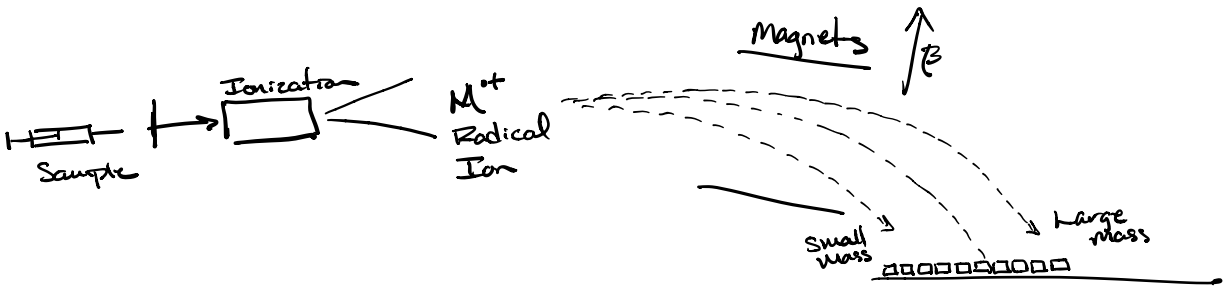
Mass Spectroscopy



Ionization Techniques

⇒ Electron Impact $e^- \rightsquigarrow \ddot{M} \rightarrow M^{+\cdot}$ Molecular ion (e^- ejected)

Electrospray $M + H^+ \rightarrow [M-H]^+$

- Mass Spec works on samples 10^{-6} g and smaller

Electron Impact (EI) — $M^{+\cdot}$ Radical Cations

Good for upto 3500 g/mol

- $M^{+\cdot}$ missing sometimes
- Polar substance don't work as well
- Fragmentations Common

Electrospray Ionization (ESI) — $[M-H]^+$

Good upto 100,000 g/mol

- Often get multiple Charges $[M-2H]^{2+}$ & $[M-3H]^{3+}$
- Fragmentations are rare

Electron Impact

$1e^- = 1/2000\ p^+$ or n°

Acetone C_3H_6O

$-e^-$

Valence e^- lost

πe^- & lone pairs

$M^{\cdot+}$ = molecular ion

$C_3H_6O^+$

Low Resolution

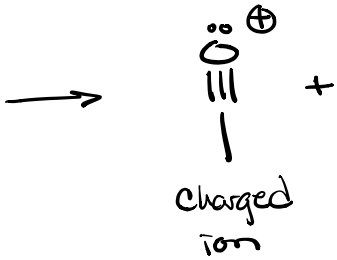
$M/z = 58$

High Resolution

$= 58.04187$

Types of fragmentations

Homolytic



Charged ion

Neutral Free Radical

$M/z = 43$

$C_2H_3O^+$

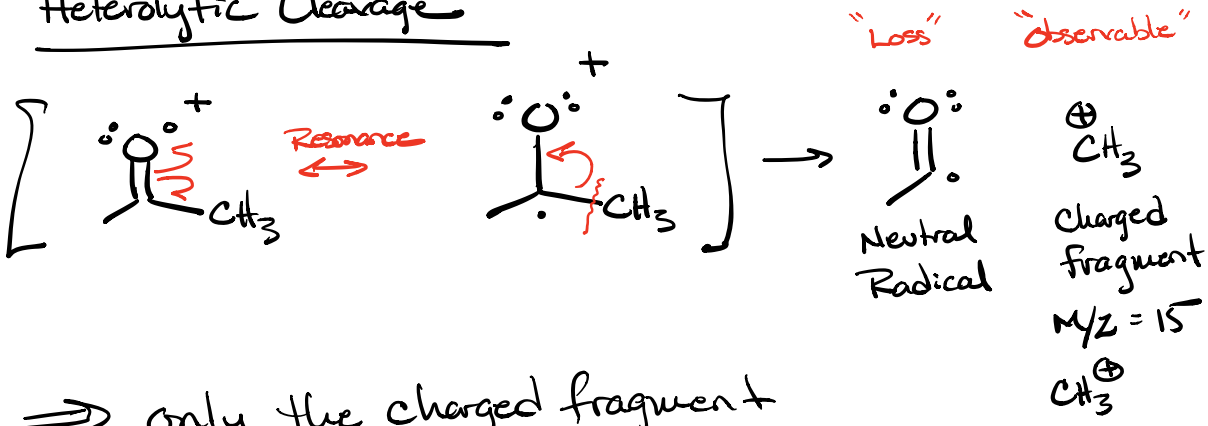
$C = 12 \times 2 = 24$

$H = 1 \times 3 = 3$

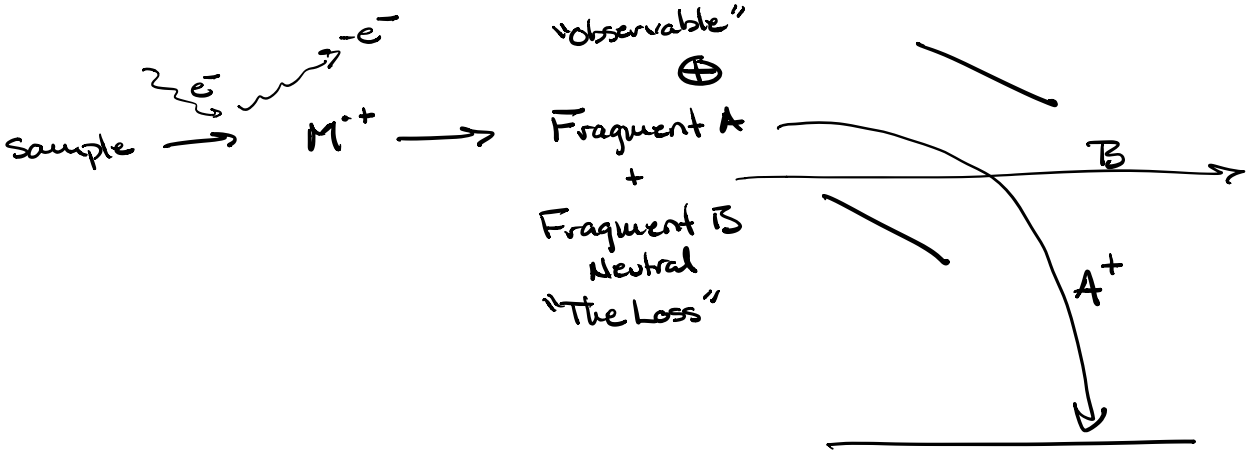
$O = 16 \times 1 = +16$

$M/z = 43$

Heterolytic Cleavage

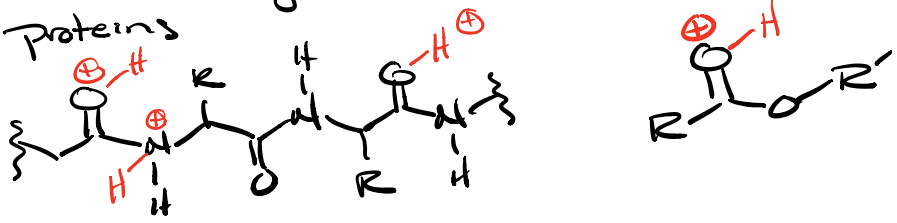


⇒ only the charged fragment is observable

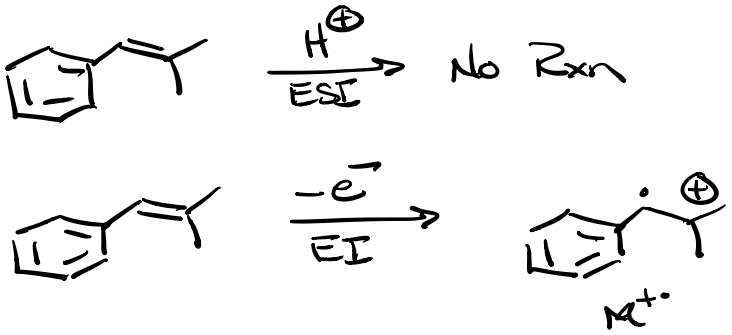


ESI (Electrospray ionization)

preferred when you have large molecules like proteins



our focus
⟹ EI preferred for small molecules & non-polar



Power of High Resolution Data

$M^{\cdot+} = 58$

Molecular Formula ?

Rule of 13 = C + H
12 + 1 = 13

4 Remainder of 6
13 | 58.0
52
6 ←

$C_4H_{4+6} = C_4H_{10}$

$4 \times 12 + 10 = 58$ ✓

O = 16 g/mol = CH_4 = 16 g/mol

O = CH_4

C_4H_{10} $\xrightarrow[+\,O]{-CH_4}$ C_3H_6O

Possible Formulas include

C_4H_{10}
C_3H_6O
$C_2H_2O_2$
} 58 g/mole

High Resolution Data

$M^{+\cdot} = 58.07825$

mass spec calculator w/ deviation ± 0.01 M/z

$58.07825 = C_4H_{10}$
$58.04187 = C_3H_6O$
} Easily distinguished between by calculators

Isotopes

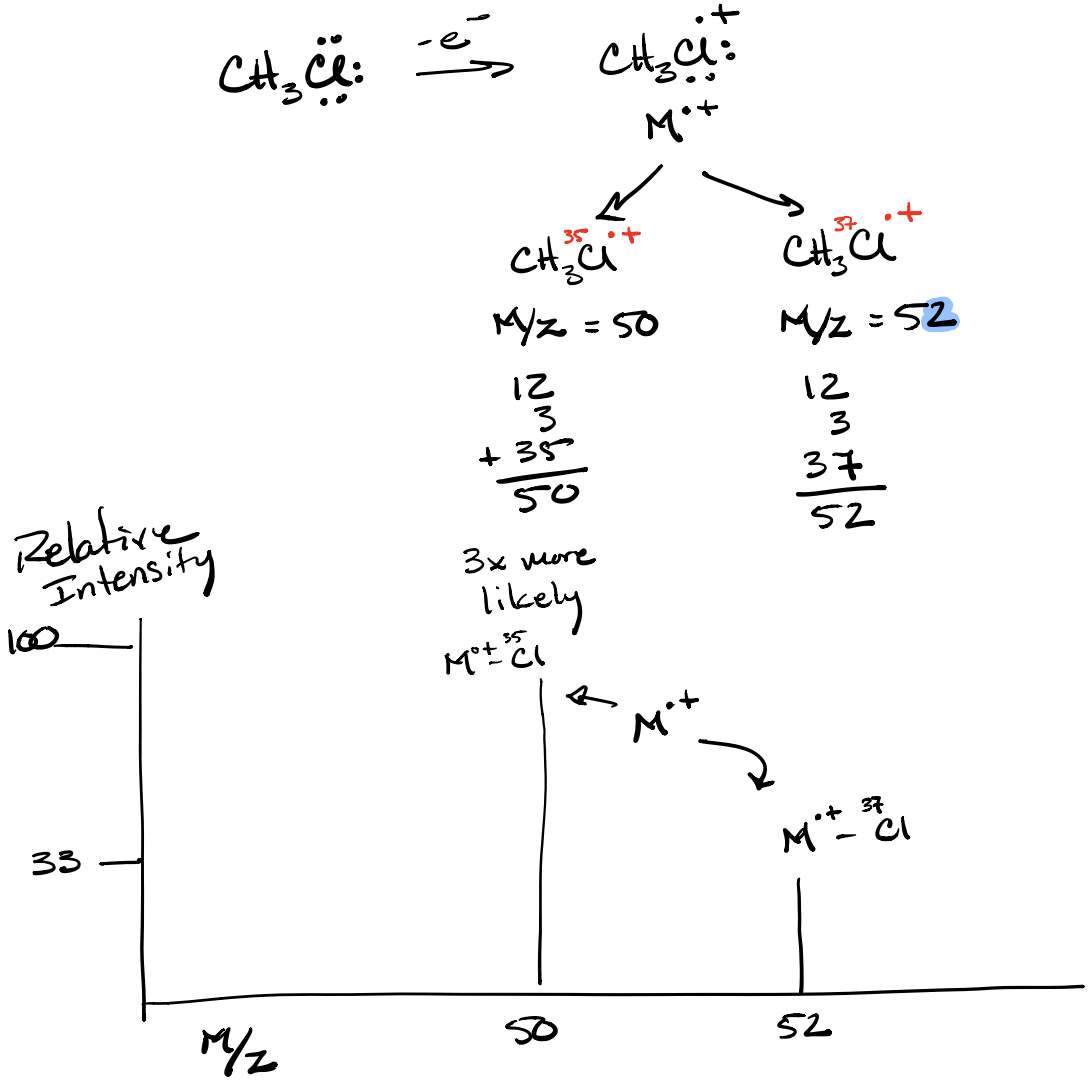
Halogens

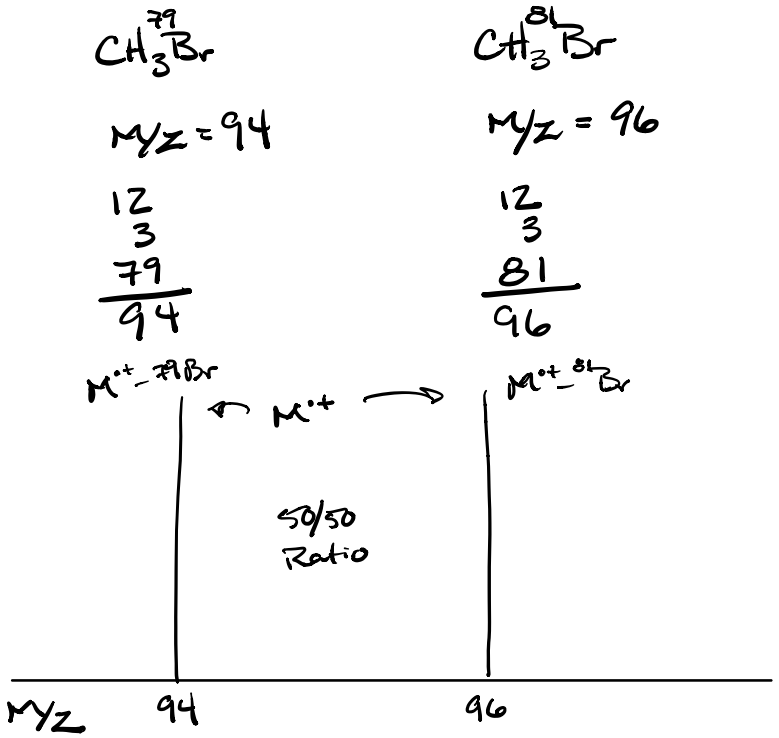
Br ^{79}Br 50.69% & ^{81}Br 49.31% ⇐ almost 50/50

Cl ^{35}Cl 75.77% & ^{37}Cl 24.23% ⇐ almost 3:1 ratio

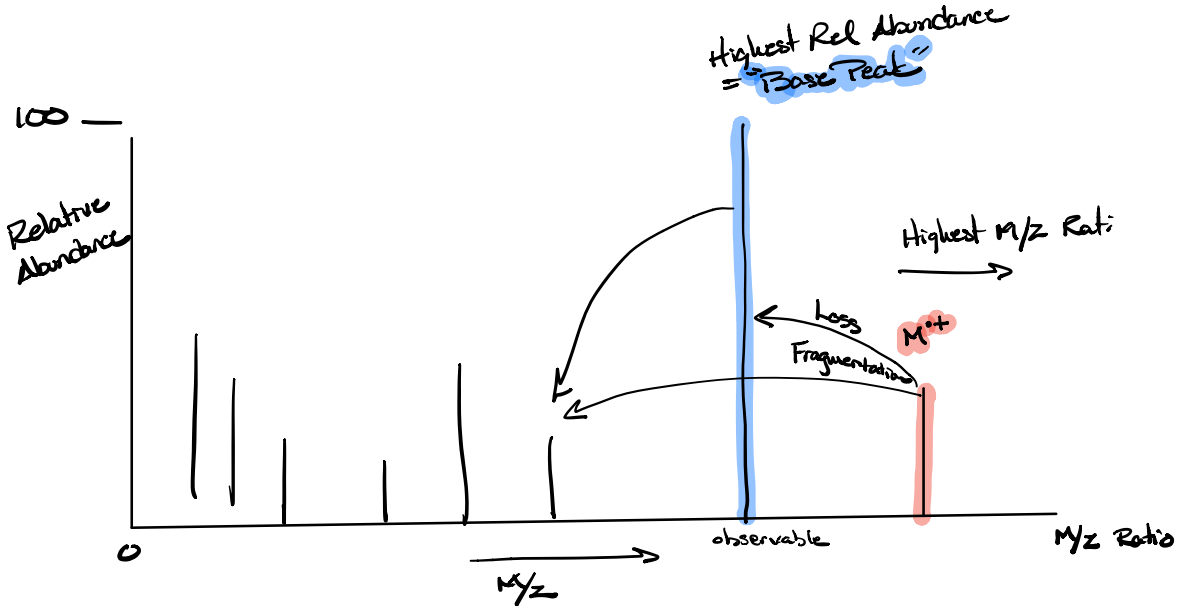
F ^{19}F 100%

I ^{127}I 100%


$CH_3Cl:$
$-e^-$
$CH_3Cl:^{+\cdot}$
$M^{+\cdot}$
$CH_3{}^{35}Cl^{+\cdot}$
M/z = 50
12
3
+ 35
50
$CH_3{}^{37}Cl^{+\cdot}$
M/z = 52
12
3
37
52
Relative Intensity
100
33
3x more likely
$M^{+\cdot} - {}^{35}Cl$
$M^{+\cdot}$
$M^{+\cdot} - {}^{37}Cl$
M/z
50
52



Mass Spectometry




$M^{+\bullet}$ = base peak