PRINCIPLES OF SPECTROSCOPY

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Introduction

Definition:

Spectroscopy generally is defined as the area of science concerned with the absorption, emission, and scattering of electromagnetic radiation by atoms and molecules, which may be in the gas, liquid, or solid phase.

Importance:

- **Spectroscopy played a key role in the development of quantum mechanics and is essential to understanding molecular properties and the results of spectroscopic experiments.**
- **It is used as a “stepping stone” to take us to the concepts of quantum mechanics and the quantum mechanical description of molecular properties in order to make the discussion more concrete and less abstract and mathematical.**
- **The results of spectroscopic experiments are represented by a ‘spectrum’ which is a graph that shows the intensity of radiation at different wavelengths or the response of the atomic or molecular system to different wavelengths of the radiation.**

Electromagnetic Radiation

- **During the nineteenth century, research in the areas of optics, electricity, and magnetism and the unification of the resulting concepts by Maxwell provided convincing evidence about electromagnetic radiation.**
- **Electromagnetic radiation consists of two sinusoidally oscillating fields or waves, an electric field and a magnetic field. In the simplest situation, which is radiation in a vacuum, these fields oscillate perpendicular to each other and perpendicular to the direction of propagation of the wave.**
- **Electromagnetic radiation is an electric and magnetic disturbance traveling through space at the speed of light (2.998×10^8 m/s). It contains neither mass nor charge but travels in packets of radiant energy called photons, or quanta.**
- **Examples of EM radiation include radio waves and microwaves, as well as infrared, ultraviolet, gamma, and x-rays.**
- **Some sources of EM radiation include sources in the cosmos (e.g., the sun and stars), radioactive elements, and manufactured devices.**
- **EM radiation exhibits a dual wave and particle nature.**

Electromagnetic Wave Parameters

- **Electromagnetic radiation can act both as a wave or as a particle or photon. Electron radiation is released as photons or bundles of light energy that travel at the speed of light as waves.**
- **Therefore electromagnetic radiation can be described by wave theory, where it is represented by its speed, frequency and wavelength.**
- **As a particle, electromagnetic radiation can be described by particle theory which describes the energy level of a photon.**
- **Frequency, wavelength, and energy are all mathematically related such that if you know one, you can calculate the others.**
- **All electromagnetic waves travel at a constant speed, known as the speed of light (c).**
- **Speed of Light (c) = 300,000,000 meters per second or 3 x 10^8 m/s (*approximately*)**

Wavelength

Electromagnetic waves have crests and troughs similar to those of ocean waves. The distance between crests is described as the wavelength. Wavelength is typically represented by the Greek letter lambda (λ). Since wavelength is measuring a distance, the base unit of measurement is a meter. Wavelength is commonly used to describe specific portions of the electromagnetic spectrum. For example, the visible and infrared portions of the electromagnetic spectrum are commonly described by their wavelength in nano or micrometers.

Common Wavelength Units

•Meters (m)

•Centimeters (cm)

•Nanometers (nm)

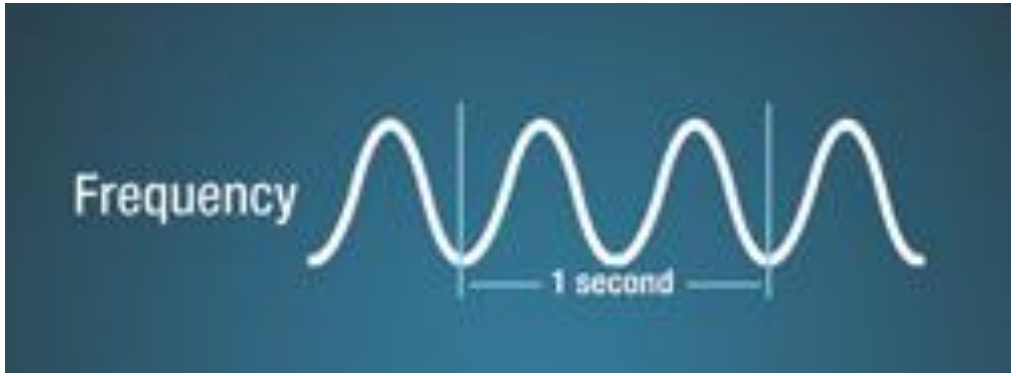
•Micrometers (µm)

Frequency

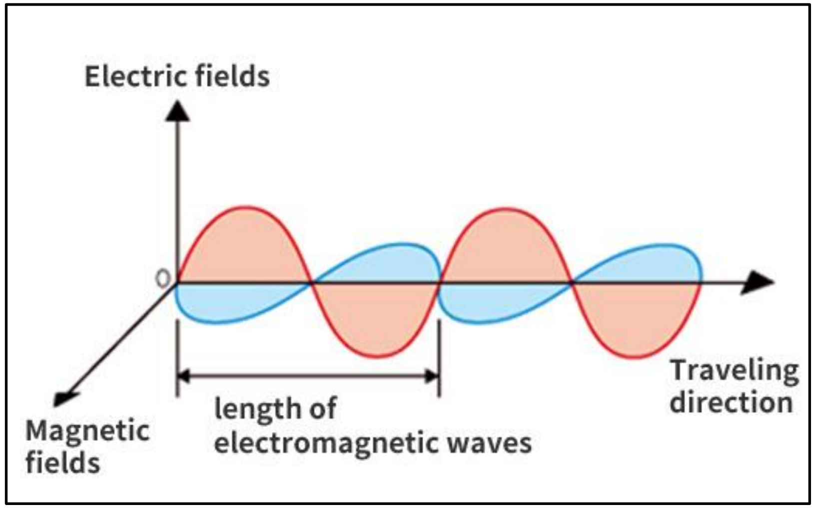
Frequency refers to the number of cycles of a wave passing a fixed point per unit of time. One wave—or one cycle per second is called a Hertz (Hz), after Heinrich Hertz who established the existence of radio waves. One Hertz can also be thought of as 1 wave cycle/second.

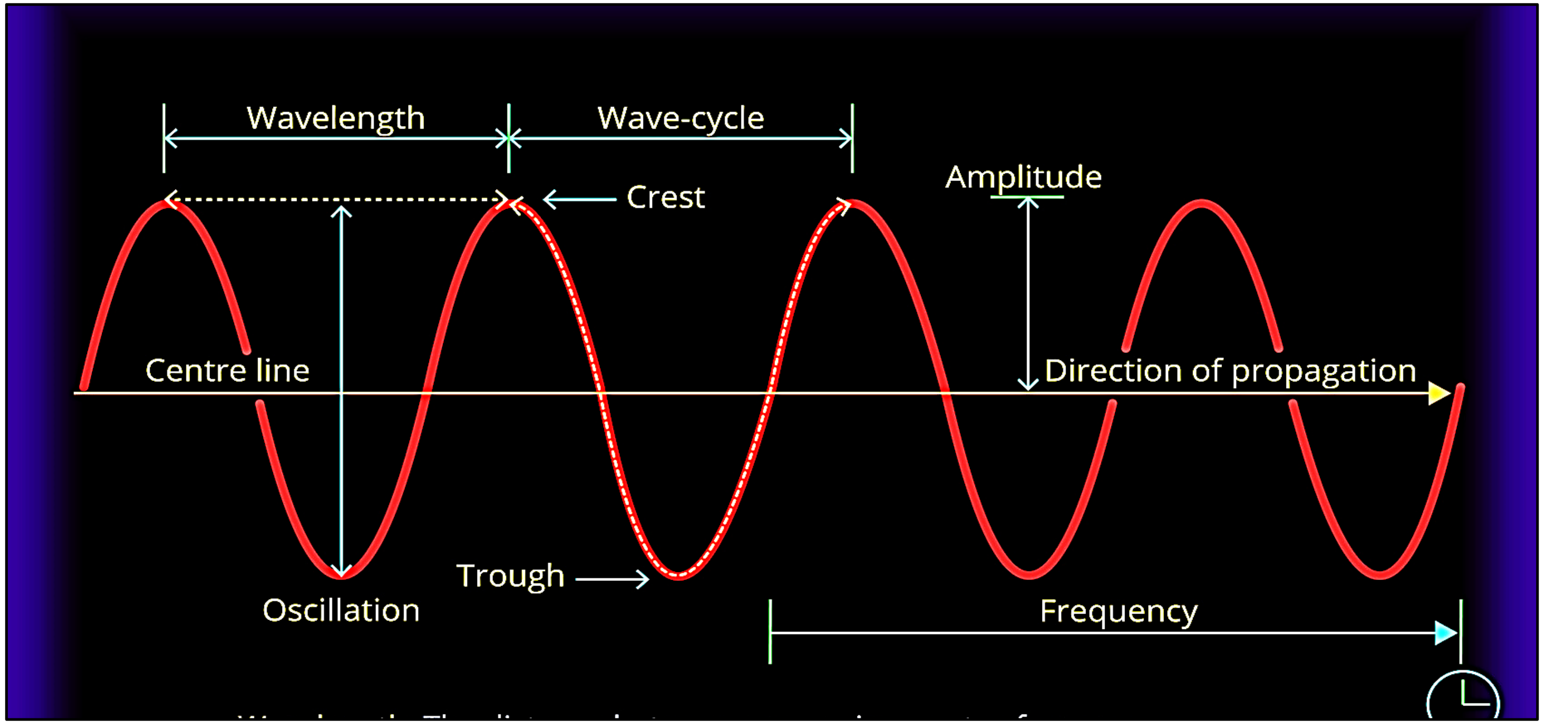
Common Frequency Units

- Hertz (Hz) (1 wave cycle/second or 1/s)
- Kilohertz (KHz)
- Megahertz (MHz)
- Gigahertz (GHz)



Features of Electromagnetic Wave





Relationship Between Wavelength and Frequency

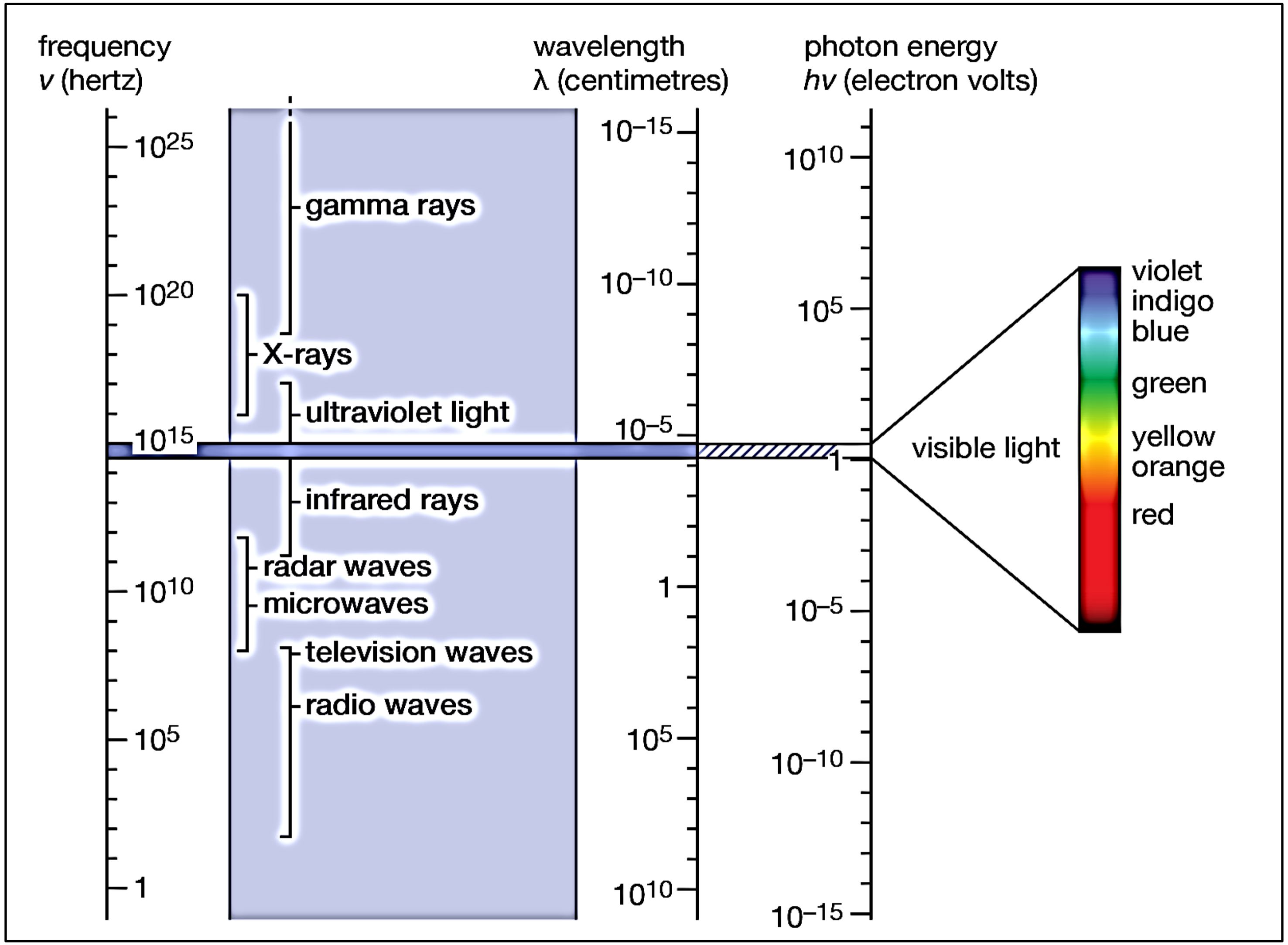
- Electromagnetic radiation travels in a waveform at a constant speed. The wave characteristics of EM radiation are found in the relationship of velocity to wavelength (the straight line distance of a single cycle) and frequency (cycles per second, or hertz, Hz), expressed in the formula

$$c = \lambda \nu$$

c = Speed of Light (3×10^8 m/sec)
λ = Wavelength in Meters
ν = Frequency in Hertz

Because the velocity is constant, any increase in frequency results in a subsequent decrease in wavelength. Therefore, wavelength and frequency are inversely proportional. All forms of EM radiation are grouped according to their wavelengths into an electromagnetic spectrum, as shown in following Figure

Electromagnetic spectrum



Relationship Between Wavelength, Frequency and Energy

- While many characteristics of electromagnetic radiation can be described by wave theory, particle theory suggests that electromagnetic radiation is composed of many discrete units called photons. The energy of a photon is described by the follow equation:

$$E = h \times \nu$$

E = energy of a photon (Joules (J))

h = Planck's constant – 6.626 X 10 $^{-34}$ Joule-Seconds

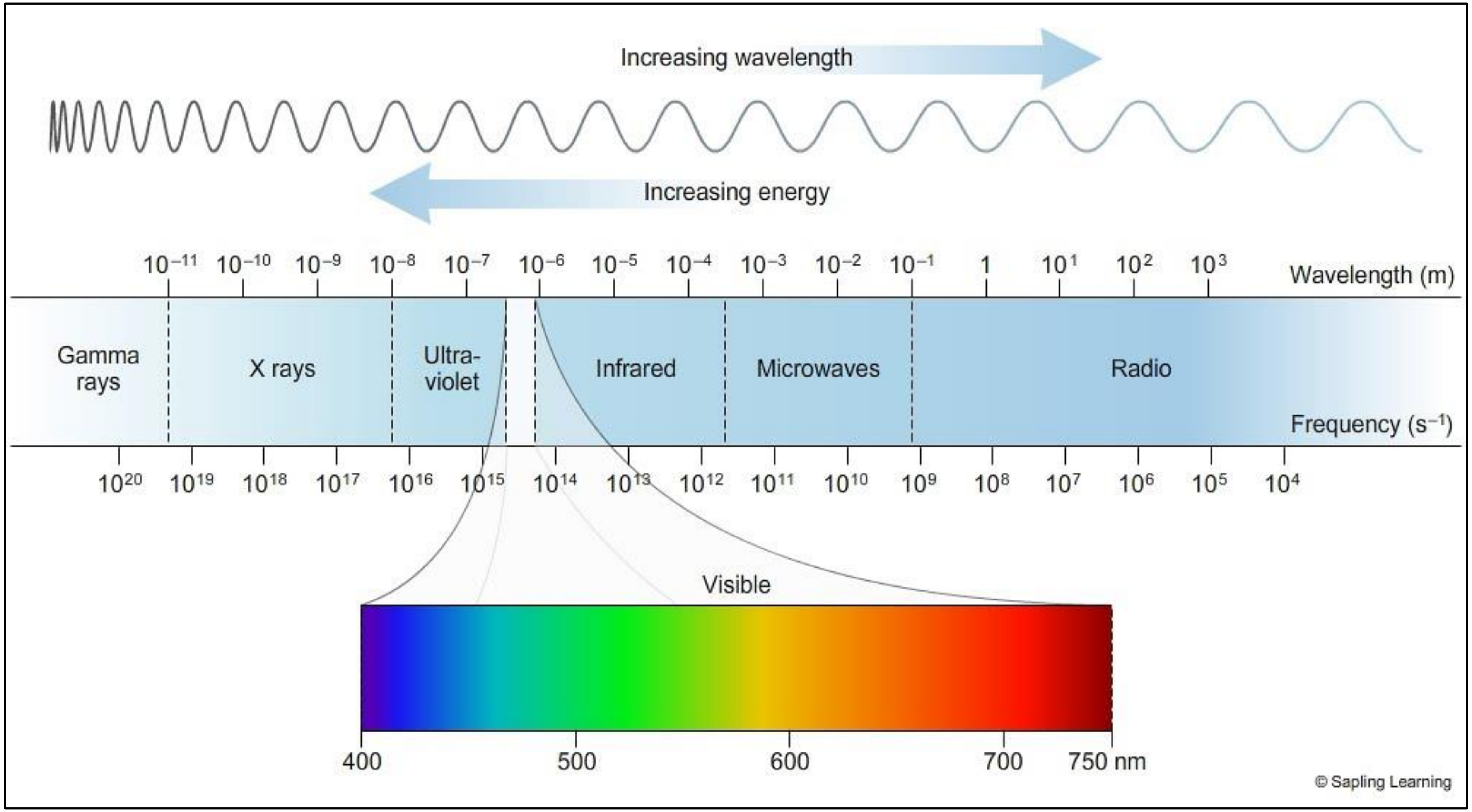
ν = Frequency (Hz)

- High frequency (short wavelength) electromagnetic radiation carries a lot of energy. Low frequency (long wavelength) electromagnetic radiation carries little energy. One of the implications of this relationship to remote sensing is that it is more difficult to detect the radiant energy of longer wavelength than shorter wavelengths (less energy to detect!).

Relationship Between Wavelength, Frequency and Energy (contd…)

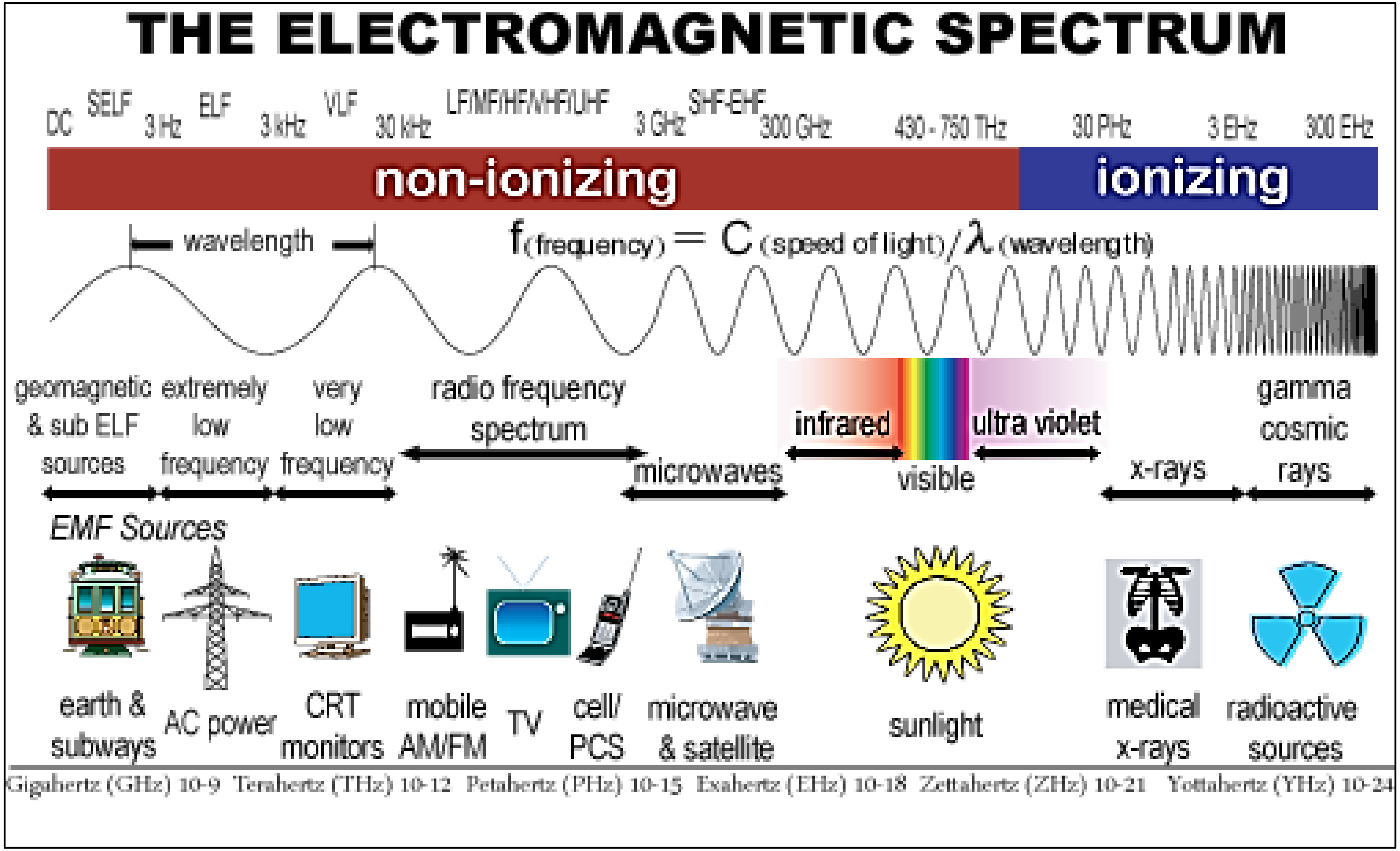
- Photon energy is directly proportional to photon frequency. Photon energy is measured in eV or keV (kilo-electron volts). The energy range for diagnostic x-rays is 40 to 150 keV. Gamma rays, x-rays, and some ultraviolet rays possess sufficient energy (>10 keV) to cause ionization.
- The energy of EM radiation determines its usefulness for diagnostic imaging. Because of their extremely short wavelengths, gamma rays and x-rays are capable of penetrating large body parts. Gamma rays are used in radionuclide imaging. X-rays are used for plain film and computed tomography (CT) imaging. Visible light is applied to observe and interpret images. Magnetic resonance imaging (MRI) uses radiofrequency EM radiation as a transmission medium.

Comparison of Energy, Wavelength and Frequency



Electromagnetic spectrum Wavelength, Frequency and Energy table

Name	Wavelength	Frequency (Hz)	Photon Energy (eV)
Gamma ray	Less than 0.01 nm	more than 10 EHz	100 kev - 300+ GeV
X - ray	0.01 - 10 nm	30 EHz - 30 PHz	120 eV - 120 keV
Ultraviolet	10 nm - 400 nm	30 PHz - 790 THz	3 eV - 124 eV
Visible	390 nm - 750 nm	790 THz - 405 THz	1.7 eV - 3.3 eV
Infrared	750 nm - 1 mm	405 THz - 300 GHz	1.24 meV - 1.7 eV
Microwave	1 mm - 1 meter	300 GHz - 300 MHz	1.24 μ eV - 1.24 meV
Radio	.1 mm - km	300 GHz - 3 Hz	12.4 feV - 1.24 meV


THE ELECTROMAGNETIC SPECTRUM
DC
SELF
3 Hz
ELF
3 kHz
VLF
30 kHz
LF/MF/HF/VHF/UHF
3 GHz
SHF-EHF
300 GHz
430 - 750 THz
30 PHz
3 EHz
300 EHz
non-ionizing
ionizing
wavelength
f(frequency) = C (speed of light) / λ (wavelength)
geomagnetic & sub ELF sources
extremely low frequency
very low frequency
radio frequency spectrum
microwaves
infrared
visible
ultra violet
x-rays
gamma cosmic rays
EMF Sources
earth & subways
AC power
CRT monitors
mobile AM/FM
TV
cell/ PCS
microwave & satellite
sunlight
medical x-rays
radioactive sources
Gigahertz (GHz) 10-9 Terahertz (THz) 10-12 Petahertz (PHz) 10-15 Exahertz (EHz) 10-18 Zettahertz (ZHz) 10-21 Yottahertz (YHz) 10-24

Regions of the Electromagnetic Spectrum

- The electromagnetic spectrum is broadly classified into different named categories based on the wavelength and characteristics of the energy.
- The names like "microwave" or "infrared" were developed for convenience to describe electromagnetic radiation with similar characteristics, but there are no definitive dividing lines between one spectral region or the next.
- The only region in the electromagnetic spectrum that is relatively consistent in the wavelength definition is the visible spectrum, as it corresponds directly with wavelengths that human eyes are sensitive to. The visible spectrum is a small window of the entire electromagnetic spectrum.

Regions of the Electromagnetic Spectrum (contd…)

Gamma Rays (Wavelength < 10^{-12} meters)

- Gamma rays have the shortest wavelengths (< 0.01 nanometers) and the most energy of any region of the electromagnetic spectrum. Gamma rays are produces by the hottest objects in the universe, including neutron stars, pulsars, supernova explosions. Gamma rays can also be created by nuclear explosions. the majority of gamma rays generated in space are blocked by the Earth's atmosphere. This is a good thing as gamma rays are biologically hazardous.

X-Rays (Wavelength 10^{-8} to 10^{-12} meters)

- X-Rays range in wavelength from 0.01 – 10 nm and are primarily generated from by super-heated gas from exploding stars and quasars. X-rays are able to pass through many different types of materials. X-rays are commonly used for medical imaging and for inspecting cargo and luggage. Similar to gamma rays, the Earth's atmosphere blocks x-ray radiation.

Regions of the Electromagnetic Spectrum (contd…)

Ultraviolet (UV) (Wavelength 10^{-7} - 10^{-8} meters)

- Ultraviolet (UV) light has wavelengths of approximately 1 – 380 nm. The Sun is a source of ultraviolet energy. The UV portion of the spectrum is subdivided into UV-A, UV-B, and UV-C. UV-C rays are the most harmful and are almost completely absorbed by our atmosphere. UV-B rays are the harmful rays that cause sunburn. Although UV waves are invisible to the human eye, some insects, such as bumblebees, can see them.

Regions of the Electromagnetic Spectrum (contd…)

Visible (Wavelength ~ 10^{-7} meters)

Visible light covers the range of wavelengths from 400 – 750 nm or 0.4 to 0.75 micrometers. This is the only region in spectrum that human eyes are sensitive to. The Sun emits the most radiation in the visible portion of the spectrum. Each individual wavelength within the spectrum of visible light wavelengths is representative of a particular color. Light at the lower end of the visible spectrum, having a longer wavelength, about 750 nm, is seen as red; light in the middle of the spectrum is seen as green; and light at the upper end of the spectrum, with a wavelength of about 380 nm, is seen as violet. When all the wavelengths of the visible light spectrum strike your eye at the same time, the color white is perceived. The visible portion of the spectrum is used extensively in remote sensing and is the energy that is recorded using photography.

Color	Wavelength
violet	380–450 nm
blue	450–495 nm
green	495–570 nm
yellow	570–590 nm
orange	590–620 nm
red	620–750 nm

Regions of the Electromagnetic Spectrum (contd…)

Infrared (Wavelength ~ 10^{-6} to 10^{-3} meters)

- The infrared portion of the spectrum ranges from approximately 0.75 µm to 100 µm (750 nm - 10,000 nm) in wavelength. It is divided up into three main regions,
- Near Infrared (NIR): 0.7 – 1.3µm,
- Shortwave Infrared (SWIR): from 1.3 – 3 µm and
- Far or Thermal Infrared from 3 - 100 µm.
- Infrared radiation is used extensively in remote sensing.
- Objects reflect, transmit, and absorb the Sun's near-infrared and shortwave radiation in unique ways and this can used to observe the health of vegetation, soil composition and moisture content.
- The region from 8 to 15 µm is referred to as thermal infrared since these wavelengths are best for studying the longwave thermal energy radiating from the Earth.

Regions of the Electromagnetic Spectrum (contd…)

Microwaves (Wavelength ~ 10^{-3} to 10^{-1} meters)

- Microwaves are essentially high frequency radio waves and have wavelengths that range 1mm to 1m. Different wavelengths or bands of microwaves are used for different applications. Mid-wavelength microwaves can penetrate haze, light rain and snow, clouds, and smoke are beneficial for satellite communication and studying the Earth from space. Radar technology sends pulses of microwave energy and senses the energy reflected back.

Radio Waves ((Wavelength >10^{-1}meters)

- Radio waves have the longest wavelengths in the electromagnetic spectrum with wavelengths ranging from approximately 1mm to several hundred meters. Radio waves are used to transmit a variety of data. Wireless networking, television and amateur radio all use radio waves. The use of radio frequencies are usually regulated by governments.

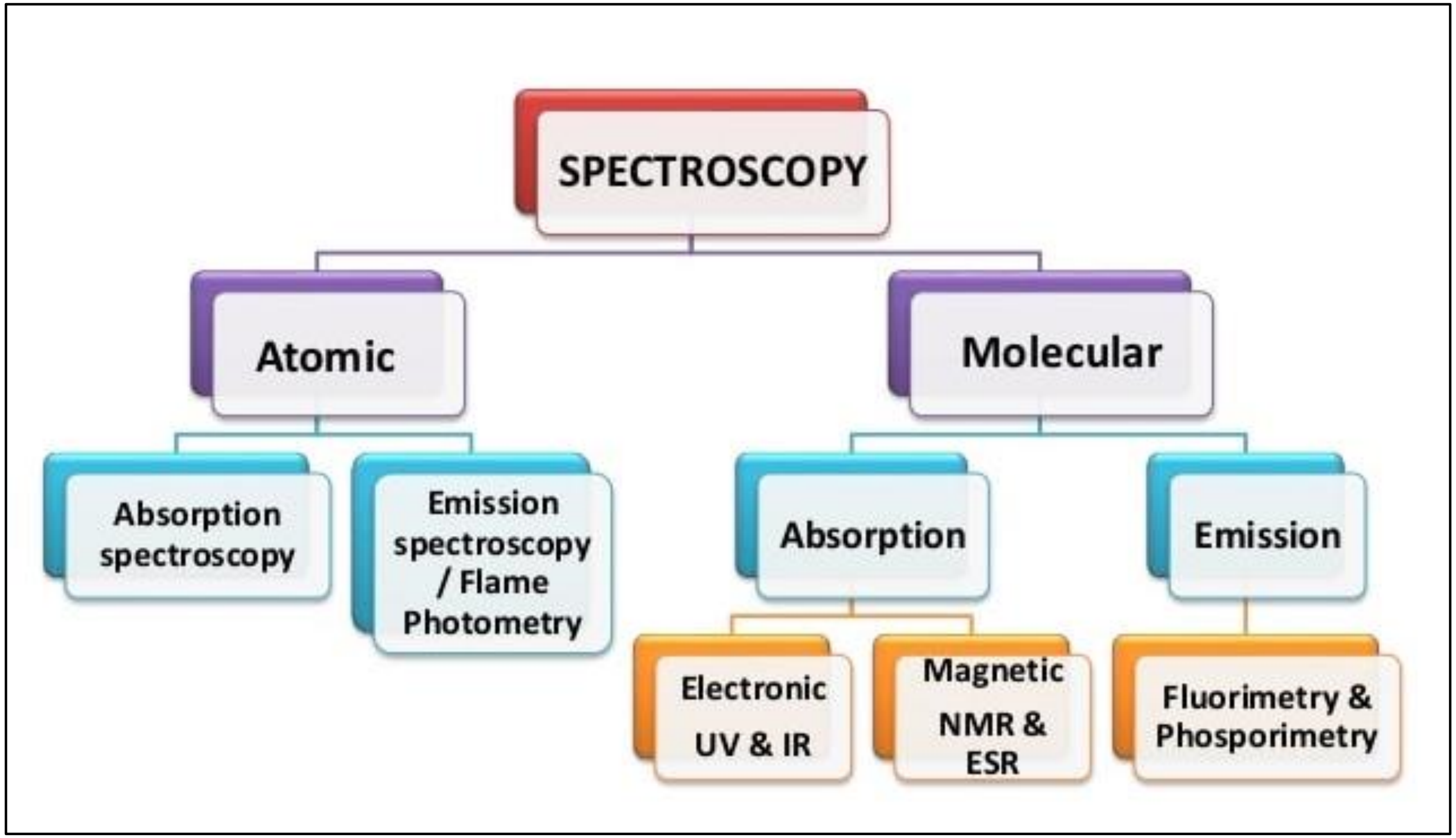
Origin of Electromagnetic spectrum

- Spectrum arises from transition of electrons between energy levels in an atom,

<u>for example:</u>

When an electron undergoes transition from lower energy level to higher energy level it absorbs energy in the form of a photon and the spectrum thus obtained is called **'Absorption spectrum'** on the other hand when it falls down from a high energy level into a lower energy level it releases the energy in the form of a photon and the spectrum thus obtained is called **'Emission spectrum'.**

Classification of Spectroscopy



Atomic Spectroscopy

- Atomic spectroscopy was the first application of spectroscopy developed.
- Atoms of different elements have distinct spectra so atomic spectroscopy can quantify and identify a sample's composition.
- The main types of atomic spectroscopy include atomic absorption spectroscopy (AAS) , atomic emission spectroscopy (AES) and atomic fluorescence spectroscopy (AFS).

➢ In AAS atoms absorb ultraviolet or visible light to transition to higher levels of energy. AAS quantifies the amount of absorption of ground state atoms in the gaseous state. AAS is commonly used in the detection of metals.

➢ In AES, atoms are excited from the heat of a flame, plasma, arc or spark to emit light. AES used the intensity of light emitted to determine the quantity of an element in a sample. Techniques that use AES include flame emission spectroscopy.

➢ In AFS, it is a beam of light that excites the analytes, causing them to emit light. The fluorescence from a sample is then analyzed using a fluorometer, and it is commonly used to analyze organic compounds.

Ultraviolet (UV) and visible (Vis) spectroscopy

- Ultraviolet (UV) and visible (Vis) spectroscopy analyses compounds using the electromagnetic radiation spectrum from 10 nm to 700 nm. Many atoms are able to emit or absorb visible light, and it is this absorption or reflectance that gives the apparent color of the chemicals being analyzed.
- UV and visible spectroscopy can be used to measure the concentration of samples using the principles of the Beer-Lambert Law, which states that absorbance is proportional to the concentration of the substance in solution and the path length.
- UV and visible spectroscopy can also be used to identify the presence of the free electrons and double bonds within a molecule.
- In addition to being an analytical technique that can be used alone, a UV/Vis spectrometer can be used as a detector for high-performance liquid chromatography.

Infrared Spectroscopy

- Infrared (IR) analyses compounds using the infrared spectrum, which can be split into near IR, mid-IR and far IR. Near IR has the greatest energy and can penetrate a sample much deeper than mid or far IR, but due to this, it is also the least sensitive.
- Infrared spectroscopy is not as sensitive as UV/Vis spectroscopy due to the energies involved in the vibration of atoms being smaller than the energies of the transitions.
- IR uses the principle that molecules vibrate, with bonds stretching and bending, when they absorb infrared radiation.
- IR spectroscopy works by passing a beam of IR light through a sample, and for an IR detectable transition, the molecules of the sample must undergo dipole moment change during vibration. When the frequency of the IR is the same as the vibrational frequency of the bonds, absorption occurs and a spectrum can be recorded.
- Different functional groups absorb heat at different frequencies depending on their structure, and thus a vibrational spectrum can be used to determine the functional groups present in a sample. When interpreting the data obtained by an IR, results can be compared to a frequency table to find out which functional groups are present to help determine the structure.

Nuclear Magnetic Resonance Spectroscopy (NMR)

- Nuclear magnetic resonance (NMR) uses resonance spectroscopy and nuclear spin states for spectroscopic analysis. All nuclei have a nuclear spin, and the spin behavior of the nucleus of every atom depends on its intramolecular environment and the external applied field.
- When nuclei of a particular element are in different chemical environments within the same molecule, there will be varied magnetic field strengths experienced due to shielding and de-shielding of electrons close by, causing different resonant frequencies and defines the chemical shift values.
- Spin-spin coupling takes into account that the spin states of one nucleus affect the magnetic field that is experienced by neighboring nuclei, via intervening bonds. Spin-spin coupling causes absorption peaks of each group of nuclei to be split into a number of components.
- There are multiple types of NMR analyses, which are hydrogen NMR, carbon 13 NMR, DEPT 90 and DEPT 135 NMR. The NMR spectrum of a compound shows the resonance signals that are emitted by the atomic nuclei present in a sample, and these can be used to identify the structure of a compound.

*DEPT = Distortionless Enhancement Polarization Transfer

Selection Rules for Electronic Transitions

- When electron gains certain quantity of energy in the form of a photon of light with just the right frequency it jumps from lower to higher energy level. Conversely if the transition takes place from higher to lower energy level, it will release a photon of light with certain frequency.
- Electronic transitions may be allowed or forbidden transitions and are governed by the following set of selection rules :

Rule 1: Spin selection rule ($\triangle S = 0$ for the transition to be allowed)

- There should be no change in spin orientation i.e. no spin inversion takes place during these transitions(Change in spin quantum number is zero).
- Thus, S→S, T→T are allowed, but S→T, T→S are forbidden transitions.

Selection Rules for Electronic Transitions (contd…)

Rule 2: $\Delta L = +1$ or -1

- **Transitions that are allowed must involve an overall change in orbital angular momentum of one unit, i.e. $\Delta L = +1$ or -1.**
- **Transitions within the same sub-level are forbidden ie change in orbital quantum number cannot be zero**

  allowed: s ---> p, p ---> d

  forbidden: d ---> d, p ---> p

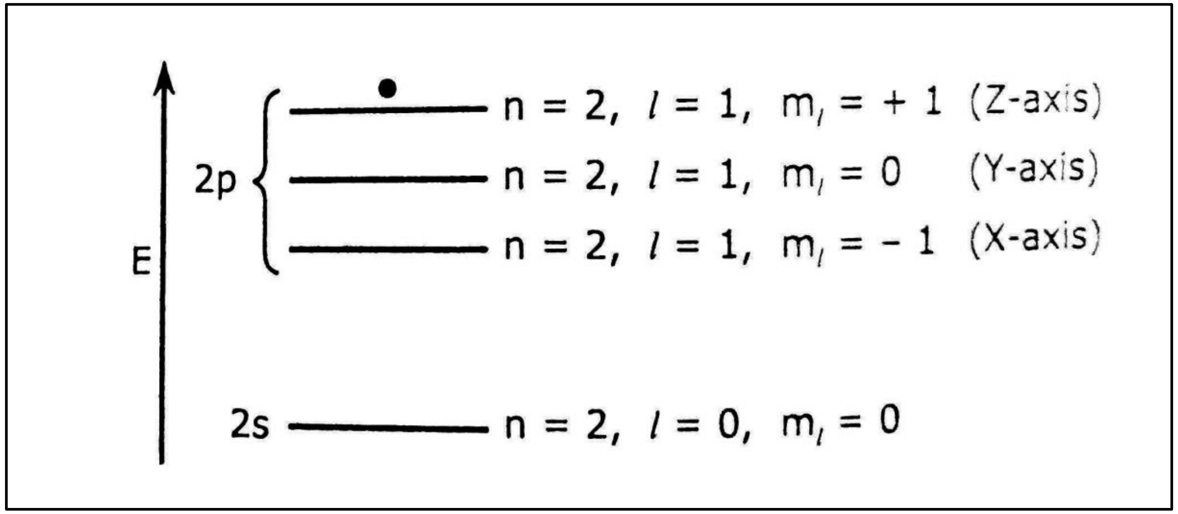
- **$\Delta L = +1$ ----- electron jumps from lower to higher**
- **$\Delta L = -1$ ----- electron jumps from higher to lower**
- **Electron cannot jump between two orbitals that differ by more than one orbital quantum number**

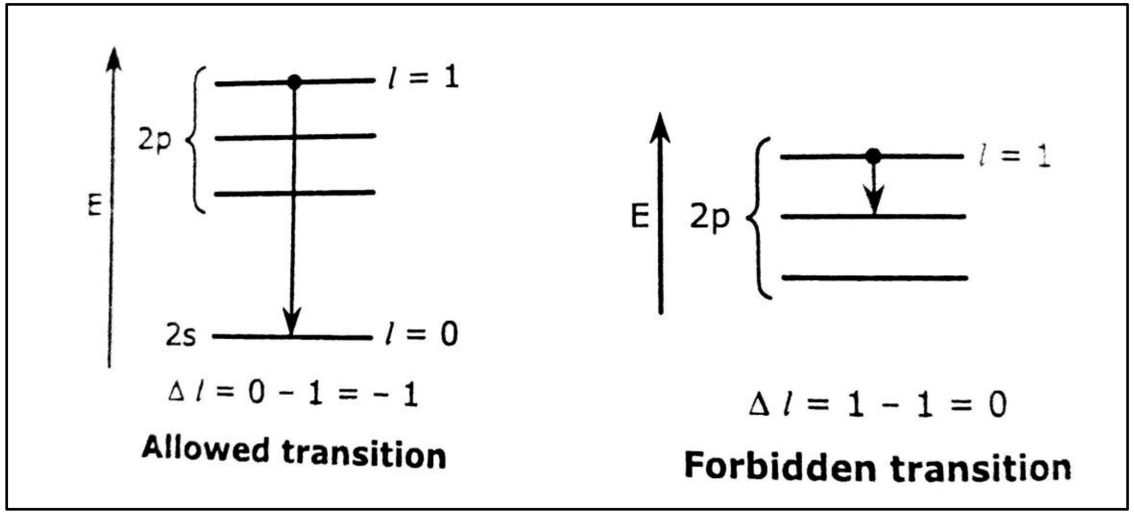
Selection Rules for Electronic Transitions (contd…)

- **Rule 3:** $\Delta m_\ell = 0, \pm 1$
- **The magnetic quantum number can change by zero or one unit.**

Example:

- **Consider a hydrogen atom having electron found in 2pz orbital and find out whether transitions to 2S and 2py are allowed or forbidden?**





- **Forbidden transitions can still take place but there is a very small probability that such transitions will actually take place.**