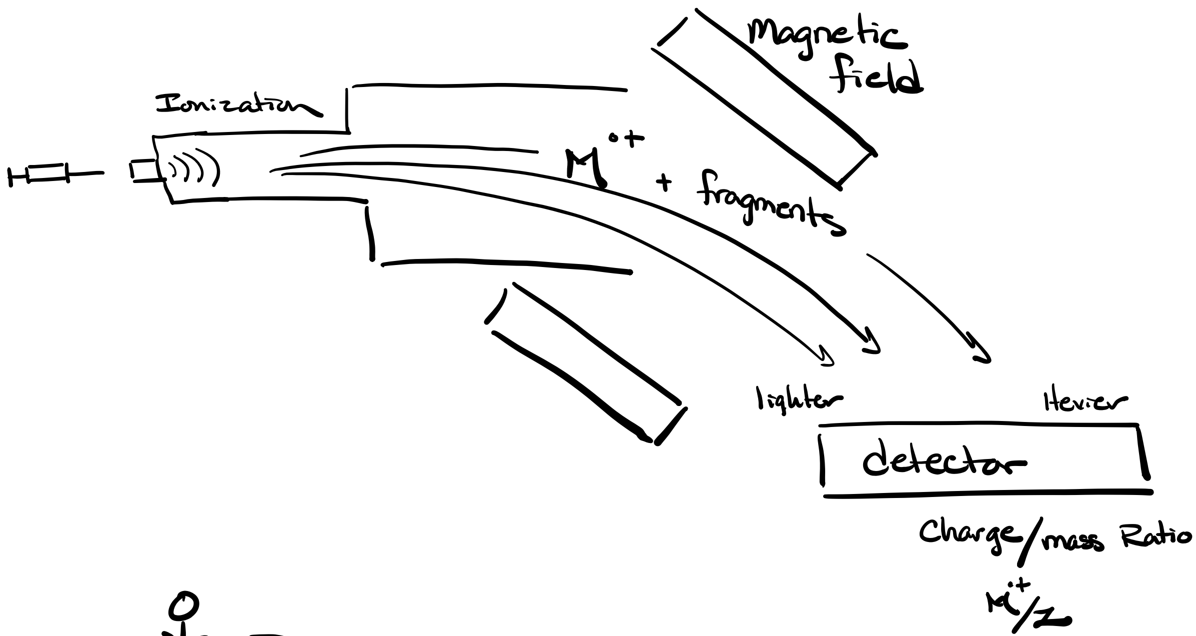
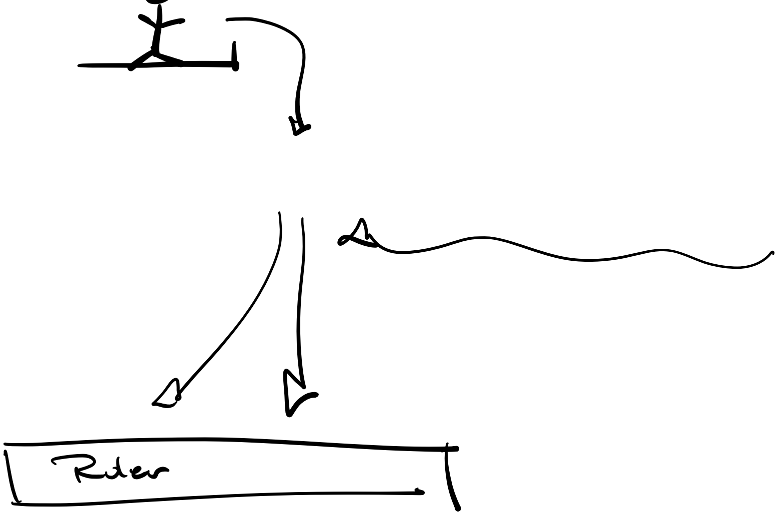
Mass Spectroscopy





- Small amount of sample needed
  usually 10^{-6} or μg quantities

Many types of Ionization

⟹ Electron Impact (EI)

$$M^{\bullet\bullet} \xrightarrow{-e^-} M^{\bullet +} + \text{fragments}$$

radical cation

molecular Ion

good for molecules upto 3500 g/mol

Electrospray Ionization (ESI)

$$M \xrightarrow{+H^+} [M-H]^+ + \text{few fragments}$$

Molecular Ion

good for molecules upto 100,000 g/mol

Instruments can be High resolution or Low resolution

High resolution - 7 or 8 Sig figs on molar Mass

$M^{\cdot +} = 58.04187$ m/z

Low resolution - 4 Sig figs on molar Mass

$M^{\cdot +} = 58.04$ m/z

Low Resolution

How many molecular formulas fit 58.04 m/z ratio?

- 16 molecular formulas by calculator that match

High Resolution Data

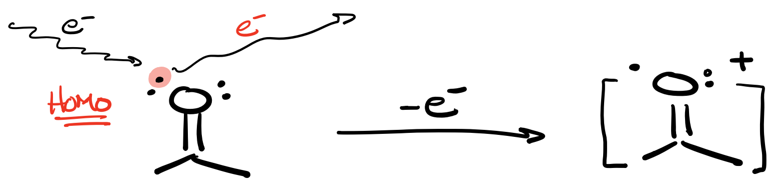
How many fit 58.04187 m/z ratio?

only 1 formula

C_3H_6O

Frequently use with mass Spec calculators which make it easier, but also frequently done by hand w/ Low Res data.

Formation of $M^{\cdot +}$



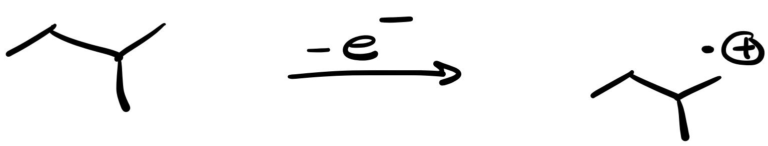
C_3H_6O

0 m/z

Molecular Ion

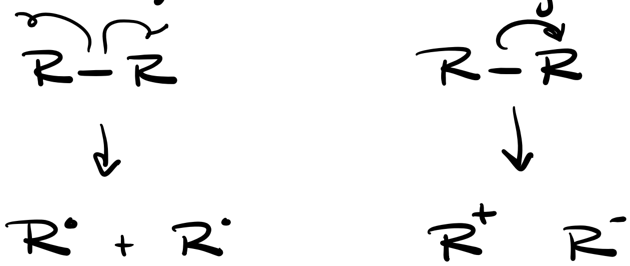
$M^{\cdot +}$

$C_3H_6O^+ = 58.04$ m/z

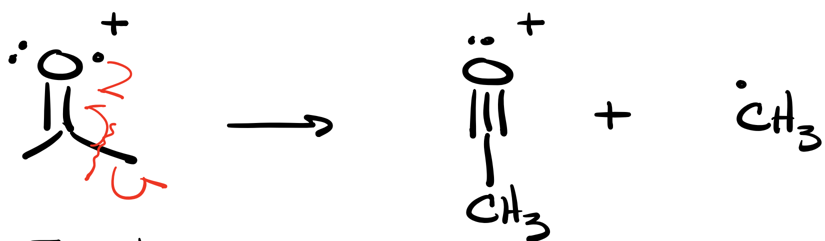


Highest occupied molecular orbital is a π e⁻ or lone pair

Molecular ions can fragment by homolytic or heterolytic Cleavage



Homolytic



m/z = 58.04

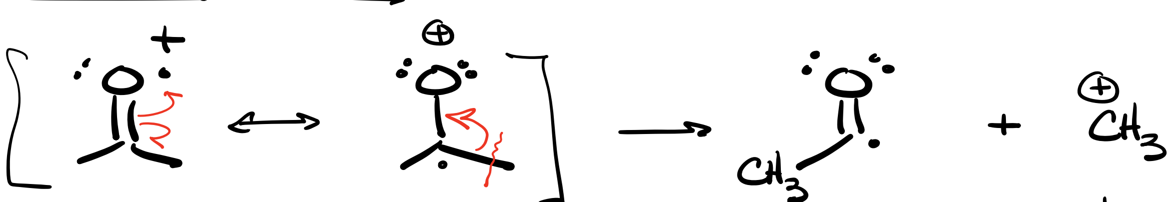
Fragment
m/z
visible

C_2H_3O

m/z = 43

Loss
Invisible to mass spec

Heterolytic



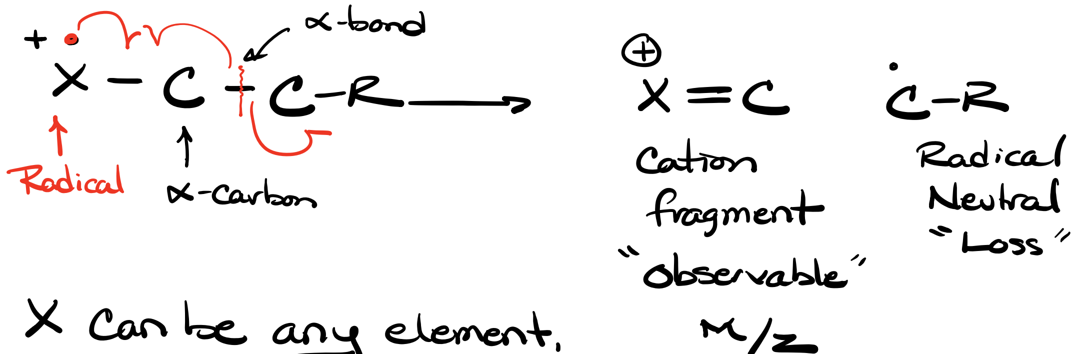
Loss

CH_3
m/z = 15

Two main types of Cleavages that we look for:

- alpha α
- McLafferty

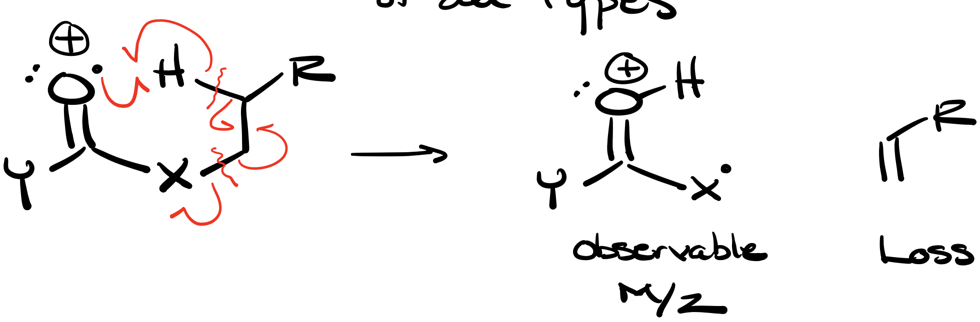
α



X can be any element.
Usually O, N, halogen, but Can also be Carbon

McLafferty

Special type with Carbonyls of all types



Molecular Ion

Three ways to find the molecular formula.

- Mass Spec Calculator
- Rule of 13
- ^{13}C isotope ratio

Rule of 13

Organic molecule will have C:H ratio that is 1:1

C–H (CH)

12 amu + 1 amu = 13 amu

M/z ratio = 86 C_xH_y

$$\begin{array}{r} 6 \\ 13 \overline{)86} \\ 78 \\ \hline 8 \end{array}$$ remainder

$$CH \overline{)C_xH_y}$$ → x

remainder = additional Hydrogens

C_xH_x

C_6H_6 + 8 amu's left

+8 → 8H's

C_6H_{14}

$6 \times 12 = 72$

$1 \times 14 = 14$

$= 86$ ✓

Try Rule 13 w/ $M/z = 212$

$$13 \overline{)212} = 16,\quad 208,\ \text{remainder } 4$$

$C_{16}H_{20}$

$16 \times 12 = 192$
$20 \times 1 = 20$
$= 212$ ✓

$1\,C = 12\,H$
12amu 12amu

$C_{15}H_{20+12} = C_{15}H_{32}$

Convert Carbons mass into hydrogen

212

$C_{16}H_{20}$ — $34 - 20 = 14$, $14 / 2 = 7$ units unsat

or

$C_{15}H_{32}$ — $32 - 32 = 0$ units unsat

What about other elements?

$$13 \overline{)86} = 6,\quad 78,\ \text{remainder } 8$$

$C_5H_{12}N$

C_6H_{14}

$-CH_4$ $+O$

$C_5H_{10}O$

$-CH_4$ $+O$

$C_4H_6O_2$

C_4H_3Cl

~~$C_3H_{15}Cl$~~

12 amu 12 amu
$1\,C = 12\,H$

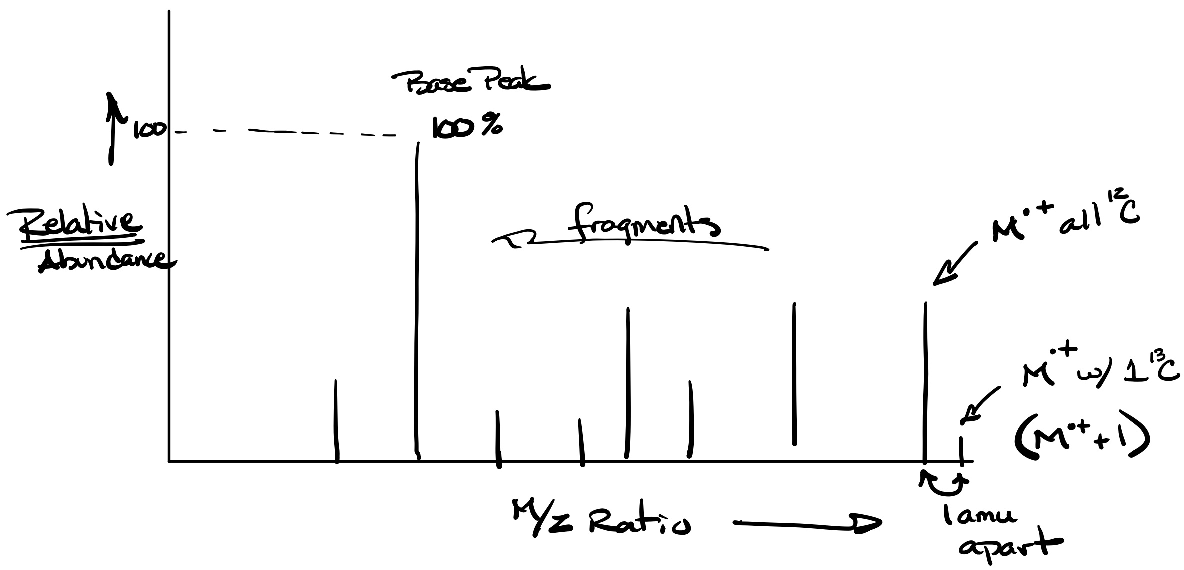
16amu 16amu
$O = CH_4$

14amu 14amu
$N = CH_2$

35amu 35amu
$Cl = C_2H_{11}$

How many Carbons are in our molecule?

$\Longrightarrow$ $^{13}C : ^{12}C$ ratio



$$\frac{\left[\dfrac{(M^{\bullet+}\text{ w/ }1\ {}^{13}C)_{\text{Relative abundance}}}{(M^{\bullet+}\text{ all }{}^{12}C)_{\text{Relative abundance}}}\right]\times 100}{1.1\%\ ({}^{13}C:{}^{12}C\text{ natural abunance})} = \#C \text{ in formula}$$