Basic Principles of FT-ICR Mass Spectrometry

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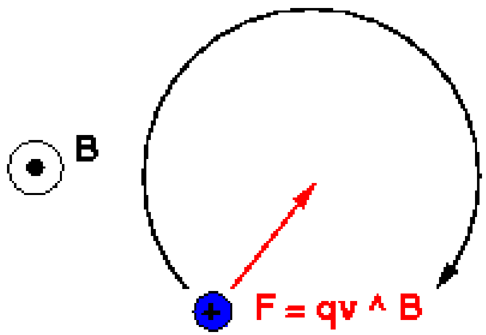
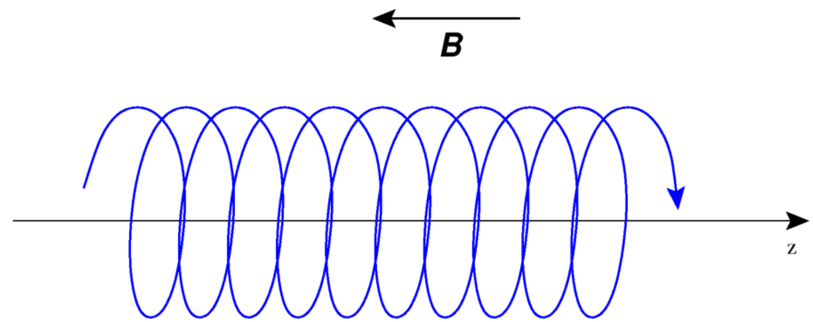
Charge displacement within a magnetic field





$$\nu_c = \frac{eB}{2\pi(m/z)} = \frac{1.535611\times 10^{7}\, B}{m/z}\ \text{Hz}$$

Cyclotron motion frequency :

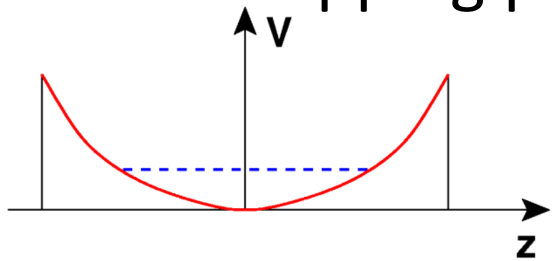
- **independent of the ions initial velocity and position,**
- **inversely related to the *m/z* ratio.**

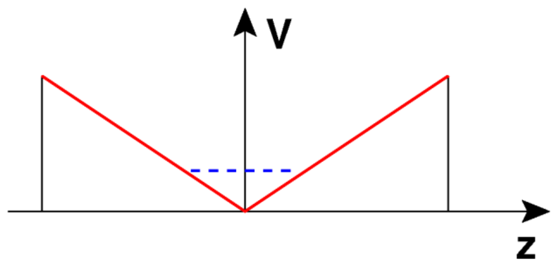
Accurate measurement of the cyclotron frequency would yield accurate measurement of the *m/z* ratio.

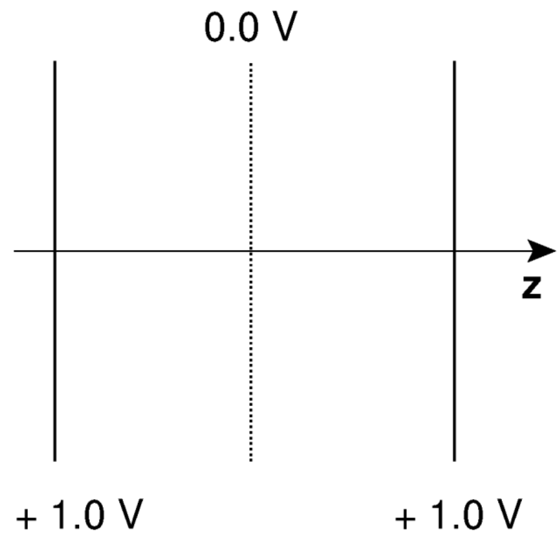
ION TRAPPING

The trapping issue

- How can the ions be confined along the *z* axis ?
- The ideal trapping potential should look like :





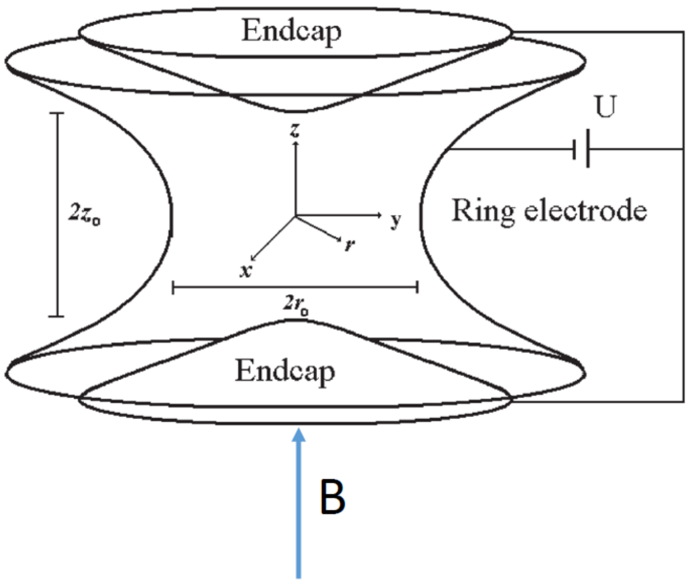


Issue : This would require infinite plates along the *xy* plane and at least a plate at $z = 0$ (at the minimum of the potential well).

Consequence : Practical implementation will all add a radial term with an electrostatic field pointing outwards from to the *z* axis.

Trapping potentials

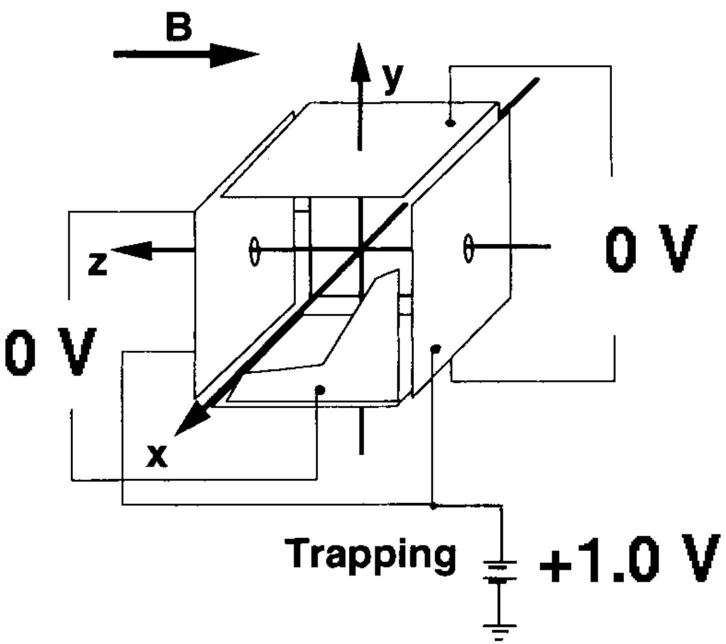
- Confining along the *z* axis requires an additionnal field.

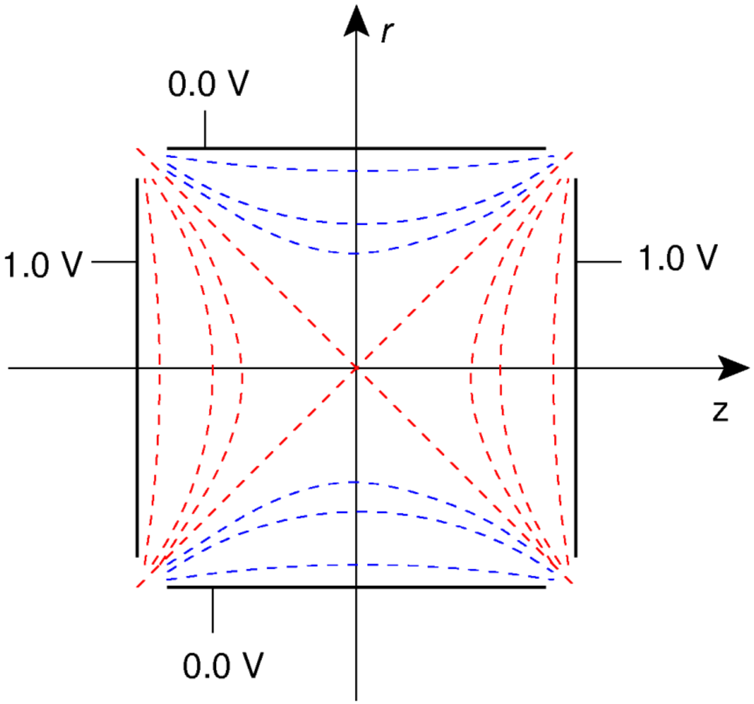


- Penning traps produce an ideal quadrupolar field, but :
  - electrodes of hyperbolic shape,
  - small ion storage capacity,
  - limits excitation amplitudes.

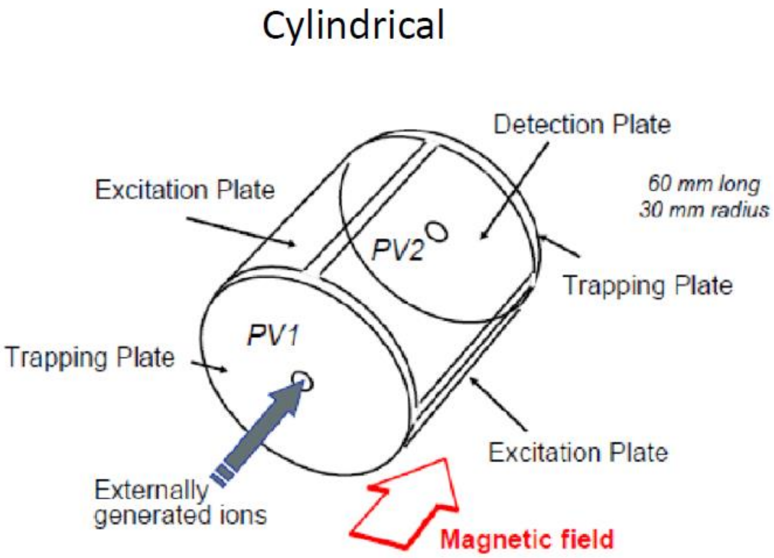
- The requirement is only to have an rotation averaged radial electric field constant for all *z* positions :
  - Other geometries can provide an approximation of this ideal situation.

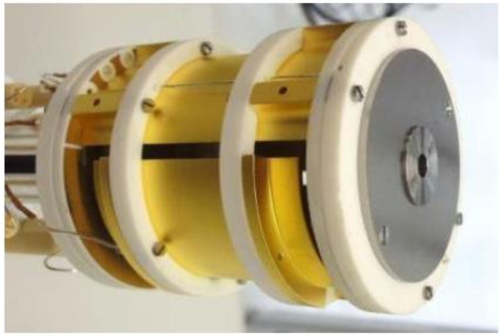
Cubic cell

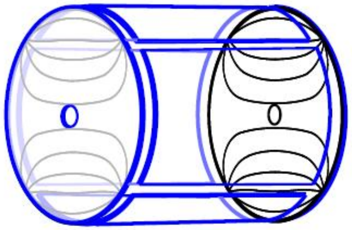


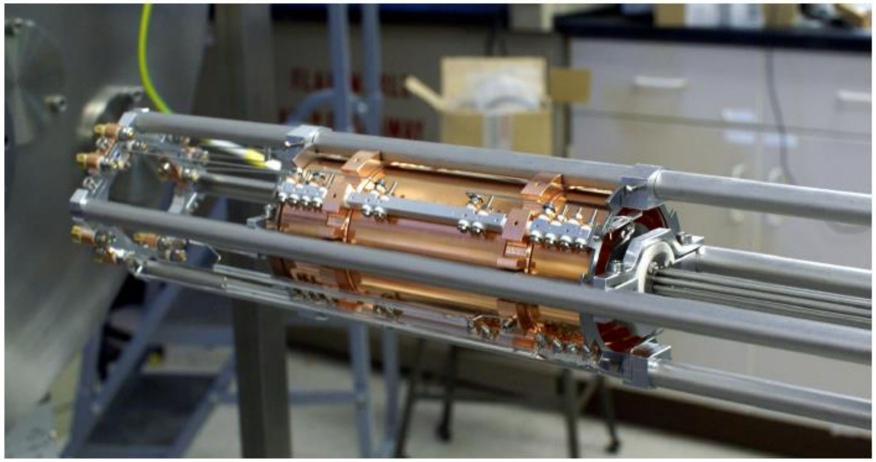


Cylindrical cell

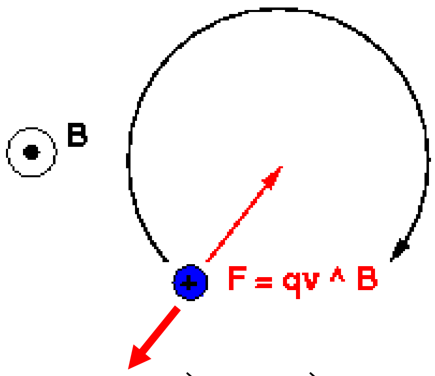








Effect of this radial electrostatic field on ion motion



Trajectories centered along the cell main axis: the radial electrostatic force opposite to the magnetic force.

$$\vec{F} = q\vec{E}(r) = \frac{qV_{trap}\alpha r}{a^2}$$

$$\omega^2 - \frac{qB_0\omega}{m} + \frac{qV_{trap}\alpha r}{ma^2} = 0$$

➡ Two solutions, so the trajectory will be a superposition of two rotations.

$$\omega_+ = \frac{\omega_c}{2} + \sqrt{\frac{\omega_c^2}{2} - \frac{\omega_z^2}{2}}$$

Reduced cyclotron frequency

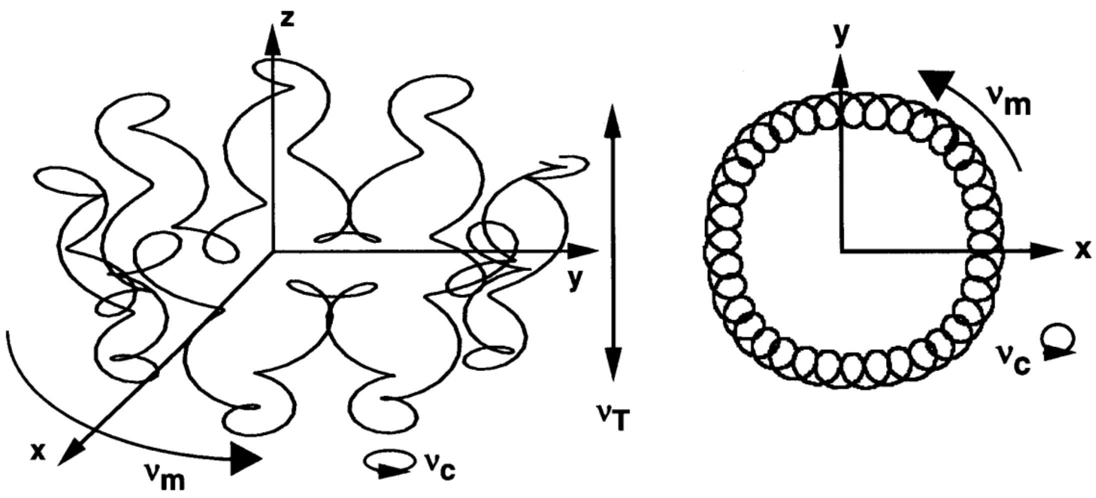
$$\omega_- = \frac{\omega_c}{2} - \sqrt{\frac{\omega_c^2}{2} - \frac{\omega_z^2}{2}}$$

Magnetron frequency

Radial oscillations limit cases

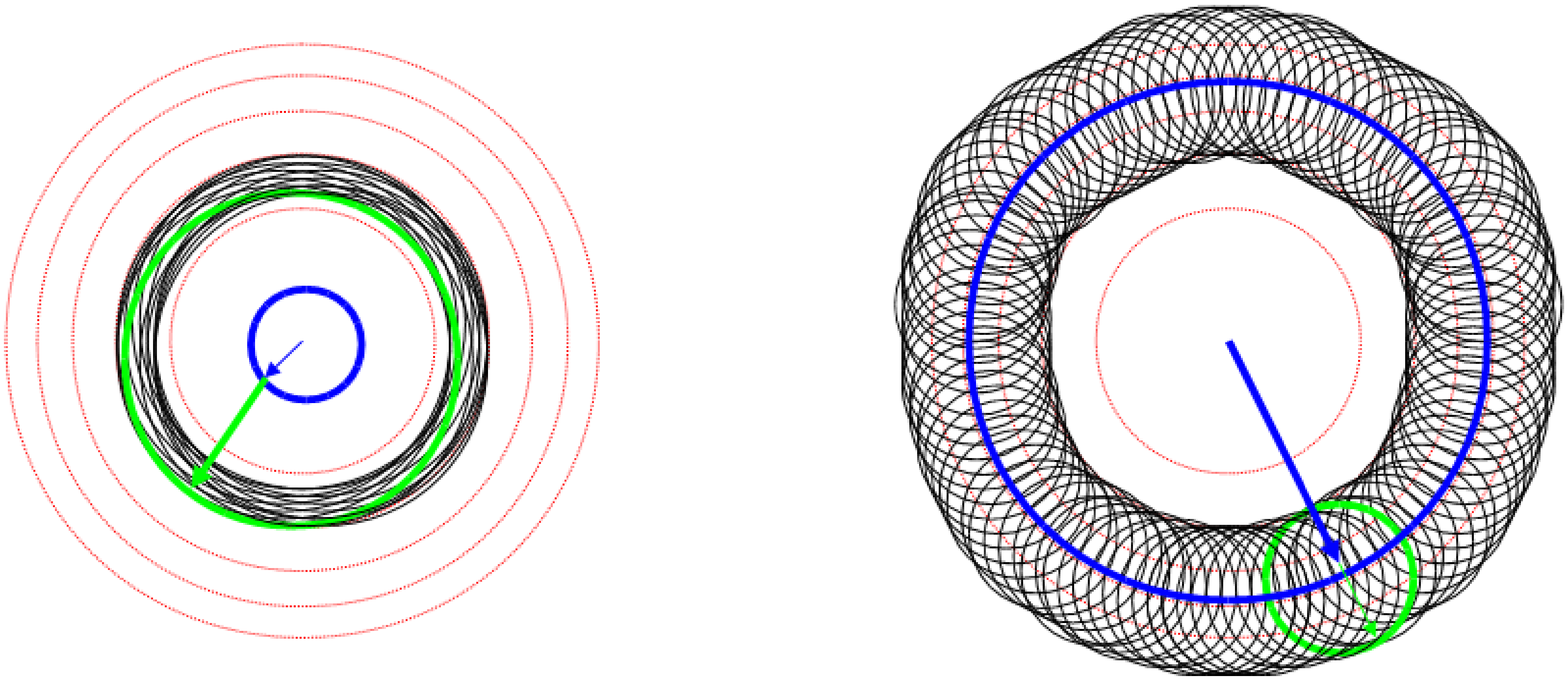
- Ions localised on the central z-axis
  - → Pure axial oscillations (trapping oscillations)
- Ion trajectories as rotations along the cell center
  - → Rotation at ω_+ : reduced cyclotron motion.
  - → Rotation at ω_- : magnetron motion.
- In the general case, the three motions will be superimposed
  - Since $\omega_+ >> \omega_-$ one can consider that cyclotron motions cycle around a circle center at reduced cyclotron frequency which itself cycles around the cell center at the magnetron frequency.

Superimposed motions of the ions



- This is a picture to show the movements but the magnetron is strongly exagerated compared to usual meausrement situations.

Trajectories for two limit situations



Initial position close to cell center, and cyclotron motion increased (for instance after excitation)

$$r_c \gg r_m$$

Initial position far from cell center, and low cyclotron motion (ions formed far from cell axis with low initial speed)

$$r_m \gg r_c$$

Cylindrical and cubic cells are non-ideal Consequences

- Ideal Penning trap:

$$\vec{E} = f(r)$$

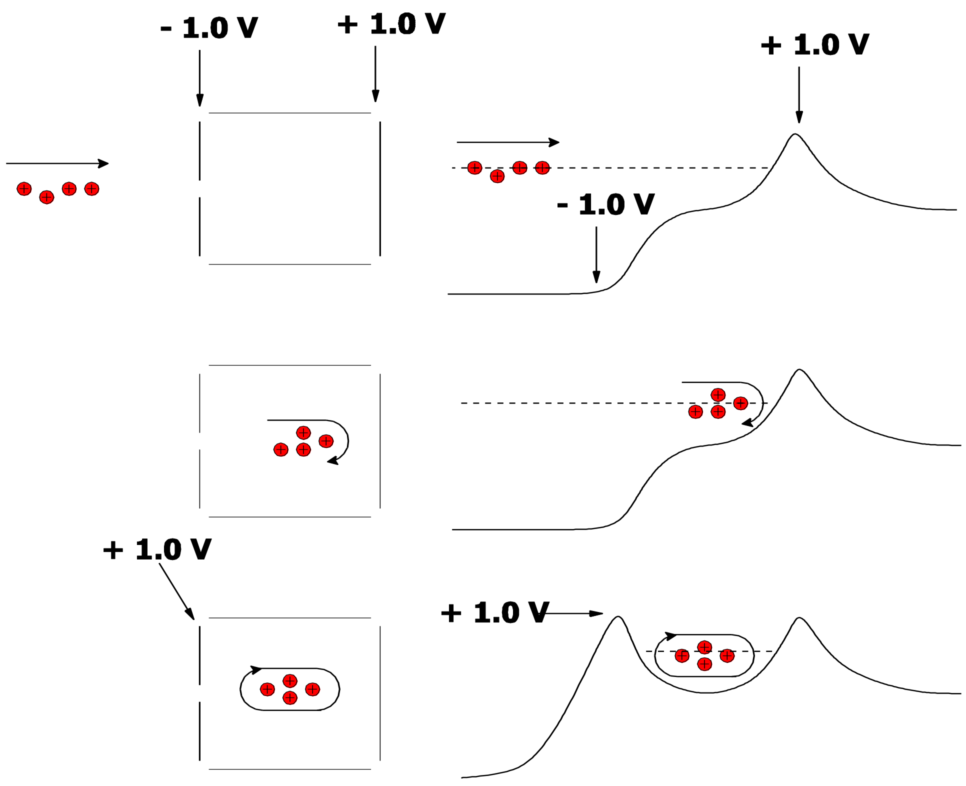
- In usual cells:

$$\vec{E} = f(r, z)$$

But ω_+ depends on the radial electric field. Thus the cyclotron frequency will depend on the axial position of ions in a cell. Axial motion is not uniform for all ions:

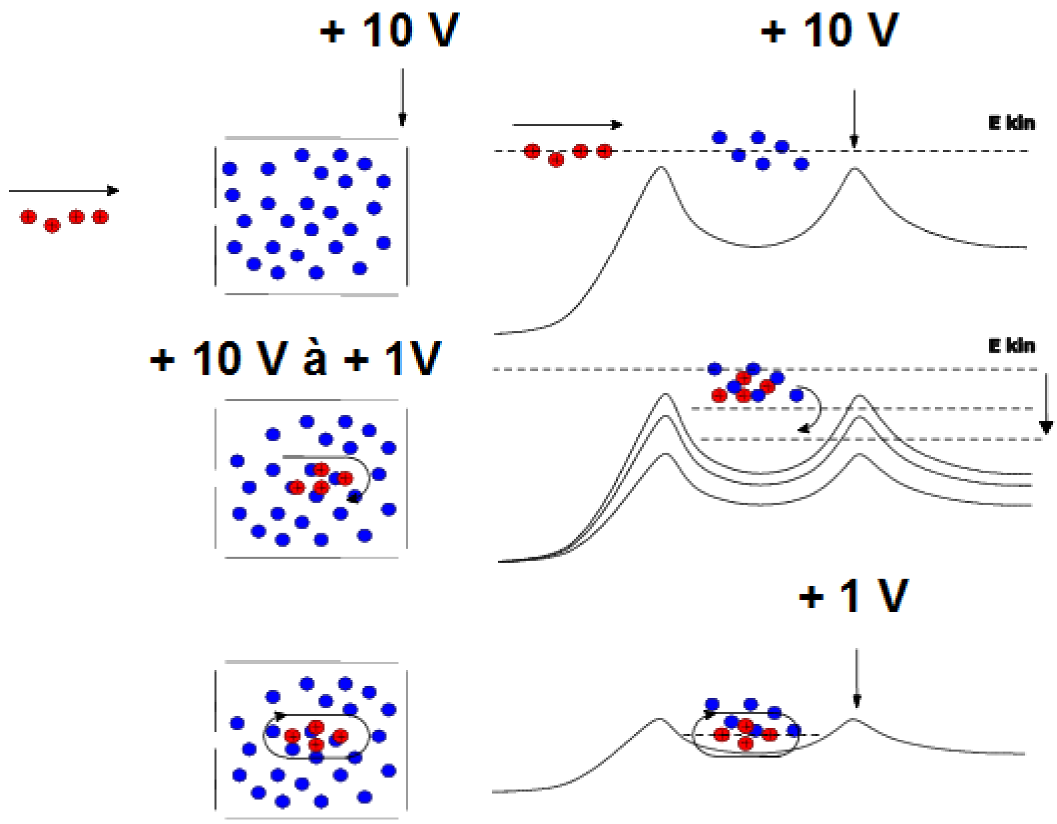
→ Peak broadening / phase shifts over time depending on the axial trapping motion.

Trapping ions from an external source: pulsed trapping



- Requires a storing stage to bunch the ions and send them in sync with the lowering of the cell voltage.
- Time of flight ion discrimintation.

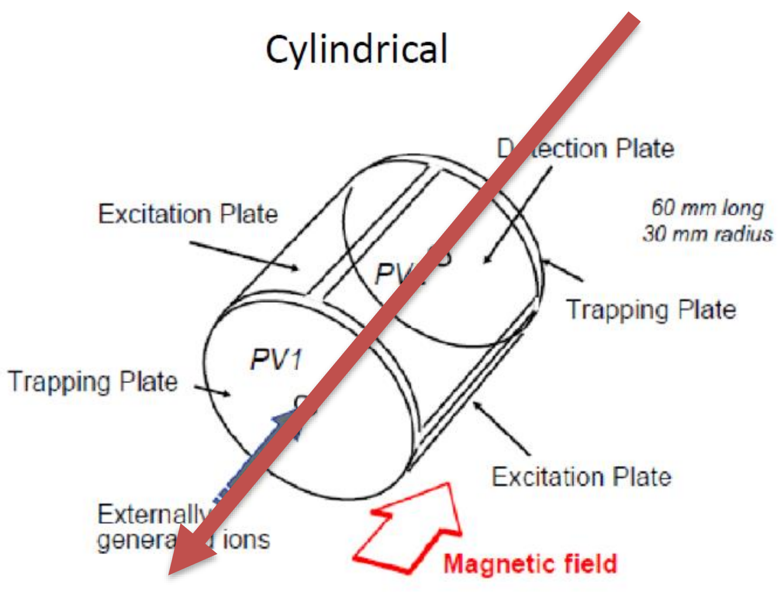
Dynamic ion trapping



- Higher voltage improves ion trapping capacity and efficiency.
- Lowering the voltage allows a reduction in non-harmonic field discrimination.
- Controlled gas buffer can be synchronised to improve trapping / ion cooling.

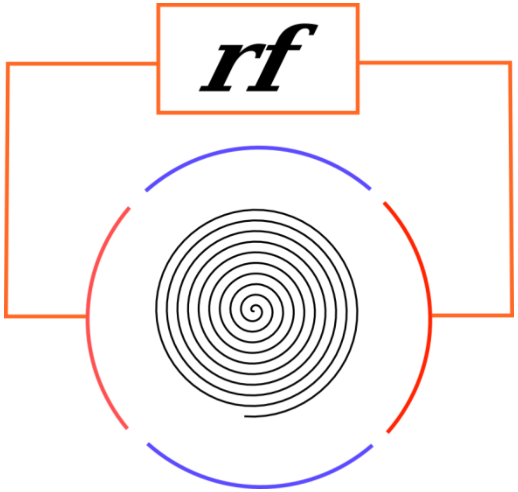
Trapping for performing ion spectroscopy

- Long storage times can be achieved (> 3000 s) without significant ion loss.
- If ion introduction done at low magnetron and cyclotron motion: ions are initially aligned along the cell axis with z trapping oscillation.
- For thermal ions (1 eV) and a 7 T magnetic field, initial radius is on the order of 0.1 mm.
- A laser beam can be shined along the z axis to interact with trapped ions.
- The length of the trap is an issue: the laser focal point cannot be adjusted to a single point in the cell.



MEASURING A MASS SPECTRUM IN AN FT-ICR CELL

Control of the cyclotron motion radius: Dipolar excitation



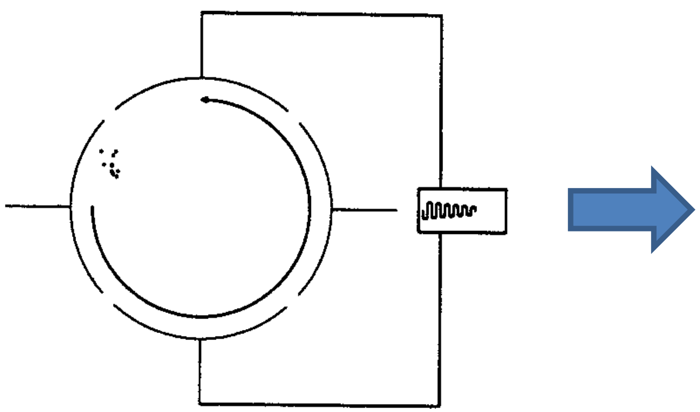
$$r = \frac{\beta_{dipolar} V_{p-p} t_{exc}}{2dB_0}$$

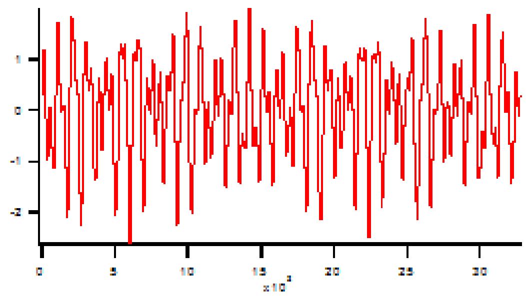
$$E_{kin} = \frac{\beta_{dipolar}^2 q^2 V_{p-p}^2 t_{exc}^2}{d^2 m}$$

- The radius is expanded to a fixed radius.
- Ion are phased together based on the phase of the excitation pulse.

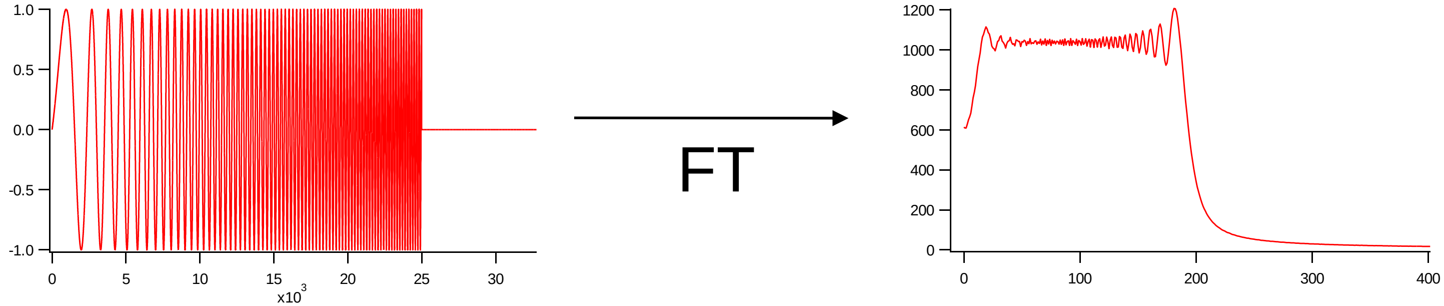
Image ion signal detection

- The ion cloud passes in front of two side plates connected through a preamplifier which allows current measurement.





Broadband excitation: Chirps

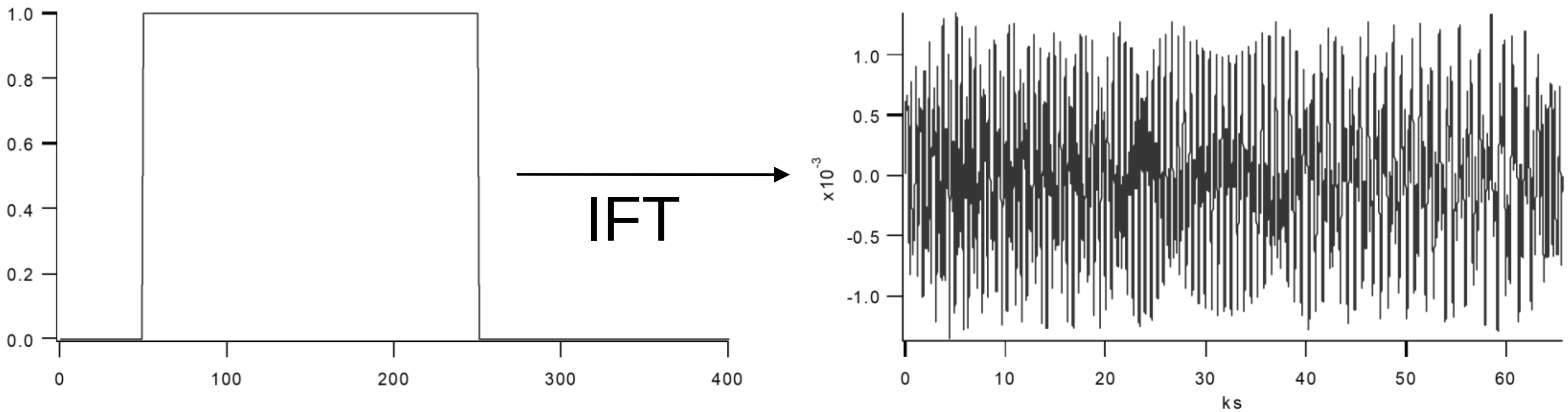


Time domain (intensity)

Frequency domain (magnitude)

- Note that the excitation magnitude is not completely flat, mostly on the sides.
- In old cells, the frequency sweep direction (upwards vs downwards) could lead to unwanted axial excitation.

Broadband excitation:
Stored Waveform Inverse Fourier Transform (SWIFT)



Frequency domain (Magnitude) Time domain (Intensity)

- Phase is not defined by the frequency domain magnitude. This will have to ba adjusted to maintain a time domain signal with appropriate bounds for the amplifier.

- The excitation can have other aspects, such as with a notch (single ion selection) or a comb (multiple ion selection).

- Due to the non-infinite duration of the signal, the power spectrum of the real waveform presents side-bands depending on the duration.

Dipolar excitation for ion detection

- Some criterions for an appropriate excitation:
  - Broadband to cover the mass range.
  - Intensity should be as homogenous as possible for signal linearity;
  - But good ion cloud coherence requires a short and intense excitation;
  - Thus excitation parameters should be chosen depending on the aim of the experiment (resolution / mass accuracy vs accuracy on the intensities)

FROM THE IMAGE CURRENT TO THE MASS SPECTRUM: SOME ELENTS ON THE FOURIER TRANSFORM

Fourier Transform

$f(t)$: $\mathbb{R} \to \mathbb{C}$

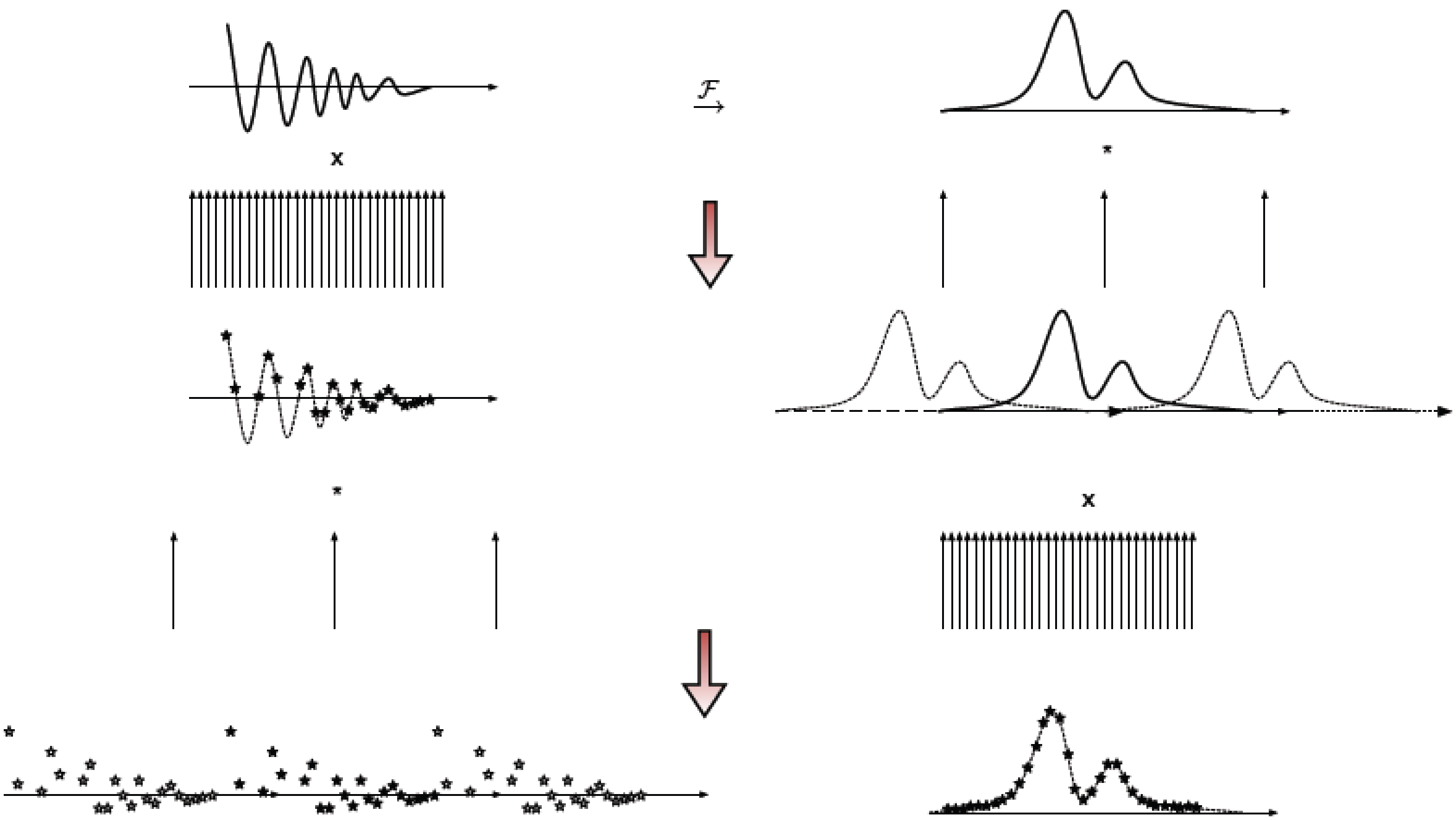
$F(\vartheta)$: $\mathbb{R} \to \mathbb{C} F(\vartheta) = \int_{-\infty}^{+\infty} f(t) e^{-2i\pi\vartheta t}\, dt$

- Inversible: two representation of the same information.
- These two representations are called reciprocal represetations:
  - t ⟷ ν (s ⟷ Hz)
- FT of the $\cos \omega t$ function is the function F which is zero everywhere except for $\vartheta = \frac{\omega}{2\pi}$.

Key reciprocal functions

	Function	Reciprocal function
1	Sine $e^{i\vartheta_0 t}$	Delta function $\delta(\vartheta - \vartheta_0)$
2	Rectangular function $t \in [-1,1]$: $f(t) = 1$ Else : $f(t) = 0$	Sine cardinal $\frac{\sin \pi\vartheta}{\pi\vartheta}$
3	Dilation $f(at)$	Contraction $\frac{1}{\|a\|} \mathrm{F}\left(\frac{\vartheta}{a}\right)$
4	Gaussian of width σ $e^{-\frac{t^2}{\sigma}}$	Gaussian of width 1/σ $\sqrt{\pi\sigma} e^{-\sigma(\pi\vartheta)^2}$
5	Comb of period T	Comb of period 1/T
6	Decreasing exponential	Lorentzian

Signal sampling and periodisation



Limits due to the sampling

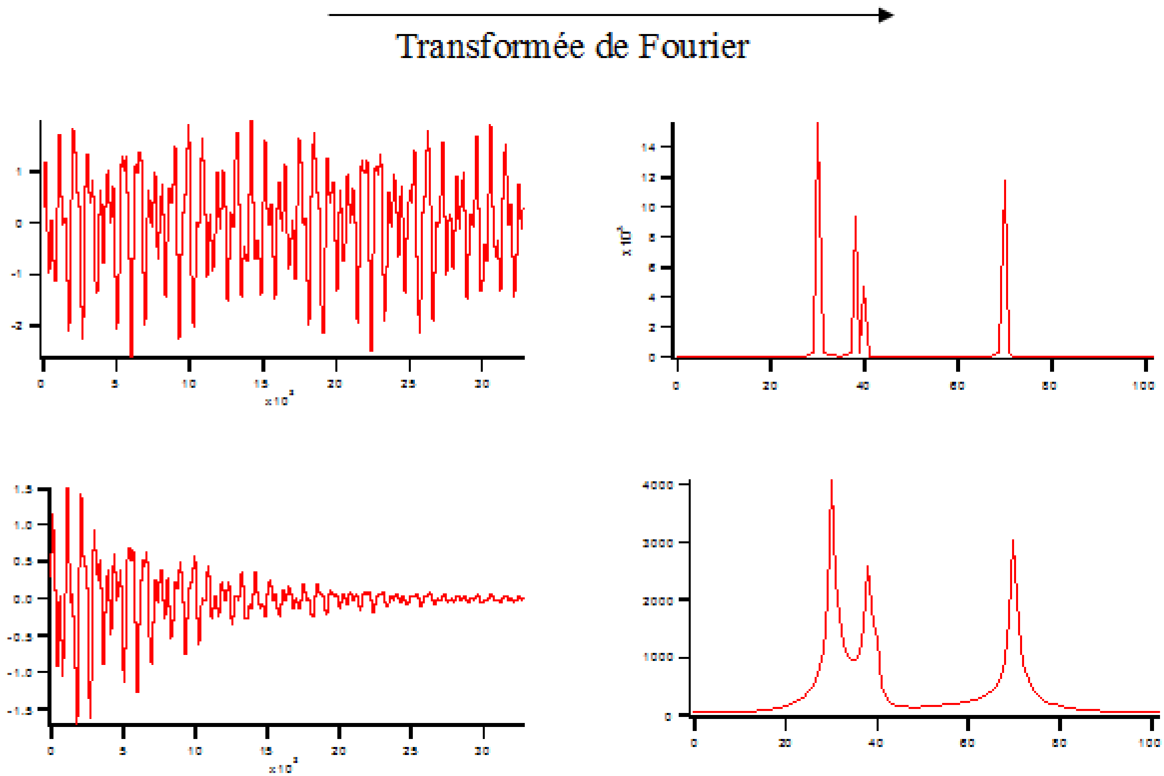
- Shannon-Niquist criterion:
  - $F_{max} = \frac{1}{2\Delta T}$
- Spacing of points in the frequency dimension:
  - $\Delta F = \frac{1}{T_{acq}}$
- Foldovers will appear when the frequencies are higher than the maximal frequency as defined by the Shannon-Niquist criterion.

Signal duration and recording

- A critical parameter:

$$\tau = 4T_{aq}$$

$$\tau = \frac{1}{10}T_{aq}$$



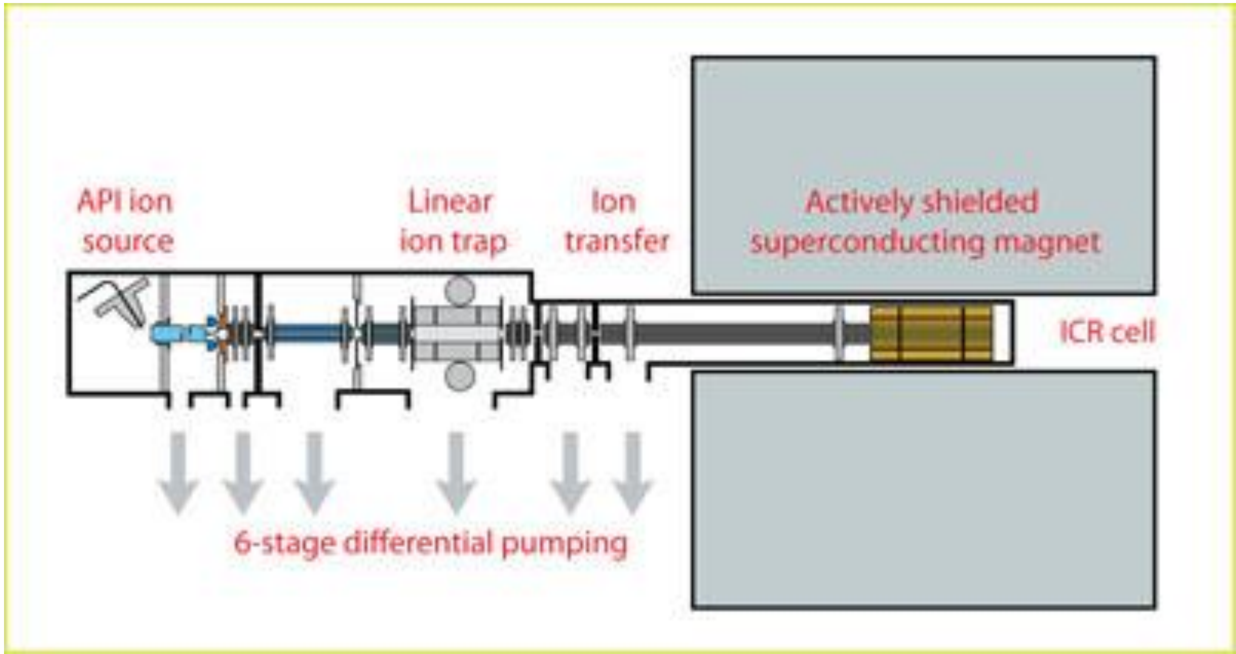
Limits to the acquisition time

- Collision with residual gas
  - High vacuum (10^{-10} mbar) since ions have to move long distances during an acquisition (~ 100 km/acquisition)

- Stability of the ion trajectories in the trap
  - In frequency (no perturbation by stray electric fields, by space charge repulsion)
  - In position (ions should remain trapped)
- Phase stability
  - Ions packets can have slightly different frequencies, due to exploring different regions of the cell. Inhomogeneity of the radial electric field will lead to slightly different frequencies of individual ions which will average as a phase shift over time of the collective motion.

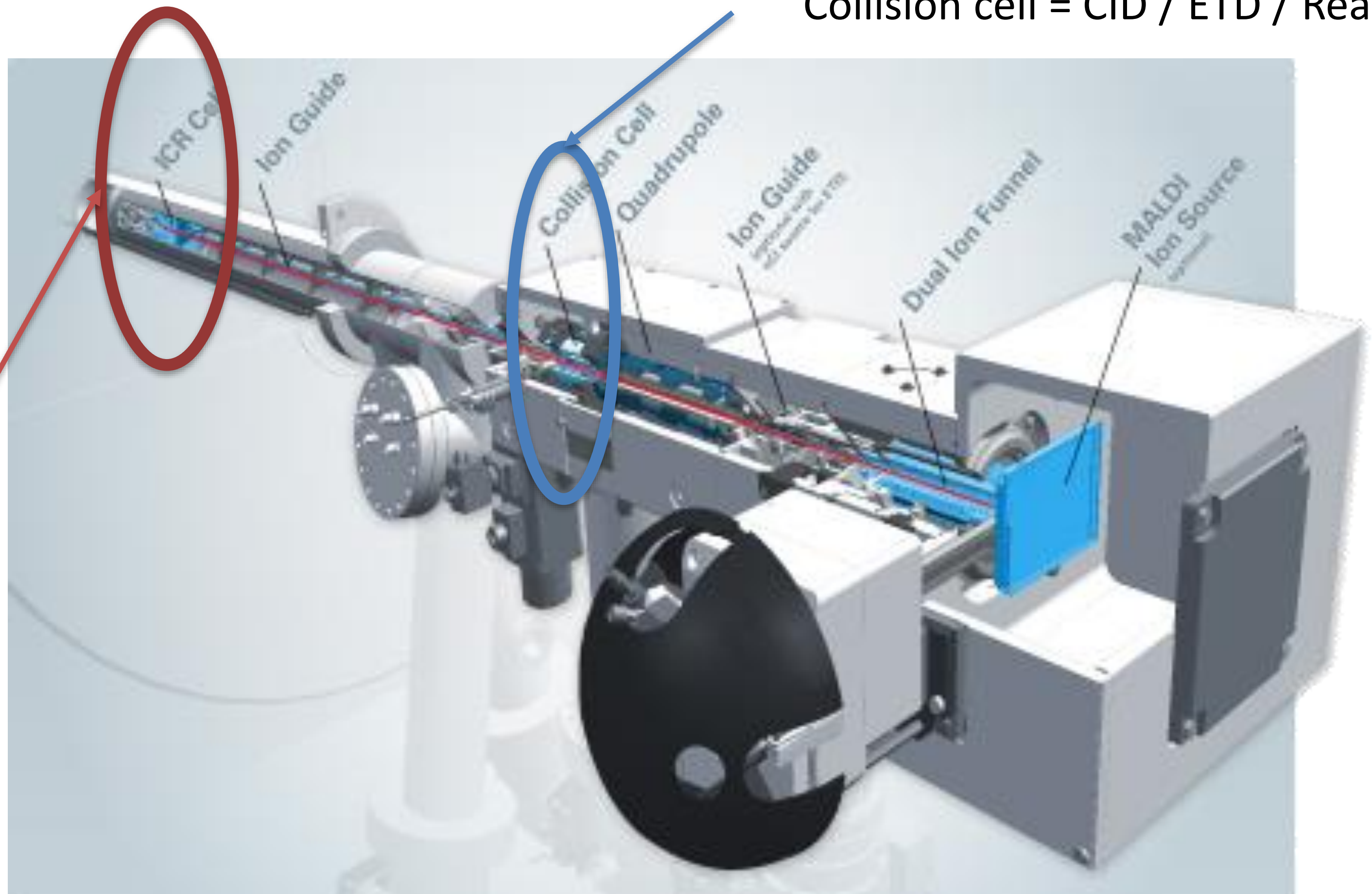
CURRENT HYBRID MASS SPECTROMETERS

Thermo LTQ-FT



Bruker SolariX

Collision cell = CID / ETD / Reactivity



ICR Cell :
(SORI–)CID
ExD
IRMPD
UVPD
BIRD
…