Basics of spectroscopy

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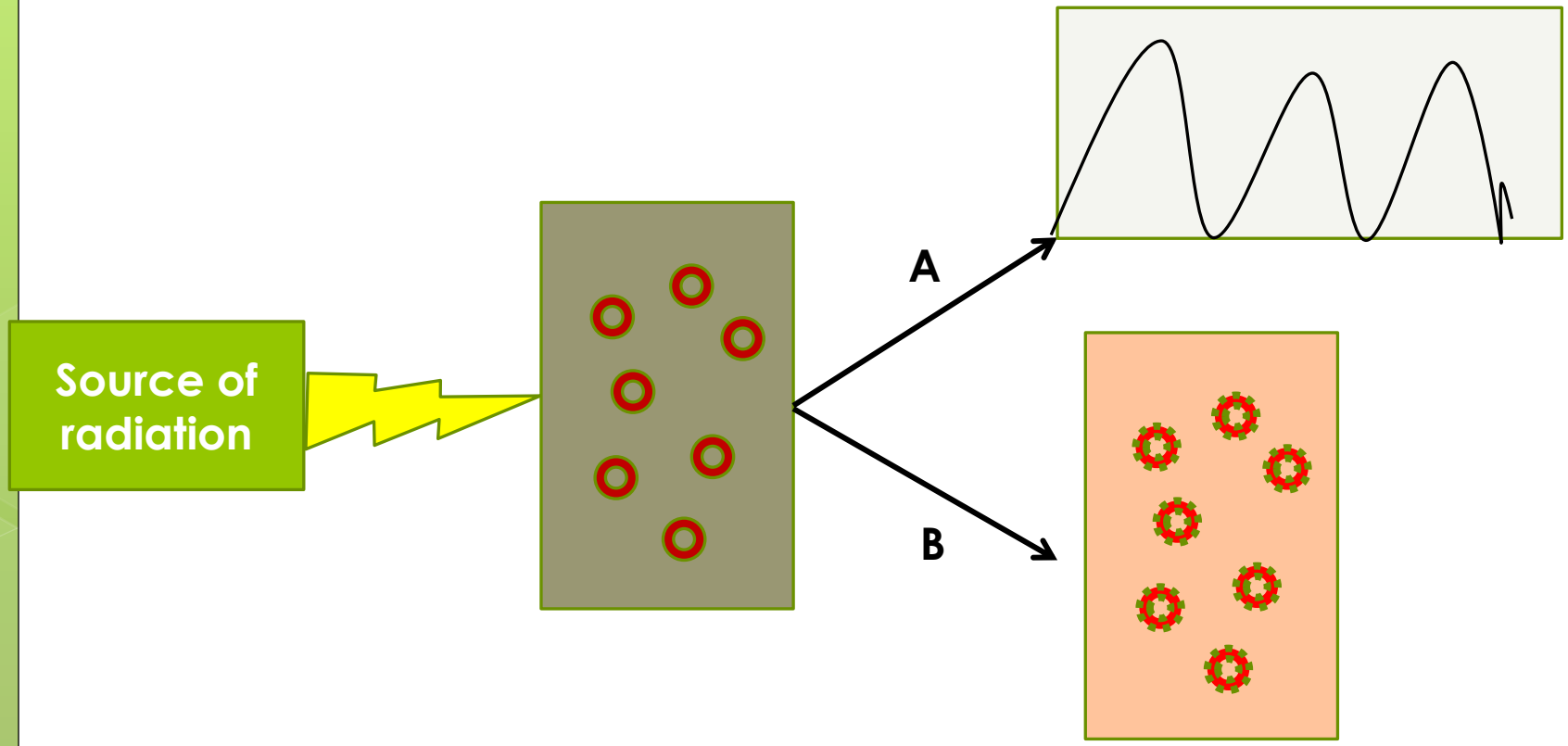
What is spectroscopy???

- In general terms spectroscopy can be simply defined as the interaction of radiation with matter. The study of interaction of light wavelength with matter and revelation of its properties is known as spectroscopy.
- The varying frequency of radiation interacts with matter at various energy levels and provide results in reference to its properties. The result obtained is known as the "spectrum".
- It not only tells about the energy level but also reveals dynamics, structure and symmetry of the molecules.

How does spectroscopic investigations help?

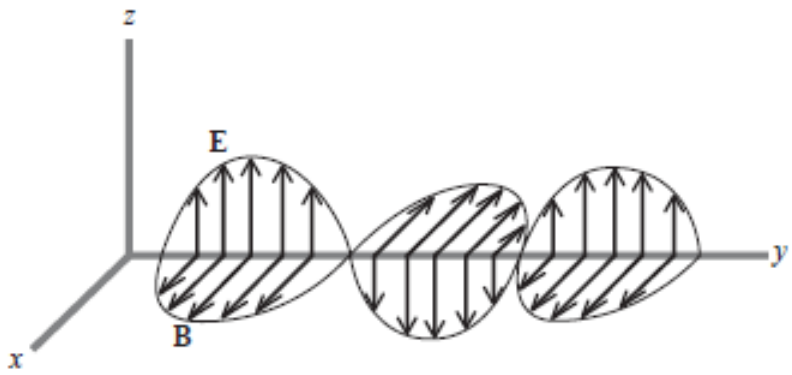
- Tells about the quality of the matter being investigated.
- Tells about the quantitative aspects of the matter under study.
- Finding about the reaction pathway and dynamics of the reaction.
- Investigation of short lived species generated during any reaction.

Interaction of light with matter

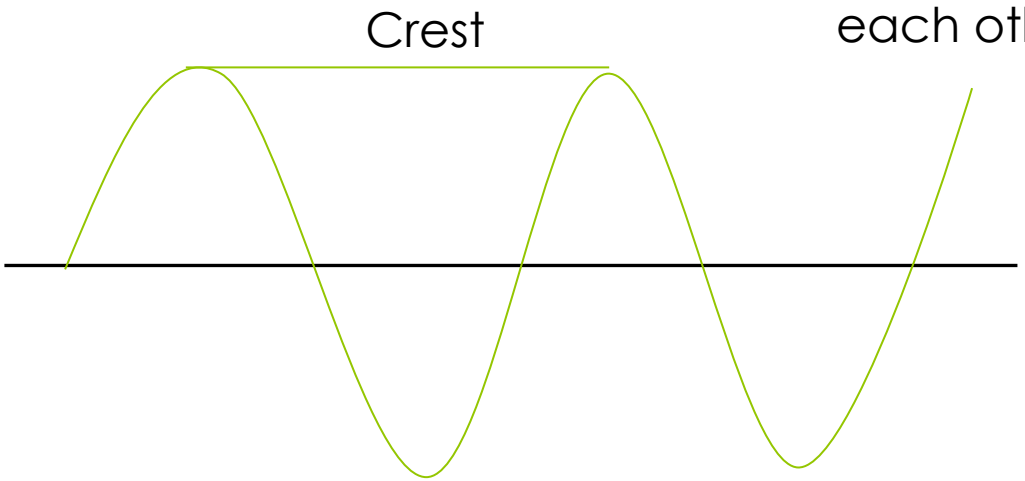


A The first process is spectroscopic data measurement

B The second one shows the molecules being excited after the irradiation and is part of photochemistry



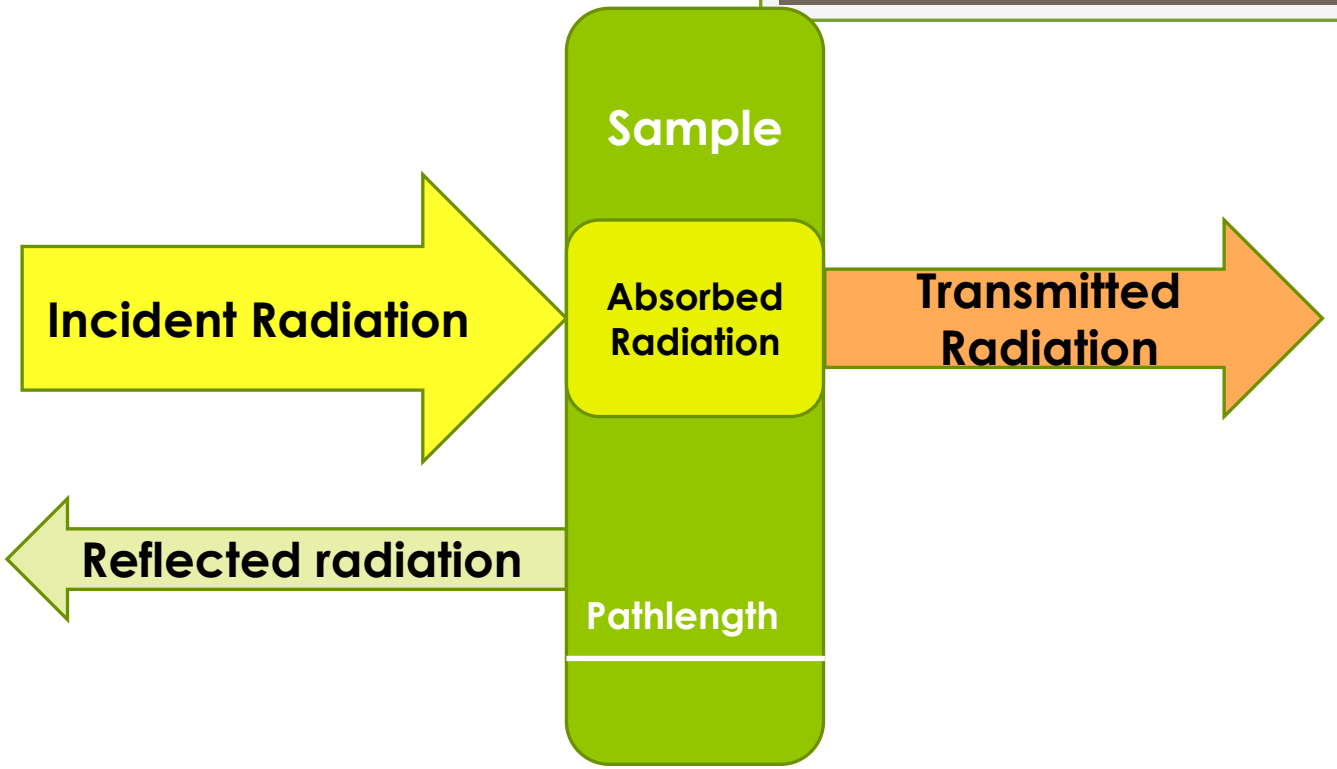
A graphical representation of how an electromagnetic radiation travels. Both electric and magnetic components are perpendicular to each other.

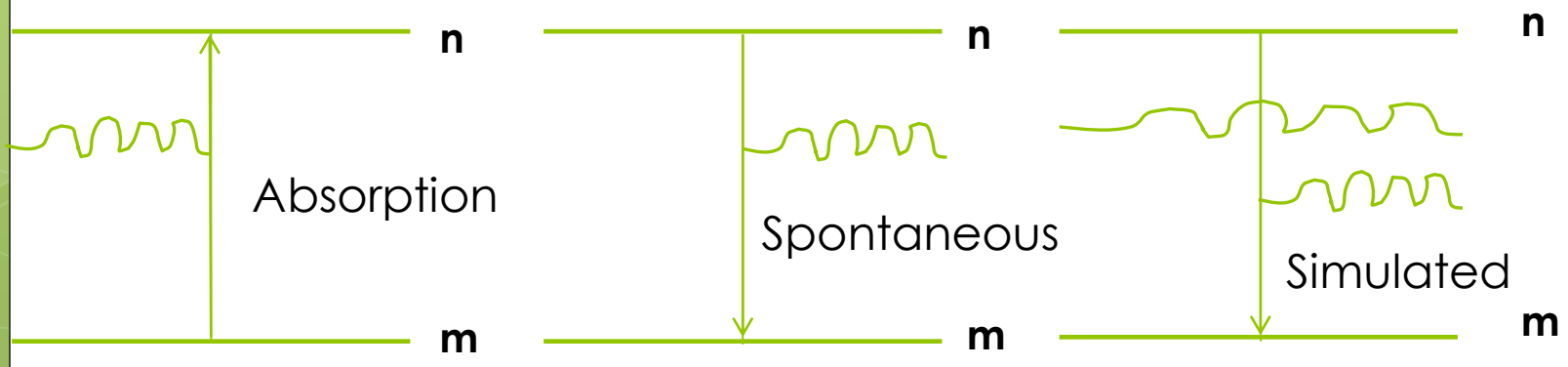


The distance between two crests is known as wavelength. One cycle is the number of waves lying between two successive crests. The frequency v of the wave is the number of cycles passing a given point per unit time.

The unit of wavelength λ is 'm' and that of frequency is hertz (H).

$E = hc/\lambda = h\nu$ where c is the velocity of light and h is Planck's Constant.


Sample
Incident Radiation
Absorbed Radiation
Transmitted Radiation
Reflected radiation
Pathlength


n
m
Absorption
n
m
Spontaneous
n
m
Simulated

When a set of frequencies is absorbed by a system the resultant spectrum is called **absorption spectrum** and the emitted frequency is known as **emission spectrum**. These emission spectra can either be a **line spectrum** which contains only discrete frequencies or a **continuous spectrum** which contains a continuous range of frequencies. Heated solids mostly give continuous spectrum and gases that are not but not at high pressure give line spectrum.

Any molecule which is in the stationary state *m* is exposed to an electromagnetic radiation, it may **absorb** a photon of frequency n and make a transition to a higher-energy state *n*. When the radiation's frequency satisfies the equation:

$$E_n - E_m = h\upsilon$$

Any molecule which is in stationary state *n (that is of higher* energy) in the absence of radiation can spontaneously go to a lower stationary state *m* with the emission of a photon with frequency:

$$E_n - E_m = h\upsilon$$

Such an emission is termed as **spontaneous emission** of radiation

When a molecule is exposed to electromagnetic radiation in the higher energy state n in such a way that its frequency satisfies the equation:

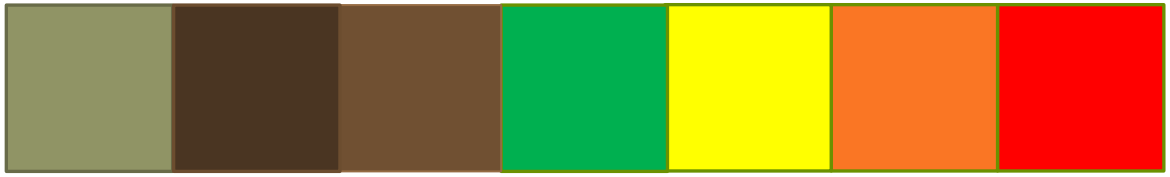
$$E_n - E_m = h\upsilon$$

There is an increase in the probability that this particular molecule undergoes a transition to the lower state m with emission of a photon of frequency υ.Such Emission which occurs due to the exposure to electromagnetic radiation is called stimulated emission

Electronic spectroscopy

- It is the earliest method of modern spectroscopy.
- The molecules interacts with the ultraviolet and visible radiation wavelengths of light.
- The bonded or non-bonding electrons in the molecules absorb the radiation and move fro ground state to the excited state.

UV Region



IR Region

- The range between 200-900 nm corresponds to UV-vis region of the wavelength.
- In common spectroscopy methods 200-400 nm is mainly applicable for UV measurements and 400-900 mainly falls for visible measurements.

Internal energy of the molecules

- $E_{total} = E_{trans} + E_{elec} + E_{vib} + E_{rot} + E_{nucl}$

Translational | Electronic | Vibrational | Rotational | Nuclear

UV/Visible | Infra Red | Microwave | Radiowave

Ultraviolet: 190~400nm

Violet: 400 - 420 nm

Indigo: 420 - 440 nm

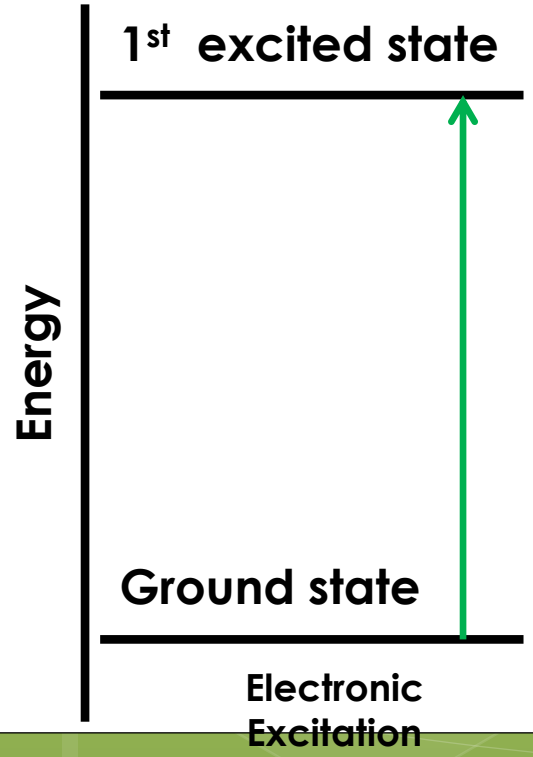
Blue: 440 - 490 nm

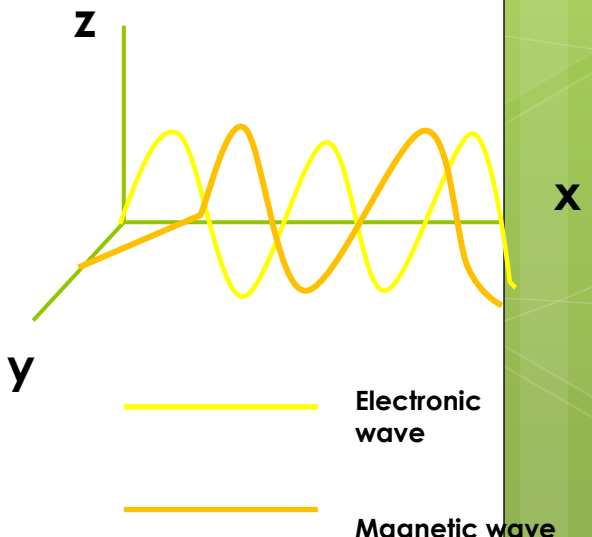
Green: 490 - 570 nm

Yellow: 570 - 585 nm

Orange: 585 - 620 nm

Red: 620 - 780 nm





- The Light waves consist of perpendicular, oscillating electric and magnetic fields " Electro- magnetic waves" and described by

- Amplitude (A)
- Frequency (ν)
- Wavelength (λ)

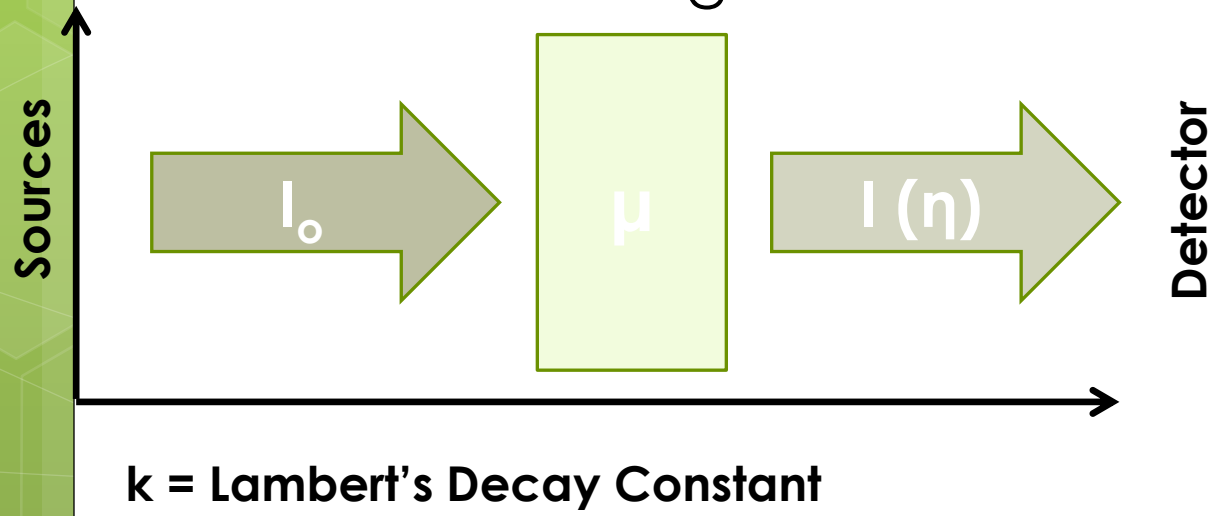
$$E = hc/\lambda = h\nu$$

- Transitions in a molecules is followed by decrease in wavelength with subsequent increases of frequency of molecular dynamics.
- For the light the freq. increases, energy increases and wavelength decreases.

Lambert's law of absorption

- Lambert described the change in the intensity with distance in an absorbing medium.
- According to him, the intensity (I_0) of light beam decreases exponentially as it passes though a uniform absorbing medium.

$I(\eta) = I e^{-\mu\eta}$



$$\frac{I}{I_0} = 10^{-k\eta}$$

k = Lambert's Decay Constant

$$k = \mu \ln 10$$

Beer's Law

- According to Beer: Lambert's decay constant k for the solution for the absorbing substance is linearly related to the concentration c by a constant ξ, known as absorptivity coeffecient, which is characteristic of an absorbing substance. The decay constant can be related to concentration as k= ξc.

The combination of both the laws gives us the equation:

A= ξc*l* ***where*** **ξ is the extinction coefficient; c is the concentration and *l* is the pathlength of the media through which light is passed.**