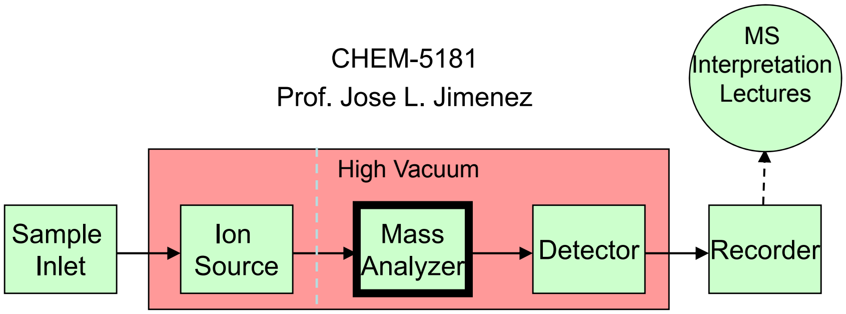
Mass Analyzers: Quadrupoles

CHEM-5181

Prof. Jose L. Jimenez



Props: quad, simul

Last Update: Oct. 2014

Some slides adapted from Fall 2007 lecture by Dr. Joel Kimmel, CU-Boulder

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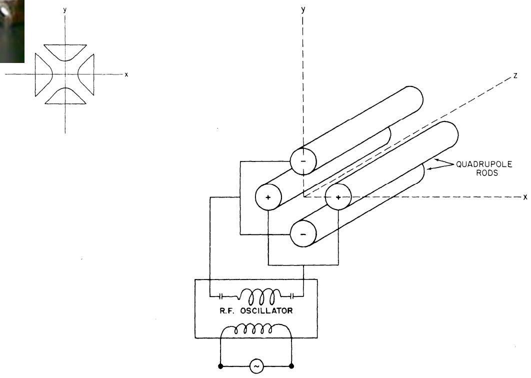
Business Items

- We will proceed soon w Labview installation
  - Instructions coming soon
  - Getting it done on time will be part of a HW
  - Folks w Macs, Bootcamp installed?
- Questions, comments?

Quadrupole Geometry



Quadrupole consists of four parallel rods

Typical length might be 10-20 cm

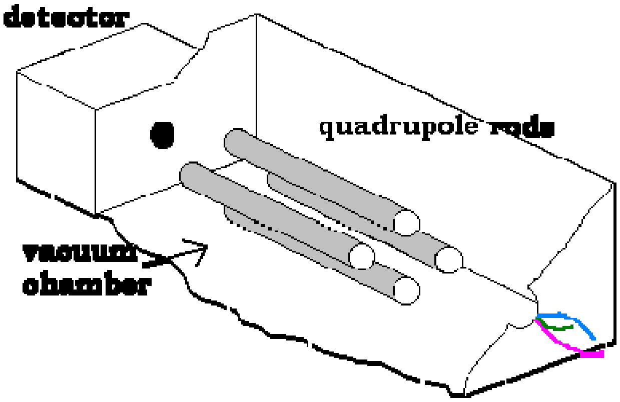
Precise dimensions and spacing

Rods connected diagonally in pairs

FIG. 4.6. Schematic diagram showing arrangement of quadrupole rods and electrical connection to RF generator; a DC potential (not shown) is also impressed on the rods. The *inset* illustrates the ideal quadrupole electric-field dispersion.

From Watson

Ion Motion inside a Quad (Animation)

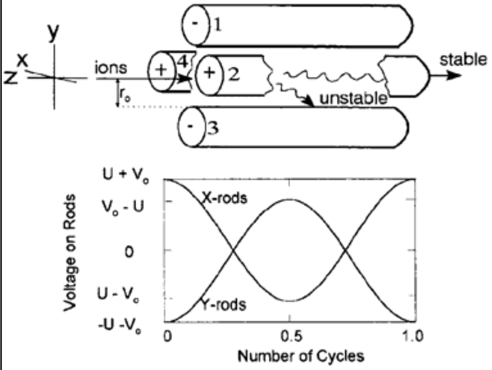


Voltages applied to rods define time-varying fields between rods and determine the m/z that is transmitted.

Q: what's wrong with this animation?

Quadrupole Voltages

- Voltage of all rods have a DC component, **U** or **-U**.
  - Q: what would happen if there was only DC?
- All rods have RF component of voltage with **MHz frequency = ω/2π** and amplitude $\mathbf{V_o}$.
- Potentials on the two sets are **out of phase by 180°**.
- Quadrupole fields cause **no acceleration along z axis**.

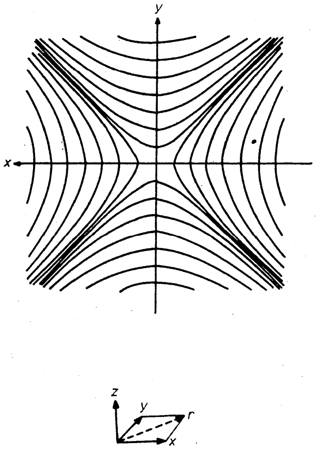


From: Steel and Henchman, *J. Chem. Ed.*, 75(8), 1049, 1998.c

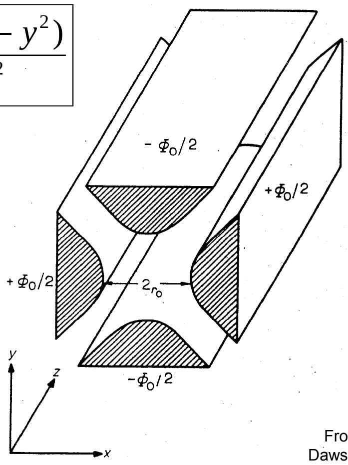
$$V_1 = V_3 = -\Phi_o = -U - V_o \cos \omega t$$

$$V_2 = V_4 = \Phi_o = U + V_o \cos \omega t$$

Quadrupole Electric Field



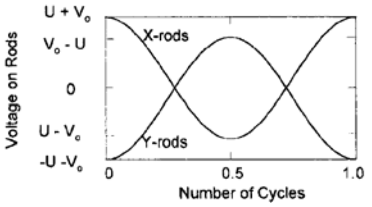
$$\Phi = \frac{\Phi_0 (x^2 - y^2)}{2 r_0^2}$$



From Dawson

Fig. 2.1. Equipotential lines for a quadrupole field where $\phi = -1/2 E_0 \lambda (x^2 - y^2)$.
Fig. 2.2. The electrode structure required to generate the potential shown in Fig. 2.1. These are the ideal quadrupole mass filter electrodes having hyperbolic cross-sections.

An (Stable) Ion in a Quadrupole Mass Spectrometer

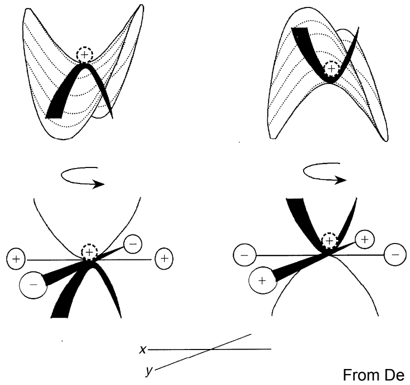


OUT OF PHASE

Symmetric voltages create clearly defined wells / ridges.

At any given moment one axis focuses ion to center (+), while the other pulls off center (-).

Rapid alternation between polarities.



From De Hoffmann

Figure 2.8
A positive ion, represented within a dotted circle, is at the center of quadrupole rods, the potential signs of which are indicated. It goes down the potential 'valley' with respect to the negative rods and acquires some kinetic energy in that direction. However, the potentials quickly change so that the kinetic energy is converted into potential energy and the ion goes back to the center of the rods, as would happen for a ball on a horse saddle that is turned quickly. The name 'saddle field' is an allusion to this phenomenon

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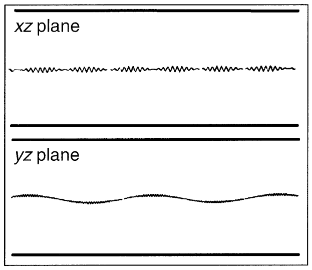
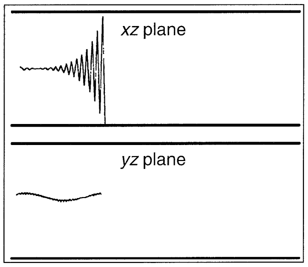
Ion Motion Inside a Quadrupole



Stable along both *x* and *y*

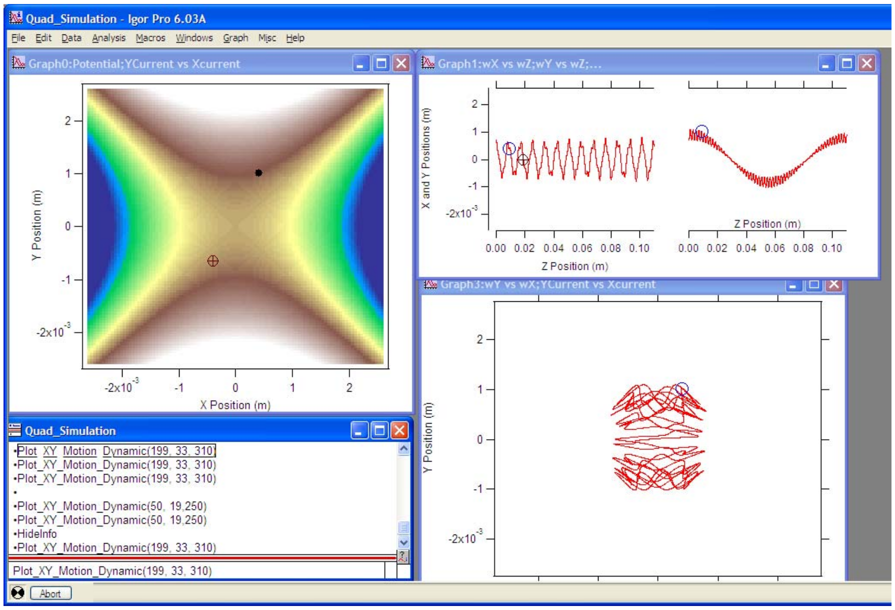


Stable along *y*, unstable along *x*

From Hoffmann

Figure 2.5
Stable and unstable trajectories of ions in a quadrupole. (Reproduced (modified) from Ref. 6 with permission)

Quad Igor Simulation



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•Plot_XY_Motion_Dynamic(199, 33, 310)
•Plot_XY_Motion_Dynamic(199, 33, 310)
•Plot_XY_Motion_Dynamic(199, 33, 310)
•
•Plot_XY_Motion_Dynamic(50, 19,250)
•Plot_XY_Motion_Dynamic(50, 19,250)
•HideInfo
•Plot_XY_Motion_Dynamic(199, 33, 310)
Plot_XY_Motion_Dynamic(199, 33, 310)
```

Forces – Generalizing for all m/z

The Laplace Equation leads to:

$$V(x,y) = (x^2 - y^2)(U + V_o \cos \omega t)/r_o^2$$

Applying Newton's Second Law:

$$F = ma = q\vec{E}$$

$$F_x = m\frac{d^2x}{dt^2} = -ez\frac{\partial V}{\partial x} = -2e(U + V_o \cos \omega t)x/r_o^2$$

Substituting:

$$\phi = \omega t/2$$

$$\alpha = \frac{8ezU}{r_o^2 m\omega^2}$$

$$q = \frac{4ezV_o}{r_o^2 m\omega^2}$$

Yields:

$$\frac{d^2x}{d\phi^2} = -(\alpha + 2q\cos 2\phi)x$$

$$\frac{d^2y}{d\phi^2} = (\alpha + 2q\cos 2\phi)y$$

Acceleration in x and y directions is described based on the terms α (or a) and q.

Note that:

α is proportional to U/m

While

q is proportional to V_o/m

For given quadrupole, r_o is constant, ω is held constant, and V and U will be variables.

Clicker Q

Q: To determine whether a quadrupole will transmit an ion of known m/z, one must know:

1. z
2. The length the quadrupole
3. The distance between rods of the quadrupole
4. The velocity of the ion before entering the quadrupole
5. The angular frequency of the applied RF potential

A. All of the above

B. 2,3,4,5

C. 1,3,4,5

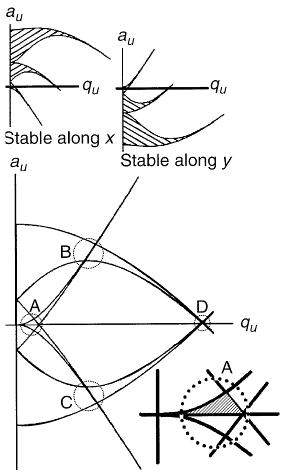
D. 3,4

E. I don't know

Stability Diagram for a Quadrupole

$$a_u = \frac{8zeU}{m\omega^2 r_o^2}$$

$$q_u = \frac{4zeV}{m\omega^2 r_o^2}$$



From De Hoffmann

a and *q* are used to define generalized stability plots

Intersections of x and y stability in a_u-q_u space define stability in quad.

Which region should we use for a quadrupole?

A. Region A

B. Regions B or C

C. Region D

D. Any of them will work similarly

E. I don't know

Stability

Stability diagram for fixed Rf frequency, fixed m/z.

An ion will have stable trajectory through quadrupole if x and y are always less than radius of quadrupole.

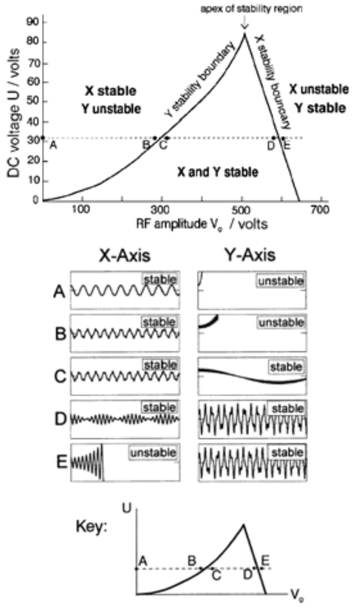
(Sim A) With no RF and positive U, positive ion is stable along X (repelled to center), attracted to negative Y rod causes instability

(Sim C) RF field has stabilized Y trajectory.

Note that with increased U, need greater V_o to achieve this stability.

(Sim E) Instable along x-axis.

Note that as U increases, lower V_o will induce this instability.



From: Steel and Henchman, *J. Chem. Ed.*, 75(8), 1049, 1998.

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m/z Scanning in a Quadrupole MS

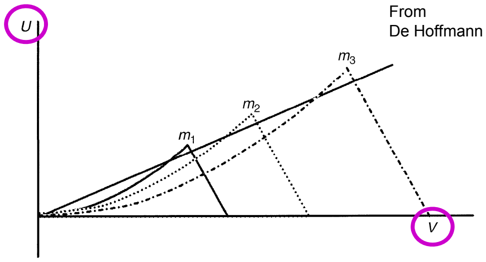
$$a_u = \frac{8zeU}{m\omega^2 r_o^2} = 0.233$$

$$q_u = \frac{4zeV}{m\omega^2 r_o^2} = 0.706$$

Scan line shows

U/Vo = ½(0.233 / 0.706)

Increase in mass requires proportional increases in U and V_o to maintain this ratio and these a and q values.



From
De Hoffmann

Figure 2.7
Stability areas as a function of U and V for ions with different masses ($m_1 < m_2 < m_3$). Changing U linearly as a function of V, we obtain a straight operating line that allows us to observe those ions successively. A line with a higher slope would give us a higher resolution, as long as it goes through the stability areas. Keeping $U = 0$ (no direct potential) we obtain zero resolution. All of the ions have a stable trajectory as long as V is within the limits of their stability area. (Reproduced (modified) from Ref. 6 with permission)

Mass Filter

Many conditions (U, V, m) fall within stability region – there is more than one way for ion to pass through

For selectivity, must also consider stability of other mass values

Apex of generalized stability diagram is at α = 0.237, q = 0.706

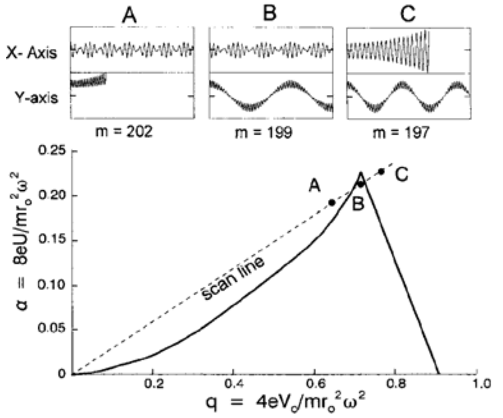
To select transmit narrow mass window, **adjust U and V_o such that α = 0.237, q = 0.706** (e.g., Ion B)

For any value m

$$\alpha/q = 2U/V_o$$

To scan values of m through narrow transmission window, hold other parameters constant and scan U and V_o with constant ratio

$$U/V_o = \tfrac{1}{2}(0.233 / 0.706)$$



From: Steel and Henchman, *J. Chem. Ed.*, 75(8), 1049, 1998

Figure limited to singly charged ions (hence lack of z in expression)

Mass Filter

For **ANY value m**

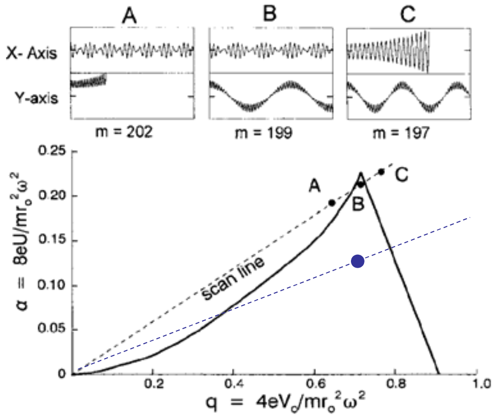
$$\alpha/q = 2U/V_o$$

For, example: Reduce U, Hold V

Still stable, slope of "scan line" is reduced

What effect does this have on resolution?

A. Increase
B. Decrease
C. Keep the same
D. I don't know



From: Steel and Henchman, *J. Chem. Ed.*, 75(8), 1049, 1998

Figure limited to singly charged ions (hence lack of z in expression)

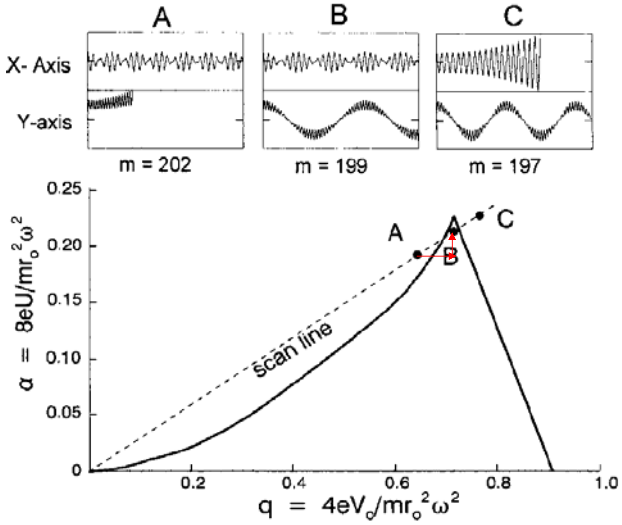
Mass Filter

Scan line shows

U/Vo = ½(0.233 / 0.706)

Increase in mass requires proportional increases in U and V_o to maintain this ratio and these a and q values.

Example, bringing 202 into stability apex requires increases in U and V

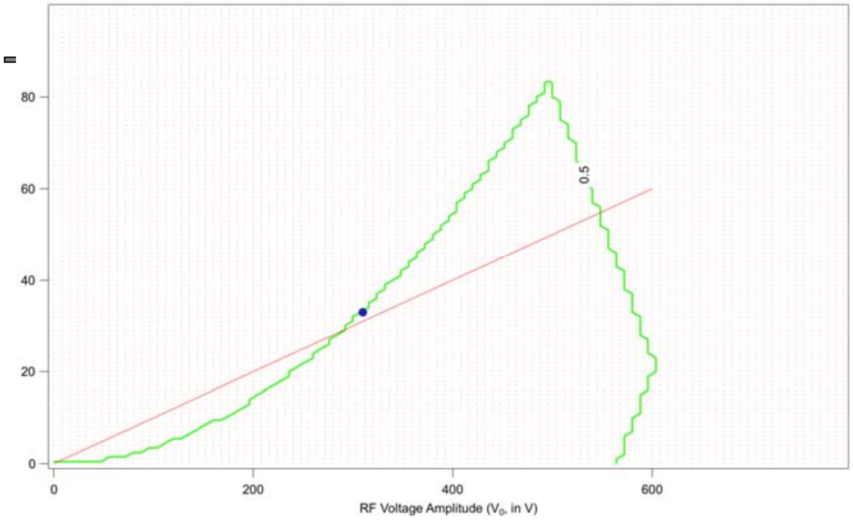


From: Steel and Henchman, *J. Chem. Ed.*, 75(8), 1049, 1998

Figure limited to singly charged ions (hence lack of z in expression)

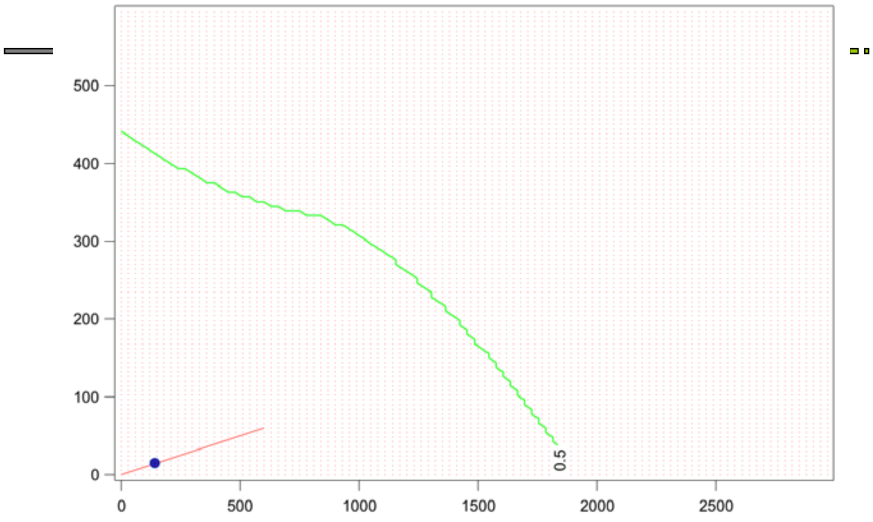
Experimenting with the model

- Experiments done by 2014 students as part of the HW
  - Let’s think about their results and whether they make sense



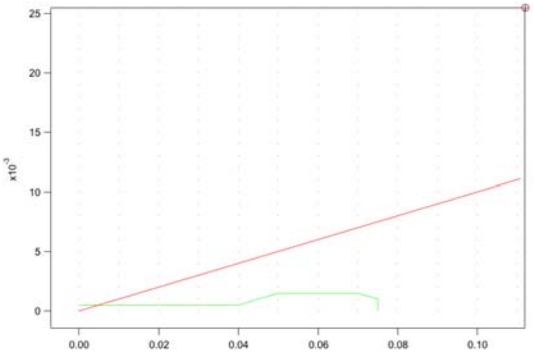
Megan H – varying initial velocity
(variable = Vz_m_s) *5 and /5

No effect on stability diagram!



Megan H – varying initial velocity
Vz_m_s*100 default!

Everything is stable (up to and beyond reasonable voltages)



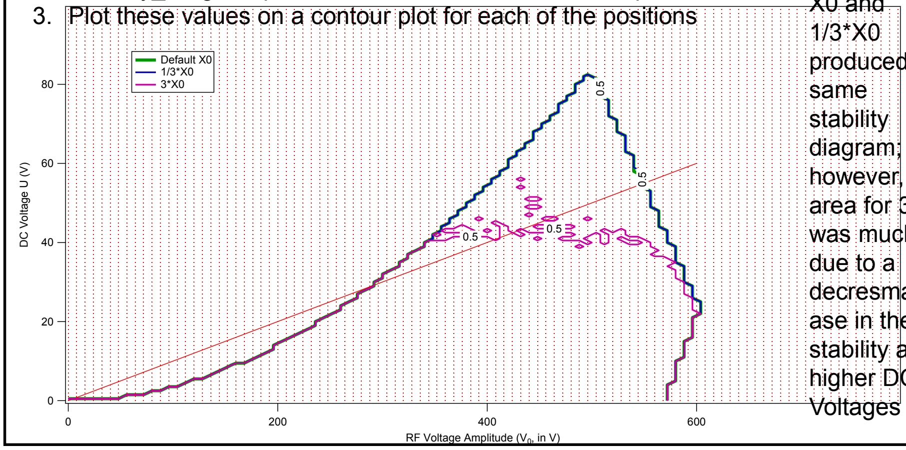
Megan H – varying initial velocity

Vz_m_s/1000 default!

Changing Initial X Position

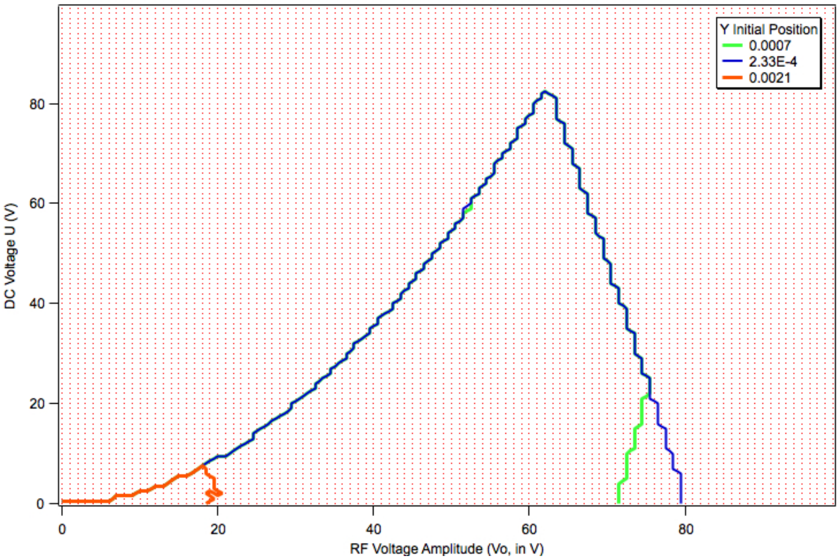
- Samantha Miller
- Description of Process:

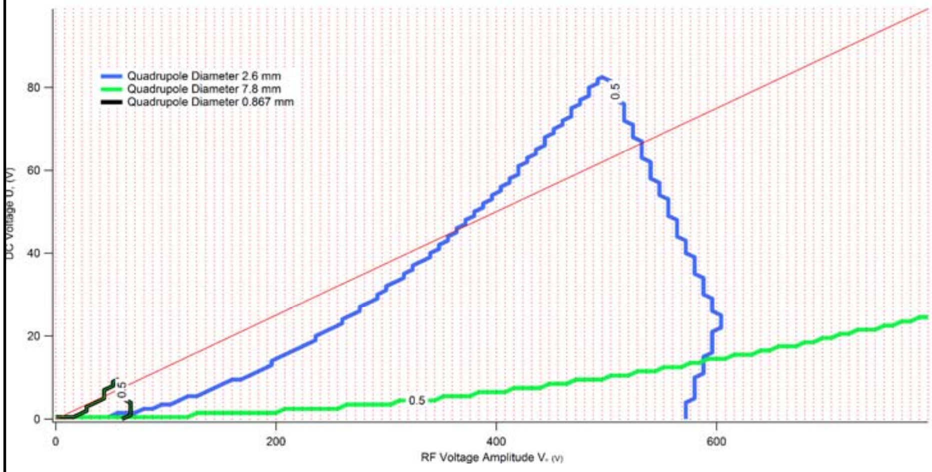
1. Call upon Stability_Diagram function for each of the values in an initial position wave (X0, 1/3*X0, and 3*X0).
2. Stability_Diagram produces matrix of stable/unstable points.
3. Plot these values on a contour plot for each of the positions



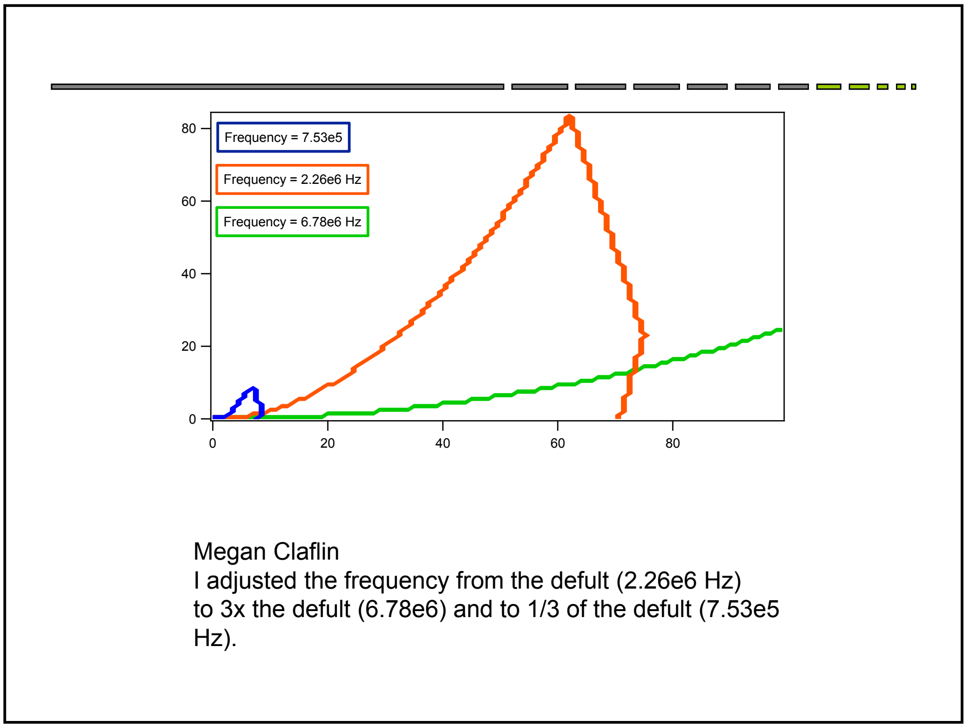
Comments: X0 and 1/3*X0 produced the same stability diagram; however, the area for 3*X0 was much due to a decresmaller ase in the stability at higher DC Voltages

Varying initial Y position (Julia)





Zack Finewax: Stability Diagrams for default quadrupole diameter, three times r0, one third r0 with scaled initial x and y positions.



Megan Claflin
I adjusted the frequency from the defult (2.26e6 Hz)
to 3x the defult (6.78e6) and to 1/3 of the defult (7.53e5
Hz).

TOFMS vs Quadrupole MS

- **TOFMS**
  - Pulse packet of ions introduced into analyzer
  - All m/z in packet reach detector ("simultaneous detection")
  - m/z determination based on <u>dispersion in time</u>
  - Based on static, DC fields
- **Quadrupole MS**
  - Continuous introduction of ions into analyzer
  - Transmit only specific m/z value to detector
  - m/z determination based on <u>band-pass filtering</u>
  - Based on time-varying, RF fields

Clicker Q

When acquiring mass spectra with unit resolution for ions originating from a continuous source (that is, ions being presented to the mass spectrometer as a steady stream) the duty cycle of a quadrupole mass spectrometer:

A. Is nearly 100%

B. Depends on the m/z range being scanned

C. Is independent of m/z range, but depends on U, V, and ω

D. Cannot be determined

E. I don't know

Clicker Q

The ratio α/q is constant for ALL m/z values, no matter what the physical dimensions and voltage settings of a quadrupole

A. True
B. False
C. Almost True
D. I don't know

Clicker Q

If two mass spectra are acquired with q = 0.706 and different α, and both generate stable conditions for m/z = 100 transmission, the spectrum collected at the ___________ U is ___________ likely to generate stable conditions for m/z = 101 transmission.

A. Higher, More
B. Higher, Equally
C. Lower, More
D. Lower, Less
E. Need to know more about quadrupole

Quadrupole Notes

- Maximum m/z ~ 4,000
- Resolution ~ 3,000
  - Quadrupoles are low resolution instruments
  - Usually operated at 'Unit Mass Resolution'
- Small, lightweight, cheaper
- Easy to couple with chromatography

Mass Discrimination on a quadrupole

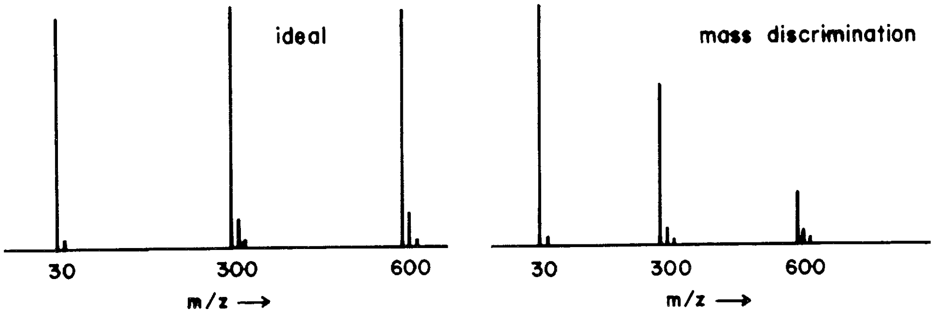
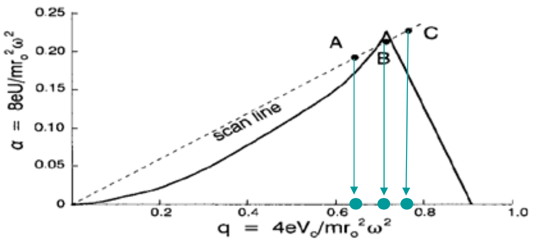


FIG. 4.9. Hypothetical mass spectra recorded by an “ideal” mass spectrometer **(left)** and one that imposes mass discrimination **(right)**.

From Watson

Rf-Only Quadrupoles



Clicker Question: an RF only quadrupole is

A. A low pass filter
B. A high pass filter
C. A band pass filter
D. None of the above
E. I don’t know

Operated with U = 0, quadrupole becomes a broad filter

Such “RF-only” quads are an important tool for transferring ions between regions of mass spectrometers.

Often denoted with small “q”

Collisional Cooling

Collisional Damping Interface for an Electrospray Ionization Time-of-Flight Mass Spectrometer

JASMS, 1998, 9, 569-579

A. N. Krutchinsky, I. V. Chernushevich, V. L. Spicer, W. Ens, and K. G. Standing

Department of Physics, University of Manitoba, Winnipeg, Canada

http://dx.doi.org/10.1016/S1044-0305(98)00027-0

- A common application of RF-only multipoles involves collisional cooling.
- In an ESI source, the expansion into vacuum produces a ion beam with broad energy distribution
- Ion optics and TOFMS experiments rely on precise control of ion energies
- Desire strategies to dampen energy from external processes
- RF-induced trajectory in high pressure region yield collisions, and reduction in energy

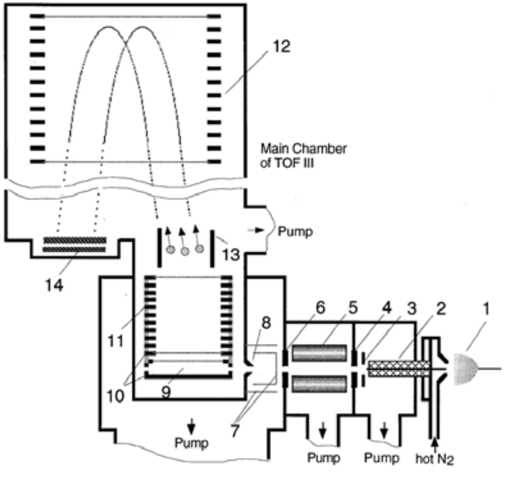


Figure 1. Schematic diagram of the time-of-flight instrument TOF III. 1—ESI ion source; 2—heated capillary; 3—focusing electrode; 4—first aperture plate; 5—rf quadrupole; 6—second aperture plate; 7—grids; 8—slit; 9—the storage region; 10—extraction electrodes; 11—acceleration column; 12—electrostatic mirror; 13—deflection plates; 14—detector.

Collisional cooling simulation paper II

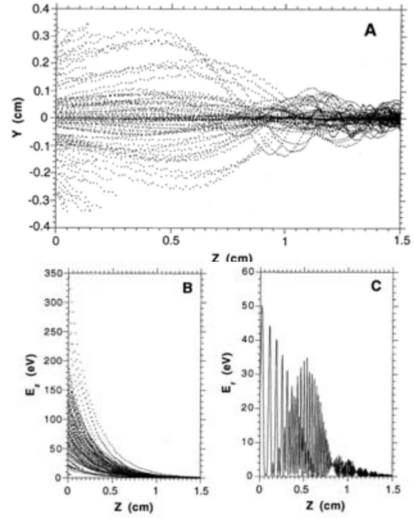


Figure 3. Computer simulation of ion motion in the quadrupole ion guide for myoglobin ions. (**A**) Projection of ion trajectories on (yz) plane. (**B**) Energy E_z of the ions as a function of position along the quadrupole z axis, where $E_z = 1/2mv_z^2$. (**C**) The energy E_r of the ions as a function of position along the quadrupole z axis, where $E_r = 1/2mv_r^2$.

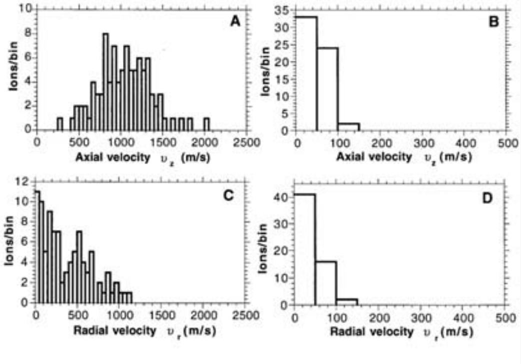
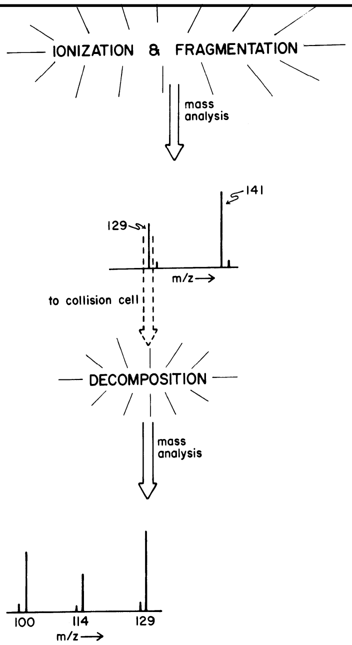


Figure 4. Histograms of the ion velocity components. (**A**) Axial velocities at the input of the quadrupole ion guide. (**B**) Axial velocities at a distance of 1.5 cm inside the quadrupole ion guide. (**C**) Radial velocities at the input of the quadrupole ion guide. (**D**) Radial velocities at a distance of 1.5 cm inside the quadrupole ion guide.

http://dx.doi.org/10.1016/S1044-0305(98)00027-0

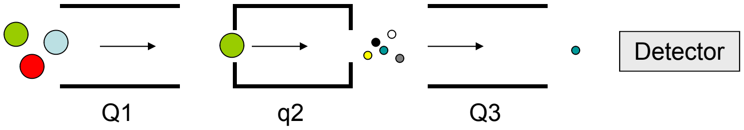
Idea of MS/MS



From Watson

FIG. 5.1. Conceptual representation of the technique of MS/MS. In this case, ions of *m/z* 129 are selected by the first mass spectrometer; these ions are directed into a collision chamber, and the decomposition products are analyzed by the second mass spectrometer to produce the product-ion spectrum of *m/z* 129 **(bottom)**.

Triple Quadrupole Mass Spectrometer



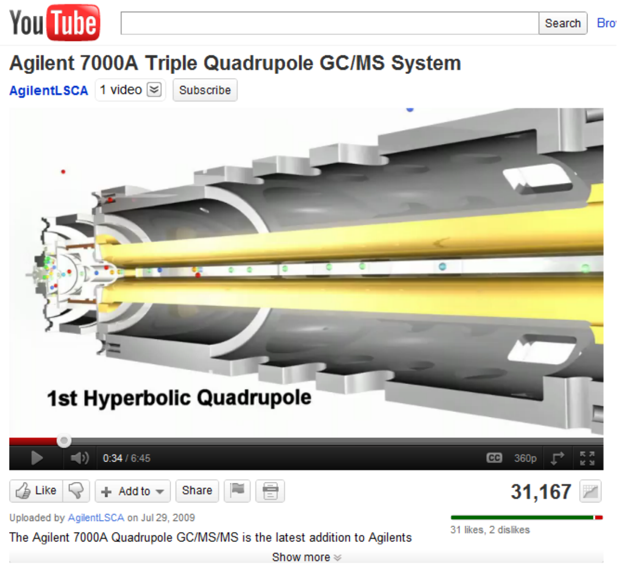
Q1 selects parent; q2 CID fragmentation inside RF-only quad; Q3 fragment analysis

Fragment Ion Scan: Park Q1 on specific parent m/z; scan Q3 through all fragment m/z to determine make-up of Q1

Parent Ion Scan: Park Q3 on specific fragment m/z; scan Q1 through all parent m/z to determine source of fragment

Neutral Loss Scan: Scan Q1 and Q3 simultaneously, with constant difference, *a*, between transmitted m/z values ($a = M_{Q1} – M_{Q3}$). Signal recorded if ion of m/z = M_{Q1} has undergone fragmentation producing a neutral of m = *a*.

Triple Quad Animation



Agilent 7000A Triple Quadrupole GC/MS System

AgilentLSCA 1 video Subscribe

1st Hyperbolic Quadrupole

0:34 / 6:45

31,167

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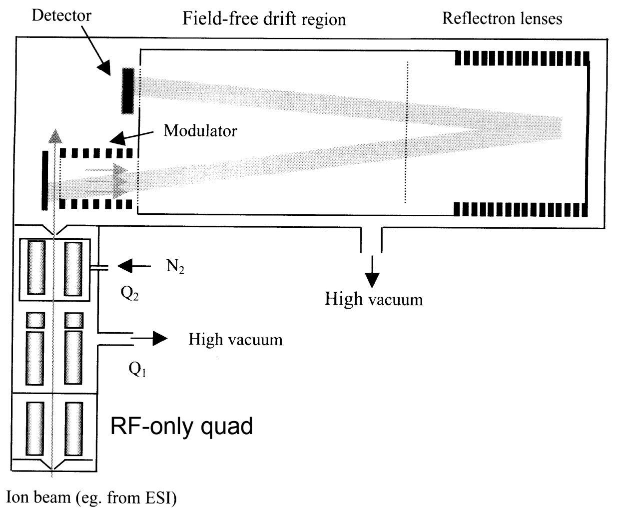
Uploaded by AgilentLSCA on Jul 29, 2009

The Agilent 7000A Quadrupole GC/MS/MS is the latest addition to Agilents

http://www.youtube.com/watch?v=PSFF6JJEFPE&NR=1

Q-TOF Hybrid Instrument



From Dass

Figure 4.7. Schematic diagram of a quadrupole–orthogonal acceleration time-of-flight hybrid tandem mass spectrometer.

Clicker Q

To operate a quadrupole in a scanning mode, where individual m/z values are transmitted one after the other (e.g., m/z = 100; 101; 102 …)

A. U is held constant, while V is scanned

B. V is held constant, while U is scanned

C. U and V are held constant, while ω is scanned

D. U and V are both changed

E. A or B