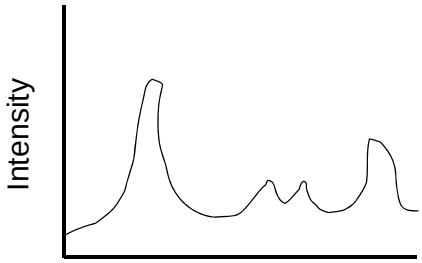
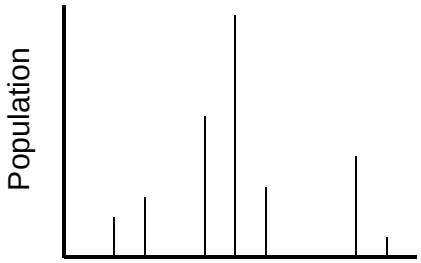
Mass Spectrometry (*technically not Spectroscopy*)

So far,



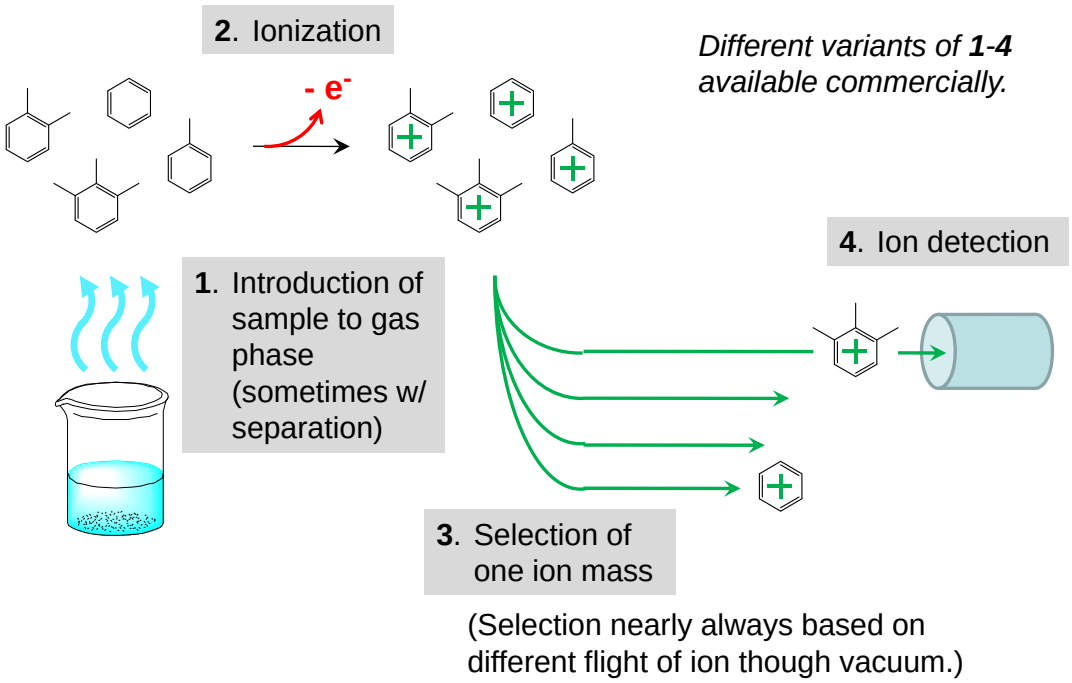
Spectroscopy *is about interaction of energy with matter. X-axis is real.*

In mass spec,



Mass ***spectrometry*** *measures population of ions with particular mass.*

General Characteristics of Mass Spectrometry

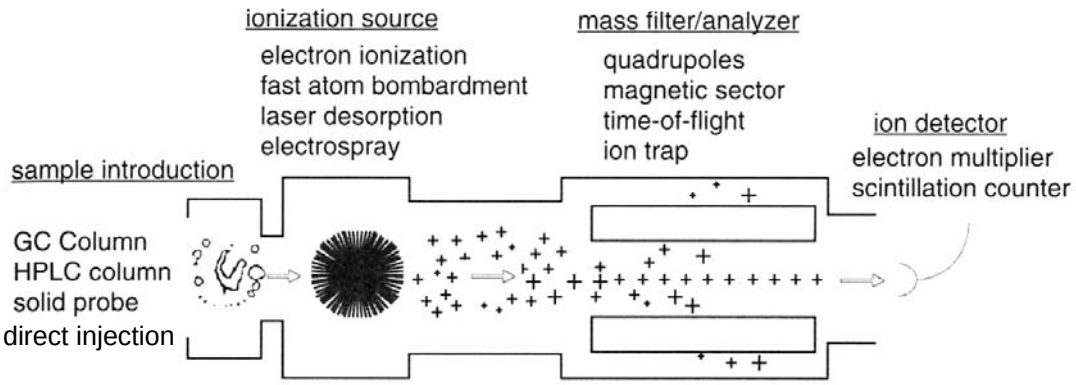


Different variants of ***1-4*** *available commercially.*

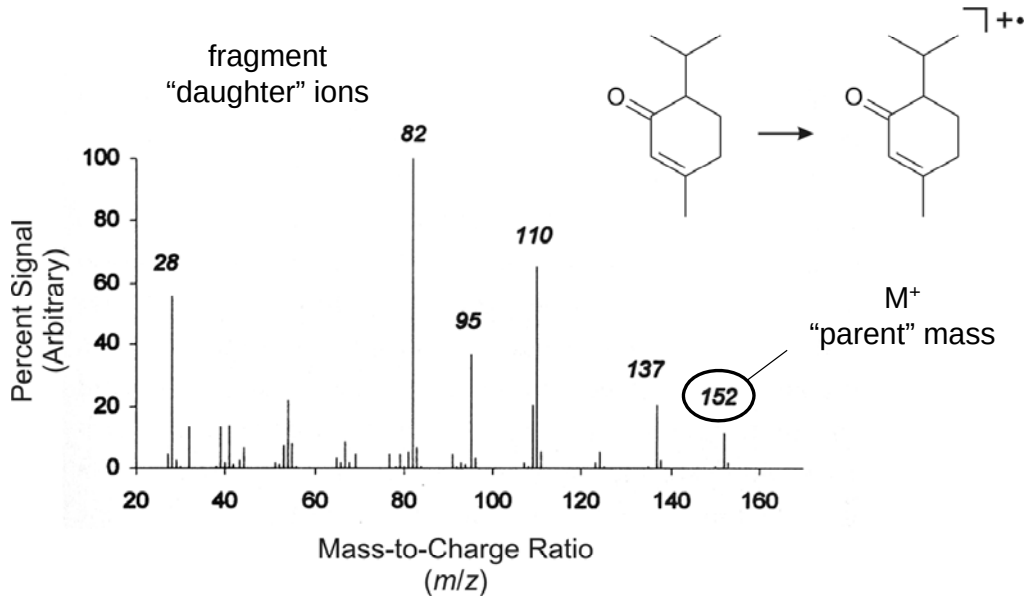
(Selection nearly always based on different flight of ion though vacuum.)

General Components of a Mass Spectrometer

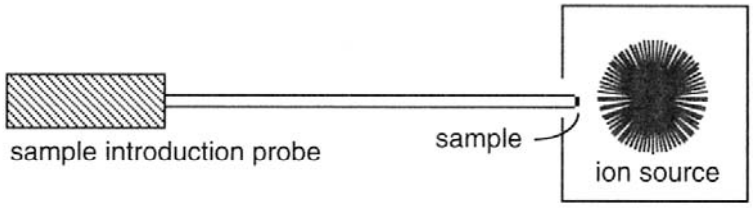
Lots of choices, which can be mixed and matched.



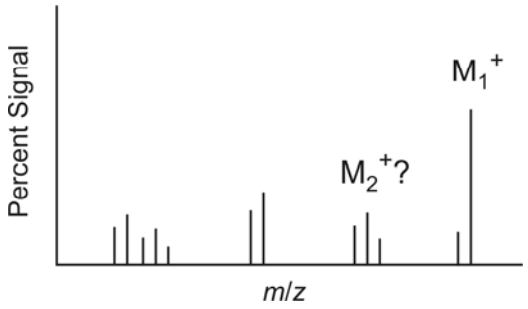
The Mass Spectrum



Sample Introduction: Direct Insertion Probe



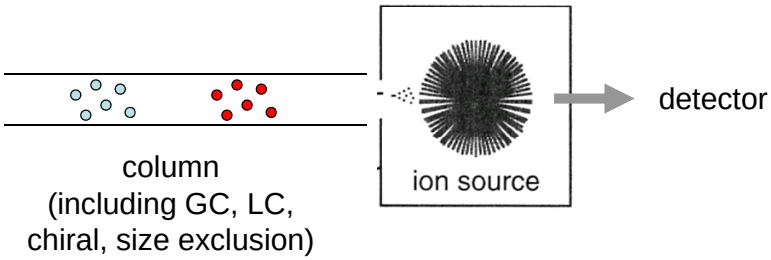
If sample is a liquid, sample can also be injected directly into ionization region.

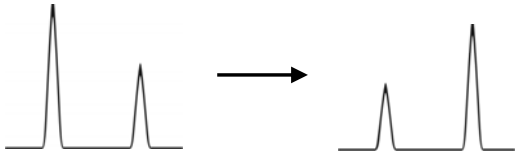


If sample isn't pure, get multiple parents (that can't be distinguished from fragments).

Capillary Column Introduction

Continous source of molecules to spectrometer.





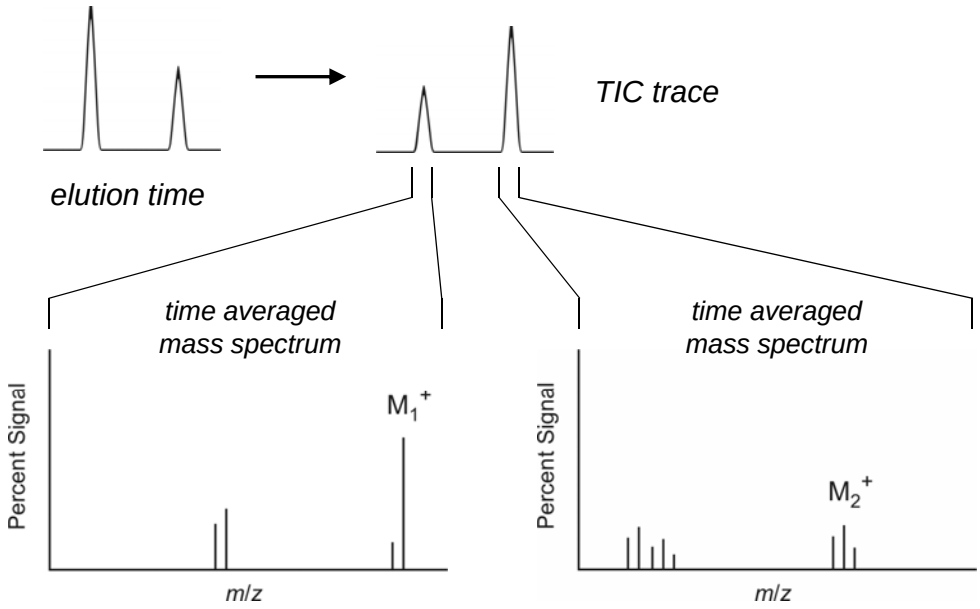
elution time

total ion current (TIC) over time

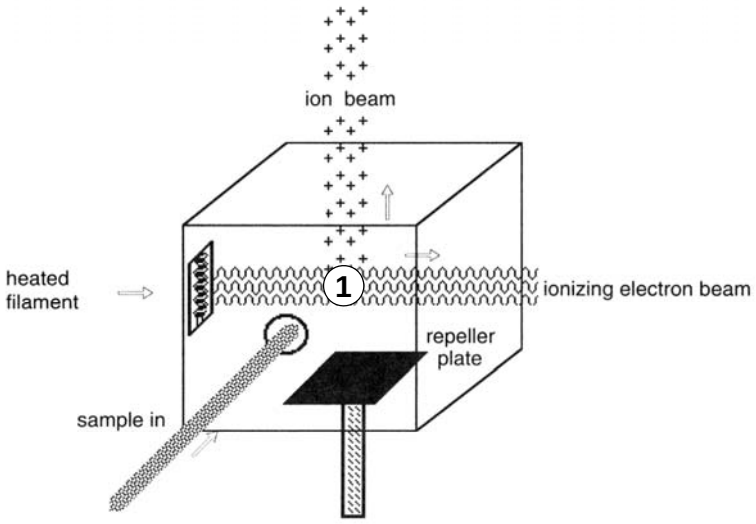
- Signal intensity depends on both amount of molecule and ionization efficiency
- To use quantitatively, must calibrate peaks with respect to quantity eluted

Capillary Column Introduction

Easy to interface with gas or liquid chromatography.

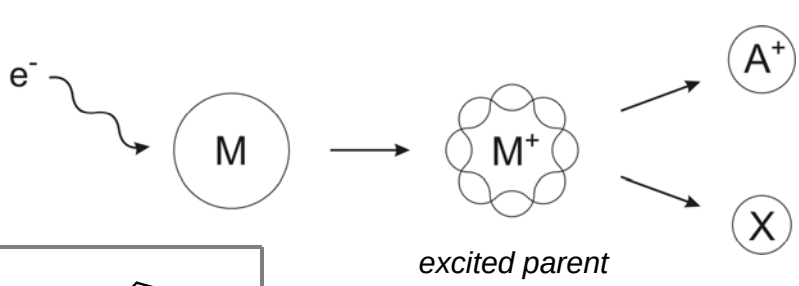


Methods of Ionization: Electron Ionization (EI)



① $M + e^- (kV\ energy) \longrightarrow M^+ + 2e^-$

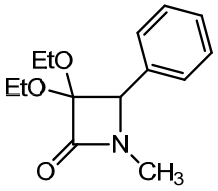
Fragmentation in Electron Ionization



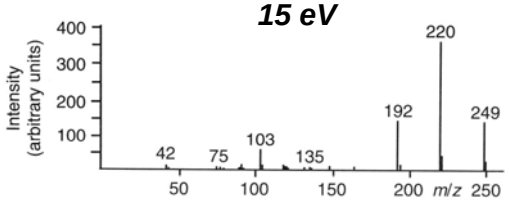
daughter ion (observed in spectrum)

neutral fragment (not observed)

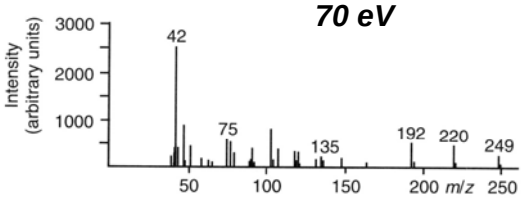
excited parent



at electron energy of ***15 eV***



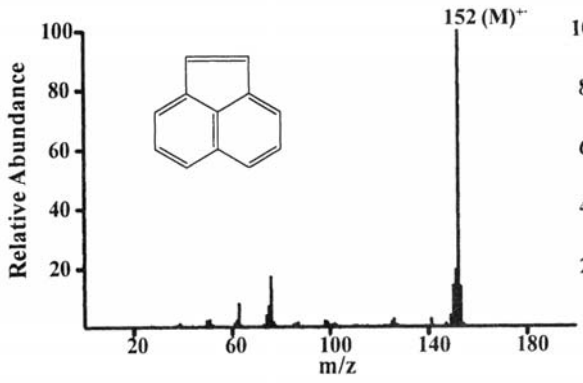
at electron energy of ***70 eV***



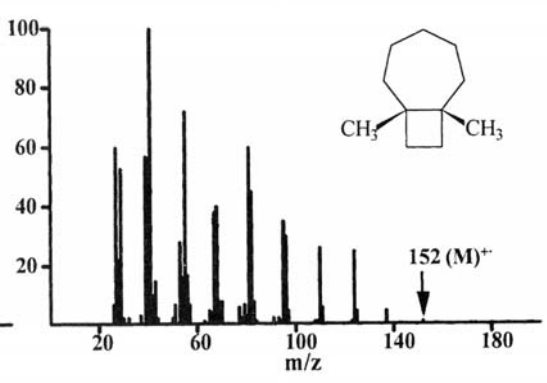
Lower electron energy yields less fragmentation, but also less signal.

Fragmentation in Electron Ionization

Degree of fragmentation in EI depends on electron energy and on molecular structure.



Little fragmentation, parent strong



Lots of fragmentation, parent nearly invisible

Electron Ionization Pros and Cons

EI Advantages

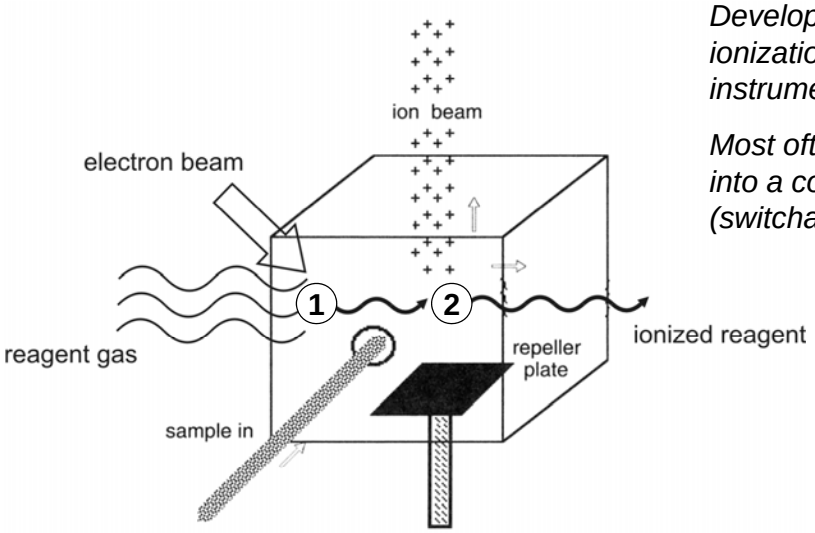
- Well-established technique.
- Fragmentation pattern gives structural information.
- Databases available for pattern identification.

EI Disadvantages

- Sample must be volatile.
- Parent molecular ion sometimes not observed (due to fragmentation).

Requires vacuum in ionization region.
Integrates well with gas chromatography (GC-MS).

Chemical Ionization (CI)



Developed as a milder ionization method for EI instruments.

Most often, integrated into a combined EI/CI (switchable) source.

(1) Electron beam generates proton donor.

(2) Proton donor protonates sample.

Chemical Ionization (CI)

CI reagent is formed via EI.

1 Electron beam generates proton donor (via EI of reagent gas).

$$CH_4 + e^- \text{(kV energy)} \longrightarrow CH_4^{+\bullet} + 2e^-$$

$$CH_4^{+\bullet} + CH_4 \longrightarrow CH_3^{\bullet} + \boxed{CH_5^+}$$ *proton donor*

or

$$NH_3 + e^- \text{(kV energy)} \longrightarrow NH_3^{+\bullet} + 2e^-$$

$$NH_3^{+\bullet} + NH_3 \longrightarrow NH_2^{\bullet} + \boxed{NH_4^+}$$ *proton donor*

2 Proton donor protonates sample.

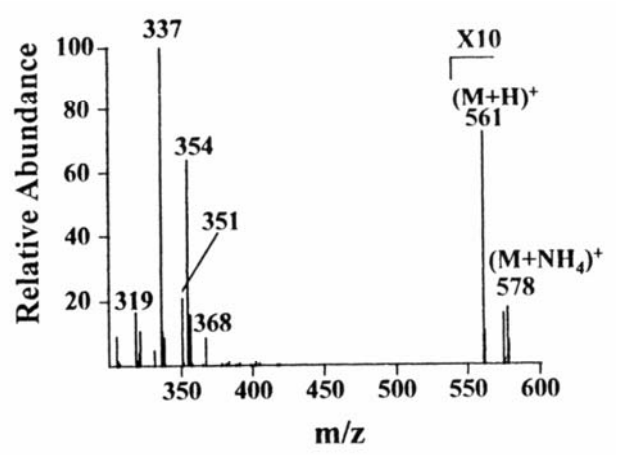
$$M + XH^+ \longrightarrow \underbrace{MH^+}_{\text{parent mass +1}} + X$$

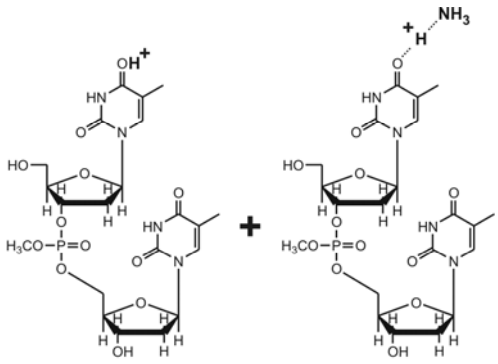
So, CI ion masses are 1 amu higher than molecular mass.

Chemical Ionization (CI)

occasionally, also

2 $$M + NH_4^+ \longrightarrow \underbrace{M{\bullet}NH_4^+}_{\text{parent mass +18}}$$





Chemical Ionization Pros and Cons

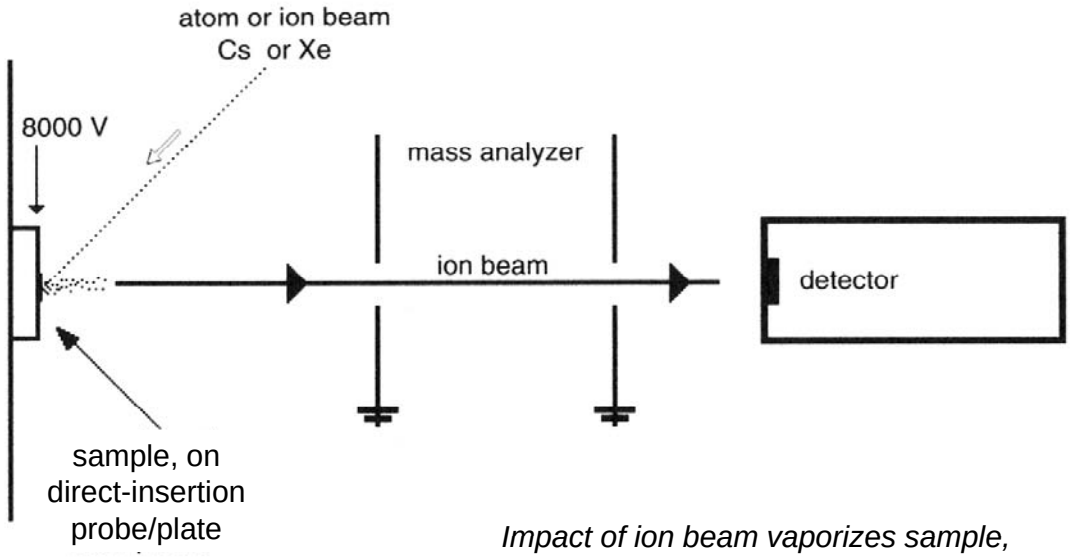
CI Advantages

- Milder ionization than EI; reduces fragmentation.
- Requires little to no additional equipment over EI.

CI Disadvantages

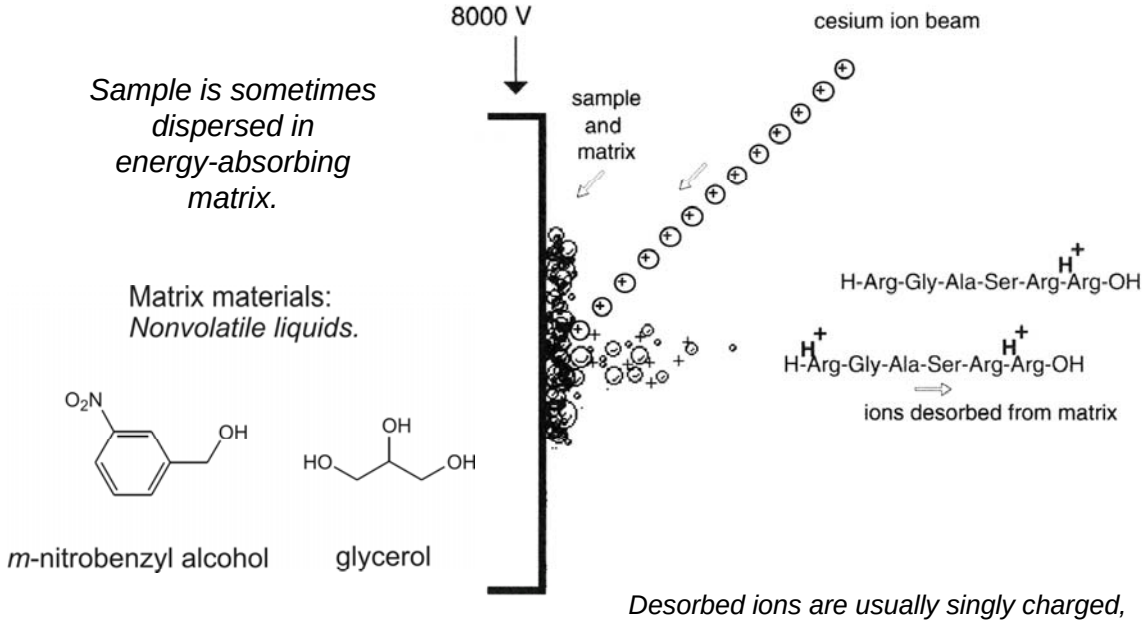
- Molecule must have a Lewis-basic or -acidic functional group.
- More external upkeep and cost (gas cylinders).

Fast Atom Bombardment (FAB) Ionization



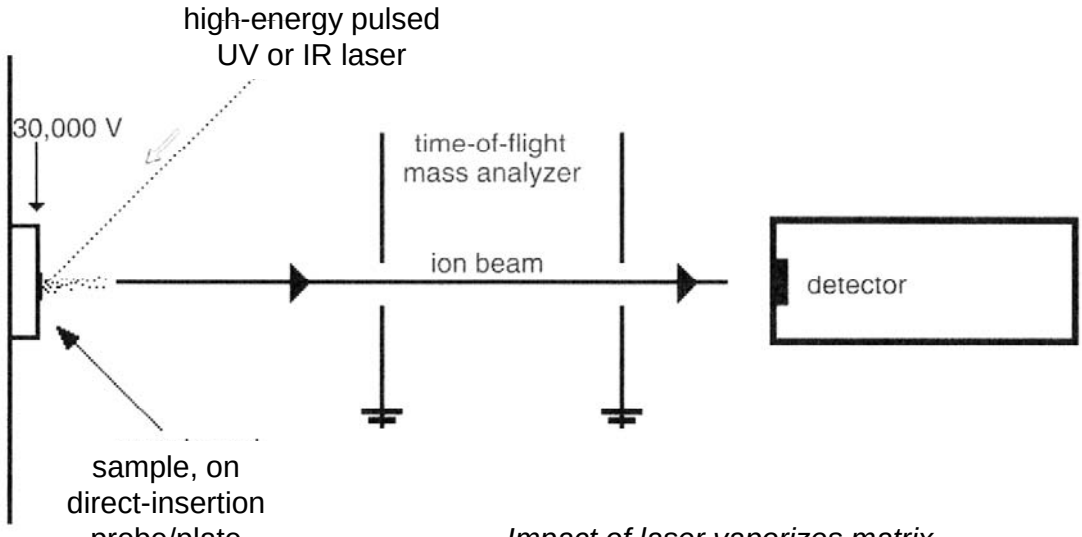
Impact of ion beam vaporizes sample, forces into mass analyzer region.

Fast Atom Bombardment (FAB) Ionization



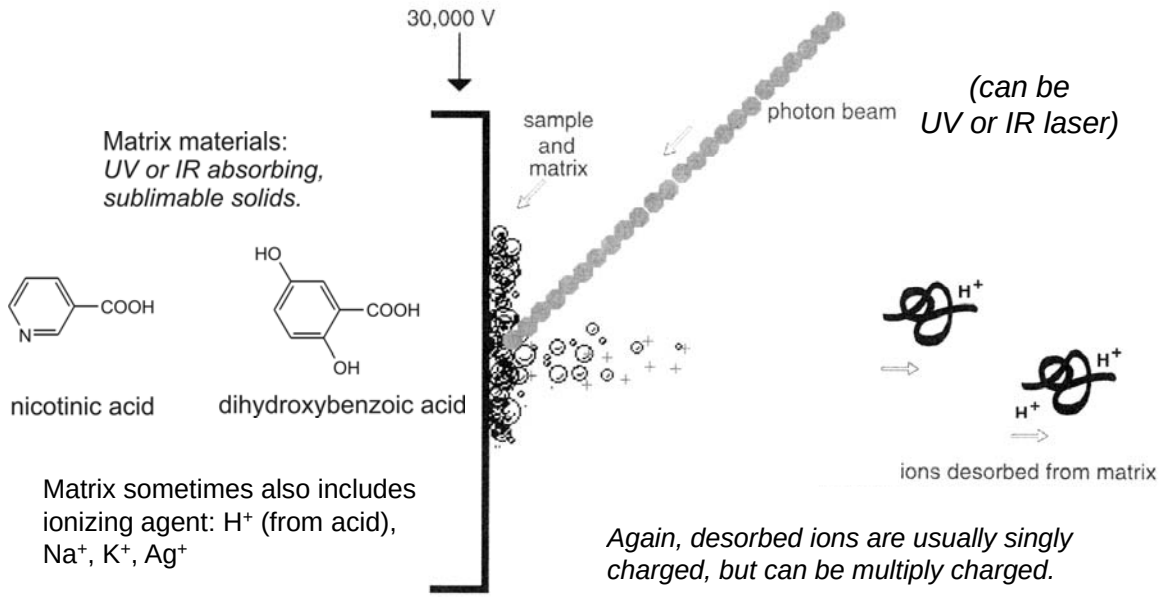
Desorbed ions are usually singly charged, but can be multiply charged.

Matrix-Assisted Laser Desorption Ionization (MALDI)



Impact of laser vaporizes matrix, which carries some analyte with it.

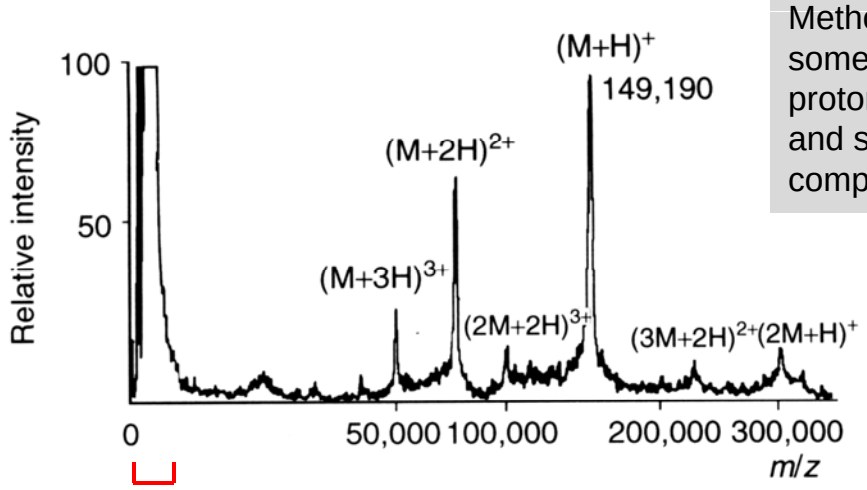
Matrix-Assisted Laser Desorption Ionization (MALDI)



Again, desorbed ions are usually singly charged, but can be multiply charged.

Very mild vaporization/ionization method.

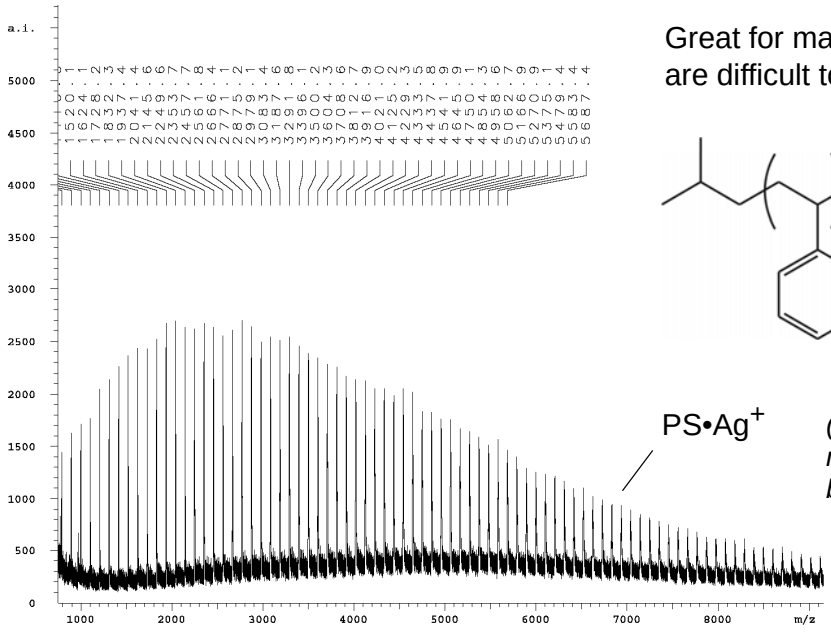
Matrix-Assisted Laser Desorption Ionization (MALDI)



Method produces some multiply protonated ions, and some ion complexes.

matrix material; blankets out m/z <350

Matrix-Assisted Laser Desorption Ionization (MALDI)



Great for macromolecules that are difficult to vaporize.

polystyrene (PS)

n = 10 - 60

PS•Ag^+

(Ag^+ works well with molecules without Lewis basic sites.)

Castro Laicer