

## LECTURE - 9

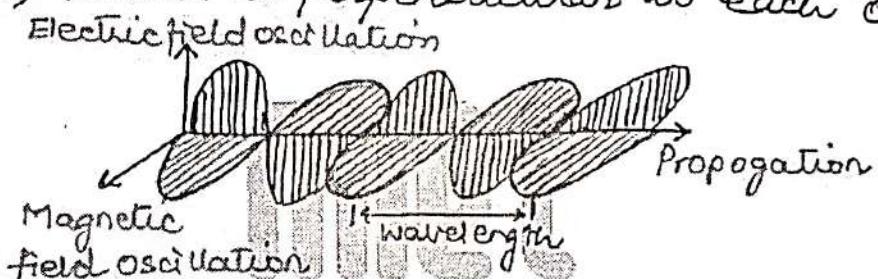
### SPECTROSCOPY

Spectroscopy is the study of the interaction of electromagnetic radiation with matter.

It is a general methodology that can be used to extract the information about the matter such as energies of electronic, vibrational, rotational states, structure, symmetry of molecules and their dynamic information.

### ELECTROMAGNETIC RADIATION (EMR) AND ITS PROPERTIES

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



Energy of photon is expressed in terms of frequency ( $\nu$ ) and wavenumber ( $\bar{\nu}$ ) as follows:

$$E = h\nu = \frac{hc}{\lambda}$$

where,  $h$  = planck's constant ( $6.626 \times 10^{-34} \text{ Js}$ )

$\lambda$  = wavelength (m)

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

Frequency of photon is given as -

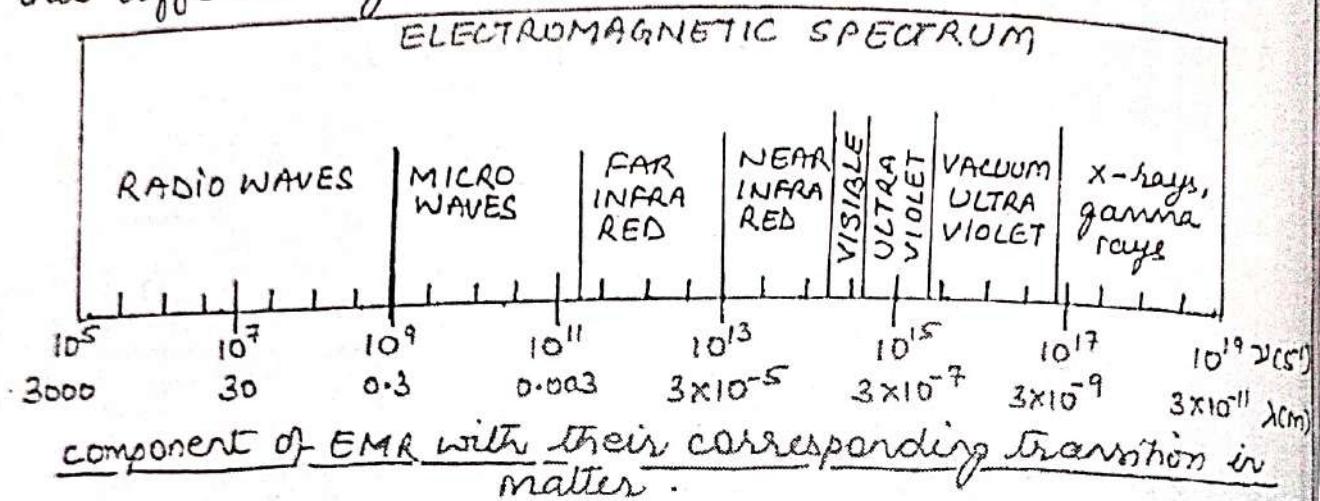
$$\nu = c/\lambda$$

unit of frequency is Hertz (Hz,  $s^{-1}$ ) or vibrations per second and that of wavenumber is  $\text{cm}^{-1}$ .

Relation between wavelength and wavenumber ( $\lambda$  and  $\bar{\nu}$  respectively)  $\bar{\nu} = \frac{1}{\lambda}$

Thus,  $E = hC\nu$

Based on energy, electromagnetic radiations has been divided into different regions.



TYPE OF RADIATION	FREQUENCY RANGE (HZ)	WAVELENGTH RANGE	TYPE OF TRANSITION
Gamma rays	$10^{20} - 10^{25}$	$< 10^{-12} \text{ m}$	Nuclear
X-rays	$10^{17} - 10^{20}$	$1\text{nm} - 1\text{pm}$	Inner electron
Ultraviolet	$7.5 \times 10^{14} - 10^{17}$	$400 - 1\text{nm}$	Outer electron
Visible	$4 - 7.5 \times 10^{14}$	$750 - 400\text{nm}$	Outer electron
Near Infrared	$1 \times 10^{14} - 10^{15}$ $4 \times 10^{14}$	$2.54\mu\text{m} - 750\text{nm}$	Outer electron molecular vibration
Infrared	$10^{13} - 10^{14}$	$254\mu\text{m} - 2.54\mu\text{m}$	Molecular vibration
Microwave	$3 \times 10^{11} - 10^{13}$	$1\text{mm} - 254\mu\text{m}$	Molecular rotation Electron spin
Radio Waves	$< 3 \times 10^{11}$	$> 1\text{mm}$	Nuclear spin

### TYPES OF MOLECULAR ENERGY

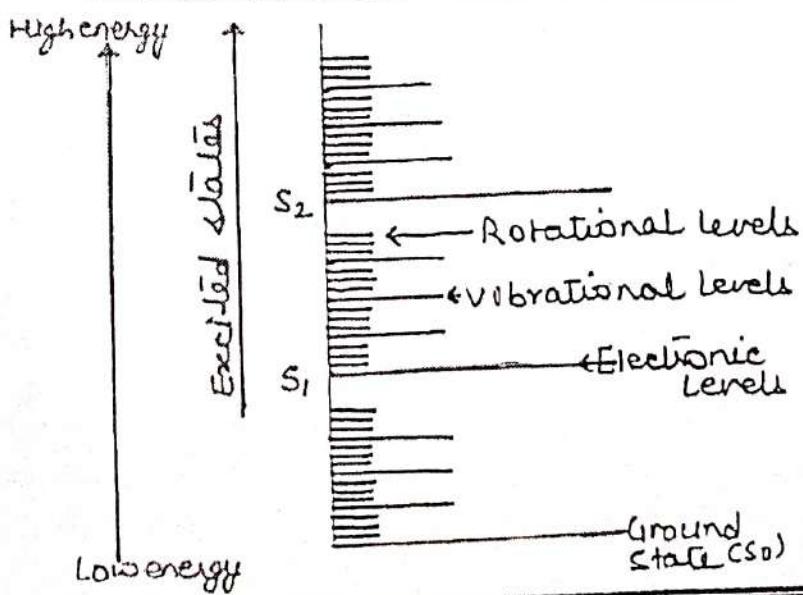
A molecule has 4 types of energy levels -

1. Electronic energy levels: The energy associated with electrons in a molecule (bonding and antibonding orbitals) are called electronic energy level. It is quantized form of energy means it can have only certain discrete values. The energy gap between these levels falls in UV-visible region.

2. Vibrational Energy levels: The bonds in a molecule always vibrate. The energy associated with the vibrational motion is called vibrational energy. It is also quantised. The energy gap between two adjacent vibrational energy levels falls in infrared region.
3. Rotational Energy levels: Molecule always rotates in space about an axis passing through the centre of mass. The energy associated with rotation of molecule is called rotational energy. Rotational energy levels are also quantised. The energy gap between rotational energy levels correspond to microwave region.
4. Translational Energy levels: Energy associated with translational motion is called translational energy. During translational motion, the position of centre of mass changes. Therefore, it appears as continuous form of energy. It is found that this energy is negligibly small.  
Hence, Total energy in the molecule can be expressed as follows

$$E_{\text{total}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}}$$

$$E_{\text{trans}} \ll E_{\text{rot}} < E_{\text{vib}} < E_{\text{elec}}$$



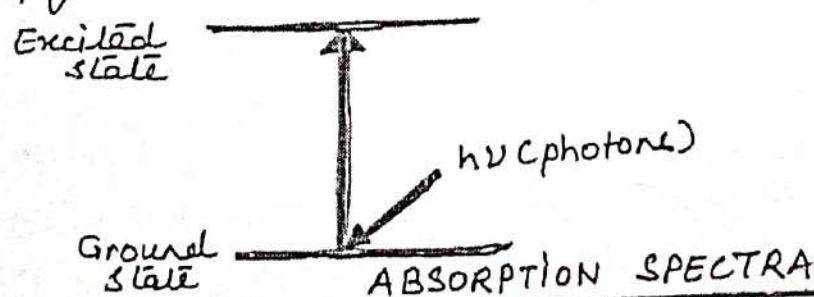
Molecular energy level diagram,  
where  $S_0, S_1$  &  $S_2$   
are ground  
electronic state,  
first electronic  
excited and  
second electronic  
excited state,  
respectively.

various transitions in molecule upon interaction with EMR

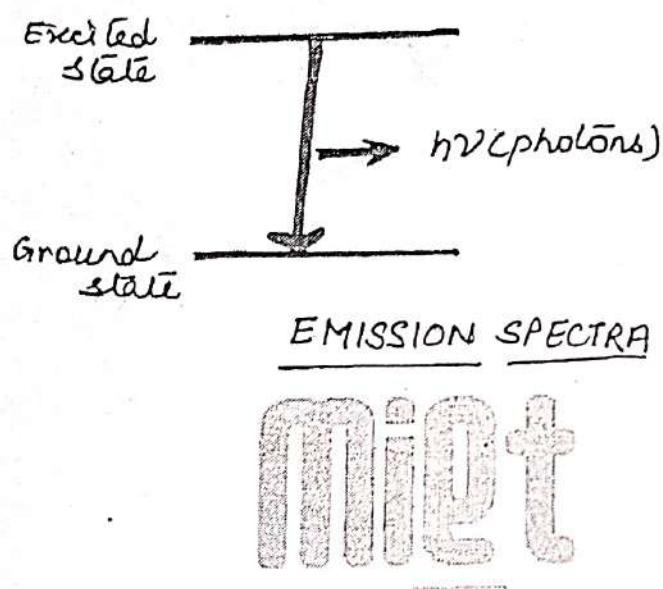
1. Electronic Transition: when a molecule absorbs ultra-violet or visible light, its electrons promote from ground electronic state to the higher electronic state. During excitation, an electron gets excited from a bonding to antibonding orbital. This transition is called electronic transition.
2. Vibrational transition: when infra-red radiations are absorbed, molecules are excited from one vibrational energy level to another vibrational energy level. Vibrational transition occurs within the same electronic state but two different vibrational energy states.
3. Rotational transition: when microwave radiation is absorbed, molecules get excited from one rotational energy level to another rotational energy level. Rotational transition occurs within same vibrational state between two different rotational energy states.

Type of spectrum exhibited by molecule upon interaction with electromagnetic radiation

Absorption spectrum: when a continuous range of radiation interact with molecule, certain frequencies are absorbed by the molecule. The spectrum obtained is called absorption spectrum which is a plot of intensity with wavelength of EMR radiation after interaction. Example: uv/visible (electronic) spectroscopy, vibrational (IR) spectroscopy.

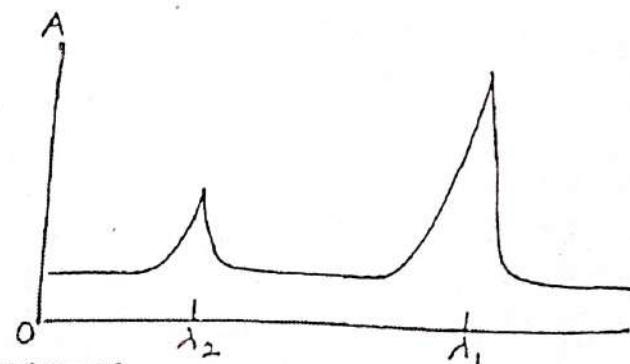
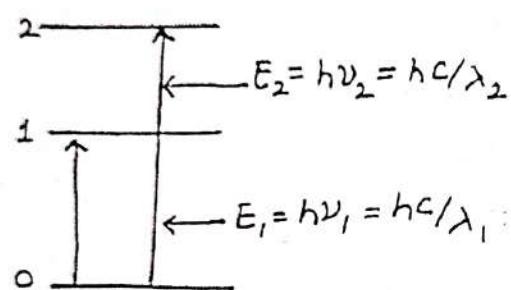


Emission Spectrum: The molecules get excited by irradiating with electromagnetic radiation. Molecules will relax back to the initial low energy state via emission of radiation. The spectrum obtained is called emission spectrum. Example: Fluorescence spectroscopy, phosphorescence spectroscopy.



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The interaction of electromagnetic radiation with matter causes the atoms and molecules to absorb energy and go to a higher energy state which is unstable. They need to emit radiations to return to their normal states, giving rise to absorption and emission spectra. Interaction of light with matter can be analysed as absorption/emission spectrum which is a plot of the intensity of radiations as a function of photon wavelength.

TYPICAL ABSORPTION SPECTRUM

Depending on frequency of EMR during light-matter interaction, following technique have been developed for the investigation of molecule.

SPECTROSCOPIC TECHNIQUE	PROCESS INVOLVED	EMR RANGE APPLICABLE	TRANSITIONS	INFORMATION OBTAINED
UV-visible spectroscopy	Absorption	350 nm — 750 nm	Electronic transition	Qualitative and quantitative information of matter.
Infrared or vibrational Spectroscopy	Absorption	750 nm — 1 mm	vibrational energy level spacing	Functional grp, force const, bond length, bond angle quantitative analysis
Microwave or Rotational Spectroscopy	Absorption	1 mm — 1 m	Rotational energy level spacing	Force constant, bond length, bond angle
Raman Spectroscopy	Scattering	532 nm, 633 nm, 780 nm, 1064 nm.	Rotational & vibrational energy level spacing	Chemical structure, phase & polymorphy, crystallinity, molecular interactions.

Q1. What is Beer-Lambert Law in UV-visible absorption spectroscopy? A compound having concentration  $10^{-3} \text{ g/L}$  resulted absorbance value 0.20 at  $\lambda_{\text{max}} = 510 \text{ nm}$  using 1.0 cm cell. Calculate its absorptivity and molar absorptivity values. Molecular weight of compound is 400 (2015-16, 2016-17, 2018-19)

Sol. The Beer-Lambert law states that, for dilute solution upon interaction with monochromatic radiation, the absorbance of a sample is directly proportional to the concentration & path length of the sample, which is as follows:

$$A \propto c l$$

$$A = E c l$$

where,  $A$  is the absorbance,  $c$  is the concentration of sample ( $\text{g/mL}$  or  $\text{mol/L}$ ),  $l$  is the path length of sample cell in cm,  $E$  is absorptivity or molar absorptivity or molar extinction coefficient. ( $\text{L/mol.cm}$ )

Numerical Given -  $c = 10^{-3} \text{ g/L}$ ; mol. wt. of compound = 400  
 $l = 1 \text{ cm}$   
 $A = 0.20$

$$\text{Molar concentration } c_m = \frac{10^{-3}}{400} = 0.25 \times 10^{-5} \text{ mol/L}$$

$$A = E_m c_m l$$

$$E_m = A / c_m \cdot l$$

$$= 0.2 / 0.25 \times 10^{-5} \times 1 = 8 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$$

Q2. State and derive the Lambert-Beer's law. The percentage transmittance of an aqueous solution of unknown compound is 20% at  $25^\circ\text{C}$  & 300 nm for  $2 \times 10^{-5} \text{ M}$  solution in a 4cm cell. calculate the absorbance and the molar extinction coefficient. (2019-20)

Sol. Lambert Beer's law statement: The decrease in the intensity of monochromatic radiation after passing through sample containing absorbing species is directly proportional to incident intensity ( $I_0$ ), thickness of and

sample (dl) and concentration (c) of the sample.

$$dI \propto -I \cdot c \cdot dl \quad (1)$$

$$dI = -k \cdot I \cdot c \cdot dl \quad (2)$$

Where constant  $k$  is called proportionality coefficient.

$$\frac{dI}{I} = -k \cdot c \cdot dl \quad (3)$$

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  $I_0$  is incident intensity and  $I$  is the final intensity of transmitted light.

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

$$\ln \frac{I}{I_0} = -Kcl \quad (5)$$

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

converting  $\ln$  to  $\log_{10}$  by replacing  $\frac{k}{2.303} = \epsilon$

$$\log_{10} \frac{I}{I_0} = -Ecl \quad (7)$$

where constant  $\epsilon$  is called absorptivity when concentration is in gm/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 becomes -

$$-\log_{10} T = Ecl \quad (8)$$

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

$$A = -\log_{10} T = Ecl \quad (9)$$

If Absorbance is zero i.e.  $A=0$  at any wavelength, it means that no light of that particular wavelength has been absorbed. At this point output intensity will be equal to incident intensity of radiation.

B. Tech I Year [Subject Name: Engineering Chemistry]

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

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

Numerical:  $\%T = 20\%$ .

concentration ( $C_m$ ) =  $2 \times 10^{-5} M$ .

Path length ( $L$ ) = 4 cm

Since,  $\%T = 20\%$ .

so,  $T = 0.2$

$$\text{Absorbance } (A) = -\log(T) = -\log(0.2) \\ = 0.699$$

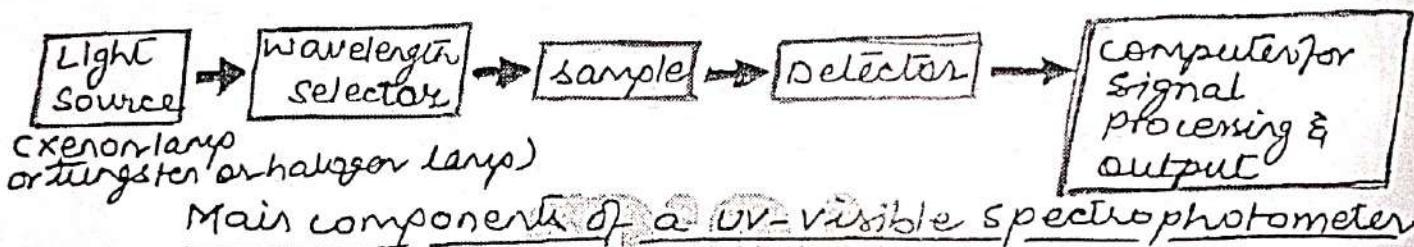
Also,  $A = E_m C_m L$

$$E_m = \frac{A}{C_m L} = \frac{0.699}{2 \times 10^{-5} \times 4} \\ = 8.74 \times 10^3 M^{-1} cm^{-1}$$

## ULTRA VIOLET - VISIBLE SPECTROSCOPY [Lecture-11]

UV-vis spectroscopy is an analytical technique that measures the amount of discrete wavelengths of UV or visible light that are absorbed or transmitted through a sample in comparison to a reference or blank sample. This property is influenced by the sample composition, providing information on what is in sample and at what concentration.

The instrument used to study UV-visible spectra is called UV-vis spectrophotometers.



The intensity of UV-visible radiation after passing through sample solution is measured as a function of wavelength of the radiation. The measurement of wavelength and intensity of radiation provides important information about its electronic structure and no. of molecules. Thus, both quantitative and qualitative information can be gathered. Information may be obtained as transmittance, absorbance or reflectance of radiation in 160 nm to 750 nm wavelength range.

- \* Ordinary UV-visible measurements are carried out from 200 nm to 800 nm. Below 200 nm, the measurements are done under vacuum to avoid absorbance signals from air components like  $\text{CO}_2$ . Therefore, region below 200 nm is called vacuum UV and corresponding technique is called vacuum UV spectroscopy.

There are 3 types of electrons which are involved in electronic transition from the molecule:

- a)  $\sigma$  electrons: Electrons forming sigma bond
- b)  $\pi$  electrons: Electrons responsible for the formation of double and triple bond.
- c)  $n$  electrons: These are unshared or non-bonded electrons.

These electrons on excitation are transmitted from their bonding orbitals to corresponding antibonding orbitals.

- \* When a molecule is subjected to UV-light, a spectrum is obtained in spectrophotometer. The spectrum consists of bands which are plots between absorbed light and wavelength. Through the study of these bands we can elucidate the molecular structure.

M.M.F.  
Q. What are chromophores and auxochromes? How do auxochromes increase the colouring power of chromophores. Explain transitions in UV spectra.  
(2014-15, 2015-16, 2016-17, 2020-21)

Ans. **CHROMOPHORE:** The part of a molecule that is responsible for absorption of EMR in Ultra violet region is known as chromophore. Chromophore may or may not produce colour in the compound.  
→ These are the functional groups containing multiple bonds capable of absorbing radiations above 200 nm, due to  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions.  
eg-  $\text{NO}_2$ ,  $\text{N}=\text{O}$ ,  $\text{C}=\text{O}$ ,  $\text{C}=\text{N}$ ,  $\text{C}\equiv\text{N}$ ,  $\text{C}=\text{C}$ ,  $\text{C}=\text{S}$  etc.  
There are two types of chromophores-  
a) chromophores containing n electrons: they undergo  $n \rightarrow \pi^*$  transitions.  
b) chromophores containing n and π electrons: they undergo  $n \rightarrow \pi^*$  as well as  $\pi \rightarrow \pi^*$  transitions.

**AUXOCHROME:** (Auxo means to enhance). It is a group which itself does not act as a chromophore but when attached to a chromophore it shifts the absorption towards longer wavelength along with an increase in the intensity of absorption. All auxochromes have one or more non bonding pairs of electrons. On attaching to the chromophore, they help in extending the conjugation by sharing their non bonding pair of electrons. Some commonly known auxochromic groups are:  $\text{OH}^-$ ,  $-\text{NH}_2$ ,  $-\text{OR}$ ,  $-\text{NHR}$ ,  $-\text{NR}_2$ .

For example- Benzene :  $\lambda_{\text{max}} = 255 \text{ nm}$   
Phenol : - OH group attached to benzene

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

Aniline: -NH<sub>2</sub> grp attached to benzene,  $\lambda_{\text{max}} = 280 \text{ nm}$

Auxochrome increase the colouring power of chromophores: The addition of auxochrome to the chromophore shifts the absorption towards higher wavelength region. This occurs due to extended conjugation by sharing their lone pair of electrons. Hence, auxochrome introduces colour to the chromophore.

### TRANSITIONS IN UV spectra

Four types of transitions of electrons which are observed in molecules on absorbing UV-visible radiations are :-

1.  $\sigma \rightarrow \sigma^*$  transitions: An electron in a  $\sigma$ -bonding orbital is excited to the corresponding  $\sigma^*$ -antibonding orbital. The energy required lies in the vacuum UV region. This type of transition is common for saturated organic molecules, without hetero atoms. Example: Methane (CH<sub>4</sub>) has C-H bonds only and can undergo  $\sigma \rightarrow \sigma^*$  transitions and shows the absorbance maxima at 125 nm.
2.  $\pi \rightarrow \pi^*$  transitions: These transitions occur when an electron from  $\pi$  bonding orbital are promoted to  $\pi^*$  anti bonding orbital. These are very intense transitions. 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 between 170 nm to 205 nm. In an aliphatic ketone, the absorption band arises at around 185 nm due to

the  $\pi \rightarrow \pi^*$  transition in carbonyl group.

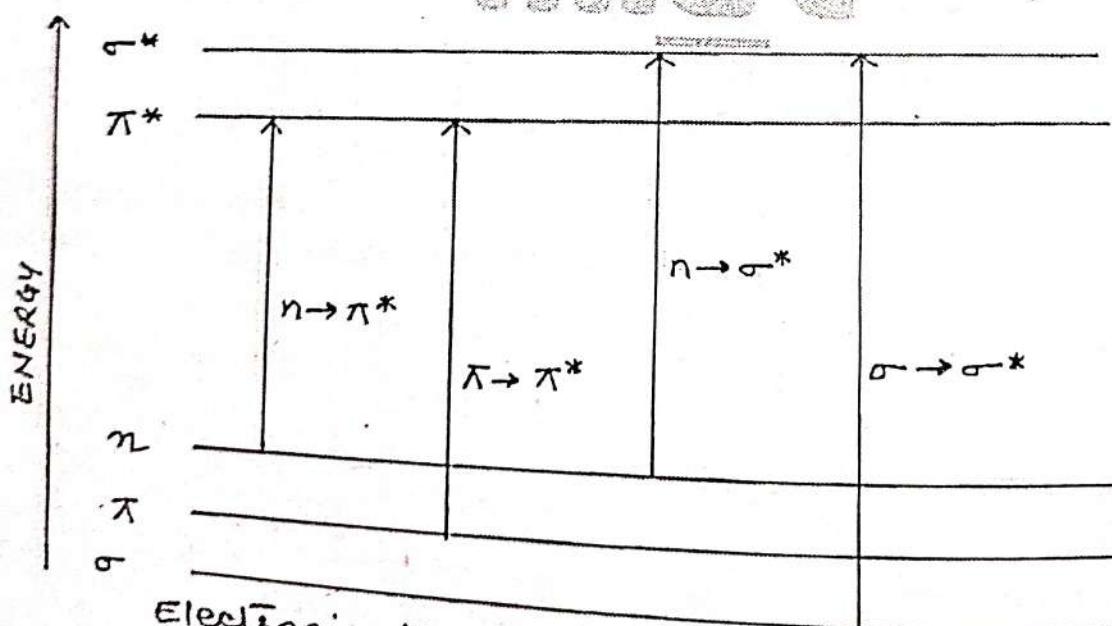
3.  $n \rightarrow \sigma^*$  transition: These types of transition occur when an electron from a non bonding orbital are promoted to  $\sigma^*$  antibonding orbital. Saturated compounds containing atoms with lone pair of electrons like O, N, S and halogens are capable of  $n \rightarrow \sigma^*$  transitions.

4.  $n \rightarrow \pi^*$  transitions: These type of transitions occur when an electron from a non bonding orbital are promoted to  $\pi^*$  antibonding orbital. These transitions are shown by unsaturated molecules which contain hetero atoms like N, O, Cl, Br, S etc. Example - any compound containing double bond ( $C=O$ ,  $C=N$ ,  $N=O$ ) undergo such transitions.

Energy required for various electronic transitions are as follows:-

$$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$$

forbidden transitions: Transitions such as  $\sigma \rightarrow \pi^*$  and  $\pi \rightarrow \sigma^*$  are called forbidden transitions which are only theoretically possible.



Electronic transitions in UV Spectroscopy

Q2. Predict electronic transitions in  $C_2H_4O$ . C2017-18)

Electronic transitions in  $\text{CH}_3\text{CHO}$ : Griner compound is an aldehyde which consists of carbonyl group with C and a hetero atom (oxygen). Thus the molecule will have non bonding orbital, bonding orbitals ( $\sigma$ ,  $\pi$ ) and antibonding ( $\sigma^*$ ,  $\pi^*$ ) orbital. Thus, the possible transitions are :

- i)  $\sigma \rightarrow \sigma^*$  : Due to  $\sigma$  electrons in  $\sigma$  bond, but not allowed (below 190 nm)
- ii)  $n \rightarrow \pi^*$  and  $n \rightarrow \sigma^*$  : These transitions are allowed and can be recorded (from 200 - 480 nm)
- iii)  $\pi \rightarrow \pi^*$  : In  $\text{C=O}$ ,  $\pi$  electrons are available but not in conjugation.

Q3. Give the possible electronic transitions (UV spectra) in  $\text{CH}_3\text{CH}_2\text{CH}_3$ ,  $\text{CH}_3\text{CH}=\text{CH}_2$ ,  $\text{CH}_3\text{CH=O}$  and  $\text{CH}_3\text{CH=CH-CH=CH-CH}_3$ .

Ans. For  $\text{CH}_3\text{CH}_2\text{CH}_3$  : It is saturated aliphatic compound which have only  $\sigma$  and  $\sigma^*$  orbital. Hence, possible transition is  $\sigma \rightarrow \sigma^*$ .

For  $\text{CH}_3\text{CH}=\text{CH}_2$  : It is unsaturated compound which have  $\sigma$ ,  $\pi$ ,  $\pi^*$  and  $\sigma^*$  orbital. Hence, possible transition is  $\sigma \rightarrow \sigma^*$  and  $\pi \rightarrow \pi^*$ .

For  $\text{CH}_3\text{CH=O}$  : It is a carbonyl compound which have  $\sigma$ ,  $\pi$ ,  $\pi^*$  and  $\sigma^*$  orbital and a non bonding ( $n$ ) orbital. Hence, possible transition is  $\sigma \rightarrow \sigma^*$ ,  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$  and  $n \rightarrow \sigma^*$ .

For  $\text{CH}_3\text{CH=CH-CH=CH-CH}_3$  : It is unsaturated conjugate compound which have  $\sigma$ ,  $\pi$ ,  $\pi^*$  and  $\sigma^*$  orbital. Hence possible transition is  $\sigma \rightarrow \sigma^*$  and  $\pi \rightarrow \pi^*$  where both the transitions will come at longer wavelength.

due to double bonds in conjugation as compared to possible transition in  $\text{CH}_3\text{CH}=\text{CH}_2$ .

Q4. Give the basic principle of UV spectroscopy.

Ans. Principle of UV spectroscopy: When a molecule absorbs UV radiations, its electrons undergoes transitions from lower electronic energy level to higher electronic energy levels in accordance with the frequency of absorbed radiations.



ABSORPTION AND INTENSITY SHIFTS

The presence of auxochrome or the solvent effect causes the absorbance maxima of the compound to be shifted to longer wavelength or/and an increase in the intensity which are known as absorption and intensity shifts respectively.

When absorption maxima of the compound shifts towards longer wavelength, it is known as bathochromic shift, whereas if it is shifted towards shorter wavelength it is known as hypsochromic shift.

Similarly when the absorption intensity ( $E$ ) of a compound decreases, it is called hypochromic shift and if the absorption intensity increases it is known as hyperchromic shift.

The above effects in the compound can be attributed to various factors including presence or removal of auxochrome, change of solvent as well as the effect of conjugation.

UV-visible spectroscopy finds various applications such as to find the extent of conjugation, to distinguish between conjugated and non-conjugated compounds, to study and distinguish between geometrical isomers, to detect the impurities in the sample, to study the kinetics of the reactions, to find the molar concentration of the compound under study, to determine the molecular weight of compounds, for quantitative analysis, to elucidate structure of organic compounds as well as for the quantitative analysis.

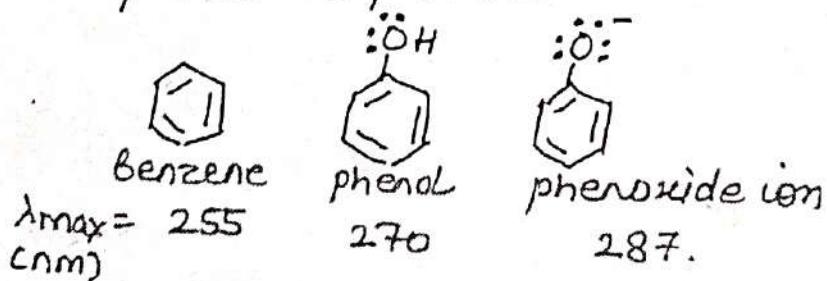
Q1. Explain the absorption and intensity shift in the UV spectroscopy and support with examples. Illustrate the effect of polar and non polar solvents on various transition in acetone (2018-19)

Ans. Absorption and Intensity shifts:

1. Bathochromic or Red shift: When absorption maxima ( $\lambda_{\text{max}}$ ) of a compound shifts to longer wavelength, it is known as Bathochromic shift or red shift. This effect is observed due to presence of auxochrome or by the change of solvent.

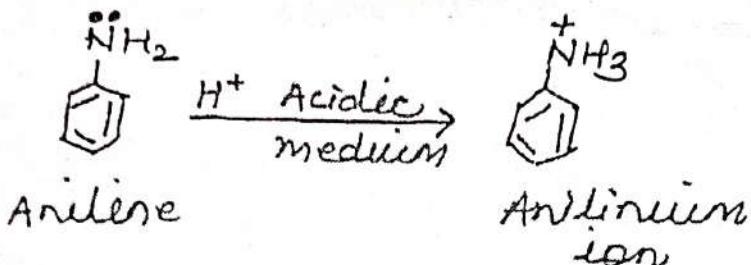
An auxochrome group like  $-\text{OH}$ ,  $-\text{OCH}_3$  causes absorption  $\pi$ - compound at longer wavelength due to increase in delocalisation of electrons in molecular framework.

This effect may also be produced due to a change in solvent. For example - Phenol in alkaline medium shows red shift as the negatively charged oxygen in phenoxide ion delocalizes more effectively as compared to phenol.

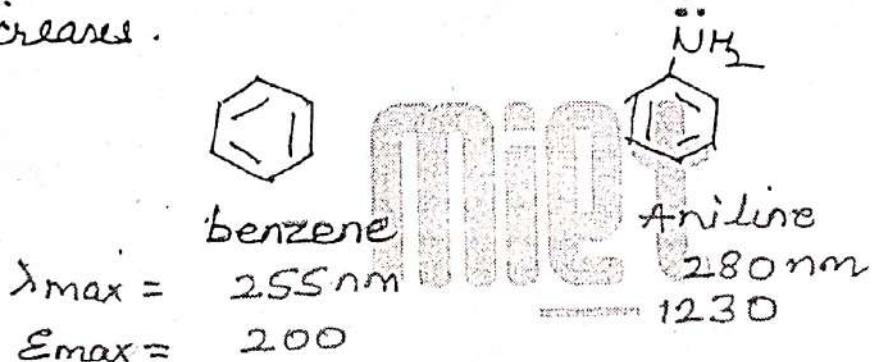


2. Hypsochromic shift or blue shift: When absorption maxima ( $\lambda_{\text{max}}$ ) of a compound shifts to shorter wavelength, it is known as hypsochromic shift or blue shift. The effect is due to presence of any group that cause a removal of conjugation or by the change of

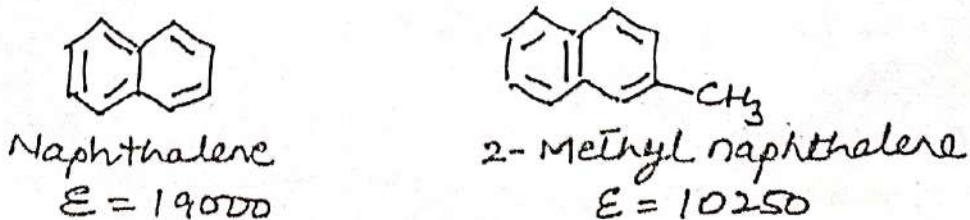
solvent. Example : Aniline shows blue shift in acidic medium, it loses conjugation due to the protonation of  $-NH_2$  group.

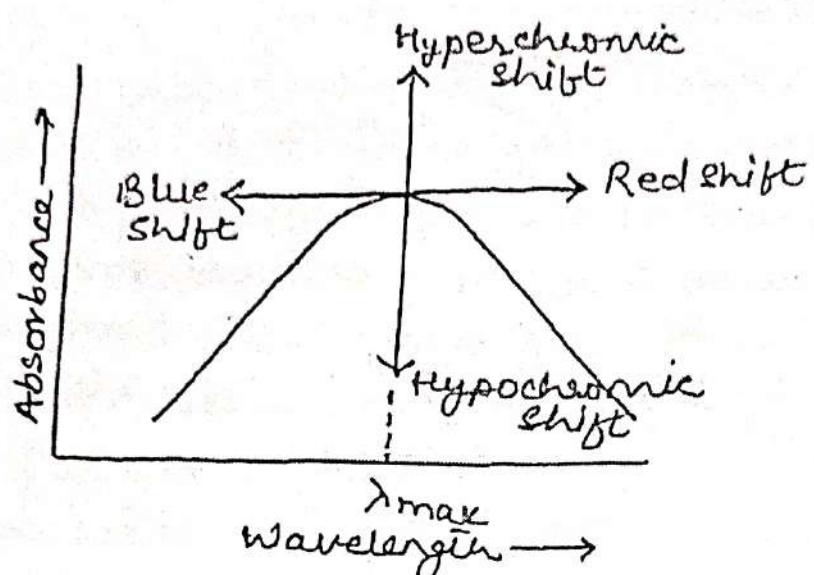


3. Hyperchromic effect: An effect which leads to an increase in absorption intensity ( $E_{max}$ ) is called hyperchromic effect. If chromophore introduces to the compound, the intensity of absorption increases.



4. Hypochromic effect: When absorption intensity ( $E$ ) of a compound is decreased, it is known as hypo chromic shift. This is caused by the introduction of a group which distorts the chromogen (any compound bearing chromophore is called chromogen) by forcing the ring out of coplanarity resulting in the loss of conjugation.





Shift in absorption position and intensity

Factors causing shift in UV-VIS Spectroscopy

1. Effect of conjugation: The higher the extent of conjugation, the more is the bathochromic shift. The increase in conjugation decreases the energy between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). So, the electronic transition becomes possible even at lower energy (higher wavelength).

Compound	$\lambda_{\text{max}}$ (nm)	$\epsilon \text{ (M}^{-1}\text{cm}^{-1}\text{)}$
$\text{HC}=\text{CH}_2$	165	15,000
	217	21,000
	256	50,000
	290	85,000
	334	125,000
	364	138,000

2. Effect of auxochrome: Auxochromes are the chemical groups that result in bathochromic shift when

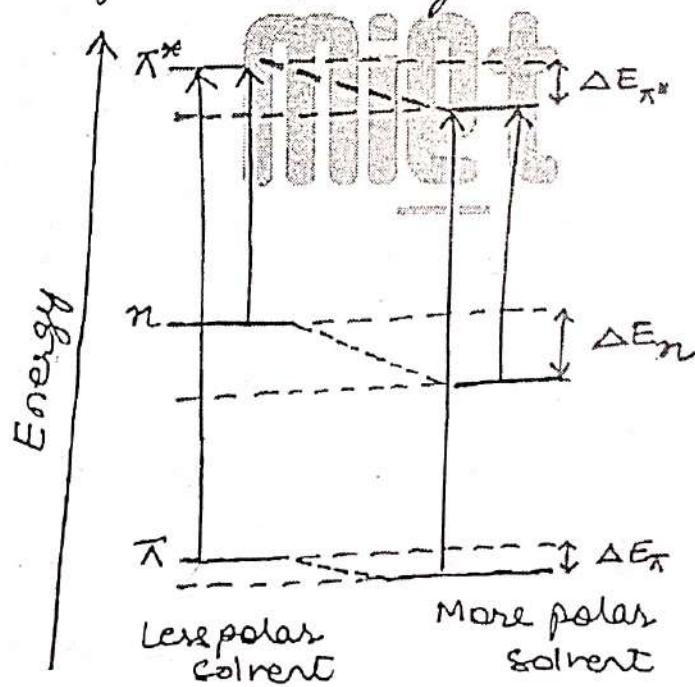
attached to a chromophore by extending the conjugation through resonance.

3. Solvent: 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 ( $n$ ,  $\pi$  and  $\pi^*$ ).

Non bonding orbital ( $n$ ) is stabilized more than antibonding  $\pi^*$  orbital and bonding  $\pi$  orbital. The order of energy of the molecular orbitals in the polar solvents is -

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

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



- a) Antibonding  $\pi^*$  orbitals are more polar than the bonding  $\pi$  orbital. Hence,  $\pi^*$  orbital is more stabilized than  $\pi$  orbital in polar solvent. This result in decrease in the energy gap between

$\pi$  and  $\pi^*$  orbital. Thus  $\pi \rightarrow \pi^*$  transition undergoes bathochromic shift with increasing polarity of solvent.

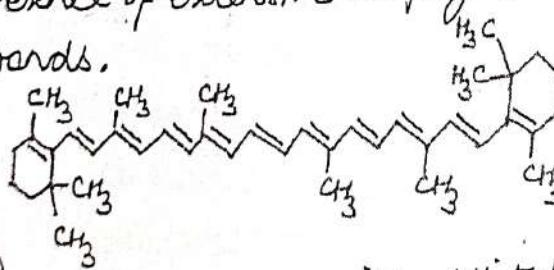
$$\Delta E_{\pi \rightarrow \pi^*}^{\text{Polar}} < \Delta E_{\pi \rightarrow \pi^*}^{\text{nonpolar}}$$

b) The dipole-dipole interaction or hydrogen bonding with a polar solvent lowers the energy of the non-bonding more than that of  $\pi$  orbital. This results in increase in the energy gap between  $n$ -orbital and  $\pi^*$  orbital. Thus, hypsochromic shift is observed for  $n \rightarrow \pi^*$  in more polar solvent.

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

Q2. Why  $\beta$  carotene absorbs light in visible region?  
(2016-2017)

Ans.  $\beta$  carotene absorbs light in blue region (visible region) of the spectra and transmits yellow-orange colour to our eyes. This is due to the presence of extensive conjugation between 11 double bonds.



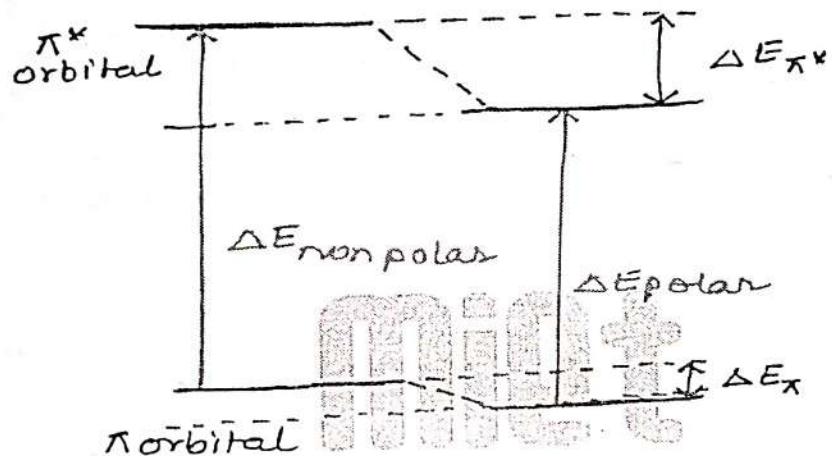
Q3. Explain which one will exhibit higher value of  $\lambda_{\text{max}}$  UV-vis spectra of  $\text{CH}_3\text{COCH}_3$  and  $\text{CH}_2=\text{CHCOCH}_3$  (2018-2019)

Ans.  $\text{CH}_3\text{COOH}$  is a compound which has only carbonyl group whereas  $\text{CH}_2=\text{CHCOCH}_3$  has carbonyl group in conjugation to double bond. So,  $\text{CH}_2=\text{CHCOCH}_3$  will have higher value of  $\lambda_{\text{max}}$  due to large delocalisation of electrons.

Q4. Illustrate effect of polar and nonpolar solvent on  $\pi \rightarrow \pi^*$  transition in acetone. (2018-2019).

### Effect of polar and non polar solvent on $\pi - \pi^*$ transition in acetone

Acetone consist of carbonyl group which has double bond between carbon and oxygen. Hence, it will have bonding  $\pi$  orbital and antibonding  $\pi^*$  orbital. Antibonding  $\pi^*$  orbital are more polar than bonding  $\pi$  orbital. Hence,  $\pi^*$  orbital is more stabilized than  $\pi$  orbital in polar solvent ( $\Delta E_{\text{R}} < \Delta E_{\text{P}}$ )



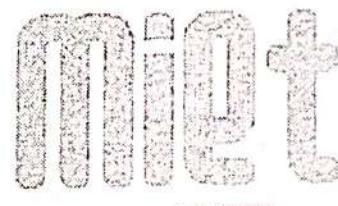
The energy gap between  $\pi$  and  $\pi^*$  orbital decrease in polar solvent. Hence,  $\pi \rightarrow \pi^*$  transition undergoes bathochromic shift with increasing polarity of solvent because  $\Delta E_{\text{polar}} < \Delta E_{\text{nonpolar}}$

Q5. Can ultra violet spectral data be useful to distinguish between the following compounds? Give reasons.  
 (2018-2019) i) Ethyl benzene and styrene  
 ii)  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$  and  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_2$

Ans. Yes, the above compounds can be distinguished by U.V spectroscopy.

i) Styrene has extended conjugation in comparison to ethyl benzene. So, it shows absorption at higher wavelength as compared to ethyl benzene in UV region

ii)  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$  is a conjugated molecular system hence delocalisation of electrons in molecular framework is larger, whereas  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$  is a non conjugated diene and have less delocalisation of electrons. So,  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$  will give the absorption band at longer wavelength than the second one in UV region.



WOODWARD - FIESER RULES

- Used to calculate  $\lambda_{max}$  for conjugated dienes.
- Each type of diene system has a certain fixed value of  $\lambda_{max}$  (nm) which is known as base value.
- Substituents such as alkyl groups or ring residues, type of double bonds, double bond extending the conjugation and polar groups such as -Cl, -Br etc also contribute to  $\lambda_{max}$  which are added to base value to get  $\lambda_{max}$  for a particular compound.

<u>Diene System</u>	<u>Base Value (<math>\lambda_{max}</math> in nm)</u>
A-cyclic & heteroannular dienes	214 & 217 respectively
Homocyclic dienes	253 nm
Increments for	
Double bond extending conjugation	30
R (alkyl substituent or ring residue)	5
Exocyclic double bond	5
Polar groups	
-OR (ether)	6
-Cl, -Br	5
-NR <sub>2</sub>	60
-OCOCH <sub>3</sub>	0
-SR (thioether)	30
-Ph (phenyl group)	60

Explanation of terminology used in Woodward-Hoffmann rule



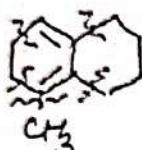
Homoannular  
diene



Heteroannular  
diene



Exocyclic double  
bond

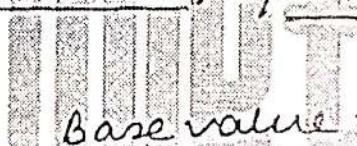
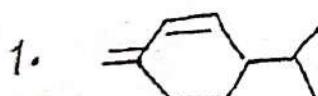


→ Represents R alkyl groups  
or ring residue.



Double bond  
extended conjugation

Examples for calculation of  $\lambda_{\text{max}}$  for given molecule

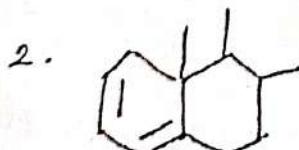


Base value = 217 nm

2 alkyl grps =  $2 \times 5 = 10$  nm

1 exocyclic double bond = 5 nm

$$\text{Hence } \lambda_{\text{max}} = 217 + 10 + 5 \\ = 232 \text{ nm}$$

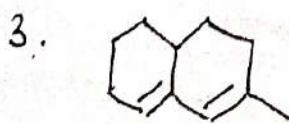


Base value = 253 nm

3 alkyl grps =  $3 \times 5 = 15$  nm

1 exocyclic double bond = 5 nm

$$\text{Hence } \lambda_{\text{max}} = 273 \text{ nm.}$$

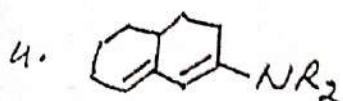


Base value = 215 nm

4 Alkyl grps =  $4 \times 5 = 20$  nm

2 exocyclic double bond = 5 nm

$$\text{Hence, } \lambda_{\text{max}} = 239 \text{ nm}$$



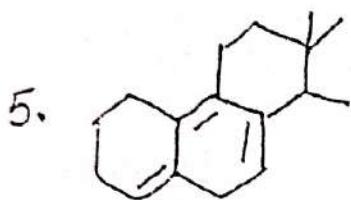
Base value = 214 nm

3 Alkyl grps =  $3 \times 5 = 15$  nm

1 polar functional = 60 nm  
grp (CNR<sub>2</sub>)

1 exocyclic double bond = 5 nm

Hence,  $\lambda_{max} = 294$  nm.



Base value = 253 nm

6 Alkyl grps =  $6 \times 5 = 30$  nm

2 exocyclic double bonds =  $2 \times 5 = 10$  nm

1 double bond exocyclic =  $2 \times 5 = 10$  nm  
to two rings

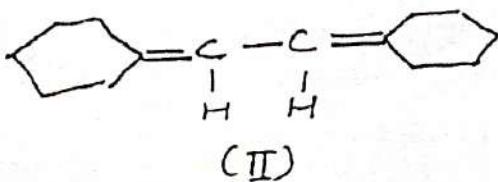
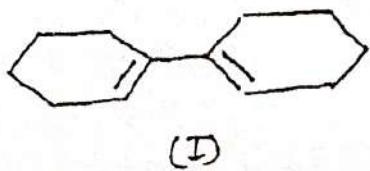
1 double bond extending = 30 nm.  
conjugation

Hence  $\lambda_{max} = 333$  nm

Q1. Give the structure of a diene having a molecular formula C<sub>4</sub>H<sub>6</sub> which shows an intense peak at  $\lambda_{max}$  217 nm in its UV spectrum. (2014-2015)

Ans. 217 nm is the absorbance given by a simple conjugated diene. The given molecular formula is C<sub>4</sub>H<sub>6</sub>. So, the structure for the diene will be C<sub>2</sub>H<sub>5</sub>=CH-CH=CH<sub>2</sub>.

Q2. Why the  $\lambda_{max}$  for the diene (I) is observed at a lower nm than (II) (2014-15)



Ans.



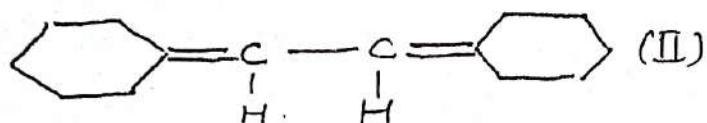
since it is acyclic diene hence base value = 214 nm

No. of exocyclic diene double bond = 0

No. of ring residues = 4

No. of extended double bond = 0

Thus,  $\lambda_{\max} = 214 \text{ nm} + 4 \times 5 \text{ nm} = 234 \text{ nm}$ .



since it is a cyclic diene hence base value = 214 nm

No. of exocyclic diene double bond = 2

No. of ring residues = 4

No. of extended double bond = 0

Thus,  $\lambda_{\max} = 214 \text{ nm} + 4 \times 5 \text{ nm} + 2 \times 5 \text{ nm}$   
 $= 244 \text{ nm}$

Therefore,  $\lambda_{\max}$  for compound II is greater than I.

## INFRA RED OR VIBRATIONAL SPECTROSCOPY [LECTURE 14]

- IR spectroscopy is used in identification of functional groups in pure compounds.
- IR radiations do not have sufficient energy to induce electronic transitions, but induces the vibrational and rotational transitions which causes net change in dipole moment in the molecule. The molecules undergoing such transitions & changes on absorption of IR radiations are called IR active such as HCl, CO etc.

✓ IR region ranges from  $4000 - 400 \text{ cm}^{-1}$ .

- If the frequency of IR radiations matches the vibrational frequency of molecule, then it absorbs the IR radiations.
- IR spectroscopy is based on Hooke's law. Suppose two atoms or masses are connected through a spring (bond), then frequency of vibration is represented as -

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{or} \quad \bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

where,  $k$  = force constant of the bond.

$\bar{\nu}$  = wave number ( $\text{cm}^{-1}$ )

$\nu$  = frequency Hz or  $\text{sec}^{-1}$

$c$  = speed of light.

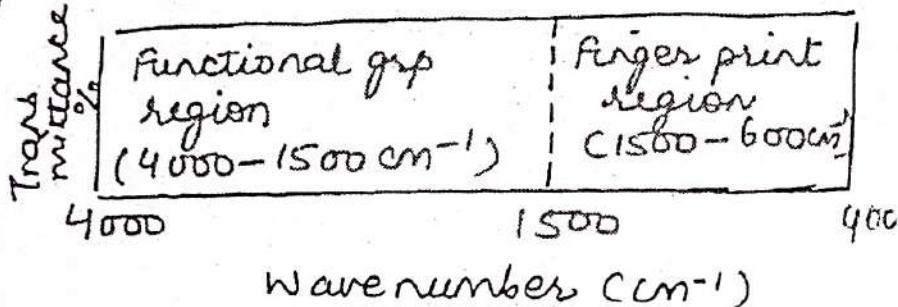
$\mu$  = reduced mass. In kg

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

where,  $m_1$  and  $m_2$  are the masses of two atoms connected through a bond.

- Stronger the bond, greater the value of force constant  $K$ , higher the frequency of vibration or wave no.
- Example :-  $C-C$      $C=C$      $C \equiv C$
- |                            |                 |                  |                  |
|----------------------------|-----------------|------------------|------------------|
| Force constt<br>(dynes/cm) | $5 \times 10^5$ | $10 \times 10^5$ | $15 \times 10^5$ |
| Wavenumber<br>$(cm^{-1})$  | 1200            | 1650             | 2100             |

IR spectrum is divided mainly into two regions:



Fundamental vibrations : The vibrations arising when molecule is promoted from ground state to lower excited (first excited) state. The fundamental vibrations for linear & non linear molecules are determined by following way :

Molecule	Degree of freedom or no. of fundamental vib.
Linear	$3n-5$
Non-linear	$3n-6$

Where  $n$  = no. of atoms present in the molecule.

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

$$\bar{v} \propto \sqrt{k} \propto \text{bond strength} \propto \text{Bond stability} \propto \frac{1}{\text{Bond length}}$$

Q1. Explain the principle of IR spectroscopy. (2014-15, 2016-17)

Ans. When molecule absorbs Electromagnetic radiations in IR region ( $4000 - 400 \text{ cm}^{-1}$ ), it undergoes transitions from lower vibrational state to excited vibrational state. These vibrational transitions are accompanied by change in dipole moment of the molecule and such molecules are called IR active molecules and can be studied using IR spectroscopy. If the dipole moment of molecule does not change, then molecule does not absorb IR radiations and molecule will be IR inactive. IR spectroscopy is based on Hooke's law which is -

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{in Hz/s or vibrations per second}$$

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

where,  $\mu$  is known as reduced mass and,

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \times \frac{1}{N_A} \times 10^{-3} \text{ kg.}$$

$K$  is the force constant

Q2. Define IR spectroscopy (2015-2016, 2017-2018)

Ans. IR spectroscopy is a tool to study the absorption of IR radiation by a molecule which shows vibrational transitions. Hence, IR spectroscopy is also known as vibrational spectroscopy.

It gives valuable information about functional groups and bonds present in the molecule.

Q3. What is finger print region and functional group region in IR spectroscopy (2013-2014, 2018-2019)

Ans. FINGER PRINT REGION: ( $1500 - 500 \text{ cm}^{-1}$ )

IR absorption spectra taken in the region of  $1500$  to  $500 \text{ cm}^{-1}$  is called finger print 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 finger print region is that each and every molecule has its own unique absorption pattern in this region. This provides confirmations about the identity of the molecules. No two compounds except enantiomers can have similar IR spectra.

#### FUNCTIONAL GROUP REGION ( $4000 - 1500\text{cm}^{-1}$ ) :

IR absorption spectra collected in the region of 4000 to  $1500\text{cm}^{-1}$  is called functional groups region. Peaks present in this region are typically associated with the stretching vibrations of the functional groups. Hence, the most common application of IR spectroscopy is the identification of functional groups in the molecules.

Ques. Give the vibrational frequency (IR radiation range) for different functional groups.

Ans.	Bond	Molecule	wavenumber ( $\text{cm}^{-1}$ )
	C-O	Alcohol, ether, carboxylic acid etc	1300 - 1000
	C=O	Alcohol, ketones, esters, carboxylic acids	1750 - 1680
	C=O	Amide	1680 - 1630
	N-H stretching	Amine, Amides	3500 - 3100
	N-H bending	Amine, Amides	1640 - 1550
	O-H	Alcohol, carboxylic acids	3650 - 3200 3300 - 2500

Bond	Molecule	wavenumber (cm <sup>-1</sup> )
C-N	Aniline	1350 - 1000
S-H	Mercaptane	2550

Ques 4. IR peak is often characterized as molecular finger prints. comment on it. or discuss the significance of finger print region. (2014-15, 2015-16, 2016-17, 2017-18, 2018-19).

Ans. Refer to Q.3.

M. Imp

Q5. Describe various molecular vibrations in IR spectroscopy. (2015-16), (2017-18), (2019-2020)

Ans. Types of fundamental vibrations observed in IR spectroscopy

There are 2 types of vibrations :-

- a) Stretching vibrations.
- b) Bending vibrations.

a) Stretching vibrations: Vibrations or oscillations along the line of bond is called stretching vibration. There occurs a change in bond length. It is of two types :-

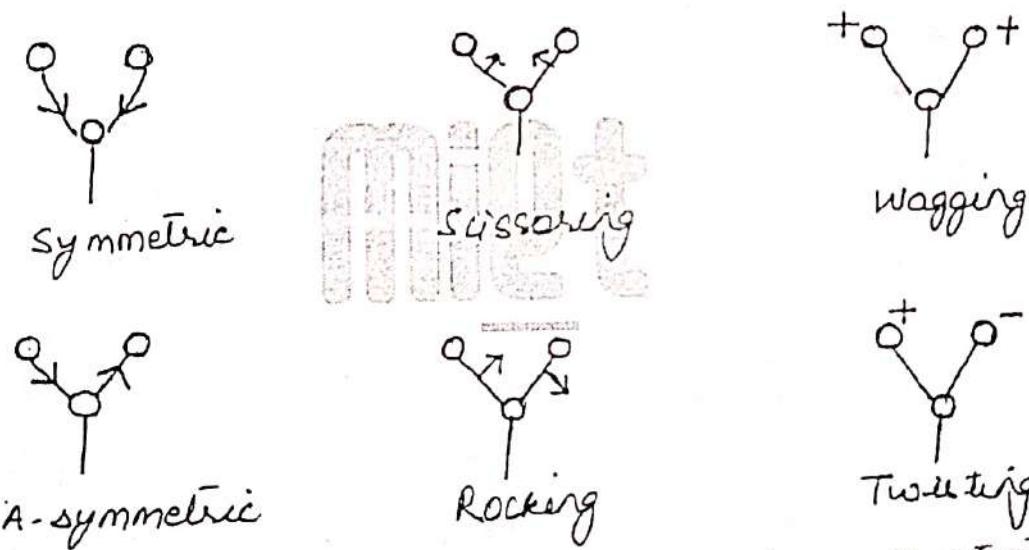
(i) Symmetric stretching - A stretching vibration is said to be symmetric if all the bonds are simultaneously stretched or compressed.

(ii) Asymmetric stretching - A stretching vibration is said to be asymmetric if one bond is being stretched while the other is being compressed.

(b) Bending vibrations :- These vibrations are not along the line of bond. Bond angle / bond axis changes during vibration which results in deformation of molecule. There are of two types :-

(1) In plane bending - It is also of two types - in this the plane remains unchanged.

- a) Scissoring: This is an in-plane bending in which two atoms approach each other and bond angles decrease or vice versa.
- b) Rocking: change of angle between two bonds due to movement of atoms takes place in the same direction.
- 2) Out Plane bending
  - a) Wagging: 2 atoms move to one side of the plane and then together to the other plane. They move up and down the plane.
  - b) Twisting: one atom moves above the plane and another atom moves below the plane.



Q6. Ques. Write short note on application of IR spectroscopy (2019-2020).

Ans. Applications of IR spectroscopy:

- a. Qualitative Analysis: Main application of IR spectroscopy is compound identification.
- b. Determination of purity of sample.

- c) To identify cis and trans isomers of a compound:  
IR frequencies are higher for trans isomers as compared to the cis ones.
- d) Distinguish between inter and intra molecular H-bonding.
- e) Structural Information: IR spectra provides information regarding molecular symmetry, dipole moments, bond strength, characteristic absorption etc.
- Q7. How many fundamental vibrational degree of freedom are expected for the following molecules  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{C}_2\text{H}_4$ ? (2020-2021).

Ans.  $\text{CO}_2$  molecule: Since it is a linear molecule so, no. of fundamental vibrations =  $3n-5$   
Here,  $n = 3$  (total 3 atoms are there).  

$$3n-5 = 3 \times 3 - 5 = 4.$$

$\text{H}_2\text{O}$  molecule: It is a linear molecule.  
so, no. of fundamental vibrations =  $3n-6$   

$$= 3 \times 3 - 6$$
  

$$= 3.$$

$\text{C}_2\text{H}_4$  molecule: It is a non linear molecule.  
so, no. of fundamental vibrations =  $3n-6$   

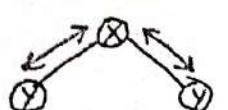
$$= 3 \times 6 - 6$$
  

$$= 12.$$

Q8. For  $\text{XY}_2$  bent molecule shows various types of stretching & bending vibrations in IR spectroscopy (2014-15, 2016-17).

Ans. Since  $X_2Y$  molecule is bent and having 3 atoms in molecule. so, the total no. of vibrational degree of freedom is  $3N - 6 = 3 \times 3 - 6 = 3$ .

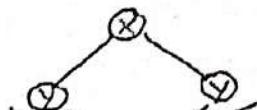
Thus, total 3 types of vibrations are there in  $X_2Y$  bent molecule, which will be symmetric stretching, A-symmetric stretching and bending vibrations.



symmetric stretching



A-symmetric stretching



Bending vibration

Q9. What is the criteria for a compound to be IR active ?

Ans. The two essential criteria's for a compound to be IR active are :

a) correct wavelength of radiation : A molecule will absorb the IR radiations only if the natural frequency of vibrations of some part of molecule is equal to the frequency of incident radiation.

b) change in dipole moment : Molecule will be IR active only if the absorption of IR radiation and the vibrational transition results in change in the dipole moment.

Q10. What is the selection rule for IR spectroscopy?

Ans. Selection rule for IR spectroscopy :-

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

b) vibrational quantum number change  $\Delta v = \pm 1$

### LECTURE -15

- There are various factors like bond order, electronic effects (inductive effect, resonance effect), hydrogen bonding etc which affects the vibrational frequency of the molecule in IR spectroscopy.
- Different functional groups have their characteristic vibrational frequency which helps in the identification of unknown molecules. But the above mentioned factors changes their characteristic vibrational frequency to some extent.
- Vibrational frequency of molecule can be calculated using the formula.

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{or} \quad \bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

where,  $k$  = force constant

$\mu$  = reduced mass

$c$  = speed of light

$\nu$  = frequency

$\bar{\nu}$  = wavenumber

- The reduced mass is calculated as -

$$\mu = \frac{m_1 \times m_2}{m_1 + m_2} \times \frac{1}{N_A} \times 10^{-3} \text{ kg.}$$

where  $m_1$  and  $m_2$  are the masses of atoms of the diatomic molecule.

Q1. Two isomers A and B of molecular formula  $C_3H_6O$  gives IR absorption at  $1650\text{ cm}^{-1}$  and  $1710\text{ cm}^{-1}$ , respectively. Assign structural formula to A and B isomers. (2018-2019).

Ans. Two isomers A and B have molecular formula  $C_3H_6O$ . So, functional group could be hydroxyl ( $\text{OH}$ ) or carbonyl ( $>\text{C=O}$ ).

i) The peak at  $1650\text{ cm}^{-1}$  corresponds to  $\text{cis}-\text{C=C}$ -stretching frequency. So, structural formula is  $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$ . Therefore A is allyl alcohol.

ii) The peak at  $1710\text{ cm}^{-1}$  corresponds to  $>\text{C=O}$  stretching frequency (ketone group). So, structural formula is  $\text{CH}_3\text{COCH}_3$ . Therefore, B is acetone.

Q2. One of the fundamental vibrational modes of  $\text{H}_2\text{O}$  occurs at  $3652\text{ cm}^{-1}$ . What would be the frequency of the corresponding vibration for  $\text{D}_2\text{O}$ . (2014-2015).

Ans. Given : -  $\bar{\nu}_{\text{H}_2\text{O}} = 3652\text{ cm}^{-1}$ .

Let us consider that force constant  $K$  of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  does not change. Then,  $K_{\text{H}_2\text{O}} = K_{\text{D}_2\text{O}}$ .

$$\bar{\nu}_{\text{H}_2\text{O}} = \frac{1}{2\pi c} \sqrt{\frac{K_{\text{H}_2\text{O}}}{\mu_{\text{H}_2\text{O}}}} \quad \text{and} \quad \bar{\nu}_{\text{D}_2\text{O}} = \frac{1}{2\pi c} \sqrt{\frac{K_{\text{D}_2\text{O}}}{\mu_{\text{D}_2\text{O}}}}$$

$$\mu_{\text{H}_2\text{O}} = \frac{m_H \times m_O}{m_H + m_O} = \frac{1 \times 16}{1 + 16} = 0.94$$

$$\mu_{\text{D}_2\text{O}} = \frac{m_D \times m_O}{m_D + m_O} = \frac{2 \times 16}{2 + 16} = 1.78$$

$$\text{The ratio} - \frac{\bar{\nu}_{\text{D}_2\text{O}}}{\bar{\nu}_{\text{H}_2\text{O}}} = \sqrt{\frac{\mu_{\text{H}_2\text{O}}}{\mu_{\text{D}_2\text{O}}}},$$

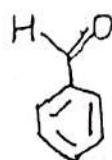
$$\text{So, } \bar{\nu}_{\text{C}_2\text{O}} = \bar{\nu}_{\text{H}_2\text{O}} \sqrt{\frac{M_{\text{H}_2\text{O}}}{M_{\text{C}_2\text{O}}}} = 3652 \times \sqrt{\frac{18}{44}} = 2654 \text{ cm}^{-1}$$

Q3. An organic compound having molecular formula  $C_7H_6O$  shows absorption peak at  $3010, 2700, 1650, 1580, 1480, 1520$ , and  $1270 \text{ cm}^{-1}$  in its IR spectrum. Suggest its structure (2015-16)

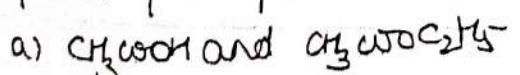
Ans. Molecular formula -  $C_7H_6O$ , the possible functional groups may be  $-OH$  or  $>C=O$ .

- a. The peak at  $1720 \text{ cm}^{-1}$  corresponds to  $>C=O$  stretching
- b. The peak at  $2700 \text{ cm}^{-1}$  corresponds to C-H stretching
- c. The peak at  $3010 \text{ cm}^{-1}$ , corresponds to  $=CH$  stretching in benzene ring.
- d. The peak at  $1650, 1580, 1520, 1480 \text{ cm}^{-1}$  corresponds to  $C=C$  in ring.

From above points it can be concluded that the above structure is benzaldehyde.



Q4. How will you distinguish between following pairs of compounds on the basis of IR spectroscopy? (2015-2016)



Ans.  $\text{CH}_3\text{COOH}$  shows strong absorption at around  $3200-3500 \text{ cm}^{-1}$  which is due to O-H bond while  $\text{CH}_3\text{COOC}_2\text{H}_5$  does not show due to absence of O-H bond.

b) If vibrational frequency is measured with varying concentration of molecule, for intramolecular Hydrogen bonding, vibrational frequency will remain unchanged, whereas for intermolecular hydrogen bonding, vibrational frequency will change for concerned bonds.

Q7: Discuss the factors affecting vibrational frequency.

Ans. Factors affecting vibrational frequency:

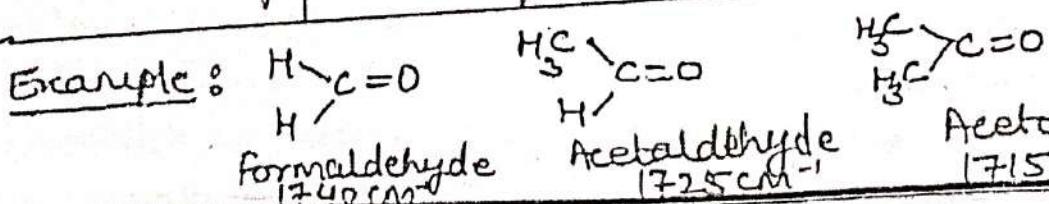
1. Bond Order: Bond order affects the position of absorption bands. Higher the bond order, larger will be the bond frequency.

Bond frequency	Bond frequency( $\text{cm}^{-1}$ )	Bond frequency( $\text{cm}^{-1}$ )
C-C	< 900	C-O 970 - 1250
C=C	1680 - 1620	C=O 1630 - 1780
C≡C	2260 - 2100	C≡O 2100

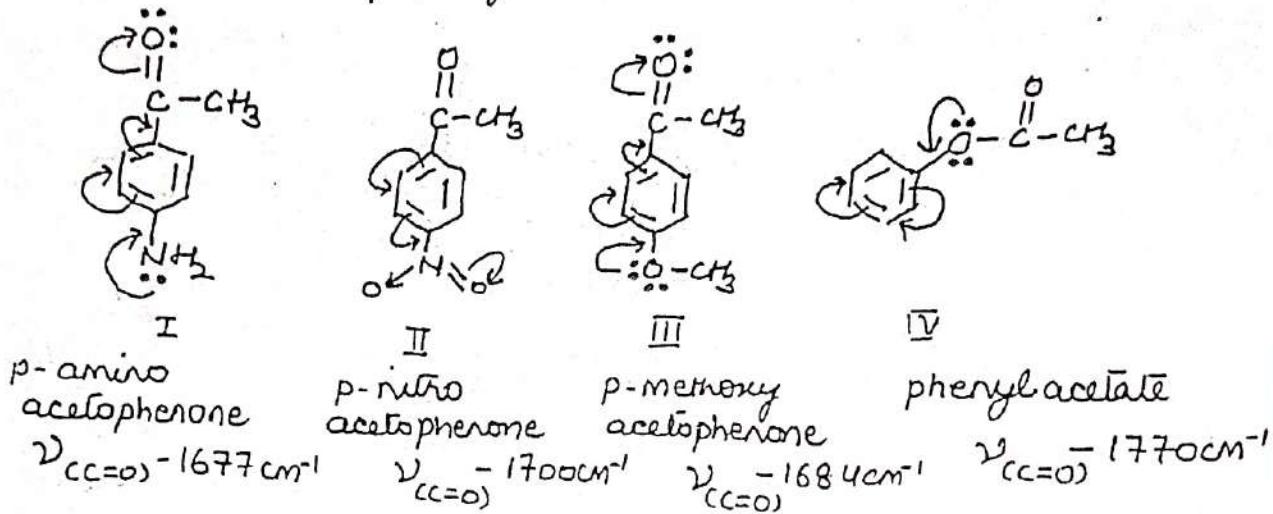
2. Electronic effect : Resonance and Inductive effects:

a) 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.

Groups	Attachment	Inductive effect	Bond length	Force constant	frequency
Electron donating	Alkyl grp	+ I	Increases	Decreases	Decrease
Electron withdrawing	Cl, Br, I, OH	- I	Decreases	Increases	Increase

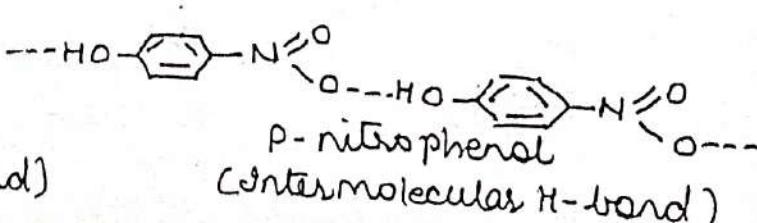
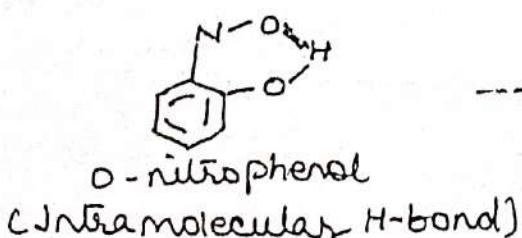
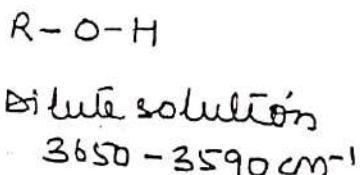
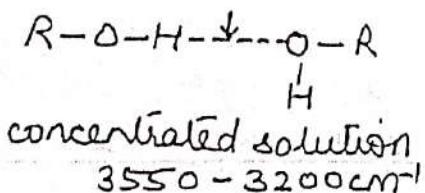


b) Resonance effect: As the molecule have  $\pi$  electrons leading to conjugation which results in delocalisation of electrons over 3-4 atoms or even more. This weakens the multiple bond (such as  $C=O$ ). This can result in decrease in vibrational frequency.



c) Hydrogen bonding: H-bonding shifts the absorption frequencies of O-H bonds of alcohols, phenols and carboxylic acids and of N-H bonds in amines.

- Stronger the H-bonding greater is the absorption shift from the normal values which results in red shift in IR spectra.
- The two types of H-bonding (inter and intra molecular) can be distinguished by the use of IR spectroscopy.

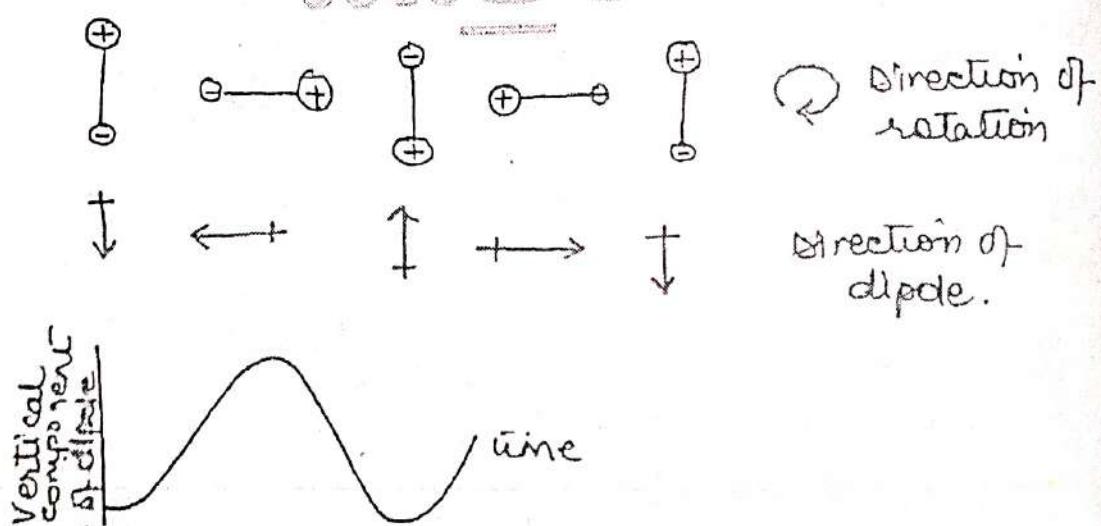


ROTATIONAL SPECTROSCOPY [LECTURE -16]

Rotational spectroscopy uses microwave radiations ( $3 \times 10^{11}$  to  $3 \times 10^{13}$  Hz) to measure the energies of rotational transitions for molecules in gas phase. Thus, rotational spectroscopy is also known as Microwave Spectroscopy.

Principle of Rotational Spectroscopy

Rotational spectroscopy is concerned with the bands in rotational energy levels in a molecule. If any molecule having permanent dipole moment rotates, it generates an electric field which interact with the electric component of the microwave radiation falling on it. During interaction, energy can be absorbed or emitted and thus gives rise to spectrum which is called rotational spectrum.



The rotation of a diatomic molecule, HCl showing the fluctuation in the dipole moment measured in a particular direction.

Rotational spectroscopy is the measurement of the energies of transitions between quantized rotational states of molecules in gas phase. The rotational degree of freedom is only possible in gas phase where distance between molecules is large enough to consider them as isolated molecule. So, microwave studies are done only in gaseous state.

Conditions for microwave absorption:

- Only those molecules which have permanent dipole moment can interact with electric field component of microwave radiation, and are called microwave active molecules.
- Rotation spectroscopy is only practical in gas phase where the rotational motion is quantized.

Q1. What is selection rule for the molecule to show rotational spectrum. (2018-19).

- Ans.
1. The molecule must have permanent electric dipole moment.
  2.  $\Delta J = \pm 1$  i.e. only those transitions are allowed in which there is an increase or decrease by unity in rotational quantum number.

Q2. Explain the microwave (rotational) spectra of diatomic molecule and write their applications. (2020-2021).

Ans. Interpretation of pure rotational spectra:  
Let us consider a rigid rotating diatomic molecule (Rigid rotor) which do not have any vibrational

degree of freedom. Rotational energy levels of rigid diatomic molecule is quantized and given by:

$$E_J = \frac{h^2}{8\pi^2 I} \cdot J(J+1) \text{ in joule}$$

where,  $J$  = rotational quantum number

$I$  = moment of inertia and,

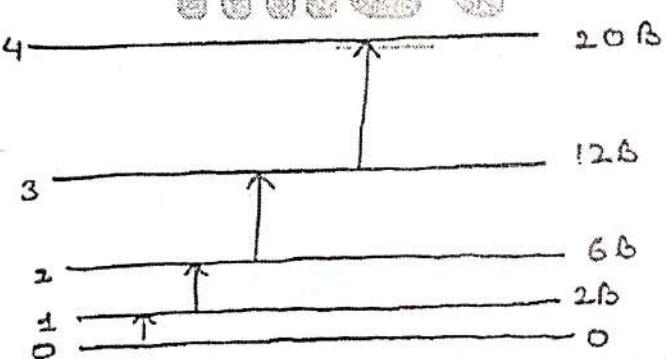
$$\boxed{I = \mu r^2} \quad \mu = \text{reduced mass of molecule in kg for the diatomic molecules.}$$

The energy of rotational state in  $\text{cm}^{-1}$  will be:

$$E_J = \frac{h^2}{8\pi^2 I C} \cdot J(J+1) \text{ in } \text{cm}^{-1}$$

$$\text{or, } E_J = B \cdot J(J+1). \quad (B = \text{rotational constant})$$

where,  $B = \frac{h^2}{8\pi^2 I C} \text{ in } \text{cm}^{-1}$



Rotational energy levels of a rigid diatomic molecule and the allowed transition.

The energy difference between two rotational levels is usually expressed in  $\text{cm}^{-1}$

$$\Delta E_{J \rightarrow J+1} = E_{J+1} - E_J = B(J+1)(J+1+1) - BJ(J+1) \\ = 2B(J+1)$$

Hence, the spacing between two rotational (successive) levels is as follows:

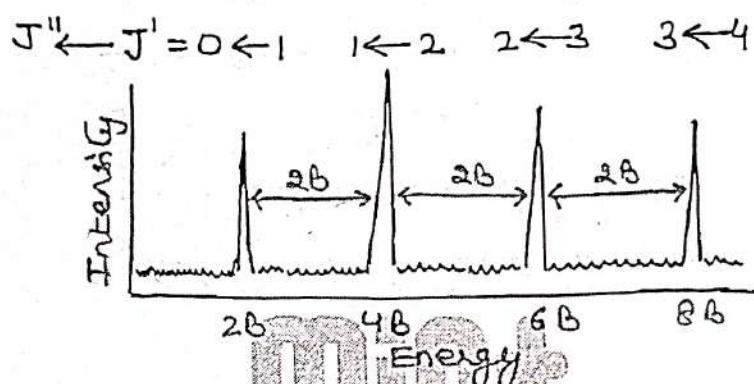
$$\Delta E_{0 \rightarrow 1} = 2B$$

$$\Delta E_{1 \rightarrow 2} = 4B$$

$$\Delta E_{2 \rightarrow 3} = 6B$$

$$\Delta E_{3 \rightarrow 4} = 8B$$

These rotational transition lines will appear in rotational spectrum as follows:



The distance between any two lines in pure rotational spectra of any molecule will be  $2B$ . The line in the rotational spectra will provide the information about the moment of inertia and bond length of the molecule.

#### Applications of rotational spectroscopy

1. Determination of symmetry and structure in a molecule.
2. Determination of dipole moment, bond length, centrifugal distortion constant and angles of gaseous molecules.
3. In some cases, information about the mechanism of chemical reactions.

[LECTURE - 17]

Determination of bond length of diatomic molecule  
(rotor)

Diatomic molecule having permanent dipole moment rotate around its moment of inertia with energy ( $E_J$ ) in  $\text{cm}^{-1}$ .

$$E_J = B \cdot J(J+1)$$

where,  $B$  = rotational constant.

$$B = \frac{h}{8\pi^2 I \cdot c} \quad \text{in } \text{cm}^{-1}$$

Rotational constant  $B$  can be determined by measuring the spacing between two rotational lines or the position of the line in the rotational spectrum.

a) spacing between two lines =  $2B$ .

b)  $n^{\text{th}}$  line in the spectrum =  $(2BCJ+1)$ , where  $n = J+1$  and  $J = 0, 1, 2, \dots$

After getting the value of  $B$ , we can calculate moment of inertia ( $I$ ) and bond distance ( $r$ ) of diatomic molecule where  $h$  is plank's constant and  $c$  is the speed of light.

$$I = \frac{h}{8\pi^2 B c}$$

$$r = \sqrt{\frac{I}{\mu}}$$

Microwave Inactive molecules

- No dipole moment
- Homonuclear diatomic molecules such as  $O_2, N_2, X_2, C_2$  etc.
- Symmetrical linear molecules such as  $CO_2, C_2H_2$ .
- Any molecule with a centre of inversion is microwave inactive such as  $CH_4, C_6H_6$  and  $SF_6$ .

Q1. Which of the following molecules will show rotational spectrum:  $H_2$ ,  $HCl$ ,  $CH_4$ ,  $CH_3Cl$ ,  $CH_2Cl_2$ ,  $H_2O$  and  $SF_6$ ? (2018-19).

Ans. Microwave active molecules are  $HCl$ ,  $CH_3Cl$ ,  $CH_2Cl_2$  and  $H_2O$ . This is because they will have permanent dipole moment whereas molecules  $H_2$ ,  $CH_4$  and  $SF_6$  will be microwave inactive because they do not have permanent dipole moment.

Q2. The first rotational line in the rotational spectrum of  $CO$  is observed at  $3.84235 \text{ cm}^{-1}$ . Calculate the rotational constant ( $B$ ) and bond length of  $CO$ . The relative atomic weight  $C = 12.00$  and  $O = 15.9994$ .

$$\underline{\text{Ans.}} \quad M_H = 12, \quad M_F = 15.9994, \quad N_A = 6.023 \times 10^{23}$$

$$\mu_{CO} = \frac{M_C \times M_O}{M_C + M_O} \times \frac{1}{N_A} \times 10^{-3} \text{ kg} = \frac{12 \times 15.9994}{12 + 15.9994} \times \frac{1}{6.023 \times 10^{23}} \times 10^{-3}$$

$$= 11.475 \times 10^{-27} \text{ kg.}$$

$$\text{Now given } 2B = 3.84235 \text{ cm}^{-1} \text{ thus } B = 1.92117 \text{ cm}^{-1}$$

$$= 192.117 \cdot n^{-1}.$$

$$I = \frac{h}{8\pi^2 BC} = \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{s}^{-1}}{8 \times (3.14)^2 \times 192.117 \text{ m}^{-1} \times 2.99 \times 10^8 \text{ ms}^{-1}}$$

$$= 14.262 \times 10^{-47} \text{ kg m}^2.$$

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{14.262 \times 10^{-47} \text{ kg m}^2}{11.475 \times 10^{-27} \text{ kg}}}$$

$$= 1.133 \times 10^{-10} \text{ m.}$$

Lecture No. 17

## Introduction

Nuclear magnetic resonance spectroscopy is a very important tool in the hands of a chemist, particularly an organic chemist. It is the study of interaction of magnetic nuclei having resultant nuclear spin ( $^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ ,  $^{13}\text{C}$ , etc.) with electromagnetic radiations in radio frequency region under the influence of an appropriate magnetic field. By studying a compound by  $^1\text{H}$  NMR (PMR) spectroscopy, one can obtain the following types of information regarding the compound:

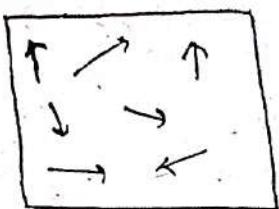
- (i) The number of types of hydrogen atoms in a molecule.
- (ii) The chemical environment of hydrogen atoms.
- (iii) The number of hydrogen atoms in a given chemical environment.
- (iv) The molecular structure and its stereochemical features.

## Basic Principle of NMR spectroscopy

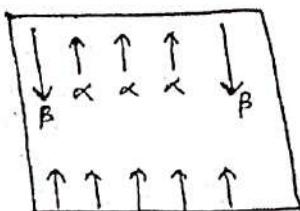
NMR involves the study of the interaction between electromagnetic radiation in radiofrequency and the nuclei of atoms. A nucleus with an odd numbers of protons or an odd number of neutrons such as  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ,  $^{19}\text{F}$  possesses nuclear spin and such nuclei can only be examined by NMR.

If a charged particle-like proton/nucleus spins about its own axis, it behaves like a tiny magnet and it generates a magnetic field called magnetic moment.

Without an external magnetic field, the nuclear spins are in random directions. When the nucleus of an atom is placed in an external magnetic field, the interaction between the magnetic moment takes place. The magnetic moment must align either with the external field or against the field.

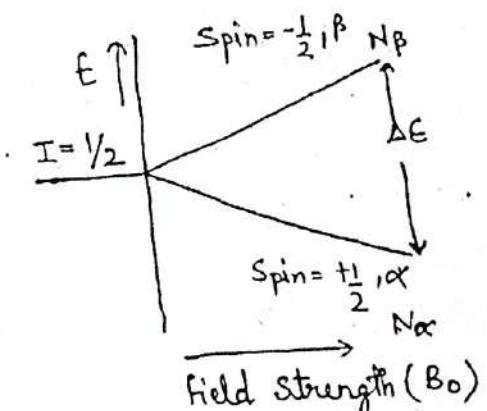
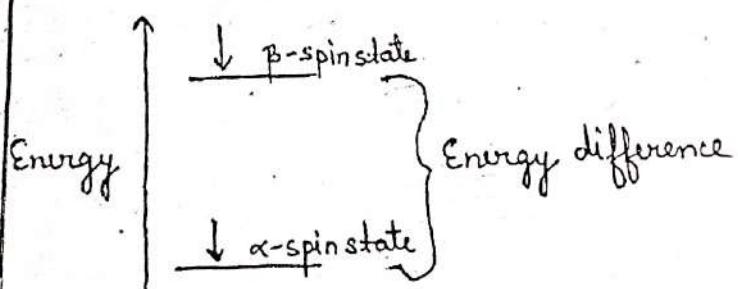


Random orientation of magnetic moment in absence of magnetic field



Orientation of magnetic moment in presence of magnetic field

If a nucleus is aligned with the magnetic field, it is said to occupy the  $\alpha$ -spin state and if it is aligned against the field, it is said to occupy the  $\beta$ -spin state. The two spin states are not equivalent in energy.



Energy gap between alpha and beta spin state and variation with external magnetic field

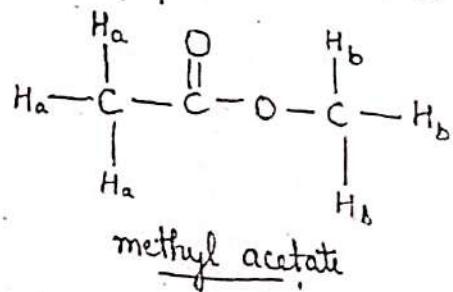
The external magnetic field establishes an energy gap between spin states. The magnitude of the energy gap depends on the

strength of the external magnetic field. The energy gap increases with increasing magnetic field strength.

When the energy between the two energy states lies within the ranges of the radiofrequency radiation, then the  $\alpha$ -spin state absorbs energy and flips to the  $\beta$ -spin state and the nucleus is said to be in nuclear magnetic resonance.

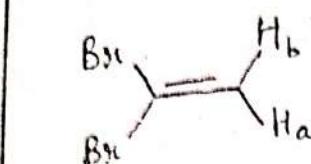
### Concept of equivalent proton in molecule

In the terminology of NMR, if the two or more proton experience same chemical environment, then those proton are called equivalent proton. All equivalent proton give rise to one NMR signal. E.g. All three  $H_a$  protons for following are chemically equivalent to each other, as are all three  $H_b$  protons. The  $H_a$  protons are, however, chemically non-equivalent to the  $H_b$  protons. As a consequence, the resonance frequency of the  $H_a$  protons is different from that of the  $H_b$  protons. Hence following molecule will give two NMR signals, one for all  $H_a$  proton and one for all  $H_b$  proton.



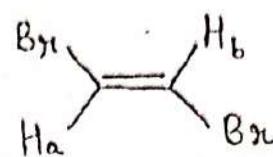
Similarly, dibromoethylene as given below can have following possible equivalent proton depending based on geometrical isomers of it.

Equivalent protons in alkenes must be cis to the same group



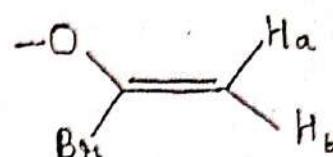
$H_a$  and  $H_b$  are both cis(trans) to the  $Br$ . They are equivalent.

One NMR signal



$H_a$  and  $H_b$  are both cis(trans) to the  $Br$ . They are equivalent.

One NMR signal



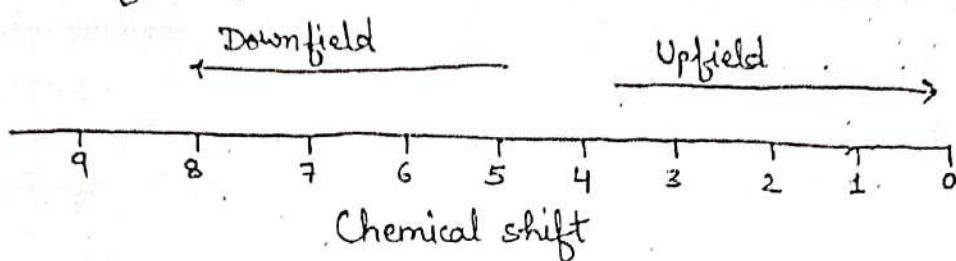
$H_a$  is cis to methoxy, while  $H_b$  is cis to the  $Br$ . They are not equivalent.

Two NMR signals (a, b) and one signal from  $CH_3$

### 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 (e.g. 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 ( $B_0$ ).

- (h) The energy gap increases causing magnetic resonance frequency to change. This changes the emissions frequency from relaxation.
- (i) This results in a greater chemical shift and the signal appears further downfield.



### Nuclear shielding and deshielding

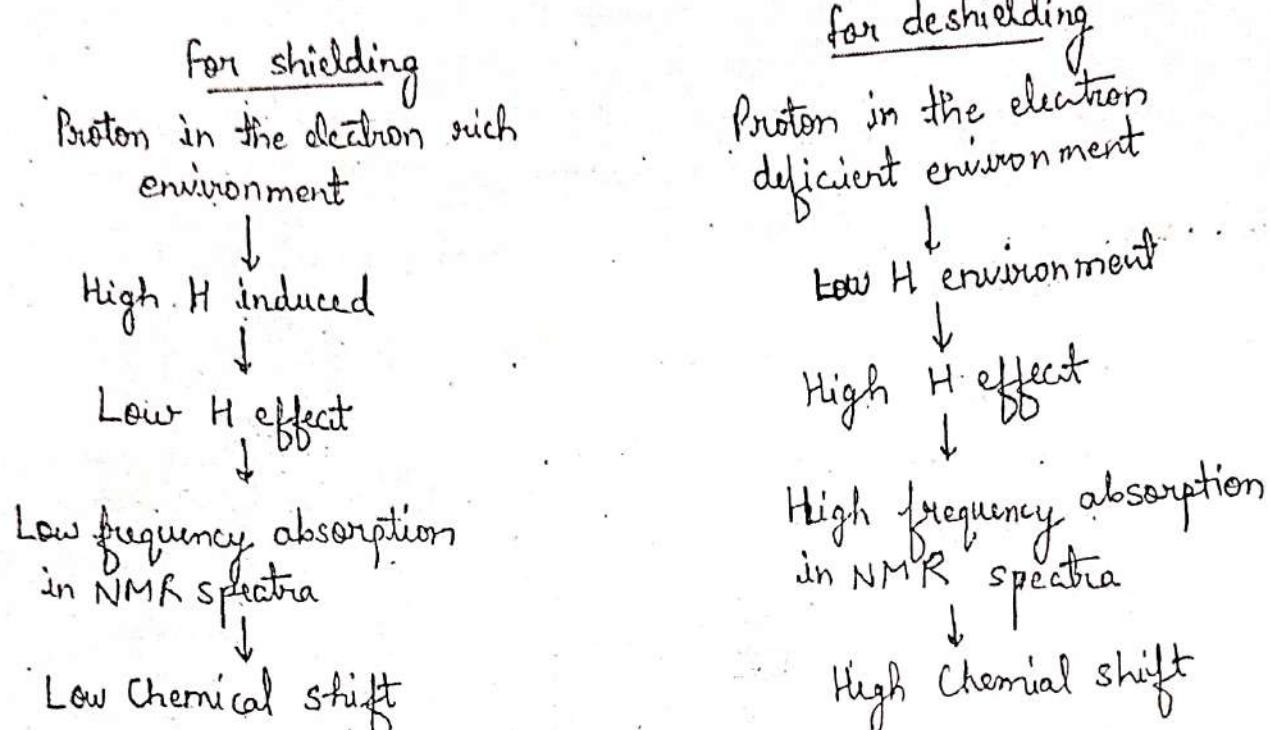
The splitting of a signal occurs due to the effects of neighbouring protons. The neighbouring proton with a different chemical shift can influence the signal of the other. If the protons are in the same chemical environment, such protons are said to be equivalent and absorb the same magnetic field strength and they behave as one proton.

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 electron 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 electron in the neighboring bond.

Thus the effective magnetic field for the different spin active nuclei can be calculated through the following equations:

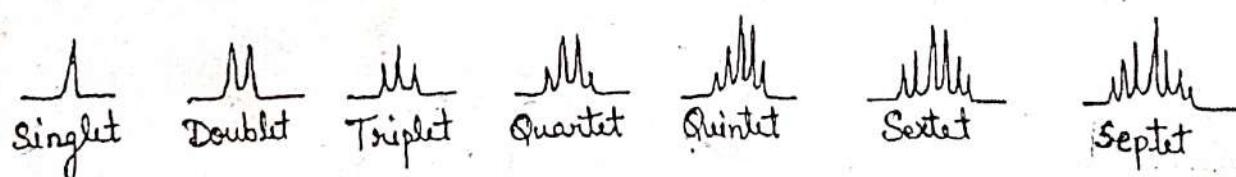
$$H_{\text{effect}} = H_0 - H_{\text{induced}}$$

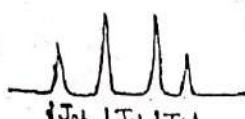
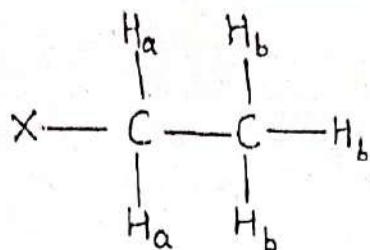
from the above equation the shielded and deshielded proton concept can be given as:



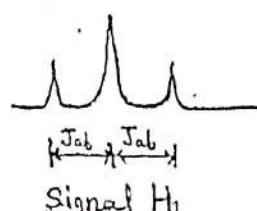
### Coupling constant (spin spin splitting in nmr spectroscopy)

If the protons are in different chemical environments, such protons are said to be non-equivalent protons and absorb different magnetic field strengths. Therefore, splitting of peak takes place. When signal splitting occurs the distance between the individual splitter peak is always constant which is called coupling constant ( $J$ ). It is measured in hertz.





Signal for  $\text{H}_a$



Signal  $\text{H}_b$

### Chemical Shift

Chemical Shift: It expresses the difference in the resonance frequency of a given proton compared to that of the methyl protons of TMS, under the experimental conditions. In practice, this difference is divided by the operating radio-frequency of the instrument and the chemical shift  $\delta$  is expressed, downfield from TMS, as per the given equation

$$\delta = \frac{\nu_s - \nu_{\text{TMS}}}{\nu_0} \times 10^6$$

where,  $\nu_s$  is sample proton frequency

$\nu_{\text{TMS}}$  is TMS proton frequency

and  $\nu_0$  is applied magnetic field frequency.

Unit of chemical shift is ppm.

### Internal standard used for NMR spectroscopy

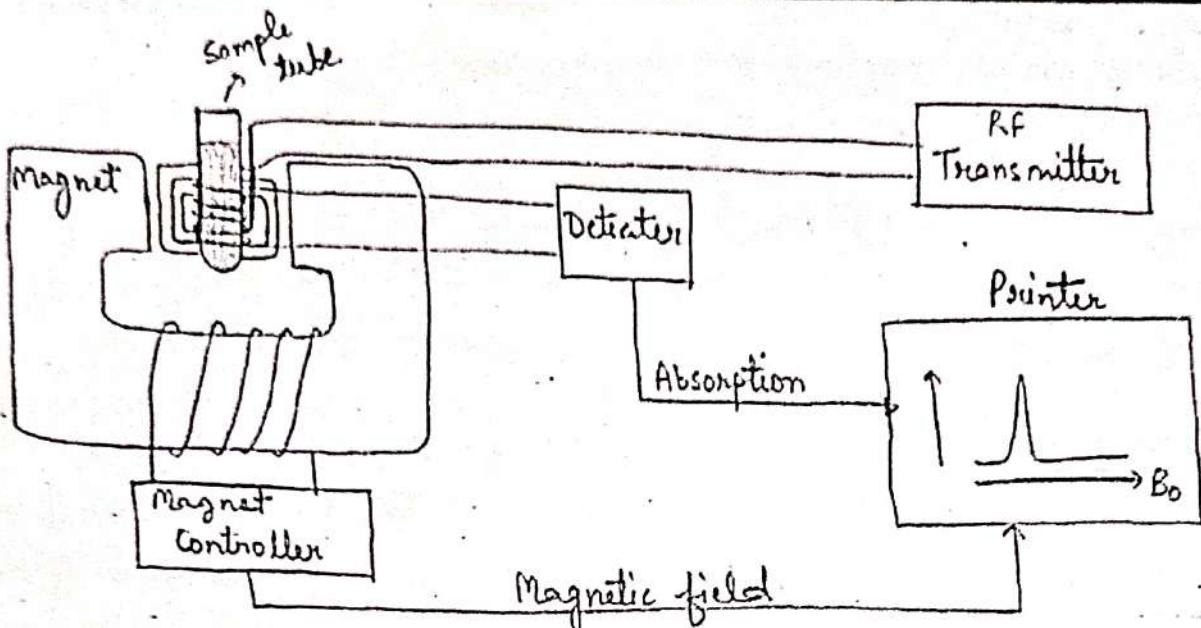
That compound which is used as a reference standard to represent the NMR signal of the compound is known as internal standard for the NMR or PMR spectroscopy.

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

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.

### Instrumentation of NMR Spectroscopy

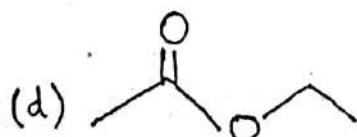
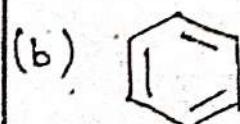
1. Sample holder: Glass tube with 8.5 cm long, 0.3 cm in diameter.
2. Permanent magnet: It provides a homogeneous magnetic field at 60-100 MHz.
3. Magnetic coils: These coils induce a magnetic field when current flows through them.
4. Sweep generator: To produce an equal amount of magnetic field pass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



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

1. NMR spectroscopy 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.

Ques. How many signals would you expect to see in the  $^1\text{H}$  NMR spectrum of each of the following compounds?



## Lecture - 1B

Stereoisomerism arises due to the difference in arrangement (configuration) of atoms or groups in space. When two or more than two isomers have the same structural formulae but having difference in the arrangement (configuration) of atoms in space are called stereoisomer and the phenomenon is called stereoisomerism.

Stereo isomerism can be further classified as

- (i) Optical isomerism
- (ii) Geometrical or cis-trans isomerism

### Optical (Configurational) isomerism

Optical isomerism is another class of stereoisomerism. The 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. Optical activity of any compound is measured by analyzing the sample in an instrument called Polarimeter. A solution of known concentration of optically active compound is when exposed to the beam of plane polarized light, the beam of plane polarized light is rotated through a certain number of degrees, either to the clockwise (right) direction or anti-clockwise (left) direction. The compound which rotates the plane polarized light towards clockwise direction is called to be

$\alpha$  is observed angle of rotation  
t is the temperature of during experiment  
 $\lambda$  is the wavelength of light used  
l is the length of the tube in decimeter  
and c is the concentration of the compounds per 100mL of solution

The angle of rotation depends upon the following factors:

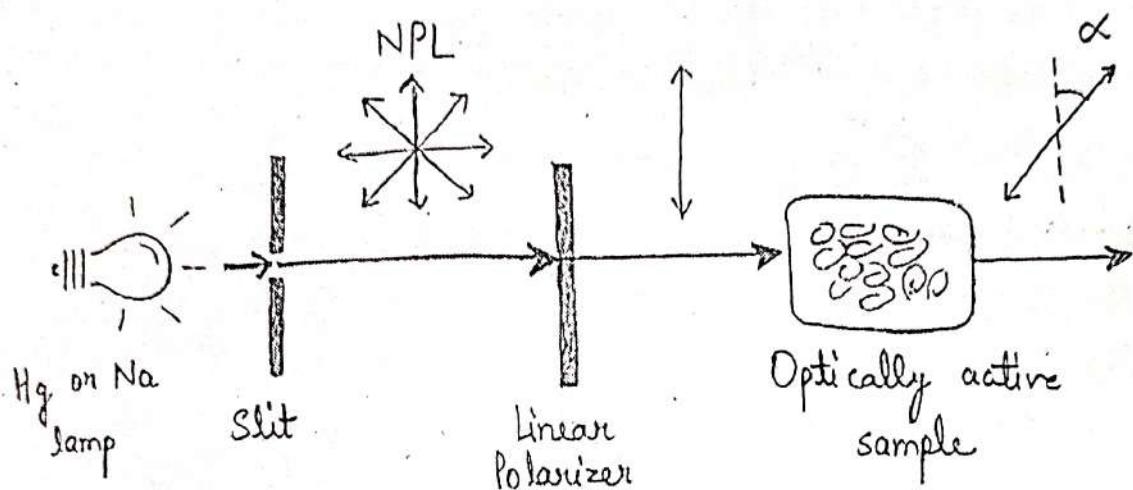
- (a) Nature of compound
- (b) Nature of solvent
- (c) Concentration of solution
- (d) Wavelength of light
- (e) Length of solution column through which light passes
- (f) Temperature

Note: Optically active compounds always exist in two isomeric forms which rotates the plane polarized light by equal degrees in opposite directions. The optical isomer which rotates the plane polarized light towards right (clockwise direction) is known as Dextrorotatory Isomer or (+)-isomer, whereas, the optical isomer which rotates the plane polarized light towards left (anticlockwise direction) is known as Levorotatory Isomer or (-)-isomer.

### Geometric Isomerism (Cis-Trans Isomerism of E-Z Isomerism)

The carbon atoms of the carbon-carbon double bond are  $sp^2$ -hybridized. The carbon-carbon double bonds consist of  $\sigma$  bond and  $\pi$ -bond. The presence of  $\pi$  bond locks the molecule in one position therefore rotation around the  $C=C$  bond is not possible.

dextrorotatory (represented by +); whereas, the compound which rotates the plane polarized light towards anti-clockwise direction is called to be levorotatory (represented by -).



Schematic representation of polarimeter.

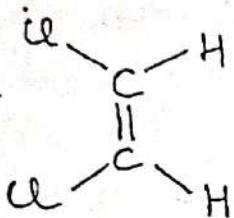
The degree of rotation depends upon the number of the molecules of the compounds falls in the path of beam. To compare the rotating power of different optically active compounds, the specific rotation of each compound is calculated and then comparison should be made. Specific rotation is defined as the degree of rotation offered for the given wavelength of plane polarized light at given temperature by a solution of 1g/mL concentration is filled in a 10cm length sample cell. Specific rotation is represented by  $\alpha$  and can be calculated as

$$\alpha_t^{\lambda} = \frac{100\alpha}{l c}$$

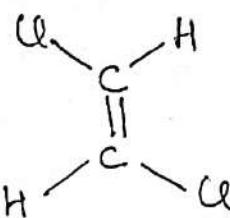
where,  $\alpha_t^{\lambda}$  is specific rotation

- This restriction of rotation about the carbon-carbon double bond is responsible for Geometric isomerism.
- The *cis* isomers is one in which two similar groups are on the same side of the double bond.
- The *trans* isomers is one in which two similar groups are on the opposite sides of the double bond.

The geometric isomers of 1,2-dichloroethene



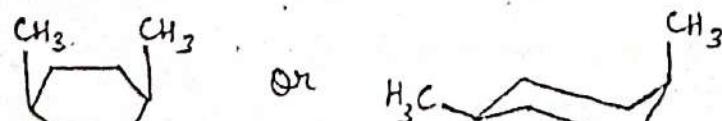
*cis*-1,2-Dichloroethene  
( $C_2H_2Cl_2$ )



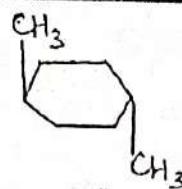
*trans*-1,2-Dichloroethene  
( $C_2H_2Cl_2$ )

### Cis and Trans for Cyclic molecules

There is geometrical isomerism whenever the rotation is restricted around any bonds, therefore presence of a double bond is not required. This is the situation for many cyclic compounds. For example, if there are two methyl groups attached to the neighbouring carbons of cyclohexane, the two substituents can be in *cis* position if these are on the same side of the plane of the non-neighbouring carbon atoms, while it is in *trans* position if these are located on the opposite sides.

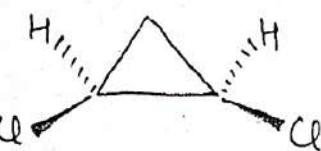


*cis*-1,4-dimethylcyclohexane

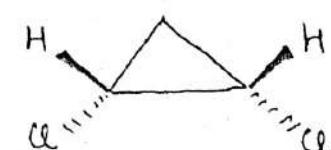


trans-1,4-dimethylcyclohexane

Cyclohexanes contain a ring of carbon atoms in which the bond angles are strained from the tetrahedral angles in the parent alkane and the ring prevents rotation around the carbon atoms, so when there are two different groups attached to two carbons in the ring, these molecules can exist as the cis- and trans-forms. For example:



cis-1,2-dichlorocyclopropane

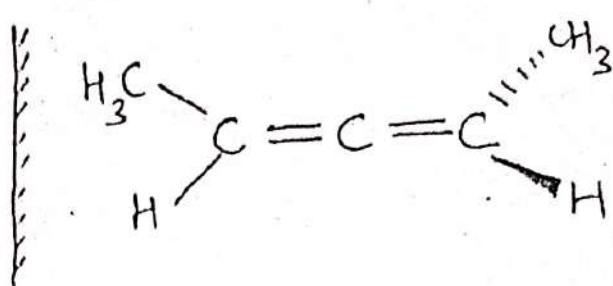
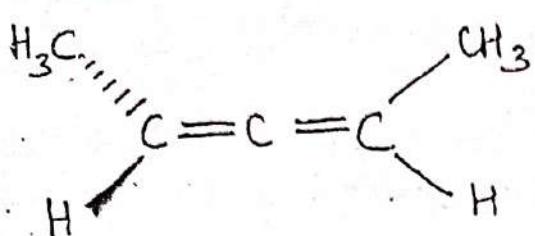


Trans-1,2-dichlorocyclopropane

### Geometrical isomer without chiral center

#### Allene Derivatives

Some derivatives of allenes ( $\text{CH}_2=\text{C=C=CH}_2$ ) exhibit optical isomerism. Example is 1,3-diphenylpropadiene. In allenes, the central carbon forms two  $\text{sp-sp}^2$  sigma bonds. The central carbon has also two p-orbitals which are mutually perpendicular. These form pi-bonds with the p-orbitals on the other carbon atoms. As a result, the substituent at one end of the molecule are in plane which is perpendicular to that of the substituent at the other end, so that the compound exists in two forms which are non-superimposable mirror images and are optically active.



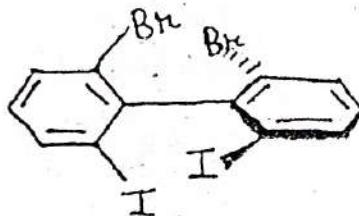
enantiomers of 2,3-pentadiene

### Biphenyl Derivatives

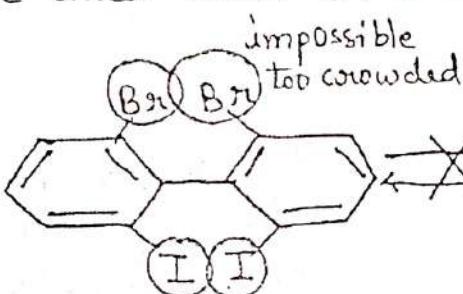
Substituted biphenyls show optical isomerism when substituents in the 2-positions are large enough to prevent rotation about the bond joining the two benzene rings. For example,

biphenyl - 2, 2'-disulphonic acid exist in two forms.

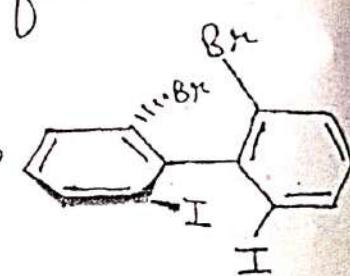
(a)



staggered conformation  
(chiral)

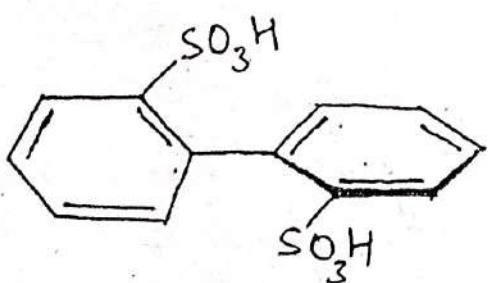


eclipsed conformation  
(symmetric, chiral)



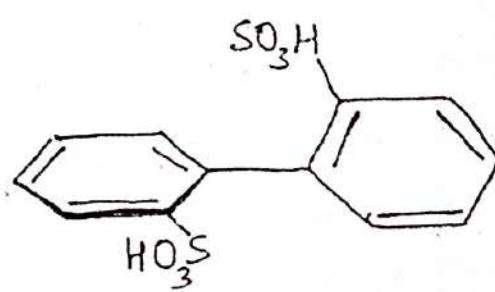
staggered  
conformation  
(chiral)

(b)



Biphenyl-2,2'-disulfonic acid  
(a Biphenyl)

Mirror

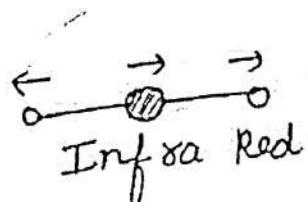
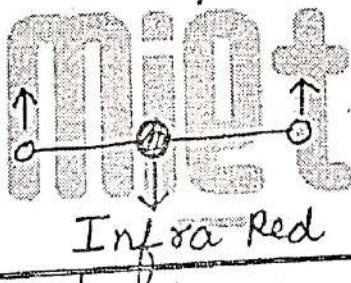
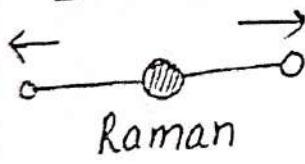


## Lecture-19

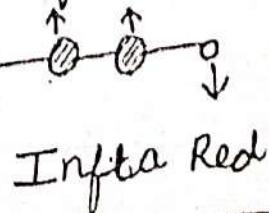
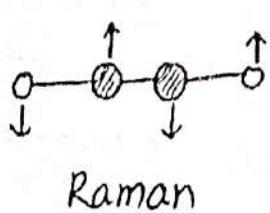
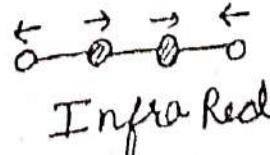
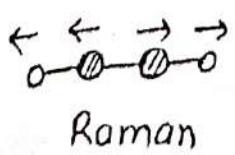
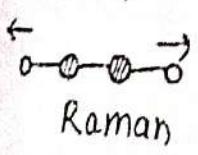
Mutual exclusion Principle

It state that no normal mode of vibration can be both infrared and Raman active in a molecule that possesses a centre of symmetry. If a molecule has a center of symmetry, all symmetric modes of vibration will be Raman active whereas all asymmetric vibration will be infrared active and vice versa. If there is no centre of symmetry in the molecule then some vibrations will be both Raman and IR active.

## Example of Mutual exclusion principle

a)  $\text{CO}_2$  Molecule

Mode of vibration of $\text{CO}_2$	Raman	Infra-red
$\nu_1$ : symmetric stretch	Active	Inactive
$\nu_2$ : Bending	Inactive	Active
$\nu_3$ : Asymmetric stretch	Inactive	Active

(b)  $\text{C}_2\text{H}_4$  Molecule

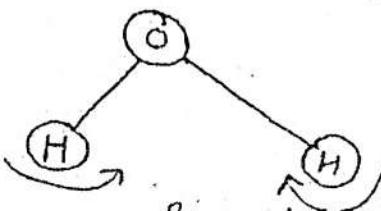
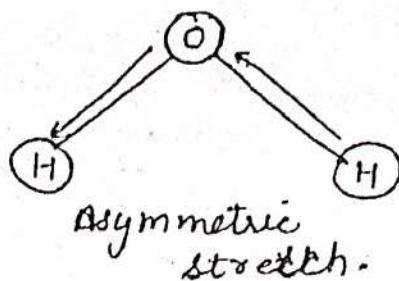
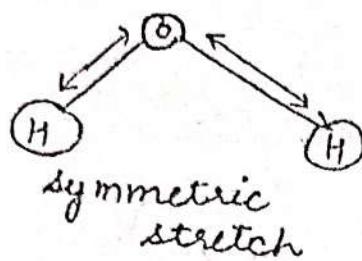
### Application of Raman Spectroscopy

- 1) Qualitative tool for identifying molecules from their vibration.
  - 2) Rapid characterization of chemical composition and structure of a sample
  - 3) Raman technique is superior to infrared for investigation of inorganic system because their aqueous solution can be employed.
  - 4) Raman spectra can be used for functional group detection and fingerprint regions that permit the identification of specific compounds.
  - 5) Raman spectroscopy can be used for biological systems because biological sample contain water which do not interfere with Raman signal from sample.
  - 6) Raman spectroscopy can be used for analysis of food and nanomaterials using Raman spectroscopy.
- Q1 Among  $F_2$ , HF,  $CO_2$ ,  $D_2O$  molecule identify which will be IR, microwave and Raman active and give reason.
- Explain different mode of vibration in  $H_2O$  molecule (2019-20)
- Solution  $\rightarrow$  HF,  $D_2O$ , asymmetric stretching and bending vibrations of  $CO_2$  are IR active because they possess change in dipole moment during vibration.
- HF and  $D_2O$  are microwave active because they have permanent dipole.

$F_2$ , HF,  $D_2O$  and symmetric vibration of  $CO_2$  is Raman active because during vibration polarizability changes.

Mode of vibration in  $H_2O$  molecule  $\rightarrow$  since  $H_2O$  is linear  $n=3$ , it has  $3n-6 = 3$  vibration and they are pictured

Below.



Q9 Which of the following would you use to measure the vibrational frequency of the following bonds? (2018 - 2019, 2019 - 2020)

- i) The stretching frequency of  $^{14}\text{N}-^{15}\text{N}$
- ii) The  $\text{C}\equiv\text{C}$  stretching in Ethyne,  $(\text{CH}\equiv\text{CH})$
- iii) The  $\text{C}=\text{O}$  stretching in acetone,  $\text{CH}_3\text{COCH}_3$
- iv) The Re-Re stretching in compound,  $(\text{CO})_5\text{Re}-\text{Re}(\text{CO})_5$

Solution →

- i) The stretching frequency of  $^{14}\text{N}-^{15}\text{N}$ : This stretching frequency can be measured using Raman spectroscopy because it has no dipole moment and can change polarizability.
- ii) The  $\text{C}\equiv\text{C}$  stretching in Ethyne,  $(\text{CH}\equiv\text{CH})$ : Respective symmetric stretching frequency can be measured by using Raman spectroscopy because it changes polarizability during vibration and has zero dipole moment.
- iii) The  $\text{C}=\text{O}$  stretching in acetone,  $\text{CH}_3\text{COCH}_3$ : This stretching frequency can be measured using IR spectroscopy because it will change dipole moment during vibration.

(IV) The Re-Re<sub>5</sub> in Compound, (CO)<sub>5</sub>-Re-Re(CO)<sub>5</sub>: Respective symmetric stretching frequency can be measured using Raman spectroscopy because it changes polarizability during vibration and has zero dipole moment.

Q3 → What is Selection Rule? (2020-2021)

Solution Selection rule state that molecule will only absorb (or emit) certain electromagnetic radiation whose energy is equal to energy difference between the two states involved in a spectroscopic transition. Selection rule predict whether the transition from one quantum number to another will occur or not. Selection rule differ from one spectroscopic technique to other.

Q4 → Write the criteria for a molecule to show Raman, IR, Rotational and UV spectra. (2020 - 2021)

Solution → Criteria for A Compound To Show Spectra

A molecule will absorb electromagnetic radiation when the energy of radiation is equal to the energy difference between two states involved in transition.

Applied Frequency = Natural frequency of vibration

- For UV spectra: 200 to 800 nm radiation will be used
- For IR spectra: IR radiation in the range of 2.5 μm to 25 μm radiation is used
- For Rotational spectra: Microwave Radiation will be used
- For Raman spectra: 478 nm, 532 nm, 780 nm will be used for Raman spectra

2) Specific Criteria

- UV Transition: a) The Total spin cannot change, ΔS = 0

b) The change in total orbital angular momentum can be  $\Delta L = 0, \pm 1$  but  $L=0 \leftrightarrow L=0$  transition is not allowed

c) The change in total angular momentum can be  $\Delta J = 0, \pm 1$  but  $J=0 \leftrightarrow J=0$  transition is not allowed

b) IR transition

A molecular vibration is IR active when molecule exhibit change in dipole moment or have permanent dipole moment.

c) Rotational transition

A molecule will be rotational active if it has permanent dipole moment.

d) Raman transition

A molecule will be Raman active if molecule exhibit change in polarizability during vibration.

B. Tech I Year [Subject Name: Engineering Chemistry]

5 Year's  
University Paper Questions  
(AKTU Question Bank)

**Meerut Institute of Engineering and Technology, Meerut**

**Topic-Wise Important Questions for AKTU End Semester Examinations**

Subject Code: BAS102		Subject Name : Engg. Chemistry		Taught in :	I Year / All Branches	
Unit No.	Topics	Q. No.	Question (Statement) - As Appeared In AKTU	Year	Marks	Remarks
Unit-2	UV-VISIBLE SPECTROSCOPY	11	Write the Beer-Lambert law. A compound having concentration $10^{-3}$ g/L resulted absorbance value 0.2 at $\lambda_{max} = 510\text{nm}$ using 1.0 cm cell. Calculate its absorptivity and molar absorptivity value. Molecular weight of compound is 400.	2018-2019, 2021-2022 (even)	2, 10	
		12	Explain various electronic transitions in UV-Visible spectroscopy. What is meant by auxochrome and chromophores? Explain various shifts observed in UV-Visible spectroscopy and what is the effect of solvent in $\pi-\pi^*$ transition?	2020- 2021,2021- 2022 (Odd,Even) 2018-2019, 2021-2022 (Odd)	10	
	IR-SPECTROSCOPY	13	Explain various types of fundamental vibrational modes observed in molecule using IR spectroscopy. How many vibrational modes will any molecule have? Give example. One of the fundamental vibrational modes of H <sub>2</sub> O occurs at 3652 cm <sup>-1</sup> . What would be the frequency of the corresponding vibration for D <sub>2</sub> O.	2021-2022 (Odd)2014- 2015	10	
		14	IR peak is often characterized as molecular fingerprint. Comment on it.	2017-2018, 2018-2019,	2	
	STERIOCHEMISTRY	15	i. Explain the term chemical shift along with shielding and deshielding in NMR spectroscopy. ii. An aromatic compound (Molecular mass=135) give the following signals in NMR Spectrum. (i) Singlet (2.09 δ),3H (ii)A distorted singlet (3.09 δ),1H (iii)A multiplet(7.27 δ),3H (iv)A multiplet (7.75 δ),2H. Predict the structure of the compound How many NMR signals will be obtained for Mesitylene?	2017-18	7	NEW CONTENT
		16	Why Tetra Methyl Silane is used as an internal indicator in NMR spectroscopy? Give the number of 1H NMR signals and their splitting pattern in the following compounds: (i) (CH <sub>3</sub> ) <sub>3</sub> COCH <sub>3</sub> (ii) CH <sub>3</sub> CH(Cl)CH <sub>2</sub> Cl (iii) CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH (iv) CH <sub>3</sub> CHCHCHO	2016-17	7	
		17	What is the importance of Green Chemistry , Describe twelve principle of Green Chemistry.			NEW CONTENT
		18	Write possible optical isomers in tartaric acid. (ii) What is the difference between enantiomers and diastereoisomers?			NEW CONTENT
		19	What is E - Z system of nomenclature ? In what way it is better than cis, trans-nomenclature ?			NEW CONTENT