“MASS SPECTROMETRY”

1. Basic Concepts

2. Instrumentation

3. Spectral Analysis

4. Fragmentation Patterns

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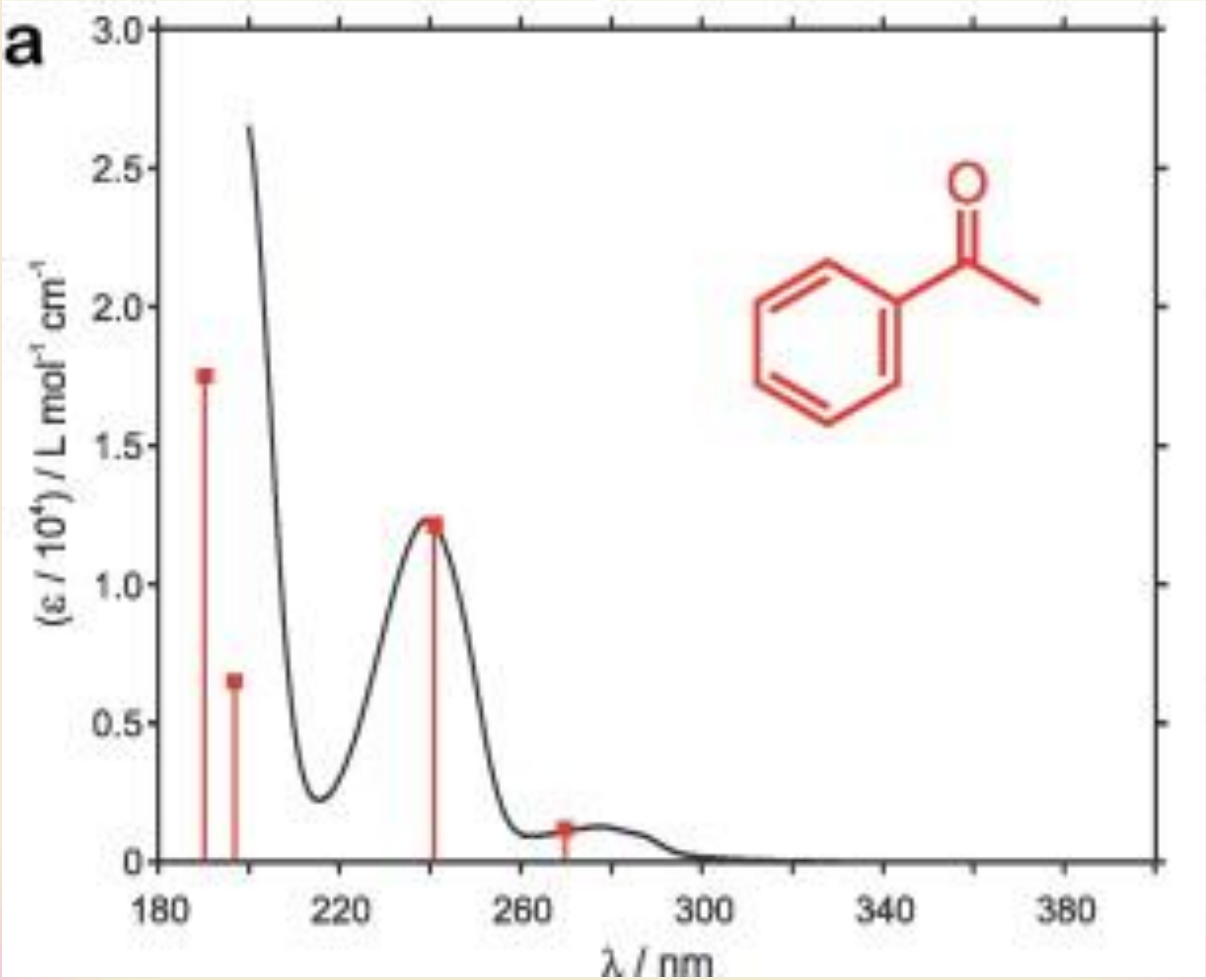
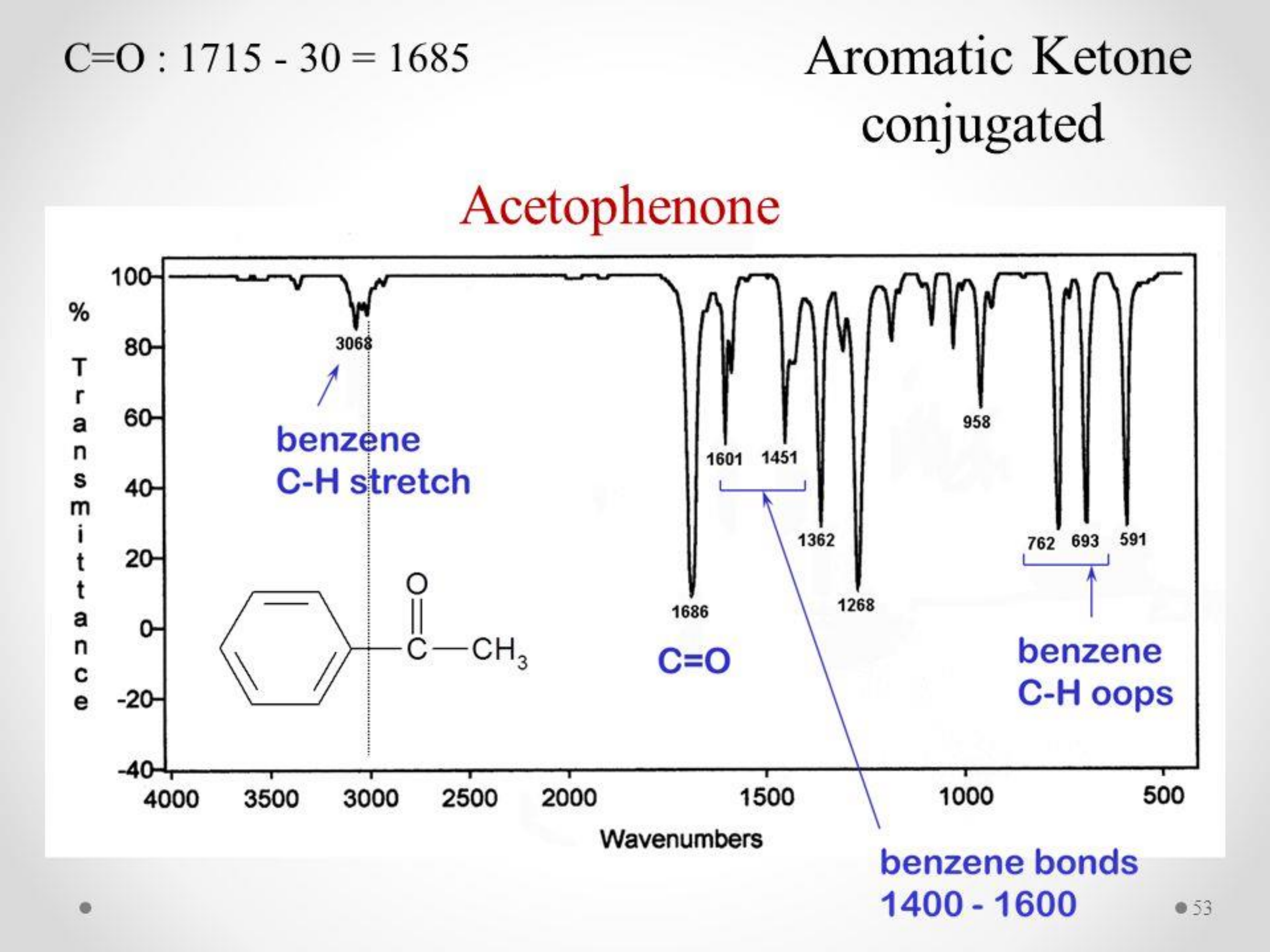
Spectroscopy and Spectrum

1. UV-vis. Spectroscopy
2. IR Spectroscopy
3. NMR Spectroscopy
4. Mass **Spectrometry**

UV-Vis. Spectrum of Acetophenone



IR Spectrum of Acetophenone



C=O : 1715 - 30 = 1685

Aromatic Ketone
conjugated

Acetophenone

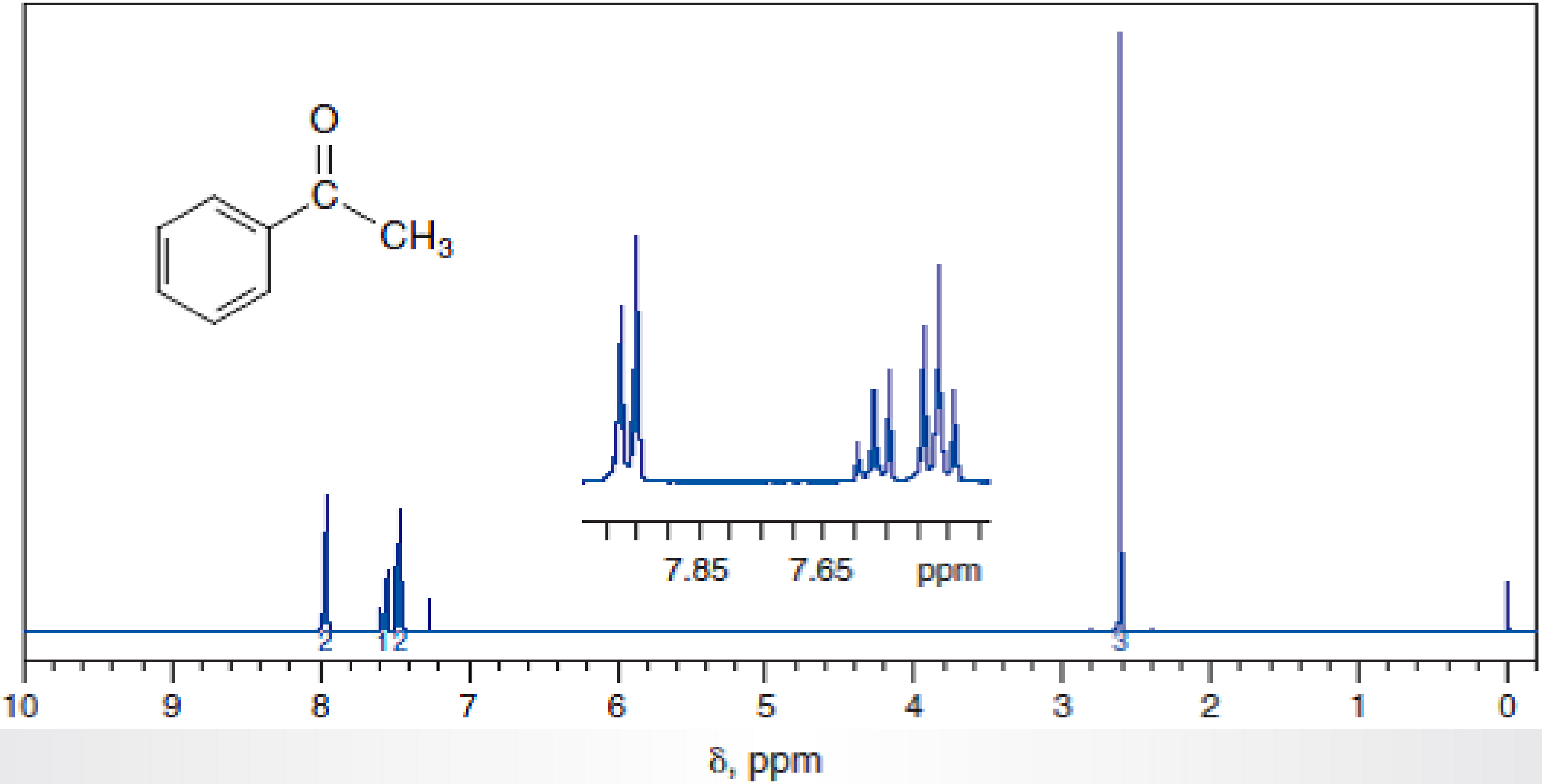
benzene
C-H stretch

C=O

benzene
C-H oops

benzene bonds
1400 - 1600

PMR (^{1}H-NMR) Spectrum of Acetophenone



Mass Spectrum of Acetophenone

?

SYLLABUS: Outline of MS

1. Basic concepts: Principle of MS
2. Instrumentation (Mass Spectrometer)
3. Types of Ions in MS
4. Types of Peaks
5. Applications: (Determination of Mol wt. & formula)
6. Fragmentation Patters of some organic compounds:
    1. Alkanes and alkenes
    2. Alcohols and phenols
    3. Amines
    4. Carbonyl compounds (aldehydes, ketones, esters and amides)

Basic Principle…

……

The basic principle of MS is……….

1. **Ionization**: **To generate ions from organic compounds by any suitable method.**
2. **Separation**: **To separate these ions by their m/z value (ratio) &**
3. **Detection**: **To detect them qualitatively and by their respective m/z value**

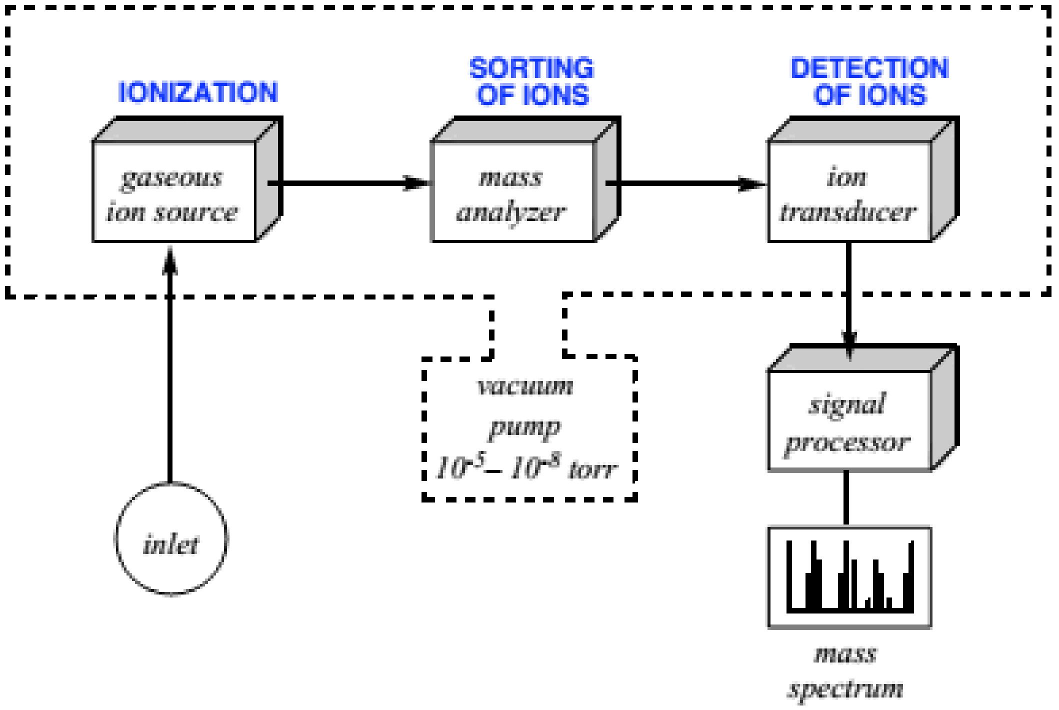
Instrument

A mass spectrometer is an instrument that …

……

produces ions, separates and detects them according to their mass-to-charge ratio (m/z).

- Instrumentation



Ionization sources

Chemical Ionisation (CI)
Atmospheric Pressure CI (APCI)
Electron Impact (EI)
Electrospray Ionization (ESI)
Fast Atom Bombardment (FAB)
Field Desorption/Field Ionisation (FD/FI)
Matrix Assisted Laser Desorption Ionisation (MALDI)
Thermospray Ionisation (TI)

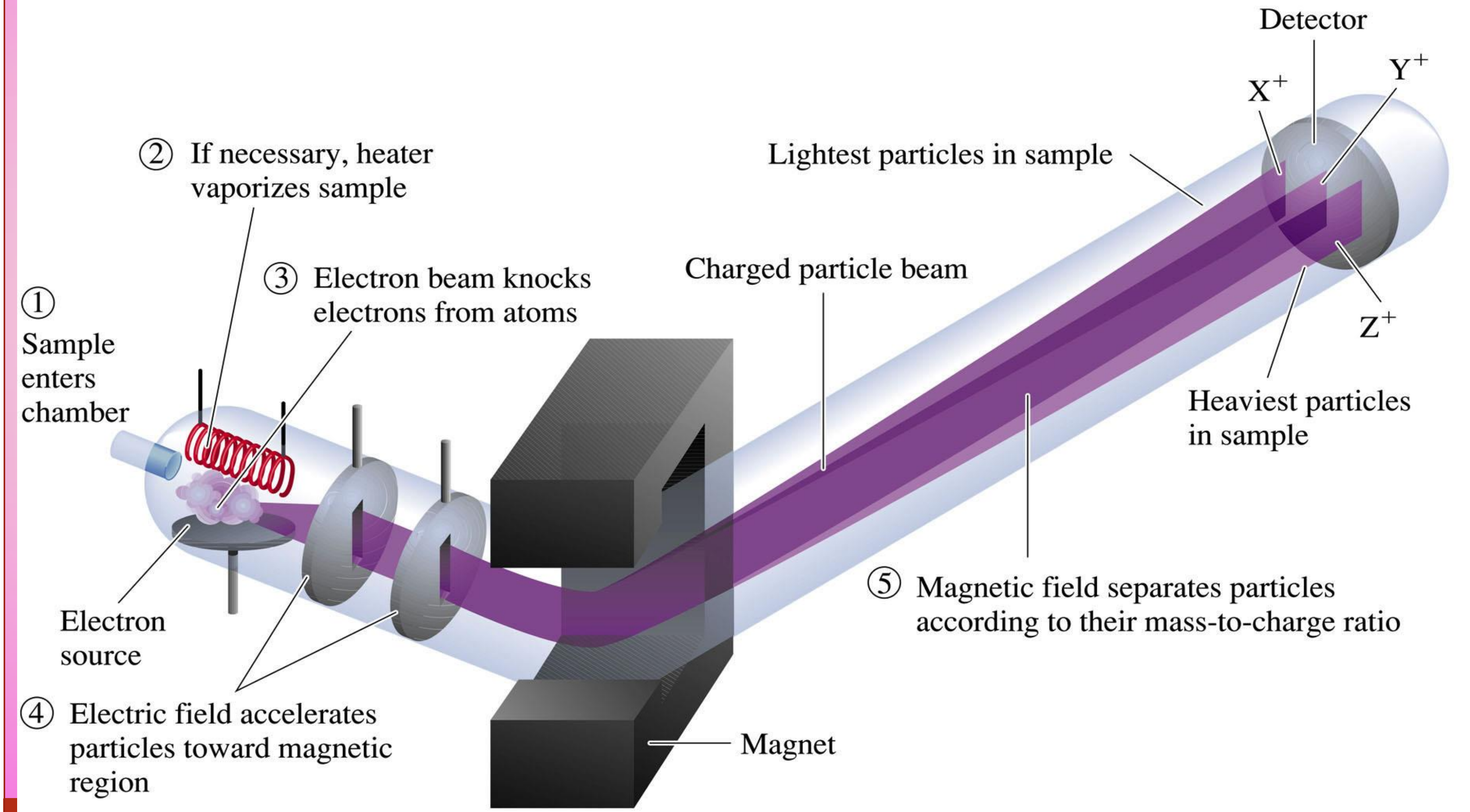
Analyzers

quadrupoles
Time-of-Flight (TOF)
magnetic sectors
Fourier transform and quadrupole ion traps

Detectors

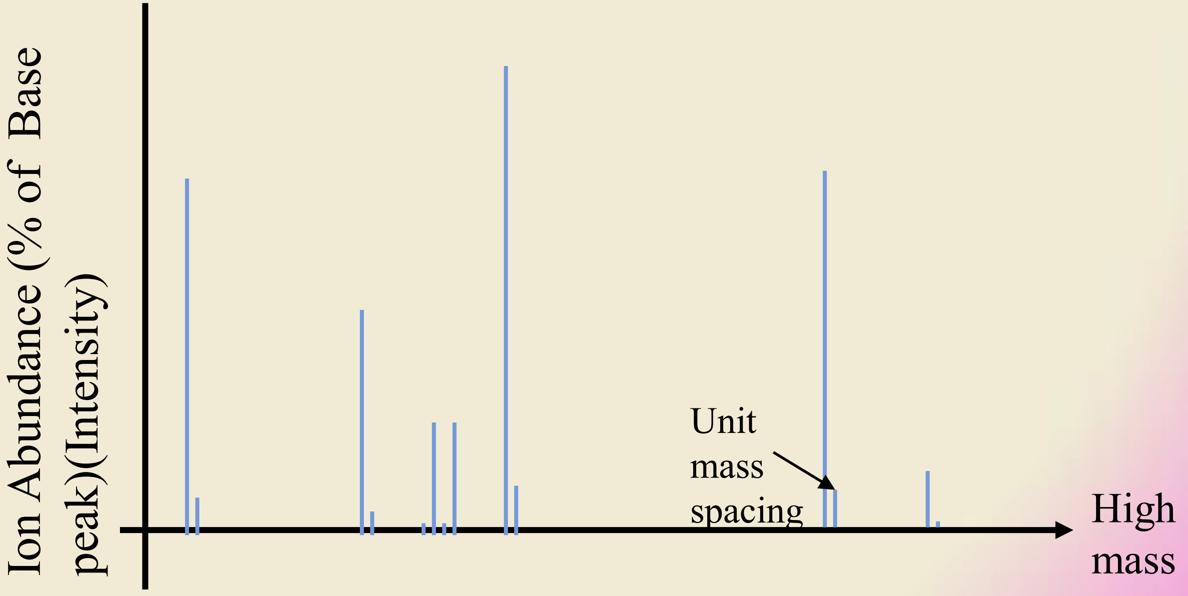
electron multiplier
Faraday cup

Instrument


Detector
X+
Y+
② If necessary, heater vaporizes sample
Lightest particles in sample
① Sample enters chamber
③ Electron beam knocks electrons from atoms
Charged particle beam
Z+
Heaviest particles in sample
Electron source
⑤ Magnetic field separates particles according to their mass-to-charge ratio
④ Electric field accelerates particles toward magnetic region
Magnet

Mass Spectrum

- Characterized by **sharp, narrow peaks**
- **X-axis:** position indicates the **m/z ratio** of a given ion.
- **Y-axis**: Height of peak indicates the **relative abundance (intensity)** of a given ion.
- **Peak intensity** indicates the **ion's stability**: ability to desorb and "fly" (some fly better than others).



Different Types of MS

- **ESI-QTOF:** Electrospray ionization source + quadrupole mass filter + time-of-flight mass analyzer
- **MALDI-QTOF:** Matrix-assisted laser desorption ionization + quadrupole + time-of-flight mass analyzer
- **GC-MS:** separates volatile compounds in gas column and ID's by mass
- **LC-MS:** separates delicate compounds in HPLC column and ID's by mass
- **MS-MS-Tandem Mass Spectrometry:** separates compound fragments by magnetic field and ID's by mass

Different Mass Analyzers

- **Magnetic Sector Analyzer** (MSA): High resolution, exact mass, original MA
- **Quadrupole Analyzer** (Q): Low (1 amu) resolution, fast, cheap
- **Time-of-Flight Analyzer** (TOF): No upper m/z limit, high throughput
- **Ion Trap Mass Analyzer** (QSTAR): Good resolution, all-in-one mass analyzer
- **Ion Cyclotron Resonance** (FT-ICR): Highest resolution, exact mass, costly

Different Ionization Methods

I. Hard methods:

1. **Electron Impact** (EI): Small molecules, 1-1000 Daltons, Structure determination.

II. Soft methods:

- **Chemical Ionization** (CI-Soft)
- **Electrospray Ionization** (ESI - Soft): peptides, proteins, up to 200,000 Daltons
- **Matrix Assisted Laser Desorption** (MALDI-Soft): peptides, proteins, DNA, up to 500 kD
- **Fast Atom Bombardment** (FAB – Semi-hard): peptides, sugars, up to 6000 Daltons.

Types of Ions and Peaks in MS

1. Molecular ions:
2. Isotope ions ([M+1] & [M+2]):
3. Metastable ions:
4. Rearrangement ions (McLafferty):
5. Fragment ions:
6. Multiply-charged ions:
7. Adduct ions:
8. Negative ions:
9. Radical ions:
10. Cluster ions:
11. Even-electron ions:
12. Daughter ions:

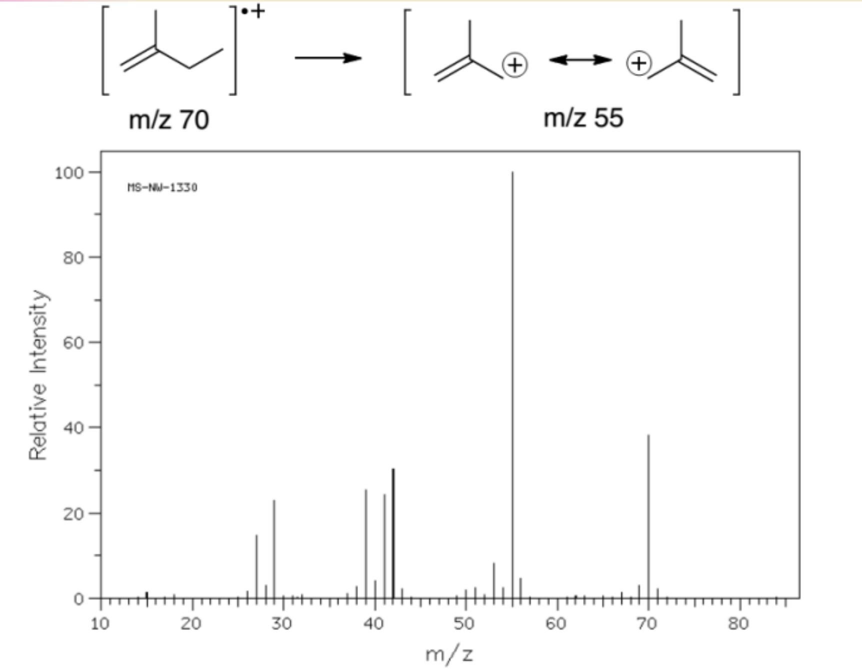
Base Peak ……………………….peak in MS with **Maximum intensity…………….**

1. Molecular ion

An ion formed by the removal of one/more electron from a molecule without fragmentation of the molecular structure.

Also called ……………….parent ion/radical cation/odd electron cation

$M + e^- \text{-----}> M^+ + 2e^-$ where M^+ = molecular ion



1.It represent the intact molecule with one electron less than molecule.

2. Its elemental composition and mass (m/z) is same as starting molecule.

3. Its m/z value gives the molecular wt. of compound that helps to find the molecular formula.

1. Molecular ion

Formation of Molecular ion:

1. **σ-bond cleavage:**

2. **π-bond cleavage:**

3. **Removal of n electron:**

Order of electron removal: σ <π<n

2. Isotope ion

Isotopes: Same number of Protons and Electrons, but a different number of Neutrons

Mono-isotopic elements: Only one naturally occurring stable isotope.

^{19}F, ^{31}P, ^{127}I

2. Isotope ion

Di-isotopic elements: Only two naturally occurring stable isotopes.

1. (X+1) elements: They are 1 amu heavier than the most abundant isotope.

- [^{1}H (99.98 %) & ^{2}H(0.01%)]
- [^{12}C (98.98 %), ^{13}C (1.1 %)]

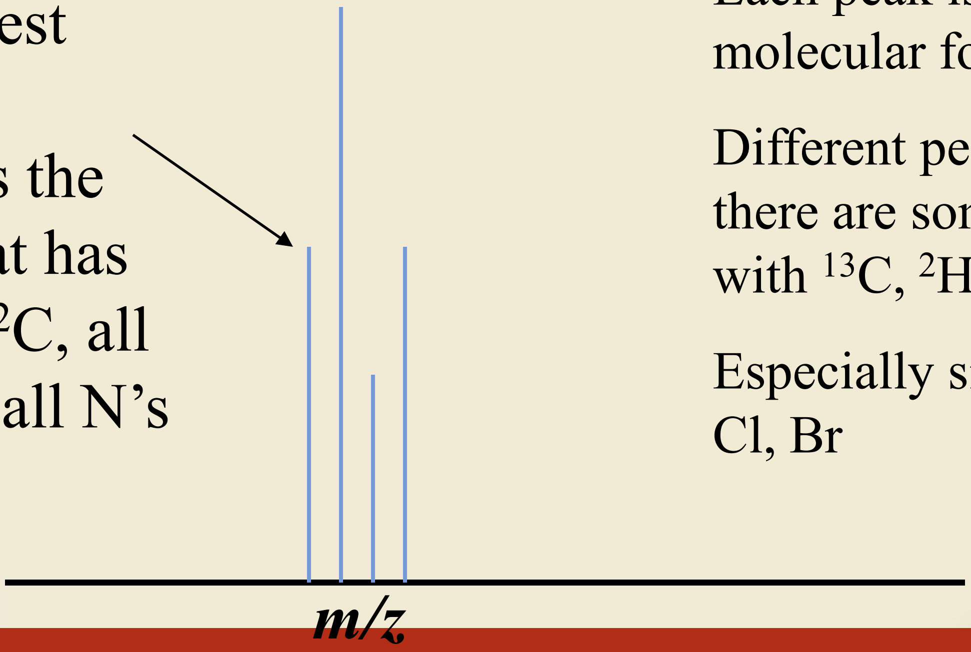
2. (X+2) elements: They are 2 amu heavier than the most abundant isotope.

- [^{35}Cl (75.8 %) & ^{37}Cl (24.2%)]
- [^{79}Br (50.5 %) & ^{80}Br (49.5 %)]

2. Isotope ion

The presence of a small peaks at high mass values than the M+. peak in MS of organic compounds are called isotopic peaks.

The *Nominal* mass is m/z of the lowest member of the cluster. This is the ***isotopomer*** that has all the C's as ^{12}C, all protons as ^{1}H, all N's as ^{14}N, etc.



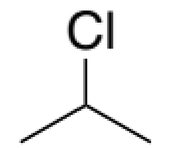
Spaced by unit mass

Each peak is for the same molecular formula

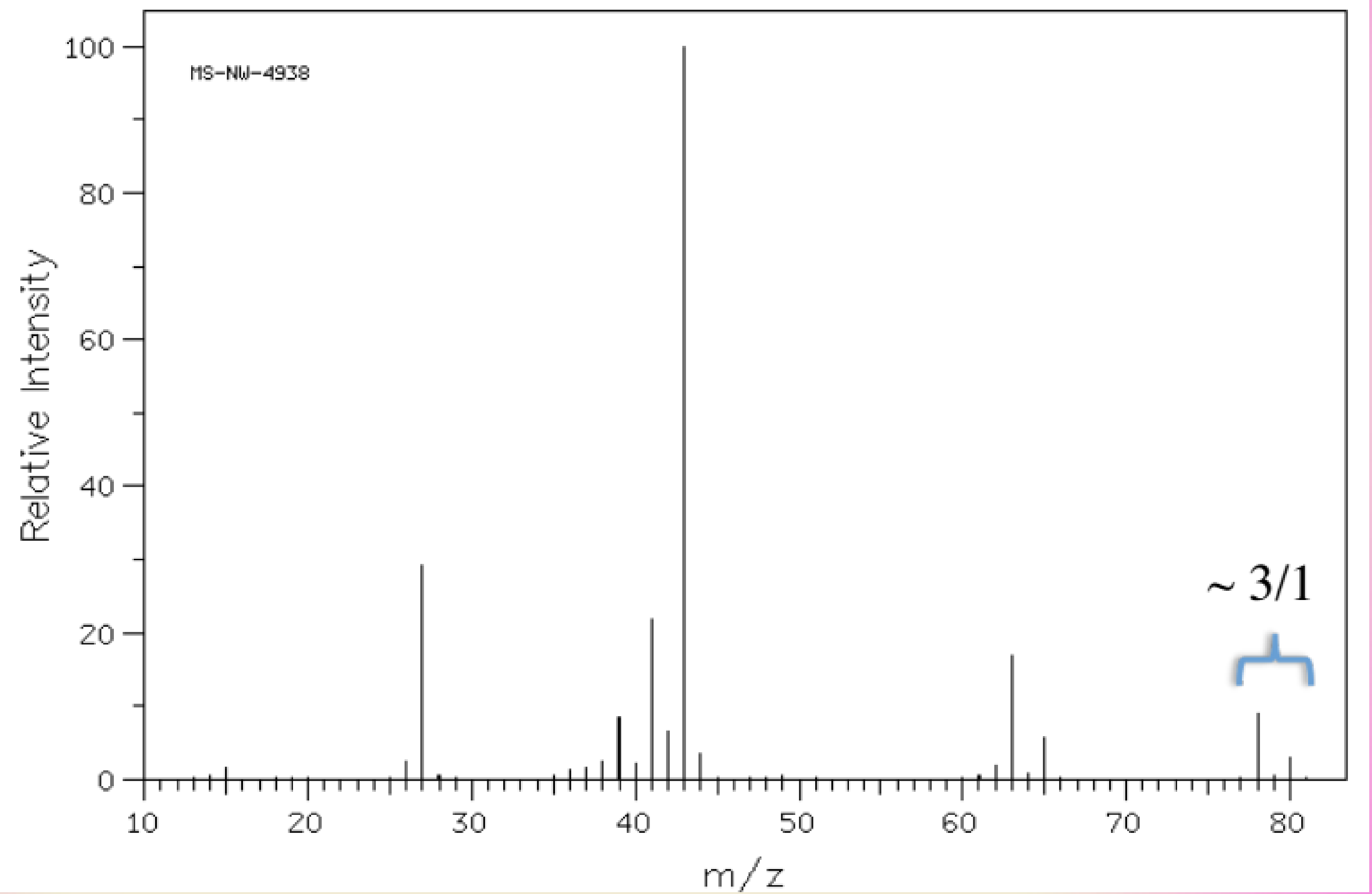
Different peaks because there are some molecules with ^{13}C, ^{2}H etc.

Especially significant for Cl, Br

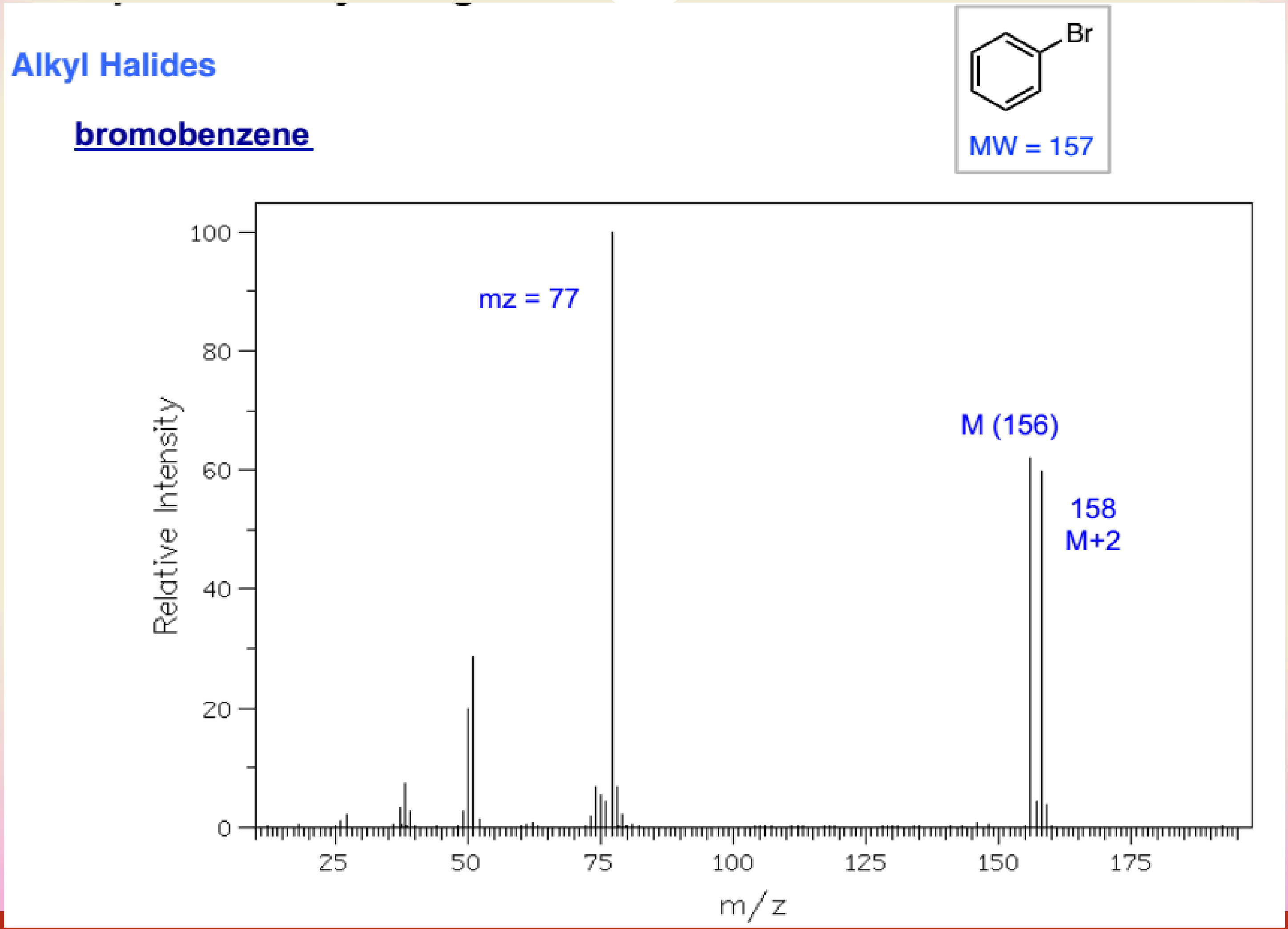
2. Isotope ion peak of Cl



m/z 78
M/M+2 = 3



2. Isotope ion peak of Br



Alkyl Halides

bromobenzene

MW = 157

3. Metastable ions

The term metastable is applied to **those ions in a MS, that have just sufficient energy to fragment sometime after leaving the ion source, but before arriving the detector**.

Or

The ions resulting from decomposition between the ion source and magnetic analyzer are called metastable ions.

3. Metastable ions

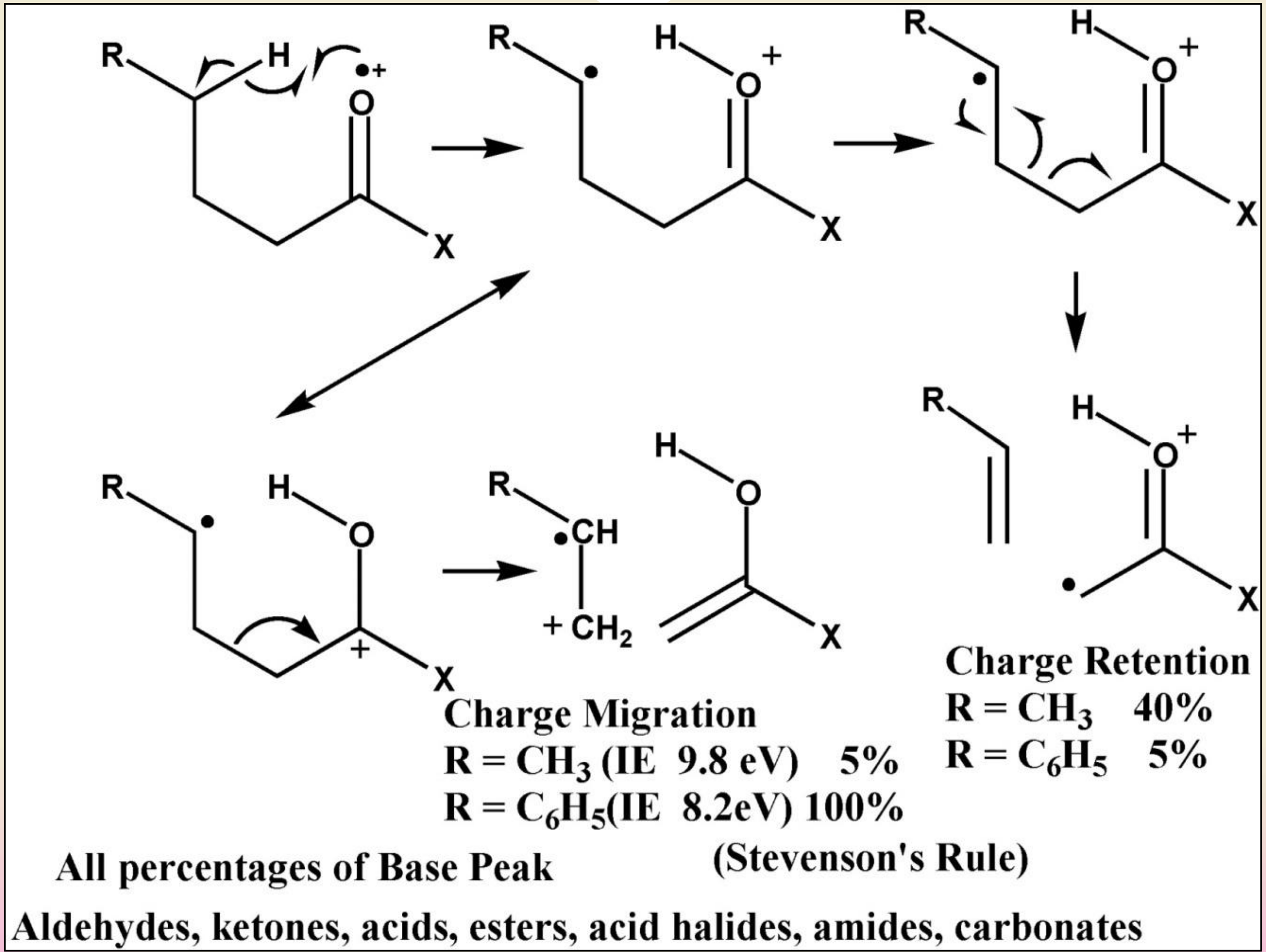
These are **appear as <u>broad & low intensity peaks</u>** at **<u>non-integral mass numbers</u>** in MS and called metastable ion peaks.

Case I: If $m_1^+ \rightarrow m_2^+$ takes place in the ion source, then the m_2^+ may travel the whole analyzer region and recorded as m_2^+ ion.

Case II: If $m_1^+ \rightarrow m_2^+$ takes place after ion source but before the collector, then the m_2^+ is called as m* ion (metastable).

$$\text{Metastable ion peak} = m^* = (m_2^+)^2 / m_1^+$$

4. McLafferty rearrangement ions



Charge Migration
$R = CH_3$ (IE 9.8 eV) 5%
$R = C_6H_5$(IE 8.2eV) 100%

Charge Retention
$R = CH_3$ 40%
$R = C_6H_5$ 5%

All percentages of Base Peak

(Stevenson's Rule)

Aldehydes, ketones, acids, esters, acid halides, amides, carbonates

5. Fragment ions

These are electrically charged dissociated fragments derived from analyte molecules by cleavage of one/more bonds M+ having m/z less than M+.

6. Multi-charged ions

These are the ions that have gained/lost more than one electrons.

Example:

Doubly charged ion: : 2 number of electrons lost/gained by atom/molecule and are recorded at ½ to that of m/z of M+.

Triply charged ion: : 3 number of electrons lost/gained by atom/molecule and are recorded at 3 to that of m/z of M+.

6. Multi-charged ions

These are the ions that have gained/lost more than one electrons.

Example:
Singly, doubly, triply charged ions: number of electrons lost/gained by atom/molecule.
Doubly charged ion: They are recorded at ½ to that of m/z of M+.

Triply charged ion: They are recorded at 3 to that of m/z of M+.

7. Adduct ions

These are the ions are formed by interaction of two species (usually ions and molecules) in ion source.

Example:

CH5+ (CH4+H+)

8. Radical ions:

These are the ions containing (anion/cation) containing unpaired electrons as it contain ion + radical.

Example:

CH4+.

9. Negative ions

These are the ions formed by taking one/more electrons.

Example:
OH-, CCl4-

10. Even-electron ions:

These are the ions containing no unpaired electrons.

Example:
CH3+, C2H5+

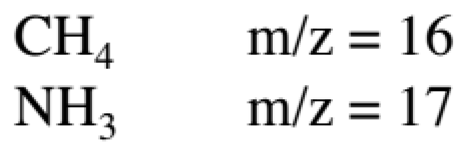
Nitrogen Rule

Nitrogen is also diagnostic in a mass spectrum due to the odd/even parity of the mass.

If a compound has ....

1. **Zero/Even number of N-atoms, its molecular ion will have an even m/z value.**

2. **Odd number of N-atoms, its molecular ion will have an odd m/z value.**



CH_4 m/z = 16

NH_3 m/z = 17

Applications of MS

It is **interdisciplinary** and versatile **analytical** method used for the

1. **characterization of molecules** ranging from **small inorganic** and **organic** molecules to **polymers and proteins**.
2. With MS we might be able to determine;
    1. **Molecular weight & formula of a molecule**
    2. **Elemental composition of a molecule**
    3. The presence of certain **functional groups**
3. Mechanistic studies of **gas-phase (ion) chemistry**: for a better understanding of the chemistry of atmosphere and in space.
4. As a **mass detector** coupled to a GC, HPLC, capillary electrophoresis (CE), and used for **qualitative and quantitative analysis of composition of complex mixtures**.
5. The structures of inorganic, organic, and biological molecules
6. The structure and composition of solid surfaces
7. **The isotopic ratios of atoms in samples**.
8. Data easier to interpret than IR and/or NMR (accurate structural analysis).

Fragmentation Pattern Guidelines

Fragmentation Reactions of $M^{+\cdot}$

The **terminology** and the **symbolism** suggested by **McLafferty** are used here as they have become universal.

Moreover, the name McLafferty is associated with a rearrangement that we will discuss later.

There are **three main classes of fragmentation** of radical cations in EIMS:

❶ **Simple cleavages**
❷ **Rearrangements**
❸ **Elimination of neutral molecules**

Fragmentation Reactions of $M^{+\cdot}$

❶Homolytic bond cleavage:

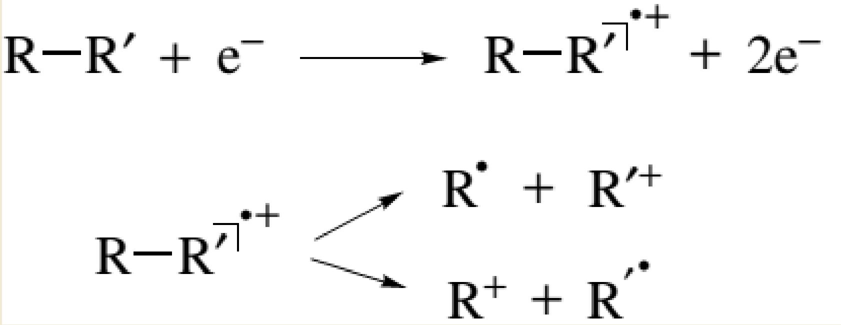
❷Hoterolytic bond cleavage:

1. **Direct σ-bond dissociation (Stevenson's rule):**
2. **Inductive Cleavage (bond adjacent to a heteroatom)**
3. **α-Clevage**
4. **β-Clevage**
5. **Benzyl- and allyl cleavage:**
6. **McLafferty rearrangement (γH abstraction with α- β bond cleavage):**
7. **Elimination (a) CO, (b) olefins, (c) acetylene, (d) water**

1. Direct Dissociation (σ): Stevenson’s rule

The **expulsion of an electron from a σ bond** can bring about the direct dissociation of $M^{+\cdot}$ also called ‘**σ fragmentations**’.

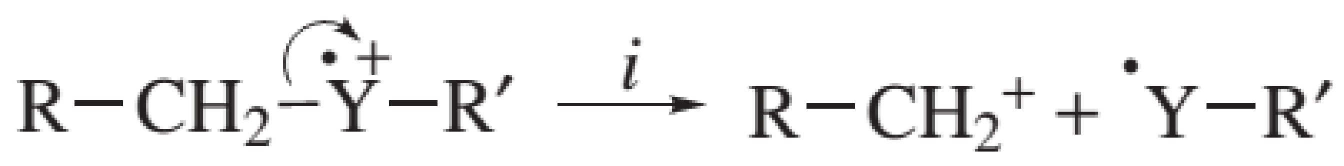
In this one of the fragments keeps the charge, while the other is a radical.



2. Inductive-Cleavage: adjacent to a heteroatom (i-Cleavage)

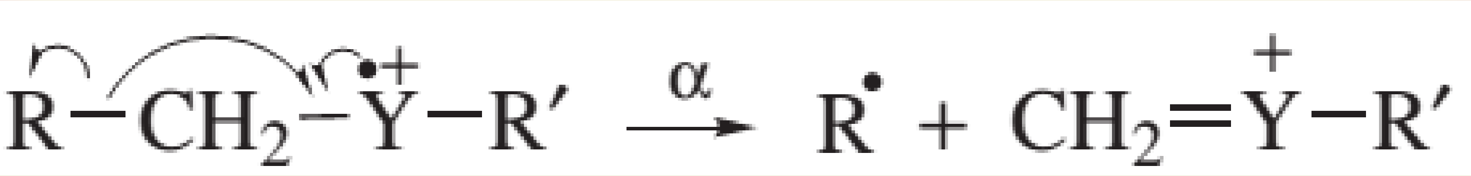
The bond adjacent to a heteroatom (O) can be broken by a **charge-site-initiated reaction**, that is by attraction of an electron pair from this bond called an **induced cleavage (i)**.

This is only happen in case of compounds containing O, S but not N.



$$R-CH_2-\overset{\bullet+}{Y}-R' \xrightarrow{i} R-CH_2^{+} + {}^{\bullet}Y-R'$$

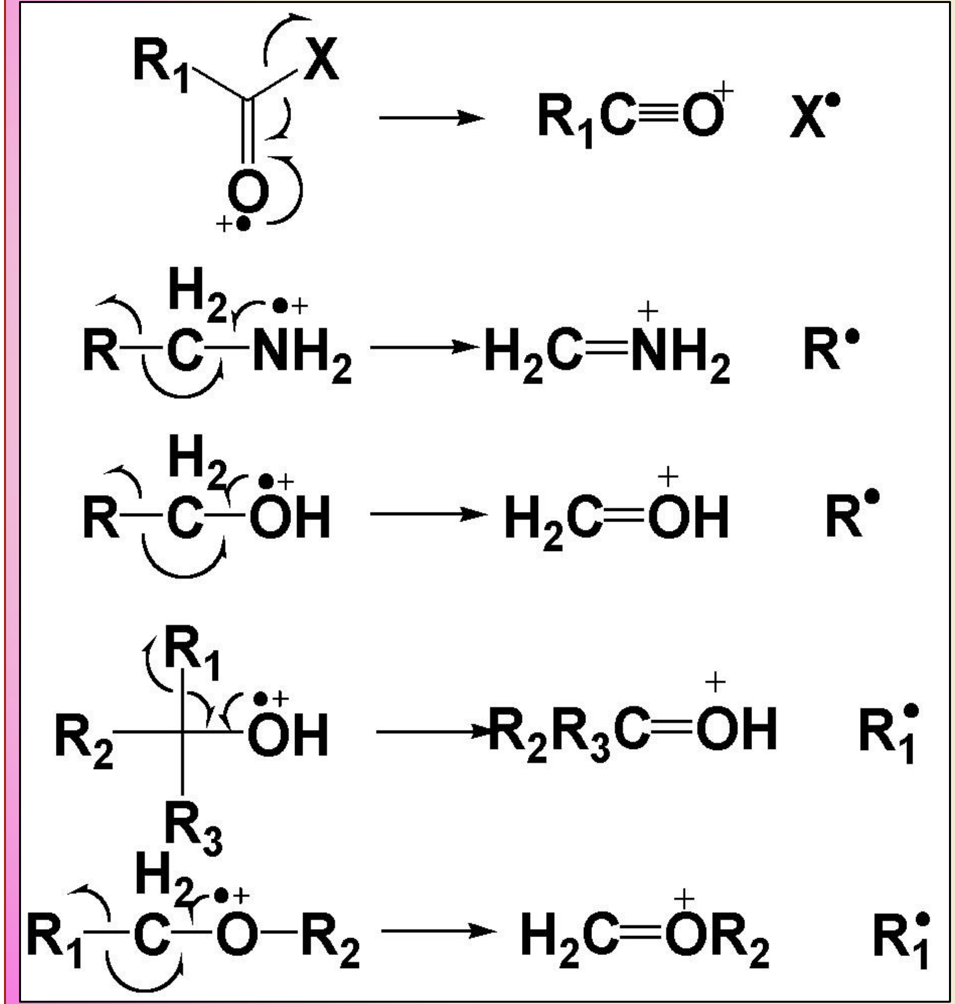
3. α-Cleavage :



$$R-CH_2-\overset{\bullet+}{Y}-R' \xrightarrow{\alpha} \dot{R} + CH_2=\overset{+}{Y}-R'$$

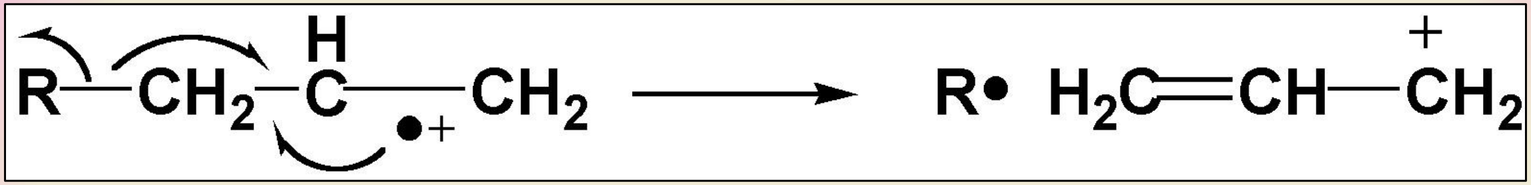
The **α-bond to the radical cation site** can be broken **by a radical-site-initiated reaction**, that is by a transfer of the unpaired electron to form a new bond to an adjacent atom (α atom) with concomitant cleavage of another bond of this atom.

3. α-Cleavage



- X = H, R, OH, OR, Cl, NH2 for aldehydes, ketones, acids, esters, acid halides and amides.
- m/z 30 is the base peak in primary amine spectra
- Primary alcohols give the m/z 31, ethers often give m/z 45, 59 . . by this reaction
- The ease of loss of alkyl groups is R1>R2>R3 where this is also the order of decreasing size.

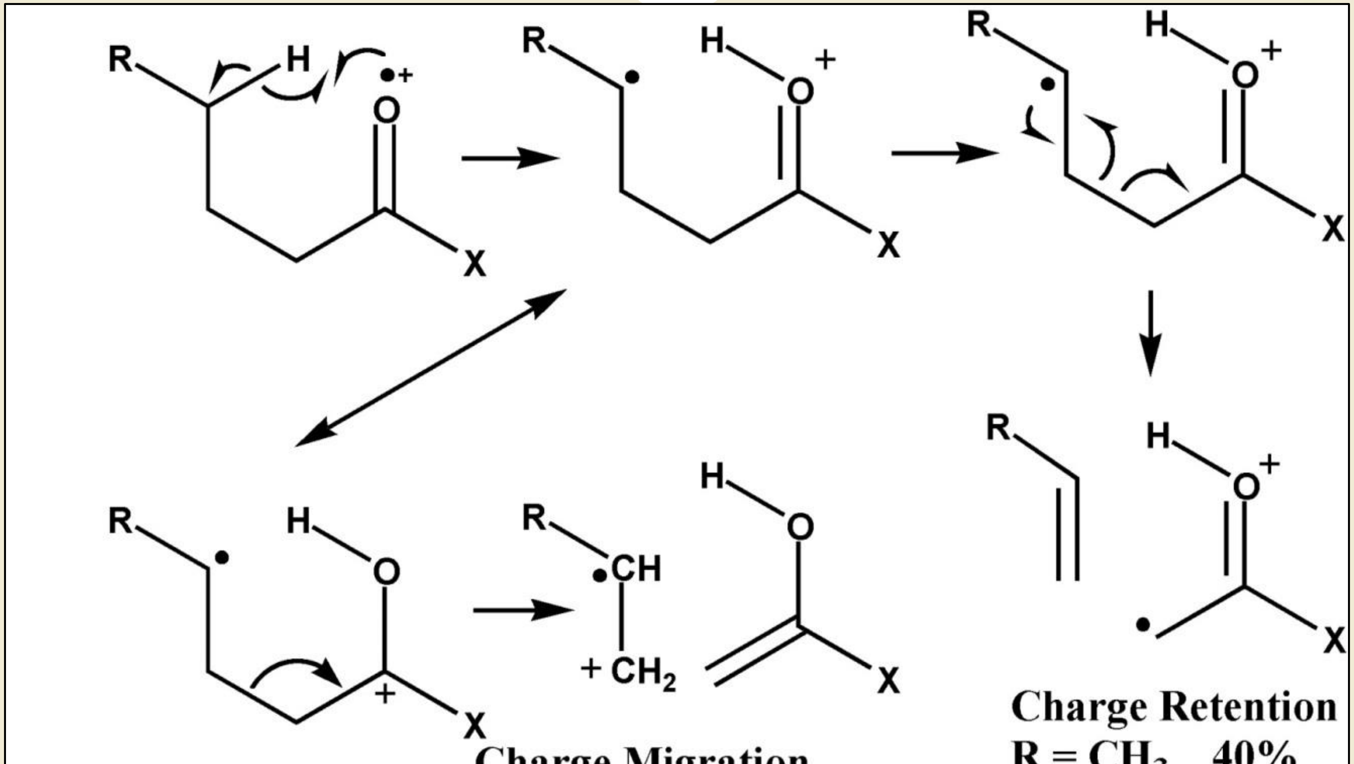
4. Allylic/benzylic cleavage



$$R-CH_2-\overset{H}{C}\underset{\bullet+}{-}CH_2 \longrightarrow R\bullet \;\; H_2C=CH-\overset{+}{C}H_2$$

- This is a **major type of fragmentation for alkenes leading to alkyl radical loss**.
- The **m/z 41** ion is the **most common ion** observed in the mass spectra of **aliphatic compounds**, together with homologues of m/z 55, 69, 83 . . .
- Unfortunately, migration of the double bond occurs before fragmentation so that the observation of ions of this type is of little structural value. The mass spectra of many alkenes, especially polyenes, tend to be independent of the position of the double bond so that isomers cannot be distinguished.

5. McLafferty rearrangement: γ-H rearrangement



Charge Migration

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$R = C_6H_5$(IE 8.2eV) 100%

Charge Retention

$R = CH_3$ 40%

$R = C_6H_5$ 5%

All percentages of Base Peak

(Stevenson's Rule)

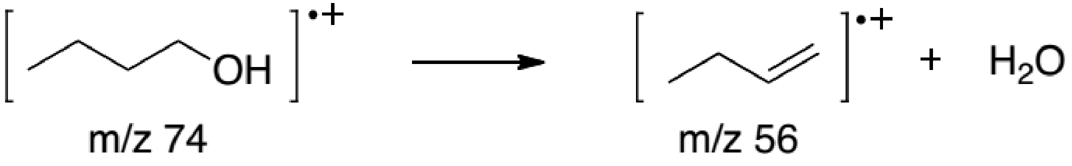
Aldehydes, ketones, acids, esters, acid halides, amides, carbonates

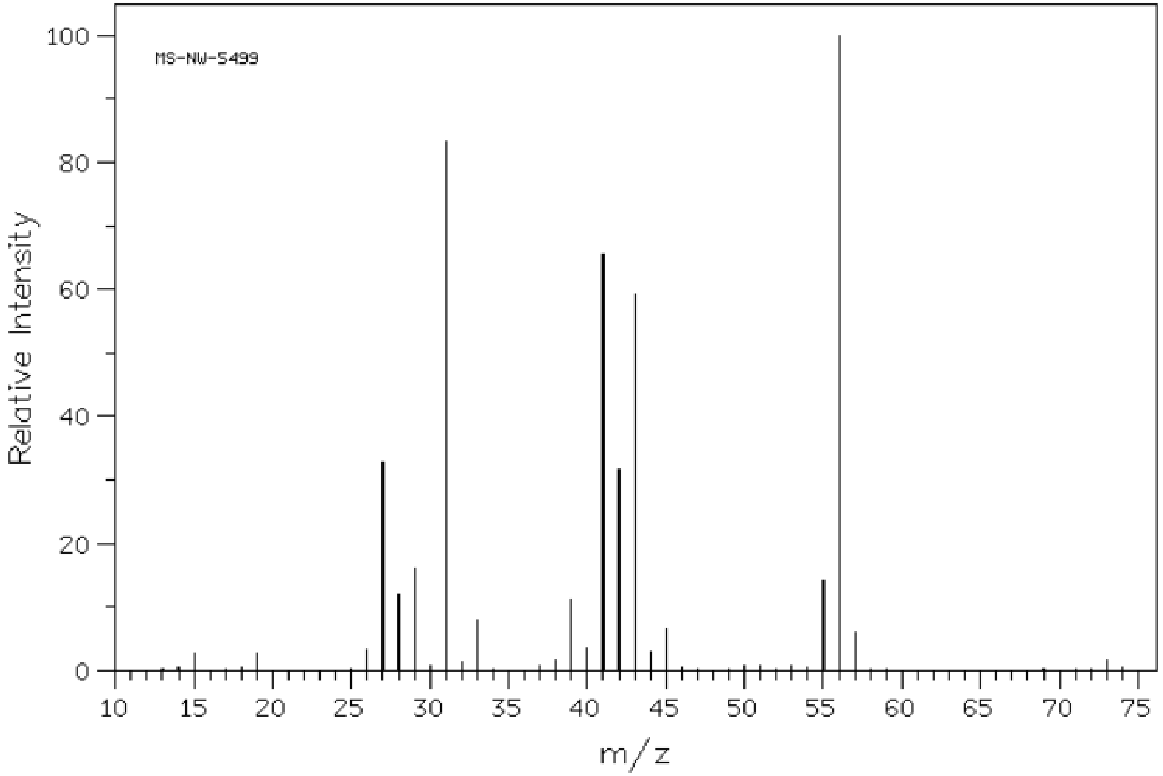
Characteristics of McLafferty

- **Deuterium labeling studies** show that a γ-H atom is transferred quite specifically through a **six-membered transition state**.
- If there are **no γ -H** atoms, the **rearrangement does not occur**.
- Note that substituents on the α-carbon atom are *retained* in the ion but substituents on the β- and γ-carbon atoms are *lost* as part of the alkene. This is useful in locating site of branching in an alkyl chain.
- If an *even* mass fragment ion is found which could be formed from the molecular ion by the **loss of 28, 42, 56, 70, . . . Da**., always suspect that it results from a McLafferty rearrangement.
- The driving force for the rearrangement is the formation of a strong bond between the H atom and the unsaturated heteroatom carrying the charge. Similar reactions occur with H-transfer to other heteroatoms.

6. Elimination of molecule
6a. Elimination of H_2O

1. Loss of H_2O: In pri. Alcohols

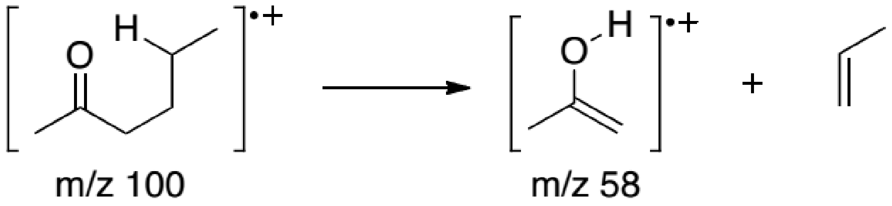


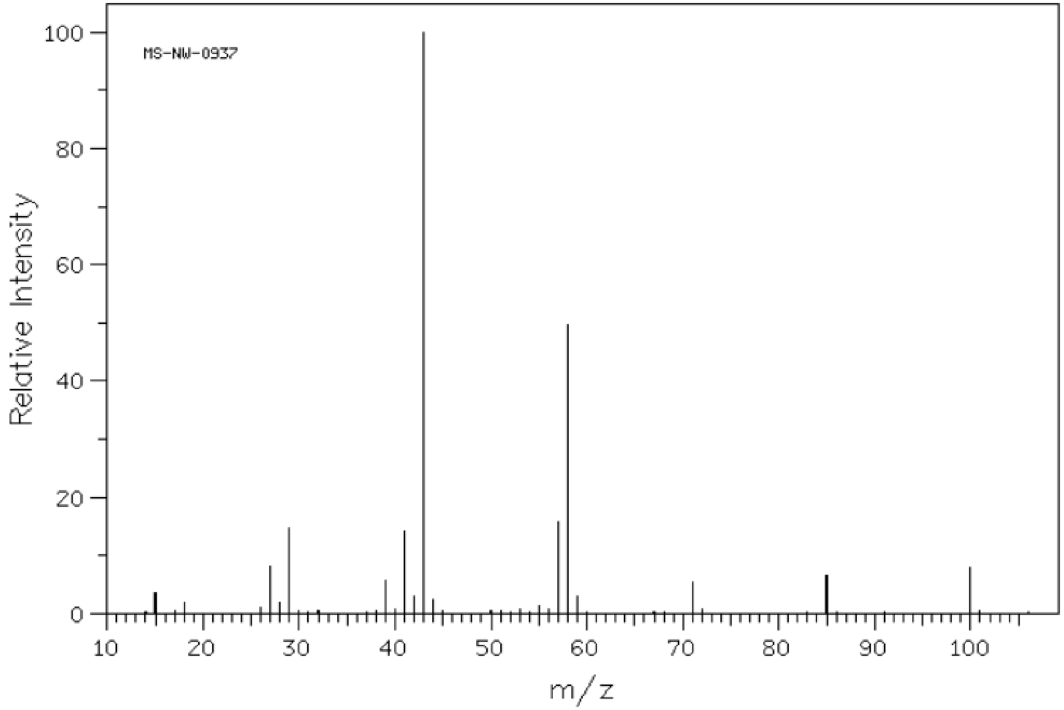


6b. Elimination of olefin

2. Loss of olefins McLafferty In compounds containing γ-H

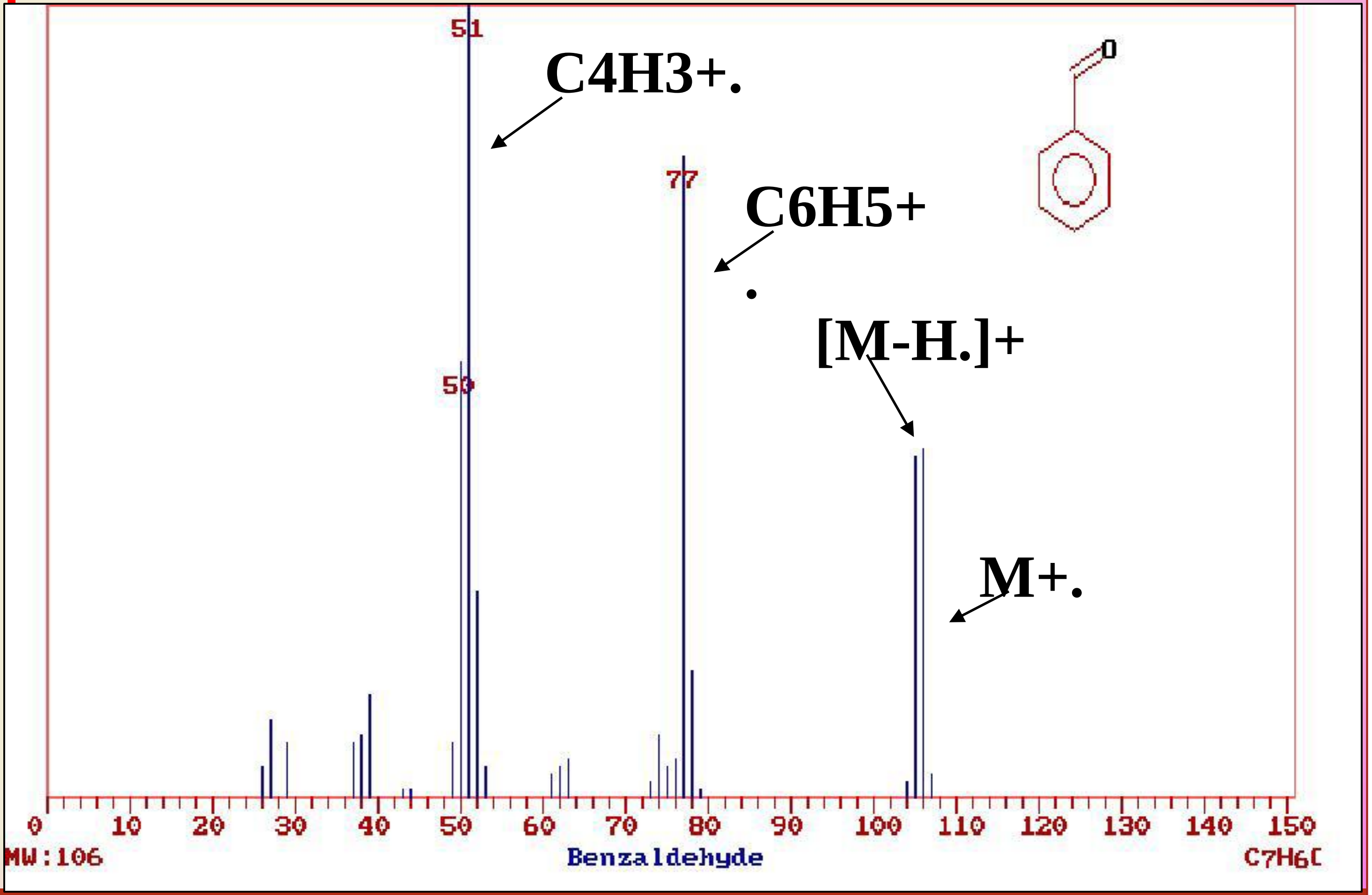
Any ketone containing a γ-hydrogen can rearrange to the enol form in a MS





6c. Elimination CO

3. Loss of CO:
In carbonyls



$C4H3+.$

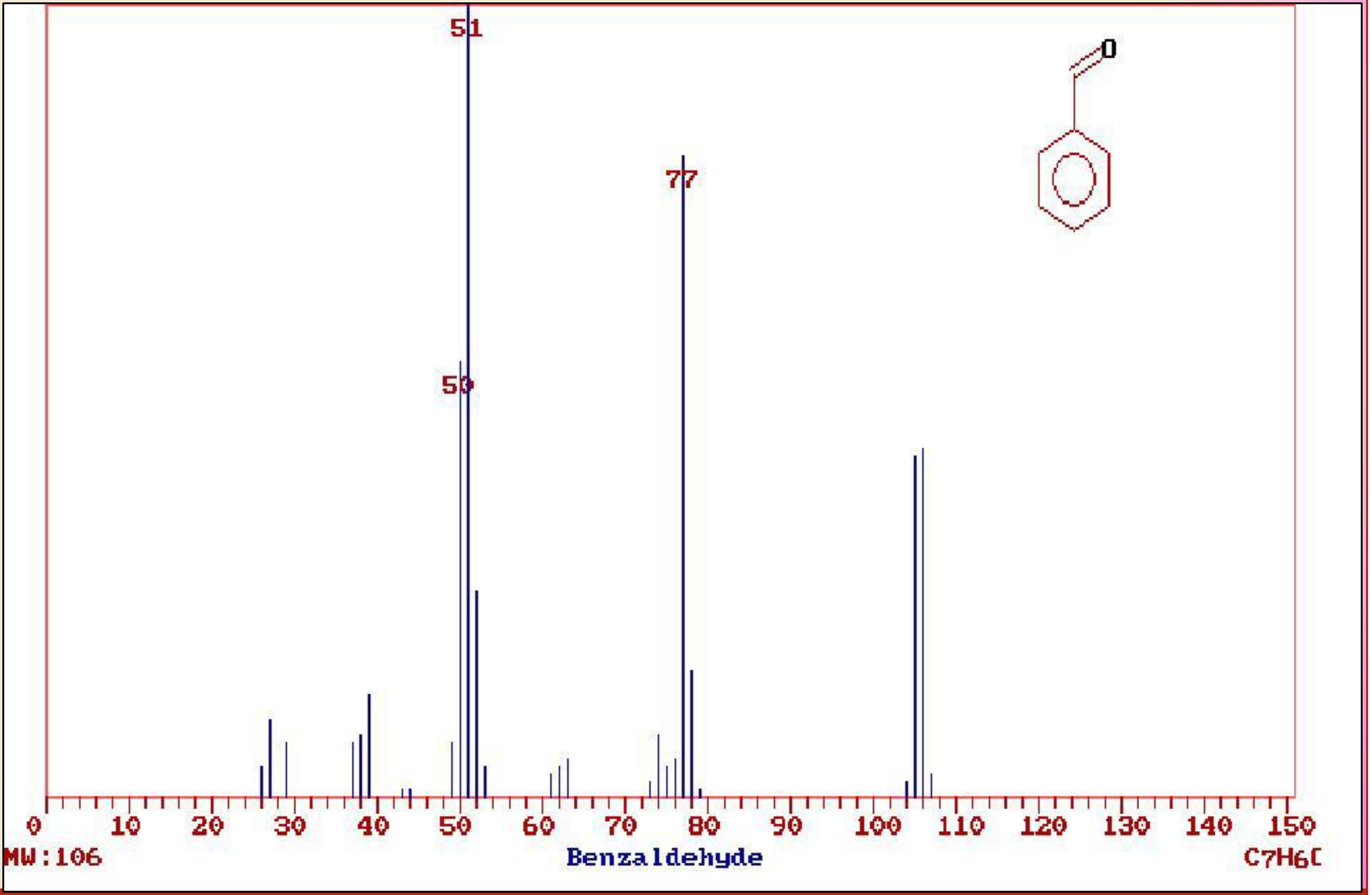
$C6H5+$

[M-H.]+

M+.

6d. Elimination acetylene

4. Loss of Acetylene: Aromatics



Fragmentation Pattern of Organic Compounds

Fragmentation Pattern of Organic Compounds

❶ Hydrocarbons:

- **(a) Alkanes**
- **(b) Alkenes**
- **(c) Aromatics**

❷ Alcohols and Phenols

❸ Amines

❻ Carbonyl compounds

- **(a) Ketones and Aldehydes**
- **(b) Acids, Esters and Amides**

1. Saturated Hydrocarbons

❶ Branched alkanes: Small/absent M^+ (Enhanced fragmentation at branch points).

❷ Long chains : Homologous series of m/z = 14 units and rarely lose methyl radical

❸ The relative height of the M+ peak decreases with chain length for a homologous series.

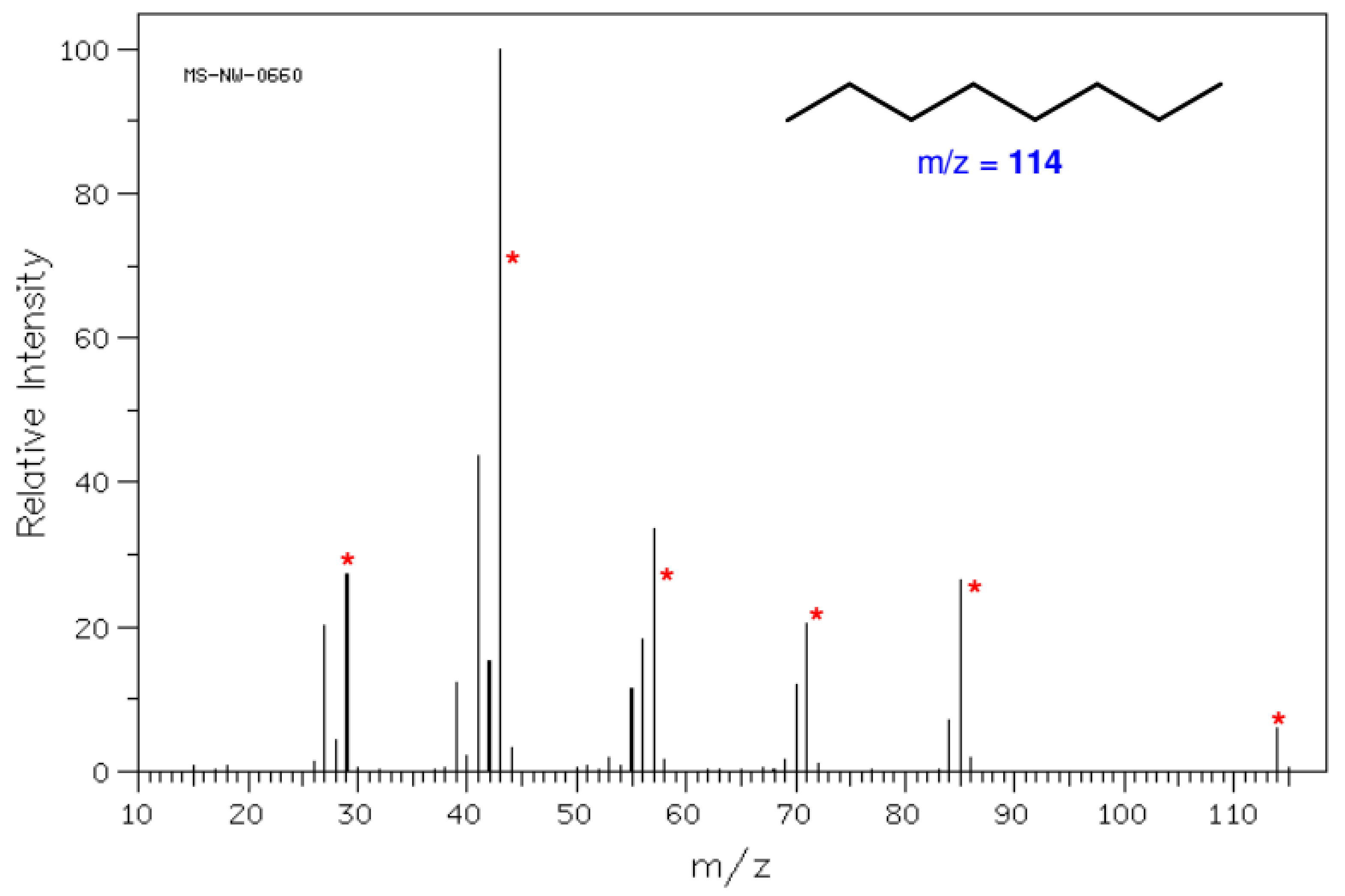
❹ Cleavage is favored at alkyl-substituted carbons, with the probability of cleavage increasing as the substitution increases.

“Stevenson’s Rule” These rules mostly arise from the fact that carbocation and radical stability show the following trend:

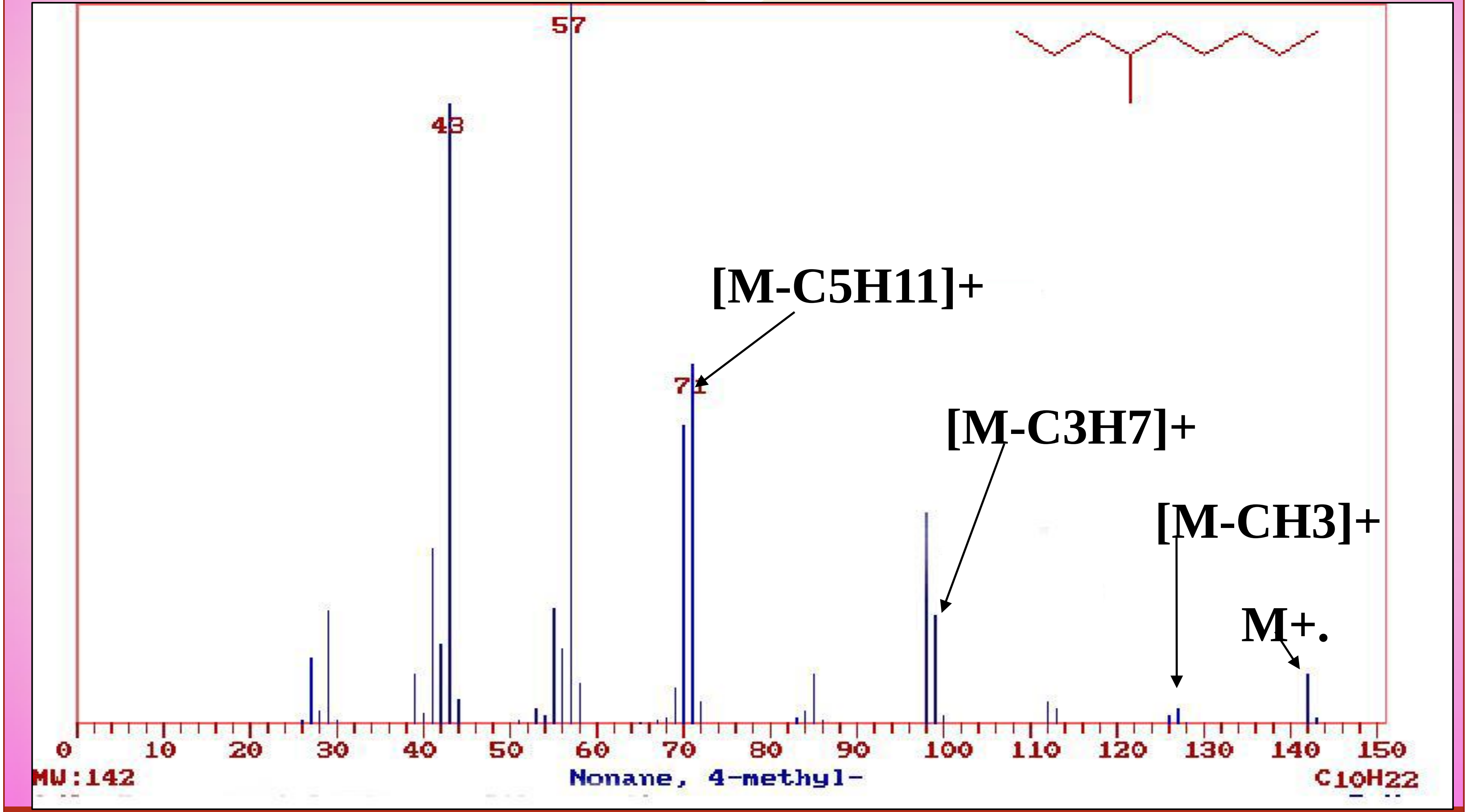
Benzylic > Allylic > Tertiary > Secondary >> Primary

At the point of breakage, the larger fragment usually takes the radical to leave the smaller cation.

1. Fragmentation Pattern of n-Octane

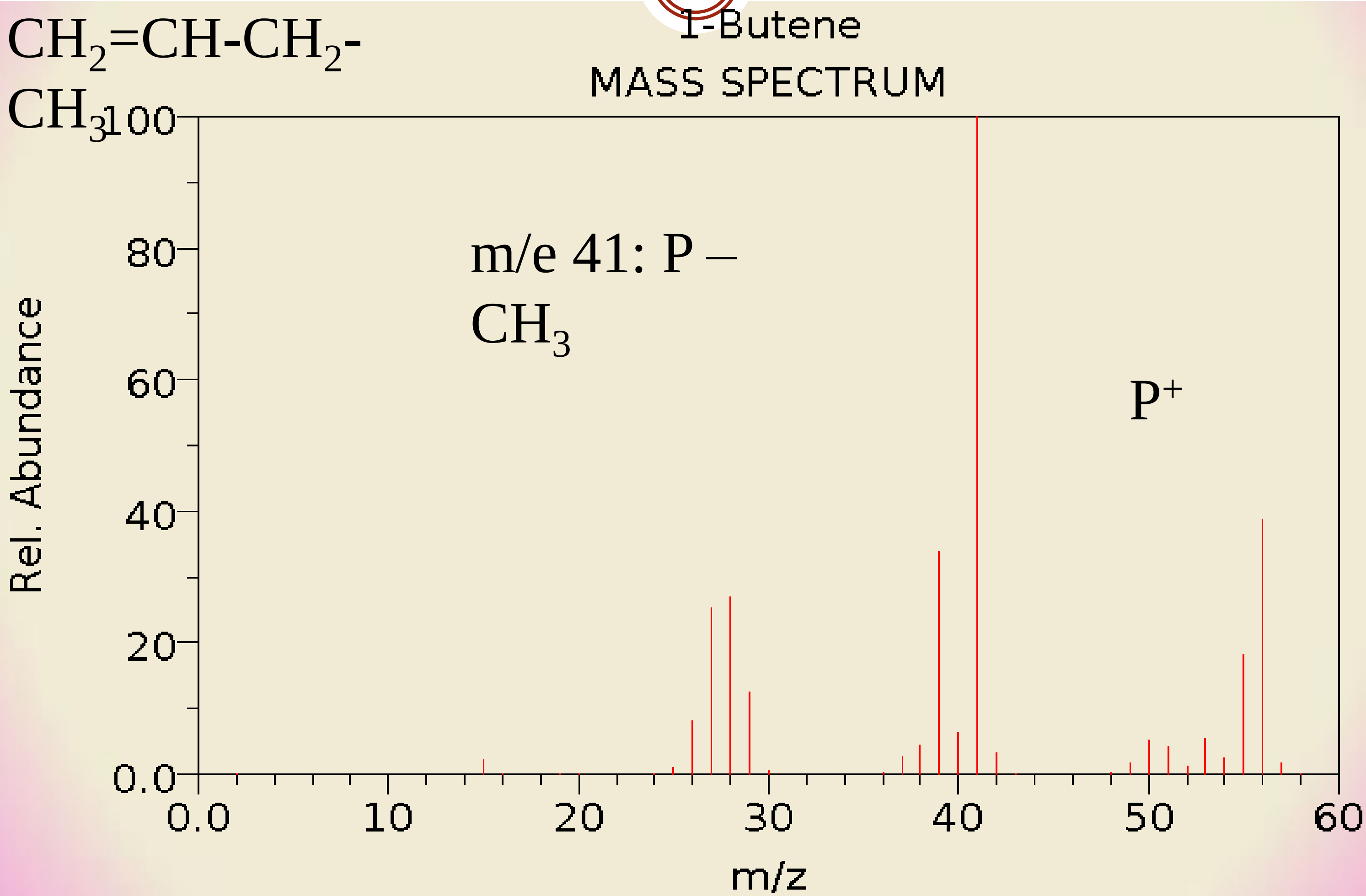


1. Fragmentation Pattern of 4-Methylnonane



1. Fragmentation Pattern of n-Butene

$CH_2=CH-CH_2-CH_3$

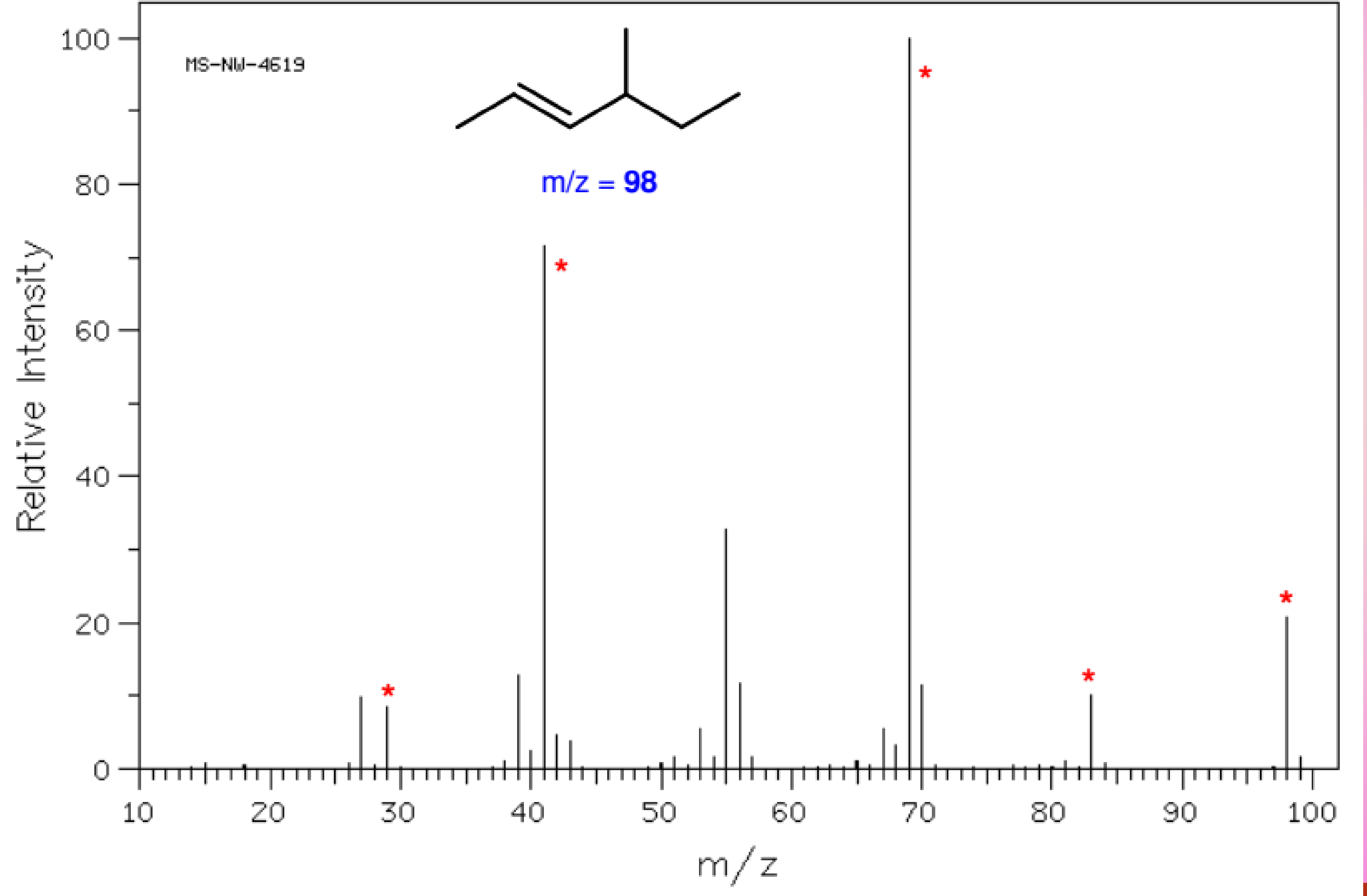


m/e 41: P – CH_3

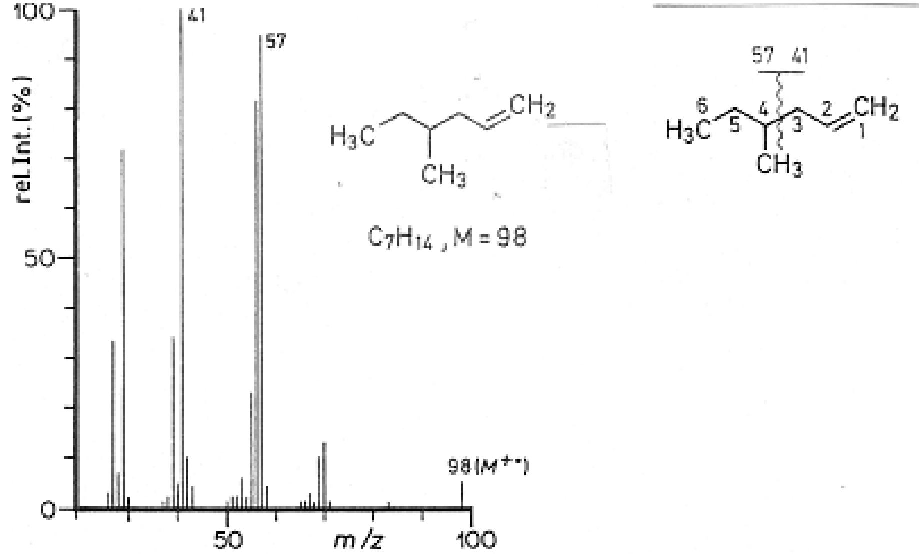
P^+

NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

1. Fragmentation Pattern of n-Hexadecane



1. Fragmentation Pattern of n-Hexadecane



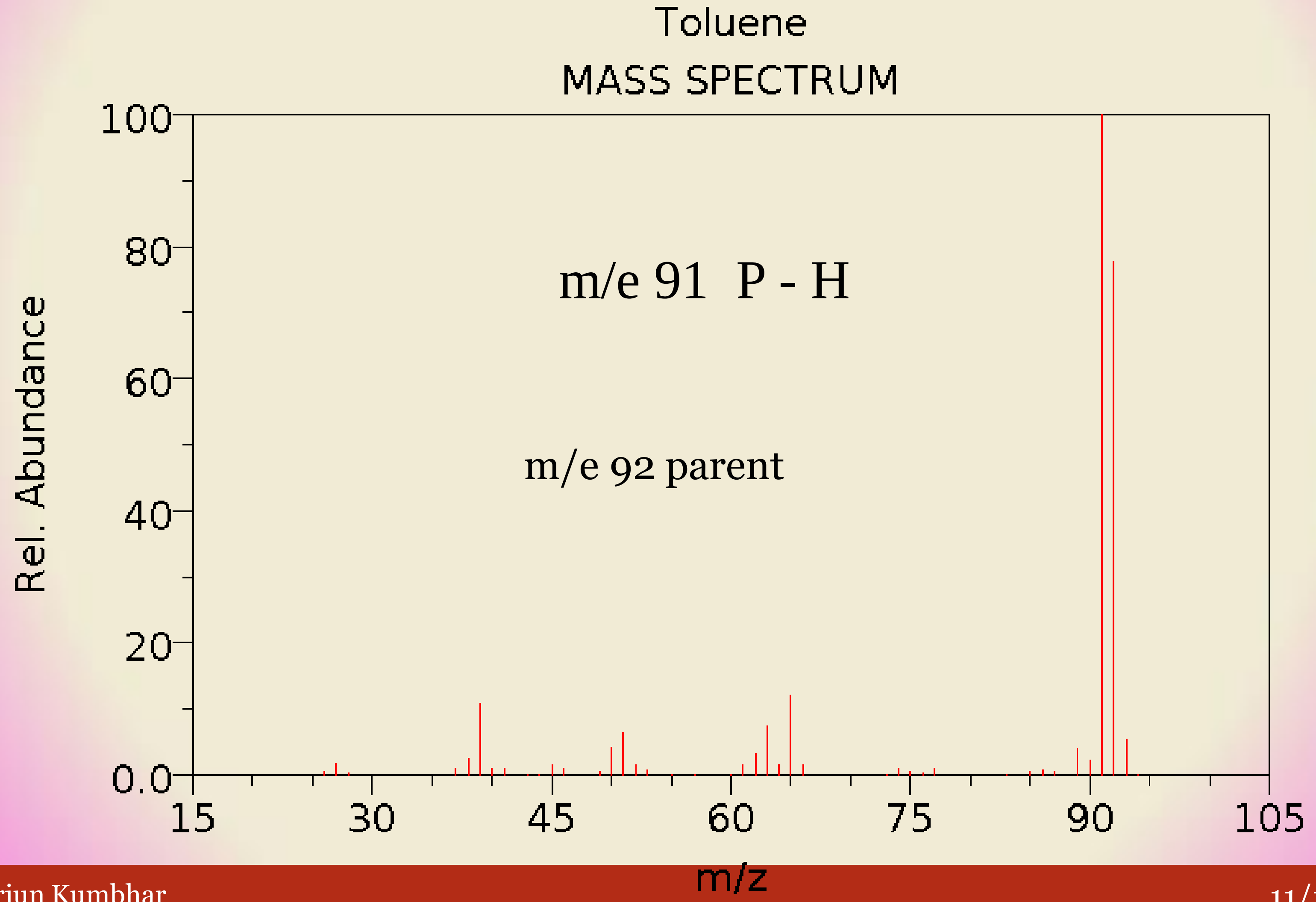
EI of 4-methyl-1-hexene

2. Aromatic Hydrocarbons

1. Aromatic hydrocarbons usually show **strong M+ peaks**, as aromatic rings are stable and have a **lower tendency to fragment**.

2. Alkyl substituted benzenes often give a **strong peak at m/z 91 due to benzyli** cleavage.

1. Fragmentation Pattern of Toluene

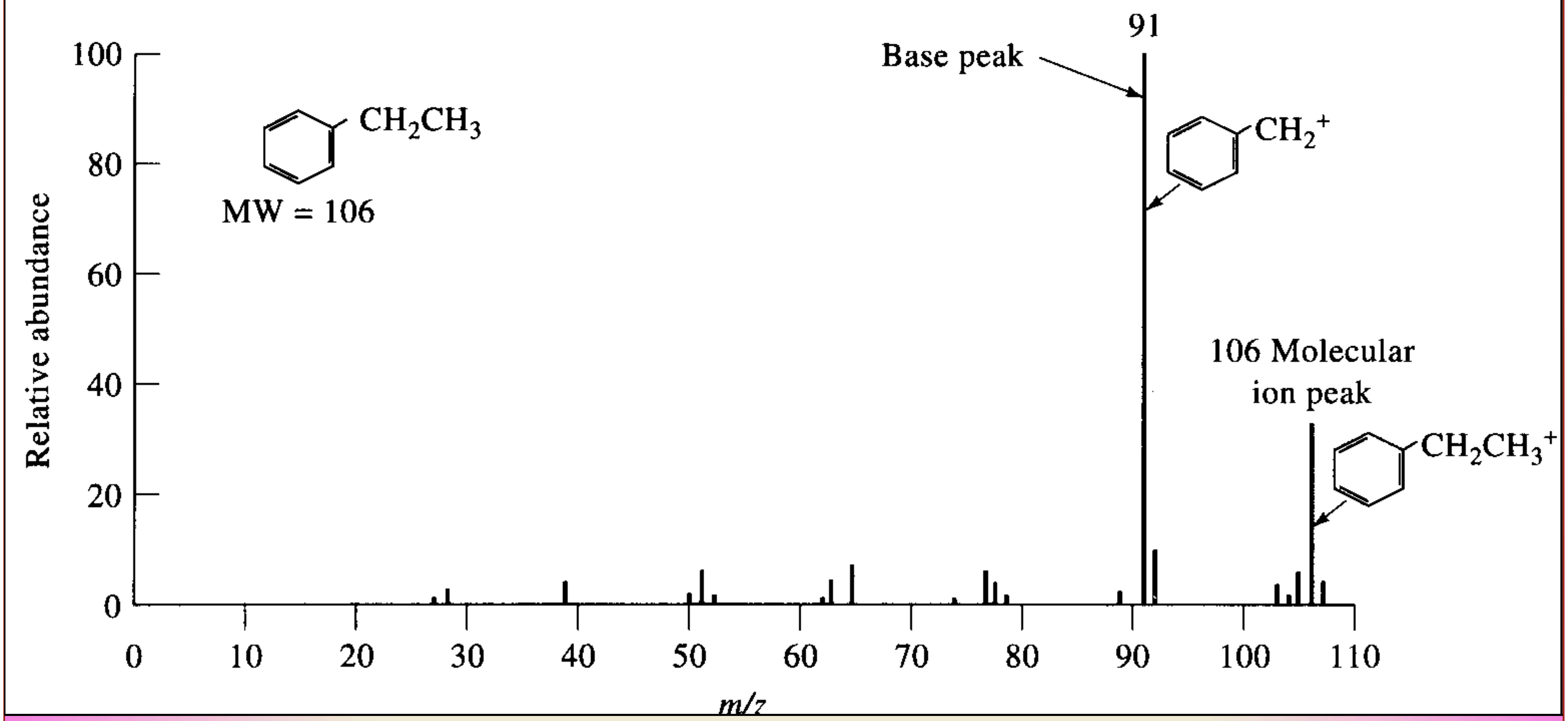


m/e 91 P - H

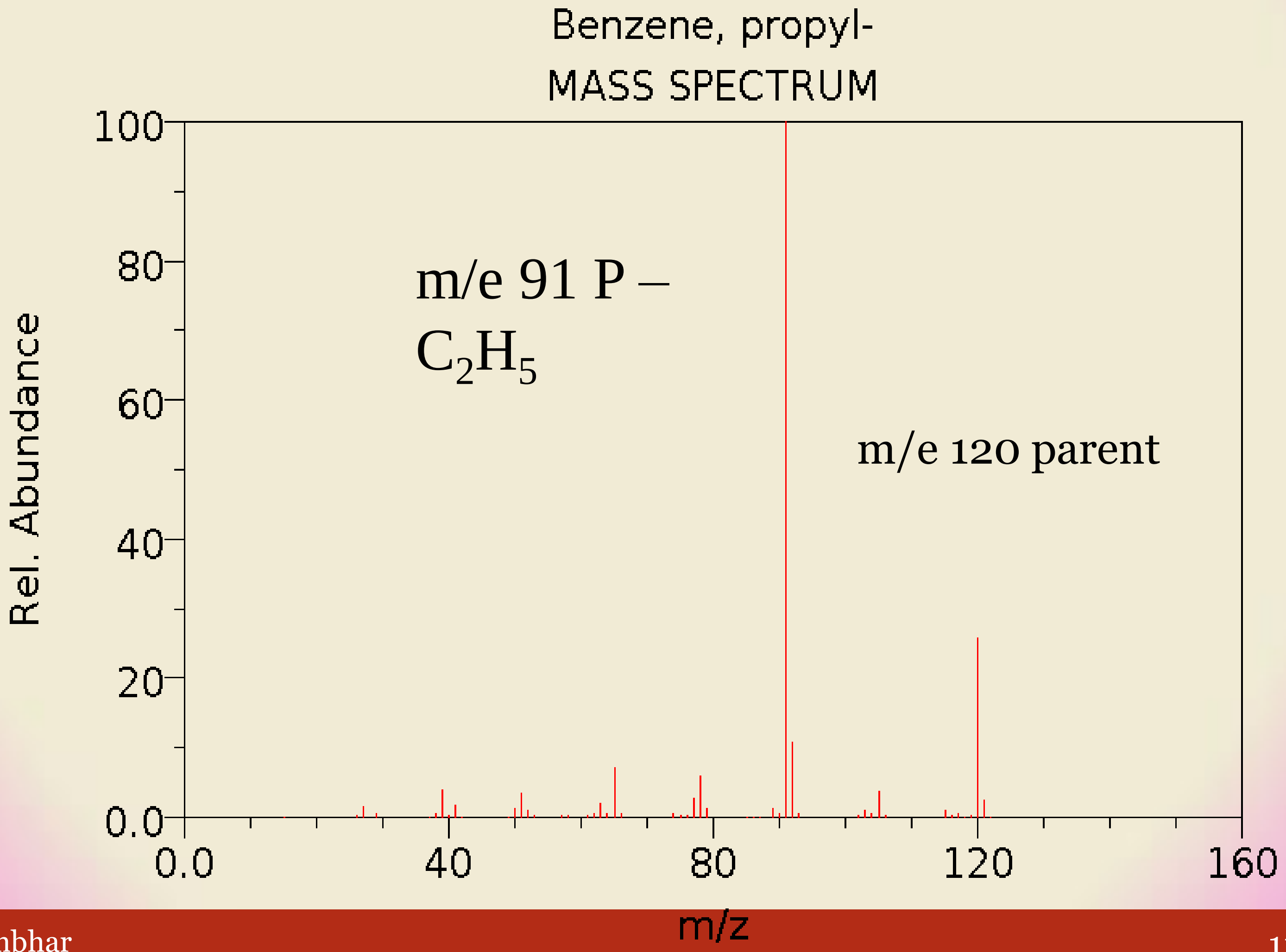
m/e 92 parent

NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Fragmentation Pattern of Ethylbenzene



Fragmentation Pattern of *n*-Propylbenzene

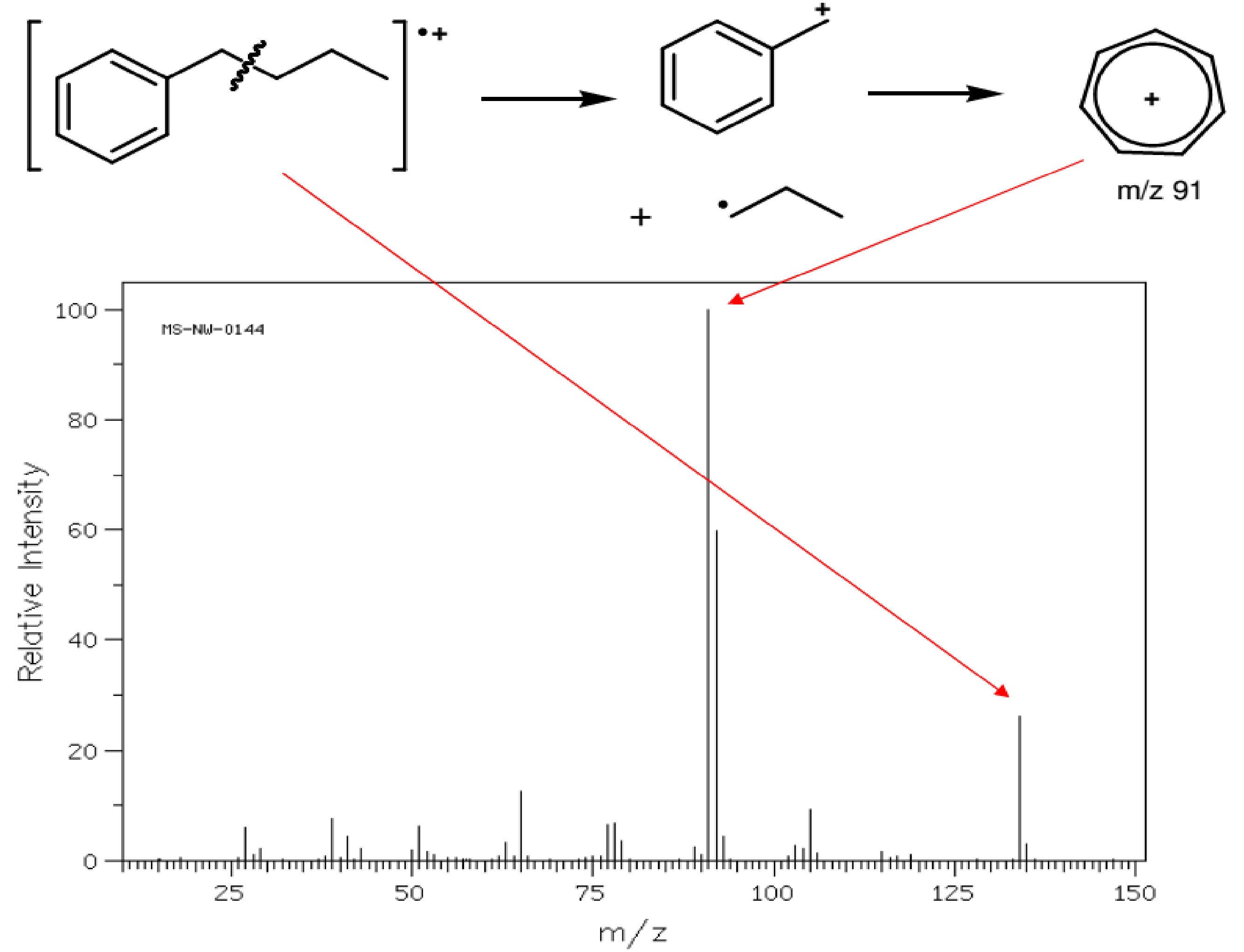


m/e 91 P – C_2H_5

m/e 120 parent

NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Fragmentation Pattern of *n*-Butylbenzene



4. Fragmentation Pattern of Alcohols

1. Alcohols show **very weak M+** peaks and many cases often do **not show M+** at all.

2. The C-C bond nearest the OH is frequently the first bond to break. Thus….

a) **primary alcohols** often show a prominent peak at **31 m/z**.

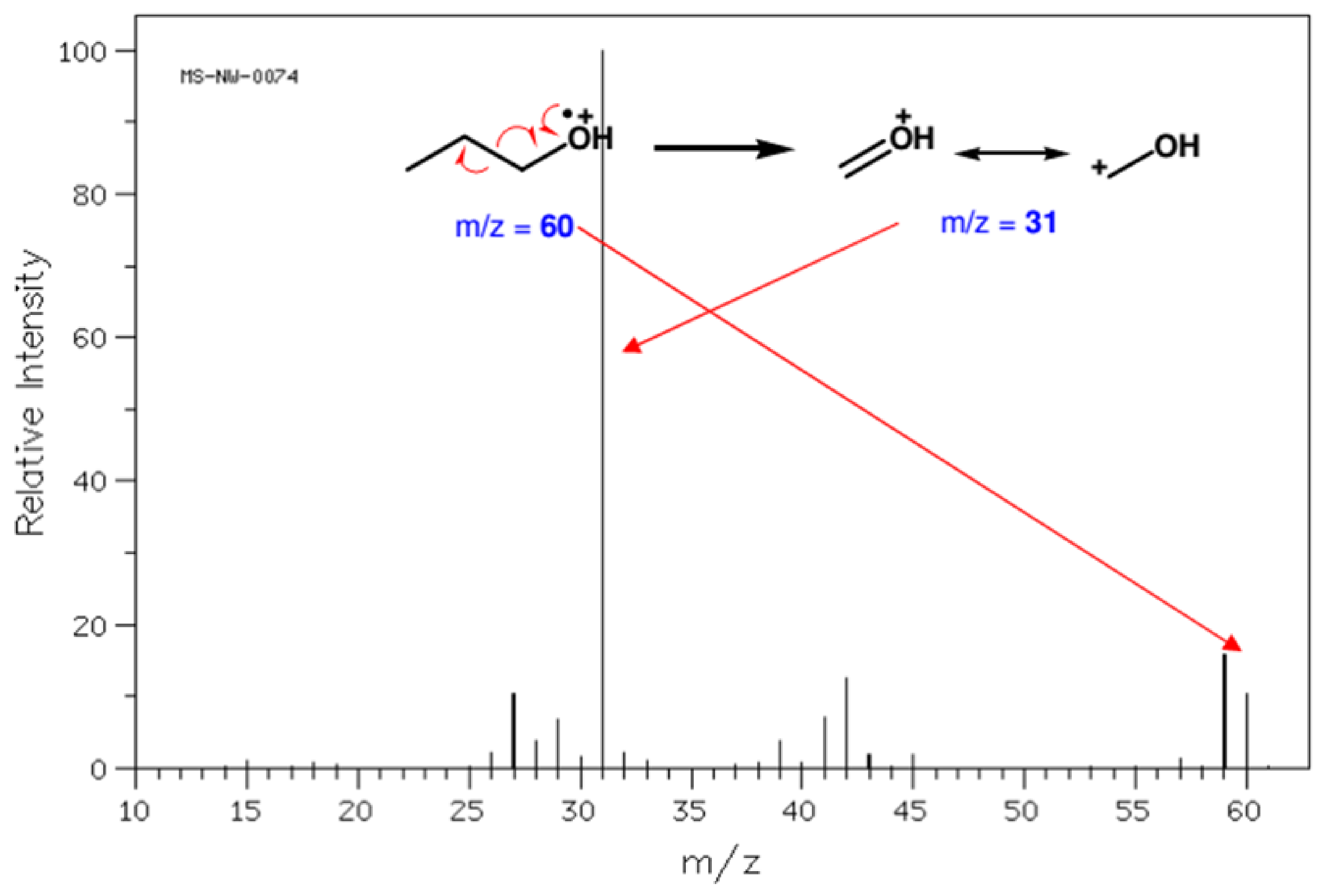
b) secondary alcohols cleave in the same way, showing a prominent **CHR-OH+ peak**.

3. M-1 peak: Sometimes the hydrogen R2CH-OH in 1 and 2 alcohols cleaves rather than an alkyl group.

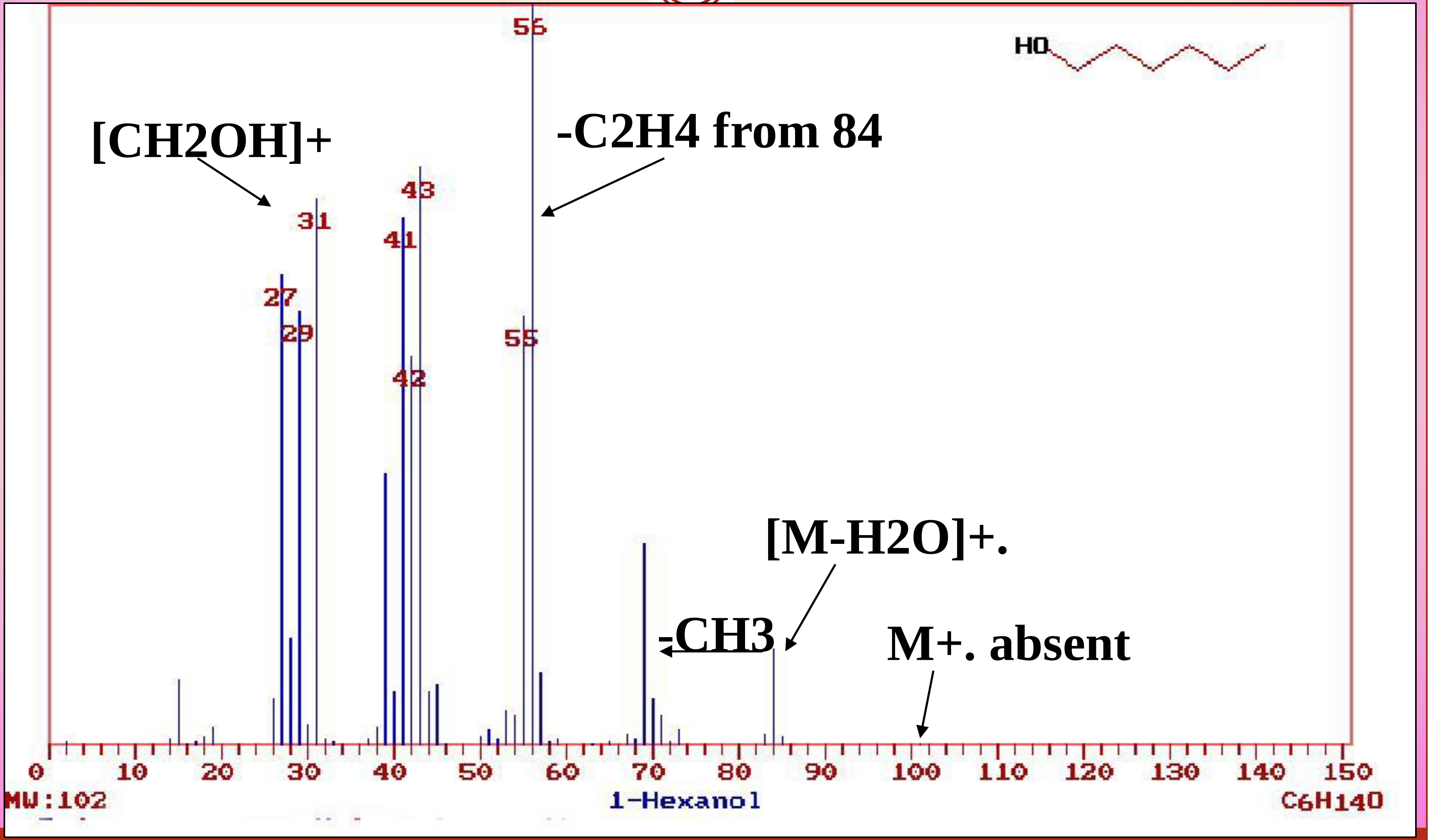
4. Alcohols can **lose a molecule of water** to show a sometimes **prominent M-18** peak (especially for primary alcohols).

5. Benzyl alcohol will usually **lose water (M-18).**

Fragmentation Pattern of Propanol



Fragmentation Pattern of Hexanol



$[CH_2OH]^+$

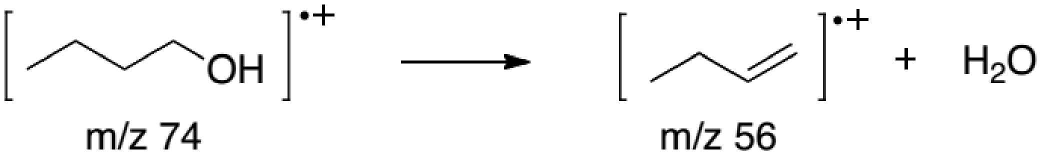
$-C_2H_4$ from 84

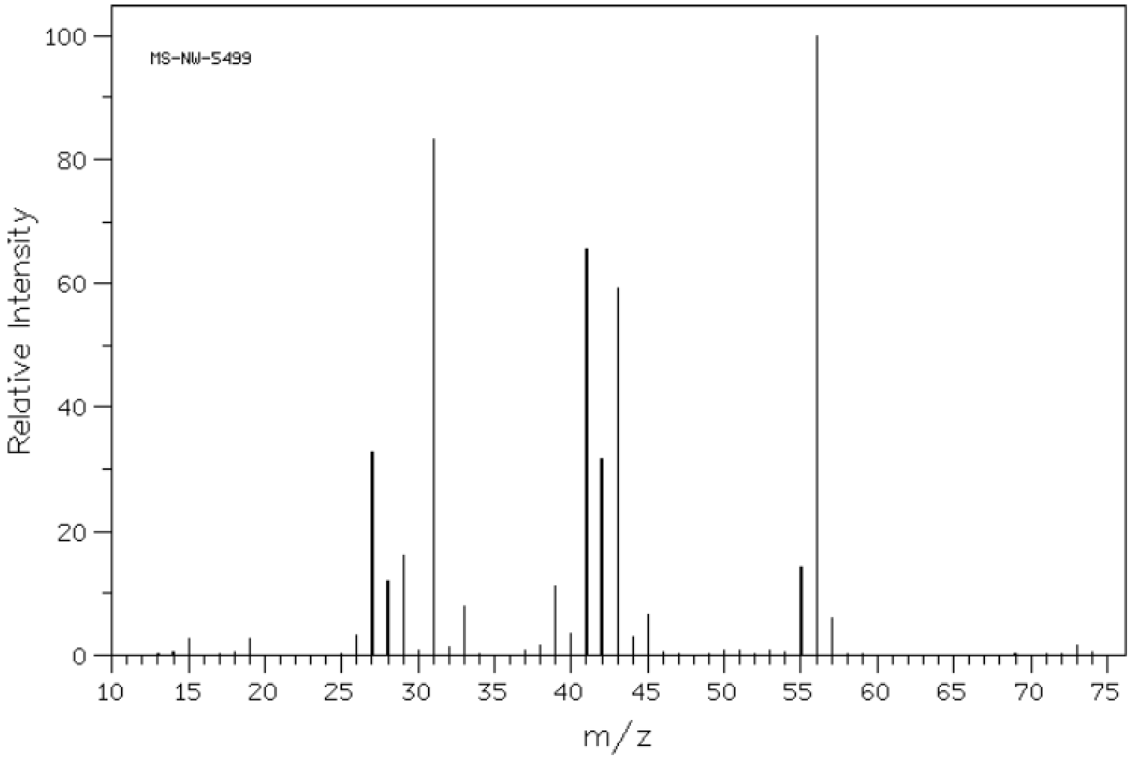
$[M-H_2O]^{+.}$

$-CH_3$

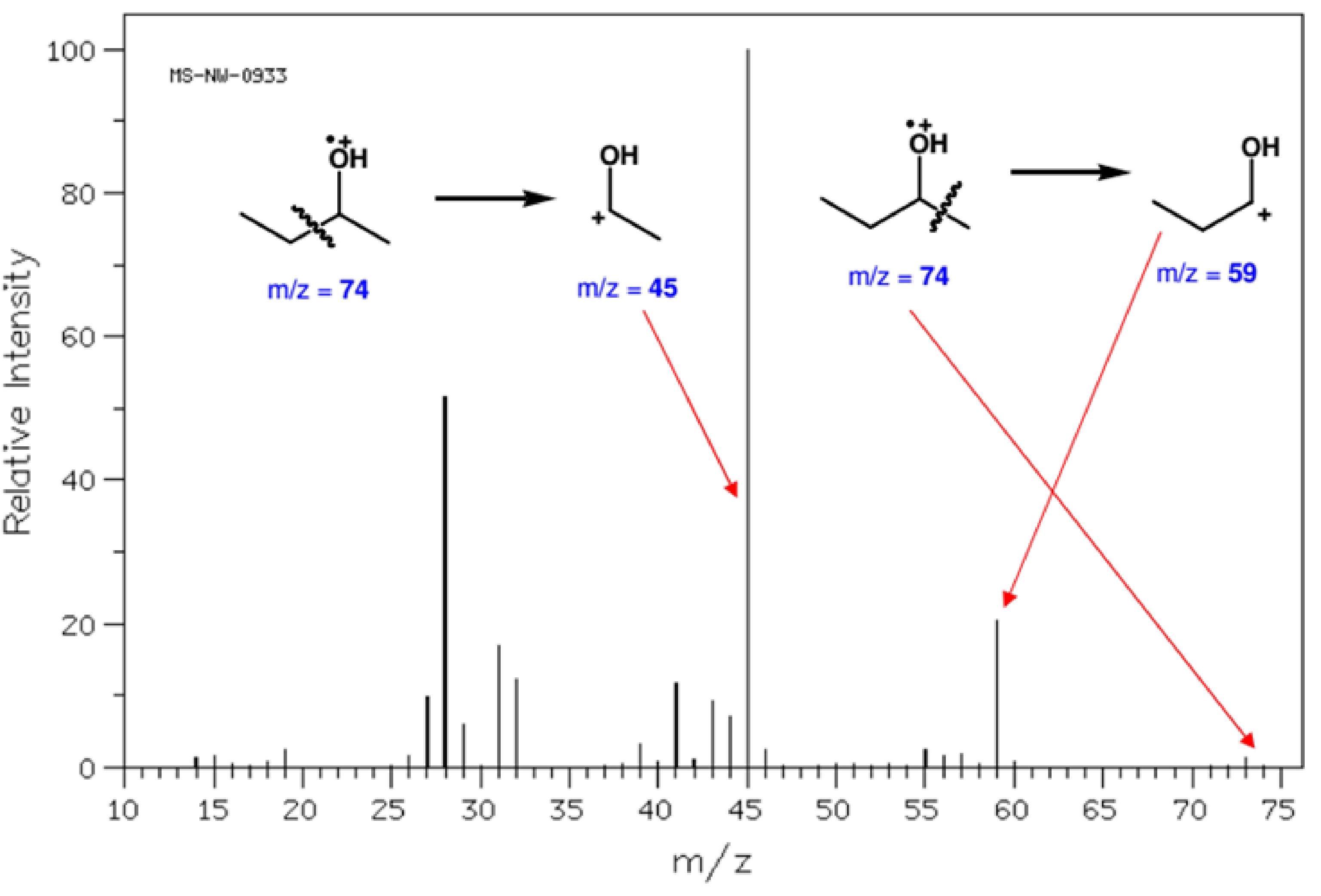
$M^{+.}$ absent

1) Loss of water

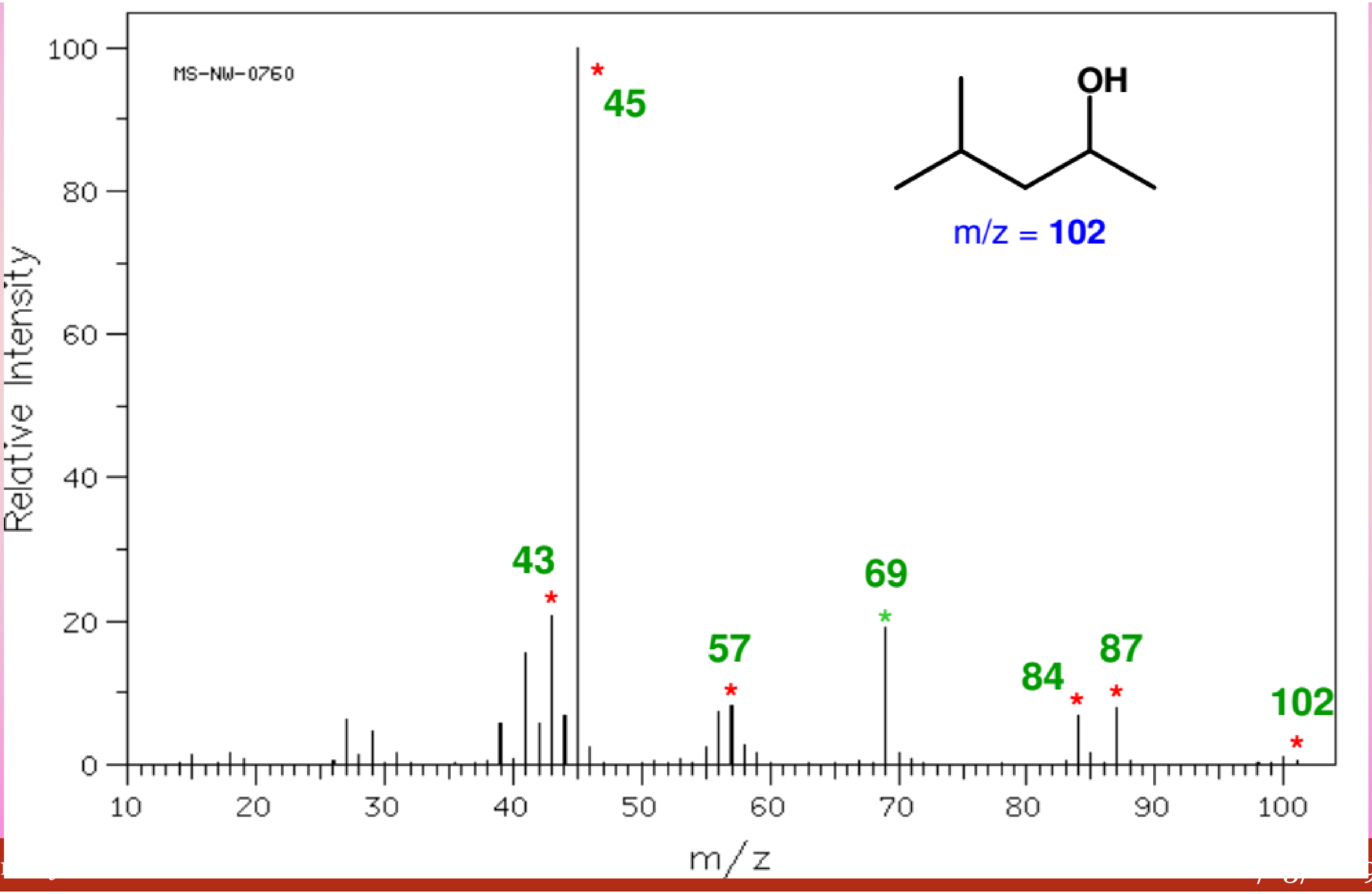




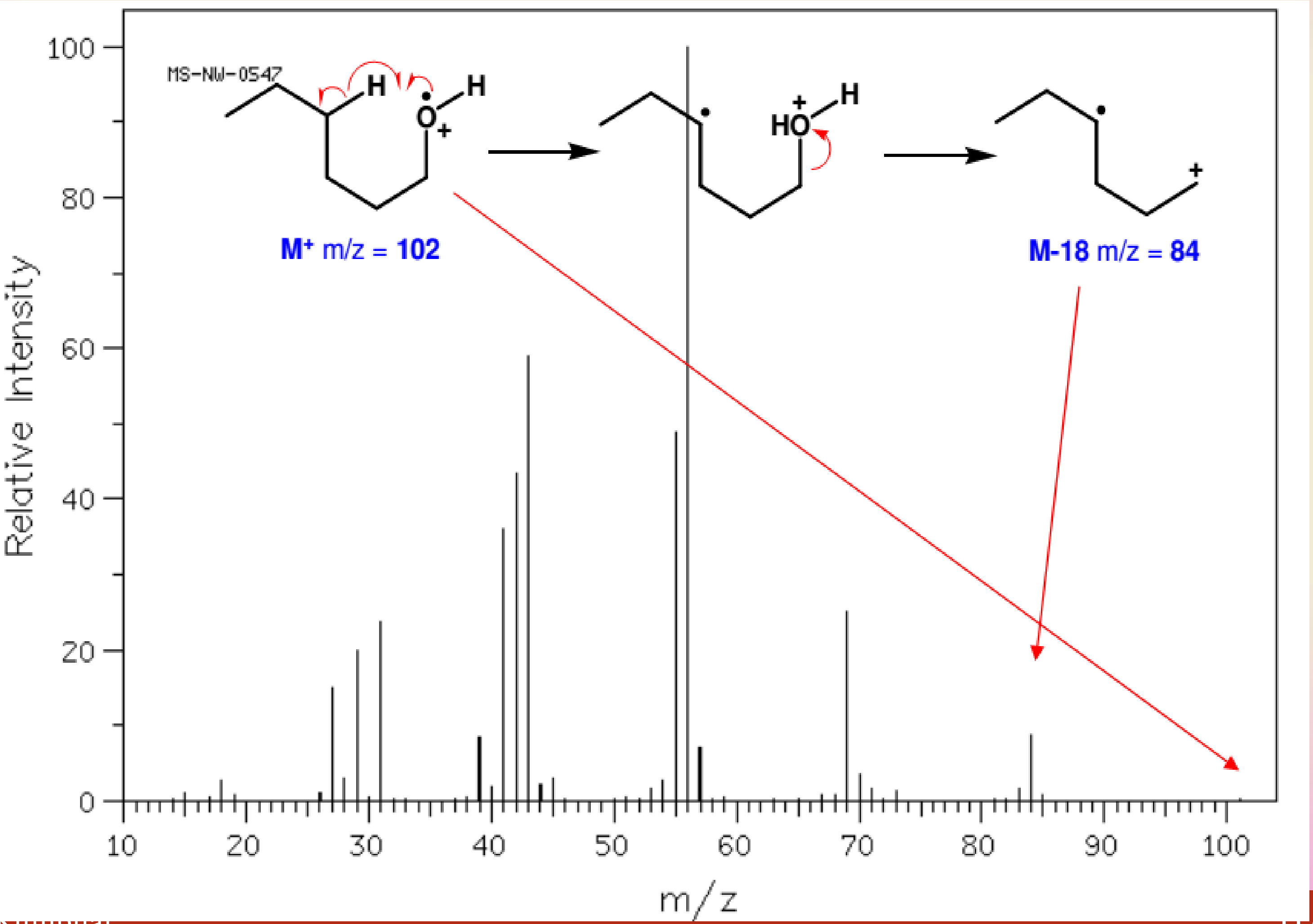
Fragmentation Pattern of 2-Butanol



Fragmentation Pattern of Alcohol



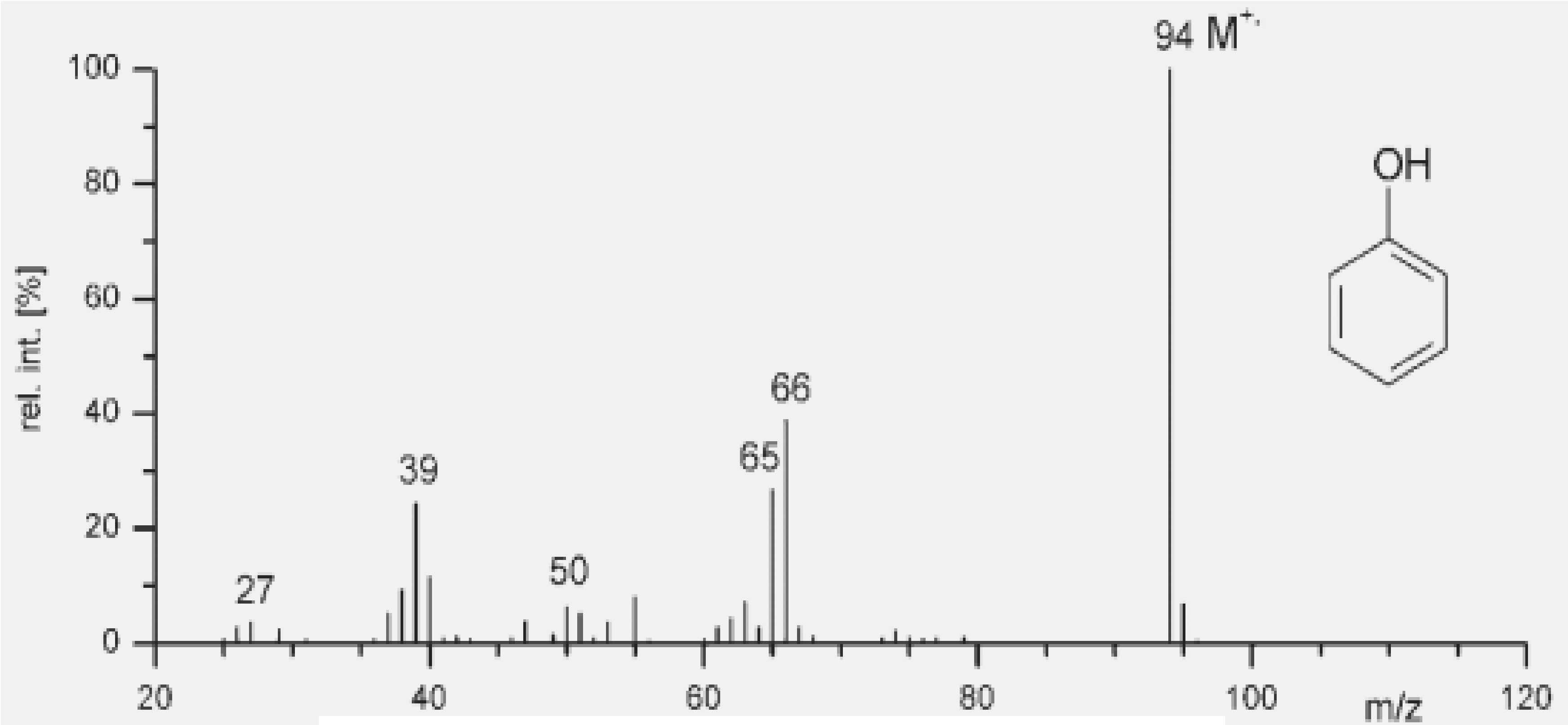
Fragmentation Pattern of Alcohol

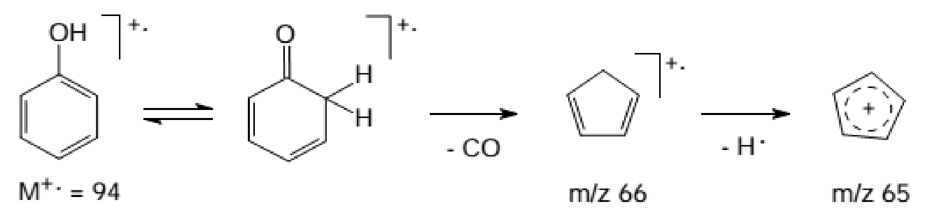


FRAGMENTATION PATTERNS OF PHENOLS

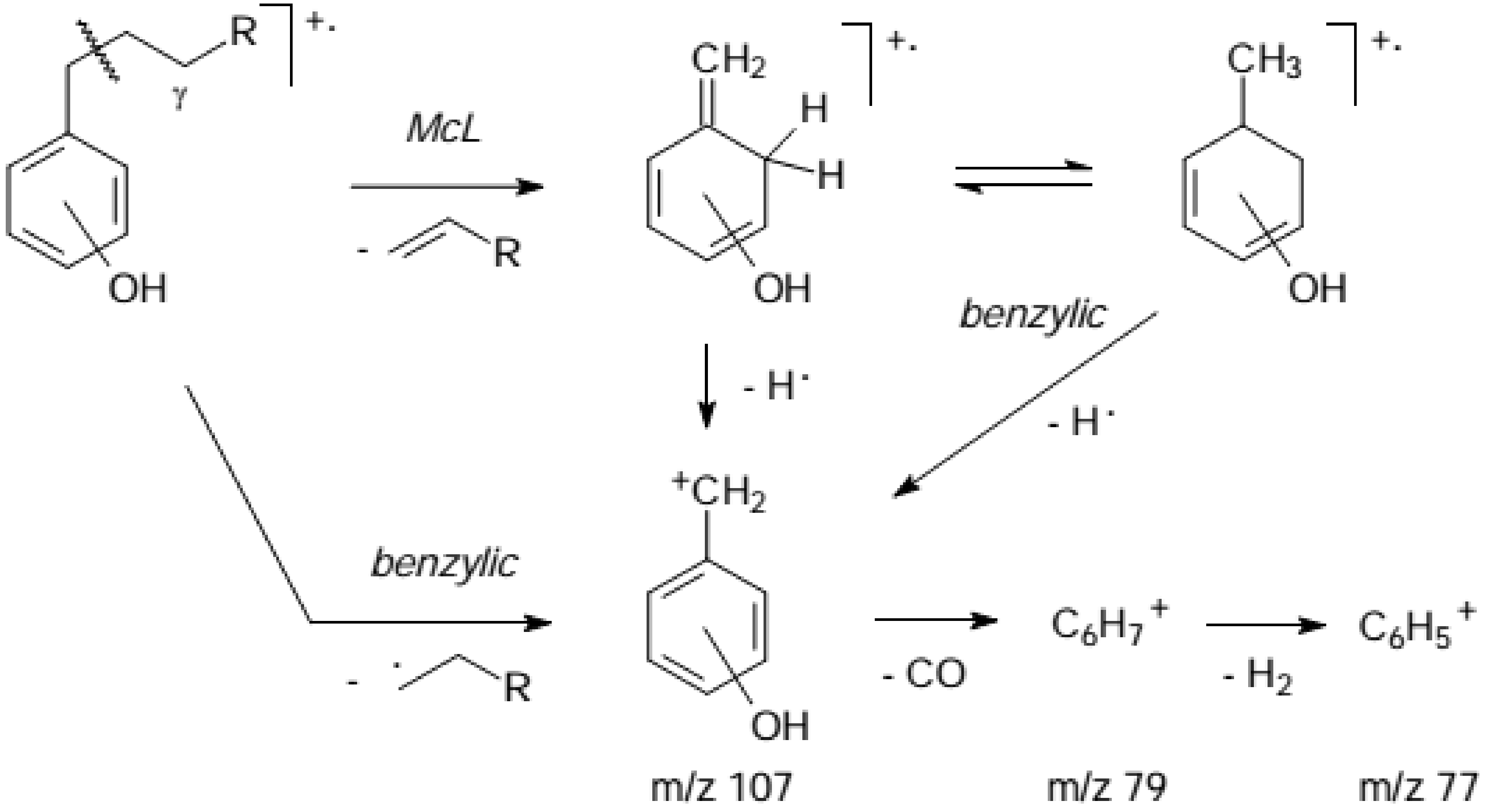
1. Phenols often show **peaks at 77 m/z** resulting from formation of **phenyl cation**,
2. Peaks resulting from **loss of CO (M-28) and CHO (M-29).**

Fragmentation Pattern of Phenol





Fragmentation Pattern of Phenol



Fragmentation Pattern of Amines

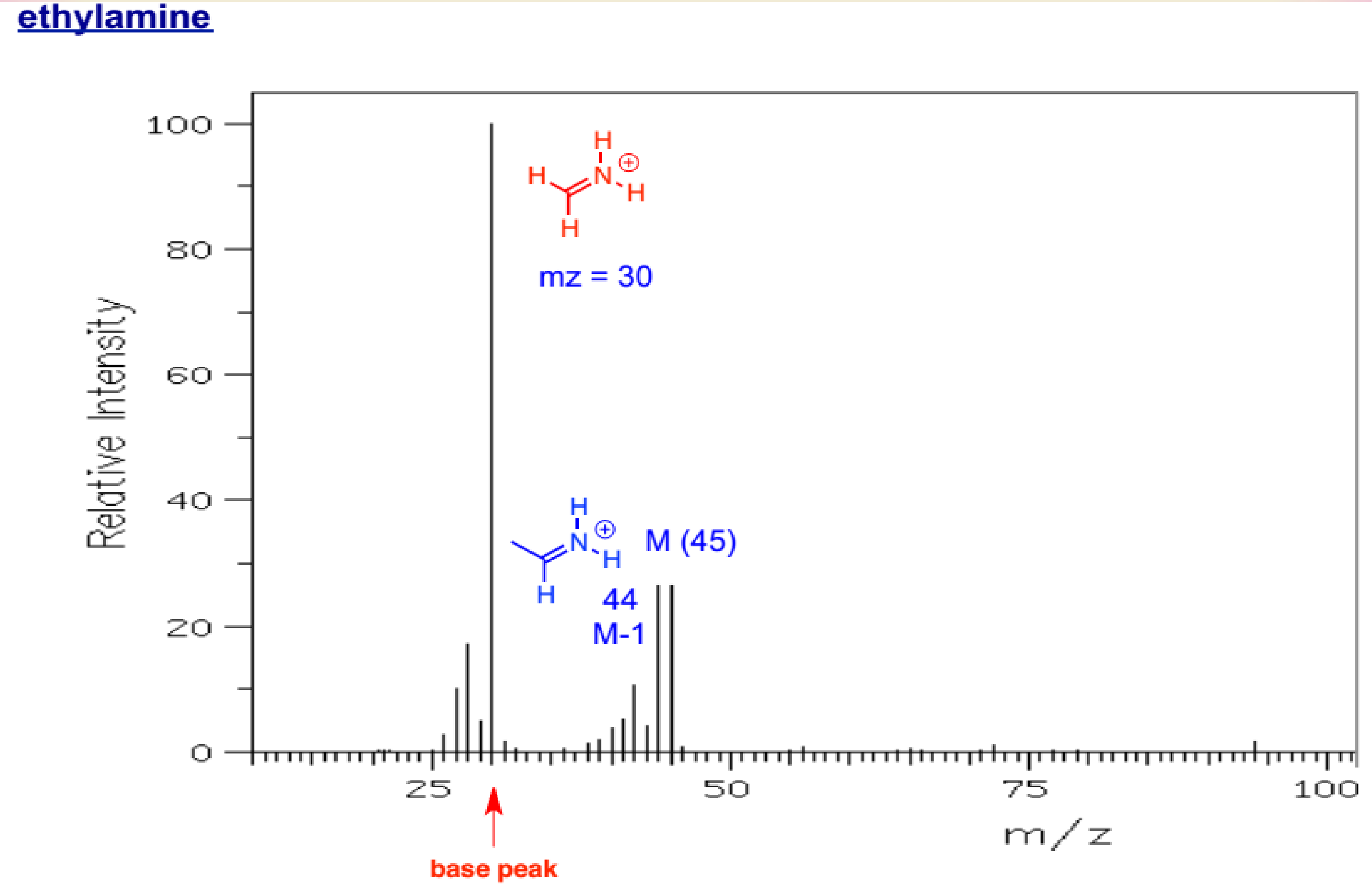
Aliphatic Amines :

1. M+ will be an odd number for monoamine; may be weak/absent
2. M-1 common
3. α-cleavage of an alkyl radical is predominate fragmentation mode largest group lost preferentially
4. McLafferty rearrangement / loss of NH3 (M-17) are not common

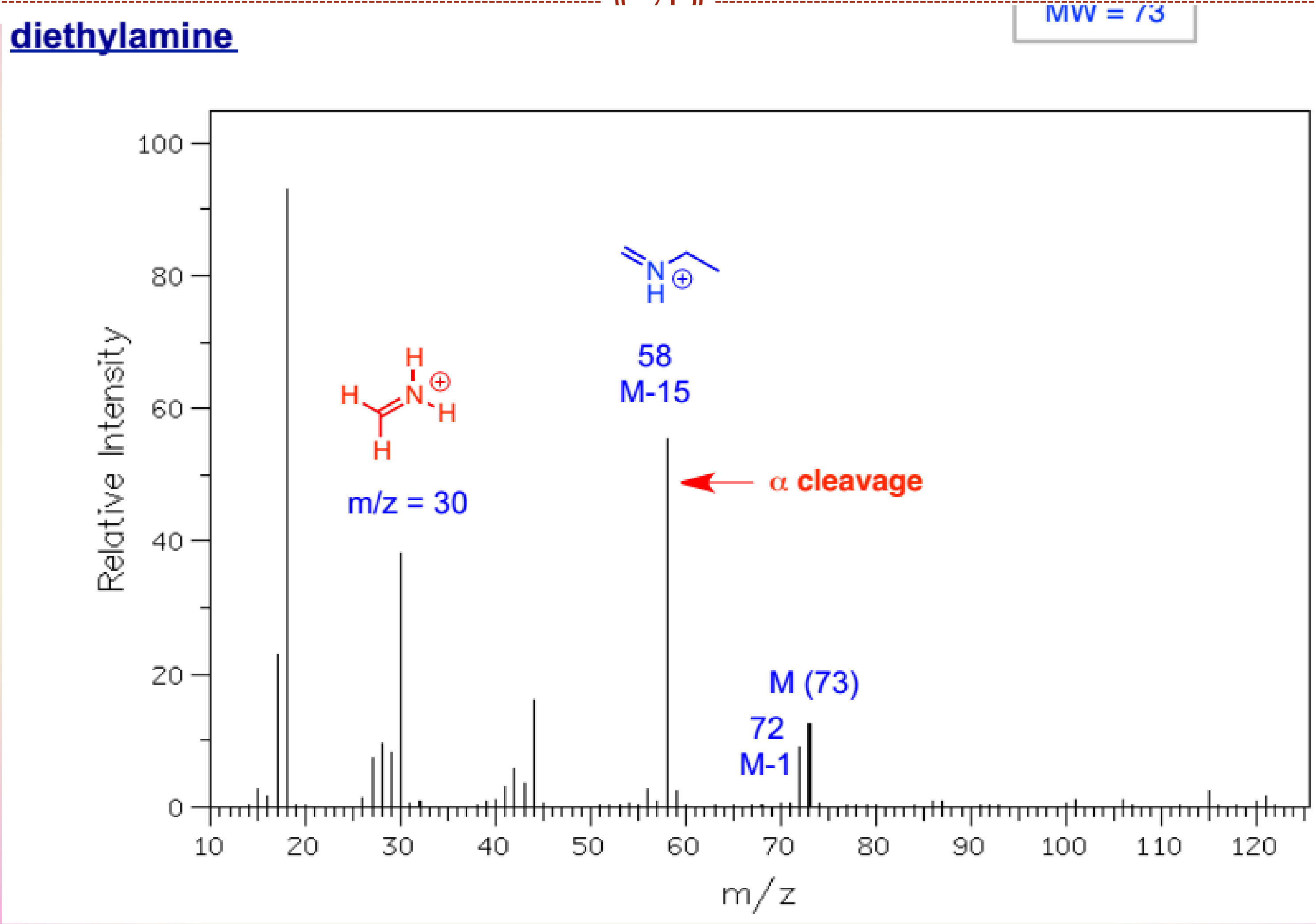
Aromatic Amines

1. M+ usually strong
2. M-1 common
3. loss of HCN is common in anilines

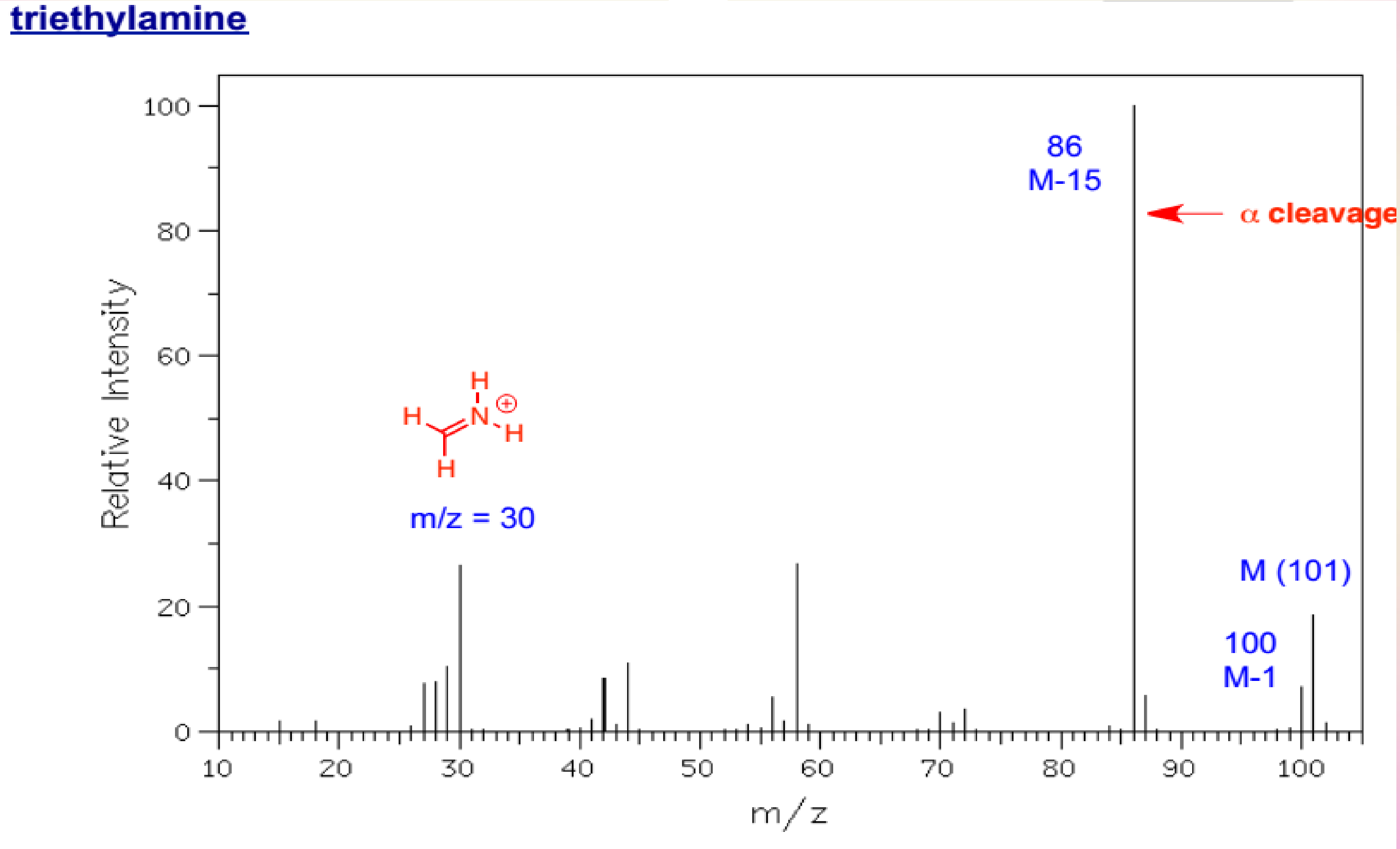
Fragmentation Pattern of Ethylamine



Fragmentation Pattern of Diethylamine

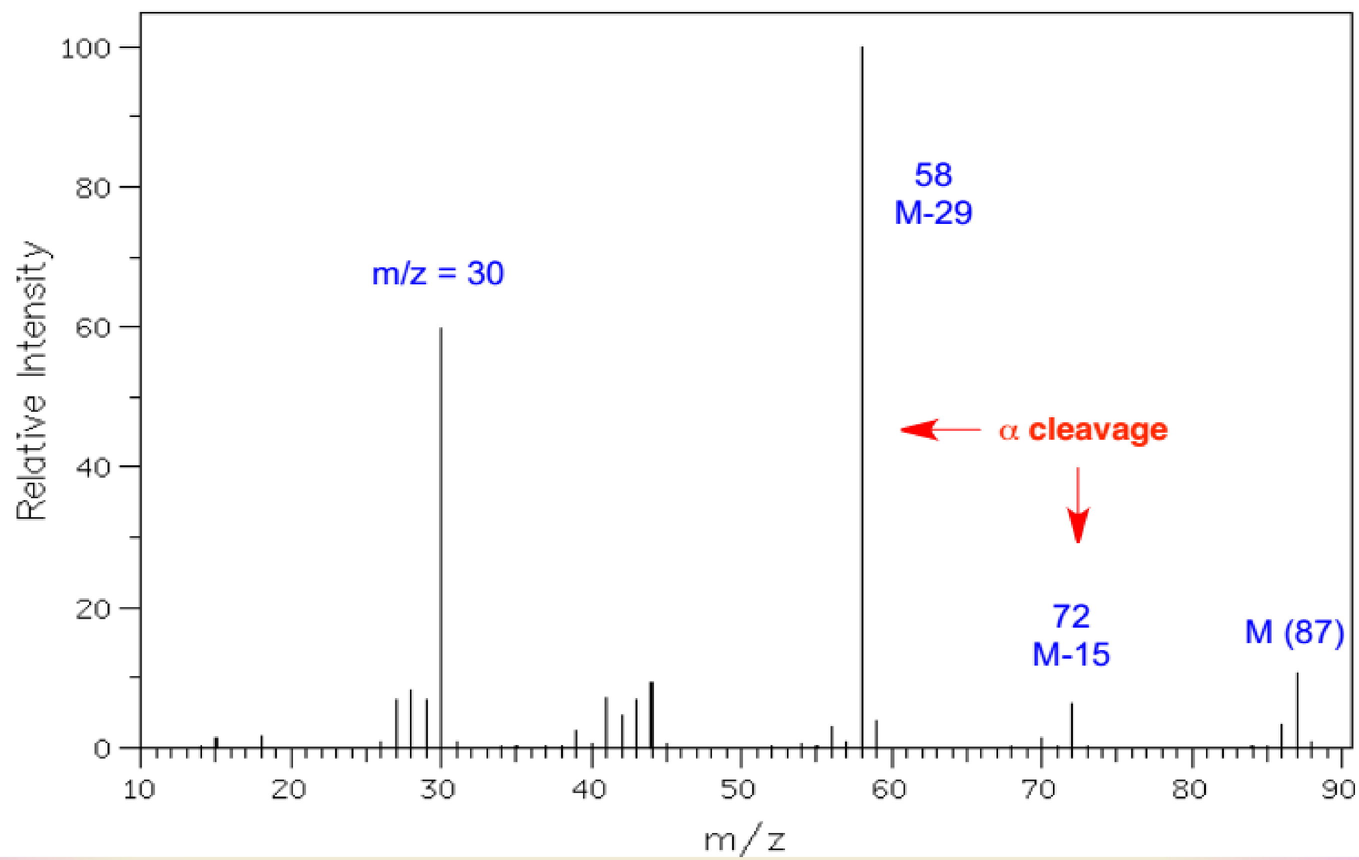


Fragmentation Pattern of Triethylamine

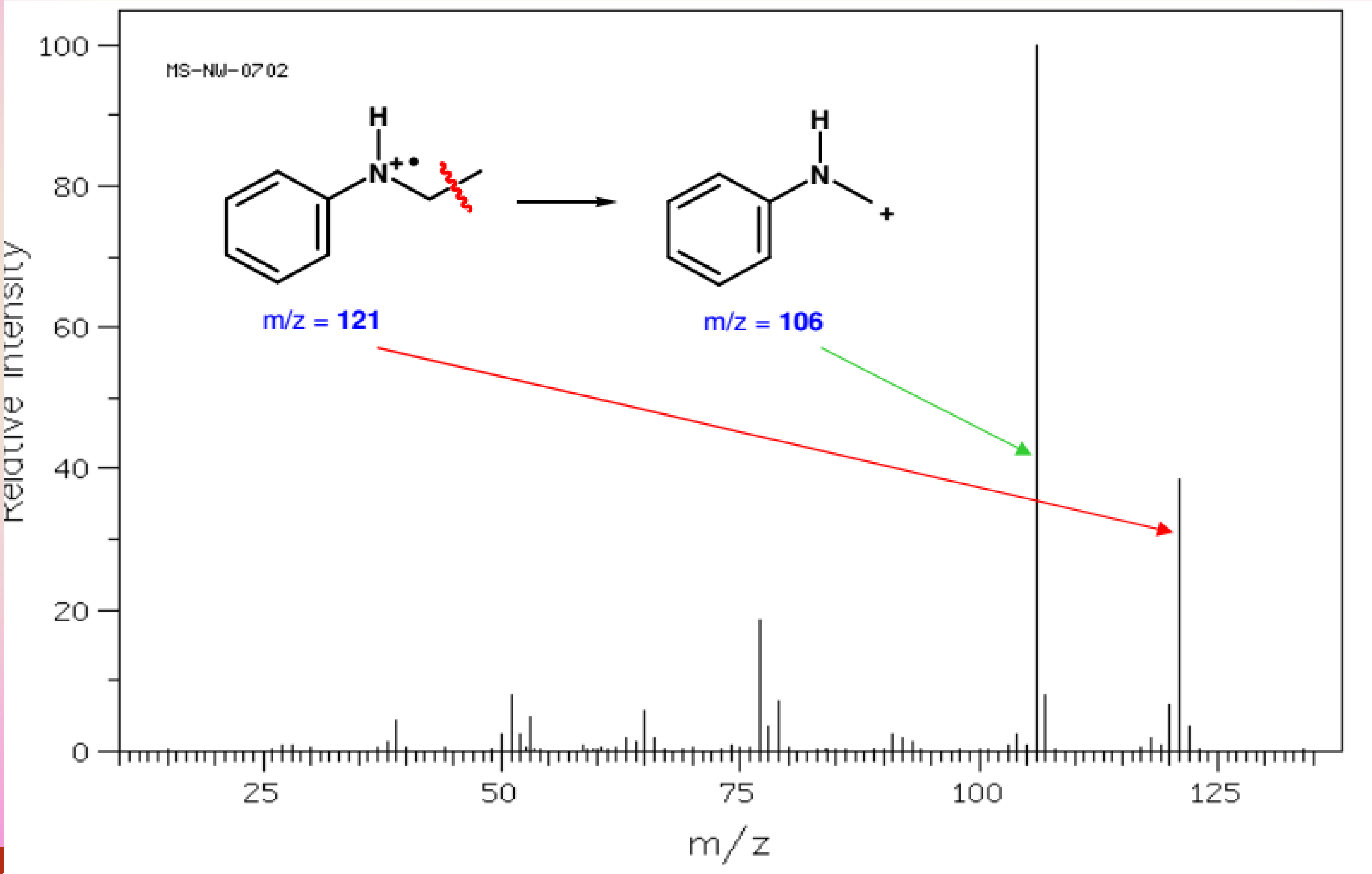


Fragmentation Pattern of Etylpropylamine

N-ethylpropylamine



Fragmentation Pattern of Amines



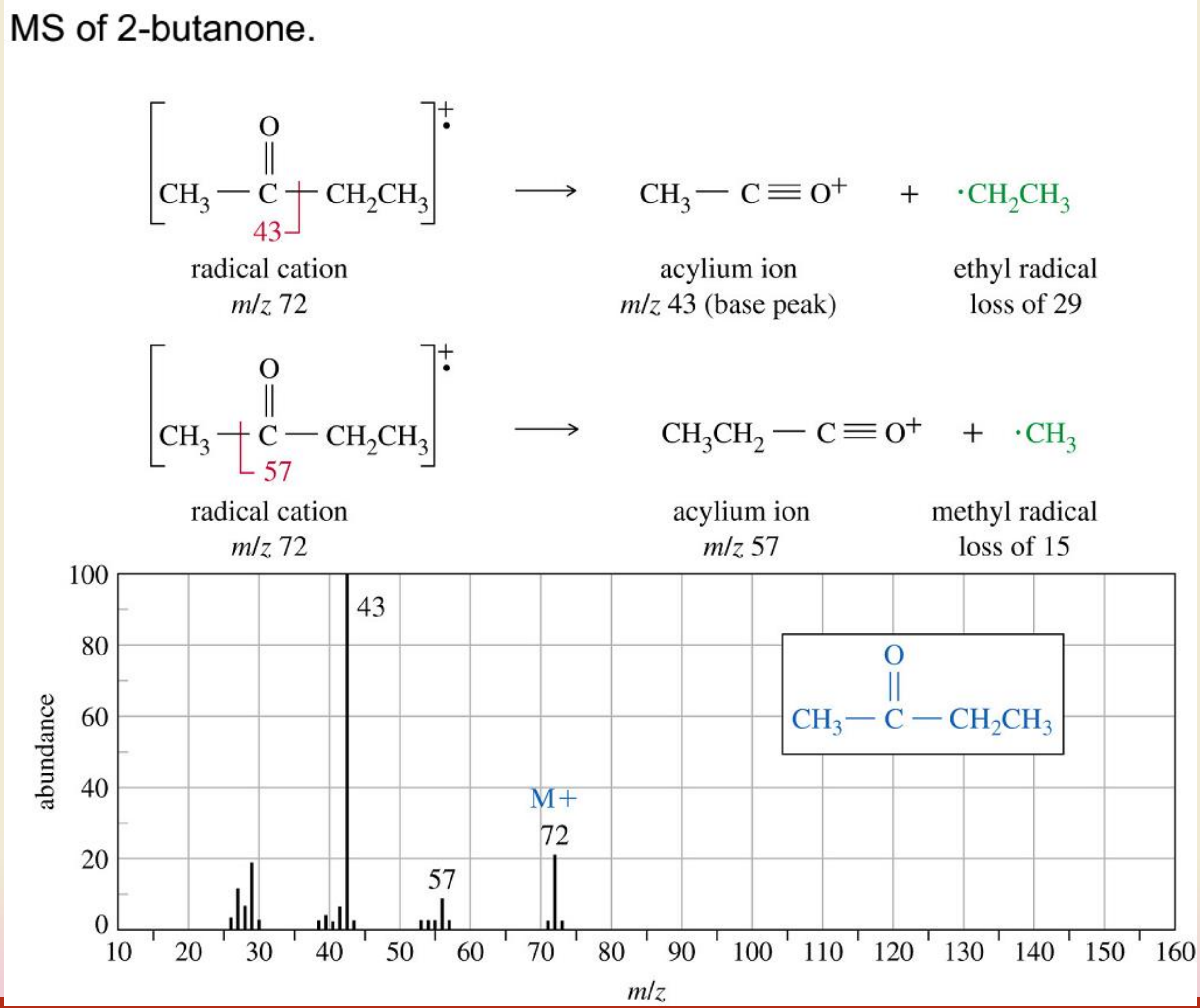
Fragmentation Pattern of Carbonyl Compounds

Fragmentation Pattern of Carbonyls

Ketones:
1. **Strong M+ peaks**.
2. A **major fragmentation pathway** involves **α-cleavage** to give an **acylium ion**.
3. McLafferty rearrangement often leads to **strong peaks**.
4. Aromatic Ketones: M+ is evident. Primary cleavage is α to the carbonyl to give a strong ArCO+ peak (m/z 105 when Ar = Ph).
5. This will lose CO to give the phenyl cation (m/z 77).
6. Aldehydes: Weak but discernable M+ peaks. Major pathways are α-cleavage and McLafferty Rearrangement.
7. Aromatic aldehydes …… are similar to aromatic ketones. M+is strong, and M-1 (α-cleavage to carbonyl) is also strong to give the ArCO+ ion (m/z 105 for Ar = Ph).

Loss of CO from this ion is common to give m/z 77 phenyl cation.

Fragmentation Pattern of Carbonyls



MS of 2-butanone.

$$\left[CH_3-\overset{\overset{\displaystyle O}{\|}}{C}\underset{43}{+}CH_2CH_3\right]^{+\cdot} \longrightarrow CH_3-C\equiv O^+ \;+\; \cdot CH_2CH_3$$

radical cation
m/z 72

acylium ion
m/z 43 (base peak)

ethyl radical
loss of 29

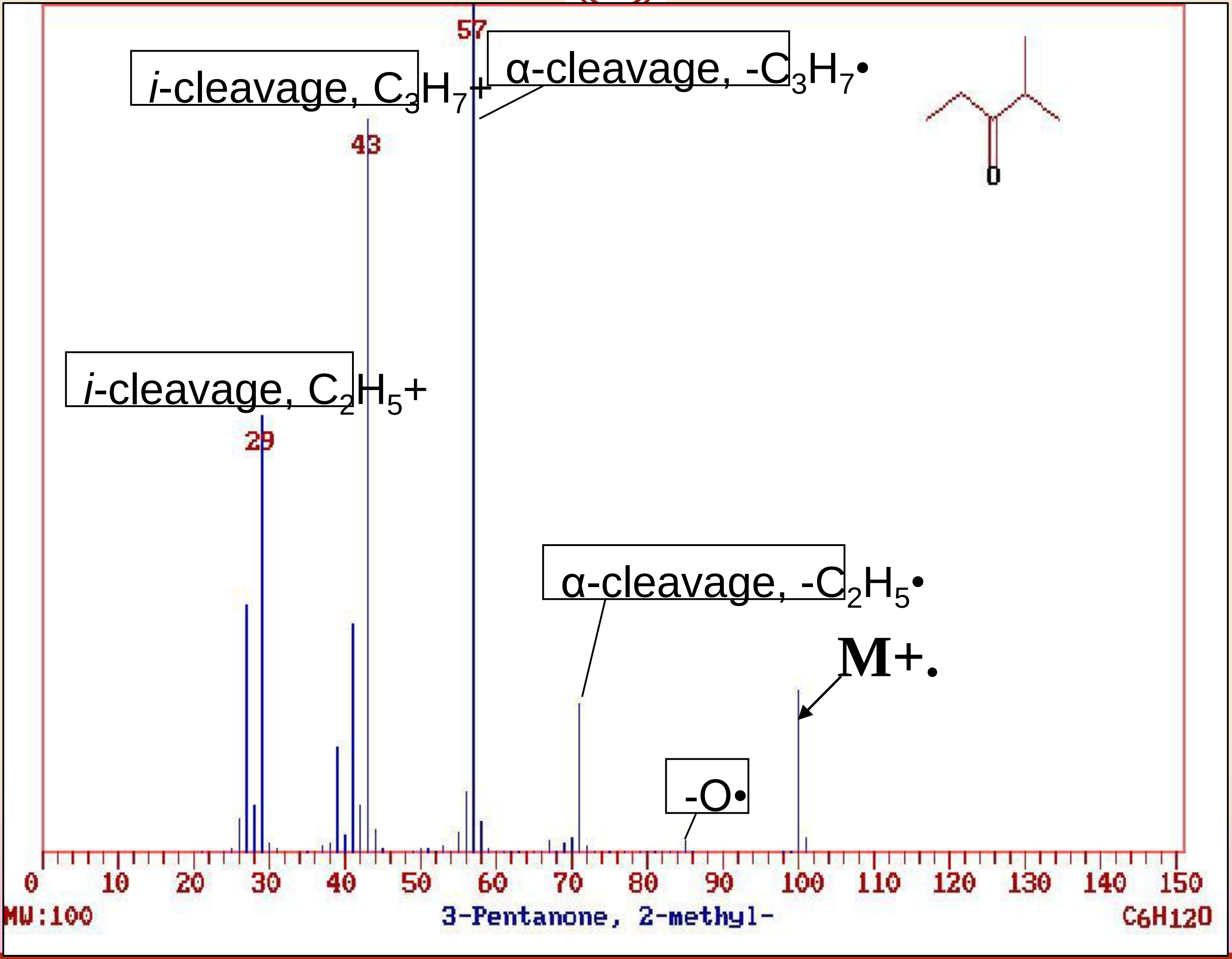
$$\left[CH_3\underset{57}{+}\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_3\right]^{+\cdot} \longrightarrow CH_3CH_2-C\equiv O^+ \;+\; \cdot CH_3$$

radical cation
m/z 72

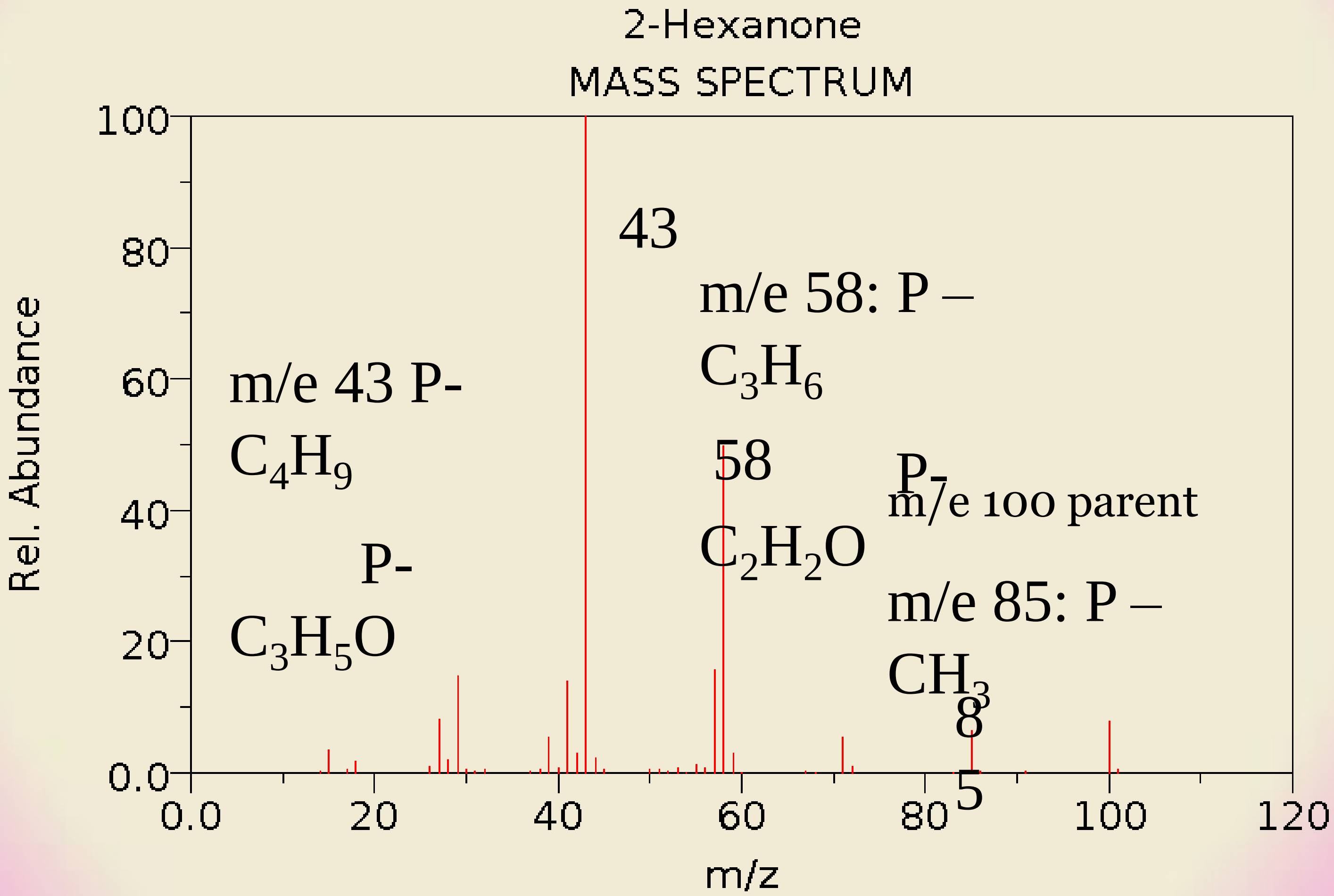
acylium ion
m/z 57

methyl radical
loss of 15

Fragmentation Pattern of Carbonyls



Fragmentation Pattern of Carbonyls



43

m/e 58: P – C_3H_6

m/e 43 P- C_4H_9

58

P-

m/e 100 parent

C_2H_2O

P-

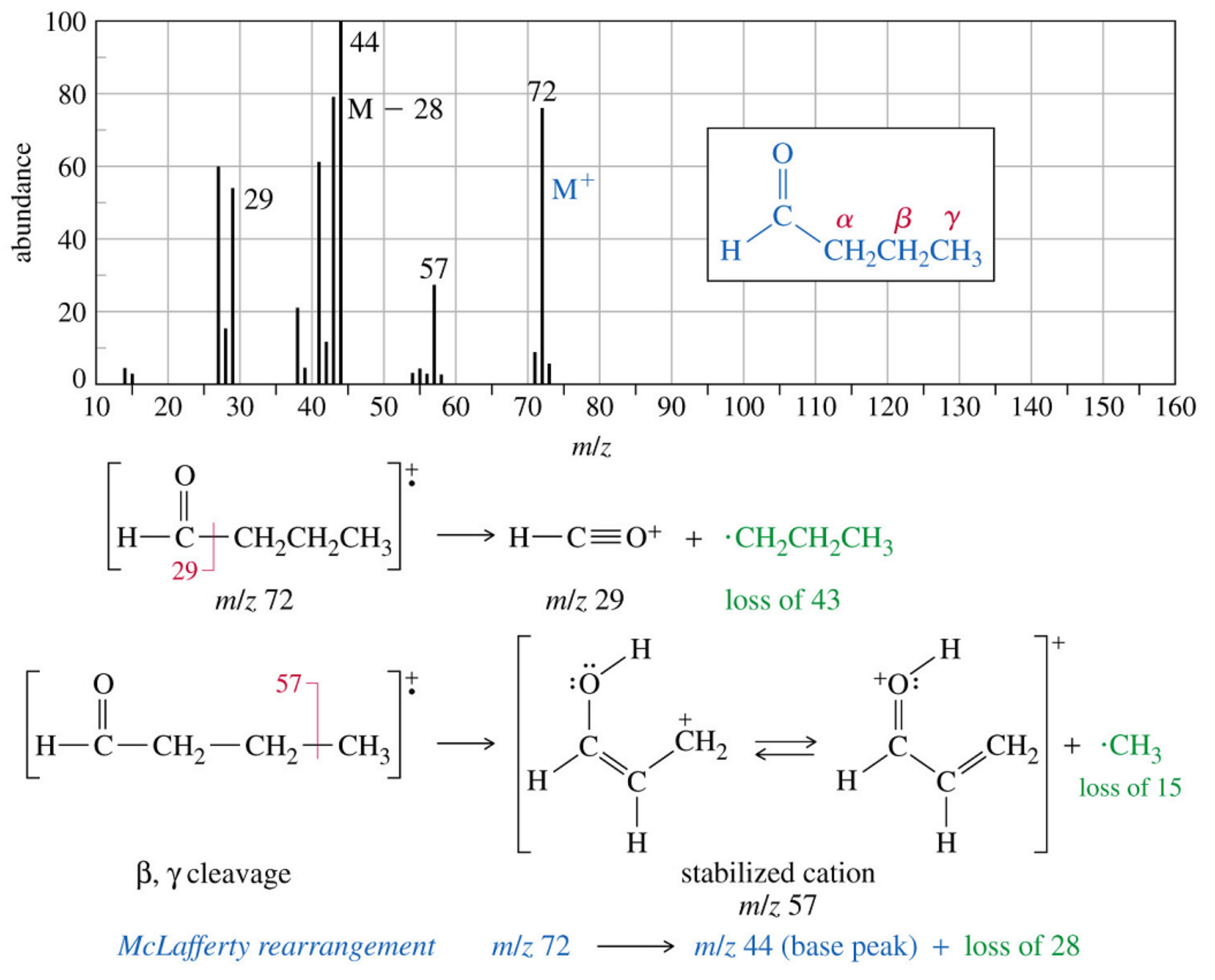
C_3H_5O

m/e 85: P – CH_3

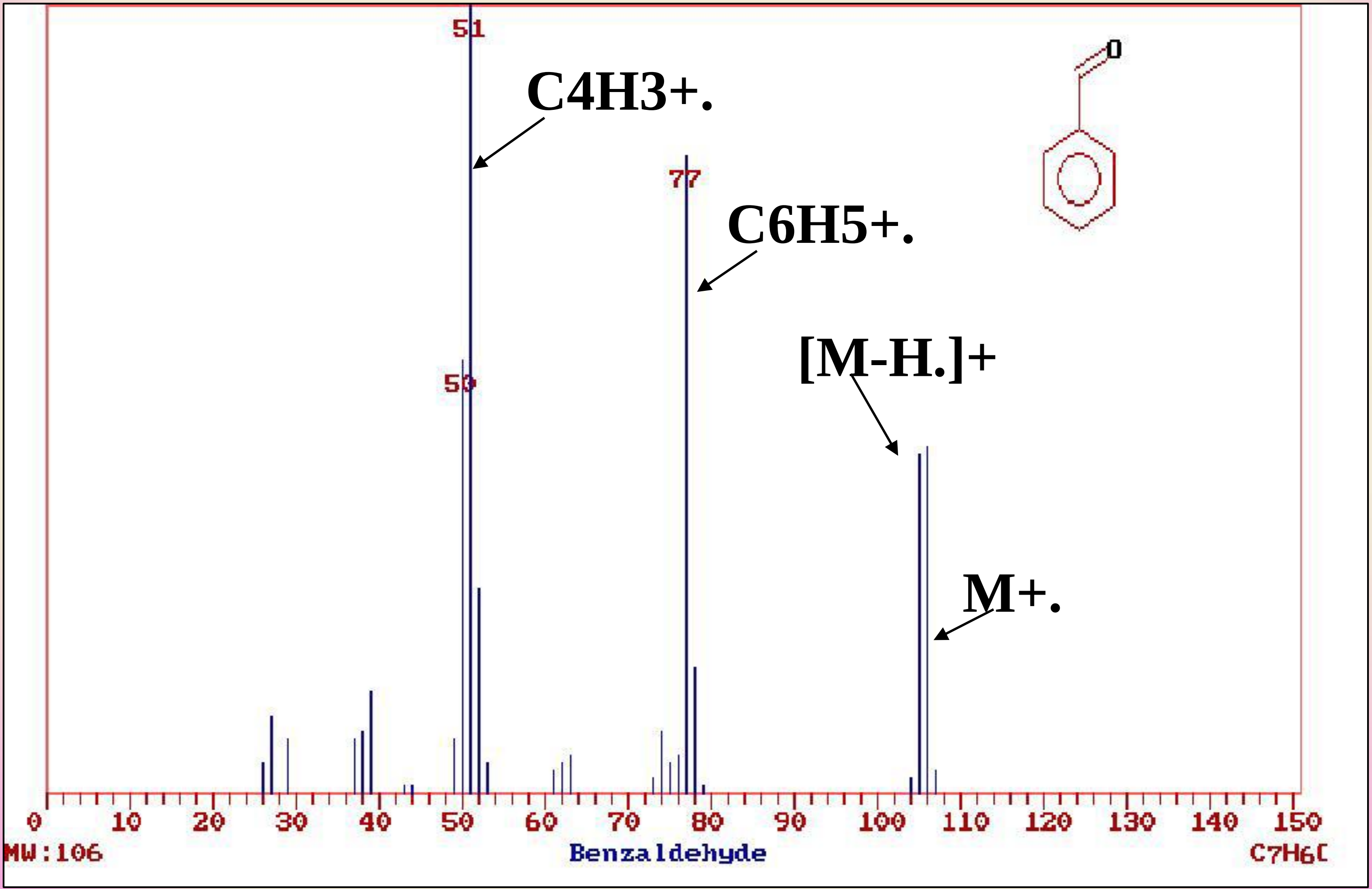
85

NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Fragmentation Pattern of Carbonyls



Fragmentation Pattern of Carbonyls



$C4H3^{+.}$

$C6H5^{+.}$

[M-H.]+

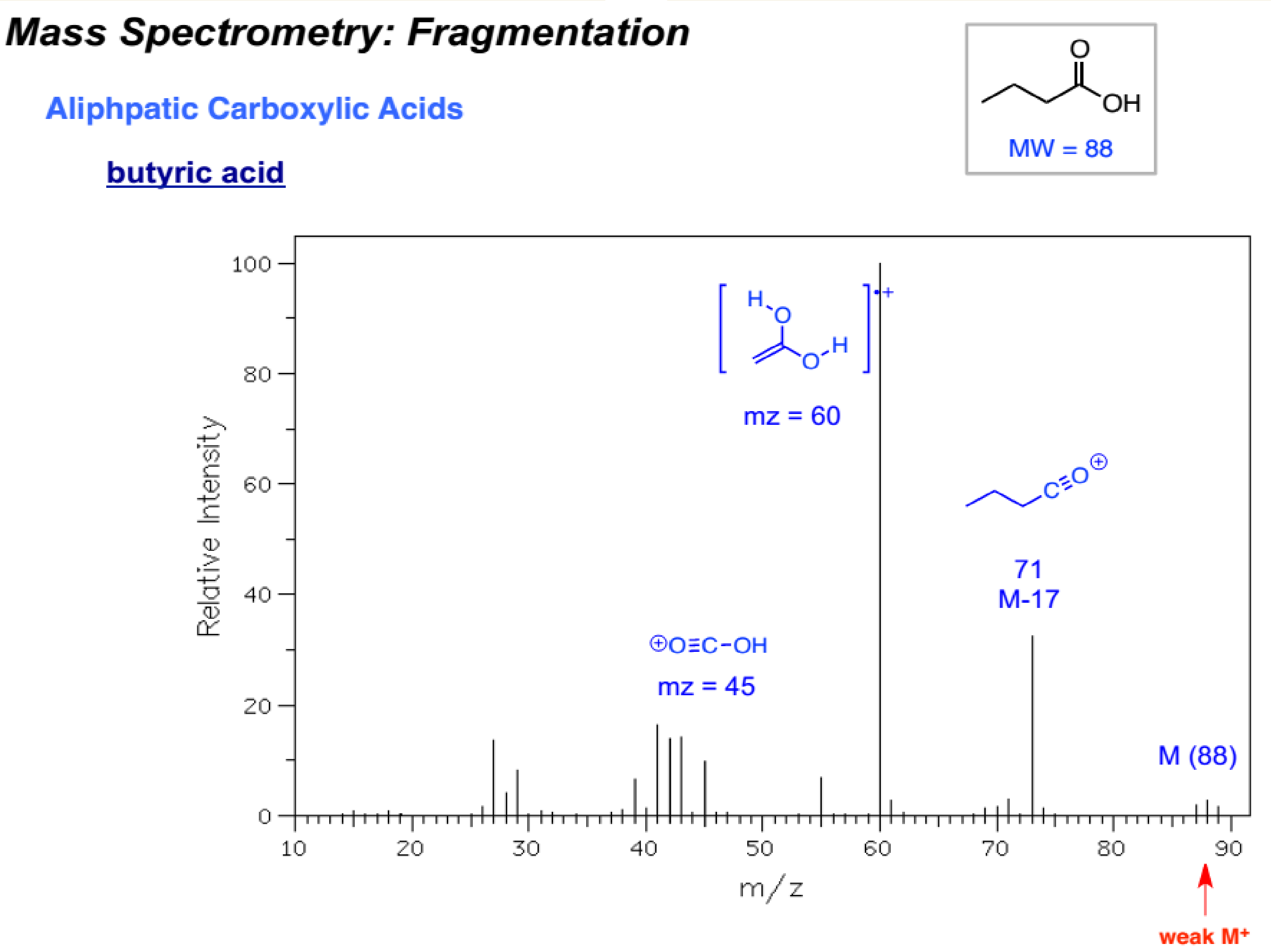
$M^{+.}$

ACIDS, ESTERS AND AMIDES

Fragmentation Pattern of Acid/Ester/Amide

Aliphatic:
M+is weak, and not always visible.
A characteristic m/z 60 peak is often present due to the McLafferty Rearrangement.
Bonds α αα αto carbonyl also frequently break to give M-OH and M-CO2H peaks.
Aromatic Acids: M+is very prominent. Common peaks are loss of OH (M-17) and loss of CO2H (M-45).
If an ortho hydrogen-bearing group is present, loss of water (M-18) is visible as well.

Fragmentation Pattern of Acid/Ester/Amide



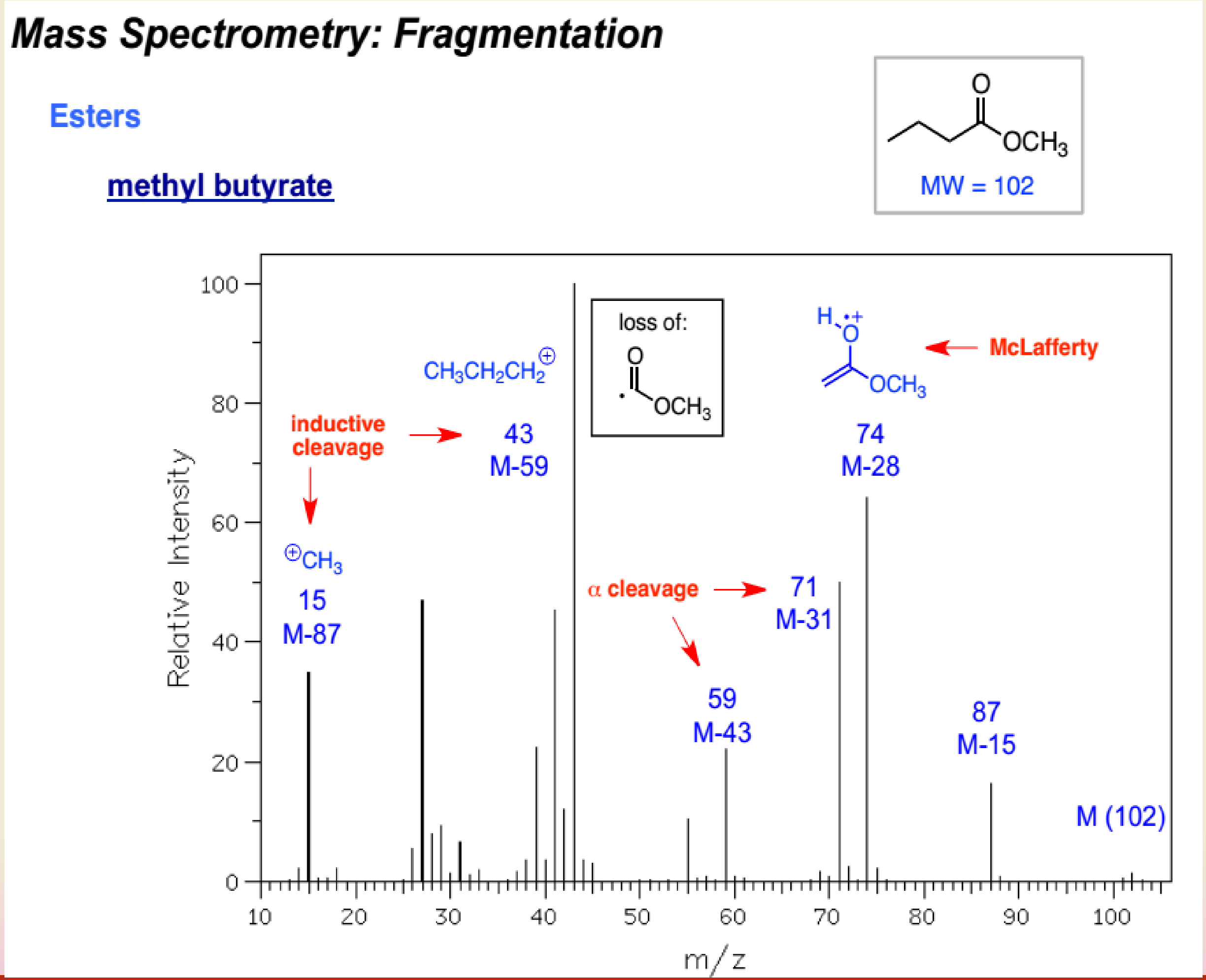
Mass Spectrometry: Fragmentation

Aliphpatic Carboxylic Acids

butyric acid

MW = 88

Fragmentation Pattern of Acid/Ester/Amide

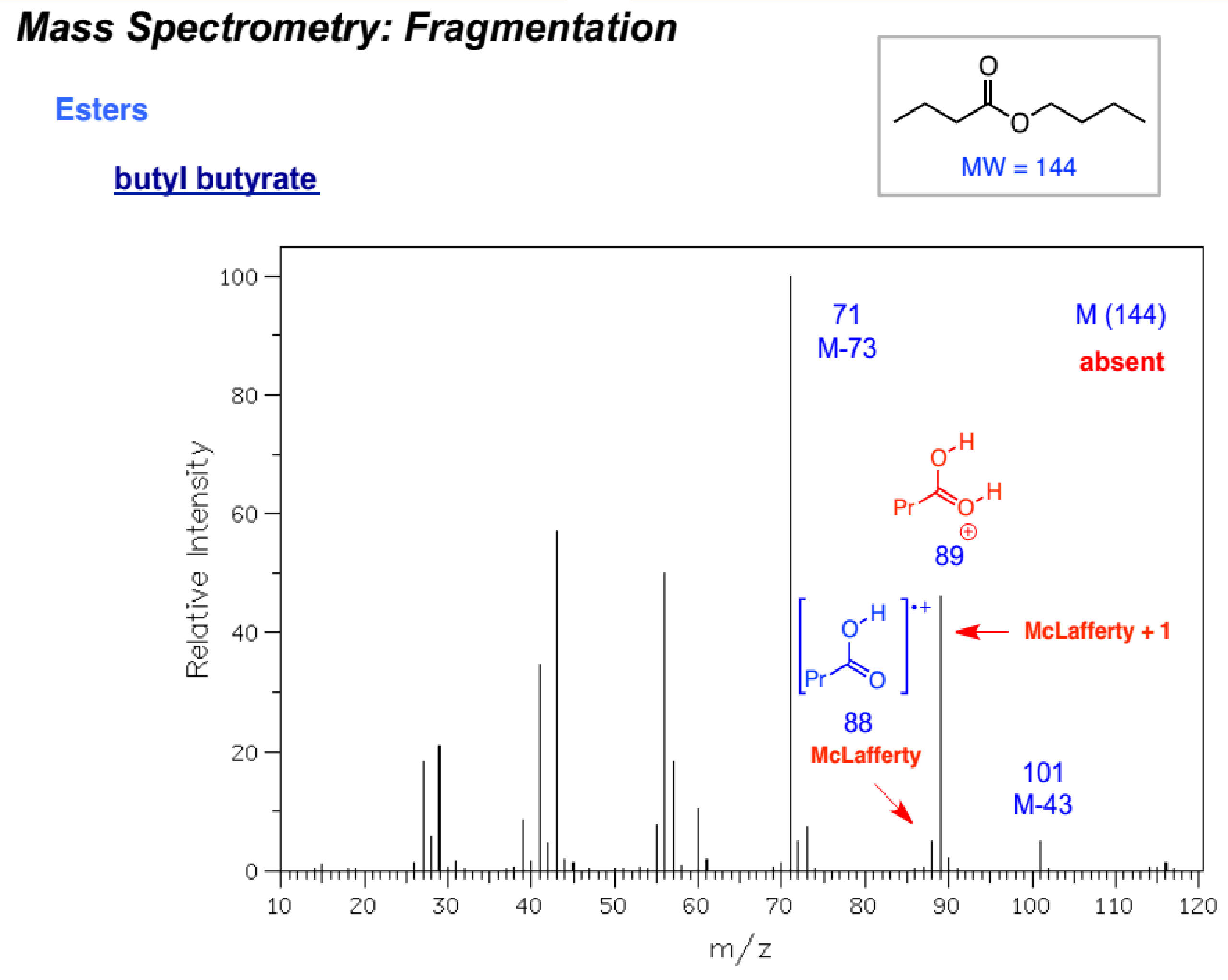


Mass Spectrometry: Fragmentation

Esters

methyl butyrate

Fragmentation Pattern of Acid/Ester/Amide

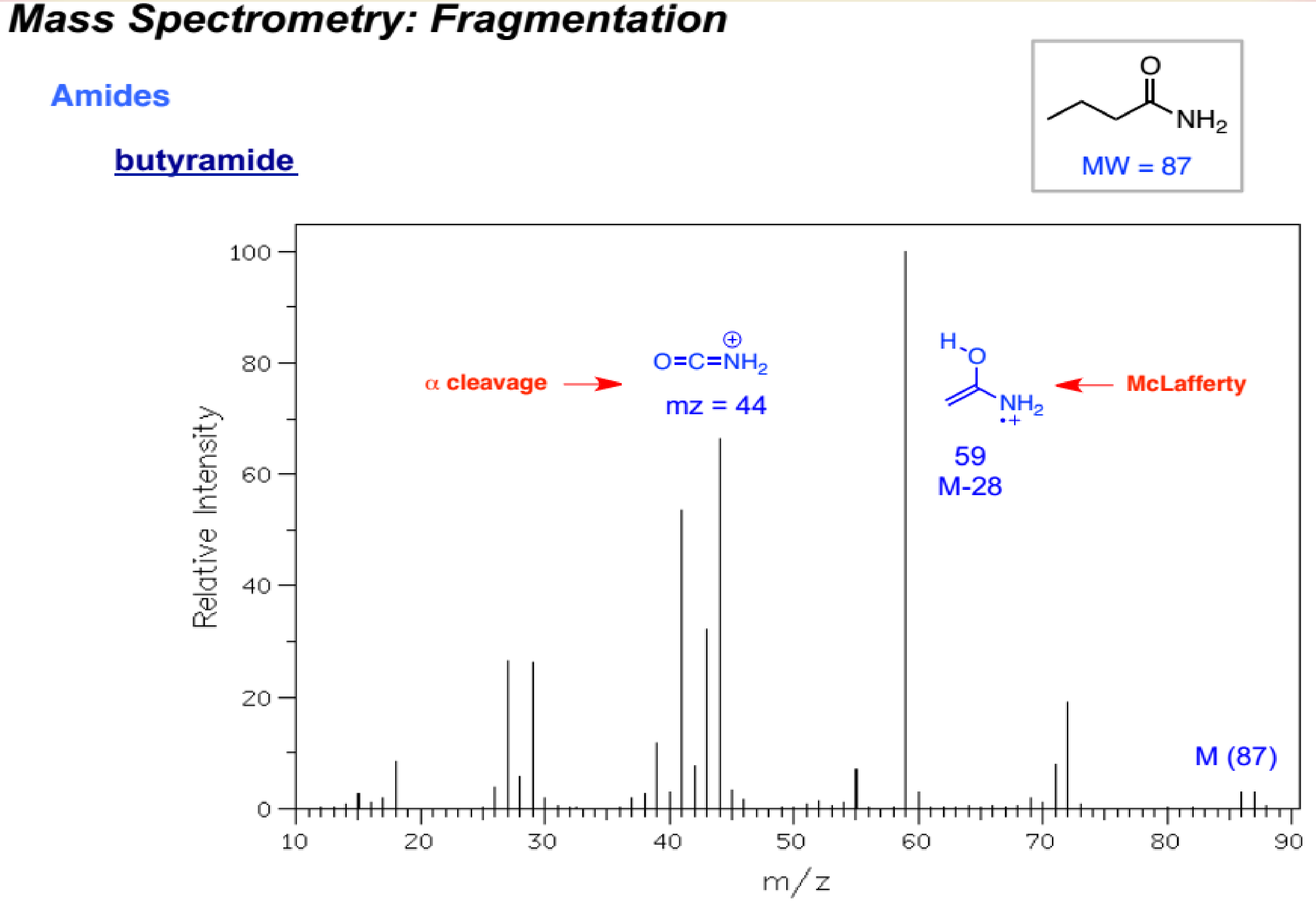


Mass Spectrometry: Fragmentation

Esters

butyl butyrate

Fragmentation Pattern of Acid/Ester/Amide



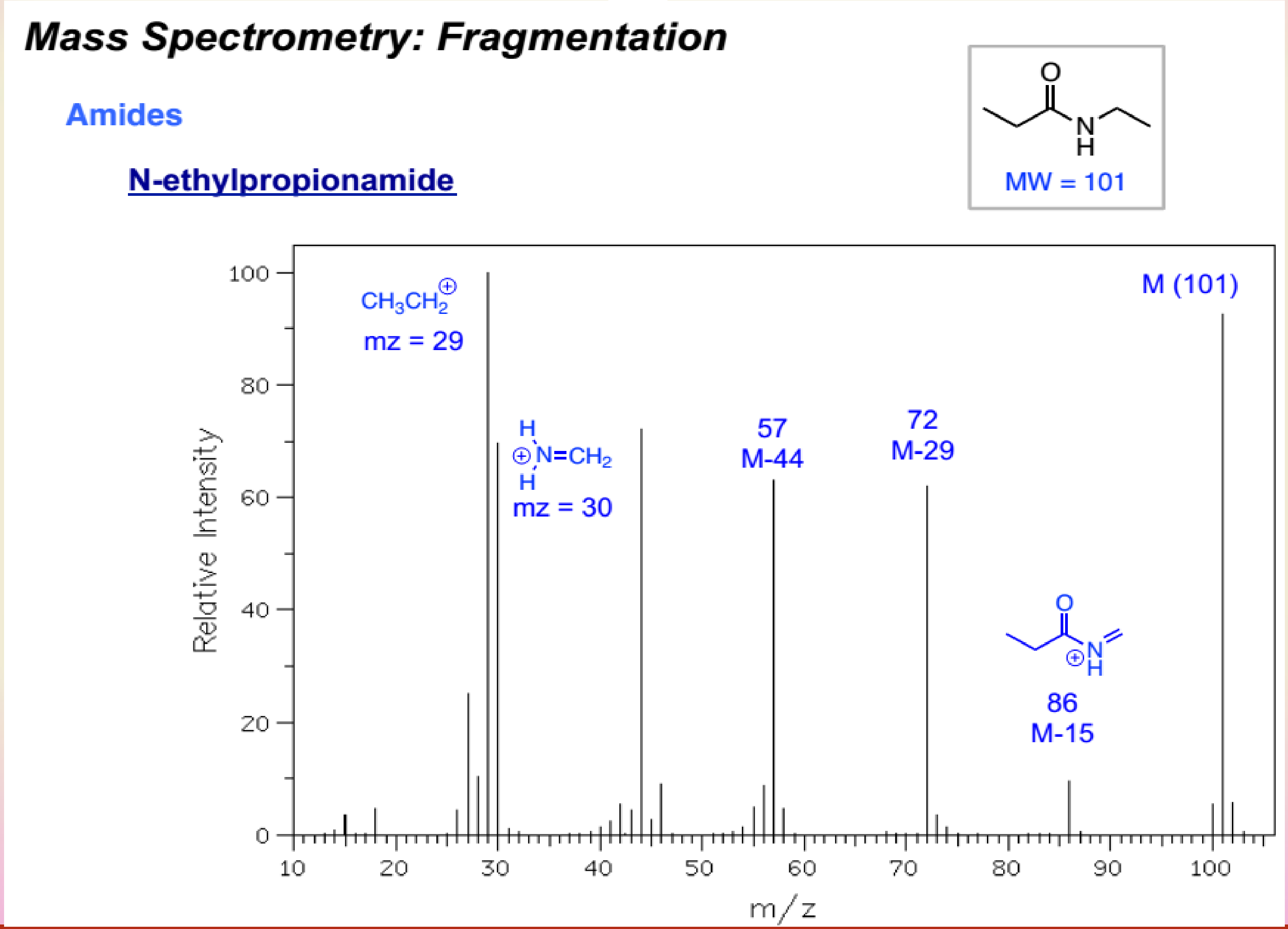
Mass Spectrometry: Fragmentation

Amides

butyramide

MW = 87

Fragmentation Pattern of Acid/Ester/Amide



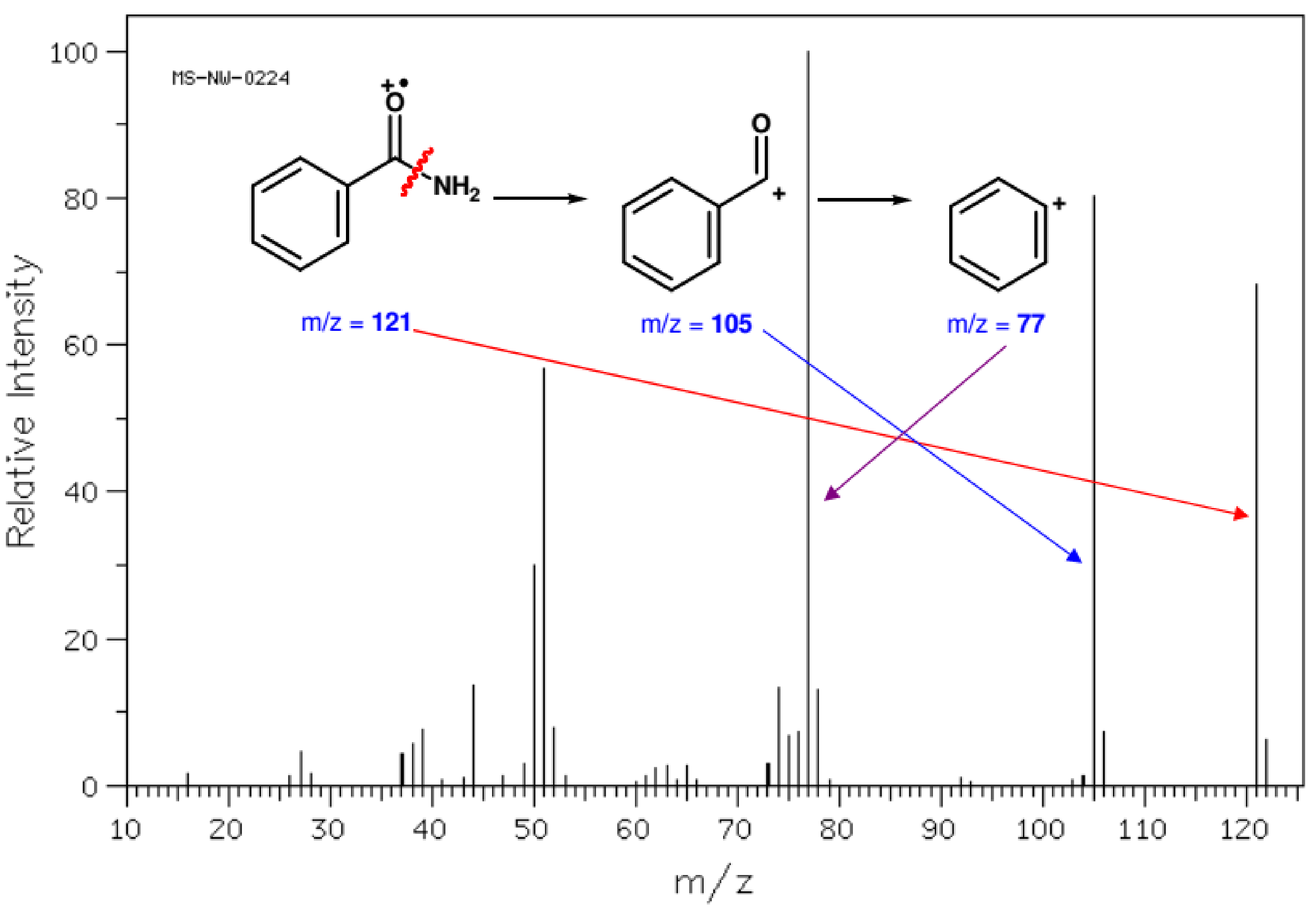
Mass Spectrometry: Fragmentation

Amides

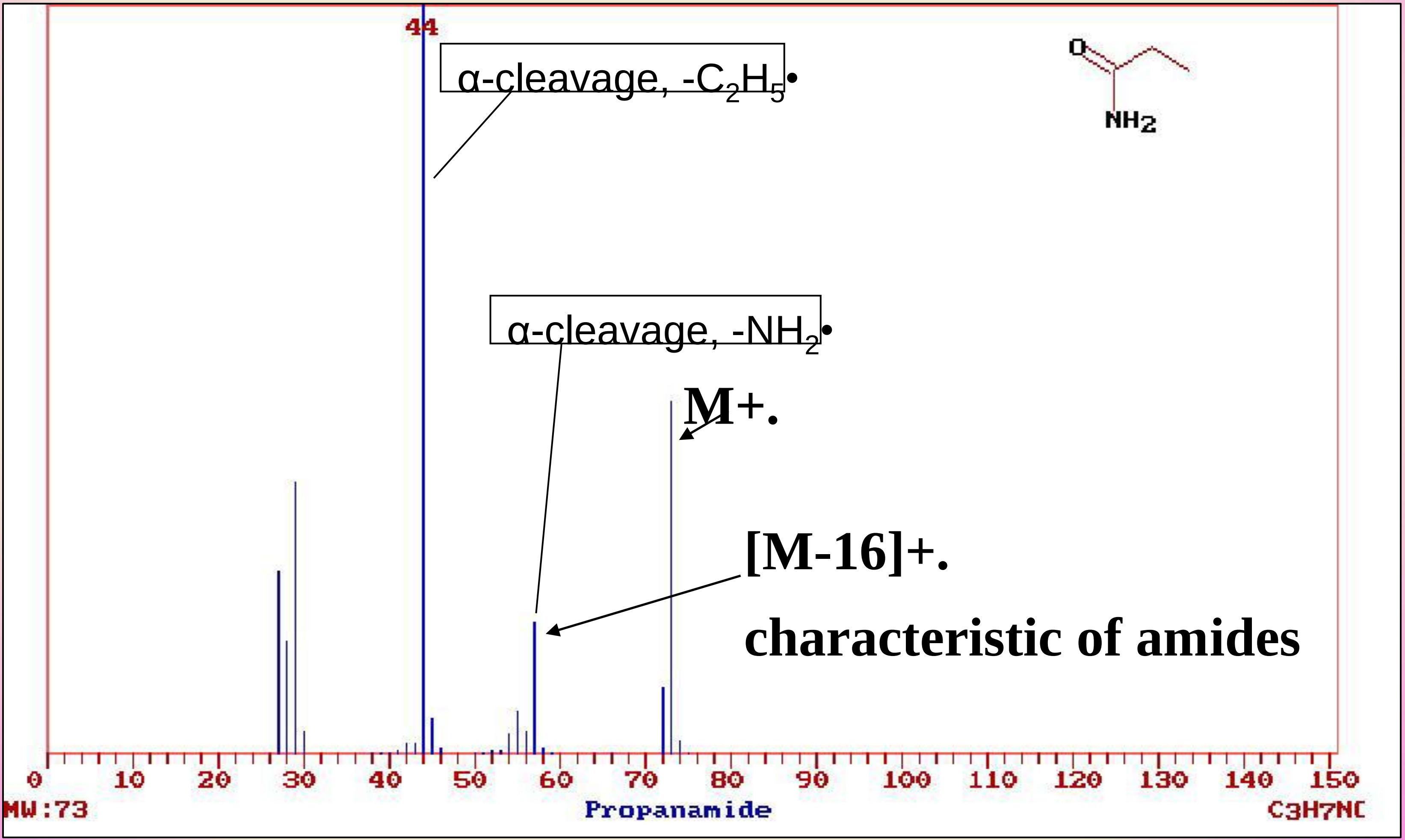
N-ethylpropionamide

MW = 101

Fragmentation Pattern of Acid/Ester/Amide



Fragmentation Pattern of Acid/Ester/Amide



α-cleavage, $-C_2H_5$•

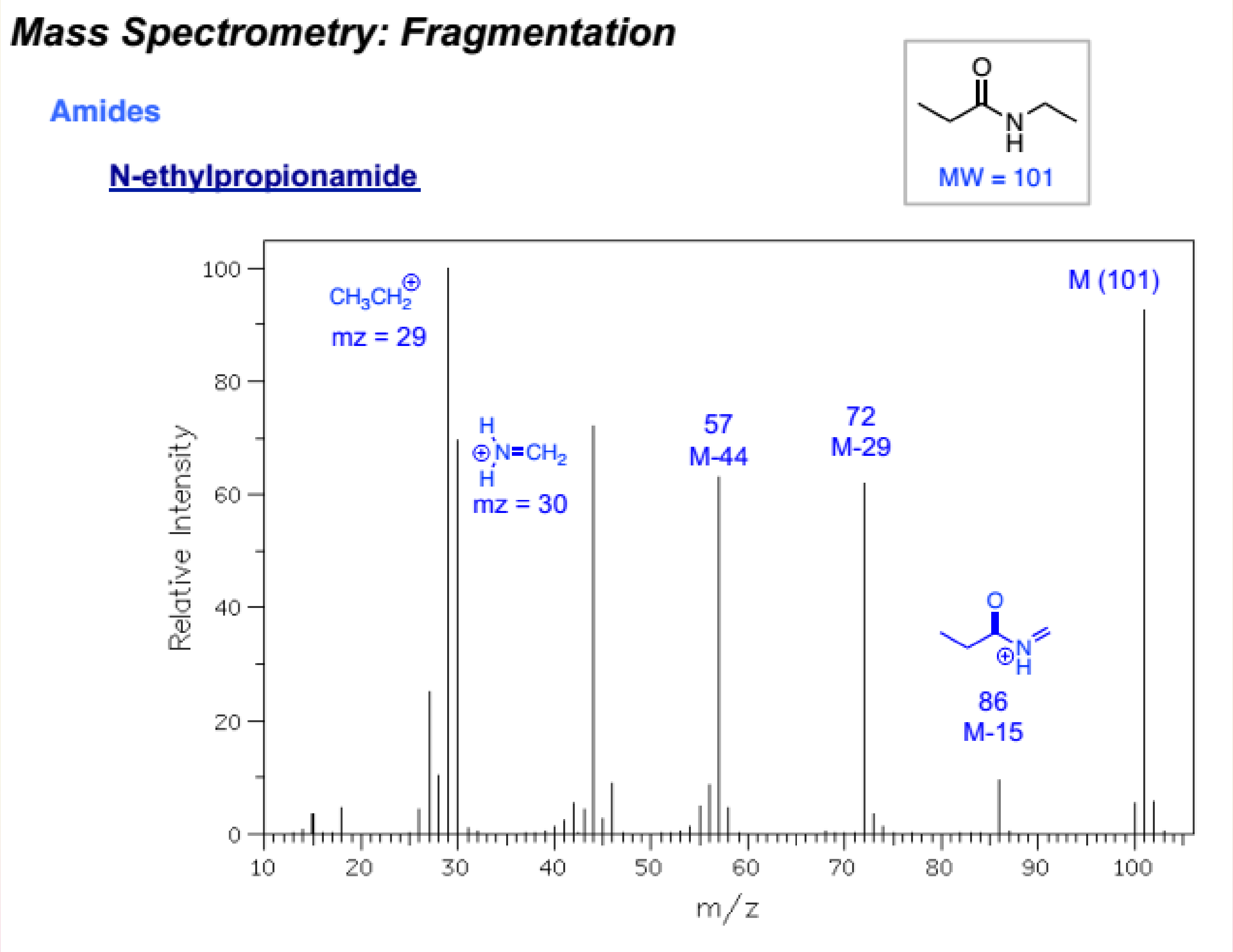
α-cleavage, $-NH_2$•

M+.

[M-16]+.

characteristic of amides

Fragmentation Pattern of Acid/Ester/Amide



Mass Spectrometry: Fragmentation

Amides

N-ethylpropionamide

MW = 101

HRMS (Determination of mol formula)

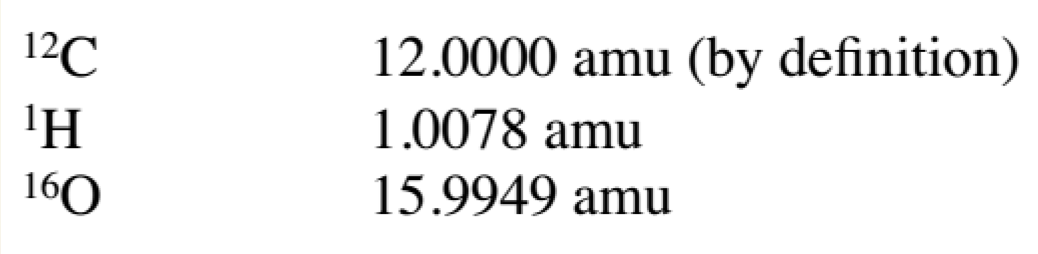
High Resolution Mass Spectrometry (HRMS): It is highly sensitivity mass spectrometers, used to determine the exact molecular formula of compounds.

HRMS can detect particle masses with an accuracy of 1/20,000 , therefore > 0.0001 amu(atomic mass units)!

In can used to distinguish compounds with a similar rough mass, but with a different molecular formula!

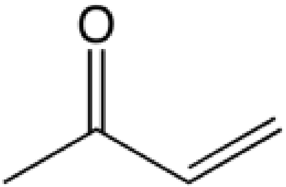
Differentiating Structures Using HRMS: Many structures may have the same integer value molecular weight, but different molecular formulas!

These structures can be differentiated with HRMS



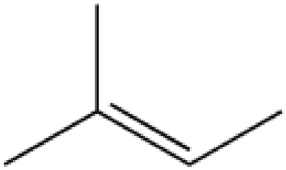
^{12}C	12.0000 amu (by definition)
^{1}H	1.0078 amu
^{16}O	15.9949 amu

For example:



$C_4H_6O_1$

70.0418 amu

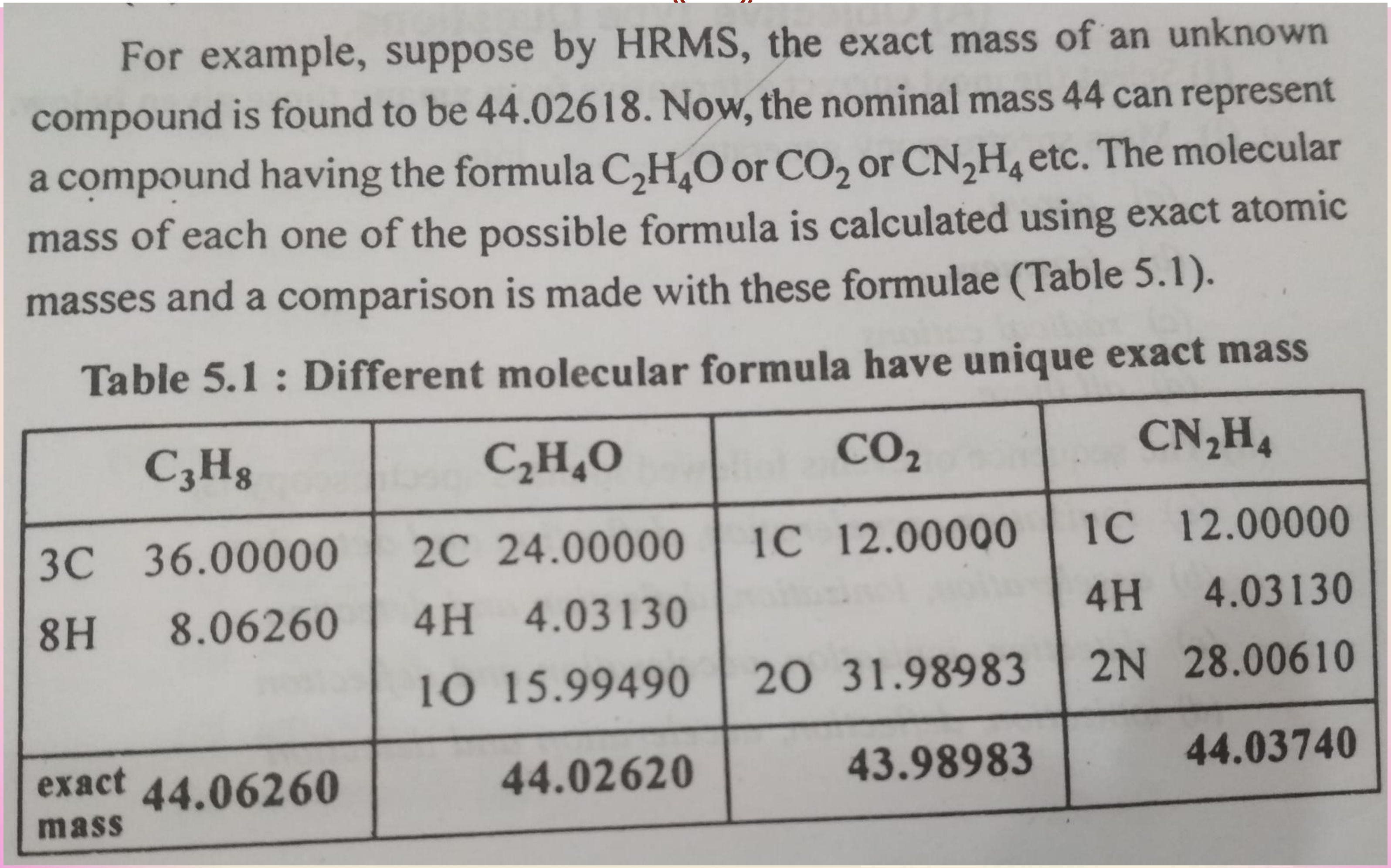


C_5H_{10}

70.0783 amu

$C_3H_6N_2$

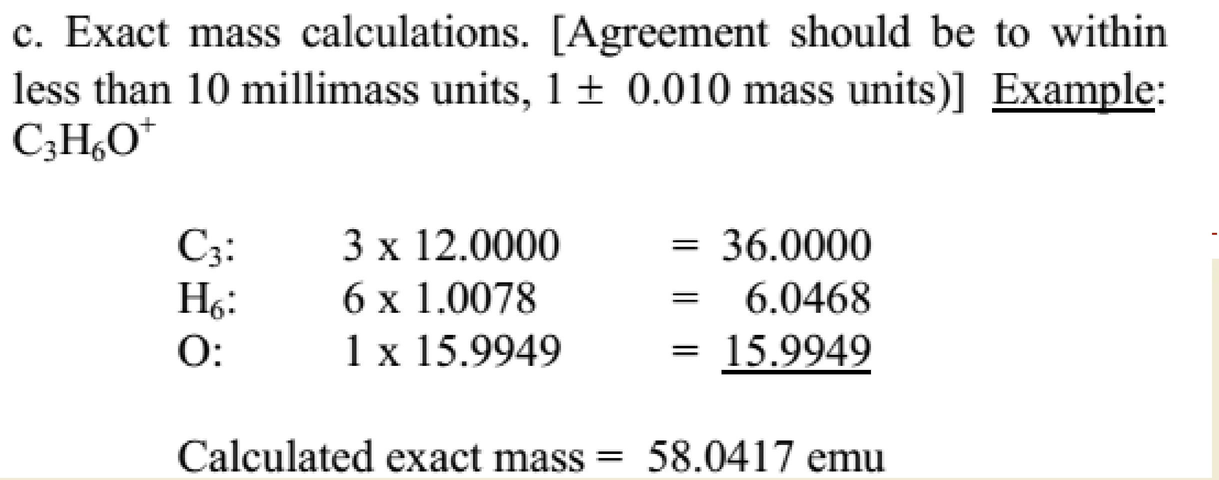
70.0531 amu



For example, suppose by HRMS, the exact mass of an unknown compound is found to be 44.02618. Now, the nominal mass 44 can represent a compound having the formula C_2H_4O or CO_2 or CN_2H_4 etc. The molecular mass of each one of the possible formula is calculated using exact atomic masses and a comparison is made with these formulae (Table 5.1).

Table 5.1 : Different molecular formula have unique exact mass

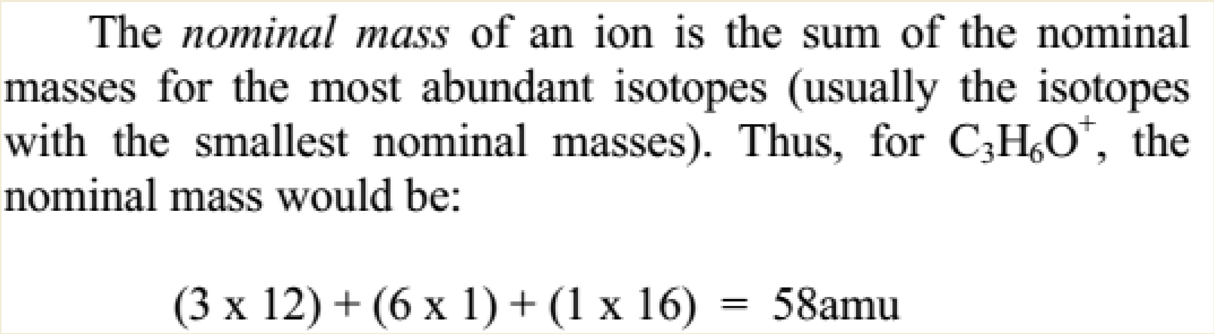
C_3H_8	C_2H_4O	CO_2	CN_2H_4
3C 36.00000 8H 8.06260	2C 24.00000 4H 4.03130 1O 15.99490	1C 12.00000 2O 31.98983	1C 12.00000 4H 4.03130 2N 28.00610
exact mass **44.06260**	**44.02620**	**43.98983**	**44.03740**



c. Exact mass calculations. [Agreement should be to within less than 10 millimass units, 1 ± 0.010 mass units)] <u>Example</u>: $C_3H_6O^+$

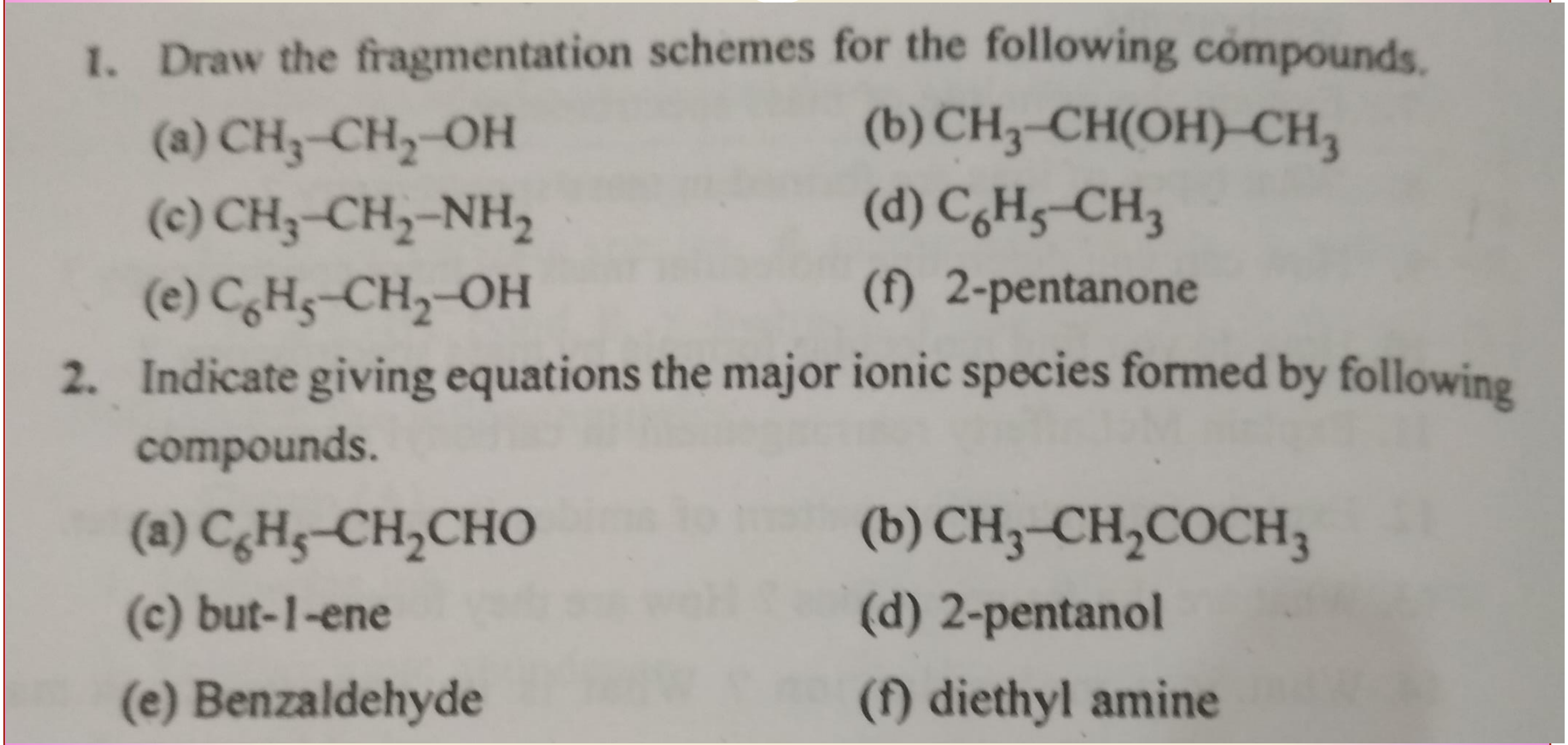
C_3: 3 x 12.0000 = 36.0000
H_6: 6 x 1.0078 = 6.0468
O: 1 x 15.9949 = $\underline{15.9949}$

Calculated exact mass = 58.0417 emu



The *nominal mass* of an ion is the sum of the nominal masses for the most abundant isotopes (usually the isotopes with the smallest nominal masses). Thus, for $C_3H_6O^+$, the nominal mass would be:

(3 x 12) + (6 x 1) + (1 x 16) = 58amu



1. Draw the fragmentation schemes for the following compounds.

   (a) CH_3–CH_2–OH (b) CH_3–CH(OH)–CH_3

   (c) CH_3–CH_2–NH_2 (d) C_6H_5–CH_3

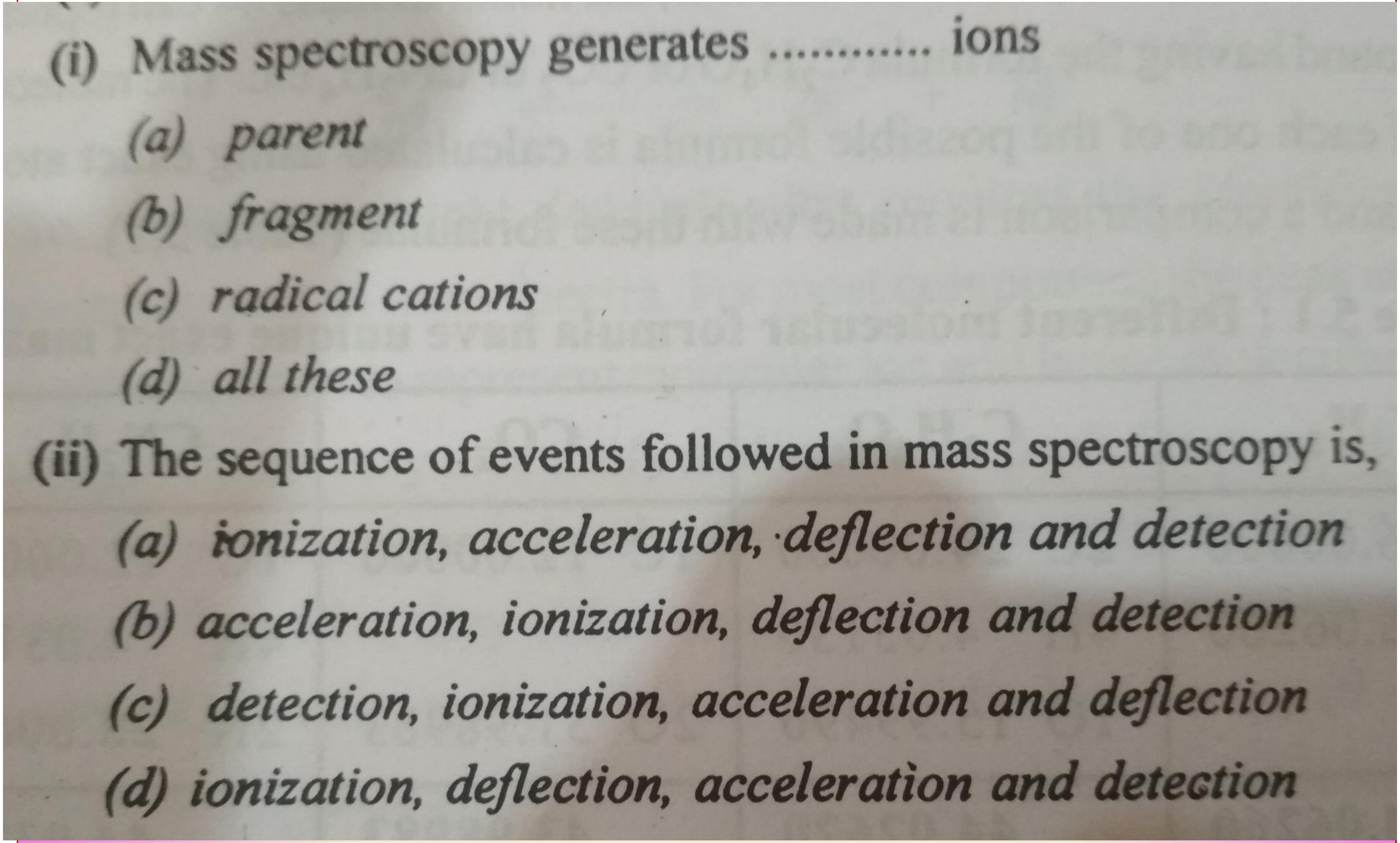
   (e) C_6H_5–CH_2–OH (f) 2-pentanone

2. Indicate giving equations the major ionic species formed by following compounds.

   (a) C_6H_5–CH_2CHO (b) CH_3–$CH_2$$COCH_3$

   (c) but-1-ene (d) 2-pentanol

   (e) Benzaldehyde (f) diethyl amine

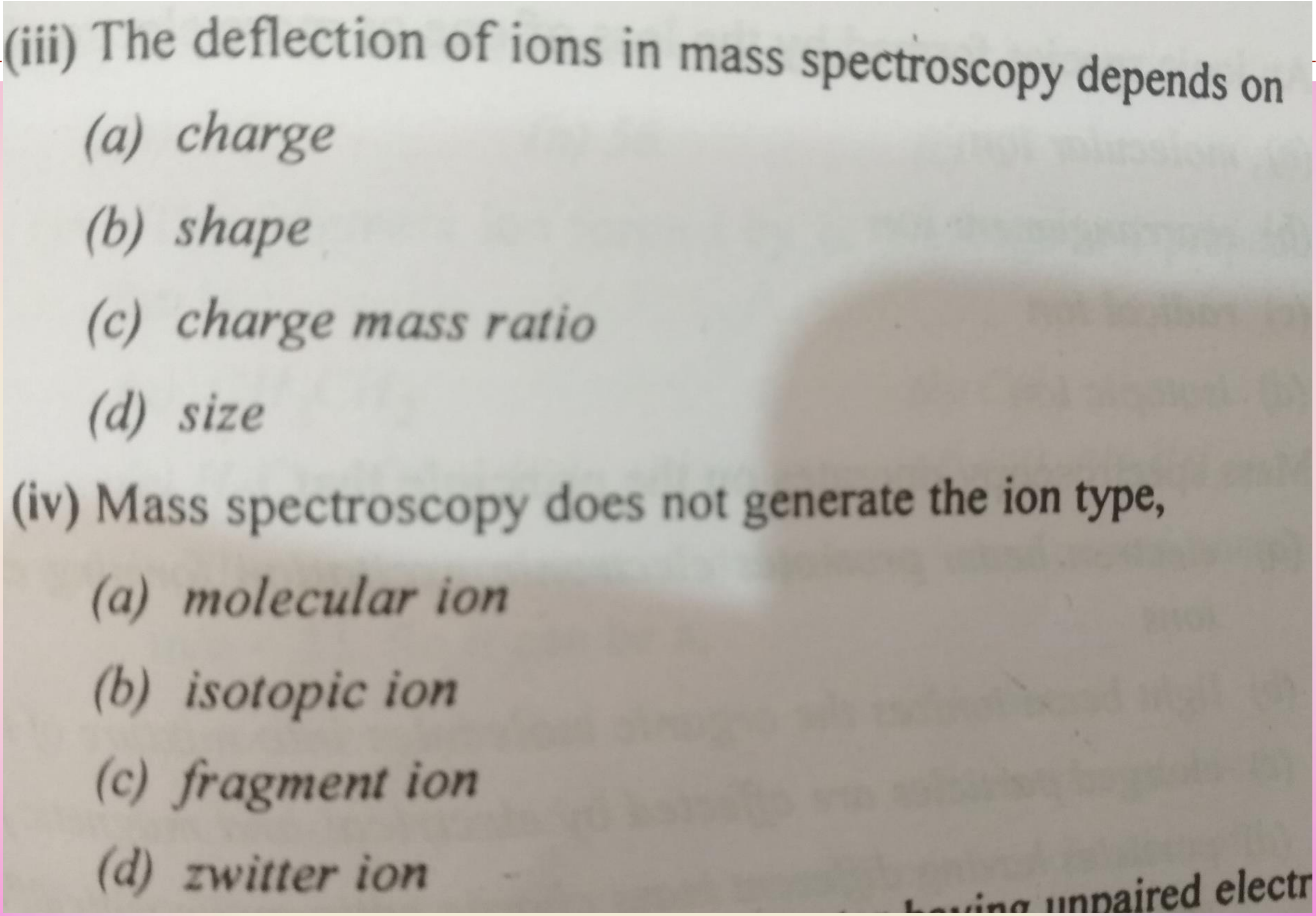


(i) Mass spectroscopy generates .... ions

- *(a) parent*
- *(b) fragment*
- *(c) radical cations*
- *(d) all these*

(ii) The sequence of events followed in mass spectroscopy is,

- *(a) ionization, acceleration, deflection and detection*
- *(b) acceleration, ionization, deflection and detection*
- *(c) detection, ionization, acceleration and deflection*
- *(d) ionization, deflection, acceleration and detection*



(iii) The deflection of ions in mass spectroscopy depends on

(a) *charge*

(b) *shape*

(c) *charge mass ratio*

(d) *size*

(iv) Mass spectroscopy does not generate the ion type,

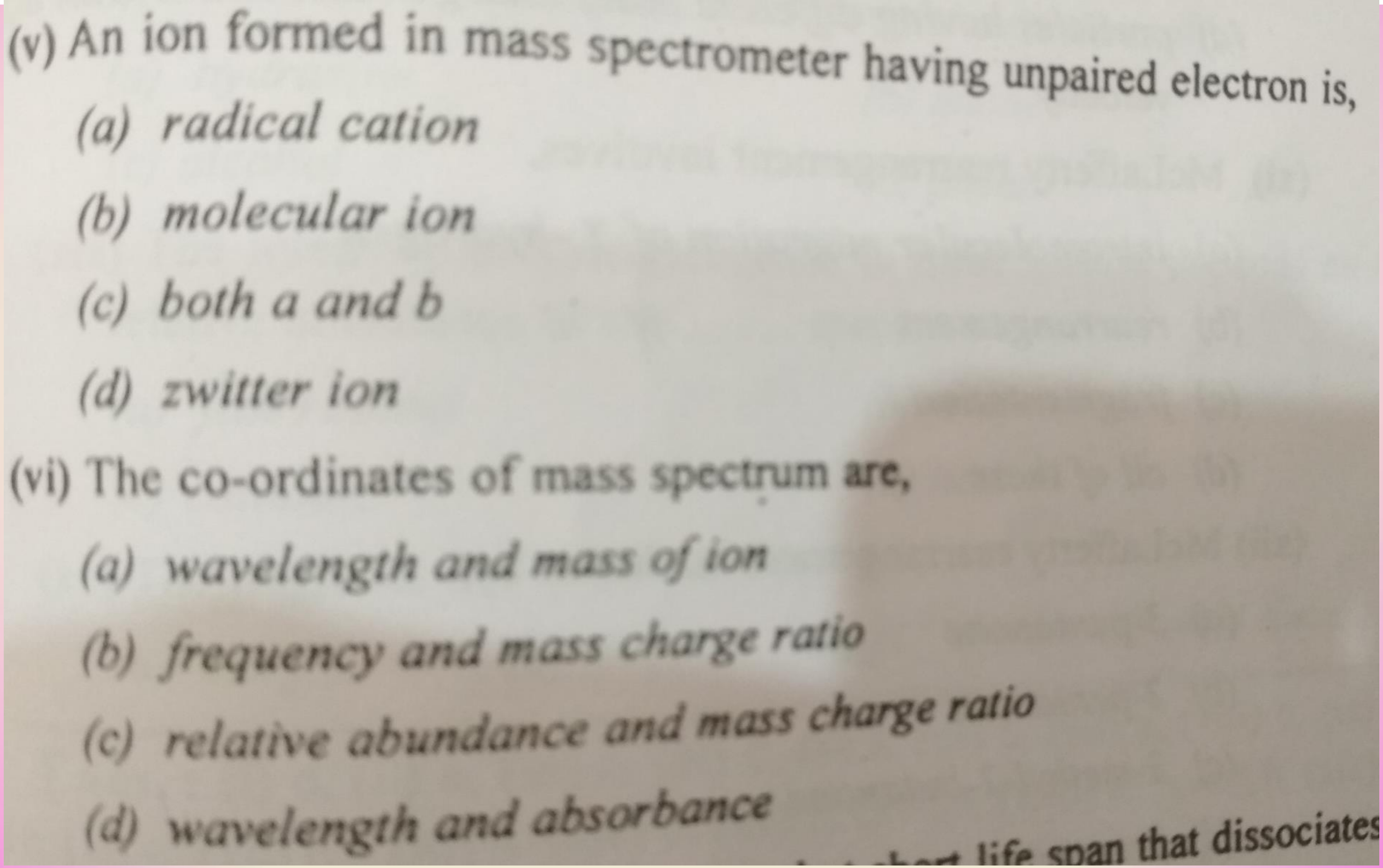
(a) *molecular ion*

(b) *isotopic ion*

(c) *fragment ion*

(d) *zwitter ion*

having unpaired electr



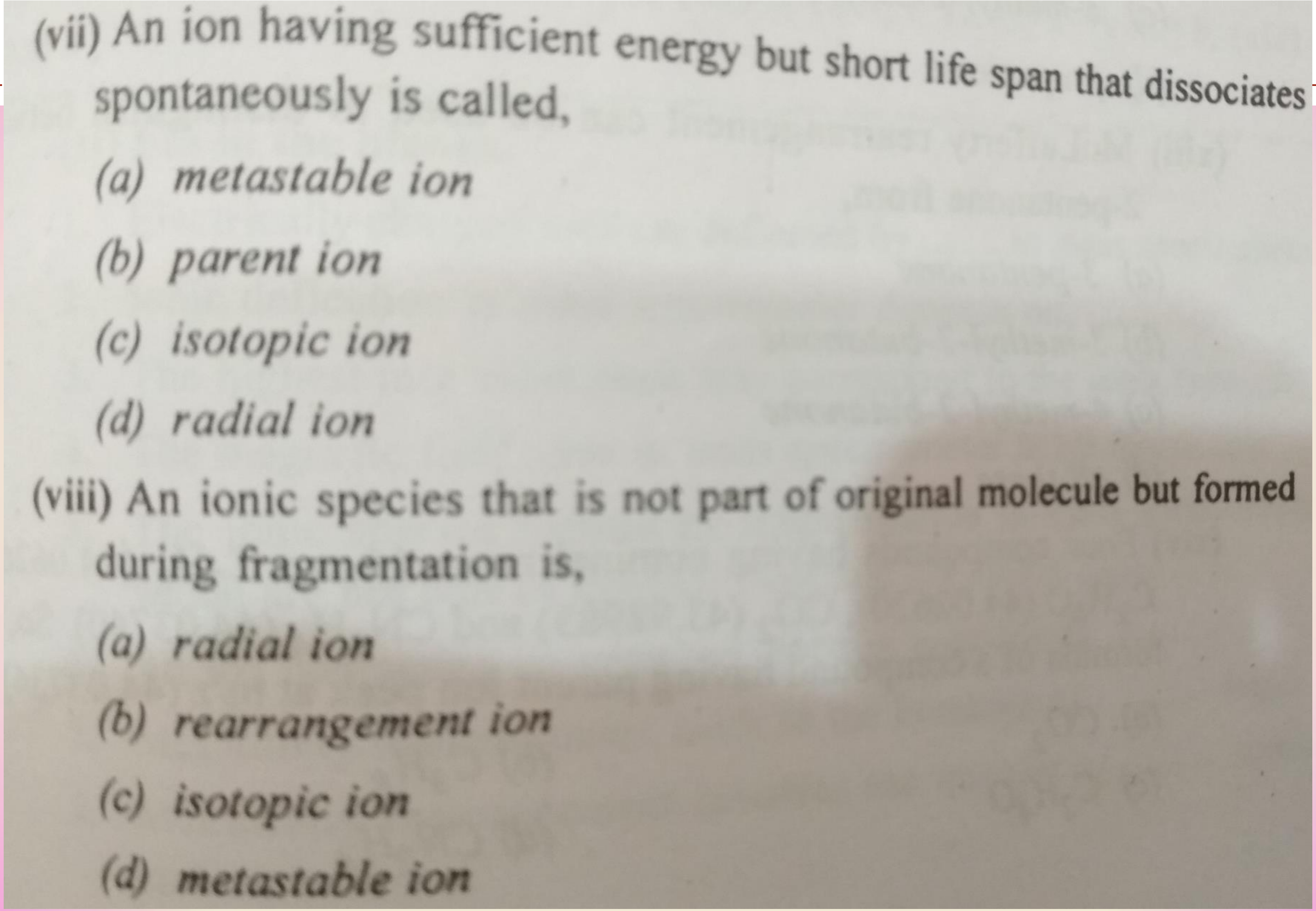
(v) An ion formed in mass spectrometer having unpaired electron is,

- *(a) radical cation*
- *(b) molecular ion*
- *(c) both a and b*
- *(d) zwitter ion*

(vi) The co-ordinates of mass spectrum are,

- *(a) wavelength and mass of ion*
- *(b) frequency and mass charge ratio*
- *(c) relative abundance and mass charge ratio*
- *(d) wavelength and absorbance*

life span that dissociates



(vii) An ion having sufficient energy but short life span that dissociates spontaneously is called,

(a) *metastable ion*

(b) *parent ion*

(c) *isotopic ion*

(d) *radial ion*

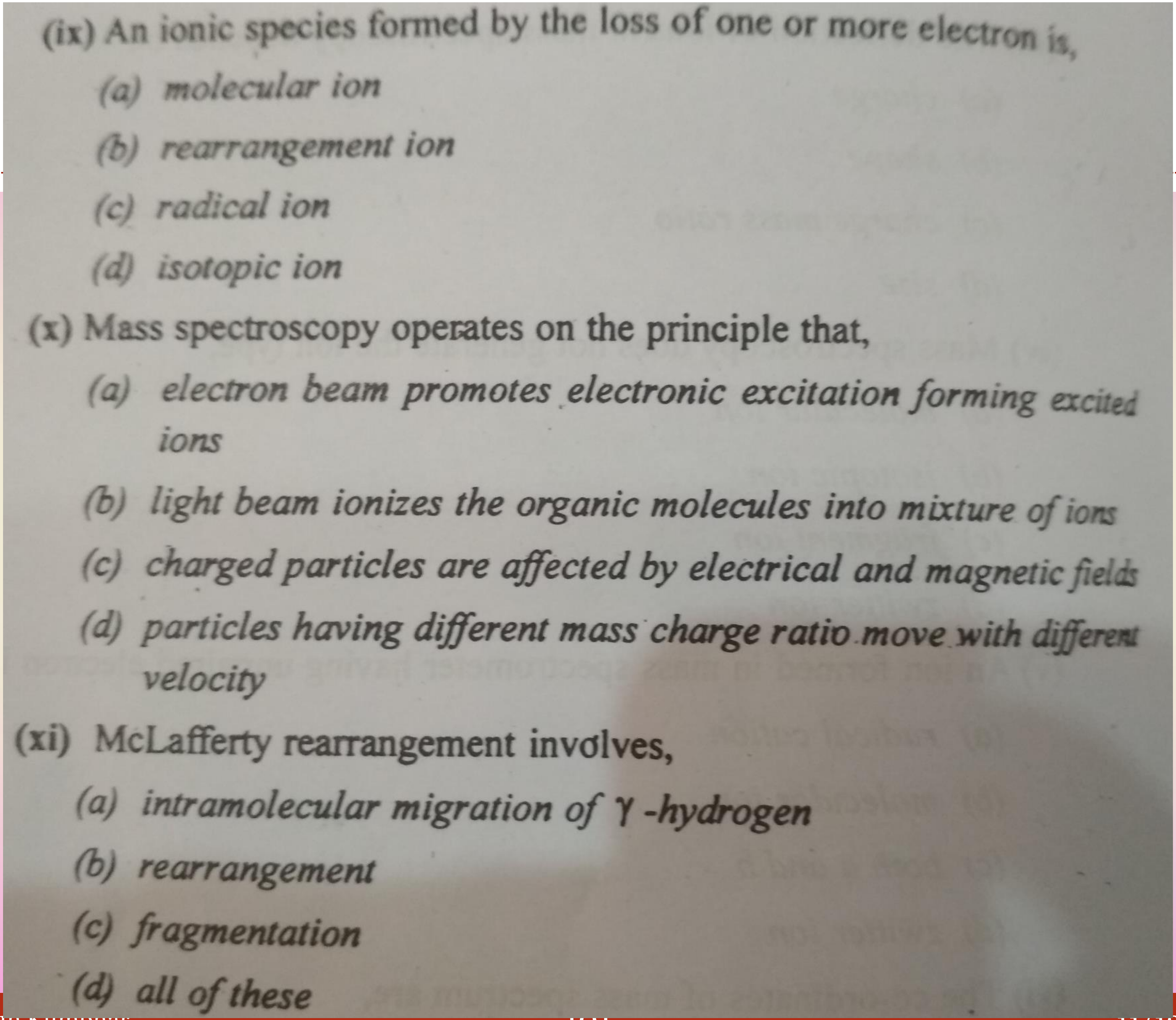
(viii) An ionic species that is not part of original molecule but formed during fragmentation is,

(a) *radial ion*

(b) *rearrangement ion*

(c) *isotopic ion*

(d) *metastable ion*



(ix) An ionic species formed by the loss of one or more electron is,

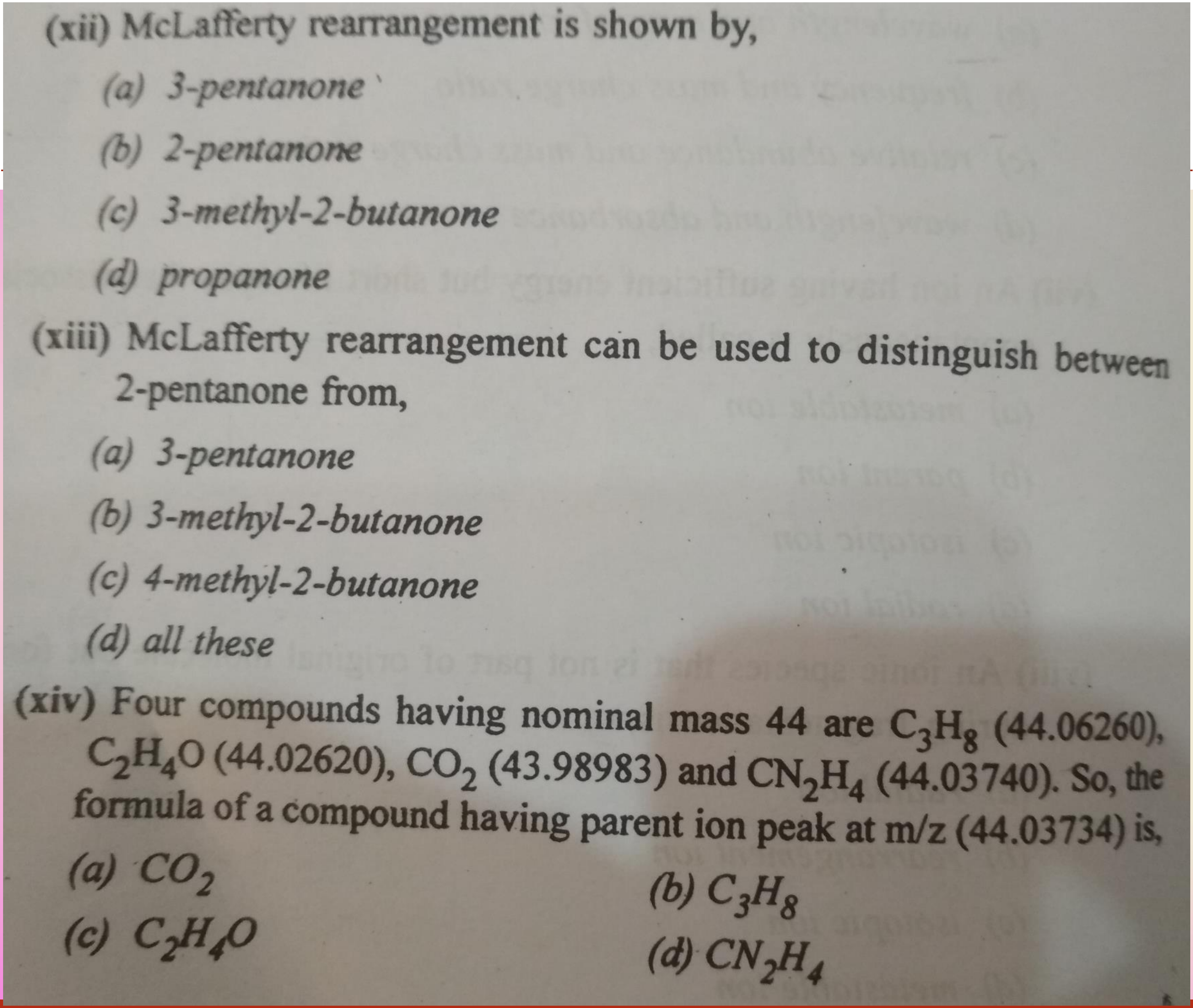
- *(a) molecular ion*
- *(b) rearrangement ion*
- *(c) radical ion*
- *(d) isotopic ion*

(x) Mass spectroscopy operates on the principle that,

- *(a) electron beam promotes electronic excitation forming excited ions*
- *(b) light beam ionizes the organic molecules into mixture of ions*
- *(c) charged particles are affected by electrical and magnetic fields*
- *(d) particles having different mass charge ratio move with different velocity*

(xi) McLafferty rearrangement involves,

- *(a) intramolecular migration of γ -hydrogen*
- *(b) rearrangement*
- *(c) fragmentation*
- *(d) all of these*



(xii) McLafferty rearrangement is shown by,

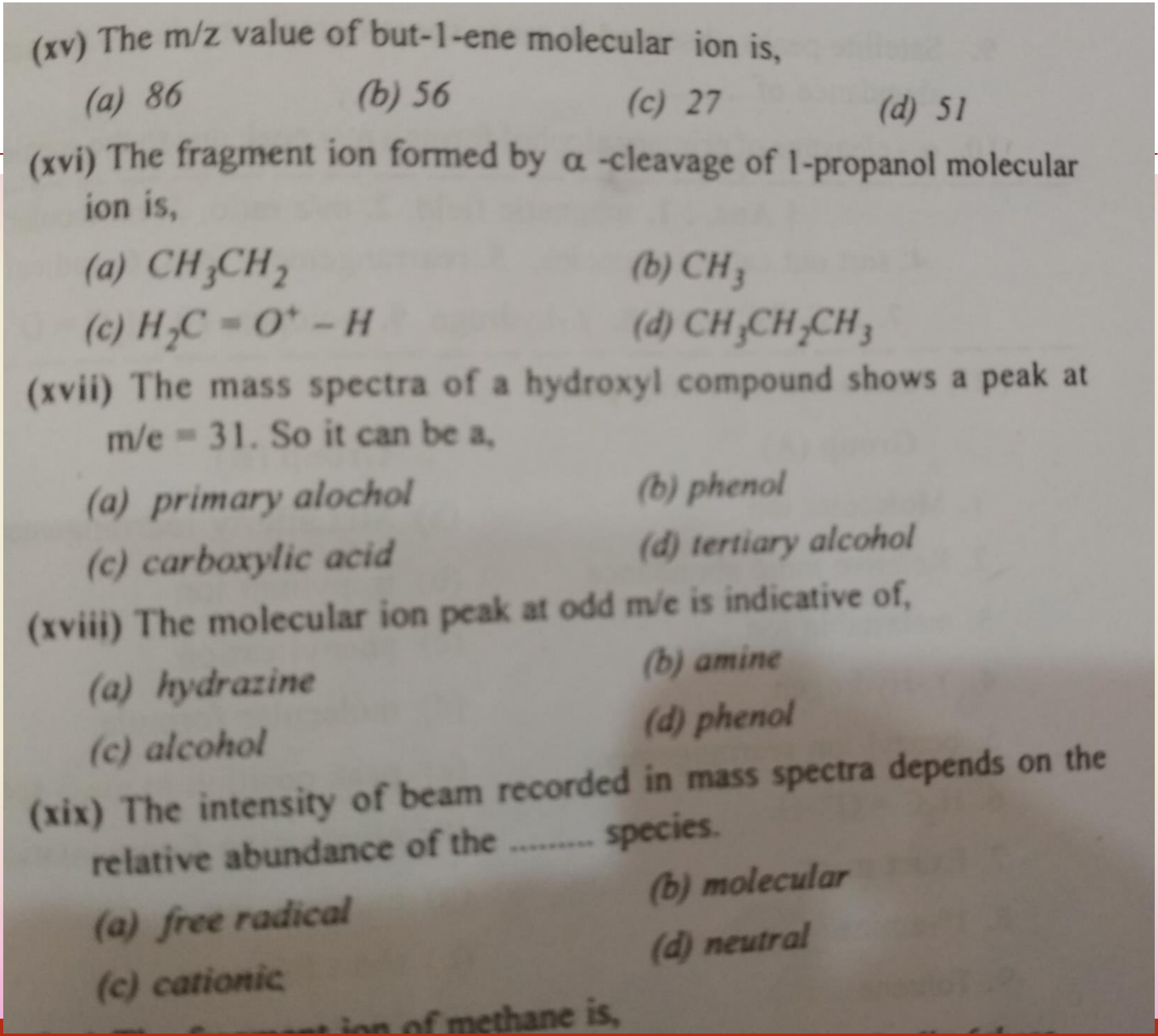
- *(a) 3-pentanone*
- *(b) 2-pentanone*
- *(c) 3-methyl-2-butanone*
- *(d) propanone*

(xiii) McLafferty rearrangement can be used to distinguish between 2-pentanone from,

- *(a) 3-pentanone*
- *(b) 3-methyl-2-butanone*
- *(c) 4-methyl-2-butanone*
- *(d) all these*

(xiv) Four compounds having nominal mass 44 are C_3H_8 (44.06260), C_2H_4O (44.02620), CO_2 (43.98983) and CN_2H_4 (44.03740). So, the formula of a compound having parent ion peak at m/z (44.03734) is,

- *(a)* CO_2
- *(b)* C_3H_8
- *(c)* C_2H_4O
- *(d)* CN_2H_4



(xv) The m/z value of but-1-ene molecular ion is,

(a) 86 *(b)* 56 *(c)* 27 *(d)* 51

(xvi) The fragment ion formed by α -cleavage of 1-propanol molecular ion is,

(a) CH_3CH_2 *(b)* CH_3

(c) $H_2C = O^+ - H$ *(d)* $CH_3CH_2CH_3$

(xvii) The mass spectra of a hydroxyl compound shows a peak at m/e = 31. So it can be a,

(a) primary alochol *(b) phenol*

(c) carboxylic acid *(d) tertiary alcohol*

(xviii) The molecular ion peak at odd m/e is indicative of,

(a) hydrazine *(b) amine*

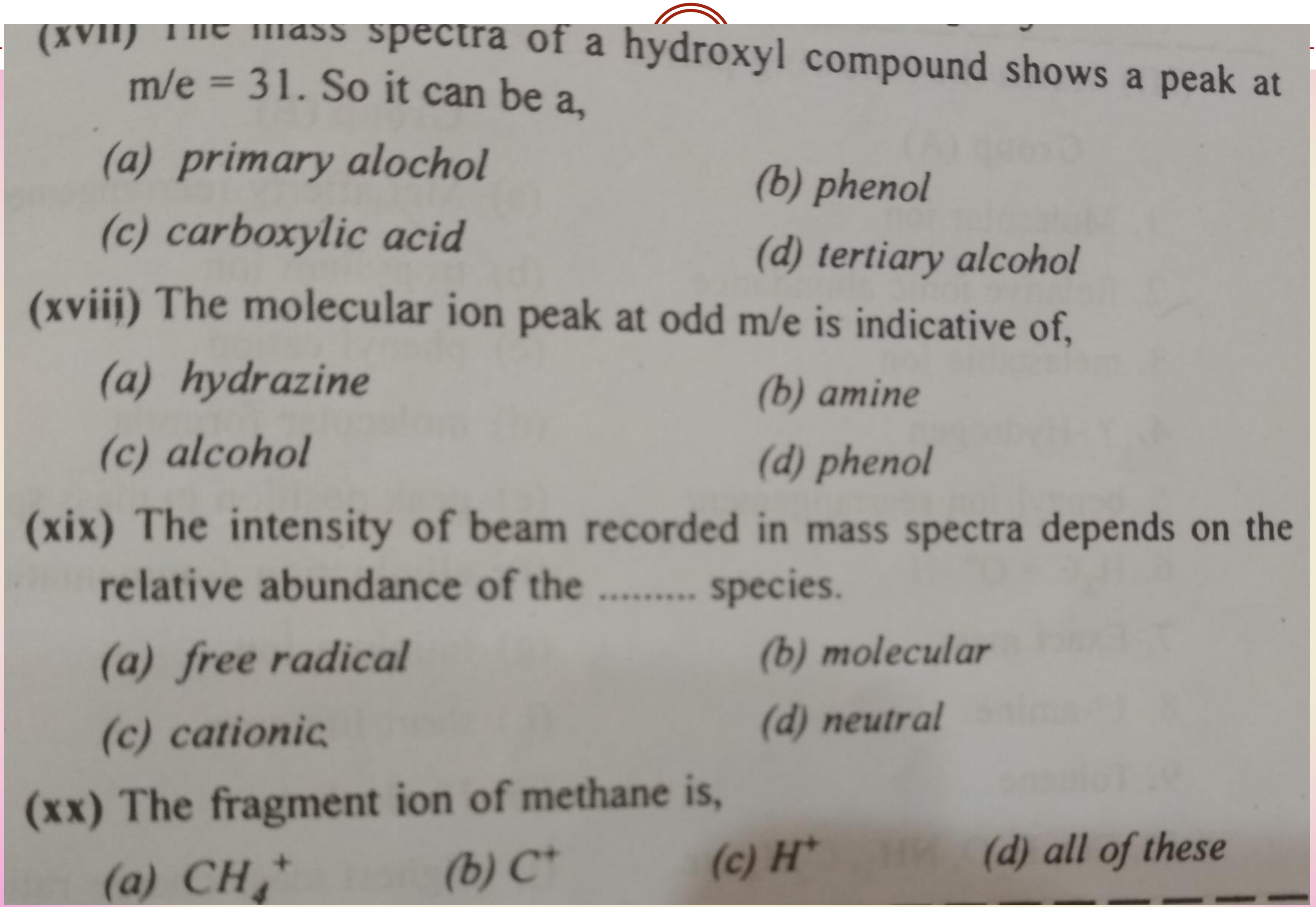
(c) alcohol *(d) phenol*

(xix) The intensity of beam recorded in mass spectra depends on the relative abundance of the .... species.

(a) free radical *(b) molecular*

(c) cationic *(d) neutral*

ion of methane is,



(xvii) The mass spectra of a hydroxyl compound shows a peak at m/e = 31. So it can be a,

(a) primary alochol *(b) phenol*

(c) carboxylic acid *(d) tertiary alcohol*

(xviii) The molecular ion peak at odd m/e is indicative of,

(a) hydrazine *(b) amine*

(c) alcohol *(d) phenol*

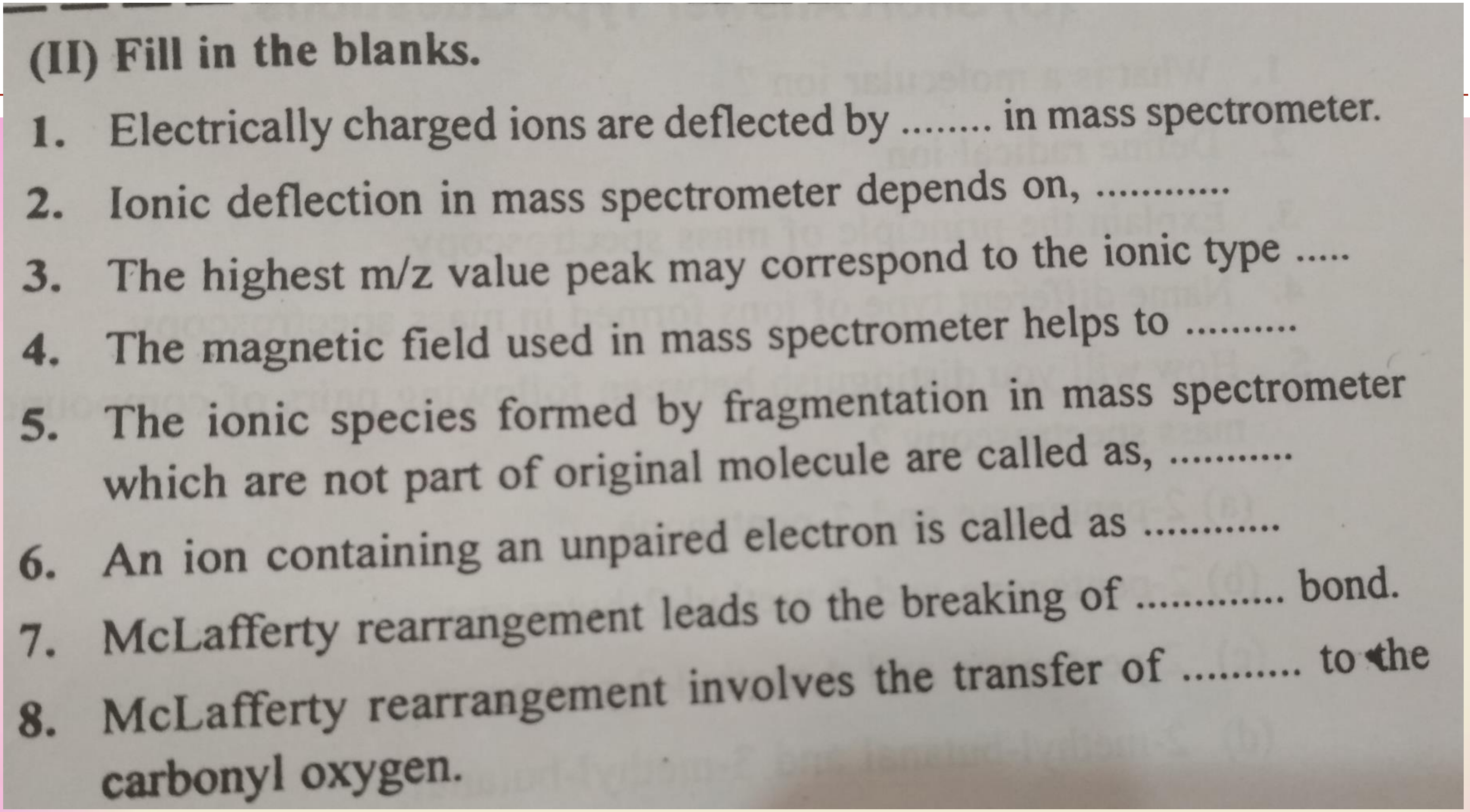
(xix) The intensity of beam recorded in mass spectra depends on the relative abundance of the .... species.

(a) free radical *(b) molecular*

(c) cationic *(d) neutral*

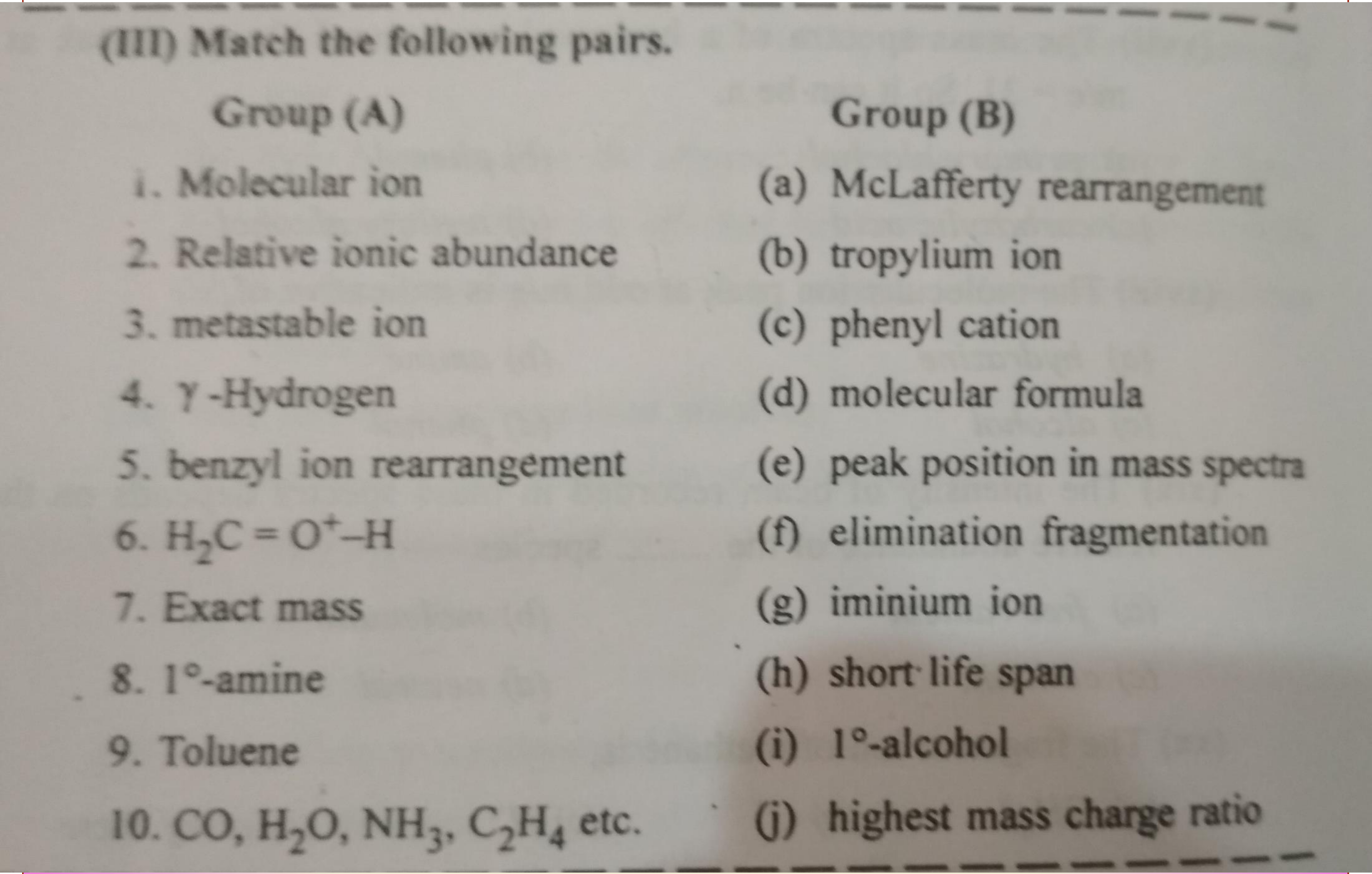
(xx) The fragment ion of methane is,

(a) CH_4^+ (b) C^+ (c) H^+ *(d) all of these*



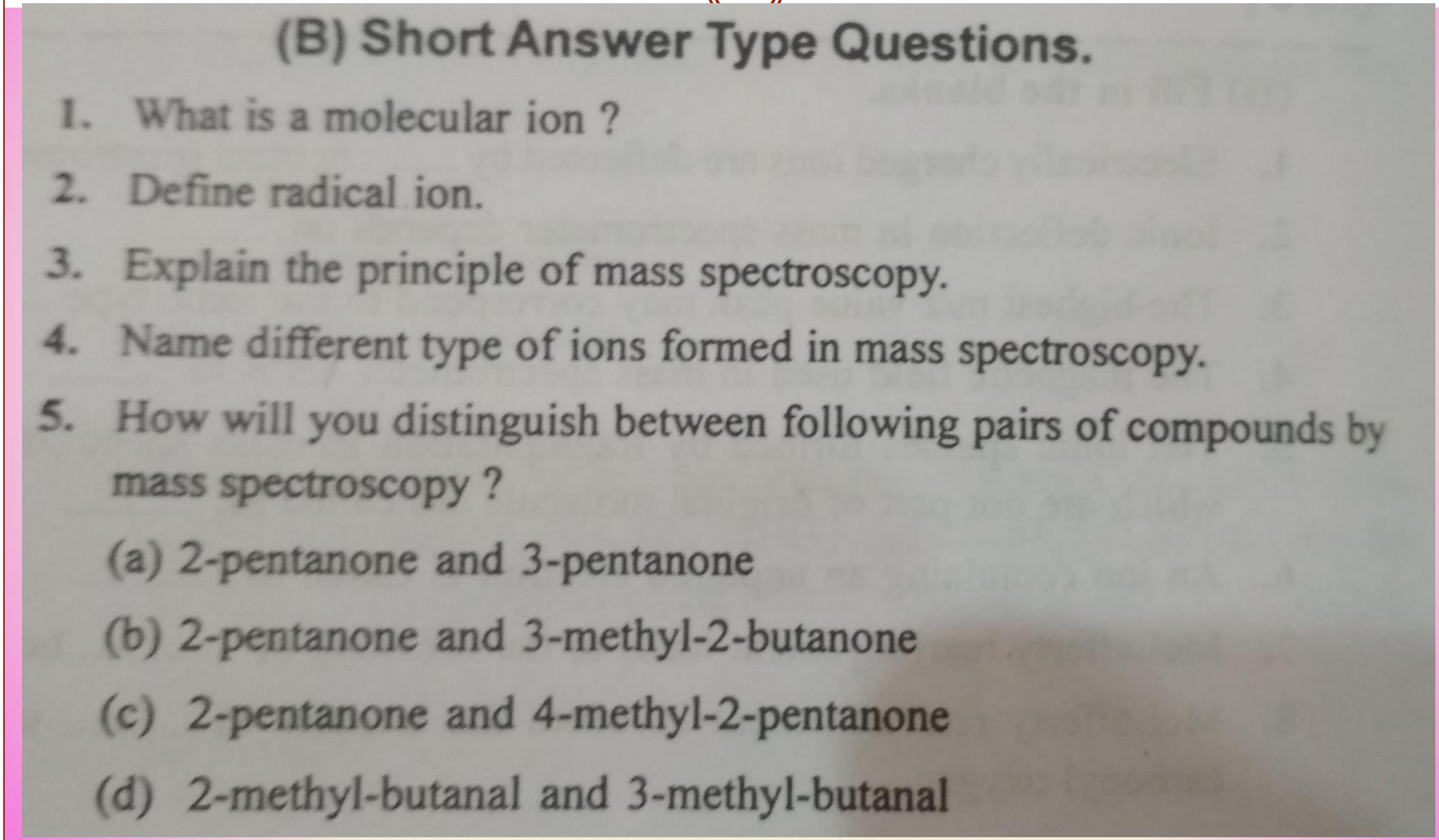
(II) Fill in the blanks.

1. Electrically charged ions are deflected by .... in mass spectrometer.
2. Ionic deflection in mass spectrometer depends on, ...
3. The highest m/z value peak may correspond to the ionic type .....
4. The magnetic field used in mass spectrometer helps to ....
5. The ionic species formed by fragmentation in mass spectrometer which are not part of original molecule are called as, ...
6. An ion containing an unpaired electron is called as ....
7. McLafferty rearrangement leads to the breaking of .... bond.
8. McLafferty rearrangement involves the transfer of .... to the carbonyl oxygen.



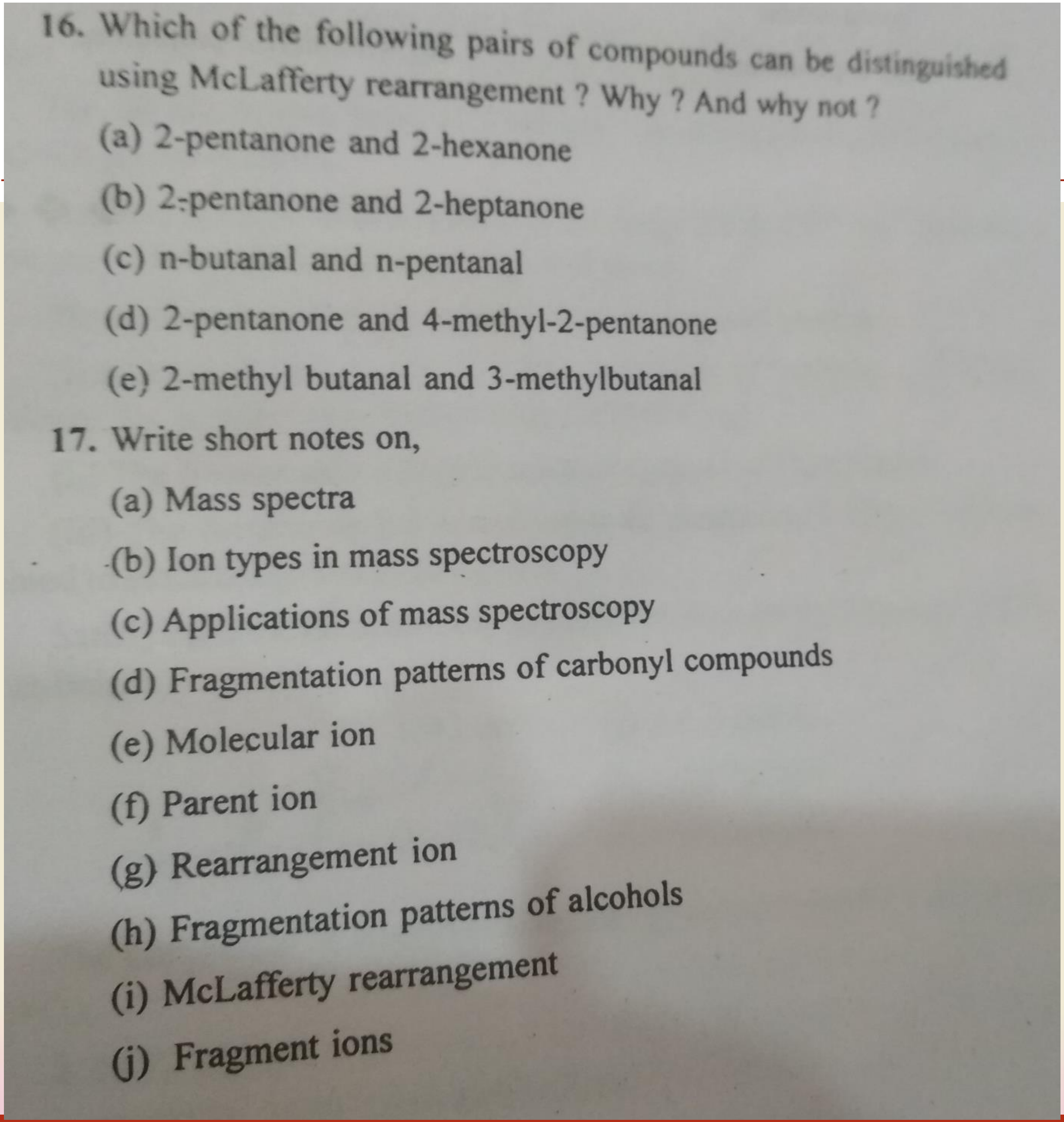
(III) Match the following pairs.

Group (A)	Group (B)
1. Molecular ion	(a) McLafferty rearrangement
2. Relative ionic abundance	(b) tropylium ion
3. metastable ion	(c) phenyl cation
4. γ-Hydrogen	(d) molecular formula
5. benzyl ion rearrangement	(e) peak position in mass spectra
6. $H_2C=O^+-H$	(f) elimination fragmentation
7. Exact mass	(g) iminium ion
8. 1°-amine	(h) short life span
9. Toluene	(i) 1°-alcohol
10. CO, H_2O, NH_3, C_2H_4 etc.	(j) highest mass charge ratio



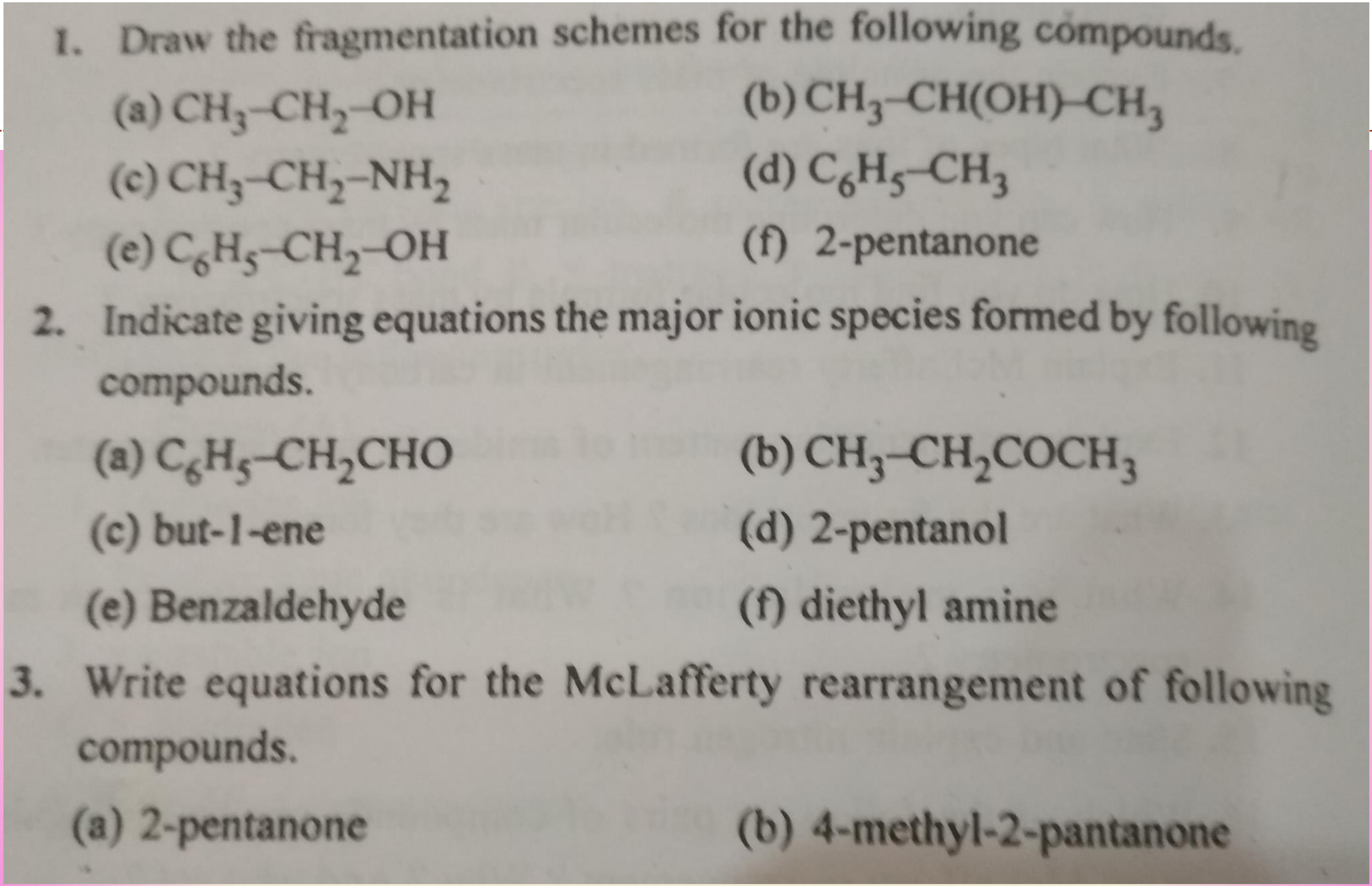
(B) Short Answer Type Questions.

1. What is a molecular ion ?
2. Define radical ion.
3. Explain the principle of mass spectroscopy.
4. Name different type of ions formed in mass spectroscopy.
5. How will you distinguish between following pairs of compounds by mass spectroscopy ?
   - (a) 2-pentanone and 3-pentanone
   - (b) 2-pentanone and 3-methyl-2-butanone
   - (c) 2-pentanone and 4-methyl-2-pentanone
   - (d) 2-methyl-butanal and 3-methyl-butanal



16. Which of the following pairs of compounds can be distinguished using McLafferty rearrangement ? Why ? And why not ?
    - (a) 2-pentanone and 2-hexanone
    - (b) 2-pentanone and 2-heptanone
    - (c) n-butanal and n-pentanal
    - (d) 2-pentanone and 4-methyl-2-pentanone
    - (e) 2-methyl butanal and 3-methylbutanal

17. Write short notes on,
    - (a) Mass spectra
    - (b) Ion types in mass spectroscopy
    - (c) Applications of mass spectroscopy
    - (d) Fragmentation patterns of carbonyl compounds
    - (e) Molecular ion
    - (f) Parent ion
    - (g) Rearrangement ion
    - (h) Fragmentation patterns of alcohols
    - (i) McLafferty rearrangement
    - (j) Fragment ions



1. Draw the fragmentation schemes for the following compounds.

   (a) CH_3-CH_2-OH

   (b) $CH_3-CH(OH)-CH_3$

   (c) $CH_3-CH_2-NH_2$

   (d) $C_6H_5-CH_3$

   (e) $C_6H_5-CH_2-OH$

   (f) 2-pentanone

2. Indicate giving equations the major ionic species formed by following compounds.

   (a) $C_6H_5-CH_2CHO$

   (b) $CH_3-CH_2COCH_3$

   (c) but-1-ene

   (d) 2-pentanol

   (e) Benzaldehyde

   (f) diethyl amine

3. Write equations for the McLafferty rearrangement of following compounds.

   (a) 2-pentanone

   (b) 4-methyl-2-pantanone


Thank You!