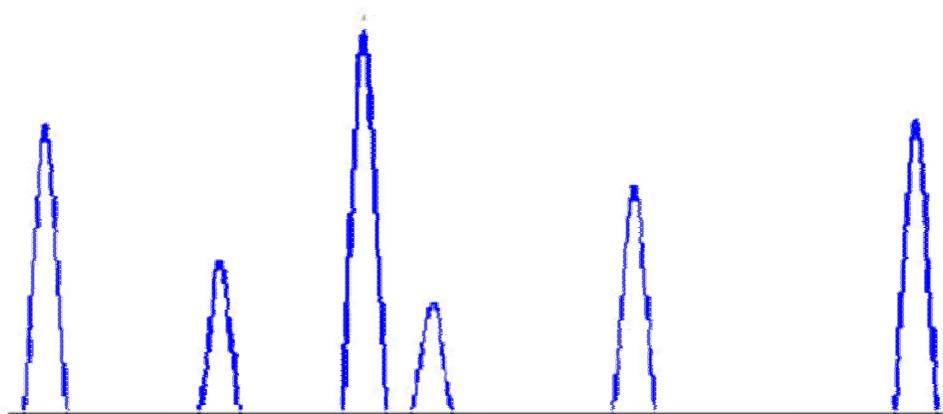


SECTION
 **2** **Principles of
Quadrupole and
Ion Trap Mass
Analyzers**

2-1

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The Mass Peak in the Quadrupole Mass Spectrum



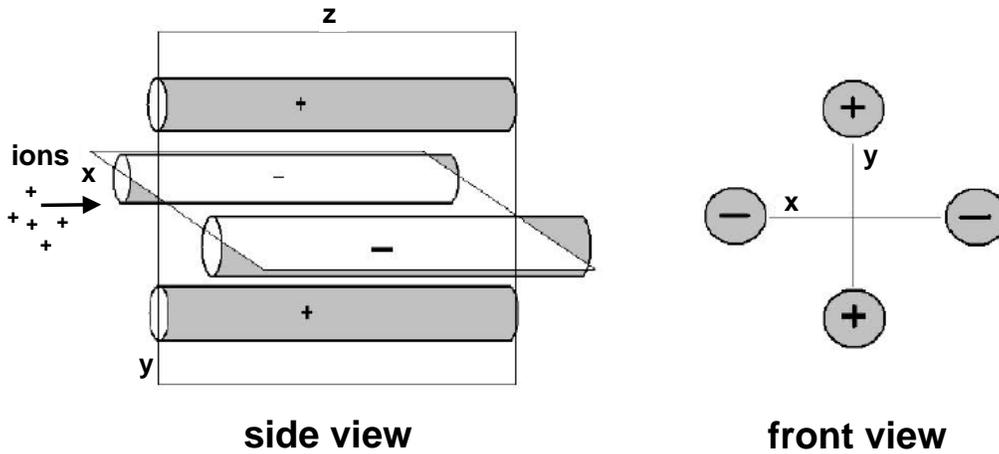
**A common phrase in texts on MS says,
“Examine the peaks in the mass spectrum.”
Why is the mass peak a *peak*?**

2-2

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Why not a single line (it's a single mass, after all)? There are a few reasons, but the most fundamental is related to the nature of the quadrupole ion filter itself. (As a starting point, ask yourself why the peak in an LC chromatogram is a peak, not a line.) The following chapter is a brief discussion of how a quadrupole mass filter actually achieves mass separation.

Some Basic Quadrupole Physics



2-3

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Quadrupole: a rectangular array of conducting rods to which variable voltages can be applied.

The poles can be metal or metal-coated ceramic.

The conventions are that x is the horizontal plane and y is the vertical plane when looking down.

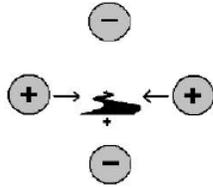
Note that the x-y convention is arbitrary. The polarities can be swapped between axes without changing anything in the following discussion (some instruments actually allow you to select the polarity to get the maximum signal).

To achieve as perfect an electric field in the quadrupole as possible, the poles should ideally have a hyperbolic cross section. In practice most instruments have poles that are circular in cross section (the latter being much less expensive to make, as well as easier to manufacture to an accurate shape).

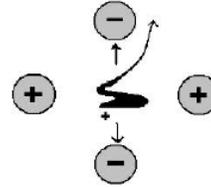
Effect of Constant Voltage (U) Only on the Quad

Voltages of the same polarity are applied to opposing pole sets.
We will trace the path of a positive ion through the quad.

Looking down the z-axis:



There is a **STABILIZING**
force in the x-z plane



There is a **DESTABILIZING**
force in the y-z plane

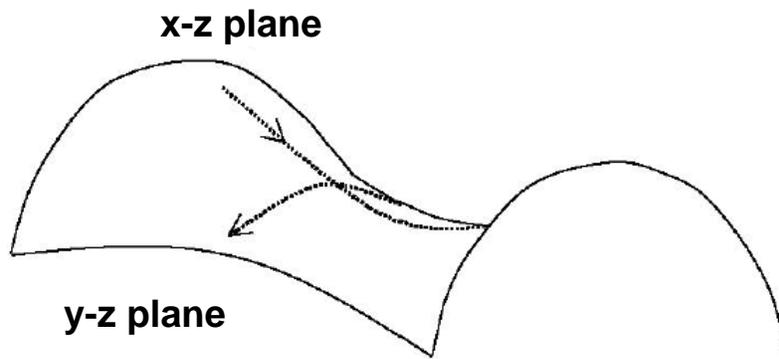
2-4

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The conventions are that the constant voltage is known as U (think of Unchanging) and the variable voltage is known as V (think of Variable).

This should make intuitive sense: like charges repel, opposite charges attract.

Forces Represented As Potential Surfaces



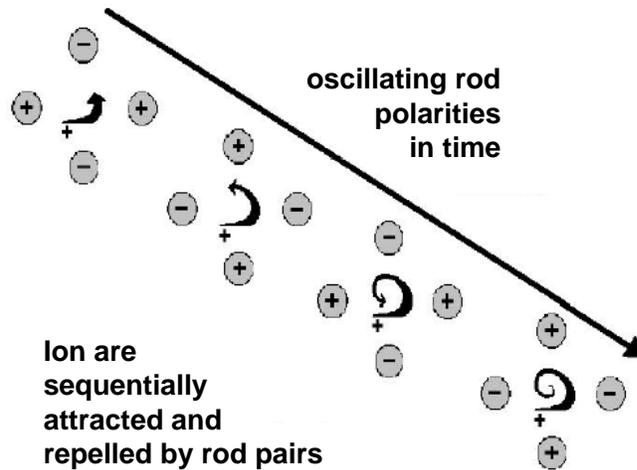
2-5

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Under these conditions the path of the ion down the quad is a metastable one. The potential energy surface can be represented as a saddle; deviations from the center in the x-z plane are uphill, and are pushed back downhill to the starting point, but deviations in the y-z plane are downhill from the start, with no restorative force back to the center. Note that the restorative force is the electric field equivalent of a simple harmonic oscillator.

Effect of Periodic Voltage (V) Only on the Quad

A stabilizing
force if
frequency is
high enough
and ion is
heavy enough



2-6

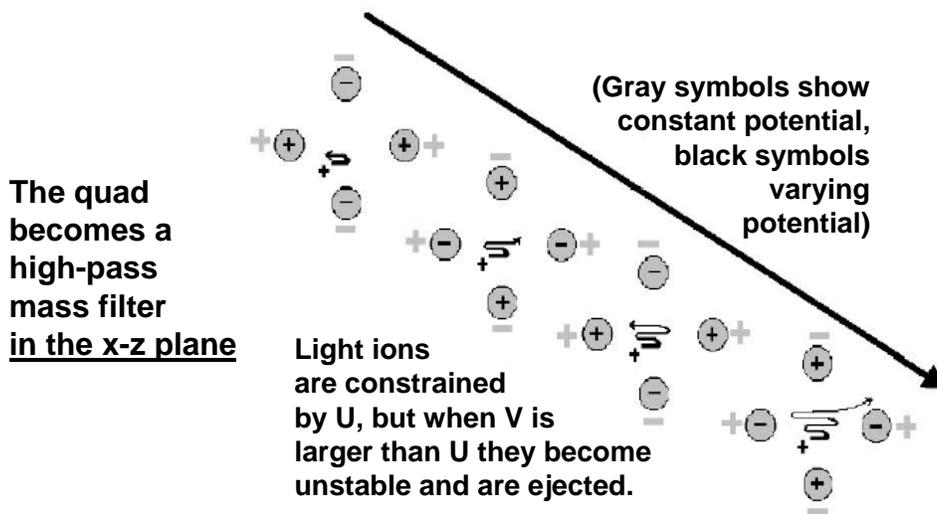
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You can think of the polarities spinning around like the spokes of a wheel; in terms of the forces, it's a bit like spinning the saddle previously mentioned around on its axis.

If the ion is too light it possesses insufficient inertia to resist the forces pulling it around; anyone who has seen a cyclone separator for particle sizing in operation will get the idea here.

If the frequency is too low it will begin to resemble a fixed voltage in the ion's reference frame; recall that a fixed voltage is metastable.

Simultaneous Constant (U) and Varying (V) Voltage



2-7

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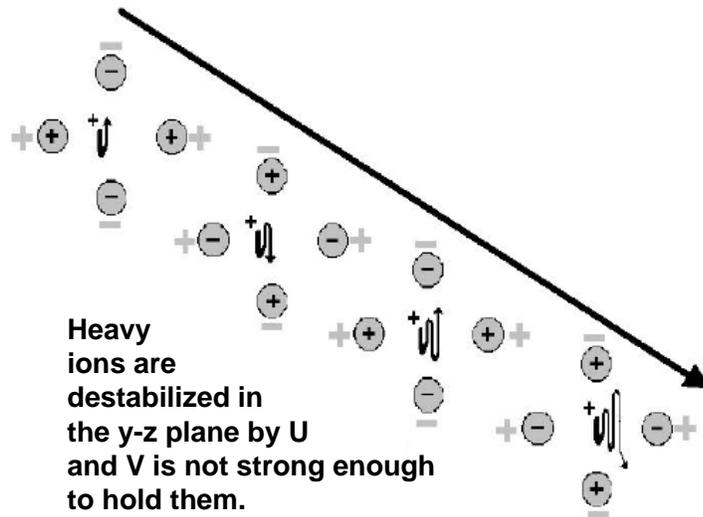
This is where it can get a bit hard to follow. The seemingly obvious answer is that the U and V values add up, and above a critical net potential the ion is pushed out. But it doesn't work that way. Remember that the potential is symmetric in the plane on either side of the z-axis, so that if the ion gets a harder shove to the left, it also gets a harder shove back to the right, so that increasing the potential actually stabilizes the ion trajectory.

The counterintuitive (and correct) answer is that the ions are pushed out when the U and V values are subtracted from each other.

In short, the ions are always trying to stay in the center, but get a periodic shove outward. The shove is sufficient for all ions below a certain mass to be lost; all higher masses have sufficient inertia to stay despite the destabilizing nudge.

Simultaneous Constant (U) and Varying (V) Voltage

The quad becomes a low-pass mass filter in the y-z plane



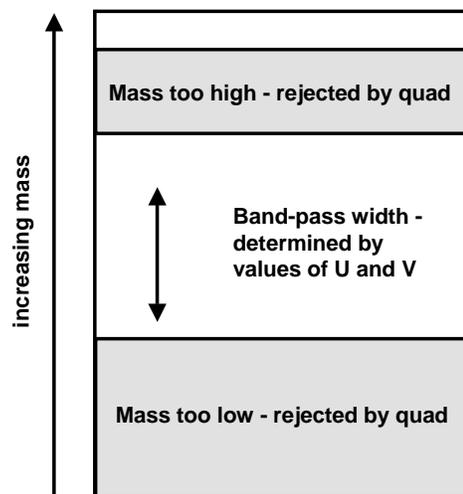
2-8

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The discussion of heavy ion instability in the x-z plane is somewhat a mirror image of the light ion discussion in the previous slide.

In short, the ions are always trying to get away in the y-z plane, but get a periodic shove back. The shove is sufficient for all ions up to a certain mass; all higher masses have sufficient inertia to escape despite the restoring nudge.

Simultaneous Constant (U) and Varying (V) Voltage



2-9

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With both U and V present, the quad rejects both ions that are either too light or too heavy.

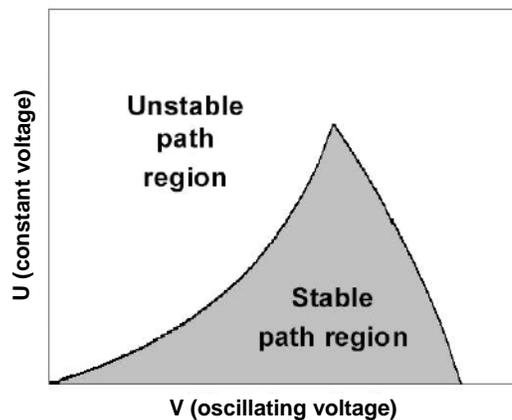
The quad becomes a band-pass mass filter.

By adjusting U and V the band-pass width (resolution) can be adjusted.

Simultaneous Constant (U) and Varying (V) Voltage

For the plot of all possible (U,V) points there are combinations where the ion path through the quad is stable and other combinations where it is unstable.

For a given m/z , the U,V plot looks like this:



2-10

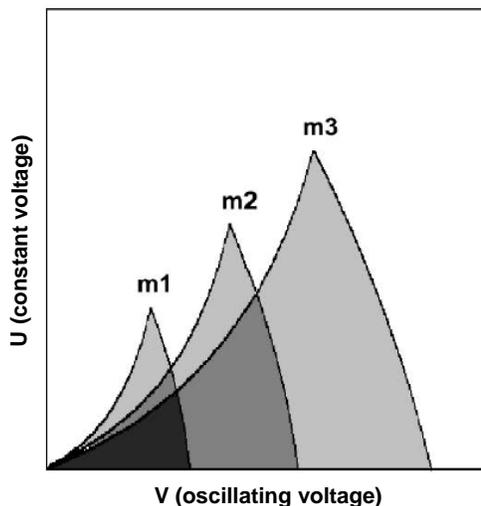
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This graph should be interpreted carefully. It is not a plot of position, even though it represents the region of stable trajectories. Rather, it is a plot of conditions, allowing ions to move in a stable path.

Note that the plot is for a particular m/z value. Each m/z value has its own plot. The peculiar shape of this plot derives from the combined equations of motion expressed in a general form known as the Mathieu equation. The portion shown here (the physically useful portion for a linear quadrupole, if you will), is a small piece of a larger and quite pretty graph.

Simultaneous Constant (U) and Varying (V) Voltage

A plot for several m/z values looks like this:



2-11

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Since the equations of ion motion contain a mass term, it should not be surprising that the shape of the plot will vary with mass.

One way of looking at it is that a heavier ion needs more force (higher potential, bigger U and V) to push it around.

Note that if $U = 0$, the quad passes all ions (a useful property, which will be exploited in multiquadrupole instruments discussed later)

As U increases, stable trajectories for each m/z become more constrained. This means that fewer ions can pass through the quad.

Simultaneous Constant (U) and Varying (V) Voltage

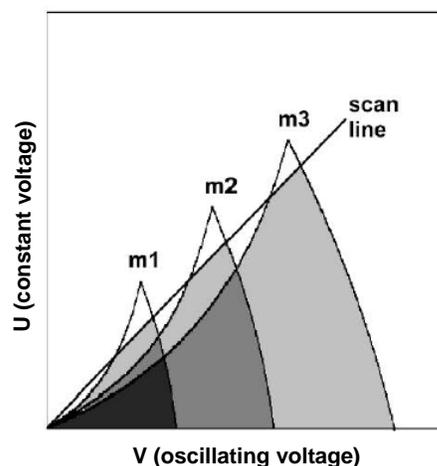
Simultaneously raise U and V, but keep the ratio U/V constant.

Superimpose this line on the plot of stable ion trajectories.

A plot U and V becomes a straight line, starting at the origin and with a slope of U/V.

Only ions above the line will pass through the quad.

Look carefully this is the MASS SPECTRUM.



2-12

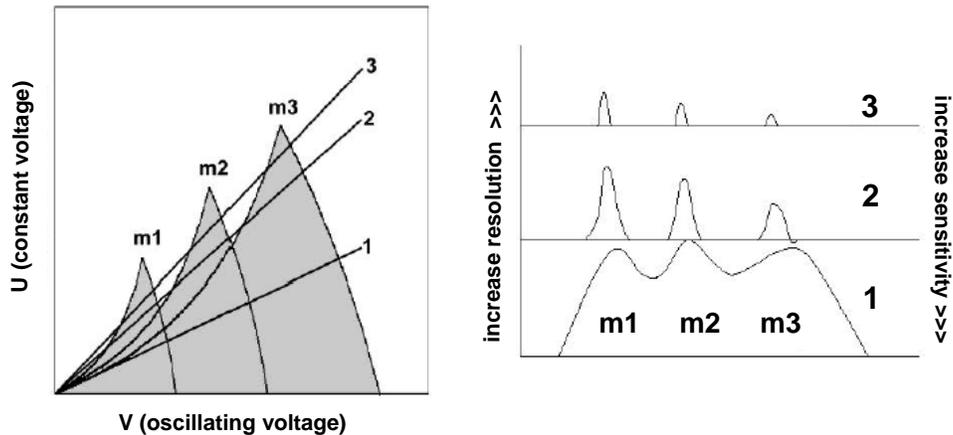
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That was a long walk, from metal rods and electric fields to a mass spectrum. Some may say it isn't essential to understand how a quadrupole works in order to use it; you can say the same thing about a UV detector. But don't you feel more confident knowing how a UV detector actually works?

Especially when it doesn't work, and you have to fix it.

Mass Resolution

Resolution is controlled by the slope of the scan line (i.e., U/V):



2-13

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Resolution is a function of several different factors in the quadrupole MS (some of which will be discussed shortly).

(One important fact that comes out of the mathematics of the quadrupole is that the maximum attainable resolution is related to the number of RF cycles the ion experiences while traversing the quad. If all the ions of whatever mass enter a quad of length L with a field of frequency f with the same total energy in the z-direction (eEz), the number of RF cycles each ion experiences is given by:

$$n = fL (m/2Eze)^{1/2}$$

Therefore, as m increases, so does n; the higher mass ions see more rf field cycles and resolution increases with ion mass.)

You can also say that for two ions of different mass but the same total kinetic energy, the heavier ion must move more slowly. Therefore it spends more time in the quadrupole and can see the field longer.

As the slope of the scan line drops the areas of stable ion trajectories begin to overlap more and more. In the limit (as U goes to zero) all the ions pass. This is called an 'rf filter', or 'operating the quadrupole in rf-only mode'.