Practical Quadrupole Theory: Resolution and Transmission as a Function of RF Frequency

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Novel Aspect:

This work probes fundamental quadrupole performance at RF frequencies much lower than used in conventional quadrupole systems (hundreds of kilohertz).

Introduction:

Modern mass spectrometers are pushing the limits of mass range. While electrospray successfully scales very large molecules down to manageable mass-to-charge ratios of conventional quadrupole mass spectrometers (typically 2000 to 4000 amu mass range for typical electrospray quadrupole systems), MALDI provides singly-charged ions to much larger mass-to-charge ratios, ideally suited to TOF mass spectrometers. Modern hybrid mass spectrometers incorporating TOF as the terminal analyzer often utilize quadrupoles for MS/MS precursor selection, as well as ion guides. This work explores the performance penalties associated with mass range extension of quadrupole devices through reduction in RF frequency. Mass range is proportional to frequency squared. Halving the frequency quadruples the mass range, but at what expense in resolution and transmission?

Methods:

A custom hybrid electrospray quadrupole time-of-flight mass spectrometer has been developed, which will be used to characterize quadrupole performance (resolution and transmission) as a function of mass and RF frequency. Ions of various masses which are generated via electron ionization or electrospray are used to measure the relative performance of this system with various RF frequencies applied to the quadrupole. Resolution-Transmission curves are used to compare resolution and transmission for a given mass at various RF frequencies, using a 9 mm rod diameter round rod quadrupole.

Preliminary Results:

Work presented by our laboratory at the 54th ASMS conference demonstrated that absolute transmission trends with the square of RF frequency when the emissivity of the ion source is much larger than the acceptance of the quadrupole. In preliminary data we also observe that ultimate resolution tends to scale linearly with RF frequency. This work extends the previous work to frequencies lower than the 0.88 MHz minimum frequency of the previous study, where unit mass resolution was easily attainable. The electrospray ionization source used in this system has a much smaller emissive area than the EI source used in the previous experiments, which should lead to less sensitivity loss as RF frequency is reduced.

I. OVERVIEW

There are many applications for quadrupoles that do not require high resolution, although some resolution is desirable.

For example the low mass cutoff in an RF-only ion guide is commonly used to get rid of solvent ions in LC/MS systems

Another example is a low resolution-high transmission quadrupole cluster deposition system where you only need enough resolution to tell one cluster from another. (I.e. a resolution of 20 to discern Cu19 from Cu20).

This poster examines the relative transmission as a function of RF frequency for a range of frequency domains, including a system with a mass range of 50,000 amu.

The objective was not to get the highest resolution, rather to explore the tradeoffs when mass range is extended via reducing RF operating frequency.

II. INTRODUCTION

No discussion of quadrupole theory would be complete without a detailed review of the Mathieu stability diagram!

Starting with 'F=ma', one could derive the Mathieu equation that describes ion motion in a quadrupole.

$$\frac{d^2u}{d\xi^2} + (a_u - 2q_u \cos 2\xi)u = 0$$

$$a_u = \frac{8eU}{m{r_0}^2\Omega^2} \qquad q_u = \frac{4eV}{m{r_0}^2\Omega^2}$$

The traditional parameterization utilizes the following definitions:

u: position along the coordinate axes (x or y)

ξ: a parameter representing Ωt/2

T: time

e: the charge on an electron

U: applied DC voltage

V: applied zero-to-peak RF voltage

M: mass of the ion

R: the effective radius between electrodes

Ω: the applied RF frequency.

Neglecting the gory details, we conclude with the following profound statements that help make quadrupole theory practical.

1. For a given RF voltage, the calculated mass is proportional to RF frequency squared.
2. For a given mass, the calculated RF voltage is proportional to RF frequency squared.

   Figure 1 shows RF and DC voltages for ions of m/z 502 at various frequencies

3. The solution of the Mathieu equation can be presented in the form of a stability diagram, wherein, any set of voltages which are inside the stability diagram for a given mass, then the ion is theoretically stable and goes through the quadrupole.
4. The stability diagram consists of two asymmetric lines, a boundary on the right hand side, and a boundary on the left hand side.

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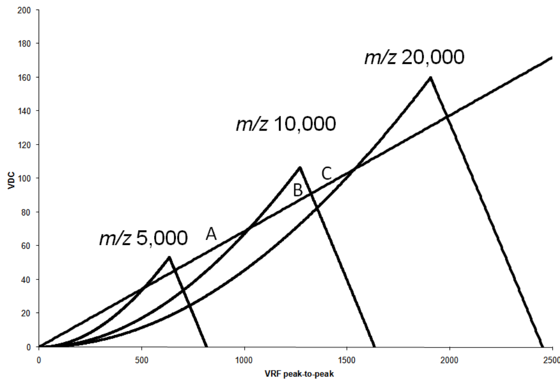

Figure 1. Stability diagrams in RF-DC space for m/z 5,000, m/z 10,000, and m/z 20,000, with a scan line at resolution = 4.0.

5. The left hand side boundary can be fit to the following equation: (valid for the range of q=0 to q= 0.706004)

$$a = 0.5016787\, q^2 - 0.01018488\, q^3 - 0.03838793\, q^4$$

6. The right hand side stability diagram boundary can be fit to the following equation: (valid for the range of q=0.706004 t0 q = 0.90803)

$$a = 1.006067 - 1.02426\, q - 0.09219\, q^2$$

7. The tippy top of the stability diagram (interception of these two equations) is

   a=0.236985

   q = 0.706004

   This puts the ratio of peak-to-peak RF voltage to DC voltage at the tip of the stability diagram at 1/11.91645 (almost 1/12).

8. When a quadrupole is scanned to determine a peak shape, it is typically scanned from low voltage to high voltage along a scan line, which typically isn't exactly straight, but will be treated as such for our purposes, and drawn through the origin in our simplification.

9. One could thus calculate the intercept of a scan line through each side of the stability diagram and calculate the theoretical peak width by projecting these intercepts onto the q axis. (In this work, we use successive approximation to estimate these intercepts and calculate theoretical peak widths).

10. We can further simplify our understanding of the stability diagram by calculating using real voltages and masses, by substituting actual values in for the parameters in the Mathieu equation.

Figure 1 shows three stability diagrams in RF-DC space calculated for a 238 kHz quadrupole power supply driving a 9 mm quadrupole to 5,000 amu, 10,000 amu, and 20,000 amu, with a scan line corresponding to a resolution of 4.0 (i.e. the 'humpogram' mass peak will have a calculated peak width of one fourth its mass number)

At point A on the scan line, the voltages are such that they are outside the stability region for all three masses.

At point B, on the scan line, only m/z 5,000 is transmitted.

At point C on the scan line, none of the three ion masses are transmitted.

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III. EXPERIMENTAL

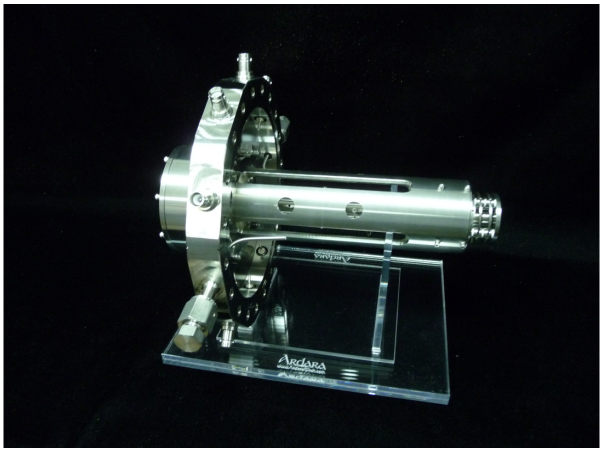

Figure 2. 9 mm quadrupole mounted to a radial flange with extraction optics and Faraday detection.

Three different quadrupole system configurations were utilized in these experiments

The first set of data was gathered in the RF frequency range of 880 kHz to 2.8 MHz. Argon at m/z 40 was leaked into the chamber background with a flange mounted mass filter assembly (RGA ionizer, eight inch long 6 mm quadrupole without pre- or post-filters, and flange mounted electron multiplier detector operated in Faraday mode).

Argon was selected as the test gas species because it is almost mono-isotopic (its isotopes have very low relative abundances).

By reducing the electron energy to 50 electron volts, the relative intensity of the doubly charged argon mass peak at m/z 20 was reduced.

A constant partial pressure of 5 X 10-5 torr of argon was maintained in the chamber background, to ensure that argon was in far excess, compared to the chamber background, yielding a single m/z value emitting from the ion source.

Data acquisition was delayed after each pumpdown, until the chamber background pressure was below 2 X 10-6 torr, to minimize the contribution of chamber background to the measured results.

The ionizer was tuned to yield reasonable peak shapes at the lowest RF frequency, exhibiting smooth mass peaks without fine structure. Ion energy was thus maintained at 6 eV for all experiments (6 Volt ion region potential, 0 volt quadrupole pole bias

Electron emission current was maintained at 0.3 mA to minimize effects of electron space charge in the ion source as a source of error.

The second set of data was gathered for the frequency range of 114 kHz to 850 kHz. m/z 502 was monitored (one of the mass peaks of perfluorotributylamine, leaked into the chamber background.)

A double quadrupole assembly was constructed consisting of an RGA ionizer mounted onto an eight inch long 12 mm quadrupole (no pre-or-post filters), which was mounted onto an eight inch long 9 mm quadrupole, which was in turn mounted onto a flange mounted electron multiplier detector.

The 12 mm quadrupole was operated at 1.44 MHz, with the resolution tuned for maximum sensitivity (~40 amu wide mass peaks that just excluded m/z 464), with the quadrupole parked at the maximum of the resulting mass peak at m/z 480.

The 9 mm quadrupole was driven using a prototype Ardara Technologies quadrupole power supply which was specially configured to allow rapid change of operating frequency. For the lowest RF frequencies (114 kHz, 235 kHz, 284 kHz), a capacitive voltage divider was used to scale down the RF amplitude to improve command resolution, and a resistive voltage divider was used for the resolving DC to similarly improve command resolution.

Ion energy was maintained at 8 eV throughout this set of experiments.

The third data set were gathered at the laboratory of Professor David Moore at Lehigh University. This cluster deposition system consists of a magnetron sputtering ion source which generates nanoamps of copper cluster singly charged negative ions, which are transmitted through a one inch rod diameter quadrupole (operated at a variable RF frequency, 40 kHz in this case), with multiple stages of differential pumping. (Model NC200U, Oxford Applied Research, Oxford England, www.oaresearch.co.uk))

Conditions were optimized for generation from the ion source and transmission through the 1 inch quadrupole of ions of m/z 10,000.

Downstream of this nanocluster source in an ultrahigh vacuum region, a 9 mm quadrupole was suspended on a radial flange with a faraday detector plate at the end. (See figure 5)

This quadrupole was operated using a similar Ardara Technologies variable frequency quadrupole power supply to that used in the second set of experiments at m/z 502.

Since only Faraday detection was available on this system, (no electron multiplier) poor signal-too-noise limited the range of peak widths that were accessible.

IV. RESULTS AND DISCUSSION

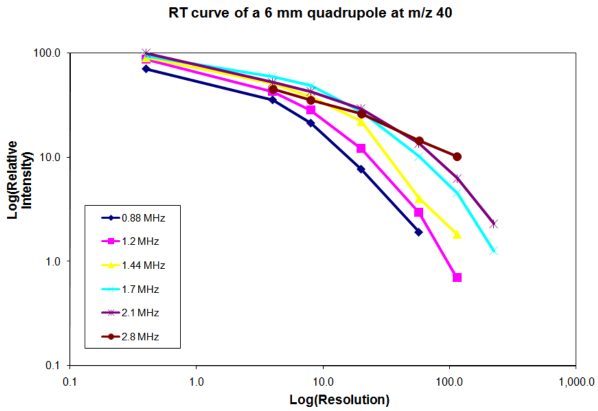

Figure 3. Resolution Transmission curves for argon intensities measured on a 6 mm quadrupole at six different RF frequencies with Faraday detection.

Figure 3 shows the resolution/transmission curves for argon measured at m/z 40 for five different RF frequencies.

Note that in all cases, the higher frequency curves demonstrate higher relative transmission.

Note that these data sets were all gathered on the same instrument, the same day, under identical conditions of partial pressure, so they are directly comparable.

Figure 4 illustrates the evolution of mass peak shape as resolution is increased for a 9 mm quadrupole operated at 284 kHz (12,000 amu mass range) on the double quadrupole system.

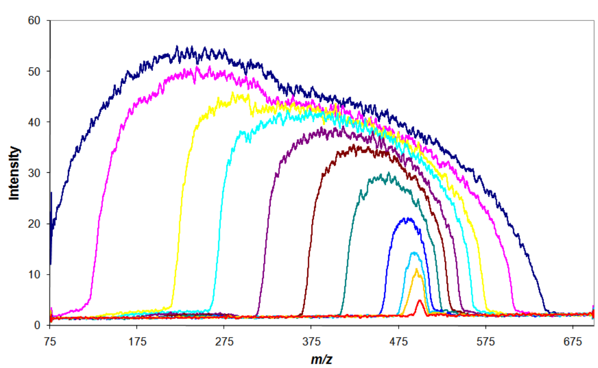

Figure 4. Evolution of m/z 502 peak shapes as resolution is increased. 284 kHz RF frequency on 9 mm quadrupole

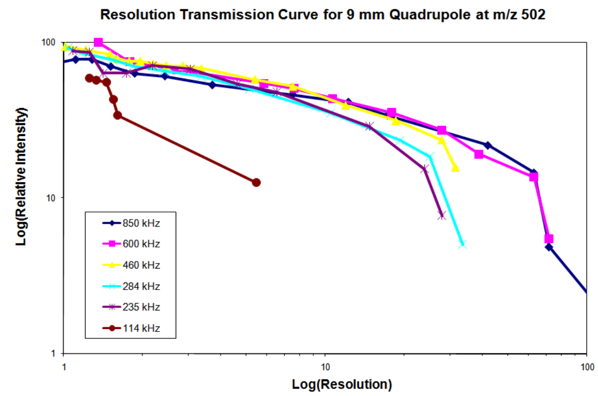

Figure 5. Resolution Transmission curves for m/z 502 intensities measured on a 9 mm quadrupole at six different RF frequencies with electron multiplier detection.

The broadest, largest intensity peak (in blue) is the RF only spectrum, with the rest of the peaks representing sequential increases in commanded resolution.

This data set is represented in Figure 8 as the turquoise trace.

The double-quadrupole m/z 502 Resolution Transmission data set shows consistent trend of reduced relative transmission as RF frequency is reduced. (See Figure 5).

Note that the tip of the stability diagram for m/z 502 in this case represents 90.84 Vpp of RF and 7.62 V of resolving DC.

Ultimate resolution in this case was hampered by the coupling of RF from the 12 mm quadrupole into the 9 mm quadrupole. At 1.44 MHz, the 12 mm quadrupole had almost 4,000 Vpp of RF!

Operating at 114 kHz, the quadrupole had a theoretical mass range of 80,000 amu, albeit at diminished performance.

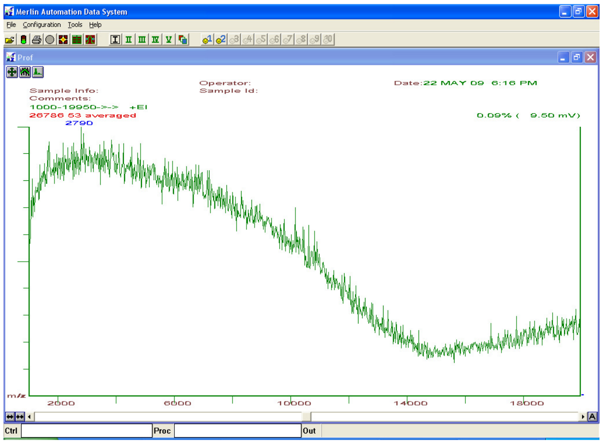

Figure 6. RF-Only Spectrum of m/z 10,000 copper clusters.

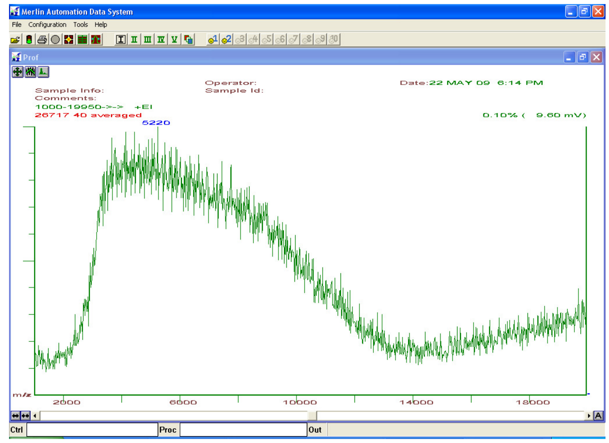

Figure 7. Commanded resolution of 1.1 spectrum of m/z 10,000 copper clusters.

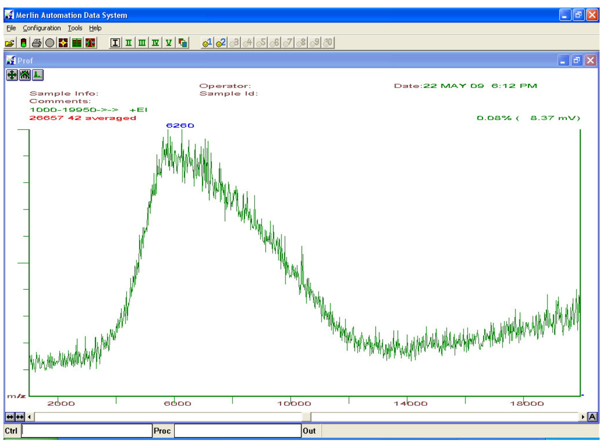

Figure 8. Commanded resolution of 1.5 spectrum of m/z 10,000 copper clusters.

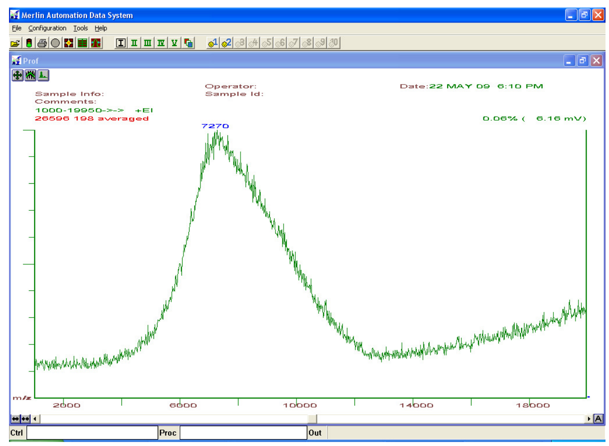

Figure 9. Commanded resolution of 2.0 spectrum of m/z 10,000 copper clusters.

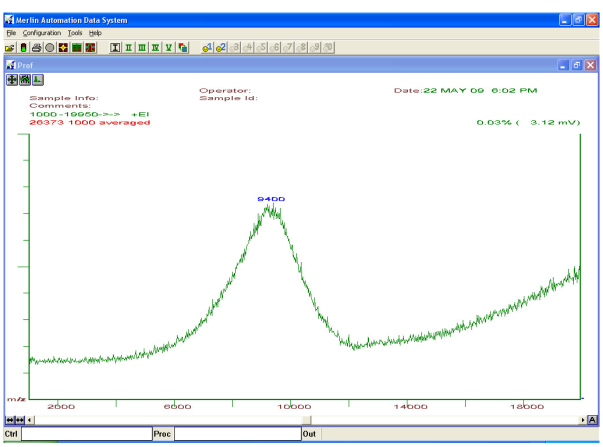

Figure 10. Commanded resolution of 4.0 spectrum of m/z 10,000 copper clusters.

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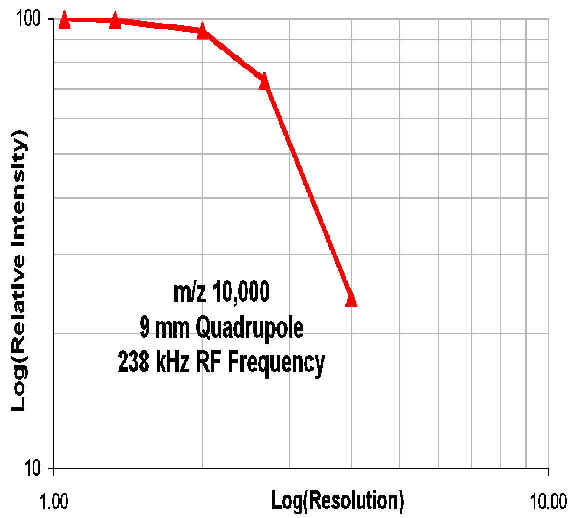

Figure 11. Resolution Transmission curve for m/z 10,000 copper clusters.

Figures 6 to 11. Measured spectra of 10,000 amu copper clusters with resulting Resolution Transmission curve. 9 mm quadrupole operated at 238 kHz (20,000 amu mass range). Note that the graphics required touch up, since the Extrel Merlin data system did not support these large mass ranges, so the systems had to be calibrated at 1/10 the nominal mass.

VI. CONCLUSIONS AND FUTURE WORK

Operation of quadrupoles at lower than traditional RF frequencies provides extended mass range at the expense of ultimate resolution, and sensitivity. (Systems used in these experiments had theoretical mass ranges as high as 80,000 amu.)

For cluster deposition applications which do not require high resolution, simply lowering the operating frequency to extend the mass range is a viable option.

The data in this poster could be much improved with electron multiplier detection for the cluster work, as it is apparent from the m/z 502 work that the ultimate resolution of the quadrupole with an electron multiplier is much higher than can be seen with Faraday detection, where the high resolution signal is lost in the noise.

The evolution of peak shape from RF-only to resolving mode can make data evaluation confusing. The apparent mass peak in RF-only mode for the 502 amu data showed a local maximum at 225 amu.

For the 10,000 amu spectra, the apparent local maximum from the RF-only spectrum is around 3,000 amu, less than one third of its actual mass.

A tried and true method to perform a coarse calibration on a quadrupole is to utilize the knowledge that RF-only spectra for a given mass has a high mass cutoff of 9/7 of the nominal mass (the a=0 boundary of the stability diagram). This is a much more reliable predictor of the actual mass of a given peak than the local maximum.

Future work includes increasing the RF power available to the power supply. Simply increasing RF voltage instead of dropping frequency is a higher performance solution.

Note that ultimately, there is a practical limit to how much RF voltage you can provide to a quadrupole, based on availability of cost effective feedthrus, as well as discharges from pressure effects.

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