UV / VISIBLE SPECTROSCOPY

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Spectroscopy

- It is the branch of science that deals with the study of interaction of matter with light.

OR

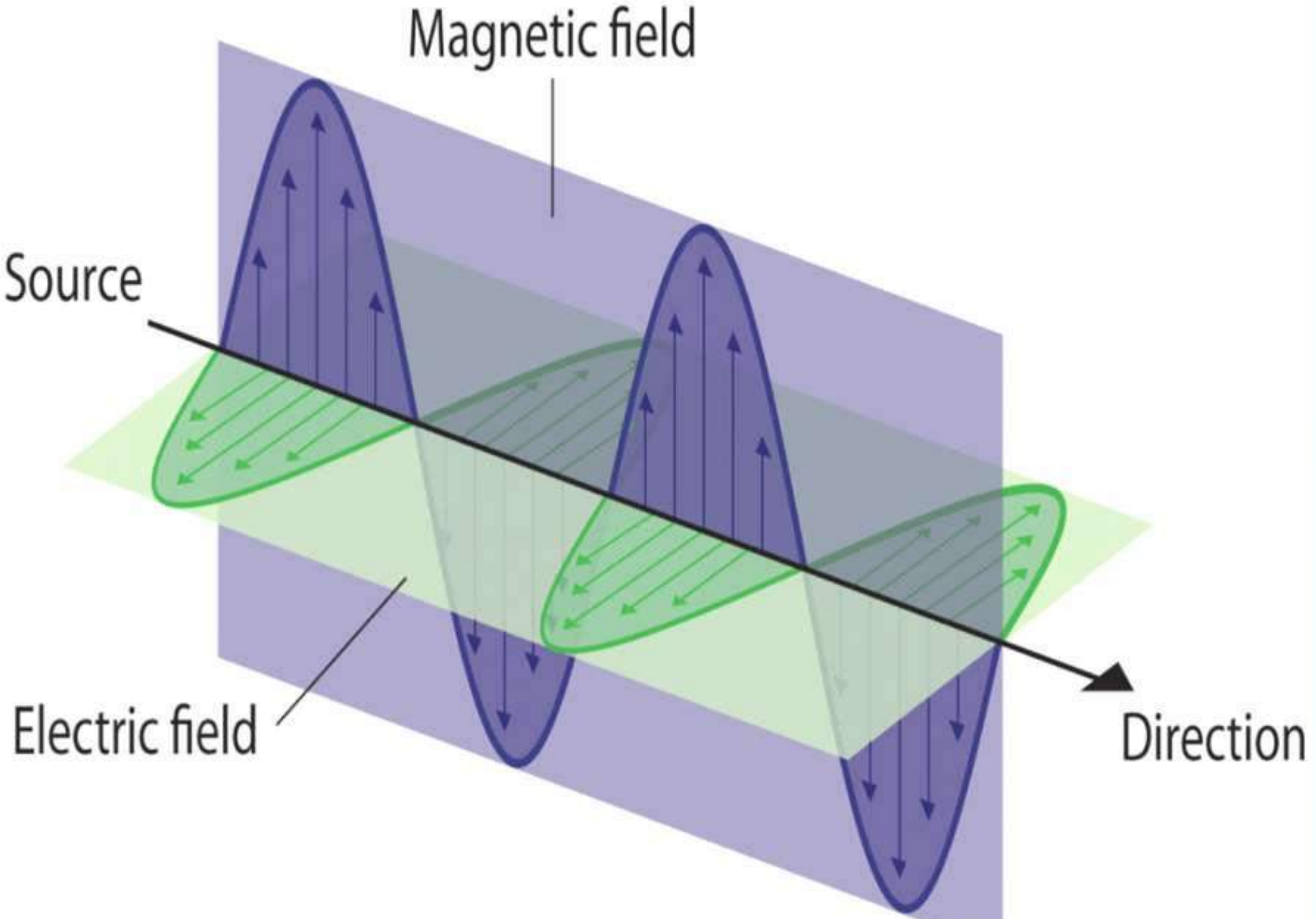
- It is the branch of science that deals with the study of interaction of electromagnetic radiation with matter.

Electromagnetic Radiation

Electromagnetic Radiation

- Electromagnetic radiation consist of discrete packages of energy which are called as photons.

- A photon consists of an oscillating electric field (E) & an oscillating magnetic field (M) which are perpendicular to each other.


Magnetic field
Source
Electric field
Direction

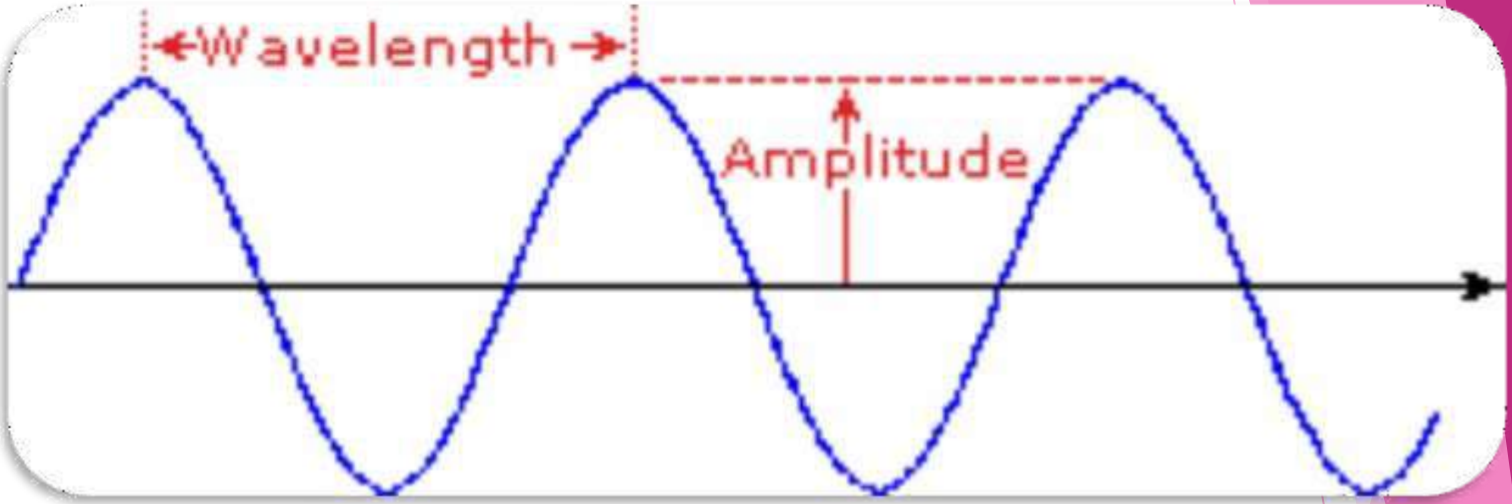
Electromagnetic Radiation

- Frequency (ν):
  - It is defined as the number of times electrical field radiation oscillates in one second.
  - The unit for frequency is Hertz (Hz).

1 Hz = 1 cycle per second

- Wavelength (λ):
  - It is the distance between two nearest parts of the wave in the same phase i.e. distance between two nearest crest or troughs.

Electromagnetic Radiation



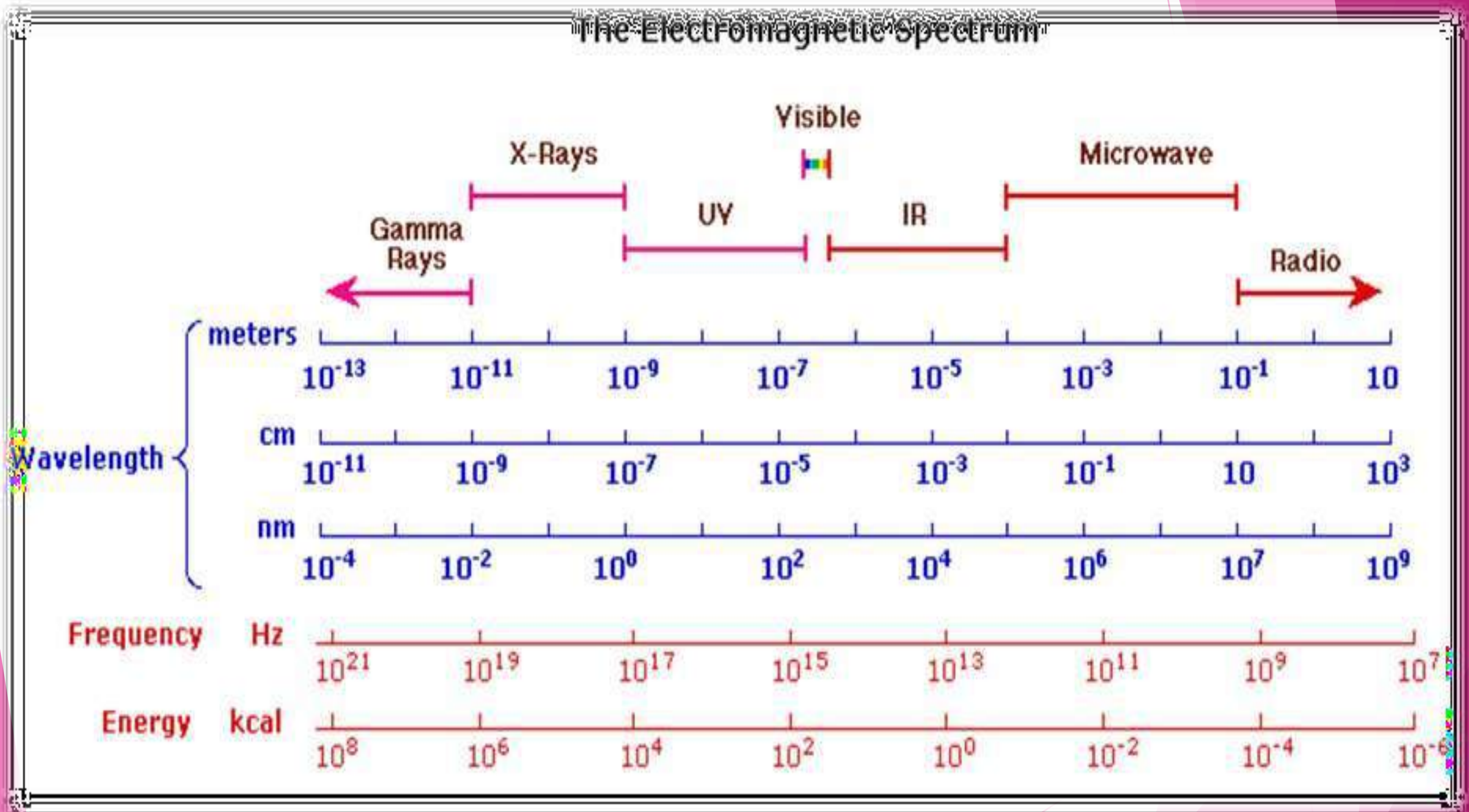
- The relationship between wavelength & frequency can be written as:

$$c = \nu \lambda$$

- As photon is subjected to energy, so

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

Electromagnetic Radiation



Principles of Spectroscopy

Principles of Spectroscopy

- The principle is based on the measurement of spectrum of a sample containing atoms / molecules.

- Spectrum is a graph of intensity of absorbed or emitted radiation by sample verses frequency (ν) or wavelength (λ).

Principles of Spectroscopy

1. Absorption Spectroscopy:

- An analytical technique which concerns with the measurement of absorption of electromagnetic radiation.

- e.g. UV (185 - 400 nm) / Visible (400 - 800 nm) Spectroscopy, IR Spectroscopy (0.76 - 15 μm)

Interaction of EMR with Matter

Interaction of EMR with matter

1. Electronic Energy Levels:

- At room temperature the molecules are in the lowest energy levels E_0.

- When the molecules absorb UV-visible light from EMR, one of the outermost bond / lone pair electron is promoted to higher energy state such as E_1, E_2, …E_n, etc is called as electronic transition and the difference is as:

$\Delta E = h\nu = E_n - E_0$ where ($n = 1, 2, 3, \ldots$ etc)

ΔE = 35 to 71 kcal/mole

Interaction of EMR with matter

2. Vibrational Energy Levels:

- These are small energy level than electronic energy levels.

- The spacing between energy levels are relatively small i.e. 0.01 to 10 kcal/mole.

- e.g. when IR radiation is absorbed, molecules are excited from one vibrational level to another or it vibrates with higher amplitude.

Interaction of EMR with matter

3. Rotational Energy Levels:

- These energy levels are quantized & discrete.
- The spacing between energy levels are even smaller than vibrational energy levels.

$$\Delta E_{\text{rotational}} < \Delta E_{\text{vibrational}} < \Delta E_{\text{electronic}}$$

Lambert's Law

Lambert's Law

- When a monochromatic radiation is passed through a solution, the decrease in the intensity of radiation with thickness of the solution is directly proportional to the intensity of the incident light.

- Let I be the intensity of incident radiation.

  x be the thickness of the solution.

  Then

Lambert’s Law

$$-\frac{dI}{dx} \alpha I$$

So, $$-\frac{dI}{dx} = KI$$

- Integrate equation between limit
  - I = Io at x = 0 and I = I at x=l,
- We get,

$$\ln \frac{I}{I_0} = -Kl$$

Lambert’s Law

$$2.303 \log \frac{I}{I_0} = -Kl$$

$$\log \frac{I}{I_0} = -\frac{K}{2.303} l$$

Where, $\log \frac{I_0}{I} = A$ Absorbance

$\frac{K}{2.303} = E$ Absorption coefficient

$A = E.l$ Lambert’s Law

Beer’s Law

Beer’s Law

- When a monochromatic radiation is passed through a solution, the decrease in the intensity of radiation with thickness of the solution is directly proportional to the the intensity of incident light as well as concentration of the solution
- Let I be the intensity of incident radiation.

  x be the thickness of the solution.

  C be the concentration of the solution.

  Then

Beer’s Law

$$-\frac{dI}{dx} \alpha\, C.I$$

- $$-\frac{dI}{dx} = K'C.I$$
- So,
- Integrate equation between limit
  - I = Io at x = 0 and
    I = I at x=l,
- We get,

$$\ln \frac{I}{I_0} = -K'C.l$$

Beer's Law

$$2.303 \log \frac{I_0}{I} = K.C.l$$

$$\log \frac{I_0}{I} = \frac{K}{2.303} C.l$$

Where, $\log \frac{I_0}{I} = A$ Absorbance

$\frac{K}{2.303} = E$ Molar extinction coefficient

$A = E.C.l$ Beer's Law

Beer’s Law

$$A = E.C.l$$

$$T = \frac{I}{I_0} \quad \text{OR} \quad -\log T = \log \frac{I}{I_0} = A$$

From the equation it is seen that the absorbance which is also called as optical density (OD) of a solution in a container of fixed path length is directly proportional to the concentration of a solution.

PRINCIPLES OF UV - VISIBLE SPECTROSCOPY

Principle

- The UV radiation region extends from 10 nm to 400 nm and the visible radiation region extends from 400 nm to 800 nm.

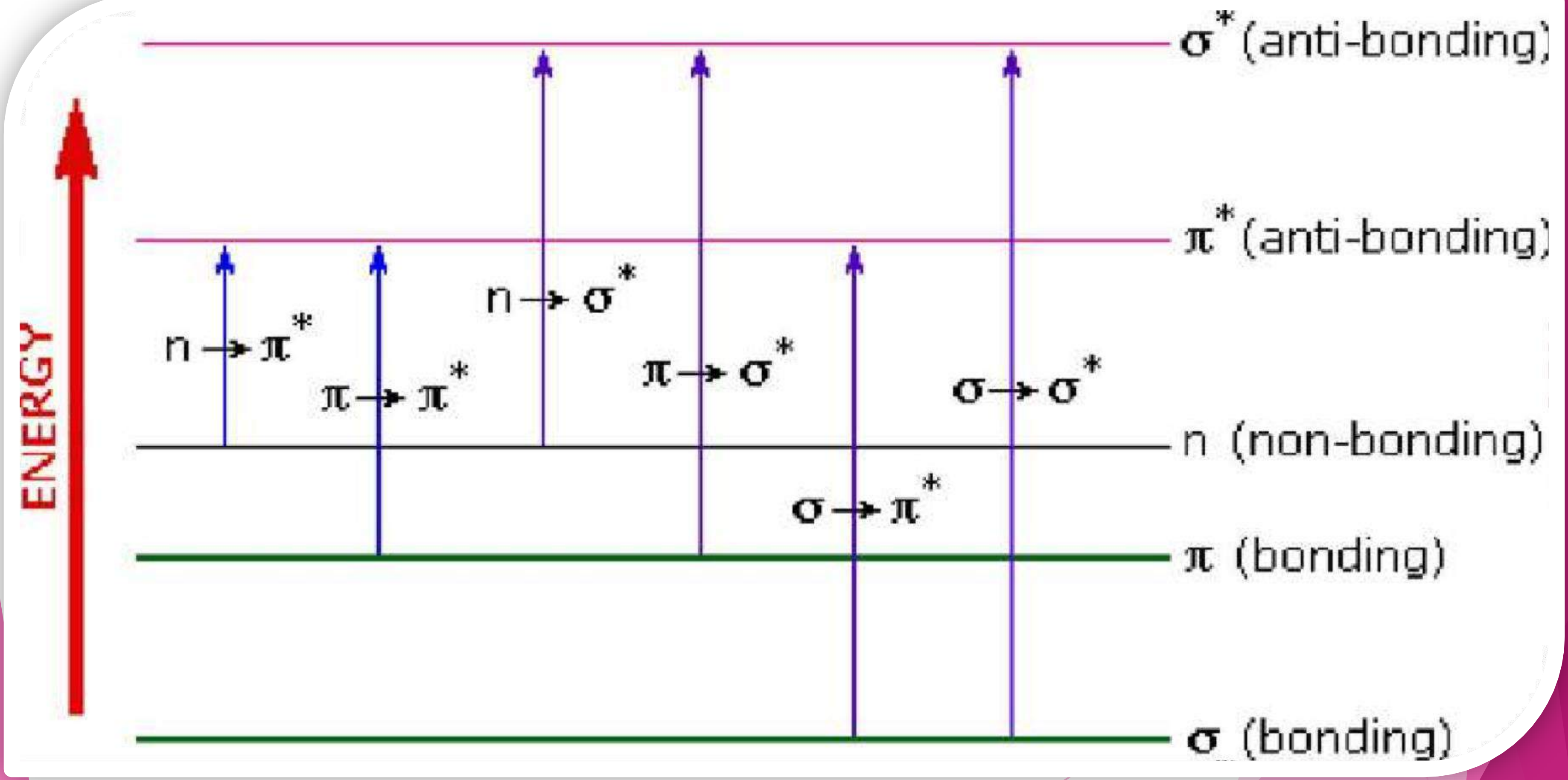
  Near UV Region: 200 nm to 400 nm

  Far UV Region: below 200 nm

- Far UV spectroscopy is studied under vacuum condition.
- The common solvent used for preparing sample to be analyzed is either ethyl alcohol or hexane.

Electronic Transitions

The possible electronic transitions can graphically shown as:



The possible electronic transitions are

1. $\sigma \rightarrow \sigma^*$ transition
2. $\pi \rightarrow \pi^*$ transition
3. $n \rightarrow \sigma^*$ transition
4. $n \rightarrow \pi^*$ transition
5. $\sigma \rightarrow \pi^*$ transition
6. $\pi \rightarrow \sigma^*$ transition

1

• σ → σ* transition

- σ electron from orbital is excited to corresponding anti-bonding orbital σ*.

- The energy required is large for this transition.

- e.g. Methane (CH_4) has C-H bond only and can undergo σ → σ* transition and shows absorbance maxima at 125 nm.

2

• $\pi \longrightarrow \pi^*$ transition

- π electron in a bonding orbital is excited to corresponding anti-bonding orbital π*.
- Compounds containing multiple bonds like alkenes, alkynes, carbonyl, nitriles, aromatic compounds, etc undergo π → π* transitions.
- e.g. Alkenes generally absorb in the region 170 to 205 nm.

3

$n \rightarrow \sigma^*$ transition

- Saturated compounds containing atoms with lone pair of electrons like O, N, S and halogens are capable of $n \rightarrow \sigma^*$ transition.

- These transitions usually requires less energy than $\sigma \rightarrow \sigma^*$ transitions.

- The number of organic functional groups with $n \rightarrow \sigma^*$ peaks in UV region is small (150 – 250 nm).

4

• n → π* transition

- An electron from non-bonding orbital is promoted to anti-bonding π* orbital.

- Compounds containing double bond involving hetero atoms (C=O, C≡N, N=O) undergo such transitions.

- n → π* transitions require minimum energy and show absorption at longer wavelength around 300 nm.

5

- σ → π* transition

&

- π → σ* transition

6

- These electronic transitions are forbidden transitions & are only theoretically possible.

- Thus, n → π* & π → π* electronic transitions show absorption in region above 200 nm which is accessible to UV-visible spectrophotometer.

- The UV spectrum is of only a few broad of absorption.

Terms used in UV / Visible Spectroscopy

Chromophore

The part of a molecule responsible for imparting color, are called as chromospheres.

OR

The functional groups containing multiple bonds capable of absorbing radiations above 200 nm due to n → π* & π → π* transitions.

e.g. NO_2, N=O, C=O, C=N, C≡N, C=C, C=S, etc

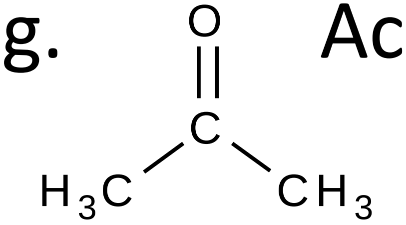
Chromophore

To interpretate UV – visible spectrum following points should be noted:

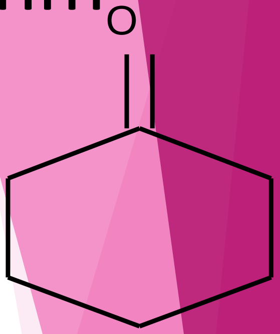
1. Non-conjugated alkenes show an intense absorption below 200 nm & are therefore inaccessible to UV spectrophotometer.
2. Non-conjugated carbonyl group compound give a weak absorption band in the 200 - 300 nm region.

Chromophore

e.g. Acetone which has λ_{max} = 279 nm



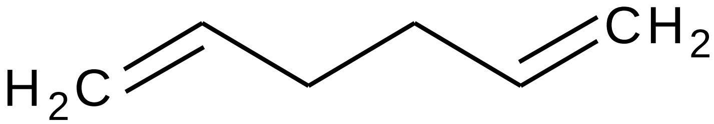
and that cyclohexane has λ_{max} = 291 nm.

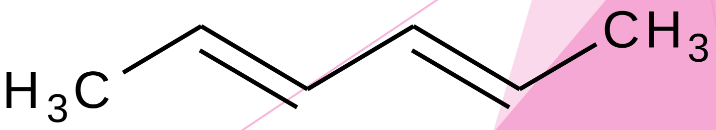


When double bonds are conjugated in a compound λ_{max} is shifted to longer wavelength.

e.g. 1,5 - hexadiene has λ_{max} = 178 nm

2,4 - hexadiene has λ_{max} = 227 nm





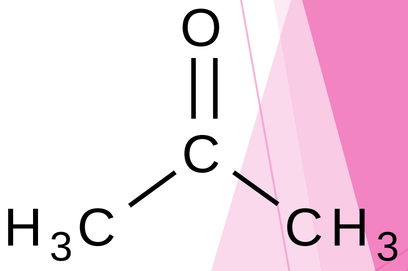
Chromophore

3. Conjugation of C=C and carbonyl group shifts the λ_{max} of both groups to longer wavelength.

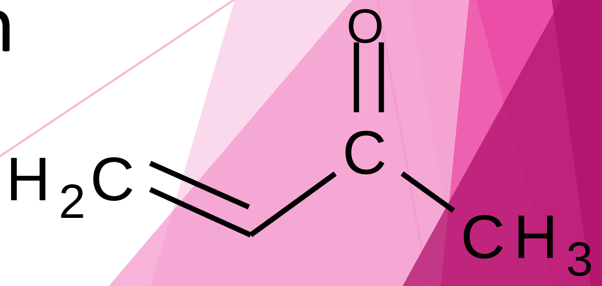
e.g. Ethylene has λ_{max} = 171 nm

$H_2C{=}CH_2$

Acetone has λ_{max} = 279 nm



Crotonaldehyde has λ_{max} = 290 nm



Auxochrome

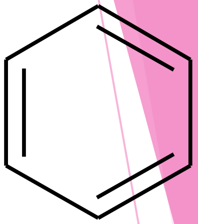
The functional groups attached to a chromophore which modifies the ability of the chromophore to absorb light , altering the wavelength or intensity of absorption.

OR

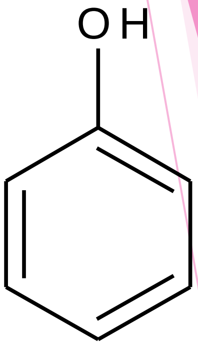
The functional group with non-bonding electrons that does not absorb radiation in near UV region but when attached to a chromophore alters the wavelength & intensity of absorption.

Auxochrome

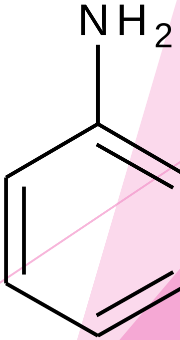
e.g. Benzene λ_{max} = 255 nm



Phenol λ_{max} = 270 nm



Aniline λ_{max} = 280 nm



Absorption & Intensity Shifts

1. Bathochromic Shift (Red Shift)
2. Hypsochromic Shift (Blue Shift)
3. Hyperchromic Effect
4. Hypochromic Effect

1

• Bathochromic Shift (Red Shift)

- When absorption maxima (λ_{max}) of a compound shifts to longer wavelength, it is known as bathochromic shift or red shift.

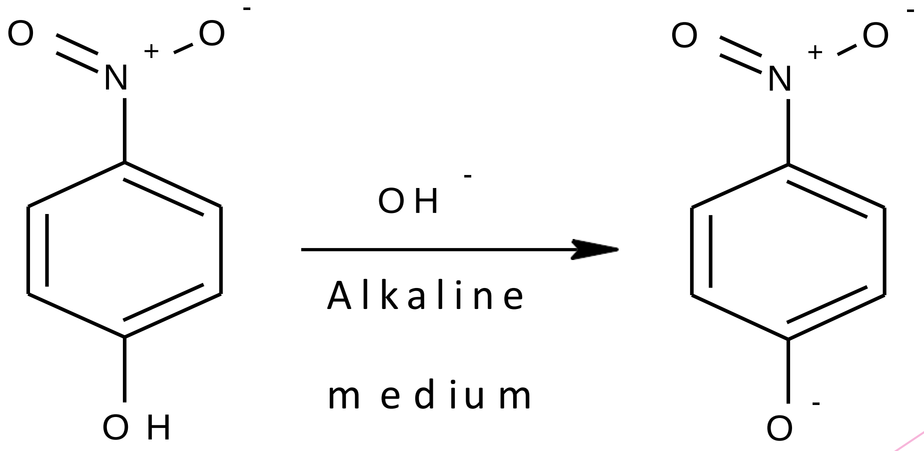
- The effect is due to presence of an auxochrome or by the change of solvent.

- e.g. An auxochrome group like $-OH$, $-OCH_3$ causes absorption of compound at longer wavelength.

1

• Bathochromic Shift (Red Shift)

- In alkaline medium, p-nitrophenol shows red shift. Because negatively charged oxygen delocalizes more effectively than the unshared pair of electron.



p-nitrophenol

λ_{max} = 255 nm λ_{max} = 265 nm

2

• Hypsochromic Shift (Blue Shift)

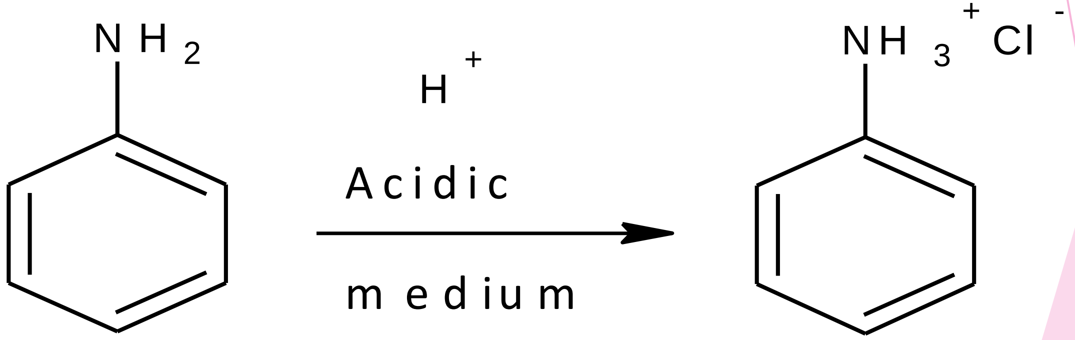
- When absorption maxima (λ_{max}) of a compound shifts to shorter wavelength, it is known as hypsochromic shift or blue shift.

- The effect is due to presence of an group causes removal of conjugation or by the change of solvent.

2

• Hypsochromic Shift (Blue Shift)

- Aniline shows blue shift in acidic medium, it loses conjugation.



Aniline

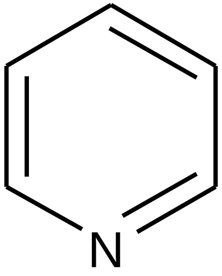
λ_{max} = 280 nm

λ_{max} = 265 nm

3

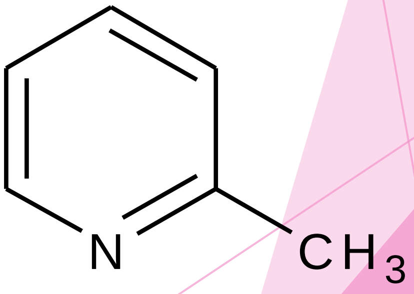
• Hyperchromic Effect

- When absorption intensity (ε) of a compound is increased, it is known as hyperchromic shift.
- If auxochrome introduces to the compound, the intensity of absorption increases.



Pyridine

λ_{max} = 257 nm



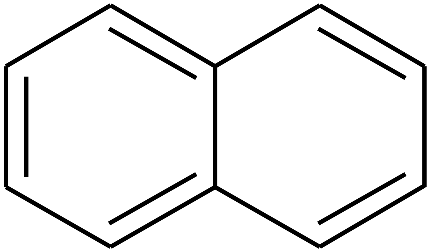
2-methyl pyridine

λ_{max} = 260 nm

4

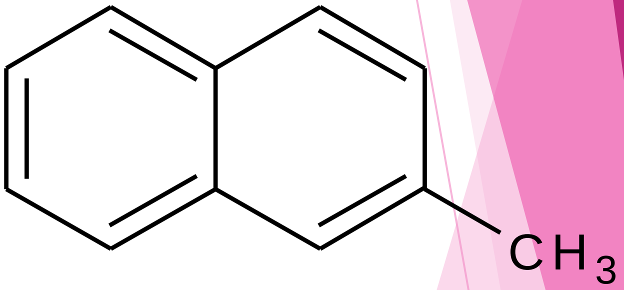
• Hypochromic Effect

- When absorption intensity (ε) of a compound is decreased, it is known as hypochromic shift.



Naphthalene

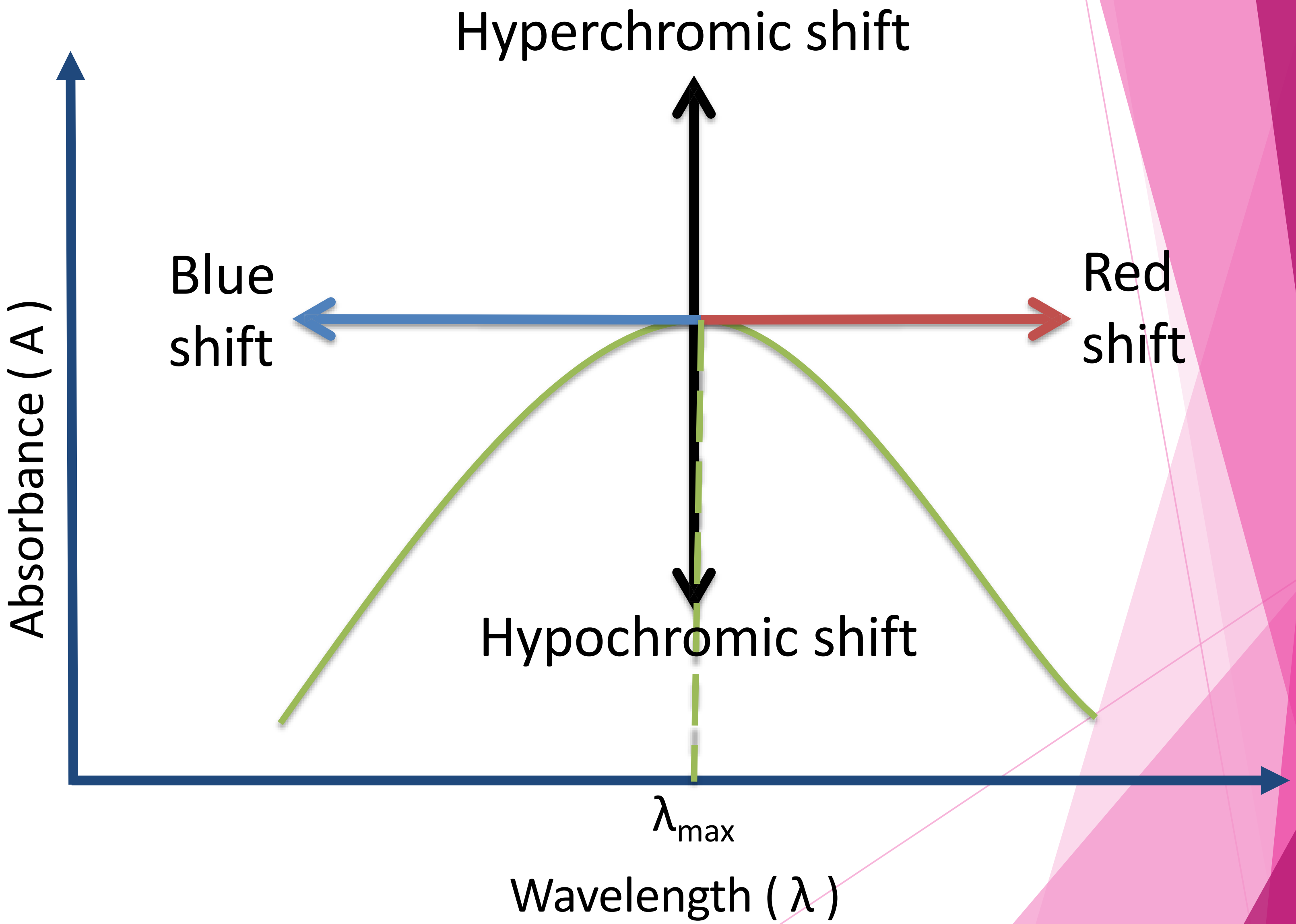
ε = 19000



2-methyl naphthalene

ε = 10250

Shifts and Effects



Hyperchromic shift

Blue shift

Red shift

Hypochromic shift

Absorbance (A)

λ_{max}

Wavelength (λ)

APPLICATIONS OF UV / VISIBLE SPECTROSCOPY

Applications

- Qualitative & Quantitative Analysis:
  - It is used for characterizing aromatic compounds and conjugated olefins.
  - It can be used to find out molar concentration of the solute under study.
- Detection of impurities:
  - It is one of the important method to detect impurities in organic solvents.
- Detection of isomers are possible.
- Determination of molecular weight using Beer's law.

Reference Books

- Introduction to Spectroscopy
  - – Donald A. Pavia
- Elementary Organic Spectroscopy
  - – Y. R. Sharma
- Physical Chemistry
  - – Puri, Sharma & Pathaniya