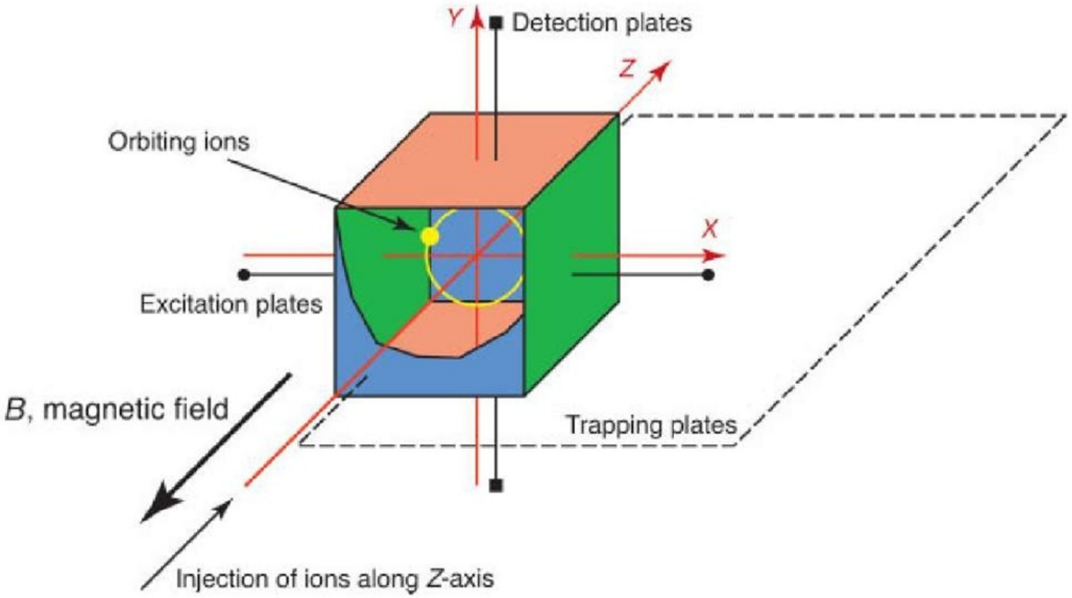
Dynamically harmonized FT ICR cell

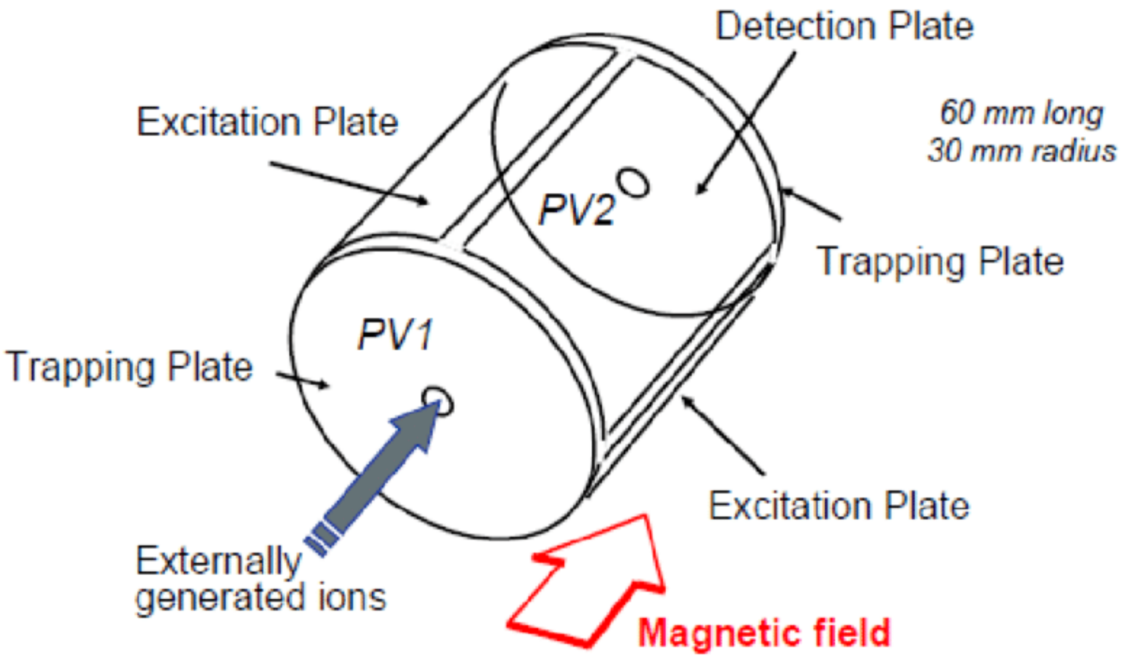
Evgeny (Eugene) Nikolaev
Skolkovo Institute of Science and Technology

First FT ICR cells

Cubic

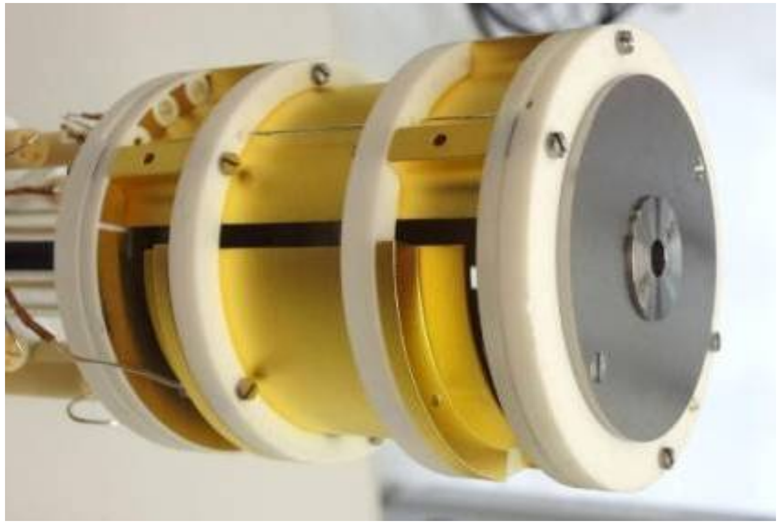


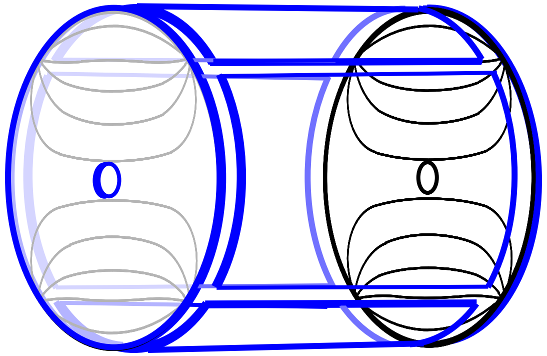
Cylindrical



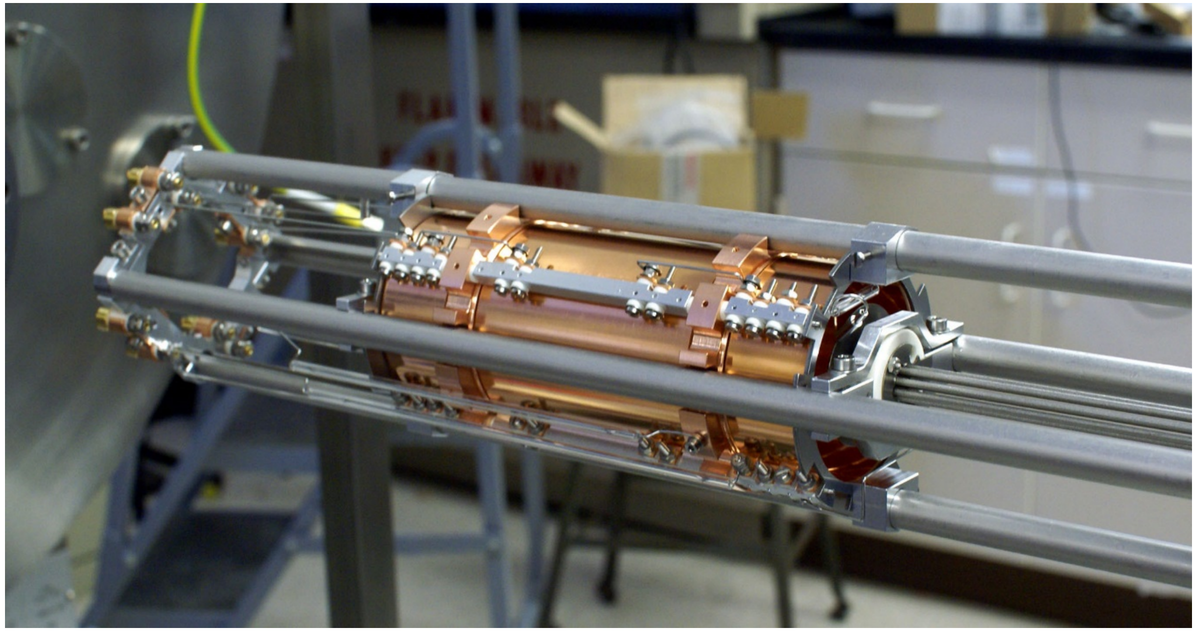
The most used ICR Cells

Bruker Infinity cell
(until 2014)





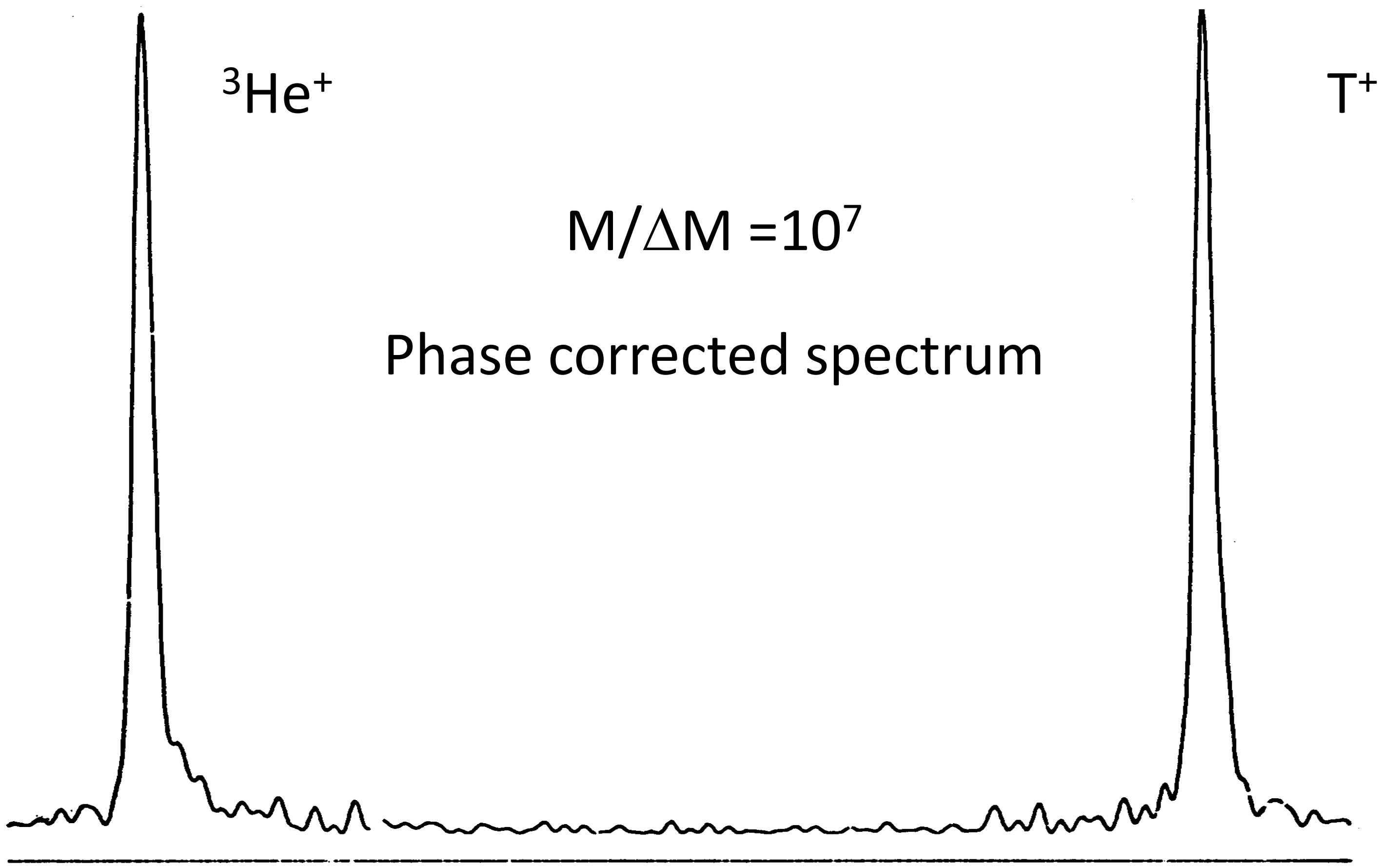
Thermo LTQ FT
(until 2006)



Why it was difficult to reach resolving power of more than 1 million on m/z close to 1000 Da?

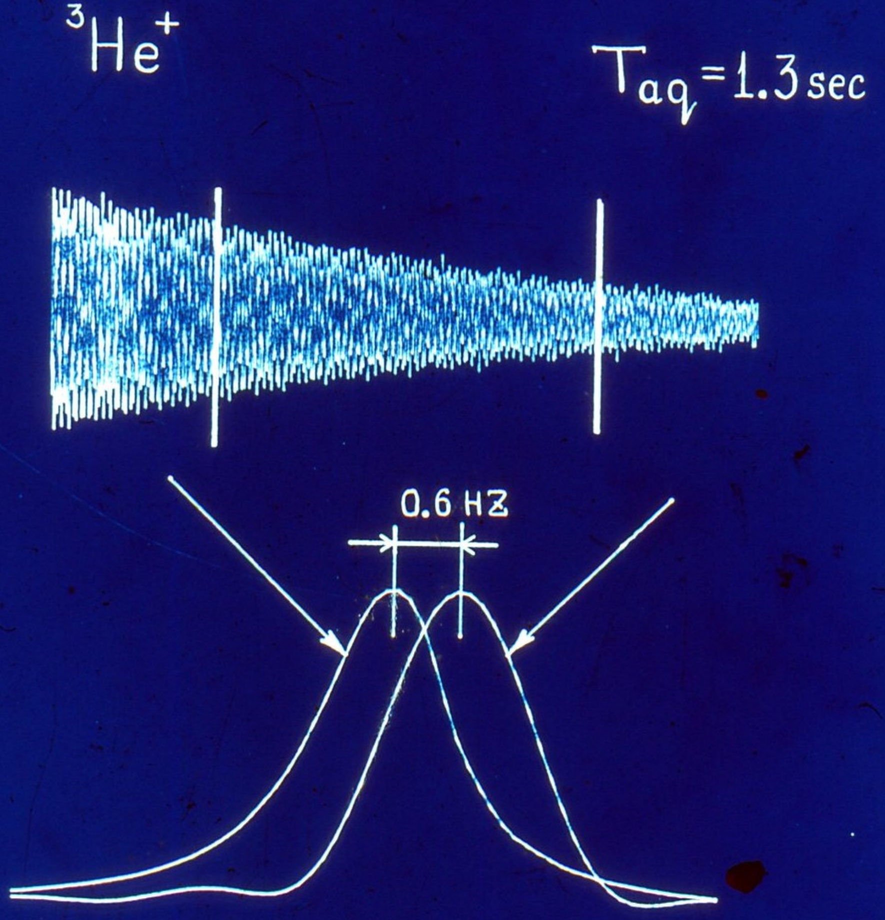
Was it the vacuum problem?
Ion-ion iteresction?

The first demonstration of $^{3}He^{+}/T^{+}$ resolution and accurate mass difference measurements 1984 year

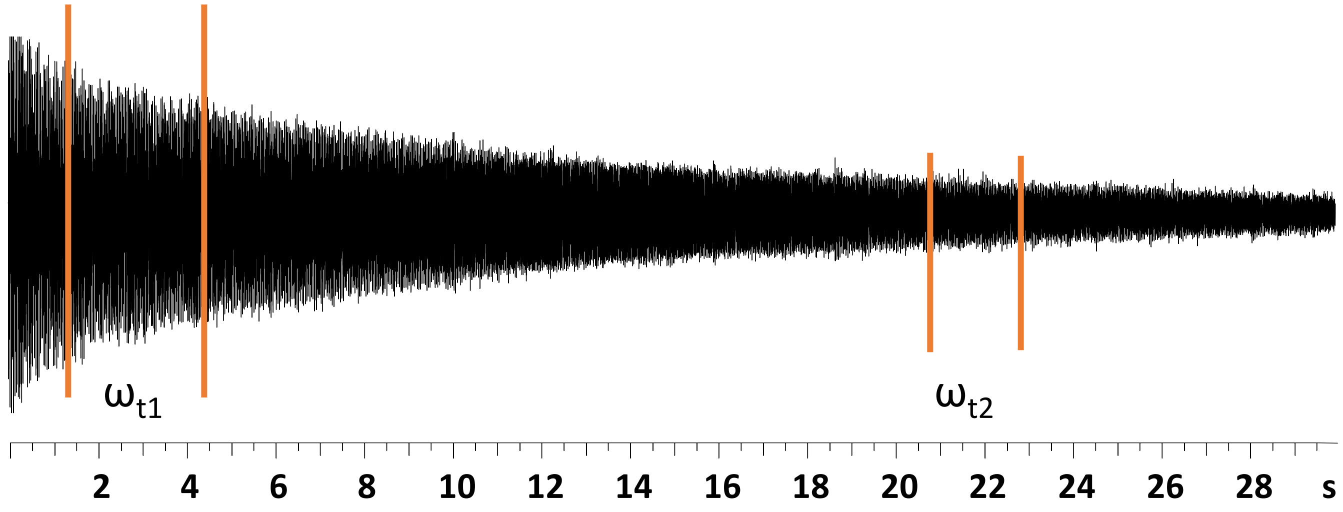


Nikolaev E.N., Neronov Y.I., Gorshkov M.V., Talroze V.L., Tarbeev N.G.
Letters to JETP (in Russian), 1084 (1984) 534-536,

Frequency drift
He/T doublet 1983



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



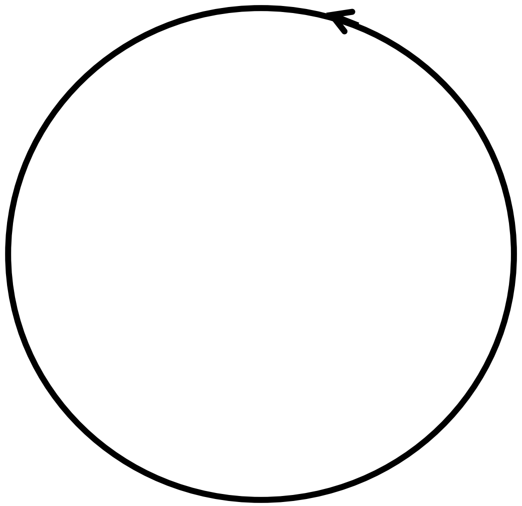
Ion motion in electric field free space

For circular motion with velocity v in magnetic field B

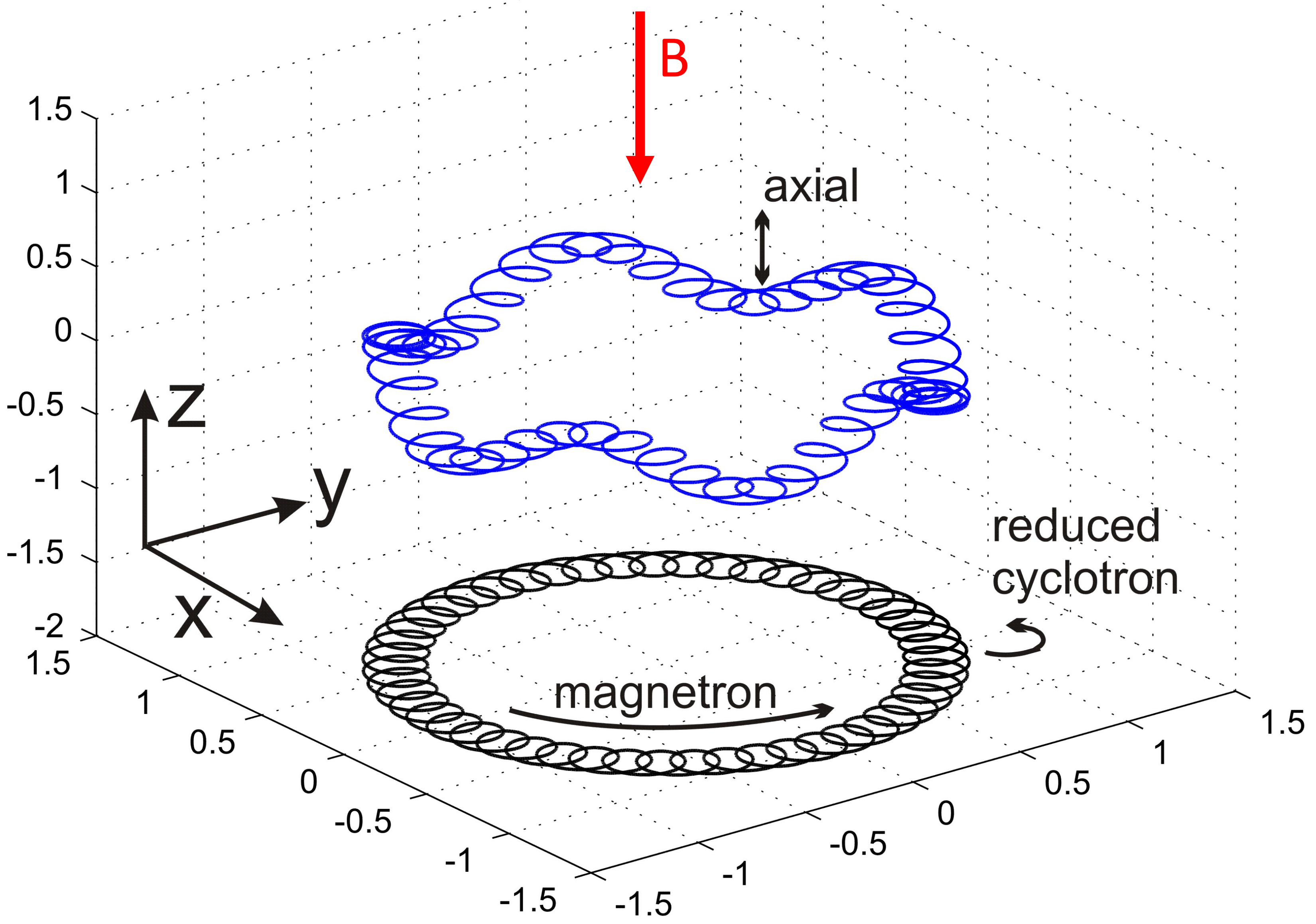
$$\vec{F} \cdot \hat{r} = ma_c = qBv$$

$$\frac{v}{r} = \frac{qB}{m}$$

$$\omega_c = \frac{qB}{m}$$

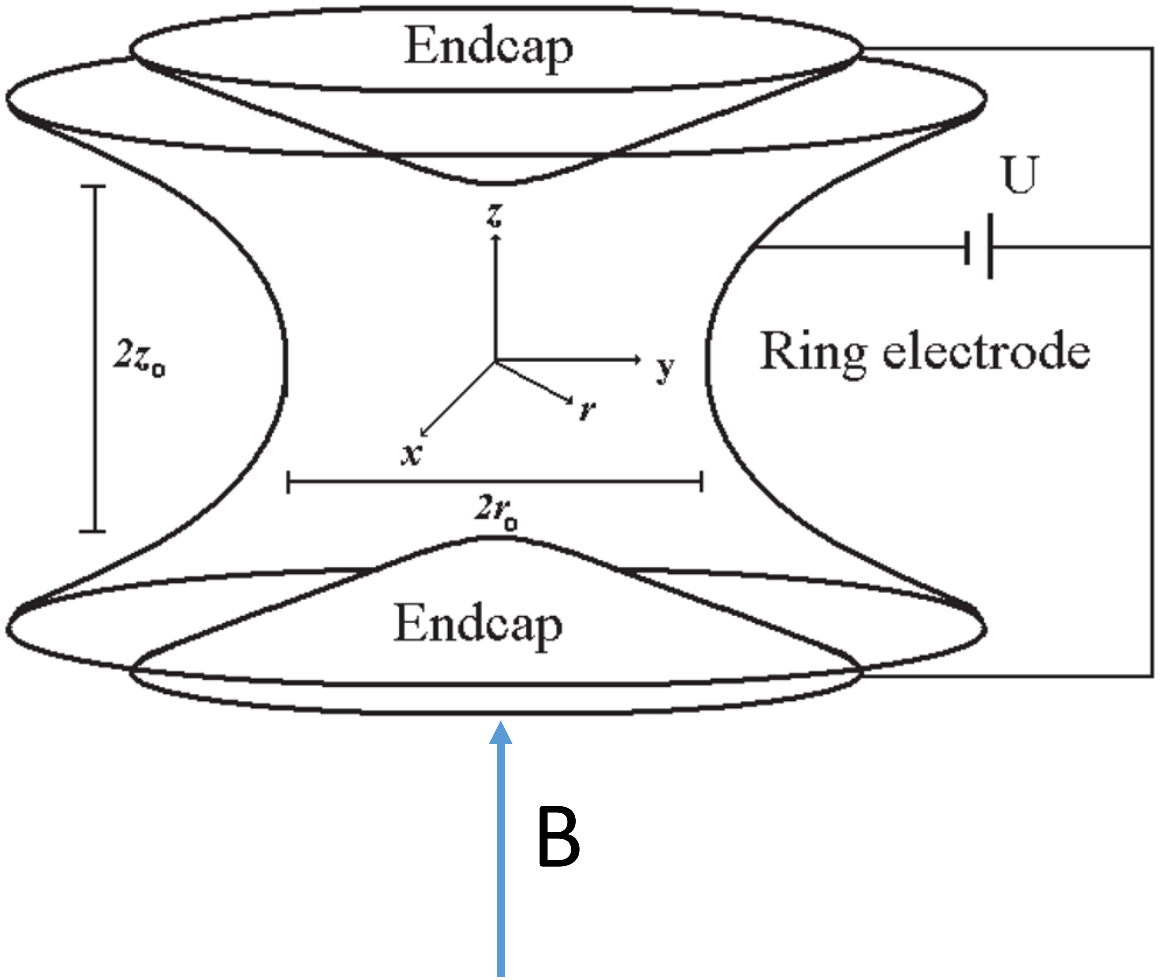


Cyclotron rotation



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

Hyperbolic Penning trap



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

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

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

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

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

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

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

$$\vec{v}\times\vec{B}\cdot\hat{x} = B\frac{\partial y}{\partial t}$$

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

$$\vec{v}\times\vec{B}\cdot\hat{y} = -B\frac{\partial x}{\partial t}$$

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

$$\vec{v}\times\vec{B}\cdot\hat{z} = 0$$

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

$$\omega_z = \sqrt{\frac{4qU_0}{m{R_0}^2}}$$

For circular motion with velocity v in magnetic field B

$$\vec{F}\cdot\hat{r} = ma_c = qBv$$

$$\frac{v}{r} = \frac{qB}{m}$$

$$\omega_c = \frac{qB}{m}$$

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

$$u = x + iy$$

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

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

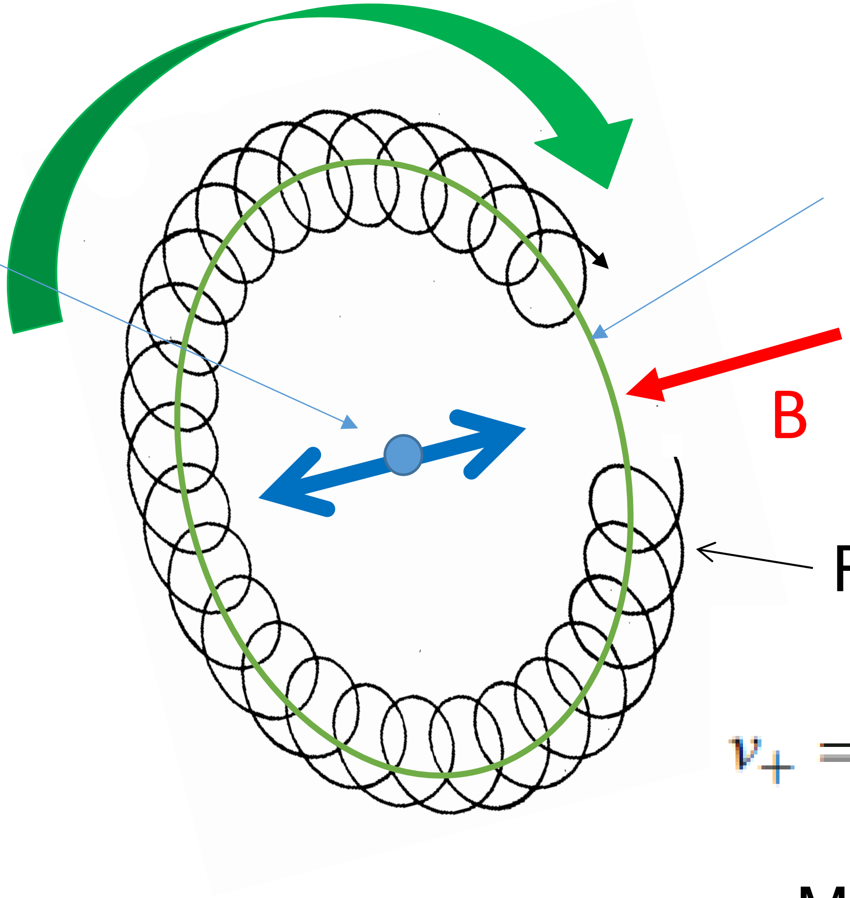
$$\ddot{z} = -\omega_z^2 z$$

$$u = e^{-i\omega t}$$

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

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

All modes of ion motion are independent

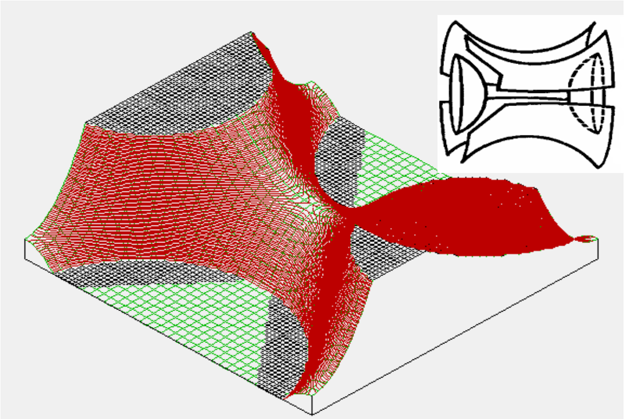


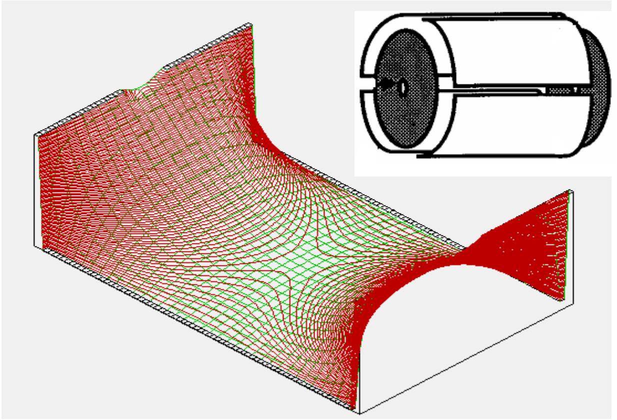
$$\nu_- = \frac{\nu_c}{2} - \sqrt{\frac{\nu_c^2}{4} - \frac{\nu_T^2}{2}}.$$

$$\nu_T = \frac{1}{2\pi}\sqrt{\frac{2\alpha z e V_T}{m a^2}}$$

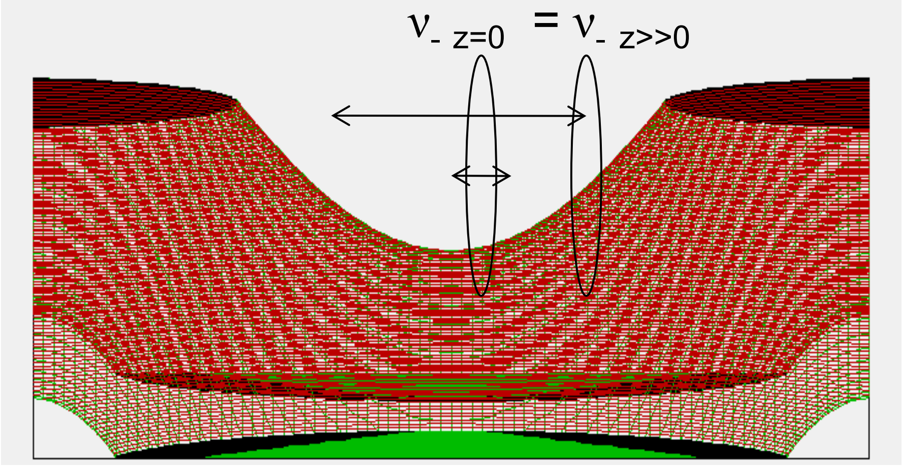
$$\nu_+ = \frac{\nu_c}{2} + \sqrt{\frac{\nu_c^2}{4} - \frac{\nu_T^2}{2}}.$$

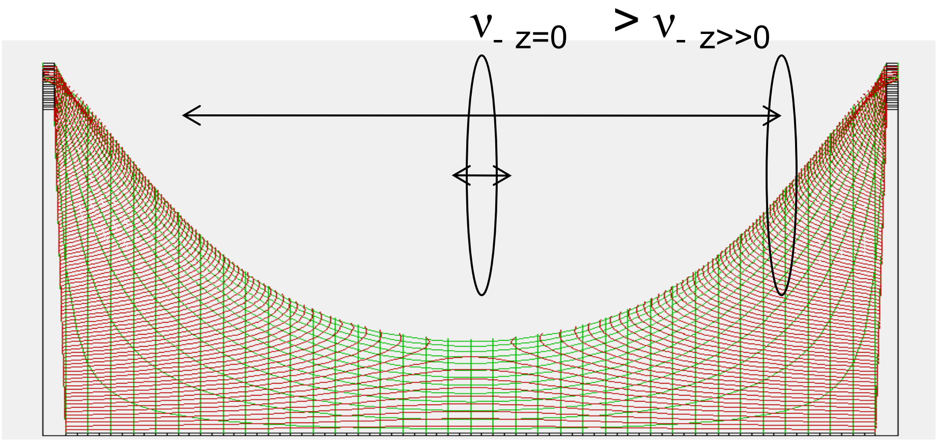
The lost of phase coherence is a result of Inharmonicity of a regular FT ICR cell field





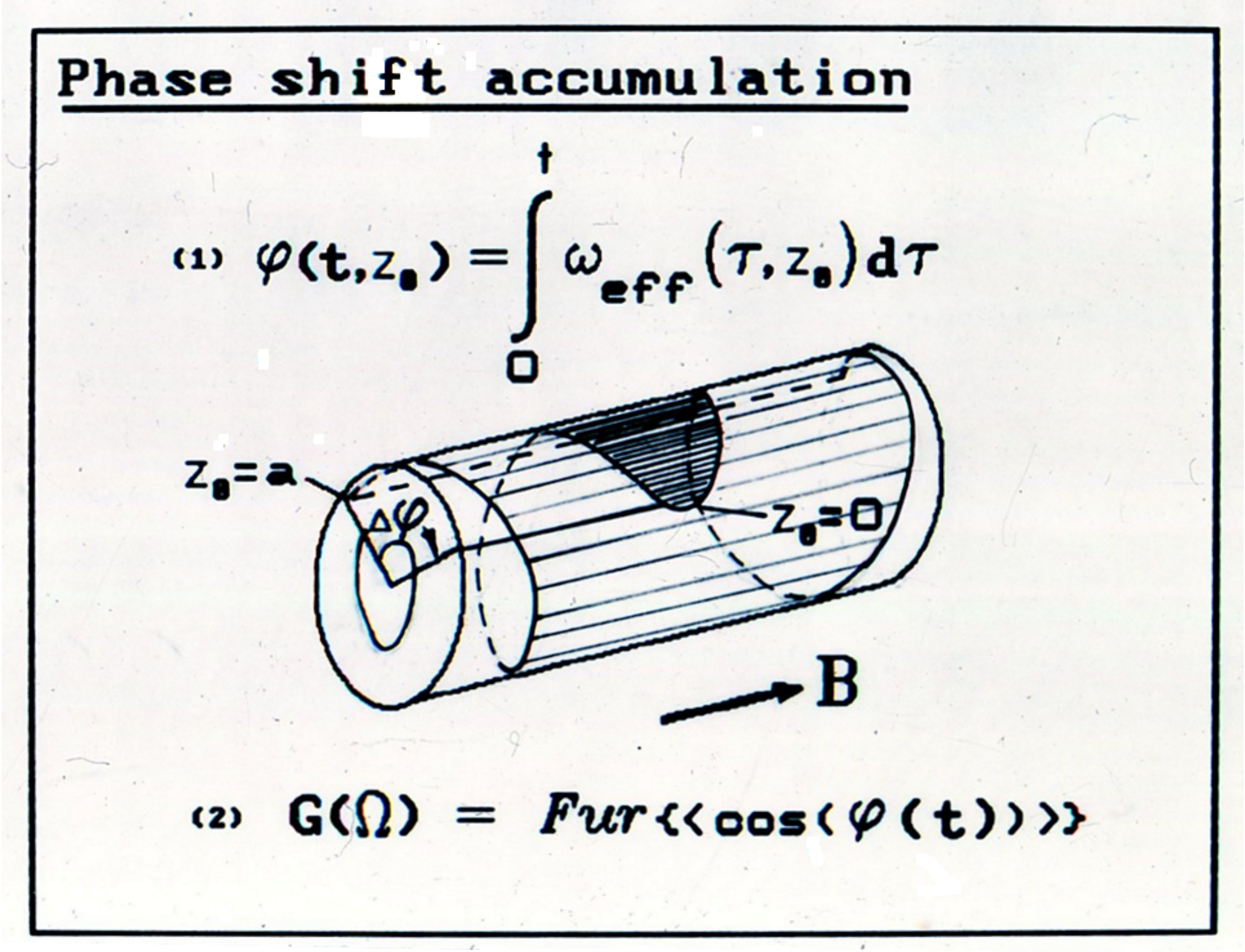
Distribution of potentials in hyperbolic (left) and rectangular or cylindrical FT ICR cells (right)



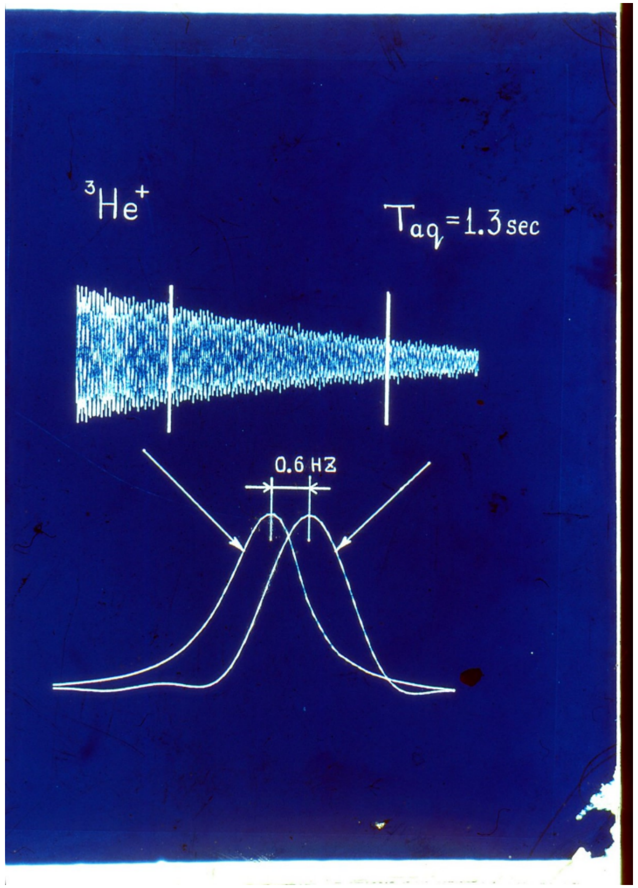


Cyclotron and magnetron frequencies are Independent on axial oscillation amplitude

Cyclotron and magnetron frequencies depend on axial oscillation amplitude



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



How do we know now that ion clouds have a comet like structure in conventional FT ICR cells?

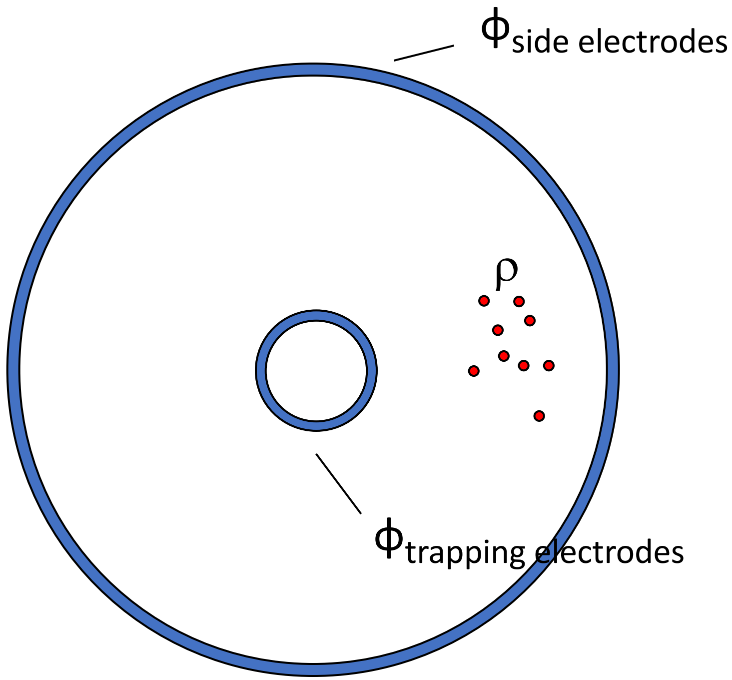
We can use SIMION

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

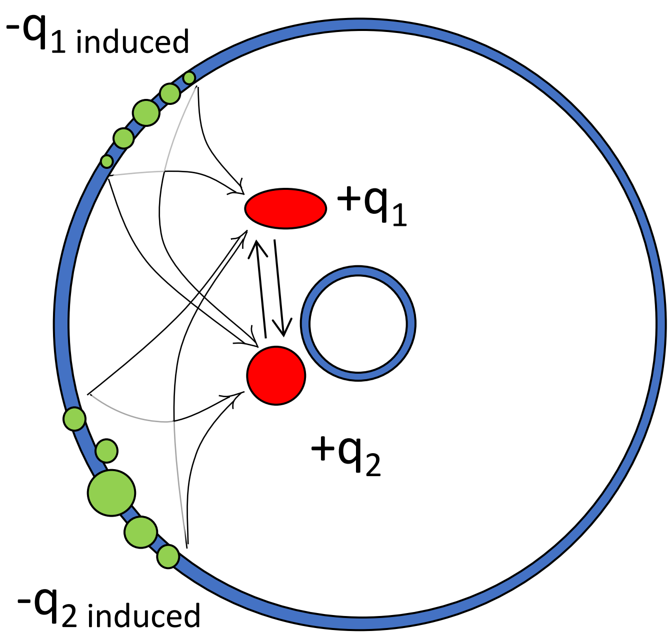
Rapid Commun. Mass Spectrom. 2007; 21,1-20



Solving Poisson Equation

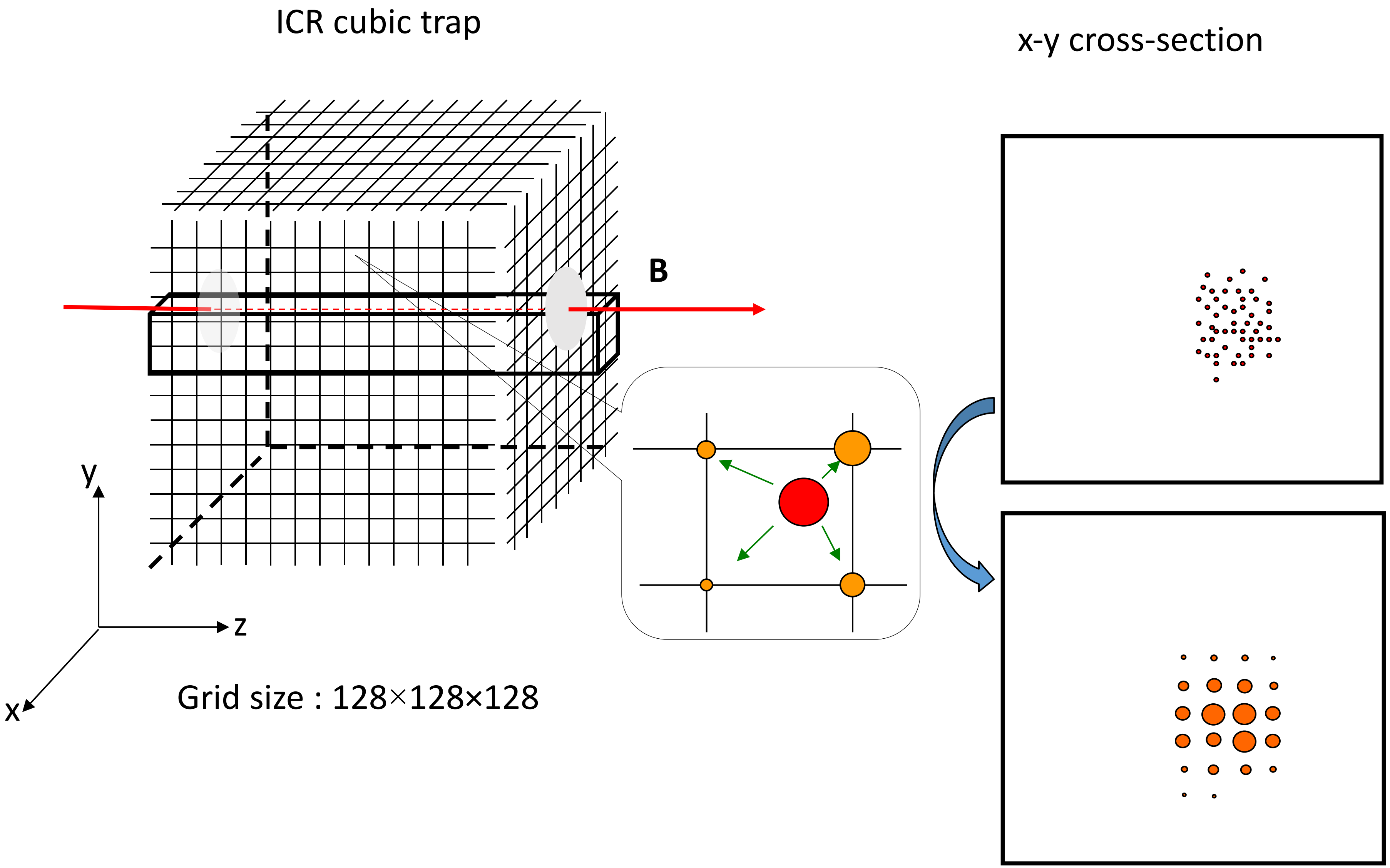
$$\nabla \cdot \nabla \varphi = \nabla^2 \varphi = -\frac{\rho}{\varepsilon}$$

Solving the equation in the region between the electrodes, using known boundary conditions (φ) and charge density (ρ) in the trap.

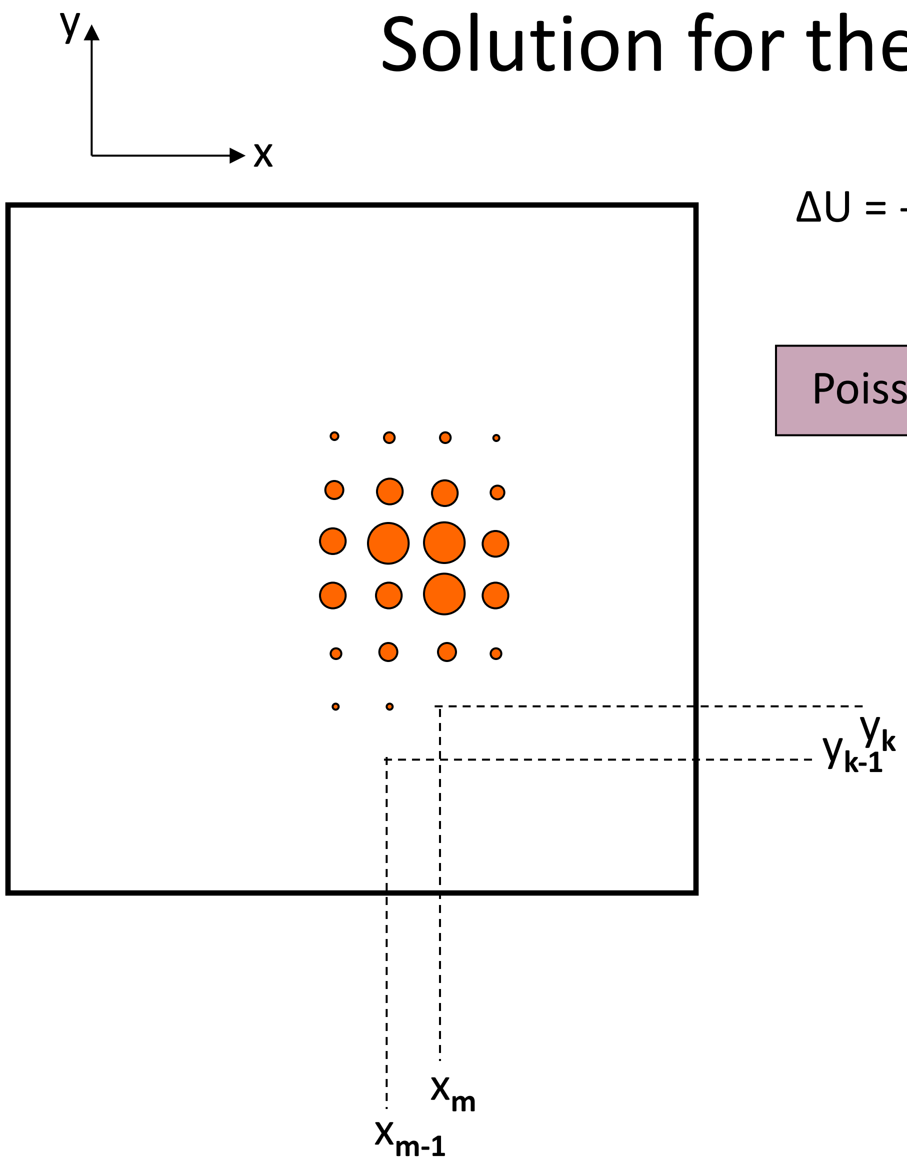


Calculate ion-ion and ion-induced charge interactions directly If we could find the charges, induced on electrodes by ions inside the trap, we could use particle-particle interaction model to calculate forces acting on those ions.

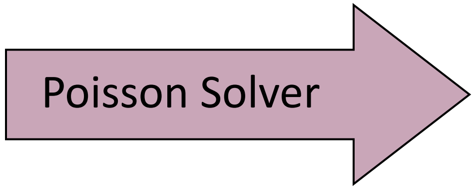
Particle-In-Cell Algorithm (first used to describe ion behavior in FT ICR cell by Dale Mitchell and Richard Smith)



Solution for the electric field

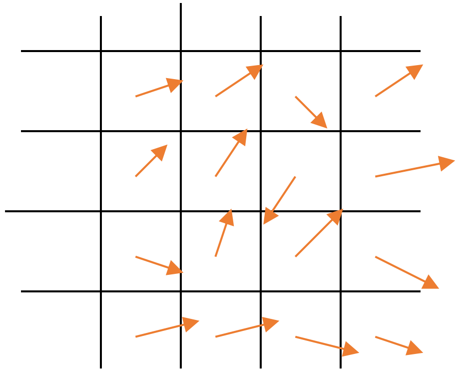


$\Delta U = -\rho(x_i, y_j, z_k)/\varepsilon_0$



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

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



Integration the equation of motion

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

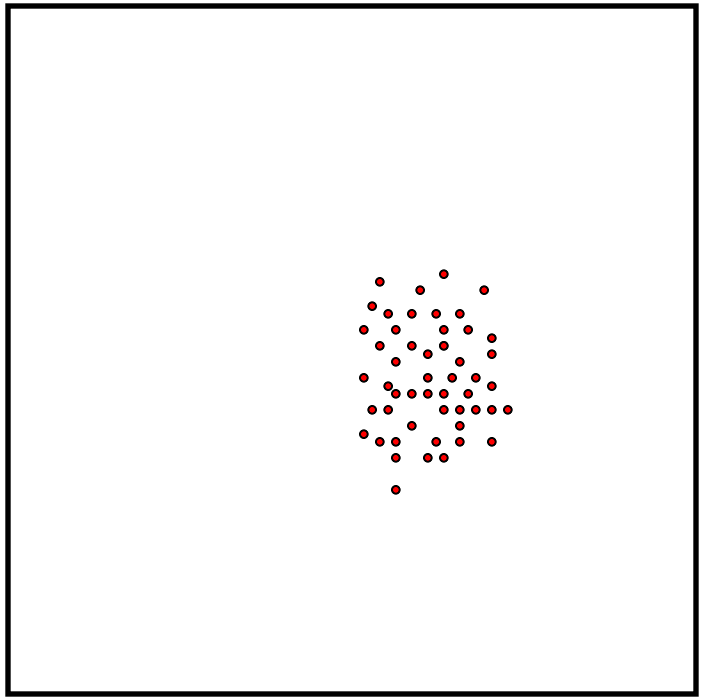
E(r_i)

v_i , r_i

Boris integrator

for every ion (i)

new v_i , r_i



Next time step

Integration the equation of motion

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

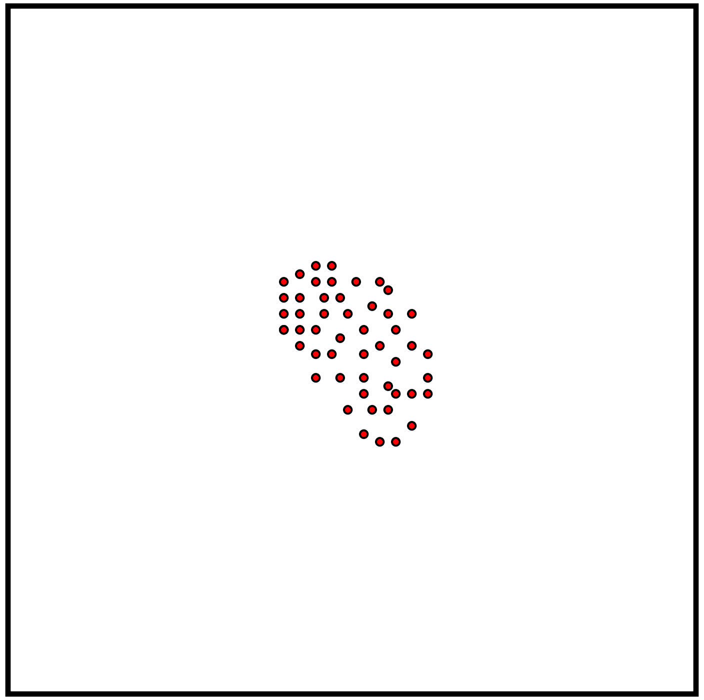
E(r_i)

v_i , r_i

Boris integrator

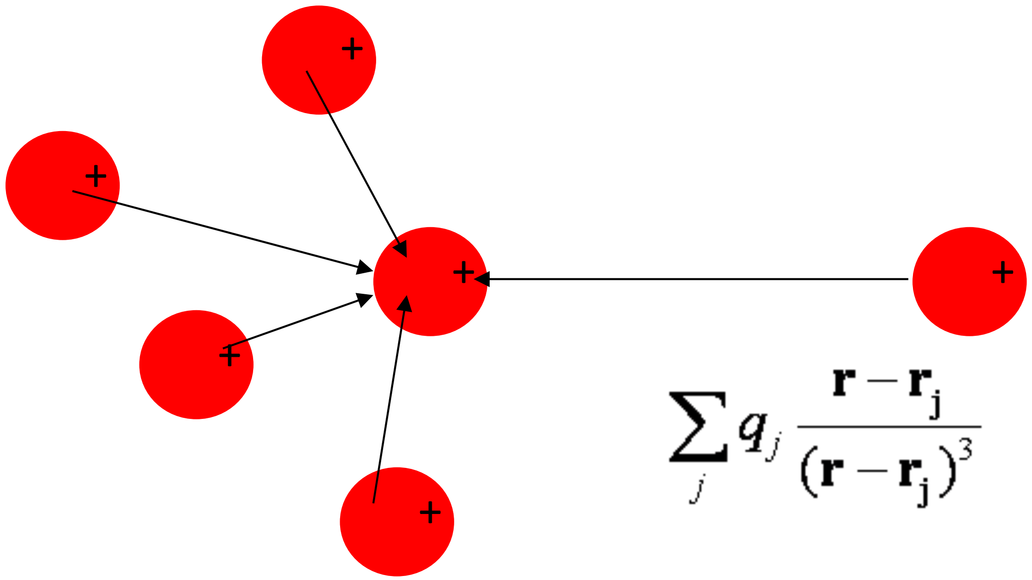
for every ion (i)

new v_i , r_i



Next time step

The Particle-Particle Method



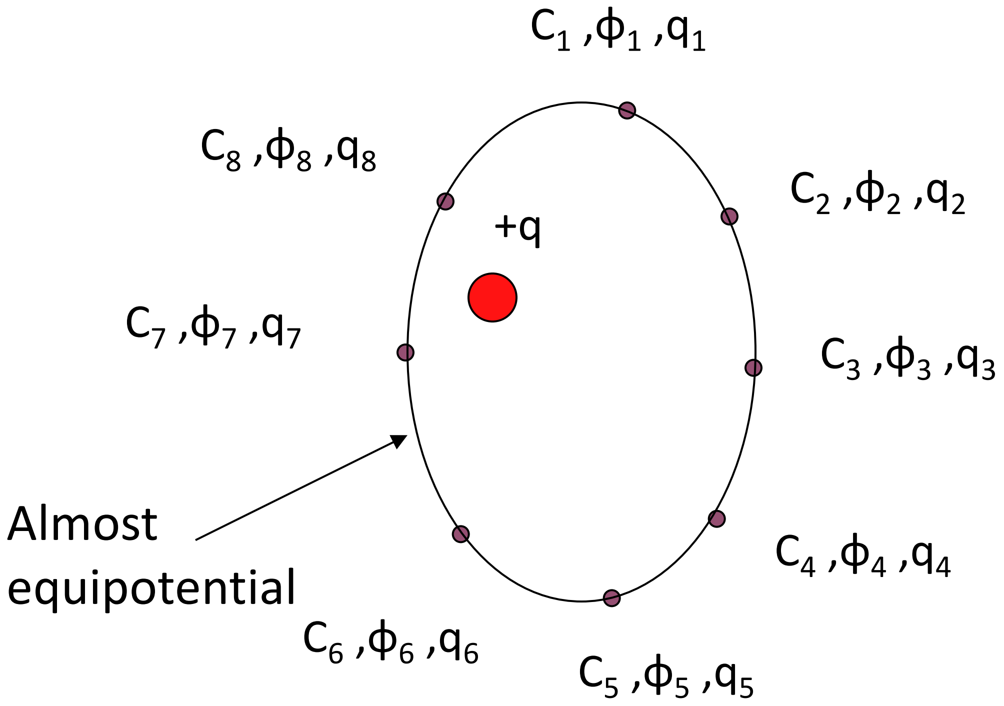
$$\sum_j q_j \frac{\mathbf{r}-\mathbf{r}_j}{(\mathbf{r}-\mathbf{r}_j)^3}$$

The main problem:

How to calculate forces from the image charge?!

Capacity matrix method for image charge calculation

$$\begin{bmatrix} q_1 \\ \vdots \\ q_n \end{bmatrix} = \begin{pmatrix} & C & \end{pmatrix} \begin{bmatrix} \varphi_1 \\ \vdots \\ \varphi_n \end{bmatrix}$$

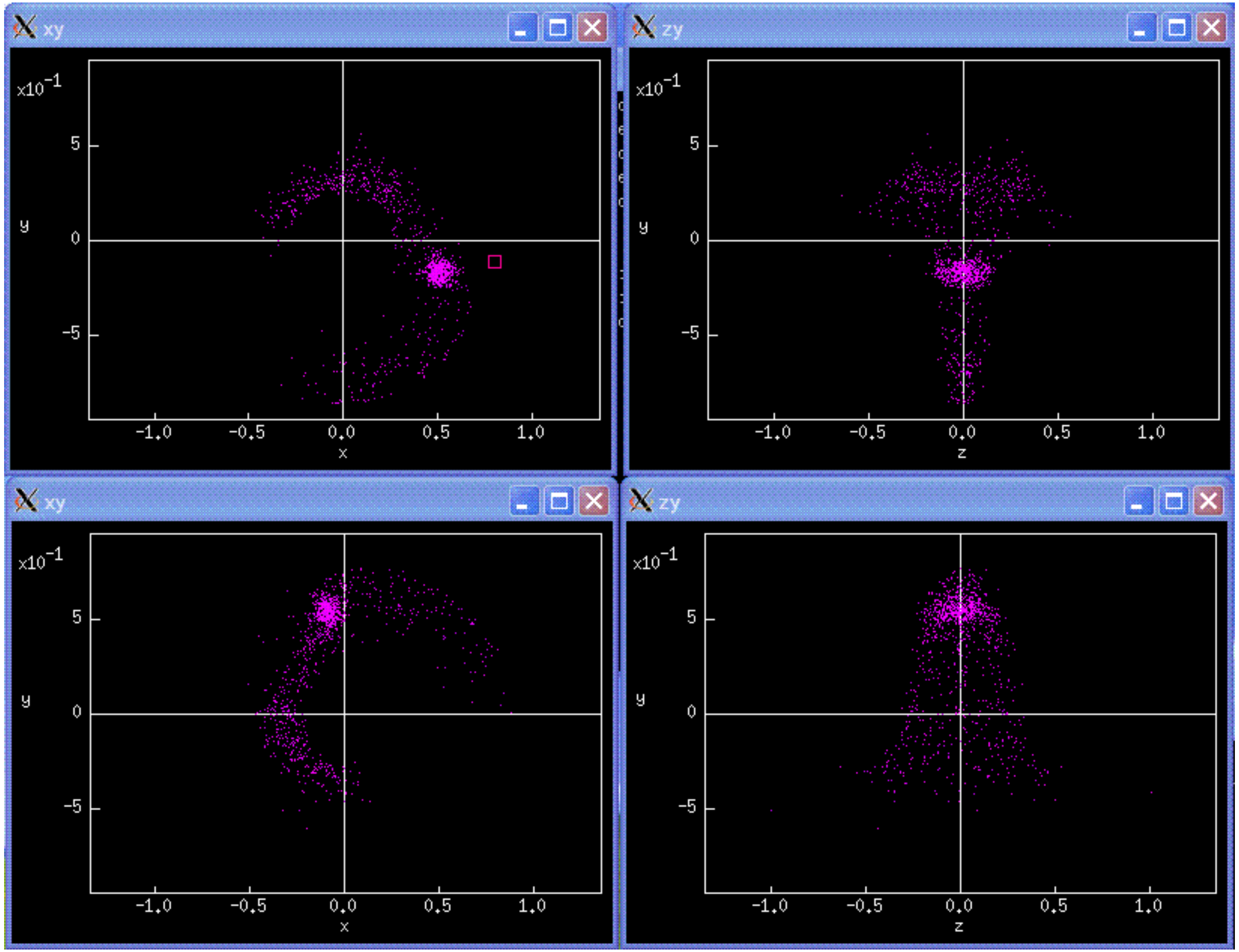


For arbitrary form surface we can find chargers located on the surface which makes it almost equipotential

Can we believe simulation results?!

Comparison PIC with particle-particle

104 charges 1T 32x32x32 mesh

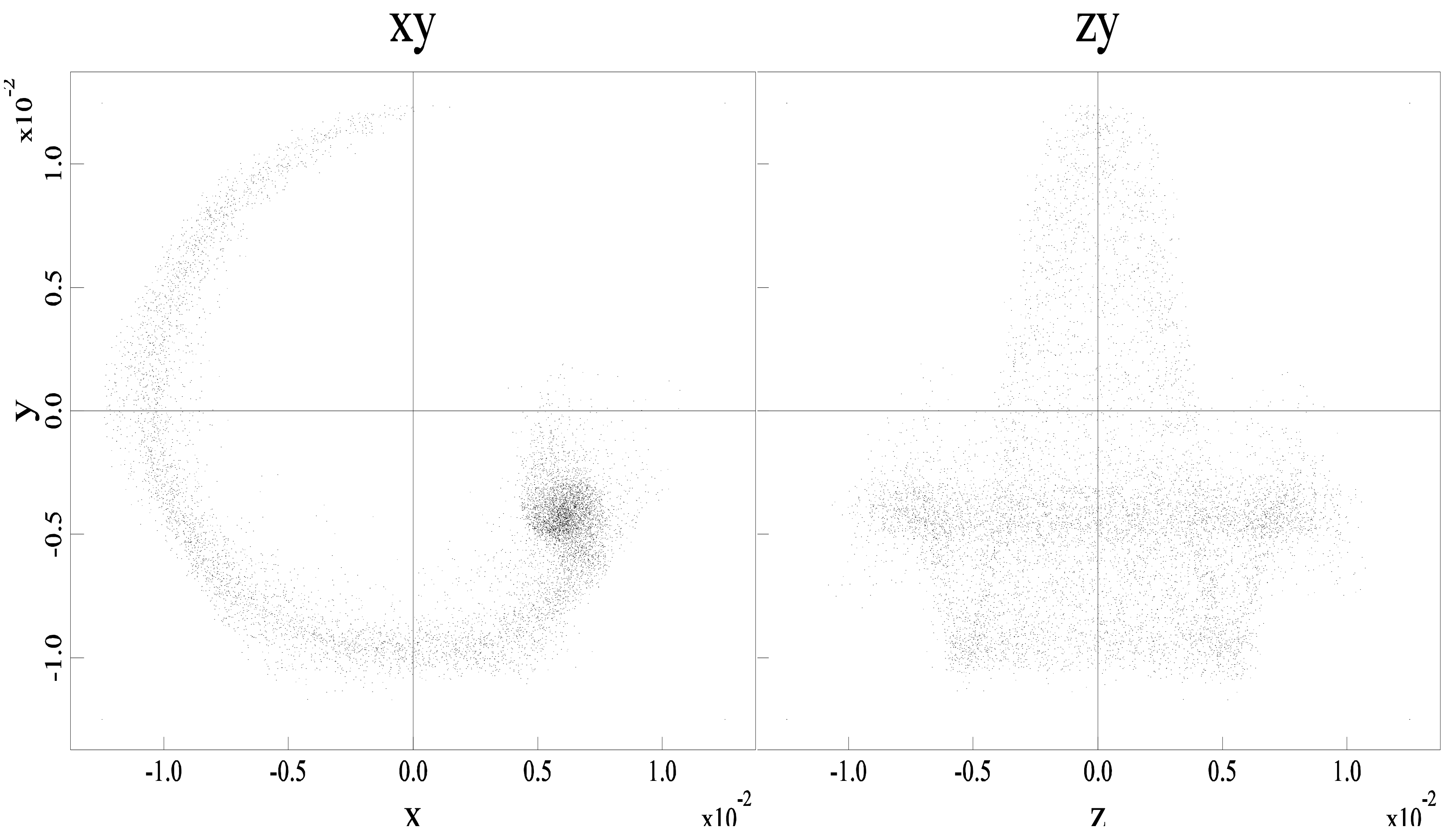


Particle-particle
No image charge

PIC

Yes, we can believe!!

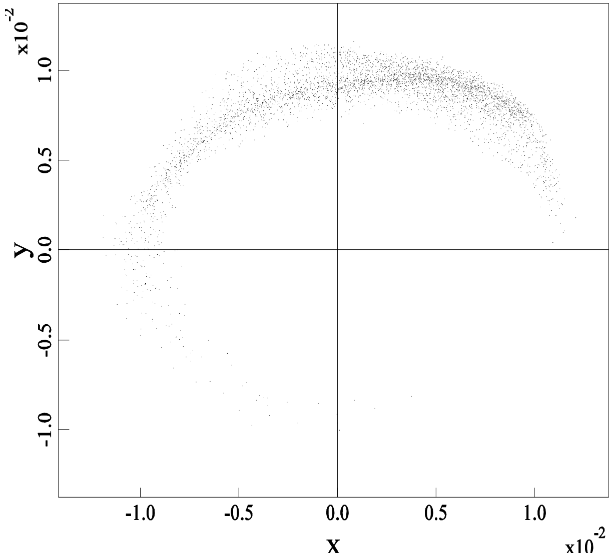
Cloud of one m/z ions in a cylindrical geometry FT ICR cell



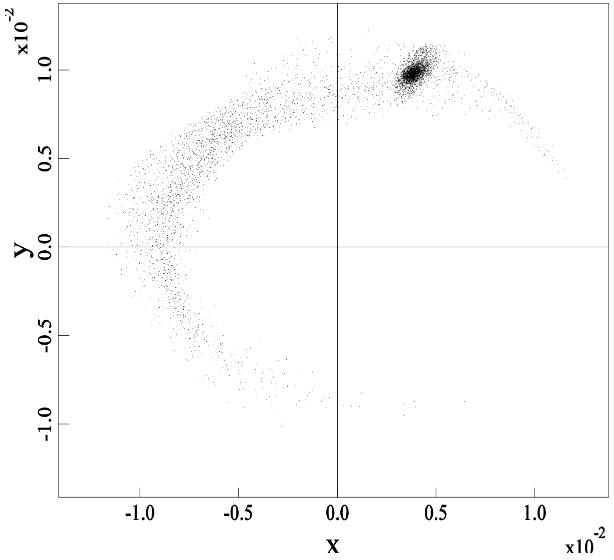
Evolution of ion clouds with different amount of ions in the cell

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

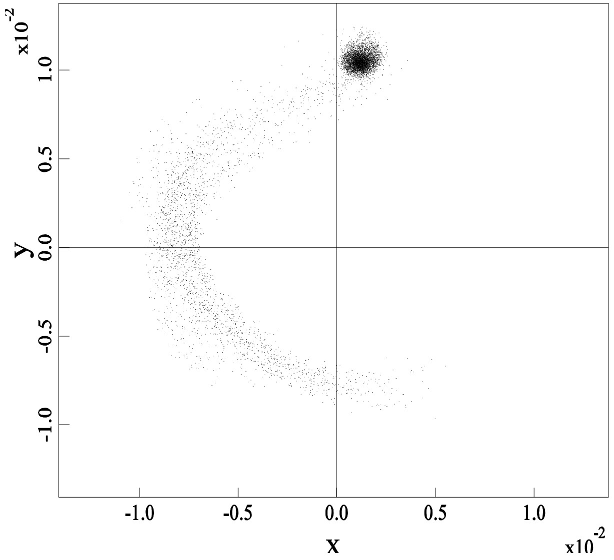
N=5000



N=20000



N=50000

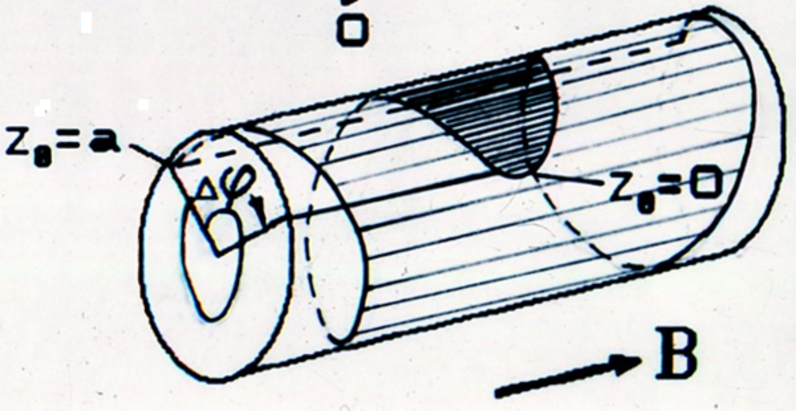


t = 3.24 ms

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

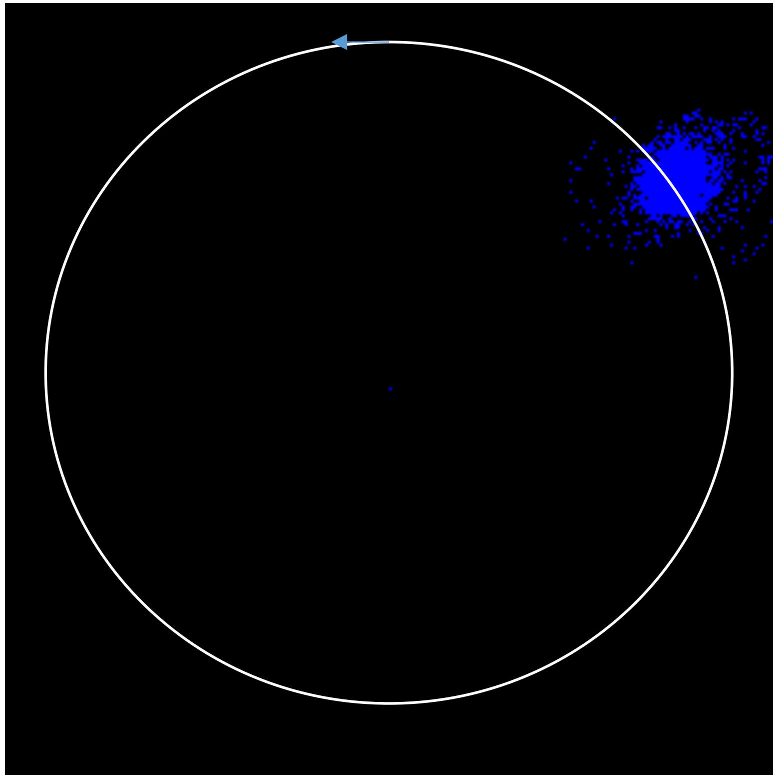
Phase shift accumulation

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

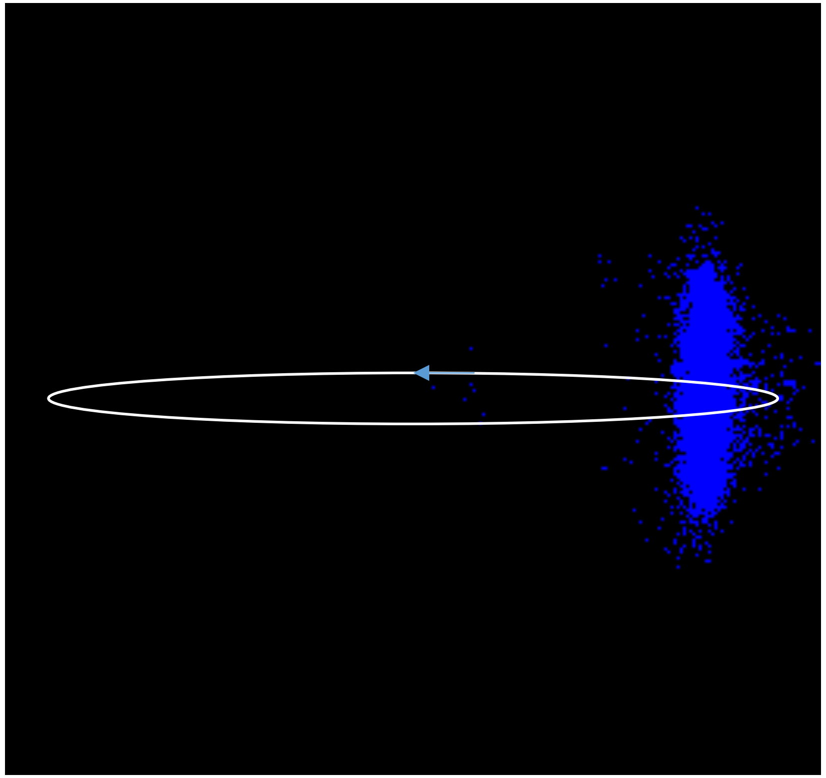


$$(2)\quad G(\Omega) = Fur\{\langle oos(\varphi(t))\rangle\}$$

Ion clouds in harmonized cells have elliptical cigar like forms



Projection on the plane orthogonal to the magnetic field



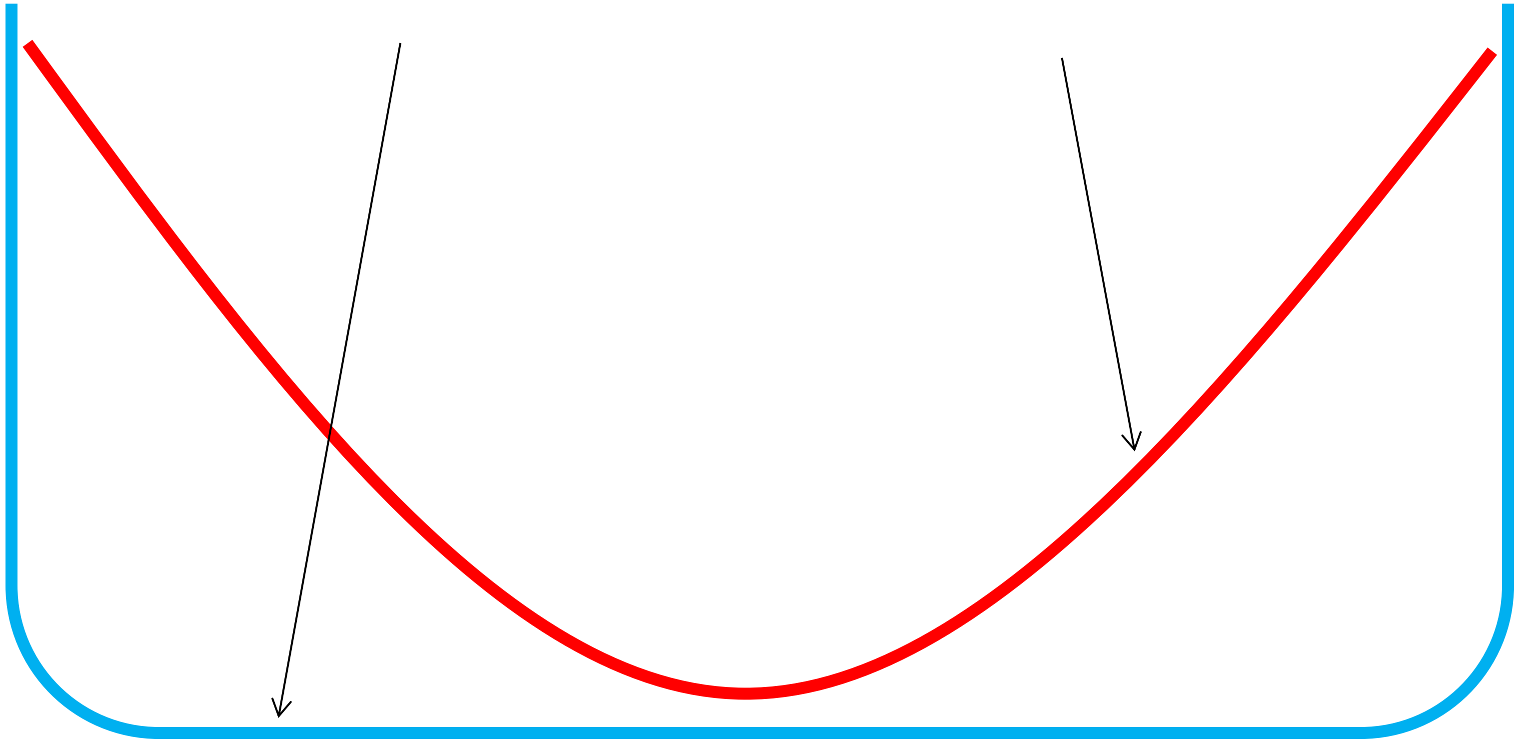
Projection on the plane almost Parallel to the magnetic field

How to get rid of comets?

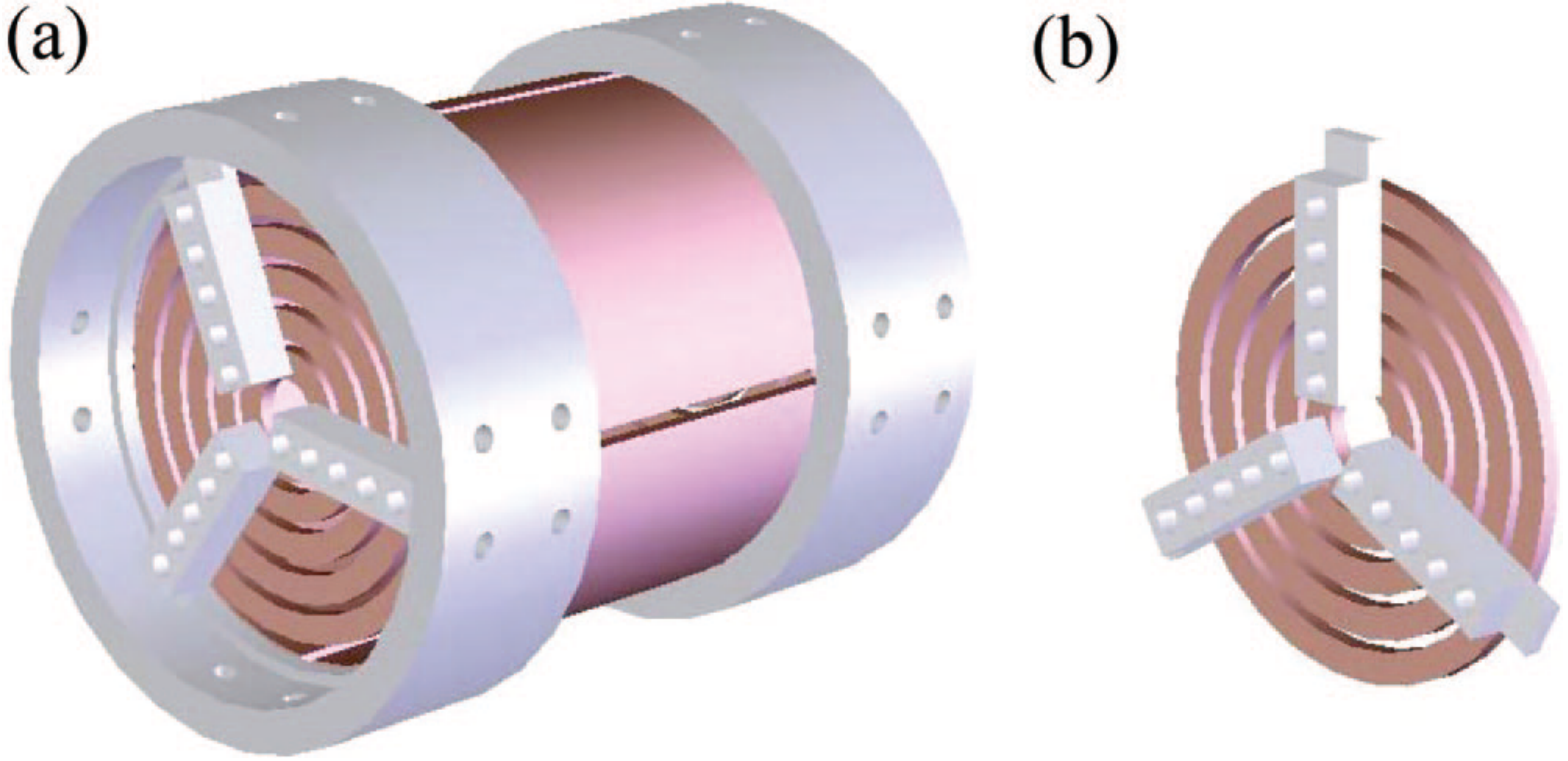
Two main approaches

Flattering potential-making field free region

Harmonization-making field distribution hyperbolic



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***



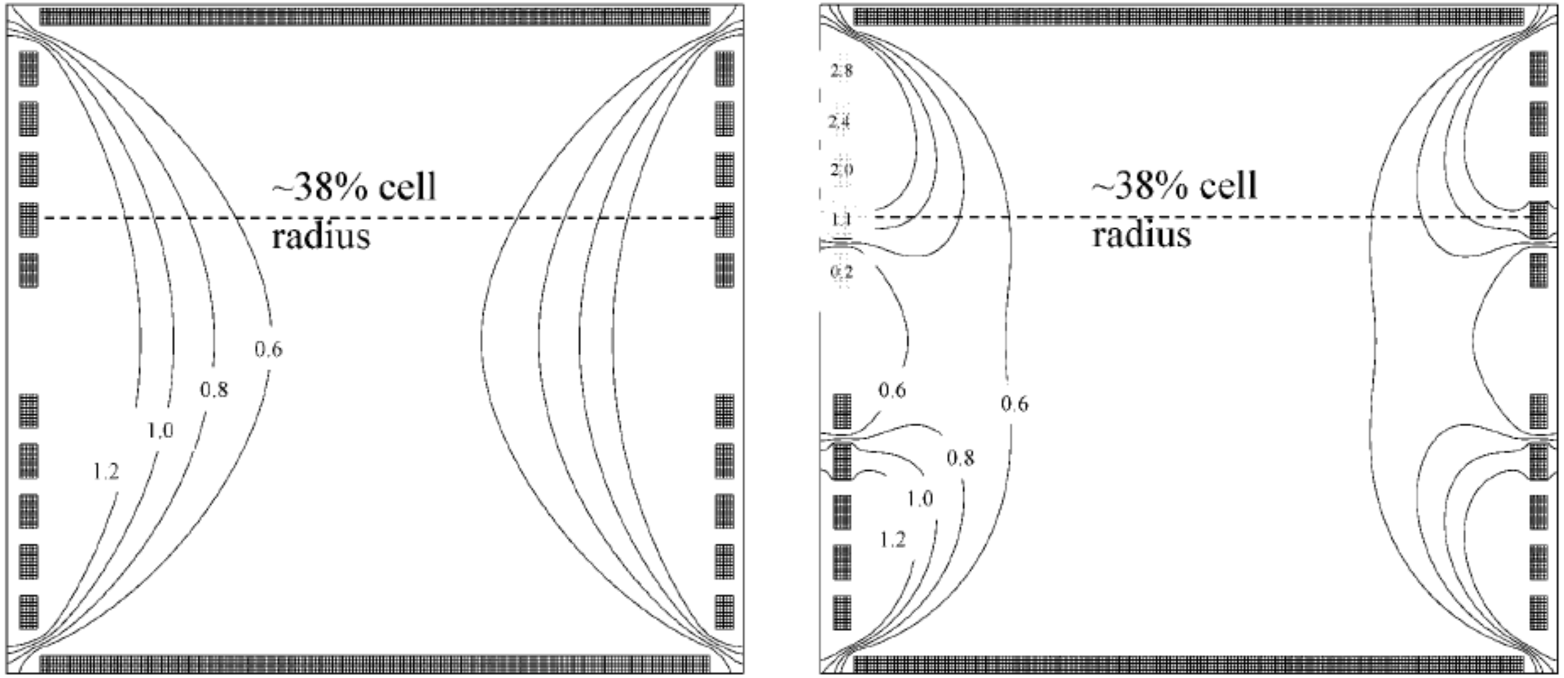


Figure 2. Equipotential contour plots are shown for (a) common 2.0 V trapping conditions and (b) the TREC trapping conditions. The voltages for the modulated (TREC) trapping conditions with increasing electrode radius are 0.2, 1.1, 2.0, 2.4, and 2.8 V respectively, as shown on the rings. A dashed line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

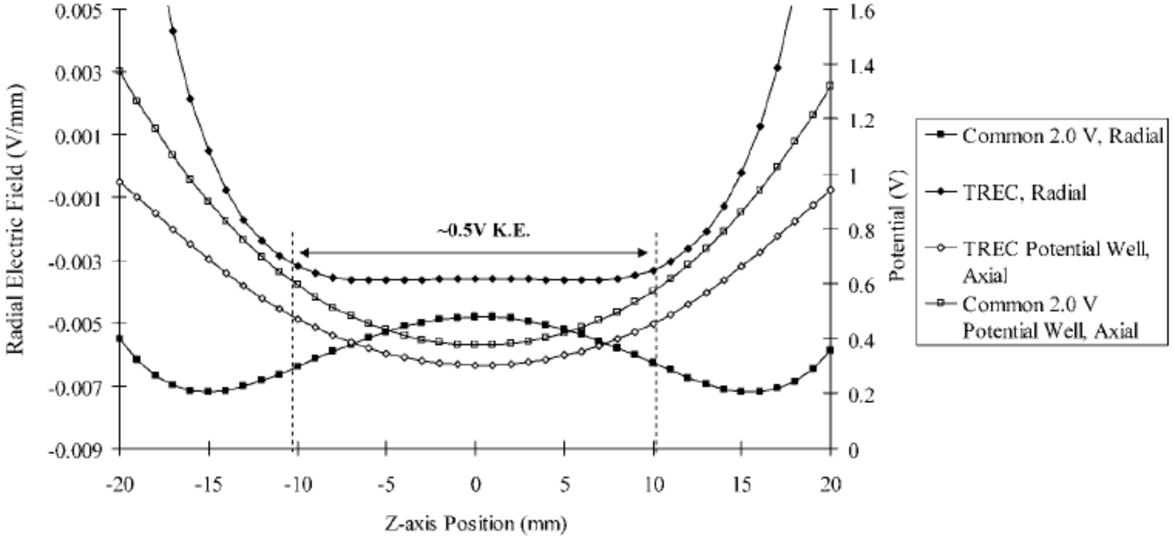
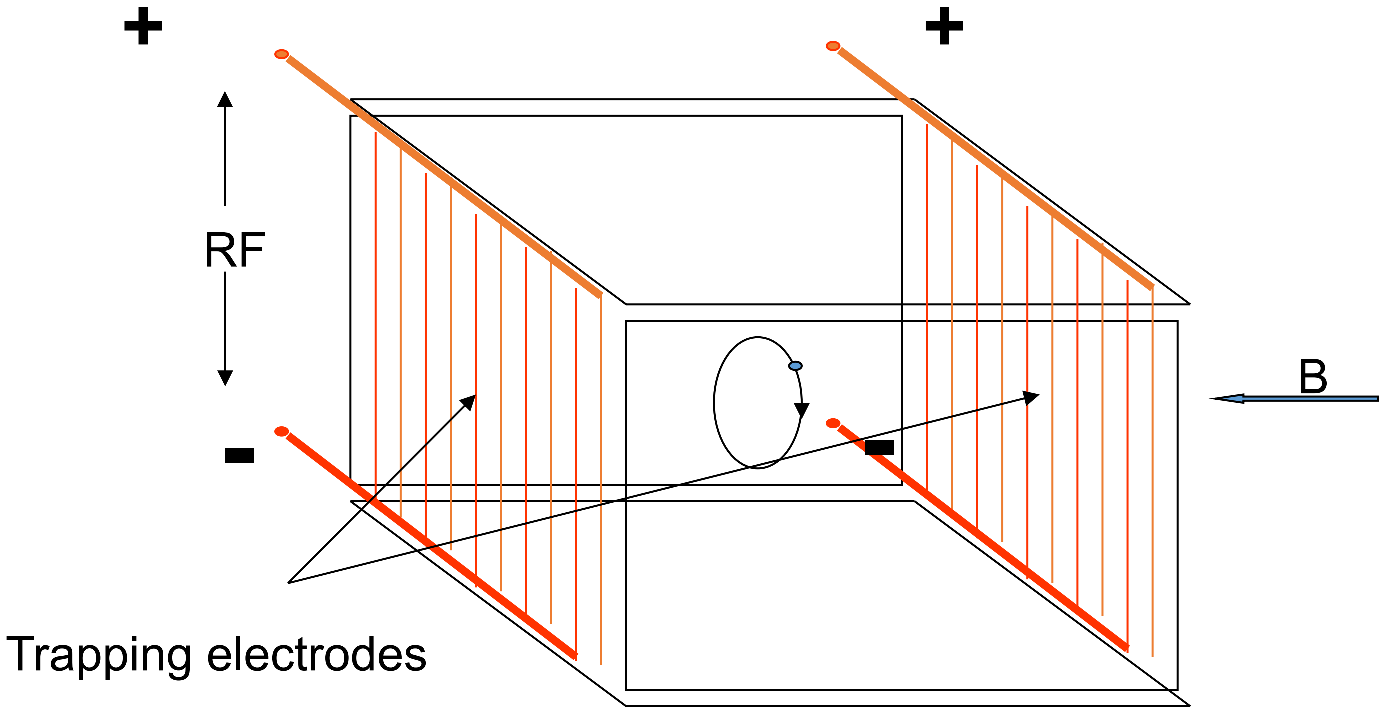
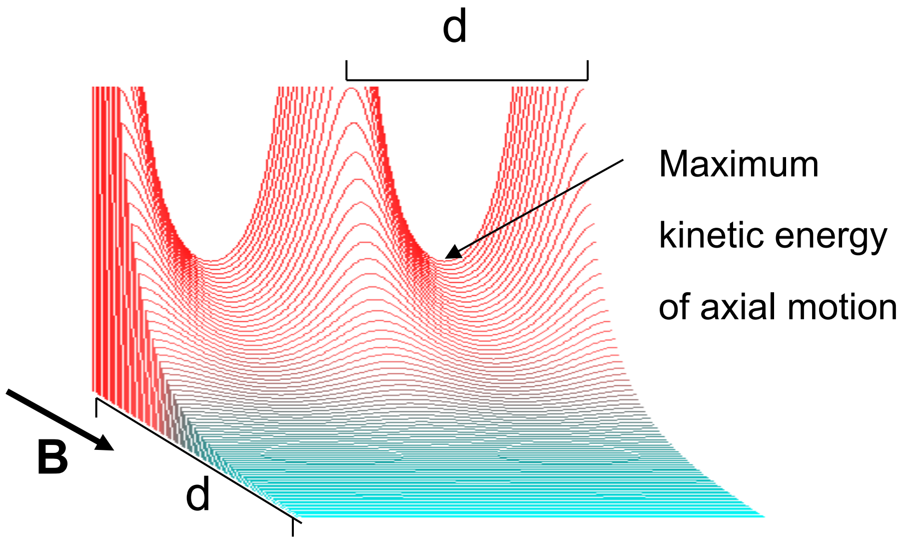
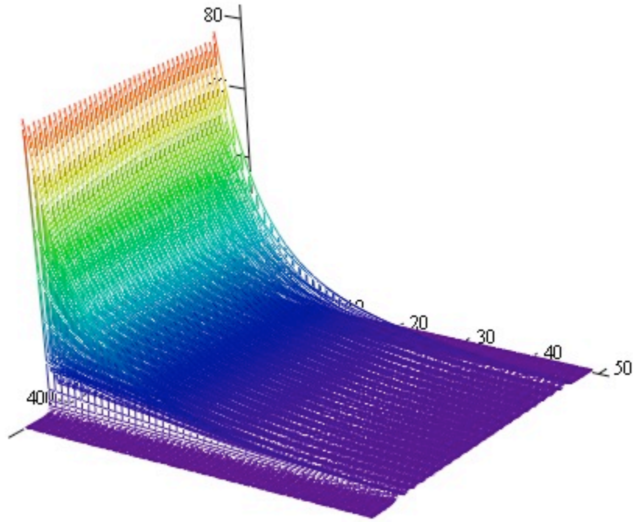


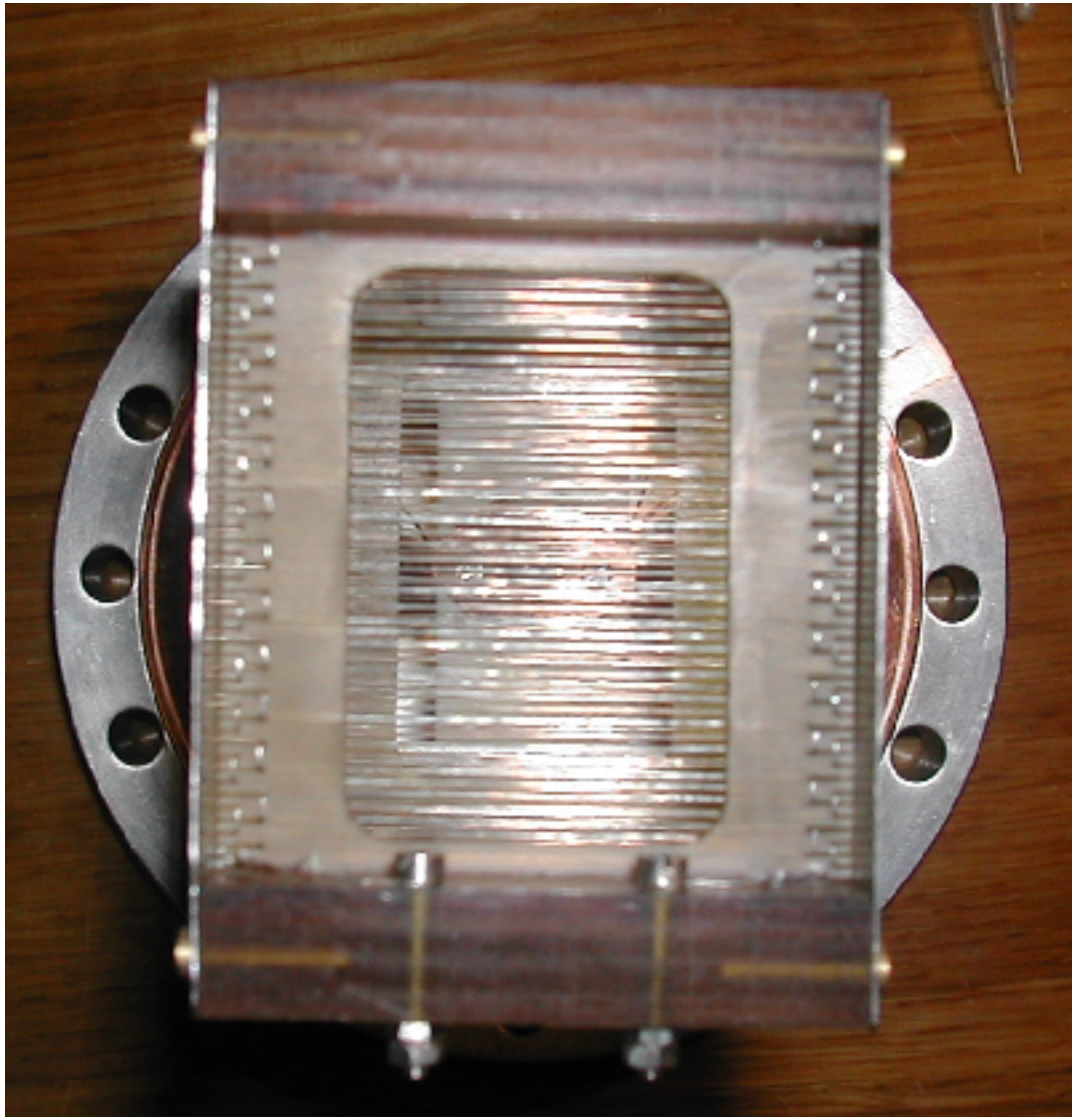
Figure 3. Radial electric field plots generated at 38% cell radius for both common 2.0 V trapping conditions and the TREC modulated conditions. A trapping potential well generated from the TREC conditions is overlaid to provide perspective.


+
+
RF
-
-
B
Trapping electrodes


d
Maximum
kinetic energy
of axial motion
B
d


80
20
30
40
50

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

(75) Inventor: **Evgenij Nikolaev**, Moscow (RU)

Correspondence Address:
KUDIRKA & JOBSE, LLP
ONE STATE STREET
SUITE 800
BOSTON, MA 02109 (US)

(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

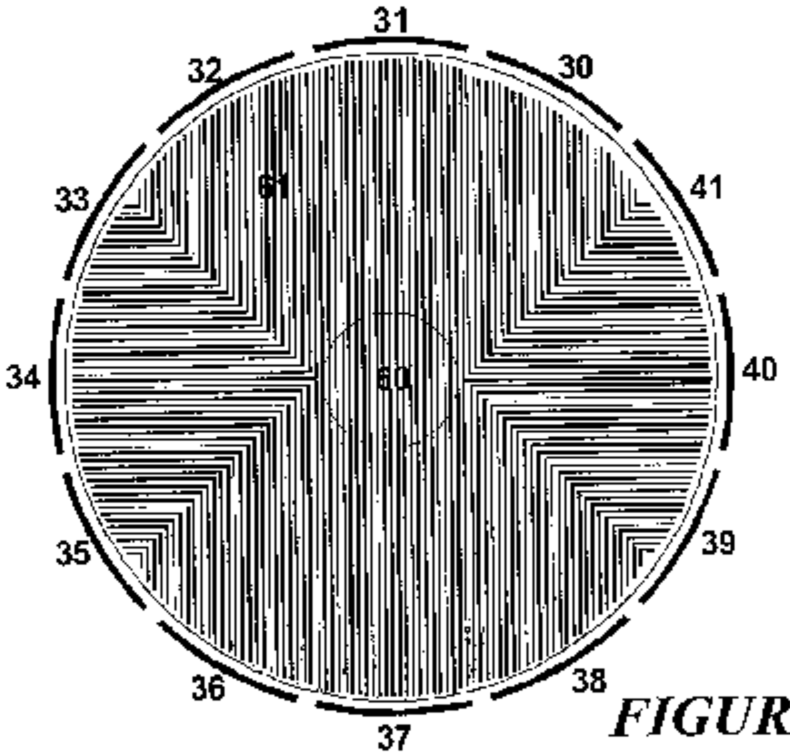
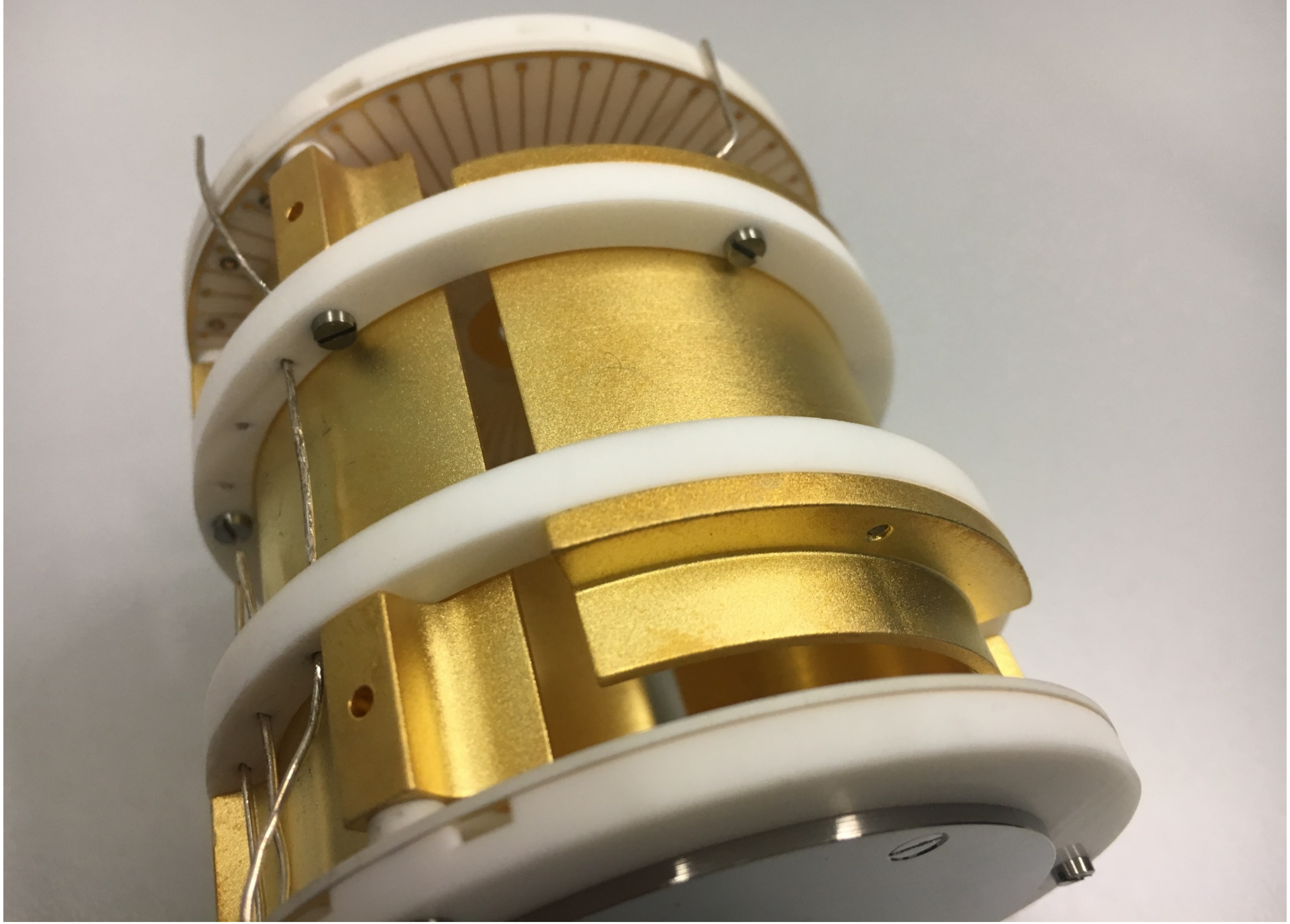
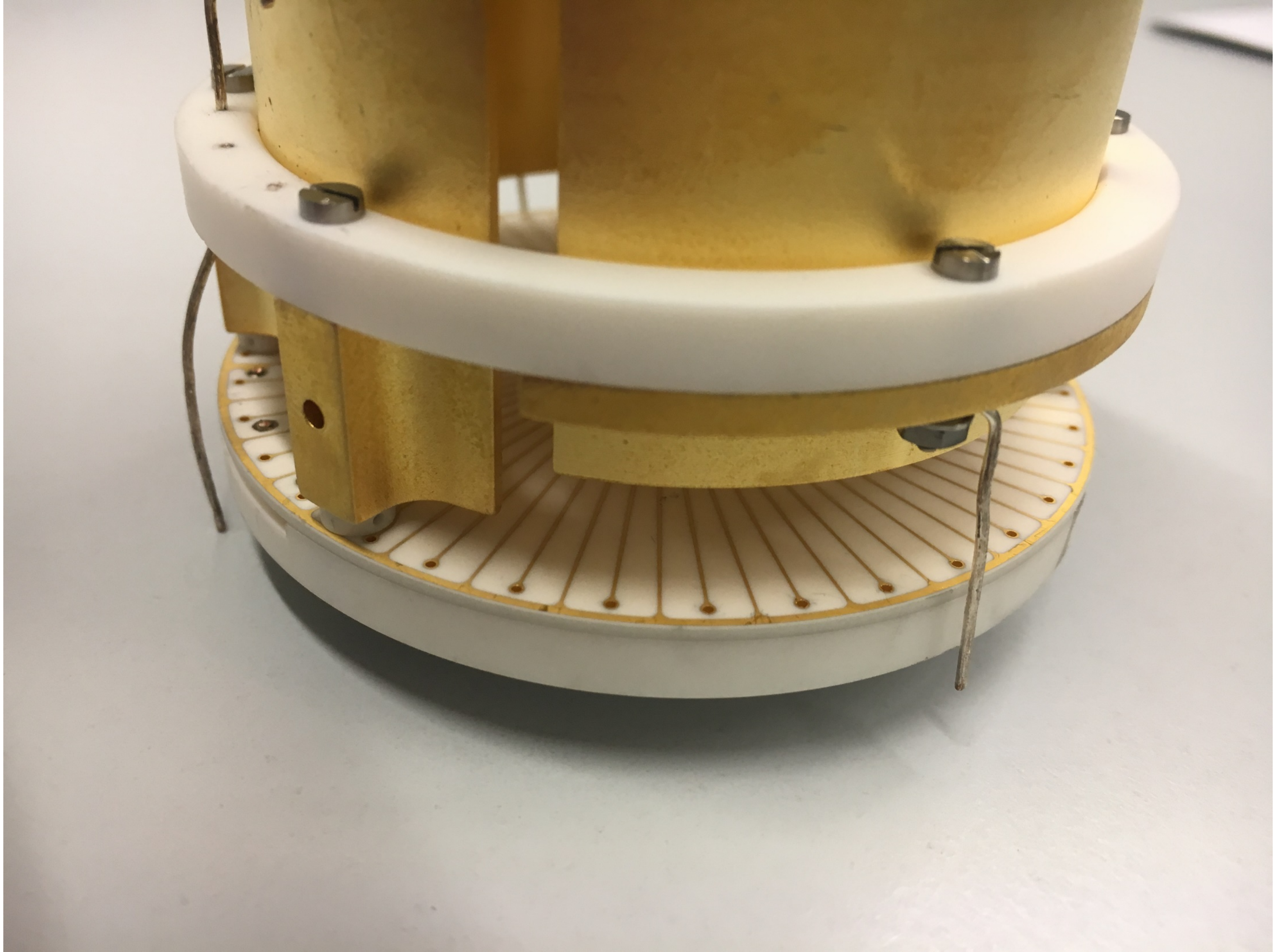
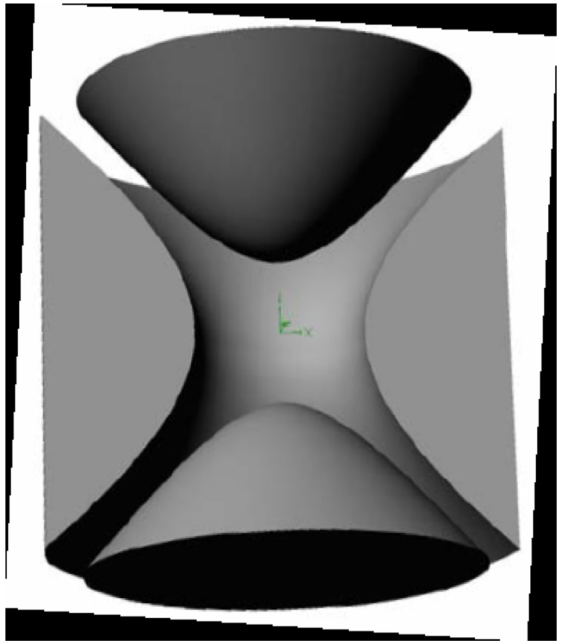


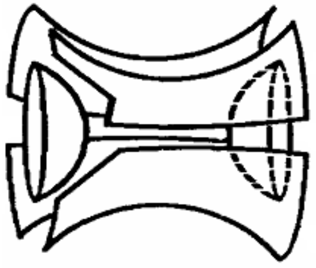
FIGURE 7

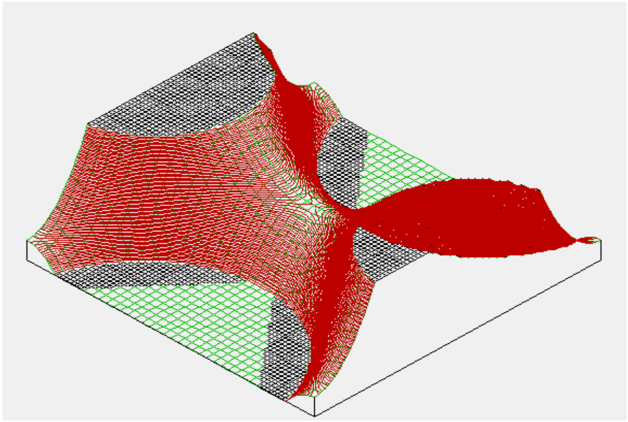


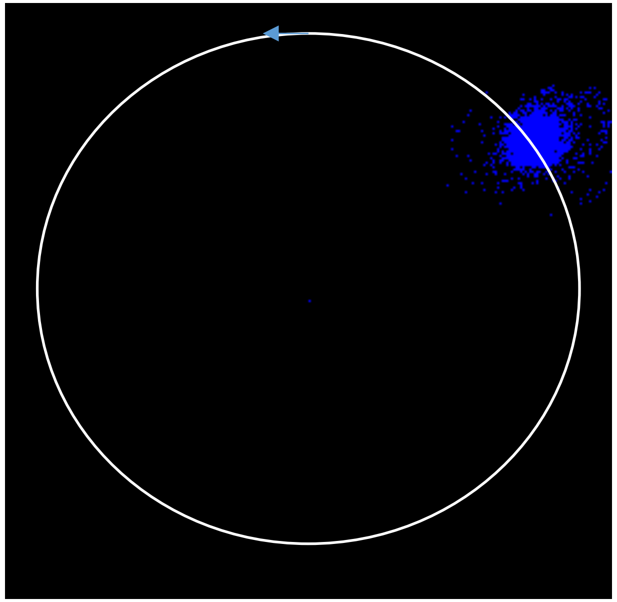


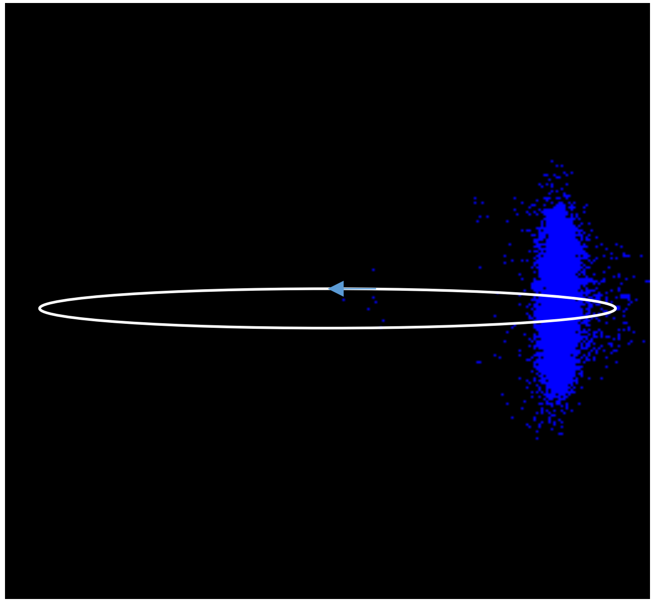
Hyperbolic cell

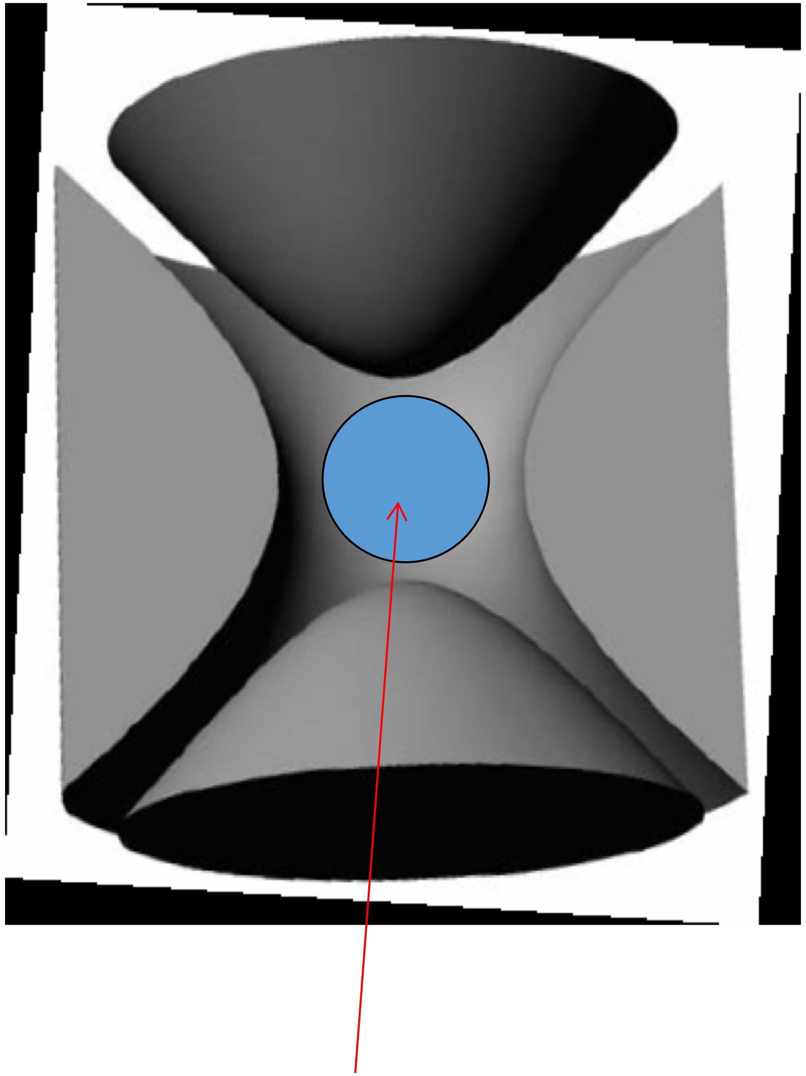




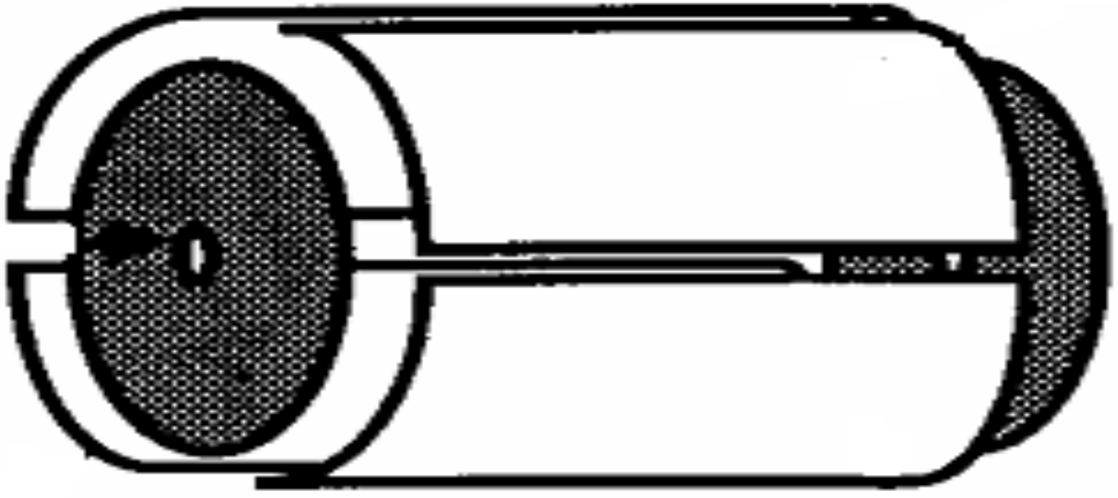


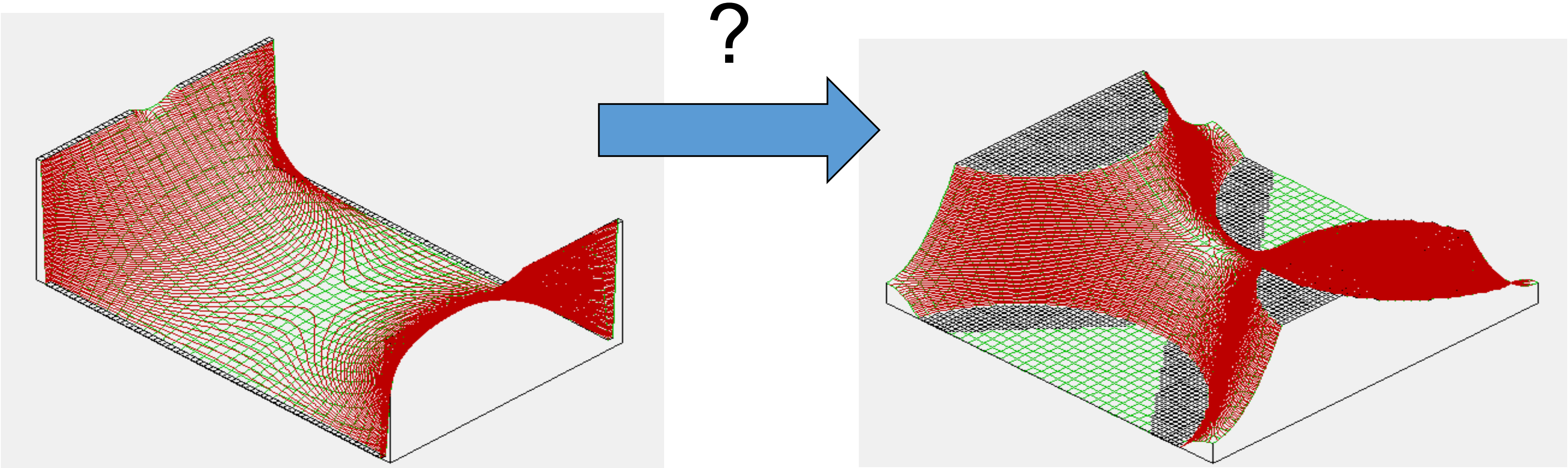




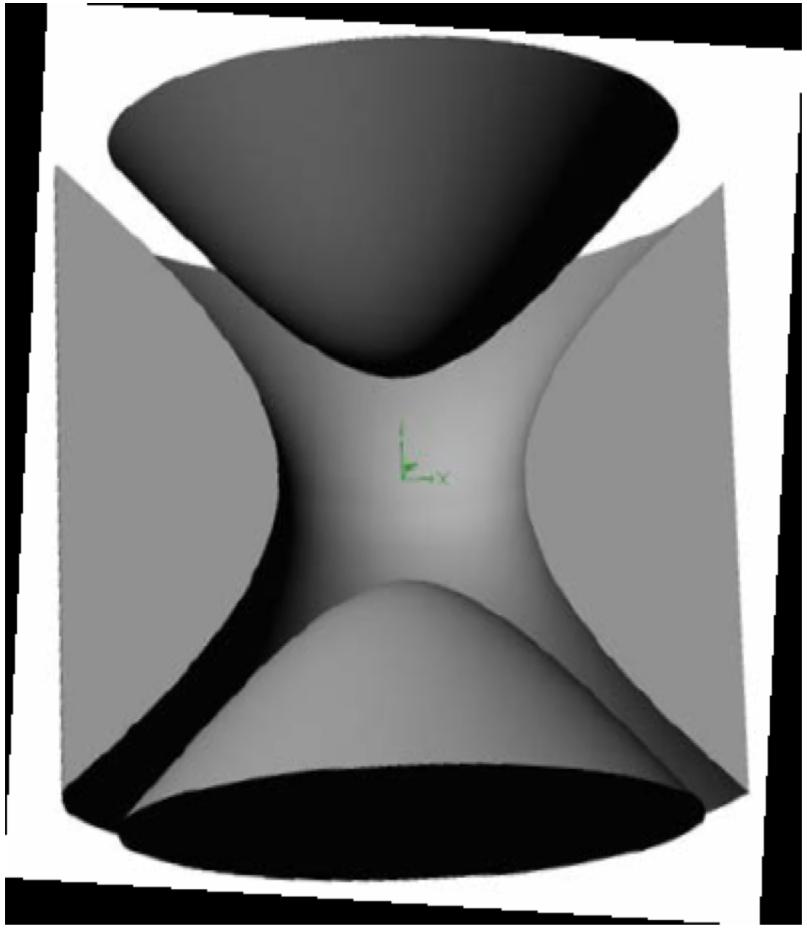


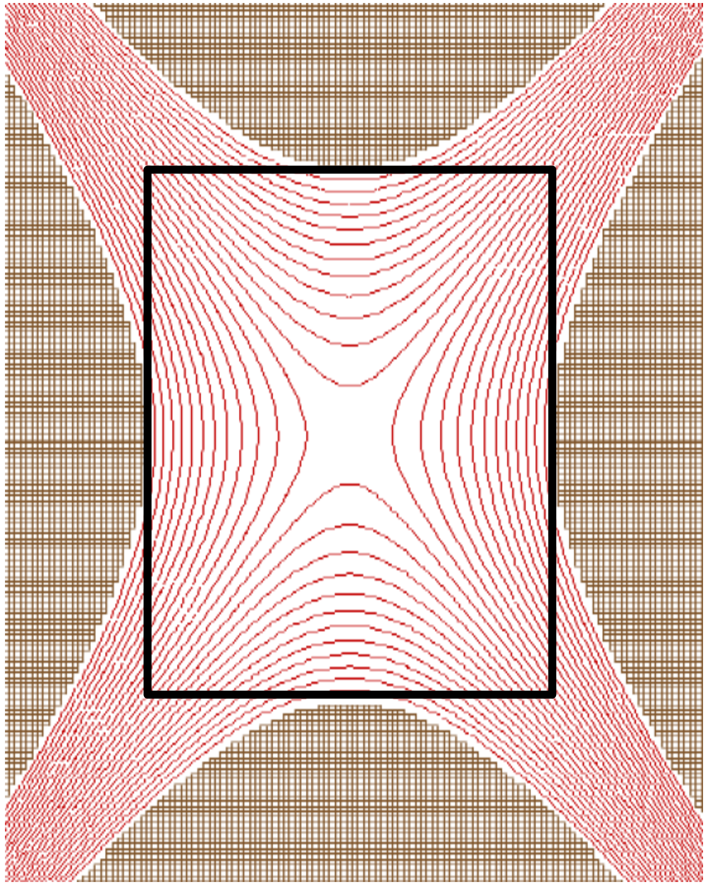
Used space



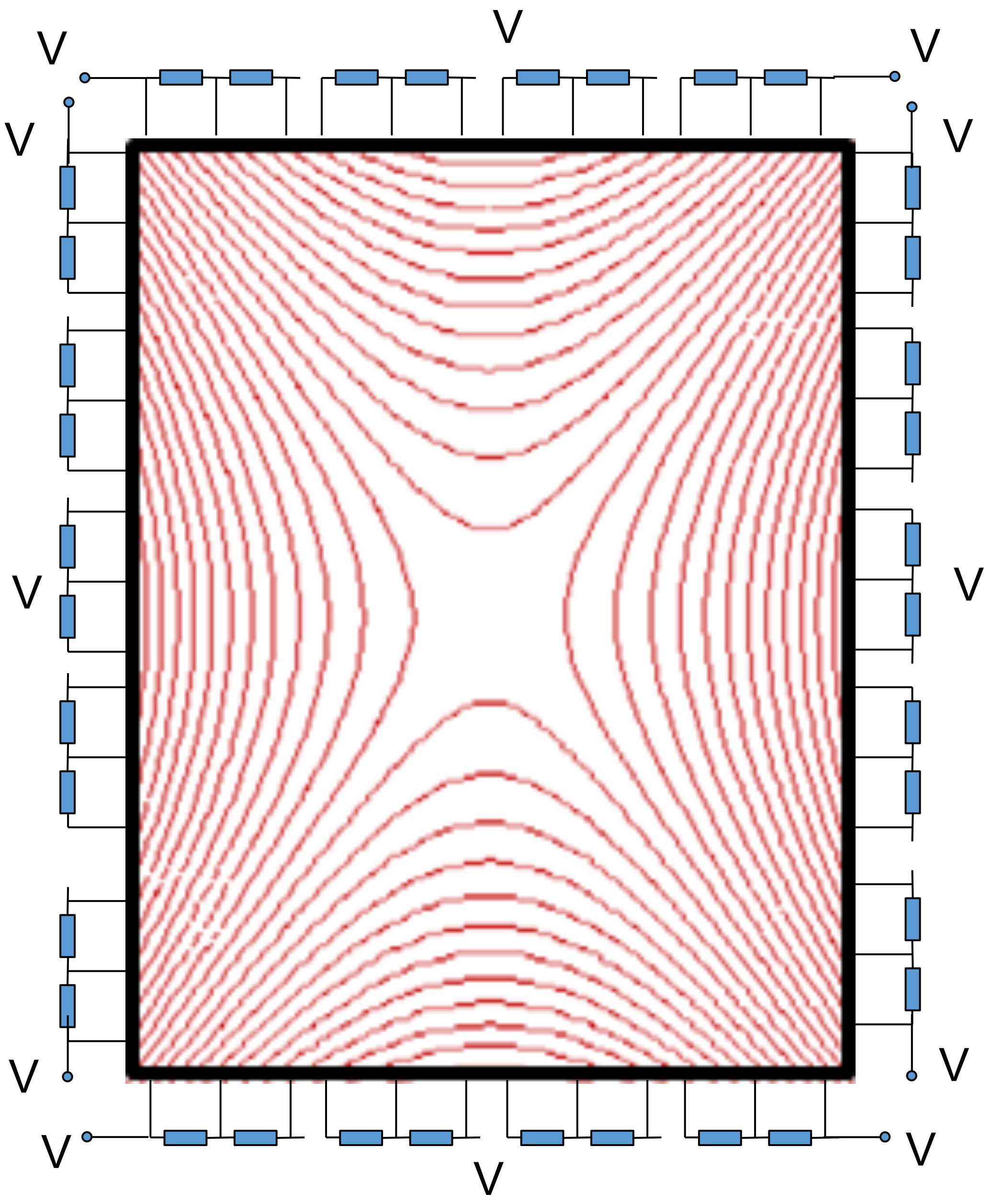


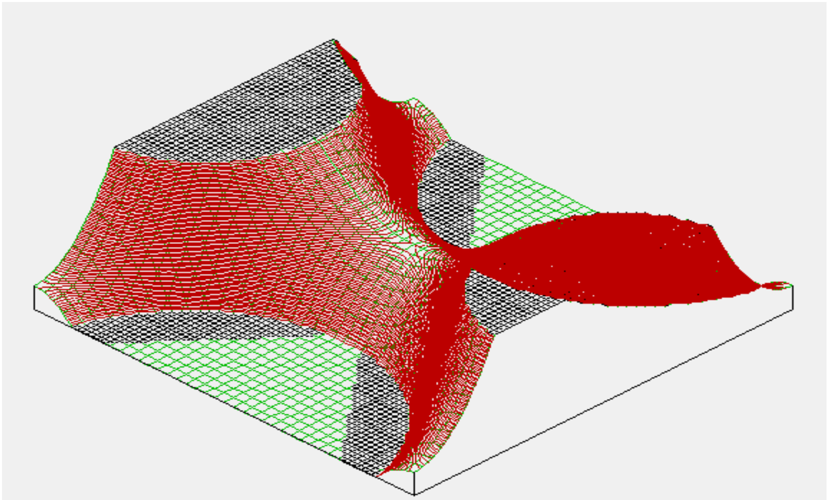
An instrument with a hyperbolic trap, however, suffers at least from inefficient use of the magnet bore and a relatively inaccessible trap interior.

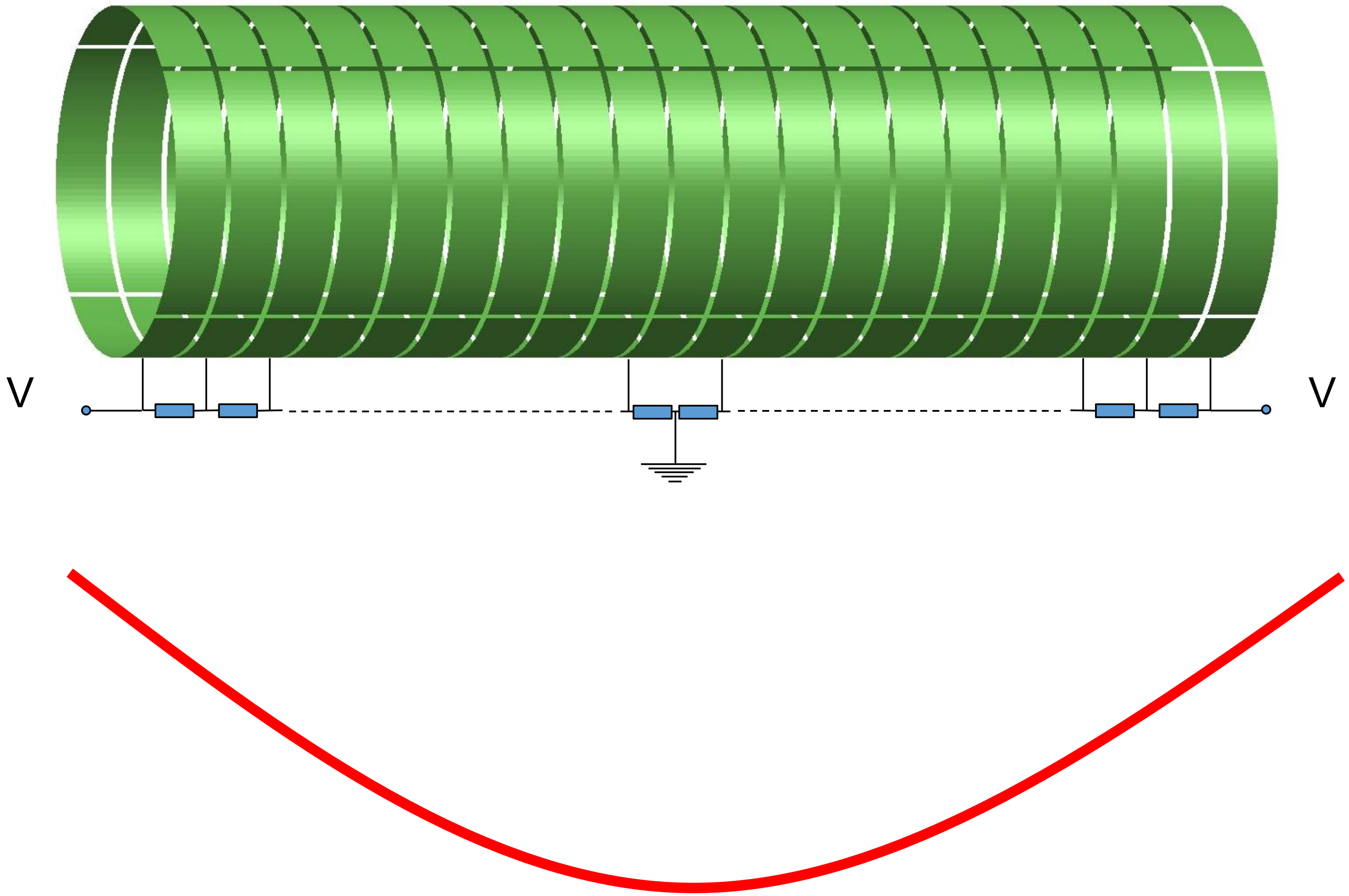




The quadrupolar potential well can also be approximated in a cylindrical or cubic trap by using simple electrode shapes and by optimizing the aspect ratio or by segmenting the electrodes
(Gerald Gabrielse)


V
V
V
V
V
V
V
V
V
V
V
V

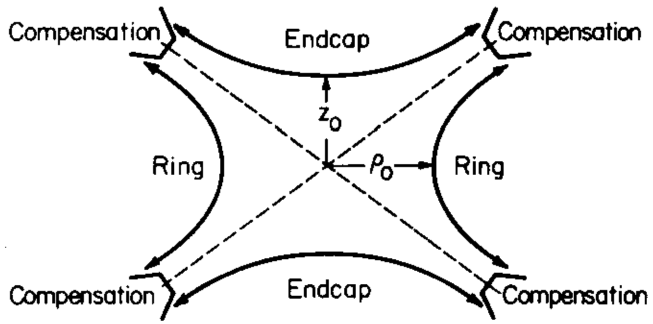



V
V

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

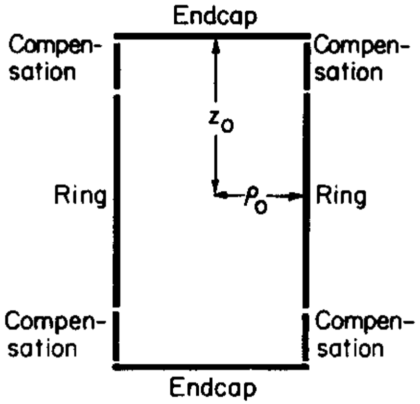
OPEN-ENDCAP PENNING TRAPS FOR HIGH PRECISION EXPERIMENTS

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



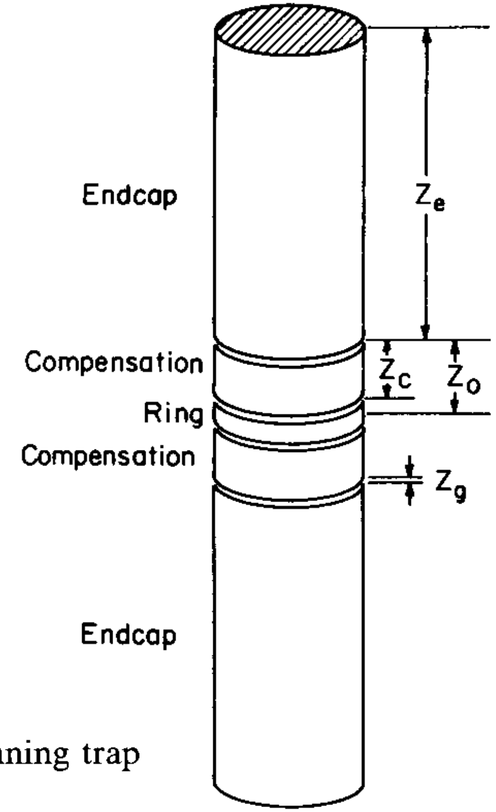
Hyperbolic Trap

(a)



Flat-endcap Cylindrical Trap

(b)



Open-endcap Penning trap

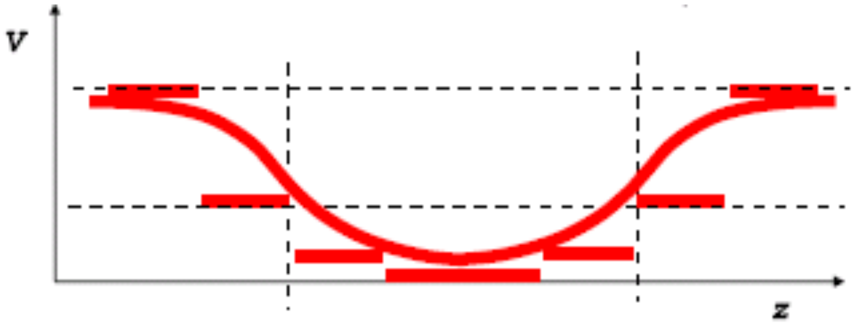
Cell potential harmonization (G.Gabrielse 1989)

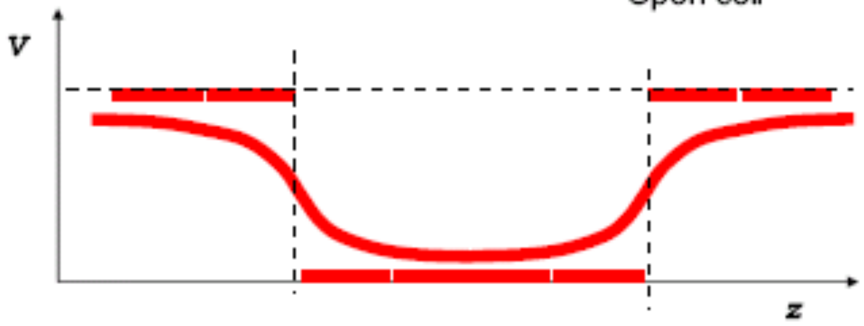
Tolmachev, A. V.; Robinson, E. W.; Wu, S.; Kang, H.; Lourette, N. M.; Pasa-Tolic, L.; Smith, R. D. Trapped-Ion Cell with Improved DC Potential Harmonicity for FT-ICR MS

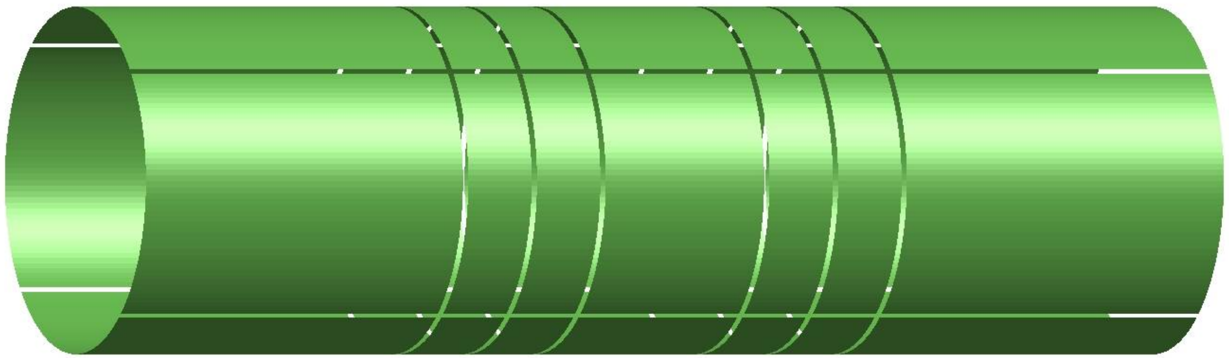
Brustkern A.M., Rempel D.L., Gross M.L. An Electrically Compensated Trap Designed to Eighth Order for FT-ICR Mass Spectrometry. J Am Soc Mass Spectrom 2008, 19, 1281–1285

Marshall’s group,

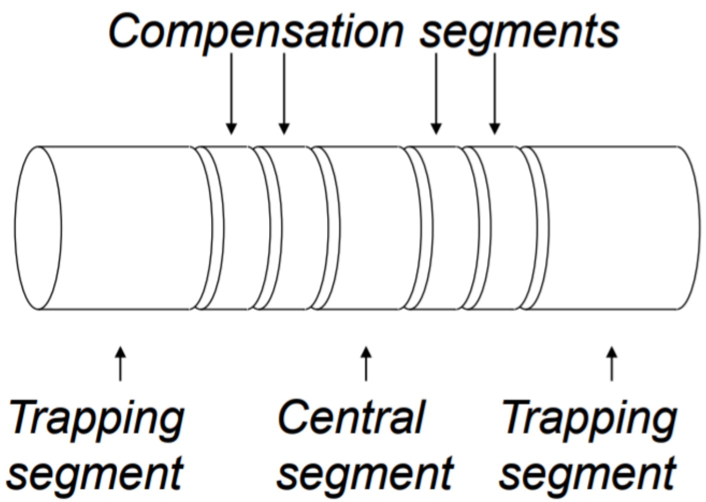
Bruker……..

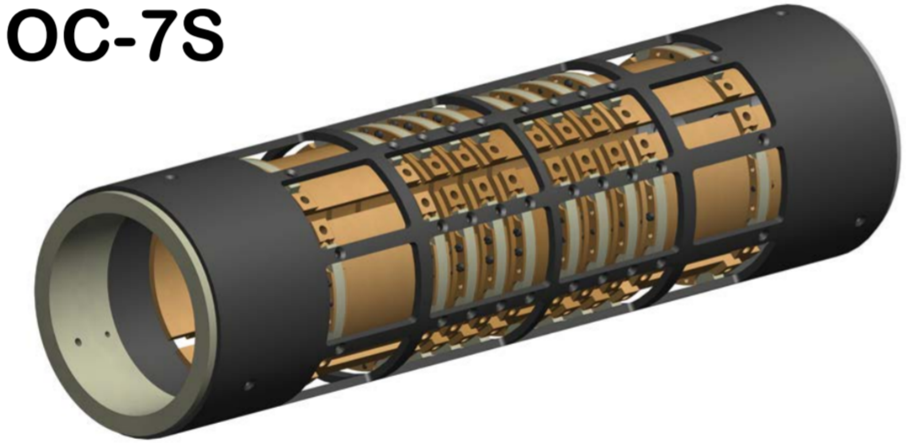




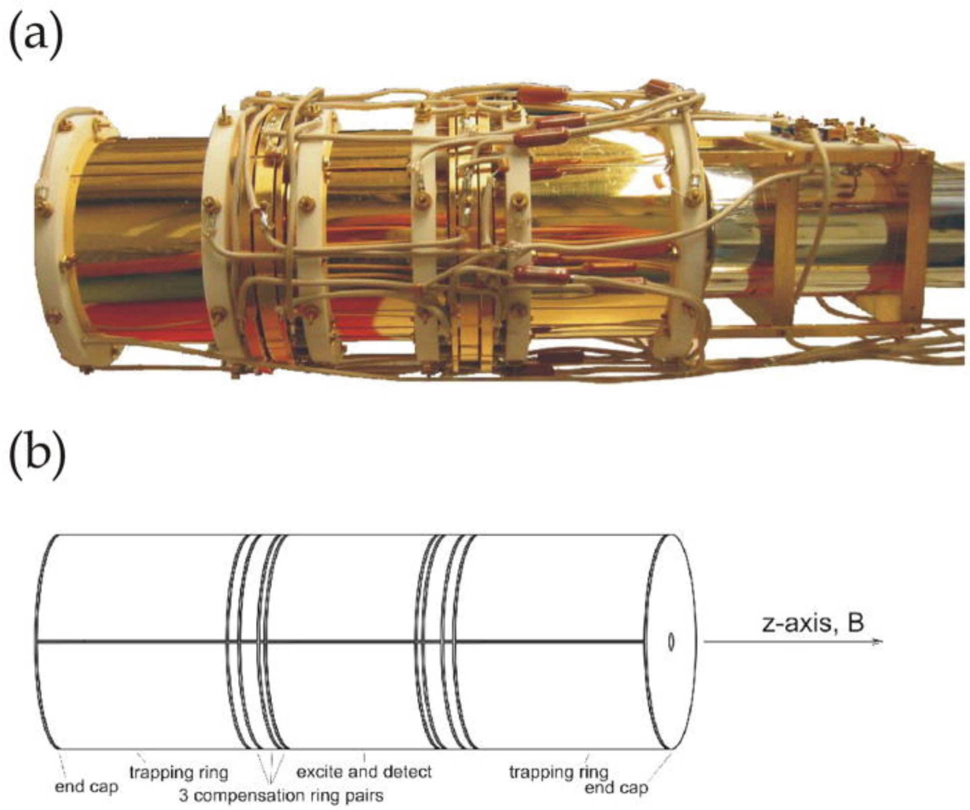


OC-7S compensation configuration

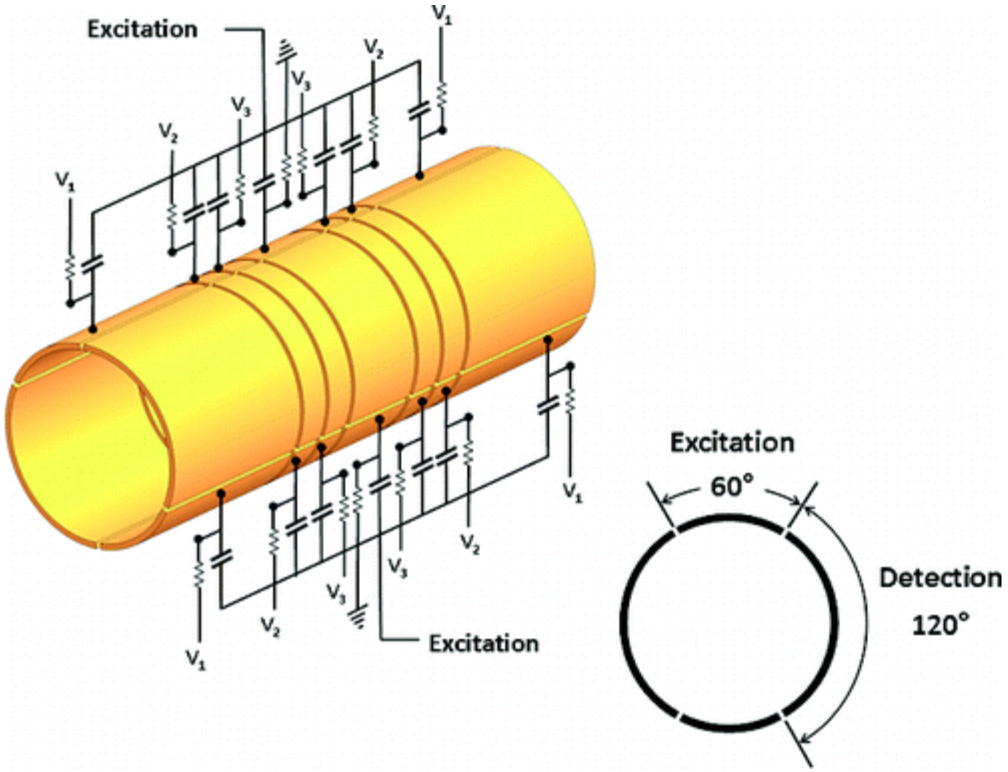




PNNL cell

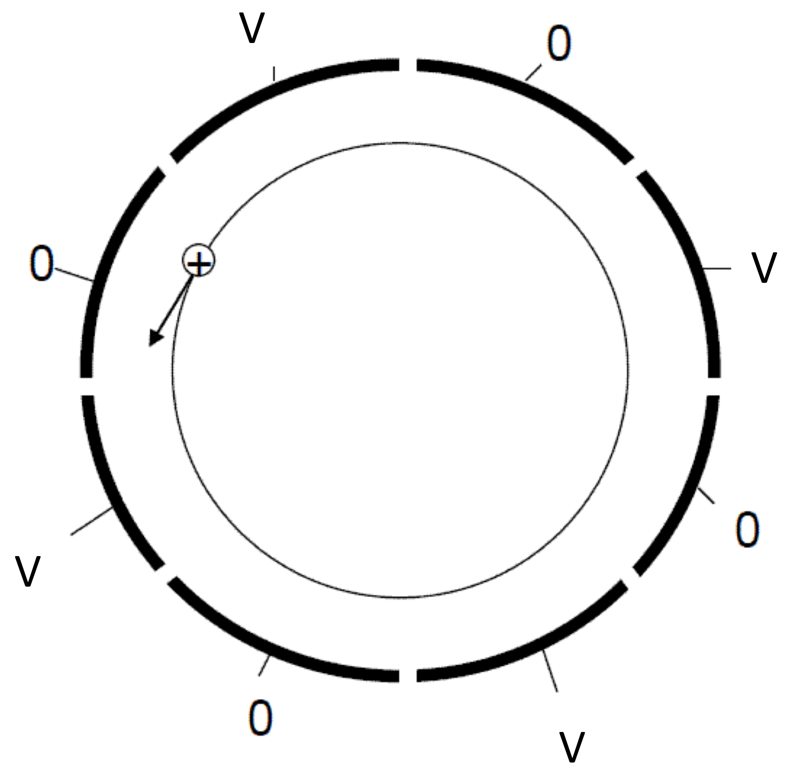


Gross group

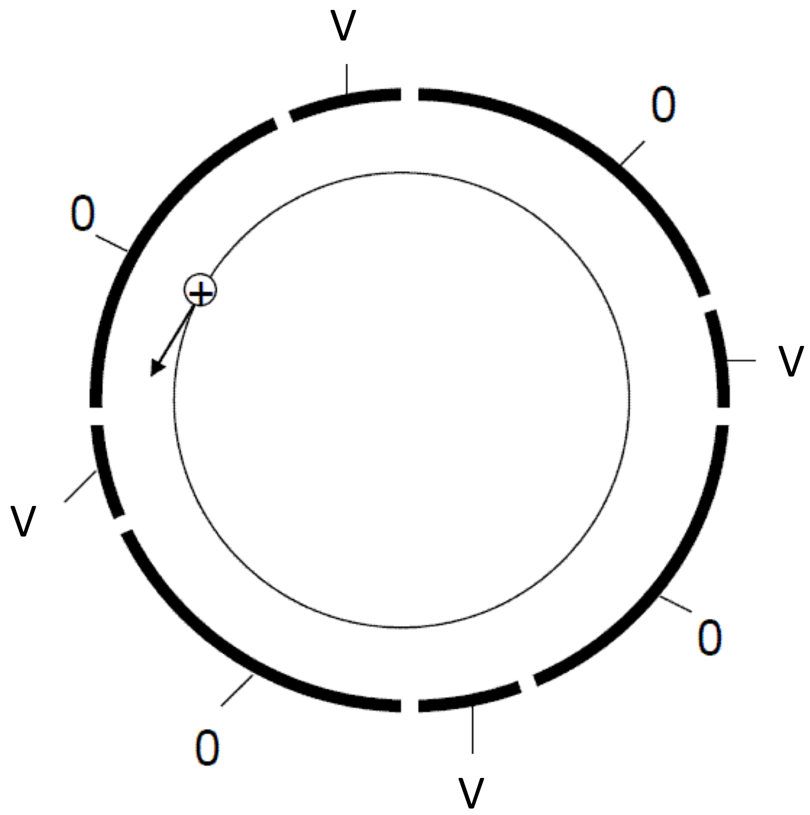


Marshall group

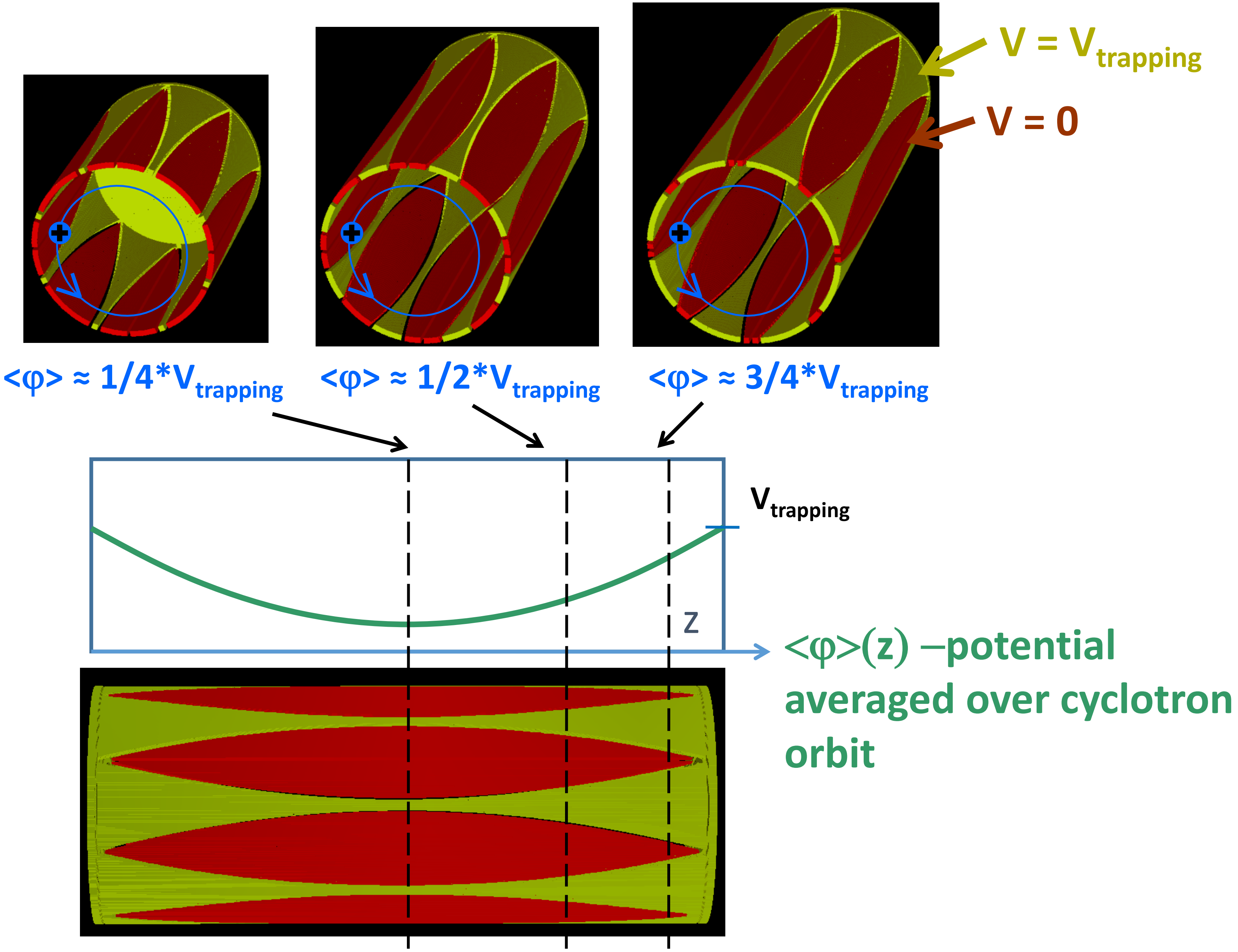
Averaging over cyclotron motion



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



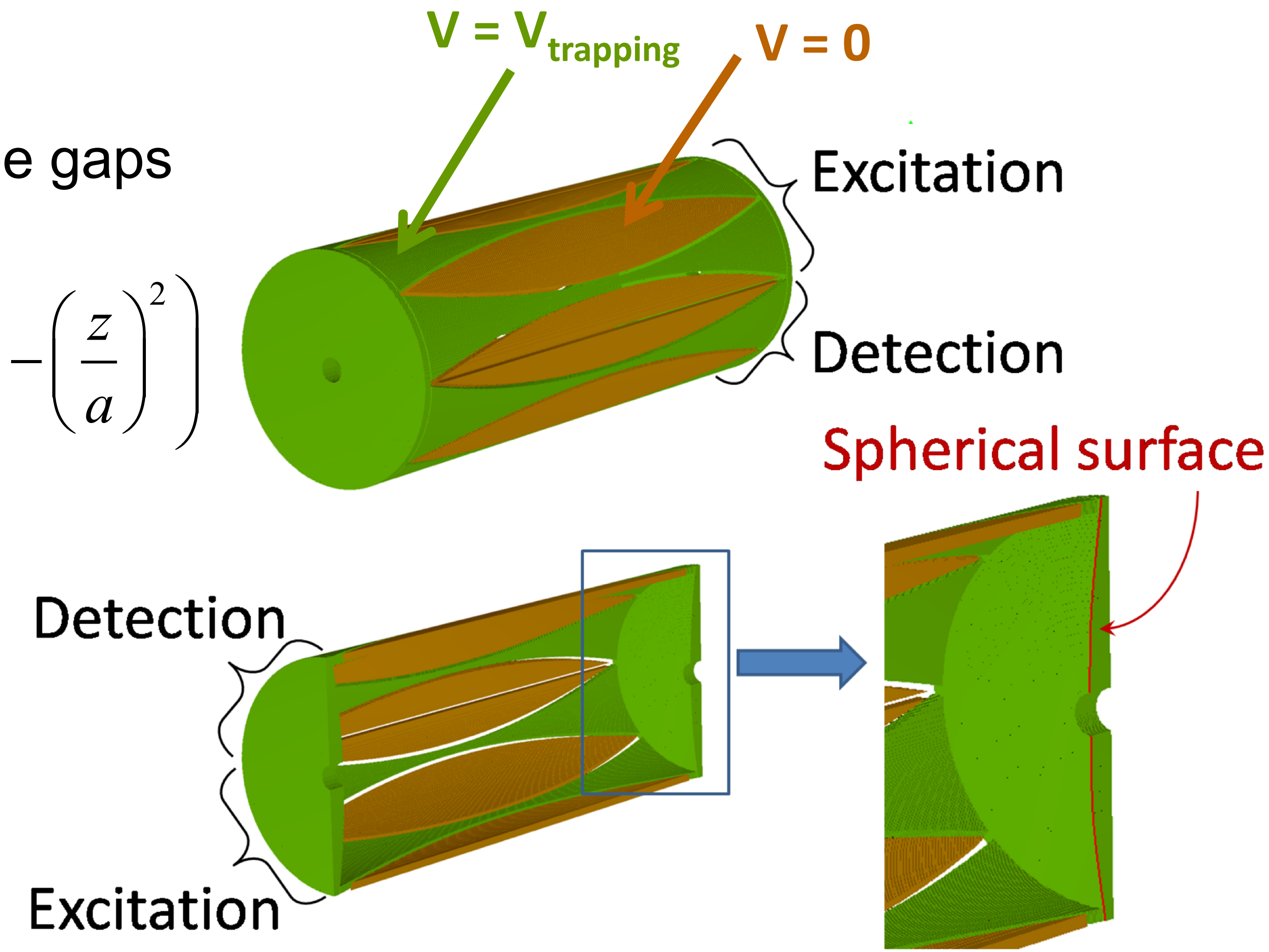
$$\langle \varphi \rangle = \frac{1}{4} V$$


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

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



How long it should be?

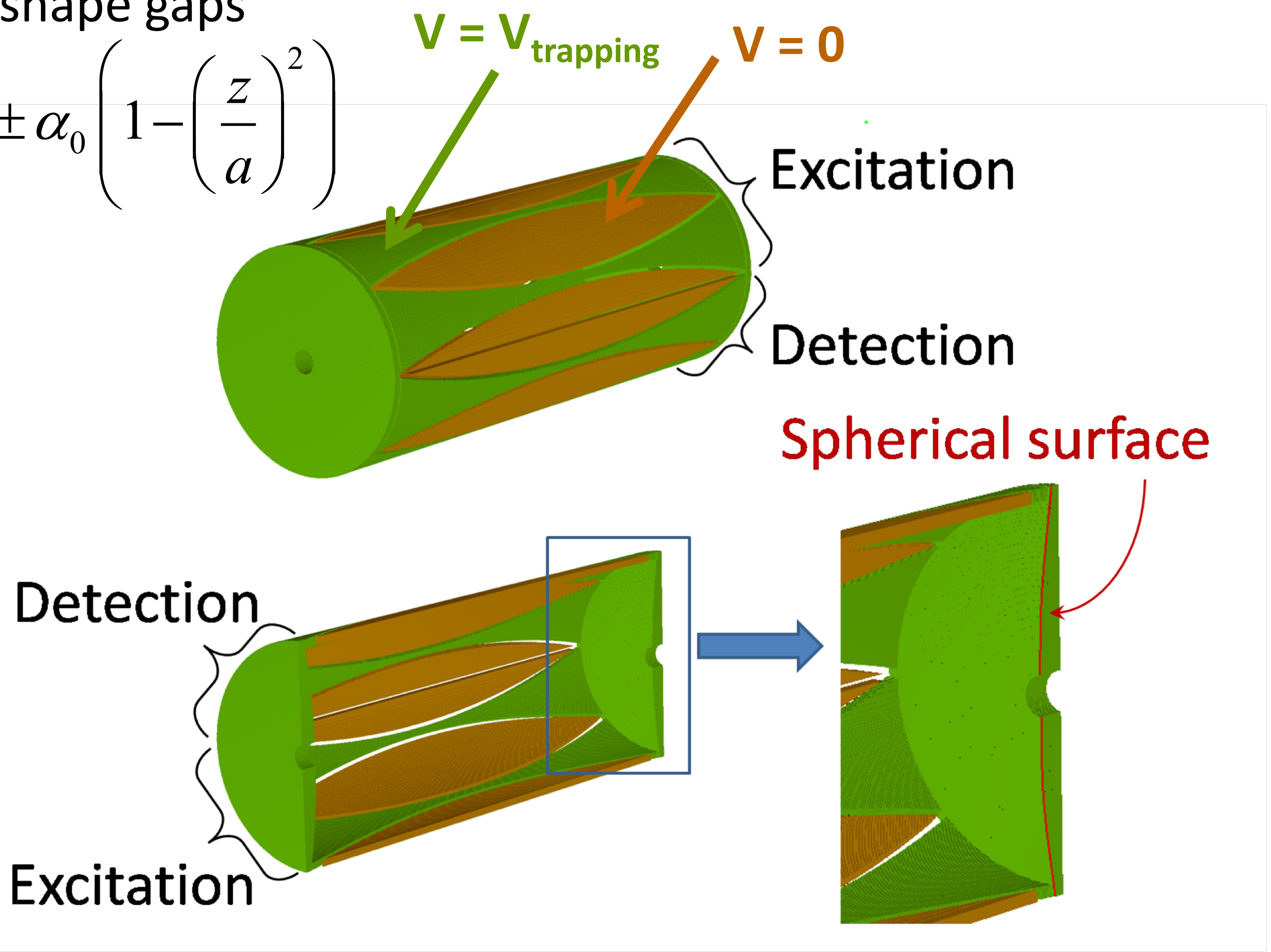
1. Homogeneous excitation

2. Simplicity of the trapping electrodes

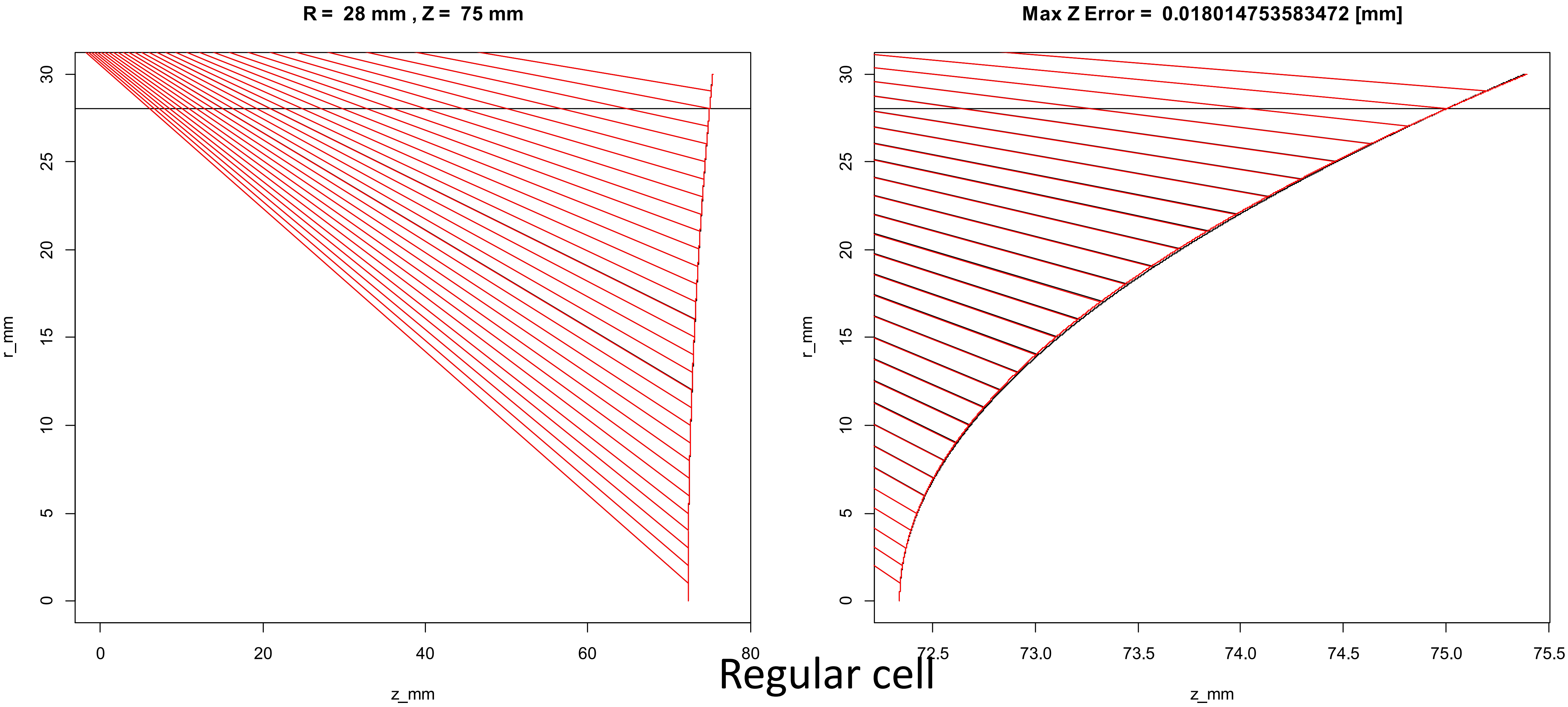
Cell design

Parabolic shape gaps

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

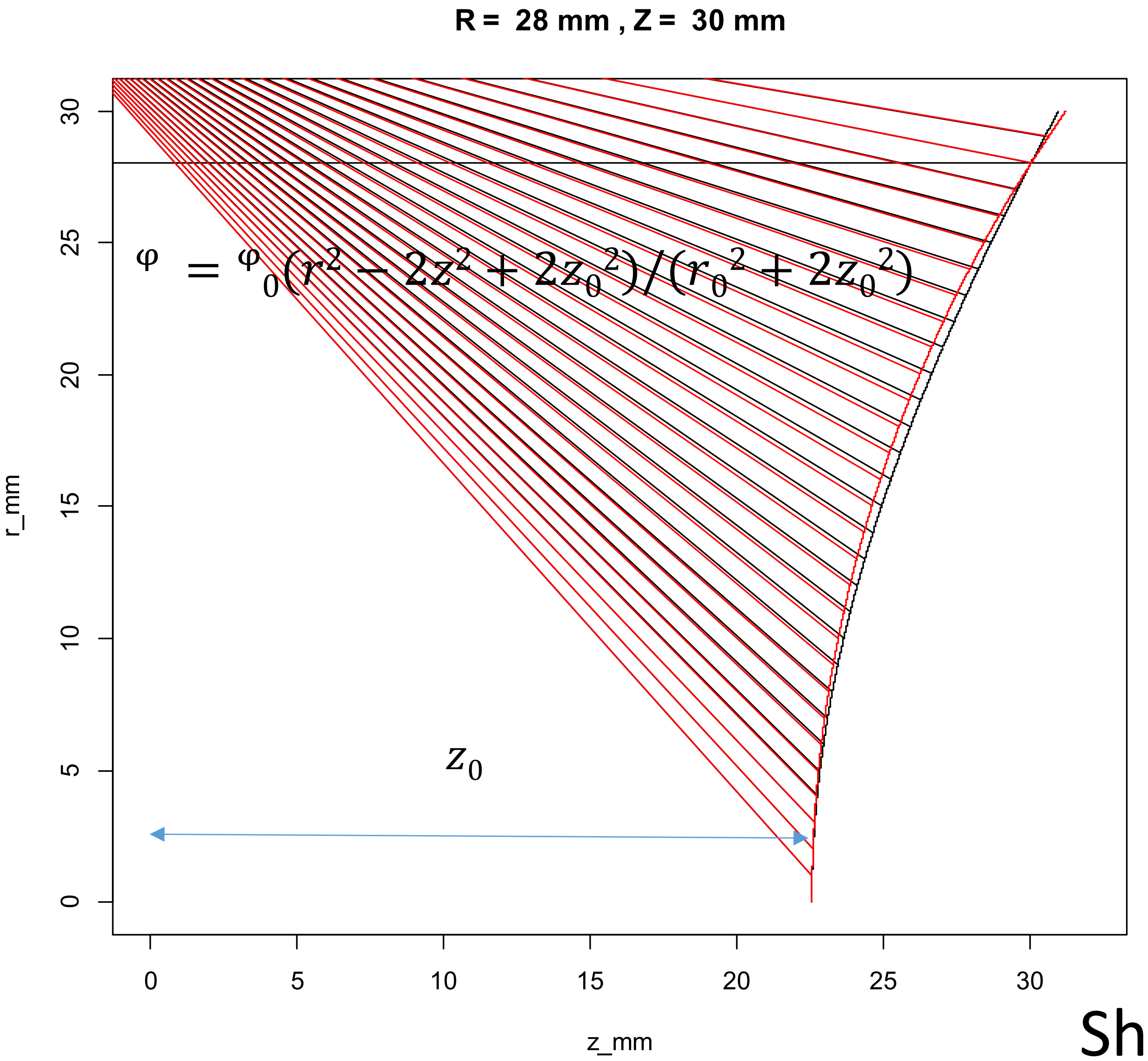


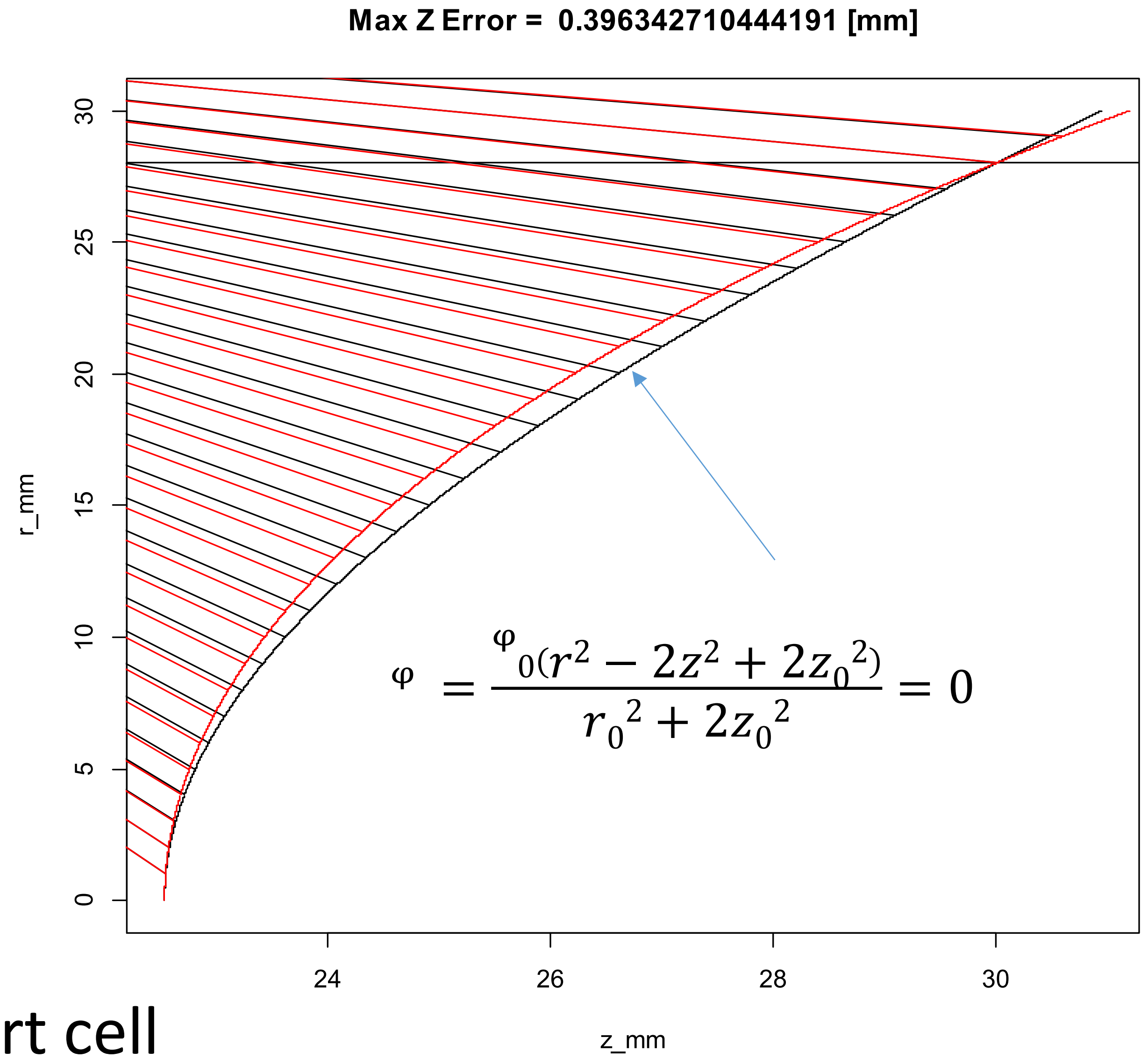
Black curve - hyperboloid
Rad curve - sphere



Regular cell

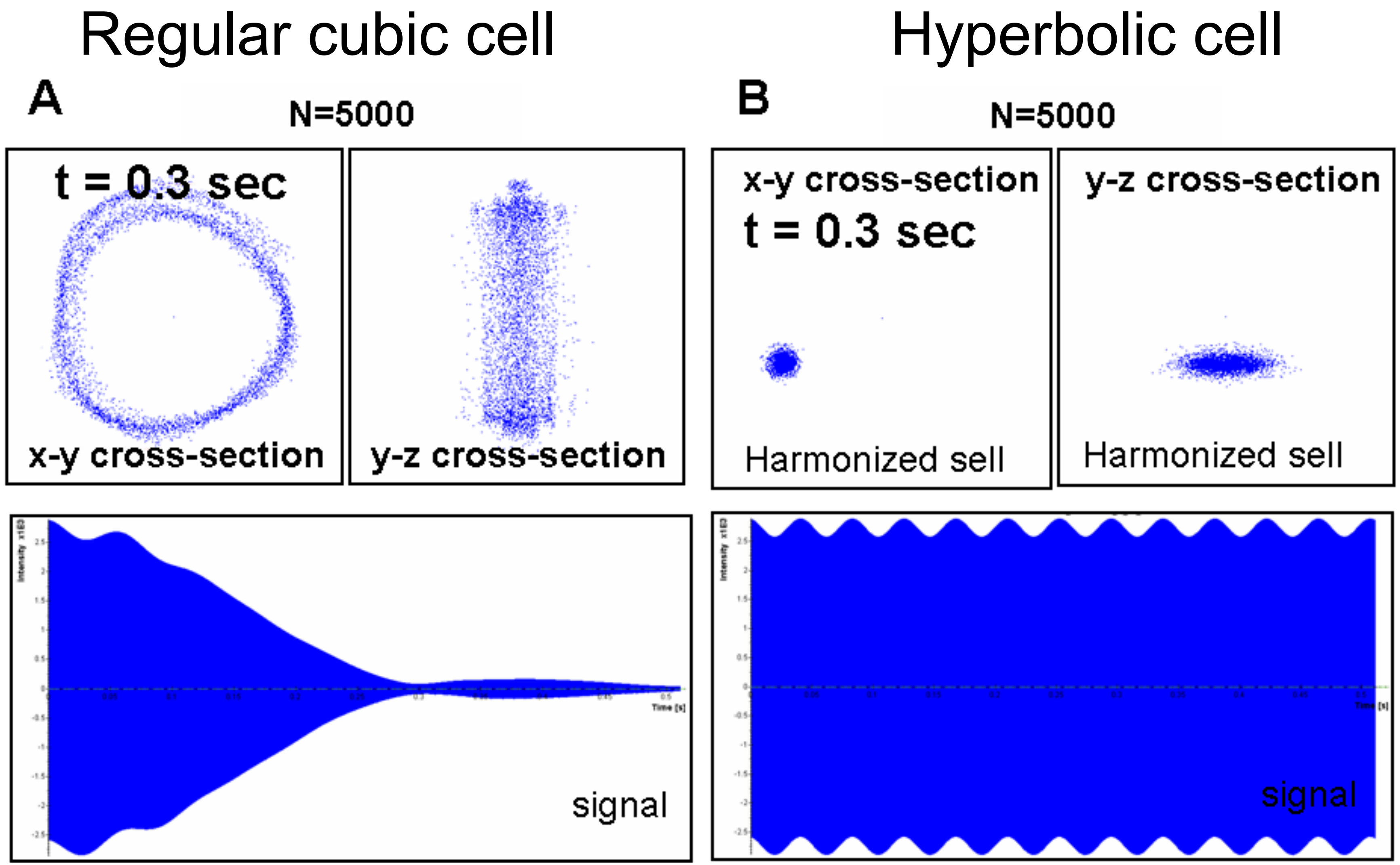
Black curve - hyperboloid
Rad curve - sphere



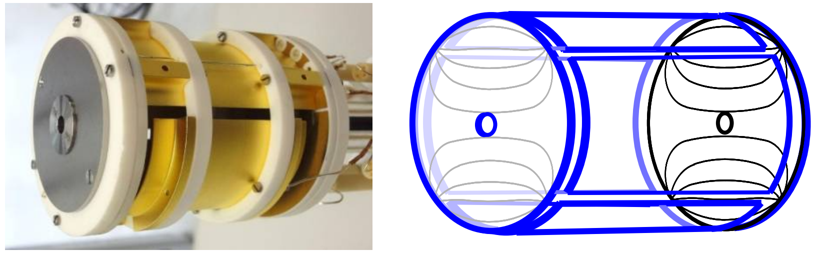


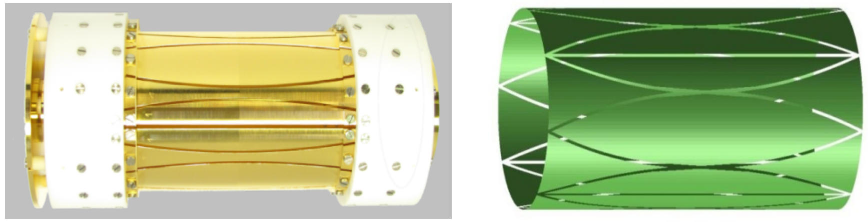
Short cell

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



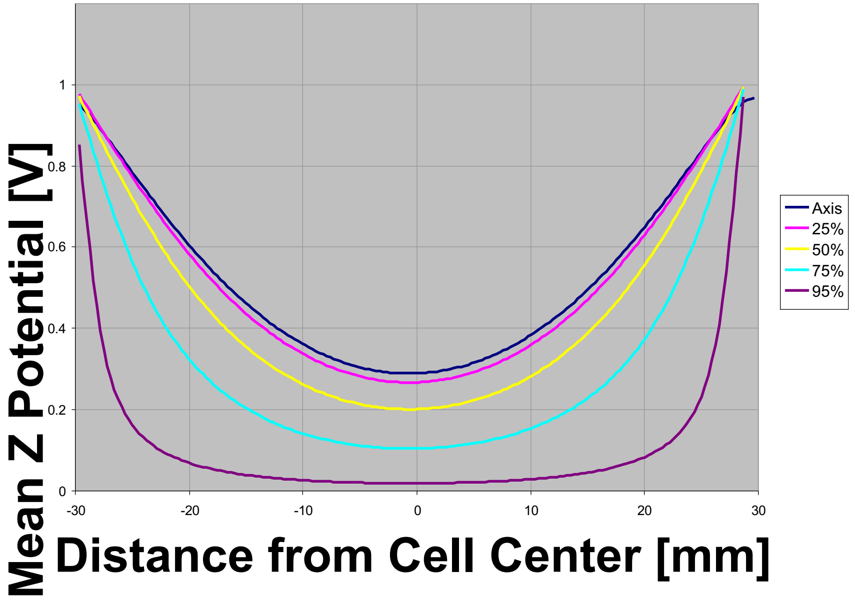
Comparison of averaged axial potential



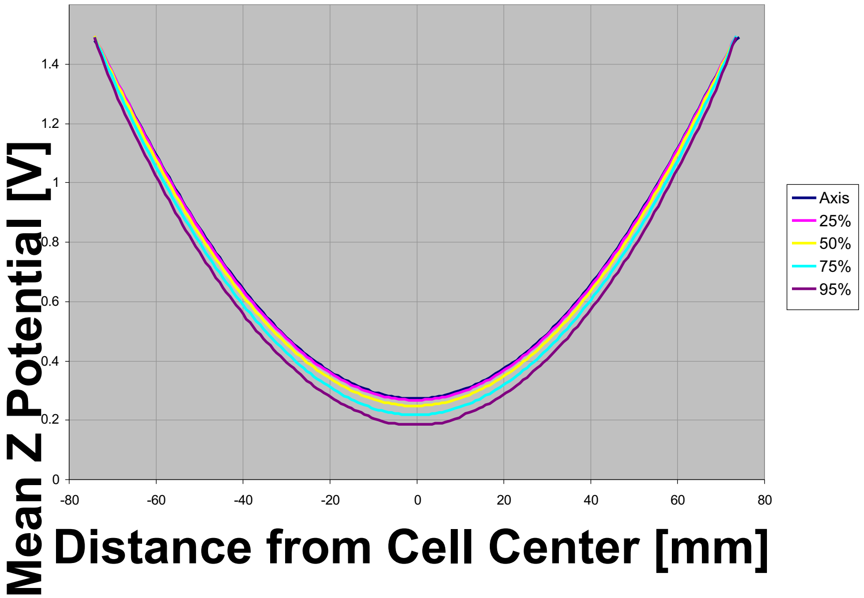


Infinity Cell

Dynamically Harmonized Cell



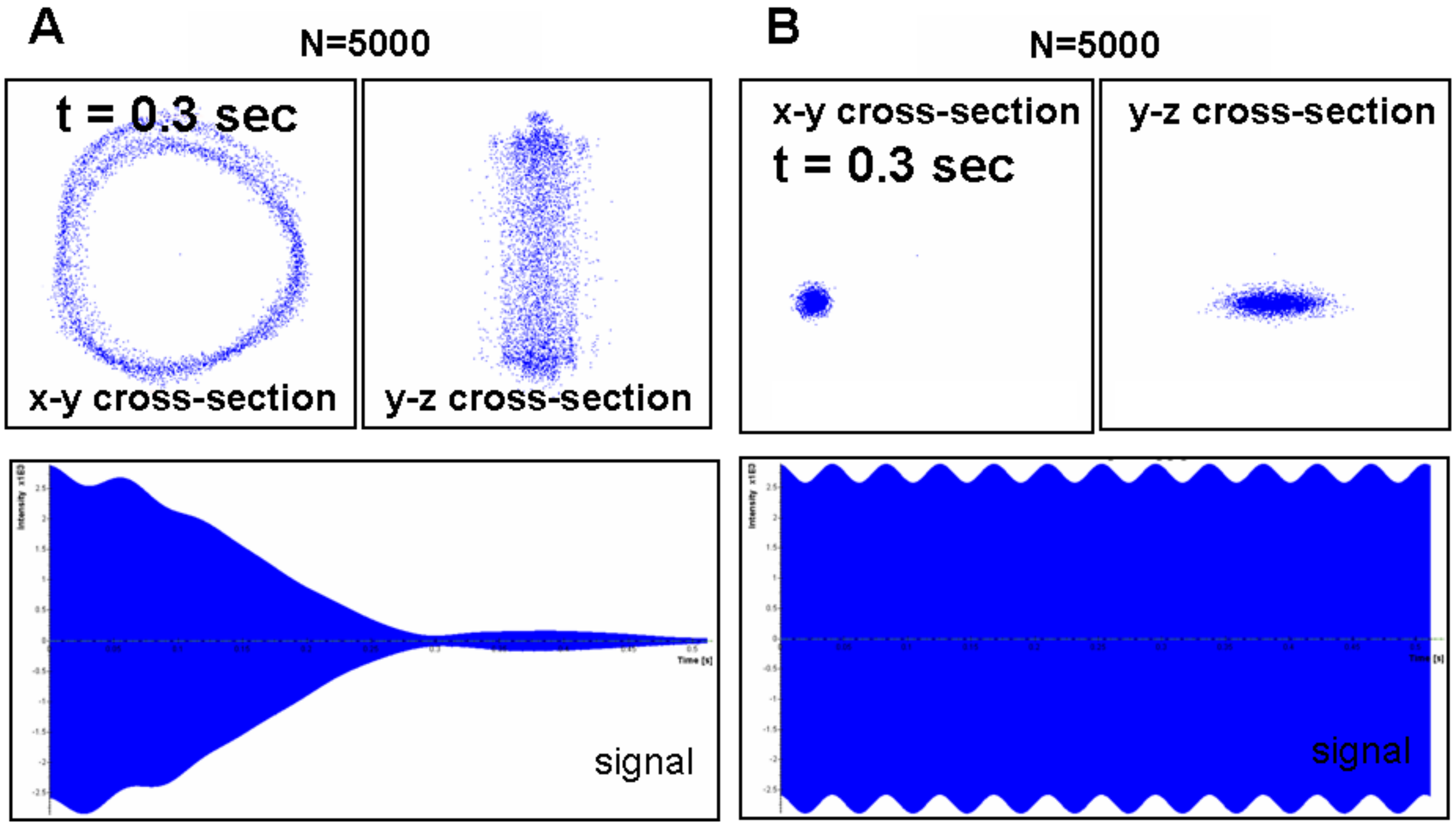
Near parabolic potential up to a cyclotron orbit of 50% of the cell radius.



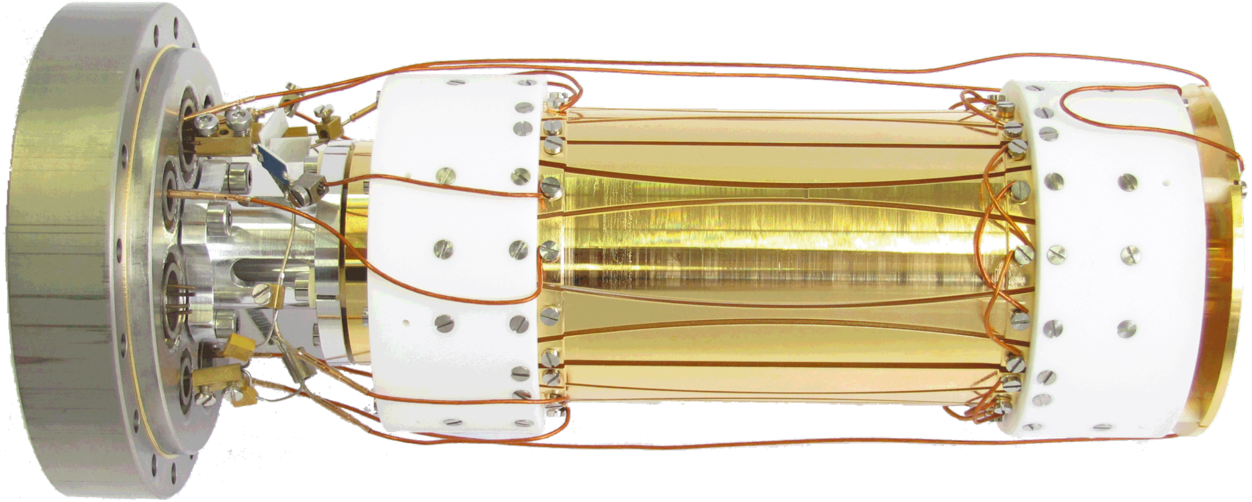
Harmonic, parabolic potential at all cyclotron orbits.

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

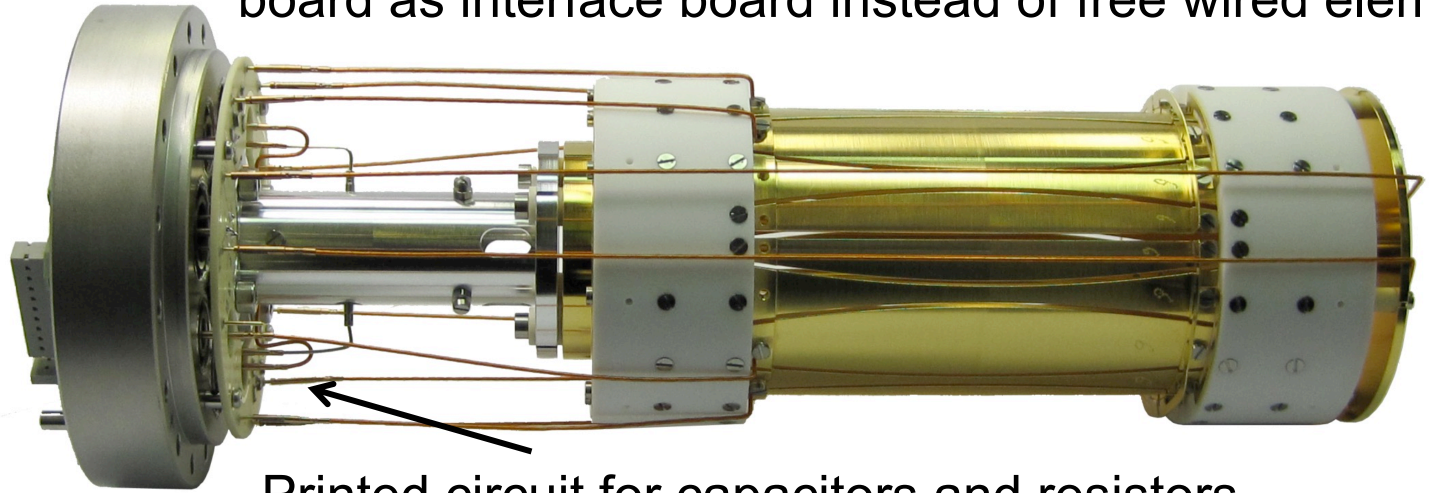
Regular cubic cell Dynamically harmonized cell



Investigation prototype:
Gold plated copper, macor insulator.
Electronic interface resistors and capacitors free wired.



Lab prototype:
Like the investigation prototype. Printed circuit ceramic board as interface board instead of free wired elements.

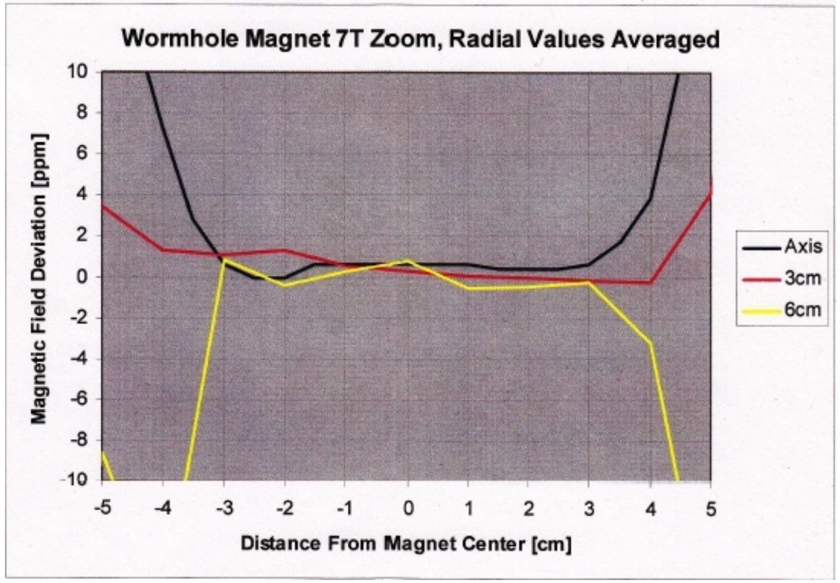


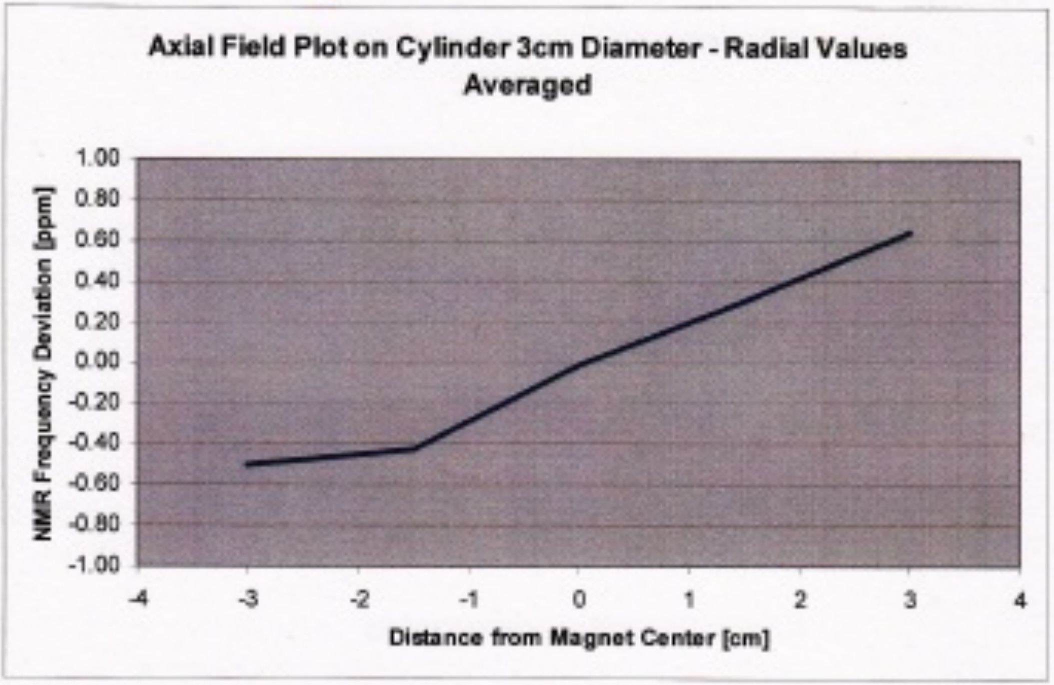
Printed circuit for capacitors and resistors

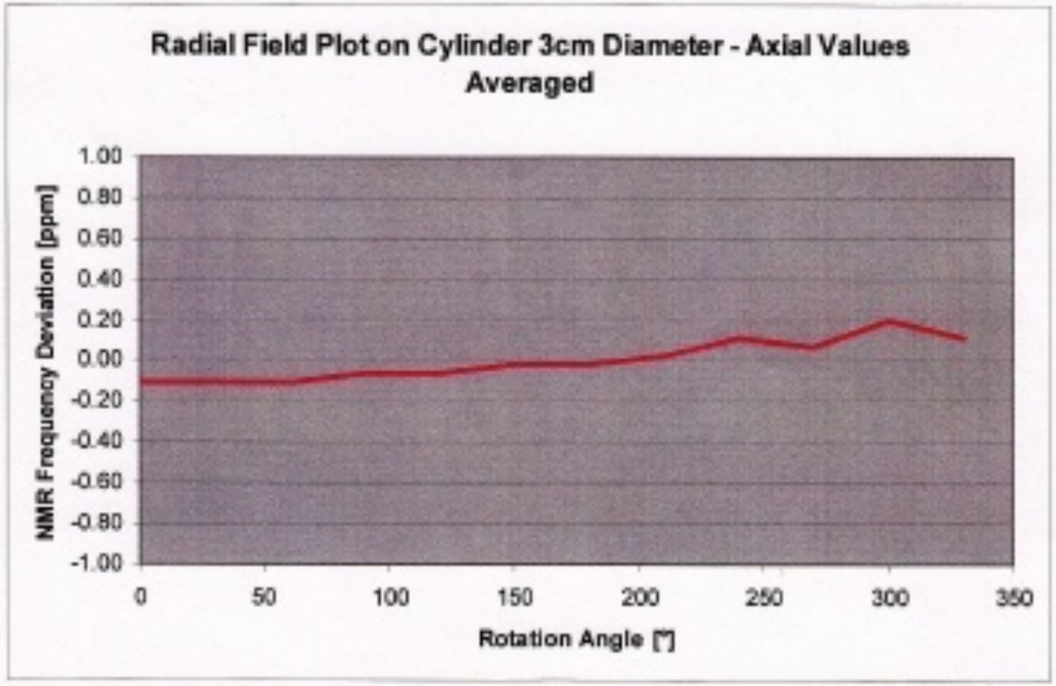
Directions of further improvements

Making cell robust and not sensitive to magnetic field inhomogeneity

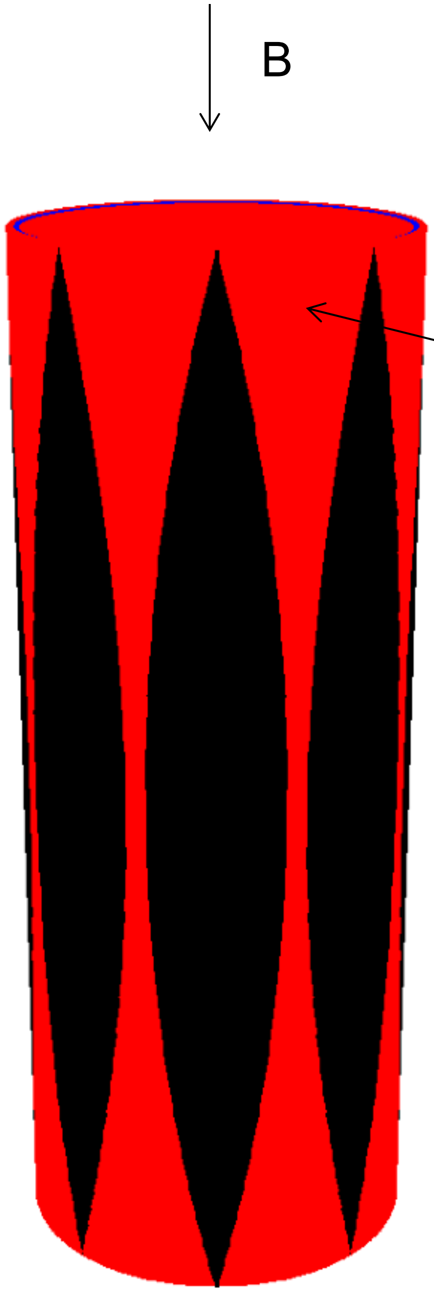
Inhomogeneity of magnetic field?

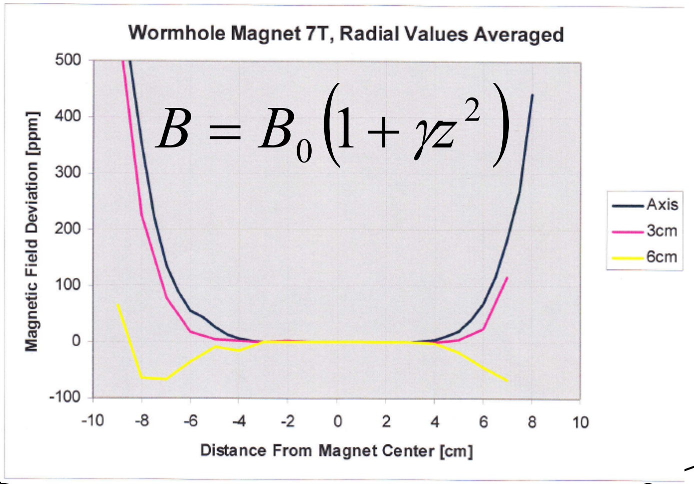






Frequency shift should not be more than 10^{-2} Hz for 100 kHz cyclotron frequency





$$B = B_0\left(1+\gamma z^2\right)$$

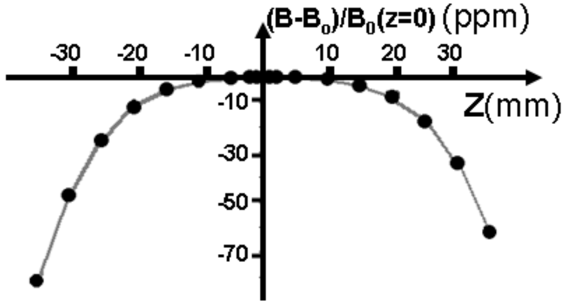
$$U = U_0 + \alpha\left(r^2 - 2z^2\right) + \beta\left(35z^4 - 30z^2r^2 + 3r^4\right)$$

Condition of cyclotron frequency independence on z-oscillation amplitude

$$0 = B_0\gamma 2z\omega + \left(\frac{2\alpha r + \beta\left(-60z^2r + 12r^3\right)}{r}\right)'_z$$

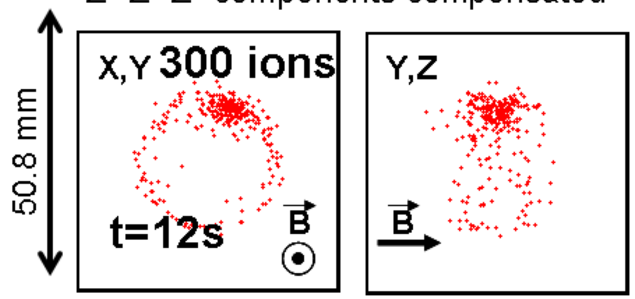
$$\beta = \frac{eB_0{}^2\gamma}{60m}$$

Inhomogeneous magnetic field:

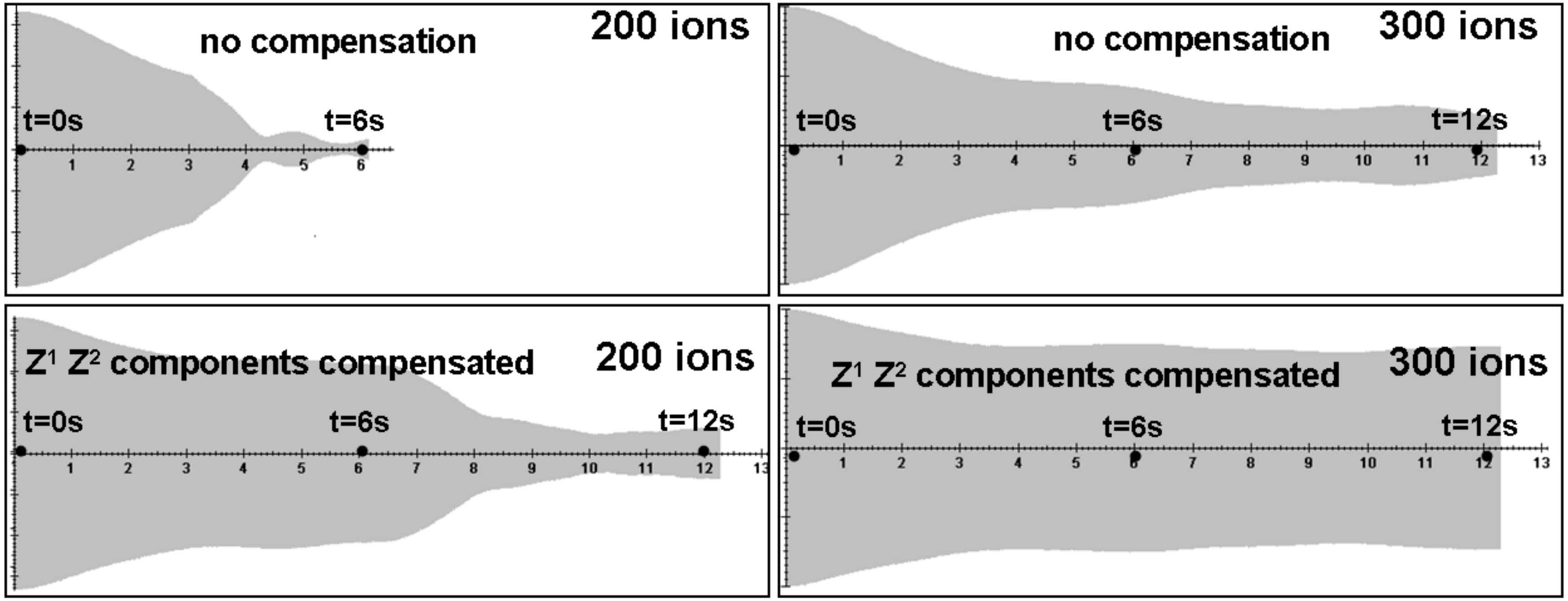


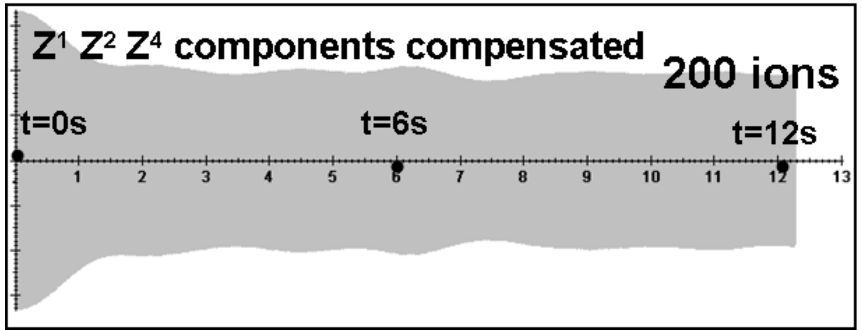
X-Y and Y-Z projection of ion cloud:

Z¹ Z² Z⁴ components compensated



Signal for 200 ions (left) and for 300 ions (right):



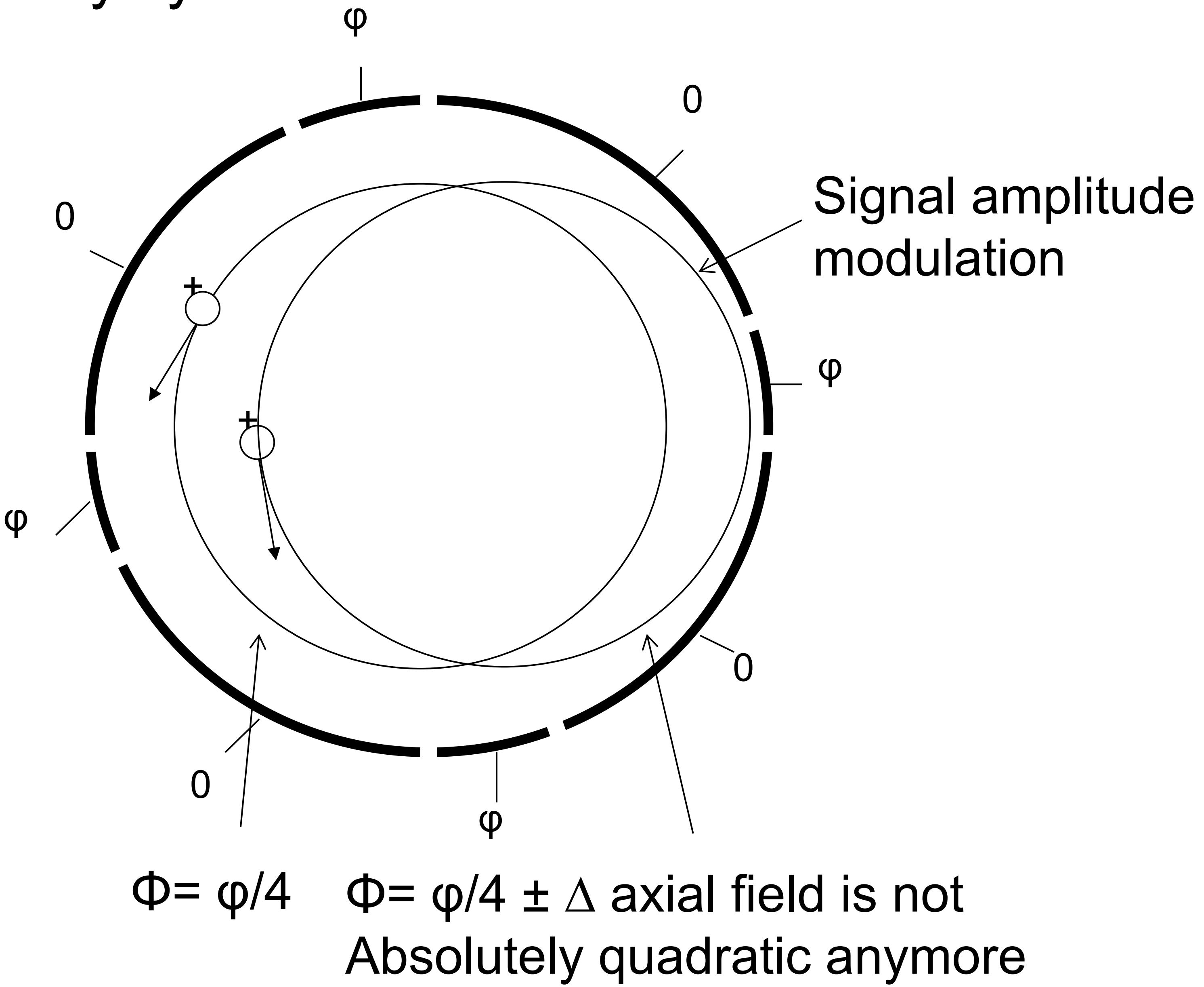


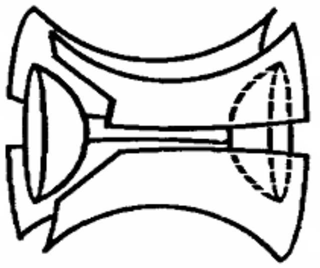
m/z=500Da; Z=1e;

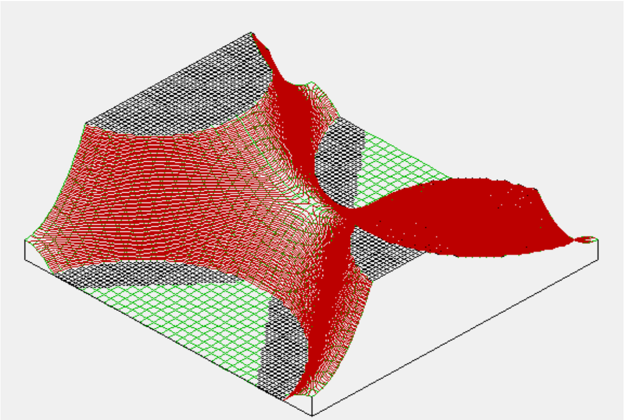
B=4.7T Spectrospin AG magnet

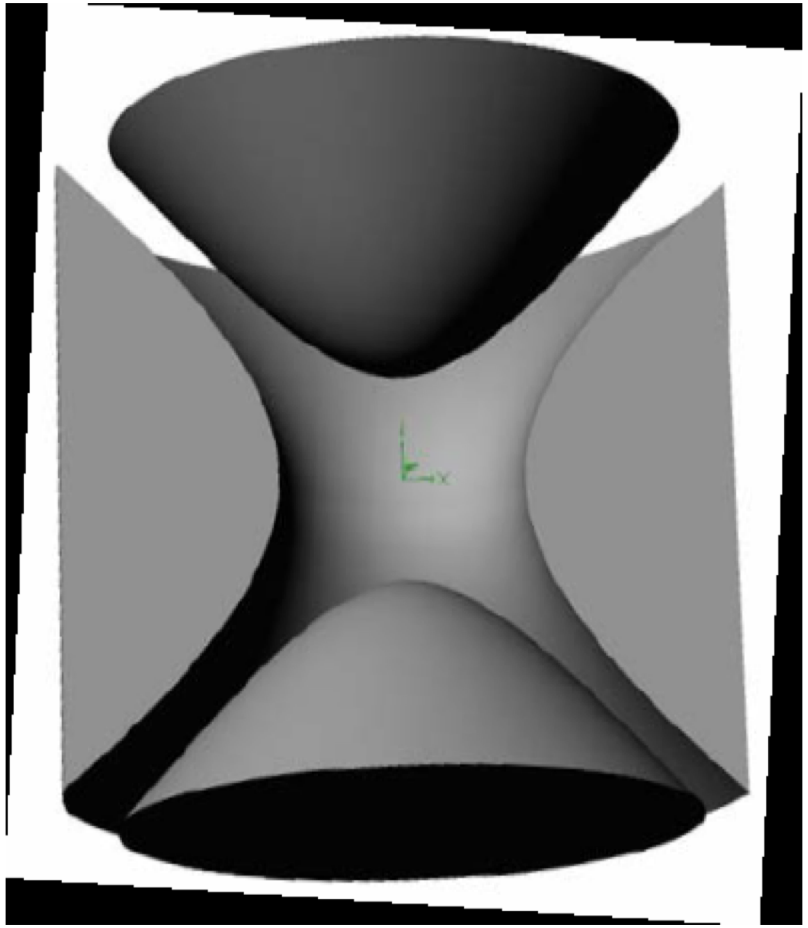
Is dynamically harmonized cell harmonized statically?

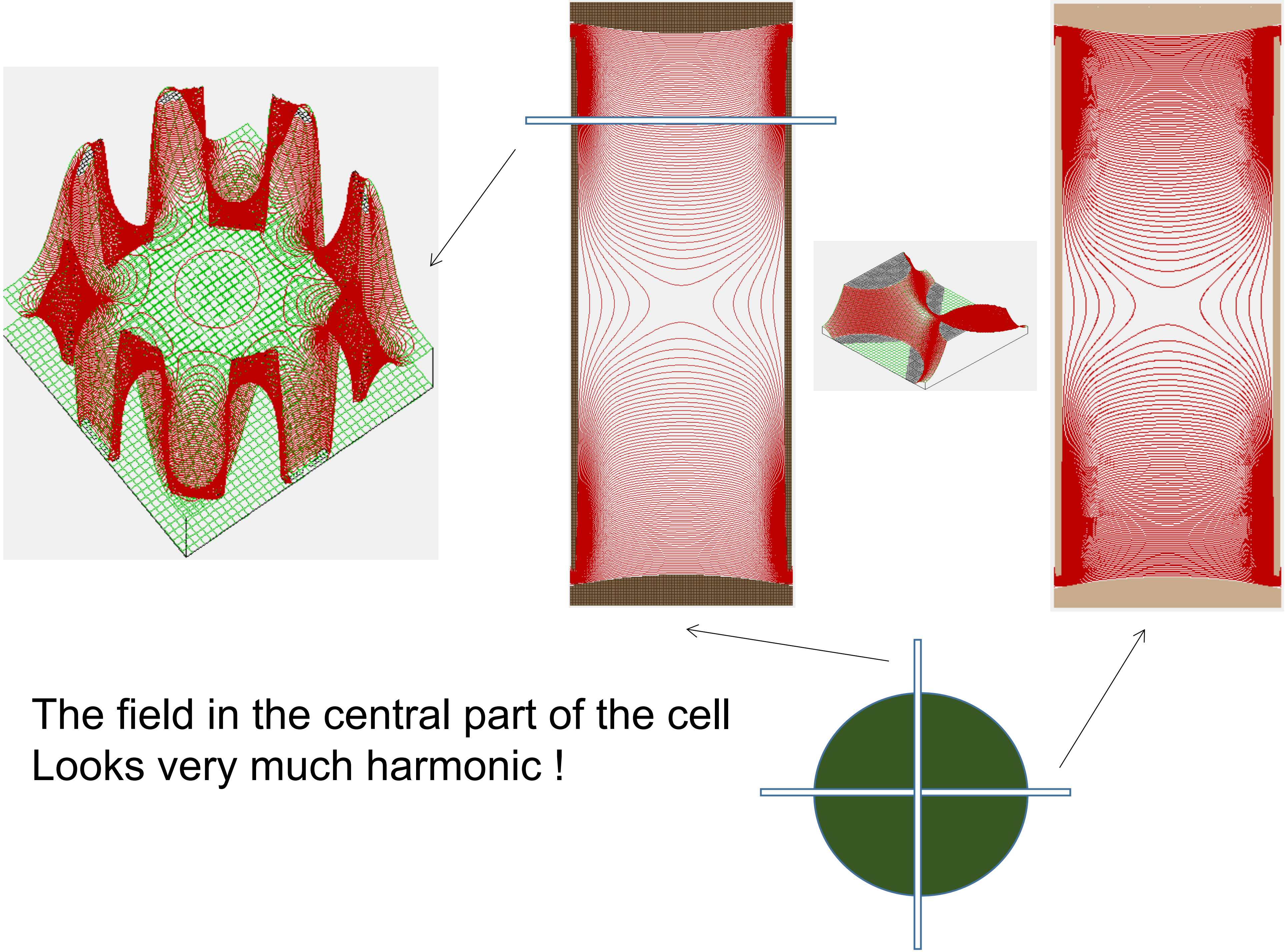
Magnetron motion problem. Averaging of the electric field potential by cyclotron motion. Combined harmonics.



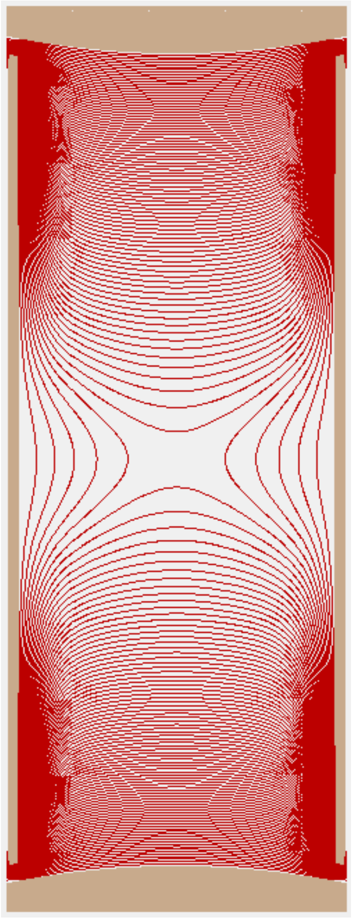


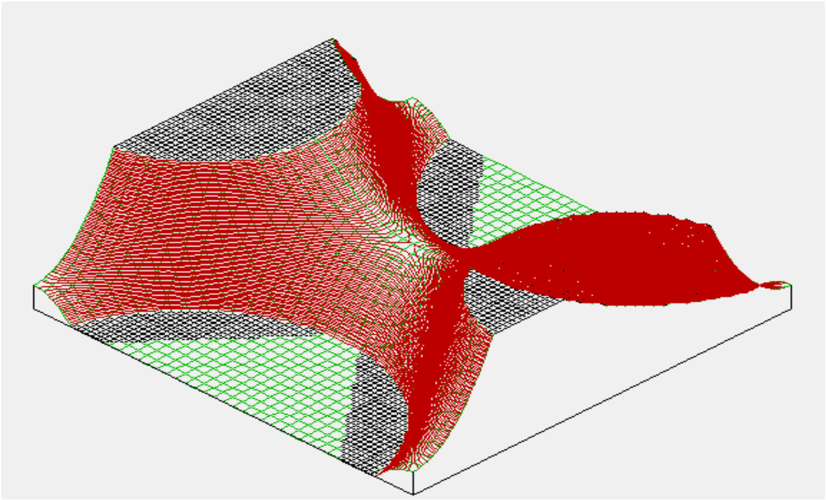


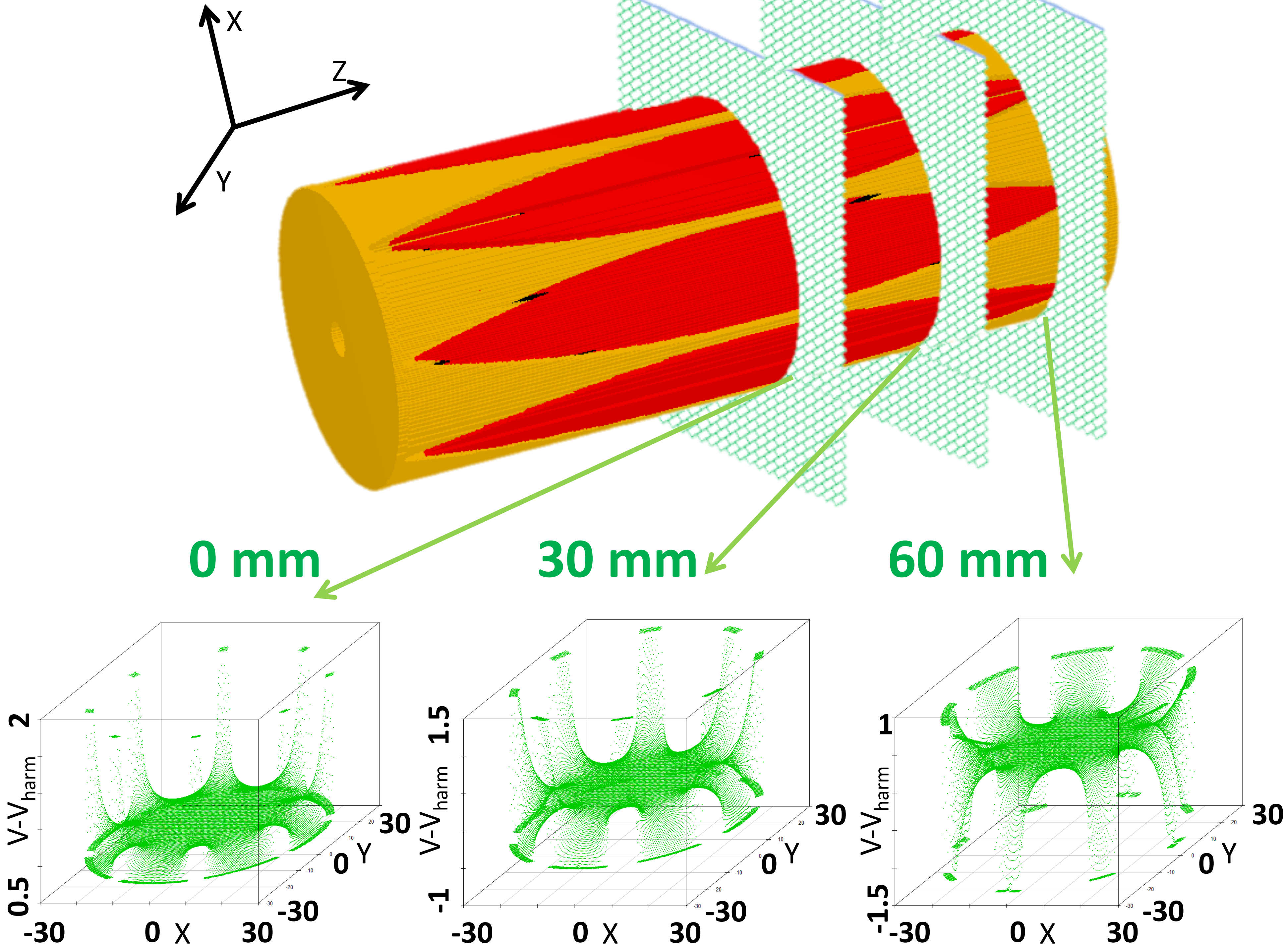


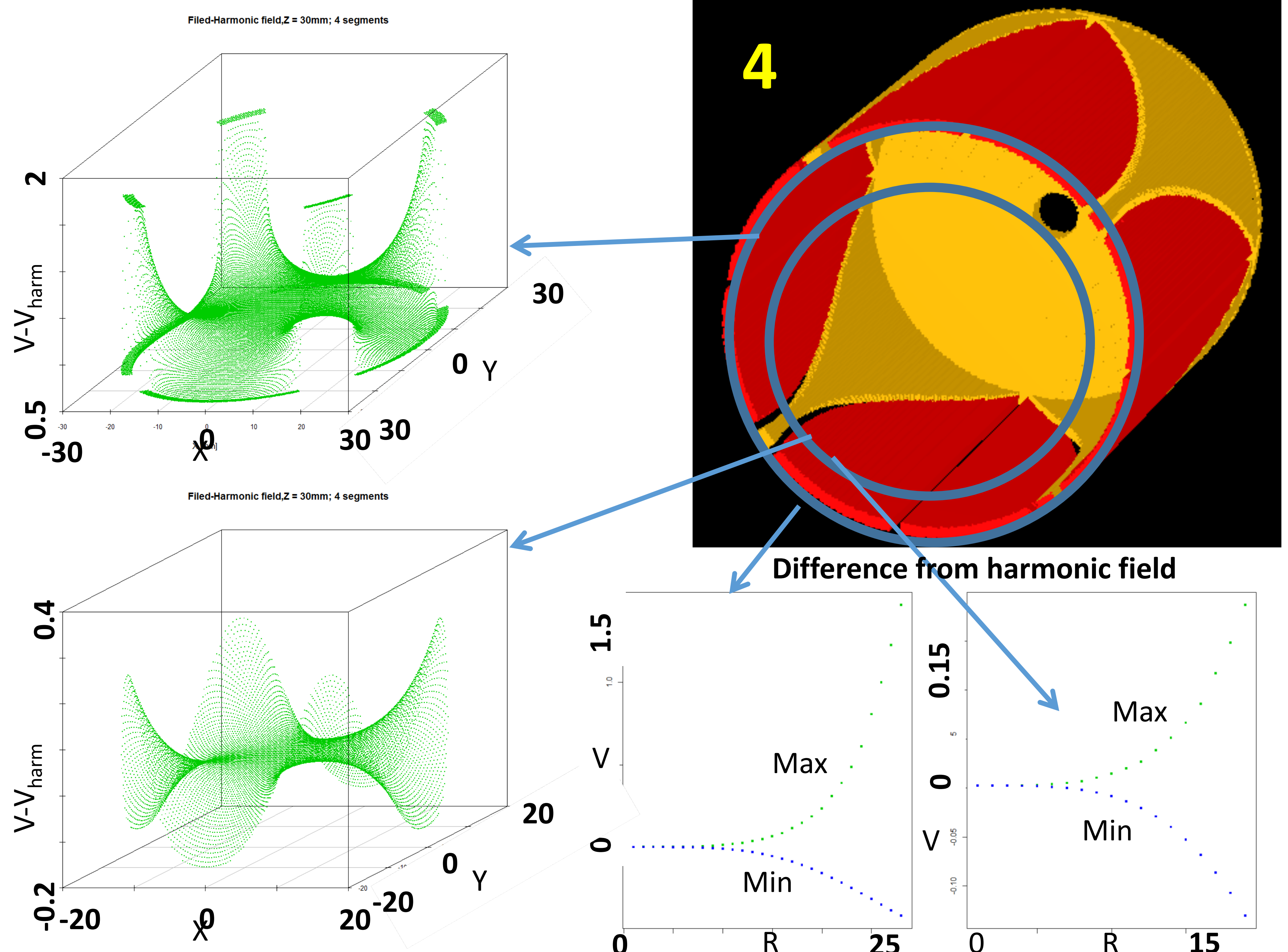


The field in the central part of the cell
Looks very much harmonic !

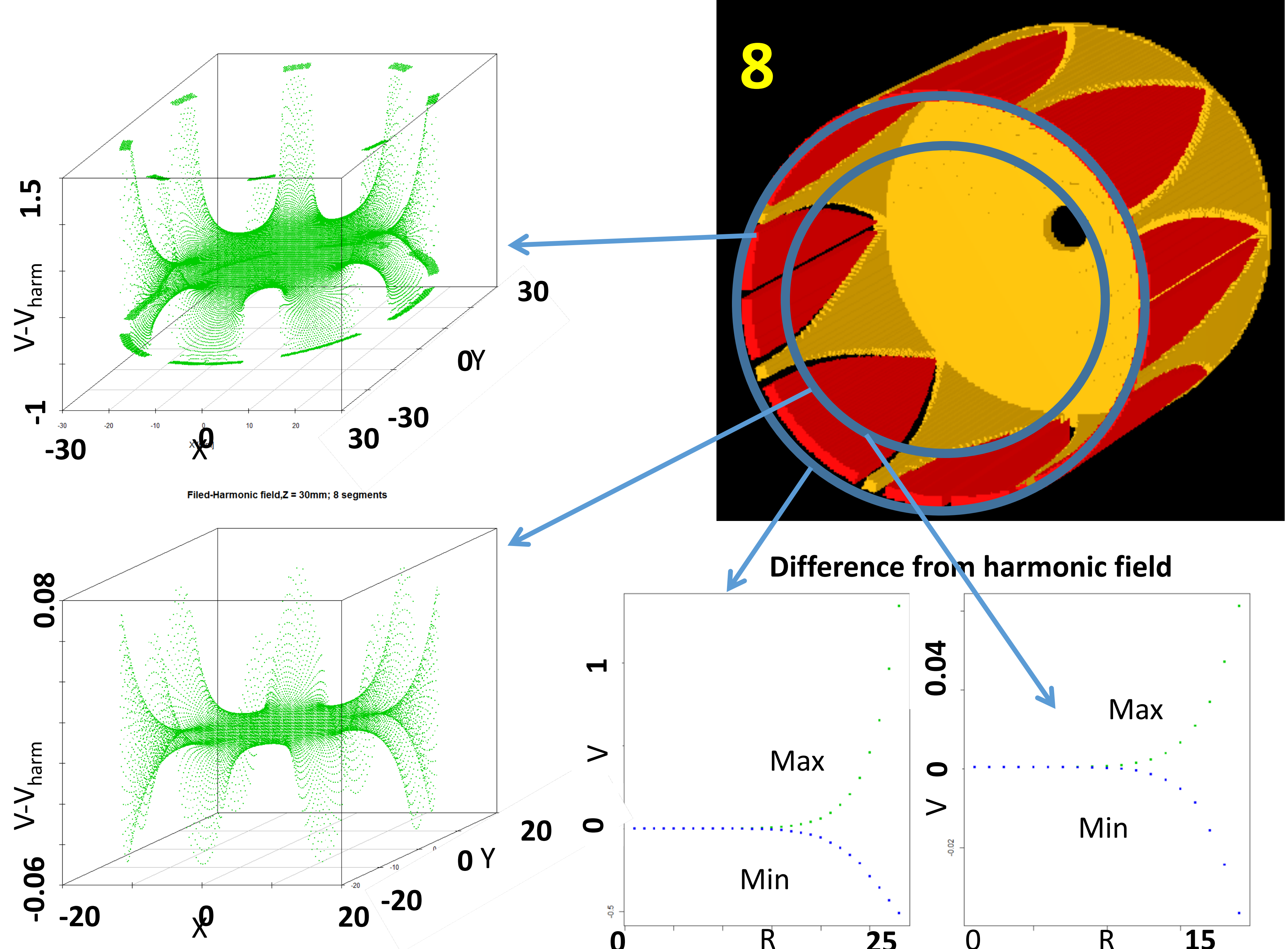




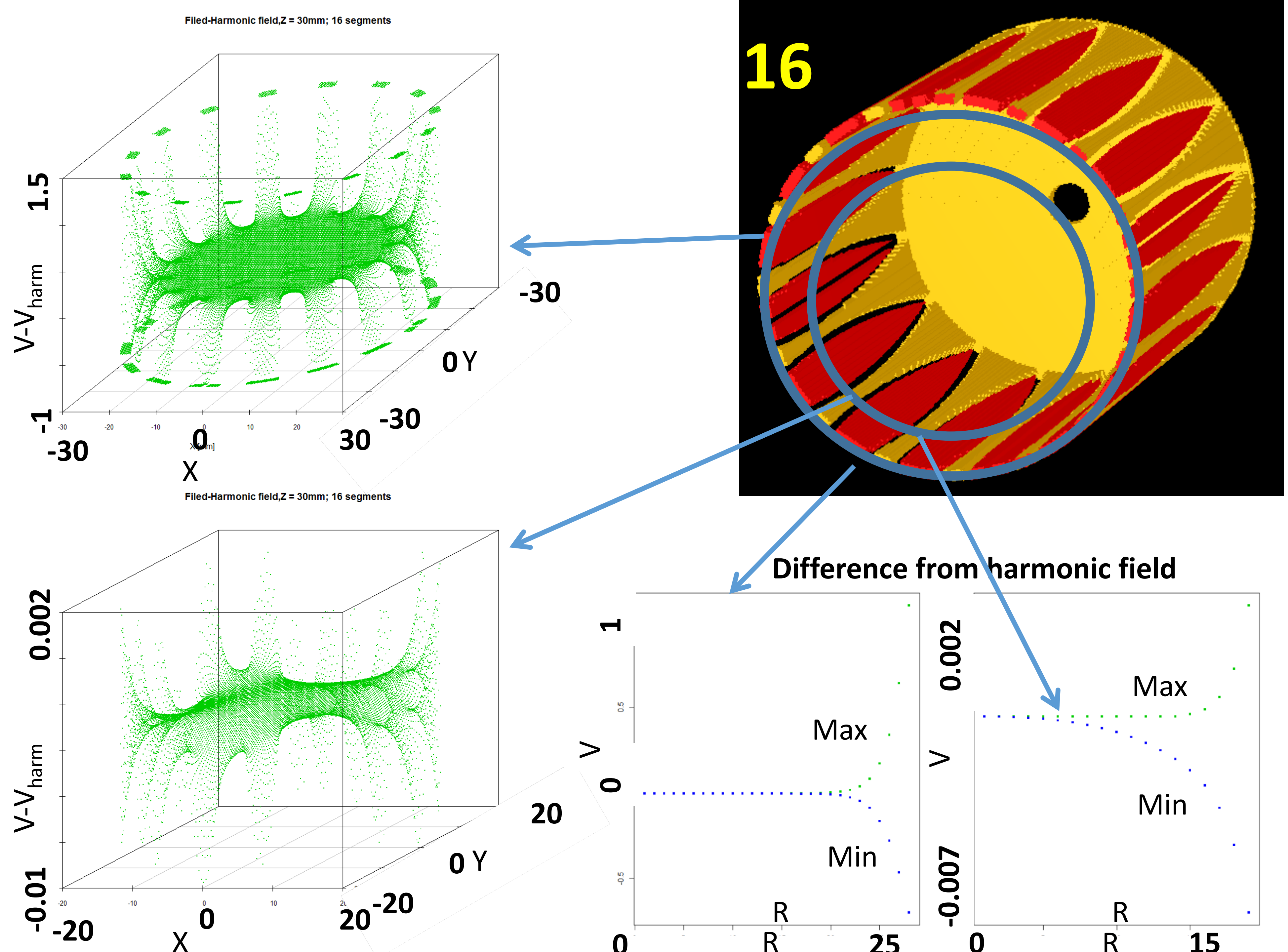

X
Z
Y
0 mm
30 mm
60 mm
V-V_harm
2
0.5
-30
0 X
30
30
0 Y
-30
V-V_harm
1.5
-1
-30
0 X
30
30
0 Y
-30
V-V_harm
1
-1.5
-30
0 X
30
30
0 Y
-30



Filed-Harmonic field,Z = 30mm; 4 segments
2
V-Vharm
0.5
-30
0
X
30
30
0
Y
30
Filed-Harmonic field,Z = 30mm; 4 segments
0.4
V-Vharm
-0.2
-20
0
X
20
-20
0
Y
20
4
Difference from harmonic field
1.5
V
0
Max
Min
0
R
25
0.15
V
0
Max
Min
0
R
15

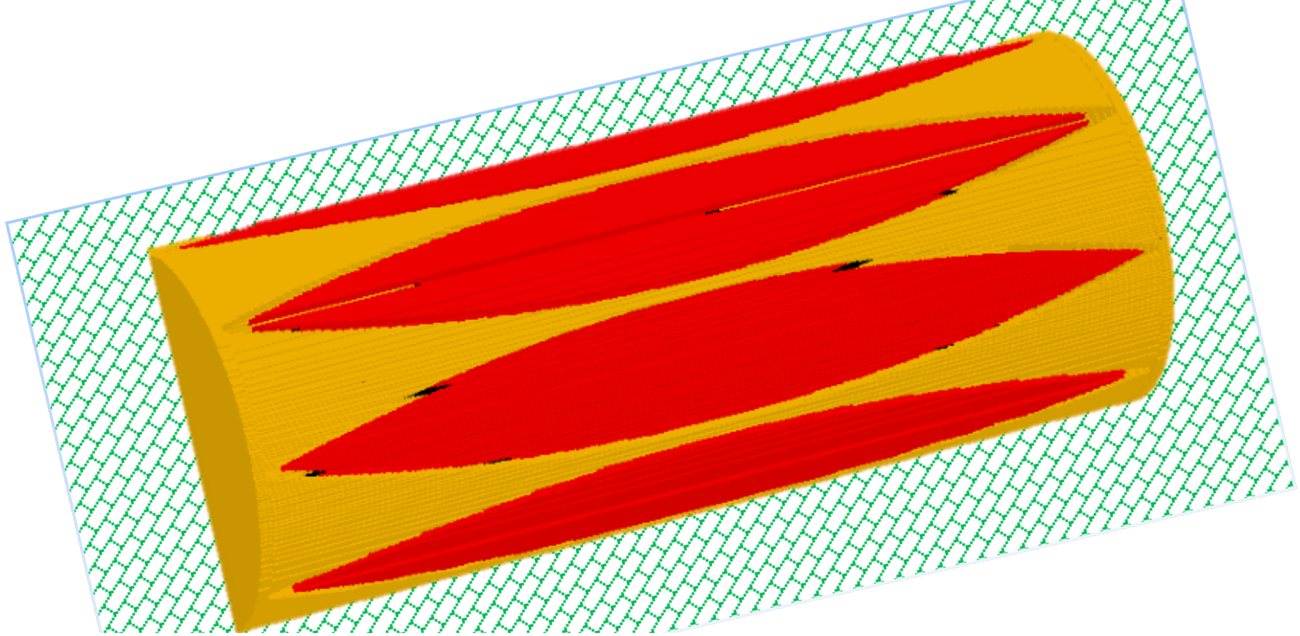


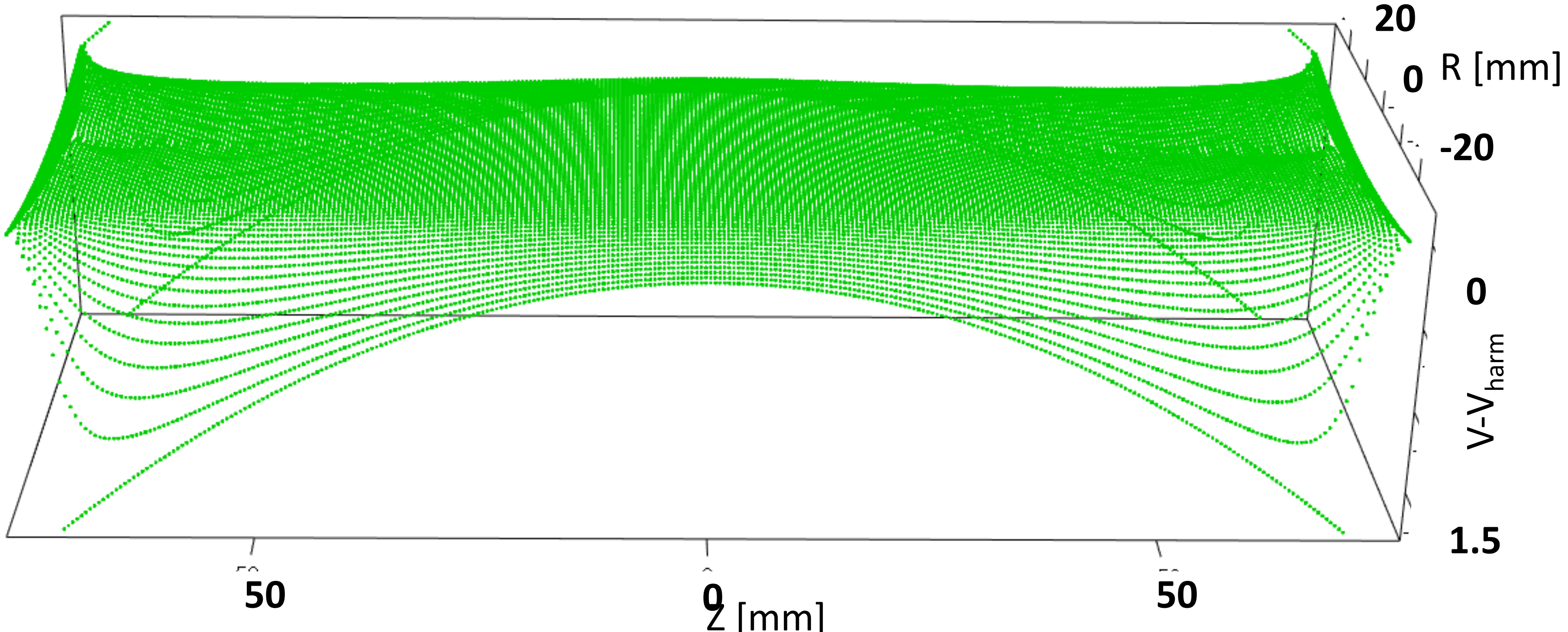
8
1.5
V-V_harm
-1
-30
0
X
30
0Y
-30
Filed-Harmonic field,Z = 30mm; 8 segments
0.08
V-V_harm
-0.06
-20
0
X
20
0 Y
-20
Difference from harmonic field
V
1
0
Max
Min
0
R
25
0.04
V 0
Max
Min
0
R
15



Filed-Harmonic field,Z = 30mm; 16 segments
1.5
V-Vharm
-1
-30
0
30
X
-30
0 Y
-30
Filed-Harmonic field,Z = 30mm; 16 segments
0.002
V-Vharm
-0.01
-20
0
20
X
20
0 Y
-20
16
Difference from harmonic field
1
V
0
Max
Min
R
0
R
25
0.002
V
-0.007
Max
Min
R
0
R
15

The field in the R-Z plane is also statically harmonized





Even for 16 segments the error of static harmonization is about units of millivolts inside the cylinder with 2/3 of cell radius!

Detection at multiple frequencies

СОЮЗ СОВЕТСКИХ
СОЦИАЛИСТИЧЕСКИХ
РЕСПУБЛИК

(19) SU (11) 1307492 A1

(51) 4 H 01 J 49/38

ГОСУДАРСТВЕННЫЙ КОМИТЕТ СССР
ПО ДЕЛАМ ИЗОБРЕТЕНИЙ И ОТКРЫТИЙ

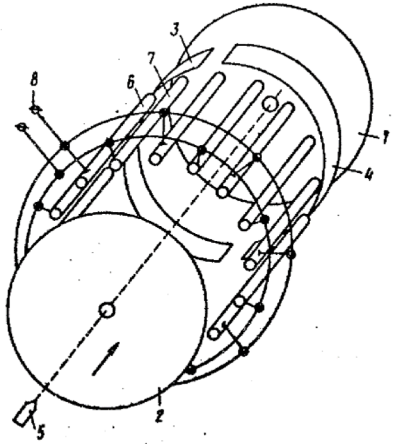
ОПИСАНИЕ ИЗОБРЕТЕНИЯ

К АВТОРСКОМУ СВИДЕТЕЛЬСТВУ

(21) 3922733/24-21
(22) 05.07.85
(46) 30.04.87. Бюл. № 16
(71) Институт химической физики АН СССР
(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

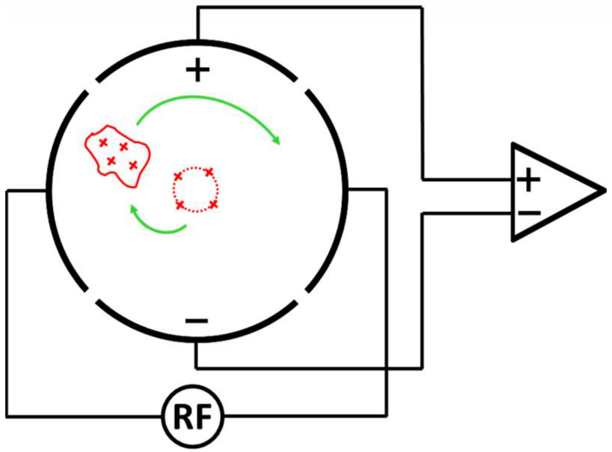
(57) Изобретение относится к области ионноплазменной техники. Ионно-циклотронный резонансный масс-спектрометр (ИЦМС) содержит пластины 1, 2 удержания ионов (И), расположенные по торцам перпендикулярно оси ИЦМС, электроды (Э) 3, 4 возбуждения И в виде полуцилиндров, установленных в одной плоскости торцами 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



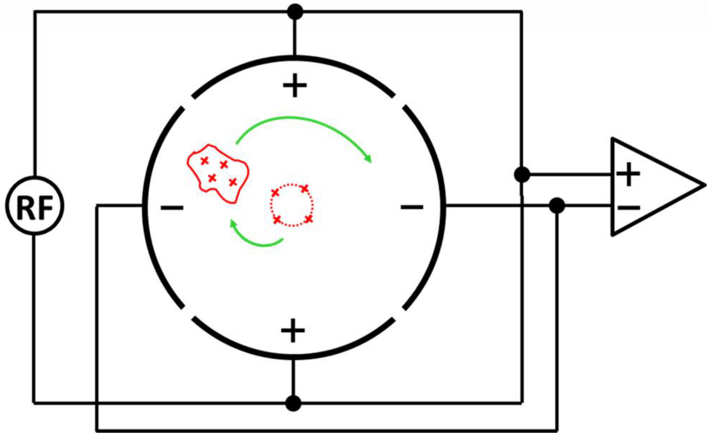
Soviet Union patent
Priority 05.07.1985
Nikolaev, Gorshkov, Mordehai, Talroze
Multi-electrode detection FT ICR cell

4 electrode FT ICR cell
Dipolar detection



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

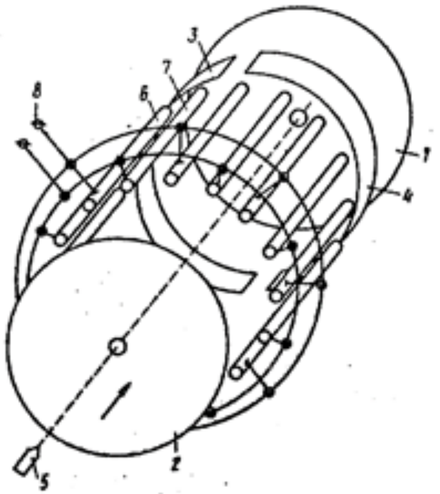
4 electrode FT ICR cell
Quadrupolar detection



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

Double resolution or double speed

2N electrode FT ICR cell
Multipolar detection



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

N times higher resolution or speed

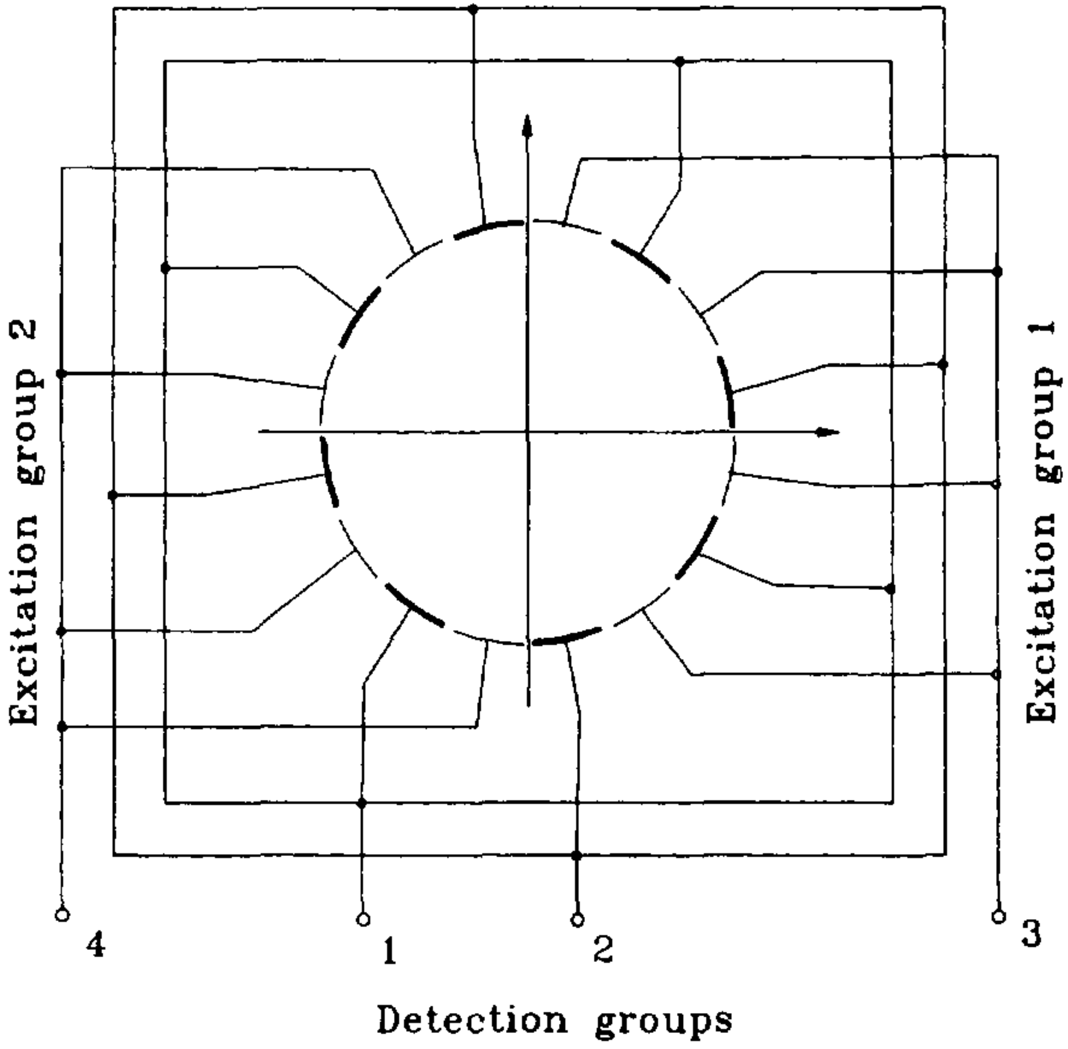
Detection on multiplied frequencies and on harmonics

$R = \omega / \Delta\omega$

$\Delta\omega \sim 1/T$

T is signal duration

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



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

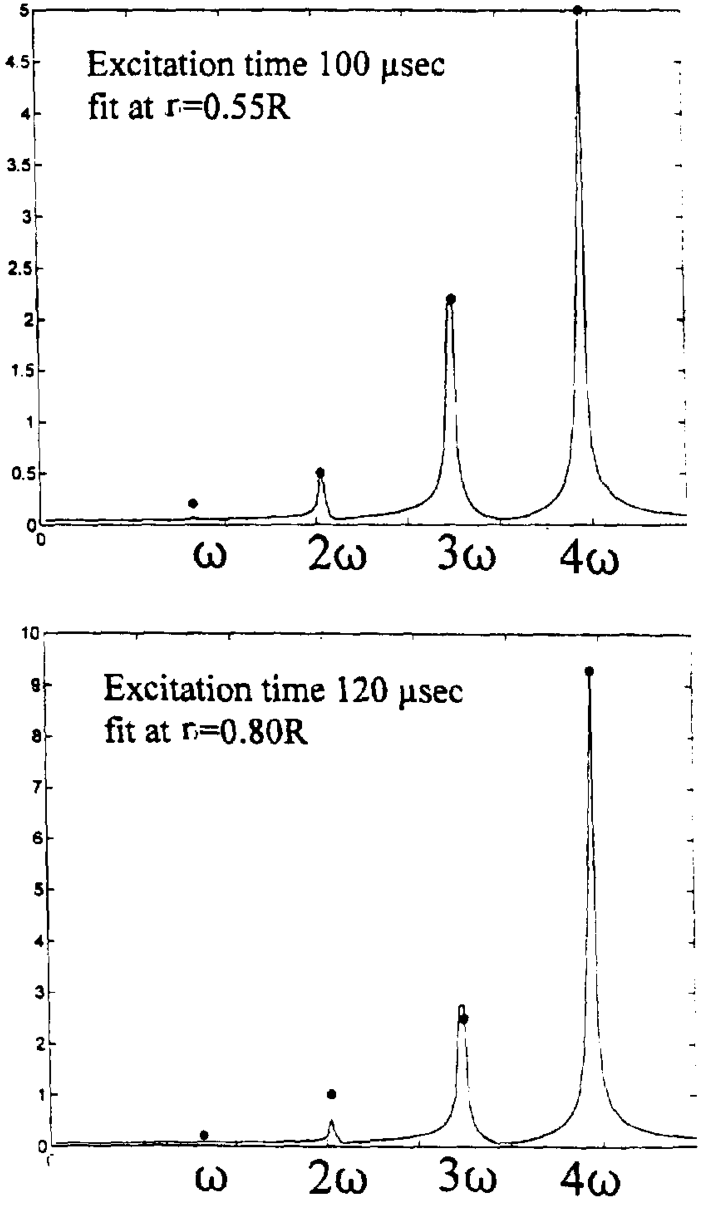
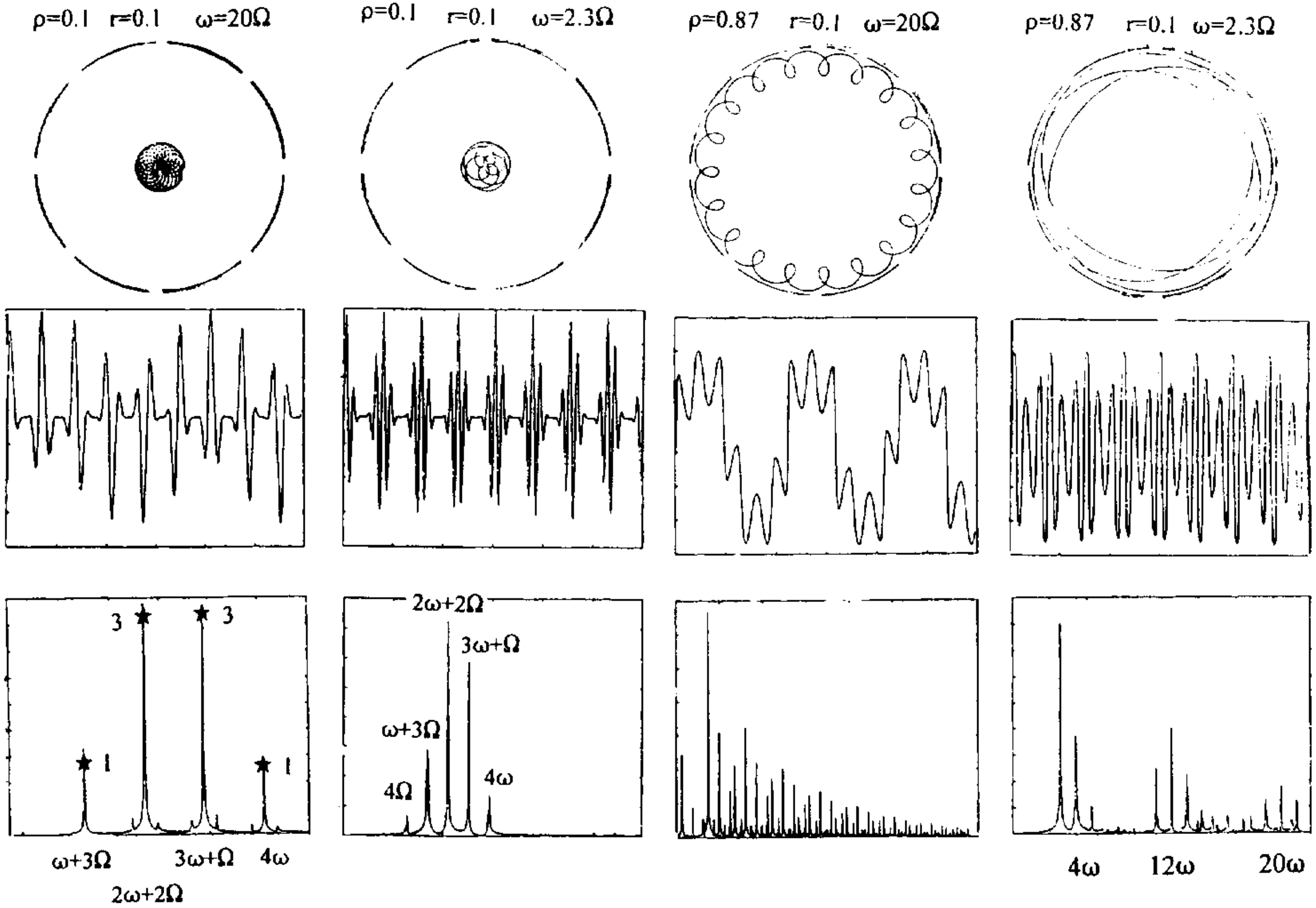
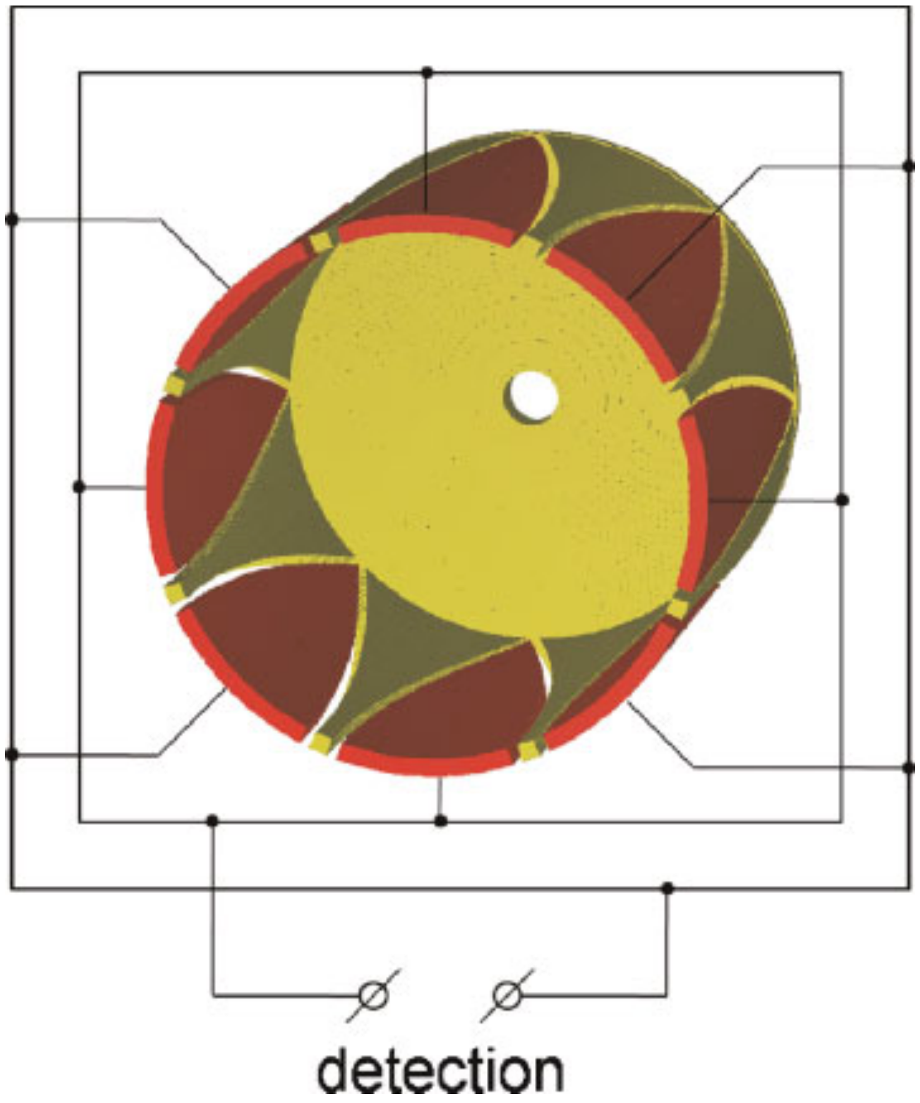


Fig. 11. Simulation for 16-electrode cell shown in . Cells radius $R = 1$. •, experimental amplitudes obtained in [7] for first four harmonics; ———, the result of computer simulation for fixed cyclotron radius, $\rho = 0.1$ and several magnetron radii. Correlation between excitation time and magnetron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

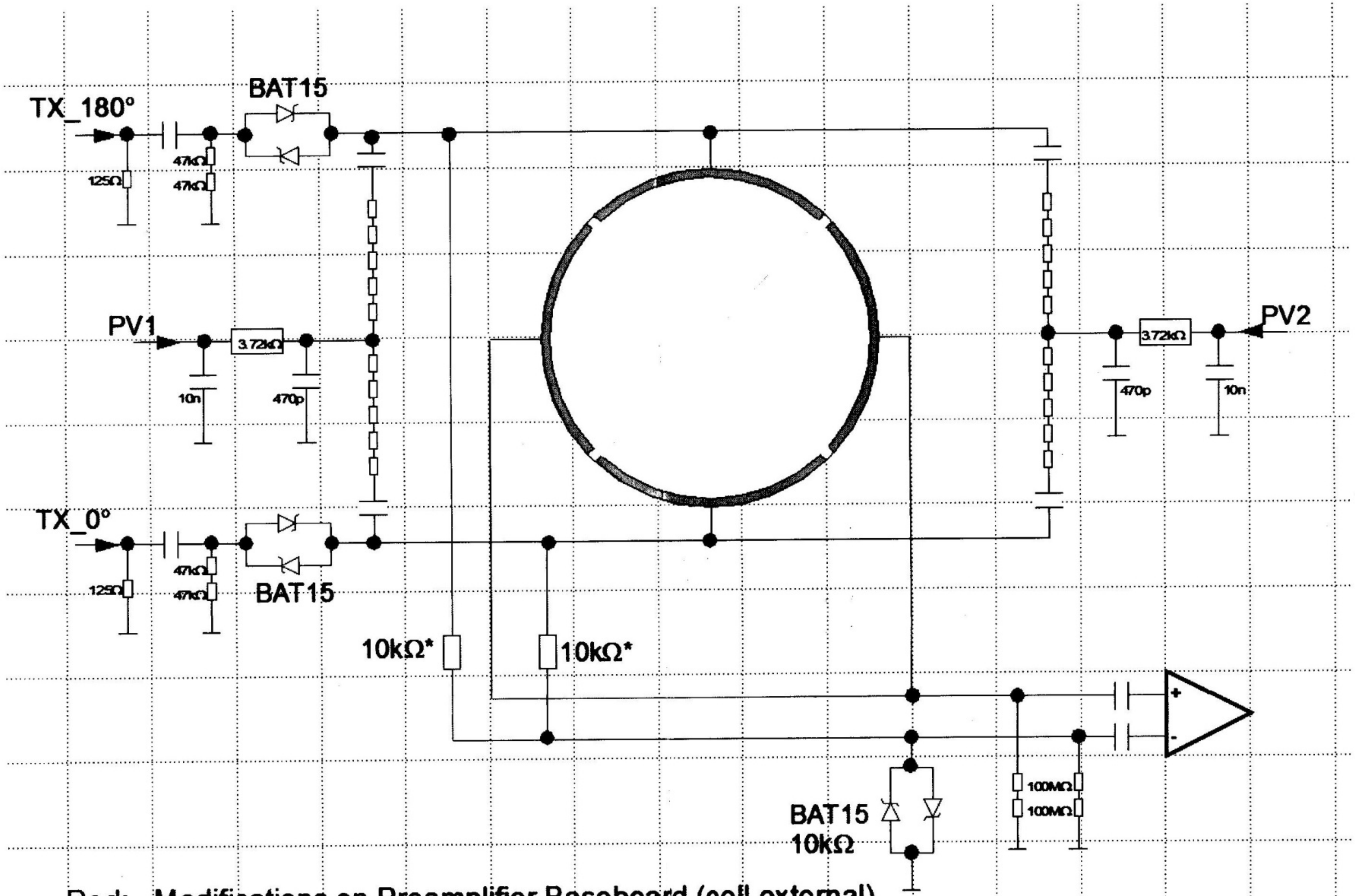
Analysis of harmonics for an elongated FTMS cell with multiple electrode detection

E.N. Nikolaev[1,a,*], V.S. Rakov[a], J.H. Futrell[a]



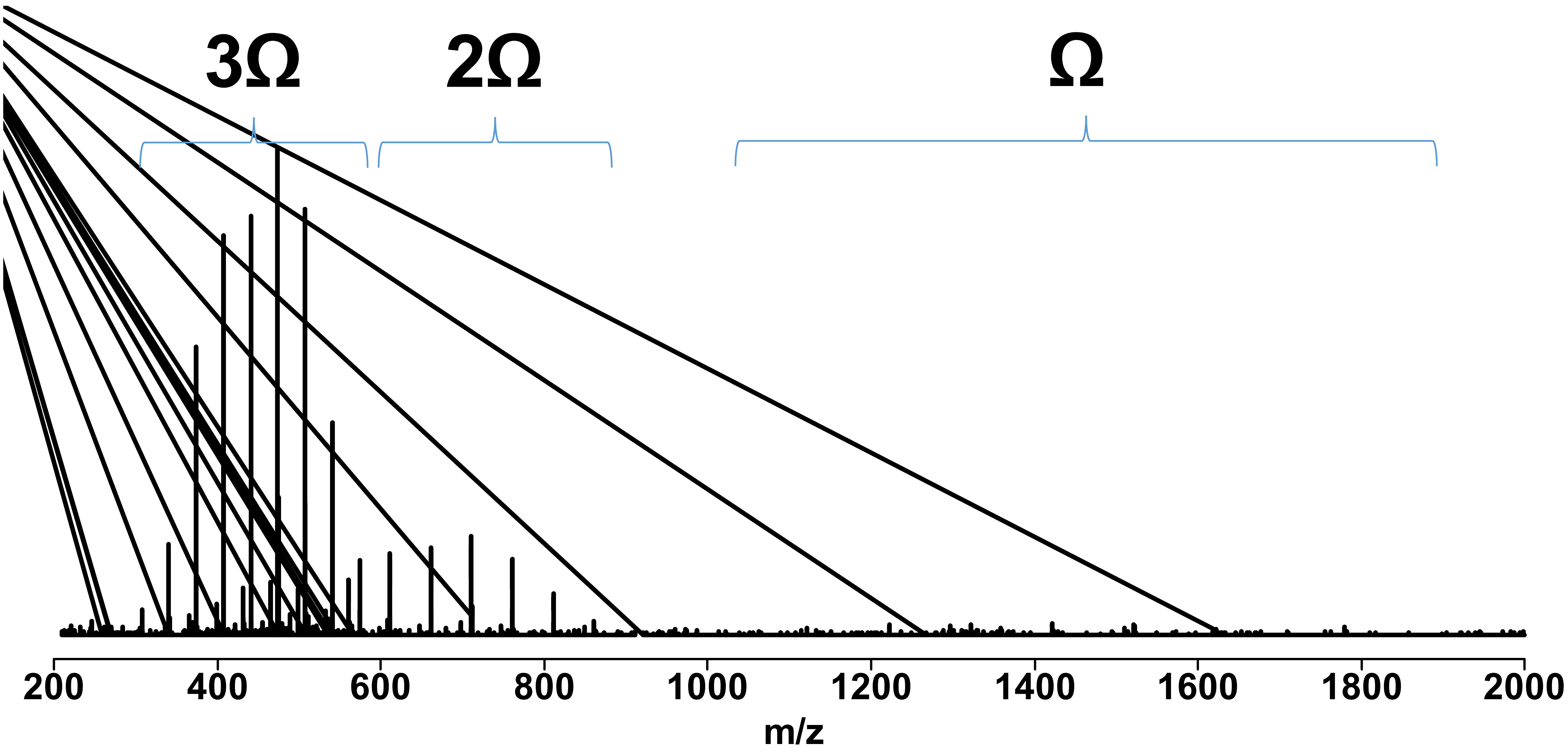


$$\omega_{signal} = 4^{*}\omega_{cyclotron}$$

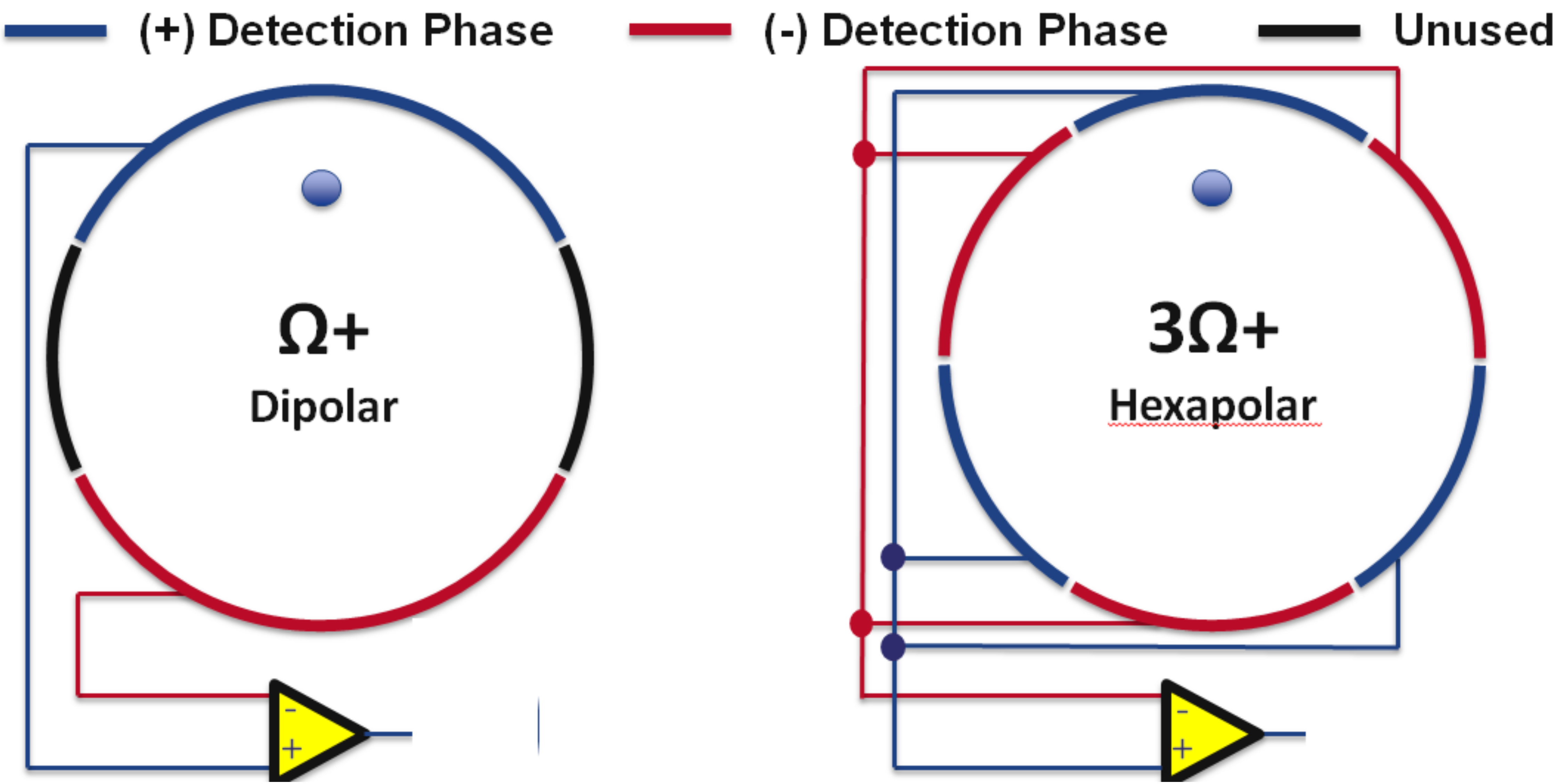


Red: Modifications on Preamplifier Baseboard (cell external)

Spectral Acquisition at 3Ω (14.5 T)

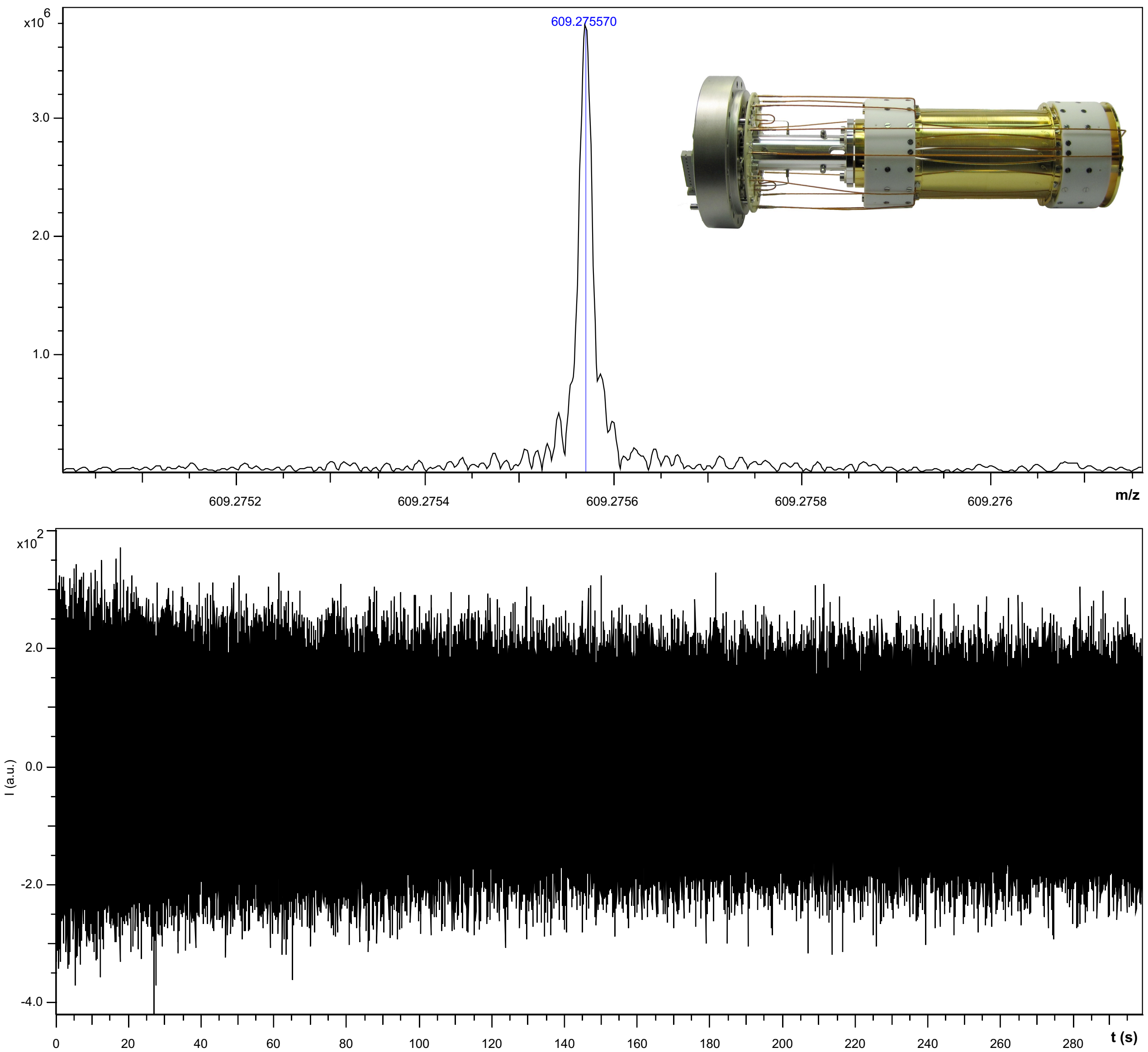


3 Ω Detection Geometry

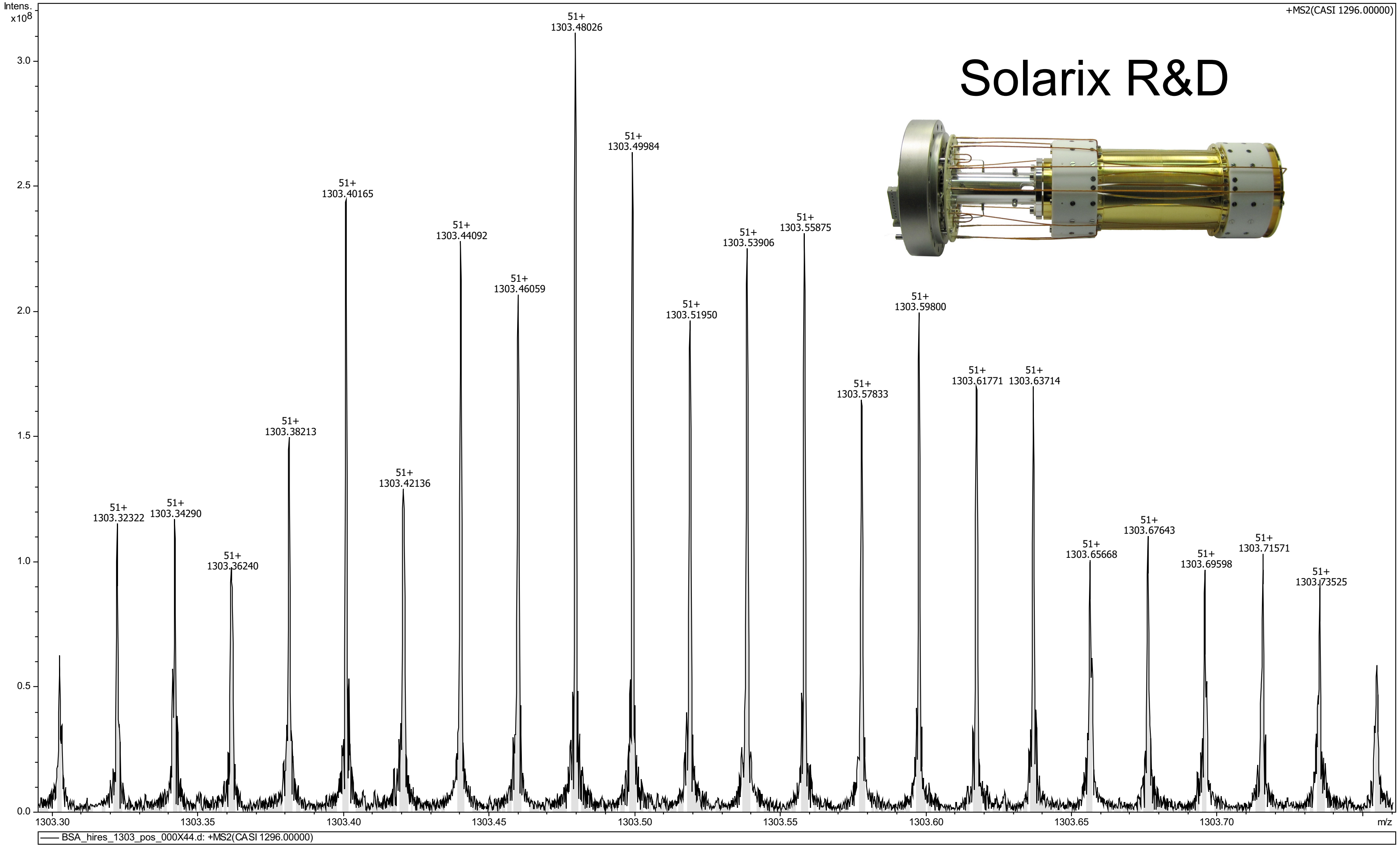


Dynamically harmonized FT ICR cell for Thermo LTQ FT

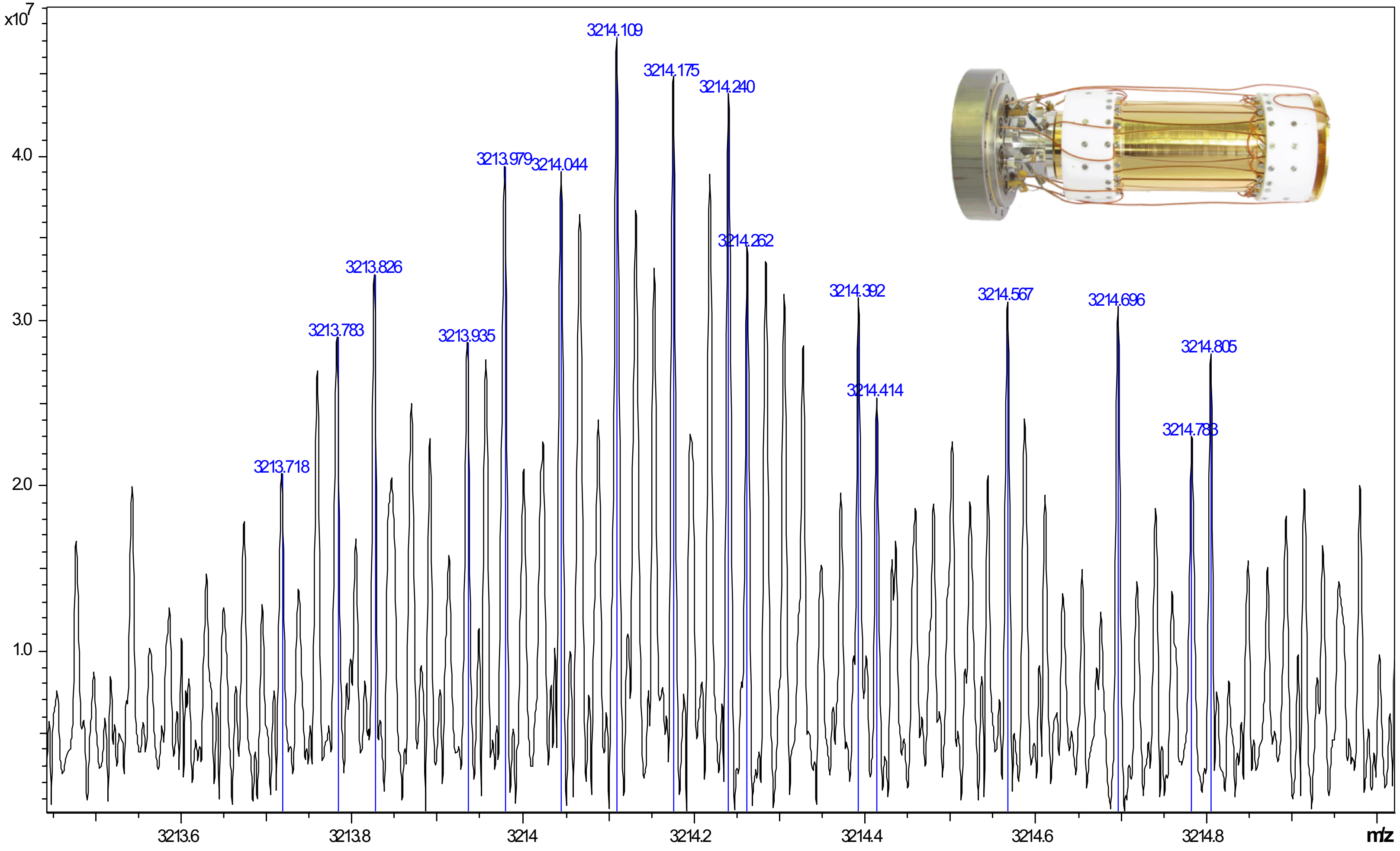
Reserpine. Lab Prototype , Solarix, 300s transient, RP 39,000,000 in magnitude mode



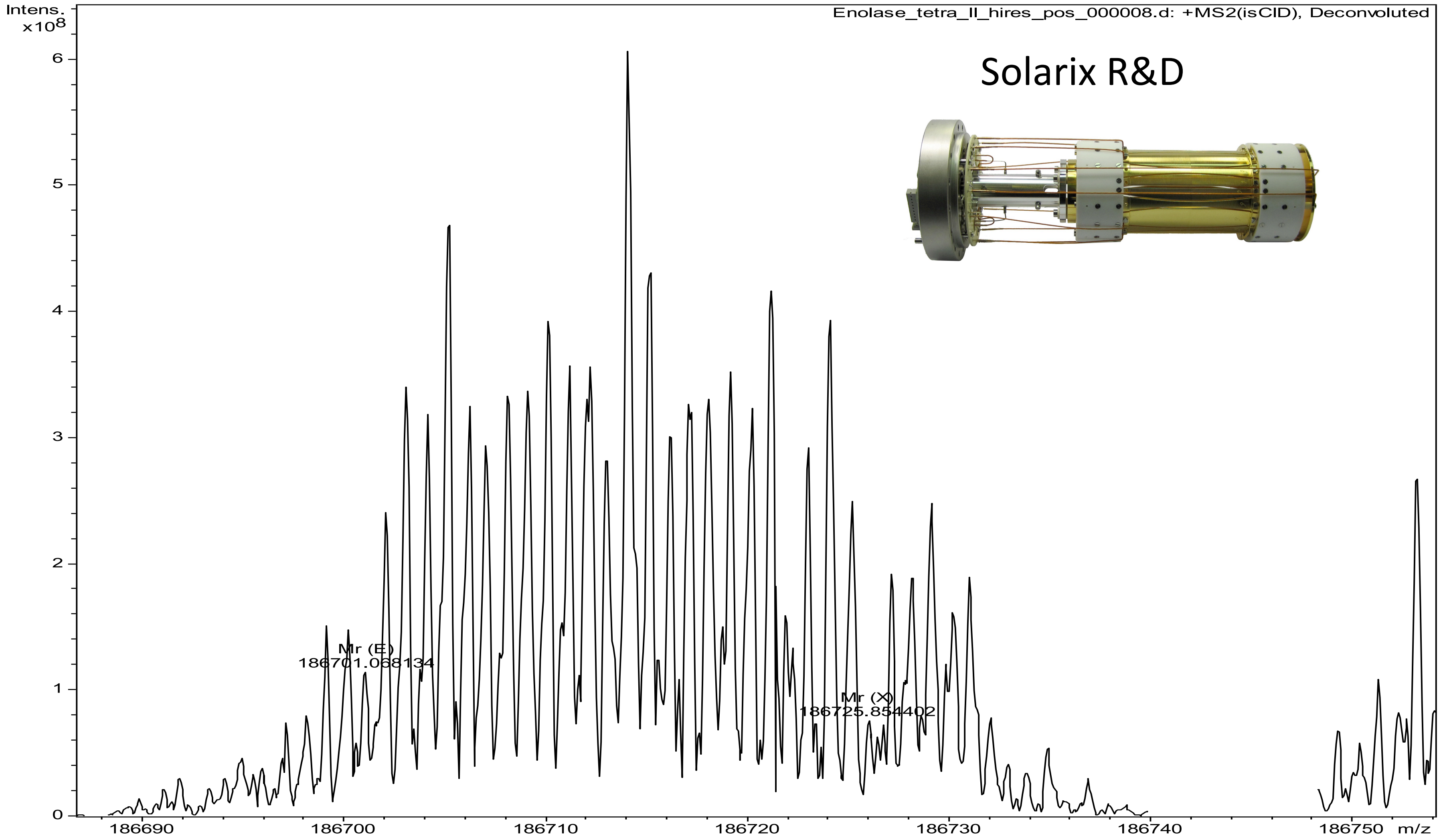
7T R&D, BSA, 51+, RP 1,700,000 28 s transient



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



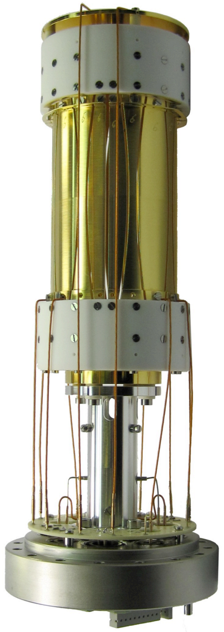
12T R&D, Enolase Tetramer, MW=**186713** Da, m/z=5835, (6мG/ml) , 32+, deconvoluted



The highest mass protein complex isotopicaly resolved

Vacuum limit of resolution is reached!

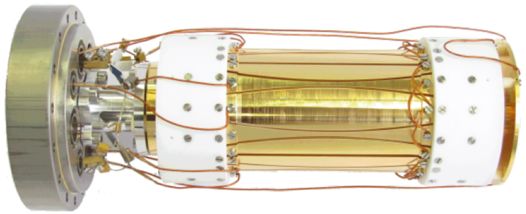
BSA	66420 Da	28 s
Yeast Enolase dimer	93340 Da	50 s
IgG	147800 Da	32 s
ADH tetramer	147530 Da	36 s
Yeast Enolase tetramer	186660 Da	38 s

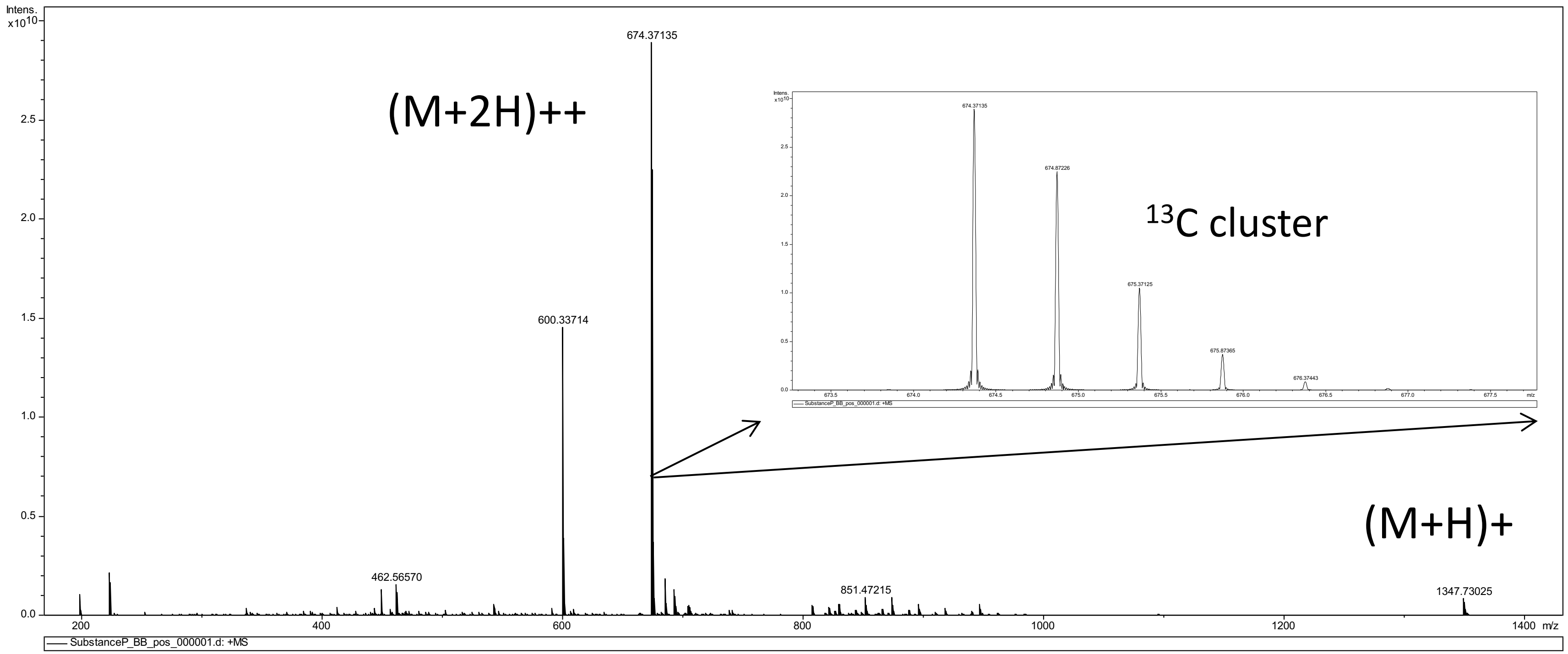


Peptide spectra fine structure

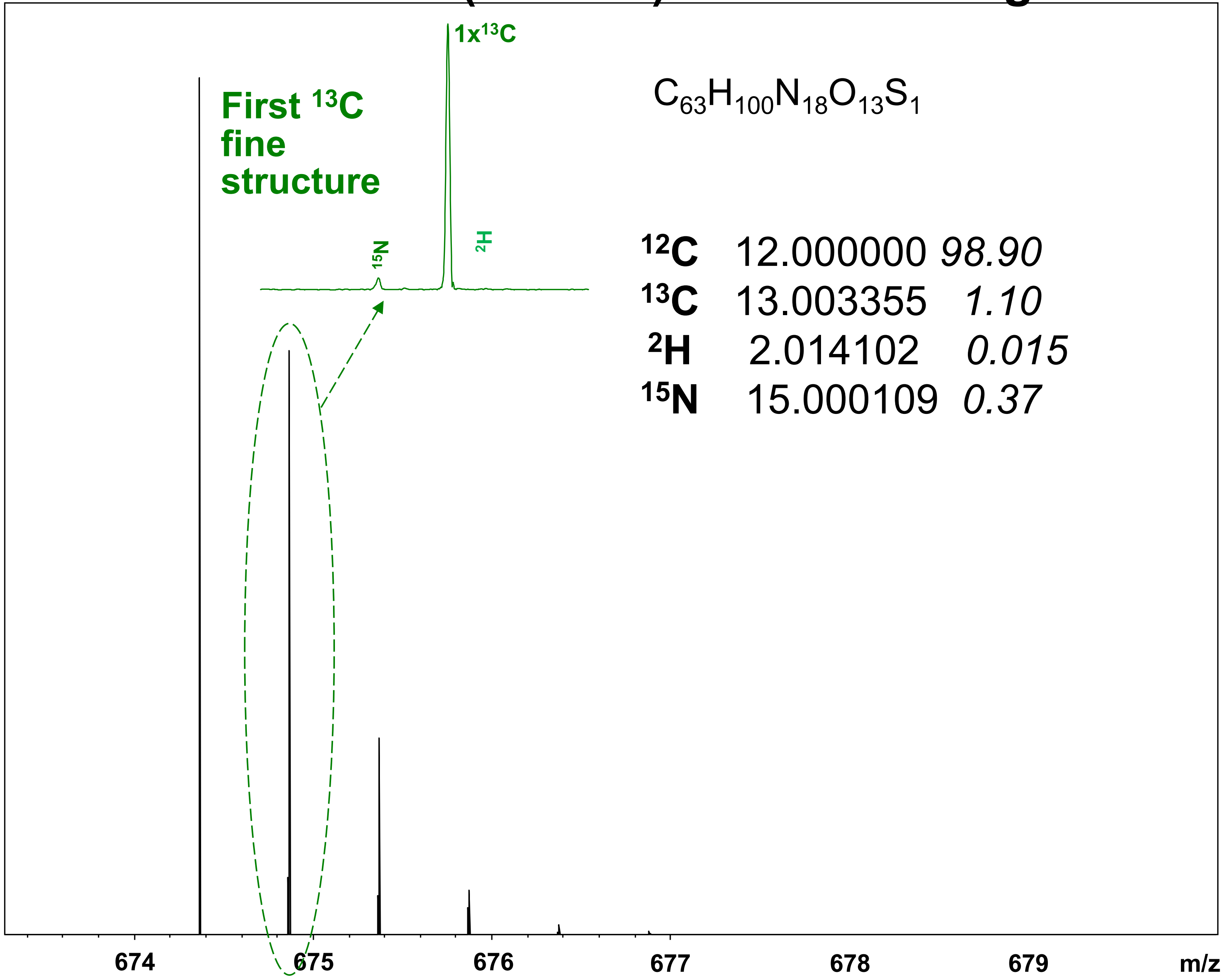
Substance P, broadband spectrum

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





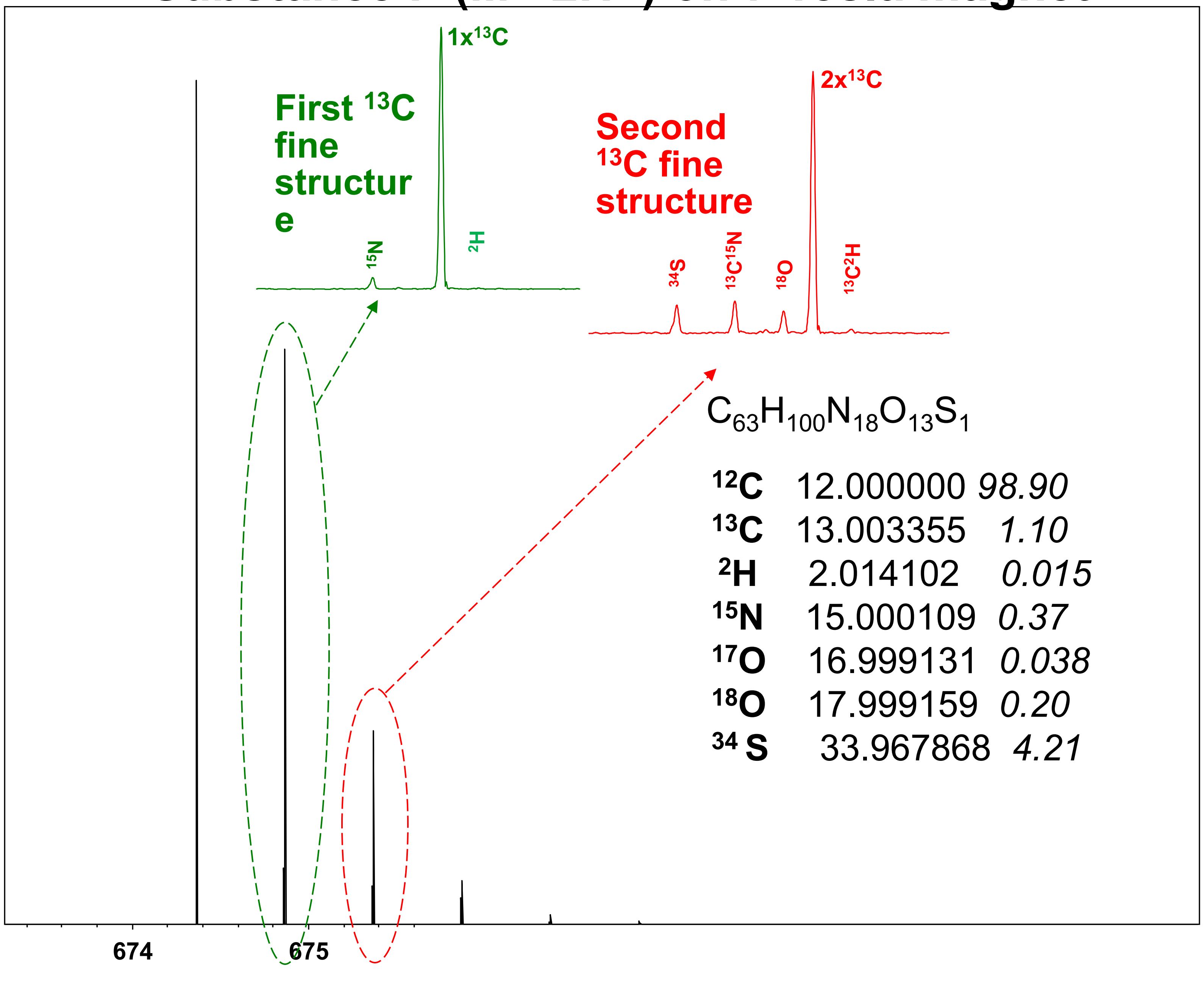
Substance P (M+ 2H⁺) on 7 Tesla magnet



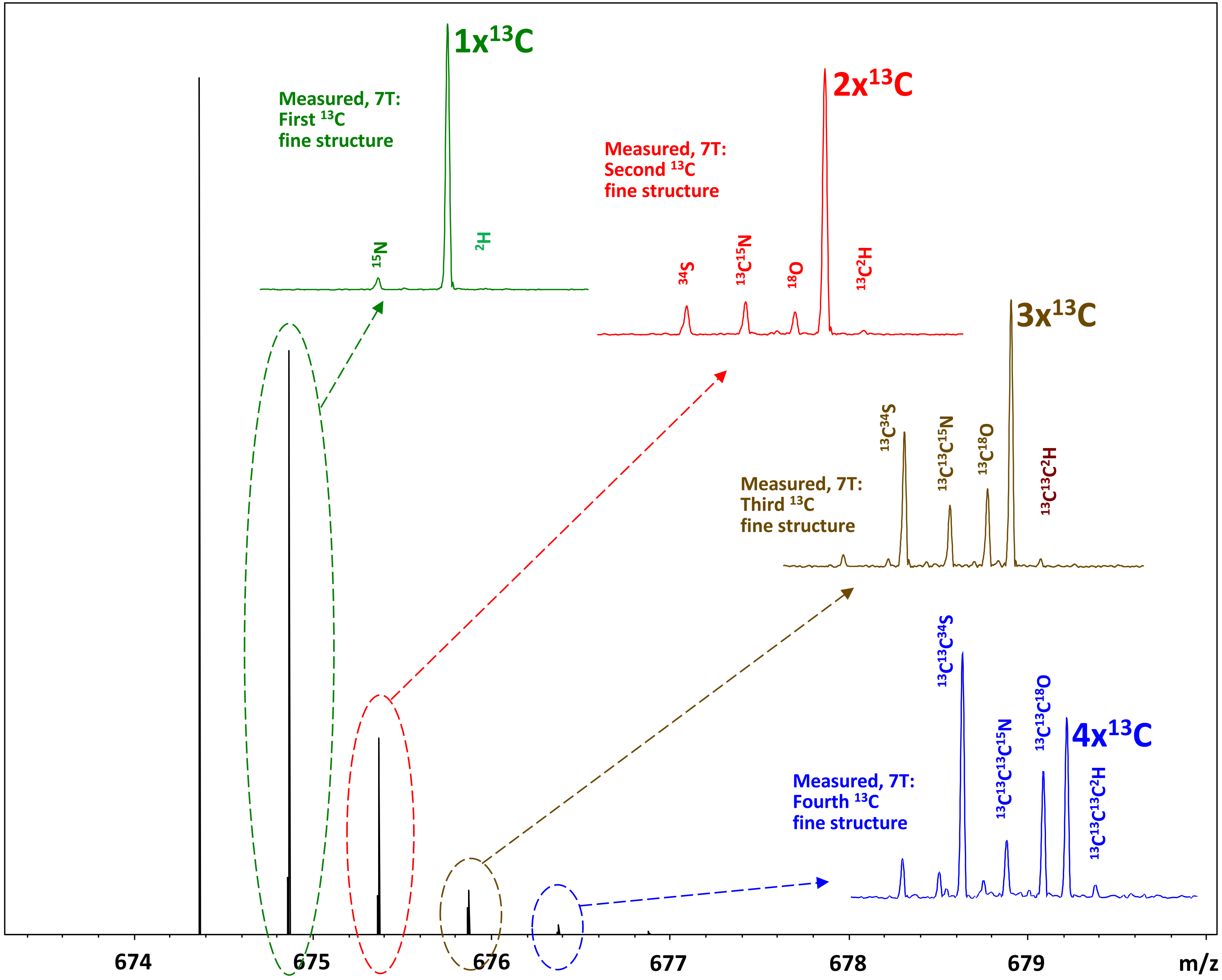
$C_{63}H_{100}N_{18}O_{13}S_1$

^{12}C	12.000000	*98.90*
^{13}C	13.003355	*1.10*
^{2}H	2.014102	*0.015*
^{15}N	15.000109	*0.37*

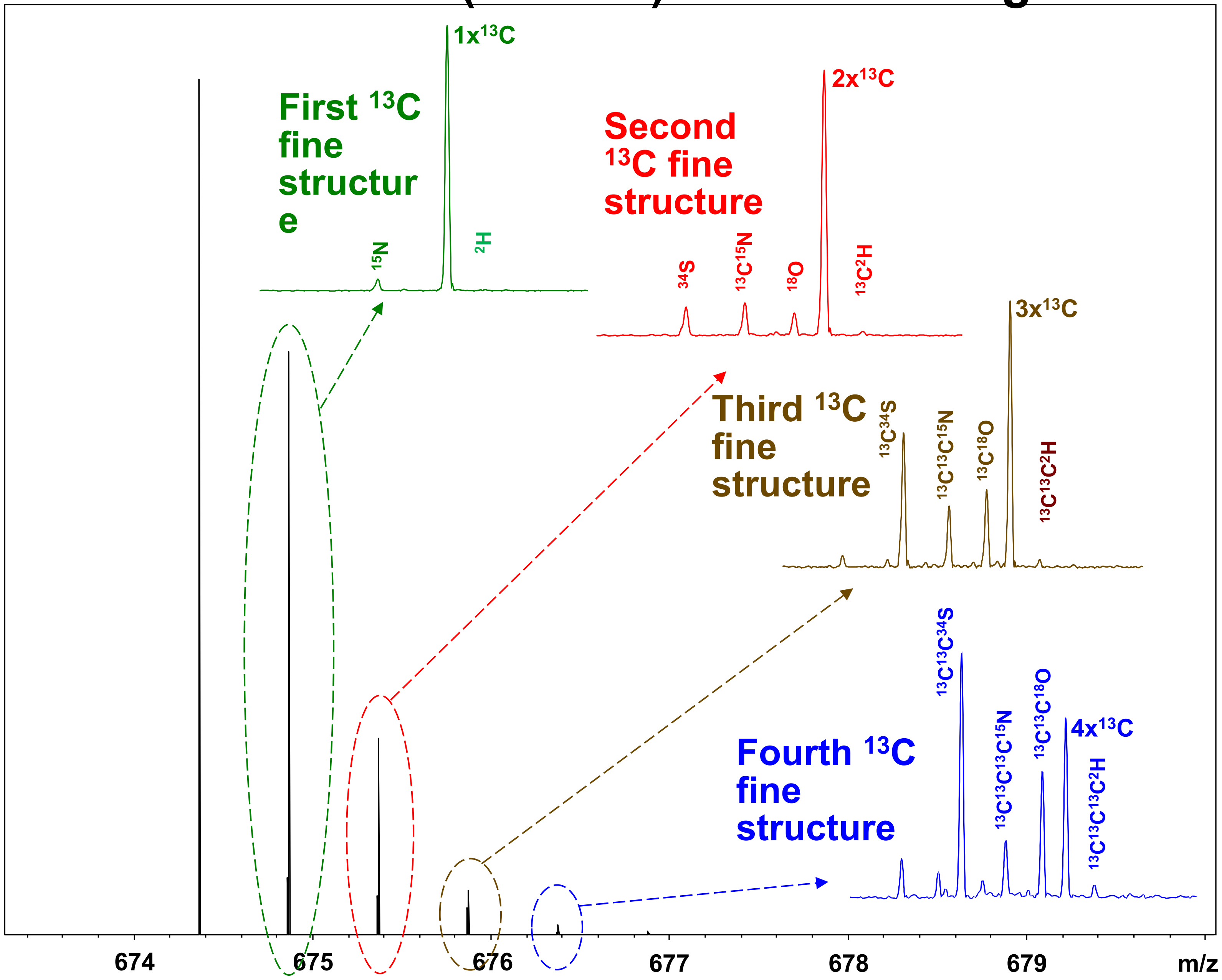
Substance P (M+ 2H⁺) on 7 Tesla magnet

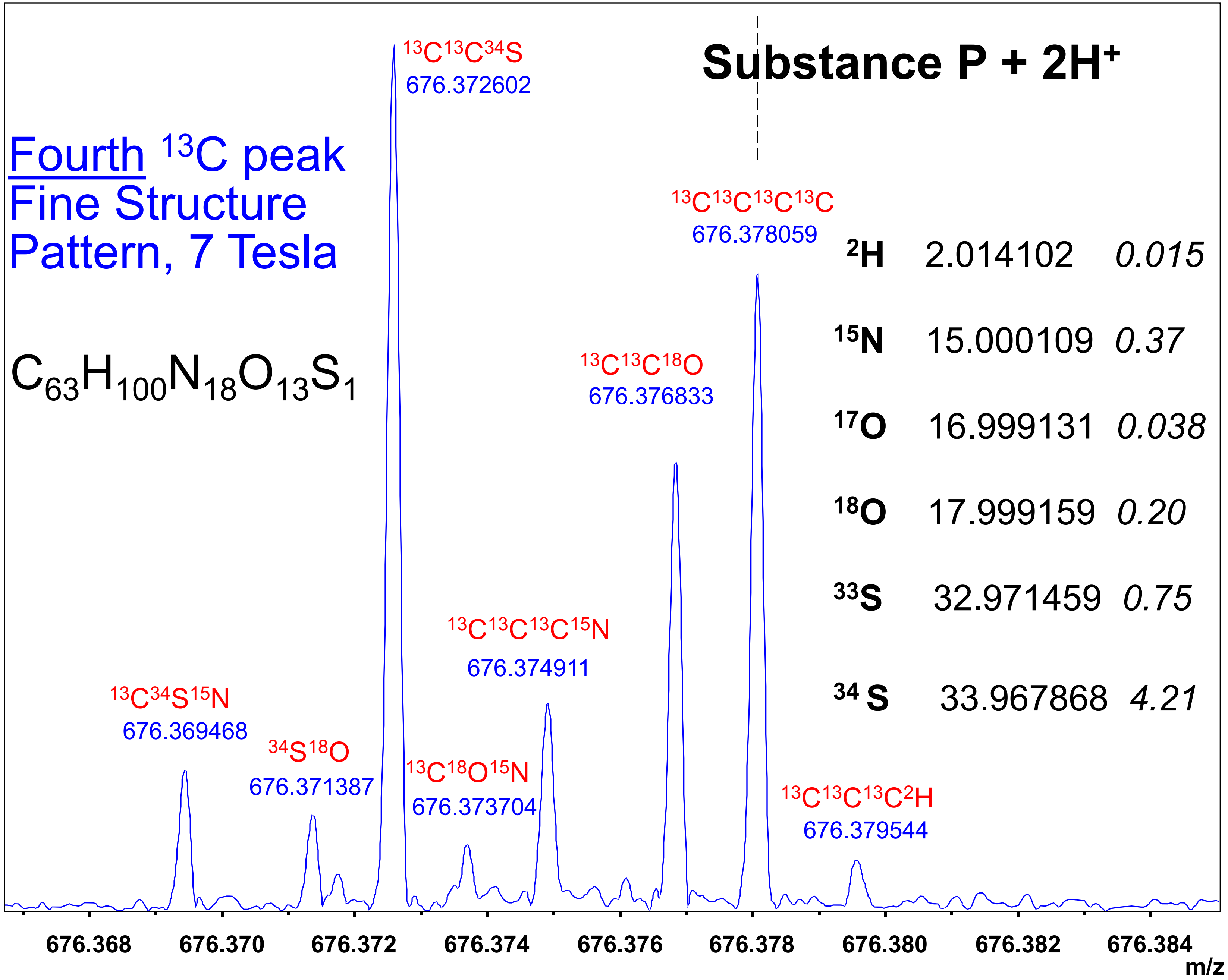


Substance P + 2H⁺ $C_{63}H_{100}N_{18}O_{13}S_1$



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





Fourth 13C peak
Fine Structure
Pattern, 7 Tesla
C63H100N18O13S1
Substance P + 2H+
13C13C34S
676.372602
13C13C13C13C
676.378059
13C13C18O
676.376833
13C13C13C15N
676.374911
13C34S15N
676.369468
34S18O
676.371387
13C18O15N
676.373704
13C13C13C2H
676.379544
2H 2.014102 0.015
15N 15.000109 0.37
17O 16.999131 0.038
18O 17.999159 0.20
33S 32.971459 0.75
34 S 33.967868 4.21
676.368
676.370
676.372
676.374
676.376
676.378
676.380
676.382
676.384
m/z

In 2015 we had Milestone events in FT ICR mass spectrometry

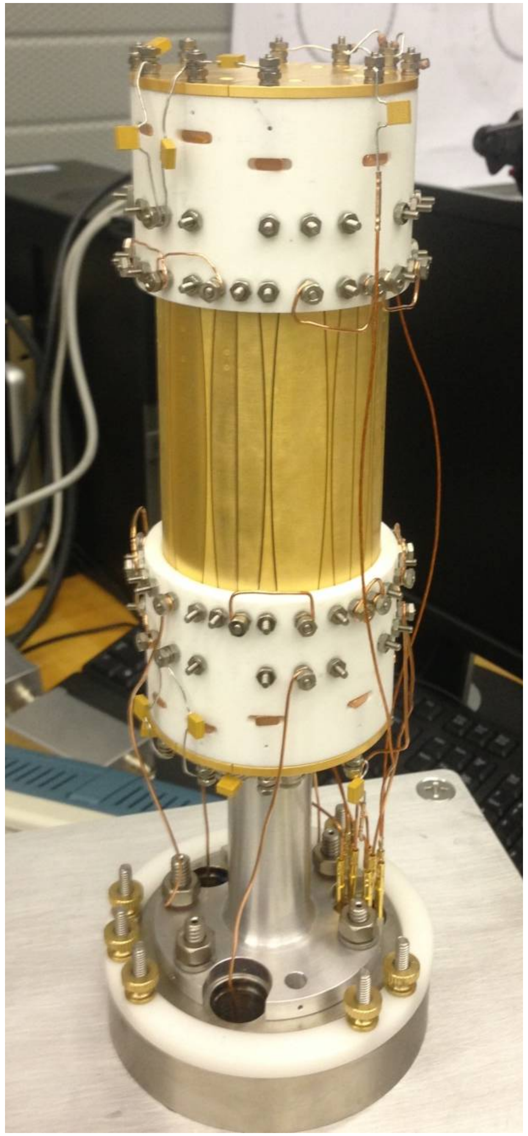
Launching two 21 tesla FT ICR mass Spectrometers

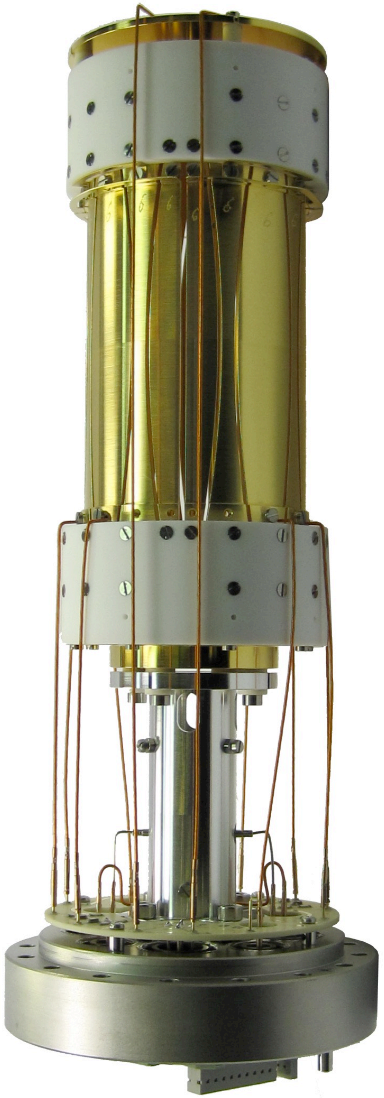
In National High Magnetic Field Laboratory NHMFL (Tallahassee Florida)

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

National High Magnetic Field Laboratory NHMFL
(Tallahassee Florida)

From Alan Marshall 10th NA FTMS 21 T talk

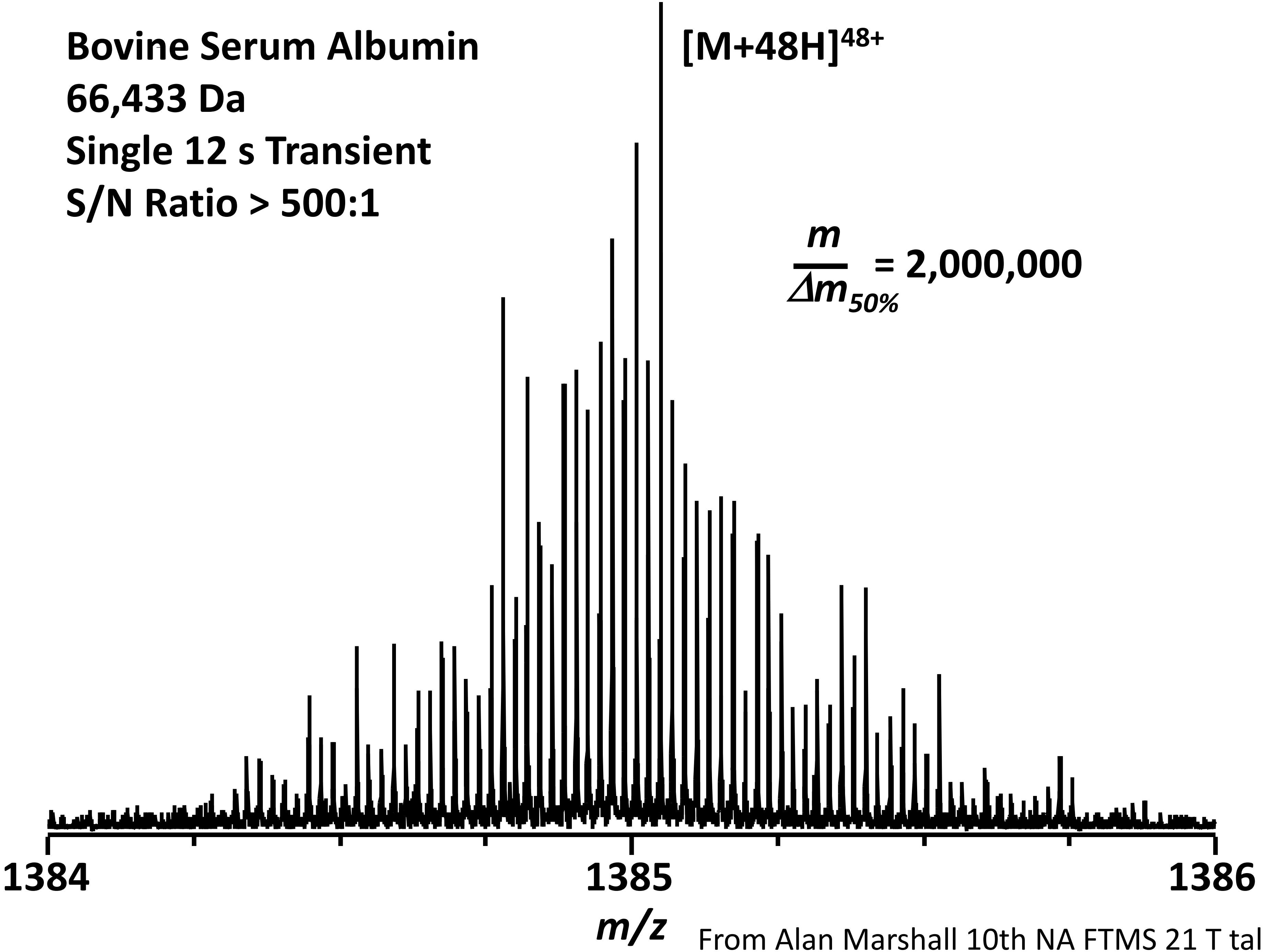


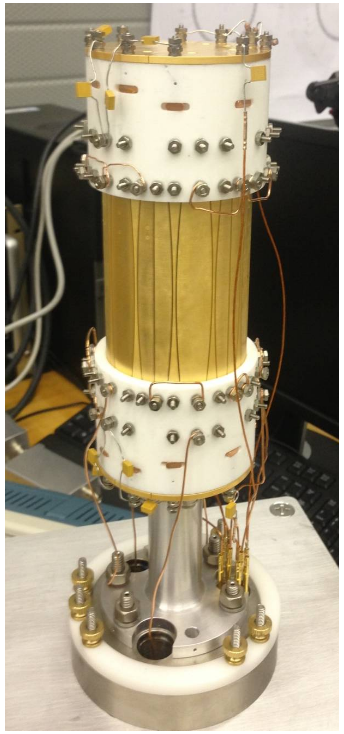


Bruker
SolariX
solariX 2xR
scimaX

From Alan Marshall 10th NA FTMS 21 T talk

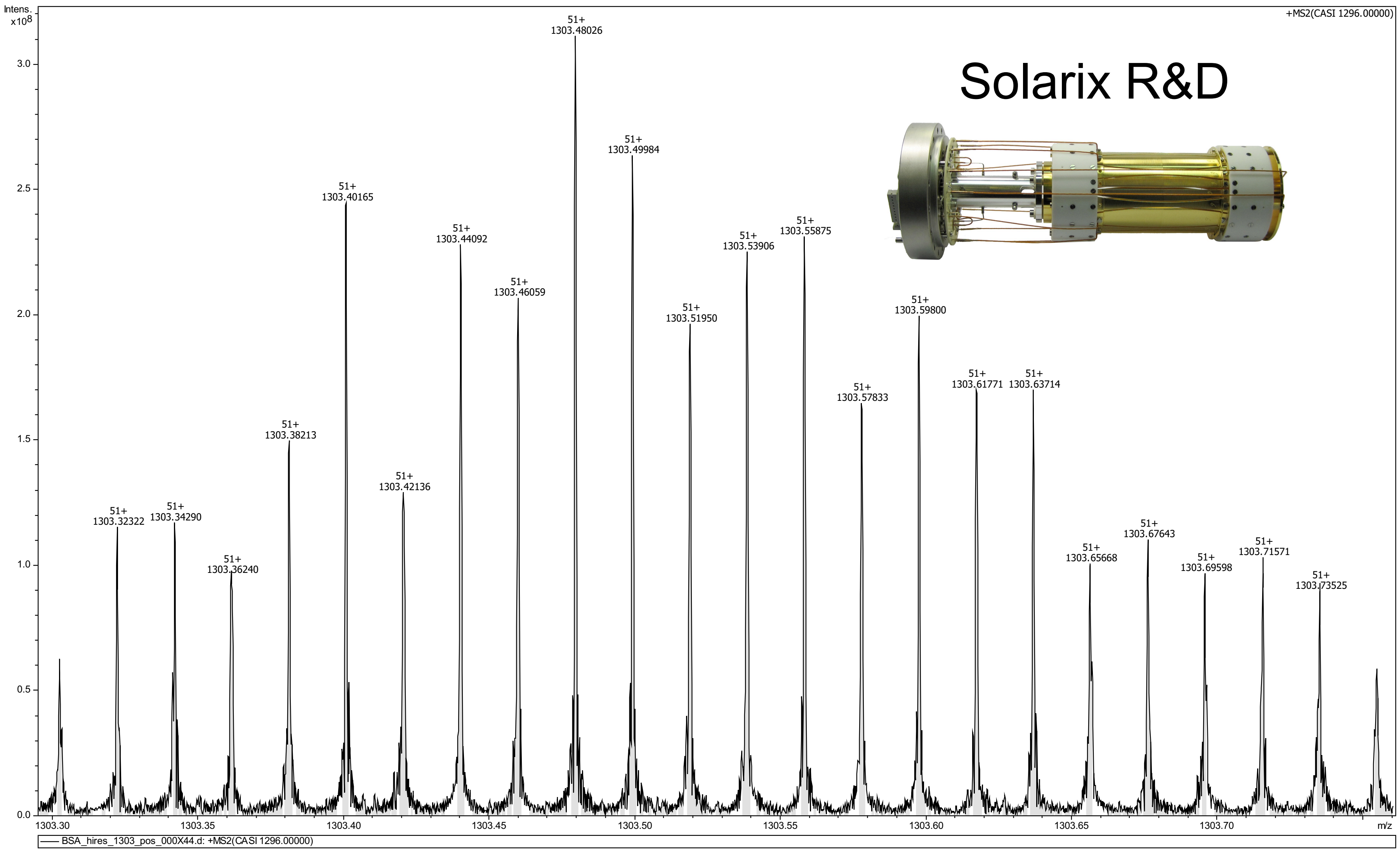
Solarix R&D



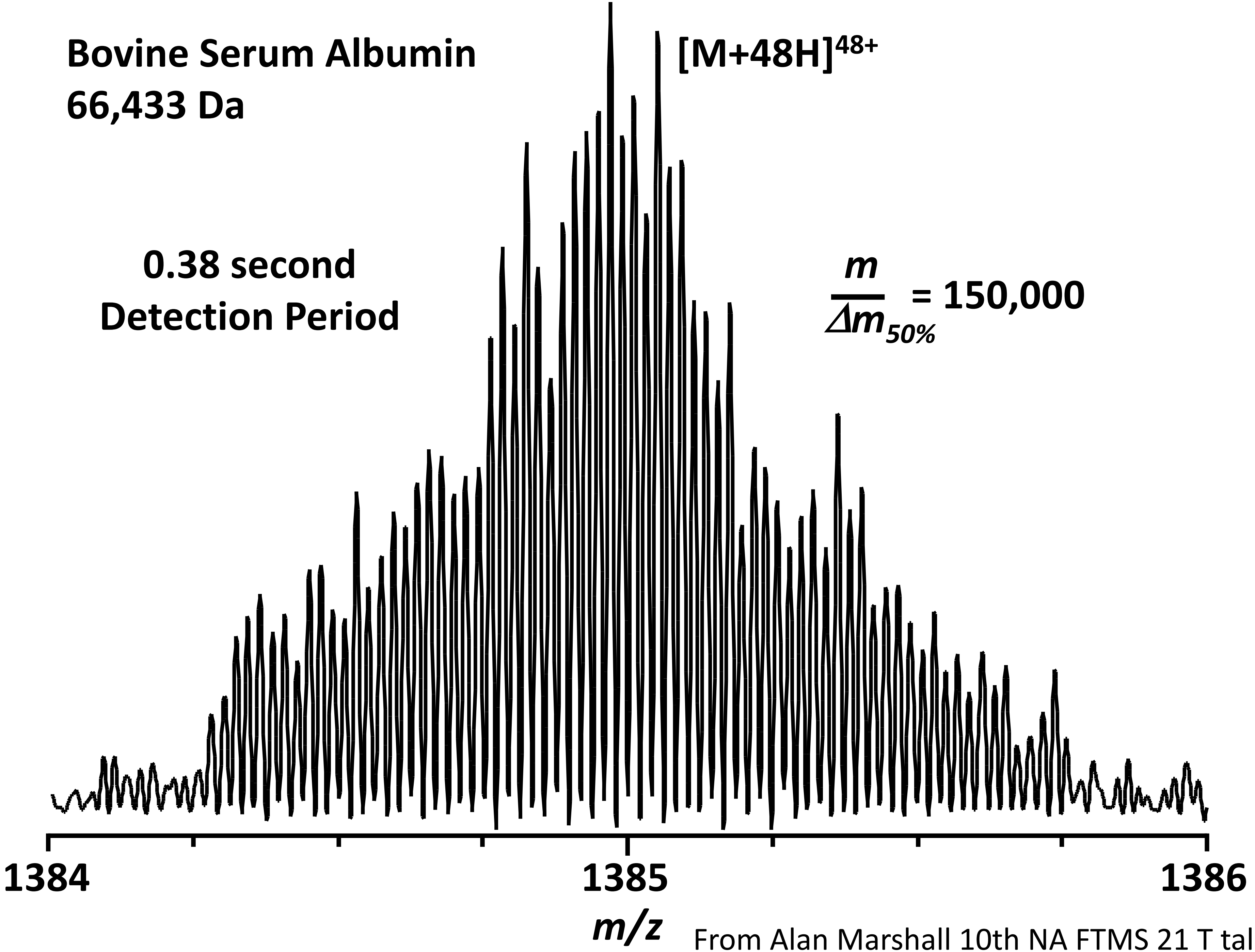


From Alan Marshall 10th NA FTMS 21 T talk

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

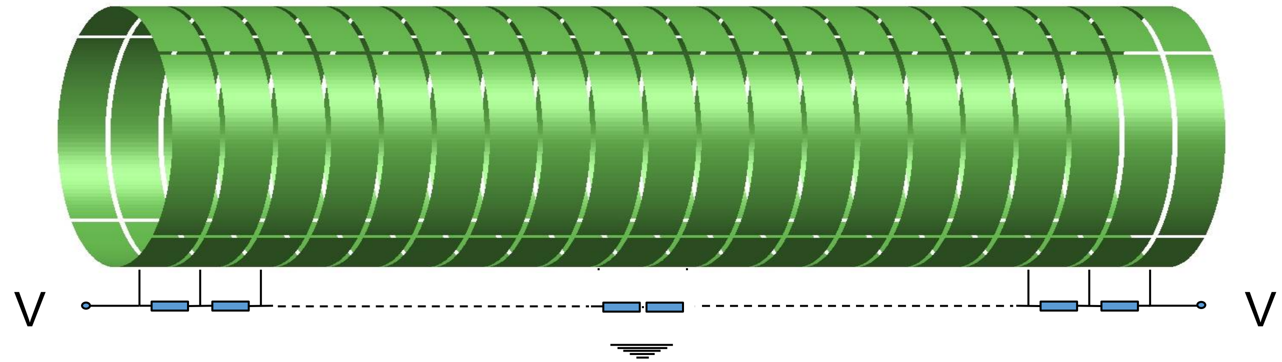


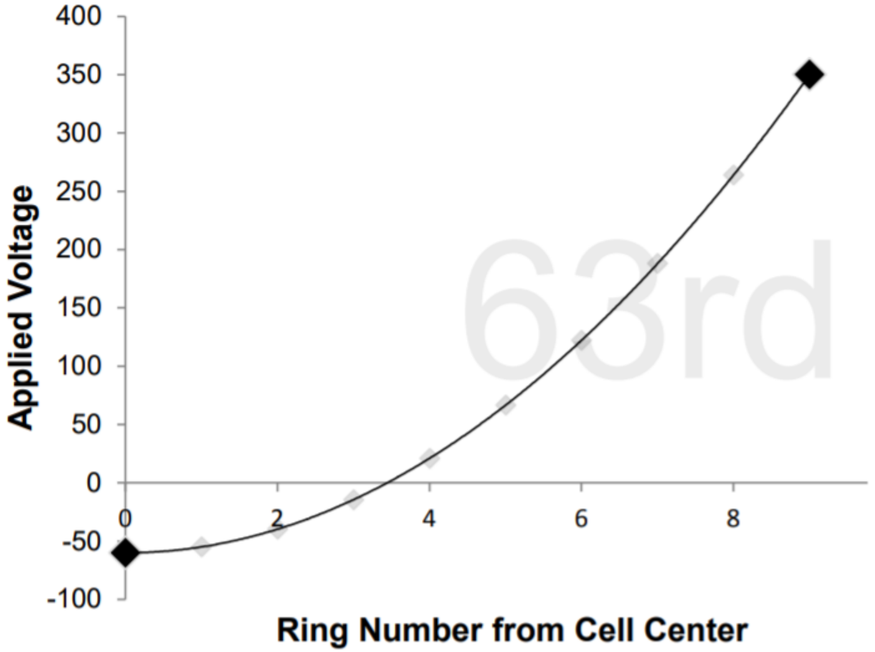
Solarix R&D

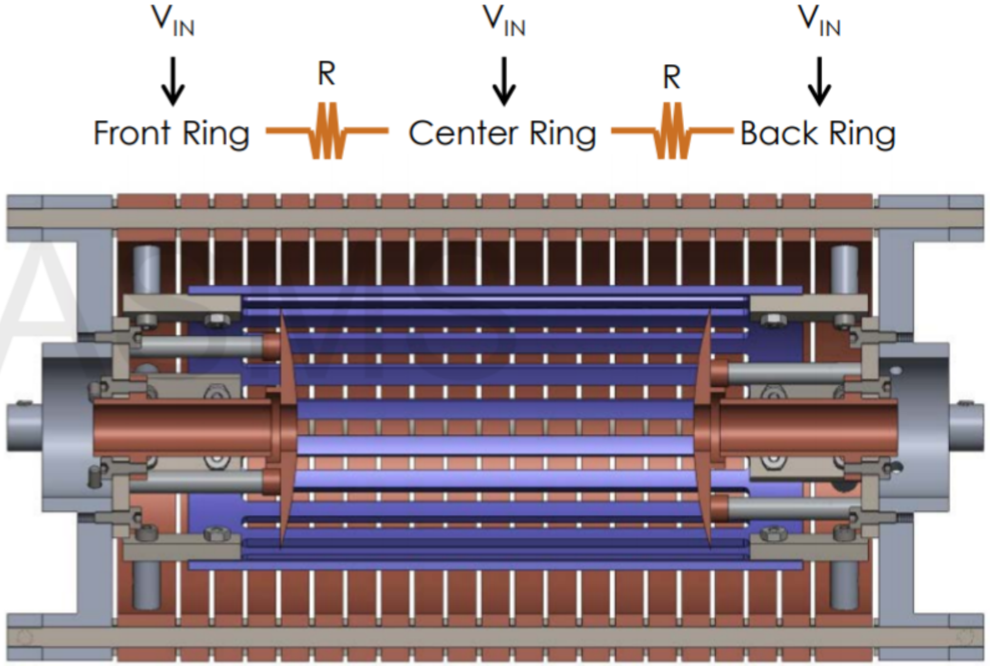


From Alan Marshall 10th NA FTMS 21 T talk

“Window” PNNL cell

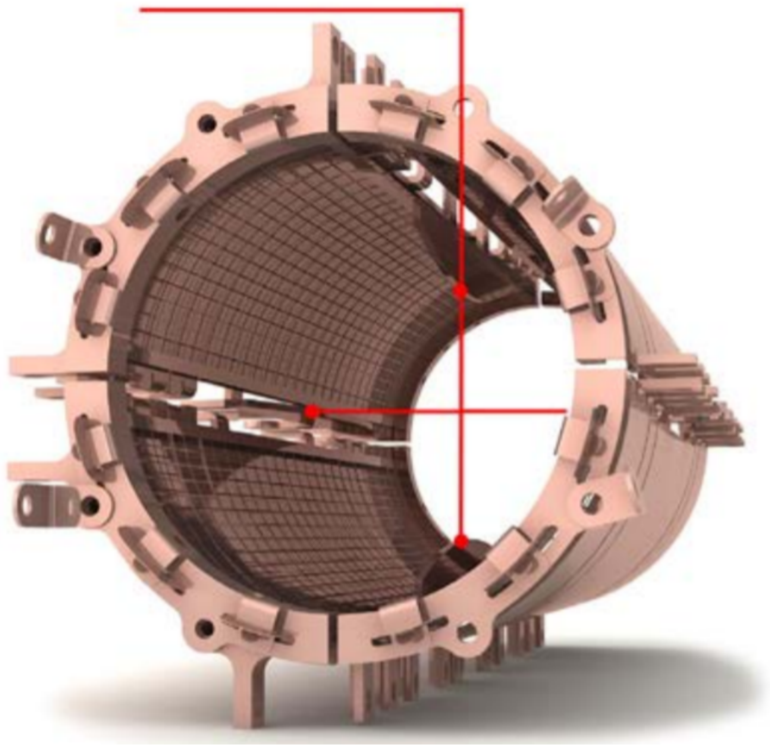




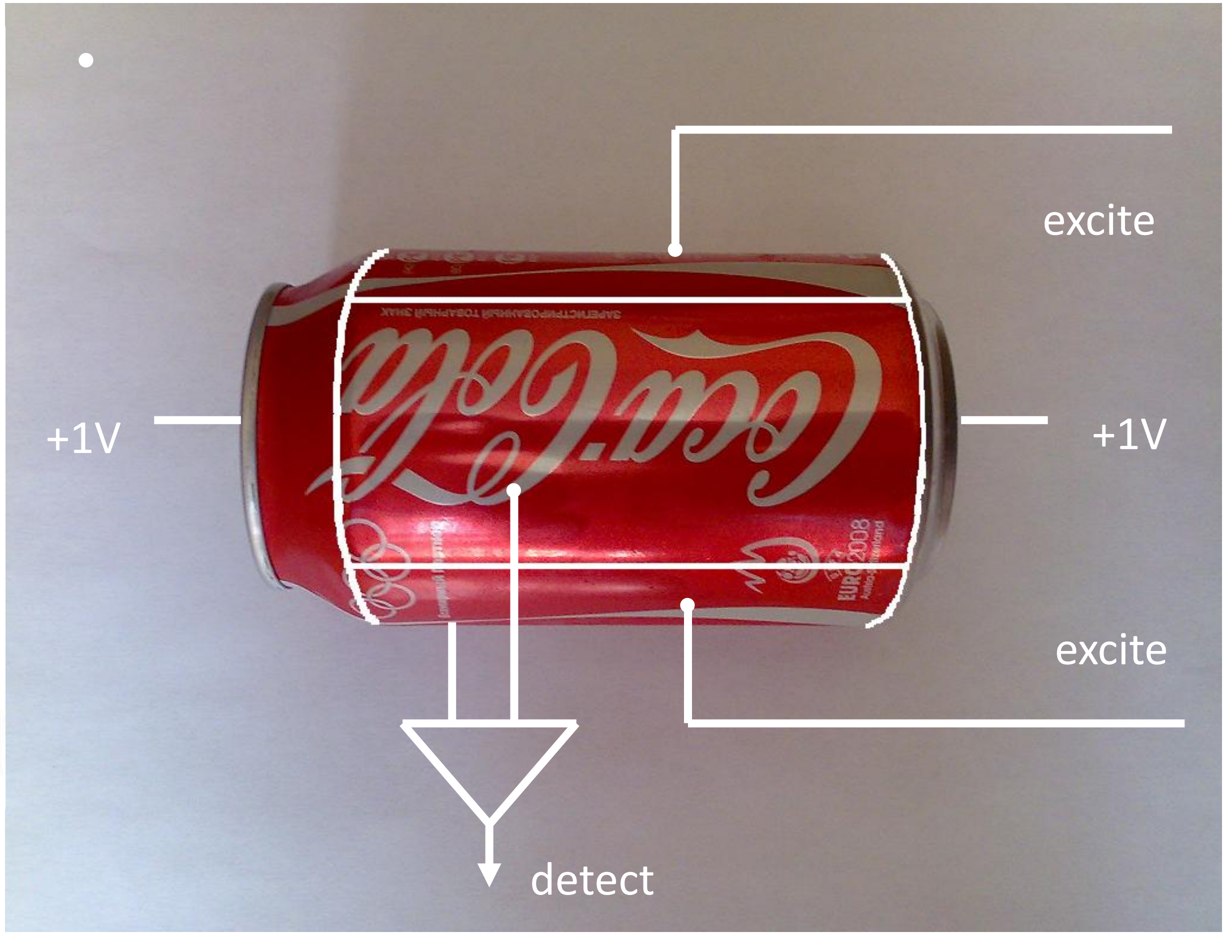


Jared Shaw ; Tzu-yung Lin ; Aleksey V Tolmachev ;Errol W Robinson ; David W Koppenaal ; Ljiljana Pasa-Tolic

Fancy cells. Not harmonized. With proper tuning more than 1 million resolution is possible as well



Spectroswiss NADEL cell



Coca Cola cell

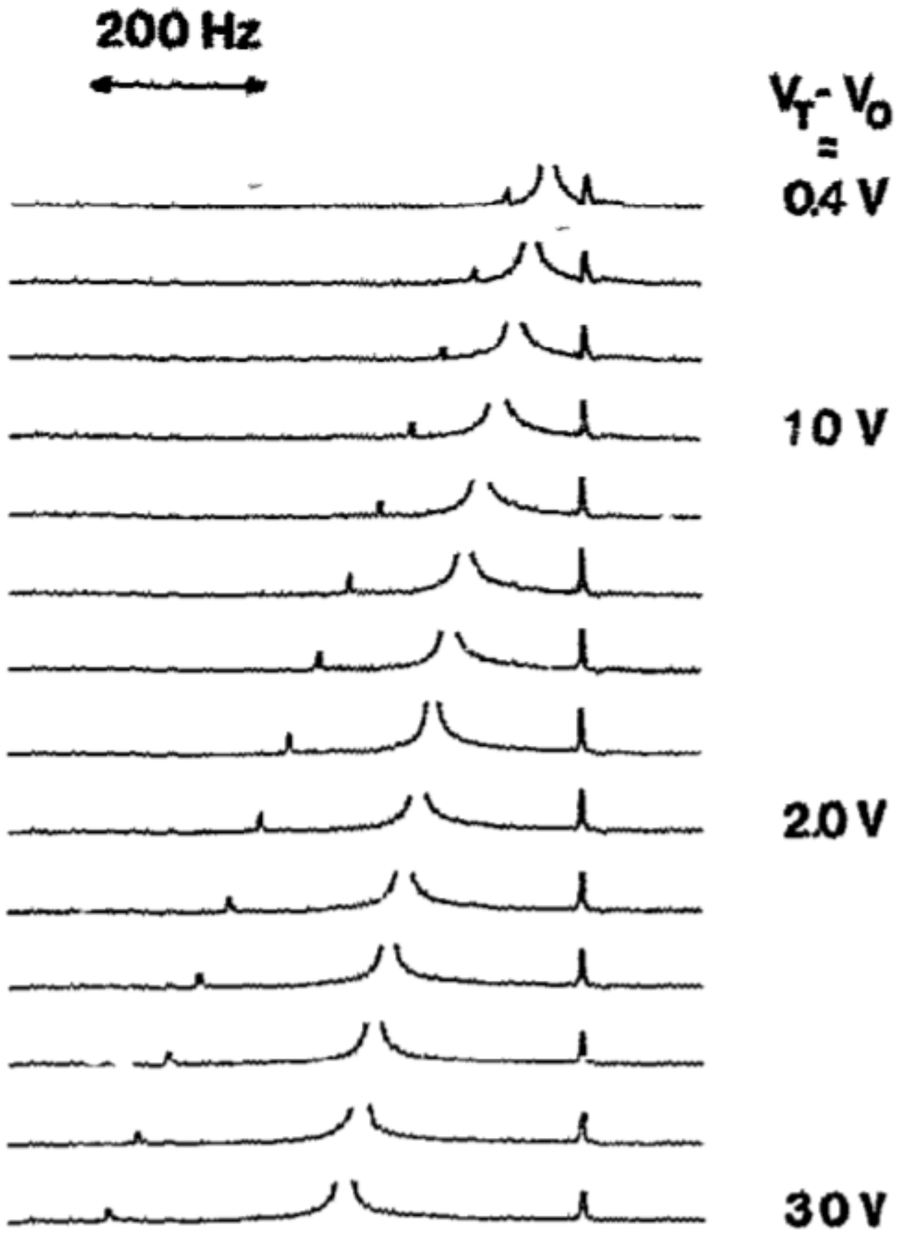


Fig. 3 Sidebands of the N_2^+ peak and their dependence upon the potential $V_t - V_0$, measured every 0.2 V

M.Alemann, H.P.Kellerhals, K.-P.Wanczek Sidebands in the ICR spectrum and their application for exact mass determination, Chemical Physics Letters, Volume 84, Issue 3, 15 December 1981, Pages 547-551

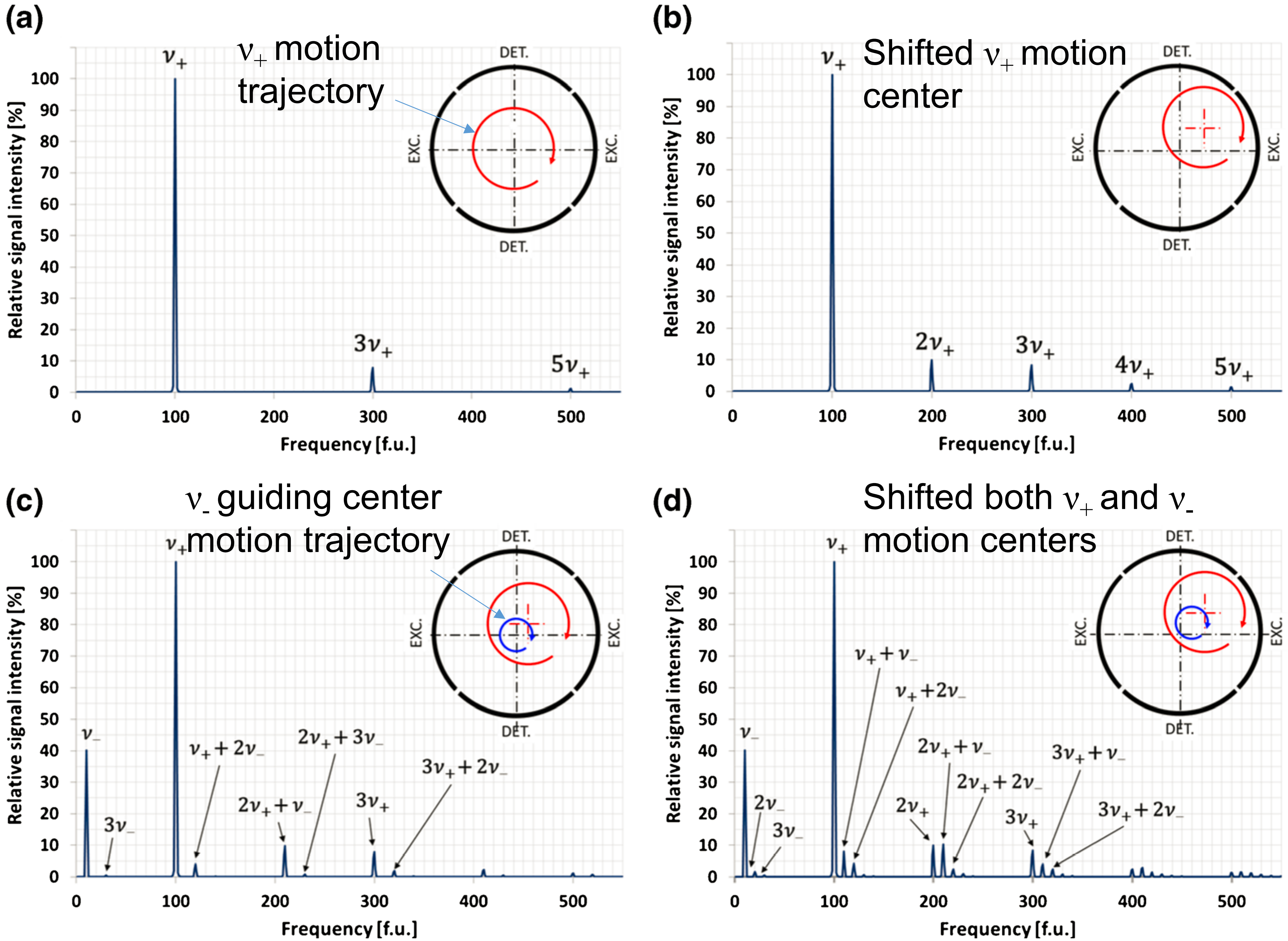
$$\omega_R \approx \omega_c + [(V_t - V_0)/a^2B]\,[(\alpha\lambda)^{1/2} - \beta]$$

$$\approx \omega_c + \omega_{cor}, \qquad (11)$$

where ω_{cor} is small compared with ω_c. Making use of relation (4).

$$\omega_R \approx \omega_c = qB/m. \qquad (12)$$

If the ICR cell has a square cross section orthogonal to the direction of the magnetic field, the sideband ω_R does not depend on cell potentials and cell dimensions and equals the cyclotron frequency ω_c



(a)
ν+ motion trajectory
DET.
EXC.
Relative signal intensity [%]
Frequency [f.u.]
ν+
3ν+
5ν+
(b)
Shifted ν+ motion center
DET.
EXC.
Relative signal intensity [%]
Frequency [f.u.]
ν+
2ν+
3ν+
4ν+
5ν+
(c)
ν- guiding center
ν+motion trajectory
DET.
EXC.
Relative signal intensity [%]
Frequency [f.u.]
ν-
3ν-
ν+ + 2ν-
2ν+ + ν-
2ν+ + 3ν-
3ν+
3ν+ + 2ν-
(d)
Shifted both ν+ and ν- motion centers
DET.
EXC.
Relative signal intensity [%]
Frequency [f.u.]
ν-
2ν-
3ν-
ν+ + ν-
ν+ +2ν-
2ν+ + ν-
2ν+
2ν+ + 2ν-
3ν+
3ν+ + ν-
3ν+ + 2ν-

Therefore the output signal of the receiver

$$U(t) = U_0 \sin(\omega_{eff} t)[1 + \epsilon \sin(\omega_d t)] \quad (8)$$

is an rf voltage $U(t)$ with frequency ω_{eff} modulated with frequency ω_d

A simple transformation yields

$$U(t) = U_0 \sin(\omega_{eff} t) - \tfrac{1}{2} U_0 \epsilon \cos[(\omega_{eff} + \omega_d) t]$$

$$+ \tfrac{1}{2} U_0 \epsilon \cos[(\omega_{eff} - \omega_d) t], \quad (9)$$

which after Fourier transformation results in a carrier frequency ω_{eff} with two symmetrically arranged side-

$$\omega_R \approx \omega_c + [(V_t - V_0)/a^2 B]\,[(\alpha\lambda)^{1/2} - \beta]$$

$$\approx \omega_c + \omega_{cor}, \quad (11)$$

where ω_{cor} is small compared with ω_c. Making use of relation (4).

$$\omega_R \approx \omega_c = qB/m. \quad (12)$$

If the ICR cell has a square cross section orthogonal to the direction of the magnetic field, the sideband ω_R does not depend on cell potentials and cell dimensions and equals the cyclotron frequency ω_c

M.Alemann, H.P.Kellerhals, K.-P.Wanczek Sidebands in the ICR spectrum and their application for exact mass determination, Chemical Physics Letters, Volume 84, Issue 3, 15 December 1981, Pages 547-551