UNIT - III

2 Marks

1. Define Beer - Lambert law ?
2. What is steric effect
3. Give the ultraviolet bands for the carbonyl compounds?
4. Give the vibractional frequency of aldehyde
5. What is solvent effect

5 Marks

1. Give the effect of solvent on electronic transition
2. Give the Fisher - woodward rules for conjugated diens.
3. Explain about ultraviolet spectrum of aromatic compound.
4. Give the characteristic vibrational frequency for following compounds
   i) Alkene   ii) Alkanes   iii) Alkynes.

10 Marks

1. Explain detail about the vibrational frequency of carbonyl compounds
2. Explain effect of solvent on electronic transition and vibrational frequency

Applications of UV and IR Spectroscopy

3.1 Ultraviolet and Visible Spectroscopy

Beer - Lambert law - The Beer-lambert law also known as Beer's law the lambert-Beer law, or the Beer-lambert-Bouguer law relates the attenuation of light to the properties of the material through which the light is travelling. The law is commonly applied to chemical analysis measurement and used in understanding attenuation in physical optics. For photons, neutrons, or rarefied gases.

Effect of solvent on electronic transition :-

A solvent which does not itself absorb in the region under investigation is the most suitable solvent for UV-visible spectroscopy. Most commonly used solvent are 95% EtOH, H_2O and hexane.

It has been observed that the intensity as well as the λ_{max} shift with the change of the polarity of the solvent. By increasing polarity of the solvent compounds like hydrocarbons doest not experi-ence any appreciable shift. Thus, value of absorption maximum for non-polar compound is same in ethanol [polar] and hexane [non-polar]

Explanation - i) $\sigma \rightarrow \sigma^*$ Transition

ii) $\pi \rightarrow \pi^*$ Transition

iii) $n \rightarrow \sigma^*$ Transition

iv) $n \rightarrow \pi^*$ Transition

Ultraviolet bands For carbonyl compounds

Absorbance in the rough neighbourhood of 270-300 nm is common For molecules containing a $C=O$ group [such as Ketones and Aldehydes] and this corresponds to a $[n \rightarrow \pi^*]$ transition.

These absorbance tend to be weak, relative to $[\pi \rightarrow \pi^*]$ transitions. Still, observing this absorbance can be important clue in the Structure determination of unknown compounds.

Diene :-

In Organic chemistry a diene is a covalent Compound that Contains two double bonds, usually among carbon atoms. They thus contain two alkene units, with the standard Prefix di of systematic nomenclature.

Conjugated Polyene :-

An cyclic hydrocarbon with a molecular Structure containing alternating carbon-carbon double bond and single bonds.

Fisher woodward rules For conjugated diene and carbonyl Compounds :-

Woodward's rules, named after Robert Burns Woodward and also known as woodward - Fisher rules are several sets of empirically derived rules which attempt to predict the wavelength of the absorption maximum (λmax) in an ultraviolet - visible spectrum of a given compound.

Inputs used in the calculation are the type of chromophores present, the auxochromes.

Example :-

  i) Conjugated carbonyl compounds

  II) Conjugated dienes and polyenes

Conjugated carbonyl compounds :-

  conjugation of a double bond to a carbonyl group transmits the electrophilic character of the carbonyl carbon to the beta-carbon of the double bond. These conjugated carbonyl are called enones or α, β unsaturated carbonyls.

Conjugated dienes :-

  conjugated dienes are two double bonds separated by a single bond. Non conjugated dienes are two double bonds are separated by more than one single bond. cumulated Dienes are two double bond connected to a similar atom.

Steric effect of biphenyl :-

  steric hindrance is a consequence of steric effects, steric hindrance between adjacent groups can also affect torsional bond angles. Steric hindrance is responsible for the observed shape of rotaxanes and the low rate of racemiz -tion of 2,2 - disubstituted biphenyl and binaphthyl derivatives.

Ultraviolet spectra of heterocyclic compounds :-

The ultraviolet spectrum of an organic compound [The pattern of its light absorption in the ultraviolet region of the spectrum] is characteristic of the π-electron system of the molecule.

i.e, of the arrangement of double bonds within the structure.

Ultraviolet spectra of aromatic compounds :-

The application of fluorescence spectroscopy in the qualitative and quantitative analysis of aromatic compounds was investigated. The replacement of hydrogen atoms of aromatic hydrocarbons by alkyl groups in some instances gives noticeable shifts in fluorescence spectra. The replacement of carbon atoms of aromatic hydrocarbons by nitrogen and by oxygen was also examined.

Unsaturated carbonyl compounds :-

A carbonyl group is a chemically organic compounds with the functional group composed of a carbon atom double-bonded to an oxygen atom [c = o]. The simplest carbonyl groups are aldehydes and ketones usually attached to another carbon compound.

It is common to several classes of organic compounds, as part of many larger functional groups. A compound containing a carbonyl group is often referred to as a carbonyl compound.

Infrared Spectroscopy
Effect of Hydrogen bonding :-

Hydrogen bonding 10 stronger the hydrogen bonding, greater is the absorption shift towards lower wave number than the normal value. The N-H stretching frequencies of amines are also affected by hydrogen bonding as that of the hydroxyl group but frequency shifts for amines are lesser than that for hydroxyl compounds.

Solvent effect on vibrational frequency :-

Solvent induced vibrational frequency shifts [SFS] have attracted interest for many years, since they provide important information on chemical bonding and solute - solvent interac -tions. The attractive interactions are usually subdivided into electrostatic, dispersive and specific ones.

Chemical exchange :-

Chemical exchange in NMR is the change in magnetic environment of a nucleus, due to a chemical reaction. This changes the resonance fre -quency of the nucleus, and the observed effect on the NMR spectrum depend on the relative size of the frequency change and the reaction rate.

Characteristic vibrational frequencies of Alkanes, Alkene, Alkynes, aromatic compounds, Alcohols. Estors, Phenol and Amine

Alcohol :-

	Type of vibration	Characorsitic Absorption	Intensity
O – H	[Stretch, H bonded]	3200 – 3600	strong, broad
O – H	[Stretch, Free]	3500 – 3700	Strong, Sharp
C – O	[Stretch]	1050 – 1150	Strong

Alkane :-

C – H	Stretch	2850 – 3000	Strong
– C – H	bending	1350 – 1480	Variable

Alkene :-

= C – H	Stretch	3010 – 3100	medium
= C – H	bending	675 – 1000	strong
C = C	Stretch	1620 – 1680	variable

Alkyne :-

C – H	Stretch	3300	strong, sharp
– C = C –	Stretch	2100 – 2260	variable

Aromatic compound :-

C – H	Stretch	3000 – 3100	medium
C = C	Stretch	1400 – 1600	medium-weak multiple band

Amine :-

N – H	Stretch	3300 – 3500	Medium
C – N	Stretch	1080 – 1360	Medium – weak
N – H	bonding	1600	Medium

Ester :-

C = O	Stretch	1735 – 1750	Strong
C – O	Stretch	1000 – 1300	two bands or more

Anhydride :-

C = O	Stretch	1800 – 1830 & 1740 – 1775	two bands

Aldehyde

C = O	Stretch	1740 – 1720	Strong
= C – H	Stretch	2820 – 2850 & 2720 – 2750	Medium, two peaks

Amide :-

C = O	Stretch	1640 - 1690	Strong
N – H	Stretch	3100 - 3500	unsubstituted
			have two bands
N – H	bending	1550 - 1640	

Ketone :-

A cyclic	Strecth	1705 - 1725	Strong
aryl ketone	Stretch	1680 - 1700	strong

Carbonyl :-

C = O	Stretch	1670 - 1820	strong

UNIT - IV

2 Marks

1. What is meant by correlation of protons?
2. Write note on chemical exchange
3. What is virtual coupling
4. What is chemical shift
5. What is coupling constant

5 Marks

1. Explain about the effect of Deuteration
2. Explain about spin-spin coupling interaction including large range coupling
3. Explain the Fourier transform technique
4. Explain Nuclear overhauser effect

10 Marks

1. Write a note on, Two dimension spectroscopy, COSY, NOESY and DEPT technique

2. Write the chemical shift, values of aliphatic olefine, alkyne, aromatic. hetero aromatic, Carbonyl Carbon.

Application of NMR spectroscopy
Proton Magnetic Resonance spectroscopy
General introduction to NMR :-

Nuclear Magnetic Resonance [NMR] is a nuceli [Nuclear] specific spectroscopy that has far reaching applications throughout the physical sciences and industry. NMR uses a large magnet to probe the intrinsic spin properties of atomic nuclei.

chemical exchange :-

Chemical exchange in NMR is the change in magnetic environment of a nucleus, due to a chemical reaction. This changes the resonance fre -quency of the nucleus, and the observed effect on the NMR spectrum depend on the relative size of the frequency change and the reaction rate.

contact shift reagent :-

EuFOD is the chemical compound with the formula $Eu(OCC(CH_3)_3 CH COC_3 F_7)_3$ also called $Eu(fod)_3$. This coordination compound is used primarily as a shift reagent in NMR spectro -scopy. It is the premier member of the lanthanide shift reagents and was popular in the 1970s and 1980s

solvent effect :-

Solvent effect are the influence of a solvent on chemical reactivity on molecular associa-tions. solvent can have an effect on solubility stability and reaction rates and choosing the appropriate solvent allows for thermodynamic and kinetic control over a chemical reaction.

Fourier transform technique :-

Fourier transform spectroscopy is a measurement technique whereby spectra are collected based on measurements of the cohe-rence of a radiative source, using time-do-main measurements of the electromagnetic radiation on space-domain measurements of the electromagnetic radiation on other type of radiation.

Nuclear overhauser effect :- [NOE]

The nuclear overhauser effect is the transfer of nuclear spin polarization from one population of spin active nuclei

E.g :-

^1H, ^{13}C, ^{15}N etc.

A phenomenological definition of the NOE in nuclear magnetic resonance spectroscopy is the change in the integrated intensity of one NMR resonance that occurs when another is saturated by irradiation with an RF field.

Effect of Deuteration :-

The incorporation of ^2H into non-exchangebl positions decreases the rate of ^{13}C and $^1H(N)$ T_2 relaxation and therefore increases the sensitivity and resolution in multidimensional NMR experiment. The suppression of proton - proton scalar couplings $[J_{HH}]$ as a result of deuteration further imp -roves linewidths.

Virtual coupling :-

The NMR spectrum for a proton in certain spin systems may be complicated by other protons to which it has a zero coupling constant. This effect, which is a virtual coupling, is shown to arise as a result of strong coupling between two or more nuclei in the system. Calculated spectra and detailed qualitative description are presented for a three - spin system along with a general discussion relating to the more comple higher spin cases. A number of illustrations are included.

Simplification of complex spectra :-

Polarizing the ^1H spin system by applying a $90°rf$ pulse at the ^1H resonance frequency. The entire sequence is repeated many times until a suitable signal - to - noise ration for ^{13}C is achieved.

Carbon 13 - NMR spectroscopy

General consideration :-

As such 13c NMR is an important tool in chemical structure elucidation in organic chem -istry.

C NMR detects only the 13c isotope of carbon whose natural abundance is only 1.1% because the main carbon isotope, 12c, is not detected by NMR since it has zero net spin.

coupling constant :-

The coupling constant, J is a measure of the interaction between a pair of protons. The implications are that the spacing between the lines in the coupling patterns are the same as can be seen in the coupling pattern from the H-NMR spectra of 1,1-dichloroethane.

Two dimensional NMR spectroscopy :-

Two dimensional NMR spectroscopy 2D [NMR] is a set of nuclear magnetic resonance spectroscopy methods which give data plotted in a space defined by two frequency axes rather than one.

Types of 2D NMR include correlation spectroscopy [COSY], J-spectroscopy, exchange spectroscopy [EXSY] and nuclear overhauser effect spectroscopy [NOESY].

COSY Technique :-

COSY is a technique for determining corre-lations through the chemical bond. In it's most used form this allows us to see which proton resonances are mutually coupled. As described in the section on 1H spectra, coupling of protons through 2, 3 or 4 bonds has a significant impact on the appearance of a proton spectrum.

EXSY Technique :-

The 2D Exchange spectroscopy [EXSY] technique is exactly the same as the same as the 2D NOESY technique. The pulse sequences are identical. The method provides off - diagonal reposes for spin which exchange slowly with one another and also between spins with NOE's.

NOESY Technique :-

A 2D NOESY experiment can be used to determine protein - ligand contacts. Because NOE cross relaxation occurs between ligand and protein while bound, cross peaks between ligand protein NMR signals can be observed in a 2D NOESY spectrum of a protein - ligand solution.

DEPT Technique :-

Distortionless enhancement by polarization transfer [DEPT] is an NMR method used for determining the presence of primary, secondary and tertiary carbon atoms. Singnals from quatornary carbons and other carbons with no attached protons are always absent.

spin-spin interaction including long range coupling :-

The structure of a molecule can be predicted using NMR spectroscopy. In fact, the interactions between different types of protons present in the molecule cause a single peak on an NMR spectrum to split into doublet, triplet, or multiplet a phenomenon known as the spin-spin coupling

First order spectra :-

In other word, the proton is only coupled to other protons that are far away in chemical shift. The spectrum is called First-order spectrum The splitting pattern depends on the magnetic field. The second order splitting at the lower field can be resolved into First order splitting pattern at the high field.

correlation proton bonded to carbon :-

The carbon peaks between 126 and 130ppm yield correlation with the proton dimension at about 7 ppm and are therefore likely to correspond to the protonated carbons of the benzyl

group.

The O–CH₂ can be assigned to the peak at 65.8 ppm, which has a proton correlation at 5.2 ppm.

Chemical shift of hetero aromatic compounds :–

The major contributions to the proton chemical shift in hetero aromatic compounds are ring current and π-electron effects, with smaller contributions due to the α, β and γ-effects of the hetero atom and the long range contribution. Initially subroutines were added to the charge programme in order to identify the hetero-aromatic systems.

Chemical shift of aromatic compounds :–

In aromatic compounds like benzene, the protons on the aromatic ring are shifted down field.

For example, six protons in benzene are magnetically and chemically eqivalent and appear at 7.33 ppm. This is farther downfield than alkene protons, which appear between 4.5 – 6.5 ppm.

Nuclear magnetic double resonance:-

Nuclear magnetic double resonance experiments are described in which the perturbing radio-frequency field is amplitude or frequency modulated, causing the processing moment vector of a group of nuclear spins (s) to mutate at a low audio frequency. Throug the action of the nuclear spin-spin coupling this modulation information is transmitted to a second group of nuclear spins (1) in the form of a selective modulation of the local magnetic field, which may be used to excite a magnetic resonance "sideband" signal.

ORGANIC CHEMISTRY

UNIT - 5   CODE : 18KP3CH09

Two marks

Write about Mass spectroscopy ?

Write the principles of mass spectroscopy ?

What is meant by Molecular ion peak ?

What is meant by metastable peak ?

What is meant by isotope peak ?

Five marks

Write a brief notes on Mc Lafferty Rearrangement ?

What is nitrogen rule ? Explain it ?

Write a short note on optical rotatory dispersion (ORD) ?

Give notes on circular dichroism (CD) ?

Ten marks

Write a brief notes on mass spectral fragmentation of organic compounds with respect to their structural determination ?

What is meant by cotton effect ? How to determine the absolute configuration of Axial halo ketone & octant rule of ketones.

UNIT- V

Mass Spectroscopy

Mass spectrometry (MS) is an analytical technique that measures the mass - to -charge ratio of ions. The results are typically presented as a mass spectrum, a plot of intensity as a function of the mass-to-charge ratio. Mass spectrometry is used in many different fields and is applied to pure samples as well as complex mixtures.

A mass spectrum is a plot of the ion signal as a function of the mass -to-charge ratio. These spectra are used to determine the elemental or isotopic signature of sample, the masses of particles and of molecules, and to elucidate the chemical identity or structure of molecules and other chemical compounds.

Introduction.

The MS principle consists of ionizing chemical compounds to generate charged molecules or molecule fragments and measurement of their mass-to-charge ratios by using the one of variety of techniques (eg, EI/CI/ESI/APCI/MALDI).

A) Introduction of Electron Ionization (EI) technique.

EI is the most appropriate technique for relatively small (m.w < 600) neutral organic molecules

which can easily be promoted to the gas phase worthout decomposition, i.e volatile.

chemical ionization (CI) technique.

CI technique is especially useful when no molecular ion is observed in EI mass spectrum of a compound, and also in the case of confirming the molecular weight of a compound. CI technique uses nearly the same ion source devices as in EI, except, CI uses tight ion source, and a reagent gas.

Electrospray Ionization (ESI) technique.

ESI technique involves spraying of a solution of the sample through a highly charged needle called ESI capillary which is at atmospheric pressure. The sprarying process can be steamlined by using a nebulizing gas. The charged droplets are produced in which the positive or negative ions are solvated with solvent molecules.

Atmospheric pressure chemical ionization (APCI) technique

PCI has also become an important ionization source because it generates ions directly from solution and it is capable of analyzing relatively non-polar compounds. Similar to sp electrospray, the liquid effluer of APCI is introduced directly into ionization source through APCI probe. Sample solution undergoes rebulization to form an aerosol spray of fine droplets

and it is rapidly heated in a stream of nitrogen desolvation gas before emerging from the probe as a stream of desolvated / vaporized sample plume. Solvent / Reagent ions are formed in the region of the corona discharge needle. These ions react with analyte molecules to form signly charged protonated or deprotonated analyte ions.

E) Atmospheric Solid analysis probe Ionization (ASAP)

ASAP ionization is used for the direct analysis of volatile, semi volatile, Solid and liquid samples at atmospheric pressure, it is also known as one of the atmospheric pressure ionization (API) technique. This technique utilizes the heated nitrogen desolvation gas to vaporize the Sample and a Corona discharge for Sample ionization and it is a useful replacement for the conventional EI / CI vacuum insertion solids probe. Reagent ions react with analyte molecules to form ions.

Ion formation,

$$N_2 + e^- \longrightarrow N_2^+ + 2e^-$$

$$N_2 + H_2O \longrightarrow H_2O^+ + N_2$$

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH^- \text{ (Reagent ion)}$$

$$H_3O^+ + A \longrightarrow AH^+ + H_2O \text{ (Analyte ion)}$$

F) Atmospheric pressure photo Ionization (APPI)

APPI also one of the atmospheric pressure

this data helps facilitate the identification of molecules.
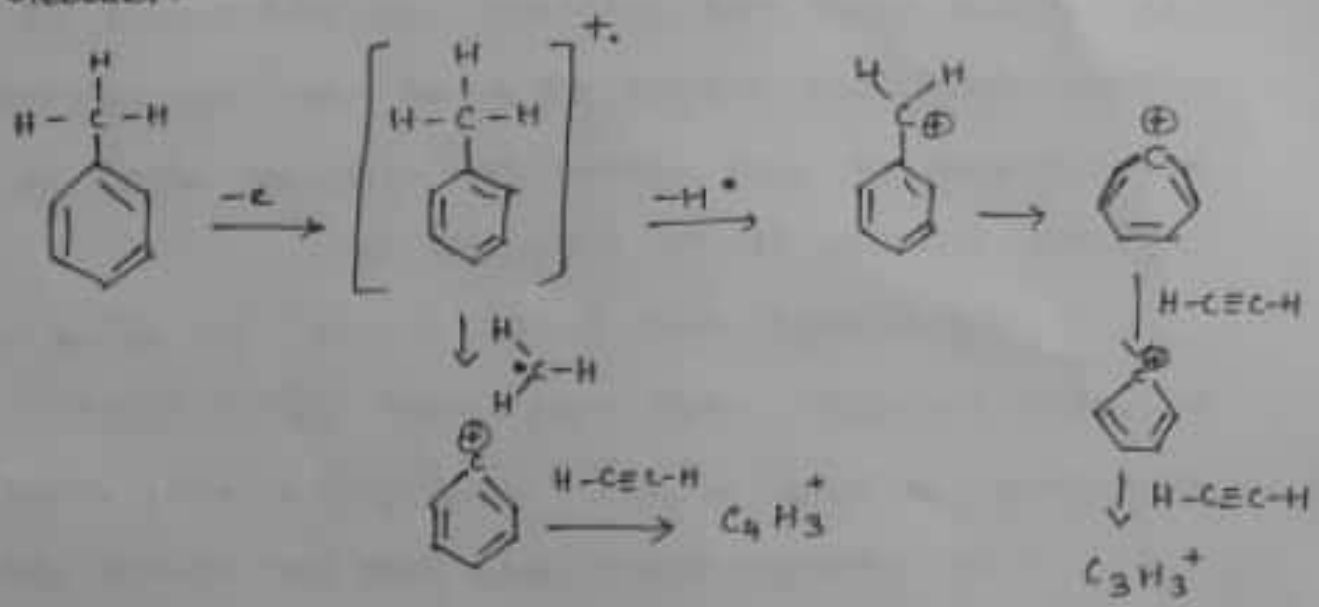
Example : Mass spectral fragmentation of phthalic acid esters.

Phthalic acid esters are among the most frequently encountered pollutants in biological extracts. They are very often detected in biological analysis using gas chromatography. Even using high resolution glass capillary columns the identification of some of these esters remains difficult. '

Fragmentation reactions.

It is a type of chemical dissociation, in which the removal of the electron from the molecule results in ionization Removal of electrons from either sigma bond, Pi bond or nonbonding orbitals because the ionization. This can take place by a process of homolytic cleavage / homolysis or heterolytic cleavage / heterolysis of the bond.

Rules for the basic fragmentation processes are

the sign of COTTON effect in ORD spectrum corresponds to that of CD.
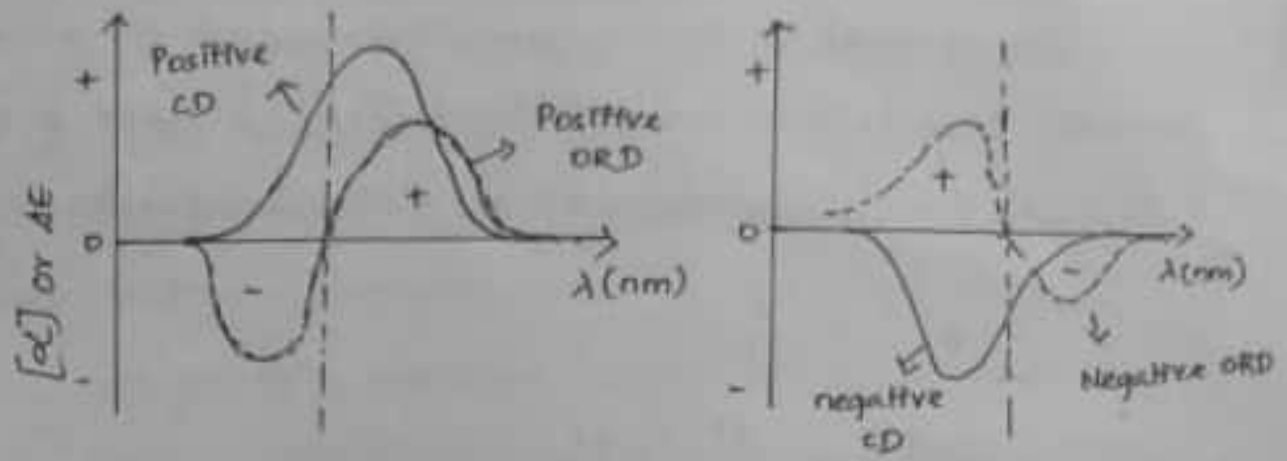
CD and ORD spectra describing (a) the positive and (b) negative CEs of a single electronic transition.

Axial Halo Ketone rule.

In Ketone formation of a strong and in-herently disymmetric chromophore due to the interaction between lone pair electrons of the axial halogen substituents at Cα associated with a strong molecular rotation and red shift at the extremum has been known as the axial haloketone rule.

Rule applies when there is an axial halogen next to the keto group of a cyclohexanone moeity. Carbonyl at the head of the chair closet to the observer, if the halogen appears at,

- Right - the compound shows strong positive cotton effect.
- left - the compound shows strong negative cotton effect.

as shown below,

(c)

+CE

≡

(or)

(a simplified Projection)

(a)

-CE
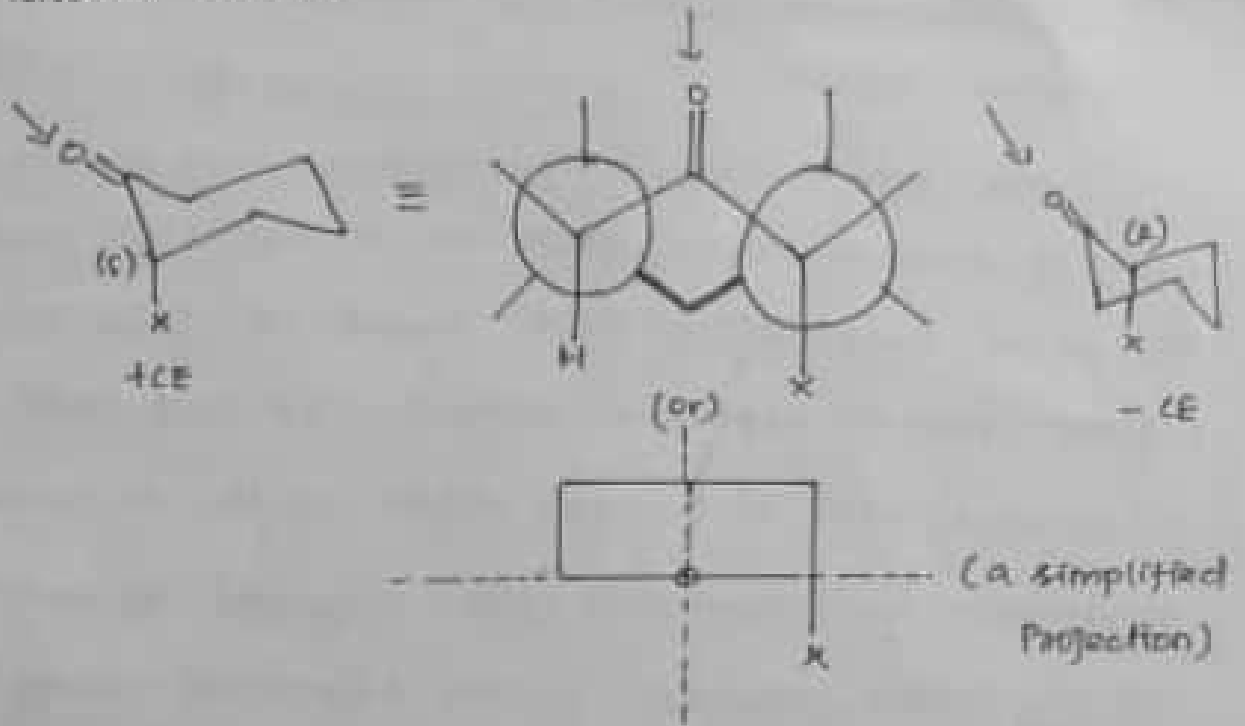
Application.

i) Determination of position of Halogen substitution.

ii) Determination of Absolute configuration.

iii) Demonstration of conformational mobility

iv) Demonstration of the existence of a boat Conformer.

Octant rule.

The <u>axial Haloketone Rule</u> and the octant Rule for Saturated ketones.

The octant rule is the most widely applied sector rule. It was developed from an earlier rule, known as the axial "halo ketone rule", based on ORD measurements carried out on steroidal ketones that had been (axially) Substituted with a halogen atom at the α-carbon. Axial Substitution (conformation) is often preferred because of the dipole-dipole repulsion in the equatorial isomer.
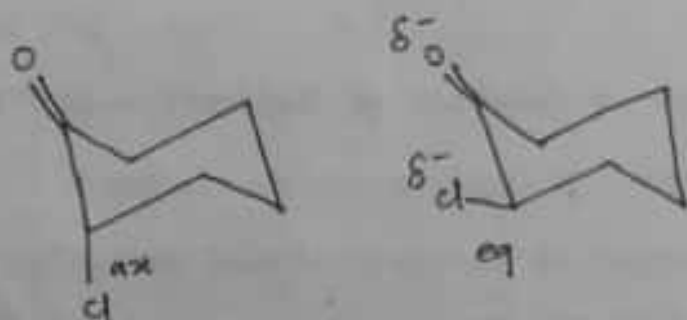
The position of the halogen was observed to influence the Sign of the cotton effect and similar effects were found for other substituents, such as NR_2, SR, SO_2R, etc.

It was suggested that prediction of the sign of the cotton effect is possible if the ketone group is viewed along the $O=C$ bond in the direction of the ring with the carbonyl carbon at the head of the chair (the major Conformer in cyclohexane ring systems). If the axial α-halogen is found on the right (as in the (s)-enantiomer), then there exists a positive cotton effect; if it appears on the left, a negative cotton effect is observed.

Source of the elliptically polarized light (Epl),(a) and definition of ellipticity ψ (b).

In analogy with the quantities related to optical rotation (i and α), a specific ellipticity $(\psi)_\lambda^T$, and a molar ellipticity $(\theta)_\lambda^T$, can defined for characterization of CD.

$$[\psi]_\lambda^T = \frac{\psi}{cl}$$

$$[\theta]_\lambda^T = \frac{M}{100}[\psi]_\lambda^T$$

Nowadays however, circular dichroism is usually obtained by measuring the difference in the molar extinction coefficients or left - E_{lcpl} and right - E_{rcpl} circularly polarized components of light.

$$\Delta\varepsilon = E_{lcpl} - E_{rcpl}$$

$\Delta\varepsilon$ is also called molar CD, and it directly correlates with the molar ellipticity $[\theta]_\lambda^T$.

$$[\theta]_\lambda^T = 3298\,\Delta\varepsilon.$$

Similarly as the ORD curve can be obtained, the measurement of the $\Delta\varepsilon$ value as a function of the wavelength λ leads to CD spectrum. In general, the measured CD effect is directly associated with the ORD anomaly, since they both reflect the interaction of the polarized light with the same chiroptical chromophore. The maximum curve of the CD curve coincides with the with the wavelength of anomalous ORD crossover, and
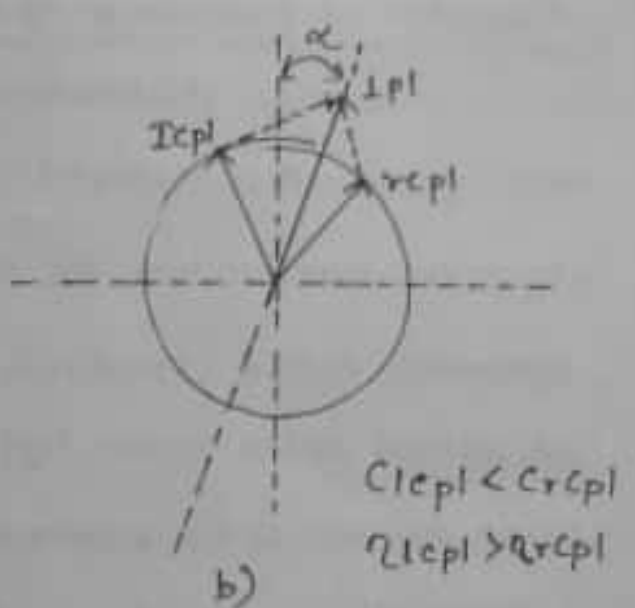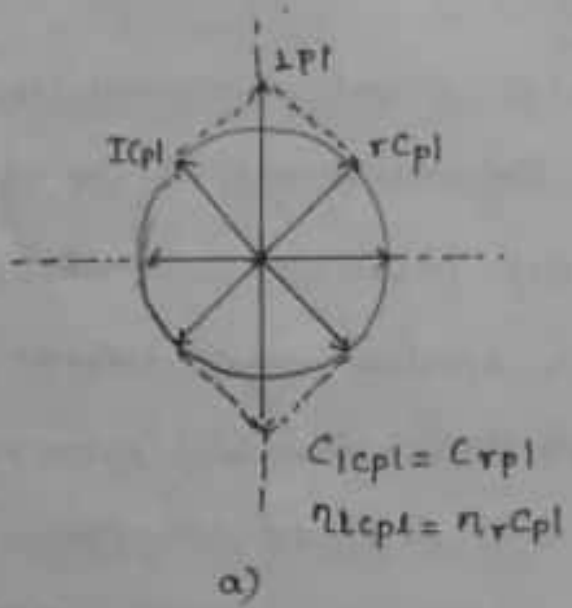
$$[\phi]_\lambda^T = \frac{M}{100} [\alpha]_\lambda^T$$

Absolute configuration of CD.

Circular dichroism (CD) is second chiroptical phenomenon most frequently applied for the assignment of the absolute stereostructure. When the linearly polarized light passes an optically active medium in a spectral region where adsorption takes place, left and right-circularly polarized rays do not only propagate with different velocities, but they are also absorbed by a chiral sample to a different extent (Alcpl ≠ Arcpl). Thereupon, the incident Lpl is converted into elliptically polarized light (Epl), and consequently, the resulting electric field vector sum traces an ellipse, which is characterized by the major and minor axes, a & b respectively and by the angle ψ, defined as the ellipticity.

a) Alcpl > Arcpl

b) ψ = arctan b/a
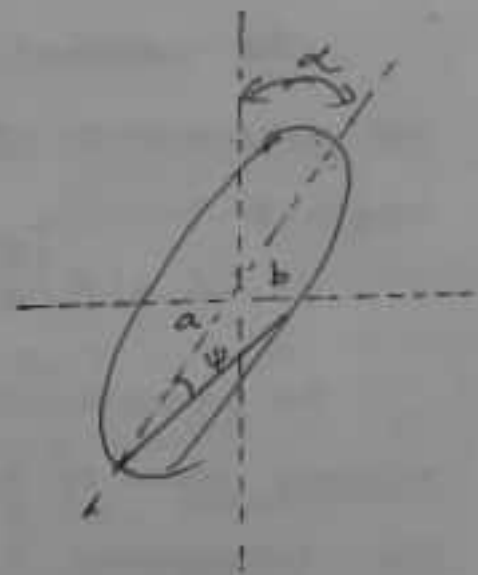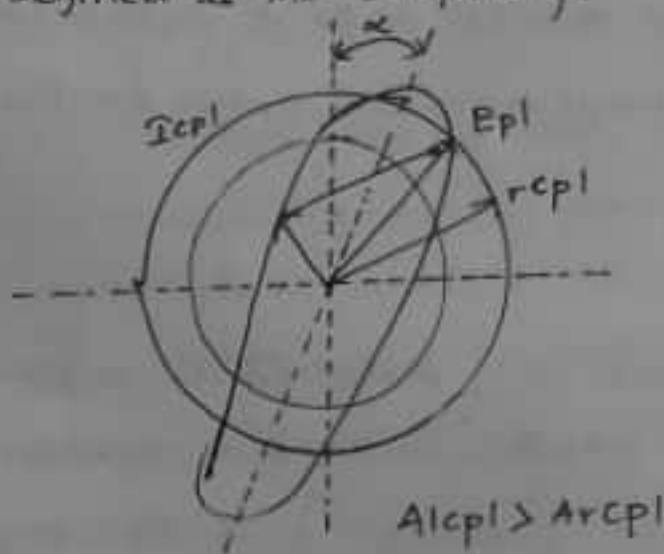
incident beam by a certain angle α, which is called optical rotation.

a)
$$C_{lcpl} = C_{rpl}$$
$$n_{lcpl} = n_{rcpl}$$

b)
$$C_{lcpl} < C_{rcpl}$$
$$n_{lcpl} > n_{rcpl}$$

Super composition of left-(lcpl) and right-(rcpl) circularly polarised light (a) in the isotopic medium, and (b) in the optically active, anisotopic environment. c_{lcpl}/c_{rcpl} and n_{lcpl}/n_{rcpl} are the respective velocities and refractive indices of the lcpl and rcpl components.

The measured optical rotation angle α depends on the concentration of the chiral compound c and on the path length l:

$$\alpha = [\alpha]_\lambda^T cl$$

The proportionality factor $[\alpha]_\lambda^T$ is defined as a specific rotatory power or specific rotation, which is a function of the temperature T and the wavelength λ of the correction for the molecular weight M of an optically active compound gives the molecular rotation $[\phi]_\lambda^T$.

Deduction of Absolute configuration in ORD

When passing linearly polarized light of a given wavelength through a chiral sample the phenomenon of optical rotation can be observed. Two enantiomers generate rotations of equal magnitude but of opposite sign and, therefore, can be easily distinguished. To comprehend the origin of the optical rotation, one has to keep in mind that the linearly polarized light can be mathematically and graphically represented as a superposition of left and right coherent rotating beams of circularly polarized light, which are enantiomeric to each other. In an optically active medium i.e, in a racemate, the two light components migrate at the same velocity c, so that the resultant vector sum, which exhibits the properties of the LPl (linearly Polarized light) does not change its orientation, that is, no rotation occurs.

If however, the linearly polarized light passes through a chiral sample, both circular components, lcpl and rcpl, are slowed down relative to their prior velocities, but to a different extent, which can be explained by an unequal, diastereomorphous interaction between the two chiral rays and the chiral molecules. The resulting linearly polarized light appears rotated relative to the

circular dichroism for spin angular momentum, (11)
and circular birefringence are manifestations of optical
activity. It is exhibited in the absorption bands of
optically active chiral molecules.

Uses.

It is used for an absorption spectroscopy, uses
circularly polarized light to investigate structural aspects
of optically active chiral media. Mostly used to biological
molecules study, and their structure and interactions
with metals and other molecules.

Cotton effect.

The cotton effect is the characteristic change in
optical rotatory dispersion and/or circular dichroism
in the vicinity of an absorption band of a substance.
In a wavelength region where the light is absorbed,
the absolute magnitude of the optical rotation at first
varies rapidly with wavelength, crosses zero at
absorption maxima and then again varies rapidly
with wavelength but in the opposite direction. This
phenomenon was discovered in 1895 by the French
Physicist Aime cotton (1869- 1951).

It is called positive if the optical rotation first
increases as the wavelength decreases, and negative
if the rotation first decreases. A protein structure
such as a beta sheet shows a negative cotton effect.

ketones, aldehydes, carboxylic acids, esters, amides, olefines, phenylalkanes. During this reaction, γ-hydrogen will transfer to the functional group at first and then subsequent α, β bond cleavage of the intermediate will take place.

5.2   Optical rotatory dispersion (ORD)   Definition

optical rotatory dispersion is the variation in the optical rotation of a substance with a change in the wavelength of light. optical rotatory dispersion can be used to find the absolute configuration of metal complexes.

Example

When plane-polarized white light from an overhead projector is passed through a cylinder of sucrose solution, a spiral rainbow is observed perpendicular to the cylinder.

Circular dichroism (CD)   Definition.

Circular dichroism (CD) is dichroism involving circularly polarized light i.e, the differential absorption of left- and right-handed light. Left-hand circular (LHC) and right-hand- circular (RHC) polarized light represent two possible spin angular momentum states for a photon, and so circular dichroism is also referred to as dichroism for spin angular momentum.

This phenomenon was discovered by Jean-Baptiste Biot, Augustin Fresnel, and Aime cotton in the first half of the 19th century.

are given by Stevenson's Rule.

$$A - B \longrightarrow A^{\bullet} + B^{\bullet}$$

Homolysis

$$A - B \longrightarrow A^{\oplus} + B^{\ominus}$$

$$A - B \longrightarrow A^{\ominus} + B^{\oplus}$$

Heterolysis.

Major categories

i) Simple bond cleavage reactions

ii) Rearrangement reactions.

i) Simple bond cleavage reactions.

Majority of organic compounds undergo simple bond cleavage reactions, in which, direct cleavage of bond take place. Sigma bond cleavage, radical site - initiated fragmentation, and charge site - initiated fragmentation are few types of simple bond cleavage reactions.

$$\overset{\oplus}{\wedge\wedge}_{CH_3} \longrightarrow \overset{\oplus}{\wedge\wedge}_{CH_2} + \overset{\bullet}{C}H_3$$
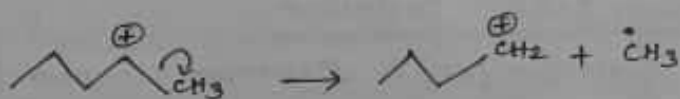
Example of sigma bond cleavage.

ii) Rearrangement reactions.

Rearrangement reactions are fragmentation reactions that form new bonds producing an intermediate structure before cleavage. One of the most studied rearrangement reaction is the Mc Lafferty rearrangement γ-hydrogen rearrangement. This occurs in the radical cations with unsaturated functional groups like

Phosphorus, Sulfur, and the halogens either have 1 an odd nominal mass that indicates an odd number of nitrogen atoms are present or 2 an even nominal mass that indicates an even number of nitrogen atoms in the molecular formula of the molecular ion.

The nitrogen rule is not a rule, per se, as much a general principle which may prove useful when attempting to solve organic mass spectrometry structures.

The nitrogen rule is only true for neutral structures in which all of the atoms in the molecule have a number of covalent bonds equal to their standard valency. Therefore, the rule is typically only applied to the molecular ion signal in the mass spectrum.

## Mass spectral fragmentation of organic compounds with respect to their structural determination.

In mass spectrometry, fragmentation is the dissociation of energetically unstable molecular ions formed from passing the molecules in the ionization chamber of a mass spectrometer. The fragments of a molecule cause a unique pattern in the mass spectrum. These reactions are well documented over the decades and fragmentation pattern is useful to determine the molar weight and structural information of the unknown molecule. Fragmentation that occurs in tandem mass spectrometry experiments has been a recent focus of research as

unit greater than the nominal mass peak are isotope peaks. The intensity of the isotope peaks relative to the intensity of the nominal mass peak can often be used in the determination of an Ion's elemental composition.

MC LAFFERTY REARRANGEMENT

The Mc lafferty rearrangement is a reaction observed in mass spectrometry during the fragmentation or dissociation of organic molecules. It is sometimes found that a molecule containing a keto-group undergoes β-cleavage, with the gain of the γ-hydrogen atom, as first reported by Nicholson working in the division of chemical physics at the CSIRO in Australia. This rearrangement may take place by a radical or ionic mechanism.

A description of the reaction was later published by the american chemist Fred Mc lafferty in 1959 leading to this name being associated with the process.
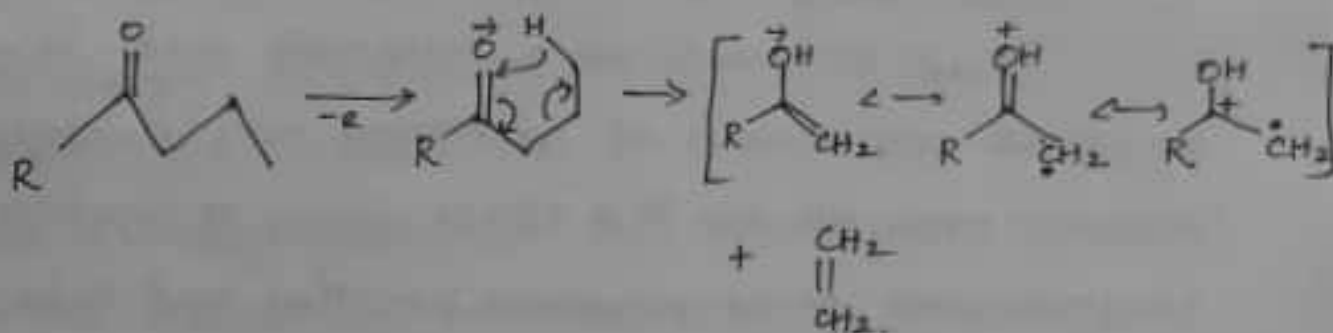
Nitrogen Rule

The nitrogen rule states that organic compounds containing exclusively hydrogen, carbon, nitrogen, silicon,

Ionizer converts a portion of the sample into ions.

→ In this technique, molecule are bombarded with a beam of energetic electrons.

⇒ The molecules are ionized and broken up into many fragments, some of which are positive ions. Each kind of which are positive ions. Each kind of ion has a particular ratio of mass to charge i,e. m/e ratio.

⇒ For most ions, the charge is one and thus, m/e ratio is simply the molecular mass of the ion.

Molecular Ion peak.

In a mass spectrum, the peak representing the molecular ion is called the molecular ion peak (symbol. M Peak). Excluding any peaks due to the presence of heavier isotopes, the molecular ion peak is the peak with the highest mass-to-charge ratio.

Meta stable peak.

Peak is known as a metastable peak. Generally, metastable peaks occur at nonintegral mass numbers, and because there usually is a kinetic energy of seperation during fragmentation of the polyatomic ion, they tend to be more diffuse than the normal mass peaks and thus are recognized easily.

Isotope peaks

The peaks representing ions that are one mass

ionization (API) technique, it is good for low to moderately polar compounds like polycyclic aromatics, Steroids, some mycotic toxins etc.

a) MALDI Technique.

Matrix-assisted laser desorption/ionization (MALDI) is a technique to allow the high molecular weight compounds such as organic macro molecules and labile biomolecular into the gas phase as intact ions. MALDI is one of the recent developments of soft ionization techniques in the field of mass spectrometry.

Principle of mass spectroscopy.

Each primary product ion derived from the molecular ion, in turn, undergoes fragmentation, and so on. The Ions are Seperated in the mass spectrometer according to their mass-to-charge ratio and are detected in proportion to their abundance. A mass spectrum of the molecule is thus produced.

A mass spectrometer generates multiple ions from the sample under investigation, It then seperates them according to their specific mass-to-charge ratio (m/z), and then records the relative abundance of each ion type.

Components.

A mass spectrometer consists of three components; an ion source, a mass analyzer, and a detector. The