

Chemistry Lecture

B.Tech First Year

Spectroscopy

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Outline

To use different spectroscopic techniques for partial evaluation of the structure of organic molecules

Introduction, UV-Vis spectroscopy: Beer Lambert's law, Types of transition

Concept of auxochrome and chromophore, factors affecting λ_{max}

Woodward-Fieser rules for calculation of λ_{max} in diene systems and numericals

✓ IR spectroscopy: Introduction, types of vibration, selection rules

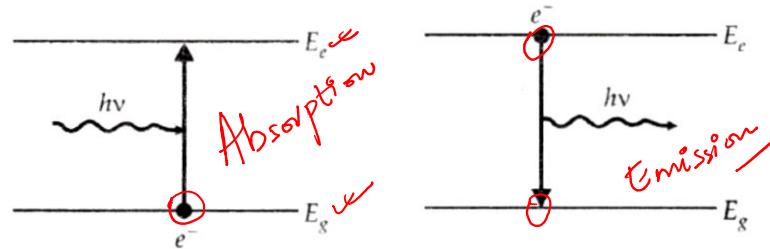
Hooke's law, identification of functional groups like C-C, C=C, -OH, -NH₂ and -C=O

Basics of NMR spectroscopy, ✓ chemical shift, Shielding and de-shielding effect

Structural elucidation of simple compounds

Introduction

Spectroscopy is the analysis of the electromagnetic radiation scattered, absorbed or emitted by molecules. It deals with the transitions that an electron in a molecule undergoes between energy levels upon absorption of suitable radiations".

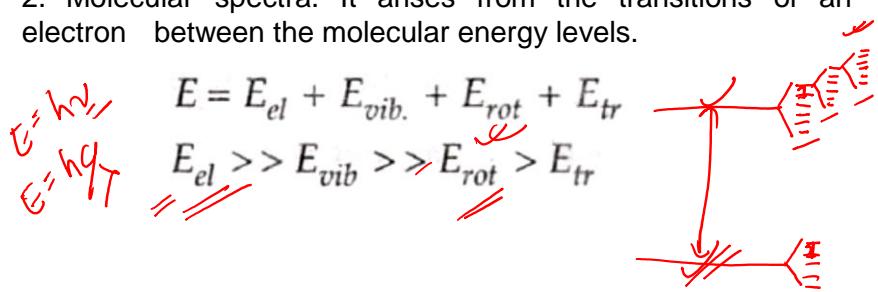


Introduction

Atomic and Molecular Spectra

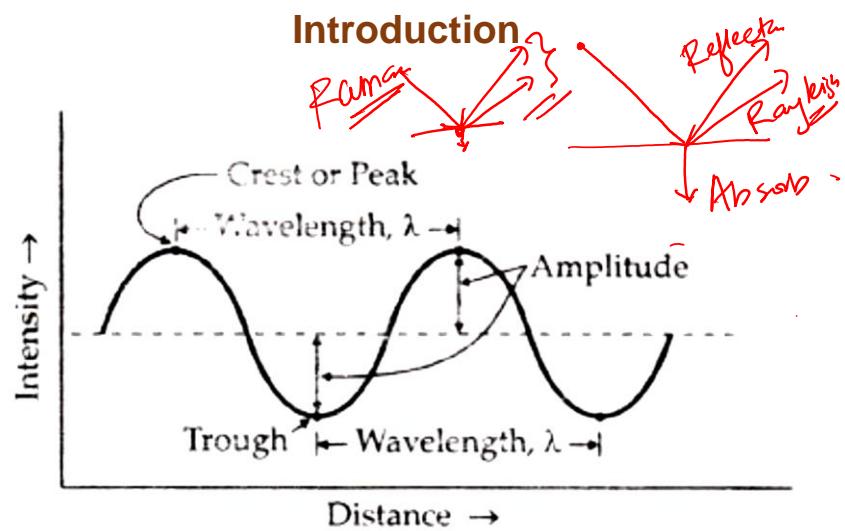
The spectra can be broadly classified into two categories :

1. Atomic spectra. It arises from the transitions of an electron between the atomic energy levels.
2. Molecular spectra. It arises from the transitions of an electron between the molecular energy levels.



Introduction

S. No.	Spectra	Transitions	Region of electromagnetic spectrum	Criteria
1.	Rotational (or microwave)	Between rotational energy levels	Microwave ($1 - 100 \text{ cm}^{-1}$)	Molecule must own permanent dipole moment e.g., HCl and H_2O
2.	Vibrational and vibrational rotational (or infrared)	Between vibrational energy levels	Infrared ($500 - 4000 \text{ cm}^{-1}$)	Dipole moment of molecule must change during vibrations.
3.	Electronic (or UV-Visible)	Between electronic energy levels	Visible ($12,500 - 25,000 \text{ cm}^{-1}$) and UV ($25,000 - 70,000 \text{ cm}^{-1}$)	Presence of chromophore in a molecule.
4.	Raman	Between vibrational and rotational levels.	Far and near infrared regions	Periodic change in polarizability due to vibrational and rotational transitions.
5.	Nuclear Magnetic Resonance (NMR)	Between magnetic energy levels of nuclei	Radio frequency	Spin quantum number of nuclei ($I > 0$)
6.	Electron Spin Resonance (ESR)	Between magnetic energy levels of unpaired electron(s)	Microwave	Presence of unpaired (or odd) electron in a molecule.



Introduction

Energy Possessed by a Wave

According to Planck's equation

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

E = energy in cal/mol

h = Planck's constant = 6.625×10^{-34} Js

ν = frequency in hertz (Hz)

λ = wavelength (in metres)

c = velocity of light = 3×10^8 m/s

UV/VIS Spectroscopy

INSTRUMENTATION OF UV/VIS AND IR SPECTROSCOPY

When radiations are passed through a transparent layer of a sample (solid, liquid, or gas), certain characteristic wavelengths are removed by the process of absorption. The absorbed energy of the electromagnetic radiations is transferred to the atoms or molecules of the sample, thereby these get excited from the ground state to the excited state. The measurement of this decrease in the intensity of radiation is the basis of spectrophotometry.

Spectrophotometer

It is an instrument used for absorption measurements. It can be made to operate in the ultraviolet, visible and infrared regions, using suitable source of radiant energy.

UV/VIS Spectroscopy

Components of Spectrophotometer

Source of Electromagnetic Radiation

Except lasers, which generates nearly monochromatic radiation, the radiation source generally produces radiation spanning a range of frequencies.

Spectroscopy	UV	Visible
Source	Hydrogen discharge lamp	Tungsten filament lamp
Sample Form	Gas or dilute solution	Gas or dilute solution

UV/VIS Spectroscopy

Components of Spectrophotometer

Wavelength Controller

For separating the frequencies of the radiation so that the variation of the absorption with frequency can be monitored, spectrometers either include a glass (or quartz) prism or a diffraction grating. This component is a dispersing element, which separates different frequencies into different spatial directions.

Sample Holder

It can be (a) test-tube (known as cuvette) in calorimetry, (b) quartz cell in UV and visible spectroscopy

UV/VIS Spectroscopy

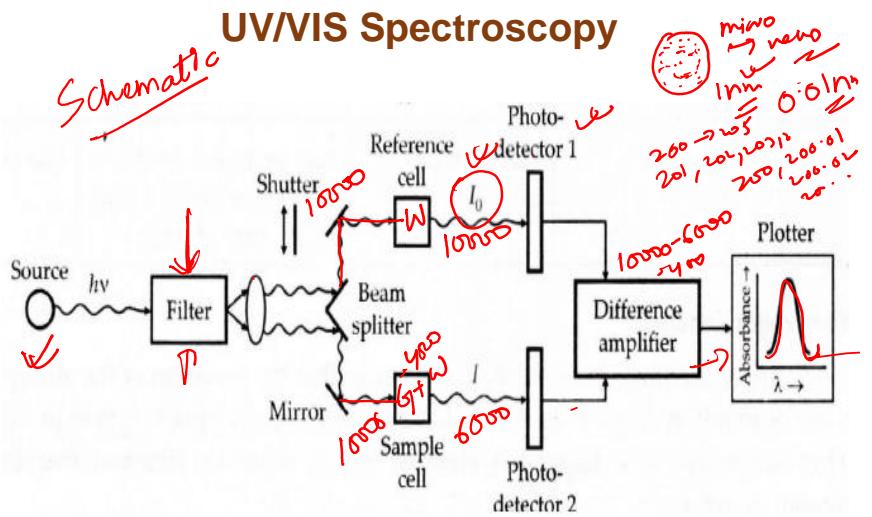
Components of Spectrophotometer

Photodetector and Receptor Unit

This unit detects and converts radiant energy into measurable electrical signal.

Amplification and Recording Unit

The radiation from a detector is chopped by a shutter that rotates in the beam so that an alternating signal is obtained from the detector. This is because an oscillating signal is easier to amplify than a steady signal.



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UV/VIS Spectroscopy

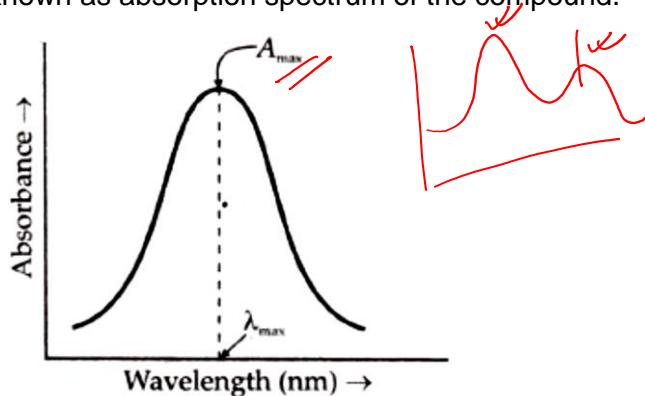


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UV/VIS Spectroscopy

Absorption Spectrum and λ_{max}

The curve showing the variation of absorbance (A) with wavelength for a given concentration of solution and thickness of the cell is known as absorption spectrum of the compound.



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UV/VIS Spectroscopy



Principle

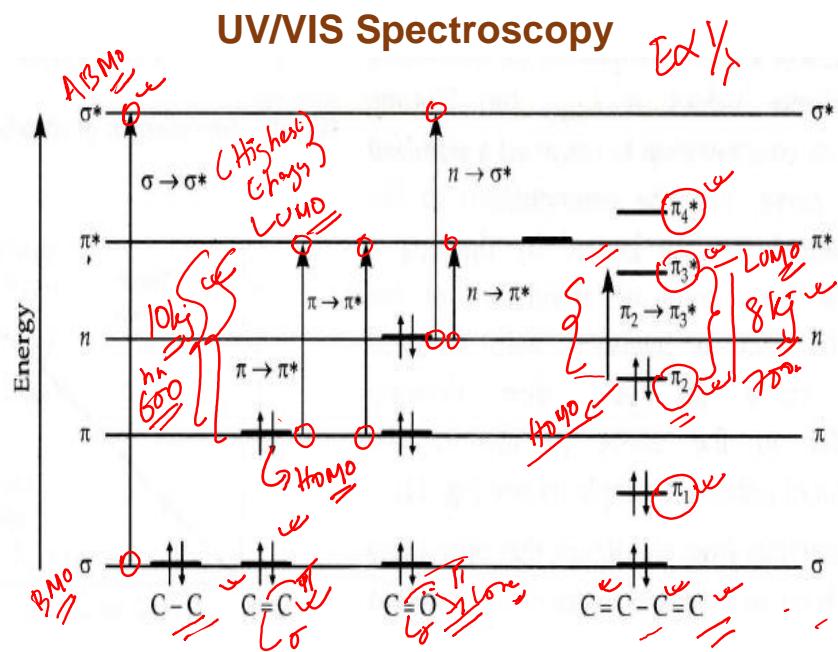
"It involves the transitions of electron(s) within a molecule or ion from a lower to a higher electronic energy level or vice-versa by the absorption or emission of radiations falling in the UV-visible range of electromagnetic spectrum."

$\sigma \rightarrow \sigma^*$ Transition. As σ electrons are held more firmly in the molecule, this transition takes place in UV or far UV region.

$\pi \rightarrow \pi^*$ Transition. This transition takes place in the near UV and visible regions.

$n \rightarrow \pi^*$ Transition. These transitions are generally of weak intensities and lie in the visible region.

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UV/VIS Spectroscopy

Alkanes	$\sigma \rightarrow \sigma^*$
Alkenes (simple)	$\pi \rightarrow \pi^*$
Saturated aliphatic ketones	$n \rightarrow \pi^*$
Conjugated dienes	$\pi \rightarrow \pi^*$

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UV/VIS Spectroscopy

Electronic Transition	Position of band and Remarks
$\sigma \rightarrow \sigma^*$	(~ 150 nm) (Requires high energy, which do not lie in UV region)
$\pi \rightarrow \pi^*$	(170 – 190 nm)
$n \rightarrow \pi^*$	(~ 280 nm) (Forbidden and hence of low intensity)
$n \rightarrow \sigma^*$	(~ 185 nm) (Allowed and hence of high intensity)
$\pi \rightarrow \pi^*$	(~ 160 nm) (Allowed and hence of high intensity)
$\pi \rightarrow \pi^*$	(~ 217 nm) (Transition is of very low energy and is due to conjugation.)

UV/VIS Spectroscopy

Chromophores and Auxochromes

Chromophore is defined as any isolated covalently bonded group that shows a characteristic absorption in the UV or the visible region. irrespective of the fact whether colour is produced or not.

Auxochromes
yellow → Bright yellow

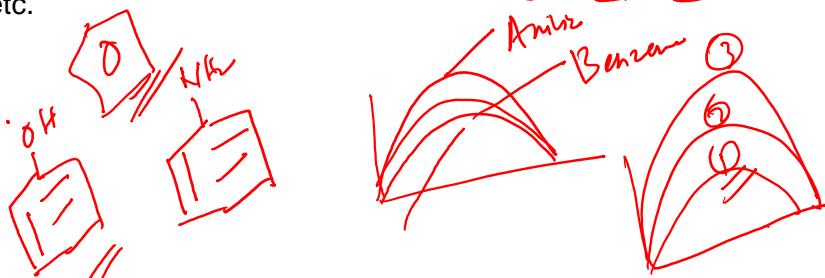
Types of Chromophores

- Chromophores, which contain π - electrons and undergo $\pi \rightarrow \pi^*$ transition. For example, ethylenes and acetylenes.
- Chromophores, which contain both π and n electrons and undergo $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. For example, carbonyls and nitriles.

UV/VIS Spectroscopy

Auxochrome is basically a colour enhancing group. It has the ability to extend the conjugation of the chromophore by the sharing of the non-bonding electrons and thus shifts the absorption band towards the longer wavelength (the red end of the spectrum). Auxochrome by itself does not act as chromophore.

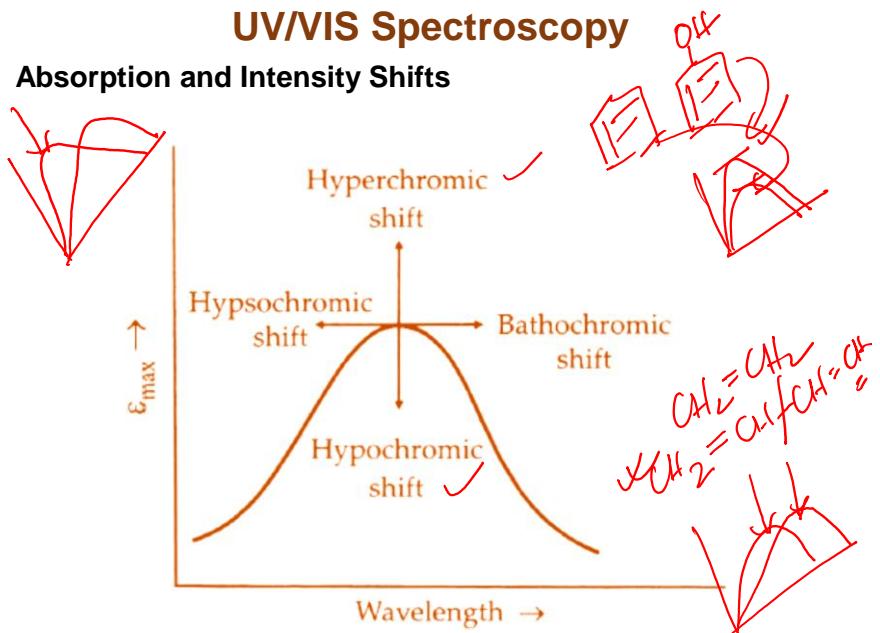
Some common auxochrome groups are - OH, -OR, - NH₂, - SH etc.



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UV/VIS Spectroscopy

Absorption and Intensity Shifts



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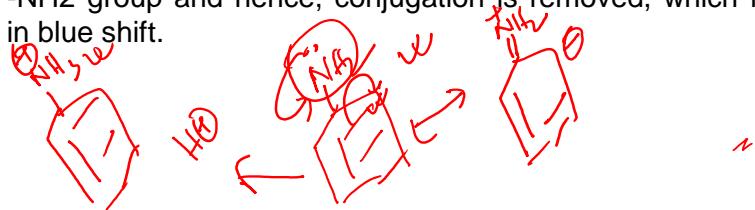
UV/VIS Spectroscopy

Hypsochromic Shift (or Effect)

It leads to the shift of absorption maximum towards shorter wavelength. It is also known as blue shift and is due to either the removal of conjugation or change in polarity of the solvent.

For example,

Absorption maximum of aniline shifts from 280 nm to 200 nm in acidic solutions, which results in the formation of $C_6H_5NH_3^+$ from $C_6H_5NH_2$. Obviously, the lone pair is no longer present on $-NH_2$ group and hence, conjugation is removed, which results in blue shift.



UV/VIS Spectroscopy

Bathochromic Shift (or Effect)

It leads to the shift of absorption maximum towards longer wavelength due to the presence of auxochrome. It is also known as red shift. It can also result by the change of solvent.

For example, the $n \rightarrow \pi^*$ transition for carbonyl compounds experience bathochromic shift when the polarity of the solvent is lowered.

Hyperchromic Effect (or Shift)

It leads to the increased intensity of absorption.

Hypochromic Effect (or Shift)

It leads to the decreased intensity of absorption.

Assignment

How can one distinguish whether a carbonyl group is part of aldehyde, ketone or ester from UV spectroscopy ?

UV/VIS Spectroscopy

Factors Affecting " λ -max and Intensity of Spectral Lines

The shape and intensity of UV/VIS absorption bands are affected by :

- (i) The electronic structure of the absorbing species, ✓
- (ii) The presence of substituents,
- (iii) The polarity of the solvent,
- (iv) The steric hindrance.

UV/VIS Spectroscopy

Woodward-Fieser Rules for Prediction of λ -max

1. First identify a principal parent chromophore system. It can be either conjugated diene or monosubstituted benzene ring or disubstituted benzene ring or conjugated carbonyl system.
2. Assign an absorption maximum value to this parent system.
3. Identify the presence of other systems (or substituents) within the parent system.
4. From the empirical rules, find how much absorption maximum shift to longer wavelength due to the presence of substituents.
5. Predict λ -max by adding up all the above values.

UV/VIS Spectroscopy

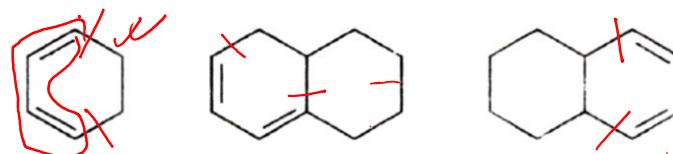
Conjugated Diene Systems ($C = C - C = C$)

	$\lambda\text{-max}$ (nm)
Base value of conjugated parent diene :	
Acyclic or heteroannular ($C = C-C = C$)	215
Homoannular diene	253
Increment for each :	
Double bond extension to diene system	30
Diene system within a ring	36
Exocyclic nature of double bond in conjugated system	5
Each alkyl substituent or ring residue	5

UV/VIS Spectroscopy

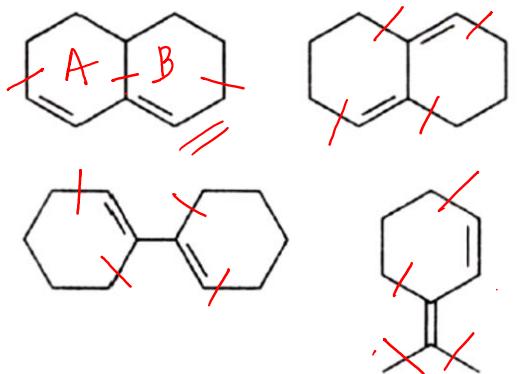
Auxochrome is

-Cl,-Br	5
-OR (alkoxy)	6
- SR(alkylthio)	30
-NR ₂ (dialkylamine)	60



Homoannular conjugated double bonds.
Conjugated double bonds present in the same ring.

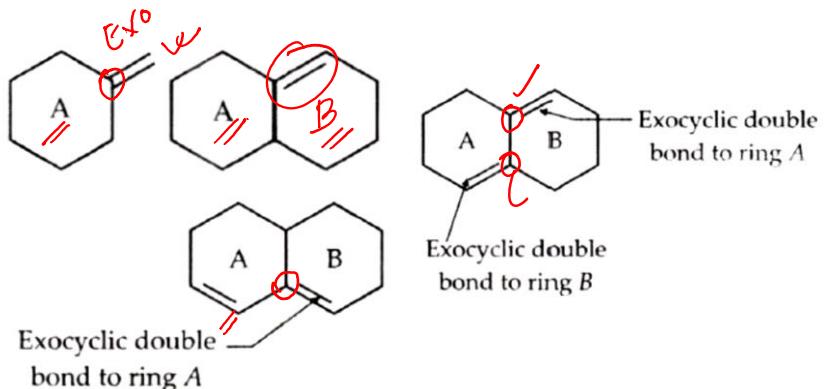
UV/VIS Spectroscopy



Heteroannular conjugated double bonds.
Conjugated double bonds which are not present in the same ring.

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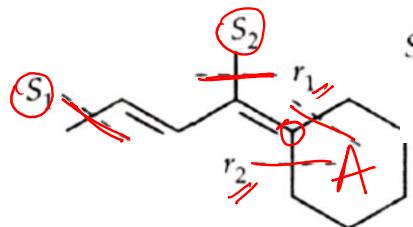
UV/VIS Spectroscopy



Exocyclic and Endocyclic double bonds. The carbon-carbon double bond projecting outside the ring is known as exocyclic.

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UV/VIS Spectroscopy



S_1 and S_2 = Alkyl substituents
 r_1 and r_2 = Ring substituents

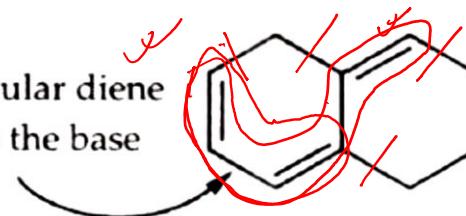
Acyclic diene
 Ring Residue $\times 2 \times 5$ 10
 Alkyl Resid $\times 2 \times 5$ 10
 Σ 235

Alkyl substituents and ring residues. Only the alkyl substituents and ring residues attached to the carbon atoms constituting the conjugated system are taken into account.

$E \propto I^0$

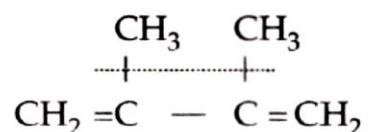
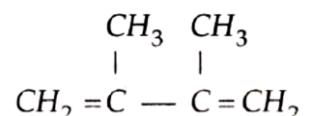
UV/VIS Spectroscopy

Homoannular diene becomes the base



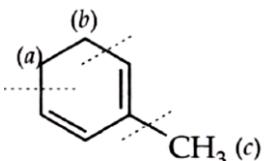
When both types of diene (viz. homo-as well as hetero-annular dienes) are present.

UV/VIS Spectroscopy



Diene	215 nm
Alkyl substituents (2×5)	10 nm
Predicted λ_{\max}	225 nm

UV/VIS Spectroscopy

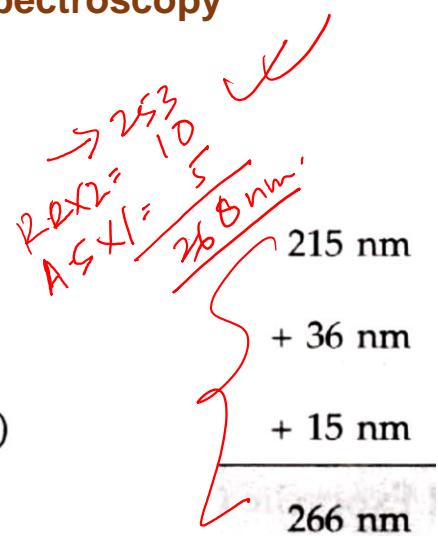


Diene

Within a ring

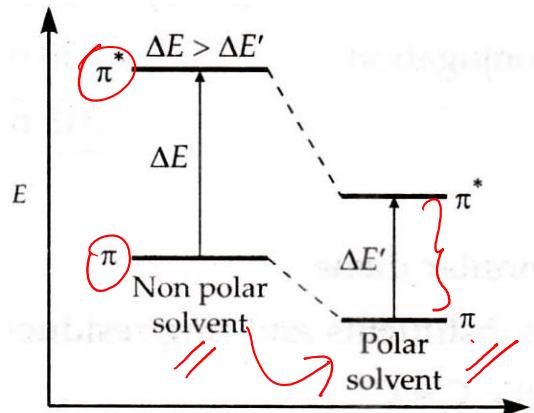
Alkyl substituents (3×5)

Predicted λ_{\max}



UV/VIS Spectroscopy

Effect of Solvents



A molecule that absorbs radiation due to a $\pi \rightarrow \pi^*$ transition exhibits a shift in the absorption maximum to a longer wavelength when the molecule is dissolved in a polar solvent compared to a non-polar solvent.

IR Spectroscopy

Vibrational spectroscopy involves the transitions between the vibrational energy levels of a molecule on the absorption of radiations falling in the spectral range of 500 cm^{-1} - $4,000\text{ cm}^{-1}$ (infra-red region)

It is to be noted that the infrared region is divided into following regions :

- (i) **Near-infrared region.** It refers to that part of the IR spectrum that is closest to the visible light (400 nm -700 nm).
- (ii) **Far-infrared region.** It refers to that part of the IR spectrum that is closest to the microwave region (3 mm- 30 cm).
- (iii) **Mid-infrared region.** It is the region between near and far infrared regions

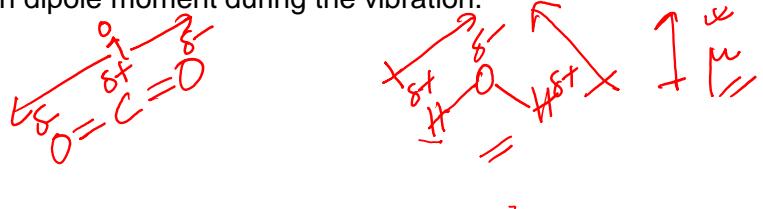
Thus, infrared waves have wavelengths longer than visible and shorter than microwaves.

IR Spectroscopy

Mechanism of Interaction between the Vibrating Molecule with Infrared Radiations

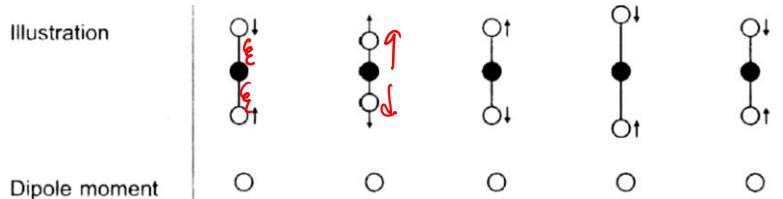
Infrared inactive molecules do not show vibrational spectra. For example, any molecule which either do not have permanent dipole moment or there occurs no change in dipole moment during vibration (O_2 , H_2 , N_2 etc.).

Infrared active molecules are those molecules, which do have a permanent dipole moment and hence, exhibit a change in dipole moment during the vibration.

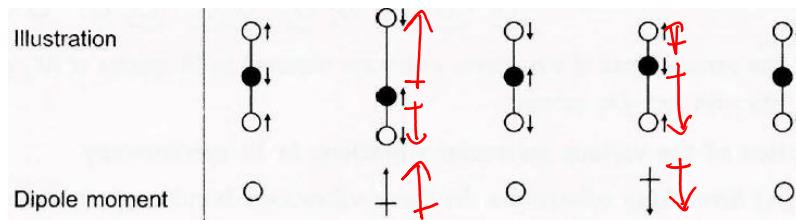


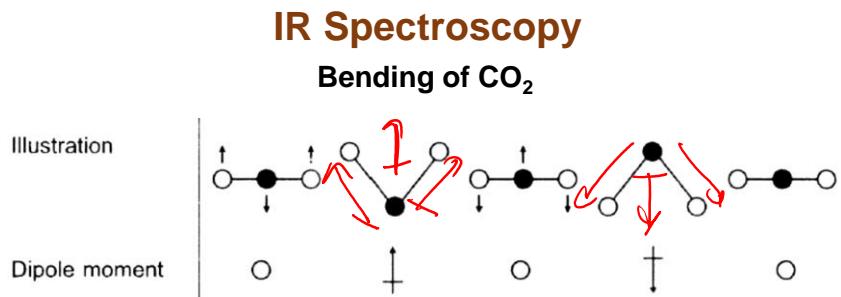
IR Spectroscopy

Symmetrical stretching of CO_2



Asymmetrical stretching of CO_2

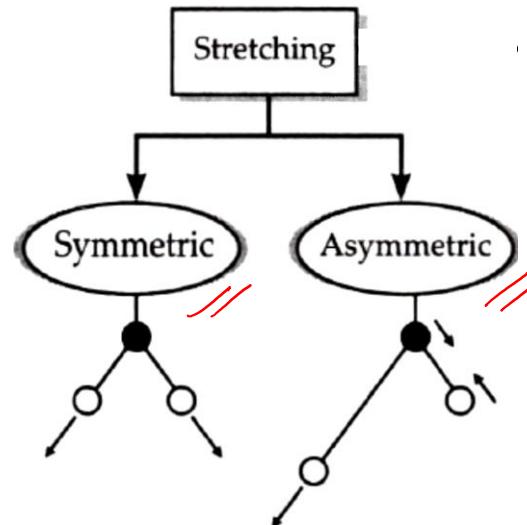




Thus, the essential condition for a molecule to show vibrational spectrum is that it must show a change in dipole moment during vibration.

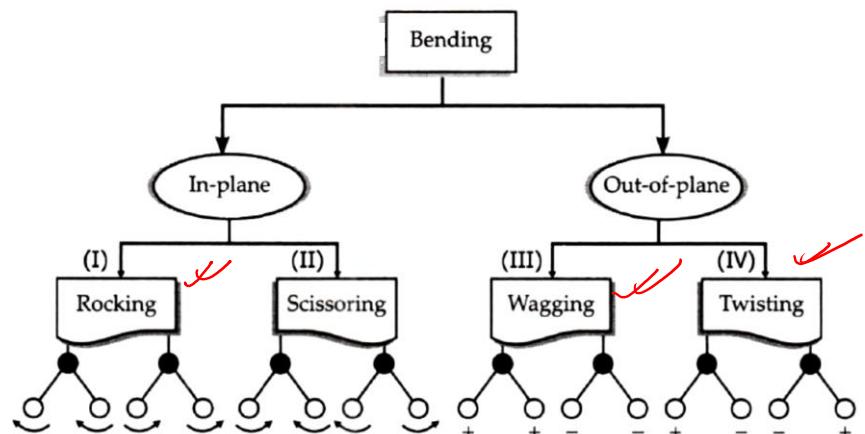
IR Spectroscopy

Fundamental Modes of Vibrations and Types



IR Spectroscopy

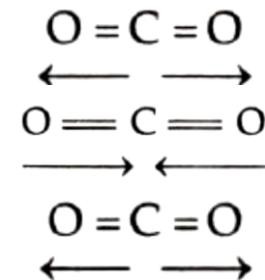
Fundamental Modes of Vibrations and Types



All these vibrations, which are accompanied with fluctuating dipole give rise to absorption bands in IR-Spectra. These vibrations are also known as fundamental vibrations.

IR Spectroscopy

Symmetric stretching vibrations.



These vibrations involve alternate stretching and compression of bonds in symmetrical manner.

IR Spectroscopy

Asymmetric stretching vibrations



These vibrations involve alternate stretching and compression of bonds in symmetrical manner.

All these vibrations, which are accompanied with fluctuating dipole (and thus a fluctuating electric field) give rise to absorption bands in IR-Spectra and are known as **fundamental vibrations**.

IR Spectroscopy

Utilisation

IR spectroscopy is an invaluable tool in organic structure determination and verification. It uses infrared (IR) radiation with frequencies between 4000 cm^{-1} and 400 cm^{-1} (wave numbers). IR radiations can be utilized in organic structure determination by making use of the fact that it is absorbed by interatomic bonds in organic compounds. Chemical bonds in different environments will absorb varying intensities and at varying frequencies.

IR Spectroscopy

Regions of IR Spectra

Functional group region.

It is the high frequency region, between 4000 cm^{-1} - 1300 cm^{-1} . This is because the characteristic stretching frequencies for important functional groups such as C=O, OH and NH occur in this region.

Fingerprint region. It is the middle frequency region, between 1300 cm^{-1} - 900 cm^{-1} . In this region, complex absorptions occur due to combinations of interacting vibrational modes, providing a unique fingerprint for every molecule. The pattern of bands in this region are dependent on the structure of the molecule and is very sensitive and changes even on minor changes in structure and stereochemistry.

IR Spectroscopy

Vibrational Frequency

A simple harmonic oscillator can be considered as a model for a vibrating diatomic molecule. The vibrational energy (E_{vib}) is thus given by

$$E_{vib} = \left(v + \frac{1}{2} \right) h\nu_0 \quad \text{Eqn.1}$$

where

v is the vibration quantum number and has the values of 0, 1, 2, ..,
 ν_0 is the fundamental vibrational frequency.

IR Spectroscopy

Vibrational Frequency

The fundamental vibrational frequency (v_0) of a molecule behaving like a simple harmonic oscillator is given by following equation

$$v_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{Eqn.2}$$

Force constant
R.M

where k is the force constant (which relates with the strength of the bond) and

μ is the reduced mass of a diatomic molecule.

IR Spectroscopy

The fundamental vibration frequency of CO is 2140 cm^{-1} . Calculate the force constant of the molecule. Given the atomic masses : $12 \text{ C} = 19.9 \times 10^{-27} \text{ kg}$ and $16 \text{ O} = 26.6 \times 10^{-27} \text{ kg}$.

Solution:

The reduced mass of CO

$$\mu = \frac{m_c m_o}{m_c + m_o}$$

$$\mu = \frac{(19.9 \times 10^{-27}) \times (26.6 \times 10^{-27})}{(19.9 + 26.6) \times 10^{-27}} = 1.14 \times 10^{-26} \text{ kg}$$

IR Spectroscopy

The fundamental vibration frequency of CO is 2140 cm^{-1} . Calculate the force constant of the molecule. Given the atomic masses : $12 \text{ C} = 19.9 \times 10^{-27} \text{ kg}$ and $16 \text{ O} = 26.6 \times 10^{-27} \text{ kg}$.

Solution:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$



IR Spectroscopy

The fundamental vibration frequency of CO is 2140 cm^{-1} . Calculate the force constant of the molecule. Given the atomic masses : $12 \text{ C} = 19.9 \times 10^{-27} \text{ kg}$ and $16 \text{ O} = 26.6 \times 10^{-27} \text{ kg}$.

Solution:

$$k = 4\pi^2 c^2 (\nu)^2 \mu$$

$$= 4(3.14)^2 (3 \times 10^{10})^2 (2140)^2 (1.14 \times 10^{-26})$$

$$= 1853 = 1853 \frac{\text{N}}{\text{m}}$$

$\cancel{1853}$

IR Spectroscopy

Calculate the force constant of the bond between H and Br using absorption maximum = $3.77 \mu\text{m}$, velocity of light = $3 \times 10^8 \text{ ms}^{-1}$, masses of H and Br atoms = 1.008 and 79.9 amu respectively.

Calculate the force constant for HCl^{35} when its fundamental vibrational frequency is $8.667 \times 10^{13} \text{ per sec}$. How does the force constant of HCl^{37} compare with it ?

IR Spectroscopy

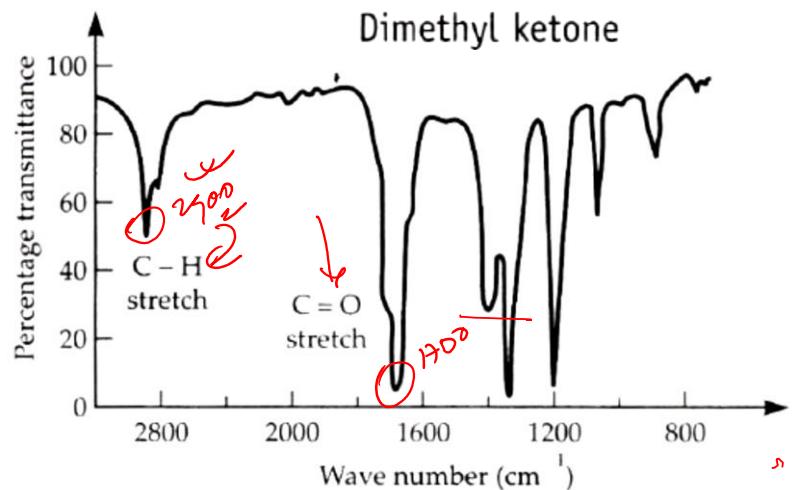
$\Sigma = 1/2$

Identification of Functional Groups in Organic Molecules

Functional Group	Frequency Range
$\text{C}=\text{O}$ stretching vibration of	
(i) Saturated ketones	$1705 - 1725 \text{ cm}^{-1}$
(ii) Unsaturated ketones	$1665 - 1685 \text{ cm}^{-1}$
Alcohol	
(i) O – H stretching	$3650 - 3590 \text{ cm}^{-1}$
(ii) O – H bending	$1150 - 1050 \text{ cm}^{-1}$

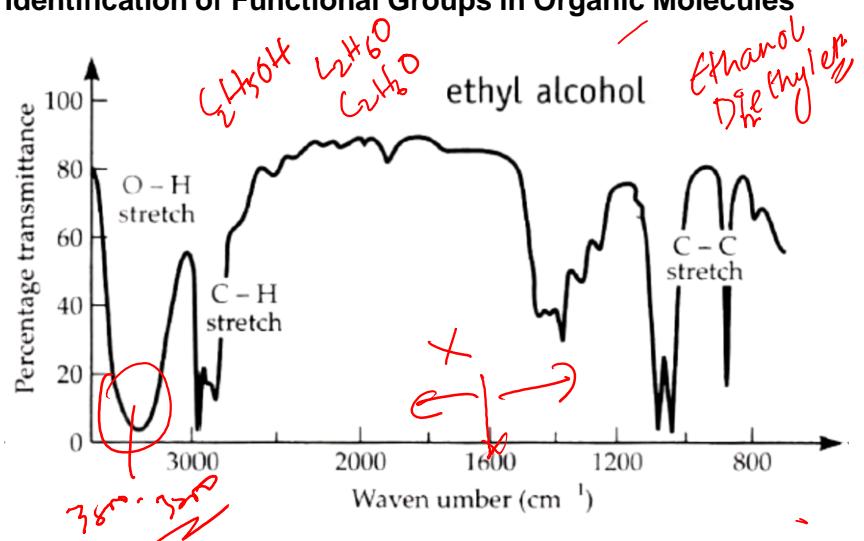
IR Spectroscopy

Identification of Functional Groups in Organic Molecules



IR Spectroscopy

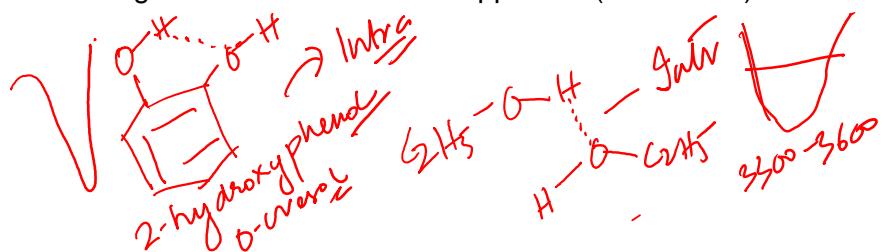
Identification of Functional Groups in Organic Molecules



IR Spectroscopy

To Distinguish Between Intra and Inter Molecular Hydrogen Bonding

It can be done by taking a series of IR spectra of the compound at different concentrations. As the concentration is increased, the absorption band, due to intermolecular hydrogen bonding increases, while ~~& at~~ due to **intramolecular hydrogen bonding remains unchanged**. It is to be noted that O-H stretching for H- bonded alcohols appear at (3200-3550).



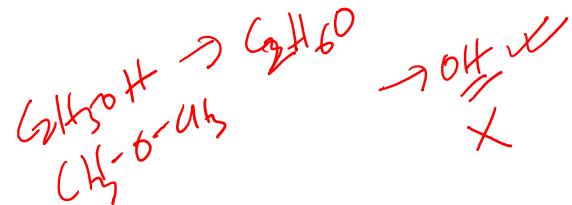
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IR Spectroscopy

How will you distinguish between ethyl alcohol and dimethyl ether on the basis of IR spectroscopy ?

Ethyl alcohol (CH₃CH₂OH) will show strong and broad O-H stretching band at (3200 -3600) cm⁻¹ region. Dimethyl ether (CH₃OCH₃) has no O-H group, thus, it will not show this band.

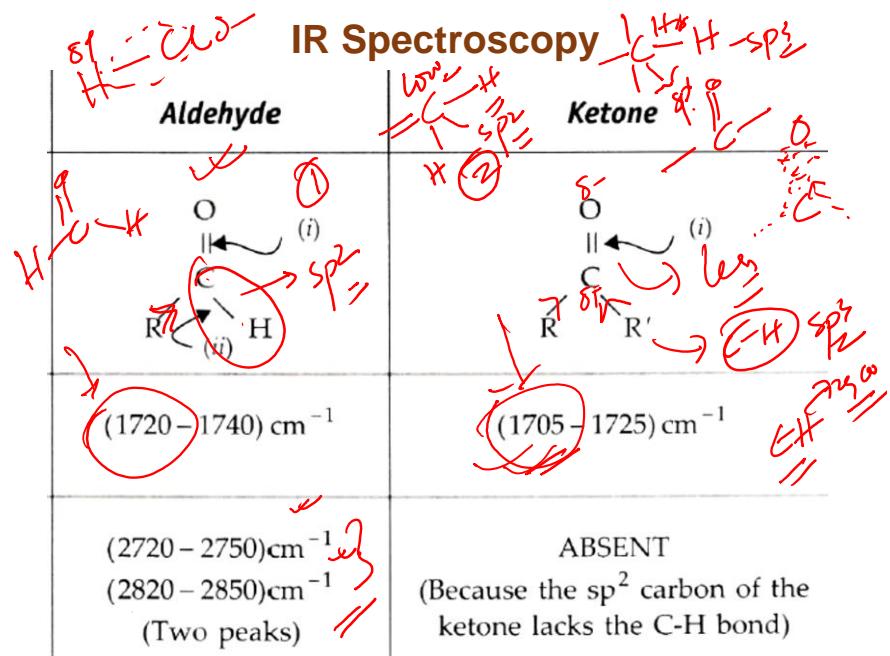
How will you distinguish the following by IR spectroscopy :

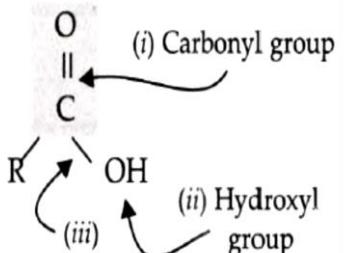
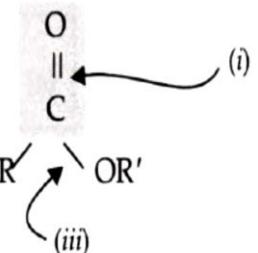


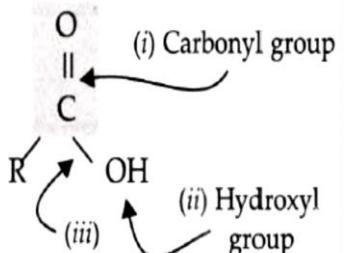
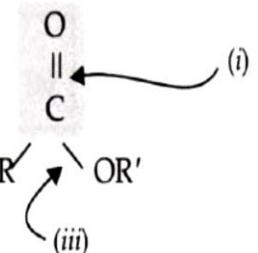
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IR Spectroscopy

How do IR spectra help in differentiating the following compounds ? (a) Aldehyde and ketone (b) Carboxylic acid and ester.



IR Spectroscopy <i>BODV</i>	
 <p>(i) Carbonyl group (ii) Hydroxyl group (iii)</p>	 <p>(i) (iii)</p>
(1700 – 1725) cm^{-1}	(1735 – 1745) cm^{-1}
(2500 – 3300) cm^{-1} (broad)	Absent

IR Spectroscopy	
 <p>(i) Carbonyl group (ii) Hydroxyl group (iii)</p>	 <p>(i) (iii)</p>
(1700 – 1725) cm^{-1}	(1735 – 1745) cm^{-1}
(2500 – 3300) cm^{-1} (broad)	Absent

NMR Spectroscopy

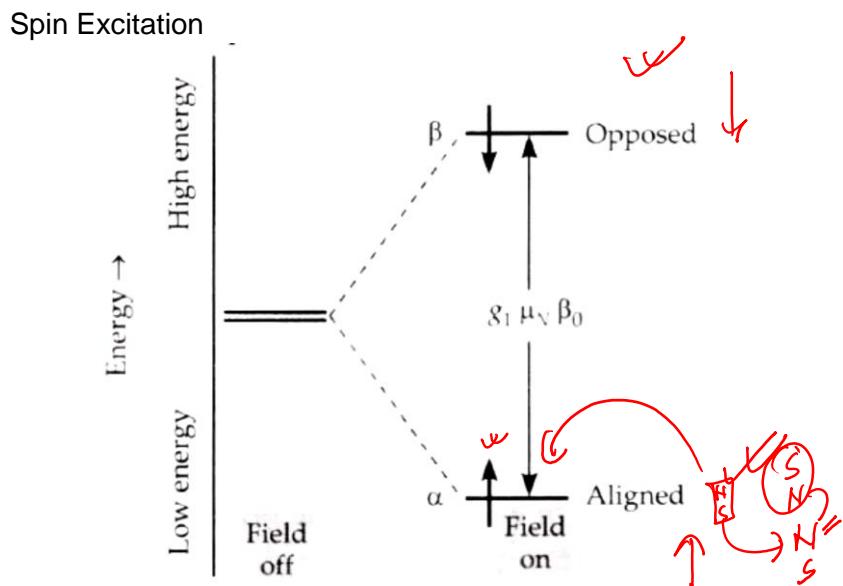
Nuclear magnetic resonance (NMR) is a branch of spectroscopy in which radio frequency waves induce transitions between magnetic energy levels of nuclei of a molecule. The magnetic energy levels are created by keeping the nuclei in a magnetic field.

The nuclei with spin quantum number (I) greater than zero can exhibit the NMR phenomenon.

For example, proton has $I = 1/2$, so it can exhibit NMR commonly known as Proton Magnetic Resonance (PMR).

The energies of nuclei in magnetic fields. The orientation of a proton is determined by the value of quantum number m ($= +1/2$ and $-1/2$), and in a magnetic field B_0 , these orientations of the nucleus have different energies

NMR Spectroscopy



NMR Spectroscopy

Theory of NMR

Quantum Description

Nuclear Spin (think electron spin)

- Nucleus rotates about its axis (spin)
- Nuclei with spin have angular momentum (p) or spin

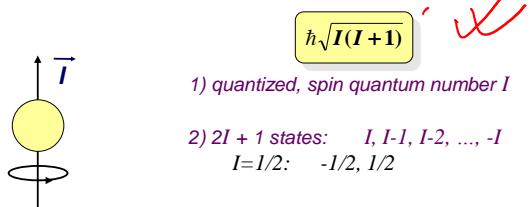
1) total magnitude

$$\hbar\sqrt{I(I+1)}$$

1) quantized, spin quantum number I

2) $2I + 1$ states: $I, I-1, I-2, \dots, -I$
 $I=1/2: -1/2, 1/2$

3) identical energies in absence of external magnetic field





NMR Spectroscopy

NMR Periodic Table

NMR "active" Nuclear Spin (I)

$I = 1/2$: $^1\text{H}, ^{13}\text{C}, ^{15}\text{N}, ^{19}\text{F}, ^{31}\text{P}$
 biological and chemical relevance

Odd atomic mass

$I = +1/2 \text{ & } -1/2$

NMR "inactive" Nuclear Spin

($I = 0$):

$^{12}\text{C}, ^{16}\text{O}$

Even atomic mass & number

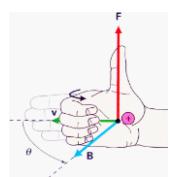
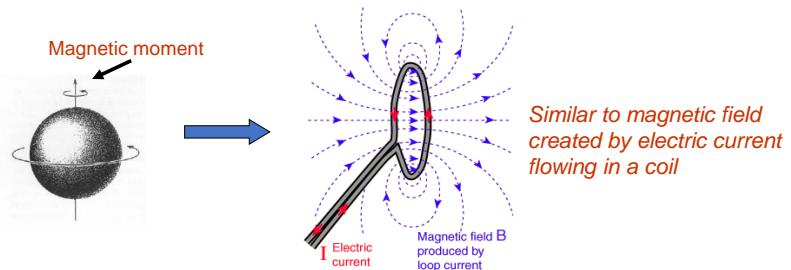
Table 1.1 Nuclear properties of some of the elements

Element	Atomic mass	Spin I	Natural abundance (%)	Receptivity ($^6\text{C} = 1.00$)	Quadrupole moment (10^{30} m^2)	Resonant frequency (MHz) at 2.348 GHz
Hydrogen	1	1/2	99.985	5670	None	100.00
Deuterium	2	1	0.015	0.0082	0.287	15.35
Tritium	3	1/2	Radioactive	None	None	106.66
Li	7	1/2	99.9994	0.0035	None	76.18
Lithium	6	1	7.42	3.58	-0.064	14.72
Lithium	7	3/2	92.58	1540	-3.7	38.87
Beryllium	9	3/2	100	20.3	2.3	15.06
Boron	10	3	19.58	22.5	7.4	10.75
Boron	11	3/2	80.42	754	4.1	32.08
Carbon	12	1/2	99.108	1.00	None	25.15
Nitrogen	14	1	99.63	5.70	1.67	7.23
Nitrogen	15	1/2	0.37	0.02	None	10.14
Oxygen	16	1/2	0.037	0.061	-2.6	13.56
Fluorine	19	1/2	100	4730	None	94.09
Neon	21	3/2	0.257	0.0036	9	7.90
Sodium	23	3/2	100	524	10	26.43
Magnesium	25	5/2	10.13	1.54	22	6.13
Aluminum	27	5/2	100	1170	14	26.08
Silicon	29	1/2	4.7	2.1	None	19.87
Phosphorus	31	1/2	100	377	None	40.48
Sulfur	32	3/2	99.76	0.998	-4.4	7.67
Chlorine	35(37)	3/2	75.53	20.29	-8.2	9.81
Potassium	39	3/2	93.1	2.69	4.67	13.51
Calcium	40	7/2	0.145	0.053	5	6.71
Sodium	45	7/2	100	1720	-22	24.33
Titanium	49(47)	7/2	5.51	1.18	24	5.64
Vanadium	51(50)	7/2	99.76	2170	-5.2	26.35
Chromium	53	3/2	9.55	0.09	-15	5.64
Manganese	55	5/2	100	1014	40	24.84
Iron	57	1/2	2.19	0.00425	None	3.24
Cobalt	59	7/2	100	1560	42	23.77
Nickel	61	3/2	1.19	0.24	16	8.93
Copper	63(65)	3/2	69.09	368	-22	26.51
Zinc	67	5/2	4.11	0.67	15	6.51
Gallium	71(69)	3/2	39.6	32	-11	30.58
Germanium	73	9/2	7.76	0.62	-17	3.48
Arsenic	75	3/2	100	144	29	17.18
Selenium	77	1/2	12.59	3.02	None	19.07
Bromine	81(79)	3/2	49.46	279	27	27.10
Krypton	83	9/2	11.55	1.24	27	3.86
Rubidium	87(85)	3/2	27.85	280	13	32.98
Sr	87	9/2	7.02	1.08	1.6	4.35
Yttrium	89	1/2	100	0.676	None	4.92
Zirconium	91	5/2	11.23	6.05	-21	3.34
Niobium	93	9/2	100	270	-32	24.55
Molybdenum	95(97)	5/2	15.72	2.92	-1.5	6.55
Technetium	99	9/2	—	—	-0.13	22.51
Ruthenium	99(101)	5/2	12.72	0.815	7.6	4.61
Rhodium	103	1/2	100	0.18	None	3.16
Palladium	105	5/2	22.23	1.43	65	4.58
Silver	109(107)	1/2	48.18	0.28	None	4.65
Cadmium	113(111)	1/2	12.26	7.69	None	22.18

NMR Spectroscopy

Magnetic Moment (μ)

- spinning charged nucleus creates a magnetic field



"Right Hand Rule"

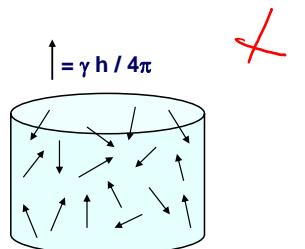
- determines the direction of the magnetic field around a current-carrying wire and vice-versa

$$\vec{F} = q\vec{v} \times \vec{B}$$

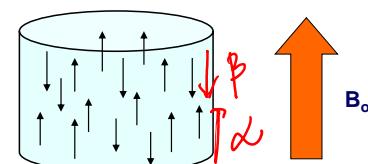
Positive test charge q

NMR Spectroscopy

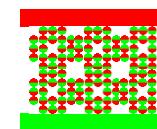
Magnetic alignment



In the absence of external field, each nuclei is energetically degenerate



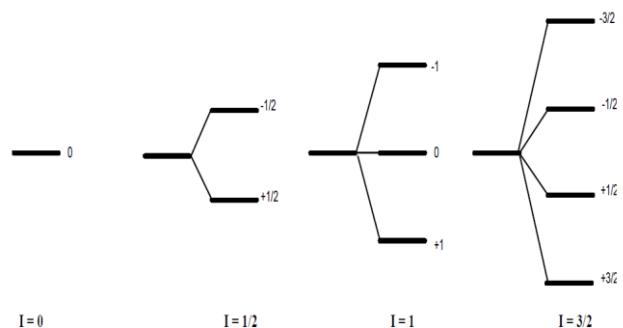
Add a strong external field (B_0) and the nuclear magnetic moment: aligns with (low energy) against (high-energy)



NMR Spectroscopy

Spins Orientation in a Magnetic Field (Energy Levels)

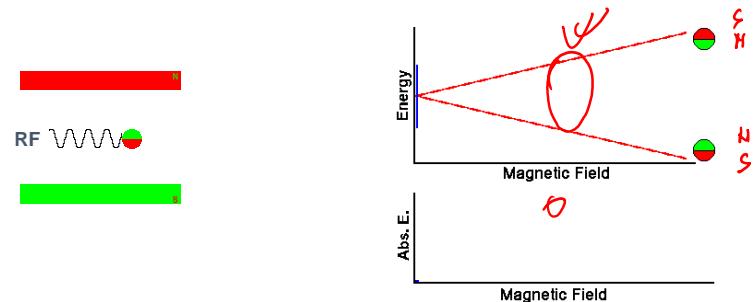
- The energy levels are more complicated for $I > 1/2$



NMR Spectroscopy

Spins Orientation in a Magnetic Field (Energy Levels)

- Transition from the low energy to high energy spin state occurs through an absorption of a photon of radio-frequency (RF) energy

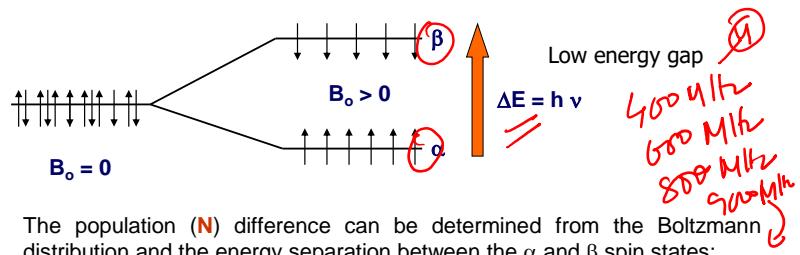


Frequency of absorption: $v = \gamma B_0 / 2\pi$

NMR Spectroscopy

NMR Signal (sensitivity)

- The applied magnetic field causes an energy difference between the aligned (α) and unaligned (β) nuclei
- NMR signal results from the transition of spins from the α to β state
- Strength of the signal depends on the population difference between the α and β spin states



- The population (N) difference can be determined from the Boltzmann distribution and the energy separation between the α and β spin states:

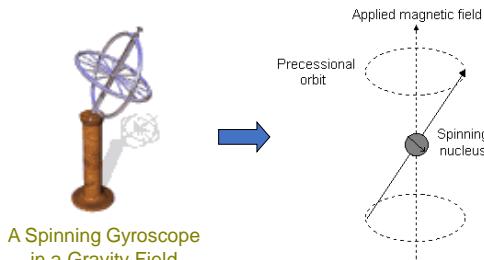
$$N_\alpha / N_\beta = e^{\Delta E / kT}$$

NMR Spectroscopy

Theory of NMR

Classical Description

- Spinning particle precesses around an applied magnetic field



NMR Spectroscopy

The Absorption of Radiation by a Nucleus in a Magnetic Field

When a proton is precessing in the aligned orientations, it has low energy. When it is irradiated with a beam of correct frequency from radio-frequency source, it will absorb the energy, provided precessing frequency is the same as the frequency of the radio-frequency beam (when this occurs, the radio frequency beam and the nucleus are in resonance, that's why it is known as *nuclear magnetic resonance*).

Suppose v is the frequency of radiation which comes into resonance with proton, then resonance condition is

$$v = \gamma \frac{B_0}{2\pi}$$

NMR Spectroscopy

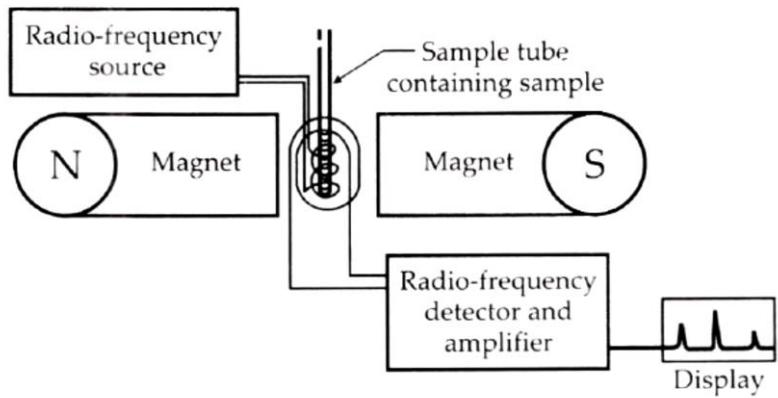
Where:

$$\gamma = \text{gyromagnetic ratio} = \frac{\text{nuclear magnetic moment (m)}}{\text{Nuclear angular momentum (I)}}$$

$\frac{\gamma B_0}{2\pi}$ is also known as **Larmor frequency**, v_L .

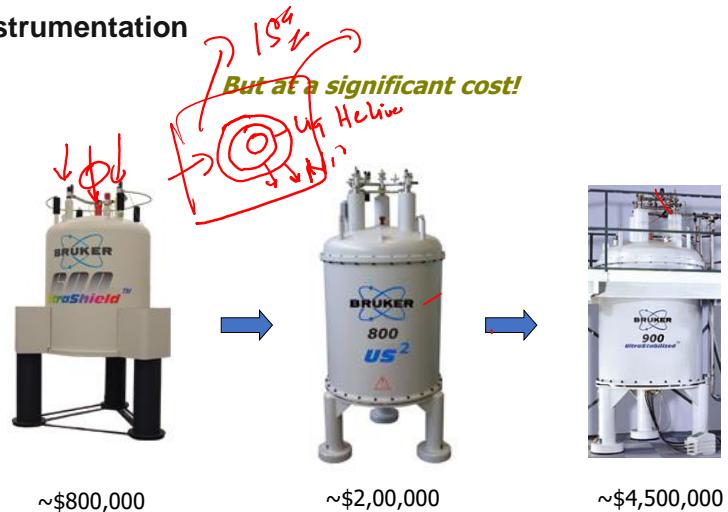
NMR Spectroscopy

Instrumentation



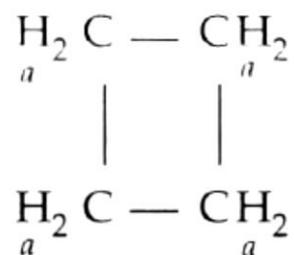
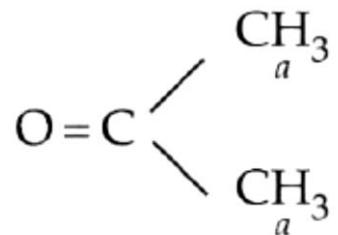
NMR Spectroscopy

Instrumentation



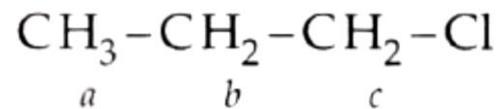
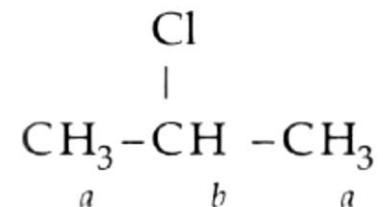
NMR Spectroscopy

NUMBER OF SIGNALS- Equivalent and Non-Equivalent Protons



NMR Spectroscopy

NUMBER OF SIGNALS- Equivalent and Non-Equivalent Protons



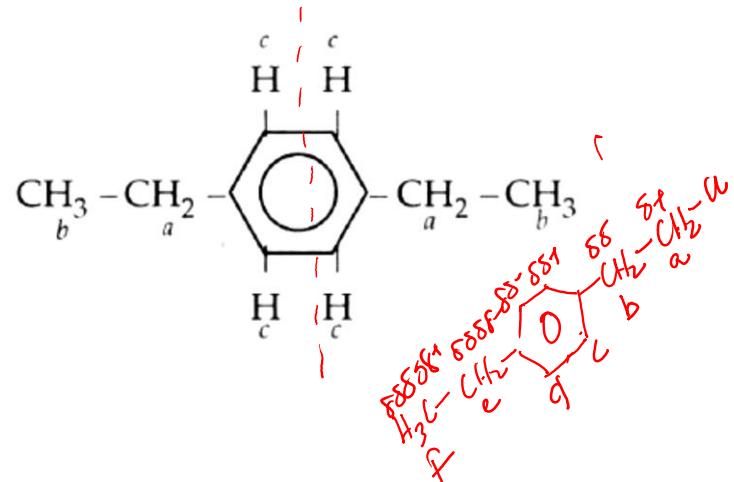
NMR Spectroscopy

NUMBER OF SIGNALS- Equivalent and Non-Equivalent Protons

S.No.	Molecule	Sets of non-equivalent protons	No. of signals in the NMR spectrum
(i)	$\text{CH}_3-\text{CH}_2-\text{OH}$ c b a	3	3
(ii)	$\text{CH}_2\text{Cl}-\text{CHCl}_2$ b a	2	2
(iii)	$\text{CH}_3-\text{CH}_2-\text{CH}_3$ b a b	2	2

NMR Spectroscopy

NUMBER OF SIGNALS- Equivalent and Non-Equivalent Protons



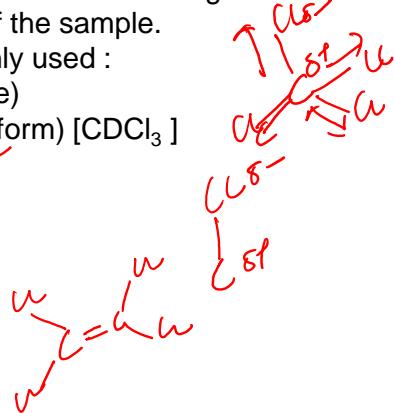
NMR Spectroscopy

SOLVENTS USED IN NMR

Aprotic solvents are preferably used for obtaining proton NMR spectra. This is because they themselves do not give an NMR spectrum to superimpose on that of the sample.

The following solvents are commonly used :

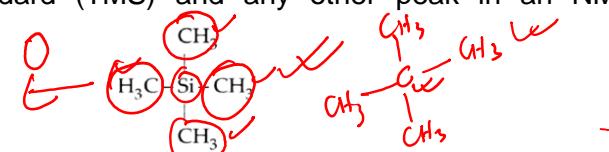
- Heavy water (or deuterium oxide) [D₂O]
- Chloroform-d (or deuteriochloroform) [CDCl₃]
- Carbon tetrachloride [CCl₄]
- Carbon disulfide [CS₂]



NMR Spectroscopy

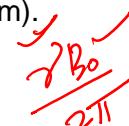
CHEMICAL SHIFT

Chemical shift is the separation between the peak of the reference standard (TMS) and any other peak in an NMR spectrum.



Delta (δ) units are generally used for expressing chemical shift positions. Delta unit is defined as proportional difference from TMS as reference standard, in parts per million (ppm).

$$(\delta) = \frac{(\nu_u - \nu_{TMS})}{\nu_0} \times 10^6$$



Let operating frequency of the instrument = (ν_0) Hz

Frequency of TMS = (ν_{TMS}) Hz

Frequency of unknown group of protons = (ν_u) Hz



NMR Spectroscopy

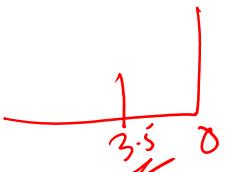
What is the shift of the resonance from TMS of a group of nuclei with $\delta = 3.50$ and an operating frequency of 350 MHz?

$$\delta = \frac{(v - v_{TMS})}{v_0} \times 10^6$$

shift

$$(v - v_{TMS}) = \frac{\delta \times v_0}{10^6}$$

$$= \frac{3.50 \times 350 \times 10^6 \text{ Hz}}{10^6} = 1225 \text{ Hz}$$



NMR Spectroscopy

Shielding and De-Shielding of Protons in NMR

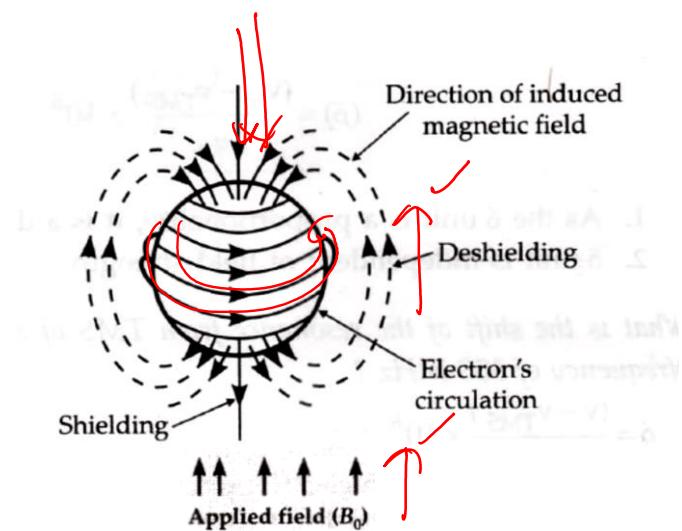
The electrons around the proton are induced to circulate in a magnetic field. These circulating electrons generate a small secondary magnetic field which acts diamagnetically (in opposition) to the applied field. The induced diamagnetic shielding effect is directly proportional to the electron density circulating around the nuclei. Hence greater the electron density, lower will be the precessional frequency of the proton.

Using this, we can easily explain the fact that CH_3 group in CH_3F comes to resonance at higher frequency than those of CH_3Cl . Since electronegativity of F > Cl so fluorine withdraws electron density from the methyl group in CH_3F to a greater extent than Cl in CH_3Cl . Due to this deshielding effect, protons of methyl group experience a greater net magnetic field and hence precess with higher frequency.

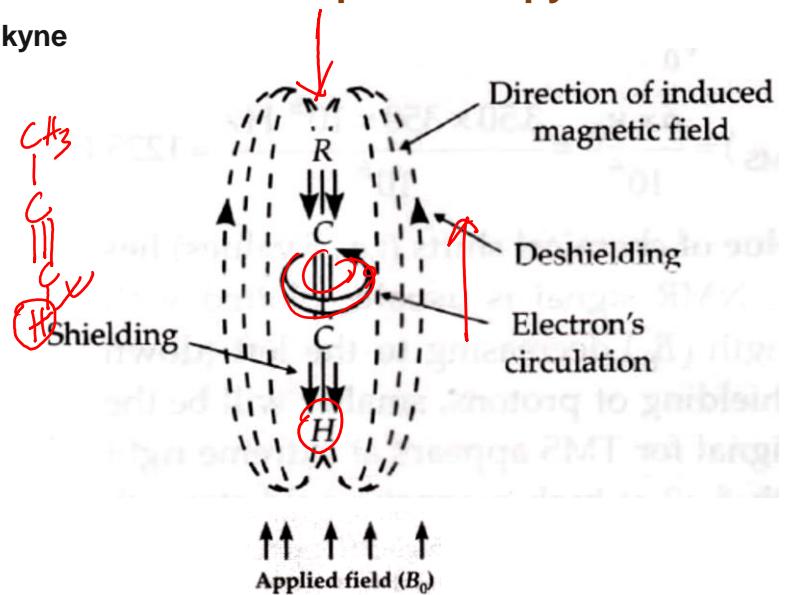
NMR Spectroscopy

Structure of Molecules and Direction of Induced Magnetic Field

Proton

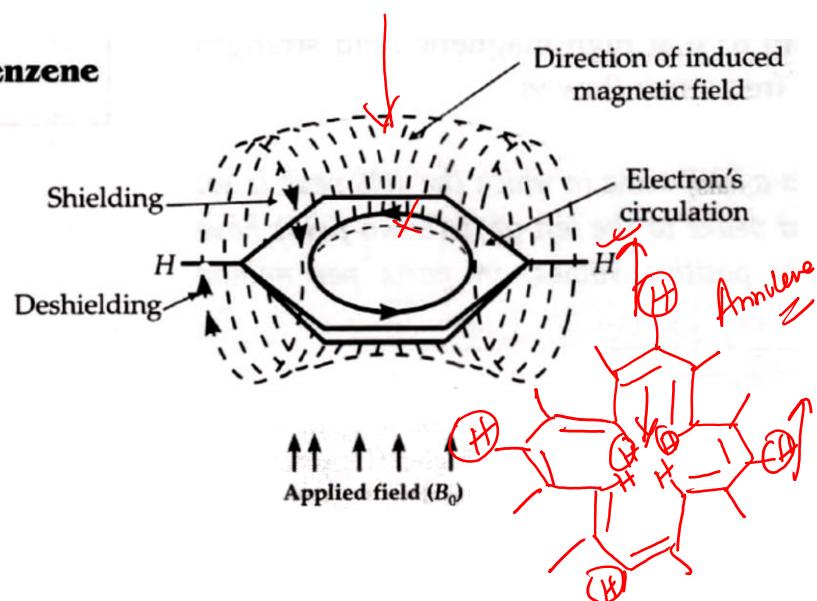


Alkyne



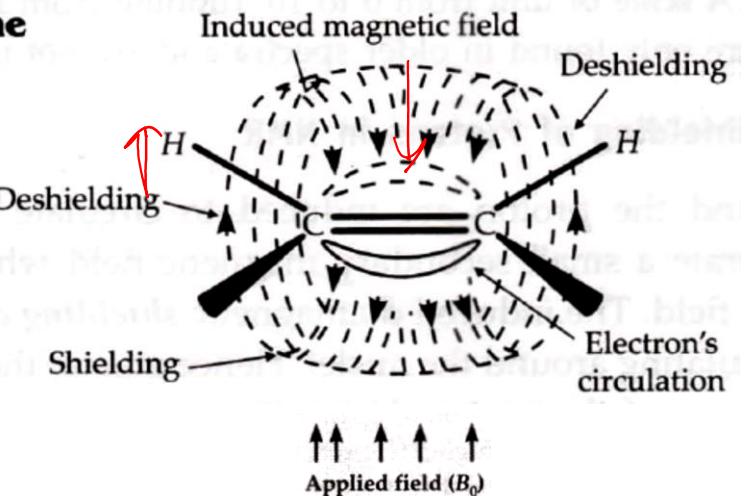
NMR Spectroscopy

Benzene

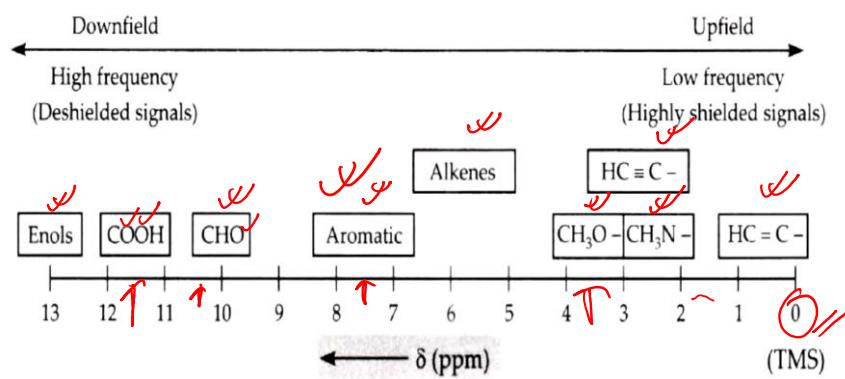


NMR Spectroscopy

Alkene

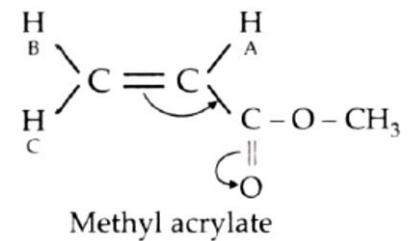
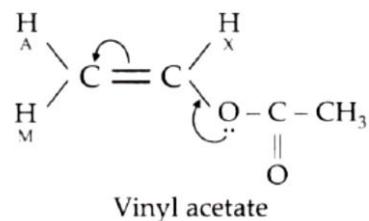


NMR Spectroscopy



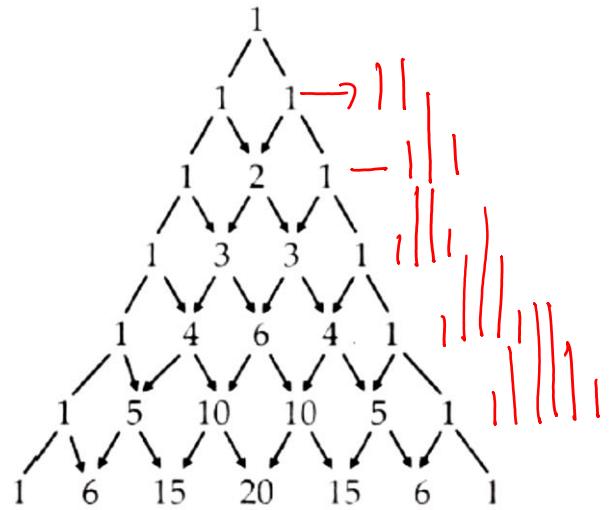
NMR Spectroscopy

How will you distinguish vinyl acetate and methyl acrylate with the help of NMR spectroscopy ?



NMR Spectroscopy

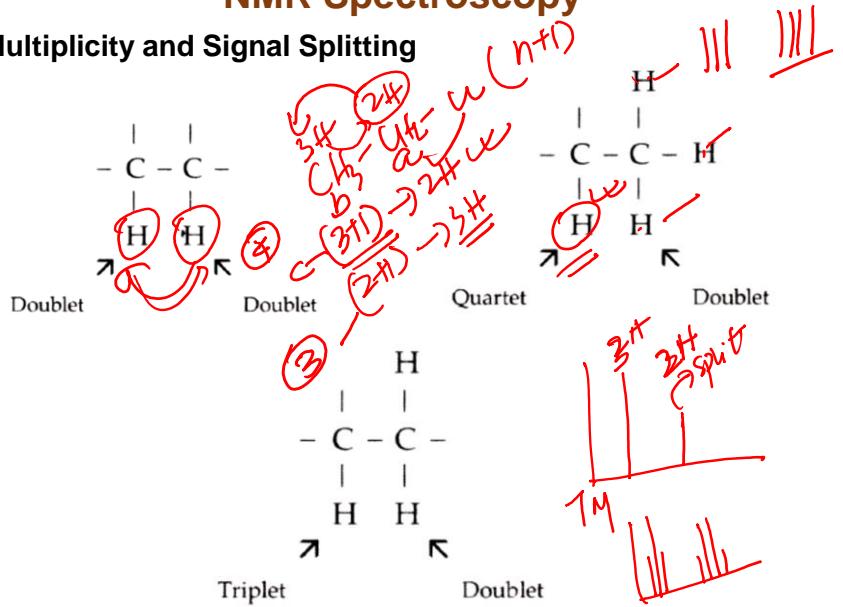
Pascal's Triangle



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NMR Spectroscopy

Multiplicity and Signal Splitting



90

45

NMR Spectroscopy

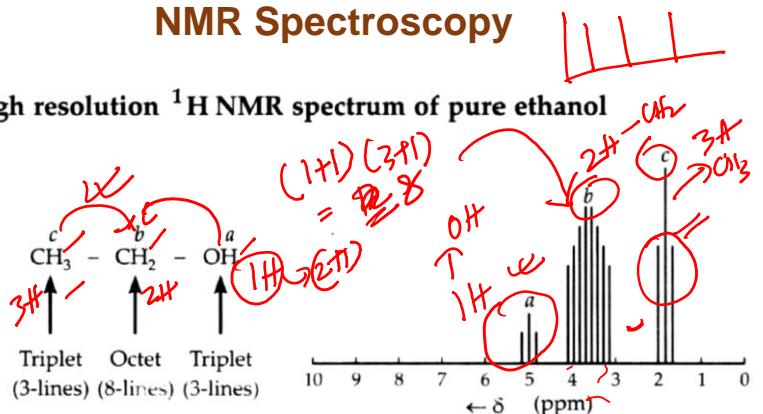
Multiplicity and Signal Splitting

<i>Neighbouring protons (n)</i>	<i>Number of signals (n + 1)</i>
0	1
1	2
2	3
3	4
4	5
5	6
6	7

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NMR Spectroscopy

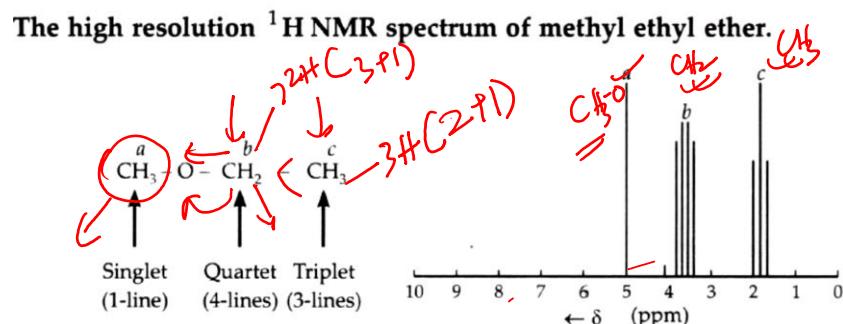
The high resolution ^1H NMR spectrum of pure ethanol



No Hydrogen Bonding

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NMR Spectroscopy



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THE LAMBERT-BEER'S LAW

It states that for a parallel beam of monochromatic radiation passing through a homogeneous solution the absorbance is proportional to the product of the concentration and path-length

$$\text{Absorbance } (A) \propto \text{Concentration } (c) \times \text{path-length } (b)$$

$$\Rightarrow A \propto bc \quad \text{or} \quad A = abc$$

where a is proportionality constant. Its value depends on the substance, the solvent, the wavelength and the units used for concentration and path-length.

The term transmittance (T) is the ratio of the intensity of the light transmitted by a sample (I) to the intensity of light incident on the sample (I_0).

$$A = \log(1/T)$$

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