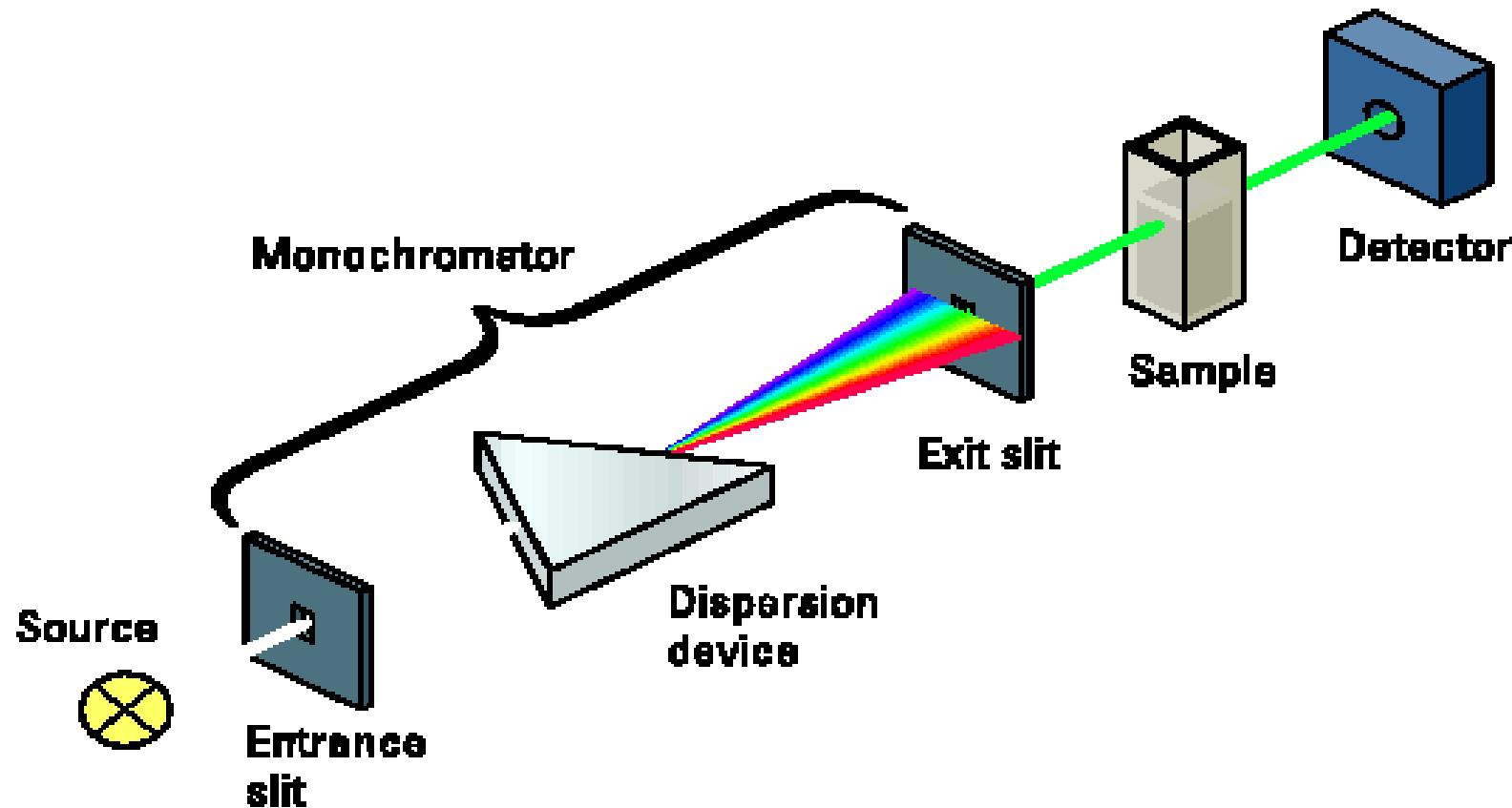


Lecture 3 - UV-Visible Spectroscopy (Instrumentation and Applications)

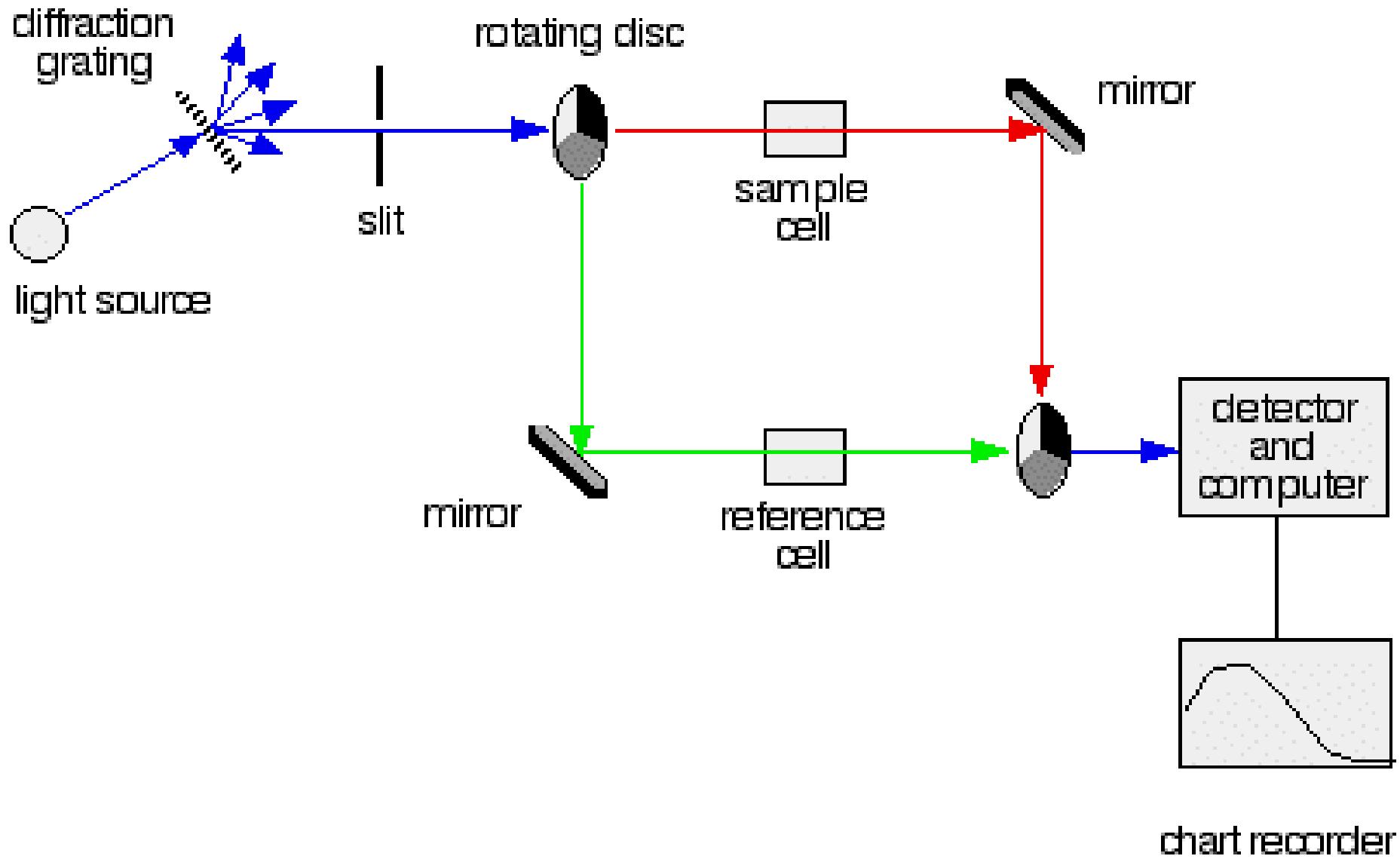


Instrumentation in UV-Visible Spectrophotometer

Schematic of a single-beam spectrophotometer



Double beam Spectrophotometer



Source of radiation: Required range of wavelength for UV-VIS is 300-700nm for this purpose, **tungsten filament lamp** used. For 200-400nm range, Quartz Hydrogen lamp is used

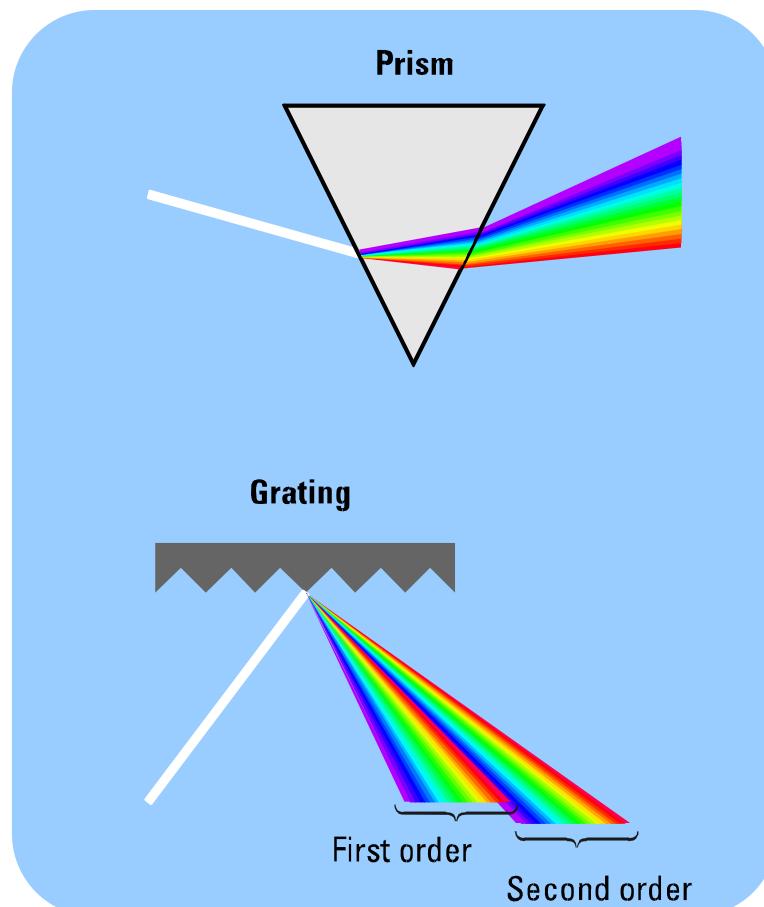
Monochromator: A monochromator consists of entrance slit, collimator, a grating or prism, exit slit. Should provide narrow range of wavelength, quartz prisms are used for this purpose.

- Non-linear dispersion
- Temperature sensitive

Gratings of two types

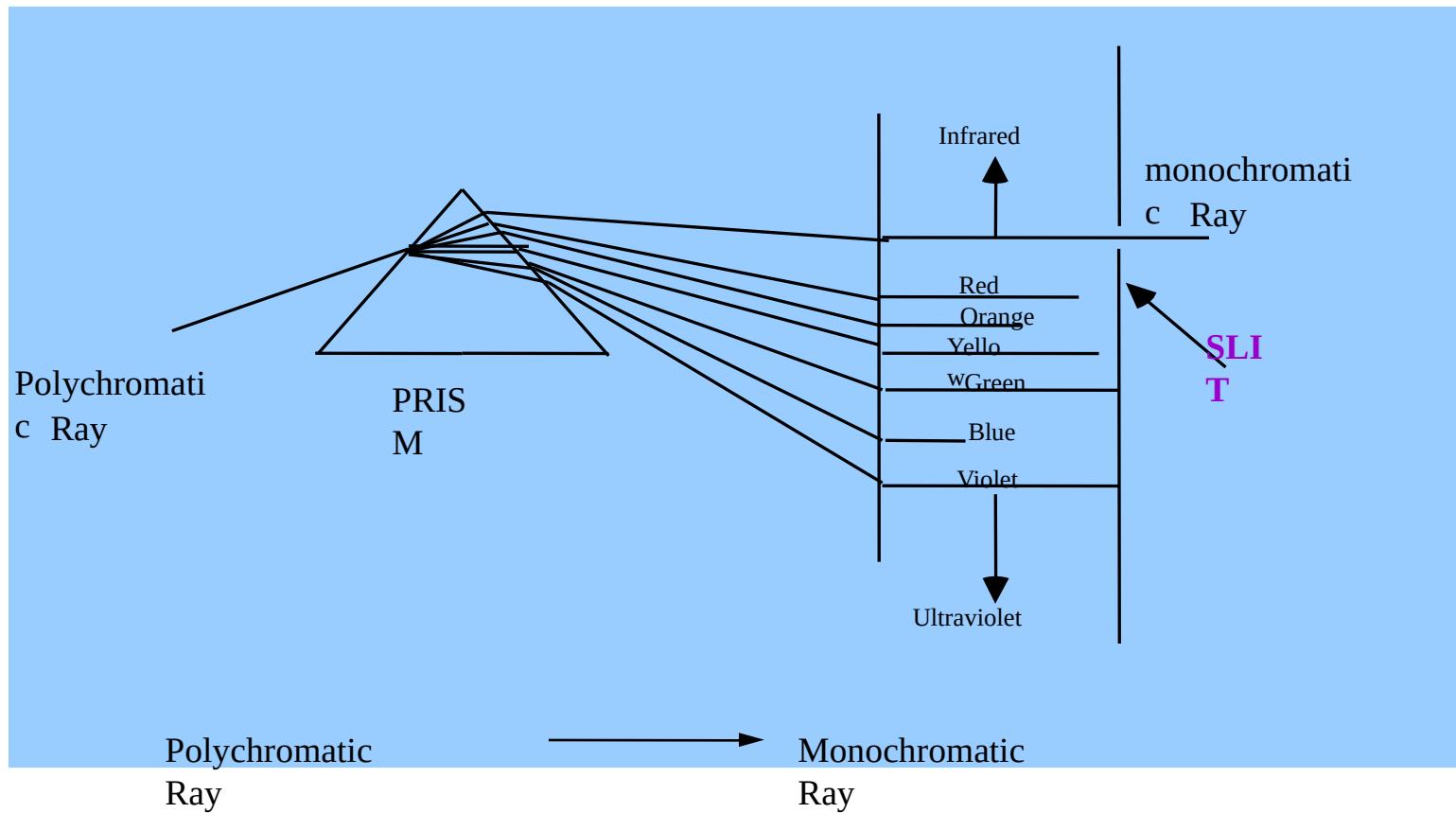
- Transmission grating
- Reflection grating

Suitable grating for UBVVIS
is **2500-5000nm**



3. Slit: The slits are used for selecting the desired wavelength from dispersed light

by the monochromator. An entrance slit and exit slit are placed on the opposite sides of the prism or grating.



4. Sample Holder: There is a special glass tube cell called cuvette which does not absorb the light from UV-visible spectrum. Quartz glass cuvettes are used for this purpose in 200-300 nm, fused glass for 300-2500nm work

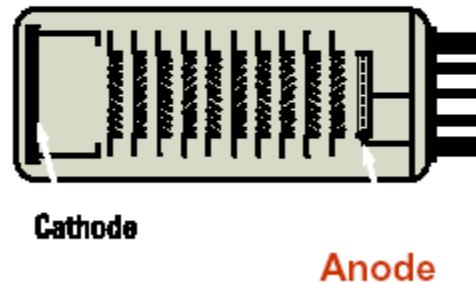


5. Detectors: A detector is a transductor that converts electromagnetic radiation into electron flow and the current produced thereby. The photocurrent is amplified if necessary. Then there is a recorder or digital display device. Various detectors like phototube used for very high sensitivity.

Phototube: Consists of evacuated bulb having in it a half cylindrical metal cathode. The inner surface of this cathode is of **oxides of Cs and Ag**. When radiation falls upon

Cathode, electrons are emitted and collected by anode. This generates current may be amplified and is

- High sensitivity at low light levels
- Cathode material determines spectral sensitivity
- Good signal/noise
- Shock sensitive



5. Amplifiers and recorder:

Signal received from detector is amplified and read on recorder.

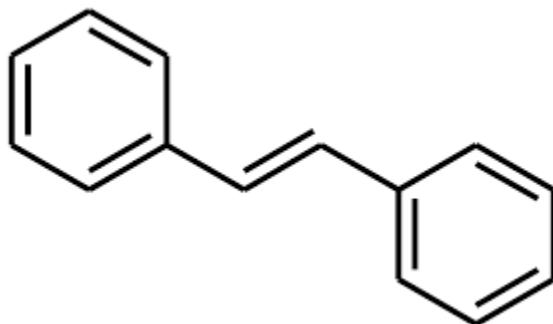
Recorder can record output either as absorption spectra or digital values as absorbance

Applications of UV-Visible Spectroscopy

1.Qualitative analysis of organic compounds: spectra of unknown compound is measured with spectrum of known compound and thus identified.

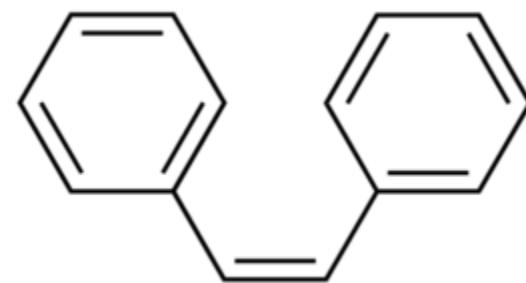
- a) Detection of functional group:** Presence of conjugation, carbonyl group or aromatic ring can be confirmed if λ_{max} above 200nm is observed.
- b) Extent of conjugation:** if number of double bond in conjugation increases, also λ_{max} gets shifted to longer wavelength.
- c) Distinguish between conjugated and non-conjugated double bond:** since isolated double bond has lower λ_{max} than conjugated double bonds
- d) Identification of unknown compound:** By comparing the spectrum of unknown compound with that of known compound, its identity can be confirmed.

2) Detection of Cis and trans isomers: This technique is used for distinguishing between cis and trans isomer



Trans-stilbene
 $\lambda_{\text{max}} = 295\text{nm}$

More co-planar due to
Less steric hindrance
Hence **higher λ_{max}**



Cis-stilbene
 $\lambda_{\text{max}} = 280\text{nm}$

Less co-planar due to
more steric hindrance
Hence **Lower λ_{max}**

1) Determination of molecular weight:

Molecular weight can be determined of the compound by recording absorbance. Using Beer Lambert law $A = \epsilon \cdot C \cdot l$, mol. Wt. can be determined.

4) Detection of Impurities: Additional peaks can be observed due to impurities in the UV spectrum of any compound. They can be detected by comparing UV spectrum of compound with that of standard raw material.

5). Quantitative analysis: Using Beer's law i.e Absorbance directly proportional to concentration, concentration of unknown can be calculated.

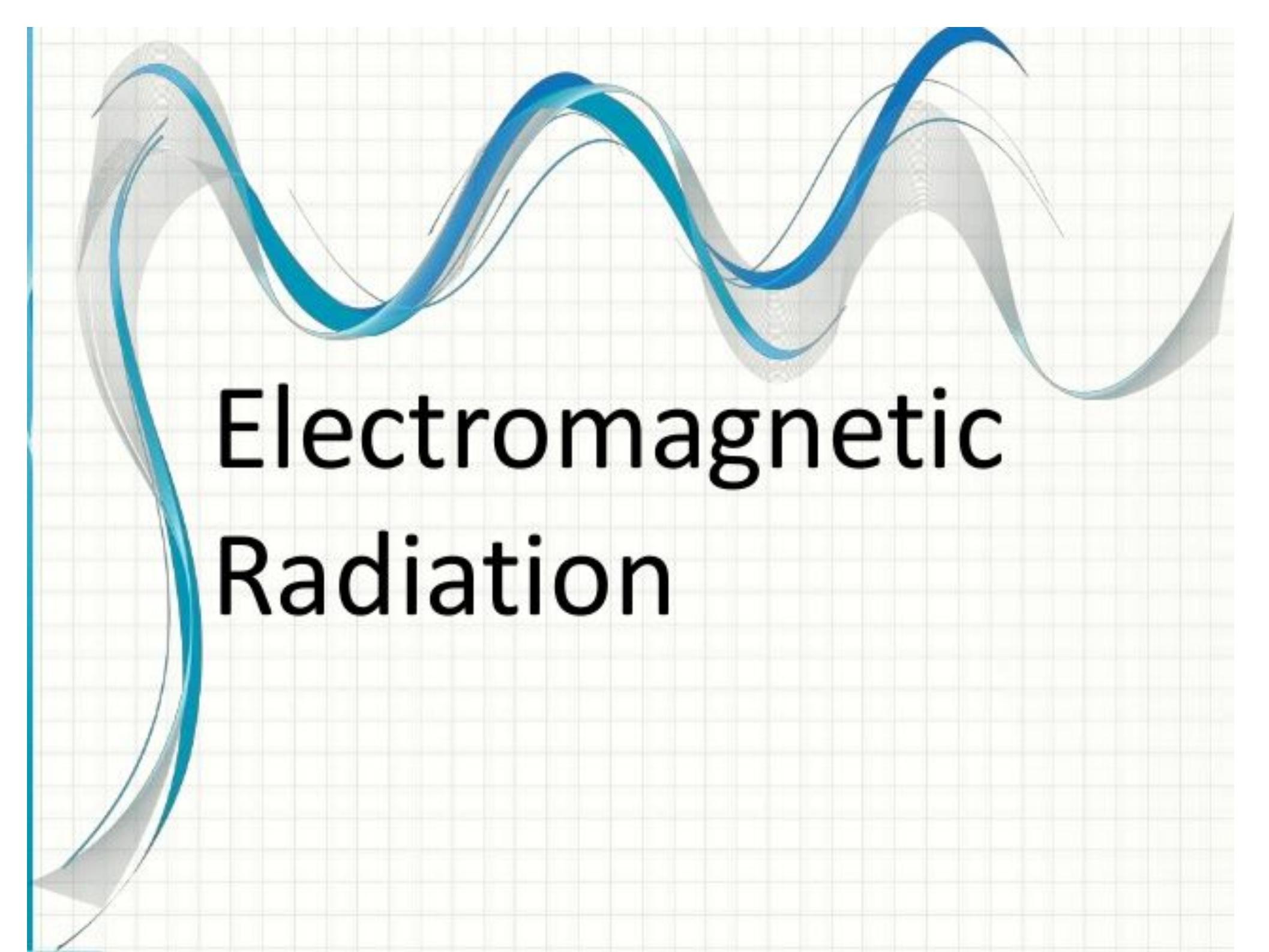
6). Chemical Kinetics: As Absorbance is directly proportion to concentration, with progress of reaction change in absorption occurs, with this rate of reaction can be determined.

Spectroscopy

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

OR

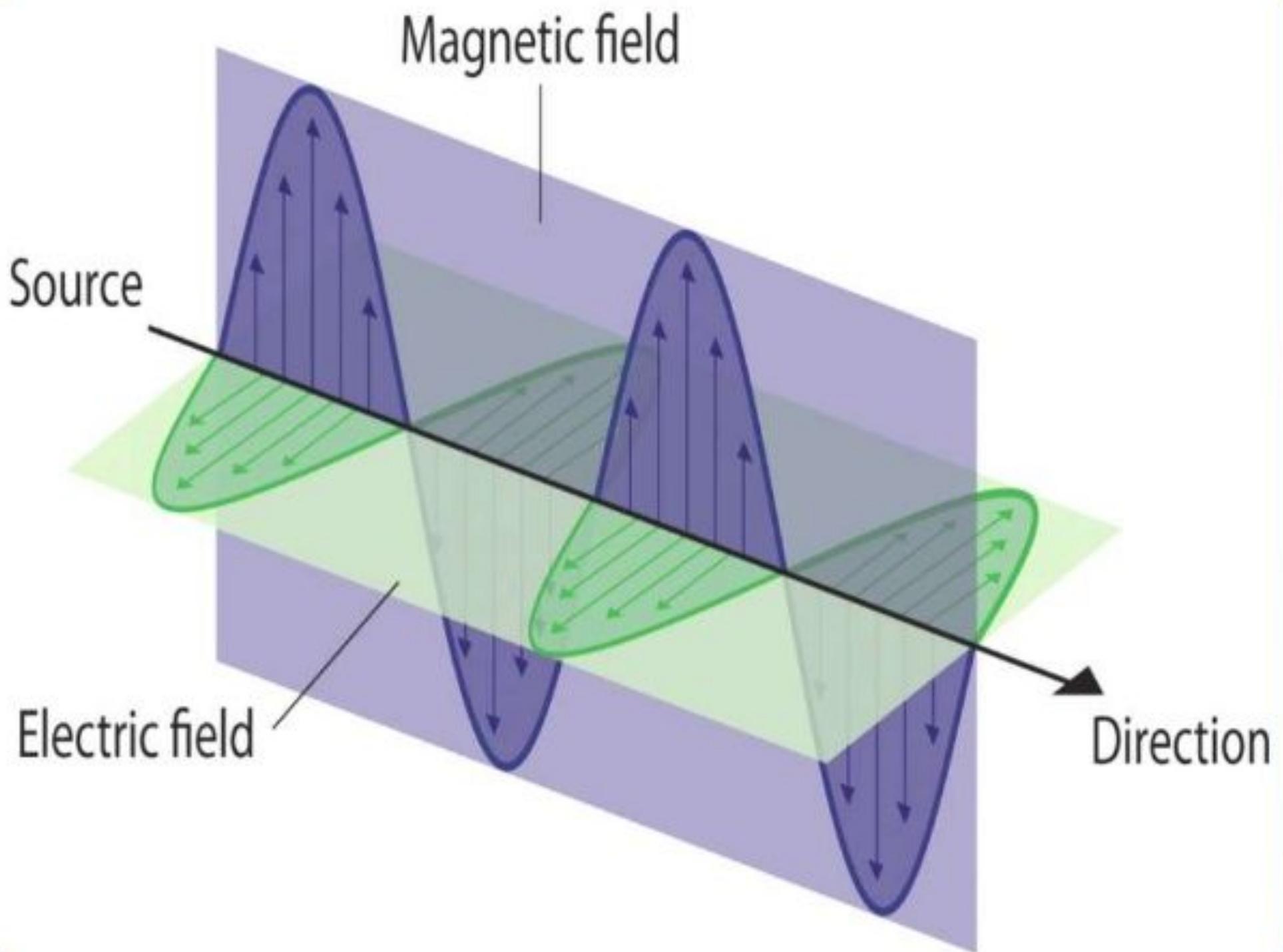
- It is the branch of science that deals with the study of interaction of electromagnetic radiation with matter.



Electromagnetic Radiation

Electromagnetic Radiation

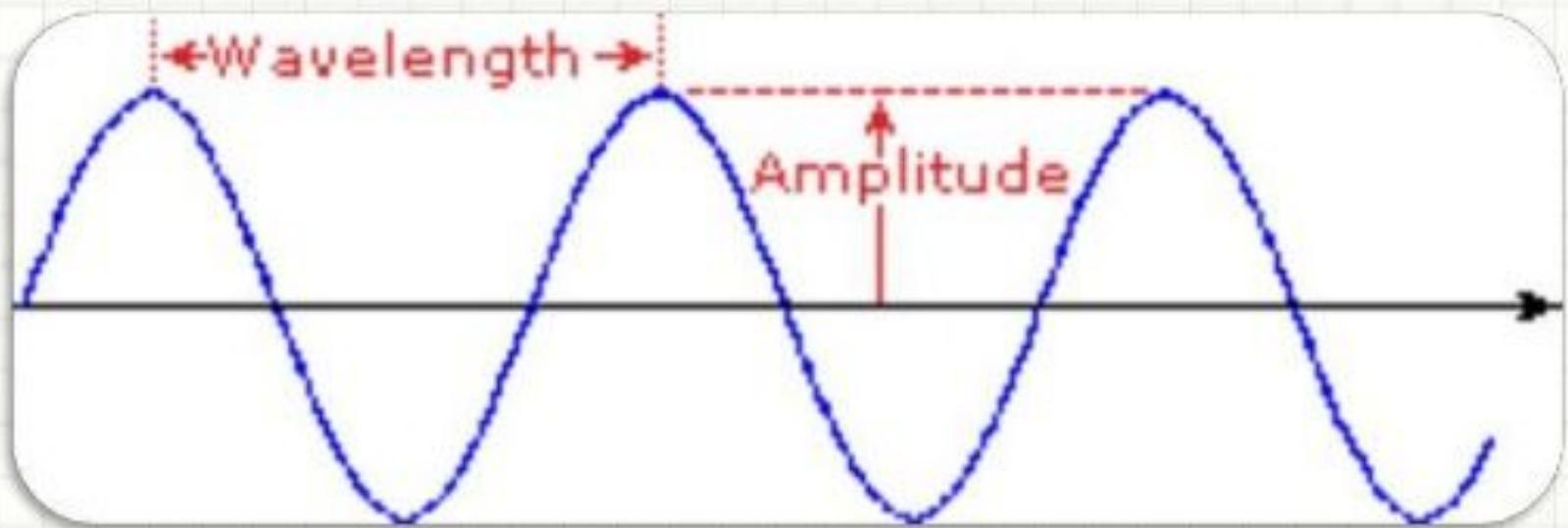
- Electromagnetic radiation consist of discrete packages of energy which are called as photons.
- A photon consists of an oscillating electric field (E) & an oscillating magnetic field (M) which are perpendicular to each other.



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).
 $1 \text{ Hz} = 1 \text{ cycle per second}$
- 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:

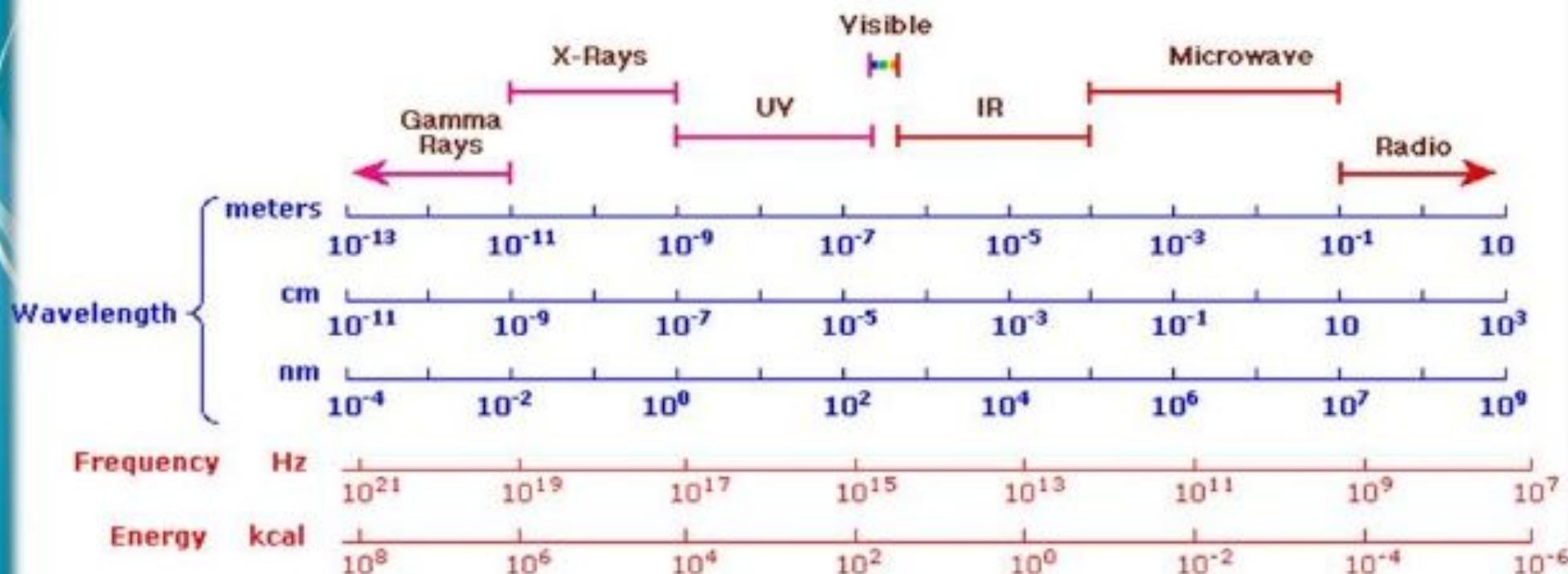
$$c = \nu \lambda$$

- As photon is subjected to energy, so

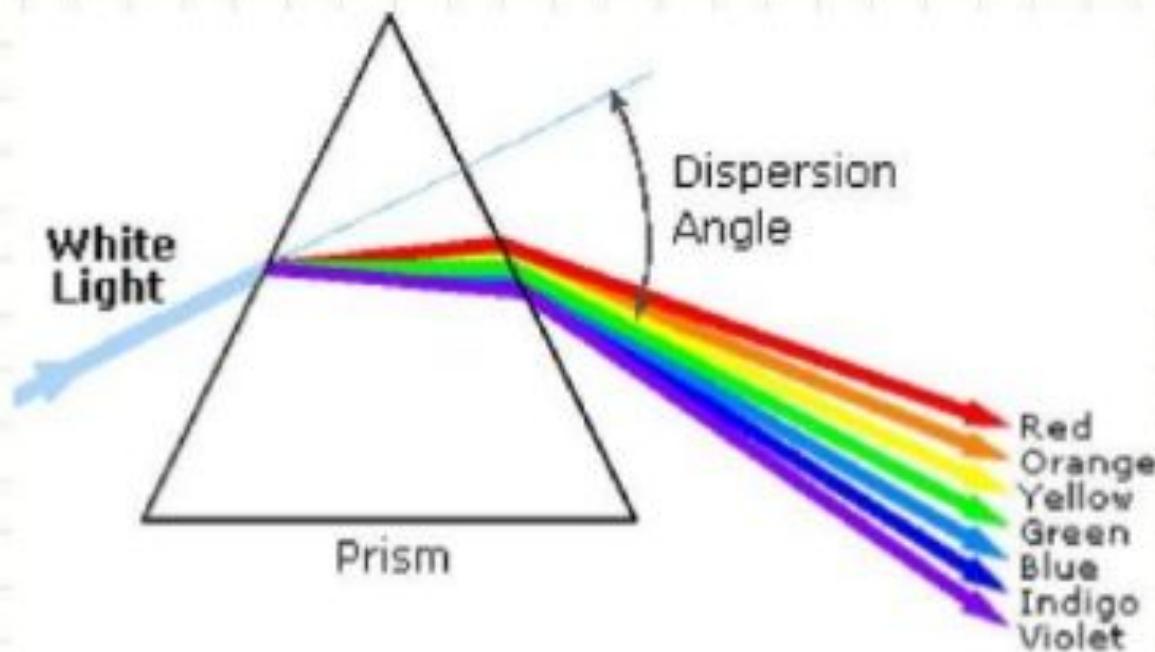
$$E = h\nu = hc/\lambda$$

Electromagnetic Radiation

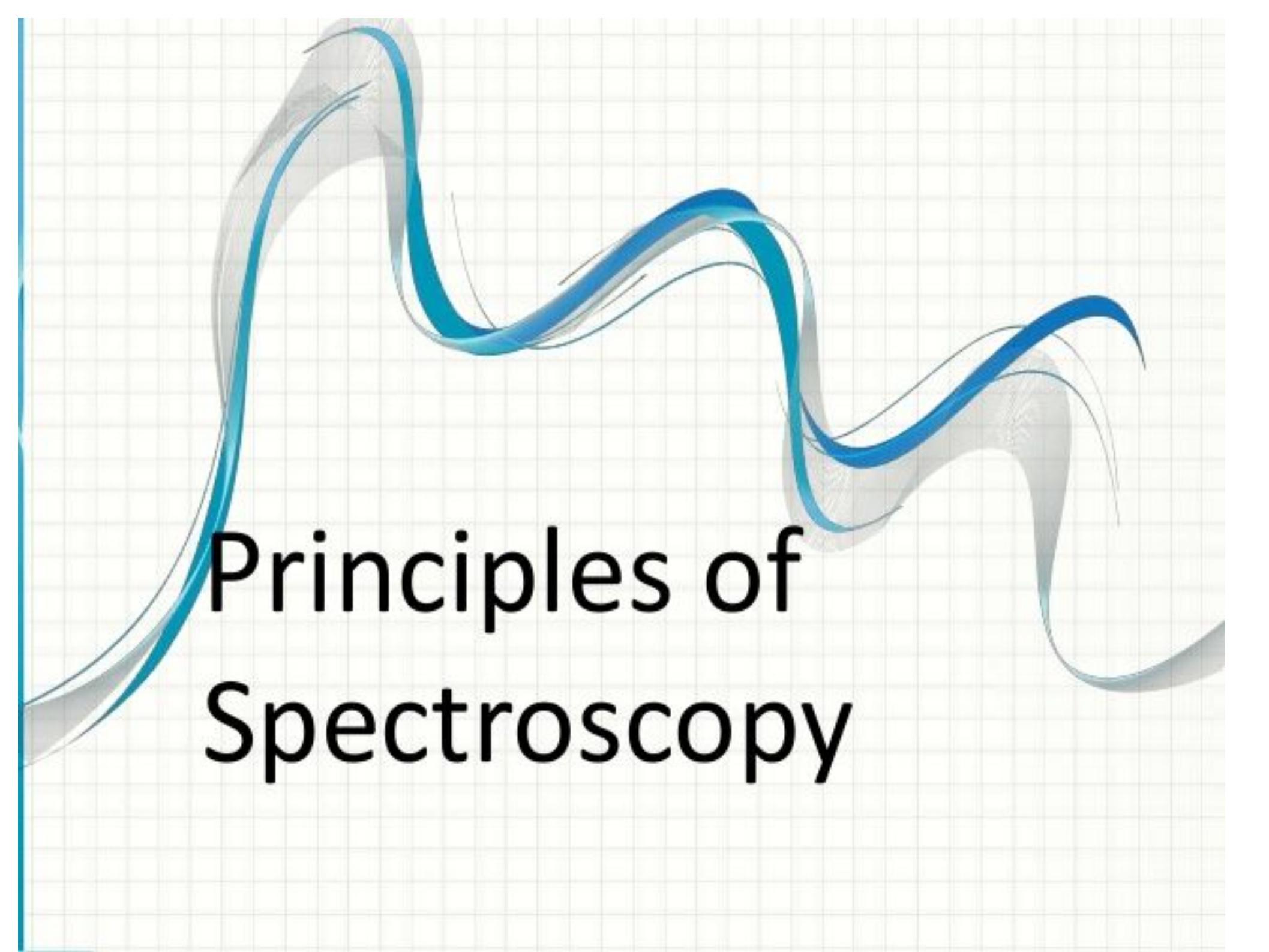
The Electromagnetic Spectrum



Electromagnetic Radiation



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

A large, stylized graphic of three wavy lines in shades of blue and grey, resembling a DNA helix or a complex signal waveform, is positioned behind the title text.

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).
- Spectrometer is an instrument design to measure the spectrum of a compound.

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)

Principles of Spectroscopy

2. Emission Spectroscopy:

- An analytical technique in which emission (of a particle or radiation) is dispersed according to some property of the emission & the amount of dispersion is measured.
- e.g. Mass Spectroscopy



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:

$$\Delta E = h \nu = E_n - E_0 \text{ where } (n = 1, 2, 3, \dots \text{ etc})$$

$$\Delta E = 35 \text{ to } 71 \text{ kcal/mole}$$

Interaction of EMR with matter

2. Vibrational Energy Levels:

- These are less 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.

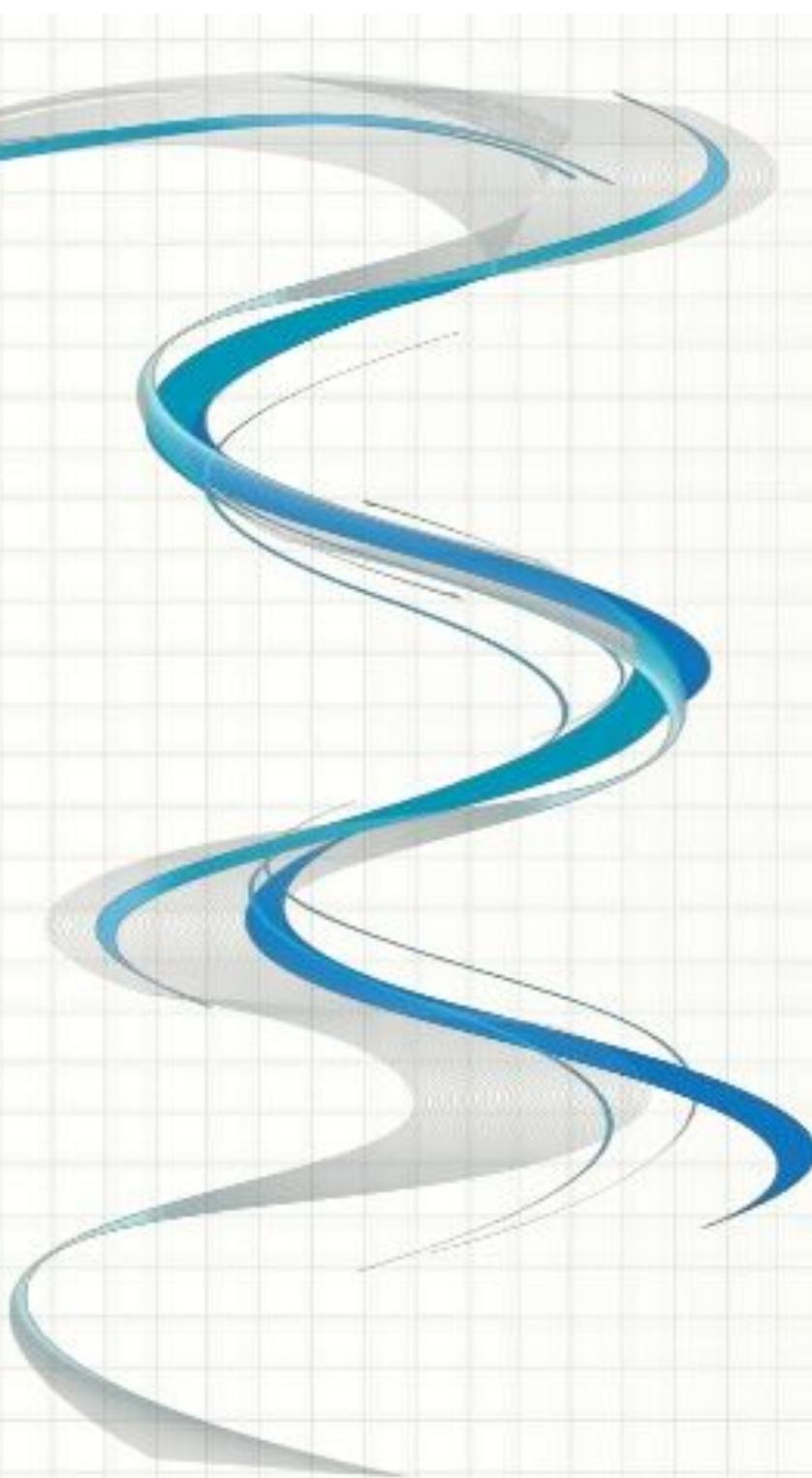
Interaction of EMR with matter

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

$I = I_0$ at $x = 0$ and

$I = I$ at $x=l$,

We get,

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

Lambert's Law

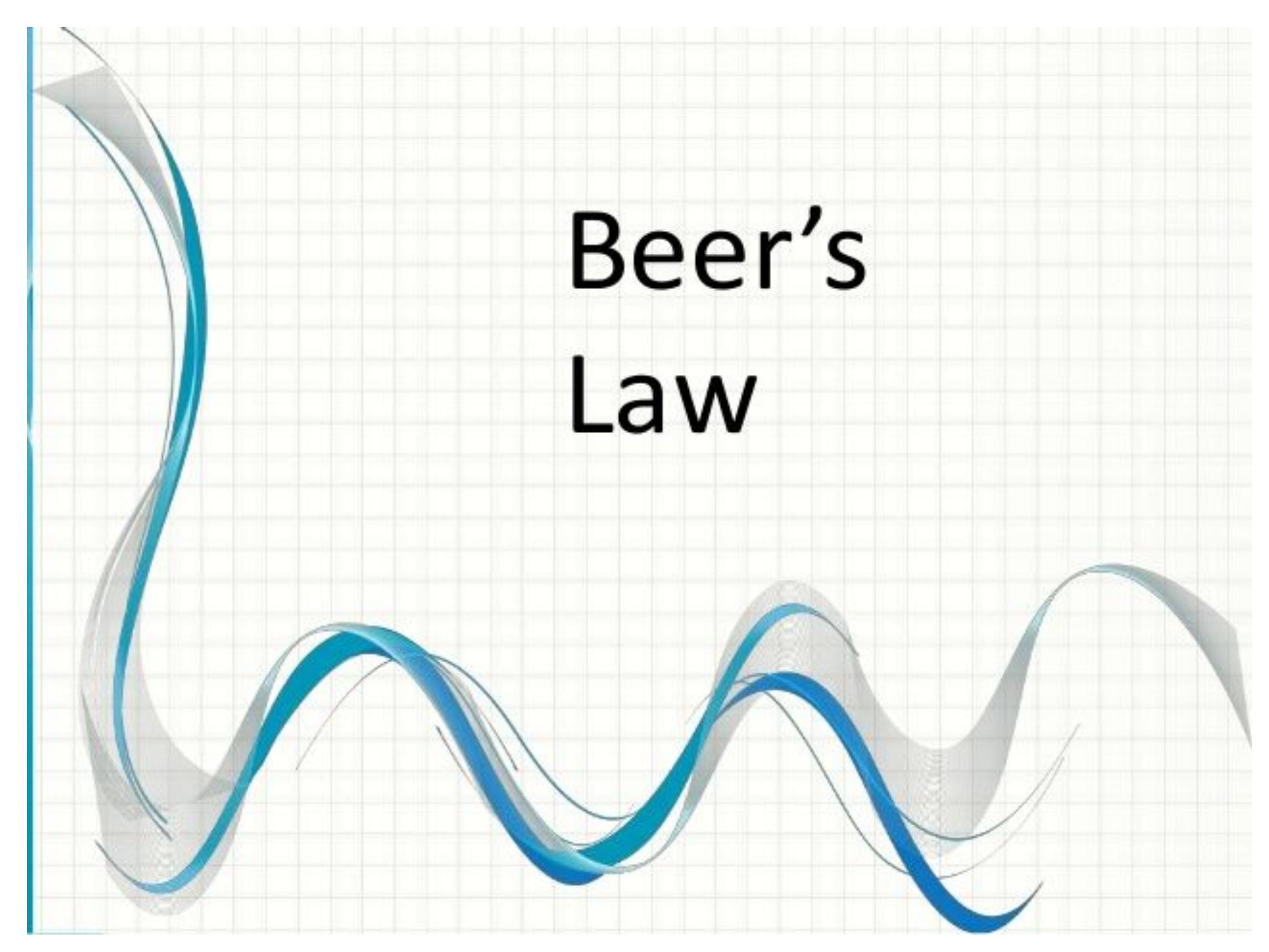
$$2.303 \log \frac{I}{I_0} = -Kl$$

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

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 intensity of the 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

$$-\frac{dI}{dx} \propto C \cdot I$$

$$\text{So, } -\frac{dI}{dx} = K' C \cdot I$$

Integrate equation between limit

$I = I_0$ at $x = 0$ and

$I = I$ at $x=1$,

We get,

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

Beer's Law

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

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

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

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

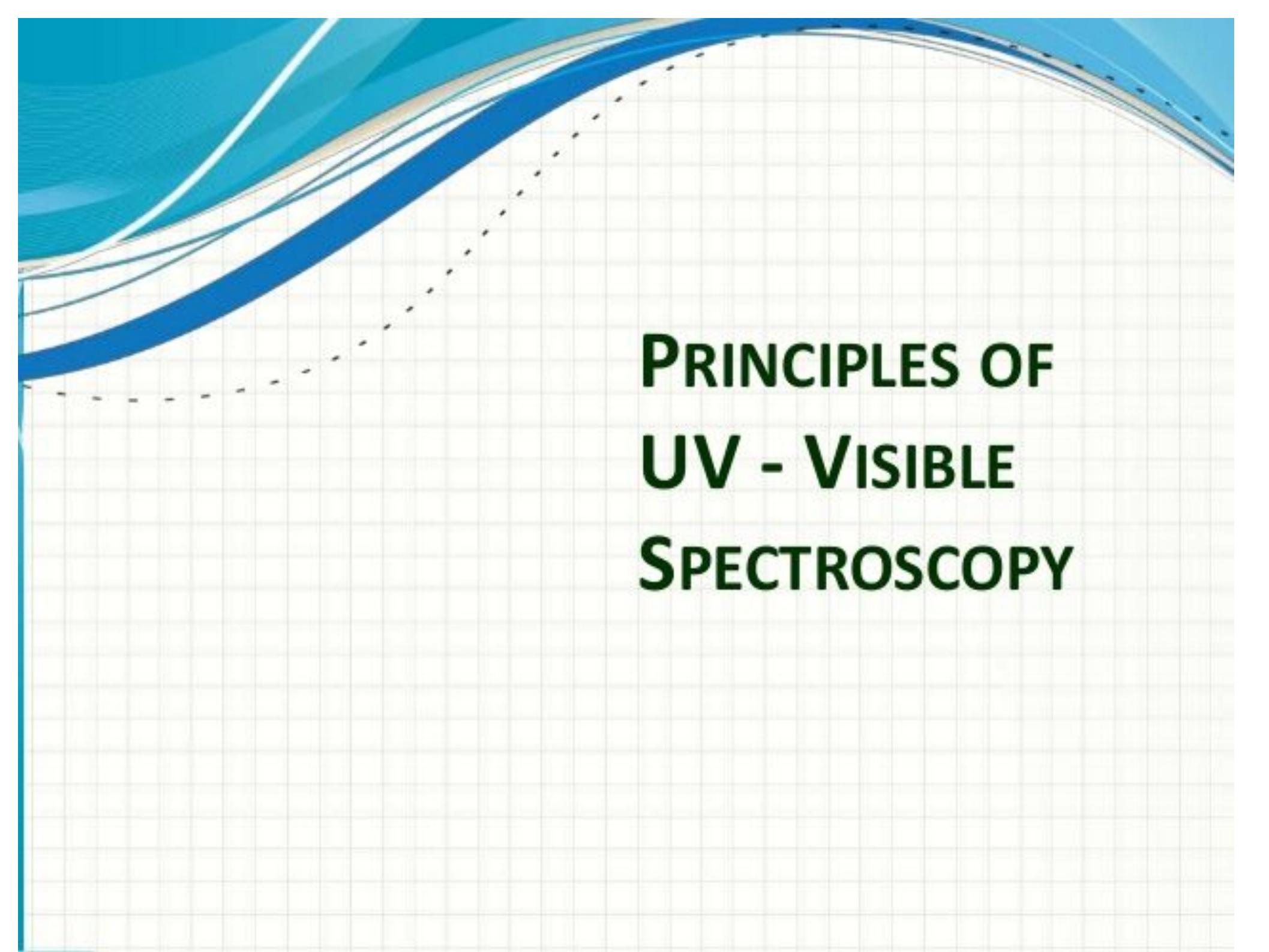
$A = E \cdot C \cdot l$ Beer's Law

Beer's Law

$$A = E \cdot C \cdot l$$

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

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

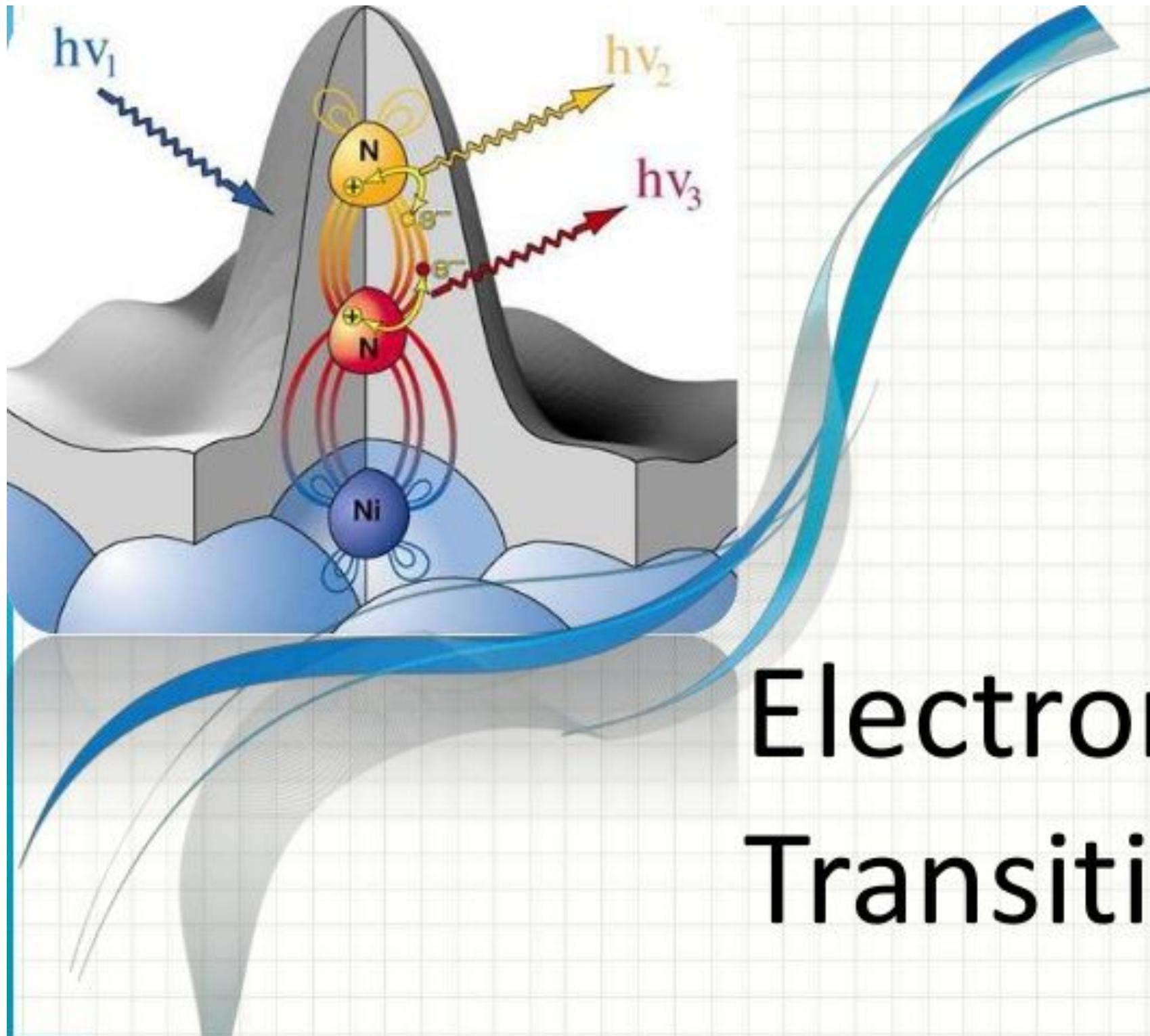
Principle

- 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

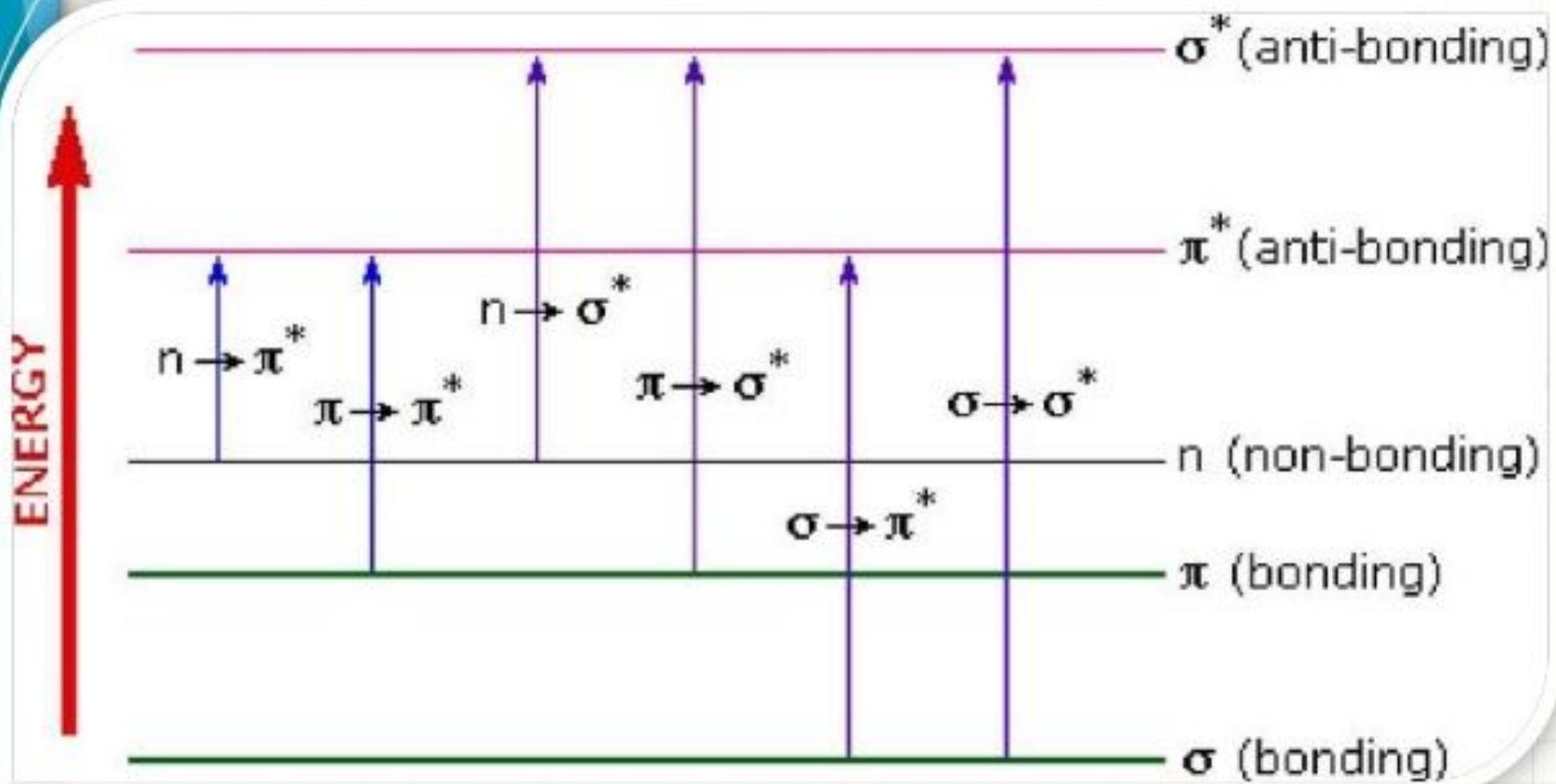
Far UV Region: below 200 nm

- 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

- $\sigma \rightarrow \sigma^*$ 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 $\sigma \rightarrow \sigma^*$ transition and shows absorbance maxima at 125 nm.

2

- $\pi \rightarrow \pi^*$ 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 $\pi \rightarrow \pi^*$ 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

• $n \rightarrow \pi^*$ transition

- An electron from non-bonding orbital is promoted to anti-bonding π^* orbital.
- Compounds containing double bond involving hetero atoms ($C=O$, $C\equiv N$, $N=O$) undergo such transitions.
- $n \rightarrow \pi^*$ transitions require minimum energy and show absorption at longer wavelength around 300 nm.

5

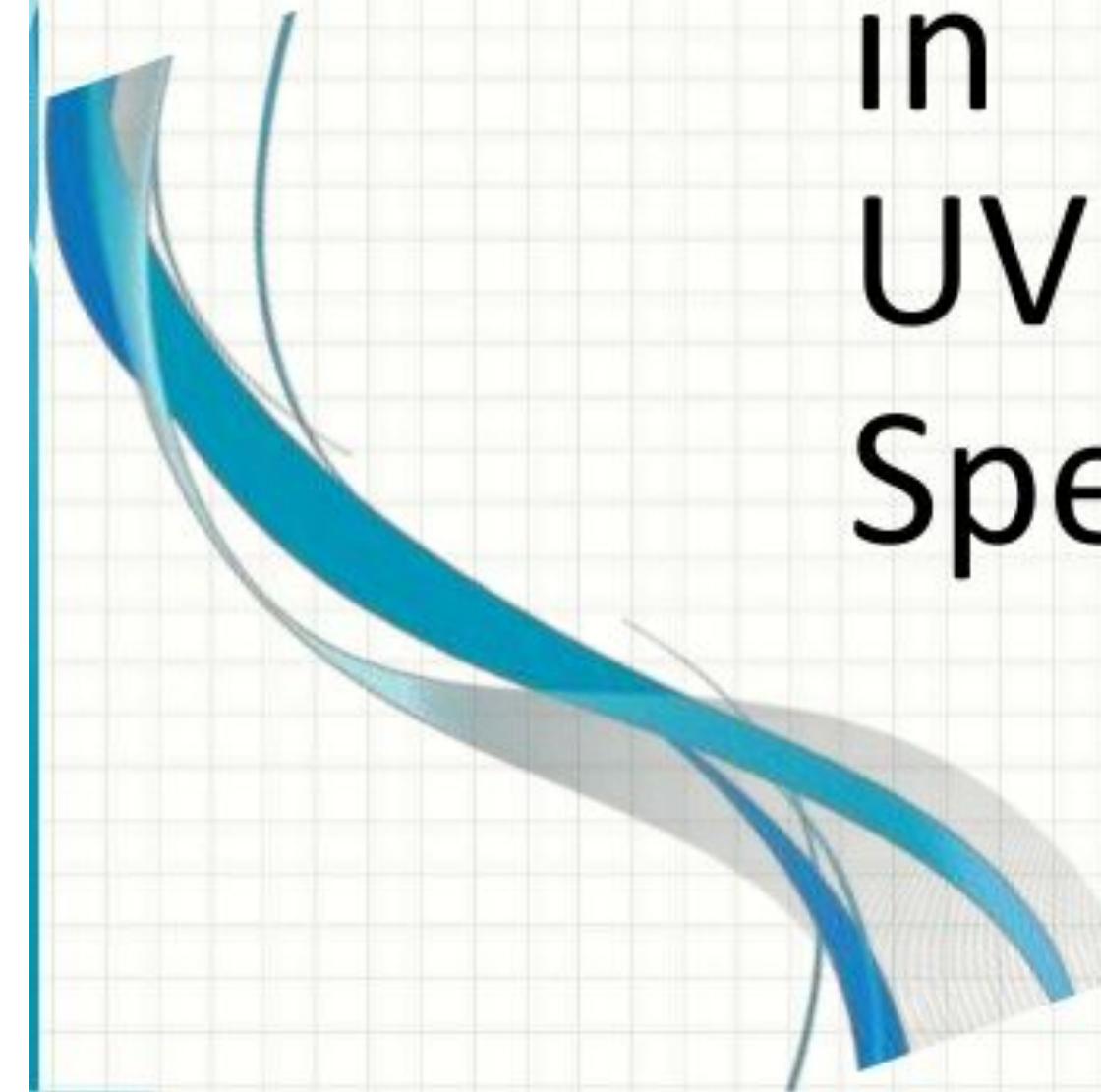
- $\sigma \rightarrow \pi^*$ transition

&

- $\pi \rightarrow \sigma^*$ transition

6

- These electronic transitions are forbidden transitions & are only theoretically possible.
- Thus, $n \rightarrow \pi^*$ & $\pi \rightarrow \pi^*$ 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 chromophores.

OR

The functional groups containing multiple bonds capable of absorbing radiations above 200 nm due to $n \rightarrow \pi^*$ & $\pi \rightarrow \pi^*$ transitions.

e.g. NO_2 , $\text{N}=\text{O}$, $\text{C}=\text{O}$, $\text{C}=\text{N}$, $\text{C}\equiv\text{N}$, $\text{C}=\text{C}$, $\text{C}=\text{S}$, etc

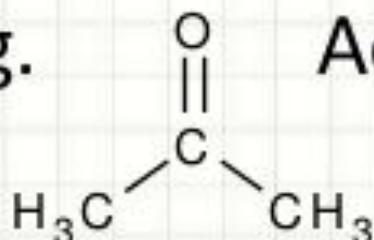
Chromophore

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.

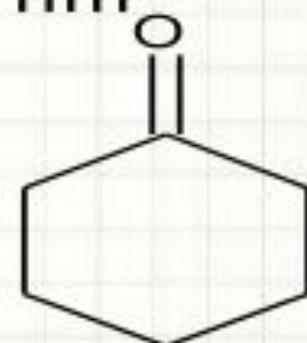
Chromophore

e.g.



Acetone which has $\lambda_{\max} = 279 \text{ nm}$

and that cyclohexane has $\lambda_{\max} = 291 \text{ nm}$.



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

e.g. 1,5 - hexadiene has $\lambda_{\max} = 178 \text{ nm}$

2,4 - hexadiene has $\lambda_{\max} = 227 \text{ nm}$

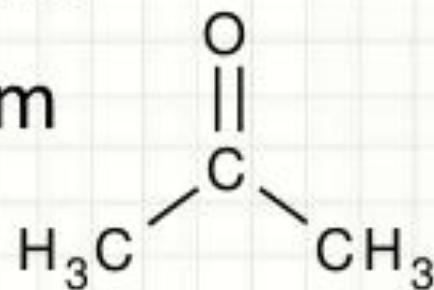


Chromophore

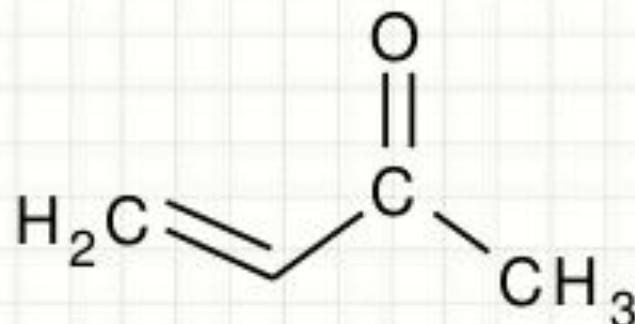
3. Conjugation of C=C and carbonyl group shifts the λ_{max} of both groups to longer wavelength.

e.g. Ethylene has $\lambda_{\text{max}} = 171 \text{ nm}$

Acetone has $\lambda_{\text{max}} = 279 \text{ nm}$



Crotonaldehyde has $\lambda_{\text{max}} = 290 \text{ nm}$



Auxochrome

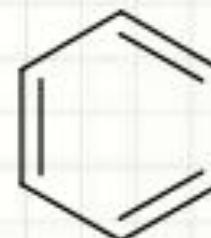
The functional groups attached to a chromophore which modifies the ability of the chromophore to absorb light , altering the wavelength or intensity of absorption.

OR

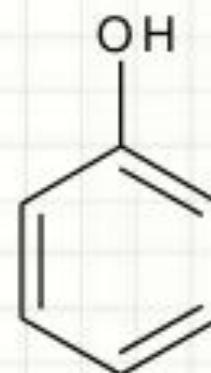
The functional group with non-bonding electrons that does not absorb radiation in near UV region but when attached to a chromophore alters the wavelength & intensity of absorption.

Auxochrome

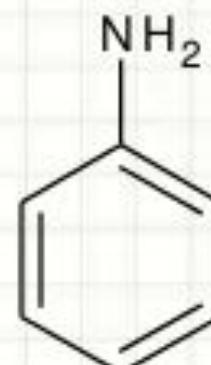
e.g. Benzene $\lambda_{\max} = 255 \text{ nm}$



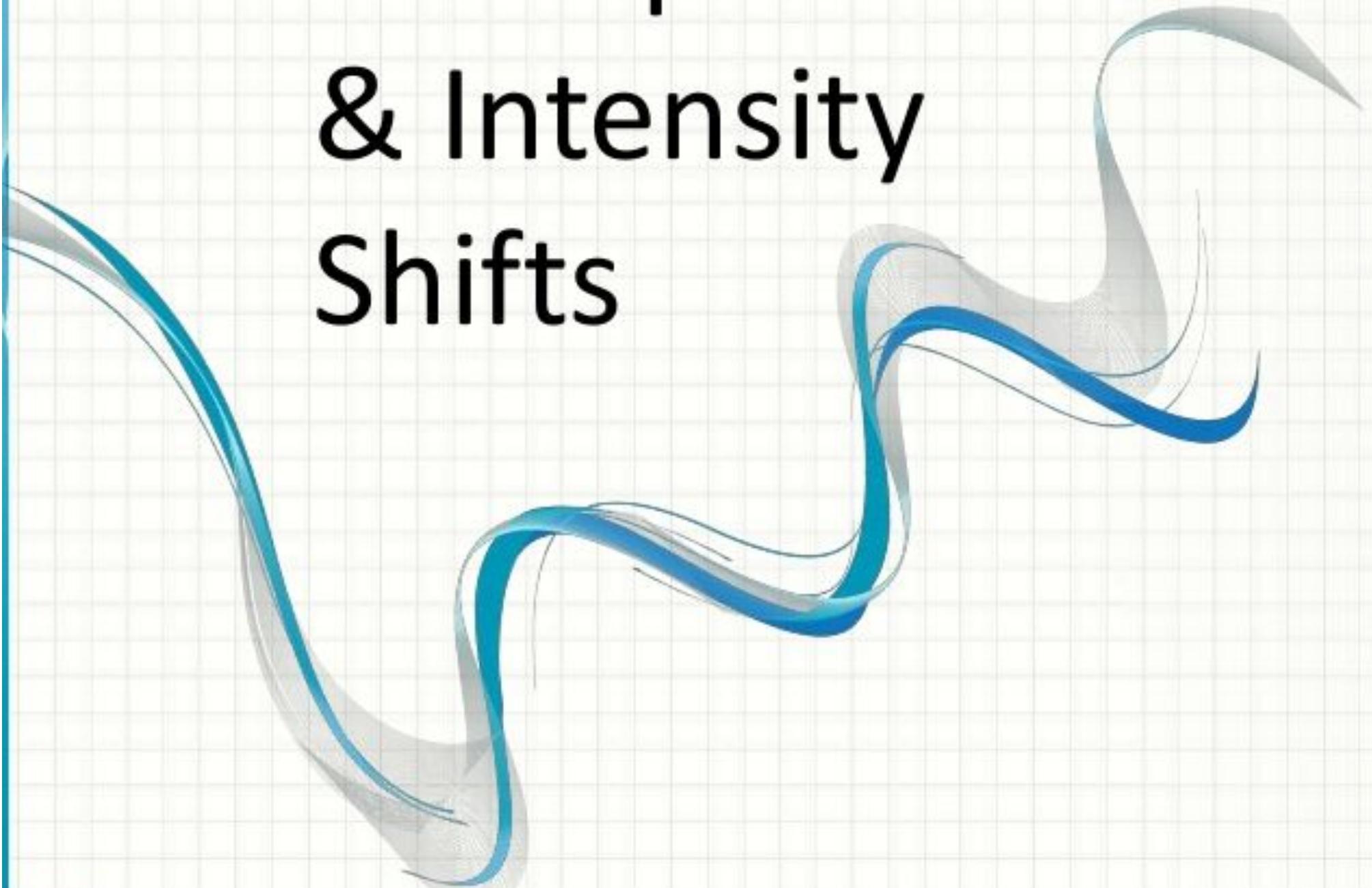
Phenol $\lambda_{\max} = 270 \text{ nm}$



Aniline $\lambda_{\max} = 280 \text{ nm}$



Absorption & Intensity Shifts



1 • Bathochromic Shift (Red Shift)

2 • Hypsochromic Shift (Blue Shift)

3 • Hyperchromic Effect

4 • Hypochromic Effect

1

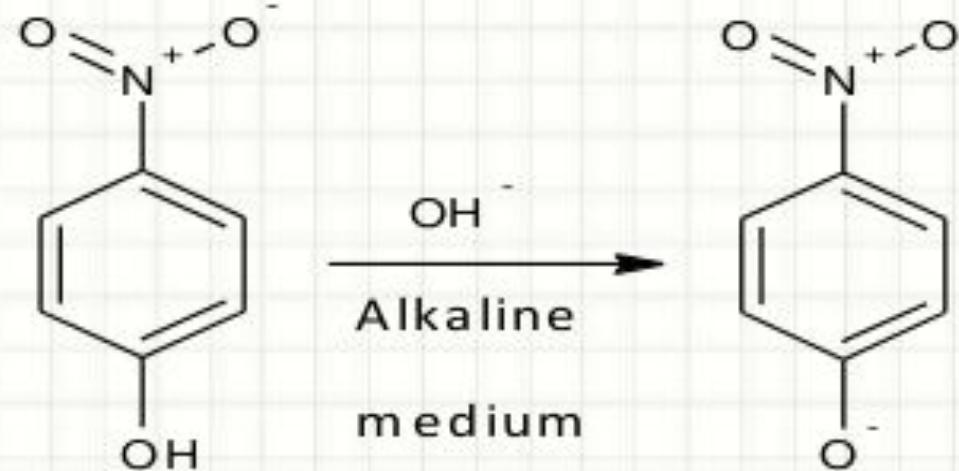
- Bathochromic Shift (Red Shift)

- 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 $-\text{OH}$, $-\text{OCH}_3$ 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

$\lambda_{\max} = 255 \text{ nm}$

$\lambda_{\max} = 265 \text{ nm}$

2

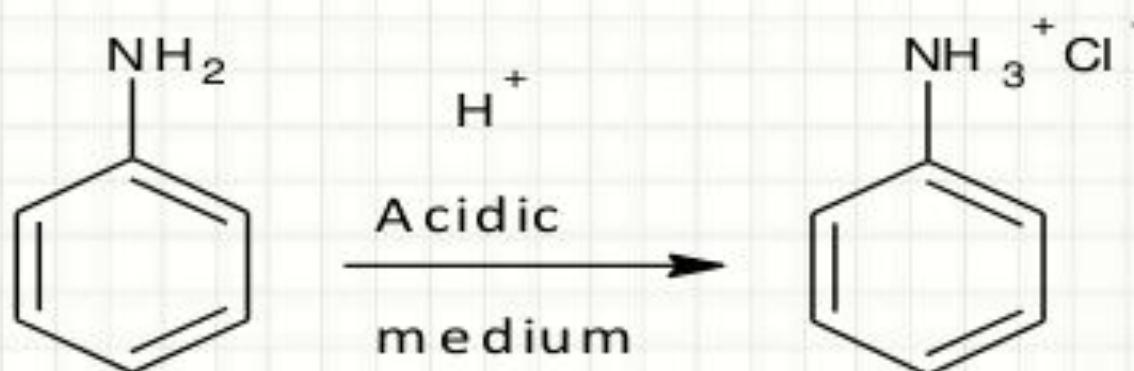
• Hypsochromic Shift (Blue Shift)

- 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

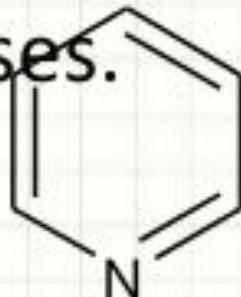
$\lambda_{\max} = 280 \text{ nm}$

$\lambda_{\max} = 265 \text{ nm}$

3

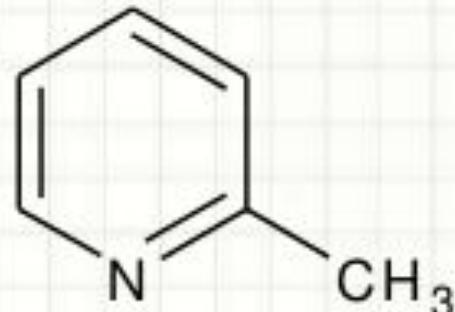
• Hyperchromic Effect

- 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

$$\lambda_{\max} = 257 \text{ nm}$$



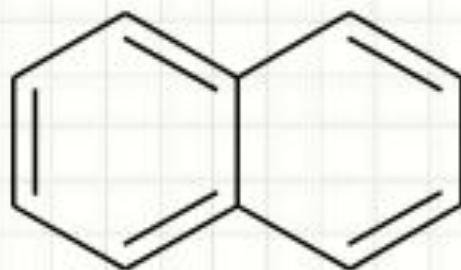
2-methyl pyridine

$$\lambda_{\max} = 260 \text{ nm}$$

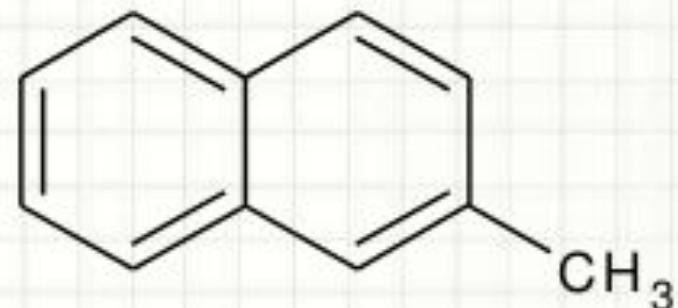
4

• Hypochromic Effect

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

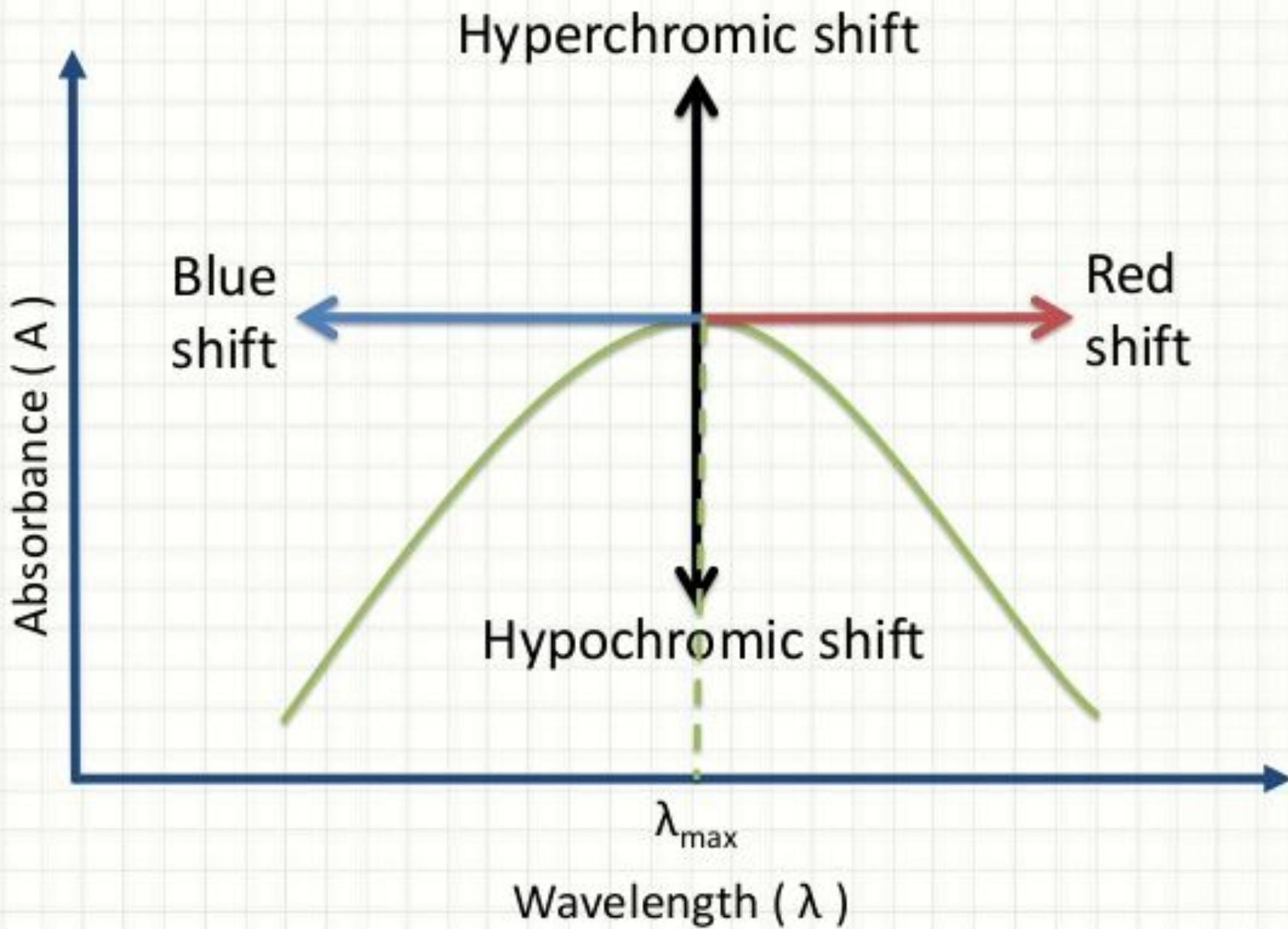


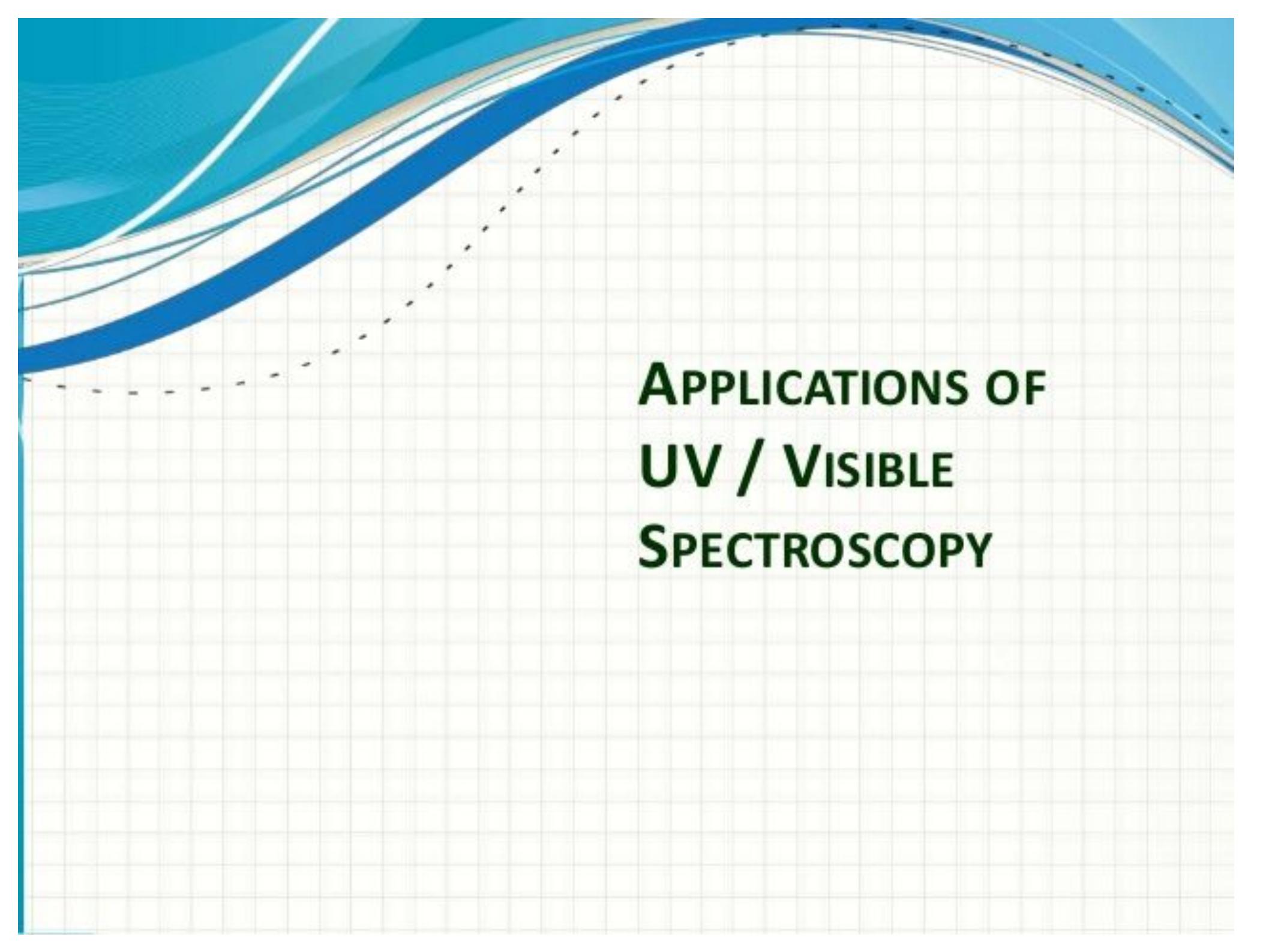
Naphthalene
 $\epsilon = 19000$



2-methyl naphthalene
 $\epsilon = 10250$

Shifts and Effects





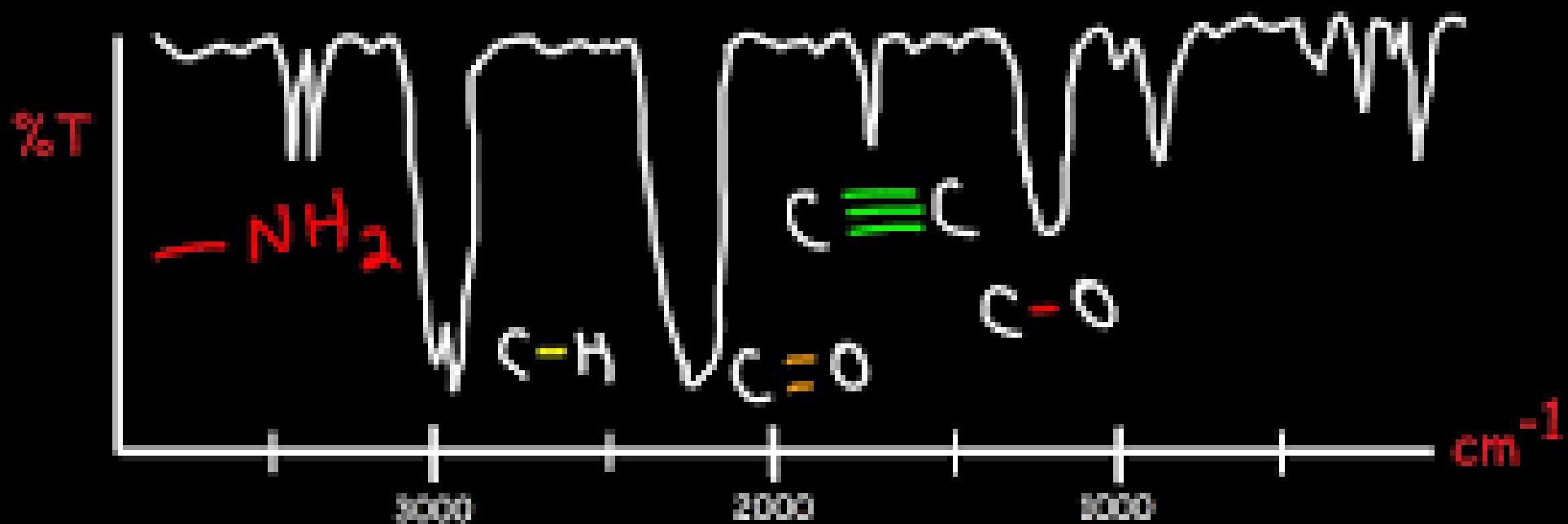
APPLICATIONS OF UV / VISIBLE SPECTROSCOPY

Applications

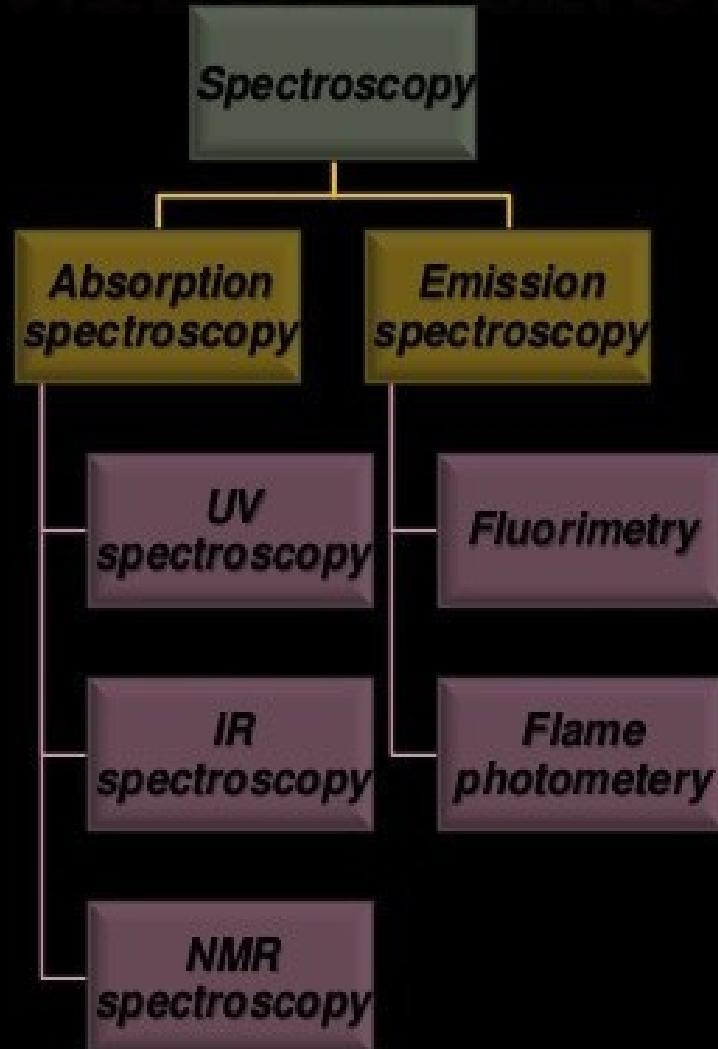
- Qualitative & Quantitative Analysis:
 - It is used for characterizing aromatic compounds and conjugated olefins.
 - It can be used to find out molar concentration of the solute under study.
- Detection of impurities:
 - It is one of the important method to detect impurities in organic solvents.
- Detection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

Infra Red (IR) Spectroscopy

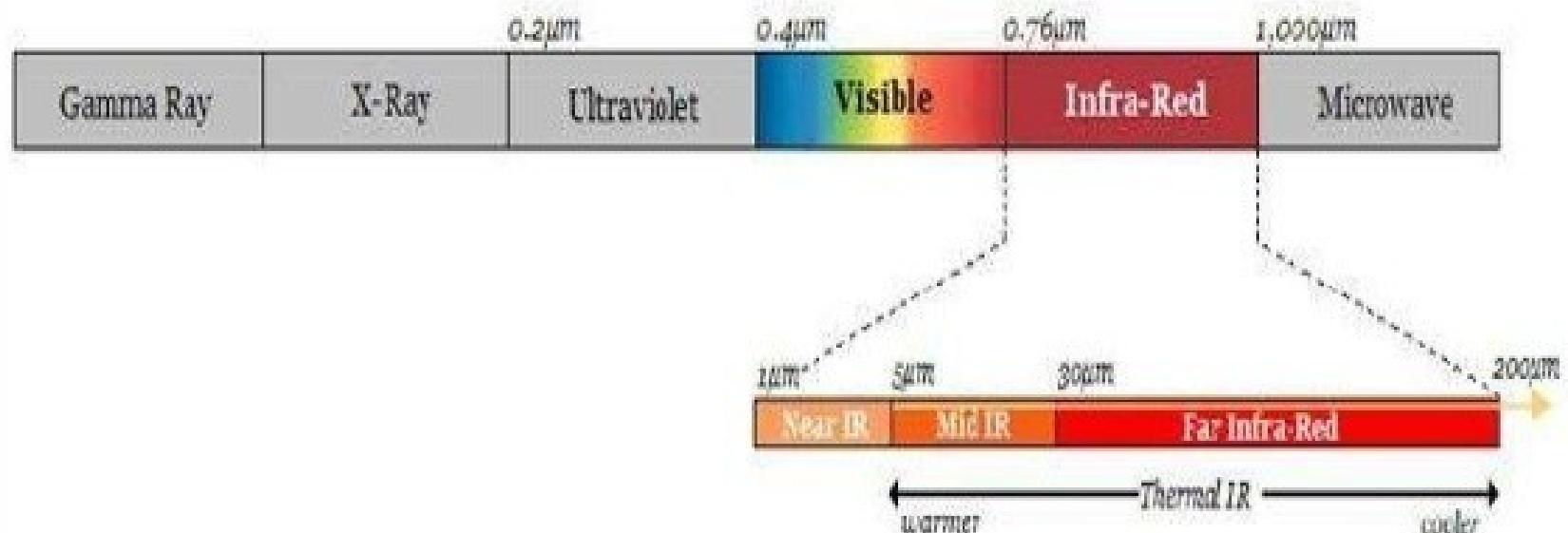
IR Spectroscopy



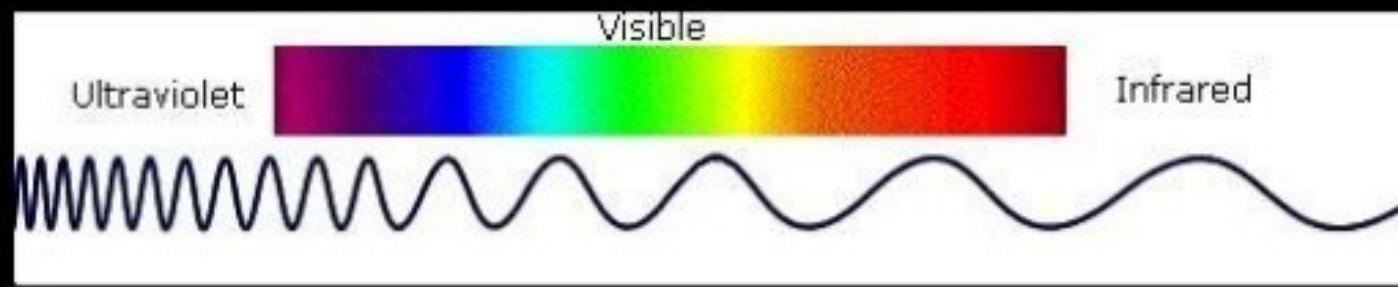
INTRODUCTION



- IR spectroscopy is the study of interaction between infrared radiations and matter.
- Infrared radiations refers broadly to that part of electromagnetic spectrum between visible and microwave region.



INFRARED REGIONS



INFRARED REGIONS	RANGE
<i>Near infrared region</i>	$0.8\text{-}2.5 \mu(12,500\text{-}4000 cm^{-1})$
<i>Main infrared region</i>	$2.5\text{-}15 \mu(4000\text{-}667cm^{-1})$
<i>Far infrared region</i>	$15\text{-}200 m \mu(667\text{-}100 cm^{-1})$



What is Spectroscopy ?

Spectroscopy is the interaction of EMR with matter to get *spectra*, which gives information like, bond length, bond angle, geometry and molecular structure

Atoms and molecules interact with electromagnetic radiation (EMR) in a wide variety of ways.

Atoms and molecules may absorb and/or emit EMR.

Absorption of EMR stimulates different types of motion in atoms and/or molecules.

The patterns of absorption (wavelengths absorbed and to what extent) and/or emission (wavelengths emitted and their respective intensities) are called '*spectra*'



Electromagnetic radiation (emr)

Electromagnetic radiation displays the properties of both particles and waves.

The particle component is called a **photon**.

The term “photon” is implied to mean a small, massless particle that contains a small wave-packet of EM radiation/light.

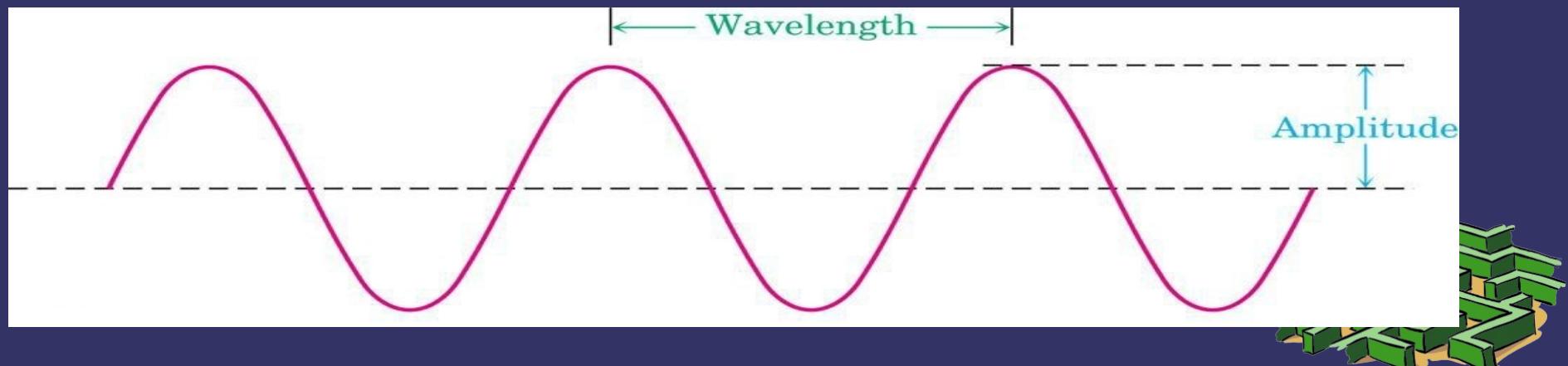
The energy (E) component of a photon is proportional to the frequency. Where **h** is Planck's constant and ν is the frequency in Hertz (cycles per second) .

$$E = h\nu$$

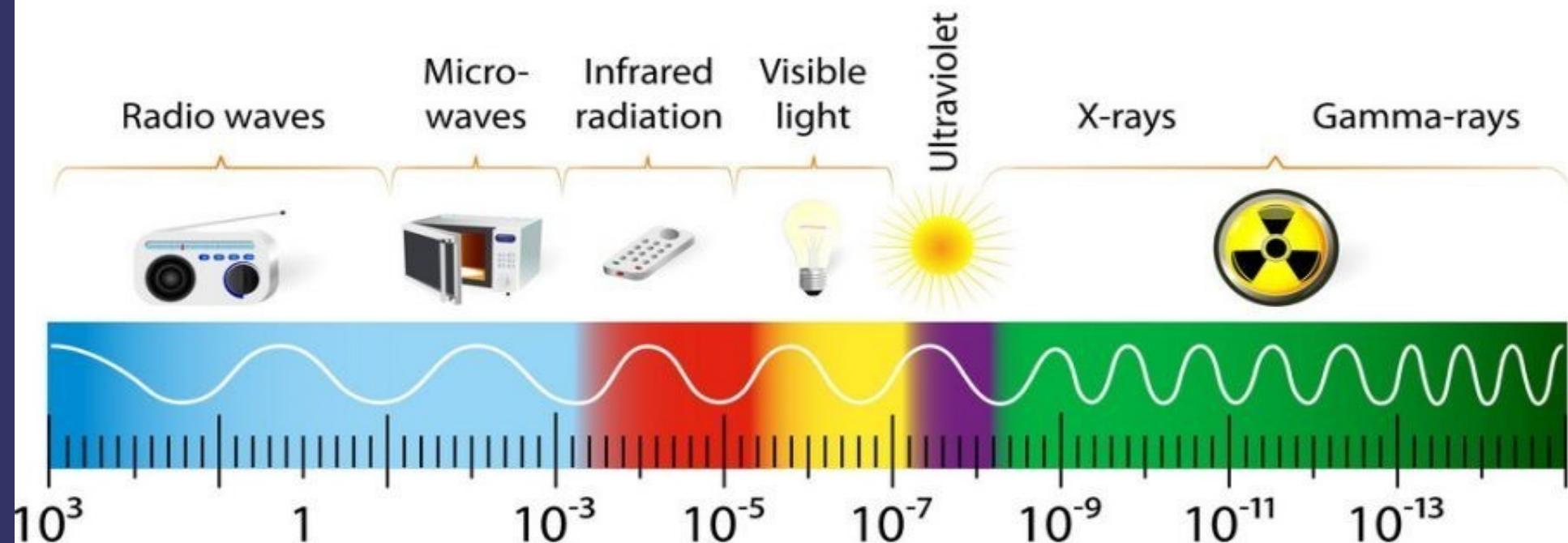
ν = frequency: waves per unit time (sec-1, Hz)

c = speed of light (3.0×10^8 m • sec-1)

h = Plank's constant (6.63×10^{-34} J • sec)

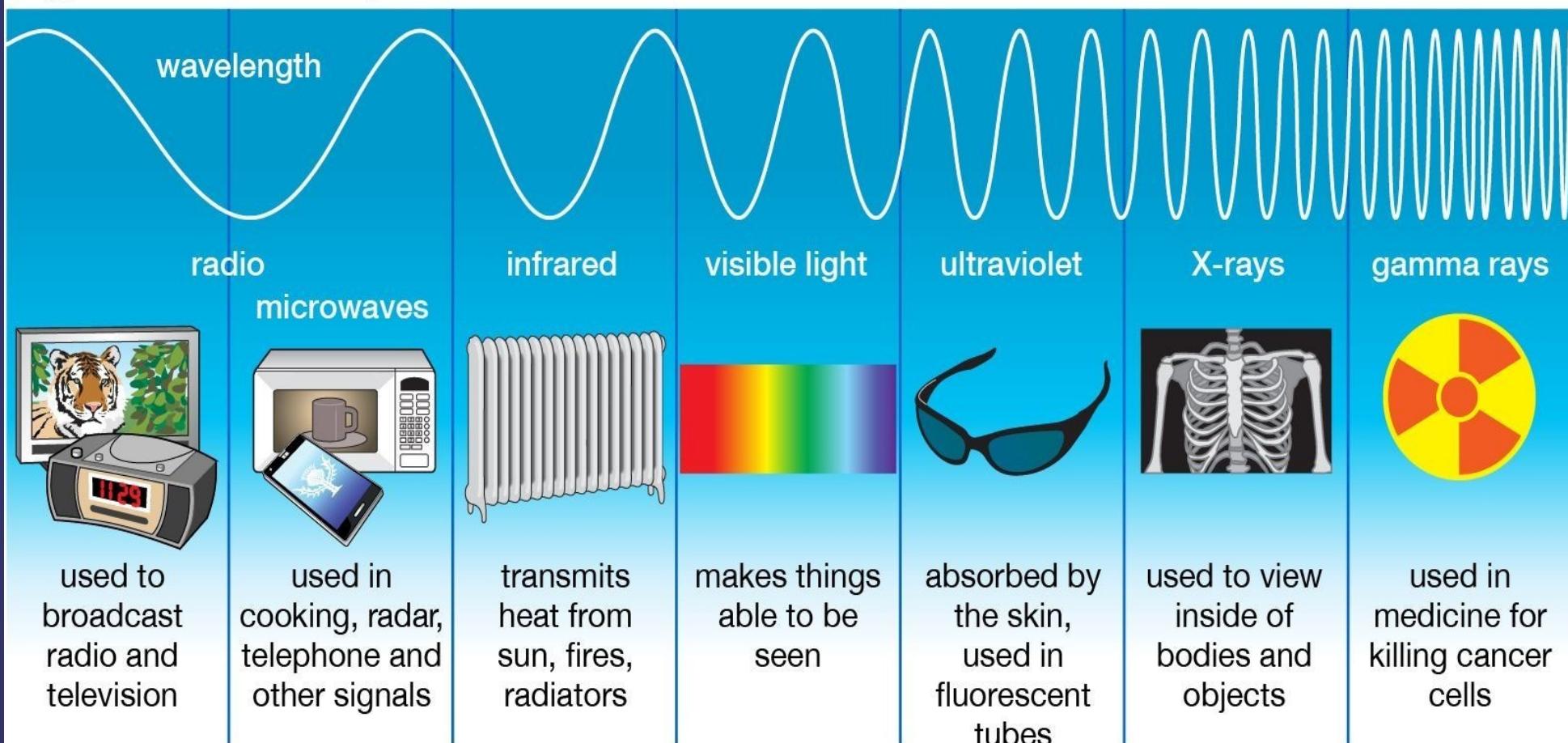


THE ELECTROMAGNETIC SPECTRUM



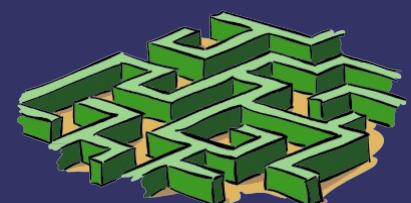
Electromagnetic spectra

Types of Electromagnetic Radiation



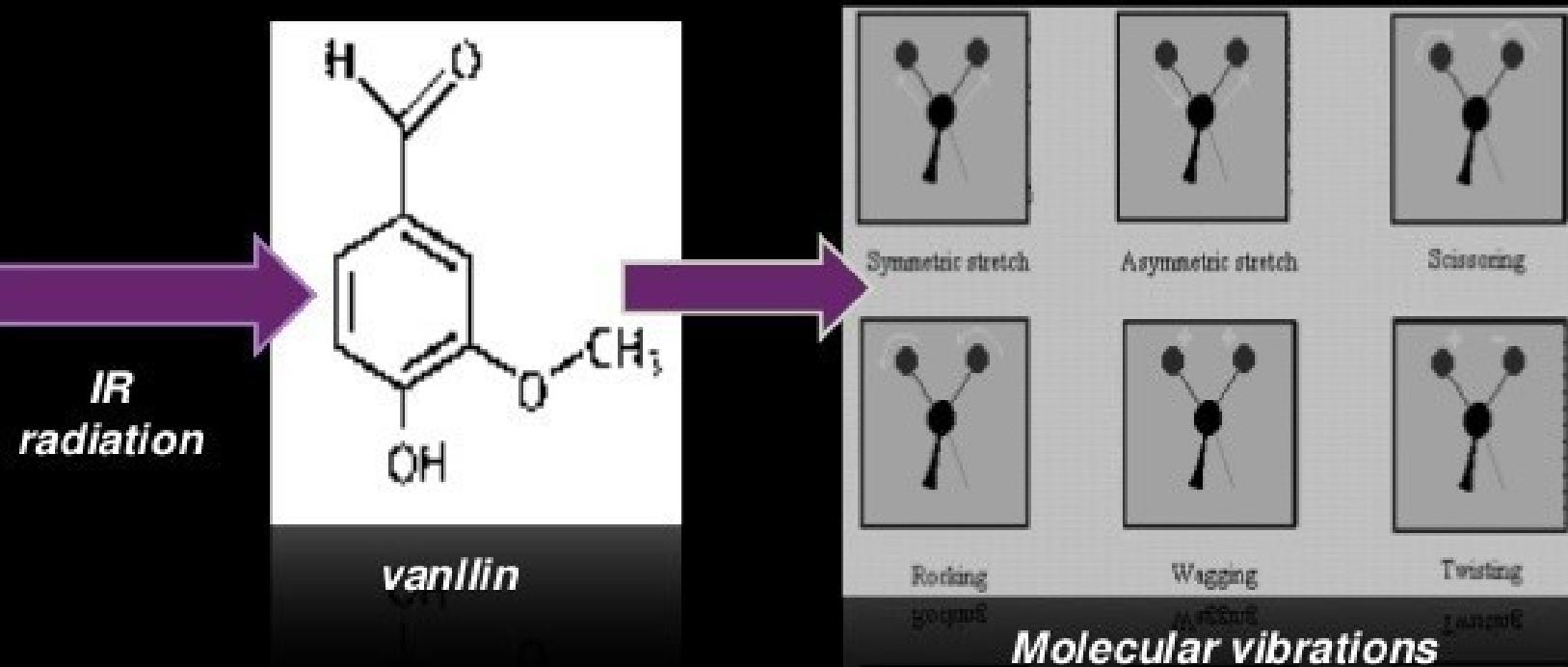
UV-Visible: valence electron transitions
- gives information about p-bonds and conjugated systems

Infrared: molecular vibrations (stretches, bends) - identify functional groups.



PRINCIPLE

- When infrared 'light' or radiation hits a molecule, the bonds in the molecule absorb the energy of the infrared and respond by vibrating.



Infrared (IR) Spectroscopy

- ◆ IR deals with the interaction of infrared radiation with matter.
- ◆ The IR spectrum of a compound can provide important information about its chemical nature and molecular structure.
- ◆ Most commonly, the spectrum is obtained by measuring the absorption of IR radiation,
- ◆ Although infrared emission and reflection are also used.
- ◆ Widely applied in the analysis of organic materials, also useful for polyatomic inorganic molecules and for organometallic compounds.

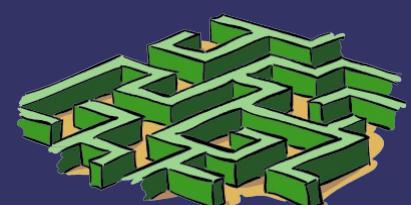
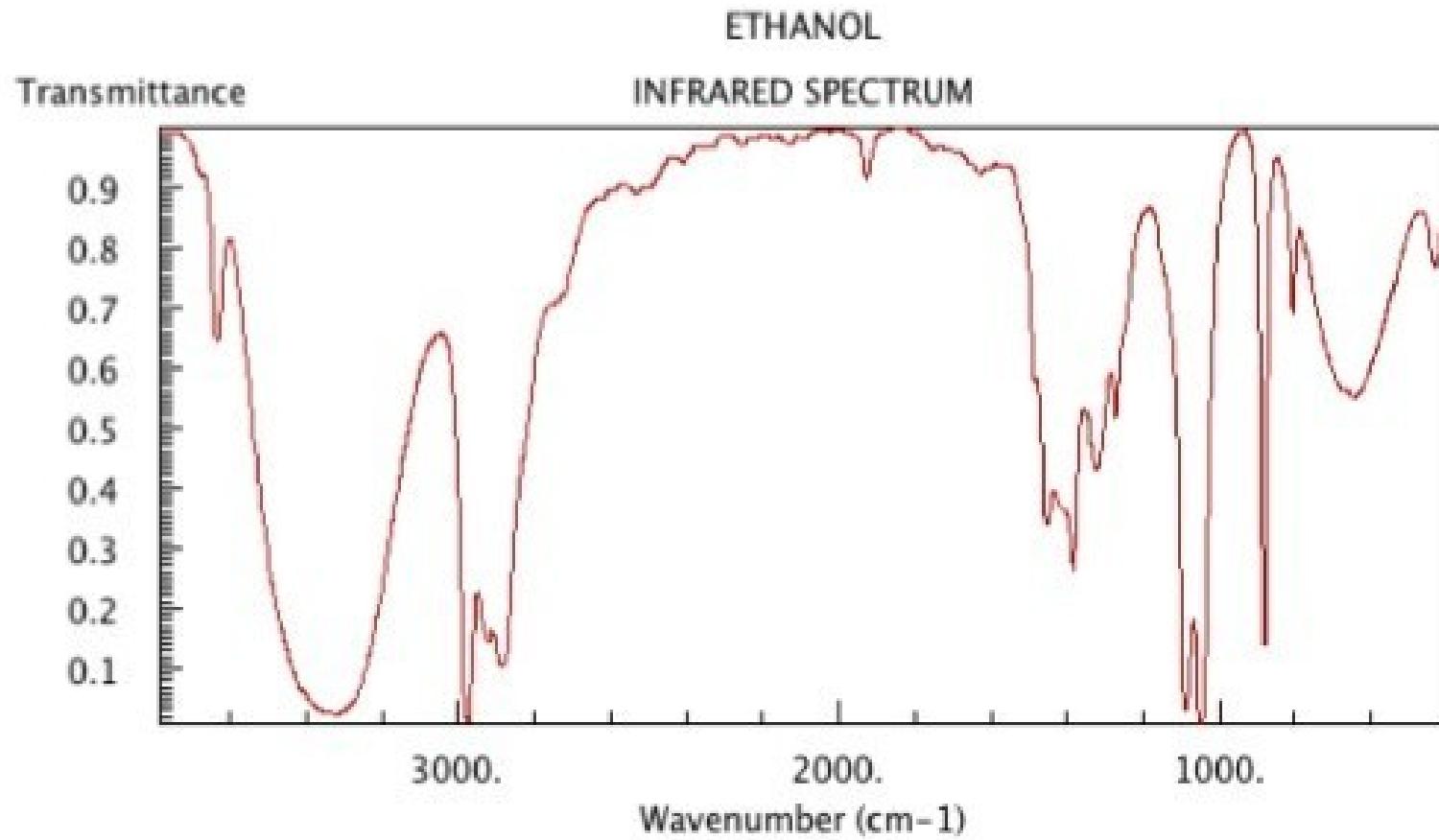


Table 13.4 Important IR Stretching Frequencies

Type of bond	Wavenumber (cm^{-1})	Intensity
$\text{C}\equiv\text{N}$	2260–2220	medium
$\text{C}\equiv\text{C}$	2260–2100	medium to weak
$\text{C}\equiv\text{C}$	1680–1600	medium
$\text{C}\equiv\text{N}$	1650–1550	medium
	~1600 and ~1500–1430	strong to weak
$\text{C}\equiv\text{O}$	1780–1650	strong
$\text{C}\equiv\text{O}$	1250–1050	strong
$\text{C}\equiv\text{N}$	1230–1020	medium
$\text{O}\text{—H}$ (alcohol)	3650–3200	strong, broad
$\text{O}\text{—H}$ (carboxylic acid)	3300–2500	strong, very broad
$\text{N}\text{—H}$	3500–3300	medium, broad
$\text{C}\text{—H}$	3300–2700	medium



IR spectrum of ethanol

Types and modes of vibrations

1. There are 2 modes of vibrations i.e. stretching and bending.
2. In polyatomic molecules ,each atom is having 3 degrees of freedom in three directions (x,y,z axes) necessary for describing its position relative to other atoms in the molecule .
3. A molecule of “n” atoms has therefore “ $3n$ ” degrees of freedom. [$3n=trans+rota+vibrational$]
4. For non linear molecules,3 degrees of freedom describe rotation and 3 translation. The remaining “ $3n-6$ ” degrees of correspond to vibrational degrees of freedom.

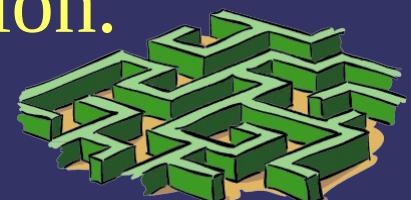


Linear molecules has “ $3n-5$ ” vibrational degrees of freedom, as only 2 degrees of freedom are required to describe rotation.

$TM=3, RM=2$ hence $3n=3+2+Vibrational\ modes$
Hence ,Vibrational modes = $3n-5$

The no. of fundamental Vibrations :

A molecule containing “ n ” atoms has “ $3n$ ” degrees of freedom ; three of which are assigned to translational, other 3 to rotational (2 in case of linear molecules like $\text{CO}_2, \text{HC}\equiv\text{CH}$) and remaining “ $3n-6$ ” {“ $3n-5$ if linear”} to vibrational motion.



Calculate the vibrational degree of freedom

1) O₂ molecule :

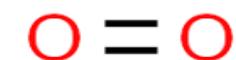
No. of atoms = 2

It is linear molecule hence

Vibrational modes = (3n-5)

$$= (3 \times 2 - 5)$$

$$= 6 - 5 = 1$$



.....

2) CO₂ molecule ,

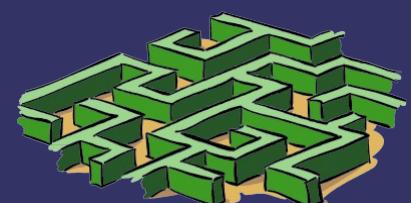
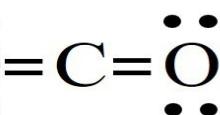
No. Of atoms= 3

It is linear molecule hence

Vibrational modes = (3n-5)

$$= (3 \times 3 - 5)$$

$$= 9 - 5 = 4$$



Calculate the vibrational degree of freedom

3) C₂H₂ molecule :

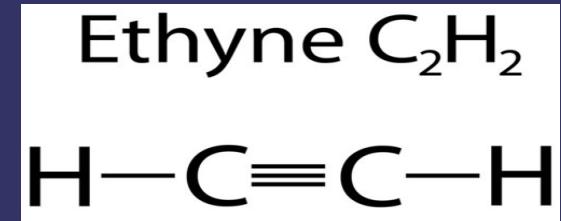
No. of atoms = 4

It is linear molecule hence

Vibrational modes = (3n-5)

$$= (3 \times 4 - 5)$$

$$= 12 - 5 = 7$$



.....

4) N₂O molecule ,

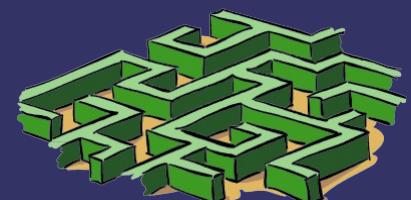
No. Of atoms = 3

It is linear molecule hence

Vibrational modes = (3n-5)

$$= (3 \times 3 - 5)$$

$$= 9 - 5 = 4$$



Calculate the vibrational degree of freedom

5) CH₂O molecule : No. of atoms

= 4 It is **non-linear molecule**

hence Vibrational modes = $(3n-6)$

$$= (3 \times 4 - 6)$$

$$= 12 - 6 = 6$$

.....

6) CH₄

molecule No.
of atoms = 5

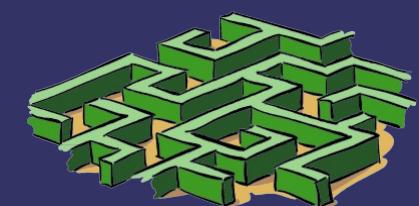
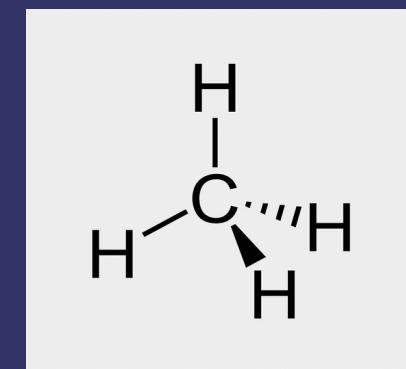
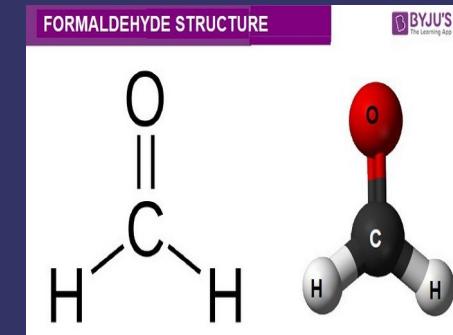
It is non-linear molecule

hence Vibrational modes

$$= (3n-6)$$

$$= (3 \times 5 - 6)$$

$$= 15 - 6 = 9$$



Calculate the vibrational degree of freedom

7) C₆H₆ molecule :

No. of atoms = 12

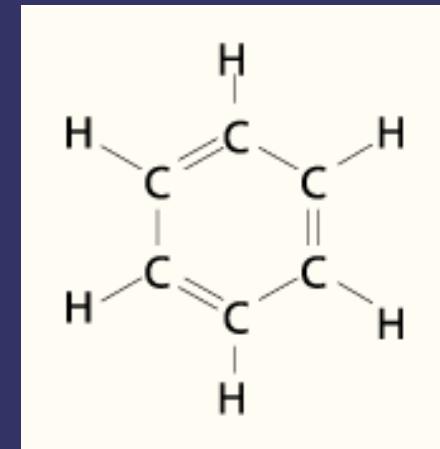
It is non-linear molecule

hence Vibrational modes

$$= (3n-6)$$

$$= (3 \times 12 - 6)$$

$$= 36 - 6 = 30$$



.....

8) CHCl₃ molecule

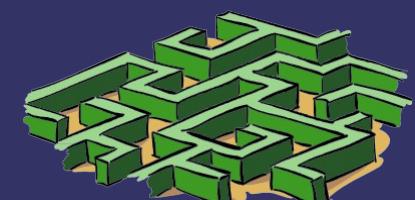
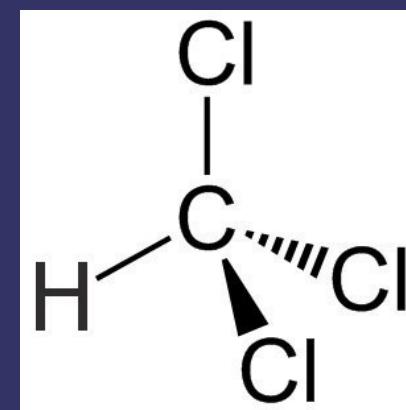
No. of atoms = 5

It is non-linear
molecule

Hence Vibrational
modes = (3n-6)

$$= (3 \times 5 - 6)$$

$$= 15 - 6 = 9$$



MOLECULAR VIBRATIONS

Fundamental Vibrations

Stretching Vibration

Symmetric

Asymmetric

Bending Vibration

In-plane Bending

Scissoring

Rocking

Out Of Plane Bending

Wagging

Twisting

Non-fundamental Vibrations

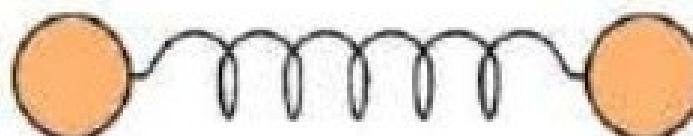
**Over Tones,
Combination
Tones,
Fermi
Resonance**

The vibration of two atoms connected by a **covalent bond** is like a system of two vibrating ball connected by a spring.

Specific bonds respond to (absorb) **specific** frequencies



equilibrium
bond length

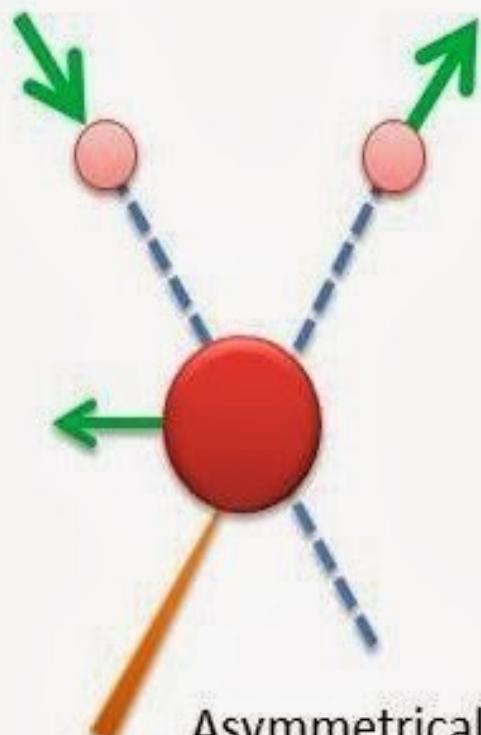


stretched

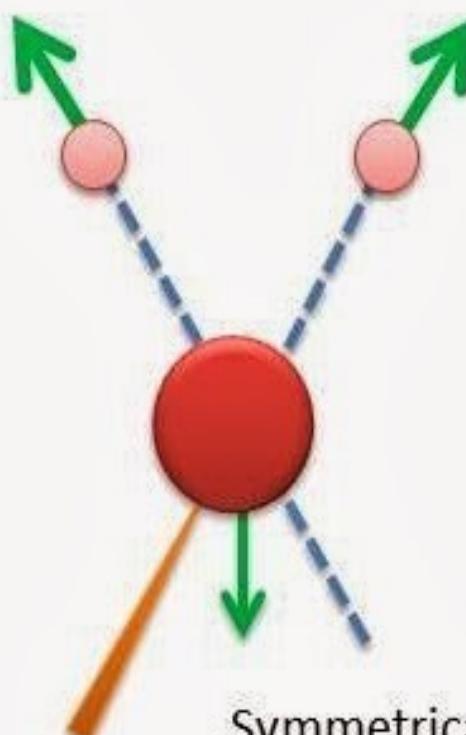


compressed





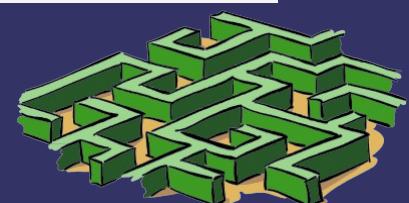
Asymmetrical
Stretching



Symmetrical
Stretching

Stretching Vibrations

Namrata Heda



the relative population in $v = 1$, compared to $v = 0$

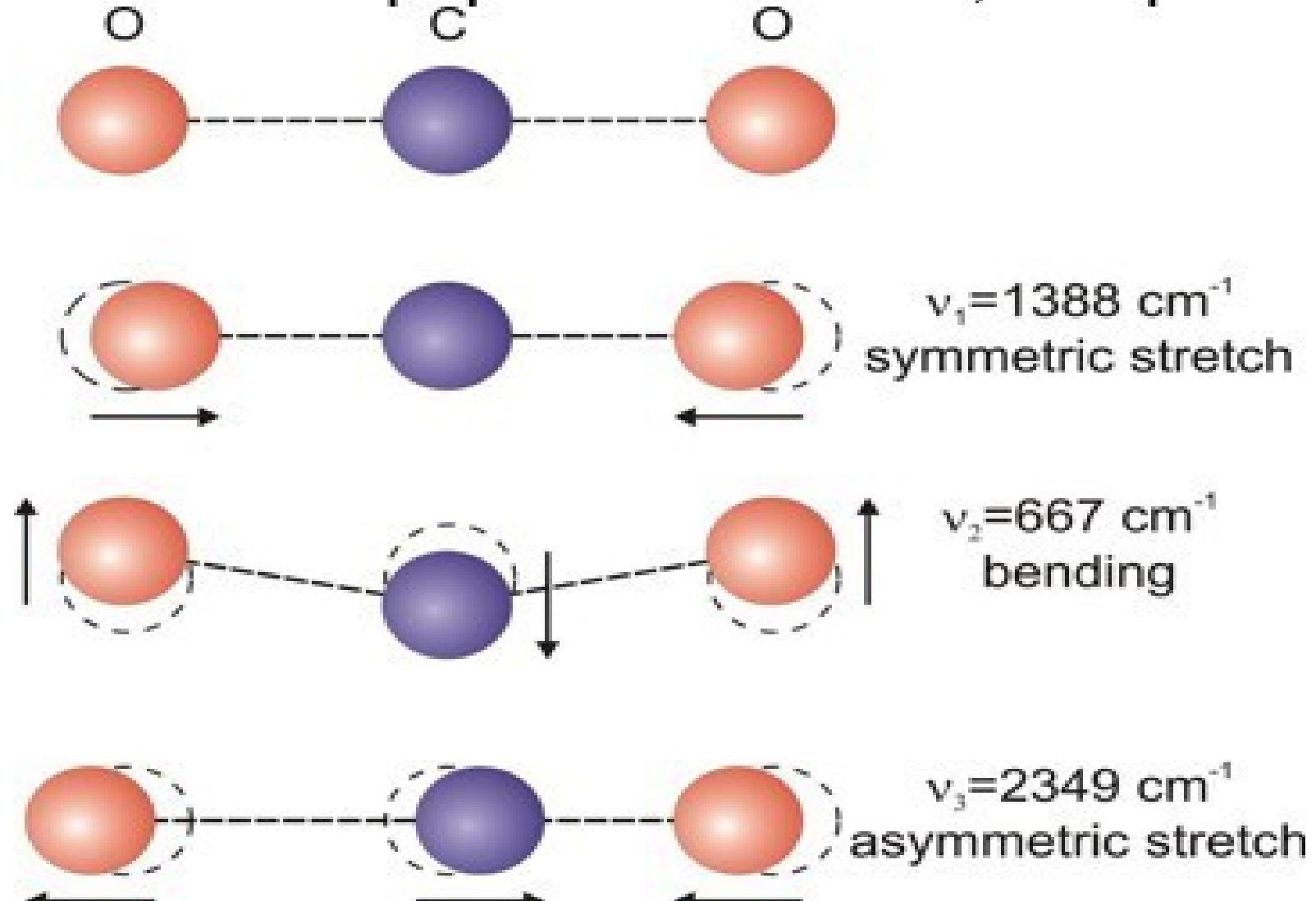
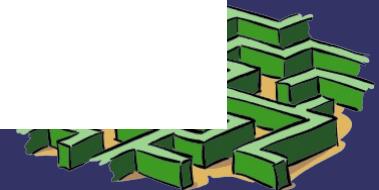
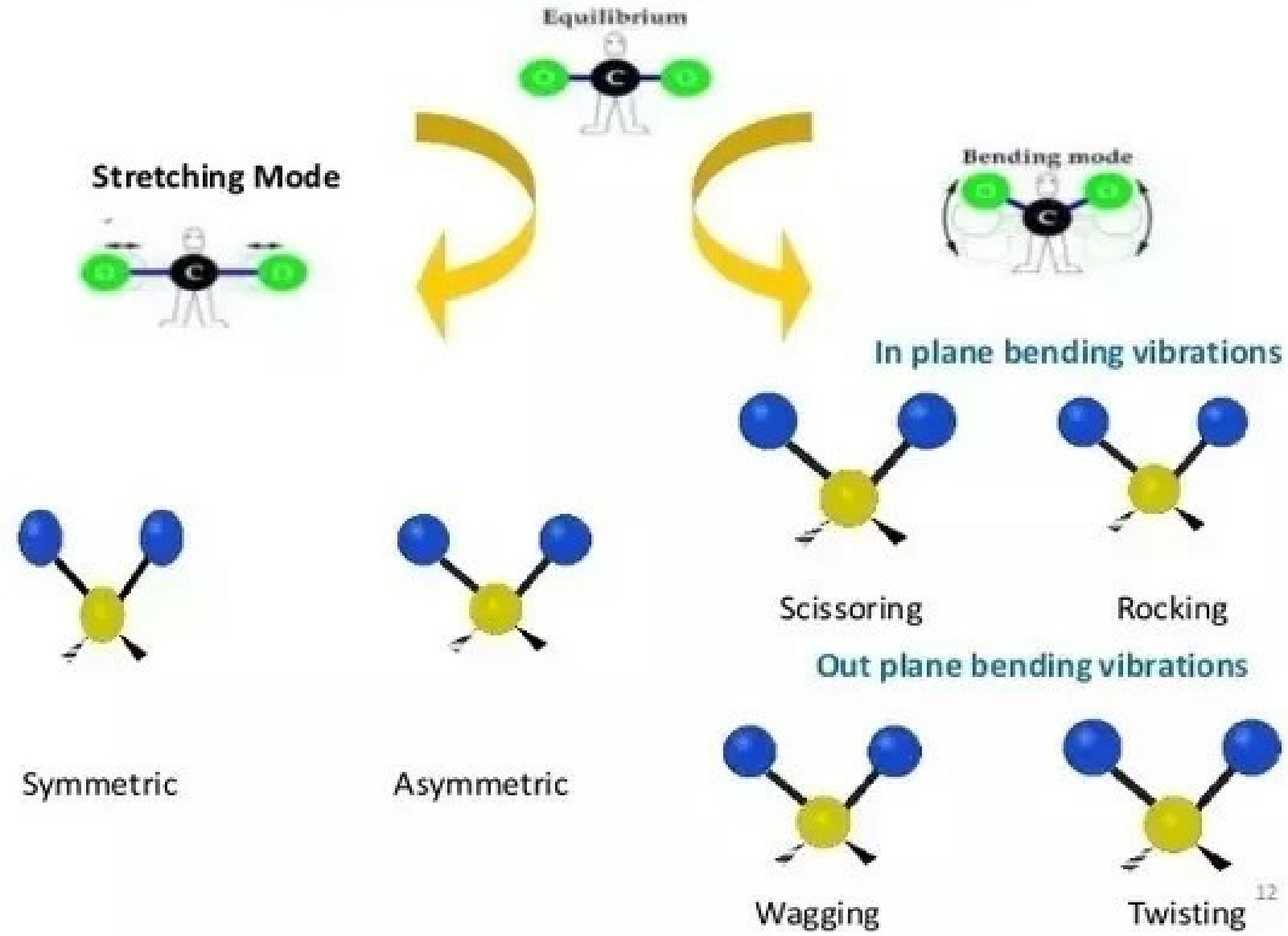


Image from <http://www.ino.it/~miomao/>

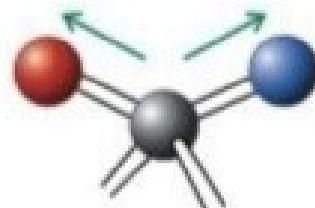


TYPES OF VIBRATIONS

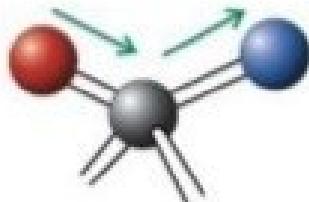


Many possible absorptions per molecule exist: stretching, bending,...

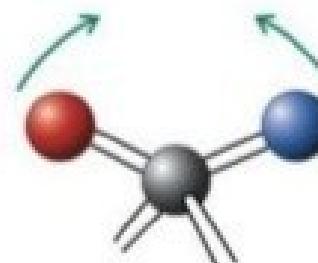
Vibrational modes leading to IR absorptions:



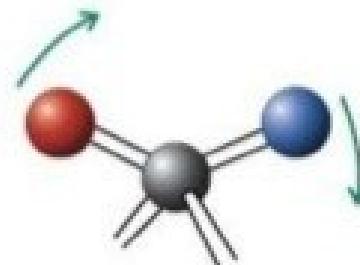
Symmetric stretching vibration (both outside atoms move away from or toward the center)



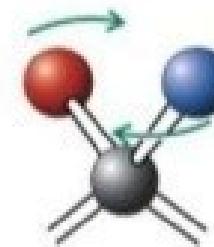
Asymmetric stretching vibration (as one atom moves toward the center, the other moves away)



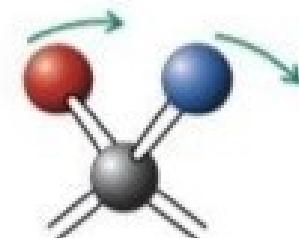
Symmetric bending vibration in a plane (scissoring)



Asymmetric bending vibration in a plane (rocking)



Symmetric bending vibration out of a plane (twisting)

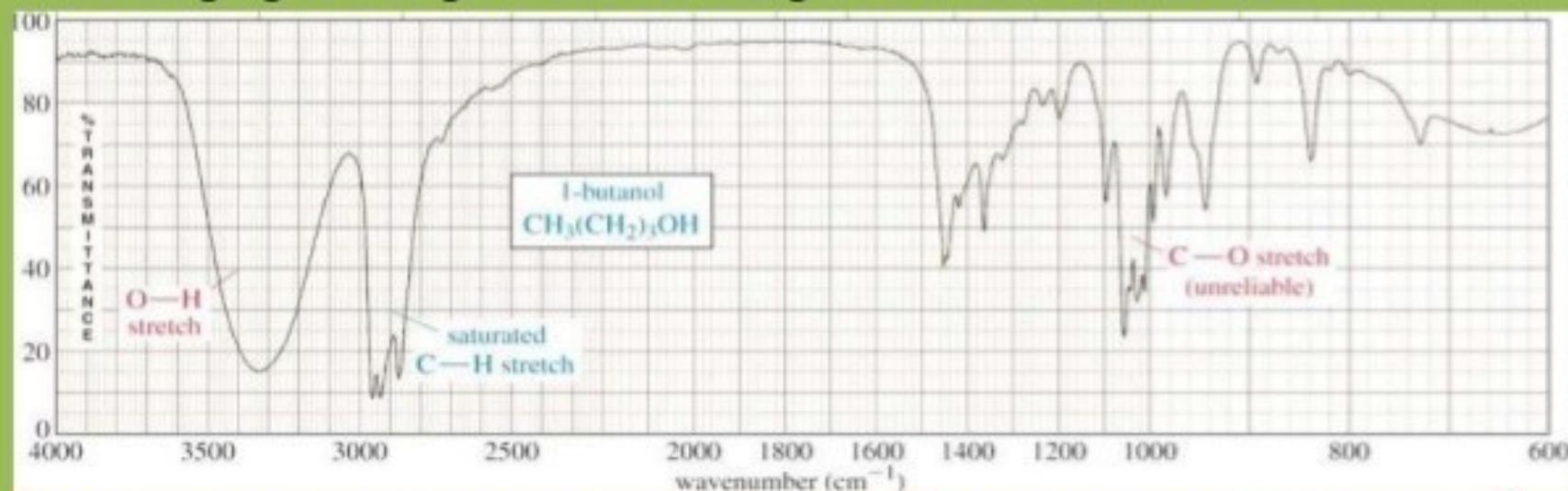


Asymmetric bending vibration out of a plane (wagging)

• The IR Spectrum

→ There are two type of IR Spectra from which we can obtained the information about the quality of molecule .

1. The Functional Group region: Identifies the functional group with the consequence of changing stretching vibrations. Ranges from 4000 to 1600 cm^{-1} .
2. The Fingerprint region: Identifies the exact molecule with the consequence of changing bending vibrations. Ranges from 1600 to 625 cm^{-1} .



Focus your analysis on this region. This is where most stretching frequencies appear

Fingerprint region: complex and difficult to interpret reliably



- **Interpretation of IR Spectra**

- Structural information about a compound is mainly derived from the presence or absence of characteristics absorption bands of various functional groups in the IR Spectrum of the compound.
- A knowledge of the band of all the major functional groups will be valuable. The band position of all the major structural bonding types have been determined in a tabular form. Characteristic absorption position of some of the more important common functional groups are presented in given table.
- This table is particularly useful for correlation when the spectrum of an unknown compound has been obtained.
- It is always more useful to make direct comparison with the spectra of closely related compound.



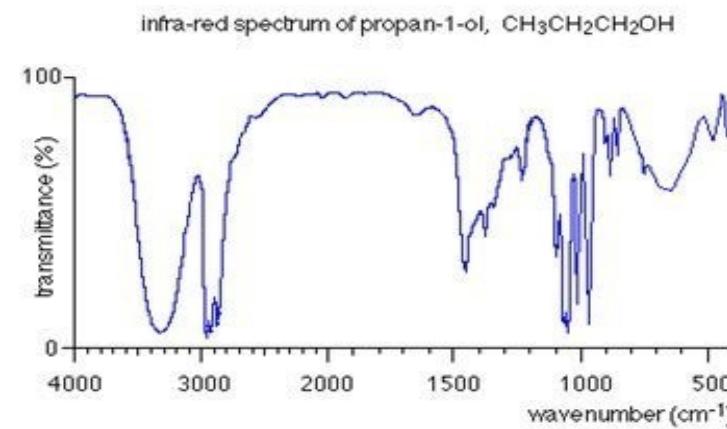
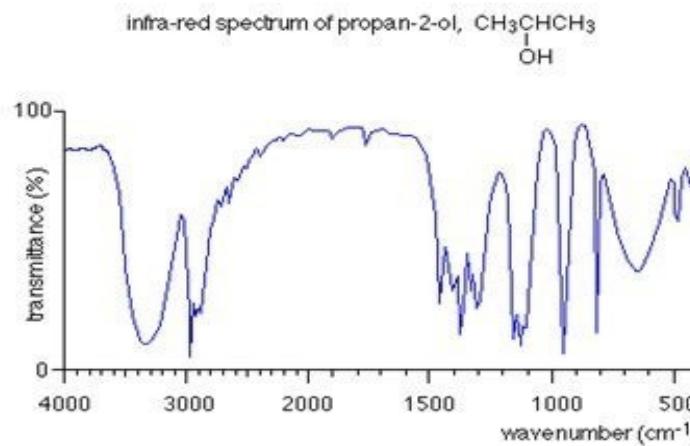
<i>Functional Group</i>	<i>Characteristic Absorption(s) (cm⁻¹)</i>
Alkyl C-H Stretch	2950 - 2850 (m or s)
Alkenyl C-H Stretch Alkenyl C=C Stretch	3100 - 3010 (m) 1680 - 1620 (v)
Alkynyl C-H Stretch Alkynyl C≡C Stretch	~3300 (s) 2260 - 2100 (v)
Aromatic C-H Stretch Aromatic C-H Bending Aromatic C=C Bending	~3030 (v) 860 - 680 (s) 1700 - 1500 (m,m)
Alcohol/Phenol O-H Stretch	3550 - 3200 (broad, s)
Carboxylic Acid O-H Stretch	3000 - 2500 (broad, v)
Amine N-H Stretch	3500 - 3300 (m)
Nitrile C≡N Stretch	2260 - 2220 (m)
Aldehyde C=O Stretch Ketone C=O Stretch Ester C=O Stretch Carboxylic Acid C=O Stretch Amide C=O Stretch	1740 - 1690 (s) 1750 - 1680 (s) 1750 - 1735 (s) 1780 - 1710 (s) 1690 - 1630 (s)
Amide N-H Stretch	3700 - 3500 (m)

s=strong, m=medium, w=weak, v=variable.



Fingerprint region

The **fingerprint region** is found on the right hand side of an infrared spectrum from about 1500-500 cm⁻¹. It can be used to compare two similar compounds.



Important areas of IR spectrum

A) Functional group region : { 4000-1300 cm⁻¹} This high frequency region corresponds to the characteristic stretching frequencies for N-H,O-H and C=O.

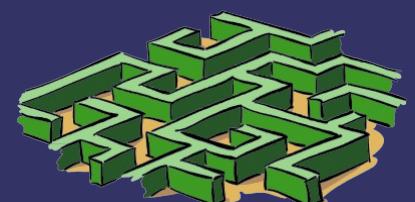
- ❖ The absence of absorption in this region indicates absence of these groups in molecule.

The presence of absorption in the 1850-1540 cm⁻¹ region indicates a structure containing a carbonyl group. Weak bands due to overtone and combination tone may appear in high frequency region.

Strong bands in 1600-1300 cm⁻¹ indicate the aromatic structures.

Broad,moderately strong bands in low frequency region suggest the presence of carboxylic dimers,amines,amides due to out of plane bending.

Olefinic structures show absorption near 1000 cm⁻¹.



B) Finger Print Region {1300-909 cm⁻¹}

1. In this region many peaks are observed and the pattern is complex,due to interacting vibrational modes.
2. A peak to peak match of an unknown spectrum with the spectrum of suspected compound in this region helps to assign structure.
3. This region is important when examined with reference to other regions .e.g. If alcoholic or phenolic OH stretching absorption appears in high frequency region and there is absorption band in 1260-1000 cm⁻¹ ,due to C-C-O bending then it makes possible to assign O-H absorption to alcohol or phenol with highly specific structure of compound.

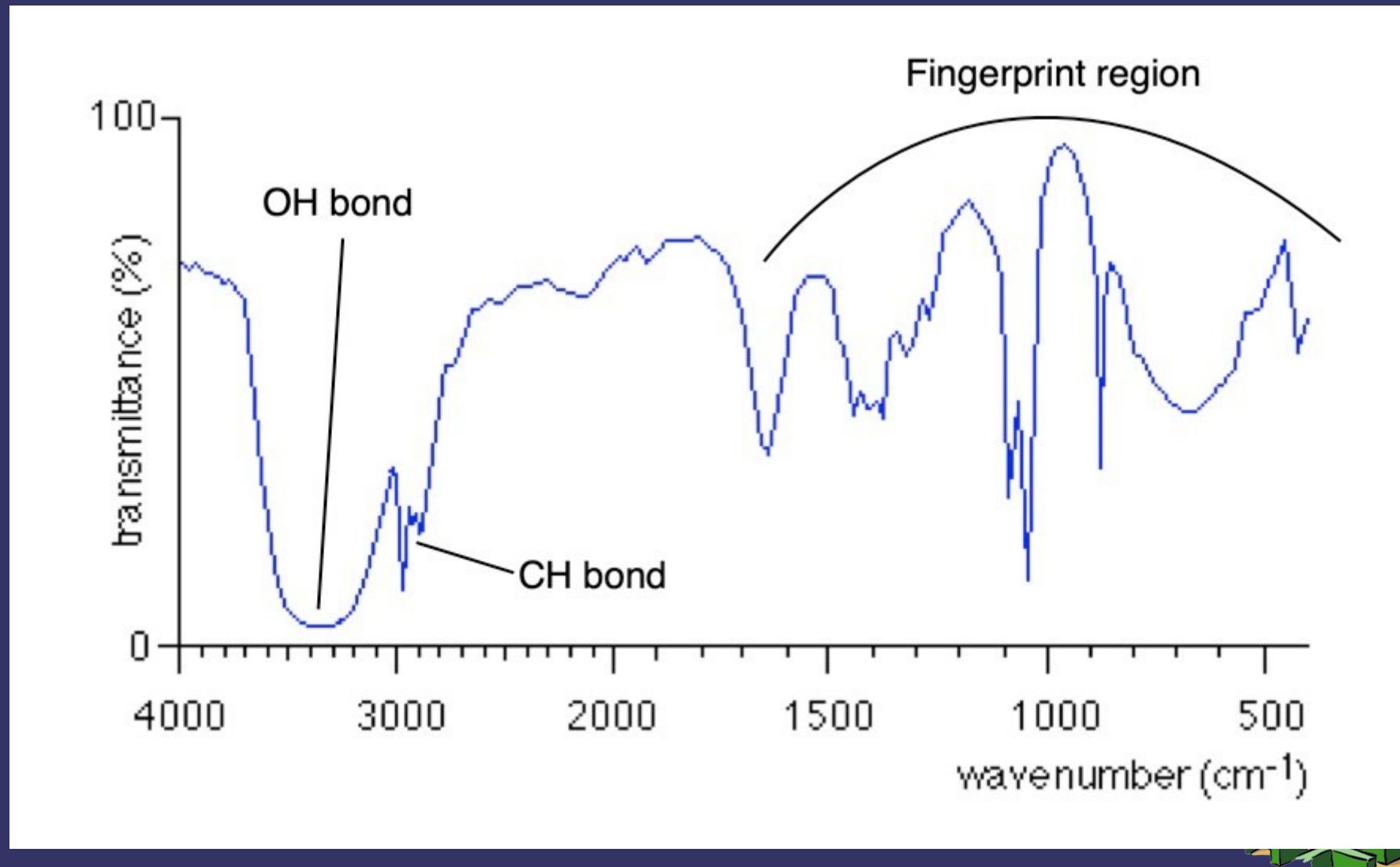


Any conclusion after examination of a particular band should be confirmed by examination of other portions of the spectrum e.g.if the carbonyl group band is observed near 1700 cm^{-1} and also a band or pair of bands are observed in $2900-2700\text{ cm}^{-1}$,it indicates that the carbonyl carbon has having hydrogen on it. i.e. The compound contains -
CHO aldehyde group.

Similarly a carbonyl absorption along with $1300-1100\text{ cm}^{-1}$ due to C-O stretch indicates presence of ester group in molecule.



IR spectrum

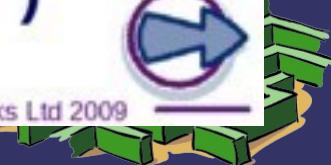
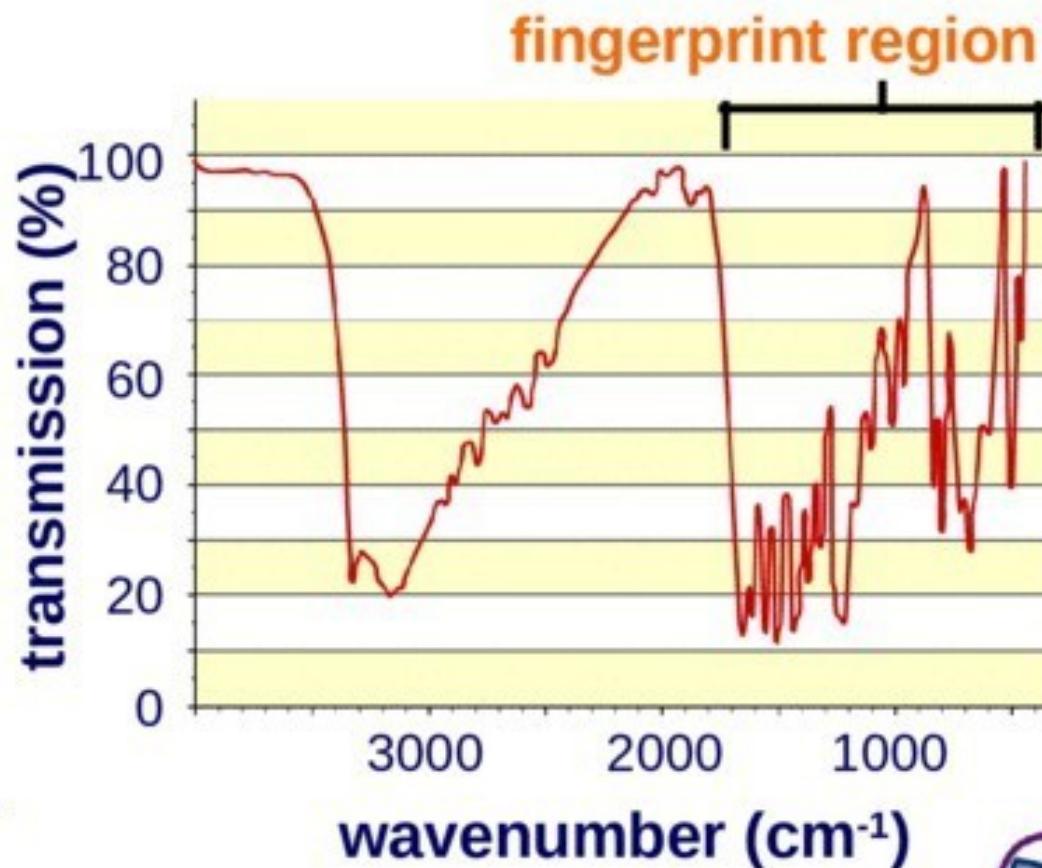


Using the fingerprint region

The region below 1500 cm^{-1} , usually called the **fingerprint region**, has many peaks that are difficult to assign. The pattern of these peaks is unique to a particular compound.

A substance may be identified by comparing the IR spectrum to a database of reference spectra.

An exact match in the fingerprint region identifies a compound.



APPLICATIONS OF IR SPECTROSCOPY

- Identification of functional groups & structure elucidation of organic compounds.
- Quantitative analysis of a number of organic compounds.
- Study of covalent bonds in molecules.
- Studying the progress of reactions.
- Detection of impurities in a compound.
- Ratio of cis-trans isomers in a mixture of compounds.
- Shape of symmetry of an inorganic molecule.
- Study the presence of water in a sample.
- Measurement of paints and varnishes.