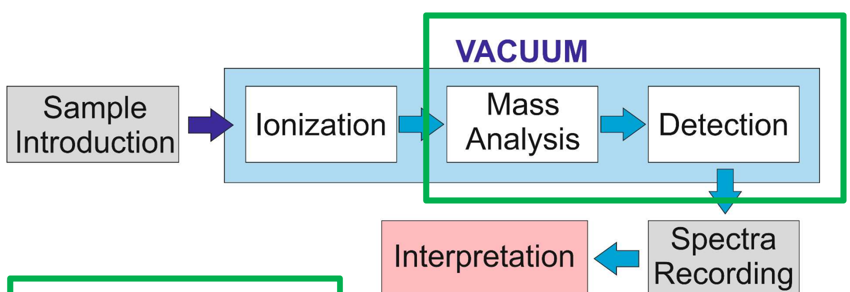
Mass analyzers

Literature: Jürgen H. Gross: Mass Spectrometry

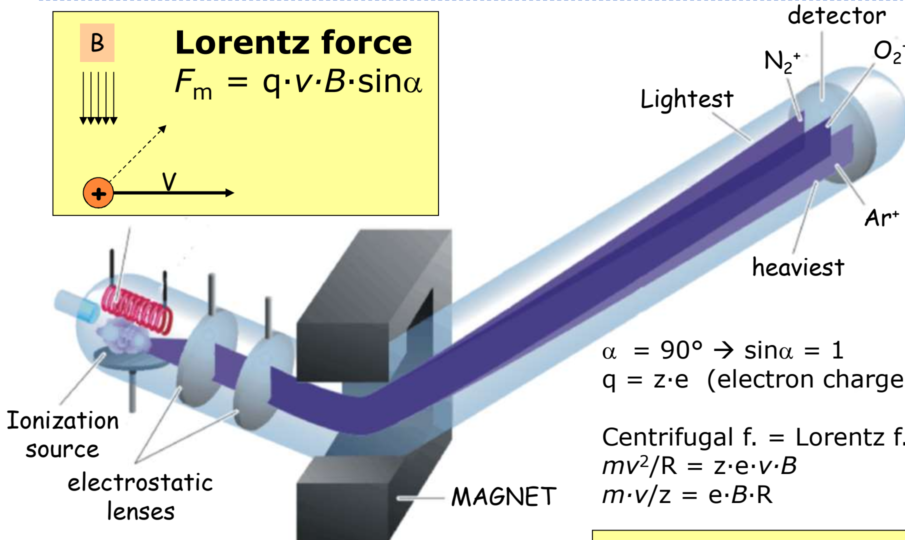
Mass Analyzers



- Magnetic analyzer
- Electrostatic analyzer
- Time-of-flight analyzer
- Quadrupoles
- Quadrupolar traps
- High resolution analyzers – ICR, Orbitrap
- Detection

Magnetic field

Lorentz force
$F_m = q \cdot v \cdot B \cdot \sin\alpha$

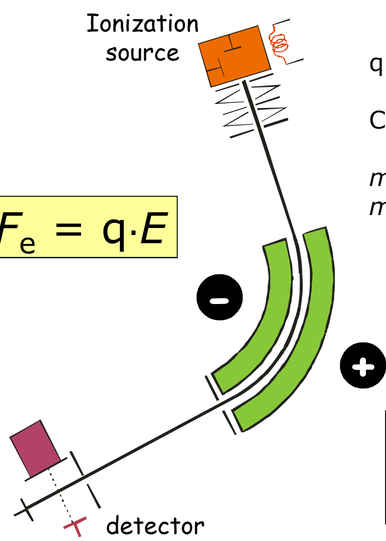


$\alpha = 90° \rightarrow \sin\alpha = 1$
$q = z \cdot e$ (electron charge)

Centrifugal f. = Lorentz f.
$mv^2/R = z \cdot e \cdot v \cdot B$
$m \cdot v/z = e \cdot B \cdot R$

$$mv/z = \text{const.}$$

Electrostatic field



$q = z \cdot e$ (electron charge)

Centrifugal f. = Electrostatic f.

$m \cdot v^2/R = z \cdot e \cdot E$
$m \cdot v^2/z = e \cdot E \cdot R$

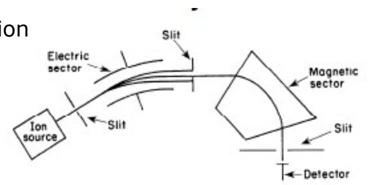
$$F_e = q \cdot E$$

$$mv^2/z = \text{const.}$$
$$2E_k/z = \text{const.}$$

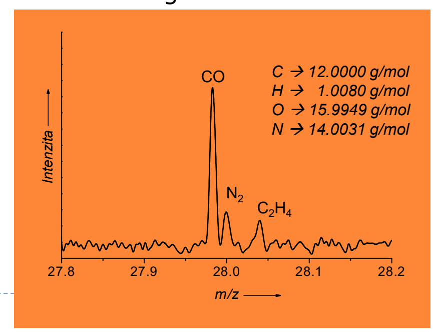
Double-focusing analyzers

- Electrostatic analyzer reduces E_k distribution
  → $2E_k/z$ = const.
- Magnetic analyzer filters m/z

$$R = \frac{mv}{qB} = \frac{\sqrt{2mE_k}}{qB}$$

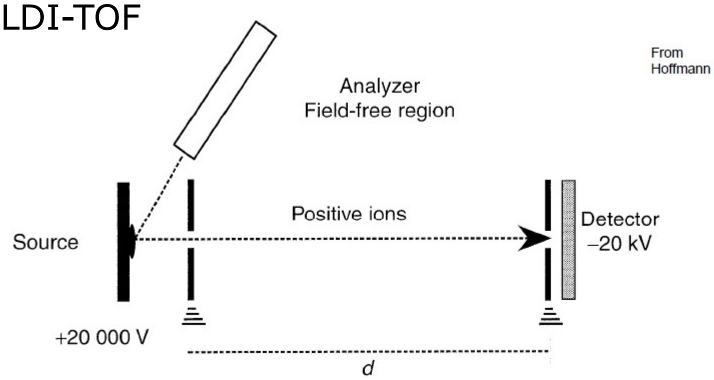


High resolution



Time-of-flight (TOF) analyzers

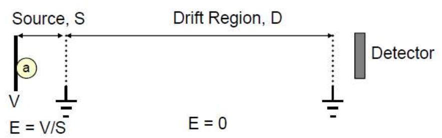
- MALDI-TOF



MALDI produces cations that are accelerated towards the analyzer
→ cations fly in a field-free region – time of flight depends on their m/z

Time-of-flight (TOF) analyzers

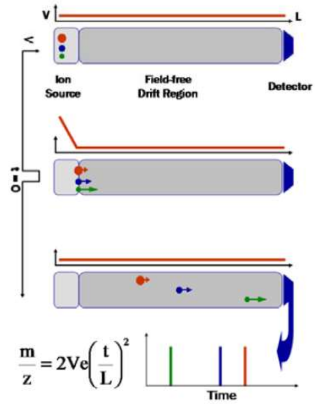
- Ions accelerated by a known potential
- Known flying distance



$$E_k = \frac{1}{2}mv^2 = qV$$

$$zeV = \frac{1}{2}m\frac{x^2}{t^2}$$

$$\frac{m}{z} = 2Ve\left(\frac{t}{x}\right)^2 = Kt^2$$

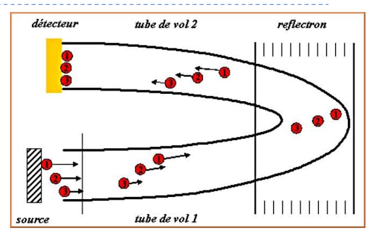


- Important factors:
  - All ions measured simultaneously → faster spectra scanning
  - Time resolution
  - "Infinite" range of masses
  - cheap

TOF renaissance

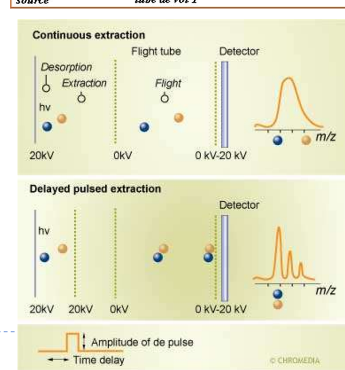
- Reflectrons
  - Series of electrodes creating a linear field with an opposite sign to the initial accelerating field
  - Ions are decelerated and turned to the opposite direction
  - Constructed so that ions are focused to the plane of the detector

  → Ions with <u>different kinetic energy, but the same m/z</u>, fly a different distance → In the end, they have <u>the same time of flight</u>

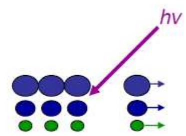


- Delayed pulsed extraction
  - Extraction of the ions is delayed by 200 – 500 ns
  - During the delay, faster ions move closer to the extraction electrode than the slower ones
    → extraction pulse accelerates the faster ions shorter time → final velocities are similar

  <u>→ Initial distribution of velocities is corrected → the same time of flight</u>

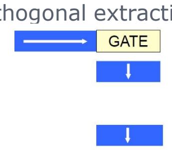


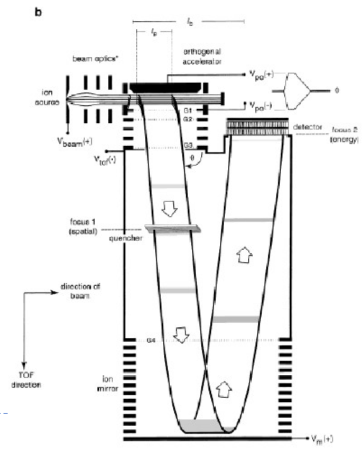
Using TOF analyzers



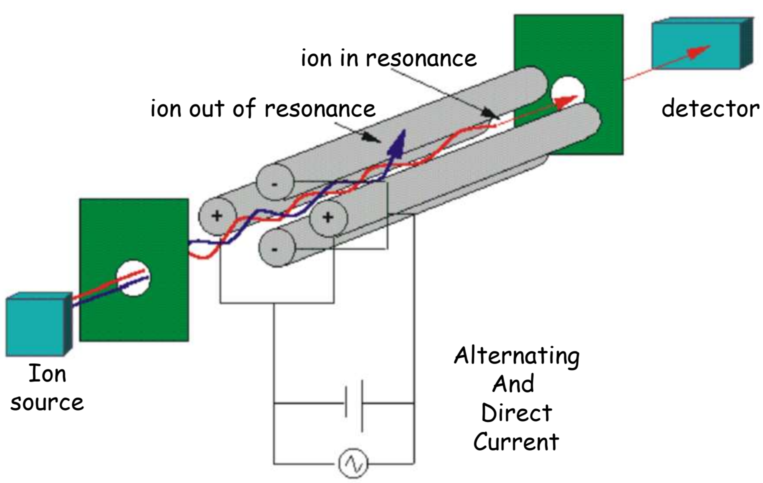
Laser Desorption: Static, solid sample probed with a pulsed laser

- TOF is an ideal detector for pulse-ionization methods such as MALDI
- For continuous ionization sources (EI, ESI, etc.) most of the ions are lost with TOF analysis
  - Shorter time of flight → decreasing of the mass range and resolution
  - Orthogonal extraction

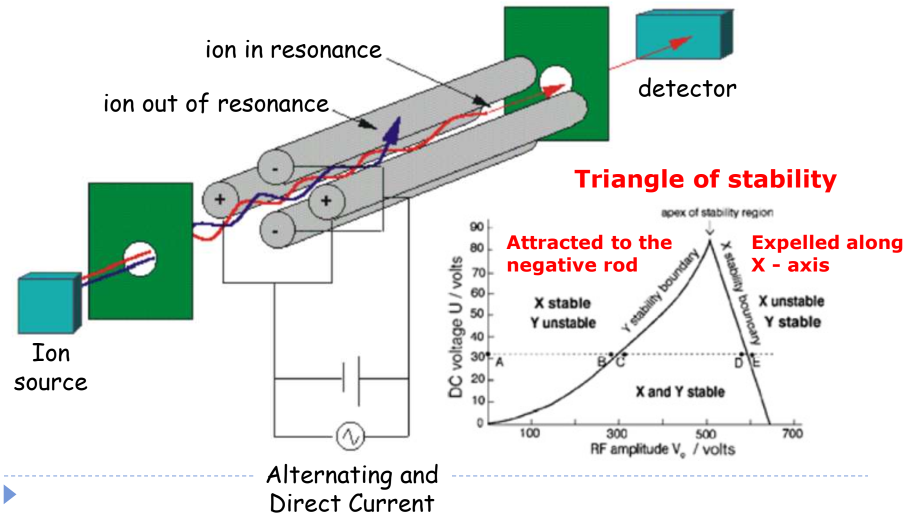




Mass selection using quadrupole

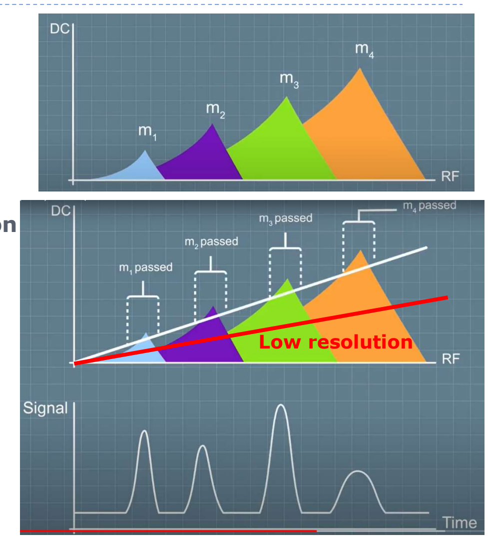


Mass selection using quadrupole



Quadrupole as mass analyzer

- Scanning along the line → **the ratio U/V_0 is kept constant**
- Maximum *m/z* ~ 4000
- Resolution ~ 3000
  - Usually used with **unit resolution**
- Small, light, cheap
- Coupling with chromatography



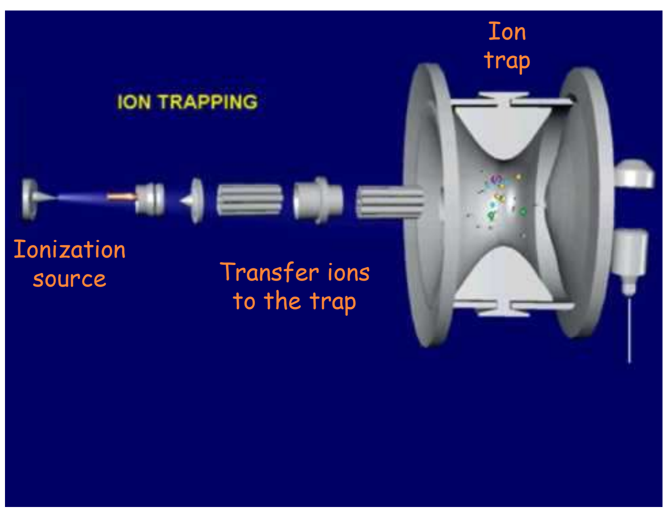
See also: https://www.youtube.com/watch?v=6_mavZ_WKoU

TOF vs. quadrupole

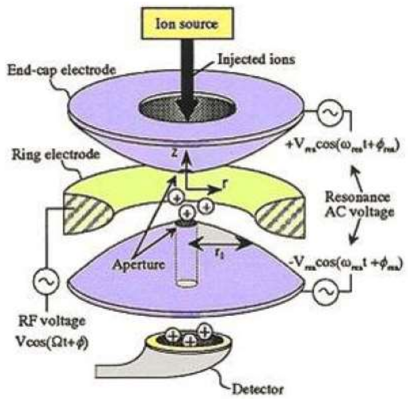
- **TOF analyzers**
  - Ions are in packets **pulsed** to the analyzer
  - All ions (all *m/z*) from the packet are analyzed simultaneously
  - *m/z* determined from dispersion of the ions in time
  - Based on static, DC field

- **Quadrupoles**
  - **Continuous** inlet of the ions
  - Only ions with specific *m/z* reach the detector
  - *m/z* determined by sequential filtering of ions
  - Based on time-dependent alternating field

Ion trap

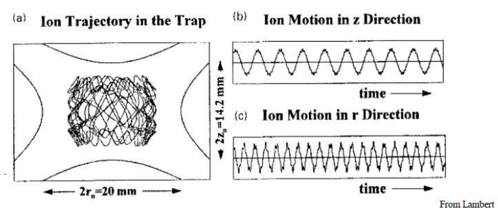


Quadrupole ion traps



- Fundamental RF at the ring electrode
  - Fixed frequency (1,1 MHz), Variable amplitude (do 7 kV)
- AC: voltage with fixed frequency at the end-cap electrodes
  - Resonance excitation for ejection or fragmentation
- Helium pressure ~1 mTorr

RF field induces oscilations along r and z axis



Stability diagram

- Stability of ion trajectories affected by combination of AC and DC → mostly DC is set to zero
- For zero DC, stability given by q_Z:

$$q_Z = \frac{8ezV}{m(r_0^2 + 2z_0^2)(2\pi\upsilon)^2}$$

- Stable trajectories up to q_Z = 0.908

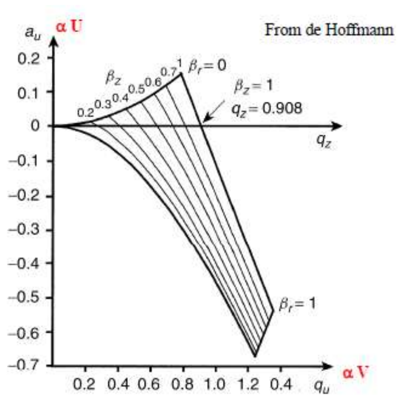


Figure 2.16
Typical stability diagram for a quadrupole ion trap. The value at $\beta_z = 1$ along the q_z axis is $q_z = 0.908$. At the upper apex, $a_z = 0.149998$ and $q_z = 0.780909$. (Data from Ref.12)

Ejection of ions

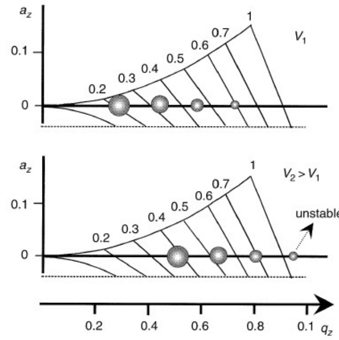


Figure 2.20
At a fixed value of the RF potential V applied to the ring electrode, heavier ions will have lower β_z values and thus lower secular frequencies. If V is increased, β_z values increase for all the ions, as do the secular frequencies. In the example given, the lightest ion now has a β_z value larger than unity and is thus expelled from the trap. The highest mass that can be analyzed depends on the limit V value that can be applied: around 7000–8000 V from zero to peak. For a trap having $r_0 = 1$ cm and operating at a ν frequency of 1.1 MHz, the highest detectable mass-to-charge ratio is about 650 Th

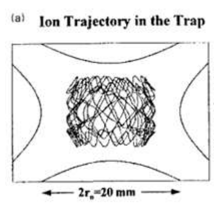
$$q_Z = \frac{8ezV}{m(r_0^2 + 2z_0^2)(2\pi\upsilon)^2}$$

- With increasing V → larger and larger *m/z* beyond q_Z = 0.908
- Pressure determines the highest V (discharges) – usually ~2000 D

Secular frequency

- Ions oscillate at secular frequency *f* that is smaller than ν
- Along *z* axis, f_z is proportional to q_z
- If RF with frequency f_z is applied to the end-cap electrodes, ions with secular frequency f_z will be in resonance and amplitude of their oscillation along the z axis will increase

→ for sufficiently large amplitudes are ions expelled
→ collisions with helium (use for fragmentation of the excited ions)

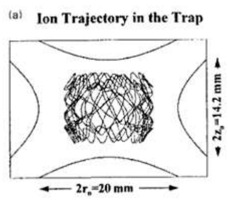


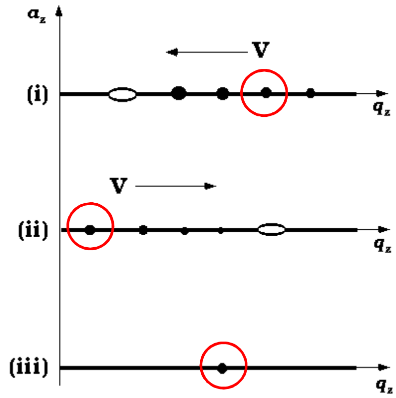
$$q_Z = \frac{8ezV}{m(r_0^2 + 2z_0^2)(2\pi\upsilon)^2}$$

Mass selection

- Apply AC field to the end cap electrodes
  → point of instability (for given f_z)

- Scan amplitude of fundamental RF
  - Scan downwards → ejection of all heavier ions
  - Scan upwards → ejection of all lighter ions





$$q_Z = \frac{8ezV}{m(r_0^2 + 2z_0^2)(2\pi\upsilon)^2}$$

MS/MS

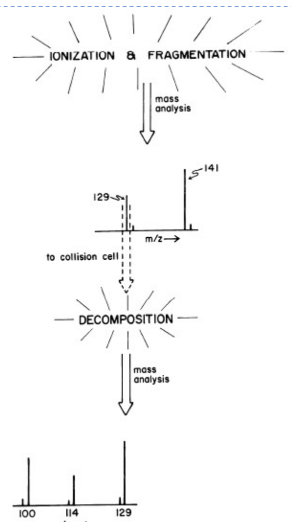


FIG. 5.1. Conceptual representation of the technique of MS/MS. In this case, ions of *m/z* 129 are selected by the first mass spectrometer; these ions are directed into a collision chamber, and the decomposition products are analyzed by the second mass spectrometer to produce the product-ion spectrum of *m/z* 129 **(bottom)**.

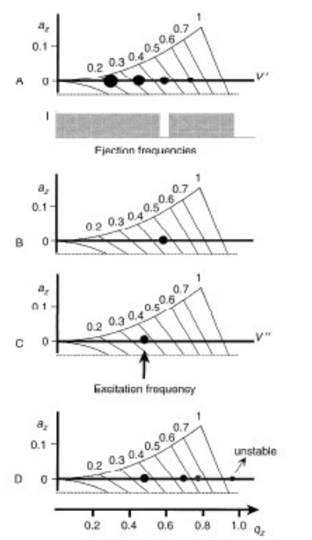
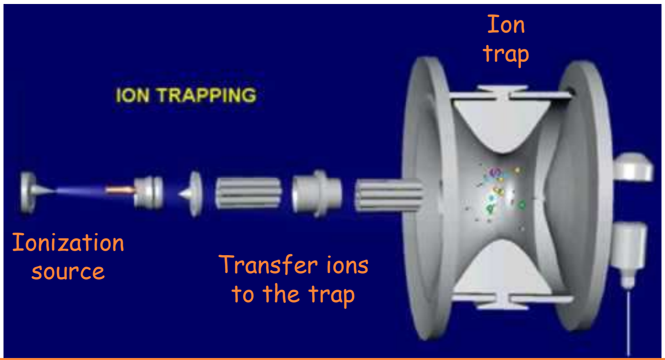


Figure 2.25
One possible sequence of events to produce an MS/MS spectrum. (A) Ions of one mass-to-charge ratio are selected by expelling all the others at their resonance frequency applied to the caps. (B) Only ions of the selected *m/z* are present in the trap. (C) Voltage *V* is adjusted so as to bring the ion in resonance with the excitation frequency applied to the caps. (D) Ions are analyzed by ejection at the stability limit

Ion trap



Ions have complicated pathways with frequency proportional to *m/z*

Ions can be analyzed according to *m/z*

Ions can be mass-selected → up to MS^{12}

Mass-selected ions can be collided with buffer gas and their fragmentations can be studied

Many other ions traps with similar properties

- Linear quadrupole traps
- Higher multipole traps

Summary:

- Magnetic analyzer (*B*)
  - continuous analysis of ions according to their momentum
- Electrostatic analyzer (*E*)
  - continuous analysis of ions according to their kinetic energy
- *B* and *E* combinations
  - double focusing – high resolution
- Time-of-flight analyzer (*TOF*)
  - pulsed analysis of kinetic energy of the ions by measuring the time required for passing a fixed distance
  - Increase of resolution – reflectrons, delayed pulsed extraction → high resolution
- Quadrupoles (*Q*)
  - continuous analysis of ions in an alternating field (combination of DC and RF)
  - usually unit resolution
- Quadrupolar traps
  - pulsed analysis of trapped ions by their sequential ejection
  - mass selection/fragmentation up to 12 times

- See you in the classroom!