

DR. A.P.J. ABDUL KALAM TECHNICAL UNIVERSITY, LUCKNOW

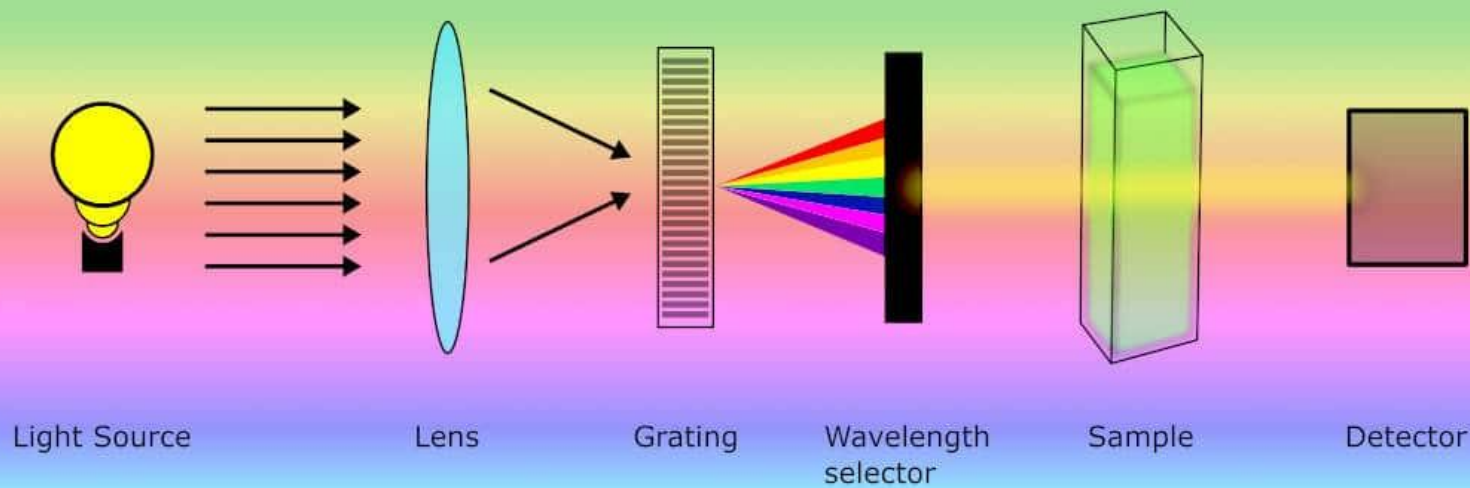


**ENGINEERING- CHEMISTRY (BAS- 102/ 202)
B. TECH. I YEAR**



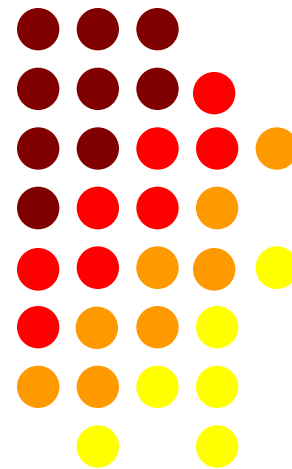
SPECTROSCOPIC TECHNIQUES AND APPLICATIONS





UV- Visible Spectroscopy

- Unit -2
- CO-2
- Lecture 9-12 (Video Lecture)
- Handbook of Engg. Chemistry, Pg. 1-9
- Engg. Chemistry by Sunita Ratan, Pg. 65-79
- Engg. Chemistry by Jain & Jain, Pg.1191-1194



Spectroscopy

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

Spectroscopy is used in physical and analytical chemistry to detect, determine, or quantify the molecular and/or structural composition of a sample. Each type of molecule and atom will reflect, absorb, or emit electromagnetic radiation in its own characteristic way.

Matter: Anything which occupies space in universe and having mass is called matter.

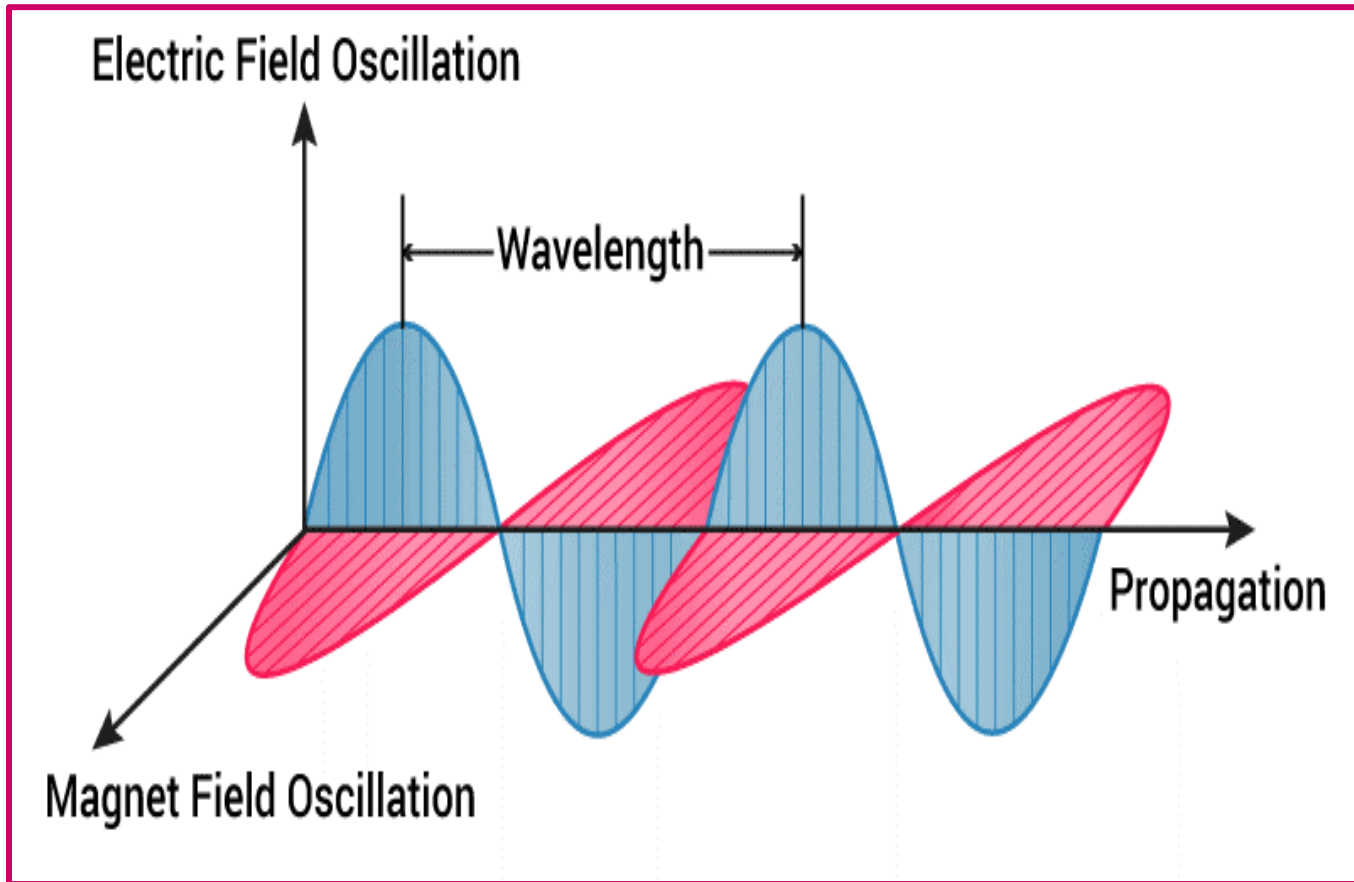


Electromagnetic radiation

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

- These are produced by the oscillation of electronic charge and magnetic field residing on an atom.
- These are characterized by their wavelengths or frequencies or wave number.





Electromagnetic radiation



Parameters of Electromagnetic radiation

Energy of a photon is given by:

$$E = h \nu$$

Since, $\nu = c / \lambda$

Therefore, $E = h c / \lambda$

Where h = Planck's constant ($6.626 \times 10^{-34} \text{ Js}^{-1}$)

λ = wavelength in m, cm, nm

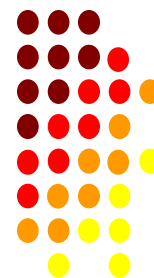
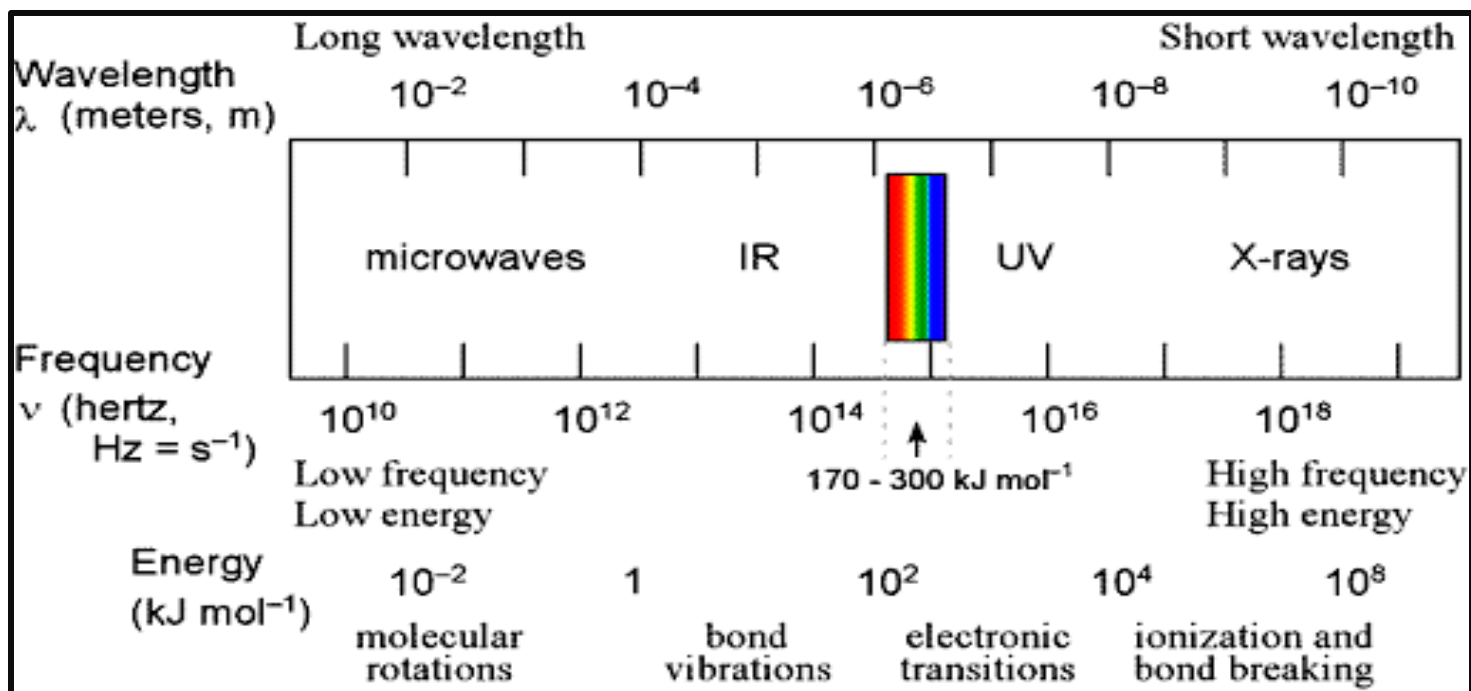
ν is the frequency in Hz, s^{-1} or vibration

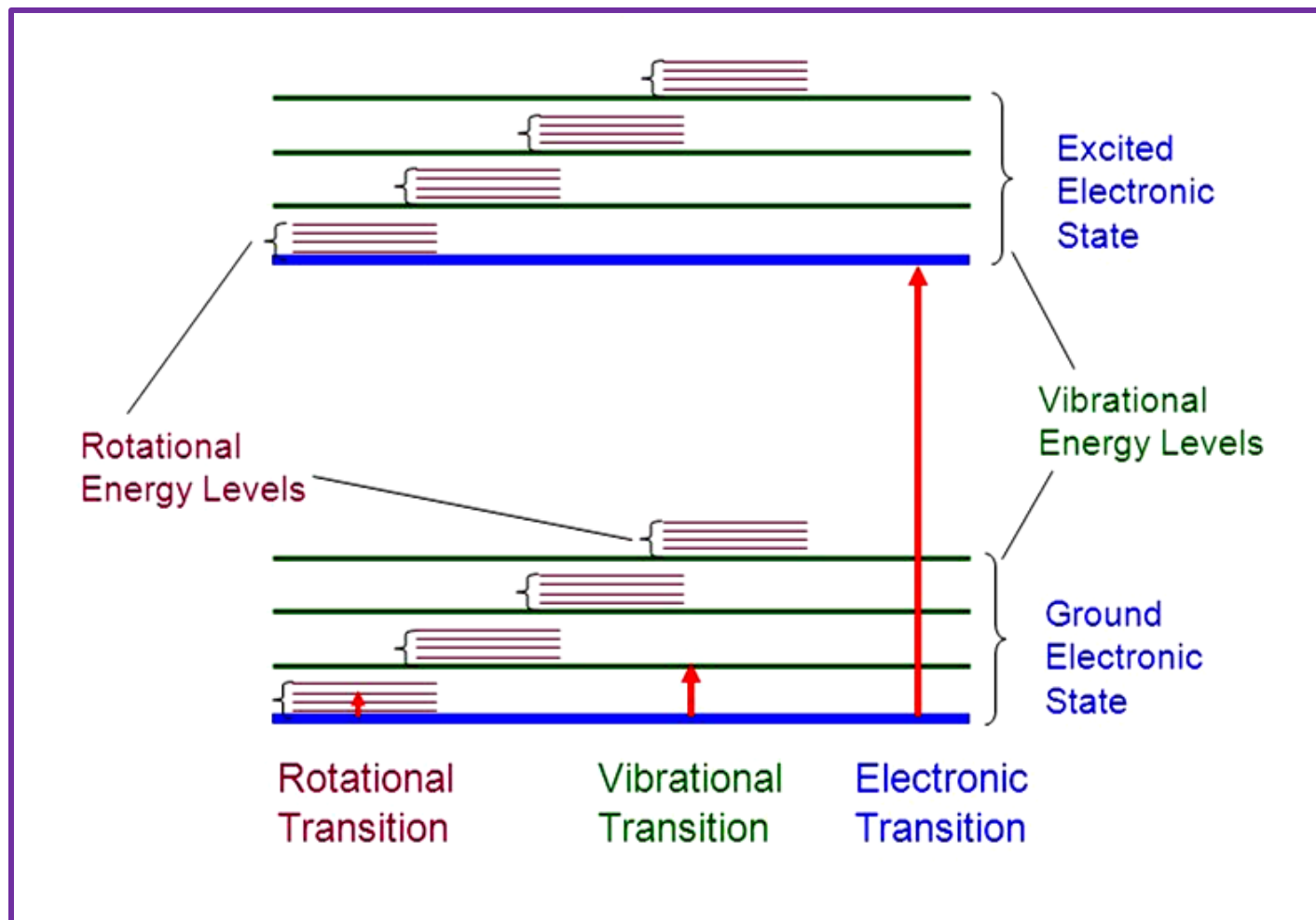
c is speed of light in vacuum = $2.99 \times 10^8 \text{ m/s}$



Electromagnetic spectrum

The arrangement of electromagnetic radiations according to increasing/decreasing wavelength or energy is known as electromagnetic spectrum.





Molecular Energy Levels



Types of Molecular Spectra

Spectroscopic technique	Process involved	EMR range applicable (nm)	Information gained about molecule	Information obtained
Electronic/ UV-Visible Spectroscopy (UV-Vis)	Absorption	390 nm - 750 nm	Electronic transition	Qualitative and quantitative information of matter
Vibrational/ Infrared Spectroscopy (IR)	Absorption	750 nm - 1 mm	Vibrational energy level spacing	Functional group, force constant, bond length, bond angle, Quantitative analysis
Nuclear Magnetic Resonance Spectroscopy (NMR)	Absorption	Radio frequency	Magnetic energy levels of nuclei	Structural determination (Peak area and proton count)



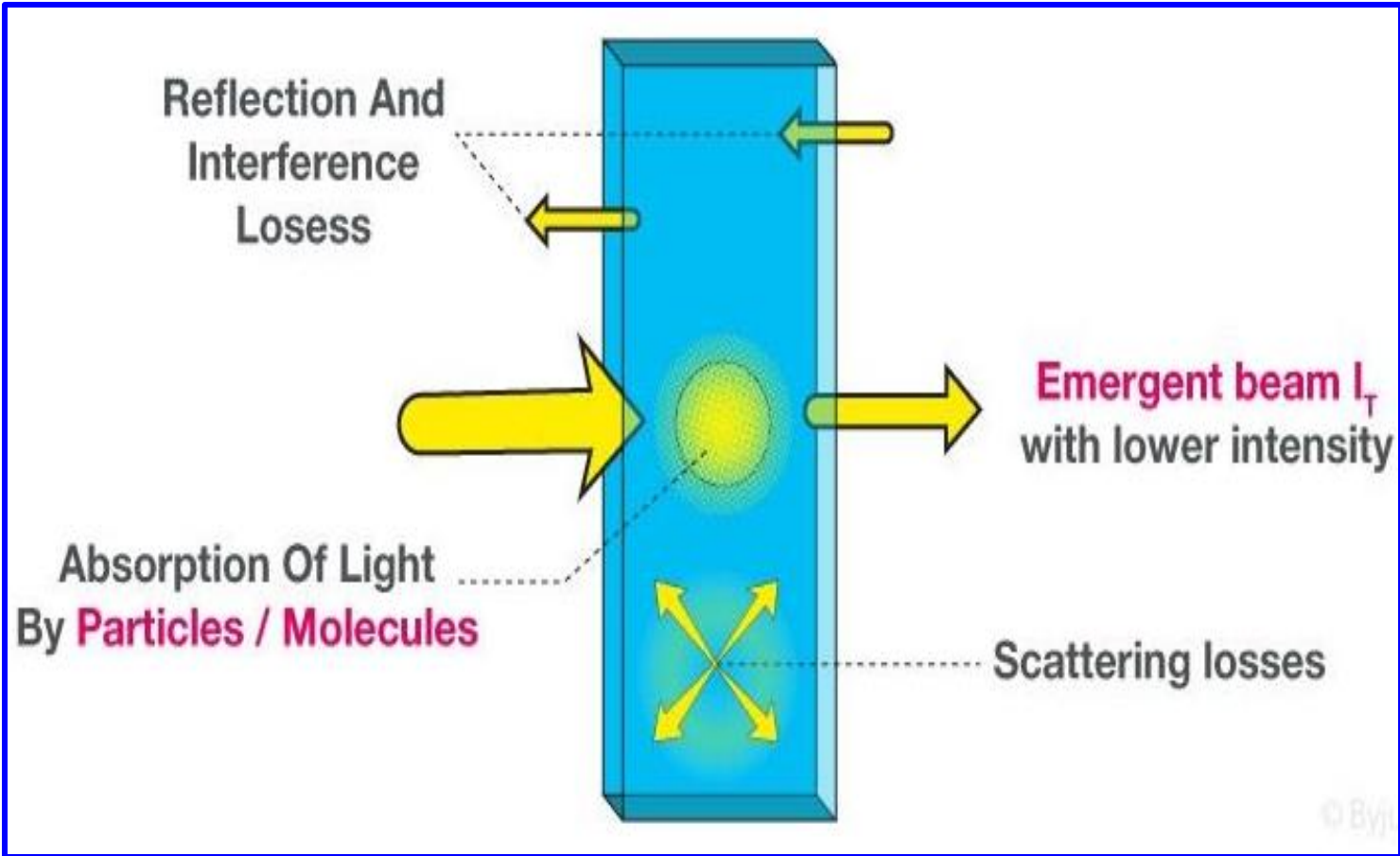
Beer-Lambert's Law:

It states that, when monochromatic radiations are passed through a homogeneous sample solution, then the absorbance of the sample is directly proportional to the concentration and path length of the sample.

$$A = \epsilon cl$$

Where A is the absorbance, c is the concentration of the molecule in mol/l or Molarity (M), and l is the path length of the sample cell in cm and ϵ is the molar absorptivity coefficient in $\text{cm}^2\text{mol}^{-1}$ or $\text{cm}^{-1}\text{M}^{-1}$.



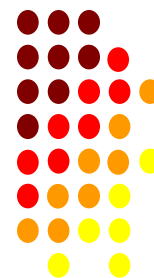


Also, Absorbance is logarithm of the reciprocal of transmittance. So,

$$A = \log_{10} (1/T) = \log_{10} (I_0/I)$$

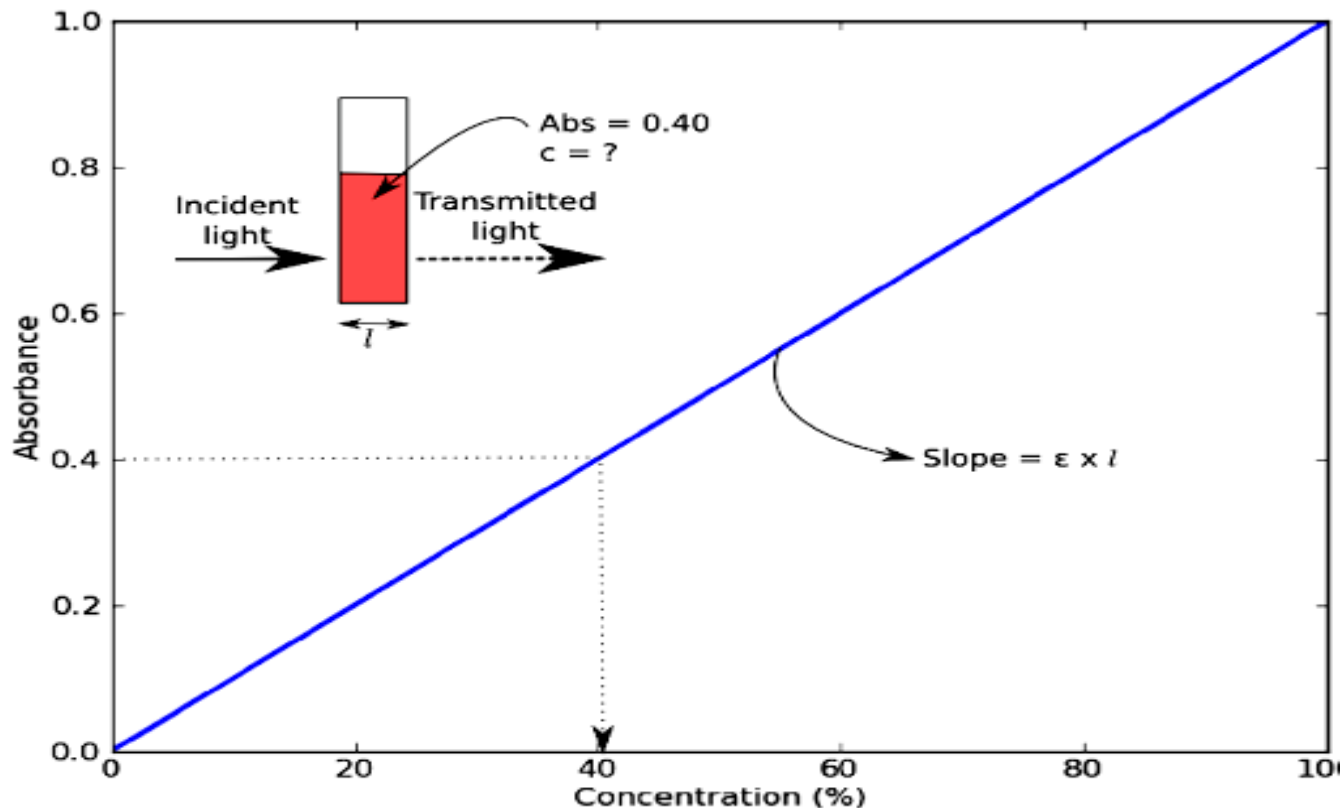
Where I_0 is the intensity of incident light, I is the intensity of transmitted light and T is transmittance.

The equation $A = \text{Log } I_0/I = \epsilon cl$ shows linear relationship between absorbance and concentration of the absorbing molecule (or chromophore).



Transmittance: It is the ratio of the intensity of light transmitted by a sample (I) to the intensity of the light incident on the sample (I_0).

$$T = I/I_0 \text{ and } \%T = I/I_0 \times 100$$



Derivation of Beer Lambert law

The decrease in the intensity of monochromatic radiation after passing through sample containing absorbing species is directly proportional to the incident intensity (I), thickness of the sample (dl) and concentration (c) of sample.

$$dI \propto -I \cdot c \cdot dl \quad \text{..... 1}$$

$$dI = -k \cdot I \cdot c \cdot dl \quad \text{..... 2}$$

Where constant k is called proportionality coefficient

$$\frac{dI}{I} = -k \cdot c \cdot dl \quad \text{..... 3}$$



At given concentration of the sample, the above equation can be integrated over 0 to l where l is the path length of the sample and I_0 to is incident intensity and I is the final intensity of transmitted light.

$$\int_{I_0}^I \frac{dI}{I} = -k \int_0^l c \cdot dl \quad \dots \dots \dots 4$$

$$\ln \frac{I}{I_0} = -kcl \quad \dots \dots \dots 5$$

$$\log_{10} \frac{I}{I_0} = -2.303kcl \quad \dots \dots \dots 6$$



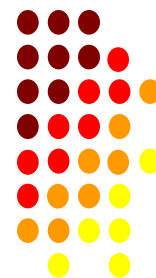
Converting \ln to \log base 10 by replacing $2.303k = \epsilon$

$$\log_{10} \frac{I}{I_0} = -\epsilon cl \quad \dots \dots \dots 7$$

Where constant ϵ is called absorptivity when concentration is in g/l, or molar extinction coefficient when concentration is in mole/l or molarity. It is the intrinsic property of the molecule which depends in wavelength.

The ratio of I/I_0 is equal to transmittance (T). Hence eq 5. Become

$$-\log_{10} T = \epsilon cl \quad \dots \dots \dots 8$$



This formula is the common form of the Beer-Lambert Law, although it can be also written in terms of absorbance (A)

$$A = -\log_{10} T = \epsilon cl \quad \dots \dots \dots 9$$

➤ An absorbance $A=0$ at some wavelength means that no light of that particular wavelength has been absorbed. It means output intensity will be equal to incident intensity of radiation.

Transmittance (T) is simply the ratio of the intensity of the radiation transmitted through the sample to that of the incident radiation which can also be represented as percentage transmittance (%T) as follows

$$\%T = T \times 100 = \frac{I}{I_0} \times 100$$



Limitations of Beer-Lambert law:

- **High sample concentration:** The Beer-Lambert law generally holds good only for dilute solutions. At higher concentrations, the molecules come in close proximity thereby influencing their electronic properties.
- **Chemical reactions:** If a molecule undergoes a chemical reaction and the spectroscopic properties of the reacted and unreacted molecules differ, a deviation from Beer-Lambert law is observed.
- **Instrumental factors:** As ϵ is a function of wavelength, Beer-Lambert law holds good only for monochromatic light. Use of polychromatic radiation will result in deviation for linearity between absorbance and concentration.



Numericals

Q1. A compound having concentration 10^{-3} g/l resulted absorbance value 0.20 at λ_{\max} 510 nm using 1 cm cell. Calculate its absorptivity and molar absorptivity values. Molecular weight of compound is 400.

Ans: Given: $c = 10^{-3}$ g/l; $l = 1$ cm; $A = 0.20$

$$A = \epsilon c l$$

$$\epsilon = A/c l = 0.20/10^{-3} \times 1 = 200 \text{ g l}^{-1} \text{ cm}^{-1}$$

Molecular wt. of compound = 400

Molar conc. $c_M = 10^{-3} / 400 = 0.25 \times 10^{-5} \text{ mol/l}$

$$A = \epsilon_m c_M l \quad \text{or} \quad \epsilon_m = A / c_M l$$

$$= 0.20 / 0.25 \times 10^{-5} \times 1 = 8 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$$



Q2: The molar absorption coefficient of tyrosine in water is $1280 \text{ M}^{-1}\text{cm}^{-1}$ at 280 nm. Calculate the concentration of a tyrosine solution in water if the absorbance of the solution is 0.34 in a 1 cm path length cell.

Ans: Given:

$$\lambda = 280 \text{ nm}; \epsilon = 1280 \text{ M}^{-1}\text{cm}^{-1}; l = 1 \text{ cm}; A = 0.34$$

From Beer-Lambert Law,

$$A = \epsilon cl$$

$$\begin{aligned} c &= A/\epsilon l = 0.32 / (1280 \text{ M}^{-1} \text{ cm}^{-1} \times 1 \text{ cm}) \\ &= 0.00025 \text{ M} = 250 \mu\text{M} \end{aligned}$$



Q3: Calculate absorbance if (%T) i.e. percentage transmittance of a solution is 80.

Ans. $A = \log (1/T) = \log(I_0/I) = \log 100/80 = 0.097$

Q4: When U.V. Light is passed through a solution, the radiant power is reduced to 50%. Calculate the absorbance.

Ans: Let radiant power of U.V. Light passed through the solution be P_0 .

So, if P is the radiant power of emitted light then,

$$P = 50/100 P_0$$

$$P = 0.5 P_0$$



Therefore, Absorbance will be given by,

$$A = \log \frac{P_0}{P}$$

$$= \log \frac{P_0}{0.5 P_0}$$

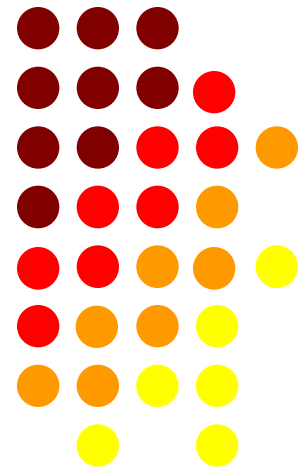
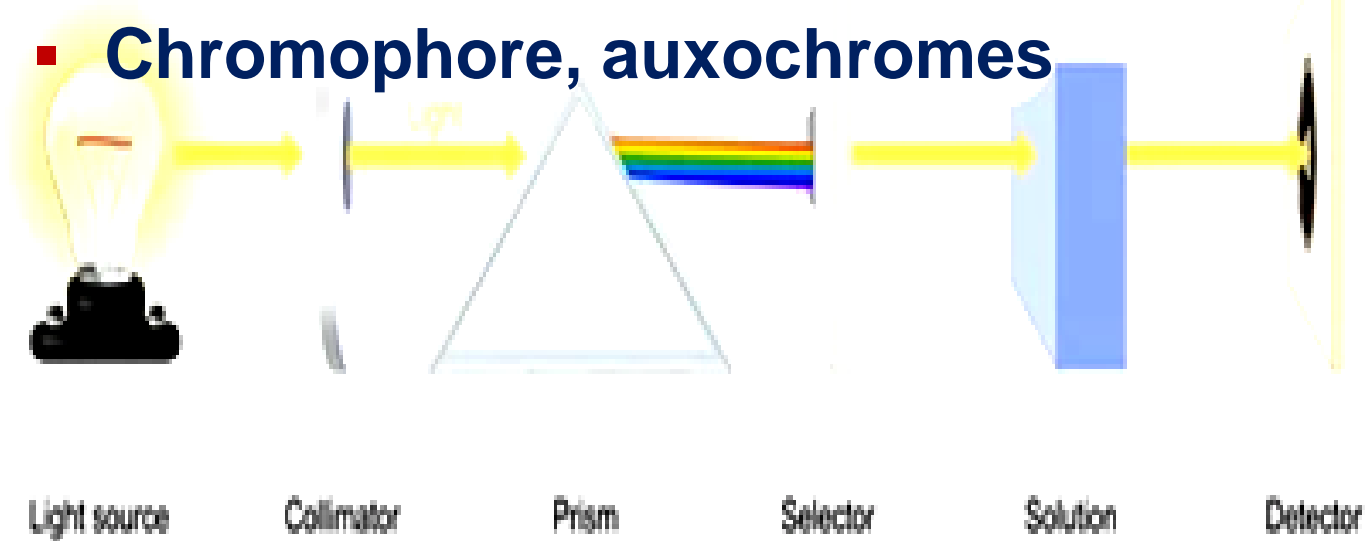
$$= \log 2$$

$$= 0.301$$



LECTURE - 11

- Principle of UV-Visible spectroscopy
- Types of electronic transitions
- Chromophore, auxochromes



Ultra Violet- Visible Spectroscopy

UV-visible spectroscopy is concerned with the study of absorption of UV-visible radiations which ranges from 200 to 800 nm (200-400nm- UV, 400-800 nm- visible).

UV region is divided into:

Type of electrons in a molecule	Orbitals involved
Near UV	250 nm – 400 nm
Far UV region	190 nm – 250 nm
Vacuum UV region	< 190 nm

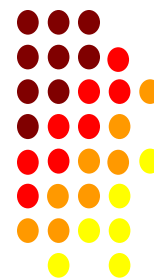
Ordinary UV-Visible measurements are carried out from about 200nm to 800 nm. Below 200nm, the measurements are done under vacuum to avoid absorbance signals from air components like CO₂. Therefore, region below 200 nm is called vacuum UV.



Type of electrons in molecule

Type of electrons in a molecule	Orbitals involved	Type of molecule
σ bonded electrons	σ orbital	Saturated compounds
π bonded electrons	π orbital	Unsaturated compounds
n (non bonded) electrons	Non bonding orbital	Compounds with atoms having lone pair of electrons

The UV spectrum of a compound gives information about its electronic structure. In other words, a sample with π electrons, with π bonds, with lone pairs, with conjugation, will show characteristic absorption of UV light.



Various Electronic transition on molecule

Various transitions that are possible in a compound on absorption of UV-Vis rays are as follows:

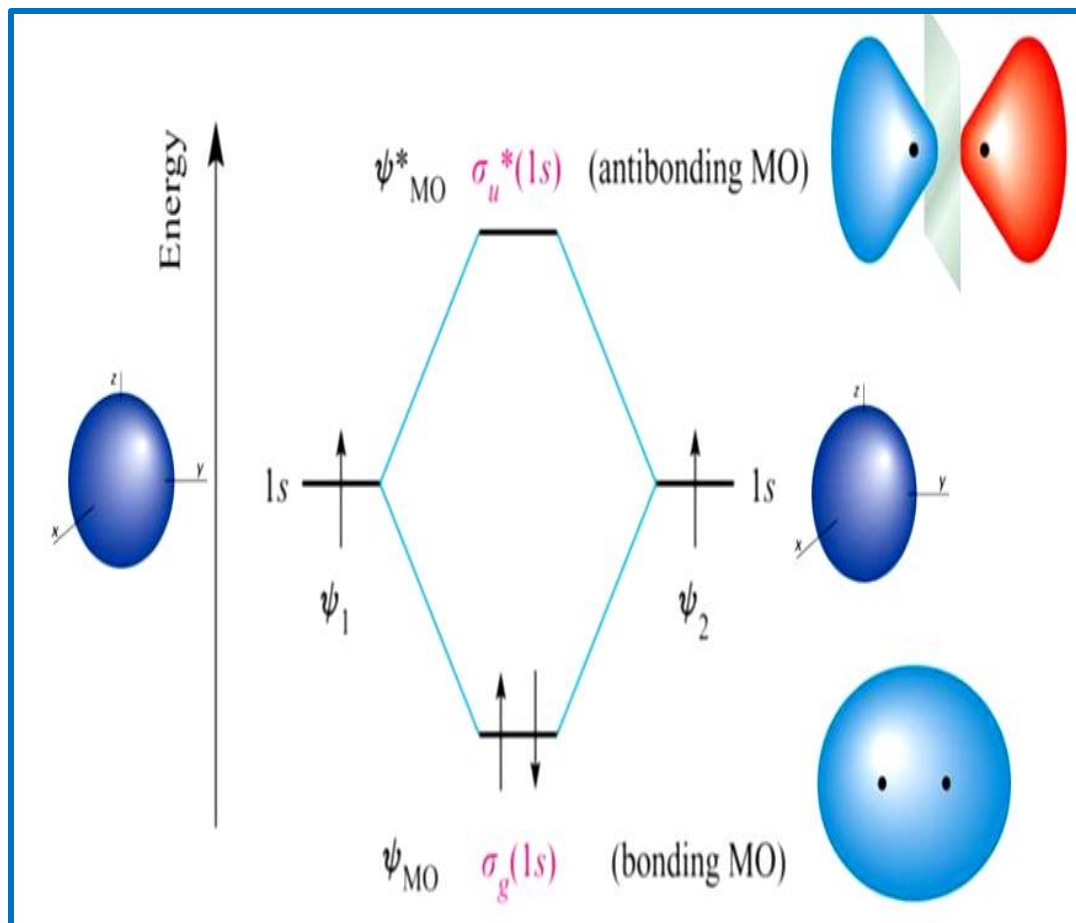
1. $\sigma \rightarrow \sigma^*$ transition:

- $\sigma \rightarrow \sigma^*$ transition is a high energy process.
- σ electrons are strongly held, so require high energy for transition.
- lies in the vacuum UV region.
- electron from σ orbital is excited to corresponding anti-bonding orbital σ^* .



- Alkanes, wherein only $\sigma \rightarrow \sigma^*$ transition is possible show absorption bands ~ 150 nm wavelength.

- e.g. Methane (CH_4) has four C-H bonds only and thus can undergo $\sigma \rightarrow \sigma^*$ transitions. It gives 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.*
- *In an aliphatic ketone, for example, the absorption band around 185 nm arises due to the $\pi \rightarrow \pi^*$ transition in the carbonyl group.*



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).*



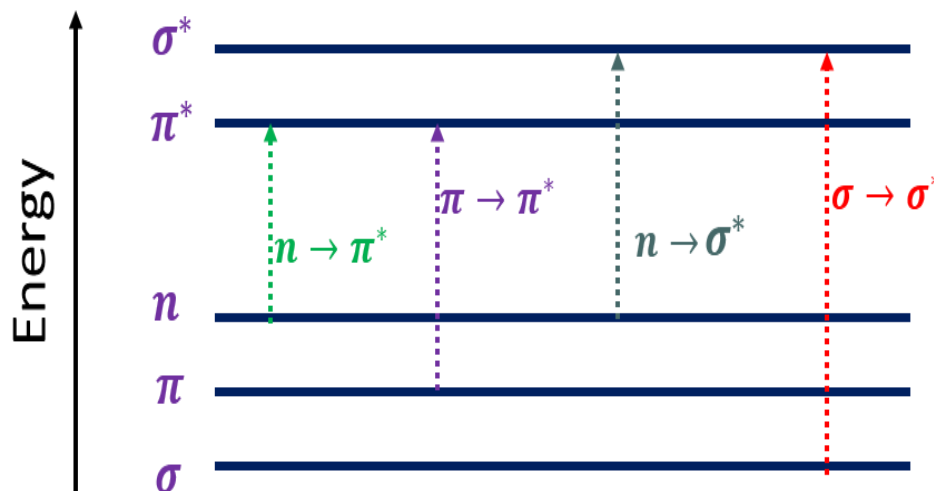
4. $n \rightarrow \pi^*$ transition:

- *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.*

Sequence of photon energy required for various electronic transitions are:



All observed electronic transitions



Forbidden Transition ($\sigma \rightarrow \pi^*$ & $\pi \rightarrow \sigma^*$)

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

Thus, only $n \rightarrow \pi^*$ & $\pi \rightarrow \pi^*$ electronic transitions show absorption in region above 200 nm which is accessible to UV-visible spectrophotometer.



Chromophore

Generally, the part of a molecule responsible for imparting colour, is known as chromophore.

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

They may or may not impart the colour to the molecule but absorbs the radiations between 200- 800 nm. 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.



Auxochrome:

- It is a group which itself does not act as a chromophore but when attached to a chromophore, it shifts the adsorption towards longer wavelength along with an increase in the intensity of absorption.
- All auxochromes have one or more non-bonding pairs of electrons.
- If an auxochromes is attached to a chromophore, it helps is extending the conjugation by sharing of non-bonding pair of electrons.



Some commonly known auxochromic groups are: -OH, -NH₂, -OR, -NHR, and -NR₂.

For example:

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

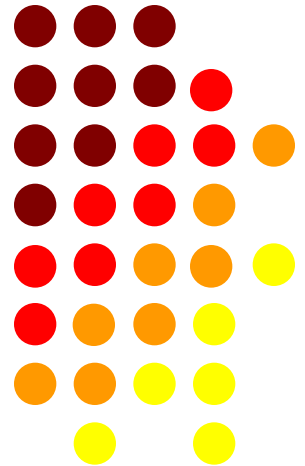
Phenol: -OH group attached to benzene,
 $\lambda_{\max} = 270 \text{ nm}$

Aniline: -NH₂ group attached to benzene,
 $\lambda_{\max} = 280 \text{ nm}$



LECTURE - 12

- Absorption and Intensity shifts.
- Factors causing shifts.
- Application of UV- Visible spectroscopy.

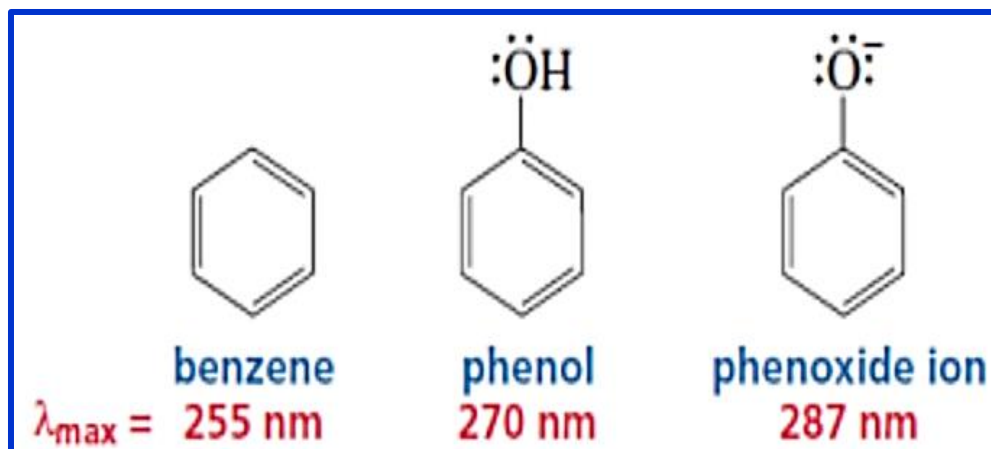


ABSORPTION AND INTENSITY SHIFTS:

1. Bathochromic Shift (Red Shift)

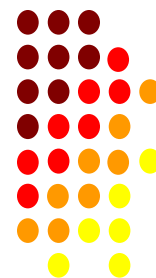
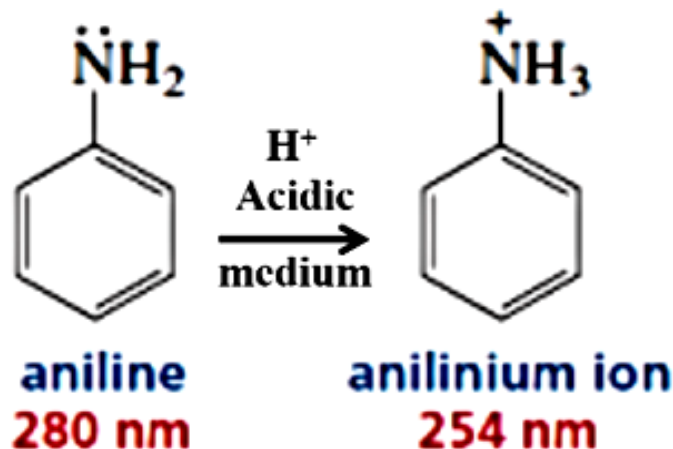
- *When absorption maxima (λ_{max}) of a compound shifts to longer wavelength, it is known as bathochromic shift or red shift.*
- *The effect is due to presence of an auxochrome or by the change of solvent. e.g. an auxochrome*

▪ *Group like – OH, –OCH₃ causes absorption of compound at longer wavelength.*



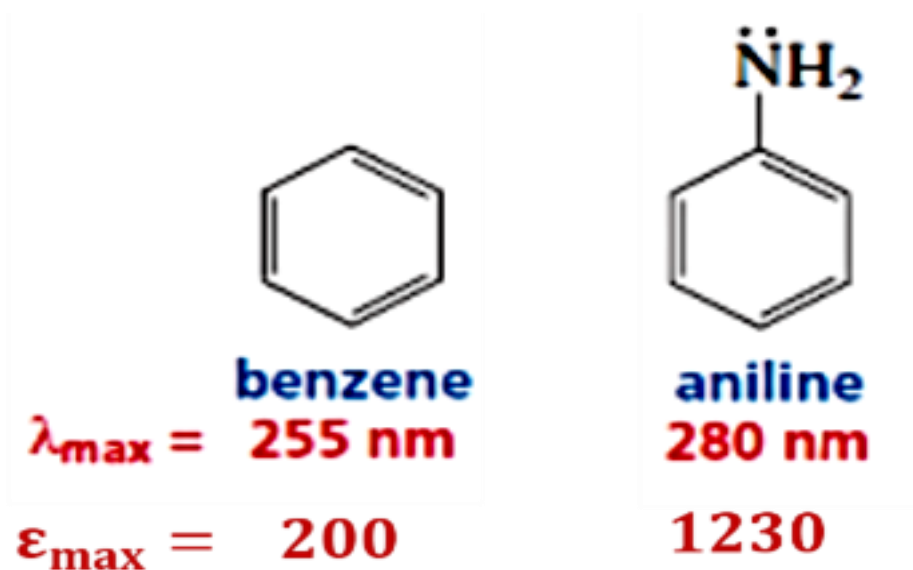
2. Hypsochromic Shift (Blue Shift)

- 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 removal of an auxochromic group which causes the removal of conjugation or by the change of solvent. e.g.: Aniline shows blue shift in acidic medium, since it loses conjugation.



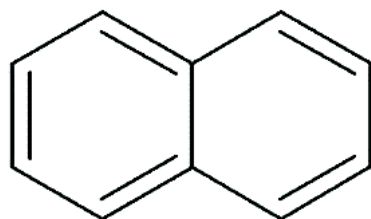
3. Hyperchromic Effect:

- 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.

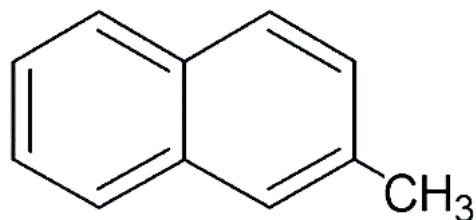


4. Hypochromic Effect:

- When absorption intensity (ϵ) of a compound is decreased, it is known as hypochromic shift.
- This is caused by the introduction of a group which distorts the chromophore by forcing the rings out of coplanarity resulting in the loss of conjugation.



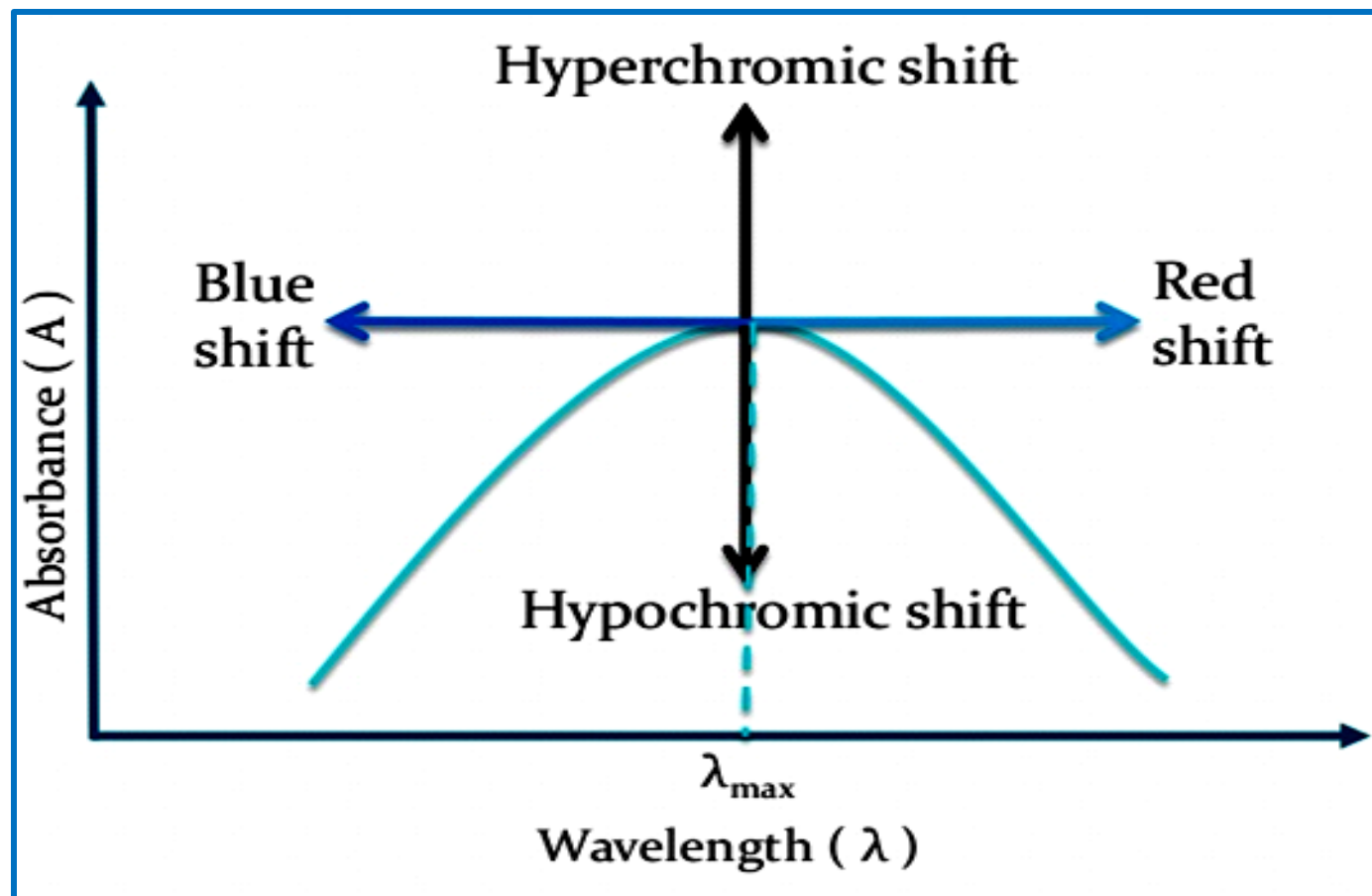
Naphthalene
 $\epsilon = 19000$



2-methyl naphthalene
 $\epsilon = 10250$

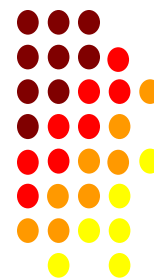
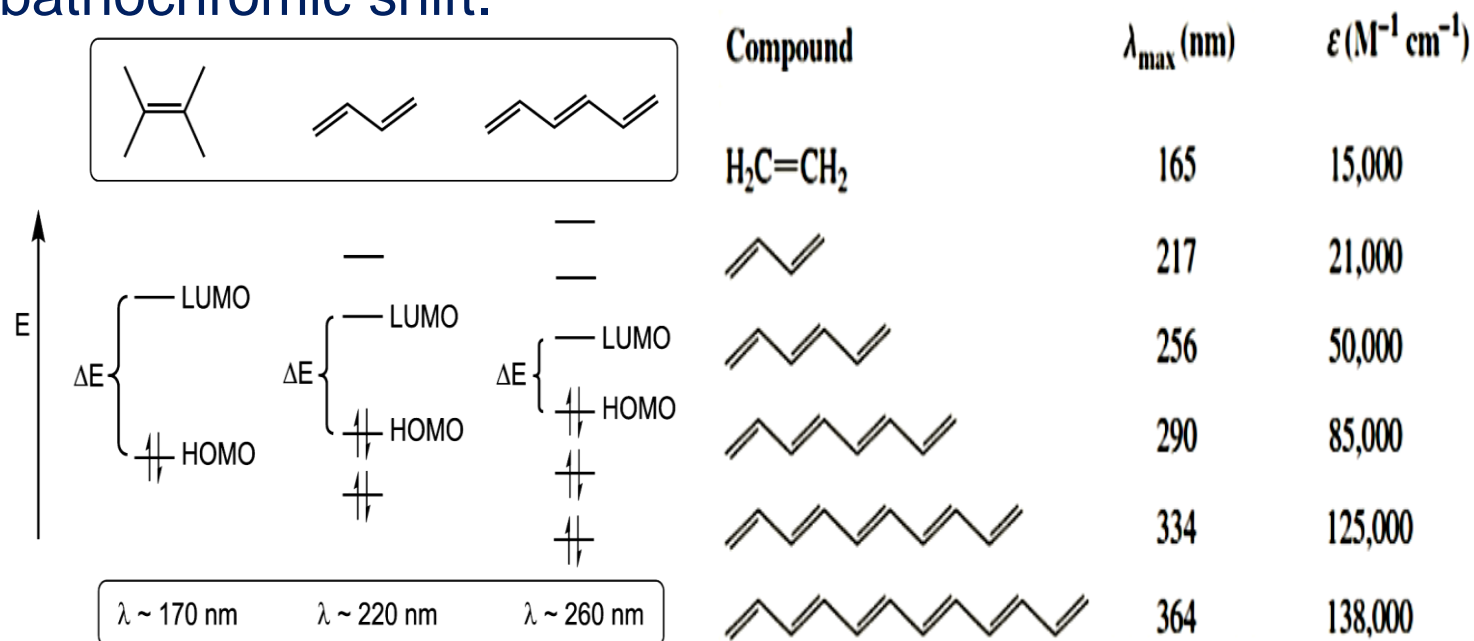


Summary of different shift in Absorption spectra



Factors responsible for shifts in UV-Vis spectroscopy:

1. Conjugation: The higher the extent of conjugation, the more is the bathochromic shift. This results in the bathochromic shift.



Auxochrome:

- Auxochromes are the chemical groups that result in a bathochromic shift when attached to a chromophore.
- They exhibit bathochromism by extending conjugation through resonance.

Solvents effect:

- The solvents used in any spectroscopic method should ideally be transparent (non-absorbing) to the electromagnetic radiation being used.

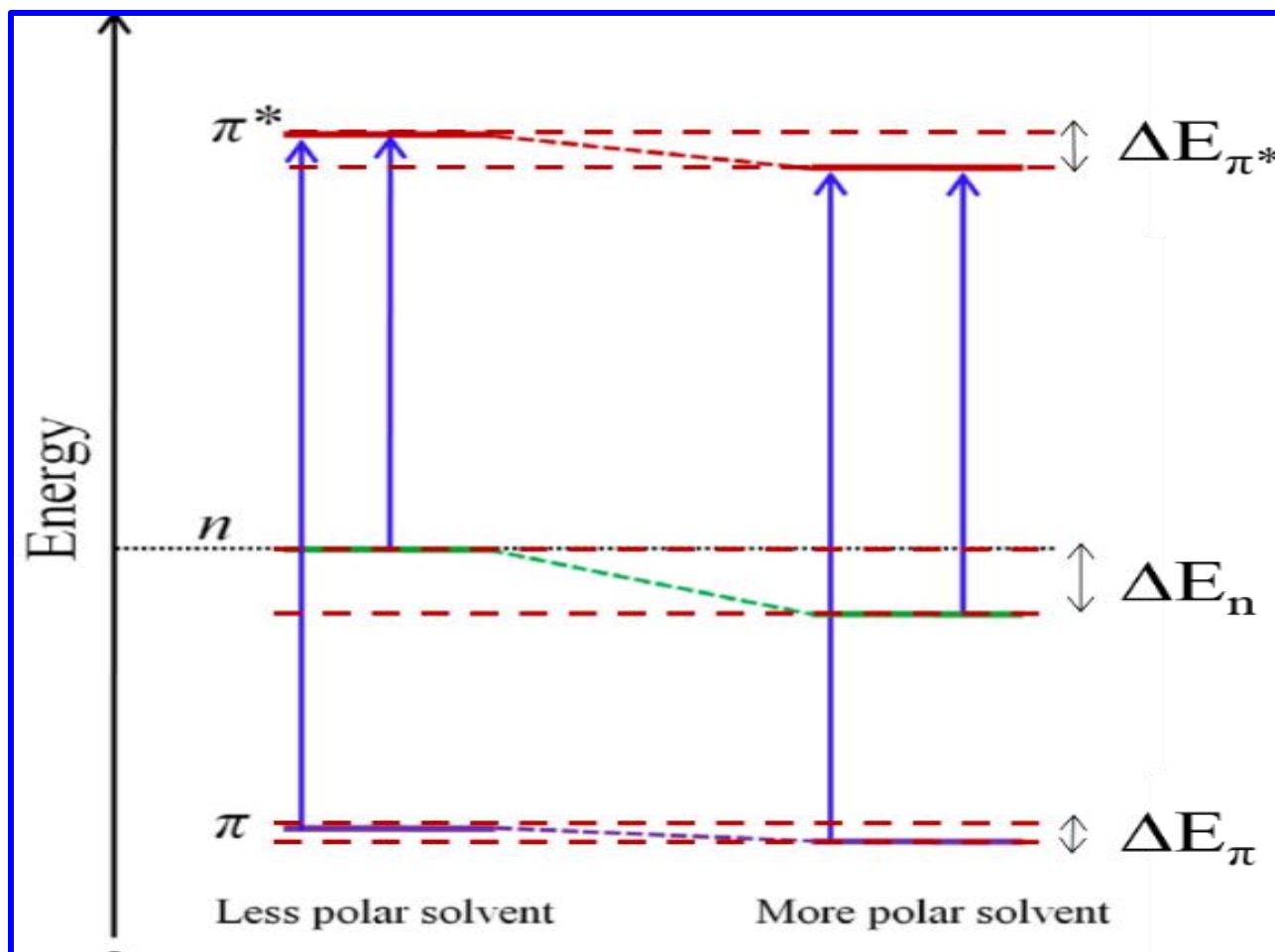


- The polarity of solvents is an important factor in causing shifts in the absorption spectra. This is because polar solvents stabilize all the three molecular orbitals (n , π , and π^*).
- Nonbonding orbital (n) stabilizes more than antibonding π^* orbital and bonding π orbital as shown in the following figure.
- Following is the order of decrease in energy of respective molecular orbital in polar solvent.

$$\Delta E_{\pi} < \Delta E_{\pi^*} < \Delta E_n$$

- Thus two electronic transitions $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respond differently to the changes in polarity.





$$\Delta E_{n \rightarrow \pi^*}^{\text{nonpolar}} < \Delta E_{n \rightarrow \pi^*}^{\text{polar}}$$

$$\Delta E_{\pi \rightarrow \pi^*}^{\text{polar}} < \Delta E_{\pi \rightarrow \pi^*}^{\text{nonpolar}}$$



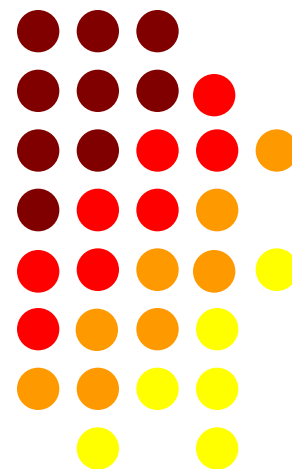
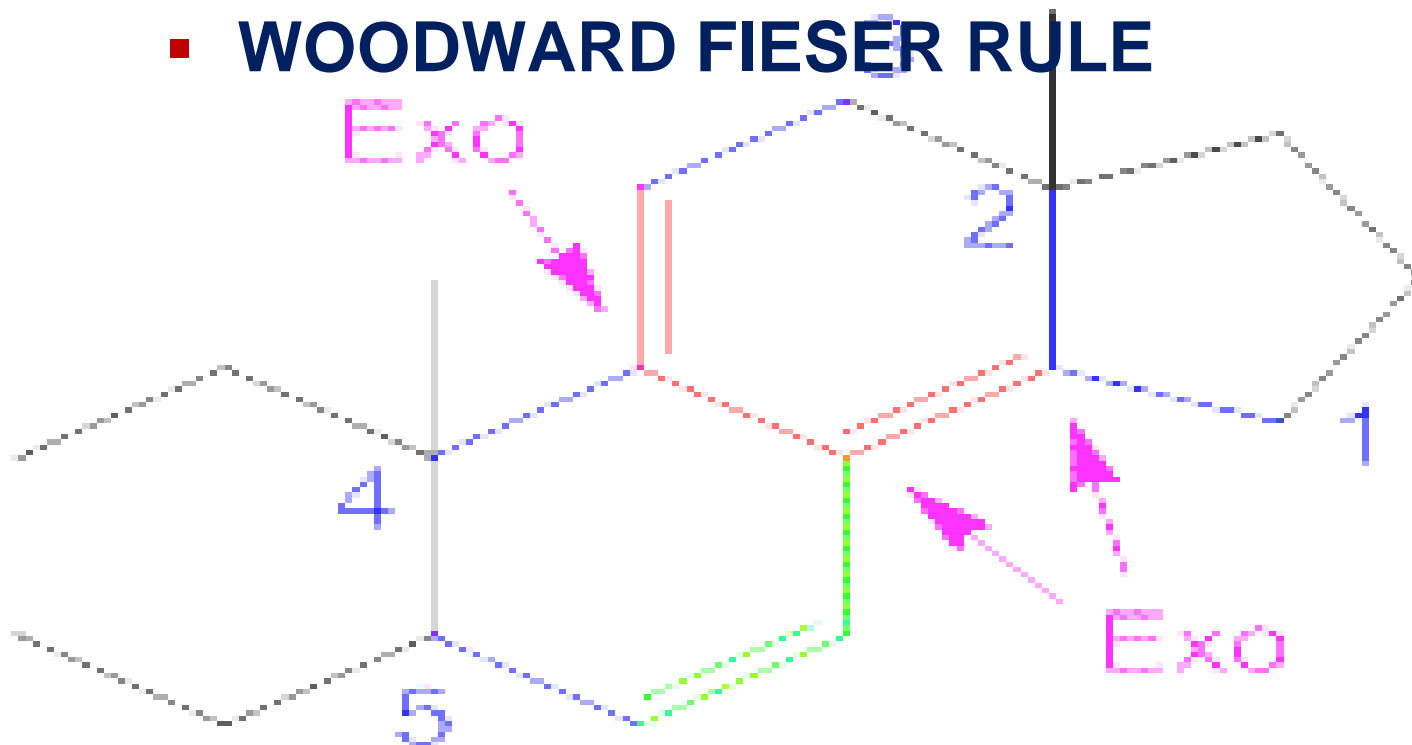
APPLICATIONS OF UV - Vis SPECTROSCOPY

- Qualitative & Quantitative Analysis:
- It is used for characterizing aromatic compound 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 .



LECTURE - 13

■ WOODWARD FIESER RULE



Woodward Fieser Rule

- Applicable for conjugated diene
- Applicable to conjugated carbonyl compound

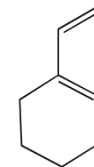
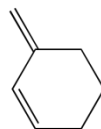
1. Type of conjugated diene

Acyclic diene

Base value: 217 nm



or

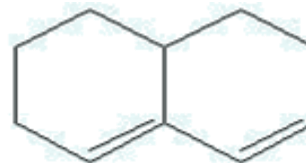


Homoannular Diene



Base Value =
253 nm

Heteroannular Diene

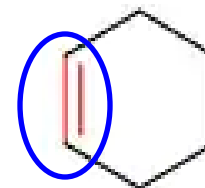


Base Value
= 214 nm

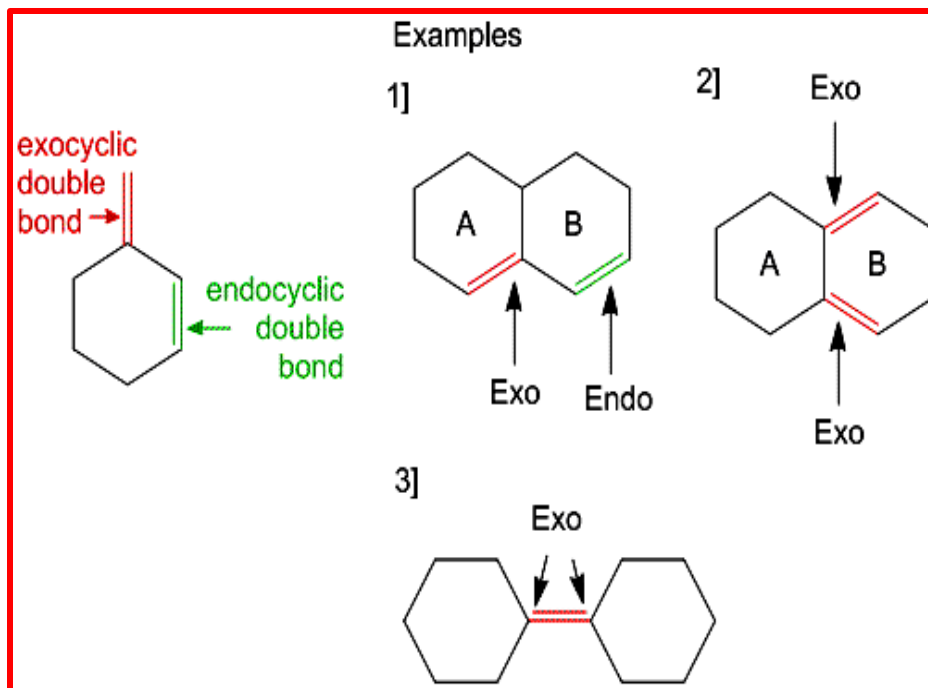


2. Type of double bond characteristic

Endocyclic double bond: Any double bond where both the carbon is a part of ring or cyclic structure concerned called endocyclic double bond.

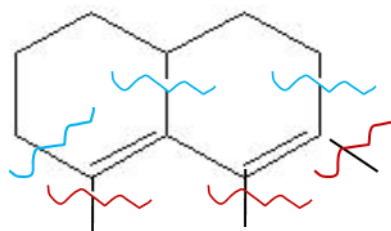


Exocyclic Double bond: Any double bond where only one of carbon is a part of ring or the concerned cyclic structure is called endocyclic double bond.



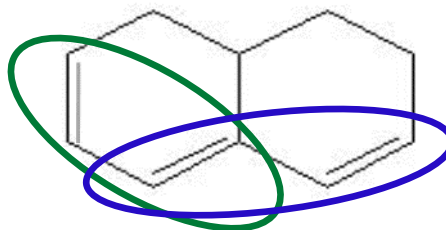
3. Alkyl group or Ring residue:

Carbon atom of the ring system or functional group connected to the carbon of conjugated diene moiety of the molecule.



4. Addition conjugated double bond:

Look for the additional double bond which extend the conjugation of double bonds.



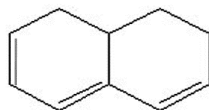
Contribution to λ_{max} of other factor

Acyclic diene	Base value = 217 nm
Homoannular diene	Base value = 253 nm
Heteroannular diene	Base value = 214 nm
Increment for	
Alkyl substituent or ring residue	5 nm
Exocyclic double bond	5 nm
Double bond extending conjugation	30nm
Polar functional group attached to diene part of molecule	
-OCOCH₃ (Acetate)	0 nm
-OR (Ether)	6 nm
-Cl	5 nm
-Br	5 nm
-NR₂ (Secondary amine group)	60 nm
-SR(Thioether)	30 nm
-Ph (Phenyl group)	60 nm



Steps for calculation of λ_{\max} using Woodward Fieser rule

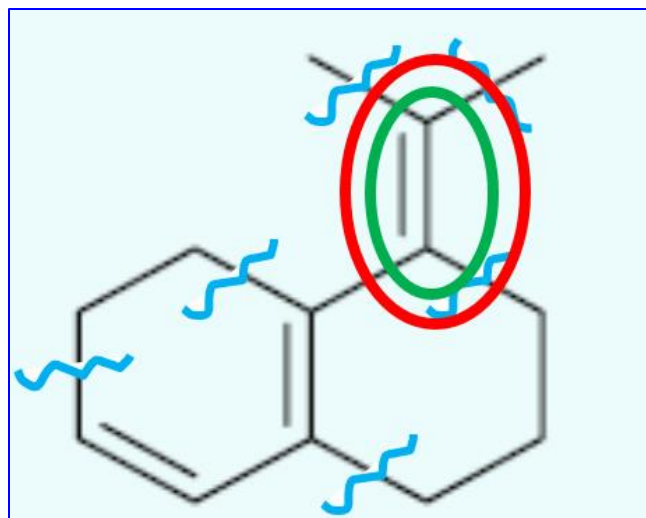
- Identify the type of diene species present in molecule. If a molecule has both homoannular diene and heteroannular diene in same molecule, then always consider homoannular diene for base value = 253 nm.



- Calculate the alkyl substituents or ring residues which are directly attached to the carbon atoms making conjugated system within the compound.
- Calculate the number of exocyclic double bond
- Calculate the number of extended double bond in conjugation to dienes



Example:



Base value = 253 nm

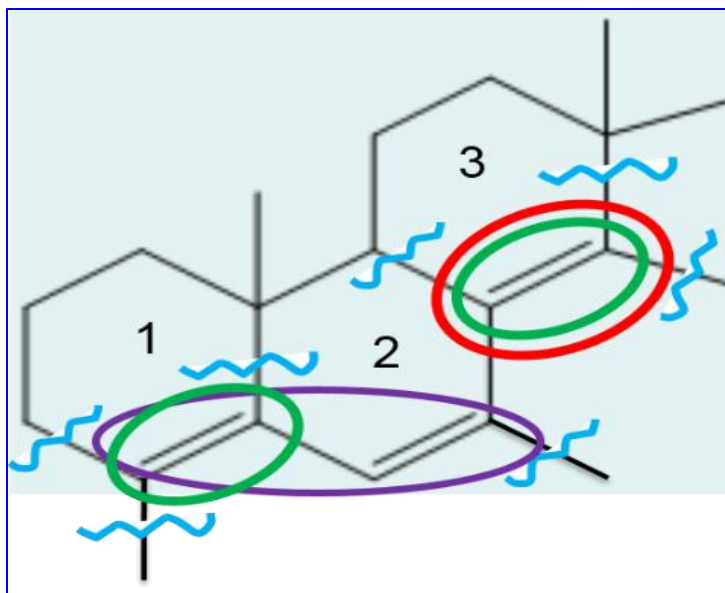
Ring residue/alkyl group = 6 x 5 nm = 30 nm

Exocyclic double bond = 1 x 5 nm = 5 nm

Extended double bond = 1 x 30 nm = 30 nm
conjugated to diene

Thus calculate $\lambda_{\max} = 318 \text{ nm}$





Base value = 214 nm

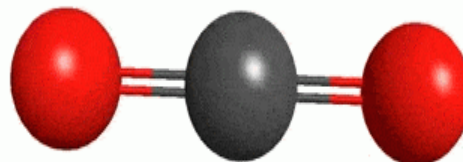
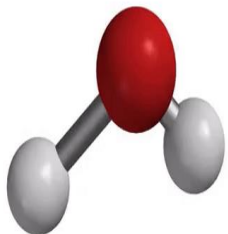
Ring residue/alkyl group = 7 x 5 nm = 35 nm

Exocyclic double bond = 2 x 5 nm = 10 nm

Extended double bond = 1 x 30 nm = 30 nm
conjugated to diene

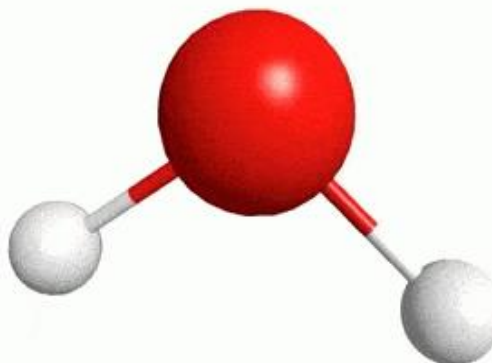
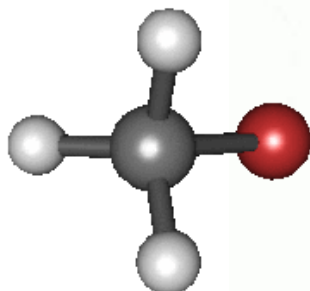
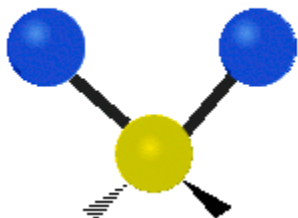
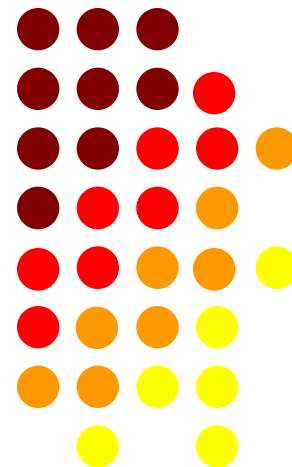
Thus calculate $\lambda_{\max} = 289 \text{ nm}$





LECTURE - 14

- Basic principle of IR spectroscopy
- Hooks law and Vibrational frequency
- Types and no. of fundamental vibrations
- Functional group and Finger Print region.



Infrared Spectroscopy

It is also known as Vibrational Spectroscopy

$$E_{\text{mol}} = E_{\text{el}} + E_{\text{vib}} + E_{\text{rot}}$$

It is the study of **Vibrational transition** in molecule which occur via *excitation of electron from vibrational ground state to vibrational excited state by absorption light in infrared radiation.*

It is mainly used in structure elucidation to determine the functional groups



Hooke's law and frequency of vibration

Each vibration in molecule can be treated as a spring where spring vibrate with frequency (ν) mentioned below. These vibration in molecule can be explained by Hooke's law which state that force acting on atom during vibration is directly proportion to the displacement given below.



$$F = -kx \quad \text{where } k \text{ is spring constant}$$

$$\mu \frac{d^2x}{dt^2} = -kx$$



By solving above second order differential equation we can get the vibrational frequency shown below-

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{in Hz, } s^{-1} \text{ or vibration per second}$$

Vibrational frequency in wavenumber

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \text{in } cm^{-1}$$

Where, c is speed of light, reduced mass of diatomic molecule

given as
$$\mu = \frac{m_1 \times m_2}{m_1 + m_2} \frac{1}{N_A} \times 10^{-3} \text{ Kg}$$



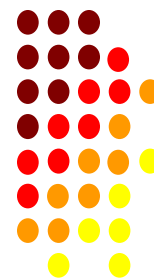
Vibrational frequency for diatomic molecule is directly proportional to stability of molecule, and inversely proportional to bond length of the molecule i.e.

$$\bar{\nu} \propto \sqrt{k} \propto \text{bond strength}$$

$$\bar{\nu} \propto \text{bond stability}$$

$$\bar{\nu} \propto \frac{1}{\text{bond length}}$$

Molecule	K (dyne/cm)	Bond length (Å)	Frequency (cm⁻¹)
HCl	527667	1.274	2990
HBr	386800	1.41	2650
HI	290000	1.61	2310
CO	1860000	1.13	2170
NO	1550000	1.15	1904



Type of Molecular Vibration:

There are 2 types of vibrations:

- Stretching vibrations
- Bending vibrations

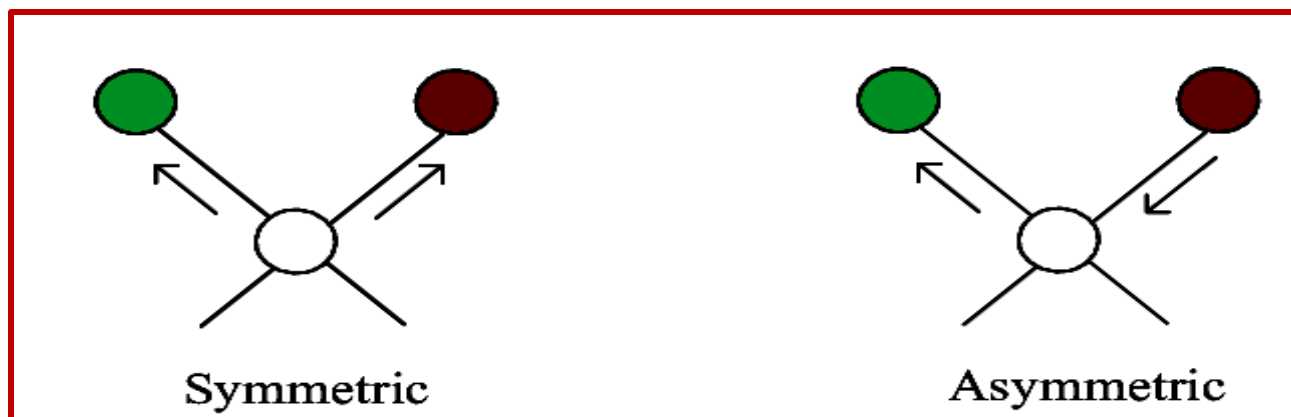
1. Stretching vibrations: Vibration or oscillation along the line of bond is called stretching vibration. There occurs a change in bond length.

2. Bending vibrations: Vibration are not along the line of bond. Bond angle changes during vibration which results in the deformation of molecule.



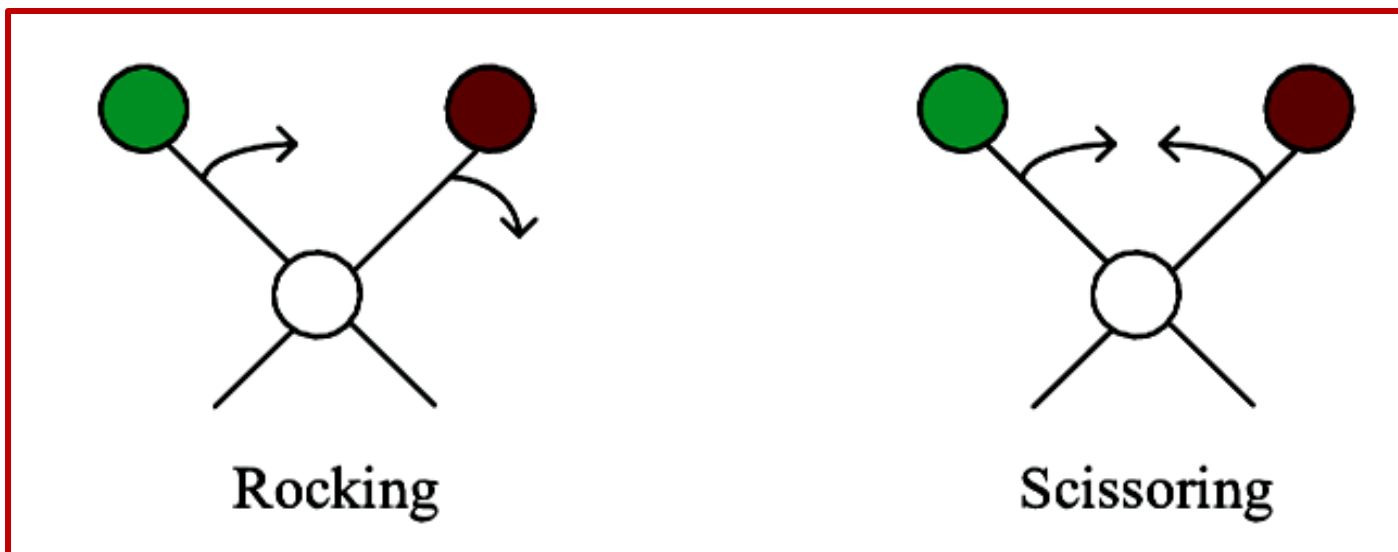
Stretching vibrations are of two types:

- **Symmetric stretching:** The bonds increase or decrease in length simultaneously. i.e. either both the atoms approach central atom or moves away from it.
- **Asymmetric stretching:** in this, one bonds length is increased and other is decreased. i.e. one of the two atoms approaches the central atom and the other moves away from it.



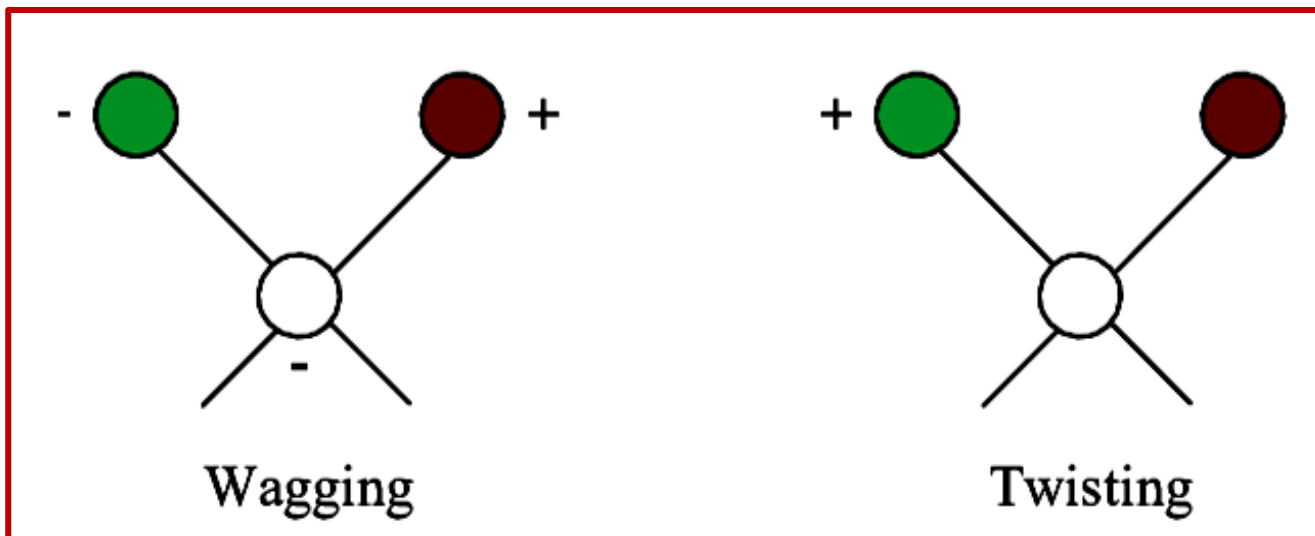
a) In plane bending

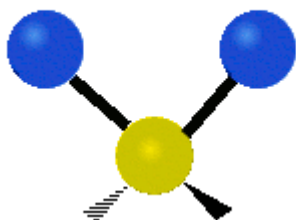
- **Scissoring**: This is an in-plane bending in which two atoms approach each other and bond angles decrease or vice versa.
- **Rocking**: Change of angle between two bonds due to movement of atoms take place in the same direction.



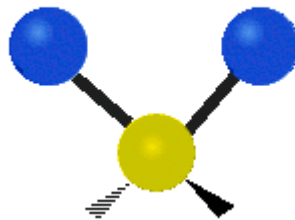
b) Out plane bending

- **Wagging**: 2 atoms move to one side of the plane. They move up and down the plane.
- **Twisting**: One atom moves above the plane and another atom moves below the plane.

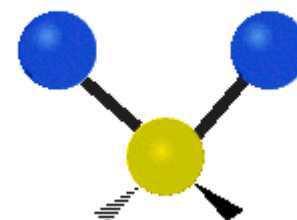




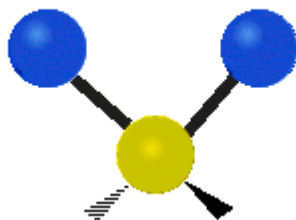
Symmetric Stretching



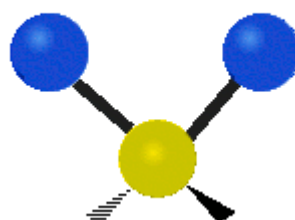
Scissoring



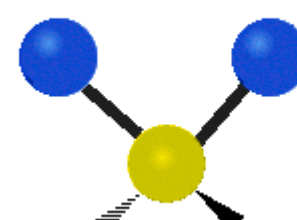
Twisting



Asymmetric Stretching

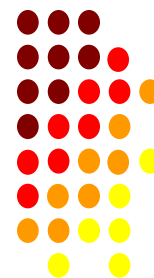


Rocking

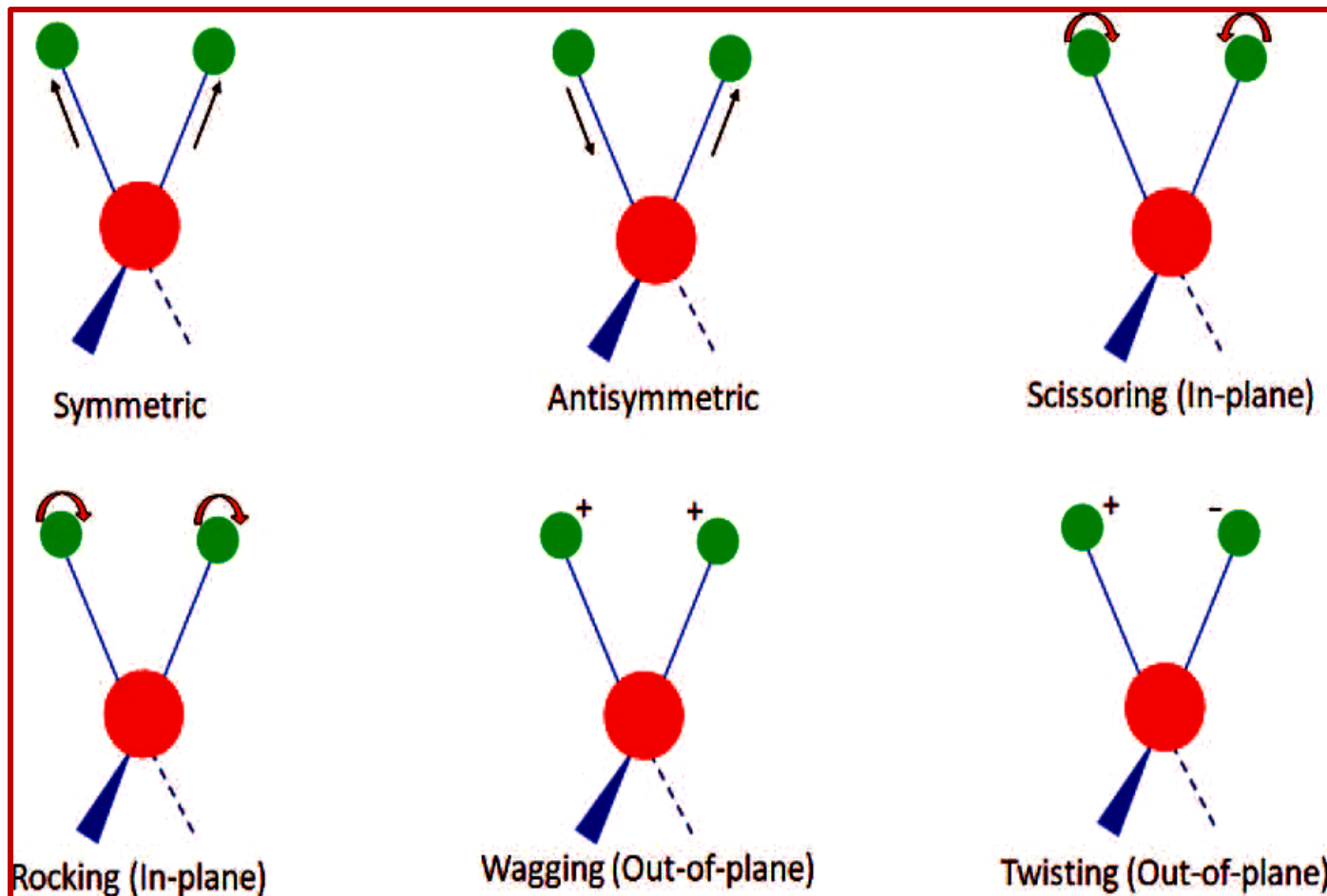


Wagging

Different types of vibration mode



Summary of different type of vibration mode



Number of fundamental vibrations:

For a linear molecule = $3N - 5$

For a non-linear molecule = $3N - 6$

Where N is the number of atoms. The following procedure should be followed when trying to calculate the number of vibrational modes:

- Determine if the molecule is linear or nonlinear. If linear, use Equation 1. If nonlinear, use Equation 2
- Calculate how many (N) atoms are in given molecule.



Example:

- **CO₂** (linear molecule)
 $n = 3,$
 no of fundamental vibrations = $3n - 5 = (3 \times 3) - 5$
 $= 4$

- **H₂O** (nonlinear molecule)
 $n = 3,$
 no of fundamental vibrations = $3n - 6 = (3 \times 3) - 6$
 $= 3$

- **CH₄** (nonlinear molecule)
 $n = 5,$
 no of fundamental vibrations = $3n - 6 = (3 \times 5) - 6$
 $= 9$



Criteria for a compound to absorb IR radiation:

The two essential criteria's for a molecule to be IR active are:

1. Correct wavelength of radiation:

A molecule to absorb IR radiation, the natural frequency of vibrations of some part of a molecule is the same as the frequency of incident radiation.

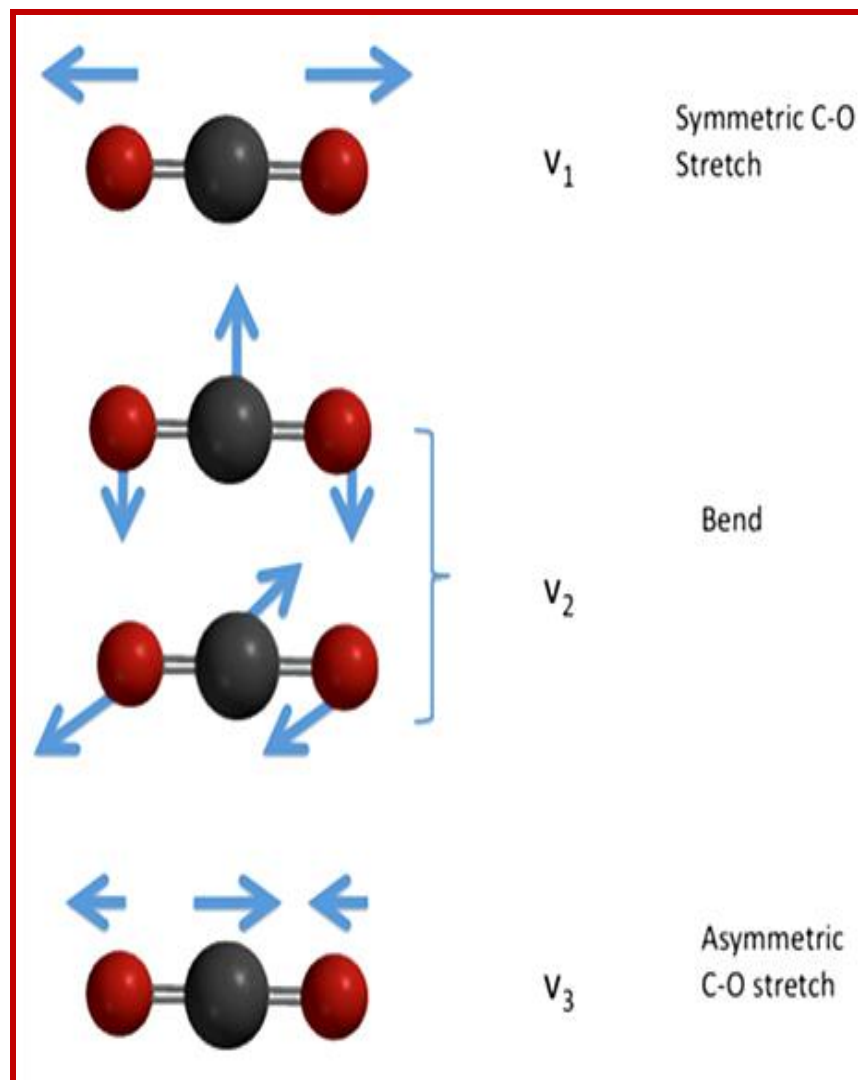
2. Change in dipole moment:

A molecular vibration is IR active i.e. it absorbs IR radiation if the vibration results in a change in the dipole moment.

All the homonuclear diatomic molecules such as H_2 , N_2 , O_2 , etc are IR inactive.



Vibration of a bond involving two atoms that have *large difference in their electronegativity* is usually IR active. Example asymmetric vibration & stretching vibrations of carbon dioxide (CO_2), on the other hand, causes a change in dipole moment & hence is IR active.



Selection rule for vibrational spectroscopy:

(a) Molecule should have permanent dipole moment or should create dipole moment during vibration

(b) Vibrational Quantum Number change $\Delta v = \pm 1$

Functional Group Region (4000-1500 cm^{-1}):

- The most common application of IR spectroscopy is perhaps to identify the functional groups. This is possible because different functional groups vibrate at different frequencies allowing their identification.



- The frequency of vibration, however, depends on additional factors such as delocalization of electrons, H-bonding, and substitutions at the nearby groups.
- Region from ***4000-1500 cm⁻¹*** in an IR spectrum is useful for identification of functional groups.
- This region shows the absorption due to stretching mode.



Functional group vibrational frequency

Bond	Molecule	Wavenumber (cm ⁻¹)
C-O	Alcohol, ethers, esters, carboxylic acid etc	1300-1000
C=O	Alcohol, Ketones, esters, carboxylic acid	1750-1680
C=O	Amide	1680-1630
N-H (stretching)	Amine, Amides	3500-3100
-N-H (bending)	Amine, Amides	1640-1550
O-H	Alcohols	3650-3200
C-N	Amine	1350-1000
S-H	Mercaptans	2550

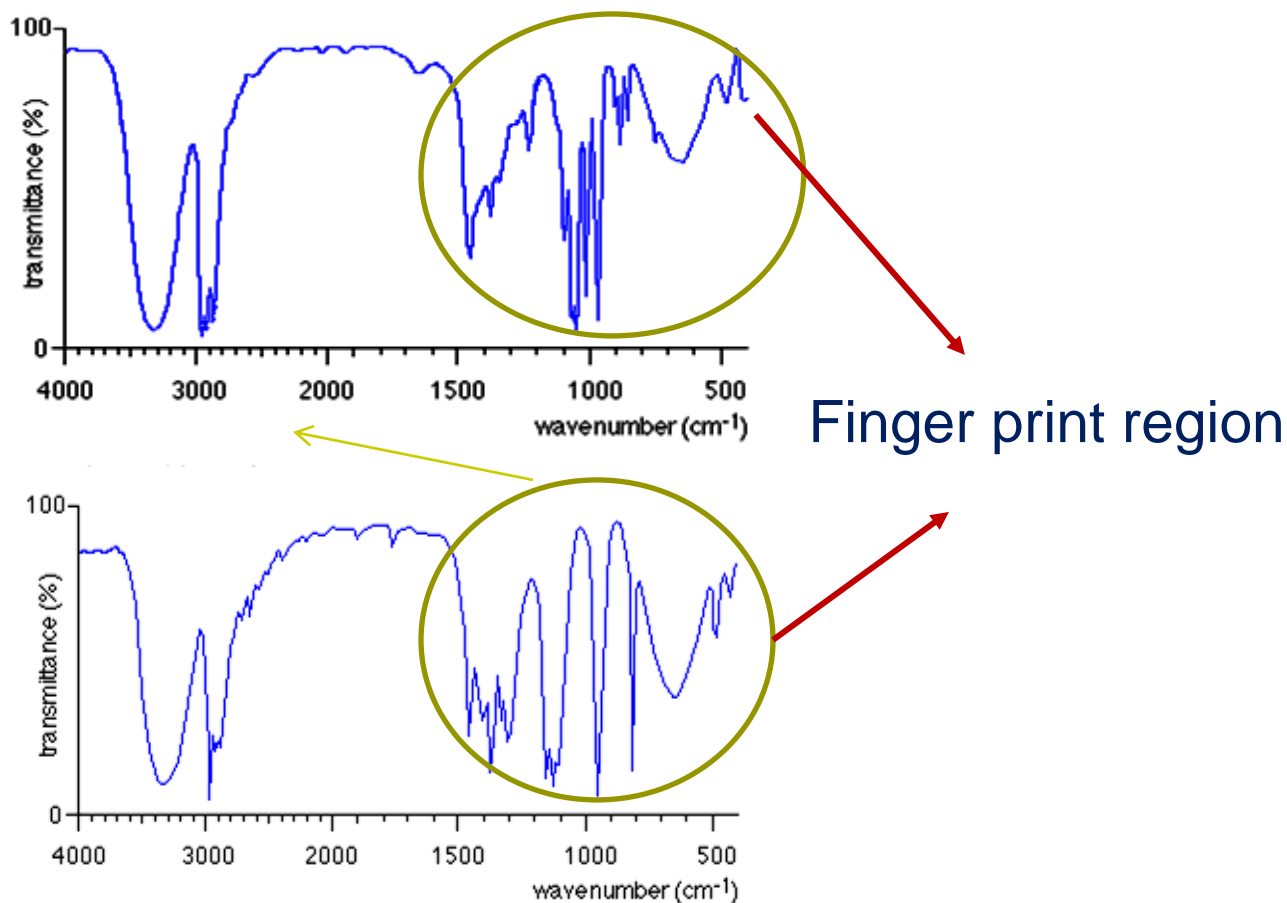


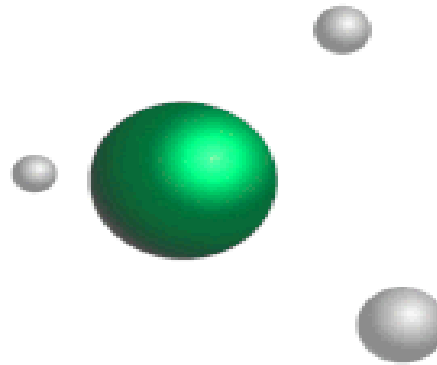
FINGER PRINT REGION (1500-600 cm^{-1}):

- IR absorption spectra taken in the region of 1500 to 500 cm^{-1} is called fingerprint region.
- It contains number of vibrations caused by bending vibrations and those resulting from the stretching vibrations of C-C, C-O and C-N.
- This region shows a number of vibrations which makes it complex.
- The importance of fingerprint region is that each different molecule has its own unique absorption pattern in this region.
- This provides confirmation about the identity of molecules. No two compounds except enantiomers can have similar IR spectra.



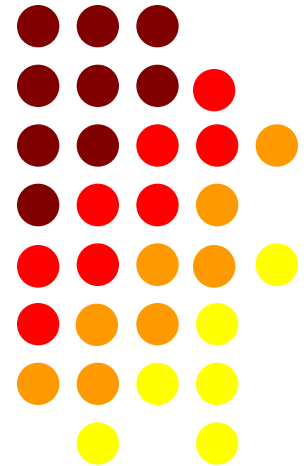
Example: Consider the example of propane-1-ol and propane-2-ol.





LECTURE - 15

- Factors affecting vibrational frequency
- Applications of Infrared spectroscopy
- Numericals on Infrared spectroscopy



Factor effecting vibrational frequency:

1. **Bond order**: Bond order affects the position of absorption bands. Higher the bond order larger is the band frequency

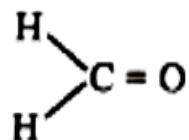
Bond	Frequency (cm ⁻¹)	Bond	Frequency	Bond	Frequency
C-C	< 900	C-O	970 - 1250	C-N	1250-1020
C=C	1680 - 1620	C=O	1630-1780	C=N	1690-1640
C≡C	2260 - 2100	C≡O	2100	C≡N	2260-2220



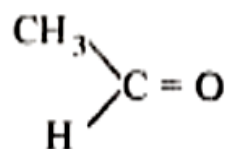
2. Electronic Effects: Resonance and Inductive

Inductive effect

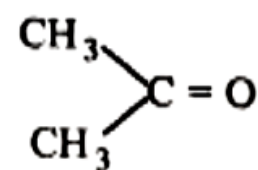
The effect on electron density in one portion of a molecule due to electron-withdrawing or electron-donating groups elsewhere in the molecule.



Formaldehyde
1740 cm^{-1}



Acetaldehyde
1725 cm^{-1}



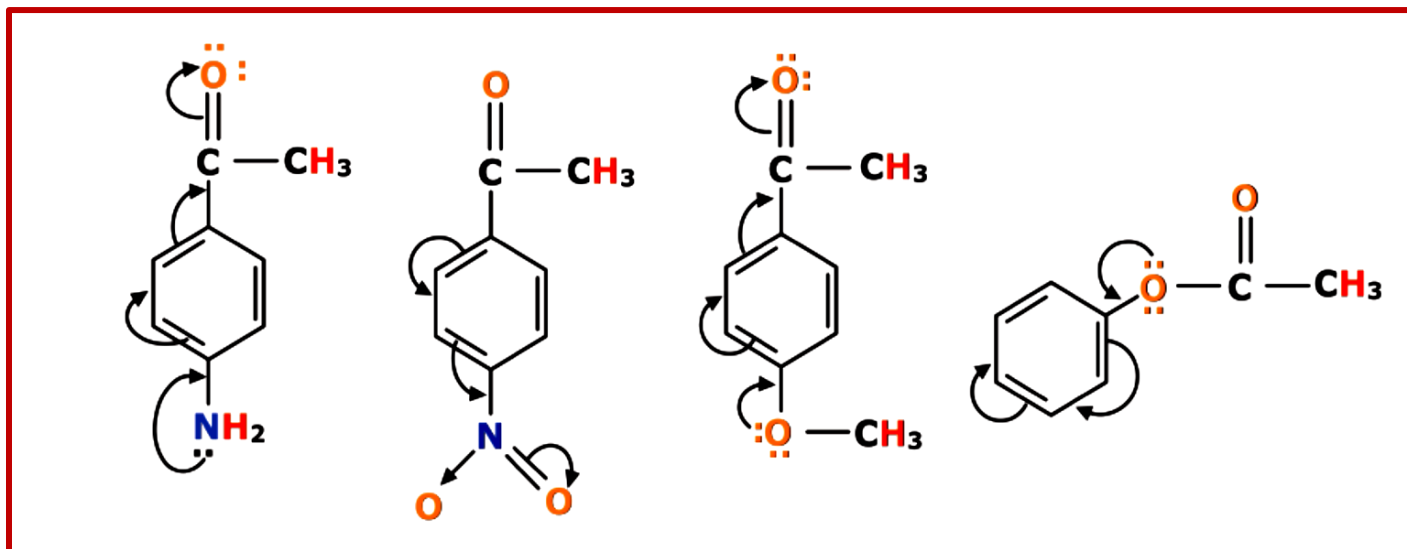
Acetone
1715 cm^{-1}

	Attachments	Inductive effect	Bond length	Force constant	Friquency
Electron releasing	Alkyl group	+i	Increases	Decreases	Decreases
Electron withdrawing	Cl, Br, I, OH	-i	Decreases	Increases	Increases



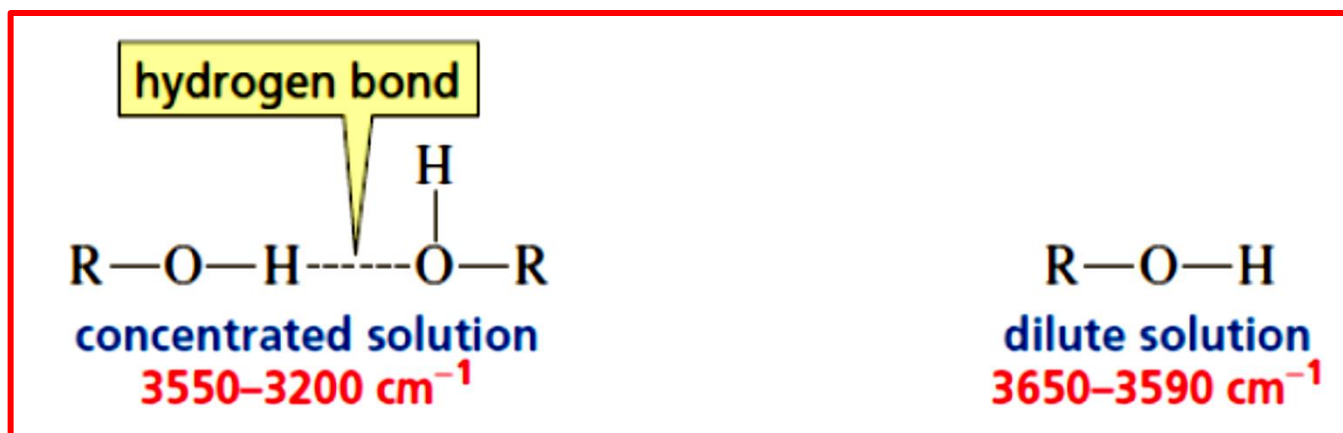
Resonance effect

As the molecule have π -electron leading to conjugation results in the delocalization of electron over 3-4 atoms or even more. This weakens the multiple bond (such as C=O). This can result in the decrease in vibrational frequency

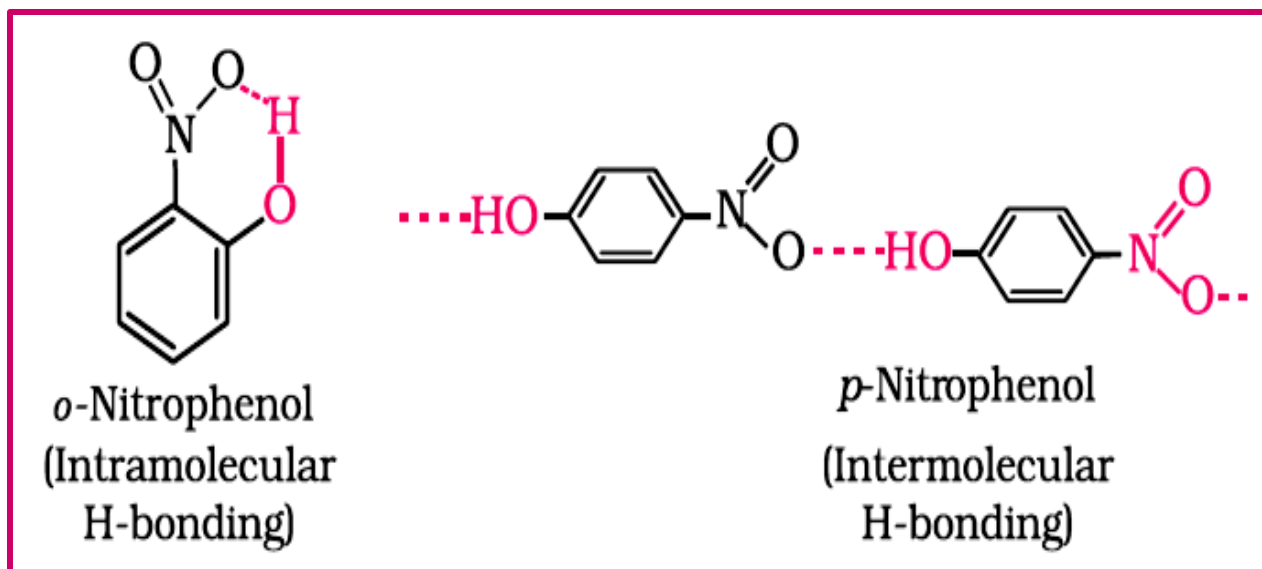


Hydrogen Bonding:

- The presence of hydrogen bonding changes the position and shape of an infrared absorption band.
- Stronger the hydrogen bonding, greater is the absorption shift from the normal values which result in red shift in IR spectra.



- The two types of hydrogen bonding (intramolecular and intermolecular) can be differentiated by the use of infrared spectroscopy.



Application of IR Spectroscopy

- **Qualitative Analysis:** Main application of IR spectroscopy is compound identification.
- **Determination of Purity of a sample.**
- **To identify cis and trans isomers of a compound.** IR absorption of a trans isomer is very weak and of cis is stronger.
- **Distinguish between inter and intra molecular H bonding.**
- **Structural information:** IR spectra provides valuable information regarding molecular symmetry, dipole moments, bond strength, characteristic absorption etc.



Numerical Example

Q1: If the stretching frequency of a hydrogen molecule is 1.2×10^{14} vibrations/sec. Calculate the wavenumber where hydrogen molecule absorption band will be observed in an IR spectrum.

Sol: The frequency of hydrogen stretching can be represented in terms of wavenumbers as follows:

$$\bar{\nu} = 1/\lambda = \nu/c \text{ cm}^{-1}$$

$$\bar{\nu} = 1.2 \times 10^{14} \text{ sec}^{-1} / 3 \times 10^{10} \text{ cm/sec} = 4000 \text{ cm}^{-1}$$

Hydrogen, however, is a homodiatomic molecule; the stretching vibration does not cause any change in the dipole moment. Therefore, hydrogen will not show absorption in the IR of 4000 cm^{-1} and consequently will not appear in an IR spectrum.



Q3. One of the fundamental vibrational modes of H_2O occurs at 3652 cm^{-1} . What would be the frequency of the corresponding vibration for D_2O .

Solution:

Since vibrational mode frequency is give as $\bar{\nu} = 3652\text{ cm}^{-1}$

Let us consider force constant of H_2O and D_2O does not change,

Then force constant $k_{H_2O} = k_{D_2O}$

$$\bar{\nu}_{H_2O} = \frac{1}{2\pi c} \sqrt{\frac{k_{H_2O}}{\mu_{H_2O}}}, \quad \text{and} \quad \bar{\nu}_{D_2O} = \frac{1}{2\pi c} \sqrt{\frac{k_{D_2O}}{\mu_{D_2O}}}$$

$$\text{Reduced mass, } \mu_{H_2O} = \frac{m_H m_O}{m_H + m_O} = \frac{1 \times 16}{1 + 16} = 0.94$$

$$\mu_{D_2O} = \frac{m_D m_O}{m_D + m_O} = \frac{2 \times 16}{2 + 16} = 1.78$$

$$\text{thus } \bar{\nu}_{D_2O} = \bar{\nu}_{H_2O} \sqrt{\frac{\mu_{H_2O}}{\mu_{D_2O}}} = 3652 \times \sqrt{\frac{0.94}{1.78}} = 2654\text{ cm}^{-1}$$



Q.4 Two isomers X and Y having molecular formula C_3H_6O give IR band near 3550 cm^{-1} and 1717 cm^{-1} respectively. Assign structural formula to X and Y consistent with their IR absorption band.

Sol: Two isomers X and Y have molecular formula C_3H_6O .

Double bond equivalence in isomer 1 and isomer 2
$$= C - H/2 + 1 = 3 - 6/2 + 1 = 1$$

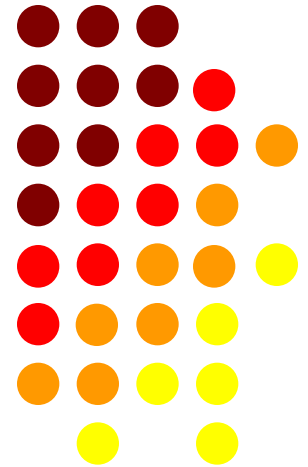
So; X and Y isomer may have one double bond thus possibilities are $C=C$ or $C=O$.

- 1) The peak at **3550 cm^{-1}** corresponds to alcoholic group ($-OH$). So, structural formula is $CH_2=CH-CH_2OH$.
- 2) The peak at 1717 cm^{-1} corresponds to $-C=O$ group stretching frequency (ketone group). So, structural formula is CH_3COCH_3 .



LECTURE - 16

Nuclear Magnetic Resonance Spectroscopy



What is Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance spectroscopy, commonly known as NMR spectroscopy or magnetic resonance spectroscopy (MRS), is a spectroscopic technique to observe local magnetic fields around atomic nuclei

- It is based on the absorption of electromagnetic radiation in the radiofrequency region ranging from 4 to 900 MHz by nuclei of the atoms.
- NMR has become the preeminent technique for determining the structure of organic compounds.



Principle of NMR Spectroscopy

1. The principle behind NMR is that many nuclei have spin and all nuclei are electrically charged. If an external magnetic field is applied, an energy transfer is possible between the lower energy to a higher energy level
2. The energy transfer takes place at a wavelength that corresponds to radio frequencies and when the spin returns to its lower level, energy is emitted at the same frequency.
3. The signal that matches this transfer is measured in many ways and processed in order to yield an NMR spectrum for the nucleus concerned.



The NMR Behavior of Some Common Nuclei

Magnetic nuclei	Nonmagnetic nuclei
^1H	^{12}C
^{13}C	^{16}O
^2H	^{32}S
^{14}N	
^{19}F	
^{31}P	

Magnetic:

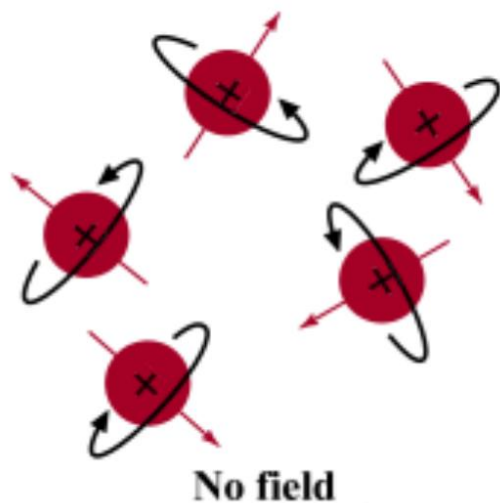
- All nuclei with odd number of protons
- All nuclei with odd number of neutrons

Nonmagnetic:

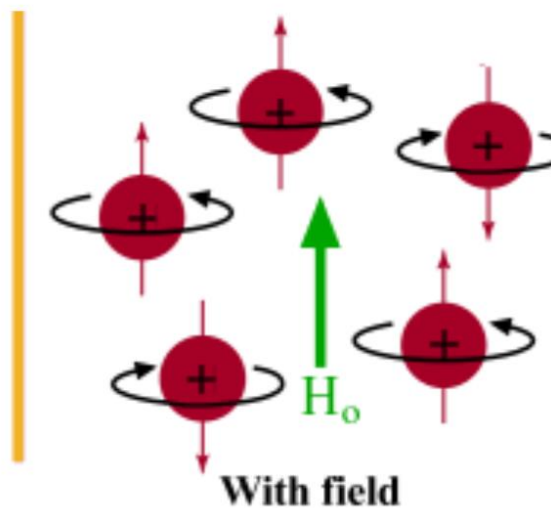
- Nuclei with even number of both protons and neutrons



Atomic nuclei in absence of magnetic field

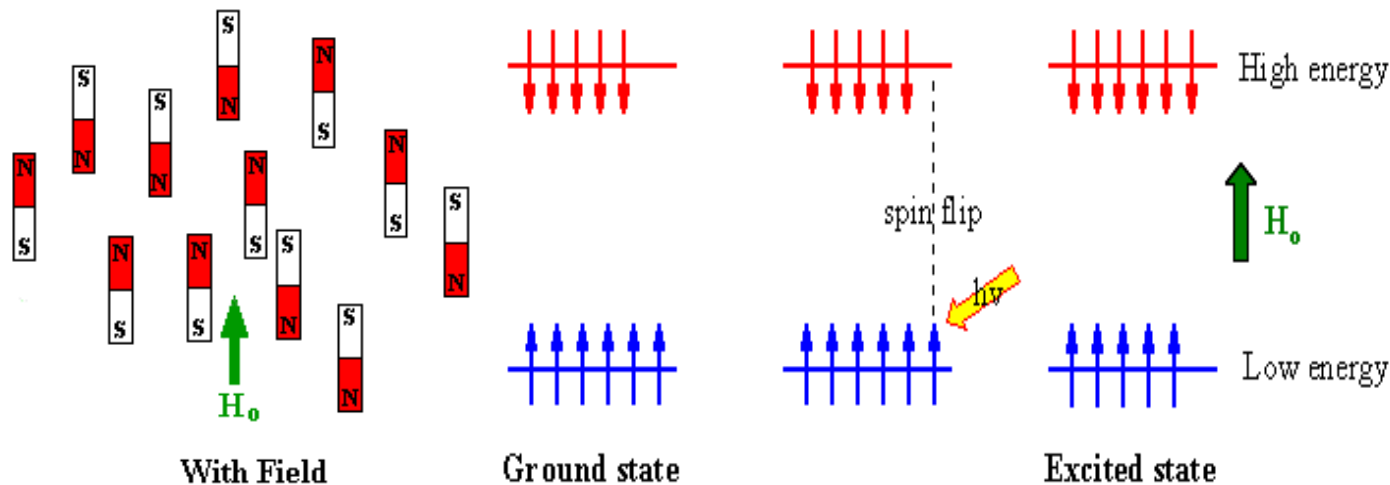


Atomic nuclei in presence of external magnetic field



Atomic nuclei can either align parallel (lower E) or antiparallel (higher E)

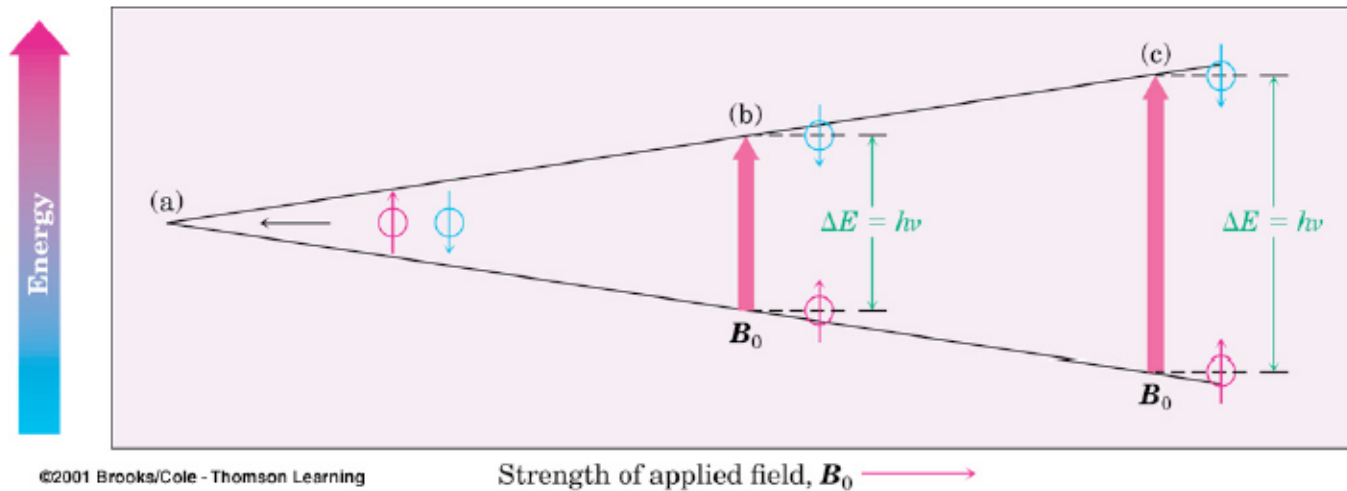




Magnetic nuclei are in resonance with external magnetic field if they absorb energy and “spin-flip” from low energy state (parallel orientation) to high energy state (antiparallel orientation).



The energy difference between aligned and opposed to the external magnetic field (B_0) is generally small and is dependant upon B_0 . Applied EM radiation (radio waves) causes the spin to flip and the nuclei are said to be in *resonance* with B_0 .



$$\Delta E = h \nu \quad \Delta E = \frac{\gamma B_0 h}{2 \pi}$$

B_0 = external magnetic field strength
 γ = gyromagnetic ratio
 $^1\text{H} = 26,752$
 $^{13}\text{C} = 6.7$

Note that $\frac{h}{2\pi}$ is a constant and is sometimes denoted as \hbar

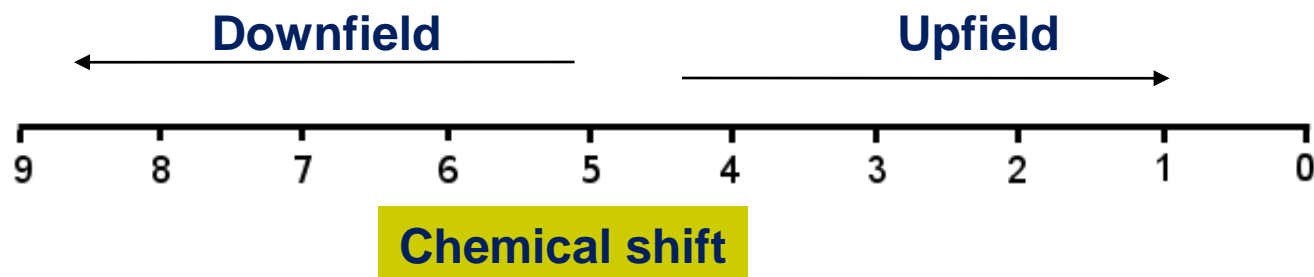


Shielding effect

- **Shielding** determines how nuclei interact with the magnetic field and the Chemical shift of the signal
- The electron cloud surrounding a nucleus opposes the applied field
- The more electrons, the greater the shielding around a proton, so the field is more strongly opposed
- As a proton becomes deshielded, it is shifted further downfield, as the magnetic field is able to affect it more
- Electronegative atoms (eg. oxygen or chlorine) will draw electron density away from the protons, deshielding them
- Less electronegative atoms like carbon will not pull electron density, leaving the proton shielded, so it is not shifted.



- As the proton's electron cloud reduces, the nucleus is exposed to more of the external magnetic field (B_0)
- The energy gap increases causing magnetic resonance frequency to change. This changes the emissions frequency from relaxation
- This results in a greater chemical shift and the signal appears further downfield



Nuclear shielding and deshielding

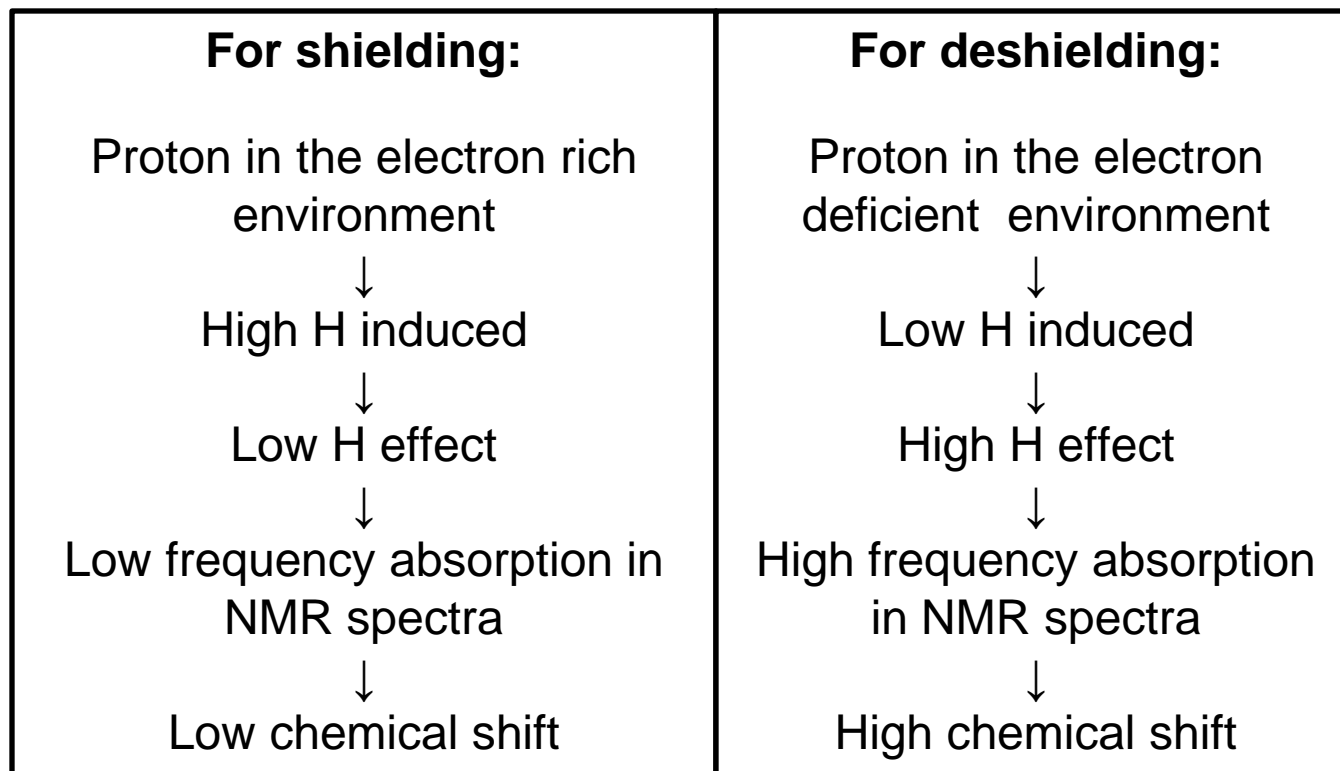
- The external magnetic field is uniform over the entire molecule and therefore cannot differentiate to the different types of the proton. However the induced magnetic field generated by the e⁻ around the nucleus is not uniform, this situation makes the different spin active nuclei (proton) to be non-equivalent. Thus each proton in the different electronic environment show slightly different magnetic field due to the circulation of e⁻ in the neighboring bond.
- Thus the effective magnetic field for the different spin active nuclei can be calculated through the following equations:

$$H_{\text{effect}} = H_0 - H_{\text{induced}}$$

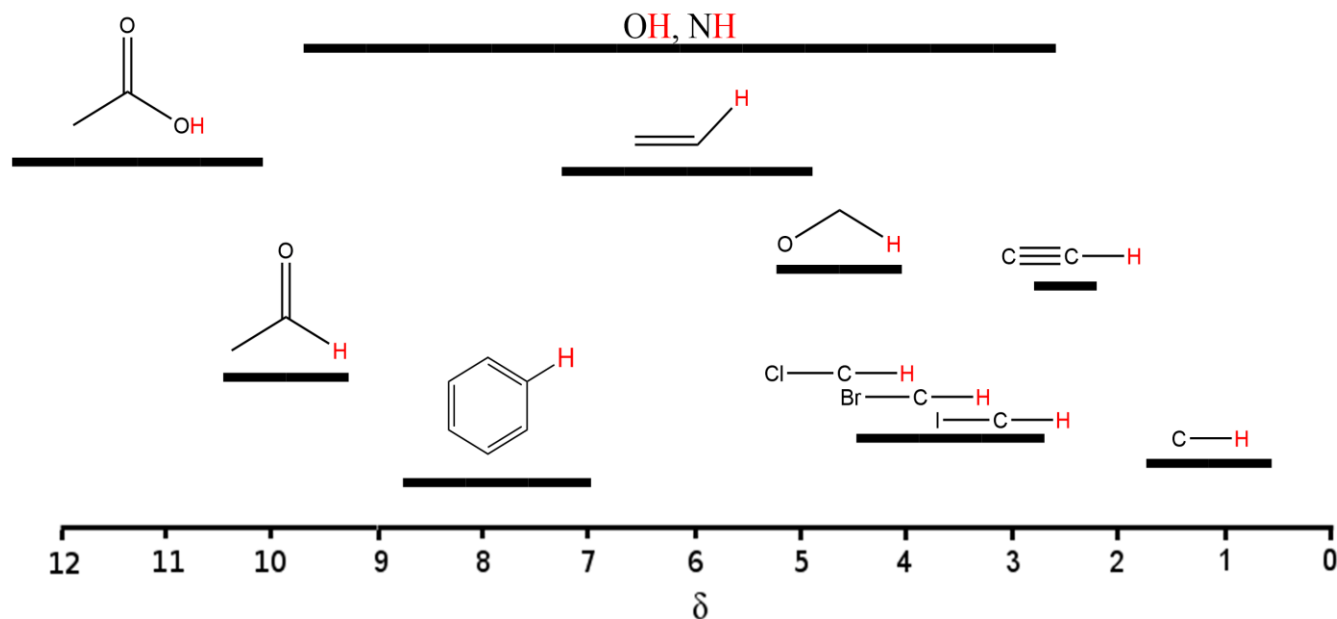


$$H_{\text{effect}} = H_0 - H_{\text{induced}}$$

Form the above equation the shielded and deshielded proton concept can be given as:



- Signals tend to fall within particular ranges, depending on the environment the proton is in
- This helps identify the signal based on the chemical shift



NMR Chemical Shift Values

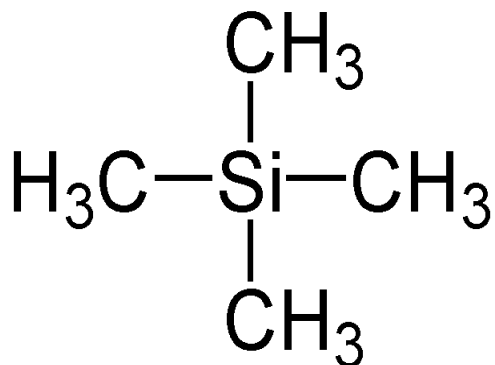
Type of Proton	Chemical Shift (ppm)	Type of Proton	Chemical Shift (ppm)
$R-CH_3$	0.9 – 1.2	$X-CH_2R$ (X: Cl, Br, I)	3.1 – 3.8
$R-CH_2$	1.2 – 1.5	$R-OH$	variable, 1 – 5
$R-CH$	1.4 – 1.9	$R-NH_2$	variable, 1 – 5
$R_2C=CHR_2$	1.5 – 2.5	$R_2C=CH$	4.5 – 6.0
$R-C(=O)CH_3$	2.0 – 2.6	$Ar-H$	6.0 – 8.5
$Ar-CH_3$	2.2 – 2.5	$R-C(=O)H$	9.5 – 10.5
$R-C\equiv C-H$	2.5 – 3.0	$R-C(=O)OH$	10 – 13
$(H)R-O-CH_3$	3.3 – 4.0		



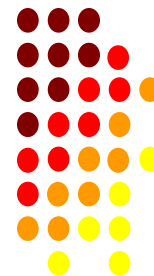
Internal standard for NMR spectroscopy:

That compound which is used as a reference standard to represent the NMR/PMR signal of the compounds is known as internal standard for the NMR or PMR spectroscopy.

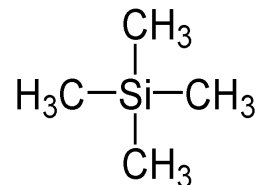
In case of PMR spectroscopy Tetramethylsilane (TMS) used as a internal standard due to the following reasons:



Tetramethylsilane



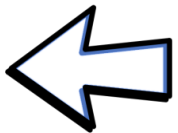
Why TMS ?



1. Due to the more shielded nature of the proton of TMS in compare to the protons of most of the organic compound.
2. It is chemically inert and miscible with large range of solvent.
3. It does not take part in intermolecular association with the sample.
4. Due to the volatile nature of TMS.



Splitting patterns

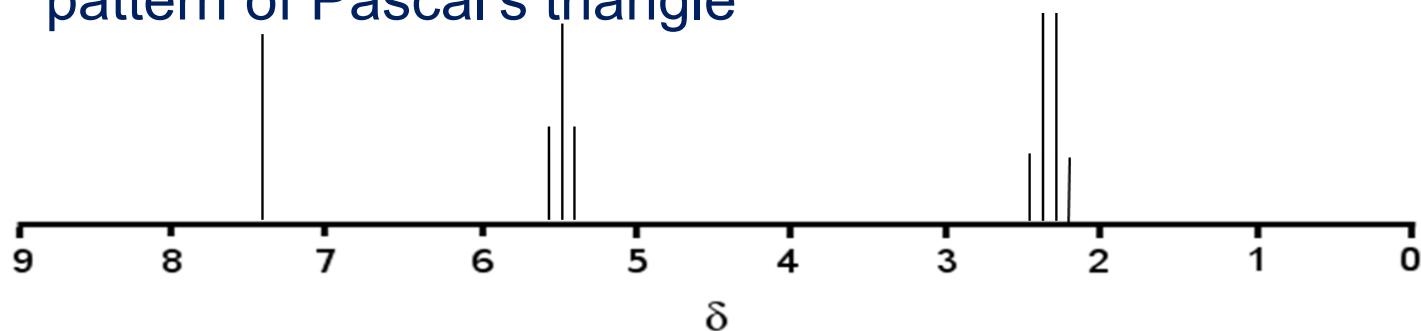


Splitting patterns

- In the spectrum below, there is a signal for each environment, however, they appear split.
- These split peaks are *multiplets*.
- The number of peaks in a multiplet provides information about neighbouring protons.
- Splitting is caused by the interaction between inequivalent protons, called *coupling*
- Proton-proton coupling usually takes place 3 bonds away from each other



- The number of peaks, or *multiplicity*, comes from the number of protons interacting
- The number of peaks follows an $n+1$ pattern, where n is the number of protons in the interacting environment
- The number of peaks observed is the *multiplicity*
- The intensity of the peaks in a multiplet follows the pattern of Pascal's triangle

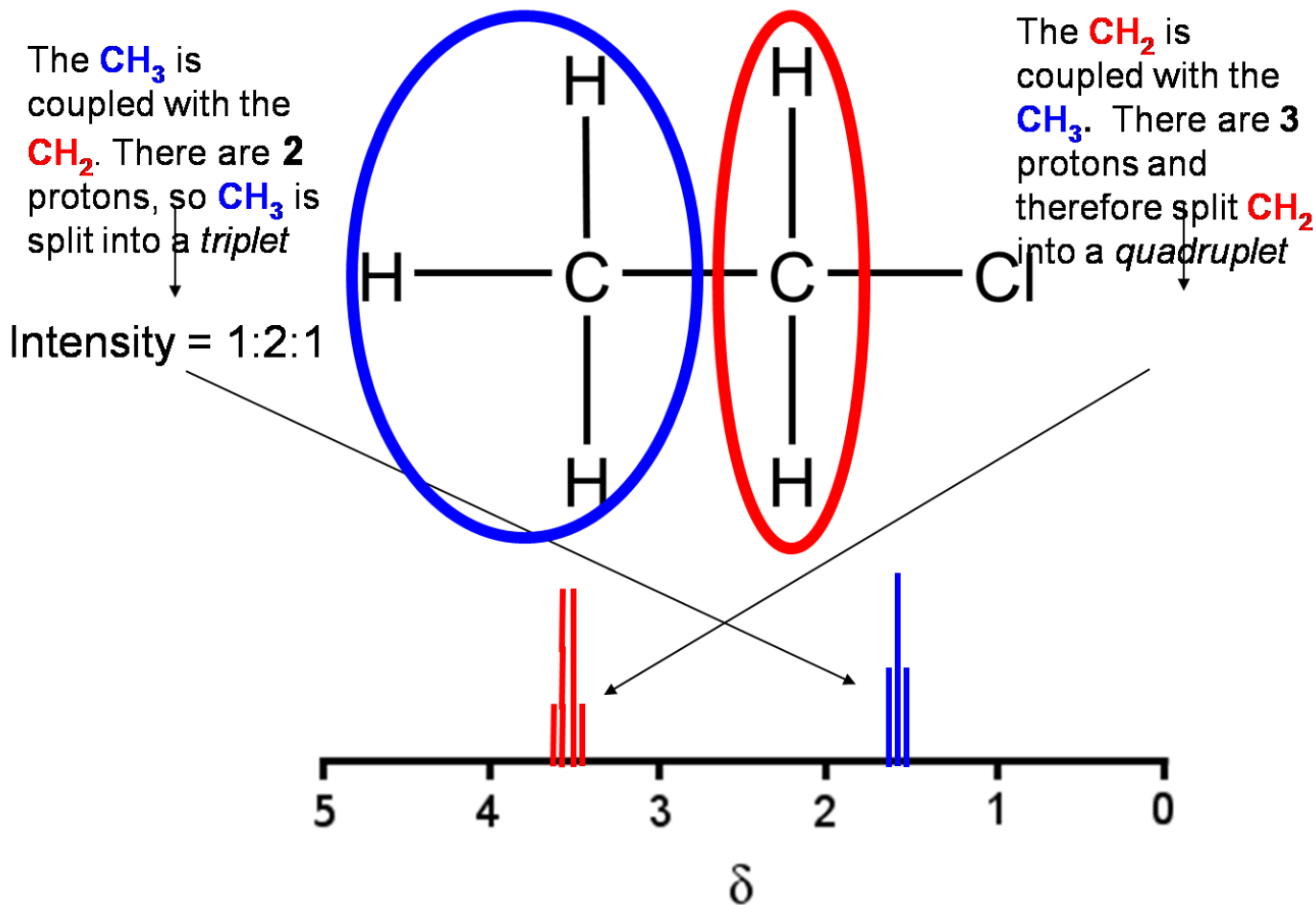


- eg. If a group of protons has 2 neighbouring equivalent protons, it will be split into a *triplet*.

0 neighbouring protons		1		Singlet	
1 neighbouring proton		1	1	Doublet	
2 neighbouring protons	1	2	1	Triplet	
3 neighbouring protons	1	3	3	1	Quartet

- This is known as Pascal's triangle.





Instrumentation of Nuclear Magnetic Resonance (NMR) Spectroscopy

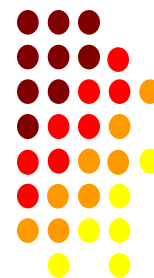
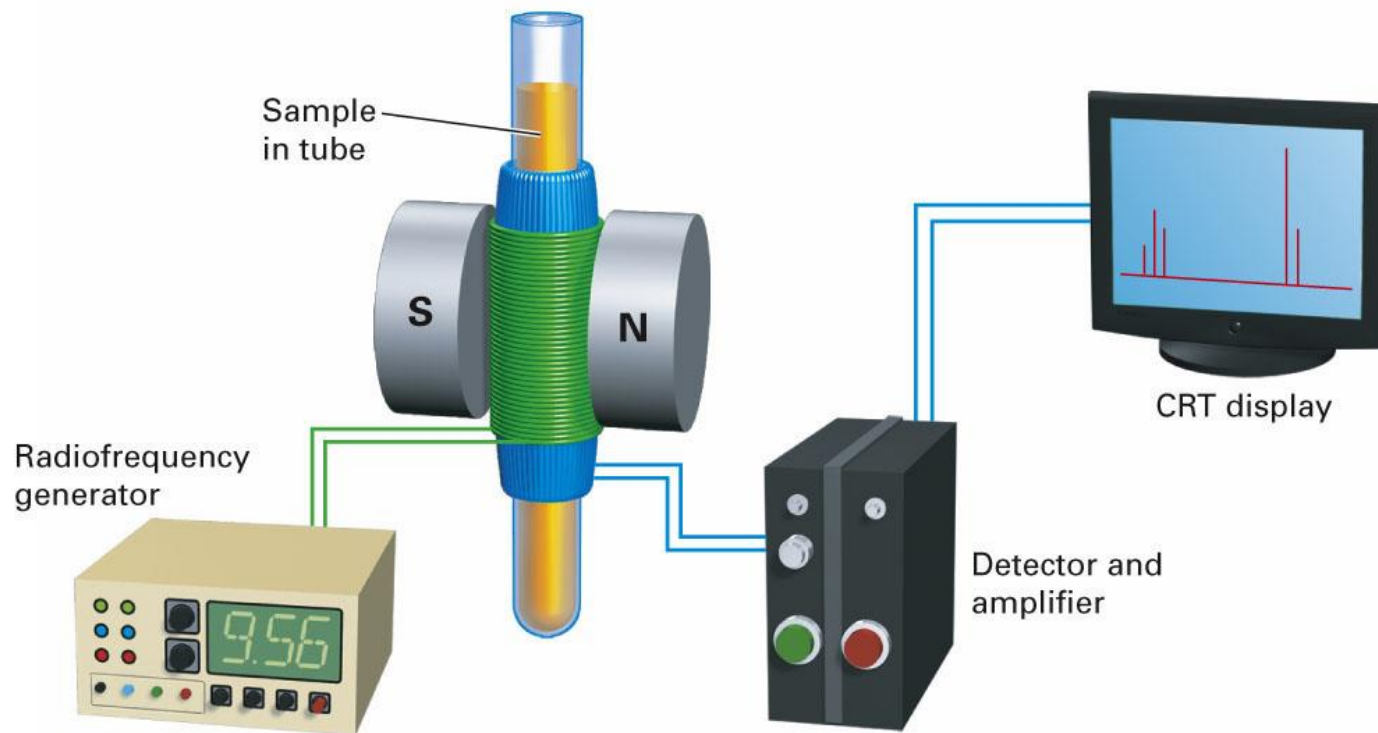
1. **Sample holder:** Glass tube with 8.5 cm long, 0.3 cm in diameter.
2. **Permanent magnet:** It provides a homogeneous magnetic field at 60-100 MHz
3. **Magnetic coils:** These coils induce a magnetic field when current flows through them
4. **Sweep generator:** To produce an equal amount of magnetic field pass through the sample



Instrumentation of Nuclear Magnetic Resonance (NMR) Spectroscopy

- 5. Radio frequency transmitter:** A radio transmitter coil transmitter that produces a short powerful pulse of radio waves
- 6. Radio frequency receiver:** A radio receiver coil that detects radio frequencies emitted as nuclei relax to a lower energy level
- 7. Read out systems:** A computer that analyses and records the data.





Working of NMR Spectroscopy

- The sample is placed in a magnetic field and the NMR signal is produced by excitation of the nuclei sample with radio waves into nuclear magnetic resonance, which is detected with sensitive radio receivers.
- The intramolecular magnetic field around an atom in a molecule changes the resonance frequency, thus giving access to details of the electronic structure of a molecule and its individual functional groups.
- As the fields are unique or highly characteristic to individual compounds, NMR spectroscopy is the definitive method to identify monomolecular organic compounds.
- Besides identification, NMR spectroscopy provides detailed information about the structure, dynamics, reaction state, and chemical environment of molecules.
- The most common types of NMR are proton and carbon-13 NMR spectroscopy, but it is applicable to any kind of sample that contains nuclei possessing spin.



Applications of NMR Spectroscopy

NMR spectroscopy is the use of the NMR phenomenon to study the physical, chemical, and biological properties of matter. Application of NMR are as follows:

1. It is an analytical chemistry technique used in quality control.
2. NMR spectroscopy is used in research for determining the molecular structure.
3. NMR can quantitatively analyze mixtures containing known compounds.
4. NMR spectroscopy techniques are being used for the determination of protein structure.
5. NMR spectroscopy techniques are used to probe molecular dynamics in solution.
6. Solid state NMR spectroscopy is used to determine the molecular structure of solids.



Problems on NMR Spectroscopy

Problem: How many protonic signals would be expected from NMR spectra of the following:

- a) $\text{ClCH}_2\text{CH}_2\text{Cl}$ b) CH_3OCH_3 c) $\text{CH}_3\text{CHClCH}_2\text{CH}_3$
 d) CH_3COCH_3 e) $\text{CH}_3\text{CH}_2\text{CHO}$ f) $\text{CH}_3\text{COOCH}_3$

Solution:

- | | |
|--|----------|
| a) $\overset{\text{a}}{\text{ClCH}_2}\overset{\text{a}}{\text{CH}_2}\text{Cl}$ | 1 signal |
| b) $\overset{\text{a}}{\text{CH}_3}\text{O}\overset{\text{a}}{\text{CH}_3}$ | 1 signal |
| c) $\overset{\text{a}}{\text{CH}_3}\overset{\text{b}}{\text{CH}}\overset{\text{c}}{\text{Cl}}\overset{\text{d}}{\text{CH}_2}\text{CH}_3$ | 4 signal |
| d) $\overset{\text{a}}{\text{CH}_3}\text{CO}\overset{\text{a}}{\text{CH}_3}$ | 1 signal |
| e) $\overset{\text{a}}{\text{CH}_3}\overset{\text{b}}{\text{CH}_2}\overset{\text{c}}{\text{CHO}}$ | 3 signal |
| f) $\overset{\text{a}}{\text{CH}_3}\text{COO}\overset{\text{b}}{\text{CH}_3}$ | 2 signal |



Numerical

Q1. A compound having molecular formula $C_6H_{10}O_2$ gave the following 1H -NMR data- δ 1.30 (6H, s); δ 2.1 (3H, s); δ 2.6 (2H, s); δ 3.9 (1H, s).

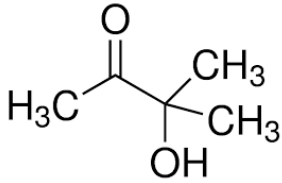
Identify the compound.

Solution: Molecular formula of compound = $C_6H_{12}O_2$

Double bond equivalence in compound

$$= C - H/2 + 1 = 6 - 12/2 + 1 = 1$$

Molecule will have one double bond

NMR data	Reason	Structure
δ 1.3 (6H, s); δ 2.1 (3H, s); δ 2.6 (2H, s); δ 3.9 (1H, s).	Since $C_6H_{12}O_2$ molecule shows 2 signals, indicates 2 sets of protons present in the molecule.	



Q2. Two isomeric compounds A and B have molecular formula $C_{10}H_{14}$. 1H -NMR spectra of these gave the following data:

Isomer A: δ 1.30 (9H, s); δ 7.28 (5H, s)

Isomer B: δ 0.88 (6H, d); δ 1.86 (1H, m); δ 2.45 (2H, d); δ 7.12 (5H, s)

Giving reasons assign the structures for the two isomers.

2022-2023

Solution:

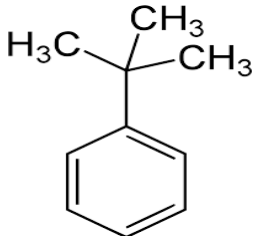
Double bond equivalence in isomer A and isomer B

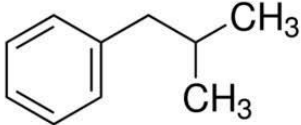
$$= C - H/2 + 1 = 10 - 14/2 + 1 = 4$$

Molecule will have three double bond and one ring thus part of the molecule will have benzene ring



Solution:

NMR data	Reason	Structure
Isomer A: δ 1.30 (9H, s); δ 7.28 (5H, s)	Since $C_{10}H_{14}$ molecule shows 2 signals, indicates 2 sets of protons present in the molecule.	 <p>The structure shows a central carbon atom bonded to a phenyl ring, a methyl group (H₃C), and two other methyl groups (CH₃).</p>

NMR data	Reason	Structure
Isomer B: δ 0.88 (6H, d); δ 1.86 (1H, m); δ 2.45 (2H, d); δ 7.12 (5H, s)	<ul style="list-style-type: none"> • Since $C_{10}H_{14}$ molecule shows 2 signals, indicates 2 sets of protons present in the molecule. 	 <p>The structure shows a phenyl ring attached to a propyl chain. The second carbon of the propyl chain has a methyl group (CH₃) attached to it.</p>



Q3 Predict the number of signals and splitting patterns in ^1H NMR of $\text{CH}_3\text{CCl}_2\text{CH}_3$ and $\text{CH}_3\text{OCH}_2\text{CH}_3$.

2022-2023

Solution:

$\text{CH}_3\text{CCl}_2\text{CH}_3$: All protons are chemically equivalent
i.e. only one signal which will be a singlet

a b c

$\text{CH}_3\text{OCH}_2\text{CH}_3$: There are 3 chemically non equivalent protons i.e. three signals

H_a : singlet

H_b : quartet

H_c : triplet



Q4 A compound having molecular formula C_4H_9Br gave the following signals in its 1H NMR spectra :

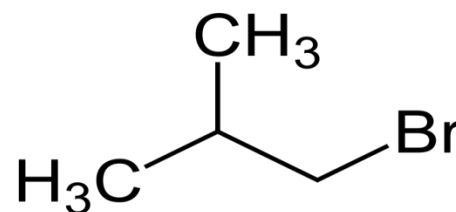
δ 1.04 (6H,d), δ 1.95 (1H,m), δ 3.33 (2H,d)

Giving reasons assign the structures for the compound.

Solution:

2022-2023

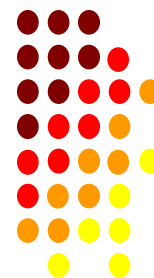
$$\begin{aligned} \text{Double bond equivalence} &= C - H/2 + N/2 + 1 - X/2 \\ &= 4 - 9/2 + 0/2 + 1 - 1/2 \\ &= 0 \end{aligned}$$



Now, $\delta = 1.04$, there is a doublet for 6 hydrogens i.e there are two CH_3 groups. therefore, $(CH_3)_2CH-$

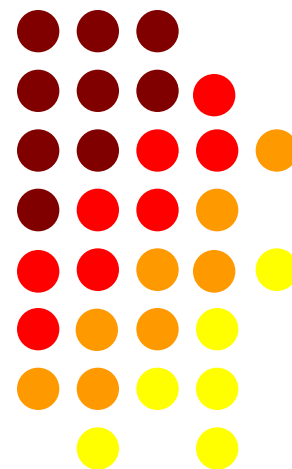
Also, $\delta = 1.95$, there is a multiplet because if one hydrogen i.e., a $CH-$ group attached to other alkyl groups

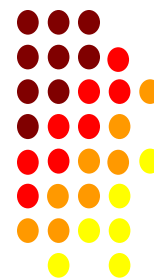
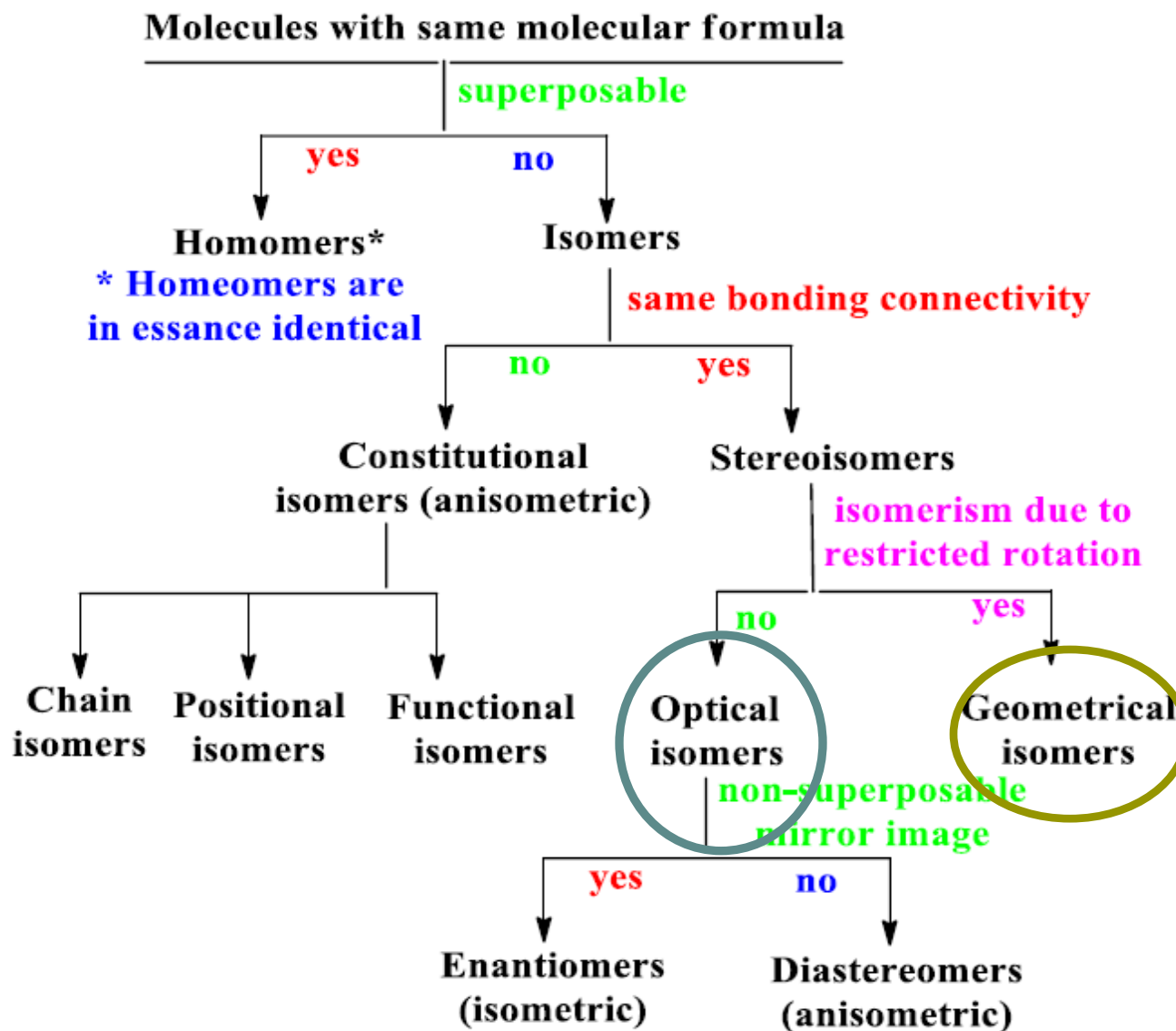
And, $\delta = 3.33$, there is a doublet due to two hydrogens i.e. a $-CH_2$ group attached to $-CH$



LECTURE - 17

Stereochemistry





Stereoisomers – compounds with the same connectivity, different arrangement in space

Enantiomers – stereoisomers that are non-superimposable mirror images; only properties that differ are direction (+ or -) of optical rotation

Diastereomers – stereoisomers that are not mirror images; different compounds with different physical properties



Asymmetric center – sp^3 carbon with 4 different groups attached

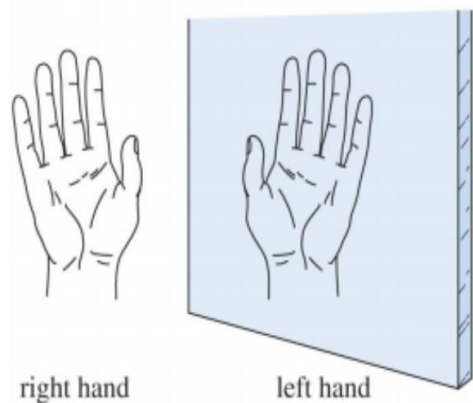
Optical Activity – the ability to rotate the plane of plane
–polarized light

Chiral Compound – a compound that is optically active
(achiral compound will not rotate light)

Polarimeter – device that measures the optical rotation of
the chiral compound

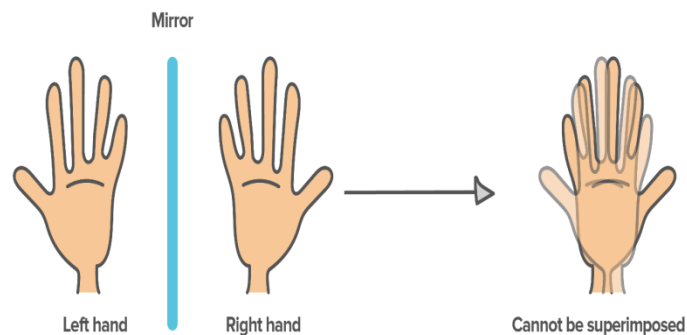


Chirality

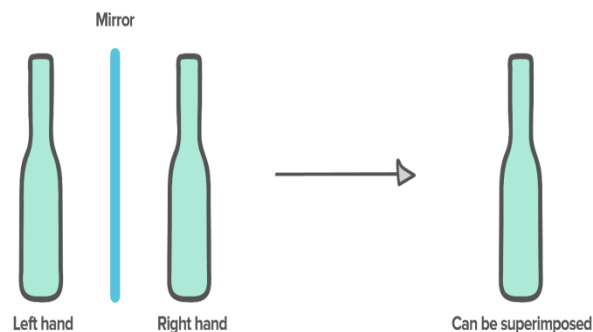


- Handedness: Right hand glove does not fit the left hand
- An object is chiral if its mirror image is different from the original object

CHIRAL OBJECTS

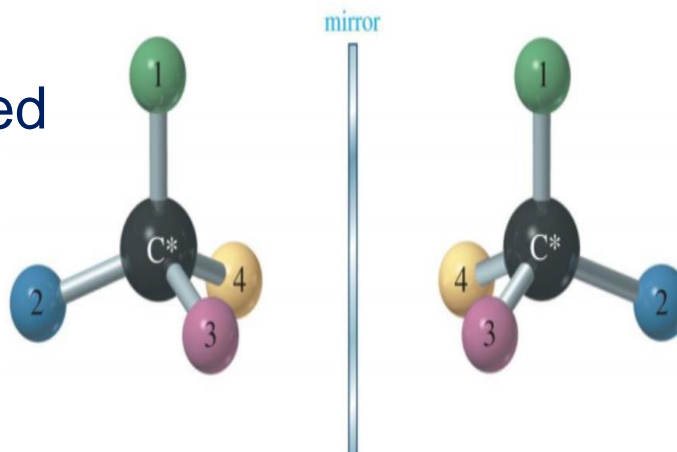


ACHIRAL OBJECTS



Chiral Carbon Atom

- Also called asymmetric carbon atom.
- Carbon atom that is bonded to four different groups is chiral.
- Its mirror image will be a different compound (enantiomer).



Stereocenters

- An asymmetric carbon atom is the most common example of a chirality center.
- Chirality centers belong to an even broader group called stereocenters. A stereocenter (or stereogenic atom) is any atom at which the interchange of two groups gives a stereoisomer.
- Asymmetric carbons and the double-bonded carbon atoms in cis-trans isomers are the most common types of stereocenters



Stereochemistry

Stereoisomers: isomers that have same formula and connectivity but differ in the position of the atoms in space. They possess one or more stereocenters.

Stereocenter: a carbon atom bearing 4 different atoms or group of atoms.

Chiral: any molecule that is non superimposable with its mirror image.

Enantiomers: stereoisomers that are non superimposable mirror images.

Racemic mixture: a 1:1 (equimolar) mixture of two enantiomers.

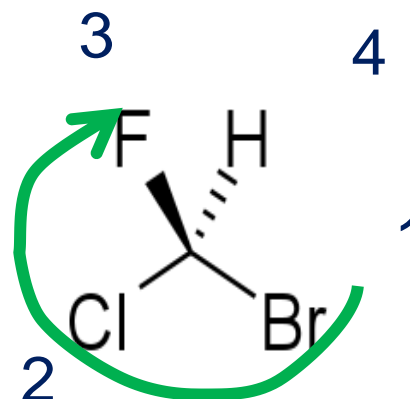
Optically Active: the ability of some compounds to rotate plane polarized light.



Cahn-Ingold-Prelog (CIP) rule

1. Assign the priorities to the groups attached to the stereocenter. Priority is based on the atomic number,

2. Orient the molecule so that the group of priority four (lowest priority) points away from the observer.



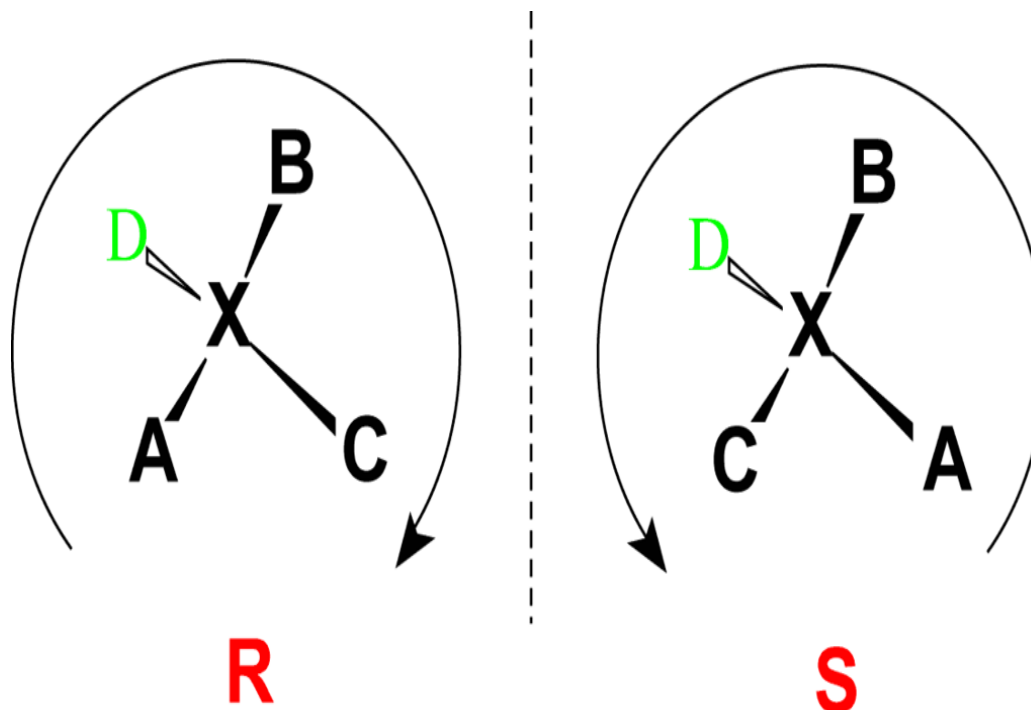
3. Draw a circular arrow from the group of first priority to the group of second priority up to third priority.

4. If this circular motion is clockwise, the enantiomer is the R enantiomer. If it is counterclockwise, it is the S enantiomer. These are known as absolute configuration

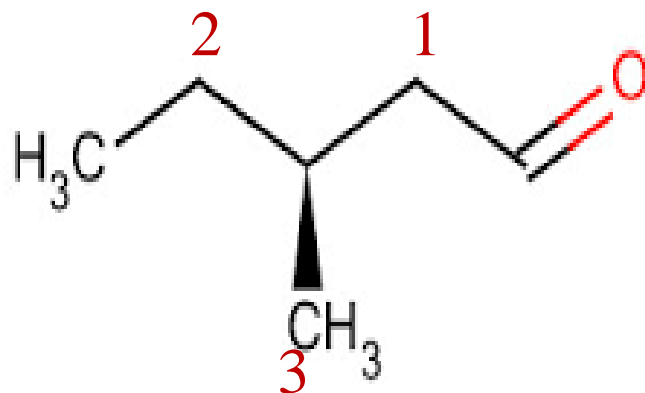
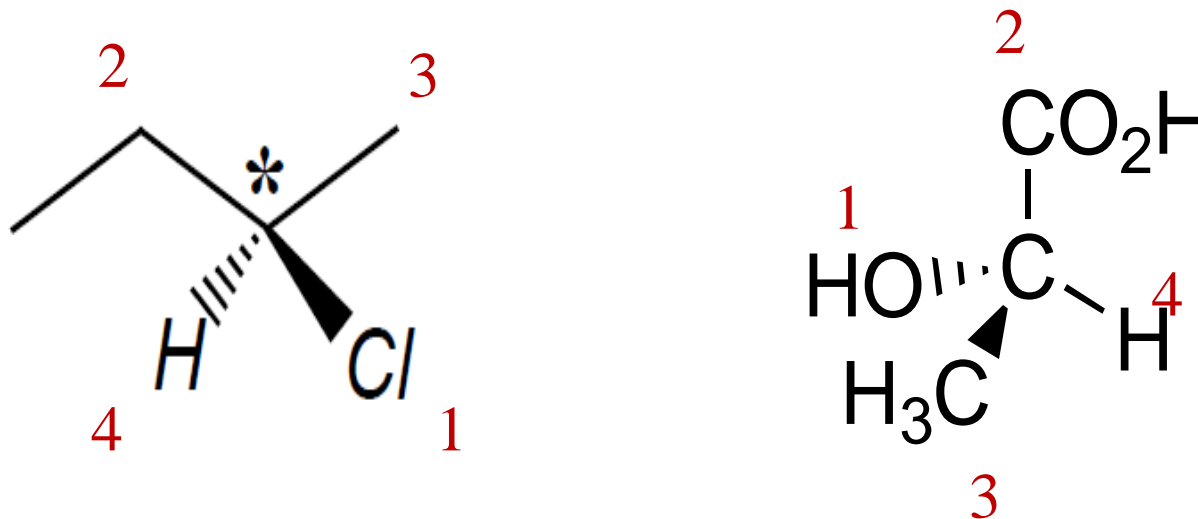


Absolute Configuration

An **absolute configuration** refers to the spatial arrangement of the atoms of a chiral molecular entity (or group) and its stereochemical description e.g. R or S

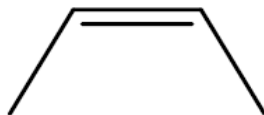


If chiral center is attached to more than one carbon atom

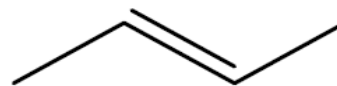


Geometrical Isomers

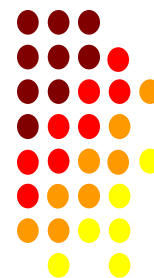
- Stereoisomerism ascribed to different directional arrangements of specifically located groups in the molecule and usually considered to be caused by prevention of free rotation in parts of the molecule (as by a double bond or a ring).
- This type of isomerism most frequently involves in compounds containing carbon-carbon double bonds with suitable substituents. Rotation of these bonds is restricted, compared to single bonds, which can rotate freely.
- This means that, if there are two different atoms, or groups of atoms, attached to each carbon of the carbon-carbon double bond, they can be arranged in different ways to give different molecules.



cis-2-Butene
 C_4H_8

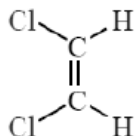


trans-2-Butene
 C_4H_8

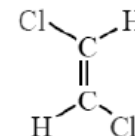


Example of geometrical isomerism:

a. 1,2 dichloro cyclopropane

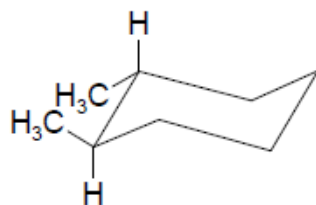


cis-1,2-Dichloroethene ($C_2H_2Cl_2$)

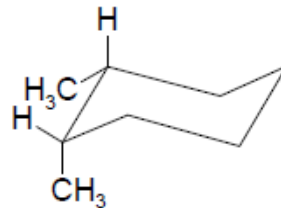


trans-1,2-Dichloroethene ($C_2H_2Cl_2$)

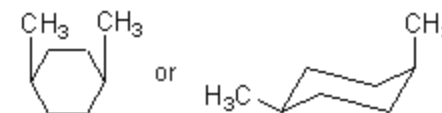
b. 1,2 dimethyl cyclohexane



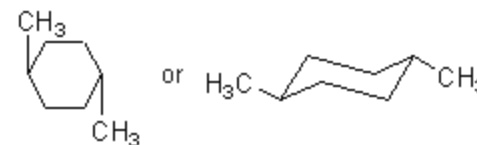
trans



cis

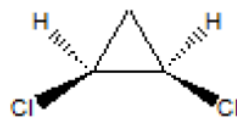


cis-1,4-dimethylcyclohexane



trans-1,4-dimethylcyclohexane

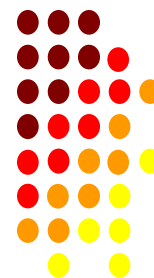
c. 1,2 dichloro cyclopropane



Cis 1,2 dichloro cyclo propane



Trans 1,2 dichloro cyclo propane



Optical Isomerisms

Organic compounds that exhibit optical isomerism must have a unique ability to rotate the plane polarized light either towards left or towards right hand directions. This unique ability is generally known as optical activity.

Enantiomers will rotate the plane of polarization in exactly equal amounts (same magnitude) but in opposite directions.

Dextrorotary designated as *d* or (+), clockwise rotation (to the right)

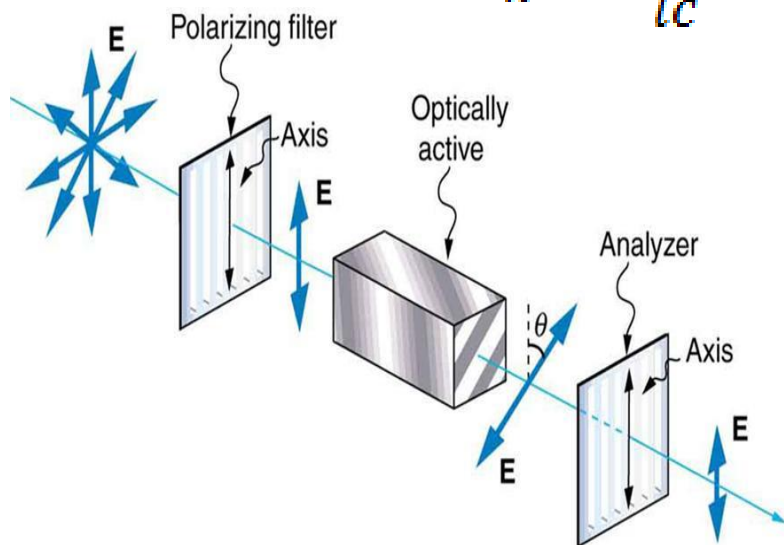
Levorotary designated as *l* or (-), anti-clockwise rotation (to the left)



Optical Activity

Optical activity is the ability of a chiral molecule to rotate the plane of plane-polarised light, measured using a polarimeter. A simple polarimeter consists of a light source, polarising lens, sample tube and analysing lens.

$$\alpha_{\lambda}^t = \frac{100\alpha}{lc}$$



- α_{λ}^T is the specific rotation in degrees $\text{cm}^3 \text{dm}^{-1} \text{g}^{-1}$.
- λ is the wavelength in nanometers,
- α is the measured angle of rotation of a substance,
- T is the temperature in degrees,
- l is the path length in decimeters,
- c is the concentration in g/ml



Determining Optical activity

Optical purity or enantiomeric excess (ee %) of a sample can be determined as follows:

$$\% ee = \frac{[\alpha]_{mixture}}{[\alpha]_{pure}} \times 100$$

If only one enantiomer is present a sample is considered to be **optically pure**. When a sample consists of a mixture of enantiomers, the effect of each enantiomer cancels out, molecule for molecule.



Problem on optical activity

Optical Activity in depth: Consider that (S)-bromobutane has a specific rotation of $+23.1^\circ$ and (R)-bromobutane has a specific rotation of -23.1°

Q1: Determine the optical purity of a racemic mixture.

Answer: The specific rotation, $[\alpha]$, of the racemate is expected to be 0, since the effect of one enantiomer cancel the other out, molecule for molecule.

$$\begin{aligned}\text{Optical purity, \%} &= 100 [\alpha]_{\text{mixture}} / [\alpha]_{\text{pure sample}} \\ &= 100 (0) / +23.1^\circ \\ &= 0\%\end{aligned}$$



Q2: Determine the enantiomeric excess of the racemic mixture.

Answer: You would expect $[R] = [S] = 50\%$.

$$\begin{aligned} ee\% &= 100 ([R]-[S]) / ([R]+[S]) \\ &= 100 (50-50) / (50+50) \\ &= 0\% \end{aligned}$$

Q3: Which isomer is dominant and what is the optical purity of a mixture, of (R)- and (S)-bromobutane, whose specific rotation was found to be -9.2° ?

Answer: The negative sign tells indicates that the R enantiomer is the dominant one.

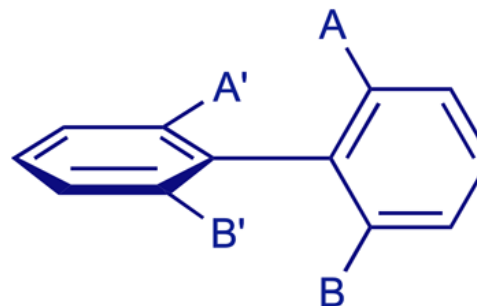
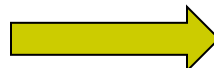
$$\begin{aligned} \text{Optical purity, \%} &= 100 [a]_{\text{mixture}} / [a]_{\text{pure sample}} \\ &= 100 (-9.2) / -23.1^\circ \\ &= 40\% \end{aligned}$$

This indicates a 40% excess of R over S!

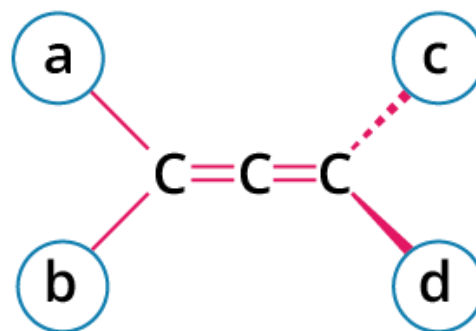


Optical isomer without chiral carbon

■ Atropisomerism



■ Allenes

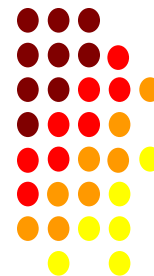
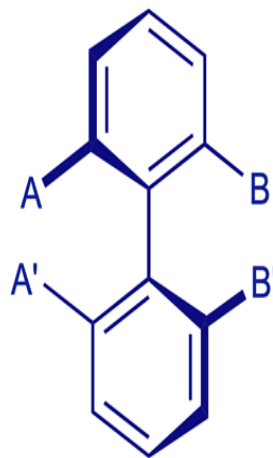


■ Spiranes



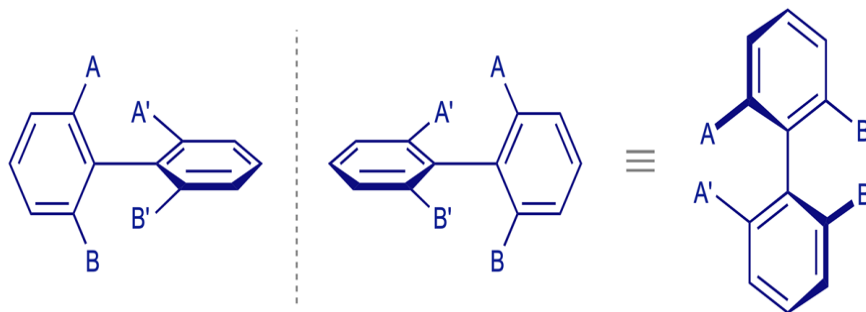
1. Atropisomerism

Atropisomers are Stereoisomers obtained due to the restricted rotation about carbon-carbon single bond are called atropisomers and the phenomenon is called atropisomerism. Such compounds also have the chirality due to the axis.



Biphenyl shows the enantiomerism when the molecule has the following properties

➤ Each ring must be unsymmetrically substituted. Each of the rings should not contain any kind of symmetry element



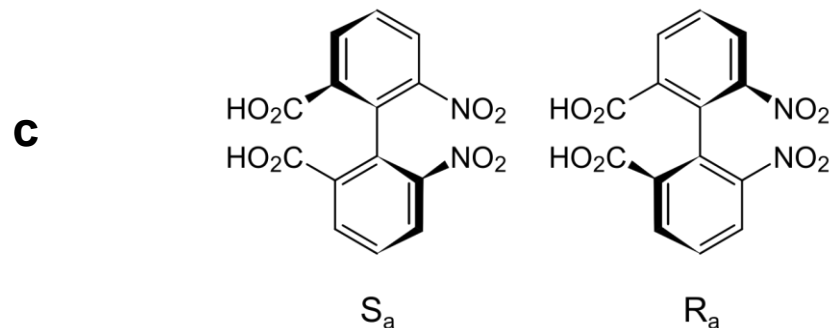
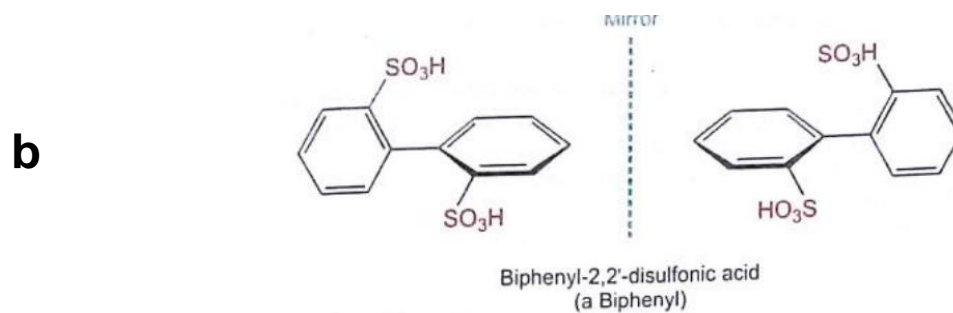
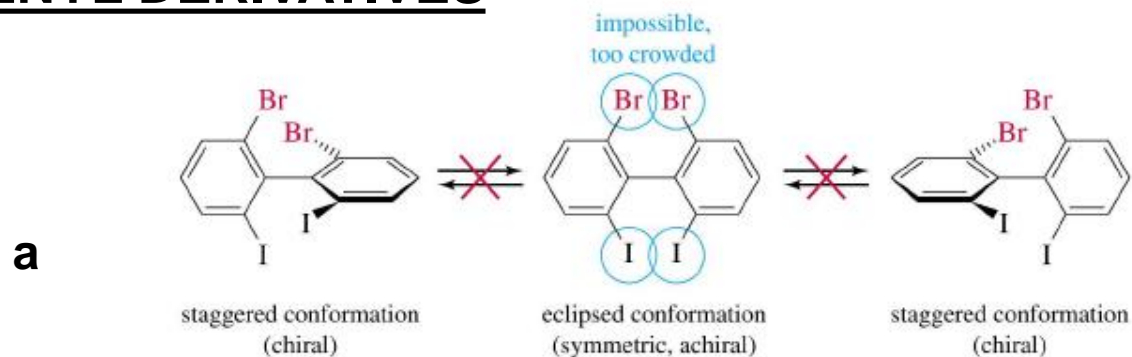
➤ Suitable substitution (at least one substitution) at *ortho*- position must be there at each rings.

➤ *ortho*- substituents must be larger in size (-Cl, -Br, -I, -COOH, -NO₂, -NHC(O)CH₃, -SO₃H, -R groups etc.).



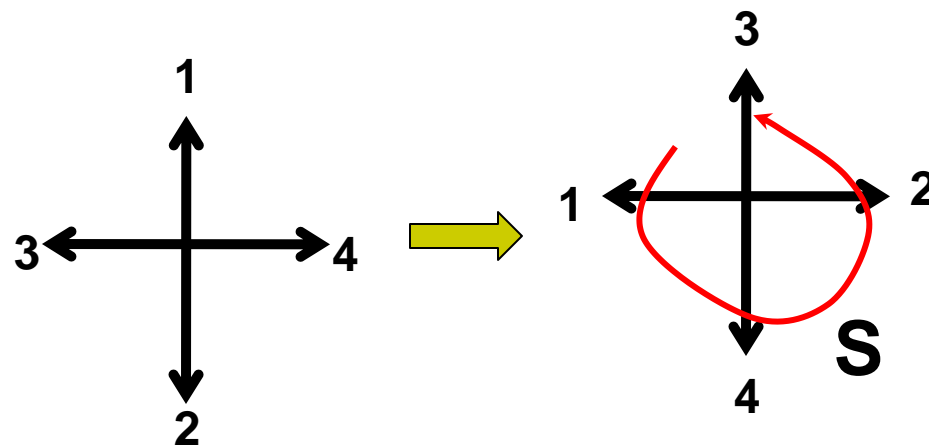
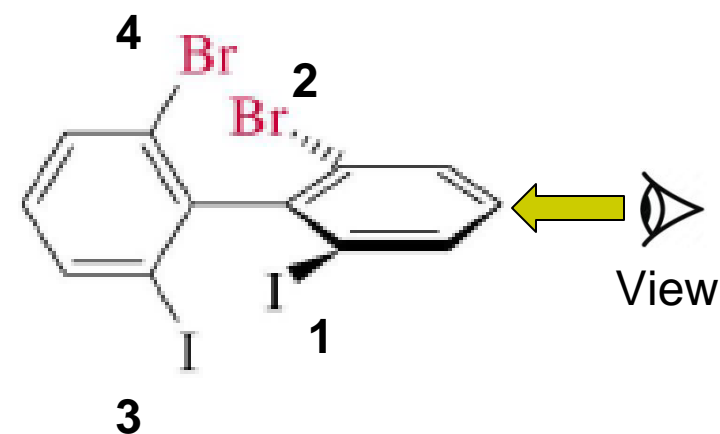
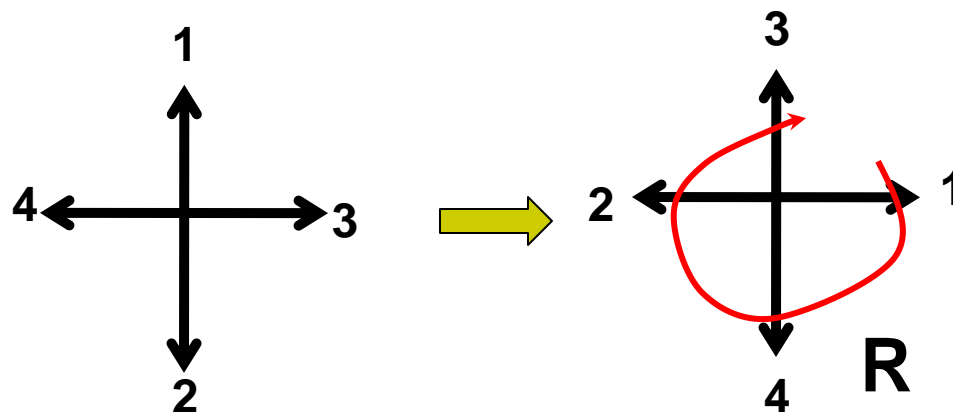
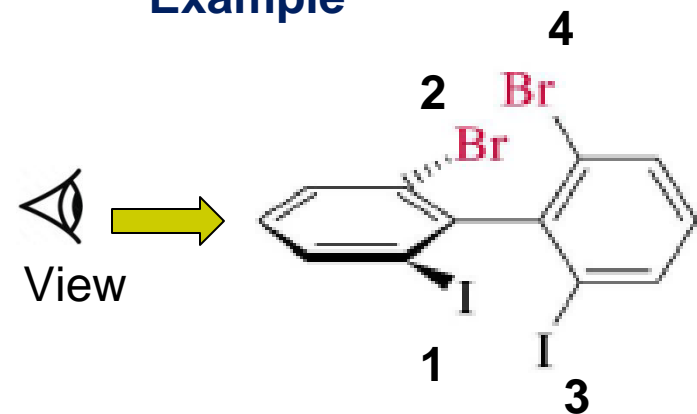
Optical isomers without chiral center

BIPHENYL DERIVATIVES



Optical Isomerism in achiral Spiro Compounds

Example



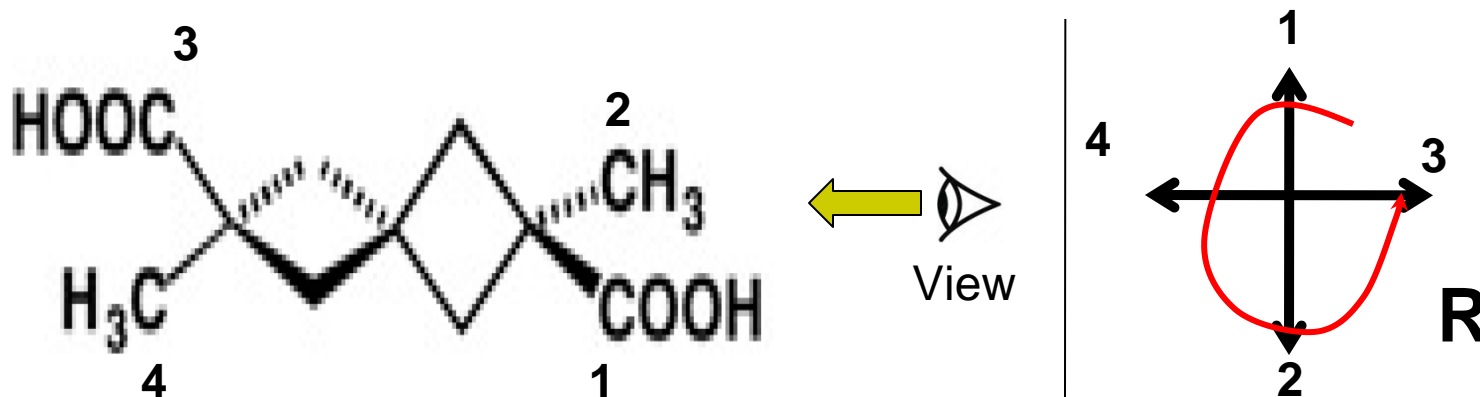
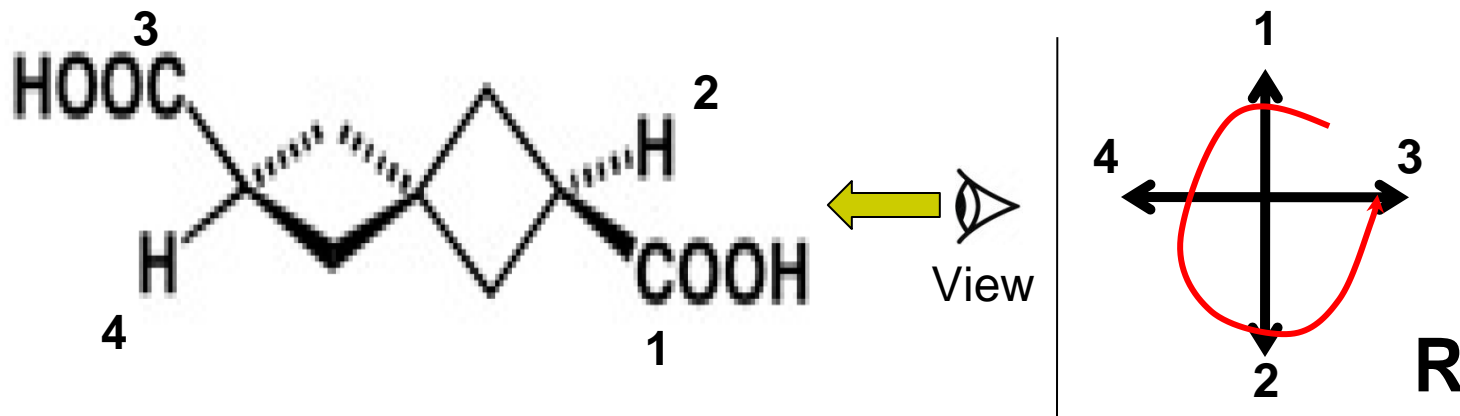
2. Optical activity in spiranes

- Stereochemistry of Spiranes: When both the double bonds in allenes are replaced with the ring system the resulting compounds are known as *spiranes* or *spiro compounds*
- The two rings of spiranes are perpendicular to each other .
- Proper substitution on the terminal carbon will make the molecule chiral and thus exhibit enantiomerism.



Optical Isomerism in achiral Spiro Compounds

Example

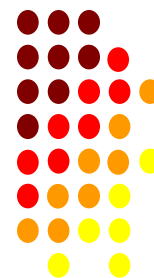


3. Optical isomerism in allenes

- Allenes are compounds with two double bonds side-by-side. Such bonds are called cumulated double bonds.
- The central carbon of allene forms two sigma bonds and two pi bonds.

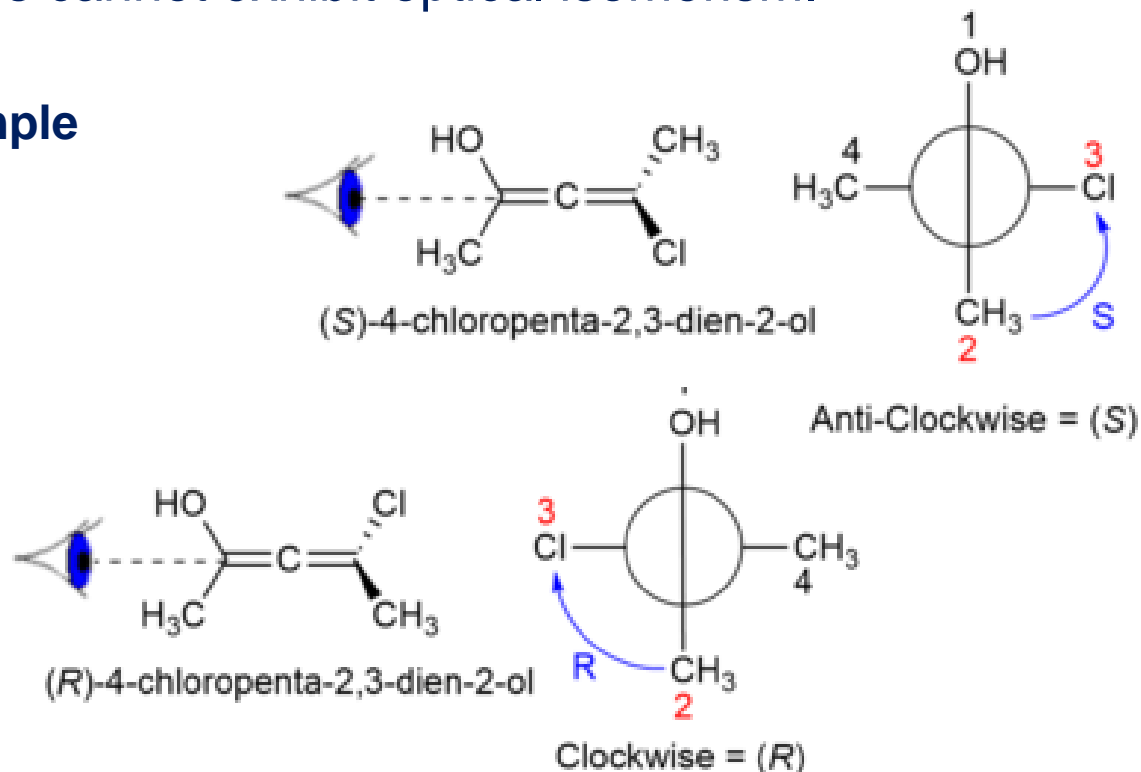


- The central carbon is sp -hybridized and the two terminal carbons are sp^2 -hybridized.
- The two π -bonds attached to the central carbon are perpendicular to each other.



- The two rings of spiranes are **perpendicular to each other**.
- Allene exhibit enantiomorphism, if each of the terminal sp^2 carbon atoms contain non-identical substituent.
- Allenes cannot exhibit optical isomerism.

Example



Problem on Stereochemistry

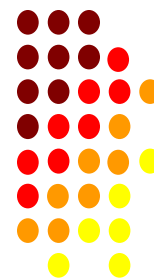
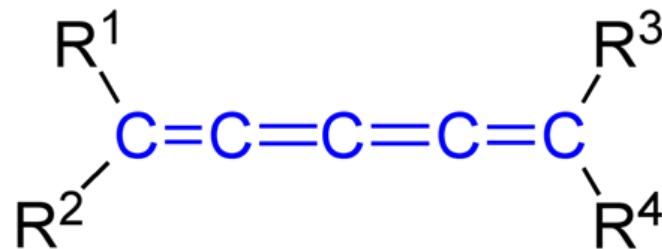
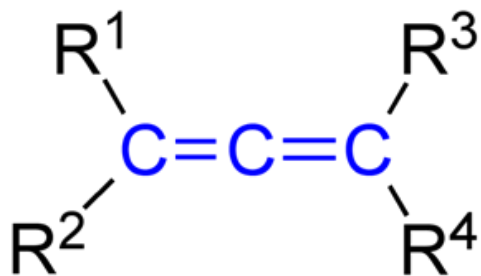
Q : Asymmetrically substituted compounds having even number of cumulative double bonds exhibit optical isomerism whereas compounds having odd number of cumulative double bonds exhibit geometrical isomerism . Explain giving proper reasons.

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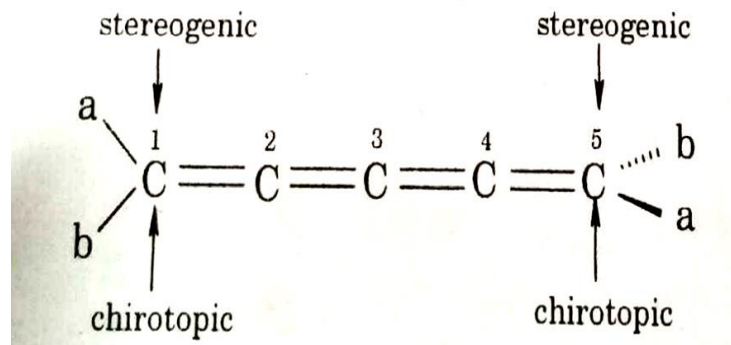


Cumulene exhibiting optical isomerism

Cumulene analogous to Allene: it having cumulative even number of double bond exhibit optical isomerism

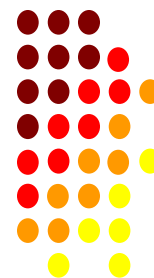
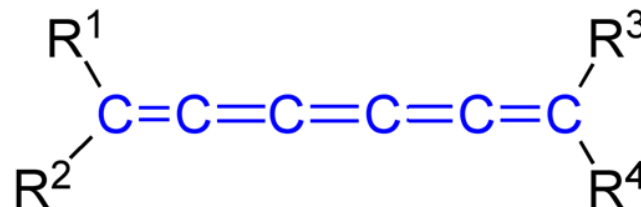
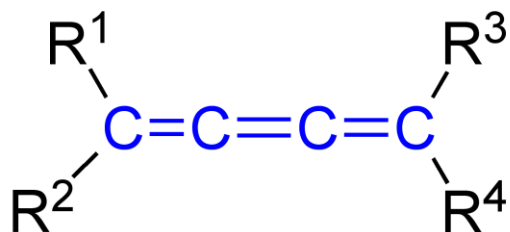


- The alternate π -bonds attached to the carbon are perpendicular to each other.
- This result in the group attached to terminal carbon are not in one plane. Hence molecule have chiral plane.
- Thus they exhibit optical isomerism (R-S configuration).



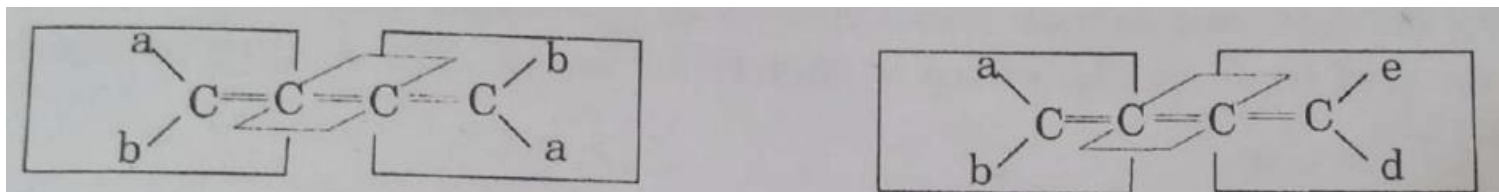
Cumulene exhibiting geometrical isomerism

Cumulene analogous to Alkene: it having cumulative odd number of double bond and exhibit geometrical isomerism

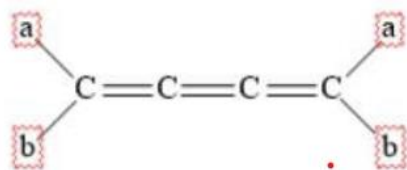


Since the alternate π -bonds attached to the carbon are perpendicular to each other.

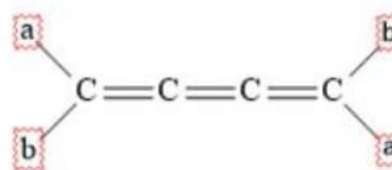
This result in the group attached to terminal carbon are in one plane.



Thus they exhibit geometrical isomerism (E-Z isomers)



cis



trans



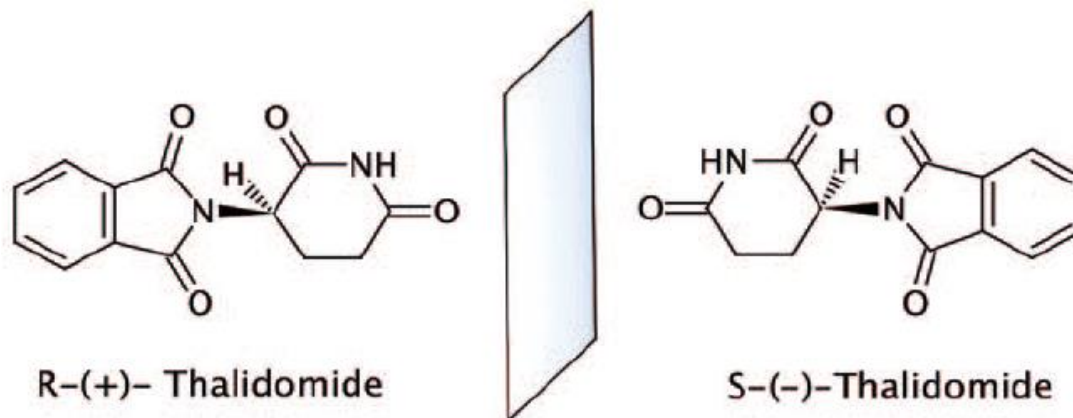
CHIRAL DRUGS

- Chemical compounds that come as mirror-image pairs are referred to by chemists as chiral or handed molecules.
- Each twin is called an enantiomer. Drugs that exhibit handedness are referred to as **chiral drugs**.
- Chiral drugs that are equimolar (1:1) mixture of enantiomers are called racemic drugs and these are obviously devoid of optical rotation.

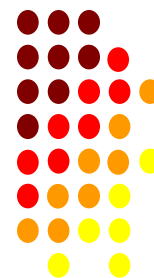


Few examples of chiral drugs whose enantiomers have vastly different properties

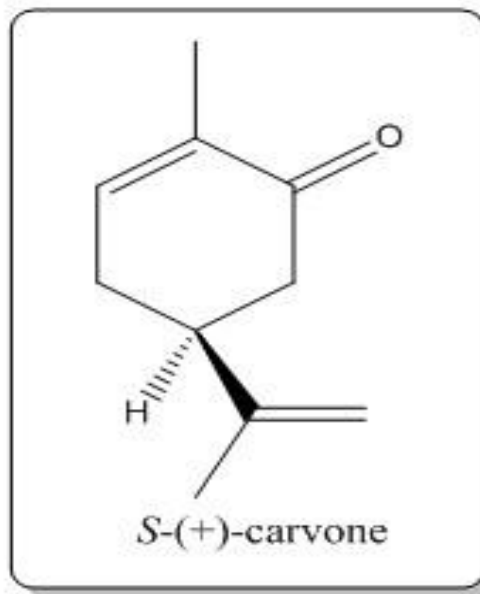
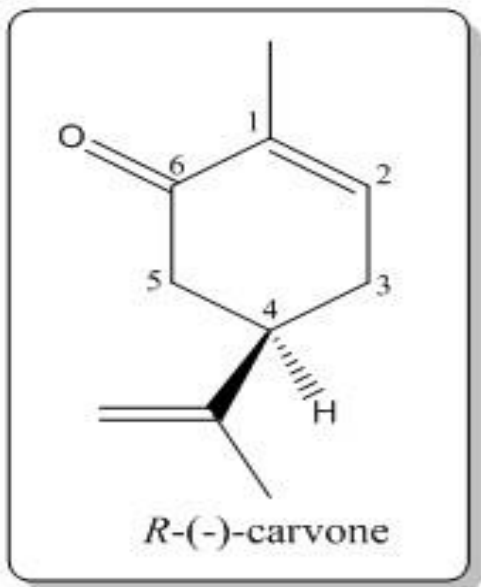
Thalidomide Chiral Drug



- R- enantiomer is an effective sedative with a soothing effect that relieves anxiety
- whereas S- enantiomer causes teratogenic birth defects.



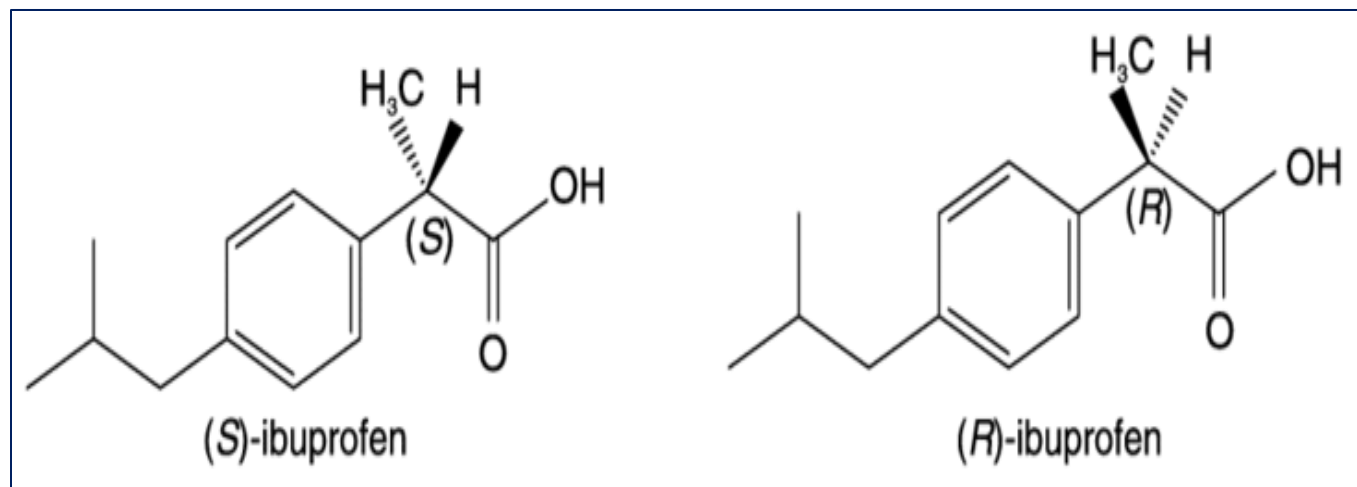
Carvone Chiral Drug



- These two smells differently. R-carvone smells like spearmint
- whereas S- carvone smells like caraway seed.



Ibuprofen Chiral Drug



- S-ibuprofen is a pain killer drug
- whereas R-ibuprofen is inactive.

