Quadrupole Ion-Trap Mass Analyzer
EAS Workshop
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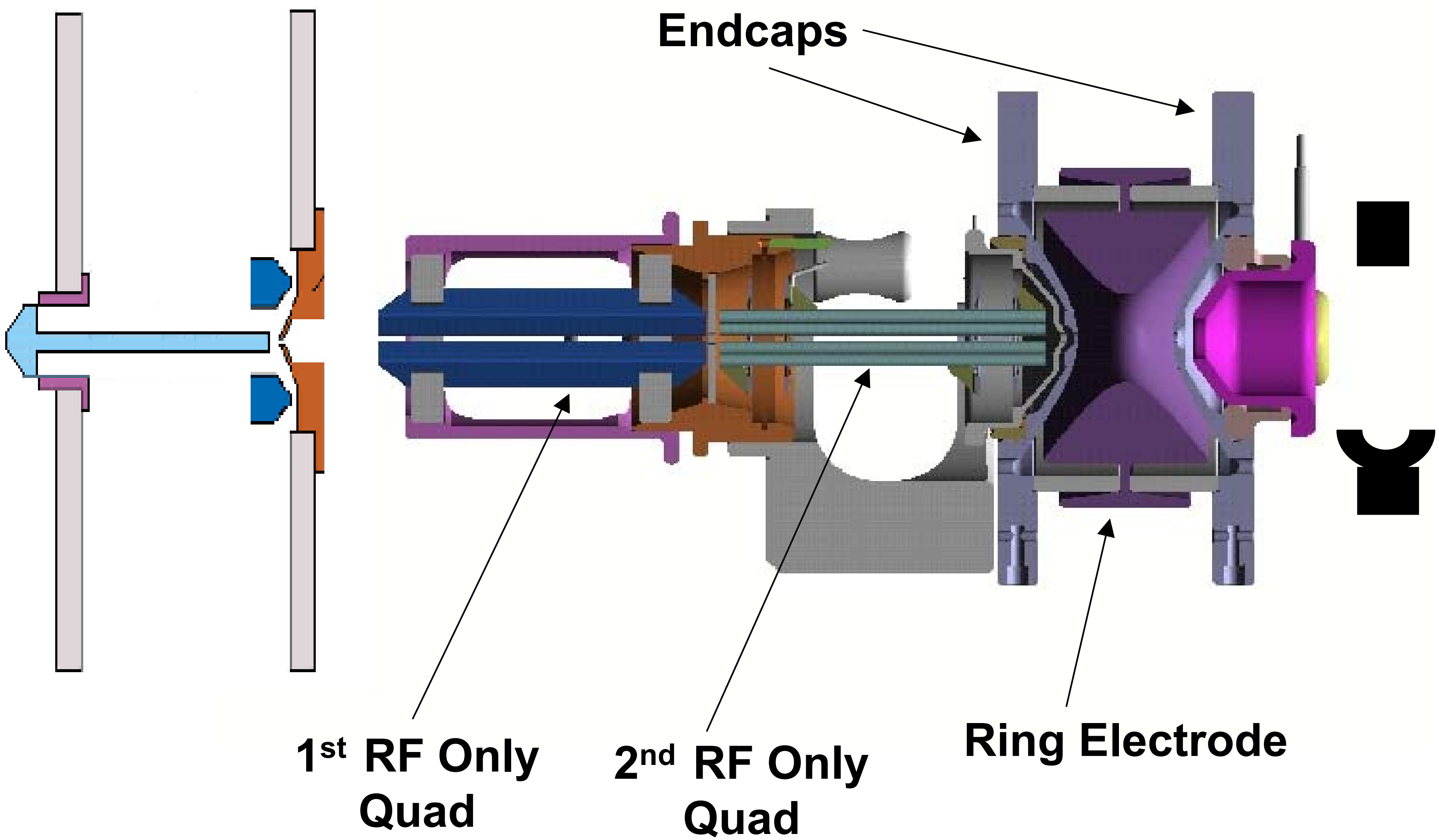
Schematic of an Ion Trap

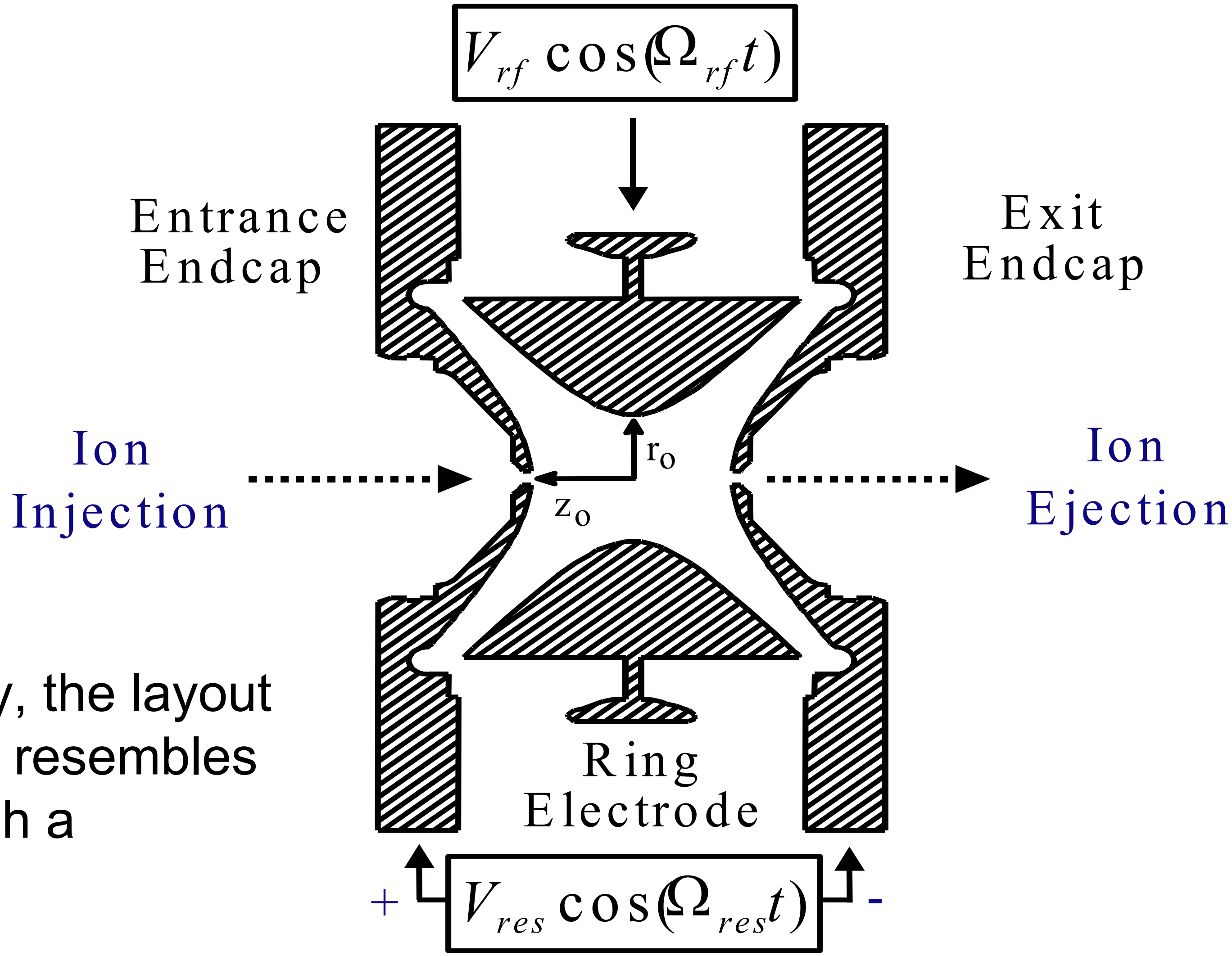


LCQ 3-D Ion Traps

FINNIGAN
LCQ Deca XP MAX

FINNIGAN
LCQ Advantage MAX

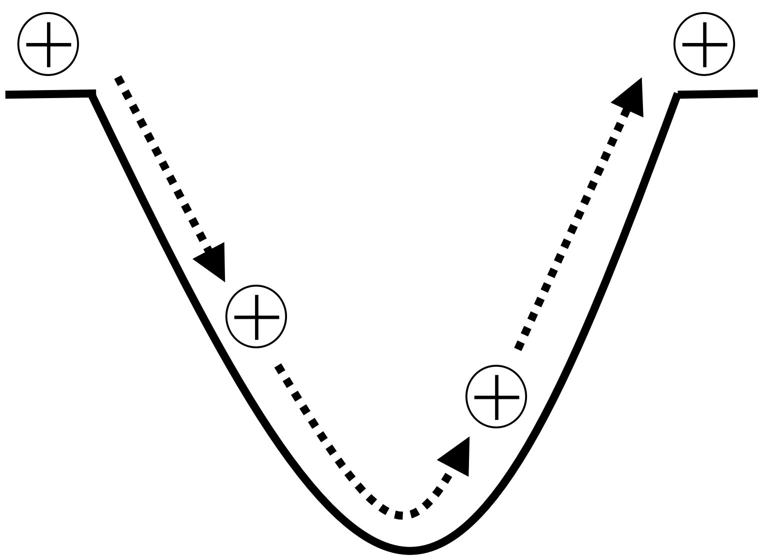
Basic Ion Trap Components



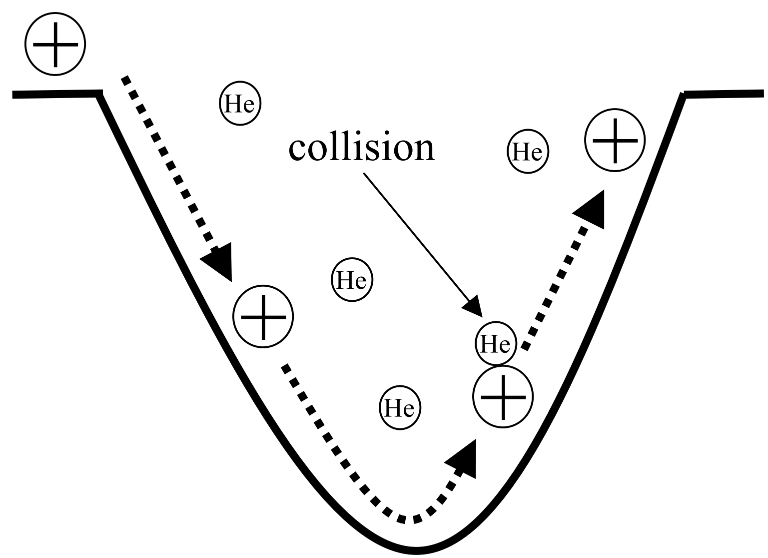
Schematically, the layout of an ion-trap resembles a slice through a quadrupole

Helium as a Damping (Buffer) Gas

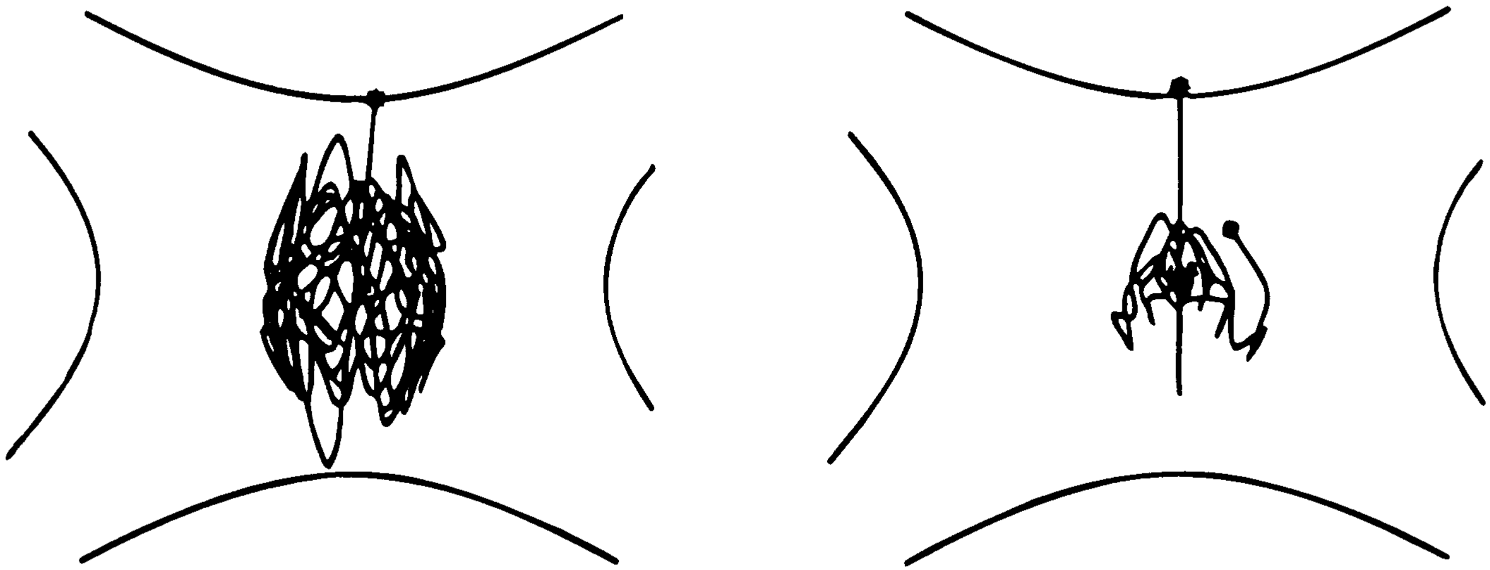
Without Helium



With Helium



Helium as a Damping Gas



Without Buffer Gas

With Buffer Gas

Purposes of Buffer Gas

- Trap injected ions by removing KE
- Damps ions to center of ion trap
- Collision gas for MS/MS

Results...

Increase sensitivity

Increase resolution

i.e. resolution is improved by giving narrower and larger peaks

Increase fragmentation efficiency

Ion Stability in the Trap

Controlled by a culmination of differential equations termed Reduced Mathieu Equations:

a = variable solution

q =solution

e= charge of trapped ion

U=DC Voltage

V=RF amplitude

m = mass of ion

Ω = constant summarizing mathematics

z_0 = distance between centre of trap to either endcap

R_0 = internal radius of ring electrode

DC on the Ring

$$a_z = -\frac{16eU}{m(r_0^2 + 2z_0^2)\Omega^2}$$

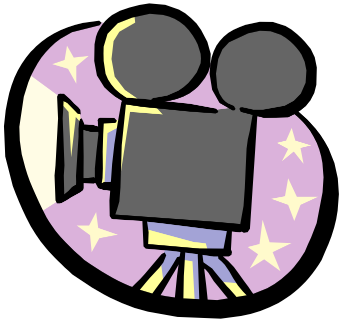
RF on the Ring

$$q_z = -\frac{8eV}{m(r_0^2 + 2z_0^2)\Omega^2}$$

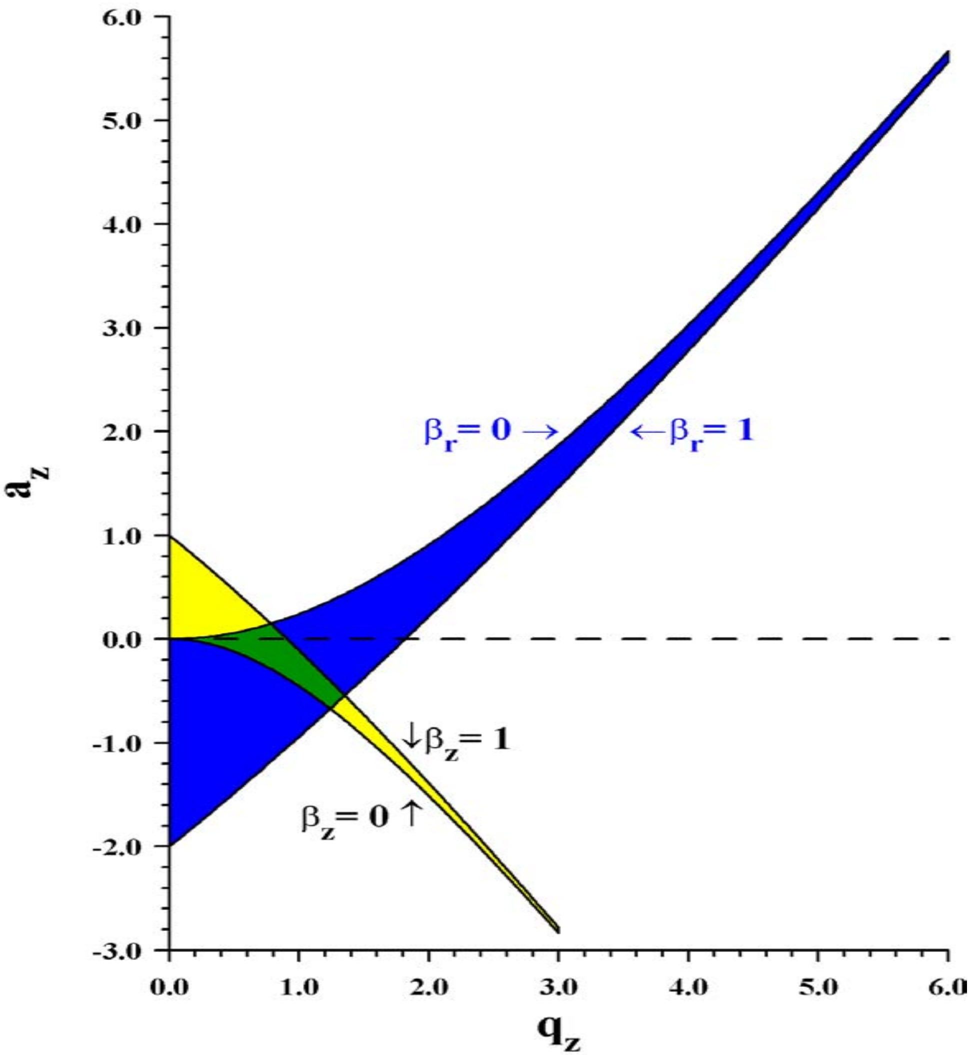
Mass

Ring Parameters

Excel Trapping Field Animation



Ion Trap Stability Diagram

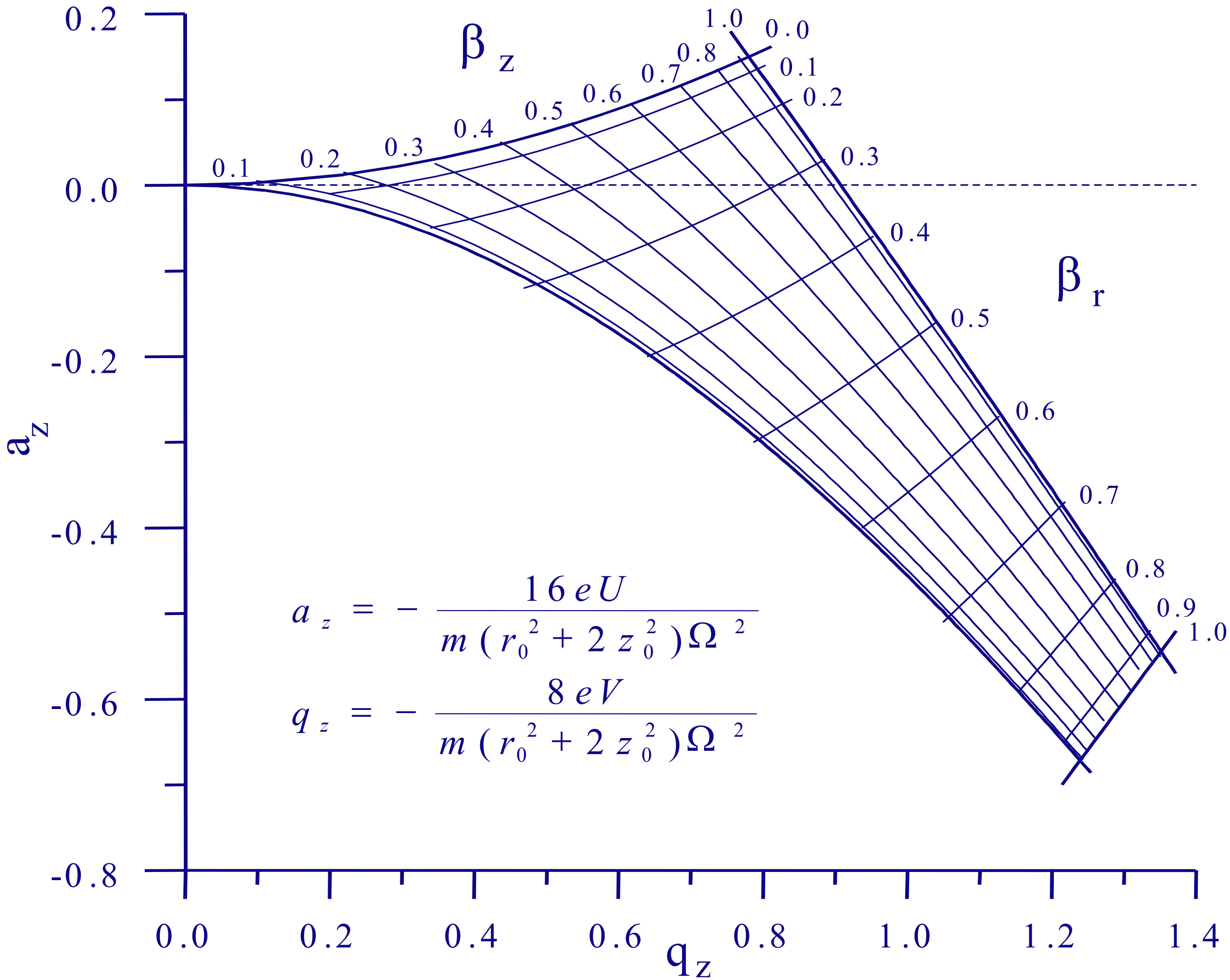


The region shaded blue indicates a (DC) and q (RF) values which provide stable trajectories in the r-direction

The region shaded yellow indicates the z-stable a and q combinations

The green area where the r- and z-stable regions overlap indicates the a and q combinations under which ions will be stable in the trap

Ion Stability Diagram



$$a_z = -\frac{16eU}{m(r_0^2 + 2z_0^2)\Omega^2}$$

$$q_z = -\frac{8eV}{m(r_0^2 + 2z_0^2)\Omega^2}$$

Mass Selective Instability

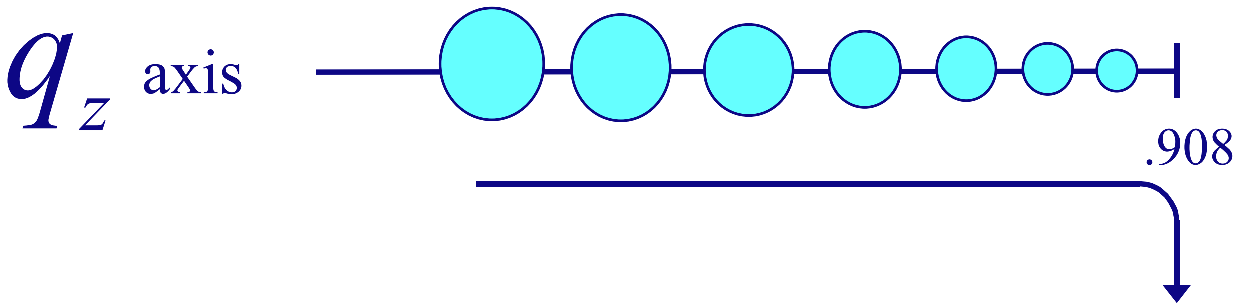
"There are two landmarks in [the history of Quadrupole Ion Traps].

The first is the invention of the ion trap [in 1953] by Wolfgang Paul and Hans Steinwedel, which was recognized by the award of the 1989 Nobel Prize in Physics . The second is the discovery, announced in 1983, of the mass selective instability scan by George C. Stafford, Jr. On these two landmarks rests the entire field of ion trap mass spectrometry."

Raymond March, John F. J. Todd in the preface of

Practical Aspects of Ion Trap Mass Spectrometry

Mass Selective Instability



$$q_z = k \frac{V}{(m/e)}$$

"Ramp RF, Ions Leave Low *m/z* to High *m/z*"

Automatic Gain Control (AGC)

Prescan before the analytical scan

- Measures the # of ions in the trap for a pre-defined time (10 – 30 ms)

- Allows software to determine optimum ion injection time

What is AGC and Why Is it Important?

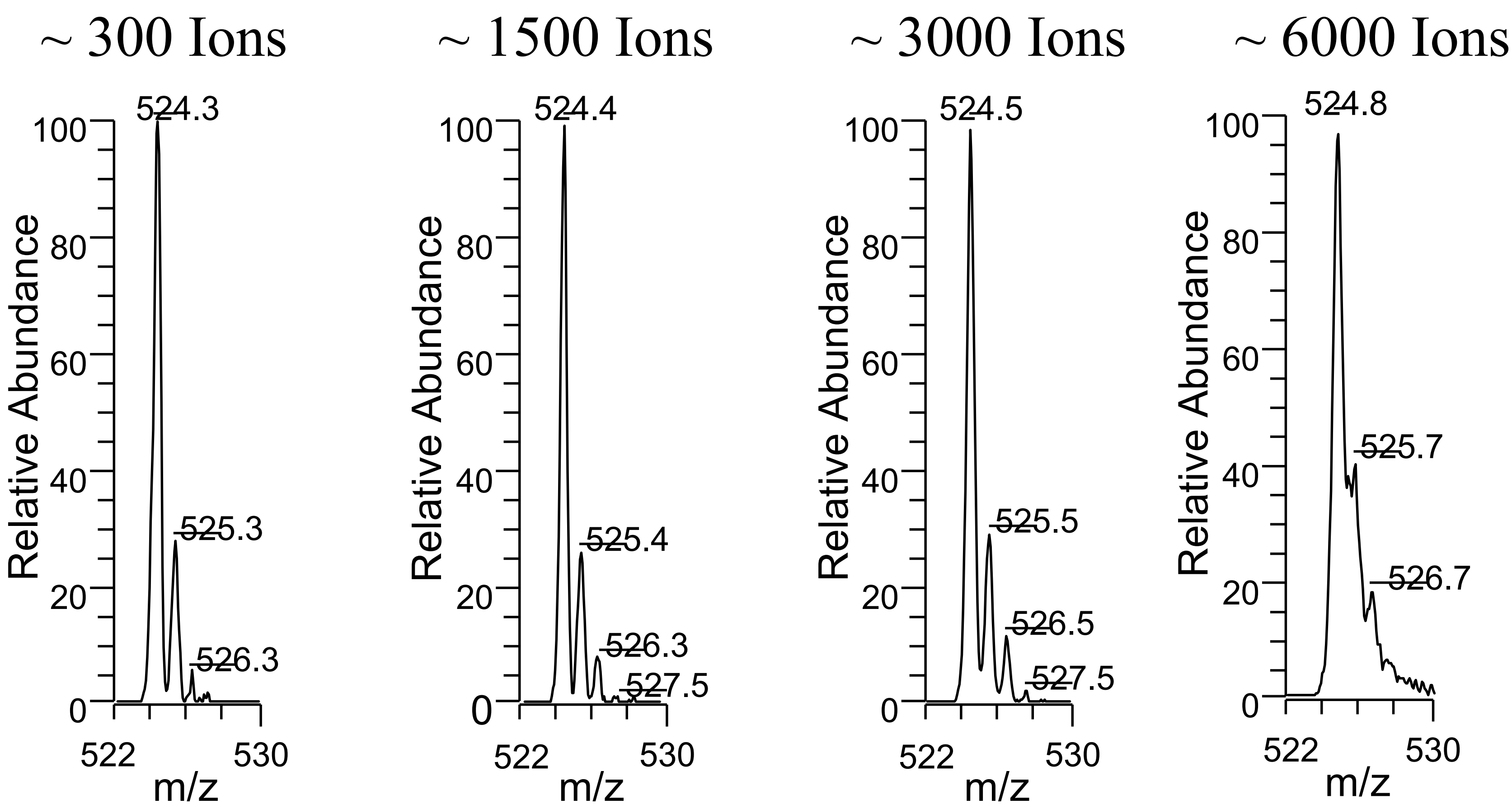
Camera AE

- Too much light degrades the image stored on film, causing a loss of color and image resolution.
- Too little light results in dark picture with no fine details visible.
- Cameras with high quality light meters and AE controls produce high quality pictures over a wide dynamic range of lighting conditions.

LCQ/LTQ Series AGC

- Controls amount of ions (light) entering the ion trap (film)
- Too many ions degrade the spectral quality in the trap, causing loss in mass resolution and mass assignment. Too few ions result in poor sensitivity to low level or minor components.
- AGC ensures excellent quality MS, SIM and MS/MS spectra, as well as excellent sensitivity over a wide dynamic range.

AGC (Ion Population Control)



Good Resolution

Poor Resolution

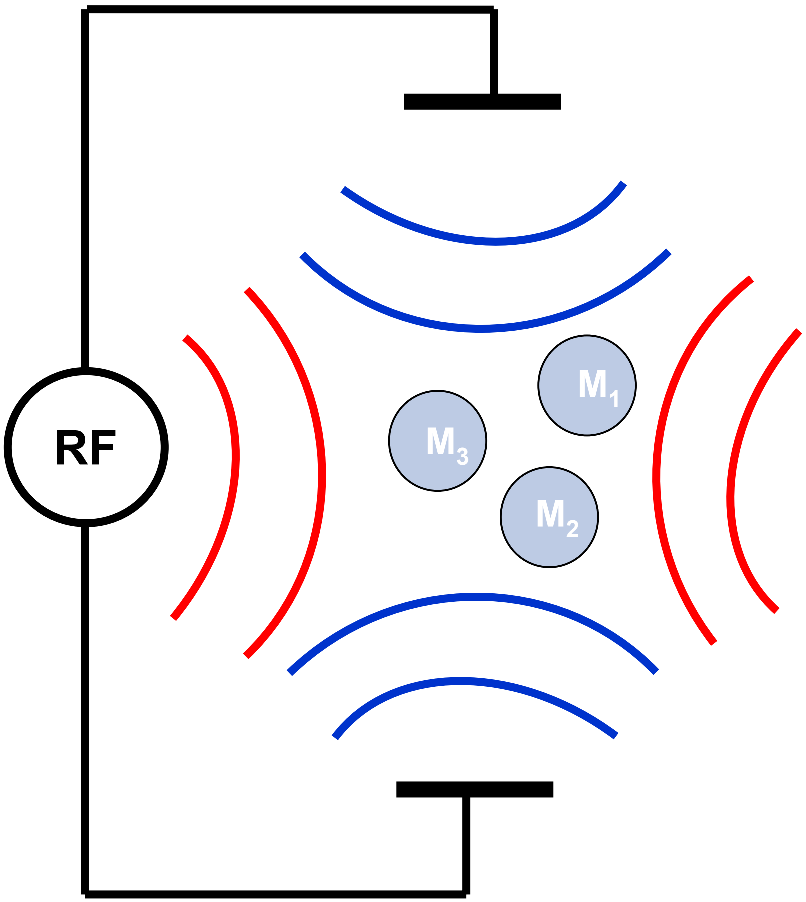
Major Strengths of Ion Trap Mass Spectrometers that make them Valuable Tools for Various Experiments

Full-Scan MS^n Sensitivity

Resonant Step-Wise Excitation

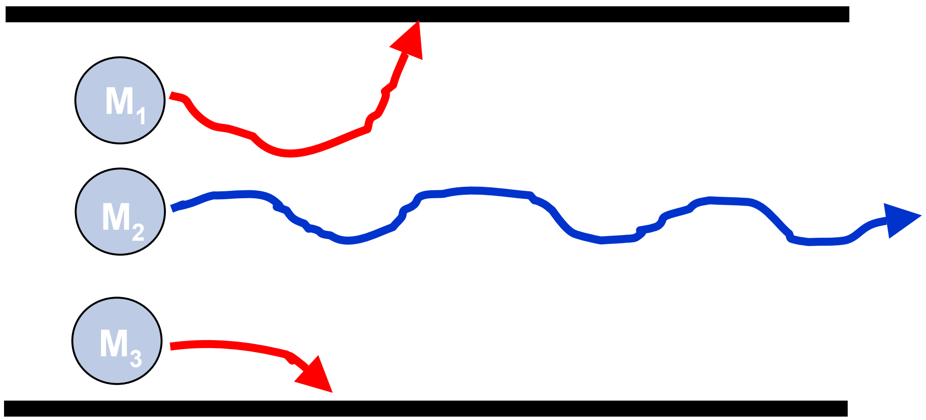
"Universal" Excitation Conditions

Full-Scan MS^n Sensitivity



3D Ion Trap: RF voltage across the ring electrode produces a quadruple field that maintains the ions over the mass range of interest in stable trajectories within the trap. As one ion mass is being scanned out of the trap to the detector, the remaining ions remain stably trapped. Excellent full-scan MS^n sensitivity.

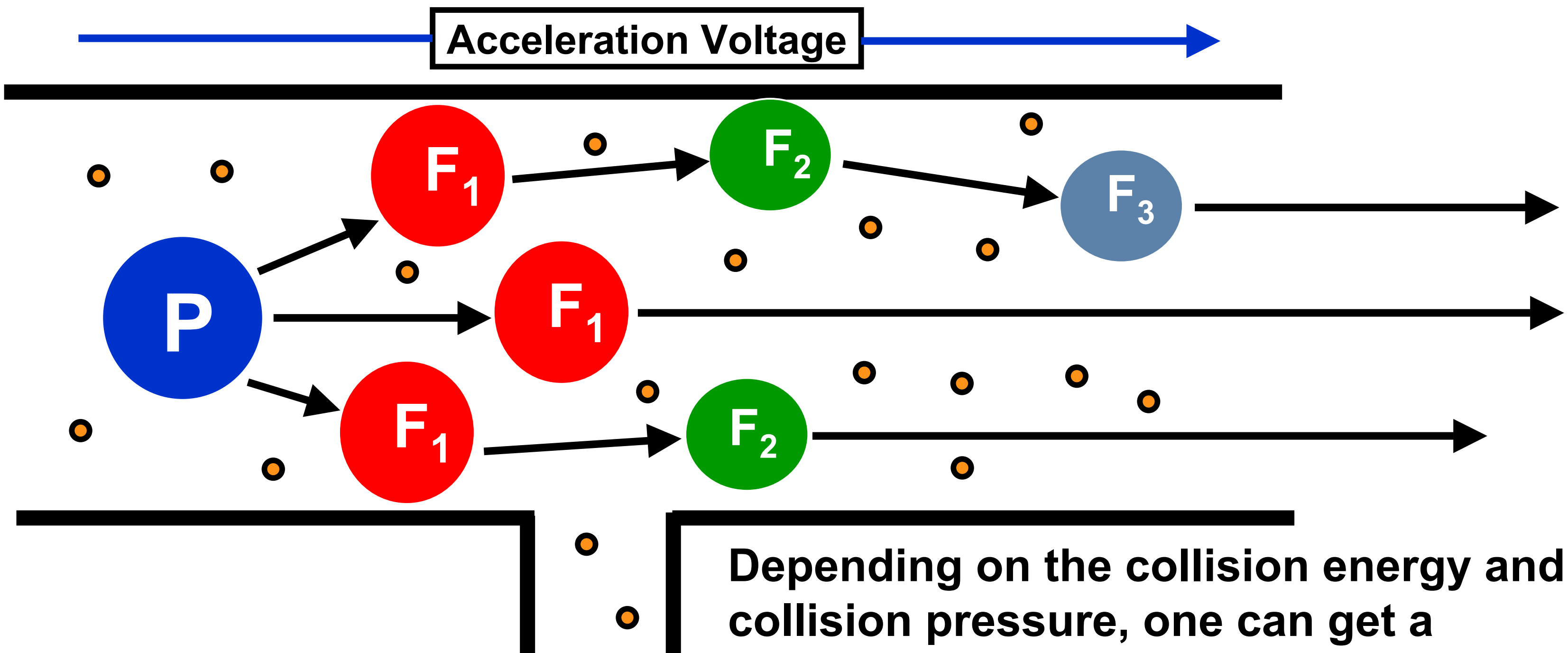
Full-Scan MS^n Sensitivity (continued)



Quadrupole: A combination of RF and DC voltages across the rods produces a stable trajectory for only one ion at a time. As one ion mass is being scanned out to the detector, the remaining ion masses are lost. Decreased full-scan MS and MS^2 sensitivity.

Resonant Step-Wise Excitation

Triple Quadrupole Collision Cell



argon

Depending on the collision energy and collision pressure, one can get a combination of MS^2, MS^3…MS^n occurring simultaneously. This can make it difficult to trace a fragment back to its parent which complicates spectral interpretations.

Unique Features of Ion Traps…

Mass separation in time – Isolation of the ions of interest and subsequent dissociation (MS/MS) are done in the same “chamber”.

Also…

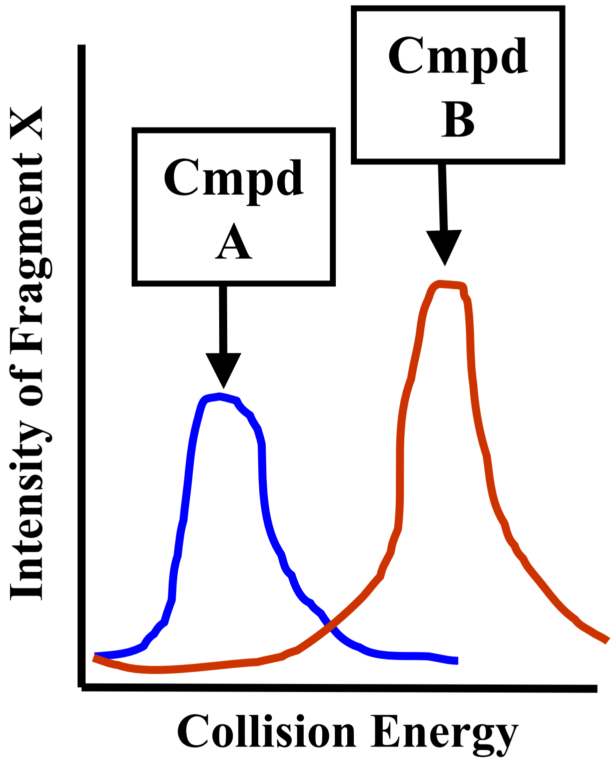
Ion Trap (resonant excitation) : Excitation energy is in resonance with only one mass at a time. Fragments, once formed, can not be further excited unless they are purposely selected for next stage of MS. Allows one to take apart a molecule in a controlled, step-wise fashion.

But…

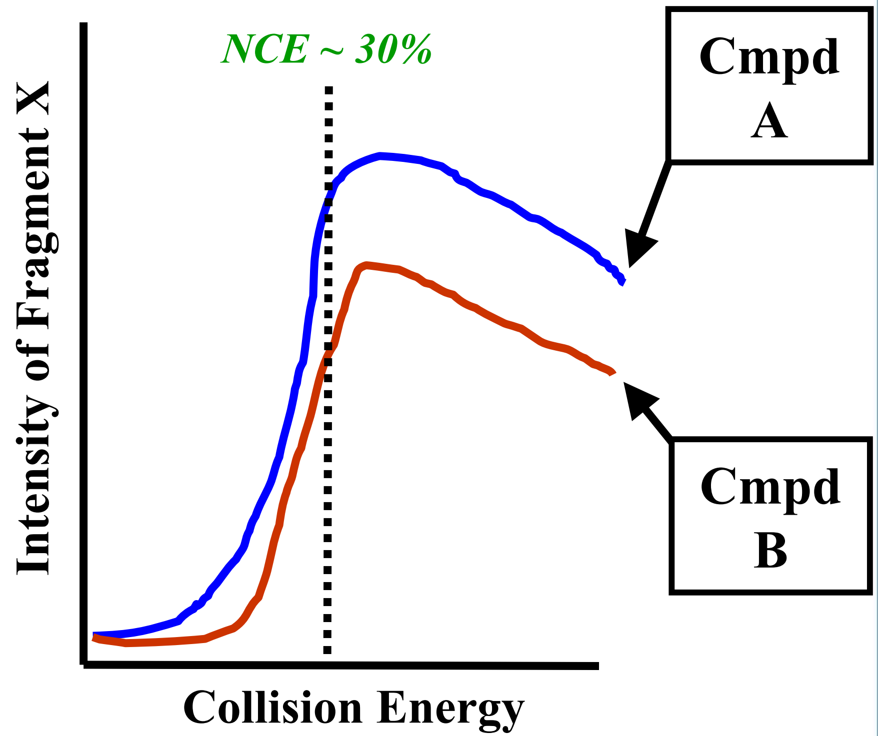
Triple Quad (nonresonant excitation) : Acceleration voltage applied equally to all masses. Get a mix of ms^2, ms^3…ms^n products.

"Universal" Excitation Conditions

Triple Quadrupole Mass Spectrometer



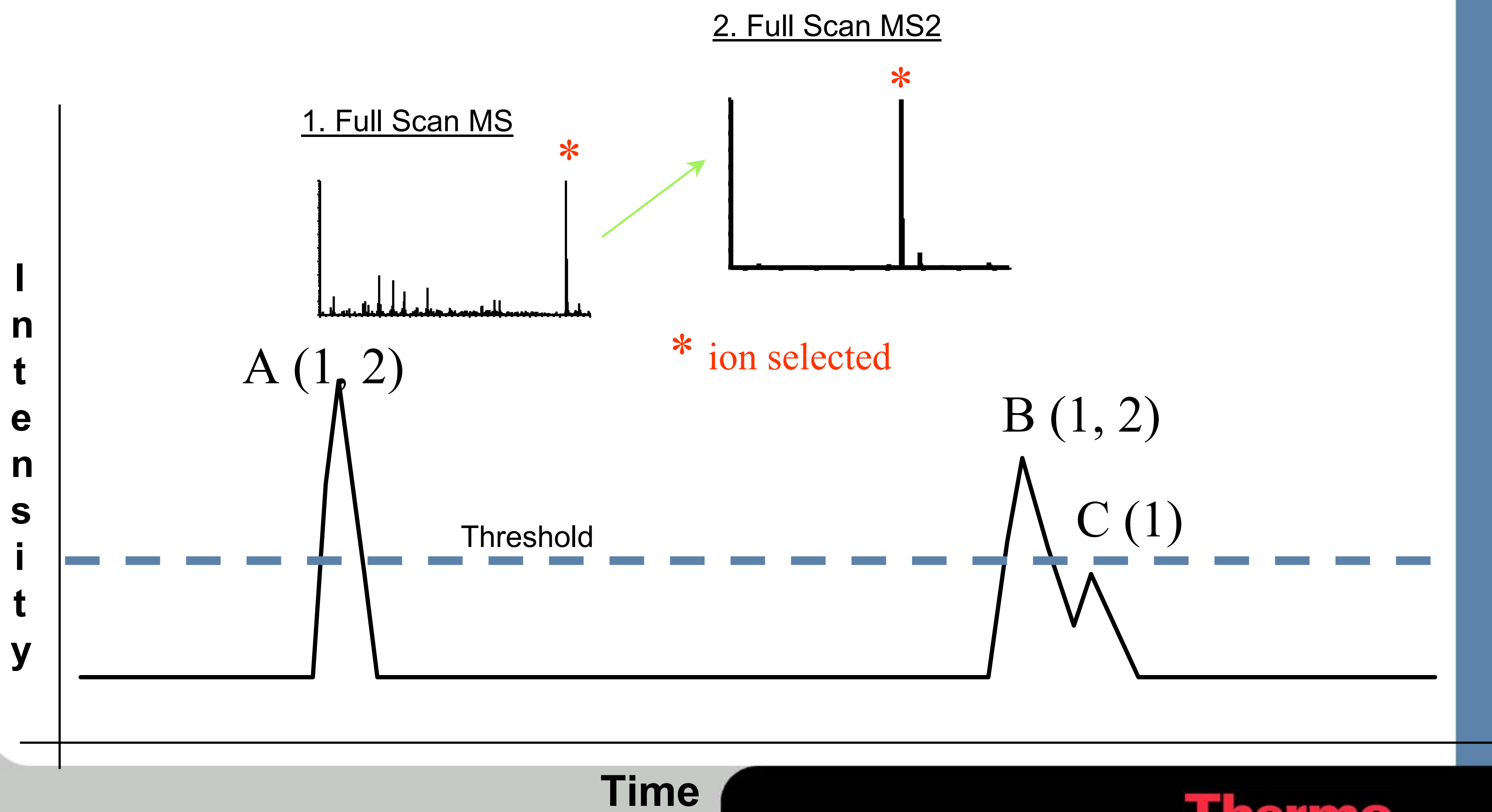
Ion Trap Mass Spectrometer



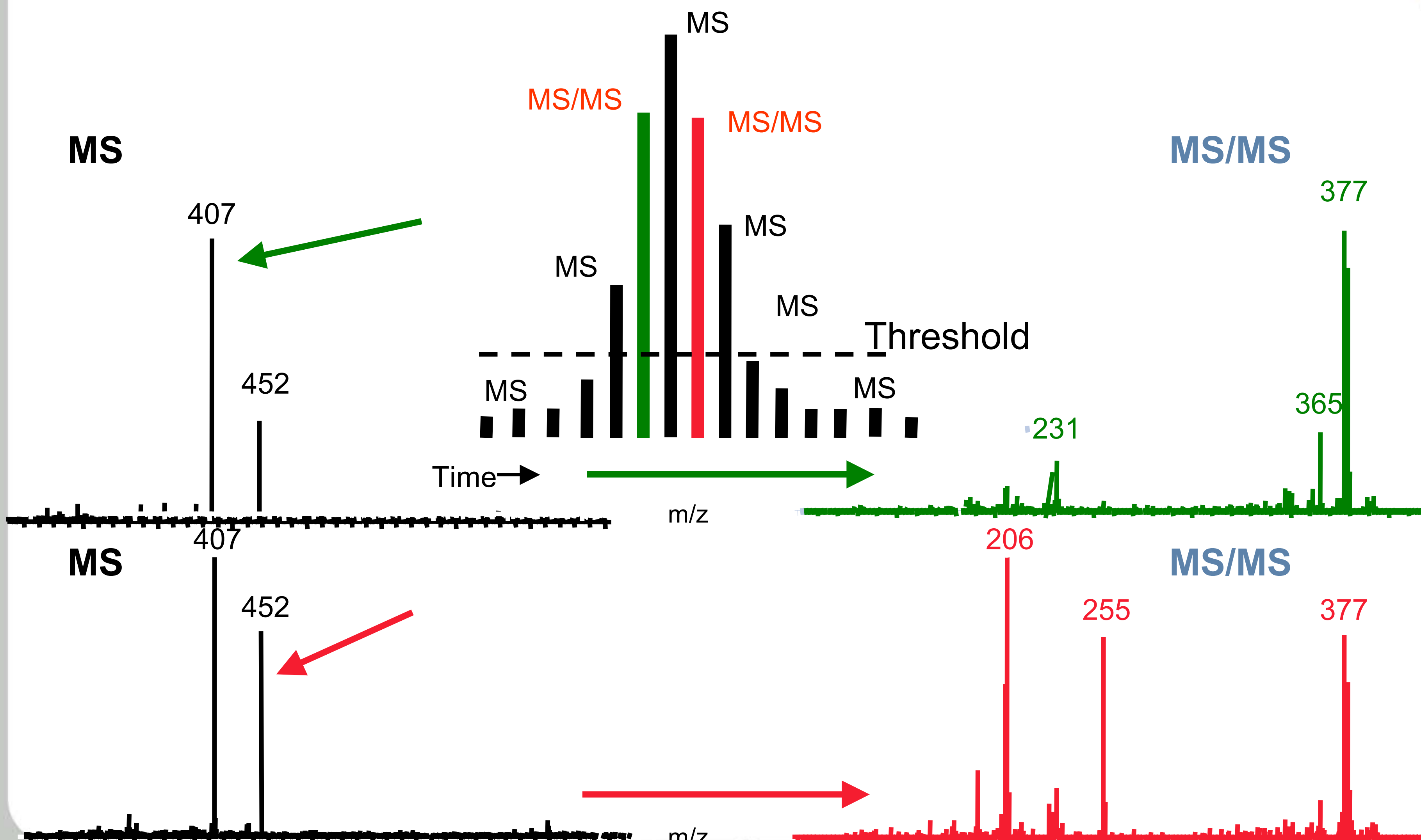
Less variability between compounds in an ion trap mass spectrometer

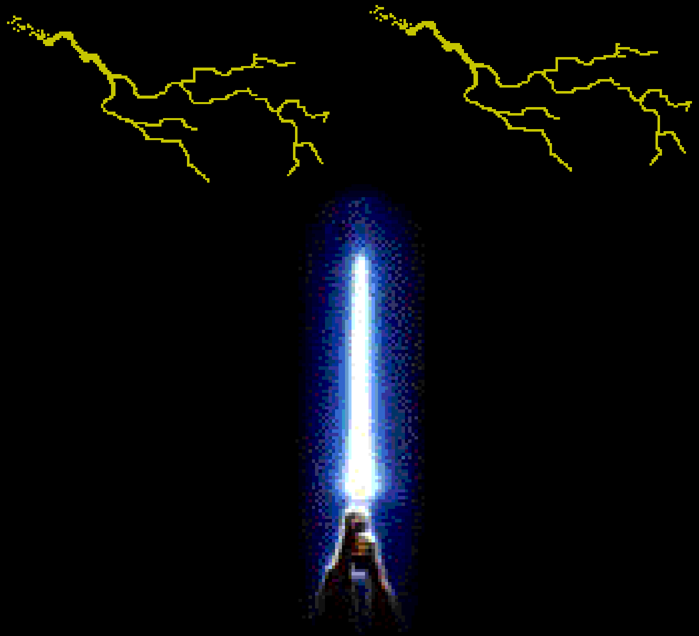
Other Interesting Aspects of Ion Traps…

Data Dependent Scanning



Dynamic Exclusion - MS and MS/MS of Coeluters

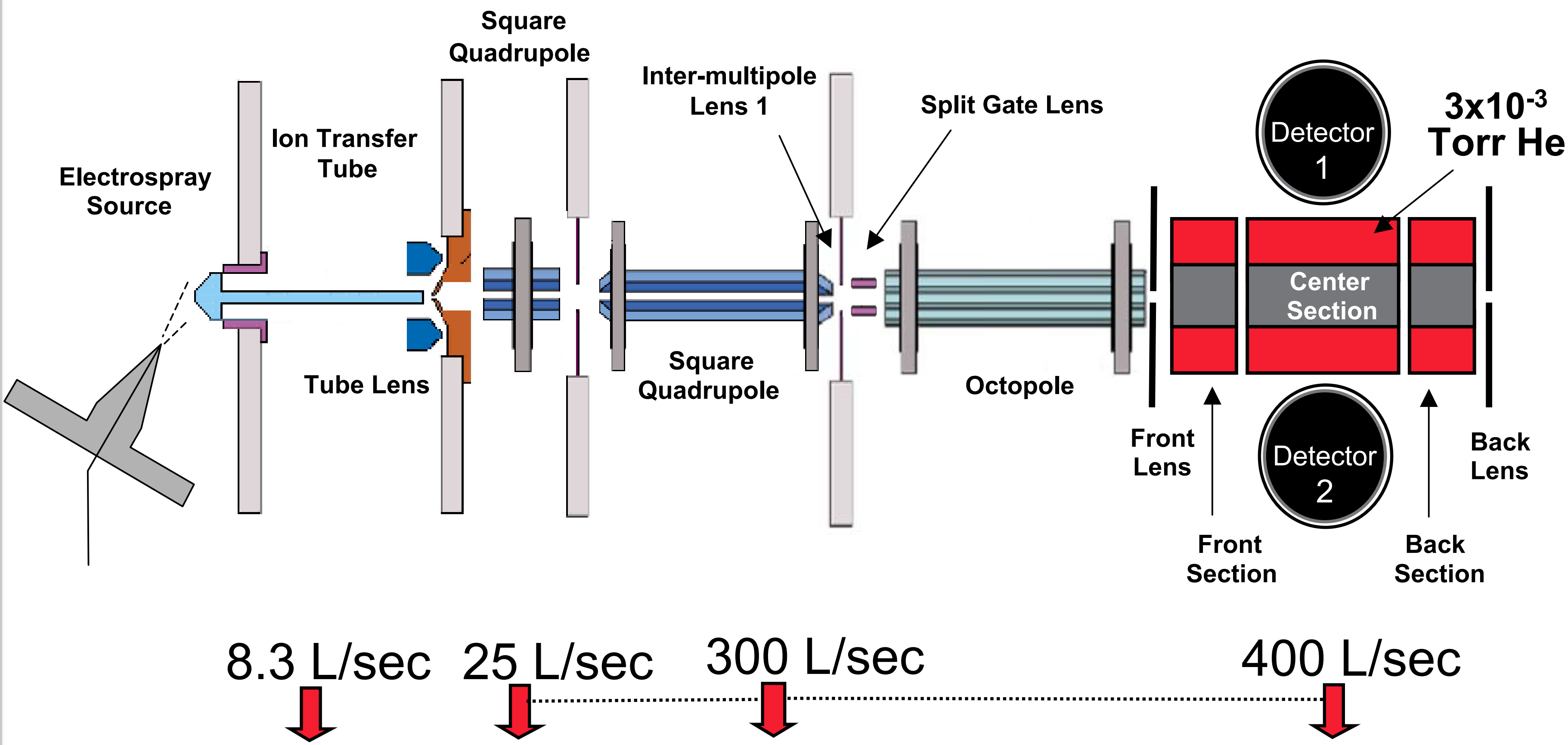




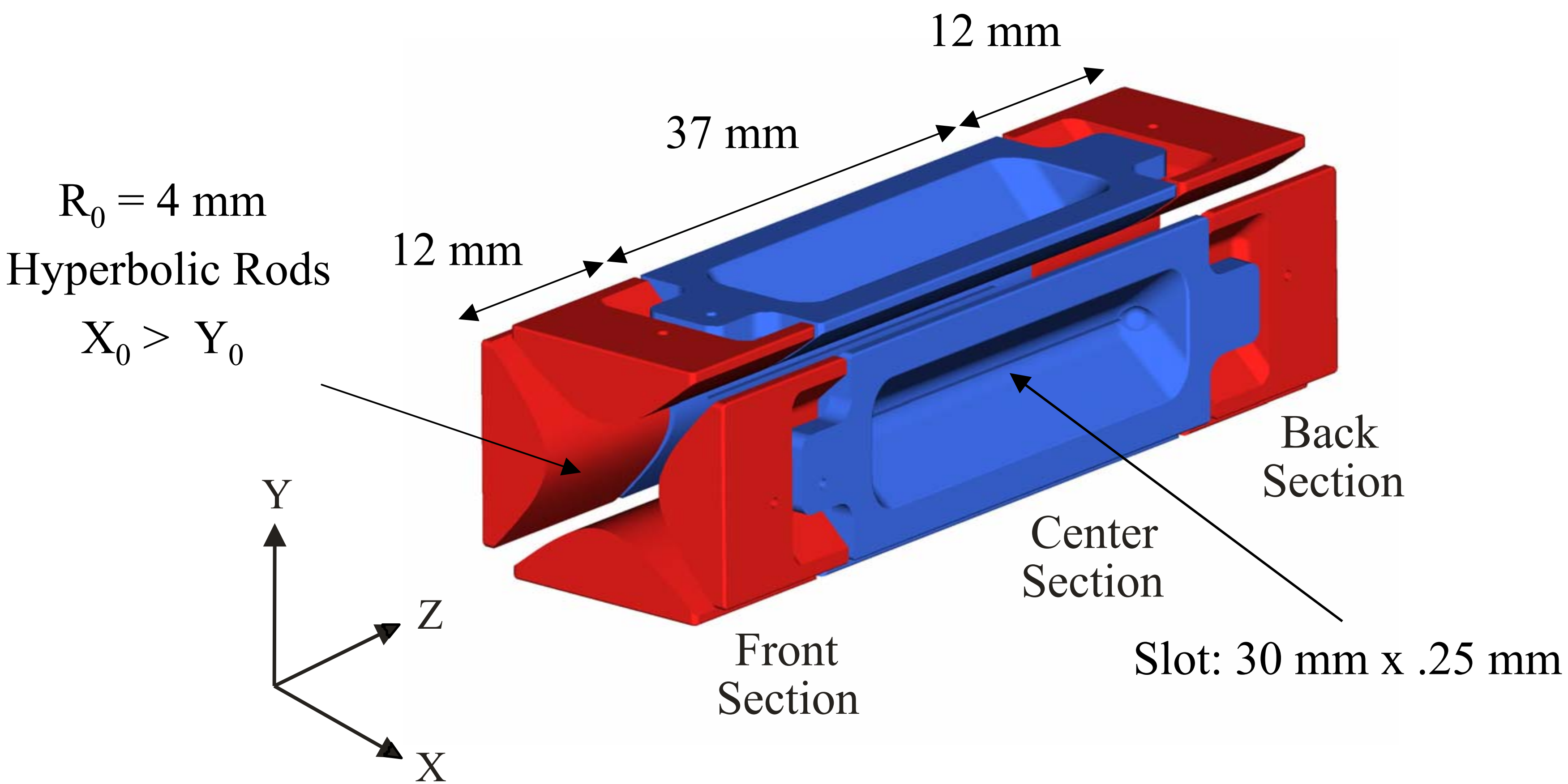
Turning it up a notch!

The Finnigan LTQ – Linear Ion Trap

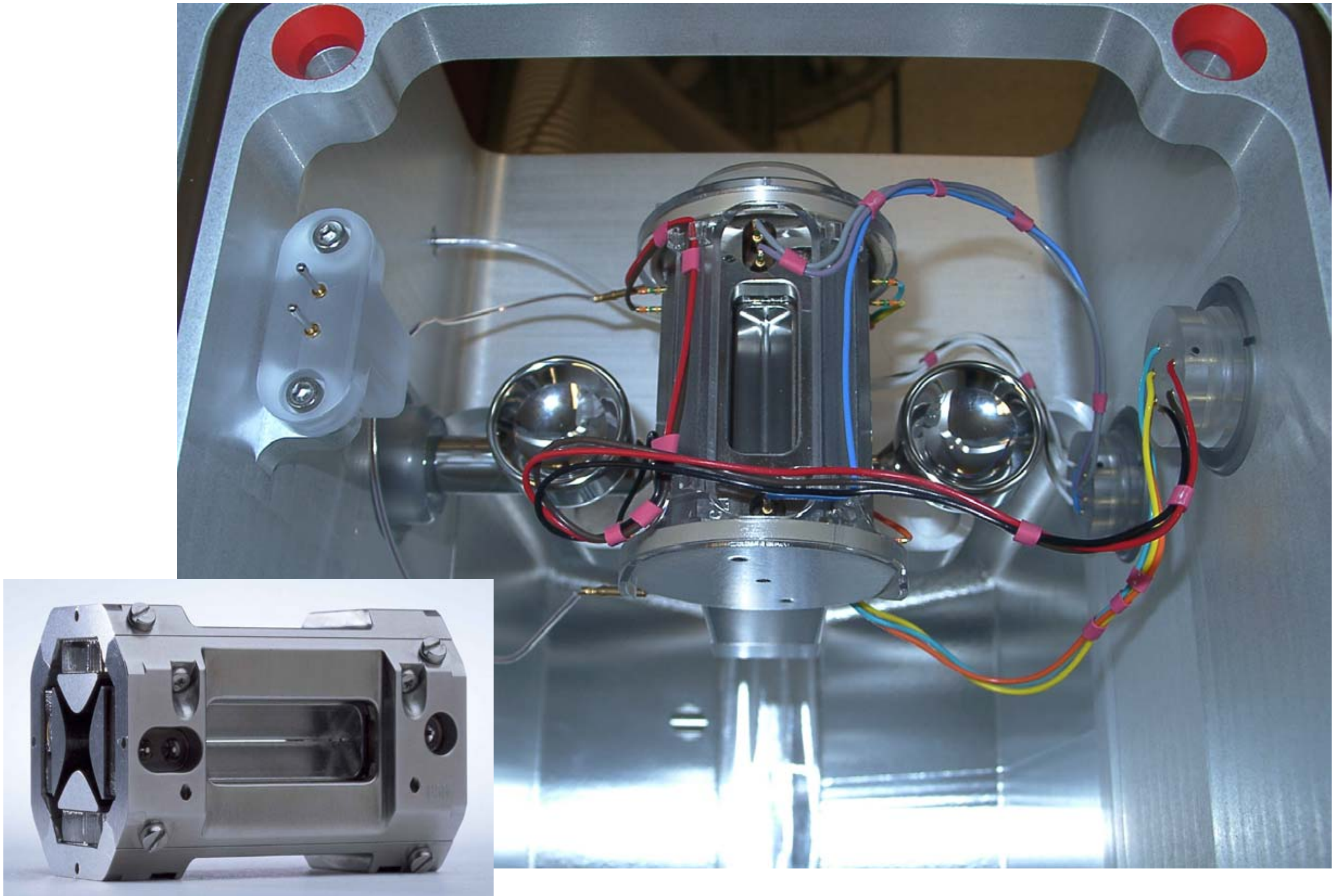
LTQ – Schematic



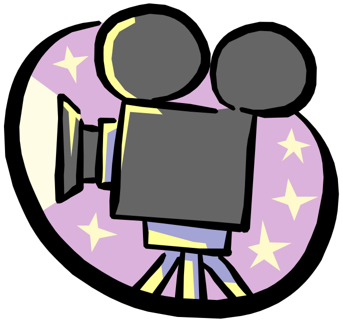
Basic Linear Trap Structure



LTQ Vacuum Chamber – Linear Trap and Dynodes



2D Ion-Trap Animation

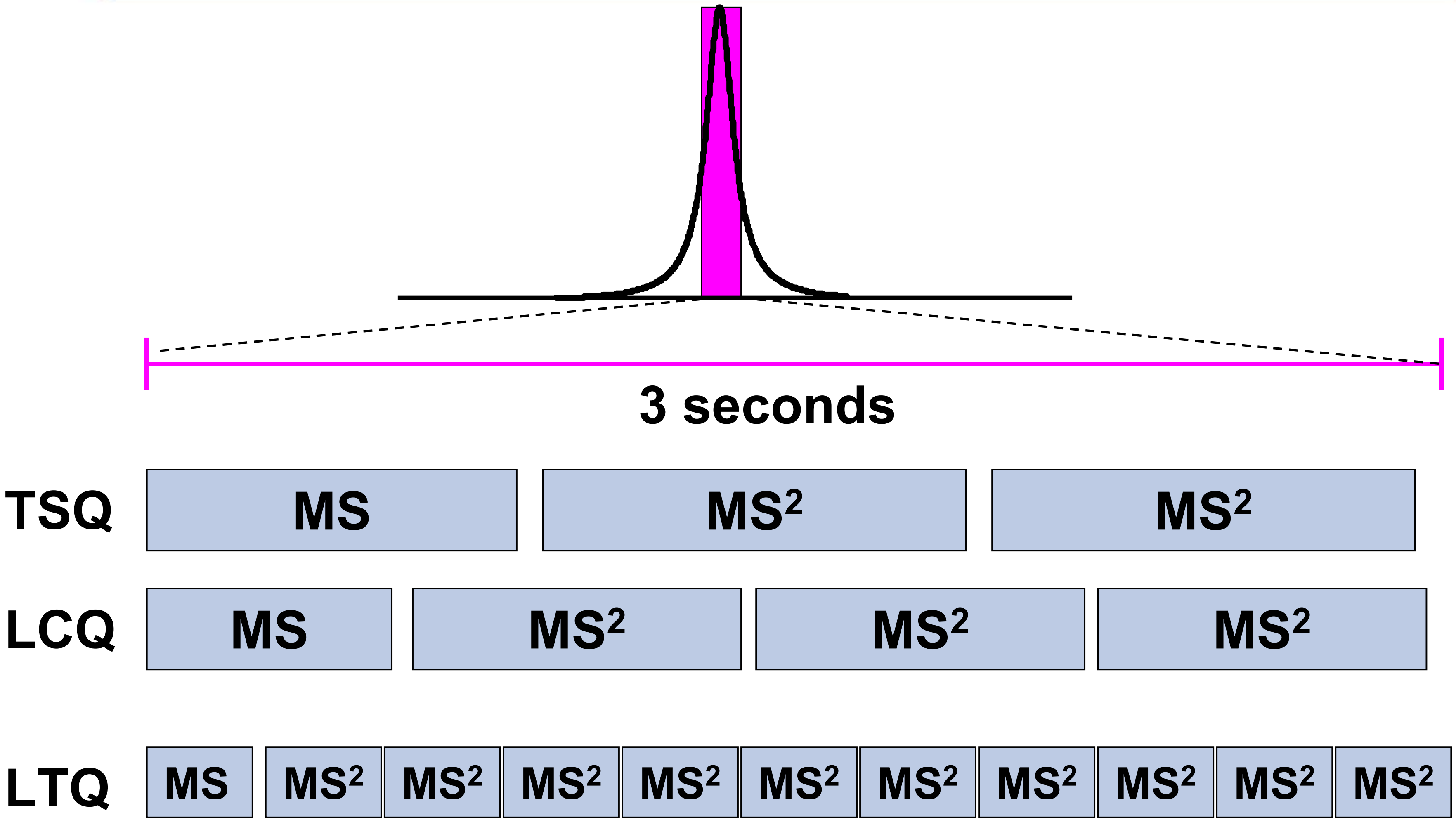


How Does the LTQ Save Time?

- Improved Cycle Time
  - *More mass spectra can be acquired across narrow chromatographic peaks*
    - Increased information content
      - *Simultaneous acquisition of MS^2 spectra from co-eluting metabolites*
      - *Acquisition of MS^2 spectra from low- level metabolites in complicated matrices*
    - Increased confidence in structural assignments based on spectral features
      - *Multiple spectra can be compared for reproducibility*

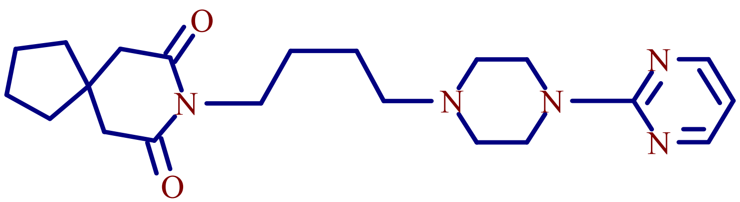
- Improved Sensitivity
  - *Lower levels of metabolite detected*
    - Less sample preparation required
    - Less re-running of samples required

Improved Cycle Time of the LTQ



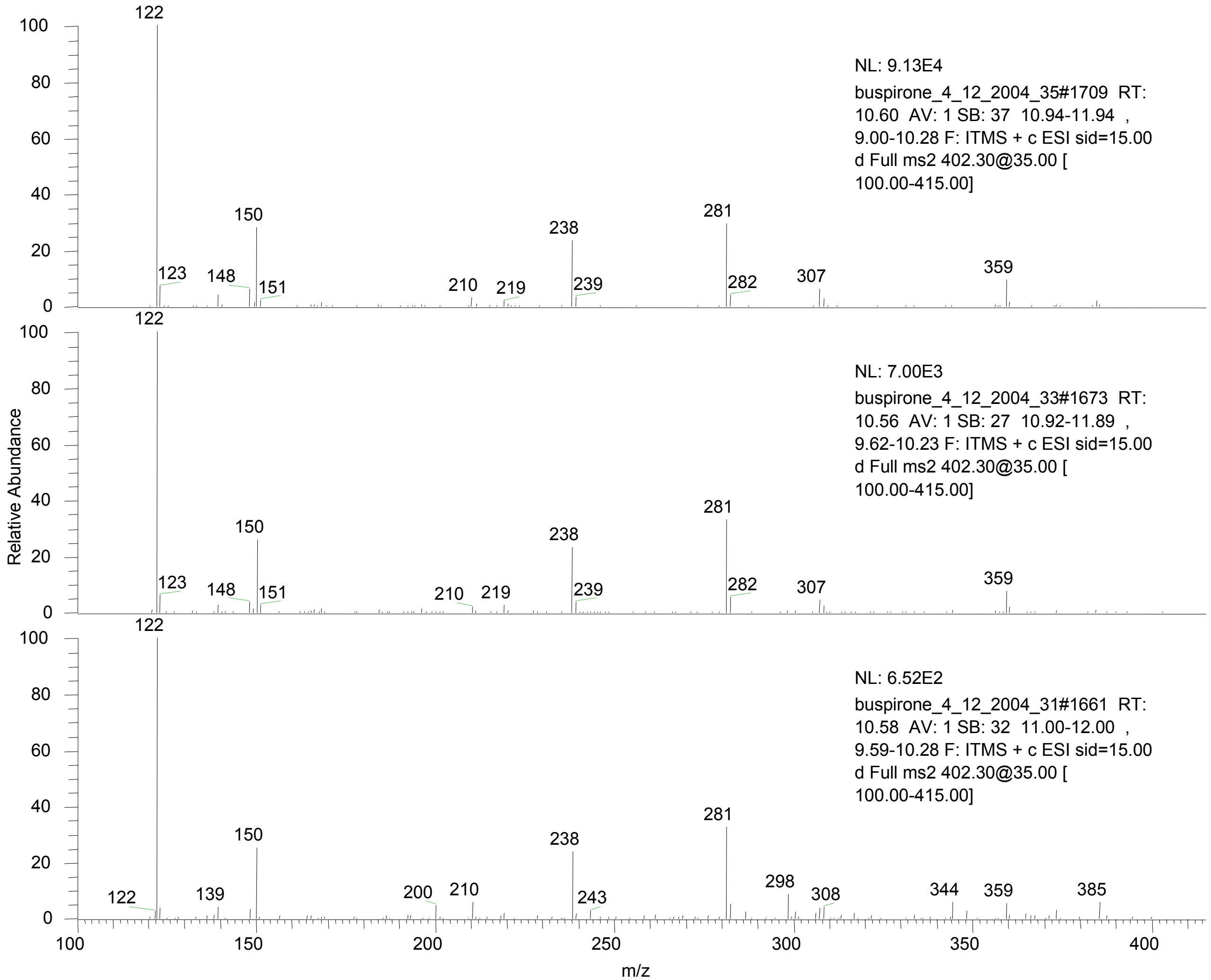
Test System

- Buspirone incubated with microsomes from male Spraque-Dawley rats
  - *Buspirone was incubated at concentrations of 0.1 uM, 1.0 uM, and 10 uM*
  - *Time points at 0 min and 60 min were acquired for each concentration*
  - *Samples were diluted in half with acetonitrile at the appropriate time to quench the reactions*
  - *Samples were centrifuged to precipitate the proteins*
  - *10 μL of supernatant from each sample was injected without any preconcentration*

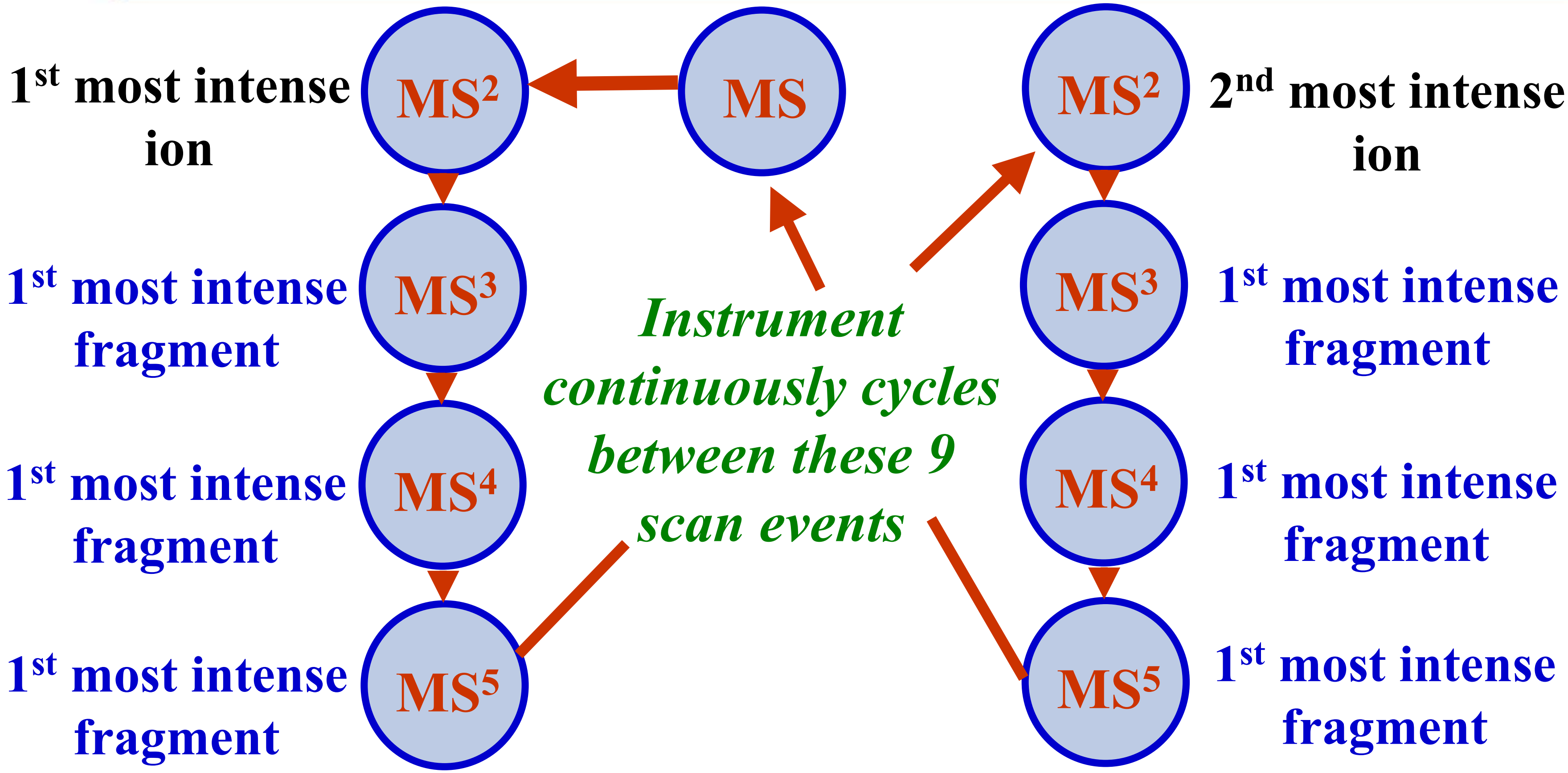


Buspirone (MH$^+$: 386)

Improved Sensitivity of the LTQ

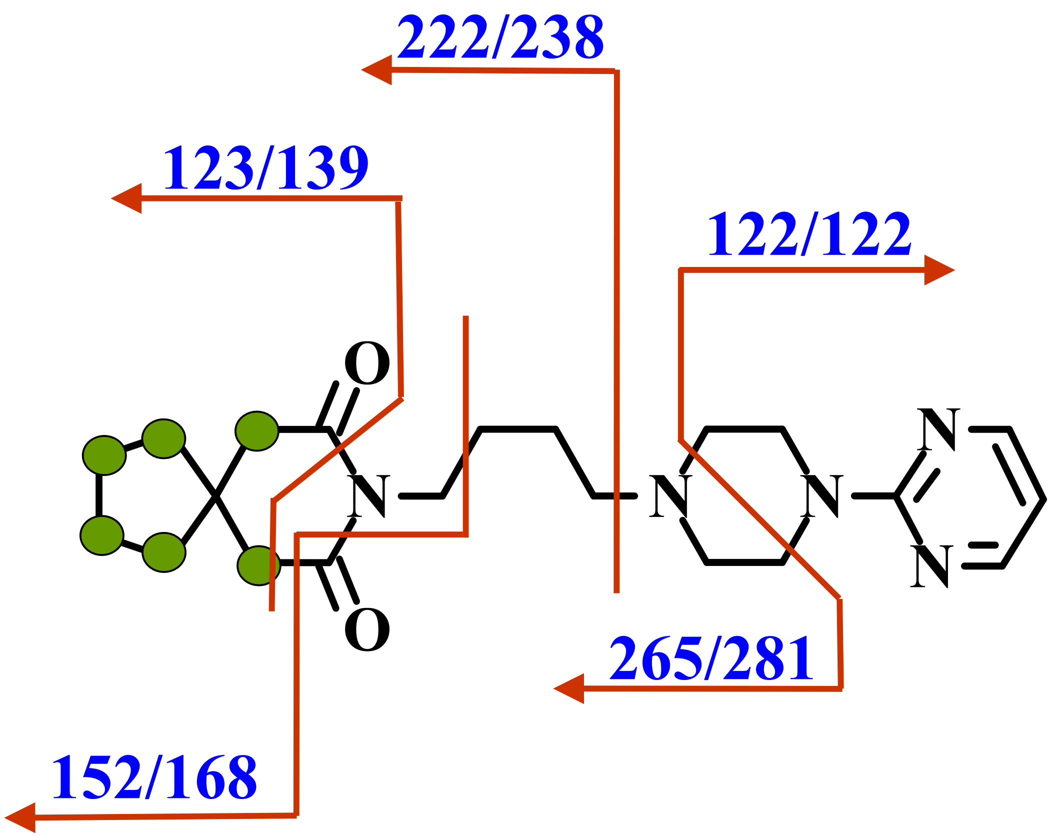


Using Higher Order MS^n Spectra to Postulate Metabolite Structures



This scanning sequence is designed to obtain MS^5 data on a smaller number of components. It is useful for when an initial MS^2 screen has been performed that limits the number of possible metabolites that need to be monitored to those on a parent mass list.

MS^n Peak Assignments for Buspirone/Hydroxy Metabolite



Potential Drawbacks of Ion Trap Mass Spectrometers that the LTQ was Designed to Overcome

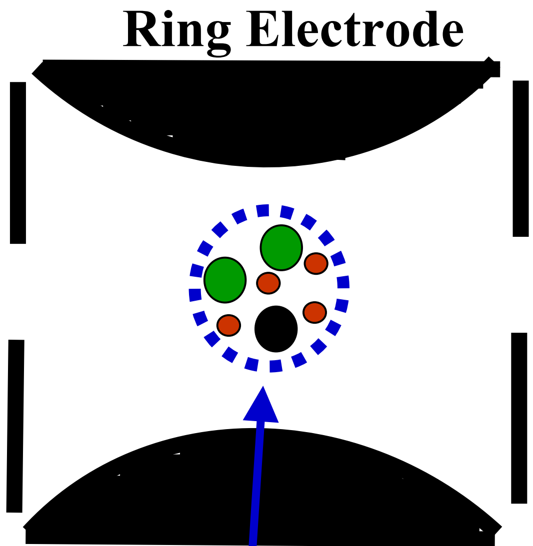
Limited Storage Capacity

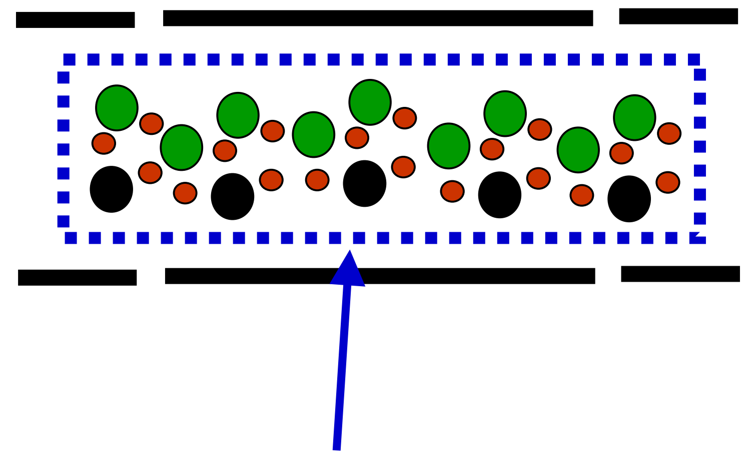
Inefficient Trapping

Storage Capacity

- There is a maximum number of ions that can be stored within an ion trap at any one time
  - *When filled beyond this maximum, "space charging" will occur*
- "Space charging" can degrade spectral resolution, mass accuracy, and sensitivity

Storage Capacity (continued)



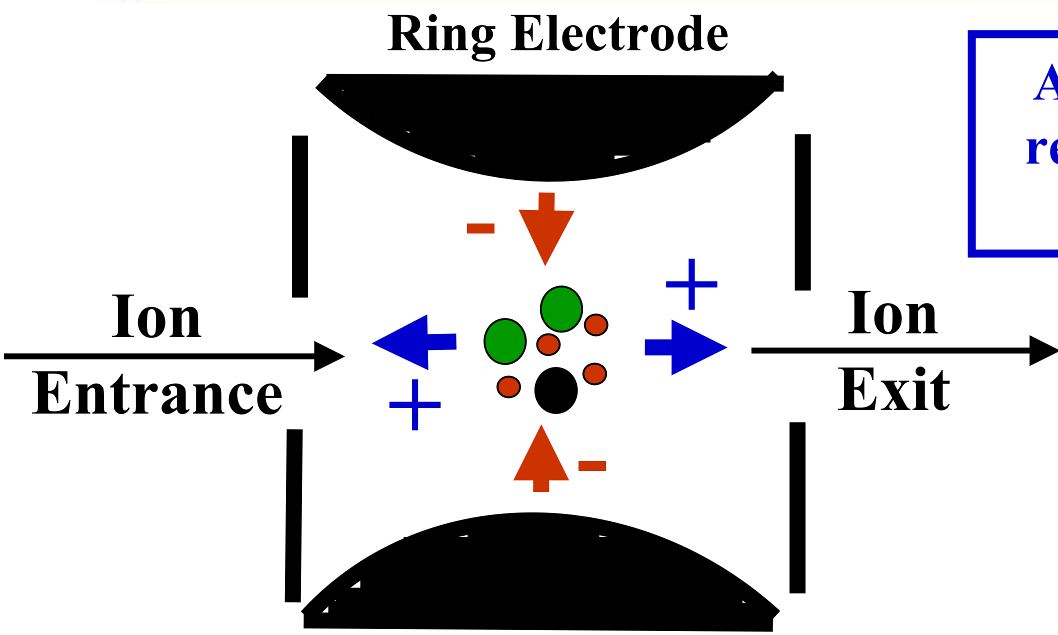


3D-Trap: Ions need to be confined to a small volume at center of trap for optimum performance

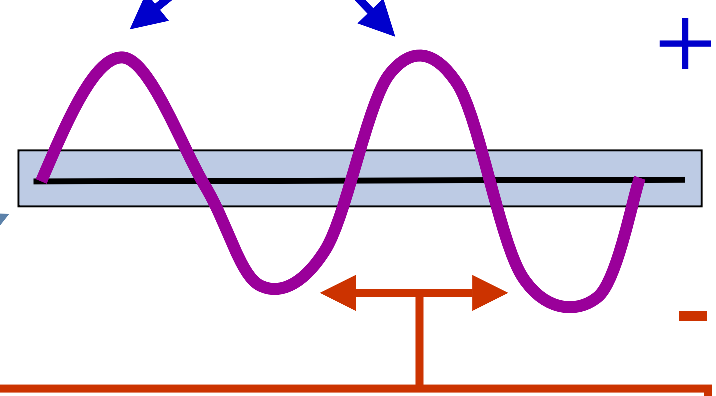
2D-Trap: Ions can spread out in the axial dimension without degrading performance

The ion storage capacity of the 2D-trap is more than 20x greater than that of the 3D-trap

Trapping Efficiency in a 3D-Trap



A positively charged ion is repelled from the trap by a positive electrical field

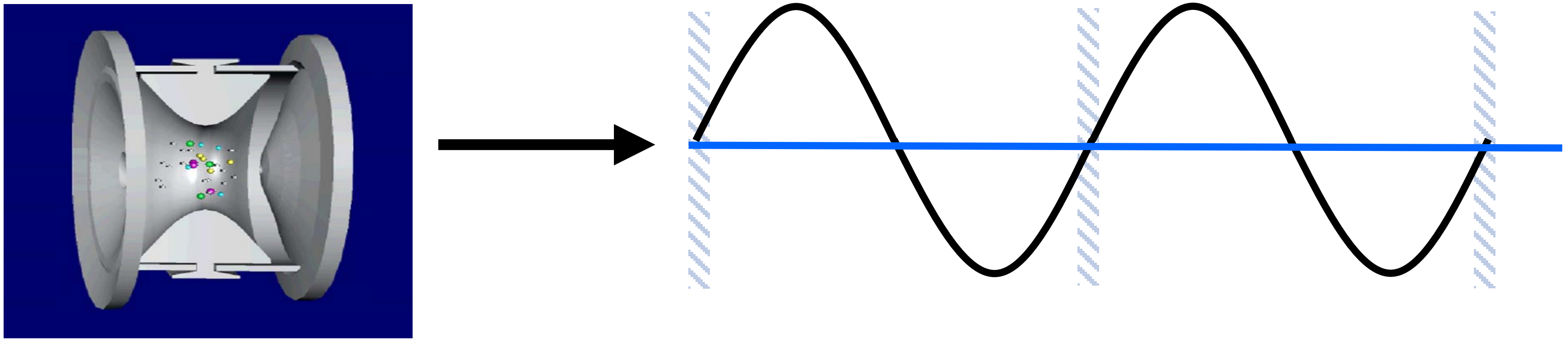


A 3D RF field exists which is unfavorable for ion trapping except for during a narrow phase window

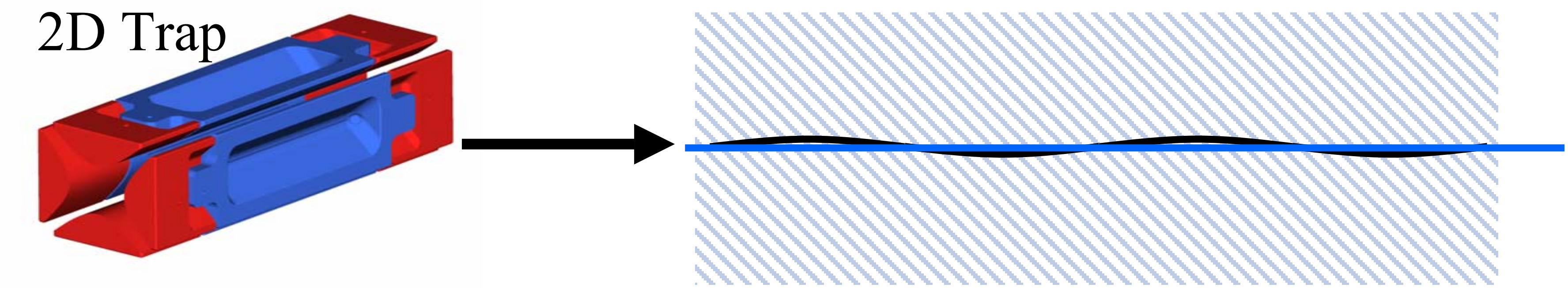
A positively charged ion is pulled through the trap by a negative electrical field

Trapping Efficiency in the LTQ 2D-Trap

3D Trap



2D Trap



In the LTQ 2D trap, the RF field is perpendicular to the ion entrance axis which reduces the problems associated with ion injection in the 3D trap. This results in a 10-15x improvement in trapping efficiencies

Summary – Analytical Improvements

- Increased Trapping Efficiency (55-75%)
- Increased Trapping Capacity (~20,000 ions)
- Increased Sensitivity (Dual detectors-2x better detection efficiency).

Which means....

Increased Dynamic Range (4-5 orders of linear Dynamic range)

Increased S/N for full Scan MS

Practical MS^n experiments

Faster Scan times (16,700 amu/sec – Normal Mode)

Resolution (FWHM) 30,000 (m/z 1522) at 27 amu/sec

Method for DD Neutral loss scanning capability

Platform for Hybridization (FT/MS)

FINNIGAN LTQ FT

Questions?