Nobel Prize 1989

H. Dehmelt

W. Paul

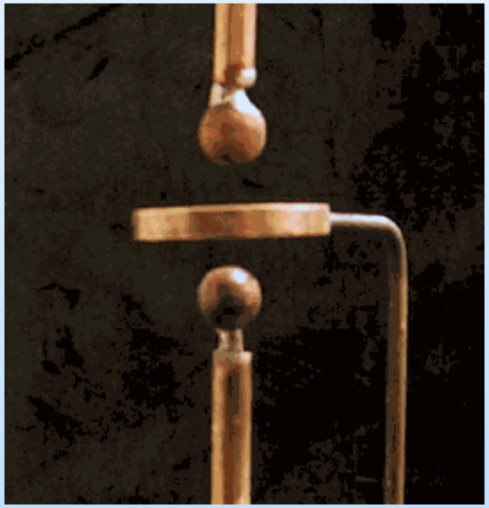
"Their development of the Ion Trap technique"

Norman F. Ramsey

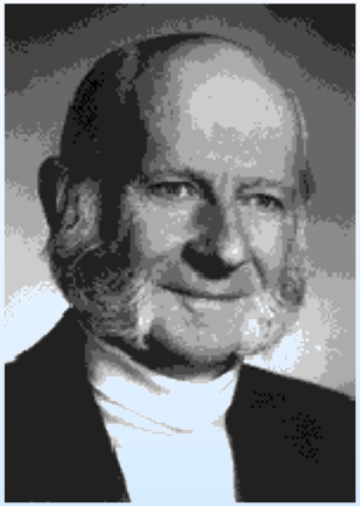
"The invention of the separated oscillator fields method and its use in the hydrogen maser and other atomic clocks"

The Simple Paul Trap

Edge View

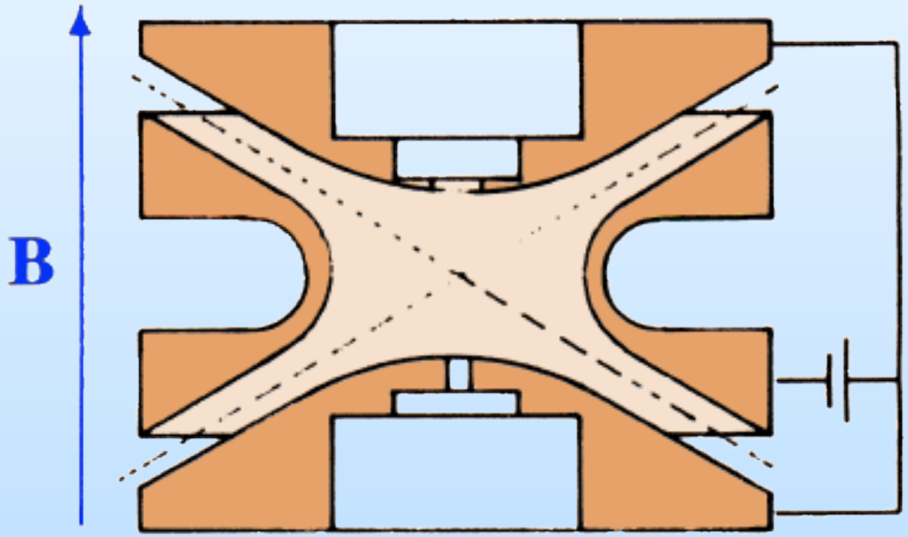


One-Quarter Up



Hans Dehmelt
University of Washington

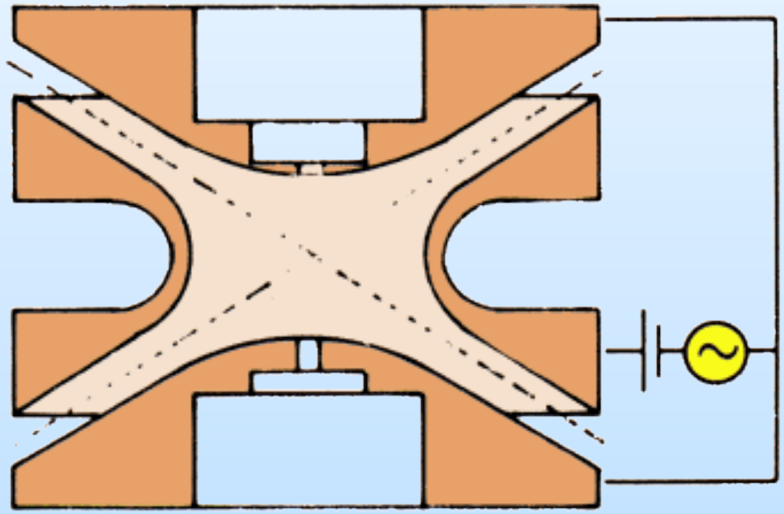
The Penning Trap



Penning trap
DC plus magnetic field

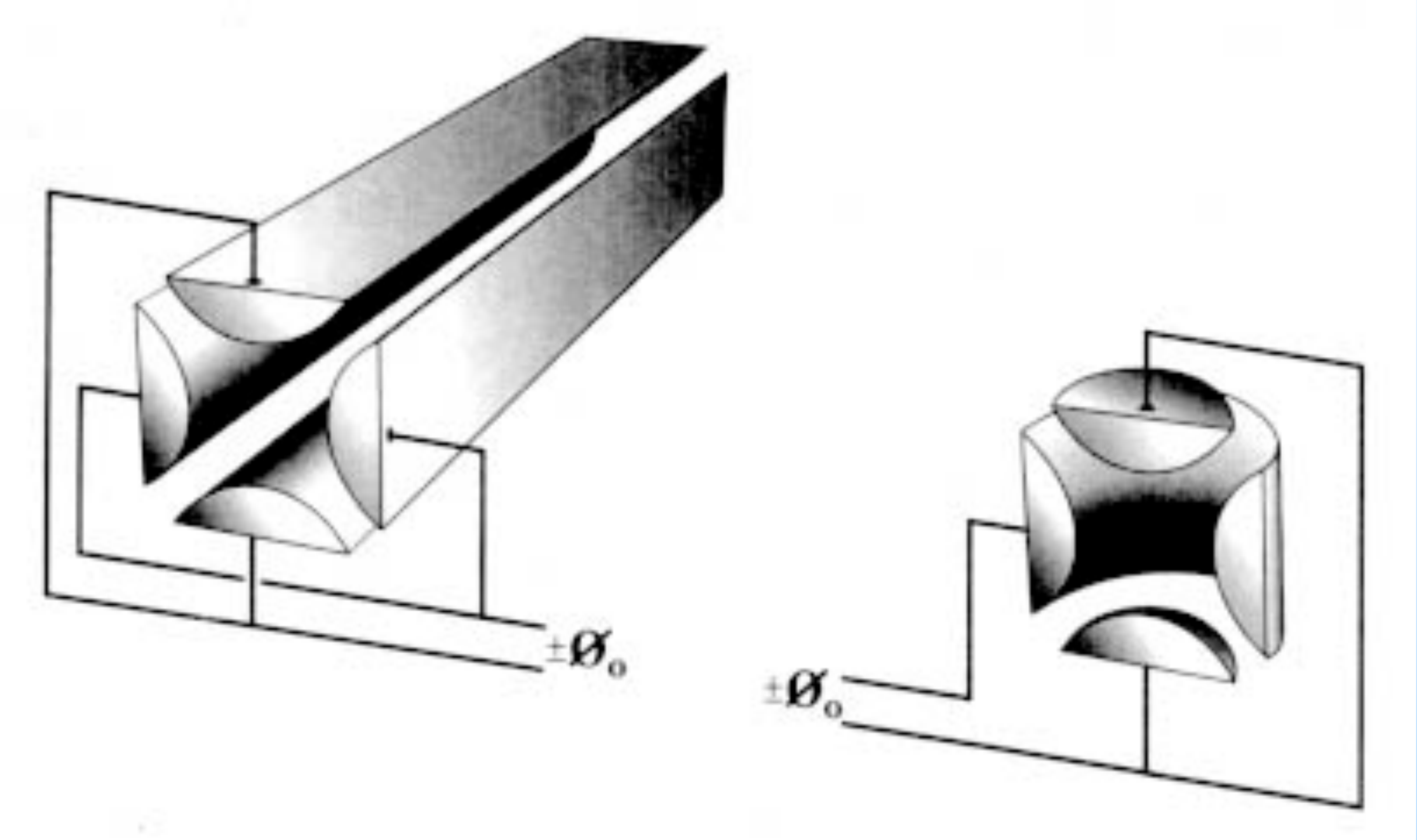
The Paul Trap

Wolfgang Paul
University of
Bonn



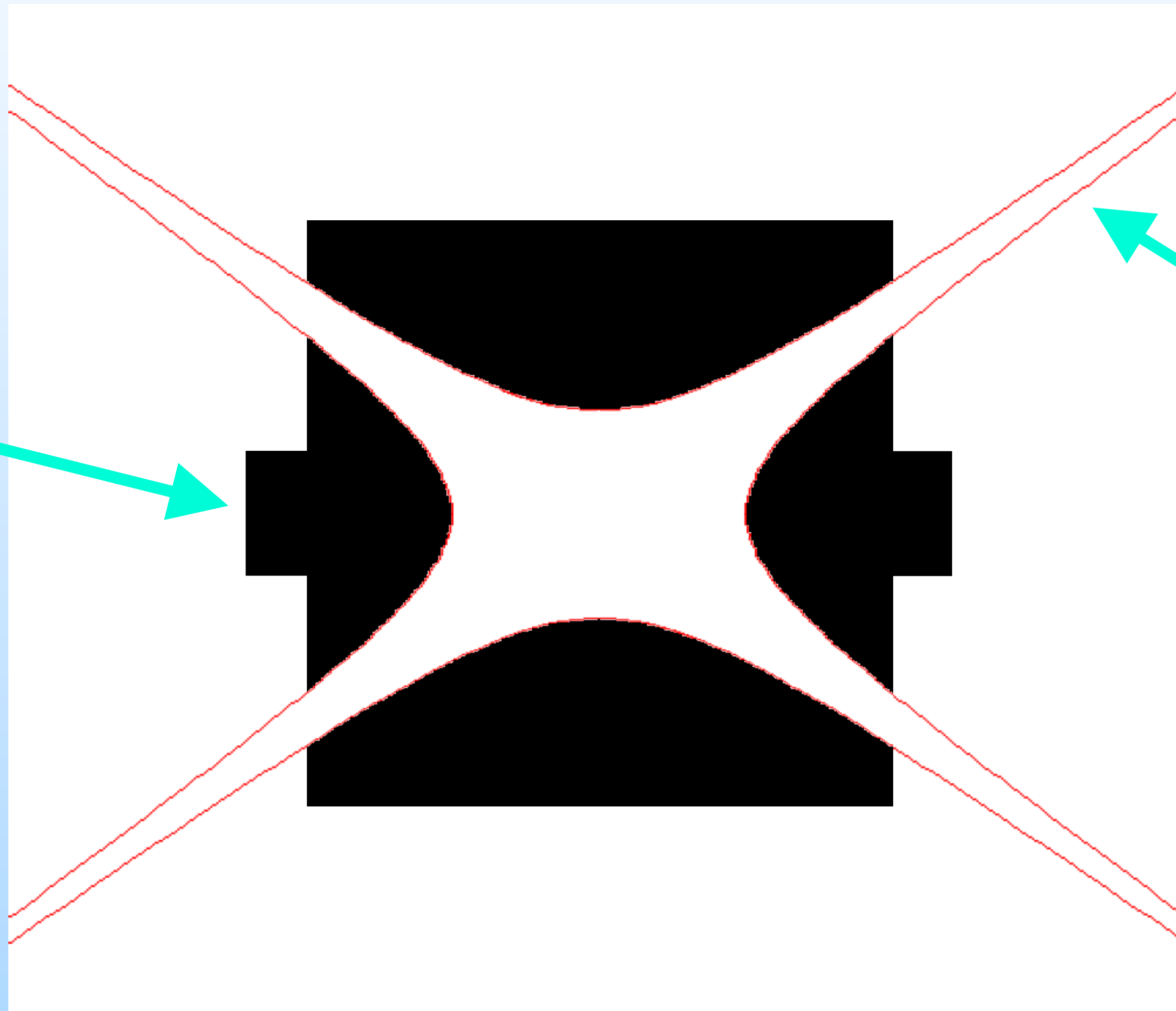
Paul trap
DC plus radiofrequency

Mass Analyzers: Quadrupole ion trap?



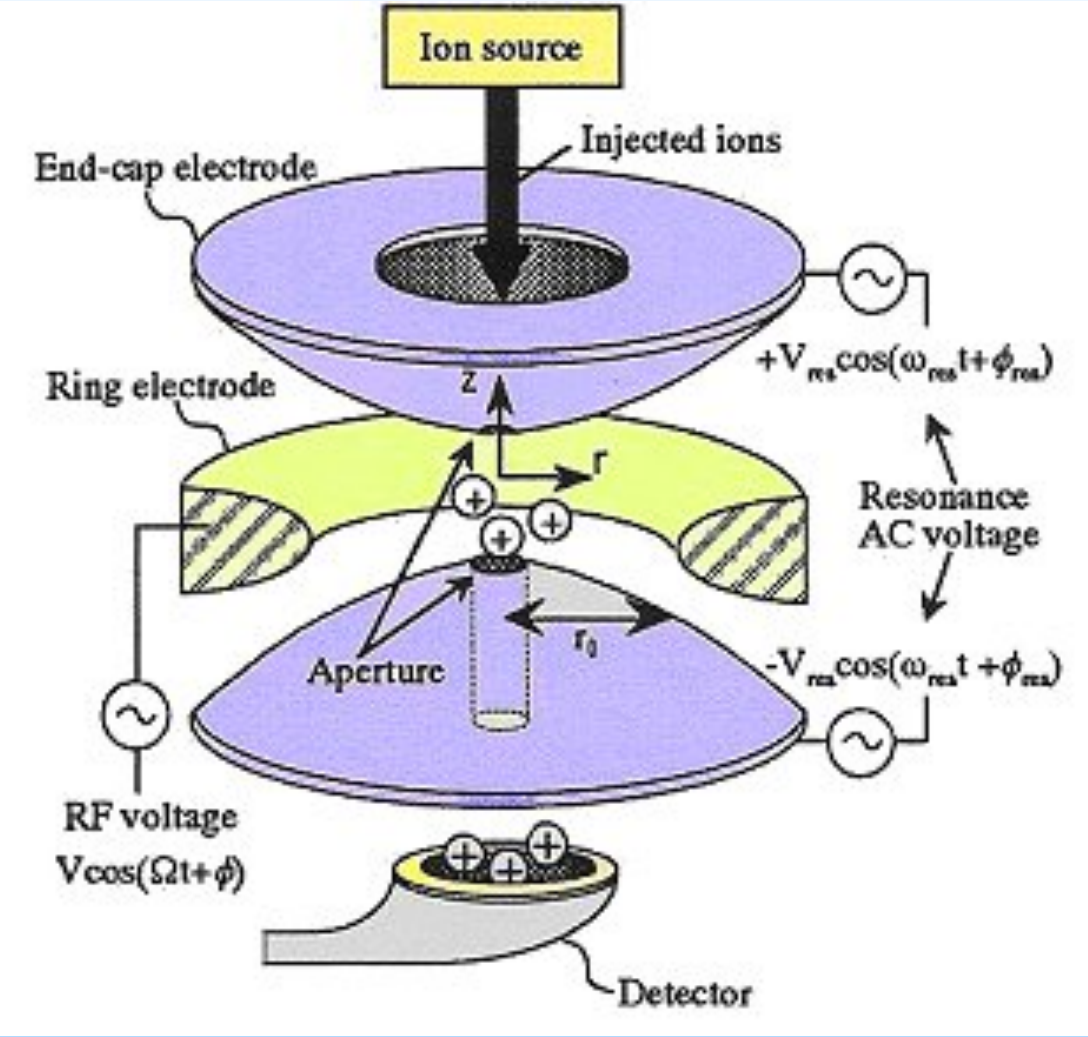
“Ideal” Geometry Quadrupole Trap

Actual physical electrodes



Theoretical “infinite” hyperbolic electrodes

Mass Analyzers: ION TRAPS



- Three-dimensional quadrupole field
- Wolfgang Paul Nobel Prize1989
- MS^n capability.

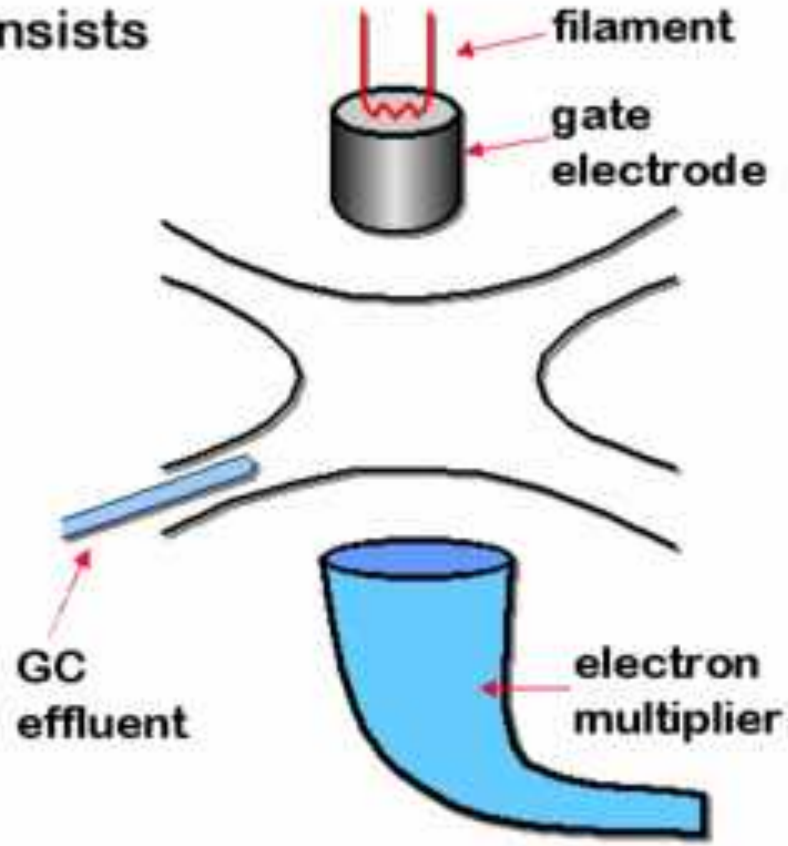
Ion trap

An ion trap analyzer consists of three electrodes.

The center electrode is doughnut shaped.

The top and bottom electrodes are hemispherical.

Ionization and mass analysis all occur in the same place.

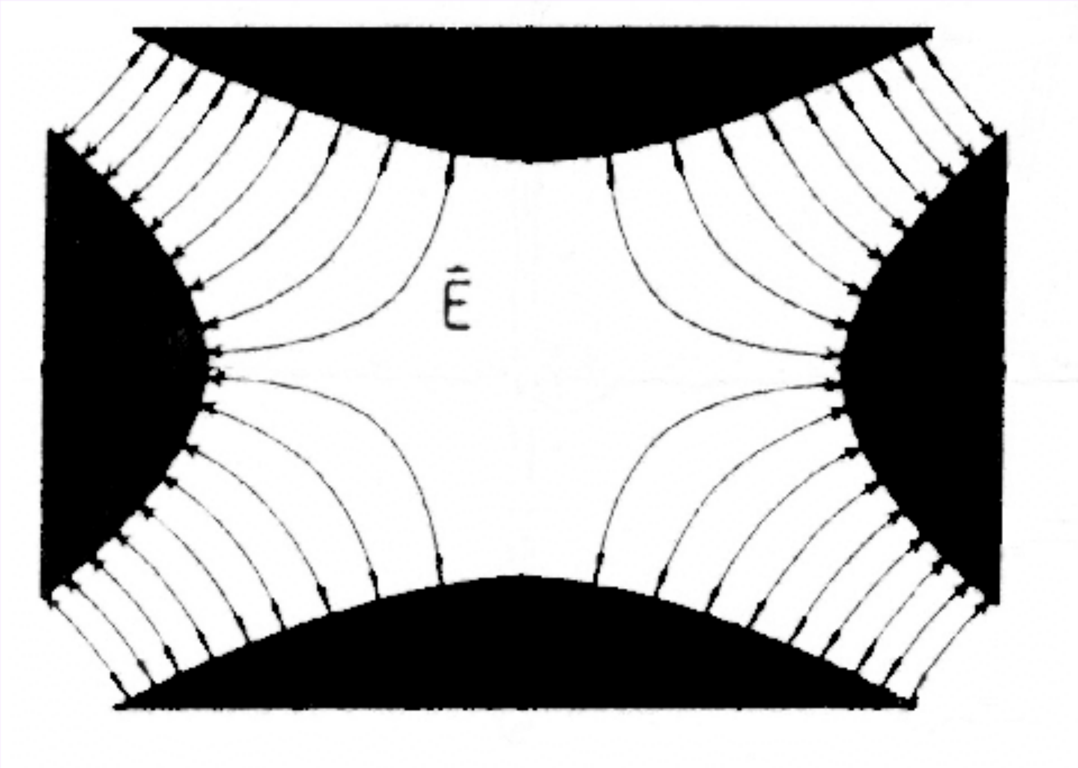


Ion trap sequence

* Do 'full' ionization of sample.
* Dump and count all ions produced.
* Based on the size of the ion pulse, adjust size of second ionization
* Do second ionization
* Acquire spectrum.

An entire spectrum (20-650 M/Z) can be obtained every second (or less).

The Quadrupole Electric Field

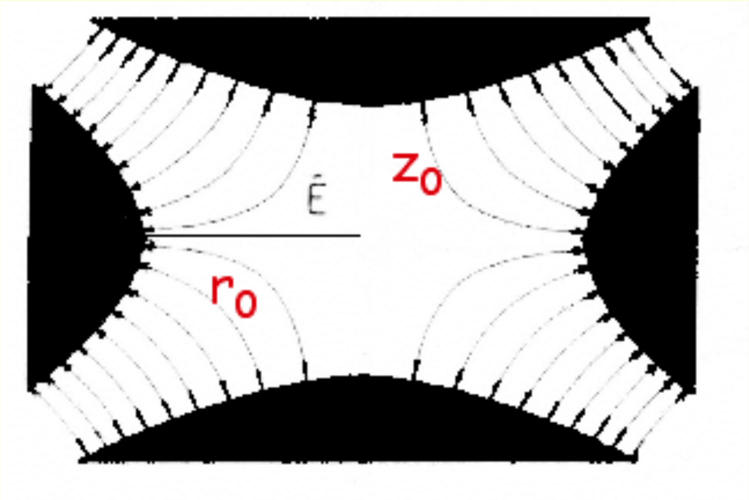


Electric Potential:

$$V(z,r) = \frac{[V_{DC} - V_{AC}\cos(\Omega t)] * [2z^2 + (r_0^{\ 2} - r^2)]}{4z_0^{\ 2}}$$

Electric Field:

$$E_z = -\frac{\partial V}{\partial z} = -\frac{(V_{DC} - V_{AC}\cos(\Omega t))}{z_0^{\ 2}} z \qquad E_r = -\frac{\partial V}{\partial r} = \frac{(V_{DC} - V_{AC}\cos(\Omega t))}{r_0^{\ 2}} r$$



Components of Force:

$$F_z = Q \cdot \left(-\frac{V_{DC} - V_{AC}\cos(\Omega t)}{z_0^{\ 2}} z \right) = M\left(\frac{d^2 z}{dt^2}\right)$$

$$F_r = Q \cdot \left(\frac{V_{DC} - V_{AC}\cos(\Omega t)}{r_0^{\ 2}} r \right) = M\left(\frac{d^2 r}{dt^2}\right)$$

Equations of Motion:

$$\frac{d^2 z}{dt^2} - \left(\frac{Q}{M}\right) \cdot \left(-\frac{V_{DC} - V_{AC}\cos(\Omega t)}{z_0^{\ 2}} z \right) = 0$$

$$\frac{d^2 r}{dt^2} - \left(\frac{Q}{M}\right) \cdot \left(\frac{V_{DC} - V_{AC}\cos(\Omega t)}{r_0^{\ 2}} r \right) = 0$$

Equations of Motion:

$$\frac{d^2z}{dt^2} - \left(\frac{Q}{M}\right) \cdot \left(-\frac{V_{DC} - V_{AC}\cos(\Omega t)}{z_0^{\,2}} z\right) = 0$$

$$\frac{d^2r}{dt^2} - \left(\frac{Q}{M}\right) \cdot \left(\frac{V_{DC} - V_{AC}\cos(\Omega t)}{r_0^{\,2}} r\right) = 0$$

Substitutions:

$$a_z = -a_r = 4\left(\frac{Q}{M}\right)\left(\frac{V_{DC}}{z_0^{\,2}\Omega^2}\right)$$

$$q_z = -2q_r = 2\left(\frac{Q}{M}\right)\left(\frac{V_{AC}}{z_0^{\,2}\Omega^2}\right)$$

$$x = \frac{\Omega t}{2}$$

Simplified Equations of Motion:

$$\frac{d^2 z}{dx^2} - \left(a_z + 2q_z\cos(2x)\right) \cdot z = 0$$

$$\frac{d^2 r}{dx^2} + 2\left(a_r - 2q_r\cos(2x)\right) \cdot r = 0$$

Equations of Motion:

$$\frac{d^2 z}{dx^2} - (a_z + 2q_z \cos(2x)) \cdot z = 0$$

$$\frac{d^2 r}{dx^2} + 2(a_r - 2q_r \cos(2x)) \cdot r = 0$$

Canonical Mathieu Equation:

$$\frac{\mathbf{d^2 u}}{\mathbf{dx^2}} + (\mathbf{a - 2q \cos(2x))u} = 0$$

Solution to Mathieu Equation:

$$u(x) = \alpha' e^{(\alpha \pm i\beta)x} \sum_{n=-\infty}^{n=\infty} C_{2n} e^{2inx} + \alpha'' e^{-(\alpha \pm i\beta)x} \sum_{n=-\infty}^{n=\infty} C_{2n} e^{-2inx}$$

Stability

$$u(x) = \alpha' e^{(\alpha \pm i\beta)x} \sum_{n=-\infty}^{n=\infty} C_{2n} e^{2inx} + \alpha'' e^{-(\alpha \pm i\beta)x} \sum_{n=-\infty}^{n=\infty} C_{2n} e^{-2inx}$$

$$\text{where } \beta = \sqrt{a + \left(\frac{q^2}{2}\right)}$$

1) $\alpha = 0$

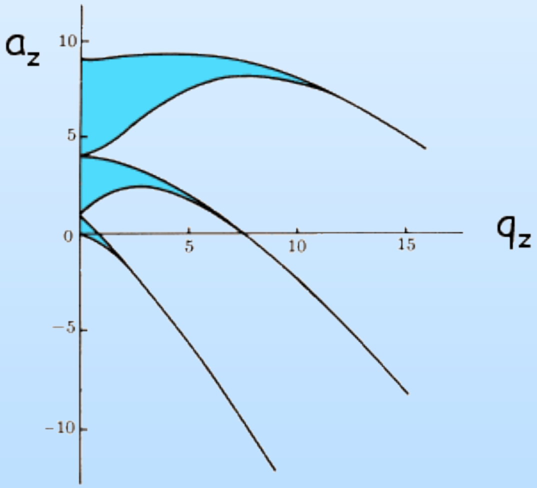
2) $\beta \neq \text{integer}$

Equations of Motion:

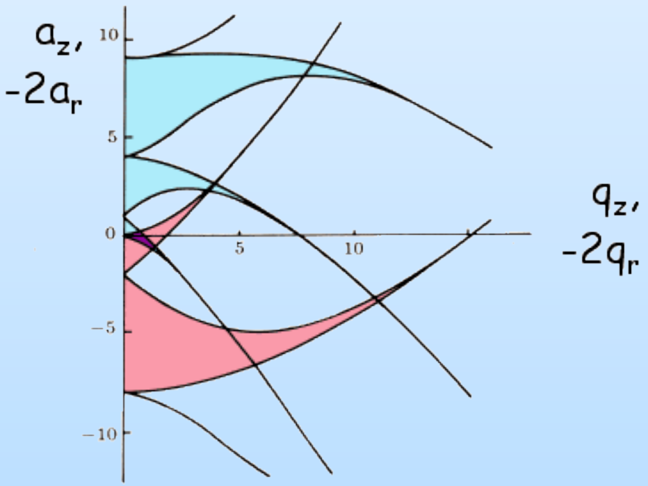
$d^2z/dx^2 - (a_z - 2q_z \cos(2x))*z = 0$

$d^2r/dx^2 + 2(a_r - 2q_r \cos(2x))*r = 0$

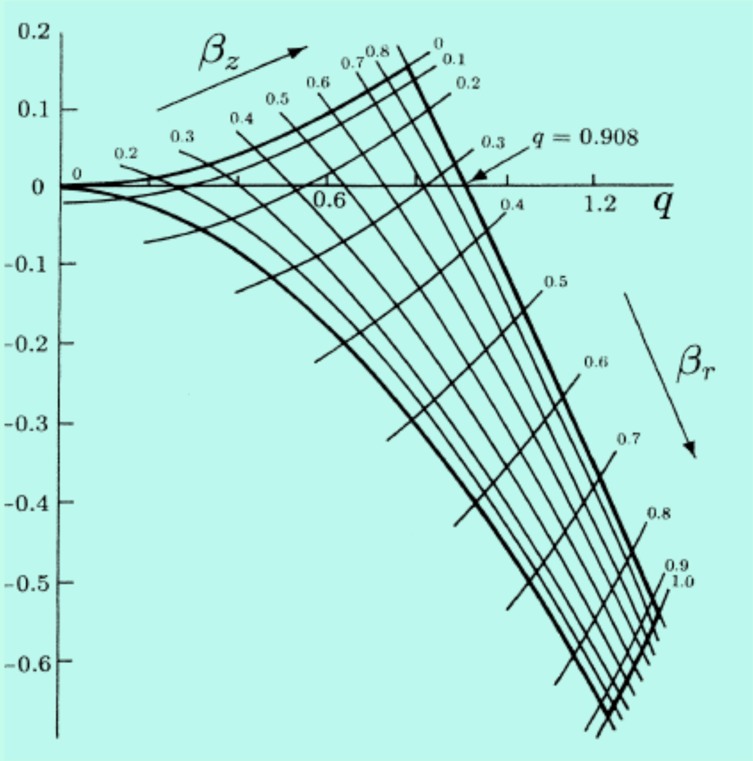
Stability Regions for the z Coordinate only



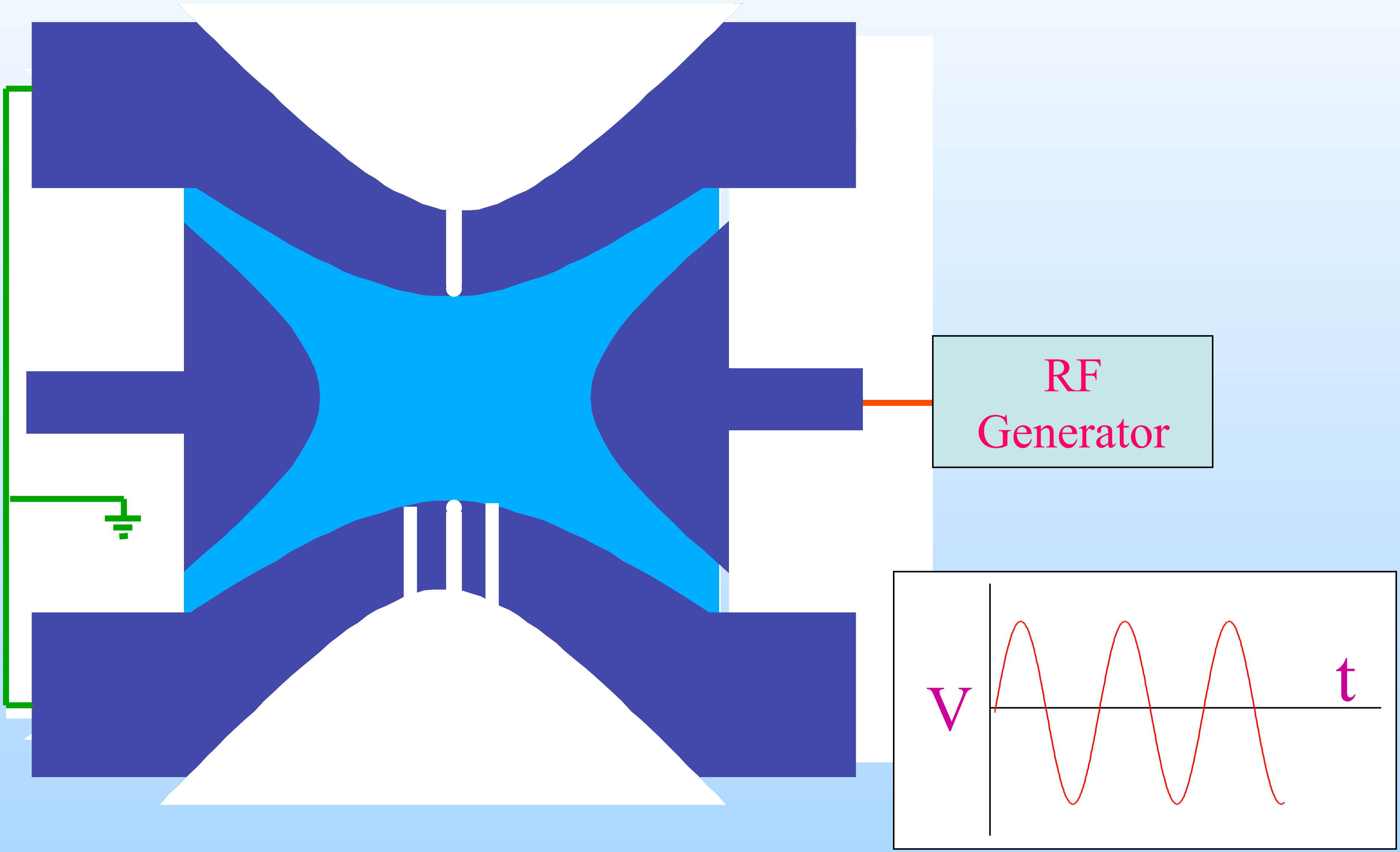
Stability Regions for z and r Coordinates



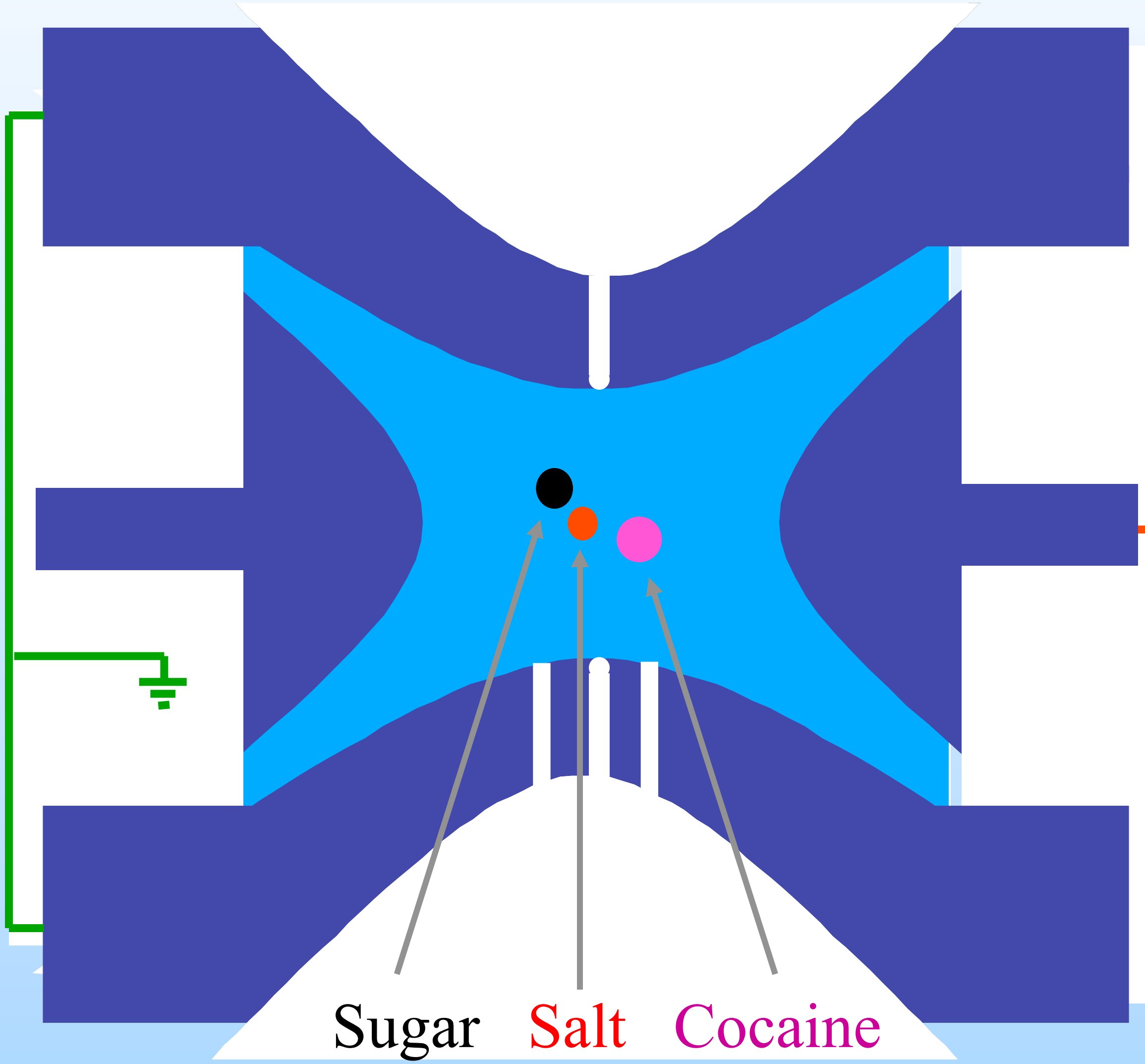
The First Stability Region



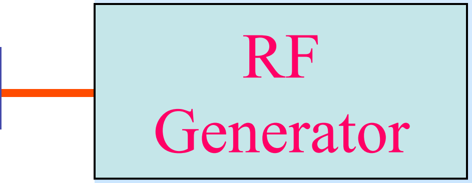
Generating Fields in an Ion Trap

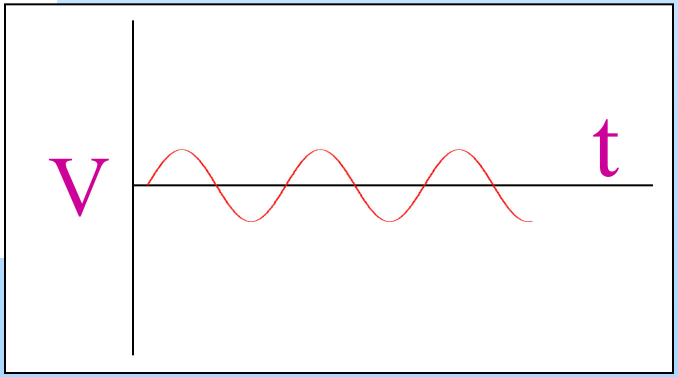


Trapping Ions

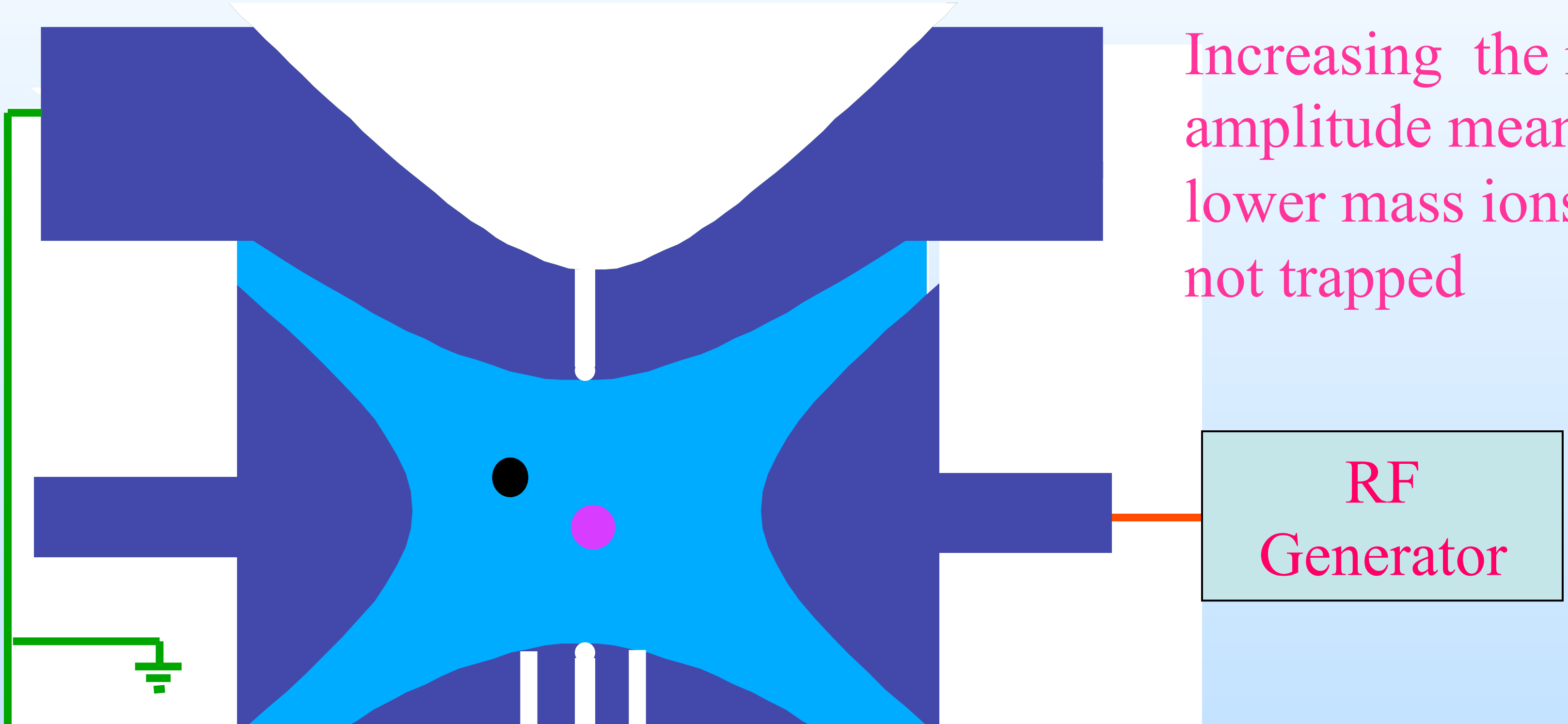


Range of masses trapped depends upon amplitude of rf voltage

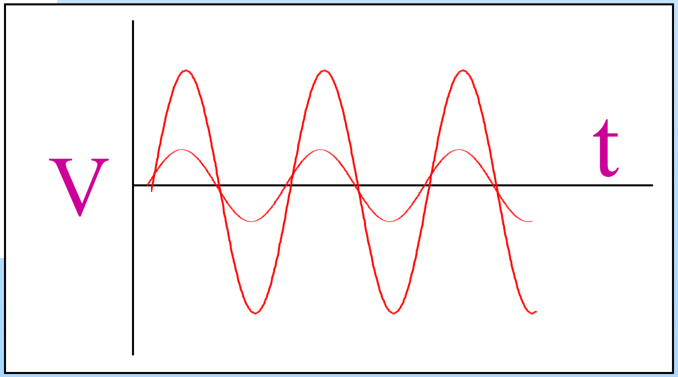




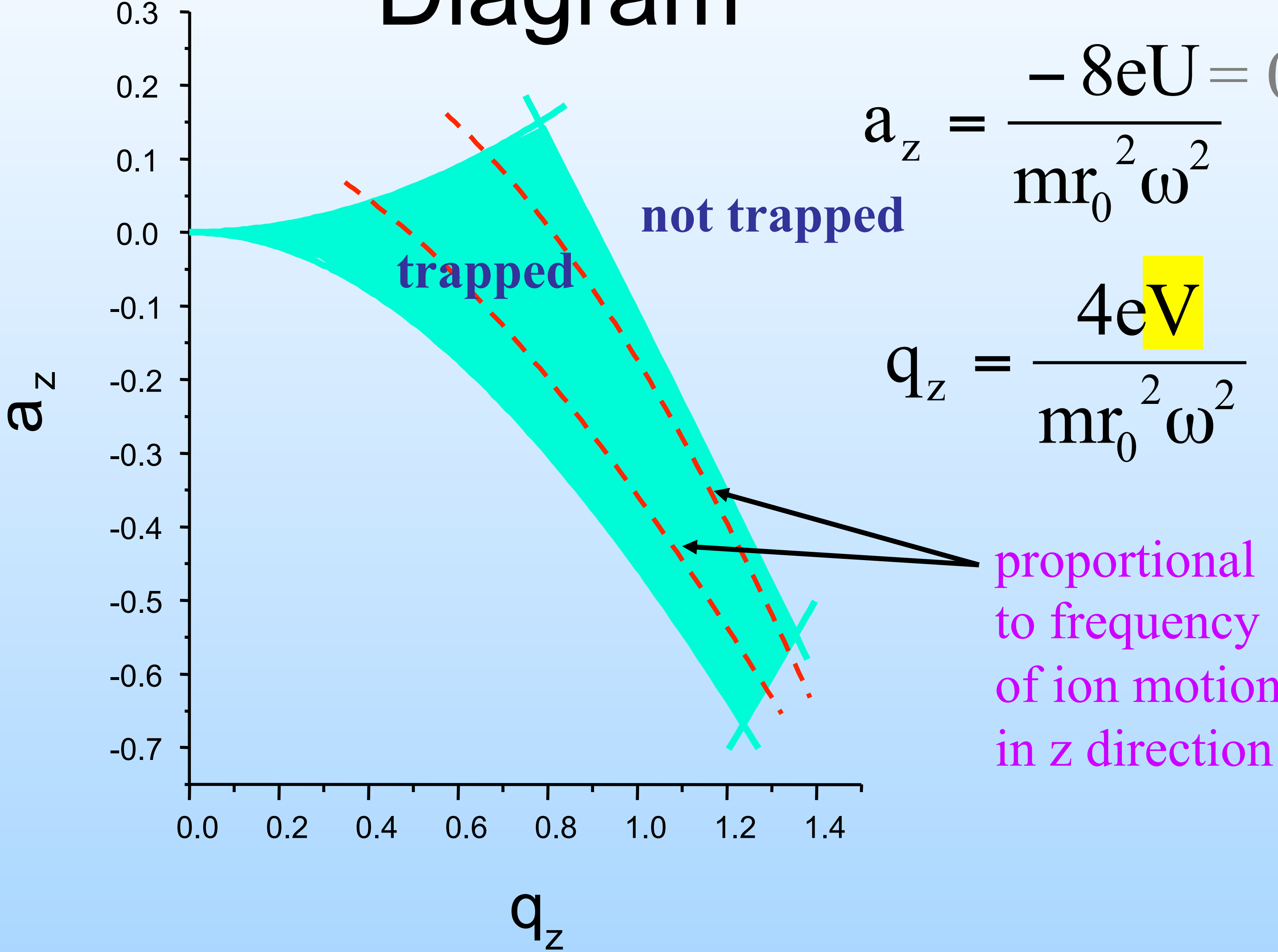
Trapping Ions



Increasing the rf amplitude means lower mass ions are not trapped



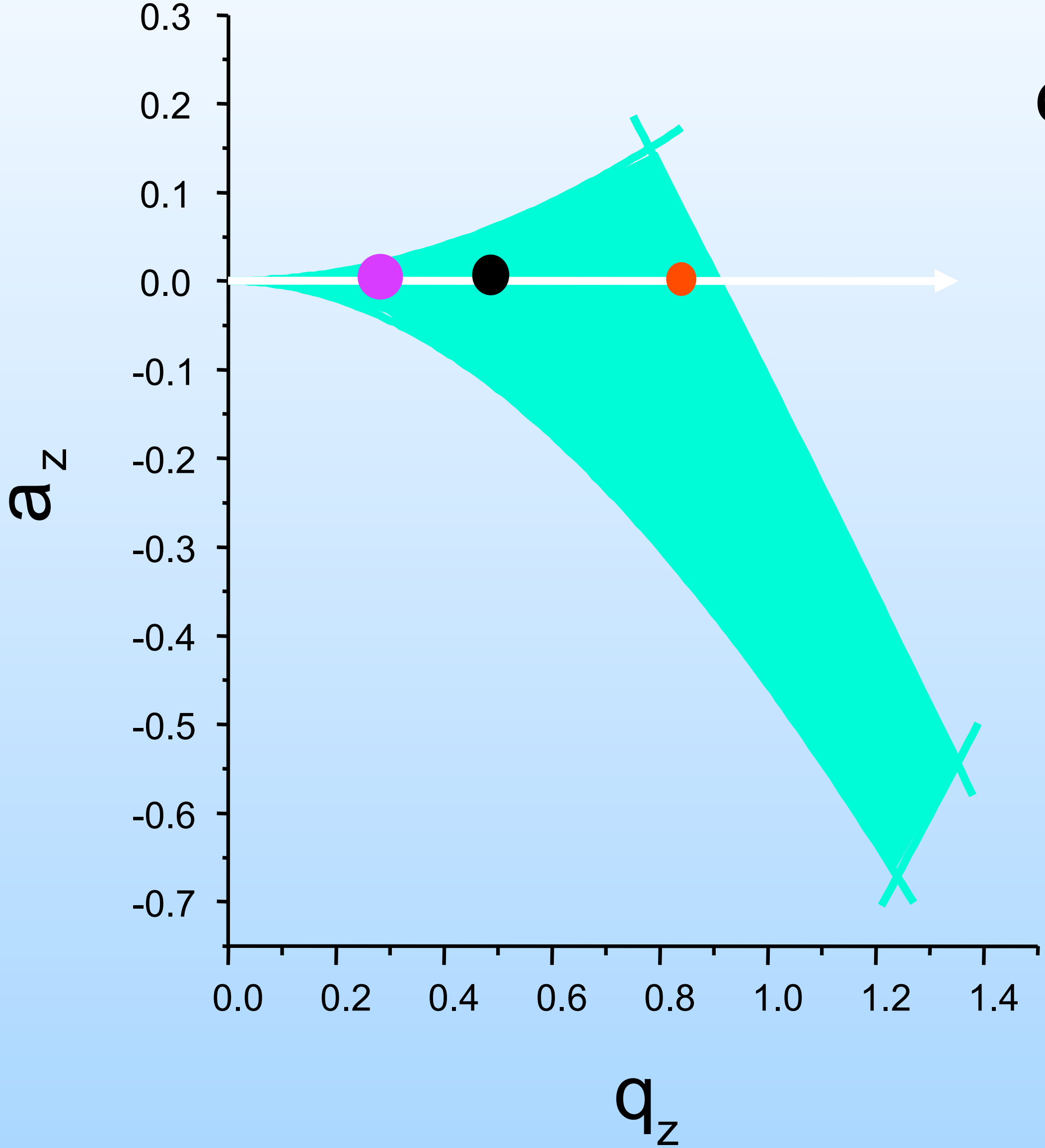
Theory - Mathieu Stability Diagram



$$a_z = \frac{-8eU}{m r_0^2 \omega^2} = 0$$

$$q_z = \frac{4eV}{m r_0^2 \omega^2}$$

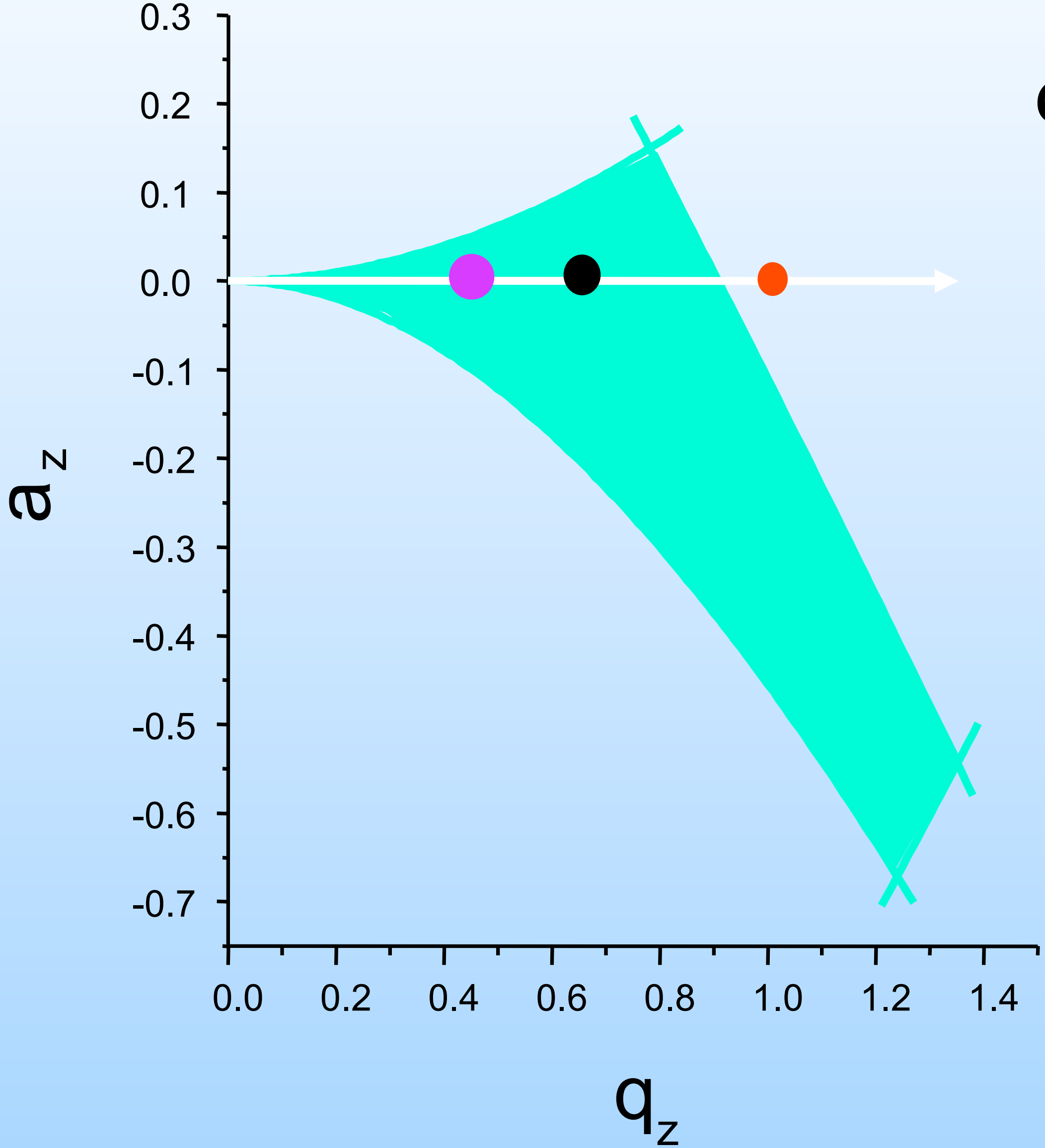
Trapping a range of ions



$$q_z = \frac{4eV}{mr_0^2\omega^2}$$

V= 600 volts

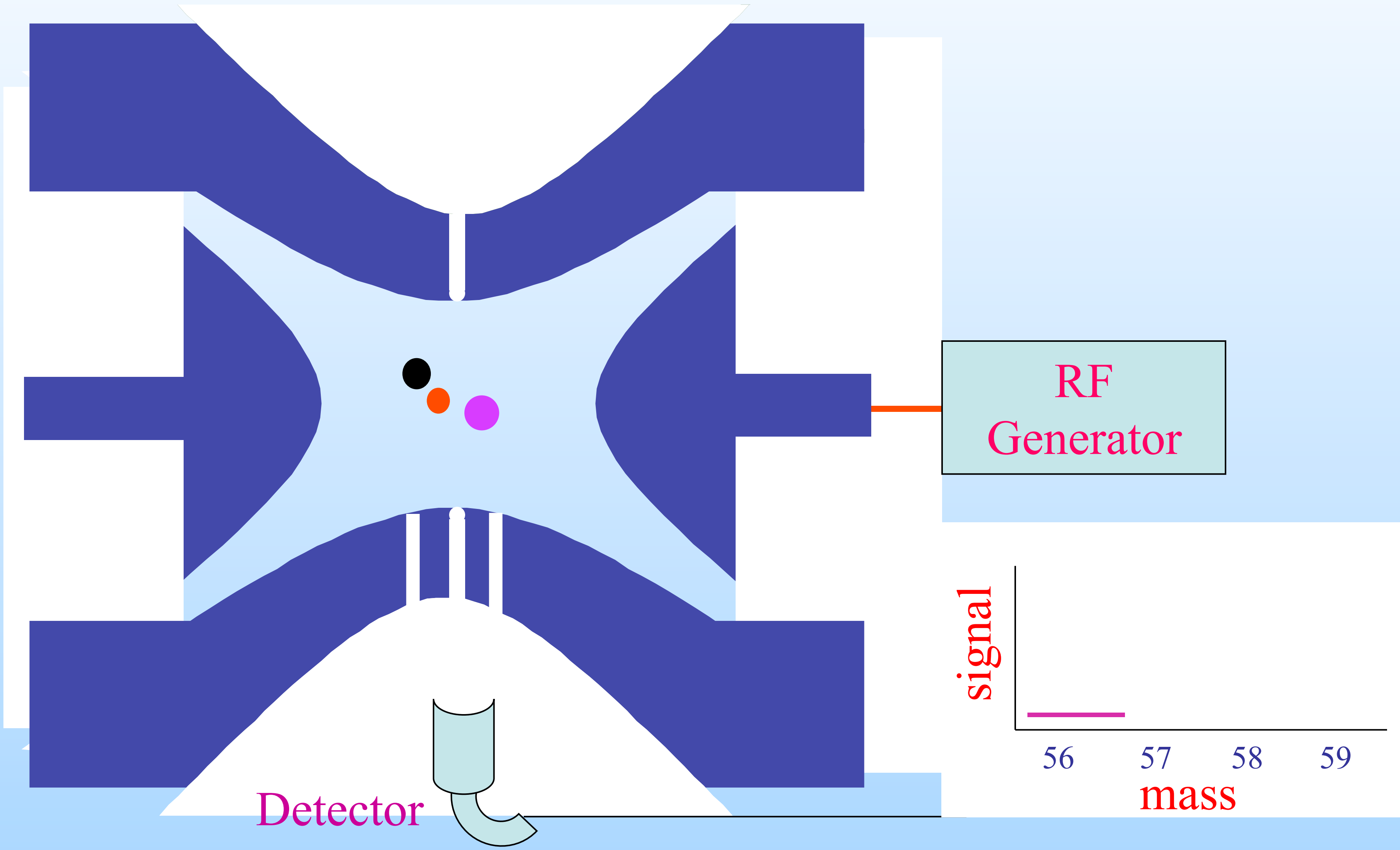
Trapping a range of ions



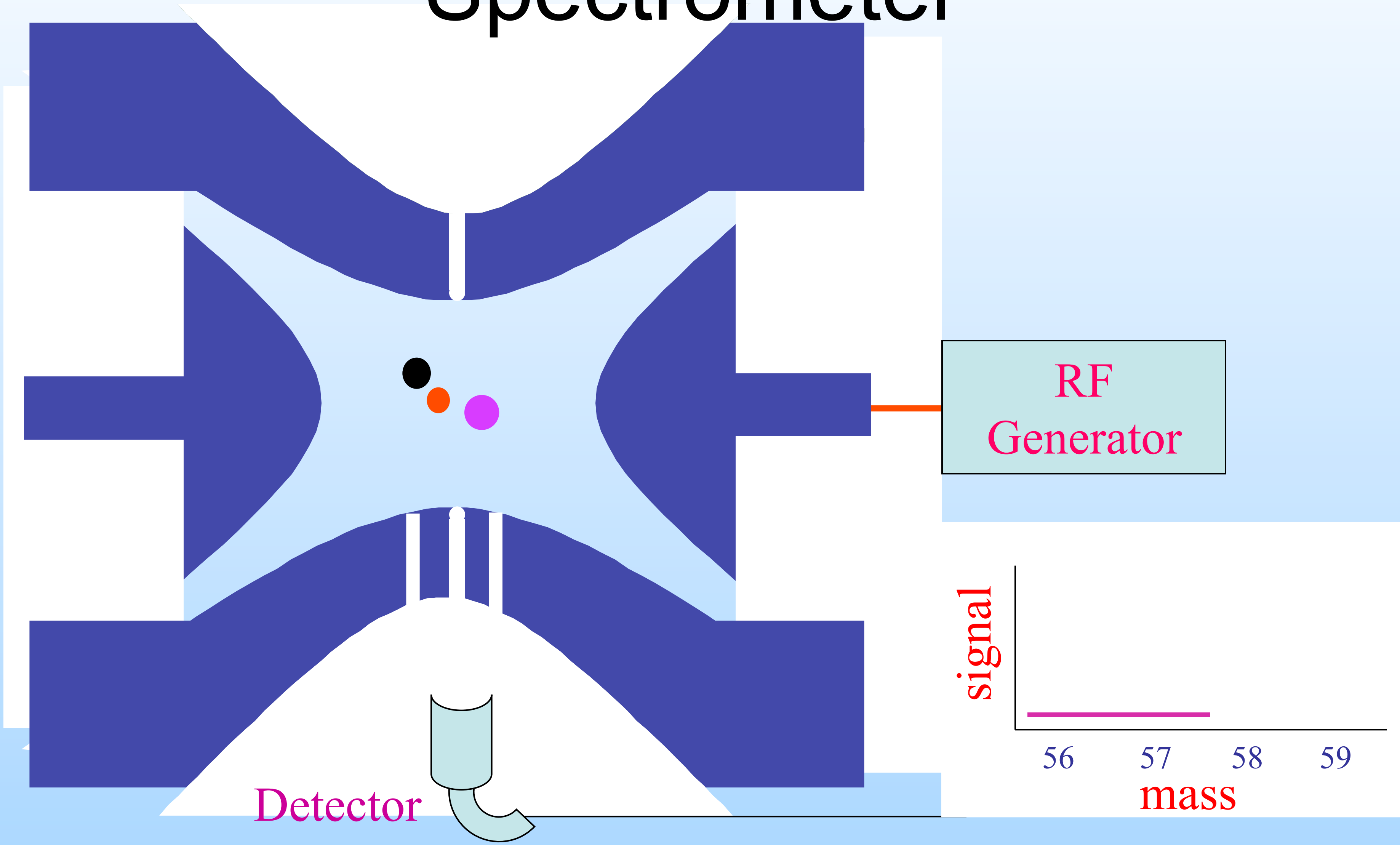
$$q_z = \frac{4eV}{m r_0^{\,2} \omega^2}$$

V= 1000 volts

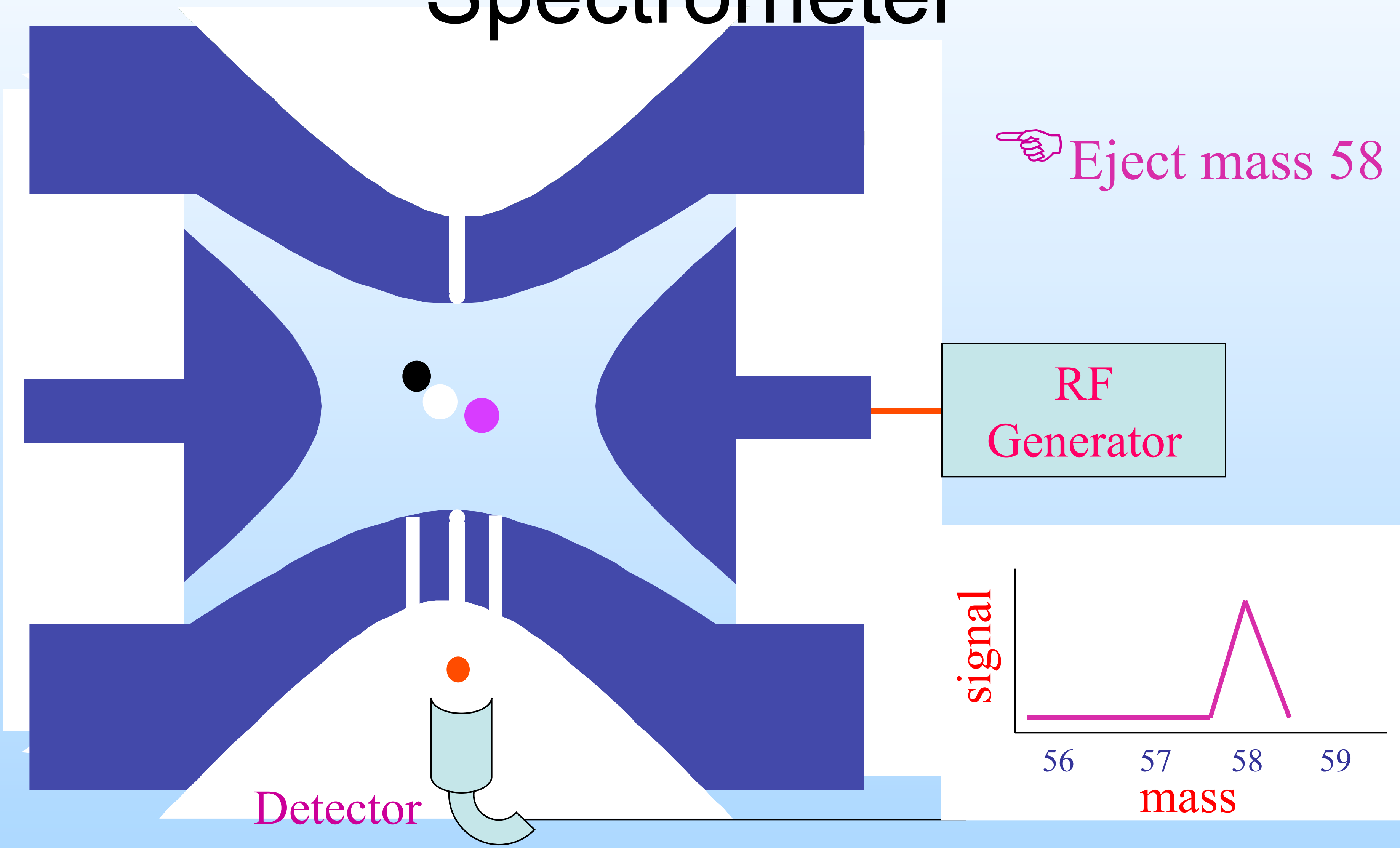
Ion Trap as a Mass Spectrometer



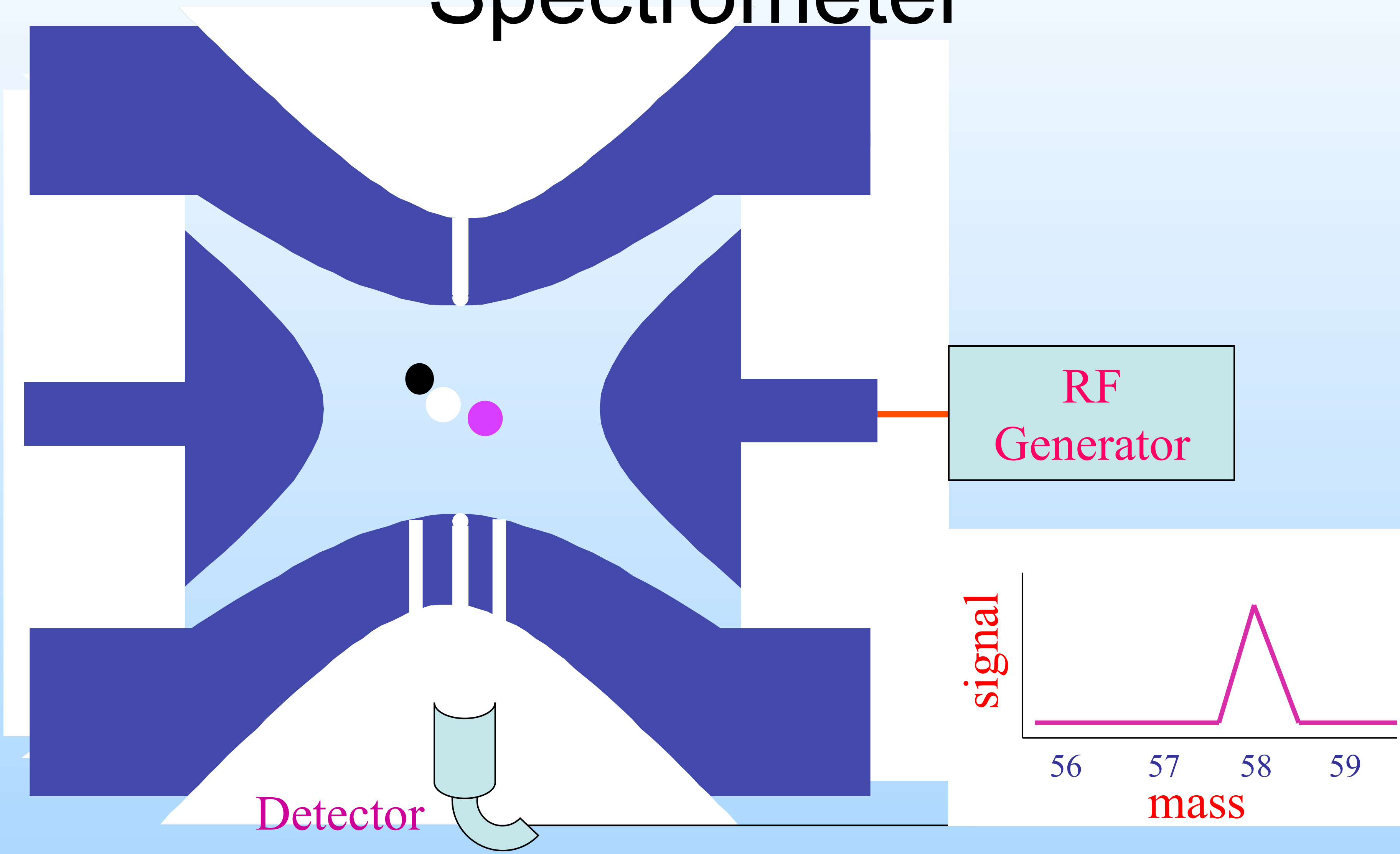
Ion Trap as a Mass Spectrometer



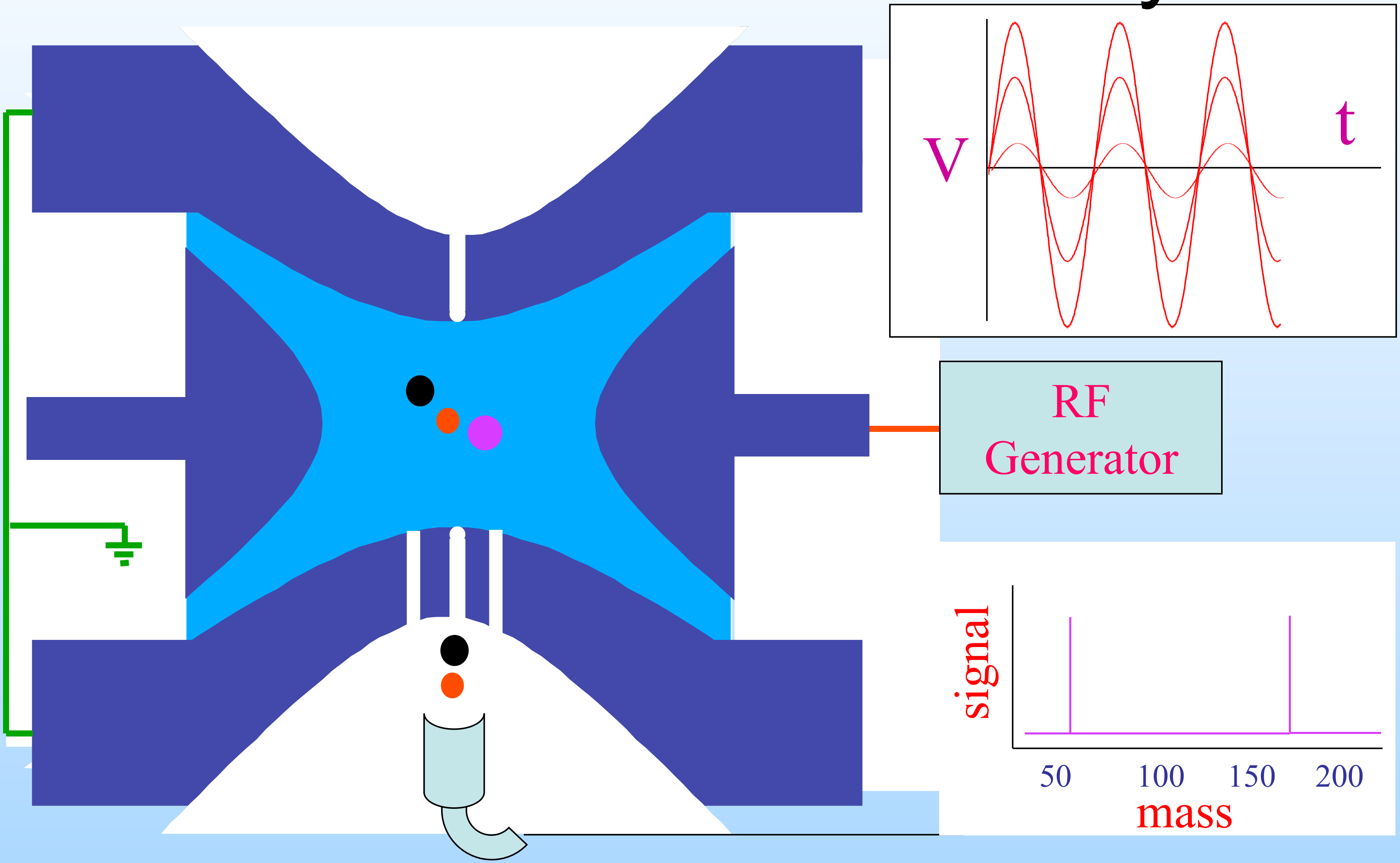
Ion Trap as a Mass Spectrometer



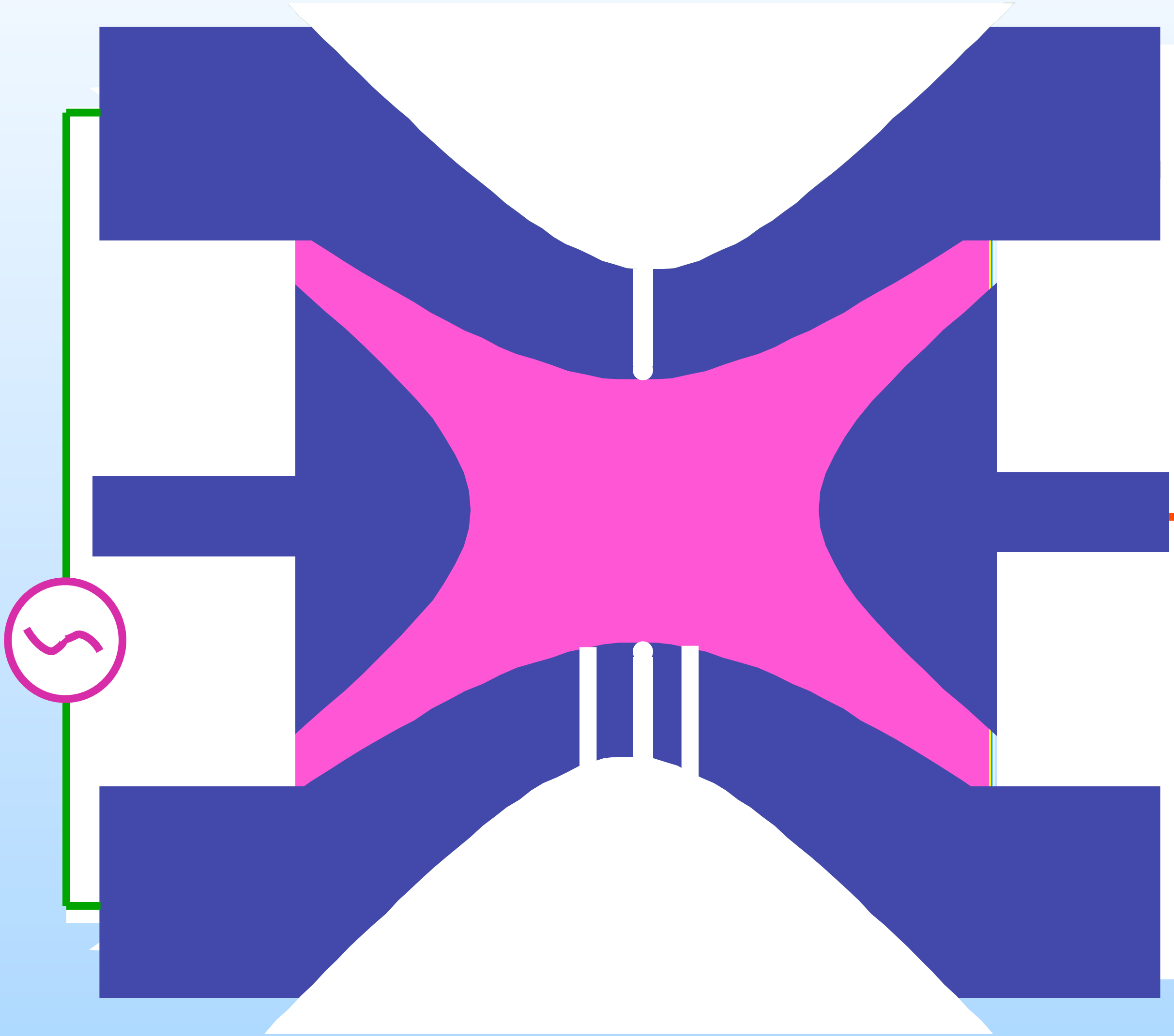
Ion Trap as a Mass Spectrometer



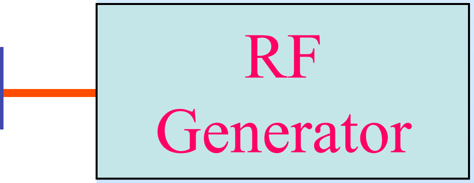
Mass-selective instability

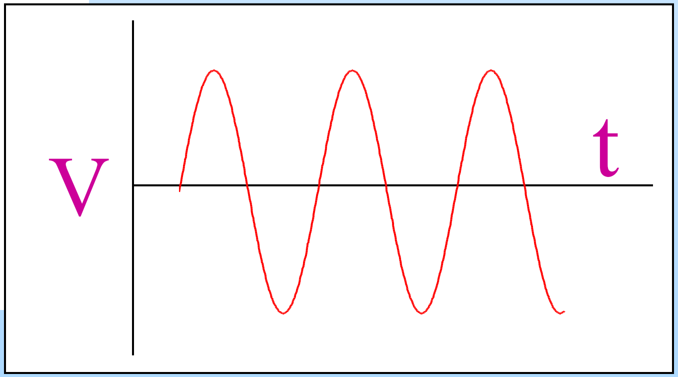


Resonance Ejection



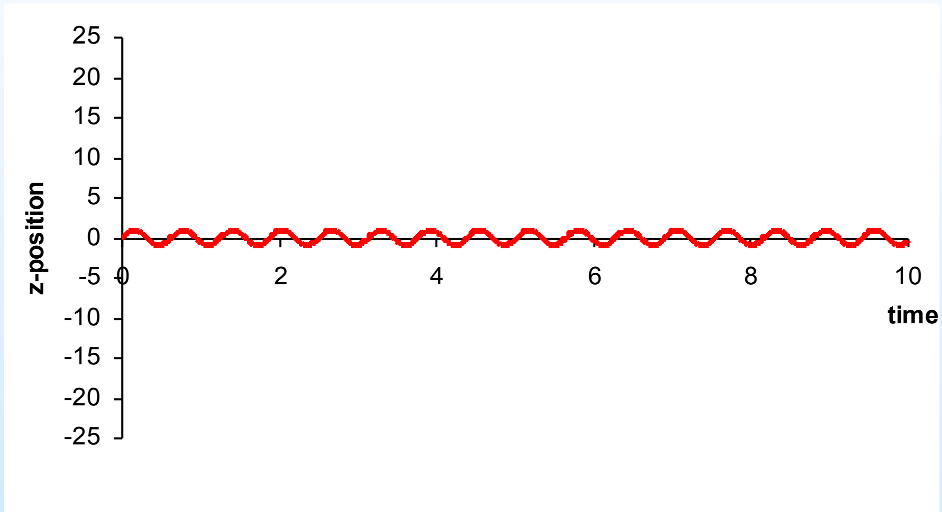
Change the electric field by applying supplemental ac voltage across end cap electrodes



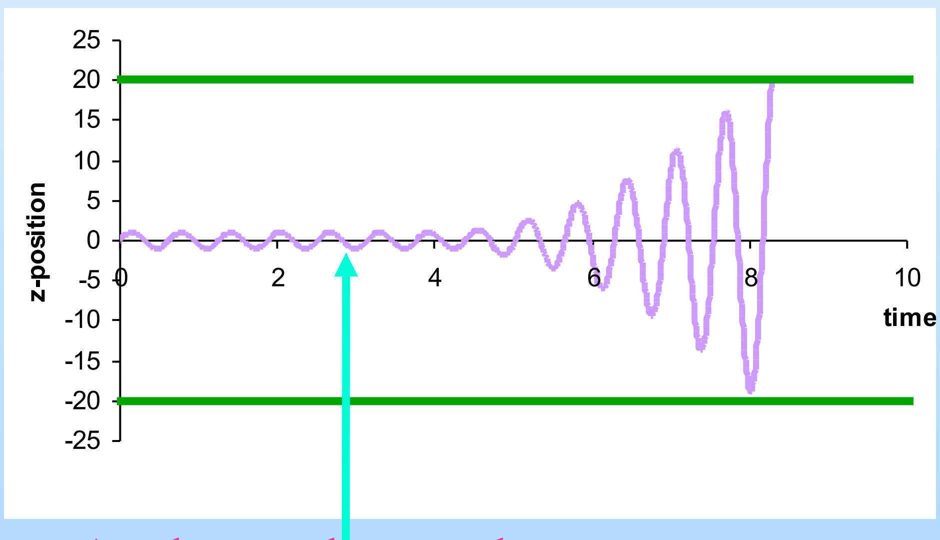


Ion Motion in Resonance Ejection

without supplemental ac end cap voltage



with supplemental ac end cap voltage



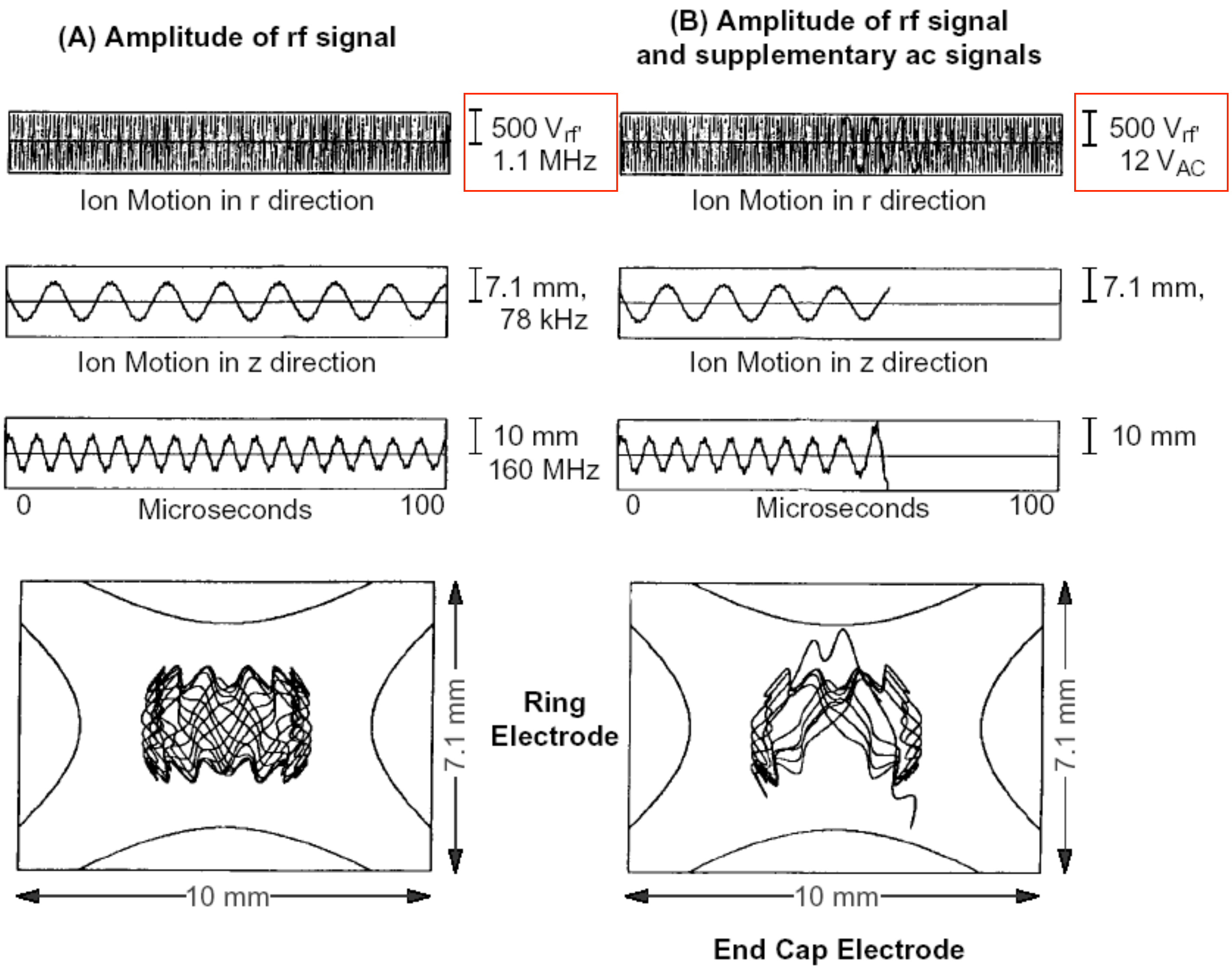
$z = z_0$

$-z = z_0$

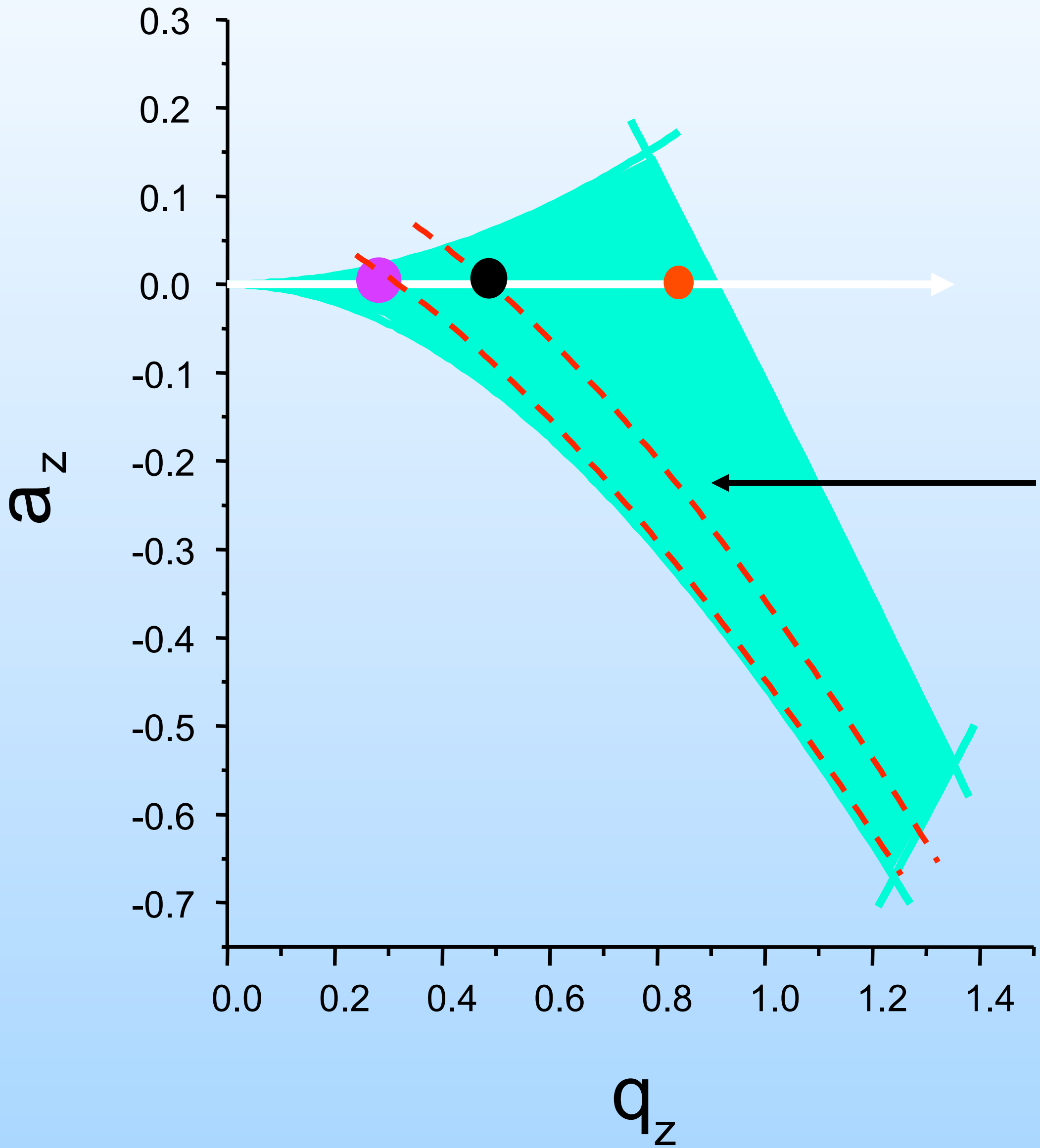
Apply supplemental ac voltage to end caps

F6

(A) A simulation of the trajectory of an ion of m/z 100 in a r_0 = 1 cm ion trap operated at a rf voltage of 500 V and a frequency of 1.1 MHz. The first three boxes are time plots of the instantaneous rf amplitude, the excursion of the ion from the center in the r-direction, and the z-excursion, respectively. The last box is a plot of r, z-motion. (B) The same simulation in which a supplementary ac voltage is applied at the time indicated to resonantly excite ion motion. (Adapted from reference 9.)

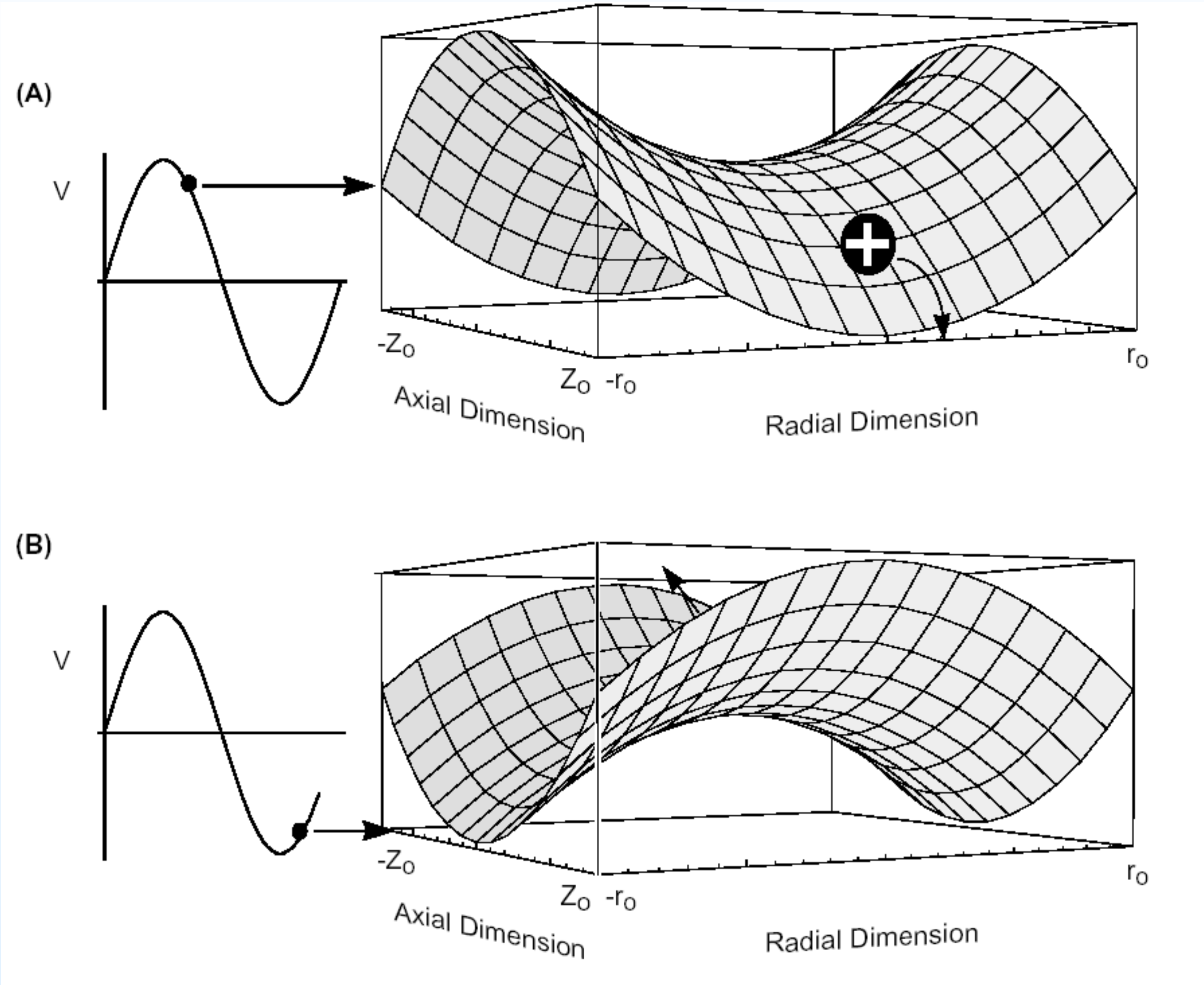


Resonance Ejection

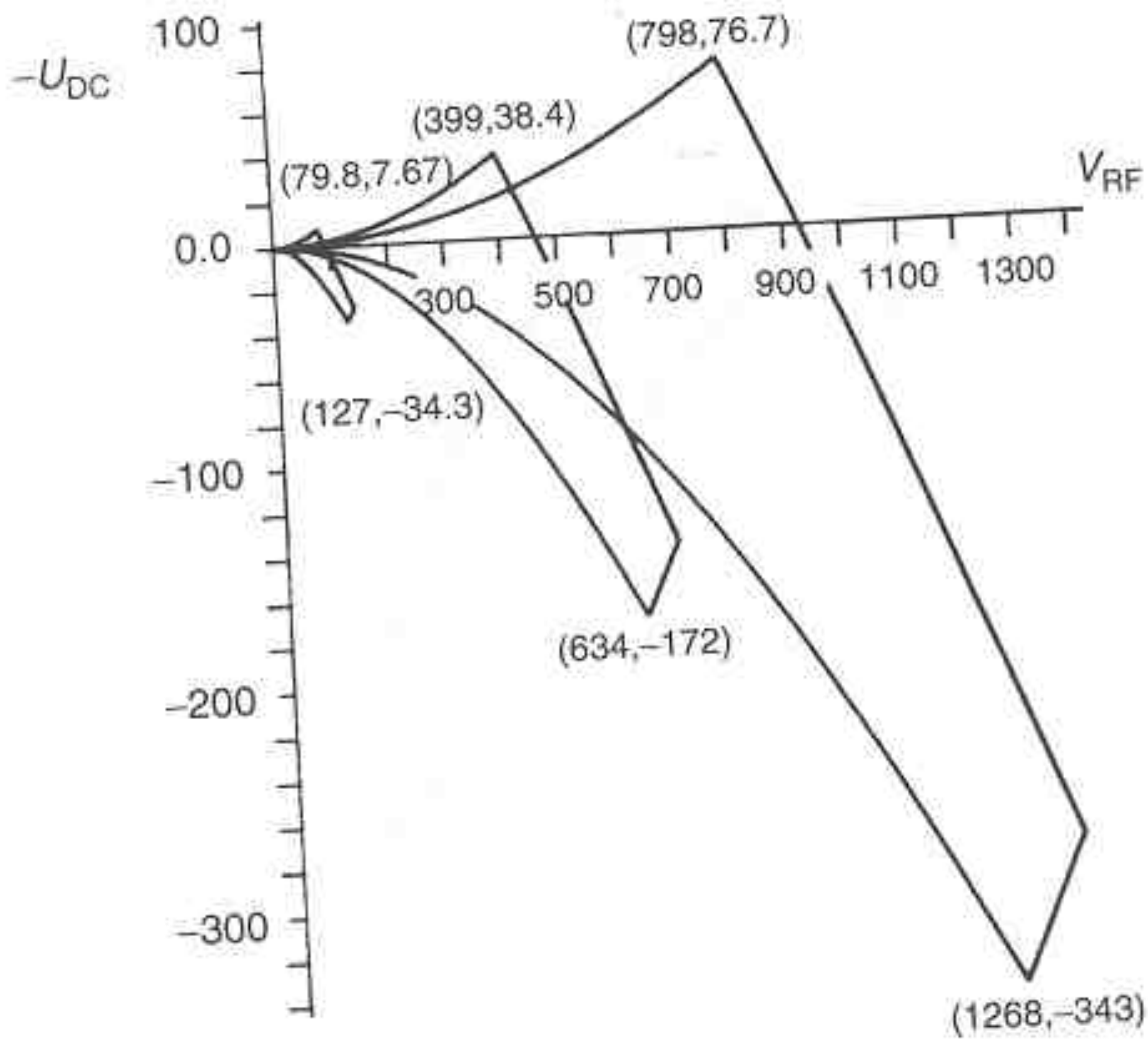


Any ion in the ion trap can be ejected

Frequency of ac voltage applied to end caps



Quadrupole.avi



100
$-U_{DC}$
(798,76.7)
(399,38.4)
(79.8,7.67)
V_{RF}
0.0
300
500
700
900
1100
1300
(127,–34.3)
–100
–200
(634,–172)
–300
(1268,–343)

Mass Analyzers: ION TRAPS

Benefits

- High sensitivity
- Multi-stage mass spectrometry (analogous to FTICR experiments)
- Compact mass analyzer

Limitations

- Poor quantitation
- Very poor dynamic range (can sometimes be compensated for by using automatic gain control)
- Subject to space charge effects and ion molecule reactions
- Collision energy not well-defined in CID MS/MS
- Many parameters (excitation, trapping, detection conditions) comprise the experiment sequence that defines the quality of the mass spectrum

Applications

- Benchtop GC/MS, LC/MS and MS/MS systems
- Target compound screening
- Ion chemistry

ION TRAPS : Time related issues MS/MS/MS

1 INJECTION.exe

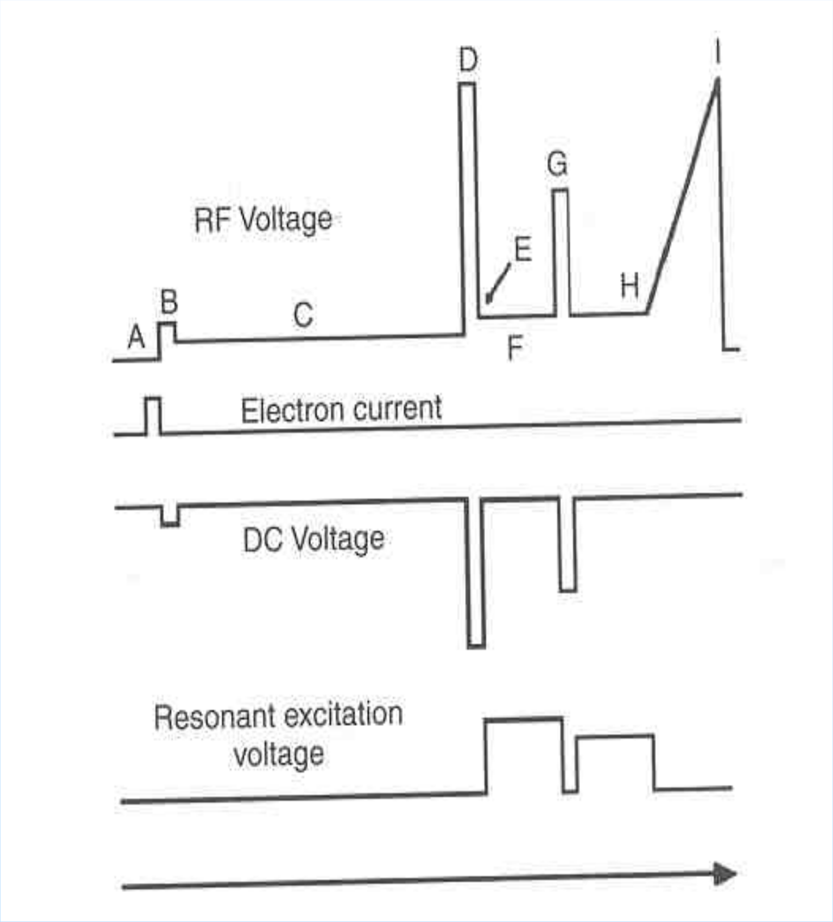
2 ISOLATION.exe

3 PARENT STABILIZATION.exe

4 EXCITATION.exe

5 DAUGHTER EJECTION.exe

6 DETECTION.exe



A: ionization

B: trapping

C: protonation

D: selection of parent ion

E: stabilization

F: CID

G: selection of daughter

H: stabilization +CID

I: Scanning of grand-daughter ions and tetection