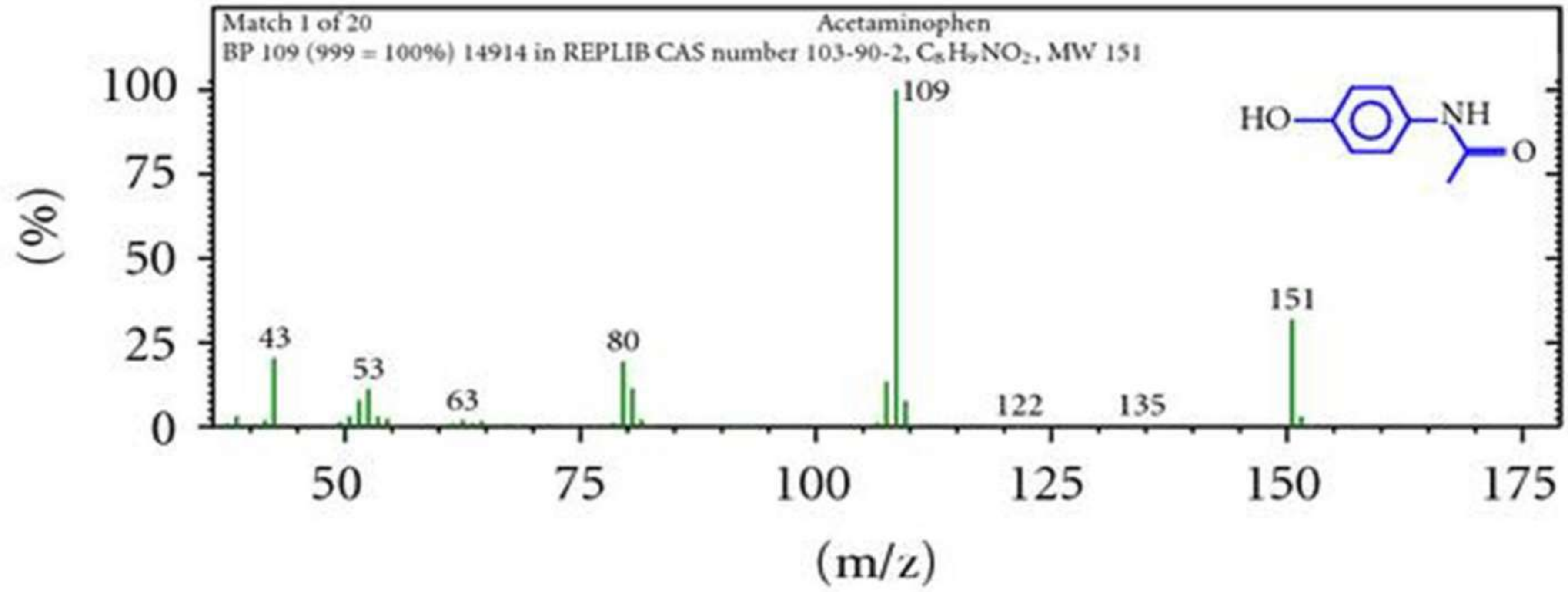
طيف الكتلة

Mass Spectroscopy

MS

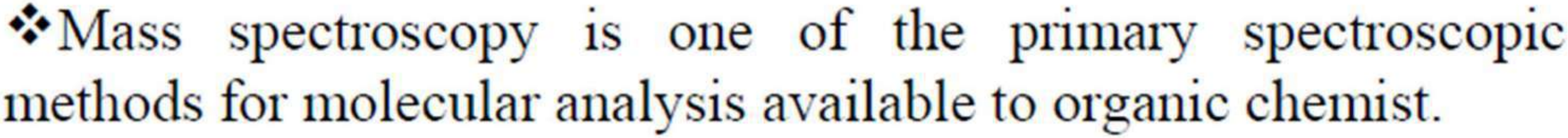


Mass Spectroscopy

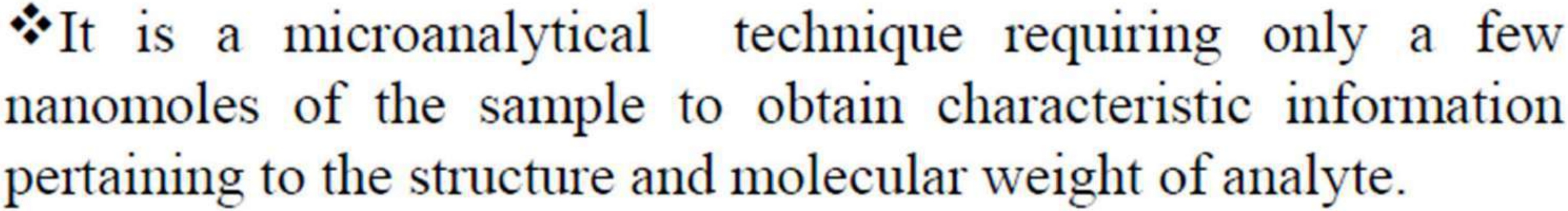
Part 1

Introduction and Basic Principles

Introduction

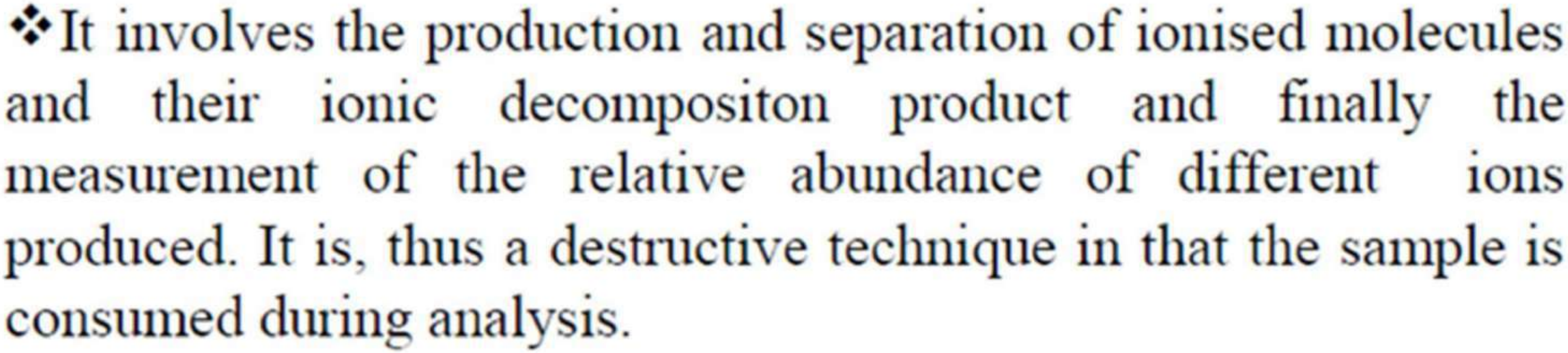


- Mass spectroscopy is one of the primary spectroscopic methods for molecular analysis available to organic chemist.



- It is a microanalytical technique requiring only a few nanomoles of the sample to obtain characteristic information pertaining to the structure and molecular weight of analyte.

- **It is classified as a destructive spectroscopy; the EMR is expected to destroy the substance under analysis "analyte"**



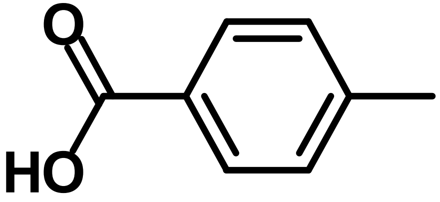
- It involves the production and separation of ionised molecules and their ionic decompositon product and finally the measurement of the relative abundance of different ions produced. It is, thus a destructive technique in that the sample is consumed during analysis.

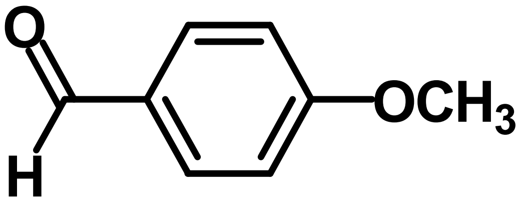
- In most cases, the nascent molecular ion of the analyte produced fragment ions by cleavage of the bond and the resulting fragmentation pattern constitutes the mass spectrum.

- Thus, the mass spectrum of each compound is unique and can be used as a “chemical fingerprint” to characterize the sample.

Eventhough; this method can guide us to differentiate between isomers; the formula C_2H_6O is the general formula of two isomers (ethanol C_2H_5OH) and ether CH_3OCH_3). Inspite of both have the same M.wt and the last peak in the spectrum for both is the same, but we have the ability to Distinguish through fragmentation peaks that are different in some of them. Also p-toluic acid and p-methoxybenzaldehyde have the same idea.

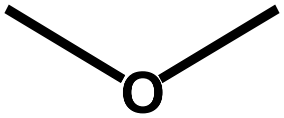
Fragments might lead for structural identification

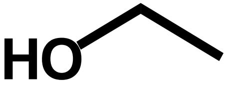




$C_8H_8O_2$

Exact Mass: 136.05





C_2H_6O

Exact Mass: 46.04

The role of mass spectroscopy in analysis

The primary role is to determine the molecular mass ;

in more details; MS is used to :-

1- Prove the identity of two compounds

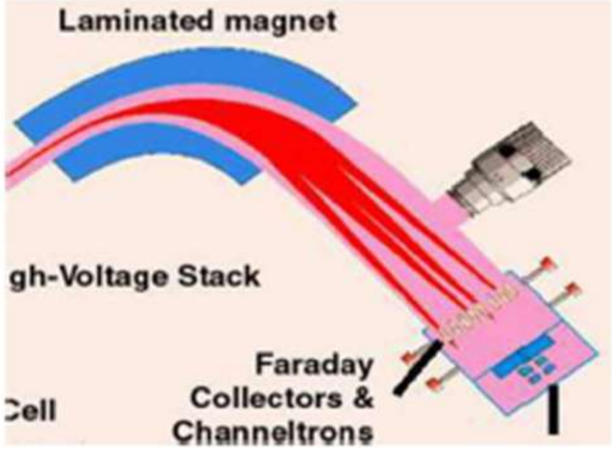
2- prove isotopes ratio

3- Establish the structure of a new compound in different ways; such as:-

a. It can give the exact molecular mass.

b. It can give a molecular formula or it can reveal the presence of certain structural units in the molecule under analysis

Mass Spectrometer



The spectrometer consists of

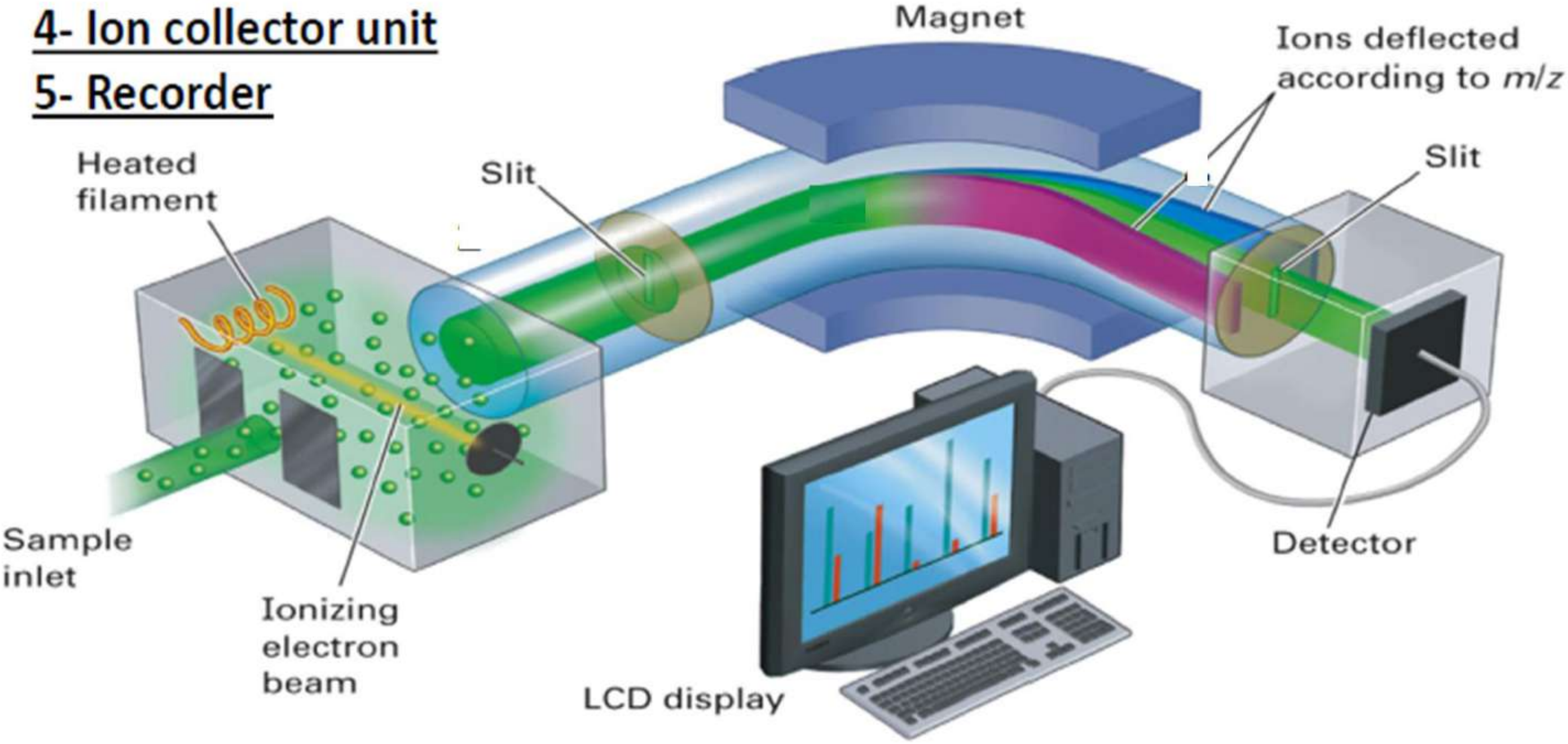
1- Sample handling unit

2- ionization chamber “unit”

3- Ion separation unit

4- Ion collector unit

5- Recorder



BASIC PRINCIPLES

Organic molecules are bombarded with electron beam

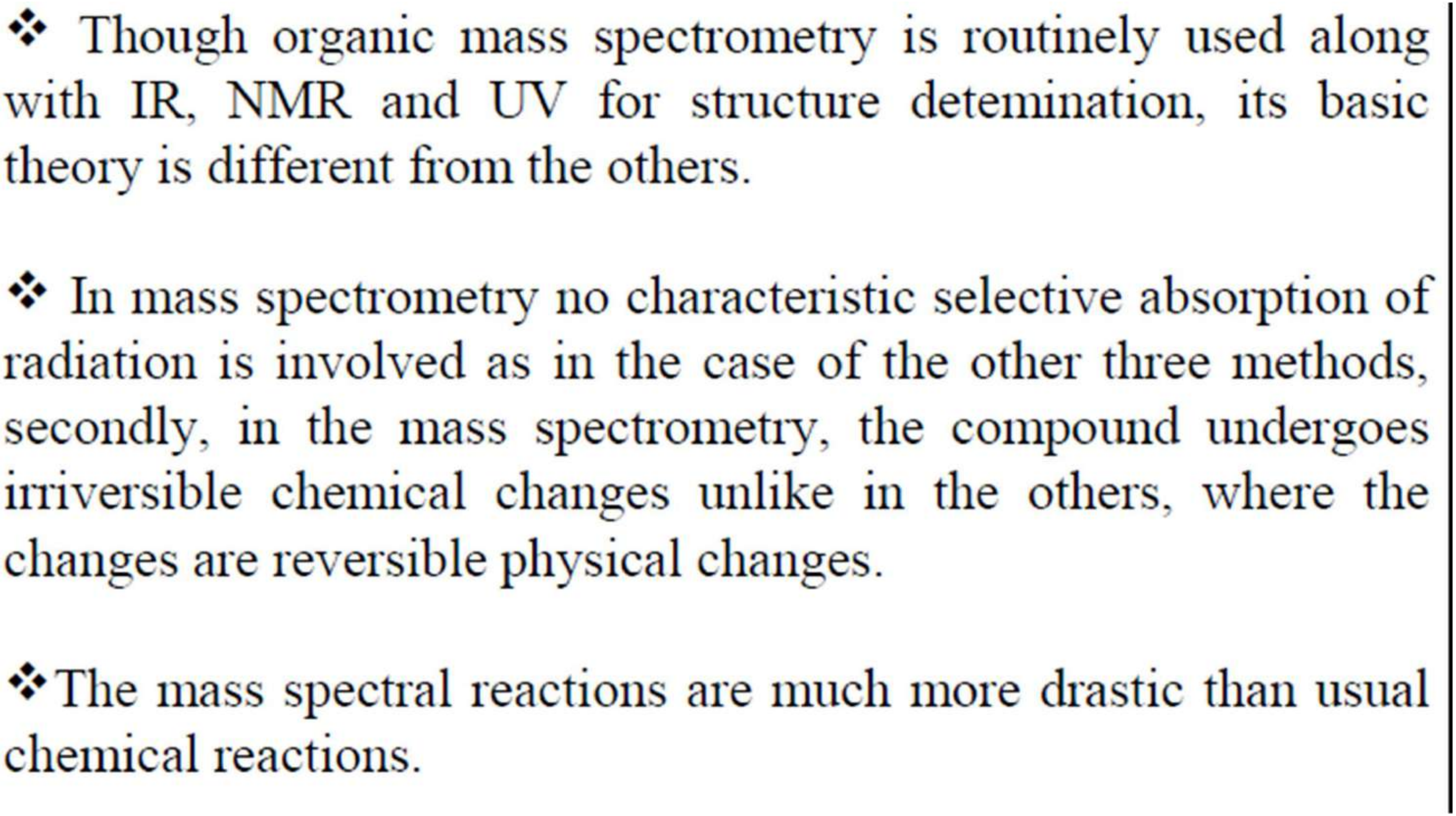
converted into Highly energetic positively charged ions (Molecular ions or Parent ions)

Further break up into smaller ions (Fragment ions or Daughter ions)

The formed ions are separated by Deflection in Magnetic field according to their Mass and Charge

MASS SPECTRUM

Basic theory and principle



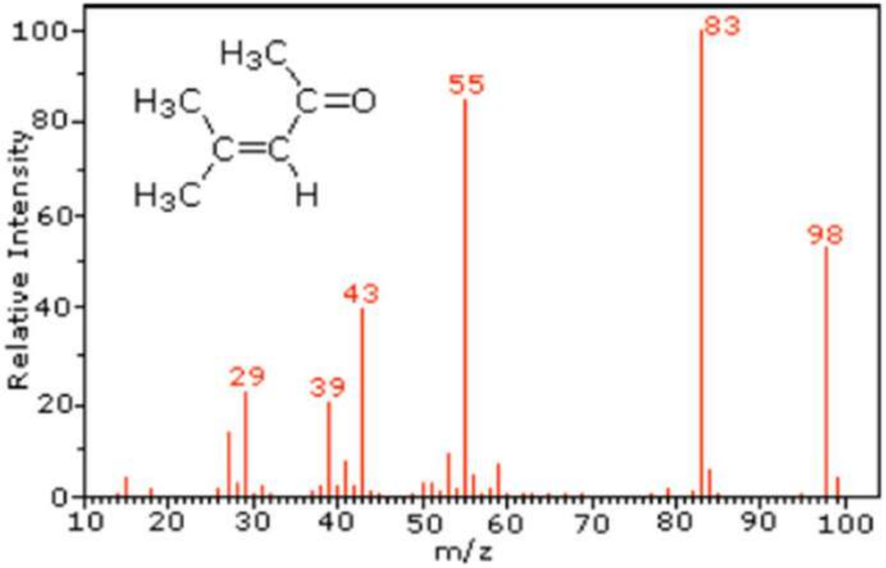
- Though organic mass spectrometry is routinely used along with IR, NMR and UV for structure detemination, its basic theory is different from the others.

- In mass spectrometry no characteristic selective absorption of radiation is involved as in the case of the other three methods, secondly, in the mass spectrometry, the compound undergoes irriversible chemical changes unlike in the others, where the changes are reversible physical changes.

- The mass spectral reactions are much more drastic than usual chemical reactions.

- Mass spectroscopy deals with the examination of the characteristics fragments(ions) arising from the breakdown of organic molecules.

- A mass spectrum is the plot of relative abundance of ions against their mass/charge ratio.



The principle of mass spectroscopy analysis

1) The basic aspect of organic mass spectrometry consist of bombarding the vapour of an organic compound with a beam of energetic electron accelarated from a filament to an energy of 10-15 eV to form +ve charged ions (molecular ion)

2) The additional energy of the elecrons is dissipated in breaking the bonds in the molecular ion, which undergoes fragmentation to yield several neutral or positively charged species.

Note:- The additional energy might reaches 50-70 eV

3) This fragmentation may result in the formation of Cations and free radical

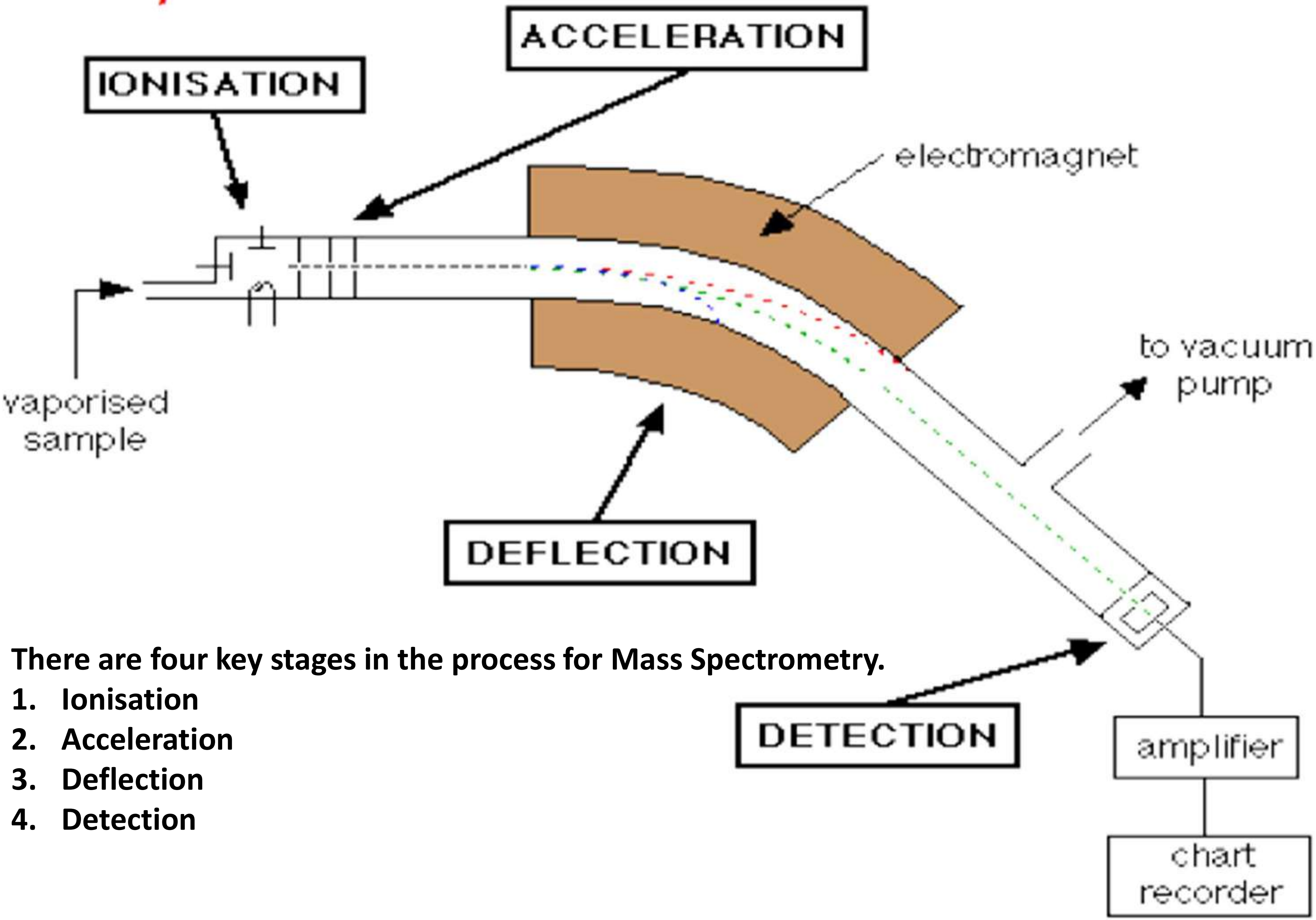
4) The various positive ions, thus formed, can be accelerated using ev pushing out and voltage difference using Cathode and anode plates and deflected using magnetic field

5) The deflection of ions, however, depends on its mass, and charge

6) When an ion hits the metal box, its charge is neutralized by an electron jumping from the metal on the ion; that leaves space in the metal, and the electrons in the wire shuffle along to fill it. And flow of electrons in the wire is detected as an electric current which can be amplified and recording

7) The clear visual presentation of a mass spectum is usually obtained by plotting m/z value against relative abundance, assigning the most abundant ion (base peak)in the spectrum as 100 per cent.

Principle and Instrumentation



There are four key stages in the process for Mass Spectrometry.

1. **Ionisation**
2. **Acceleration**
3. **Deflection**
4. **Detection**

➢Ionisation

- ❖The atom is ionised by knocking one or more electrons off to give a positive ion. (Mass spectrometers always work with positive ions).

- ❖The particles in the sample (atoms or molecules) are bombarded with a stream of electrons to knock one or more electrons out of the sample particles to make positive ions.

- ❖Most of the positive ions formed will carry a charge of +1.

- ❖These positive ions are persuaded out into the rest of the machine by the ion repeller which is another metal plate carrying a slight positive charge. “cathode” and by the effect of the focusing ev from the electron source “50-70 ev”.

Q1] What does ionization mean in ms?

Q2] What is the source of such ionization? Why I is known as thermal ionization?

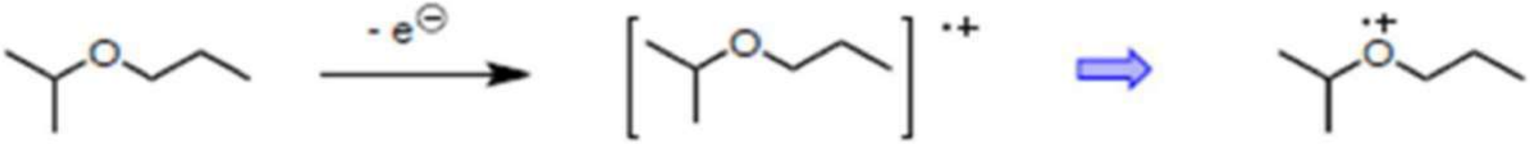
Q3] It is important to start with lower of ev then gradually increasing to higher energy ev?

Q4] What is the role of metal plate?

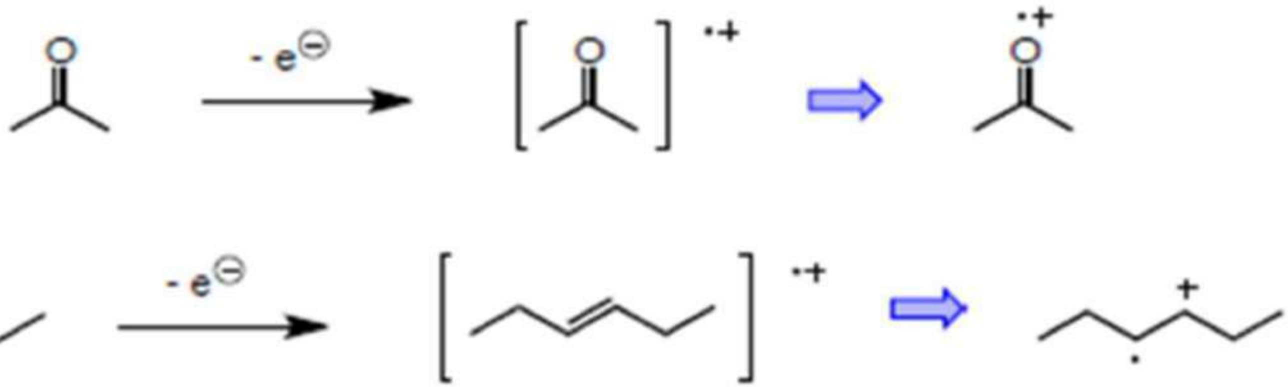
Initial loss of electrons

More easy | non-bonding orbital > π-orbital > σ-orbital | **Less easy**

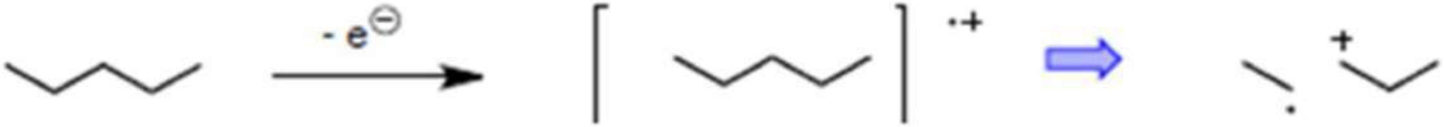
from a non-bonding orbital



from a π orbital

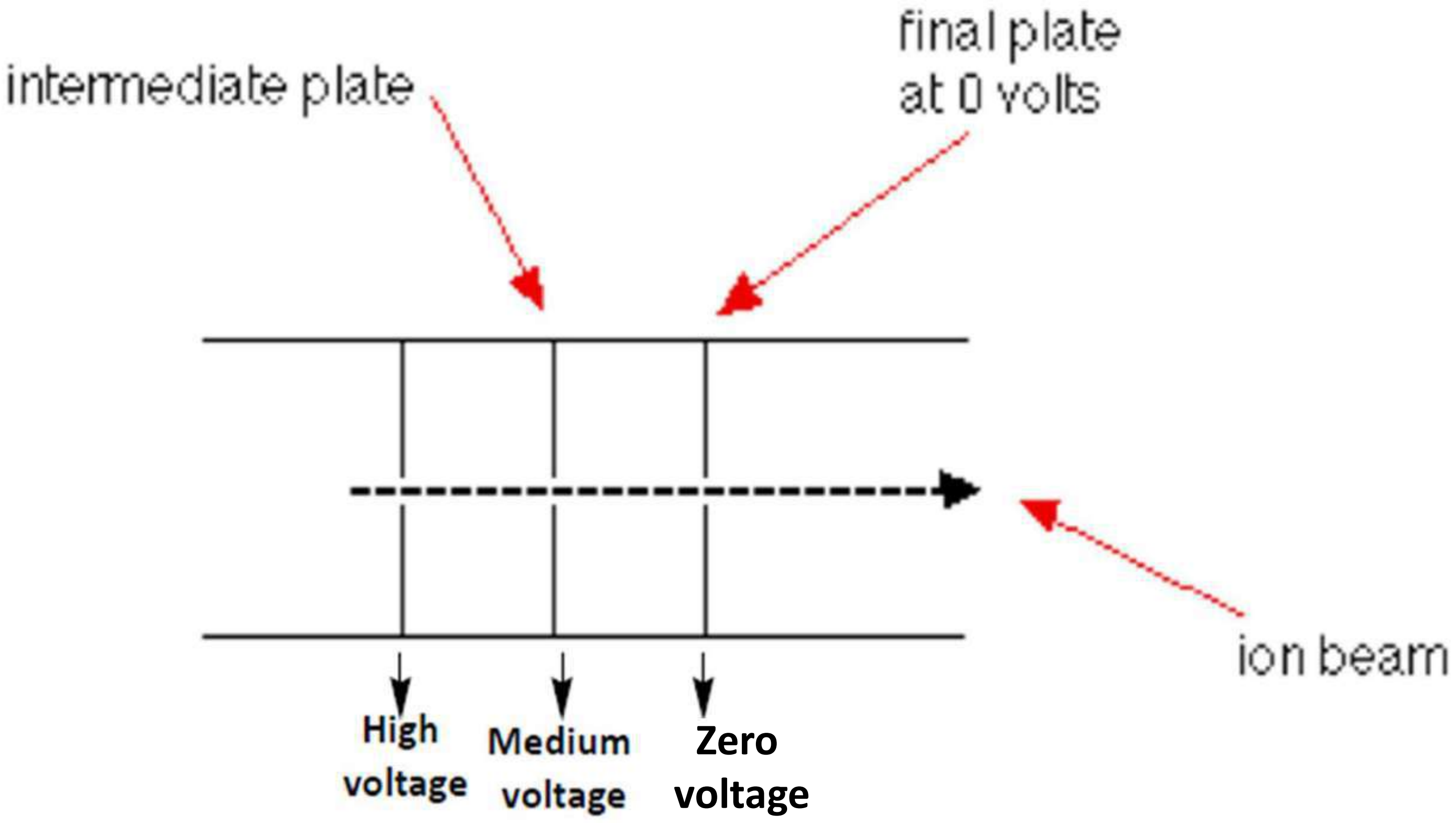


from a σ orbital



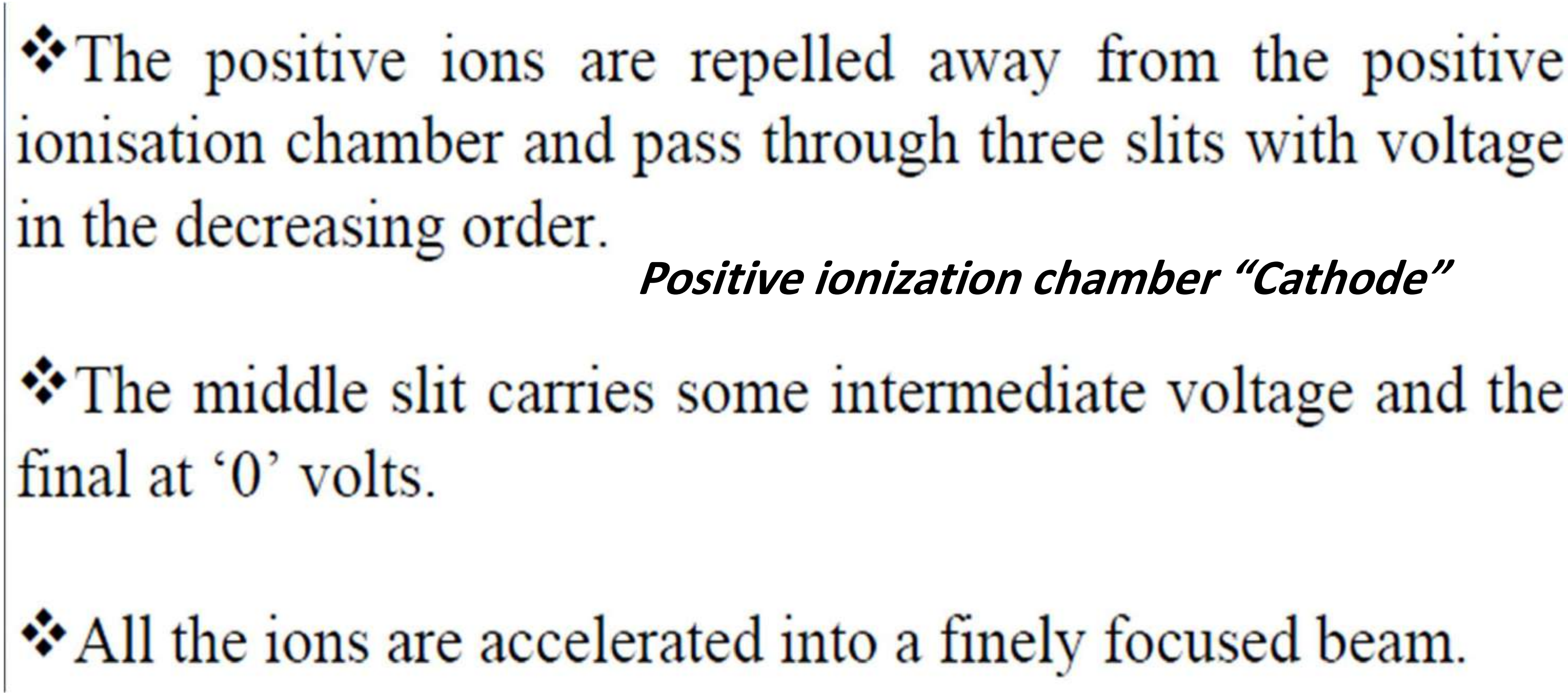
➢ Acceleration

❖ The ions are accelerated so that they all have the same kinetic energy.



Q1] What does acceleration mean in mass spectroscopy?

Q2] What is the source of such acceleration?



- The positive ions are repelled away from the positive ionisation chamber and pass through three slits with voltage in the decreasing order.

Positive ionization chamber “Cathode”

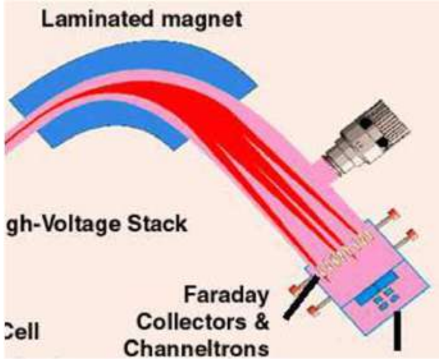
- The middle slit carries some intermediate voltage and the final at ‘0’ volts.

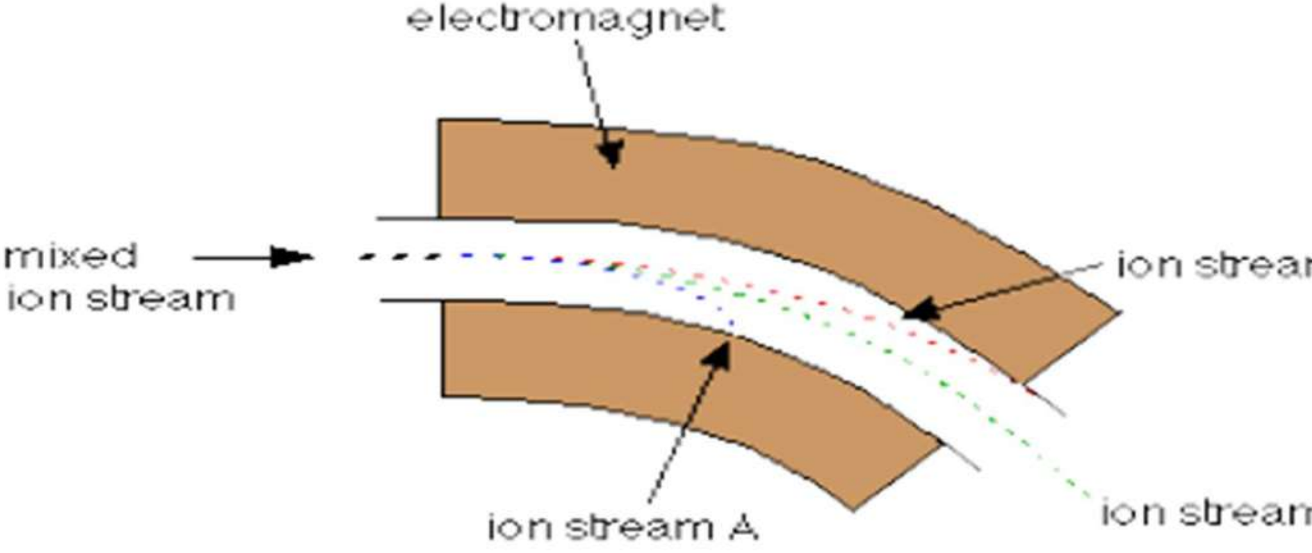
- All the ions are accelerated into a finely focused beam.

➢ Deflection

❖The ions are then deflected by a magnetic field according to their masses. The lighter they are, the more they are deflected.

❖The amount of deflection also depends on the number of positive charges on the ion -The more the ion is charged, the more it gets deflected.





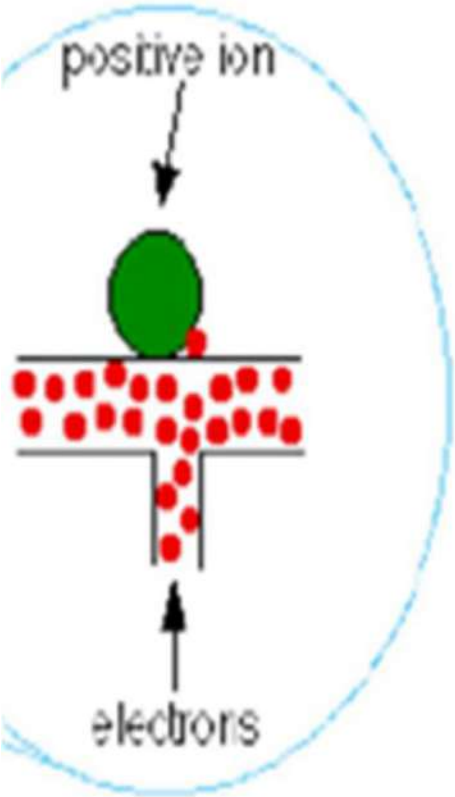
- Different ions are deflected by the magnetic field by different amounts. The amount of deflection depends on:

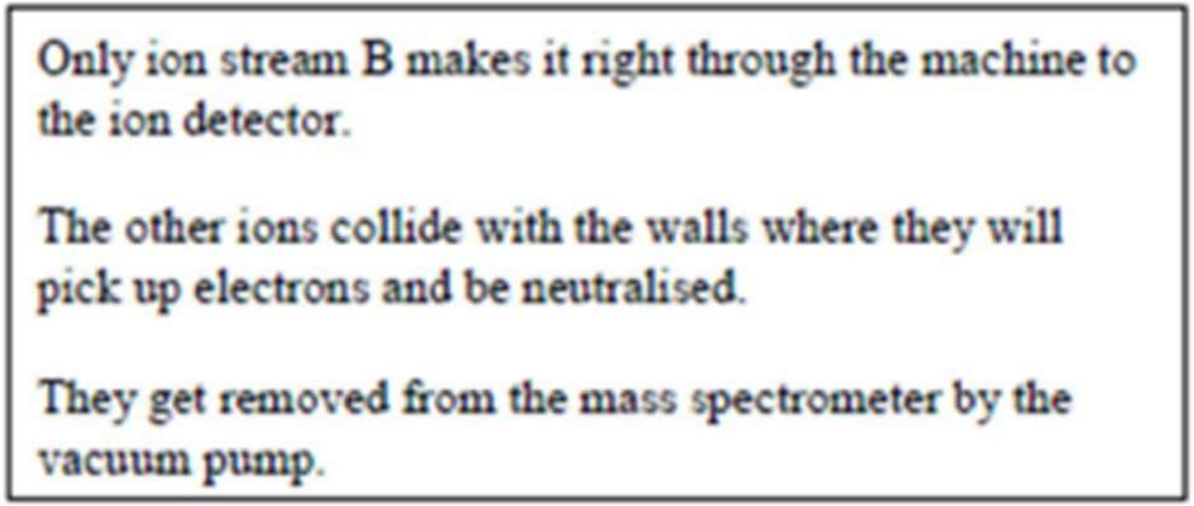
- *The mass of the ion*: Lighter ions are deflected more than heavier ones.

- *The charge on the ion*: Ions with 2 (or more) positive charges are deflected more than ones with only 1 positive charge.

➢ *_Detection*

❖ The beam of ions passing through the machine is detected electrically.




Only ion stream B makes it right through the machine to the ion detector.

The other ions collide with the walls where they will pick up electrons and be neutralised.

They get removed from the mass spectrometer by the vacuum pump.

The detector records either the charge induced or the current produced when an ion passes by or hits a surface.

- When an ion hits the metal box, its charge is neutralised by an electron jumping from the metal on to the ion.
- That leaves a space amongst the electrons in the metal, and the electrons in the wire shuffle along to fill it.
- A flow of electrons in the wire is detected as an electric current which can be amplified and recorded. The more ions arriving, the greater the current.

What is the difference between metal plate in ionization unit and metal plate "metal box" In the detection unit?

Ionization methods

There are several methods; just we'll focus on

1. **Electron Impact Ionization (E.I.I)**
2. **Chemical Ionization.(C.I)**
3. **Field Ionization. (F.I)**
4. **UltraViolet. (U.V)**
5. **Laser Microprobe.(L.M)**

1] Electron Impact Ionization (E.I.I)

- **It is the most common method of ionization in mass spec. It includes the gaseous substance entrance to the ionization unit which is evacuated from air and temperature inside is 200 °C .**
- **The substance molecules are exposed to an electron beam with 10-15 ev that arises from hot filament.**
- **When the molecule is exposed to this high energy electrons; they are ionized forming cations "positive ions“.**

Note:-

- **The used voltage 10 ev is enough to give only one molecular ion that means; it gives one peak that matches the M. Wt without any fragmentation in the original molecule.**

- **But increasing the value of voltage " ev" 50-70; causes many fragments formed which is good in the case of trying to identify the full structure through puzzle reconstruction but for unstable molecules it is not good.**

Disadvantages of E.I.I

1. Unstable molecules are broken and fragmented for very small ions difficult to be interpreted .
2. The molecular ion might not been seen because of its destruction from the beginning.
3. Incomplete evacuating leads to the appearance of sort of overlapping peaks (gases are still there).

2] Chemical Ionization (CI):-

- In this method; gas (methane, butane or ammonia) is used alongside the sample in high concentration.

- Methane is ionized due to the effect of its exposure to an electron beam after entering the ionization unit alongside with sample under analysis.

- Then methane ions react with sample molecules; causing altering in charges (proton transfer). It is known as indirect ionization

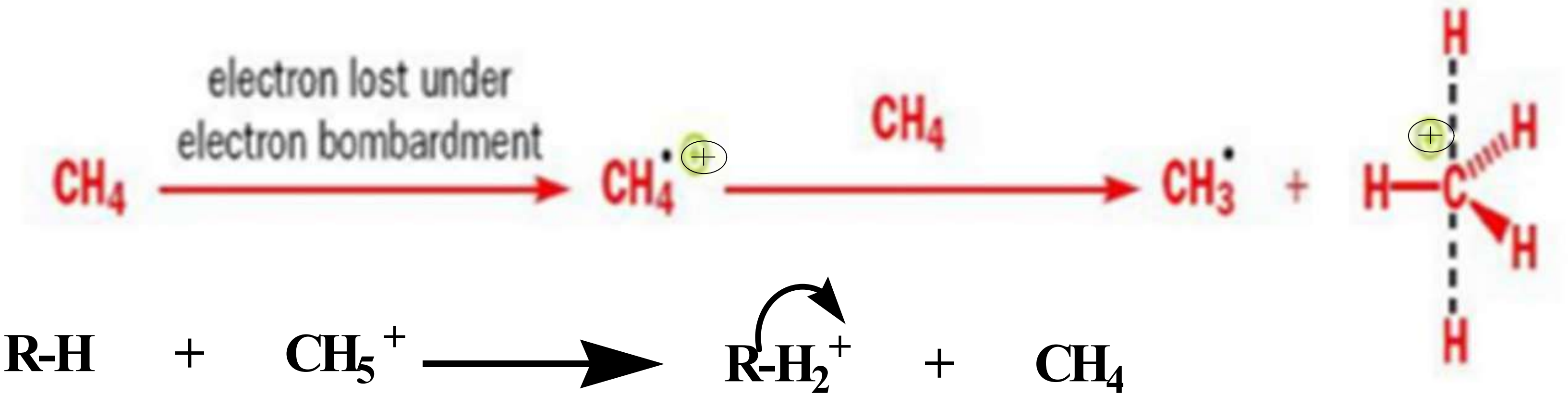
- This method is very suitable for unstable molecules that are broken and fragmented into very small fragments when different methods are used to get analysis done.

Chemical Ionization Mechanism

$$CH_4 \longrightarrow CH_4^{\bullet +}$$

$$CH_4^{\bullet +} + CH_4 \longrightarrow CH_5^{+} + {}^{\bullet}CH_3$$

$$CH_4^{\bullet +} + H^{\bullet} \longrightarrow CH_5^{+}$$



$$R\text{-}H + CH_5^{+} \longrightarrow R\text{-}H_2^{+} + CH_4$$

proposed structure of CH_5^{+}
the two black bonds share two electrons

You might see an M+1 peak

$$R\text{-}H_2^{+} \longrightarrow R^{+} + H_2$$

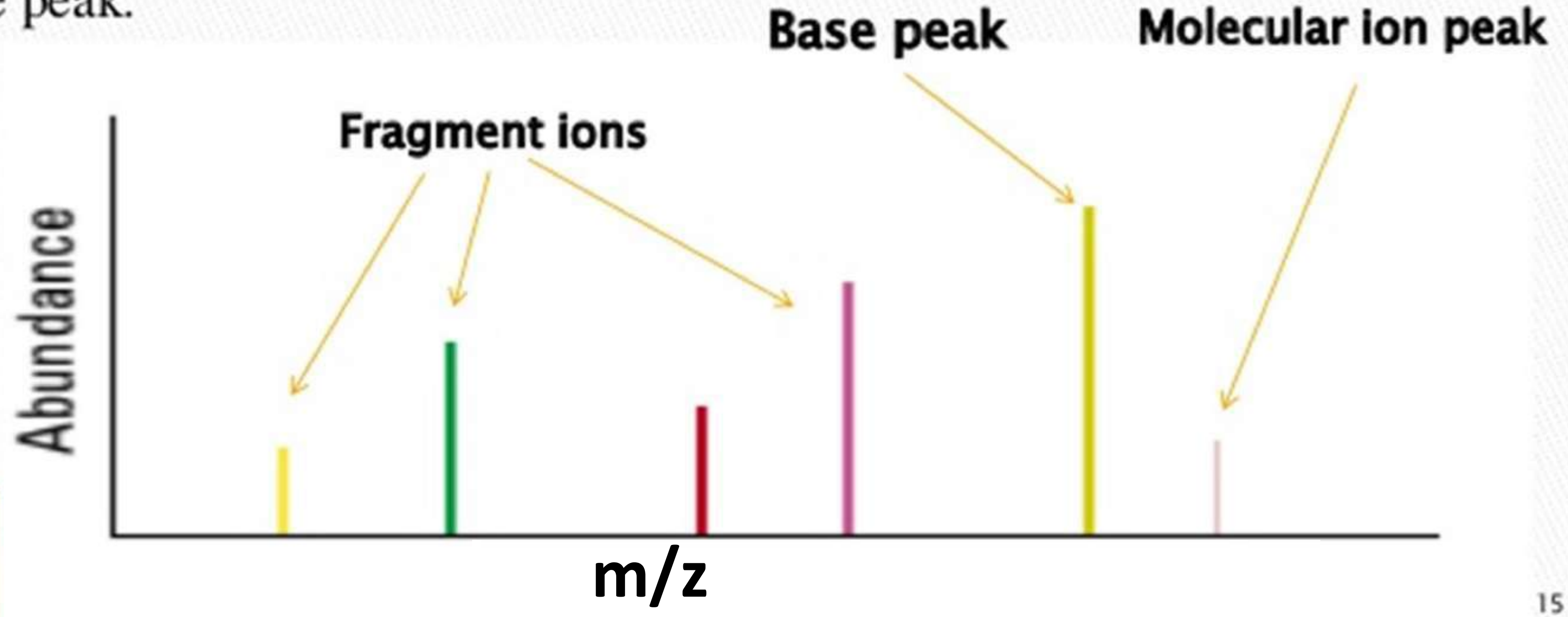
Mass Spec. Terminology

- Molecular ion - The ion obtained by the loss of one electron from the molecule (m^+)
- Base peak - The most intense peak in the MS, assigned 100% intensity
- Fragment ions - Lighter cations (and radical cations) formed by the decomposition of the molecular ion.
- m/z - mass to charge ratio

MOLECULAR ION PEAK:

The ion formed from a molecule by removal of one electron of lowest ionization potential is known as molecular ion.

The molecular ion is detected as mass to charge ratio that corresponds to molecular weight of molecule. The molecular ion peak gives the molecular weight of compound . The molecular ion peak is highest mass number except isotope peak.



Mass Spectroscopy

Part 2

Fragmentation Patterns

Fragmentation process:

❖Bombardment of molecules by an electron beam with energy between 10-15ev usually results in the ionization of molecules by removal of one electron (Molecular ion formation).

❖When the energy of electron beam is increased between 50-70ev, these molecular ions acquire a high excitation resulting in their break down into various fragments. This process is called “ Fragmentation process”.

Fragmentation Patterns

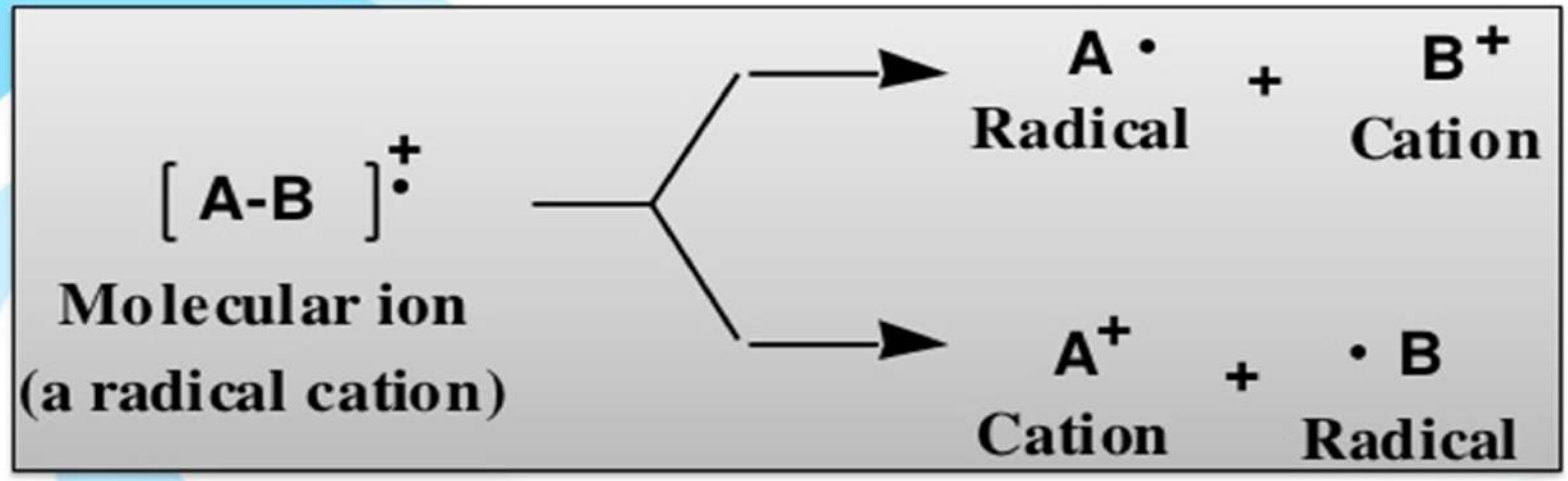
- **The impact of the stream of high energy electrons often breaks the molecule into fragments, commonly a cation and a radical.**
  - Bonds break to give the most stable cation.
  - Stability of the radical is less important.

- **There are several rules for such fragmentation.**

Fragmentation of the Molecular ion

Fragmentation of a molecular ion, M, produces a radical and a cation.

-Only the cation is detected by MS.



$[A\text{-}B]^{+\bullet}$

Molecular ion

(a radical cation)

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

Radical + Cation

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

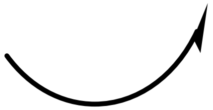
Cation + Radical

$$[A\text{—}B]^{\oplus\bullet} = A\bullet\!\!-\!\!\circ B$$

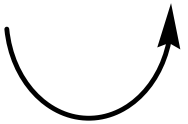
More on Conventions…

When a molecule is ionized by EIMS, must decide which electron to remove. Always best to remove an electron from a *π-bond*, or from a *heteroatom lone pair*. It will become more clear which is the better choice when we look at individual examples.

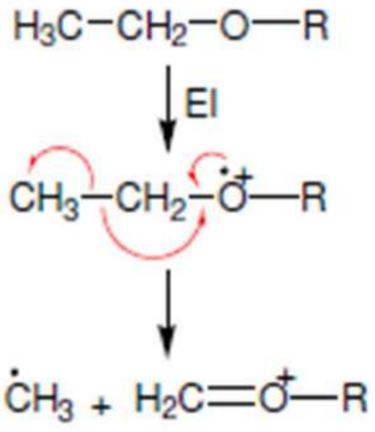
The bond breaking can be done either by *homolytic* or *heterolytic* cleavage.



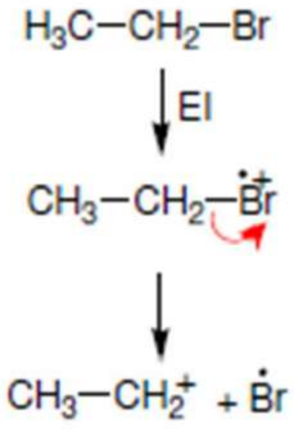
One electron movement (homolytic)



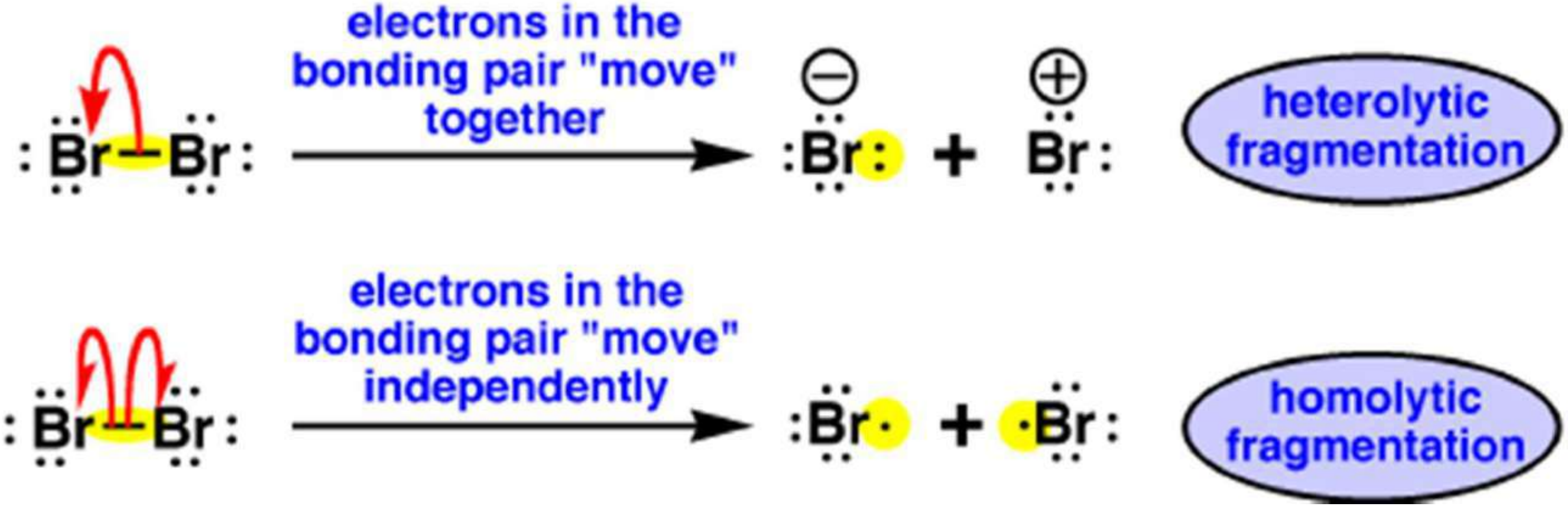
Two electrons movement (heterolytic)



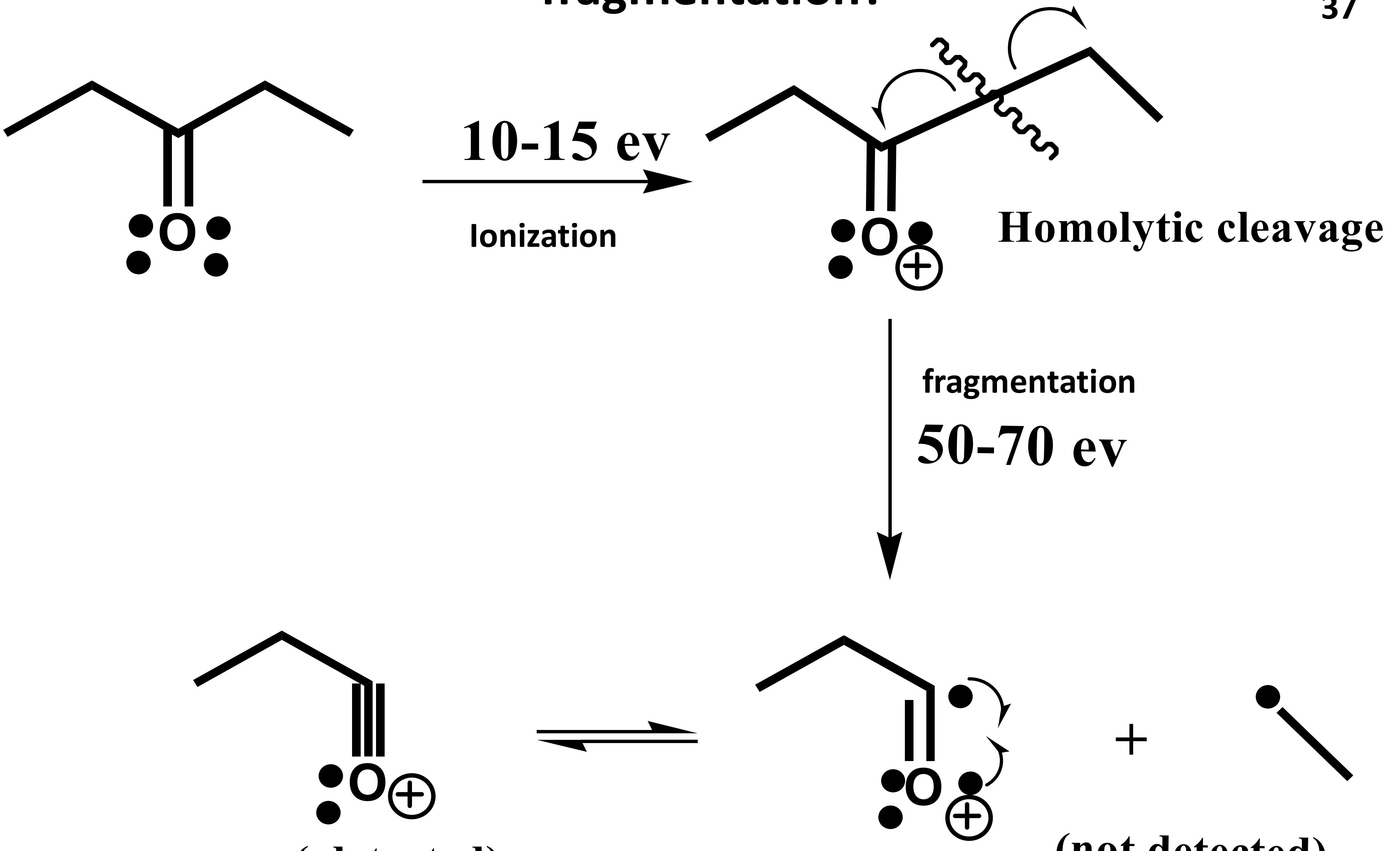
Homolytic



Heterolytic


electrons in the bonding pair "move" together
heterolytic fragmentation
electrons in the bonding pair "move" independently
homolytic fragmentation

How can both radical and cation be formed through fragmentation?



10-15 ev

Ionization

Homolytic cleavage

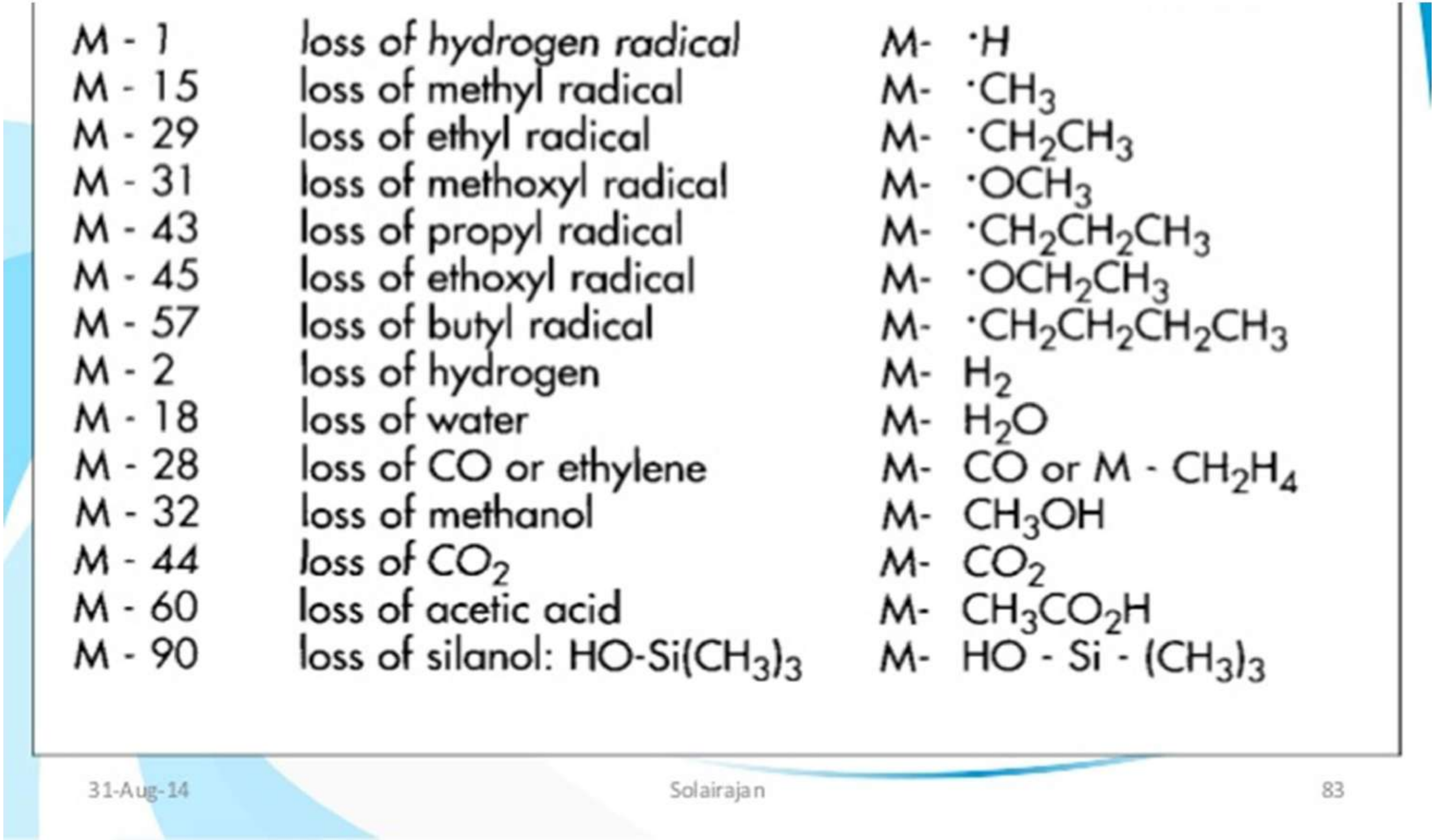
fragmentation

50-70 ev

(detected)
seen in the spectrum

(not detected)
not seen in the spectrum

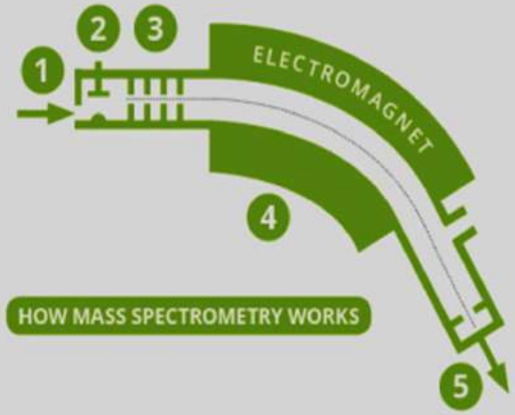
Some common and well-known fragments (F.)



M - 1	loss of hydrogen *radical*	M- $^{\cdot}H$
M - 15	loss of methyl radical	M- $^{\cdot}CH_3$
M - 29	loss of ethyl radical	M- $^{\cdot}CH_2CH_3$
M - 31	loss of methoxyl radical	M- $^{\cdot}OCH_3$
M - 43	loss of propyl radical	M- $^{\cdot}CH_2CH_2CH_3$
M - 45	loss of ethoxyl radical	M- $^{\cdot}OCH_2CH_3$
M - 57	loss of butyl radical	M- $^{\cdot}CH_2CH_2CH_2CH_3$
M - 2	loss of hydrogen	M- H_2
M - 18	loss of water	M- H_2O
M - 28	loss of CO or ethylene	M- CO or M - CH_2H_4
M - 32	loss of methanol	M- CH_3OH
M - 44	loss of CO_2	M- CO_2
M - 60	loss of acetic acid	M- CH_3CO_2H
M - 90	loss of silanol: HO-Si$(CH_3)_3$	M- HO - Si - $(CH_3)_3$

A GUIDE TO INTERPRETING MASS SPECTRA

Mass spectrometry is an analytical technique that allows us to measure the masses of atoms and molecules. The most important peak in a mass spectrum is the molecular ion peak, which can be used to determine the mass of the molecule, but fragment ions can also provide information on chemical structure.



HOW MASS SPECTROMETRY WORKS

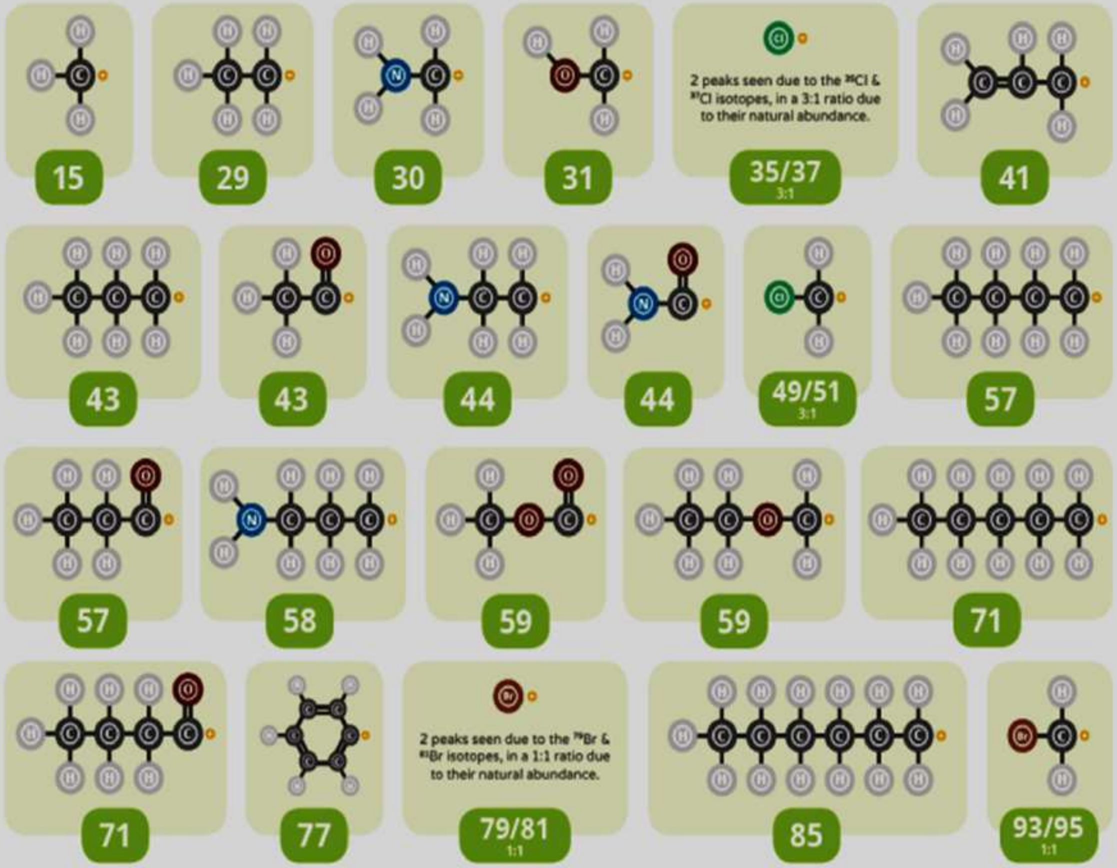
① The sample is introduced to the mass spectrometer. Only very small samples are required. A heater is often present to vapourise the sample.

② An electron gun ionises molecules in the sample by knocking out electrons, producing positive ions. Some molecules break into smaller ions & fragments.

③ The positive ions generated are passed through an electric field which accelerates them into a magnetic field generated by an electromagnet.

④ As the positive ions pass through the magnetic field, they are deflected. Lighter ions are deflected more than heavier ions, as are those with higher charges.

⑤ The positive ions hit a charged plate & accept electrons, creating a signal. The more ions that hit, the greater the signal. The output is a complex stick diagram.



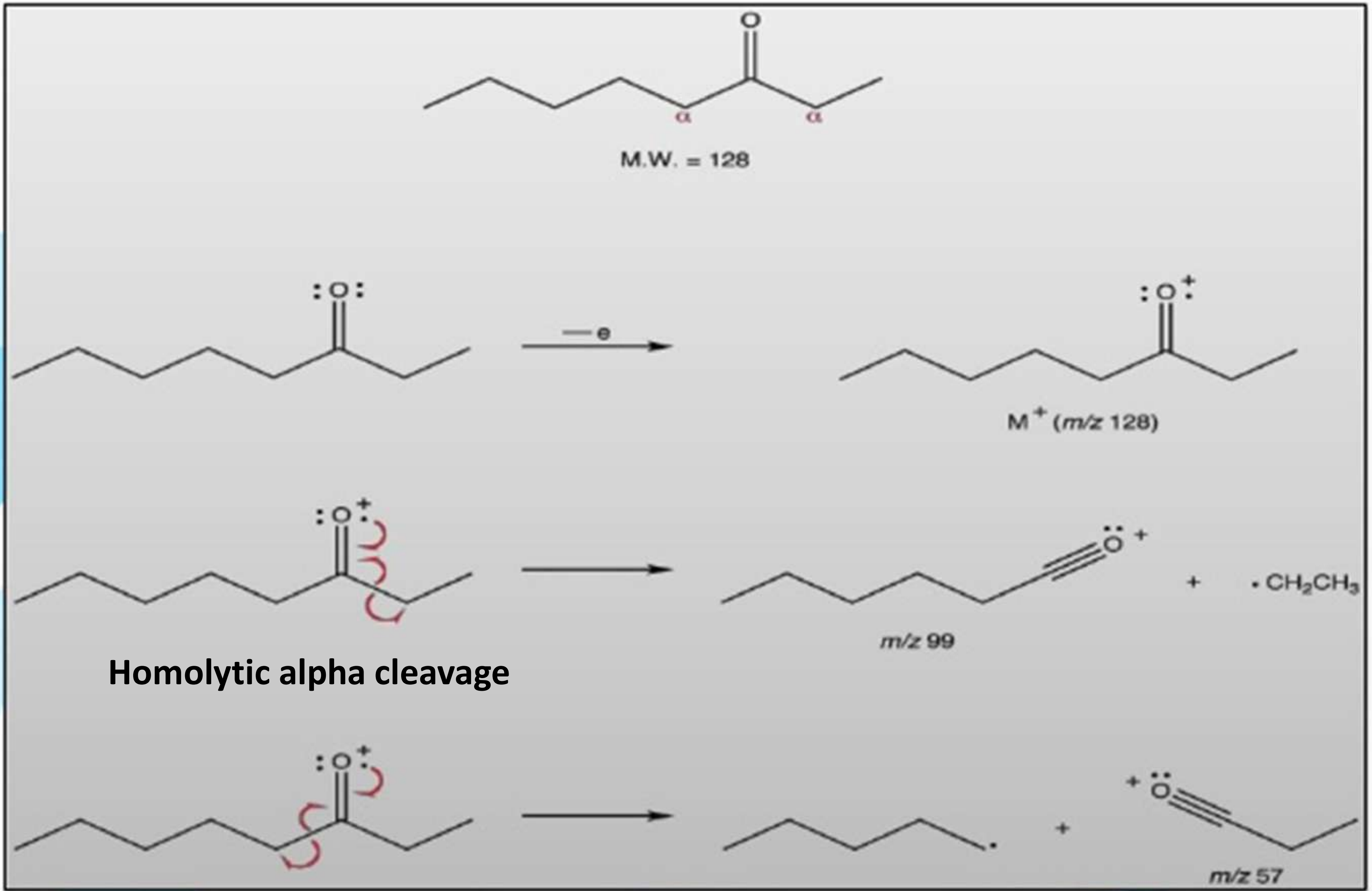
2 peaks seen due to the ^{35}Cl & ^{37}Cl isotopes, in a 3:1 ratio due to their natural abundance.

2 peaks seen due to the ^{79}Br & ^{81}Br isotopes, in a 1:1 ratio due to their natural abundance.

Above are shown a selection of common fragment ions seen in mass spectra, along with their masses. Note that the structures shown are general representations, and it can also be possible for isomeric structures (those with the same constituent atoms, but a different structure) to cause the peaks in spectra. There are also many more fragments possible than those shown, but knowledge of these should suffice to interpret spectra of most simple molecules.

α cleavage

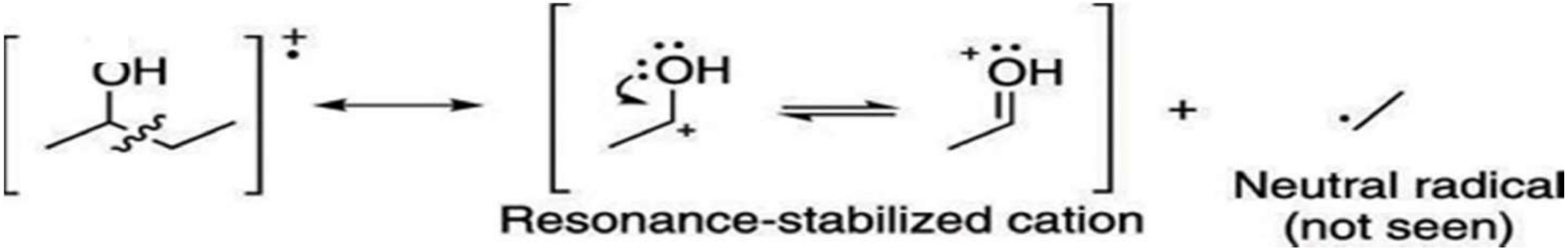
- Alpha cleavage in mass spectrometry is a characteristic fragmentation of the molecular ion derived from carbonyl compounds, in which the bond linking the carbonyl carbon to the atom occupying an alpha position breaks.
- It is an expected pathway for carbonyl compounds,ethers,halides,alcohols,and amines.

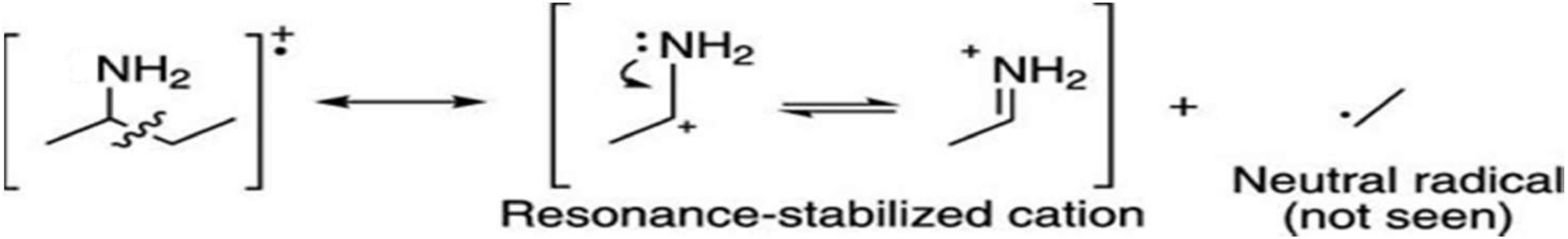


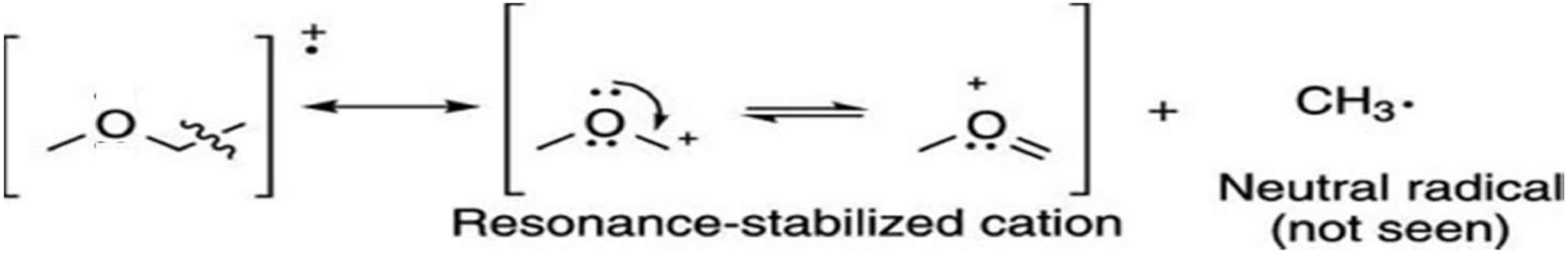
Homolytic alpha cleavage

Alpha cleavage in alcohols, amines and ethers

When a molecule contains heteroatoms (elements such as oxygen, sulfur, and nitrogen), breaking next to these atoms makes cations that are resonance stabilized. For example, breaking the C-C bond next to an alcohol (carbinol) group creates a resonance-stabilized carbocation. This type of break is called alpha cleavage and is commonly seen in alcohols, amines and ethers.





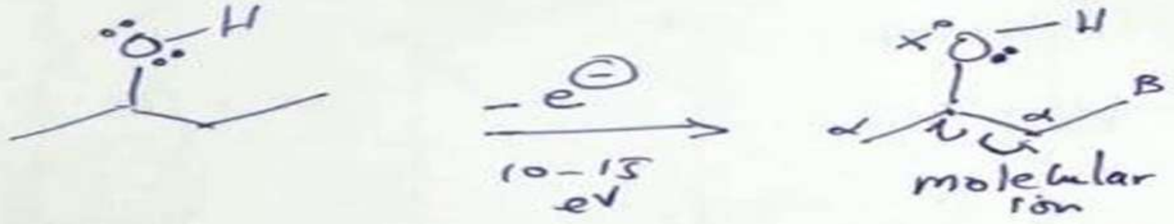


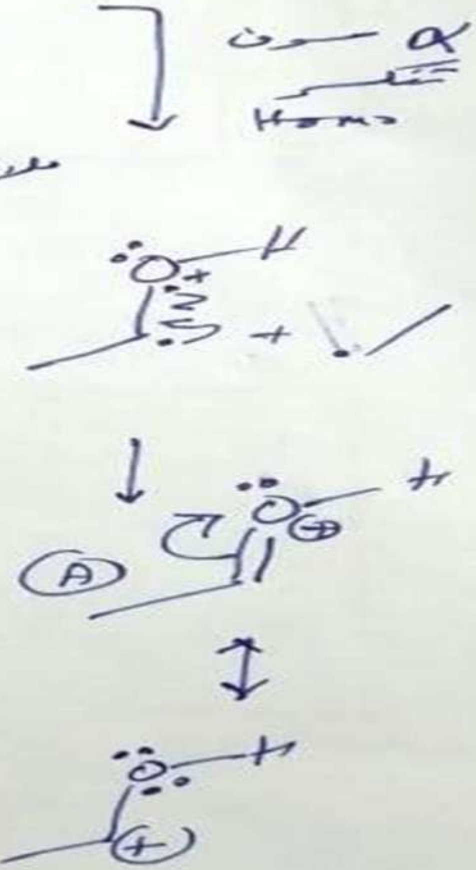
إنتبهوا !!

كيف حدث هذا الأمر ؟!!

حتى يكون هناك إلتباس في النسخة هذا

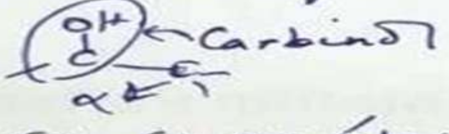
ركزوا معي .





ملاحظة: α هي بين الكربينول وأول ذرة كربون بعدها

هذا معناه α_cleavage

كربينول 

← عندما يكون هناك ذرتان متجاورتان مع كل واحدة منهما جذر حر سيشكلون رابط ثنائية وأحيانا ثلاثية

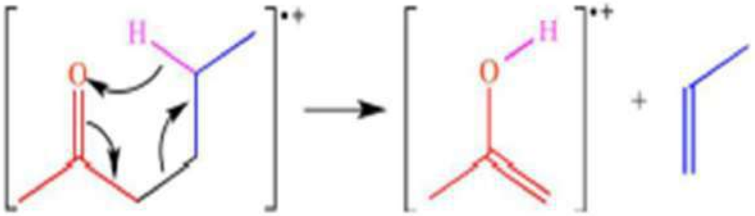
لا زال الاكسجين موجبا، لأنه حواليه في الالكترونات وليس 6

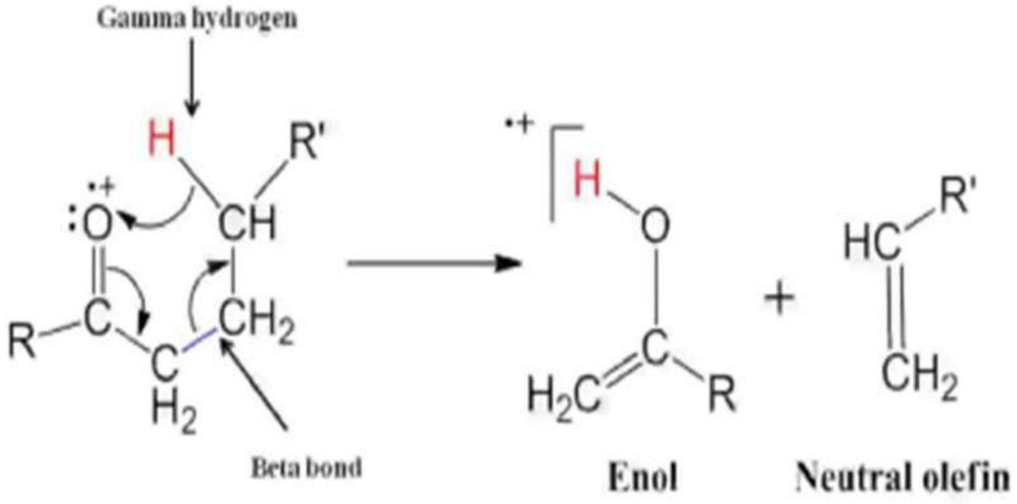
∴ المركب A له شكل رنيني

الآن تحرك زوج الالكترونات رابطة π
و تعادل شحنة الاكسجين (أصبحوا 6)
طبعا مع حساب ذرة الكربون التي أصبحت +ve

Mclafferty Rearrangement

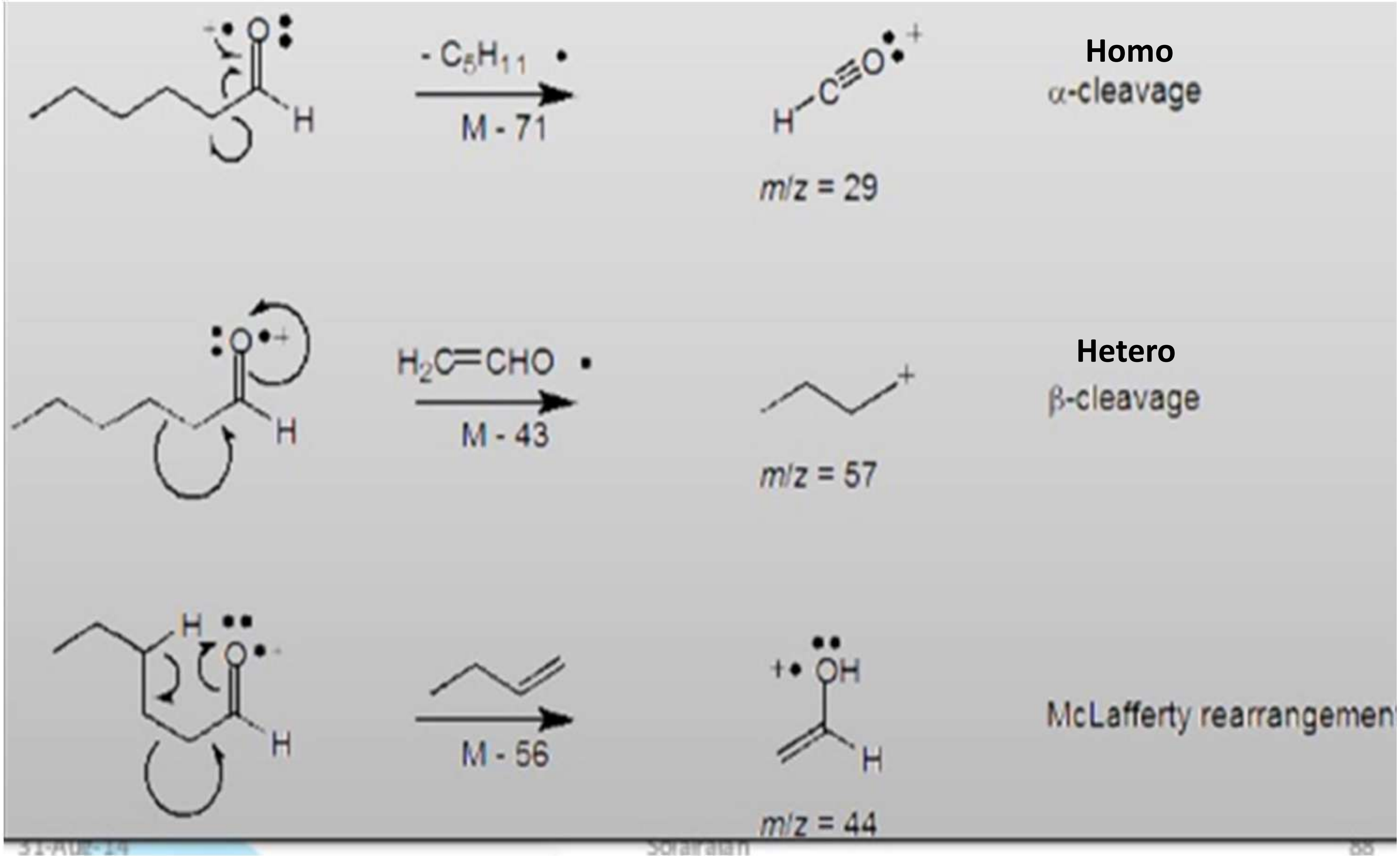
Mechanism: Abstraction of Gamm Hydrogen Followed by cleavage of Beta bond to form two fragments (i) Olefin (Alkene) (ii) Enol





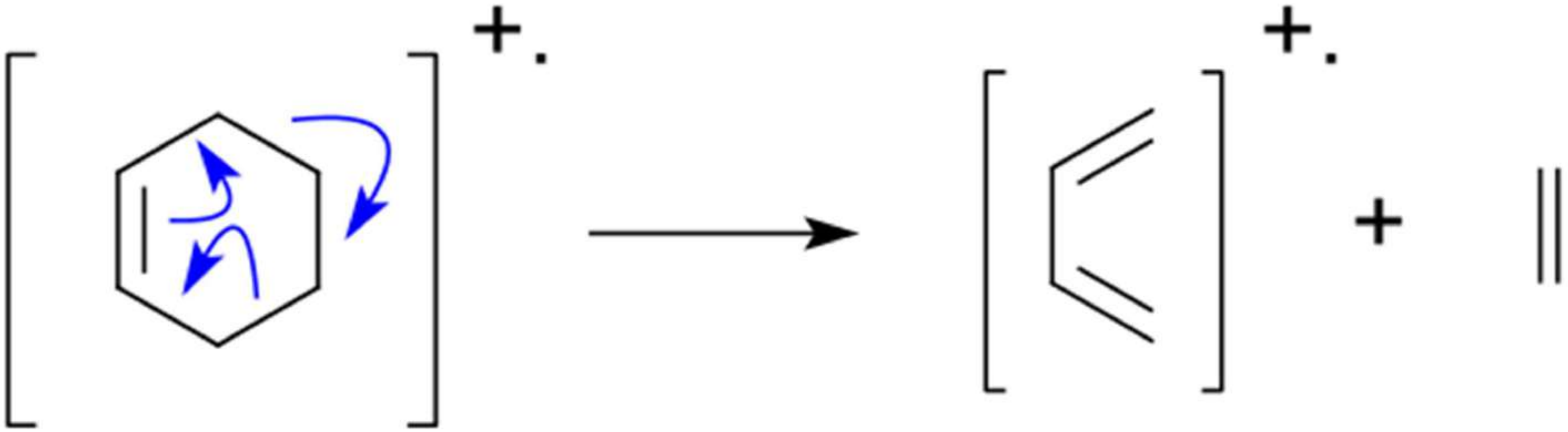
Aldehyde might undergo alpha, beta and Mclafferty rearrangement. Explain

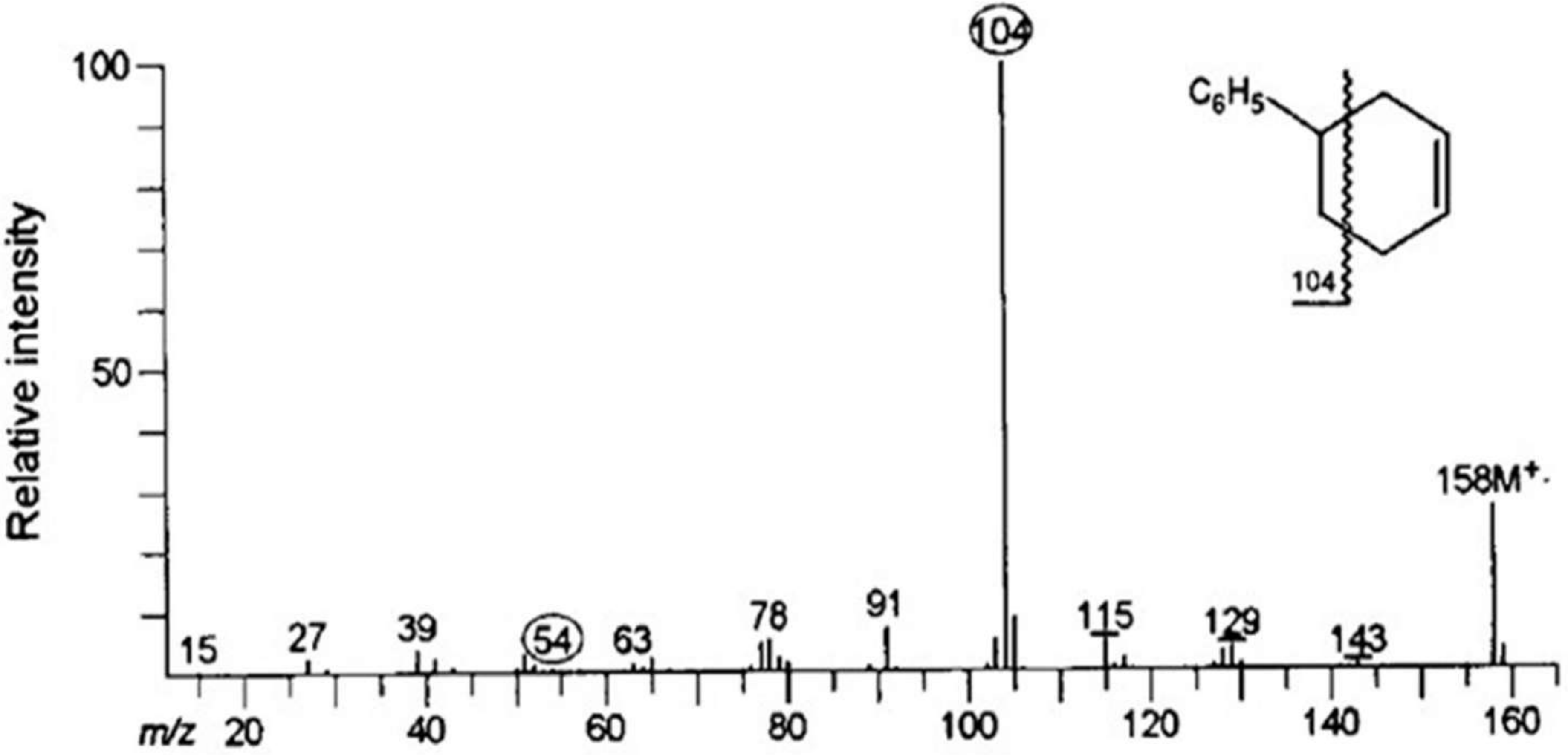
Note:- For breaking bonds; any atom left or right to carbonyl is known as alpha



Retro Diels-Alder fragmentation

This reaction occurs mainly in cyclohexene and its derivatives. Upon ionization, the pi electrons are excited and generate a charge site and a radical site. Following this, two successive α cleavages yield a butadiene radical and a neutral ethene




Relative intensity
100
50
m/z
20
40
60
80
100
120
140
160
15
27
39
54
63
78
91
104
115
129
143
158M+·
C6H5
104

Mass Spectroscopy

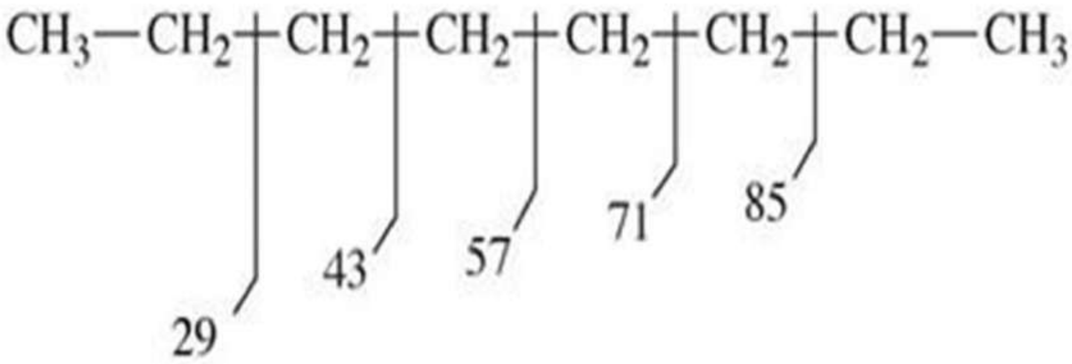
Part 3

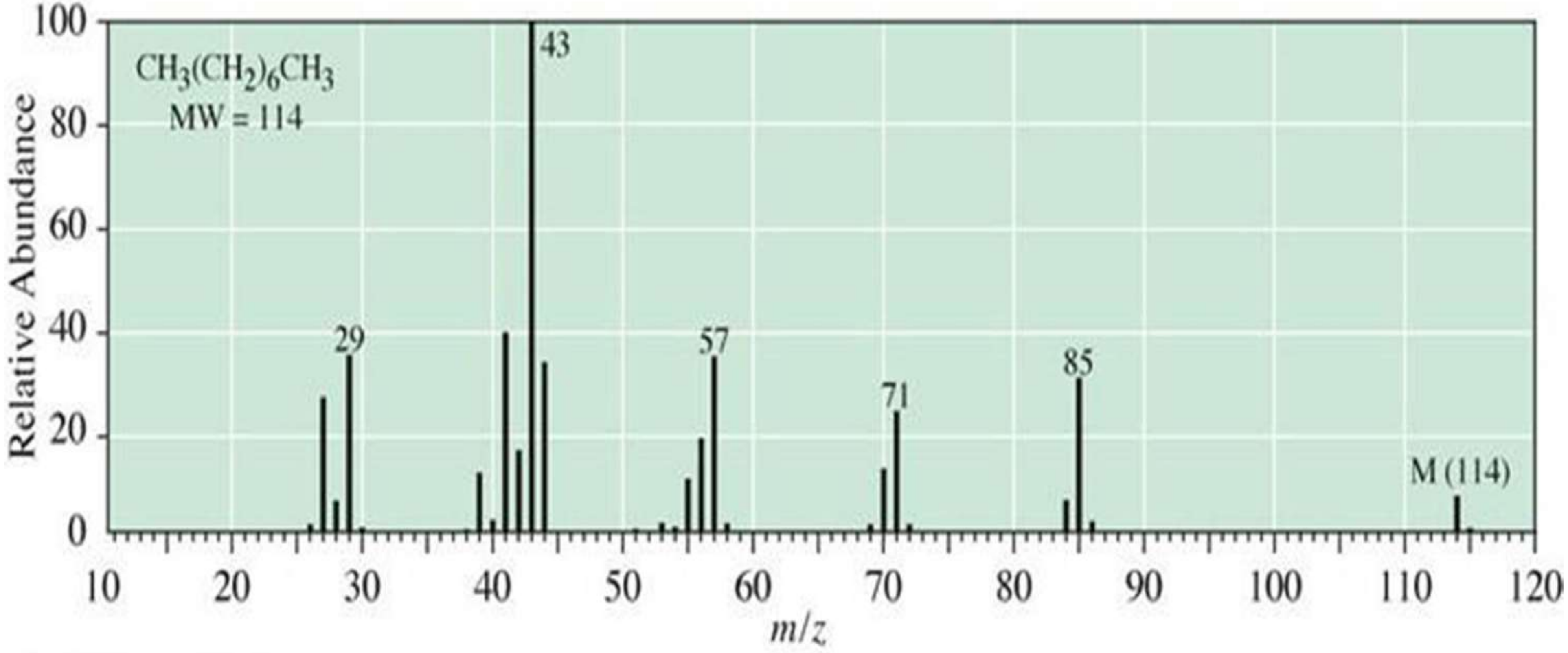
Application

Fragmentation Patterns

- Alkanes
  - Fragmentation often splits off simple alkyl groups:

Loss of methyl	$M^+ - 15$
Loss of ethyl	$M^+ - 29$
Loss of propyl	$M^+ - 43$
Loss of butyl	$M^+ - 57$


CH3—CH2—CH2—CH2—CH2—CH2—CH2—CH3
29
43
57
71
85


CH3(CH2)6CH3
MW = 114
Relative Abundance
m/z
43
29
57
71
85
M (114)
0
20
40
60
80
100
10
20
30
40
50
60
70
80
90
100
110
120

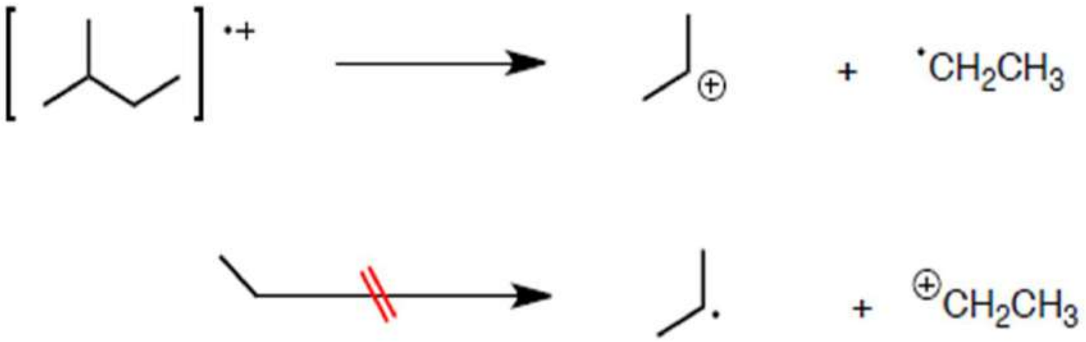
Basic Fragmentation Processes

Stevenson's Rule

- The most probable fragmentation is the one that leaves the positive charge on the fragment with the lowest ionization energy
  - fragmentation processes that lead to the formation of more stable ions are favored over processes that lead to less stable ions

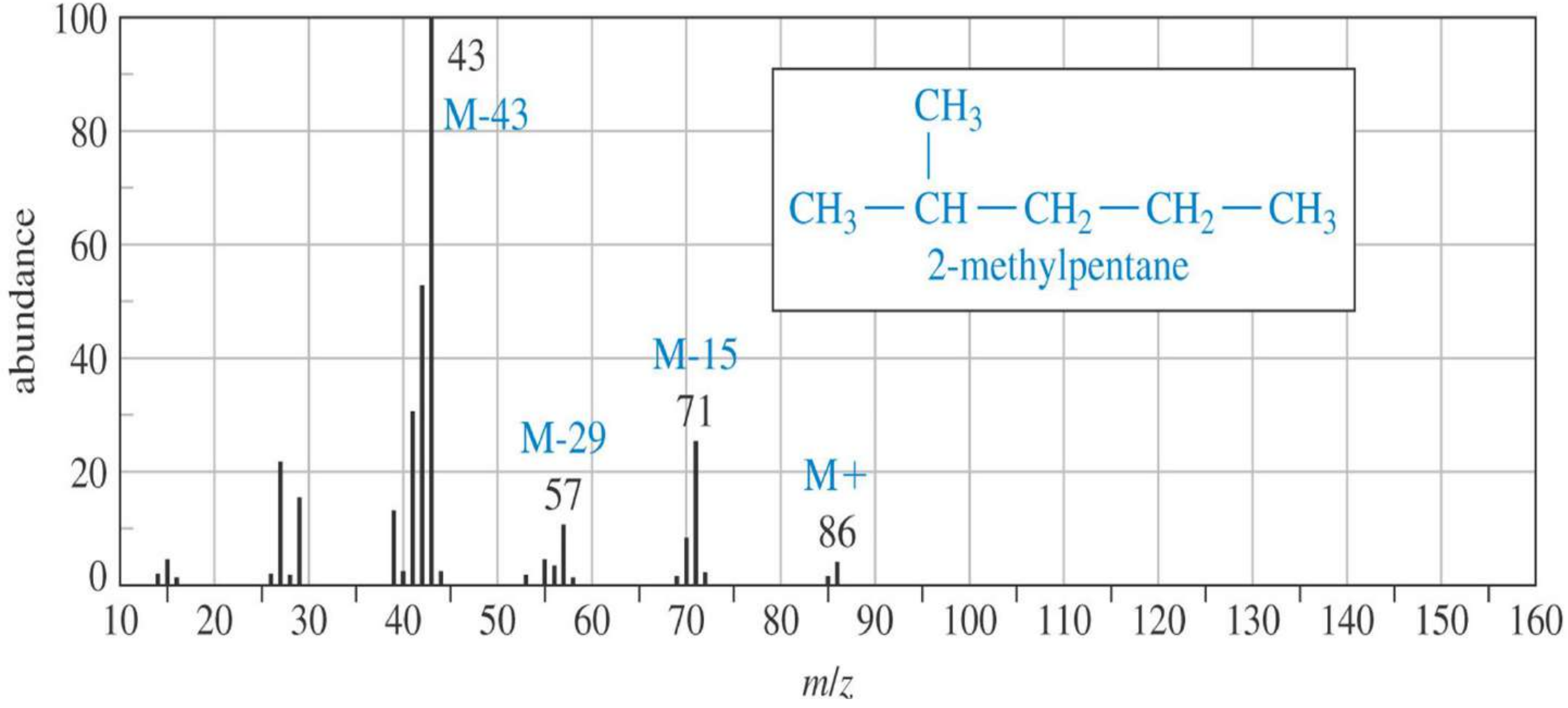
- Cleavages that lead to formation of more stable carbocations are favored
  - cation stability is more important than radical stability

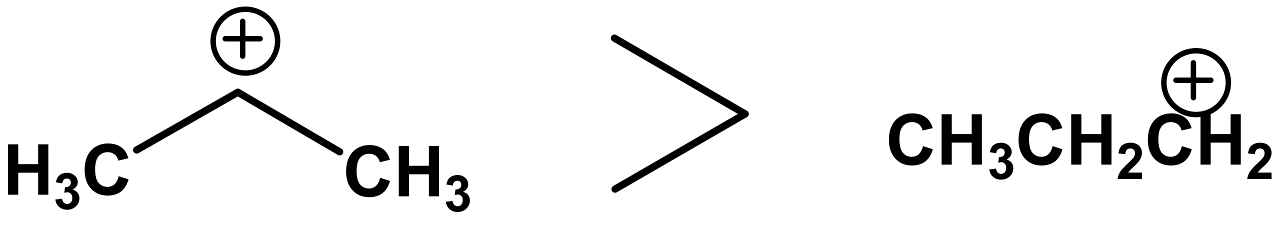
- When loss of more than one radical is possible, the largest alkyl radical will be lost preferentially



Fragmentation Patterns

- **Mass spectrum of 2-methylpentane**





Mass Spectrometry

Basic Fragmentation Processes

Ease of Fragmentation

less fragmentation

higher relative abundance of M^+

aromatics
alkenes
unbranched hydrocarbons
ketones
amines
esters
ethers
carboxylic acids
branched hydrocarbons
alcohols

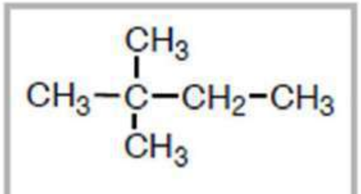
more fragmentation

lower relative abundance of M^+

Mass Spectrometry: Fragmentation

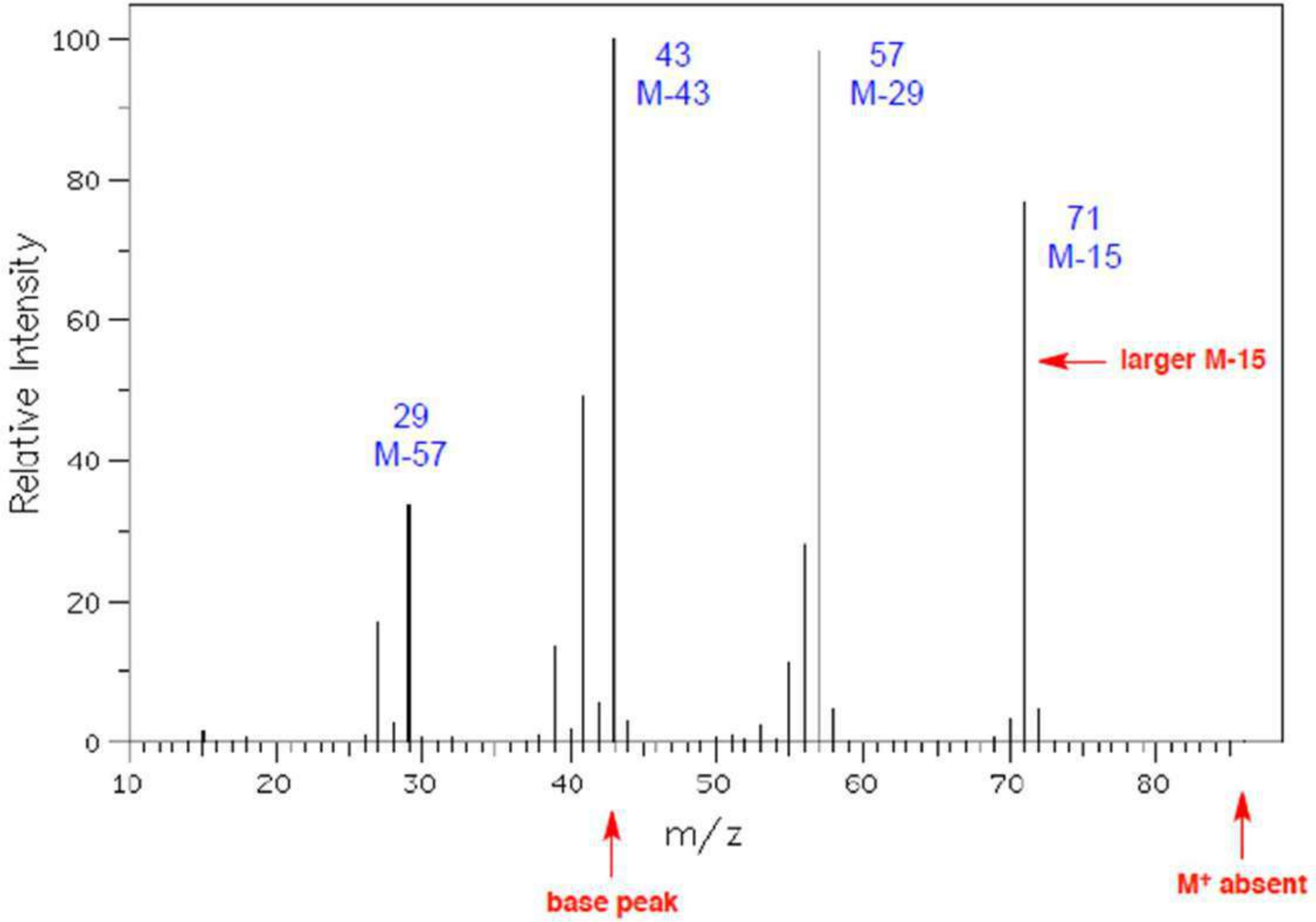
Branched Alkanes

2,2-dimethylbutane



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2-CH_3$$

MW = 86



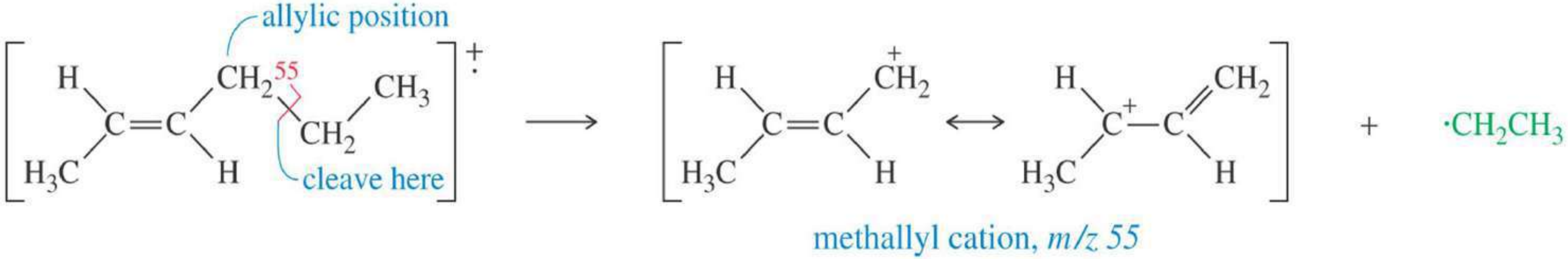
larger M-15

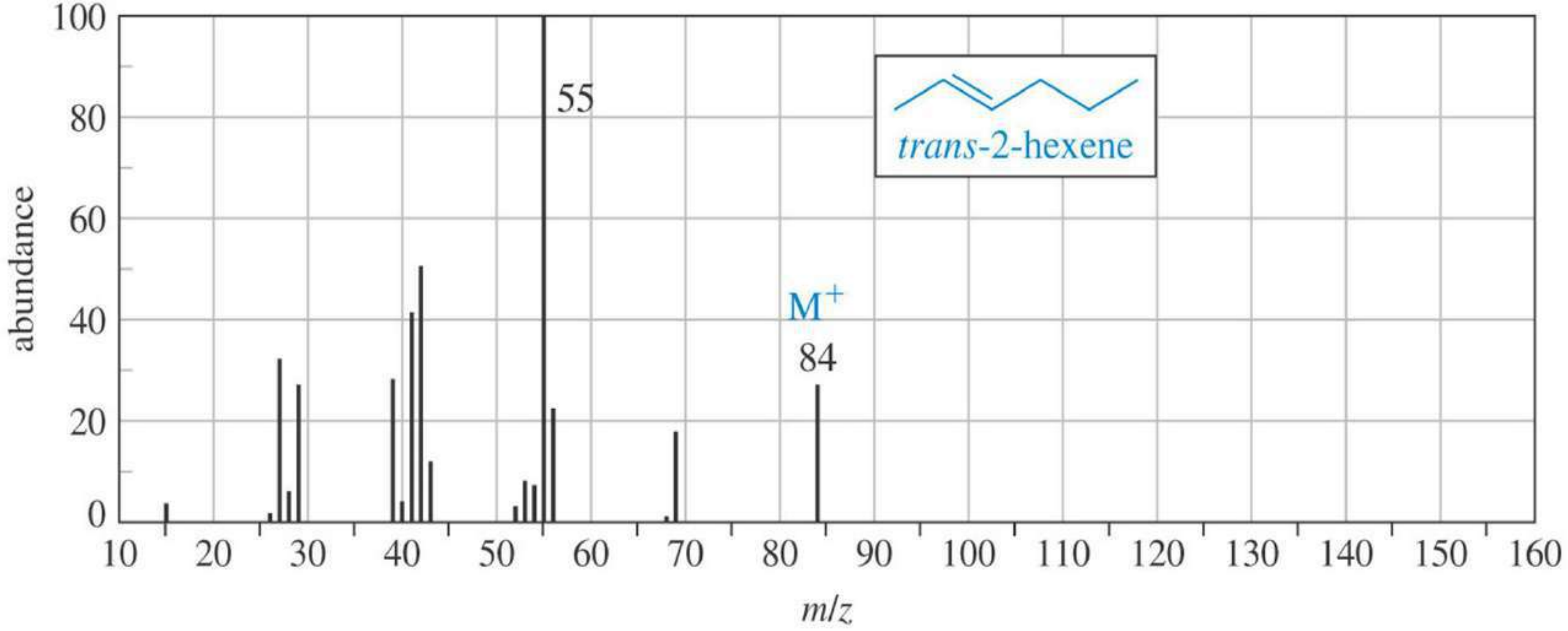
base peak

M^+ absent

Fragmentation Patterns

- **Alkenes:**
  - **Fragmentation typically forms resonance stabilized allylic carbocations**

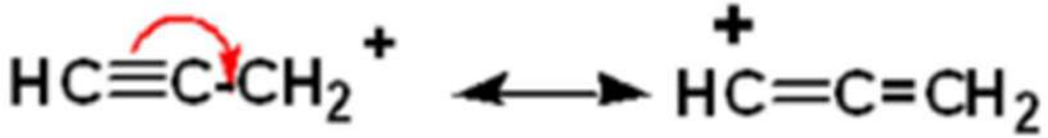




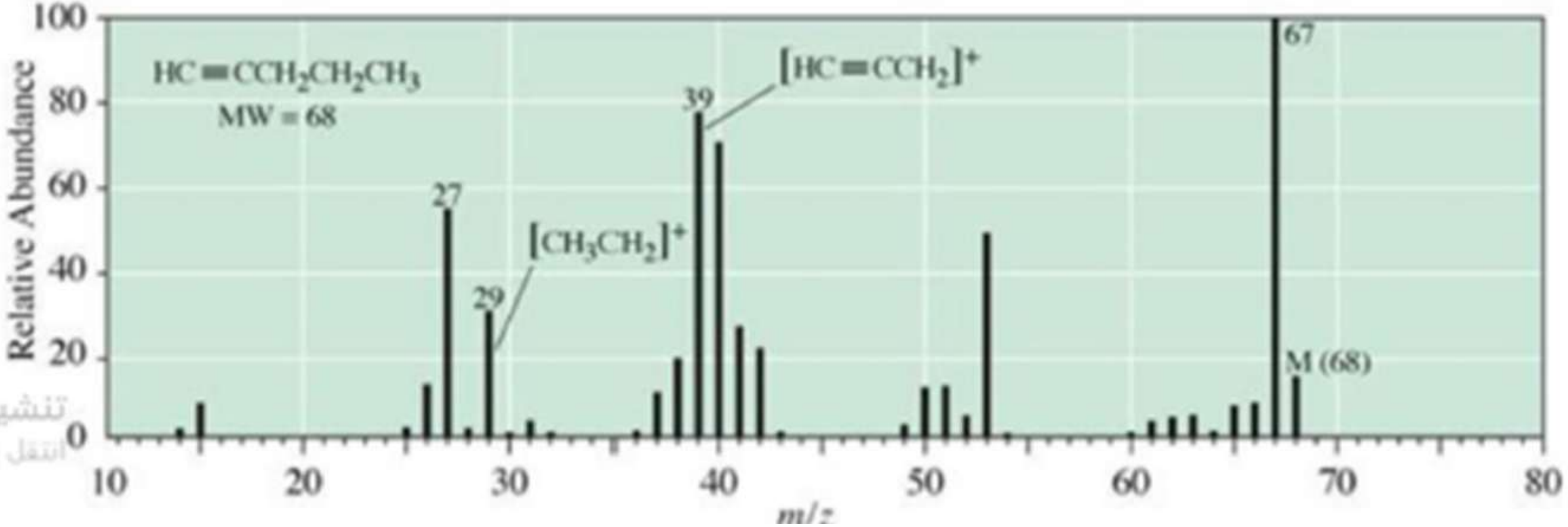
Alkynes

- Alkynes typically
  - show a strong molecular ion peak.
  - cleave readily to form the resonance-stabilized propargyl cation or substituted propargyl cations.

3-Propynyl cation (Propargyl cation)

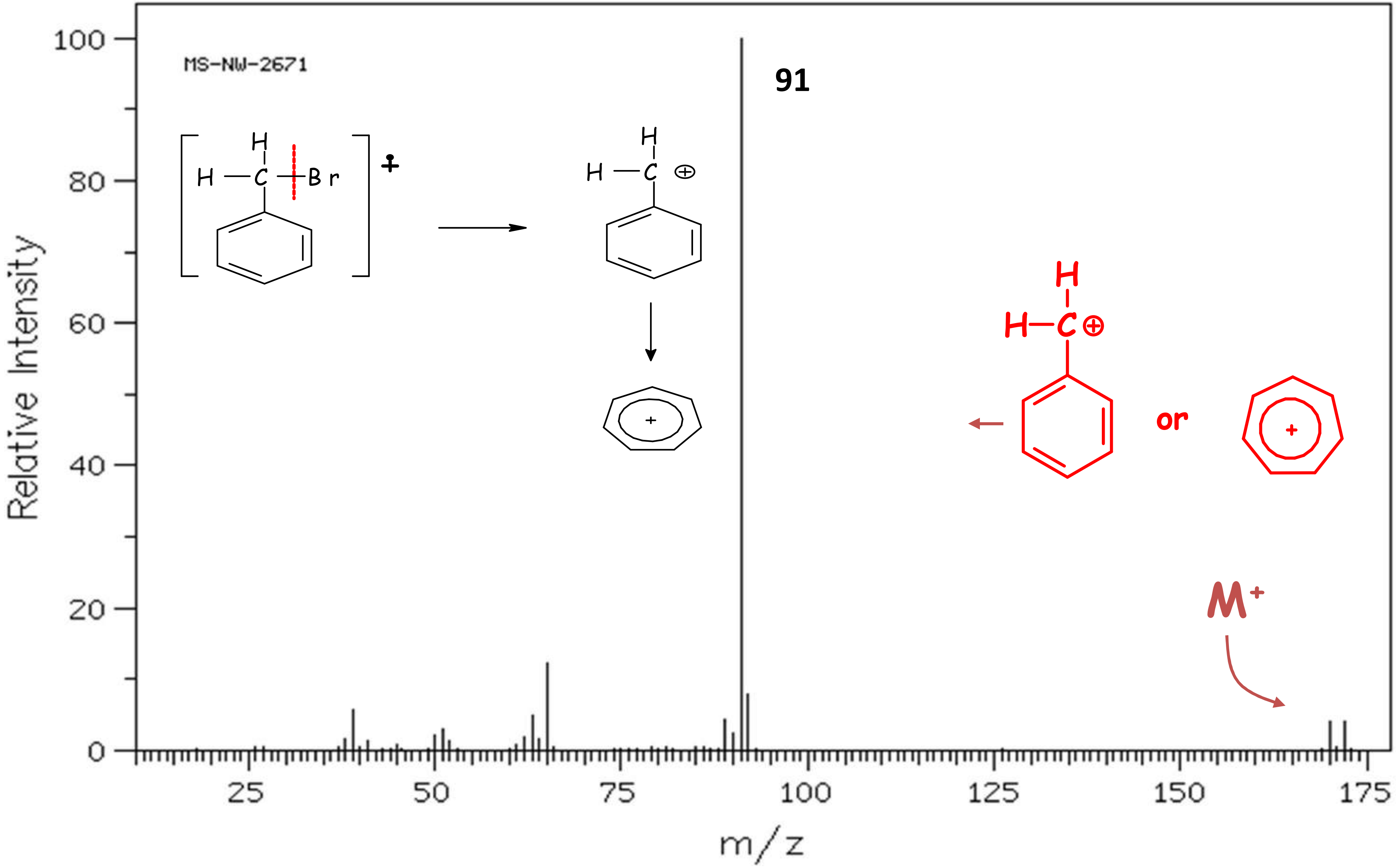


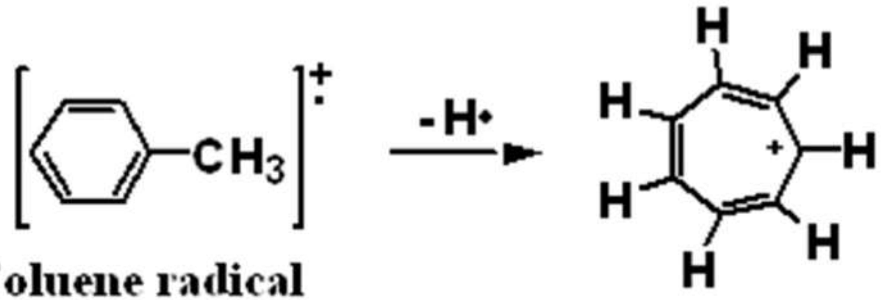
$$HC{\equiv}C{-}CH_2^{+} \longleftrightarrow H\overset{+}{C}{=}C{=}CH_2$$



Fragmentation Patterns

- **Aromatics:**
  - **Fragment at the benzylic carbon, forming a resonance stabilized benzylic carbocation (which rearranges to the tropylium ion)**

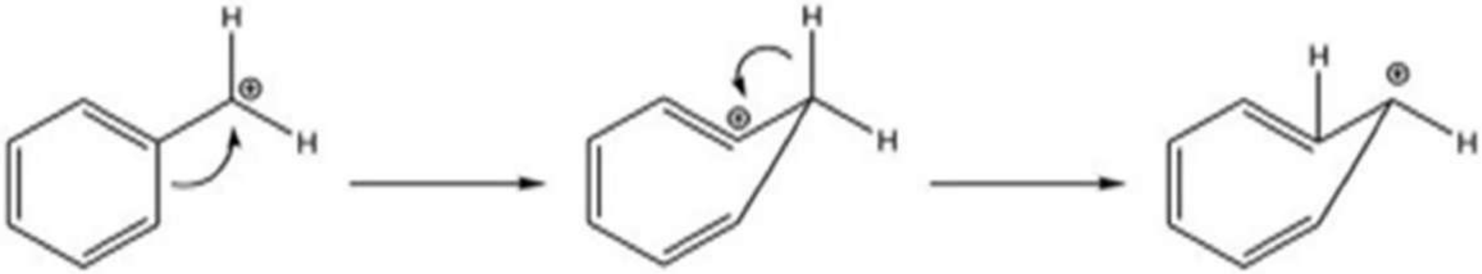




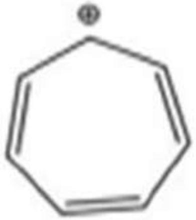
Toluene radical cation

Tropylium cation (m/z 91)

➢Tropylium ion formation

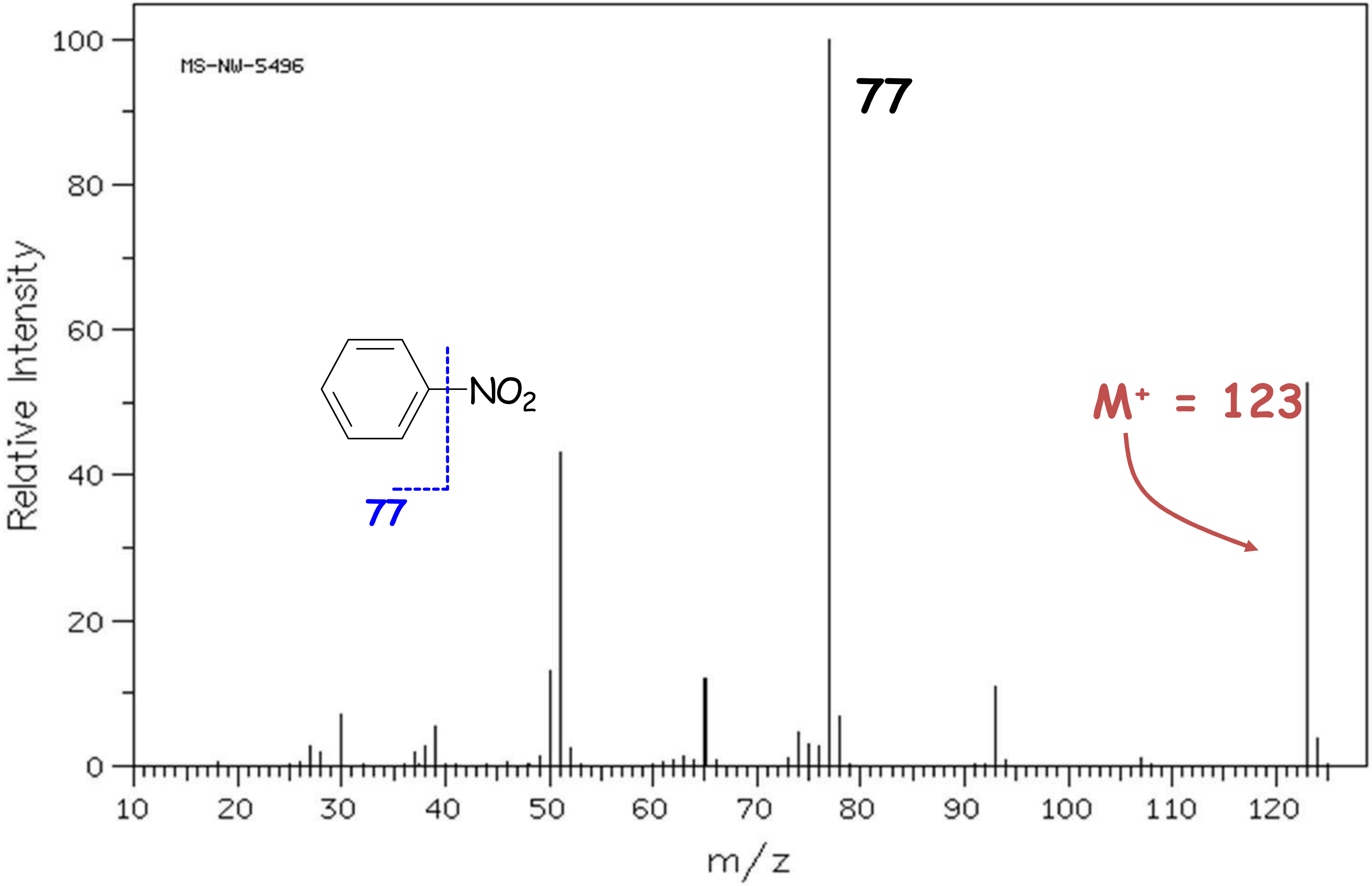


➢Tropylium ion structure:



Fragmentation Patterns

Aromatics may also have a peak at m/z = 77 for the benzene ring.



Fragmentation Patterns

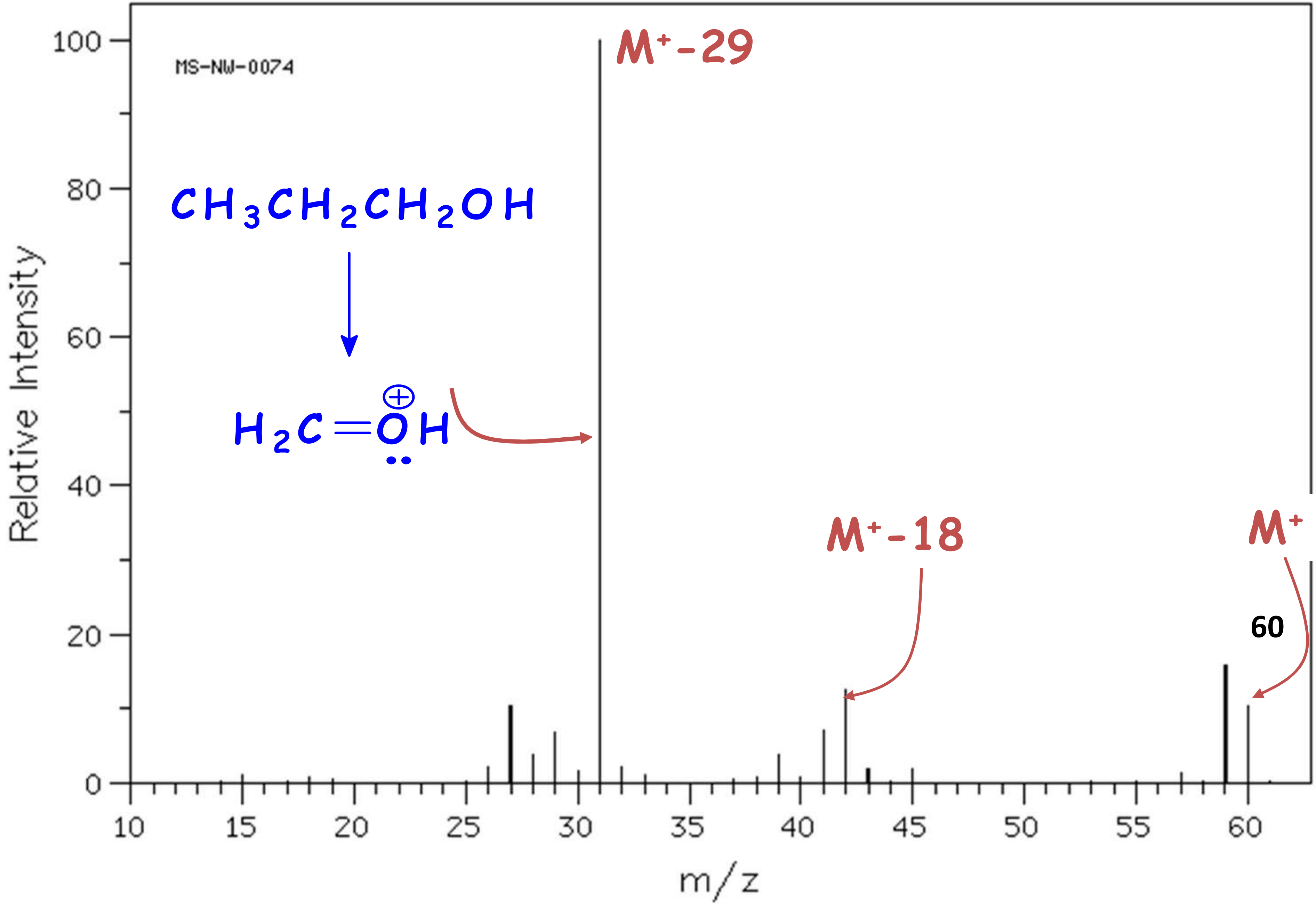
- Alcohols (M^+ - 17 or M^+ - 18)
  - Fragment easily resulting in very small or missing parent ion peak
  - May lose hydroxyl radical

or water

    - M^+ - 17 or M^+ - 18

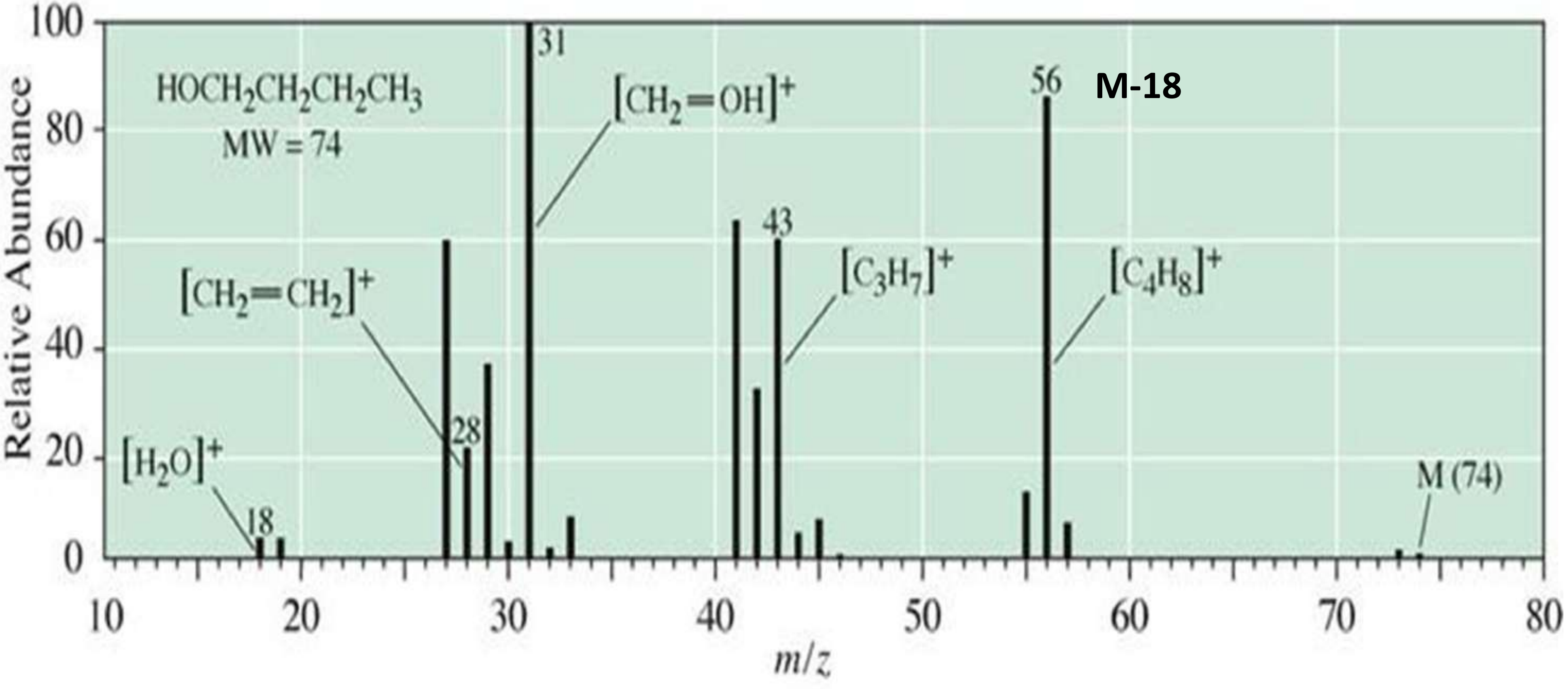
  - Commonly lose an alkyl group attached to the carbinol carbon forming an oxonium ion.
    - 1^o alcohol usually has prominent peak at m/z = 31 corresponding to $H_2C{=}OH^+$

Fragmentation Patterns

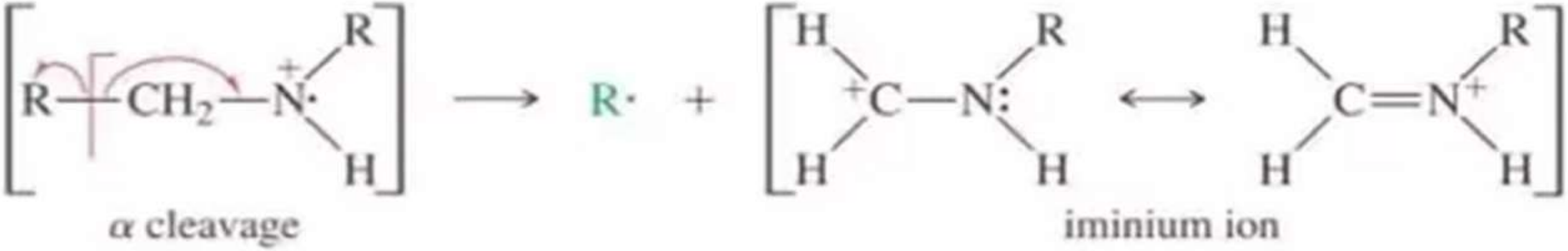


من ضمن الاسئلة المشهورة

Provide a clear interpretation for each given fragment

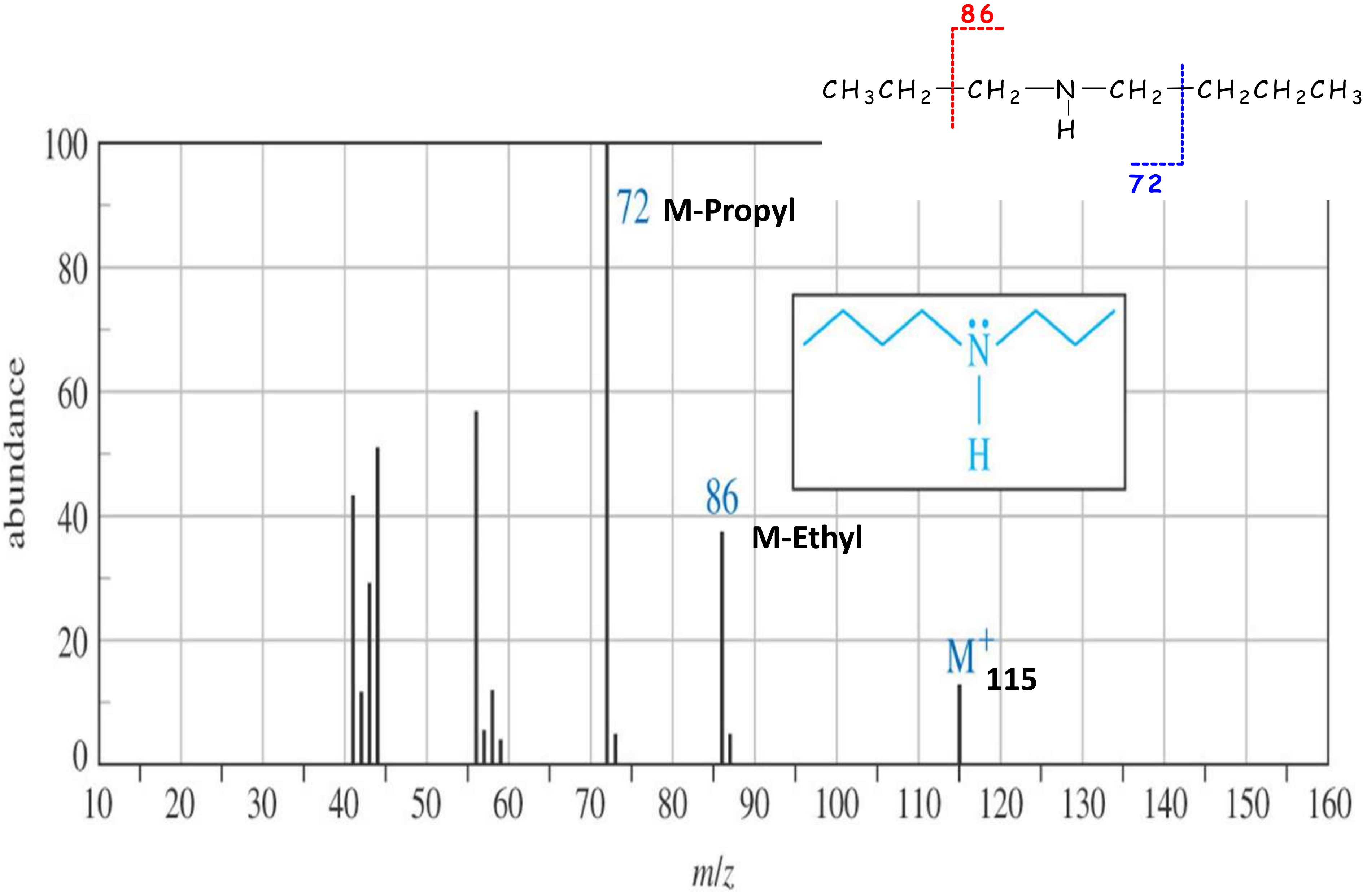


Alpha Cleavage of Amines



- The most common fragmentation of amines is α-cleavage to give a resonance-stabilized cation—an iminium ion.

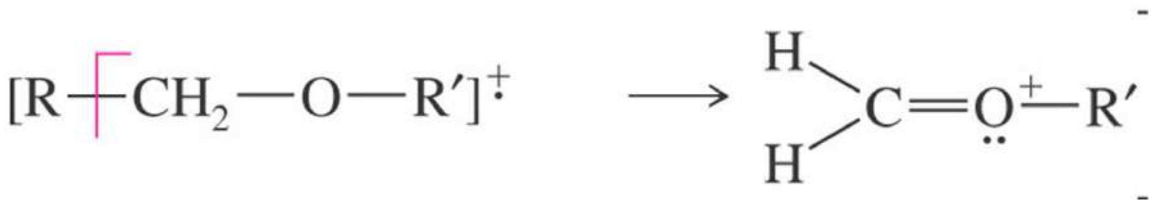
Fragmentation Patterns



$$CH_3CH_2-CH_2-\underset{\displaystyle H}{\underset{|}{N}}-CH_2-CH_2CH_2CH_3$$

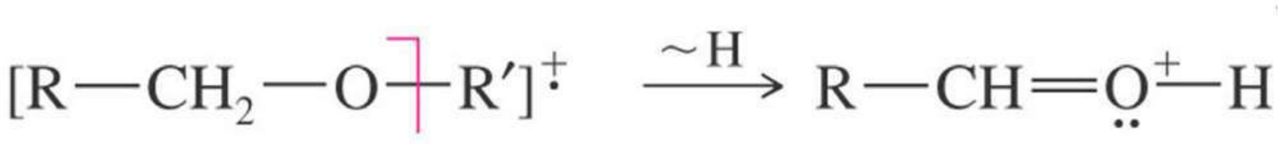
Fragmentation Patterns

- **Ethers**
  - **α-cleavage forming oxonium ion**



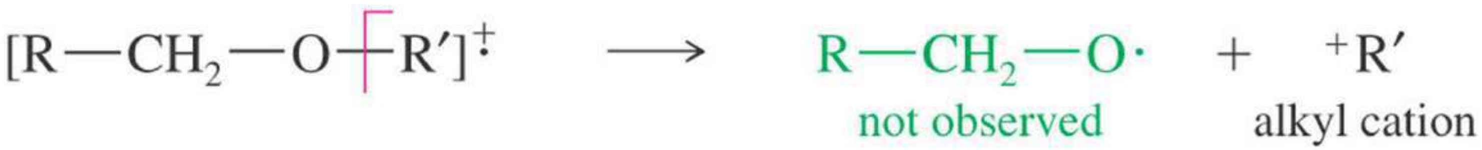
$$[R-CH_2-O-R']^{+\cdot} \longrightarrow H_2C=\ddot{O}^{+}-R'$$

  - **Loss of alkyl group forming oxonium ion**



$$[R-CH_2-O-R']^{+\cdot} \xrightarrow{\sim H} R-CH=\ddot{O}^{+}-H$$

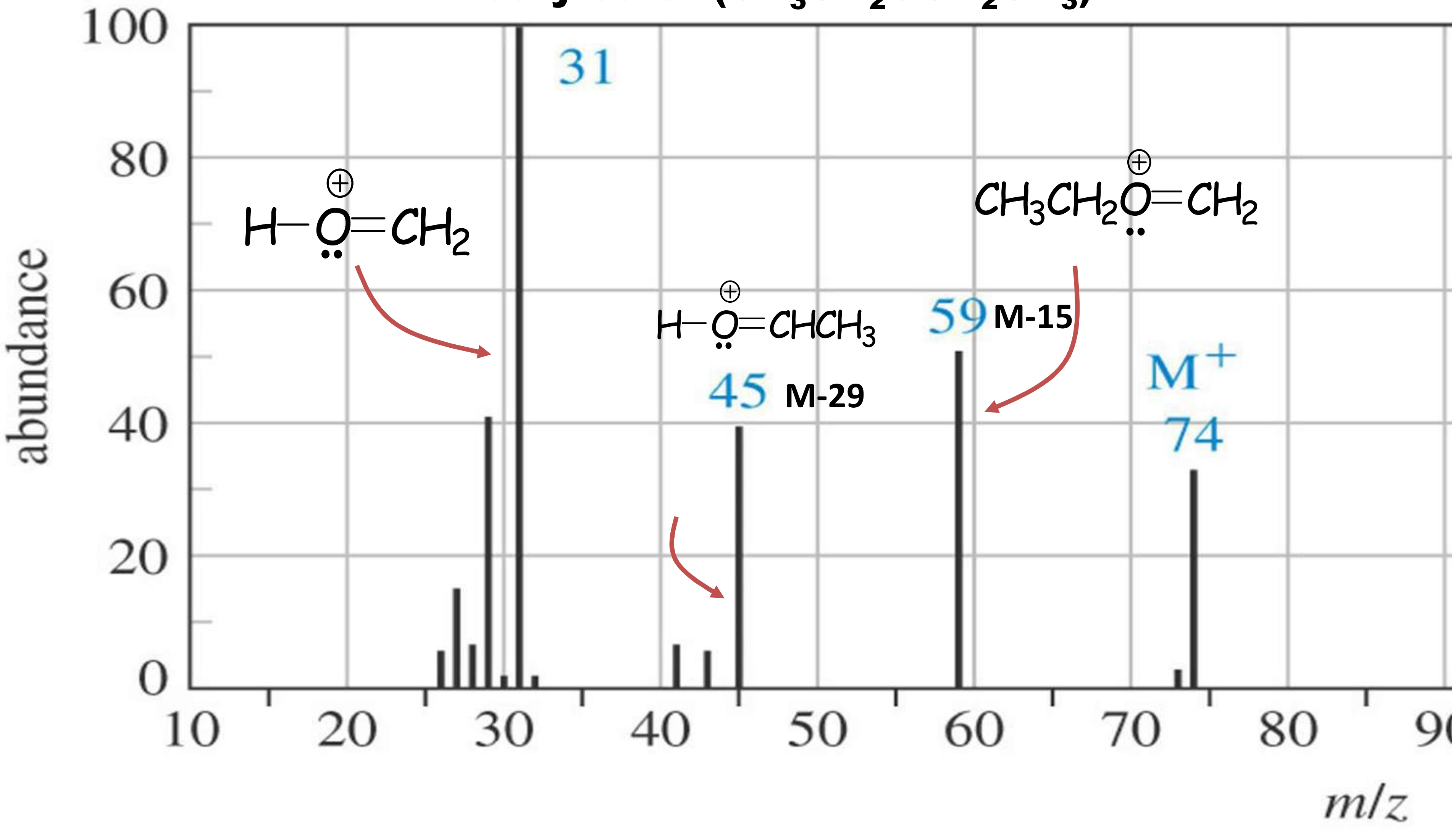
  - **Loss of alkyl group forming a carbocation**



$$[R-CH_2-O-R']^{+\cdot} \longrightarrow R-CH_2-O\cdot \;+\; {}^{+}R'$$

Fragmentation Patterns

Diethylether ($CH_3CH_2OCH_2CH_3$)



Fragmentation Patterns

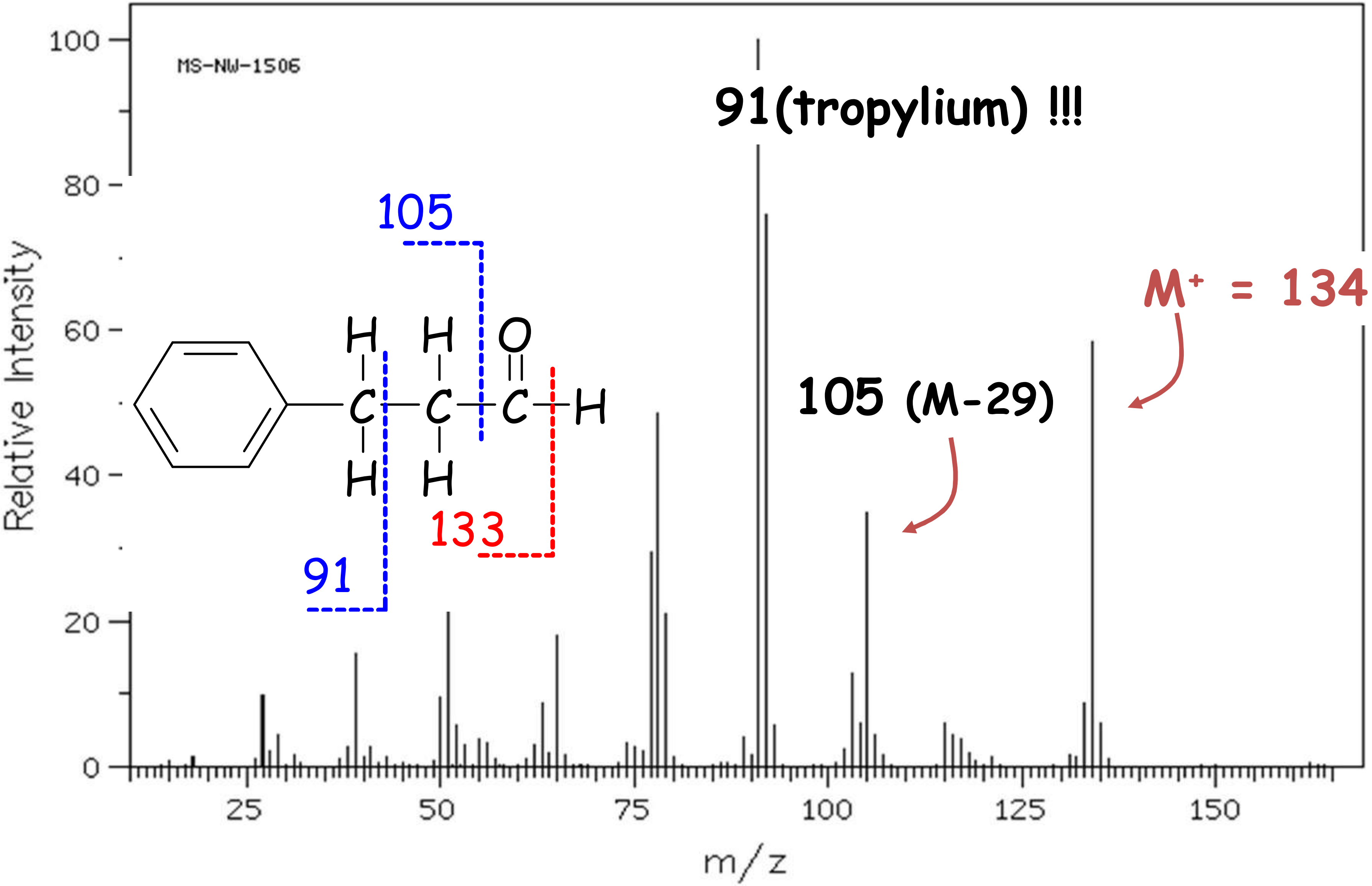
- **Aldehydes (RCHO)**
  - **Fragmentation may form acylium ion**

$$RC\equiv\overset{\oplus}{O}:$$

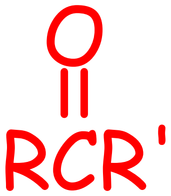
  - **Common fragments:**
    - **M^+ - 1 for** $RC\equiv\overset{\oplus}{O}:$
    - **M^+ - 29 for** $R\oplus$ (i.e. RCHO - CHO)

Fragmentation Patterns

- **Hydrocinnamaldehyde**

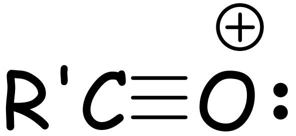


Fragmentation Patterns



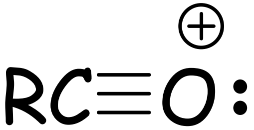
$$\overset{O}{\overset{\|}{RCR'}}$$

- **Ketones**
  - Fragmentation leads to formation of acylium ion:
    - Loss of R forming



$$R'C\equiv\overset{\oplus}{O}:$$

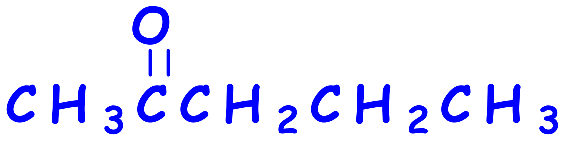
    - Loss of R’ forming



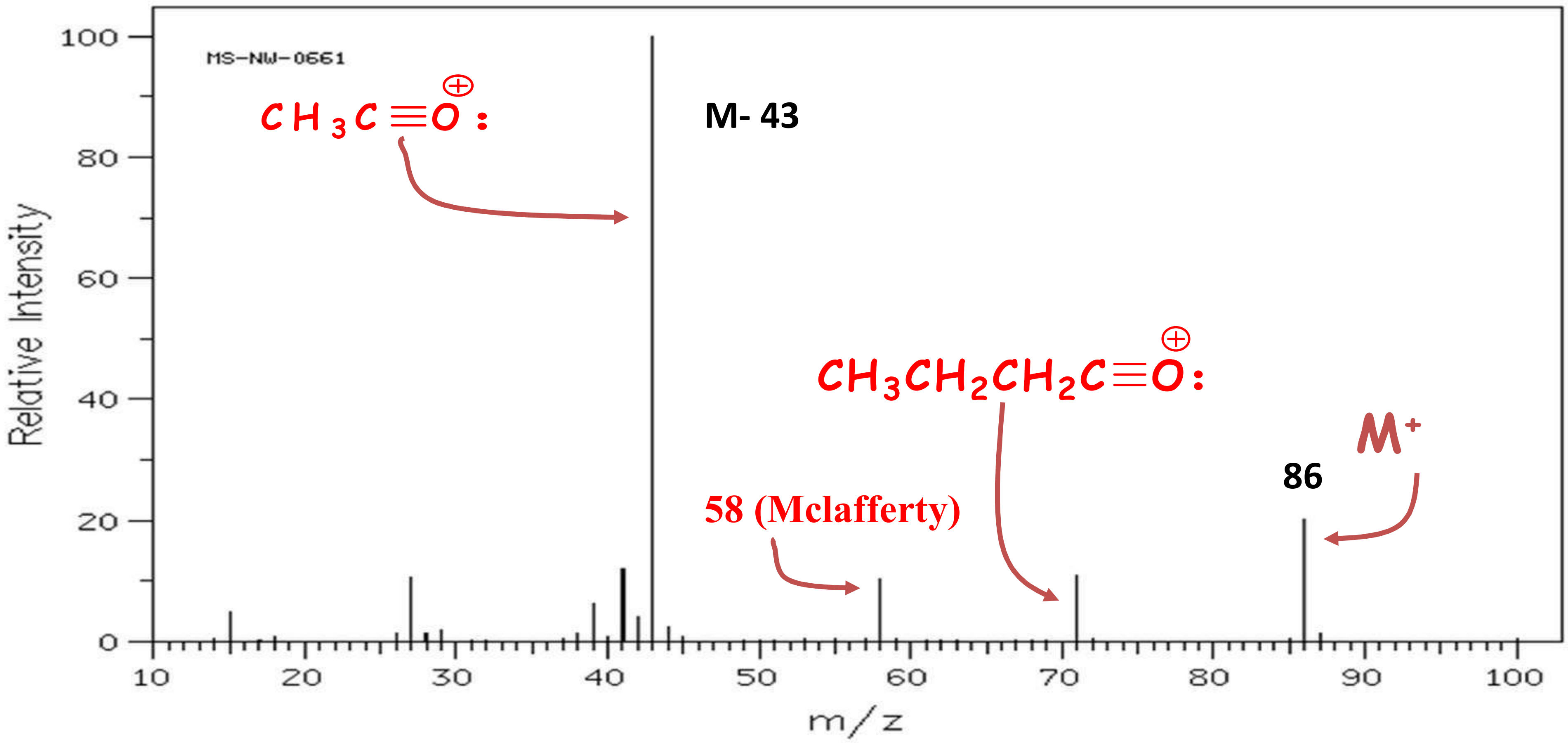
$$RC\equiv\overset{\oplus}{O}:$$

Fragmentation Patterns

- MS for 2-pentanone



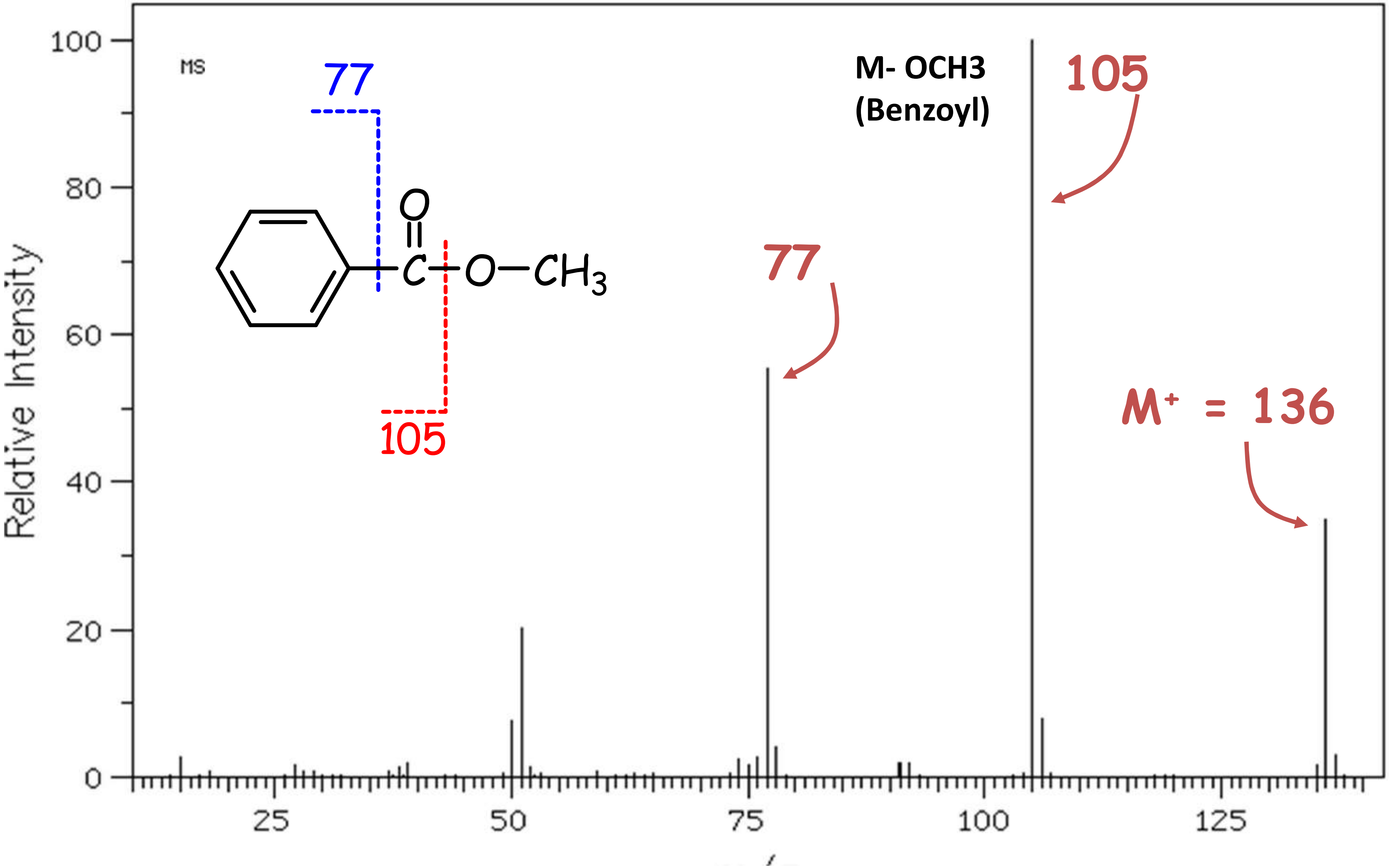
$$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH_3$$



Fragmentation Patterns

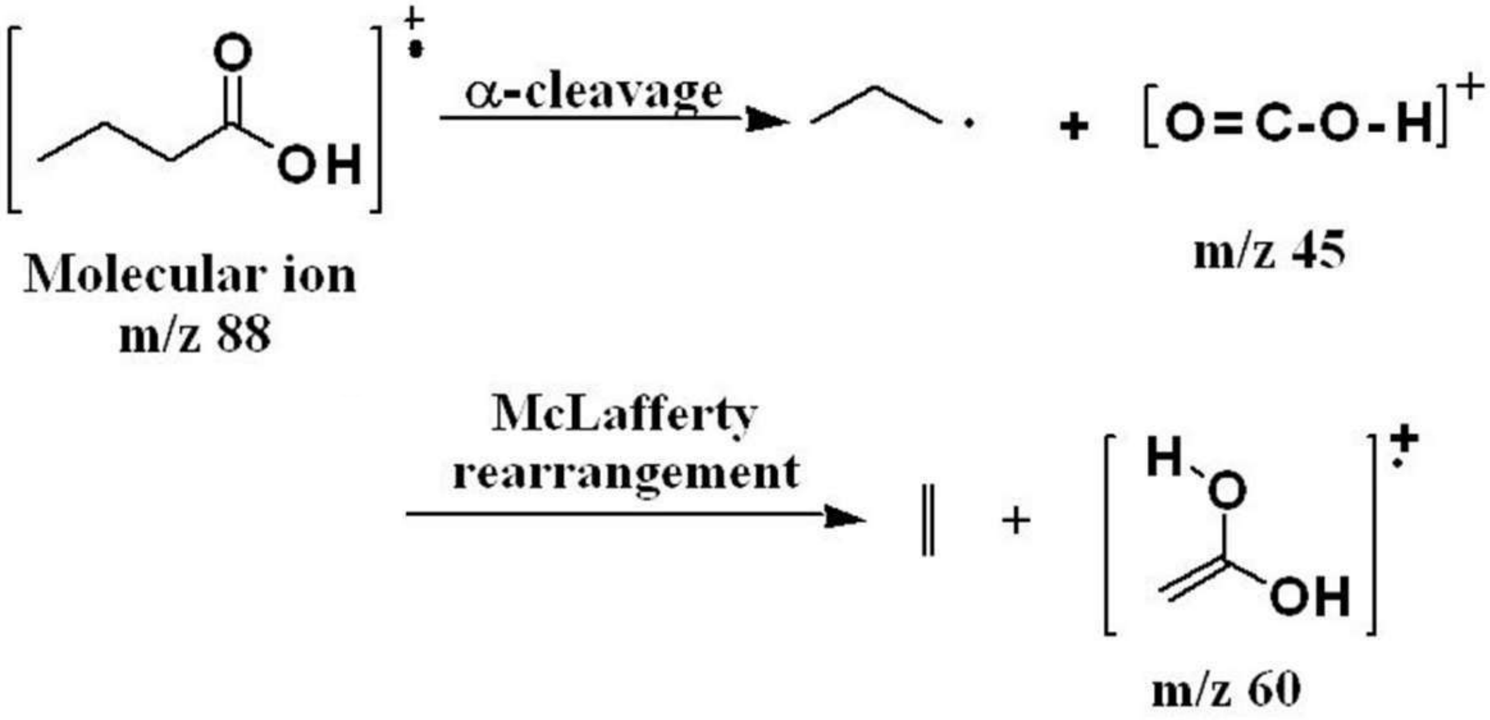
- Esters (RCO_2R')
  - Common fragmentation patterns include:
    - Loss of OR'
      - peak at M^+ - OR'
    - Loss of R
      - peak at M^+ - R

Fragmentation Patterns



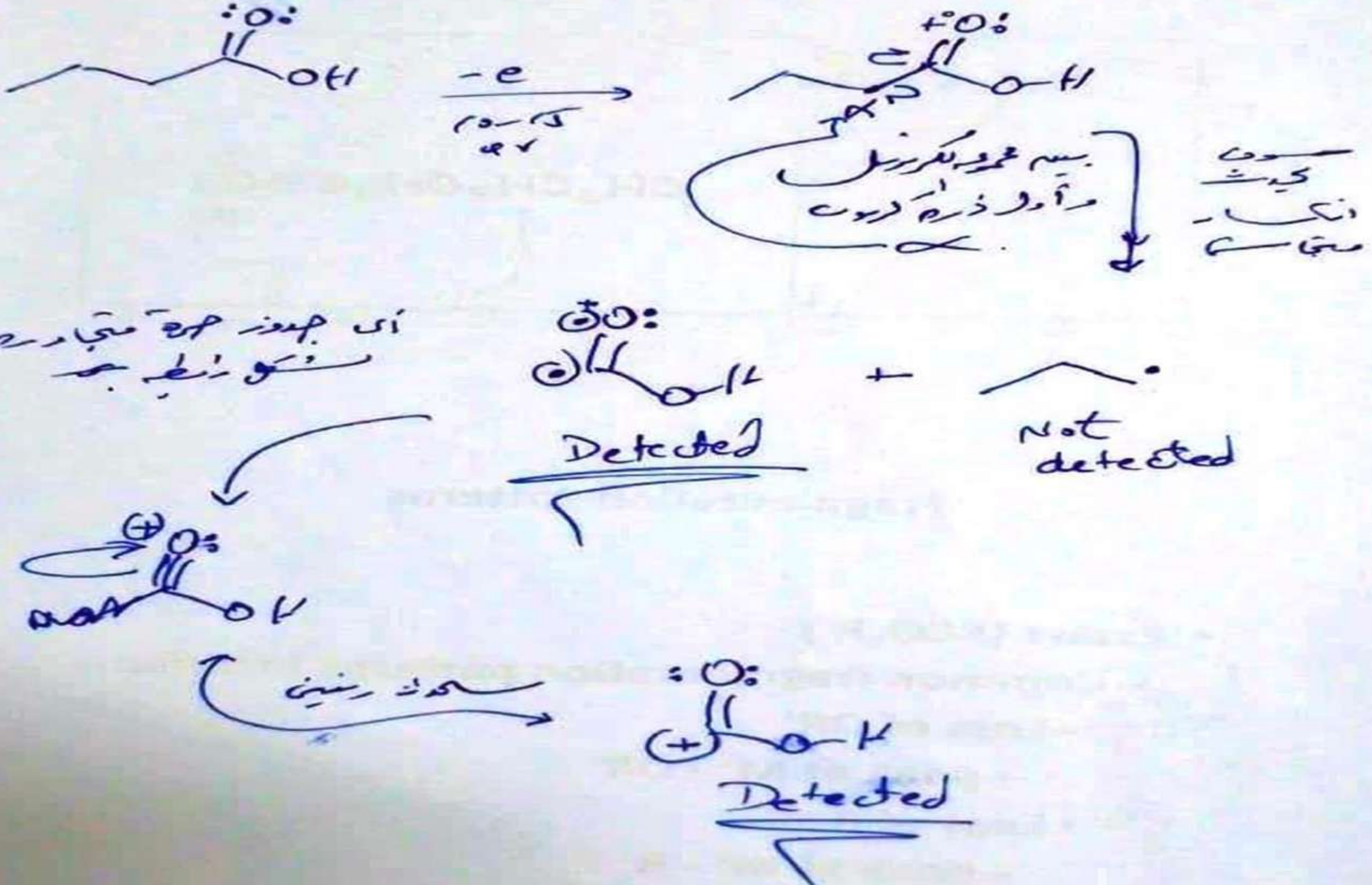
Carboxylic Acids

- Characteristic fragmentation patterns are α-cleavage to give the ion $[CO_2H]^+$ with *m/z* 45.
  - – McLafferty rearrangement.



إنتبهوا !!!

بخصوص α_cleavage في هذا الحمض الكربوكسيلي



بيتم كسر مجموعة الكربونيل مع أول ذرة كربون α.

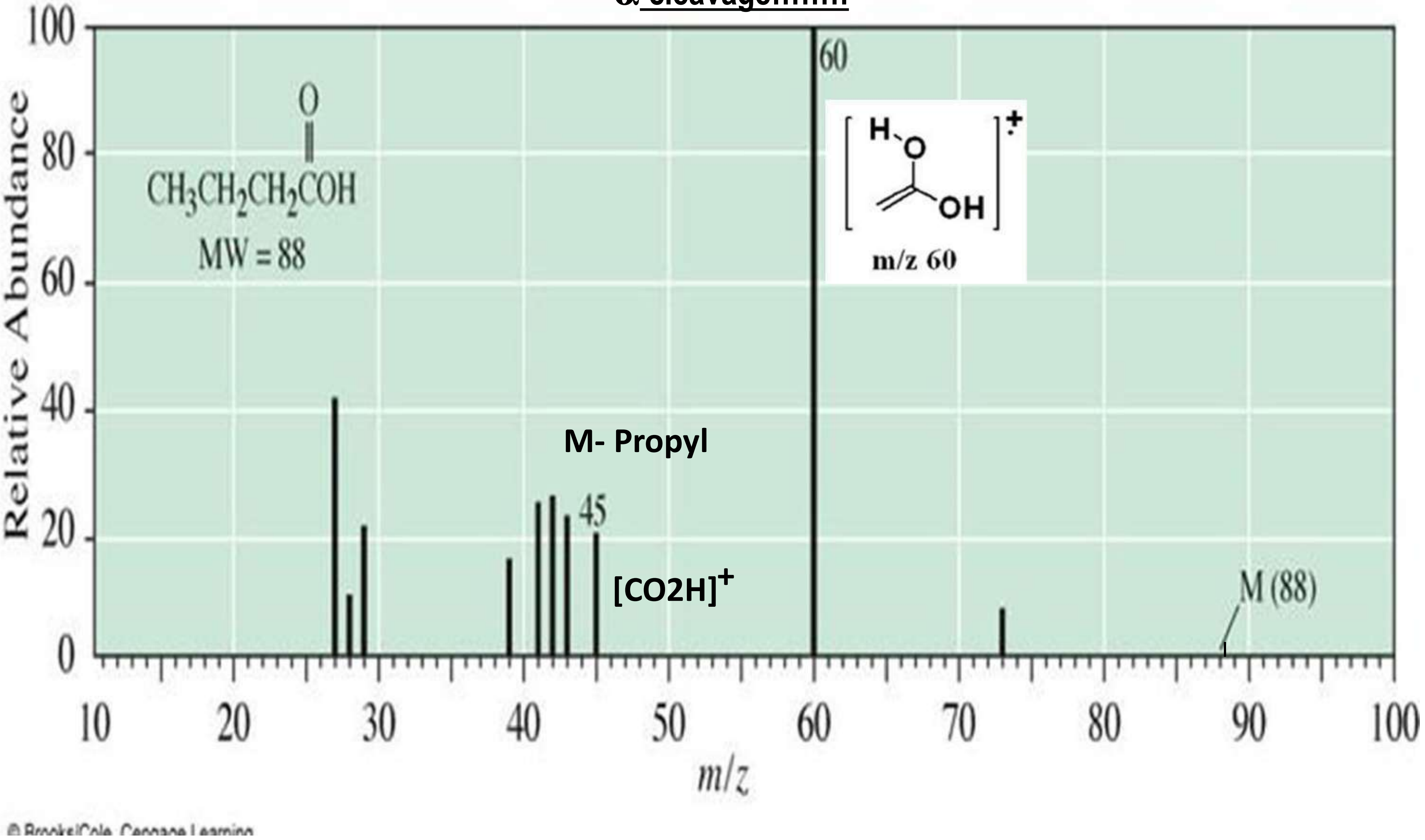
سوف يحدث انكسار متجانس

أي جذور حرة متعادلة [illegible]

سحب رنيني

Provide clear interpretation for the peak 60 and 45

N.B:- take care when it is carboxylic acid or ester
(just think about Mclafferty rearrangement and
α cleavage!!!!!!!!



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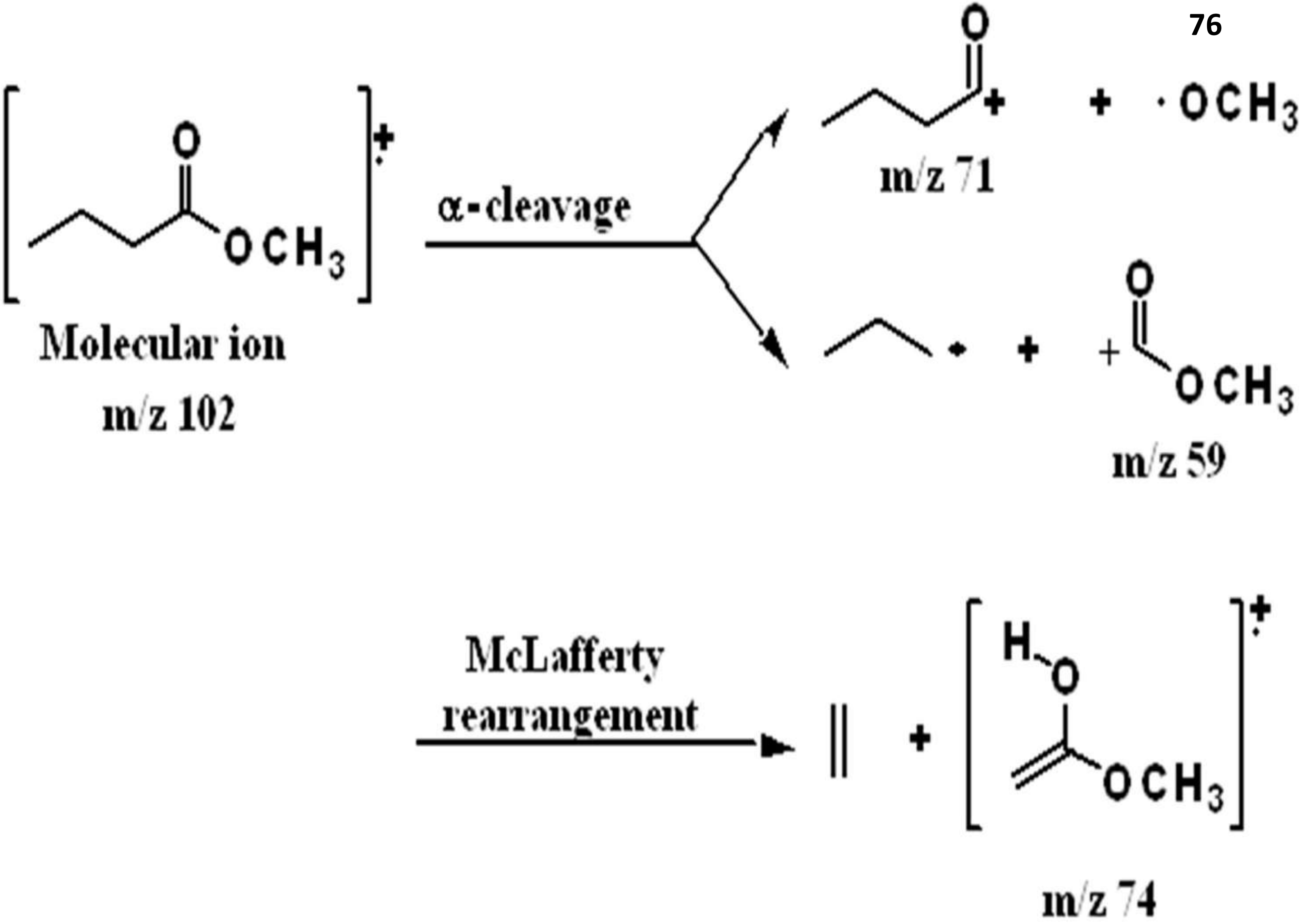
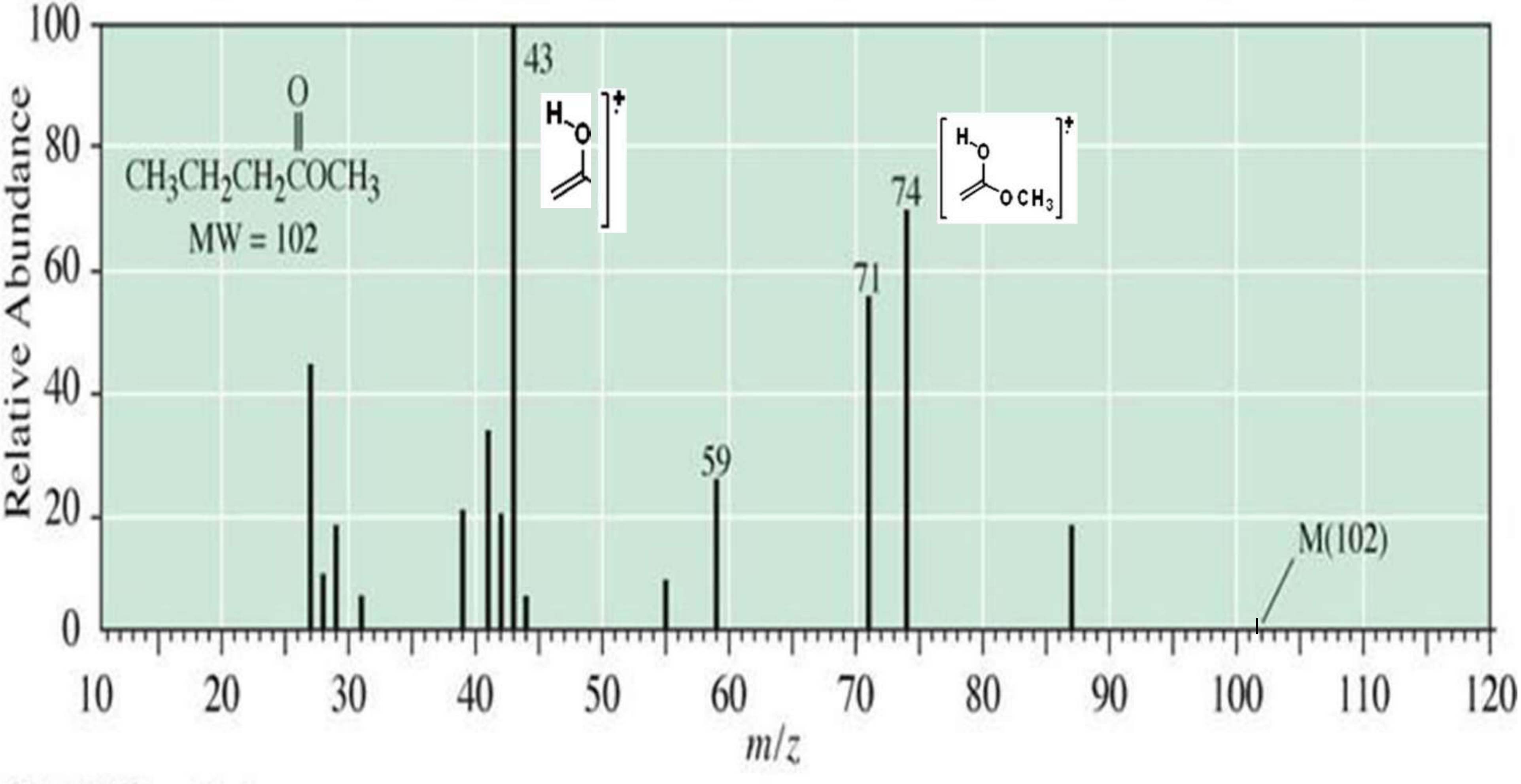

OCH3
Molecular ion
m/z 102
α-cleavage
m/z 71
·OCH3
m/z 59
McLafferty
rearrangement
H
O
OCH3
m/z 74

Provide clear interpretation for all given numerical peaks

N.B:- take care when it is carboxylic acid or ester (just think about Mclafferty rearrangement and alpha cleavage!!!!!!!!



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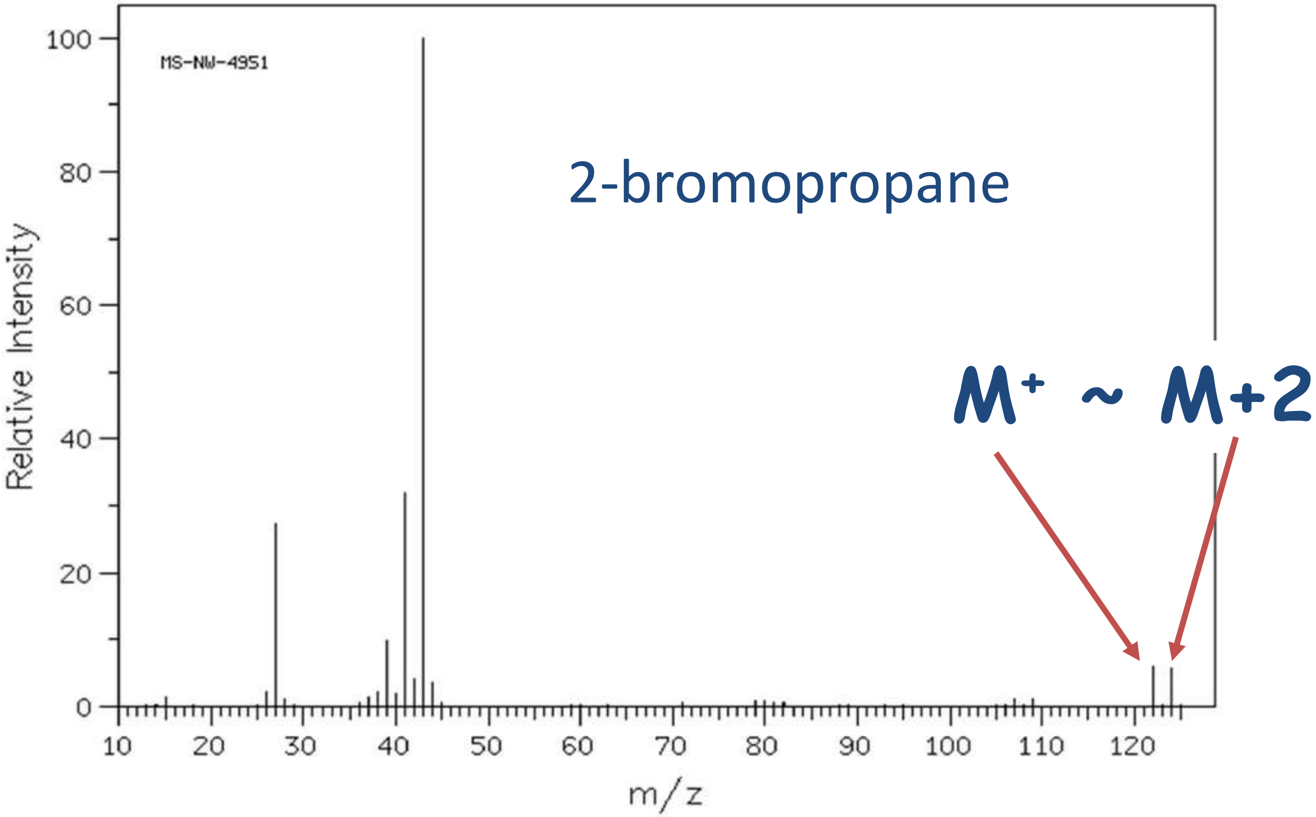
Natural Occurring Isotopic Abundances of Common Elements

Element	M+	M+ +1	M+ +2
hydrogen	^{1}H 100.0%		
carbon	^{12}C 98.9%	^{13}C 1.1%	
nitrogen	^{14}N 99.6%	^{15}N 0.4%	
oxygen	^{14}O 99.8%		^{18}O 0.2%
sulfur	^{32}S 95.0%	^{33}S 0.8%	^{34}S 4.2%
chlorine	^{35}Cl 75.5%		^{37}Cl 24.5 %
bromine	^{79}Br 50.5%		^{81}Br 49.5%
iodine	^{127}I 100.0%	Mono isotpoic feature	

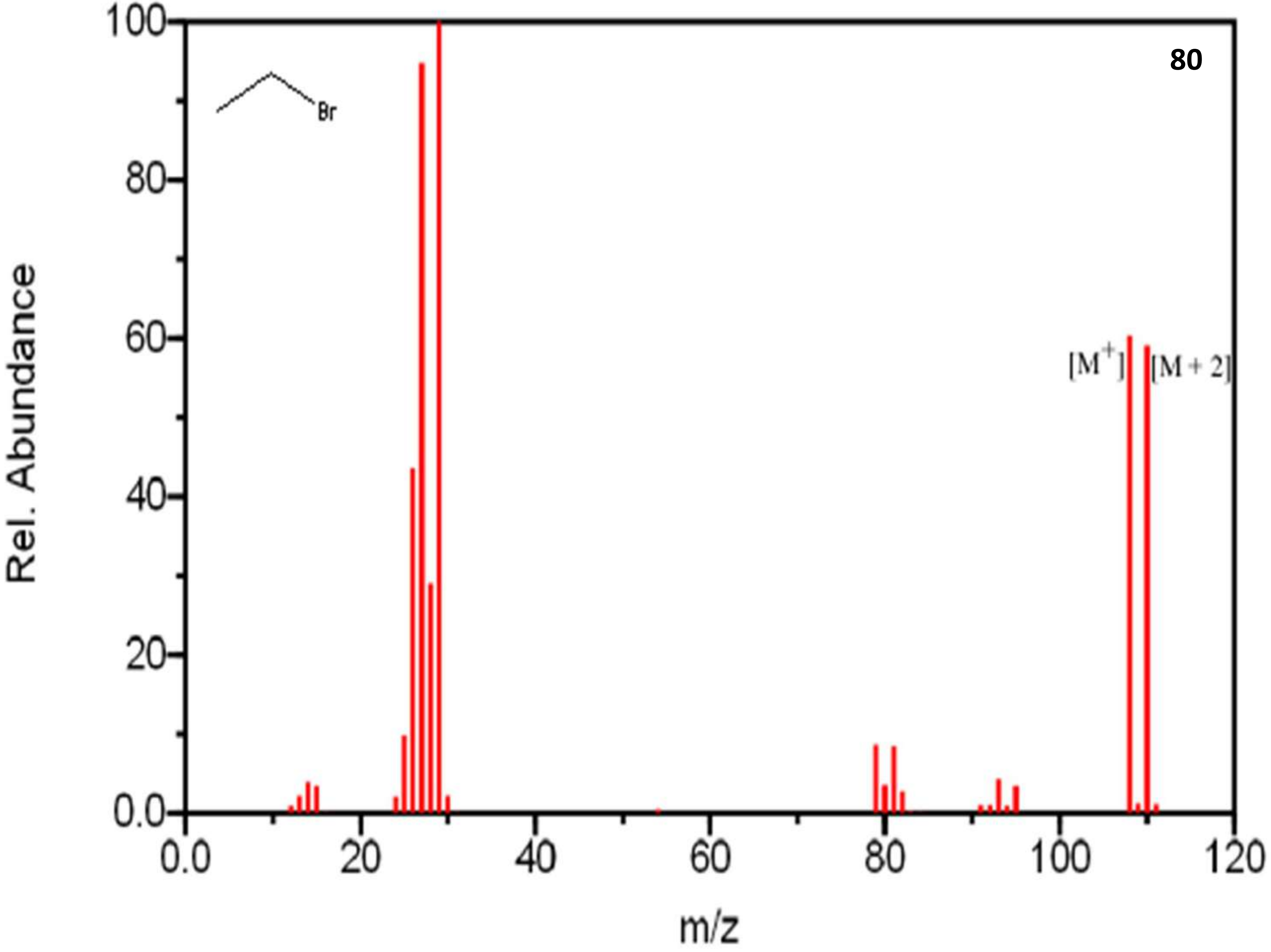
Easily Recognized Elements in MS

- **Bromine:**
  - $M^+ \sim M+2$ (50.5% ^{79}Br/49.5% ^{81}Br)



2-bromopropane

$M^+ \sim M+2$

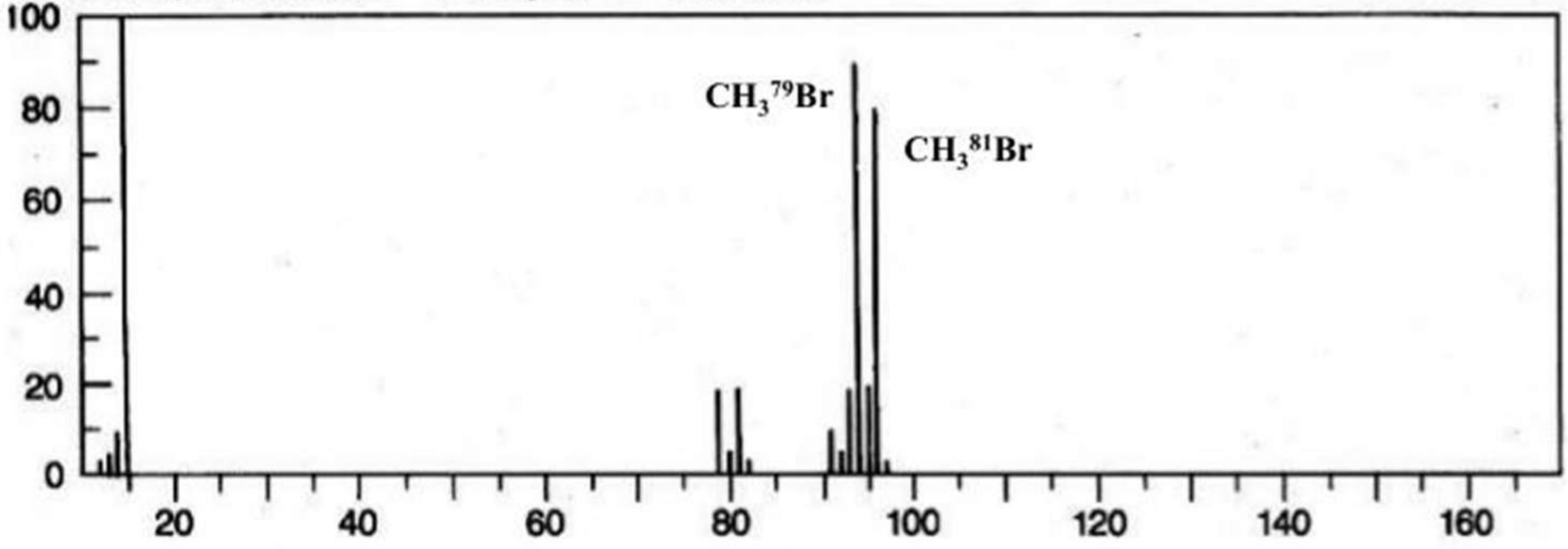

Br
Rel. Abundance
100
80
60
40
20
0.0
m/z
0.0
20
40
60
80
100
120
[M⁺]
[M + 2]

Isotope effects

Molecular weight
Br = 79.9040

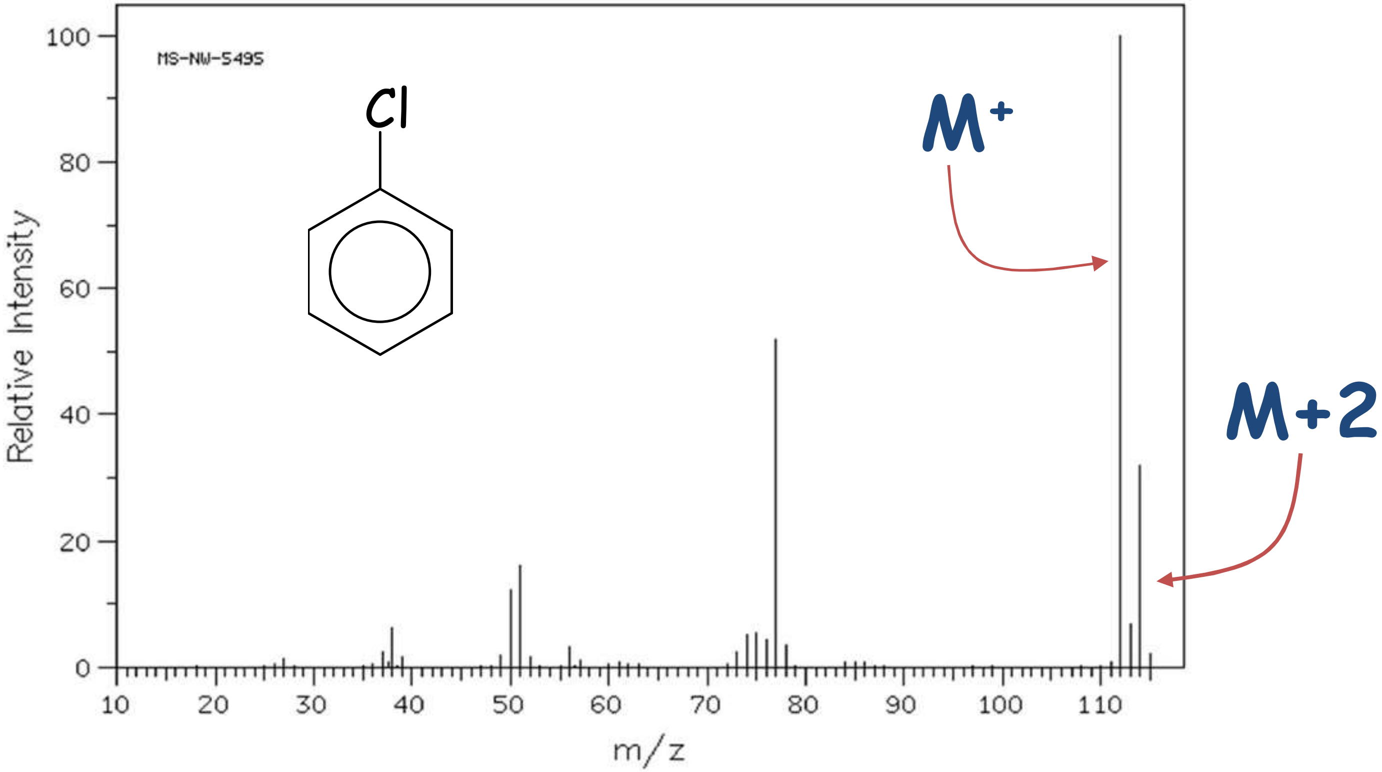
Br isotopic abundance
$^{79}Br = 50.5$ %
$^{81}Br = 49.5$ %

Methyl bromide CH_3Br 93.94181



Easily Recognized Elements in MS

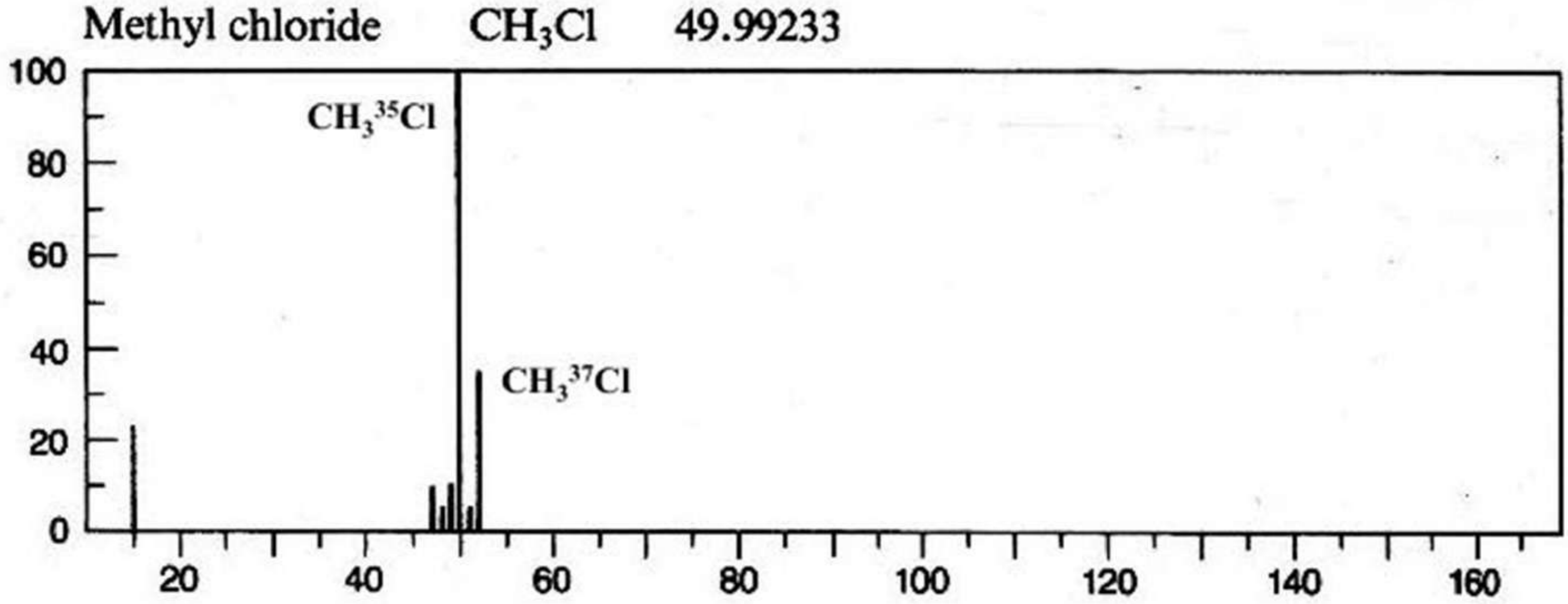
- **Chlorine:**
  - M+2 is ~ 1/3 as large as M^+

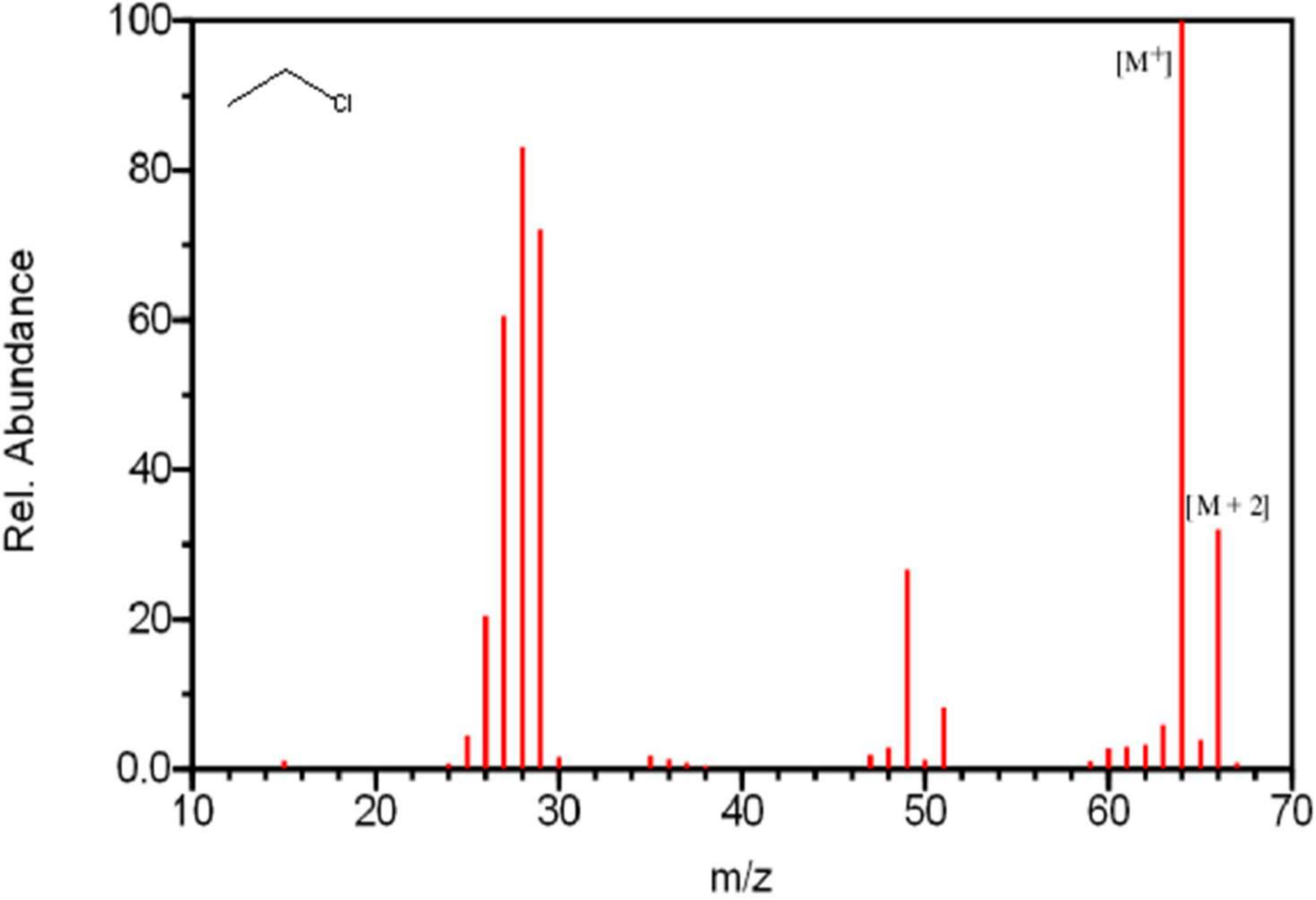


Isotope effects

Molecular weight
Cl = 35.453

Cl isotopic abundance
^{35}Cl = 75.4 %
^{37}Cl = 24.6 %
^{35}Cl : ^{37}Cl Ratio = 3:1

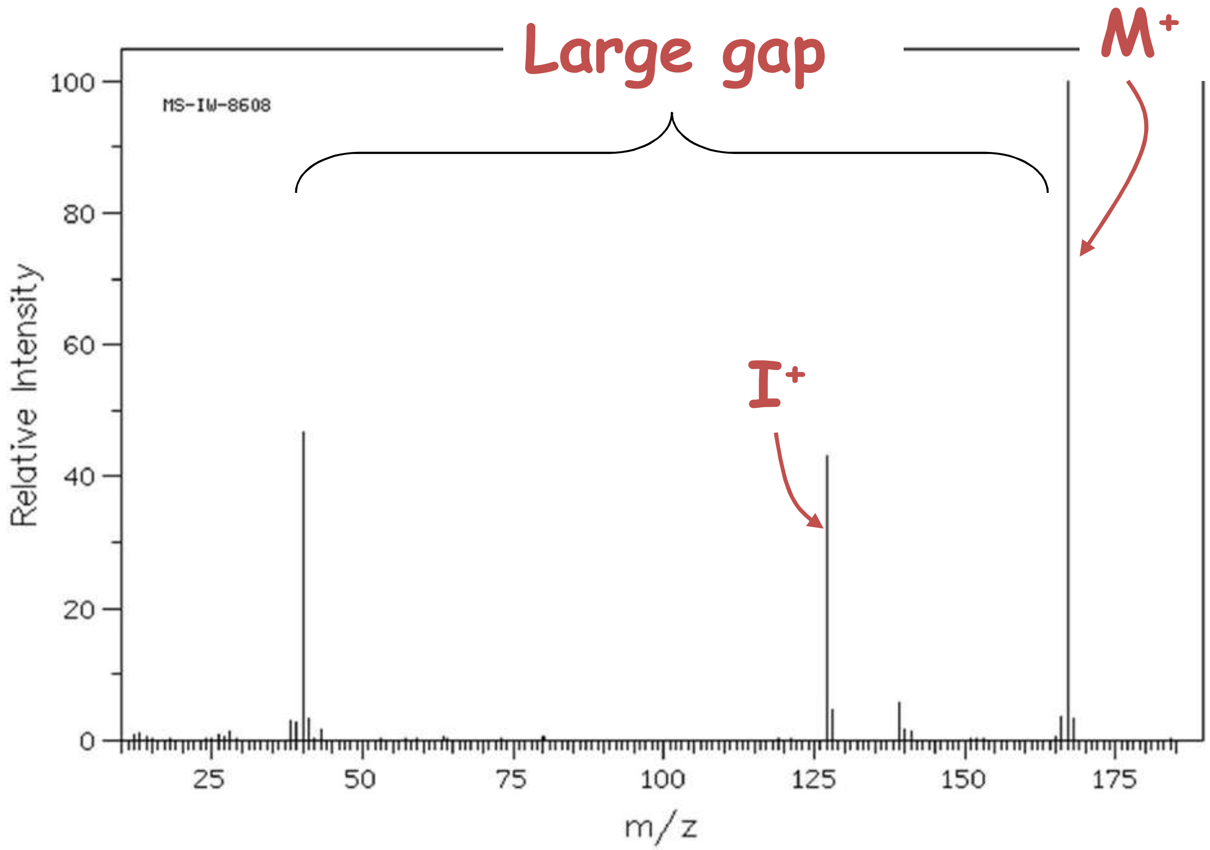


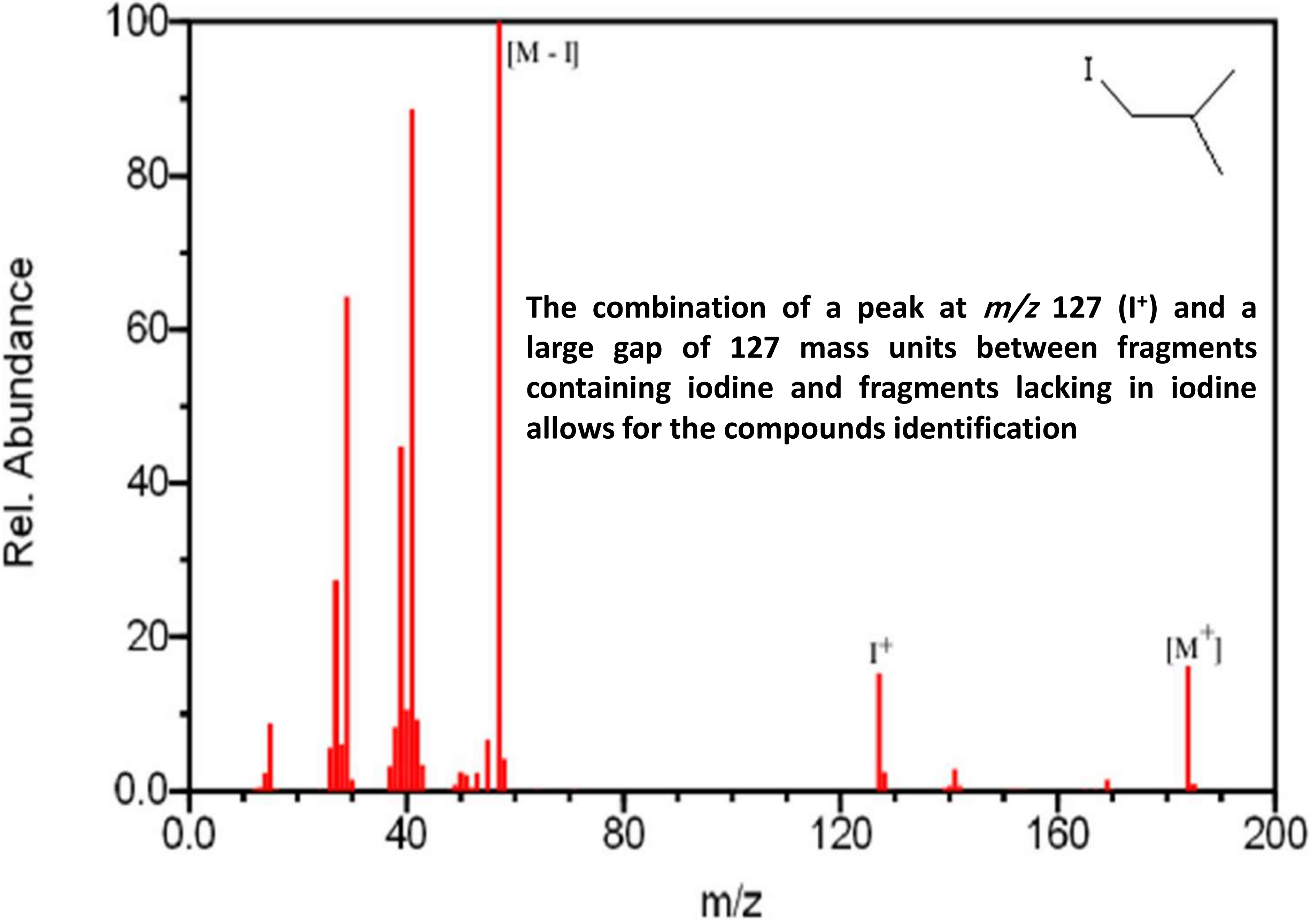

Cl
[M+]
[M + 2]
Rel. Abundance
100
80
60
40
20
0.0
10
20
30
40
50
60
70
m/z

Easily Recognized Elements in MS

- Iodine
  - I^+ at 127
  - Large gap

ICH_2CN

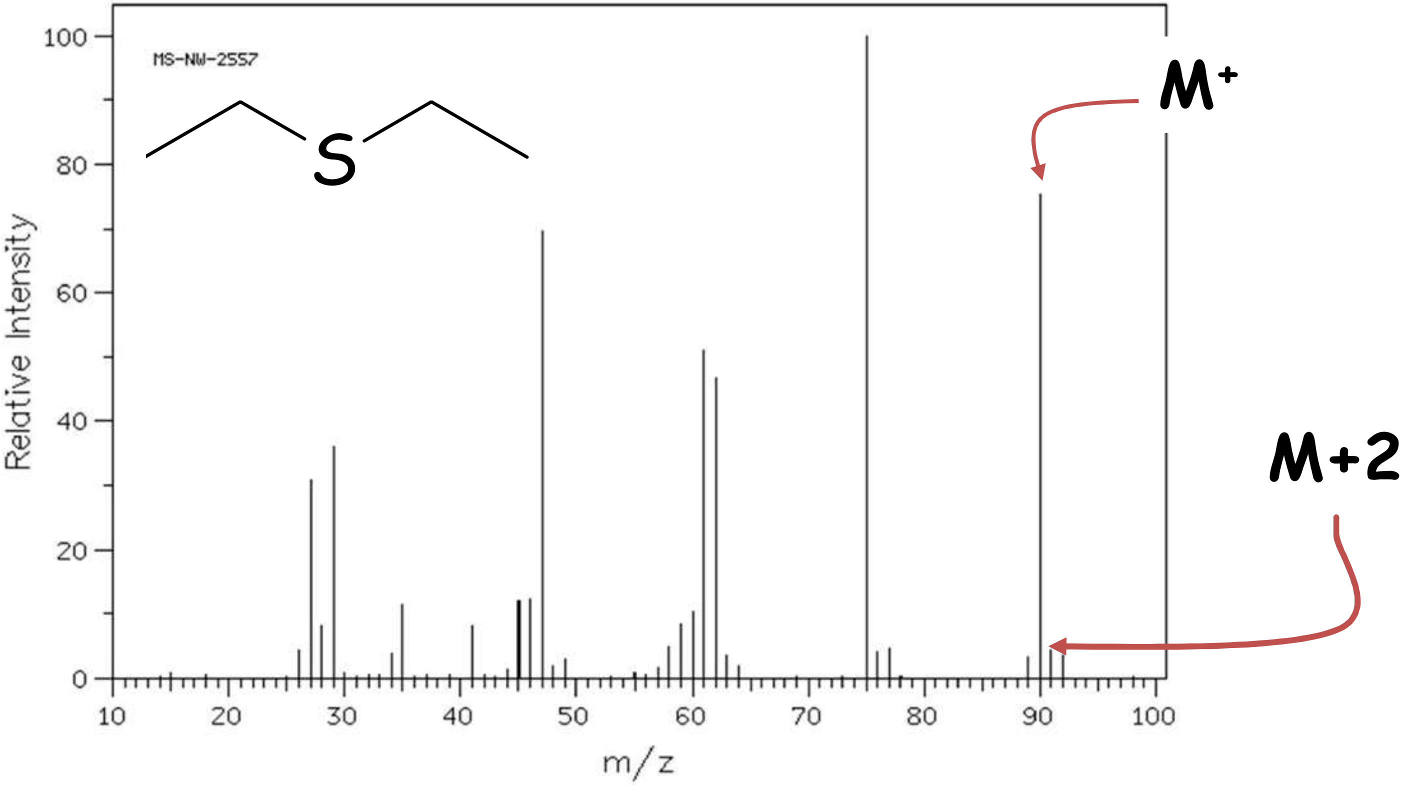




The combination of a peak at *m/z* 127 (I^+) and a large gap of 127 mass units between fragments containing iodine and fragments lacking in iodine allows for the compounds identification

Easily Recognized Elements in MS

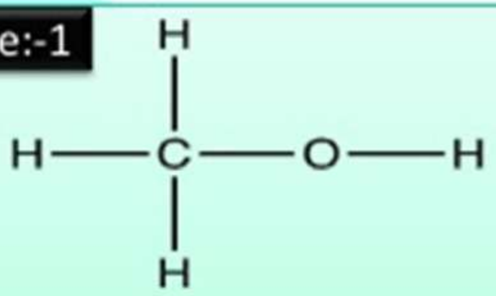
- **Sulfur:**
  - M+2



Nitrogen rule:-

The nitrogen rule states, that a molecule that has no or even number of nitrogen atoms has an even nominal mass, whereas a molecule that has an odd number of nitrogen atoms has an odd nominal mass.

Example:-1



CH_3OH

molecular formula = CH_4O

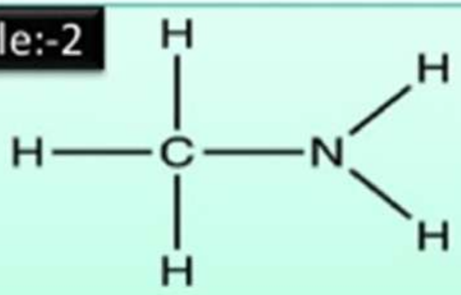
nominal mass = (1x12) + (4x1) + (1x16)

= 32 ←

N atoms = 0

nominal mass = 32 (even #)

Example:-2



CH_3NH_2

molecular formula = CH_5N

nominal mass = (1x12) + (5x1) + (1x14)

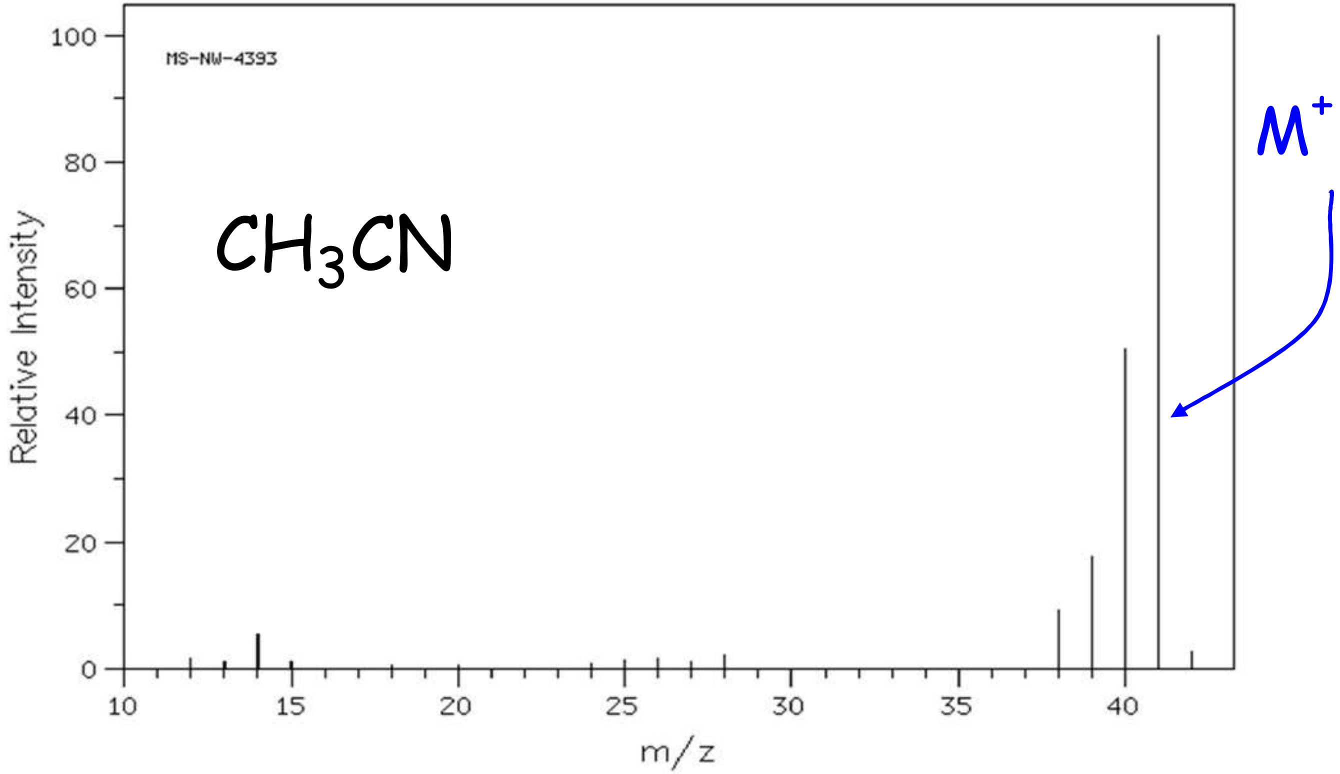
= 31 ←

N atoms = 1 (odd #)

nominal mass = 31 (odd #)

Easily Recognized Elements in MS

- **Nitrogen rule**
  - Odd number of N = odd MW
  - Even or zero number of N = even MW

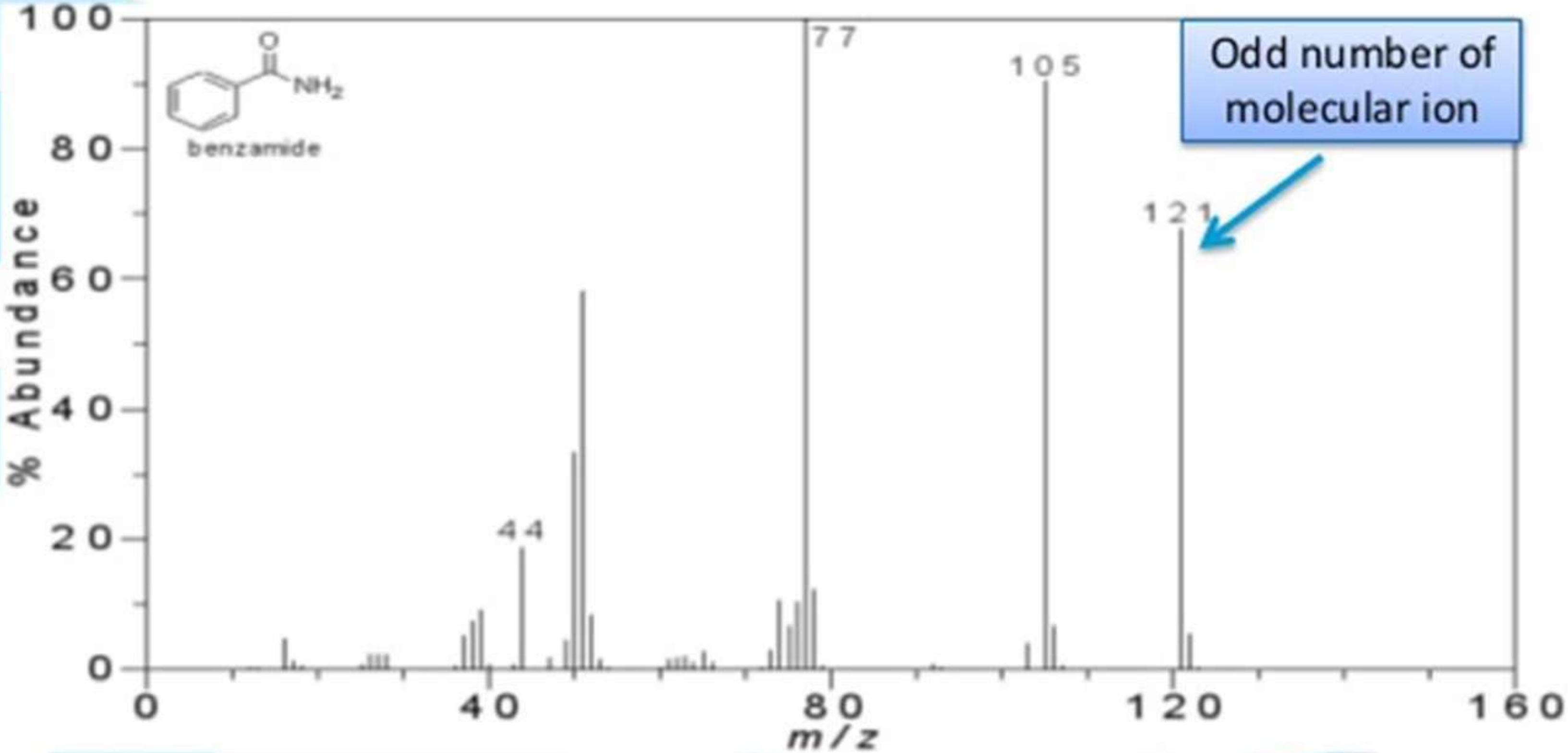


CH_3CN

$M^+ = 41$

Contd….

The molecular ion appears at m/z 121, indicating an odd number of nitrogen atoms in the structure.



Odd number of molecular ion