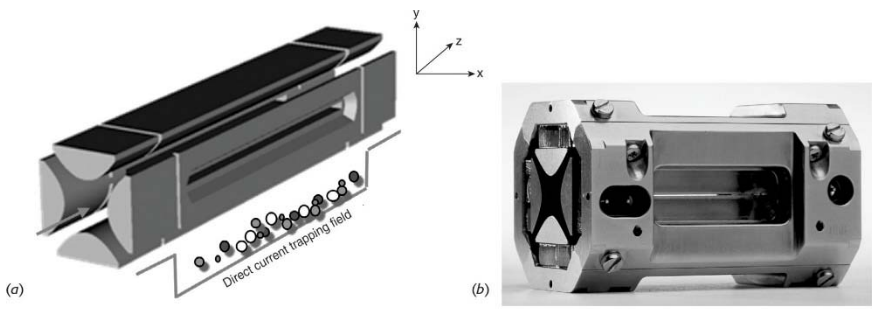
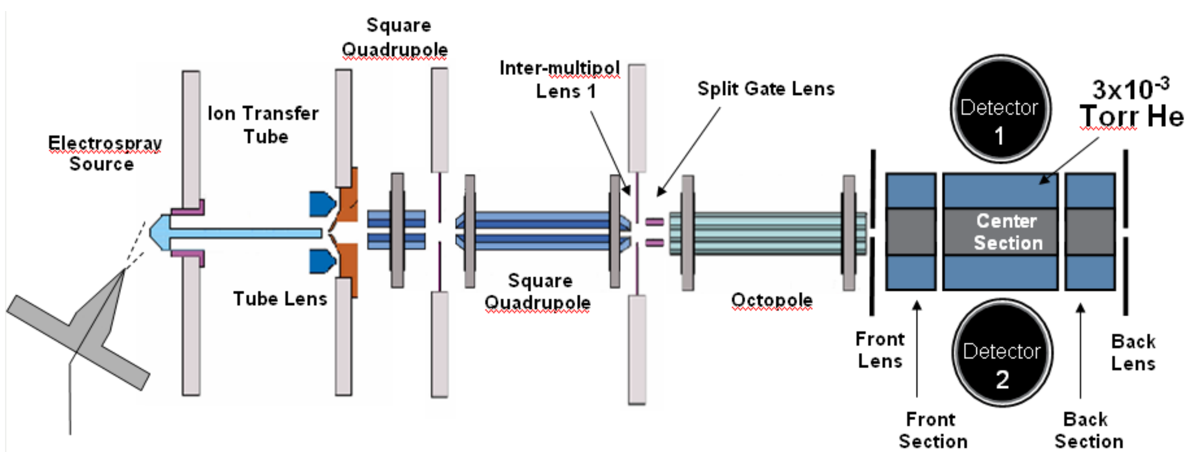
Linear (2-D) ion trap (LIT)

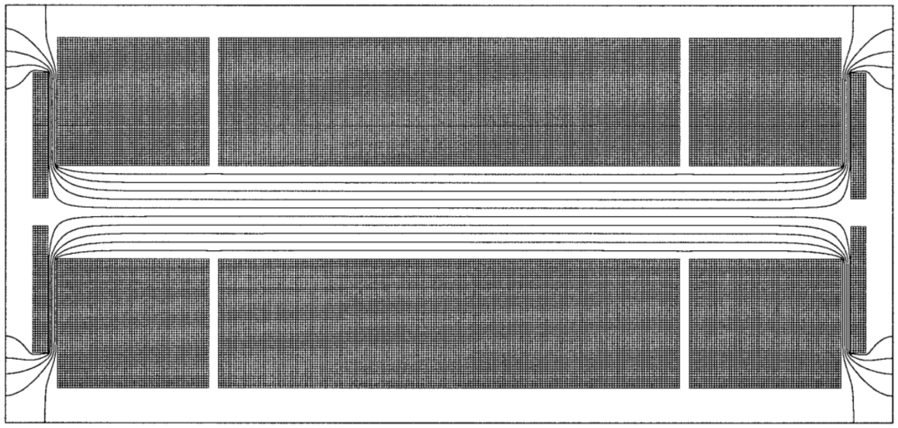


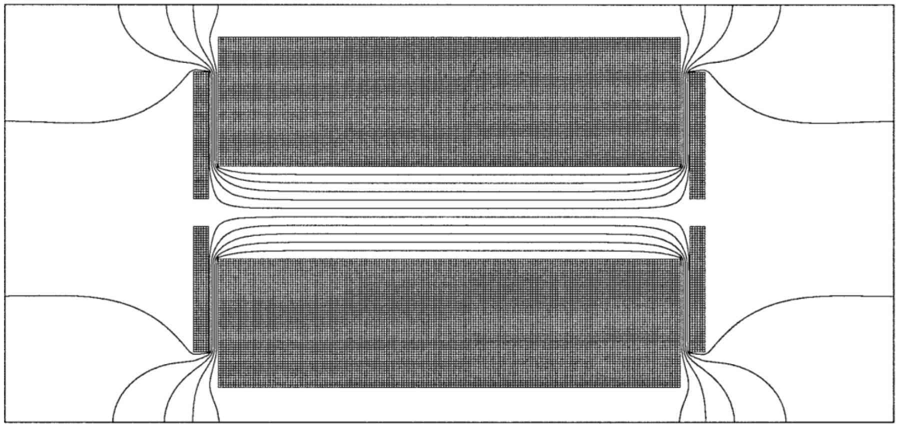
	LTQ	3D Traps	Increase
•Trapping efficiency	~ 55-70%	~5%	~ 11-14x
•Detection efficiency	~ 50-100%	~50%	~ 1-2x
•Trapping capacity	~ 20,000 ions	~500 ions	~ 40x



Characteristics of LIT

- **Higher trapping efficiency** (> 10 X) than 3-D QIT.
  - Less perturbed from fringing fields at the inlet of LIT.
- **Higher storage capacity** (> 30 X) than 3-D QIT.
  - Overcome the space-charge effect.





J. Am. Soc. Mass Spectrom. (2002) **13**, 659

Time-of-flight (TOF) mass analyzer : Working principle

- When formed at the surface of the backing plate, ions are accelerated through the entire source-extraction region to the same final kinetic energy:

$$\frac{mv^2}{2} = zeV$$

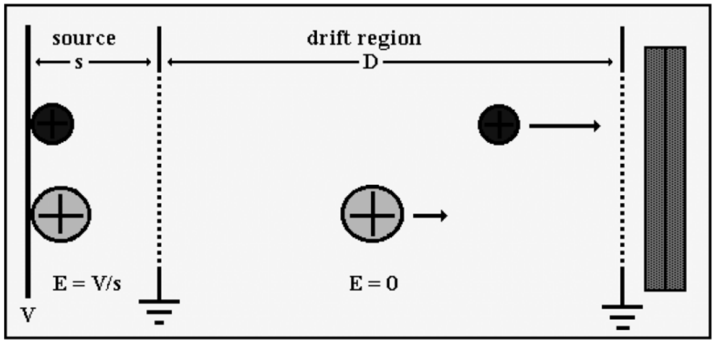
- The extracted ions cross the drift region with velocities (v):

$$v = \left(\frac{2zeV}{m}\right)^{1/2}$$

- From $D = vt$, the flight times of ions (t):

$$t = \left(\frac{m}{2zeV}\right)^{1/2} D$$

  - Thus, the **flight times** of ions depend on the **square root** of their *mass to charge ratios*.



Linear ToF mass spectrometer

s: Short source region with a high electric field (E).

D: Longer field-free drift region ($E = 0$).

Mass resolution

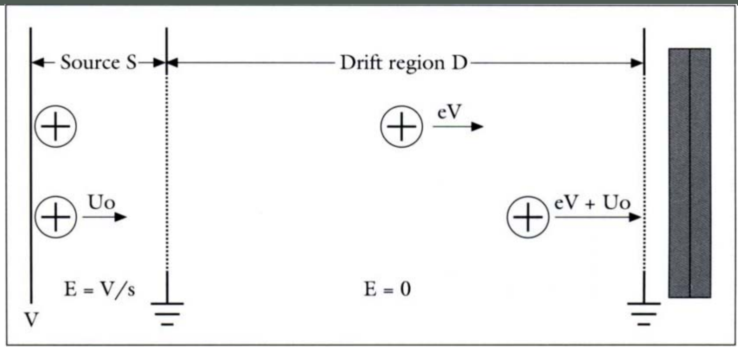
$$\frac{m}{\Delta m} = \frac{t}{2\Delta t}$$

R.J. Cotter, *Time-of-Flight Mass Spectrometry* (1997)

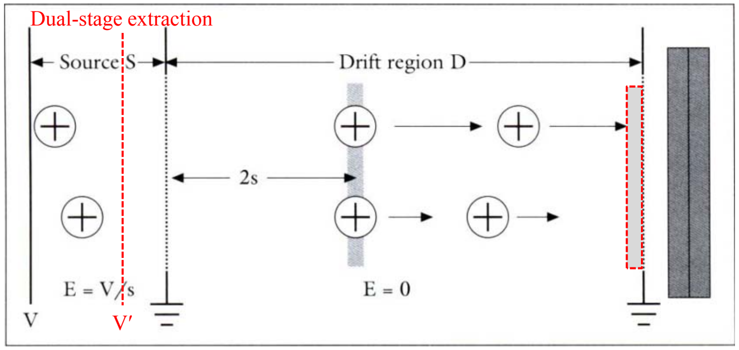
Initial kinetic energy & Spatial distributions of ions

- Mass resolution is reduced by the **spread** in **initial ion kinetic energy** (U_0) prior to acceleration.
  - How is it improved?
  - (a) High accelerating voltage
  - (b) Reflectron
- Mass resolution is reduced by the **spread** in **initial positions** of the ions in the ion source.
  - **Space-focus plane (@ 2s)**: A *focal point* in the drift region at which faster ions formed toward the rear of the source catch up with slower ions formed near the front of the source.
  - How is it improved?
  - (a) Dual-stage extraction to move the *space-focus plane*.
  - (b) Reflectron

R.J. Cotter, *Time-of-Flight Mass Spectrometry* (1997)



Two ions with different initial kinetic energies

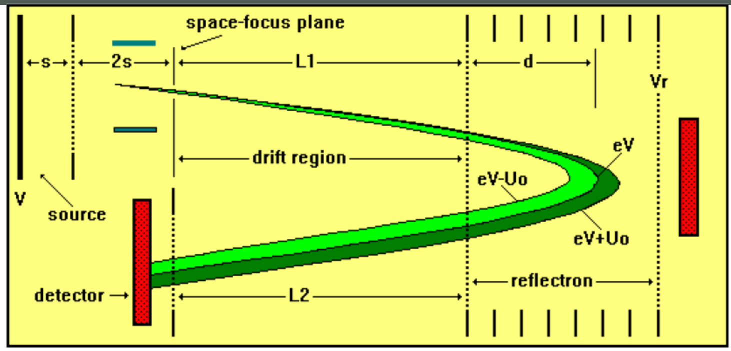


Two ions formed in different locations

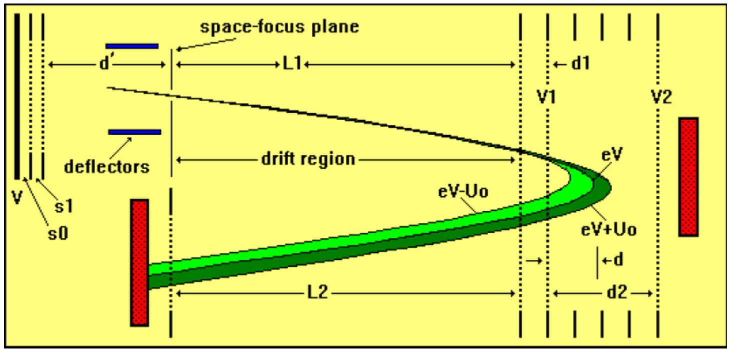
Reflectron (Ion mirror)

- **Single-stage reflectron**: Utilizes only a single retarding/reflecting field.
  - Set the voltage (V_r) at the back of the reflectron to some value greater than the initial accelerating voltage (V) at the source backing plate: $V_r > V$.
  - **Penetration depth** (d): The distance at which the ions turn around from the entrance of the reflectron.
  - Reflected ions reach a *new space-focus plane* at the grid in front of the detector.
- **Dual-stage reflectron**: Two linear retarding voltage (constant field) regions, separated by an extra grid.
  - Provides *second-order* energy correction.

R.J. Cotter, *Time-of-Flight Mass Spectrometry* (1997)



Single-stage ion extraction & single-stage reflectron



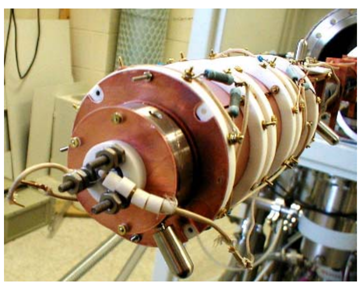
Dual-stage ion extraction & dual-stage reflectron

Characteristics of TOF

Benefits	Limitations
Fastest MS analyzer (μs order of acquisition time)	Requires pulsed ionization method or ion beam switching
High ion transmission	Fast digitizers used in TOF can have limited dynamic range
Highest practical mass range of all MS analyzers	Limited precursor-ion selectivity for most MS/MS experiments
MS/MS information from post-source decay	
Well suited for pulsed ionization methods	

Applications
Almost all MALDI systems
Very fast GC/MS systems

Fourier Transform (FT) Spectrometers
: Ion cyclotron resonance (ICR)



Fourier Transform (FT) Spectrometers
: Ion cyclotron resonance (ICR)

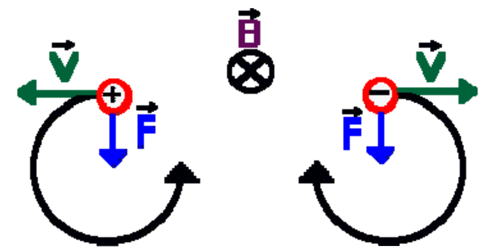
- It is a form of **ion trap**, but one in which "ion cyclotron resonance (**ICR**)" occurs.

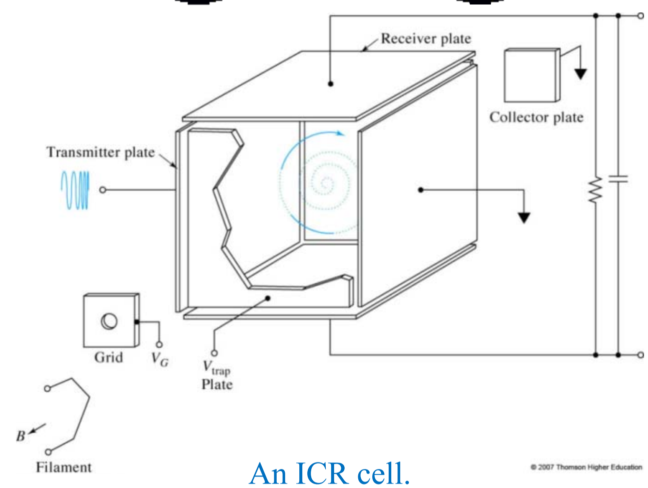
- When an ion travels through a strong magnetic field, it starts *circulating in a plane perpendicular to the field* with an **angular frequency** ω_c:

$$F_M = Bzev \;\&\; F_c = \frac{mv^2}{r} \quad \Rightarrow \quad zeB = \frac{mv}{r}$$

$$f = \frac{v}{2\pi r} \quad \& \quad \omega_c = 2\pi f$$

$$\boxed{\omega_c = \frac{v}{r} = \frac{zeB}{m}}$$

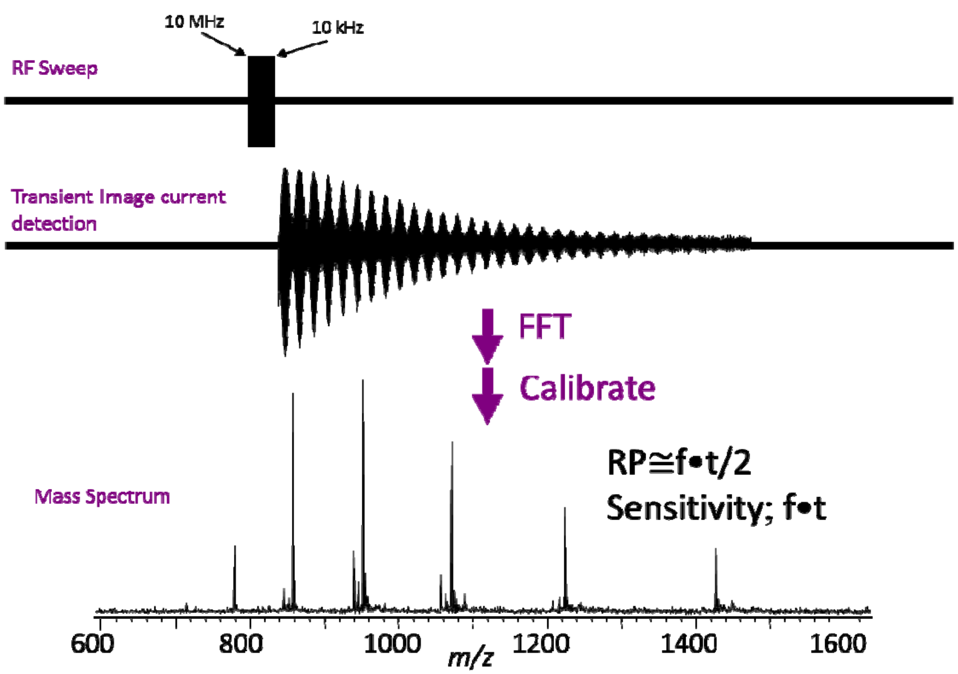


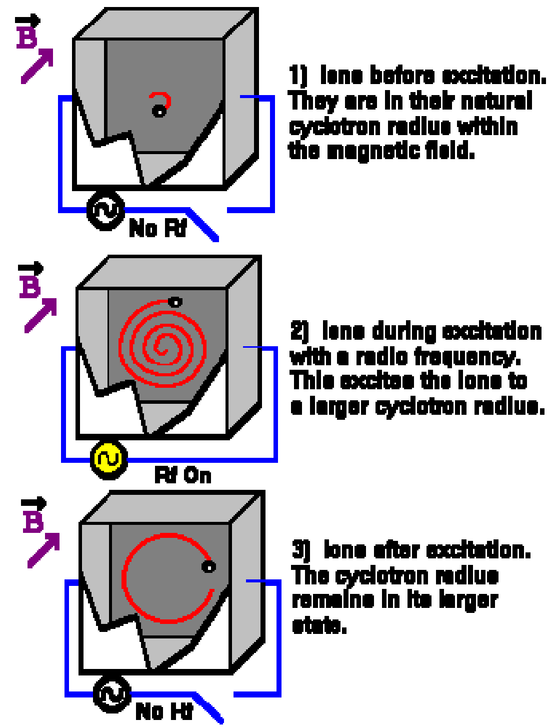


An ICR cell.

D. A. Skoog, et al., *Principles of Instrumental Analysis* **(2007)**

Measurement of the ICR signal : Image current





http://panomics.pnnl.gov/training/tutorials/ft_icr_tutorial.stm

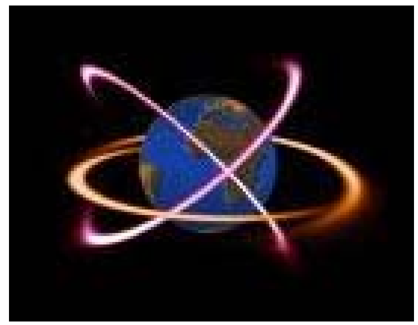
Characteristics of FT-ICR

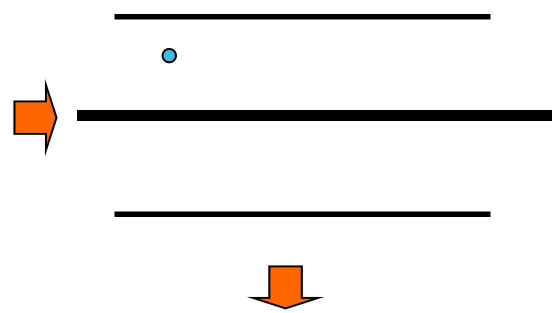
Benefits	Limitations
The highest recorded mass resolution	Limited dynamic range
Powerful for ion chemistry & MS/MS experiments	Strict low-pressure requirements
Well-suited for pulsed ionization methods	Subject to space-charge effects & ion-molecule reactions
Non-destructive ion detection	High cost for purchase & maintenance
Multistage MS (MS^n)	

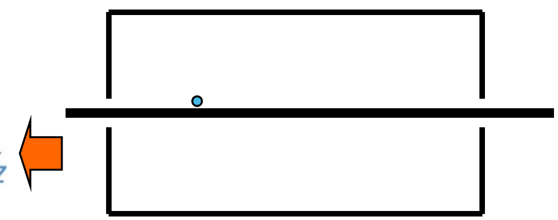
Applications
High-resolution for high-mass analytes
Study ion chemistry

Orbitrap mass spectrometer
: Working principle

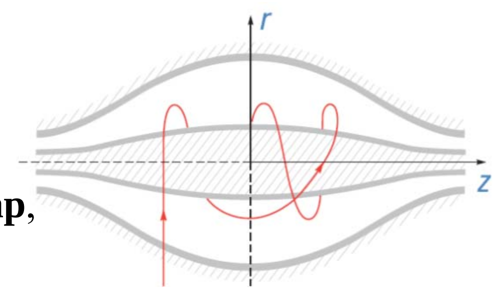
- The **Orbitrap** is an ion trap with *no RF or magnet fields*!
- Moving ions are trapped around an electrode: Electrostatic attraction is compensated by centrifugal force arising from the initial tangential velocity.
- **Potential barriers** created by end-electrodes *confine the ions axially*.
- One can control the frequencies of oscillations (especially the axial ones) by shaping the electrodes appropriately.
- This idea results in an **invention of the orbitrap**, which consists of a *spindle-shaped central electrode* surrounded by a pair of *bell-shaped outer electrodes*.







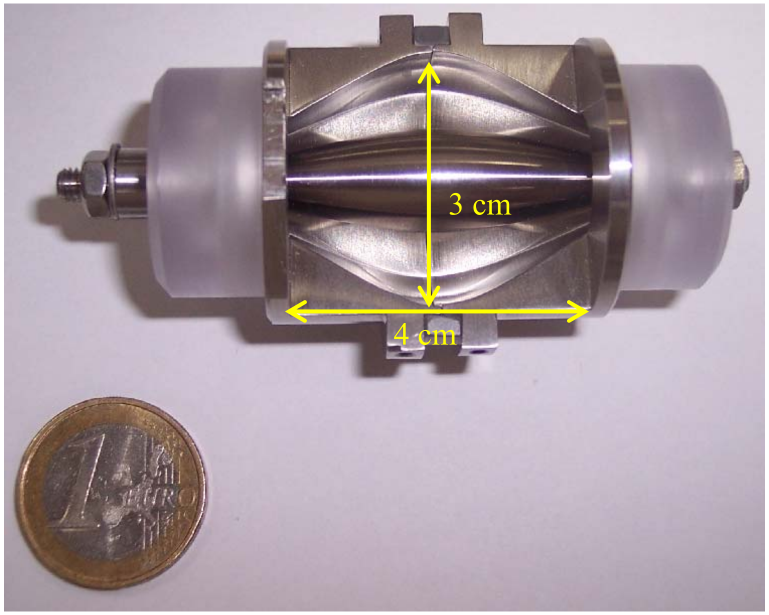
Orbital traps
Kingdon (1923)



www.thermofisher.com

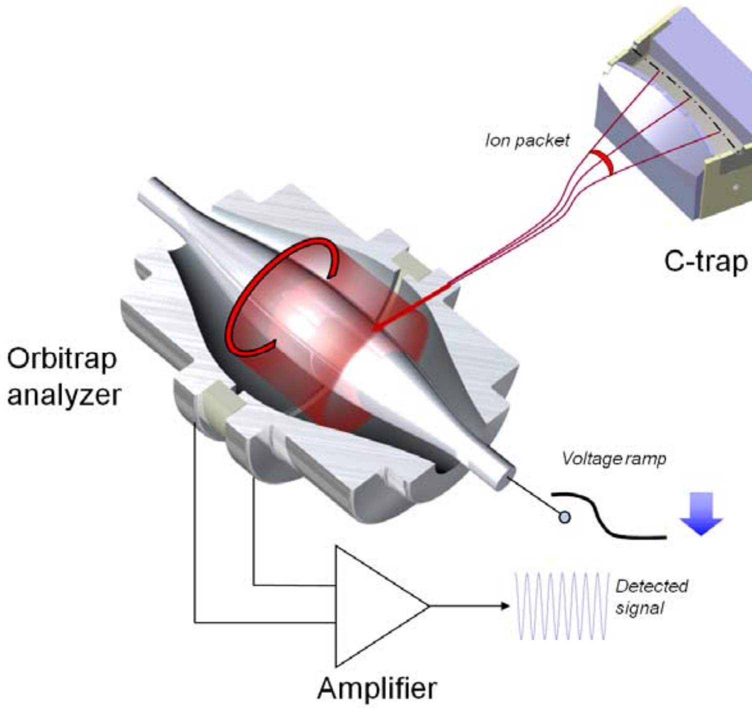
Orbitrap
: Inventor & strumentation

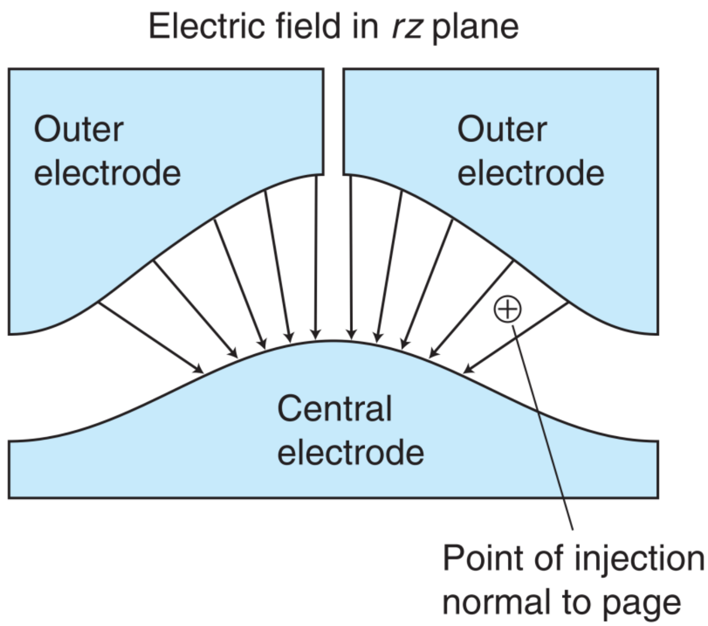
Dr. Alexander Makarov



Shape of orbitrap

Orbitrap
: Instrumentation



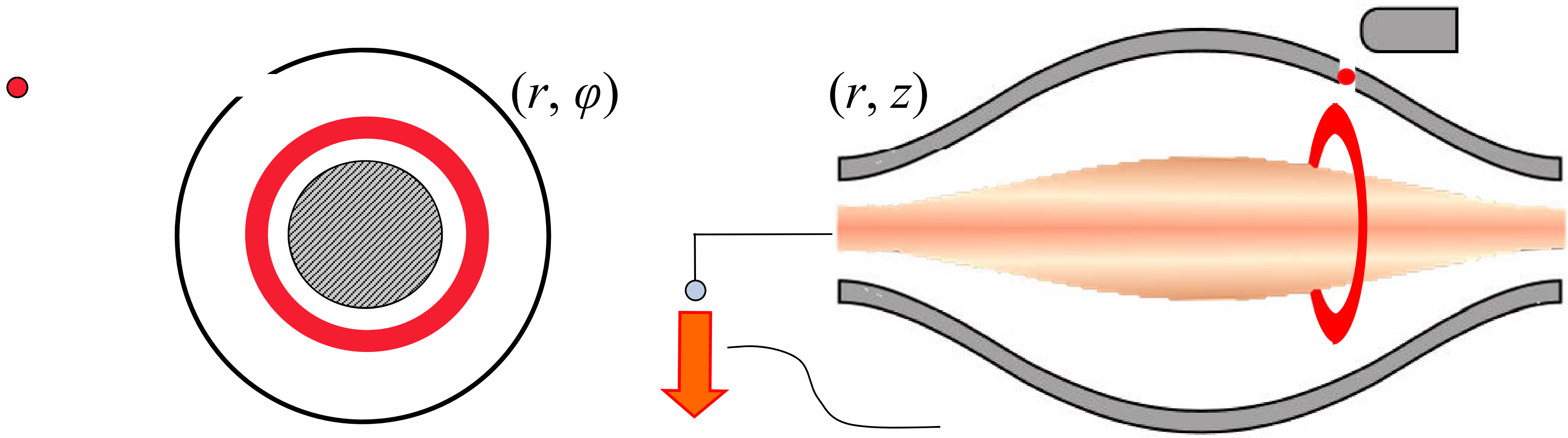


Electric field in orbitrap

www.thermofisher.com

Ion rotation in the Orbitrap

- A short ion packet of one *m/z* enters the field *tangentially, off-equator*.
- Ions are squeezed toward the central electrode *by decreasing voltage* on the central electrode.
- In the axial direction, ions are forced to move away from the narrow gap toward the wider gap near the equator.
- This initiates axial oscillations. After the voltage decrease stops, ion trajectories become a *stable spiral*.



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Ion trajectories in the Orbitrap

- There are three characteristic frequencies:
  - Frequency of rotation: ω_φ

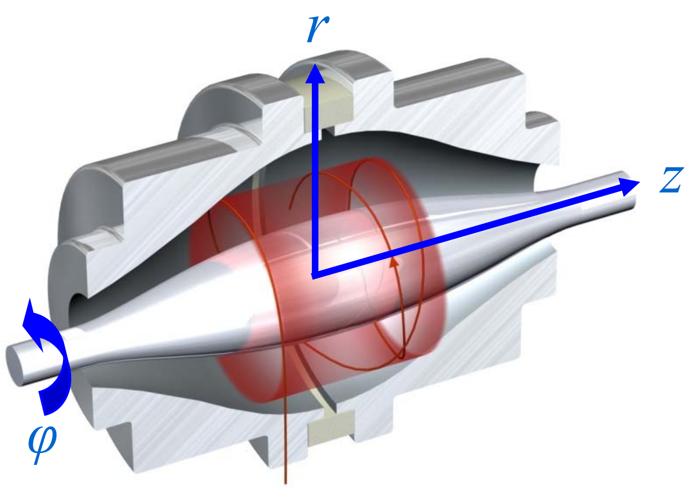
$$\omega_\varphi = \frac{\omega_z}{\sqrt{2}}\sqrt{\left(\frac{R_m}{R}\right)^2 - 1}$$

  - Frequency of radial oscillation: ω_r

$$\omega_r = \omega_z\sqrt{\left(\frac{R_m}{R}\right)^2 - 2}$$

  - Frequency of axial oscillation: ω_z

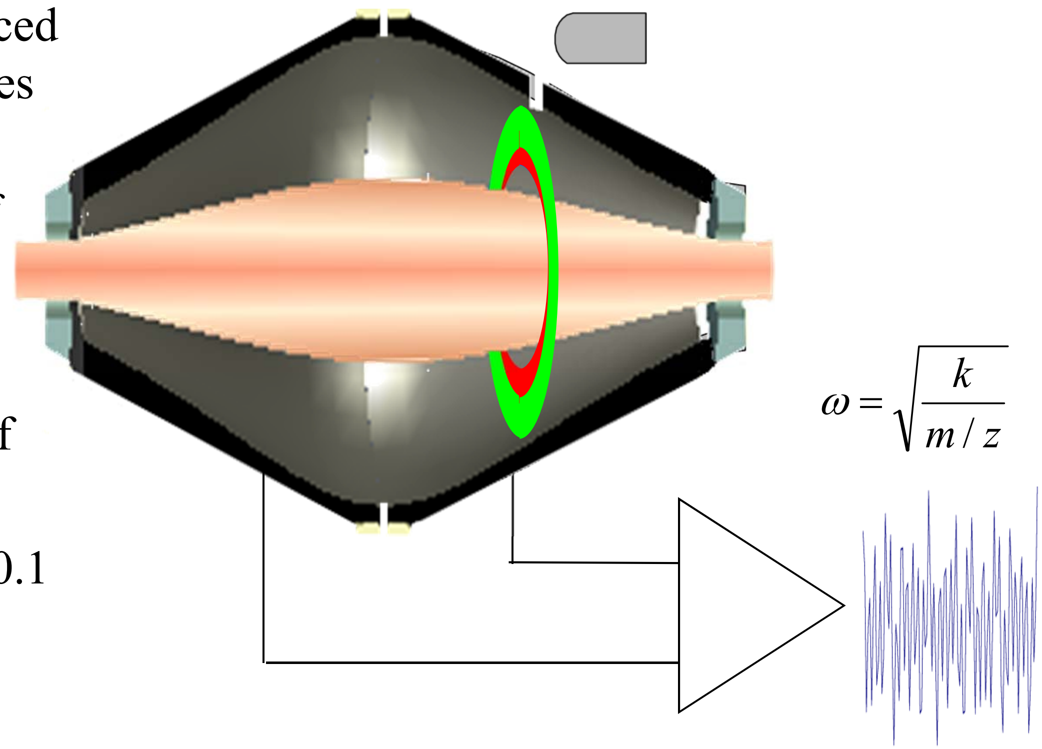
$$\boxed{\omega_z = \sqrt{\frac{k}{m/z}}}$$



Anal. Chem. (2000) **72**, 1156

Detection of ions with image charge (current) in the Orbitrap

- **Image charge**: An opposite charge induced by ions oscillating between the two halves of the orbitrap.
  - An **amplifier** connected to the two halves of the split outer electrode measures the image current.
- The orbitrap contains ions with different *m/z* values, each creating a component of current with a different frequency.
- After recording the current for a time (~0.1 to 1.5 s), a computer decomposes the current into its component frequencies through *Fourier transform*.



$$\omega = \sqrt{\frac{k}{m/z}}$$

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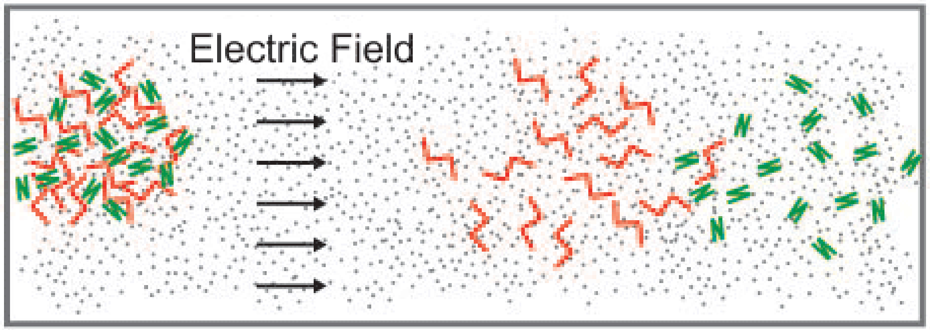
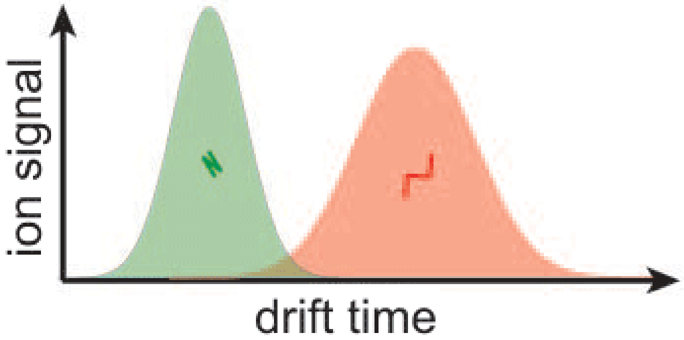
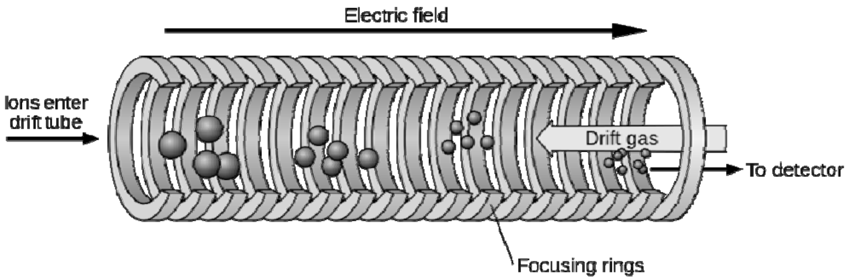
Ion mobility spectrometer (IMS)
: Gas-phase electrophoresis

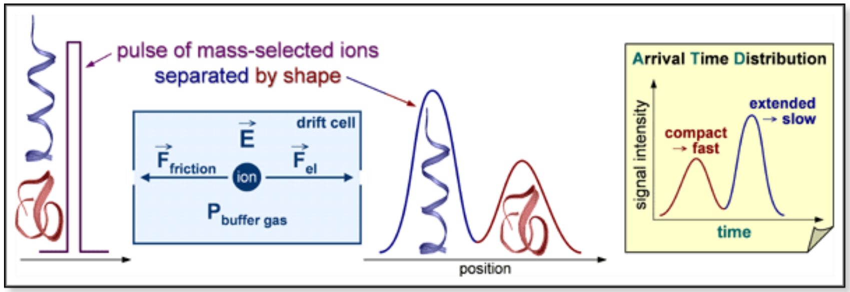
- **Instrumentation**







http://en.wikipedia.org/wiki/Ion-mobility_spectrometry



http://bowers.chem.ucsb.edu/theory_analysis/ion-mobility/index.shtml