LECTURE NOTE ON UV / VISIBLE SPECTROSCOPY

By

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The Electromagnetic Spectrum (EMS)

The EMS is a broad spectrum of rays which overlap to form the white light

	λ (m)	ν (Hz)
Cosmic Rays	10^{-14}	10^{22}
Gamma Rays	10^{-11}	10^{19}
X-Rays	10^{-9}	10^{17}
Far UV	10^{-7}	10^{15}
UV	10^{-7}	10^{15}
Visible	10^{-6}	10^{14}
IR	10^{-5}	10^{13}
Far IR	10^{-4}	10^{12}
µ-wave	10^{-3}	10^{11}
Radar	10^{-2}	10^{10}
Television	10^{0}	10^{8}
NMR	10	10^{7}
Radio	10^{2}	10^{6}
Alternating Current (AC)	10^{6}	10^{2}

$\nu = c/\lambda = ms^{-1}/m = s^{-1}$ This is quoted in Hertz (Hz)

$\bar{\upsilon}$ (wave number) = $1/\lambda$

e.g for $\lambda = 10^{-6}$ m = 10^{-4} cm; $\bar{\upsilon} = 1/10^{-4}$ m = 10^{4} cm^{-1}

$\nu = c/\lambda = 3 \times 10^{8}\ ms^{-1}/\ 10^{-6}\ m = 3 \times 10^{14}\ s^{-1}$.

UV Spectroscopy

- EMS region: 200 – 400 nm = UV; 400 – 800 nm = visible
- UV deals with the study of conjugation in molecules (conjugated chromophores in molecules).

Characteristics of UV absorption

i. The wavelength λ and ii. Intensity

- For any symmetry allowed absorption, the intensity, which is indicated by the molar absorptivity (ϵ) is usually > 10,000 ; absorptions not symmetry allowed have $\epsilon < 1000$.
- The values of λ and ϵ are very important for any particular absorption.

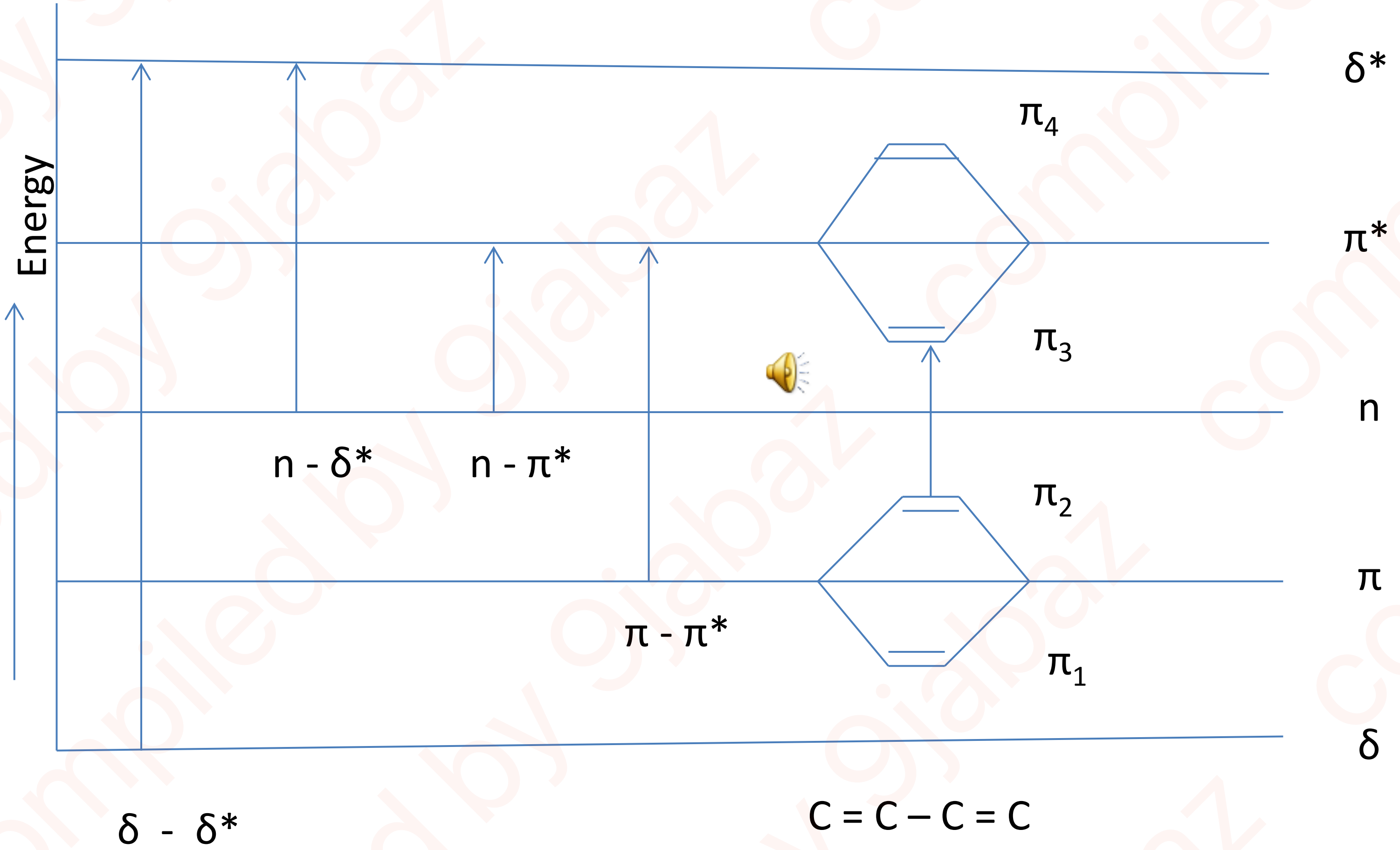
Beer/Lambert Law

- Transmittance $T = I/I_o$;
  Absorbance $A = \log_{10} 1/T = \log_{10} I_o/I =$ Єcl
- Where: I_o = Incident light; I = Transmitted light;
  A = Absorbance; Є = molar absorptivity; l = path length and
  c = concentration in moles/litre.
- Electronic Transitions
- This involves the promotion of electrons from HOMO (Highest Occupied Molecular Orbital) to LUMO (Lowest Unoccupied Molecular Orbital)
- As the energy (E) required for transition increases, the gap between HOMO & LUMO increases; hence λ decreases.
- Energy: $E \alpha 1/\lambda$, $E = hc/\lambda$.

Types of Electronic Transitions

- (a). $\delta - \delta^*$ Transition. This is electronic transition from sigma bonding orbital to sigma anti-bonding orbital. This transition is observed in saturated organic molecules – the Alkanes. It is a high energy transition hence low λ value (150 nm), which does not encroach the UV range, therefore the alkanes are said to be UV inactive
- (b). $n - \delta^*$ Transition. This is transition from non-bonding molecular orbital to sigma anti-bonding orbital. This transition is of lower energy than $\delta - \delta^*$ but the energy requirement is high enough that the λ value is below UV range e.g alkyl halides, alkoxides etc
- (c).). $n - \pi^*$ Transition. This is movement of electrons from non-bonding molecular orbital to anti-bonding pie molecular orbital. It is a low energy transition hence high λ value (280 nm). It is quite useful in UV diagnosis. In symmetry terms it is a forbidden transition hence it's a low intensity transition, e.g. aldehydes and ketones
- (d). $\pi - \pi^*$ Transition. This is electronic transition from bonding pie molecular orbital to anti-bonding pie orbital. The energy involved in this transition is higher than in $n - \pi^*$, the resulting λ value (190 nm) is below UV range, e.g. alkenes, aldehydes and ketones.
- (e). $\pi_2 - \pi_3^*$ Transition (Conjugated system). Very low energy transition. The higher the extent of conjugation the lower the energy of transition hence the higher the λ value.

Energy Profile of Electronic Transitions in Molecular Orbitals



Electronic Transitions in Common Groups

	Group	**λ_{max} (nm)**	**ε ($10^{-2}m^2mol^{-1}$)**	**Transitions**
i	$C = C$	175	14,000	$\pi - \pi^*$
ii	$C = O$	160	18,000	$\pi - \pi^*$
		185	5000	$n - \delta^*$
		280	15	$n - \pi^*$
iii	$C = C - C = C$	217	20,000	$\pi - \pi^*$
Iv	$C = C - C = O$	220	10,000	$\pi - \pi^*$
		315	30	$n - \pi^*$

Effect of Conjugation on Electronic Transition

S/No	Group	λ_{max} (nm)	ε
1	Ethylene	175	15,000
2	1,3-butadiene	217	21,000
3	1,3,5-hexatriene	258	35,000
4	β-carotene	465	125,000
5	Ethanone ($\pi - \pi^*$)	189	900
	Ethanone ($n - \pi^*$)	280	12
6	3-buten-2-one ($\pi - \pi^*$)	213	7,100
	3-buten-2-one ($n - \pi^*$)	320	27

Definition of Terms

(i). Chromophore. Unsaturated group of atoms in a molecule responsible for UV absorption and impartation of colour

(ii). Auxochrome. Saturated group of atoms with lone pair of electrons. An auxochrome does not absorb UV light but when attached to a chromophore, they affect the UV absorption of the chromophore, e.g –OH; -SH; -NH etc.

(iii). Bathochromic Shift. This is the shift of absorption from shorter λ to longer λ. It is sometimes referred to as Red shift.

(iv). Hypsochromic shift. Shift of absorption to shorter λ. It is otherwise called a Blue shft.

(v). Hyperchromic effect. Any effect that result in increased absorption intensity

(vi). Hypochromic effect. Any effect that result in decreased absorption intensity

Solvent Effect

Changes may take place in λ – value due to changes in solvent used

For changes to solvents of increased polarity:

i. No significant shift in absorption band for conjugated dienes & aromatic hydrocarbons

ii. Significant shift (both Red & Blue shifts) occur in α- β- unsatd. carbonyl compounds.

Red Shift is due to $\pi - \pi^*$ transition while

Blue shift due to $n - \pi^*$ transition

Explanation:

Polar protic solvent stabilizes π, π^* and n – orbitals in order of:

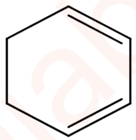
$$n > > \pi^* > \pi.$$

Computation of λ_{max} value (Woodward-Fieser Rules)

A. For Conjugated Dienes

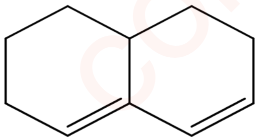
	λ_{max} (nm)Parent
Basic Heterocyclic or Acyclic diene	214
Basic Homoanular diene	253
ADDITIONS:	
Alkyl substituent/ Ring residue	+5
Double bond exocyclic to a ring	+5
Double bond extending conjugation	+30
-Oac (-OCOCH$_3$)	0
-OR (Alkoxy)	+6
-SH (Thioether)	+30
-Cl, -Br	+5

Explanation of Terms Used in Woodward-Fieser Rules



Homoannular diene

The conjugated double bonds are within the same ring

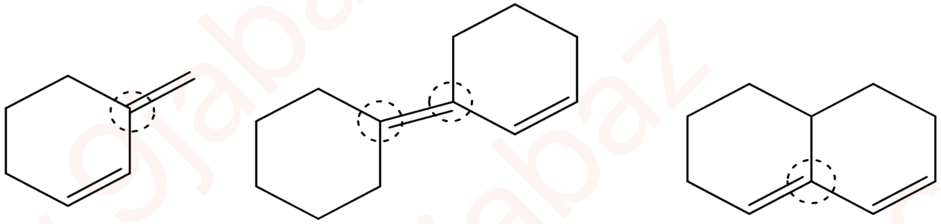


Heteroannular diene

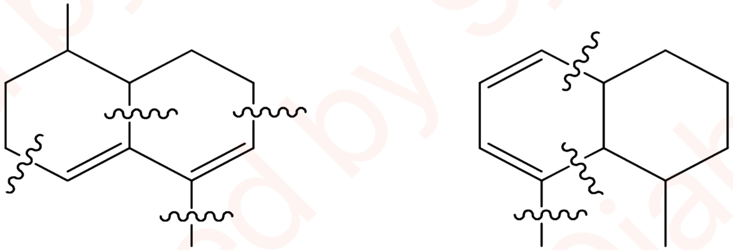
The conjugated double bonds are contained in different rings

Acyclic diene

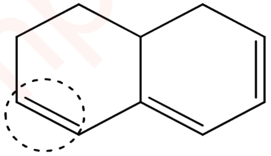
The conjugated double bonds are not cyclic



Exocyclic nature of a double to ring(s)



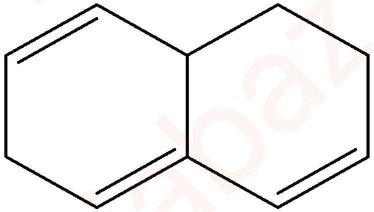
∿∿∿∿ = Alkyl substituent group or Ring residue



= Double bond extending conjugation

Practice Exercise

λ nm

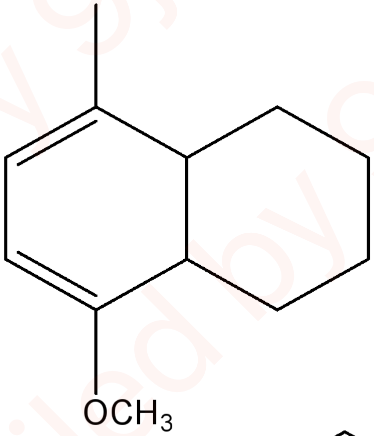


Parent heterocyclic diene = 214

1 Exocyclic double bond = 5

3 Ring residue = 15

Calculated = 234

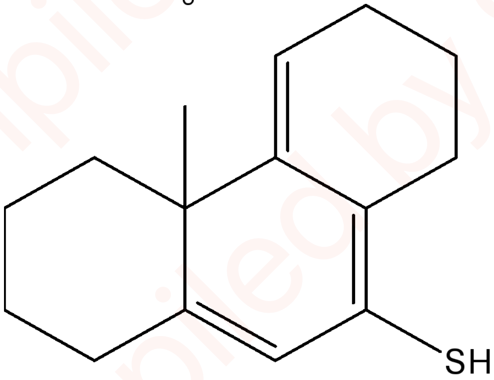


Parent homoanular diene = 253

3 Ring residue = 15

-OCH_3 group = 6

Calculated = 274



Parent homoanular diene = 253

5 Ring residues = 25

-SH group = 30

3 Exocyclic double bonds = 15

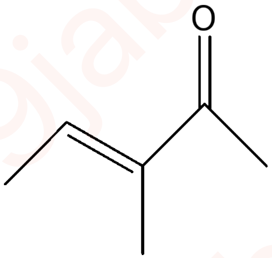
Calculated = 323

B. α,β-Unsaturated carbonyl compounds

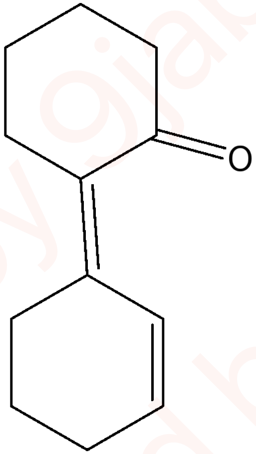
	λ_{max} (nm)Parent			
Parent α,β-Unsatd. 6-membd. ring or acyclic Ketones	215			
Parent α,β-Unsatd. 5-member ring ketones	202			
Parent α,β-Unsaturated aldehydes	207			
Parent α,β-Unsaturated acids and Esters	197			
ADDITIONS	α ;	β ;	γ ;	δ.
Double bond extending conjugation	+30			
Homoannular diene component	+39			
Alkyl or Ring residue	10 ;	12 ;	18 ;	18 .
-OAc (-$OCOCH_3$)	6 ;	6 ;	6 ;	6.
-OR (Alkoxy)	35;	30 ;	17;	31.
-SR (Thioether)	- ;	80;	- ;	- .
-Cl	15 ;	12 ;	12 ;	12.
-Br	25 ;	30 ;	25 ;	25.
-NR_2	- ;	95 ;	- ;	- .

Practice Exercise

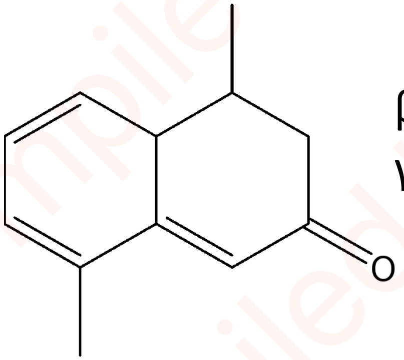
λ nm



Parent acyclic ketone = 215
α - substituent group = 10
β - substituent group = 12
Calculated = 237



Parent cyclic ketone = 215
α -Ring residue = 10
β -Ring residue = 12
γ - Ring residue = 18
Double bond extg. conjugation = 30
2 exocycli nature of double bond = 10
Calculated = 295



Parent cyclic ketone = 215
β -Ring residue = 12
γ - Ring residue = 18
ω - Ring residue = 18
2 Double bond extd. conjugation = 60
Homo. diene component = 39
Exocyclic D. bond = 5
Calculated = 365

LECTURE NOTE ON IR SPECTROSCOPY

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Unit of Vibrational frequency ν

- $\nu = c/\lambda = ms^{-1}/m = s^{-1}$
- $\bar{\upsilon}$ (wave number) = $1/\lambda$
- In the context of infra red spectroscopy, frequency (ν) is measured in "wavenumber", which has the unit cm^{-1}.

Infra red region: *near*, *mid* and *far* infra red

Near	12800 – 4000 (cm^{-1});	0.78 – 2.5 µm
Middle	4000 – 200 (cm^{-1});	2.5 – 50 µm
Far	200 – 10 (cm^{-1});	50 – 1000 µm

The useful IR region lies between 4000 – 400 cm^{-1} (2.5 – 25 µm)

The IR spectrum can be divided into two main parts:

i. The Functional group region (stretching vibration region)

ii. The Finger-print region (bending vibration region)

Theory of infra red absorption

- Infrared spectroscopy is used in identification of functional groups in pure compounds.
- When a molecule absorbed electromagnetic radiation in IR region, it undergoes vibrational transitions which causes net change in the dipole moment in the molecule, the molecule is said to be **IR active, for example HCl, CO etc, but if dipole moment does not change in the molecule then it is IR inactive (for example: O_2, H_2, N_2 etc.) i:e they do not absorb IR radiation.**
- If the frequency of IR radiation matched with the vibrational frequency of a bond in the molecule, then the molecule absorb radiation.

Molecular vibrations

The positions of atoms in a molecule are not fixed; they are subject to a number of different vibrations. Vibrations fall into the two main categories : *stretching* and *bending*.

- **Stretching:** Change in inter-atomic distance along bond axis. There are two types: Symmetric and Asymmetric
- **Bending:** Change in angle between two bonds. There are four types of bend:

Rocking; Scissoring; Wagging; Twisting

Degree of Freedom/Mode of Vibration

- The degree of freedom of a molecule = Sum of degree of freedom of individual atoms
- A molecule with n atoms possesses 3n degree of freedom (becos an atom's motion is 3 dimensional: x, y, z)

For Linear Molecules

2 degree of freedom describe Rotational mode

3 degree of freedom describe Translational mode hence

(3n – 5) degree describe Vibrational mode.

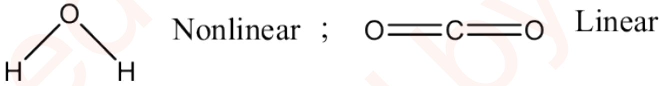
For Non-Linear Molecules

3 degree of freedom describe Rotational mode

3 degree of freedom describe Translational mode hence

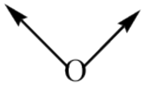
(3n – 6) degree describe Vibrational mode.

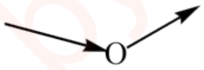
For example CH_4 a nonlinear molecule theoretically will possess 9 vibrational modes (3x5 – 6)



AX_2 System e.g CH_2

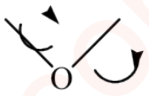
I Stretching vibration; Two types:

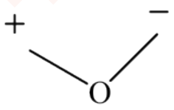

Symmetric stretching (2900 - 2853 cm^{-1})

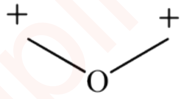

Asymmetric stretching (3000 - 2926 cm^{-1})

II Bending vibration; Four types:


Scissoring (1465 cm^{-1})


Rocking (720 cm^{-1})


Twisting (1350 -1150 cm^{-1})


Wagging 1350 - 1150 cm^{-1})

- The above are referred to as Fundamental frequency

III Modulated Vibration (Modulation of fundamental frequency)

- i. Overtone : Expressed as 2x, where x = fundamental frequency
- ii. Beats: Combination of frequencies; x and y fundamental frequencies interact to give another weaker absorption at (X±Y) cm^{-1}

Factors Affecting Vibrational Frequency v

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi}\sqrt{\left(\frac{k}{m1m2/m1+m2}\right)}\,. \qquad \mu = \frac{m1\;x\;m2}{m1+m2}$$

Where, κ is force constant of the bond, which is a function of bond strength, v is the frequency, and μ is reduce mass of atoms with masses(m1 and m2)

1.

$$\text{V} \propto k.\, the\ higher\ the\ value\ of\ k, the\ bond\ strength\ the\ higher\ the\ vibrational\ frequency$$

$C{=}O$ & $C{=}C$ will have higher v than $C{-}O$ & $C{-}C$ respectively

This is because bond strength is in order of: $C{\equiv}C > C{=}C > C{-}C$

2.

$$V \propto \frac{1}{\mu}.\, the\ higher\ the\ value\ of\ \mu, the\ lower\ the\ vibrational\ frequency$$

$C{-}H$ & $O{-}H$ will have higher v than $C{-}C$ & $C{-}O$ respectively

This is because the reduced mass of C - H is lower than that of C - C

Factors Affecting Vibrational Frequency contd

3. Vibrational Coupling

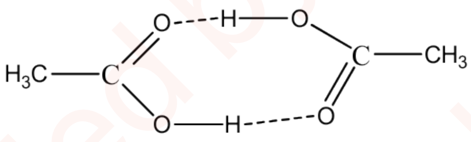
This takes place between 2 bonds vibrating with similar V if the bonds are close in the molecule. The coupling vibrations may be fundamentals as in AX_2 System or a fundamental may couple with modulated vibration (Fermi Resonance). Coupling usually result in symmetric and anti-symmetric vibrations:

Group	Ant-Symmetric	Symmetric
$-CH_2$	3000	2900
$-NH_2$	3400	3300
$-NO_2$	1550	1400
$-SO_2$	1350	1150
$-COO^-$	1600	1400

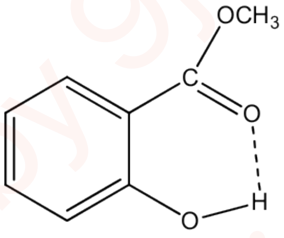
4. H_2 Bonding

H-bonding lowers vibrational v and leads to broadening of -OH band. The stronger the H-bonding the lower the v and broader the band.

H_2 bonding can be intermolecular or intramolecular:



Intermolecular H_2 bonding between two molecules of ethanoic acid



Intramolecular H_2 bonding in methtylsalicylate

Factors Affecting Vibrational Frequency contd

Effect of H-bonding contd

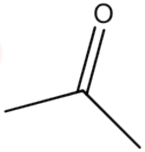
The effect of Intermolecular H-bonding can be reduced or totally removed in dilute solution (depending on extent of dilution) but dilution doesn't affect intramolecular H-bonding.

e.g in dilute ethanoic acid -O – H (free i:e non H-bonded) v = 3550s cm-1

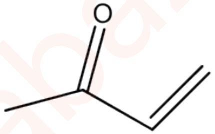
However in concentrated solution (H-bonded) v = 3300- 2500s (broad)

5. Electronic Effects

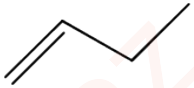
i. Conjugation: It reduces k value hence lowers v. The higher the extent of conjugation the lower the v.



A



B



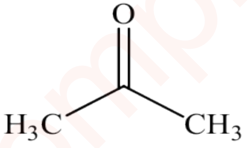
D

E

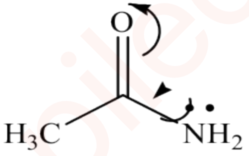
In A, C=O bond v value is 1720; in B C=O band is 1700. In D C=C band is 1650 but in E absorption band is 1600 cm-1

ii. Mesomeric: In amides generally, the relative movement of the lone pair on N-atom and the pie electrons in carbonyl bond because both are conjugated usually leads to weakening of the C=O bond (increase of s-character) thereby lowering v

Mesomeric effect:



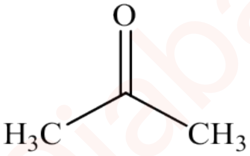
$V_{C=O\ stretch}$ = 1720 (s)



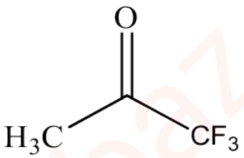
$V_{C=O\ stretch}$ = 1690 (s)

+ M effect due to lone pair electron in N-atom increasing the s-character of C=O hence reducing the k and v values of the C=O bond

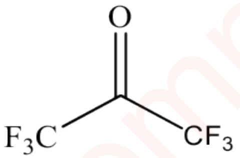
iii. Inductive effect



$V_{C=O\ stretch}$ = 1720 (s)



$V_{C=O\ stretch}$ = 1760 (s)



$V_{C=O\ stretch}$ = 1790 (s)

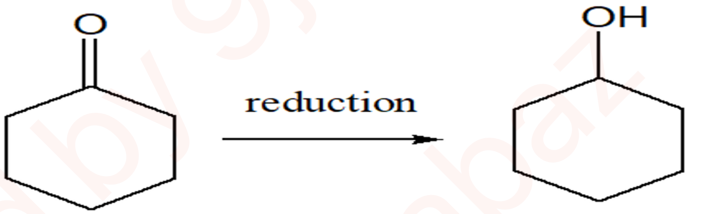
Application of IR Spectroscopy

a) Identification of different functional group (different functional groups have different v values.

b) Distinction between intermolecular and intra-molecular hydrogen bonding.

c) Identification of purity of the compound, if compound is impure then additional peaks are observed in the IR spectrum.

d) Study/monitoring of chemical reaction:



C=O (1710 cm^{-1})

O-H (3300 cm^{-1})
hydrogen bonded

IR correlation chart

Functional Group	Types of Vibration	Frequency (cm^{-1})
Alkane	C – C stretching	1200
	C – H stretch	2980 – 2840
	CH_2 bending	1465
	CH_3 bending	1375
	CH_2 rocking	720
Alkene	C = C stretch	1650
	=C – H stretch	3095 – 3010
	=C – H bend	1000 – 650
Alkyne	$C\equiv C$ stretch	2100
	$\equiv C-H$ stretch	3300
	$\equiv C-H$ bend	700 – 600
Aromatic	C = C stretch	1600
	=C – H stretch	3040 – 3010
	=C – H bend	Below 900
C = O stretch	Amide	1680
	Ketone	1745 - 1715

IR correlation chart Contd.

C = O stretch	Aldehyde	1740 – 1720
	Caboxylic acid (dilute)	1760
	Esters	1750 – 1725
	Acid Chloride	1800
	Anhydride (2 bands)	1810 (I) & 1760 (II)
C – O Stretch		1300 – 1000
O – H	Alcohol/Phenol (Free)	3600
	H-bonded	3400 – 3200
	Carboxylic acid	3400 – 2400
N – H stretch (Amine)	NH_2 (2 bands) stretch	3440 & 3350
	-N – H bend	1650 – 1580
	C – N stretch	1350 - 1000
Amide	-N – H stretch	3370 & 3150
Nitrile	$C \equiv N$	2250
Imine	C = N	1690 – 1640

Mass Spectroscopy

By

Akin Akinlua

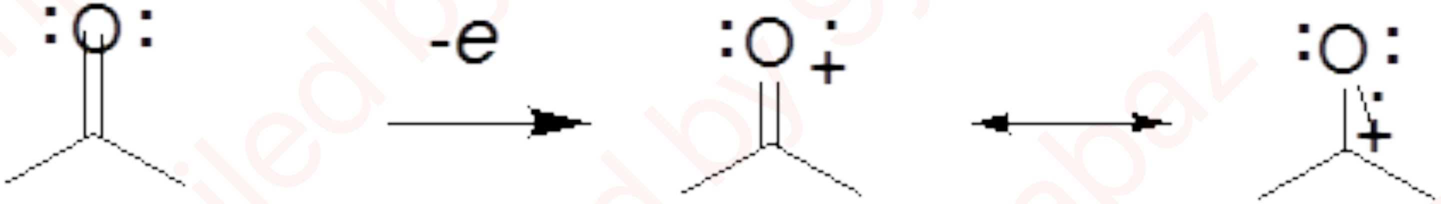
Introduction

- Consider the expression $M \xrightarrow{-e} M^{\cdot +}$

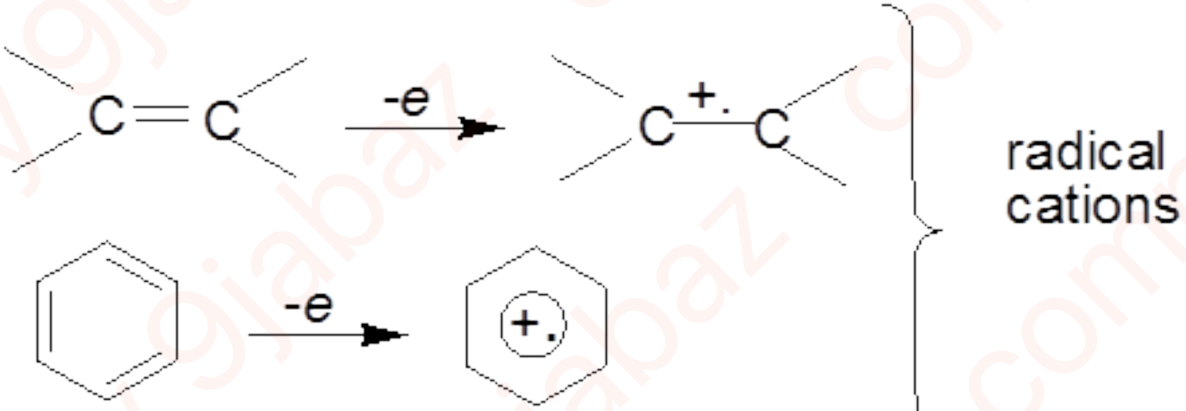
- The product of this operation is a radical cation because it has both positive and radical (.).

- It is also called the molecular ion because it has the same relative molar mass as M itself.

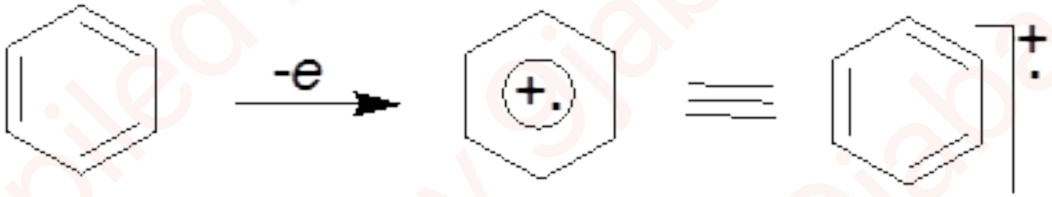
- In the case of the carbonyl compound, it has been concluded that the most facile ionization process corresponds to the removal of one of the lone pair of electrons on the oxygen atom.



- The position of removal and the ease with which you can remove an electron depend on the actual compound.

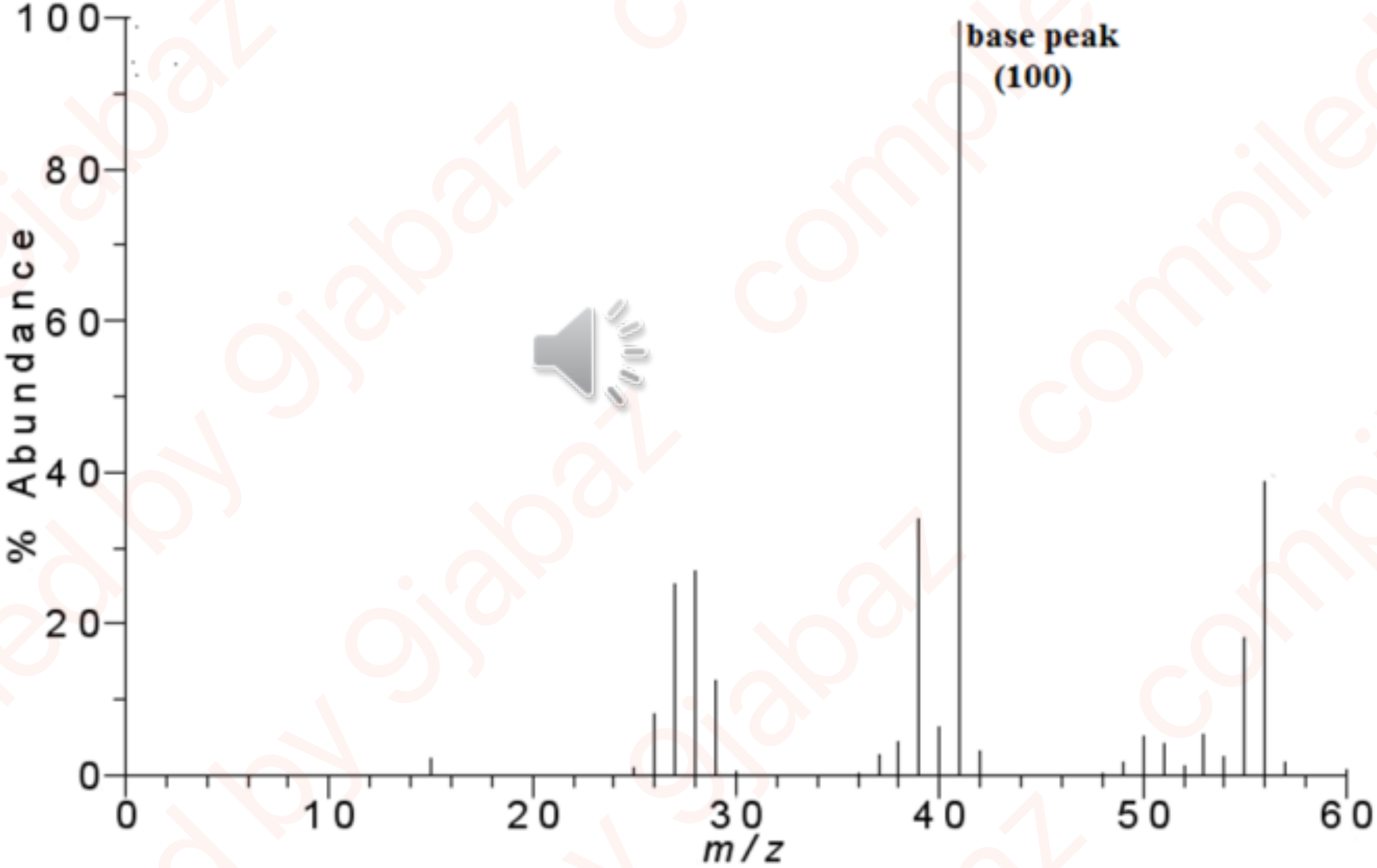


- At times, it is not convenient to write radical cations in the above forms. Hence another method writing this has been introduced.

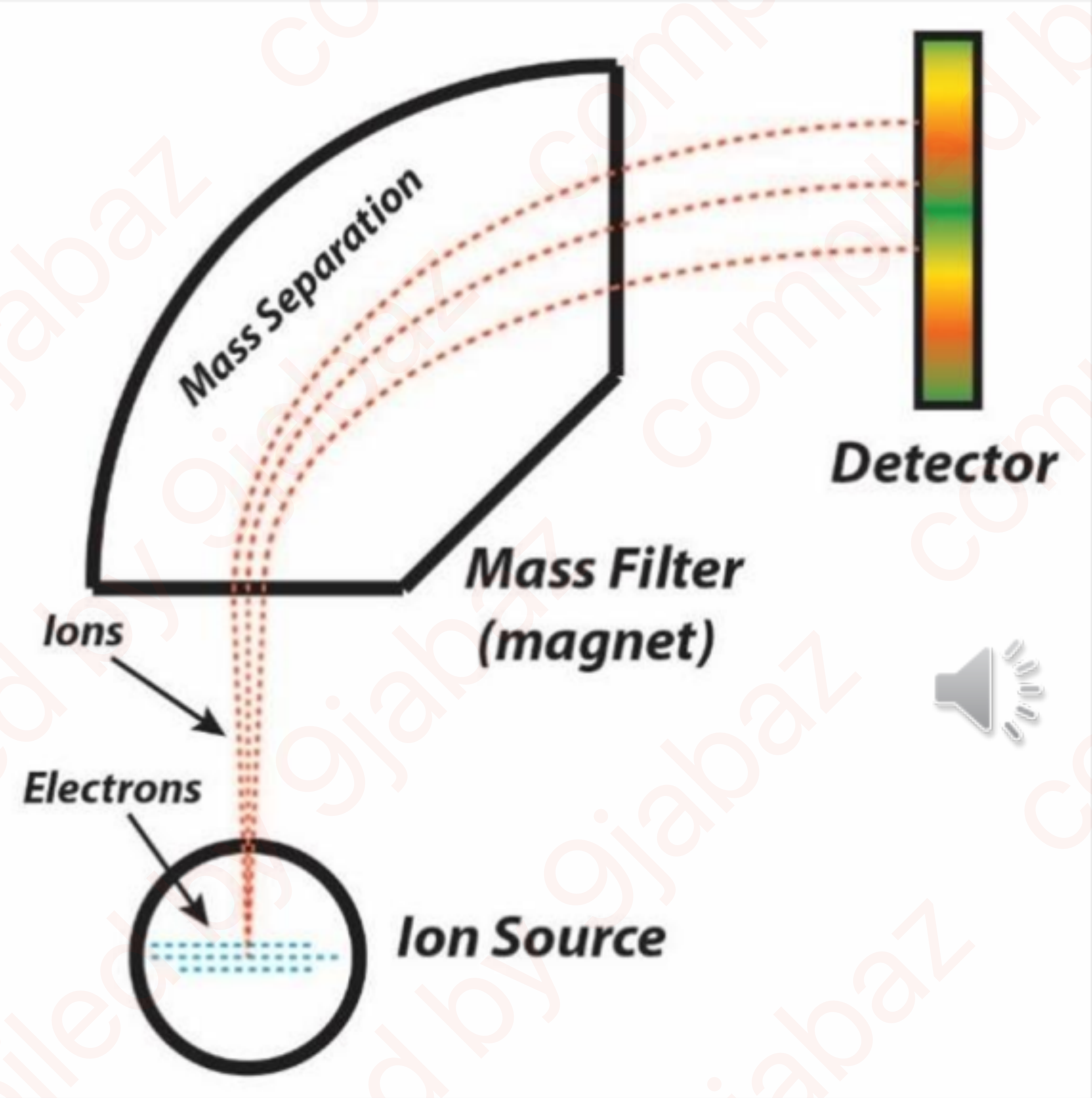


- If an electron is lost from $H_3C - CH_2 - CH_2 - CH_3$, then we can write $H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_3 \xrightarrow{-e} \left.H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_3\right]^{+\cdot}$

What is mass spectrum and how do we obtain it?



The Mass Spectrometer



The Molecular Ion Peak

- The molecular ion peak arises from the molecular ion, but often, it does not always appear in the mass spectrum.

- The importance of the parent peak is that it gives in the molecular weight of the compound concerned.

- If the measurement is on a high resolution mass spectrometer that gives the mass/change ratios to four places of decimal.

- **For Accurate Mass**

  ^{1}H = 1.0078246
  ^{12}C = 12.0000000
  ^{16}O = 15.994941
  ^{13}C = 13.003354
  ^{14}N = 14.003074

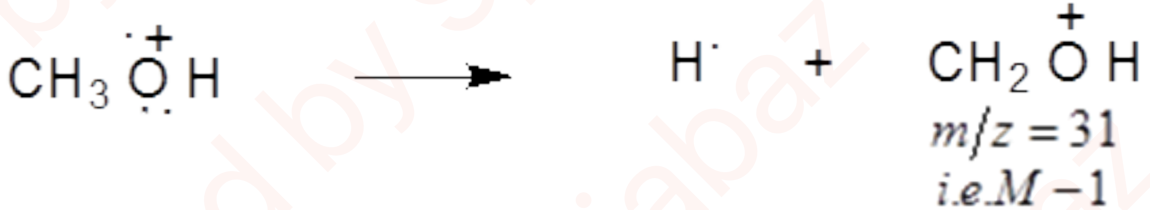
- Suppose we have a compound whose low resolution mass spectroscopy shows that it has a molecular weight of 28. This can be CO or N_2.

Formation of and Disintegration of Molecular Ion

Formation:

$$CH_3\ddot{O}H + e \longrightarrow CH_3\overset{\cdot +}{O}H + 2e$$

Disintegration:

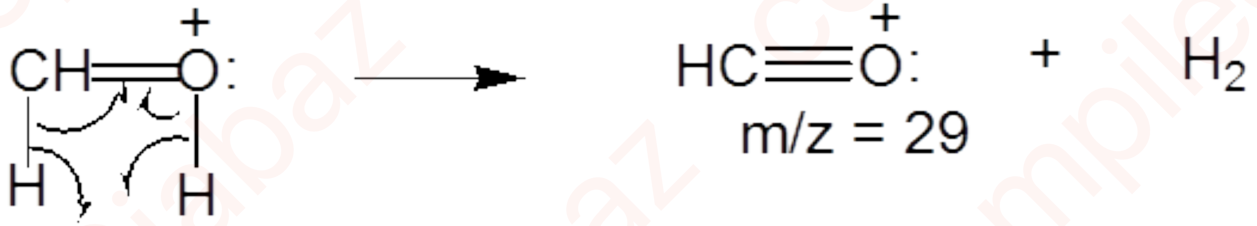


$$CH_3\overset{\cdot +}{O}H \longrightarrow H^{\cdot} + CH_2\overset{+}{O}H$$

- It may be required to show the movement of electrons during the fragmentation.

$$H{-}CH_2{-}\overset{\cdot +}{O}{-}H \longrightarrow H^{\cdot} + CH_2{=}\overset{+}{O}{-}H$$

- It is possible to lose one mole of hydrogen and in this case, we shall have



- It is also possible to have another mode of fragmentation as

- Note that a molecular ion will disintegrate to give a positive ion and a radical.

Rules for Predicting the Prominent Peaks in a Spectrum

- The relative height of the molecular ion peak is greatest for the straight chain compound and decreases as the degree of branching increases.

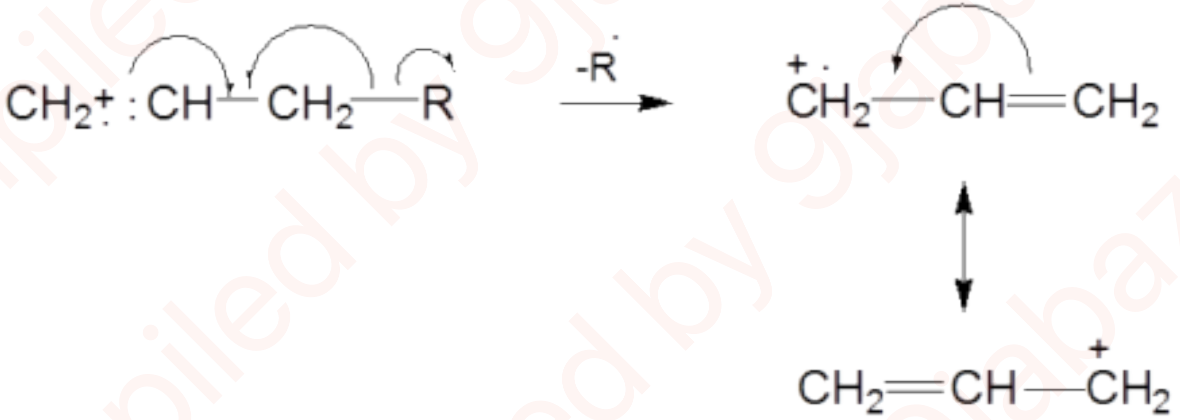
- The relative height of the molecular ion peak usually decreases with increasing molecular weight in a homologous series. Fatty acid esters are exceptions.

- Cleavage is favoured at branched c-atoms; the more branched, the more likely is cleavage. This in a consequence of increased stability of carbonium ion which is of the order. $3^{\circ}>2^{\circ}>1^{\circ}$

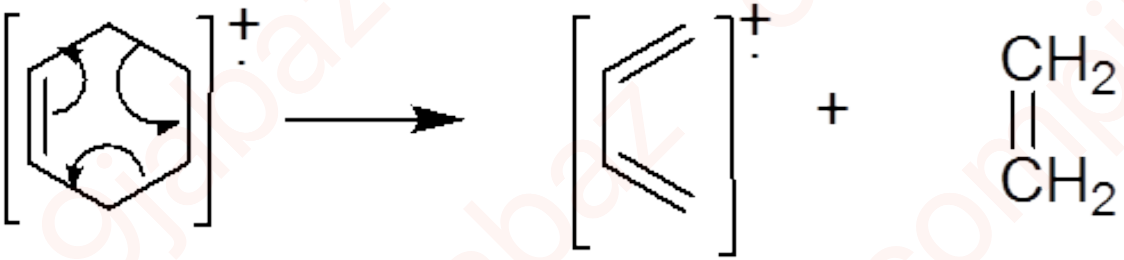
- Generally, the largest substituents at a branch is eliminated most readily as a radical, presumably because a long chain radical can achieve some stability by delocalization of the lone electron.

- Double bonds, cyclic structures and especially aromatic (or heteroaromatic) rings stabilize the molecular ion and thus increase the probability of its appearance.

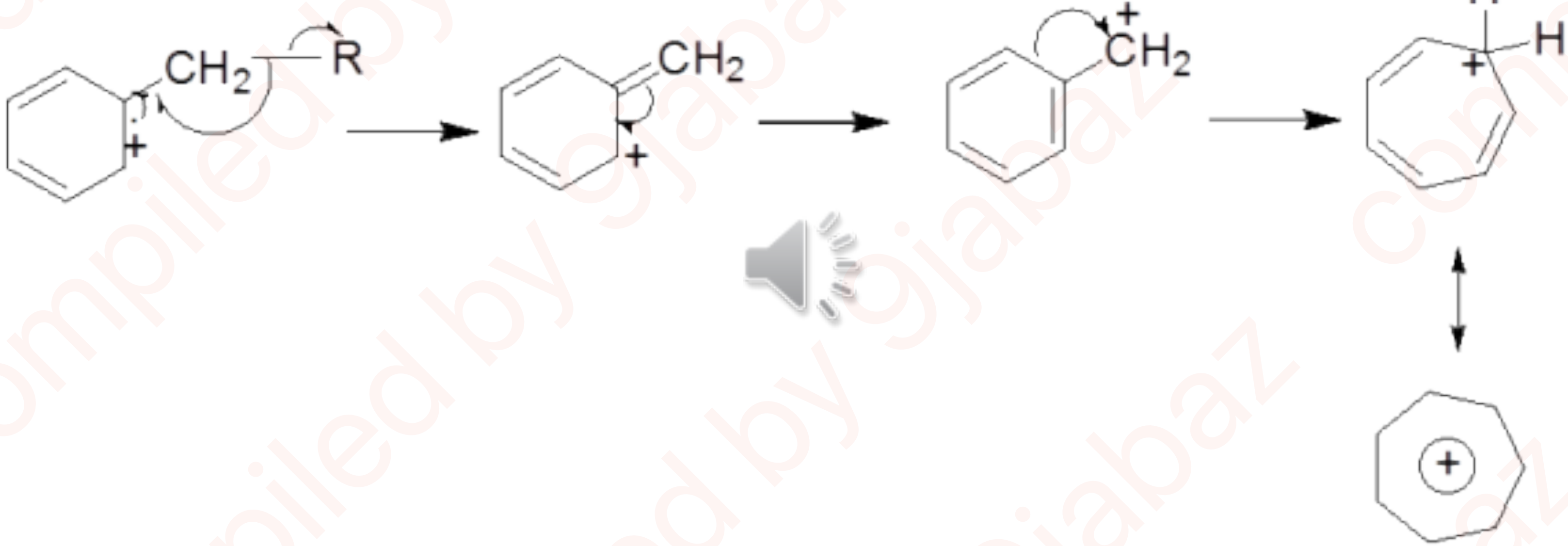
- Double bonds, favour allylic cleavage and give the resonance stabilized allylic carbonium ions.



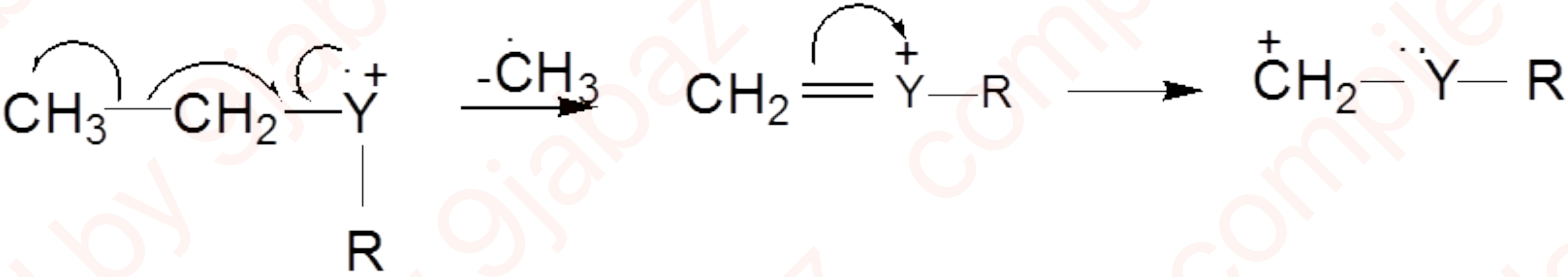
- Saturated rings tend to lose side chains at the ∝ bond. This is merely a special case of branching (rule 3). The positive change tends to stay with the ring fragment. Unsaturated rings can undergo a retro-Diels-Alder reaction.



- In alkyl substituted aromatic compounds cleavage is very probable at the bond beta to the ring, giving the resonance stabilized benzyl ion or, more likely, the tropylium ion directly.



- C – C bonds next to a hetero atom are frequently cleaved, leaving the charge on the fragment containing the hetero-atom where non-bonding electrons provide resonance stabilization.

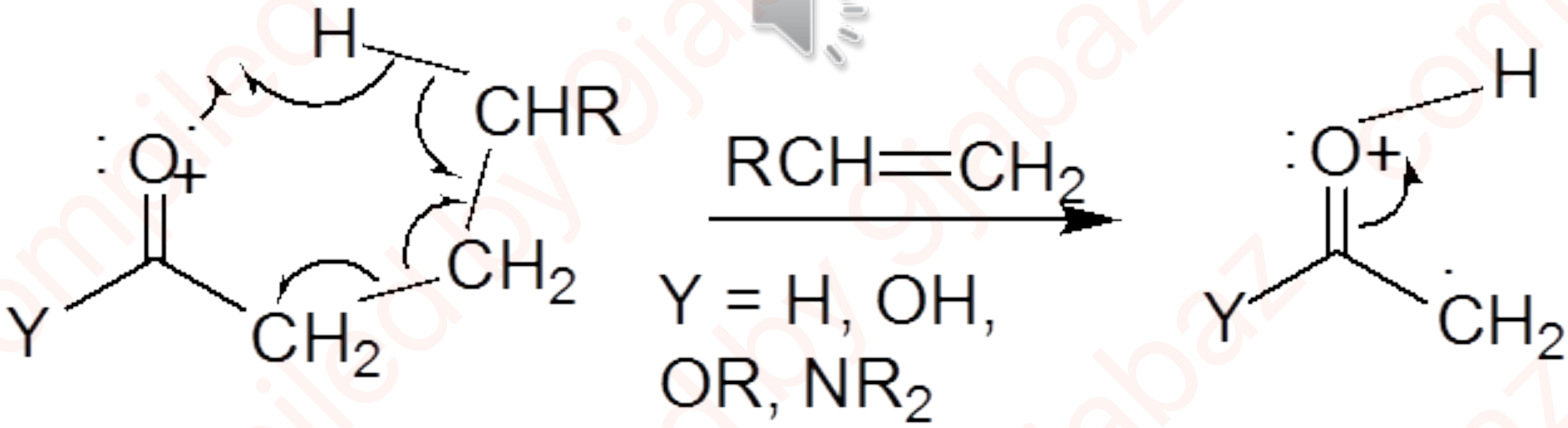


- Cleavage is often associated with elimination of small, stable molecules such as CO, olefins, water, NH_3, H_2S, HCN or alcohols.

Rearrangements

- Rearrangement ions are fragments whose origin cannot be described by simple cleavages of bonds in the parent ion; but are as a result of intermolecular atomic rearrangements during fragmentation e.g McLafferty rearrangement.

- To undergo a McLafferty rearrangement, a molecule must possess the appropriately located hetero-atoms (e.g O), π electron system (usually a double bond) and a ∝ - hydrogen atom.



Mass Spectra of Some Chemical Classes

Saturated hydrocarbons

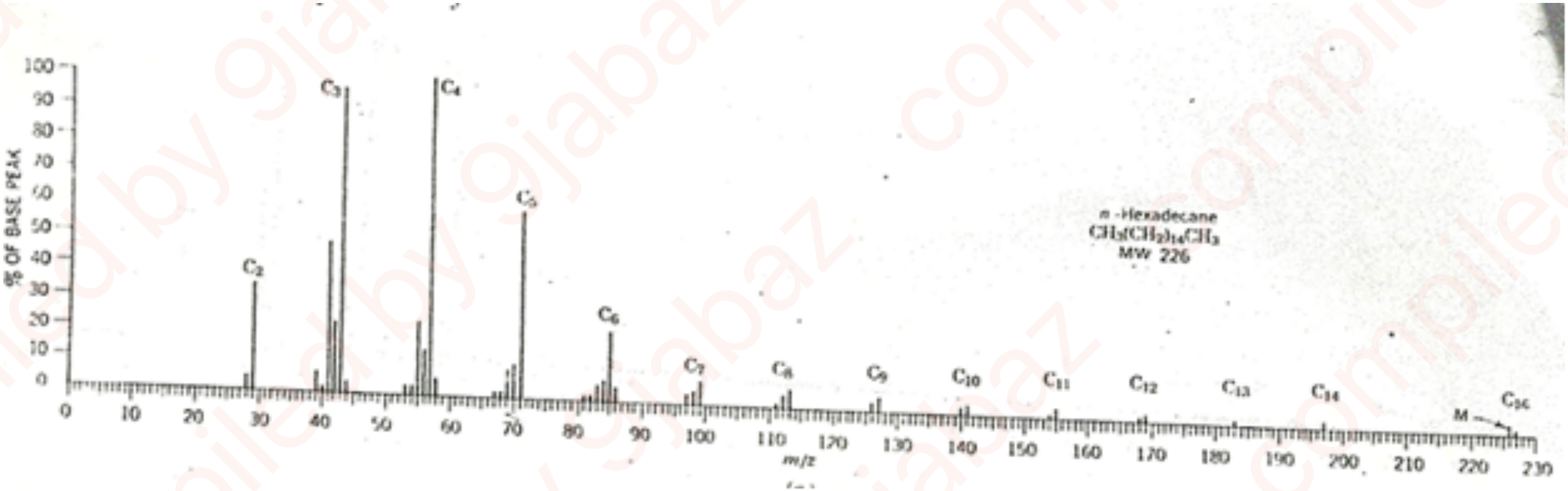
- The molecular ion peak of a straight chain saturated hydrocarbon is always present, though of low intensity for long-chain compounds.

- The fragmentation pattern is characterized by cluster of peaks and the corresponding peaks of each cluster are 14 (CH_2) mass units apart.

- The largest peak in each cluster represents C_nH_{2n+1} fragment. This is accompanied by CnH_2n and C_nH_{2n-1} fragments.

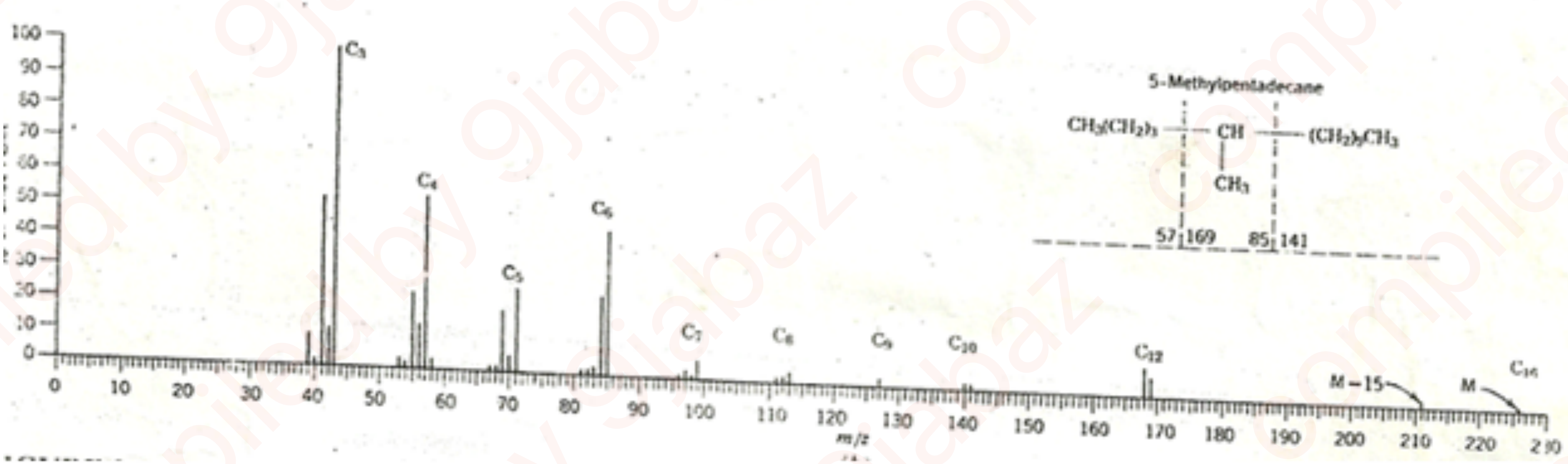
- The most intense fragment is $C_4H_9^+$ or $C_3H_7^+$, the intensities decrease in a smooth curve down to M-C_2H_5.

- The M-CH_3 peak is characteristically very weak or missing.



Branched chain saturated hydrocarbons

- Spectra of branched chain saturated hydrocarbons are grossly similar to those of straight – chain compounds, but the smooth curve of decreasing intensities is broken by preferred fragmentation at each branch.



Olefins

- The molecular ion peak of olefins, especially poly-olefins is usually distinct. Location of the double bond in cyclic olefin is difficult because of its facile-migration in the fragment.

- Cyclic olefins usually show a distinct molecular ion peak. A unique mode of cleavage is a type of homolytic retro-Diels Alder reaction as shown by limonene.

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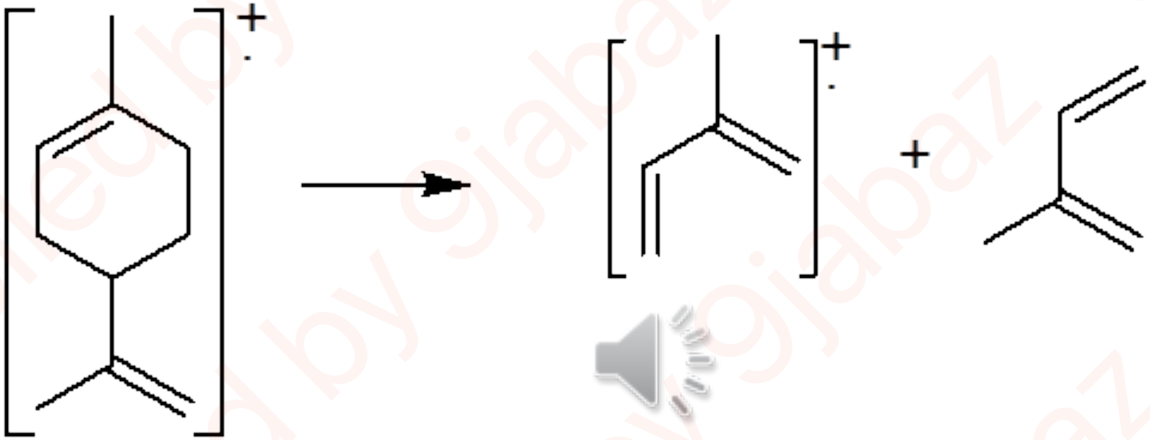
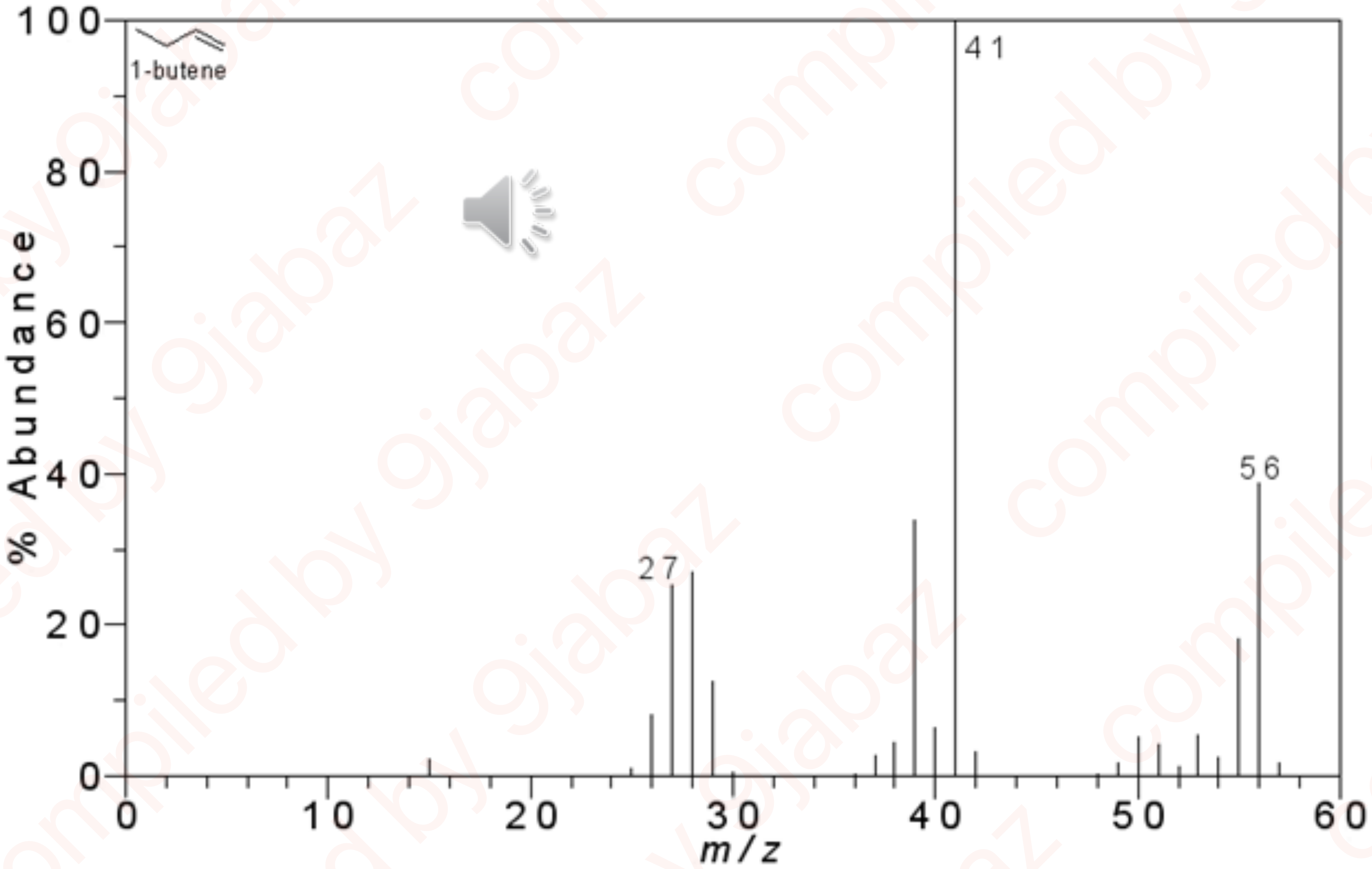
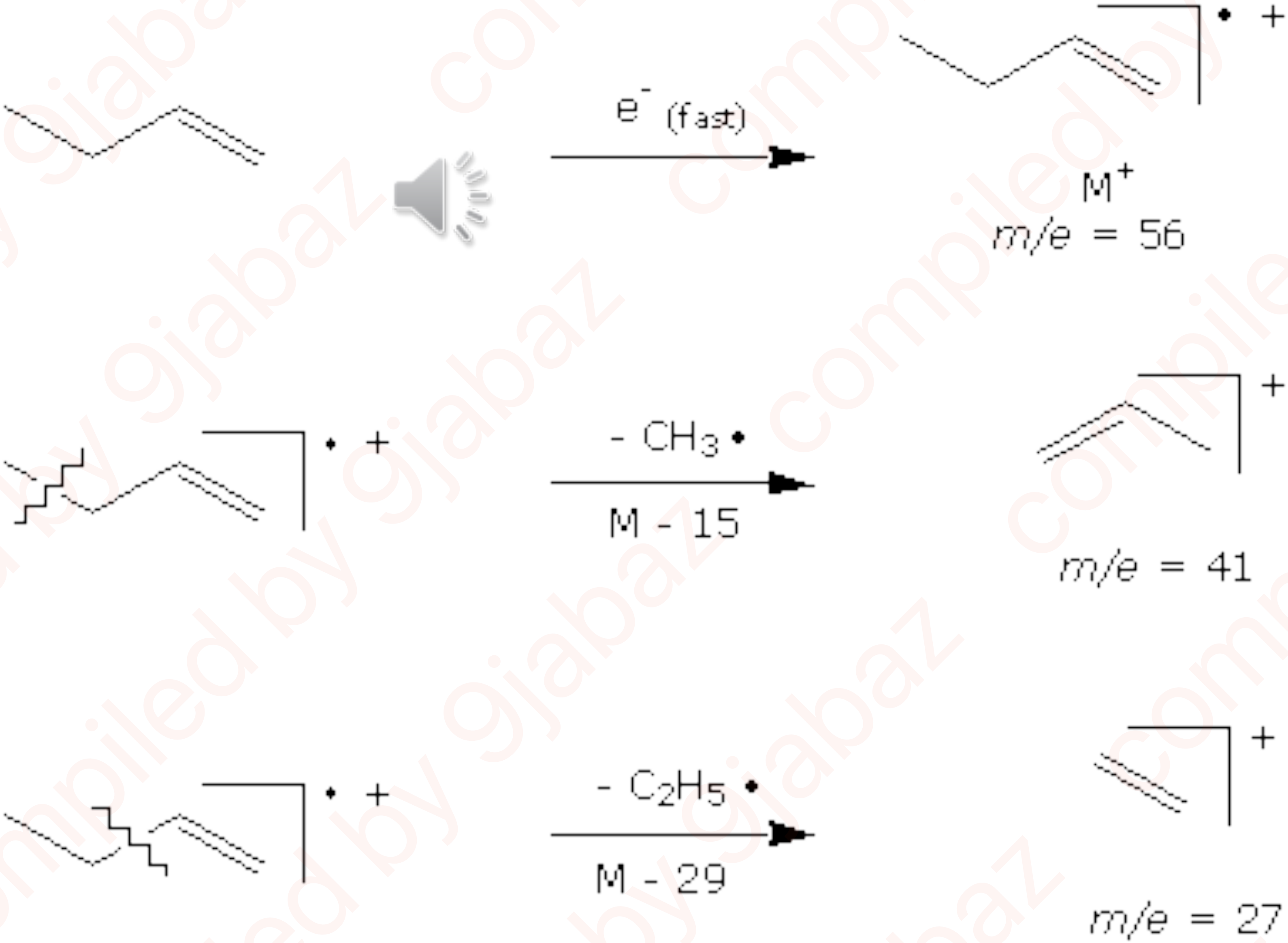
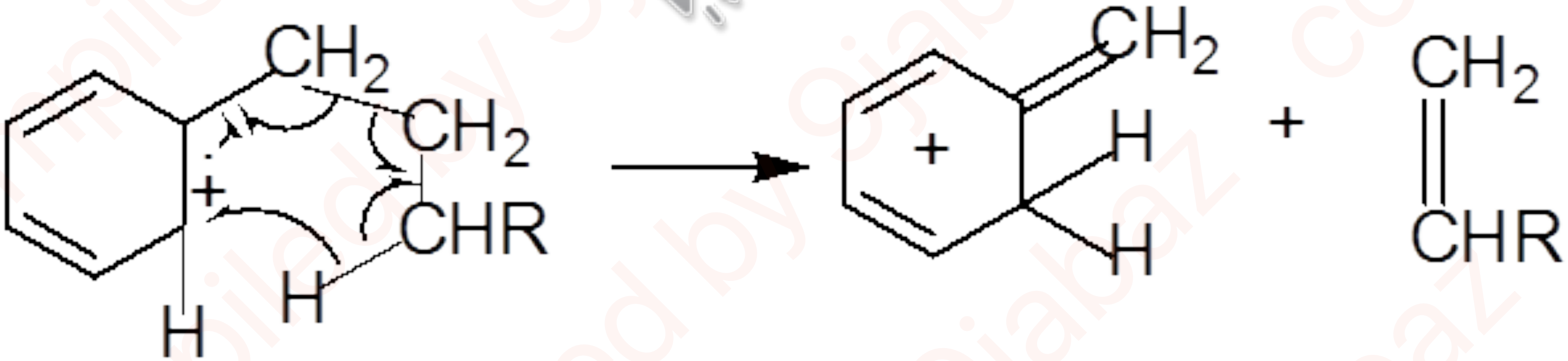




Mass spectrum of an alkene


e^- (fast)
M^+
m/e = 56
$-\ CH_3\bullet$
M - 15
m/e = 41
$-\ C_2H_5\bullet$
M - 29
m/e = 27

Aryl-alkyl hydrocarbons



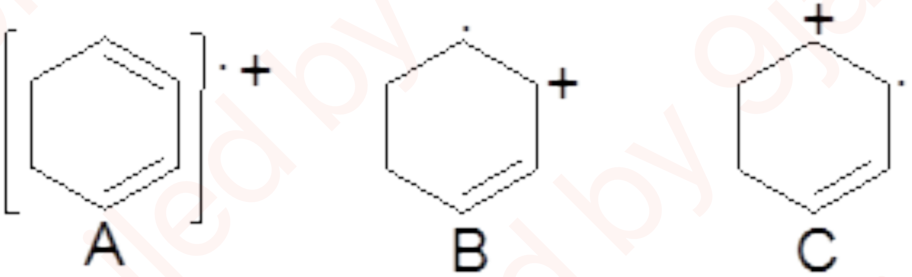
Fragmentation

- The rationalizations used to correlate spectral patterns with structure can rather be considered elegant.

- The insight provided by the pioneers such McLafferty, Beynon and others led to a number of rational mechanisms of fragmentation.

- The tendency is to represent the molecular ion with a delocalized change. The positive charge is localized on either a bond (except in conjugated systems) or on a hetero atom.

- For example, structures A & B represent the molecular ion of cyclohexadiene.

- 

- Generally, fragmentation is initiated by EI. Only small part of the driving force for fragmentation is energy transferred as of result of the impact. The major driving force is the cation – radical character that is imposed on the structure.

- Fragmentation of the odd-e- molecular ion (radical cation, M.T) may occur by homolytic or heterolytic cleavage of a single bond. In homolytic cleavage, each e-moves independently; the fragments produced are an even-e- cation and a free radical (odd electron).

- In heterolytic cleavage, a pair of e-s move together toward the charged site; the fragments produced are an even e-cation and a radical, but here the charge is on the alkyl product.

Hydroxyl-Compounds – Alcohols

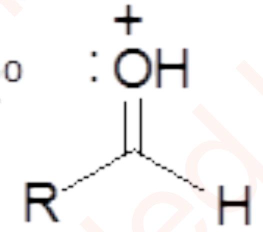
- The molecular ion peak of a 1° or 2° alcohol is quite small and for 3° alcohol is undetectable.

- Cleavage of the C-C next to O–atom is of the general occurrence (|Rule 8). Thus, 1° alcohols show a prominent peak due to

$CH_2=\overset{+}{O}H$

- 2° and 3° cleave analogously to give prominent peaks due to:-

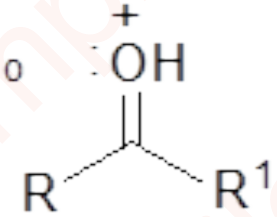
2°



(m/z 45, 59, 73, etc)

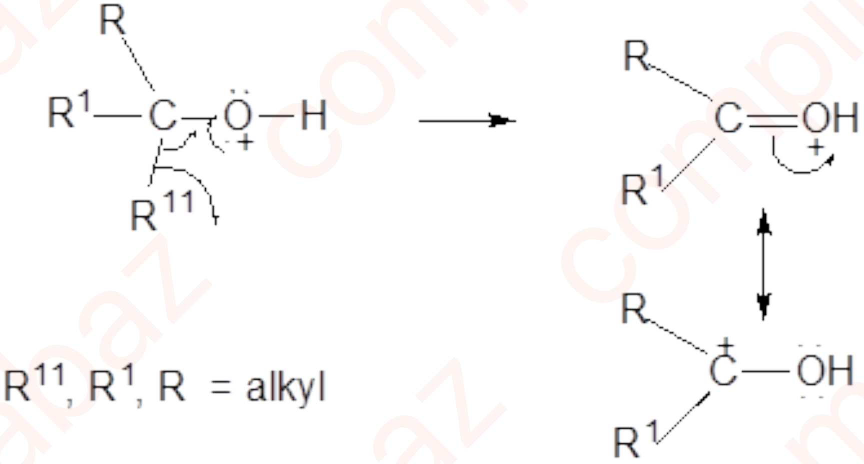
or

3°

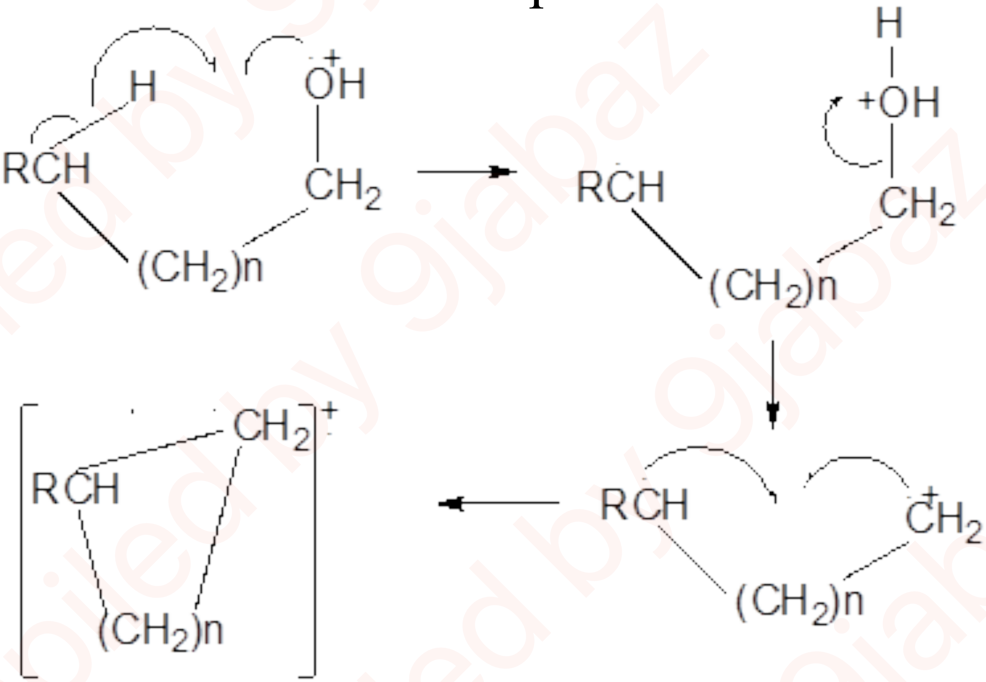


(m/z 45, 59, 73, 87 etc)

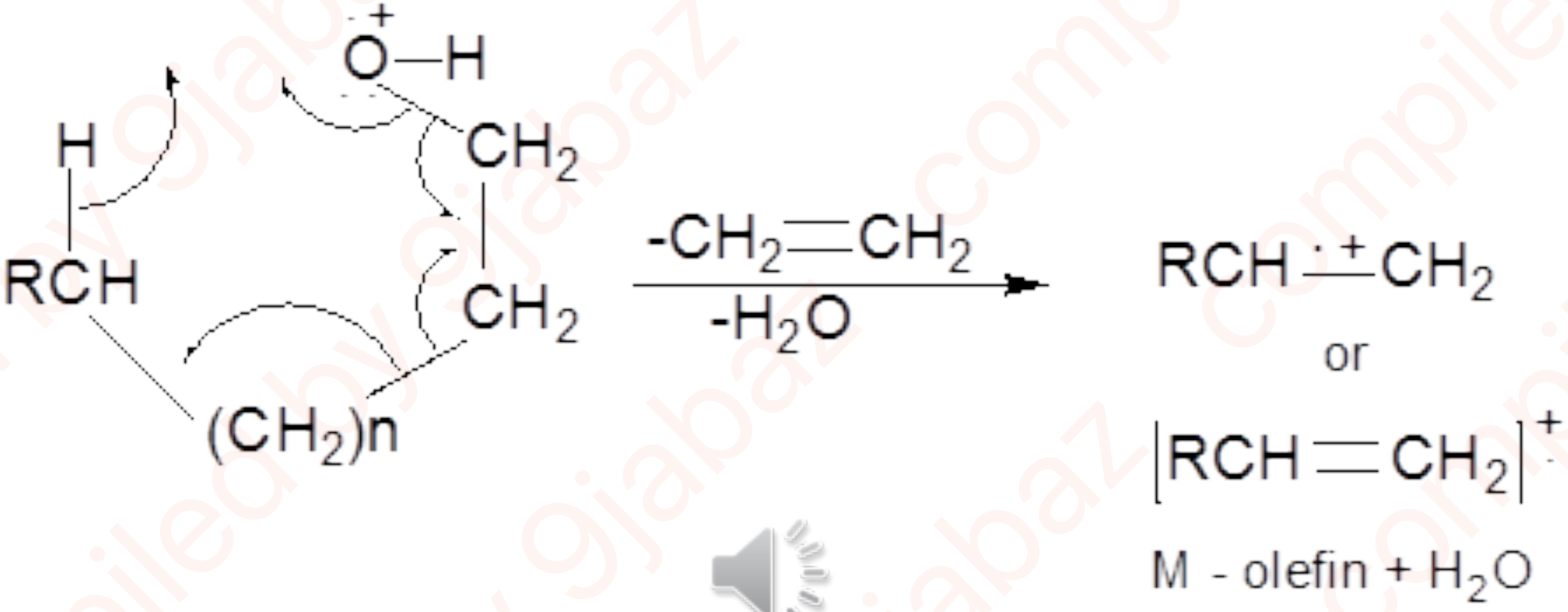
- The largest substituent is expelled most readily (Rule 3) e.g

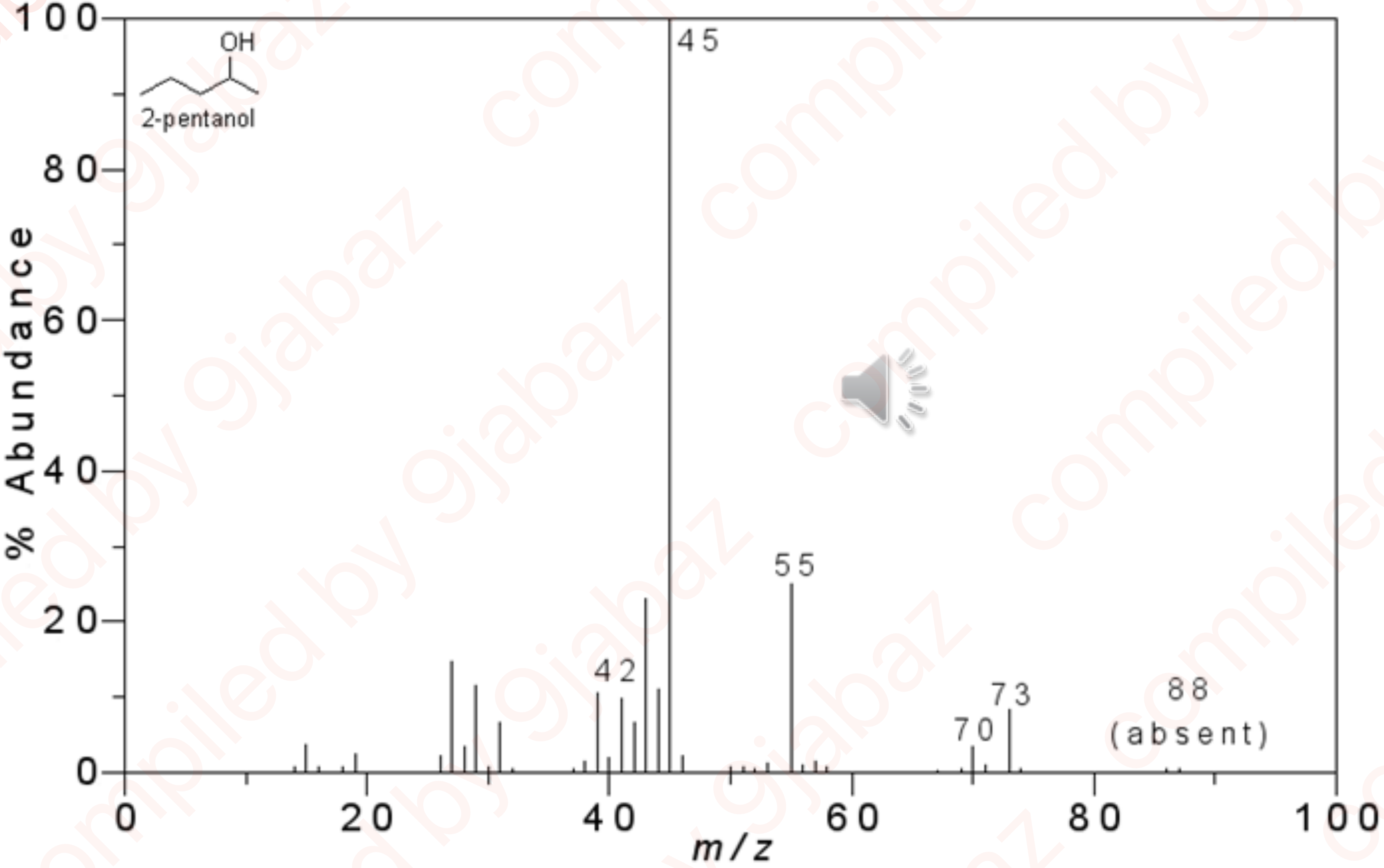


- A distinct peak can usually be found at M-18 from loss of H_2O. This peak is most noticeable in the spectra of 1° alcohols.

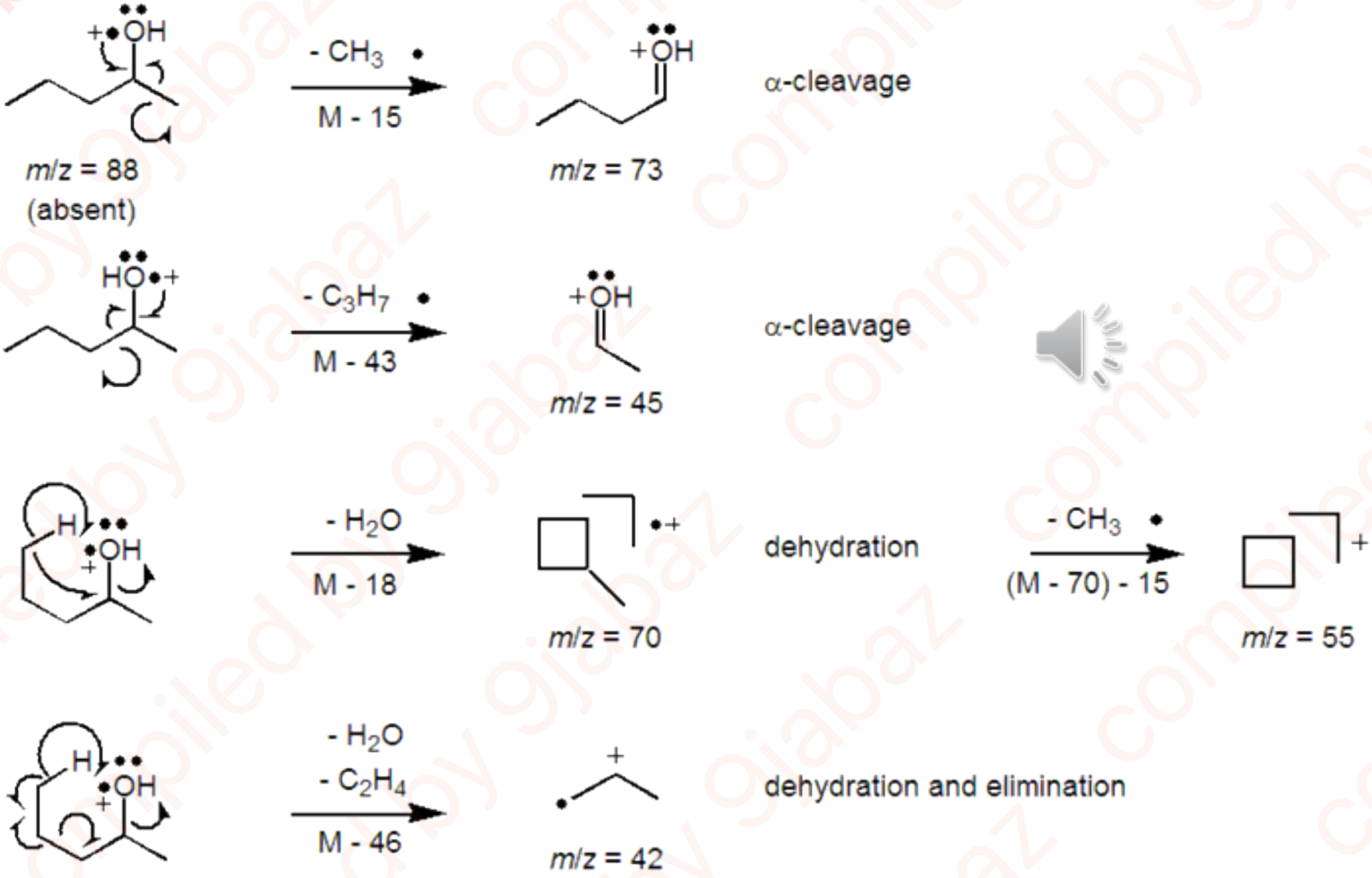


- Elimination of water, together with elimination of an olefin from 1° alcohol accounts for the presence of a peak at M (olefin + H_2O) is a peak at M-46; M-74, M-102 etc.
-





A typical mass spectrum of alcohol



$m/z = 88$ (absent) $\xrightarrow[M - 15]{- CH_3 \bullet}$ $m/z = 73$ α-cleavage

$\xrightarrow[M - 43]{- C_3H_7 \bullet}$ $m/z = 45$ α-cleavage

$\xrightarrow[M - 18]{- H_2O}$ $m/z = 70$ dehydration $\xrightarrow[(M - 70) - 15]{- CH_3 \bullet}$ $m/z = 55$

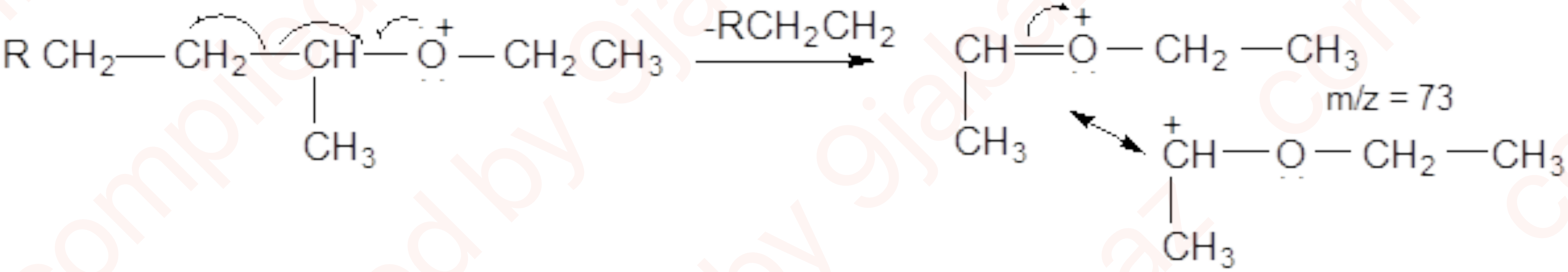
$\xrightarrow[M - 46]{- H_2O,\ - C_2H_4}$ $m/z = 42$ dehydration and elimination

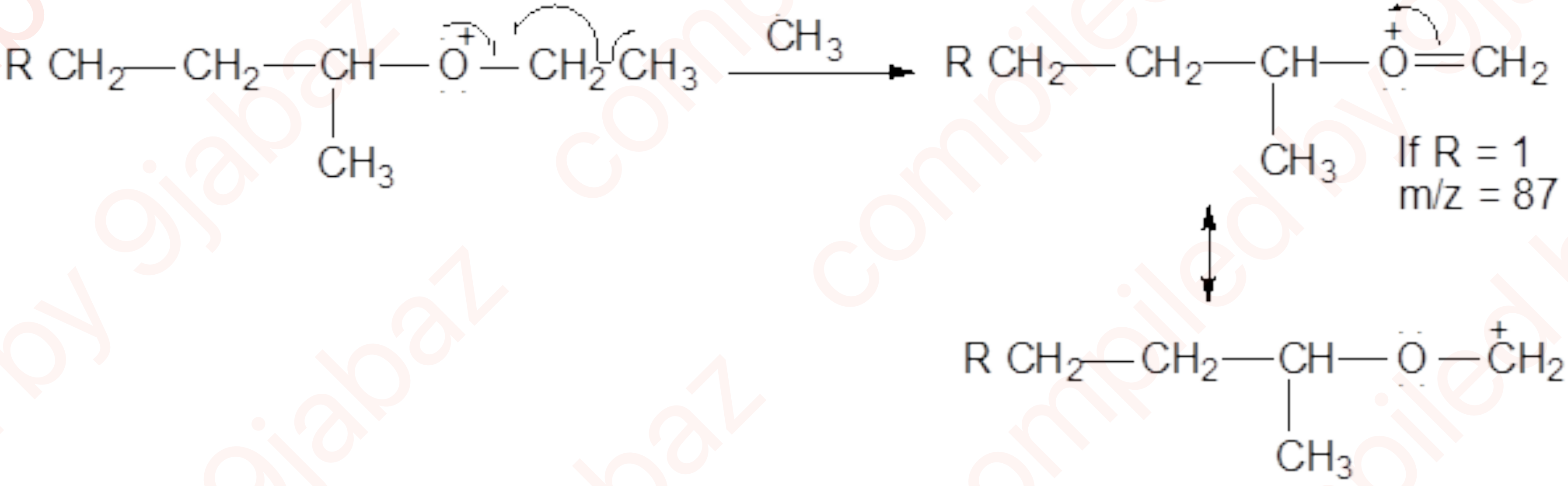
Ethers (Aliphatic)

- The molecular ion peak (which is 2 mass units larger than that of an analogous hydrocarbon) is small.
-
- Presence of an oxygen atom can be deduced from strong peak at m/z 31, 45, 59, 73. These fragments represent the RO^+ and $ROCH_2^+$fragments.

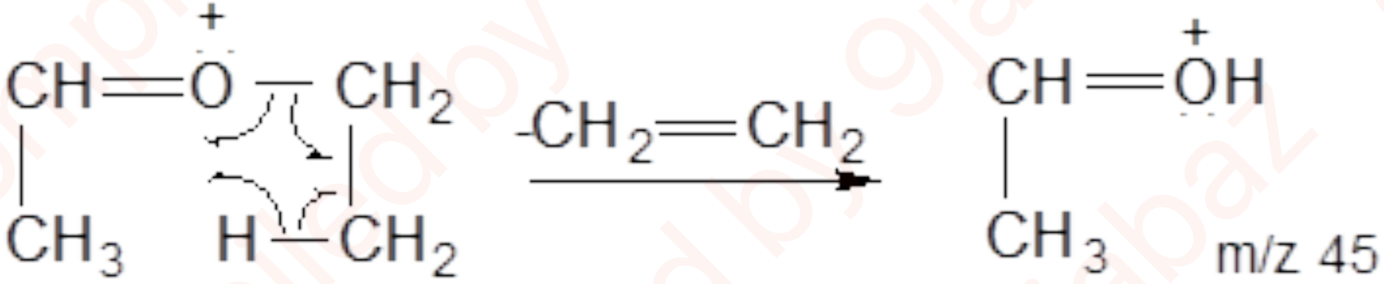
- Fragmentation occurs in two principal ways:-

(a) Cleavage of C-C bond next to the oxygen atom (- bond Rule 8)

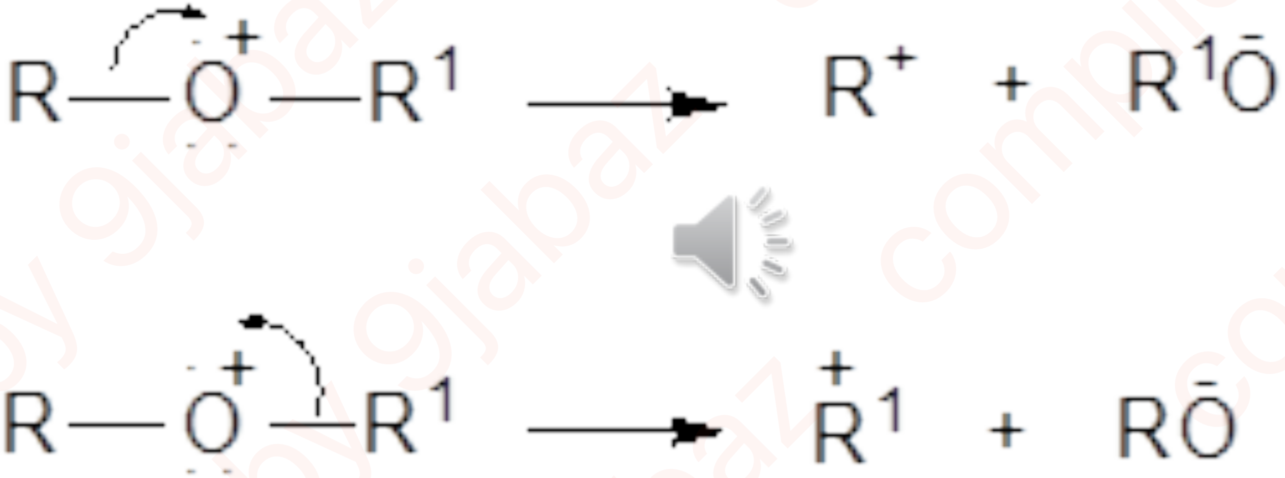




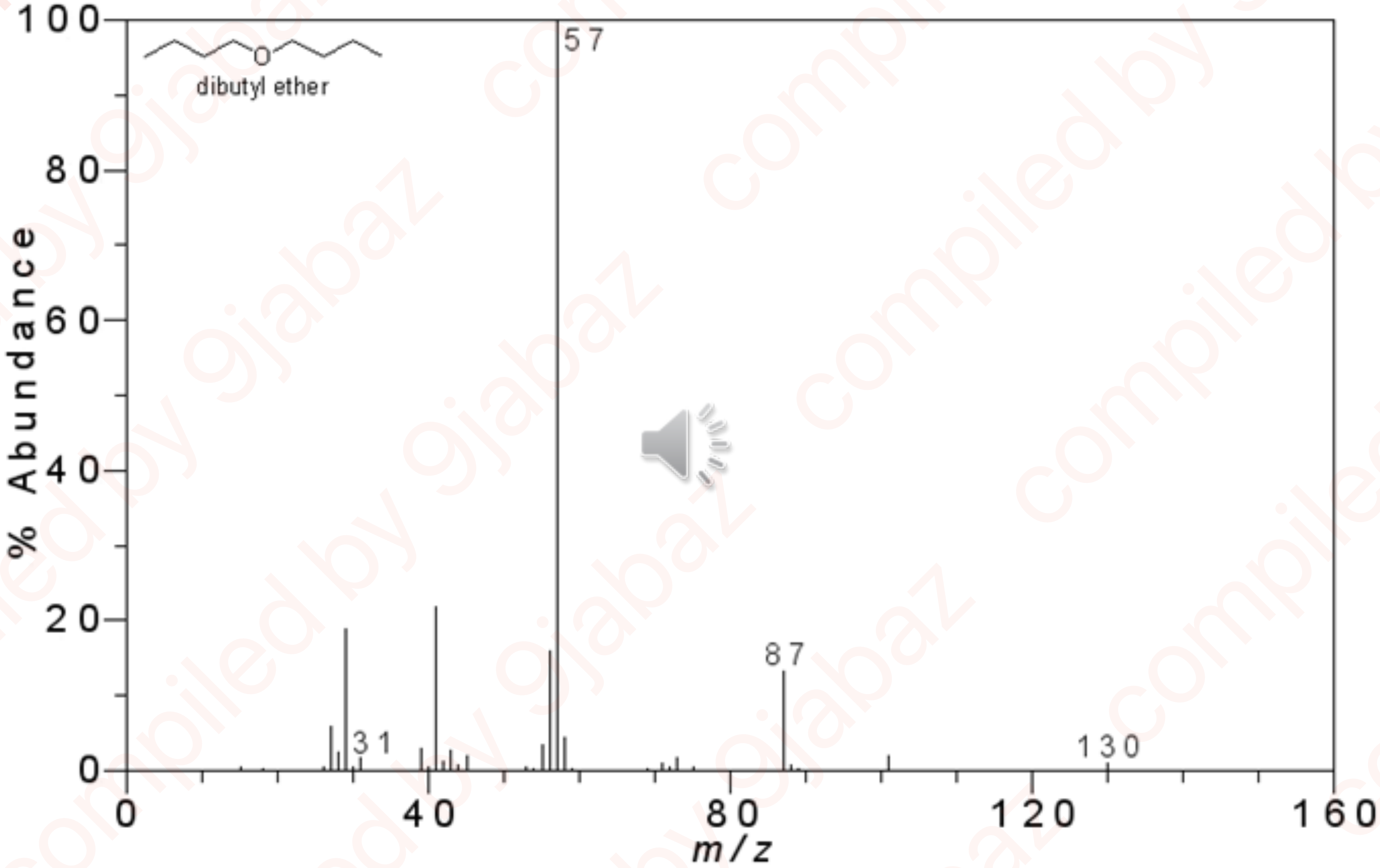
- One of these oxygen containing ions may account for the base peak.
- In the case shown, the 1st cleavage is at the branched C-atom to lose the larger fragment is preferred.
- Thus, the first formed fragment decomposes further by the following mechanism to give the base peak. The decomposition is important when -carbon is branched.



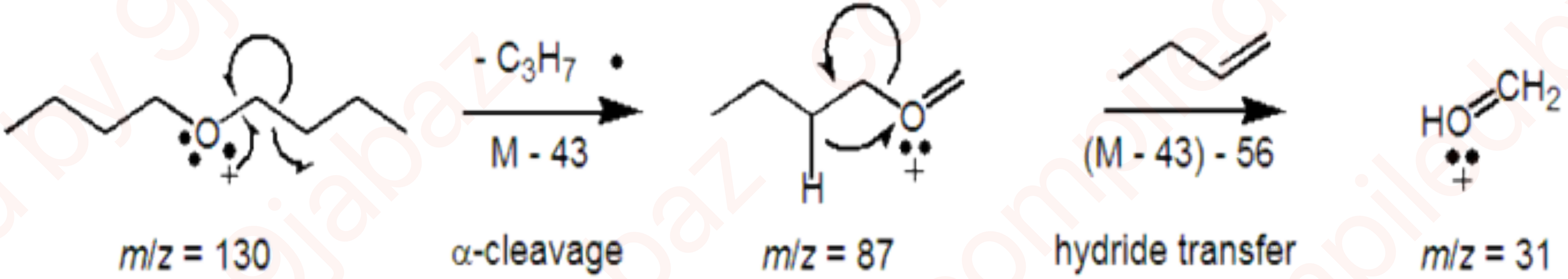
(b) C-O- bond cleavage with charge remaining on the alkyl fragment.

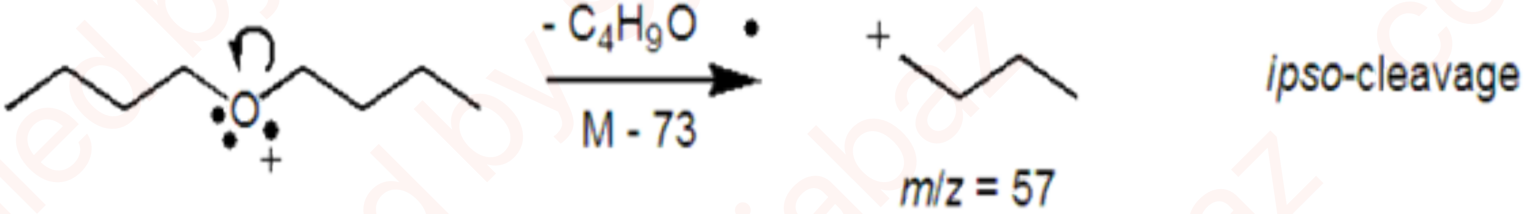


- As expected, the spectra of long chain ethers become dominated by the hydrocarbon pattern.



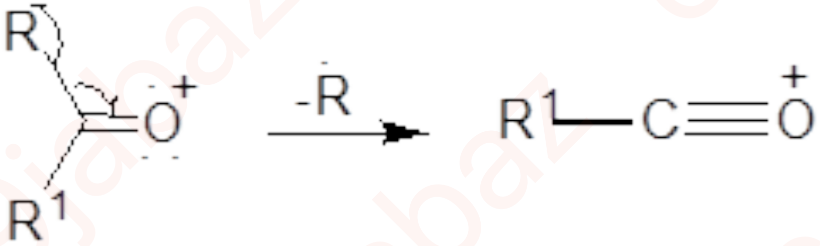
A typical mass spectrum of ether


m/z = 130
$- C_3H_7 \bullet$
M - 43
α-cleavage
H
m/z = 87
(M - 43) - 56
hydride transfer
$HO{=}CH_2$
m/z = 31

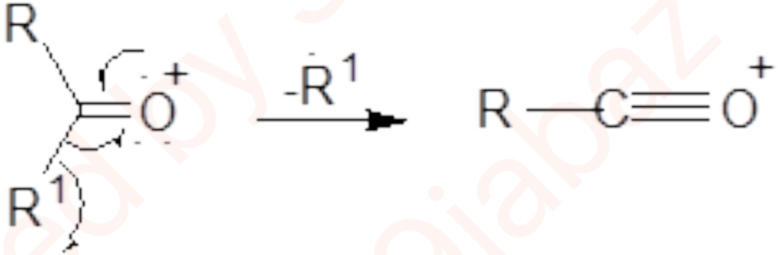

$- C_4H_9O \bullet$
M - 73
m/z = 57
ipso-cleavage

Ketones – (Aliphatic)

- As with alcohols and ethers, cleavage is again at the C-C bond next to oxygen atom.

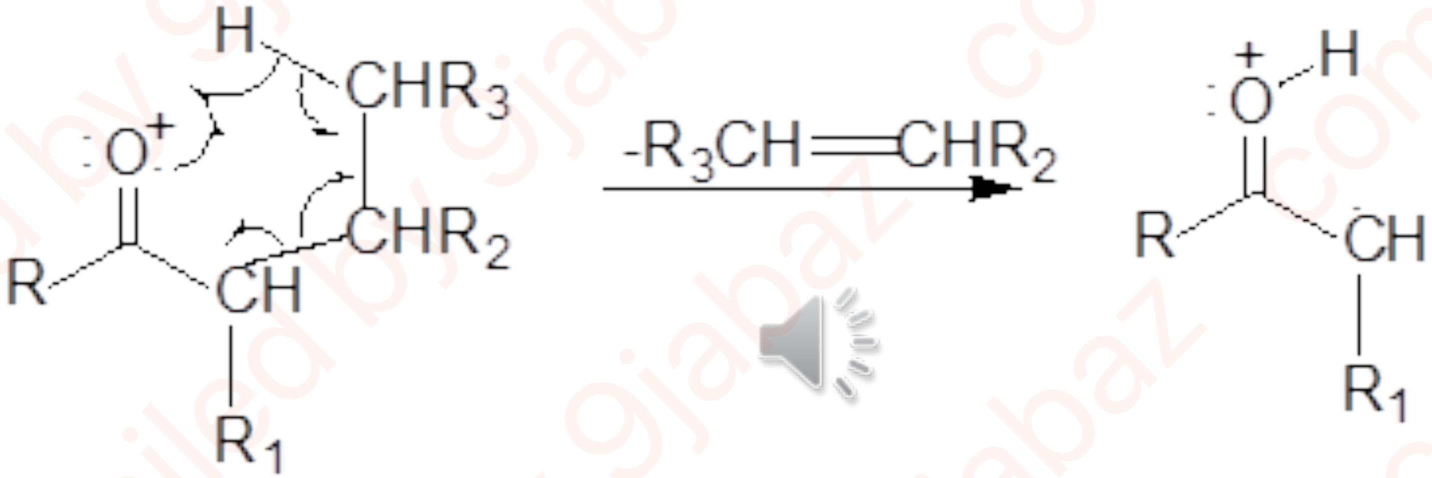


- This cleavage gives rise to a peak at m/z 43 or 57.



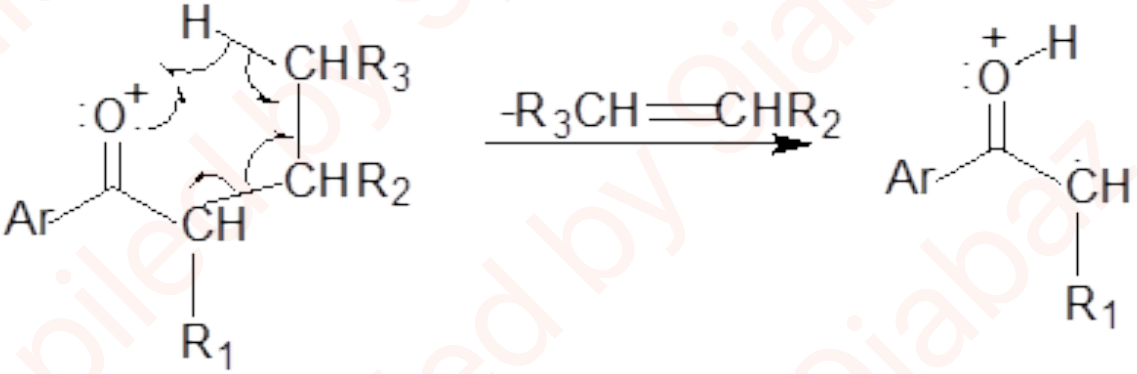
- The base peak very often results from the loss of the larger alkyl group.

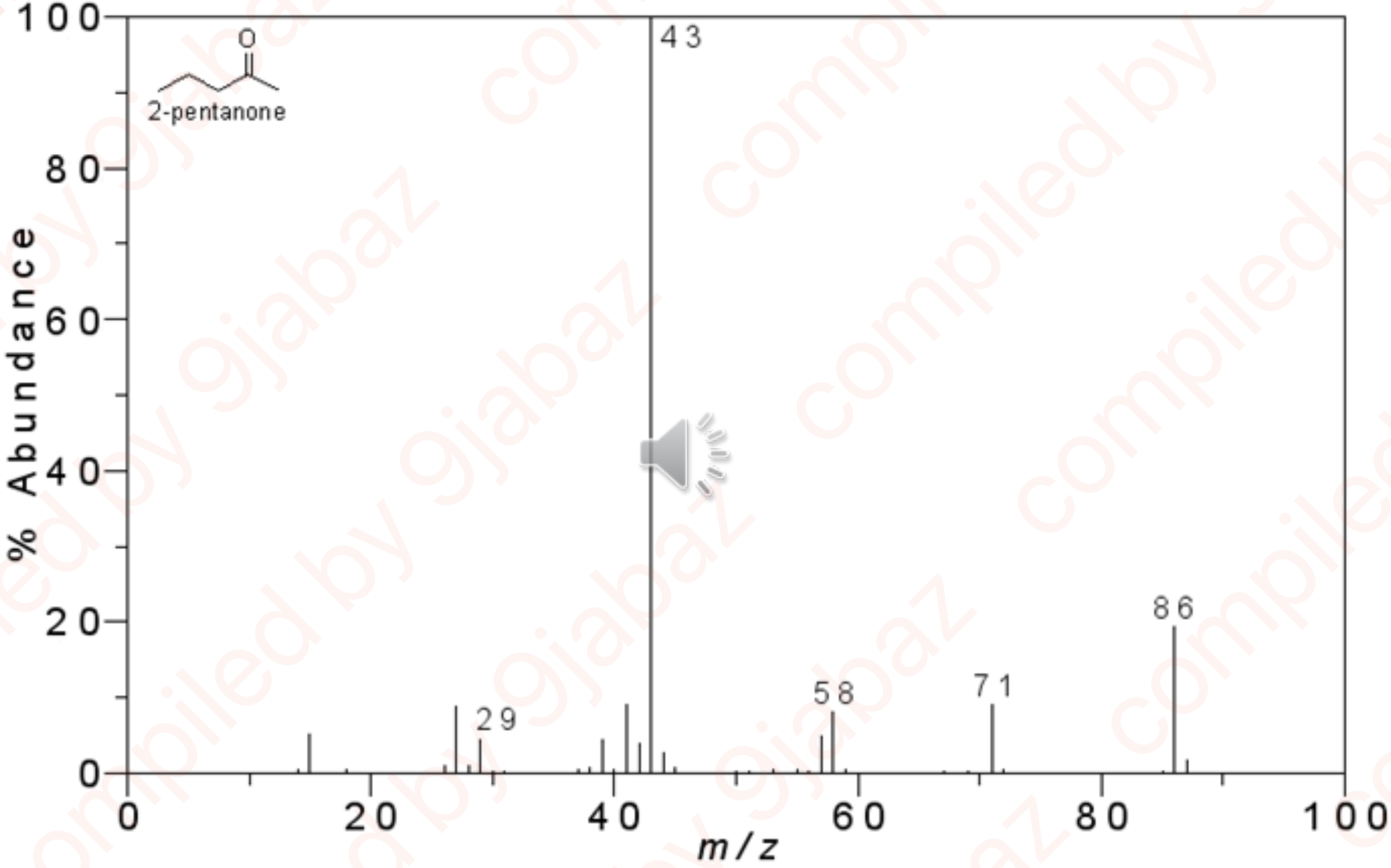
- When one of the alkyl chains attached to the C = O group is C_3 or larger, cleavage of the C-C bond once removed from the C=O group occurs with hydrogen rearrangement to give a major peak at m/z 58 or 72 or 86 (McLafferty rearrangement).



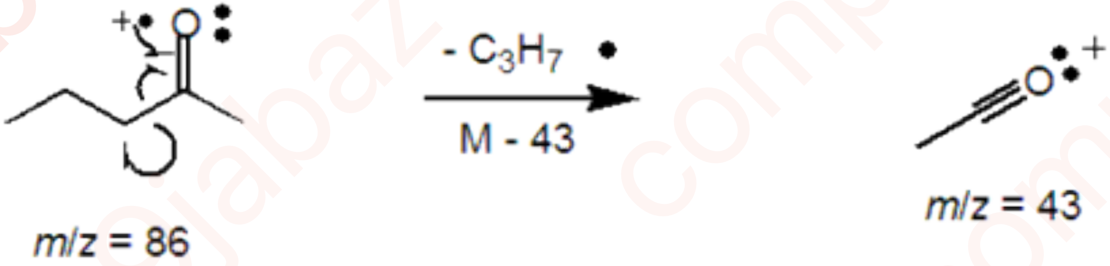
Aromatic Ketones

- The molecular ion peak of aromatic ketones is prominent.
- Cleavage aryl alkyl ketone occurs at the bond beta to the ring, leaving a characteristic $ArC\equiv\overset{+}{O}$ fragment which usually accounts for the base peak.
- Loss of CO from this fragment gives the phenyl ion (m/z 77 in case of acetophenone).
- Cleavage of bond adjacent to the ring to form a $RC\equiv\overset{+}{O}$ fragment is less important though can be enhanced by electron –withdrawing groups (and diminished by electron donating group) in the preposition of the aromatic ring.
- When the alkyl is C_3 or larger and there is a γ-hydrogen, McLafferty rearrangement can be achieved as with aliphatic ketones.

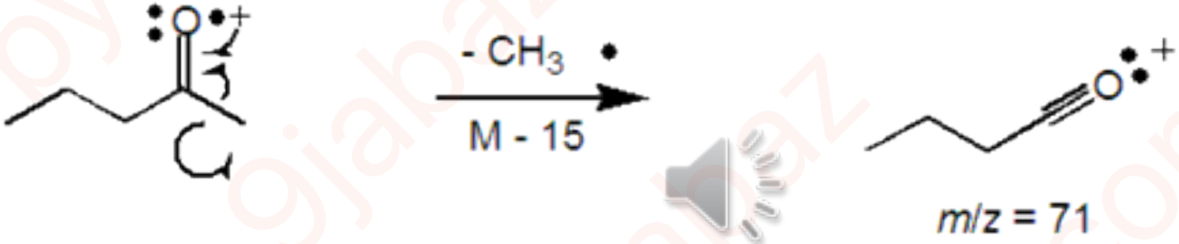




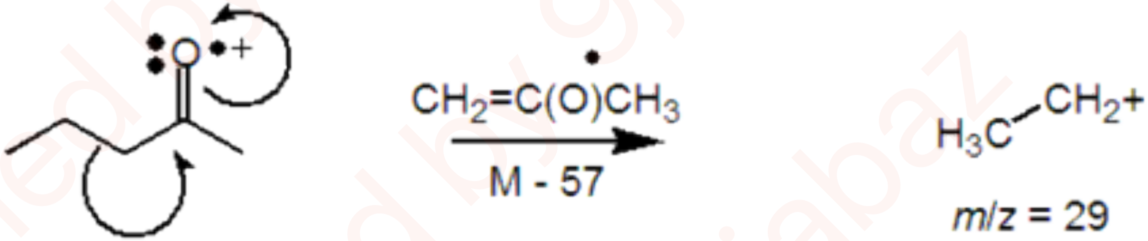
A typical mass spectrum of ketone



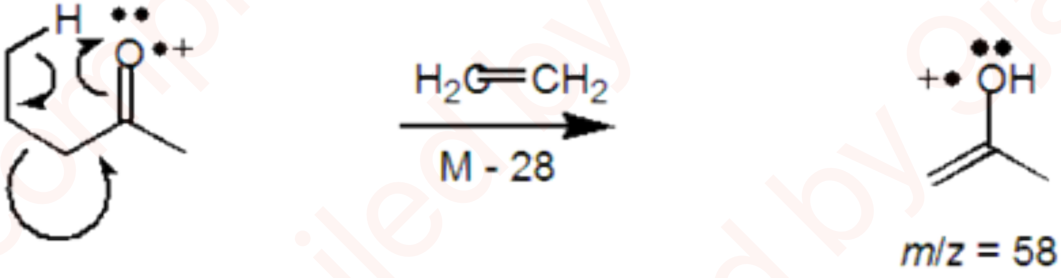
α-cleavage



α-cleavage



β-cleavage



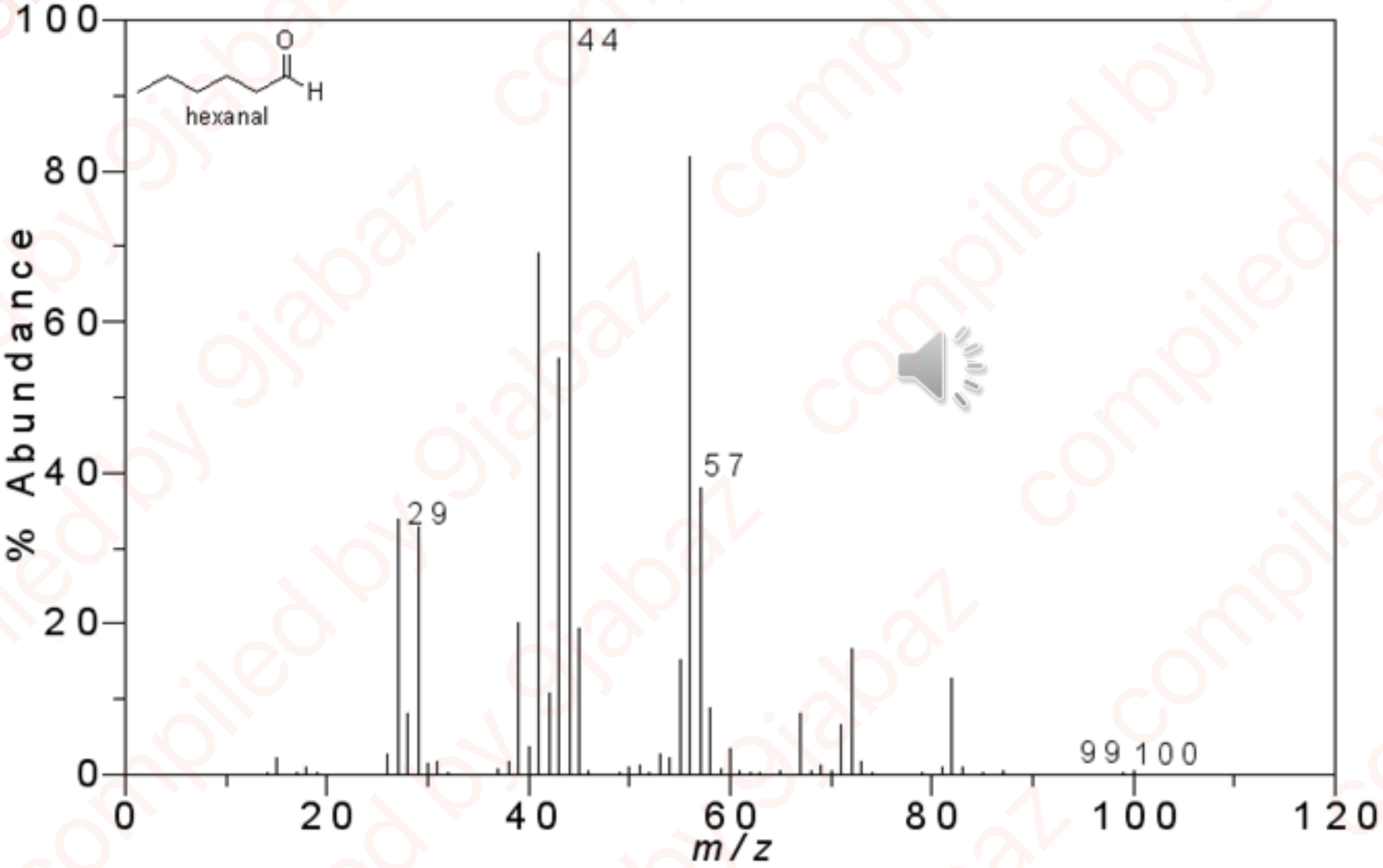
McLafferty rearrangement

Aliphatic Aldehydes

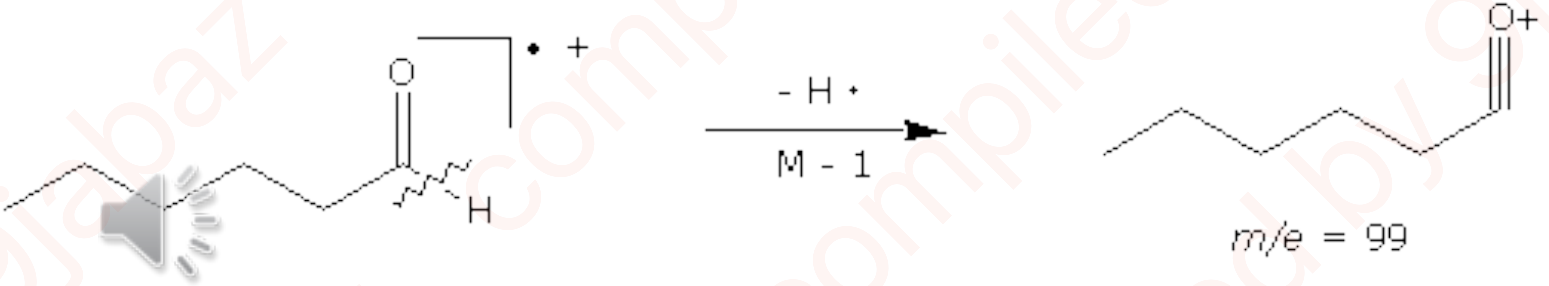
- The molecular ion peak is present.

- Cleavage of the C-H and C-C bond next to the O-atom results in an M-1 peak and in an M-R peak (m/z 29, CHO^+).

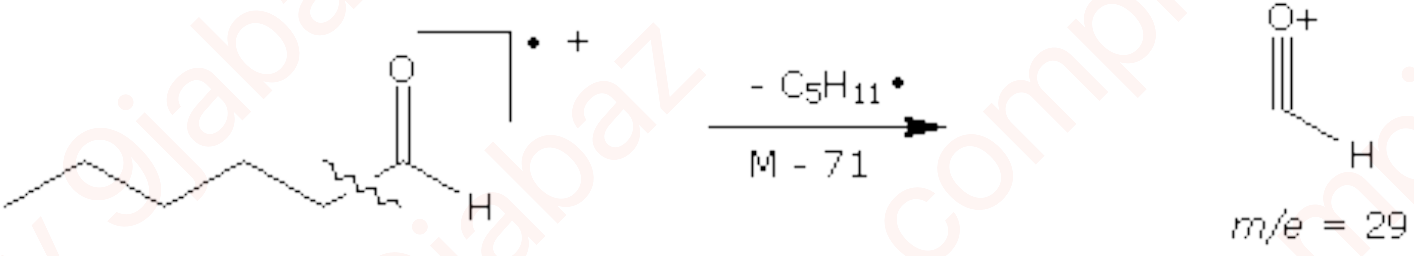
- The M-1 peak is a good diagnostic peak even for long chain aldehydes



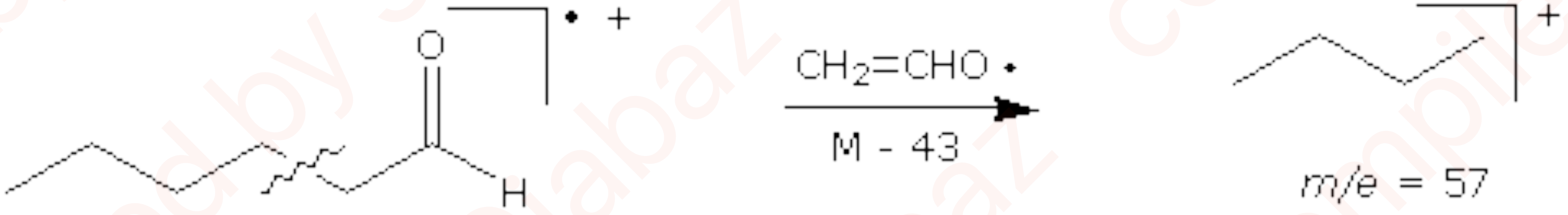
A typical mass spectrum of aldehyde



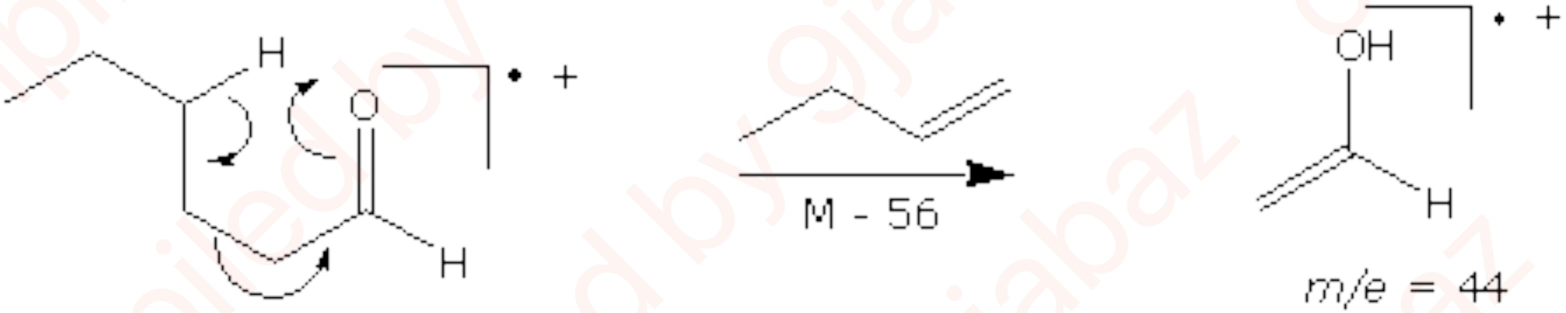
O
H
- H •
M - 1
O+
m/e = 99



O
H
- C5H11 •
M - 71
O+
H
m/e = 29



O
H
CH2=CHO •
M - 43
+
m/e = 57



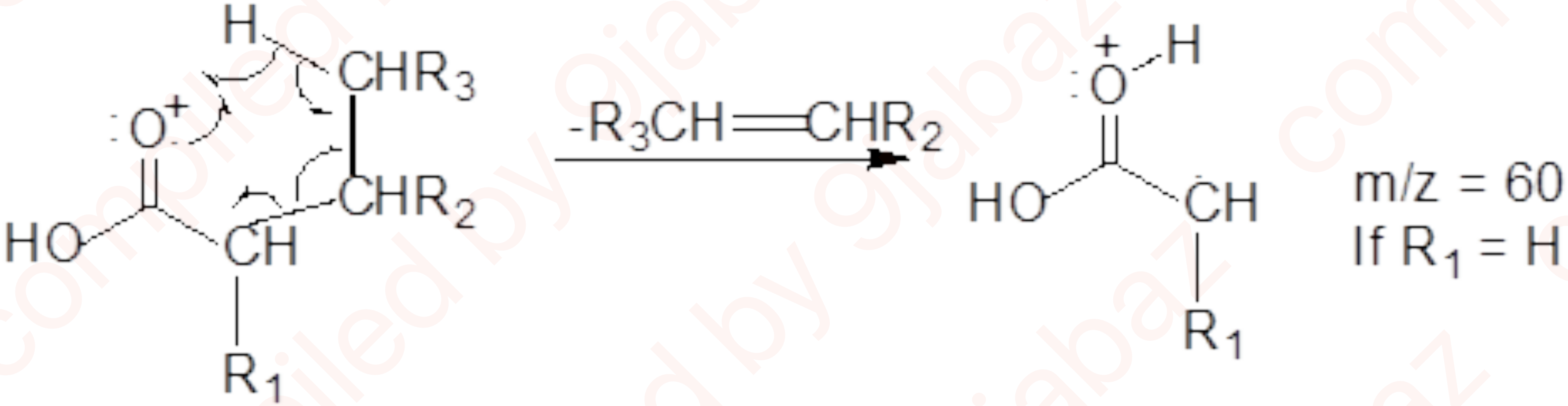
H
O
H
M - 56
OH
H
m/e = 44

Aliphatic Carboxylic Acids

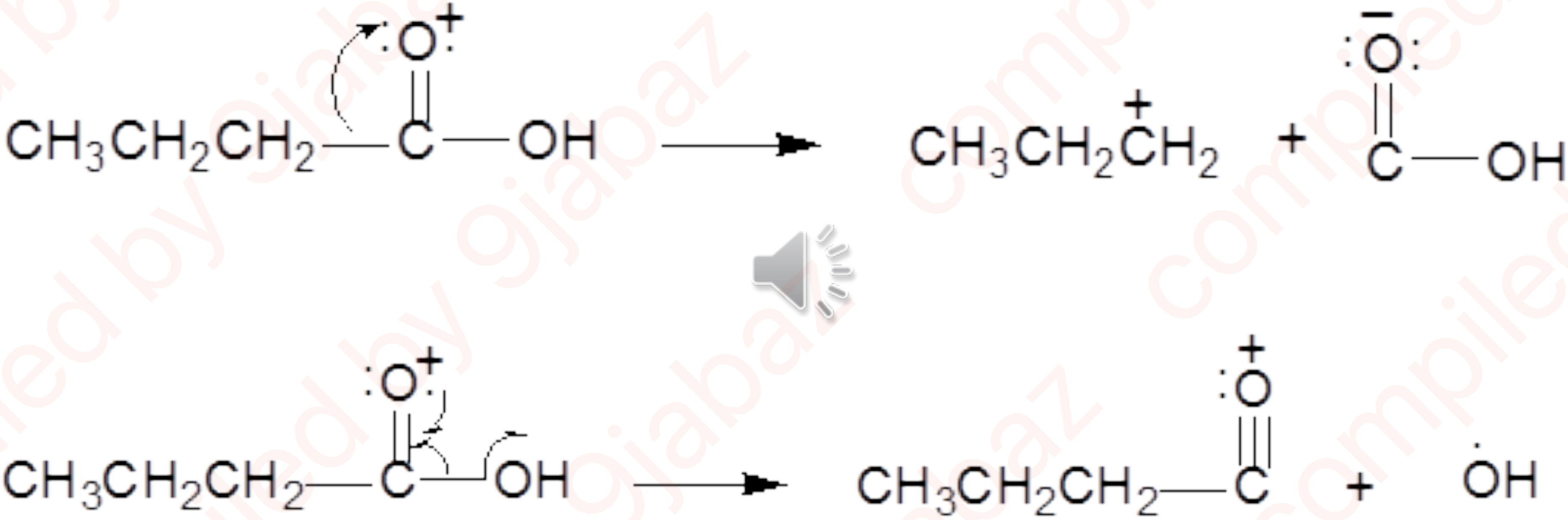
- The molecular ion peak of straight chain mono-carboxylic acid is weak but can be obtained.

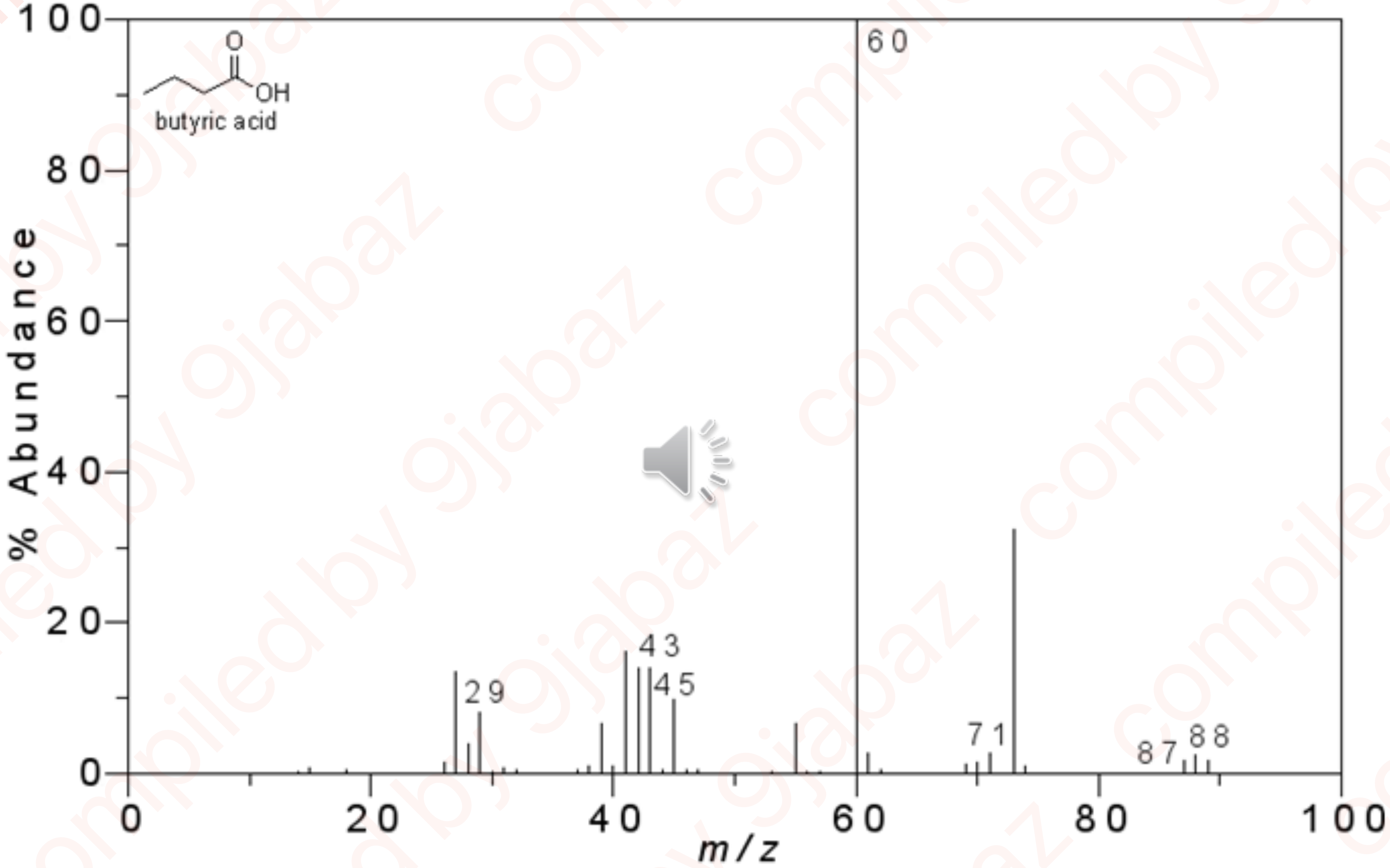
- The most characteristic peak (sometimes the base peak) is m/z 60 due to McLafferty rearrangement.

- Branching at the α-carbon increases the fragment by the mass of the substituent.

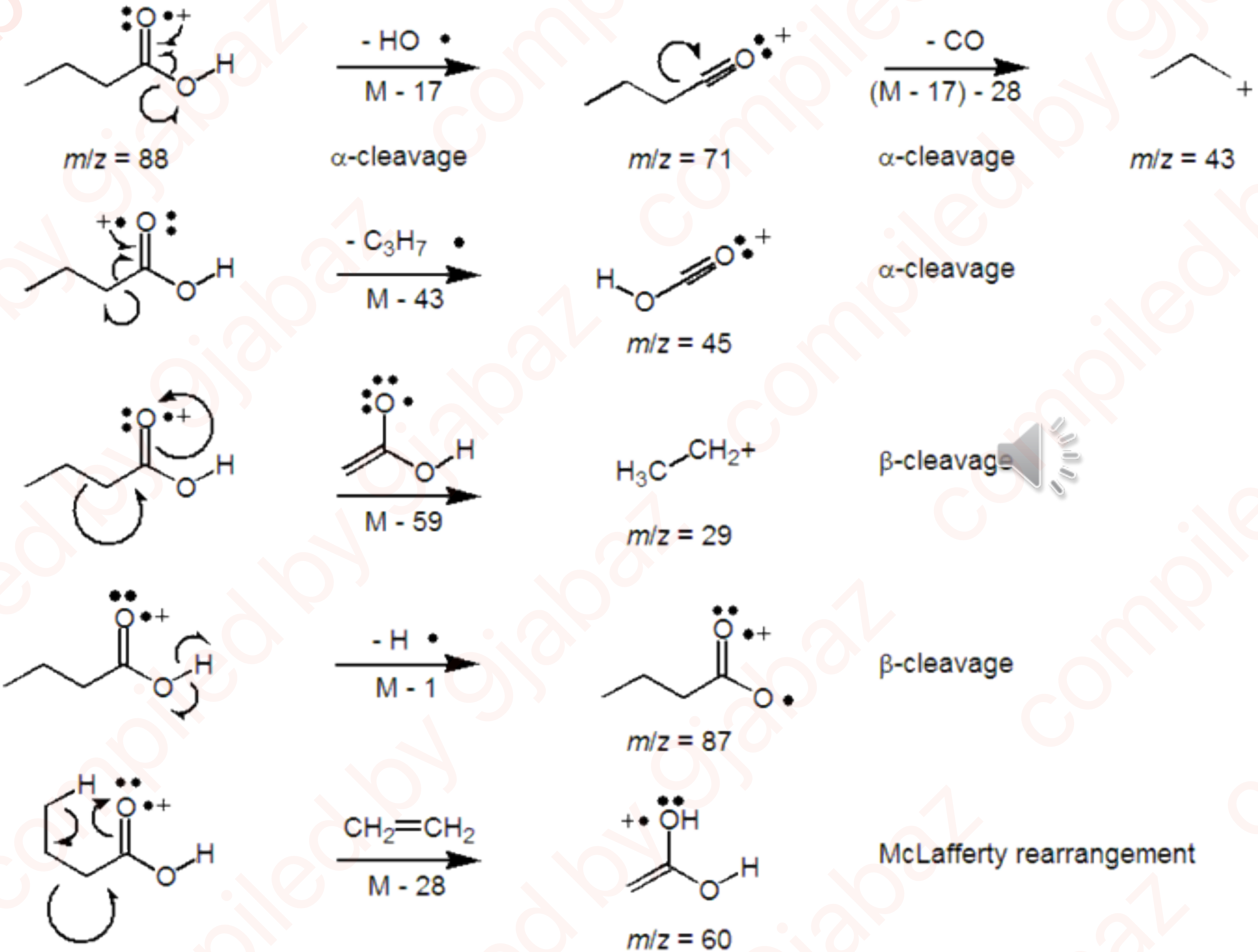


- In short-chain acids, peaks at M-OH and M-COOH are prominent. These represent cleavages of bonds next to C=O i.e.





A typical mass spectrum of carboxylic acid

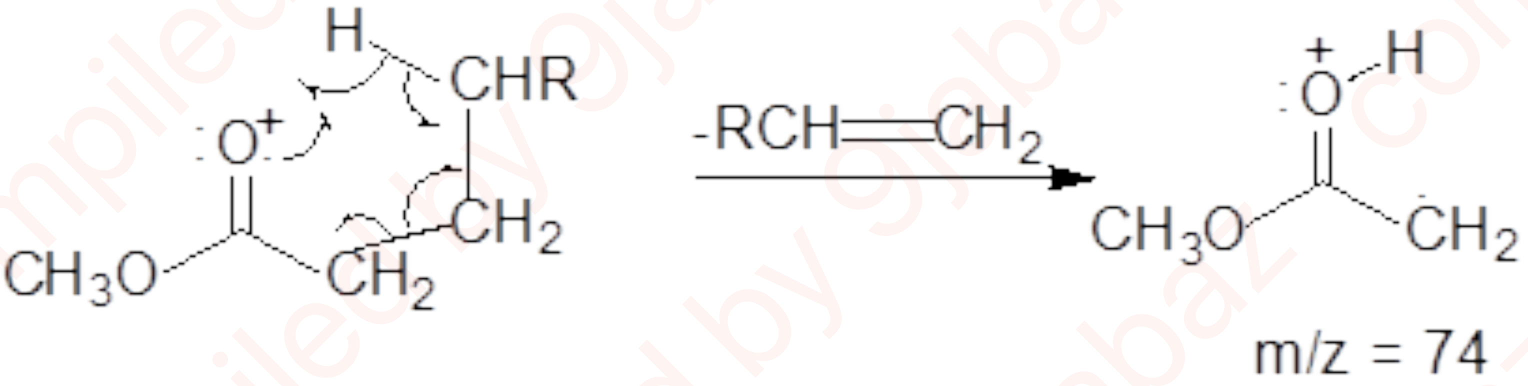

- HO •
M - 17
α-cleavage
- CO
(M - 17) - 28
α-cleavage
m/z = 88
m/z = 71
m/z = 43
- C3H7 •
M - 43
α-cleavage
m/z = 45
M - 59
H3C-CH2+
m/z = 29
β-cleavage
- H •
M - 1
m/z = 87
β-cleavage
CH2=CH2
M - 28
m/z = 60
McLafferty rearrangement

Aliphatic Esters

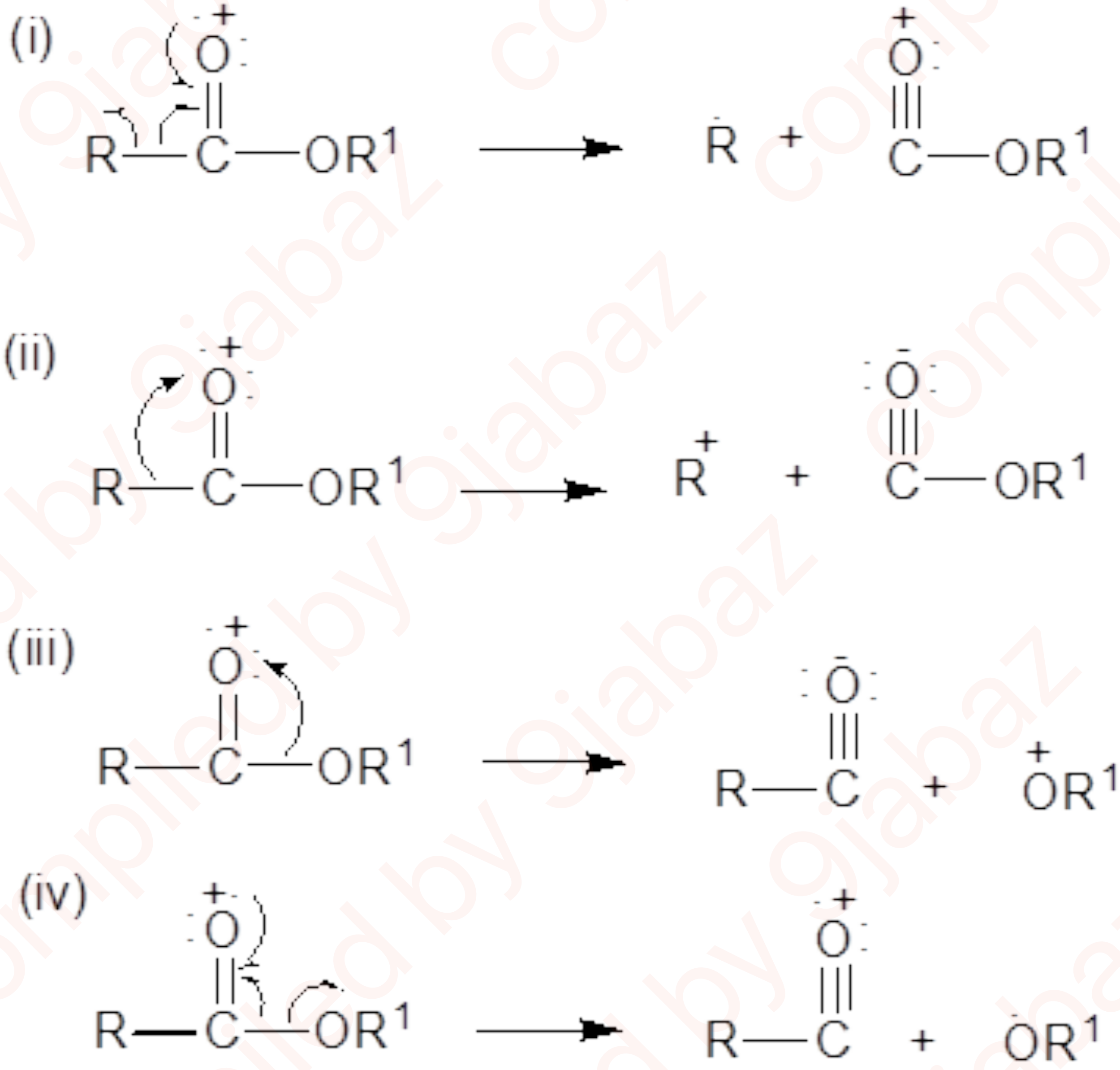
- The molecular ion peak of a methyl ester of a straight chain aliphatic acid is usually distinct.

- The most characteristics peaks are due to McLafferty rearrangement and cleavages of one bond removed from the C=O group.

- Thus, a methyl ester of an aliphatic acid, unbranched at the α-carbon gives strong peak at m/z 74, which is the base peak in straight chain methyl esters from $C_6 - C_{26}$.

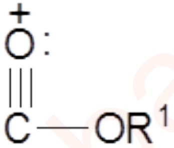


- Four ions can result from bond cleavage next to the C=O.

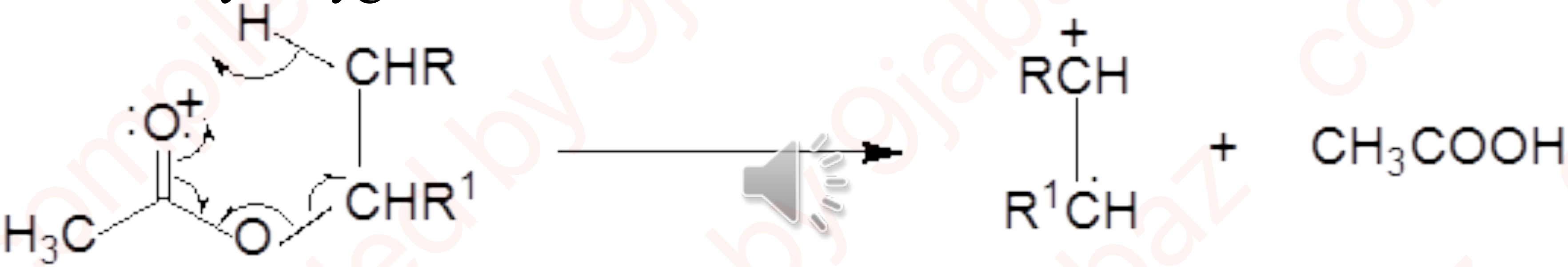


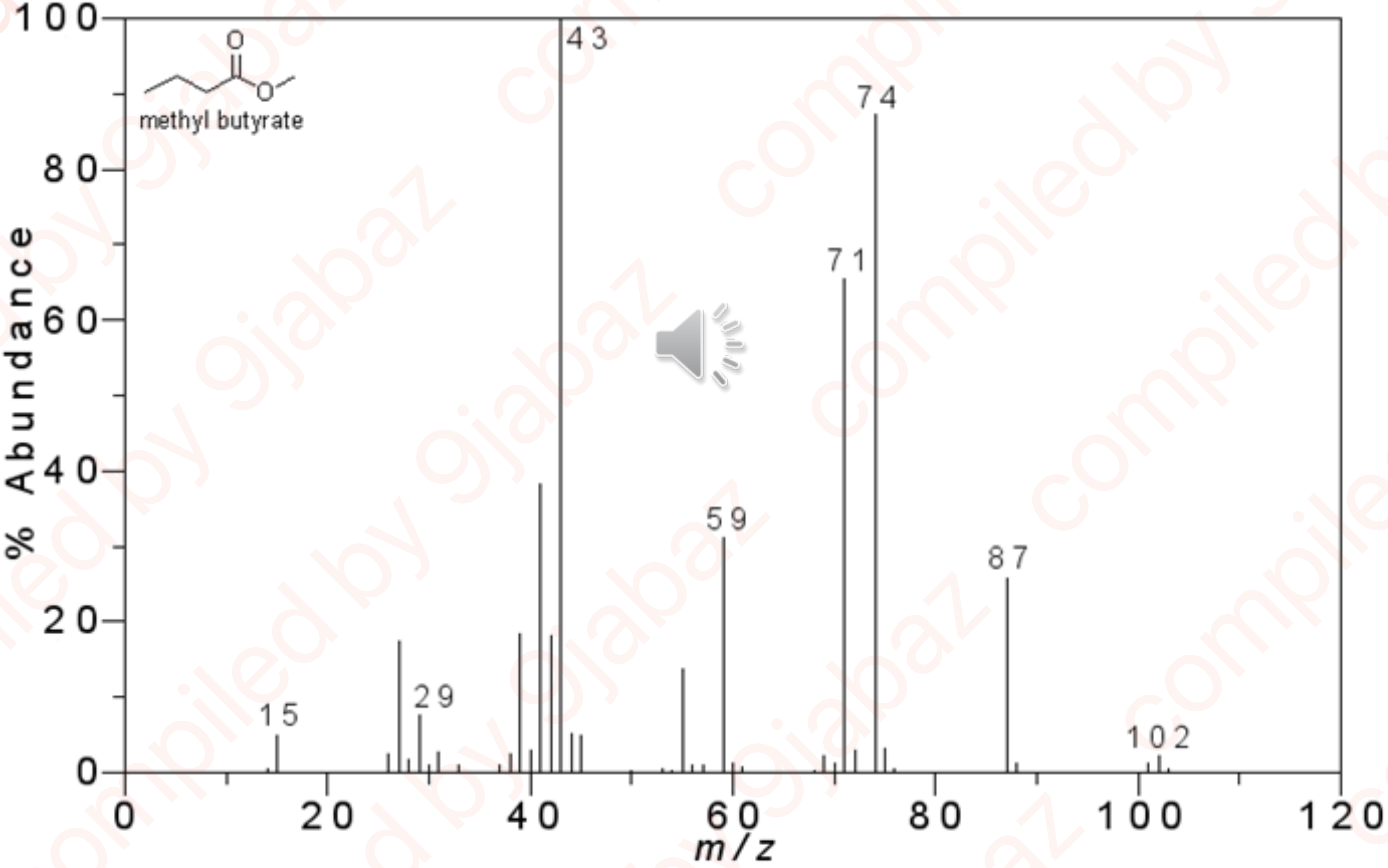
- The ion R^+ is prominent in short chain esters, but diminishes rapidly with increasing chain length.

- The ion $RC\equiv O^+$ gives an excellent diagnostic peak for esters. In methyl esters, it occurs at M-31.

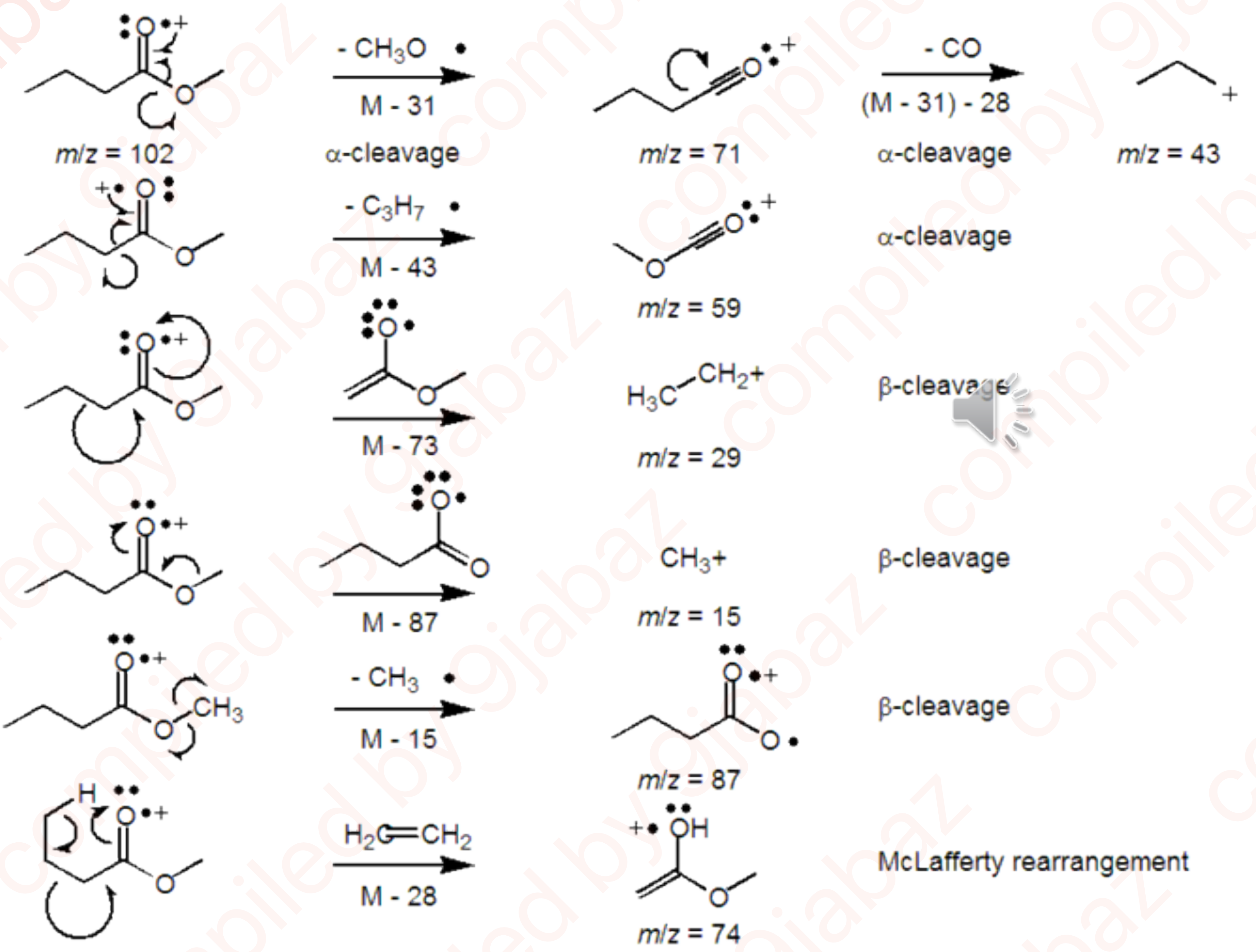
- The ions $(OR^1)^+$ and  $\overset{+}{O}{:}\equiv C-OR^1$ are usually of little importance.

- The loss of ethanoic acid, propanoic acid and benzoic acid from the corresponding ethanoates, propanoates and benzoates respectively can be viewed as follows. It involves hydrogen transfer to the carbonyl oxygen.





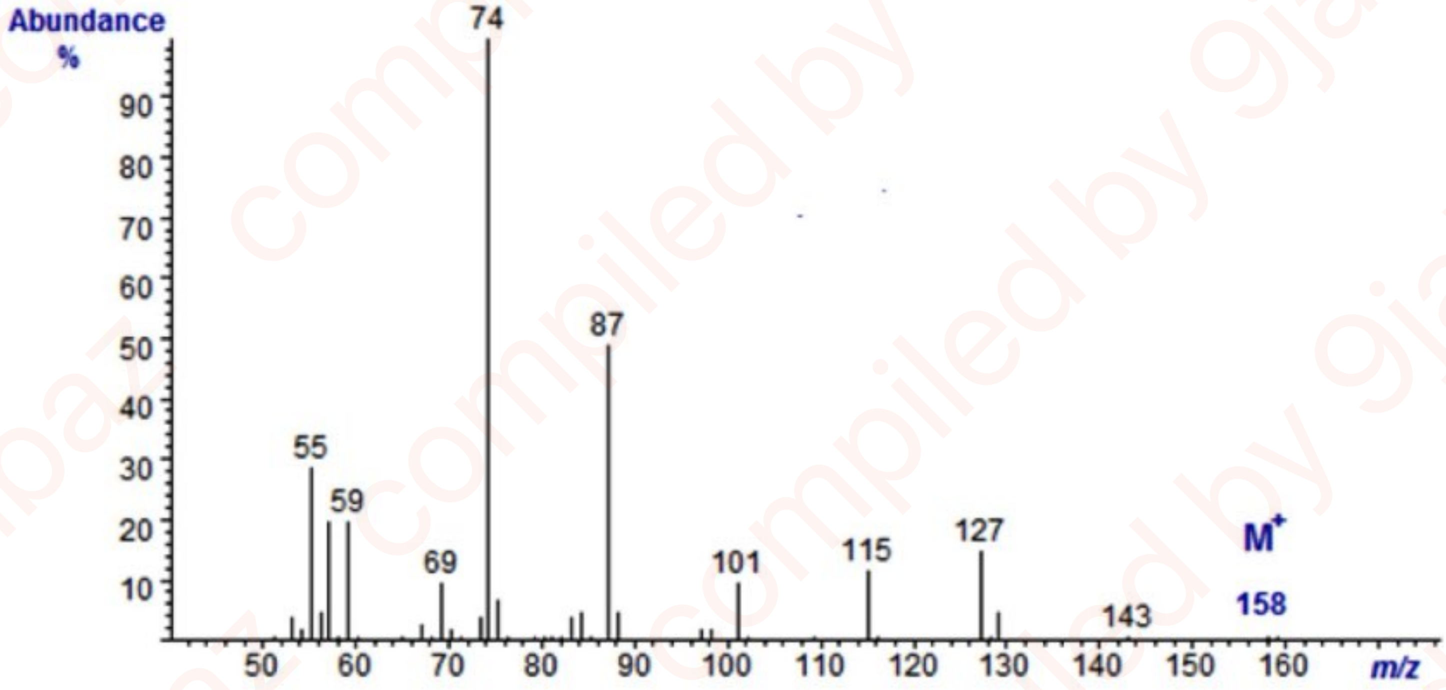
A typical mass spectrum of ester


m/z = 102
- CH3O •
M - 31
α-cleavage
m/z = 71
- CO
(M - 31) - 28
α-cleavage
m/z = 43
- C3H7 •
M - 43
α-cleavage
m/z = 59
M - 73
H3C CH2+
m/z = 29
β-cleavage
M - 87
CH3+
m/z = 15
β-cleavage
CH3
- CH3 •
M - 15
m/z = 87
β-cleavage
H
H2C=CH2
M - 28
OH
m/z = 74
McLafferty rearrangement

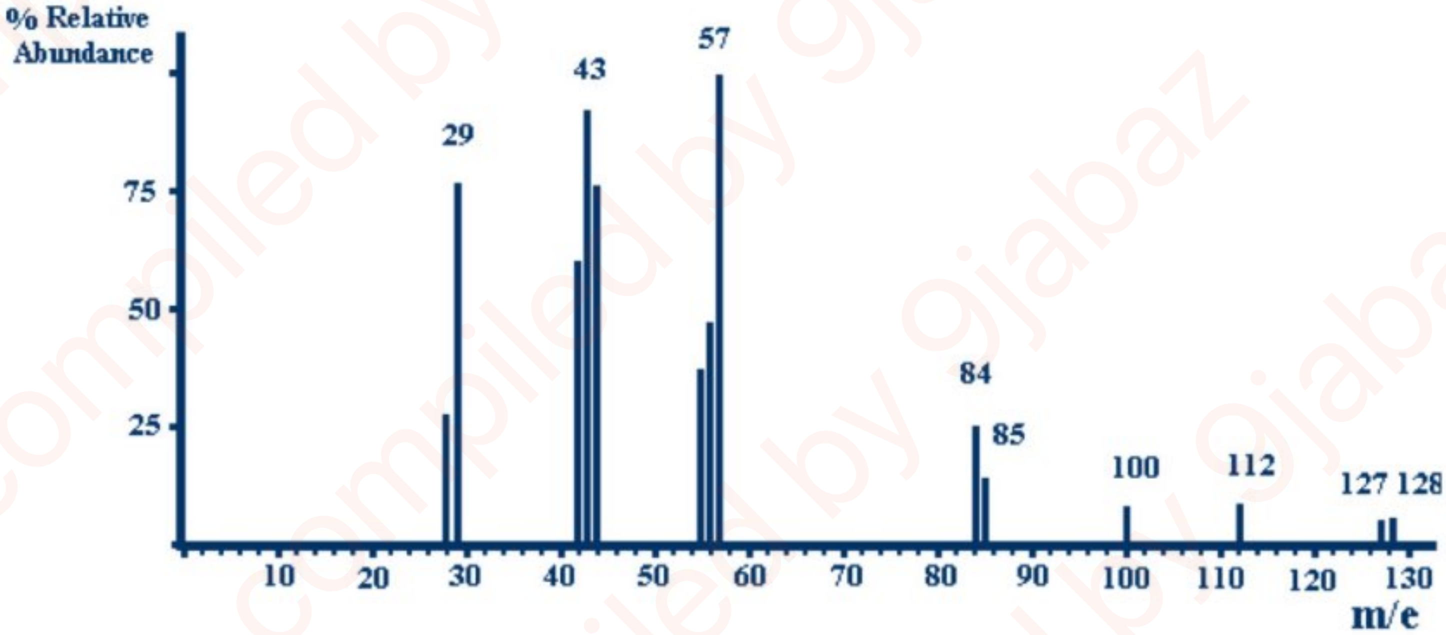
1. The mass spectrum of compound **A**, which is a volatile derivative of a compound that is not volatile is presented below.

(a) Interpret the spectrum and identify the compound

(b) Show the mechanism of fragmentation that resulted in the following ion peaks; m/z 59 and 74.



2. Compound **B** is a product of a reaction between a carboxylic acid and thionyl chloride. Compound **B** was reduced to compound **C** using lithium aluminium tri(t-butoxy) hydride $[LiAlH(OBu\text{-}t)_3]$. The electron impact (EI) mass spectrum of compound **C** is appended below.



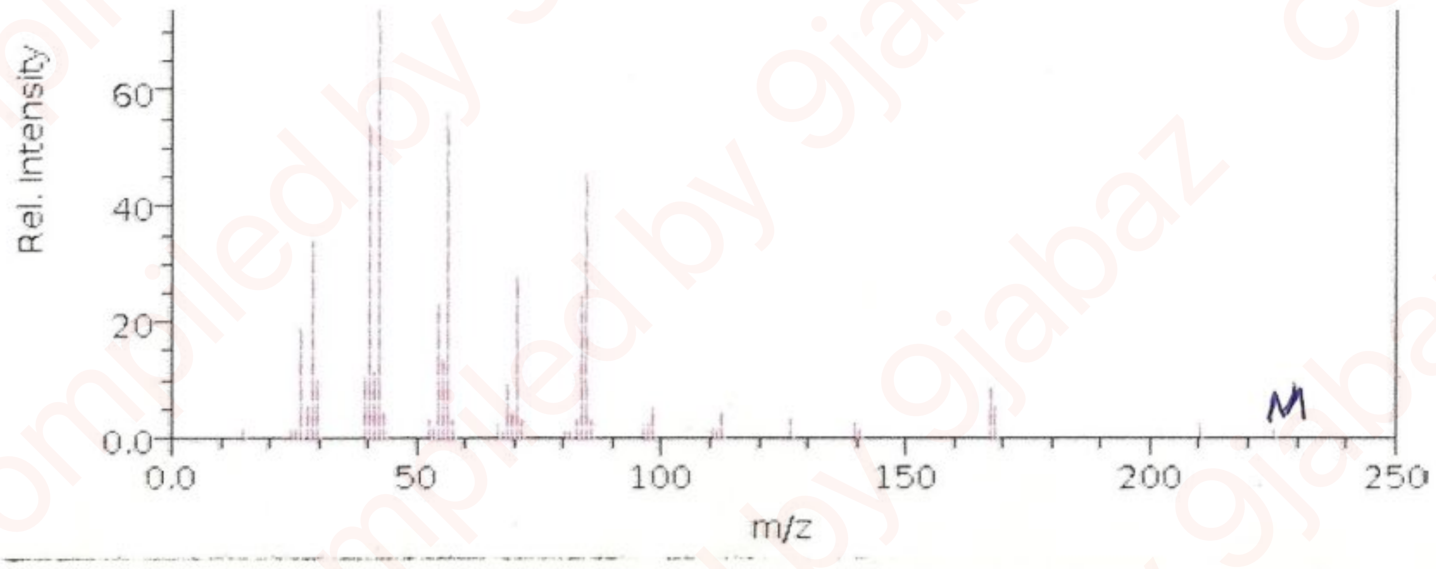
Mass spectrum of compound **C**

a. Interpret the spectrum and identify the compound.
b. Account for the following peaks in the mass spectrum of compound **C**; m/z 29, 57 and 127 and show detailed mechanisms of fragmentations that resulted in the ions of these peaks.
c. What is compound **B**?
d. Write a balanced chemical equation for the synthesis of compound **B** from the carboxylic acid and thionyl chloride as stated above.
e. Write a balanced chemical equation for the reduction of compound **B** to compound **C** as stated above.

3 a. (i) What is the difference between electron impact (EI) technique and direct inlet probe (DIP) technique?
(ii) What is the advantage of using chemical ionization (CI) technique in mass spectrometry?

b. (i) What are the conditions that a molecule must fulfill to undergo McLafferty rearrangement?
(ii) Account for the following peaks in the mass spectrum of butanoic acid; m/z 43, 60 and 71. The mechanism of fragmentation that resulted in each peak must be clearly shown.

c. Compound A represented by an electron-impact spectrum below is a non-polar compound.



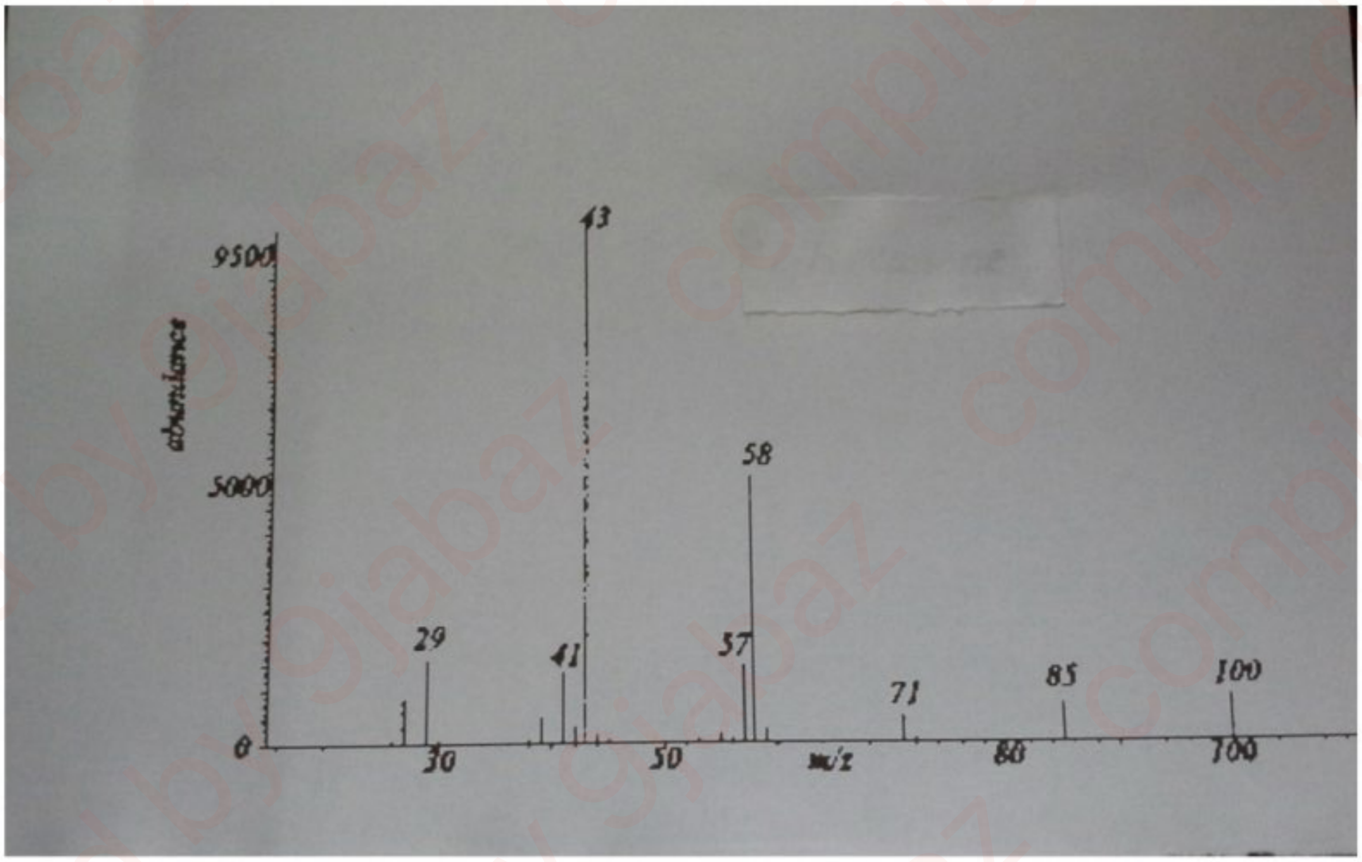
Mass spectrum of compound A

a. Interpret the spectrum and identify the compound.

b. Account for the following peaks in the spectrum; m/z 57, 85, 141 and 169.

4. a. Account for the following peaks in the mass spectrum of 2-pentanol; m/z 42, 45, 55, 70 and 73. The mechanism of fragmentation that resulted in each peak must be clearly shown.

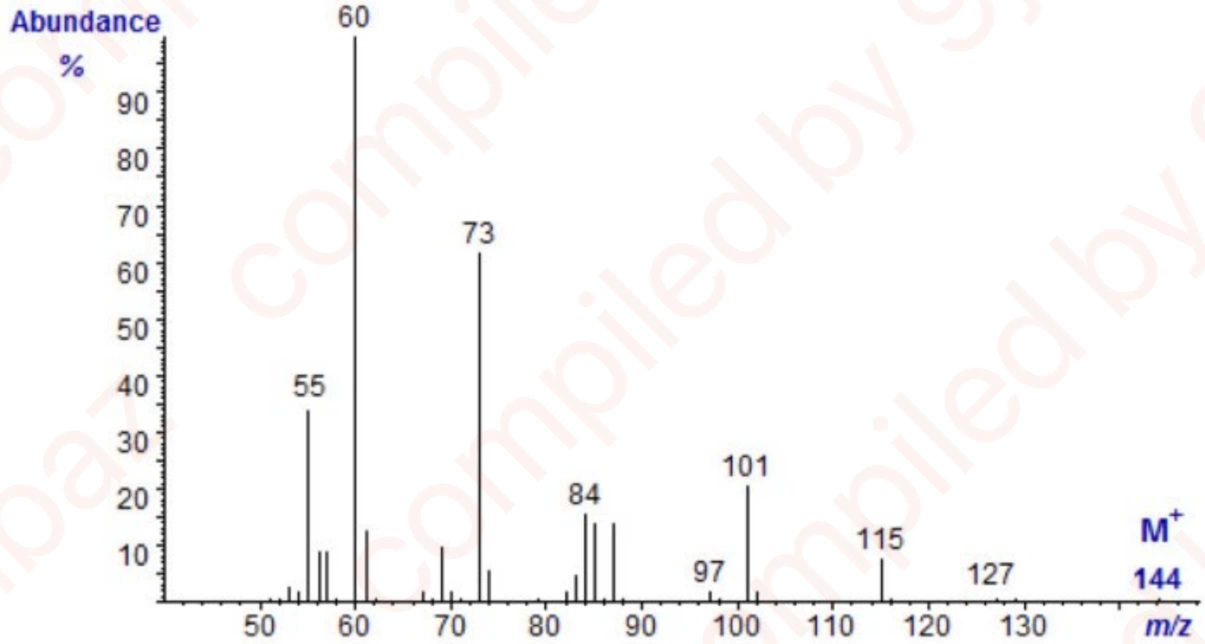
5. The electron impact mass spectrum of compound A, which may be prepared by the reaction of an acid chloride with an organocopper compound, is presented below.



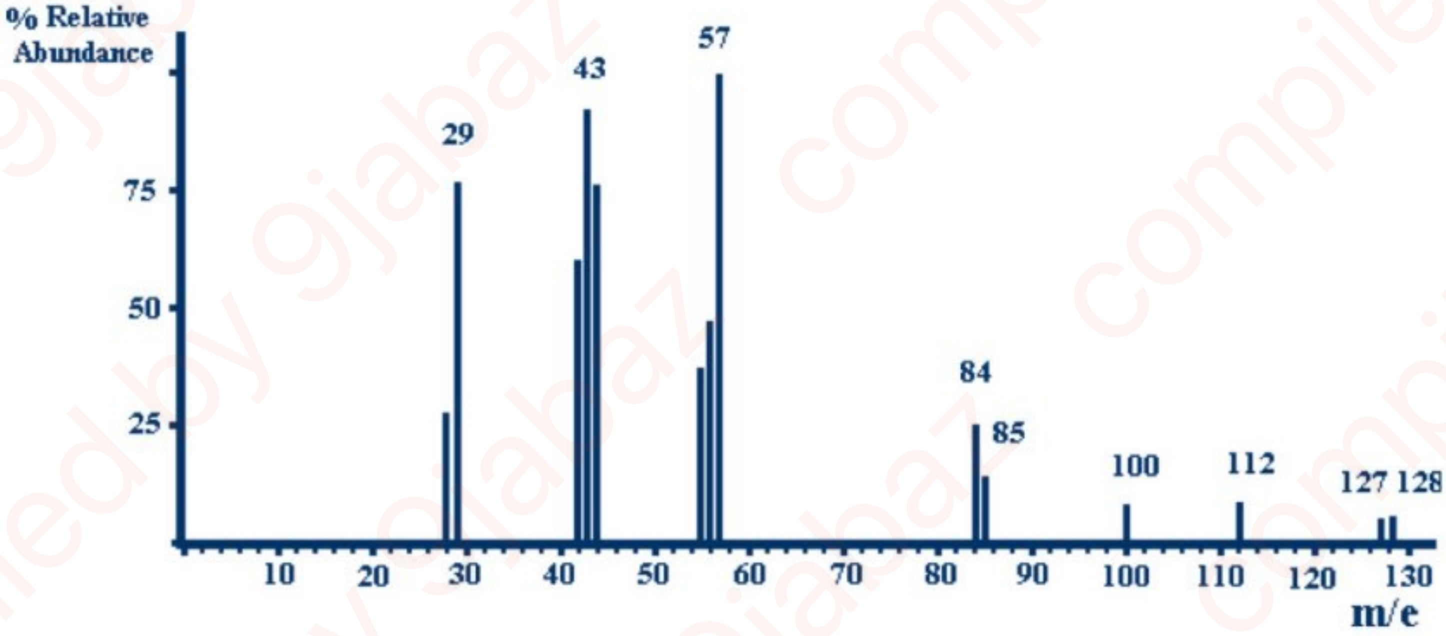
(a).Interpret the spectrum and identify the compound.

Show clearly the mechanism of fragmentation that resulted in the following ion peaks; m/z 43, 58 and 85.

6. Compound **A** is a direct product of oxidation of compound **B**. The reaction of compound A with ethanol will produce a volatile compound that can be detected easily by gas chromatography.



Mass spectrum compound **A**



Mass spectrum compound **B**

a. Interpret the spectra and identify the compounds **A** and **B**.

b. Show the mechanism of fragmentation that resulted in the following ion peaks; m/z 60 and 127 in the mass spectrum of compound **A**

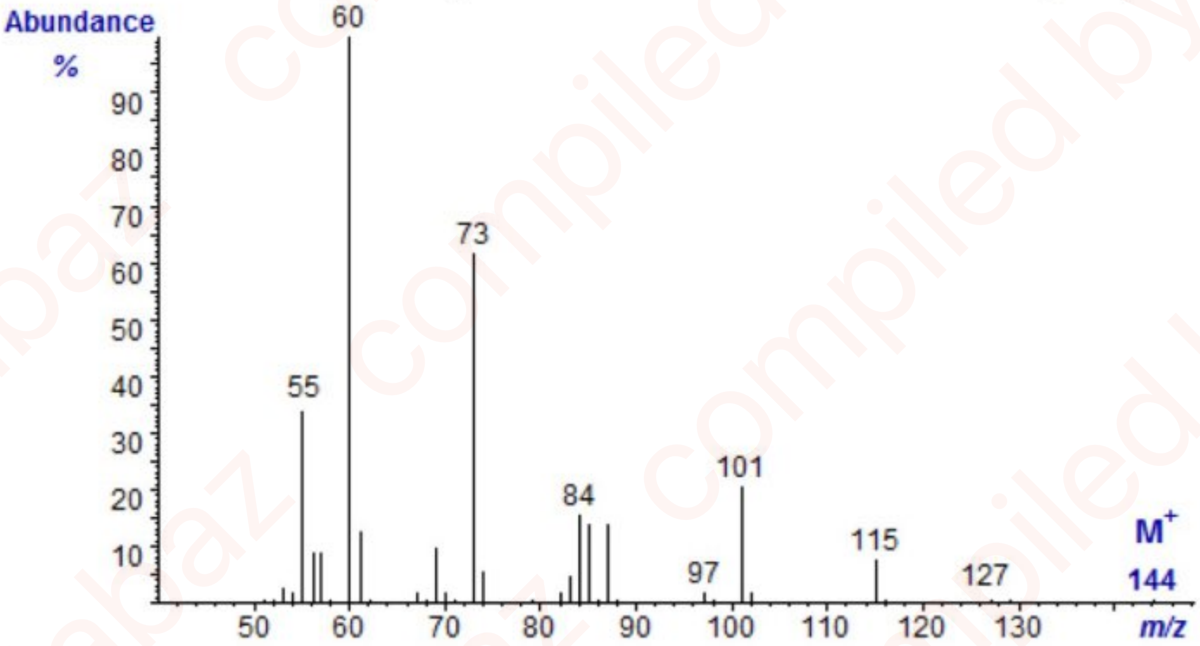
c. Account for the following peaks in the mass spectrum of compound **B**; m/z 29, 57 and 127 and show detailed mechanisms of fragmentations that resulted in the ions of these peaks.

d. Write a balanced equation for the reaction between compound **A** and ethanol.

7. Below is a mass spectrum of a non-volatile compound B from which a fruity volatile compound can be produced.

a. Interpret the spectrum and identify the compound

b. Show the mechanism of fragmentation that resulted in the following ion peaks; m/z 60 and 127



Mass spectrum of compound **B**

CHM 307:
Nuclear Magnetic Resonance (NMR) Spectroscopy technique for structural elucidation

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Acknowledgments:

-►Maitland Jones Jr, 1995. Organic Chemistry, 3rd edition, W.W. Norton & Co
Inc United States of America

-►Francis A. Carey and Robert M. Giuliano 2011. Organic Chemistry, 8th Edi
McGraw-Hill, Singapore

-►Tewari, K. S. and Vishnoi N. K. 2007. A textbook of Organic Chemistry, 3rd
Edition,Vikas Publishing House PVT Ltd, New Delhi

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Compounds, 6th Edition, Courier Westford, United States of America

-►Michigan State University-NMR Presentation

-►Northern Kentucky University_ch11_141s

Spectroscopy

- ► An area of study that probes molecular structure with electromagnetic adiation
- ►Electromagnetic spectrum: Gamma rays → X rays → UV-visible →IR →microwave →Radio waves
- ►From the spectrum: UV or vis, IR, NMR (radio waves) spectroscopy techniques
- ►These techniques yield a great deal of structural information

Advantages of Spectroscopy techniques in structural elucidation

- A very small sample is required and can be recovered
- The methods are rapid, give results within few minutes
- Give structural information that are accurate

Application of Spectroscopy Techniques
Column Chromatography

→

***Artemisia annua* –**

Artemisinin – Artesunate, anti-malaria drug

Spectroscopic techniques are required to identify the isolated compound

Nuclear Magnetic Resonance Spectroscopy (NMR)

► For identification and analysis of molecules and matters

► technique is based on the absorption of electromagnetic radiation in

he radio frequency region by certain atomic nuclei

► involves energy much smaller than those in IR, UV or vis spectroscopy

► Absorption is determined by the characteristics of the molecule.

^{1}H NMR

(Proton Nuclear magnetic resonance spectroscopy)

-► is one of the most powerful tools for elucidating the number and position of hydrogen (proton) in the compound

-►Like the electron, the nucleus has spin

-►Nuclei with non zero spin number absorb energy in the radio frequency region (NMR Active)

The following nuclei have spin number (I) that are not zero:

-►Nuclei that have odd atomic number (e.g $_{1}$H, $_{7}$N)
-►An odd mass number (e.g ^{13}C, ^{15}N, ^{17}O , ^{19}F)
-►Both an odd atomic number and odd mass number $^{15}_{7}N$

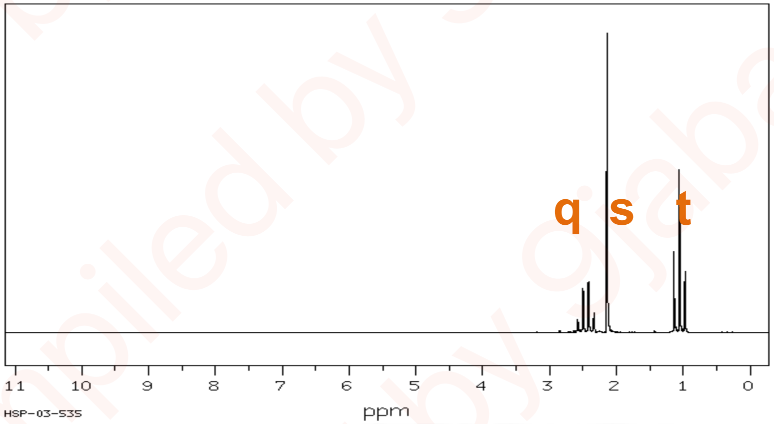
-►Some nuclei have even atomic number and even mass number:

e.g $^{12}_{6}C$

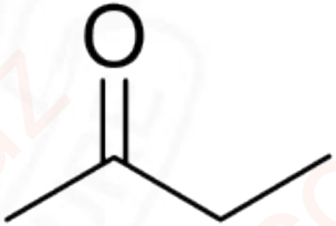
spin number (I) = 0

-►Only nuclei with non zero spin number will give NMR Spectra

-



^{1}H NMR Spectrum



Compound

The Nobel Prize in Physics 1952

-▶ "for their development of new methods for nuclear magnetic precision measurements and discoveries in connection therewith "

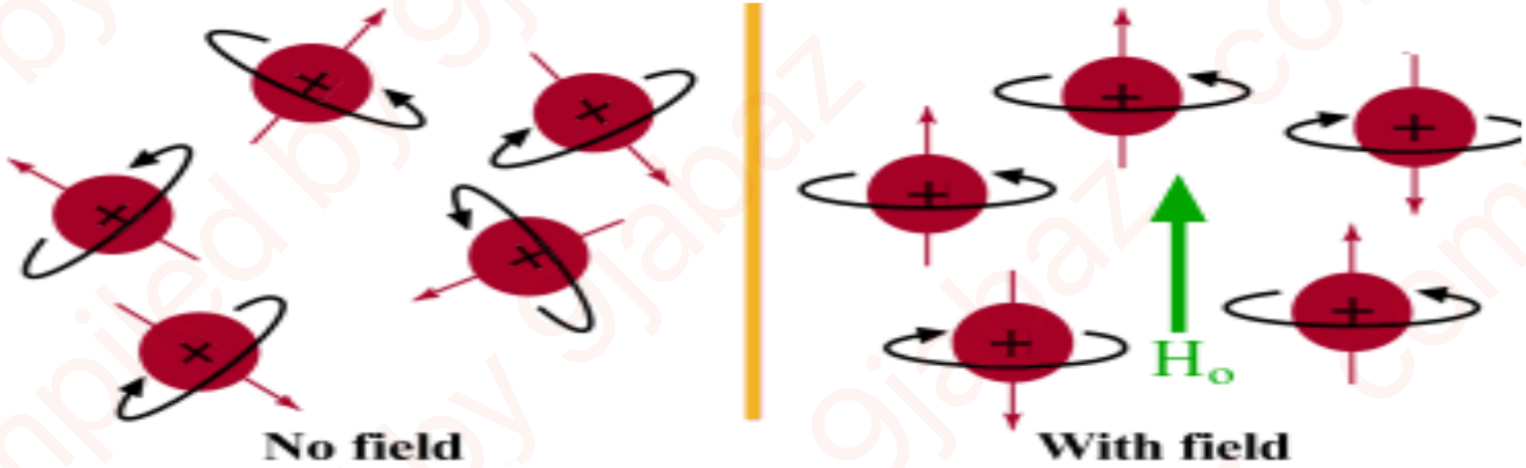
Felix Bloch

Edward Mills Purcell

-► Each nucleus has a characteristic magnetic dipole moment (↑) and behaves like a small magnet

-► When nuclei with spin are placed between poles of a powerful magnet

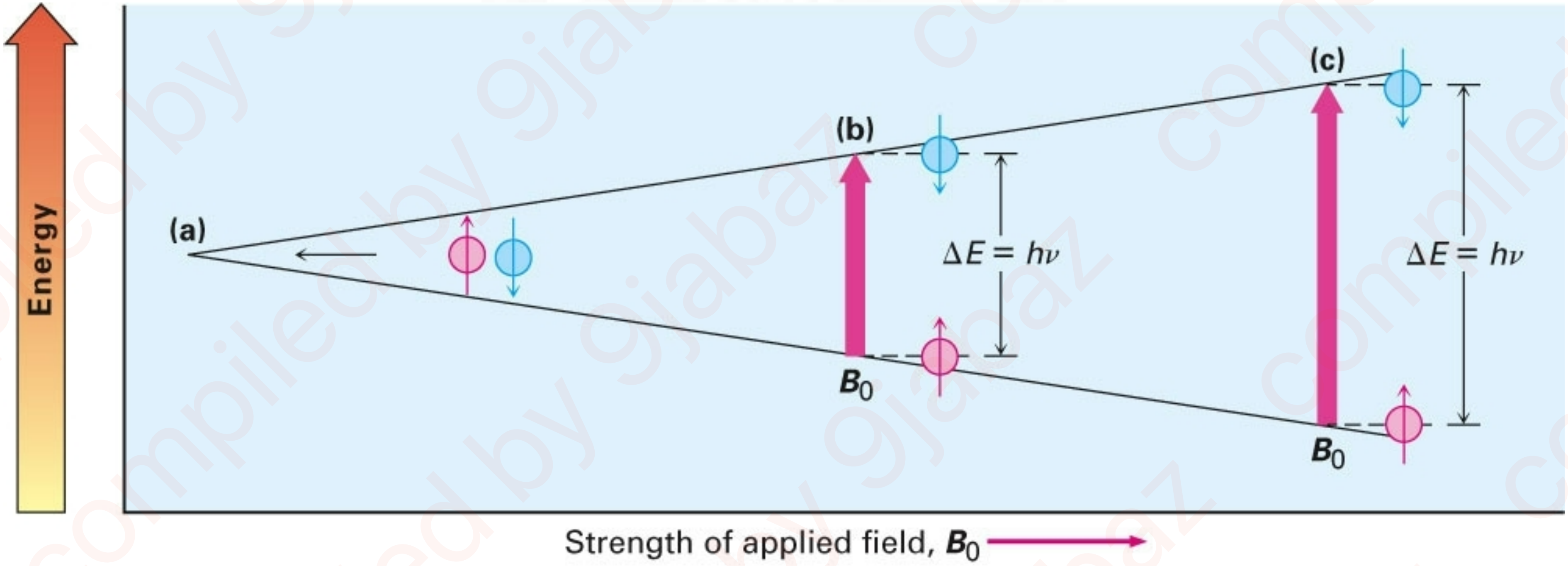
-► they either align their field (lower energy state) or against the field (higher energy state) of the magnet



atomic nuclei in absence of magnetic field

atomic nuclei in presence of magnetic field

-► Amount of energy required to move from one state to another (hv) Depend on (i) the strength of the external magnetic field (ii) Nuclear moment



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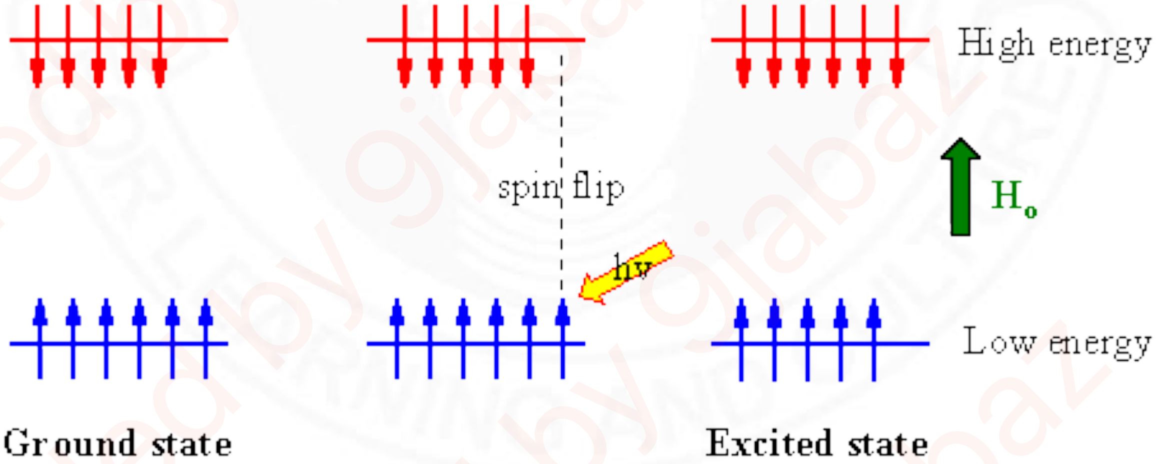
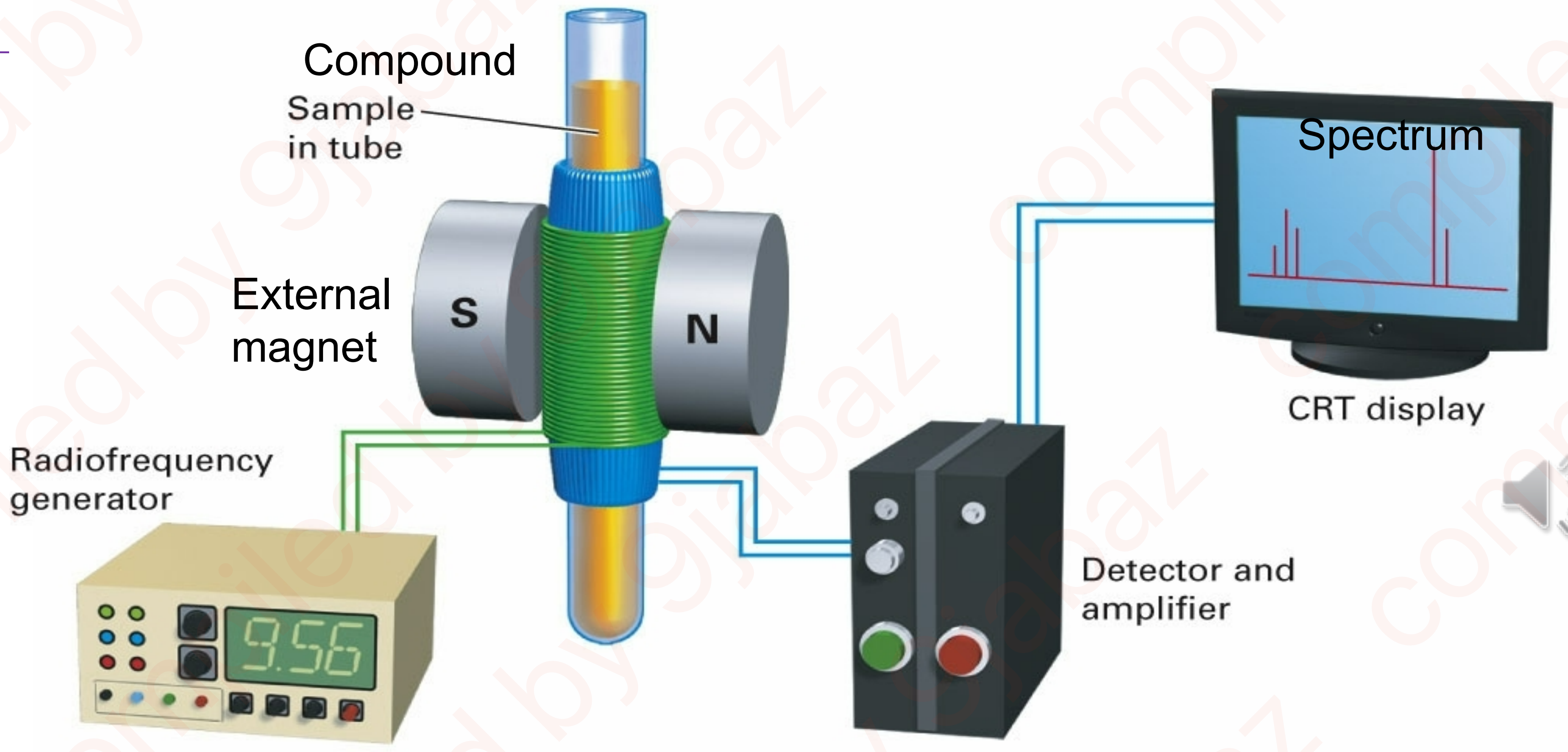
-►By applying energy in the radio frequency region, nuclei in the lower energy state can be excited to higher energy state

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

-►Hence the term **Nuclear Magnetic Resonance**



^{1}H NMR Spectrum



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NMR Spectrometer

-► **An NMR spectrum is a plot of the intensity of a peak against its chemical shift**

-►Spectra of molecules are obtained in solution (except pure liquid)

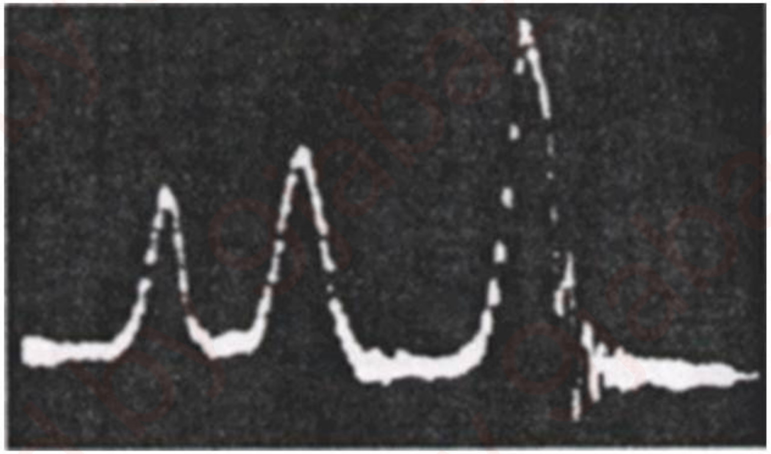
-►Commonly used solvents in NMR have no hydrogen to give interfering absorption e.g CCl_4

-►Deuterated solvents in which all hydrogen have been replaced by deuterium are also widely used -deuterium (D) absorbs in a different region from hydrogen:

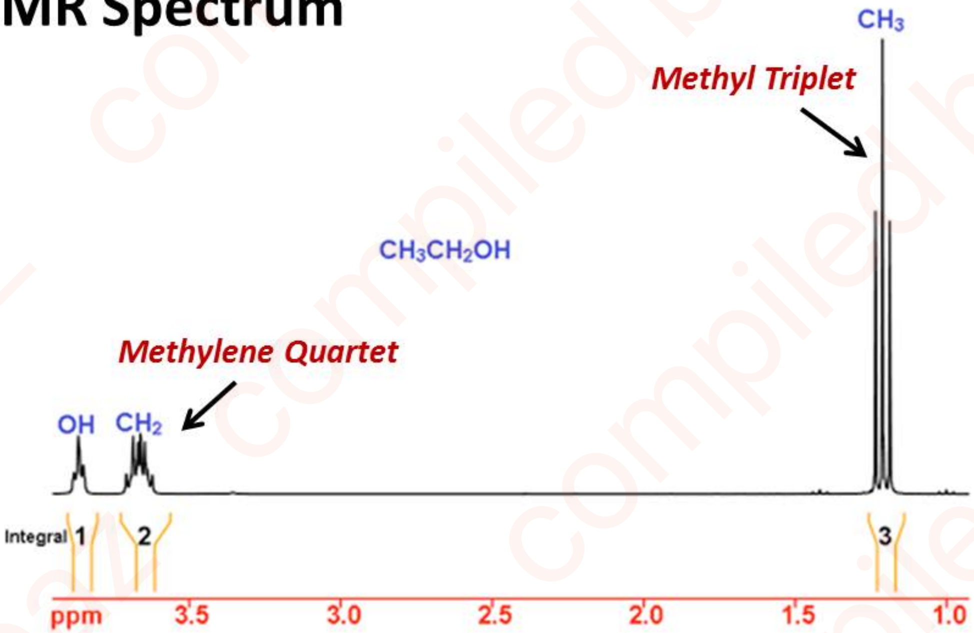
i)$CDCl_3$ Deuterated chloroform

ii)CD_3OD deuterated methanol

Ethanol ^{1}H NMR Spectrum



First ^{1}H NMR Spectrum of ***ethanol*** at ***30 MHz*** -1951 Stanford Univ



^{1}H NMR Spectrum of ***ethanol*** at 700 MHz

-► Information from ^{1}H NMR Spectra

1.The number of signals in a spectrum indicates different kinds of protons (hydrogens) present in a given molecule
2. The positions of the signals chemical shift give information about the electronic environment of each proton.
3. The splitting patterns give information about the environment of a proton with respect to other protons.
4. We can determine how many protons are present in each environment by integration.

MANY THANKS FOR YOUR ATTENTION

CHM 307:
Nuclear Magnetic Resonance (NMR) Spectroscopy technique for structural elucidation (2)

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Acknowledgments:

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Edition,Vikas Publishing House PVT Ltd, New Delhi

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Compounds, 6th Edition, Courier Westford, United States of America

-►Michigan State University-NMR Presentation

-►Northern Kentucky University_ch11_141s

-►NMR Presentation B_ch13, -► Chemistry Steps.com

Revision_ NMR Active Nuclei

-► Nuclear spin quantum number (I) ≠ 0, (**NMR active**)

-► Even atomic mass nuclei that have odd atomic number have an integer spin quantum number (I = 1, 2, 3, etc)

-► Both odd atomic number and mass number nuclei have half-integer spin quantum number

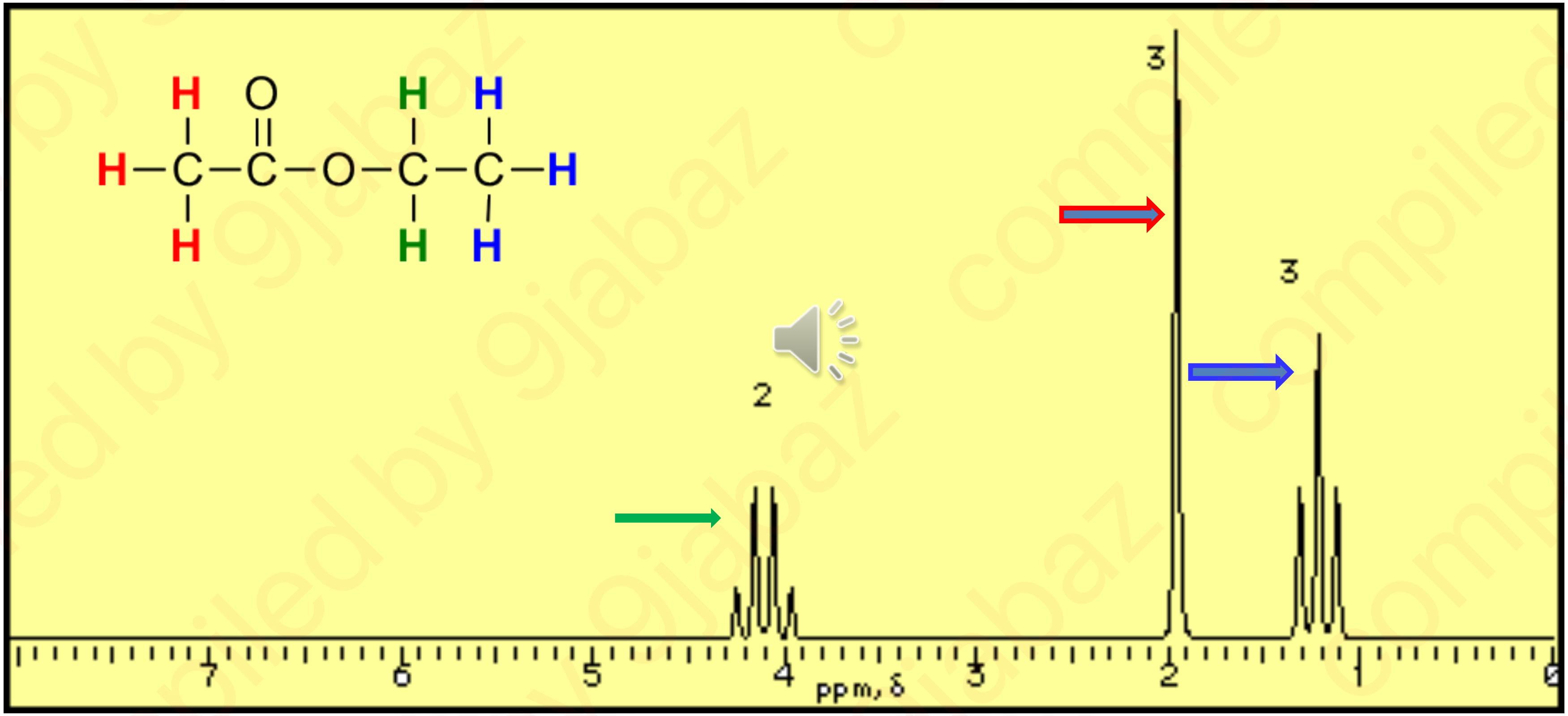
(I = 1/2, 3/2, 5/2, etc)

I= **½** ► **^{1}H**, **^{13}C**, ^{19}F, ^{31}P
I= **1** ► ^{2}H, ^{14}N
I= **3/2** ► ^{15}N

-► Even mass nuclei that have even atomic number have I = 0 (NMR inactive)

I= 0 ► ^{12}C, ^{16}O

Revision_ ^{1}H NMR Spectrum



^{1}H NMR Spectrum

-► Different nuclei absorb EM radiation in the radio frequency region to obtain energy required to bring about resonance

-► Nuclei of a given type, will resonate at different energies depending on their chemical and electronic environment.

-► The position of an NMR signal (*chemical shift*, δ) and its *splitting* pattern (*multiplicity*) gives important information about the chemical environment of the nuclei.

-► The *integration* of the signal is proportional to the number of nuclei giving rise to that signal

Chemical shift, δ and Nuclear Shielding

-► **Chemical shift**:

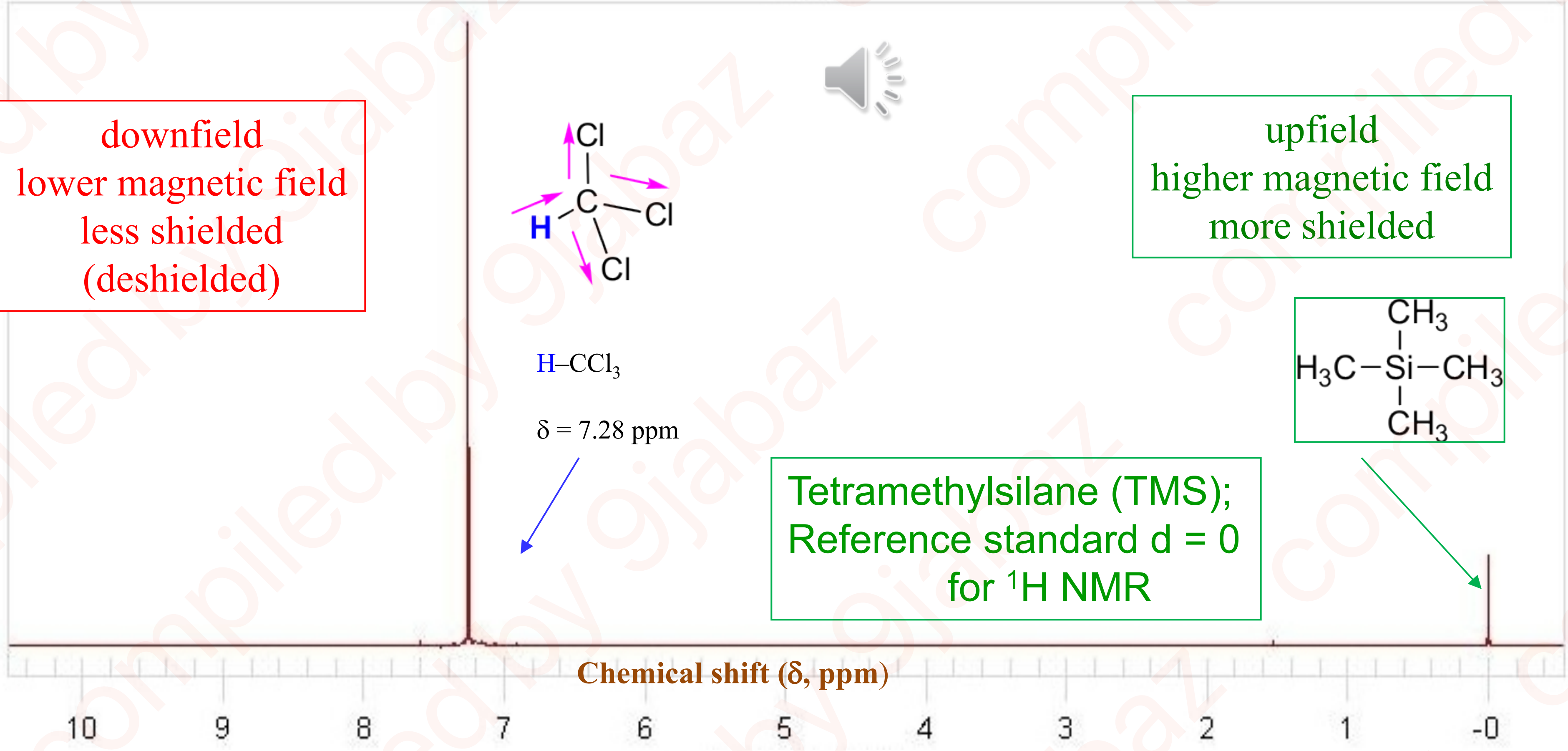
i) the absorption position of a proton (H) relative to the absorption position of a reference standard (TMS)

ii) exact field strength (in ppm) that a nuclei comes into resonance relative to a reference standard (TMS).

-► **Shielding**: influence of neighbouring functional groups on the electronic structure around a nuclei and consequently the chemical shift of their peak(s).

Electron clouds “shield” nuclei from the external magnetic field ausing them to resonate at slightly higher energy

Shielding determines Chemical Shift of a proton



downfield
lower magnetic field
less shielded
(deshielded)

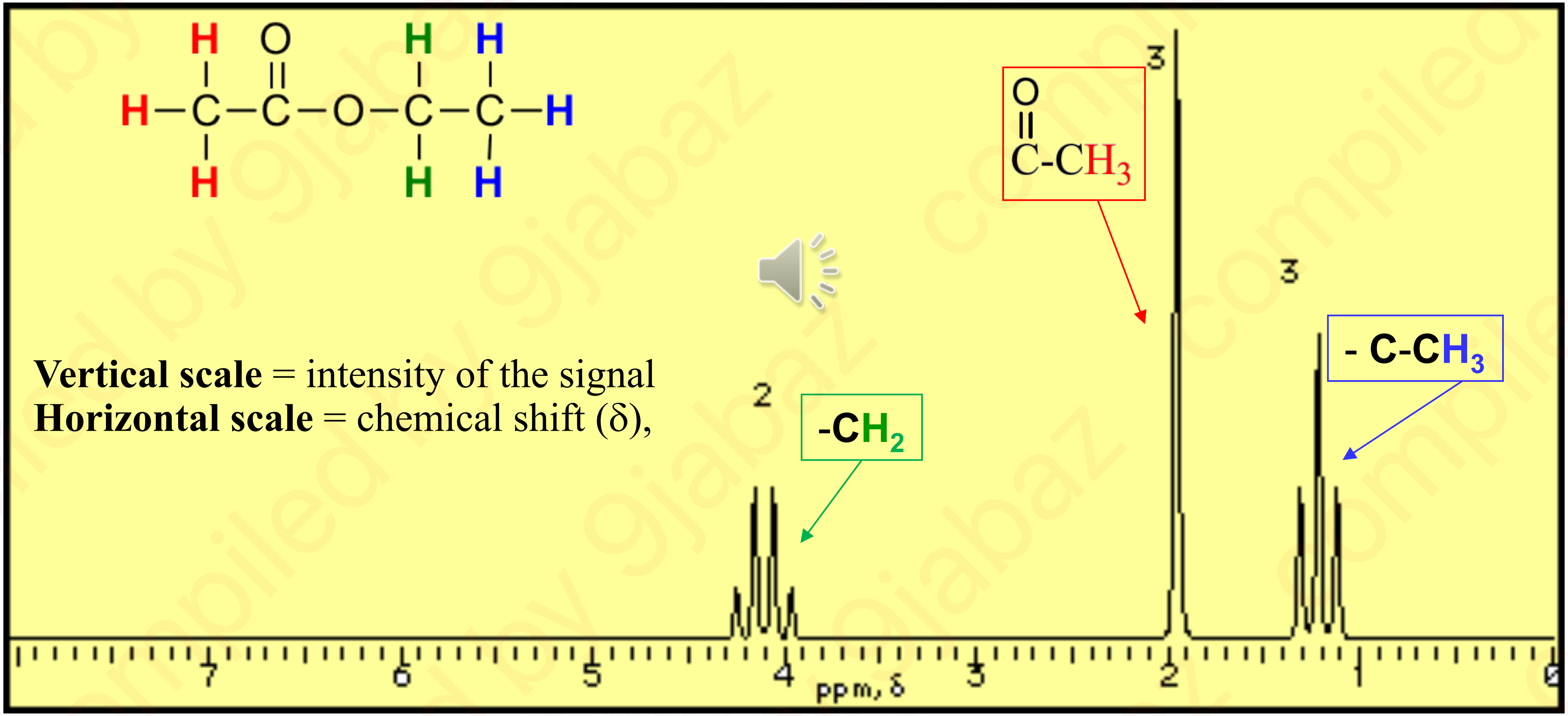
$H–CCl_3$

δ = 7.28 ppm

upfield
higher magnetic field
more shielded

Tetramethylsilane (TMS);
Reference standard d = 0
for ^{1}H NMR

^{1}H NMR Spectrum_ Position of Peaks (Signals)



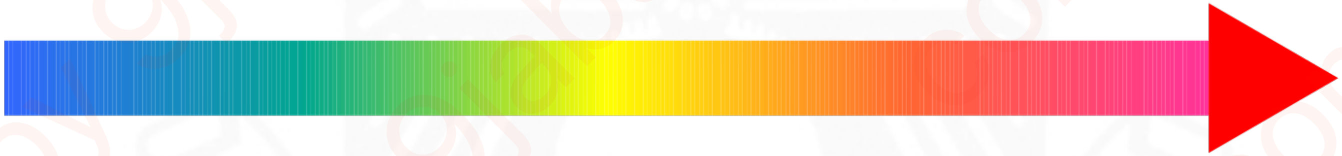
Vertical scale = intensity of the signal
Horizontal scale = chemical shift (δ),

Factors influencing Chemical Shift

Inductive Effect

)

less shielded *more shielded*



$H_3C\text{-}F$ $H_3C\text{-}O\text{-}CH_3$ $(H_3C)_3\text{-}N$ $H_3C\text{-}CH_3$ $(H_3C)_4\text{-}Si$

δ 4.3 δ 3.2 δ 2.2 δ 0.9 δ 0.0

Electronegative substituents deshield nearby protons

Inductive Effect

ii)

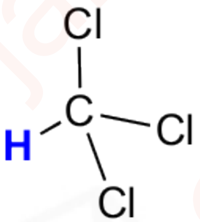
The deshielding effect of an electronegative group falls off as he number of bonds between the substituent and proton ncrease increases

$$O_2N\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

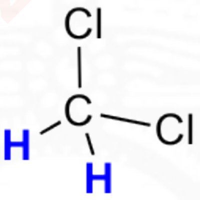
$\delta =$ 4.3 2.0 1.0

Inductive Effect

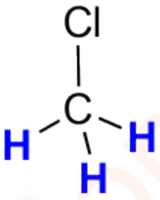
(iii) The influence of neighboring groups (electronegative) on ^1H chemical shifts is cumulative



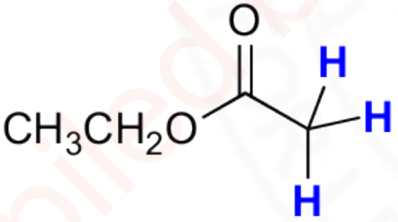
δ = 7.3



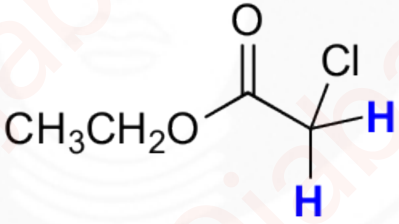
5.3



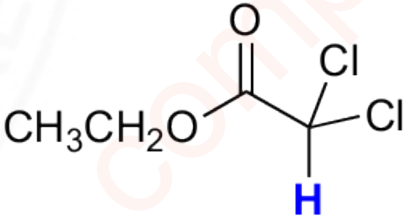
3.1 ppm



δ = 2.1

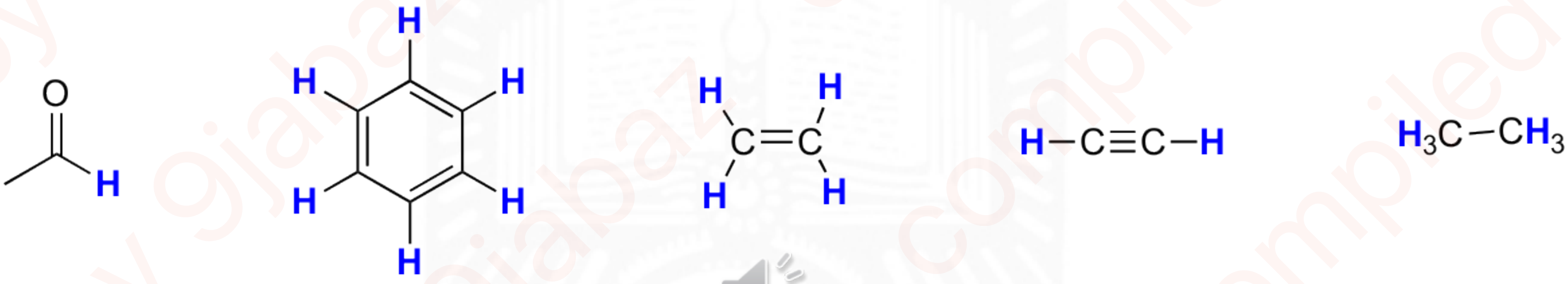


4.06



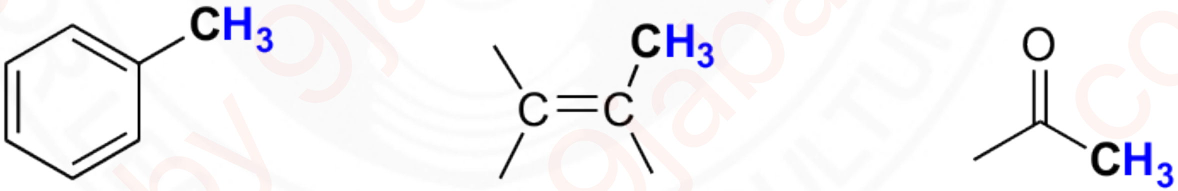
5.96 ppm

Protons attached to sp^2 and sp hybridize carbons are more deshielded relative to protons attached to sp^3 hybridized carbons



δ = 9.7 7.3 5.3 2.1 0.9-1.5 ppm

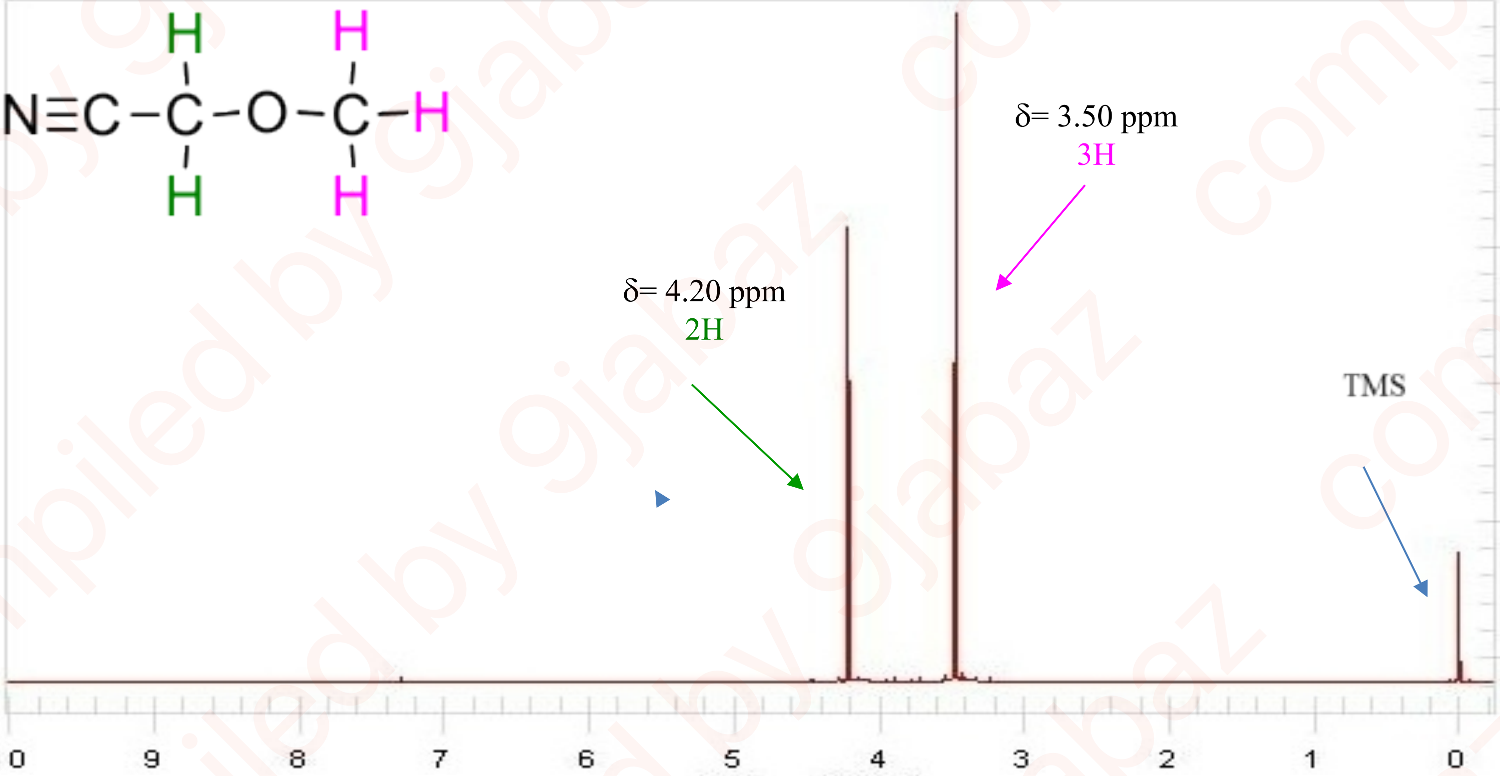
Please read about ring current effects of π-bonds in my NMR Lecture Note

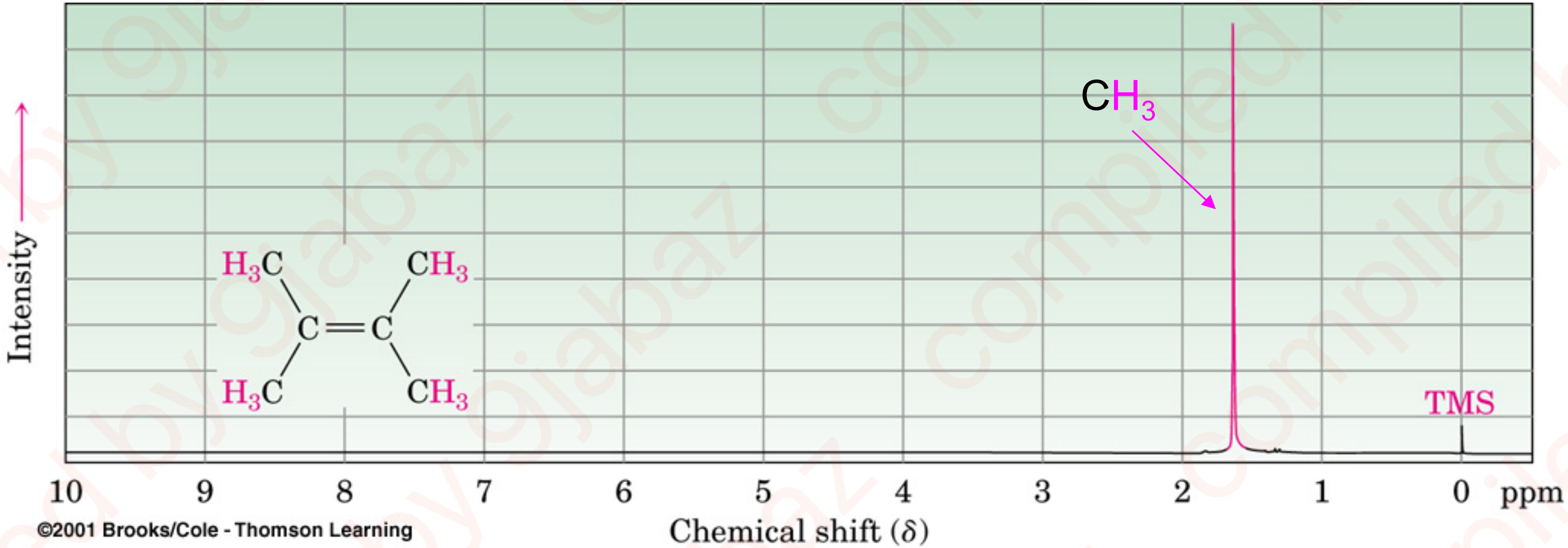


δ = 2.3 - 2.8 1.5 - 2.6 2.1-2.5 ppm

Interpreting ^{1}H NMR Spectra

Chemical-shift equivalence: chemically and magnetically equivalent nuclei (proton in the same environment) resonate at the same energy and give a single signal or pattern





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Chemically equivalent nuclei do not normally give separate resonance (signal) in the NMR spectra

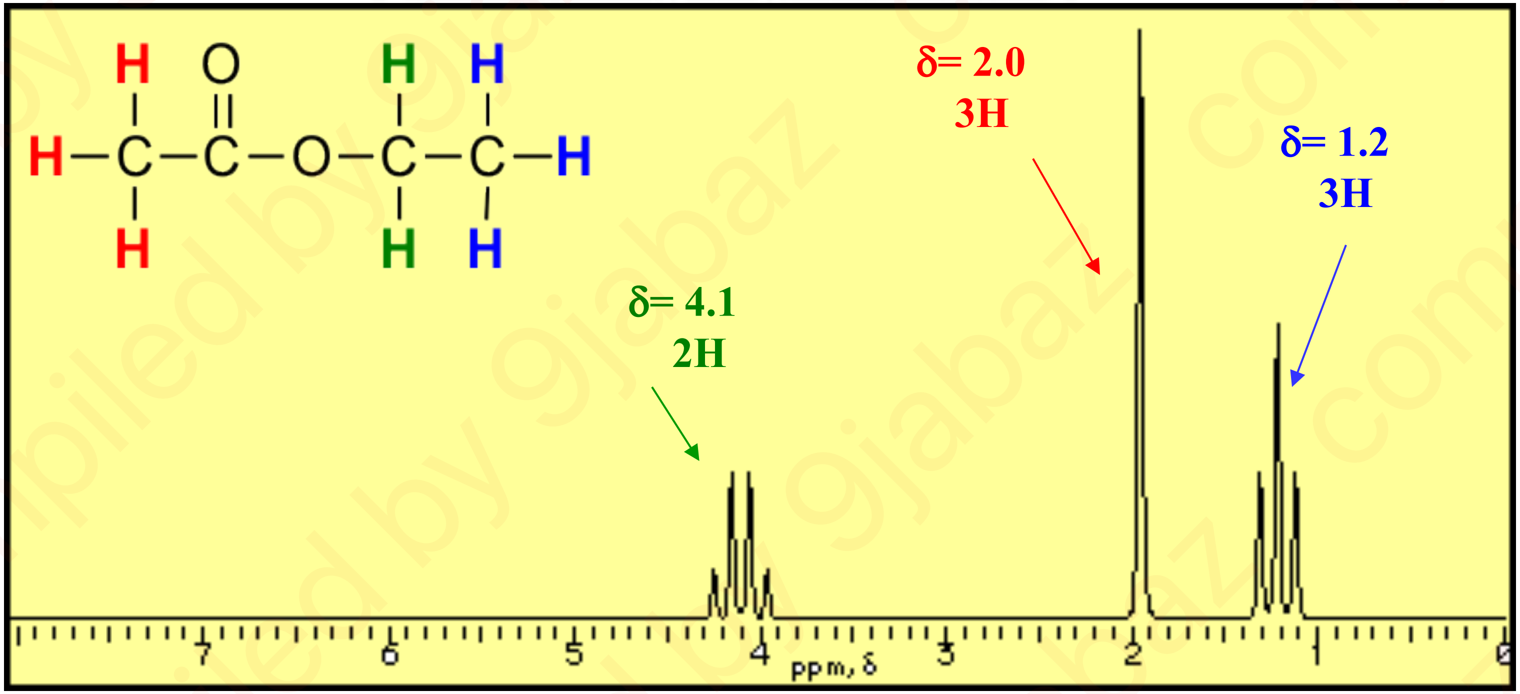
If the labeled methyl groups are not identical, the nuclei are not chemically equivalent and can give rise to different resonances in the NMR spectra

Spin-spin splitting in ^{1}H NMR spectroscopy

-► protons on adjacent carbons (that are not equivalent) will interact and “split” each others resonances into multiple peaks (multiplets)

-► **n + 1 rule**: equivalent protons that have n protons on the adjacent carbon will be “split” into n + 1 peaks

-► **the resonance at δ = 1.2 must split the resonance at δ = 4.2**.



Multiplicity of Peaks

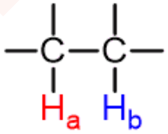
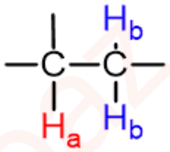
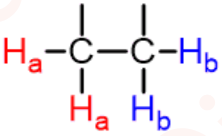
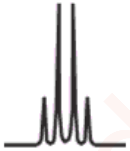
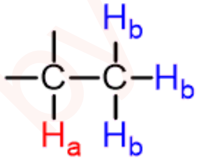
-►The number of peaks and the pattern

-► Common multiplicities patterns and relative intensities

-►There is no correlation between multiplicity of peaks and number of protons

Summary of Signal Splitting Patterns in ^{1}H NMR Spectroscopy

The pattern is that n protons split the signal into n+1 peaks, which is known as the **n+1 rule**.

Multiplicity	N +1	H_a	Signal	H_b	N +1	Multiplicity
Doublet	1+1 = 2		 $-\underset{H_a}{\overset{\vert}{C}}-\underset{H_b}{\overset{\vert}{C}}-$		1+1 = 2	Doublet
Triplet	2+1 = 3		 $-\underset{H_a}{\overset{\vert}{C}}-\overset{H_b}{\underset{H_b}{C}}-$		1+1 = 2	Doublet
Triplet	2+1 = 3		 $H_a-\underset{H_a}{\overset{\vert}{C}}-\underset{H_b}{\overset{\vert}{C}}-H_b$		2+1 = 3	Triplet
Quartet	3+1 = 4		 $-\underset{H_a}{\overset{\vert}{C}}-\overset{H_b}{\underset{H_b}{C}}-H_b$		1+1 = 2	Doublet

^{1}H NMR Coupling Constant (J value)

Coupling constant: distance between peaks in a multiplet

J is expressed in Hz.

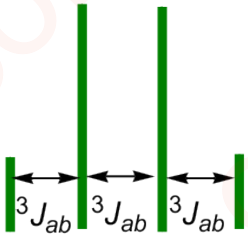
-► Protons coupled to each other have the same coupling constant *J*.

-► J value depends on the structural relationship between coupled protons

-► J value is larger between trans related protons 13-16 Hz

-► J value for cis related protons ≤ 12 Hz

Aromatic protons (phenyl ring)



-► Ortho related proton 6-9 Hz

-► Meta related protons 1-3 Hz

-► Para related protons 0

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Obafemi Awolowo University, Ile - Ife

CHM 307:
Nuclear Magnetic Resonance (NMR) Spectroscopy technique for structural elucidation (3)

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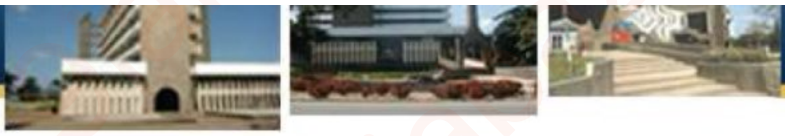

Acknowledgments:

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-► Tewari, K. S. and Vishnoi N. K. 2007. A textbook of Organic Chemistry, 3rd Edition,Vikas Publishing House PVT Ltd, New Delhi

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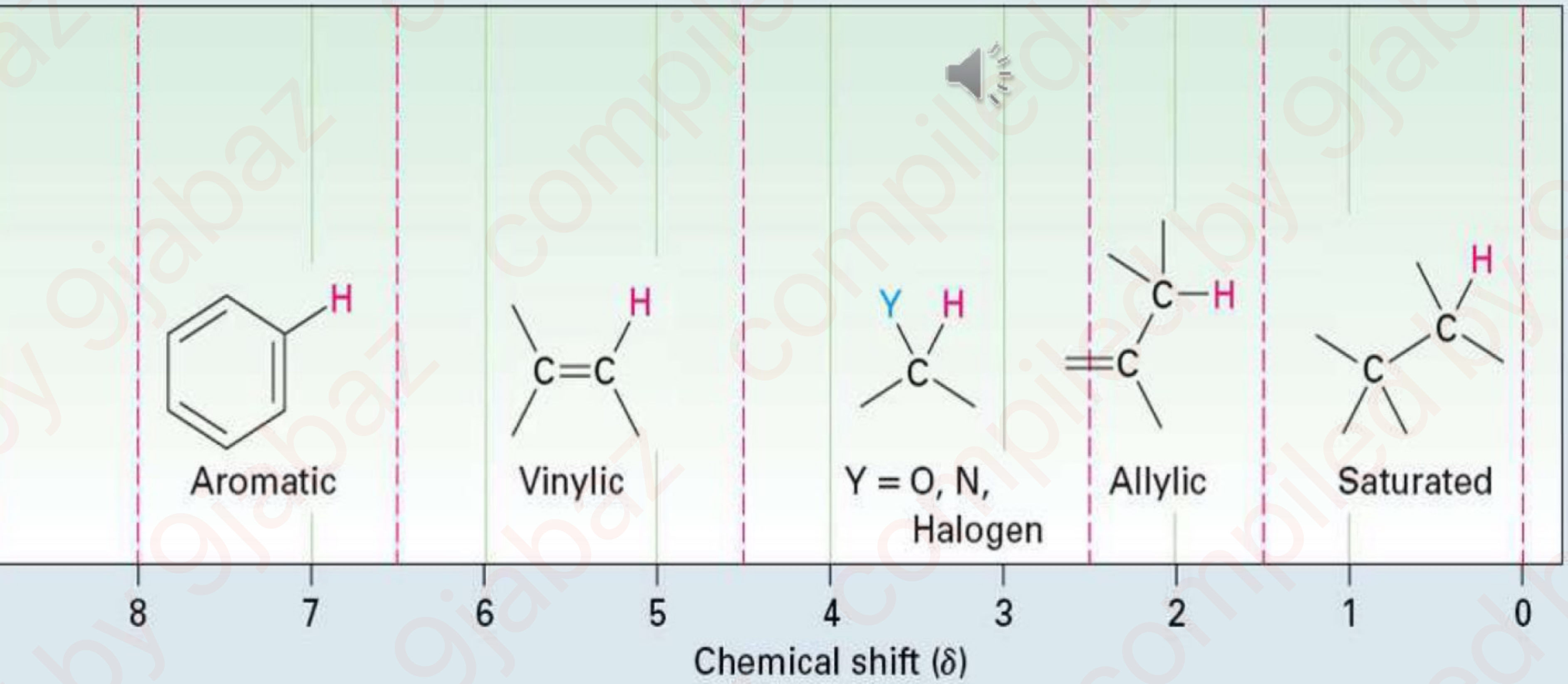
-► Michigan State University-NMR Presentation

-► Northern Kentucky University_ch11_141s

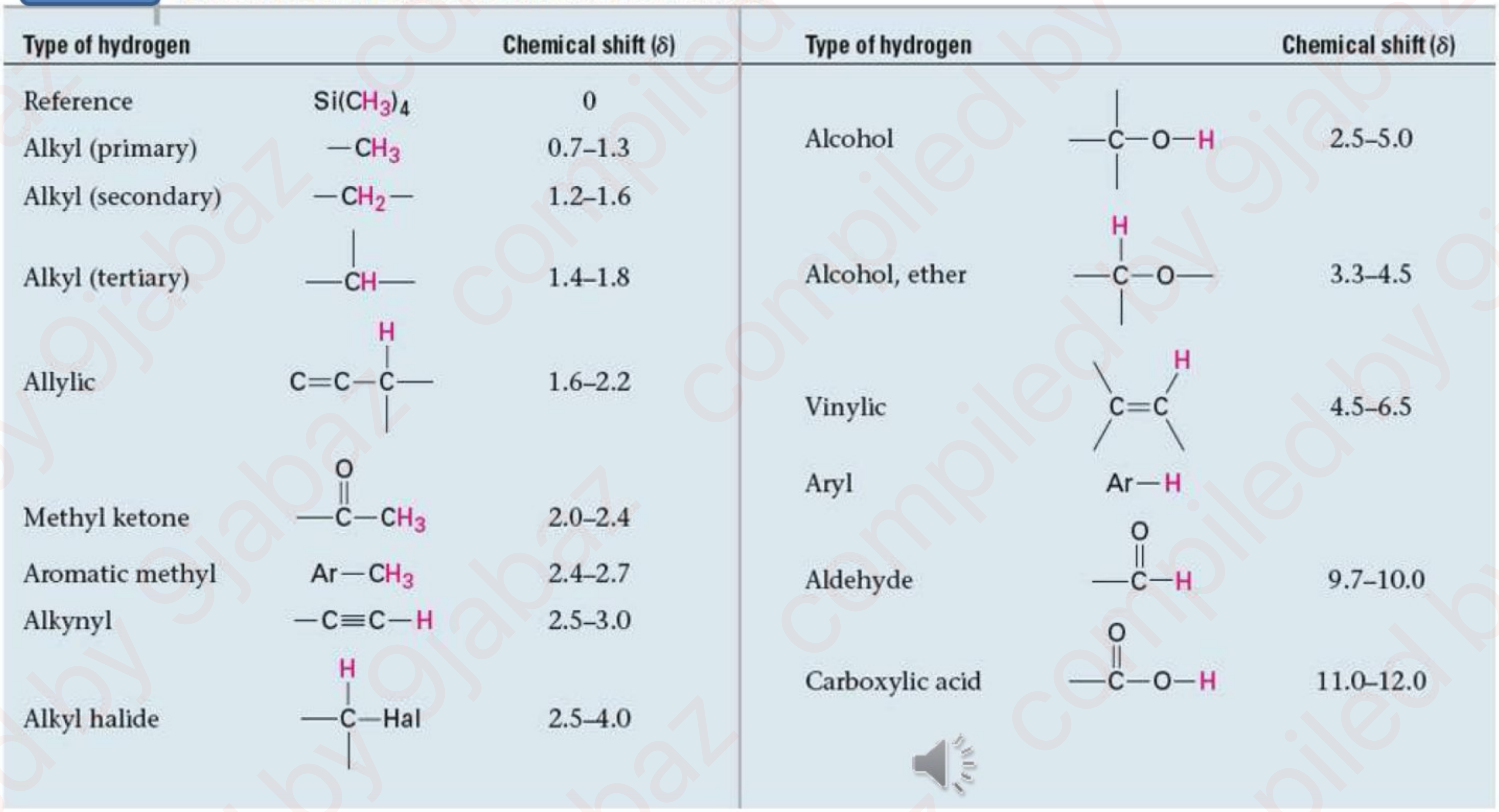
-► NMR Presentation B_ch13, -► Chemistry Steps.com

-► NMR Chemical Shift Values Table - Chemistry Steps.com

Regions of the ^{1}H NMR Spectrum



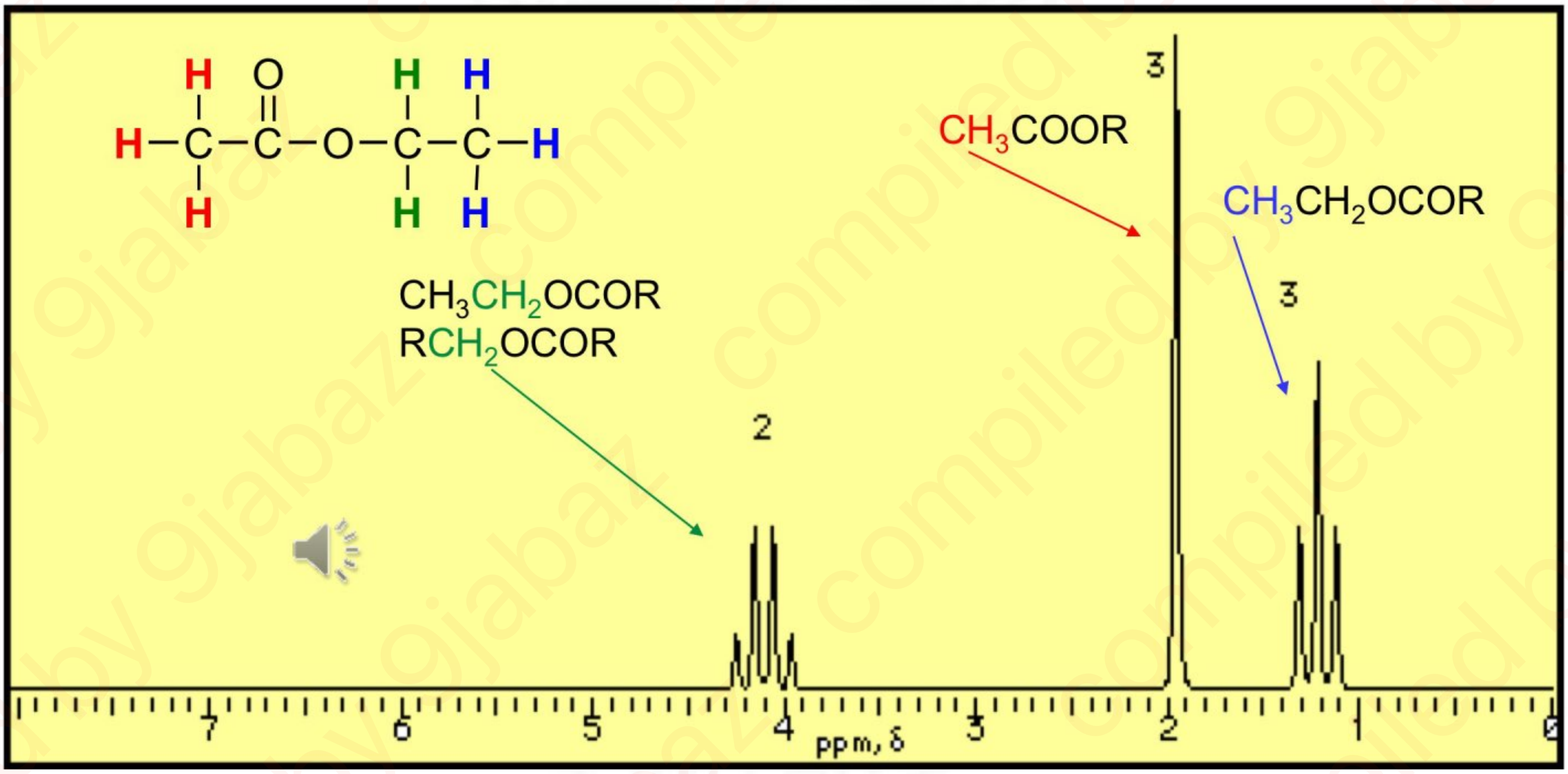
Correlation of ^1H Chemical Shift with Environment



Type of hydrogen		Chemical shift (δ)
Reference	$Si(CH_3)_4$	0
Alkyl (primary)	$-CH_3$	0.7–1.3
Alkyl (secondary)	$-CH_2-$	1.2–1.6
Alkyl (tertiary)	$-\underset{}{\overset{\vert}{C}}H-$	1.4–1.8
Allylic	$C{=}C-\overset{H}{\underset{\vert}{\overset{\vert}{C}}}-$	1.6–2.2
Methyl ketone	$-\overset{O}{\overset{\Vert}{C}}-CH_3$	2.0–2.4
Aromatic methyl	$Ar-CH_3$	2.4–2.7
Alkynyl	$-C{\equiv}C-H$	2.5–3.0
Alkyl halide	$-\overset{H}{\underset{\vert}{\overset{\vert}{C}}}-Hal$	2.5–4.0

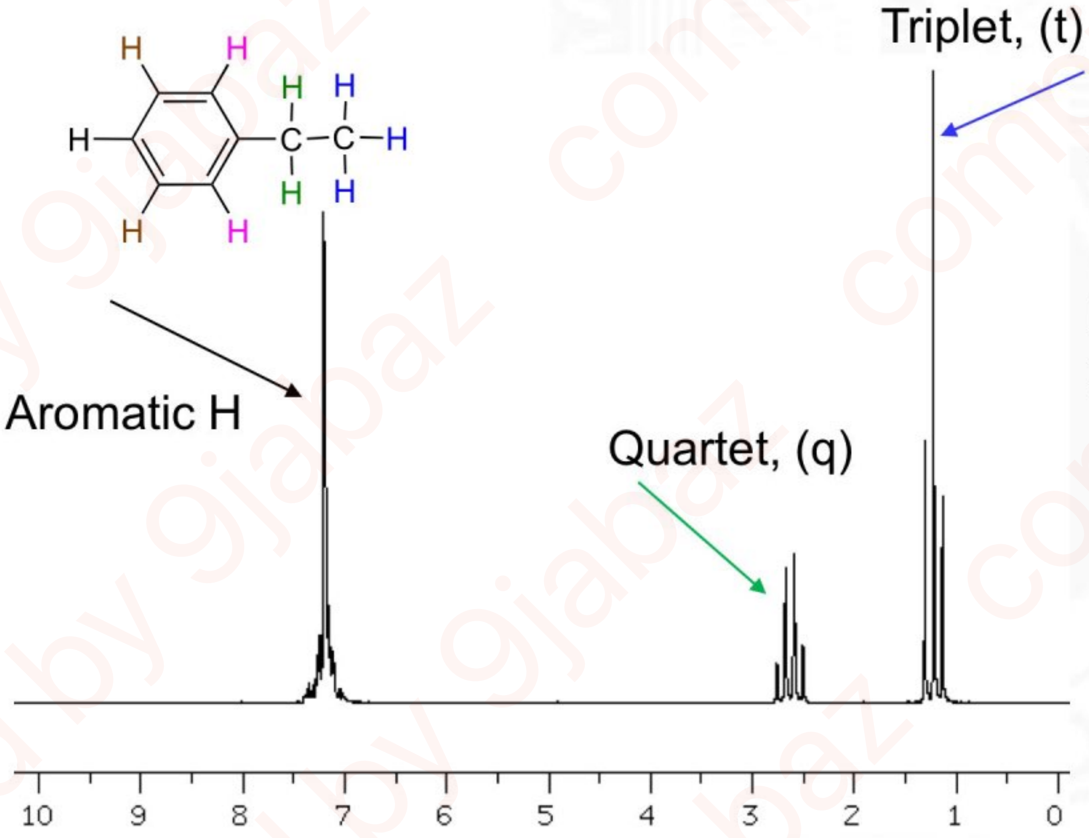
Type of hydrogen		Chemical shift (δ)
Alcohol	$-\underset{\vert}{\overset{\vert}{C}}-O-H$	2.5–5.0
Alcohol, ether	$-\overset{H}{\underset{\vert}{\overset{\vert}{C}}}-O-$	3.3–4.5
Vinylic	$>C{=}C<^{H}$	4.5–6.5
Aryl	$Ar-H$	
Aldehyde	$-\overset{O}{\overset{\Vert}{C}}-H$	9.7–10.0
Carboxylic acid	$-\overset{O}{\overset{\Vert}{C}}-O-H$	11.0–12.0

^{1}H NMR Spectrum of Ethyl Acetate



^{1}H NMR Spectrum_ Common Splitting Patterns

(1)Ethyl group

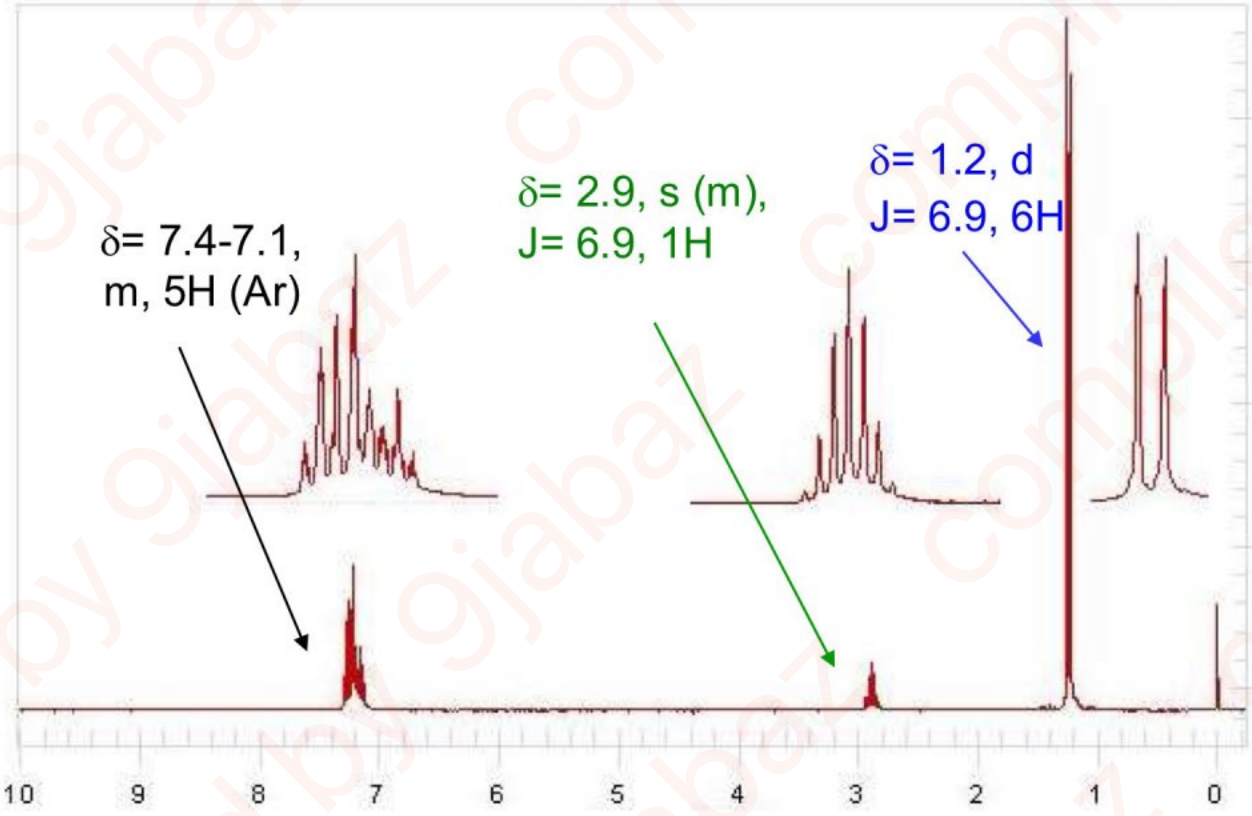


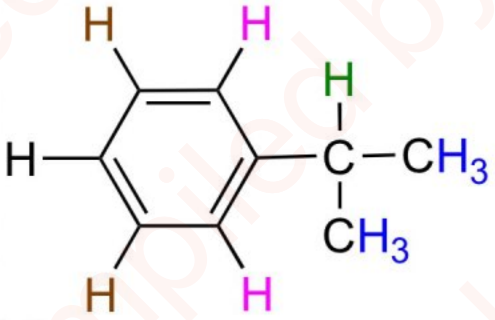
Multiplicity of methyl H= n+1,
2+1= 3, triplet (t)

Multiplicity of methylene H= n+1,
3+1=4, quartet, (q)

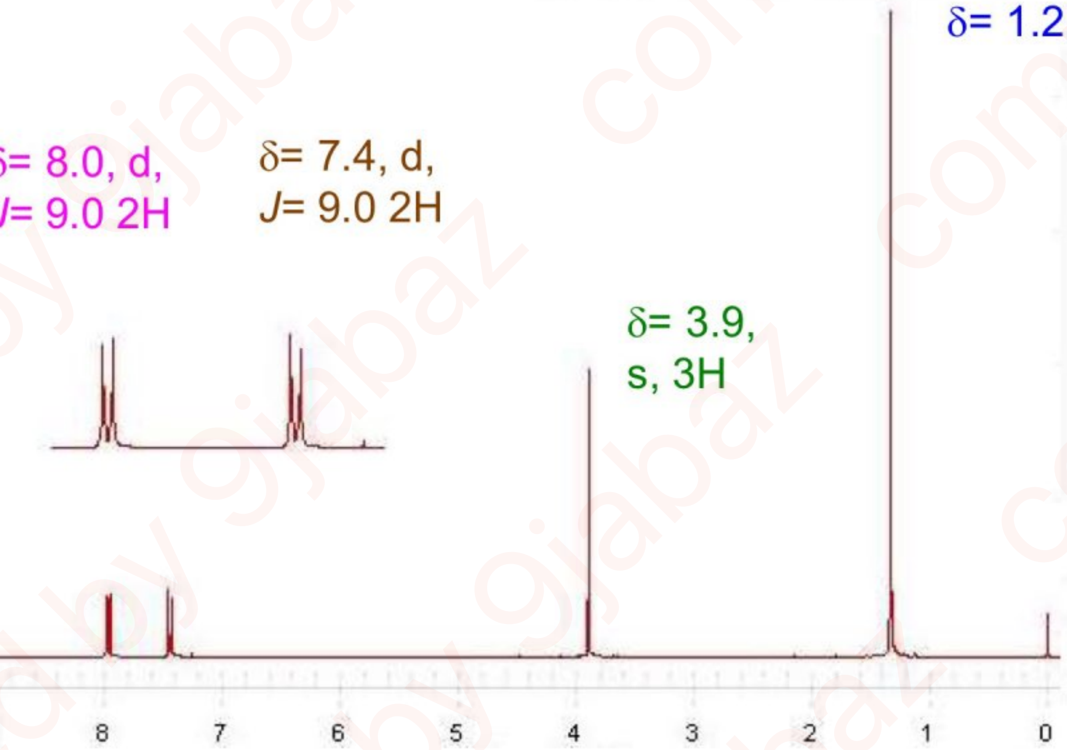
The Isopropyl Group

- ►One proton (H) on the adjacent carbon will split six equivalent protons into a septet (s)
- ►Six equivalent protons(H) will split a proton into a doublet (d) (m)
- ► five aromatic protons appear as a multiplet





Pairs of Doublets _^{1}H NMR Spectrum

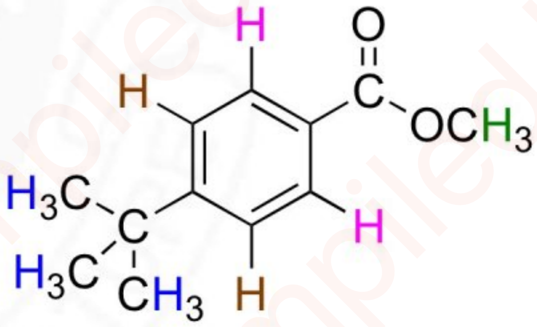


= 8.0, d,
= 9.0 2H

δ= 7.4, d,
J= 9.0 2H

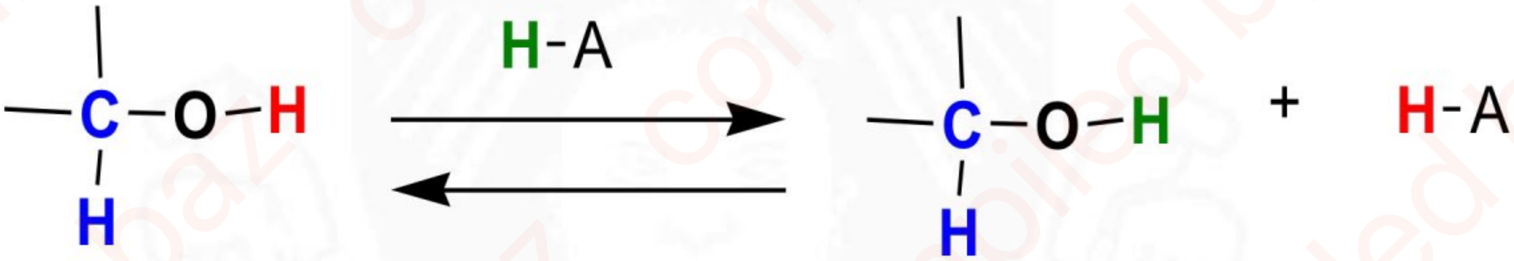
δ= 3.9,
s, 3H

δ= 1.2, s, 9H



^{1}H NMR Spectra of Alcohols

- **S**pin-spin coupling between the O–H proton and neighbouring protons on carbon do not occur normally
- Exchange reaction

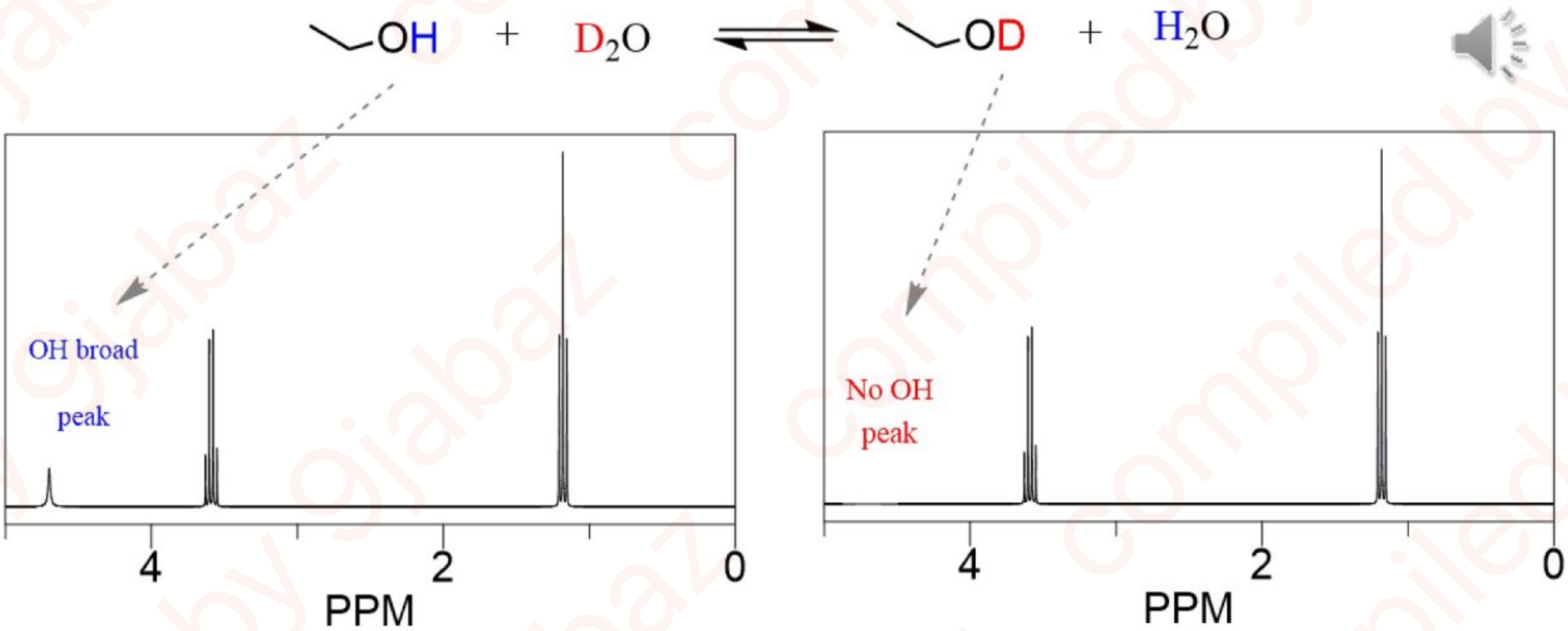


- The chemical shift of the -OH proton occurs over a large range (2.0 - 5.5 ppm).
- This proton usually appears as a broad singlet.
- It is not uncommon for this proton not to be observed.

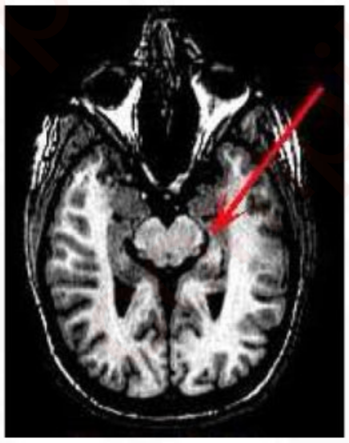
(H = deuterium)

Hydrogen–Deuterium Exchange in NMR Spectroscopy

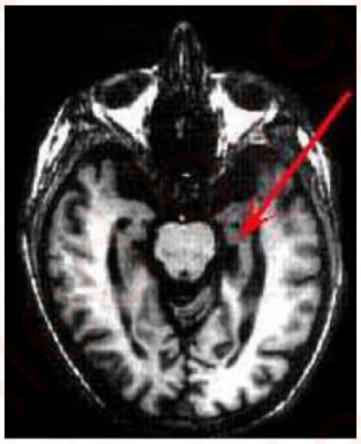
One way of testing if the peak is from an OH, is adding a drop of a deuterated solvent (D_2O or MeOD). Because of the exchange with the D, **the peak disappears since the deuterium is NMR inactive <u>at the proton's frequency!</u>**



Magnetic Resonance Imaging (MRI): uses the principles of nuclear magnetic resonance to image tissue



Normal
25 years old



Alzheimer's Disease
78 years old

- MRI uses the magnetic resonance of protons on water to obtain images
- Other nuclei within the tissue e.g. ^{31}P can also be used

MANY THANKS
FOR
YOUR
ATTENTION

① UV–Vis Electronic Spectra

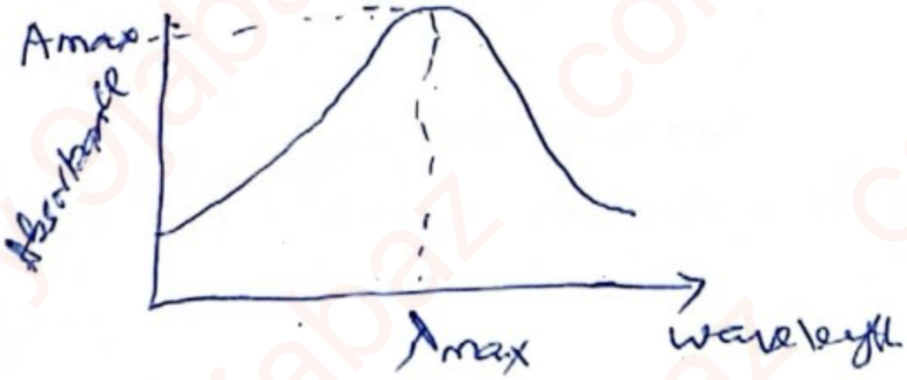
A characteristics feature of Many d-block metal complexes is their colour, which arise because they absorb light in the visible region. Studies of electronic spectra of metal complexes provide information about structure and bonding, although interpretation of the spectra is not always straightforward. Absorptions arise from transitions between electronic energy levels.

⇒ Intra Ligand transitions (transitions within the Ligands give rise to $\pi-\pi^*$, $n-\pi^*$. occur in the UV region

⇒ Transitions between metal-centred Orbitals possesing d-character (d–d transitions)

⇒ transitions between metal- and Ligand-centred MO which transfer charge from metal to Ligand or Ligand to metal (Charge transfer bands)

⇒ Absorption bands are described in terms of λmax corresponding to the absorption maximum Amax.



The wavelength is usually given in nm, but the Position of the absorption may also be reported in terms of wavenumbers, $\bar{\nu}$ (cm⁻¹). $\left[\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}\right]$

[400 nm corresponds to 25000 cm⁻¹; 200 nm ⇒ 50000 cm⁻¹

The Molar extinction coefficient (or Molar absorptivity) ε_{max} of an absorption Indicates how Intense an Absorption is and is related to A_{max} by equation below

$A = \varepsilon c l$ $$\varepsilon_{max} = \frac{A_{max}}{c \times l} \quad (\varepsilon_{max} \text{ in } dm^3 mol^{-1} cm^{-1})$$

The value of ε_{max} range from close to zero (a weak absorption to $> 10,000\ dm^3 mol^{-1} cm^{-1}$ (an intense absorption).

⇒ important points:

- d^1, d^4, d^6 and d^9 complexes consist of one broad band
- d^2, d^3 d^7 and d^8 complexes consist of three broad absorptions
- d^5 complexes consist of a series of weak, relatively sharp absorptions.

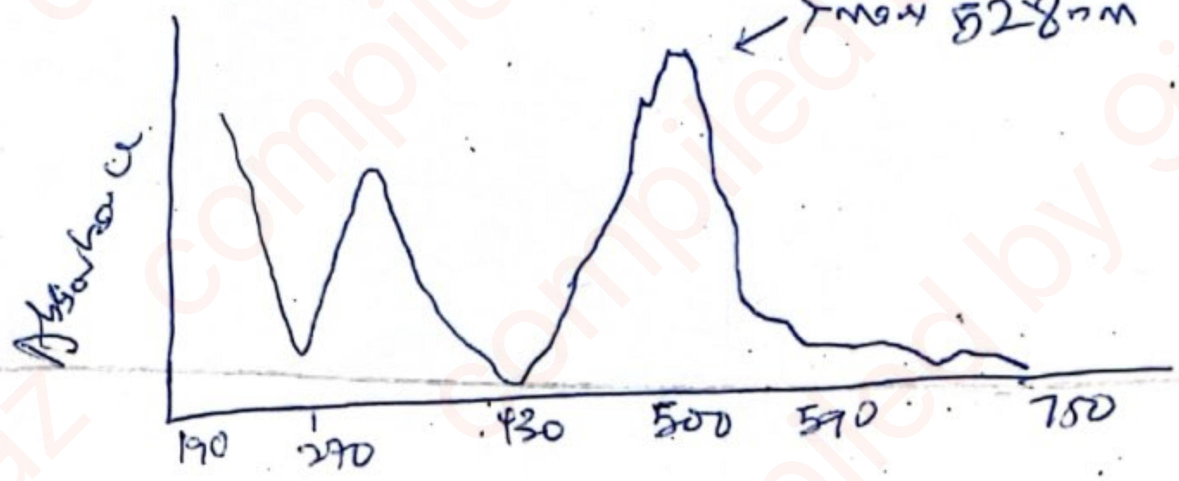
Charge transfer absorptions

In metal complexes, intense absorptions (typically in the UV or visible part of the electronic Spectrum) may arise from Ligand-centred $n-\pi^*$ or $\pi-\pi^*$ transitions, or from the transfer of electronic charge between ligand and metal orbitals. There are two types of charge transfer

- transfer of an electron from an orbital with primarily Ligand character to one with primarily metal character (Ligand-to-metal charge transfer, LMCT)
- transfer of an electron from an Orbital with primarily metal character to one with primarily Ligand character (metal-to-Ligand charge transfer, MLCT).

③ Since electron transfer from metal to Ligand corresponds to metal oxidation and Ligand reduction, an MLCT transition occurs when Ligand that is easily reduced is bound to a metal centre ~~(usually one in high oxidation state)~~ that is redily ~~reduced~~ oxidised. Conversely LMCT occurs when a Ligand that is easily oxidised is bound to a metal centre to this readily reduced.

For example, The deep purple colour of aqueous solutions of $KMnO_4$ arise from an intense charge transfer (LMCT) absorption in the visible spectrum.



The following series of complexes illustrate the effects of the metal Ligand and oxidation state of the metal on the position (λmax) of the charge transfer band.

$[MnO_4]^-$ (528 nm), $[TcO_4^-]$ (286 nm) $[ReO_4]^-$ (227 nm)
$[CrO_4^{2-}]$ (373 nm) $[MoO_4]^{2-}$ (225 nm) $[WO_4]^{2-}$ (109 nm)
$[FeCl_4]^{2-}$ (220 nm) $[FeBr_4]^{2-}$ (244 nm) $[OsCl_6]^{3-}$ (282 nm)
$[OsCl_6]^{2-}$ (370 nm)

589
645
871

14th January

21 Sc $3d^1 4s^2$

22 Ti $3d^2 4s^2$

23 V $3d^3 4s^2$

24 Cr $3d^5 4s^1$

25 Mn $3d^5 4s^2$

26 Fe $3d^6 4s^2$

27 Co $3d^7 4s^2$

28 Ni $3d^8 4s^2$

29 Cu $3d^{10} 4s^1$

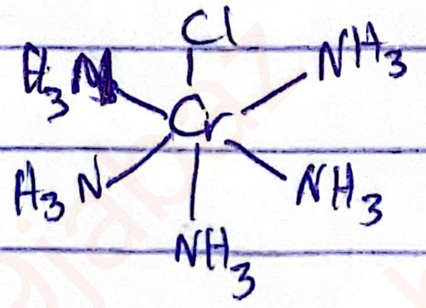
30 Zn $3d^{10} 4s^2$

What type of transition will you expect in $Ti^{3+} \Rightarrow d^1$

A d-d transition is expected in the visible region (400 — 8

because d orbitals is partially filled

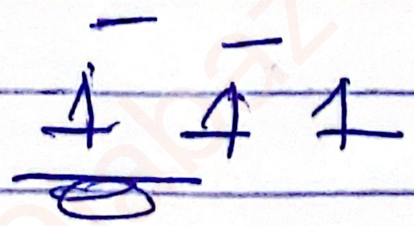
$[CrCl(NH_3)_5]^{2+} \rightarrow [CrCl(NH_3)_5]$



$G + (-1) + 0 = +2$

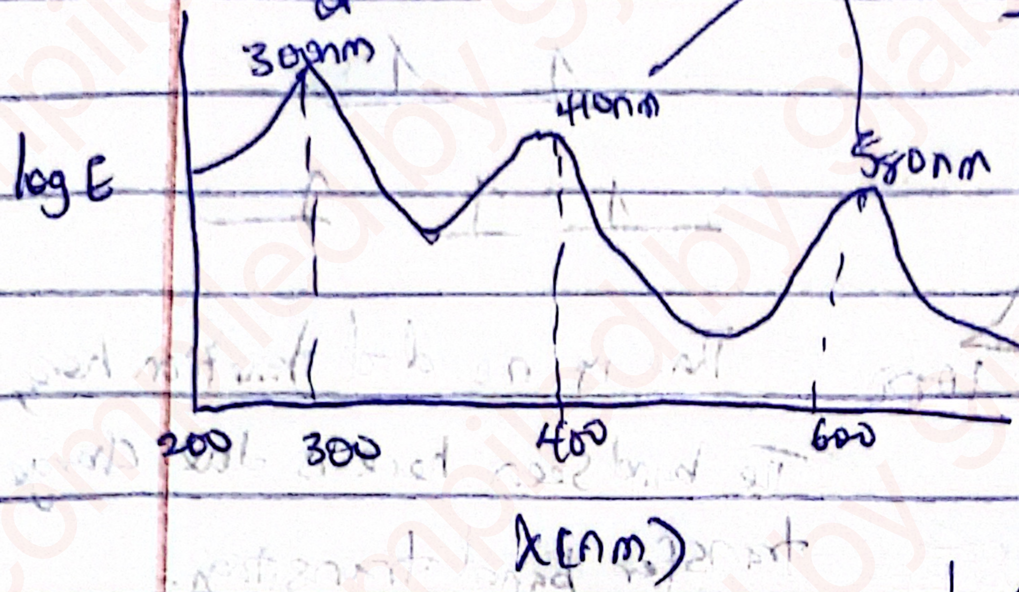
$Cr = +3$

Cr^{3+}



Cr^{3+}

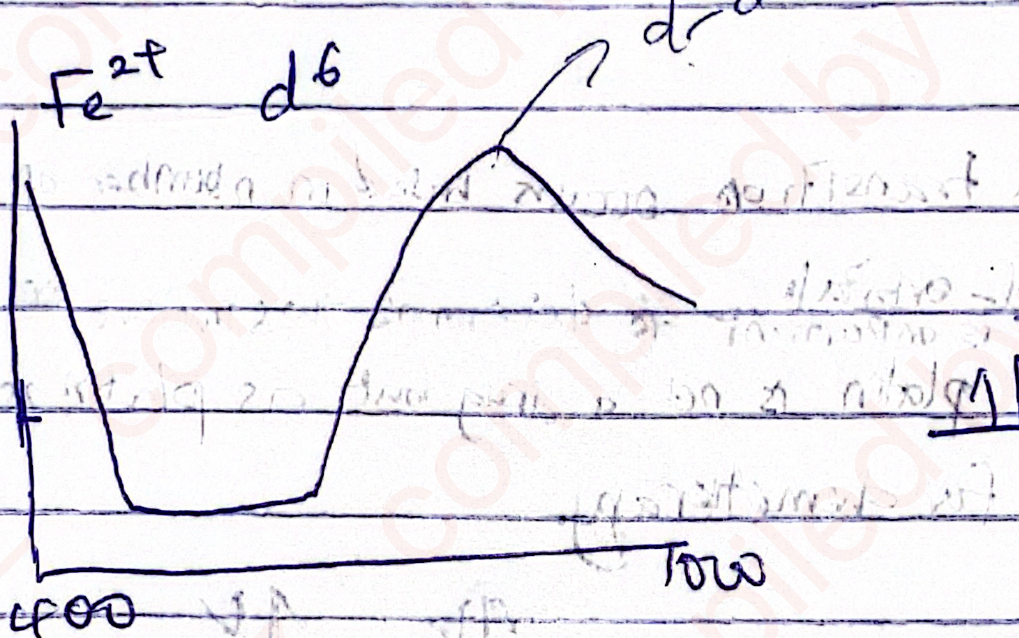
d^3 ion

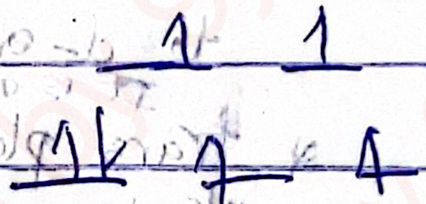


These are due to d-d transition

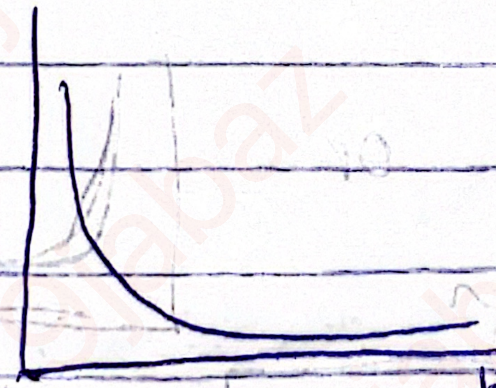
The prominent band at 300nm is due to charge transfer band

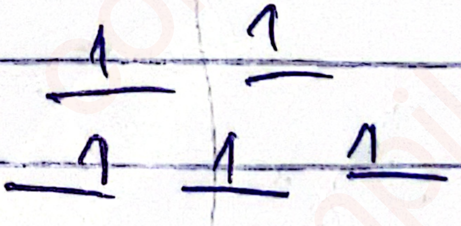
Fe^{2+} d^6





Fe^{3+} d^5

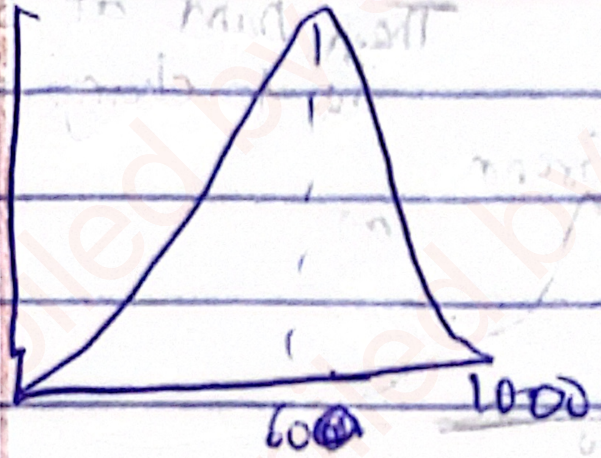


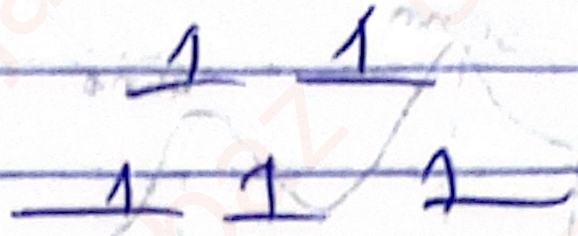


Because Fe^{3+} is ~~partially~~ half filled/partially filled, there is no transition expected

* The number of electrons in the d-orbital will determine the types of transitions that occurs.

Mn, d^5



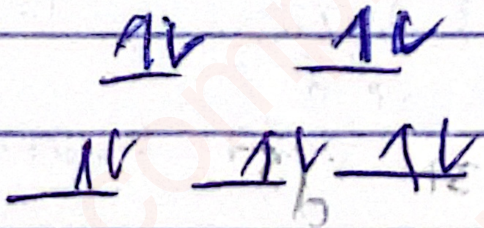


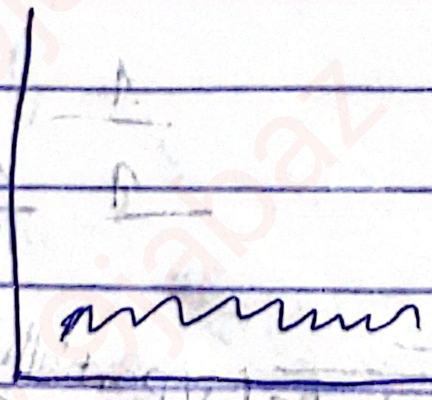
There is no d-d transition here, The band seen here is due charge transfer band transition.

* d-d transition occurs based in number of electron in the d-orbitals.
It is important to ~~determine the structure of our compounds~~

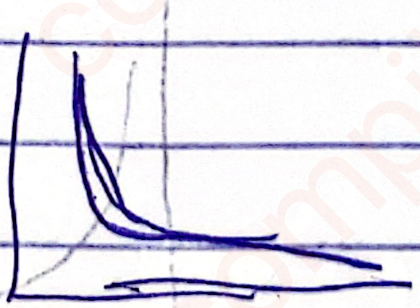
* trans platin is not a drug but cis platin is a ~~used~~ drug used for chemotherapy.

Zn, d^{10}

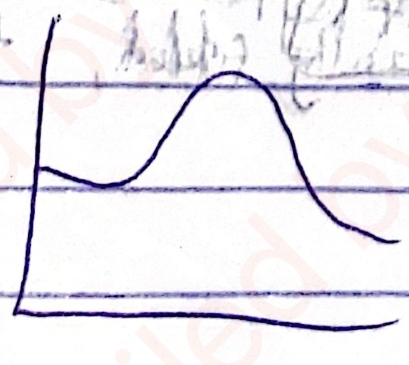




or



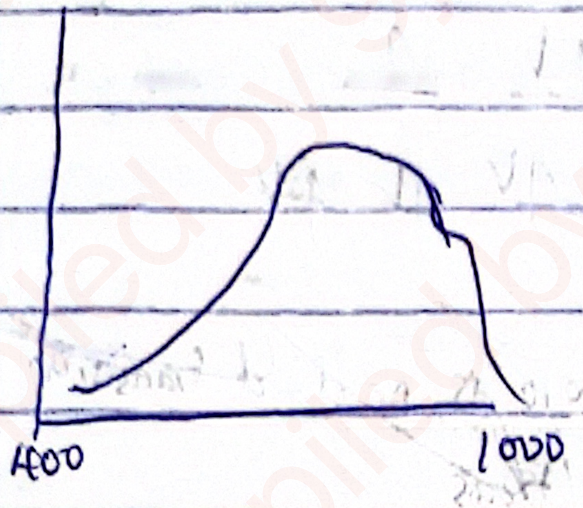
no transition



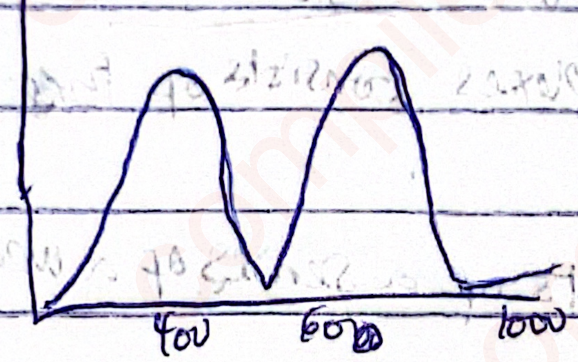
This transition is due to charge transfer band.

$t_{2g} \to e_g$

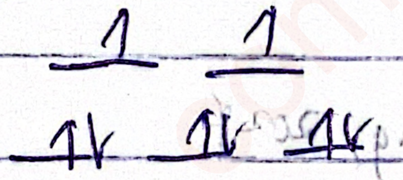
Ti^{3+} $3d^1$

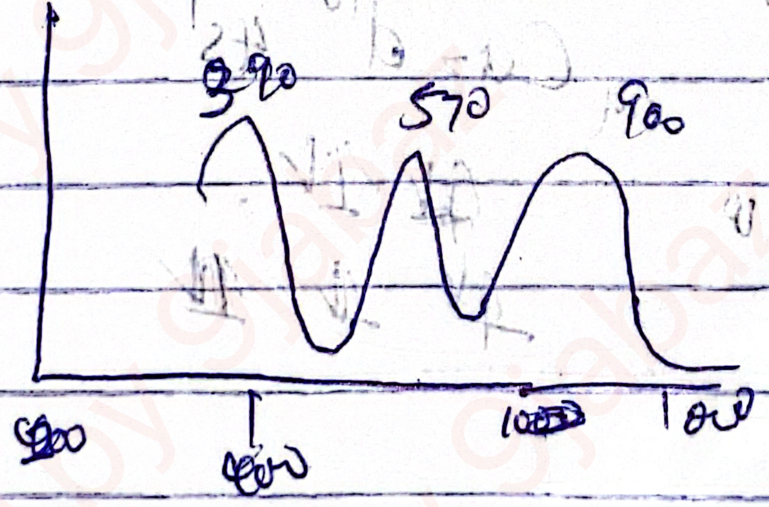


Cr^{3+} d^3



Ni^{2+} d^8





Nickel complex

Transitions

① charge transfer band

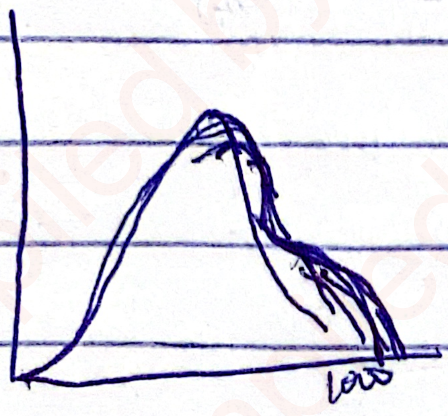
(ii) d-d transition

4 d^1 d^6 & ~ one

d^2 d^3 d^7 d^8

Cu^{2+}

d^9



↑↓ ↑

↑↓ ↑↓ ↑↓

~~There is no d-d transition here,~~

~~The trans~~

Very Important point

d^1, d^4, d^6 and d^9 complexes consists of one broad band

d^2, d^3, d^7 & d^8 complexes consists of three broad absorption band

d^5 complexes consists of a series of a weak relatively sharp absorption.

18th January, 2024

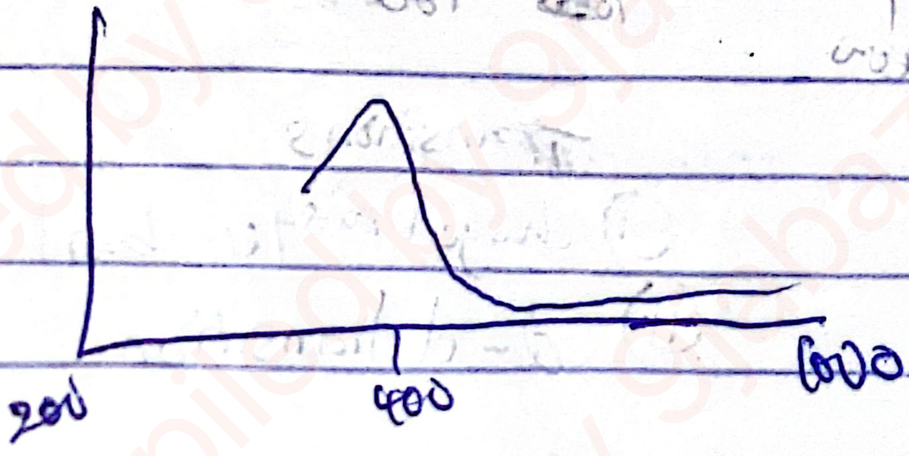
$[CuL_2]^{+1}$

$_{29}Cu = d^{10}\ 4s^1$

$Cu^+ = d^{10}$

↑↓ ↑↓

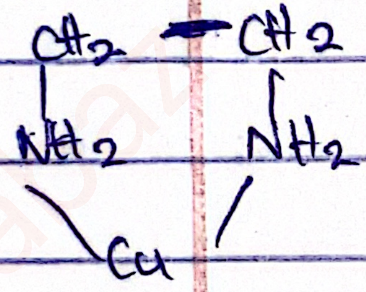
↑↓ ↑↓ ↑↓



$\lambda = 400nm$, The only transition that occured is the charge transfer band transition. The d-d transition did not ~~occur~~ because the d orbital is completely filled

monodentate : $\ddot{N}H_2$, $\ddot{N}H_3$

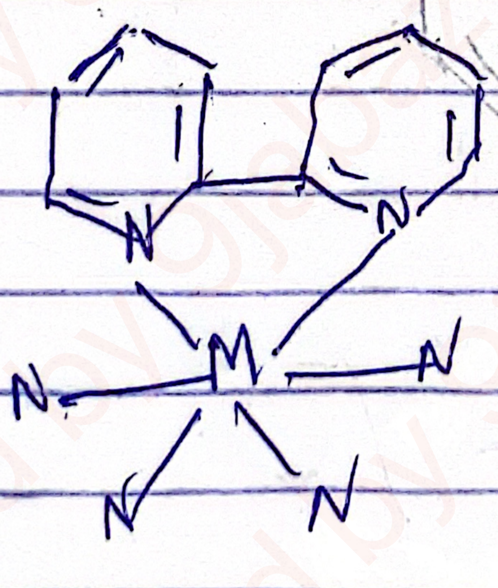
Bidendatee : Ethylene diammine, oxa



	IR
OH	3300
NH	3200 - 3100
C=O	1700

C=N C=C 1600 - 1550

C=N ~~Ligand~~ free ligand 1565cm⁻¹ shifted to 1570cm⁻¹ in the Zn

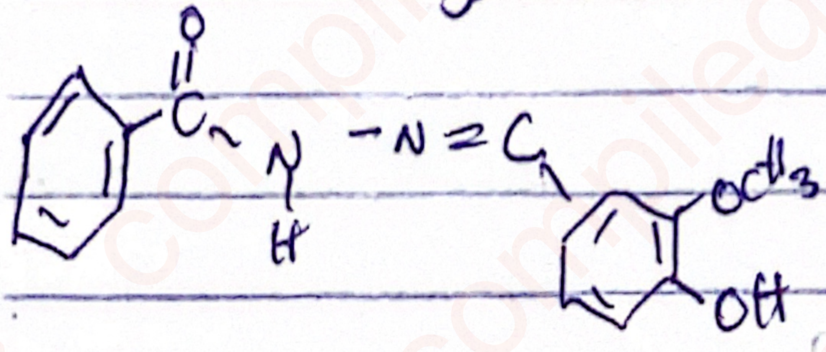


An octahedral complex has 8 sides

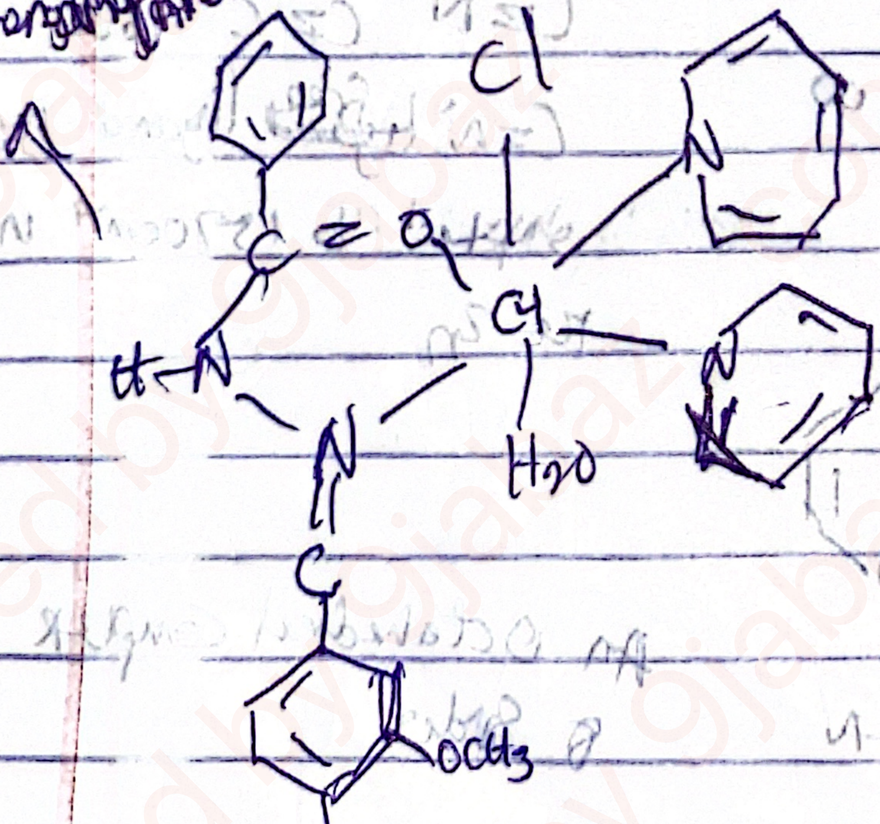
After binding to the metal, the functional group belongs to the metal is lengthened, i.e vibrational frequency is reduced, as energy is also reduced.

A shift shows that the ~~metal~~ ~~ligand~~ ligand has been to the metal.

21st January, 2024

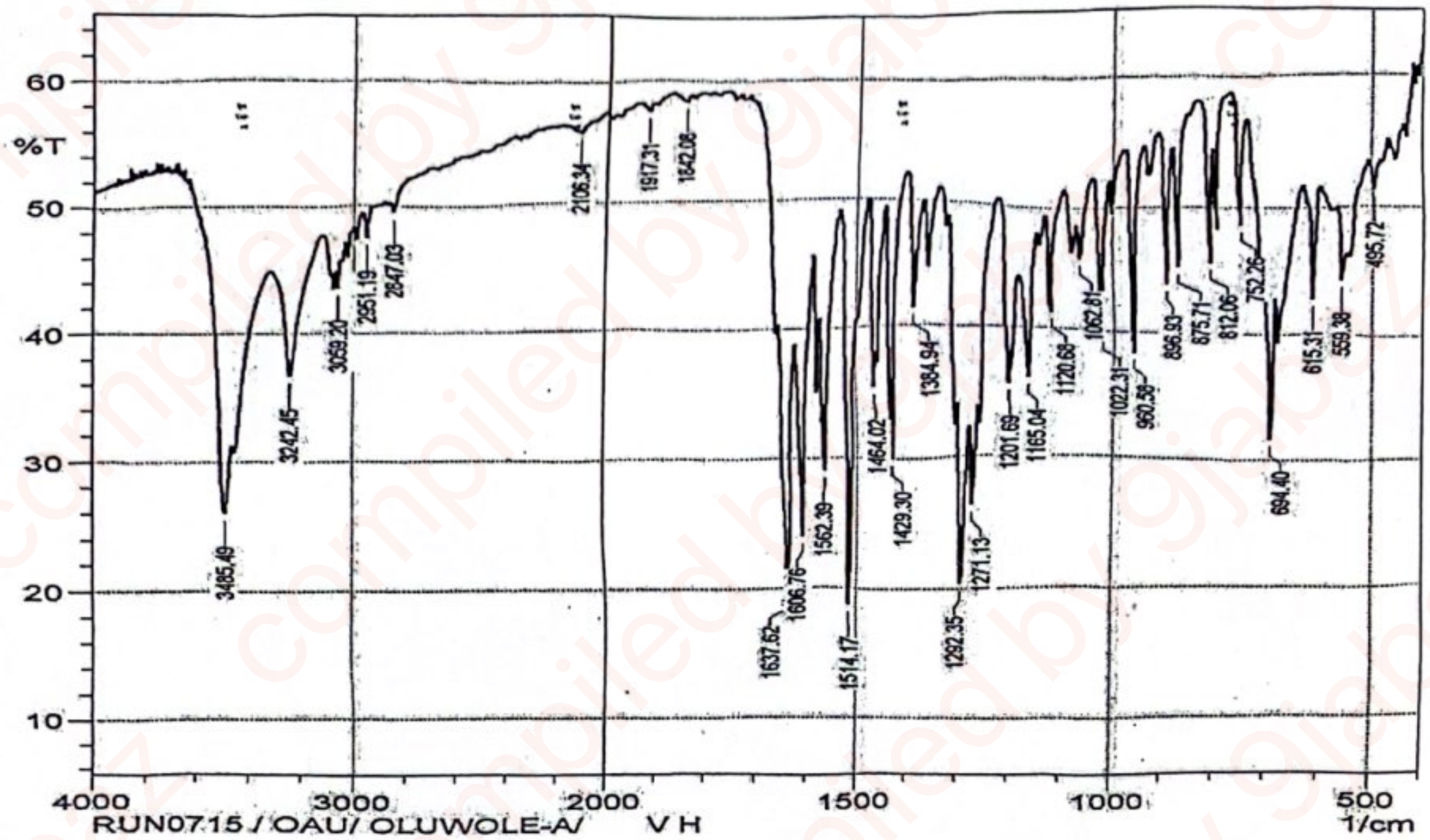


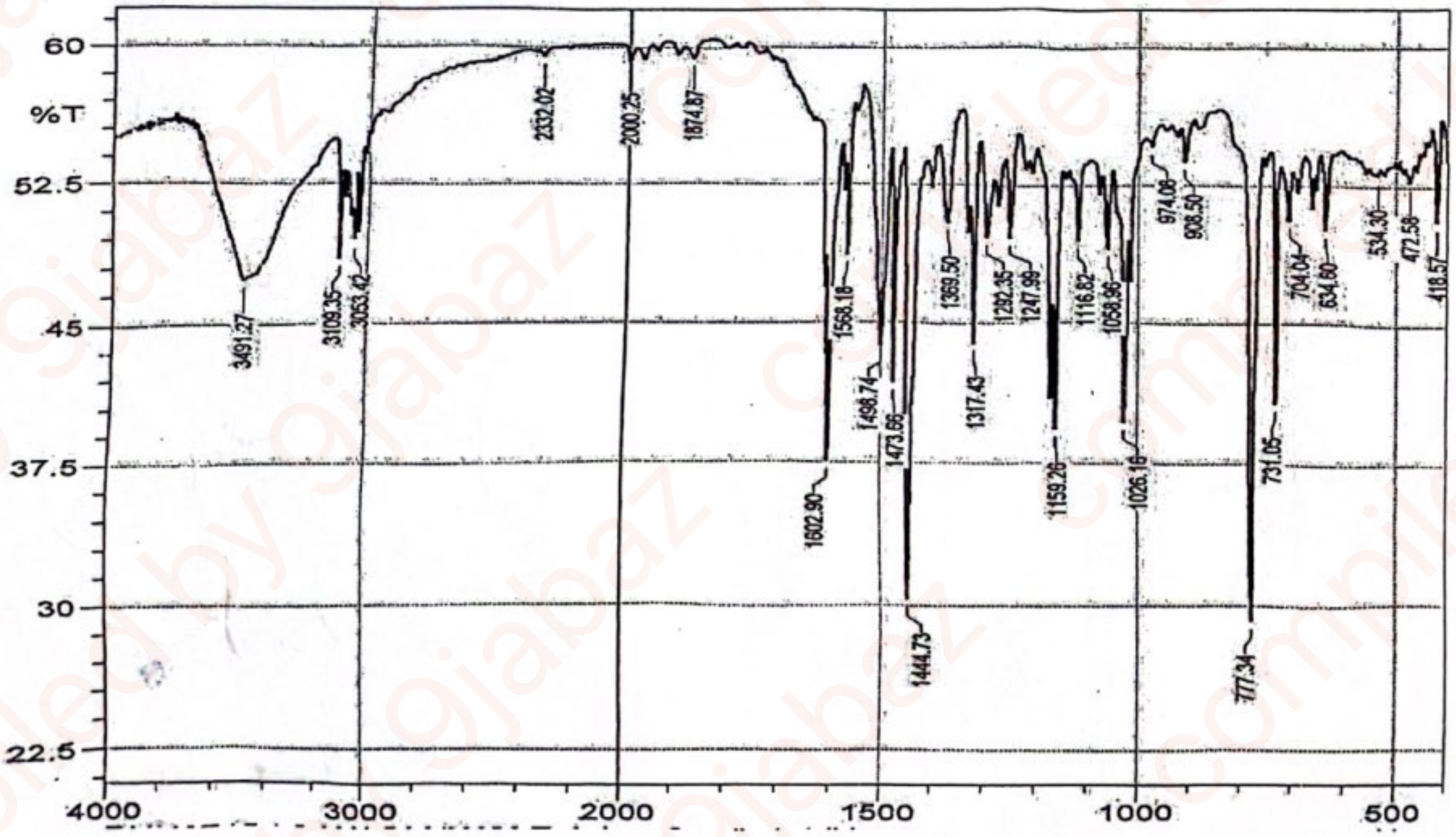
C10, phenylhydrazone



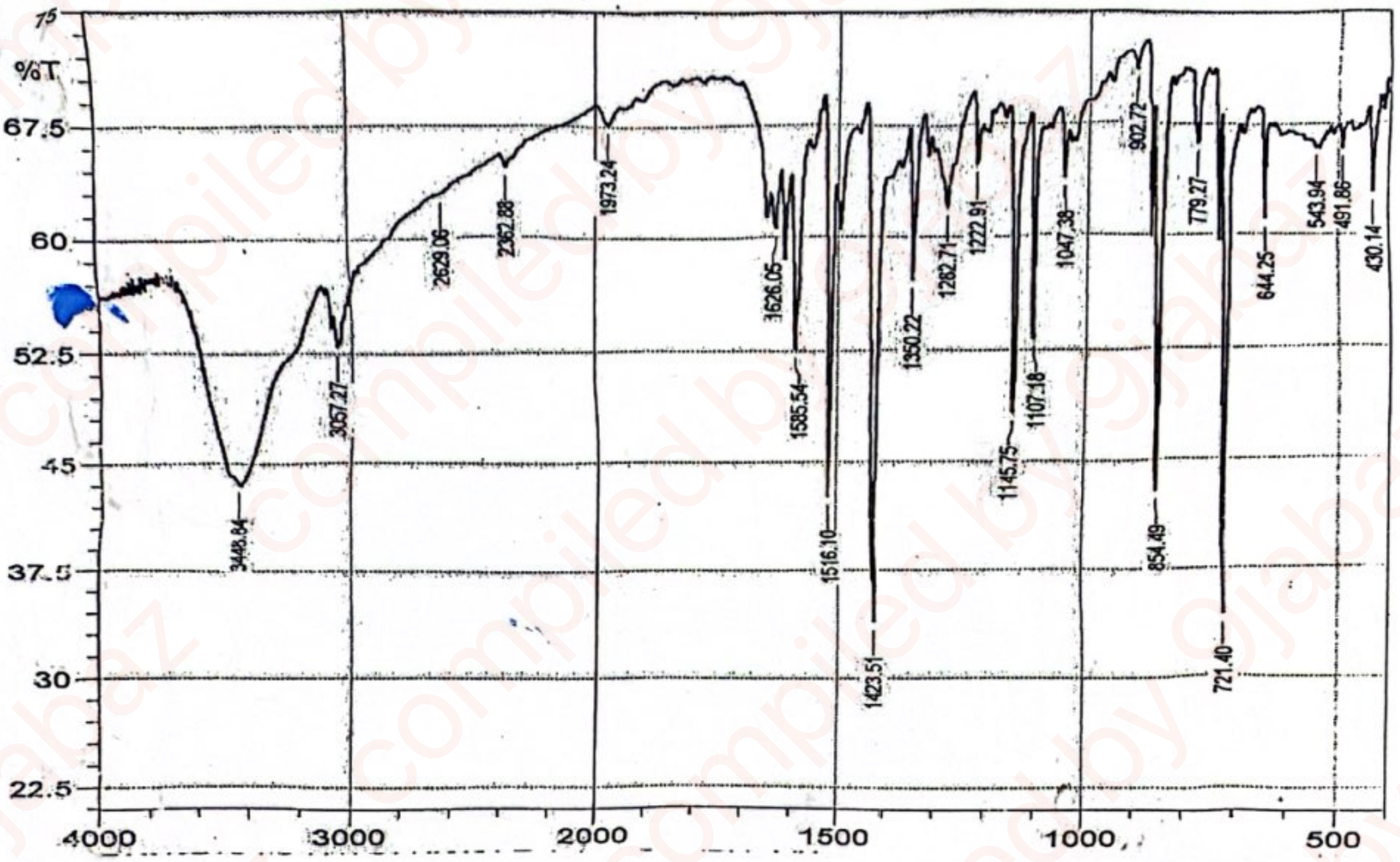
2,2-bipyridine

VBH





(Cu(VBH)By(H_2O)Cl)



Cu(VBH)Phen$(H_2O)_2$Cl

Ligand spectral

OH = 3486 cm^{-1}

C=O = 1637 cm^{-1}

N-H = 3240 cm^{-1}

C=N = 1606 cm^{-1}

Metal complex Spectral

~~OH, N-H disappeared~~

C=O, N-H disappeared on forming a metal complex

OH → 3491 cm^{-1} undergoes hydrogen bond which might make it to shift

C=N → 1602 cm^{-1} an indication that the ligand thus interacted with the metal

Metal-Ligand Spectral

It is usually taken in the fingerprint region

M-O = 634 cm^{-1}

M-N = 418 cm^{-1}

1,10, phenanthroline

C=N (base) = 1568 cm^{-1}

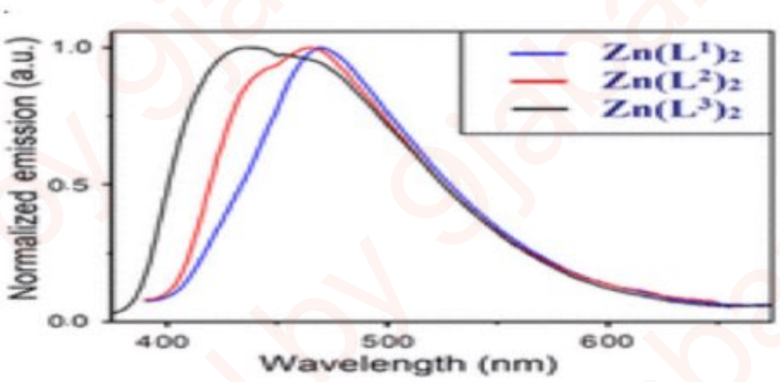


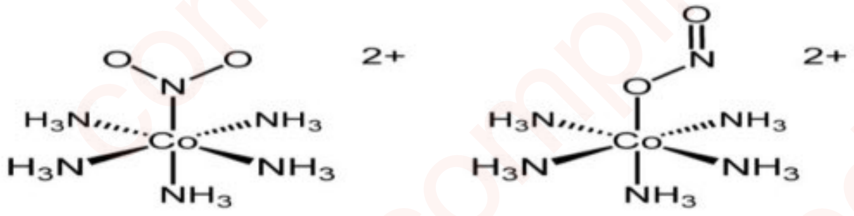
Figure 1: UV-Visible spectra of zinc(II) complexes.

5a. The electronic spectra above (Fig. 1), belong to zinc(II) complexes.

i. What is the origin of these bands?

ii. Explain your answer in (1a), above.

5b. The two compounds drawn below (Fig. 2), exhibit linkage isomerism. The yellow isomer is named pentaamminenitrito-N-cobalt(III) ion and red isomer is pentaamminenitrito-O-cobalt(III) ion. How would you use infrared spectroscopy (IR) to distinguish between the two isomers?



Yellow

Red

Figure 2: Cobalt(II) complexes displaying linkage isomerism.

5c. The diagrams of the structure of Ligand and its zinc(II) complex are given in (Fig. 3). below. The Infrared spectra (IR) of the Ligand and its zinc(II) complex is given in (Fig. 4; A and B respectively), while C is the Mass spectrum of the zinc(II)complex.

i. What are the functional groups where the binding of the ligand to zinc(II) occur ?

ii. Interpret the IR spectra to elucidate the formation of the complex.

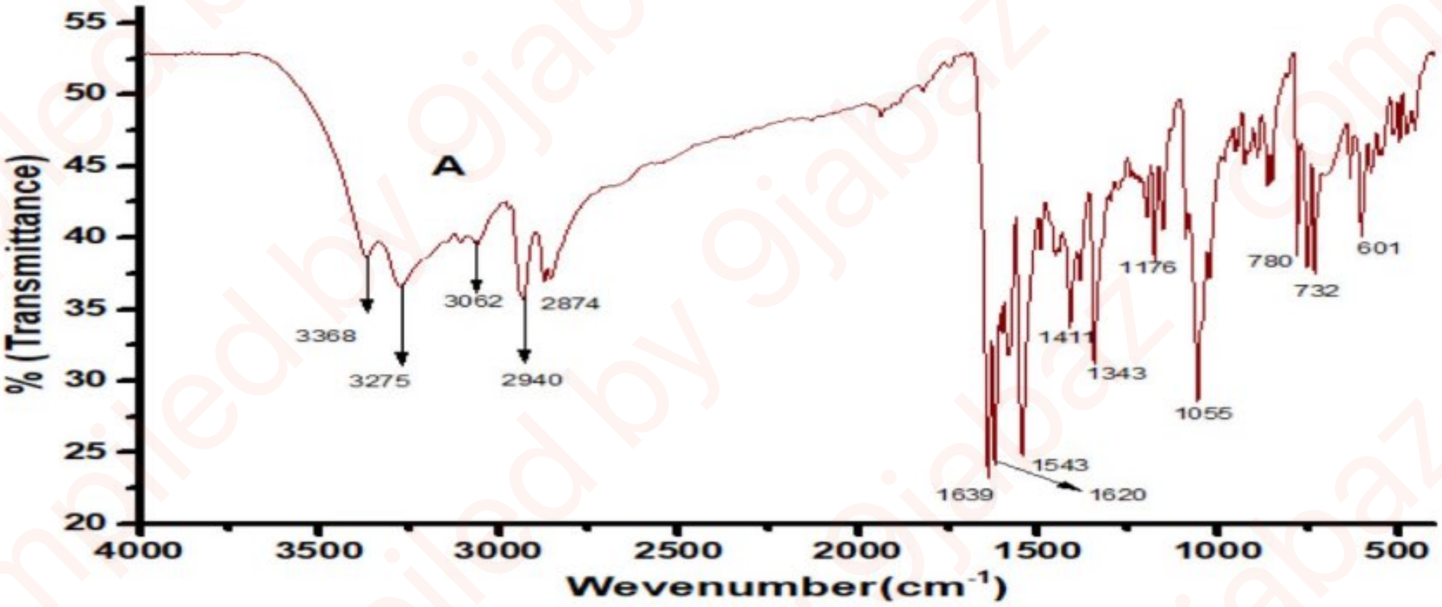
iii. In the Mass spectrum, account for the molecular ion peak and the m/z peak at 322.07.

iv. What structural orientation does the zinc(II) complex exhibit?

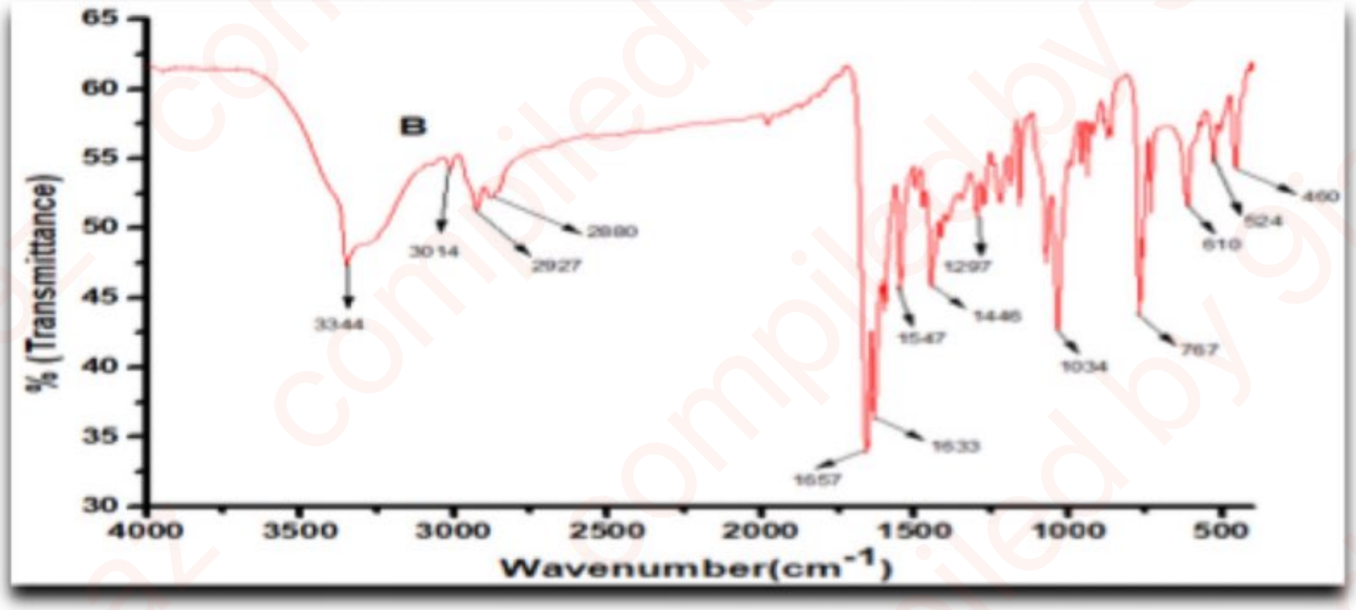
Ligand

zinc(II) complex

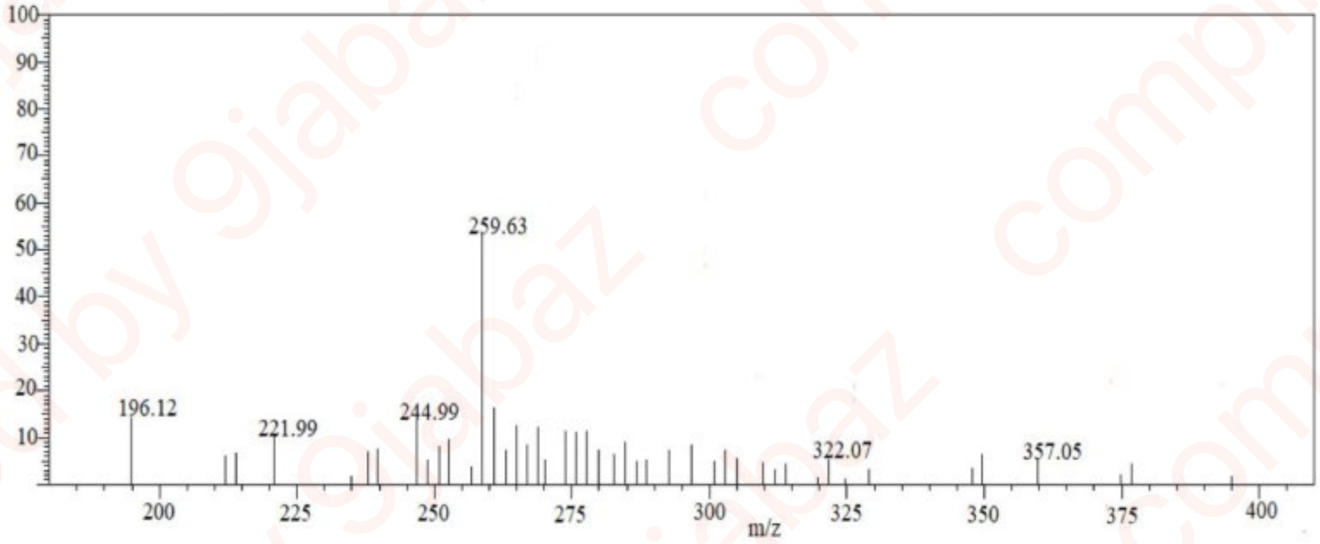
Figure 3: Structure of ligand and Zinc(II) complex



(A): IR Spectrum of Ligand.



(B): IR Spectrum of zinc(II) complex



(C): Mass spectrum of zinc(II) complex.

Figure 4: A and B are the infrared spectrum of the Ligand and zinc(II) complex.

C is the mass spectrum of the zinc(II) complex.

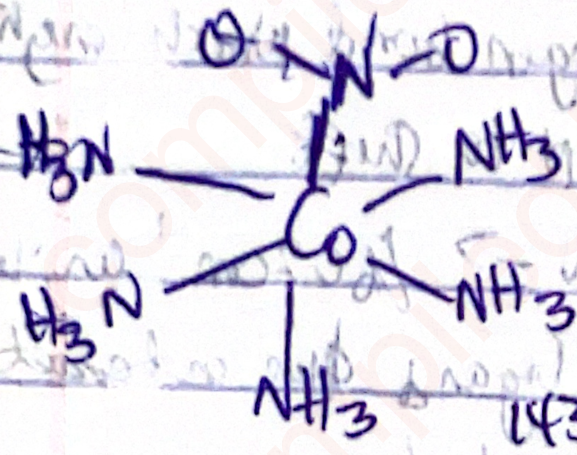
Spectra culled from https://www.ncbi.nlm.nih.gov/pmc/articles/PMC9669718/

How would you use IR to differentiate the two $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5(SO_4)]Br$

1104 cm^{-1} — 1040 cm^{-1}

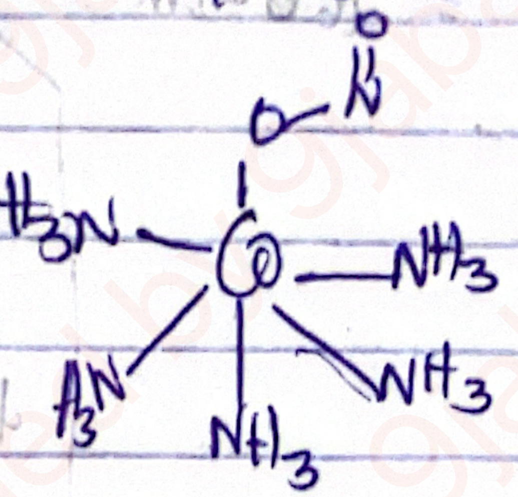
613 cm^{-1} — 1120 cm^{-1}

970 cm^{-1}



1430 cm^{-1}

825 cm^{-1}



1460 cm^{-1}

1060 cm^{-1}

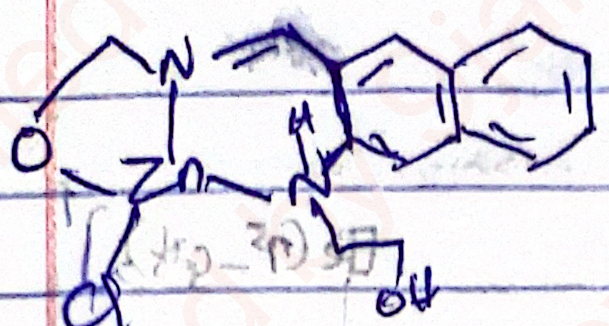
Geometry: octahedral

Metal
C=N ⇒ 1620 cm^{-1}
O-H ⇒ 3368 cm^{-1}
N-H ⇒ 3275 cm^{-1}

Zn Complex
C=N ⇒ 1633 cm^{-1}
N-H ⇒ 3014 cm^{-1}
C-O ⇒ 1034 cm^{-1}

Zn - ligand
Zn-O ⇒ 610 cm^{-1}
Zn-N ⇒ 460 cm^{-1}

	O-H (cm^{-1})	N-H (cm^{-1})	C=N (cm^{-1})	C-O (cm^{-1})	Zn-O	Z
Ligand	3368 cm^{-1}	3275	1620	1055	—	—
Zn (II) Complex		3014	1633	1034	610	460

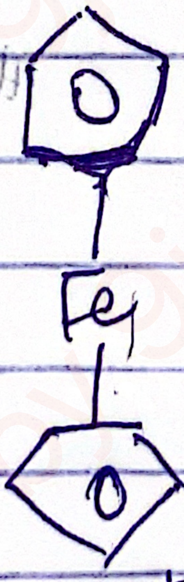


Orientation: tetrahedral

* Organo metallic compound is the direct bond between a metal and a carbon. They are used mainly as catalyst

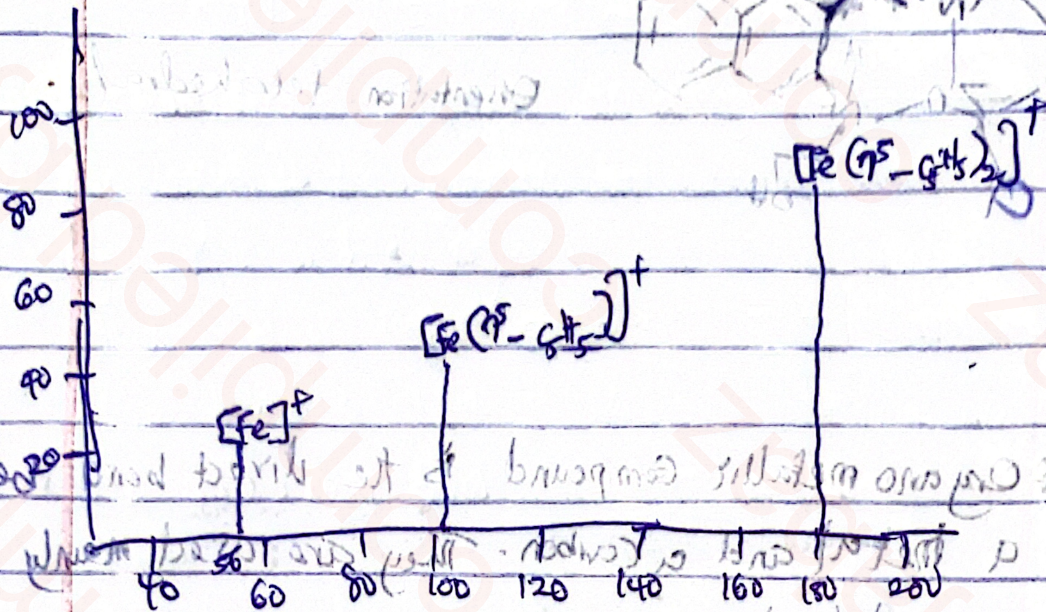
frequency ⇒ 2080 cm^{-1}
bridging ⇒ 1850 cm^{-1}

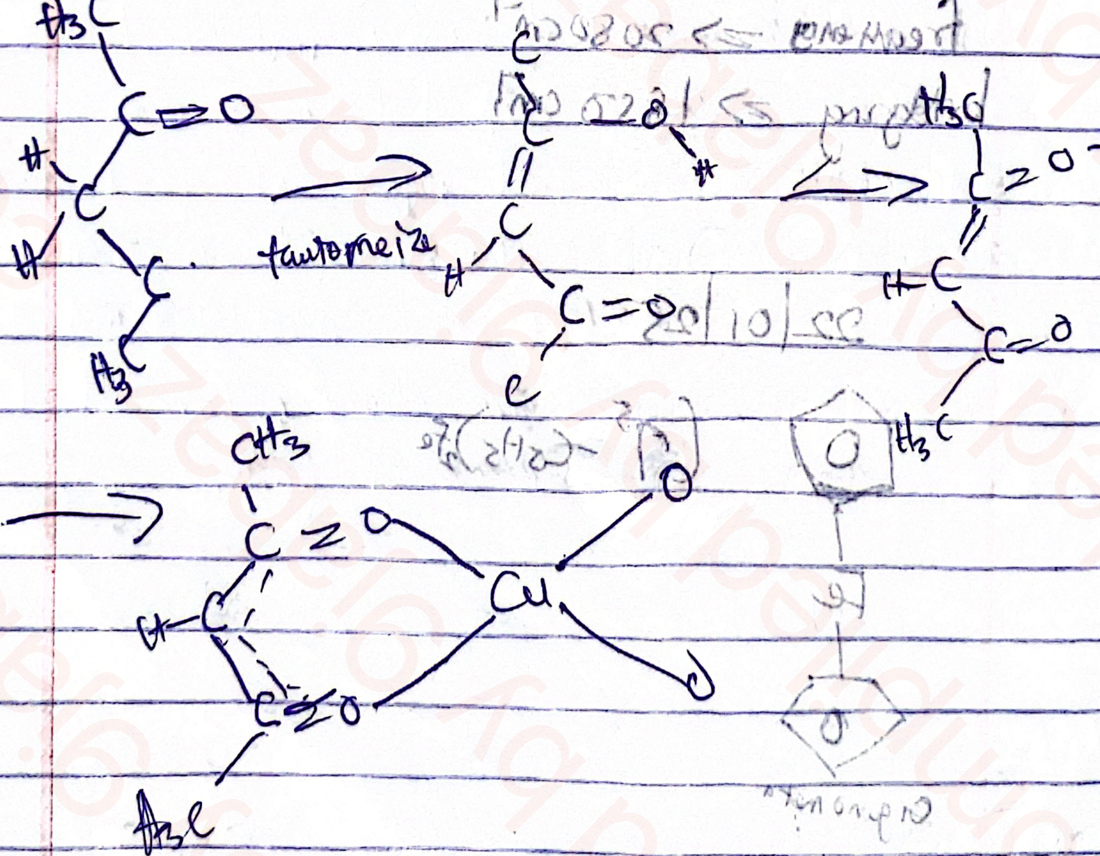
22/01/25

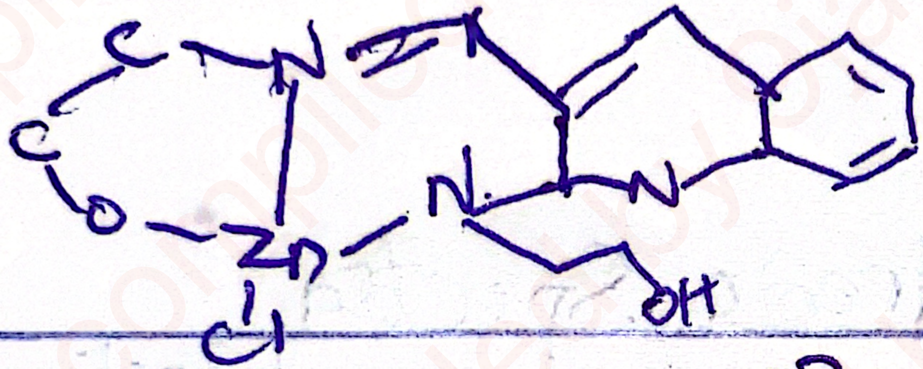


$(\eta^5-C_5H_5)_2Fe$

Organo meta


100
80
60
40
20
40
56
60
80
100
120
140
160
180
200
$[Fe]^+$
$[Fe(\eta^5-C_5H_5)]^+$
$[Fe(\eta^5-C_5H_5)_2]^+$


tautomerize



$[C_{14}H_{16}O_2N_3ZnCl] = 358.5$

Po ·CS

1—16

CHEMISTRY DEPARTMENT

OBAFEMI AWOLOWO UNIVERSITY,

ILE-IFE.

73
66
139
75

CHM 307

APPLICATION OF SPECTROSCOPIC TECHNIQUES.

TUTORIAL MANUAL.

Nuclear Magnetic Resonance (NMR)

1. The nmr. spectrum of $C_9H_{10}O_2$ shows three single peaks at 7.29 (area 84); 5.00 (area 34) and 1.98 ppm (area 50).

   What is the structural formula of the compound?

2. The nmr spectrum of a dichloro compound (M.W. 113) has a quintet at 2.20 and triplet at 3.70 ppm. What is the structure of this compound Assign the absorption peaks to specific protons.

3. Predict what the high-resolution nmr spectra of the following compounds would look like. Indicate the approximate values for the different groups of equivalent protons in these compounds.

   (a) propanone
   (b) ethanoic acid
   (c) chloroethane
   (d) 1-bromo-3-chloropropane
   (e) ethyl benzene
   (f) propamamide
   (g) 2-iodobutane

4. Interpret and discuss the nmr. spectra of the following compounds and suggest a structure for the compound. Indicate the nature of any additional spectroscopic information which would help you verify your prediction.

   (a) Compound A C_4H_8O NMR: 1.0 (triplet, J 5.0 Hz), 2.20 (siglet) and 2.51 ppm (quartet, 5.0 Hz)

Tab.l

C_3H_8O. NMR: 1.21 doublet, (J 4.80 H_z 1.62)

c) and 4.00 ppm (septet, J 4.8 H_z).

$C_5C_4H_8O$ NMR: 10.00(triplet) , 1.6 (multiplet), 2.5

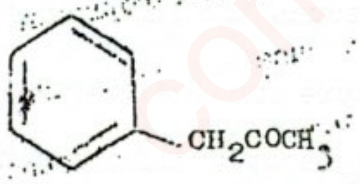
plet) and 9.82 ppm (triplet).

(d) Compound D $C_9H_{10}O_2$ NMR: 1.98 (singlet , 50 squares),
5,00 (singlet, 34 squares) and 7.29 ppm (singlet, 84 squares).

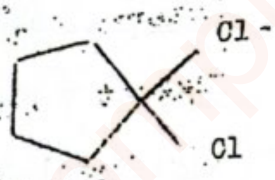
5. State the different types, (indicating multiplicity where applicable), of signals you would expect to find in the NMR spectra of the following compounds, and state the protons giving rise to each signal (e.g. triplet due to $CH_3.CH_2-$, etc.)

5 (a) $CH_3\ CH_2COCH_2COCH_2C{\equiv}CH$

(i)



(ii)



(iii)

(b) A compound (D) $C_{10}H_{12}O$, IR: 2720,1700cm^{-1} is oxidisable to 1,3-benzene dicarboxylic acid. In NMR, it absorbs at the following frequencies (delta values): 10.20 (singlet, [illegible] squares); 7.45 (multiplet 18.2 squares); 2.87 (septet, [illegible] squares) and 2.34 (doublet 26.8 squares).

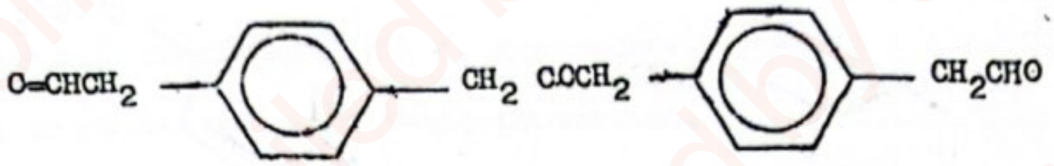
(i) Deduce the [illegible]

(ii) Describe [illegible] re of the [illegible]

6. How many different types of signals would you expect to find in the proton NMR spectrum of each of the following compounds. (Ignore coupling)

(a) $CH_3\,CHBr\,CH_3$

(b) $CH_3\,CH_2\,COOC_2H_5$

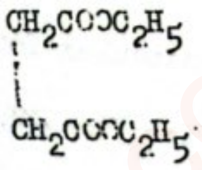
(c) 

7. The proton NMR spectrum of a compound $C_2H_4Cl_2$ showed signals at the following frequencies (δ values):

2.5 (3H, doublet), 5.8 (1H, quartet).

Deduce th structure of the compound.

8. (i) Sketch the NMR spectrum (60 MHz) that you would expect for

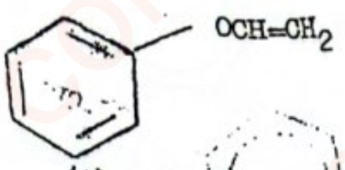


$$\begin{array}{l} CH_2COOC_2H_5 \\ | \\ CH_2COOC_2H_5 \end{array}$$

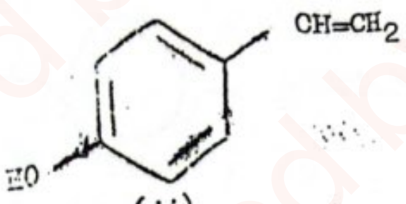
showing the relative chemical shifts and signal intensities.

(ii) Briefly explain the <u>relative</u> chemical shifts of the protons (by simply showing why specified protons absorb at higher or lower frequencies than others).

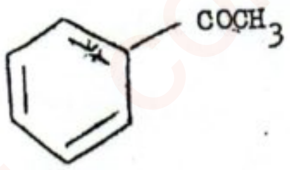
9. Give main features of the NMR of the following isomeric compounds which will aid their identification.



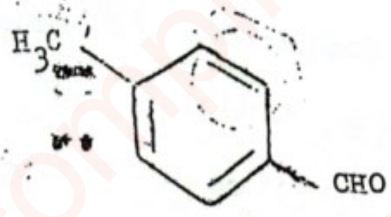
(i)



(ii)



(iii)



(iv)

10. A hydrocarbon A of molecular formula $C_{11}H_{14}$ has weak absorption at about ν_{max} 1620 cm^{-1}. The PMR shows signals at δ 1.1 (6H, d, $J = 3H_z$);
2.9 (1H, heptet, $J = 3H_z$); 5.4 (2H, d, $J = 5H_z$);
5.9 (1H, t, $J = 5H_z$); 6.9 (2H, d, $J = 10\ H_z$);
7.3 (2H, d, $J = 10\ H_z$).

Ozonolysis of A followed by appropriate work up of reaction product gave two compounds B and C of molecular formulae $C_{10}H_{12}O$ and CH_2O respectively.

C was further oxidised and methylated to give D $C_2H_4O_2$. D gave PMR signals at δ 3.8 (3H, s) and 9.0 (1H, s). Deduce the structures for A, B, C and D.

11. A compound **X**, C_4H_7NO, gives a yellow precipitate with sodium hypoiodite solution. The nmr spectrum shows only two signals, at 3.25 and 1.63 ppm, unsplit, with relative area 1 and 6, respectively. Write a structure for X which is consistent with these properties.

Mass Spectra

1. The mass spectral data for compounds A, B and C are given below:

(a) Suggest structures for the compounds.

(b) How could these structures be confirmed by other spectroscopic methods?

Compound A $C_4H_8O_2$

m/e	88	73	60	45	29
relative abundance	15	40	100	25	20

Compound B $C_4H_{11}N$

m/e	73	42	30
relative abundance	10	5	100

Compound C C_7H_6O

m/e	106	105	77	51	29
relative abundance	99	98	100	60	15

2. The mass spectrum on an organic compound liquid shows a very large peak at m/e 31. There are also small peaks at m/e 15, 27, 29, 45 and 46. Deduce the structure of the compound.

3. (a) (i) State [illegible] associated with the [illegible] of the [illegible] organic compound.

(ii) [illegible]

(iii) What is the significance of the molecular ion peak in the elucidation of the structure of an organic compound?

3. (b) Which fragment ions would you expect to give the most significant peaks in the mass spectra of:

(i) $CH_3.COOCH_2.C_6H_5$.

(ii) $CH_3(CH_2)_2CO(CH_2)_2CO(CH_2)_5CH_3$.

Briefly indicate the origin of these fragment ions.

4. The mass spectrum of alkylbenzenes often shows a prominent peak of mass 92. Write a likely mechanism for breakdown of n-propylbenzene to give a fragment of mass 92.

5. Decane and 4,4-dimethyloctane are structural isomers of formula $C_{10}H_{22}$.

(i) With the aid of equations to depict their fragmentation pattern, outline how MS could be used to differentiate between them.

(ii) Which of the two compounds would you expect to show a more intense molecular ion peak in its MS and why?

6. (a) Heptan-3-one, $CH_3CH_2COCH_2CH_2CH_2CH_3$ showed the following peaks in its MS:

m/e	27	28	29	41	57	72	85	114
R.A.(%)	35	10	70	22	100	20	22	10

- Using conventional signs and equations, show how the peaks at m/e 27, 29, 57, 72 and 85 are formed upon electron impact on the molecule in a mass spectrometer. State the mode of each type of fragmentation you use.

6. (b) Write the structures of the fragment ions, which you would expect to give the two most significant peaks in the MS of each of

(i) $C_6H_5CH_2OCH_3$

(ii) $C_6H_5CH_2CH_2CH_2OH$.

Show how the fragment ions are formed.

7. The mass spectrum of an aliphatic compound containing carbon, hydrogen and oxygen only showed major peaks at m/e 29, 47, 75, 85, 103, 143 and 187. Account for these peaks in interpreting the spectrum.

8. A monoamine has the following mass spectrum.

m/e	115	100	58
relative abundance	17	50	100

What is the structure of the amine?

9. Briefly explain the following terms:

   (a) Mass spectrum

   (b) Base peak

   (c) Molecular ion

   (d) Metastable ion

   (e) McLafferty rearrangement

10. What roles do metastable ions play in the application of mass spectroscopic techniques?

11. Describe the situations in which the recognition of the molecular ion peak in the mass spectrum of an organic compound, may be difficult.

12. The following peaks were observed in the MS of ethyl sec-butyl ether: m/e 29/35%): 45(100%): 57(18%): 73(50%) and 87(5%). Write feasible structures for the ions at the stated m/e values.

13. Deduce the structure of a compound of molecular formula $C_4H_{11}N$ which showed the following peaks in its MS:

m/e	30	42	73
R.A.	100	5	10

14. 1-pentanol and 2-methyl-2butanol are isomeric alcohols; with the aid of equations do depict their fragmentation pattern,. outline how MS could be used to differentitate between them.

15. Compound A, $C_7H_{14}O$, gives a crystalline precipitate with 2,4-dinitrophenyldrazine. In the MS, the following peaks were observed:

m/e	114	85	72	57	29
R.A.	10	22	20	100	70

Write feasible structures, using conventional signs and equations to show how they are formed, for the ions at the stated m/e values - after deducing the structure of **A**.

16. Compound B, $C_9H_{10}O_2$, can be converted to compound C, C_7H_8O, by treatment with aqueous NaOH. Compound C does not give a precipitate with 2,4-dinitrophenyldrazine. Compound B absorbs strongly in the IR at 1745 cm^{-1}. It gives the following peaks in the MS: m/e 150(30%); 108(100%); 91/88%); 79(22%) and 43(72%). Deduce the structure of **B**.

17. Describe the methods for determining the molecular formular of a compound by mass spectrometry. Compare their relative advantages.

18. Phenyl propanoate and benzyl ethanoate are structural isomers having molecular formular $C_9H_{19}O_2$. Outline how MS could be used to differentiate between them.

19. Using equations and converntional sugns to represent relevant modes of fragmentation, explain why:-

(i) 2-methylpropane has a lower intensity molecular ion peak than butane.

(ii) All primary alchols, R CH_2CH_2OH, have a prominent fragment cation at m/e = 31.

20. a) 2-Methylpentanal, $CH_3CH_2CH_2CH(CH_3)$ CHO has the following mass spectrum:-

m/e 27/18%); 29/22%); 41/30%) 43(100%) 58(95%);
71(17%) and 100(5%).

Using conventional signs and equations only, show how the peaks are formed upon electron bombardment on the molecule in a mass spectrometer.

b) What gragment ions would you expect to give the most significant peaks in the mass spectrum of hept-1-en-6-one.

21. 3, 3-Dimethylheptane and nonane are structural isomers of molecular formular C_9H_{20}. With the aid of equations to depict their fragmentation patterns, describe how mass spectrometry could be used to differentiate between them.

22. The mass spectrum of a compound containing C, H, O and N gives a maximum m/e of 121. Its IR spectrum show peaks at 700, 750, 1520, 1685 and 3100 cm^{-1}, and a twin peak at 3440 cm^{-1}. What is a reasonable structure for the compound?

COMBINED SPECTRA

1.(a) Compound A, C_5H_8O has the following absorption bands in the ir spectrum: 3020, 2900, 1690, and 1620 cm^{-1}; In the uv spectrum it absorbs at 227 nm. ($E = 10^4$). Propose a structure and say whether it is the only possible one. The compound gives negative Tollen's and Fehling's tests.

(b) Compound (F) C_5H_8O has absorption bands in the infrared spectrum at 3020, 2900, 1690 and 1620 cm^{-1}. In its ultraviolet spectrum, it shows maximum absorption at 226nm. (E max 10^4). It does not react with either Tollens' or Fehling's reagent. Propose the most probable structure for F.

(c) An unknown substance B, $C_6H_{10}O$ has a strong band in the infrared spectrum at 1681 cm^{-1}, and in the ultraviolet spectrum it absorbs at 226nm (E_{max}7,900).

The compound gave a negative iodoform test. Deduce the structure of the compound B.

(d) An unknown substance C, $C_7H_{12}O$ has a strong band in the infrared spectrum at 1690cm^{-1} and in the ultraviolet spectrum it absorbs at 227nm. The compound gave a positive iodoform test. Deduce the structure of compound A.

COMBINED

Derive structural formulae that are consistent with the data given for the following compounds. In cases where the molecular formula is not given, the compound may contain nitrogen and/or halogen in addition to C, H and O.

(a) M.F. : $C_{15}H_{14}O$.

IR : 1710 cm^{-1}

NMR (delta values): 2.20 (singlet, area 3),

5.08 (singlet, area 1) and

7.25ppm (singlet, area 10 units).

(b) M.S. : m/e 58 (parent peak)

UV : no absorption above 210 nm.

IR : 2941 (m) and 1458 cm^{-1} (m).

NMR (delta values): 4.75 (triplet, J = 7.1 Hz, 29.4 squares) and 2.75 (quintet, J = 7.1 Hz, 14.6 squares).

(c) MS. m/e 72 (parent peak)

UV: maximum absorption 274nm (E 17).

IR: 2941-2857 (m), 1715 (s) and 1460 cm^{-1} (m)

NMR (delta) 2.48 (quartet, J = 7.3 Hz, 12.0 squares),

2.12 (singlet, 17.6 squares) and

1.07 (triplet, J = 7.3 Hz, 18.2 squares).

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(d) MS : m/e 104 (parent peak)

UV : maximum absorption 203nm (E 40, water)

IR : 3125–2857 (m), 2695 (w), 1718 (s) and 1449 cm^{-1}

NMR (delta): 10.95 (singlet, 5.4 squares), 4.13 (singlet, 11.0 squares), 3.66 (quartet, J = 7.1 Hz, 10.6 squares) and 1.27 (triplet, J = 7.1 Hz, 16.2 squares).

(e) MS: m/e 110 (parent peak)

UV: maximum absorption 239 nm, (E 21, 400)

IR: 3077–2857 (m), 1661 (s), 1608 (w) and 1449 cm^{-1} (m).

NMR: (delta); 6.00 (singlet, 6.4 squares), 1.90 (singlet, 17.9 squares) and 1.83 (singlet, 18.6 squares).

(f) MS: m/e 158 (parent peak).

UV: maximum absorption 225nm (E 50, hexane)

IR: 3077–2857 (m), 1828 (s), 1757 (m) and 1456 cm^{-1} (m).

NMR: (delta): 2.70 (septet, J = 6.7 Hz, 6.4 squares), 1.20 (doublet, J = 6.7 Hz, 37.2 squares).

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3. Compound **A**, C_5H_8O, has the following absorption bands, amongst others, in the IR spectrum: 3020, 2900, 1690, and 1620, 970 cm^{-1}. In the UV spectrum it absorbs at 227 nm ($E = 10^4$). The compound gives negative Tollen's and Fehling's tests. Propose a structure and, indicate whether it is the only possible one.

4. Compound **L** ($C_9H_{10}O$) shows IR: 1710 and 1602 (weak) cm^{-1}. NMR: singlets at 2.10, 3.60 and multiplet at 7.25ppm. Formulate a structure of L. Suggest 2 chemical tests to confirm the structure. Write structures for two isomers of L one, (x), of which shows a pair of triplets and the other, (y), which shows a triplet and a quartet in the NMR.

5. Compound **M** ($C_{10}H_{18}O_4$) shows no UV absorption above 200 nm. IR: 2985, 1735 and 1150 cm^{-1}. NMR: 1.02 (doublet, 11.9 squares), 1.32 (triplet, J. 6.4 Hz, 12.1 squares), 2.34 (multiplet, 1.94 squares), 2.98 (doublet, 1.96 squares) and 4.20 ppm (quartet, J. 6.4 Hz, 8.1 squares).

   (i) Formulate the structure of **M**.

   (ii) Assign all the bands to specific functionalities.

   (iii) Compound M is refluxed with aqueous potasium hydroxide, acidified and heated strongly to give a compound **N** $C_5H_{10}O_2$. What is the structure of N? Predict its NMR spectrum.

   (iv) Outline a possible synthesis of M.

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6. Compound, Q ($C_7H_{14}O_2$) does not absorb significantly in the UV. In the IR, it absorbs strongly at 2982, 1702 and 1220 cm^{-1}. Its NMR shows singlets at 1.28, 2.10, 2.50 and 3.20 ppm with area ratios: 17.9 : 9.1 : 5.9 : 9.2. Formulate the structure of Q and assign the frequencies to specific protons. Suggest 2 chemical tests to confirm the structure.

7. Compound H has molecular mass 102. IR: 1380, 1370, 1130, 1110, cm^{-1}. NMR: 1.10 (doublet J 5.1 Hz, 35.9 squares) and 3.61 ppm (septet, J 5.1 Hz, 6.1 squares). Propose a structure for H.

8. Compound I (M.M. 131) contains C, H, O, and N. It is water-insoluble, but dissolves in aqueous hydrochloric acid. IR: 2850, 2790, 1748, 1234 and 1040 cm^{-1}. NMR: 1.95 (singlet, 14.9 squares), 2.20 (singlet, 30.2 squares), 2.45 (triplet, J 6.4 Hz, 9.8 squares) and 4.10 ppm (triplet, J 6.4 Hz, 9.8 squares). Propose a structure for I. Assign all spectral frequencies as much as possible.

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Compound J has molecular mass 90, and analyses for C 53.30 H 11.18%, balance O.

IR: 2980, 1300-1100 (strong and broad) cm^{-1}

NMR: 1.20 (doublet, J, 5.0 Hz, 14.92 squares) 3.32 (singlet, 30.40 squares) and 4.62 ppm (quartet, J, 5.0 Hz, 5.1 squares).

(a) Formulate structure of J.

(b) How will J react (if at all) with

i. aqueous sodium hydroxide

ii. aqueous hydrochloric acid? Formulate mechanism.

(c) How can J be prepared? What important experimental conditions must be observed in order to obtain a good yield in the preparation?

10. Compound K has molecular mass around 109 and contains C, H, O and Cl only.

IR: 3010, 1728 and 1220 cm^{-1} (broad and intense).

NMR: 2.82 (triplet, J, 6.2 Hz, 6.4 squares), 3.71 (triplet, J, 6.2 Hz, 6.3 squares) and 10.75 ppm (singlet, 3.1 squares). Formulate the structure of K and the structure of the product of the reaction of K with a hot aqueous solution of potassium hydroxide.

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11. Compound N, $C_4H_{10}O$, does not absorb in the IR above $3000\ cm^{-1}$. Write 3 possible structures for N. Its NMR shows 3 distinct bands: a singlet, a doublet and a septet. What is the most probable structure of N? Assign each band to specific protons.

12. Compound A, $C_6H_{10}O$, gives a crystalline precipitate with 2, 4-dinitro-phenylhydrazine. The compound gave the following spectral data:

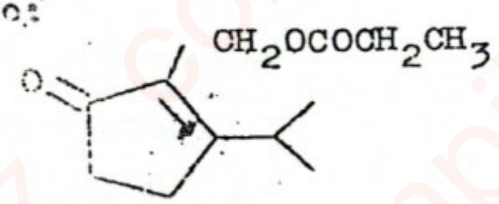
NMR: (delta): 1.9 (3H, singlet), 2.1 (6H, singlet) and 6.15 ppm (1H, singlet).

UV: maximum absorption 238 nm (ε 11,700)

IR: 1620 (m), 1695 (s) cm^{-1}.

Deduce the structure of the compound A.

13. In 1925, the following structure was proposed for a natural product on the basis of evidences obtained from chemical degradations of the molecule:



Given a sample of this compound, discuss in detail how you would test the validity of the structure with the aid of the common spectroscopic techniques. Clearly specify the spectral properties you would expect the compound to show, and indicate the structural features which are responsible for these properties.

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α-Terpinene, $C_{10}H_{16}$ is a natural oil isolated from turpentine. On hydrogenation, it gives 4-methyl-1-isopropylcyclohexane. Its NMR spectrum indicates the presence of two vinyl protons. It absorbs strongly ($E_{max} > 10^4$) in the UV at a wavelength above 200nm. It also undergoes the Diels- Alder reaction with reactive dienophiles. Deduce the structure of α - Terpinene.

15. You are given the essential spectroscopic properties of a compound X. Examine the spectral data very carefully and hence deduce the most probable structure which is consistent with the given data.

IR: 2820 (m), 2750 (m), 1685 (s), 1630 (m), 970 (s), 745 and 688 (m) cm^{-1}.

NMR:(delta) 6.62 (1H, dd); 7.40 (1H, d); 7.41 (5H, m); 9.66 (1H, d).

MS m/e 133 (4), 132 (45), 131 (77), 103 (74), 91 (6), 77 (88), 51 (100), 29 (14).

UV: maximum absorption 285 nm (E 20,000)

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16. An ester D, $C_{11}H_{14}O_2$ was synthesised from two components E and F, whose NMR (in delta values) are as follows:

E, ($C_8H_{10}O$) gave singlets at 2.5, 3.7, 4.4 ppm. with relative integral values (intensities) in the ratio 3:1:2 respectively. In addition, there were two pairs of doublets (J = 10 Hz) at 6.9 and 7.3 ppm., each of which has the same intensity as the peak at 4.4.

F, ($C_3H_6O_2$) signals at 1.1, (triplet); 2.4 (quartet) and 10.0 ppm. (broad singlet) with relative integral values of 3:2:1 respectively. The signals at 3.7 in E and 10.0 in F are exchangeable with D_2O. Deduce the structures for D, E and F.