Spectroscopic Identification of Organic Molecules

Mass Spectroscopy

Exclusively for the graduate course at
Myongji University

2008.09

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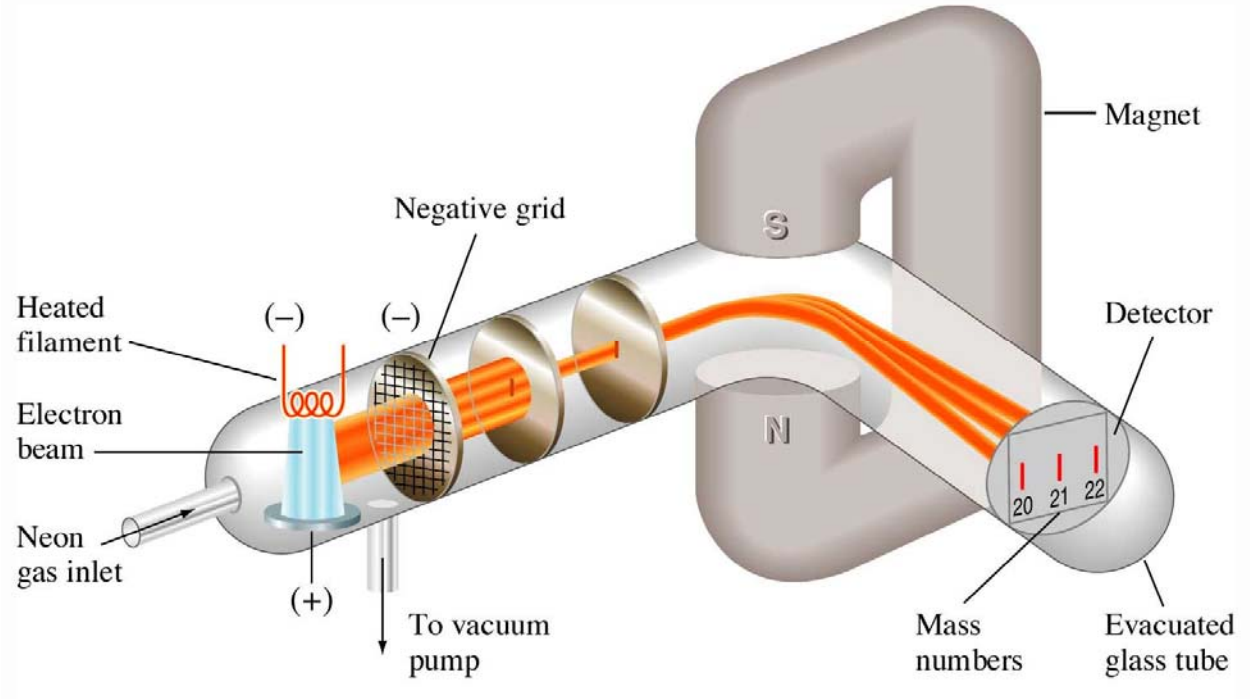
1. Mass Spectroscopy

1.1 Introduction

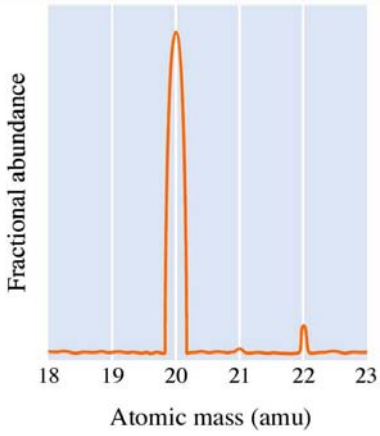
►**Basic Concept:** Ionized compounds are separated on the basis of their mass to charge ratio (*m/z*)



Spectrum

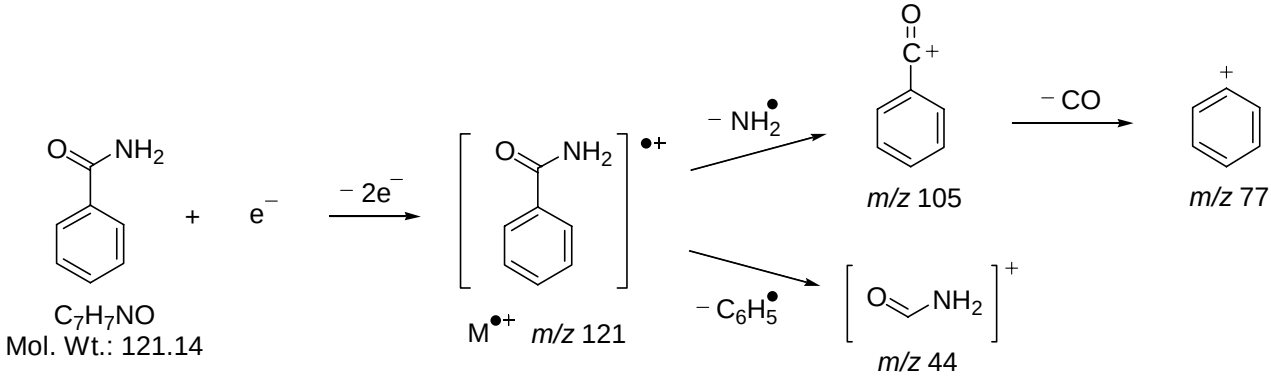
Vertical – peak intensity

Horizontal – m/z number



Molecular ion: Intact molecule minus one electron $M^{\bullet+}$

Fragment ion:



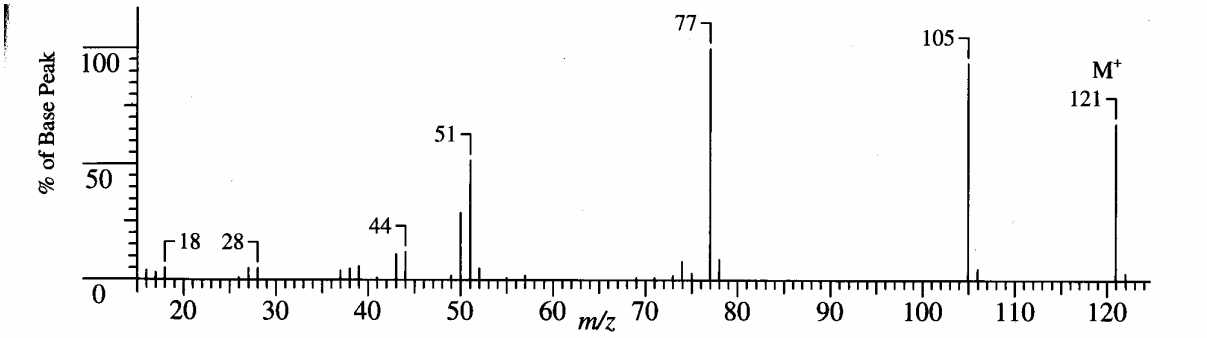


FIGURE 1.1 The EI mass spectrum of benzamide above which is a fragmentation pathway to explain some of the important ions.

Combined with GC or LC for sample introduction (GC-MS, LC-MS)

1.2 Ionization Methods

a) Gas-Phase Ionization Methods

Good for non-ionic organic molecules with **MW < 1,000**

a-1) Electron Impact Ionization (EI)

Vapor phase sample molecules are bombarded with high energy electrons (70 eV) to produce a radical cation (**molecular ion**).

Ionization potential (IP) of typical organic compounds – less than 15 eV

Excess energy is dissipated by breaking covalent bonds (3 ~ 10 eV) to provide **fragmented ions** – characteristics of compounds (unique property)

Databases contain EI mass spectra of over 390,000 compounds

a-2) Chemical Ionization (CI)

Soft ionization technique – Reagent gas (methane, isobutene, ammonia) is introduced into the source, and ionized. Then, sample molecules collide with the ionized reagent gas molecule (CH_5^+, $C_4H_9^+$, etc) in the relatively high-pressure CI source.

Secondary ionization

$[M+1]^+$: Quasimolecular ion – by proton transfer

$[M+15]^+$, $[M+24]^+$, $[M+43]^+$, $[M+18]^+$ (with NH_4^+) – by electrophilic addition

$[M]^+$ – by charge exchange (rare case)

$[M-1]^+$ – by hydride abstraction

The excess energy transferred to the sample molecule is less than 5 eV, so much less fragmentation takes place. Molecular ion can be easily detected, but less information on the structure can be provided.

CI MS is not useful for structural elucidation. Its main use is to detect molecular ion or molecular weight.

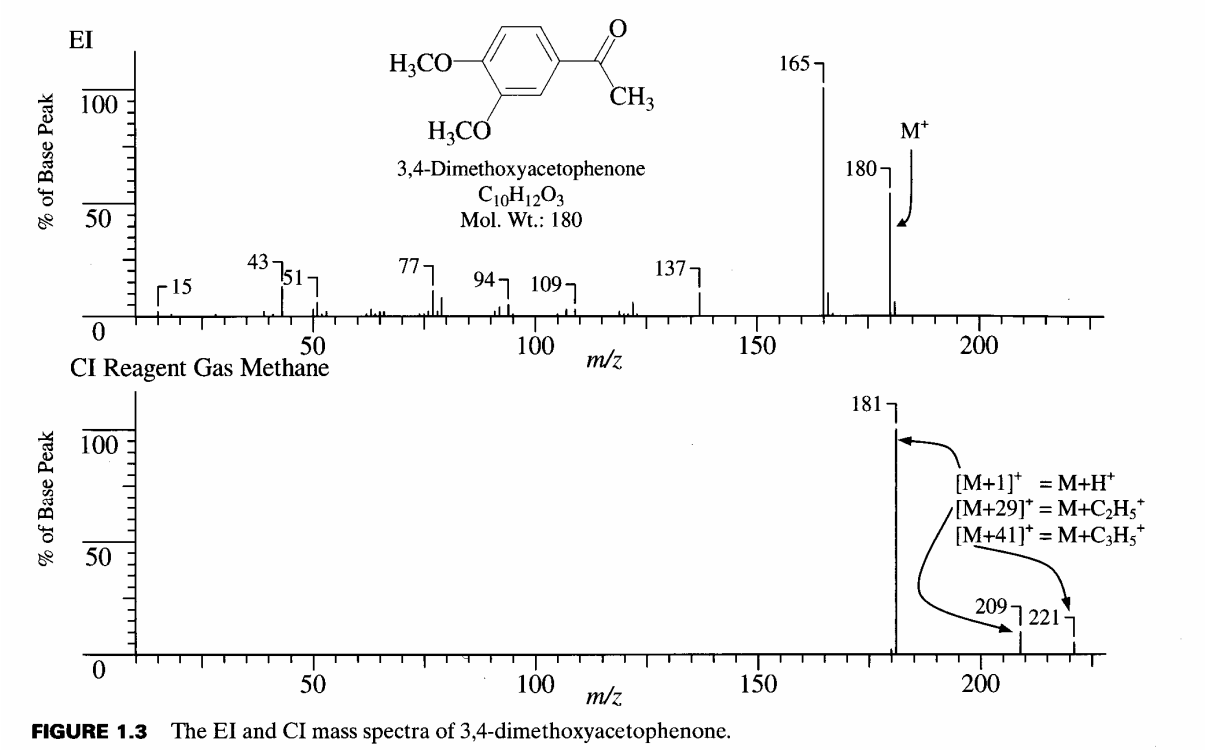


FIGURE 1.3 The EI and CI mass spectra of 3,4-dimethoxyacetophenone.

$[M+29]^+$

$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$

$[M+41]^+$

$CH_4 + C_2H_5^+ \rightarrow C_3H_5^+ + 2H_2$

b) Desorption Ionization Methods

Sample molecules are emitted directly from a condensed phase into the vapor phase as ions.

Used for large, nonvolatile, or ionic compounds.

Information is limited, primarily used to provide MW or in some case to obtain exact mass.

Spectra are often complicated by abundant matrix ions.

b-1) Field Desorption Ionization

High voltage gradients at the tips of the needles in a metal emitter remove an electron from the sample, and the resulting cation is repelled away from the emitter.

Molecular ion is usually the only significant ion (minimal fragmentation).

Useful for non-polar compounds, and low level of background ions

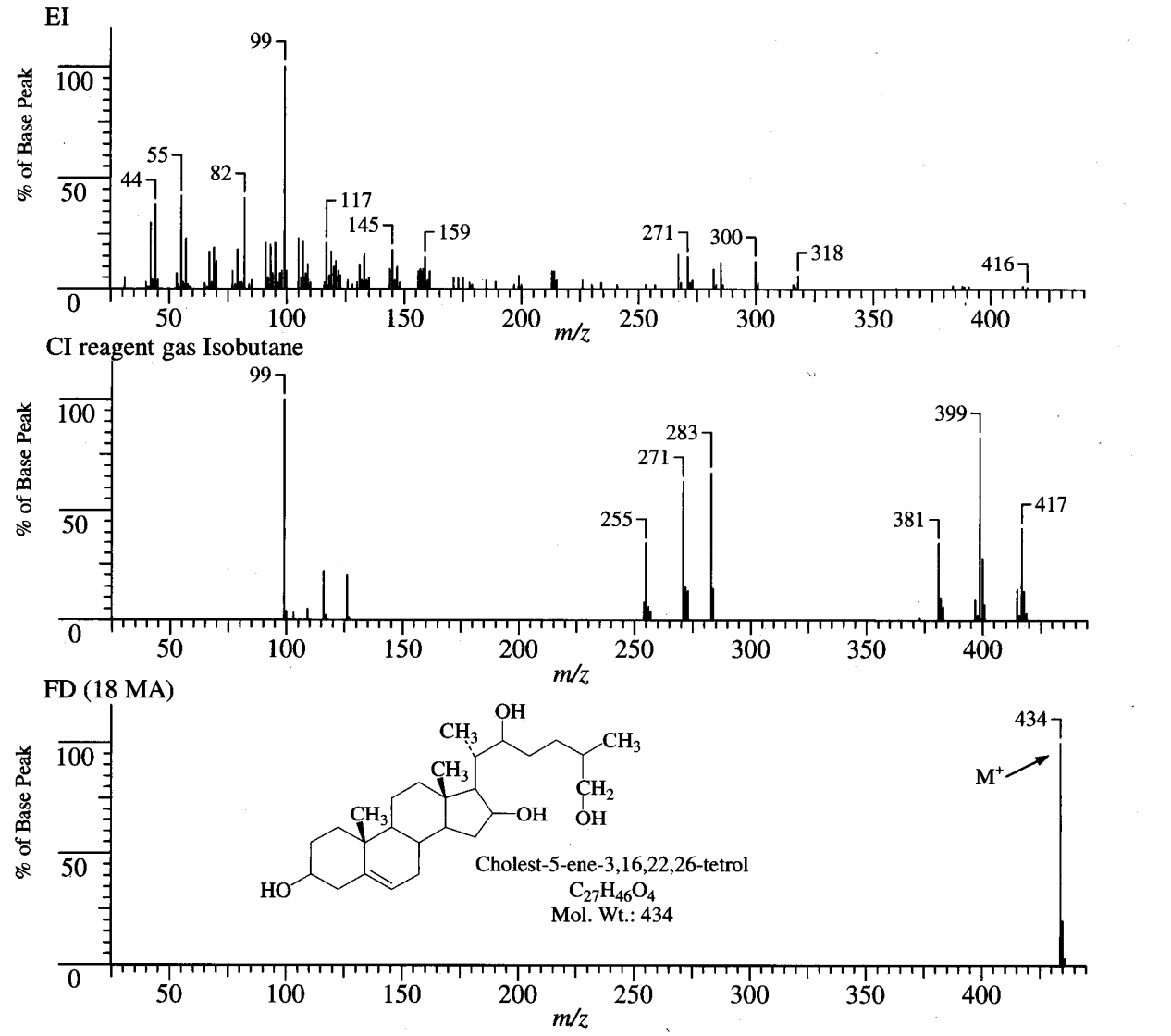


FIGURE 1.4 The electron impact (EI), chemical ionization (CI), and field desorption (FD) mass spectra of cholest-5-ene-3, 16, 22, 26-tetrol.

b-2) Fast Atom Bombardment Ionization (FAB)

FAB uses high-energy **Xe** (xenon) or **Ar** (argon) atoms (6-10 KeV) to bombard samples dissolved in a liquid of low vapor pressure (e.g. glycerol). The matrix protects the sample from excessive radiation damage.

Used for high resolution mode and for large non-volatile molecules, particularly to determine MW.

Low mass ranges are composed of ions produced by the matrix (drawback).

A method of sequencing polysaccharides and peptides – fragmentation usually occurs at the glycosidic and peptide bonds, respectively.

The upper mass limit is between 10 and 20 KDa and useful up to 6 KDa.

LSIMS (liquid secondary ionization mass spectrometry) is similar to FAB except that it uses somewhat more energetic **Cs** (cesium ions) (10-30 KeV).
Positive ions: $[M+1]^+$ or **$[M+23, Na]^+$** by cation attachment
Negative ions: $[M-1]^+$ by deprotonation

b-3) Plasma Desorption Ionization

Specialized technique used exclusively with a time of flight (TOF) mass analyzer.
The fission products from Californium 252 (**^{252}Cf**) with energies in the range of 80-100 MeV are used to bombard and ionize the sample.
Each time a ^{252}Cf splits, two particles are produced moving in opposite directions. One of the particles hits a triggering detector and signals a start time. The other particle strikes the sample matrix ejecting some sample ions into a time of flight mass spectrometer (**TOF-MS**).
Ions are of low energy and useful fragmentation is rarely observed.
MW up to 45 KDa.

※ TOF principle

All of the ions arriving at the beginning of the drift have the same energy given by $zeV = mv^2/2$, then ions of different mass will have different velocities: $v = (2zeV/m)^{1/2}$.
In a drift tube length of L, the time of flight for an ion is **t** = $L/(2zeV/m)^{1/2} = (L^2\mathbf{m}/2zeV)^{1/2}$.
The mass for a given ion can be calculated.

b-4) Laser Desorption Ionization

A pulsed laser beam can be used to ionize samples, and it must be used with either a time of flight (TOF) or Fourier transformation (FT) mass spectrometer.
Laser source: CO_2 laser (far IR region) or Nd/YAG laser (UV region at 266 nm)
MW less than 2KDa without matrix assistance

Matrix assisted laser desorption ionization (MALDI)

Matrix materials: nicotinic acid and sinapinic acid
MW up to 200~300 KDa
Ions have little excess energy and show little propensity to fragment

c) Evaporative Ionization Methods

Ions (or rarely neutral compounds) in solution (often containing formic acid) have their solvent molecules stripped by evaporation, with simultaneous ionization leaving behind the ions for mass analysis. Used as a combination with LC (LC-MS).

c-1) Thermospary Mass Spectrometry

A solution of the sample is introduced into mass spectrometer by means of **a heated capillary tube**. The tube nebulizes and partially vaporizes the solvent forming a stream of fine droplets, which enter the ion source. When the solvent completely evaporates, the sample can be analyzed.

c-2) Electrospray Mass Spectrometry

The electrospray (**ES**) ion source is operated at or near atmospheric pressure (**API**: atmospheric pressure ionization)

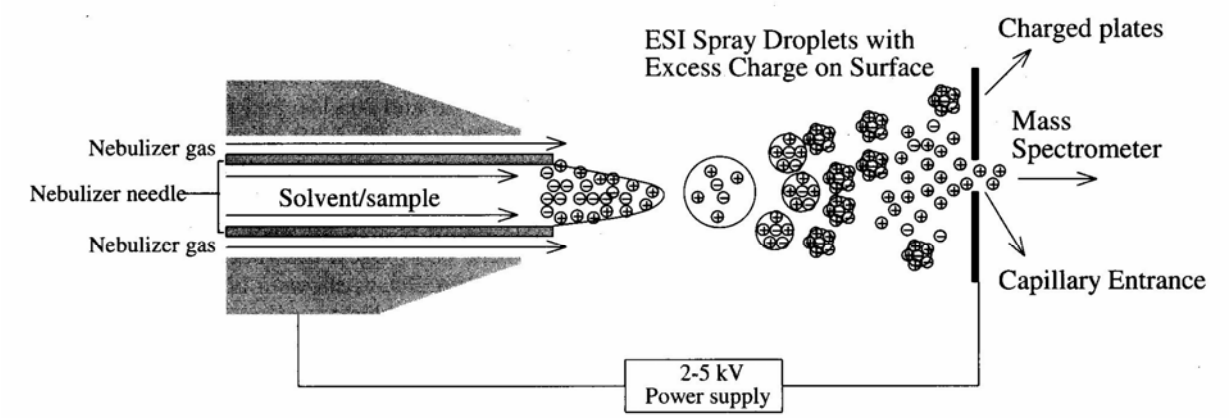


FIGURE 1.5 A diagram showing the evaporation of solvent leading to individual ions in an electrospray instrument.

►Operating Principle

The sample in solution (a polar, volatile solvent) enters the ion source through a stainless steel capillary, which is surrounded by a co-axial flow nitrogen (nebulizing gas). The tip of the capillary is maintained at a high potential. The potential difference produces a field gradient of up to 5 KV/cm. As the solution exits the capillary, an aerosol of **charged droplets** forms. Droplet in the aerosol shrink as the solvent evaporates, thereby concentrating the charged sample ions. When the electrostatic repulsion among the charged sample ions reaches a critical point, the droplet undergoes "***Coulombic explosion***," which releases the sample ions into vapor phase. The vapor phase ions are focused with a number of sampling orifices into the mass analyzer.

►Multiple Charges and MW calculation

With proteins, ions with **multiple charges (n)** are formed – mass values of 1/2, 1/3, …, 1/n of their actual masses are recorded. MW up to 100KDa (40 charges) can be detected.

If two peaks, which differ by a single charge, can be identified, the **MW can be calculated**.

Each ion of the sample molecule (M_s) has the general form $(M_s + ZH)^{Z+}$.

H: mass of a proton (1.0079 Da); Z: the number of charge

For two ions differing by one charge,

$M_1 = [M_s + (Z+1)H]/(Z+1)$

$M_2 = [M_s + ZH]/Z$

Solve the above two equation for Z, then

$Z = (M_1 - H)/(M_2 - M_1)$

EI-MS of Lactose is useless – low vapor pressure and thermally labile.

ES-MS shows molecular ion m/z 342 and $[M+23]^+$, the molecular ion plus Sodium, which is ubiquitous in aqueous solution. Sodium adducts are very common.

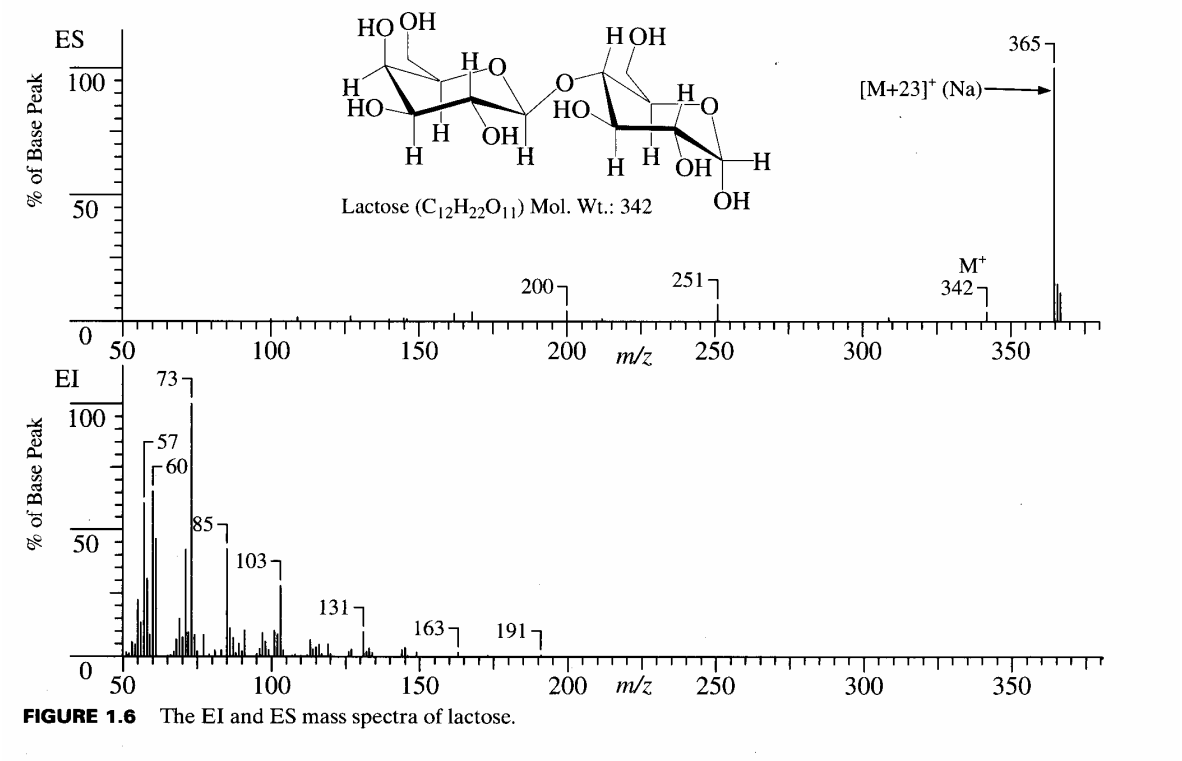


FIGURE 1.6 The EI and ES mass spectra of lactose.

ES-MS for Tetra-peptide: Valine-Glycine-Serine-Glutamic acid (VGSE)

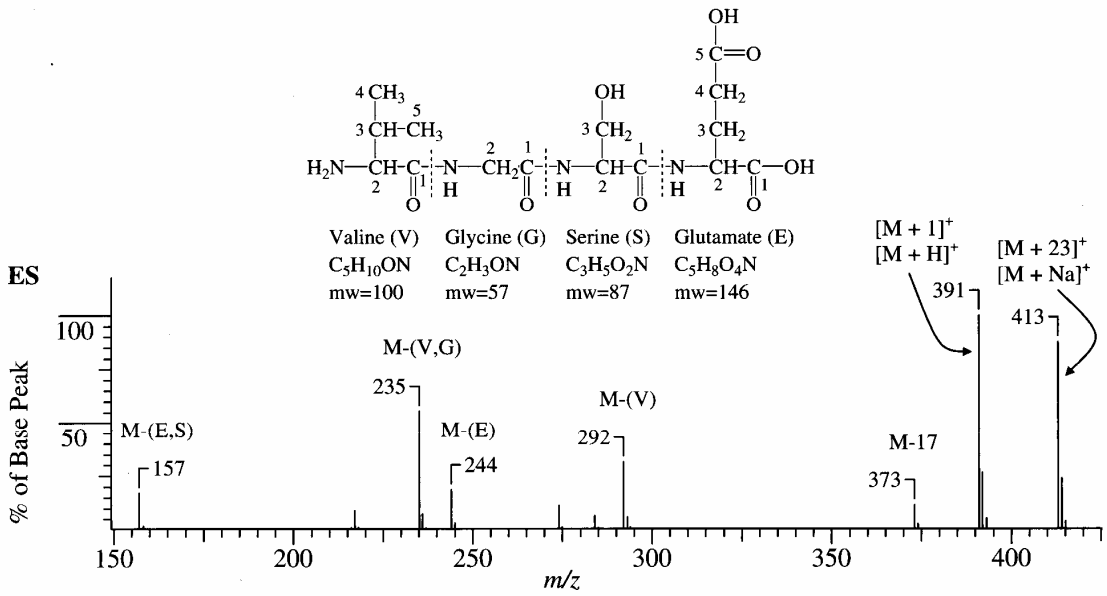


FIGURE 1.7 The electrospray (ES) mass spectrum for the tetra-peptide whose structure is given in the figure. See text for explanation.

m/z 391 $[M+1]^+$

m/z 413 $[M+23]^+$

some valuable fragmentation information characteristic of each of the amino acids.

TABLE 1.1 Summary of Ionization Methods.

Ionization Method	Ions Formed	Sensitivity	Advantage	Disadvantage
Electron impact	M^+	ng–pg	Data base searchable Structural information	M^+ occasionally absent
Chemical ionization	M + 1, M + 18, etc	ng–pg	M+ usually present	Little structural information
Field desorption	M^+	μg–ng	Non volatile compounds	Specialized equipment
Fast atom bombardment	M + 1, M + cation M + matrix	μg–ng	Non volatile compounds Sequencing information	Matrix interference Difficult to interpret
Plasma desorption	M+	μg–ng	Non volatile compounds	Matrix interference
Laser desorption	M + 1, M + matrix	μg–ng	Non volatile compounds Burst of ions	Matrix interference
Thermospray	M^+	μg–ng	Non volatile compounds	Outdated
Electrospray	M^+, M^{++}, M^{+++}, etc.	ng–pg	Non volatile compounds interfaces w/ LC Forms multiply charged ions	Limited classes of compounds Little structural information

1.3 Mass Analyzers

TABLE 1.2 Summary of Mass Analyzers.

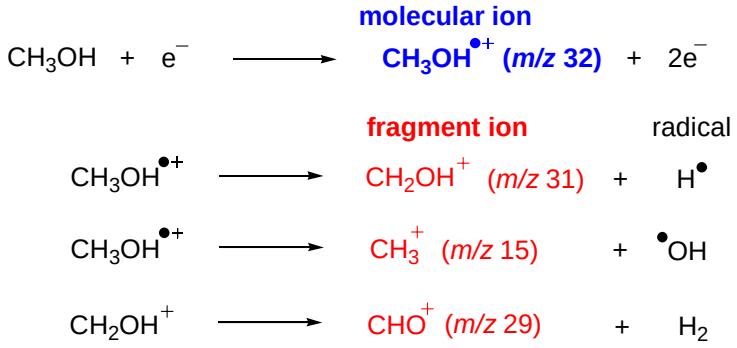
Mass Analyzer	Mass Range	Resolution	Sensitivity	Advantage	Disadvantage
Magnetic Sector	1–15,000 *m/z*	0.0001	Low	High res.	Low sensitivity Very expensive High technical expertise
Quadrupole	1–5000 *m/z*	unit	High	Easy to use Inexpensive High sensitivity	Low res. Low mass range
Ion trap	1–5000 *m/z*	unit	High	Easy to use Inexpensive High sensitivity Tandem MS (MS^n)	Low res. Low mass range
Time of flight	Unlimited	0.0001	High	High mass range Simple design	Very high res.
Fourier transform	up to 70 kDa	0.0001	High	Very High res. and mass range	Very expensive High technical expertise

1.4 Interpretation of EI Mass Spectra

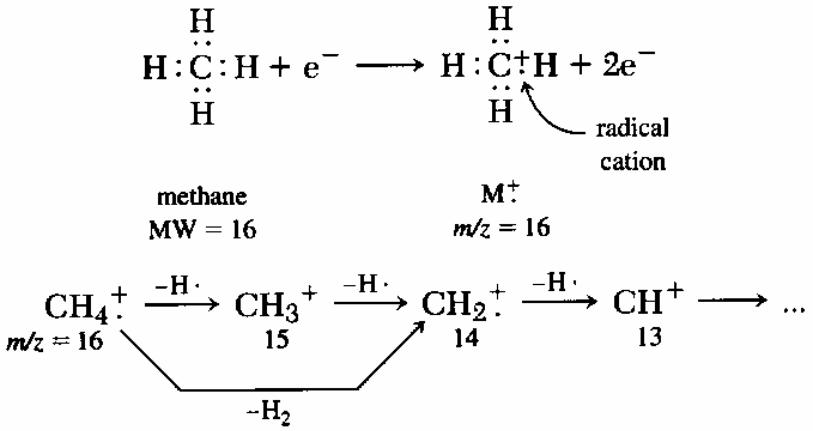
A mass spectrum is a presentation of **the masses of the positively charged fragments** including molecular ion versus their relative concentrations.

Base peak: the most intense peak in the spectrum (assign a value of 100%).

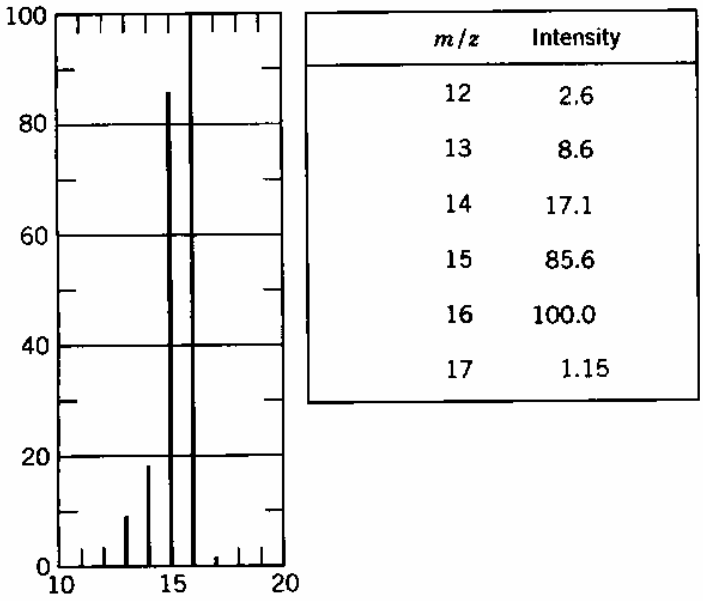
The other peaks are reported as percentages of the base peak



The **molecular ion** is frequently not detected in aliphatic alcohols, nitrites, nitrates, nitro compounds, nitriles, and highly branched compounds.



In Figure 8.2, the peaks are seen at 16, 15, 14, and 13, corresponding to th species in the above equation.



m/z	Intensity
12	2.6
13	8.6
14	17.1
15	85.6
16	100.0
17	1.15

Figure 8.2 Mass spectrum of CH_4 in both bar graph and tabular form.

► **Isotope peaks** (at M+1, M+2, etc.)

Determination of molecular formula

For compound $\mathbf{C_nH_mN_xO_ySi_aS_bCl_cBr_d}$

$\%(M+1) \approx (1.08 \cdot n) + (0.0115 \cdot m) + (0.369 \cdot x) + (0.0381 \cdot y) + (5.08 \cdot a) + (0.800 \cdot b)$

$\%(M+2) \approx (1.08 \cdot n)^2/200 + (0.205 \cdot y) + (3.35 \cdot a) + (4.52 \cdot b) + (32.0 \cdot c) + (97.3 \cdot d)$

Ex)

C_5H_5N:

$\%(M+1) = 1.08 \times 5 + 0.0115 \times 5 + 0.369 \times 1 = 5.8265$

$\%(M+2) = (1.08 \times 5)^2/200 = 0.1458$

C_7H_5O:

$\%(M+1) = 1.08 \times 7 + 0.0115 \times 5 + 0.0381 \times 1 = 7.6556$

$\%(M+2) = (1.08 \times 7)^2/200 + 0.205 \times 1 = 0.4908$

Home works

1. Calculate the abundances of the M+1 and M+2 peaks for C_2H_4, CO, and N_2
2. Calculate the abundances of the M+1 and M+2 peaks for C_3H_4O, C_4H_8, and $C_2H_4N_2$
3. Calculate the abundances of the M+1 and M+2 peaks for $C_6H_{12}Br_2$, $C_6H_{12}BrCl$, and $C_6H_{12}Cl_2$

Masses and Isotope Abundance Ratios

Formula	*m/z* Ratio	M+1	M+2
C_2H_4	28.0313	2.28	0.01
CO	27.9949	1.15	0.20
N_2	28.0062	0.74	0.00

TABLE 1.3 Relative Isotope Abundances of Common Elements.

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

►High-Resolution Molecular Ion

Accurate mass measurement determines molecular formula (masses are not integers).

The exact mass of the most abundant isotope must be used, not the elemental mass from the periodic table.

Low-Resolution Mass of 28 – CO, N_2, CH_2N, and C_2H_4

CO = 12.0000 + 15.9949 = 27.9949

N_2 = 2 x 14.0031 = 28.0062

CH_2N = 28.0187

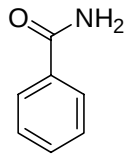
C_2H_4 = 28.0312

►Index of Hydrogen Deficiency (by Molecular Formula) – Degree of Unsaturation

# of rings + # of double bonds + (# of triple bonds) x 2

For $\mathbf{C_nH_mX_xN_yO_z}$

Index = (n) – (m/2) – (x/2) + (y/2) + 1

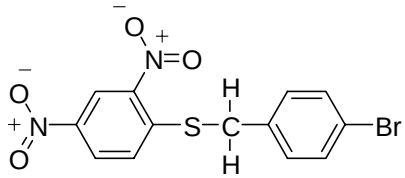


Oxygen and Sulfur (divalent) are not counted.

Ex) C_7H_7NO Index = 7 – 3.5 + 0.5 + 1 = 5

In general, compounds of $\alpha_I\ \beta_{II}\ \gamma_{III}\ \delta_{IV}$

Index = (IV) – (I/2) + (III/2) + 1



α: mono-valent (H, D, or Halogen)

β: di-valent (O, S)

γ: tri-valent (N, P)

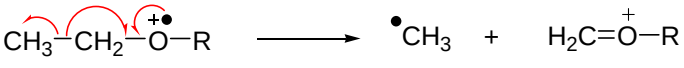
δ: tetra-valent (C, Si)

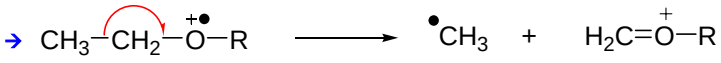
Ex) $C_{13}H_9N_2O_4BrS$ Index = 13 – 10/2 + 2/2 + 1 = 10

►Fragmentation

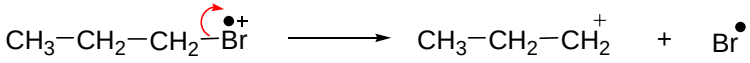
Fragmentation is initiated by electron impact. The major driving force is the cation-radical character that is imposed upon the structure.

Homolytic cleavage: each electron moves independently

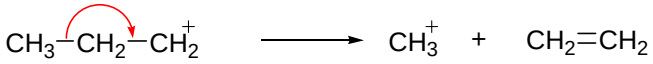




Heterolytic cleavage: a pair of electrons moves together toward the charged site



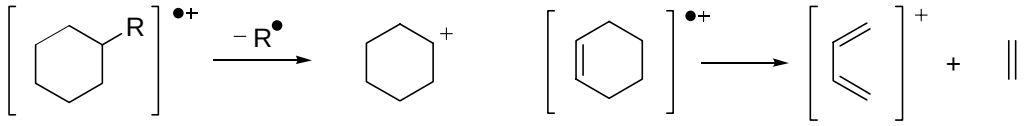
Further fragmentation of an even-electron cation → even-electron cation and even-electron neutral molecule or fragment



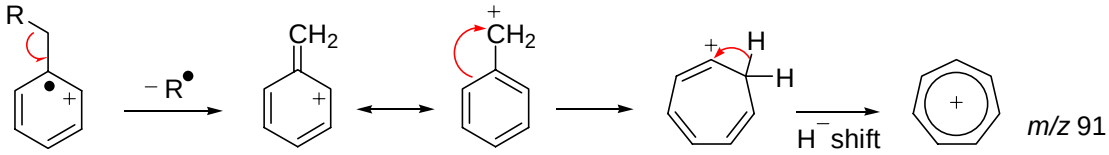
※The probability of cleavage of a particular bond is related to the bond strength.

General Rules Predicting Prominent Peaks in EI Spectra

1. Cleavage is favored at alkyl-substituted carbon atoms. The largest substituent at a branch eliminated readily as a radical.
2. Double bonds, cyclic structures, especially aromatic rings stabilize the molecular ion.
3. Double bond (cyclic compound) favor allylic cleavage and give the resonance stabilized allylic carbocation.
4. **Saturated rings** tend to lose alkyl side chains at the α-bond.



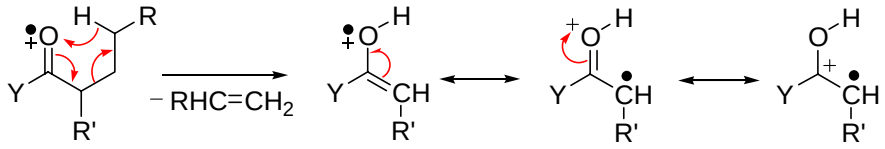
5. **Unsaturated rings** can undergo a retro-Diels Alder reaction
6. **Alkyl-substituted aromatic compounds** – cleavage at the bond β to the ring to produce benzyl ion or tropylium ion.



7. The C–C bonds next to a heteroatom are frequently cleaved.
8. Cleavage is often associated with elimination of small, stable, neutral molecules, such as CO (28), H_2O (18), NH_3 (17), H_2S (34), HCN (27), olefins, mercaptans, ketene, or alcohols.

►Rearrangements

McLafferty rearrangement – migration of hydrogen atoms in molecules that contain a heteroatom.



Y = H, R, OH, OR, NH_2

Requirement – heteroatom (O), π system, γ hydrogen to the C=O system.

Rearrangement peaks can be recognized by considering the mass (m/z) number for fragment ions and for their corresponding molecular ions.

Simple cleavage: even number molecular ion → odd number fragment ion (and vice versa)

Rearrangement: even number molecular ion → even number fragment ion (odd to odd)

or, a fragment ion mass different by 1 unit from that expected for a simple cleavage.

1.5 Mass Spectra of Some Chemical Classes

►Hydrocarbons

Fragmentation pattern is characterized by cluster of peaks, and the corresponding peaks of each cluster are 14 mass units (CH_2) apart. The largest peak in each cluster represent C_nH_{2n+1} fragment at $m/z = 14n + 1$.

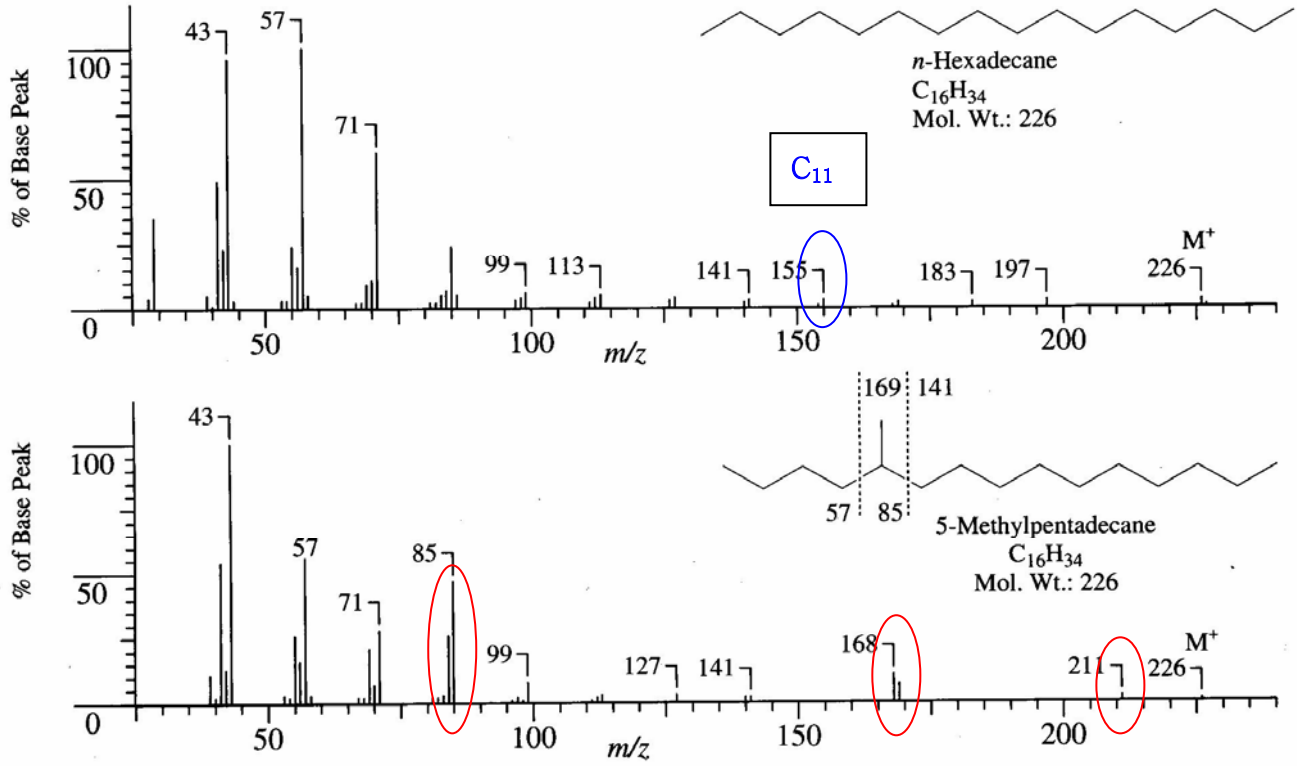


FIGURE 1.14 EI mass spectra of isomeric C_{16} hydrocarbons.

Saturated ring in a hydrocarbon

Increased intensity of the molecular ion peak

Fragmentation – characterized by loss of two carbon atoms as **C_2H_4 (28)** and C_2H_5 (29).

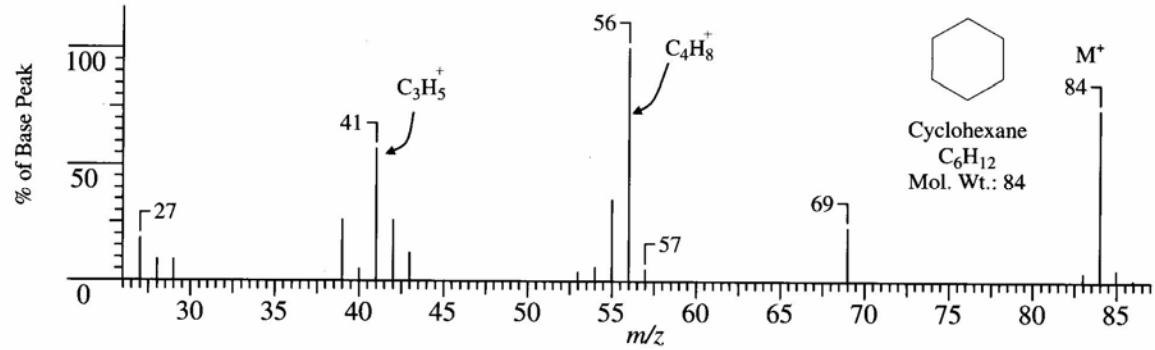


FIGURE 1.15 EI mass spectrum of cyclohexane.

Intense molecular ion,

56: loss of C_2H_4; 41: C_nH_{2n-1} for n = 3

►Olefins

Location of the double bond in acyclic alkenes is difficult because of its facile migration in the fragments.

In cyclic alkenes, location of the double bond is frquently evident as a result of allylic cleavage without migration.

C_nH_{2n-1} and **C_nH_{2n}** peaks are more intense than C_nH_{2n+1}

β-myrcene

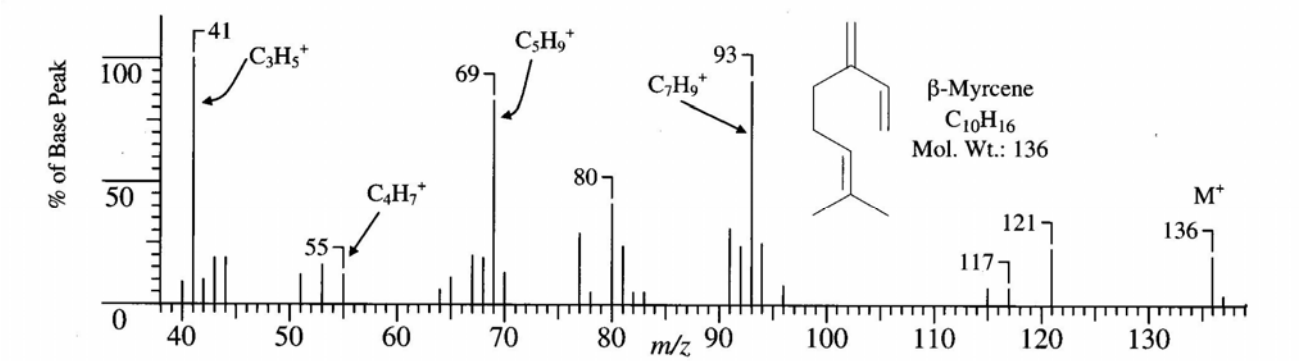
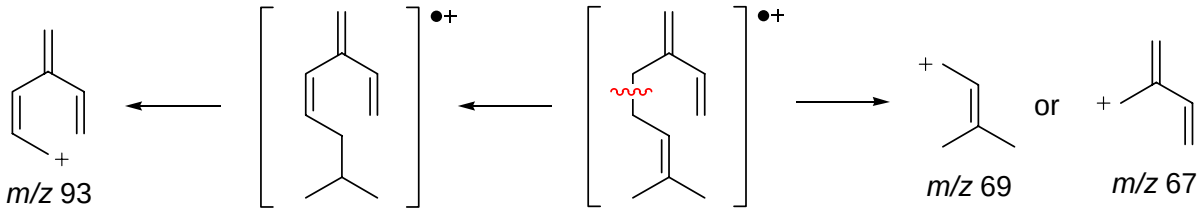


FIGURE 1.16 EI mass spectrum of β-myrcene.

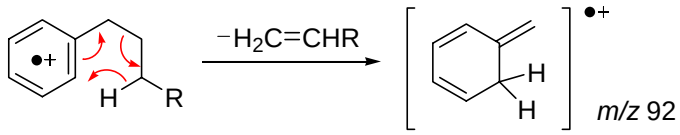
41, 55, 69: C_nH_{2n-1} for n = 3, 4, 5

93: $C_7H_9^+$ by double bond isomerization (increased conjugation)



►Aromatic and Aralky Hydrocarbons

1. Alkyl-substituted benzene ring gives a prominent peak at *m/z* 91 (β-cleavage).
2. $[M–1]^+$: benzylic cleavage of C–H bond
3. Rearrangement: hydrogen migration with elimination of a nutral alkene at *m/z* 92.

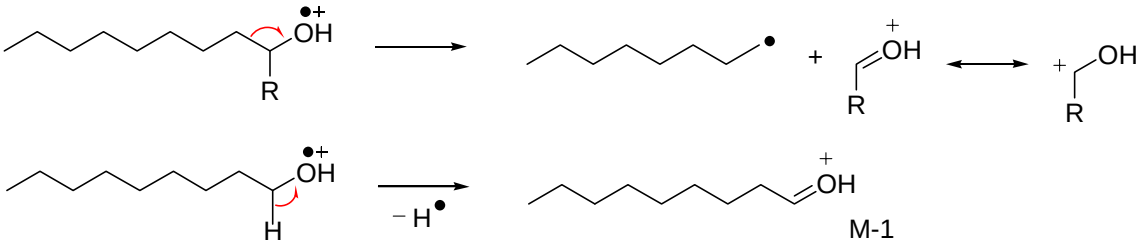


4. A characteristic cluster of ions resulting from α-cleavage and hydrogen migration at *m/z* 77 ($C_6H_5^+$), 78 ($C_6H_6^+$), and 79 ($C_6H_7^+$).

►Alcohols

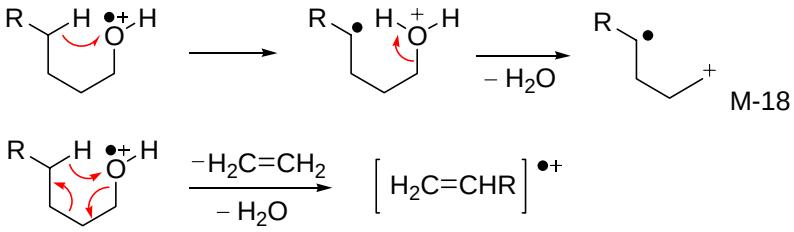
1. The molecular ion peak is usually quite small. CI may be used to obtain MW.
2. Cleavage of the C–C bond next to the oxygen atom: ***m/z* 31 [$^+CH_2$–OH] for primary alcohol**; *m/z* 45, 59, 73 etc. [$^+$CHR–OH] for secondary; *m/z* 59, 73, 87, etc. [$^+$CHRR'–OH] for tertiary.

3. M-1 peak: cleavage of C–H bond next to the oxygen atom



4. M–18 peak from loss of H_2O (prominent for primary alcohol)

5. M–46, M–74, M–102 etc.: M – (alkene + H_2O)



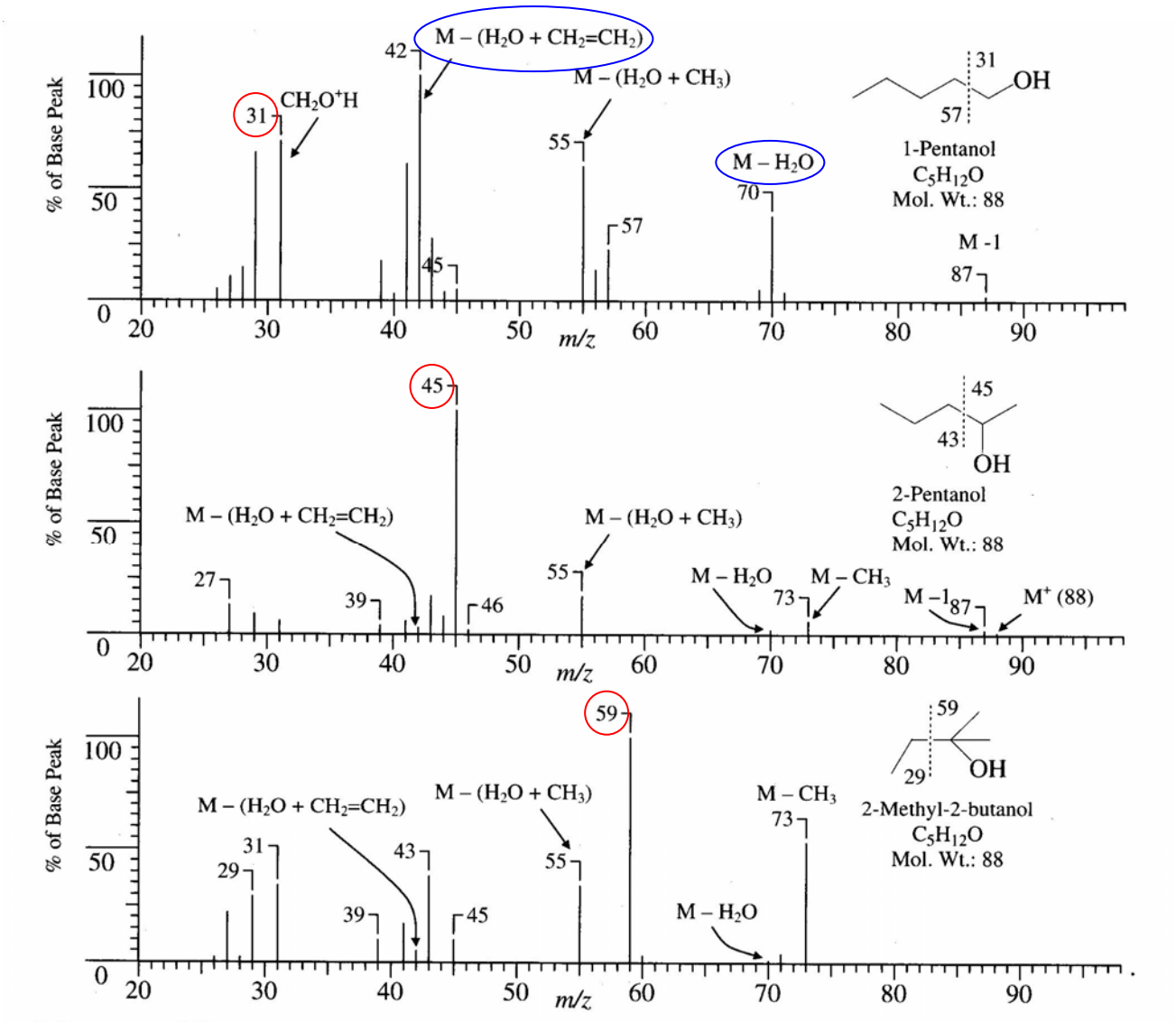
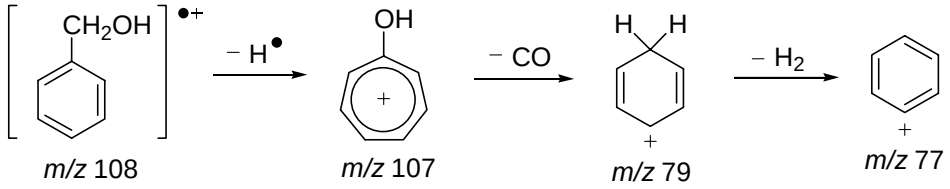


FIGURE 1.18 EI mass spectra of isomeric pentanols.

Benzyl alcohol

1. Strong molecular ion peak
2. M–OH peak (benzylic peak) by β-cleavage
3. Framentation: M–1, $C_6H_7^+$ (–CO), $C_6H_5^+$ ($–H_2$)



►Ethers

1. Strong peaks at *m/z* 31, 45, 59, 73 etc (presence of oxygen atom by **β-cleavage**: RO^+, $ROCH_2^+$)
2. C–O bond cleavage: similar to hydrocarbon pattern

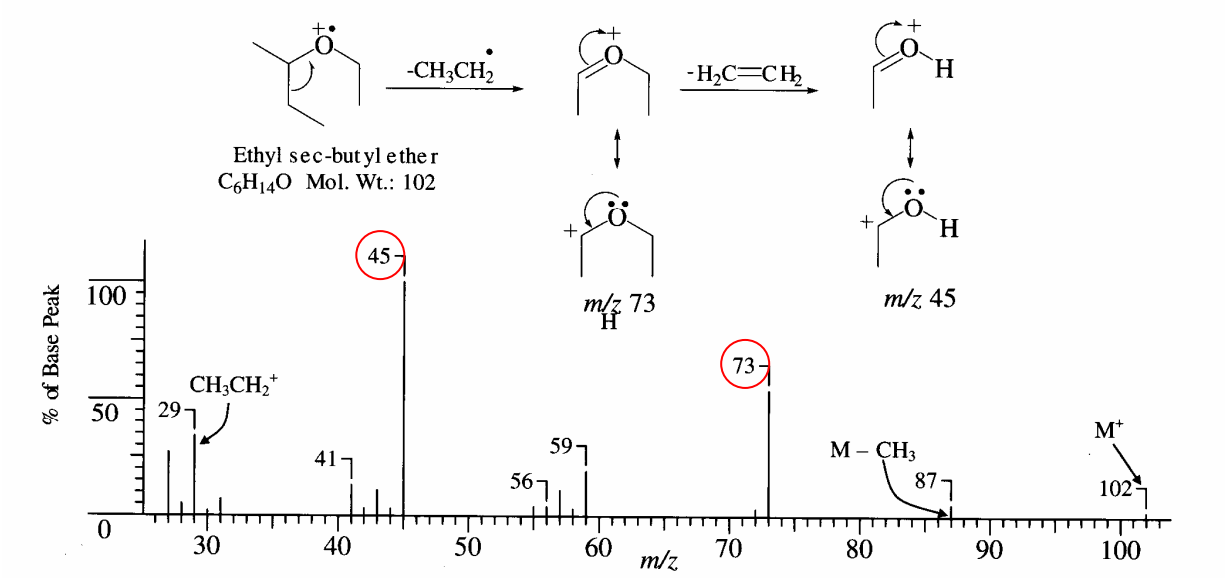


FIGURE 1.20 EI mass spectrum of ethyl *sec*-butyl ether.

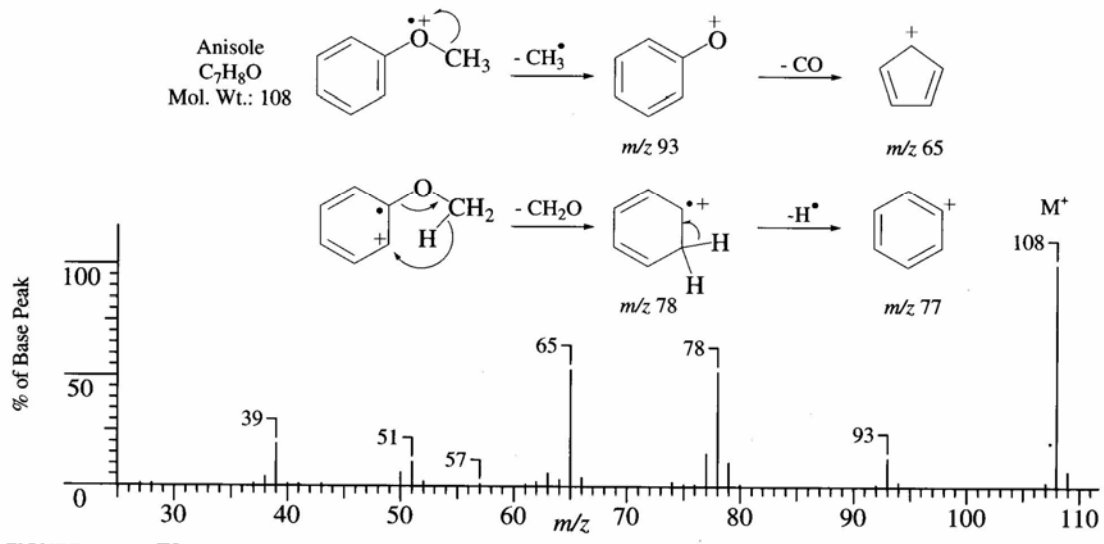
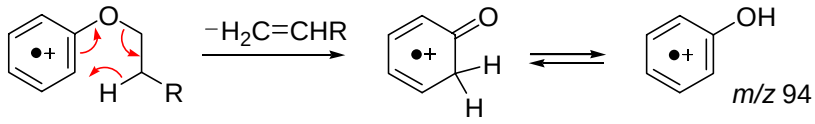


FIGURE 1.21 EI mass spectrum of anisole.

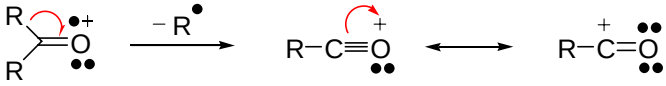
3. β-Cleavage with hydrogen migration



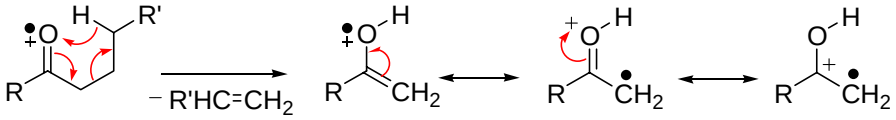
►Ketones

1. Molecular ion peak is strong

2. Fragmentation: Cleavage at one of the C–C bonds adjacent to the carbonyl group (α-cleavage). Peaks at m/z 43, 57, 71 ....



3. McLafferty rearrangement for alkyl groups of C_3 or longer.



Cyclic ketones

1. Molecular ion peak is prominent.

2. Fragmentation: α-cleavage and then further cleavage.

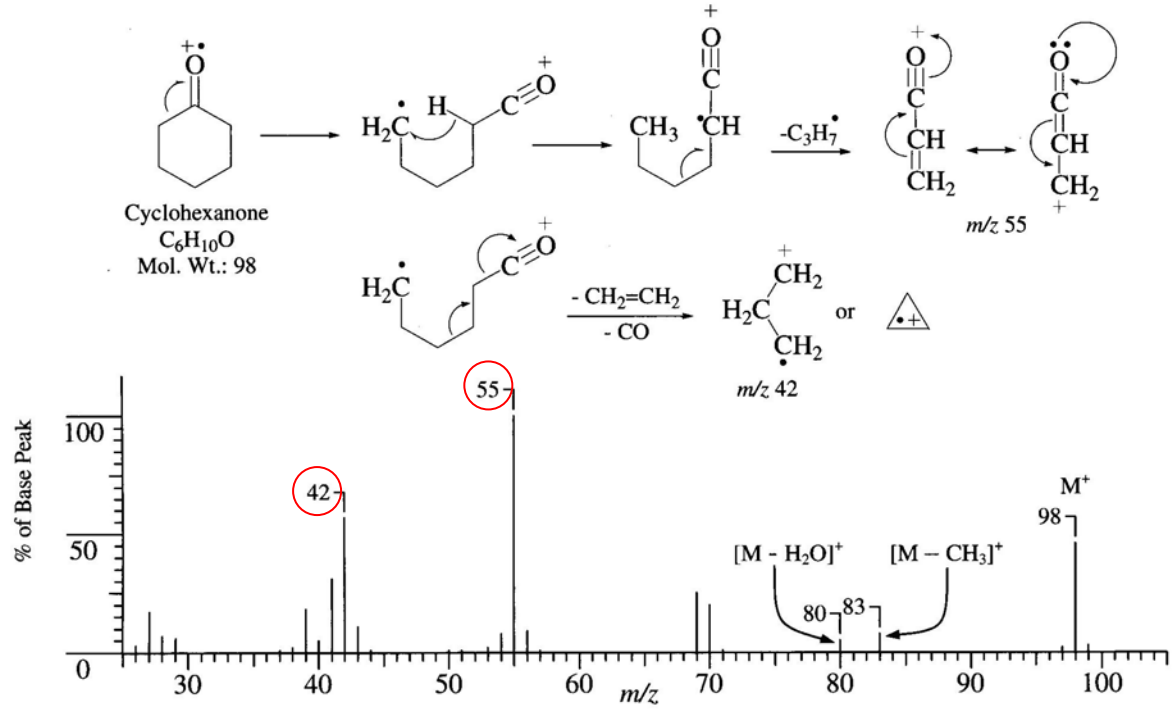


FIGURE 1.22 EI mass spectrum of cyclohexanone.

Aromatic ketone

1. The molecular ion peak is prominent.

2. Cleavage of aryl alkyl ketones at the β bond to the aromatic ring giving $ArC{\equiv}O^+$ fragment. Loss of CO from this fragment gives aryl ion. [$ArC(=O)R \rightarrow ArC{\equiv}O^+ \rightarrow Ar^+$]

p-Chlorobenzoquinone

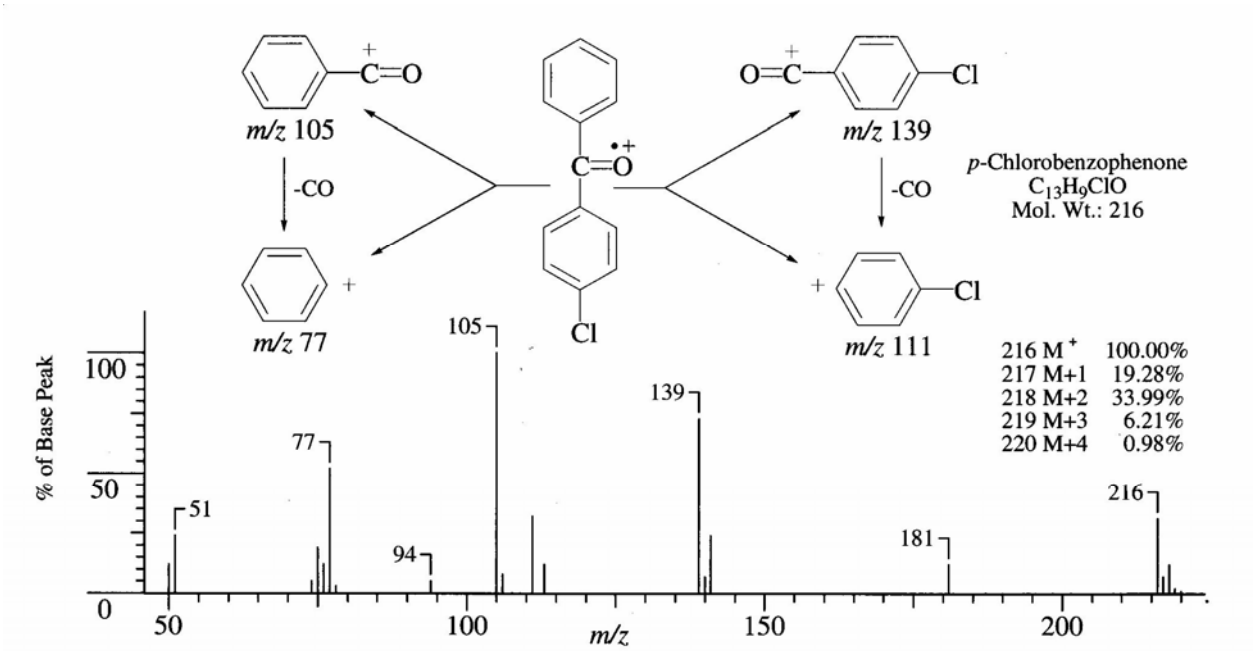


FIGURE 1.23 EI mass spectrum of *p*-chlorobenzophenone.

►Aldehydes [RC(=O)H]

1. The molecular ion peak is usually discernable.

2. α-Cleavage gives M–1 peak and M–R peak (*m/z* 29, CHO^+). The *m/z* 29 peak in C_4 or higher aldehyde could be from the hydrocarbon $C_2H_5^+$ ion.

3. McLafferty cleavage: m/z 44, 58, 72 .....

4. In a straight-chain aldehydes, M–18 (–H_2O), M–28 (–ethylene), M–43 (loss of CH_2=CH–O•), M–44 (loss of CH_2=CH–OH).

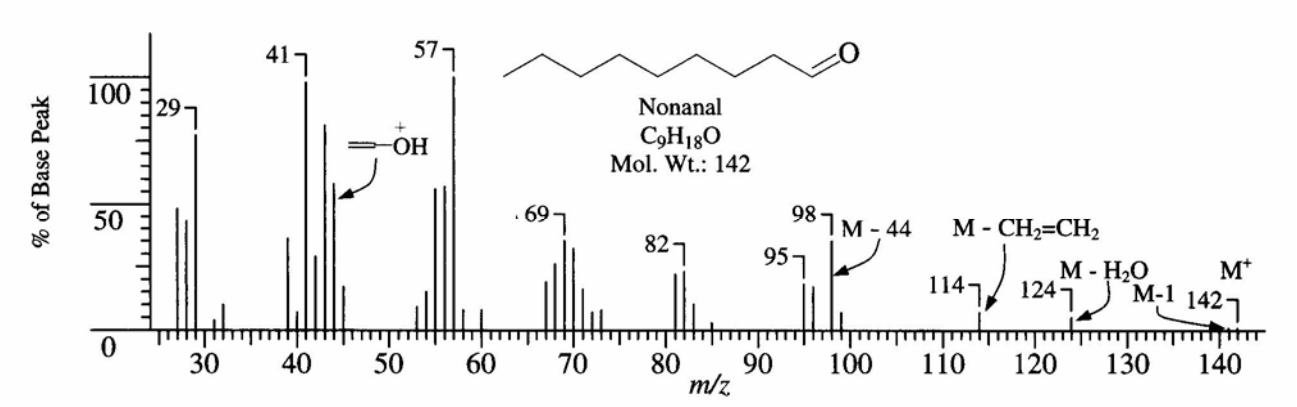
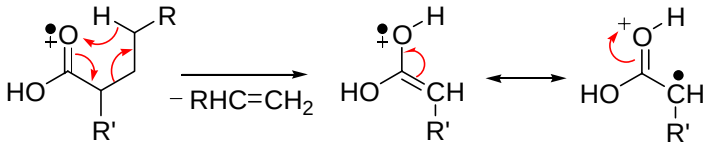


FIGURE 1.24 EI mass spectrum of nonanal.

►Carboxylic acids

1. The molecular ion peak is weak but discernable.
2. The most characteristic peak is m/z 60 resulting from McLafferty rearrangement.



3. In short-chain acid, M–OH and M–CO_2H are prominent.
4. In long-chain acid, cleavage at each C–C bond produces both the oxygen-containing fragment (m/z 45, 59, 73, 87, ...) and the alkyl fragment (m/z 29, 43, 57, 71, 85,.....)

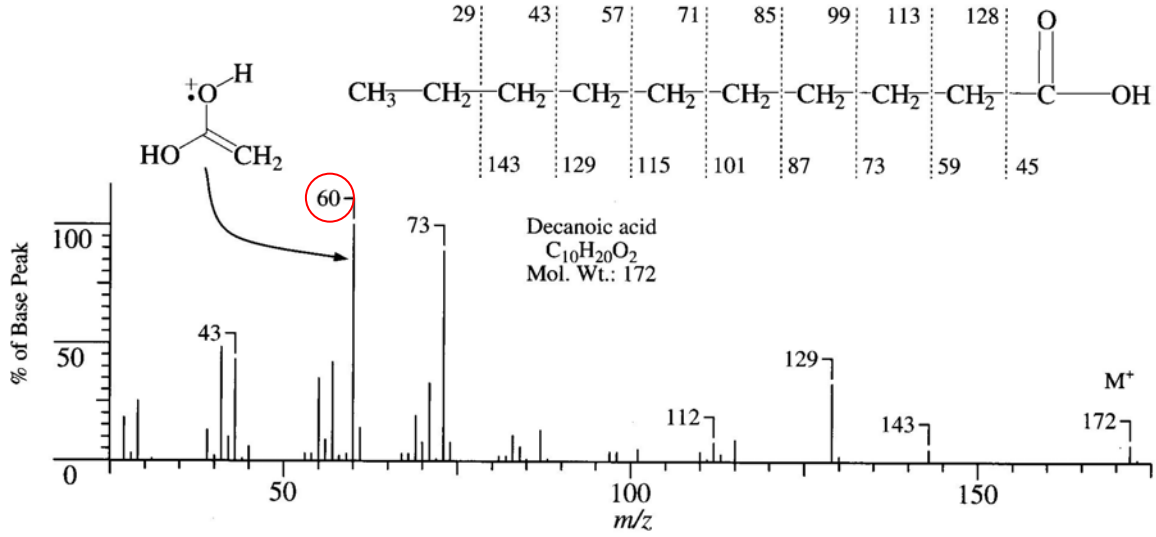
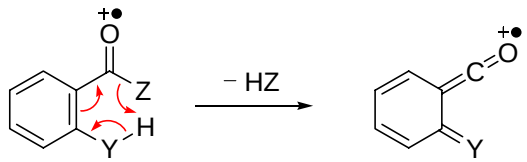


FIGURE 1.25 EI mass spectrum of decanoic acid.

Aromatic acids

1. The molecular ion peak is large.
2. The prominent peaks are M–17 (OH), M–45 (CO_2H).
3. M–18 (H_2O) is important when a hydrogen-bearing ***ortho*** group is available.

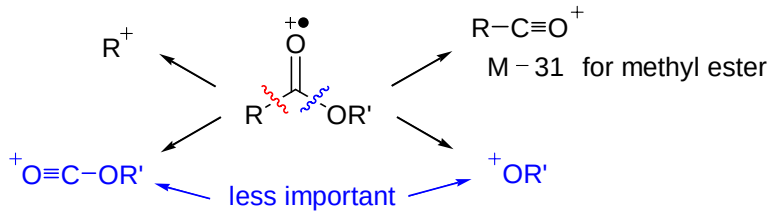


Z = OH, OR, NH_2; Y = CH_2, O, NH

►Carboxylic Esters

1. The molecular ion of a methyl ester of a straight-chain aliphatic acid is usually distinct.
2. The most characteristic peak results from McLafferty rearrangement. α-Unbranched methyl ester gives the value of ***m/z* 74**.

3. For general ester, four ions can result from bond cleavage next to C=O



Cleavage at each C–C bond gives an alkyl ion (m/z 29, 43, 57, 71, 85,.....) and an oxygen-containing ion, $C_nH_{2n-1}O_2^+$ (m/z 59, 73, 87, ...)

Methyl octanoate

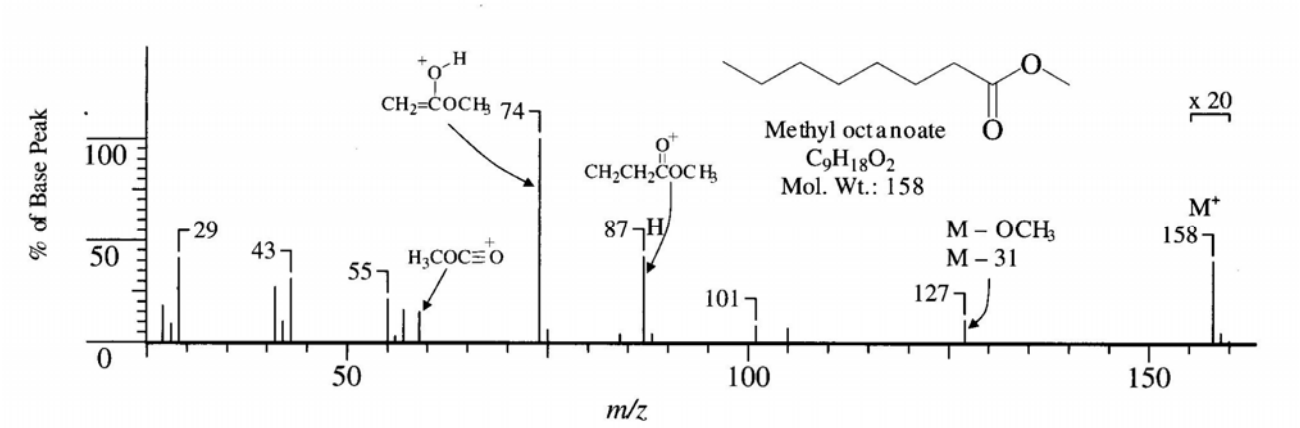


FIGURE 1.26 EI mass spectrum of methyl octanoate.

►Lactones

1. The molecular ion peak of five-membered ring lactones is distinct but is weaker when an alkyl substituent is present at C_4.

2. Facile cleavage of the side chain at C_4 gives a strong peak at M–alkyl..

γ-Valerolactone

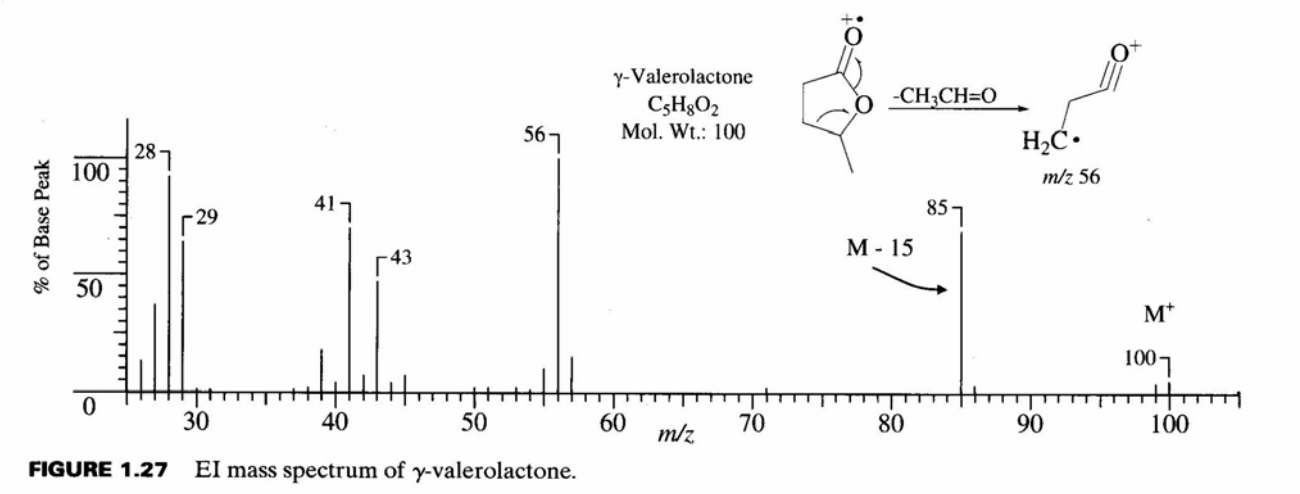


FIGURE 1.27 EI mass spectrum of γ-valerolactone.

►Amines

1. The molecular ion peak of aliphatic monoamine (odd number) is usually weak, and undetectible in long-chain or highly branched amines.

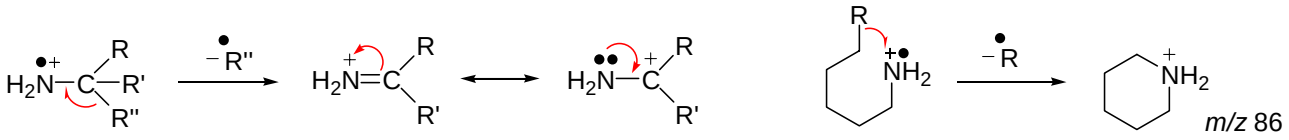
2. The base peak is from C–C cleavage next to the nitrogen atom (β-cleavage).

***m/z* 30** ($CH_2NH_2^+$) amines with no α-branch.

3. M–1 peak is usually visible when no α-brnaching.

4. Primary straight-chain amine shows the characteristic peak cluster resulting from $C_nH_{2n+2}N$ ion (*m/z* 30, 44, 58....)

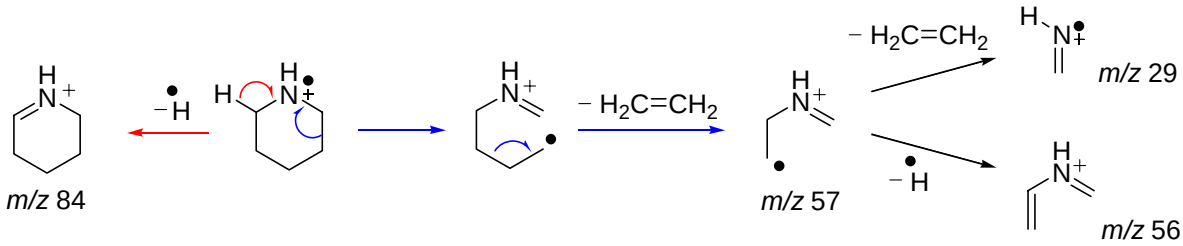
Cyclic fragments



Cyclic amines

1. The molecular ion peak of cyclic amine is usually intense unless there is substitution at the α-position.

2. Primary cleavage (β-cleavage):

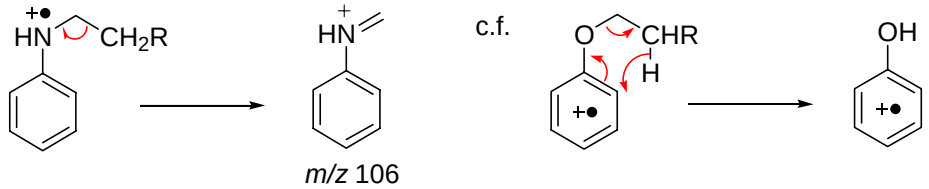


Aromatic amines

1. The molecular ion peak (odd number) is intense.

2. Loss of one of the amino H atoms gives moderately intense M–1 peak.

3. Cleavage of alkyl aryl amine: C–C cleavage next to the nitrogen atom



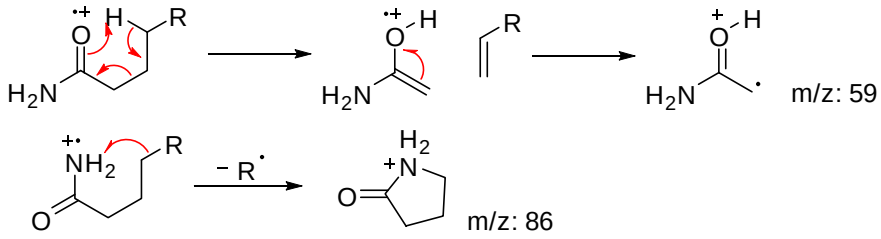
►Amides

1. The molecular ion peak of straight-chain monoamides is usually discernable.

2. The base peak [***m/z* 59**, $H_2NC(=OH^+)CH_2^{\cdot}$] in all straight-chain primary amides (>C_3) results from the McLafferty rearrangement.

3. A strong peak at ***m/z* 44**: Cleavage of the R–$CONH_2$ bond to give $O{=}C{=}NH_2^+$.

4. A moderate peak at ***m/z* 86**: γ,δ C–C cleavage by cyclization



►Nitriles

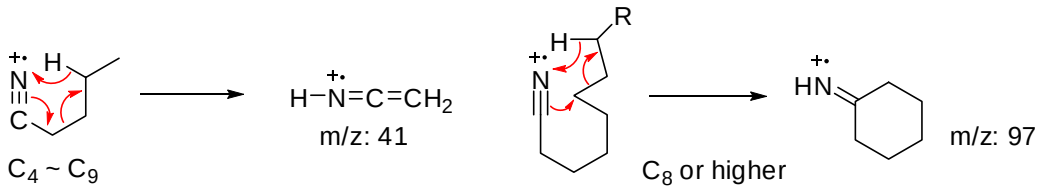
1. The molecular ion peak of aliphatic nitrile is weak or absent, but M+1 peak can be seen by increasing the sample size.

2. M–1 peak: loss of α-hydrogen to form $RCH{=}C{=}N^+$.

3. The base peak of straight-chain nitriles between C_4 and C_9 is *m/z* 41.

4. A peak at *m/z* 97 is characteristic and intense in the straight-chain nitrile of C_8 or higher.

5. Simple cleavage at each C–C bond gives a series of peaks at *m/z* 40, 54, 68, 82... resulting from $(CH_2)_nC{\equiv}M^+$ ions.



►Nitro Compounds

1. The molecular ion peak (odd number) of an alphatic mononitro compound is weak or absent.

2. The main peaks are attributed to the hydrocarbon fragments up to M–NO_2.

3. Presence of nitro group is indicated by an appreciable peak at ***m/z* 30** (NO^+) and smaller peak at ***m/z* 46** (NO_2^+).

Aromatic nitro compounds

1. The molecular ion peak is strong (odd number for one N atom).

2. Prominent peaks result from elimination of an NO_2 radical (M–46) and a neutral NO molecule with rearrangement to form the phenoxy cation (M–30).

►Sulfur Compounds

1. ^{34}S isotope (4.4%) gives M+2 peak. The number of sulfur atoms can be determined from the size of the contribution of the ^{34}S isotope to the M+2 peak.

2. The mass of alkyl groups can be obtained by the subtraction of the mass of the sulfur atom(s) from the molecular weight.

Aliphatic Mercaptans (Thiols)

1. The molecular ion peak of aliphatic mercaptan is usually strong enough to measure the M+2 peak.

***m/z* 47**: cleavage of C–C bond (α,β–bond) next to SH group to give $CH_2=SH^+$ ion.

2. The intensities decrease along the series (*m/z* 47, 61, 75) but increase at *m/z* 89 due to stabilizing mechanism by cyclization (5-membered ring formation).

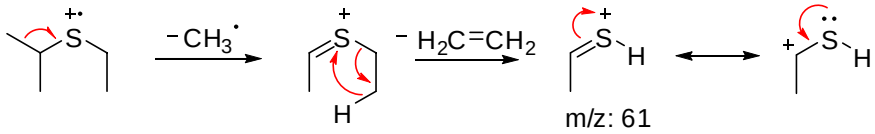
M–34 peak: loss of H_2S and then homologous series $M–H_2S–(CH_2=CH_2)_n$ arises.

M–33 peak: loss of HS for secondary mercaptans.

Aliphatic Sulfides

1. The molecular ion peak is usually intense so that M+2 peak can be measured.

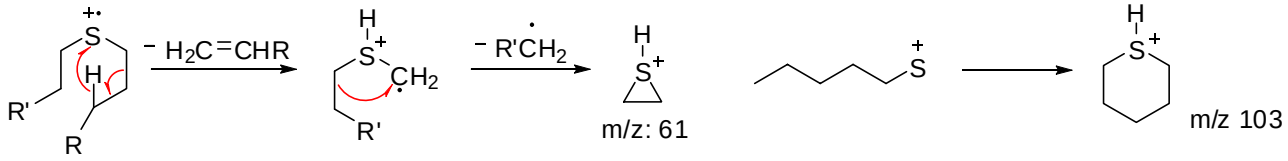
β-Cleavage:



※ For a sufide unbrached at either α-carbon, $CH_2=SH^+$ (***m/z* 47**) is seen, which may lead to confusion with mercaptans. However, *the absence of M–H_2S or M–SH peaks* in sulfide make the distinction.

2. Strong peak at ***m/z* 61** except tertiary sulfides

3. Cleavage of the C–S bond (α-cleavage): 32+CH_3, 32+C_2H_5, 32+C_3H_7 etc.



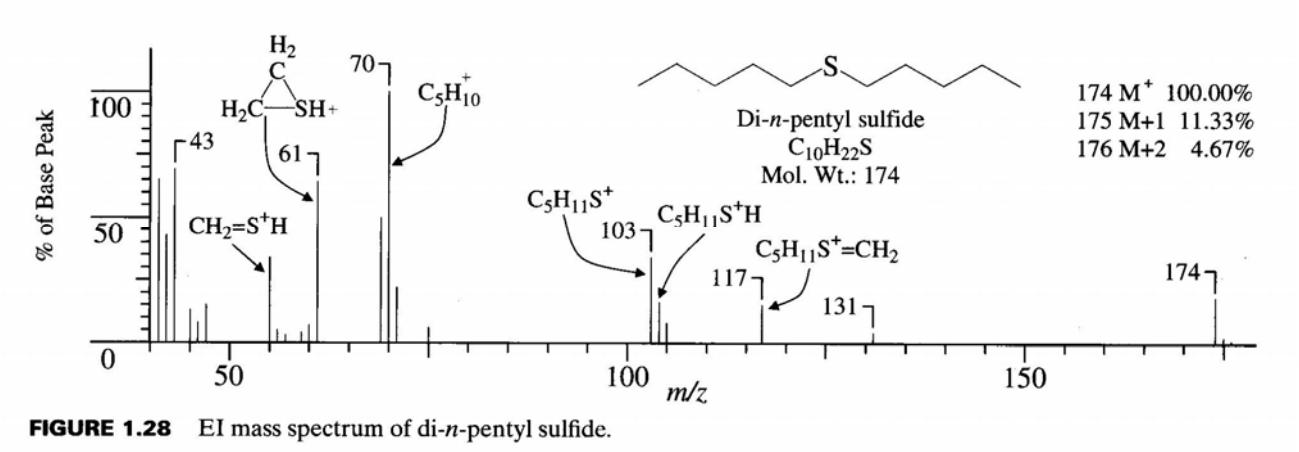


FIGURE 1.28 EI mass spectrum of di-*n*-pentyl sulfide.

►Halogen Compounds

1. One ^{37}Cl isotope contribute M+2 peak, which has 1/3 intensity of the molecular ion.

2. One ^{81}Br isotope will give M+2 peak, which has almost equal intensity to the molecular ion.

3. Two chlorine atoms, or two bromine atoms, or one chlorine and one bromine atoms will show

M+4 peaks, in addition to the M+2 peak.

4. The number of chlorine and/or bromine atoms can be calculated by the number of alternate peaks beyond the molecular ion peak.

5. The application of isotope contribution is useful for aromatic halogen compounds, but is limited by the weak molecular ion peak of aliphatic halogen compounds with more than six straight-chain carbon atoms (or fewer branched carbon atoms).

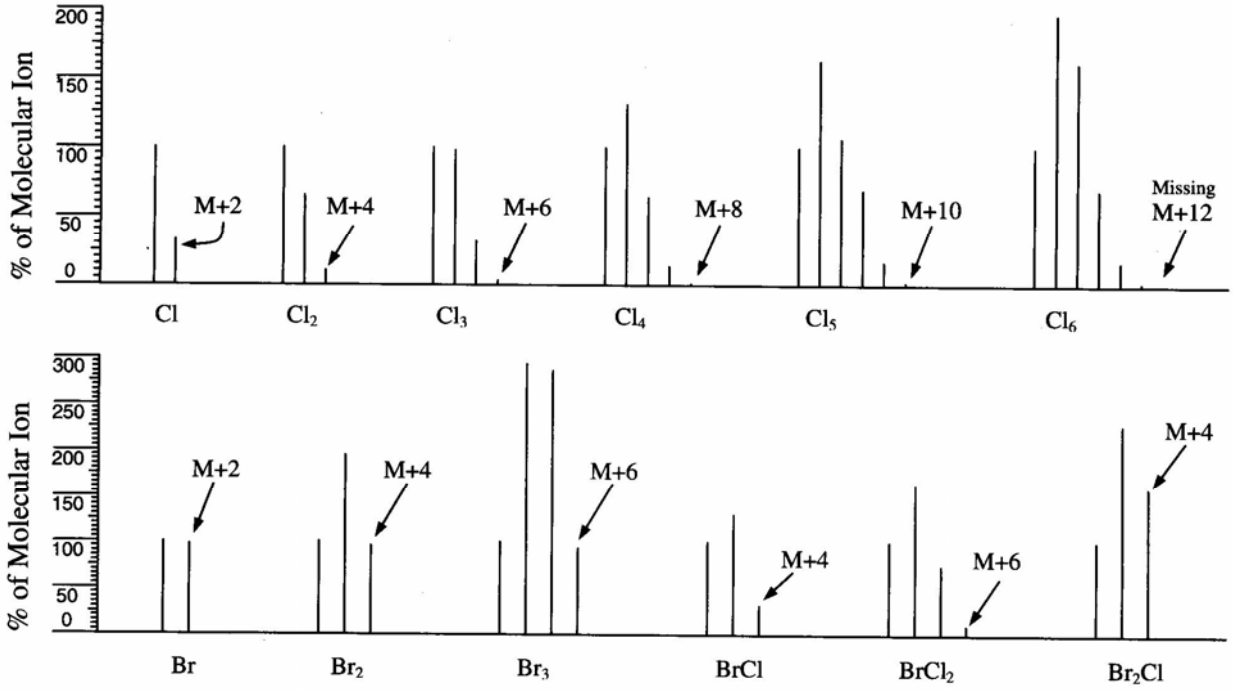


FIGURE 1.29 Predicted patterns of M, M + 2, M + 4, . . . for compounds with various combinations of chlorine and bromine.

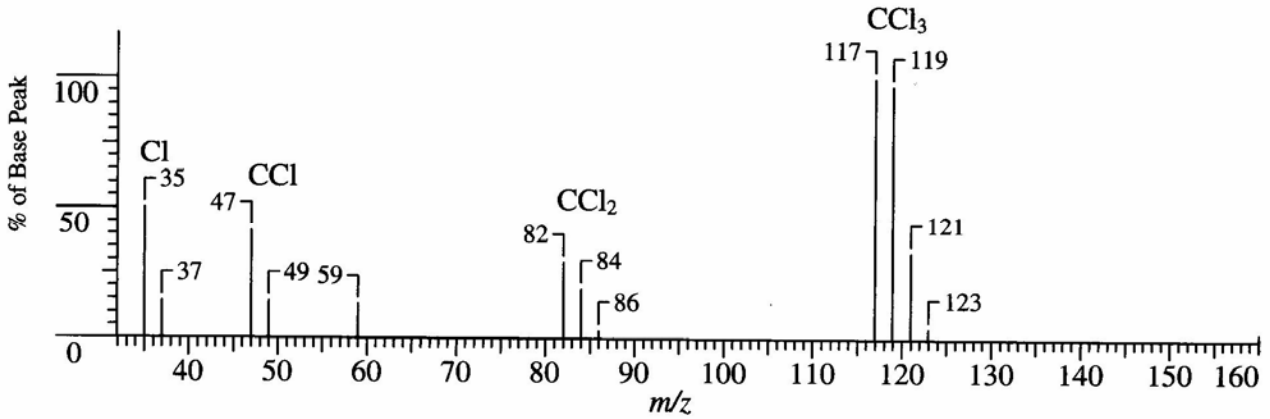


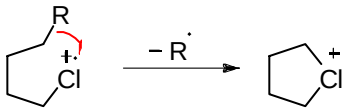
FIGURE 1.30 EI mass spectrum of carbon tetrachloride (CCl_4).

Aliphatic Chlorides

1. The molecular ion peak is detectable only in the lower monochlorides.

2. The C–C cleavage adjacent to the chlorine atom accounts for a weak peak at *m/z* 49 (CH_2=Cl^+) and the isotope peak at *m/z* 51.

3. The C–Cl cleavage leads to small Cl^+ peak and to a R^+ peak (prominent only for lower chloride < C_5).



m/z 91

4. Straight-chain chlorides longer than C_6 give $C_3H_6Cl^+$, $C_4H_8Cl^+$ (the most intense), $C_5H_{10}Cl^+$ ions.

5. M–36 peak: loss of HCl by 1,3-elimination.

Aromatic Halides

1. The molecular ion peak is readily apparent.

2. The M–X peak is large, in which X is directly attached to the ring.