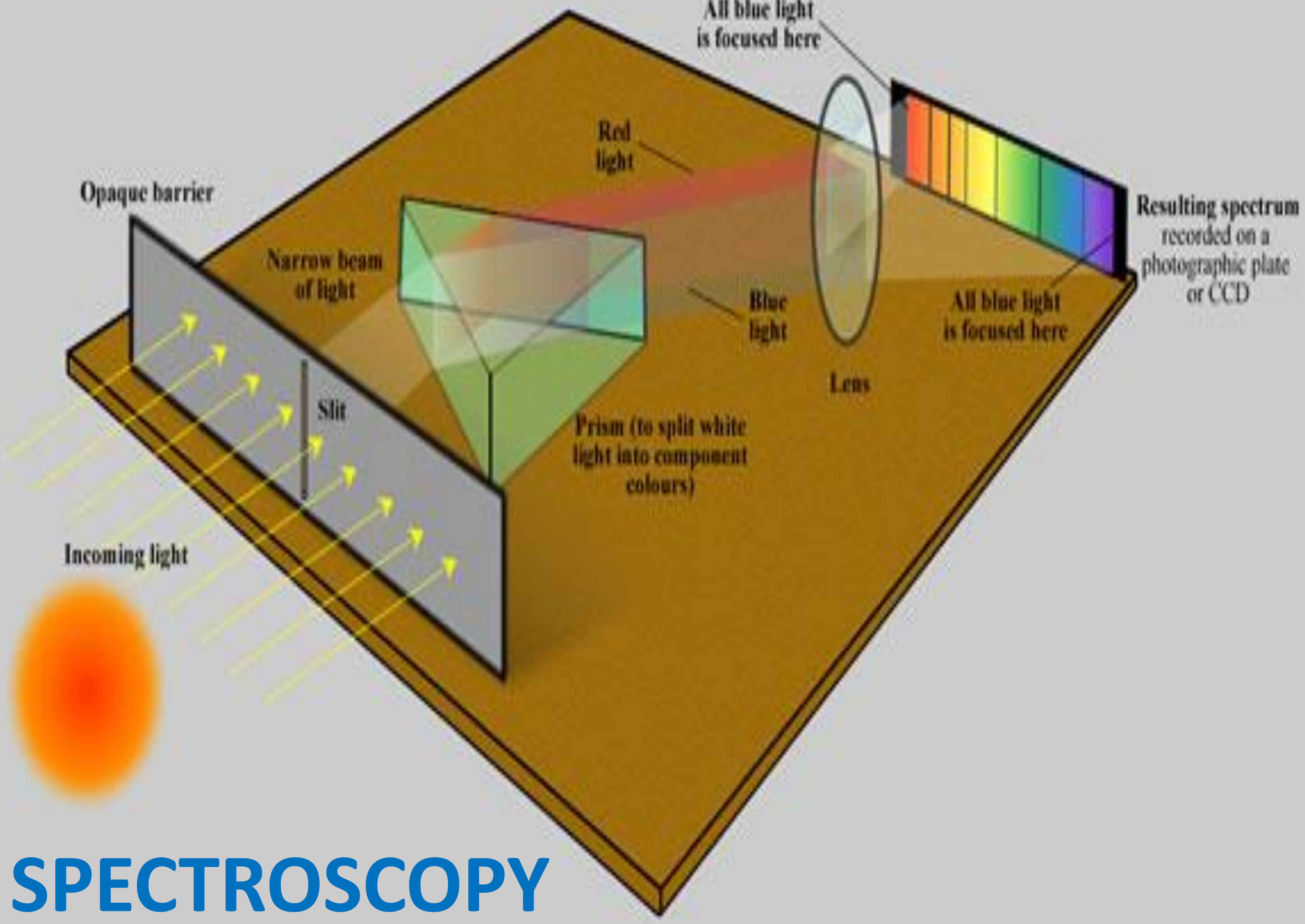


SPECTROSCOPY

Introduction

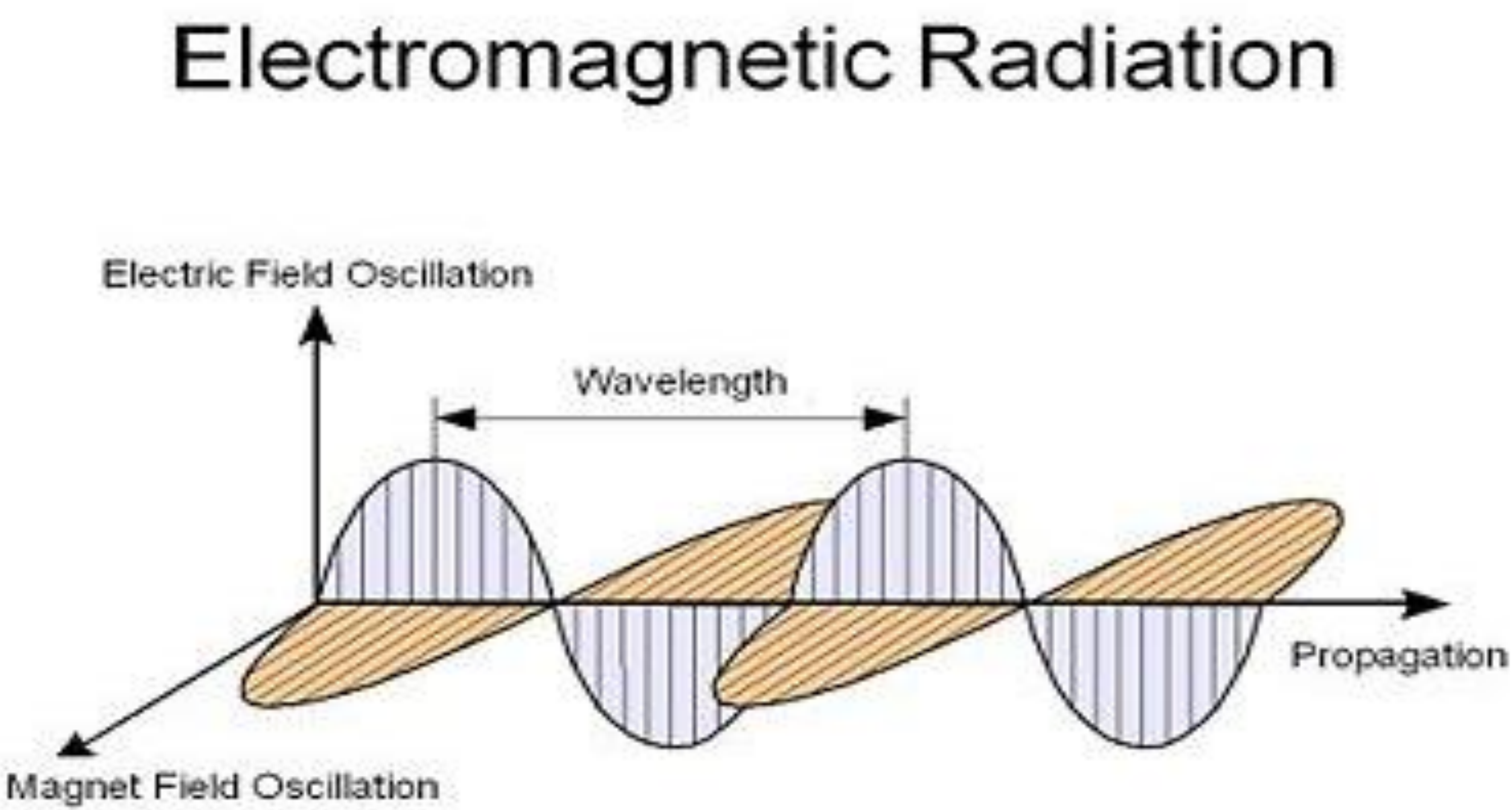
- Spectroscopy is the study of the interaction between electromagnetic radiation and matter. The matter can be atoms, molecules or ions , or solid.
- The nature of the interaction between radiation and matters may include – absorption, emission or scattering .
- It is the absorption, emission or scattering of radiation by matter that is used to quantitatively or qualitatively study the matter or to study physical process.

- A study of the wavelength absorbed or emitted by an atom or a molecule will give information about its identity and this technique is known as qualitative spectroscopy.
- Measurement of total amount of radiation will give information about the number of absorbing or emitting atom or molecules and is called quantitative spectroscopy.

Electromagnetic radiation

- Electromagnetic radiation is a form of energy that is all around us
- Electromagnetic radiation is a form of energy and has both electrical and magnetic characteristics
- Electricity and magnetism were once thought to be separate forces
- **<u>James clerk maxwell</u>** developed a unified theory of electromagnetism
- The study of electromagnetism deals with how electrically charged particles interact with each other and with magnetic fields

- The electric and magnetic fields in a electromagnetic wave oscillate along directions perpendicular to the propagation direction of the wave



Electromagnetic spectrum

- A short wavelength means that the frequency will be higher because one cycle can pass in a shorter amount of time according to the **University of Wisconsin**.
- Similarly a longer wavelength has a lower frequency because each cycle takes longer to complete

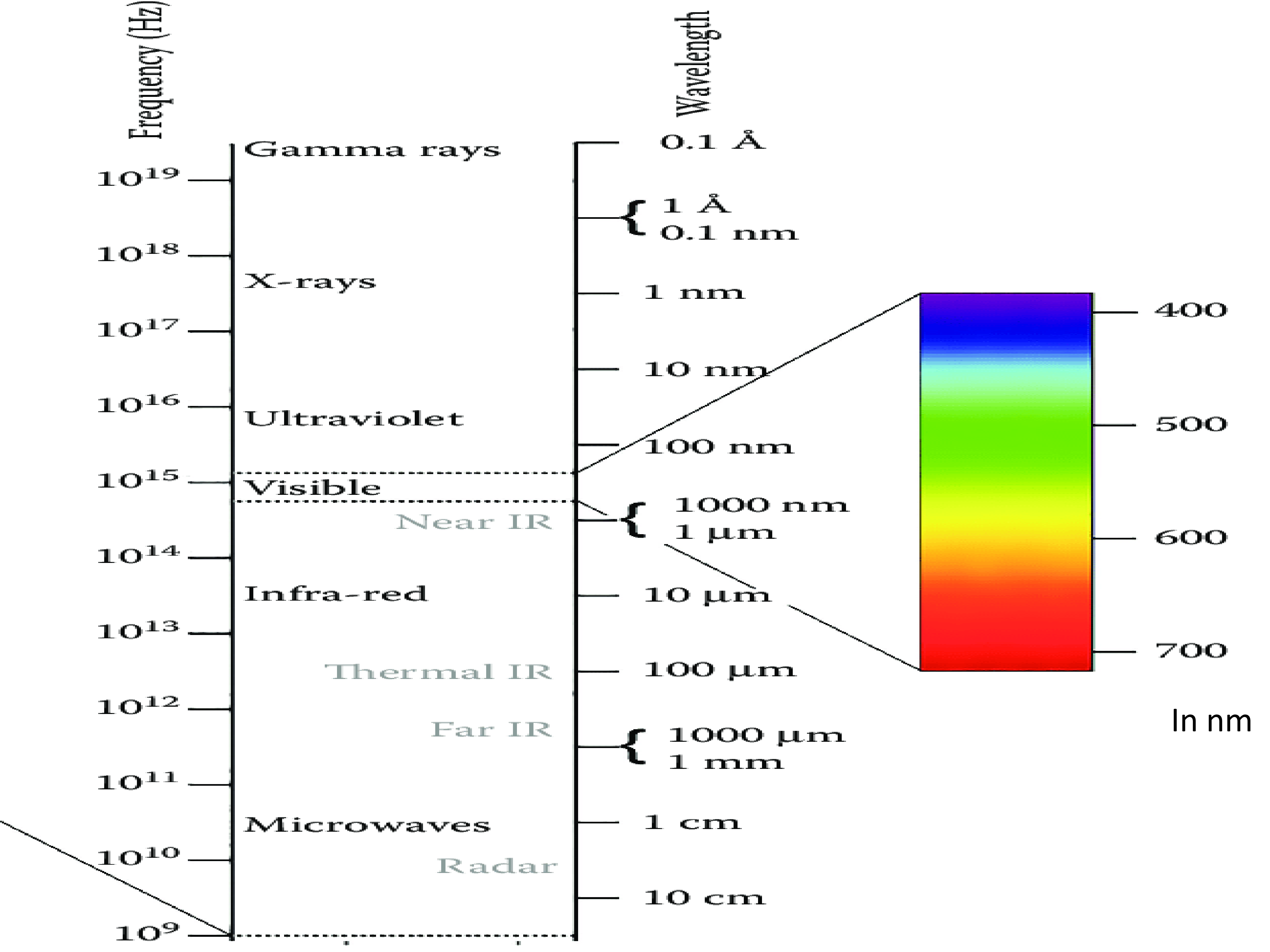
Various terms...

- **Frequency** :- number of waves produced each second (measured in Hz).
- **Wavelength** (λ) :- the distance between two successive waves (measured in m).
- **Amplitude** :- is the maximum distance a wave extends beyond its middle position

Electromagnetic spectrum

- Electromagnetic spectrum ranges from very short wavelength (gamma rays) to very long wavelengths(radio waves).
- The visible region of the spectrum extends approximately over the wavelength range 400-700nm
- The shorter wavelengths being the blue end of the spectrum and the longer wavelength the red

- The wavelength between 400 and 200nm make up the near ultraviolet region of the spectrum
- The wavelength above 700nm to approximately 2000nm(2μm) the infrared region.



Frequency (Hz)
Wavelength
Gamma rays
X-rays
Ultraviolet
Visible
Near IR
Infra-red
Thermal IR
Far IR
Microwaves
Radar
10^{19}
10^{18}
10^{17}
10^{16}
10^{15}
10^{14}
10^{13}
10^{12}
10^{11}
10^{10}
10^{9}
0.1 Å
1 Å
0.1 nm
1 nm
10 nm
100 nm
1000 nm
1 µm
10 µm
100 µm
1000 µm
1 mm
1 cm
10 cm
400
500
600
700
In nm

PRINCIPLE

- When radiation fall on homogeneous medium , a portion of incident light is reflected, a portion is absorbed remainder is transmitted.
- The two laws governing the absorption of radiation are known as **Lambert's law** and **Beer's law** .
- In the combined form they are referred to as **Beer-Lambert law**.

- **BEER’S LAW** = when a ray of monochromatic light passes through an absorbance medium, its intensity decreases exponentially as the concentration of the absorbing medium increases, provided the length of the absorbing medium is constant.

Equation : $I = K_1 I_0 C$

Where as,

I = Intensity of transmitted ray

I_o = Intensity of the incident ray .

K_1 = constant

C = concentration of he absorbing medium

- **LAMBERT'S LAW** = when a ray of monochromatic light passes through an absorbing medium, its intensity decreases exponentially as the light of the absorbing medium increases, provided the concentration of the absorbing medium is constant.

Equation = $I = I_0 e^{-k_2 l}$

Where as,

I = Intensity of transmitted ray

I_o = Intensity of the incident ray .

K_2 = constant

L= path length of he absorbing medium

Transmittance (T)

Transmittance is the ratio of intensities and usually expressed as a percentage (%)

Equation: $T = I/Io$ $\quad \% T = I/Io \times 100$

The absorbance A or extinction E is expressed as :

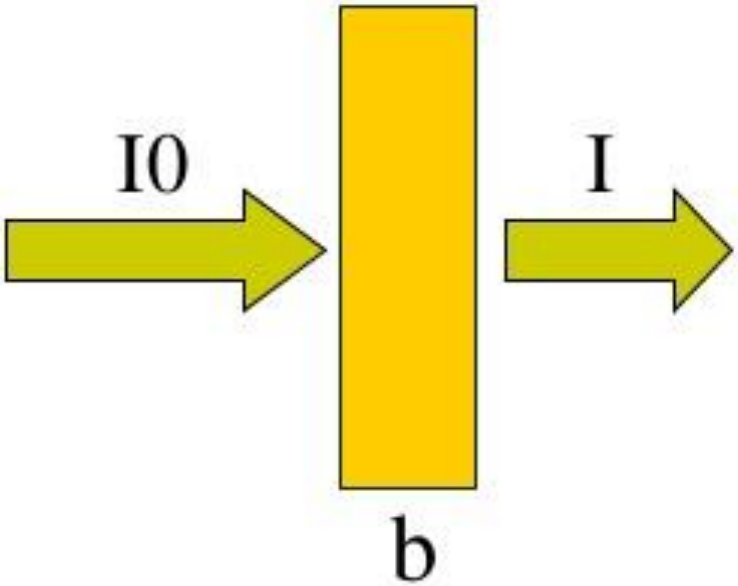
$E = \log I/Io$

According to the beer's lambert's law the extinction or absorbance is propotional to the concentration of the absorbing solution (C) and to the thickness of the absorbing medium (L) i.e. $A \propto C$ & $A \propto L$

Therefore, $A = \dot{\varepsilon} CL$

Where, $\dot{\varepsilon}$= molar extinction co-efficient for absorbing medium.

Transmittance



$$T = \frac{I}{I_0} \Rightarrow \frac{dI}{I_0} = kcdb$$

$$\int_{I_0}^{I} \frac{dI}{I_0} = -kc\int_0^b db$$

$$\Rightarrow \ln(\frac{I}{I_0}) = -kbc = 2.303\log(\frac{I}{I_0})$$

$$\Rightarrow -\log(\frac{I}{I_0}) = -\log T = A = \varepsilon bc$$

$$\varepsilon = \frac{k}{2.303}$$

Classifications

- Spectroscopy can be defined by the type of radiative energy involved.
- The intensity and frequency of the radiation allows for a measurable spectrum.
- Electromagnetic radiation is a common radiation type and was the first used in spectroscopic studies.
- Both infrared (IR) and near IR use electromagnetic radiation, as well as terahertz and microwave techniques.

- Both electrons and neutrons are also a source of radiation energy due to their de Broglie wavelength.
- Mechanical methods can be applied to solids for radiation, and acoustic spectroscopy uses radiated pressure waves.
- Another way of classifying spectroscopy is by the nature of the interaction between the energy and the material.

- These interactions include absorption, emission, resonance spectroscopy, elastic and inelastic scattering.
- The materials used can also define the spectroscopy type, including atoms, molecules, nuclei and crystals.

Atomic Spectroscopy

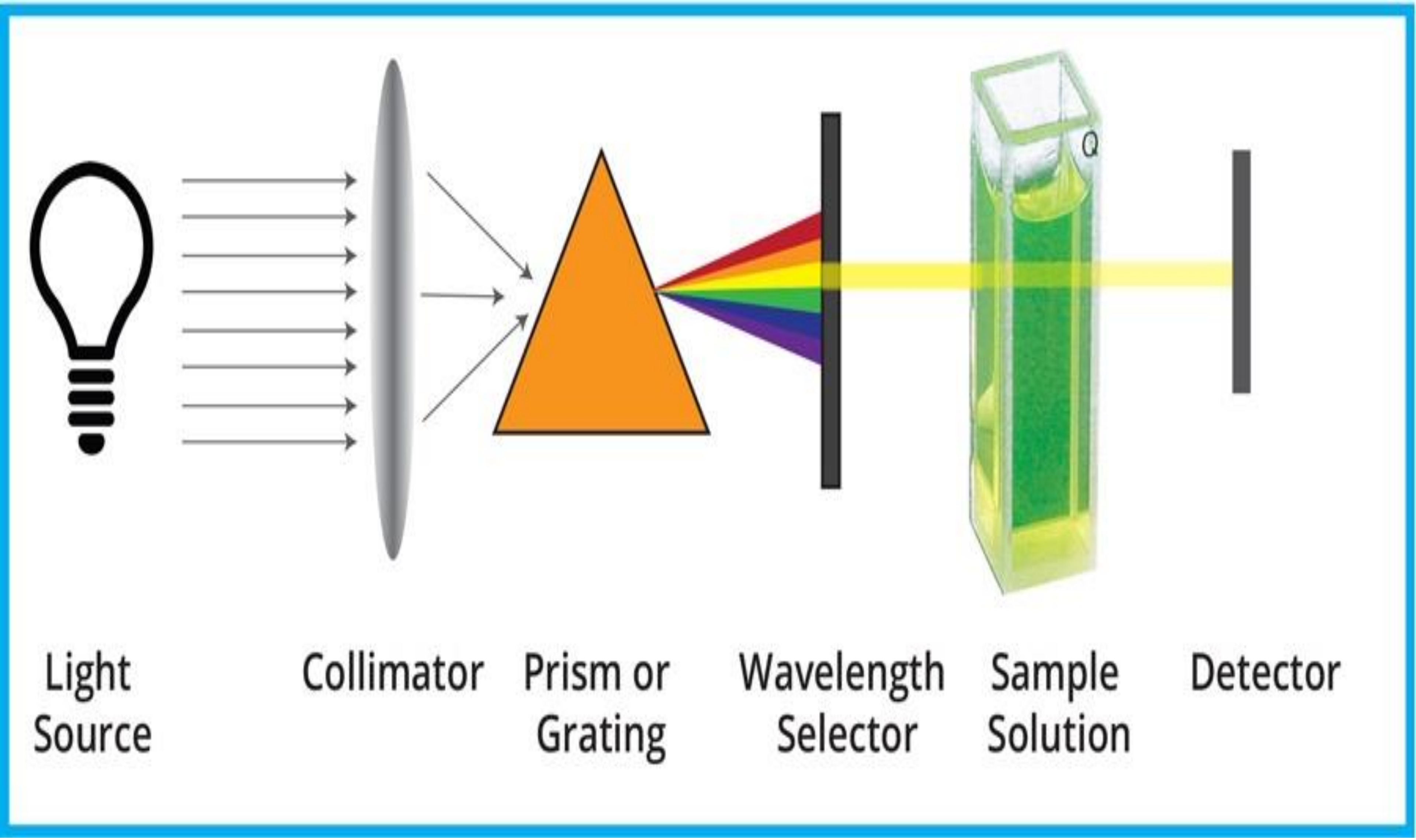
- Atomic spectroscopy was the first application of spectroscopy developed, and it can be split into atomic absorption, emission and fluorescence spectroscopy.
- Atoms of different elements have distinct spectra so atomic spectroscopy can quantify and identify a sample's composition.
- The main types 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, inductively coupled plasma atomic emission spectroscopy, and spark or arc atomic 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 analysed using a fluorometer, and it is commonly used to analyse organic compounds.

Ultraviolet and Visible 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 colour of the chemicals being analysed.



Ultraviolet and Visible Spectroscopy

- The absorption of visible and UV radiation is associated with excitation of electrons from a low energy ground state into a high energy excited state, and the energy can be absorbed by both non-bonding **n -electrons** and **π-electrons** within a molecular orbital.
- Wavelengths of light all have a particular energy associated with them, and it is only light with the right amount of energy that causes transitions from one level to another for absorption. For larger gaps between energy levels, more energy is required for promotion to the higher energy level, so there will be higher frequency and shorter wavelength absorbed.

- 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.
- As well as for measuring the concentration of a sample, UV and visible spectroscopy can 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.

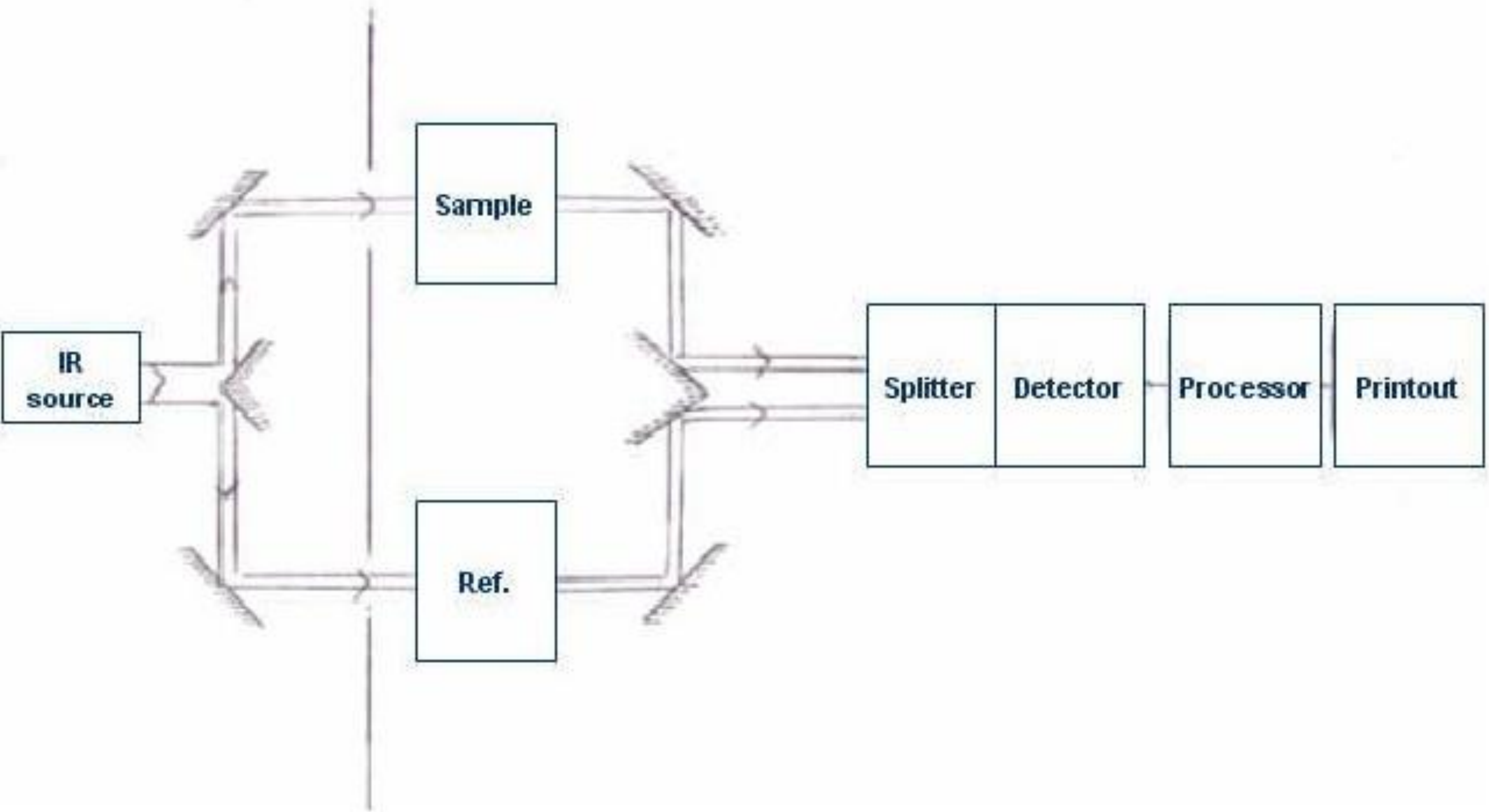


FIG :- IR SPECTROSCOPY

- 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 dependent upon 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.

Raman Spectroscopy

- Raman spectroscopy is similar to IR in that it is a vibrational spectroscopy technique, but it uses inelastic scattering.
- The spectrum of Raman spectroscopy shows a scattered Rayleigh line and the Stoke and anti-Stoke lines, which is different to the irregular absorbance lines of IR.

- Raman spectroscopy works by the detection of inelastic scattering, also known as Raman scattering, of monochromatic light from a laser in the visible, near infrared or ultraviolet range.
- For a transition to be Raman active, there must be a change in the polarizability of the molecule during the vibration and the electron cloud must experience a positional change.

- The technique provides a molecular fingerprint of the chemical composition and structures of samples, but Raman scattering gives inherently weak signals.
- Techniques such as Surface Enhanced Raman Spectroscopy (SERS) have been developed to enhance sensitivity when using Raman spectroscopy.