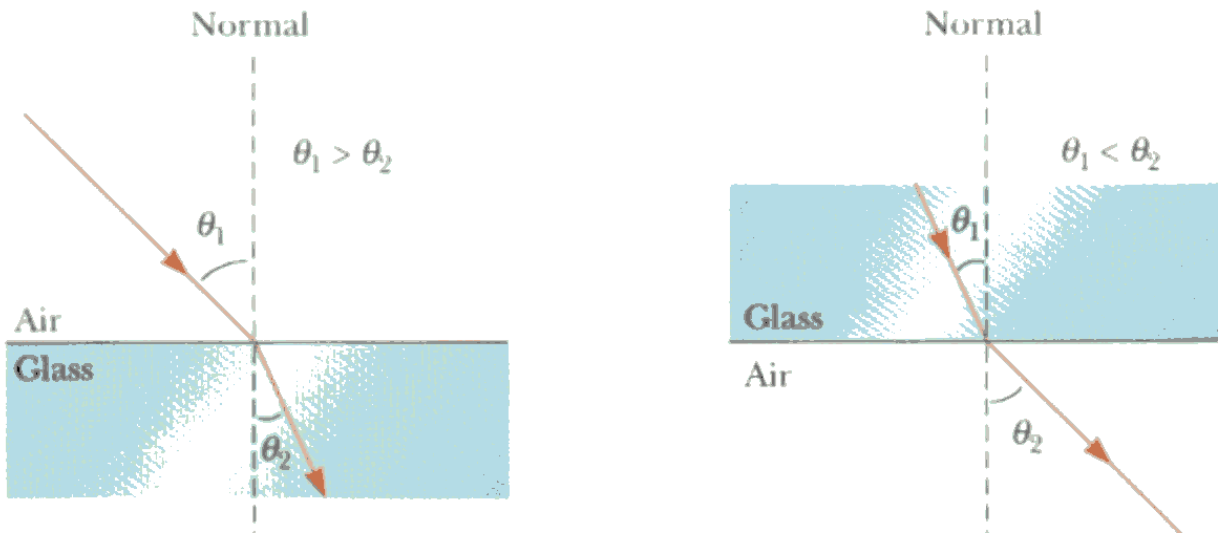
**Anomalous Dispersion:**

Frequency ranges in which a sharp change in  $\eta$  is observed.

Dispersion curves are imp. when choosing materials for the optical components of spectrometer. ND( lenses) AD(prisms)

# 6B-8 Refraction of Radiation

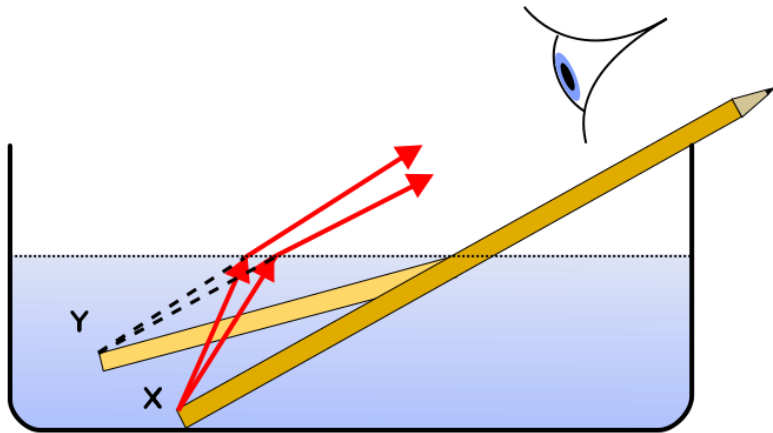
- **Refraction** is the change in direction of **propagation** of a wave due to a change in its transmission medium.
- Refraction of light in passing from less dense to a more dense medium, bending is towards the normal.
- If the beam passes from more dense to a less dense medium, bending away from the normal occurs



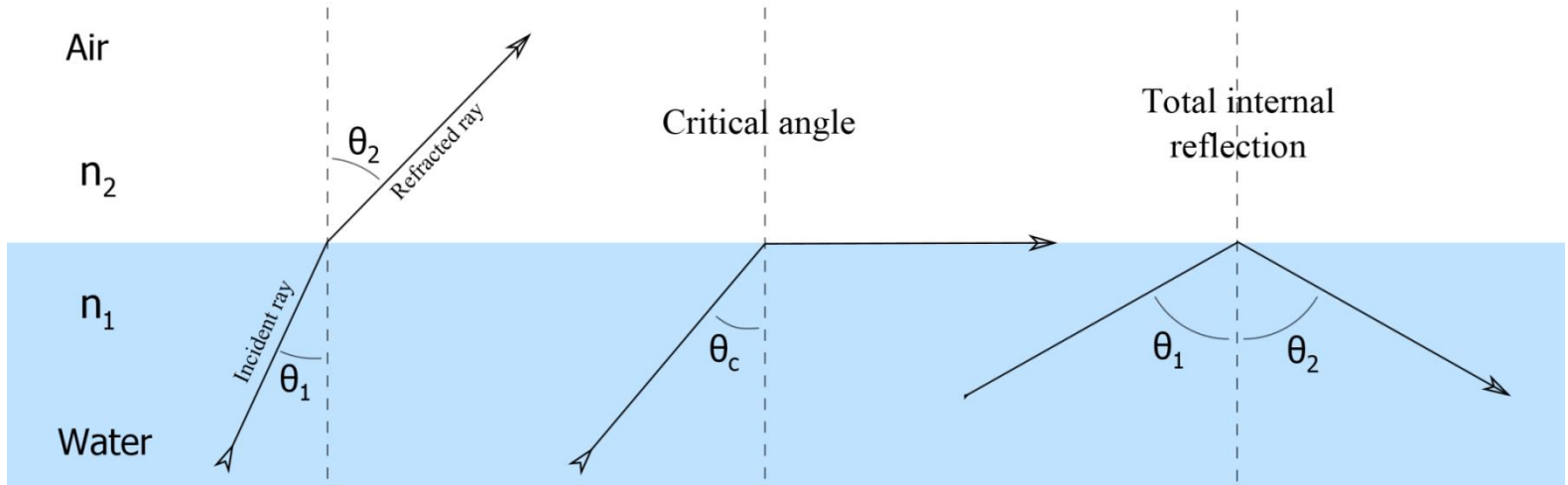
- The extent of refraction is given by ,

**Snell's Law:**  $n_1 \sin \theta_1 = n_2 \sin \theta_2$     $v_2 \sin \theta_1 = v_1 \sin \theta_2$     $\frac{\sin \theta_1}{\sin \theta_2} = \frac{v_1}{v_2} = \frac{n_2}{n_1}$ .

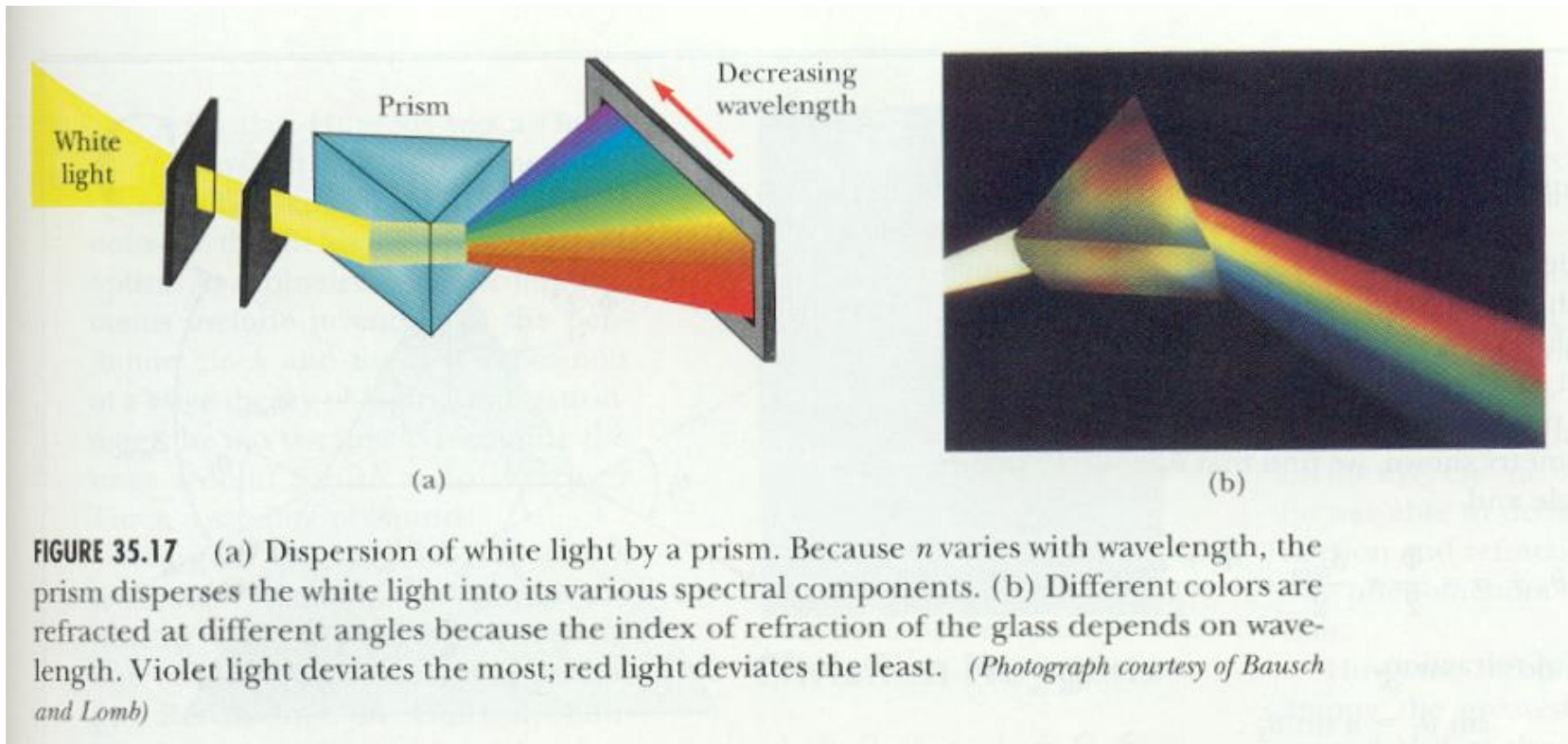
# Refraction:



An object (in this case a pencil) partially immersed in water looks bent due to refraction

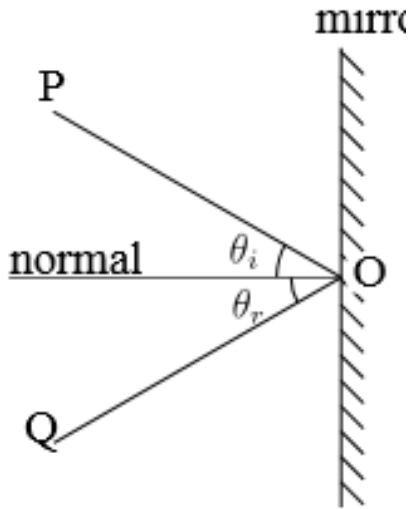


Another example of refraction is the dispersion of white light into its individual colors by a glass prism. As visible light exits the prism, it is refracted and separated into a magnificent display of colors.



## 6B-9 Reflection of Radiation

**Reflection** is the change in direction of a wavefront at an interface between two different media so that the wavefront returns into the medium from which it originated.



For monochromatic light hitting a flat surface at  $90^\circ$

$$\frac{I_r}{I_0} = \frac{(n^2 - n^1)^2}{(n^2 + n^1)^2}$$

$I_0$ : intensity of incident light  
 $I_r$ : reflected intensity

### Laws of reflection:

1. The incident ray, the reflected ray and the normal to the reflection surface at the point of the incidence lie in the same plane.
2. The reflected ray and the incident ray are on the opposite sides of the normal.

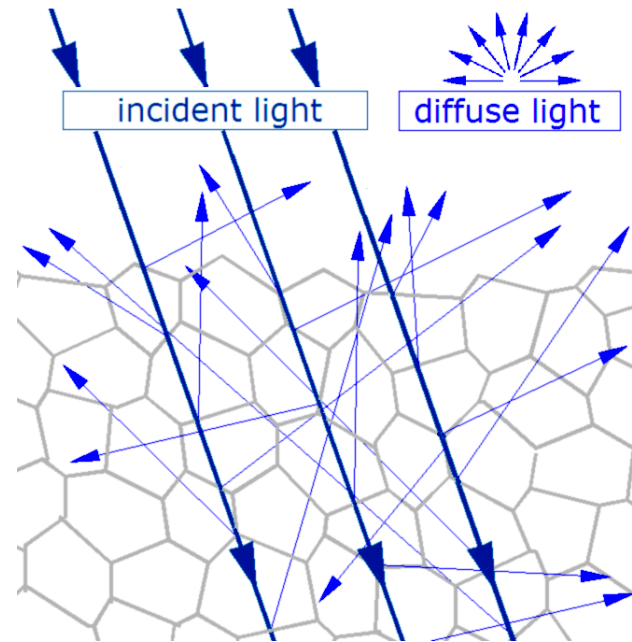
# Reflection of Radiation

**Specular reflection:** Reflection of light from a smooth surface (mirror like)



Reflections on still water are an example of specular reflection

**Diffuse reflection:** Reflection of light from a rough surface. (retaining the energy but losing the image)



# $\rho(\lambda)$ at different interfaces

Reflectance is the fraction of the incident radiant energy reflected.

**TABLE B-2**

Reflectances for several interfaces

Interface	Spectral reflectance	Interface	Spectral reflectance
Glass-air	0.0403	NaCl-air	0.045
Glass-H <sub>2</sub> O	0.0035	KCl-air	0.038
Glass-1 M KCl	0.0031	Sapphire-air	0.076
Glass-benzene	$1.1 \times 10^{-7}$	Sapphire-H <sub>2</sub> O	0.0198

**TABLE B-1**

Refractive indices of optical materials at 20°C

Material	$\eta$ at 589 nm	Material	$\eta$ at 589 nm
Air	1.003	AgCl	2.000 (3.9 $\mu\text{m}$ )
H <sub>2</sub> O	1.333	Sapphire	1.769 (579 nm)
Fused silica	1.458	NaCl	1.544
	1.513 (240 nm)		1.522 (4.0 $\mu\text{m}$ )
Borosilicate	1.517	ZnS	2.35
Crown glass	1.548 (313 nm)	Cryolite	1.34
KCl	1.490	ADP	1.525 ( $\eta_o$ , 579 nm)
	1.471 (4.71 $\mu\text{m}$ )		1.479 ( $\eta_e$ , 579 nm)
KI	1.666	KDP	1.510 ( $\eta_o$ , 579 nm)
	1.627 (4.13 $\mu\text{m}$ )		1.469 ( $\eta_e$ , 579 nm)
MgF <sub>2</sub>	1.378 ( $\eta_o$ )	Calcite	1.658 ( $\eta_o$ )
	1.390 ( $\eta_e$ )		1.486 ( $\eta_e$ )
Crystal quartz	1.544 ( $\eta_o$ )	MgO	1.773 (361 nm)
	1.553 ( $\eta_e$ )		1.723 (1.01 $\mu\text{m}$ )
KBr	1.560	Benzene	1.500
	1.535 (4.26 $\mu\text{m}$ )		
1 M KCl (aq)	1.342		



# 6B-10 Scattering of Radiation

The fraction of radiation transmitted at all angles from its original path

- **Rayleigh scattering** : Molecules or aggregates of molecules with dimensions significantly smaller than  $\lambda$  of radiation. Intensity is proportional to the inverse fourth power of the wavelength.  $I \propto 1/\lambda^4$ 
  - Blue color of the sky.
- **Scattering by big molecules (Tyndall effect):**
  - Colloidal dimensions particles, scattering can be seen by naked eye.
  - used for measuring particle size and shapes of polymer molecules
- **Raman Scattering:**
  - Involves quantized frequency changes. These changes are the results of vibrational energy level transitions that occur in the molecule as a consequence of the polarization process.

# 6B-11 Polarization of Radiation

- The interaction involved in transmission can be ascribed to periodic polarization of the atomic and molecular species that make up the medium.
- Polarization in this context means the temporary deformation of the electron clouds associated with atoms or molecules that is brought about by the alternating electromagnetic field of the radiation.
- Provided that the radiation is not absorbed, the energy required for polarization is only momentarily retained ( $10^{-14}$  to  $10^{-15}$  s) by the species and is reemitted without alteration as the substance returns to its original state.
- Since there is no net energy change in this process, the frequency of the emitted radiation is unchanged, but the rate of its propagation is slowed by the time that is required for retention and reemission to occur.
- Thus, transmission through a medium can be viewed as a stepwise process that involves polarized atoms, ions, or molecules as intermediates

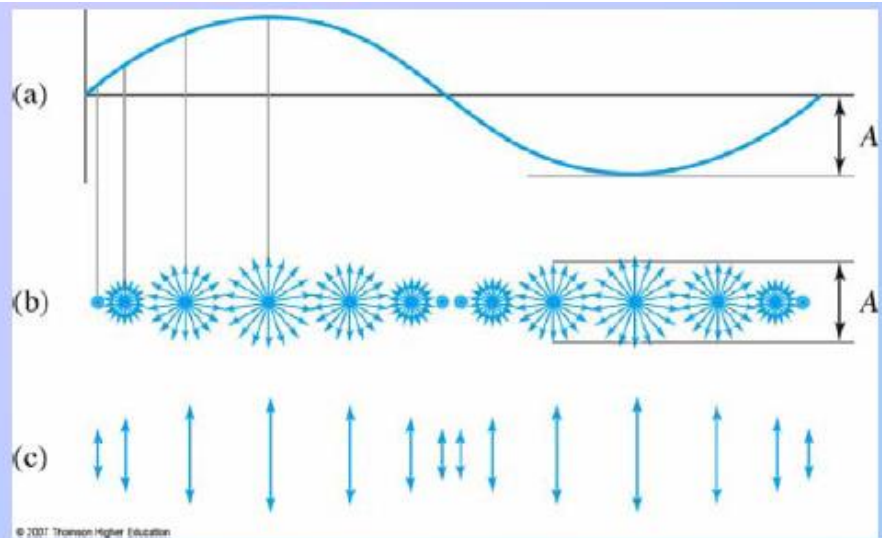


FIGURE 6-11 Unpolarized and plane-polarized radiation: (a) cross-sectional view of a beam of monochromatic radiation, (b) successive end-on view of the radiation in (a) if it is unpolarized, (c) successive end-on views of the radiation of (a) if it is plane polarized on the vertical axis.

•Figure 6-12a shows a few of the vectors depicted in Figure 6-11b at the instant the wave is at its maximum. The vector in anyone plane, say  $XY$  as depicted in Figure 6-12a. can be resolved into two mutually perpendicular components  $A$  and  $B$  as shown in Figure 6-12b.

•If the two components for all of the planes shown in Figure 6-12a are combined, the resultant has the appearance shown in Figure 6-12c. Removal of one of the two resultant planes of vibration in Figure 6-12c produces a beam that is *plane polarized*.

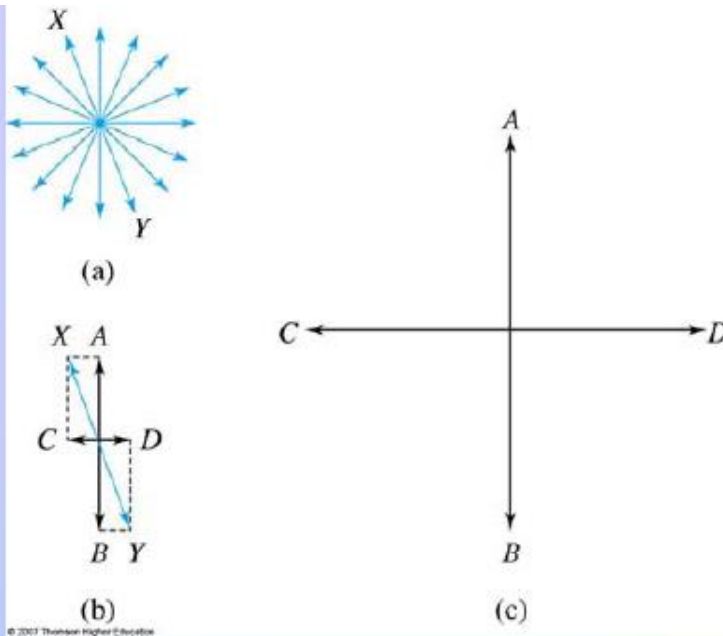
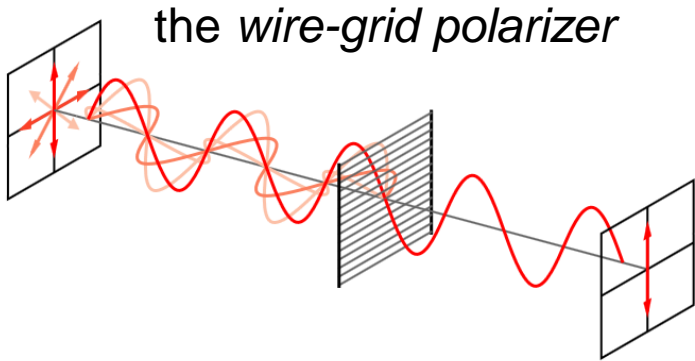


FIGURE 6-12 (a) A few of the electric vectors of a beam traveling perpendicular to the page. (b) The resolution of a vector in a plane  $XY$  into two mutually perpendicular components. (c) The resultant when all vectors are resolved (not to scale).

*The resultant* electric vector of a plane-polarized beam then occupies a single plane. Figure 6-11c shows an end-on view of a beam of plane-polarized radiation after various time intervals.

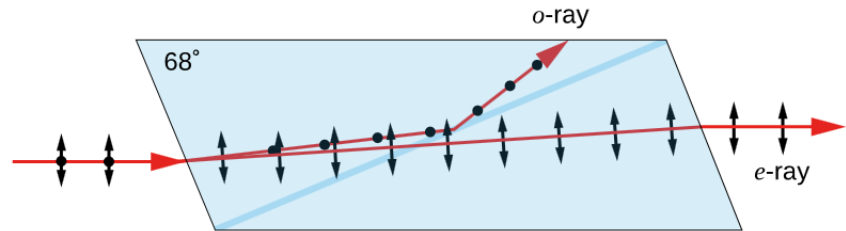
# Polarizers:



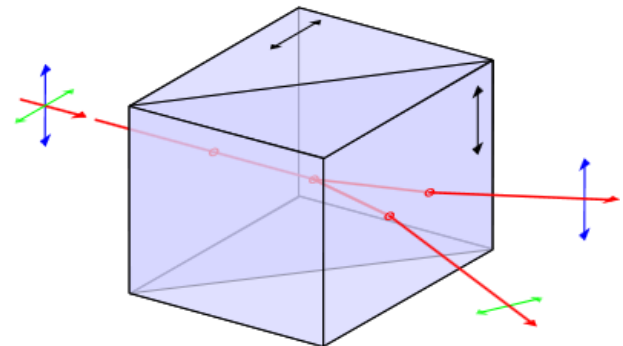
the *wire-grid polarizer*

- the *wire-grid polarizer*, which consists of a regular array of fine parallel metallic wires, placed in a plane perpendicular to the incident beam. Electromagnetic waves which have a component of their [electric fields](#) aligned parallel to the wires induce the movement of [electrons](#) along the length of the wires. Since the electrons are free to move in this direction, the polarizer behaves in a similar manner to the surface of a [metal](#) when reflecting light, and the wave is reflected backwards along the incident beam (minus a small amount of energy lost to [joule heating](#) of the wire).<sup>15</sup>

a Nicol prism- Birefringent polarizer that consists of a crystal of calcite which has been split and rejoined with [Canada balsam](#). The crystal is cut such that the o- and e-rays are in orthogonal linear polarization states

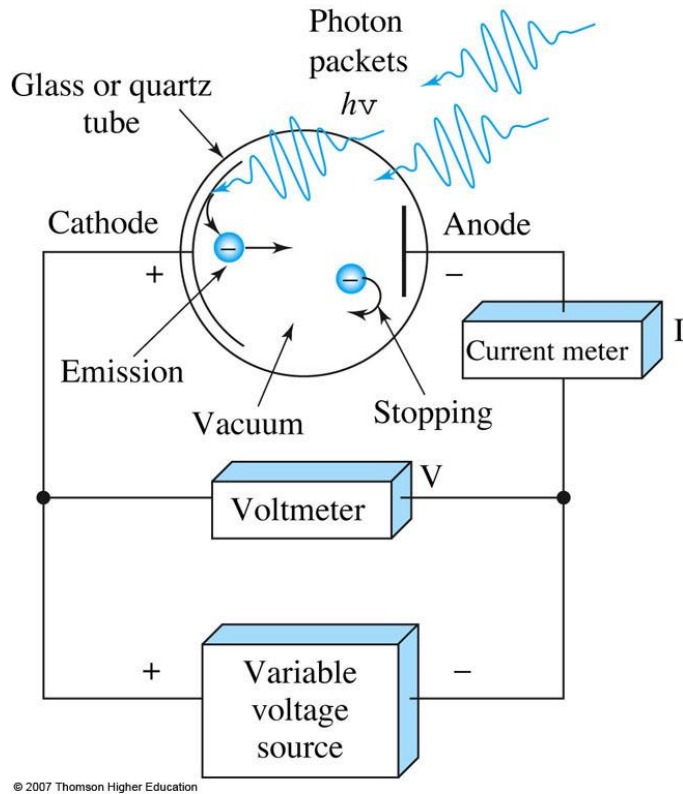


A [Wollaston prism](#) is another birefringent polarizer consisting of two triangular calcite prisms with orthogonal crystal axes that are cemented together. At the internal interface, an unpolarized beam splits into two linearly polarized rays which leave the prism at a divergence angle of  $15^\circ - 45^\circ$ .



# 6C-Quantum-Mechanical Properties of EMR

## 6C-1 The Photoelectric Effect

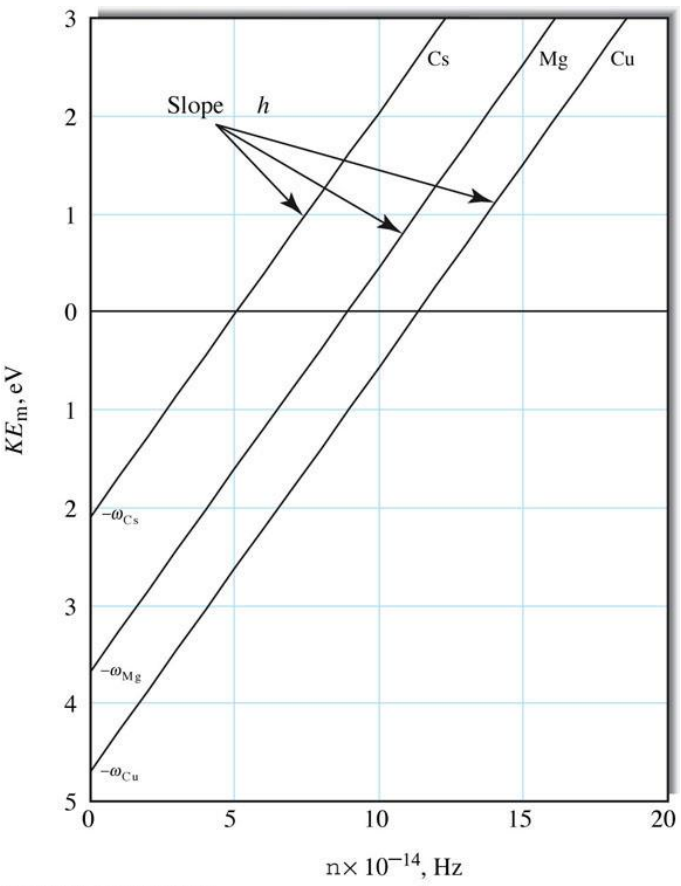


- The photoelectrons are attracted to the anode when it is positive with respect to the cathode.
- When the anode is negative as shown, the electrons are “stopped”, and no current passes.
- The negative voltage between the anode and the cathode when the current is zero is the stopping potential.

FIGURE 6-13

Apparatus for studying the photoelectric effect. Photons enter the phototube, strike the cathode, and eject electrons.

- Current is proportional to the intensity of the radiation
- $V_0$  depends on the frequency of the radiation and the chemical composition of the coating on the photocathode
- $V_0$  independent of the intensity of the incident radiation



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FIGURE 6-14 Maximum kinetic energy of photoelectrons emitted from three metal surfaces as a function of radiation frequency. The *y-intercepts* ( $-\omega$ ) are the work functions for each metal. If incident photons do not have energies of at least  $h\nu = \omega$ , no photoelectrons are emitted from the photocathode.

$$KE_m = h\nu - \omega$$

$h$ : Planck's constant =  $6.62 \times 10^{-34} \text{ J}\cdot\text{sec}$ .

$\omega$ : work function

: energy required to remove an  $e^-$  from the surface

$$E = h\nu = KE_m + \omega$$

The photoelectric effect cannot be explained by a classical wave model but requires instead a quantum model, in which radiation is viewed as a stream of discrete bundles of energy, or photons

# Energy States of Chemical Species

- Quantum theory by Planck (1900)
- Black body radiation
- Atoms, ions, and molecules exist in discrete states
- Characterized by definite amounts of energy
- When changes of state involve, the absorption or emission of energy occur

- $E_1 - E_0 = h\nu = hc/\lambda$

where :

$E_1$  is the energy of the higher state and

$E_0$  the energy of the lower state.

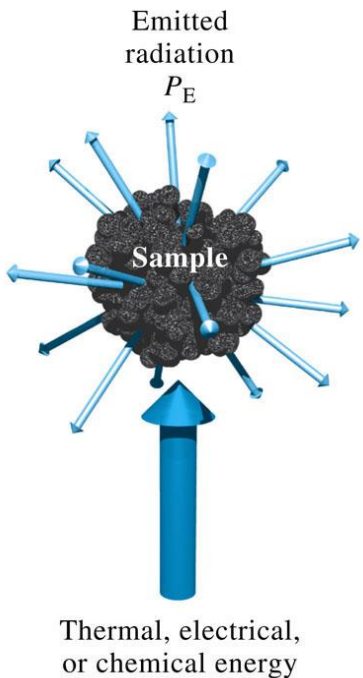
$c$  : the speed of light and

$h$ : the Planck constant,

respectively.

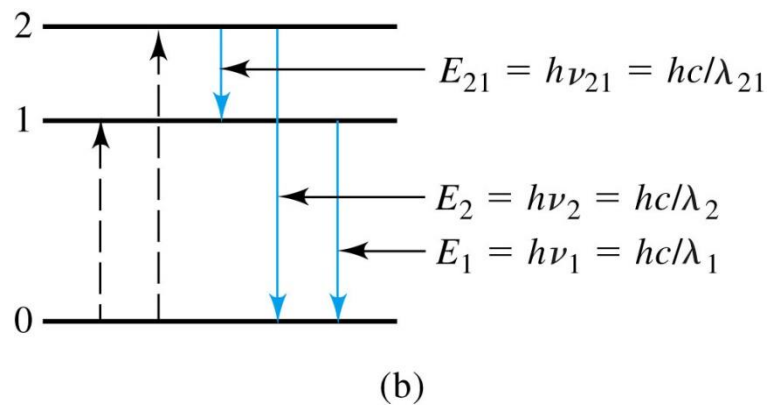
# Interaction of Radiation and Matter:

## Emission and Chemiluminescence Process



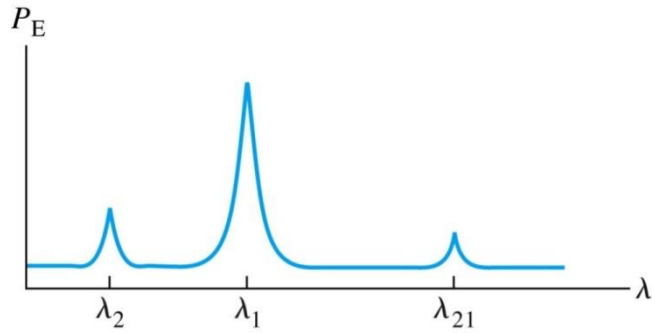
(a)

In (a), the sample is excited by the application of thermal, electrical, or chemical energy.



(b)

In the energy level diagram (b), the dashed lines with upward-pointing arrows symbolize these non-radiative excitation processes, while the solid lines with downward-pointing arrows indicate that the analyte loses its energy by emission of a photon.



(c)

In (c), the resulting spectrum is shown as a measurement of the radiant power emitted  $P_E$  as a function of wavelength,  $\lambda$ .

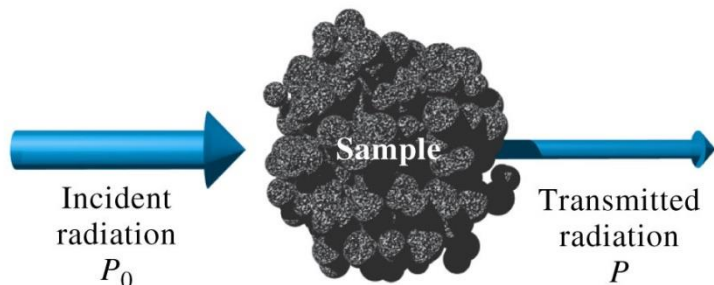
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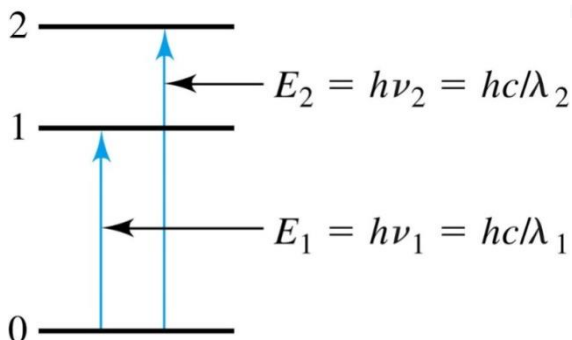
# Interaction of Radiation and Matter

## Absorption Process:

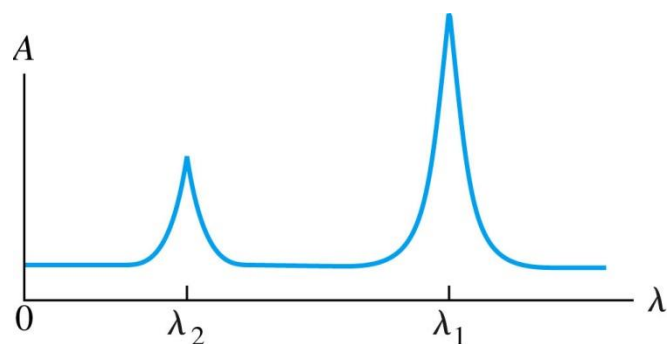


(a)

When some of the incident radiation is absorbed, it promotes some of the analyte species to an excited state. In absorption spectroscopy, we measure the amount of light absorbed as a function of wavelength. This can give both qualitative and quantitative information about the sample.



(b)



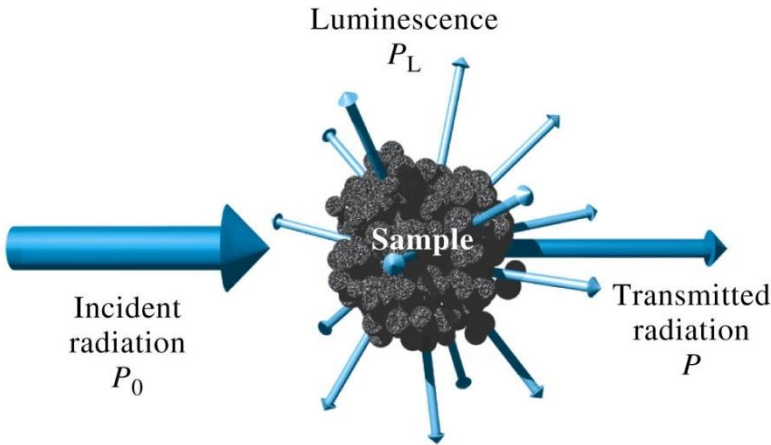
(c)

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).

# Interaction of Radiation and Matter

## Photoluminescence method (Fluorescence and phosphorescence)

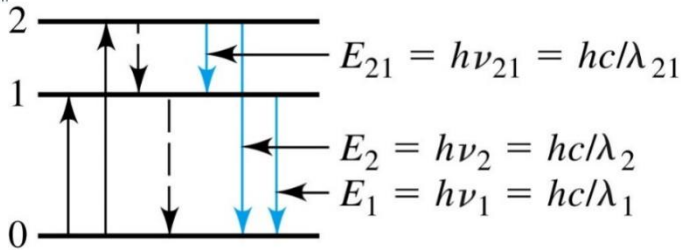
In photoluminescence spectroscopy the emission of photons is measured after absorption. The most important forms of photoluminescence for analytical purposes are fluorescence and phosphorescence spectroscopy.



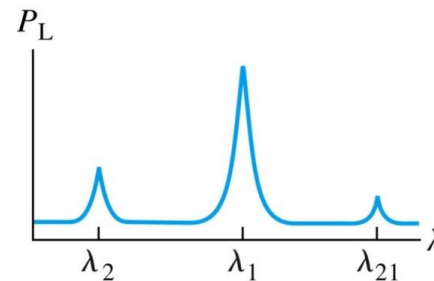
(a)

FIGURE 6-17(a) Photoluminescence methods  
(a) Fluorescence and phosphorescence result from absorption of electromagnetic radiation and then dissipation of the energy emission of radiation

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).



(b)



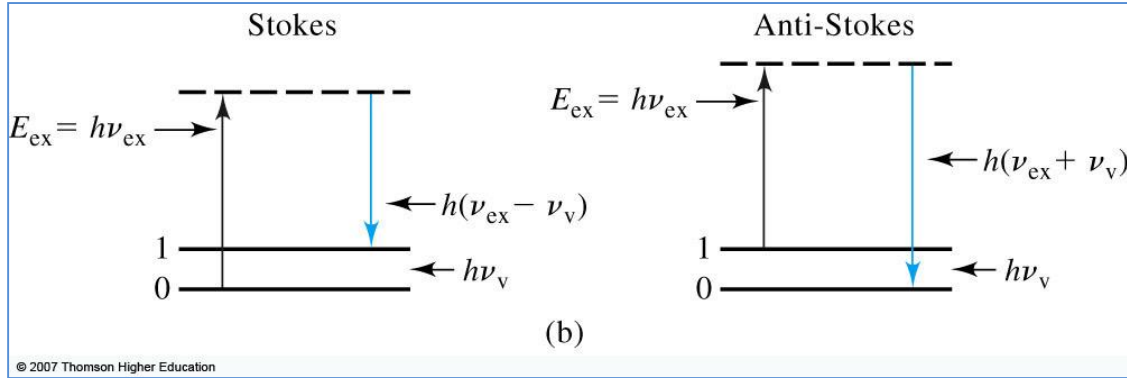
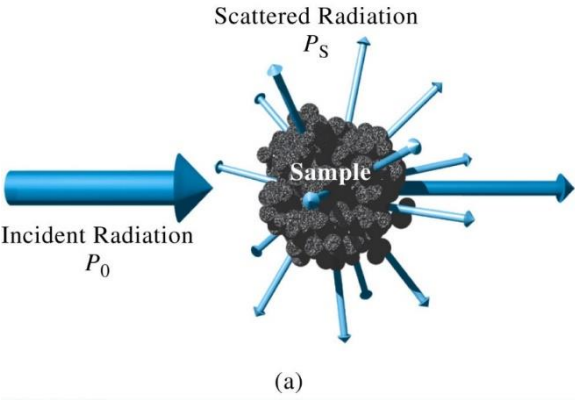
(c)

(c) The emission occurs over all angles, and the wavelengths emitted 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.

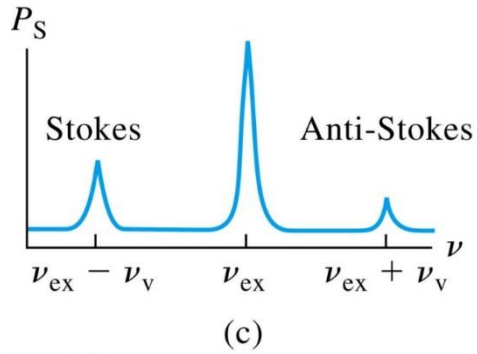
# Interaction of Radiation and Matter

## Inelastic Scattering in Raman Spectroscopy

When radiation is scattered, the interaction of the incoming radiation with the sample may be elastic or inelastic. In elastic scattering, the wavelength of the scattered radiation is the same as that of the source radiation. The intensity of the elastically scattered radiation is used to make measurements in nephelometry and turbidimetry, and particle sizing.



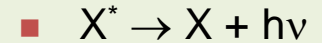
Raman spectroscopy, which is mentioned briefly in Section 6B-10 and is discussed in detail in Chapter 18, uses inelastic scattering to produce a vibrational spectrum of sample molecules. In this type of spectroscopic analysis, the intensity of the scattered radiation is recorded as a function of the frequency shift of the incident radiation. The intensity of Raman peaks is related to the concentration of the analyte.



# Emission of Radiation:

Electromagnetic radiation is produced when excited particles (atoms, ions, or molecules) relax to lower energy levels by giving up their excess energy as photons.

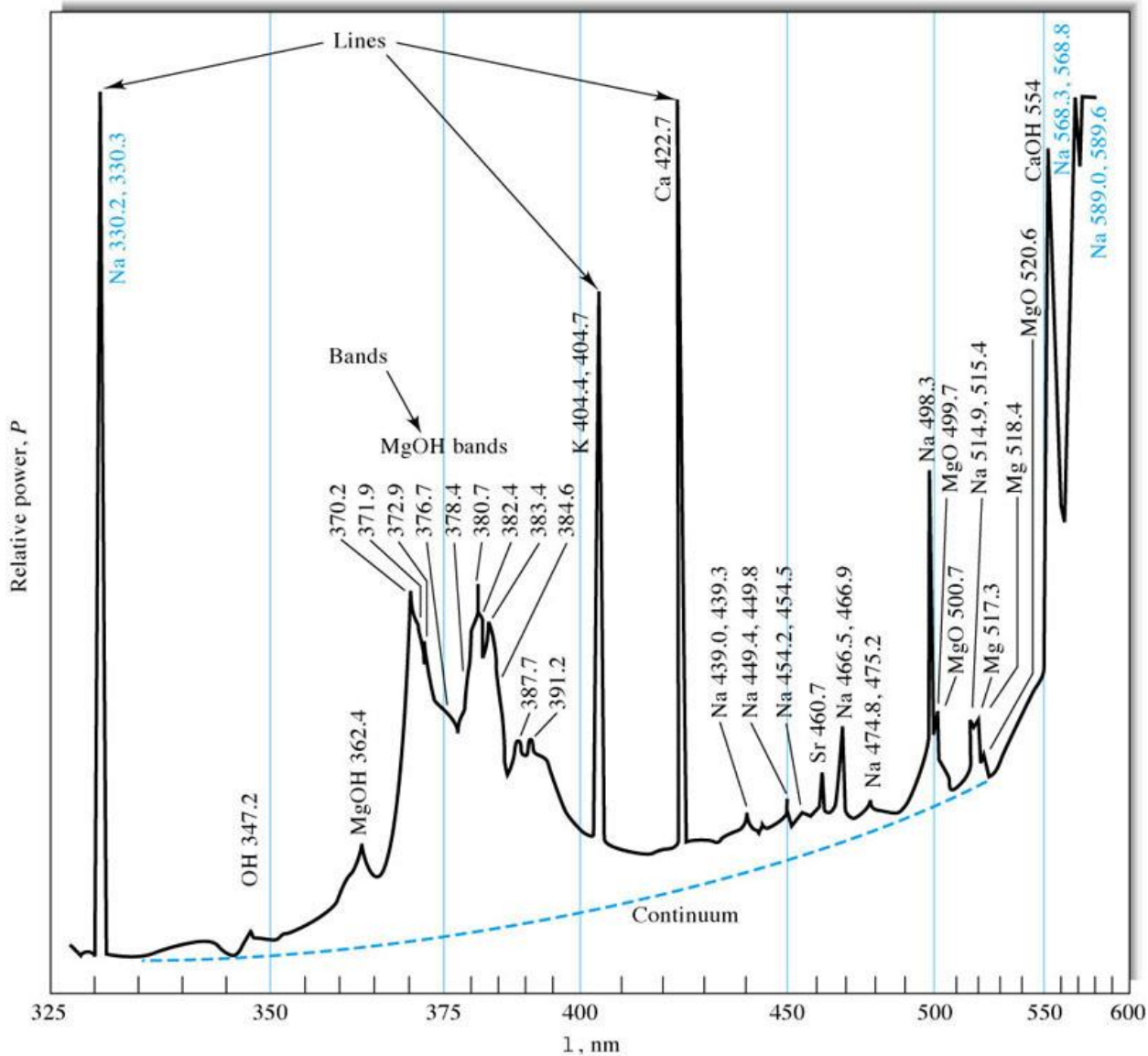
## Emission



## Excitation needs energy!

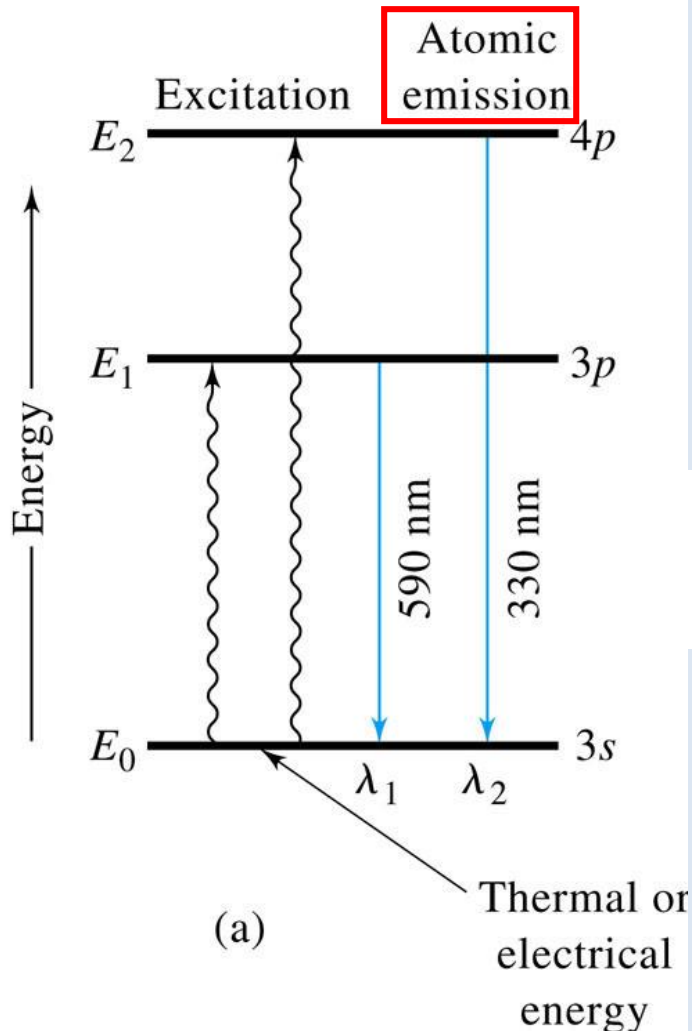
- bombardment with electrons or other elementary particles, which generally leads to the emission of X-radiation;
- exposure to an electric current, an AC spark, or an intense heat source (flame, DC arc, or furnace), producing ultraviolet, visible, or infrared radiation;
- irradiation with a beam of electromagnetic radiation, which produces fluorescence radiation; and
- an exothermic chemical reaction that produces chemiluminescence

# Emission: Saltwater in a flame



# Line Spectra

- Arises from individual, well separated atoms in a gas phase
- Sharp lines ( $10^{-4}$  Å)



$E_0$  : the lowest, or ground-state energy of the atom.  
 $E_1$  and  $E_2$  : two higher-energy electronic levels

- the single outer electron in the GS for a sodium atom is located in the  $3s$  orbital.
- when this electron has been promoted to the  $3p$  state by absorption of thermal, electrical, or radiant energy.
- After perhaps  $10^{-8}$  s, the atom returns to the ground state, emitting a photon whose frequency and wavelength are given by

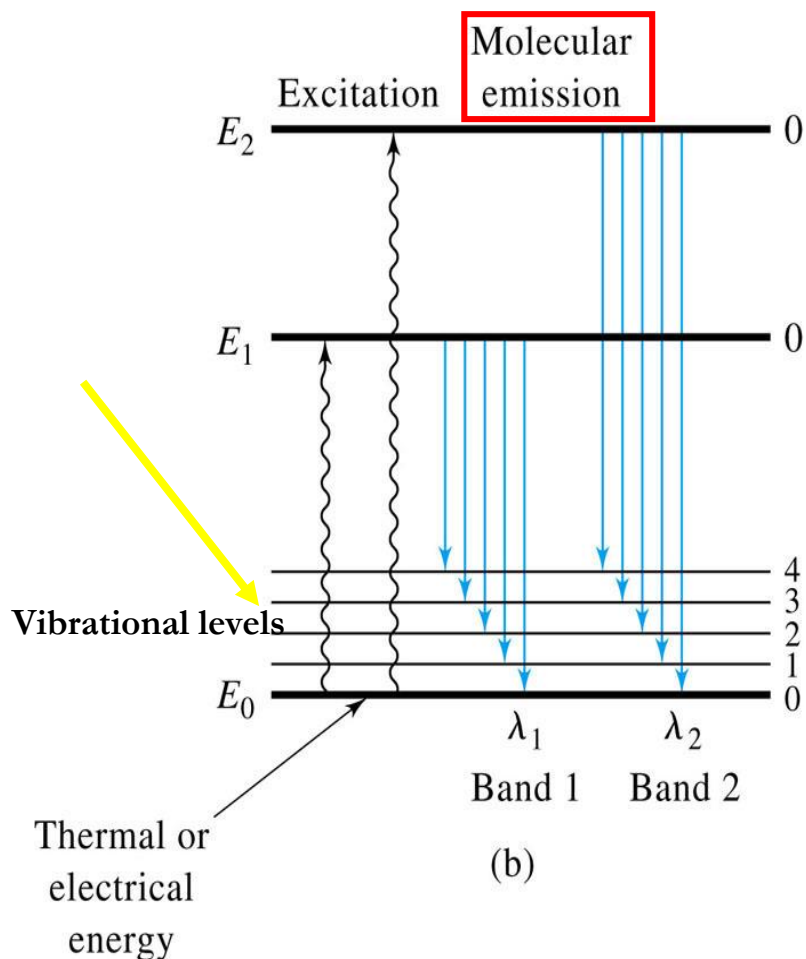
$$\nu_1 = (E_1 - E_0)/h$$

$$\lambda_1 = hc/(E_1 - E_0)$$

- The line at about 590 nm is the result of the  $3p$  to  $3s$  transition.
- For the sodium atom, corresponds to the more energetic  $4p$  state; the resulting emitted radiation  $\lambda_2$  appears at a shorter wavelength or a higher frequency. The line at about 330 nm results from this transition.

# Band Spectra

- Arises from small molecules and radicals
- consist of a series of closely spaced lines that are not fully resolved by the instrument
- numerous quantized vibrational levels that are superimposed on the ground-state electronic energy level of a molecule are involved

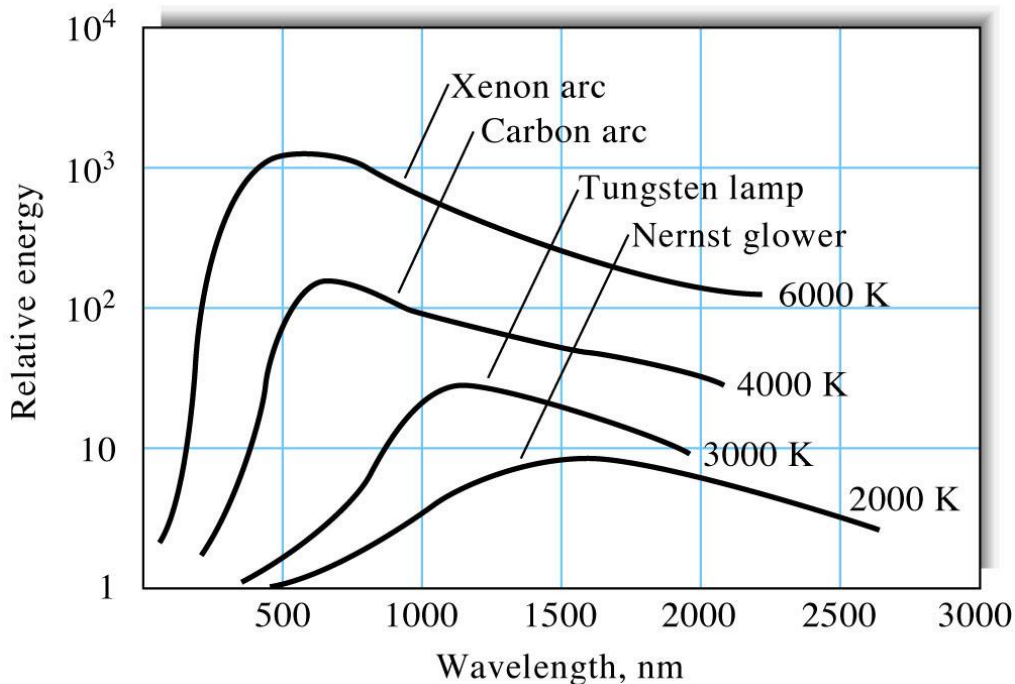


(b)

- an electron excited to one of the higher vibrational levels of an electronic state relaxes to the lowest vibrational level of that state before an electronic transition to the ground state can occur.
- Therefore, the radiation produced by the electrical or thermal excitation of polyatomic species nearly always results from a transition from the lowest vibrational level of an excited electronic state to any of the several vibrational levels of the ground state
- The mechanism by which a vibrationally excited species relaxes to the nearest electronic state involves a transfer of its excess energy to other atoms in the system through a series of collisions. This process takes place at an enormous speed. Relaxation from one electronic state to another can also occur by collisional transfer of energy, but the rate of this process is slow enough that relaxation by photon release is favored.
- For a real molecule, the number of individual lines is much larger because in addition to the numerous vibrational states, a multitude of rotational states are superimposed on each.
- The differences in energy among the rotational levels are perhaps an order of magnitude smaller than that for vibrational states. Thus, a real molecular band would be made up of many more lines than we have shown in Figure and these lines would be much more closely spaced.

# Continuum Spectra

- When solids are heated to incandescence, thermal radiation called Blackbody Radiation is produced
- This radiation is characteristic of the temperature of the emitting surface rather than the material composing that surface.
- Blackbody radiation is produced by the innumerable atomic and molecular oscillations excited in the condensed solid by the thermal energy.
- Note that the energy peaks in Figure shift to shorter wavelengths with increasing temperature. It is clear that very high temperatures are needed to cause a thermally excited source to emit a substantial fraction of its energy as ultraviolet radiation



- Heated solids are important sources of infrared, visible, and longer-wavelength ultraviolet radiation for analytical instruments
- in the flame spectrum shown in Figure 6-19 is probably thermal emission from incandescent particles in the flame. Note that this background decreases rapidly as the ultraviolet region is approached.



# Blackbody Radiation

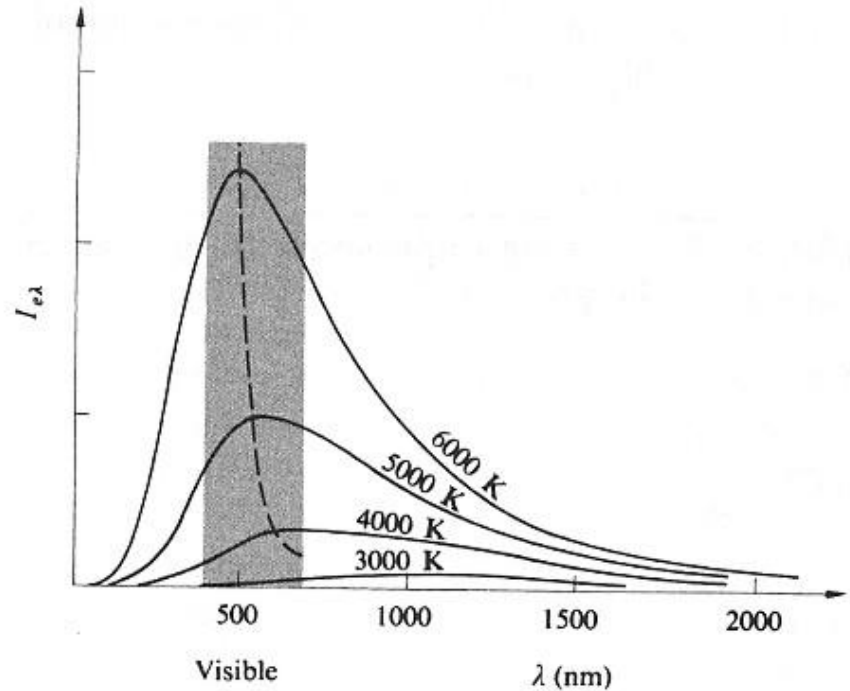
*Wien's Displacement Law  
for blackbody radiators*

$$\lambda_{\max} = \frac{2.897 \times 10^6 \text{ K nm}}{T}$$

*Stefan-Boltzman Law*

$$P = \sigma T^4$$

$$\sigma = 5.6697 \times 10^{-12} \text{ Wcm}^{-2}\text{K}^{-4}$$

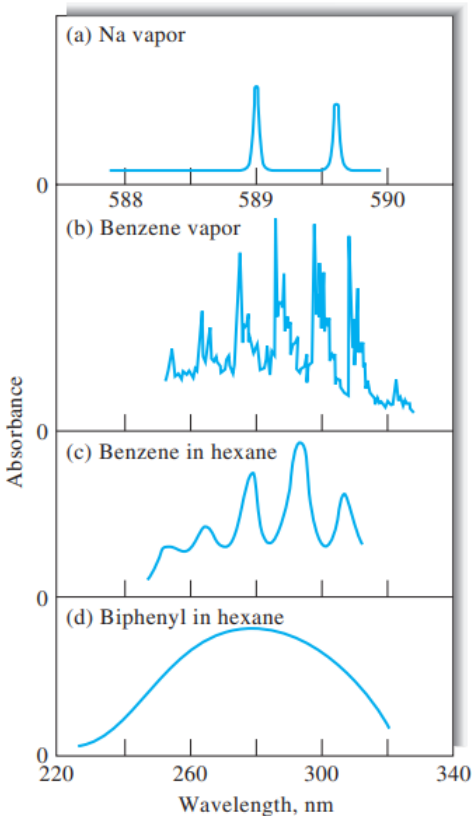
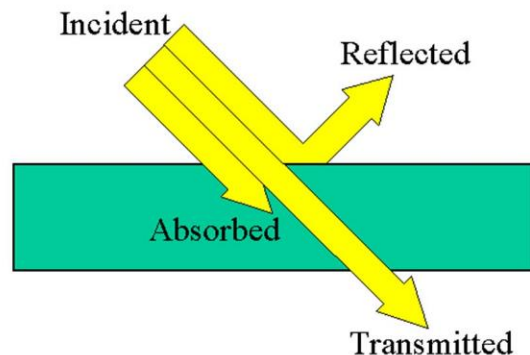


**Figure 13.2** Blackbody radiation curves. The hyperbola passing through peak points corresponds to Wien's Law.

Both  $\lambda_{\max}$  and radiation power (P) are related to TEMPERATURE and current!

## 6C-5 Absorption of Radiation

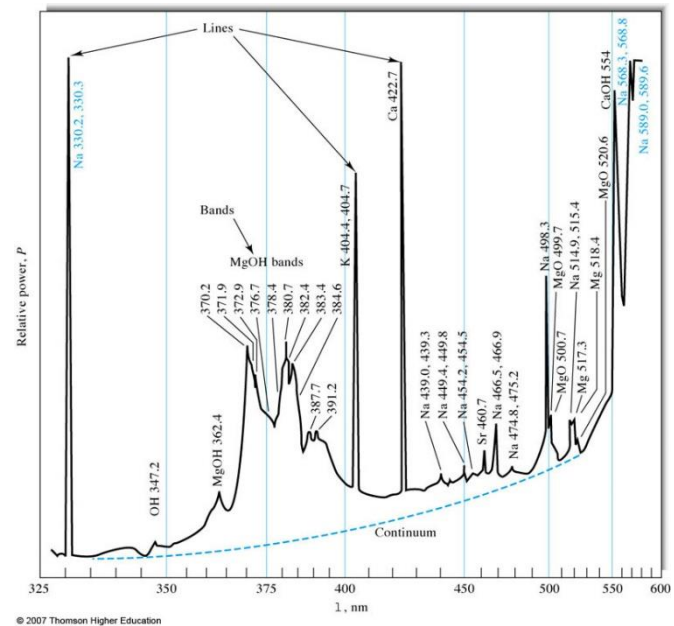
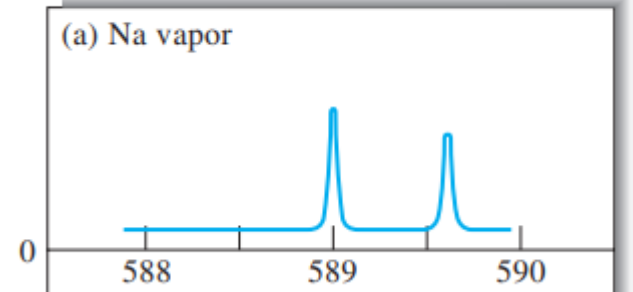
- When radiation passes through a solid, liquid, or gaseous sample, certain frequencies may be selectively removed by absorption, a process in which electromagnetic energy is transferred to the atoms, ions, or molecules composing the sample.
- Absorption promotes these particles from their normal room temperature state, or ground state, to one or more higher-energy excited states.



- According to quantum theory, atoms, molecules, and ions have only a limited number of discrete energy levels; for absorption of radiation to occur, the energy of the exciting photon must exactly match the energy difference between the ground state and one of the excited states of the absorbing species.
- Since these energy differences are unique for each species, a study of the frequencies of absorbed radiation can be used to characterize and identify the constituents of a sample. For this purpose, a plot of absorbance as a function of wavelength or frequency is experimentally determined
- Typical absorption spectra are shown in Figure 6-23, reveal that absorption spectra vary widely in appearance; some are made up of numerous sharp peaks, while others consist of smooth continuous curves.
- In general, the nature of a spectrum is influenced by such variables as the complexity, the physical state, and the environment of the absorbing species. More fundamental, however, are the differences between absorption spectra for atoms and those for molecules<sup>50</sup>

# Atomic Absorption

- When polychromatic ultraviolet or visible radiation passes through a medium that consists of monoatomic particles, such as gaseous mercury or sodium, absorption can occur at a few well-defined frequencies.
- The relative simplicity of such spectra is due to the small number of possible energy states for the absorbing particles.
- Ultraviolet and visible radiation have enough energy to cause transitions of the outermost, or bonding, electrons only. X-ray frequencies, on the other hand, are several orders of magnitude more energetic and are capable of interacting with electrons that are closest to the nuclei of atoms. Absorption peaks that correspond to electronic transitions of these innermost electrons are thus observed in the X-ray region



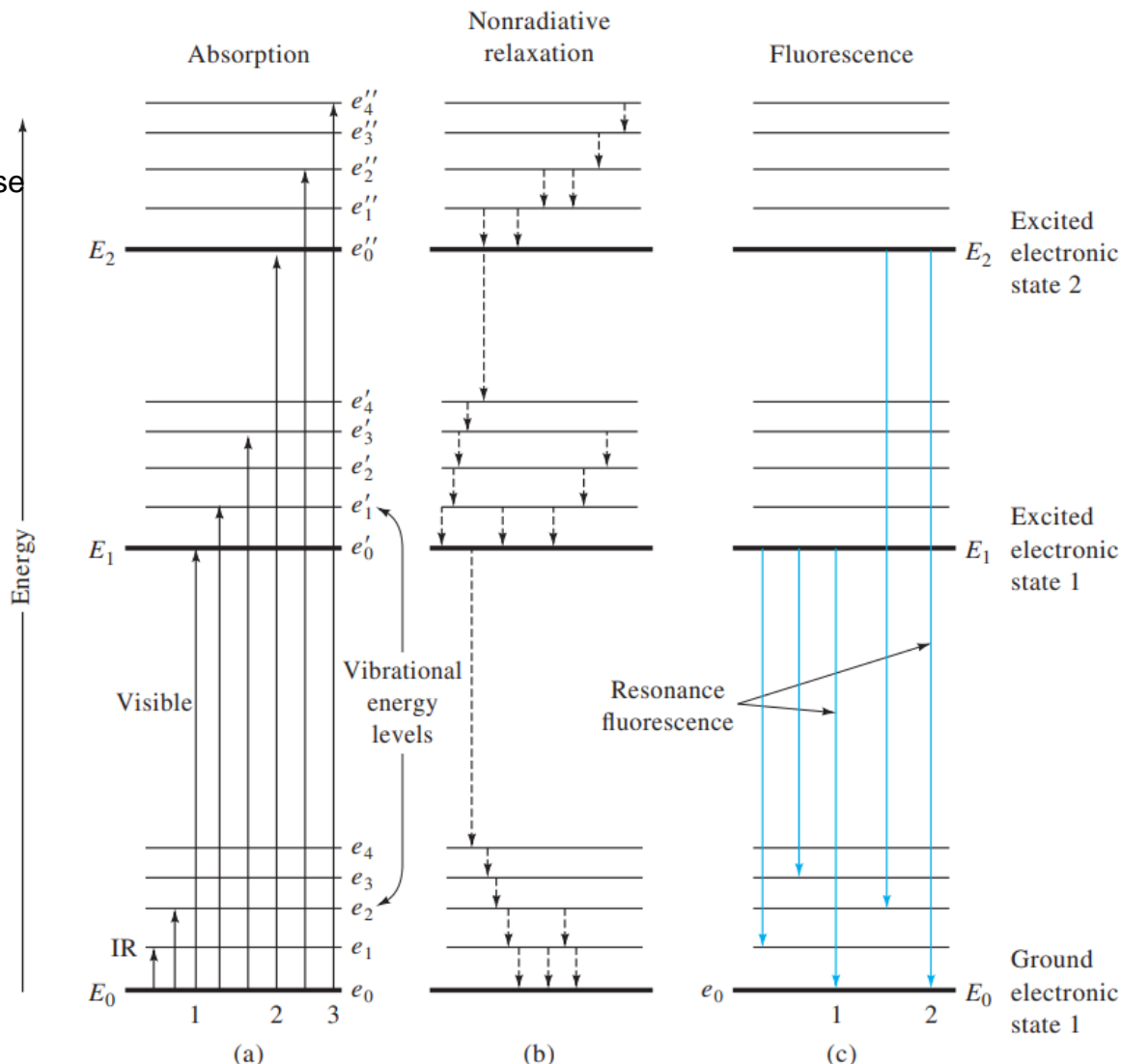
# Molecular Absorption

- Absorption spectra for polyatomic molecules are considerably more complex than atomic spectra because the number of energy states of molecules are generally enormous when compared with the number of energy states for isolated atoms.
- The energy  $E$  associated with the bands of a molecule is made up of three components. That is

$$E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}}$$

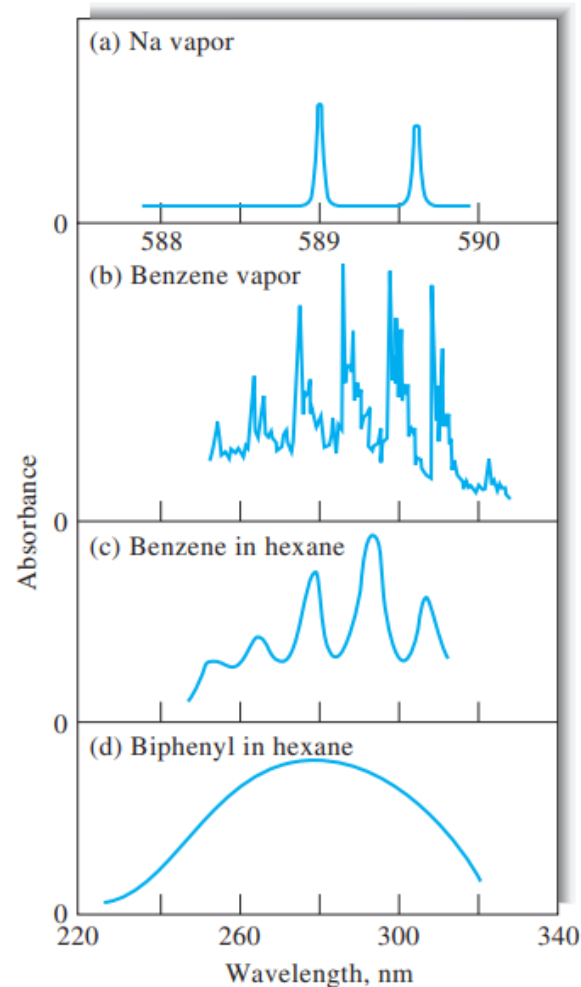
Number of levels/states

$$E_{\text{el}} < E_{\text{vib}} < E_{\text{rot}}$$



**FIGURE 6-24** Partial energy-level diagrams for a fluorescent organic molecule.

- In contrast to atomic absorption spectra, which consist of a series of sharp, well-defined lines, molecular spectra in the ultraviolet and visible regions are ordinarily characterized by absorption regions that often encompass a substantial wavelength range (see Figure 6-23b,c).
- Molecular absorption also involves electronic transitions. Several closely spaced absorption lines will be associated with each electronic transition, because of the existence of numerous vibrational states. Furthermore, as we have mentioned, many rotational energy levels are associated with each vibrational state. As a result, the spectrum for a molecule usually consists of a series of closely spaced absorption lines that constitute an absorption band, such as those shown for benzene vapor in Figure 6-23b. Unless a high-resolution instrument is used, the individual peaks may not be detected, and the spectra will appear as broad smooth peaks such as those shown in Figure 6-23c.
- Finally, in the condensed state, and in the presence of solvent molecules, the individual lines tend to broaden even further to give nearly continuous spectra such as that shown in *Figure 6-23d*. *Solvent effects* are considered in later chapters.



! 6-23 Some typical ultraviolet absorption spectra.

# 6C-6 Relaxation Processes

## Nonradiative Relaxation

- *nonradiative relaxation* involves the loss of energy in a series of small steps, the excitation energy being converted to kinetic energy by collision with other molecules. A minute increase in the temperature of the system results.
- relaxation can also occur by emission of fluorescence radiation.

## Fluorescence and Phosphorescence Emission

- Species are excited by absorption of a beam of electromagnetic radiation;
- radiant emission then occurs as the excited species return to the ground state.
- Fluorescence occurs more rapidly than phosphorescence and is generally complete after about  $10^{-5}$  s from the time of excitation. Phosphorescence emission takes place over periods longer than  $10^{-5}$  s and may indeed continue for minutes or even hours after irradiation has ceased.
- Fluorescence and phosphorescence are most easily observed at a  $90^\circ$  angle to the excitation beam.
- *Resonance fluorescence* describes the process in which the emitted radiation is identical in frequency to the exciting radiation.
- Resonance fluorescence is most commonly produced by *atoms* in the gaseous state, which do not have vibrational energy states superimposed on electronic energy levels.
- *Nonresonance fluorescence* is caused by irradiation of molecules in solution or in the gas phase.

## 6C-7 The Uncertainty Principle

- first proposed in 1927 by Werner Heisenberg,
- who postulated that nature places limits on the precision with which certain pairs of physical measurements can be made.
- The uncertainty principle, which has important and widespread implications in instrumental analysis, can be derived from the principle of superposition, which was discussed in Section 6B-4. Applications of this principle will be found in several later chapters that deal with spectroscopic methods.
- Let us suppose that we wish to determine the frequency  $\nu_1$  of a monochromatic beam of radiation by comparing it with the output of a standard clock, which is an oscillator that produces a light beam that has a precisely known frequency of  $\nu_2$ . To detect and measure the difference between the known and unknown frequencies,  $\Delta\nu = \nu_1 - \nu_2$ , we allow the two beams to interfere as in Figure 6-5 and determine the time interval for a beat (A to B in Figure 6-5). The minimum time  $\Delta t$  required to make this measurement must be equal to or greater than the period of one beat, which as shown in Figure 6-5, is equal to  $1/\Delta\nu$ . Therefore, the minimum time for a measurement is given by

$$\Delta t \geq 1/\Delta\nu$$

or

$$\Delta t \Delta\nu \geq 1$$

*Note that to determine  $\Delta\nu$  with negligibly small uncertainty, a huge measurement time is required. If the observation extends over a very short period, the uncertainty will be large.*

Let us multiply both sides of Eqn. by Planck's constant,  $h$ , to give

$$\Delta t \cdot (h\Delta\nu) = h$$

Heisenberg uncertainty principle.

$$\Delta t \cdot \Delta E = h$$

### Meanings of the Heisenberg uncertainty principle in words

- If the energy  $E$  of a particle or system of particles—photons, electrons, neutrons, or protons—is measured for an exactly known period of time  $\Delta t$ , then this energy is uncertain by at least  $h/\Delta t$ .
- Therefore, the energy of a particle can be known with zero uncertainty only if it is observed for an infinite period. For finite periods, the energy measurement can never be more precise than  $h/\Delta t$ .

## 6D Quantitative Aspects of Spectrochemical Measurements

**TABLE 6-2** Major Classes of Spectrochemical Methods

Class	Radiant Power Measured	Concentration Relationship	Type of Methods
Emission	Emitted, $P_e$	$P_e = kc$	Atomic emission
Luminescence	Luminescent, $P_l$	$P_l = kc$	Atomic and molecular fluorescence, phosphorescence, and chemiluminescence
Scattering	Scattered, $P_{sc}$	$P_{sc} = kc$	Raman scattering, turbidimetry, and particle sizing
Absorption	Incident, $P_0$ , and transmitted, $P$	$-\log \frac{P}{P_0} = kc$	Atomic and molecular absorption

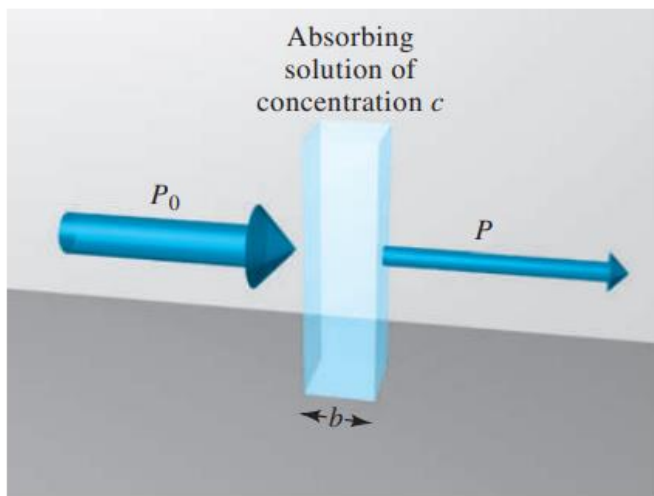
- there are four major classes of spectrochemical methods. All four require the measurement of radiant power  $P$ ,
- *radiant power*  $P$ , which is the energy of a beam of radiation that reaches a given area per second.
- In modern instruments, radiant power is determined with a radiation detector that converts radiant energy into an electrical signal  $S$ .
- Generally,  $S$  is a voltage or a current that ideally is directly proportional to radiant power. That is, where  $S = kP$ , and  $k$  is a constant.
- Many detectors exhibit a small, constant response, known as a **dark signal or dark response**,  $k_d$  (usually a current or voltage),  $S = kP + k_d$  of radiation. In those cases, the total signal is described by the relationship
- The dark signal is generally small and constant. Spectrochemical instruments are usually equipped with a compensating circuit that reduces  $k_d$  to zero whenever measurements are made.



## 6D-1 Emission, Luminescence and Scattering Methods

- As shown in column 3 of Table 6-2, in emission, luminescence, and scattering methods, the power of the radiation emitted by an analyte after excitation is ordinarily directly proportional to the analyte concentration,  $c$ , ( $P_e = k.c$ ).
- Combining this equation with Equation 6-27 gives  $S = k'.c$  (6-29) where  $k'$  is a constant that can be evaluated by measuring  $S$  after excitation of one or more standards of known concentration.

## 6D-2 Absorption Methods



**FIGURE 6-25** Attenuation of a beam of radiation by an absorbing solution. The larger arrow on the incident beam signifies a higher radiant power than is transmitted by the solution. The path length of the absorbing solution is  $b$ , and the concentration is  $c$ .

$$T = \frac{P}{P_0}$$
$$A = \log \frac{P_0}{P}$$

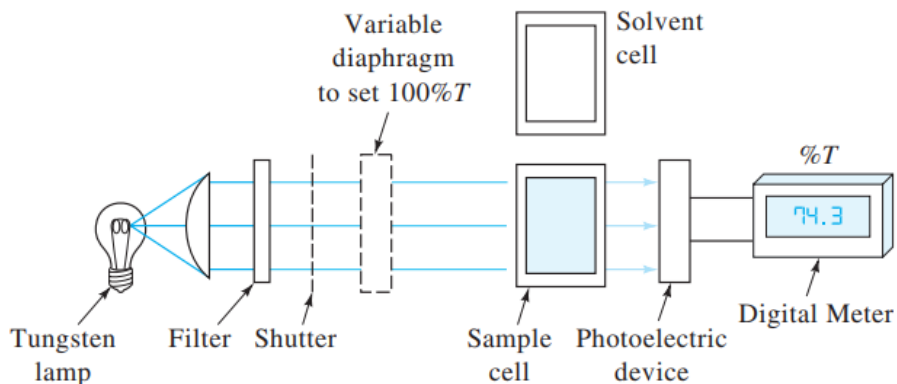
- quantitative absorption methods require two power measurements: 1) before a beam has passed through the medium that contains the analyte ( $P_0$ ) and 2) the other after passing through the medium ( $P$ ).
- Two terms, that are widely used in absorption spectrometry and are related to the ratio of  $P_0$  and  $P$ , are transmittance and absorbance

$$A = abc$$

$a$  : proportionality constant called absorptivity. The magnitude of  $a$  depends on the units used for  $b$  and  $c$ . When the concentration in Equation 6-33 is expressed in moles per liter and the cell length is in centimeters, the absorptivity is called the molar absorptivity and is given a special symbol,  $\epsilon$ . Thus, when  $b$  is in centimeters and  $c$  is in moles per liter,  $\epsilon$  has the units  $L \text{ mol}^{-1} \text{ cm}^{-1}$ .

$$A = \epsilon bc$$

## Measurement of Transmittance and Absorbance



**FIGURE 6-26** Single-beam photometer for absorption measurements in the visible region.

- A photometer, is used for measuring the transmittance and absorbance of aqueous solutions with a filtered beam of visible radiation.
- The radiation from a tungsten bulb passes through a colored glass filter that restricts the radiation to a limited band of contiguous wavelengths. The beam then passes through a variable diaphragm that permits adjustment of the power of the radiation that reaches the transparent cell that contains the sample. A shutter can be imposed in front of the diaphragm that completely blocks the beam.
- With the shutter open, the radiation strikes a photoelectric transducer that converts the radiant energy of the beam to a signal (current or voltage) that can be measured with a digital meter as shown.