Mass Spectroscopy

Mass Spectroscopy is a technique causing the formation of the gaseous ions with or without fragmentation; the gas phase ions are then characterized by their mass to charge ratios (m/z) and their relative abundances.

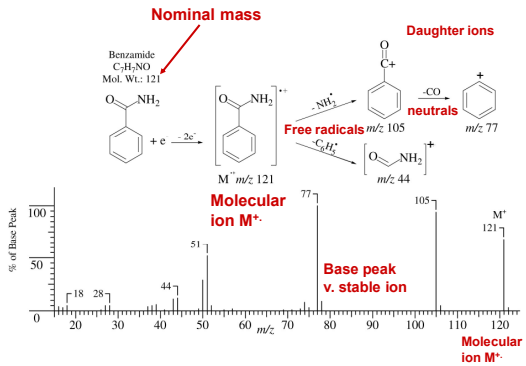
In MS, compounds are ionized. The ionized molecule often fragments into smaller ions/radicals.
The positively charged fragments produced are separated based on their nominal_mass/charge (m/z) ratio.

$$M \xrightarrow{\text{ionization}} \underset{\text{Parent ion}}{M^{+\cdot}} \xrightarrow{\text{fragmentation}} \underset{\text{daughter ions, radicals, neutrals}}{M^{+}_{1} + M^{+\cdot}_{2} + .. + N_1 + N_2 \cdot + \ldots..}$$

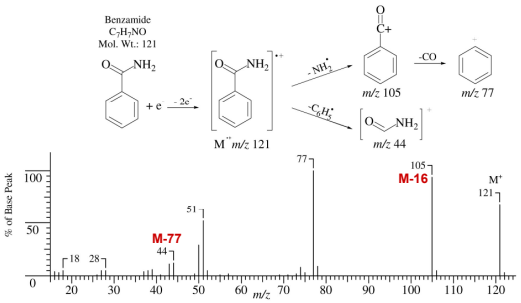
Most of the ions has z=+1, thus in a given ion, m/z = mass of the fragment.
A plot of relative abundance of ions vs m/z of all charged particles is the mass spectrum.

If the quantity of energy supplied to a molecule is greater than it's ionization energy a molecular ion is formed (parent ion).

The Mass spectral pattern is unique to a molecule (fingerprint), especially EI.



Mass Spectrum presented as a bar graph.



Parent/Molecular Peak $M^{+\cdot}$:

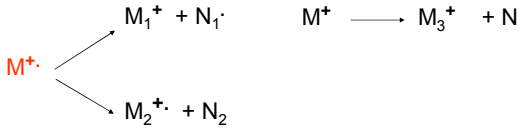
An molecular ion that has not lost/gained atoms.
The nominal mass of which is calculated with the mass numbers of the predominant isotopes of atoms.

Base peak:

Base peak is the peak from the most abundant ion, which is often the most stable ion.

Fragment peaks other than the molecular ion peak is given the symbol A, then it's isotopic peaks would be A+1, A+2, ,,,

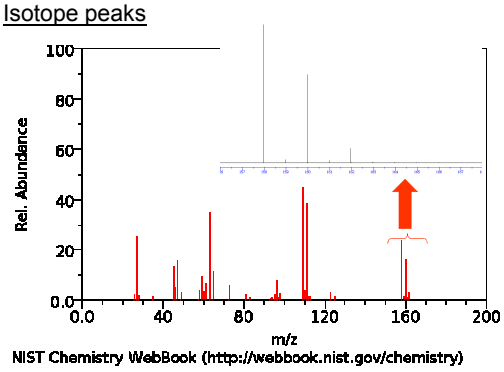
Fragmentation:



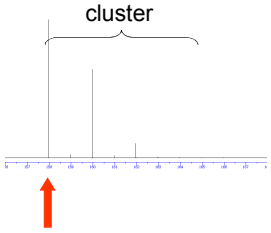
$M^{+\cdot}$ Radical ion (odd e)
$N\cdot$ Neutral radical (odd e)
N Neutral (even e)

M^{+} *(even e) would not break up into a radical ion….*

Isotope peaks



Cl-CH_2-CH_2-S-CH_2-CH_2-Cl



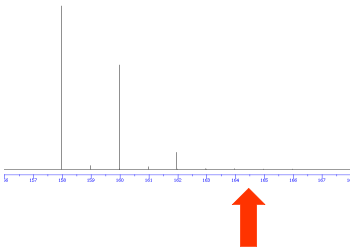
A peak made up of the principal isotopes of atoms making up the ion.

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				

E.g.
$\%M+1=(0.012n_H+1.08n_C+0.369n_N+0.038n_O+5.08n_{Si}+0.801n_S)$

Cl-CH_2-CH_2-S-CH_2-CH_2-Cl
Cl-*CH_2-CH_2-S-CH_2-CH_2-Cl
Cl-CH_2-*CH_2-S-CH_2-CH_2-Cl
***Cl**-CH_2-CH_2-S-CH_2-CH_2-Cl
***Cl**-*CH_2-CH_2-S-CH_2-CH_2-Cl
Cl**-CH_2-CH_2-S-CH_2-CH_2-Cl**



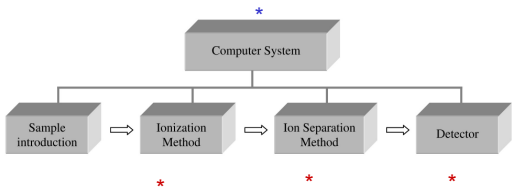
MS *cannot* distinguish between isotopomers (isomers having the same number of each isotopic atom but differing in their positions).

Mass Spectrometer:

Create gas-phase ions of sample.

Separate ions in space or time basis based on m/z ratio accomplished by mass analyzers.

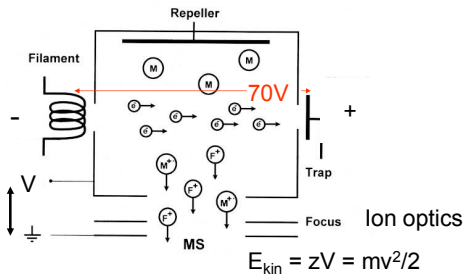
Detect the quantity of ions of each ion based on the m/z ratio.



Ionization:

Electron Ionization (Electron Impact, EI)
Chemical Ionization (CI)
Field Desorption (FD) Ionization
Fast Atom Bombardment (FAB)
Matrix Assisted Laser Desorption Ionization (MALDI)
Thermospray Ionization
Electrospray (ESI)
Atmospheric Pressure Ionization (API)
Atmospheric Pressure Chemical Ionization (APCI)
Inductively Coupled Plasma (ICP)

Electron impact ionization (EI)



Ion optics

$E_{kin} = zV = mv^2/2$

70eV – high energy electrons,
molecular ion - very energetic, low/no abundance.

Volatilized compound is ionized by electron impact. An electron beam is generated by a accelerating the electrons from a heated filament through an applied voltage.

The electron energy is defined by the potential difference between the filament and the source housing and is usually set to 70 eV (~1.12×10^{-17}J).

A field keeps the electron beam focused across the ion source and onto a trap (collimating magnets).

Upon impact with a 70 eV electron, the gaseous molecule may lose one of its electrons to become a positively charged radical ion, daughter ions, etc.

Chemical ionization (CI):

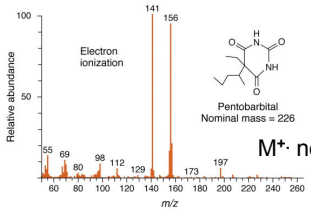
Interaction of the molecule M with a reactive ionized reagent species (gaseous Bronsted acids). E.g.., EI of methane, generates $CH_4^{+\cdot}$ which then reacts to give the Bronsted acid CH_5^+;

$$CH_4^{+\cdot} + CH_4 \rightarrow CH_5^+ + CH_3^{\cdot}$$

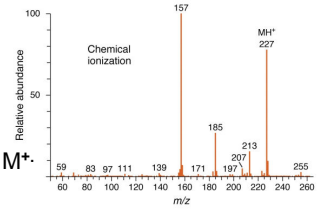
If M in the source has a higher proton affinity than CH_4, the protonated species MH^+ will be formed by the exothermic reaction.

$$M + CH_5^+ \rightarrow MH^+ + CH_4$$

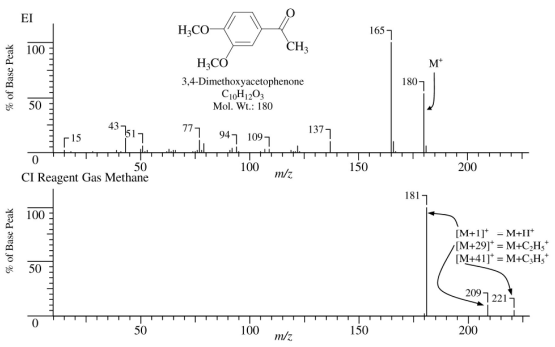
CI is a softer ionization process.

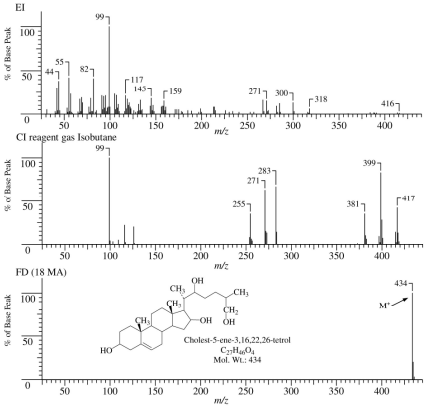


$M^{+\cdot}$ nearly nonexistent.



Abundant $M^{+\cdot}$.

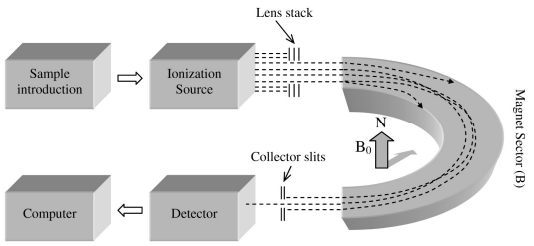




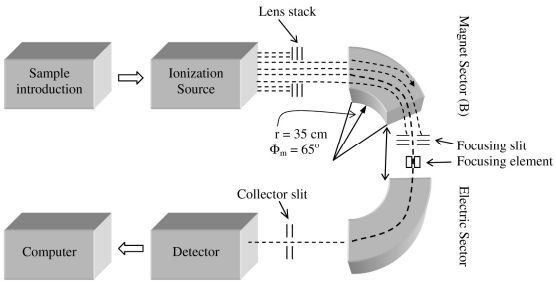
Some Chemical Ionization Reagents

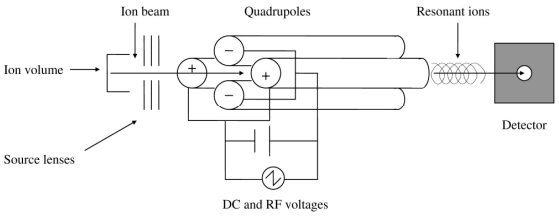
Reagent Gas	Reagent Ion	Analyte Ion/Quasi-molecular Ion	Comment
H_2	H_3^+	$(M+H)^+$	Very energetic, considerable fragmentation
CH_4	CH_5^+	$(M+H)^+$	Energetic protonating agent
CH_4	$C_2H_5^+$, $C_3H_5^+$	$(M+C_2H_5)^+$ $(M+C_3H_5)^+$	Form adduct ions
i-C_4H_{10}	$C_4H_9^+$	$(M+H)^+$	Mild protonating agent, ionizes all nitrogen
NH_3	NH_4^+	$(M+NH_4)^+$	Selective; little fragmentation
NH_3-CH_4	NH_4^+	$(M+H)^+$	Selective protonative agent
Biacetyl	CH_3CO^+	$(M+CH_3CO)^+$	Acetylating agent
Ar	$Ar^{+\cdot}$	$M^{+\cdot}$	Energetic charge exchange agent
CS_2	$CS_2^{+\cdot}$	$M^{+\cdot}$	Mild charge exchange agent
CH_3ONO-CH_4	CH_3O^-	$(M-H)^-$	Mild proton abstraction reagent
NF_3	F^-	$(M-H)^-$	Proton abstraction reagent
$CHCl_3$, -CH_4	Cl^-	$(M+Cl)^-$	Chloride addition reagent

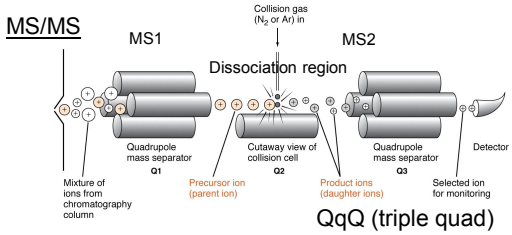
Mass Analyzers:
Magnetic Sector Mass Analyzer
(Single/Double Focusing)
Quadrupole
Quadrupole Ion Trap
Fourier-Transform Mass Spectrometry (FTMS)
Time-of-flight (TOF)
Tandem Mass Spectrometry MS-MS$^{(n)}$



Ion Detection:
Faraday Cup
Electron Multiplier
Photomultiplier Conversion Dynode







Scan with MS1 (only) turned on – entire MS spectrum.

Set MS1 to filter fragment of interest, dissociate further in q collisionally and mass analyze by scanning with MS2.

EI Spectra

EI spectra are rich in fragments thus useful in structure determination (thro' interpretation).

Parent ion may be absent (aliphatic alcohols, nitrites, nitrates, nitro compounds nitriles and highly branched compounds).

Intensity of peaks depends on the stability of the ion.

Characteristic losses point to characteristic moieties in the molecule e.g. O(16), OH (17), H_2O (18) losses from alcohols. (M-3 to M-14 and M-19 to M-25 peaks are unlikely, exceptions exist; HF(20) loss)

Molecular Ion Peak

The highest mass ion in the spectrum. Provides the most valuable information; molecular mass of the molecule. That leads to elemental composition. Structural fragments are then fitted into the elemental composition. (CI and FAB).

$M^{+\cdot}$: MW (unit mass) in terms of the most abundant isotope of each element present. It is an OE ion. It yields ions in the high mass range by loss of logical neutral species.

Nitrogen Rule:

Molecule of even nominal mass must contain zero or even number of N atoms. An odd numbered nominal mass requires an odd number of N.

Nitrogen Rule (molecules and OE molecular ions, $M^{+\cdot}$)

Nearly all molecules are even electron systems.

If the nominal mass is even, the compound contain an even number of N atoms; 0,2,4,6,…
If the nominal mass is odd, the compound contain an odd number of N atoms; 1,3,5,7,…

Nitrogen Rule (EE molecular ions)

EE precursor ions $(M+H)^+$, $(M+Na)^+$, $(M+Cl)^-$ etc; the N rule is;

If the nominal mass is odd, the compound contain an even number of N atoms; 0,2,4,6,…
If the nominal mass is even, the compound contain an odd number of N atoms; 1,3,5,7,…

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Parent Peak leads to molecular formula. (Appendix A)

Molecular formula leads to the structural (/partial) features of the possible molecular structure.

Unsaturation can be calculated from the molecular formula of M or fragments (octet rule) of the parent ion.

$$U = R + DB + 2TB = c - h/2 + n/2 + 1$$

$c = \#C \ \& \ Si$; $h = \#H \ \& \ halogens$; $n = \#N, P, As..$

ignore divalent atoms (O,S)

OE fragments generate integral U values, EE fragments generate U values which are odd multiples of 0.5.

m/z=74

MF	Unsaturation
$C_2H_2O_3$	2.0
$CH_2N_2O_2$	2.0
C_6H_2	6.0
C_3H_3FO	2.0
$C_2H_3FN_2$	2.0
$C_3H_6O_2$	1.0
$C_2H_6N_2O$	1.0
C_4H_7F	1.0
$C_4H_{10}O$	0.0
$C_3H_{10}N_2$	0.0

Rule of Thirteen:

Used to generate possible formula for a given molecular mass.

1. Generate a *base formula*;

$$\frac{MM}{13} = n + \frac{r}{13} \longrightarrow C_nH_{n+r}$$

2. Calculate the index of U for the base formula.

$$U = \frac{n - r + 2}{2}$$

3. If needed to find the formula with n_O of O for the same MM;

New formula = Base formula + n_O O – n_OC – $4n_O$H which changes U to U+n_O ;

4. If needed to find the formula with n_N of N for the same MM,

New formula = Base formula + n_N N – n_N C – $2n_N$ H and recalculate U; Fractional U's – unlikely formula.

U < 0 is an impossible combination, indicates likely presence of O and N.

Useful Links

http://www.colby.edu/chemistry/NMR/NMR.html
http://www.colby.edu/chemistry/PChem/Fragment.html

http://www.chemcalc.org/ Main Page
MF finder

http://www.chem.uni-potsdam.de/tools/index.html

High Resolution MS:

Using mass number for isotopes of atoms is approximate. Actual mass of a given isotope deviates this integer by a small but unique amount ($\Delta E = \Delta mc^2$). Relative to ^{12}C at 12.0000000, the isotopic mass of ^{16}O is 15.9949146 amu., etc.

High resolution mass spectrometers that can determine m/z values accurately to four/more decimal places, making it possible to distinguish different *molecular formulas* having the same *nominal mass*.

TABLE 1.4 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

MF	Unsaturation	Exact Mass
$C_2H_2O_3$	2.0	74.00040
$CH_2N_2O_2$	2.0	74.01163
C_6H_2	6.0	74.01565
C_3H_3FO	2.0	74.01679
$C_2H_3FN_2$	2.0	74.02803
$C_3H_6O_2$	1.0	74.03678
$C_2H_6N_2O$	1.0	74.04801
C_4H_7F	1.0	74.05318
$C_4H_{10}O$	0.0	74.07316
$C_3H_{10}N_2$	0.0	74.08440

Isotope Peaks

The peaks from the isotopes.

The intensity ratios (relative intensities) in the isotope patterns are arising from the natural abundance of the isotopes, thus are valuable to ascertain the atomic composition of ions.

M+1 peaks are primarily due the presence of ^{13}C in the sample.

M+2, M+4, .. indicative of presence of Br, Cl, S; (^{79}Br:^{81}Br = 1:1, ^{35}Cl : ^{37}Cl = 3:1)

Isotope peak abundance depends on the molecular constitution. Example, halogens Cl, Br.

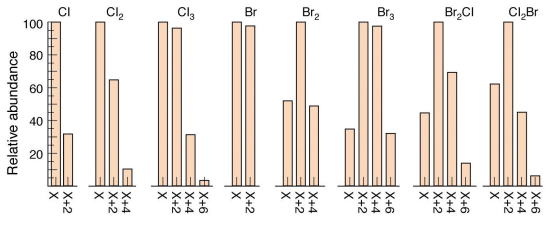


TABLE 1.5 Intensities of Isotope Peaks (Relative to the Molecular Ion) for Combination of Chlorine and Bromine.

Halogen Present	% M+2	% M+4	% M+6	% M+8	% M+10	% M+12
Cl	32.6					
Cl_2	65.3	10.6				**M=100%**
Cl_3	97.8	31.9	3.5			
Cl_4	131.0	63.9	14.0	1.2		
Cl_5	163.0	106.0	34.7	5.7	0.4	
Cl_6	196.0	161.0	69.4	17.0	2.2	0.1
Br	97.9					
Br_2	195.0	95.5				
Br_3	293.0	286.0	93.4			
BrCl	130.0	31.9				
$BrCl_2$	163.0	74.4	10.4			
Br_2Cl	228.0	159.0	31.2			

Calculating isotope peak abundances (%) to confirm fragment and parent peaks.

Table 22-2 Isotope abundance factors (%) for interpreting mass spectra

Element	X+1	X+2	X+3	X+4	X+5	X+6
H	0.012*n*					
C	1.08*n*	0.005 8*n*(*n* − 1)				
N	0.369*n*					
O	0.038*n*	0.205*n*				
F	0					
Si	5.08*n*	3.35*n*	0.170*n*(*n* − 1)	0.056*n*(*n* − 1)		
P	0					
S	0.801*n*	4.52*n*	0.036*n*(*n* − 1)	0.102*n*(*n* − 1)		
Cl	—	32.0*n*	—	5.11*n*(*n* − 1)	—	0.544*n*(*n* − 1)(*n* − 2)
Br	—	97.3*n*	—	47.3*n*(*n* − 1)	—	15.3*n*(*n* − 1)(*n* − 2)
I	0					

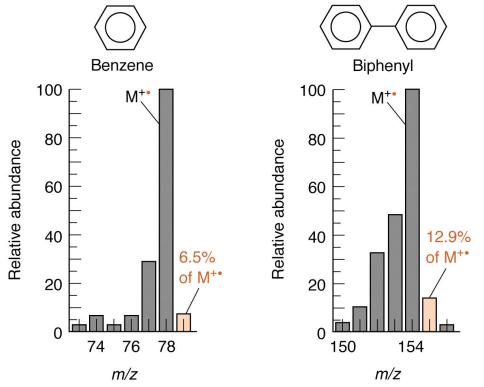
EXAMPLE: For a peak at *m/z* X containing *n* carbon atoms, the intensity from carbon at X+1 is *n* × 1.08% of the intensity at X. The intensity at X+2 is *n*(*n* − 1) × 0.005 8% of the intensity at X. Contributions from isotopes of other atoms in the ion are additive.

X=M or A

E.g.
$\%M+1=(0.012n_H+1.08n_C+0.369n_N+0.038n_O+5.08n_{Si}+0.801n_S)$

(M+1)/M ratio is paticularly useful to estimate the #C in the species.

$$\#C \le \frac{\%M+1}{\%M}\times 100$$



Fragmentation:

Unreasonable losses from molecular ion:

M - [3-14] and M – [19-25] are unreasonable losses.

Reasonable losses from molecular ion
Neutral fragments expelled by simple cleavage

$OE^{+\bullet} \rightarrow EE^{+} + OE^{\bullet}$

Neutral fragments expelled by multi-centered fragments

$OE^{+\bullet} \rightarrow OE^{+\bullet} + EE$

If molecular ion cleaves at a single bond (N rule corollary) then,

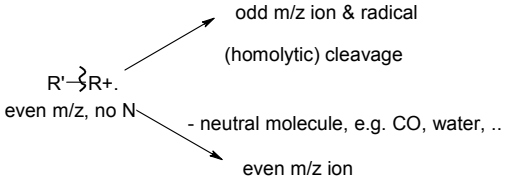
$M^{+\bullet} \rightarrow M^{+} + M^{\bullet}$

Mass: even even even (odd #N)
even odd odd (even #N)
(even #N, 0,2,4,..)

odd odd even (even #N)
odd even odd (odd #N)
(odd #N; 1,3,5,..)

N atoms found here. If more than one N atom is present the other fragment may contain N atoms.

Nominal mass of parent ion containing C, H, O, S, Si, P and halogens is even.

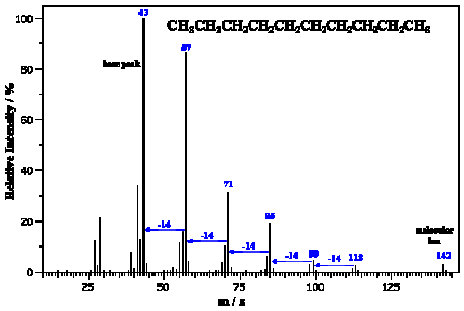


Examine the MS; M+• Downwards

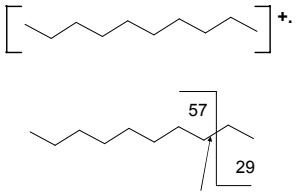
Fragment	Due to loss of…	Interpretation
$M^{+\bullet}$ -1	-H•	Aldehydes, tert. Alcohols, amines,
$M^{+\bullet}$ -2	Multiple -H•	Secondary alcohols
$M^{+\bullet}$ -3	Multiple -H•	Primary alcohols
$M^{+\bullet}$ -4 to -13	?	Consider contaminants
$M^{+\bullet}$ -14	?	CH_2• , N• not good losses
$M^{+\bullet}$ -15	CH_3•	Available methyl groups, methylesters
$M^{+\bullet}$ -16	O•	Peroxides
$M^{+\bullet}$ -17	OH•	Alcohols, phenols, RCO_2H
$M^{+\bullet}$ -18	H_2O	alcohols
$M^{+\bullet}$ -19	-F•	Fluoro compound
$M^{+\bullet}$ -20	-HF	Fluoro compound
$M^{+\bullet}$ -21 to -25	-	
$M^{+\bullet}$ -26	HC≡CH	
$M^{+\bullet}$ -27	•HC=CH2 or HCN	HCN from pyridine, anilines
$M^{+\bullet}$ -28	C≡O or CH_2=CH_2	Verify McLafferty rearrangement

Fragmentation pattern:

From the fragment losses the parent peak may be predicted by working back.

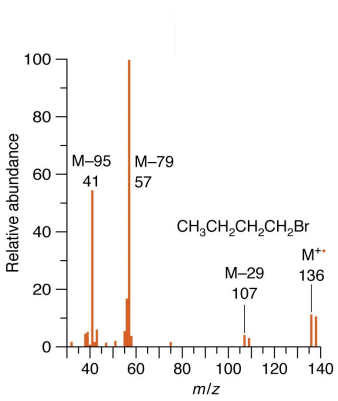


Notation:

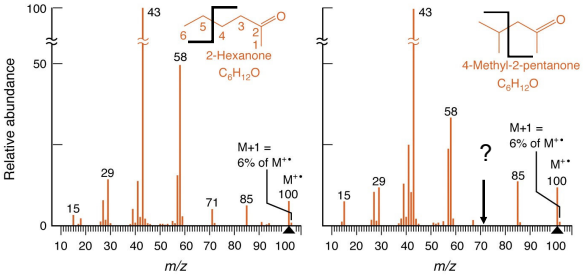


cleavage here

Unique isotope peak patterns are useful for the analysis.



m/z=100



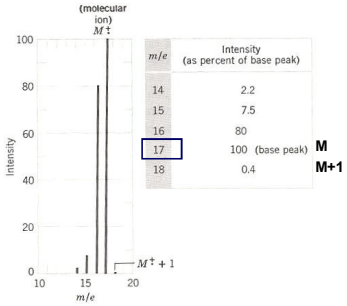


Fig. E3

Fig. E3

M = odd, 17 one N

M+1 0.4% no C

↑

Consistent with 1N

Nominal mass

17

14 – 1N

3 →3H

NH_3

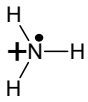
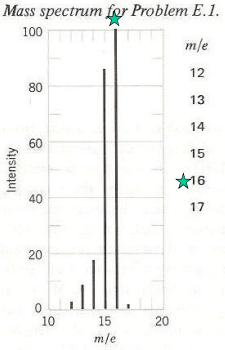


FIG. E.4 *Mass spectrum for Problem E.1.*



PE1

M = even

M+1 1.1% 1 C

→

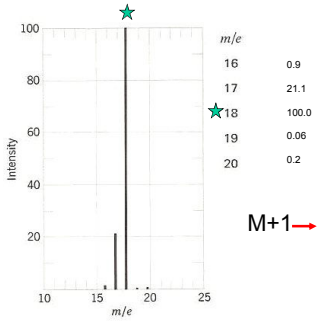
Nominal mass

16

12 – 1C

4 →4H

CH_4



M+1→no C

FIG. E.5 *Mass spectrum for Problem E.2.*

PE2

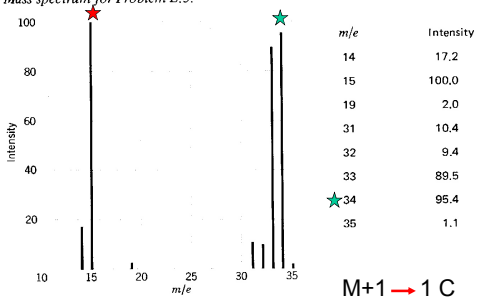
1 O present

2 H present

M+1, M+2 peaks confirm H_2O.

FIG. E.6 *Mass spectrum for Problem E.3.*

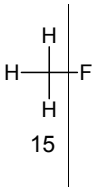
Data:Contains 3 elements, one is F.



M+1 → 1 C

PE3

Nominal mass
34
12 – 1 C
22
19 - 1 F
3 → 3 H



CH_3F

Further 34-15=19

Fragment intensities depend on the stability of the ion and the probability of formation.

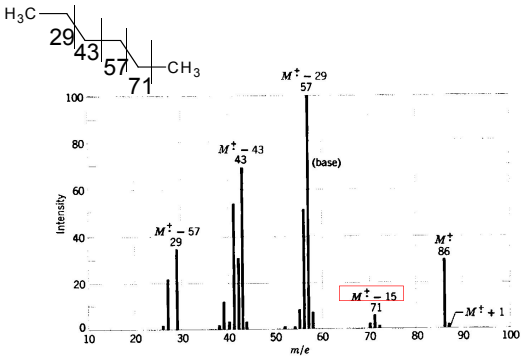
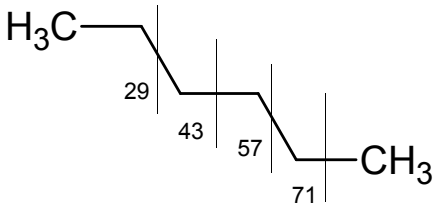
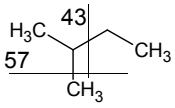


FIG. E.9 *Mass spectrum of hexane.*





Electron repelling methyl group stabilizes the carbocation.

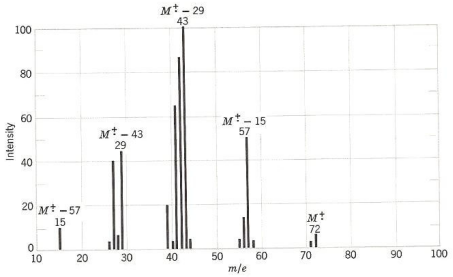
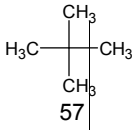
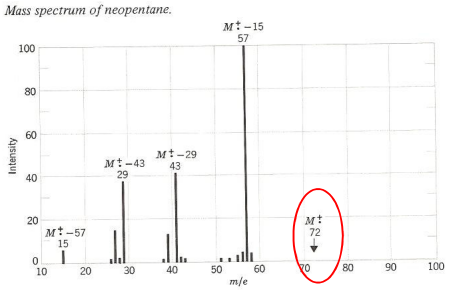


FIG. E.10 *The mass spectrum of 2-methylbutane.*

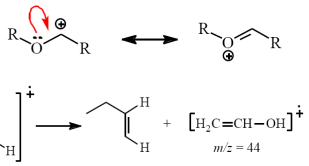


Four ways to form carbocation

FIG. E.11 *Mass spectrum of neopentane.*



two electron movement

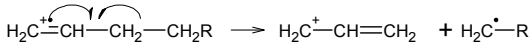


one electron movement

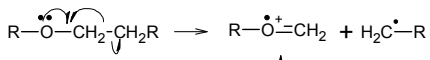
m/z = 43

Stabilization of carbocations:

1. Alkenes frequently undergo fragmentations that yield allylic cations

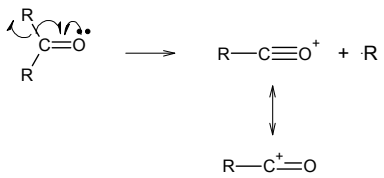


2. Carbon-carbon bonds next to an atom with an unshared electron pair usually break readily because the resulting carbocation is resonance stabilized.

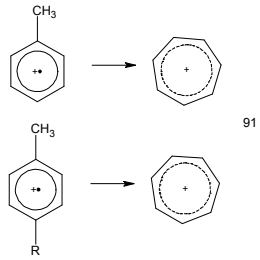


N, 0, or S; R may also be H.

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.

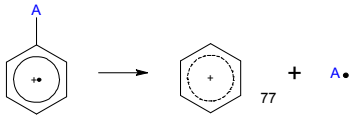


4. Alkyl-substituted benzenes undergo loss of a hydrogen atom or methyl group to yield the relatively stable tropylium ion. This fragmentation gives a prominent peak (sometimes the base peak) at *m/z* 91.



91

5. Substituted benzenes also lose their substituent and yield a phenyl cation at *m/e* 77.

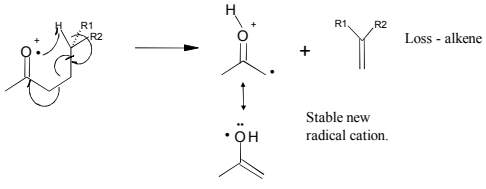


77

A =halogen,-NO_2.-Keto group,-R. etc.

McLafferty Rearrangement

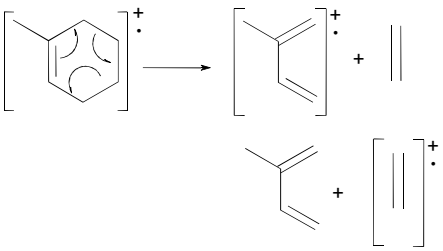
Radical cations localized on keto-type oxygen give β cleavage.
Requires a H atom on a γ sp^3 carbon.
Candidates, ketones, esters, carboxylic acids.



Stable new radical cation.

Retro Diels-Alder Cleavage

Candidates, cyclohexenes; capable of forming a 6-membered transition state; may include heteroatoms (N,O).



Structure Determination Protocol using MS Spectra

Determine the molecular weight, possible elemental compositions, isotopic abundances (to narrow the possibilities) and unstauration.

Identify prime, smaller mass losses like water, etc.; and as many as possible of the major peaks

Based on NMR, IR formulate structure candidates or partial structures, e.g. functional groups

Using MS, predict some fragments your structure would generate, calculate the masses and verify MS.

Go back and forth with other data spectral or otherwise, to corroborate or eliminate structures.

Sequential losses possible.

INTENSITY

m/e (AS PERCENT OF BASE PEAK)

14	8.0	
15	38.6	
18	16.3	
28	39.7	
29	23.4	
42	46.6	
43	10.7	
★44	100.0 (base)	
73	86.1 $M^{+\cdot}$	*100*
74	3.2	3.72
75	0.2	0.23

Mass spectrum for Problem E. 7.

FIG. E.8

Recalculating intensities to base peak

Using Molecular ion isotope peaks:

$N_C := \frac{3.2}{86.1} 100$ $N_C = 3.717$

73

36 - 37 3C from M+1

14-23 1N odd M

16-7 1O from M+2

7H

C_3H_7NO C_3H_7NO 1.0

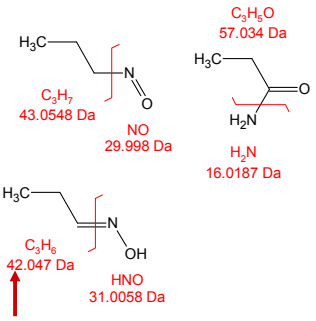
14	8.0	
15	38.6	
18	16.3	
28	39.7	
29	23.4	
42	46.6	73-31
43	10.7	
★44	100.0 (base)	
73	86.1 $M^{+\cdot}$	*100*
74	3.2	3.72
75	0.2	0.23

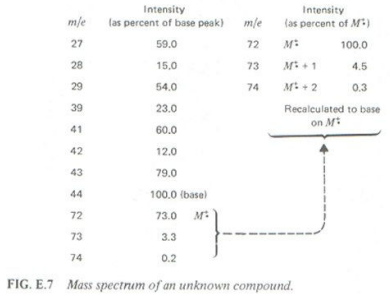
Mass spectrum for Problem E. 7.

FIG. E.8

Confirming MF

C3H7NO 3.81 0.25 73.0528 o 1





m/e	Intensity (as percent of base peak)	*m/e*	Intensity (as percent of $M^{+\cdot}$)
27	59.0	72	$M^{+\cdot}$ 100.0
28	15.0	73	$M^{+\cdot}+1$ 4.5
29	54.0	74	$M^{+\cdot}+2$ 0.3
39	23.0		Recalculated to base on $M^{+\cdot}$
41	60.0		
42	12.0		
43	79.0		
44	100.0 (base)		
72	73.0 $M^{+\cdot}$		
73	3.3		
74	0.2		

FIG. E.7 *Mass spectrum of an unknown compound.*

No halogens

Probably 1 O; (M+2)

4 C ; M+1

Nominal mass

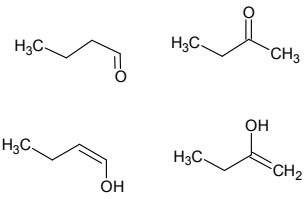
72

48 – 24 4 C

16 - 8 1 O

8 H

Calculation; C4H8O 4.56 0.28 72.0575 o 1

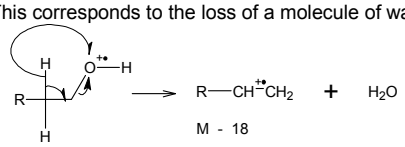


72-44=28 loss of 28 from M to form base peak

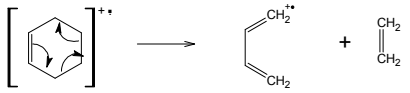
No straight forward cleavage possible; probably a rearrangement occurs before cleavage.

Cleavage of Two bonds:

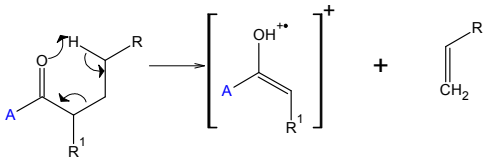
1. Alcohols frequently show a prominent peak at M - 18. This corresponds to the loss of a molecule of water.



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



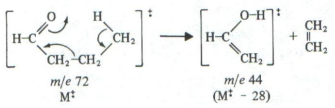
3. Carbonyl compounds with a hydrogen on their -γ-carbon undergo a fragmentation called the *McLafferty rearrangement.*



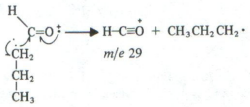
A may be R, H, OR, OH, etc.

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, N_2, NH_3, CO,HCN, H_2S, alcohols, and alkenes.

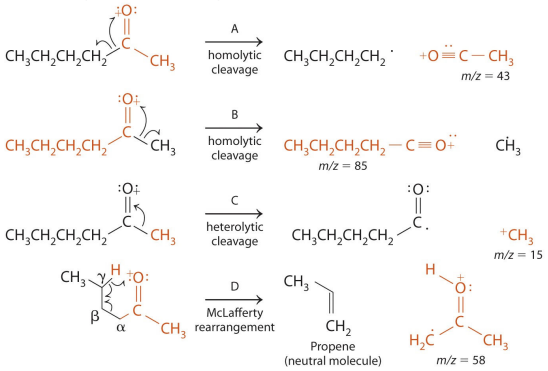
The compound is butanal. m/z = 44 arises from the McLafferty rearrangement.



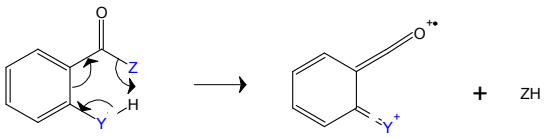
m/z=29 arises from acylium ion.



Cleavage α to C=O group



Carboxylic acids



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

Aromatic –CO_2H; M-17, M-45, M -18 (ortho effect)
Aliphatic –CO_2H; M-17, M-45

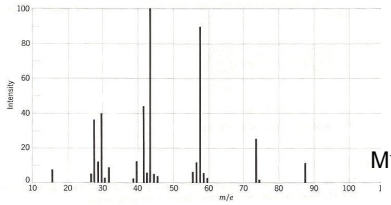
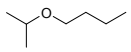


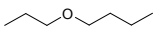
FIG. E.13 *Mass spectrum for Problem E.13.*

M^+=116

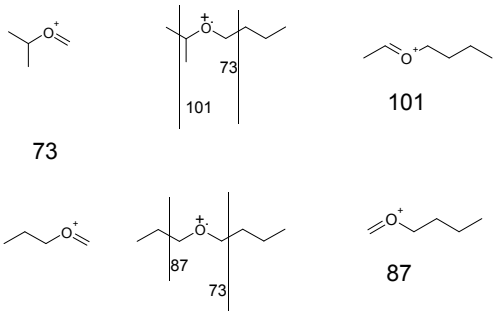
MS of which compound?



Isopropyl butyl ether



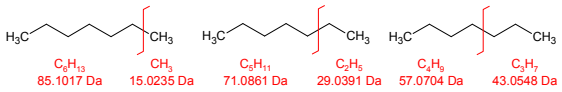
Propyl butyl ether



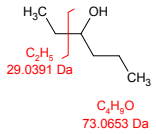
Characteristic Cleavages by Functional Group

Patterns in mass spectra of compounds ionized by EI ionization.

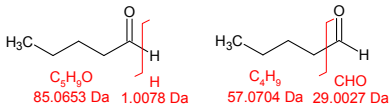
Alkanes: Molecular ion present, may be low intensity, clusters of peaks 14 mass units apart appear.



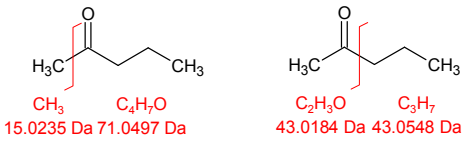
Alcohols: Molecular ion is small or non-existent. Cleavage of the C-C bond next to the oxygen usually occurs. A loss of H_2O may occur.



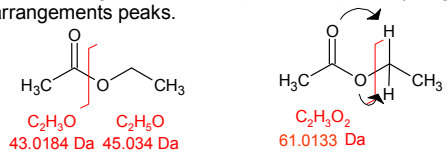
Aldehydes: Cleavage of bonds next to the carboxyl group results in the loss of hydrogen (M-1) or the loss of CHO (M-29).



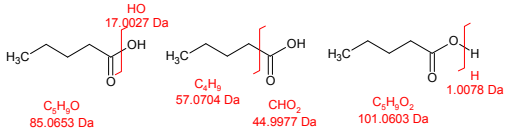
Ketones: cleavage of the C-C bonds adjacent to the carbonyl.



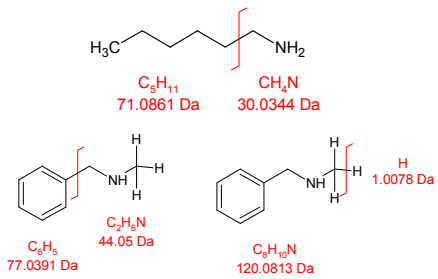
Esters: cleavage next to C=O (loss of -OR) and hydrogen rearrangements peaks.



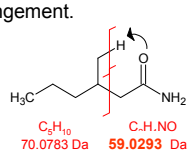
Carboxylic Acids: In short chain acids, loss of OH (M-17) and COOH (M-45) are prominent due to cleavage of bonds next to C=O. (M-1) present.



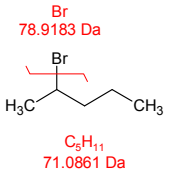
Amines: molecular ion - odd number. α cleavage dominates in aliphatic amines.



Amides: Primary amides show a prominent peak due to the McLafferty rearrangement.



Halides: isotopic peaks are diagnostic.



Ethers: cleavage α to the oxygen atom (C-C bond next to the oxygen).