Mass spectrometry

• Electron impact Mass spectrometry

Bombard your molecules with high energy electrons

$$M \xrightarrow[\text{(BANG!)}]{e^- \; 70\ \text{eV}} M^{\bullet +} + 2\,e^-$$

• 70 eV = 1614 kcal/mol
  - contrast with energy from IR (1-10 kcal/mol) or NMR (0.2 cal/mol)
  - typical C-C bond = 100 kcal/mol
• Point: lots of energy in play here
  - you can eject electrons, break bonds, etc.

• don't call it spectroscopy (absorption of electromagnetic radiation)

• Electron impact Mass spectrometry

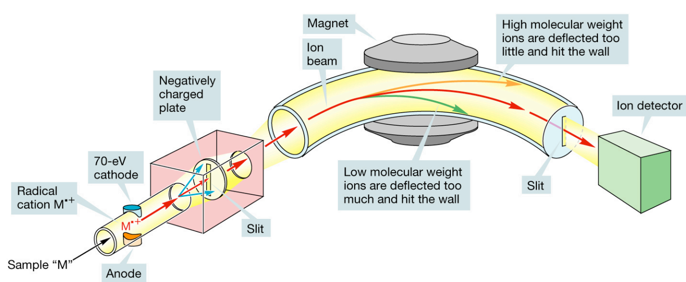


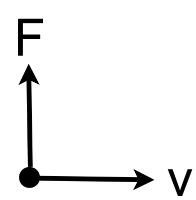
Figure 15.04

• Upon ionization, radical cations (M+) are accelerated toward a negatively charged plate with a slit. Some of the ions pass through the slit to form a beam.

• ions follow a curved path between poles of a magnet.

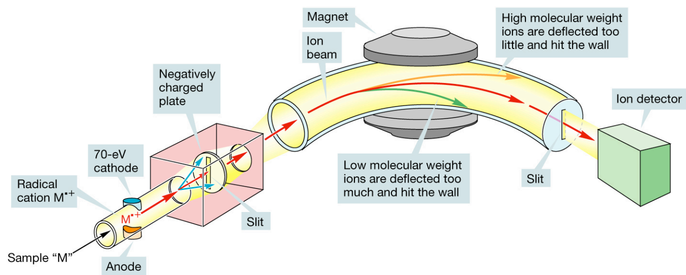
uniform circular motion in the magnetic field

F = zvB
where z= point charge
v= velocity
B = Field stregnth



particles follow circular pathway as a function of time

• Electron impact Mass spectrometry



$F = \frac{mv^2}{R} = zvB$ R = radius

rearranged:

$\frac{m}{z} = \frac{RB}{v}$

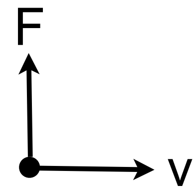
thus, we can observe different masses by holding velocity and radius constant, and varying B

usually, z = 1, so m/z = m

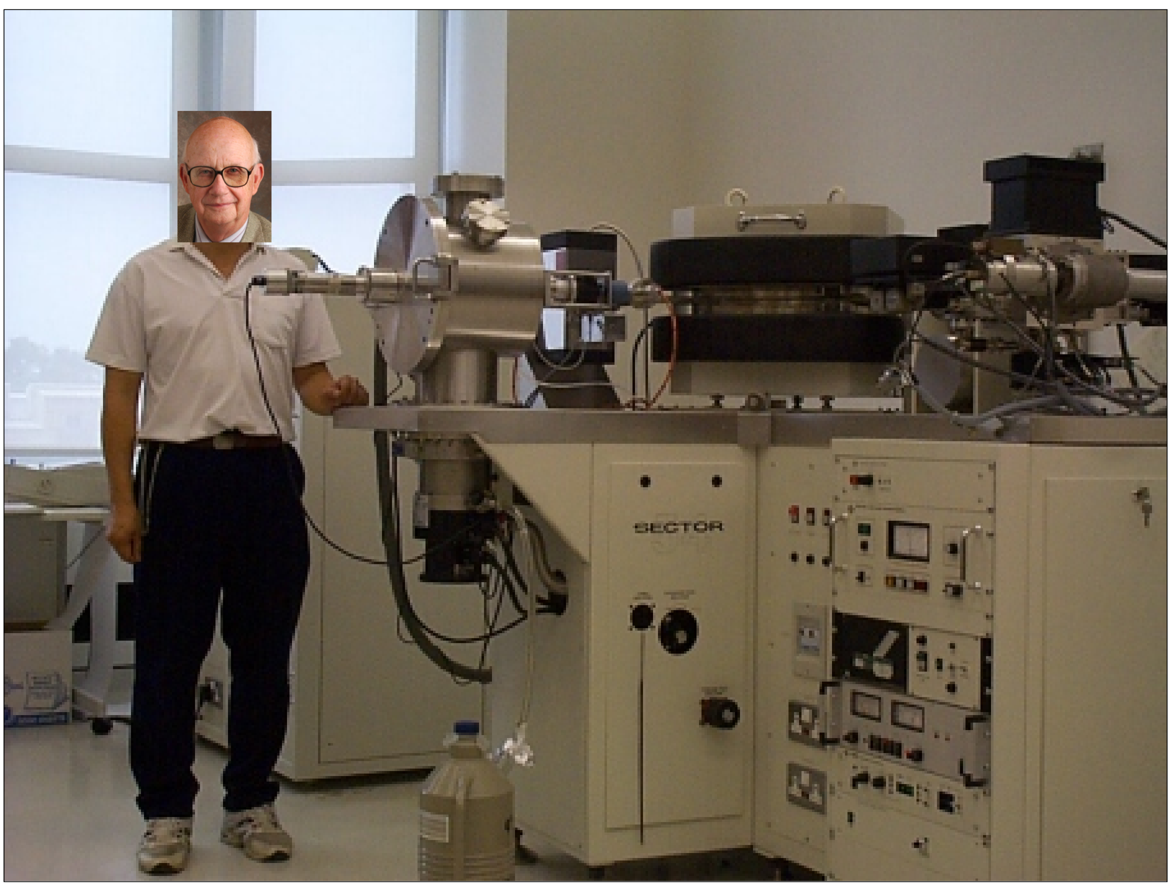
uniform circular motion in the magnetic field

F = zvB

where z= point charge
v= velocity
B = Field stregnth



particles follow circular pathway as a function of time



Isotope	Abundance	Isotope	Abundance
^{1}H	99.985	^{17}O	0.038
^{2}H (D)	0.015	^{18}O	0.200
^{12}C	98.90	^{35}Cl	75.77
^{13}C	1.10	^{37}Cl	24.23
^{14}N	99.63	^{79}Br	50.69
^{15}N	0.37	^{81}Br	49.31
^{16}O	99.762	^{127}I	100

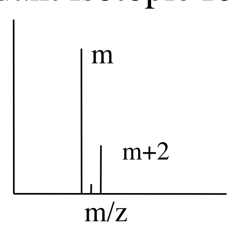
TABLE 15.1 Some Common Isotopes and Their Abundances

Molecular Weight vs Exact Mass

Molecular Mass refers the average mass of molecules made from their natural isotopic abundance:

Exact Mass: The mass of the most abundant isotopic form of a molecule.

Example: $HOCH_2CH_2Cl$



Molecular Weight:

2 x C: 2 x 12.011 : 24.022

1 x O: 1 x 15.999: 15.999

1 x Cl: 1 x 35.453: 35.453

H x 5: 5 x 1.008: <u>5.040</u>

MW: 80.514

Exact Mass:

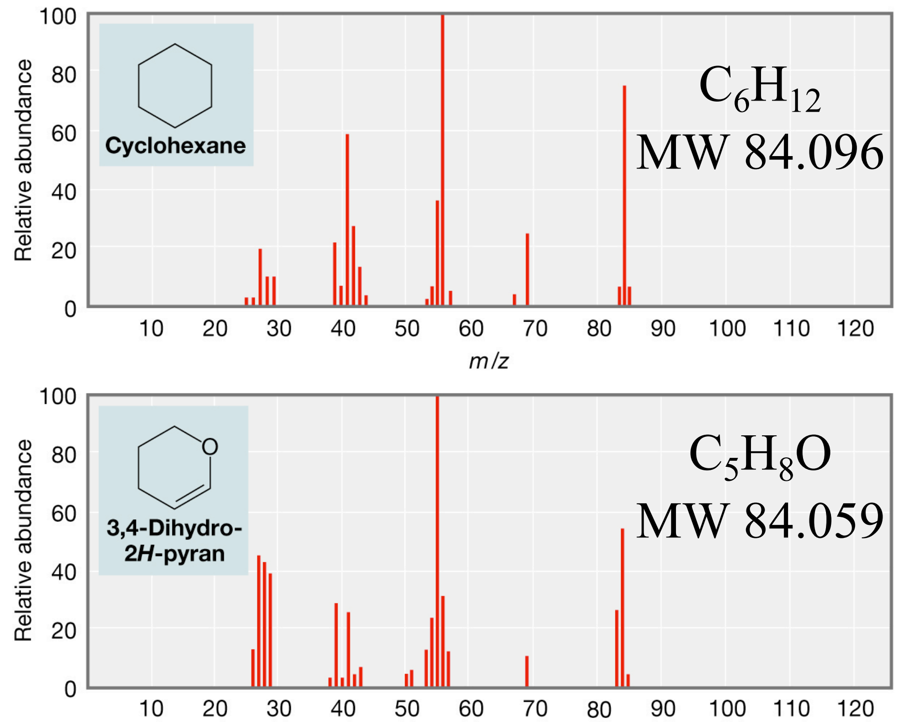
2 x C: 2 x 12.000 : 24.000

1 x O: 1 x 15.9949: 15.9949

1 x Cl: 1 x 34.9689 : 34.9689

H x 5: 5 x 1.0078: <u>5.0390</u>

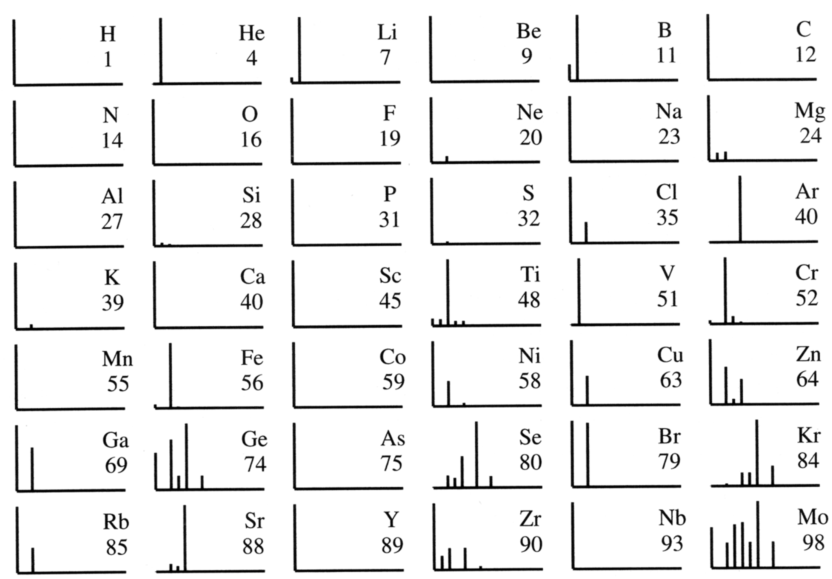
Exact Mass: 80.003



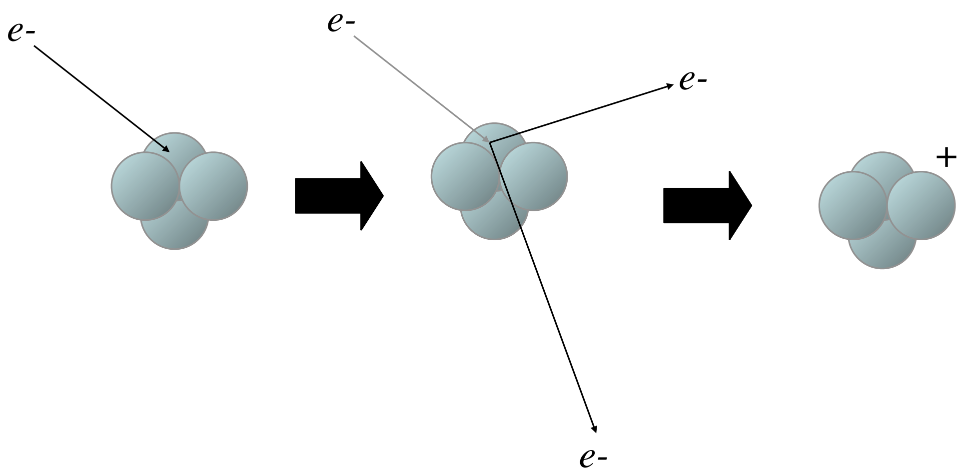
High-Resolution MS can determine the exact molecular formula

Isotopic Abundance

Isotope Patterns of Naturally Occurring Elements

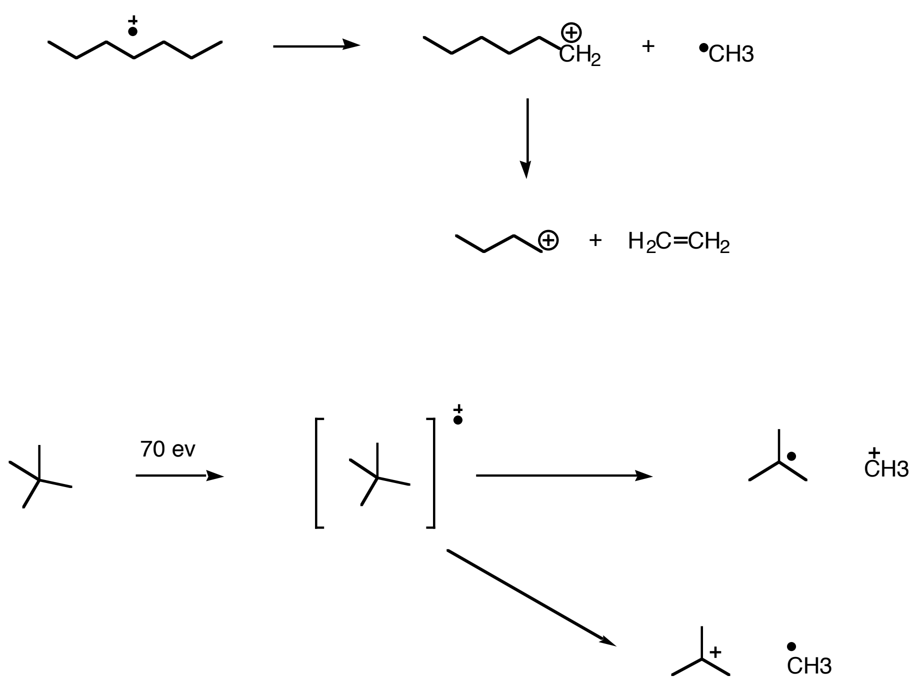


Ionization:



- Lone pair electrons are more easily displaced than bonding electrons.
- Electrons in pi-bonds are more easily displaced than those in single bonds

Fragmentation : Alkanes



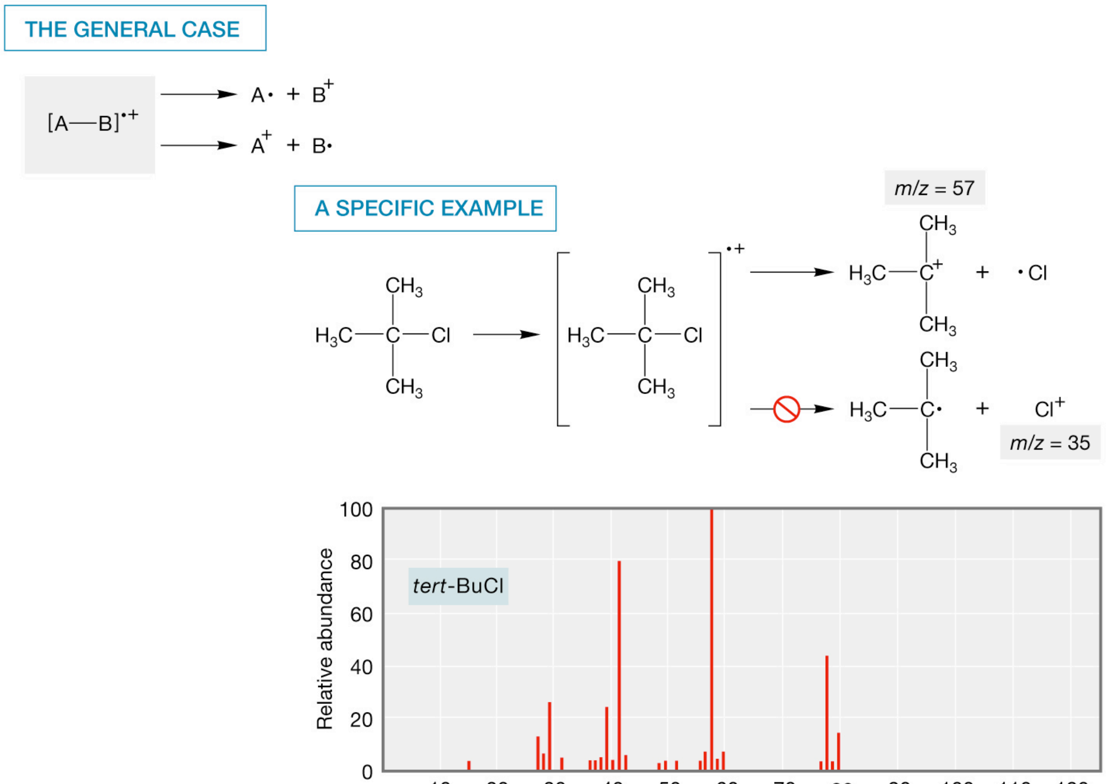
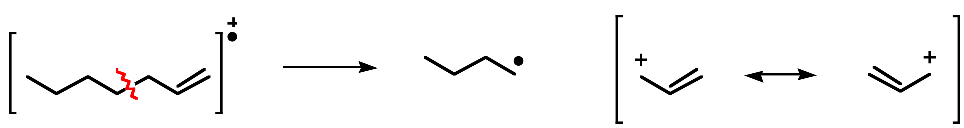
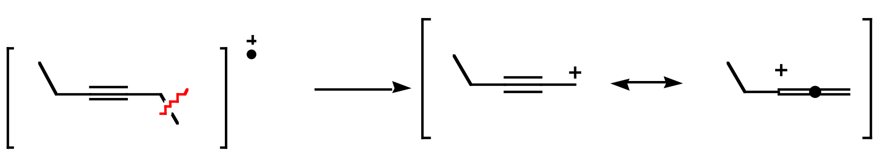


Figure 15.08

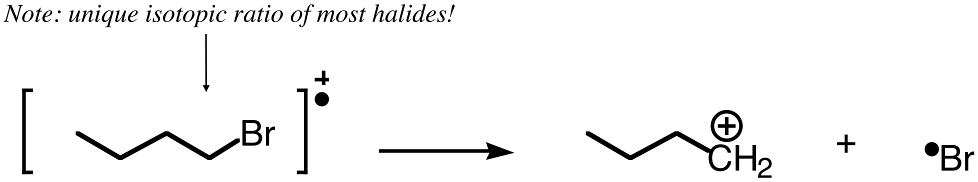
Alkenes/Alkynes



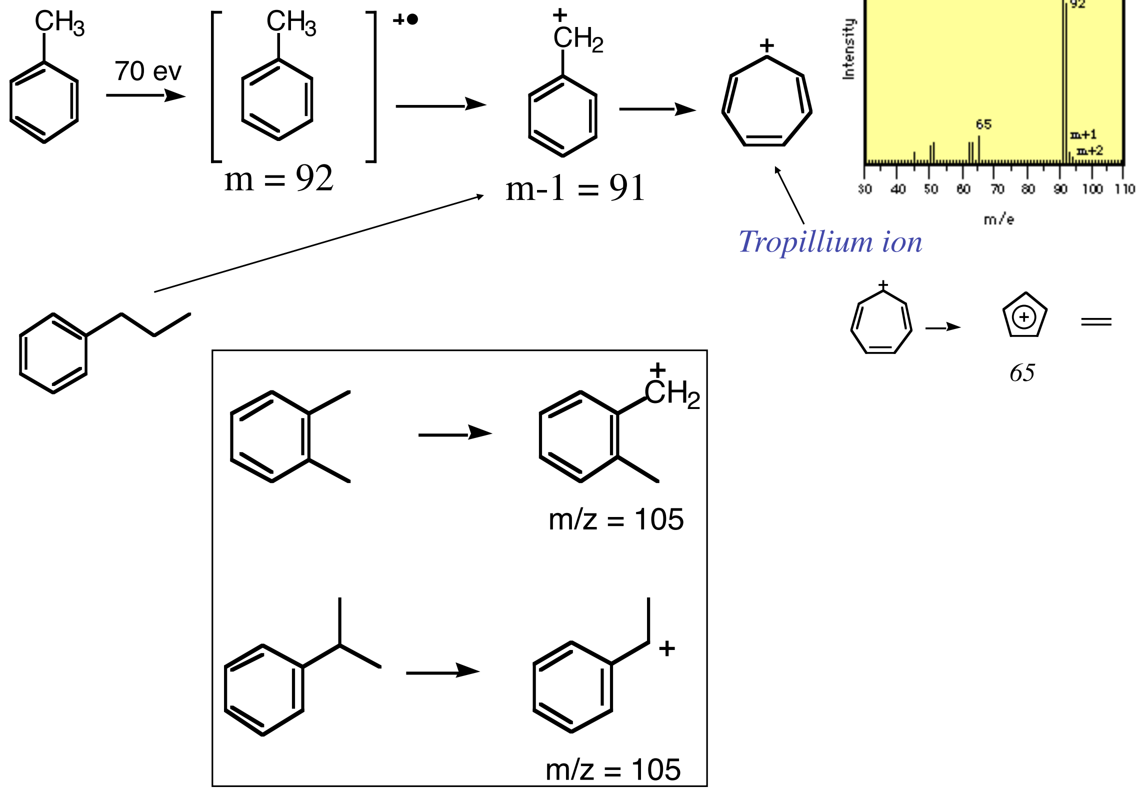


Halides:

Note: unique isotopic ratio of most halides!



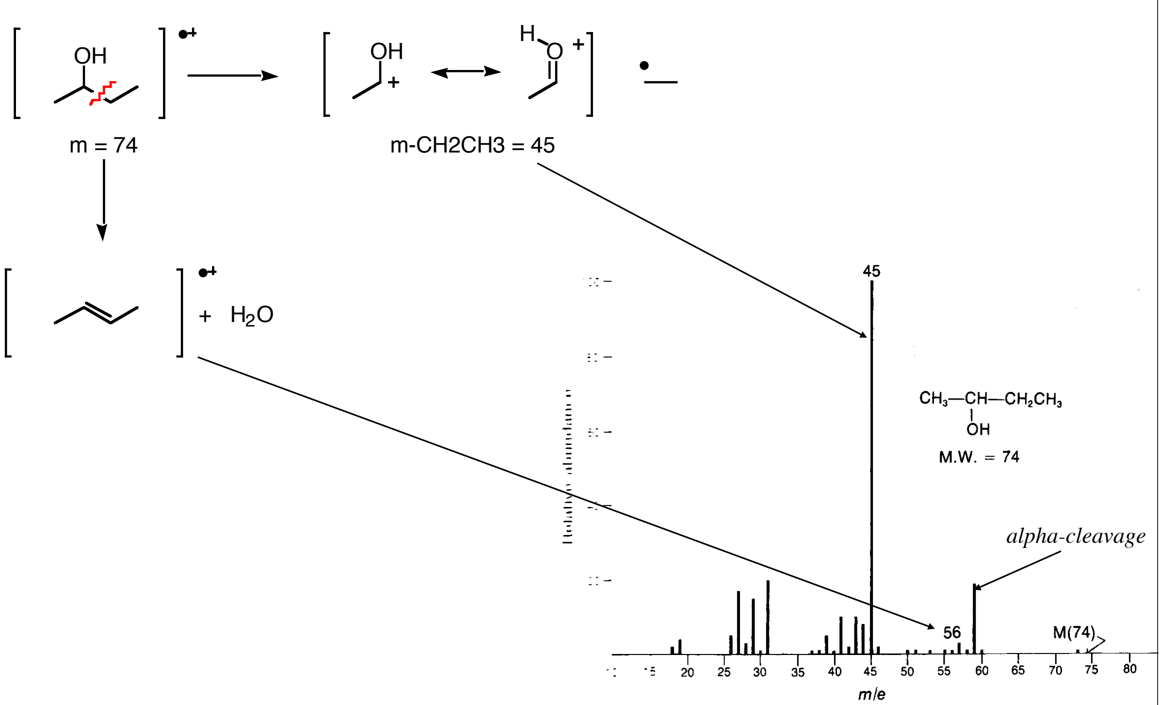
Aromatic:



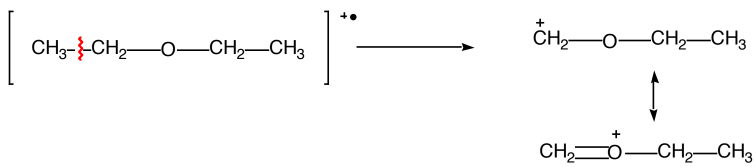
ROH Alcohols

Note: molecular ion is often weakor absent.

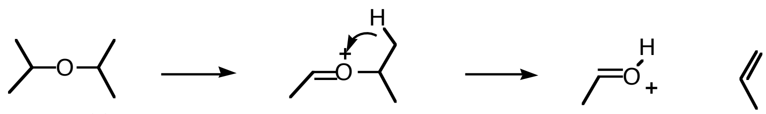
alpha cleavage and dehydration are common fragmentations



ROR Ethers
Notes: molecular ion is often weak
alpha cleavage a are common fragmentations



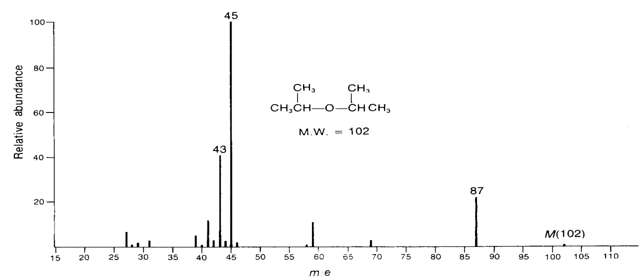
Ethers with branched alpha carbons tend to undergo secondary fragmentation



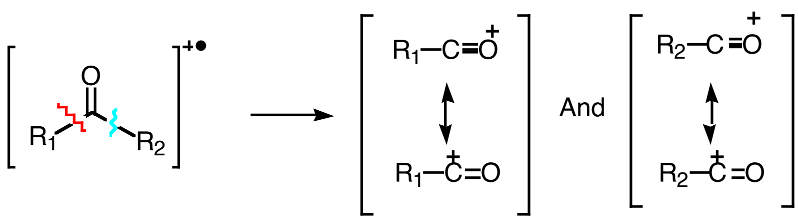
m = 102

m-15 = 87

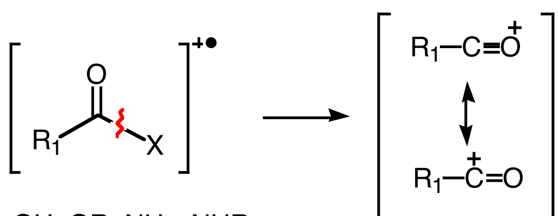
m/z = 45



Ketones and Aldehydes:
Major Fragmentation pattern is alhpa cleavage resulting in loss of side-chain and formation of acylium inon
Also McLafferty Rearrangement where possible!



Esters, Acids, Amides:
Major Fragmentation pattern is alhpa cleavage resulting in loss of side-chain and formation of acylium inon
Also McLafferty Rearrangement where possible!



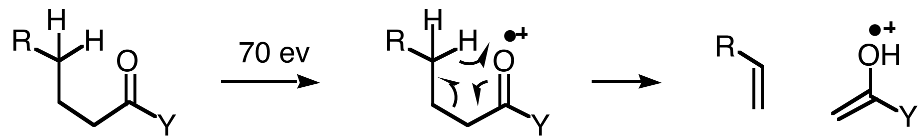
X = OH, OR, NH_2, NHR

note:

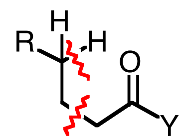
$HO-C\equiv O^+$ m/z = 45

$H_2N-C\equiv O^+$ m/z = 44

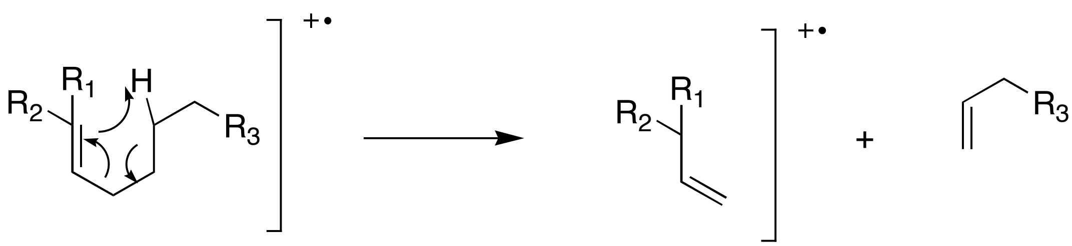
The McLafferty Rearrangment:



must have gamma proton

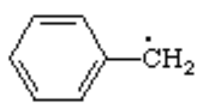


Alkene Fragmentation Revisited



McLafferty - like rearrangement of Alkenes.

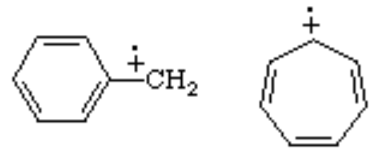
Commonly Lost Fragments

m-15	$\cdot CH_3$
m-17	$\cdot OH$
m-26	$\cdot CN$
m-28	$H_2C=CH_2$
m-29	$\cdot CH_2CH_3$ $\cdot CHO$
m-31	$\cdot OCH_3$
m-35	$\cdot Cl$
m-43	$CH_3\dot{C}=O$
m-45	$\cdot OCH_2CH_3$
m-91	

Common Stable Ions

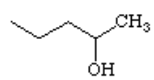
m/e = 43 $CH_3-\overset{+}{C}\equiv O$

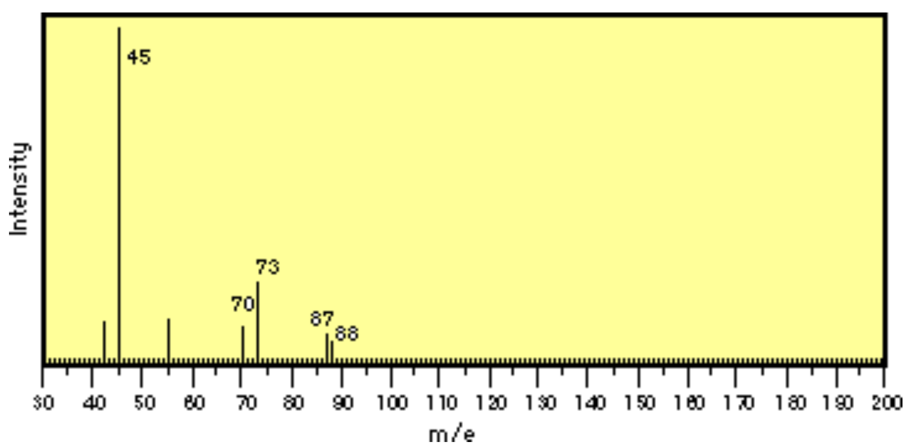
m/e = 91

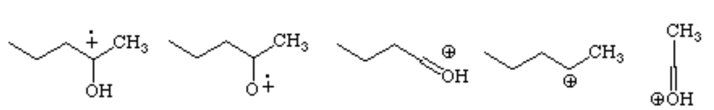


m/e = m-1

C5H12O MW = 88.15

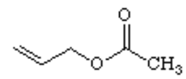


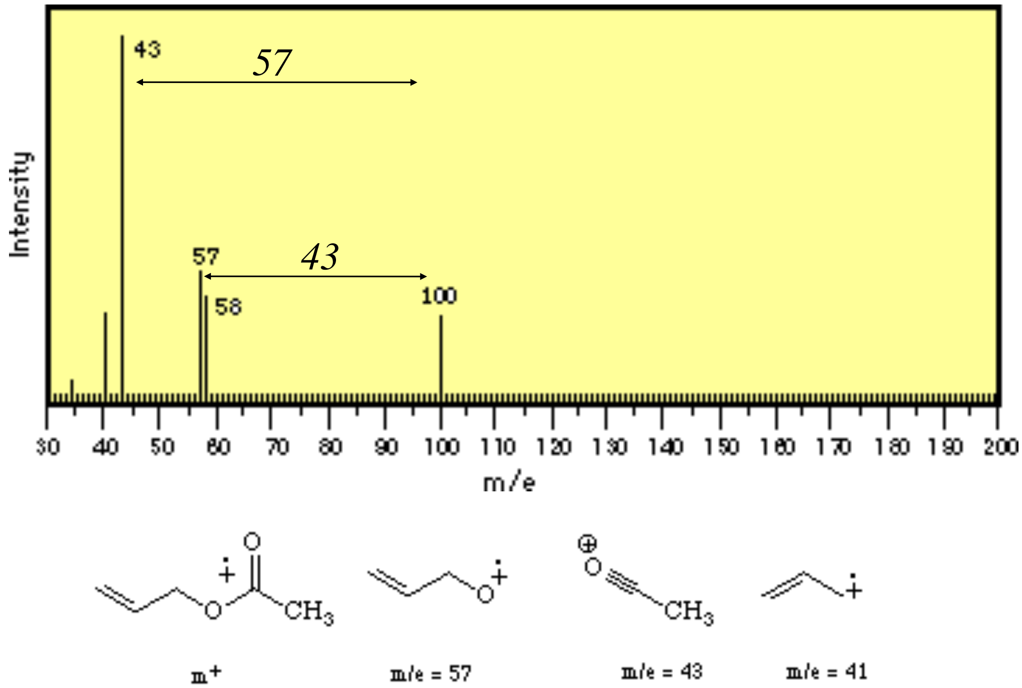




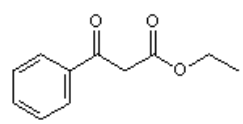
m+ m-1 m-15 m-17 m/e = 45

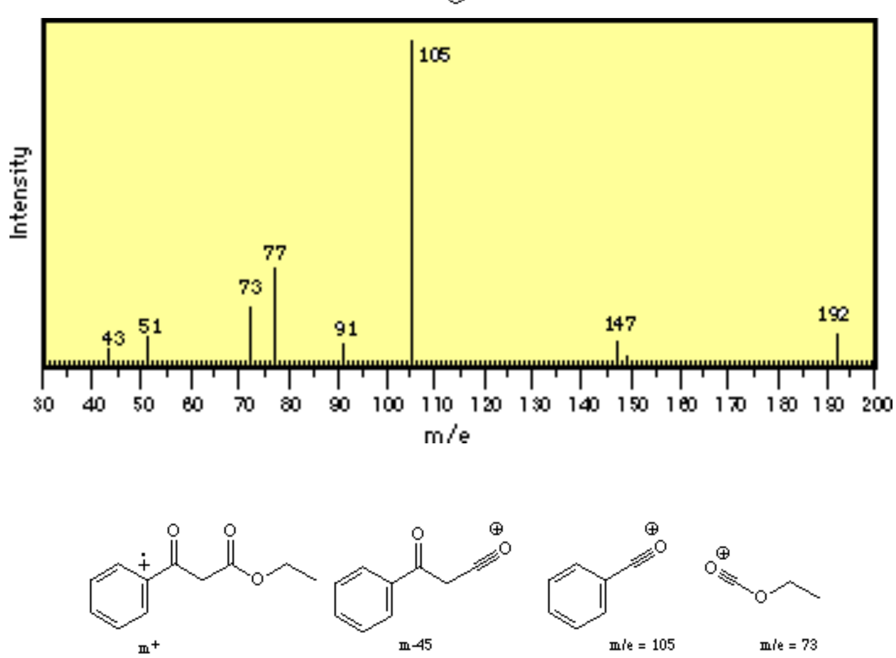
$C_5H_8O_2$ MW = 100.12



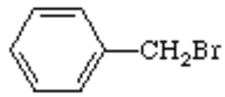


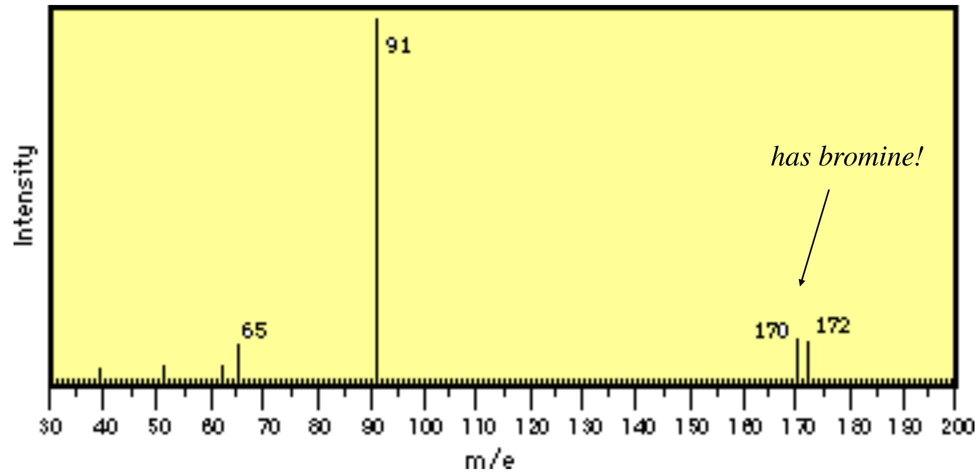
$C_{11}H_{12}O_3$ MW = 192.21

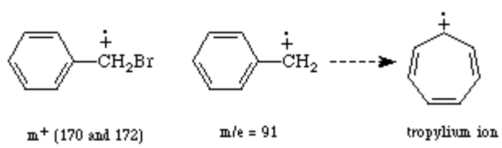




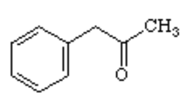
Problem:
C_7H_7Br

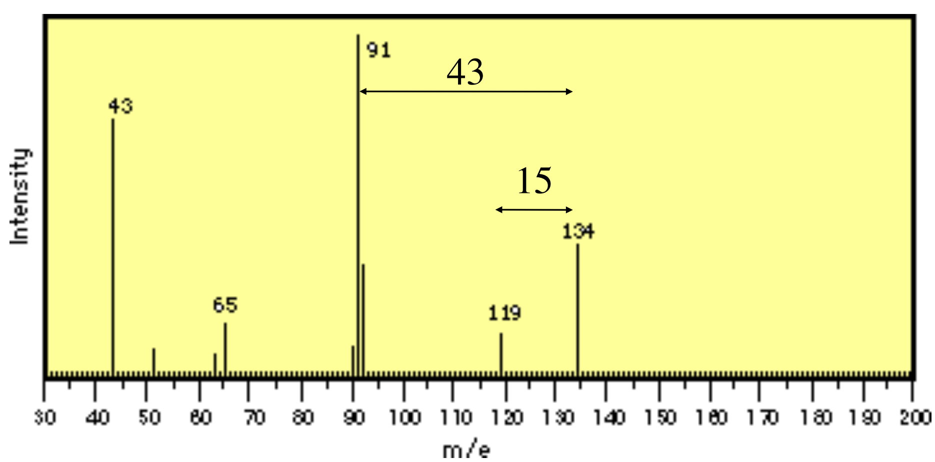


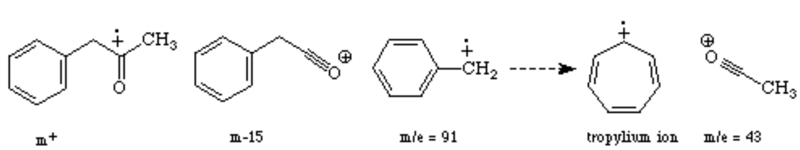




Problem:
$C_9H_{10}O$ MW = 134.18







$C_{12}H_{24}O$

13-C NMR

210, s

43.1 t

42.6, t

31.4, t

30.6, t

23.3, t

22.8, t

22.5, t

22.1, t

14.1, t

12.1, q

10, q

1H-NMR

2.45 (broad triplet, J=7.6 Hz, 4H)

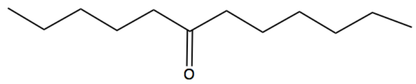
1.60 (m, 4H)

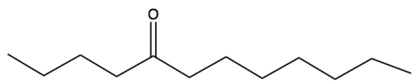
1.2-1.4 (m, 10H)

0.96 (broad triplet, J = 6.8 Hz, 6H)

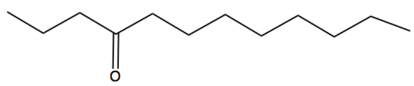
MS:

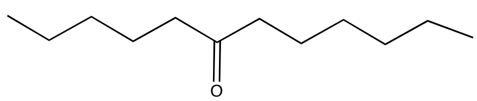
184.2 (5), 128.1(98), 114.1(100), 99.1(8), 113.1(10),



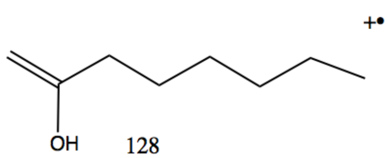


which is it?

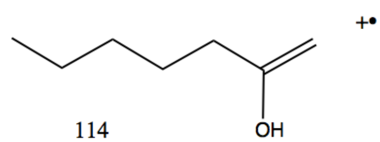




McLafferty

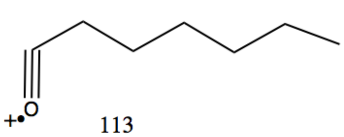


128

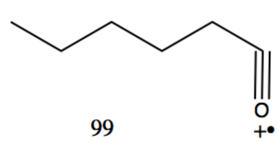


114

acylium



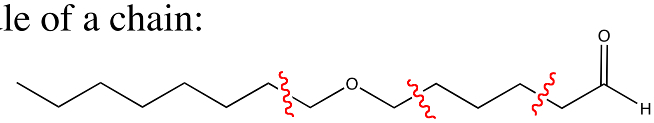
113



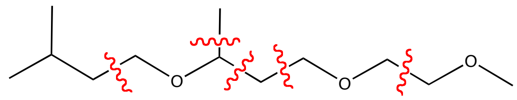
99

When MS really helps:

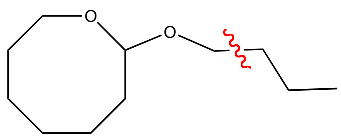
Middle of a chain:



Assembly of subunits



Identification of ring substitutions.



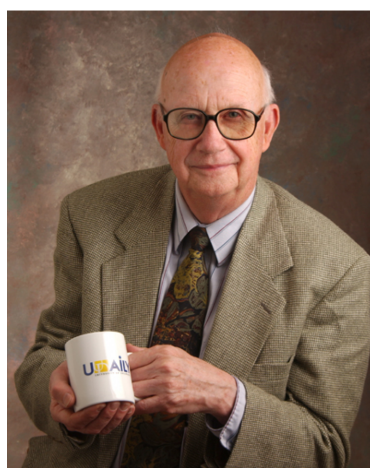
What is MS good for?

- The complex fragmentation patterns can be used as a finger print to identify a compound.
- MS is extremely sensitive! fempto-mole quantities can be detected!
- As seen on TV! Used in crime seen investigation to detect trace evidence.

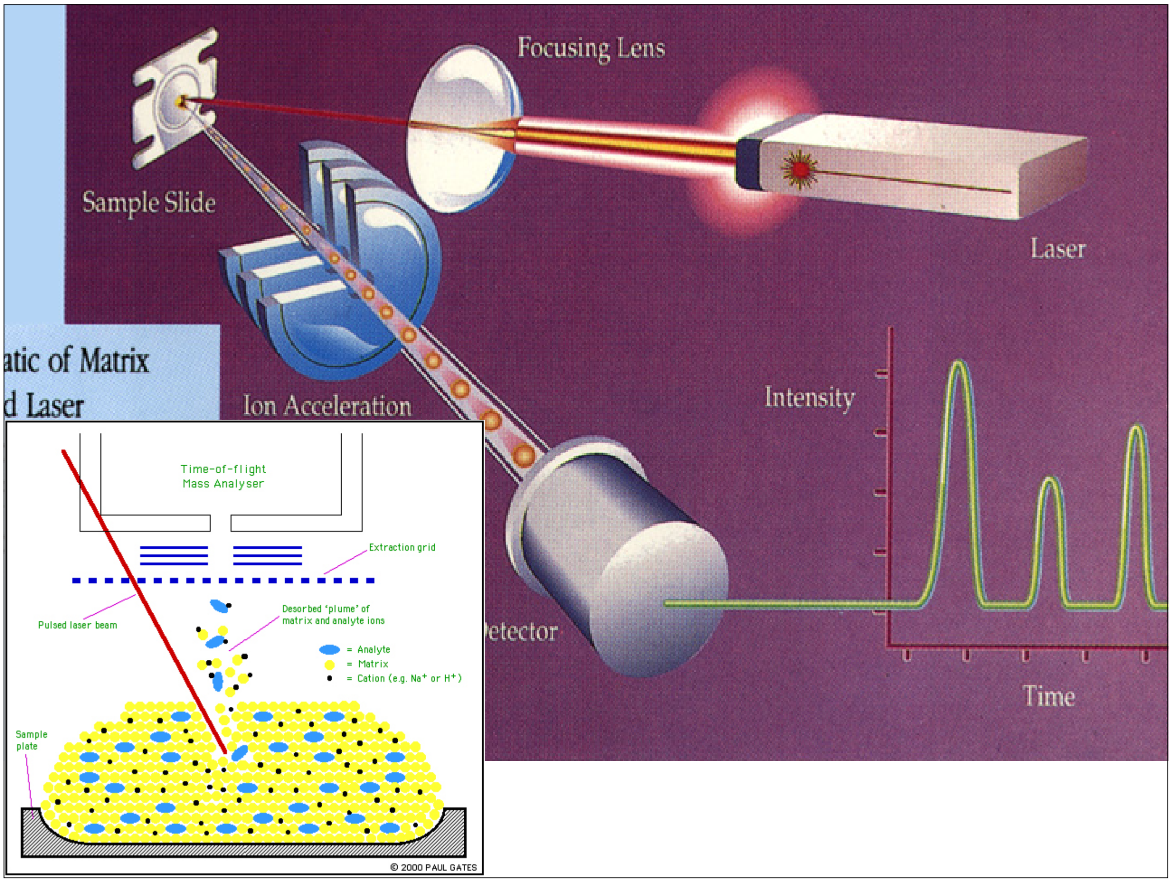
Wanted: Better methods to ionize molecules without the molecule falling apart

Ionization Methods

- Electron Impact. High velocity electrons.
- Chemical Ionization: A carrier gas (eg Methane) is activated by EI. Radical cations protonate analyte.
- Fast Atom Bombardment: High Energy Atoms (Xe or AR) strike a sample leading to desorption and ionization.
- Electrospray - Formation of charged liquid Droplets which lose solvent to form ionized molecules.
- MALDI (Matrix Assisted Laser Desobtion) Sample dissolved in organic matrix that absorbs light energy from high-intensity laser.



One early major breakthrough, described by M.S.B. Munson and F.H. Field in 1966 [1], was the use of chemical ionisation (CI), which for the first time made it possible to ionise thermo-labile biomolecules. In CI, abundant reagent gas ions are first formed by electric discharge of a reagent gas, and the reagent ions then in turn ionise volatilised molecules of interest.



SIMS Imaging

(Secondary Ionization Mass Spectrometry)