

Resolution and Transmission of Quadrupoles: RF-DC and RF-Only Operation

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Requirements for increased mass range (electrospray, clusters...) have challenged the performance of quadrupole mass spectrometers. Because increased mass range translates into increased required mass resolution, and increased mass resolution generally results in decreased transmission, the quadrupole is generally described as discriminating against high mass. In our laboratory, we have demonstrated that for limited mass range systems (large quadrupoles, high RF frequency) the penalty in transmission for going from RF-only operation to RF-DC operation is minimal (as high as 80% transmission); whereas the penalty for high mass operation (small diameter quadrupoles, low RF frequency) is much greater, typically significantly less than 1% relative transmission for masses greater than 1000 amu with RF-DC operation relative to RF-only operation. We have explored alternative RF-only operations of the quadrupole which offer high resolution high sensitivity operation. In this poster we will present experimental results from an evaluation of a number of quadrupoles of various rod radii and RF frequencies in RF-DC and resolving RF-only modes of operation. Emphasis will be placed on the following figures of merit: absolute transmission, relative transmission, ultimate resolution, abundance sensitivity, and peak shape.

I. INTRODUCTION

Quadrupole mass spectrometers are used in a wide variety of applications from the analysis of hydrogen, deuterium, tritium and helium [1], to the analysis of cluster and large biomolecules (thousands of amu mass range, less than unit mass resolution).

The mass range of a quadrupole mass spectrometer is dependent upon the RF frequency, the RF and DC voltages available, and the rod radius (for round rods), as well as the mode of operation (RF-only, first stability region, second stability region...). There is a variety of combinations of RF frequency, voltage and rod radii which yield equivalent mass ranges for a given input power. We have investigated the performance of quadrupole systems using some of these combinations with the goal of identifying which combinations yield the highest performance for a given input power/voltage.

The resolving RF-only mode of quadrupole operation was identified and refined in the 1970's using retarding potentials and specialized ion detectors [2-4]. In contrast with normal RF-DC quadrupole operation, RF-only operation relies on the strong focusing fields at the $a=0$, $q=0.906$ edge of the first stability region, requiring 9/7 times as much RF voltage to get to a given mass.

We have demonstrated high performance operation of a quadrupole using a retarding exit lens potential in our standard ion detector hardware. Dramatic increases in resolution and transmission are seen for high mass ions over the conventional first stability region, with unspectacular performance for very light ions.

II. EXPERIMENTAL

All experiments were performed in this study using standard Extrel EXM series probe assemblies consisting of a flange mounted analog electron multiplier, quadrupole in a grounded housing with entrance and exit lenses, and an Extrel 041-11 axial ionizer. All of these experiments used the same exact ionizer and detector, with the two quadrupoles swapped out between the two sets of experiments, with each set of experiments on a given quadrupole size performed in a single eight hour time period. All quantitative experiments utilized an emission current of 5.0 mA, and a partial pressure of perfluorotributylamine of 5×10^{-6} torr.

The ion energy for experiments in each quadrupole size was kept constant, with the rest of the tune elements optimized for best sensitivity and peak shape at each frequency.

The measurement of absolute transmission was performed

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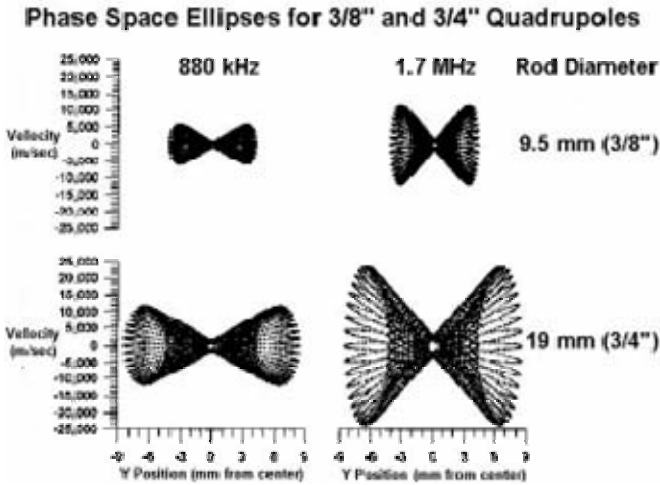


Figure 1. Phase space acceptance ellipses for 3/8" and 3/4" quadrupoles at 880 kHz and 1.7 MHz RF frequency.

by adjusting only the entrance lens, exit lens, and resolution for maximum sensitivity with no peak splitting, with resolution adjusted to just eliminate the valley between a given peak and its isotope. This methodology was found to be more reproducible than some arbitrary valley depth.

The same 3/4" quadrupole probe assembly was used for both the RF-only and the RF-DC experiments, changing only the tuning of the ionizer and quadrupole entrance and exit lenses and the presence or absence of the resolving DC voltage.

Calculations were performed using a modified version of HyperIon, a BASIC program developed by one of the authors (REP) at the University of Florida which uses a Runge-Kutta

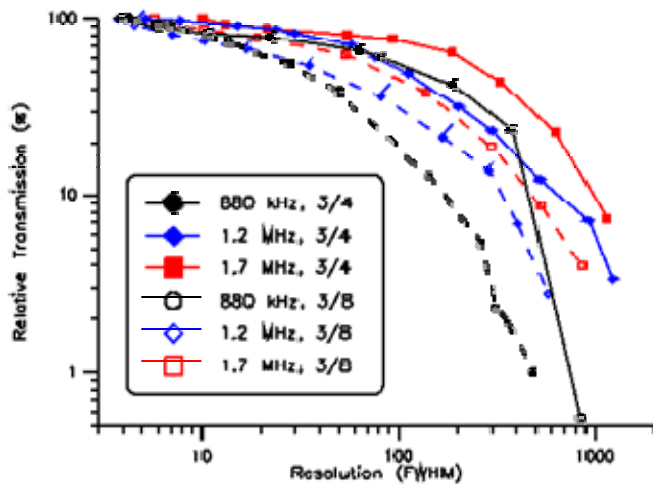


Figure 2. m/z 69: Relative transmission as a function of resolution for various combinations of rod diameter and RF frequency.

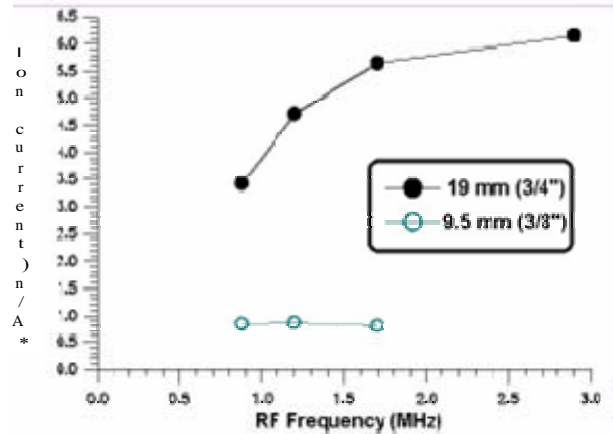


Figure 3. Absolute transmission for m/z 69 as measured on a Faraday detector.

numerical integration algorithm to solve the Mathieu equation of ion motion for a quadrupole mass spectrometer.

III. RESULTS AND DISCUSSION

A. Phase Space Acceptance Ellipses

One method of representing the calculated trajectories of an ion through a quadrupole is to plot the calculated trajectories into position-velocity space. The position velocity pairs corresponding to a given RF phase are seen to lie on the same ellipse. The area of these ellipses can be used as a predictor of quadrupole transmission. The transmission of a quadrupole system could be predicted based on some combination of the matching of the emittance of the ionizer with the phase space acceptance ellipses of the quadrupole.

Table 1. Absolute ion intensities (in pA) from perfluorotributylamine measured at various masses for different combinations of rod diameter and RF frequency. Note: The column of se for m/z 69 is plotted in Figure 3.

	m/z					
	50	69	131	219	414	502
3/8" 880 kHz	17	840	154	137	4	5
3/8" 1.2 MHz	17	860	160	94	3.9	2.7
3/8" 1.7 MHz	14.6	800	208	157	9.4	7
3/4" 880 kHz	55	3416	881	676	40.7	52.3
3/4" 1.2 MHz	82	4670	1290	905	31	28.2
3/4" 1.7 MHz	90	5650	1148			
3/4" 2.9 MHz		6140				

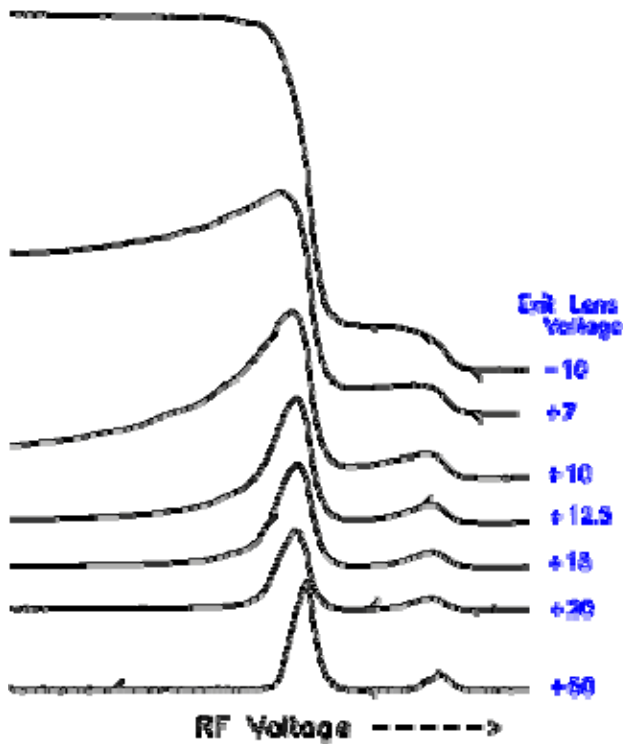


Figure 4. Evolution of peak shapes for the RF-only separation of m/z 664 and 665 of perfluorotributylamine.

Consider the case (shown in Figure 1) of the operation of a quadrupole at two frequencies 880 kHz and 1.7 MHz, almost a factor of two difference. The phase space ellipses are seen to double their dimensions in the velocity direction with a corresponding doubling in the area of the ellipses.

If one considers instead, the doubling of the rod radius

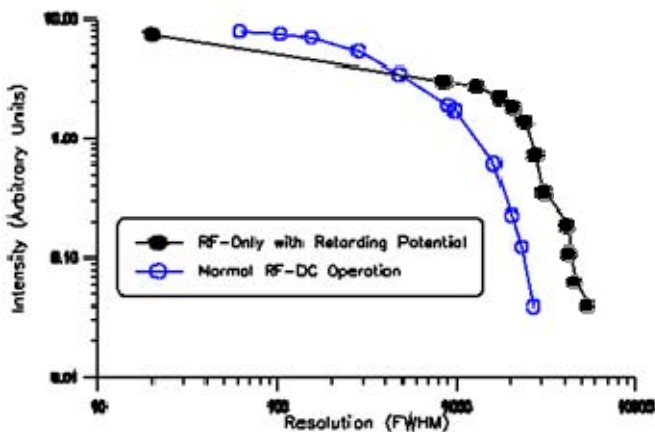


Figure 5. RF-only and RF-DC Intensity/Resolution curves for m/z 664.

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with maintenance of the same frequency, the resulting family of ellipses have four times the area, from a two-fold stretch in both the position and velocity directions.

The implications of these musings is the prediction that if one assumes that the emittance of the ionizer is well collimated (i.e. has little transverse velocity components), then a four-fold increase (2X in x direction, and 2X in y direction) in transmission would be expected for a doubling of rod radius, with negligible increase in transmission with the doubling of RF frequency.

Figure 1 contains representative phase space acceptance ellipses for the Y direction (negative DC voltage applied to the rods) for the four combinations of 3/8" and 3/4" diameter rods at 880 kHz and 1.7 MHz.

B. Transmission of RF-DC Quadrupoles

The resolution/transmission curves for various quadrupole configurations are presented in Figure 2. Note that for almost all

cases, relative transmission at higher frequencies is greater than relative transmission at lower frequencies. Relative transmission for the 3/4" quadrupole is better at all frequencies than relative transmission for the 3/8" quadrupole.

As can be seen in Figure 3, the absolute transmission follows the trend in relative transmission (two sides of the same coin). The data for absolute transmission for the 3/8" quadrupole does not seem to exactly follow the trend of increased transmission as with increased RF frequency, presumably due to tuning of the lens voltages.

The most striking information evident in this data is the greater than four-fold increase in absolute transmission for the 3/4" quadrupole over the 3/8" quadrupole at all frequencies. This can be interpreted to imply that the ionizer yielded a reasonably well collimated ion beam with emissive area wider than the acceptance area of both the 3/8" and 3/4" quadrupoles.

Table 1 contains the experimental results of the measurement of absolute transmission (measured on a Faraday collector) of various quadrupoles operated at various RF frequencies. All currents are in picoAmps.

C. High Resolution RF-Only Operation

An RF-only quadrupole can be converted from a band pass filter to high resolution mode by simply changing the tune voltages (primarily the quadrupole entrance and exit lens voltages), and utilizing the strong focusing capabilities at the boundary of the Mathieu stability diagram at $a=0$, $q=0.906$.

In high resolution RF-only quadrupole operation, the transition from high pass mass filter to high resolution is controlled through changes in the exit lens 'retarding' potential. Figure 4 demonstrates the transition in resolution as the exit 'retarding' lens is adjusted to more and more positive values for the analysis of m/z 664 of perfluorotributylamine.

As can be seen in Figure 5, the transmission as a function of resolution for high resolution RF-only mode is better than normal RF-DC operation, but from Figure 4, the abundance sensitivity is better for RF-DC except for the highest RF-only resolutions.

IV. CONCLUSIONS

Bigger is Better! Transmission scales roughly with the square of the rod radius. Larger diameter quadrupole rods require lower (more power efficient) frequencies to yield the same mass range. By increasing the rod radius instead of frequency, the same magnitude of applied voltage yields dramatically better transmission and resolution. Larger diameter quadrupole rods allow for larger diameter ion volumes (longer electron path length for electron ionization), which allows for increased source emittance. For a well collimated ion source emittance, an increase in RF frequency yields increased resolution and relative transmission with marginal increase in sensitivity.

For high mass ions, RF-only operation with a retarding potential offers twice the ultimate resolution and higher transmission at all resolutions albeit at sacrificed abundance sensitivity for the lower resolutions. High resolution RF-only operation requires 129% of the RF voltage as normal RF-DC operation to yield the same mass range. High resolution RF-only operation works better for heavier ions than lighter ions, and is predicted to offer dramatic improvements in sensitivity for higher mass range systems (smaller diameter quadrupoles, lower RF frequencies). Predicted applications include cluster analysis and deposition and the analysis of large bio-molecules.

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