INSTRUMENTAL ANALYSIS II

Unit 1

Introduction to Spectroscopy

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UNIT ONE
1. INTRODUCTION TO SPECTROSCOPY

Objectives

At the end of this chapter the students will be able to:

- Explain the electromagnetic radiation
- Explain the wave and particle nature of the electromagnetic radiation
- Describe the phenomenon observed during the interaction of EMR with matter
- Describe the quantum mechanical properties of EMR
- Explain the photoelectric effect
- Describe the quantized energy states of atoms and molecules
- Describe the EMR spectrum

Introduction

- Spectroscopy is the study of the interaction of electromagnetic radiation and matter.

- Spectrometry is the measurement of these interactions and an instrument which performs such measurements is a spectrometer or spectrograph.

- A plot of the interaction is referred to as a spectrum.

- Spectroscopy is often used in physical and analytical chemistry for the identification and quantification of substances through the spectrum emitted from or absorbed by them.

- The science that deals with light and its absorption and emission by solutions and other material substances is called **spectroscopy** or **spectrometry. OR**

- Spectroscopy is the science that deals with the interactions of radiation with matter (atomic and molecular).

- Spectrometric methods are a large group of analytical methods
- Spectrophotometer is an instrument that measure the amount of light absorbed by a substance.
- The most widely used spectrometric methods are based on electromagnetic radiation (light, gamma rays, X-rays, UV, microwave, and radio-frequency).

- The most interesting types of interactions in spectroscopy involve transitions between different energy levels of chemical species.

Types of spectrometers

- Photometers: operate at one or more fixed wavelengths, and are used almost exclusively for quantitative analysis, *e.g.*, HPLC detector
- Spectrophotometers: are capable of scanning through wavelength to record a spectrum. They are more versatile because (a) qualitative and quantitative information can be obtained; (b) quantitative measurements can be made at any desired wavelength.

Electromagnetic Radiation

- In 1873, James Clerk Maxwell proposed that light consists of electromagnetic waves.
- According to his theory, an electromagnetic wave has an electric field component and a magnetic field component.
- Electromagnetic radiation is the emission and transmission of energy in the form of electromagnetic waves.
- The wave properties of electromagnetic radiation are described by two interdependent variables, frequency and wavelength.
- Wavelength (λ, *Greek lambda) is the distance* between any point on a wave and the corresponding point on the next wave; that is, the distance the wave travels during one cycle.

- Wavelength is commonly expressed in meters, but since chemists often deal with very short wavelengths the nanometer, picometer and the angstrom are also used.

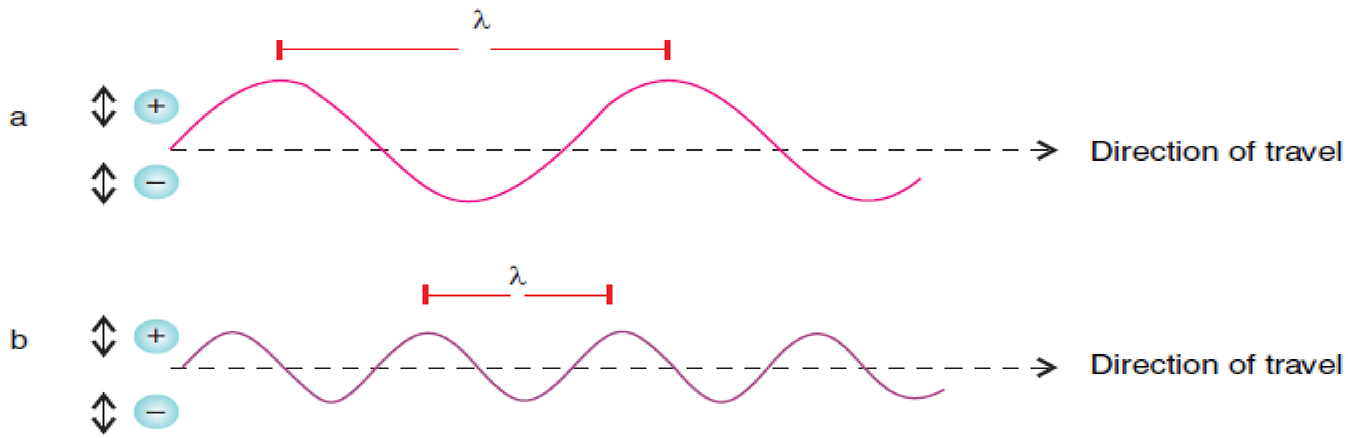


Figure 2.4 Electromagnetic waves.

- Frequency (ν, Greek nu) is the number of cycles that pass a given point in space per second, expressed in units of s^{-1} or hertz (Hz).
- The speed of the electromagnetic wave (light), *c (distance travelled per unit time, in* meters per second), is the product of its frequency (*cycles per second) and its* wavelength (*metres per cycle),*

$$c = \nu \times \lambda \text{ ....} (2.1)$$

- In vacuum, light travels at a speed of 2.9979×10^8 m s^{-1} (3.00×10^8 m s^{-1}

- **<u>Amplitude</u>**, the height of the crest (or depth of the trough) of the wave.
- The amplitude of an electromagnetic wave is a measure of the strength of its electric and magnetic fields.
- Thus, amplitude is related to the intensity of the radiation, which we perceive as brightness in the case of visible light.

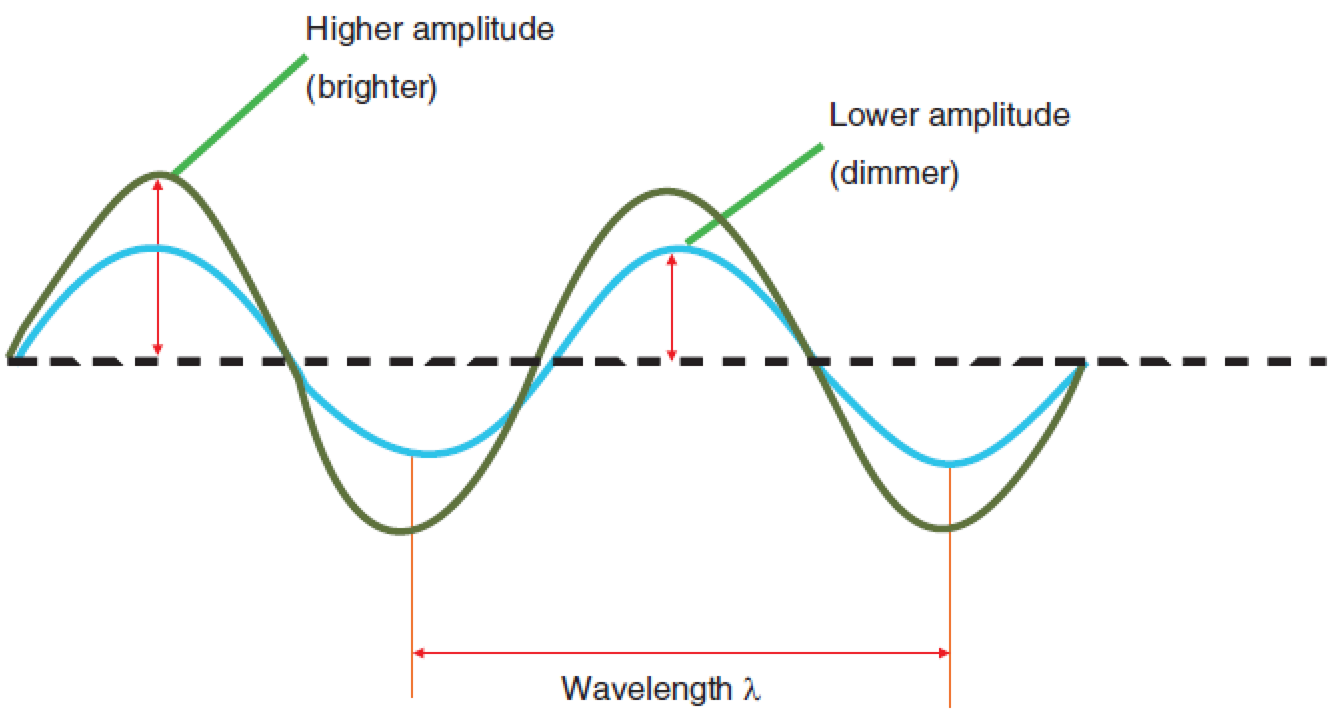


Figure 2.5 Amplitude (intensity) of waves.

- The electromagnetic waves in the different spectral region travel at the same speed but differ in frequency and wavelength.

- We perceive different wave lengths *(or frequencies) of visible light as different* colours, from red (λ = 750 nm) to violet (λ = 400 nm).

- Light of a single wavelength is called *monochromatic* (*Greek "one colour"), light of many wavelengths is* polychromatic (*Greek "many colours").White light is polychromatic*.

- The most widely used spectrometric methods are based on electromagnetic radiation (light, gamma rays, X-rays, UV, microwave, and radio-frequency).

How does a spectrophotometer work- -.MP4

How a Simple UV-visible Spectrophotometer Works -.MP4

Definitions:

- **Wavelength, λ.** Light of only one wavelength is called monochromatic light.
- Light that consists of more than one wavelength is called polychromatic light.
- White light is an example of polychromatic light.
- The units of wavelength are the micrometer (1 μm = 10^{-6} m), usually called micron.
- The unit widely used in spectroscopy is the angstrom (1A = 10^{-10}m).

Wave number ($\bar{\nu}$) is the number of waves per unit distance ($\bar{\nu} = \frac{1}{\lambda}$).

The unit most commonly used for wave number is the reciprocal cm (cm^{-1}).

- ***Amplitude* (A)** – The maximum length of the electric vector in the wave (Maximum height of a wave).

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

- ***Radiant Power* (*P*)** - The amount of energy reaching a given area per second. Unit in watts (W)

- ***Intensity* (*I*)** - The radiant power per unit solid angle.

- ***Frequency* (V)** – is the number of complete wavelength unit which pass a fixed point per unit of time

  - The units of frequency are cycles per second or Hertz (Hz)

Relationship Between These Variables

Speed of light = Wavelength x Frequency

- $c = \lambda V$
- $\lambda = c/V$
- $V = c/\lambda$

$$\nu = \frac{C}{\lambda} = \bar{\nu}\,C \quad , \qquad \left(\bar{\nu} = \frac{1}{\lambda}\right)$$

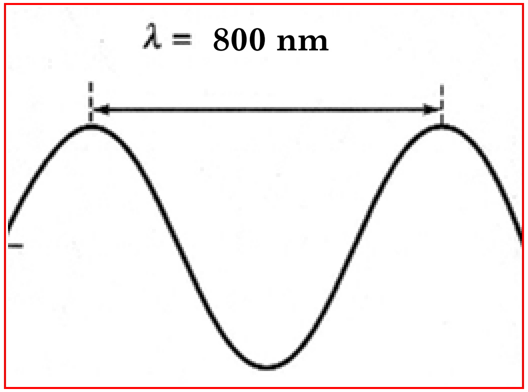
- For Electromagnetic Waves the Speed *(c) is a Constant*
- This Constant Speed Means a Direct, Inverse Relationship Between Wavelength and Frequency

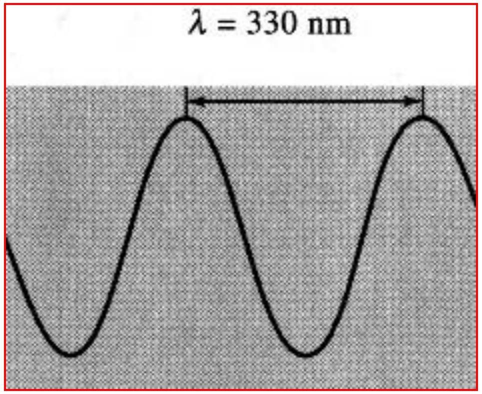
$$\lambda \propto 1/V$$

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

The Relationship Between Frequency and Wavelength

- These relationship means that if the wavelength is longer, the frequency is lower.





Infrared radiation
V = 3.75 x 10^{14} s^{-1}

Ultraviolet radiation
V = 7.50 x 10^{14} s^{-1}

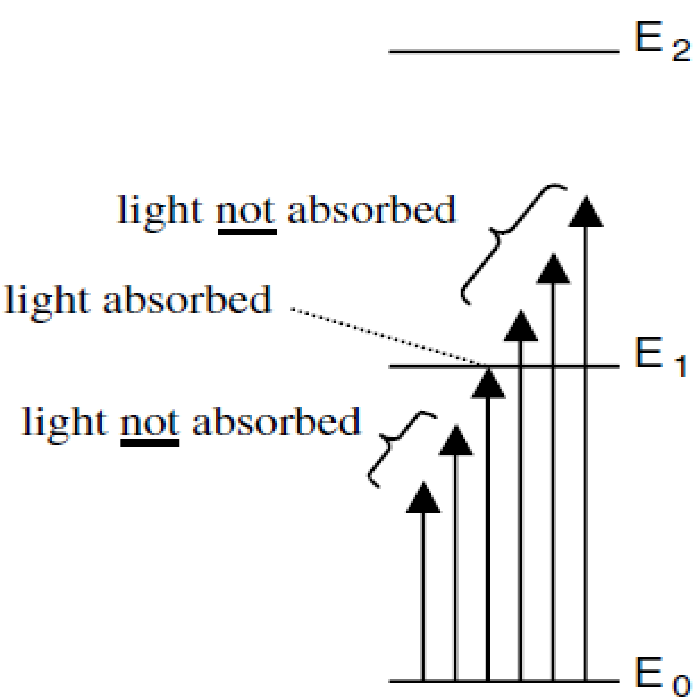
Wavelength is inversely proportional to frequency

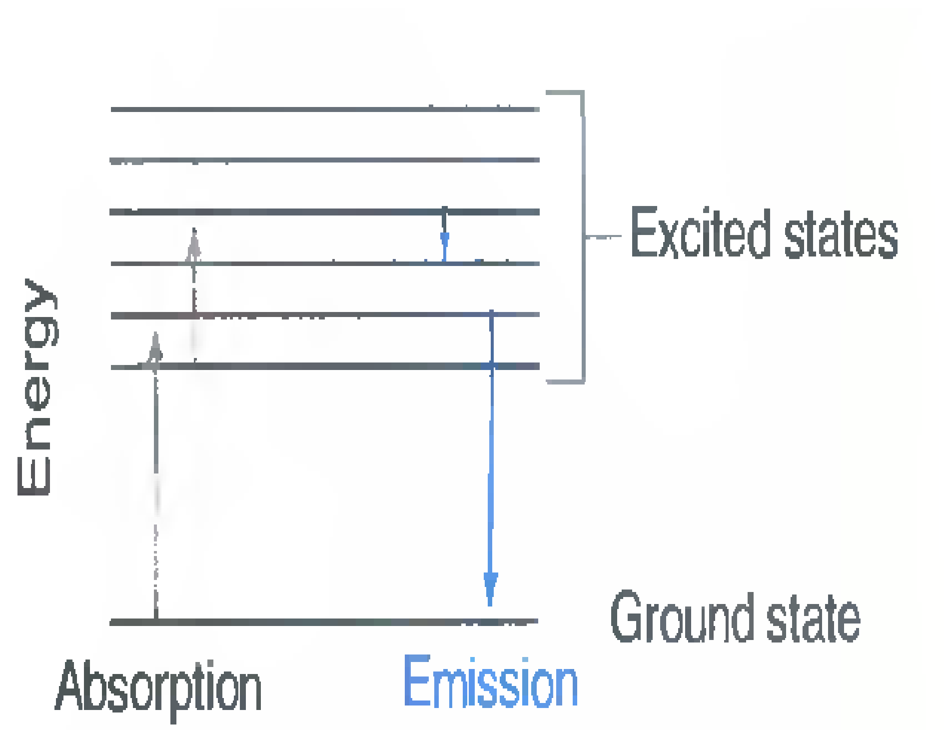
1.3. Absorption and Emission of Light

- When a molecule absorbs a photon, the energy of the molecule increases & the molecule is promoted to an excited state. If a molecule emits a photon, the energy of the molecule is lowered.
- The lowest energy state of a molecule is called the ground state.
- The amount of light absorbed is called the absorbance(A).
- When radiation passes through a layer of solid, liquid/gas, certain frequencies may be absorbed, a process in which EM energy is transferred to the sample.
- It is important to keep in mind that the light coming in must be exactly the same energy as the energy difference between the two electronic levels; otherwise, it will not be absorbed at all.

Cont…

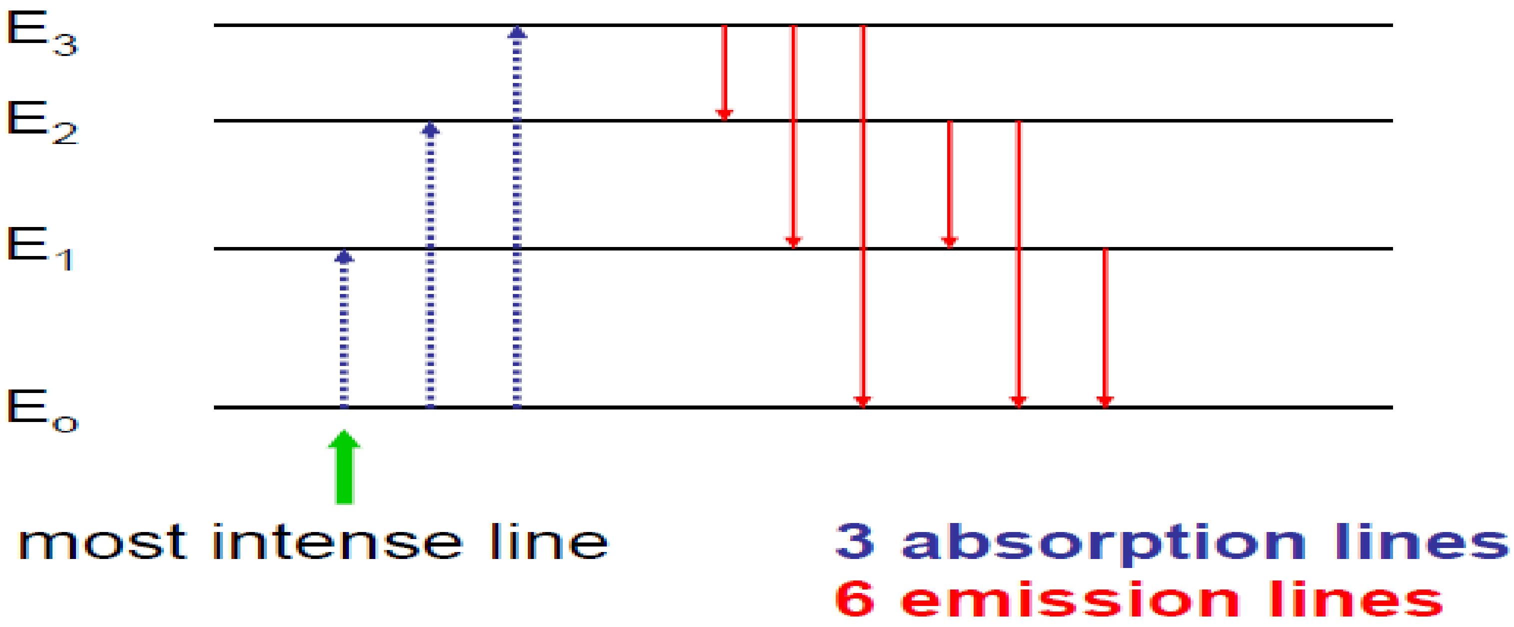
- An energy level diagram of an atom showing the fact that some wavelengths possess too much or too little energy to be absorbed, while another possesses the exact energy required and is therefore absorbed

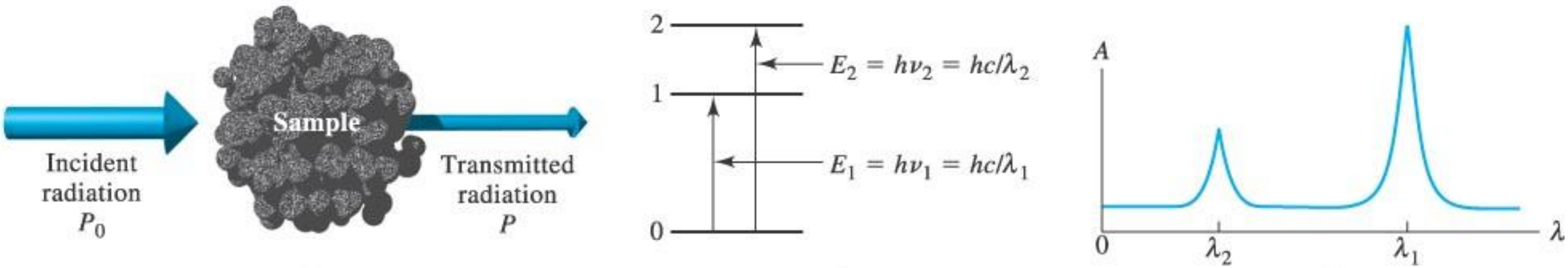




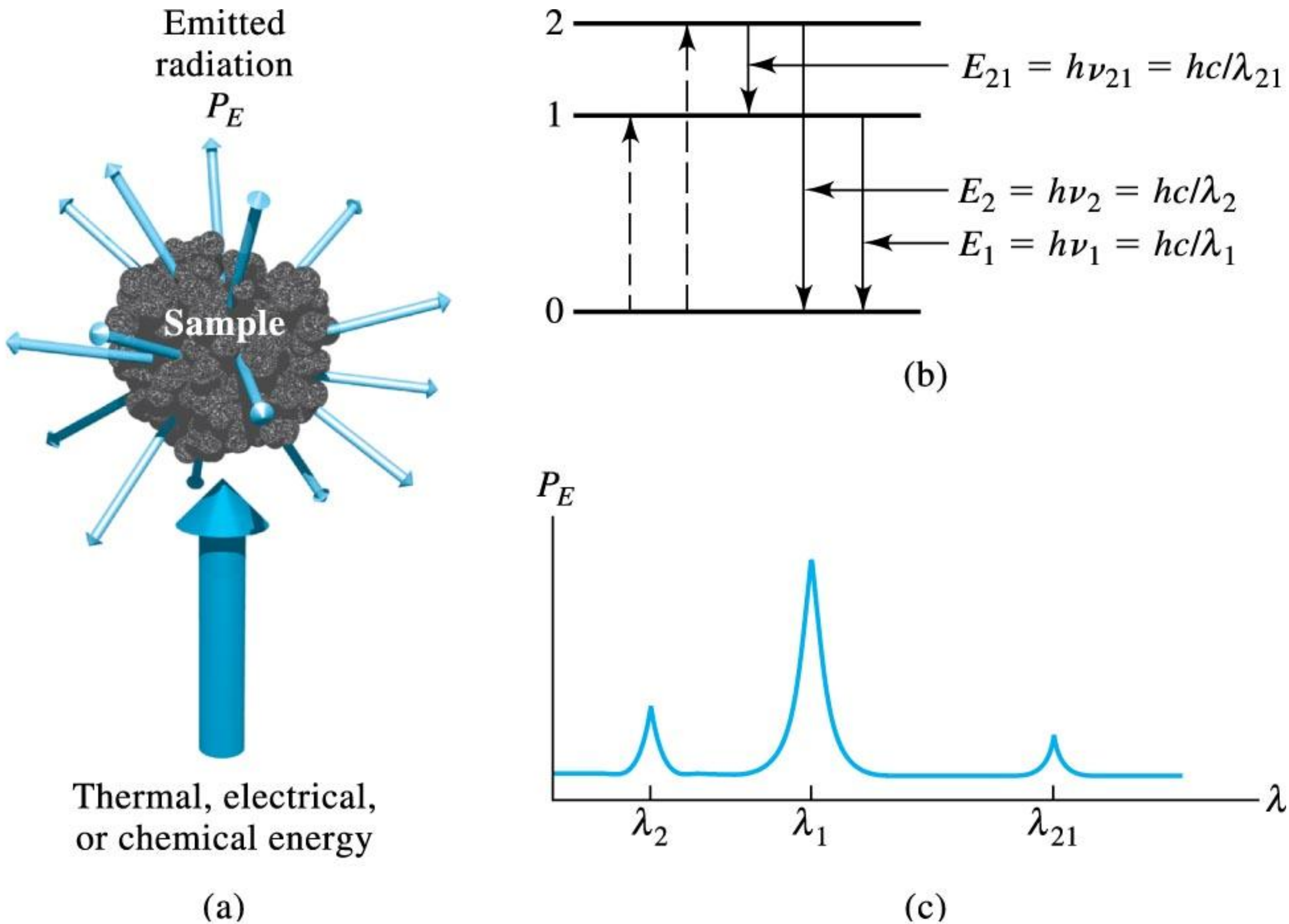
Absorption and emission lines

- **Absorption** is produced when electron absorbs incoming photon and jumps from a lower orbit to a higher orbit
- **Emission** is produced when electron jumps from a higher orbit to a lower orbit and emits a photon of the same energy



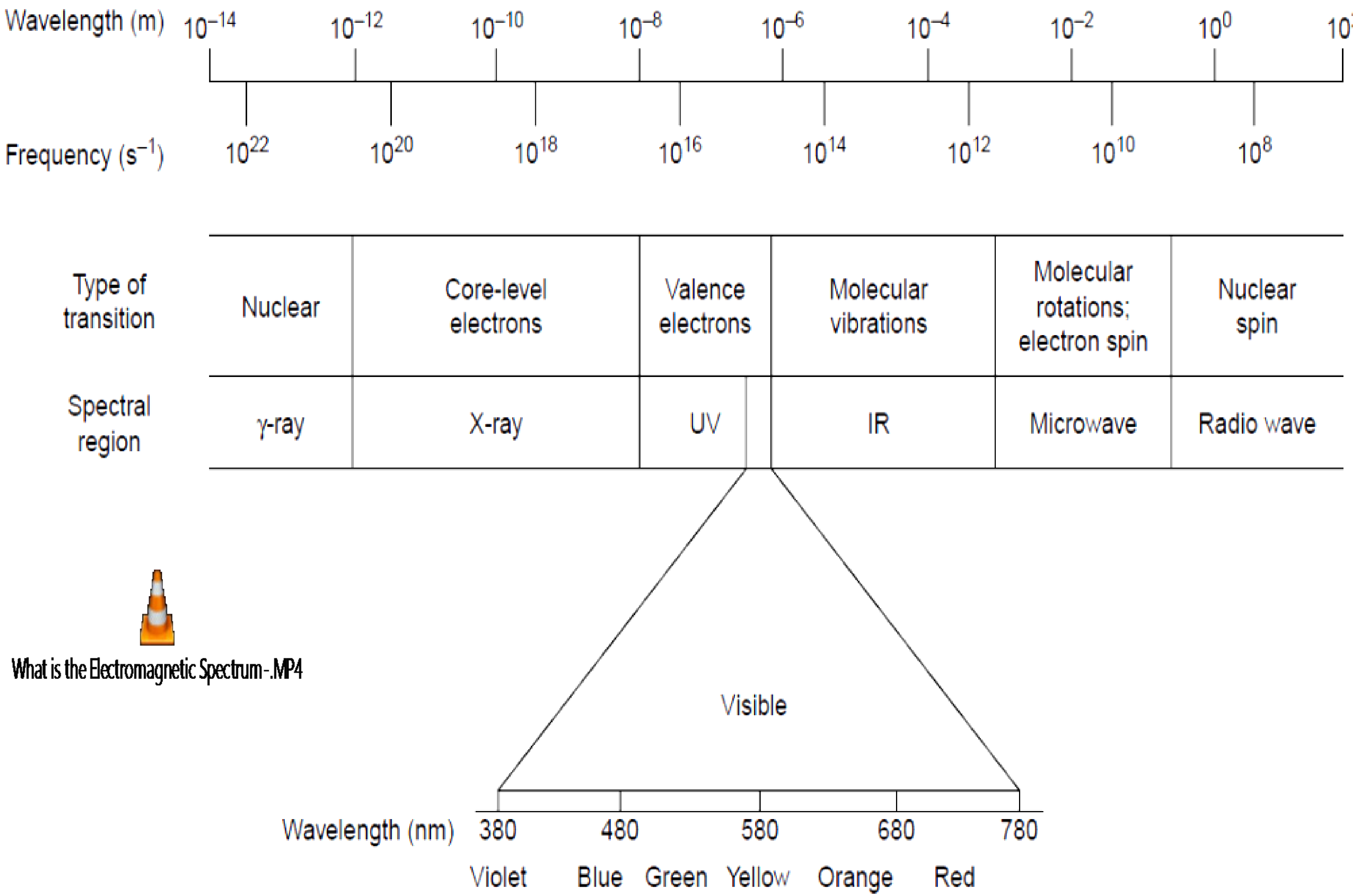

Incident
radiation
P_0
Sample
Transmitted
radiation
P
2
1
0
$E_2 = h\nu_2 = hc/\lambda_2$
$E_1 = h\nu_1 = hc/\lambda_1$
A
0
λ_2
λ_1
λ

(a) (b) (c)



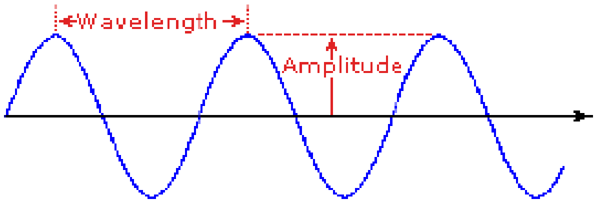
Emitted radiation P_E
Sample
Thermal, electrical, or chemical energy
(a)
2
1
0
$E_{21} = h\nu_{21} = hc/\lambda_{21}$
$E_2 = h\nu_2 = hc/\lambda_2$
$E_1 = h\nu_1 = hc/\lambda_1$
(b)
P_E
λ
λ_2
λ_1
λ_{21}
(c)

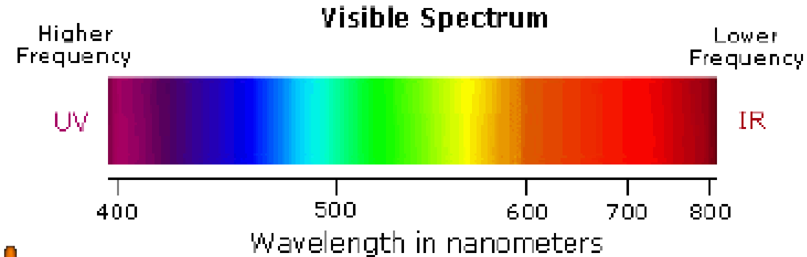
Type spectroscopy	Type of transitions	Wavelength range
Gamma rays	Nuclear	$(10^{-10} - 10^{-14})$ m
X-rays	Inner K-and L-shell electrons	$(10^{-9}) - (6\times10^{-12})$ m
Ultraviolet rays	Valence and middle-shell electrons	$(3.8\times10^{-7}) - (6\times10^{-10})$ m
Visible	Valence electrons	$(7.8 - 3.8)\times10^{-7}$
Infrared	Molecular vibrations and rotations	$(10^{-3}) - (7.8\times 10^{-7})$m
Microwave	Molecular rotations	0.3m-1mm



What is the Electromagnetic Spectrum-.MP4

Fig. the electromagnetic spectrum





The Electromagnetic Spectrum.MP4

- **Violet:** 400 - 420 nm
- **Indigo:** 420 - 440 nm
- **Blue:** 440 - 490 nm
- **Green:** 490 - 570 nm
- **Yellow:** 570 - 585 nm
- **Orange:** 585 - 620 nm
- **Red:** 620 - 780 nm

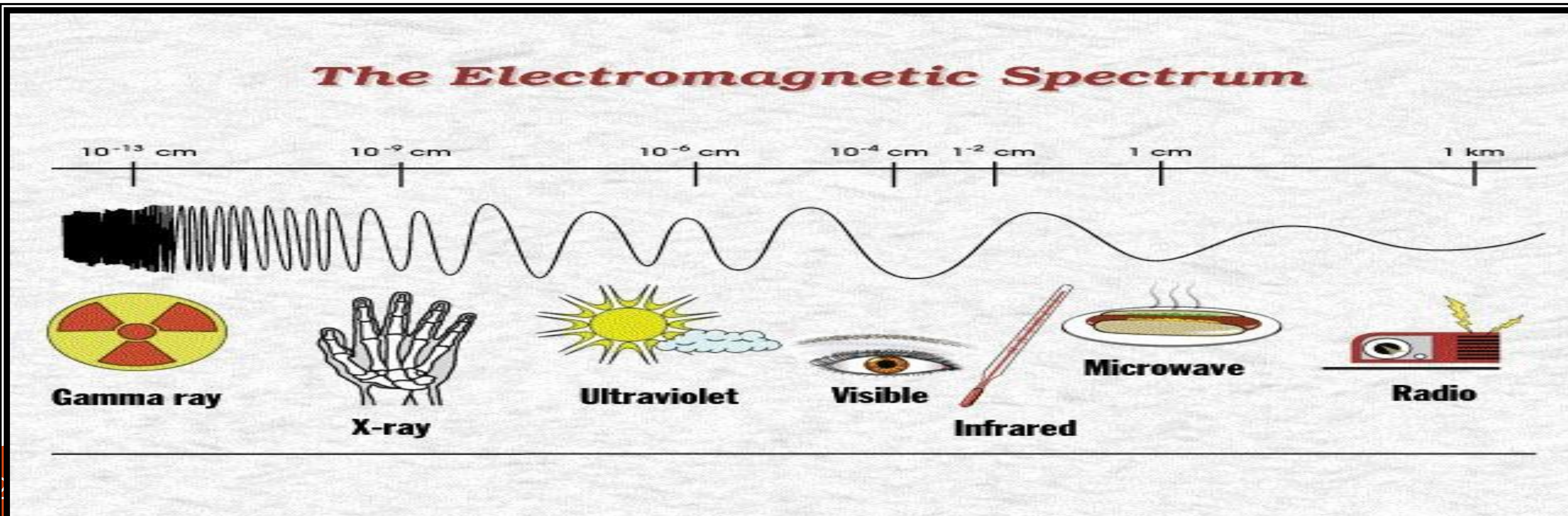


Table. Common Wavelength Symbols and Units for Electromagnetic Radiation

Unit	Symbol	Length (m)	Type of radiation
Angstrom	Å	10^{-10}	X-ray
Nanometer	nm	10^{-9}	UV, visible
Micrometer	µm	10^{-6}	IR
Millimeter	mm	10^{-3}	IR
Centimeter	cm	10^{-2}	Microwave
Meter	m	1	Radio

Prefixes for Units

Prefix	Symbols	Multiplier
giga-	G	10^{9}
mega-	M	10^{6}
kilo-	k	10^{3}
deci-	d	10^{-1}
centi-	c	10^{-2}
milli-	m	10^{-3}
micro-	μ	10^{-6}
nano-	n	10^{-9}
pico-	p	10^{-12}
femto-	f	10^{-15}
atto-	a	10^{-18}

Example 1

1. The yellow light given off by a sodium lamp has a wavelength of 589 nm. What is the frequency of this radiation?
2. A dental hygienist uses X-ray (λ = 1.00 Å) to take a series of dental radiographs while the patient listens to an FM radio station (λ = 325 cm) and looks out the window at the blue sky (λ = 473 nm). What is the frequency (in s^{-1}) of the electromagnetic radiation for each source?

Solution: 1) convert nm to m

$$\mathbf{V = c/\lambda}$$

$$\nu = \frac{3.00 \times 10^{8}\,\text{m/s}}{589\,\text{nm}} \times \frac{10^{9}\,\text{nm}}{1\,\text{m}} = 5.09 \times 10^{14}\ \text{s}^{-1}$$

For X-ray,

$$\lambda = 1.00\ \cancel{\text{Å}} \times \frac{10^{-10}\,\text{m}}{1\,\cancel{\text{Å}}} = 1.00 \times 10^{-10}\ \text{m}$$

$$\lambda = c_o/\lambda = \frac{3.00 \times 10^{8}\,\text{m/s}}{1.00 \times 10^{-10}\,\text{m}} = 3.00 \times 10^{18}\ \text{s}^{-1}$$

For the radio station,

$$\lambda = 325\ \text{cm} \times \frac{1\,\text{m}}{100\ \text{cm}} = 3.25\ \text{m}$$

$$\nu = \frac{3.00 \times 10^{8}\,\text{m/s}}{3.25\,\text{m}} = 9.23 \times 10^{7}\ \text{s}^{-1}$$

For the blue sky,

$$\lambda = 473\ \text{nm} \times \frac{10^{-9}\,\text{m}}{1\,\text{nm}} = 4.37 \times 10^{-7}\ \text{m}$$

$$\nu = \frac{3.00 \times 10^{8}\ \text{m/s}}{4.73 \times 10^{-7}\,\text{m}} = 6.34 \times 10^{14}\ \text{s}^{-1}$$

Exercise 2

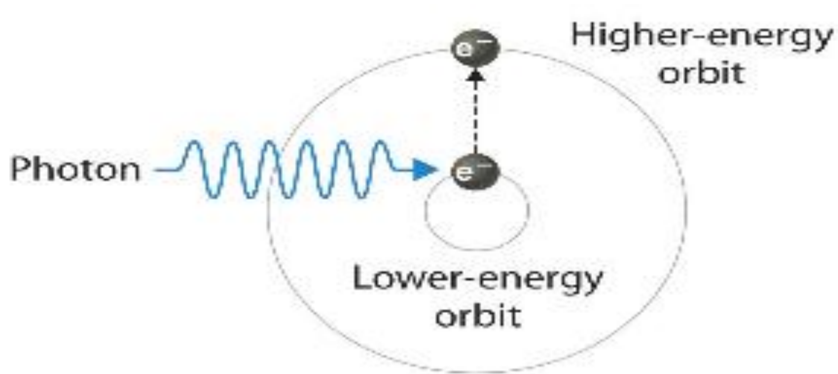
1. Some diamonds appear yellow because they contain nitrogeneous compounds that absorb purple light of frequency 7.23×10^{14} s^{-1}. Calculate the wavelength (in nm) of the absorbed light.
2. The FM station broadcasts traditional music at 102 MHz on your radio. Units for FM frequencies are given in megahertz (MHz). Find the wavelength of these radio waves in meters (m), nanometers (nm), and angstrom (Å).

Answer

1. 415 nm
2. 2.94 m, 2.94×10^{9} nm, 2.94×10^{10} Å

Electromagnetic Radiation(ER) And Its Interaction With Matter

- Electromagnetic radiation, or light, is a form of energy whose behavior is described by the properties of both waves and particles duality.
- The optical properties of ER, such as diffraction, scattering, reflection are explained best by describing light as a wave.
- Many of the interactions between electromagnetic radiation and matter, such as absorption and emission, however, are better described by treating light as a particle, or photon.



(a) Electronic absorption transition

Wave-Particle Duality of Light.MP4

2 The Quantum Theory and Photon

- The quantum theory is concerned with the rules that govern the gain or loss of energy from an object.
- In 1900, the German physicist Max Planck came to an entirely new view of matter and energy.
- He proposed that a hot glowing object could emit (or absorb) only certain amounts of energy.
- Radiant energy is quantized and can only be emitted in discrete (separate) amounts called quanta. A quantum of radiation is a photon.

$$E = nh\nu$$

where E *is the energy of the radiation*, in joules (J)

ν *is the frequency*, in second (s^{-1})

n *is a positive integer* ($n = 1, 2, 3, \ldots$) *called quantum number*

h is proportionality constant now called Planck's constant.

h has units of J s; ($h = 6.626 \times 10^{-34}$ J s)

- Planck's work was the observation of the radiant energy absorbed or emitted by matter.
- (An object can gain or lose energy by absorbing or emitting radiant energy.)

Electromagnetic radiation and its quantum mechanical property

Particle properties of Light: Photons

- In some cases it is more convenient to consider light as a stream(packets) of particles. We call particles of light photons.
- With regard to energy, it is more convenient to think of light as particles called **photons** or *quanta*.
- Photons are characterized by their energy, E.
- The energy of a photon, in joules, is related to its frequency, wavelength, or wave number by;

$$\boldsymbol{E = h\nu = hc/\lambda = hc\tilde{V}}$$

- where E is the energy in joules (J),

  h is Planck's constant, 6.626×10^{-34} J s, and

  ν is the frequency in inverse seconds (Hz).

Quantum mechanics

- QMs founded on the bases of two very important principles.
- These are the uncertainty and dual nature of matter principles.
- The development of wave mechanics is base on the following basic concepts.

1. de – Broglie's idea of dual nature of matter.

de Broglie postulated that matter has a wave like properties .

- $E = h\nu$ (When it behaves the nature of light)
- $E = mc^2$ (it behaves the nature of particle)

2. Heisenberg's uncertainty principle.

(Bohr's model was unable to determine the position and momentum (energy and time) of a particle simultaneously)

- locating (observing) the particle with high energy radiation, we have changed its momentum.
- As a result, it is impossible to determine both the position and momentum simultaneously to greater accuracy than some fundamental quantity.

3. Schrodinger's wave equation.

Activity

1. Is it possible to know the exact location of an electron? Defend your suggestion.
2. Do electrons have a particle nature or a wave nature?

Answer :

1. Predicting the exact location of an electron, according to quantum theory, is only a matter of probability. The Heisenberg uncertainty principle states that it is impossible to know both the location and direction of an electron. You can know the location, but then the direction of the electron will change. If you find the direction, the location will change.
2. Electrons have dual natures – particle and wave natures. The atomic models are the manifestations of its particle nature, and the spectral lines indicate its wave nature.

Example 3

- Calculate the amount of energy (*that is, the quantum of energy*) *that an* object can absorb from yellow light, whose wavelength is 589 nm.

Solution:

$$\Delta E = h\nu \;; \quad h = 6.626 \times 10^{-34}\ Js.$$

The frequency, ν, *is calculated from the* given wavelength,

$$\nu = C_o / \lambda = 5.09 \times 10^{14}\ s^{-1}.$$

Thus, we have:

$$\Delta E = h\nu = 6.626 \times 10^{-34}\ J\,s \times 5.09 \times 10^{14}\ s^{-1}$$

$$= \underline{3.37 \times 10^{-19}}\ \mathrm{J}$$

The Photoelectric Effect

- Light shining on a clean metallic surface can cause the surface to emit electrons. This phenomenon is known as the photoelectric effect.
- In 1905, Albert Einstein, He assumed that the radiant energy striking the metal surface is a stream of tiny energy packets. Each energy packet, called a photon, is a quantum of energy, $h\nu$.

$$E_{ph} = h\nu$$

where E_{ph} *is the energy of a photon*.

- If a photon has more than the minimum energy required to free an electron, the excess energy appears as the kinetic energy of the emitted electron. This situation is summarized by the equation

$$h\nu = E_k + E_b \qquad \ldots(2.5)$$

where E_k *is the kinetic energy of the ejected electron, and*

E_b *is the binding energy of* the electron in the metal.

- Rewriting equation (2.5), using
  - $E_k = ½\, m_e v^2 \quad and \quad E_b = h\nu_o$
- Results in
  - $h\nu = h\nu_o + ½\, m_e v^2$

where m_e *is mass of an electron, and*

ν_o *is the* minimum frequency of light (*threshold frequency)*

- The higher the frequency of the light, the greater will be the kinetic energy of the emitted electrons.
- we have equations to quantify these observations
  - $\Delta E = h\nu = h\nu_o + ½\, m_e v^2$ ....*(2.6)*

where ν_o *is the threshold frequency,*

m_e *is the mass of the electron and*

v *is the* velocity of the emitted electron.

Example 4

- The maximum kinetic energy of the photoelectrons emitted from a metal is 1.03×10^{-19} J when light that has a 656 nm wavelength shines on the surface. Determine the threshold frequency, $\mathbf{v}_o$, *for this metal.*

Given quantities: $h = 6.626 \times 10^{-34}\ J\ s$,

$\lambda = 656\ nm$, *kinetic energy of photoelectron*

$E_k = 1.03 \times 10^{-19}\ J.$ (emitted from a metal)

Solution:

- Solve for **v** from $\boldsymbol{Co = v \times \lambda}$

$$v = c_o/\lambda \quad \frac{3.00\times10^{+8}\,\mathrm{m/s}}{656\mathrm{nm}\times10^{-9}\,\mathrm{m/mn}} = 4.57 \times 10^{14}\ \mathrm{s}^{-1}$$

- Rearrange Equation 2.5 and solve for $\boldsymbol{v_o}$

$$\boldsymbol{hv = E_k + E_b \ \ \& \ \ E_b = hv_o}$$

$$\nu_o = \frac{h\nu - E_k}{h}$$

$$\nu_o = \frac{(6.626\times10^{-34}\ \mathrm{J\,s}\times4.57\times10^{14}\ \mathrm{s^{-1}})-(1.03\times10^{-19}\ \mathrm{J})}{6.626\times10^{-34}\ \mathrm{J\,s}} = 3.02\times10^{14}\ \mathrm{s^{-1}}$$

- Therefore, a frequency of **3.02×10^{14} Hz** is the minimum (threshold) required to evoke the photoelectric effect for this metal.
- ***Note!***

$$\lambda_o = c/\nu_o$$

$$\lambda_o = \frac{3.00\times10^{8}\ \mathrm{m/s}}{3.02\times10^{+14}\ \mathrm{s^{-1}}} = 9.93\times10^{-7}\ \mathrm{m\ or\ 993\ nm.}$$

- Photoelectrons will not be emitted from the surface of this metal unless the wavelength of the light is shorter than 993 nm.
- Remember that higher energies are associated with higher frequencies and shorter wavelengths.

Exercise

1. List the similarities between microwaves and ultraviolet radiation.
2. How does intensity of a radiation affect the kinetic energy of photons during photoelectric effect?
3. The threshold frequency for metallic potassium is $5.46 \times 10^{14}\ s^{-1}$. Calculate the maximum kinetic energy and velocity that the emitted electron has when the wavelength of light shining on the potassium surface is 350 nm. (The mass of an electron is 9.11×10^{-31} kg.)
4. A laser produces red light of wavelength 632.8 nm. Calculate the energy, in kJ, of one mole of photons of this red light.
5. Two members of the boron family owe their names to bright lines in their emission spectra. Indium has a bright indigo-blue line (451.1 nm), and thallium has a bright green line (535.0 nm). What are the energies of these two spectral lines?

Answers

1. Both are electromagnetic waves with similar poles and charges (north/south, positive/ negative) and the same constant speed.
2. For a given frequency of incident radiation, the rate at which photoelectrons are ejected is directly proportional to the intensity of the incident light. An increase in the intensity of the incident beam increases the magnitude of the photoelectric current.

3. $$\Delta E = h\nu = \frac{hc}{\lambda} = \frac{6.626\times10^{-34}\,Js\times3\times10^{8}\,ms^{-1}}{350\times10^{-9}\,m} = 5.678\times10^{-19}\,J$$

$$h\nu_o = 6.626\times10^{-34}\,Js\times5.46\times10^{14}\,s^{-1} = 3.617\times10^{-19}\,J$$

$$\Delta E = h\nu = h\nu_o + E_k$$

$$E_k = h\nu - h\nu_o = 5.678\times10^{-19}\,J - 3.617\times10^{-19}\,J = 2.06\times10^{-19}\,J$$

$$E_k = \frac{1}{2} m_e v^2 ; \; v = \sqrt{\frac{2E_k}{m_e}} = 6.7 \times 10^5 m/s$$

4. $$\frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} Js \times 3 \times 10^8 ms^{-1}}{632.8 \times 10^{-9} m} = 3.14 \times 10^{-19} J/photon$$

$$\Delta E = 3.14 \times 10^{-19} J/photon \times 6.02 \times 10^{23} photon/mol = 1.89 \times 10^2 kJ/mol$$

5. In = 4.4×10^{-19} J; Th = 3.7×10^{-19} J

Atomic Spectra

- Atomic or line spectra are produced from the emission of photons of electromagnetic radiation (light).

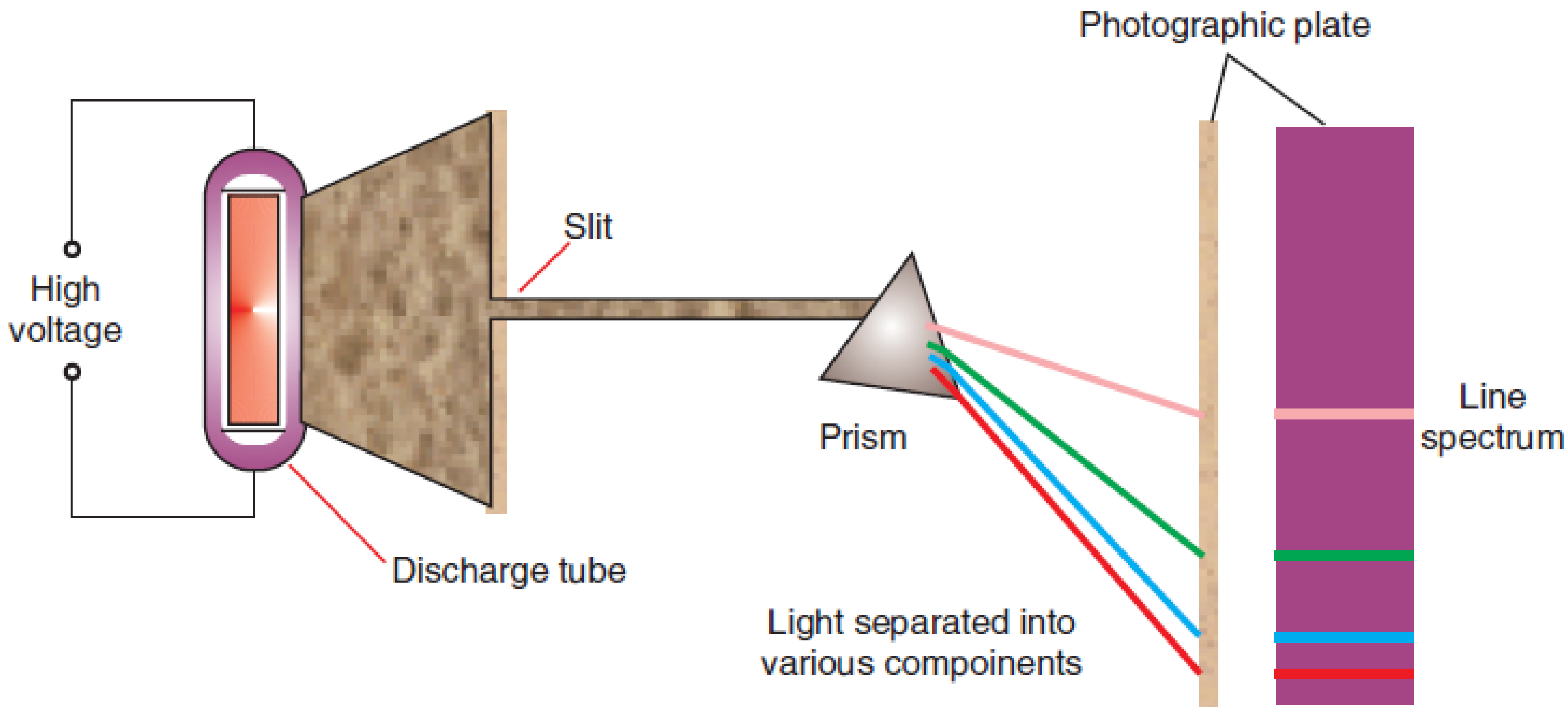


Figure 2.7 An experimental arrangement for studying the emission spectra of atoms and molecules.

WAVE NATURE OF ELECTROMAGNETIC RADIATION.MP4