NEPHAR 201
Analytical Chemistry II

Chapter 2
An introduction to spectrometric methods

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Electromagnetic Radiation

- **Spectroscopy:** is the study of the interaction between matter and electromagnetic radiation.
- **Optical spectrometry:** techniques for measuring the distribution of light across the optical spectrum, from the UV spectral region to the visible and infrared.
- **Mass spectrometry:** an analytical technique that measures the mass-to-charge ratio of charged particles.
- **Parameters of electromagnetic radiation:**

  Wavelength (λ)

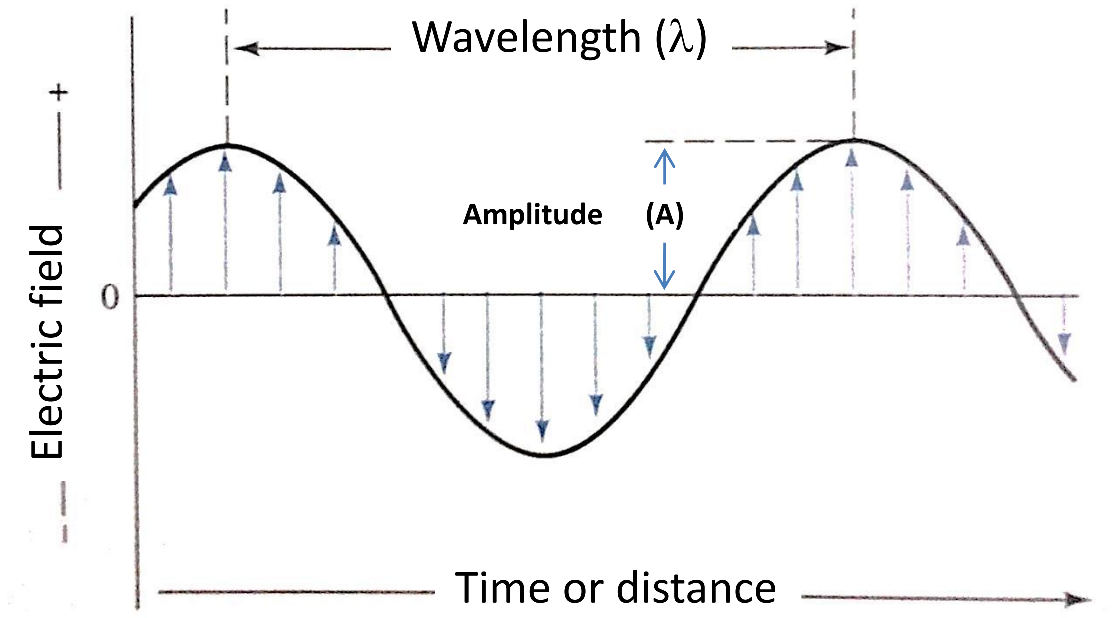
  Frequency (ν)

  Amplitude (A)

  Period (p)

  Wave number ($\overline{\nu}$)

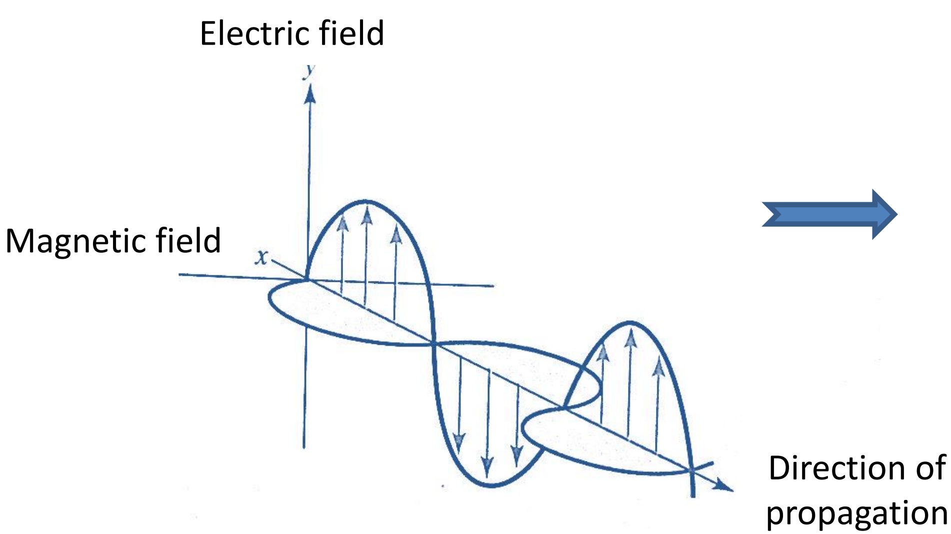
  Velocity (ν_i)

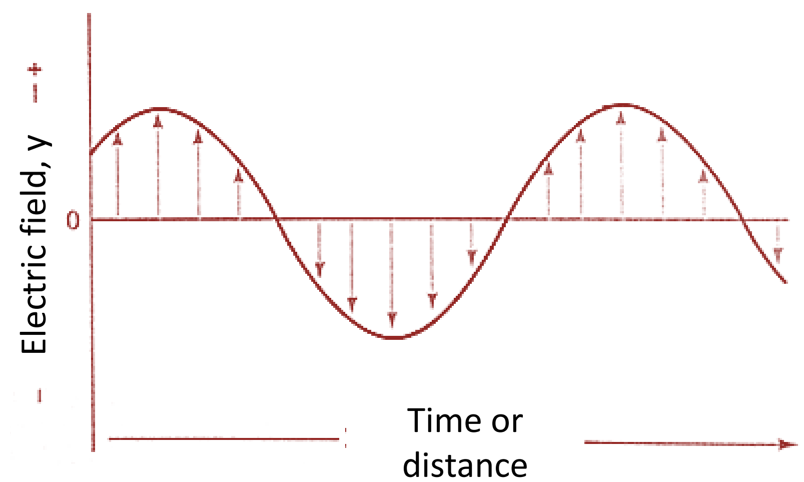


Wave parameter	Definition	Unit(s)
Wavelength (λ)	The linear distance between any two equivalent points on successive waves (e.g., maxima or minima).	mm, cm, µm, nm, ..
Amplitude (A)	The length of the electric vector at a maximum in the wave.	mm, cm, µm, nm,..
Frequency (ν)	The number of oscillations of the field that occur per second.	s^{-1} (Hz)
Period (p)	The time in seconds required for the passage of successive maxima or minima through a fixed point in space.	s
Wave number ($\overline{\nu}$)	The number of waves in a certain distance.	cm^{-1},..

Electromagnetic Radiation

- Requires no supporting medium for its transmission and thus passes readily through a vacuum,
- Consists of photons (i.e., packets of discrete particles having specific energy),
- Has a wave-particle duality properties (i.e., has some properties of waves and some of particles),
- Made up of electric and magnetic components,
- Plane-polarized electromagnetic radiation consists of either electric or magnetic component.





- Velocity of radiation (or speed of light) has its maximum value in vacuum and is given the symbol “c”.

- In vacuum, $\boldsymbol{c = 3.00 \times 10^{8}\ m/s}$

- In air, the velocity of radiation differs only slightly from c (about 0.03 % less).

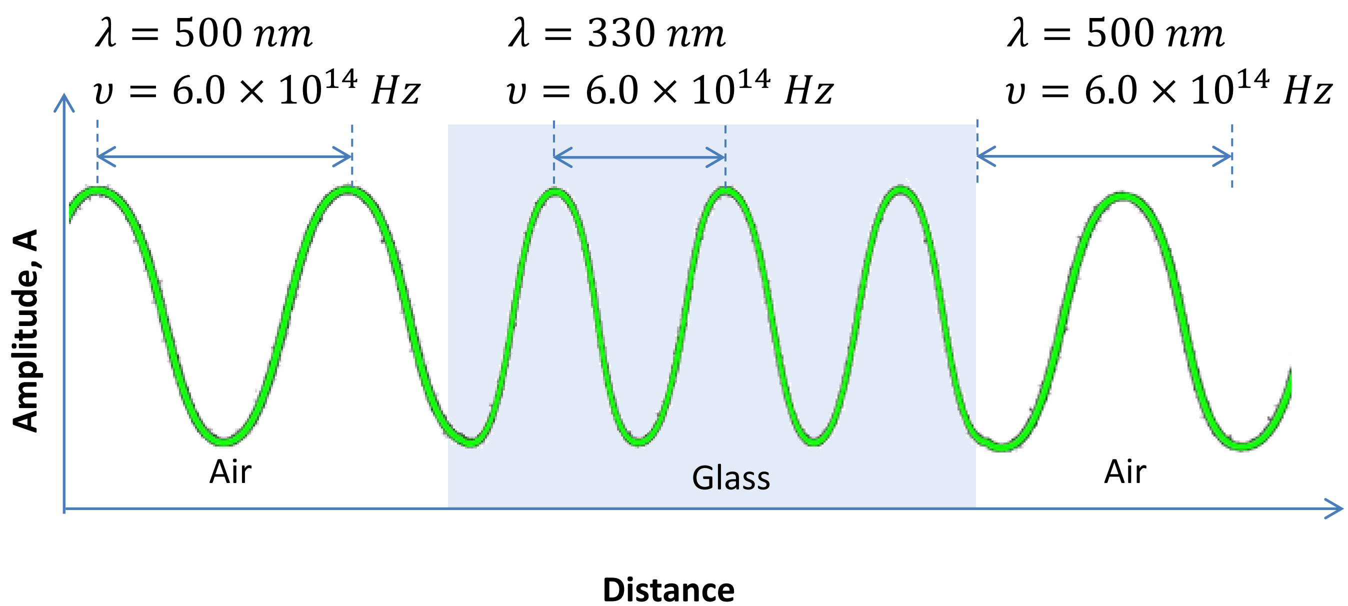
- In any medium containing matter, propagation of radiation is slowed due to interaction of radiation with bound electrons in the matter.

$$c_{\ (m/s)} = \lambda_{(m)} \times \nu_{\ (/s)}$$

Velocity of radiation | Wavelength | Frequency

Example

Effect of medium on a beam of radiation



Using the wave properties given in the figure above, calculate the velocity of radiation in:

a) air
b) glass

Solution

a) In air:

$$c = \lambda \times \nu$$

$$\lambda = 500\ \cancel{nm} \times \frac{1\ m}{10^9\ \cancel{nm}} = 5.0 \times 10^{-7}\ m$$

and

$$\nu = 6.0 \times 10^{14}\ Hz = 6.0 \times 10^{14}\ s^{-1}$$

$$c = \lambda \times \nu = 5.0 \times 10^{-7}\ m \times 6.0 \times 10^{14}\ s^{-1} = 3.0 \times 10^{8}\ m/s$$

b) In glass:

$$\lambda = 330\ \cancel{n}m \times \frac{1\ m}{10^{9}\ \cancel{n}m} = 3.3 \times 10^{-7}\ m$$ and $$\nu = 6.0 \times 10^{14}\ Hz = 6.0 \times 10^{14}\ s^{-1}$$

$$c = \lambda \times \nu = 3.3 \times 10^{-7}\ m \times 6.0 \times 10^{14}\ s^{-1} = 1.98 \times 10^{8}\ m/s$$

Conclusions:

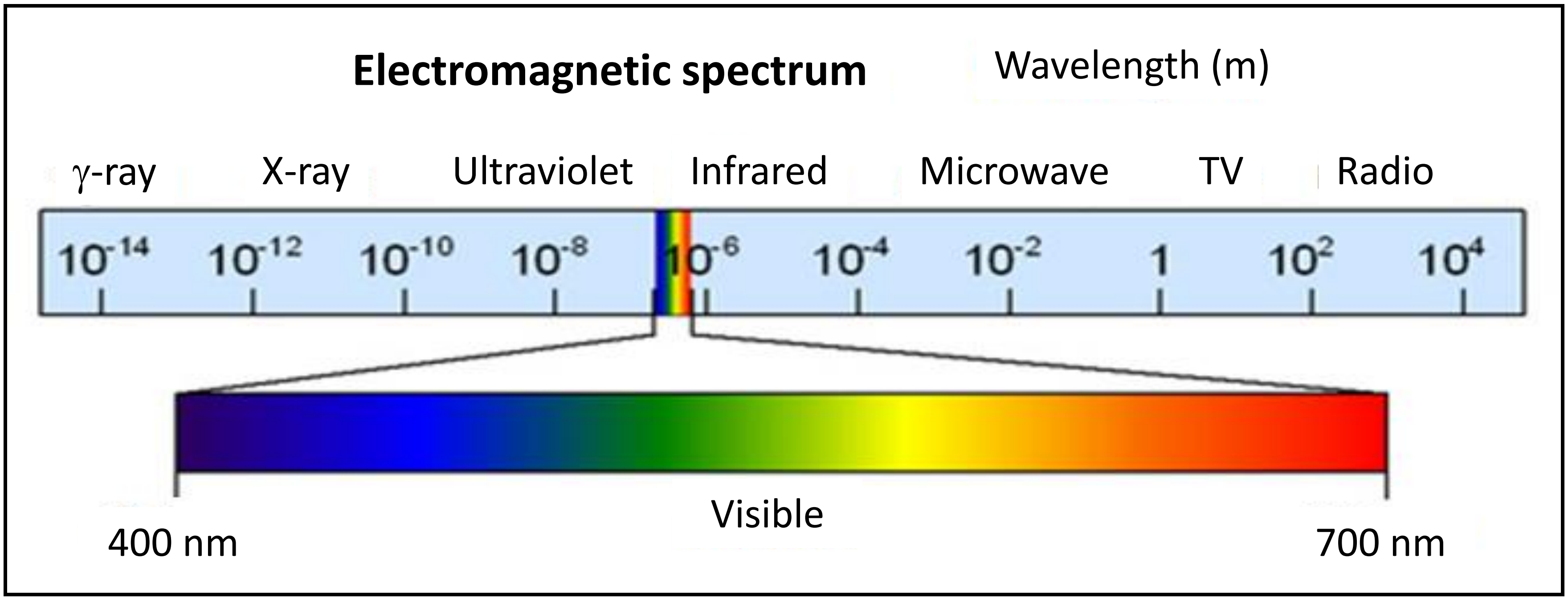
When the radiation beam passes from air to glass:

- its wavelength decreases,
- its frequency remains constant,
- its velocity decreases. This is due to more interactions with matter in the glass.

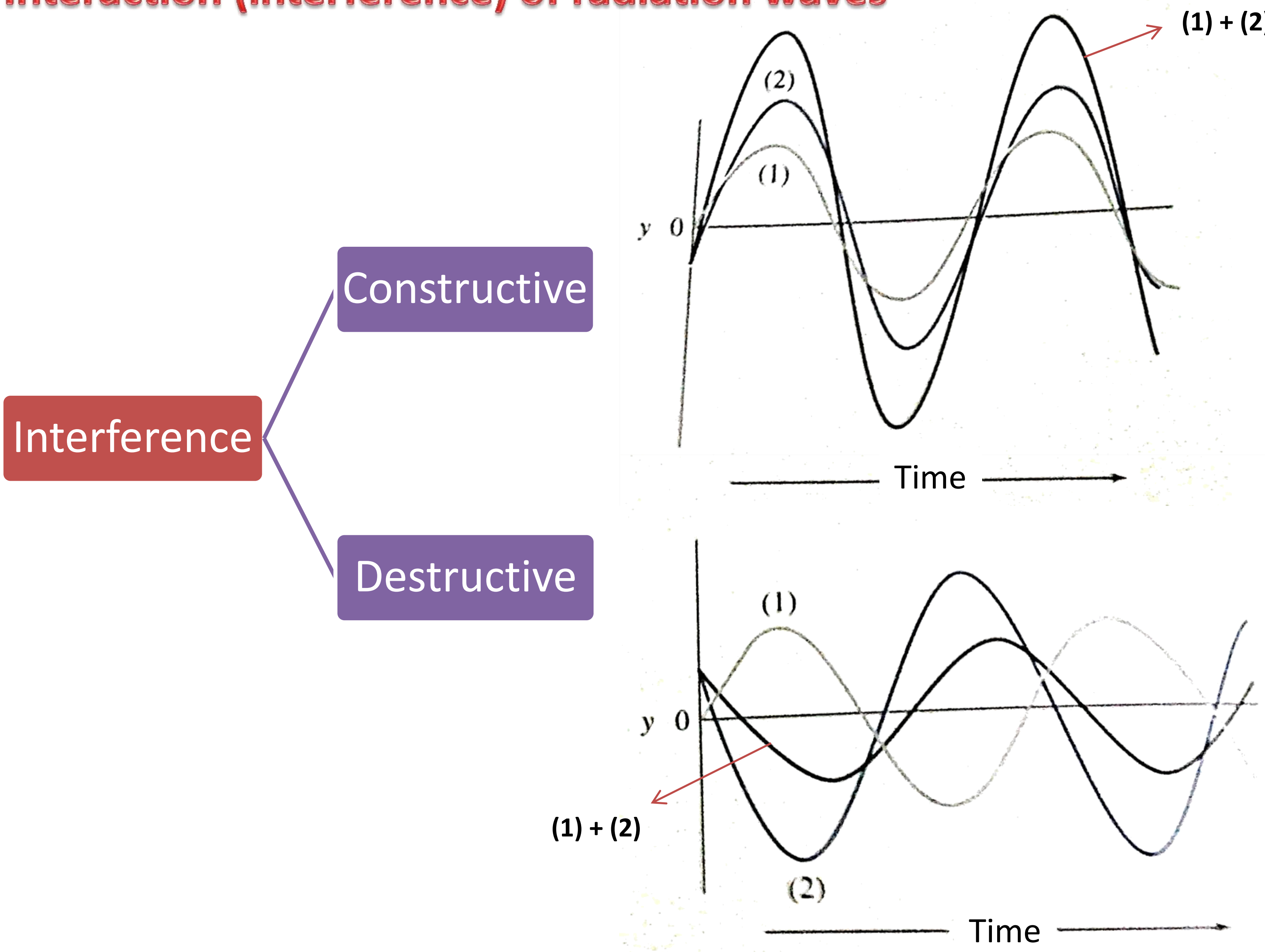
Electromagnetic Spectrum

- High energy
- High frequency
- Low wavelength

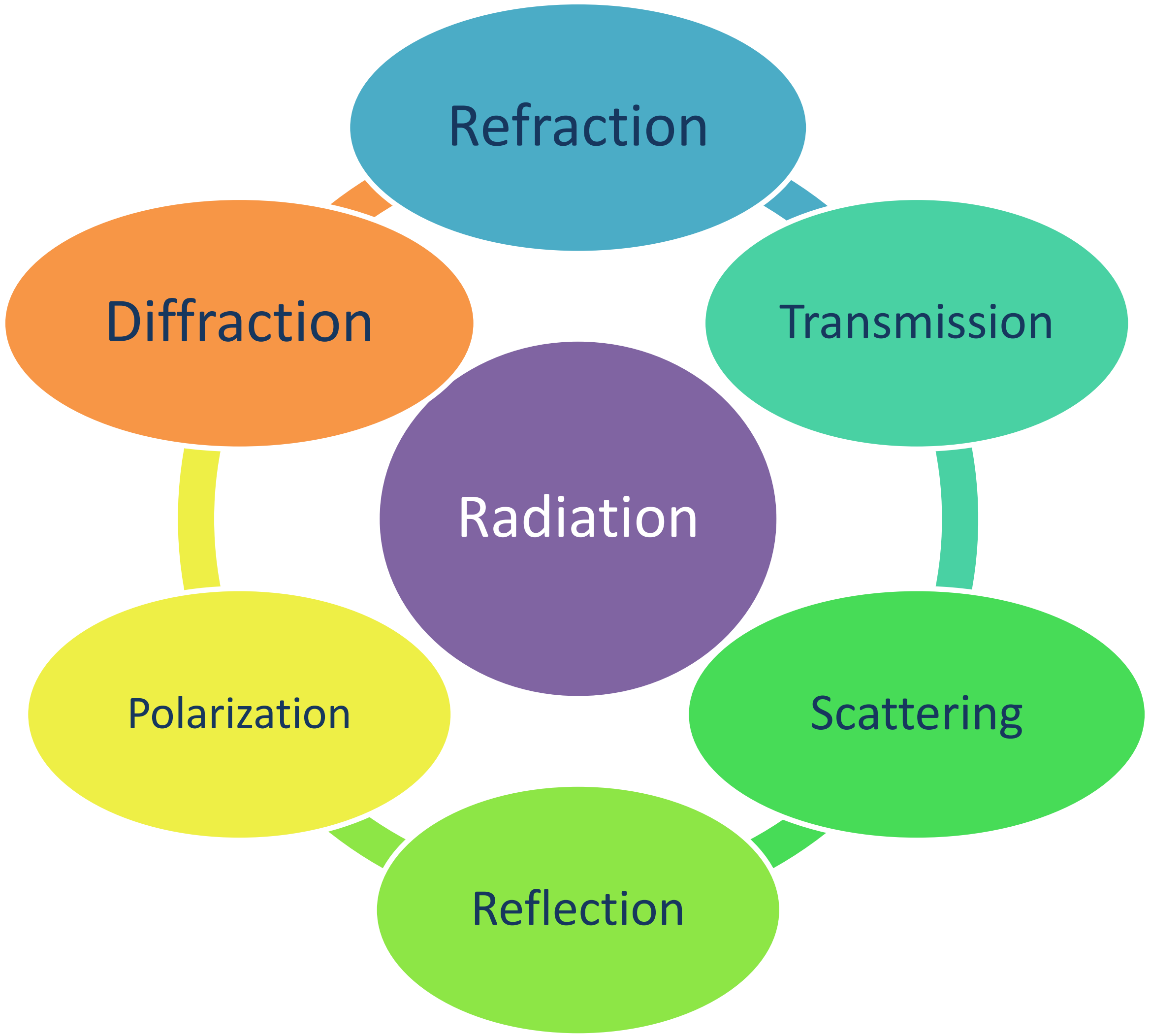
- Low energy
- Low frequency
- High wavelength



Interaction (interference) of radiation waves

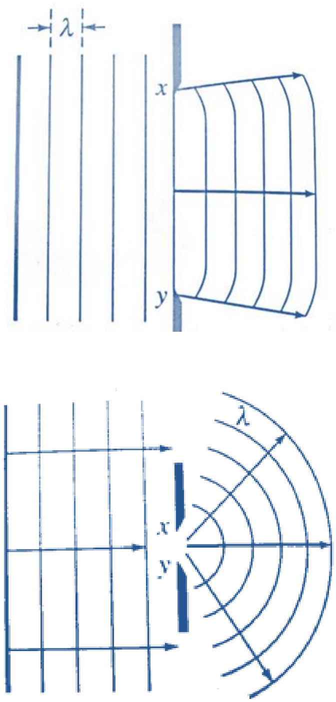


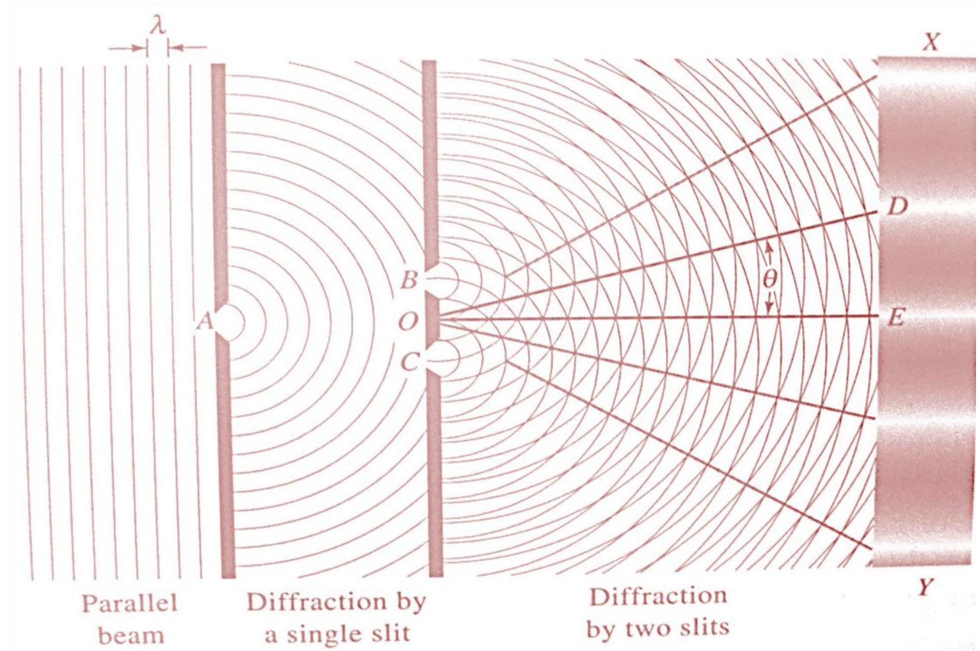
Changes of Radiation



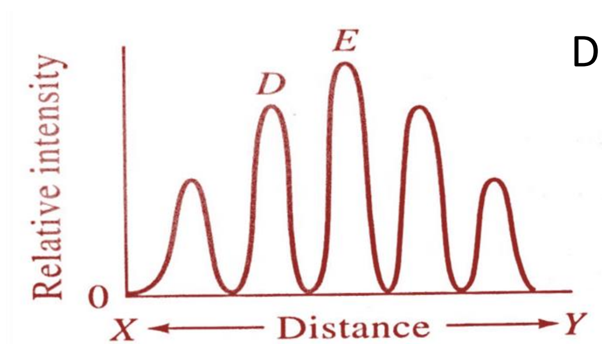
1) Diffraction of radiation

Diffraction is a process in which a parallel beam of radiation is bent as it passes by a sharp barrier or through a narrow opening. Diffraction is a consequence of interference.





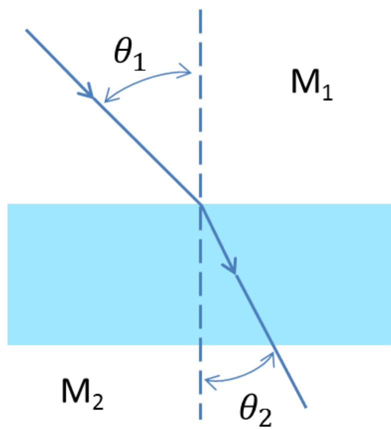
Propagation of a wave through slit



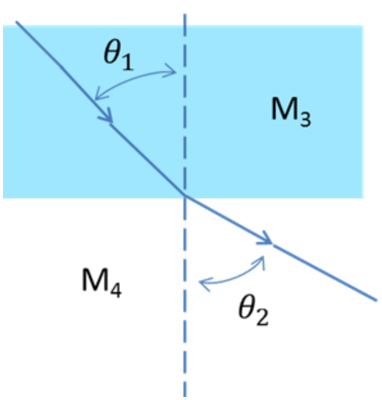
Diffraction of radiation by slits

2) Refraction of radiation

- When radiation passes at an angle through the interface between two transparent media that have different densities, an abrupt change in direction (**refraction**) of the beam is observed as a consequence of a difference in velocity of the radiation in the two media.
- **Refractive index** (η) of a medium is a dimensionless number that describes how light, or any other radiation, propagates through that medium.



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

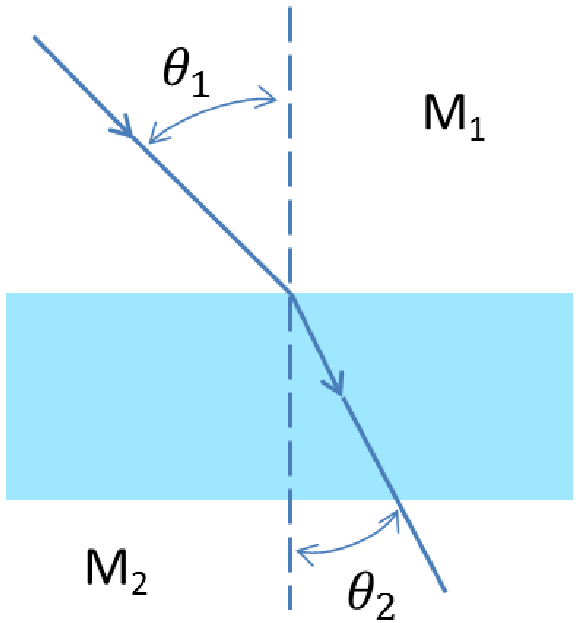


Refraction of light in passing from a **more** dense medium M_3 into a **less** dense medium M_4, where its velocity is **higher**.

- The extent of refraction is given by Snell's law.

Snell's Law:

$$\boxed{\frac{\sin\theta_1}{\sin\theta_2} = \frac{\eta_2}{\eta_1} = \frac{v_1}{v_2}}$$



In this equation:

η_1: refractive index of medium M_1,

η_2: refractive index of medium M_2,

v_1: velocity of radiation in medium M_1,

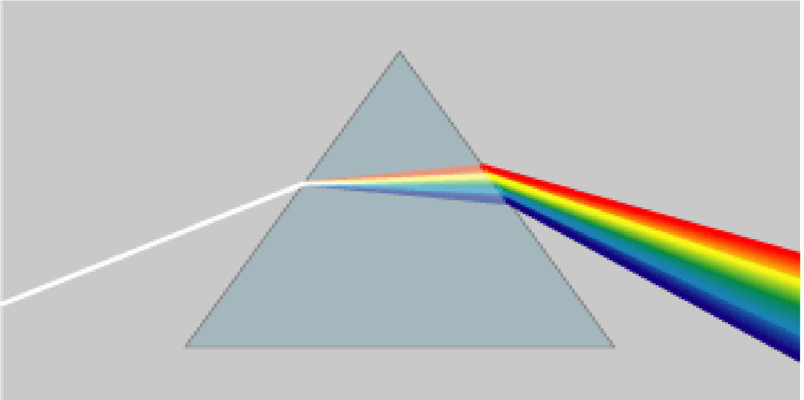
v_2: velocity of radiation in medium M_2.

1) If M_1 is vacuum, $\boldsymbol{\eta_1 = 1}$ and $\boldsymbol{v_1 = c = 3.0 \times 10^8\ m/s}$

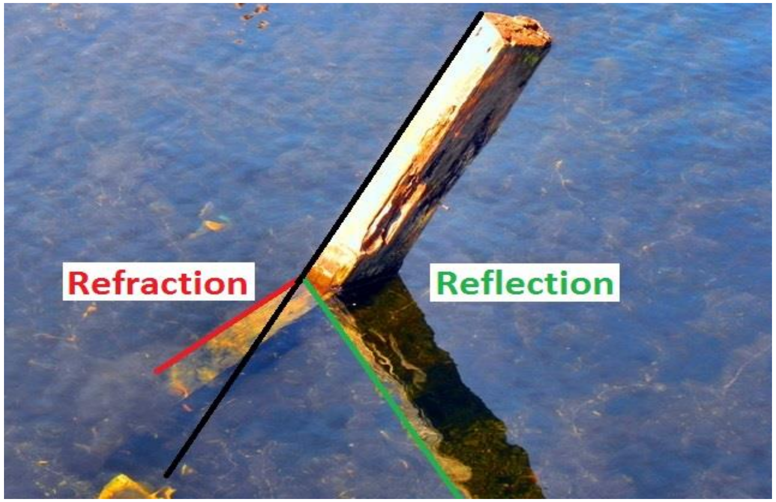
$$\eta_2 = \frac{(\sin\theta_1)_{vac}}{\sin\theta_2} = \frac{v_2}{c}$$

2) $\eta_{vac} = 1.00027\,\eta_{air}$

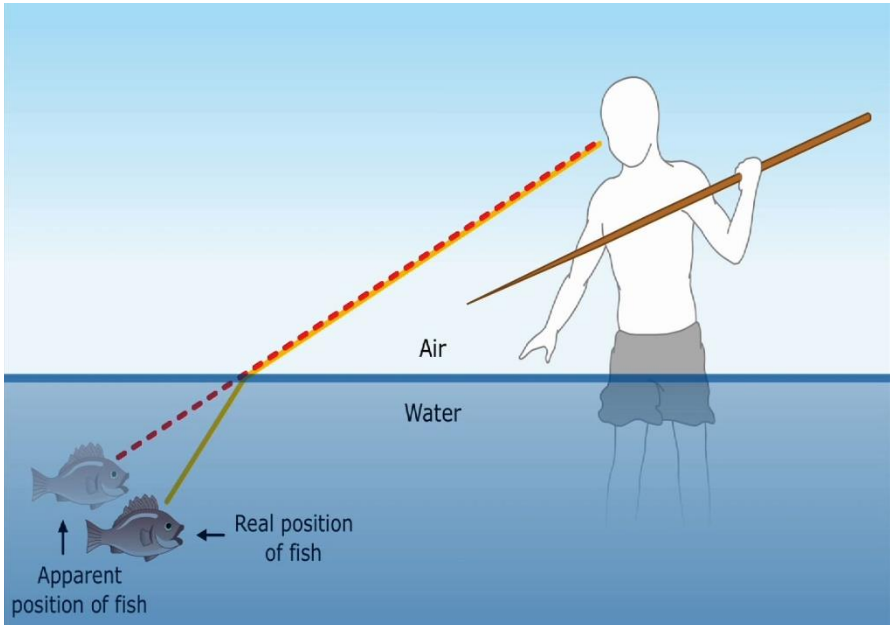
η_{air} is used instead of η_{vac} because it is easier to measure.



In a prism dispersion causes different colors to refract at different angles, splitting white light into a rainbow of colors.

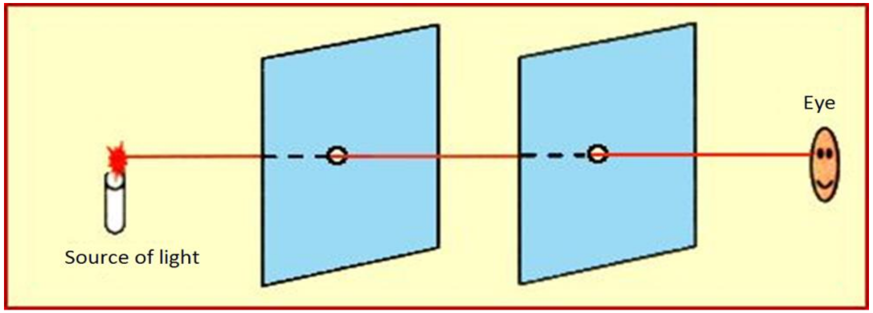


The difference between reflection and refraction of light.



Consequences of refraction

3) Transmission of radiation



- The path a light follows is called a "**beam**".

- **Transmission** of radiation is the moving of electromagnetic waves (whether visible light, radio waves, ultraviolet etc.) through a material. This transmission can be reduced or stopped when light is reflected off the surface, or absorbed by atoms, ions or molecules in the material.

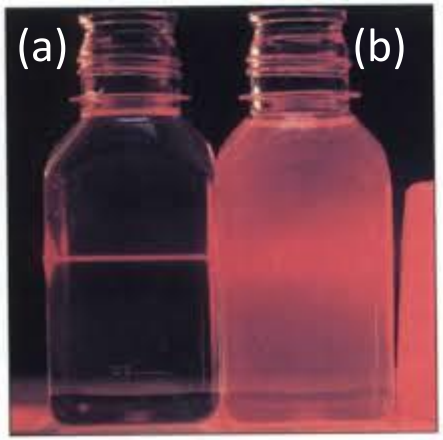
- Unless absorbed by the material, the rate of propagation of radiation decreases slightly due to this interaction of radiation with atoms, ions or molecules.

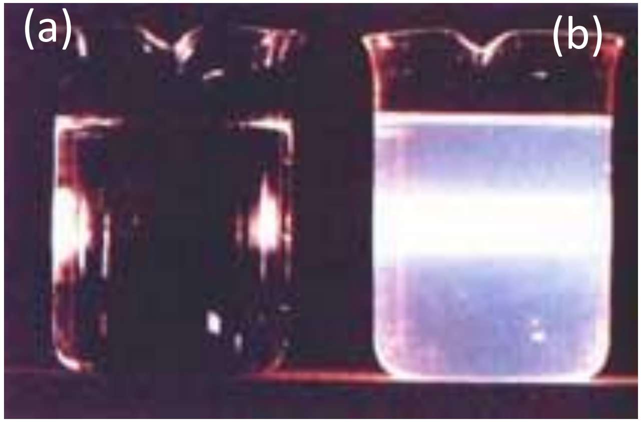
- Provided that it is not absorbed, radiation is retained by the atoms, ions or molecules for a very short time (10^{-14}-10^{-15} s) before it is reemitted unchanged.

- If the particles are small (e.g., dilute NaCl in water), the beam will travel in the original path. However, if the particles are large enough (e.g., milk), the beam will be scattered in all directions.

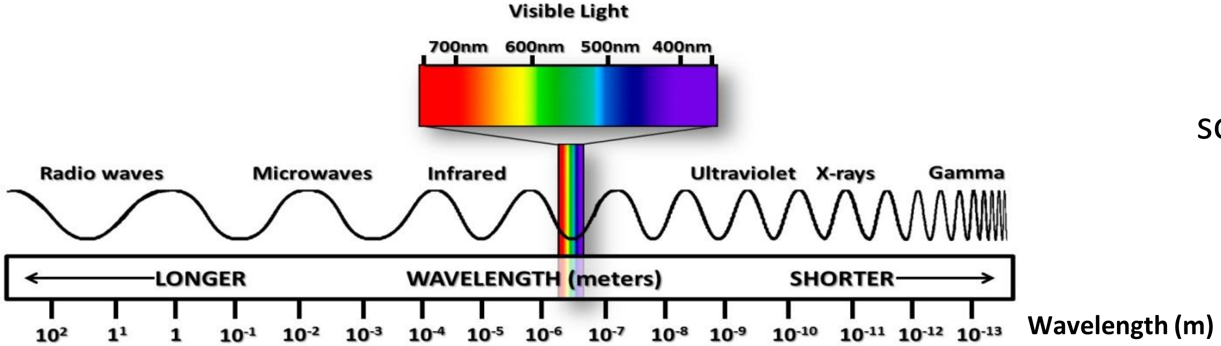
4) Scattering of radiation

- **Scattering of radiation**: Transmission of light in other directions than the original path due to large particle.
- Intensity of scattered light increases with increasing the size of particles in the solution.
- An everyday manifestation of scattering is the blue color of the sky, which results from the greater scattering of the shorter wavelengths of the visible spectrum (the blue and violet).



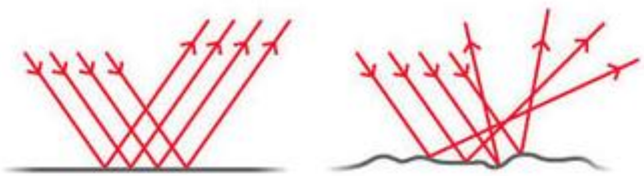


(a) A solution containing small particles (low scattering), (b) A solution containing large particles (high scattering)



5) Reflection of radiation

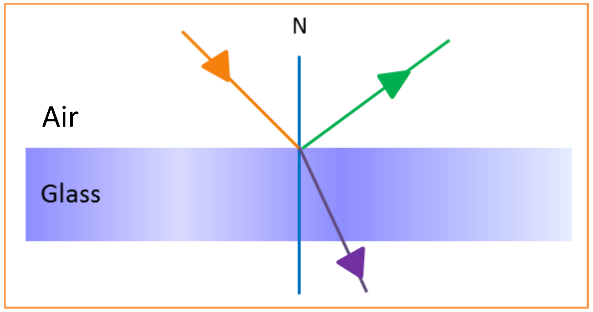
- **Reflection** of light: is when light bounces off an object. If the surface is smooth and shiny, like glass, water or polished metal, the light will be reflected at the same angle as it hits the surface. This is called **specular reflection**.



Specular reflection　　Diffuse reflection

- **Diffuse reflection** is when light hits an object and reflects in lots of different directions. This happens when the surface is rough.

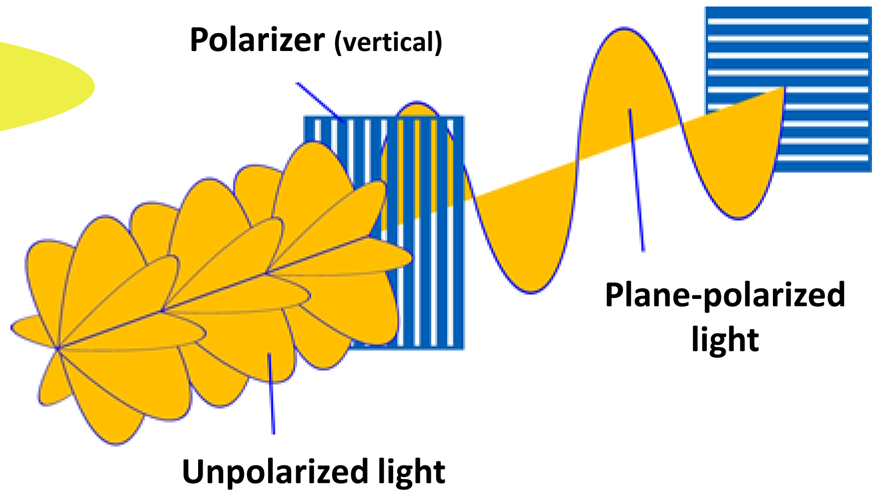
- Reflected light has the same properties of the incident light (i.e., wavelength, frequency, velocity etc.). The direction alone is what is different.
- Reflection and refraction are consequences of different refractive indices and may occur at the same time.

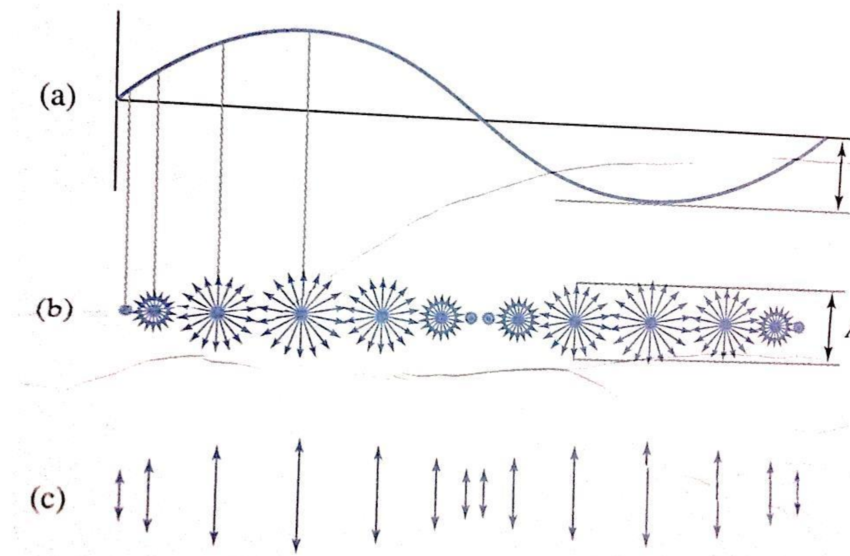


Refraction vs reflection

6) Polarization of radiation

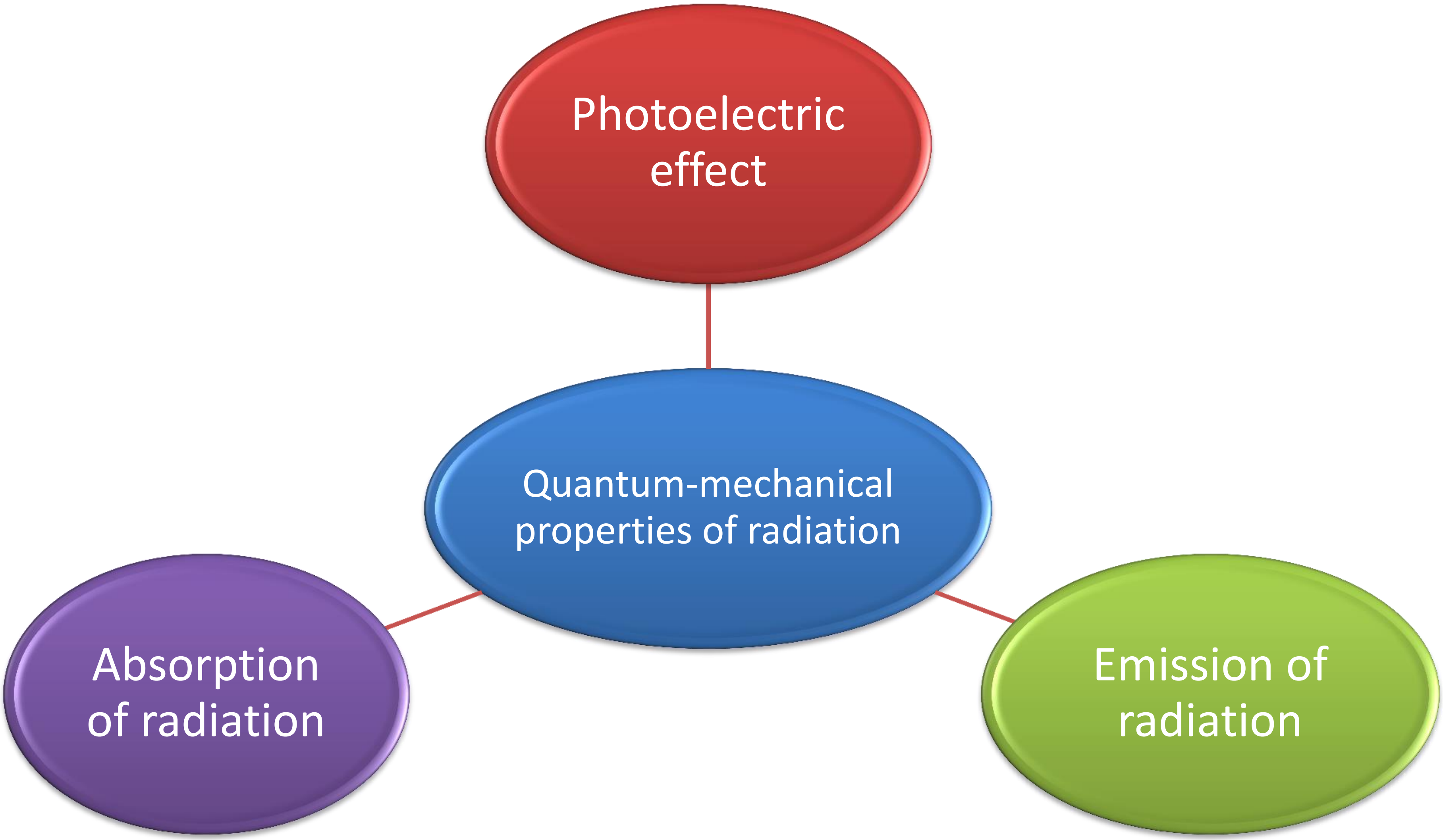
- Normally, radiation is made up of electric and magnetic components (unpolarized light),
- **Plane-polarized light** consists of one of these components (either electric or magnetic),
- If a beam of unpolarized light is passed through a vertical or horizontal polarizer, one of these components is removed and a polarized light is obtained,
- Plane-polarized light is used to determine analytes, e.g., organic molecules in medicines.





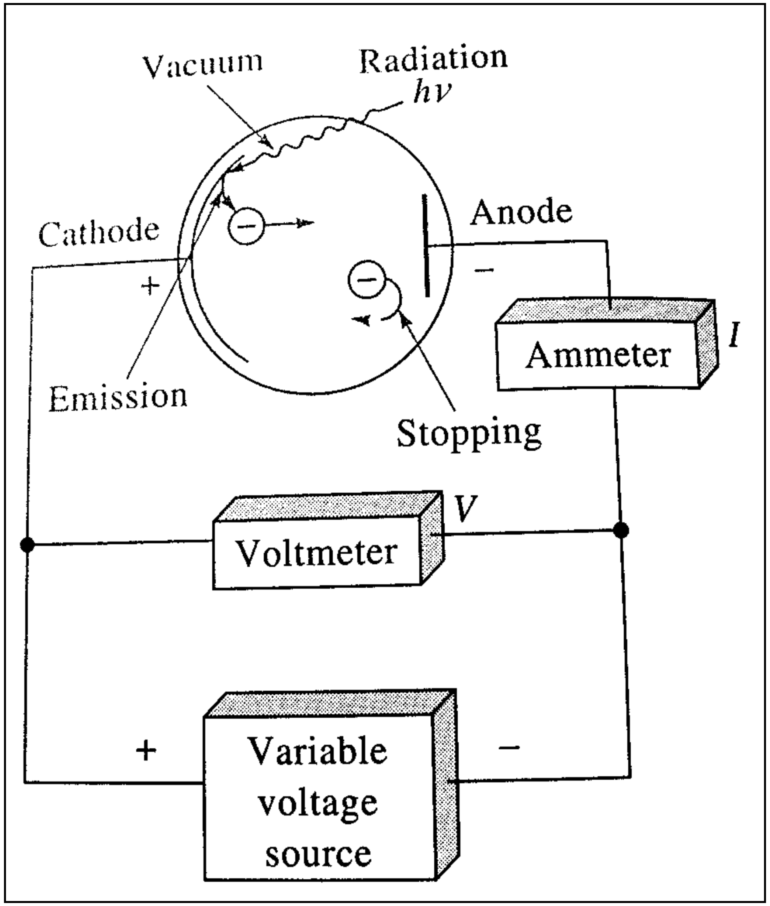
(a) A beam from light source, (b) unpolarized components of light, (c) plane-polarized light.

Quantum-mechanical properties of radiation



① Photoelectric effect

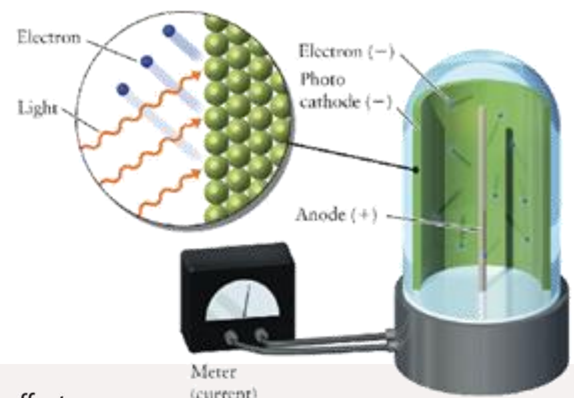
- The photoelectric effect is the observation that many metals (generally, alkali metals) emit electrons when light shines upon them. Electrons emitted in this manner can be called **photoelectrons**.
- Photons hit the cathode and emit electrons which are swept to the anode and produce a current.
- Since the anode is also negative, it repels the electrons and current becomes zero. Electrons with higher kinetic energy can still reach the anode and produce current.
- The applied voltage is increased until the most energetic electrons are stopped from reaching the anode. That voltage is called the "**stopping voltage**" which is used to measure kinetic energy of electrons.



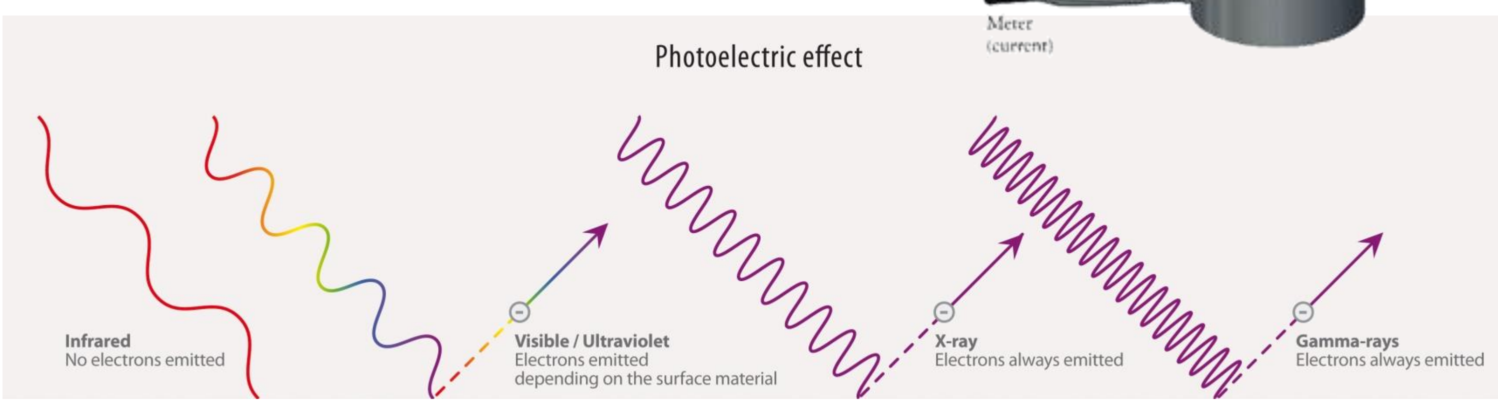
Apparatus for studying the photoelectric effect

Why is the photoelectric effect important?

- The need to use the wave-particle model to understand the interaction between light and matter was realized upon the observation of the photoelectric effect.
- Energy of light (photons), wavelength, frequency etc. were better understood.
- The working principles of detectors in many analytical instruments rely on the photoelectric effect.



Some detectors in analytical instruments rely on the photoelectric effect.



Dependence of energy of ejected electron on incident light

Planck Equation

$$\boldsymbol{E \propto \nu}$$

$$E \propto \frac{1}{\lambda}$$

$$\boxed{E = h\nu = \frac{hc}{\lambda}}$$

Symbol	Meaning
E	Energy
h	Planck constant ($= 6.63 \times 10^{-34}\ J.s$)
ν	Frequency
c	Speed of light ($= 3.00 \times 10^{8}\ m/s$)
λ	Wavelength

a) Calculate the energy in electron volt (eV) of (a) an X-ray having a wavelength of 5.3 Å and (b) a visible light with a wavelength of 530 nm.

Solution

a) Angstrom (Å) is a distance unit. 1 Å = 10^{-10} m, Planck constant (h = 6.63 × 10^{-34} J.s)

1 J = 6.24 × 10^{18} eV

$$E = h\nu = \frac{hc}{\lambda}$$

$$E = \frac{6.63 \times 10^{-34}\ \text{J.}\cancel{\text{s}} \times 3.00 \times 10^{8}\ \text{m.}\cancel{\text{s}}^{-1}}{5.3\ \cancel{\text{Å}} \times 10^{-10}\ \text{m}/\cancel{\text{Å}}} = 3.75 \times 10^{-16}\ \text{J}$$

1 J = 6.24 × 10^{18} eV

$$E = 3.75 \times 10^{-16}\ \cancel{\text{J}} \times \frac{6{,}24 \times 10^{18}\ \text{eV}}{1\ \cancel{\text{J}}} = \mathbf{2.34 \times 10^{3}\ eV}$$

b) 1 nm = 10^{-9} m

$$E = h\nu = \frac{hc}{\lambda}$$

$$E = \frac{6.63 \times 10^{-34}\ \mathrm{J.\cancel{s}} \times 3.00 \times 10^{8}\ \mathrm{m.\cancel{s}^{-1}}}{530\ \mathrm{\cancel{n}m} \times 10^{-9}\ \mathrm{m/\cancel{n}m}} = 3.75 \times 10^{-19}\ \mathrm{J}$$

1 J = 6.24×10^{18} eV

$$E = 3.75 \times 10^{-19}\ \cancel{\mathrm{J}} \times \frac{6.24 \times 10^{18}\ \mathrm{eV}}{1\ \cancel{\mathrm{J}}} = \mathbf{2.34\ eV}$$

One conclusion

The energy of one X-ray photon (**2.34 × 10³ eV)**, can be 1000 times higher than the energy of a photon in the visible region (**2.34 eV).**

To calculate the frequency of the photons given in (a) and (b):

$$E = h\nu = \frac{hc}{\lambda} \Rightarrow \cancel{h}\nu = \frac{\cancel{h}c}{\lambda} \Rightarrow \nu = \frac{c}{\lambda}$$

(a)

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \cancel{m}.s^{-1}}{5.3\ \cancel{Å} \times 10^{-10}\ \cancel{m}/\cancel{Å}}$$

$= 5.66 \times 10^{17}\ s^{-1}$

(b)

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \cancel{m}.s^{-1}}{530\ \cancel{nm} \times 10^{-9}\ \cancel{m}/\cancel{nm}}$$

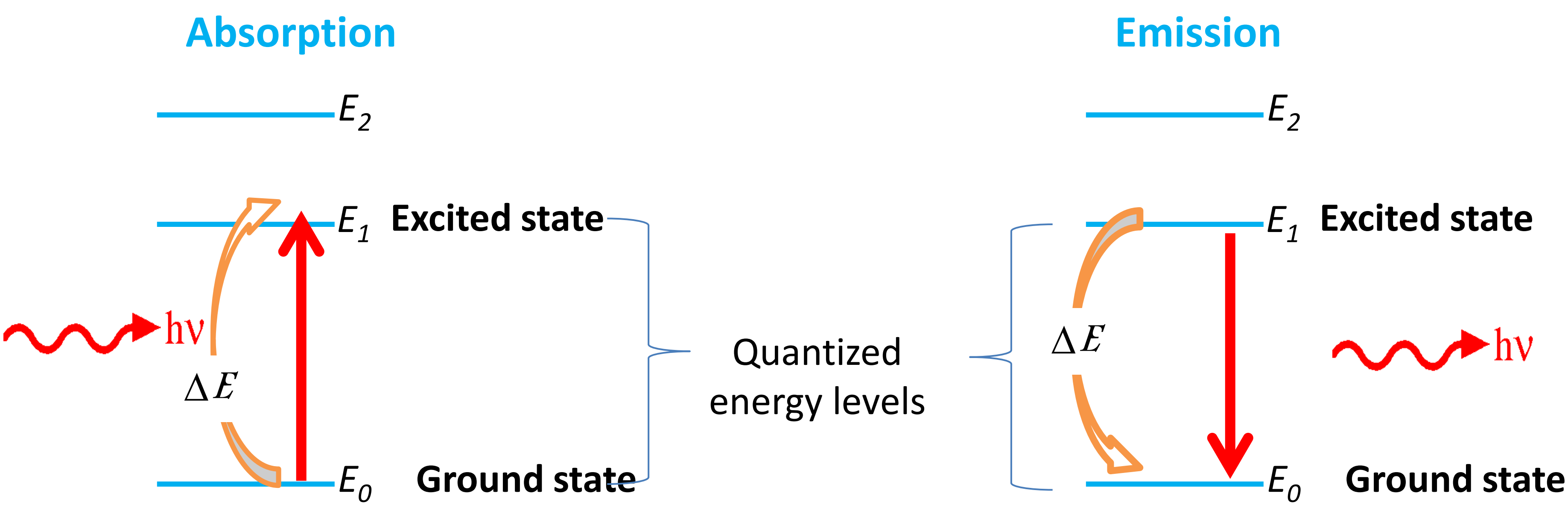
$= 5.66 \times 10^{14}\ s^{-1}$

Another conclusion

The frequency of one X-ray photon (**5.66×10^{17} s^{-1}**), can be 1000 times higher than the frequency of a photon in the visible region (**5.66×10^{14} s^{-1}**).

Energy States of Chemical Species

- A chemical species (e.g., atom, ion, molecule) can only exist in certain discrete states, characterized by definite amounts of energy (**quantized energy levels**).
- If a species is to change its state from a **low** energy level to a **higher** energy level, it must **absorb** energy that is exactly equal to the difference between the two states.
- If a species is to change its state from a **high** energy level to a **lower** energy level, it **emits** energy that is exactly equal to the difference between the two states.

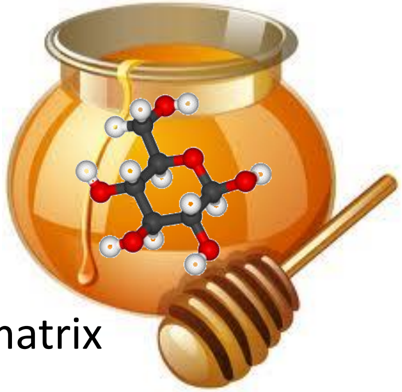


$$\Delta E = E_1 - E_0$$

$$= h\nu = \frac{hc}{\lambda}$$

Interaction of radiation with matter

- Spectroscopic techniques make use of the interaction between radiation and matter to gain information about the **analyte** in a sample.
- **Analyte**: The chemical species (e.g., atom, ion, molecule, etc.) which are to be determined in a biological or non-biological sample. Ex., glucose in honey, heavy metals in water, benzene in air, etc.
- **Matrix**: all components in a sample other than the analyte

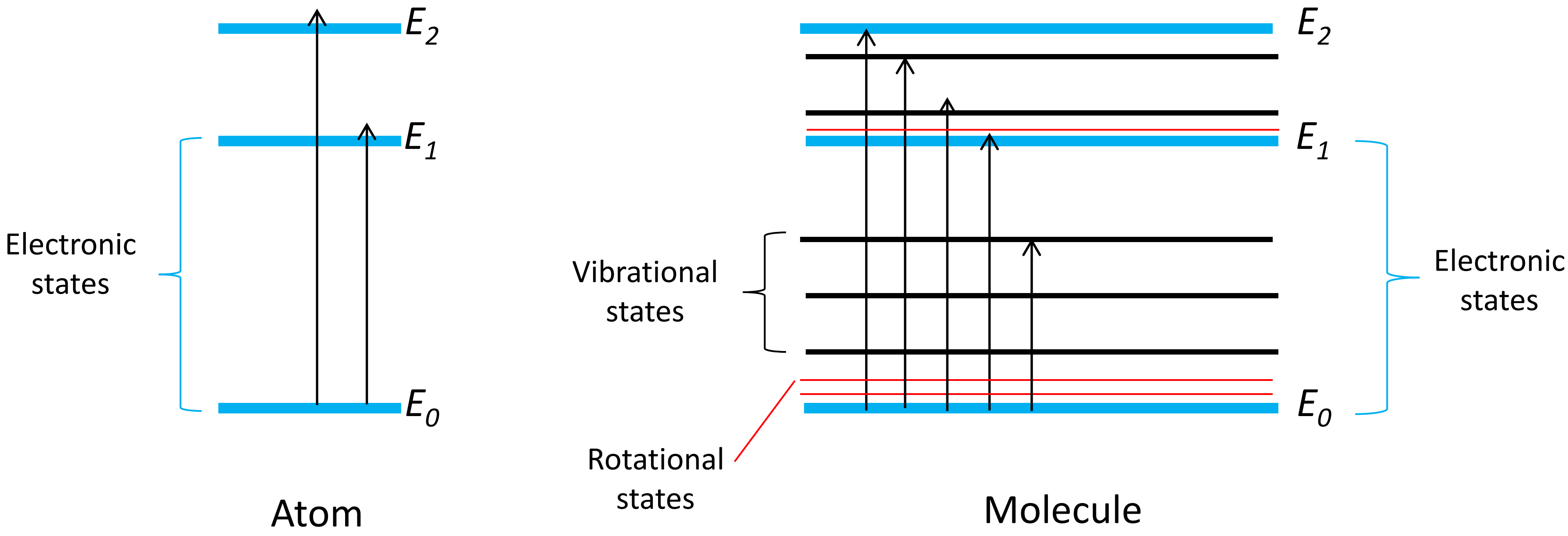


Honey sample = glucose (analyte) + matrix

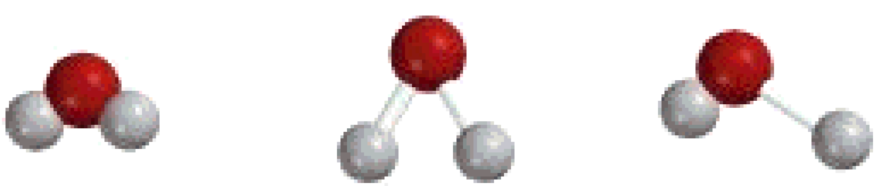
② Absorption of radiation

- In absorption techniques, the analyte is excited with a radiation. The analyte absorbs some of the radiation and is excited from the ground state to a higher energy level.
- The absorbed radiation gives **quantitative** (amount, concentration) and **qualitative** (identity) information about the analyte. The results are reported as a graph which is termed as a "**spectrum**".
- The analytes can be atomic or molecular. Thus, absorption techniques are called as "**Atomic Absorption**" or "**Molecular Absorption**", respectively.

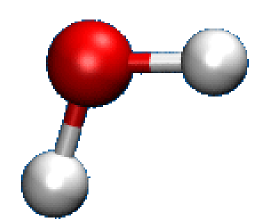
- In <u>atoms</u> there are only **electronic states**. One the other hand, <u>molecules</u> have **electronic**, **vibrational** and **rotational** states.



States in atoms vs. molecules and absorption diagrams

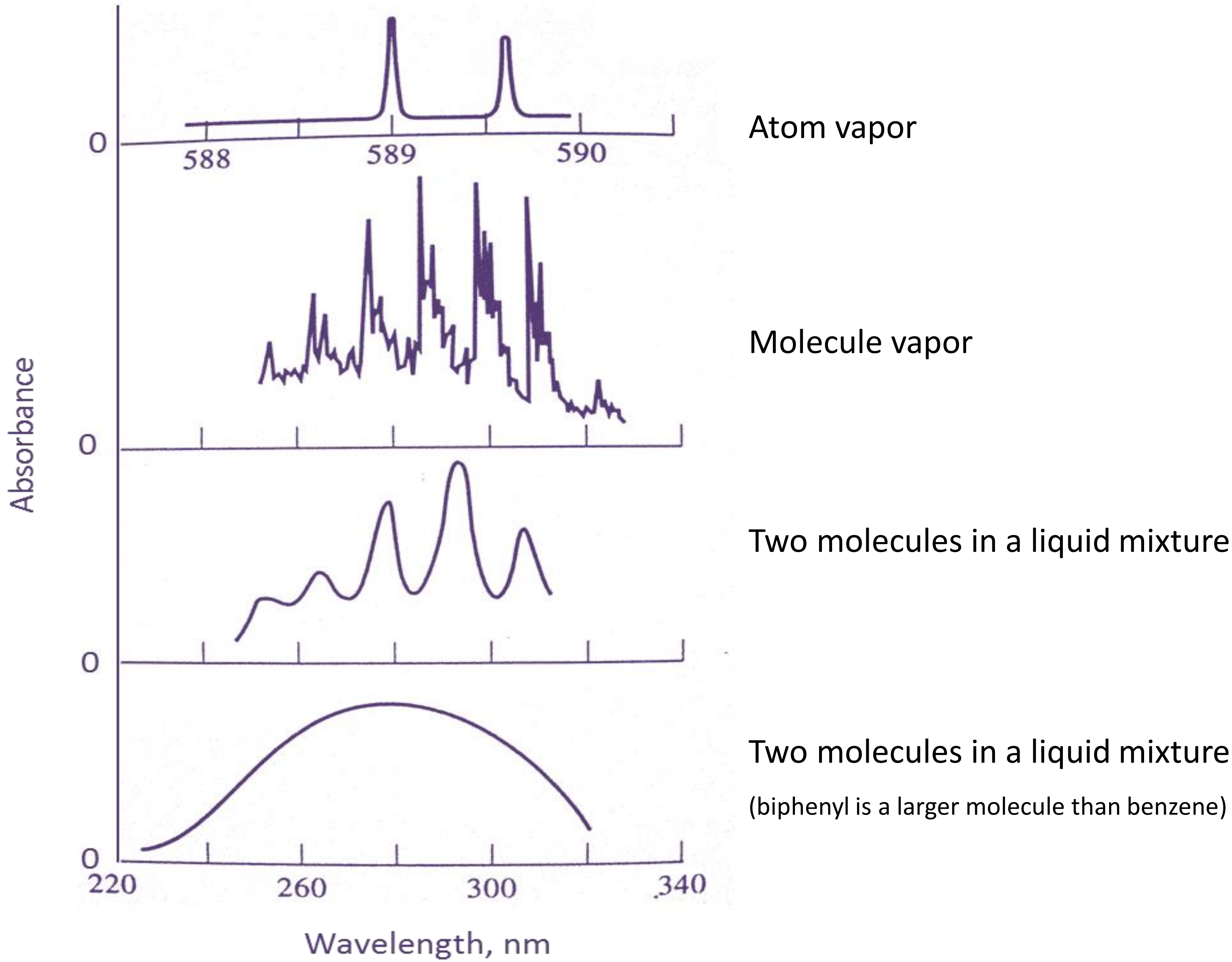


Modes of vibration in molecules



Rotational mode in molecules

Atomic vs. molecular absorption spectra

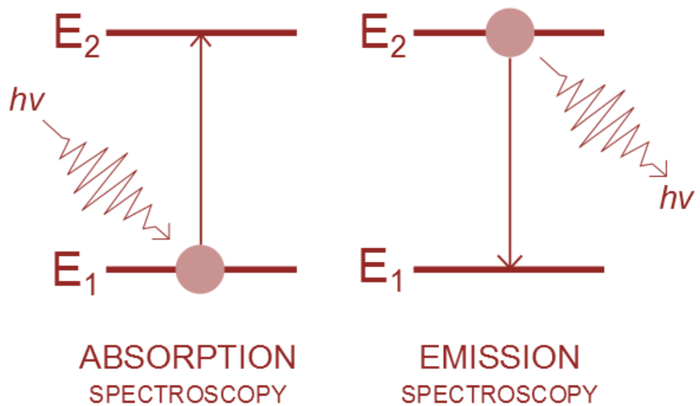


Typical UV absorption spectra

③ Emission of radiation

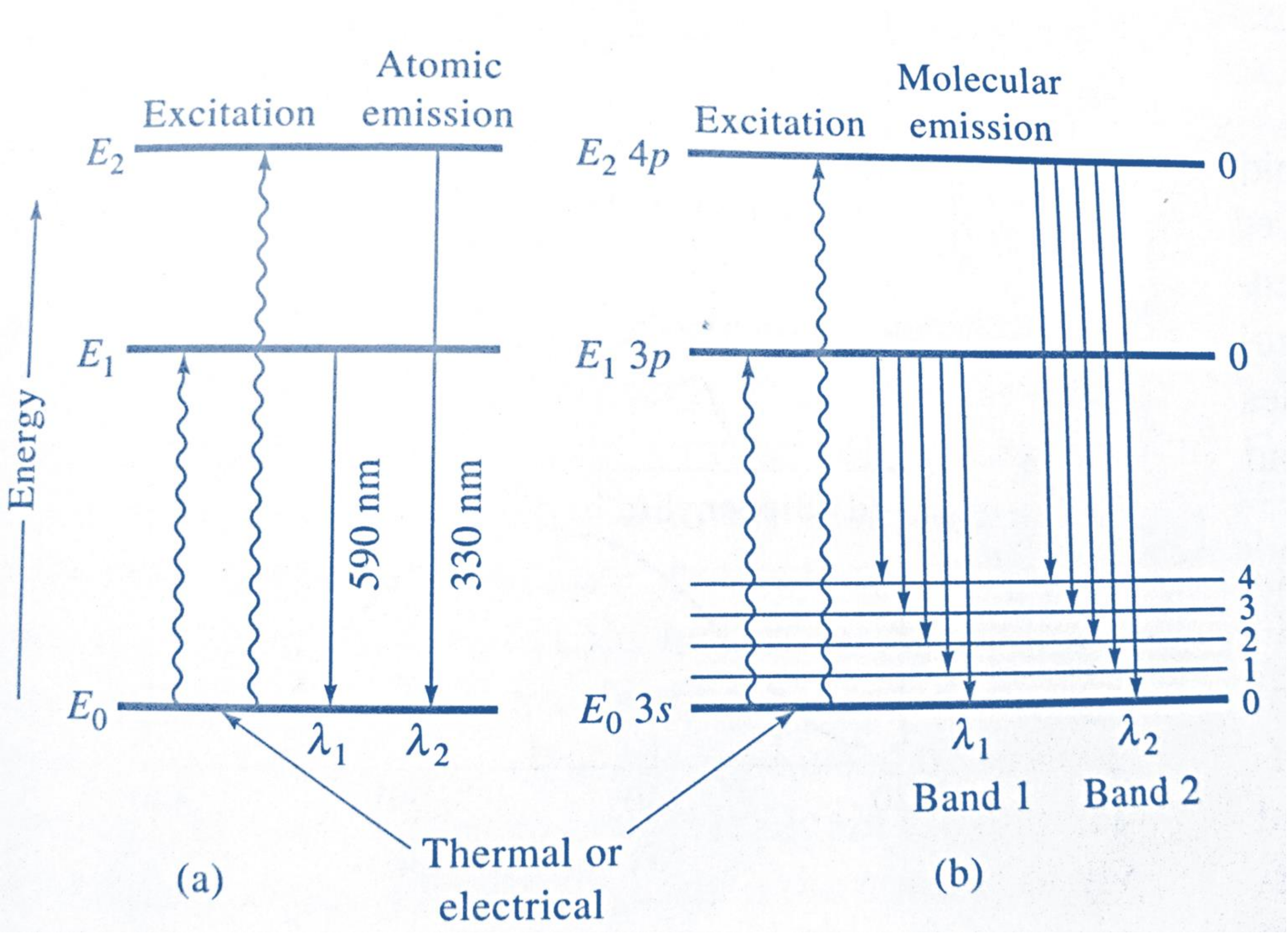
- In emission techniques, the analyte is excited by **electrical current, heat, bombardment with electrons or other subatomic particles, heat from exothermic reactions**.
- When the analyte returns to its ground state, it emits radiation.
- The emitted radiation is measured, a spectrum is plotted and information (quantitative and qualitative) about the **analyte** is obtained.
- Like in absorption techniques, the analyte can be atomic or molecular. Hence, there are "**Atomic Emission**" and "**Molecular Emission**" techniques.

Absorption spectroscopy: a photon is **absorbed** ("lost") as the molecule is raised to a higher energy level.



Emission spectroscopy: a photon is **emitted** ("created") as the molecule falls back to a lower energy level.

Atomic vs. molecular emission diagrams



Energy-level diagrams for (a) a sodium atom, and (b) a simple molecule

Types of spectra

Spectra

Line

Band

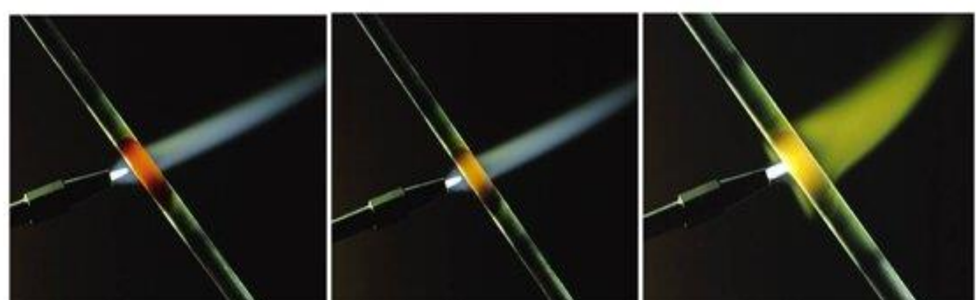
Continuum

Line: Produced from **atomic** species in the gas phase

Band: Produced from **molecular** species in the gas phase

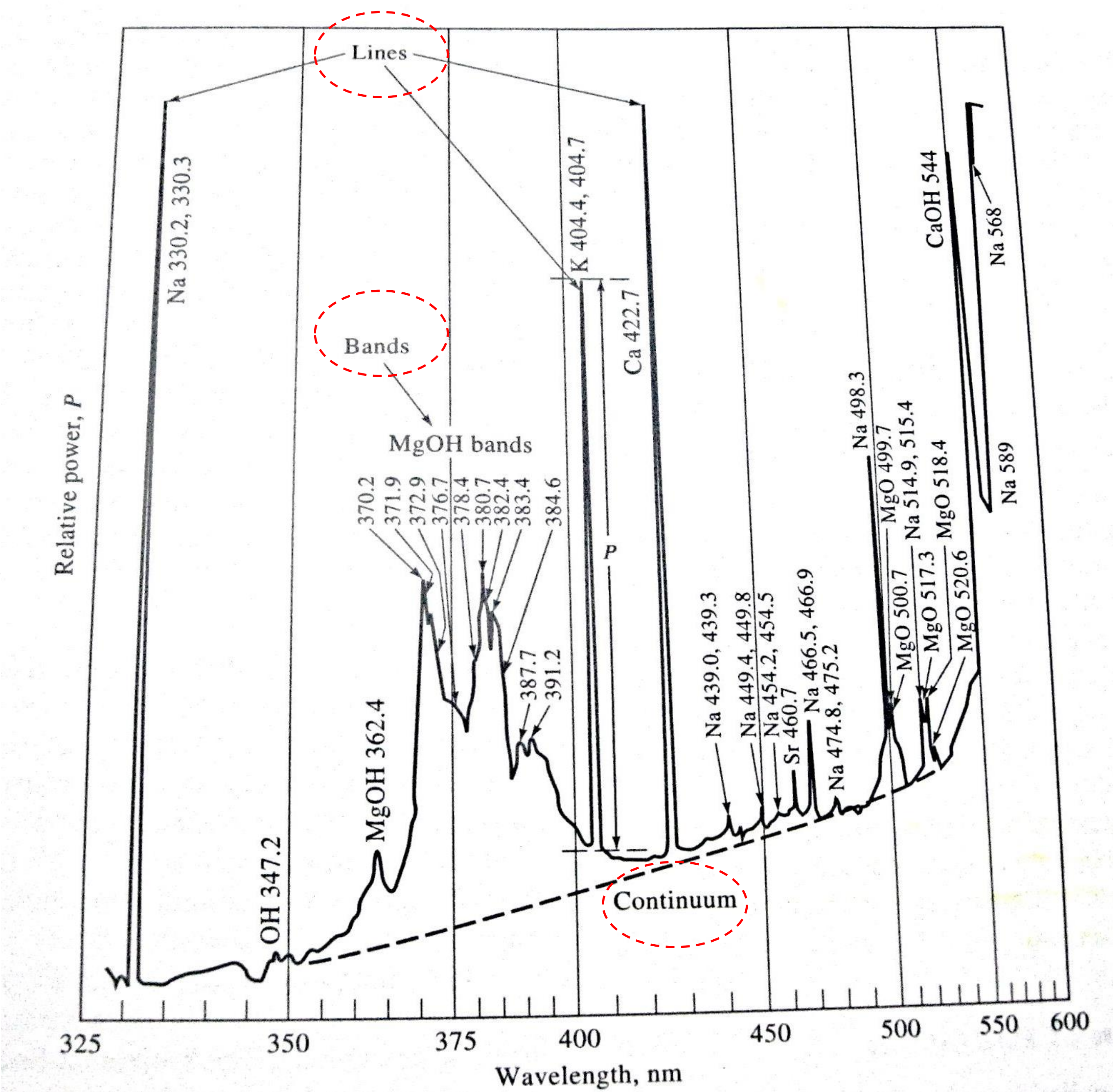
Continuum: Produced when solids are heated to incandescence. The resulting radiation is called "**black-body radiation**"

Left to right: an iron bar is heated to incandescence. As temperature increases, the energy of the emitted radiation increases. This is called "**black-body radiation**".

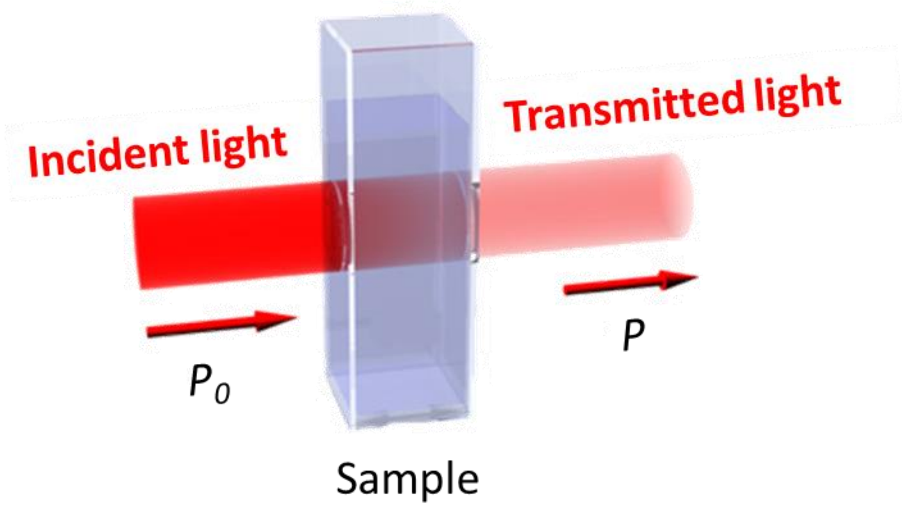


An example of emission spectrum

Emission spectrum of sea water using a flame. The spectrum is a sum of line, band and continuum spectra.



Measurement of Transmittance and Absorbance

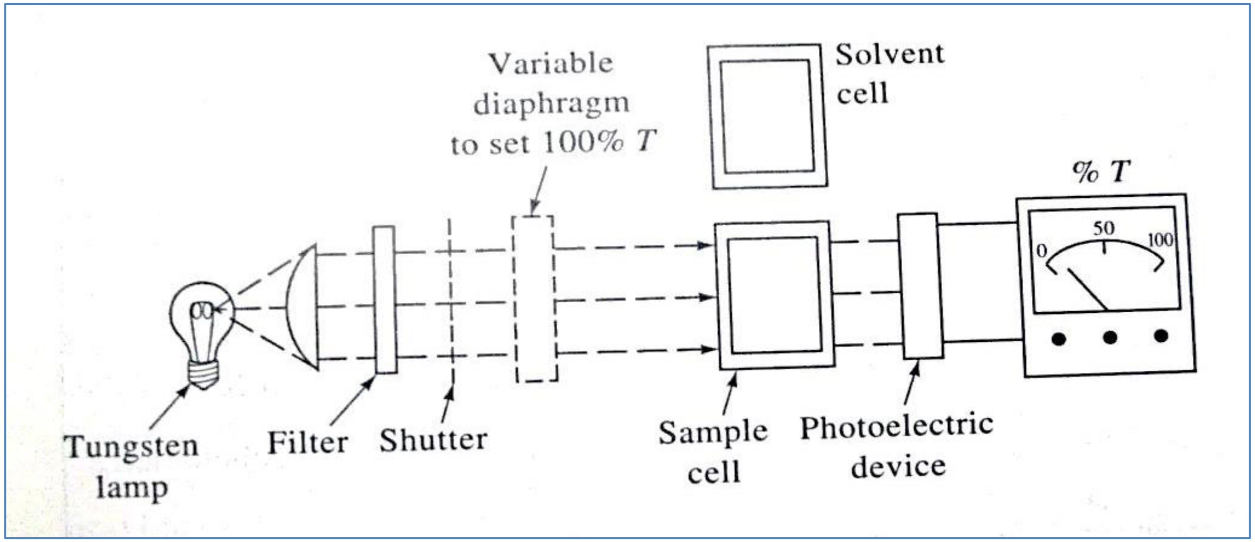


$$T\ (Transmittance) = \frac{P}{P_0}$$

$$\%\ T = \frac{P}{P_0} \times 100\%$$

$$A\ (Absorbance) = -logT = log\frac{P_0}{P}$$

Single-beam photometer for measurement of absorption in the visible region.



Example — Converting absorption to transmittance

Convert 0.375 absorbance into percent transmittance.

Solution

$$A = -logT \Rightarrow 0.375 = -logT \Rightarrow T = antilog(-0.375)$$

$$T = 0.42 \Rightarrow \%T = 0.42 \times 100 = 42\ \%$$

Example — Converting transmittance to absorption

Convert 92.1 percent transmittance into absorbance.

Solution

$$\%T = 92.1 \Rightarrow T = \frac{92.1}{100} = 0.921$$

$$A = -logT \Rightarrow A = -log0.921 = 0.036$$

Beer's Law

$$\boldsymbol{A = \epsilon b c}$$

Symbol	Meaning	Unit
$\boldsymbol{A}$	Absorbance	-
$\boldsymbol{\epsilon}$	Molar absorptivity	$L\ mol^{-1}\ cm^{-1}$
$\boldsymbol{b}$	Path length	cm
$\boldsymbol{c}$	Concentration	$mol\ L^{-1}$

A compound has a molar absorptivity of $4.05 \times 10^3 L\ mol^{-1}\ cm^{-1}$. What concentration of the compound would be required to produce a solution that has an absorption of 0.375 in a 1.00-cm cell?

Solution

$$\boldsymbol{A = \epsilon bc} \quad \Rightarrow \quad c = \frac{A}{\epsilon b} = \frac{0.375}{4.05 \times 10^3 L\ mol^{-1}\ \cancel{cm}^{-1} \times 1.00\ \cancel{cm}}$$

$$= 9.26 \times 10^{-5}\ mol\ L^{-1}$$

A solution of an organic compound having a concentration of $1.06 \times 10^{-4}\ mol\ L^{-1}$ shows an absorbance of 0.520 in a 1.50-cm cell. What is the molar absorptivity of this compound?

A compound has a molar absorptivity of $2.17 \times 10^3 L\ mol^{-1}\ cm^{-1}$. What concentration of the compound would be required to produce a solution that has a percent transmission of 8.42% in a 2.50-cm cell?

Solution

$$\%T = 8.42 \Rightarrow T = \frac{8.42}{100} = 0.0842$$

$$A = -logT \Rightarrow A = -log0.0842 = 1.07$$

$$\boldsymbol{A = \epsilon bc} \Rightarrow c = \frac{A}{\epsilon b} = \frac{1.07}{2.17 \times 10^3 L\ mol^{-1}\ cm^{-1} \times 2.50\ cm}$$

$$= 1.97 \times 10^{-4}\ mol\ L^{-1}$$