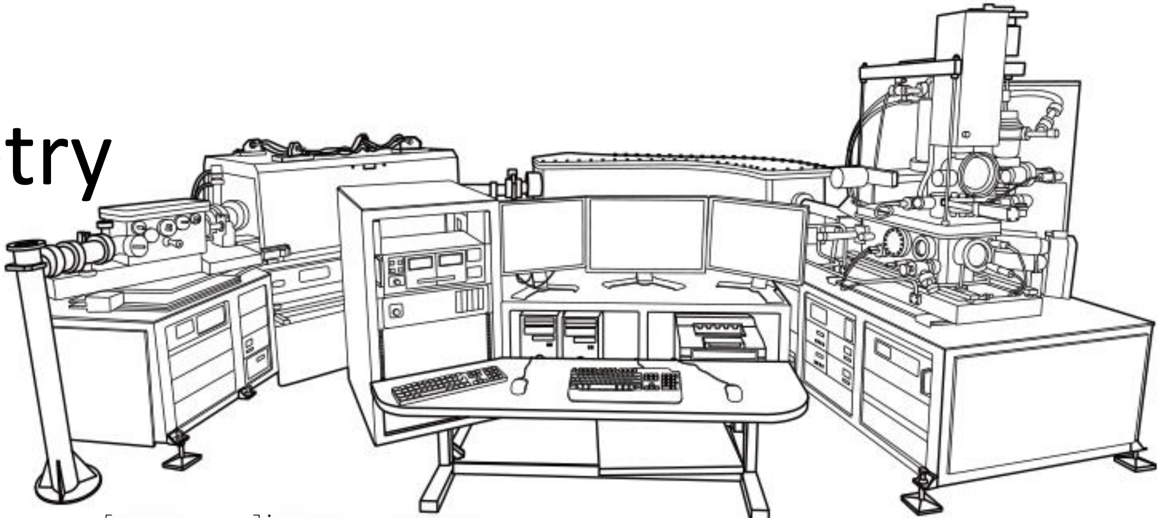
Instrumental Chemical Analysis

Mass Spectrometry



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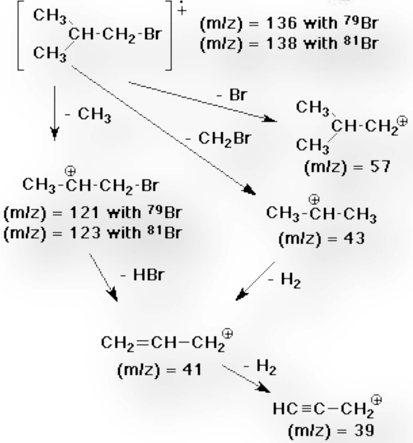
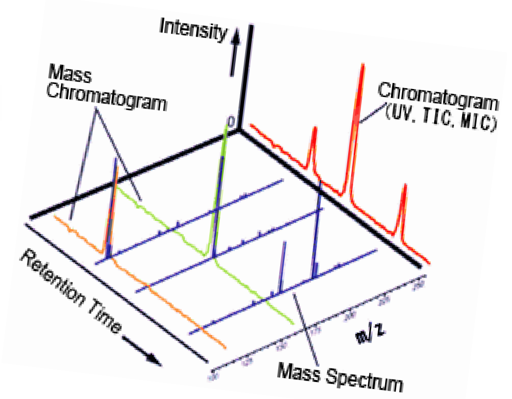
1st semester, 2021/2023



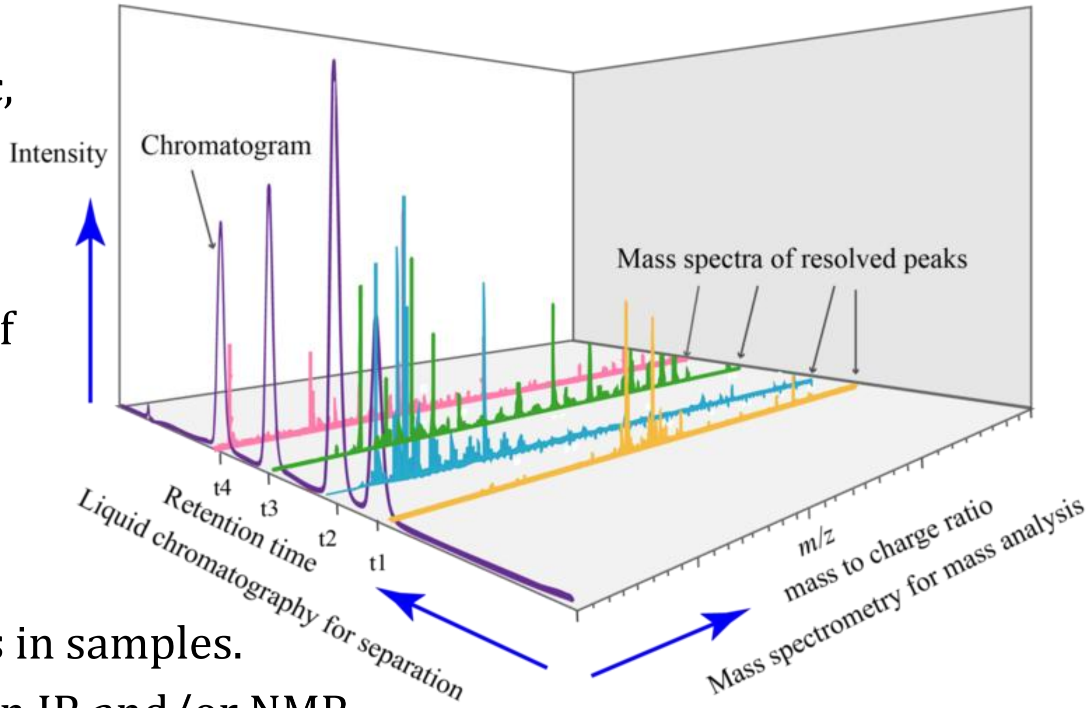


Mass Spectrometry

- **Mass spectrometry** (**MS**) is an analytical technique that produces spectra of the masses of the atoms or molecules comprising a sample of material.
- The spectra are used to determine the elemental or isotopic signature of a sample, the masses of particles and of molecules, and to clarify the chemical structures of molecules.
- Mass spectrometry works by ionizing chemical compounds to generate charged molecules or molecule fragments and measuring their **mass-to-charge ratios.**
- **In a typical MS procedure:**
  - ❖ Sample, which may be solid, liquid, or gas, is ionized.
  - ❖ The ions are separated according to their mass-to-charge ratio.
  - ❖ The ions are detected by a mechanism capable of detecting charged particles.
  - ❖ Signal processing results are displayed as spectra of the relative abundance of ions as a function of the mass-to-charge ratio. The atoms or molecules can be identified by <u>correlating known masses to the identified masses</u> or through a <u>characteristic fragmentation pattern</u>.

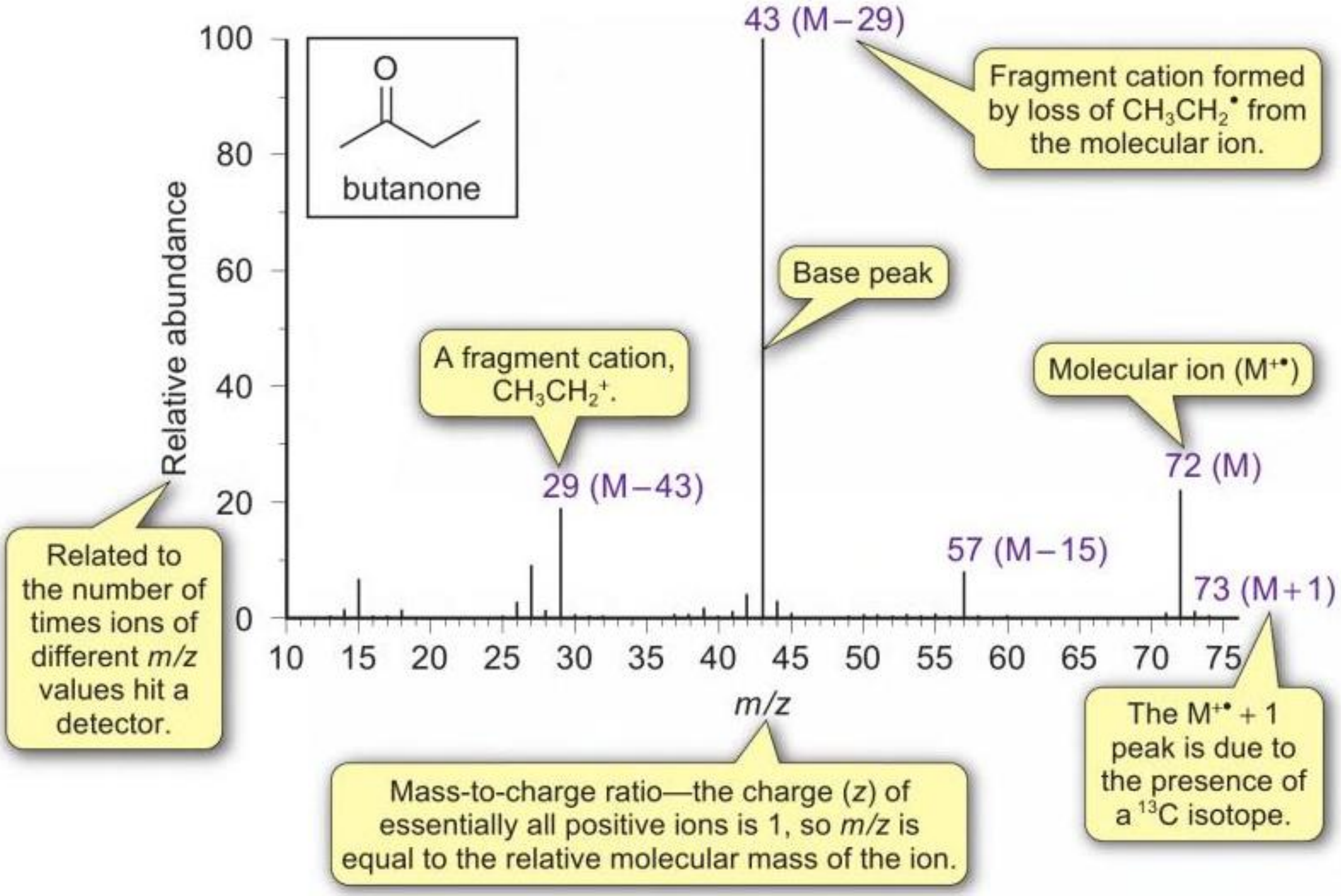
Mass Spectrometry

- **Mass spectroscopy provides information about:**
  - accurate MW of sample
  - the elemental composition of samples
  - the structures of inorganic, organic, and biological molecules
  - the qualitative and quantitative composition of complex mixtures
  - the structure and composition of solid surfaces
  - the isotopic ratios of atoms in samples.
  - data easier to interpret than IR and/or NMR



Mass Spectrometry

MS Spectrum



Fragment cation formed by loss of $CH_3CH_2^{\bullet}$ from the molecular ion.

Base peak

A fragment cation, $CH_3CH_2^+$.

Molecular ion ($M^{+\bullet}$)

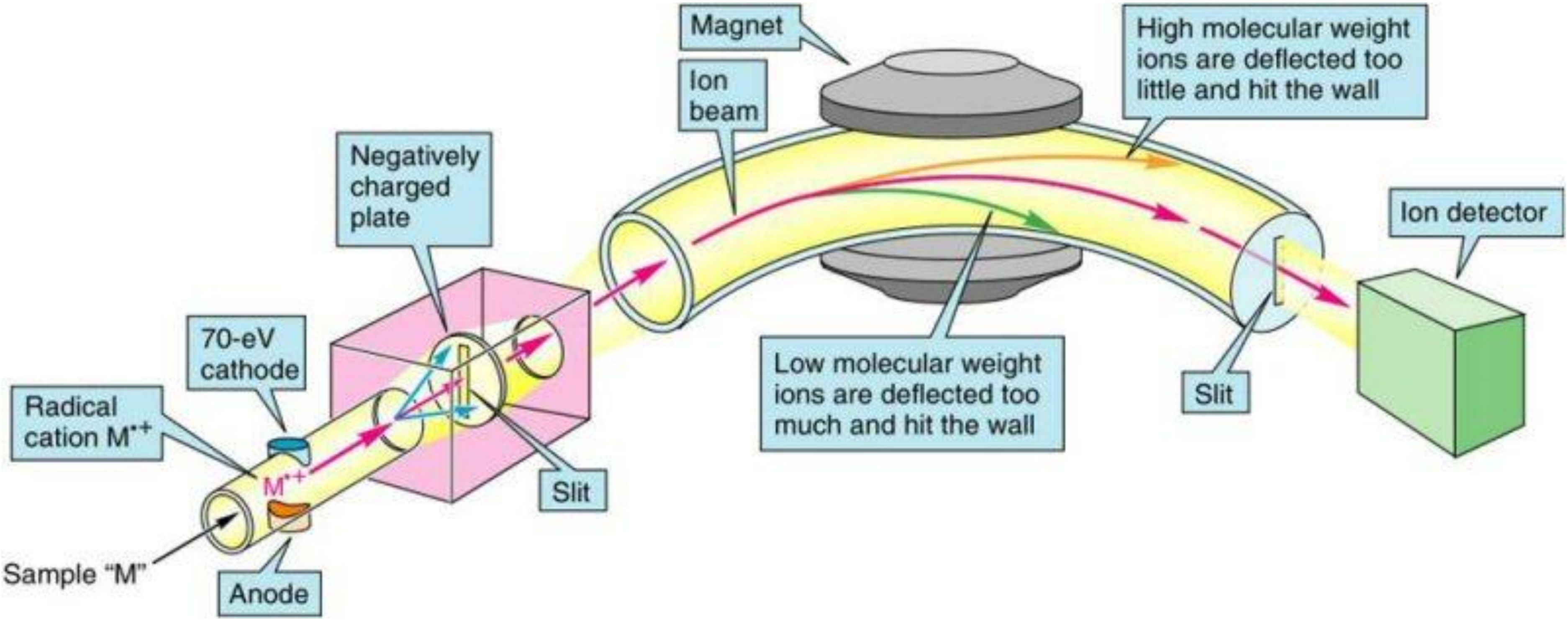
Related to the number of times ions of different *m/z* values hit a detector.

Mass-to-charge ratio—the charge (z) of essentially all positive ions is 1, so *m/z* is equal to the relative molecular mass of the ion.

The $M^{+\bullet} + 1$ peak is due to the presence of a ^{13}C isotope.

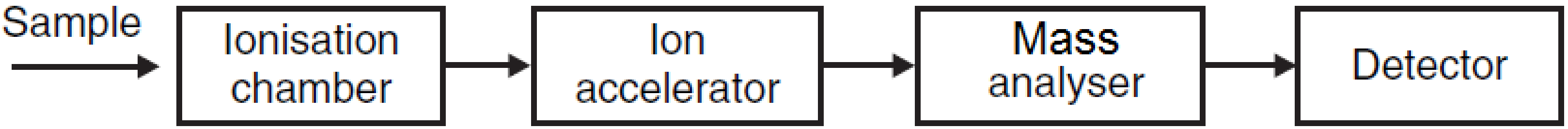
Mass Spectrometry

MS Instrumentation



Mass Spectrometry

MS Instrumentation : Parts of a mass spectrometer


Sample → Ionisation chamber → Ion accelerator → Mass analyser → Detector

- ***Stage 1: Ionization***
  The molecule is ionized by knocking one or more electrons off to give a positive ion. This is true even for negative ions (chlorine, for example).

- ***Stage 2: Acceleration***
  The ions are accelerated so that they all have the same kinetic energy.

- ***Stage 3: Mass Analyzer (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. New instruments also include an electrostatic sector that can be located between the ion accelerator and the magnetic sector (forward geometry, ‘EB’) or after the magnetic sector, (reversed geometry, ‘BE’). The function of the electric sector is to focus the energy of ions produced in the source. Energy focusing leads to a significant improvement in resolution.

- ***Stage 4: Detection***
  The beam of ions passing through the machine is detected electrically.

Mass Spectrometry

MS Instrumentation : Parts of a mass spectrometer

Ionization

- Soft and Hard ionization
  - ⇢ Ion sources could be classified as being **hard sources** or **soft sources**.
  - ⇢ **Hard sources** impart sufficient energy to analyte molecules so that they are left in a highly excited energy state. Relaxation then involves break of bonds, producing fragment ions that have mass-to-charge ratios less than that of the parent molecular ion.

    The many peaks in a hard source spectrum provide useful information about the kinds of functional groups and thus structural information about analyte.
  - ⇢ **Soft sources** cause little fragmentation. Consequently, the resulting mass spectrum consists of the molecular ion peak and only a few, if any other peaks.

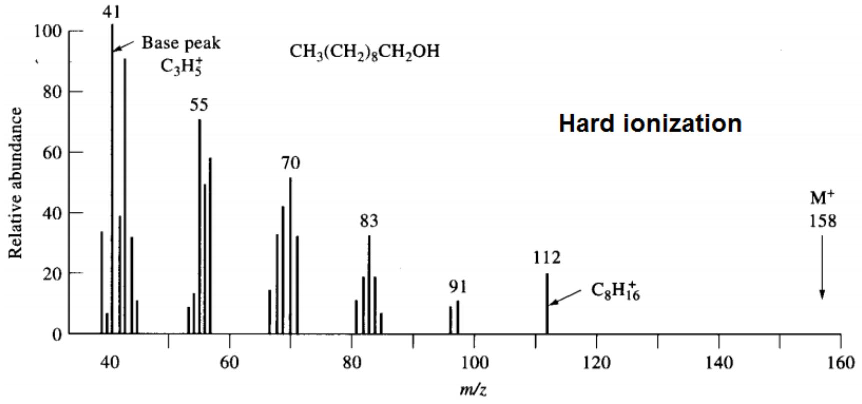
    Soft source spectra are useful because they supply accurate information about the molecular weight of the analyte molecule or molecules

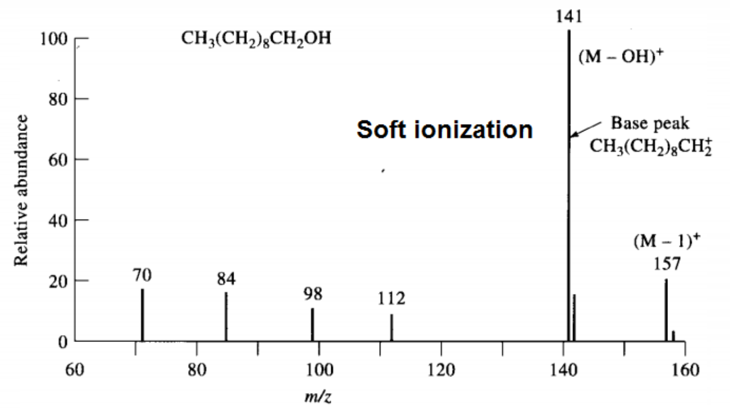
Mass Spectrometry

MS Instrumentation : Parts of a mass spectrometer

Ionization

- Soft and Hard ionization





- Popular ionization techniques:
  - ❖ Electron Ionization (EI) (Hard)
  - ❖ Chemical Ionization (CI) (Soft)
  - ❖ Electrospray Ionization (ESI) (Soft)
  - ❖ Atmospheric Pressure Chemical Ionization (APCI) (Soft)
  - ❖ Matrix-assisted Laser Desorption/Ionization (MALDI) (Soft)

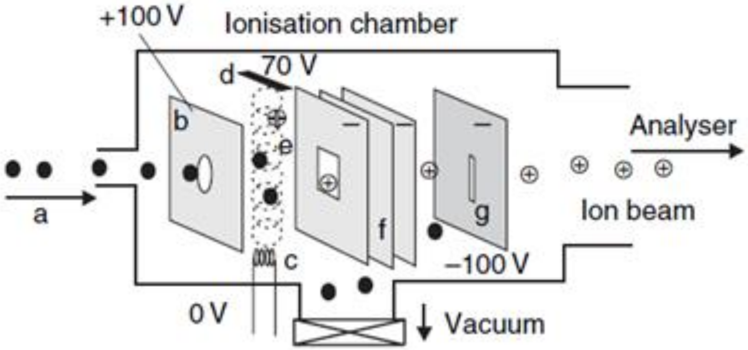
Mass Spectrometry

MS Instrumentation : Parts of a mass spectrometer

Ionization

Electron Ionization (EI), (also called Electron Impact)

- The electrically heated metal coil in the ionization chamber gives off electrons which are attracted to the electron trap which is a positively charged plate.
- The vaporized sample passes into the ionization chamber.
- The particles in the sample (atoms or molecules) are therefore bombarded with a stream of **high energy electrons**, leading to knock one or more electrons out of the sample particles to make positive ions.



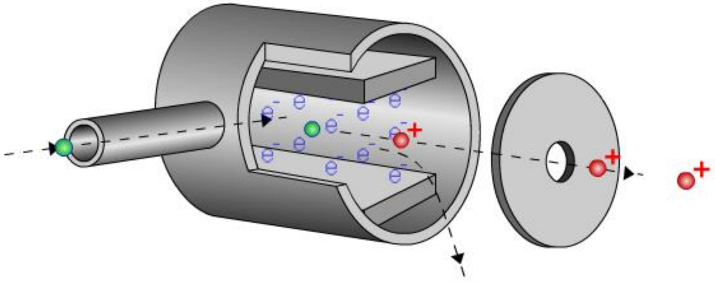
a - Sample entrance
b - **Repeller**
c - Tungsten filament
d - Discharge anode
e - Electron beam
f - Extraction plates
g - Exit slit to the MS

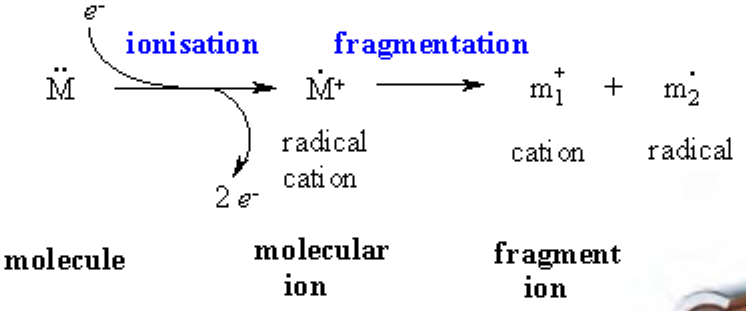
- Most of the positive ions formed will carry a charge of +1 because it is much more difficult to remove further electrons from an already positive ion.
- These positive ions are persuaded out into the rest of the machine by the ion repeller which is another metal plate carrying a slight positive charge.

Mass Spectrometry

MS Instrumentation : Parts of a mass spectrometer

Electron Ionization (EI)





$$\ddot{\mathrm{M}} \xrightarrow[2e^-]{e^-\ \text{ionisation}} \dot{\mathrm{M}}^+ \xrightarrow{\text{fragmentation}} \mathrm{m}_1^+ + \dot{\mathrm{m}}_2$$

radical cation

cation

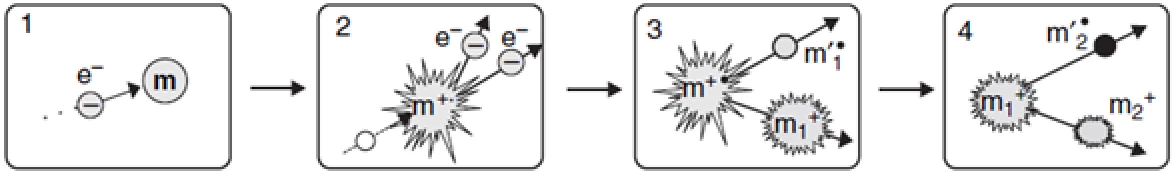
radical

molecule

molecular ion

fragment ion

Molecular ions hold high energy, this , making some chemical bonds to break, or causing rearrangements to break into multiple fragment ions or positive ions at an instantaneous rate.



$$\underset{m}{C_6H_6} \xrightarrow{e^-} \underset{m^{+\bullet}}{\left.C_6H_6\right]^{+\bullet}} \xrightarrow{-H^\bullet} \underset{m_1^{+\bullet}}{\left.C_6H_5\right]^{+}} \xrightarrow{-C_2H_2} \underset{m_2^{+}}{\left.C_4H_3\right]^{+}}$$

Mass Spectrometry

MS Instrumentation : Parts of a mass spectrometer

Chemical Ionization (CI)

Produces less fragmentation than electron ionization, so there is a high probability of obtaining the molecular ion. For chemical ionization, the ionization source is filled with a *reagent gas such as methane, isobutane,* or ammonia, at a pressure of 100 Pa (1 mbar, 1 Torr). Energetic electrons (100–200 eV) convert CH_4 into a variety of reactive products:

Primary reactions: $CH_4 + e^- \longrightarrow CH_4]^{+\bullet} + 2e^-$ *(Ionisation)*

Secondary reactions: $CH_4]^{+\bullet} \longrightarrow CH_3]^{+} + H^{\bullet}$

$CH_4]^{+\bullet} + CH_4 \longrightarrow CH_5]^{+} + CH_3^{\bullet}$ *(Autoprotonation)*

$CH_3]^{+} + CH_4 \longrightarrow C_2H_5]^{+} + H_2$

Collisions with M: $CH_5]^{+} + M \longrightarrow MH]^{+} + CH_4$ (ion at $M+1$)

$C_2H_5]^{+} + M \longrightarrow MC_2H_5]^{+}$ (ion at $M+29$)

If M is of the type RH: $CH_5]^{+} + RH \longrightarrow R^{+} + CH_4 + H_2$ (ion at $M-1$)

If it is a tert-butyl cation: $(CH_3)_3C]^{+} + M \longrightarrow MH]^{+} + CH_2{=}C(CH_3)_2$

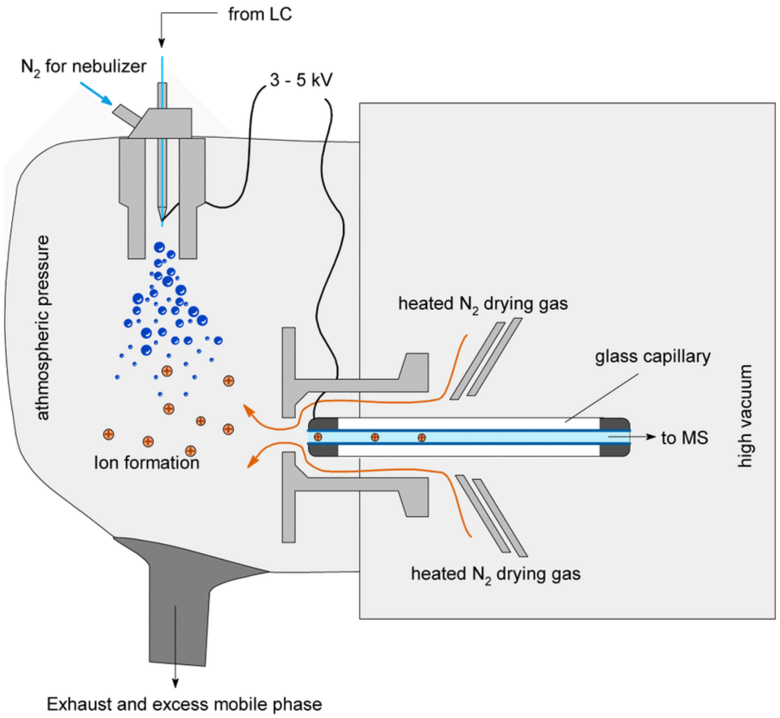
Generally the ion corresponds to molecular weight appears at $(M+1)^+$ or $(M-1)^+$ and some times at $(M+29)^+$ or others, depending on the reagent gas and ionization source energy.

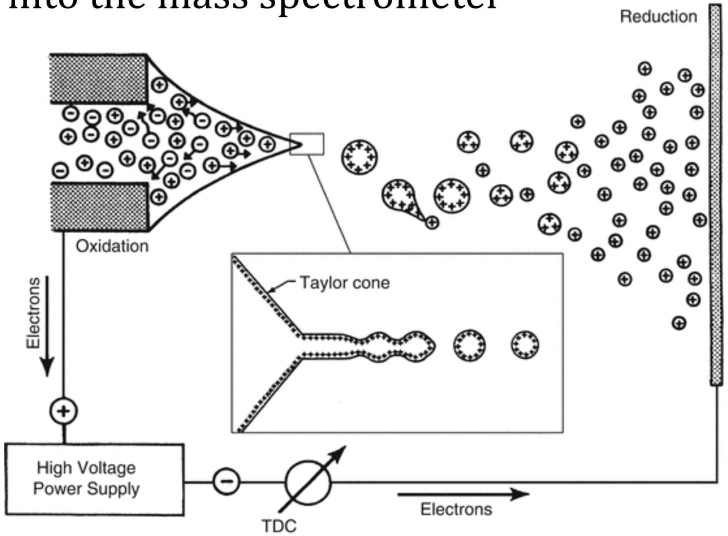
Mass Spectrometry

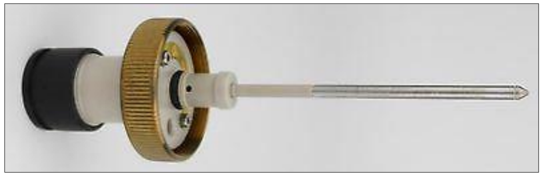
MS Instrumentation : Parts of a mass spectrometer

Electrospray Ionization (ESI)

Charge is transferred to the analytes during the nebulization process by high voltage at the end of the nebulizer needle tip; the droplets are reduced in size until the repulsion of the equally charged analyte particles leads to a sudden burst of the droplet creating smaller droplets (coulomb explosion); This process is repeated until single ions are emitted from the droplet surface and dragged through the glass capillary into the mass spectrometer





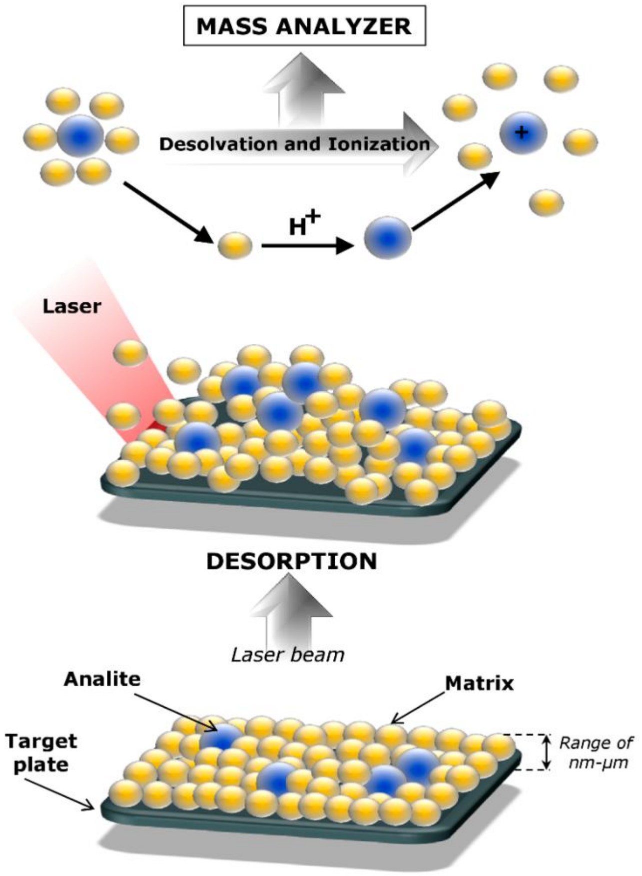


Mass Spectrometry

MS Instrumentation : Parts of a mass spectrometer

Matrix-assisted Laser Desorption/Ionization (MALDI)

- It is an ionization technique that uses a laser energy absorbing matrix to create ions from thermally instable large molecules (like biopolymers such as DNA, proteins, peptides and sugars) with minimal fragmentation.
- MALDI typically produces far fewer multi-charged ions.
- MALDI methodology is a three-step process.
  - ↳ First, the sample is mixed with a suitable matrix material and applied to a metal plate.
  - ↳ Second, a pulsed laser irradiates the sample, triggering ablation and desorption of the sample and matrix material.
  - ↳ Finally, the analyte molecules are ionized by being protonated or deprotonated in the hot cloud of ablated gases, and then they can be accelerated into whichever mass spectrometer is used to analyse them.

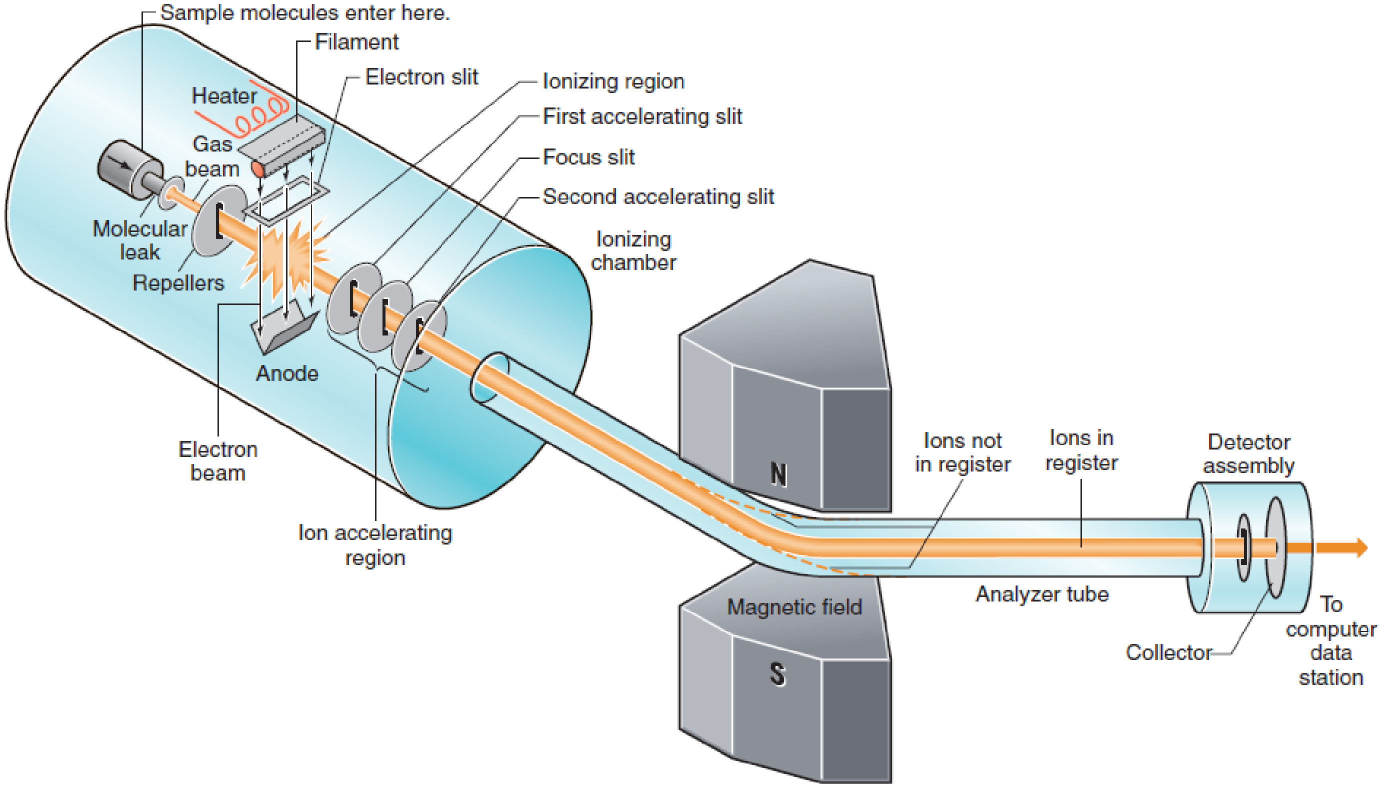


Mass Spectrometry

MS Instrumentation : Parts of a mass spectrometer

Acceleration

- The positive ions are accelerated using an electric field so that they all have the same kinetic energy. The positive ions are repelled away from the very positive ionization chamber and pass through slits (ion gun). All the ions are accelerated into a finely focused beam.



Mass Spectrometry

MS Instrumentation : Parts of a mass spectrometer

Mass Analyzer / Deflection

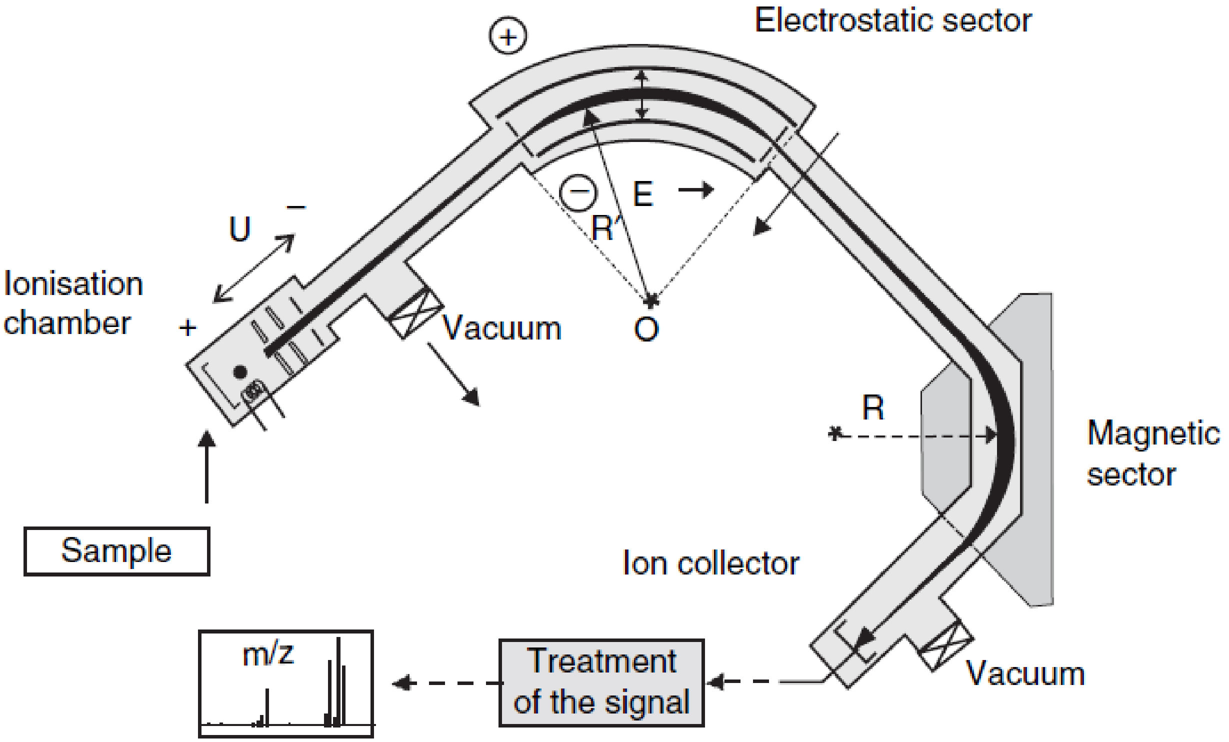
- Different ions are deflected by the magnetic field by different amounts. The amount of deflection depends on:
  - **The mass of the ion**. Lighter ions are deflected more than heavier ones.
  - **The charge on the ion**. Ions with 2 (or more) positive charges are deflected more than ones with only 1 positive charge.
- These two factors are combined into the ***mass/charge ratio.*** Mass/charge ratio is given the symbol m/z (or sometimes m/e).
- Ions with the smallest mass/charge ratio are the most deflected. Ion stream least deflected contains ions with the greatest mass/charge ratio.
- Most of the ions passing through the mass spectrometer will have a charge of 1+, so that the mass/charge ratio will be the same as the mass of the ion.

Mass Spectrometry

MS Instrumentation : Parts of a mass spectrometer

Mass Analyzer / Deflection

'EB' or 'BE' geometry mass analysers



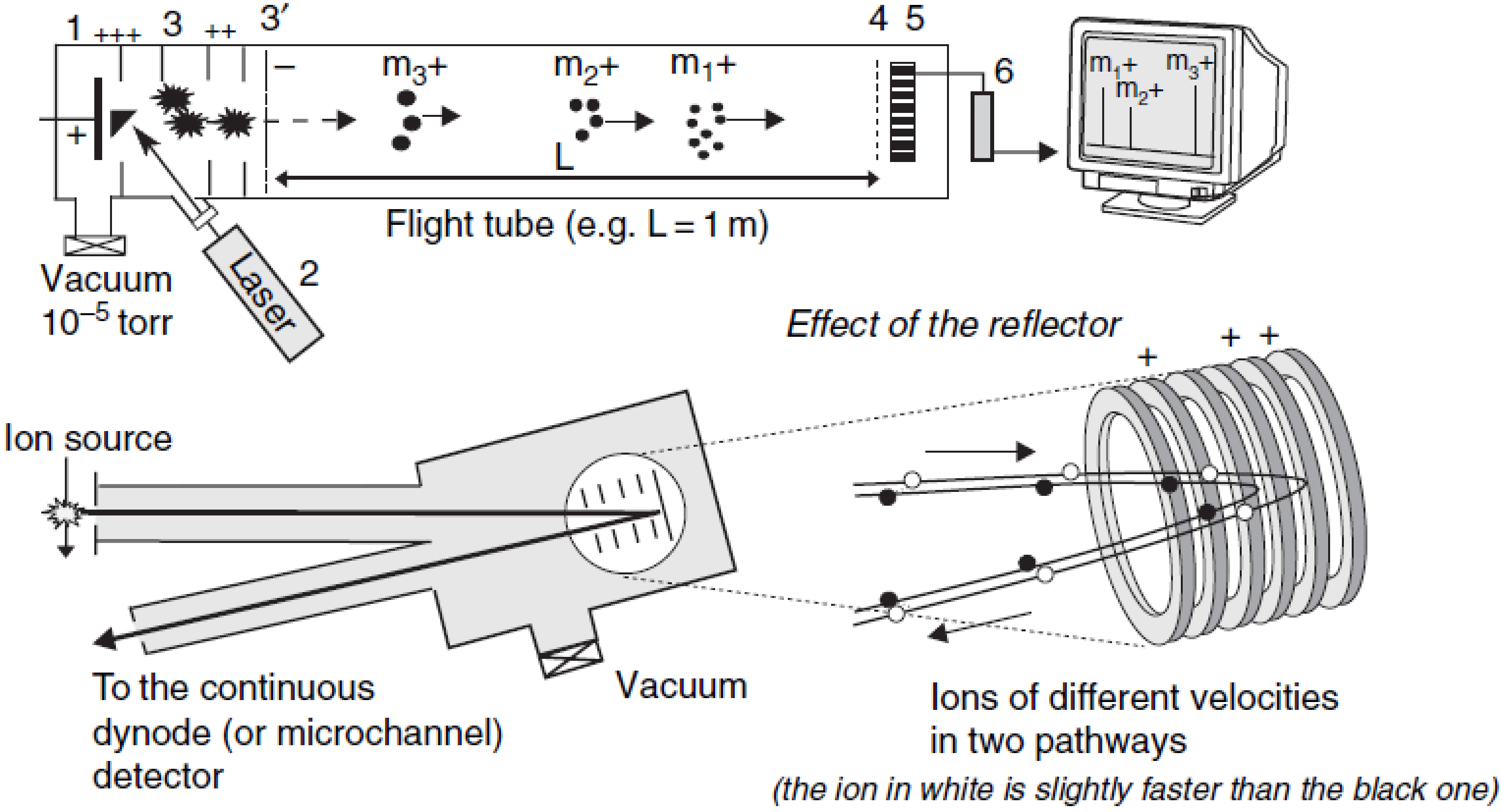
Arrangement of a double focusing spectrometer

Mass Spectrometry

MS Instrumentation : Parts of a mass spectrometer

Mass Analyzer / Deflection

Time of flight analysers (TOF)

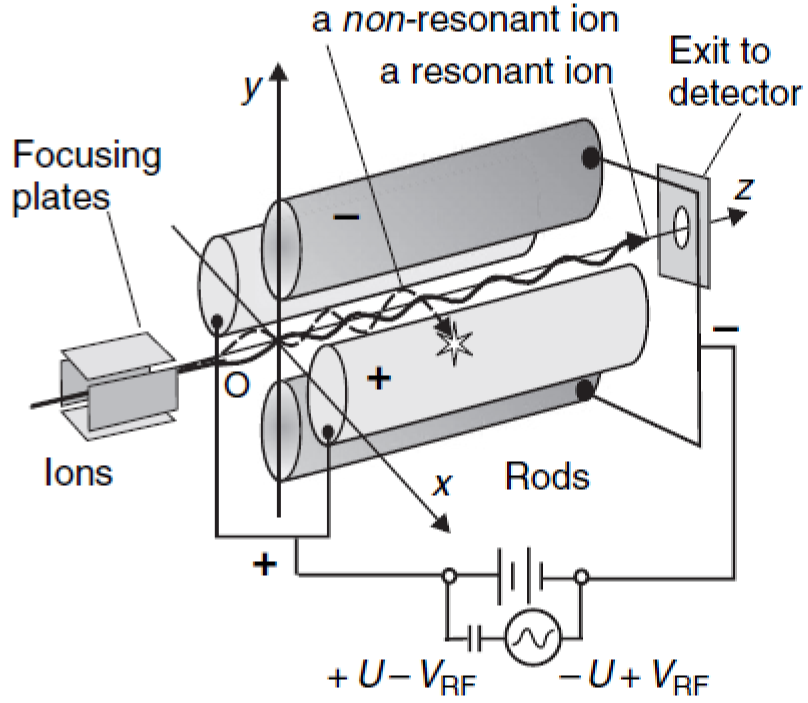


Mass Spectrometry

MS Instrumentation : Parts of a mass spectrometer

Mass Analyzer / Deflection

Quadrupole analysers

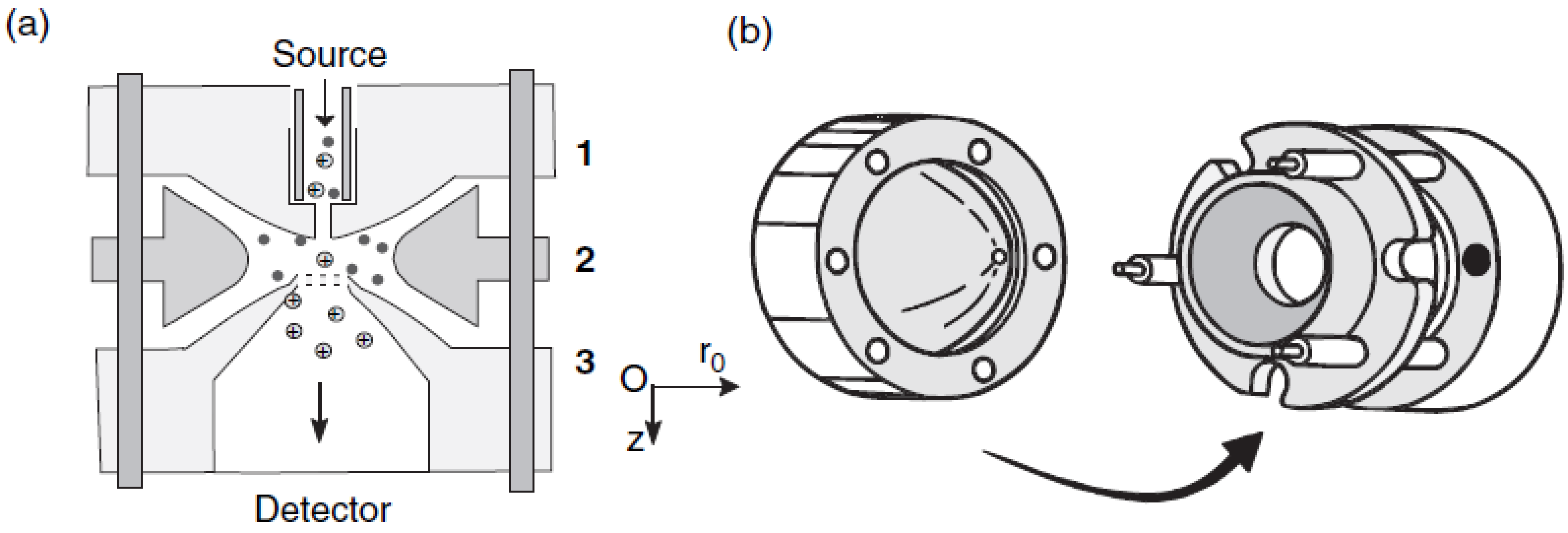


Mass Spectrometry

MS Instrumentation : Parts of a mass spectrometer

Mass Analyzer / Deflection

Quadrupole ion trap analysers



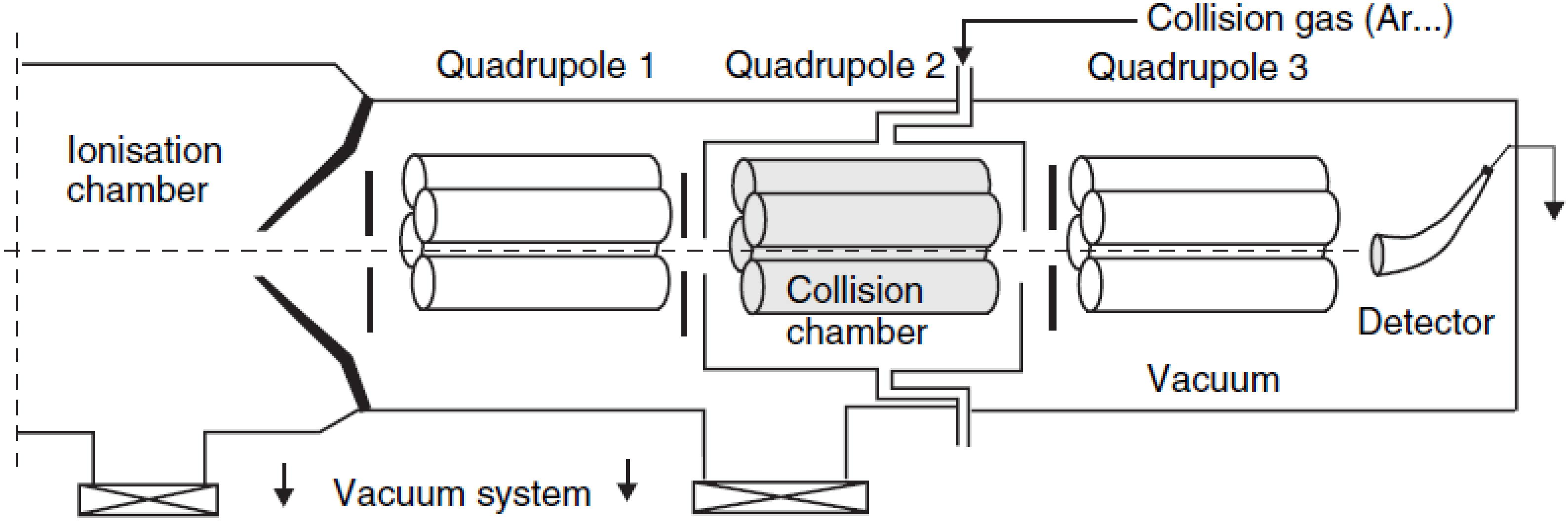
Ion-trap spectrometer. (a) Design of the electrodes in an ion trap; (b) Diagram giving a perspective of the end-cap and annular electrodes

Mass Spectrometry

MS Instrumentation : Parts of a mass spectrometer

Mass Analyzer / Deflection

Tandem mass spectrometry (MS/MS)



A triple quadrupole (QQQ-MS-MS). The middle quadrupole is used as a collision chamber. It is operated in the radiofrequency voltage mode only, where it will transmit all masses. A gas is introduced in this middle quadrupole for collision activation.

Mass Spectrometry

MS Instrumentation : Parts of a mass spectrometer

Detection

- When an ion hits the metal box, its charge is neutralized 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.

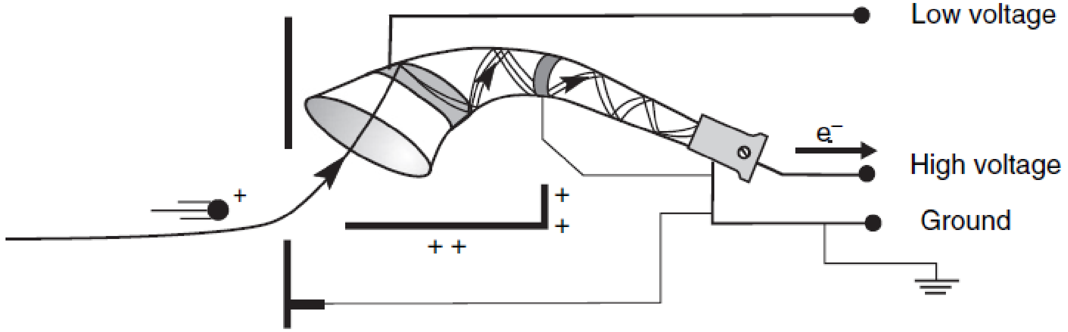
- Typically, some type of electron multiplier is used, although other detectors including Faraday cups and ion-to-photon detectors are also used. Because the number of ions leaving the mass analyzer at a particular instant is typically quite small, considerable amplification is often necessary to get a signal. Microchannel plate detectors are commonly used in modern commercial instruments.

Mass Spectrometry

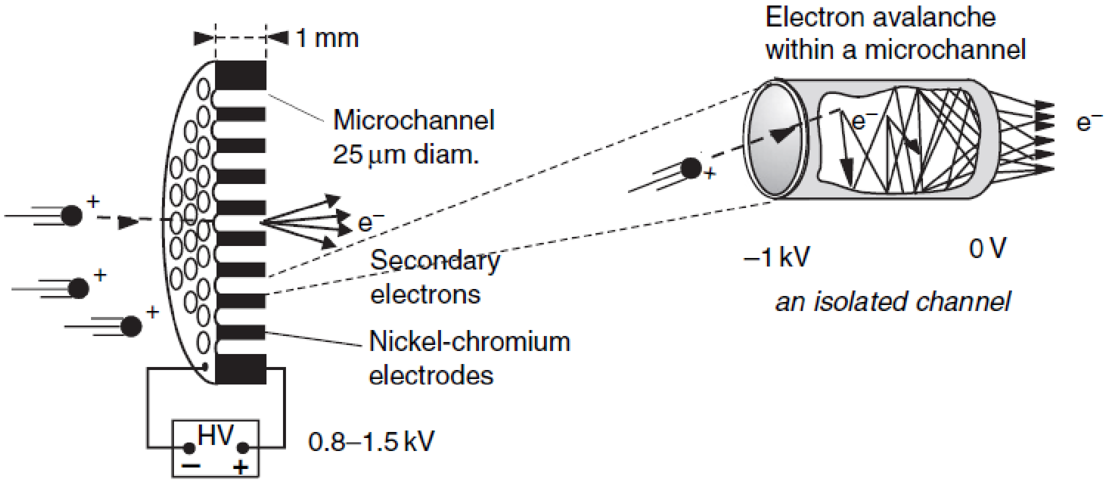
MS Instrumentation : Parts of a mass spectrometer

Detection

Continuous dynode detector
single-channel electron multiplier



Microchannel plate (MCP) detector
(20–100 mm diam.)

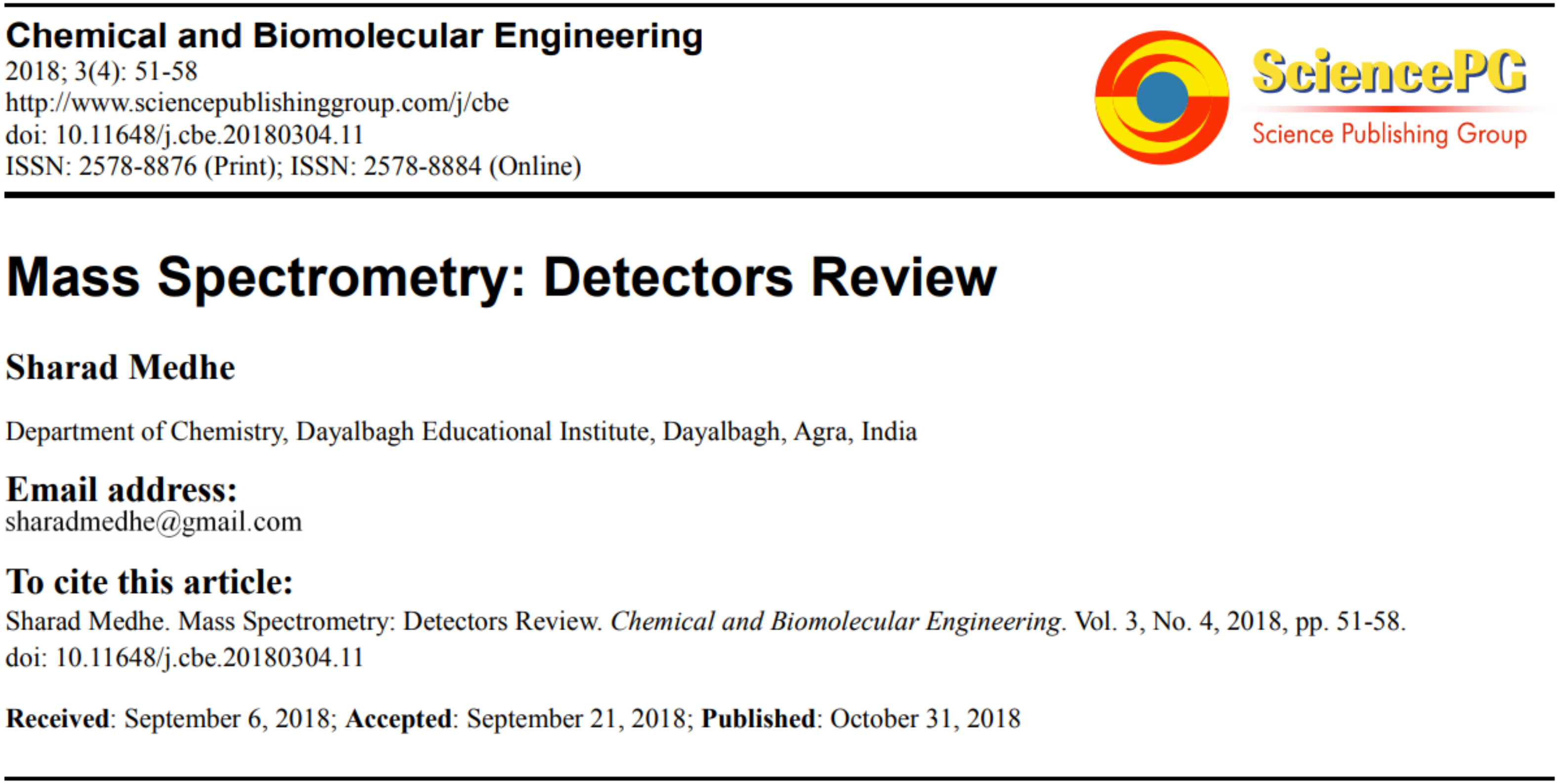


Mass Spectrometry

MS Instrumentation : Parts of a mass spectrometer

Detection

- For more information about detectors an how does they are work, please look at the following review.



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Mass Spectrometry: Detectors Review

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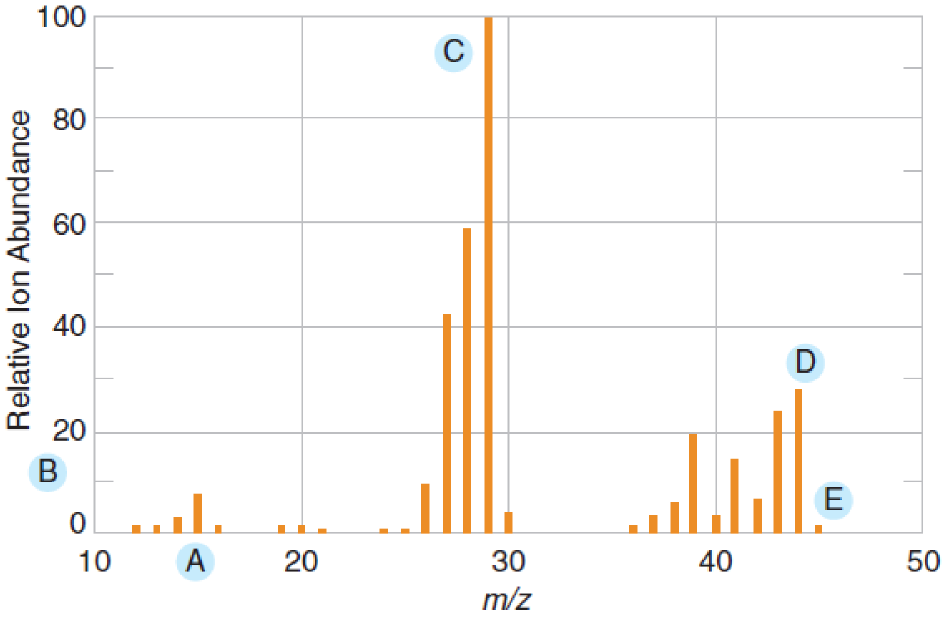
Mass Spectrometry

MS Spectrum



- A The *x*-axis, in units of *m/z*, represents the formula weight of the detected ions. ***m/z*** is the mass (*m*) to charge (*z*) ratio. Because z is typically +1, *m/z* represents the formula weight of each ion.
- B The *y*-axis represents the relative abundance of each detected ion.
- C The most abundant ion (tallest peak) is called the **base peak.** The base peak is usually an easily formed fragment of the original compound. In this case it is an ethyl fragment ($C_2H_5^+$, *m/z* 29).
- D One of the higher value *m/z* peaks may or may not represent the **molecular ion** (the ion with the formula weight of the original compound). When present, the molecular ion (*m/z* 44 in the case of propane) is usually not the base peak, because ions from the original molecule tend to fragment, resulting in the other *m/z* peaks in the spectrum.
- E Small peaks having *m/z* values 1 or 2 higher than the formula weight of the compound are due to ^{13}C and other isotopes

Mass Spectrometry

Determination of a molecular formula

Relative Isotopic Abundances of Common Elements

Element	**Isotope**	**Relative Abundance**	**Isotope**	**Relative Abundance**	**Isotope**	**Relative Abundance**
Carbon	$^{12}\mathrm{C}$	100	$^{13}\mathrm{C}$	1.11		
Hydrogen	$^{1}\mathrm{H}$	100	$^{2}\mathrm{H}$	0.016		
Nitrogen	$^{14}\mathrm{N}$	100	$^{15}\mathrm{N}$	0.38		
Oxygen	$^{16}\mathrm{O}$	100	$^{17}\mathrm{O}$	0.04	$^{18}\mathrm{O}$	0.2
Fluorine	$^{19}\mathrm{F}$	100				
Silicon	$^{28}\mathrm{Si}$	100	$^{29}\mathrm{Si}$	5.1	$^{30}\mathrm{Si}$	3.35
Phosphorus	$^{31}\mathrm{P}$	100				
Sulfur	$^{32}\mathrm{S}$	100	$^{33}\mathrm{S}$	0.78	$^{34}\mathrm{S}$	4.4
Chlorine	$^{35}\mathrm{Cl}$	100			$^{37}\mathrm{Cl}$	32.5
Bromine	$^{79}\mathrm{Br}$	100			$^{81}\mathrm{Br}$	98
Iodine	$^{127}\mathrm{I}$	100				

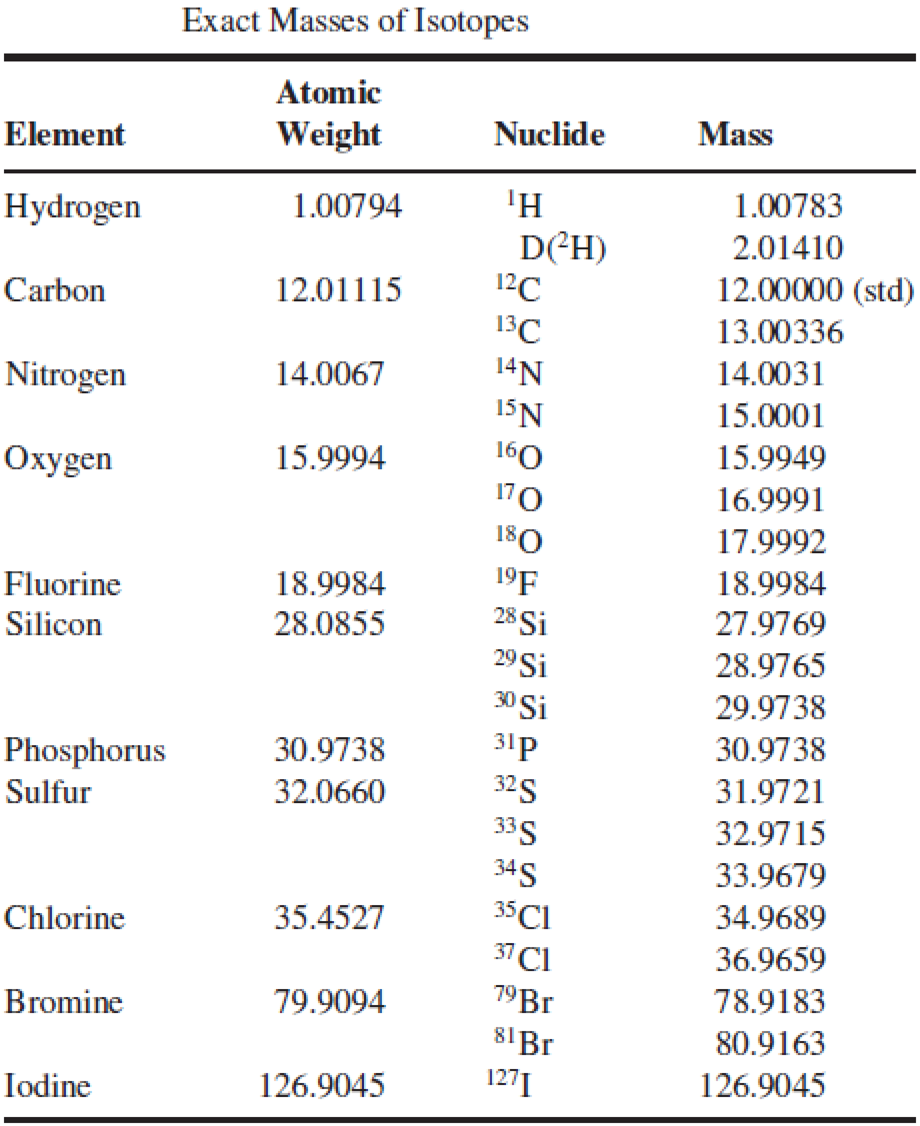
M^+

$M^+ +1$

$M^+ +2$

Mass Spectrometry

Determination of a molecular formula

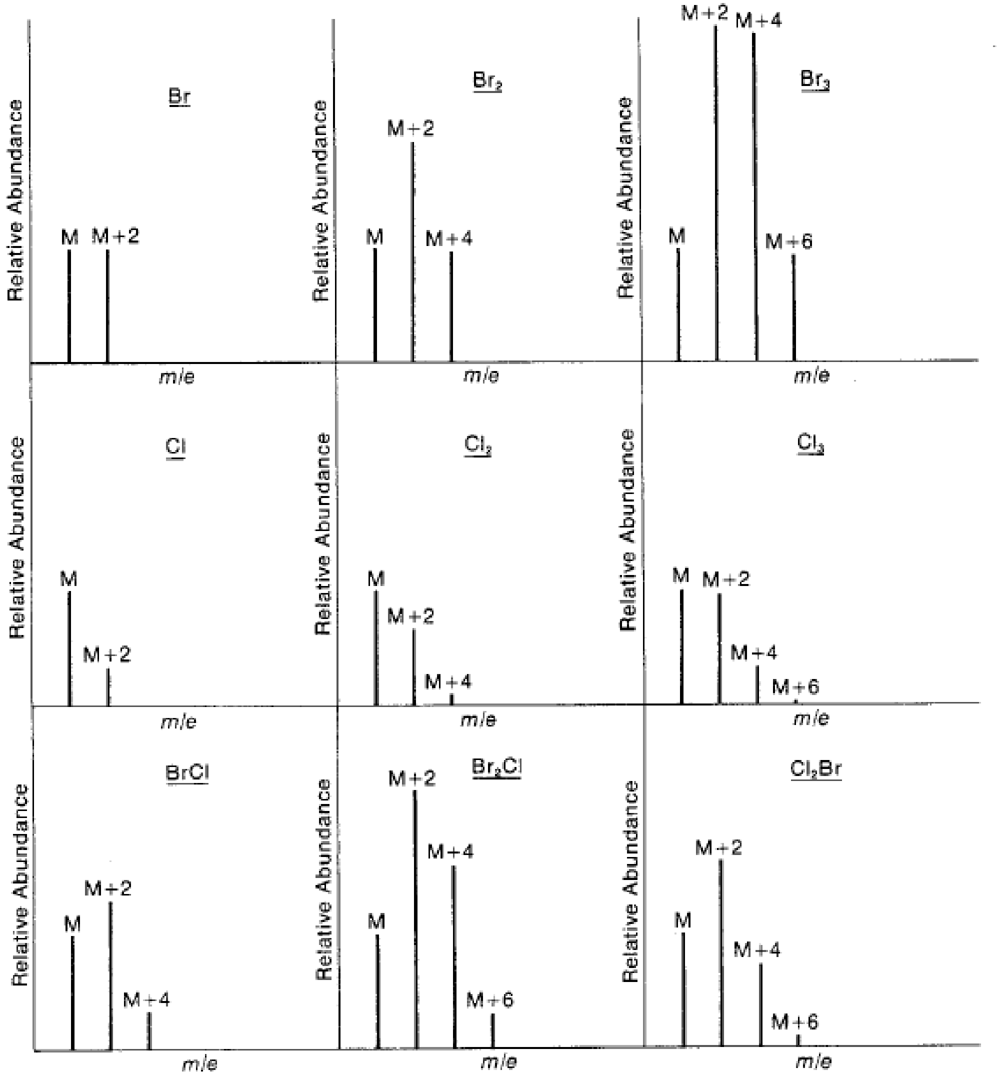


Exact Masses of Isotopes

Element	Atomic Weight	Nuclide	Mass
Hydrogen	1.00794	^{1}H	1.00783
		D(^{2}H)	2.01410
Carbon	12.01115	^{12}C	12.00000 (std)
		^{13}C	13.00336
Nitrogen	14.0067	^{14}N	14.0031
		^{15}N	15.0001
Oxygen	15.9994	^{16}O	15.9949
		^{17}O	16.9991
		^{18}O	17.9992
Fluorine	18.9984	^{19}F	18.9984
Silicon	28.0855	^{28}Si	27.9769
		^{29}Si	28.9765
		^{30}Si	29.9738
Phosphorus	30.9738	^{31}P	30.9738
Sulfur	32.0660	^{32}S	31.9721
		^{33}S	32.9715
		^{34}S	33.9679
Chlorine	35.4527	^{35}Cl	34.9689
		^{37}Cl	36.9659
Bromine	79.9094	^{79}Br	78.9183
		^{81}Br	80.9163
Iodine	126.9045	^{127}I	126.9045

Mass Spectrometry

Determination of a molecular formula



Mass Spectrometry

Determination of a molecular formula Rules

- M^+ is the molecular ion = M.wt.
- $M^+ + 1$ is for C, H and N isotopes [^{13}C, ^{2}H, ^{15}N]
- $M^+ + 2$ is for O, S, Cl and Br isotopes [^{18}O, ^{34}S, ^{37}Cl, ^{81}Br]
- If M^+ is odd then it contains odd # of N atoms
- If M^+ is even then it contains even # of N atoms or zero.
- # of C atoms = $[(M^+ + 1 / M^+) \times 100\%]/1.1$ or less, <u>(N and S will contribute in $M^+ + 1$ also but with small amount , 0.38 and 0.78 respectively)</u>
- $(M^+ + 2 / M^+) \times 100\%$ will be used to calculate # of O, S, Cl and Br atoms if present.
- After calculating # of C, O, N …etc. , # H atoms will be calculated from M^+– mass of C, N,O….etc.

Mass Spectrometry

Determination of a molecular formula

- For the molecular formula C_2H_5Cl, calculate the relative intensity for M+1 and M+2

$\%M+1 \approx (1.1 \text{ x number of C})/100 = 1.1 \text{ x} 2 = 2.2\%$

$\%M+2 \approx (1.1 \text{ x number of C})^2/200 + (32.5 \text{ x number of Cl})/100$

$= 2.2^2/200 + 32.5/100 = 32.5$

- Calculate the relative intensity for M+1 and M+2 for C_7H_7NO

$\%M+1 \approx (1.1 \text{ x number of C})/100 + (0.38 \text{ x number of N})/100$

$=(1.1\text{x}7)/100 + (0.38\text{x}1)/100 = 8.1\%$

$\%M+2 \approx (1.1 \text{ x number of C})^2/200 + (0.2 \text{ x number of O})/100$

$=(7.7^2/200) + 0.2/100 = 0.5\%$

Mass Spectrometry

Determination of a molecular formula

Example: Determine the molecular formula of the following compounds

a. Comp. I

m/z	Intensity
86	10.0
87	0.56
88	0.03

86 (10%) = $[M]^+$

$[M+1]^+$=(0.56/10.0)x100%=5.6%
⇨ 5.6/1.1 ≈ 5 #C

$[M+2]^+$=(0.03/10.0)x100%=0.3%
this is too small for S, Si, Cl or Br
We can try it for O only
⇨ 0.3/0.2=1.5 ⇨one O atom could be present

so the formula is in the form of $[C_5H_?O]$
86-(5x12)-(1x16)=10
⇨10 H
⇨ $C_5H_{10}O$

Mass Spectrometry

Determination of a molecular formula

b. Comp. II

m/z	Intensity
42	46.6
43	10.7
44	100.0
73	86.1
74	3.2
75	0.2

73 (86.1%) = $[M]^+$
Odd M.wt ⇨ odd #N atom (1, 3,5 ,,,, etc.)

$[M+1]^+$=(3.2/86.1)x100%=3.7%
⇨ 3.7/1.1=3.4 ≈ 3 #C

$[M+2]^+$=(0.2/86.1)x100%=0.23%
0.23/0.2=1.165 ⇨ one O atom could be present

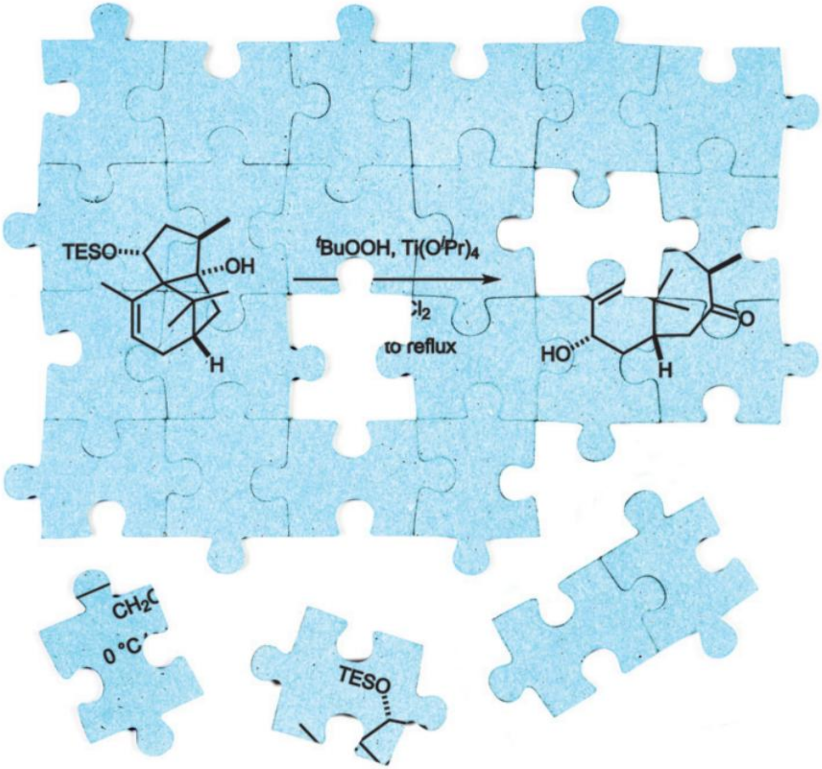
$[C_3H_?NO]$
73-(3x12)-(1x14)-(1x16)=7
⇨7 H
⇨ C_3H_7NO

Mass Spectrometry

Fragmentation

- Molecular ions formed by EI mass spectrometry are highly energetic species, and in the case of complex molecules, a great many things can happen to them including homolytic cleavage, heterolytic cleavage of the bond or rearangments. A molecular ion (parent ion) can break apart in a variety of ways, the fragments that are produced can undergo further **fragmentation,** and so on.

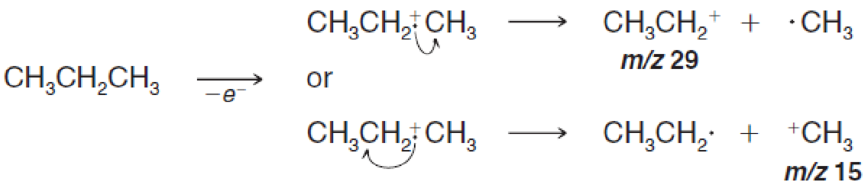
- Collecting the structural information for these small fragments will lead to draw the whole structure of the parent molecule.



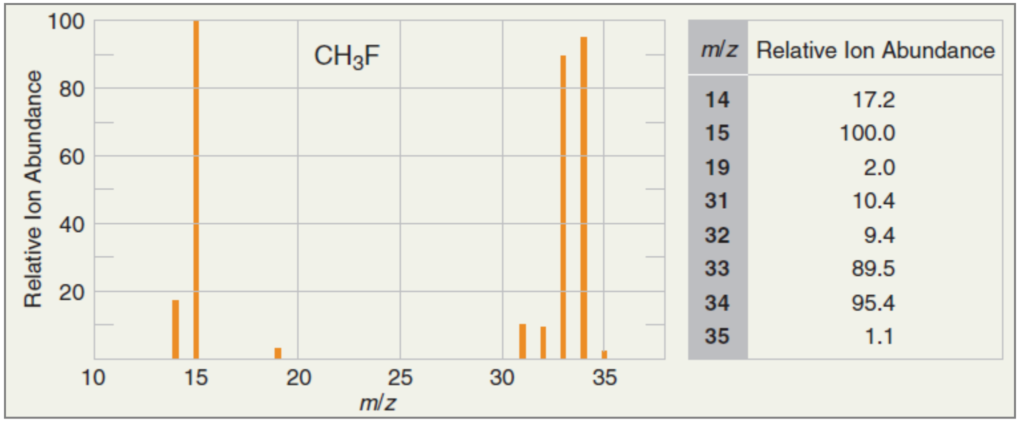
Mass Spectrometry

Fragmentation

- ❑ Fragmentation by Cleavage at a Single Bond



MS detect only the charged fragment, the two reactions have different rate, therefore the relative abundance for CH_3 and CH_3CH_2 are not equal.



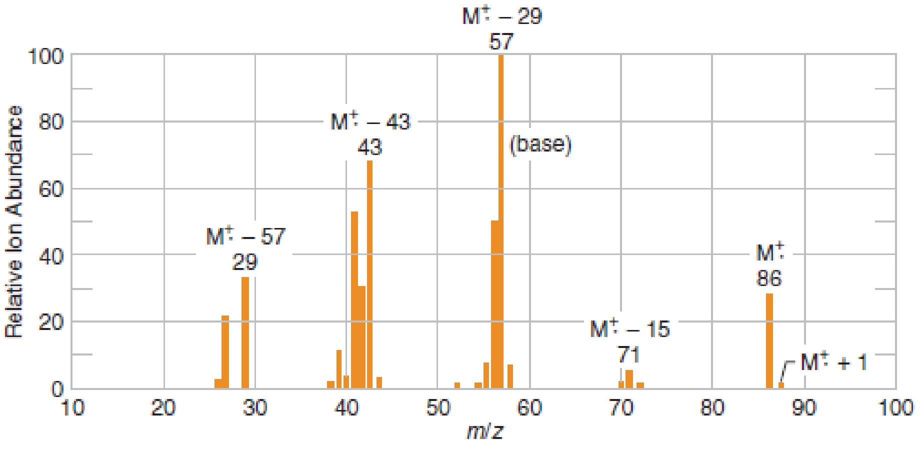
m/z	Relative Ion Abundance
14	17.2
15	100.0
19	2.0
31	10.4
32	9.4
33	89.5
34	95.4
35	1.1

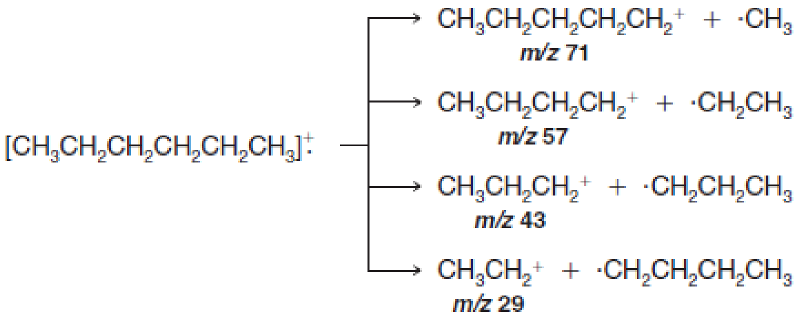
Mass Spectrometry

Fragmentation

- ❑ Fragmentation of Longer Chain and Branched Alkanes

The mass spectrum of hexane shown in Fig. 9.37 illustrates the kind of fragmentation a longer chain alkane can undergo. Here we see a reasonably abundant molecular ion at *m/z* 86 accompanied by a small $M^{+\cdot} + 1$ peak. There is also a smaller peak at *m/z* 71 ($M^{+\cdot} - 15$) corresponding to the loss of $\cdot CH_3$, and the base peak is at *m/z* 57 ($M^{+\cdot} - 29$) corresponding to the loss of $\cdot CH_2CH_3$. The other prominent peaks are at *m/z* 43 ($M^{+\cdot} - 43$) and *m/z* 29 ($M^{+\cdot} - 57$), corresponding to the loss of $\cdot CH_2CH_2CH_3$ and $\cdot CH_2CH_2CH_2CH_3$, respectively.





$[CH_3CH_2CH_2CH_2CH_2CH_3]^{+\cdot}$

$\rightarrow CH_3CH_2CH_2CH_2CH_2^{+} + \cdot CH_3$ **m/z 71**

$\rightarrow CH_3CH_2CH_2CH_2^{+} + \cdot CH_2CH_3$ **m/z 57**

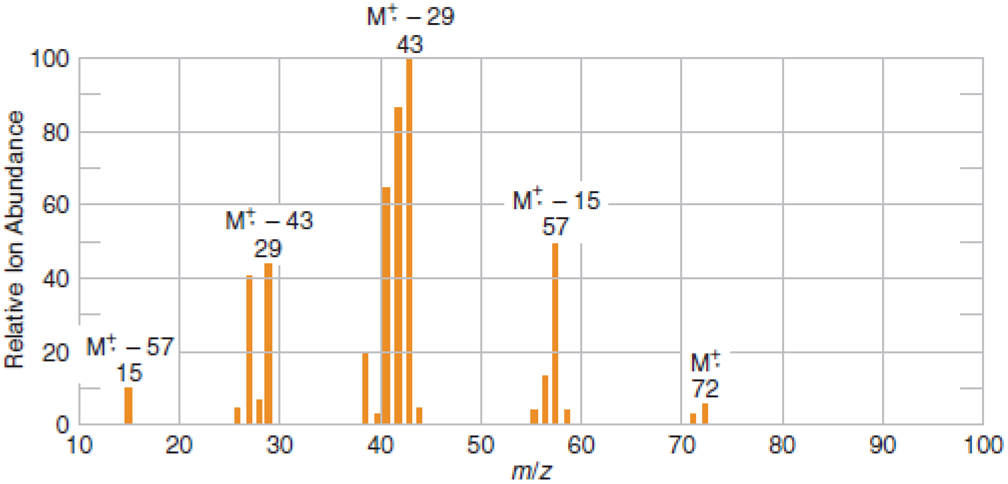
$\rightarrow CH_3CH_2CH_2^{+} + \cdot CH_2CH_2CH_3$ **m/z 43**

$\rightarrow CH_3CH_2^{+} + \cdot CH_2CH_2CH_2CH_3$ **m/z 29**

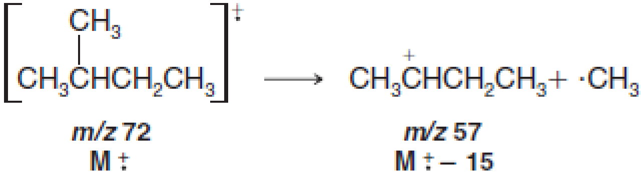
Mass Spectrometry

Fragmentation

Chain branching increases the likelihood of cleavage at a branch point because a more stable carbocation can result. When we compare the mass spectrum of 2-methylbutane with the spectrum of hexane, we see a much more intense peak at $M^{+\cdot} - 15$.



Loss of a methyl radical from the molecular ion of 2-methylbutane can give a secondary carbocation:



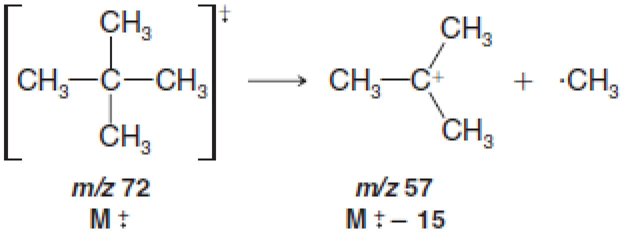
$$\left[\begin{array}{c} CH_3 \\ | \\ CH_3CHCH_2CH_3 \end{array}\right]^{+\cdot} \longrightarrow CH_3\overset{+}{C}HCH_2CH_3 + \cdot CH_3$$

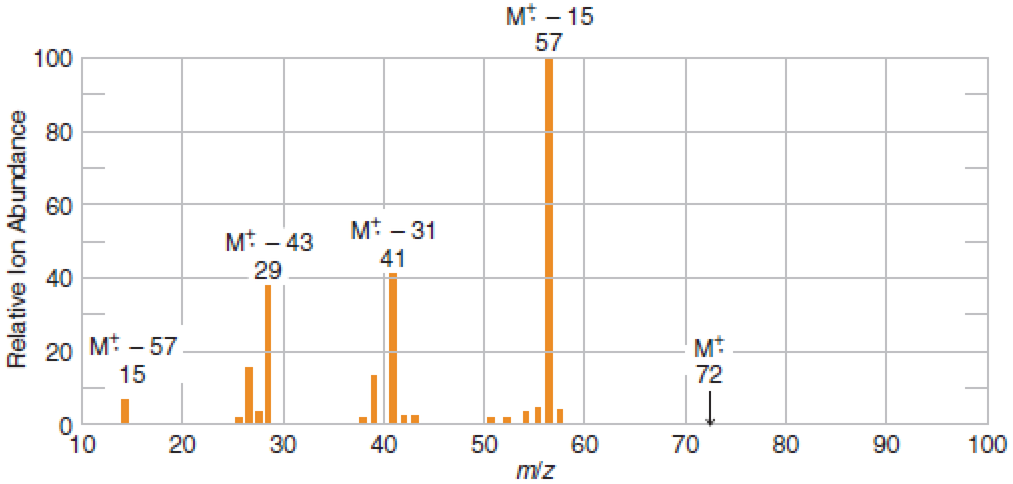
whereas with hexane loss of a methyl radical can yield only a primary carbocation.

Mass Spectrometry

Fragmentation

With neopentane , this effect is even more dramatic. Loss of a methyl radical by the molecular ion produces a *tertiary* carbocation, and this reaction takes place so readily that virtually none of the molecular ions survive long enough to be detected:





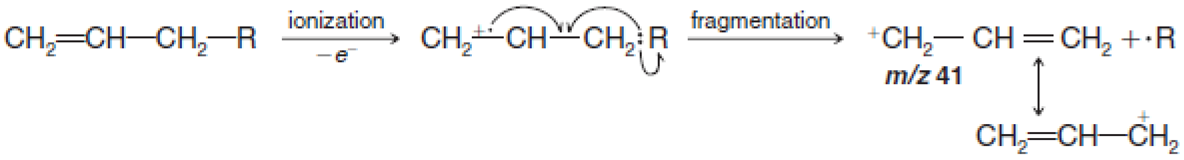
Q. Explain why the peak at M⁺-29 has very high intensity if compared to the peak at M⁺-15 in the mass spectrum of 3-methylpentane?

Mass Spectrometry

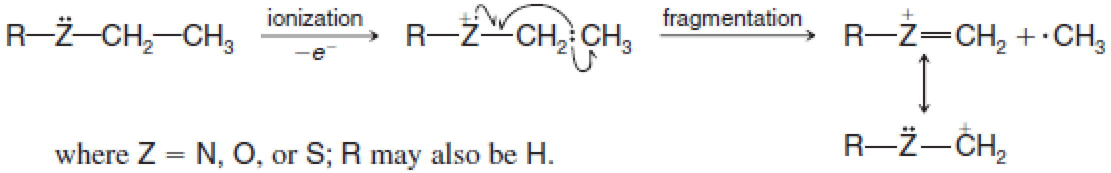
Fragmentation

- ❑ Fragmentation to Form Resonance-Stabilized Cations

1. Alkenes ionize and frequently undergo fragmentations that yield resonance-stabilized allylic cations:

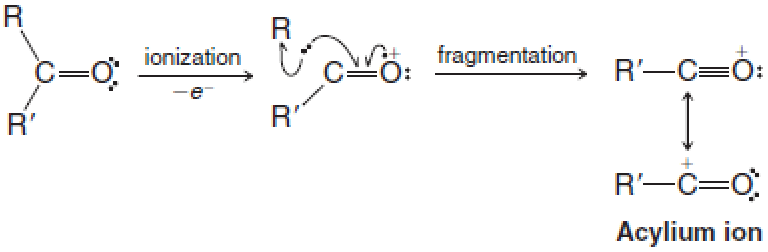


2. Carbon–carbon bonds next to an atom with an unshared electron pair usually break readily because the resulting carbocation is resonance stabilized:



where Z = N, O, or S; R may also be H.

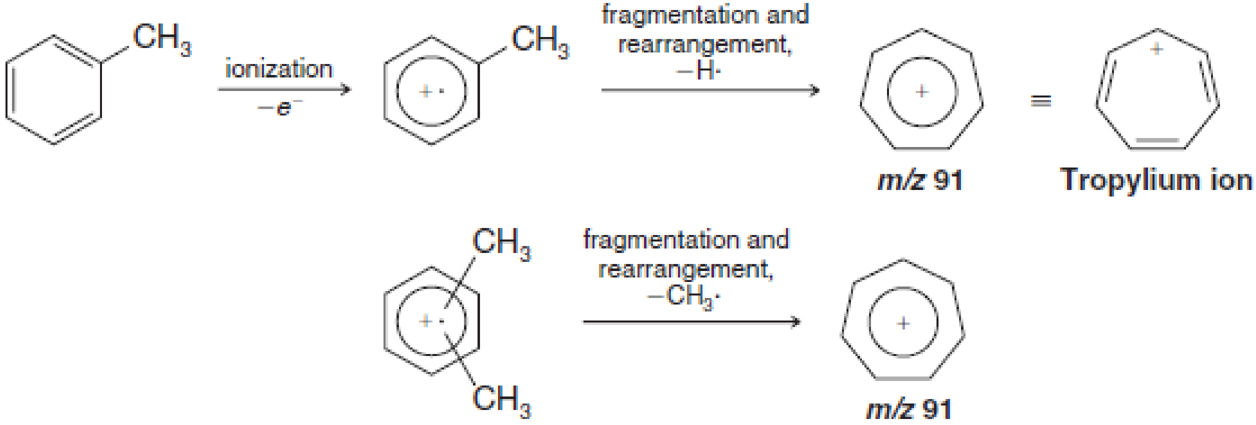
3. Carbon–carbon bonds next to the carbonyl group of an aldehyde or ketone break readily because resonance-stabilized ions called **acylium ions** are produced:



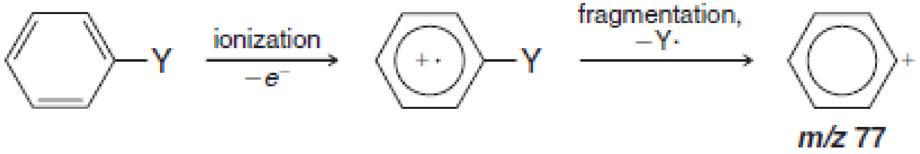
Mass Spectrometry

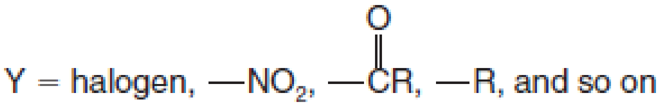
Fragmentation

4. Alkyl-substituted benzenes ionize by loss of a π electron and undergo loss of a hydrogen atom or methyl group to yield the relatively stable tropylium ion (see Section 14.7C). This fragmentation gives a prominent peak (sometimes the base peak) at *m*/*z* 91:



5. Monosubstituted benzenes with other than alkyl groups also ionize by loss of a π electron and then lose their substituent to yield a phenyl cation with *m*/*z* 77:



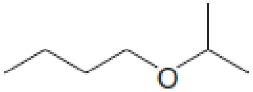


$Y = \text{halogen},\ \text{—}NO_2,\ \text{—}\overset{\displaystyle O}{\overset{\|}{C}}R,\ \text{—}R,\ \text{and so on}$

Mass Spectrometry

Fragmentation

Which spectrum for which molecule?



Butyl isopropyl ether

Butyl propyl ether

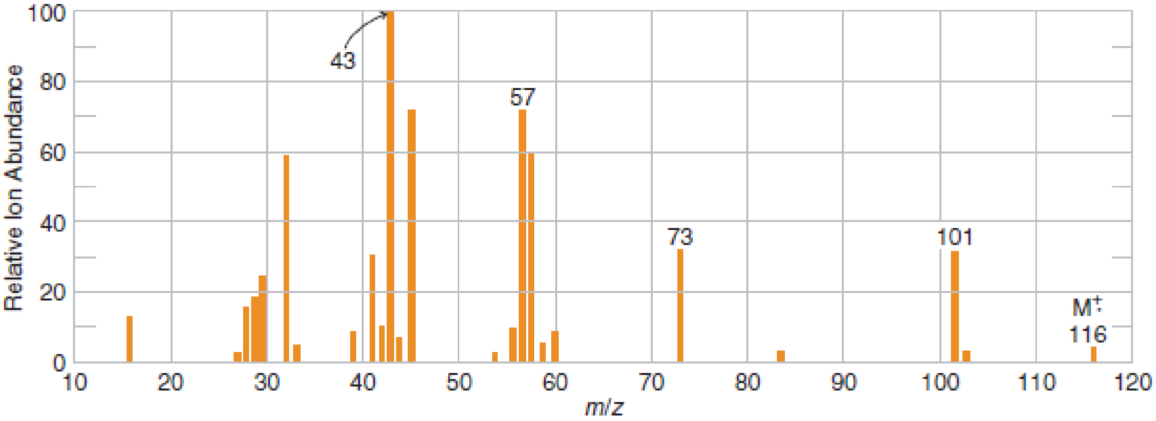
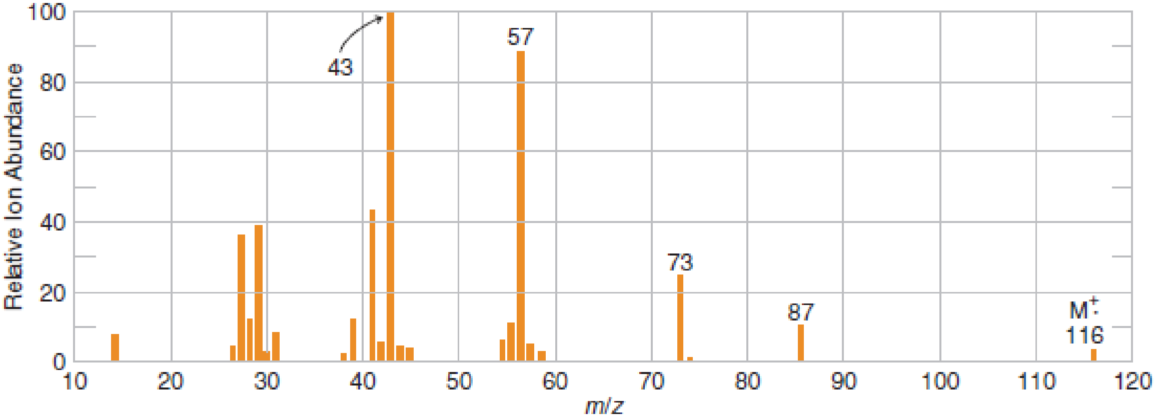


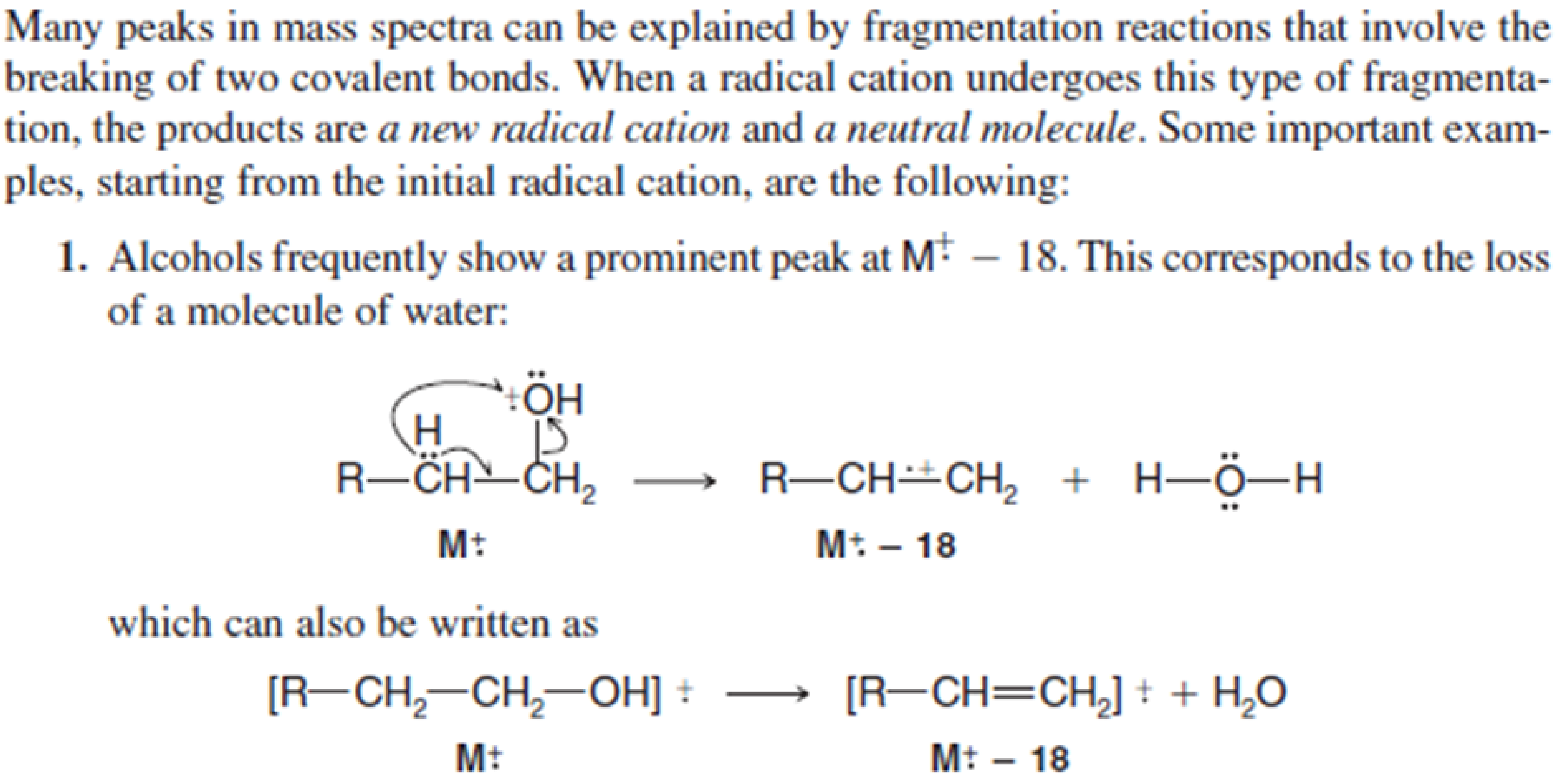
Figure 9.40 Mass spectrum for Review Problem 9.18.



Mass Spectrometry

Fragmentation

- Fragmentation by Cleavage of Two Bonds



Many peaks in mass spectra can be explained by fragmentation reactions that involve the breaking of two covalent bonds. When a radical cation undergoes this type of fragmentation, the products are *a new radical cation* and *a neutral molecule*. Some important examples, starting from the initial radical cation, are the following:

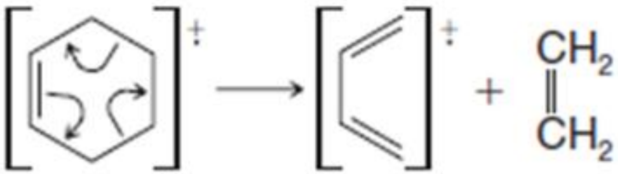
1. Alcohols frequently show a prominent peak at $M^{+\cdot} - 18$. This corresponds to the loss of a molecule of water:

$$\underset{M^{+\cdot}}{R{-}\overset{H}{\ddot{C}H}{-}\overset{\overset{+\cdot}{\ddot{O}H}}{CH_2}} \longrightarrow \underset{M^{+\cdot}-18}{R{-}CH\overset{\cdot+}{=}CH_2} + H{-}\ddot{\underset{\cdot\cdot}{O}}{-}H$$

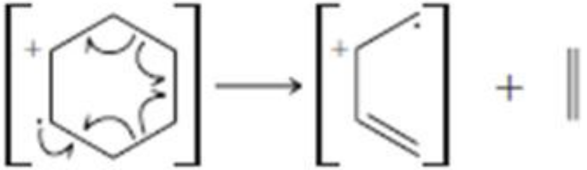
which can also be written as

$$\underset{M^{+\cdot}}{[R{-}CH_2{-}CH_2{-}OH]^{+\cdot}} \longrightarrow \underset{M^{+\cdot}-18}{[R{-}CH{=}CH_2]^{+\cdot}} + H_2O$$

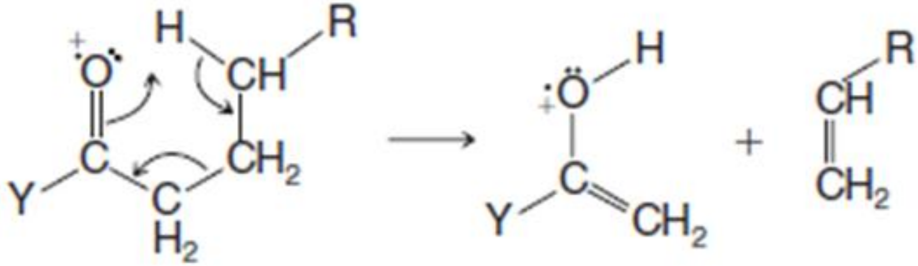
2. Cycloalkenes can undergo a retro-Diels–Alder reaction that produces an alkene and an alkadienyl radical cation:



which can also be written as



3. Carbonyl compounds with a hydrogen on their γ carbon undergo a fragmentation called the *McLafferty rearrangement*.

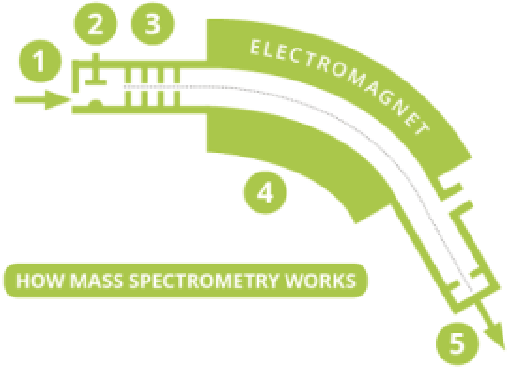


where Y = R, H, OR, OH, and so on.

In addition to these reactions, we frequently find peaks in mass spectra that result from the elimination of other small stable neutral molecules, for example, H_2, NH_3, CO, HCN, H_2S, alcohols, and alkenes.

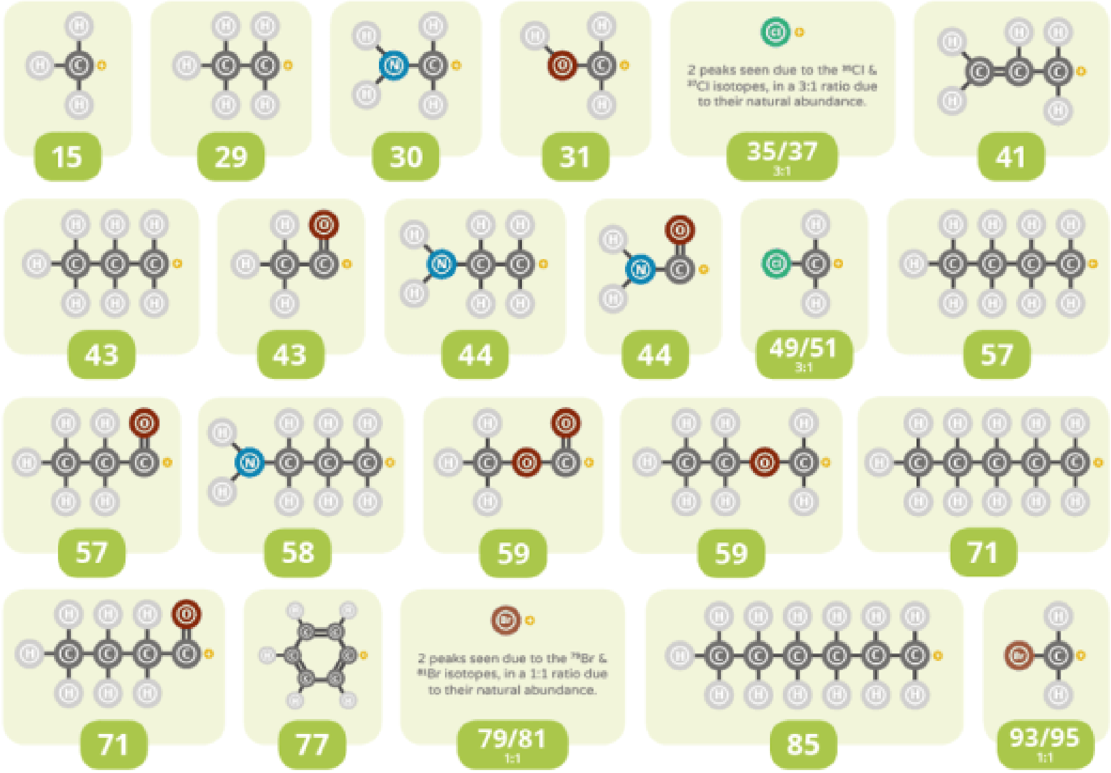
A GUIDE TO INTERPRETING MASS SPECTRA

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.



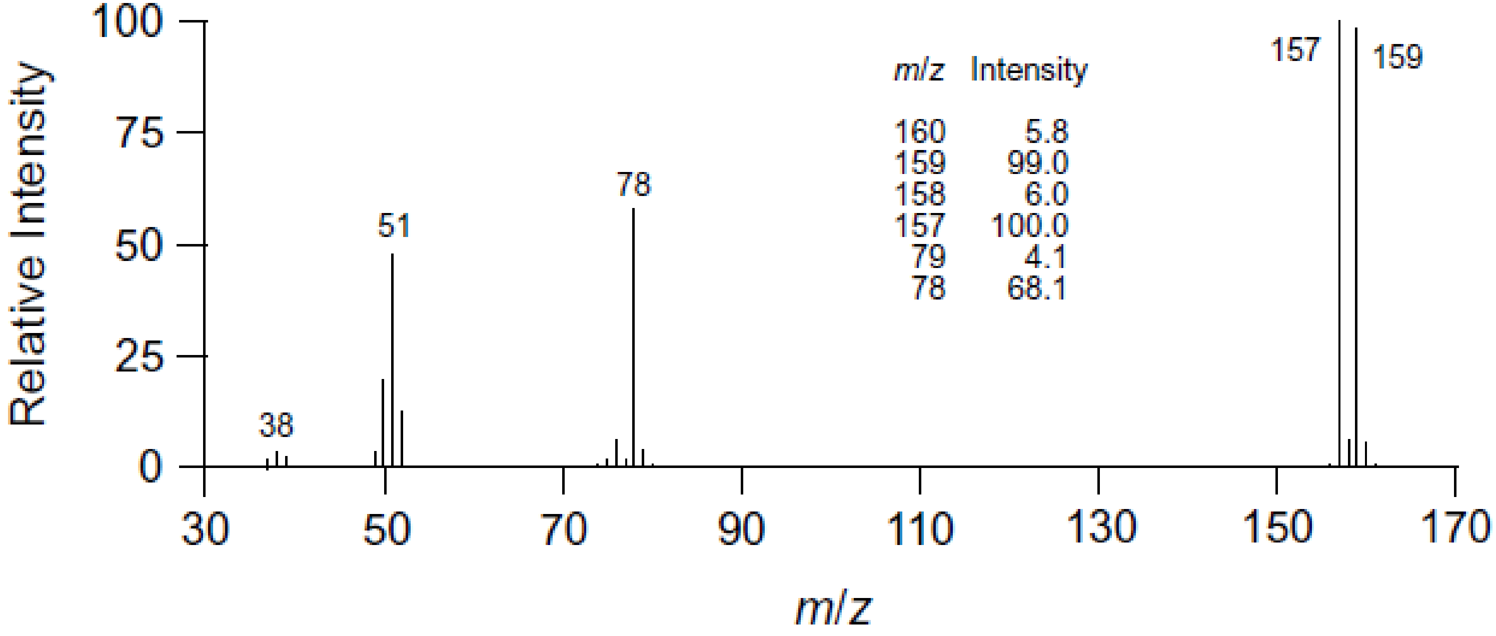
2 peaks seen due to the ^{35}Cl & ^{37}Cl isotopes, in a 3:1 ratio due to their natural abundance.

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.

Questions

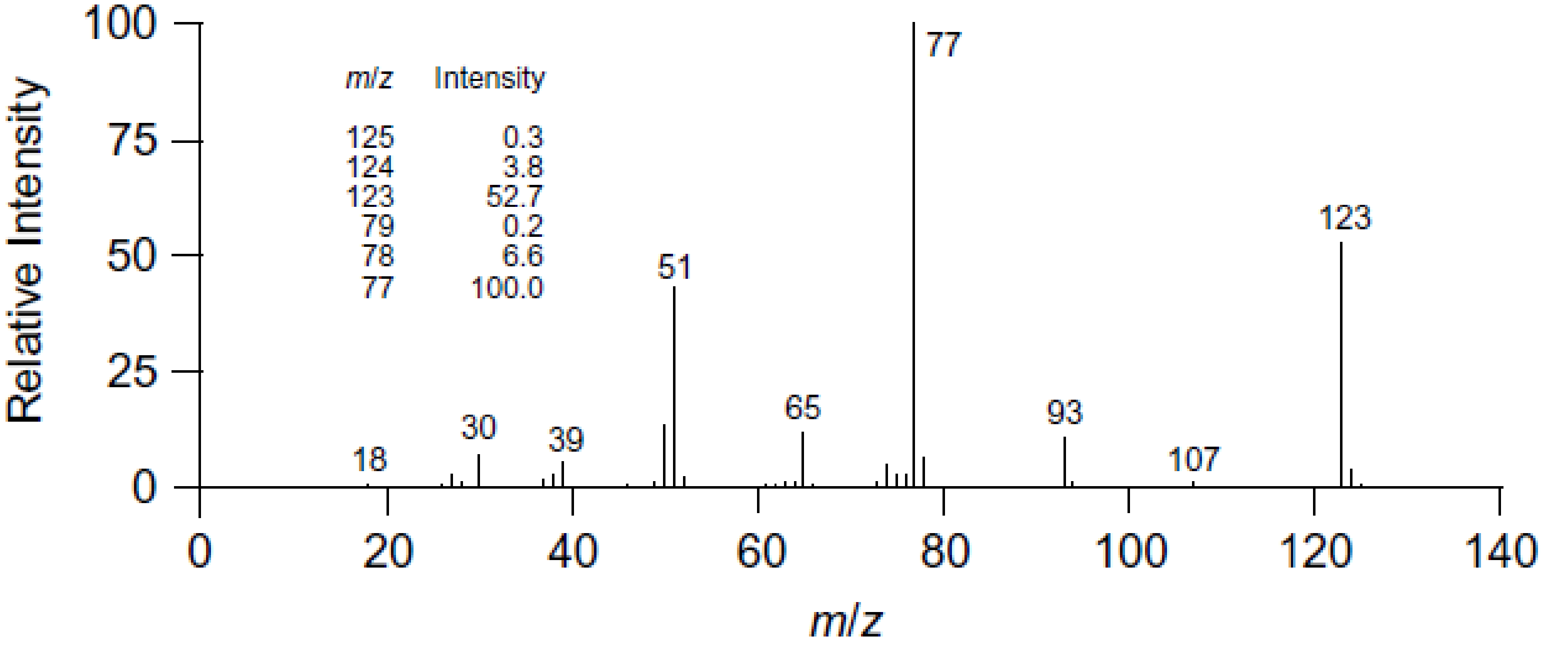
- Using Mass spectra, draw the chemical structure of the compound?



m/z	Intensity
160	5.8
159	99.0
158	6.0
157	100.0
79	4.1
78	68.1

Questions

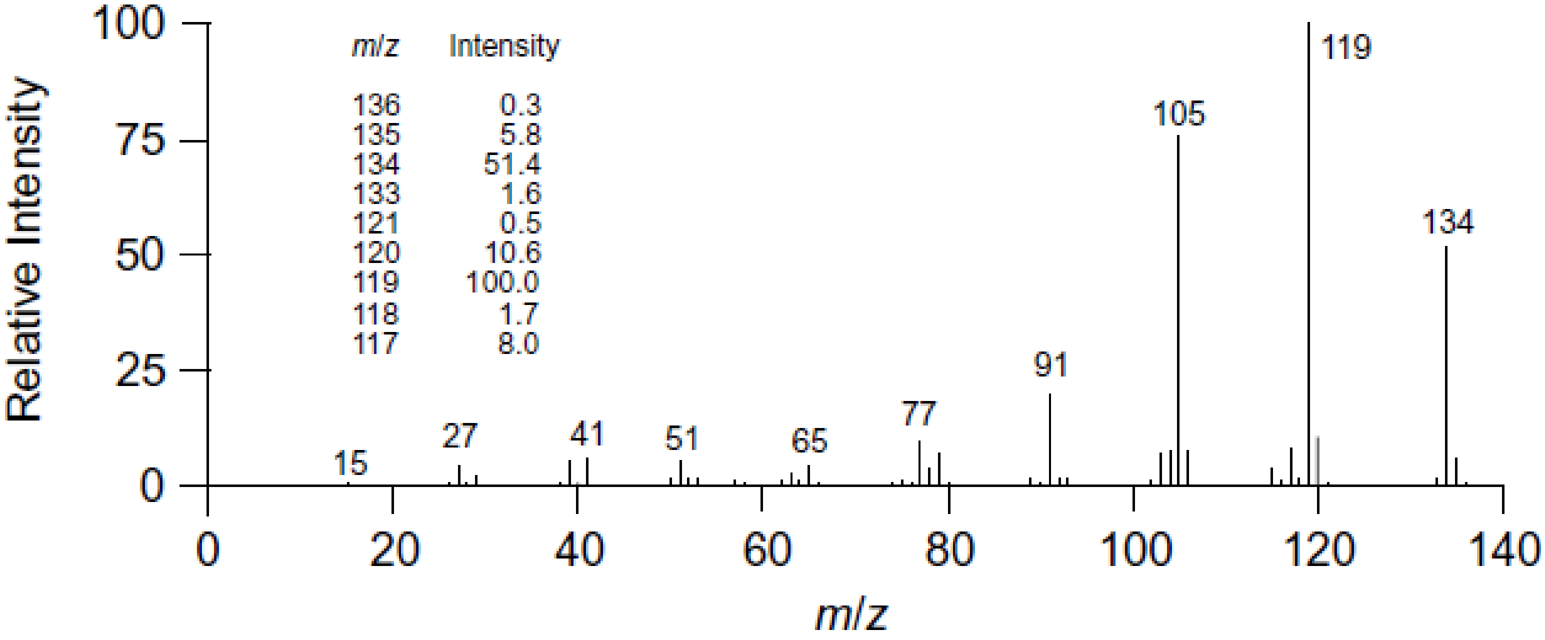
- Using Mass spectra, draw the chemical structure of the compound?



m/z	Intensity
125	0.3
124	3.8
123	52.7
79	0.2
78	6.6
77	100.0

Questions

- Using Mass spectra, draw the chemical structure of the compound?



m/z	Intensity
136	0.3
135	5.8
134	51.4
133	1.6
121	0.5
120	10.6
119	100.0
118	1.7
117	8.0