RF-Only Quadrupole Mass Spectrometry for High Sensitivity at High Mass Resolution.

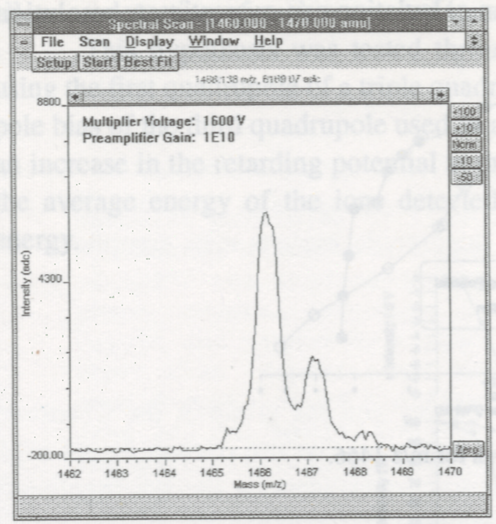

Figure 1. Typical high resolution RF/DC spectrum of m/z 1466.

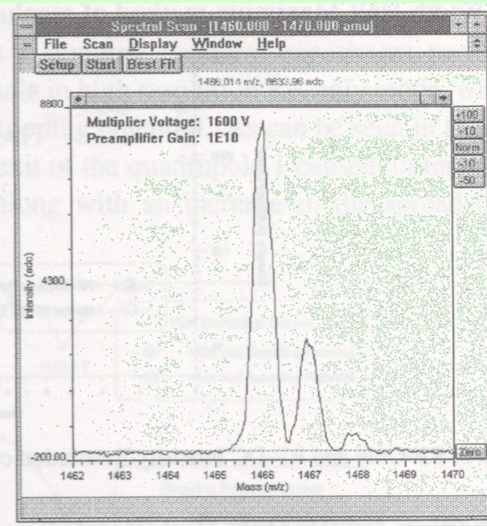

Figure 3. Typical high resolution RF Only spectrum of m/z 1466.

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High Resolution High Sensitivity RF-Only Quadrupole Mass Spectrometry for Cluster Characterization and Deposition

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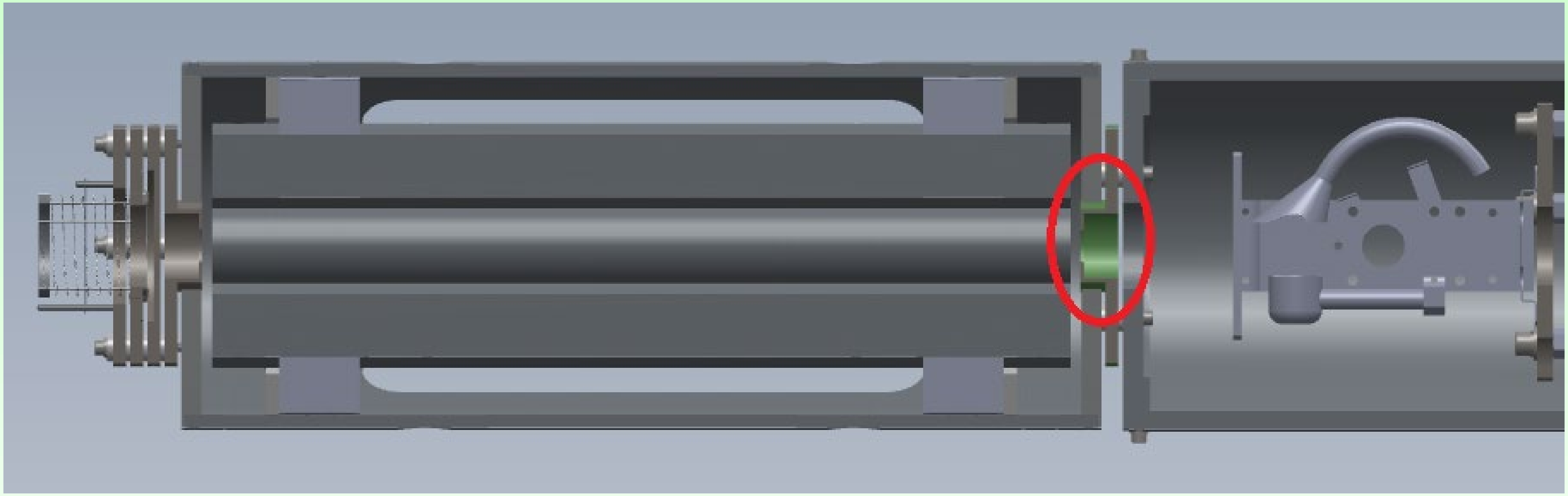
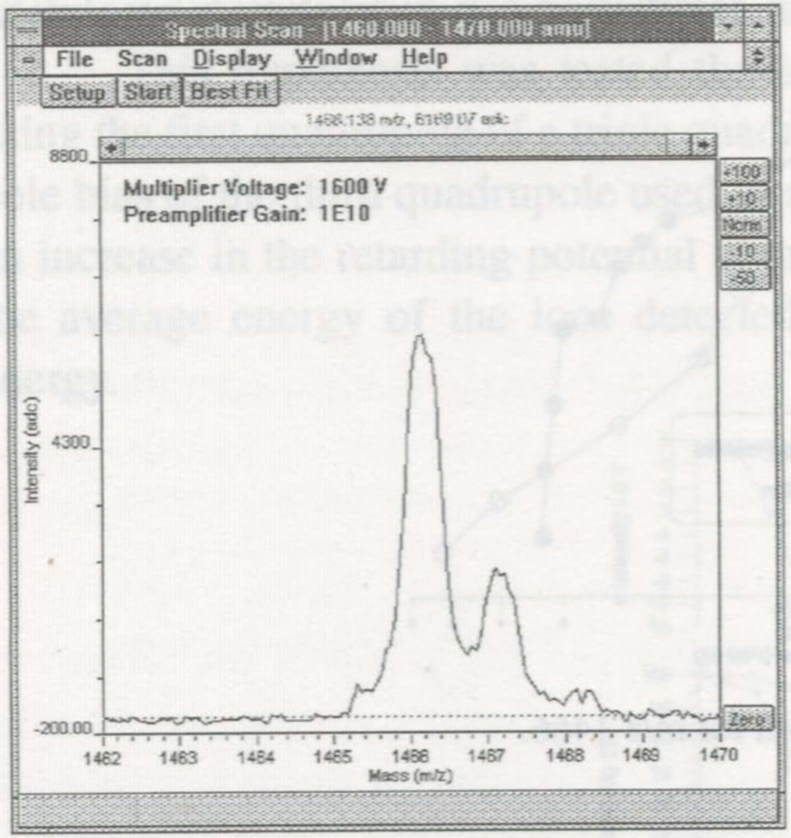
What happens when quadrupole exit lens potential is higher than an ion's effective birth potential?

Quadrupole exit lens is inside red circle below.



- If the quadrupole exit lens is ion optically thick, it should stop any and all ions, whose effective birth potential is lower than the applied exit lens potential.

But something magic can happen in RF-only mode.



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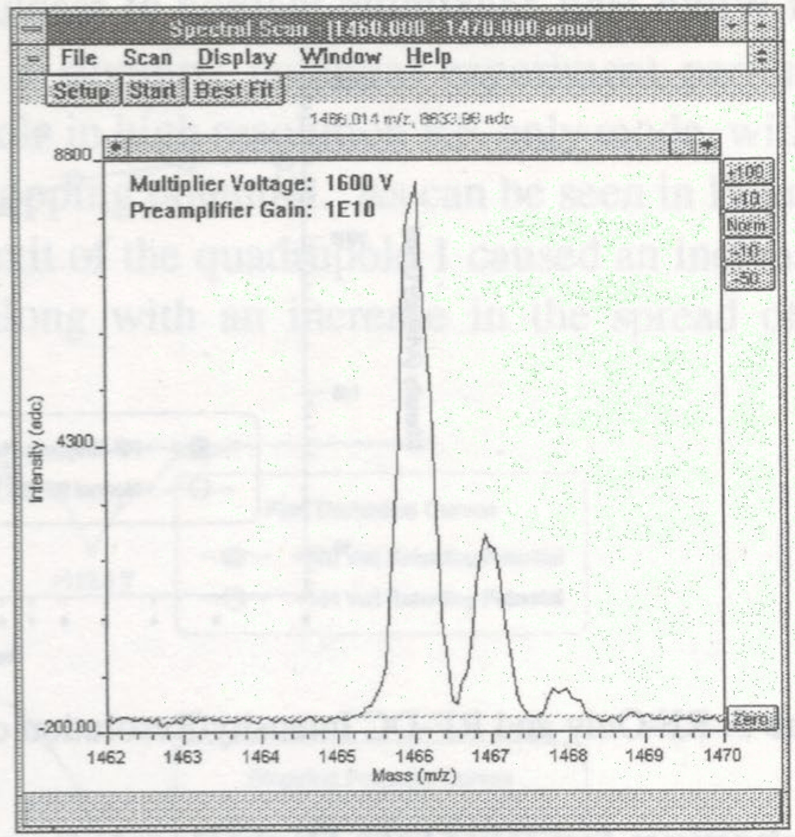

Figure 3. Typical high resolution RF Only spectrum of m/z 1466.

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Evolution of Peak Shape at Various Mass Resolutions

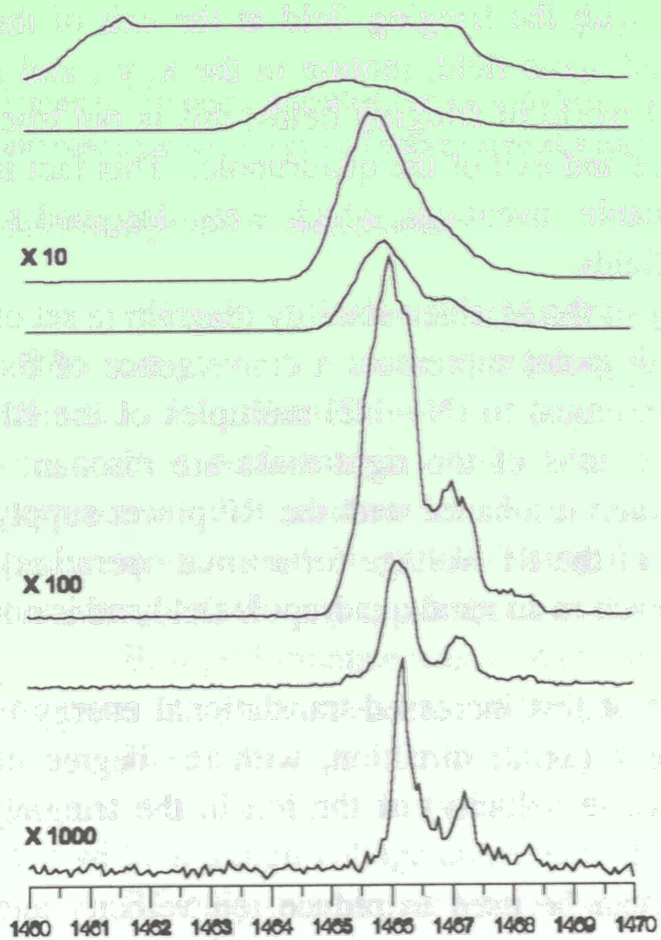

Figure 2. RF/DC peak shapes for m/z 1466 at various resolutions.

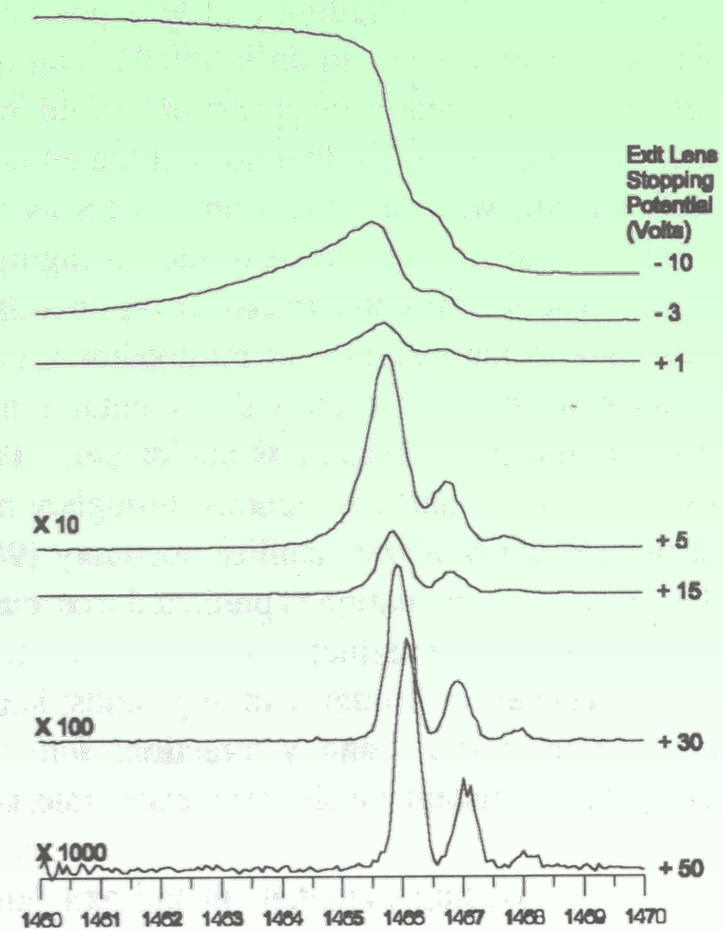

Figure 4. RF-Only peak shapes for m/z 1466 at various resolutions.

Resolution – Transmission Curves

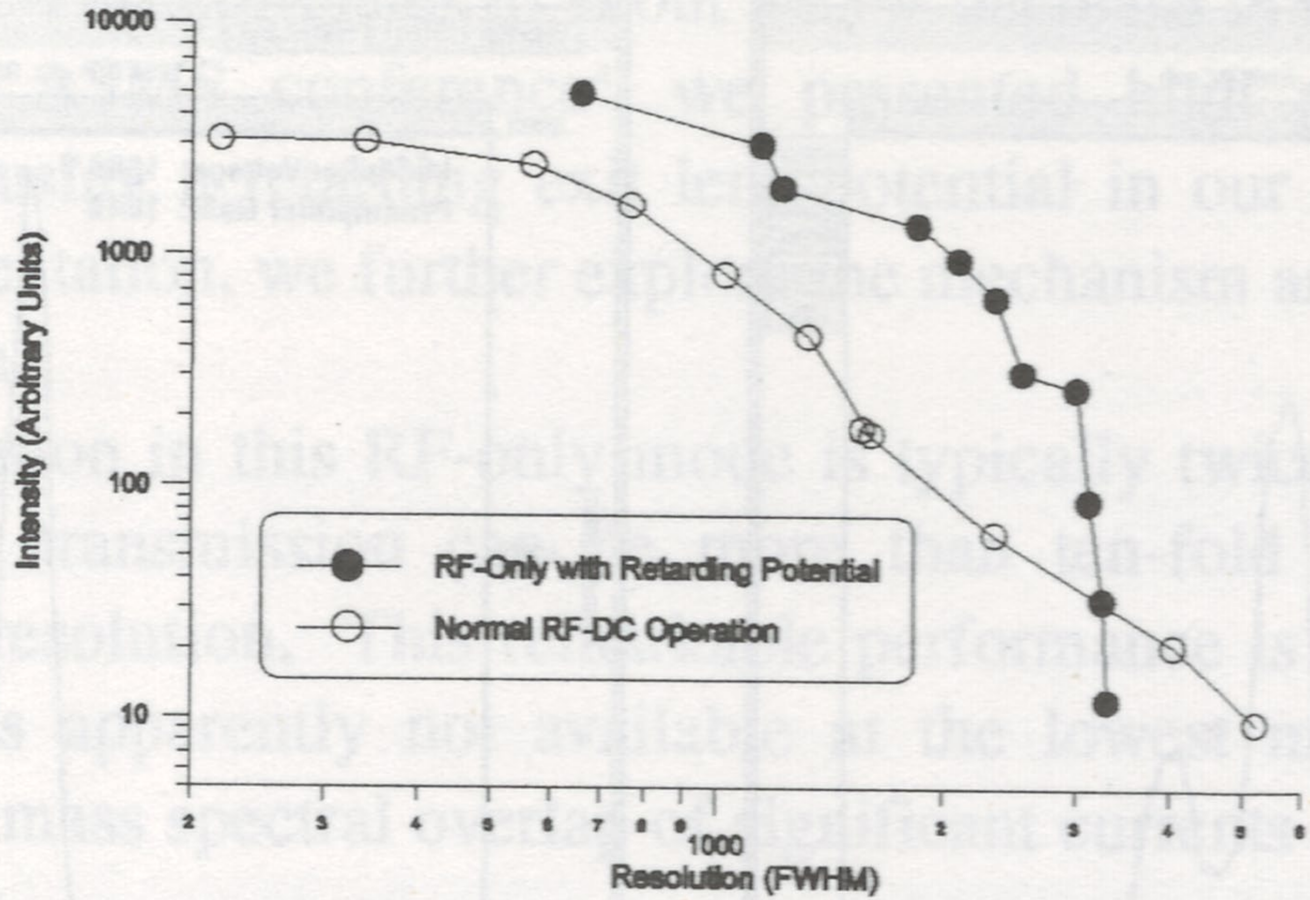

Figure 5. RF-Only and RF-DC Intensity/Resolution curves for m/z 1466.

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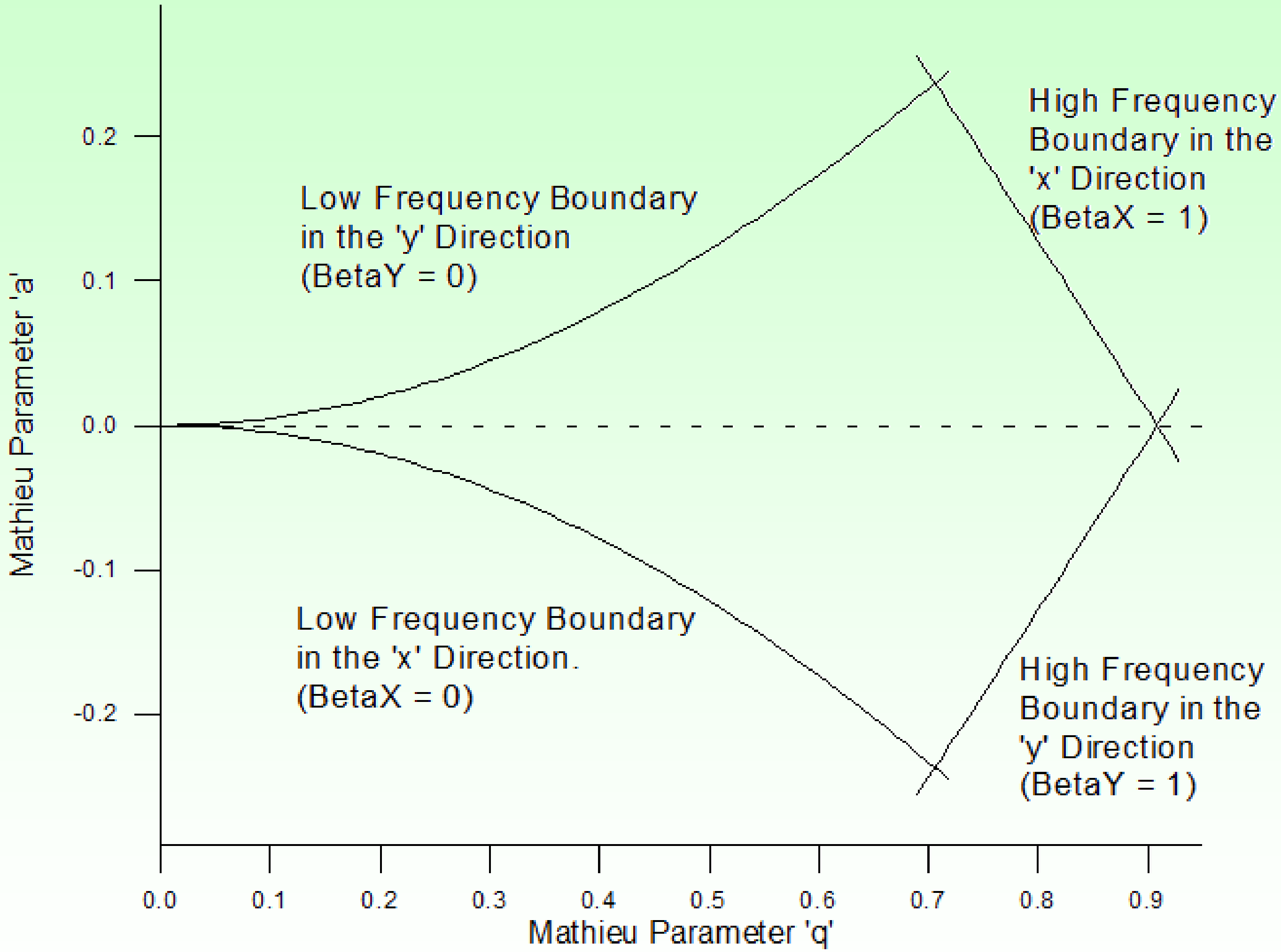
What is this Magic?

- Assuming an infinitely long quadrupole, trajectories in the X, Y and Z directions are decoupled, and can be treated independently.
- But in the real world, quadrupoles have finite length.
- And, at the entrance and exit of a quadrupole mass filter, there are fringing fields, where the X, Y and Z velocity vectors get coupled, (Cross terms in the equations of motion).
- When you reach either the BetaX = 1 boundary or the BetaY = 1 boundary of the stability diagram, an ion becomes unstable either the X or Y direction, dramatically increasing its X or Y velocity vector, ultimately striking one of the rods.
- Now in RF-only mode, the BetaX = 1 and BetaY = 1 converge, so an ion crossing this converged boundary at the right hand side of the stability diagram will be pumped with energy in both directions, increasing both its X and Y velocity vectors at the same time.

What is this Magic – Part 2

- A retarding potential on the exit lens can be used to reduce ion velocity and increase residence time in the fringing field.
- Ion of all masses are slowed down, but only those ions whose mass corresponds with the stability boundary get significant resonance excitation from the RF drive voltage, which by definition, exactly double the resonant frequency of motion for the ion in question.
- Coupling of this increased X and Y translational energy into the Z direction by the fringing field results in enough gain in Z axis translational energy to overcome the retarding potential, allowing these ions to poke through the retarding potential and be detected.

Mathieu Stability Diagram for a Quadrupole



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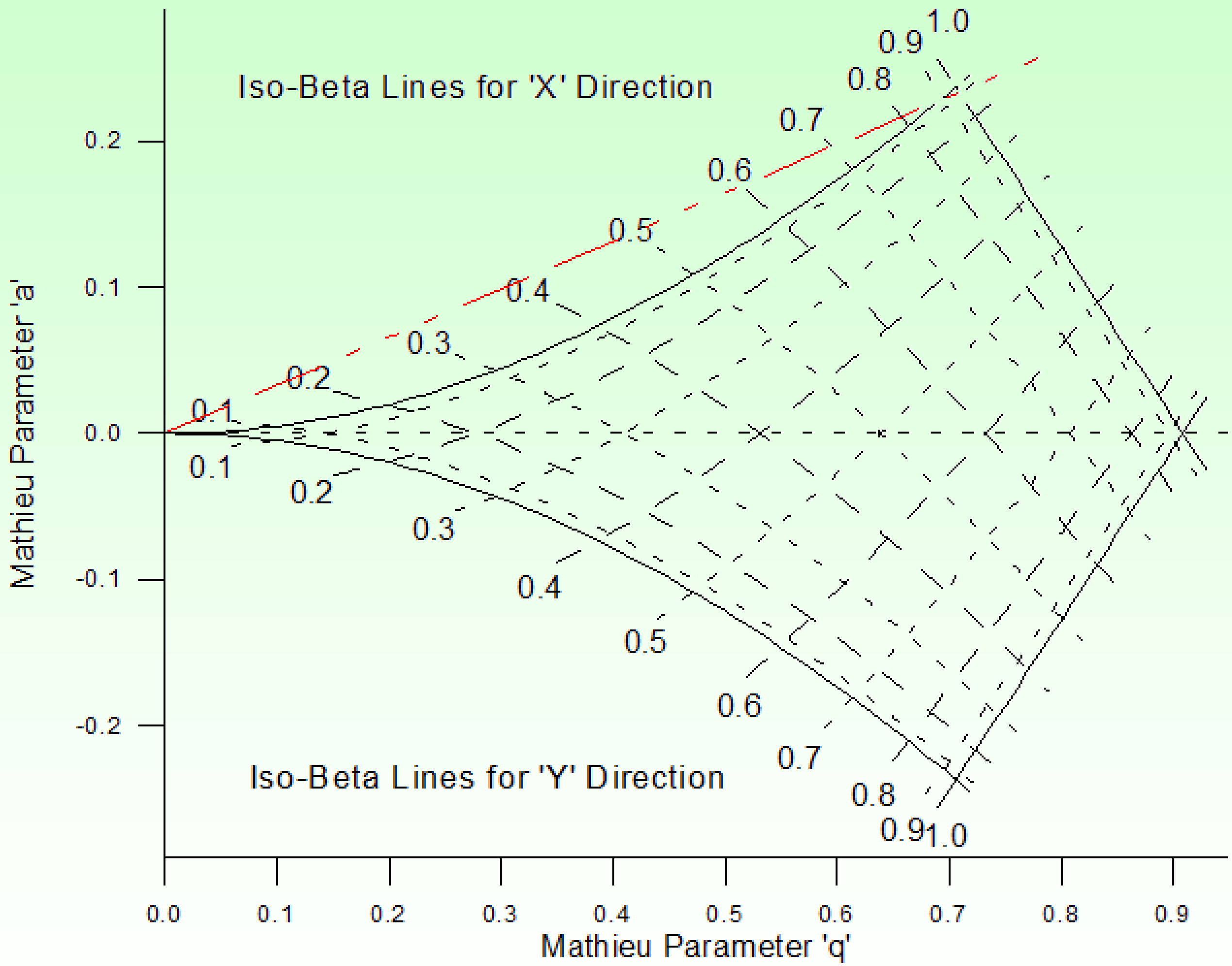

Secular Frequency = Beta / 2 * RF Drive Frequency

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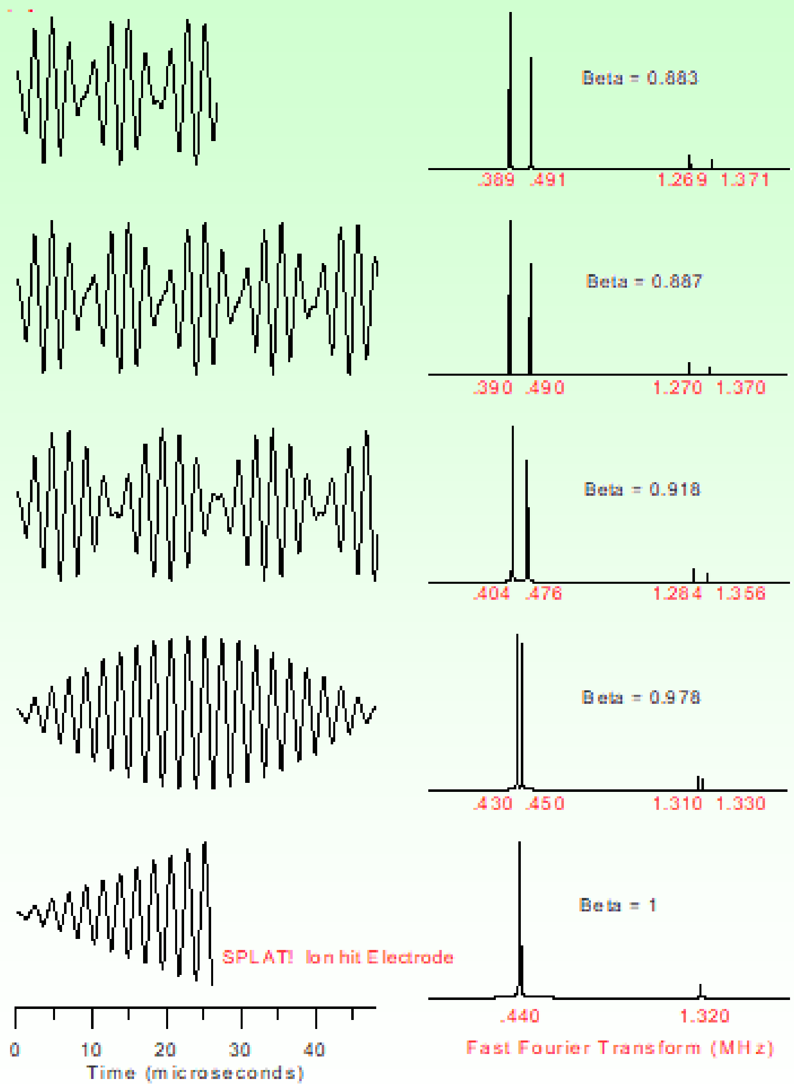
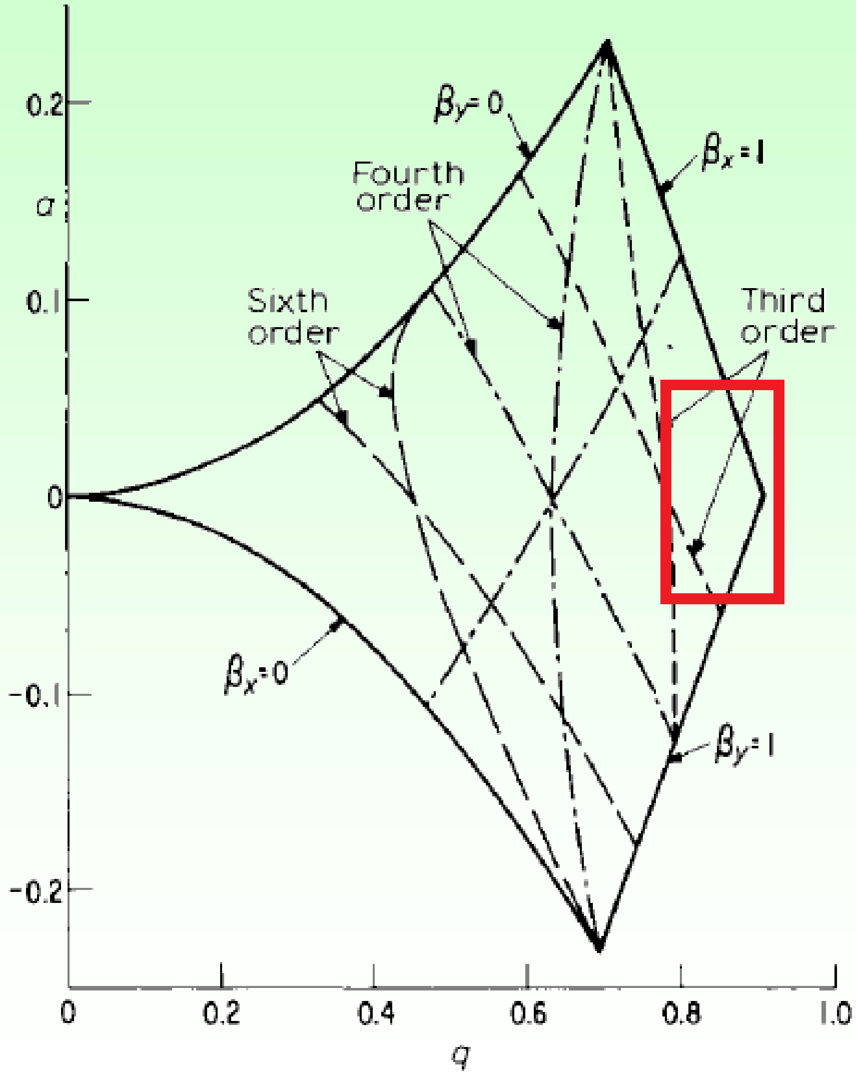
Ion Secular Frequency as you approach Beta=1 boundary:



RF-Only Axis of Stability Diagram doesn't show Non-Linear Resonances near the q=0.906, Beta=1 Boundary, Yielding Pretty Peak Shapes!



Prove it!

- A stopping potential experiment can demonstrate the average energy and energy spread of a beam of ions.
- In this case, first quadrupole of a triple quadrupole tandem mass spectrometer system was set to the Beta =1 boundary (q=0.906), with a stopping potential applied to its exit lens.
- The pole bias of the center quadrupole was varied, with the third quadrupole set to RF-only, but not at the right hand edge of the stability diagram.
- Intensity was measured for a series of Q2 pole bias settings, with the first derivative of the measured ion intensity plotted against retarding potential, showing the energy distribution of the ions.

Stopping Potential Curves for two different Retarding Potentials

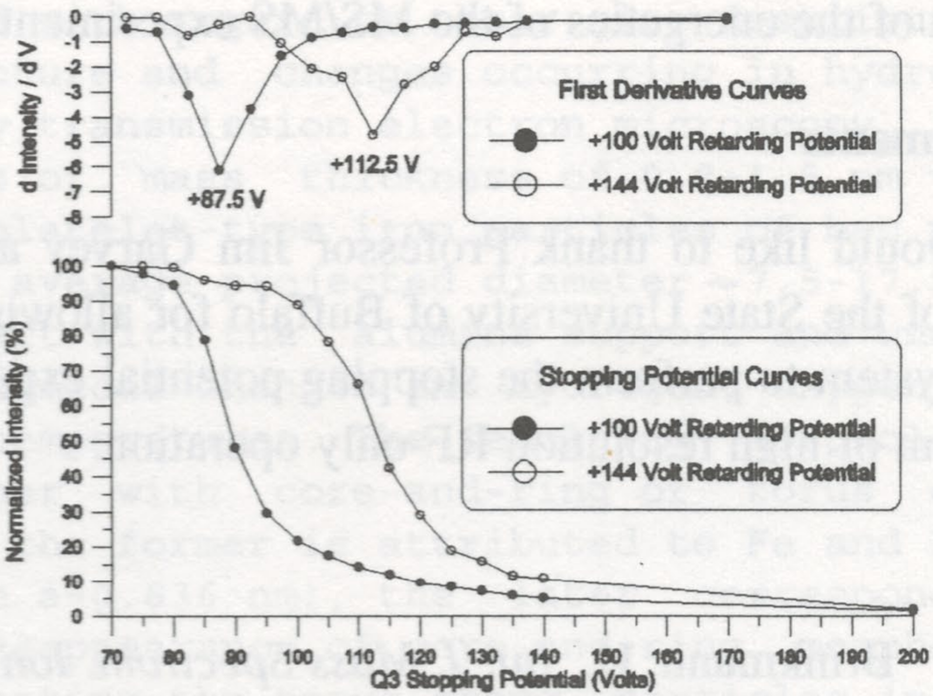


Figure 6. Stopping potential curves with first derivatives for two exit lens retarding potentials, showing an increase in axial energy and energy spread with increase in exit lens retarding potential.

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Advantages of High Resolution RF-only Quadrupole Operation

- RF-only quadrupole operation with a retarding exit lens voltage demonstrates higher sensitivity (as much as 10X) and greater ultimate resolution (typically 2X) than conventional RF/DC operation.
- Since there are no non-linear resonances near the q=0.906 boundary of the stability diagram, high resolution RF-only operation seems more immune to poor mechanical tolerances.

Disadvantages:

- Requires 9/7 (~28%) higher RF voltage per mass than conventional RF/DC operation. (q=0.906/0.706).
- The mass analysis method adds energy and broadens the ion beam's energy distribution, making this approach problematic where narrow ion energy matters.
  - Precursor ion selection in MS/MS systems.
  - Deposition of ions onto a surface.
- Peak shapes for lower mass ions are not as well resolved, since RF amplitude is smaller, relative to the retarding potential, the Magic fringing field coupling is less effective.

Final Notes:

- Miniaturization:
  - Since all the hard work happens between the end of the quadrupole and the retarding exit lens,
    - How long does it take to establish the secular ion motion?
    - Can we therefore make the quadrupole a lot shorter?

- Simplicity (Co$t)
  - Since the right hand side (q=0.906, Beta=1) boundary is so boring, without all of those pesky non-linear resonances,
  - Can we reduce the mechanical tolerance requirements to something more sloppy?
  - Can we 3D print a high performance quadrupole?

Acknowledgments and References

Acknowledgments

We would like to thank Professor Jim Garvey and his group at the Chemistry Department of the State University of Buffalo for allowing our use of their Extrel triple quadrupole system to perform the stopping potential experiments for the investigation of the mechanism of high resolution RF-only operation.

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