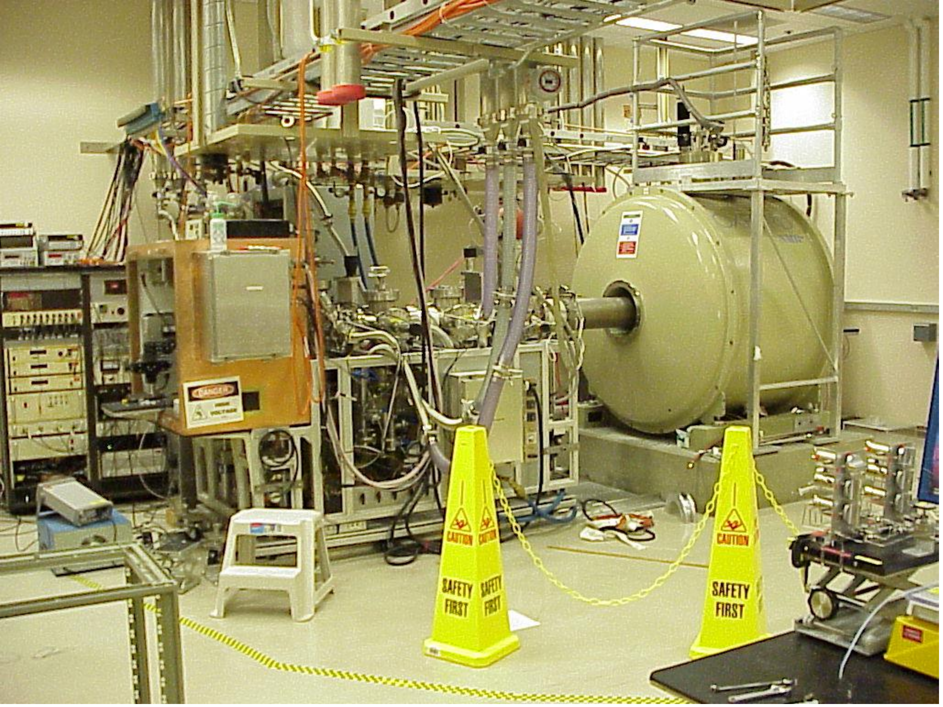
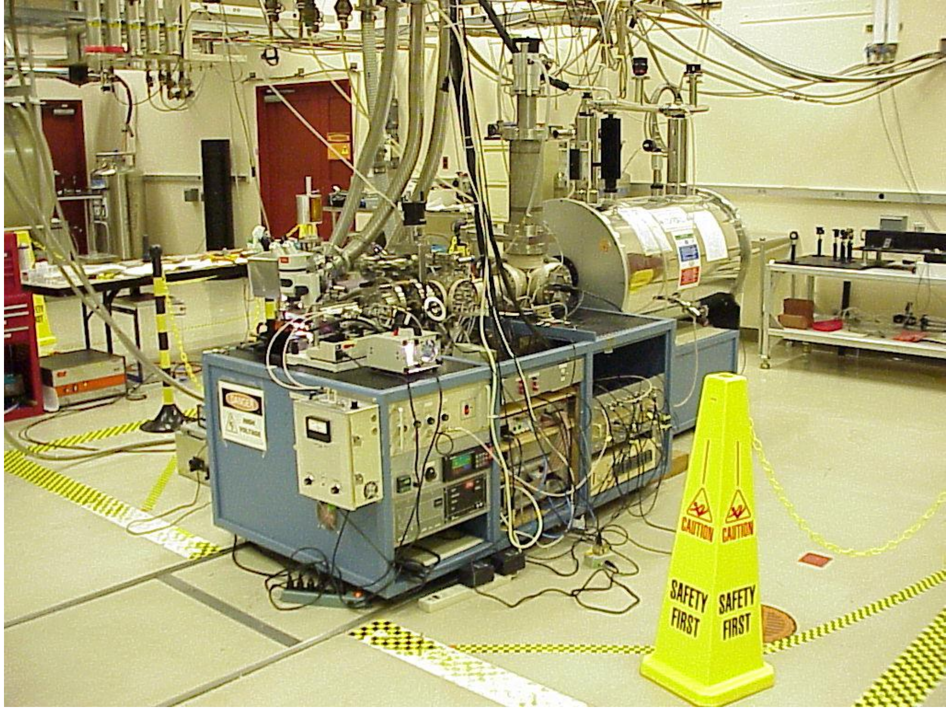
FT ICR cell: How to make the best

Evgeny Nikolaev
Skolkovo Institute of Science and Technology

Since introduction in 1974 FT ICR continue to be the best in resolving power and mass measurement accuracy!


DANGER
CAUTION
SAFETY FIRST


DANGER
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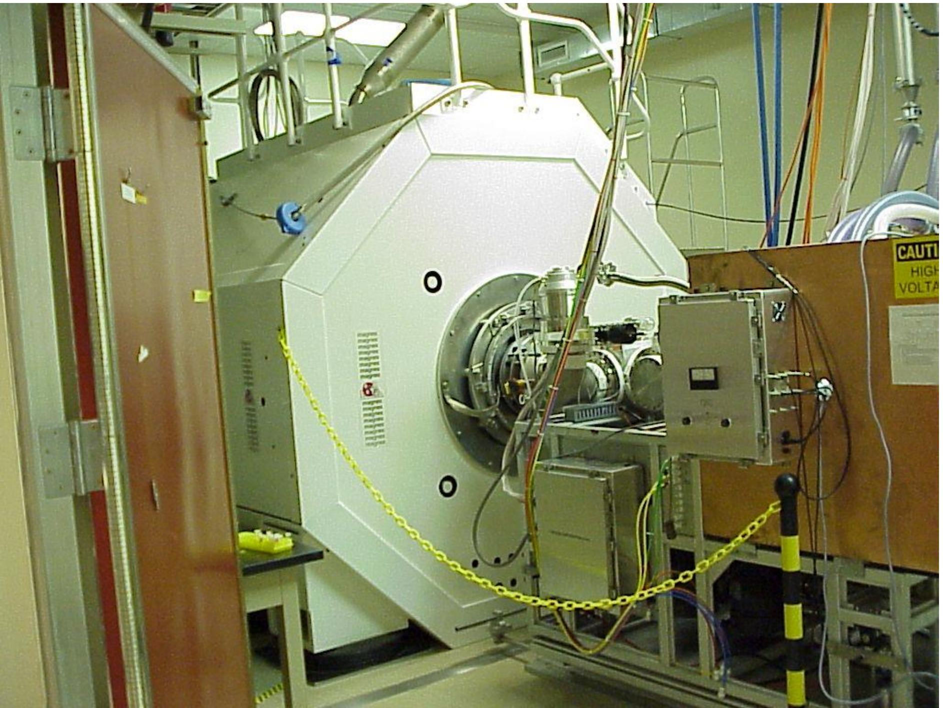
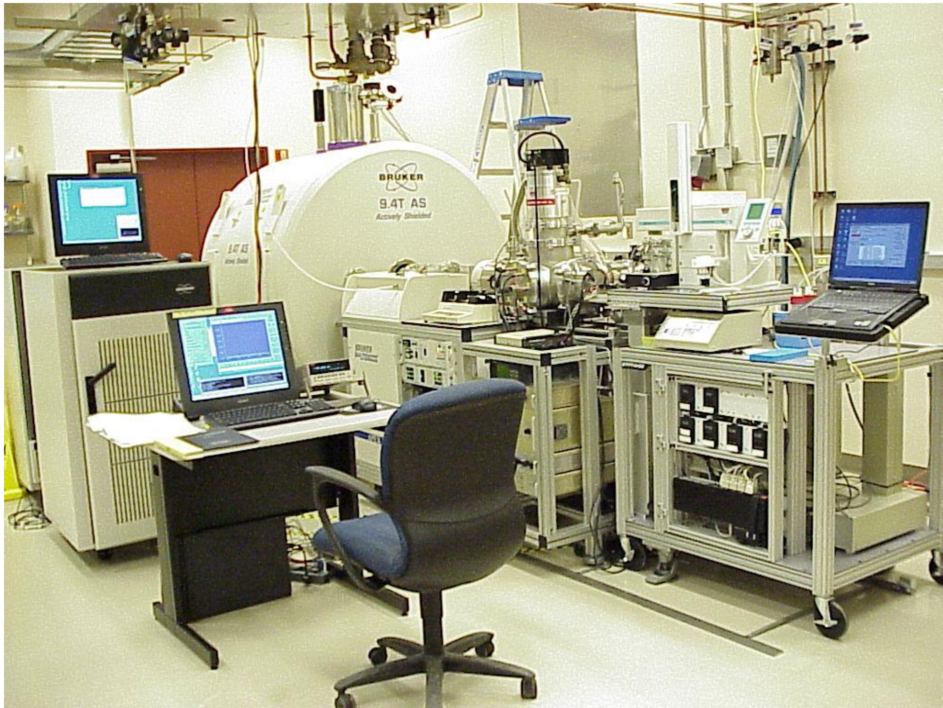
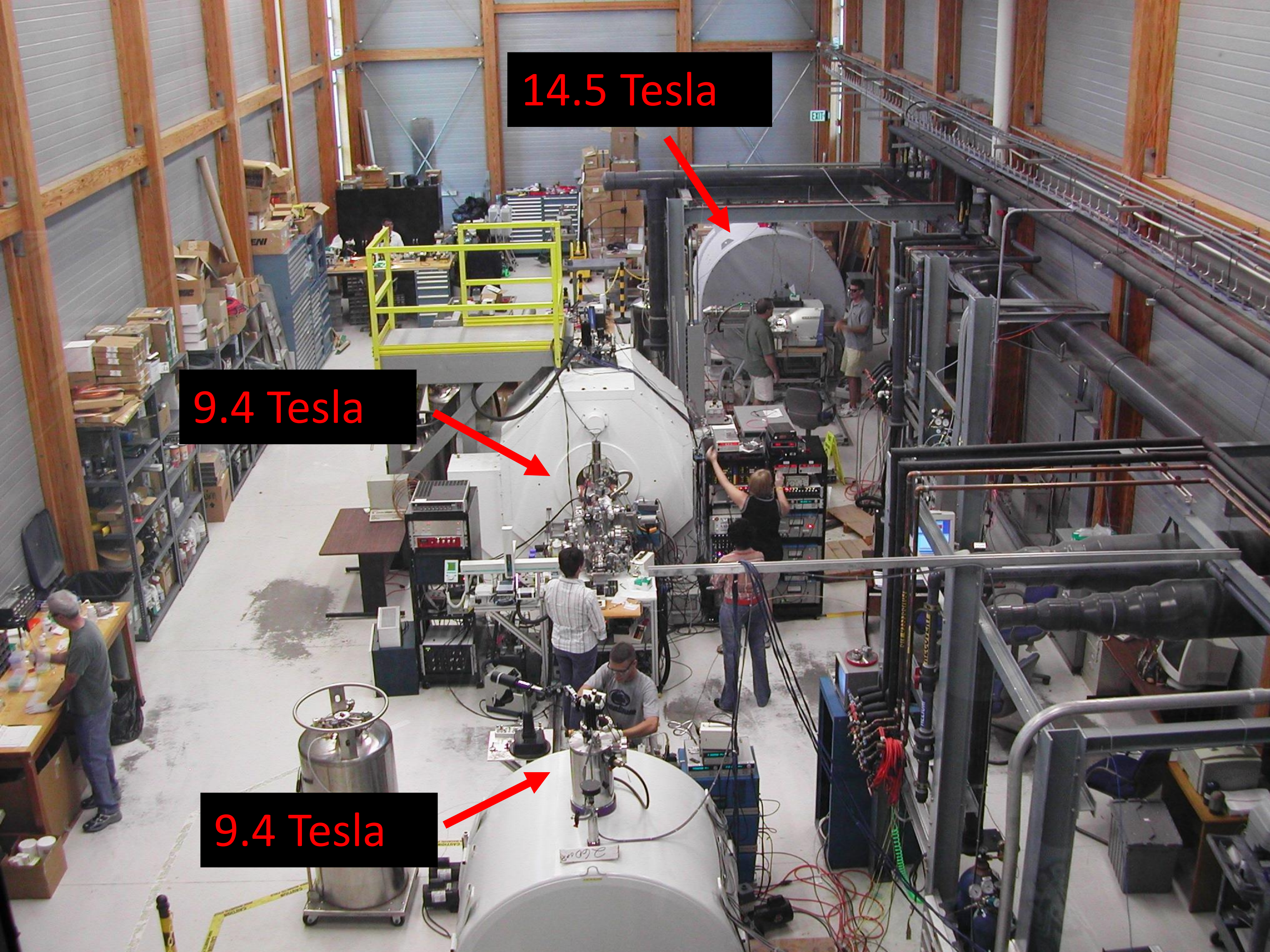
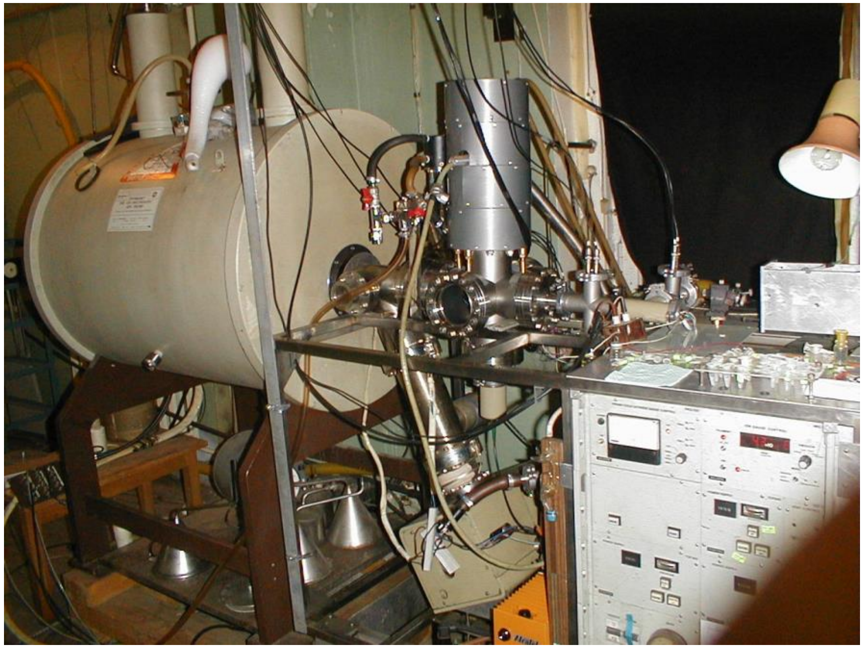



BRUKER
9.4T AS
Actively Shielded


14.5 Tesla
9.4 Tesla
9.4 Tesla

National High Magnetic Field Laboratory NHMFL
(Tallahassee Florida)

From Alan Marshall 10th NA FTMS 21 T talk

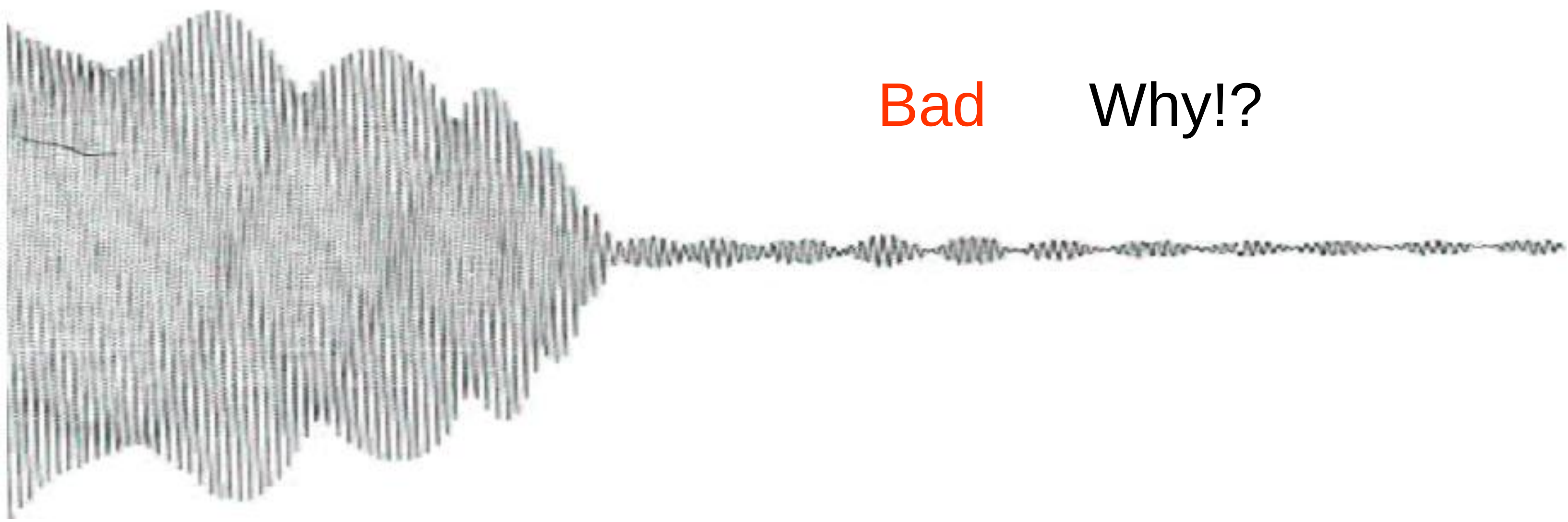


Moscow FT ICR instruments

After 47 years since introduction of FT ICR do we understand how it works?

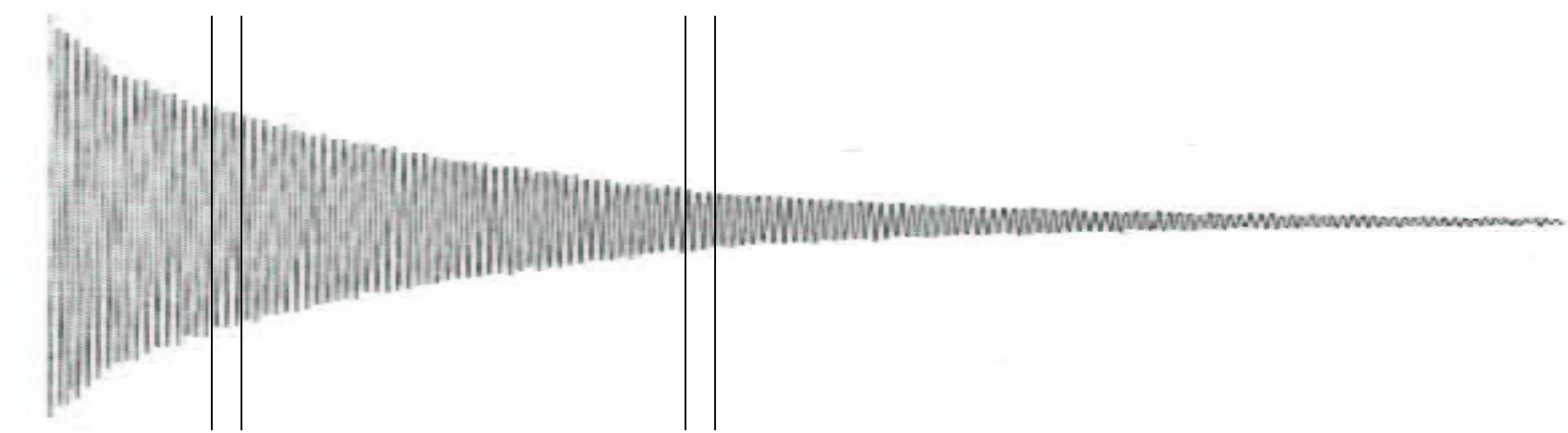
Good!

Signals from same m/z ions



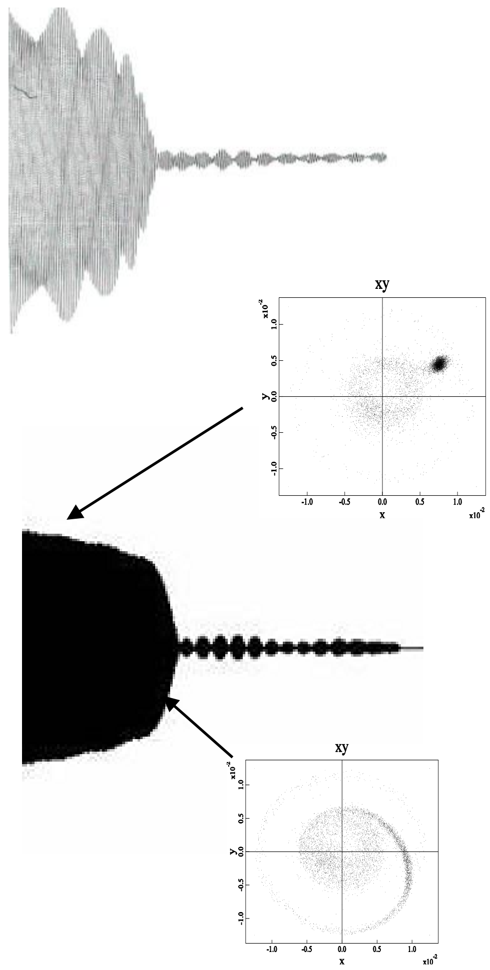
Bad Why!?

$\Omega(t)$ $\Omega(t+\Delta t)$



$\Omega(t+\Delta t) \neq \Omega(t)$ Why!?

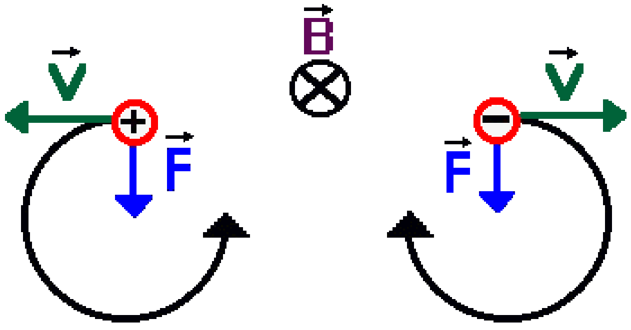
Strange signal forms



Experimental

Simulated

Charged particle in magnetic field



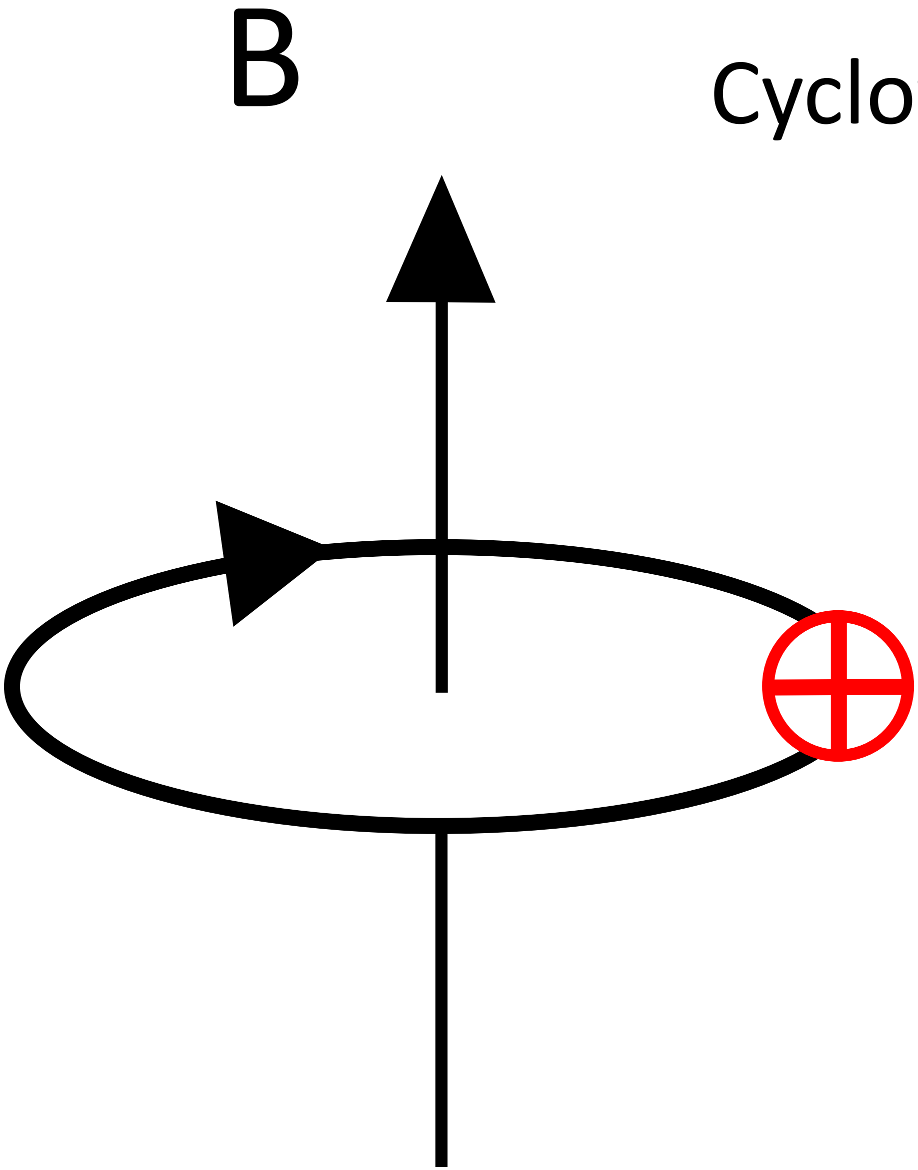
Lorentz force F=ze*v*B = m*v²/r

v/r = 2πω,

ze*B = m*2πω

ω = B*ze/2πm (cyclotron frequency)

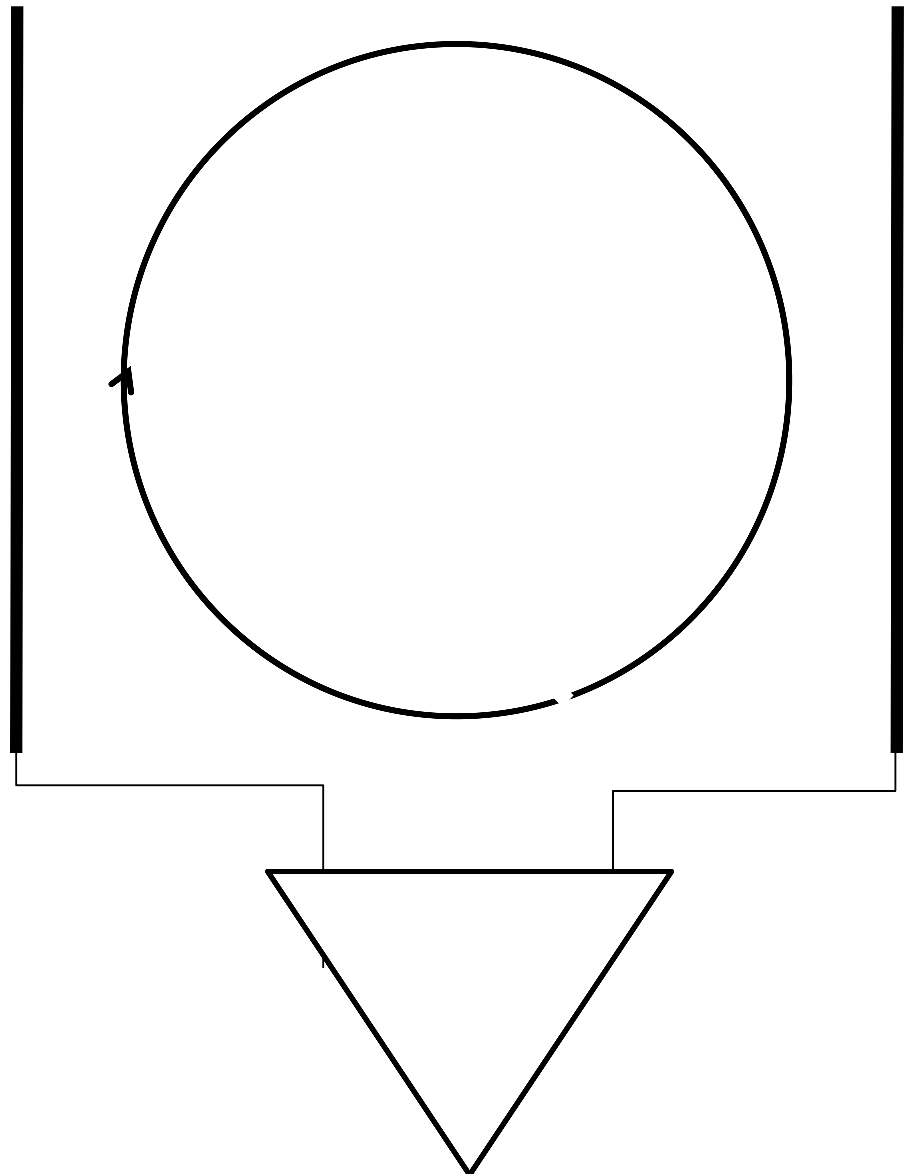
Cyclotron motion of ions



$$\omega = \frac{Z e B}{m}$$

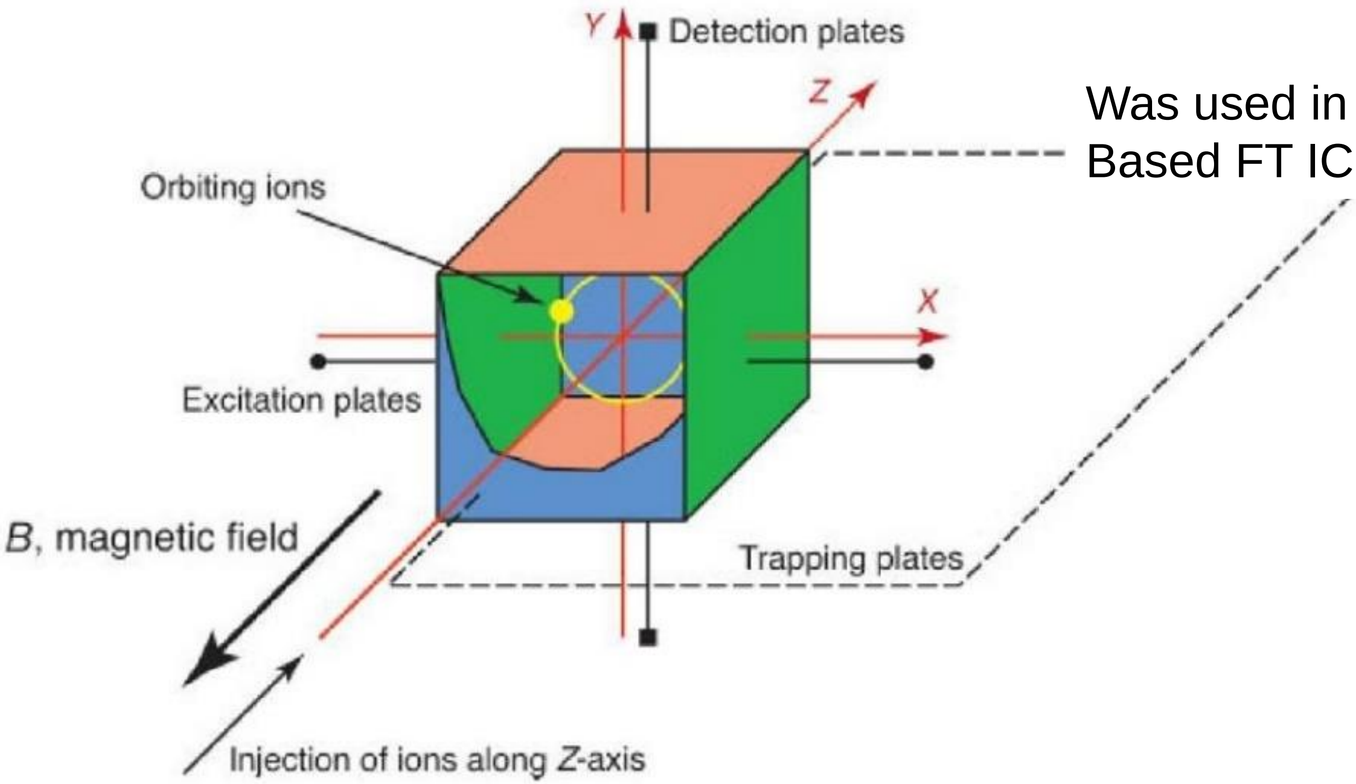
Ion motion in electric field free space

$$\omega_c = \frac{|eB|}{mc}$$

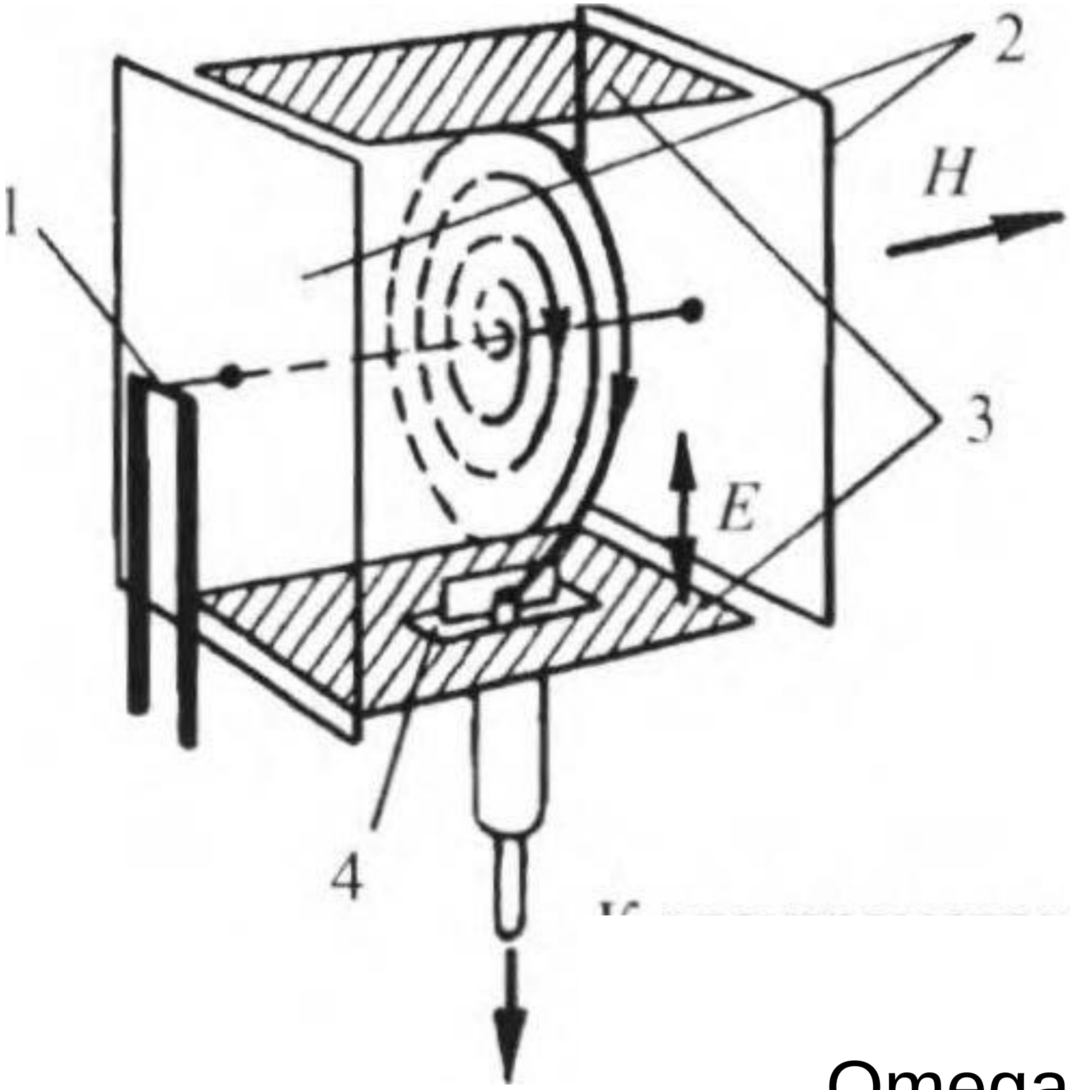


To excite cyclotron motion and detect the signal we need to trap ions

ICR Cells (Penning trap)

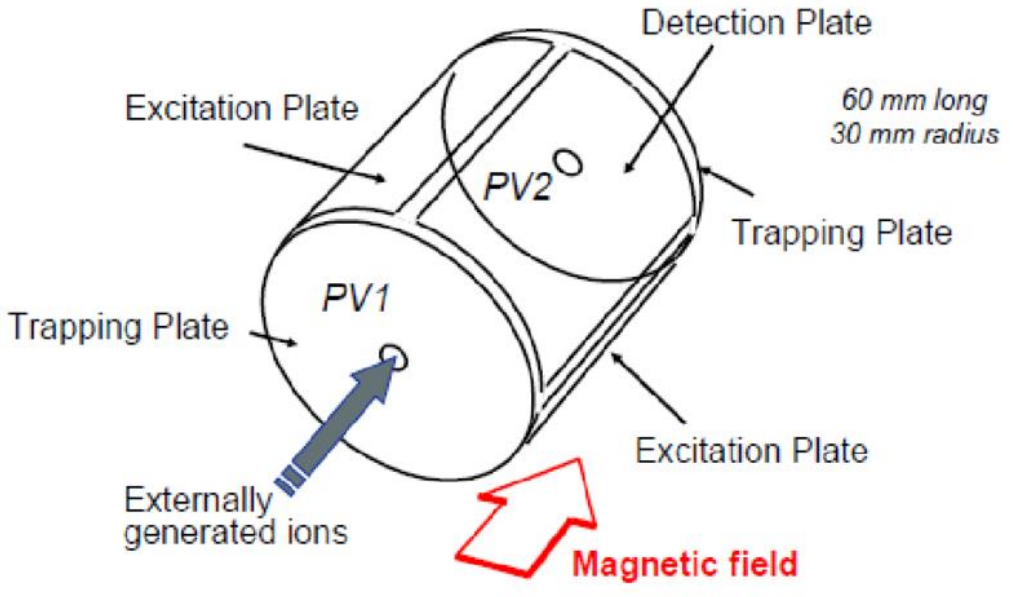


Was used in electromagnet
Based FT ICR instruments



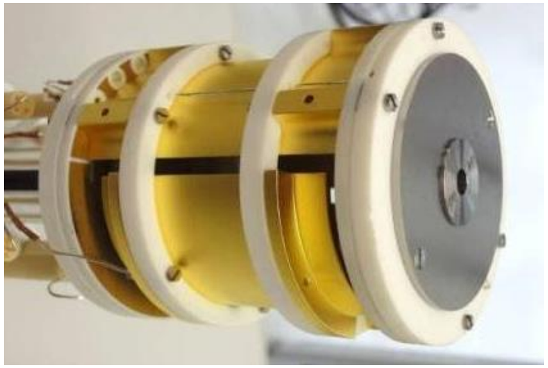
Omegatron

For superconductive magnets with cylindrical symmetry

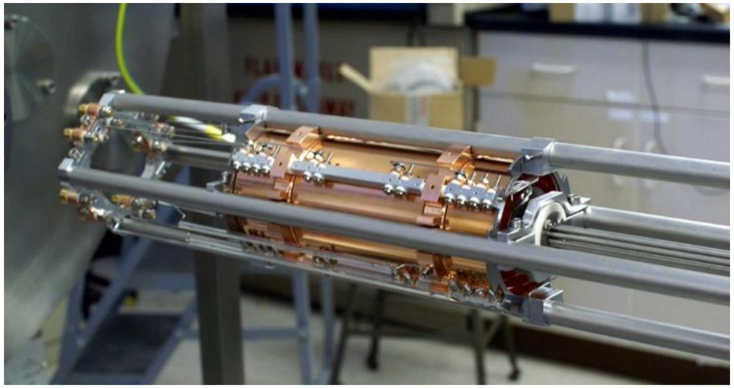


Most used cells

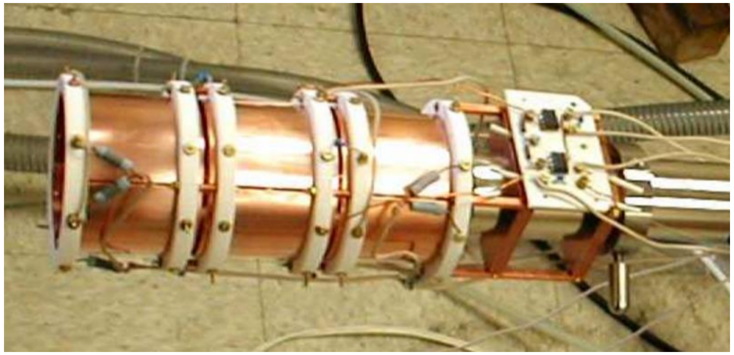
Bruker
Infinity cell
(until 2014)



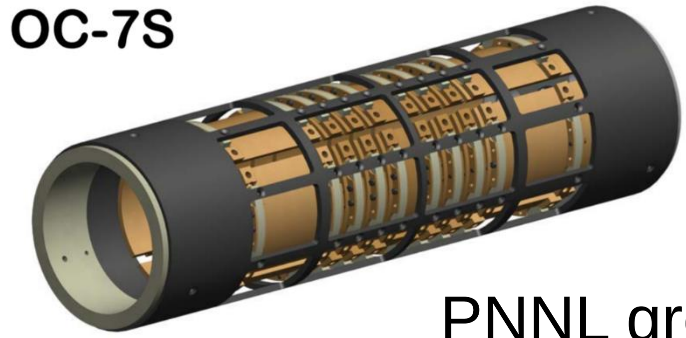
Thermo
LTQ FT
(until 2006)



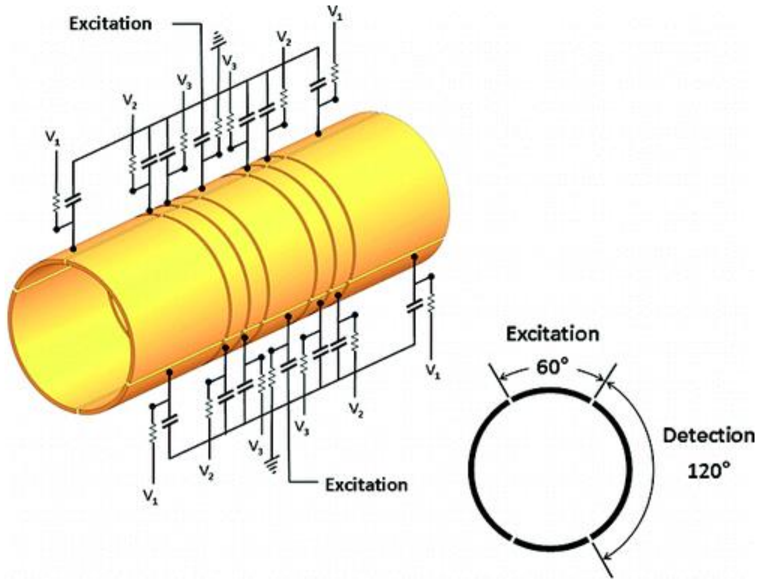
IonSpec Varian

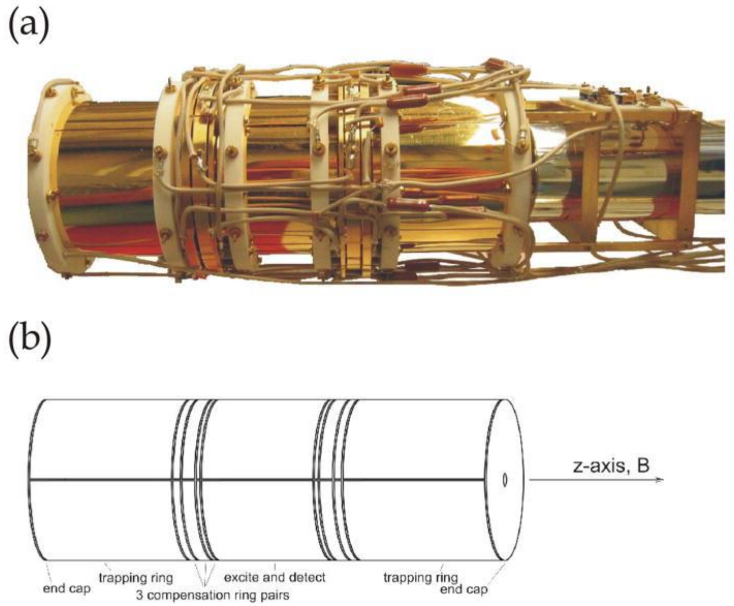


Compensated cells



PNNL group



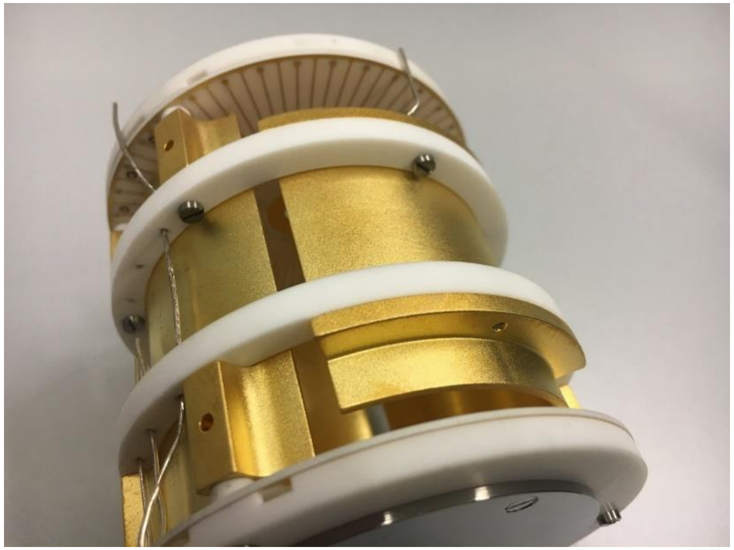


Marshall group

Gross group

Cells with trapping by pseudopotential

Nikolaev

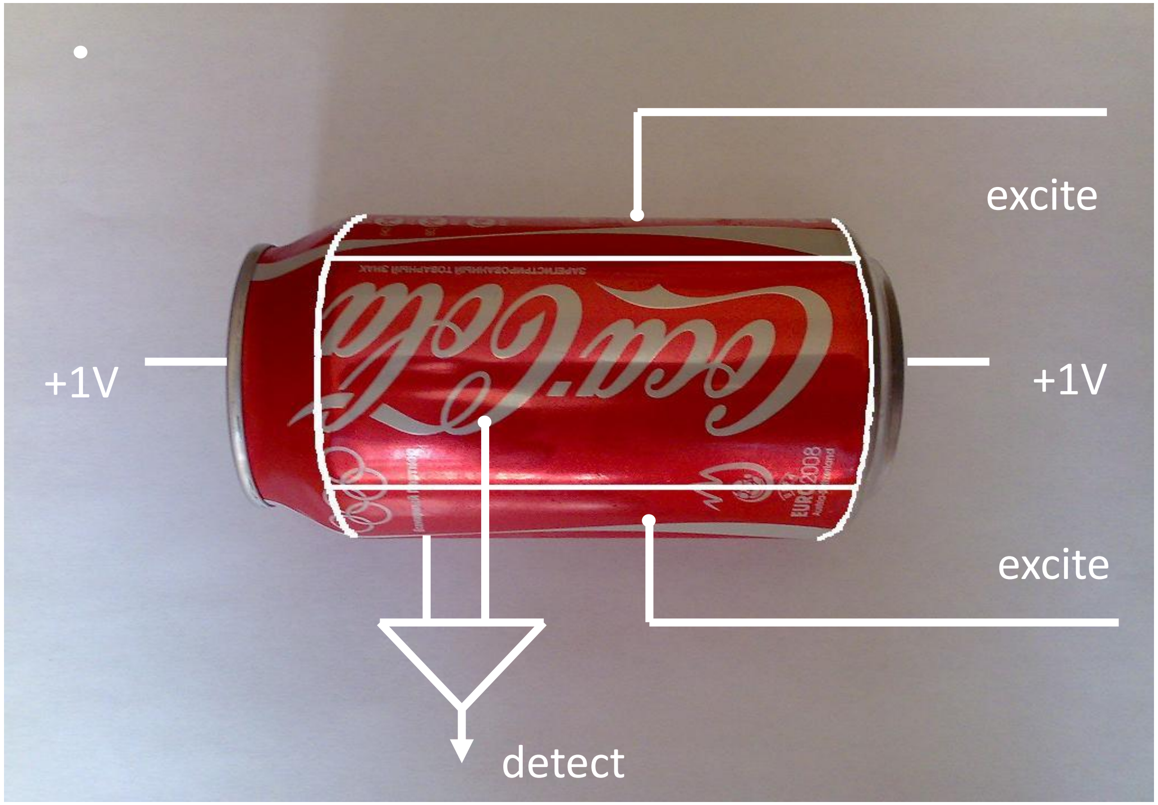


Bruker-Nikolaev

Cell with segmented trapping electrodes

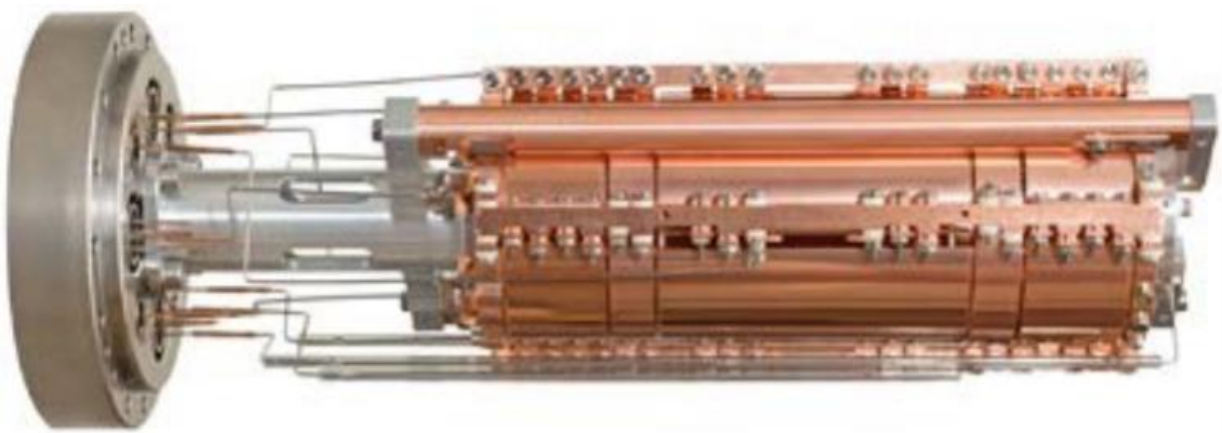
Bruce

Fancy cells

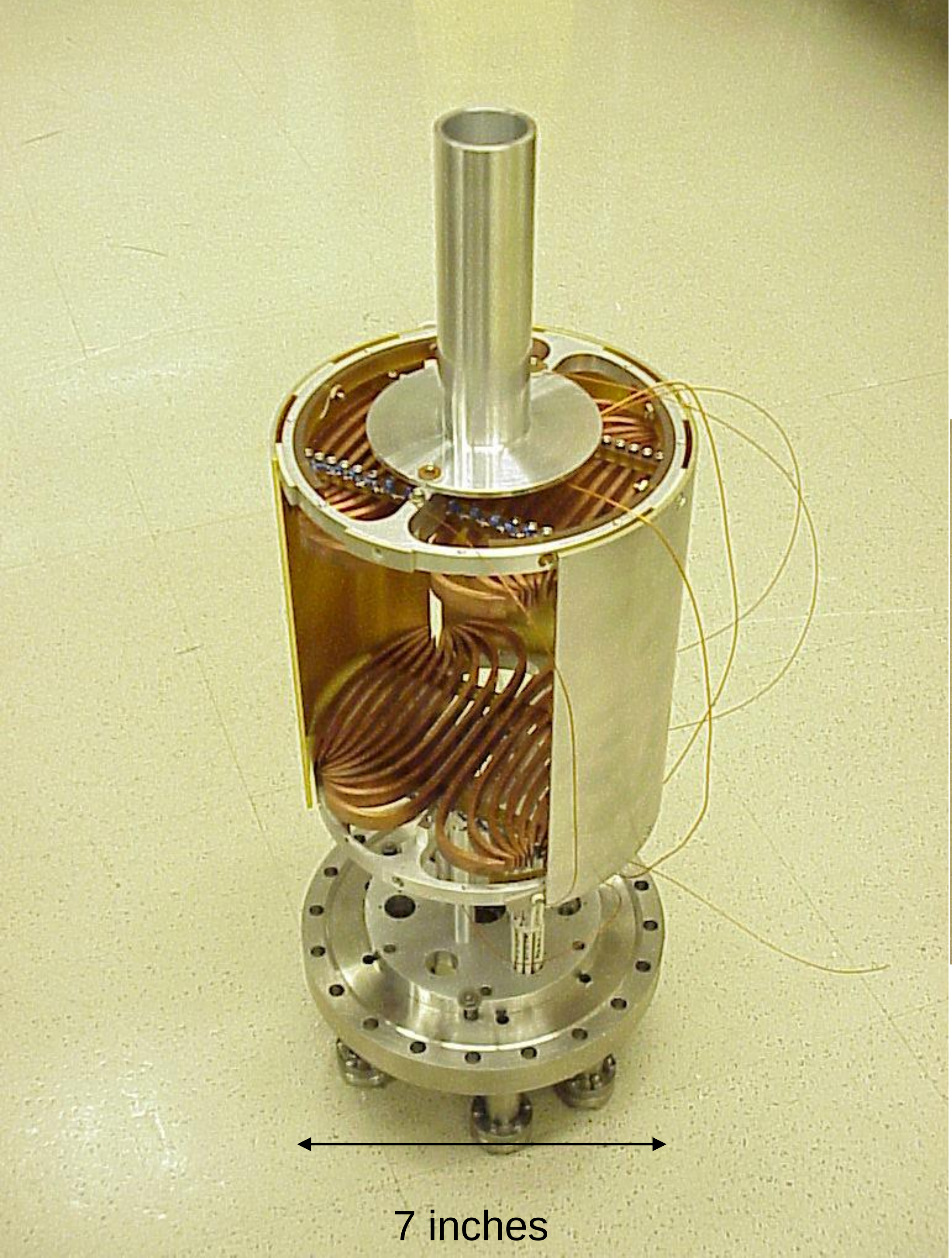


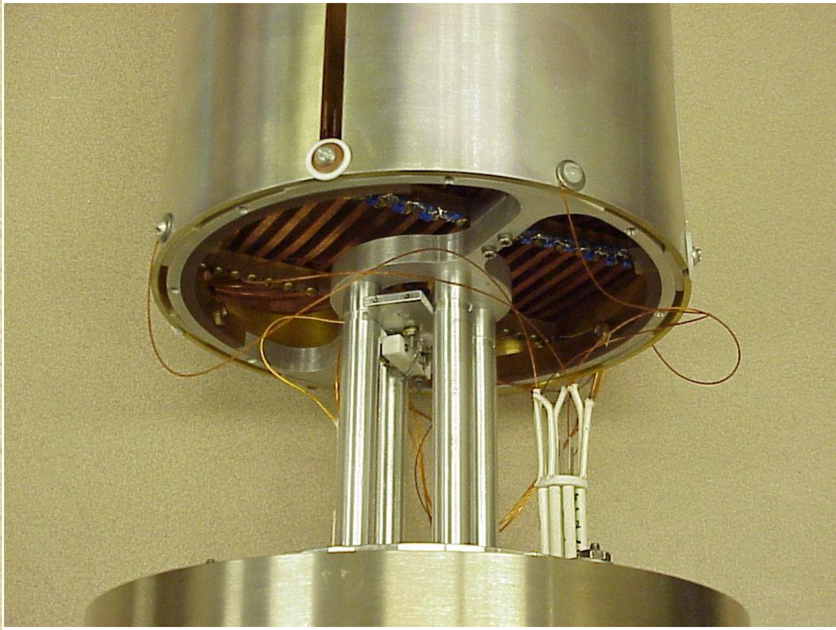
Coca-Cola cell

Spectroswiss NADEL cell



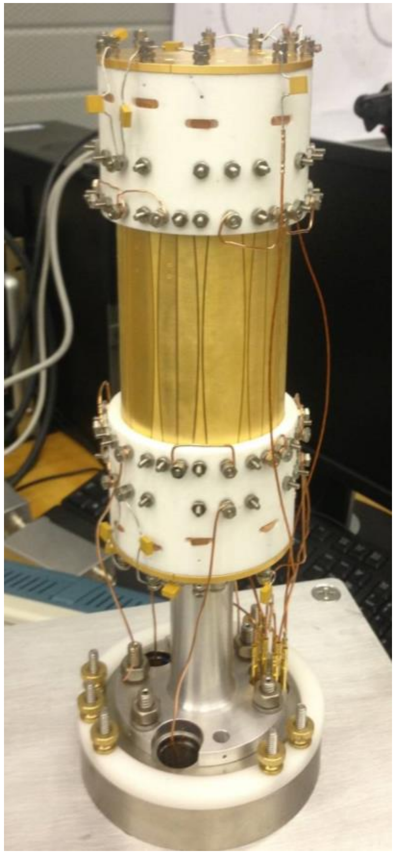
BIG
7 inches FT ICR cell



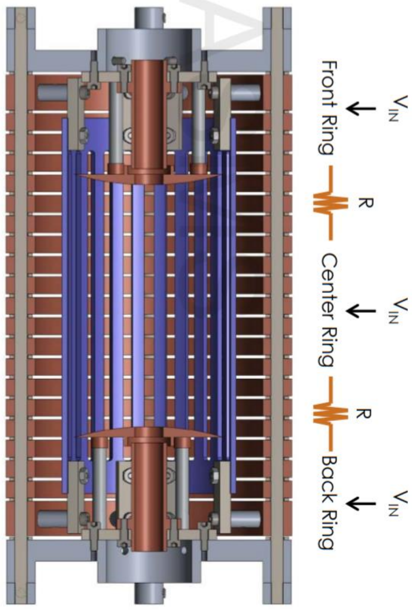


Dynamically harmonized cells

Bruker Solarix R&D



NHMFL cell From Alan Marshall 21 T talk



PNNL window cell

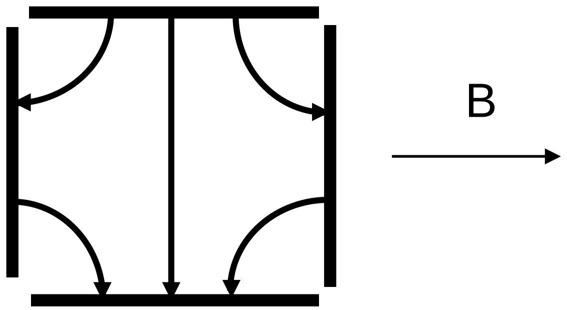
Dynamically harmonized FT ICR cell for Thermo LTQ FT

Why so many designs?

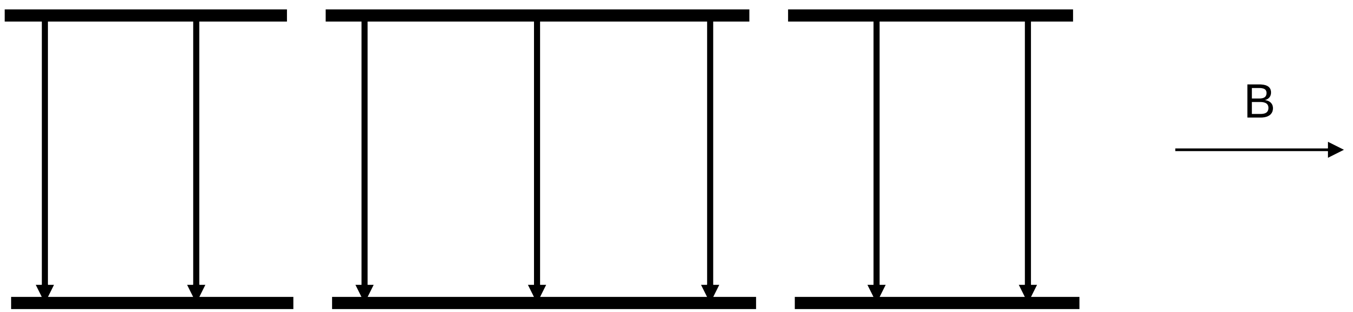
What is the problem?

The first problem was homogeneity of excitation
Field distribution

Cubic and cylindrical

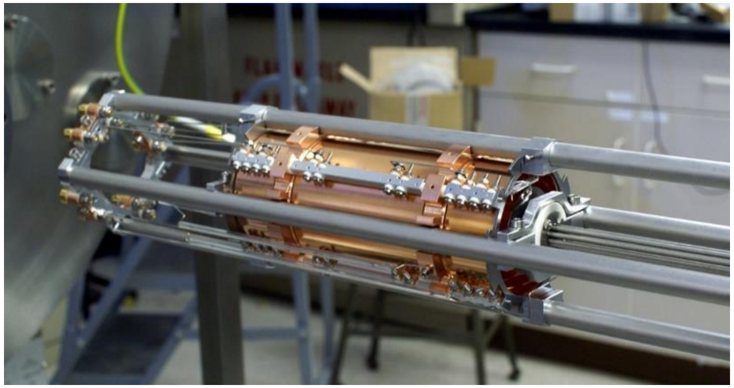


Elongated open cell

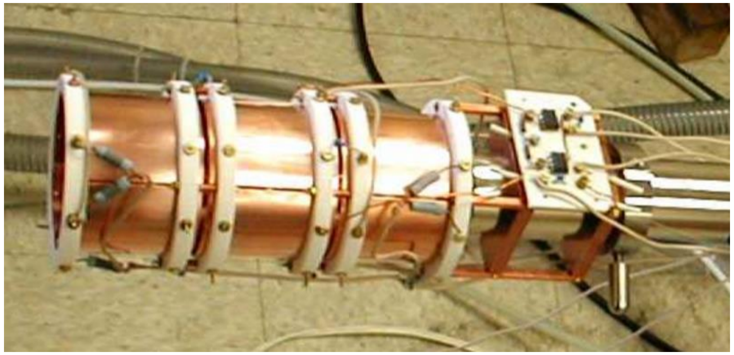


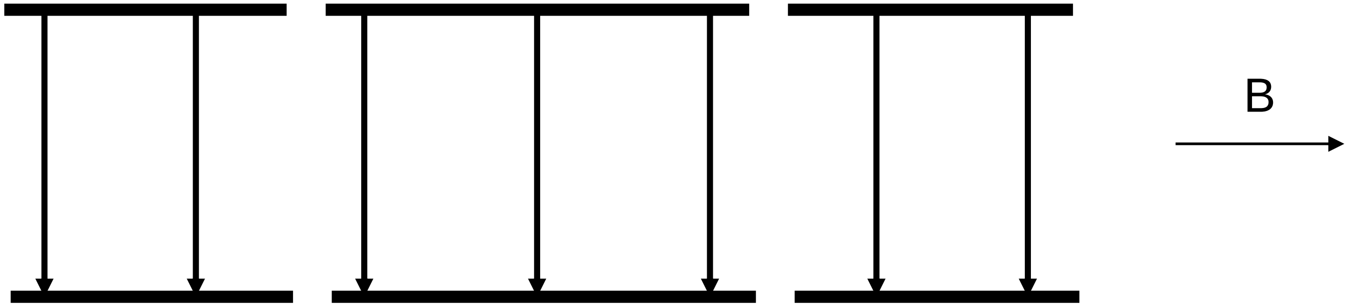
Elongated open cells

Thermo
LTQ FT
(until 2006)

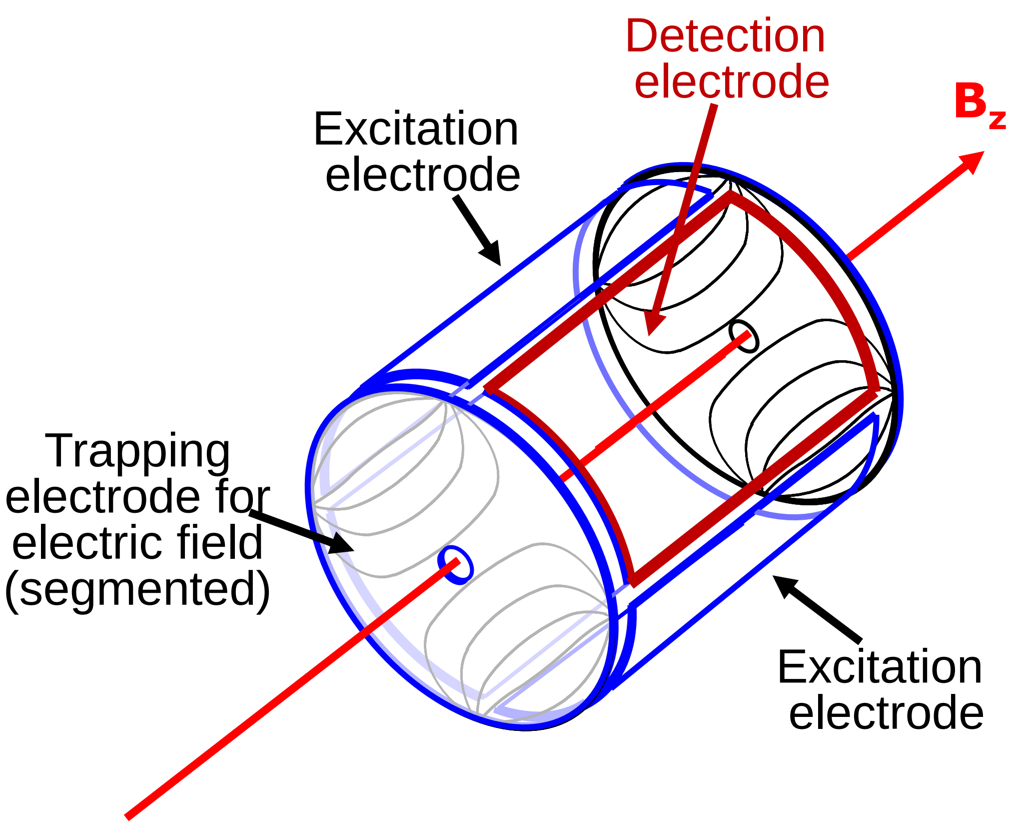


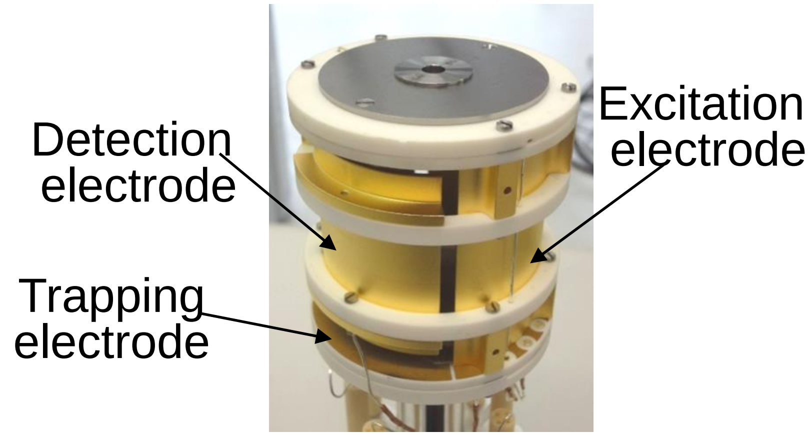
IonSpec Varian



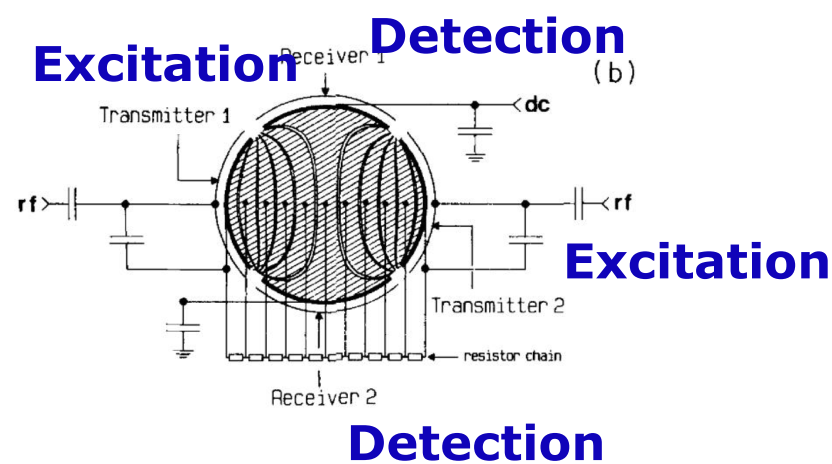


Infinity cell



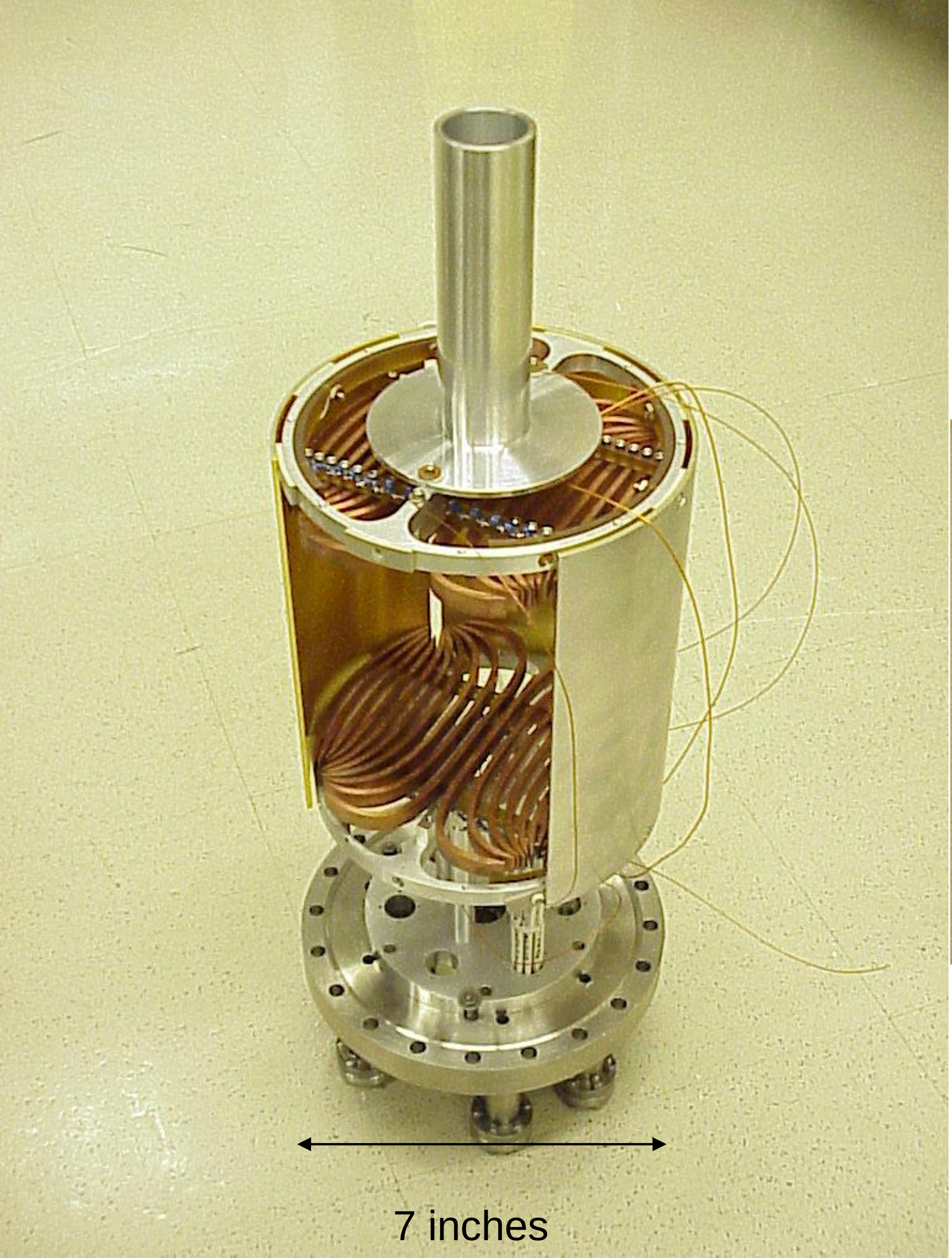


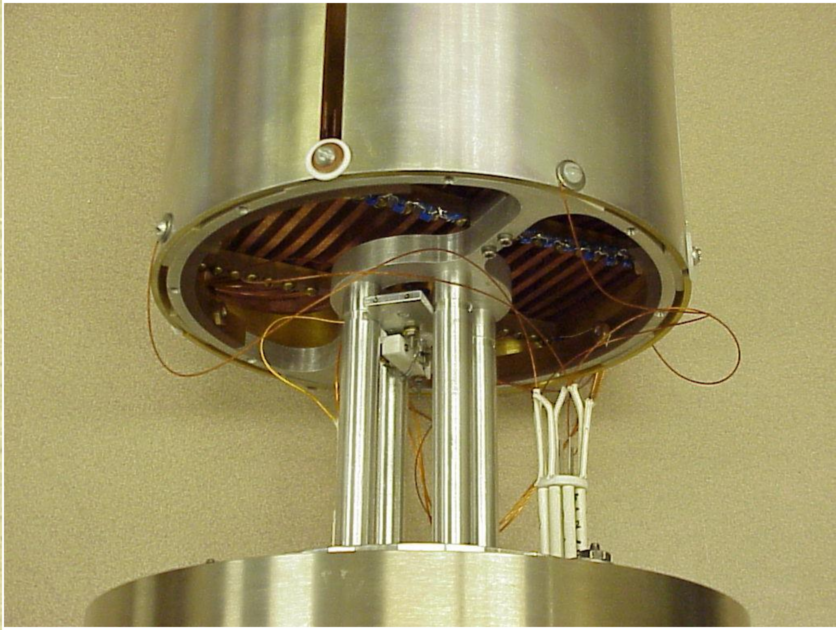
diameter: 60 mm
length: 60 mm



➔ Infinity trapping segments realize a dipolar excitation field, as if the ICR cell would be "infinitely" long.

BIG
7 inches FT ICR cell



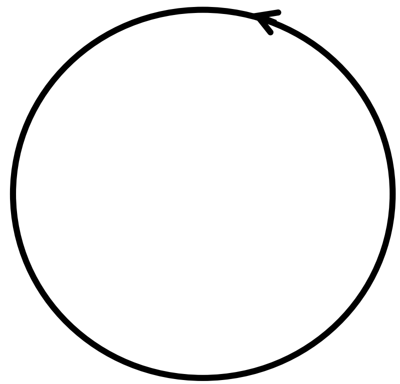


The second problem was:

Why we could not reach resolving power of more than 1 million at m/z close to 1000 Da?

Is it the vacuum problem?

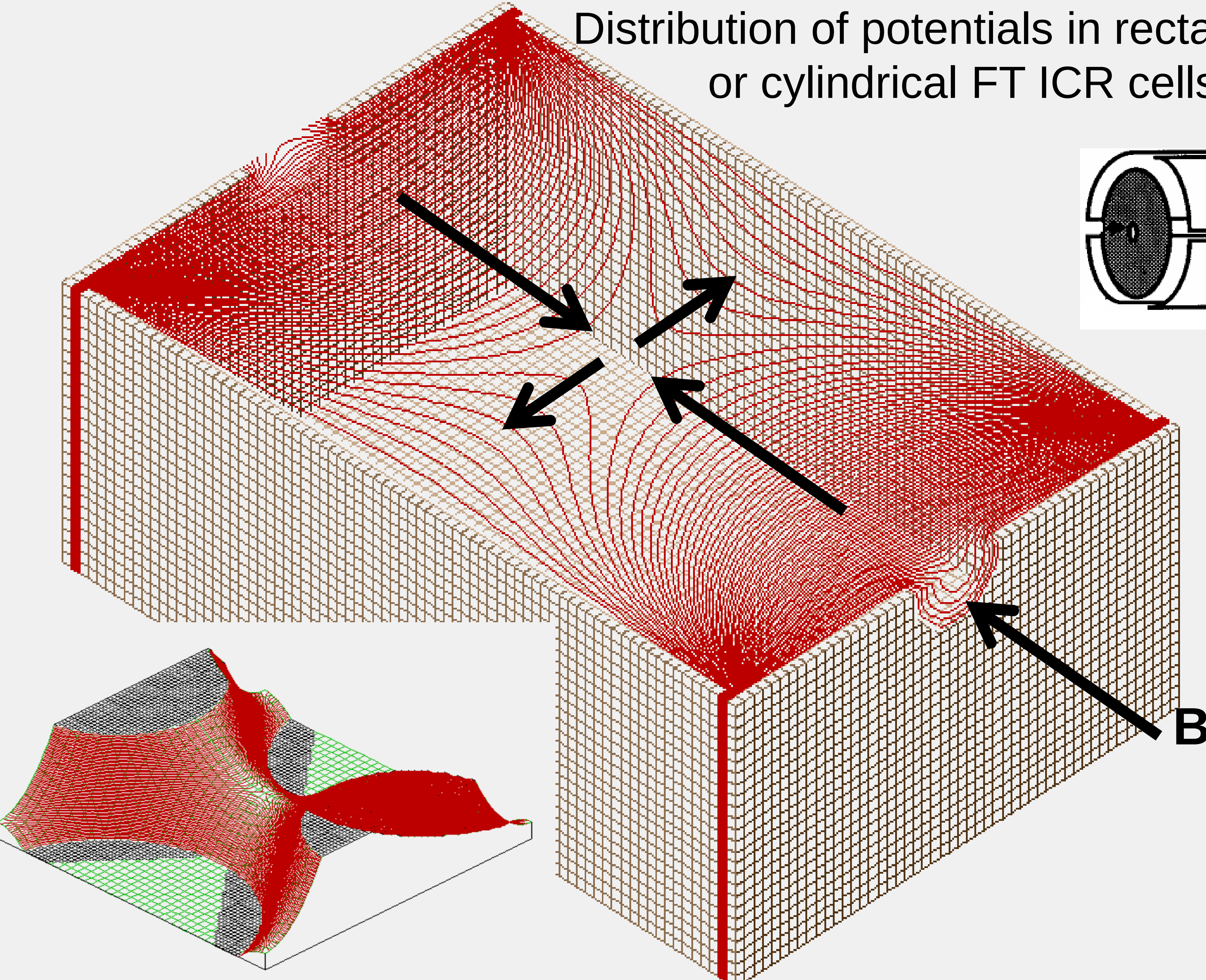
Ion motion in electric field free space

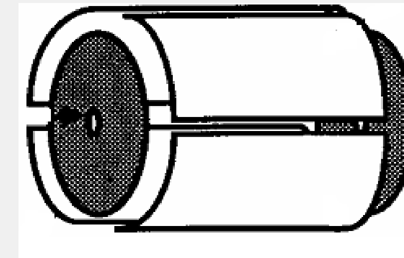


Cyclotron rotation

$$\omega_c = \frac{|eB|}{mc}$$

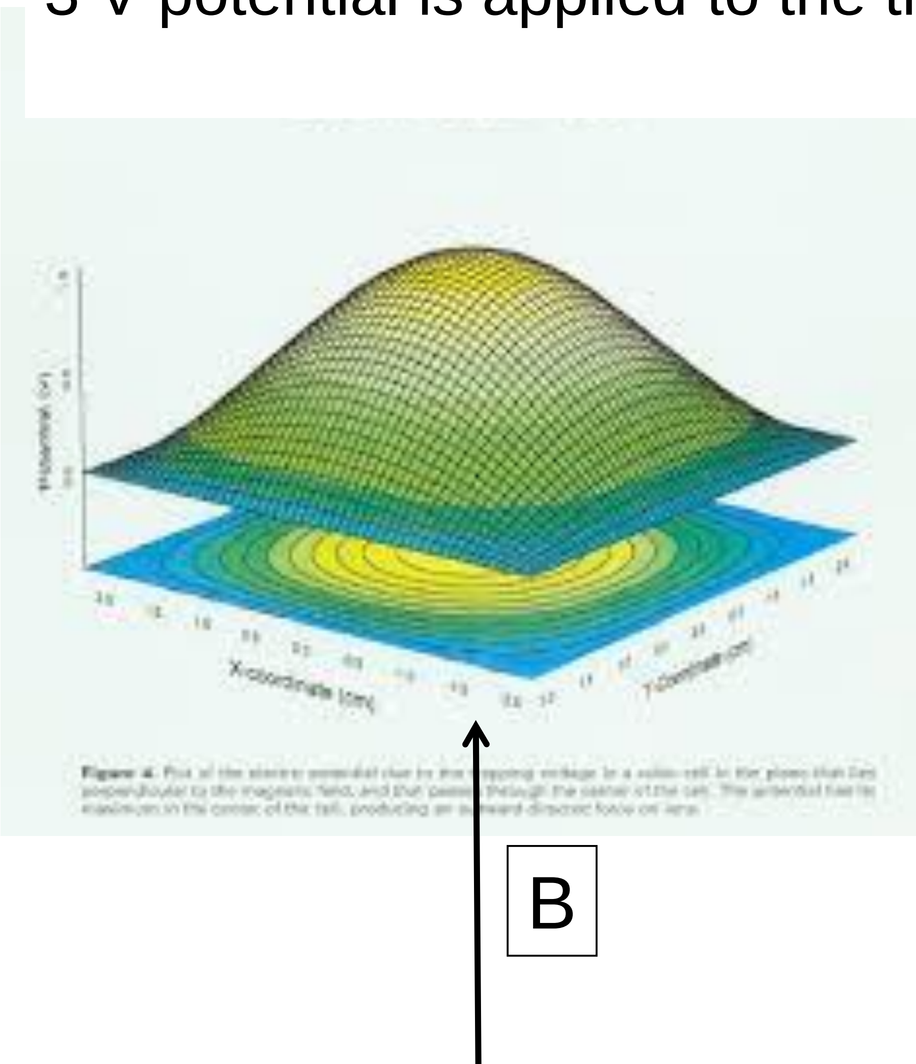
Distribution of potentials in rectangular or cylindrical FT ICR cells

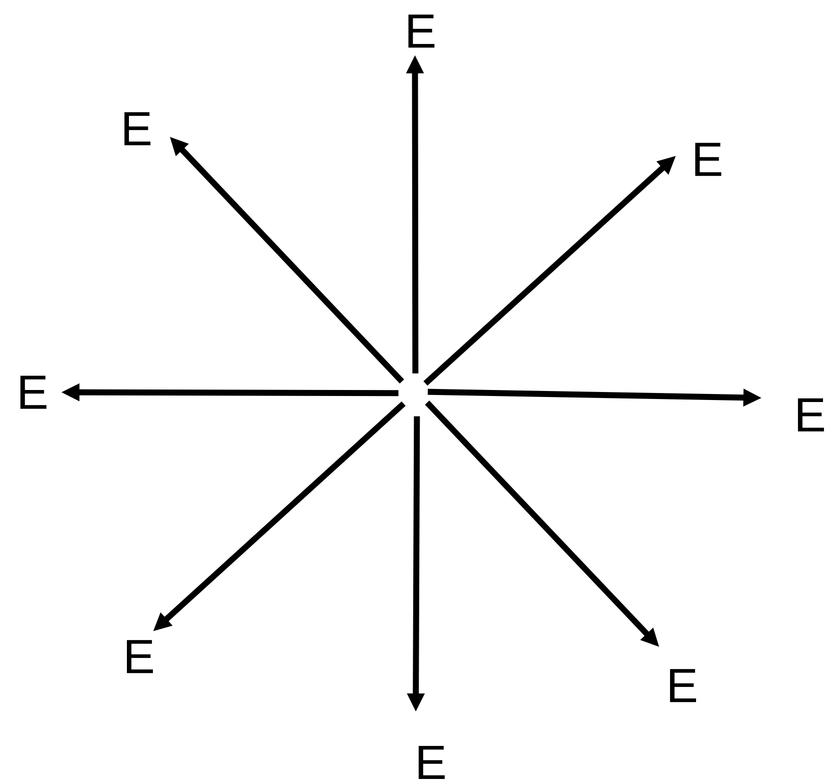




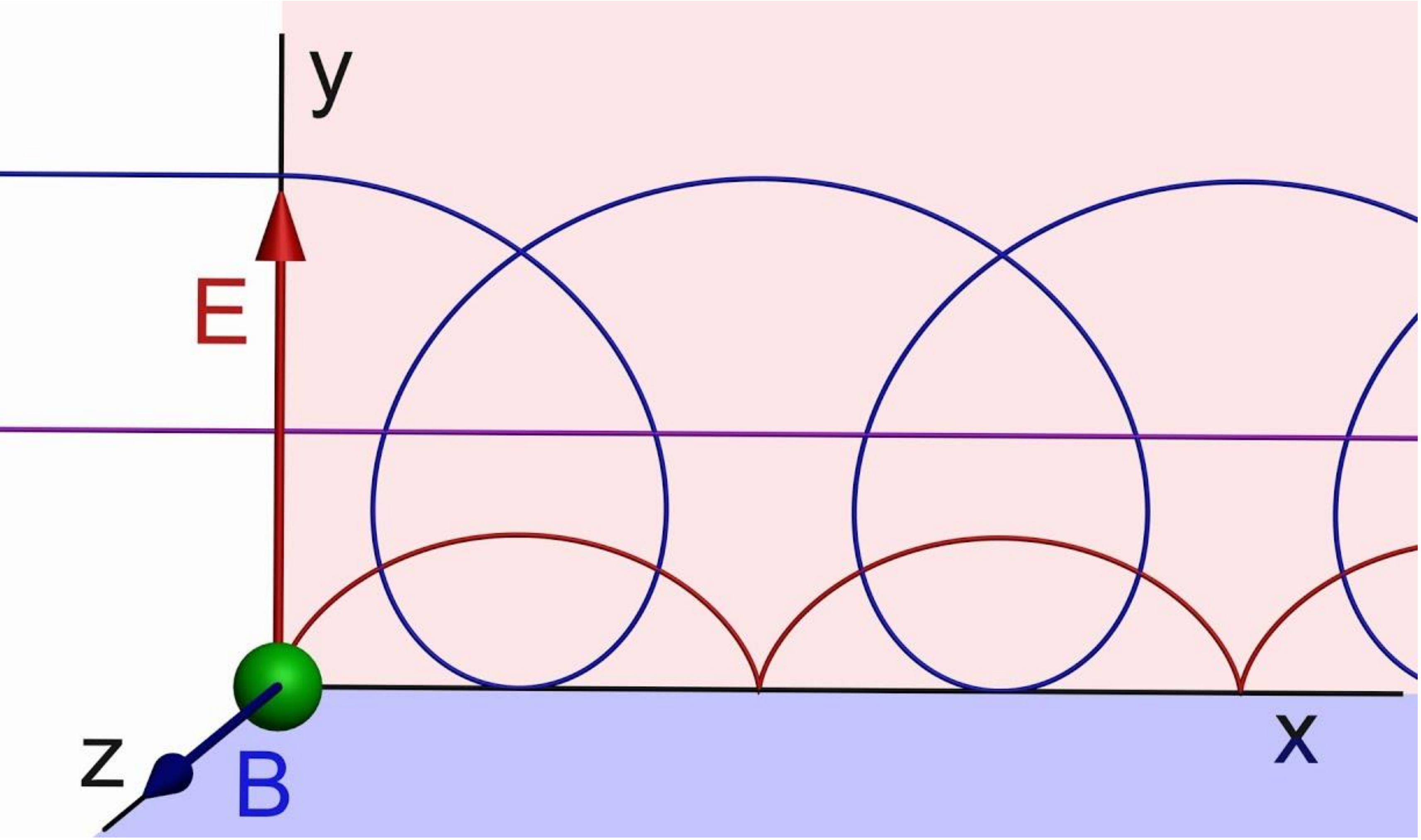
Motion of ions in crossed E/B fields

Cell potential plot in the xy plane of a cubic FT ICR cell.
3 V potential is applied to the trapping electrodes

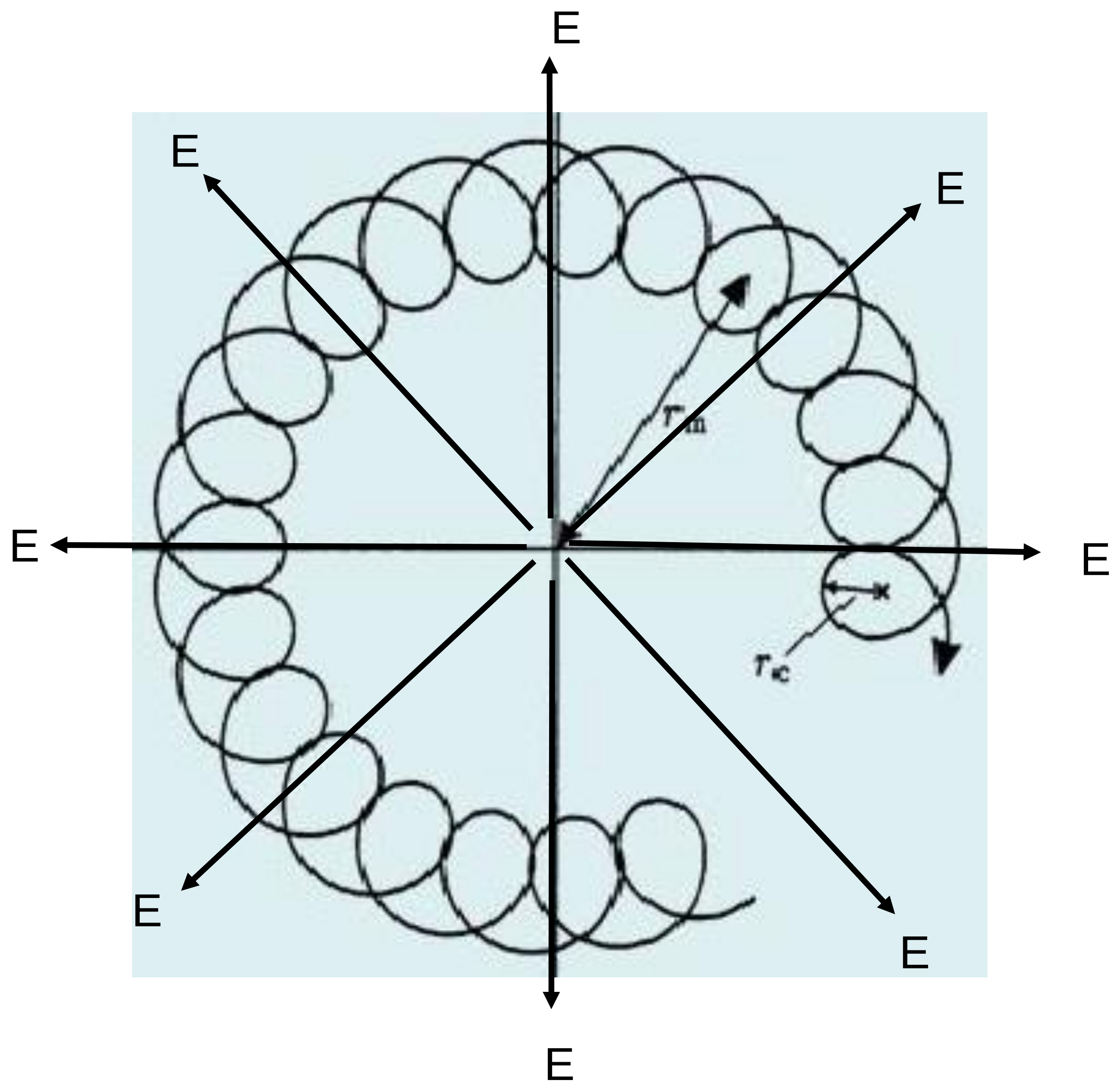




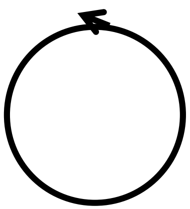
Motion of ions in crossed E/B fields



Magnetron motion. No excitation of cyclotron motion



Ion motion in electric field free space



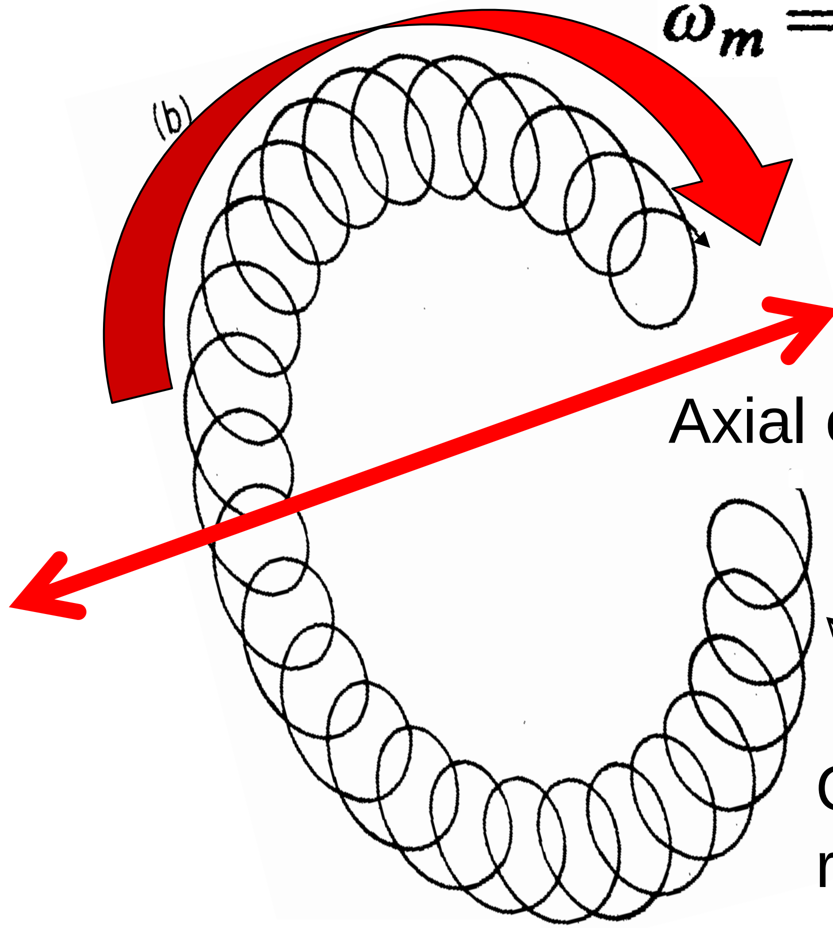
Cyclotron rotation

$$\omega_c = \frac{|eB|}{mc}$$

Ion motion in an electrostatic trap

Magnetron rotation

$$\omega_m = \omega_z^2 / 2\omega_c'$$



Axial oscillation

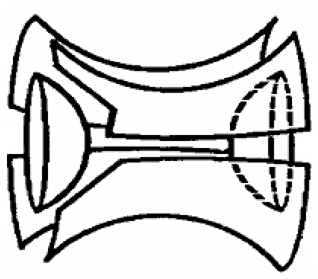
Cyclotron rotation

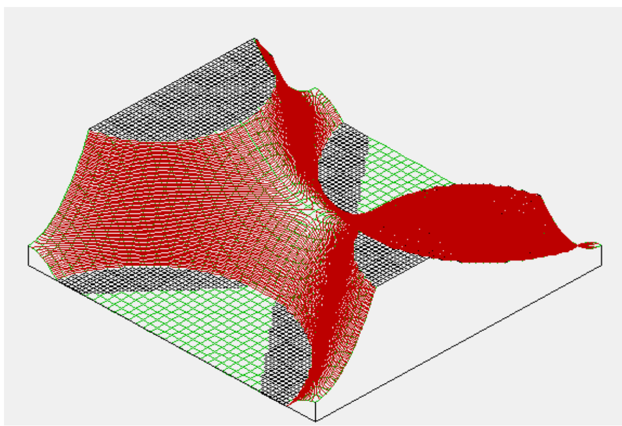
$$\omega_c = \frac{|eB|}{mc}$$

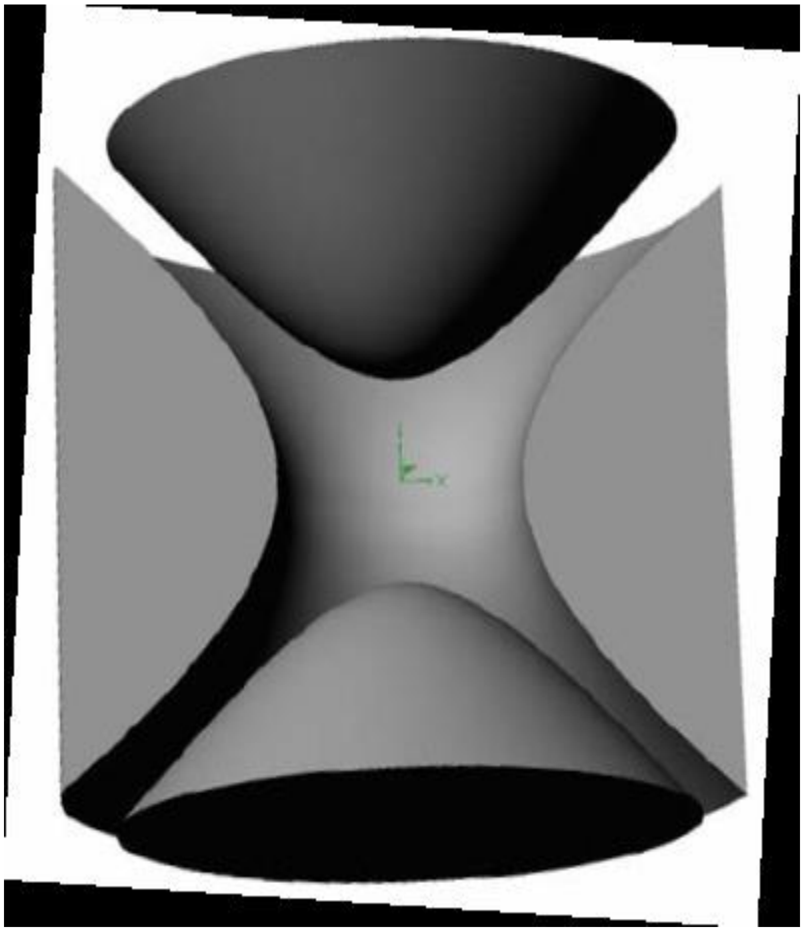
$$\omega_c' = \omega_c - \omega_m$$

Measured frequency

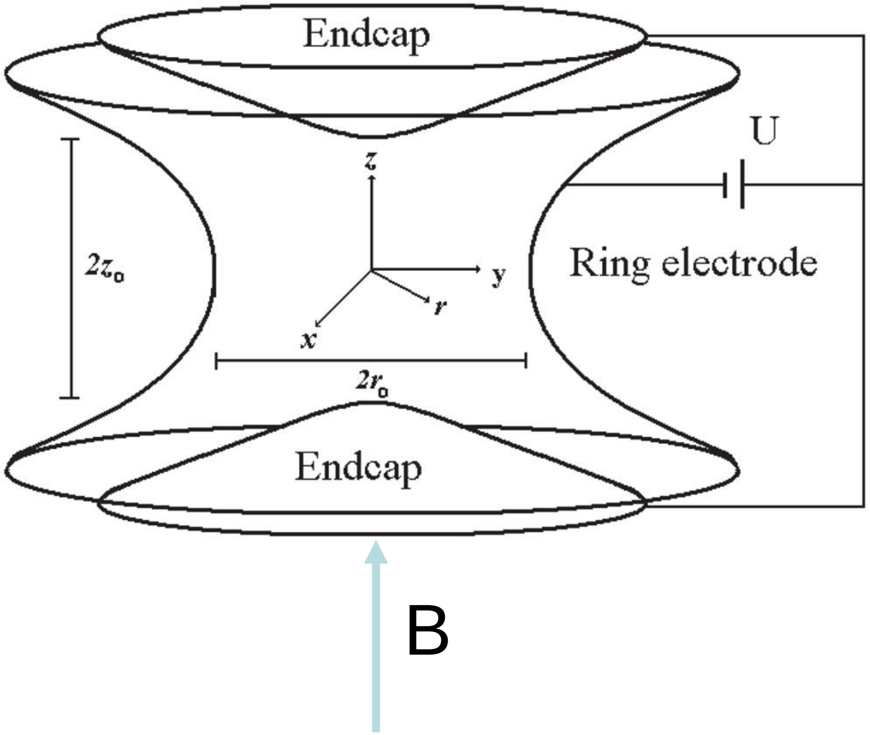
Hyperbolic cell





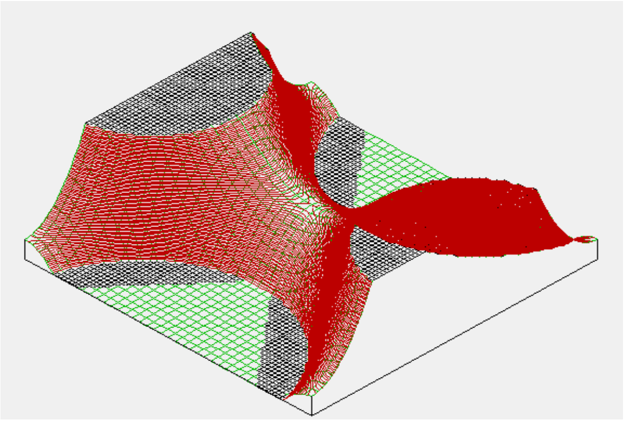


Hyperbolic Penning trap



$$\phi(r,z) = \frac{U_0}{{R_0}^2}(r^2 - 2z^2)$$

$$R_0^2 = r_0^2 + 2z_0^2$$



$$\vec{F} = q(\vec{E} + \vec{v} \times \vec{B})$$

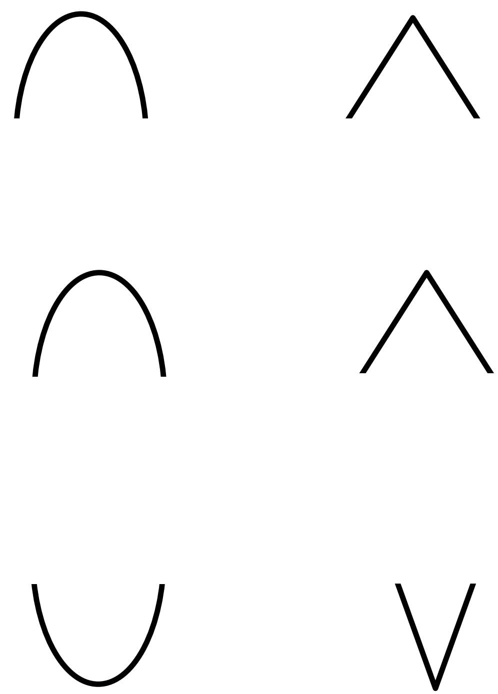
Linear dependence of electric field on coordinates in hyperbolic ion trap

Electric field distribution

$$E_x = -\frac{\partial \phi(x,y,z)}{\partial x} = -\frac{2U_0}{R_0^2}x$$

$$E_y = -\frac{\partial \phi(x,y,z)}{\partial y} = -\frac{2U_0}{R_0^2}y$$

$$E_z = -\frac{\partial \phi(x,y,z)}{\partial z} = \frac{4U_0}{R_0^2}z$$



Potential distribution

$$\frac{\partial^2 x}{\partial t^2} = \frac{qB}{m}\frac{\partial y}{\partial t} - \frac{2qU_0}{mR_0^2}x$$

$$\frac{\partial^2 y}{\partial t^2} = -\frac{qB}{m}\frac{\partial x}{\partial t} - \frac{2qU_0}{mR_0^2}y$$

$$\frac{\partial^2 z}{\partial t^2} = \frac{4qU_0}{mR_0^2}z$$

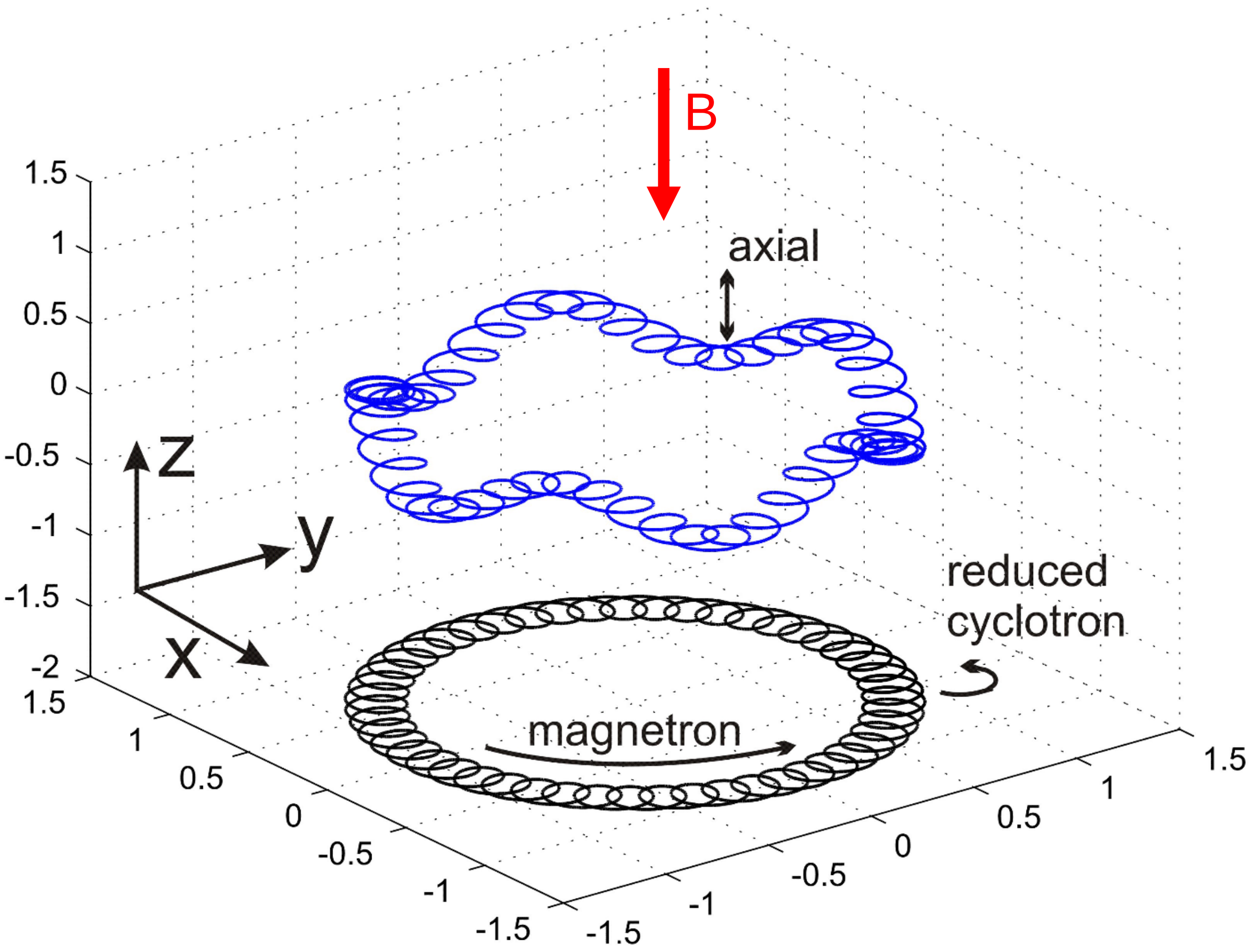
$$\ddot{x} = \omega_c \dot{y} + \frac{\omega_z^2 x}{2} \qquad u = x + iy$$

$$\ddot{y} = -\omega_c \dot{x} + \frac{\omega_z^2 y}{2} \qquad \ddot{u} = -i\omega_c \dot{u} + \frac{1}{2}\omega_z^2 u$$

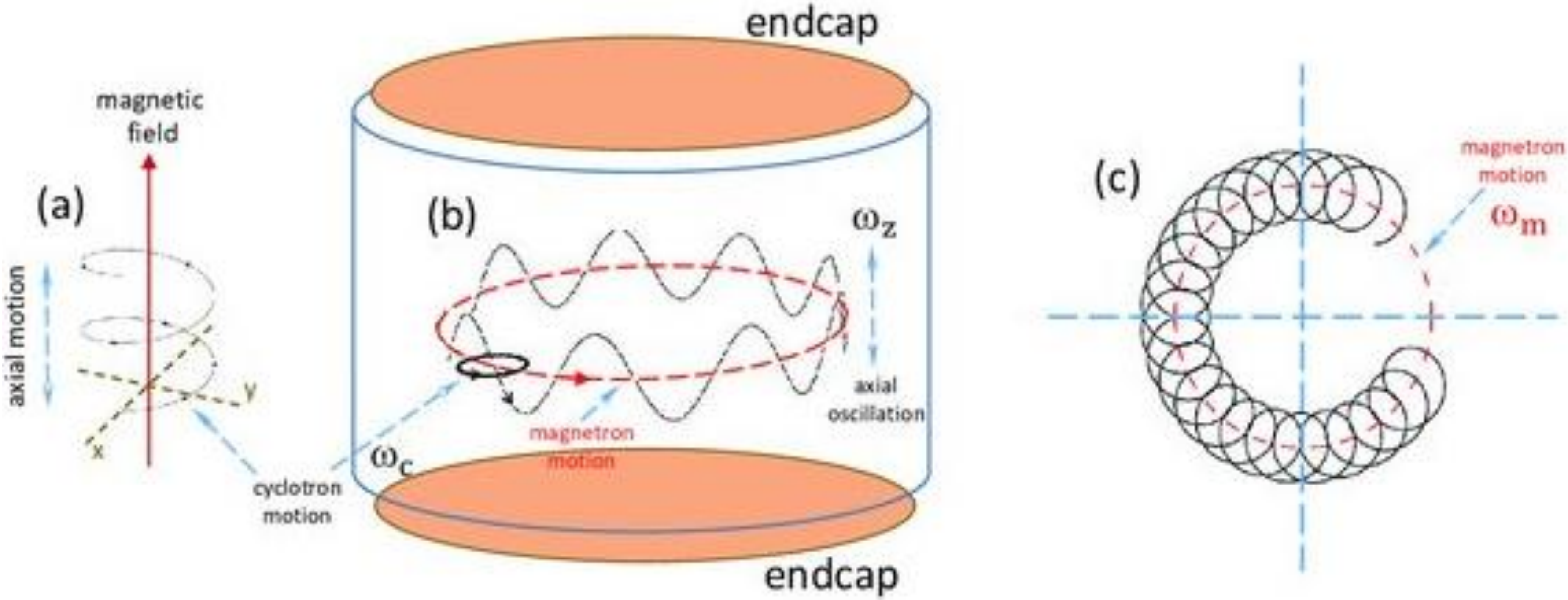
$$\ddot{z} = -\omega_z^2 z \qquad u = e^{-i\omega t}$$

$$\omega_c' = \frac{\omega_c + \sqrt{\omega_c^2 - 2\omega_z^2}}{2} \qquad \omega_m = \frac{\omega_c - \sqrt{\omega_c^2 - 2\omega_z^2}}{2}$$

$$\omega_c^2 > 2\omega_z^2 \qquad \omega_c' \approx \omega_c \gg \omega_z \gg \omega_m$$

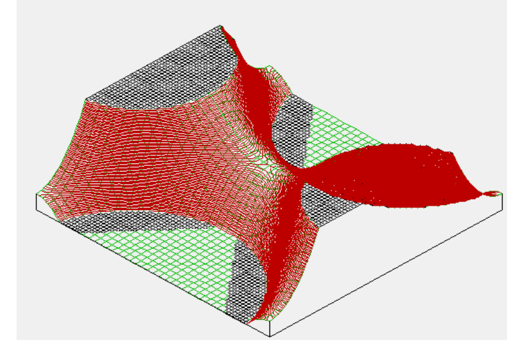


https://www.diva-portal.org/smash/get/diva2:413035/FULLTEXT01.pdf



endcap
magnetic field
(a)
axial motion
y
x
cyclotron motion
(b)
ω_z
axial oscillation
magnetron motion
ω_c
endcap
(c)
magnetron motion
ω_m

In ideal hyperbolic trap all modes of ion motion are independent

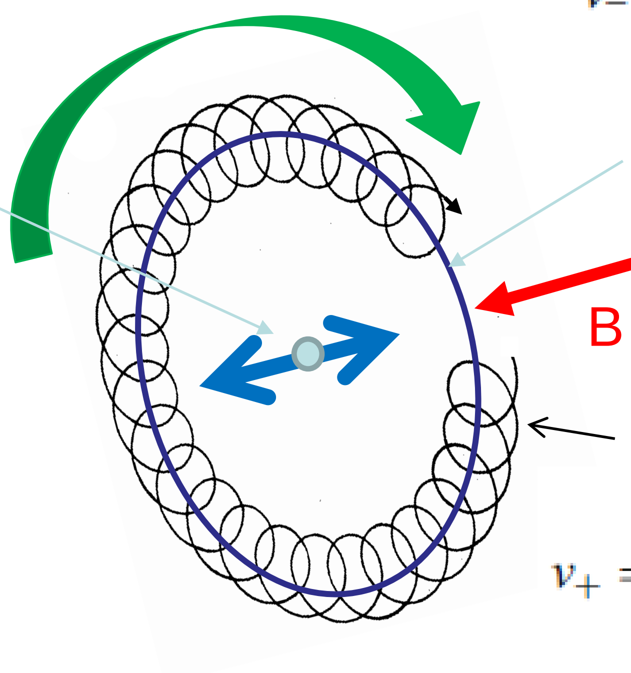


Magnetron rotation

$$\nu_- = \frac{\nu_c}{2} - \sqrt{\frac{\nu_c^2}{4} - \frac{\nu_T^2}{2}}.$$

Magnetron rotation center

Equipotential of the trapping field



Axial oscillation

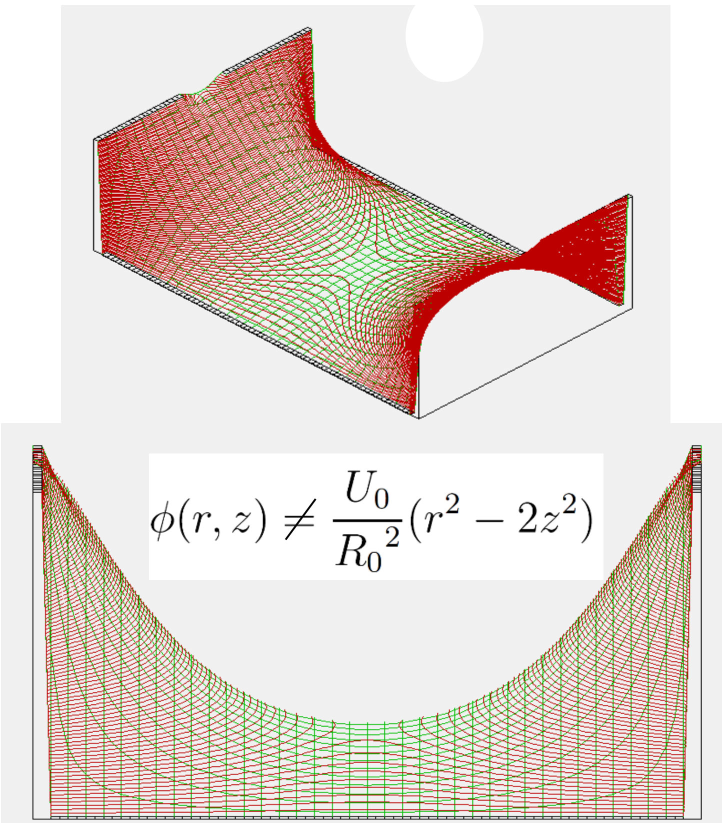
$$\nu_T = \frac{1}{2\pi}\sqrt{\frac{2azeV_T}{ma^2}}$$

Reduced cyclotron rotation

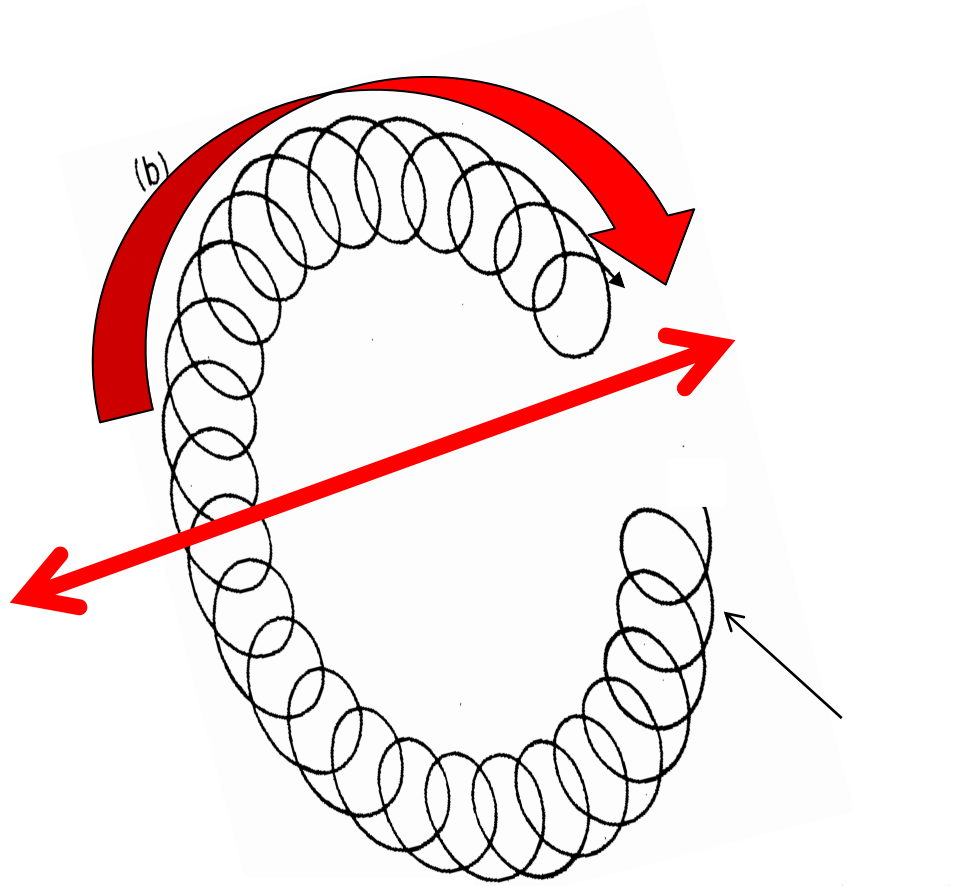
$$\nu_+ = \frac{\nu_c}{2} + \sqrt{\frac{\nu_c^2}{4} - \frac{\nu_T^2}{2}}.$$

Measured frequency

Distribution of potentials in rectangular or cylindrical FT ICR cells



Axial and magnetron frequencies depend on axial oscillation amplitude

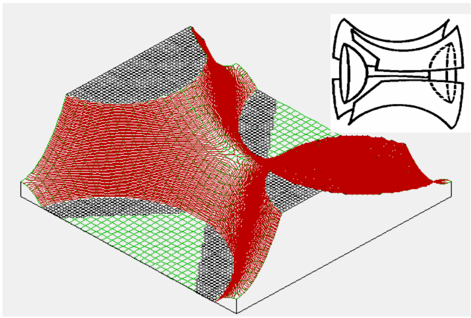


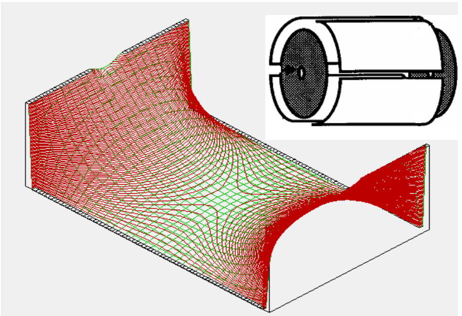
$$\omega'_c = \omega_c - \omega_m(\mathrm{Z})$$

$$\omega_c = \frac{|eB|}{mc}$$

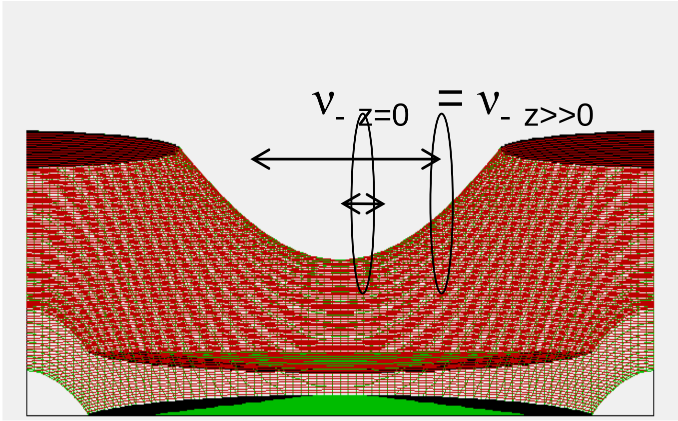
Measured frequency

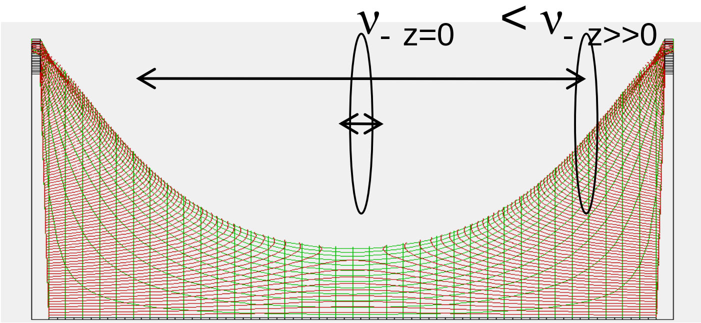
The lost of phase coherence is a result of Inharmonicity of a regular FT ICR cell field





Distribution of potentials in hyperbolic (left) and rectangular or cylindrical FT ICR cells (right)

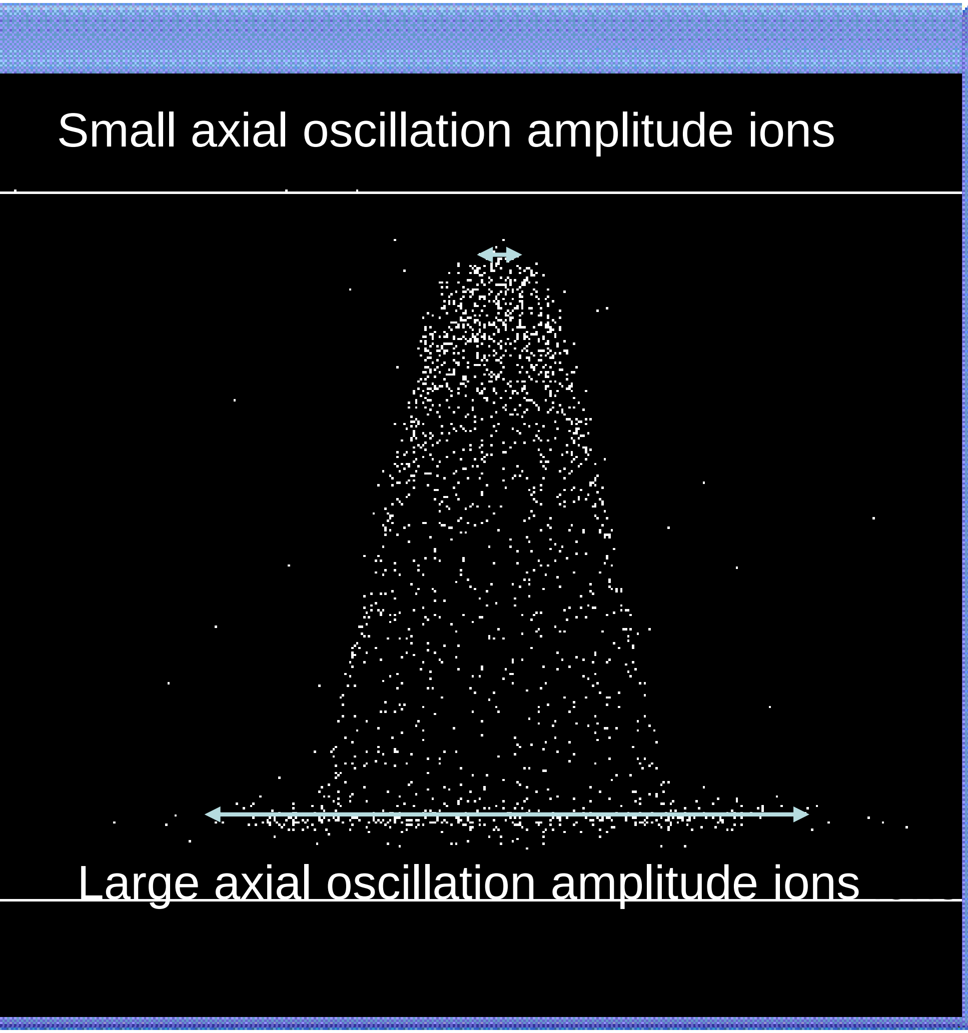


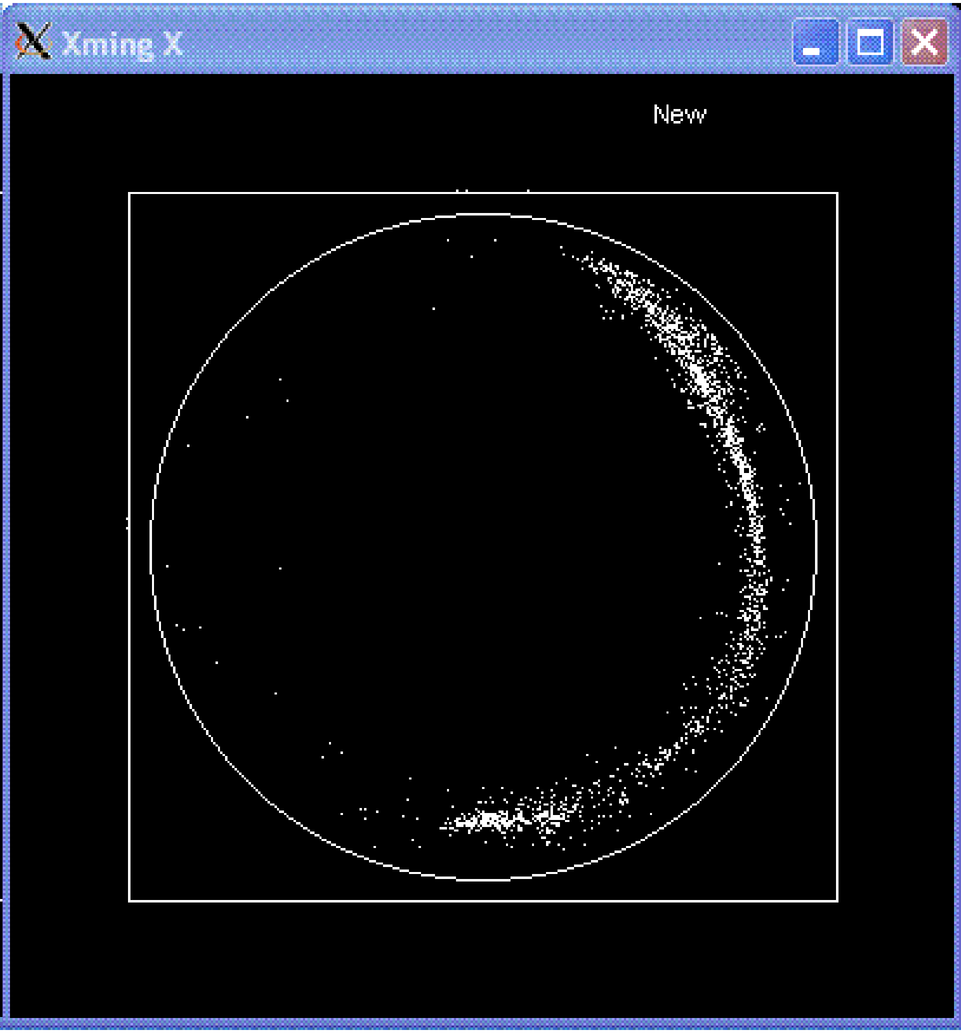


Cyclotron and magnetron frequencies are Independent on axial oscillation amplitude

Cyclotron and magnetron frequencies depend on axial oscillation amplitude

Comets in conventional FT ICR cell

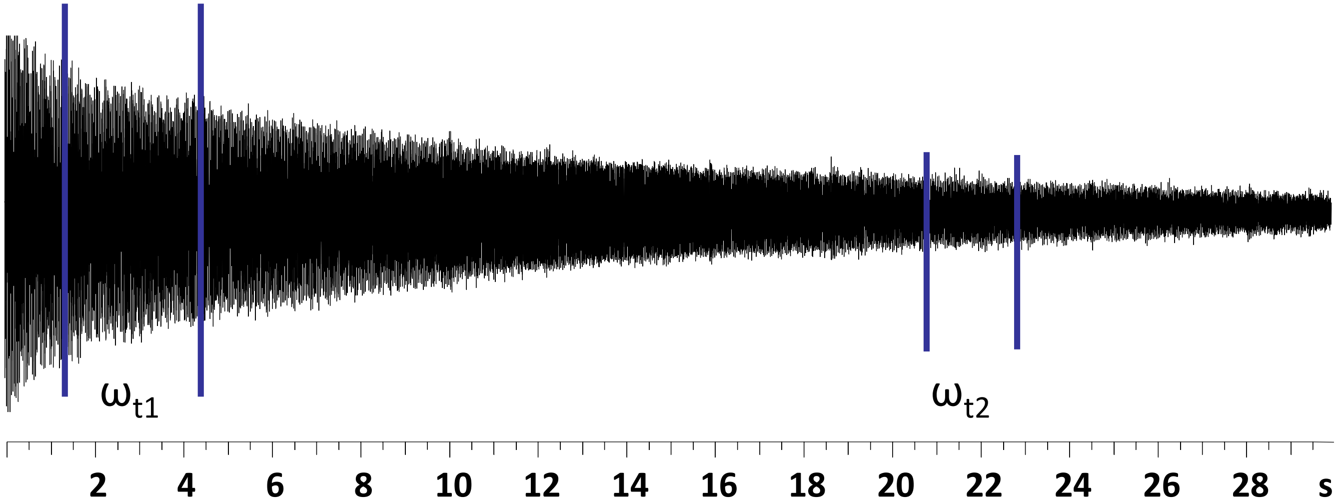




Comet in conventional
(cubic, cylindrical, “infinity”..)
FT ICR cells

$\omega_{t1} \neq \omega_{t2}$

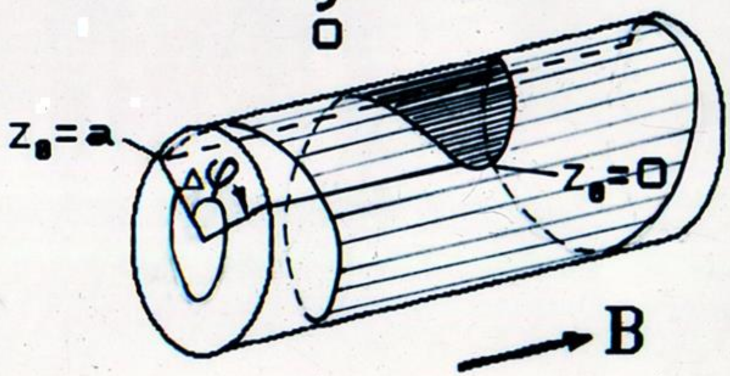
Because ion-ion interaction inside comets is changing in time



How do we know about comets?

Phase shift accumulation

$$(1)\quad \varphi(t, z_0) = \int_0^t \omega_{eff}(\tau, z_0)\, d\tau$$



$$(2)\quad G(\Omega) = Fur\{\langle\cos(\varphi(t))\rangle\}$$

Nikolaev EN. 9th Asilomar Conference on Mass Spectrometry, Trapped Ions: Principle, Instrumentation and Applications, Sep 27–Oct 1, 1992

Two different approaches to simulation of ion cloud dynamics in FT ICR cell

1. Calculation of ion-ion and ion image charges interaction directly
2. Solving Poisson equation

ELSEVIER International Journal of Mass Spectrometry and Ion Processes 148 (1995) 145–157

International Journal of Mass Spectrometry and Ion Processes

Evolution of an ion cloud in a Fourier transform ion cyclotron resonance mass spectrometer during signal detection: its influence on spectral line shape and position

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[a]*Institute for Energy Problems of Chemical Physics, Russian Academy of Sciences, Moscow 117829, Russian Federation*
[b]*Department of Applied Physics and Chemistry, University of Electro-Communications, Chofu-shi, Tokyo 182, Japan*

Received 19 August 1994; accepted 31 May 1995

Simulation was carried out on a Fujitsu AP1000 parallel computer, which is a "multiple instruction multiple data" (MIMD) machine with 512 independent 25 MHz processors. **(One processor per ion)**

We were trying to explain:

Why ICR frequency is changing during detection?

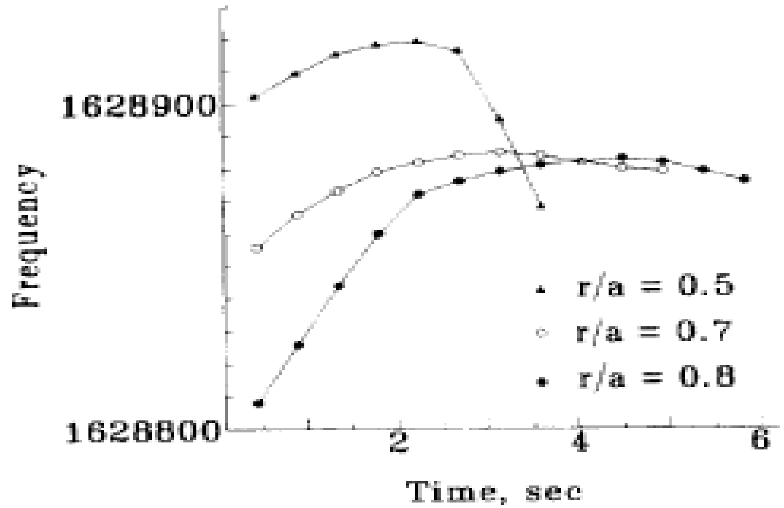
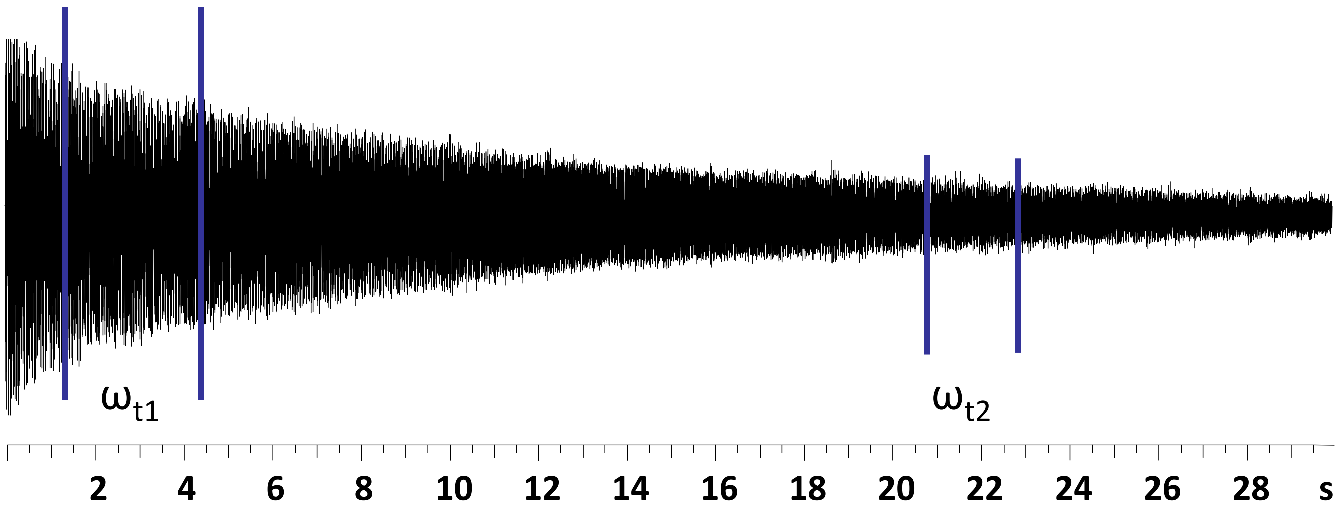
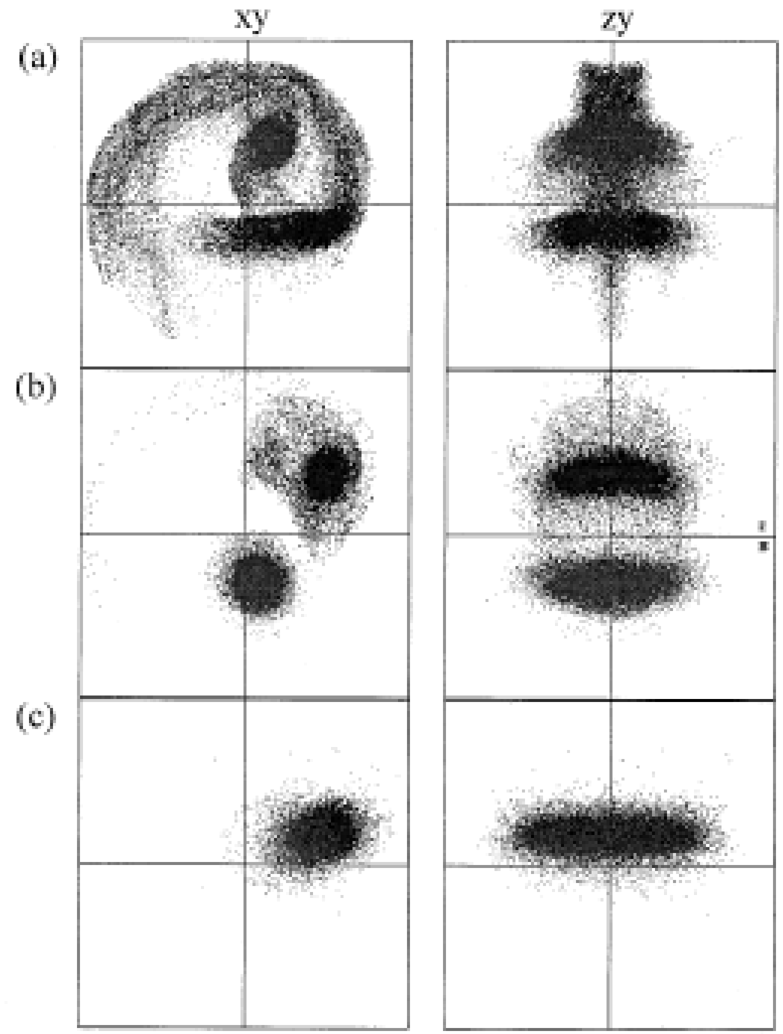


Fig. 1. Experimental ICR frequency of externally produced Cs⁺ ions as a function of time. The three curves correspond to different ratios of cyclotron radius to cell radius.



The Particle-Mesh Method

Dale Mitchell and Richard Smith
1996



Snapshots in *xy* perspective (left) and *zy* perspective (right) at a late time during the detection period. **(a)** 50,000, **(b)**150,000, and **(c)** 350,000 ions.

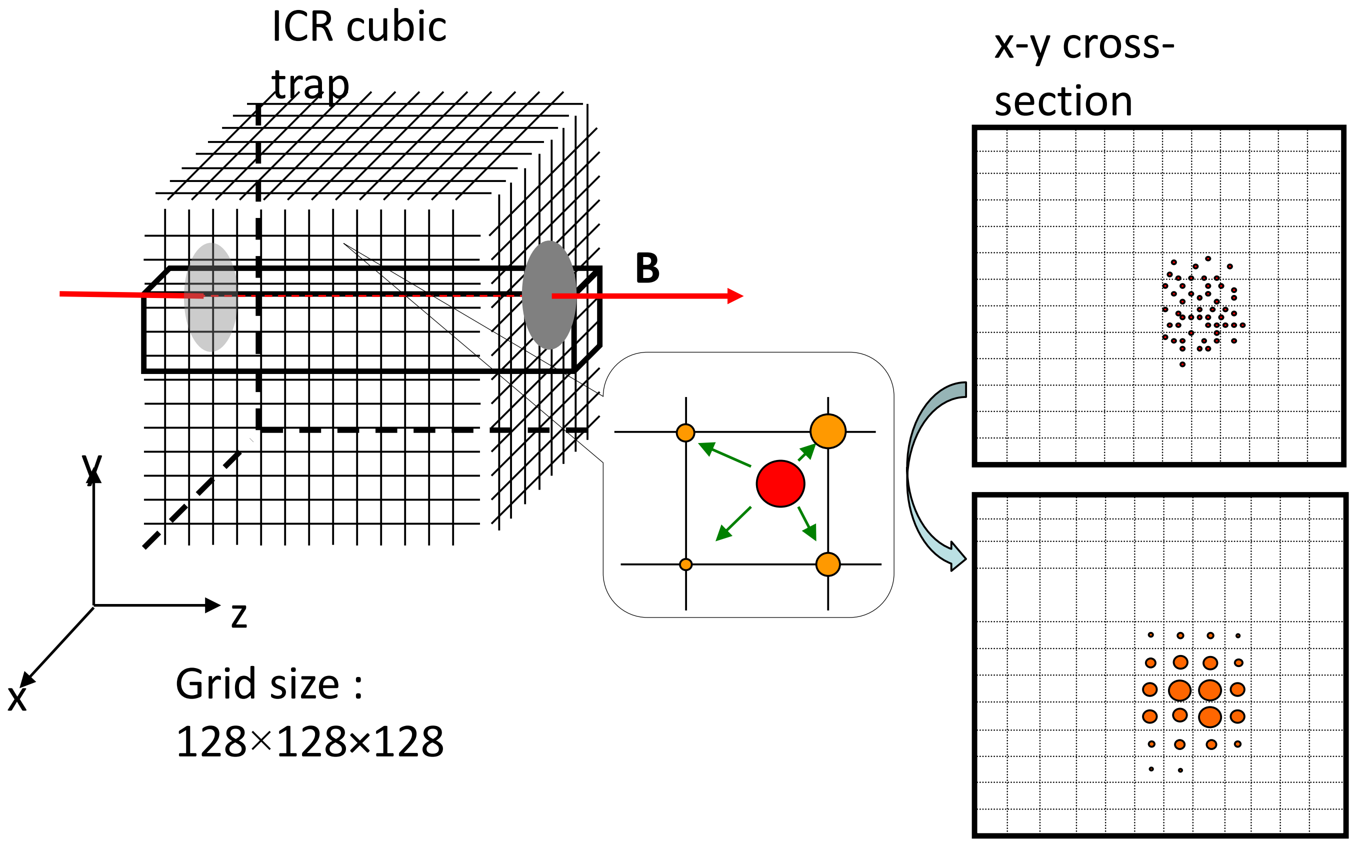
Solving Poisson equation using supercomputer

Eugene N. Nikolaev; Ron M.A. Heeren; Alexander M. Popov; Alexander V Pozdneev; Konstantin S Chingin;

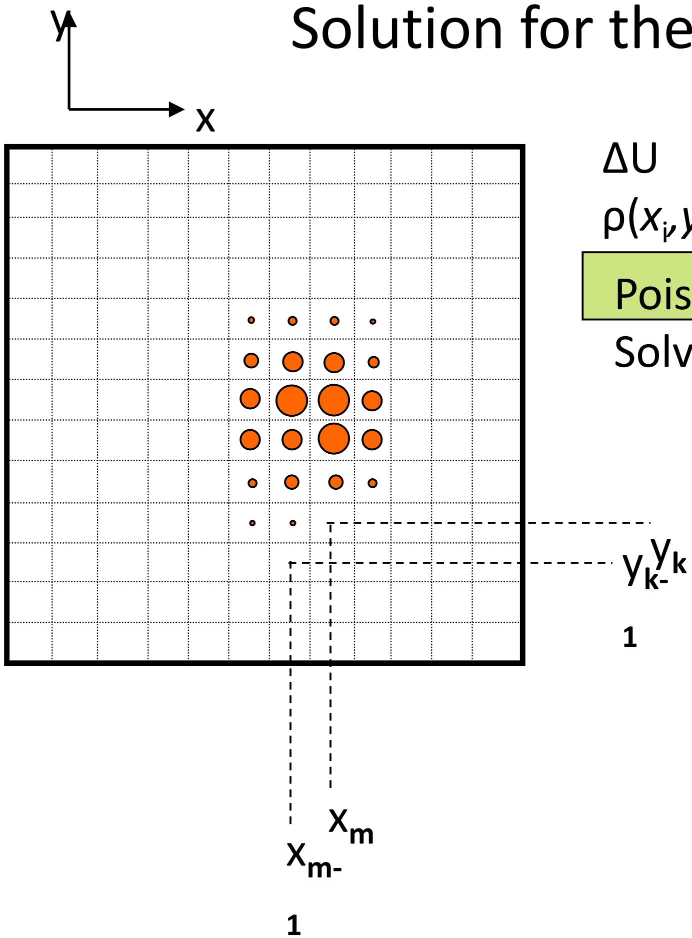
Realistic modeling of ion cloud motion in Fourier transform ion cyclotron resonance cell by use of a particle-in-cell approach

Rapid Commun. Mass Spectrom. 2007; 21,1-20

Particle-In-Cell Algorithm (first used to describe ion behavior in FT ICR cell by Dale Mitchell and Richard Smith)



Solution for the electric field

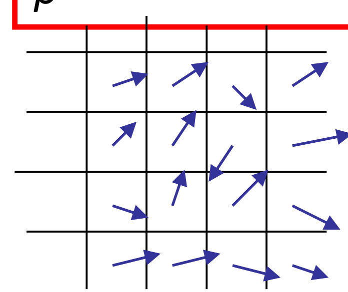


$\Delta U = -\rho(x_i, y_j, z_k)/\varepsilon_0$

Poisson Solver

$\mathbf{U}(x_i, y_j, z_k)$ *i, j, k=1-p*

$\mathbf{E}(x_i, y_j, z_k)$ *i, j, k=1-p*



Integration the equation of motion

$$m\frac{d^2\vec{r}}{dt^2} = q\vec{E} + q\left(\frac{d\vec{r}}{dt}\times\vec{B}\right)$$

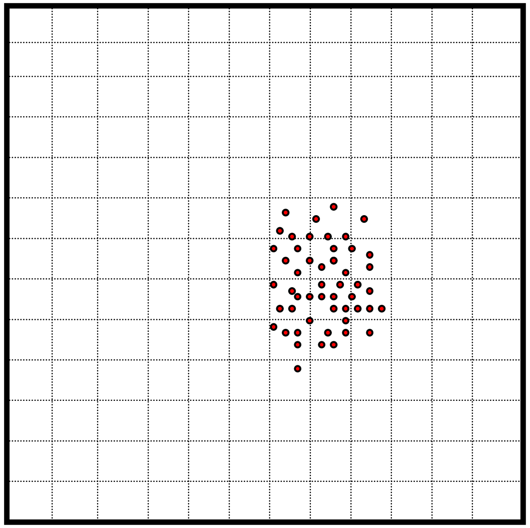
E(r_i)

v_i , r_i

Boris integrator

new v_i , r_i

for every ion (i)



Next time step

Integration the equation of motion

$$m\frac{d^2\vec{r}}{dt^2} = q\vec{E} + q\left(\frac{d\vec{r}}{dt}\times\vec{B}\right)$$

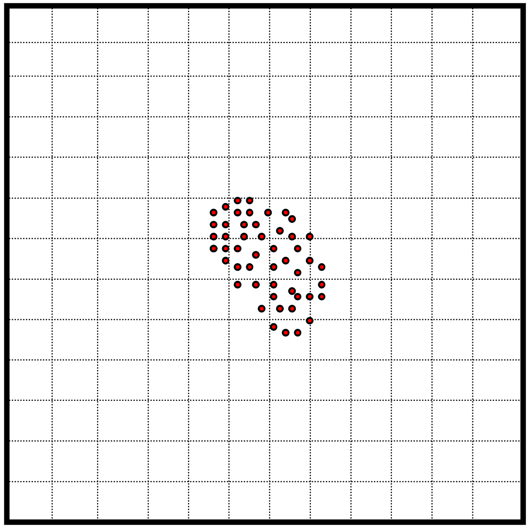
E(r_i)

v_i , r_i

Boris integrator

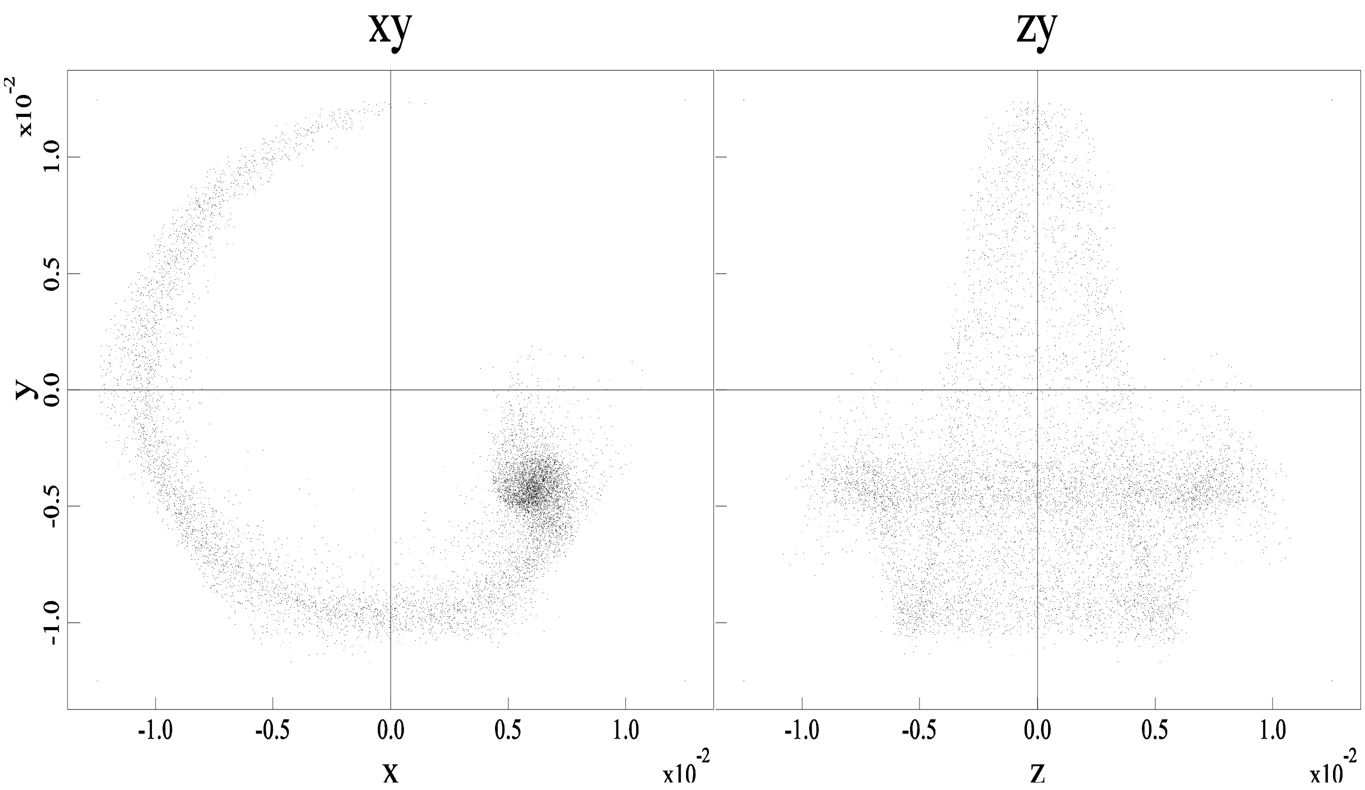
new v_i , r_i

for every ion (i)



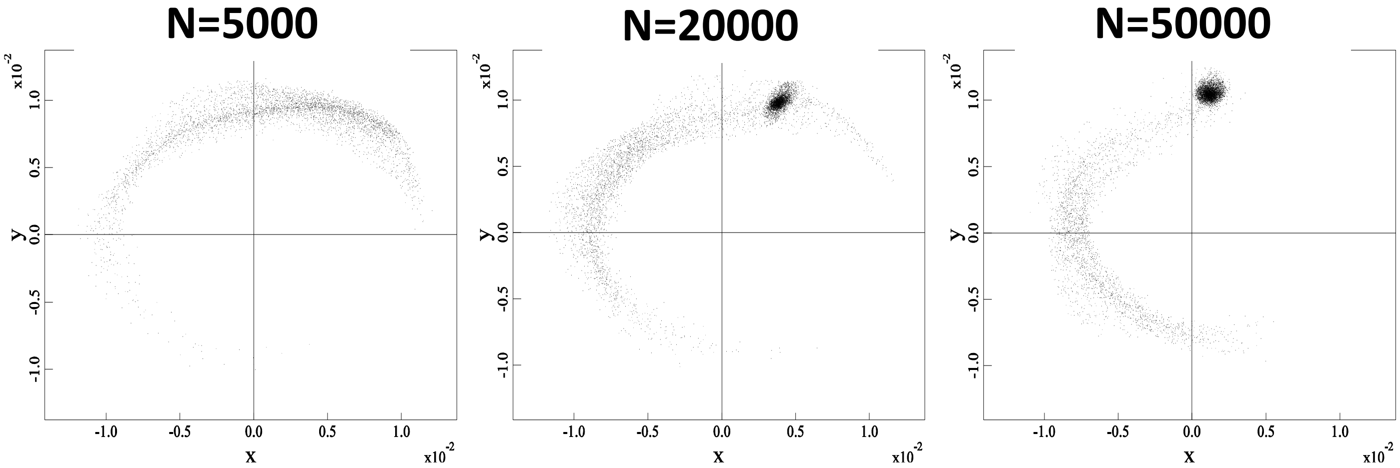
Next time step

Cloud of one m/z ions in a cylindrical geometry FT ICR cell



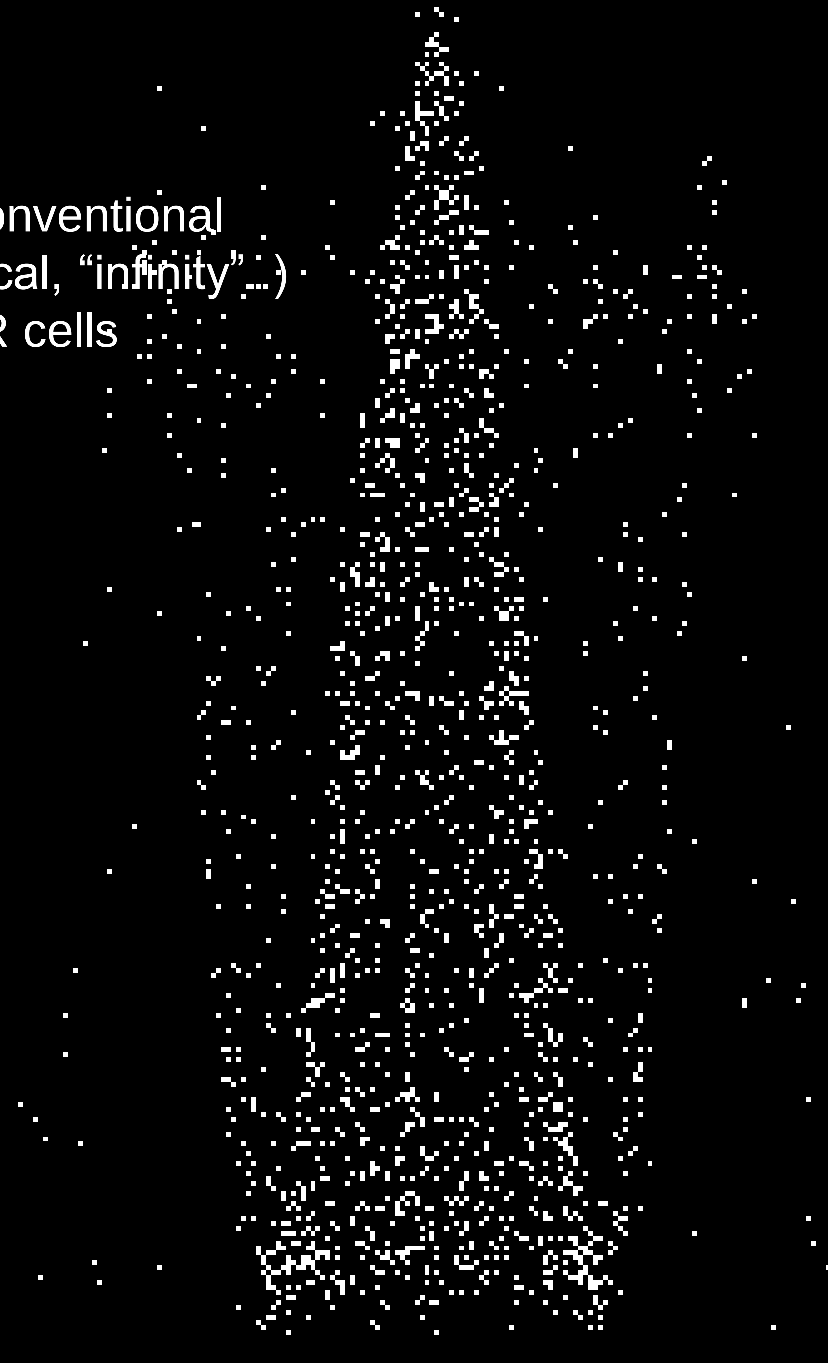
Evolution of ion clouds with different amount of ions in the cell

cloud initial radius 0.15 cm
cloud initial length 0.10 cm
T_{exc}= 0.07 ms , T_{detect}= 30 ms

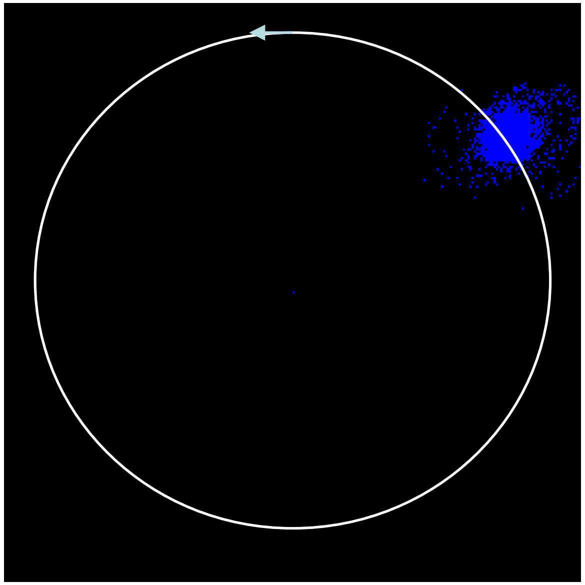


t = 3.24 ms

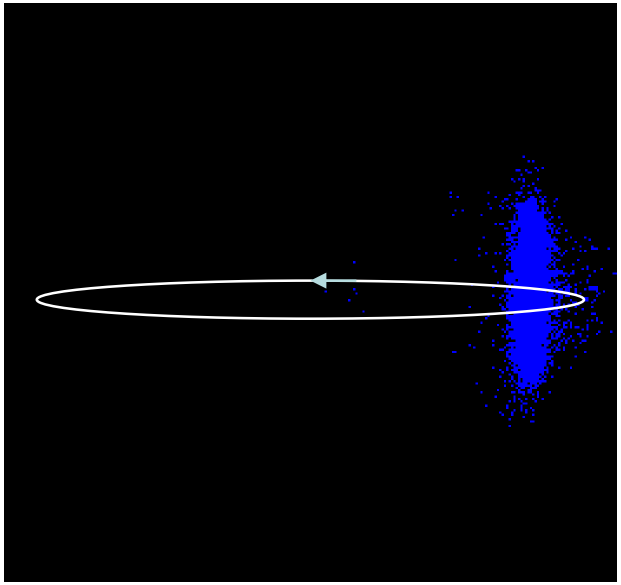
Comet in conventional
(cubic, cylindrical, “infinity”...)
FT ICR cells



Ion clouds in harmonized cells have elliptical cigar like forms



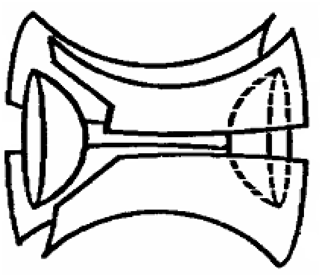
Projection on the plane
orthogonal to the magnetic field

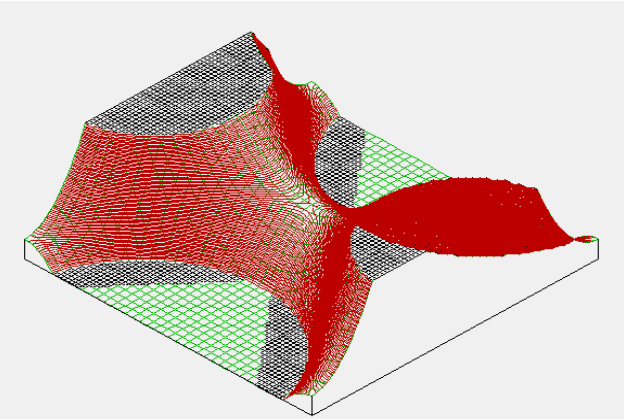


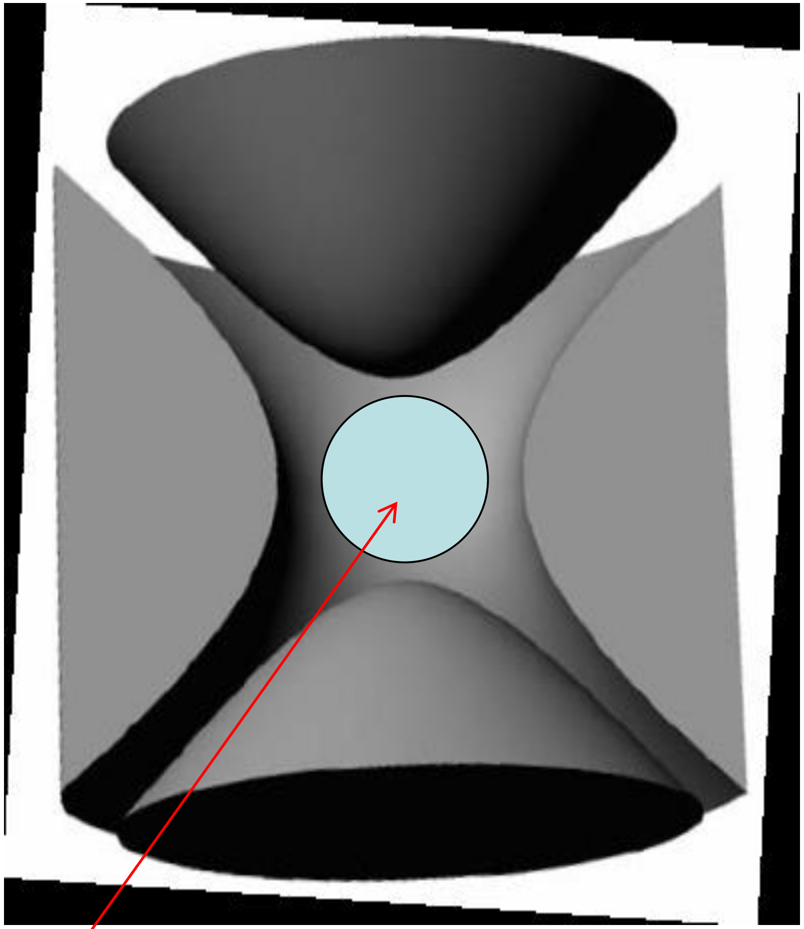
Projection on the plane almost
Parallel to the magnetic field

How to get rid of these comets?

The simple solution: use hyperbolic cell





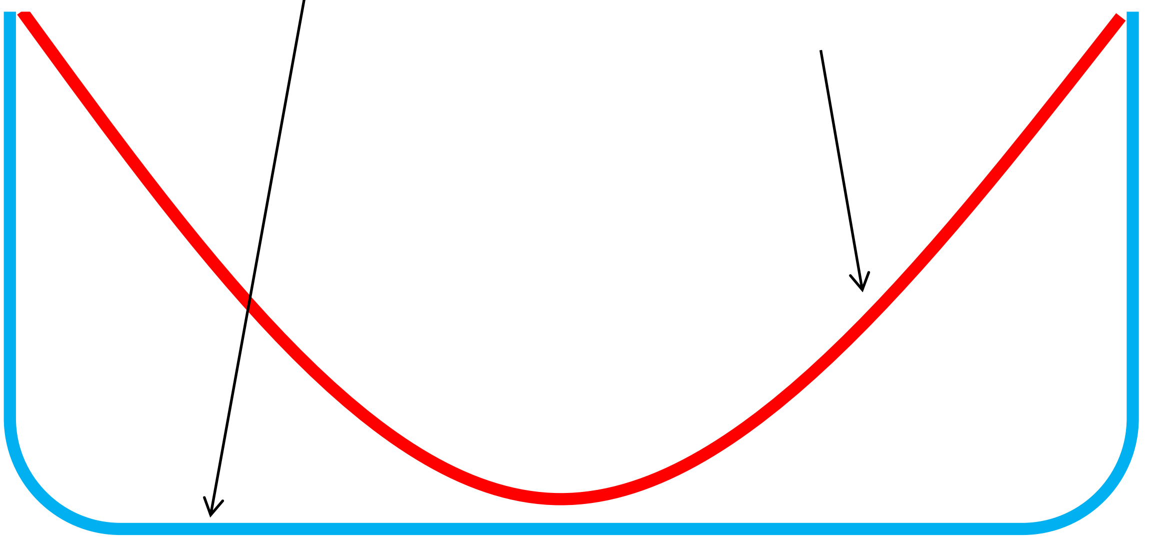


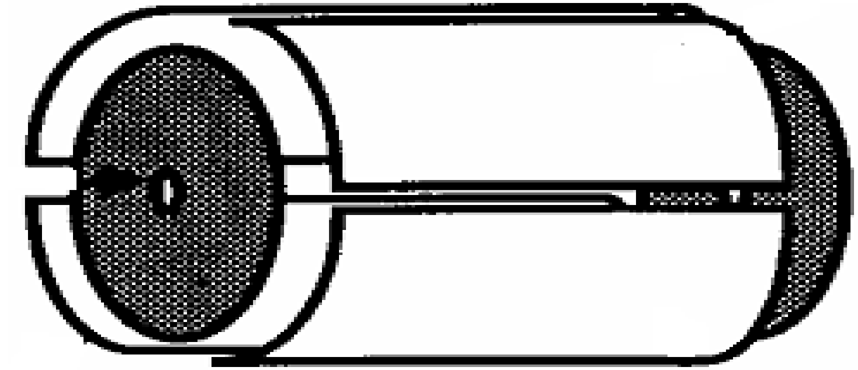
Used space

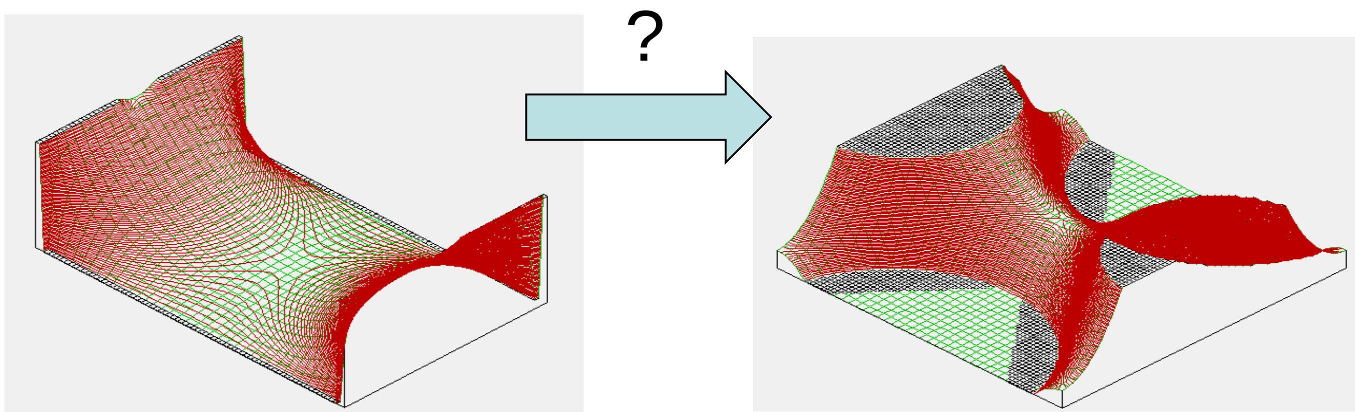
Other approaches

Flattering potential

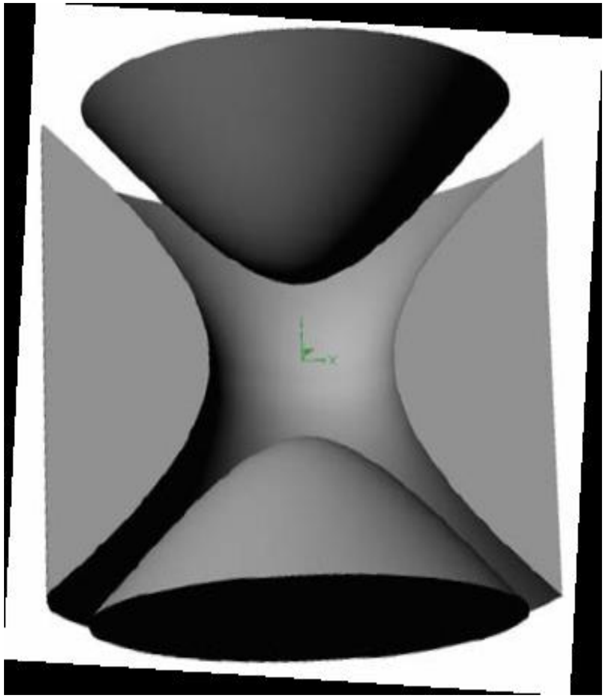
Harmonization - making the field quadratic along z and r coordinates

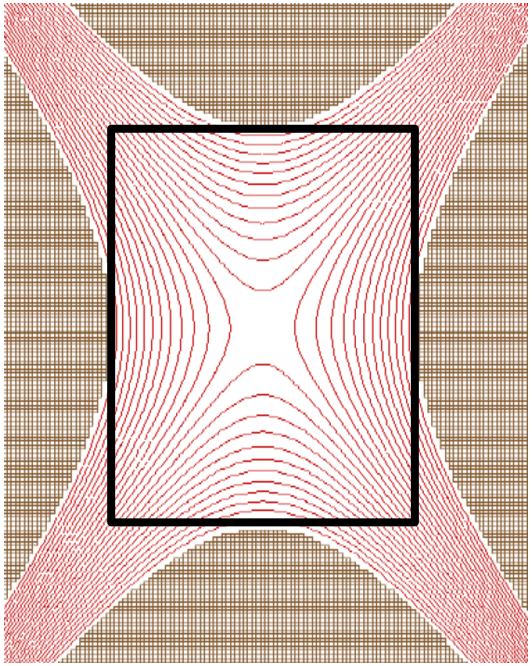






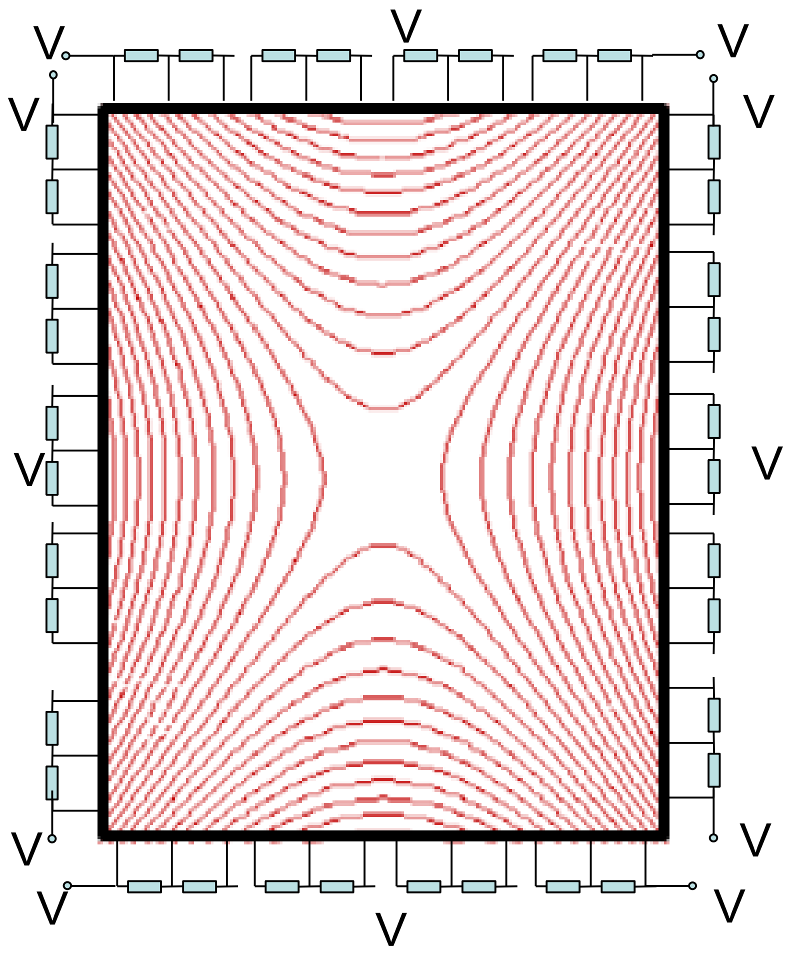
An instrument with a hyperbolic trap, however, suffers at least from inefficient use of the magnet bore and a relatively inaccessible trap interior.





The quadrupolar potential well can also be approximated in a cylindrical or cubic trap by using simple electrode shapes and by optimizing the aspect ratio or by segmenting the electrodes

(Gerald Gabrielse)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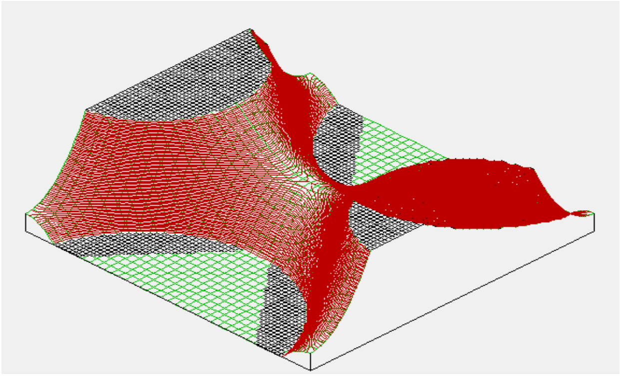

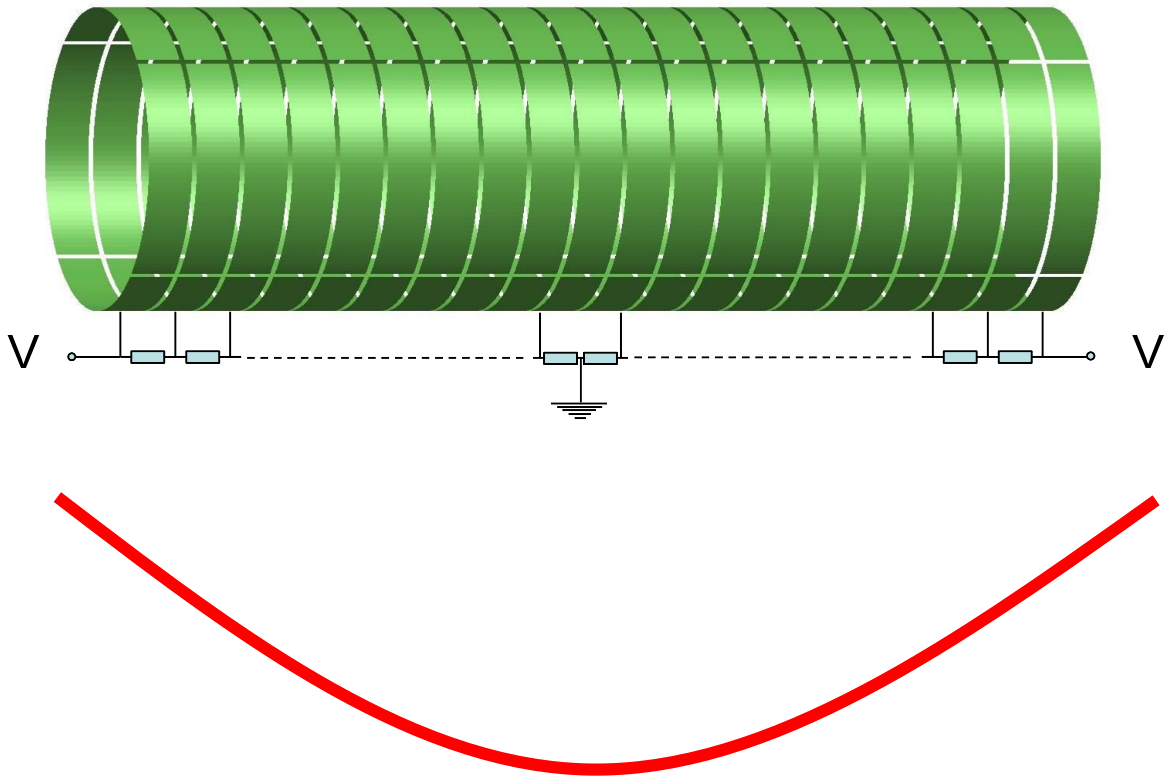
V
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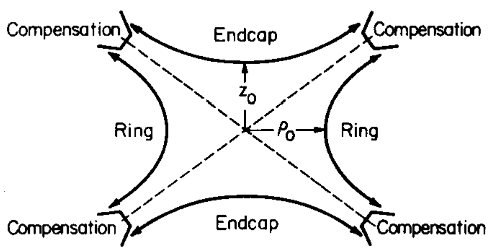
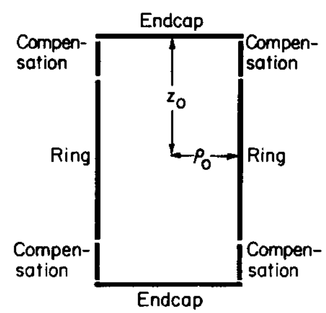
G. GABRIELSE, L. HAARSMA and S.L. ROLSTON

OPEN-ENDCAP PENNING TRAPS FOR HIGH PRECISION EXPERIMENTS

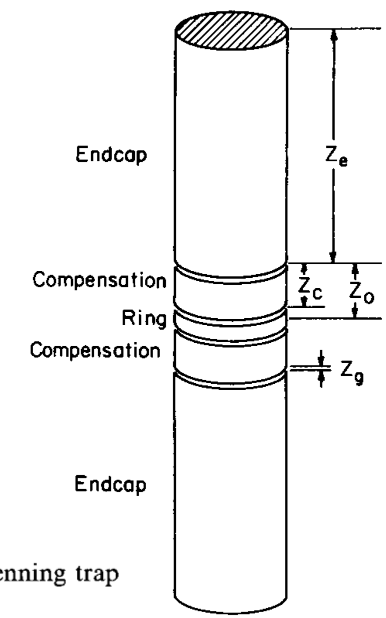
International Journal of Mass Spectrometry and Ion Processes, 88 (1989) 319–332



Hyperbolic
Trap
(a)



Flat-endcap
Cylindrical Trap
(b)



Open-endcap Penning trap

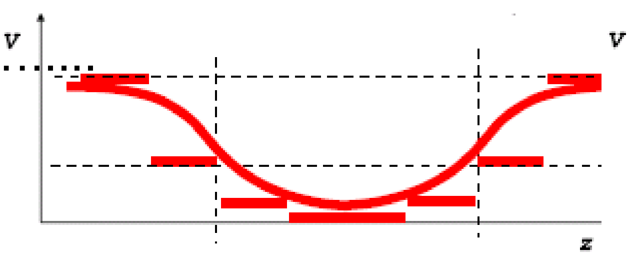
Harmonization of cell's electric potential (G.Gabrielse 1989)

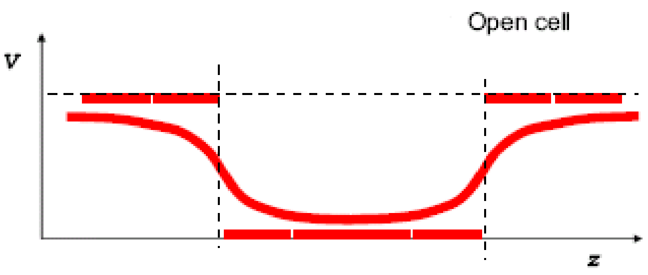
Tolmachev, A. V.; Robinson, E. W.; Wu, S.; Kang, H.; Lourette, N. M.; Pasa-Tolic, L.; Smith, R. D. Trapped-Ion Cell with Improved DC Potential Harmonicity for FT-ICR MS

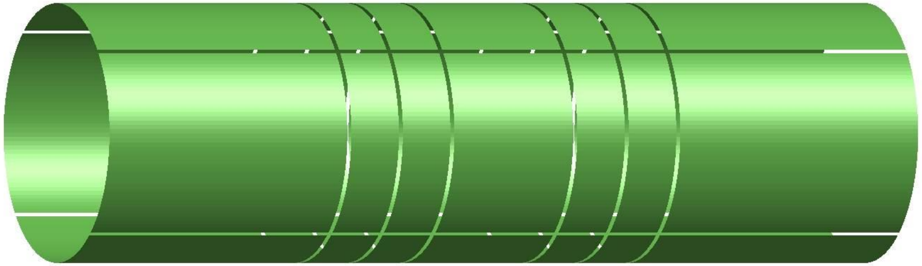
Brustkern A.M., Rempel D.L., Gross M.L. An Electrically Compensated Trap Designed to Eighth Order for FT-ICR Mass Spectrometry. J Am Soc Mass Spectrom 2008, 19, 1281–1285

Marshall's group,

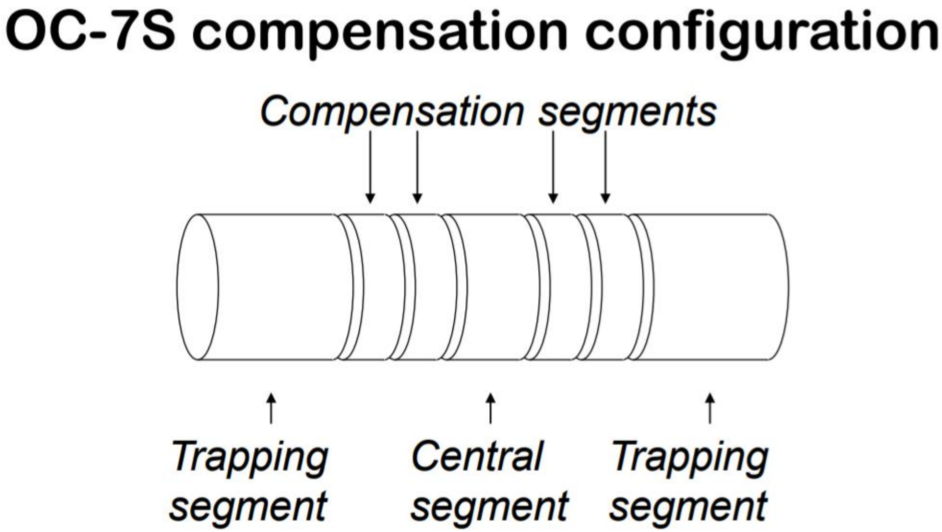
Bruker…….



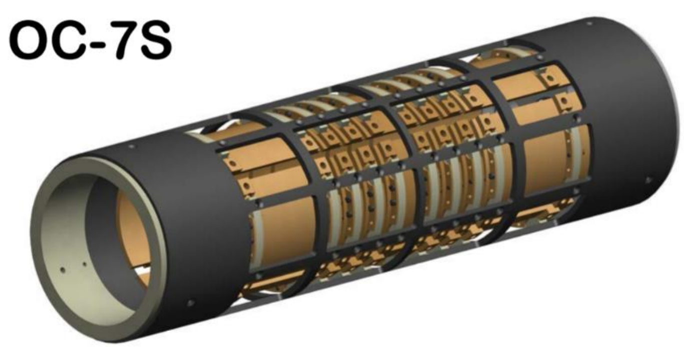




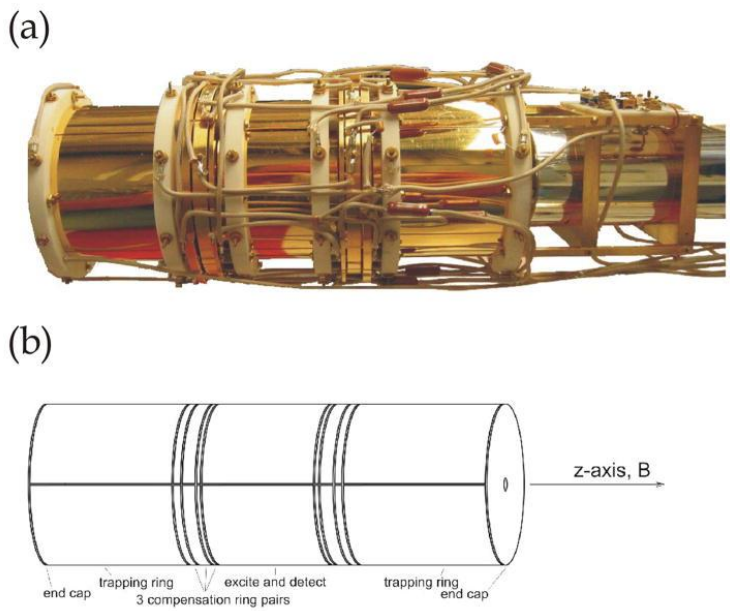
PNNL cell



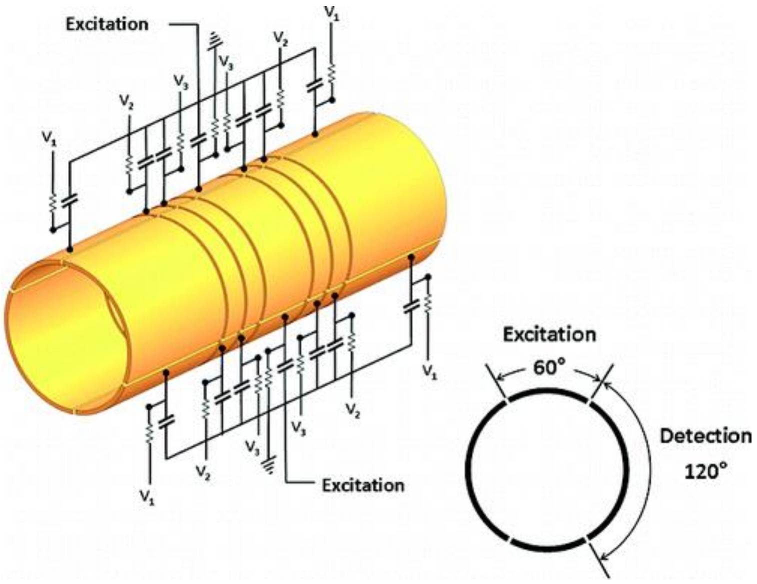
OC-7S compensation configuration
Compensation segments
Trapping segment
Central segment
Trapping segment



OC-7S

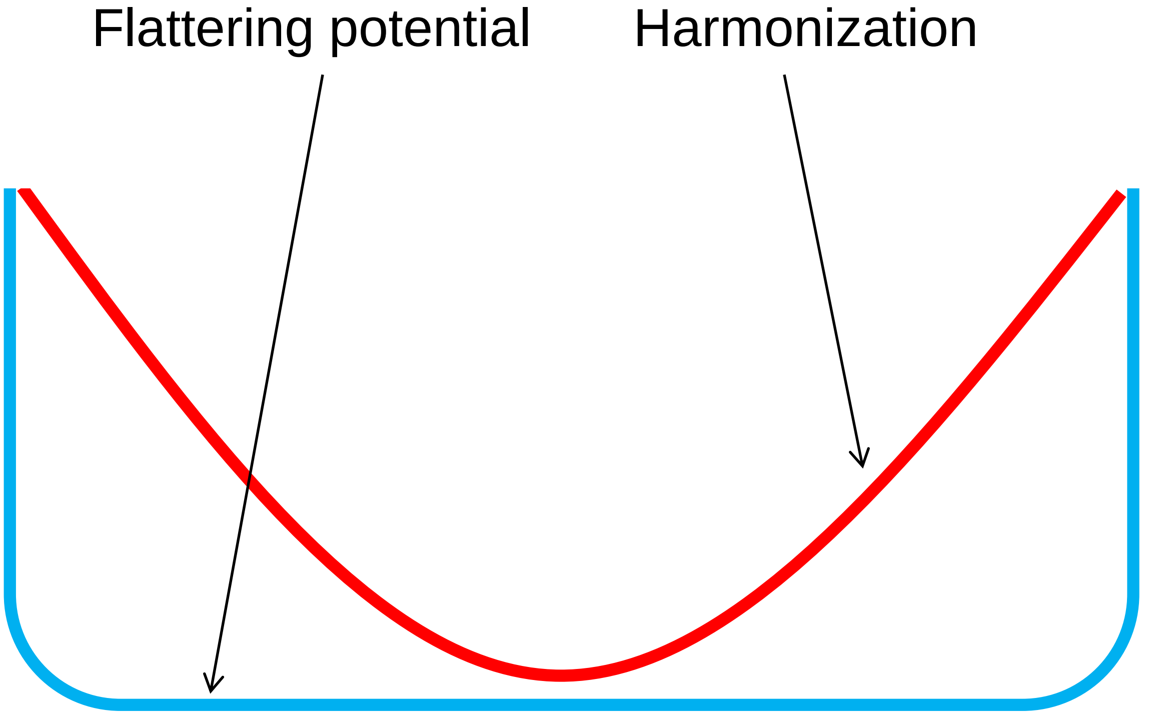


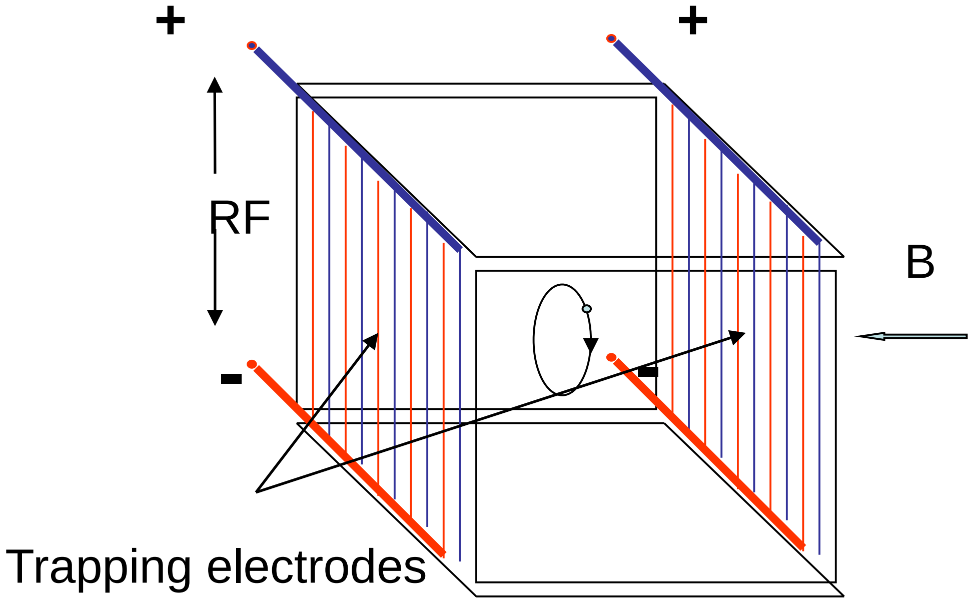
Gross group

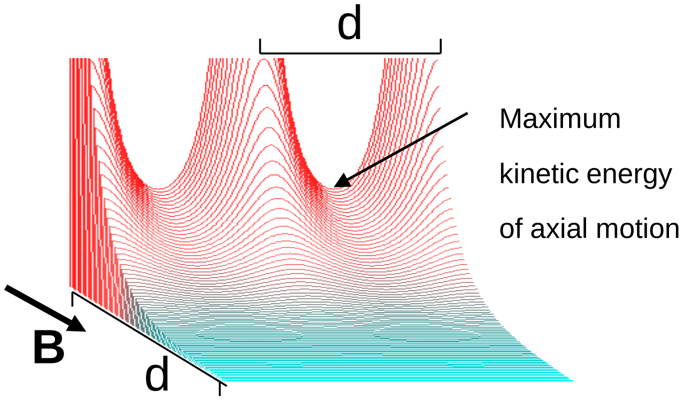


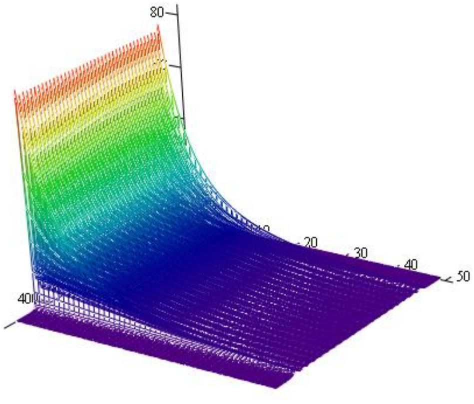
Marshall group

Two main approaches



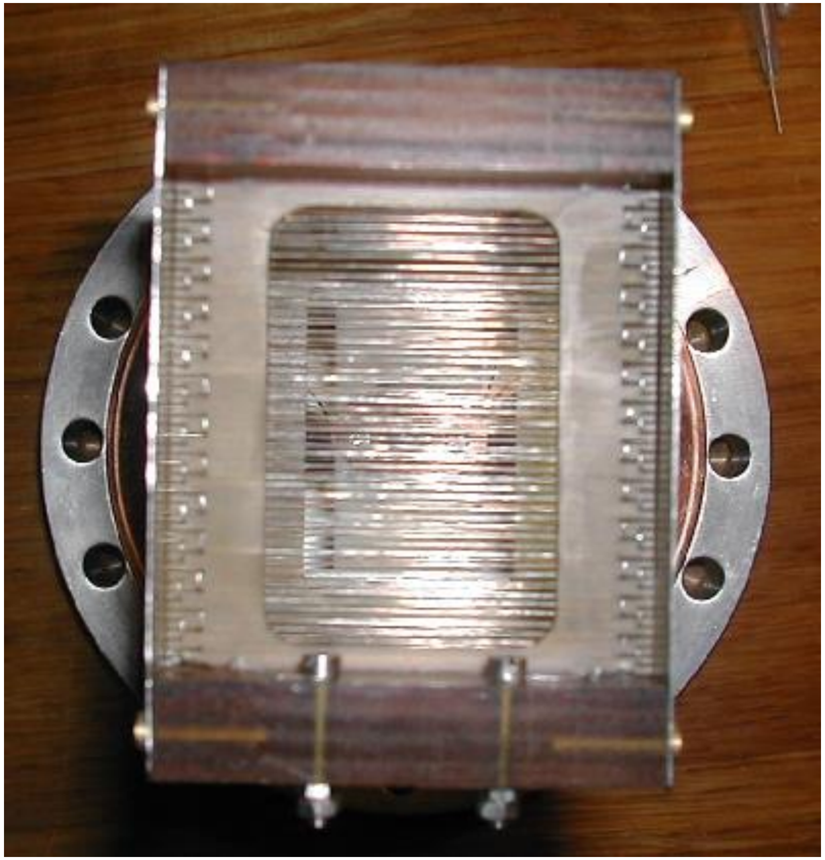

+
+
RF
B
-
-
Trapping electrodes


d
Maximum
kinetic energy
of axial motion
B
d



FT ICR cell with mesh trapping electrodes creating pseudopotential

Wire cell trapping electrode
(1 mm distance between adjacent wires)



US 20050242280A1

(19) United States
(12) Patent Application Publication
Nikolaev
(10) Pub. No.: US 2005/0242280 A1
(43) Pub. Date: Nov. 3, 2005

(54) **ION CYCLOTRON RESONANCE MASS SPECTROMETER**

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(73) Assignee: **Bruker Daltonik GMBH**, Bremen (DE)

(21) Appl. No.: **10/833,938**

(22) Filed: **Apr. 28, 2004**

Publication Classification

(51) **Int. Cl.**[7] **H01J 49/38**

(52) **U.S. Cl.** **250/291**

(57) **ABSTRACT**

The invention describes an ion cyclotron resonance (ICR) mass spectrometer with an ICR trap, the ICR trap having as trapping electrodes two ion reflecting electrode structures operated by RF voltages without any DC voltage. The usual apertured ion trapping electrodes are replaced by multitudes of structural elements, electrically conducting, and repeating spatially in one or two directions of a surface, neighboring structure elements being connected each to different phases of an RF voltage. In the simplest case a grid of parallel wires can be used. The surface of such structures reflects ions of both polarities, if the mass-to-charge ratio of the ions is higher than a threshold.

(12) **United States Patent**
Franzen et al.

(10) **Patent No.: US 7,368,711 B2**
(45) **Date of Patent: May 6, 2008**

(54) **MEASURING CELL FOR ION CYCLOTRON RESONANCE MASS SPECTROMETER**

(75) Inventors: **Jochen Franzen**, Bremen (DE); **Evgenij Nikolaev**, Moscow (RU)

(73) Assignee: **Bruker Daltonik GmbH**, Bremen (DE)

5,019,706	A *	5/1991	Allemann et al.	.... 250/291
5,572,035	A	11/1996	Franzen	
6,403,955	B1	6/2002	Senko	
7,223,965	B2 *	5/2007	Davis	.... 250/282

FOREIGN PATENT DOCUMENTS

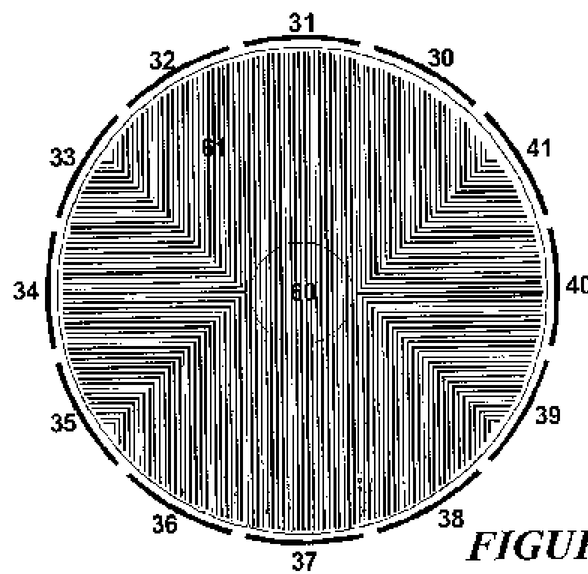
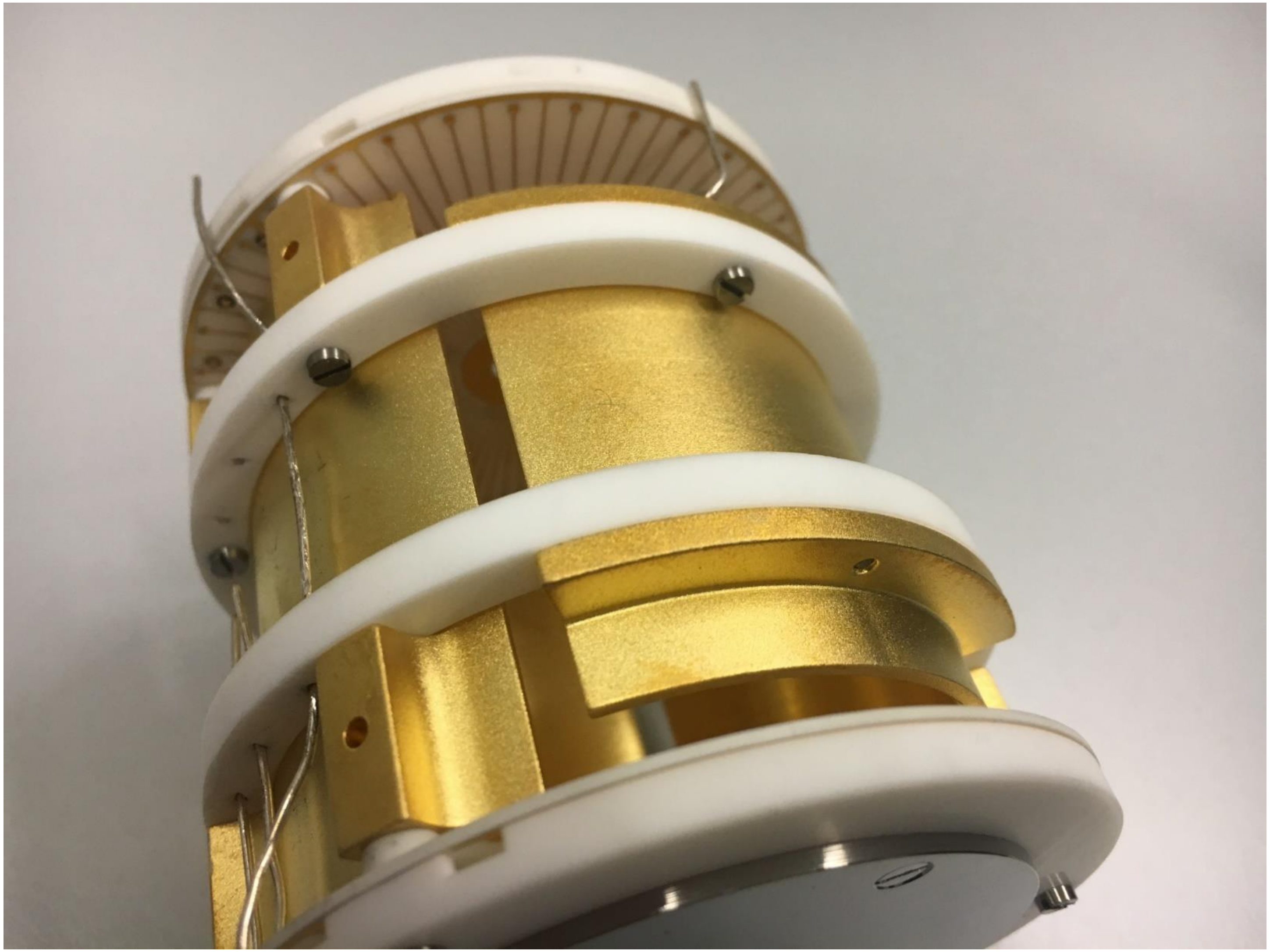
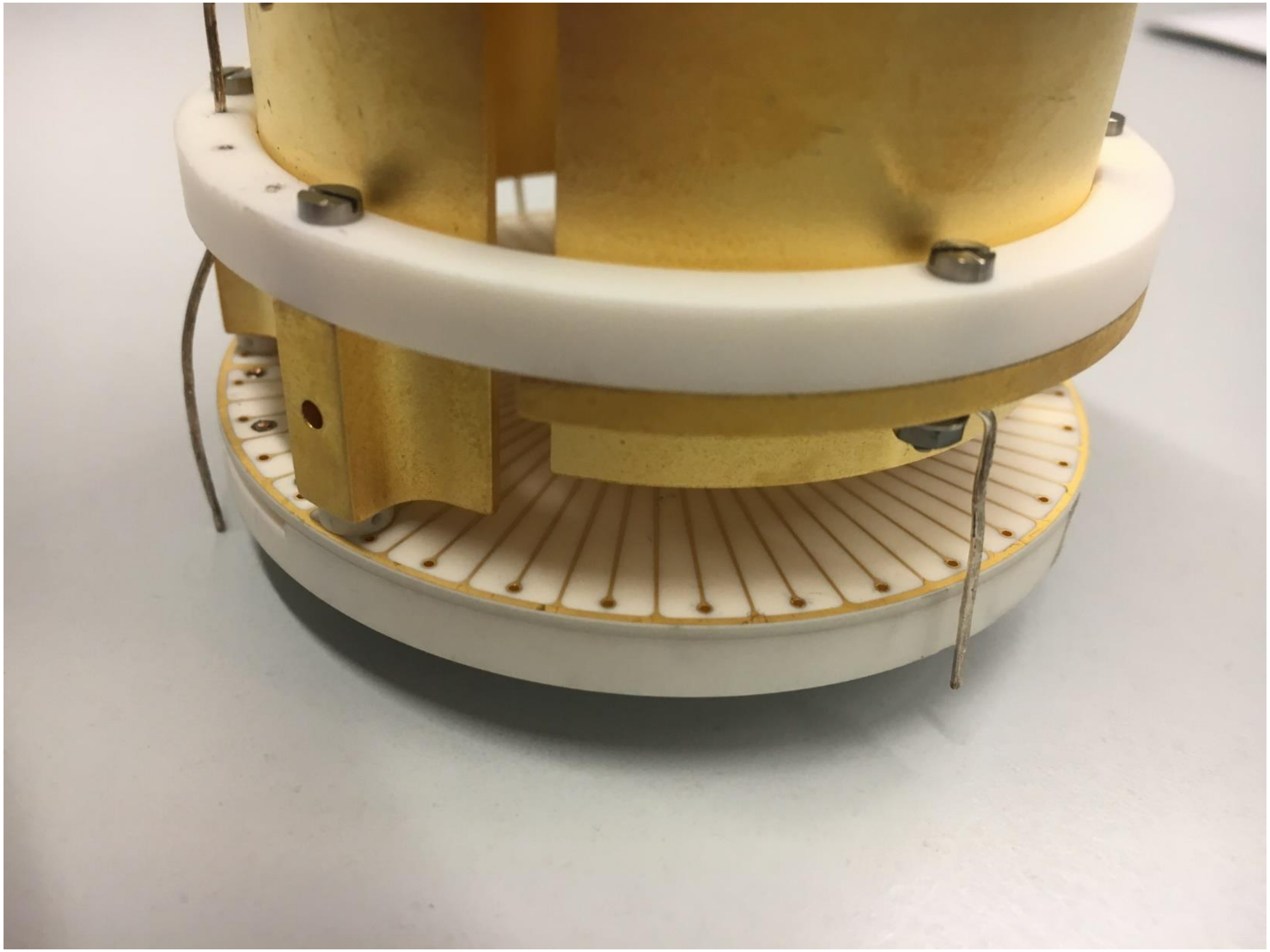


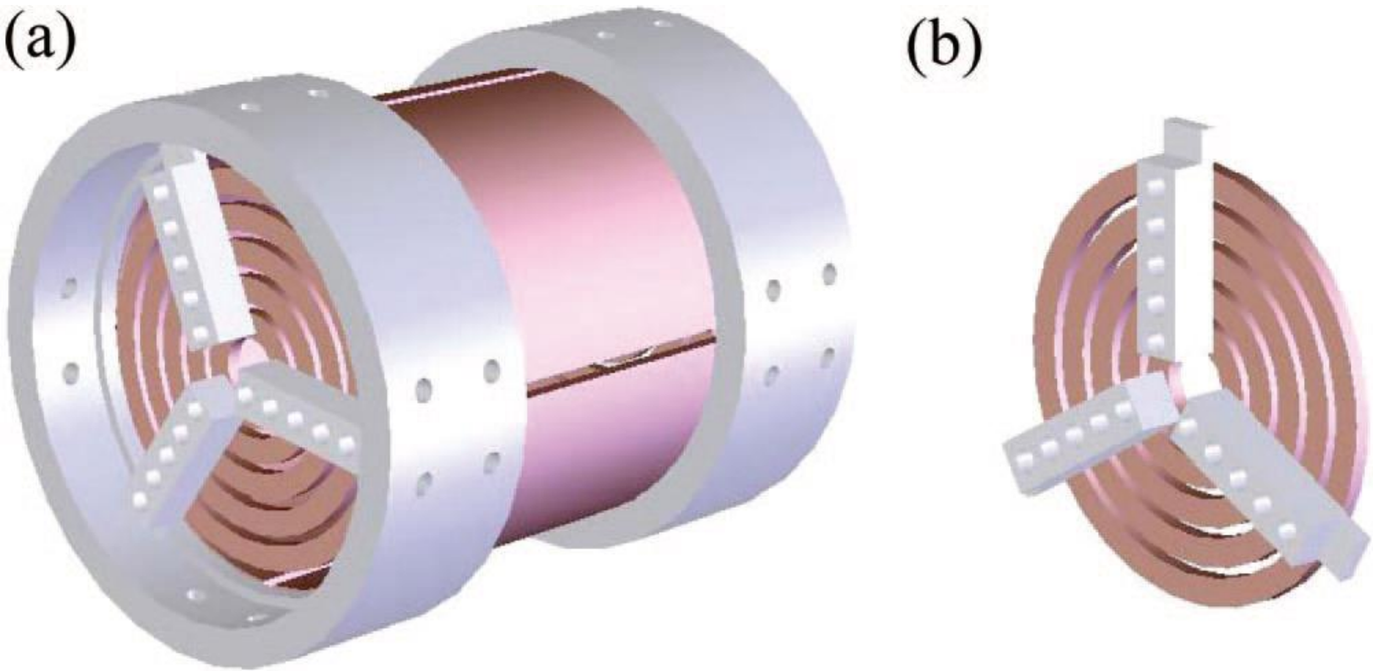
FIGURE 7





Cell with trapping electrodes segmented to rings

Chad R. Weisbrod, Nathan K. Kaiser, Gunnar E. Skulason, and James E. Bruce*
Trapping Ring Electrode Cell: A FTICR Mass Spectrometer Cell for Improved Signal-to-Noise and Resolving Power *Anal. Chem. 2008, 80, 6545–6553*



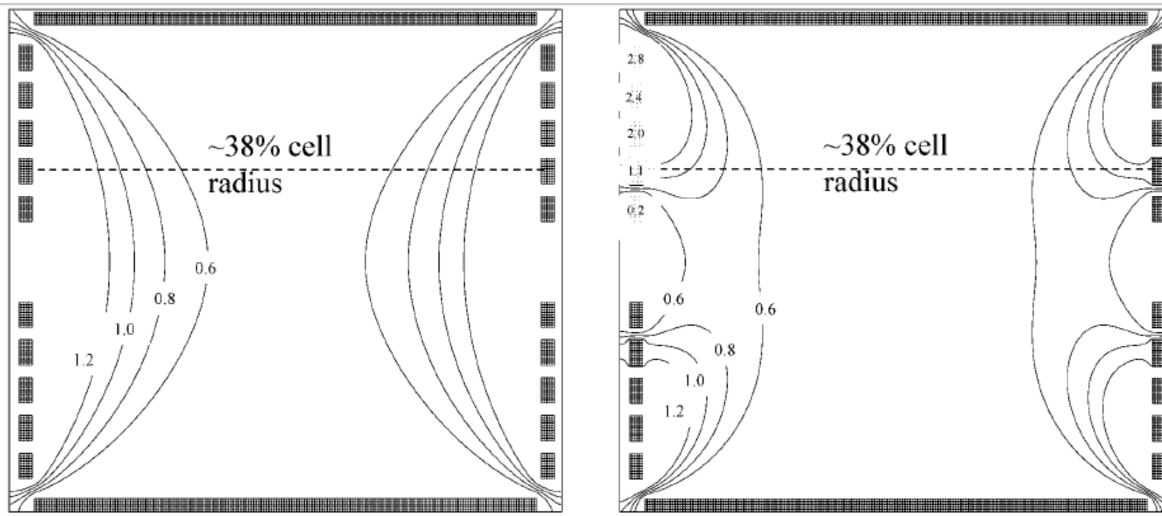


Figure 2. Equipotential contour plots are shown for (a) common 2.0 V trapping conditions and (b) the TREC trapping conditions. The voltages for the modulated (TREC) trapping conditions with increasing electrode radius are 0.2, 1.1, 2.0, 2.4, and 2.8 V respectively, as shown on the rings. A dashed line through the cell located at 38% cell radius is depicted.

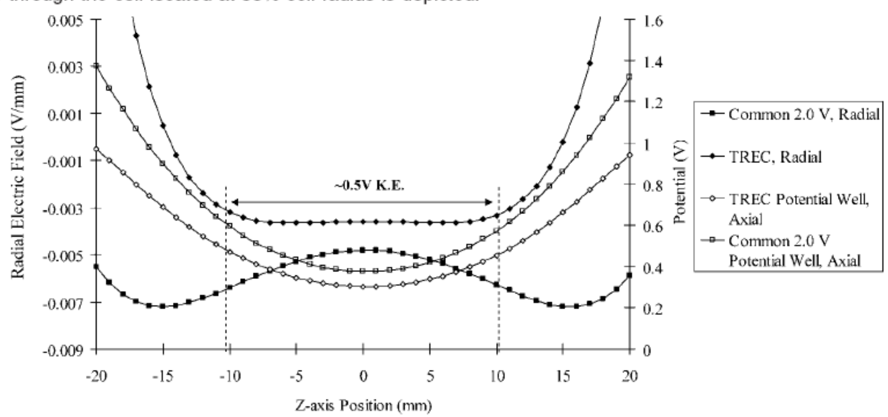
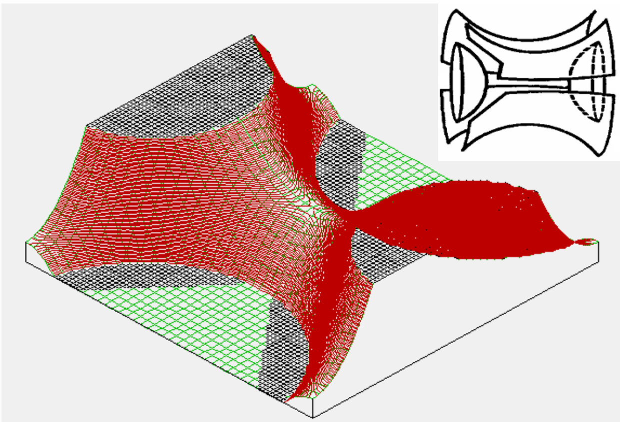
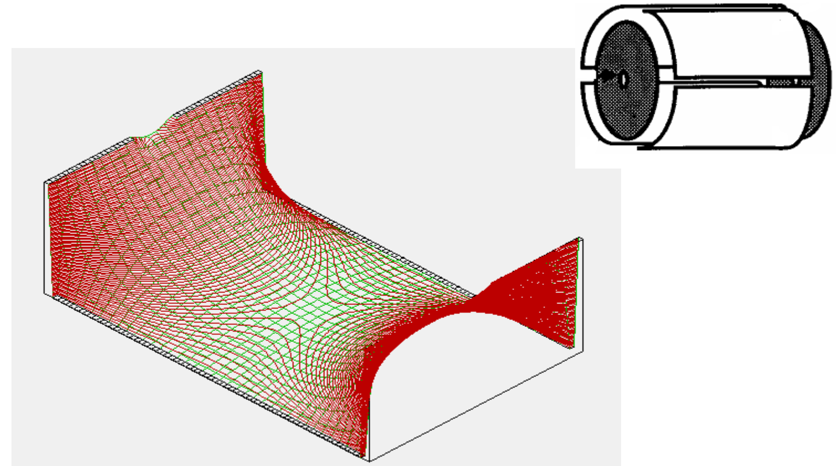


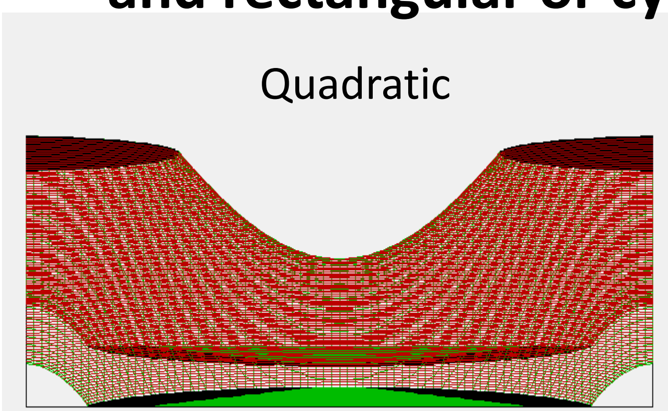
Figure 3. Radial electric field plots generated at 38% cell radius for both common 2.0 V trapping conditions and the TREC modulated conditions. A trapping potential well generated from the TREC conditions is overlaid to provide perspective.

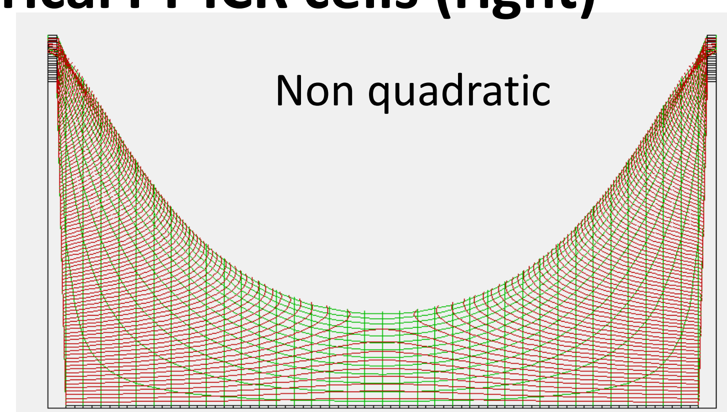
The lost of phase coherence is a result of Unharmonicity of a regular FT ICR cell field





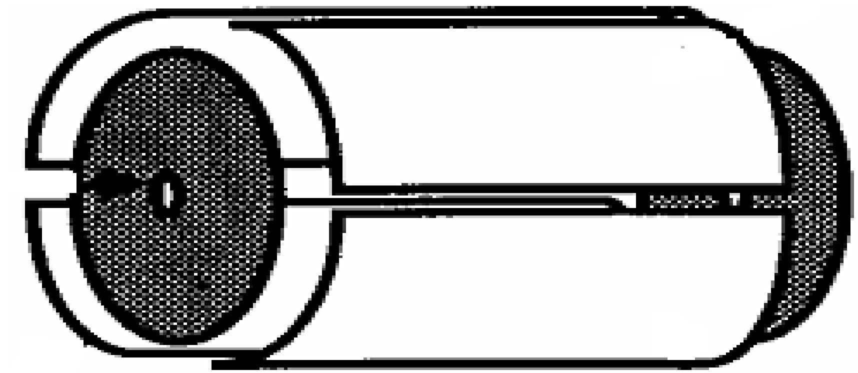
Distribution of potentials in hyperbolic (left) and rectangular or cylindrical FT ICR cells (right)

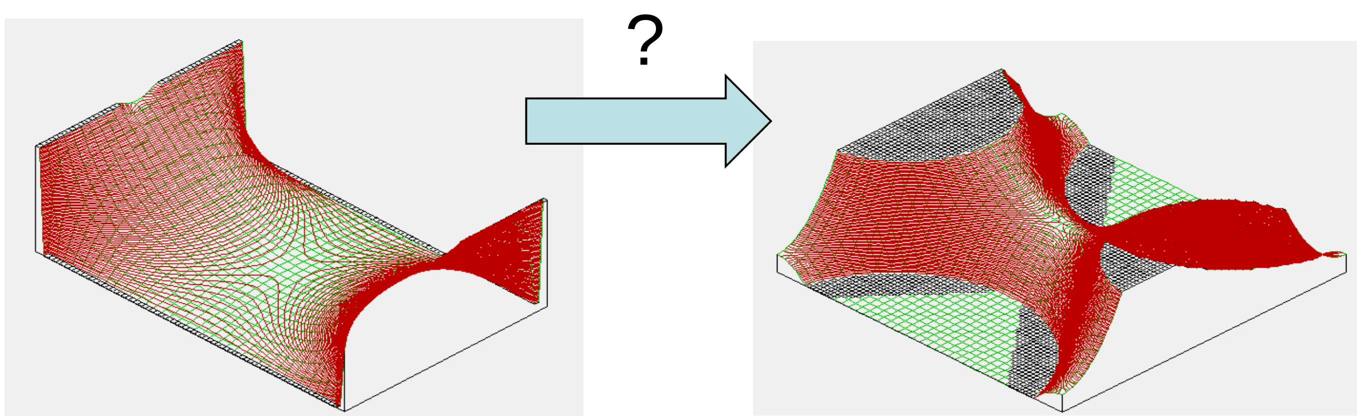




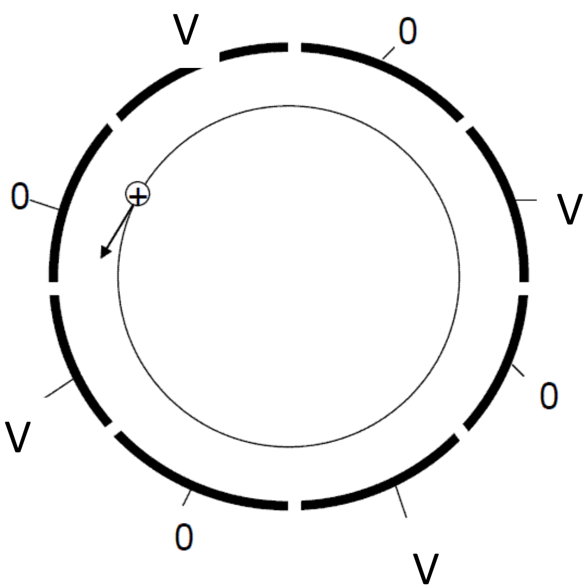
Axial and magnetron frequencies are Independent on axial oscillation amplitude

Axial and magnetron frequencies depend on axial oscillation amplitude

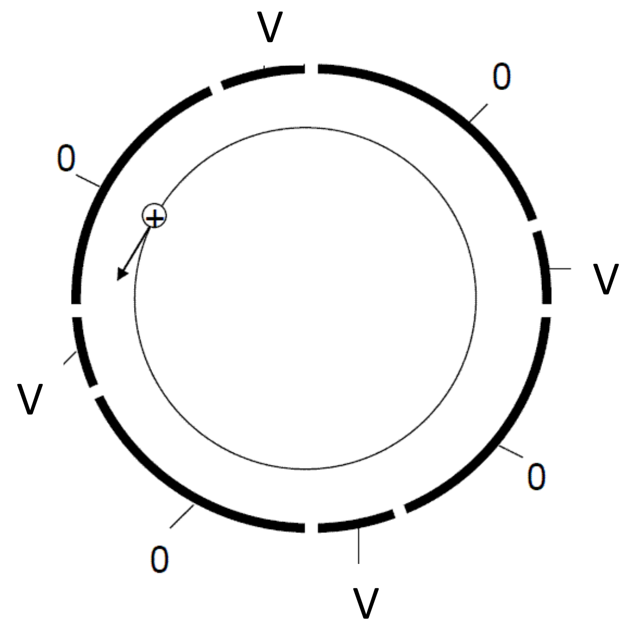




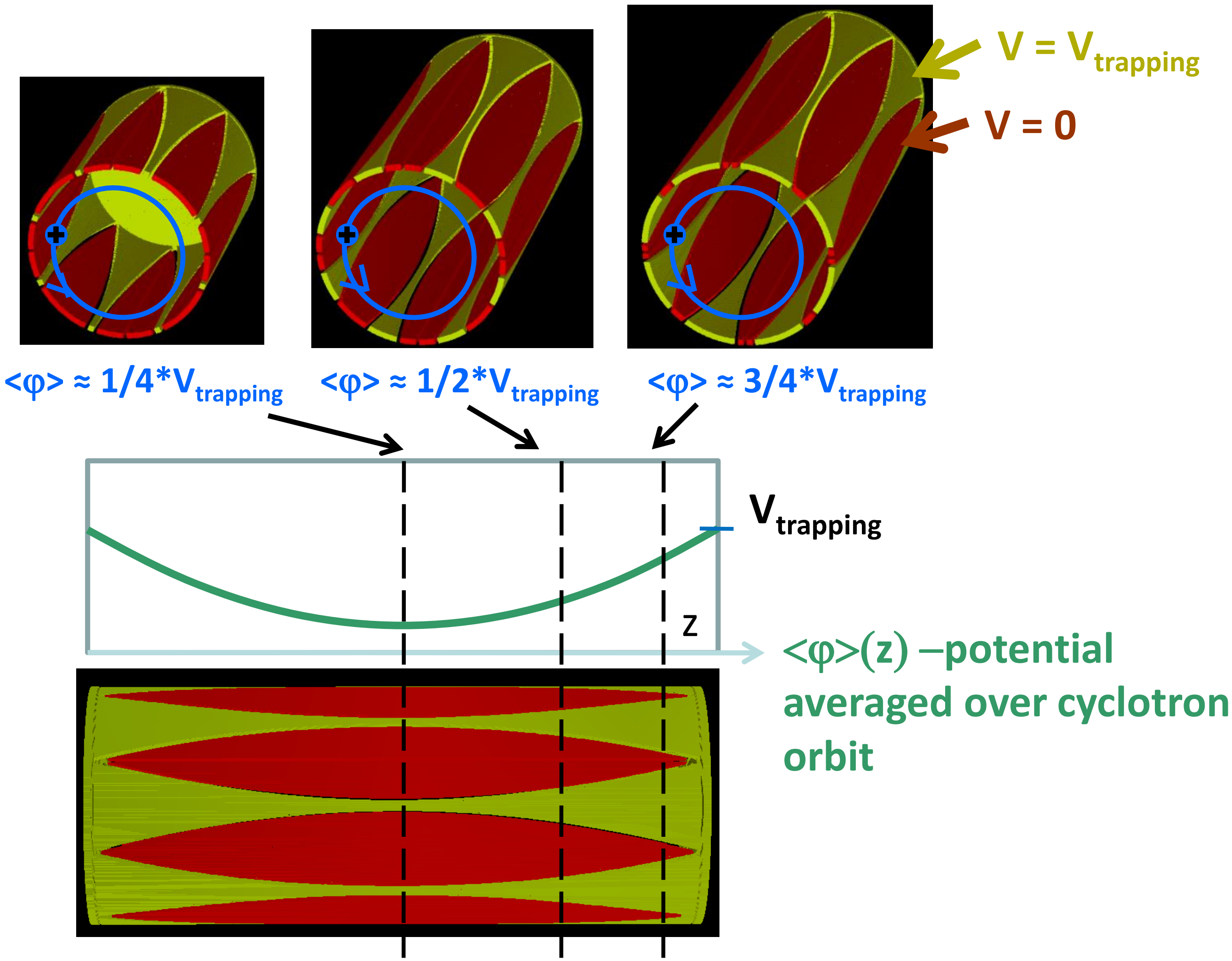
Averaging over cyclotron motion



$$\langle \varphi \rangle = \frac{1}{2} V$$



$$\langle \varphi \rangle = \frac{1}{4} V$$

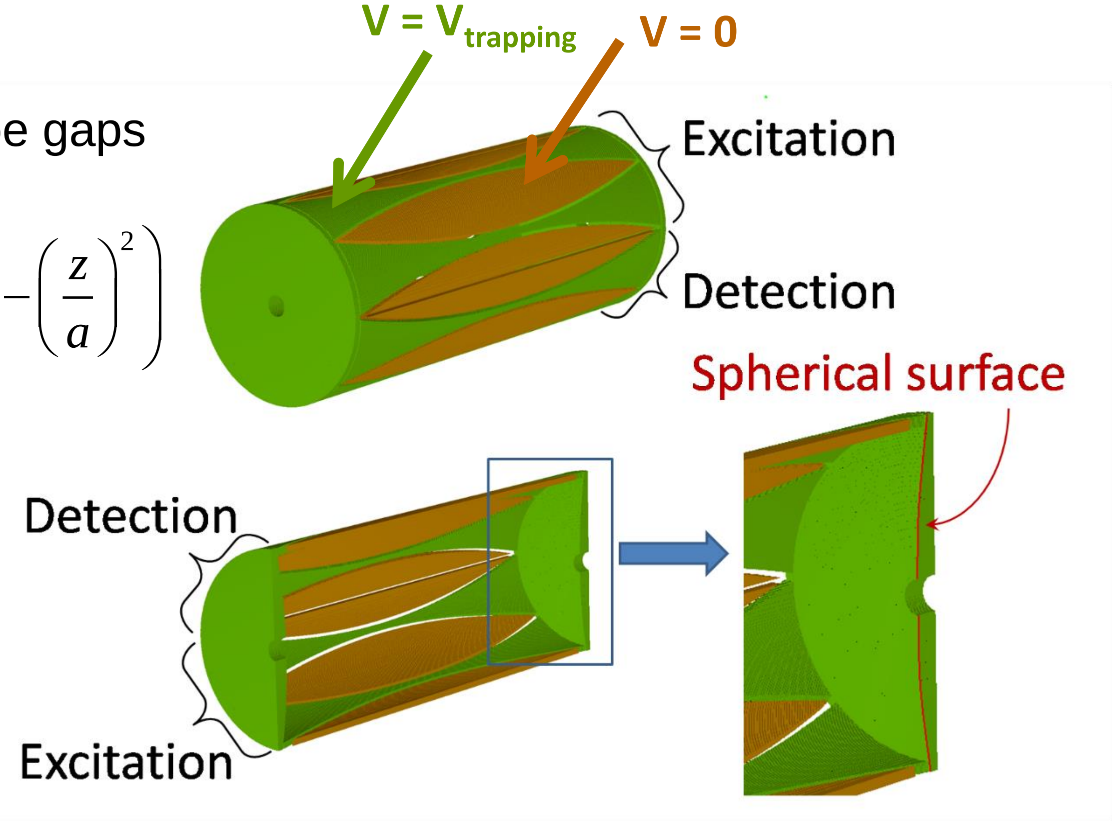


V = V_trapping
V = 0
<φ> ≈ 1/4*V_trapping
<φ> ≈ 1/2*V_trapping
<φ> ≈ 3/4*V_trapping
V_trapping
z
<φ>(z) –potential averaged over cyclotron orbit

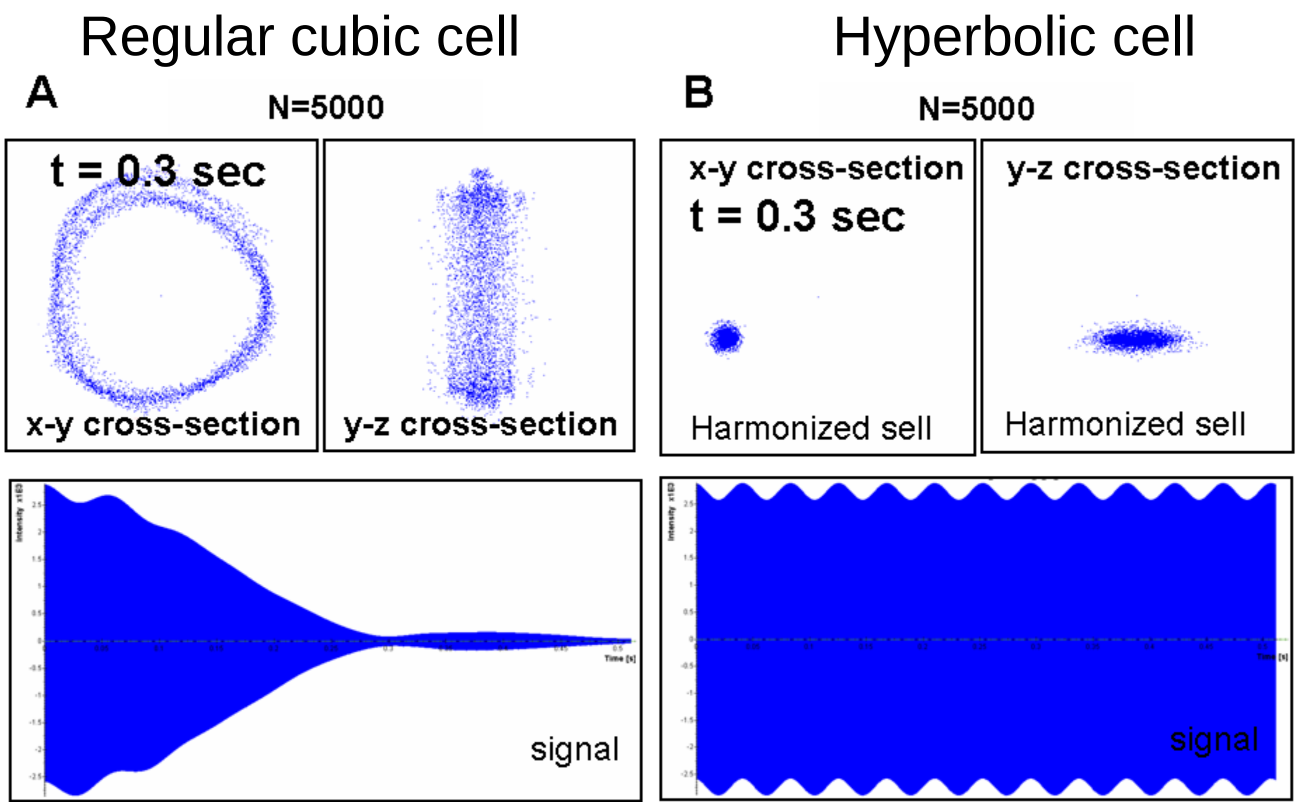
Dynamically harmonized FT ICR cell

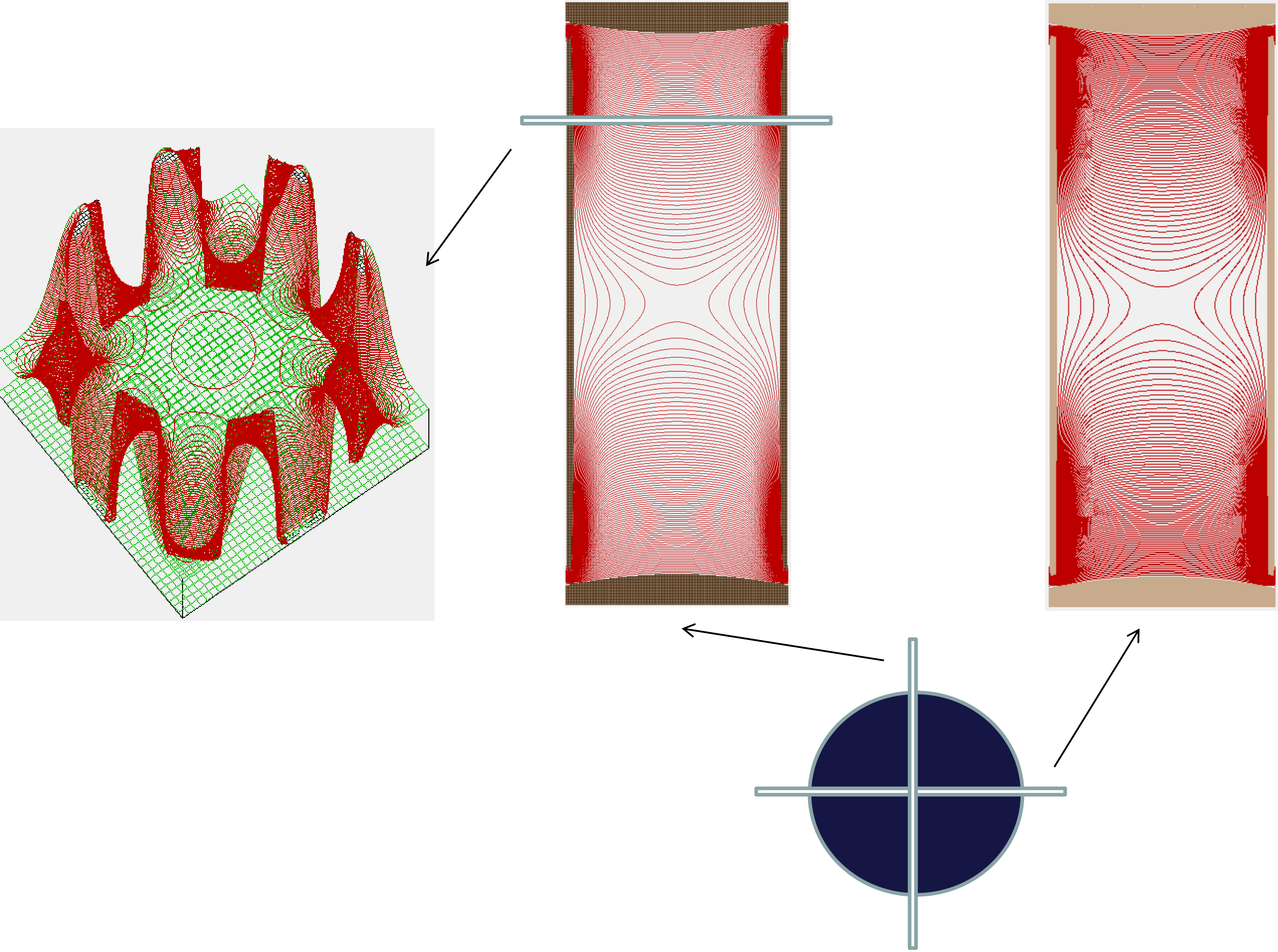
Parabolic shape gaps

$$\alpha = \frac{2\pi}{N} n \pm \alpha_0 \left(1 - \left(\frac{z}{a} \right)^2 \right)$$

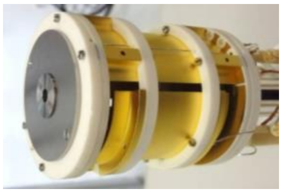


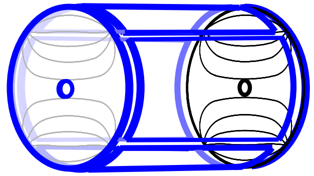
Evolution of ion cloud m/z = 500 Да, Z=1 in 7 T
0.5 s detection time.

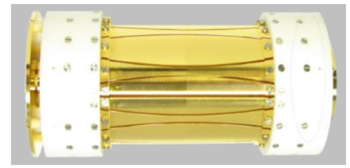


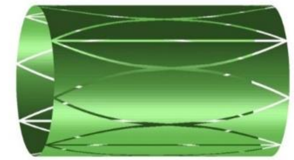


Comparison of averaged axial potential

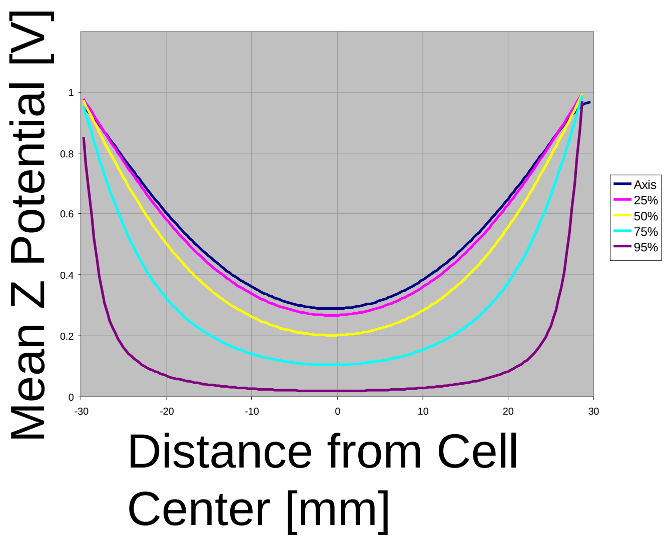




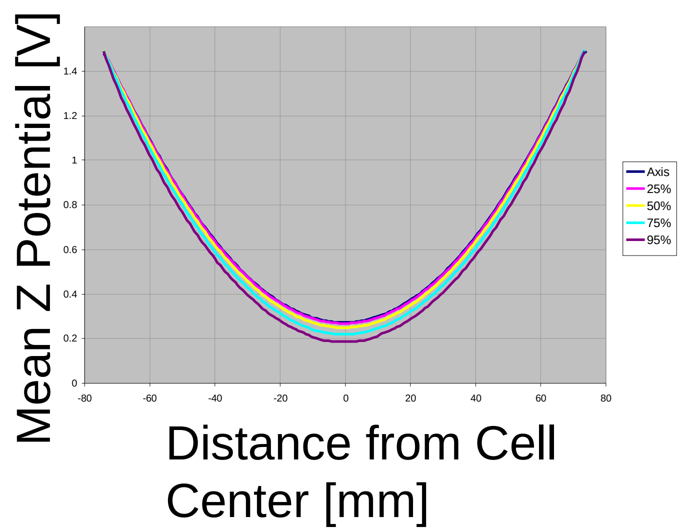




Infinity Cell



Dynamically Harmonized Cell

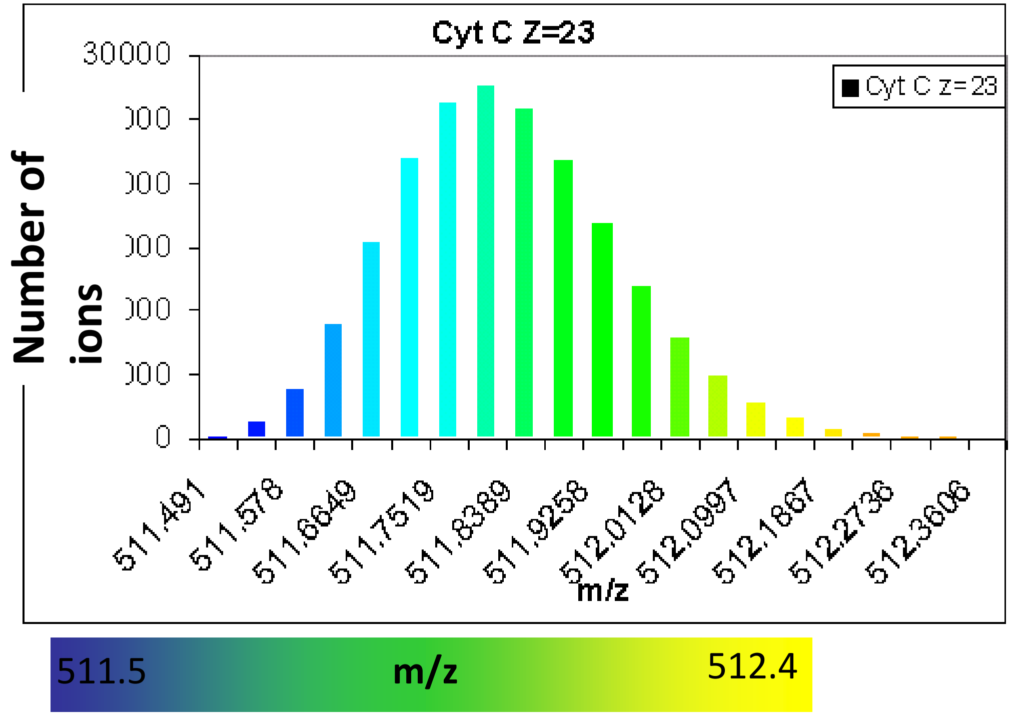


Near parabolic potential up to a cyclotron orbit of 50% of the cell radius.

Harmonic, parabolic potential at all cyclotron orbits.

Isotopic cluster of Cyt C (charge state Z=23)

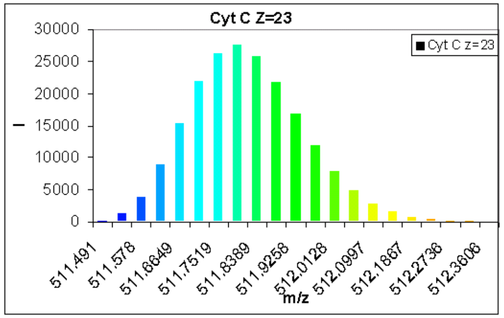
Theoretical isotopic distribution



7T, 21T ; 0.3 sec detection; >100 steps per minimal cyclotron period;

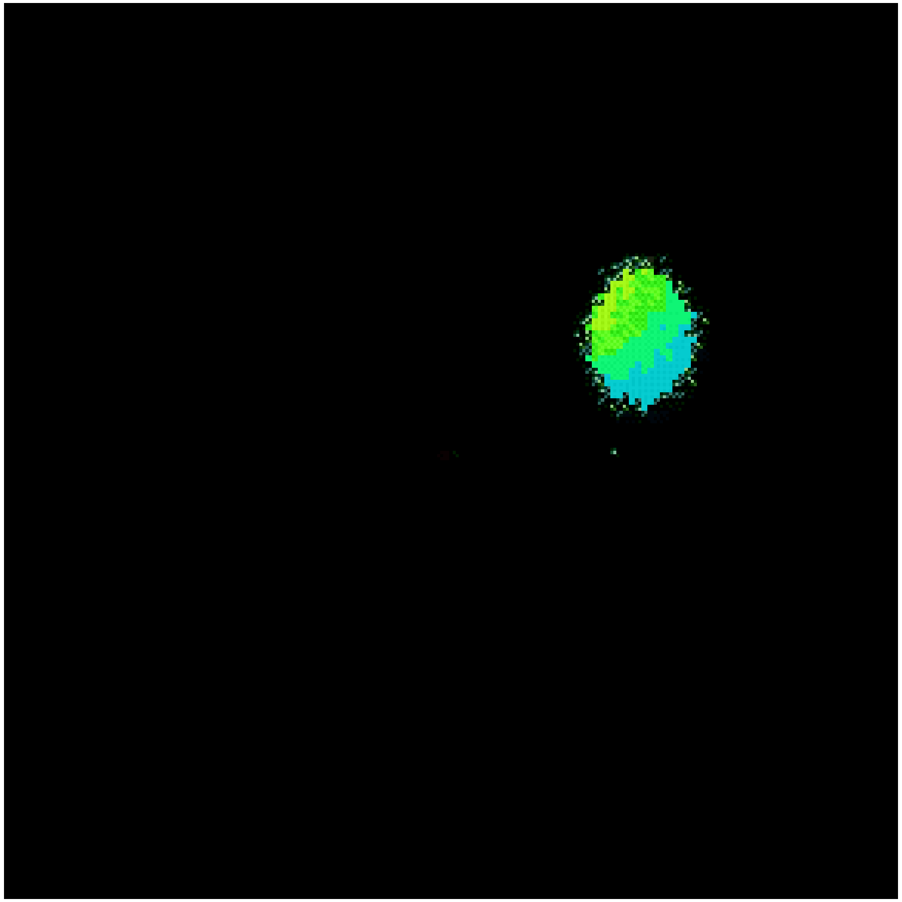
0.0004 sec, 50V p-p excitation "chirp" excitation *; 5V trapping potential*

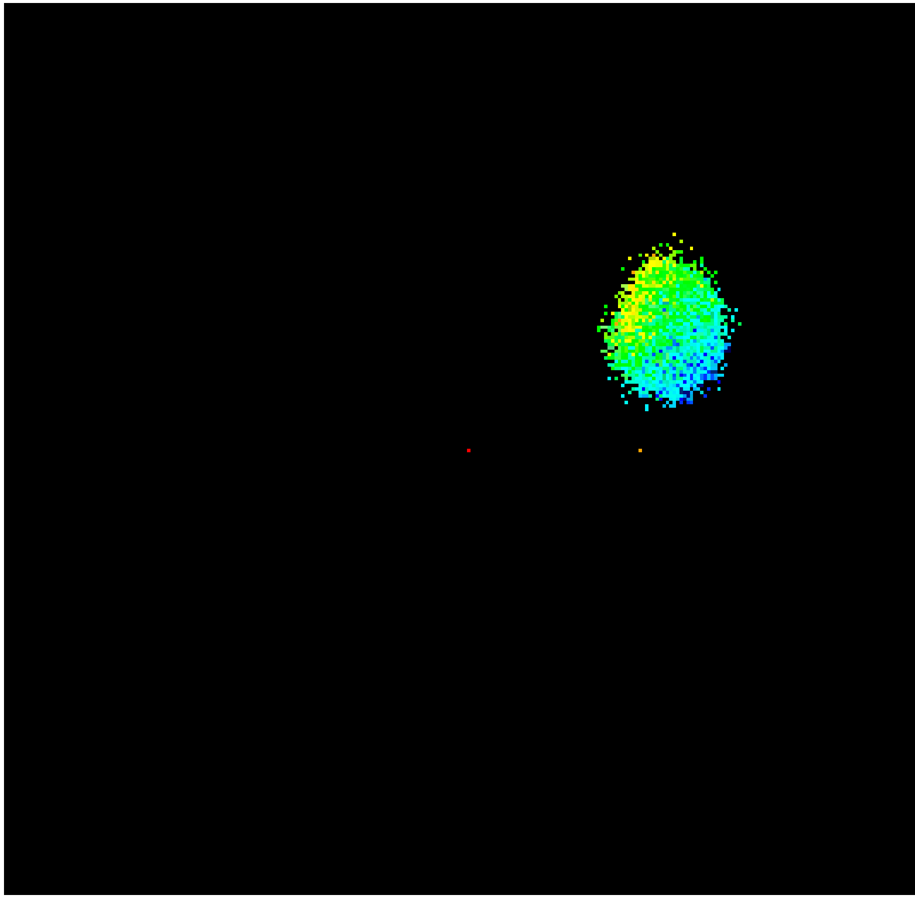
7T Cyt C 100000 charges



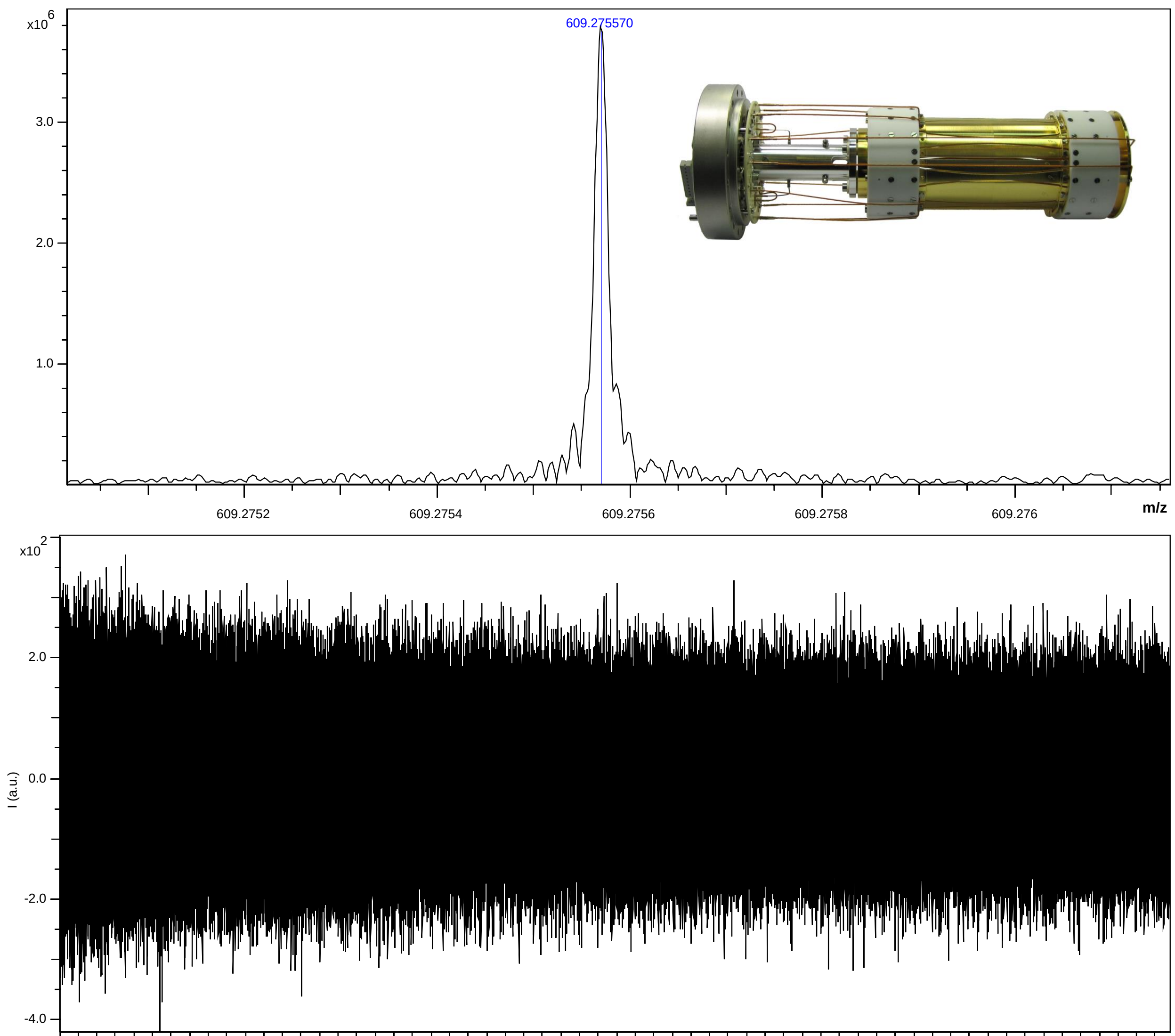
Cylindrical, cubic

Hyperbolic, dynamically harmonized

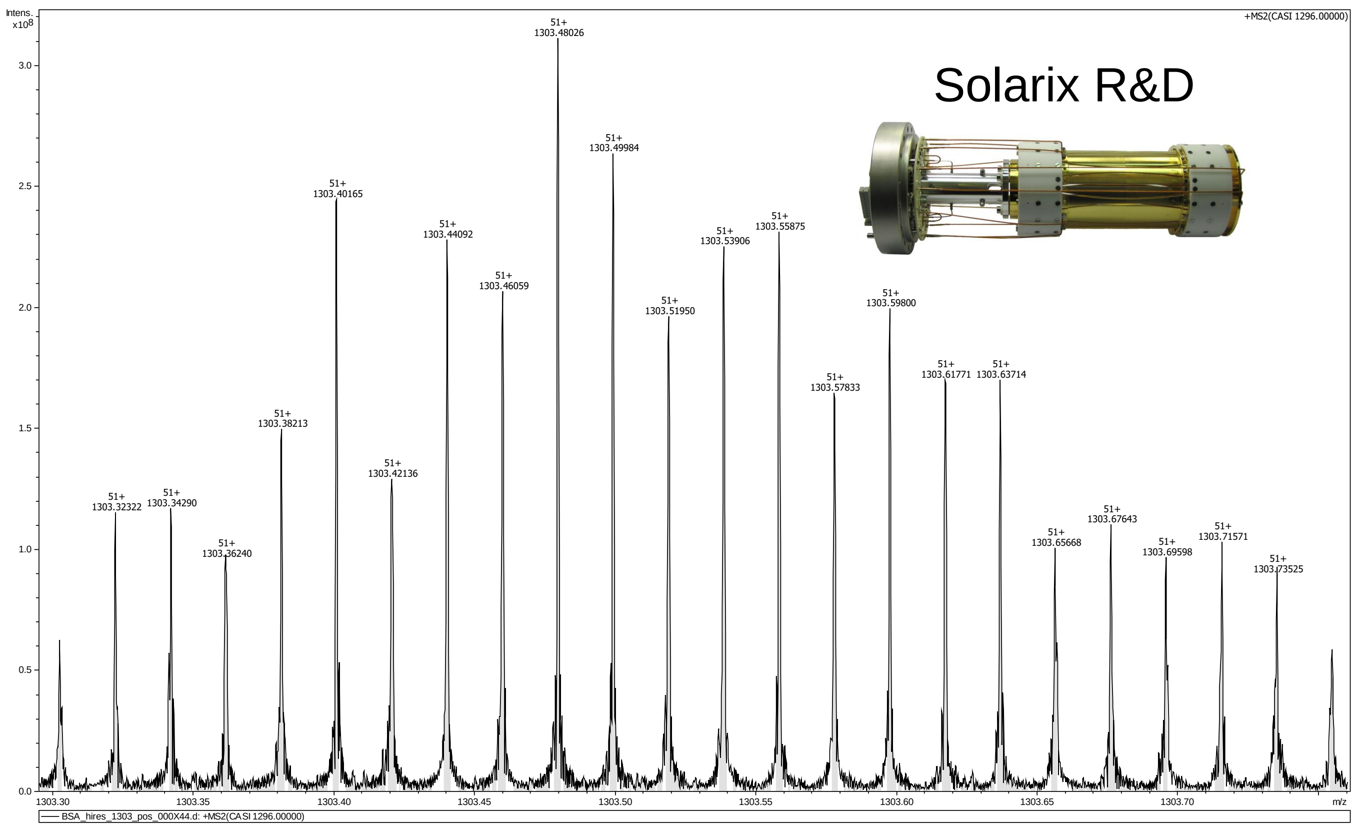




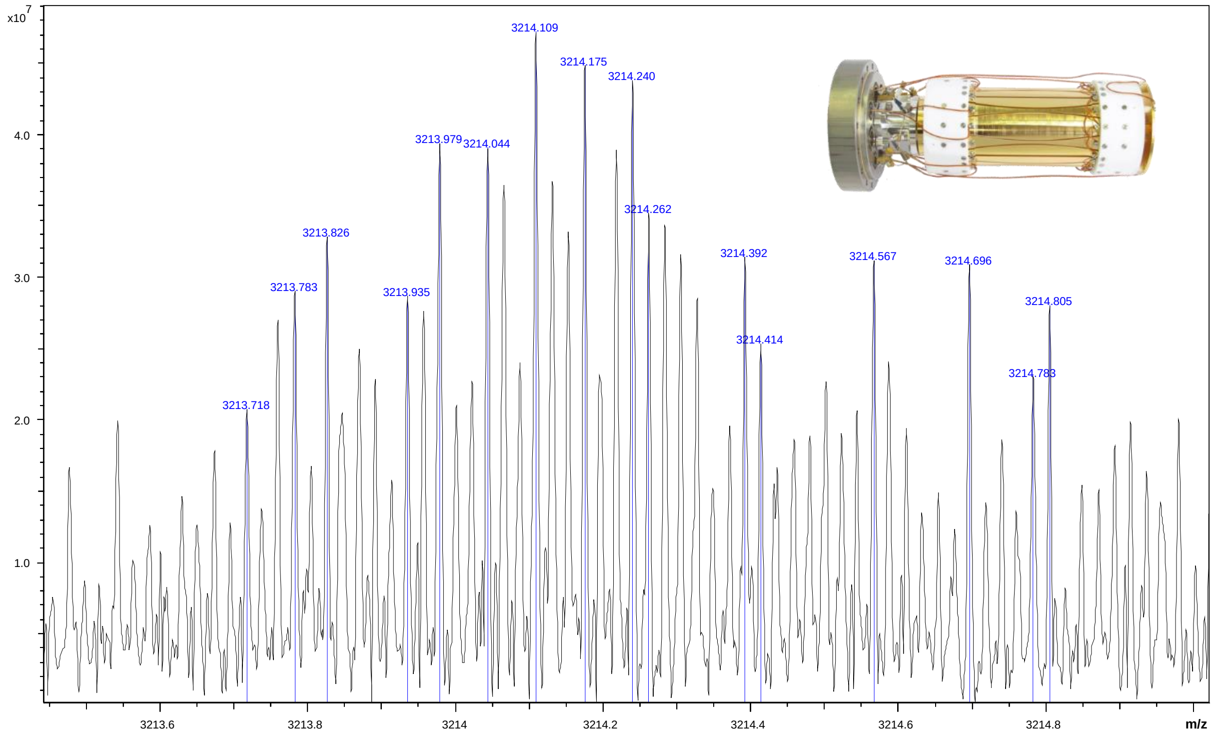
Reserpine. Lab Prototype , Solarix, 300s transient, RP 39,000,000 in magnitude mode



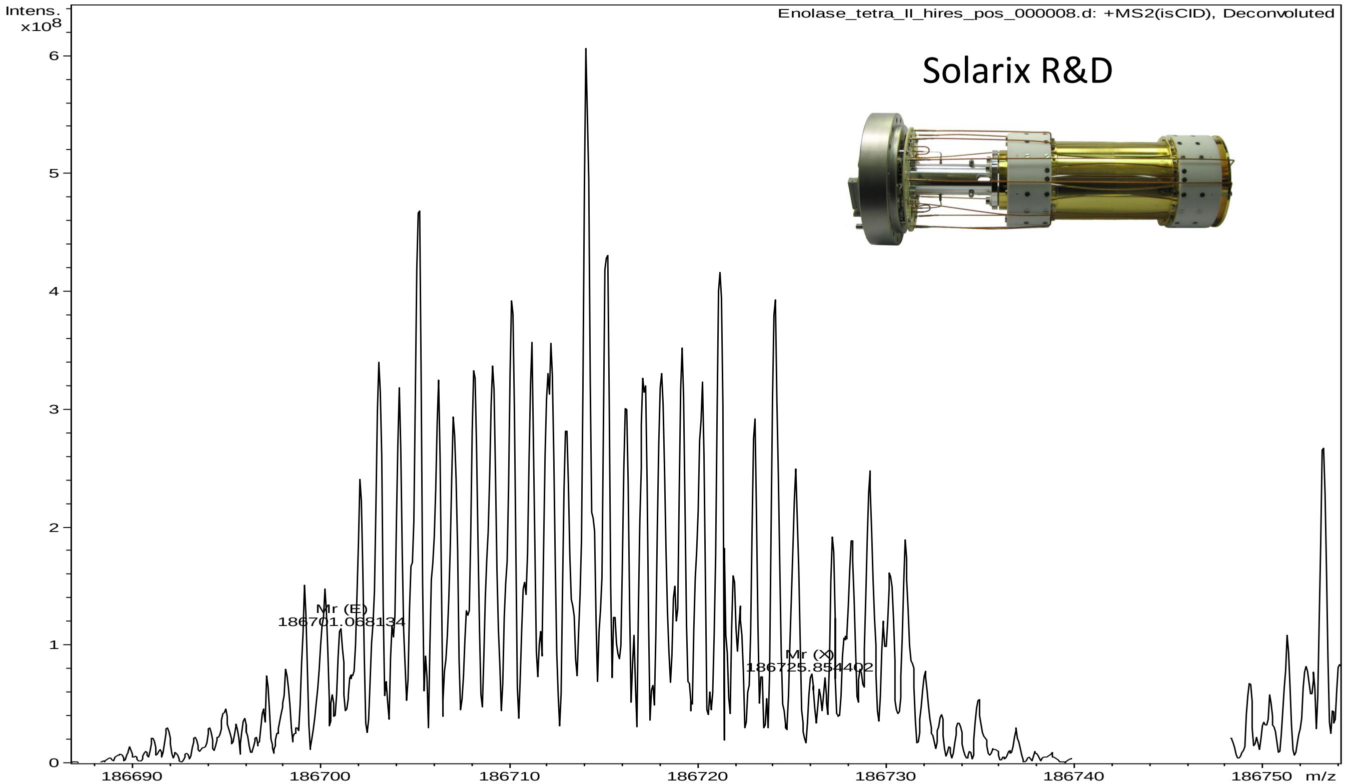
7T R&D, BSA, 51+, RP 1,700,000 28 s transient



IgG1 (MW =147800 Da), 46+, RP 500 000



12T R&D, Enolase Tetramer, MW=**186713** Da, m/z=5835, (6мG/ml) , 32+, deconvoluted

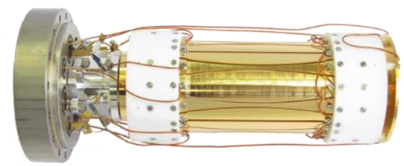


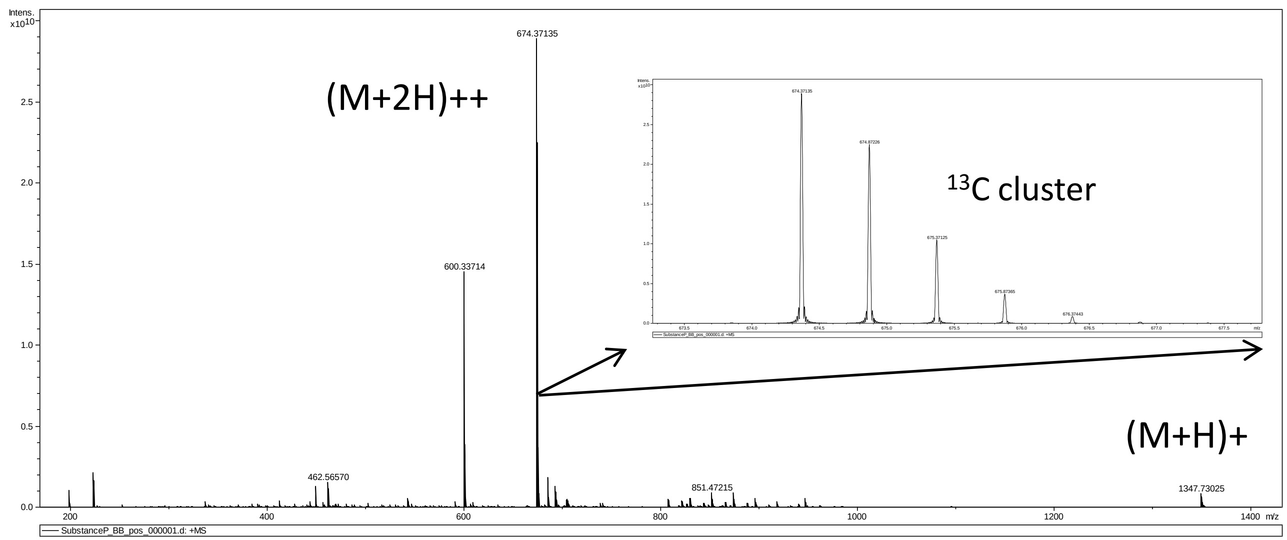
The highest mass protein complex isotopicaly resolved (2012)

Peptide spectra fine structure

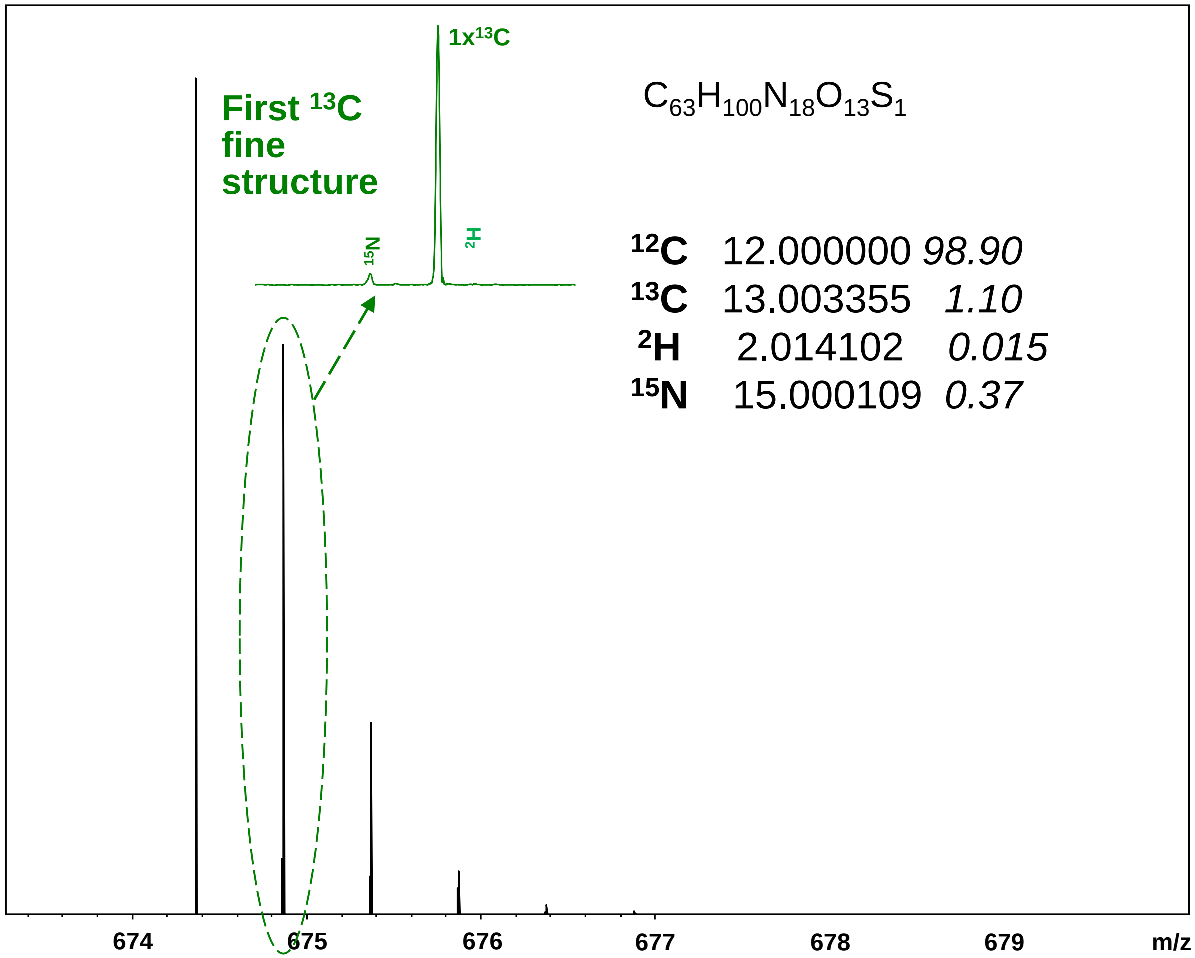
Substance P, broadband spectrum

$C_{63}H_{100}N_{18}O_{13}S_1$

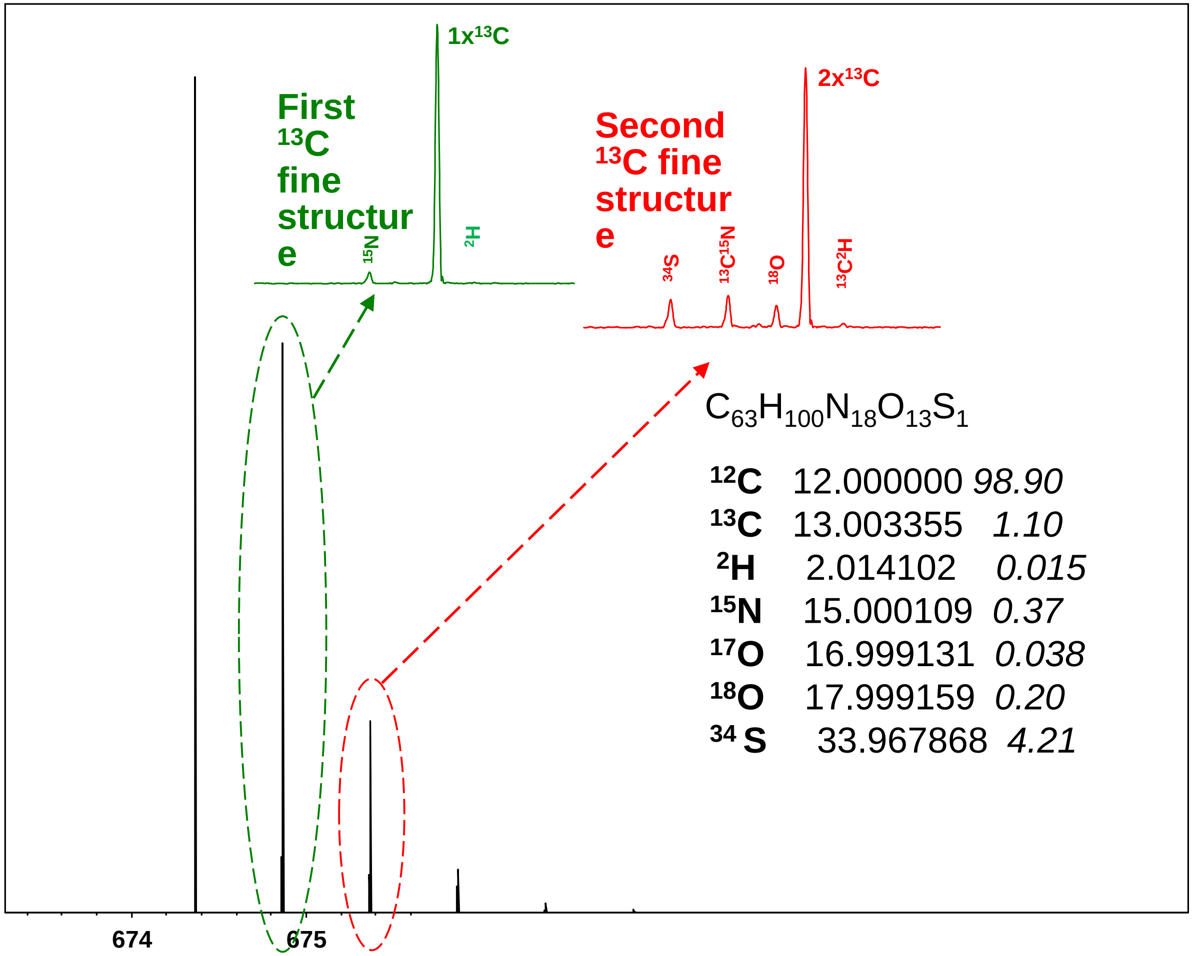




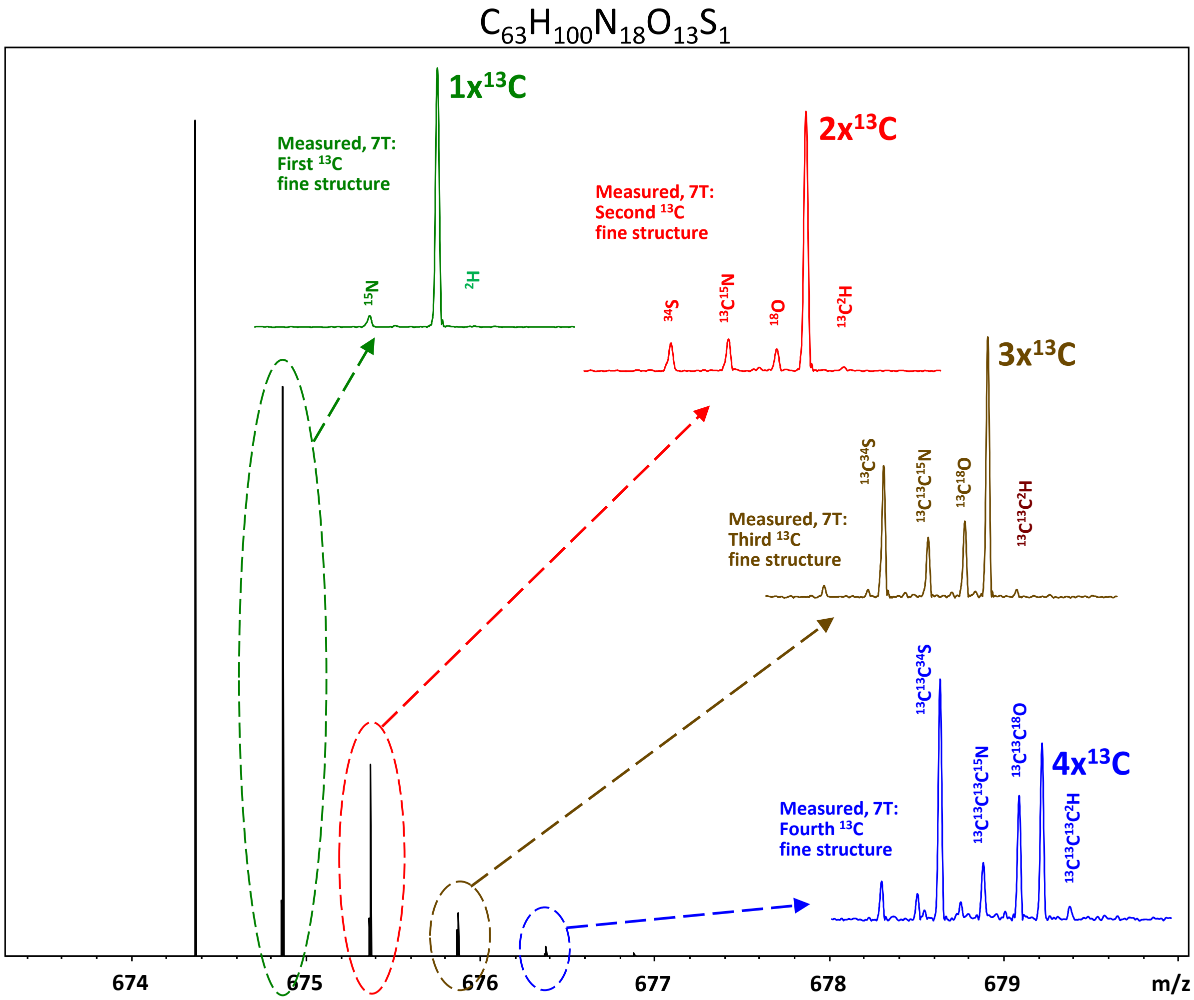
Substance P (M+ 2H$^+$) on 7 Tesla magnet



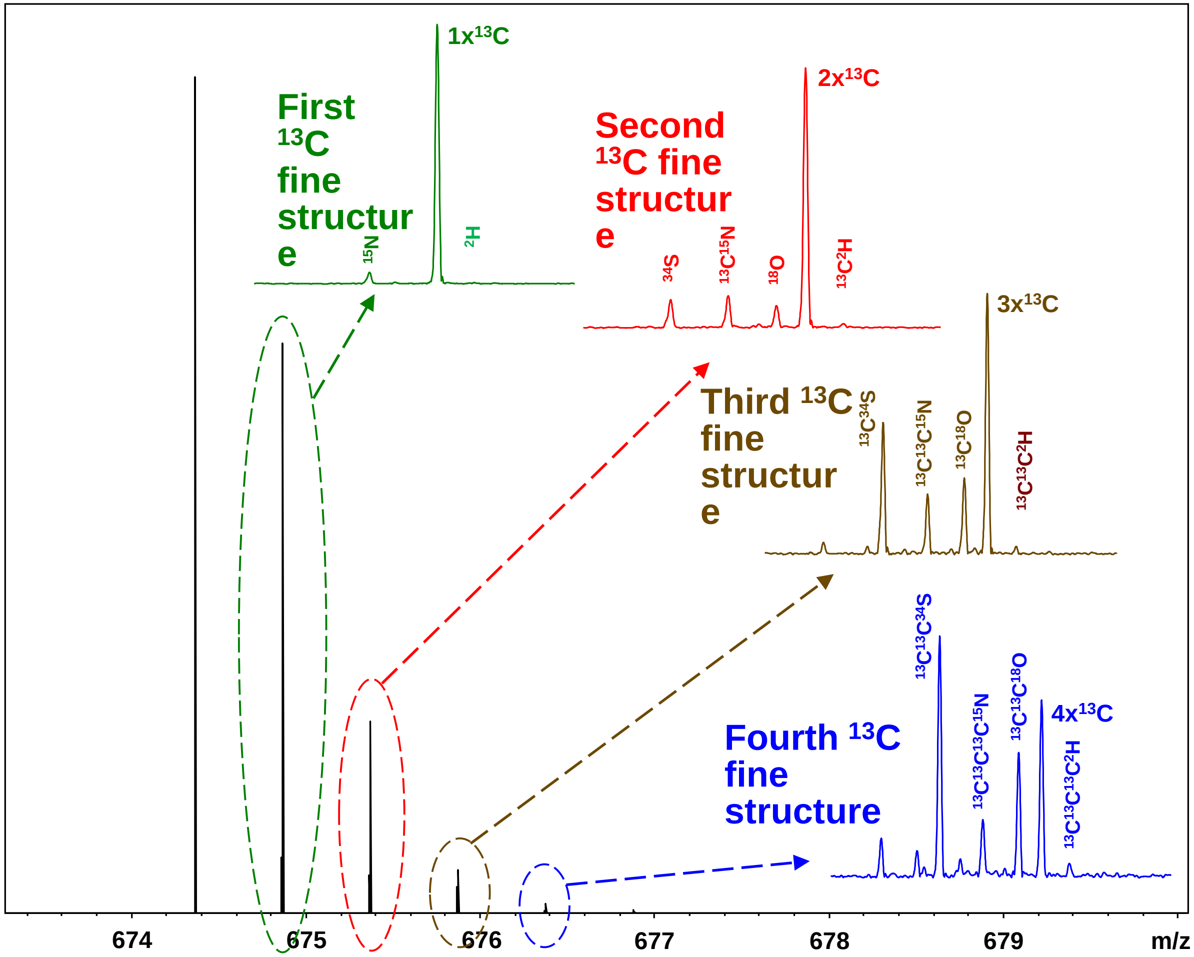
Substance P (M+ 2H$^+$) on 7 Tesla magnet



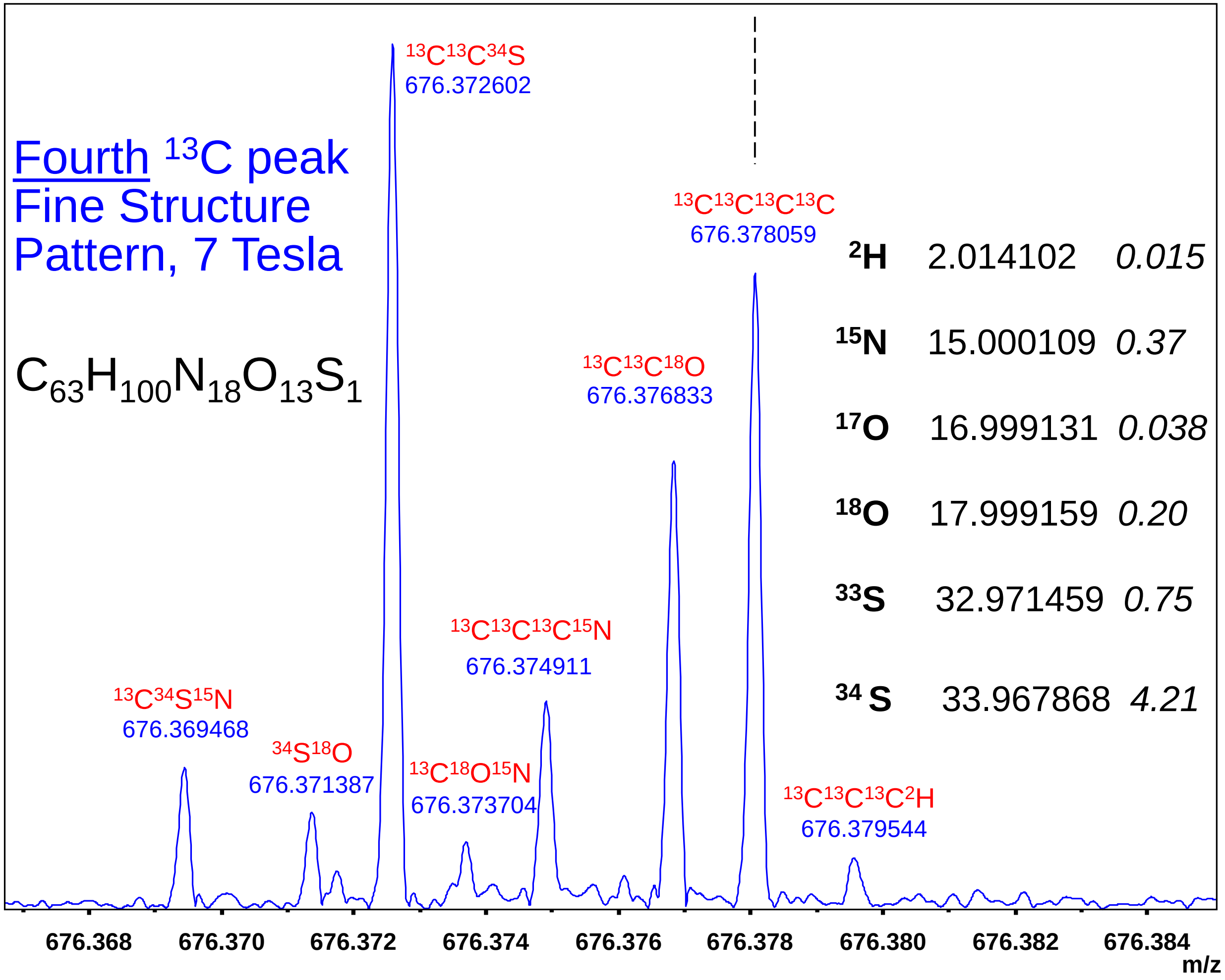
Substance P (M+ 2H$^+$) on 7 Tesla magnet



Substance P ($M+ 2H^+$) on 7 Tesla magnet

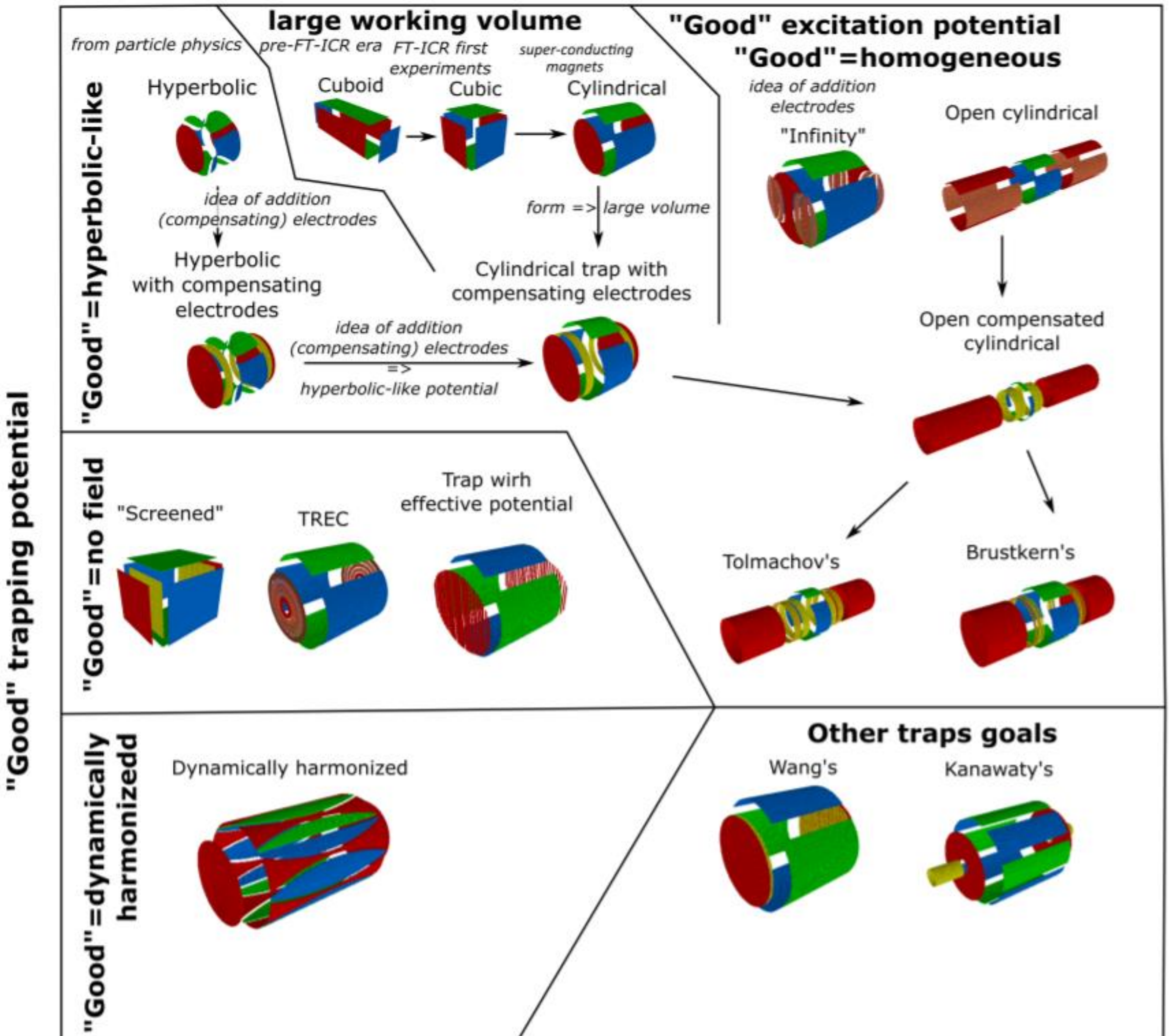


Substance P (M+ 2H$^+$) on 7 Tesla magnet

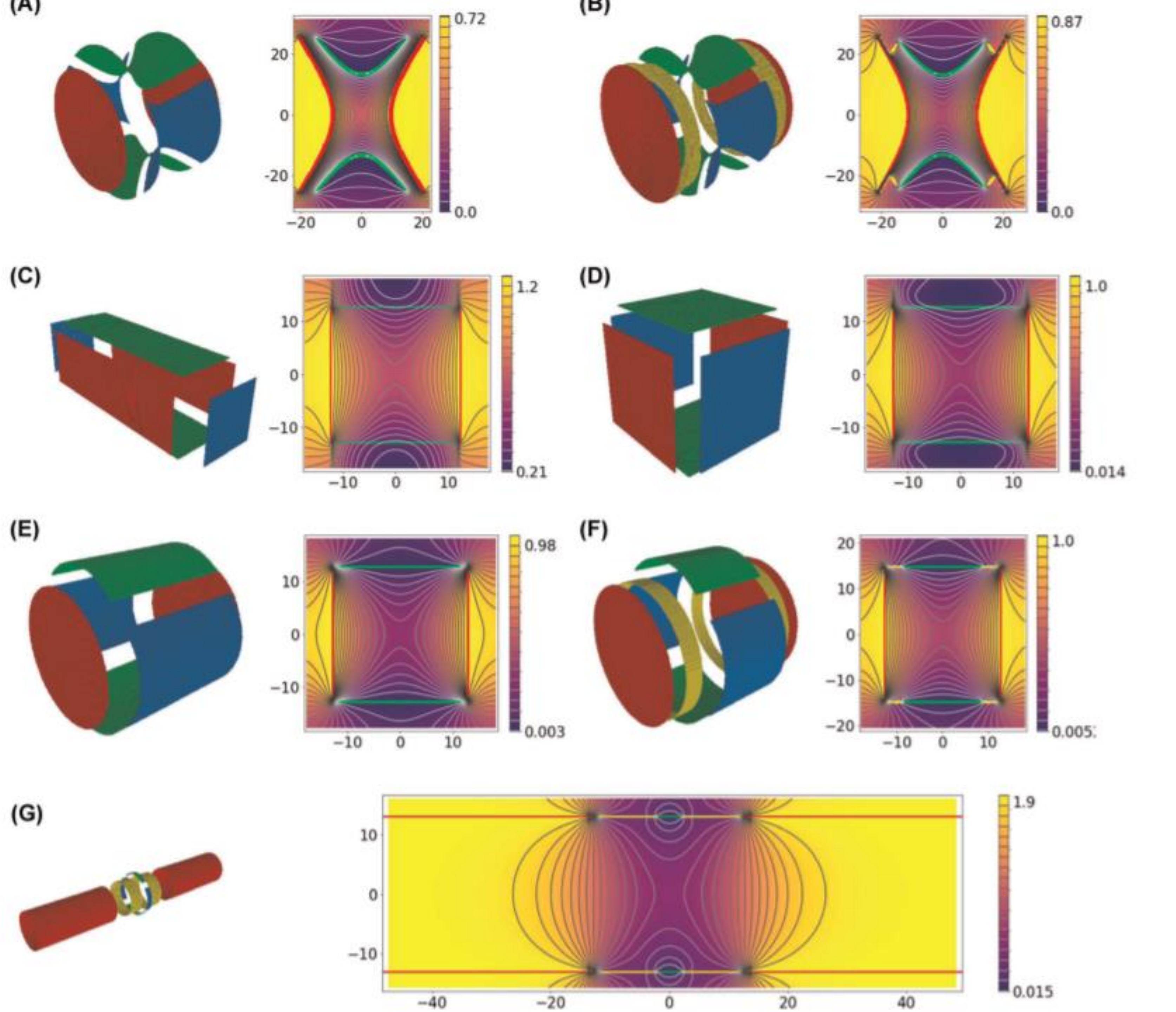


How to evaluate the cell quality?

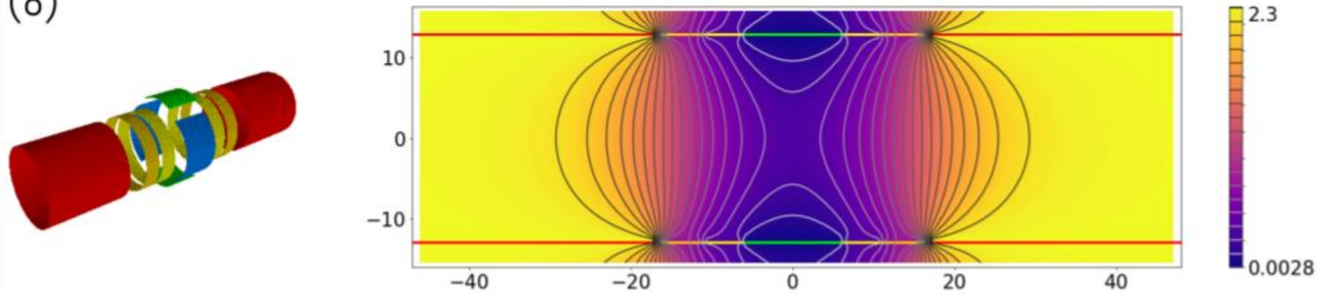
E.Nikolaev, A.Lioznov
Evaluation of major historical ICR cell designs using electric field simulations
Mass Spec Rev. 2020;1–22



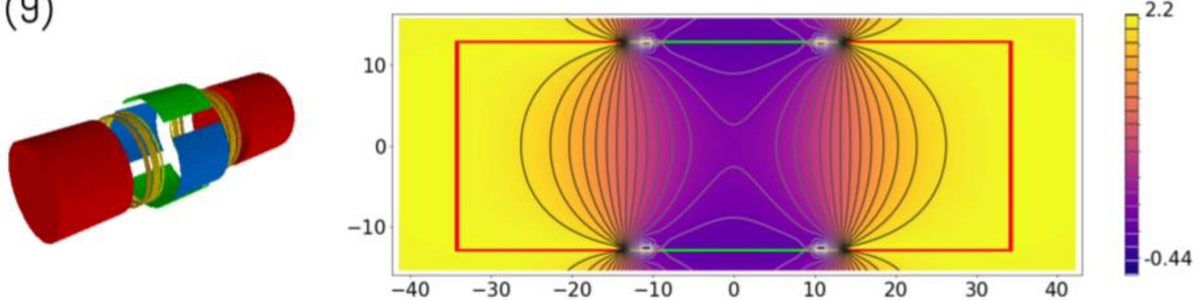
Skoltech
Skolkovo Institute of Science and Technology


(A)
0.72
0.0
(B)
0.87
0.0
(C)
1.2
0.21
(D)
1.0
0.014
(E)
0.98
0.003
(F)
1.0
(G)
1.9
0.015

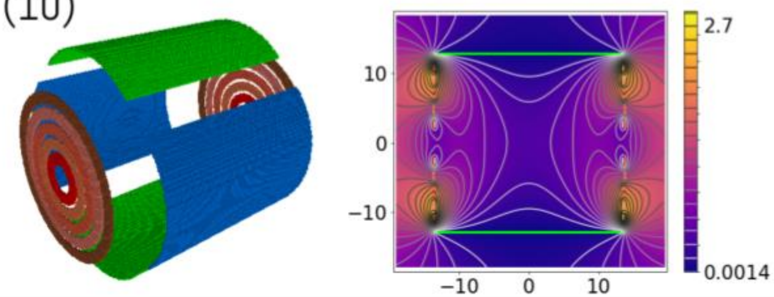
(8)


10
0
−10
−40
−20
0
20
40
2.3
0.0028

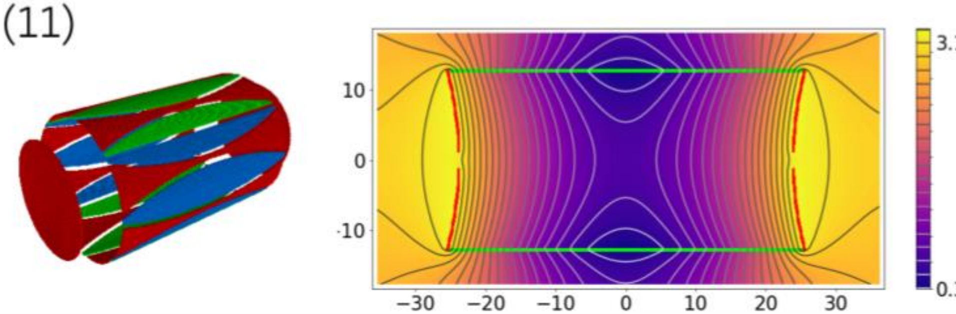
(9)


10
0
−10
−40
−30
−20
−10
0
10
20
30
40
2.2
-0.44

(10)


10
0
−10
−10
0
10
2.7
0.0014

(11)


10
0
-10
−30
−20
−10
0
10
20
30
3.1
0.3

The electric field inside any ion cell may be presented as Spherical Harmonic Decomposition

$$\phi(r,\theta,\varphi) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} A_{lm} Y_{lm}(\theta,\varphi)\cdot r^l$$

We take into account only first significant nonzero terms: $A_{20} r^2 Y_{20}$, $A_{40} r^4 Y_{40}$, $A_{60} r^6 Y_{60}$ and present the main mode of rotation ion frequency as

$$\omega_+(\rho, z) = \frac{qB}{2m} + \left[\left(\frac{qB}{2m}\right)^2 - \frac{q}{m}\{A_{20} + A_{40}(48z^2 - 12\rho^2) + \right.$$
$$\left. + A_{60}(240z^4 - 360z^2\rho^2 + 30\rho^4)\}\right]^{1/2}$$

Theory

The time of comet formation can be estimated as

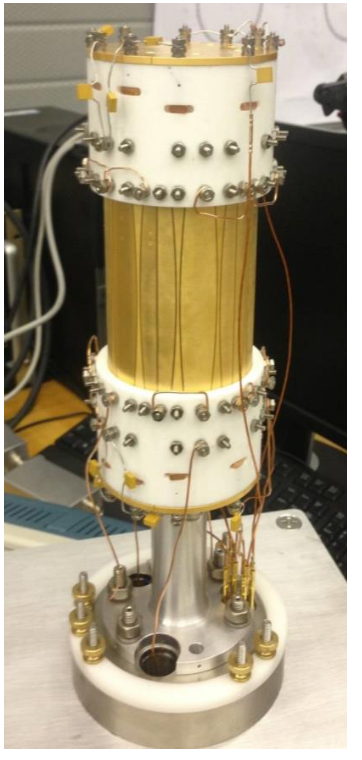
$$T_{\text{comet formation}} = \frac{2\pi}{\max_{r,z} \omega_+ - \min_{r,z} \omega_+}$$

Relative time of synchronized motion of ions in different FT ICR cells

Trap name	A_{20}	A_{40}	A_{60}	t_{comet}, s
Hyperbolic trap	4.3e-01	-2.0e-05	4.5e-06	5.3e+00
Hyperbolic trap with compensating electrodes	4.3e-01	-1.9e-07	2.4e-06	1.8e+01
Cuboid cell	1.9e+00	-2.0e-02	-9.8e-02	3.2e-02
Cubic cell	5.2e-01	4.7e-03	-2.9e-03	2.4e-02
Cylindrical cell	5.3e-01	1.0e-02	-3.6e-03	1.4e-02
Cylindrical trap with compensating electrodes	5.8e-01	2.0e-06	-3.1e-03	3.3e-02
Open cylindrical cell with compensating electrodes	5.3e-01	2.4e-08	-5.9e-04	1.3e-01
Trap with compensating electrodes by Tolmachov	7.6e-01	7.2e-05	-1.3e-03	1.8e-01
Trap with compensating electrodes by Brustkern	5.8e-01	1.6e-02	-3.5e-03	1.3e-02
Dynamically Harmonized Cell or Paracell	1.6e+00	-4.4e-05	2.6e-04	7.0e+00

Dynamically harmonized cells are providing the highest resolving power

Bruker's cell



NHMFL cell

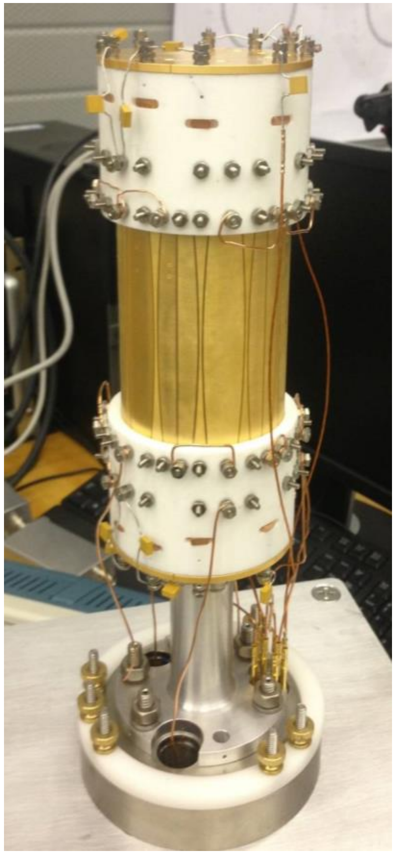
In 2015 we had Milestone events in FT ICR mass spectrometry

Launching two 21 tesla FT ICR mass Spectrometers

In National High Magnetic Field Laboratory NHMFL (Tallahassee Florida)

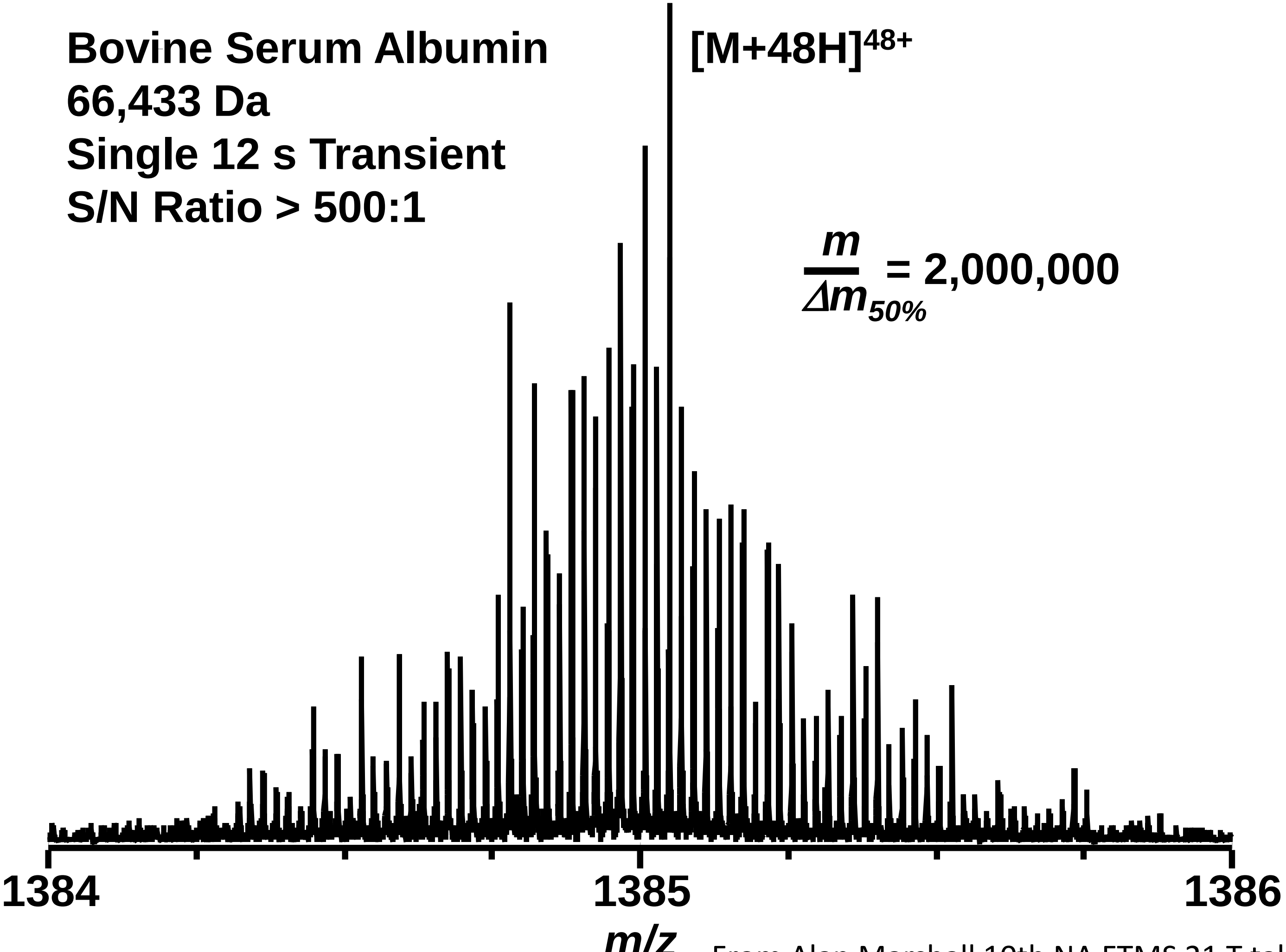
and in Pacific North West National Laboratory PNNL (Richland, Washington)


BRUKER
21T FT-ICR

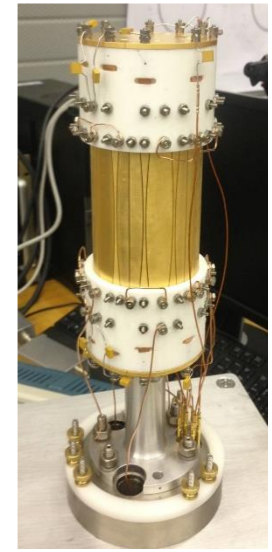


From Alan Marshall 10th NA FTMS 21 T talk

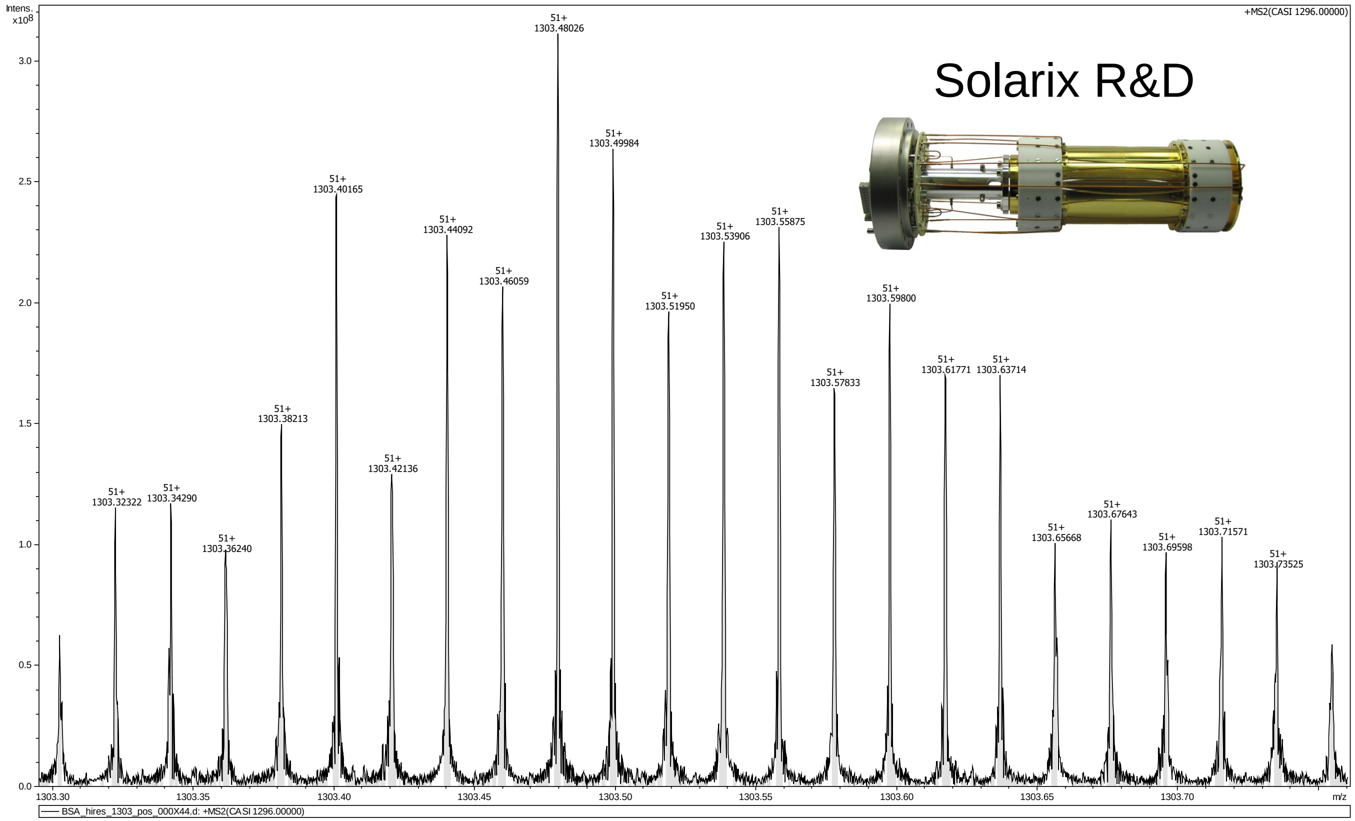
Solarix R&D

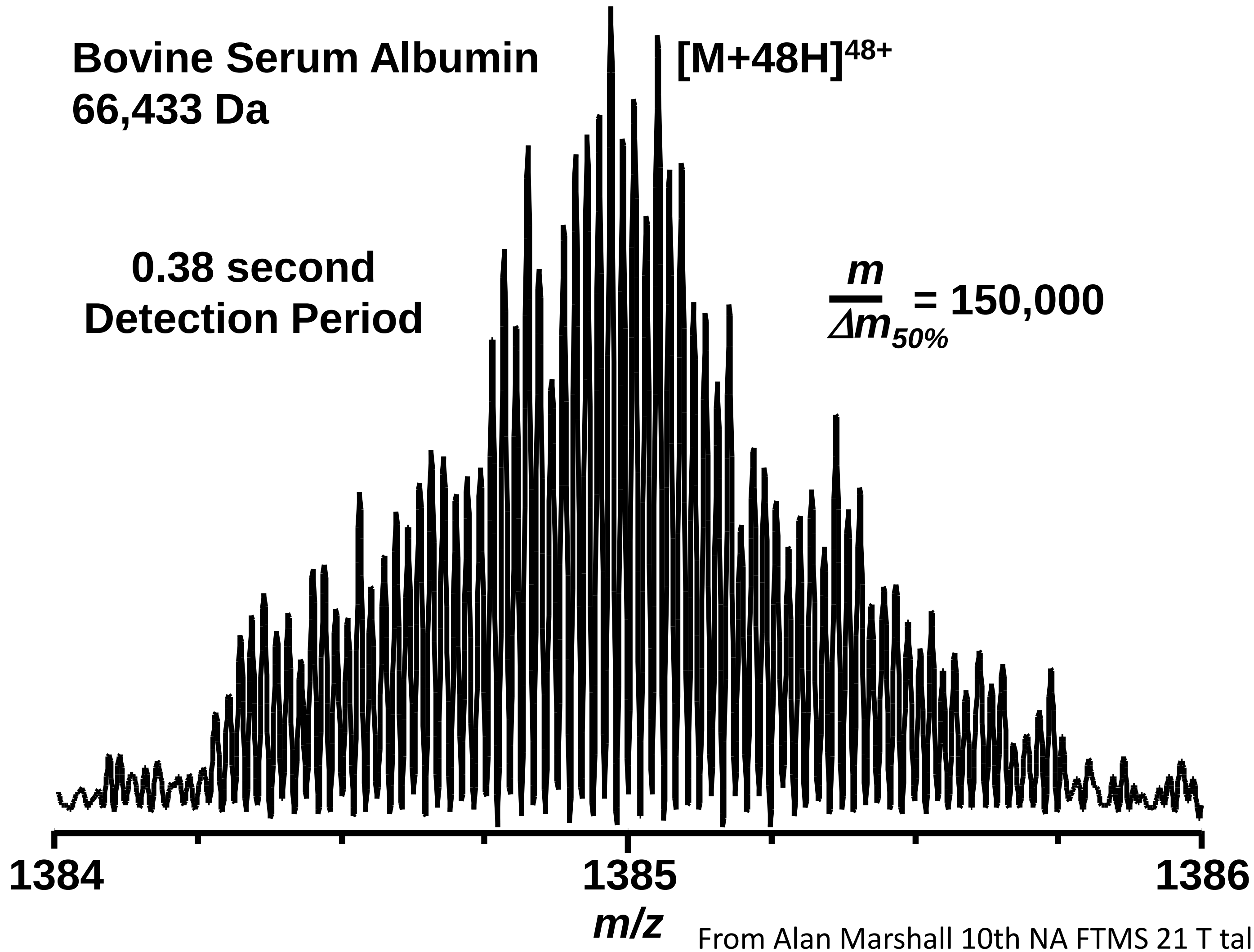


From Alan Marshall 10th NA FTMS 21 T talk



7T R&D, BSA, 51+, RP 1,700,000 28 s transient



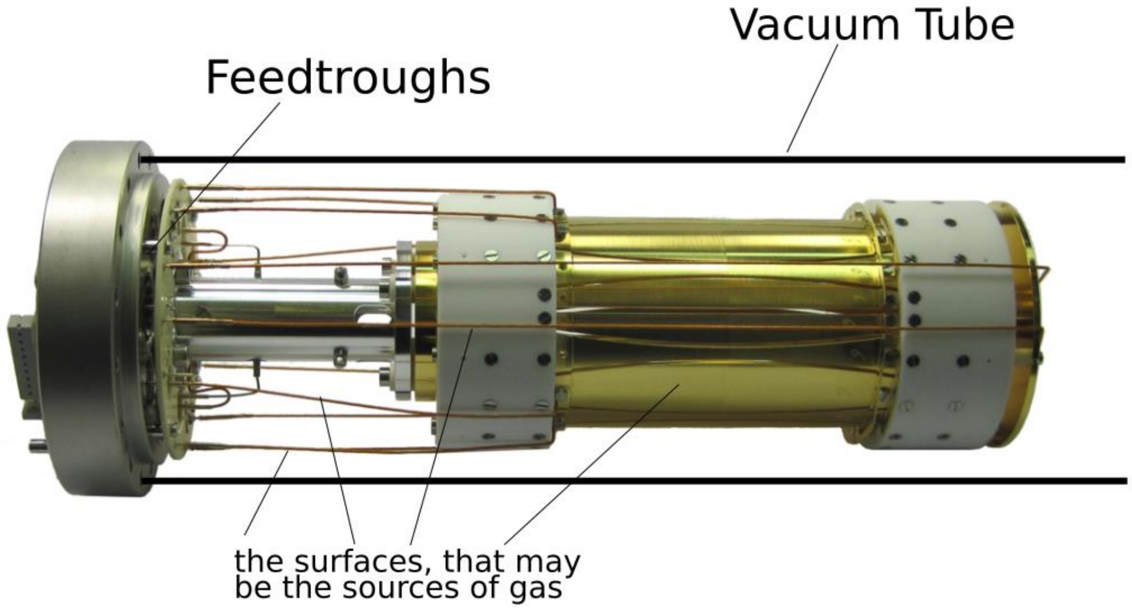


From Alan Marshall 10th NA FTMS 21 T talk

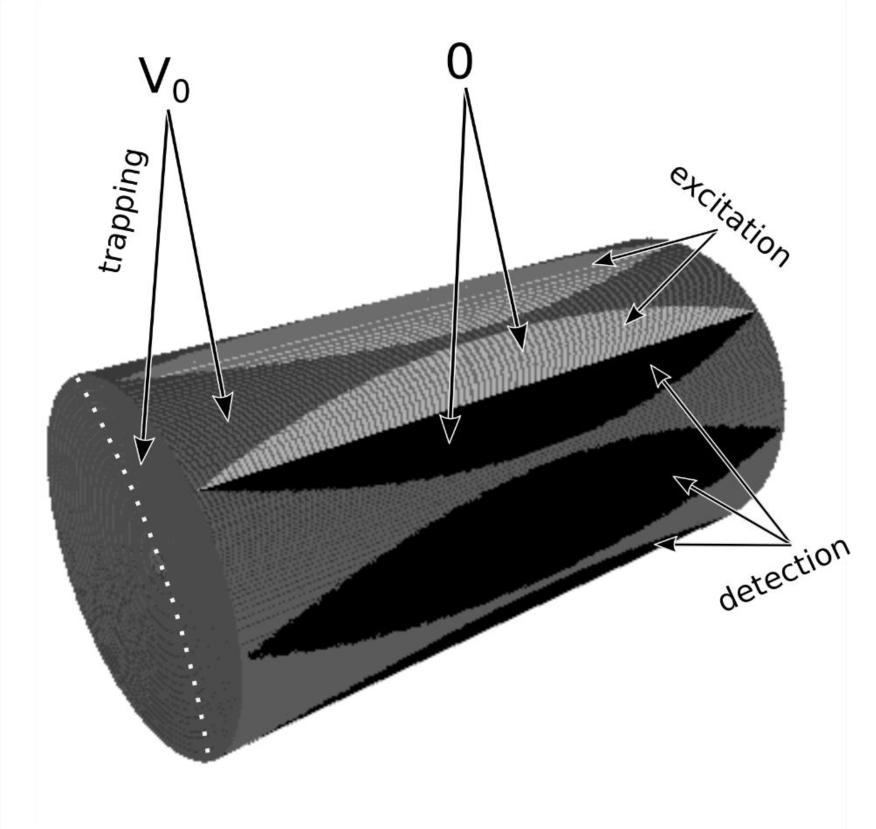
Highly developed surface with large «vacuum memory»

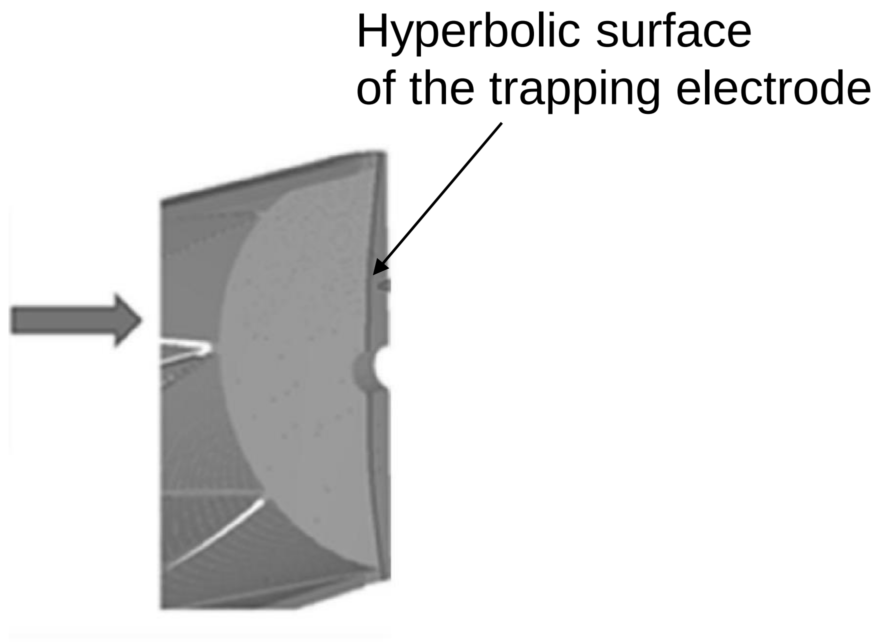
- Long pumping time;
- Not highest avalible final vacuum;
- Potential leakage in feedthroughs.
- Closed volume of the

  cell



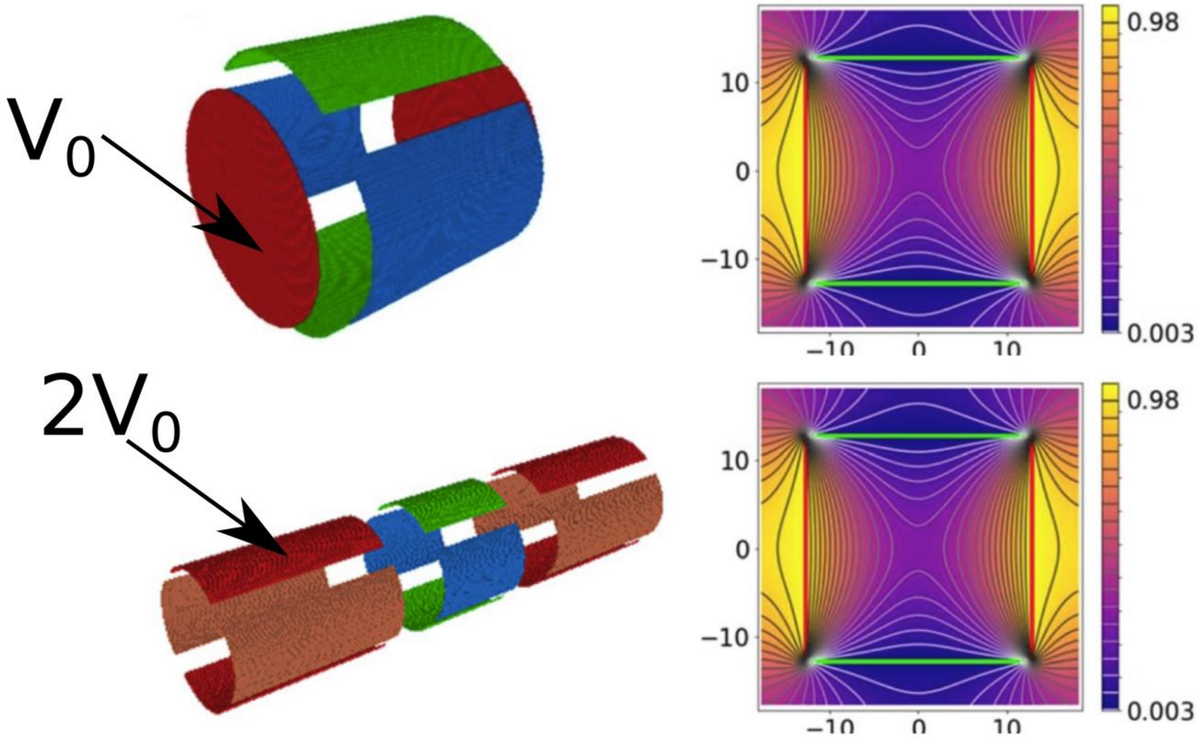
«Standard» (closed) DHC



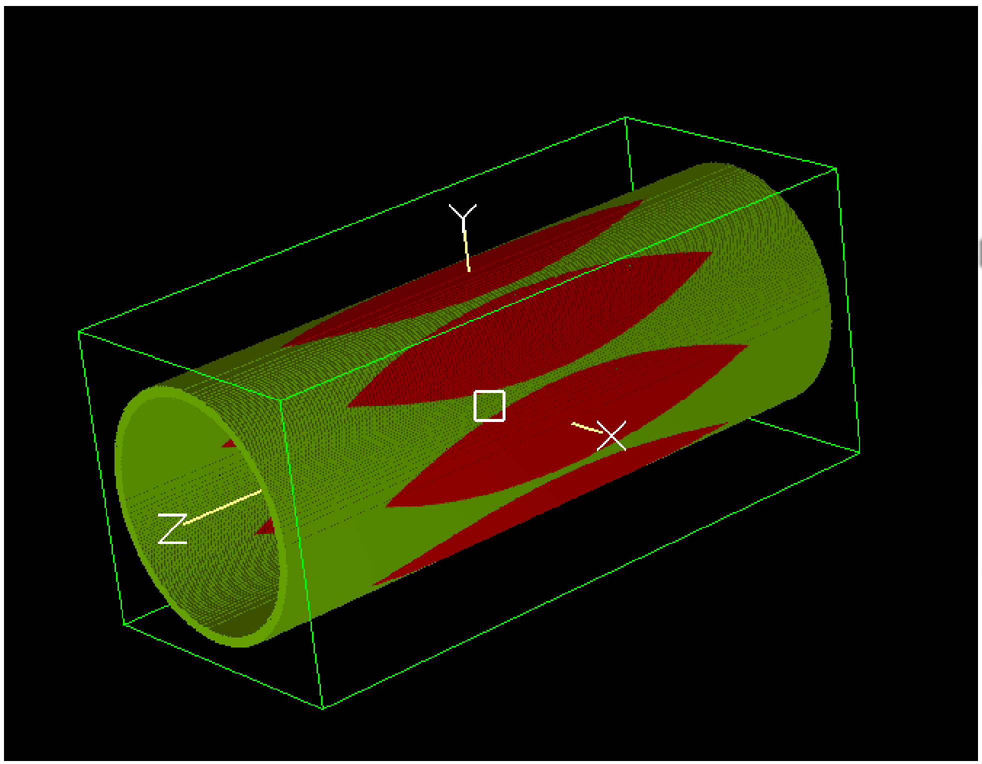


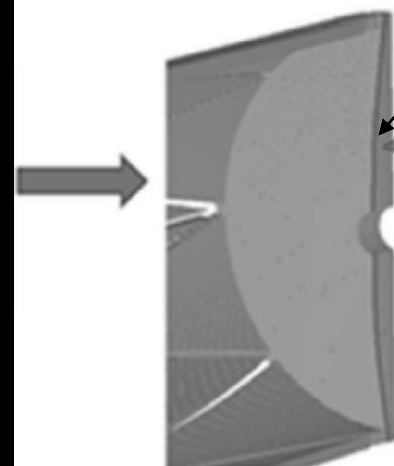
How to “open” dynamically harmonized cell?

It is easy to «Open» a simple Cylindrical Cell Substituting flat trapping electrodes by cylinders

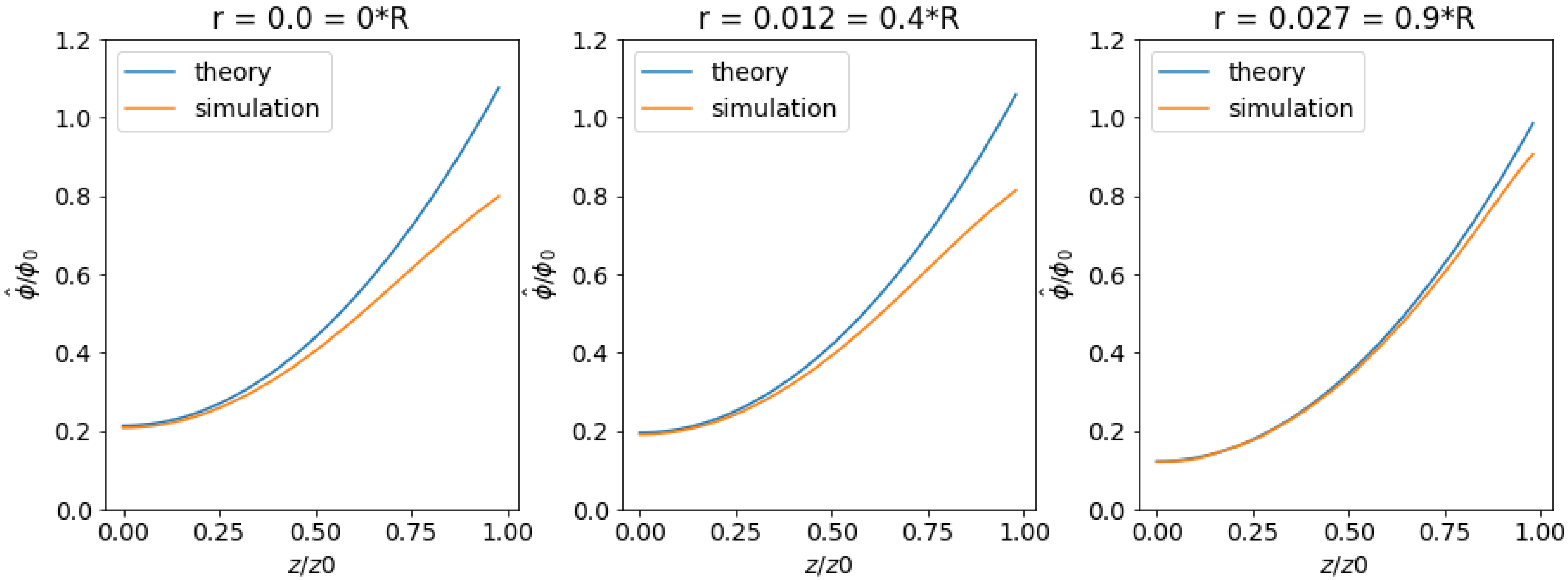


If we substitute in DHC the hyperbolic shape trapping electrodes by cylinders...



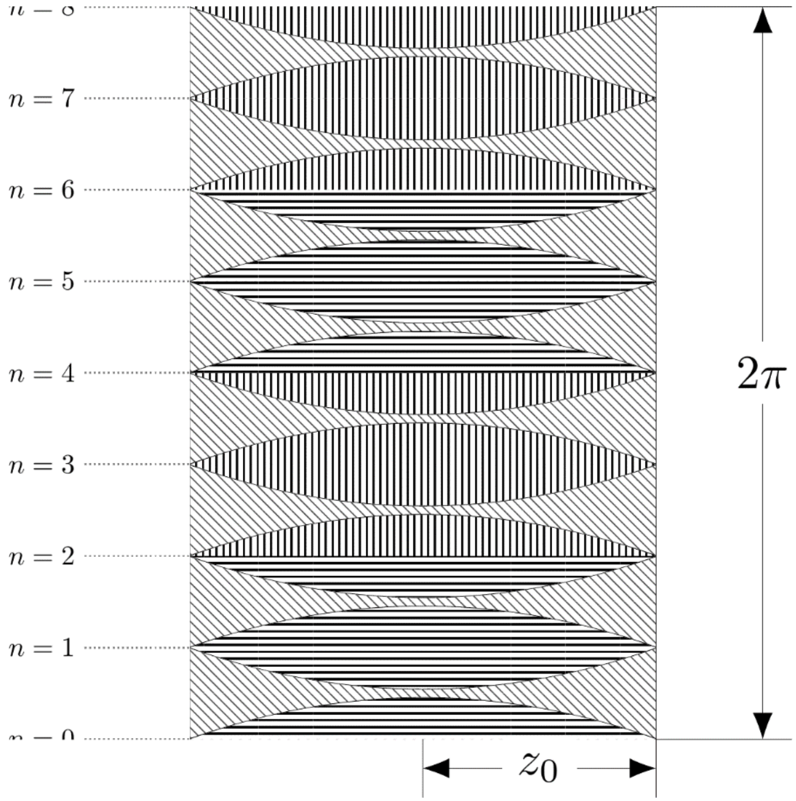


We will not obtain hyperbolic field inside the cell!

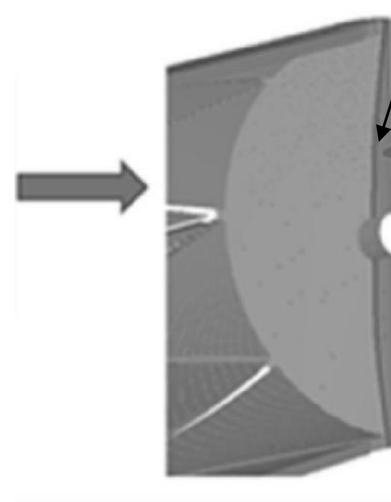


The 2D-unrolled electrode configuration for a closed DHC

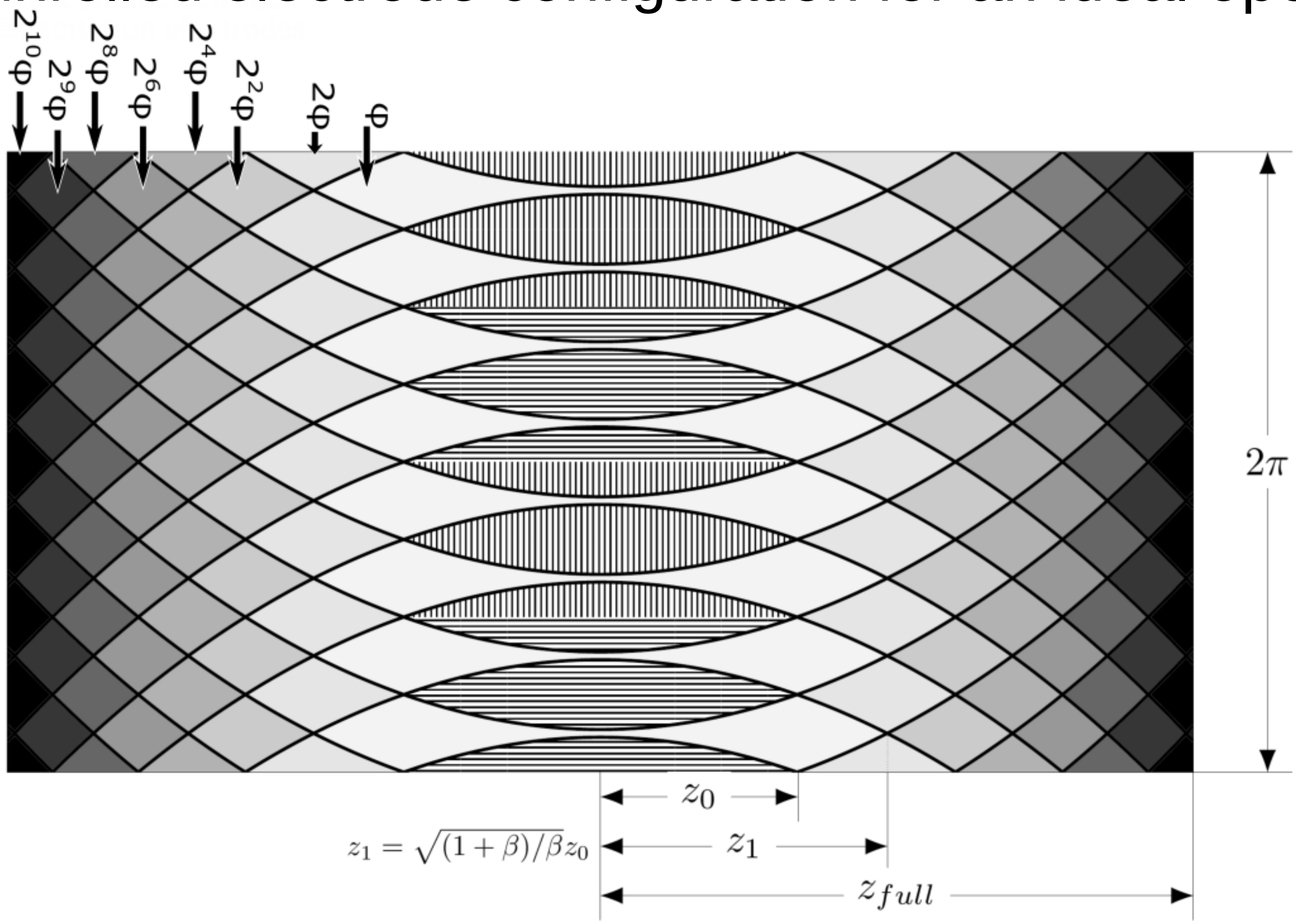
detection electrodes
excitation electrodes
trapping electrodes



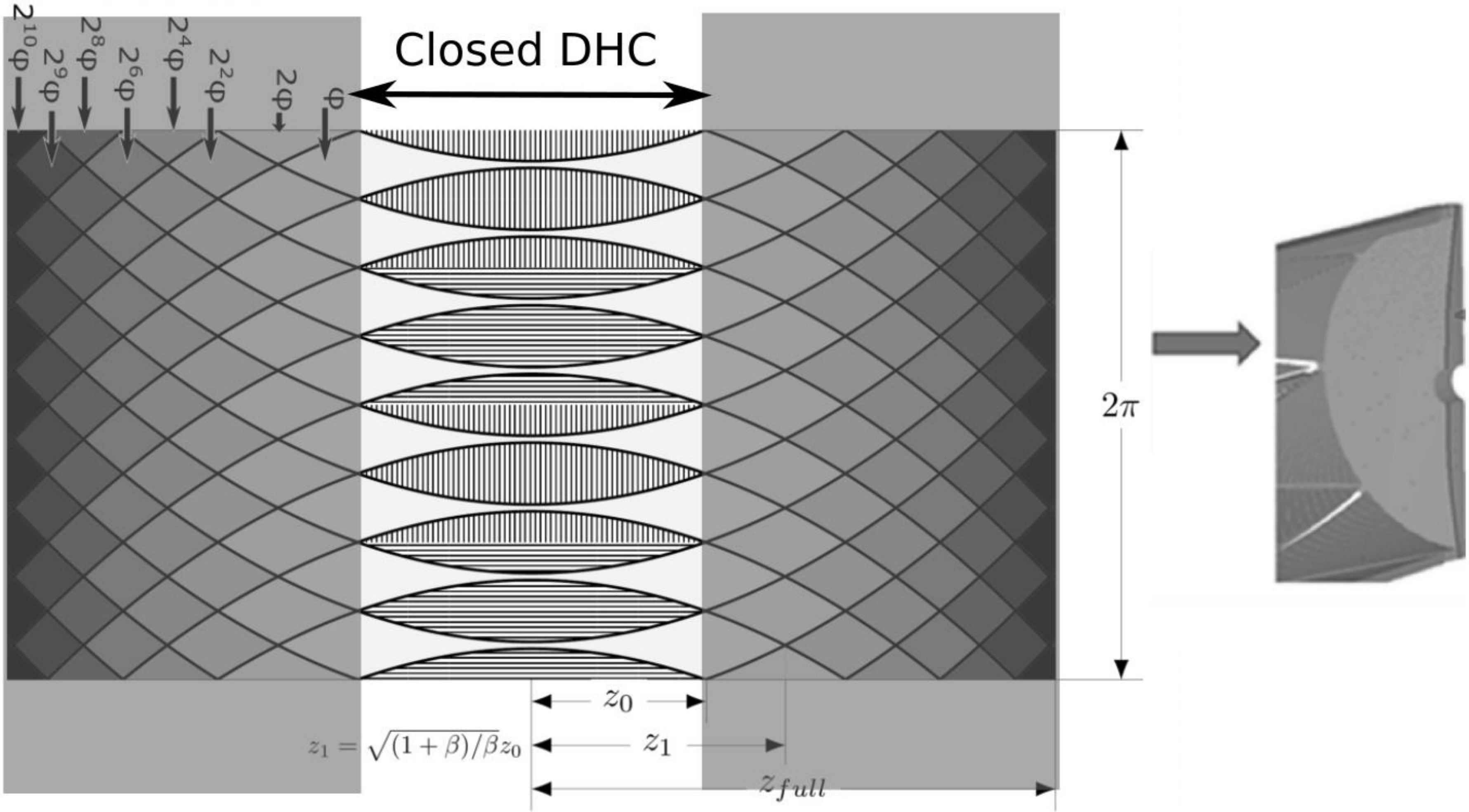
Hyperbolic surface
of the trapping electrode



The 2D-unrolled electrode configuration for an ideal open DHC



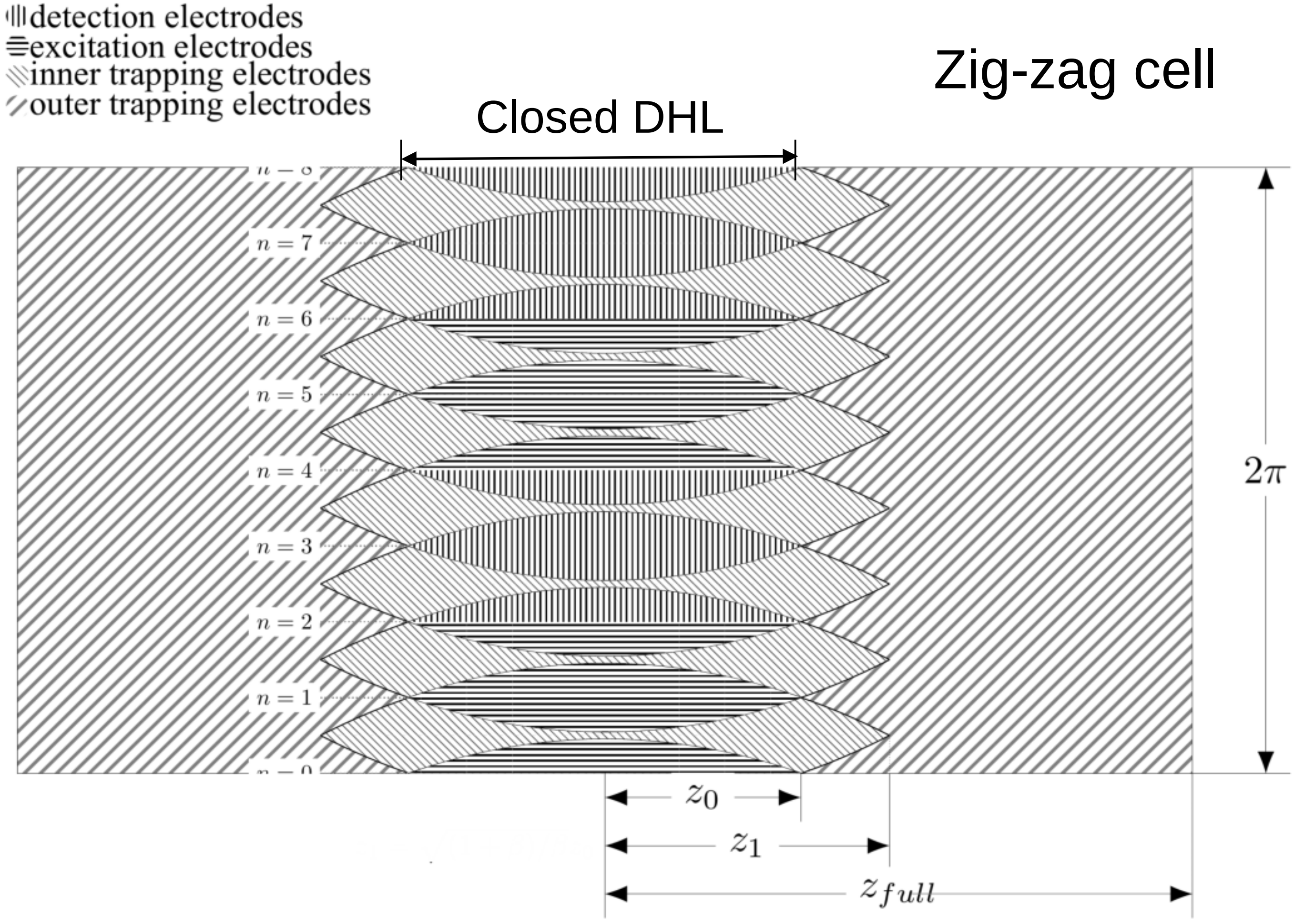
The 2D-unrolled electrode configuration for an ideal open DHC



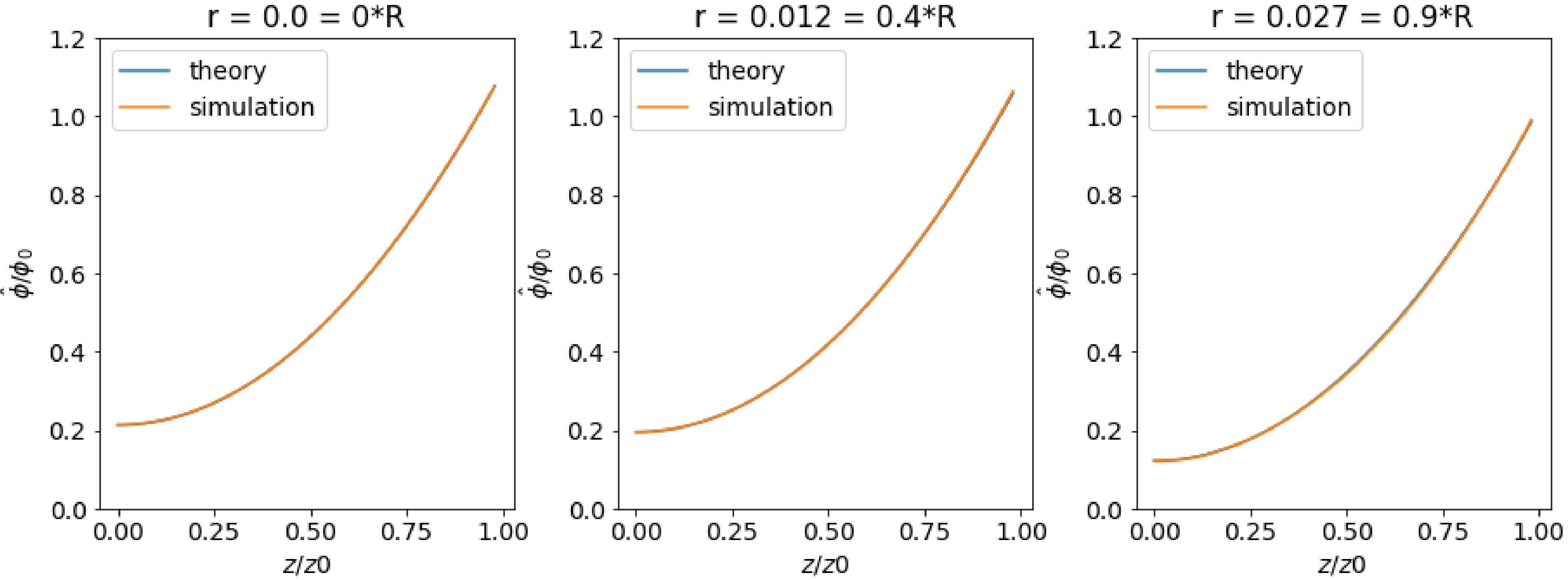
Reducing number of electrodes

- The set of electrodes shown above creates the needed field, but it is hard to build it.
- We have shown that the electrodes located far from the trap center has low effect on the field inside the working volume of the cell. Thus, we can merge all these electrodes into one.

The 2D-unrolled electrode configuration of realizable open DHC



The ideal and simulated distribution of the electric potential inside the open DHC



Z-component of electric field at different distance (r) from the cell axis

The deviations from the ideal field

The electric field distribution inside the Open Dynamically Harmonized «Zig-Zag» Cell is not absolutely ideal. But the field deviation is bellow numerical errors of simulations.

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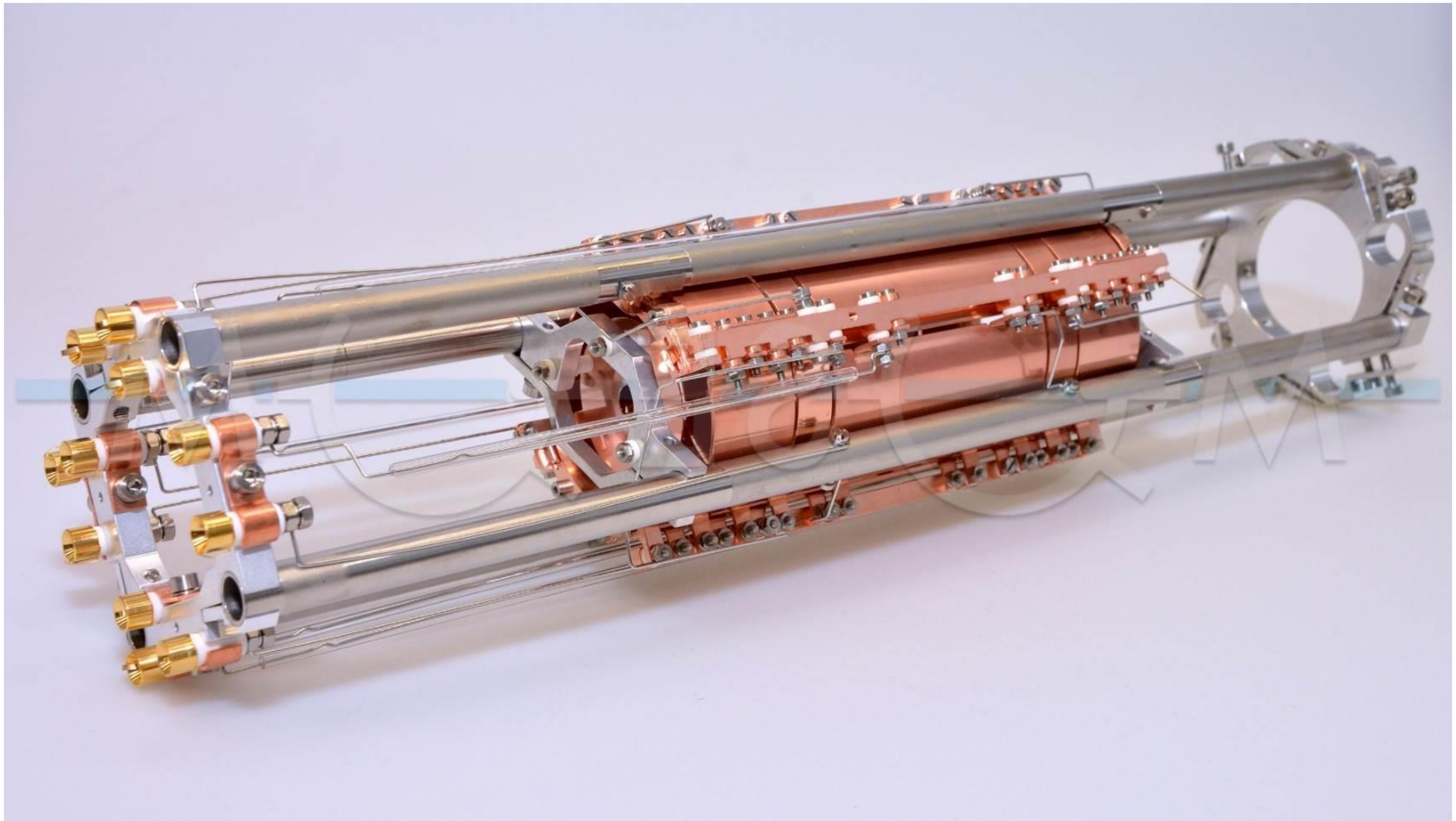
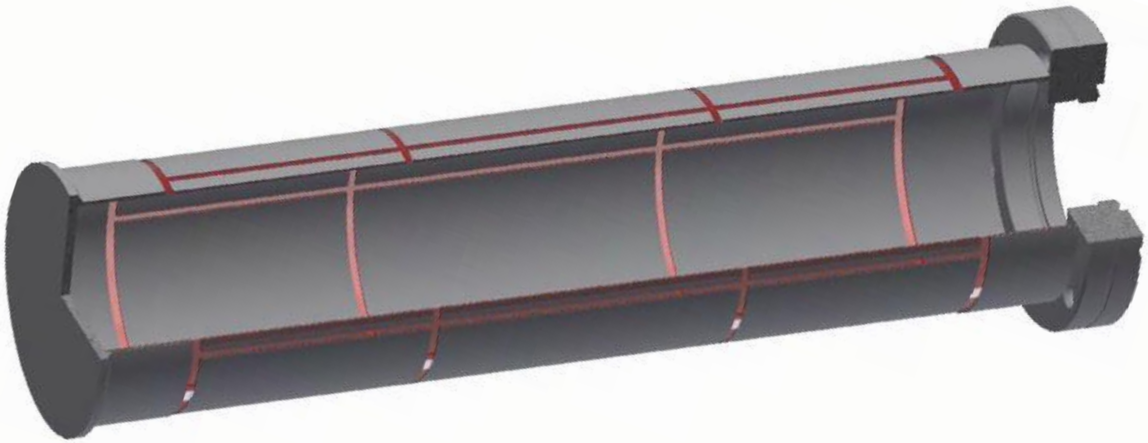
Tired of cells…

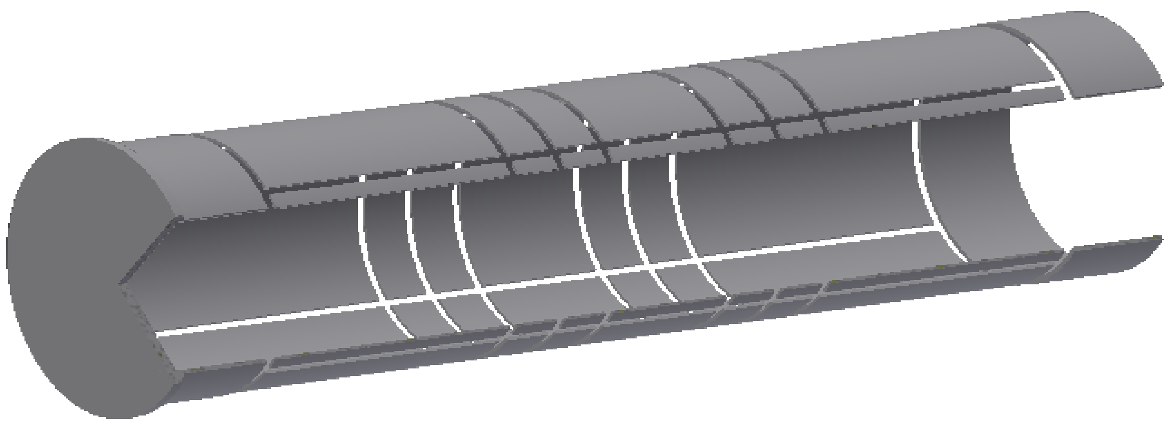
Is it possible to get rid of the cell as a **separate** element of FT ICR mass spectrometer?



Trap walls are the walls of the vacuum chamber:
Different geometries could be implemented



Open cylindrical cell



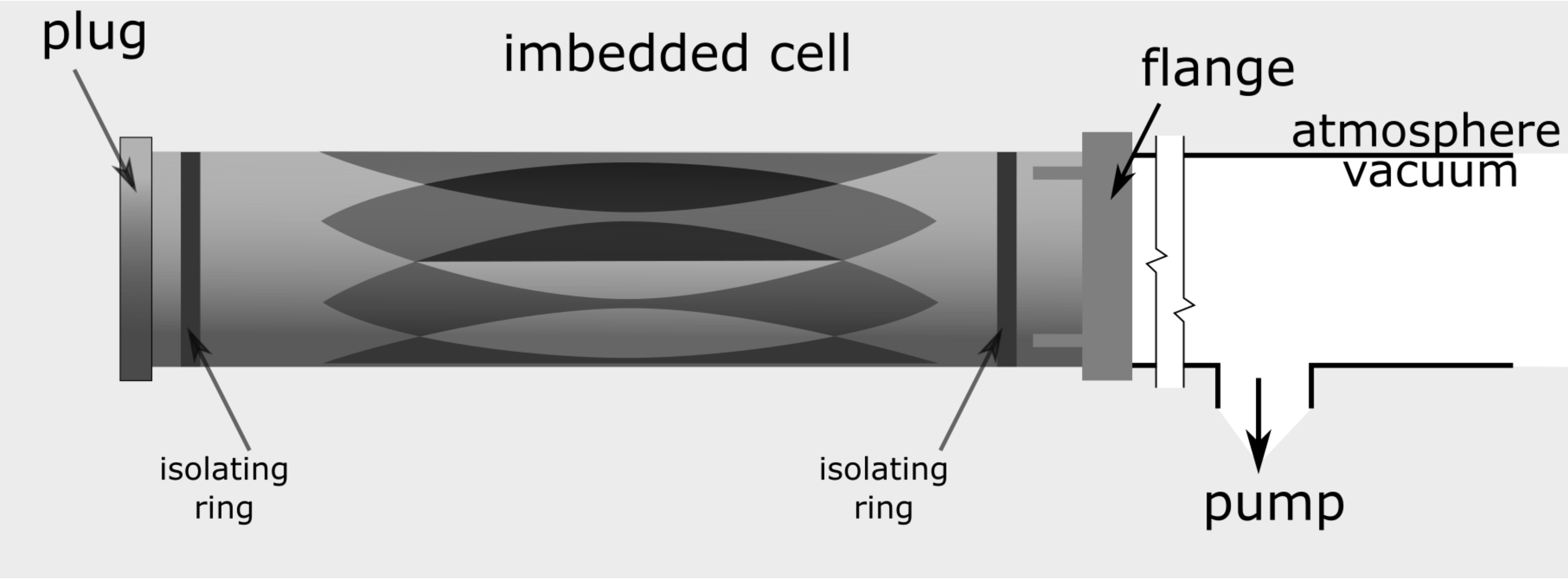
Open compensated cylindrical cell

Advantages of vacuum system wall imbedded cell

No feedthroughs (can apply voltages from outside)
No wires inside
Extremely low surface (only surfaces of the electrodes)
Easy to align to magnetic field
Low diameter of room temperature bore magnet could be used

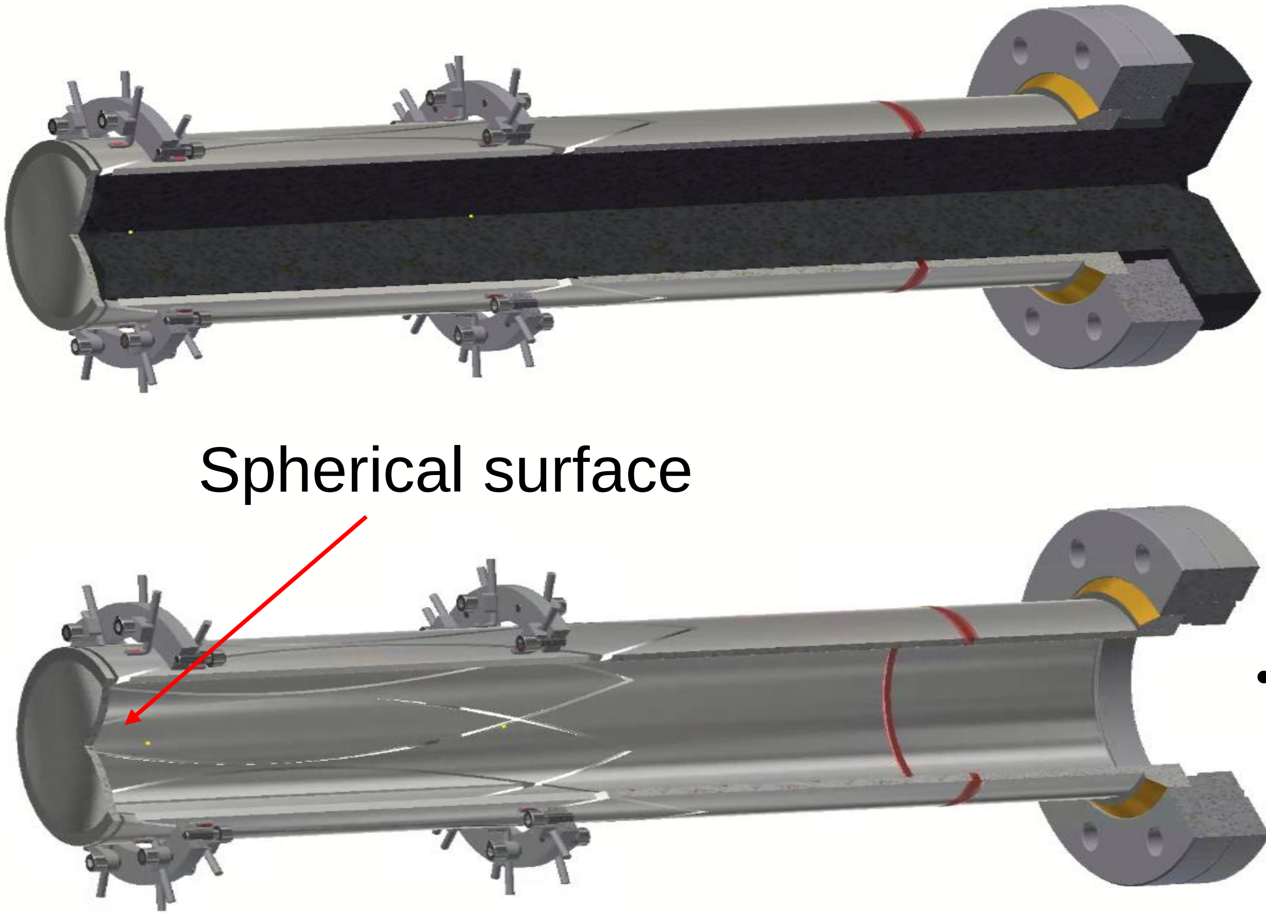
Is it possible to incorporate an open DHC into the vacuum tube wall?

New Open DHC



plug
imbedded cell
flange
atmosphere
vacuum
isolating ring
isolating ring
pump

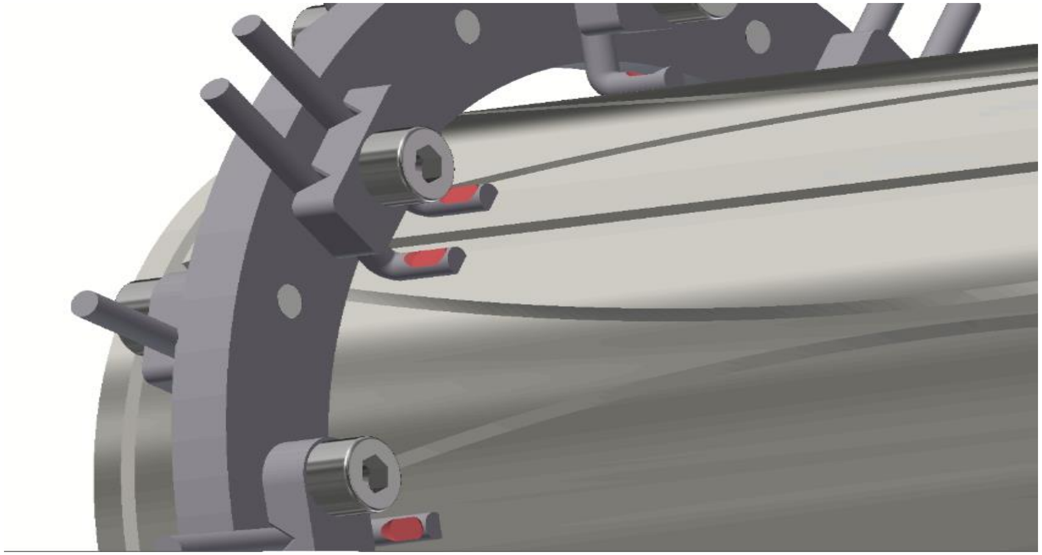
The open dynamically harmonized cell could be made from a single cylinder



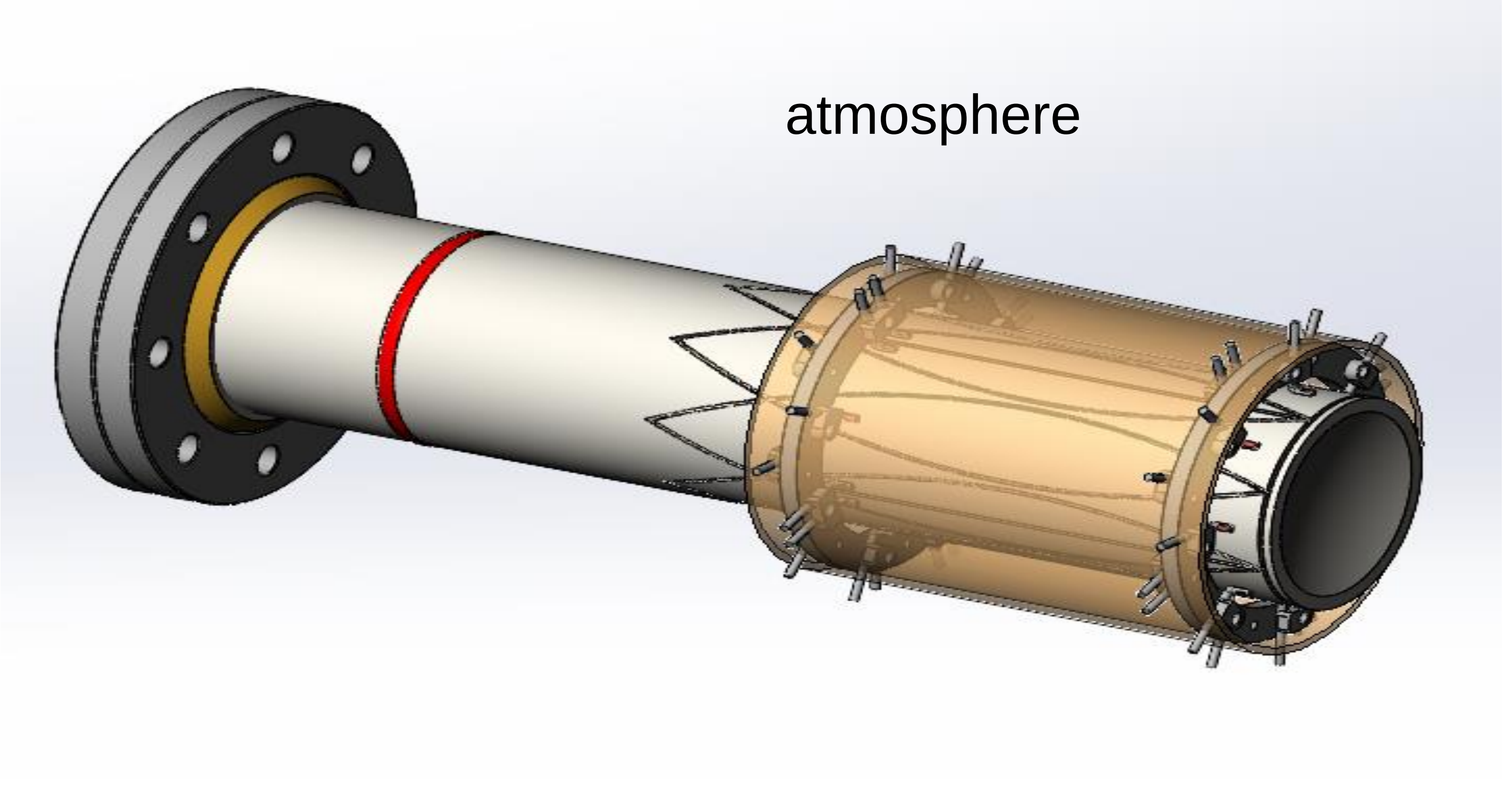
The cell opened from one side

- Fabrication of ICR trap-vacuum chamber consists of the following steps
- 1) A titanium adapter for a CF63 flange is welded to a 62 mm diameter BT1-0 titanium tube
- 2) In certain places on the tube by means of contact welding, pieces of 2mm BT1-00св titanium wire are welded
- 3) The pipe is cut into individual electrodes
- 4) Temporary fasteners are installed to hold the electrodes
- 5) A graphite insert is placed inside the pipe, and then the cut points are filled with a special ceramic powder. Then the billet is annealed in the furnace.

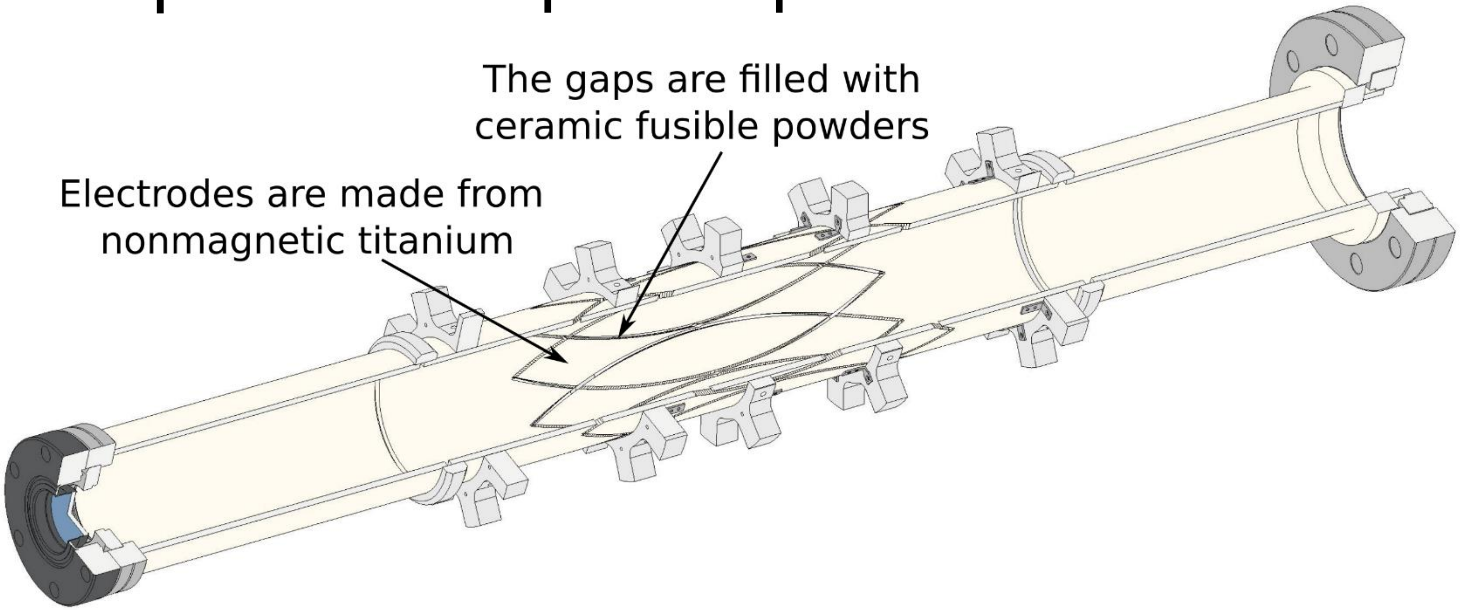
The voltage to the cell electrodes could be applied from outside



Amplifier could be installed directly on ICR trap using Flexible PCBs



Open “atmospheric pressure” DHC

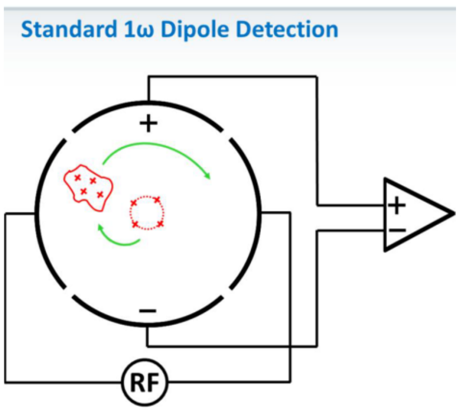


The titanium and the ceramics have the similar coefficient of thermal expansion, which allows annealing a vacuum system

Detection at multiple frequencies

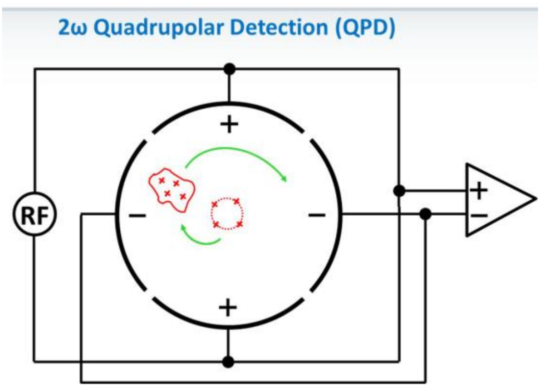
Detection with more than two electrodes

4 electrode FT ICR cell dipolar detection



$\omega_{signal} = \omega_{cyclotron}$

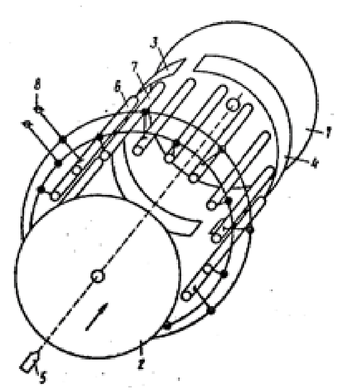
4 electrode FT ICR cell quadrupolar detection



$\omega_{signal} = 2*\omega_{cyclotron}$

Double resolution or double speed

2N electrode FT ICR cell multipolar detection



$\omega_{signal} = N*\omega_{cyclotron}$

N times higher resolution or speed

Detection on multiplied frequencies and on harmonics

$R = \omega / \Delta\omega$

$\Delta\omega \sim 1/T$

T is signal duration

If $\omega' = n * \omega$, $R' = n * R$

СОЮЗ СОВЕТСКИХ СОЦИАЛИСТИЧЕСКИХ РЕСПУБЛИК

(19) SU (11) 1307492 A1

(51) 4 H 01 J 49/38

ГОСУДАРСТВЕННЫЙ КОМИТЕТ СССР ПО ДЕЛАМ ИЗОБРЕТЕНИЙ И ОТКРЫТИЙ

ОПИСАНИЕ ИЗОБРЕТЕНИЯ

К АВТОРСКОМУ СВИДЕТЕЛЬСТВУ

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(22) 05.07.85
(46) 30.04.87. Бюл. № 16

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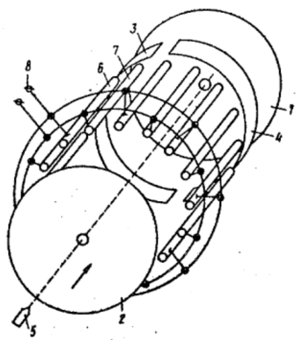
(72) Г.Н.Николаев, М.В.Горшков, А.В.Мордехай и В.Л.Тальрозе

(53) 621.384.6 (088.8)

(56) Леман Т., Берси М. Спектрометрия ионного циклотронного резонанса. М.: Мир, 1980, с.13-41.
Патент США № 3742212, кл.250-291, 1973.

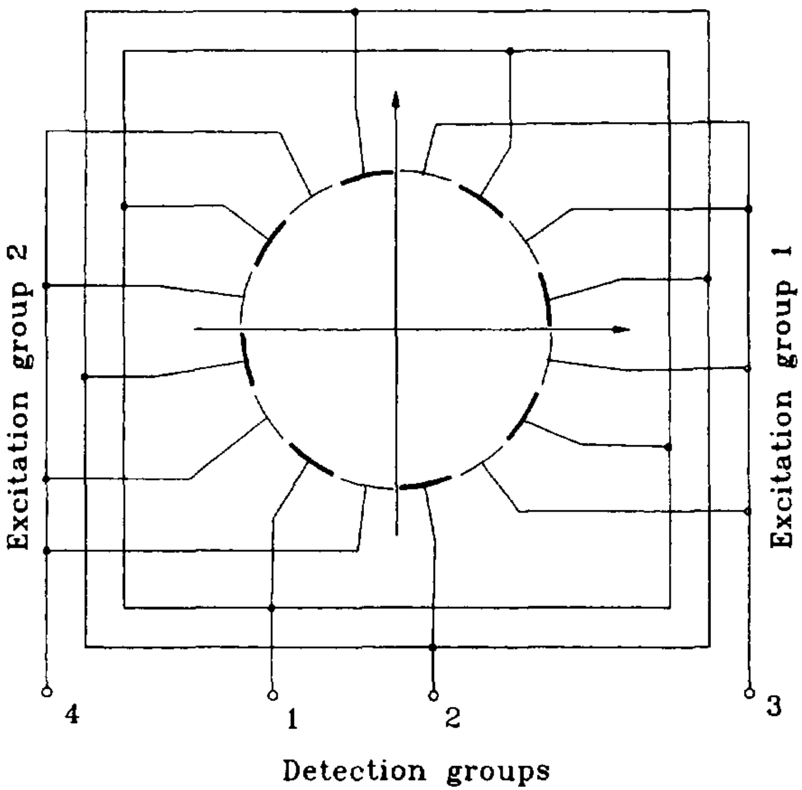
(54) ИОННО-ЦИКЛОТРОННЫЙ РЕЗОНАНСНЫЙ МАСС-СПЕКТРОМЕТР

(57) Изобретение относится к области ионноплазменной техники. Ионно-циклотронный резонансный масс-спектрометр (ИЦМС) содержит пластины 1, 2 удержания ионов (И), расположенные по торцам перпендикулярно оси ИЦМС, электроды (Э) 3, 4 возбуждения И в виде полуцилиндров, установленных в одной плоскости торцами друг к другу, детектор 5 И и электронную систему управления и обработки данных. Выполнение детектора 5 И в виде четного числа Э 6, 7, размещенных по окружности с центром на оси ИЦМС и гальванически соединенных в две группы таким образом, что два соседних Э расположены в разных группах, позволяет расширить диапазон исследуемых масс и увеличить разрешающую способность ИЦМС за счет детектирования сигнала на частоте, кратной циклотронной. Изобретение позволяет исследовать ионно-молекулярные реакции в газовой фазе, особенно И тяжелые биологических молекул. 1 ил.



(19) SU (11) 1307492 A1

Soviet Union patent
Priority 05.07.1985
Nikolaev, Gorshkov, Mordehai, Talroze
Multi-electrode detection FT ICR cell



E.N. Nikolaev, M.V. Gorshkov, A.V. Mordehai and V.L.Talrose, Rapid Communications in Mass Spectrometry, 4 (1990) 144.

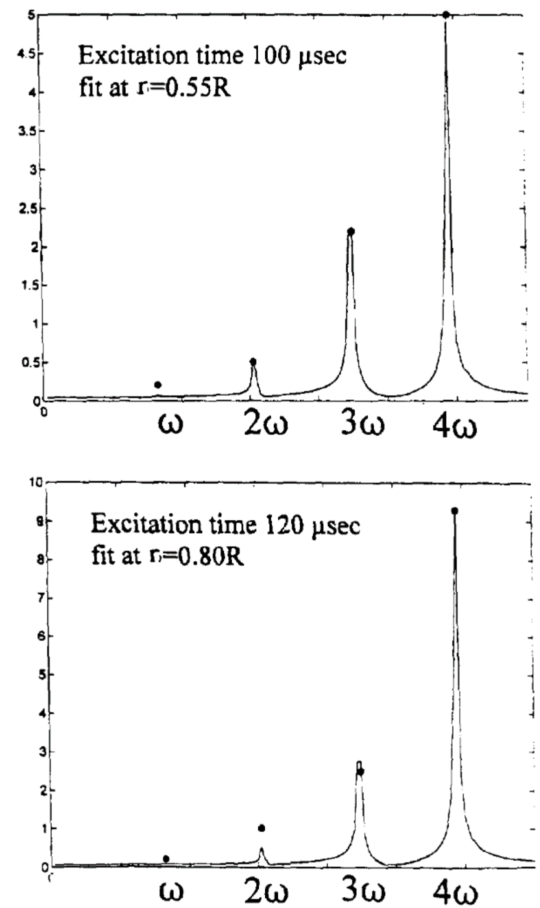
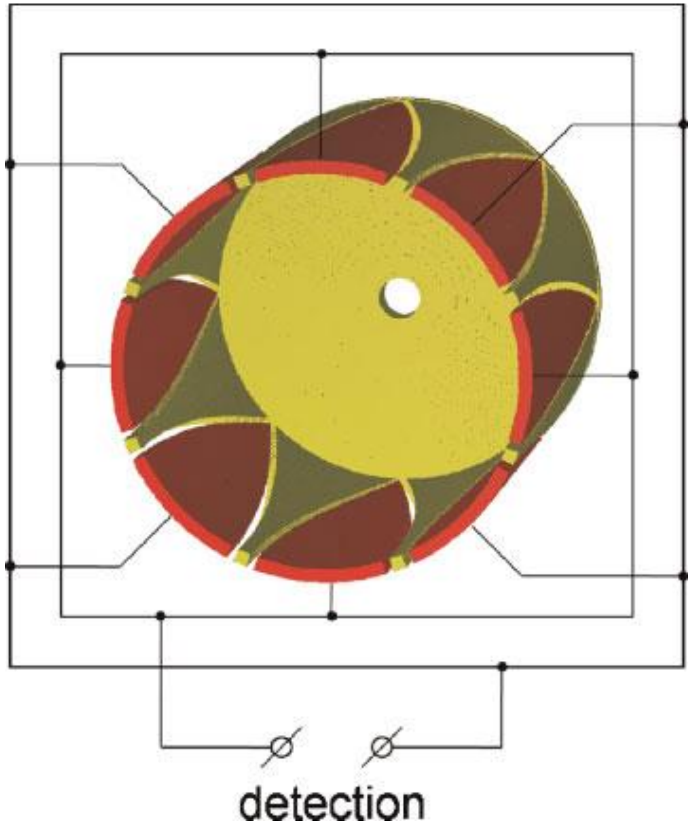
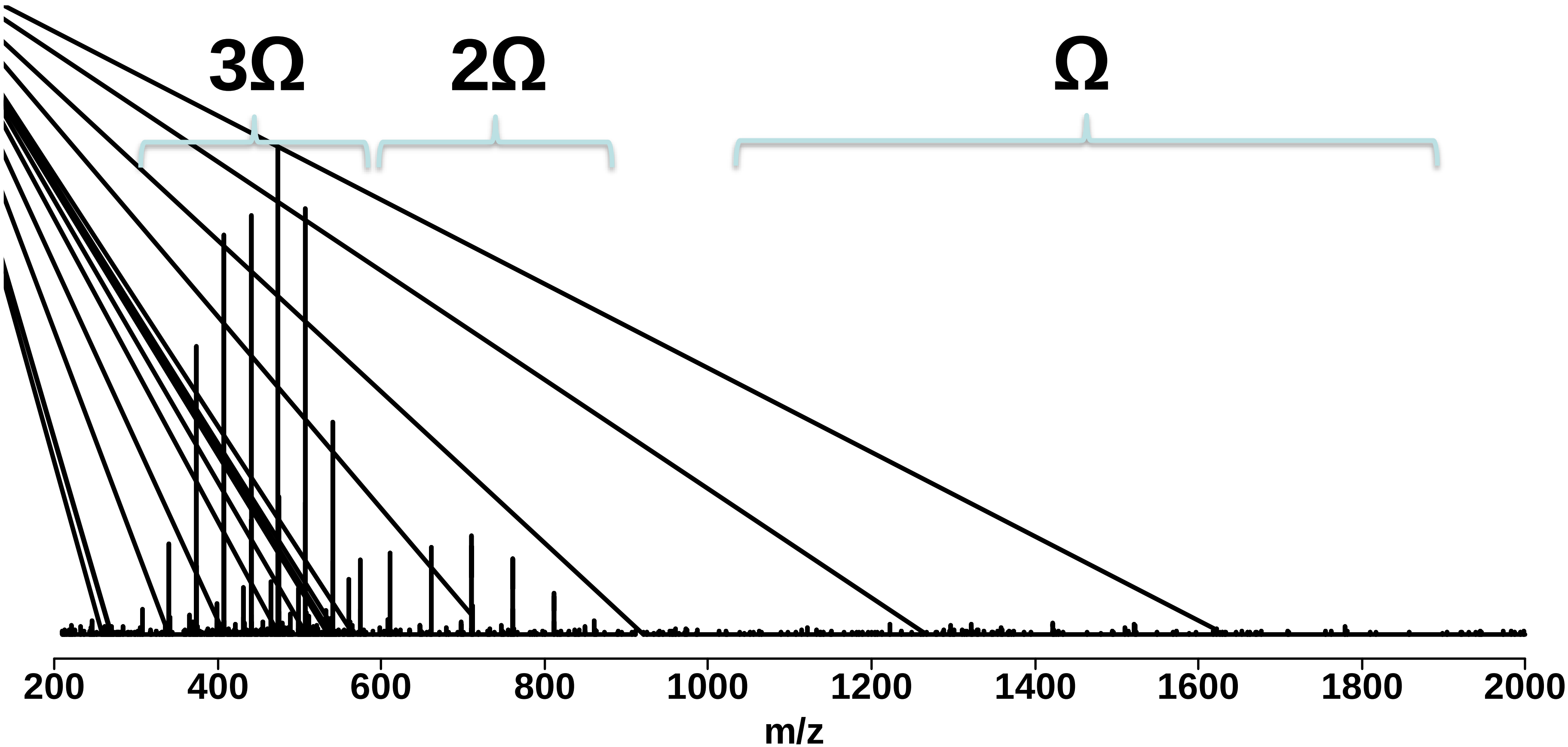


Fig. 11. Simulation for 16-electrode cell shown in . Cells radius $R = 1$. •, experimental amplitudes obtained in [7] for first four harmonics; ———, the result of computer simulation for fixed cyclotron radius, $\rho = 0.1$ and several magnetron radii. Correlation between excitation time and magnetron radius is pronounced.



$$\omega_{signal} = 4*\omega_{cyclotron}$$

Spectral Acquisition at 3Ω (14.5 T)



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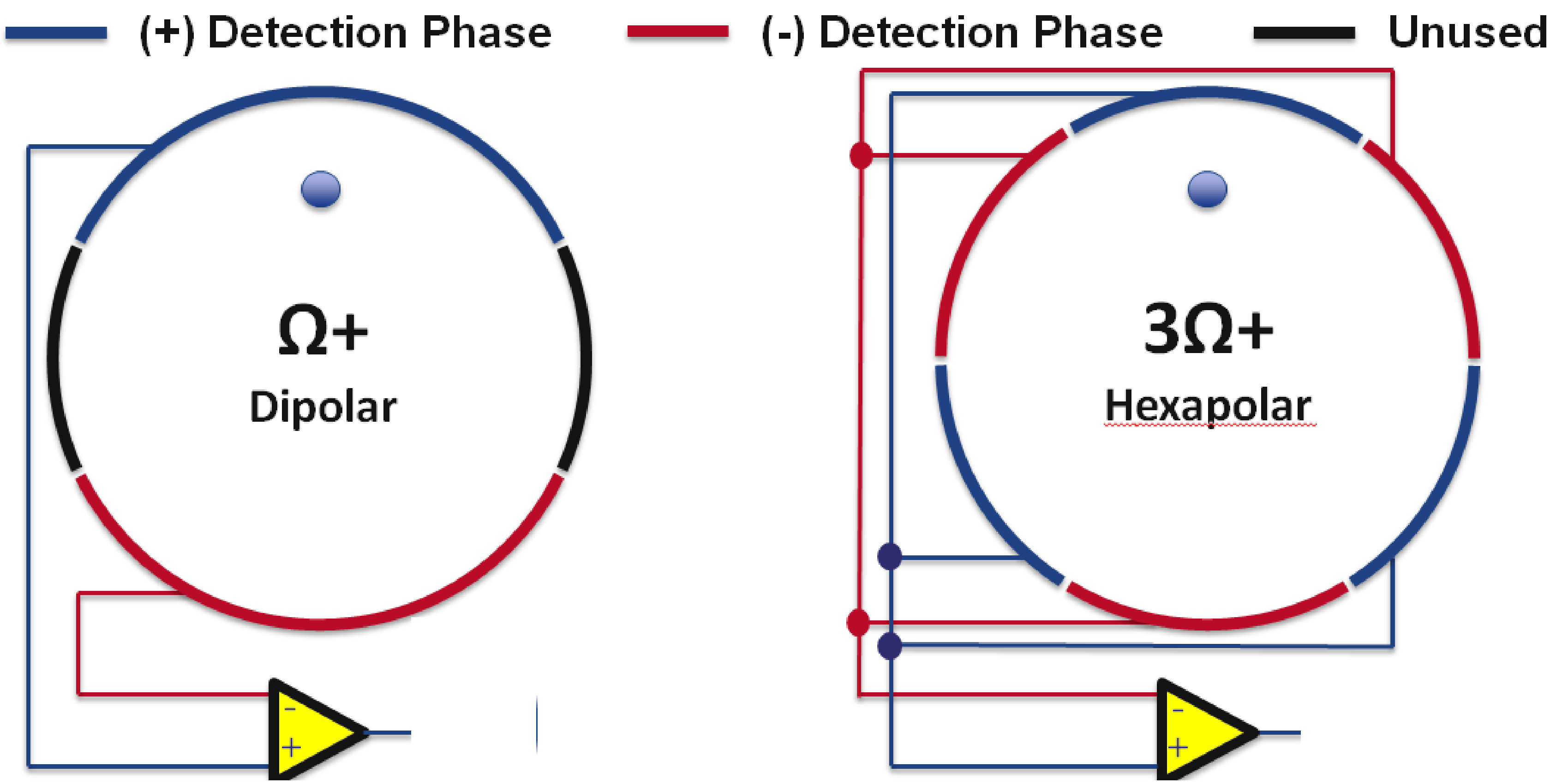
26 April, 2018

3 Ω Detection Geometry



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Thank you!

Acknowledgement to

HORIZON 2020 FT ICR network programm