ORBITRAP Mass Spectrometry

D. Grinfeld, A. Makarov

Thermo Fisher Scientific,
Hanna-Kunath Str 11, 28199 Bremen, Germany

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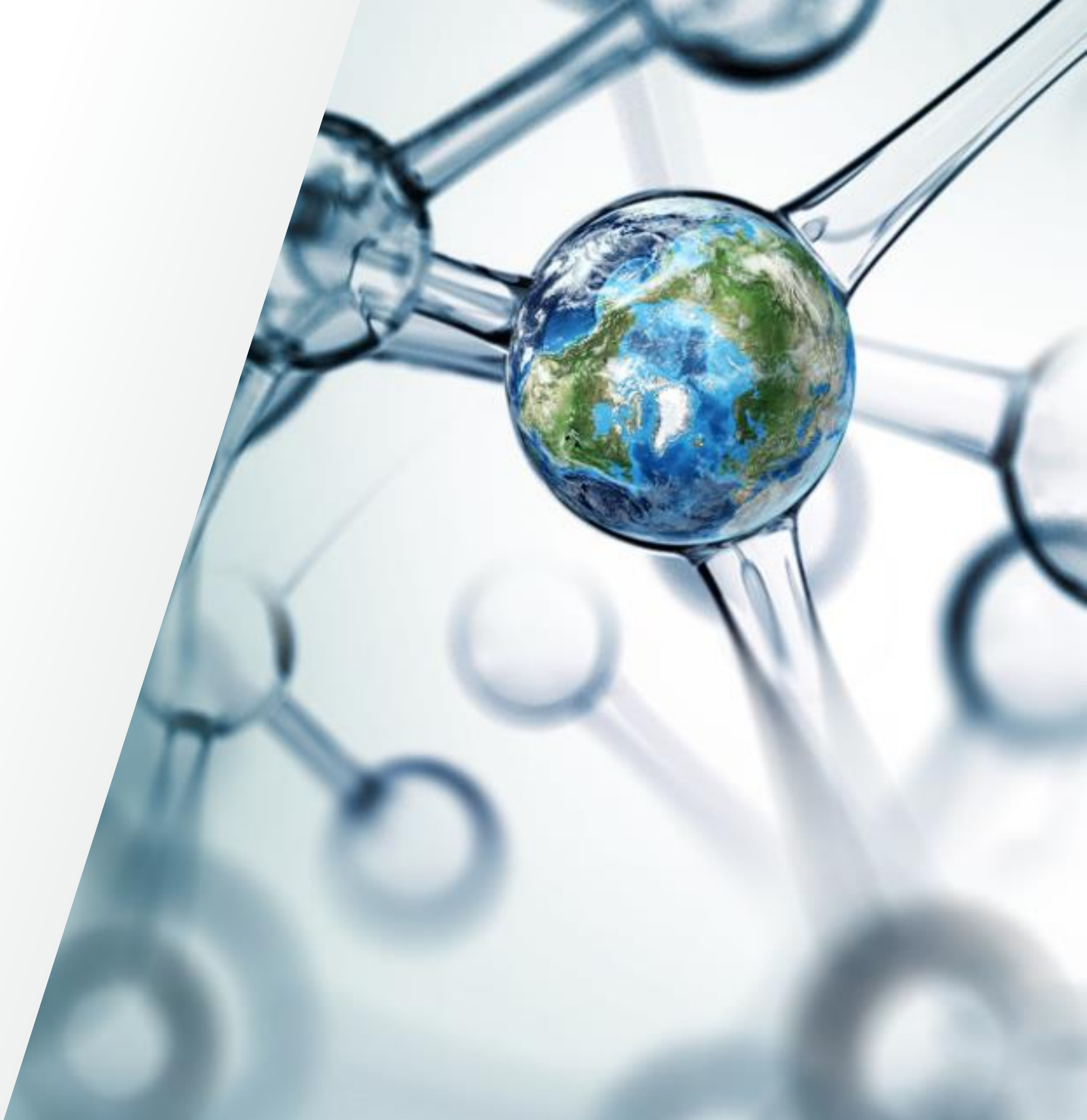
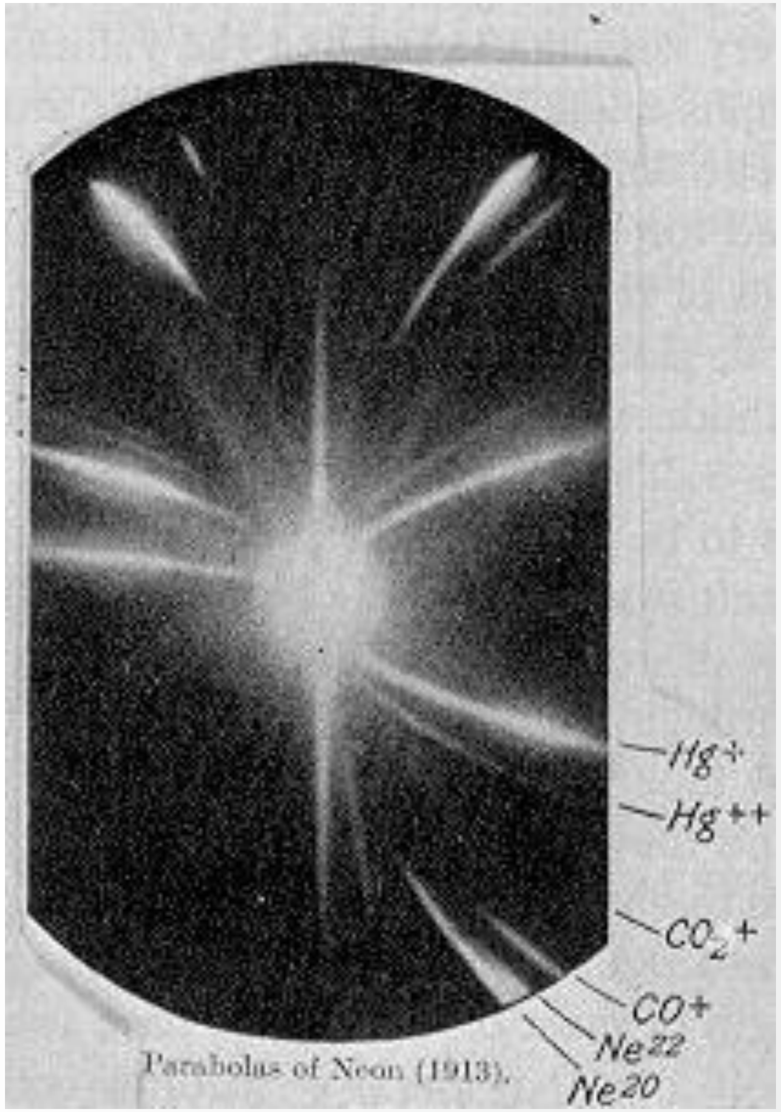


110 years of mass spectrometry since 1913



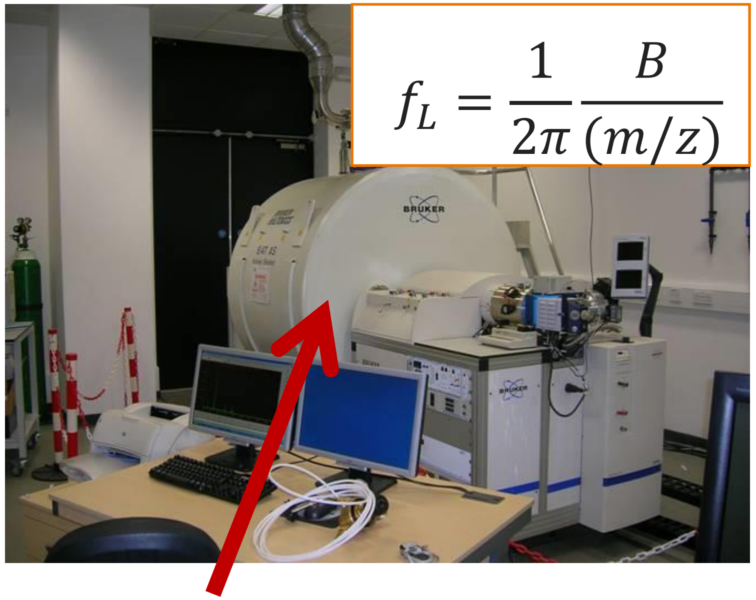
Joseph J. Thomson deflected the 'rays of positive electricity' in magnetic and electric fields and obtained mass spectrum of the atmospheric gases.

<u>Resolving power ~ 20</u>

Fourier Transform Mass Spectrometry

<u>***Magnetic trapping***</u>

$$f_L = \frac{1}{2\pi}\frac{B}{(m/z)}$$

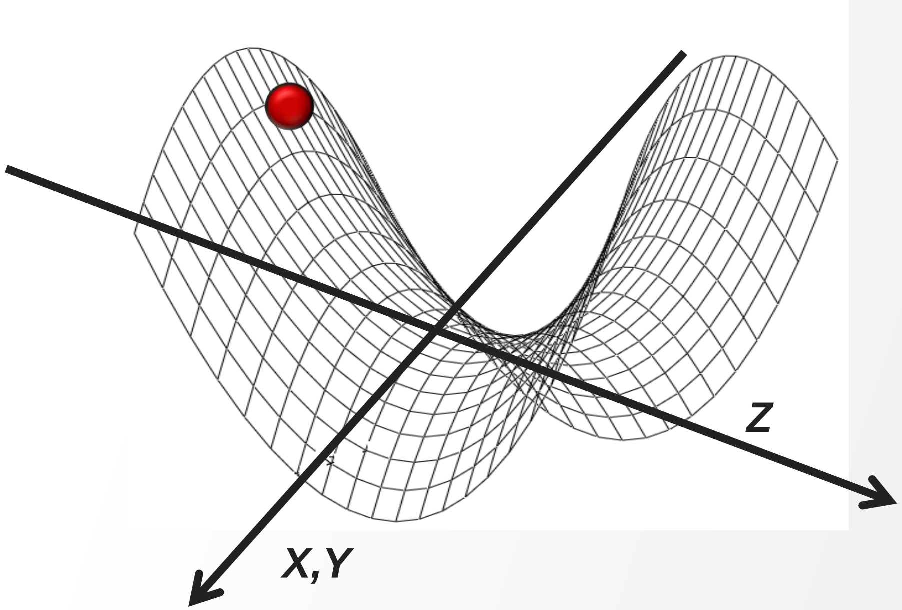


Cyclotron frequency (non-relativistic) depends on m/z.

But a superconductive magnet is

Big, Heavy, Expensive

<u>***Electrostatic trapping***</u>



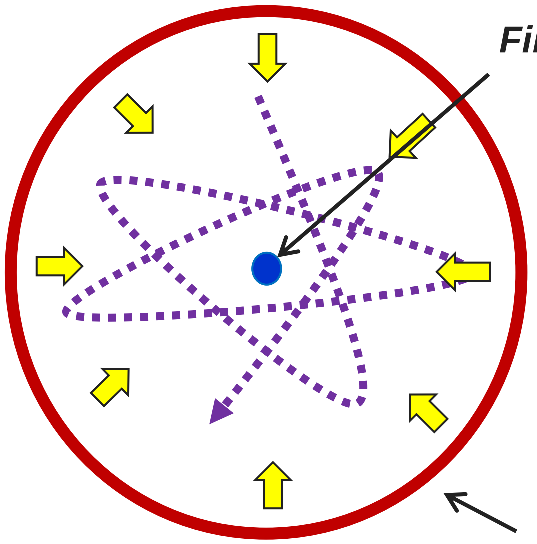
There is no stationary equilibrium in an electrostatic field...

(Earnshaw's theorem, 1842)

…but what about trapping in motion?

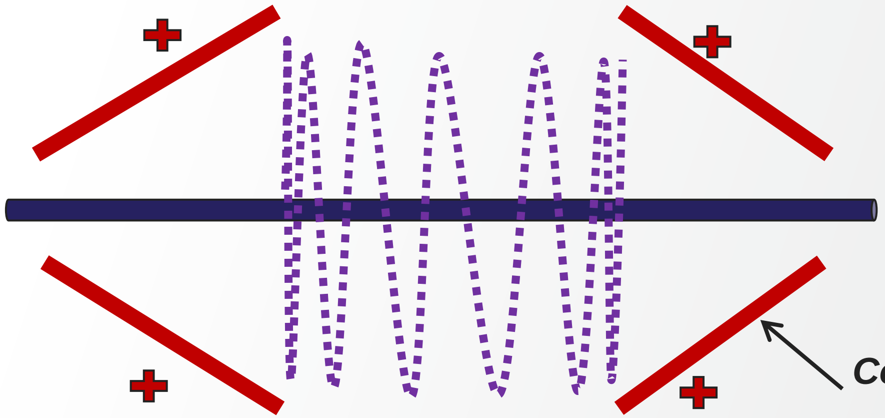
Some history of electrostatic ions traps

Orbital ion trap. Kingdon, 1923



$$\varphi\,(r) = C\ln\frac{r}{r_m} + const$$

Axial confinement with conical electrodes (Knight, 1981)

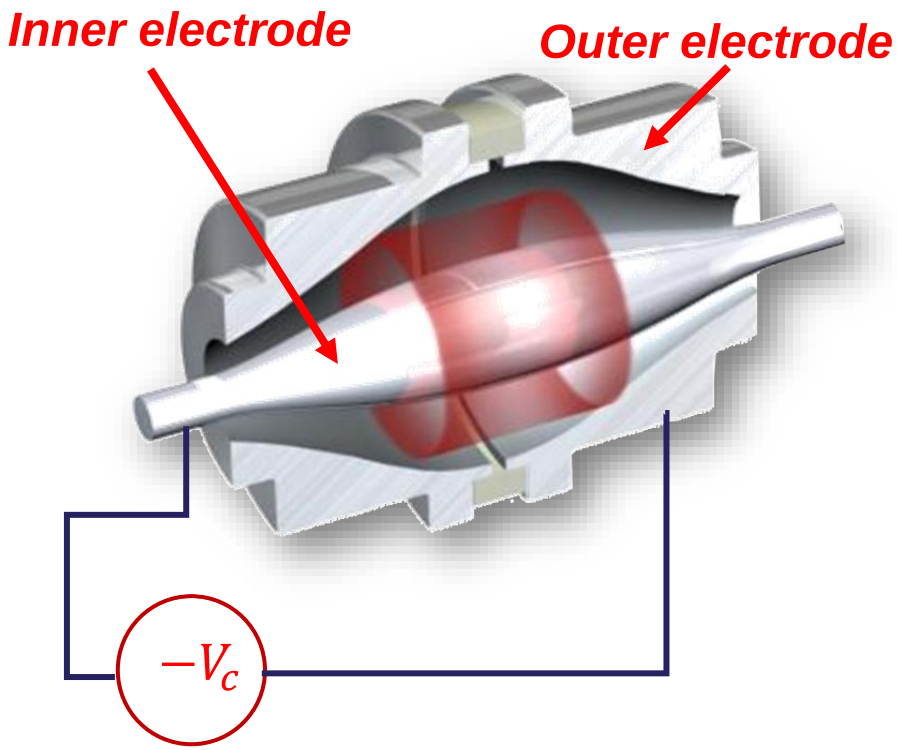


Quadro-Logarithmic field

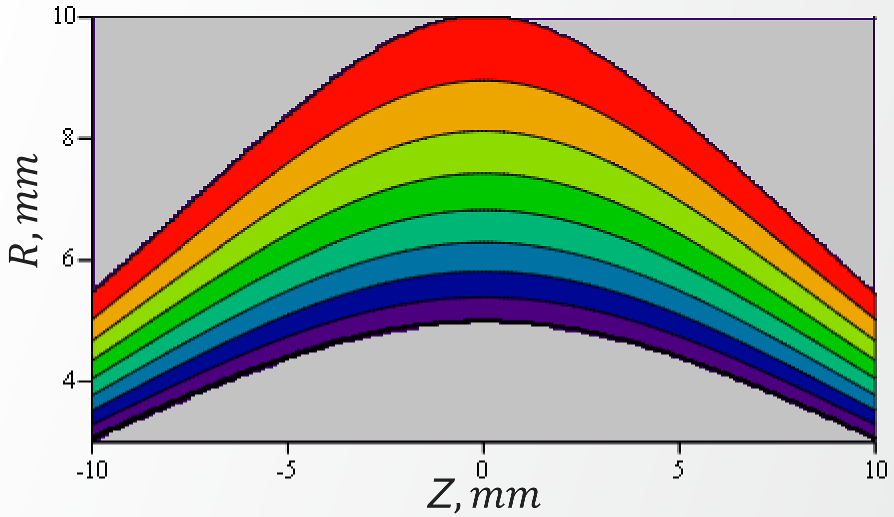
$$\varphi(z,r) = \frac{kV_c}{2}\left(z^2 - \frac{r^2}{2} + r_m^2 \ln\frac{r}{r_m}\right) + const$$

Axial oscillations are harmonic and the frequency is constant

$$f_z = \frac{1}{2\pi}\sqrt{\frac{ekV_c}{m/z}}$$



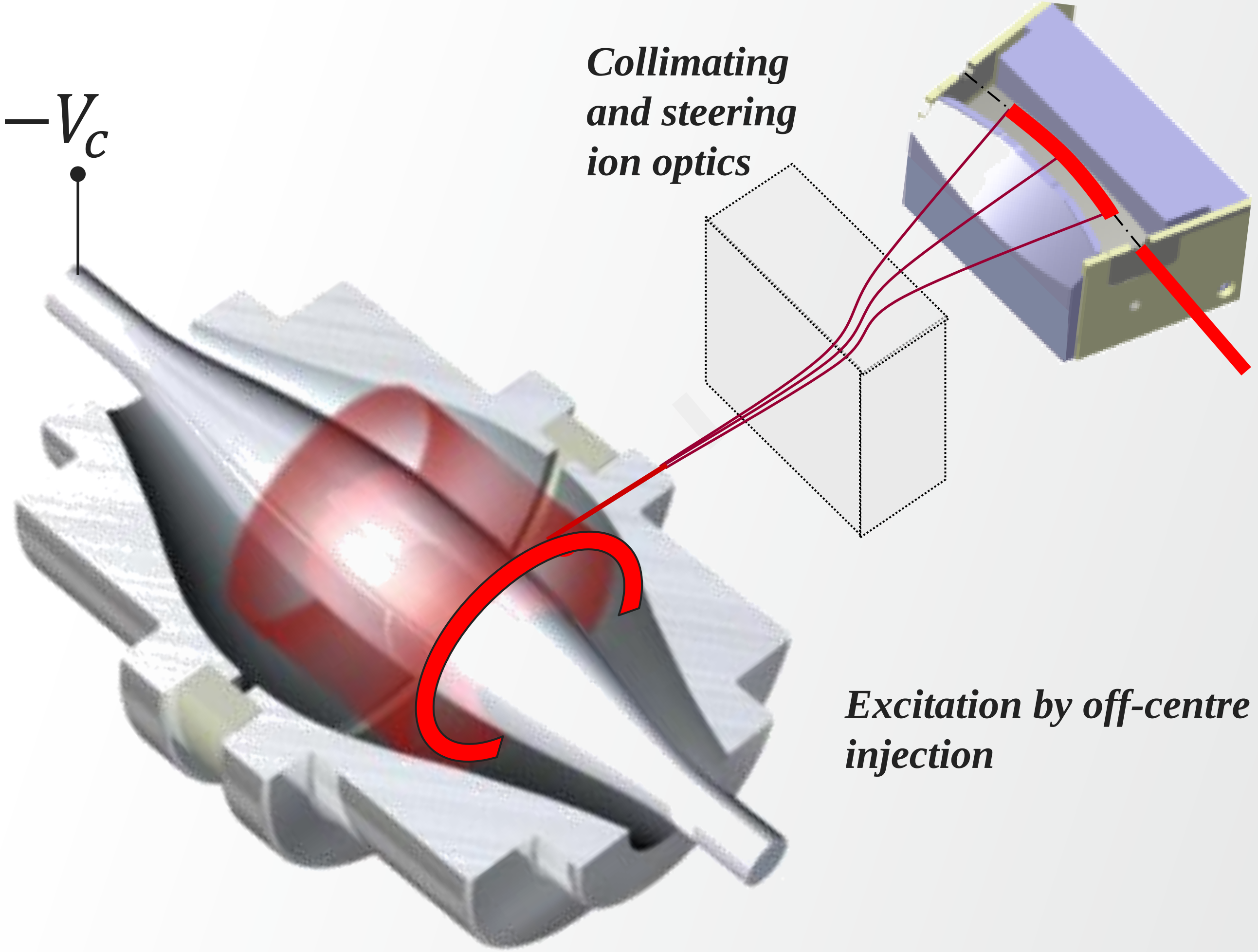
Electrodes are fabricated to follow equipotential surfaces of the QL-field



Precision of setting up the electric field is the corner-stone of the technology

Core of Orbitrap technology

- ***Pulsed ion source***
- *Off-axis injection*
- *Dynamic squeezing*
- *Signal detection and processing*



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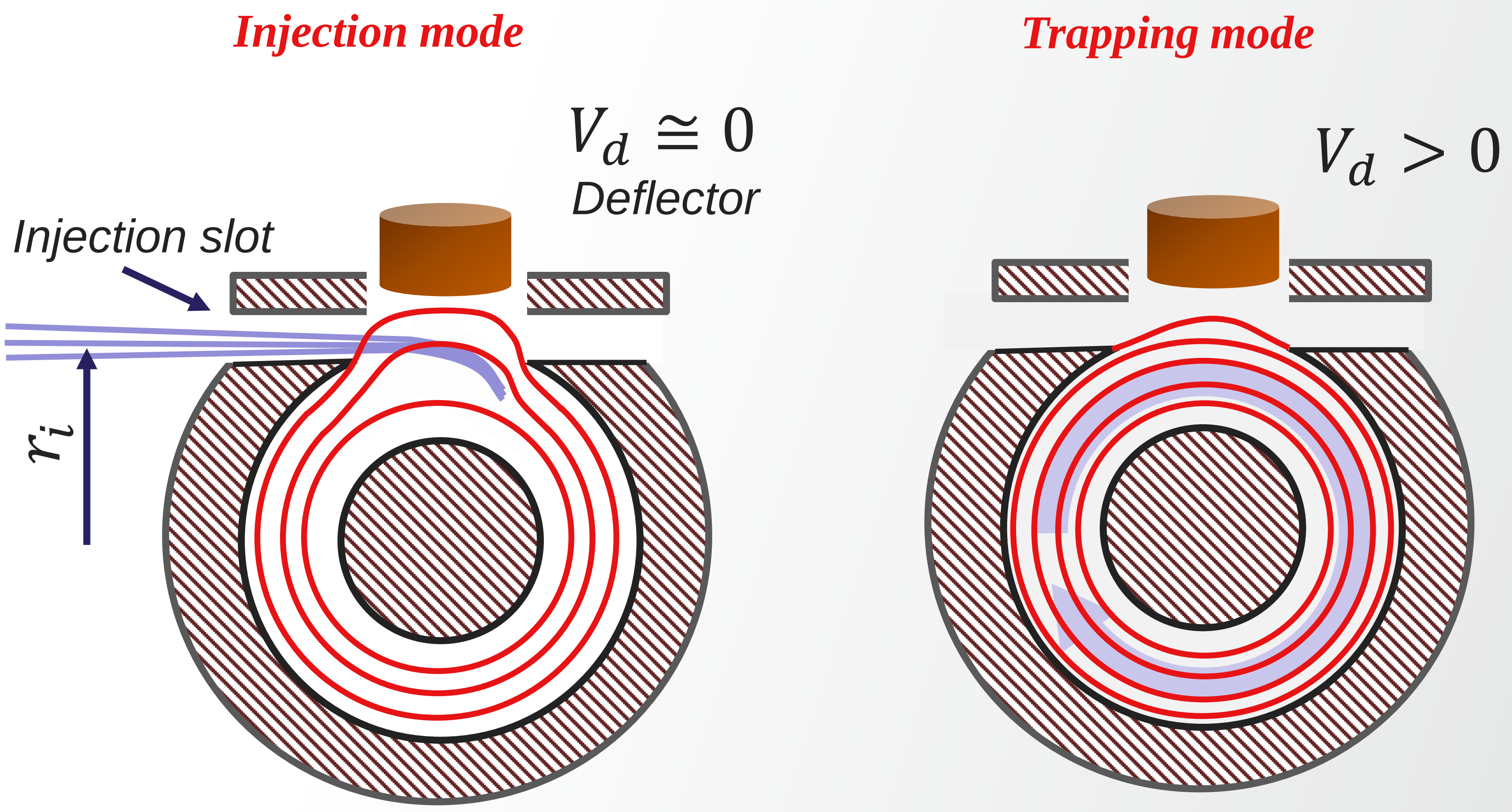


Deflector is set to steer ions into orbital motion

Deflector is set to compensate for the field bulging into the injection slot

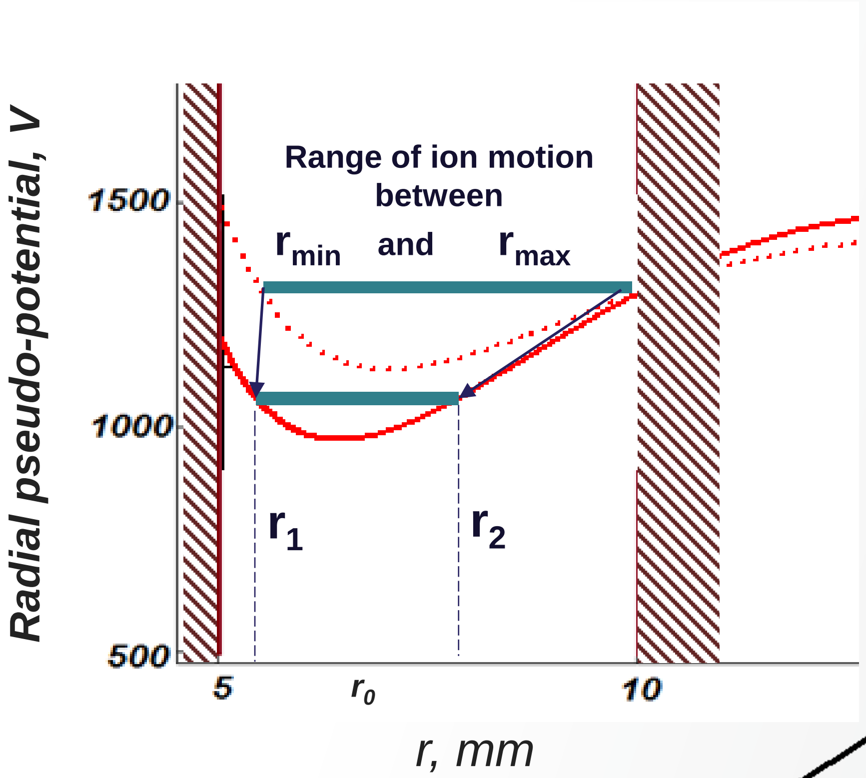
An ion acquires the angular momentum $K = mvr_i = \sqrt{2m\,zeU_a}\,r_i$

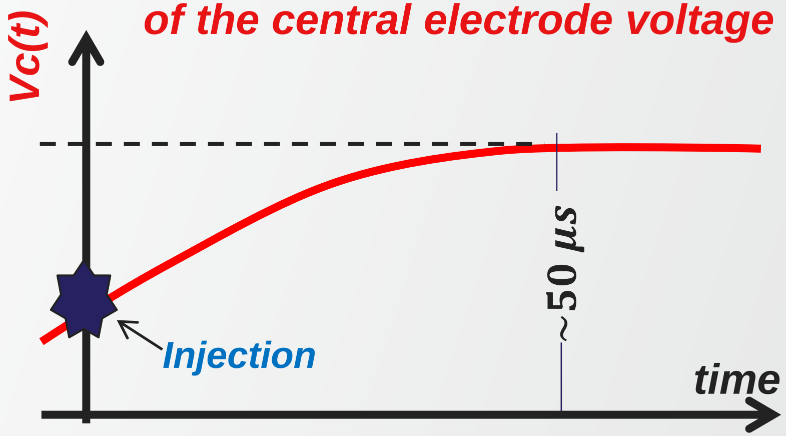
Core of Orbitrap technology

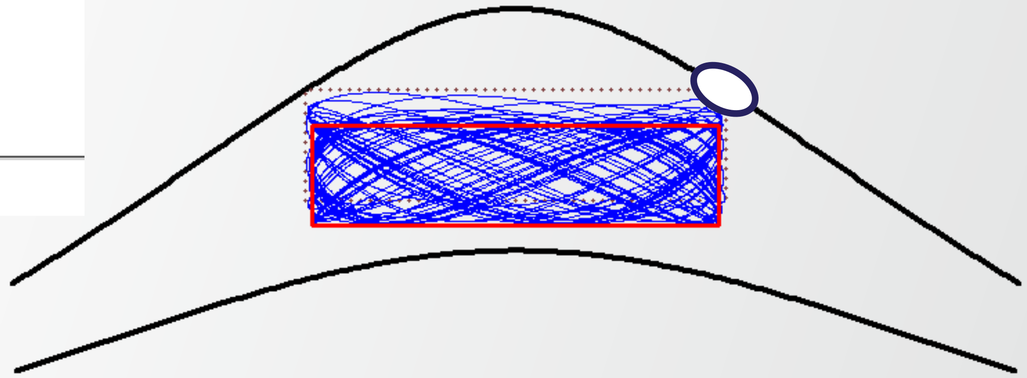
- *Pulsed ion source*
- *Off-axis injection*
- ***Dynamic squeezing***
- *Signal detection and processing*

$$U(r,t) = \frac{k^2 V_c(t)}{2}\left(r_m^2 \ln\frac{r}{r_m} - \frac{r^2}{2}\right) + \frac{K^2}{2m^2 r^2}$$

(centrifugal force)





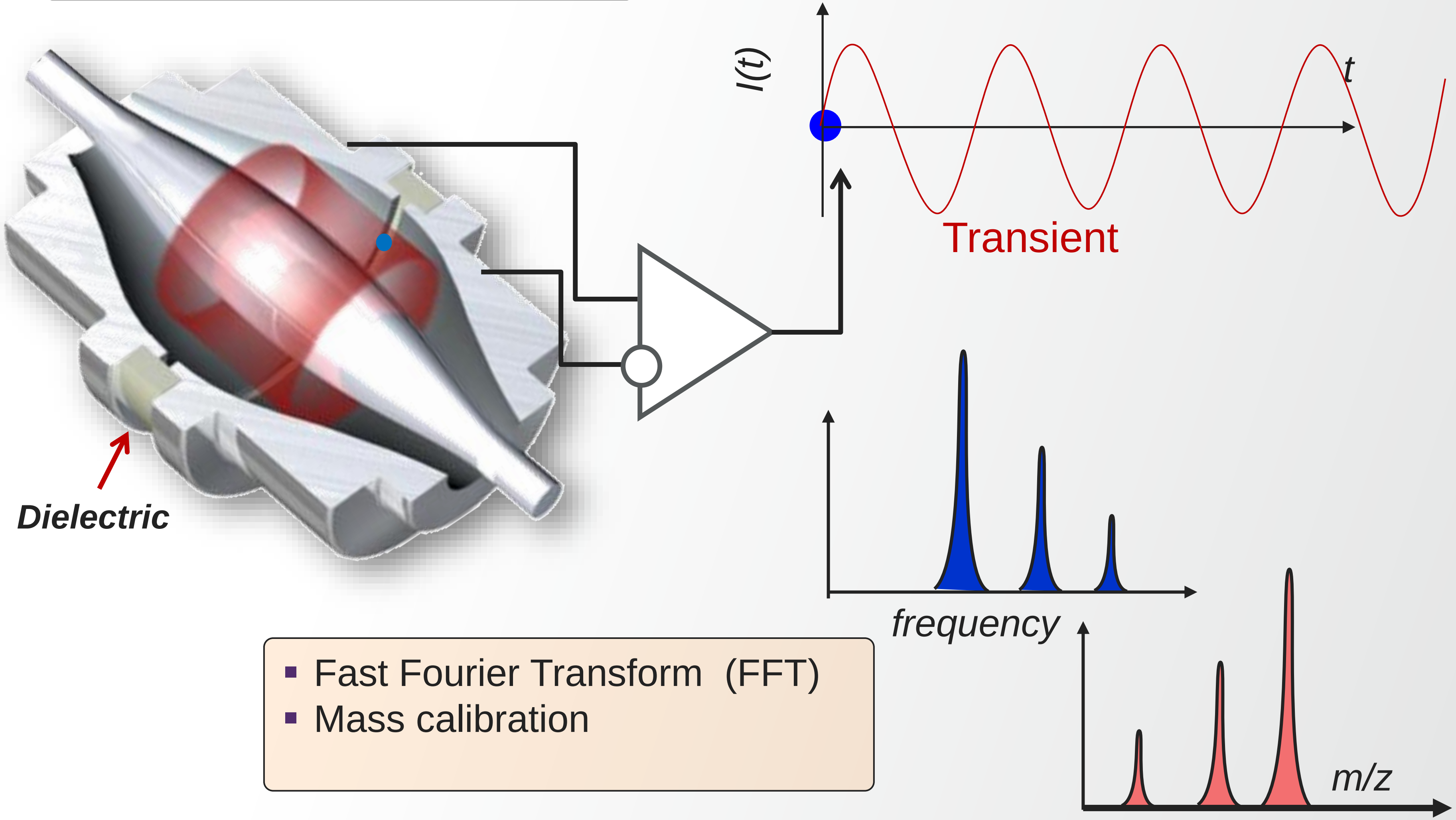


Core of Orbitrap technology

- *Pulsed ion source*
- *Off-axis injection*
- *Dynamic squeezing*
- ***Signal detection and processing***

- The outer electrode is split into two isolated sections

- The differential induced current signal is amplified and digitalized



- Fast Fourier Transform (FFT)
- Mass calibration

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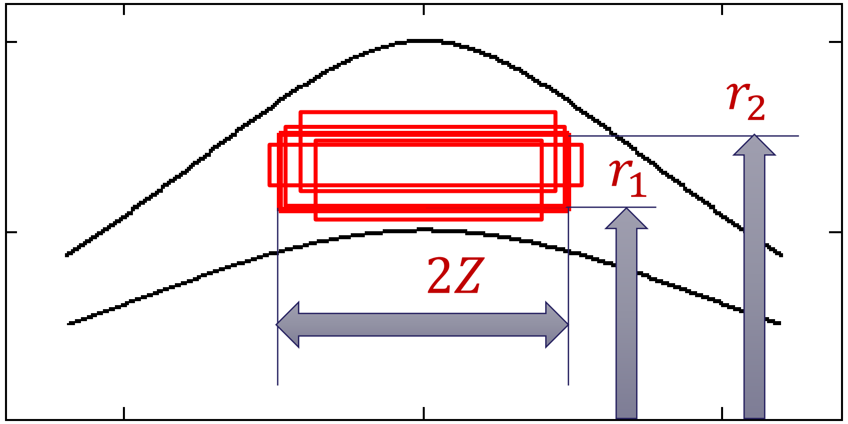
Is Orbital Trap precise enough?

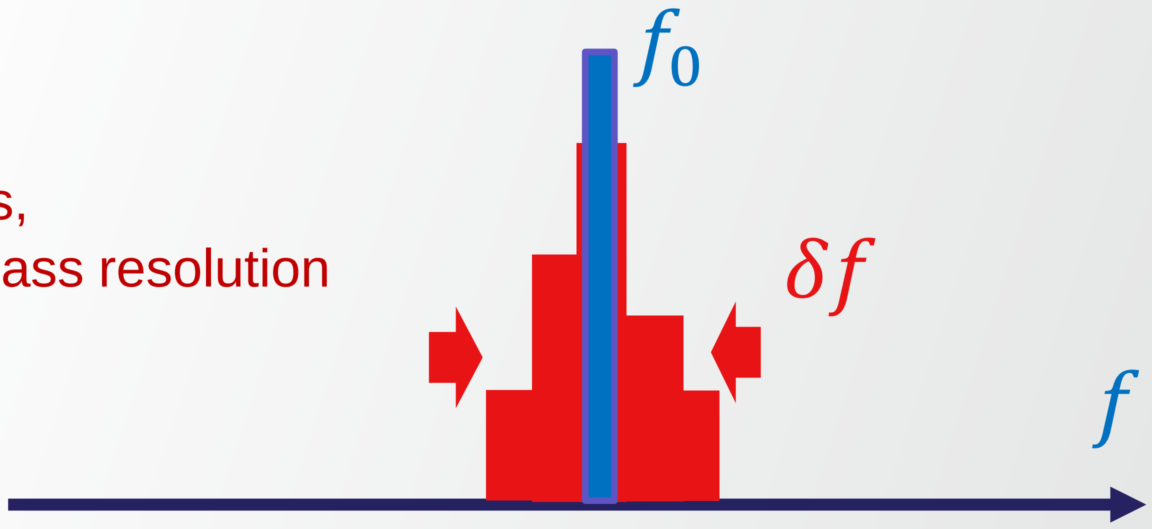
An ion orbit is characterized by three parameters Z, r_1, r_2. Different orbits are populated.



Ideal trap
with exact QL field $f_0 = \frac{C_0}{\sqrt{m/z}}$

(frequency is independent on the ion orbit)

Non-ideal trap: $f = f_0 + \delta f(Z, r_1, r_2)$



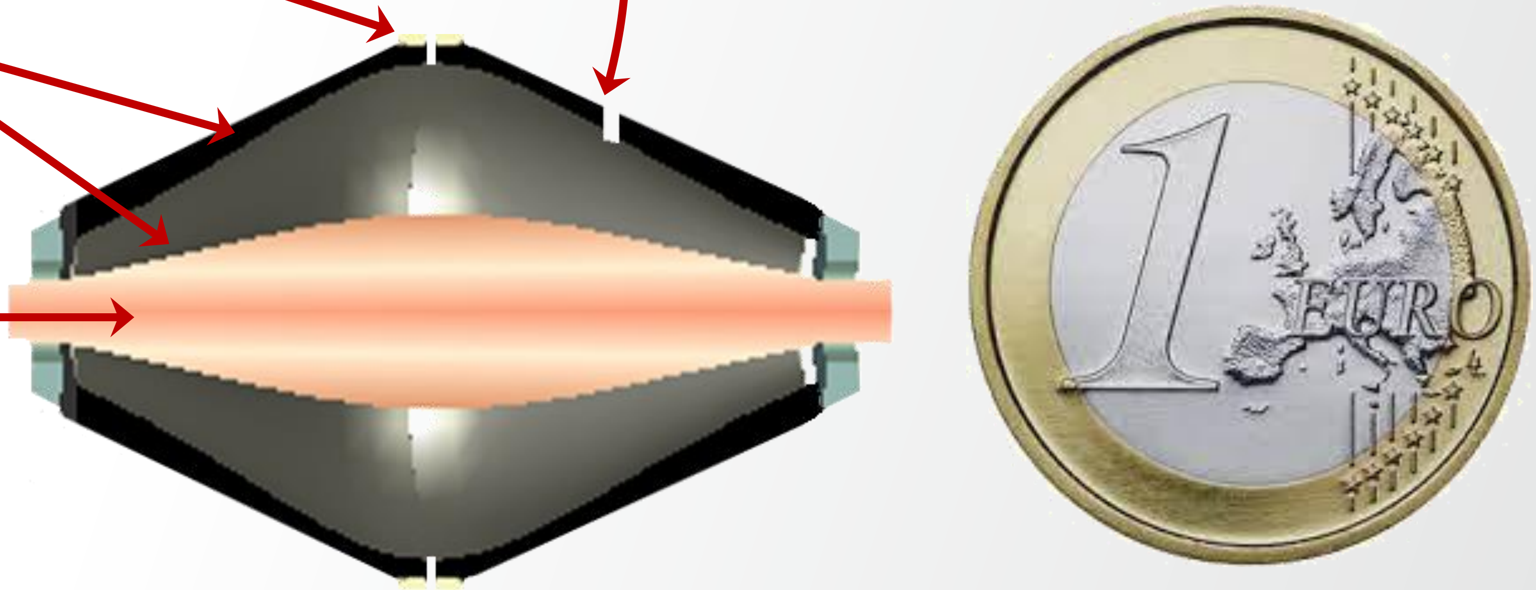
Ions have somewhat different oscillation frequencies,
resulting in an extra frequency spread and loss of mass resolution

Why the field distribution is not exact

Machining precision
- Injection slot
- Central slot
- Roundness
- Roughness

Assembly precision
- Shift and tilt
- End fringes

Potential perturbations
- Surface chemical potential
- Space charge



Some aspects of the perturbation theory

Ion motion in the **ideal** field

$$\ddot{Z} + \omega^2 Z = 0$$

$$Z(t) = Z_0 \cos(\omega t + \zeta_0)$$

Some aspects of the perturbation theory

Non-ideal
ion trap

$$\ddot{Z} + \omega^2 Z = -\frac{e}{m}\nabla_z \delta\varphi$$ ← Field error

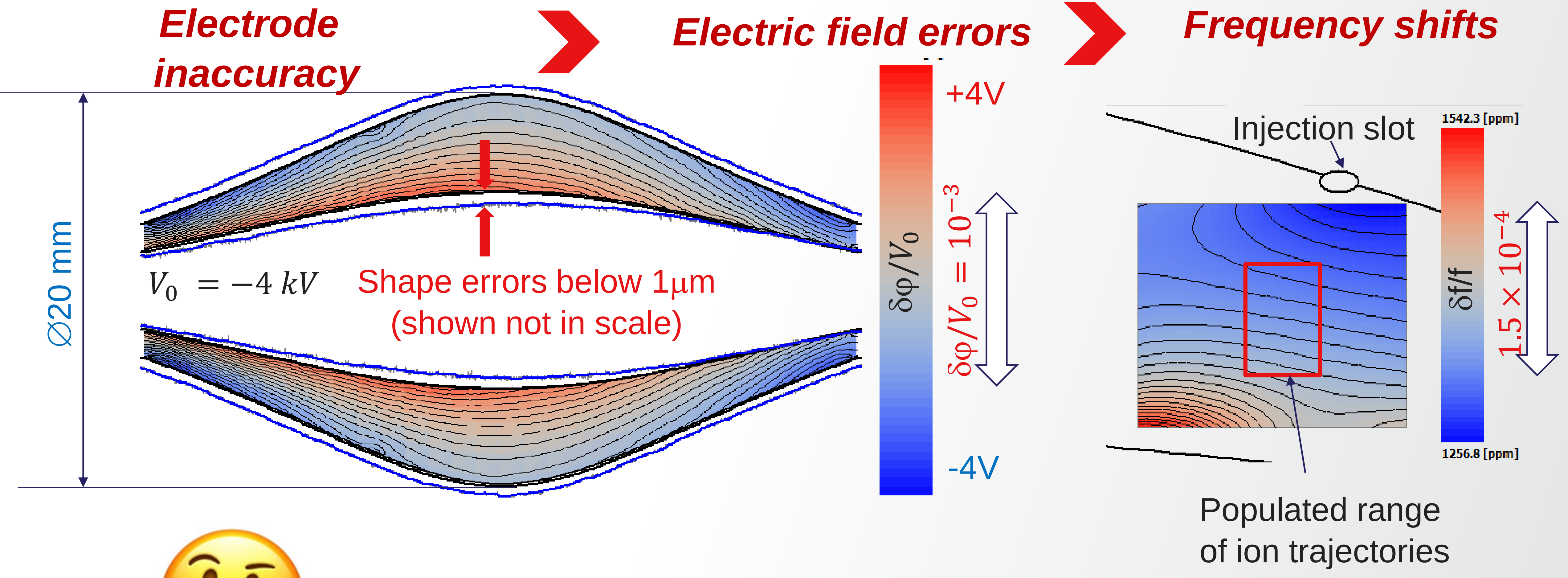
$$Z(t) = Z_0(t)\cos(\omega t + \zeta(t))$$

The amplitude *Z* and the phase offset ζ are *slow* functions of time defined by the ODEs

(Frequency perturbation) $$\dot{\zeta} = \frac{e}{2\pi m Z} \times \underset{r_1 \dots r_2}{\text{average}}\left(\int_0^{2\pi} \nabla_z \delta\varphi\,(Z\cos\xi, r)\cos\xi\ d\xi\right)$$

(Amplitude evolution) $$\dot{Z} = \frac{e}{2\pi m} \times \underset{r_1 \dots r_2}{\text{average}}\left(\int_0^{2\pi} \nabla_z \delta\varphi\,(Z\cos\xi, r)\, sin\,\xi\ d\xi\right)$$

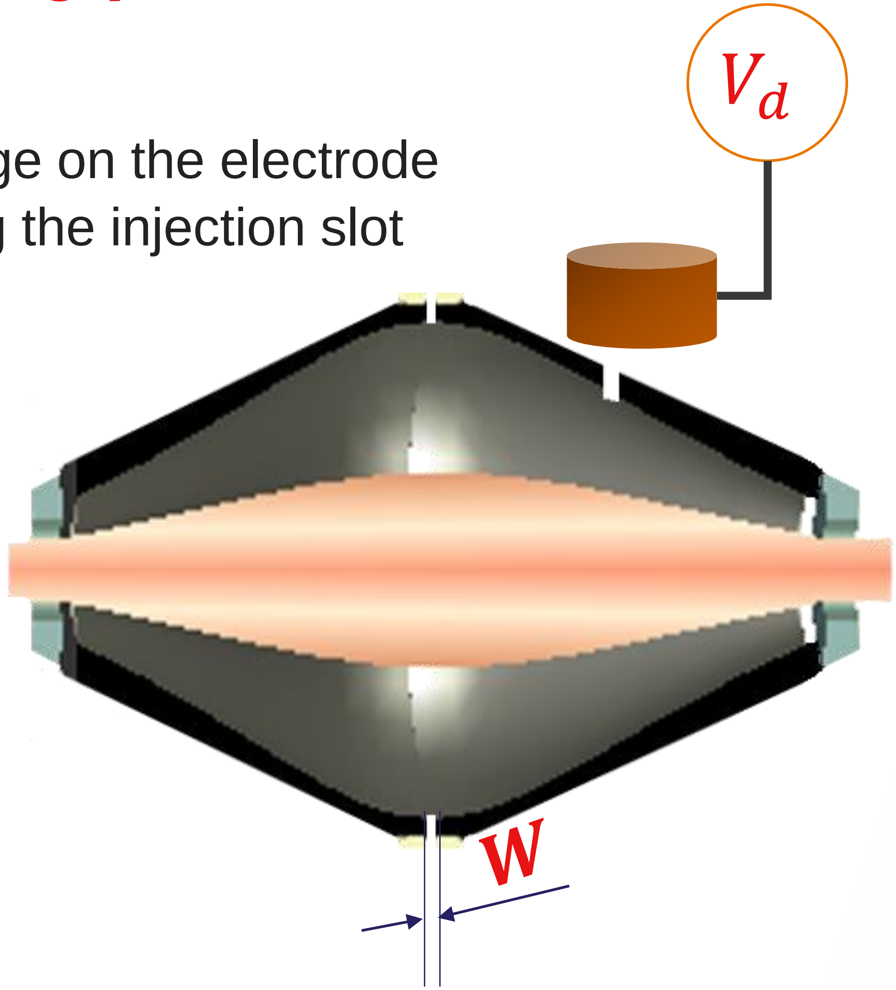
Electrode manufacturing errors



The mass resolution may narrowly reach ***10,000.*** Not really exciting...

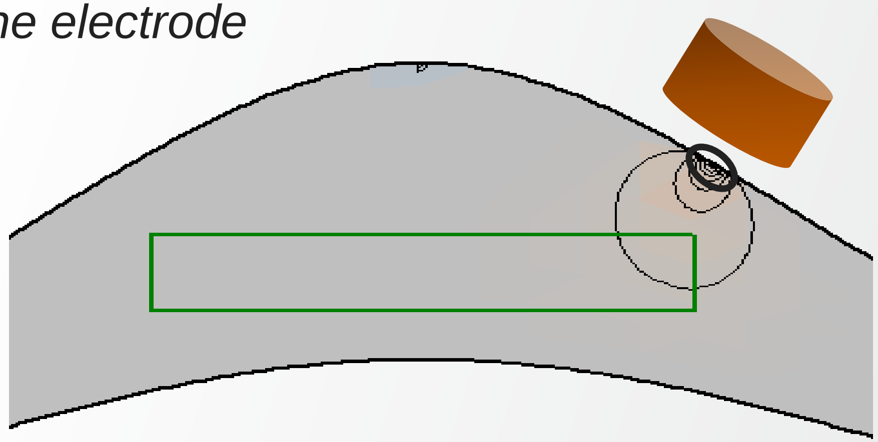
Tuning parameters

Voltage on the electrode facing the injection slot

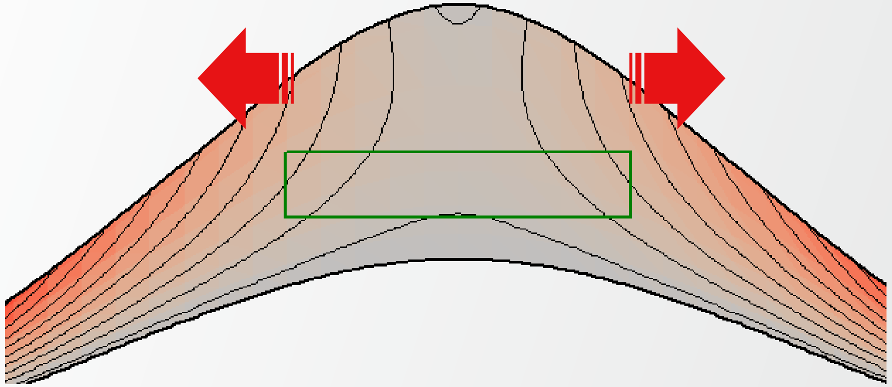


Width of the dielectric (quartz) spacer between the outer electrodes

More positive voltage applied to the electrode

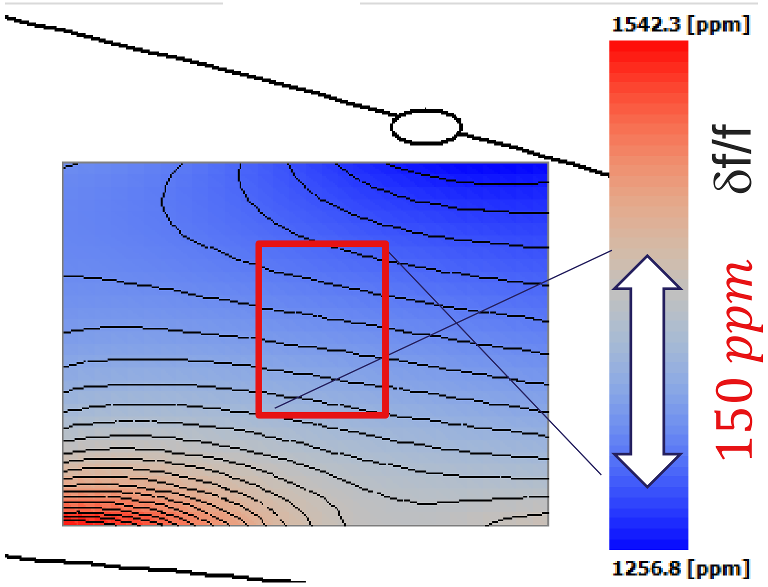


Separation between outer electrodes is modified by a few microns



Tuning parameters

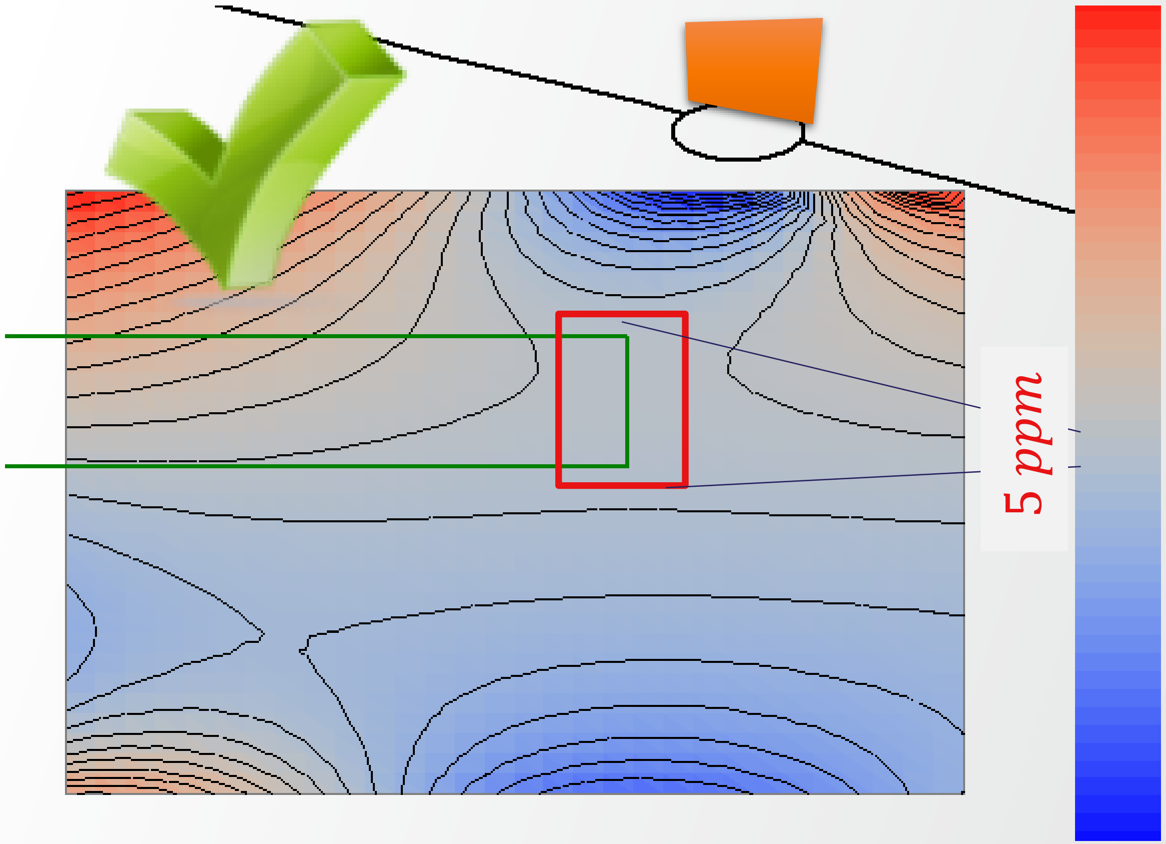
Before tuning:



After tuning:

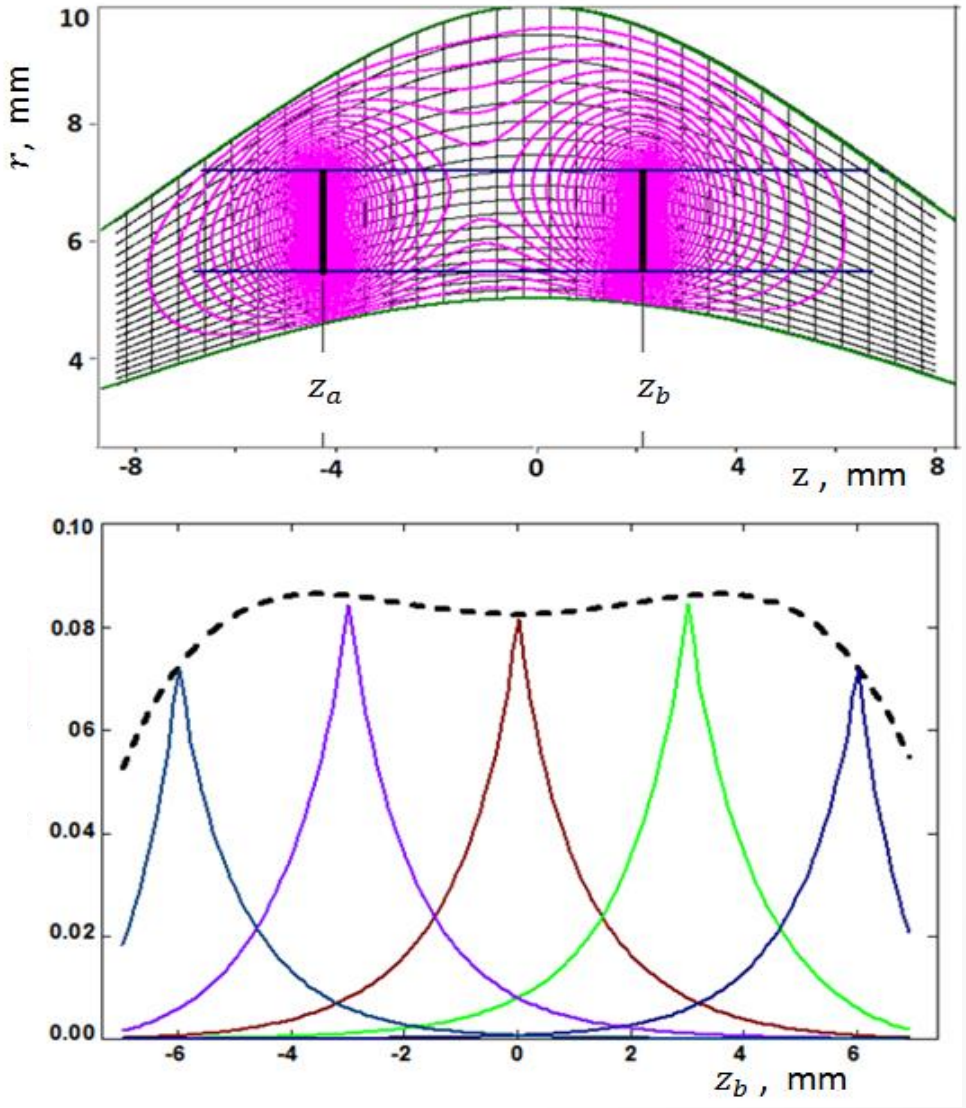
$\Delta W = 2.5\ \mu m$

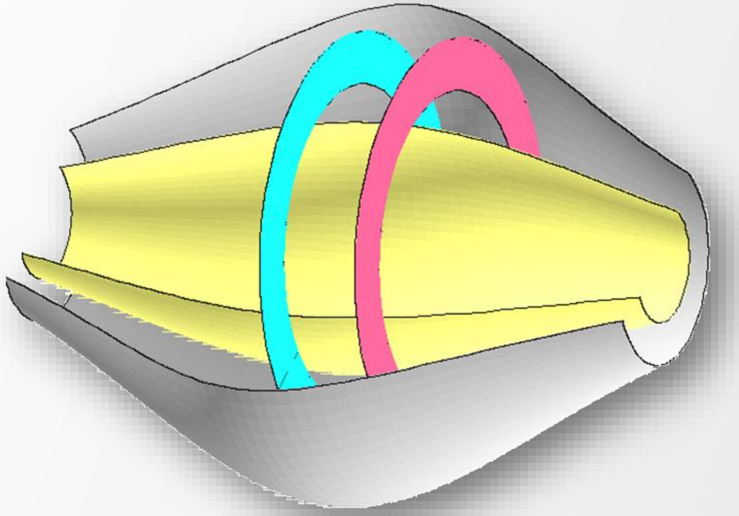
$\Delta V_d = +\,80\ V$



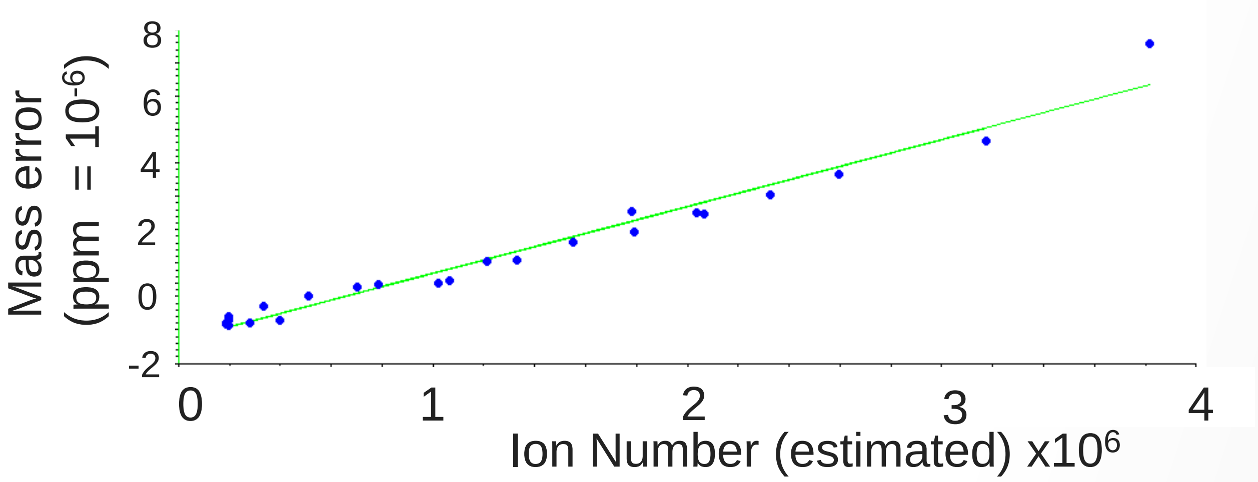
Individual tuning settings of only two parameters make the frequency shift level off inside the ion-populated domain. The mass resolving power improves by factor $10 \div 100$

Some aspects of space-charge dynamics



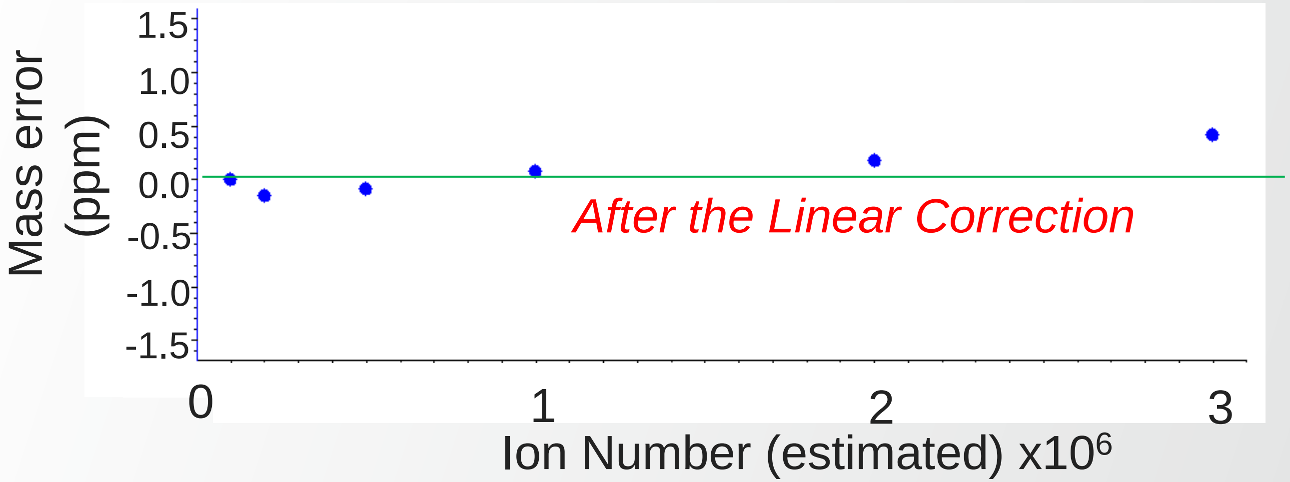


The cloud space charge

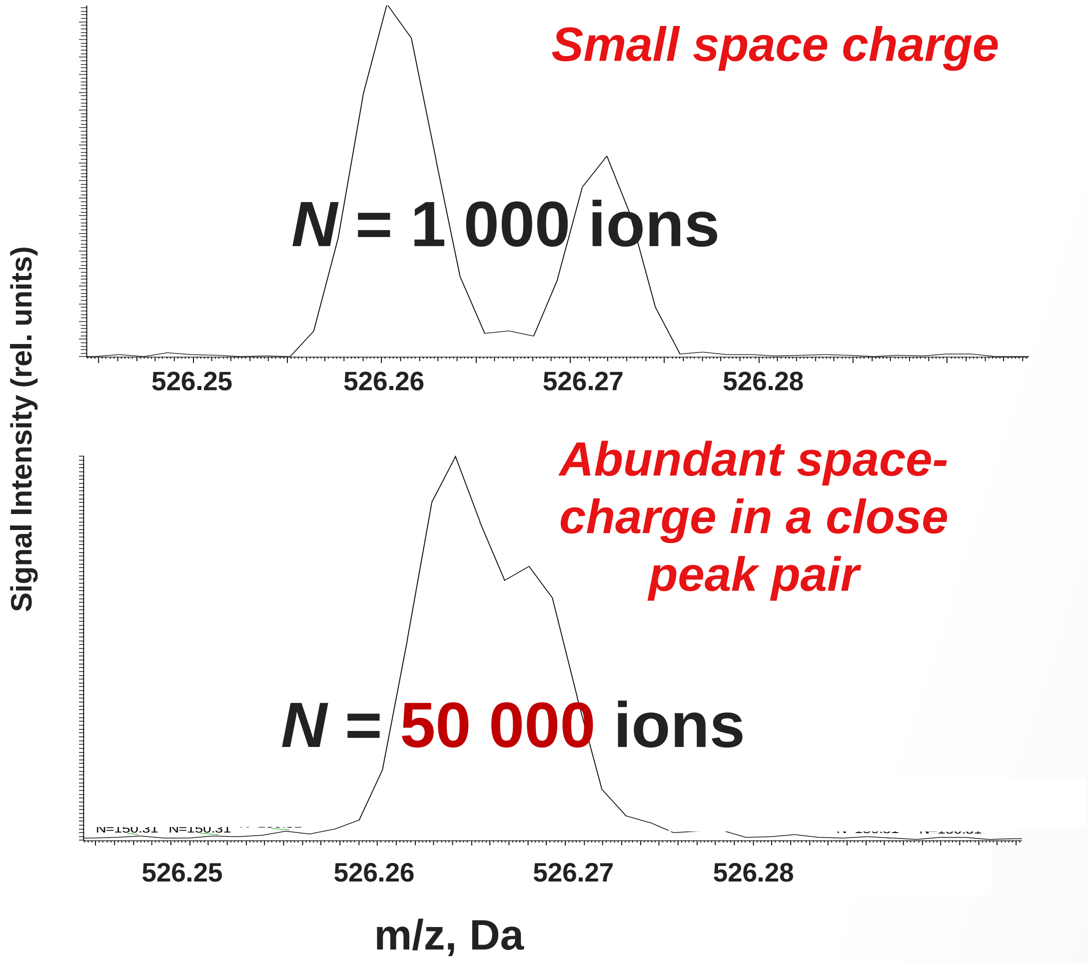


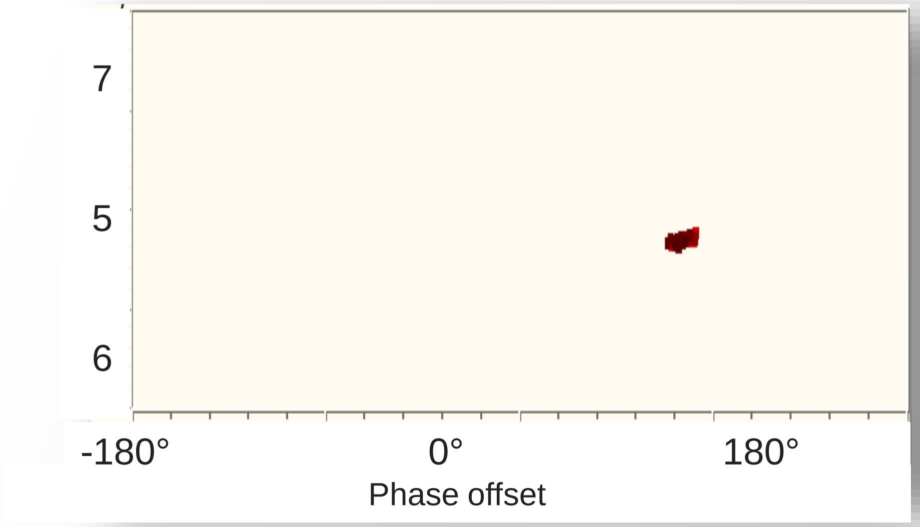
The space-charge generates a coherent frequency shift, and measured ion masses seem higher than they are.

In the practical range with below 1M charges trapped, the shift is around 1 ppm and is easily calibrated out.

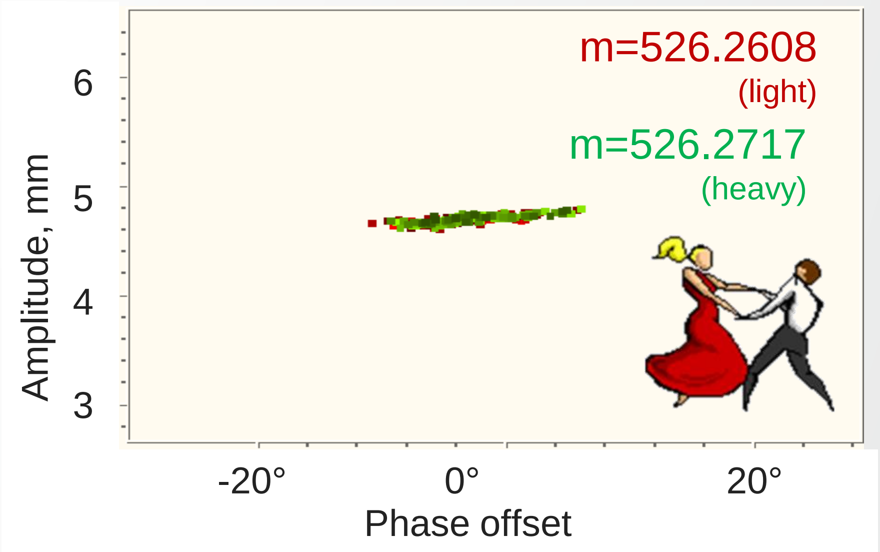


Resonant space-charge effects in close m/z peaks (self-bunching, coalescence)



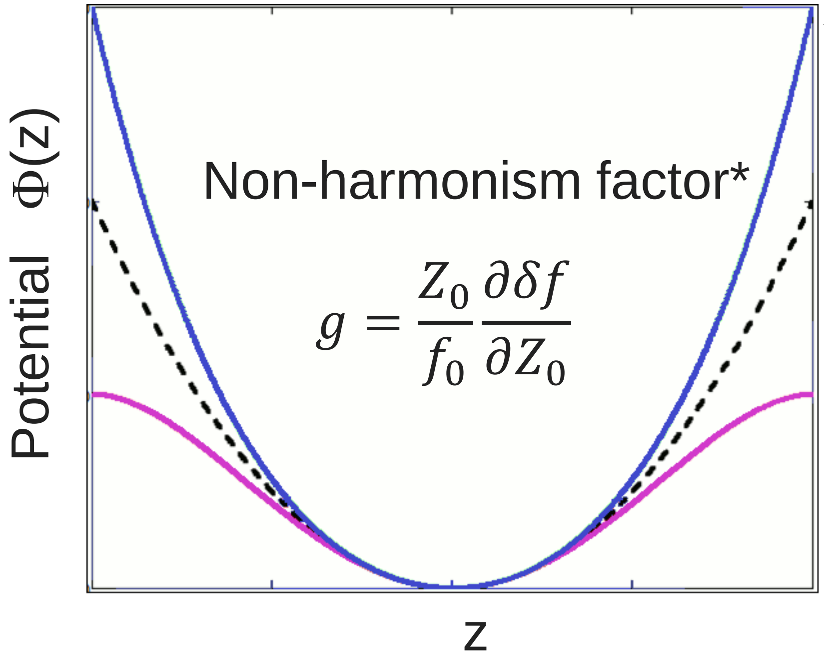


Ion energy is constant, the phases diverge



Energy is re-distributed between ions. Phases are locked

The coalescence v.s. perturbations

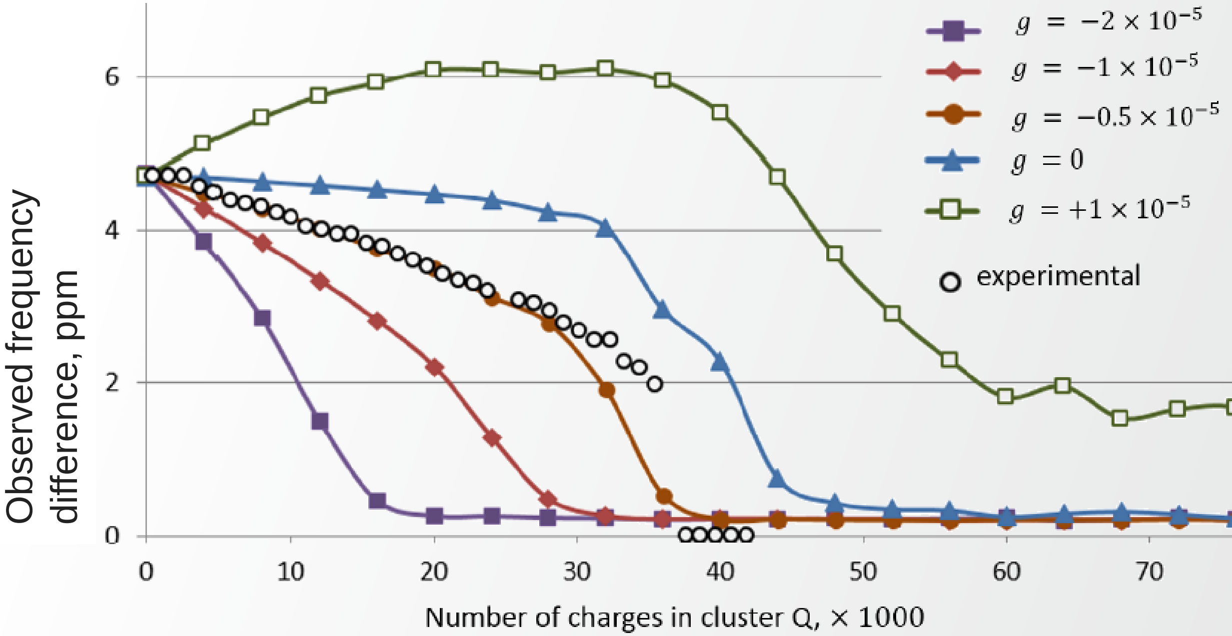


‘Hard’ potential well ($g > 0$)
steeper than quadratic

‘Ideal’ quadratic potential well
($\omega = \omega_0$ = *const*)

‘Soft’ potential well ($g < 0$)
shallower than quadratic

**frequency slightly (ppm level) changes with the oscillation amplitude*



Family of Orbitrap Mass Spectrometers

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Acknowledgements

Orbitrap Exploris team

Orbitrap Eclipse team

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Thank you for your attention!

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