OPTIMIZATION OF THE CYLINDRICAL ION TRAP GEOMETRY FOR MASS ANALYSIS AT HIGH PRESSURE

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ABSTRACT

Dmitriy Chernookiy: Optimization of the Cylindrical Ion Trap Geometry for Mass Analysis at High Pressure
(Under the direction of J. Michael Ramsey)

The cylindrical ion trap (CIT) provides many advantages for implementing mass spectrometry at elevated background pressures, presenting a practical route for the realization of a hand-portable device with performance that is suitable for many critical applications. This objective can be achieved through favorable scaling properties whereby high drive frequencies combined with small trap dimensions compensate for the loss of mass resolution from higher collisional damping rates. However, the simplified geometry of the CIT from the ideal hyperbolic electrode profile gives rise to higher-order fields that must be optimized for satisfactory performance.

Previous investigations of CIT geometry have addressed performance at relatively low background pressures (ca. 1 mTorr) with only a few trap configurations. In this work, a practical range of CIT geometry parameters was experimentally evaluated at pressures between ca. 20 to 1000 mTorr of helium at a drive frequency of 9 MHz for ring electrodes with a 0.500 mm radius. Mesh-covered endcap electrodes were substituted for the traditional aperture-style design to mitigate alignment concerns, which proved to be robust and not inherently limiting to resolution. The study focused on the major parameters of ring electrode thickness (0.600, 0.650, 0.700, 0.750 and 0.800 mm) and ring-to-endcap spacing (varied between 0.075 to 0.300 mm) for a total of 20 unique traps. The optimization results are reported in terms of these dimensions and are also generalized by correlating
performance changes to specific multipole fields. The octopole was found to be strongly correlated with trends in resolution at all pressures, with the dodecapole serving a minor role; the effects of all higher terms were confirmed to be inconsequential on a first-approach basis. At lower pressures resolution was primarily improved through an extension of the overall field linearity and the enhancement of an octopolar nonlinear resonance for double-resonance ejection, while at higher pressures it appears to benefit from the dynamic stabilization offered by more-than-linear fields. Thus, the optimal trap geometry was found to vary with the degree of damping and the mode of mass analysis. However, the spectral peak width was minimized over the widest pressure range with octopole strengths near 10% relative to the quadrupole.
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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS:

2D Two-dimensional
3D Three-dimensional
AC Alternating current
CF ConFlat (flange)
CIT Cylindrical ion trap
DAPI Discontinuous atmospheric pressure interface
DAQ Data acquisition (system)
DC Direct current
EI Electron (impact) ionization
EM Electron multiplier
FT-ICR Fourier transform ion cyclotron resonance
FWHM Full width at half maximum
GC Gas chromatograph(y)
GD Glow discharge
HMCO High-mass cutoff
HPMS High-pressure mass spectrometry
LIT Linear ion trap
LMCO Low-mass cutoff
MS Mass spectrometry
QIT Quadrupole ion trap
QMF Quadrupole mass filter
RF  Radio frequency
SMA  Subminiature version A (RF connector)
S/N  Signal-to-noise ratio
SWaP  Size, weight, and power
TOF  Time of flight

LATIN SYMBOLS:

A  Normalized potential difference between electrodes
An  Multipole weighting coefficient
C  Fixed floating potential or offset
\( \bar{D}_z \)  Pseudopotential well depth in the axial trap dimension
e  Charge of ion in coulombs
E  Electric field vector
\( E_z \)  Electric field component in the axial dimension
F  Force vector
\( f_d \)  Ordinary drive frequency in hertz
\( F_z \)  Component of force in the axial dimension
m  Ion mass
m/z  Mass-to-charge ratio of an ion
\( P_n \)  Legendre polynomial of order \( n \)
q  Charge of particle in coulombs
\( q_u \)  Dimensionless Mathieu stability parameter in \( u \) dimension
\( r_0 \)  Radius of the ring electrode
\( R^2 \)  Coefficient of determination
\[ S_n \] Dimensional weighting factors

\[ t \] Time

\[ u \] Coordinate dimension in \( x, y, z \) or \( r \)

\[ U \] DC voltage

\[ V \] Amplitude of AC (RF) voltage

\[ z_0 \] Axial distance from the center of a trap to the apex of an endcap electrode

**GREEK SYMBOLS:**

\[ \beta_u \] Dimensionless trapping parameter in the \( u \) dimension

\[ \theta \] Polar angle

\[ \xi \] Dimensionless phase or time interval

\[ \rho \] Radial distance in the spherical coordinate system

\[ \rho_{\text{max}} \] Maximum ion density

\[ \varphi \] Azimuthal angle

\[ \phi \] Electric potential

\[ \phi_0 \] Potential applied to the ring electrode

\[ \omega_{u,n} \] Secular frequency in \( u \) dimension of order \( n \)

\[ \omega_z, \omega_{z,0} \] Fundamental axial secular frequency

\[ \Omega \] Angular drive frequency

**SPECIAL UNITS:**

\[ \text{Th} \] Thomson, unit of \( m/z \), defined as \( \text{Da}/e \) (daltons per elementary charge)

\[ V_{0-p} \] Zero-to-peak amplitude of an AC potential

\[ V_{p-p} \] Peak-to-peak amplitude of an AC potential

\[ \text{WPI} \] Wires per inch (in one dimension of a square grid)
CHAPTER 1
INTRODUCTION

The search for balance between capability and convenience is not a new struggle. This age-old equation persists because practicality usually places the variables at odds with each other. When an imbalance is created out of necessity, it can be corrected by shifting the fulcrum through advances in science and technology. It is interesting to consider, then, that while we no longer depend on horses for transportation or homing pigeons for communication, there is still widespread use of trained dogs for chemical detection.

When it comes to analytical instrument development, the traditional mindset of lab-based analysis is primarily concerned with figures of merit, without placing much emphasis on the footprint. Hence, decades of research have led to great improvements in performance, but without broadening accessibility outside the lab environment or increasing affordability. Long-standing centralization of specialized equipment and personnel largely restricted chemical analysis to these locations, with little recourse for remote or unique samples. However, bolstered by the fabrication tools from the microelectronics industry, a new movement began near the end of the twentieth century to redesign instruments into smaller, faster, and more efficient systems.

This new frontier in analytical chemistry is in the process of expanding the discipline in many respects, already encompassing a variety of techniques. Among these, mass spectrometry (MS) is poised to offer the advantages it has in the laboratory to a new wave of portable devices. MS is useful for determining an analyte's molecular weight, and
the characteristic ion fragmentation patterns provide detailed structural information. High sensitivity is readily achieved when mass analyzers are coupled with detectors such as electron multipliers. Additionally, a wide variety of ionization sources have been developed to accommodate diverse compounds across samples of ranging complexity. Even though the concept of miniature MS spans decades, with a number of commercial models already available, much work remains in adapting the components into a convenient form factor while closing the gap in performance compared to established systems.

This dissertation is focused on a few aspects of a specific mass analyzer—the cylindrical ion trap (CIT). It is one of many forms in the general family of ion trap mass analyzers, which are collectively among the most promising candidates for handheld MS. The remainder of this chapter gives a brief review of miniature mass spectrometers, then covers some essential background theory and principles to provide a clear perspective for the project objectives stated at the end, while the next chapter explains the methods and instrumentation employed in this study. Chapter 3 contains the experimental results of optimizing the CIT geometry for high-pressure operation, including some considerations of secondary geometric features and other factors affecting resolution. This is followed by analysis in Chapter 4 with regards to the electric field composition in order to generalize the results across different trap structures. Chapter 5 closes with conclusions and the future outlook of this work.

1.1 The Mobilization of Mass Spectrometry

The ideal portable mass spectrometer would be no more of a burden to carry than a modern cell phone while providing unquestionable specificity and rapid answers to the demands of critical tasks such as the detection of chemical and biological warfare agents,
searching and screening for explosives, and urgent medical diagnostics. Mitigating imminent threats is only the beginning of a long list of applications that would benefit from this device, including the monitoring of industrial production lines, tracking pollutants, mineral exploration, forensics, and the identification of possible contraband substances. These all share common concerns regarding sampling. In some cases, results are needed on the spot and there is insufficient time to transport the sample to a distant facility. In others, the sample may be unstable or difficult to collect, or perhaps the time and manpower required are simply cost-prohibitive. Whatever the reason, the alternative approach to conventional sampling is to bring the mass spectrometer to the field for in situ analysis.

1.1.1 General Developments

Perhaps the most extreme example of sampling involves remote extraterrestrial analysis by unmanned vehicles. In this case, sending an instrument to make measurements on-site is preferable to facing the logistics and expense of recovering a multitude of samples, with the added risk of contamination. Due to the high costs of carrying a payload into space, there are clear advantages to having the smallest and lightest instrument possible. In fact, the need to perform mass spectral analysis on such missions is one of the earliest driving forces for transforming standard laboratory instruments so they can be taken into the field. In the mid-1970s, NASA’s Viking program launched two probes to study the atmosphere and soil composition of Mars. Each of these had a sector mass spectrometer on board, coupled with a gas chromatograph (GC).

Further development was slow until interest picked up in the 1990s to study the miniaturization of existing mass analyzers, with focus shifting the following decade towards applying this knowledge in building small but fully integrated mass spectrometers.
Throughout this time, various degrees of portability have been achieved. As defined by Lammert, a transportable system is one that is detached from its environment but must be conveyed on wheels (vehicle or cart) or carried by a few people. A person-portable system is small enough to be carried by a single individual, as in a backpack. The smallest system is hand-portable, only imposing a minor load and easily added as an accessory item. This range exists because of the inherently inverse relationship between performance and the instrument’s size, weight, and power consumption (SWaP). Since it is not yet possible to have the best of both worlds in one package, tradeoffs must be made, and thus a spectrum of tailored devices is necessary to meet demand.

In order for the device to remain useful, the performance cannot be overly compromised for the sake of portability, and vice versa. A balance point can be reached by setting the target performance according to the minimum requirements of the intended application. For example, in many cases unit mass resolution would be sufficient, which greatly eases many of the engineering difficulties of a hand-portable system. Resolution concerns can be lowered further by employing automated statistical analysis and reference libraries. This is a good solution when the detection of a limited number of analytes is needed with high throughput—a low rate of false negatives can be maintained while relying on relatively crude raw data. Another advantage of such processing is that one of the largest and most expensive elements of an MS system becomes optional: the skilled technician who usually interprets the data. An obvious drawback, however, is decreased versatility.

Portable MS has not yet been widely adopted, pending better solutions to industry problems. A variety of challenges remain to be solved, centered on the mass analyzer but extending to all the other MS components and supporting equipment. Furthermore,
shrinking the mass analyzer does not generally translate to a reduction in SWaP for the other hardware, which includes the ionization source, detector, electronics, and pumps. Power is itself ultimately another manifestation of size and weight in miniature systems. It has little bearing when drawn from an outlet, but becomes a scarce resource when supplied by batteries. Given the present limitations of energy storage technology, batteries are still among the largest and heaviest parts.

1.1.2 Strategies for Inadequate Pumps

The vacuum system is typically the most expensive and difficult to manage in terms of SWaP. Consequently, its design and shortcomings are the primary obstacles in miniature MS research. There are currently no satisfactory pumps available with the necessary specifications for a hand-held device that can maintain the high vacuum conditions usually required in a mass spectrometer (well below $10^{-3}$ Torr), although there are some commercial options for less portable purposes. As long as pumping capacity remains deficient, alternative strategies must be employed to undertake MS under the constraints of existing pumps. For mass analyzers that depend on low pressure to achieve good performance, the gas load imposed by sample introduction can be reduced in one of two ways. Under continuous operation with a constant gas stream, a smaller orifice can be used at the inlet for lower conductance. However, the smaller flow rate directly affects the ion throughput and thus the sensitivity. Conversely, a discontinuous atmospheric pressure interface (DAPI) can be used to pulse the gas in short bursts between longer pump-down segments. Although sensitivity isn’t curtailed during the brief low-pressure period when analysis is possible, this cyclical action makes DAPI unsuitable for high sampling rates, considering the normal 1% duty cycle. It is possible to sidestep the pumping issue
somewhat by implementing a vacuum tethering strategy: the device is initially evacuated at some designated station, after which vacuum is maintained for a limited period of time by a small pump such as an ion getter. In this interval the spectrometer is free to be transported as needed, with the caveat that it is not self-sustaining. A pulsed sample introduction method akin to DAPI must be used to avoid overwhelming the pumps. In some circumstances a semipermeable membrane may be a good solution for continuous sampling without exceeding pumping capacity, but its chemically selective nature precludes general use.11,12

To circumvent the issues of modest pumping technology, a profoundly different approach can be taken to system design. The goal of high-pressure mass spectrometry (HPMS) is to perform mass analysis entirely at the elevated pressures typical of such pumping conditions (≥100 mTorr).13 This means that each component of the system must be capable of operating at high pressure, with unique hurdles presented for the ionization source, detector, and the mass analyzer. This dissertation is a continuation of previous work in this group based on the HPMS strategy.

1.1.3 Ion Sources for HPMS

Electron ionization (EI) is a commonly used technique for converting neutral analytes into positively charged ions, particularly for organic compounds. The traditional electron source is a resistively heated filament combined with accelerating and focusing potentials to direct the beam as needed. These thermionic emitters are inappropriate for HPMS, the foremost reason being their incompatibility with high pressures, especially if air is the background gas. Due to the extreme temperatures involved they are subject to rapid oxidation and other destructive reactions. Additionally, the heating current is responsible
for relatively high power consumption. A glow discharge (GD) source, on the other hand, is a good alternative. They are intrinsically suited for high pressure conditions and can be operated in EI mode by extracting electrons from the plasma. With occasional cleaning their lifetime is indefinite, and power draw is a slight fraction of a hot cathode’s. There is ongoing research into next-generation field effect sources based on novel materials and microfabricated structures to further improve ionization efficiency and reduce power consumption to negligible levels.

Although the aforementioned internal ionization sources are ideal for volatile samples, they are not the best choice for field applications due to their comparatively low throughput. Ambient ionization techniques paired with atmospheric pressure interfaces enable the analysis of samples in their natural state with no prior workup and are applicable to nonvolatile substances. Desorption electrospray ionization (DESI) and direct analysis in real time (DART) are well-known options. When constrained by poor pumping speed, these ion sources face heavy disadvantages in non-HPMS systems (from workarounds such as DAPI).

1.1.4 Detectors for HPMS

A pressure-tolerant detector is also necessary to successfully conduct HPMS. The most sensitive ion detectors are electron multipliers, providing gains on the order of $10^7$ before any electronic amplification of the signal takes place. Unfortunately, they are also inherently not fit for pressures much above $10^{-6}$ Torr. When this threshold is exceeded, ion feedback from secondary electrons colliding with residual gas begins to increase noise counts. Eventually ion runaway catastrophically damages the emissive surface coating.
few versions have been designed expressly for miniature MS operation into the $10^{-2}$ Torr range, but this is still insufficient for HPMS.

For trapped-ion mass analyzers where periodic motion of the ion is relatable to its mass, image current detection can be implemented with Fourier transformation to convert the measured frequencies into a mass spectrum, with no added risk of electrical breakdown. In ultra-high vacuum conditions this method has given tremendous resolving power to some mass analyzers, namely Fourier transform ion cyclotron resonance (FT-ICR)\textsuperscript{19} and the orbitrap.\textsuperscript{20} It is nondestructive and thus extended ion re-measurement increases the number of samples and leads to superior frequency resolution. Yet, coherent pickup is impaired at high pressure—the ion collisions with neutrals destabilize periodicity. Furthermore, the collapsing ion trajectories induce weaker currents in the detection circuitry which decreases signal strength.\textsuperscript{21} The extended measurement time also translates to slower data acquisition rates.

Another pressure-tolerant detection scheme is the Faraday cup, which uses a circuit tied to a biased sensor electrode to amplify the charges that are transferred from impinging ions. Except for their indifference to pressure, they are inferior to electron multipliers in most respects. The gain is lower by many orders of magnitude, and narrow bandwidth can distort peak shape. Nonetheless, for HPMS they are currently the most viable choice.\textsuperscript{22,23}

1.1.5 Pros and Cons of Common Mass Analyzers

Mass analyzers separate ions according to their mass-to-charge ratios ($m/z$) by influencing their trajectories in space, time, or frequency using electric and/or magnetic fields. The thompson (Th) is a unit of $m/z$, defined as Da/e (daltons per elementary charge).\textsuperscript{24} In almost all cases, the mass analyzer must be operated in high vacuum to
minimize the detrimental effects of ion-neutral collisions on performance. While a reduction in analyzer size can decrease the total number of collisions at a given pressure by shortening the ion pathlength, there is usually no further recourse to running it at greater pressures. Moreover, in some analyzers the spatial confinement itself will adversely affect resolution. Yet, at smaller dimensions all mass analyzers naturally need lower voltages to maintain electric field strengths, which alleviates the strain on supporting electronics. Beyond this, each analyzer holds special challenges, as well as benefits, and thus selecting one for a miniature system has not been a straightforward process. As reported in 2000, there was comparable representation from all common analyzers in miniaturization research. By a 2009 review, however, the strong advantages of ion traps had emerged and led to their commercial dominance, continuing to grow through the present. These superior aspects are discussed in §1.1.6 below.

Time-of-flight (TOF) analyzers are the simplest in regards to fabrication, consisting of a field-free drift tube (although this is offset somewhat by the intricacies of the high bandwidth detector and the injection of ions with uniform kinetic energy). While they require high vacuum, this can be mitigated by shortening the tube and ion flight path, as mentioned earlier. However, since mass resolution is intrinsically dependent on the length of the tube, it strongly counters any miniaturization efforts of the TOF. Nevertheless, working within these bounds, several systems have been produced. This includes small benchtop units, several iterations of person-portable suitcase packages, and even a micro-sized device with an integrated ion source and detector.

Sector mass analyzers share the size-dependent resolution issue with TOF, and also possess no special tolerance for rough vacuum conditions. Of the different possible configurations, the Mattauch-Herzog geometry is especially attractive for miniaturization
since it uses only static electric and magnetic fields, which makes it possible to implement small permanent magnets and simple electronics. The associated simultaneous transmission of all ions, rather than scanning them, lends itself to rapid data acquisition. As a classic mass analyzer of widespread use, the sector was the first to attract attention for miniaturization.\textsuperscript{25} Despite this, they have not been demonstrated as amenable to hand portability, with interest waning after the turn of the century.\textsuperscript{33–36}

The prevailing ambitions of FT-ICR development are in stark contrast with the goals of miniaturization. To achieve maximum resolution, these instruments utilize ever larger and more powerful superconducting magnets. A stringent vacuum is necessitated for long and unperturbed ion lifetimes, otherwise the benefits of image current detection are diminished. In spite of these detractors, a portable FT-ICR would be competitive even if it retains just a slight fraction of the resolving power seen in its full form. While the practical limit is still beyond hand-portability, a briefcase-sized device operating at $10^{-7}$ Torr with a 0.44 Tesla permanent magnet has been demonstrated with resolving power on the order of 500-1000.\textsuperscript{37,38}

The quadrupole mass filter (QMF) is based on principles very similar to ion traps, in that the physics governing ion stability have the same origin. The differences in electrode configuration and operating parameters, however, clearly distinguish them in terms of capability and performance. The QMF derives its name from the mass-selective stability that ions have when traversing along two pairs of rods that confine them orthogonally via RF (radio frequency) and DC potentials (which are scanned to pass single $m/z$ values over time). Consequently, it shares the drawbacks of other beam-type analyzers when it comes to high-pressure operation. Although ion confinement in the radial plane features dynamic stability in the manner of ion traps (see §1.4.2) this does not extend to the axial flight path.
With increased pressure, scattering caused by ion-neutral collisions prevents ions from reaching the detector, lowering sensitivity. As with ion traps, though, the QMF is readily parallelized; arrays of rods can be used to moderate lower sensitivity due to pressure and other effects, such as space charge.\textsuperscript{39} While not as favorable as ion traps in many regards, the QMF has wide market share, finding appeal particularly as a residual gas analyzer.\textsuperscript{40} These have been successfully tested up to 10 mTorr.\textsuperscript{41}

It is worth mentioning the role of ion mobility spectrometry and its variants in the history of portable detection, though it is distinct from mass spectrometry (separating ions according to size and shape in addition to mass). As a predecessor that found popularity in the 1990s among applications that miniature MS has also targeted, it suffers from high false-positive rates amid background interferents due to its relative lack of selectivity. Yet, they continue to rival MS in terms of sensitivity and detection limits, size, ease of use, and response time.\textsuperscript{42–45}

1.1.6 Advantages of Ion Trap Mass Analyzers

Ion traps have a broad set of advantages for portable MS, but what makes them truly exceptional is their unique relationship with background pressure. Even without any special adaptation for portable systems (i.e. at their normal laboratory scale) they not only tolerate pressures that are many orders of magnitude higher than found in other analyzers, they actually require them for optimal performance. This extends into the 1 mTorr range for light buffer gas species such as helium, which are deliberately added for collisional cooling effects. Kinetic energy is removed without scattering the ions, thereby collapsing their trajectories to the center of the trap; this narrows their distribution and ultimately improves resolution. Furthermore, the acceptable level of damping is relative to the drive
frequency of the dynamic trapping field, which serves as an effective counterbalance. Specifically, the resolving power is inversely proportional to pressure, but directly proportional to drive frequency (see §1.4.2). This compensation is the key enabling factor of HPMS, opening the door to practical mass analysis at hundreds of millitorr. The resulting high-pressure environment also reduces the extent of sample rarefaction, increasing ionization efficiency and sensitivity.

Decreasing the size of an ion trap leads to a quadratic reduction in working voltage, which translates to a quartic reduction in power. This is an important point considering that HPMS pushes the frequency and voltage envelope to the limits of any RF amplifier that is efficient enough for portability. Keeping the voltage in check is also essential because the operating conditions of HPMS span a pressure regime that exacerbates electrical breakdown. According to Paschen’s Law, the pressure-distance product for miniature ion traps and their environments is near the minimum breakdown voltage for standard background gases, which is made worse by RF potentials and smaller electrode radii.46,47

Ion storage capacity drops with trap size due to the mutual repulsion of like charges. The induced space charge distorts the trapping potential and is deleterious to performance long before saturation prevents the accumulation of any more ions (see §1.2.5). However, these issues can be remedied by implementing large arrays of traps that perform mass analysis in parallel.48–50 It is estimated that for a given footprint, an array of \( n \) traps will have a factor of \( n^{1/2} \) greater capacity than a single trap occupying the same area.51 Alternatively, instead of a uniform array, the trap elements can have a multiplex configuration with varying specifications to expand the capabilities through flexible figures of merit. For example, Misharin et al. have demonstrated a 4-channel design that is able to simultaneously analyze different compounds via independent ion sources and detectors.52
On the other hand, arrays are more susceptible to degradation of resolution as a result of fabrication or alignment imprecision. For nominally uniform arrays, trap-to-trap variability contributes directly to electric field irregularity, causing ensemble peak broadening. Therefore, arrays require tighter tolerances relative to a single trap to achieve the same resolution.

Standard-sized ion traps are fairly small to begin with (having interior diameters on the order of 2 cm) and prompt considerable concern towards tolerances in fabrication and assembly. Miniaturization only aggravates the situation (enough to warrant manifold research topics, including this present work). Although resolution is not fundamentally limited by trap size, poor surface quality and faults in geometry and alignment will lead to inferior performance. In order to avoid larger relative errors from a mechanical standpoint, the absolute tolerances must improve in concert with trap size. Consequently, conventional machining becomes unreliable for traps with features on scales under 1 mm. Although micromilling tools can extend this range by another order of magnitude, these serial production techniques are easily surpassed in terms of precision, time, and cost by microfabrication technologies that have batch processing capabilities.

Ion traps can execute tandem MS studies within a single analyzer by virtue of selective ion manipulation and partitioning the separation stages over time. Tandem MS improves the overall selectivity and facilitates the analysis of more complex samples by reducing chemical noise and augmenting structural elucidation methods. This ability and the previously mentioned advantages are shared across an assortment of ion trap devices, which can be classified by whether the ions are confined in a two- or three-dimensional (2D or 3D, respectively) oscillating field. The 3D versions are rotationally symmetric, with ions confined towards a central point. In 2D traps, this point is extended along a line, which
increases charge capacity proportionately. Axial ion injection along this line can also significantly enhance trapping efficiency. For these reasons, 2D traps have superseded 3D traps, despite arriving much more recently. The most common 2D variant, the linear ion trap (LIT), utilizes additional static potentials at the ends to confine ions axially. In a toroidal ion trap, the ends are joined to form a continuous circular track for ion containment. Numerous geometric simplifications of all these exist as well.

Almost all miniature ion trap systems are still designed for relatively low pressure work and thus have not broken through the pumping barrier to achieve hand portability. This excludes those that are based on a vacuum tethering strategy (discussed in § 1.1.2), since that only temporarily bypasses the major SWaP constraints facing portable spectrometers. For instance, the smallest ion trap MS reported to date employs this strategy to attain a weight of just 1.5 kg and average power usage of 5 W, but with large tradeoffs in sampling capability and performance. On the other hand, extensive development at Purdue University has led to progressively smaller standalone instruments, namely the Mini 10 (at 10 kg and 70 W) and Mini 11 (5 kg and 35 W) iterations. Of the sparse published examples of portable MS in action, the Mini 10 underlines such utility with fast analysis of toxic industrial compounds at detection limits well below permissible exposure levels. Hyphenated instruments (which combine the selectivities of different analytical techniques) are available commercially, with a 13 kg GC-MS offered by Torion in a suitcase package. Other companies have focused on transportable benchtop solutions, such as the MMS-1000 (8 kg) from 1st Detect and model 824 (23 kg) from Griffin Analytical. The M908 from 908 Devices is currently the only hand-portable device to have put HPMS into practice with ion traps, and as such weighs in at just 2 kg.
The HPMS approach is not clear-cut, of course, otherwise an ultraportable MS solution would have emerged long ago and there would be no competition to meet today’s needs. Although the intent has never been to compete with the performance level of standard MS, the prospect of improvement will continue to drive research. To understand how the interplay of the many ion trap parameters and conditions restrains the goals of HPMS, it is necessary to review the guiding theory and principles of operation.

1.2 Ion Trap Theory

As discussed in the previous section, there are multiple ion trap designs. Due to variations in structure and symmetry between 2D and 3D ion traps, there are some differences in theory that have important consequences, particularly with regard to the characteristics of their stability diagrams and relationships among nonlinear resonances. Since the results presented in this dissertation deal only with 3D traps, the following theoretical treatment is limited in scope accordingly. The reference works of March et al. provide comprehensive coverage of these and many other ion trap topics.68–73

1.2.1 Origins and Structure

The invention of the 3D ion trap is credited to Paul and Steinwedel,74 who reported it in 1953, although it took several decades of further development and serendipitous discoveries before ion traps became popular in mass spectrometry (more so for versatility than the relatively modest performance). In its more ideal form, the 3D ion trap is also known as the quadrupole ion trap (QIT), where the name is derived from the quadrupolar shape of the trapping potential established by the electrodes. Before describing it physically, however, it is perhaps more informative to first consider the question of how a charged particle can be contained in 3D space. Rather than following the actual
chronological order of historical events surrounding ion traps, this approach starts with
basic principles to show a logical route to their conception. After examining the physics of
ion containment and determining the relevant stability parameters, it becomes apparent
that mass analysis is a natural extension and can be readily enacted.

As codified by Earnshaw’s theorem, it is not possible to trap a charged particle in
three dimensions by means of electrostatic fields alone. The static fields of the closely
related Penning trap (the basis of the FT-ICR) are not an exception, since a magnetic field is
used for confinement in two of the dimensions. It is, however, possible to confine ions by
means of an oscillating potential that imparts dynamic stability, alternating such that the
ions are focused towards a single point in space that is an effective, but not absolute,
potential energy minimum. For the sake of simplicity, harmonic ion motion is desired (this
allows an analytical expression to be derived that describes the motion in terms of stability
and frequency). The restoring force $F$ acting on the ions, therefore, should increase linearly
with displacement $r$ in any direction from a central point:

$$ F \propto -r $$ (1.1)

The next step is to determine the general form of the electric potential $\phi$ in 3D space that
will produce this condition. From the Lorentz force law in the absence of a magnetic field, a
particle of charge $q$ in an electric field $E$ will experience the force

$$ F = qE $$ (1.2)

Since the electric field is the gradient of the potential,

$$ E = -\nabla \phi \quad \text{or} \quad E = \left( \frac{\partial}{\partial x} \hat{x} + \frac{\partial}{\partial y} \hat{y} + \frac{\partial}{\partial z} \hat{z} \right) \phi $$ (1.3)
a simple substitution shows that the force is related to the potential as

\[ F = -q \nabla \phi \]  

(1.4)

It is clear, then, that in order for \( F \) to be linear as in eq 1.1, \( \phi \) must be a quadratic function.

In Cartesian coordinates, the most general form of this potential is

\[ \phi(x, y, z) = A(S_1x^2 + S_2y^2 + S_3z^2) + C \]  

(1.5)

where \( A \) is the normalized potential difference between the electrodes, \( C \) is an adjustment for any potential offset, and the \( S_n \) weighting factors along each dimension are associated with the symmetry of the electrodes. It is reasonable to assume that the trapping volume has negligible charge density; so, in order to satisfy Laplace’s equation for the potential,

\[ \nabla^2 \phi(x, y, z) = 0 \]  

(1.6)

and given that \( A \) is non-zero, we find that the weighting factors must meet the condition

\[ S_1 + S_2 + S_3 = 0 \]  

(1.7)

The rotational symmetry of the QIT around the \( z \) axis dictates the equivalence of the \( x \) and \( y \) dimensions, which can be accounted for by setting \( S_1 = S_2 = 1 \) and \( S_3 = -2 \). In fact, for convenience, we can convert to the cylindrical coordinate system using \( r^2 = x^2 + y^2 \) whereby the potential is then

\[ \phi(r,z) = A(r^2 - 2z^2) + C \]  

(1.8)

A direct way to establish a potential of this form is to shape the electrodes to follow the equipotential contours, which means they should be hyperbolic surfaces. In practice, three axially-symmetric electrodes are used, consisting of a central \textit{ring} electrode that is interposed between two identical \textit{endcap} electrodes, with mirror symmetry across the
radial plane as shown in Figure 1.1a. The radius of the ring electrode is denoted as \( r_0 \) and the axial distance from the center of the trap to the apex of an endcap electrode is denoted as \( z_0 \). Although the electrodes are constrained to share common asymptotes, Knight\(^{76} \) demonstrated that there are no restrictions on the relation between \( r_0 \) and \( z_0 \) and that the general cross-sectional geometry follows

\[
  r^2 - 2z^2 = r_0^2
\]

for the ring electrode and

\[
  r^2 - 2z^2 = -2z_0^2
\]

for the endcap electrodes. However, it was common in the past to conform the dimensions to the ratio of \( r_0^2 = 2z_0^2 \) since it was perceived to be ideal, if only to maximize the effective confinement volume.\(^{77} \)

To determine the values of constants \( A \) and \( C \) in eq 1.8 within the system of the trap, the internal potential \( \phi_0 \) is best defined as the relative difference in potentials applied between the ring and endcap electrodes:

\[
  \phi_0 = \phi_{\text{ring}} - \phi_{\text{endcaps}}
\]

In terms of eq 1.8 and the electrode boundaries we know that

\[
  \phi_{\text{ring}} = \phi(r_0,0) = A(r_0^2) + C
\]

and

\[
  \phi_{\text{endcaps}} = \phi(0,z_0) = A(2z_0^2) + C
\]
Substituting these into eq 1.11 and solving for \( A \) returns

\[
A = \frac{\phi_0}{r_0^2 + 2z_0^2}
\]  
(1.14)

so that eq 1.8 becomes

\[
\phi(r,z) = \frac{\phi_0 (r^2 - 2z^2)}{r_0^2 + 2z_0^2} + C
\]  
(1.15)

Given that the QIT is typically operated with the endcaps at (or very near) ground potential, such that we know \( \phi(0,z_0) = 0 \), the constant \( C \) can be evaluated from eq 1.15 to obtain the final form of the potential within the trap:

\[
\phi(r,z) = \frac{\phi_0 (r^2 - 2z^2)}{r_0^2 + 2z_0^2} + \frac{2\phi_0 z_0^2}{r_0^2 + 2z_0^2}
\]  
(1.16)

The potential applied to the ring electrode can combine a DC voltage component \( U \) along with an RF component of amplitude \( V \) (expressed as volts zero-to-peak, \( V_{0-p} \)) and angular frequency \( \Omega \) (equal to \( 2\pi f_d \) where \( f_d \) is the ordinary drive frequency in hertz) that alternates over time \( t \) as a sinusoidal function:

\[
\phi_0 = U + V \cos \Omega t
\]  
(1.17)

The quadrupolar equipotential lines of eq 1.16 in the \( r-z \) plane are shown in Figure 1.1b for a QIT that holds the \( r_0^2 = 2z_0^2 \) ratio.

### 1.2.2 Stability Parameters

Due to the absence of cross-dimensional terms in the quadrupolar potential, we are able to treat ion motion in each direction independently. Therefore, considering the
movement of an ion of charge $e$ and mass $m$ in just the axial dimension at first, applying eq 1.4 to the potential in eq 1.16 gives the $z$-component of force as

$$F_z = \frac{4e(U + V \cos \Omega t)}{r_0^2 + 2z_0^2}z$$  \hspace{1cm} (1.18)$$

where eq 1.17 has been substituted for $\phi_0$. To complete the equation of motion, this force can be related to the ion’s acceleration by Newton’s second law,

$$F_z = ma = m \frac{d^2z}{dt^2}$$ \hspace{1cm} (1.19)$$

so that we have the following second-order differential equation

$$\frac{d^2z}{dt^2} = \frac{4e(U + V \cos \Omega t)}{m(r_0^2 + 2z_0^2)}z$$ \hspace{1cm} (1.20)$$

Equations of this class have been solved and applied in many areas of physics, so it is convenient to simply adopt the corresponding solutions for this case. Specifically, eq 1.20 resembles the well-known Mathieu equation, which has the form

$$\frac{d^2u}{d\xi^2} = -(a_u - 2q_u \cos 2\xi)u$$ \hspace{1cm} (1.21)$$

where $q_u$ and $a_u$ are dimensionless stability parameters, $u$ is a spatial coordinate, and $\xi$ is a dimensionless phase or time interval. Following the approach taken by March78 and others, an exact conformation can be obtained by making the following transformation via the chain rule

$$\frac{d^2u}{d\xi^2} = \frac{4}{\Omega^2} \frac{d^2u}{dt^2}$$ \hspace{1cm} (1.22)$$

20
and with a change of variables, whereby $\xi$ is set to $\Omega t/2$, so that eq 1.21 is rewritten as

$$\frac{d^2u}{dt^2} = -\left(\frac{\Omega^2}{4} a_u - \frac{\Omega^2}{2} q_u \cos\Omega t\right)u \quad (1.23)$$

With a final expansion of eq 1.20,

$$\frac{d^2z}{dt^2} = \left(\frac{4eU}{m(r_0^2 + 2z_0^2)} + \frac{4eV}{m(r_0^2 + 2z_0^2)} \cos\Omega t\right)z \quad (1.24)$$

it becomes evident by direct comparison of eqs 1.23 and 1.24 that the stability parameters for the QIT in the $z$ dimension are

$$q_z = \frac{8eV}{m(r_0^2 + 2z_0^2)\Omega^2} \quad (1.25)$$

and

$$a_z = \frac{-16eU}{m(r_0^2 + 2z_0^2)\Omega^2} \quad (1.26)$$

This exercise can be repeated for ion motion in the radial dimension, whereupon it is determined that the stability parameters are related as $q_r = -\frac{1}{2} q_z$ and $a_r = -\frac{1}{2} a_z$, stemming from the values chosen for the weighting factors in eq 1.5.

For the present purpose, it is not necessary to investigate the complete integration of the Mathieu equation, as would be needed to follow ion trajectories over time. The nature of the solutions has been thoroughly characterized elsewhere in terms of the stability parameters, and these general properties are sufficient to understand the consequences for ion containment (and ultimately mass analysis, covered in § 1.2.4). As summarized by March and Todd, there are two possible types of periodic solutions, and
they take different forms according to the values of $q_u$ and $a_u$. Unbounded solutions cause the ion trajectory amplitude to increase towards infinity from the center of the trap as $\xi$ increases, and are therefore \textit{unstable}. Due to the finite boundaries of the physical trap, these ions may either be neutralized after colliding with the walls of the electrodes, or they may escape through holes that are incorporated for this reason. Bounded solutions for ion motion are able to confine the oscillation amplitude within the trap volume, and are therefore \textit{stable}. This concept of stability is quantified by yet another dimensionless parameter $\beta_u$ that is a function of $q_u$ and $a_u$ (see § 1.2.3 below). Integer values of $\beta_u$ demarcate the boundaries of stable and unstable motion, while rational non-integer values represent stability; all other values of $\beta_u$ (i.e. complex numbers) are unstable.

These $\beta_u$ values can be used to map out domains of ion stability in $q_u$ and $a_u$ space, which are the coordinates of parametric plots referred to as \textit{stability diagrams} (Figures 1.2 and 1.3). To improve readability, it is common to convert the radial stability parameters to their axial counterparts $q_z$ and $a_z$ so that they all lie in the same quadrants, which means they are off by a factor of $-2$ in the diagrams. In order to be trapped in all dimensions, an ion must reside in stable regions of $\beta_z$ and $\beta_r$ simultaneously by virtue of all the operating variables embedded in the stability parameters. The most practical area of overlapping stability is for $0 < \beta_u < 1$, which is the region closest to the origin, labeled $A$ in Figure 1.2. This is because the values of $q_u$ and $a_u$ are directly proportional to the operating voltages $V$ and $U$, respectively. An expanded view of region $A$ is shown in Figure 1.3; this stability diagram is central to many ion trap concepts. Notably, the intersection of $\beta_z = 1$ with the $q_z$ axis at $q_z = 0.908$ marks the lowest $m/z$ ion that can theoretically be stored when operating a trap in the common RF-only mode, termed the \textit{low-mass cutoff} (LMCO).
1.2.3 Frequencies of Ion Motion

Solutions of the Mathieu equation return a superposition of frequencies that describe ion motion, also called the secular frequencies. This series can be calculated for different orders of \( n \) (integer values) from already familiar terms:

\[
\omega_{u,n} = \begin{cases} 
(n + \frac{1}{2} \beta_u) \Omega & \text{for } 0 \leq n < \infty \\
-(n + \frac{1}{2} \beta_u) \Omega & \text{for } -\infty < n < 0
\end{cases}
\] (1.27)

where \( \omega_{u,n} \) necessarily has the same units as \( \Omega \). The magnitudes of the higher order frequencies diminish quickly, so only those corresponding to values of \( n \) up to \( \pm 2 \) are usually given consideration.\textsuperscript{69} The fundamental frequency components at \( n = 0 \) are predominant and outline the ion’s axial and radial harmonic oscillations that originate from the quadrupolar potential surface. The axial secular frequency \( \omega_{z,0} \) is of particular importance in 3D traps since it is commonly used for the purposes of ion excitation, selection, and manipulation; hereafter it will simply be denoted as \( \omega_z \). Ions approaching the \( \beta_z = 1 \) boundary will reach a maximum \( \omega_z \) of \( \Omega/2 \) before becoming unstable. Under a fixed set of operating conditions, ions of a given \( m/z \) will have secular frequencies unique from other ions. On the stability diagram in Figure 1.3, iso-\( \beta_u \) lines for intermediate values of \( \beta_u \) (between 0 and 1) delineate these conditions of constant frequency.

The accuracy of the calculated secular frequency depends on the accuracy with which \( \beta_u \) is known. Because there is no exact closed-form expression for \( \beta_u \) in terms of \( q_u \) and \( a_u \), the error level can only be lowered through iterative evaluations of the following continued-fraction formula:
\begin{equation}
\beta_u^2 = a_u + \frac{q_u^2}{(\beta_u + 2)^2 - a_u - \frac{q_u^2}{\beta_u + 4)^2 - a_u - \frac{q_u^2}{(\beta_u + 6)^2 - a_u - \cdots}} + \frac{q_u^2}{(\beta_u - 2)^2 - a_u - \frac{q_u^2}{\beta_u - 4)^2 - a_u - \frac{q_u^2}{(\beta_u - 6)^2 - a_u - \cdots}}}
\end{equation}

At sufficiently small values of \( q_u \) and \( a_u \) (below 0.4), where ion motion can be treated as consisting of simple harmonic oscillation in both \( r \) and \( z \), an error of around 1% can be achieved with the Dehmelt approximation: \(^6\)

\begin{equation}
\beta_u^2 = a_u + \frac{1}{2} q_u^2
\end{equation}

More accurate approximations are provided in Appendix A, which are necessary for large \( q_u \) and \( a_u \) values; these were used to generate the stability diagrams presented here.

1.2.4 Modes of Mass Analysis

In the context of stability diagrams, an examination of the variables comprising the stability parameters (eqs 1.25 and 1.26) makes it clear that ion confinement within the trap is subject to experimental control. If the parameters of a stable ion are changed to unstable values, the ion can be ejected from the trap through suitable apertures and steered to a detector by means of external fields. To achieve this manipulation, it would be much less practical to change the dimensions of the trap or the drive frequency than it is to apply different voltages to the ring electrode. As per the earlier derivation, the endcaps are held at ground potential in the modes discussed here, at least in regards to the trapping field. Normally an axial stability boundary is employed so that ions are ejected only along this direction, although with a pure quadrupolar field they have equal probability of exiting.
either endcap. Ions are also usually injected into the trap through the endcaps, or formed internally with an axial EI source that is positioned opposite the detector.

Since the mass and charge of an ion are accounted for in the stability parameters, mass analysis can be effected by deliberate navigation within or across the limits of $\beta_u$. Long before the QIT became mainstream, the main mode of operation was to set the parameters so that a single $m/z$ was stable in the trap. This corresponds to adjusting both $V$ and $U$ so that only one $m/z$ fits in the upper or lower apex of the stability diagram, analogous to the manner by which a quadrupole mass filter transmits specific $m/z$ values. A full mass spectrum is collected by stepping the voltages across the $m/z$ range of interest between intervals of ionization and detection. Accordingly, this mode is called the *mass-selective stability scan*.\textsuperscript{80,81}

Preferable to the previous mode is the utilization of the simpler *mass-selective instability scan* (also known as *boundary ejection*), which was conceived as part of an effort by Finnigan Corp. to commercialize the QIT.\textsuperscript{82} No DC potential is applied, so the method is completely described by the $q_z$ parameter alone (eq 1.25). Ions are first accumulated and stored at a fixed RF amplitude along the $q_z$ axis, after which the voltage is ramped linearly to increase their $q_z$ values and slide them over the $\beta_z = 1$ boundary in order of low to high $m/z$. As each ion exceeds the working point at $q_z = 0.908$ it is quickly ejected out one of the endcaps, and by correlating their sequential arrival time at the detector with the calibrated RF amplitude a mass spectrum is generated. The *high-mass cutoff* (HMCO) is set by the maximum amplitude of the RF ramp. Considering electrical breakdown, the HMCO is about 650 Th for the QIT parameters standardized by Finnigan ($r_0 = 10$ mm and $f_d = 1.1$ MHz).

The capabilities of mass analysis are greatly expanded by the application of an auxiliary RF signal. Since the ion secular frequencies are known, they can be selectively...
brought into resonance with this supplementary potential. The oscillation amplitude of resonant ions is increased through power absorption from the additional field. Axial excitation can be achieved a number of ways, the most common of which is bipolar application of a fixed frequency that is connected 180° out-of-phase to each endcap. This superimposes an approximate dipolar field. If the potentials are in-phase, a quadrupolar field is formed. Monopolar excitation results from unipolar application, where one endcap remains grounded.

If the supplementary RF is applied just below $\Omega/2$, ion ejection is enhanced at the $\beta_z = 1$ boundary during a typical mass-selective instability scan. This is called *axial modulation* and it improves resolution and sensitivity by better defining the point of instability and ejecting ions after fewer cycles of the drive RF. If the voltage and duration of the signal are sufficient, the ion amplitude will grow enough to leave the trap despite being in a stable region of the stability diagram. With *resonance ejection*, just as in boundary ejection, the ions are scanned along the $q_z$ axis by ramping the drive RF voltage; however, they will instead be ejected at the $\beta_z$ point corresponding to the frequency of the supplementary field as they come into resonance with it. Since this occurs at a lower drive RF voltage, the mass range is extended by a factor proportional to the reduction of $q_z$.

Resonant excitation is also implemented to increase the kinetic energy of stored ions to induce fragmentation by using lower voltages that do not lead to ejection.
1.2.5 Pseudopotential Well Model and Space Charge

In order to estimate charge density and the kinetic energy of stored ions, it is useful to know the potential energy drop within the QIT. However, since this potential well minimum is not formed electrostatically, a pseudopotential well model has been developed to approximate the equivalent DC trapping potential over stability parameter values where ion motion is simplifiable. If the ion motion is averaged at low values of $q_u$ where $\omega_{u,0}$ is much lower than $\Omega$, the high frequency micromotion can be disregarded while the macromotion is reduced to simple harmonic oscillation in a parabolic pseudopotential well. These are the same conditions for which eq 1.29 holds true. So, in the axial dimension for the case where $a_z = 0$, one form of the pseudopotential well $\bar{D}_z$ in units of volts is

$$\bar{D}_z = \frac{mz_0^2\Omega^2}{16e} q_z^2 \quad (1.30)$$

In the event that $r_0^2 = 2z_0^2$ and by replacing one $q_z$ with its terms from eq 1.25, the equation can be shortened to

$$\bar{D}_z = \frac{1}{8} V q_z \quad (1.31)$$

and the pseudopotential well in the radial dimension becomes half this value. As ion motion approaches instability at large $q_u$ values and energy is transferred into other modes of oscillation, the pseudopotential well model loses physical meaning.

Spectral resolution is improved by a deep potential well that focuses the ions strongly in the center of the trap, thereby narrowing their spatial distribution, whereas a shallow well can lead to trajectory excursions close to the electrode walls where the effects of imperfections are more pronounced on ion packets. Likewise, ion storage is subject to this confining potential. So far, the presented theory has not accounted for multiple charges.
within the QIT. Realistically, the long range effects of coulombic repulsion among many stored ions results in an effective DC space charge that is added to the total potential. Due to the finite volume of the trap, this limits the number of charges that can be contained. Furthermore, an excess level of space charge begins to affect resolution and cause spectral mass shifts well before the trap is saturated with ions. It has a defocusing effect that enlarges the ion cloud, spreading the ejection events over a longer time and thus broadening peaks. The signal level at which this becomes unacceptable in some way is referred to as the spectral space charge limit. The linear dynamic range is also naturally affected by the restricted ion accumulation.

The pseudopotential well model can be used to estimate the charge density in the trap volume as limited by space charge. An approach based on defining the total space charge limit as a balance of the well potential with the collective electrostatic potential from the stored ions gives the maximum ion density $\rho_{\text{max}}$ as

$$\rho_{\text{max}} = \frac{3}{64\pi} \frac{m\Omega^2}{e^2} q_z^2$$

A standard QIT holds around $10^5$–$10^6$ ions before space charge effects begin to significantly affect mass spectral performance. It is estimated that on a scale of $r_0 = 1 \mu$m, operating the trap with more than a single ion will exceed the spectral space charge limit.

1.3 Higher-Order Fields and Their Effects

It is necessary to address several assumptions held for the preceding theory, which dealt strictly with ideal quadrupolar fields that could only be formed by electrodes that extend infinitely along their common asymptotes and are constructed and aligned perfectly. In practice, ion traps have mechanical imperfections that introduce potentials
that increase more than quadratically with displacement from the center, and these make nonlinear contributions to the total electric field. Such terms, even if seemingly small, can have strong influences on ion storage and mass analysis. These effects on ion behavior can be deleterious or beneficial, depending on the strength and nature of the nonlinearities. Previous characterization studies can be used for guidance in avoiding the unwanted attributes while enhancing performance. For quantitative control and analysis, the potential generated by arbitrary geometries needs to be fully described.

1.3.1 Generalized Potential from Multipole Expansion

A standard way of representing the general potential within a system of electrodes that establish rotationally symmetric boundaries is with a series of continuous functions that can provide any level of accuracy through continued expansion of the terms. Following earlier conventions and using spherical coordinates, the potential at a point that is a distance $\rho$ from the center of the trap at angles of $\theta$ and $\phi$ can be written

$$
\phi(\rho, \theta, \phi) = \phi_0 \sum_{n=0}^{\infty} A_n \left( \frac{\rho}{r_0} \right)^n P_n(\cos \theta)
$$

(1.33)

where $r_0$ is the chosen normalization length and the $P_n$ functions are Legendre polynomials of order $n$ that define the spatial distributions of the multipole components that are weighted by the $A_n$ coefficients. Each term in this superposition satisfies Laplace’s equation. To arrive at the full polynomial form, Rodrigues’ formula can be used

$$
P_n(x) = \frac{1}{2^n n!} \frac{d^n}{dx^n} (x^2 - 1)^n
$$

(1.34)

with $\cos \theta$ substituted for $x$, and transforming into cylindrical coordinates whereby $\cos \theta = \frac{z}{\rho}$ and $\rho^2 = r^2 + z^2$. The solutions for the first several multipoles in the series, as
constituents of the total potential, are

\[
\phi(r, z) = \phi_0 \left( A_0 + A_1 \frac{z}{r_0} - A_2 \frac{r^2 - 2z^2}{2r_0^2} - A_3 \frac{3r^2 z - 2z^3}{2r_0^3} + A_4 \frac{3r^4 - 24r^2 z^2 + 8z^4}{8r_0^4}
\right.
\]

\[
+ A_5 \frac{15r^4 z - 40r^2 z^3 + 8z^5}{8r_0^5} - A_6 \frac{5r^6 - 90r^4 z^2 + 120r^2 z^4 - 16z^6}{16r_0^6}\]

(1.35)

They are identified, in sequential order of \(n\) from 0 to 6, as the monopole, dipole, quadrupole, hexapole, octopole, decapole, and dodecapole fields. Surface plots of some of these terms are shown in Figure 1.4. Each term has \(n\) pairs of poles; for even values of \(n\), opposite poles have the same polarity, while for odd terms the polarity is reversed. The monopole is position independent and is equivalent to the constant \(C\) in eq 1.15, and a trapping field dipole is not present under the operational modes discussed here. For a pure quadrupolar field, all coefficients other than \(A_2\) would be 0; this is not the case for real traps where higher order fields exist due to various nonidealities. Along with possible geometric flaws, they are certainly induced by truncation of the electrodes to practical sizes, the addition of endcap apertures for injecting and ejecting ions, and external field penetration through such openings. Even multipoles are generated by symmetric trap distortions, and vice versa. If a trap is symmetric about the \(z = 0\) plane, and the axial symmetry under consideration is not broken, then odd multipoles do not exist.

### 1.3.2 Multipole Characteristics

The spatial overlap of the higher multipoles with the quadrupole can be either constructive or destructive. Positive even multipoles are defined as those that increase the electric field strength along the \(z\) axis — these have positive \(A_n\) coefficients when following the natural signs of the expansion (as in eq 1.35). This designation does not apply to odd
multipoles due to their inversion across the origin. The lower-order terms are more influential in the center of the trap than those of higher order. Even for sizable weighting coefficients, higher-order terms have a weaker presence close to the origin due to the higher powers in their spatial expressions. Conversely, near the fringes of the trapping volume these terms can easily dominate the field. This is exemplified by a comparison of the potential surfaces of the octopole and the 12th order tetraikosipole in Figure 1.4c,f (although the relative potential scaling belies the difference in magnitudes). In pure form, the higher multipoles have found widespread use as ion guides, where the larger ‘field-free’ zone is advantageous for the simultaneous transmission of a broad mass range of ions, but at the cost of focusing ability.87

The superposition of higher order terms on a pure quadrupole produces an electric field that is no longer linear. Consequently, ion motion in the \( r \) and \( z \) dimensions cannot be treated independently, and this coupling allows energy to be exchanged between different modes. With such anharmonic oscillation, the secular frequencies become amplitude dependent. When the electric field is strengthened by nonlinearities, the oscillation frequency of an ion increases with its amplitude; when the nonlinearity weakens the field, it has the opposite effect. Thus, positive even multipoles shift up the frequency, while negative even multipoles shift it down. With odd multipoles the net effect is much weaker because during each oscillation cycle of the ion the frequency is shifted alternately in both directions.88 This frequency shift explains why the octopole and other even multipoles stabilize ions against resonant losses—they interfere with the continual uptake of energy by shifting the ion off resonance before it is excited enough to leave the trap. Ions are further stabilized by the greater restoring forces of the higher terms that steepen the pseudopotential well at the edges of the trap, prolonging storage times.69
Although the frequency shift helps prevent ion losses, it can be detrimental to mass resolution. For example, ion ejection is delayed when operating under the mass-selective instability scan with a negative even multipole contribution. After crossing the $\beta_z = 1$ boundary and gaining amplitude, a shift to lower frequency momentarily returns the ion to stable conditions, establishing a hunting oscillation that increases the temporal linewidth. However, positive even multipoles will instead accelerate the ion into unstable conditions and can thus be used to compensate for negative fields and greatly improve resolution. Methods of tuning multipoles for enhanced performance are discussed in §1.3.5.

In addition to these effects, higher order terms can create resonant conditions where ion motion can actually absorb energy from the trapping field at specific frequencies despite lying within a stable region of the stability diagram. The circumstances leading to this are discussed next.

### 1.3.3 Nonlinear Resonances

Unlike a pure quadrupole where ion stability depends only on the $q_a$ and $a_q$ Mathieu parameters, nonlinear fields have cross-dimensional products in their expressions that complicate the equations of motion such that there are no known analytical solutions. Nonetheless, with weak superpositions of higher terms on the quadrupole, the original QIT theory can be modified by treating the additional fields as perturbations that are split from the linear portion. Wang et al. have derived a set of rules that are necessary for a resonance to occur, along with predictions for their relative strengths. In these results, a resonance condition arises within the stable region bounded by $\beta_r \geq 0$ and $\beta_z \leq 1$ when the denominator of a certain expression becomes 0, which in simplified form is

$$n_r \beta_r + n_z \beta_z = 2v \quad (1.36)$$
where \( n_r, n_z \) and \( \nu \) are integer values. Using the relation of the \( \beta_u \) terms to the fundamental secular frequencies defined in eq 1.27, \( \omega_u = \beta_u \Omega / 2 \), this condition can be rewritten as

\[
n_r \omega_r + n_z \omega_z = \nu \Omega \quad (1.37)
\]

A physical interpretation of eq 1.37 is that resonances are produced when linear combinations of secular frequency harmonics match a harmonic of the drive frequency.

Various restrictions on \( n_r, n_z \) and \( \nu \) yield different classes of resonances. For \( \nu = 0 \), only coupling resonances are formed where energy is simply exchanged between the \( r \) and \( z \) oscillations. Resonances can pick up energy from the drive RF when \( \nu = 1 \), which includes the one-dimensional axial resonances where \( n_r = 0 \) and the radial resonances where \( n_z = 0 \), as well as sum resonances where \( n_r \) and \( n_z \) have the same sign and both directions are energized simultaneously. Difference resonances, where \( n_r \) and \( n_z \) have opposite signs, result in \( r \) and \( z \) energy exchange, and less is picked up from the field. Based on rotational symmetry, \( n_r \) must be even for all multipoles, while \( n_z \) must be even only for even multipoles. The order \( N \) of a resonance is defined as

\[
N = |n_r| + |n_z| \quad (1.38)
\]

Resonances can only exist for values of \( N, N - 2, N - 4 \), etc. and the maximum number of them is \( 2N \). The strongest resonances for a given multipole are of equivalent order, so that \( N = n \); furthermore, across different multipoles, those of lowest order are predicted to have the most intense resonances.\(^{69,89}\)

The theoretically predicted resonances have been experimentally confirmed through high-resolution probing of a non-commercial QIT stability diagram, revealing a prolific network of resonance lines.\(^{90}\) The convergence of many of these lines at the apexes
can make it difficult to isolate ions in that vicinity. Even so, the vanishing strength of the higher order resonances leaves the low-\(q_u\) region of the stability diagram free of perturbing forces, where ions can be successfully stored even for relatively heavy contributions from higher order fields. For common trap designs, the lower-order multipoles and their resonances are the most important, as determined from theory and their larger weighting coefficients. They can be mapped onto stability diagrams by converting their \(\beta_r\) and \(\beta_z\) coordinates in \(q_u\) and \(q_u\) space (per approximations of eq 1.28). Following the assumption that \(N = n\), the resulting even-order octopole and dodecapole resonances are shown in Figure 1.5 and the odd-order hexapole and decapole resonances are shown in Figure 1.6.

1.3.4 Ion Ejection via Nonlinear Resonances

The effects of nonlinear resonances were first observed during tandem MS experiments where product ions were undesirably eliminated from the trap under special circumstances. This occurred when the ions were formed at certain points in the stability diagram, but only if they were displaced far from the center of the trap, supported by the fact that pre-existing ions with moderate kinetic energy do not exhibit unstable behavior if moved to these same points. Since multipole fields are the sources of nonlinear resonances, they share spatial attributes. This means that nonlinear resonances are essentially nonexistent near the center of a typical trap, and in order for an ion to come into resonance with nonlinear fields, it must first have sufficient amplitude.

Nonlinear resonances can be exploited for better resolution during mass analysis performed in the resonance ejection mode (described at the end of §1.2.4). With normal boundary or resonance ejection, an ion’s amplitude increases linearly prior to ejection; with a nonlinear resonance, though, the rate of amplitude increase is related to powers of \(n - 1\)
(n being the multipole order). Thus, if ions are excited by means of a supplementary dipole onto a nonlinear resonance, the ejection can occur much faster and minimize contributions to peak broadening—this enhanced mode of mass analysis is called double-resonance ejection. Since the dipole has a constant field strength it is able to displace ions from the center of the trap, unlike higher multipoles. However, due to the time dependence associated with scanning the secular frequencies with the drive RF voltage, the supplementary dipole frequency and voltage must be selected so that the ion amplitude is already at the optimum level for interaction with the nonlinear resonance when their frequencies coincide. Hence, the supplementary frequency is tuned just below the expected nonlinear resonance point.

The hexapole and octopole resonances are widely utilized and studied. The hexapole resonance at $\beta_z = 2/3$ is highly active and known to rapidly extract ions in double-resonance ejection mode (thereby improving resolution and allowing fast scan speeds) so it is often deliberately engineered into a trap’s design. Since the octopole is an even term, most of its resonances are self-quenching (by the mechanism described in § 1.3.2). Even as ions absorb energy from the octopole, a concurrent frequency shift moves them off resonance, inhibiting further energy transfer. Interestingly, this does not apply to the octopole sum resonance $\beta_r + \beta_z = 1$, which is also quite intense and leads to sharp double-resonant ejection. The axial and radial motions compensate for one another such that the resonance is maintained despite the shifting frequencies. These two nonlinear resonances have also been used in parallel to achieve consistent unidirectional ejection (doubling the signal reaching the detector) by forming an asymmetrical beat resonance. The Bruker HCT mass spectrometer employs them with careful supplementary dipole phase control to mitigate space charge effects (through prolonged selective excitation prior to ejection).
1.3.5 Control of Higher Order Fields in the QIT

The initial response to the presence of nonlinearities within the QIT was one of avoidance, though this is not entirely possible even with exacting mechanical tolerances. Subsequent characterization and theory have revealed that these additional fields can be beneficial, but this was not apparent beforehand. One of the largest issues presented to the developers of the first commercial QIT at Finnigan was an unacceptable level of compound-dependent mass shift errors. This was ultimately solved by the rather serendipitous discovery that stretching the endcaps to increase $z_0$ by 10.8% (without an accompanying change in electrode geometry)\textsuperscript{95} introduced adequate positive even multipoles (with ca. +1.4% octopole relative to the quadrupole) to counteract the negative ones ($\sim 0.14\%$ octopole) caused by electrode truncation\textsuperscript{69} and holes in the endcaps.\textsuperscript{96} Unit mass resolution was also attained with this change. A later study showed that with large slot apertures in the endcaps (to accommodate a laser beam) a stretch of 23% is required to subdue mass shifts.\textsuperscript{97}

Although stretching $z_0$ reverses the signs of the higher order fields, it is not the best approach because it introduces relatively strong terms of higher order than the octopole, which can have unwanted effects such as impacting the injection of ions from external sources. One alternative is to slightly distort the hyperbolic angle between the electrodes, with no changes to the other dimensions. The induced fields are positive like with stretching, but the relative octopole field can be made stronger while keeping the dodecapole weak.\textsuperscript{69} Moreover, the standard size of a benchtop QIT makes it amenable to precise control of the electrode geometry. Therefore, exact superpositions of weak multipoles are possible by conforming the electrode profiles to the desired potential contours.\textsuperscript{98} For dynamic control of the multipole distributions, variable potentials can be
applied to the electrodes (with possible subdivisions) so that a single trap can optimize the fields to suit different analytical purposes.\textsuperscript{99,100}

\subsection*{1.4 Additional Considerations for Mass Analysis}

The versatility of ion traps permits a wide range of operating conditions that can greatly influence performance and the quality of mass spectra. The roles of several major factors in mass analysis are discussed below. Integrating these aspects with the fundamental principles of ion traps reveals clear implications for HPMS.

\subsubsection*{1.4.1 Scan Rate}

The standard methods of mass analysis with ions traps include ramping the drive RF voltage to scan the ion secular frequencies across the stability diagram to some point of instability. The rate at which this is done has consequences on throughput (time to collect a spectrum), mass resolution, and spectral S/N (signal-to-noise ratio). Mass resolution depends on the coherence of each $m/z$ ion packet—fast scan rates are prone to destabilizing the ions at different times, thus broadening the distribution. Ultimately, resolution is a function of the total number of resonance cycles the ions go through prior to ejection.\textsuperscript{72} By slowing down the scan rate, ions undergo more secular oscillations for a given voltage sweep. Schwartz et al. have demonstrated resolving powers greater than 30,000 by scanning at 27.8 Th/s, which is about 200 times slower than the normal rate for their instrument.\textsuperscript{101} There is a tradeoff with S/N because the signal is spread out in time, which decreases peak height, while noise fluctuations are unaffected.\textsuperscript{70} This limits the technique to high abundance peaks, whereas practical data acquisition times restrict high resolution scanning to narrow mass ranges. The relationship of scan rate to resolution is quantified in § 1.4.3.
1.4.2 Background Pressure

Elevated pressures were originally expected to be exclusively detrimental to QIT performance, as experienced with other mass analyzers. Contrary to this, the introduction of a light buffer gas improves both resolution and sensitivity; this surprising discovery at Finnigan Corp. successfully led to the first commercial ion trap in 1983 as a GC detector.69 The effects of ion-neutral collisions are subject to the relative mass of the species, among other things. If the ion’s mass is much greater than the neutral’s, which is likely the case if helium is used as the buffer gas, then the ion’s average change in kinetic energy per collision will be small. The overall effect is viscous damping of ion oscillations such that they are cooled to the center of the trap, decreasing the size of the ion cloud. Resolution improves because the effective starting conditions and spatial distribution of the ions are narrowed, while sensitivity is better because radial compression improves the efficiency of ejection through the small endcap apertures. Since higher order fields are weakest in the center, their effects are minimized as well. On the other hand, if the neutral is much heavier, the collision events can scatter the ions by suddenly imparting excessive kinetic energy or disrupting the oscillation phase and deflecting their trajectories. This randomization degrades resolution and triggers premature ion losses from the trap.68

For constant operating conditions at typical experimental mass scan rates, greater collisional damping increases the secular frequency line widths, which are directly related to mass resolution. However, it has been demonstrated theoretically that resolution also depends on the number of ion-neutral collisions per oscillation cycle.102–104 In short, resolving power \( \frac{m}{\Delta m} \) is proportional to the drive frequency (since secular frequency scales with \( \Omega \)) and inversely proportional to the background gas pressure \( P \).
Therefore, mass resolution can be reconciled with raised operating pressures by increasing
the drive frequency. This unique trait among ion traps is the premise of HPMS and the
impetus behind research aimed at extending mass spectrometry into the 10^3 mTorr regime.
For most benchtop QIT systems, optimum damping for mass analysis occurs at helium
pressures of 1 mTorr or less. Miniature ion trap systems that do not employ frequency
compensation struggle to perform well by 15 mTorr of air,^6^10 with peak widths (full width
at half maximum, FWHM) above 2.0 Th reported near 50 mTorr (for a rectilinear ion trap
with critical dimensions near 1 cm and operated at 1.08 MHz).^7^

1.4.3 Resolution Dependencies

A more complete expression for resolution than eq 1.39 can be written based on the
model developed by Goeringer et al.^102^ and extended by Arnold et al.^103^ for resonance
ejection, which incorporates ion-neutral collisions, secular frequency, and scan rate, among
other parameters. Since it is built on the assumption of simple damped harmonic motion
under the pseudopotential well model, it cannot be readily applied for operation at high q_z
values. It also does not consider higher-order fields or their nonlinear resonances, which
can strongly affect resonance excitation. Despite these limitations, the model is useful for
predicting and explaining general trends.

From an examination of ion cloud dynamics at the moment of ejection, the temporal
linewidth \( \Delta t \) for a given \( m/z \) ion packet can be approximated as

\[
\Delta t = \frac{\Delta A}{dA/dt}
\]  
(1.40)
where $\Delta A$ is the axial amplitude dispersion and $dA/dt$ is the rate of increase in ion oscillation amplitude. The amplitude dispersion term as given by Arnold et al. for ions at equilibrium with the background gas is

$$\Delta A = \frac{1}{\omega_z} \left( \frac{kT}{m} + \frac{C^* M}{3 m} \frac{4m + M}{2m + M} v_d^2 \right)^{1/2}$$

(1.41)

where $\omega_z$ is the fundamental axial secular frequency at ejection, $k$ is Boltzmann’s constant, $T$ is temperature, $C^*$ is a constant close to unity, $m$ is the mass of the ion, $M$ is the mass of the neutral background gas, and $v_d$ is the axial drift speed. In the final oscillation cycle before leaving the trap, the ions will have traversed an amplitude of $z_0$ in a quarter-period of $\omega_z$ such that the average drift speed is $2z_0 \omega_z / \pi$. In the condition that $m \gg M$, the amplitude dispersion can be condensed to

$$\Delta A = \left( \frac{kT}{m\omega_z^2} + \frac{M}{m} \frac{8z_0^2}{3\pi^2} \right)^{1/2}$$

(1.42)

Additionally, the two limiting cases given for $dA/dt$ by Arnold et al. can be combined, with a conversion to $z_0$ to undo the assumption that $r_0^2 = 2z_0^2$ and substitution for the amplitude decay relaxation time $\tau$ with $2/c$, the reduced ion-neutral collision frequency:

$$\frac{dA}{dt} = z_0 a_\omega \left( \pi a_\omega + c^2 \right)^{-1/2}$$

(1.43)

where $a_\omega$ is the secular frequency scan rate. The value of $c$, which is proportional to pressure, can be estimated from the collision frequency $\nu$ as

$$c = \nu \left( \frac{M}{m + M} \right)$$

(1.44)
Substitution of eqs 1.42 and 1.43 into eq 1.40 will return $\Delta t$, and this can be related to mass resolution from the fact that $\Delta \omega_z = a_\omega \Delta t$ and $m/\Delta m = \omega_z / \Delta \omega_z$ for $q_z < 0.4$ as shown by Goeringer et al. Under the Dehmelt approximation it is convenient to further relate the frequency scan rate to the mass scan rate $a_m$ (with units of Th/s) by $a_\omega = a_m \omega_z / (m/z)$ so that the final resolving power is

$$\frac{m}{\Delta m} \approx \frac{\omega_z}{\left[ \frac{\pi a_m \omega_z}{m/z} + c^2 \left( \frac{kT}{mz_0^2 \omega_z^2} + \frac{8M}{3\pi^2 m} \right) \right]^{1/2}}$$  \hspace{1cm} (1.45)

This equation predicts that resolving power generally scales with $1/c$, which is consistent with eq 1.39. There is also a $1/a_m^{1/2}$ dependence that lessens with greater damping—higher pressures extend the range over which resolving power is independent of scan rate. With sufficient damping, the secular frequency relationship is linearized (for typical operating conditions), which brings eq 1.39 into full accordance with this model.

1.5 Ion Trap Challenges for HPMS

There are many engineering difficulties in applying the theory behind HPMS to a real-world mass analyzer that can satisfy the need for a portable device. Under the constraints of practicality there is a necessary departure from the ideal and predictable nature of theory in order to maximize the possible benefits. When the prospects of high-pressure operation with ion traps are evaluated, limitations on the structure of the QIT are found.

1.5.1 Analyzer Geometry Simplification

Beginning with the provision that resolving power can be maintained with elevated background pressure by increasing the drive frequency (eq 1.39), we can follow the
intertwined parameters to determine the consequences that emerge for electrode shape. From the $q_z$ parameter (eq 1.25), it is evident that for the mass range to remain constant with a rise in frequency, the drive RF voltage can be increased quadratically. However, to avoid higher power consumption and electrical breakdown issues, the size of the trap can be decreased proportionally instead. Based on anticipated operating conditions and desired performance, the reduced dimensions and complex features of the trap inevitably extend beyond the capabilities of available fabrication technology. The QIT has been made as small as $r_0 = 2.5 \, \text{mm}$ for the purposes of mass range extension, but even with this modest four-fold reduction the trap exhibited poor resolution and spectral artifacts due to field faults. While significant effort and resources can be expended to construct QITs with ideal hyperbolic geometries on the submillimeter scale, this is in conflict with the objectives of an affordable device.

Fortunately, it has long been known that simpler ion trap geometries largely retain the characteristics of a QIT and are thus viable for mass spectrometry. The most basic of these and the easiest to produce with existing microfabrication tools is the cylindrical ion trap (CIT), which has a right circular cylinder for the ring electrode and planar electrodes for the endcaps, as illustrated in Figure 1.7a. Even though the flat electrode profiles are significant deviations from the hyperbolic shapes that are needed for a pure quadrupolar field, the prevailing potential is still of the quadrupolar form. A qualitative comparison of the potential contours in the central region of the CIT (shown in Figure 1.7b) with those of the QIT (Figure 1.1b) corroborates this fact. The CIT is essentially a QIT with strong contributions from higher order fields, the distinction being that with a CIT the nonlinearities are intractable, whereas in a QIT the nonlinearities are relatively weak and can be independently tuned via arbitrary changes to the geometry. Ions trapped in a CIT
are subject to the same solutions of the Mathieu equation, especially within the vicinity of
the trap center where higher order multipoles are usually negligible. That is not to say the
stability parameters can be calculated with the same degree of accuracy, but with proper
calibration the standard modes of mass analysis can be successfully implemented. Although
the magnitude of higher multipole terms can be quite large with CITs, they are typically
designed to keep the perturbations at moderate levels, such that the extended theory of
nonlinear resonances is directly applicable.

1.5.2 Prior Work with Cylindrical Ion Traps

The CIT has been around for almost as long as the QIT, first proposed by Langmuir
et al. in 1962 as an ion containment device\textsuperscript{106} and later explored for MS and demonstrated
in the mass-selective stability mode in 1977 and 1980.\textsuperscript{107,108} Its use for mass analysis in the
superior boundary ejection mode nearly two decades later by Wells et al. garnered much
broader interest and also showed the important role geometry plays in performance.\textsuperscript{109}
Here, the geometry of an $r_0 = 10$ mm CIT was altered through $z_0$ stretching with the aim of
decreasing higher-order field content and reducing mass shifts. Badman et al. performed
coarse geometry optimization on a reduced scale of $r_0 = 2.5$ mm, further establishing the
compensatory nature of the octopole and dodecapole terms, neither of which can be
eliminated in a CIT without grossly affecting the other.\textsuperscript{56} An even smaller trap of
$r_0 = 0.5$ mm was demonstrated shortly thereafter by Kornienko et al. in the boundary
ejection mode, with similar trap proportions to Wells et al. but lower spectral resolution.\textsuperscript{57}
In general, performance is independent of trap size and geometry, except that relative
dimensional error is worse for smaller sizes and can thus lead to inexact fields. In this case,
though, the fault was attributed to spectral jitter caused by electrical noise, underscoring
the fact that performance can be negatively affected by a number of secondary experimental factors.

Moxom et al. showed that double-resonance ejection can dramatically enhance resolution in CITs, and that the strength of nonlinear resonances can vary significantly with moderate adjustments in electrode spacing.\textsuperscript{110} With mounting evidence that there were yet unrealized geometries that could yield favorable performance, optimization studies were undertaken to identify them. Although CITs generate a plethora of higher order field arrangements, analysis is typically simplified to the dominant octopole and dodecapole terms. In the practical range of parameters, the octopole can be made either positive or negative, while the dodecapole always remains negative. Wu et al. found empirically that the best resolution is achieved when the sum of these terms relative to the quadrupole is close to $-10\%$, based on a scheme to maximize the axial electric field linearity.\textsuperscript{111} Since this rule was developed for performance under boundary ejection, it does not account for double-resonance ejection behavior.

The CIT represents fixed sets of multipole distributions that depend on its geometric proportions. Although it is possible to make judgements about the desirability of certain terms according to their known character, they cannot be tuned separately. Therefore, the otherwise-attractive method of numerical optimization through objective functions has limited utility, in that solutions tend to lie outside of reasonable parameter space. This was verified by Tallapragada et al., who advocated for additional geometric degrees of freedom in the form of raised steps on the ring or endcaps in order to expand the range of possible field combinations.\textsuperscript{112} However, even simple features like these are not trivial to fabricate and are tough to justify without first determining that satisfactory options are unavailable with the basic CIT. A similar concept is to employ two additional
compensation electrodes in the cylindrical sandwich to adjust the potential, with which both the octopole and dodecapole terms can be reduced to zero.\textsuperscript{77} Alternatively, the ring could be split into numerous smaller electrodes to have greater control of the field composition.\textsuperscript{113} For some applications this added complexity is worthwhile, such as eliminating anharmonicities in spectroscopy work, but it has not yet outweighed the more practical trap designs for miniature mass spectrometry.

Microfabricated CITs push the envelope of scale considerably. Mass spectra have been collected with a 256 element array of $r_0 = 20 \mu m$ traps driven at 100 MHz, albeit with poor resolution and low signal intensity.\textsuperscript{51} Massive arrays of $r_0 = 5 \mu m$ traps have also been tested, but without achieving mass analysis.\textsuperscript{114} Traps on this scale face additional operational challenges, such as higher loading capacitance on the drive RF amplifier and susceptibility to charging of exposed dielectric material. Although they are representative of the ultimate goals of HPMS, it is more feasible to converge on these sizes incrementally as the body of knowledge grows.

1.5.3 Project Objectives and Approach

Most of the earlier progress in CIT development was not directed towards high-pressure operation, which left several performance aspects open to inquiry, particularly in regards to geometry. The intricacies of the CIT preclude generalization of the published optimization data to unexplored geometric parameters. Furthermore, without a complete understanding of the complex ion dynamics under harsh damping conditions, results obtained at low pressure cannot be readily extended to the high-pressure regime. The primary goal of the research in this dissertation pertains to CIT geometry optimization with respect to these gaps in empirical data.
Even with some reliance on a priori assumptions about the interactions of the different nonlinear fields and their overall influence on performance, an expansive set of parameters remained to be investigated. The objective was to identify performance trends across these parameters and determine the boundaries of workable geometries. A systematic method of mapping the parameter space was undertaken after narrowing the scope of optimization. This included focusing the study on the thickness of the ring electrode and the spacing between it and the endcaps. Additionally, a step size of 10% (relative to $r_0$) was selected under the presumption that local extrema would not be overlooked if performance proved to be a sufficiently smooth function of geometry. The principal figure of merit for evaluating the geometries was spectral resolution over a pressure range of 20 to ca. 1000 mTorr of helium.

Ordinarily, simulations would be the preferable option for such a study due to the greater insight offered into ion behavior at all points of the mass analysis process. However, at the time this project was undertaken the collision modeling in available software was intended for low-pressure investigations, such that the increased collision rate of higher pressures proved too computationally intensive. Hence, an experimental approach was necessitated. The results of this and other pertinent work are presented and discussed in the following chapters.
Figure 1.1 Structure and potential contours of the QIT following the $r_0^2 = 2z_0^2$ relationship with electrodes truncated at 2.5$r_0$ along asymptotes. (a) Bisected hyperboloid electrodes, illustrating the critical dimensions $r_0$ (inscribed radius) and $z_0$ (center-to-endcap axial distance). (b) Nominally ideal quadrupolar equipotential lines computed with voltage applied to ring electrode [B] and with endcaps [A] and [C] grounded.
Figure 1.2 Extended Mathieu stability diagram for the QIT in terms of $a_u$ and $q_u$ parameters. The boundaries demarcate stable and unstable ion motion in the $r$ or $z$ dimensions, with trapping in 3D space possible in the labeled overlapping regions. It is customary to use $q_z$ and $a_z$ for the coordinates, such that $q_r$ and $a_r$ coordinates are scaled by a factor of $-2$. *This figure is adapted from Quadrupole Ion Trap Mass Spectrometry, 2nd ed. by March and Todd.*
Figure 1.3  Enhanced view of the stability region that is most practical for mass analysis, labeled A in Figure 1.2. The plot is further subdivided by iso-$\beta_{u}$ lines that represent constant secular frequency along their length. In the RF-only modes of mass analysis ions lie on the $q_{z}$ axis ($a_{z} = 0$) and can be axially ejected in order of low to high mass at the $\beta_{z} = 1$ boundary by ramping their $q_{z}$ values through the 0.908 point.
Figure 1.4  Potential surfaces and projected contour lines of a few pure multipole terms of order $n$ computed from the general potential in eq 1.33. Shown are (a) the quadrupole, $n = 2$; (b) the hexapole, $n = 3$; (c) the octopole, $n = 4$; (d) the decapole, $n = 5$; (e) the dodecapole, $n = 6$; and (f) the tetraikosipole, $n = 12$. The vertical potential axis (not shown) is scaled for best qualitative fit in each plot.
Figure 1.5 Predicted even-order nonlinear resonances for $\nu = 1$. The octopole resonances are [A] $\beta_r + \beta_z = 1$, [B] $2\beta_r = 1$, and [C] $2\beta_z = 1$. The dodecapole resonances are [D] $3\beta_z = 1$, [E] $3\beta_r = 1$, [F] $2\beta_r + \beta_z = 1$, and [G] $\beta_r + 2\beta_z = 1$. 
Figure 1.6  Predicted odd-order nonlinear resonances for $v = 1$. The hexapole resonances are [A] $3\beta_z = 2$ and [B] $2\beta_r + \beta_z = 2$. The decapole resonances are [C] $5\beta_z = 2$, [D] $4\beta_r + \beta_z = 2$, and [E] $2\beta_r + 3\beta_z = 2$. 
Figure 1.7  Structure and potential contours of the CIT. (a) Bisected trap showing the cylindrical cavity of the ring electrode [B] with radius \( r_0 \) and the planar endcap electrodes [A] and [C] separated by the distance \( 2z_0 \) about the center. (b) Compared to the QIT (Figure 1.1b), the equipotential lines of the CIT have a similar quadrupolar shape in the trap center but are distorted by higher order fields at larger displacements.
CHAPTER 2
INSTRUMENTATION AND METHODOLOGY

This chapter describes the mass spectrometer system used for the high-pressure CIT geometry optimization study and associated experiments that are discussed subsequently. Most of the methods and hardware are based on previous development work within this and external research groups and these are referenced accordingly for more detailed information. A modular benchtop HPMS device was designed to facilitate frequent trap reassembly and quick pump-down time. Due to the focus of this project on one particular aspect of CIT performance, special considerations were made to minimize randomness from other experimental factors.

2.1 Instrument Electronics

The mass spectrometer electrical system consists of a mixture of commercial and custom-built equipment that provide the necessary flexibility for a wide range of operating conditions. Their function and purpose are explained in this section in the context of the high-pressure study, while the other physical instrument components are covered in § 2.2.

2.1.1 System Overview

Mass analysis with an ion trap generally entails the introduction and trapping of ions followed by their mass-dependent ejection and external detection (see § 1.2.4). Although much variation exists, a conventional process was desirable in this case to make the results more comparable to typical experiments, insofar as the HPMS strategy allows.
As illustrated in Figure 2.1, a glow-discharge (GD) ionization source, the CIT, and an electron multiplier (EM) for detection were integrated in a vacuum chamber with appropriate electrical feedthroughs and coordinated for data collection with a single computer running a custom LabVIEW program (National Instruments, Austin, TX). This commercial software and driver package communicates with a National Instruments data acquisition (DAQ) platform configured with an output board (PXI-6733) and input board (PXIe-6356) that have multiple analog and digital channels. The foundation of the LabVIEW control program is described in another dissertation, with additional capabilities added later such as automation and calibration of the mass scan rate. A sampling rate of 1 MS/s was used for all analog signals. Most of the electronics were controlled through digital pulses for their on/off state, while the drive RF amplitude was set proportionally through an analog modulation waveform.

A typical timing diagram is shown in Figure 2.2 with the relative trigger points for different functions during a single mass analysis scan. It begins with an ion generation period on the order of 1 to 10 ms with the drive RF amplitude set to an appropriate level to accumulate ions. The specifics of the ion sources are addressed in § 2.2.2. This is followed by a ‘cool down’ period (ca. 3 ms) at which point ionization stops and the electron multiplier (DeTech 2300, Palmer, MA) is activated. At low pressures this idle time serves to collisionally cool the ions to the center of the trap to reduce their spatial distributions and improve performance, and while at high pressure this step is unnecessary for ion cooling, it is retained to allow the detector voltage to stabilize. Pulsing the EM is necessary to prevent overloading during the ionization stage, which is a simpler alternative to leaving it on continuously and deflecting ions instead. The EM was operated in positive-ion detection mode with the cathode set to ca. −1500 V DC and the anode terminated at ground, using
the built-in collector pin to measure the signal, which is fed to a current amplifier (SR570, Stanford Research Systems, Sunnyvale, CA) operated at a gain of 200 nA/V before digitization and recording as a function of time by an input DAQ channel. The next stage is mass analysis, where the drive RF amplitude on the ring electrode is linearly ramped over a timescale of about 5 ms to sequentially destabilize the ions and eject them to the EM. The supplementary RF on the endcap electrodes can also be applied simultaneously to utilize the resonance or double-resonance ejection modes. The RF system is covered separately in § 2.1.3. Prior to the next mass analysis scan the EM is deactivated and the drive RF is lowered to clear out any remaining trapped ions (3 ms).

The EM and the GD ion source both required the application of a discontinuous DC high voltage. For the EM a TTL pulsed circuit was previously developed within our group based on off-the-shelf negative high voltage modules and an optocoupler, having a range of −200 to −2000 V with sufficiently fast rise times.22 For the GD rear electrode a 1 kV floatable power supply was purchased (230-01F, Spellman, Hauppauge, NY), which was pulsed using another home-built MOSFET switching circuit driven with TTL logic.15

2.1.2 Data Processing

The mass spectra were usually low-pass filtered in post-processing at a cutoff frequency of 150 kHz and mass calibrated from the time domain to units of \(m/z\) using known ion peak positions. For a measure of peak width uncertainty in evaluating resolution for the high-pressure geometry optimization study, a Gaussian fit was performed on the 108 Th peak of anisole (molecular ion), and the error that is reported in later chapters is the confidence interval at the 95% level for this fit at FWHM. Due to common peak tailing or fronting features, it was often more accurate to perform the fit
using an exponentially-modified Gaussian function, but the error was still reported for a pure Gaussian fit. In this sense, the error is an indication of the degree to which the peak profile is not Gaussian.

The peak width uncertainty for all reported measurements was greatly reduced through high spectral averaging counts, whereby a large sample size of $n$ spectra reduces the standard deviation (and improves S/N by a factor of about $n^{1/2}$). This is qualitatively illustrated for a typical CIT in Figure 2.3, where each panel contains ten mass spectra collected sequentially that were each averaged the labeled number of times. Since the CIT signal levels are fairly low, averaging the spectra with only $n = 10$ leads to significant variation in peak shape, but with $n > 1000$ the spectra are quite reproducible. A statistical analysis of each set of 10 spectra is made in Figure 2.4, which gives the mean peak width and standard deviation. For the high-pressure study the minimum averaging count was 1000 to keep the relative standard deviation below ca. 5%; greater averaging was necessary at high pressure to maintain repeatability, with $n$ often exceeding 5000 for final measurements. Longer averaging times are more susceptible to artificial peak broadening from drive RF amplitude drift, but it was measured to be negligible over short periods (<5 minute scale).

### 2.1.3 RF Configuration

The CIT was operated at a drive frequency of 9 MHz for the high-pressure geometry study, which necessitated ramping the amplitude to less than 500 $V_{\text{pp}}$ for the mass range of interest (depending on the $z_0$ dimension). A diagram of the RF system for symmetric trapping field operation is provided in Figure 2.5a. The initial sinusoidal waveform was delivered by a precise analog signal generator (SMB100A, Rohde and Schwarz, Columbia,
MD) at low power (<10 μW). This was fed to a preamplifier with a ca. 40 dB gain (ENI 603L) before final amplification with a home-built power amplifier capable of 300 W output (AR305 kit purchased from Communications Concepts, Beavercreek, OH). The AR305 was powered with a 48 V DC supply (1685B, B&K Precision, Yorba Linda, CA). A standard series LC (inductive-capacitive) resonance circuit was then employed to transform the RF to high voltage, accomplished by matching the capacitive trap reactance with a variable air-core inductor preceding it in the circuit. The resonant frequency is tuned according to the relationship $1/(2\pi(LC)^{1/2})$ with the help of a small air variable capacitor (<15 pF) positioned in parallel with the CIT ring electrode. The drive RF voltage was measured just before the trap with a 100X oscilloscope probe (P5100A probe with DPO3034 oscilloscope, Tektronix, Beaverton, OR).

For resonance ejection modes of mass analysis a supplementary RF was supplied to the endcap electrodes in bipolar mode with an arbitrary 2-channel function generator (AFG3022B, Tektronix), with which the phase was easily adjusted for a 180° difference between the endcaps. The endcaps were pulled to ground with 50 Ω resistors to impedance-match them the function generator, and purely reactive low-pass filters were installed to shunt the drive RF to ground. A maximum of 10 V$_{pp}$ could be applied this way to each endcap. For the high-pressure geometry study the supplementary RF was applied continuously during all stages of the mass analysis scan function and the amplitude was fixed (not scaled with the drive RF).

For asymmetrical trapping fields, whereby a hexapolar field was induced for ejection at the $\beta_z = 2/3$ nonlinear resonance, passive field cancellation was employed via a capacitive voltage divider on the detector-side endcap, as shown in Figure 2.5b (differences highlighted in red). A large resistor was used in parallel with the voltage divider to avoid
ionic charging of the endcap while minimizing phase shifting. The supplementary RF could still be applied in unipolar mode to the ionization-side endcap, but a second purely reactive low-pass filter was installed before the 50 Ω resistor to maintain the trapping field phase. The drive RF voltage was measured on both endcaps with P5100A oscilloscope probes to calculate the resultant changes to the multipole distribution.

Instability of the drive RF amplitude was initially a concern for this project, with the previous generation of RF hardware exhibiting large and sudden voltage drifts, electromechanical and line noise, and interference from (and with) other equipment. This had a severe impact on the mass spectral resolution. These issues were primarily resolved through better thermal regulation of the amplifier, adequate system grounding, heavy shielding of all RF circuits, threaded connectors, and the application of bypass filters on the DC switching power supply to minimize noise and RF feedback. Additionally, a custom-built rigid tuning inductor with a soldered center tap was utilized in place of a previous commercial roller inductor that had high contact resistance and was subject to shifting with slight vibration. The final RF system could produce at least 600 V_{o-p} with low harmonics and no stability problems (long-term drift was not addressed). The amplitude stability at 9 MHz and 400 V_{o-p} was measured via amplitude demodulation on a spectrum analyzer (FSVR7, Rohde and Schwarz) to be better than ±0.1% over timescales of single mass analysis scans.

RF instability is not expected to have had a significant influence on resolution in the high-pressure geometry optimization study. This was determined through the superimposition of 1 MHz white noise (uniform distribution randomized over 125 ramp waveforms) at various levels and recording the effects on mass spectra. Figure 2.6 shows this qualitatively, starting with no added noise (only intrinsic noise present) that
demonstrates good resolution, and ending with ±3.0% amplitude fluctuation that drastically impairs both resolution and S/N. Noise levels of ±0.2% can be seen to have a small but noticeable effect, such that even slight RF instability is not tolerated well. Although the intrinsic RF noise may still be responsible for slight degradation of resolution, the fact that it is present at a constant level allows the performance among different trap geometries to be compared on a relative basis.

2.2 Instrument Design

While the focus of this project was the CIT mass analyzer, high background pressures have consequences on all of the instrument components. For ionization, the traditional hot-cathode EI source can be replaced with a glow-discharge cell that is highly compatible with the pressure range of interest. However, there is currently no substitute for the electron multiplier that offers similar high gain and bandwidth. In order to retain the benefits of the EM, a differential vacuum chamber was implemented whereby the detector can reside in a low-pressure environment while the trap is operated at high pressure. Since portability is not a concern for laboratory research, larger pumps can be used for greater experimental capabilities.

2.2.1 Vacuum Chamber

A general schematic of the vacuum system is given in Figure 2.7 and a 3D drawing of the differential vacuum chamber is shown in Figure 2.8. The chamber is designed around a fixed pumping manifold with removable modules for the glow discharge source, the ion trap, and the detector. The manifold was mounted by way of a 1-1/3 in. ConFlat (CF) gate valve onto a previously existing vacuum chamber (that was used for the low-pressure experiments) consisting of a 6 in. CF cube that was evacuated by a turbo pump (TMP361,
Oerlikon Leybold, Cologne, Germany) backed by a dry scroll pump (nXDS10i, Edwards Vacuum, Crawley, England). With the addition of a separate roughing line to the scroll pump, the chamber could be vented and pumped down without stopping the turbo pump. The detector module was mounted at an angle to maximize gas conductance through the manifold and was maintained below ca. 1 mTorr during experiments (monitored with an MKS Instruments 925 MicroPirani transducer). Gas flow from the trap module was limited by the detector-side endcap of the CIT, which featured a smaller aperture (0.4 mm diameter) than the ionization-side endcap. Vacuum sealing between the modules was accomplished with Viton O-rings held in place by retaining rings.

The trap and glow discharge modules comprise the high-pressure side of the chamber. Helium gas (UHP grade, Airgas National Welders) was introduced directly into the glow discharge cell with a mass flow controller (FMA5402, Omega Engineering) at a rate of ca. 1 standard cm\(^3\)/min, with the pressure in the cell maintained near 1 Torr (estimated). A single orifice on the front GD electrode (0.34 mm diameter, roughly aligned with the ring electrode) passed the helium to the trap module. The gas in the trap module was pumped out through the CIT and a separate port leading to the turbo pump through a series of conductance-limiting valves. This enabled the pressure (as measured on a capacitance monometer, 727A, MKS Instruments) to be varied from ca. 15 to 800 mTorr with no change in the helium flow rate. The open architecture of the CIT assembly (see § 2.2.3) assured high gas conductance throughout the trap to prevent a large pressure drop in the ring electrode cavity due to pumping through the detector-side endcap outlet. Therefore, the pressure measurements made at the trap module are expected to accurately reflect the pressure in the trap itself. The ultimate vacuum of the trap module was typically less than 5 \(\mu\)Torr after 12 hours. Organic analyte (degassed via a single freeze-pump-thaw
cycle) was introduced to the trap through a heated precision leak valve (ULV-150, MDC Vacuum) and measured with an ionization gauge to ca. 8 μTorr above background with maximum pumping conductance (uncorrected, using an MKS MIG sensor). Due to the use of conductance regulation to vary the helium pressure, the analyte pressure was also affected; the leak rate and the ionization time were adjusted during experiments to maintain a constant MS signal level at all background pressures.

2.2.2 Ionization Sources

The majority of the results presented in this dissertation were obtained with the differential chamber, but some earlier work was performed on a similar instrument that was composed of a single isobaric pressure chamber with a maximum He pressure of 50 mTorr (the 6 in. CF cube on which the differential chamber was later mounted). This applies to all results showing xenon as the analyte (99.999%, Nova Gas Technologies), particularly the trap charge capacity measurements. The only other noteworthy difference between the systems was the use of a hot-cathode EI source (ES-525, Kimball Physics) biased at −70 V DC with a gate electrode to block the electron beam during mass analysis and detection.

The glow-discharge cell was originally intended to also serve as an EI source similar to published specifications for an air GD source with a 1 cm electrode gap.⁴⁴ Since helium was used in this study, the electrode separation was increased to 3 cm to operate closer to the Paschen curve minimum near 4 Torr cm.⁴⁶ However, the most stable operation was obtained with a different ionization mechanism, whereby the rear electrode was pulsed to a negative voltage relative to the front electrode (ca. −500 V DC) and both electrodes were offset to ca. −150 V DC relative to ground. With no analyte present, many fragments were
observed that correspond to published mass spectra of Teflon, which is the material used for the GD cell insulation. However, upon gradual analyte introduction the Teflon fragments vanished incrementally while analyte peaks appeared. This is a soft ionization technique, apparently based on charge exchange. Since analyte fragmentation was low, a mixture of two analytes with similar vapor pressures was used for mass calibration purposes (anisole and 4-fluoroanisole, 99%, Sigma-Aldrich). Charge exchange also occurred between the two analytes at high pressure, such that the anisole signal increased at the expense of the 4-fluoroanisole signal, leading to persistent boundary ejection of anisole from ions formed during the mass analysis ramp after resonance ejection.

### 2.2.3 CIT Components

The trap electrodes and their assembly are shown in Figure 2.9; their critical dimensions are given with the experimental results. The detector-side endcap was isolated from the chamber ground potential using a Teflon insulator so that supplementary RF could be applied to both endcaps. The endcaps were fabricated commercially from beryllium-copper sheets (ca. 0.250 mm thick) through an isotropic electrochemical etching process (Towne Technologies, Somerville, NJ). A copper mesh (2.5 mm diameter TEM grid, 200 wires per inch, SPI Supplies, West Chester, PA) was affixed to the endcaps used in the high-pressure geometry study by soldering on a hotplate with minute quantities of fine solder paste such that the mesh was wicked flat to the supporting electrode surface. To prevent oxidation and charging issues, the entire mesh endcap was then lightly gold plated in an electrochemical bath (commercially available solutions from Gold Plating Services, Kaysville, UT). A photograph of an ionization-side mesh endcap is shown in Figure 2.10. The electrode spacing was controlled using lapped 99.6% alumina washers (±0.002 mm
tolerance, Valley Design, Santa-Cruz, CA). The spacing could be adjusted in 0.025 mm increments from 0.075 mm and wider using combinations of 0.075, 0.100, 0.125 and 0.150 mm thick washers.

The ring electrodes with \( r_0 = 0.500 \) mm were CNC milled from 304 stainless steel, deburred, and lapped flat to the necessary thicknesses with a Logitech PM5 lapping system. The thickness tolerance was maintained to within ±1% of the reported values (as measured with a Starrett 3732XFL-1 micrometer). Precise cylindrical cavities were attained using miniature carbide reamers (Magafor part #88860001000) after an initial pilot hole was drilled with a smaller bit. The final diameter and tolerance was measured to be 1.000 ± 0.005 mm or better for the traps used in this study (optical measurements performed with a Keyence VHX-2000 digital microscope). A typical electrode is shown in Figure 2.11. The surface finish was also sufficiently smooth to discount any major influences to the electrode field from asymmetries; a typical ESEM side-profile image is shown in Figure 2.12 (FEI Quanta 200 environmental scanning electron microscope).
Figure 2.1  Basic schematic diagram of electrical system components and wiring to perform mass analysis with the CIT. The glow discharge electrodes were accessible outside the vacuum chamber, while feedthroughs were used to make all other connections shown crossing the dashed line.
Figure 2.2  A typical timing diagram to perform a single mass analysis scan with the various MS components, with the different stages labeled. The drive RF amplitude is modulated in direct proportion to the shown waveform, while the other signals simply indicate the on/off state.
Figure 2.3 Qualitative effects of averaging on mass spectra, showing improved repeatability with larger sample sizes. Ten spectral traces are shown in each panel, and each trace is the result of averaging together the indicated number of mass spectra. The \( m/z \) 108 peak is the molecular ion of anisole.

Experimental conditions: 20 mTorr helium background pressure, \( r_0 = 0.500 \) mm CIT with 0.600 mm thick ring and 0.200 mm electrode spacing, 9 MHz drive RF, operated in double-resonance ejection mode utilizing the octopolar nonlinear resonance near \( \beta_z = 0.70 \).
Figure 2.4  Statistical analysis of each set of ten spectra from Figure 2.3, showing the mean with error bars representing the standard deviation (red) and the relative standard deviation (blue). The abscissa shows the number of times $n$ that each individual spectrum from a set was averaged (on a logarithmic scale).
Figure 2.5  Diagrams of the electrical systems used for generating and applying the drive RF to the ring electrode and the supplementary RF to the endcaps. (a) Shows the typical setup for most experiments with a symmetrical trapping field and (b) shows the modifications to induce odd multipoles through an asymmetrical trapping field by means of field cancellation via a capacitive voltage divider [C] on the detector-side endcap [EC2]. A large parallel resistor [R] is added to avoid charging of the endcap. Low-pass filters [LPF] are included to protect the function generator and minimize phase shifting in (b).
**Figure 2.6** Qualitative effects of drive RF amplitude instability on mass spectral performance. Uniform white noise was superimposed on the RF ramp at a write rate of 1 MHz and randomized over 125 sequential modulation waveforms. Each panel shows the modulation signal for a single ramp, with which there are approximately 50 noise fluctuations per peak.

Experimental conditions: anisole (molecular ion at $m/z$ 108) in 20 mTorr helium background pressure, $r_0 = 0.500$ mm CIT with 0.650 mm thick ring and 0.250 mm electrode spacing, 9 MHz drive RF, operated in double-resonance ejection mode utilizing the octopolar nonlinear resonance near $\beta_z = 0.70$. 

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Figure 2.7  Schematic of the vacuum and pressure-control system used for the high-pressure experiments. The helium pressure in the trap module could be varied from ca. 15 to over 1000 mTorr, while the detector was maintained at pressures below ca. 1 mTorr (depending on flow from trap module).
**Figure 2.8** Drawing of the differential pressure vacuum chamber used for the high-pressure geometry optimization study. Several pumping and pressure gauge ports are obscured due to the viewing angle and cross-sectioning.
Figure 2.9  Configuration of the cylindrical ion trap electrodes and their assembly within the vacuum chamber module. Electrical connections were made via wire soldered to the electrodes and mechanically fastened to the SMA feedthroughs with set screws.
Figure 2.10 Photograph of a gold-plated ionization-side endcap electrode with a 200 WPI TEM grid soldered over the central 2.5 mm diameter aperture. The visible electrode side faces the ring electrode in the trap assembly.
Figure 2.11  Typical ring electrode diameter and concentricity measurements, showing the front (a) and back (b) of a 0.650 mm thick electrode ($\bar{r}_0 = 0.500$ mm) relative to the milling operation. The front is always slightly larger due to initial run-out of the reamer entering the pilot hole. The measurement tolerance itself is on the order of ±0.005 mm.
Figure 2.12  ESEM image of typical ring electrode surface finish within the cylindrical cavity from the reaming and lapping fabrication process ($r_0 = 0.500$ mm, 0.600 mm thick).
CHAPTER 3

EXPERIMENTAL RESULTS OF CIT GEOMETRY OPTIMIZATION

This chapter examines various aspects of CIT geometry optimization from strictly an experimental viewpoint, focusing on the primary parameters of ring electrode thickness and ring-to-endcap spacing, but also exploring the effects of mesh endcap size and electrode alignment. An interpretation of the results with respect to the electric field composition is reserved for Chapter 4. The first section introduces the full body of work.

3.1 Overview of Studies

As discussed in the introduction, the many complex facets of mass analysis with the CIT necessitates an experimental approach to determine the effects of geometry on performance, as opposed to simulations. Strong emphasis was placed on double-resonance ejection due to the superior resolution possible compared to other common modes of mass analysis. Consequently, each geometry requires extensive tuning of the amplitude and frequency of the supplementary dipole field imposed between the endcaps to determine the conditions for best performance with a given nonlinear resonance. Moreover, with each increase in pressure this supplementary RF signal has to be retuned to compensate for resonance damping. The multiplicative effort of this task is best suited for an experimental undertaking, especially when coupled with the need for large ion populations to adequately cover the range of possible ion trajectory starting conditions. With a physical instrument (described in Chapter 2) mass spectra can be rapidly collected, whereas simulations of
hundreds of spectra per geometry at high pressure would require tremendous computational power with a program like SIMION. This shortcoming in simulation capabilities is currently being addressed within our group by implementing GPU-accelerated methods for handling parallelizable calculations such as ion-neutral collisions and gas flow, which can shorten the processing time of a single spectrum from hours to minutes. While this will be highly advantageous for future work, these tools were unavailable for the present study.

3.1.1 Parameter Space

Even with just a few basic geometry parameters, a vast range of field distributions are achievable with the CIT. To make systematic experimental evaluation feasible, limits were first placed on the trap proportions according to prior knowledge of multipole characteristics from the literature, while also staying within practical operating conditions. The sample size was further reduced by determining an appropriately coarse dimensional step size. The rationale for paring the parameter space to its final size is discussed below.

The traditional geometric parameters of a CIT that incorporates endcap apertures are given in Figure 3.1a. The endcap thickness and outer extension of the electrodes (beyond \( r_0 \)) are minor parameters in that they do no significantly affect the field composition, as also noted by Wu et al. The endcap aperture size can have a strong influence, however, especially for relatively small \( z_0 \) values. Larger apertures generally decrease the value of even-order multipoles (typically making the dodecapole term more negative and the octopole less positive or more negative). For this reason the apertures can be considered detrimental to the overall field composition and their size is minimized at the expense of ion transfer efficiency. Although the aperture size can be useful for fine-tuning
the fields or compensating for an overly-positive octopole in some cases, it is commonly accepted that ideally they would not be present. Their inclusion also complicates and slows trap assembly due to the need for concentric electrode alignment for optimum ion transfer and preserving axial symmetry (see §3.2.2). Elimination of the apertures as parameters from the geometry study is therefore advantageous, while not sacrificing much in the range of interesting field compositions (in that nearly the same combinations of the octopole and dodecapole can still be attained, albeit with different higher-order field additions). If the holes in the endcaps are instead covered by a mesh that is sufficiently fine to approximate a uniform surface (Figure 3.1b), the only remaining critical parameters are the ring thickness and electrode spacing. Although this is ultimately a variation of $z_0$, it is not equivalent to $z_0$ variation with the QIT since more than one degree of freedom is involved. The extent to which mesh can be assumed to be a uniform surface that is transparent to ions is explored in §3.2.1, which is important in ensuring that it does not affect the results of the geometry optimization.

The trap size was fixed at $r_0 = 0.500$ mm for the geometry study because it is convenient in several regards. At this scale conventional machining tools still offer good mechanical precision, with a tolerance of ±0.5% or better readily achieved with miniature reamers (see Chapter 2 for trap design and fabrication details). The size is small enough to access a sufficiently high drive frequency at moderate voltages for surveying helium pressures up to ca. 1 Torr (by which point nonlinear resonances are damped out), yet also large enough so that a coarser and more robust mesh can be used. Each tested ring thickness required a separate ring electrode; these were machined and then lapped flat to within ±1% of the nominal dimension. The ring-to-endcap electrode spacing was controlled by alumina washers that were commercially lapped to within ±0.002 mm of the stated
thickness. With no discernible alignment concerns and reasonably tight dimensional
tolerances, along with the RF amplitude control and stability discussed in Chapter 2,
differences in trap performance can be attributed more certainly to the changes in the
trapping field from variation of the ring and spacer thicknesses.

Although this chapter does not address the multipole fields as they pertain to
performance, they are needed to bring the final geometry selection into context (their
determination is covered in § 4.1.2). As in other published studies, attention was placed on
the lowest order even multipoles (mainly the octopole and dodecapole). The available
parameter space is shown in Figure 3.2, which relates the ring and electrode spacer
thickness to the octopole and dodecapole coefficient values (relative to the quadrupole).
Twenty geometries were chosen (as indicated in the figure) for the main high-pressure
optimization study, guided by a few facts. The published characteristics for the octopole
preclude negative or overly positive superpositions since they are detrimental to resolution,

hence the selection bounds are roughly between 0–20%. Within this space, the dodecapole
is always undesirably negative. Increasing the electrode spacing for a given ring thickness
is naturally limited by a maximum value for the dodecapole, whereupon it tends to
decrease again through the examined range of spacer thicknesses (0.6 mm). Furthermore,
before this limit is reached it becomes impractical to keep increasing $z_0$ through spacing
since this leads to large ejection voltage requirements. Thicker rings allow the greatest
dodecapole values, but they are also constrained by voltage and by very large octopole
contributions at wider spacings. In order to access the shown parameter space with thick
rings (those above ca. 0.8 mm), the electrode spacing must be reduced to the point that trap
capacitance pulls excessive power from the RF amplifier.
In order to subdivide the remaining pool of geometries, the empirical rule of Wu et al. was followed, whence sums of the octopole and dodecapole coefficients (relative to the quadrupole) near −10% were found to be optimal. The parameter space is reconstructed in these terms in Figure 3.3, again showing the selected geometries among the different ring and spacer thicknesses. Preliminary work showed that in the asymptotically flat portions of the curves (where the multipole values are less sensitive to changes in spacing) the performance is also fairly constant among different spacings for a given ring thickness. This is assumed to be true for all ring thicknesses, although the increased ejection path length is likely unfavorable at high pressure. Therefore, in the interest of minimizing $z_0$ and the ejection voltage, the geometries associated with the asymptotic regions were not explored in the final high-pressure study. On the sloped portions of the curves, the geometry evaluation order was randomized to avoid systematic error over the period of the study. The initial goal was to find the best resolution for each ring thickness through spacer variation, until overall trends in performance across all ring thicknesses were identified. As discussed later, further geometry exploration in the more-positive region of parameter space remains interesting to add to the study. The exact multipole compositions of the twenty geometries tested in the high-pressure study are given in Appendix B. It should be noted that the nominal spacing values given throughout the dissertation are actually less by the thickness of the mesh grid attached to the inner face of each endcap (ca. −0.018 mm).

3.1.2 Study Comparison and Optimization Routine

Two separate geometry optimization studies were carried out, the full experimental details of which are covered in Chapter 2. Some important points and differences are
summarized here. The first study utilized an isobaric pressure chamber, such that all geometries were evaluated at a constant helium background pressure of 10 mTorr, with xenon as the analyte (7.5 MHz drive RF). Although the results were affected by several issues, this preliminary data set was instructive in developing the subsequent high-pressure study.

Trap charge capacity was investigated only in the low-pressure study where a hot-cathode EI source was employed that could provide a constant electron flux (discussed in § 3.4.3). The particular glow discharge mode used in the high-pressure study was not suitable for saturating the trap with charge since the ionization efficiency dropped quickly after the initial turn-on pulse (see § 2.2.2). The results pertaining to resolution in the low-pressure study are excluded from analysis, however, due to three issues (which were resolved in the high-pressure experiments). The most severe of these was random electrode spacing error (and possibly endcap warping) due to incompressible debris from the brittle ceramic spacers, which occasionally chipped at the edges during trap assembly. This was corrected after discovery late in the low-pressure study by a final examination of all parts of the electrode stack under magnification. The extent to which this affected the study is not known, but it is the likely cause for several deviations from the general trend.

The high-pressure results are more directly comparable among the different geometries because they were consistently calibrated to a mass scan rate of 20 Th/ms. Before this capability was added to the control software, a constant drive RF voltage ramp rate was used instead (120 V\text{pp}/ms for the low-pressure study), which contributed to peak width fluctuation since the mass scan rate varied. Another difference between the two studies is the application mode of the supplementary dipole potential to the endcaps. In the low-pressure study it was applied in unipolar mode, with the detector-side endcap
grounded and supplementary RF on the ionization-side endcap only. This was found to be problematic in cases where the supplementary RF amplitude exceeded ca. 4 V<sub>p-p</sub> due to the appearance of spurious peaks in the mass spectra. When applied in bipolar mode, with the supplementary RF on both endcaps 180° out-of-phase, spurious peaks were never observed as a function of amplitude. Additionally, resolution tended to be slightly better in bipolar mode; thus, it was used in the high-pressure study.

The most important results came from the high-pressure study, namely due to the extension across a broad pressure range and refinements in methodology. The selection of some of the experimental conditions that are constant throughout the study, such as drive frequency and scan rate, are covered in § 3.3.1. Mass spectra were collected in the RF-only mode (no DC potential applied to the ring electrode). The investigated pressure range varied with geometry according to how quickly the resolution decreased. The performance was evaluated at the following pressures for all geometries: 20, 50, 75, 100, 150, 200, 250, 300, 400, and 500 mTorr (set to within ±0.5%). In almost all cases the pressure continued to be increased until the peak width broadened to over 1 Th FWHM, at which point analysis became uncertain due to peak crowding. The trapping voltage for ion accumulation prior to the mass analysis ramp was optimized at 20 mTorr for each geometry based on maximum trapping efficiency and remained fixed across the pressure range. The spectral signal was kept low and adjusted for consistent peak height across all data. Although this means that the total number of trapped ions increased as peaks broadened at higher pressure, space charge effects appeared to be negligible.

A nonlinear resonance search was also performed at 20 mTorr for each geometry by sweeping the supplementary dipole frequency and amplitude across areas of interest, first with a coarse step size and then finely (in β<sub>z</sub> steps of ca. 0.002) to pinpoint the best
performance. The identified nonlinear resonances that exhibited good resolution under
double-resonance ejection were then investigated at the higher pressures. Since the
nonlinear resonance frequency bandwidth broadened with damping (see §4.5), only the
amplitude was retuned as the pressure was increased. The octopole nonlinear resonance
along $\beta_r + \beta_z = 1$ (which crosses the $q_z$ axis near $\beta_z = 0.704$) was investigated with each
gallery to monitor its transformation. When this resonance was active it produced the
best performance. Most other resonances did not merit high-pressure investigation due to
poor performance; for a few geometries the dodecapole resonance $2\beta_r + \beta_z = 1$ (crossing $q_z$
at $\beta_z = 0.522$) was explored. Ordinarily there were no odd-order field resonances; an
electrically-induced hexapole is discussed separately in §4.6. Although boundary ejection
resolution was consistently quite poor at low pressure, it was investigated at high pressure
in several cases as a benchmark.

3.2 Ancillary Geometry Concerns

Although the systematic geometry optimization studies only dealt with the ring
electrode and spacer thickness, there are secondary elements that had to be accounted for,
mainly to ensure that their influences could be made negligible. The experimental tests
covered in this section are not definitive, but were assumed to generally apply to all CIT
geometries for the purposes herein.

3.2.1 Effects of Endcap Mesh Size

The use of mesh-covered endcaps poses several potential problems. They are
typically avoided in commercial benchtop instruments because mesh is not readily formed
into arbitrary shapes with good precision and it is more prone to charging from residue
build-up than endcaps with large apertures since it is not completely transparent to passing
ions. With planar endcaps the mesh is much easier to handle, and concerns about charging are mitigated by the ability to entirely replace the endcaps as needed (since they are cheap enough to be disposable). Three pairs of mesh endcaps were cycled throughout the high-pressure geometry study to minimize residue build-up; introducing more endcap sets would have unnecessarily increased the chances for random error. The fabrication of mesh endcaps is covered in §2.2.3.

There are several factors to consider in choosing a mesh size. Higher screen densities are better at approximating a uniform surface (effectively decreasing surface roughness) but tend to have lower ion transmittance, which lowers ionization and ejection efficiency. Thus, the best-suited screen size would be just dense enough to avoid affecting the trapping field with changes in endcap position. However, another important consideration seems to be the cross-sectional area of the mesh wires, presumably in direct relation to the electrical conductivity of the grid.

Without a simple method for calculating the RF power dissipation by the mesh on the endcaps, the conductivity requirements are not obvious. Initially, in the interest of maximizing mesh smoothness, a screen size of 1000 wires-per-inch (WPI) was selected, which consisted of a square grid of wires that are ca. 6 μm wide and spaced apart by ca. 18 μm (shown in Figure 3.4a). The small wire width in this case gives ion transmission near 55%. However, the electroformed mesh sheet was only ca. 4 μm thick on account of the narrow wires. With the mesh soldered across a 2.5 mm diameter aperture on the endcap support electrode, the electrical resistance may be too high for the mesh to be near ground potential. This is likely related to a mass spectral peak-shifting phenomenon observed with this specific mesh size. The strange behavior usually manifested as seemingly random
repositioning of some of the mass peaks either above or below the expected value by less than 0.5 Th (example given in Figure 3.4b).

Although reminiscent of the historical mass shift errors with the QIT, this shifting was highly inconsistent: the peaks frequently and erratically repositioned with changes in the scan function timing (any operation that interrupted the drive or supplementary RF signals). After a shift occurred, the peaks almost always remained stationary until triggered by another timing change, occasionally drifting back into their expected positions. Sometimes instead of the peaks shifting, the resolution was severely degraded instead. Although this behavior is not yet understood or well characterized, it has been associated with the 1000 WPI mesh after extensive experimental testing. The phenomenon has been repeated across different instruments with separate hardware and trap electrodes, with this mesh size as the common factor. More significantly, the peak shifting was never observed under the same conditions but with the endcaps exchanged for those covered by a thicker mesh (such as a 200 WPI screen size with wires ca. 34 μm in width and ca. 18 μm thick, spaced ca. 90 μm apart). Several other mesh sizes with larger wires were tested as well with no abnormal behavior. Without further study of the peculiar dynamics involved, it is only speculated that the trapping field is affected by the electrical resistivity of the mesh. At a drive frequency of 7.5 MHz, the RF skin depth is ca. 24 μm, so the mesh conductivity is expected to improve until the outer wire dimensions exceed twice this value. Alternatively, there may be some unique interaction with the 1000 WPI mesh with frequencies near the tested 7.5 MHz, such as reflection. The peak shifting was resolved by using a thicker mesh sheet, but this entailed a coarser wire grid as well.

The mesh wire density relative to the size of \( r_0 \) is less critical for a single CIT than for an array of traps, where the field differences from variable wire position across an
ensemble can randomize peak position and average into broader peaks. Although the geometry optimization studies utilized single traps, it was necessary to find a mesh size that could be repositioned arbitrarily from trap to trap without significantly affecting the performance, such that electrode alignment could be fully excluded as a factor. Overly fine mesh was ruled out on the basis of the peak-shifting problem.

With these defined limits on mesh properties, several sizes were tested to determine the most suitable one. Interestingly, the performance under double-resonant ejection did not vary much across a broad range of mesh sizes for a constant set of experimental conditions (with the same trap geometry other than mesh). The results for three of the mesh sizes are shown in Figure 3.5, which includes mass spectra of similar resolution for screen densities of 1000, 200 and 75 WPI. Although the overall performance of the 75 WPI mesh was similar to the others, the supplementary RF for double-resonant ejection had to be reoptimized to maintain resolution upon lateral repositioning this endcap by a fraction of its grid size (both frequency and amplitude), which indicates that there are field differences. The boundary ejection performance with the 75 WPI mesh also varied considerably with lateral endcap shifts, as shown in Figure 3.6. This is not surprising given that this coarse mesh provides much less coverage than a typical aperture endcap. The experimental conditions and performance for mesh sizes between 1000 and 200 WPI were found to be highly repeatable (other than the peak shifting exclusive to the 1000 WPI mesh). The 200 WPI mesh was selected for the geometry optimization study at \( r_0 = 0.5 \) mm, which covers the ring cavity with about 7 wires in each direction. This wire size is robust and the spacing gives reasonable ion transmission (approximately 53%). An additional comparison study of electrode alignment with a similar mesh size (250 WPI) is presented in the next section.
3.2.2 Electrode Alignment

For the high-pressure geometry optimization study, the trap architecture was modified slightly. In the low-pressure study, identical mesh endcaps were used on both sides of the trap, with the wire screen suspended across large 2.5 mm diameter openings. The gas conductance through such traps is too high for the differential-pressure chamber used in the high-pressure study. The use of a small aperture endcap on the detector side of the trap limits the conductance sufficiently, but reintroduces alignment issues due to the nonuniform electrode potential surface. This was resolved by simply covering the small aperture with mesh as well (see Figure 3.7). However, the mesh wire length is effectively much shorter in this case, such that differences in electrical conductivity between the endcaps could affect the trapping field. To ensure that alignment would not be an issue, the effects of misalignment were assessed.

Preliminary work with traditional aperture-style endcaps showed that a high degree of concentricity of the ring electrode with the endcap apertures does not significantly improve resolution, although ionization and ejection efficiency decrease quickly with misalignment. To achieve high accuracy and precision of concentricity (within a few micrometers) for these traps, a die bonder was used that permanently epoxied the electrodes together. This was not an ideal solution for systematically investigating misalignment because of the limited availability of precision-machined ring electrodes. The performance of the highly concentric traps was compared to many tests made with pin-aligned traps, where the alignment tolerance was ±15% at best and yet the achievable resolution was frequently just as good. The use of mesh endcaps presented an opportunity to evaluate performance as a function of alignment. It is possible to see the relative
concentricity of the electrodes through the transparent mesh, and the same electrodes can be reused throughout the experiments.

The electrode alignment study consisted of two endcap electrode configurations, both of which used a plain mesh covering for the endcap on the ionization-side of the trap (250 WPI). In one case, the detector-side endcap had a single aperture that was 40% the size of the ring electrode (Figure 3.7a), while in the other case an identical aperture endcap was used but it was covered by mesh (Figure 3.7b). Three degrees of alignment were tested with each configuration, qualitatively shown in Figure 3.7 and referred to as [1] Aligned, [2] Misaligned, and [3] Severely Misaligned. All tests were done with an \( r_0 = 0.500 \) mm ring electrode (0.600 mm thick with 0.300 mm electrode spacing) at 20 mTorr He with 9 MHz drive RF.

A comparison of spectral resolution for all six traps under octopolar double-resonant ejection near \( \beta_z = 0.70 \) is made in Figure 3.8. The only notable difference in operating conditions is that the bare-aperture traps required a smaller supplementary RF amplitude for optimal resolution (ca. 0.4 versus 0.6 V\(_{pp}\)). The results are consistent with previous observations that the resolution in this ejection mode is very similar regardless of the degree of misalignment. The peak width of the ‘severely misaligned’ mesh-covered aperture trap (b3) is broader by about 25%, but this is a secondary effect of the misalignment, not directly related to changes in the trapping field. As the alignment images show, the misalignment is so extreme in this case that there is minimal overlap with the center of the trap, where most ion ejection occurs. Consequentially, the ejection efficiency was very low and this trap gave a weak signal unless it was overloaded with ions. The detected ions thus experienced harsh space charging effects, which are known to degrade resolution (see § 1.2.5). Furthermore, the extreme aperture displacement from the axial
center means that the mass spectrum is composed predominantly of the ion population that had to pass through the fringing trap fields where nonlinearities are much more influential and can negatively affect the trajectories.

The similarity of the results obtained in the octopolar double-resonance mode are not representative of the full situation. While the appeal of the octopolar resonance is enhanced by its robustness against changes in alignment, the other resonances and modes of mass analysis are not as resilient. A broader perspective of performance is offered by mapping the nonlinear resonances of the trap by sweeping the frequency of the supplementary dipole field, as done in Figure 3.9 for the ‘misaligned’ aperture endcap trap (a2). A very similar resonance map was observed for the ‘severely misaligned’ aperture endcap trap (a3). Compared to the aligned aperture endcap trap (a1) and all of the mesh-covered aperture traps (Figure 3.7b), there are several important differences evident. First, there is spurious ejection near $\beta_z = 0.84$, which can be seen as the peaks labeled [A] just before boundary ejection—the cause of this will be examined shortly. The spurious peaks disappear along with the boundary ejection peaks when a strong nonlinear resonance is encountered earlier in the ramp that succeeds in ejecting all the ions from the trap, such as the aforementioned octopole, labeled [D]. As long as ejection via these earlier resonances is complete, the spurious ejection does not interfere with the assignment of a unique $m/z$ to each ion peak. Although the octopolar nonlinear resonance produced the best resolution in all cases, the dodecapolar resonances near $\beta_z$ values of 0.40 and 0.52 ($\beta_r + 2\beta_z = 1$ and $2\beta_r + \beta_z = 1$, respectively) were quite active when the aperture endcap was not covered by mesh. The $\beta_z = 0.52$ resonance actually produced a much stronger signal than the octopole, suggesting that ion ejection directionality may strongly favor the detector-side endcap for the dodecapole in this case.
Spurious ion ejection via a nonlinear resonance is not common with CITs during typical mass analysis modes because despite the presence of many higher order fields they are quite weak in the center of the trap. Ions usually require pre-excitation in amplitude to be influenced by the nonlinear resonances (see § 1.3.4). The observed peaks at $\beta_z = 0.84$ in Figure 3.9 are therefore surprising, in that they are ‘auto-ejected’ with no excitation by a supplementary dipole field. This indicates that the responsible nonlinear resonance is related to abnormally strong fields induced by the electrode misalignment. The spurious nature of these peaks is not fully clear from Figure 3.9, where they may be mistaken for the boundary ejection of a lower $m/z$ ion, even though such peaks are absent from the resonantly ejected portion. The spurious behavior was confirmed by collecting mass spectra in the boundary ejection mode with both endcaps grounded (no supplementary RF). When both endcaps of a trap were covered in mesh, only the expected peaks appeared in the spectra regardless of the degree of misalignment, as seen in Figure 3.10a. When the detector-side endcap was just a bare aperture (configured as in Figure 3.7a) and aligned with the ring electrode, the spurious ejection remained absent (Figure 3.10b). However, in both the ‘misaligned’ and ‘severely misaligned’ arrangements the $\beta_z = 0.84$ nonlinear resonance caused auto-ejection.

Another surprising aspect of the $\beta_z = 0.84$ resonance is that it is not theoretically predicted for any of the multipoles under the assumptions of radial symmetry with $\nu = 1$ (see § 1.3.3). However, given that the endcap aperture misalignment clearly establishes radial asymmetry, as well as asymmetry across the radial plane, not only can the hexapolar resonances be active, but the otherwise necessary condition that $n_r$ is even in eq 1.36 no longer holds true. Consequently, the previously forbidden hexapole resonance $\beta_r + 2\beta_z = 2$ may be active, which happens to cross the $q_z$ axis near $\beta_z = 0.838$, the observed spurious
ejection position. This hexapolar resonance has not been noticed with pin-aligned traps where both endcaps had small apertures with no mesh, and where high degrees of misalignment are routine. Yet, in the presented results, only a relatively small amount of misalignment was necessary to cause auto-ejection at this resonance. This suggests that a high degree of asymmetry across the $z = 0$ plane may also be needed to first induce a strong hexapolar field, which is expected when a mesh endcap is paired with a sizable aperture endcap. It is possible that other CIT geometries would behave differently under these circumstances.

For the geometry optimization studies, the use of mesh on both endcaps appears to eliminate alignment concerns. To help ensure good reproducibility, and to maximize ejection efficiency, approximate concentric alignment was maintained for all tested geometries through visual inspection (as in the ‘aligned’ cases here). Although the geometry optimization focused on only the ring thickness and electrode spacing, it is clear that other factors such as mesh and aperture size can also be important to performance. Whether or not they can be used to enhance performance, however, remains to be investigated.

3.3 Experimental Considerations

Resolution is the primary figure of merit investigated in the geometry optimization study. However, it is not a fixed attribute for any given CIT, but depends on variable experimental conditions such as drive frequency, mass scan rate, and buffer gas species. In order to directly compare the trap geometries relative to one another, a single set of conditions needed to be determined. The background gas pressure was not limited to one value since trends across a wide range are of interest.
3.3.1 Competing Resolution Factors

As discussed in § 1.4.3, the mass resolution scales with drive frequency, which additionally increases the potential well depth and trap charge capacity. In practice, then, the highest possible drive frequency is desirable, with the usual restraint being the voltage necessary to achieve a certain mass range with the RF ramp. A qualitative example of resolution enhancement in the range of 6 to 13 MHz is given in Figure 3.11 for a single trap geometry with \( r_0 = 0.500 \). Within the expected \( z_0 \) geometry optimization range for the chosen analytes, a drive frequency of 9 MHz (precise to 0.001 Hz) was selected to minimize the chances of electrical breakdown and to ensure a stable operating voltage (below ca. 600 V\(_{\text{op}}\)).

As mentioned earlier, a constant mass scan rate of 20 Th/ms was employed in the high-pressure study so that differences in resolution could be attributed strictly to changes in geometry. This scan rate value was a reasonable compromise between maximizing resolution and keeping the mass analysis scan time reasonable. In Figure 3.12a it can be seen that with typical trap parameters the length in time for a single mass analysis ramp increases rapidly as the scan rate is decreased further; with spectral averaging the total acquisition rate can get very slow.

The peak widths appear to be linearly related to the mass scan rate in Figure 3.12a because the data was collected in a narrow linear portion of the otherwise asymptotic curve. Since the double-resonance ejection mass analysis mode was used, the supplementary RF amplitude had to be retuned with each change in scan rate and pressure for optimal excitation, hence the lack of data points at slow scan rates where there is only a slight dip from linearity. For better comparison with theory,\(^{102,103}\) the data points are replotted on a logarithmic scale in Figure 3.12b. With lower damping (pressures 15 to
100 mTorr) the resolving power approaches the maximum predicted trend with $1/a_m^{1/2}$ (see end of § 1.4.3). At lower scan rates and with greater damping the resolving power starts to become independent of scan rate, consistent with eq 1.45. By extrapolating to the low scan rate limit, it can be seen that the resolving power reaches a pressure-dependent maximum. For a given pressure, the peak width can be reduced by decreasing the scan rate, which increases the interaction time of the ions with the resonance field (or the total number of secular oscillations). However, in order to reduce the curve offset due to damping, it is necessary to increase the number of secular frequency oscillations per ion-neutral collision. The differences in resolution due to geometry in the optimization study are expected to scale proportionally with changes in drive frequency.

### 3.3.2 Buffer Gas Damping

The effect of drive frequency on the relationship of peak width with pressure is demonstrated in Figure 3.13. With helium as the buffer gas, an increase in drive frequency from 6 to 9 MHz offset the curve to lower peak widths and caused the slope to decrease (lower rate of peak width increase versus pressure). For this reason, most of the geometries in the optimization study were evaluated at close to 1 Torr without the need for peak deconvolution due to crowding. At a fixed drive frequency of 9 MHz, a change in the buffer gas from helium to nitrogen had a more drastic effect in this test. The peak width jumped significantly at low pressure and the slope was much greater under the same conditions. Additionally, the double-resonance ejection behavior was markedly different, with the effects of tuning the supplementary RF quickly diminishing as the pressure increased, indicative of the nonlinear resonance being damped out. This happened at a much lower pressure with nitrogen than helium. The more massive neutral collisional partner can lead
to strong scattering of ion trajectories without an appropriate compensation in drive
frequency. Due to this large change in collision dynamics, the geometry optimization
results obtained with helium are not as readily generalized to heavier buffer gas species
without further experimental verification.

The stability diagram boundaries are theoretically expected to shift by a factor
directly related to collisional damping,\textsuperscript{104} which in turn affects ion ejection voltage and
mass calibration. A brief investigation was made to characterize the spectral peak shifting
behavior with higher background pressures under typical experimental conditions.
Although the shifting was consistent across all modes of mass analysis, boundary ejection
was employed to probe the $f_2 = 1$ stability boundary and avoid the shifting also caused by
tuning the supplementary dipole field for resonance ejection. Figure 3.14 shows that the
stability boundary initially shifts steadily with pressure to lower $q_z$ ejection points, but after
passing ca. 400 mTorr the shifting almost ceases through 1 Torr. If pure QIT theory is
approximately applied to the CIT in this experiment, it is found that the value of $q_z$ shifts
about 0.015 units across the full pressure range, corresponding to a drop of less than 2% in
ejection voltage. Peak shifting due to pressure and other experimental conditions was
accounted for by recalibrating the mass scan rate prior to saving spectra, relying on the
presence of known $m/z$ peaks.

In order to utilize the double-resonance mass analysis mode at higher pressures, the
damping needed to be compensated for by increasing the supplementary RF amplitude. If
the excitation force is not increased, the ions will collapse to the center of the trap due to
collisional cooling where they are not influenced by nonlinear resonances. This is
illustrated in Figure 3.15, in which the resonantly ejected peaks are gradually quenched as
the pressure is increased with a constant supplementary RF amplitude, such that by 150
mTorr nearly all the ions are retained in the trap until the $\beta_z = 1$ boundary is crossed. Xu et al. found that a linear increase in supplementary RF amplitude is required to maintain optimum resolution with resonant ejection.\textsuperscript{117} However, in the course of the present geometry optimization study, this was not true for all the tested traps (see § 4.4.2).

The typical optimization goals for the supplementary RF are to minimize peak width and to maximize the number of ions that are resonantly ejected (to avoid $m/z$ assignment conflicts from dual ejection points when some ions remain trapped till the stability boundary). In the geometry studies, the two objectives were usually accomplished in parallel, but with some traps they were mutually opposed. The more common case is described in Figure 3.16, which applied to trap geometries operated in the octopolar double-resonance ejection mode ($\beta_z = 0.70$) where the multipole composition had a sum for the octopole and dodecapole coefficients greater than ca. –11% relative to the quadrupole. As the supplementary RF amplitude was increased at a given pressure, the ion population transitioned to resonant ejection and the peak width narrowed. Ideally, the resonant ejection signal was maximized before or at the amplitude at which the peak width minimum was reached. The amplitude range over which the peak width minimum was maintained varied with pressure. However, in most cases the optimum supplementary RF amplitude was the lowest one necessary to reach the minimum peak width because exceeding this voltage usually caused the total signal level to start dropping and could strongly affect peak shape (such as initiating peak splitting). As the pressure was increased, higher amplitudes were required to shift the ions from boundary to resonant ejection, and the peak width became much less sensitive to changes in the amplitude. Additionally, higher pressures increased the difference in amplitude required to stop boundary ejection and minimize peak width.
Trap geometries where the octopole and dodecapole coefficient sum was less than ca. –11% tended to behave opposite to the previous case, as seen in Figure 3.17. At pressures ca. 20 mTorr and below, the tuning mechanism was actually similar in that the peak width initially decreased with higher supplementary RF amplitude. However, at higher pressures the peak width simply increased with amplitude until reaching a maximum near the amplitude at which boundary ejection was minimized. Although greater supplementary RF amplitudes increased the number of resonantly-ejected ions like before, in this case it was at the expense of resolution. This tradeoff between resolution and eliminating boundary ejection led to geometries with this tuning behavior having the worse high-pressure performance, as discussed later. For all traps in the geometry studies, minimizing boundary ejection was prioritized over peak width in tuning the supplementary RF amplitude, such that the reported peak widths do not necessarily represent the best resolution possible in the double-resonance ejection mode.

3.4 Results of High-Pressure Geometry Optimization

The complete optimization results are presented and discussed in terms of the geometric parameters to directly relate the selection of trap dimensions to expected performance under a variety of conditions. Further analysis is made in Chapter 4 with reference to the electric field composition to establish clearer trends and generalize them beyond the specific traps examined in this study. Unless otherwise noted, all data were obtained with helium background gas, a trap size of $r_0 = 0.500$ mm, and drive frequency of 9 MHz.
3.4.1 Resolution as a Function of Pressure

The central goal of optimizing the CIT geometry in this study was to improve selectivity, especially at the higher pressures necessitated by the HPMS strategy. Resolution is quantified by reporting the peak widths (FWHM) for the molecular ion of anisole at 108 Th. This measure is experimentally intuitive and relatable to the common standard for unit mass separation. A qualitative example of the typical changes observed in mass spectra across a broad pressure range for the double-resonance and boundary ejection modes is given in Figure 3.18. The trap in this case performed well in the double-resonance mode; the peak width increased steadily with pressure but remained under 1 Th by 700 mTorr. Although the resolution was poor in the boundary ejection mode at low pressure, the peak width varied much less over the same pressure range. The rate of peak width increase versus pressure is an interesting comparison point among the geometries.

For most CITs, the best resolution was obtained in the double-resonance ejection mode using the octopolar nonlinear resonance near $\beta_2 = 0.704$. The peak widths obtained in this mode over a wide pressure range are presented in Figure 3.19 for all tested traps. The spectra were analyzed by the method described in §2.1.2, and the error bars represent the confidence interval at the 95% level for a Gaussian fit of each peak; the error bars are not shown in later plots for cleaner presentation. It is expected that the observed changes with pressure are relative to the drive frequency. Although this plot is rather crowded, making it difficult to discern trends related to the geometry parameters, several aspects of the data stand out that will be examined closer in later sections. First, the peak width for the majority of the traps did not vary as much in the low-pressure range (<100 mTorr), with most falling within a 0.1 Th window. However, in the approach towards 200 mTorr, there is distinct nonlinear variation in peak width that creates a substantial spread between traps.
Beyond 200 mTorr, the relative differences in peak widths between most of the traps was maintained over the tested pressure range due to a constant rate of peak width increase.

The biggest exceptions are the 0.800/0.200 (thickness/spacing) and 0.750/0.250 traps, where a slightly improving peak width was seen through ca. 500 mTorr. These geometries exhibited poor resolution in the low-pressure end and correspond to the thicker ring electrodes with the greatest $z_0$ values.

The nonlinear increase in peak width across the low-pressure range (ca. 50 to 200 mTorr) for most of the geometries is not yet understood. The extreme changes throughout this narrow pressure range are responsible for establishing a second 'starting position' for each geometry near 200 mTorr from which the peak width increases regularly thereafter. The curves most closely resemble a sigmoid function, which is more clearly seen in the inset of Figure 3.19. Following the driven damped nonlinear oscillator model for ion motion in this case, it can be assumed that the nonlinear resonance component (octopole) of the double-resonance ejection passes through the critical damping point by the end of this pressure range, and enters an overdamped state for all higher pressures. An examination of resonance damping in §4.5 shows that double-resonance ejection is quenched into standard resonance ejection in this same range. How this translates into nonlinear increases of peak width remains to be answered. These changes are also coincident with a rapid transition of pressure regimes based on Knudsen number approximations, with viscous drag effects becoming more likely beyond the rarified conditions experienced below 50 mTorr. Any resulting effects on collision dynamics are best suited for computer modeling to explain. Another interesting dynamic that could be influential on resolution is the secondary consequence of the ion cloud collapsing with greater damping, whereby the closer ion proximity induces greater mutual space charge
perturbance. Although the ion spatial distribution decreases as they are packed closer in the center of the trap, the extent of collapse is balanced by Coulombic repulsion that could negatively affect the trapping field in turn.

In the boundary ejection mode, the resolution of all tested traps was quite poor. Since deconvolution was required to determine peak widths, full analysis over a wide pressure range was performed on a subset of traps; these results are shown in Figure 3.20, with a comparison to the respective octopolar double-resonant ejection results as well. The peak width dispersion between traps at low pressure was much more extensive in this mode, but the differences quickly narrowed at elevated pressures. As with octopolar double-resonance ejection, the peak width variation in boundary mode was not linear up to ca. 150 mTorr, except that there was an initial improvement in resolution instead (with especially large improvements in peak width observed for the 0.600 mm thick ring). This is likely a direct result of the ion cloud collapsing further to the center of the trap. At higher pressures the peak widths increased linearly, but much slower than in the double-resonant mode. Due to this difference in rates, the peak width curves for the two modes eventually intersect; the performance of the 0.600 mm thick ring was specifically investigated at higher pressures to see if the double-resonance curves leveled off to match the boundary-ejected peak widths. As evident in the figure (green and purple dashed lines), this was not the case. Rather, in double-resonance mode the peak widths continued to increase at much the same rate as before, with minor leveling at the high-pressure end. Therefore, the application of supplementary RF to perform resonance ejection after a certain level of damping is reached seems to be more detrimental to the secular frequency coherence than boundary ejection without axial modulation. This suggests that for some trap geometries, if
the drive RF is insufficient to counter damping at high background pressures, it is beneficial to simply use the boundary ejection mode.

Besides the octopole nonlinear resonance at $\beta_z = 0.704$, the only other strong resonances routinely encountered during exploration were from the dodecapole at $\beta_z$ values of 0.404 and 0.522. It is possible that other strong resonances were overlooked since the search (through scanning the supplementary dipole frequency and amplitude) was not exhaustive. The dodecapole resonances were always active (or inactive) together, but much better resolution was obtained for the one near $\beta_z = 0.522$. The resolution with the octopole was usually superior, but for at least two of the tested trap geometries the dodecapole was competitive (Figure 3.21). In these cases, the $\beta_z = 0.522$ resonance was slightly better at low pressure, but above 300 mTorr the peak widths with the octopole were significantly lower. The peak widths increased nonlinearly in the low-pressure end just as with the octopole, but in the linear portion above 300 mTorr the slope of the dodecapole curves was larger, so that the difference in peaks widths between the resonances increased with pressure. This is in agreement with theory – at higher pressures the nonlinear resonance advantages are removed due to overdamping, and the trap is left operating at a lower $\beta_z$ point where the secular frequency is lower than it could be. According to eq 1.45, this results in lower resolving power. For some other traps (data not shown in the figure) the dodecapole also gave good resolution near 20 mTorr, but the peak width increased much quicker at greater pressures than for the traps in Figure 3.21. The fact that good resolution can be obtained at all with the dodecapolar resonances is interesting because negative multipoles are predicted to be detrimental when mass analysis is performed with a forward (increasing) secular frequency scan (see § 1.3.4).118,119
3.4.2 Resolution as a Function of Geometry

In order to better differentiate the performance of all the tested CITs, the results are separated by pressure in this section. Since the best resolution obtained with most traps was in the double-resonance ejection mode via the octopole (near $\beta_z = 0.704$), this was the most suitable method to survey the parameter space. Thus, the study can actually be considered an optimization of the octopolar nonlinear resonance. Cases where the resolution could be improved by utilizing other mass analysis modes are discussed elsewhere (see the dodecapole results above and §4.5).

One of the most common geometry adjustments made with the QIT is a variation of electrode spacing, where the constant ring dimensions give way to the ratio $z_0/r_0$ serving as the sole optimization parameter. This term is not appropriate for CITs because the ring thickness adds another degree of freedom to $z_0$ manipulation. If a correlation with $z_0/r_0$ is attempted for the present results, as done in Figure 3.22 for the peak widths at 20 mTorr and the peak width versus pressure rate, it becomes clear that traps with different ring thicknesses do not have equivalent performance at a given $z_0/r_0$ value. Rather than localizing the data to individual curve lines, it is convenient to separate the $z_0$ parameters for 2D correlation on contour plots.

The peak width results are presented in a more useful contour plot format in Figure 3.23 for eight different background pressures. These plots were generated using OriginPro v2015, with documentation available that describes the algorithm (such as triangulation, interpolation, and smoothing). Light smoothing was applied to the contour lines, but not so much as to distort the apparent trends (total points increase factor of 200, and thin plate spline smoothing parameter of 0.005). The round markers are the experimental data points overlaid on the plot without smoothing so that the exact peak
width is not obscured. Since the peak width trends are not disrupted by abrupt fluctuations or deviations across any of the tested geometries, the interpolated values for untested parameters are expected to be reasonably accurate. That is, undiscovered local extrema are unlikely within this space. The peak width trend is mostly in one direction, as indicated by the arrows in Figure 3.23a, but involves both the ring thickness and the electrode spacing. The contour lines are arc-shaped, with a minimum peak width valley extending across the full parameter range (approximately following the dashed line). Accordingly, as the ring thickness decreases along this minimum, a wider electrode spacing is needed to maintain resolution. This corresponds with the shift of the peak width curve minimums to higher $\frac{z_0}{r_0}$ values in Figure 3.22a. Although changes in pressure did not affect the direction of the trend (Figure 3.23b–h), the minimum peak width band shifted towards higher $z_0$ values throughout the entire pressure range, as illustrated in Figure 3.23h by the significant shift of the dashed line marking the approximate minimums at 20 and 700 mTorr. So, for the octopolar nonlinear resonance, loss of resolution due to greater damping can be offset to a degree for some traps by adjusting either the electrode spacing or ring electrode thickness.

The rates at which the peak widths increased with higher pressure were also dependent on changes in $z_0$ due to ring thickness and electrode spacing. However, as both Figures 3.22b and 3.24 show, in general a minimum rate was not reached (the data boundaries are not the endpoints of the trend). The slope, which was determined through ordinary least squares fitting of the curves in Figure 3.19 in the linear portions above ca. 250 mTorr, continually decreased with larger ring thickness and spacing (as indicated by the arrow) to the extent that it became negative for the 0.800 mm thick ring. However, the lowest rates were observed with traps that also had the worst resolution at low pressure, such that they would only be attractive for use at high pressures where their peak widths
were comparable with the other traps. A shortcoming of this study is that the traps with low slopes were not tested at high enough pressures to stabilize their peak width versus pressure curves (due to an ionization source issue whereby only a single reliable $m/z$ value was present at high pressure, preventing accurate mass calibration). Unlike most other geometries that have nonlinear behavior through only ca. 250 mTorr, the traps with low slopes seem to have a nonlinear relationship with pressure through at least 700 mTorr. For example, with reference to Figure 3.19, by 800 mTorr the trap with the narrowest observed peak width is the 0.750 mm ring with a spacing of 0.250 mm, where the slope of the curve appears to finally begin entering the linear relationship stage. Likewise, the slope of the trap with the 0.800 mm thick ring stopped decreasing by 700 mTorr, and is presumed to start increasing soon after. Nevertheless, at pressures of 1 Torr and above, traps with these dimensions are expected to have the best resolution. Another important consideration, however, is the ion storage capacity (discussed in §3.4.3), which decreases substantially for these traps and strongly detracts from their overall performance.

The peak widths observed in the boundary ejection mode had a very similar trend to those in the octopolar double-resonance mode, as shown in Figure 3.25. The analysis of these results was limited to 20 mTorr, and the plot excludes the 0.800 mm thick ring due to its especially poor resolution and signal level in this mode. By direct comparison with Figure 3.23a, it can be seen that the relationship of the peak width to ring thickness and electrode spacing is nearly identical, as is the location of the peak width minimum valley. However, in boundary ejection mode the range of peak widths was greater, so that the geometries with better resolution are more starkly contrasted to the rest.

The fact that the best resolution was obtained with the same geometries in the boundary and double-resonant ejection modes is advantageous for situations where both
modes of analysis are desired for an instrument. This also indicates that the two modes benefit from at least one common feature of the electric field, despite utilizing different ejection pathways. An examination of the higher order fields is necessary to interpret this, which is the focus of Chapter 4. The changes in supplementary RF requirements with geometry provide hints about ion energetics and nonlinear resonance dynamics, but this is also best discussed in the context of the multipole composition.

3.4.3 Ion Storage Capacity

Preliminary experiments with trap geometry showed that the signal level varied considerably with changes in $z_0$ for a constant $r_0$ dimension. Since S/N is important for quantitative analysis, the geometry optimization study included an investigation of the ion storage capacity. The most likely mass analysis mode to be used with CITs is double-resonance ejection via the octopole, making it best suited for evaluating the signal level. However, resonance dynamics are known to affect the efficiency of ejection, so the results do not necessarily apply to other analysis modes.

There are several options for assessing the maximum signal level of a trap. The spectral space charge limit is the most practical figure of merit for traps that have analytical purposes, since high levels of space charge are detrimental to resolution and mass accuracy. Commercially, an arbitrary limit on mass shift error is one method used to quantify the spectral space charge limit. An example for the Bruker Esquire 3000plus and HCT instruments is given by March and Todd,72 wherein the mass shift is recorded as a function of the total number of ions stored in the trap. Two regimes are reported for the mass shift rate: at lower space charge levels the mass shift rate is slow, while at high space charge levels the mass shift error accumulates much faster. At the linear intersection of
these two regimes the mass spectrum starts to become distorted, and this is the accepted spectral limit. This analysis was tested with one CIT geometry (0.600 mm thick ring, 0.300 mm spacing), the results of which are shown in Figure 3.26a. Under otherwise constant experimental conditions, the spectral peaks shifted to higher values as the amount of charge stored in the trap increased. Curiously, though, the mass shift rate decreased after the critical intersection point of the two space charge regimes, which is opposite to the behavior of the commercial QITs. Additionally, the spectra became distorted well before the mass shift rate changed. Consequently, the point at which the peak width begins to increase due to space charge may be a better metric for CITs. For the same data set, the change in peak width is shown in Figure 3.26b, which starts to increase with half as many stored ions compared to the change in mass shift rate. This result is more intuitive and confirms that the spectral space charge limit with CITs is just a small fraction of the total charge capacity. While this peak width increase and mass shift behavior was consistent for all tested CITs, it is unknown whether the change in mass shift rate varies with geometry.

For the systematic evaluation of the charge capacity with geometry, it is useful to have a theoretical comparison. While this would be overly complex if the spectral space charge limit was examined, a model has been developed for estimating the maximum ion density in the ideal QIT (see end of § 1.2.5), from which the maximum number of stored ions can be predicted. Following the example of Dehmelt, an ellipsoid trapping volume is assumed for the CIT, which in terms of the geometry parameters is

\[
V_{\text{CIT}} = \frac{4}{3} \pi z_0 r_0^2
\]  

(3.1)
Although this is likely inaccurate, it will only be used to determine the expected trend. From the expression for the maximum ion density in eq 1.32, the maximum number of ions contained in this volume is

\[ N_{\text{max}} = \frac{m(qzr_0\Omega)^2}{16e^2} z_0 \]  

(3.2)

Therefore, under constant experimental conditions with a fixed \( r_0 \) dimension, the space-charge-limited ion storage capacity is predicted to increase linearly with \( z_0 \). This is contrary to the results obtained in the present study, where the signal level consistently decreased as \( z_0 \) was increased.

As discussed in § 3.1.2, charge capacity was only investigated in the first set of geometry optimization experiments (Xe analyte in 10 mTorr He with EI source), with which there were some issues. In order to make objective measurements of the maximum storable charge in each trap, the ionization time was gradually increased until the spectral signal level stopped increasing due to charge repulsion. The total integrated spectral area was then used to compare charge capacity among traps (with the spectral space charge limit expected to follow the same relative trend). However, in some cases the normally asymptotic increase in signal level was affected by doubly-charged species, which further contributed to random error. Coupled with the other issues, this accounts for the deviations observed in the trendlines of Figure 3.27, which appear to be linear overall for individual ring thicknesses. In addition to the charge capacity decreasing with larger \( z_0 \) due to electrode spacing, it is clear that it dropped with thicker ring electrodes at a constant \( z_0 \) value. This is an important factor in choosing the most suitable trap geometry for an application. At very high pressures (above the equivalent of 800 mTorr at 9 MHz drive RF) the thicker ring electrodes (with appropriate electrode spacing) are promising candidates.
for best spectral resolution, but their low signal levels makes them far less appealing. The
fact that they had poor resolution at low and mid-range pressures is another reason they
are less likely to be analytically useful. The charge capacity variation with geometry is
revisited in §4.7, where correlation with nonlinear fields helps explain the strong
discrepancy between CIT experiments and ideal QIT theory.

3.5 Conclusions

While the results in this chapter can guide the selection process of an applicable
CIT, the geometry set is limited by the particular parameters utilized in the study. Since
alternative electrode structures (such as endcaps with macro apertures) will change the
electric field composition, the ring thickness and electrode spacing values given here
cannot be directly applied for those cases. However, by transforming the data from
gEometric terms into the domain of multipolar coefficients, the performance of other trap
designs can be predicted as well. This extension is made in Chapter 4.

Due to the wide range of possible applications and the lack of a fixed set of
operating conditions, it would be incorrect to label any one geometry as the best overall.
Restrictions on the mode of mass analysis will affect the geometry hierarchy, but it is
assumed here that this aspect is flexible in favor of optimal performance. It is also
important to remember that the results are not absolute, but will scale relative to a factor
consisting of pressure, drive frequency, and background gas characteristics. Although this
factor is not quantitatively expanded for the present study, different zones of operation can
be outlined in order to narrow the geometry selection pool. The range can be described
qualitatively as operation under low, intermediate, and high damping conditions. Low
damping, where low pressure and/or high drive frequency prevail, benefits from strong
nonlinear resonance activity such that true double-resonance ejection can be performed (see § 4.5). This corresponds approximately with helium pressures below 100 mTorr at 9 MHz; for HPMS applications where the pressure is higher or the neutral gas is heavier, the drive RF would have to be increased adequately for the damping to be considered low, which may not be practical. Among the top choices for this zone (employing octopolar double-resonance mode near $\beta_z = 0.70$), the 0.650/0.250 trap (ring thickness/electrode spacing in mm) tested quite well, but there are many similar options available from both other experimentally evaluated traps and their interpolated counterparts, as seen in Figure 3.23a–c.

In the intermediate damping zone the ion secular frequency is increasingly overwhelmed by some combination of high pressure, low drive frequency, and/or heavy neutral collisions (approximately 150 to 600 mTorr He for the presented data). Double-resonance ejection loses its advantage over normal resonance ejection, but stabilization due to higher-order fields (see Chapter 4) leads to even greater differences in resolution, with geometries like the 0.700/0.175 trap demonstrating superiority. While intermediate damping is an achievable range for HPMS, it is likely that low-power applications may dictate operation under high damping conditions (above the equivalent of ca. 700 mTorr at 9 MHz). This is the least-explored pressure range of this study, but it was also clear from the results that another class of geometries begins to predominate in terms of resolution (such as the 0.750/0.250 and 0.800/0.200 traps). Although these geometries have weaker signal levels, they may provide enough of an advantage in selectivity to justify their use. However, at yet higher pressures (between 1 to 2 Torr), it is predicted that all geometries that are operated in the resonance ejection mode will yield supremacy to geometries operated in the boundary ejection mode. At some damping point, the additional gain in
secular frequency from operating at $\beta_z = 1$ appears to supersede the influence of a supplementary dipole field at a lower $\beta_z$ value. Since performance in the boundary ejection mode was not consistently tested at high pressure, it is not obvious which geometries would be preferable for these cases. On the other hand, operation under severe damping conditions is a compromise rather than an objective of HPMS, and the trends suggest that geometry plays a comparatively minor role in resolution at such extremes.
3.6 Figures

Figure 3.1  CIT geometry optimization parameters for a fixed $r_0$ size. In both cases $z_0$ is set by the sum of half the ring thickness $t_r$ and the electrode spacer thickness $t_s$. Differences in the outer radius of the electrodes $R$ are not significant if $R \gg r_0$. (a) The traditional CIT with apertures of diameter $d_e$ in the endcaps for ion injection and ejection, where the endcap thickness plays a minor role in the field composition. (b) A CIT with mesh endcaps; if the mesh is sufficiently fine to approximate a uniform surface, the only remaining optimization parameters are $t_r$ and $t_s$. 
Figure 3.2  CIT geometry optimization parameter space, relating the ring thickness and electrode spacing to the dominant multipole terms, the octopole and the dodecapole (as fractions of the quadrupole). Each trace represent a different ring thickness (labeled) while each data point represent a different spacing that increases from left-to-right in the range of 0.025 to 0.600 mm with a 0.025 mm increment (not labeled). The experimentally evaluated geometries are noted. Each data point is color-coded to the boundary ejection voltage predicted from QIT theory for that geometry.
Figure 3.3 CIT geometry optimization parameter space with respect to the sum of the octopole and dodecapole coefficients relative to the quadrupole. Each trace is unique to the labeled ring thickness, with the multipole sum increasing as a function of both larger ring and electrode spacer thicknesses. A previous study\textsuperscript{111} and preliminary testing found the performance to be best near sums of $\sim$10\% at low pressure.
Figure 3.4  Peak shifting phenomenon exhibited by CITs employing mesh endcaps with small wire sizes. (a) Digital microscope image at a 30° angle of mesh endcap (1000 wires/inch) overlaying an $r_0 = 0.500$ mm ring electrode. (b) Two mass spectra of xenon collected 15 seconds apart with this mesh size (each spectrum average of 500 scans, 7.5 MHz drive RF), with the only change in experimental conditions being the drive RF ramp duration (max voltage slightly decreased), which triggered the shift. Peak position was otherwise stable.
Figure 3.5 Effects of mesh endcap wire density on spectral resolution, showing only minor differences even with very coarse size. The mean FWHM peak widths (with standard deviations) for m/z 131 and 132 Th are (a) $0.39 \pm 0.02$, (b) $0.40 \pm 0.02$, and (c) $0.39 \pm 0.03$. The listed nominal densities are in wires/inch, with wire widths and gaps of (a) 6 $\mu$m by 18 $\mu$m, (b) 34 $\mu$m by 90 $\mu$m, and (c) 58 $\mu$m by 275 $\mu$m. The green inscribed circles show the relative size of the ring electrode ($r_0 = 0.500$) to the mesh. Data was collected under octopole double-resonance ejection near $\beta_z = 0.70$ (Xe in 40 mTorr He with 7.5 MHz drive RF, with 1000 scan average). The optimal supplementary RF amplitude was slightly different for each mesh size. In all cases the ring thickness was 0.60 mm and the spacing 0.30 mm, except as varied slightly by mesh thickness.
Figure 3.6  Boundary ejection performance of CIT with 75 WPI mesh endcaps; the two spectra were collected under identical conditions except that the trap was reassembled (after collecting red spectrum) with the endcaps shifted laterally on the order of 0.1 mm for the subsequent blue spectrum. The exact endcap positions were not quantified. The experimental conditions are the same as the trap described in Figure 3.5c, but at 10 mTorr He and no supplementary RF applied.
Figure 3.7  Endcap configurations and relative positions used in the trap electrode alignment study. The ionization-side endcap (top) in both cases had a 250 WPI mesh supported across a 2.5 mm diameter aperture. In set (a) the detector-side endcap (indicated by arrow) featured a single 0.4 mm diameter aperture, while in set (b) this endcap was also covered by 250 WPI mesh. The traps labeled [1] were approximately concentric, while in traps [2] and [3] the ring and detector-side endcap aperture were increasingly misaligned. The alignment images were taken by a digital microscope (top-down view) with variable z-focusing, hence the pixels for the ionization-side mesh are partially subtracted wherever the bottom endcap was in focus.
Figure 3.8  Mass spectra collected with the traps described in Figure 3.7 in the double-resonance mode of ejection utilizing the octopolar nonlinear resonance near $\beta_z = 0.70$. The peak widths (FWHM) for $m/z$ 108 Th are given alongside each peak. A supplementary RF amplitude (bipolar mode) of 0.4 $V_{pp}$ was required in (a) and 0.6 $V_{pp}$ in (b) for best resolution. The test analyte was anisole, and the spectra are offset for better display.
Figure 3.9 Nonlinear resonance map obtained experimentally for the ‘misaligned’ aperture endcap trap detailed in Figure 3.7a(2) by sweeping the frequency of the supplementary dipole field at a constant amplitude of $0.4 \, V_{pp}$ (bipolar application) with $\beta_z$ increments of 0.0044 between each mass spectrum. The two major peaks in each spectrum belong to separate analytes, anisole (108 Th) and 4-fluoroanisole (126 Th). A soft ionization technique was used, hence there was only minor fragmentation. Note that the spectral baseline is masked by light coloration. The peaks that shift to later ejection times with higher $\beta_z$ are due to resonant or double-resonant ejection, while most of the stationary peaks are due to boundary ejection. There are several notable features, including a spurious peak [A] occurring just before boundary ejection. The frequency of this nonlinear resonance is around $\beta_z = 0.84$, as determined by the intersection of the resonantly-ejected peaks with the stationary ones near [B]. The dodecapolar resonances [C] are quite strong and it produces a larger signal near $\beta_z = 0.52$ than the octopole near $\beta_z = 0.70$ [D].
Figure 3.10 Mass spectra collected in the boundary ejection mode to confirm the presence of a strong nonlinear resonance near $\beta_z = 0.84$ that can cause spurious ejection when an aperture endcap is misaligned. (a) When both the ionization and detector-side endcaps are covered by mesh, only the expected molecular ion peaks for both analytes are observed (smaller protonated peaks at 109 and 127 Th are masked by poor resolution). (b) Spectra collected for traps where detector-side aperture endcap has no mesh. If the aperture endcap is aligned (black trace) there is no change. If the aperture endcap is misaligned (red trace) spurious peaks appear. Although not shown in this figure, the results for the ‘severely misaligned’ traps in Figure 3.7 (a3) and (b3) were the same as for the ‘misaligned’ traps.
Figure 3.11 Mass spectra of anisole collected at variable drive frequencies in 20 mTorr He under octopolar double-resonance ejection near $\beta_z = 0.70$ for an $r_0 = 0.500$ mm trap with mesh endcaps, a 0.650 mm thick ring, and 0.250 mm electrode spacing.
Figure 3.12 Typical effects of mass scan rate on mass resolution and analysis time at variable buffer gas pressures. Data was collected at 9 MHz drive RF with an $r_0 = 0.500$ mm trap with 0.600 mm thick ring and 0.300 mm thick spacer. Analysis was done on anisole peak at 108 Th under octopolar double-resonance ejection near $\beta_z = 0.70$. (a) Peak widths vs mass scan rate on a linear scale. Dashed line represents the relative ramp length (which is directly proportional to analysis time) compared to a scan rate of 1 Th/ms. (b) Resolving power vs mass scan rate, with both on a logarithmic scale for comparison to theory.
Figure 3.13 Peak width increase with pressure at different drive frequencies and buffer gas species (helium and nitrogen) using double-resonance ejection near $\beta_z = 0.70$ (supplementary RF retuned as needed). All other parameters were fixed, including geometry ($r_0 = 0.500$ ring at 0.650 mm thickness with 0.250 mm spacing) and the mass scan rate at 20.0 Th/ms. Analysis was performed on the 108 Th peak of anisole.
Figure 3.14 Mass spectra collected in the boundary ejection mode to qualitatively illustrate the shifting of the $\beta_z = 1$ stability boundary to lower $q_z$ values with increase in helium background pressure. The mass scan rate was calibrated to 20.0 Th/ms at 20 mTorr; no other experimental parameters were adjusted as pressure was increased except the ionization time to maintain an approximately constant signal level. Each spectrum shows the $m/z$ peak of 108 Th from anisole, with a minor shoulder from a small 109 Th peak. Experiment performed at 9 MHz drive RF at $r_0 = 0.500$ with a 0.600 mm thick ring and 0.200 mm electrode spacing (mesh endcaps).
Figure 3.15 Quenching of double-resonant ejected peaks when background gas pressure is increased without a corresponding increase in the supplementary RF amplitude. The peaks on the left are ejected via the octopole nonlinear resonance at $\beta_z = 0.70$, while ions that were insufficiently excited in amplitude are ejected at the $\beta_z = 1$ boundary (broader peaks on right side). The only experimental condition changed with the spectra was the helium pressure. The largest peaks belong to the molecular ion of anisole, 108 Th. The drive frequency was 9 MHz, $r_0 = 0.500$ mm, ring thickness was 0.600 mm, and electrode spacing 0.300 mm.
Figure 3.16 Effects of tuning the supplementary RF amplitude on peak width under double-resonance ejection mode at $\beta_z = 0.70$ for traps where $A_4/A_2 + A_6/A_2$ was greater than ca. $-11\%$. The amplitude was optimized for minimum peak width at each pressure, with a concurrent reduction in the boundary ejection signal level. Analysis was performed on the 108 Th peak of anisole with helium buffer gas at a 9 MHz drive frequency ($r_0 = 0.500$ mm, ring thickness of 0.650 mm, electrode spacing of 0.250 mm). The percent resonant ejection signal was computed as the integrated area of the resonantly ejected peaks relative to the total spectral signal area for that $m/z$ value (resonant and boundary). The resonant ejection signal did not reach 100% due to incomplete baseline subtraction and a charge-transfer reaction particular to this glow-discharge ionization source whereby ions are formed during the mass analysis ramp in between resonant and boundary ejection points (see §2.2.2).
Figure 3.17  Unfavorable tuning results of supplementary RF amplitude exhibited by traps where $A_4/A_2 + A_6/A_2$ was less than ca. −11%. At pressures above 20 mTorr the peak width increased as more ions were transitioned from boundary ejection to resonant ejection earlier in the ramp. Experimental conditions were identical to those in Figure 3.16 except that a different trap was used, with a 0.700 mm thick ring and 0.100 mm electrode spacing.
Figure 3.18  Typical example of mass spectral changes observed with increase in helium buffer gas pressure in different mass analysis modes. Peak at 108 Th corresponds to molecular ion of anisole. Trap ring thickness was 0.650 mm and electrode spacing was 0.250 mm for all spectra. (a) Spectra collected in double-resonance ejection mode via octopole near $\beta_z = 0.70$ with the supplementary RF amplitude reoptimized for pressure changes. (b) Spectra collected in boundary ejection mode.
Figure 3.19 Mass spectral peak widths obtained for all tested geometries in the double-resonance ejection mode of mass analysis via the octopole nonlinear resonance near $\beta_0 = 0.70$ for the 108 Th peak of anisole. The trace color corresponds to the ring thicknesses in the legend, while the electrode spacing value is used as the data point markers. Each trap geometry was evaluated at the same helium pressures through 500 mTorr, after which the interval and final stopping point varied. The error bars represent the confidence intervals at the 95% level for a Gaussian fit to the peak, from which the peak width was extracted.
Figure 3.20 Mass spectral peak widths obtained in the boundary ejection mode for some tested trap geometries, along with a comparison to the octopolar double-resonant ejection peak widths obtained with the same traps. Most other trap geometries not represented here exhibited significantly worse high-pressure performance in the boundary ejection mode.
Figure 3.21 The best spectral resolution obtained with the dodecapole nonlinear resonance at $\beta_z = 0.522$ (from the $2\beta_r + \beta_z = 1$ condition) in the double resonance ejection mode, compared to the octopole nonlinear resonance (at $\beta_z = 0.704$). Typically the resolution observed with the dodecapole resonance was inferior to the octopole, but for these two geometries it was better at low pressure.
Figure 3.22 Correlation of geometry optimization results to the $z_0/r_0$ ratio, showing (a) peak widths obtained at 20 mTorr and (b) the rate of peak width increase vs pressure in the double-resonance ejection mode (near $\beta_z = 0.70$). The rates correspond to the slopes obtained from linear fitting performed on peak widths collected above 250 mTorr (error bars are confidence intervals at the 95% level). Since the ring thickness shifts the field distribution, the performance is offset across different $z_0/r_0$ values.
Figure 3.23 Contour plots of peak width (FWHM) variation in the double-resonance ejection mode near $\beta_z = 0.70$ for CITs with different ring thicknesses and electrode spacing. The peak widths increased with helium background pressure, but with an accompanying shift in the minimum to geometries with larger $z_0$. The contour line increment is 0.025 Th. The data points are mapped directly to the color scale, and interpolated values are smoothed.
Figure 3.24 Contour plot of slopes of the curves in Figure 3.19 at pressures above ca. 250 mTorr where the peak width increases linearly with pressure for most geometries. The trend appears to be interrupted by a couple of the traps of lower $z_0$ (e.g. the 0.600 mm ring at 0.200 mm spacing) but this is not actually statistically significant (the estimated error typically spans multiple contour lines, which are incremented 0.05 Th/Torr; see Figure 3.22b). Smoothing is applied to interpolated values between discrete data points.
Figure 3.25  Contour plot of peak widths (FWHM) obtained in the boundary ejection mode at 20 mTorr for 19 of the 20 evaluated geometries. The trend and minimum values are very similar to those determined for the octopolar double-resonance ejection mode (see Figure 3.23a). Smoothing is applied to the interpolated values. The contour lines are incremented by 0.05 Th.
Figure 3.26 Two possible methods for quantifying the spectral space charge limit with CITs. The total number of ions stored in the trap is directly proportional to the integrated spectral signal. (a) Mass shift error relative to the peak position with fewest stored ions in trap (peaks shifted to greater apparent mass). Each curve had two linear regimes with different mass shift rates. (b) Increase in peak widths due to greater space charge levels. The rates for the m/z 126 ion are different in both cases due to lower space charge after the ejection of m/z 108 ions.

Experimental conditions: \( r_0 = 0.500 \text{ mm}, \ 0.600 \text{ mm} \) ring thickness, 0.300 mm electrode spacing, 9 MHz drive frequency, 17 mTorr helium background pressure. The molecular ions of anisole (108 Th) and 4-fluoroanisole (126 Th) were analyzed, generated with a glow-discharge ionization source. Trap operated in double-resonance ejection mode utilizing the octopolar nonlinear resonance near \( \beta_z = 0.70 \).
Figure 3.27  Space-charge-limited ion storage capacity of CITs as a function of $z_0$, including ring thickness and electrode spacing. The maximum signal corresponds to the total integrated spectral area when the trap was saturated with charge. The double-resonance ejection mode was used near $\beta_z = 0.70$. Experiments were performed at 10 mTorr of helium background pressure, 7.5 MHz drive RF, and xenon as the analyte, with $r_0$ fixed at 0.500 mm. A hot-cathode EI source was employed at 70 eV of energy.
CHAPTER 4
CORRELATION OF PERFORMANCE WITH CIT FIELD COMPOSITION

While the experimental optimization results and characterizations in the previous chapter can be used to guide the selection process of the most appropriate CIT for various applications, the focus on physical dimensions restricts the options to the particular geometric parameters investigated. In order to generalize the results beyond traps with straight-walled ring electrodes and mesh endcaps, a separate treatment in terms of the electric field composition is necessary. By attributing the performance changes to certain low-order multipole components and assuming negligible secondary effects from higher-order fields, the present data may be useful in designing traps with alternative electrode geometries, such as those possessing aperture-style endcaps or non-cylindrical ring electrodes. Additionally, after relating the performance trends to specific multipoles, the influence and behavior of the electric field is better understood.

4.1 Higher-Order Fields

In the context of QIT geometry and mass spectral performance, much work in the literature is directed towards maximizing electric field linearity, with the ideal case being a pure quadrupolar field. Although the CIT is inherently a nonlinear device, a focus on field linearity is still relevant because higher order fields are quite weak near the centers of typical CITs (see § 1.3). Consequently, even though ion motion is perturbed by nonlinearities, QIT theory can be directly carried over to describe and predict CIT behavior.
While field linearity is more closely examined in §4.2.3, it is useful to begin the discussion of field composition and the resulting effects on performance by comparing the experimental results of Chapter 3 with field linearity trends in geometry parameter space.

4.1.1 CIT Field Linearity

The overall field linearity varies with CIT geometry due to the positive and negative superpositions of higher order fields. These nonlinear terms dominate the field strength close to the electrode surfaces, where an evaluation of linearity is not as meaningful. On the other hand, since ions reside primarily within a narrow spatial distribution at the center of the trap for most of the time leading up to excitation and ejection, the cumulative effects of this central semi-linear region can be expected to have a large influence on performance. Under typical circumstances, the ion trajectories are unlikely to extend beyond about halfway along the axial dimension (z/z₀ = 0.5) except for the final few oscillation cycles before leaving the trap. The z-axis can be taken as representative of field linearity in this space if the ion cloud is small and considering that mass analysis is not performed in the radial dimension.

The degree of field linearity for the geometries from the high-pressure optimization study (see §3.1) was determined with coefficient of determination (R²) values from least-squares linear fitting of the electric field for each trap. The axial electric field was computed in SIMION 8.1 and exported to OriginPro v9.1 for linear fitting, with the results shown in Figure 4.1. From one perspective, it may appear that the fields are highly linear in all cases, given that the R² values are close to unity (no less than 0.9984). Yet, the relatively small differences lead to a clear trend with geometry that closely matches the experimental performance results presented in Chapter 3. This includes the peak widths obtained at
20 mTorr in the octopolar double-resonance ejection mode (Figure 3.23a) and under boundary ejection (Figure 3.25), with the minimum peak width valleys positioned where the greatest field linearity is observed (along the $R^2 = 1.0000$ contour of Figure 4.1). This suggests that under low damping conditions, both mass analysis modes benefit from operating with an electric field that is close to purely quadrupolar, despite relying on significantly different ejection mechanisms. However, as the background gas pressure increases in Figure 3.23, the peak width minimum contour shifts to higher $z_0$ values, which corresponds to fields with increasing nonlinearity. Likewise, a comparison of the trend in the rate of peak width increase versus pressure (Figure 3.24) to the variation in field linearity (Figure 4.1) shows a strong correlation, where greater nonlinearity appears to lower the rate at which the peak width increases.

The consistent relationship with experimental results also illustrates that the field nonlinearity at high versus low $z_0$ geometries is not equivalent, in that only the higher-order field contributions obtained with larger $z_0$ traps were beneficial against greater damping. The question becomes, then, what are the specific aspects of the nonlinearity that affect performance? To answer this, the different trapping fields can be broken down into the constituent multipoles, which can then be correlated with different performance metrics either individually or in limited combination.

4.1.2 Multipole Composition Determination

The multipole coefficients for the $r_0 = 0.500$ traps from the high-pressure geometry optimization study were introduced in § 3.1.1, with the raw values for some of the terms given in Appendix B. This section covers the computational methods employed and their accuracy. The mathematical definitions and background theory for multipole components,
which can be used to describe the electric field of any arbitrary geometry via an infinite
polynomial expansion, are provided in §1.3.1.

A numerical approach was taken to determine the multipole coefficient values, with
the electric potential of each geometry first calculated using SIMION 8.1, wherein the
endcap electrodes were set to 0 V, the ring electrode set to 10 kV, and the convergence
objective set to 0.1 μV. The 200 WPI mesh endcaps were modeled as simpler solid
electrodes that had no openings, and all the electrodes were truncated at a 3 mm radius
from the trap center. The resultant 3D potential array had a spatial resolution of 1 μm. The
geometries included ring thicknesses between 0.400 to 1.000 mm with a 0.025 mm step size,
and symmetric ring-endcap spacings between 0.025 to 0.600 mm (also incremented by
0.025 mm). Due to the rotational symmetry, a 2D cross-section of the potential array was
directly extracted into the (r, z) domain with a 95% boundary in each dimension from the
trap center. A nonlinear surface fit was performed on the data using the Curve Fitting
Toolbox of MATLAB R2014b for the first 26 multipole terms in the polynomial generated
by eq 1.33 (with the highest even coefficient being A_{24}).

The numerical fitting error for the coefficients in Appendix B is not reported
because it was significantly lower than the error introduced by trap fabrication and
assembly tolerances. The accuracy of the coefficients for multipoles that do not have a
strong presence near the center of the trap (terms higher than about A_8) is expected to be
poor, but their inclusion in the fit improves the accuracy of the lower-order terms, which
are the focus of this study. It would be necessary to include terms of much higher order to
accurately fit the multipoles comprising the fringing trap fields, especially if the mesh was
modeled realistically. This is demonstrated in Figure 4.2, which compares the actual electric
field magnitude of a trap (a) to fields that are calculated from the polynomial terms of
eq 1.33 (converted from potential to field magnitude) with coefficients obtained under
different fitting conditions. In Figure 4.2b the field was calculated using coefficient values
for $A_0$ to $A_{24}$ as returned by fitting the innermost 95% of the electric potential surface of (a),
while the field in (c) was calculated with coefficients up to $A_{30}$ from a fit of 100% of the
original potential data. It is clear that the field contours of both (b) and (c) are different
from (a) in the vicinity of the trap electrodes, but with fewer noticeable deviations in (c)
due to a more complete fit. However, in all cases the field in the central half of the trap was
consistent, and the multipole coefficient differences between (b) and (c) were low for the
first few terms, diverging with greater multipole order ($\Delta A_2 = 0.00\%, \Delta A_4 = 0.08\%$,
$\Delta A_6 = 0.16\%, \Delta A_8 = 3.7\%, \Delta A_{10} = 14.8\%, \Delta A_{12} = 28.2\%$, etc.). Therefore, while it would be
inappropriate to analyze trap performance with reference to high-order coefficients, the
accuracy of the lower terms is sufficient (the present study only considers terms up to $A_8$).
Since the least-squares fitting is computationally intensive, including more multipole terms
to improve accuracy is an unnecessary tradeoff here. A separate internal validation against
published data found excellent agreement with the methods used by Wu et al.\textsuperscript{111} and
Tallapragada et al.\textsuperscript{112} for the multipoles of interest (lower order terms).

4.1.3 Multipole Significance

The benefits and influences of the lower-order multipoles (particularly the octopole)
are well established in the literature (see § 1.3.2 and § 1.5.2) and as such they are prime
candidates for optimizing ion trap performance. However, with simple electrode
configurations like the CIT these terms are not independently controllable — the field
includes a multitude of higher terms of which many are strongly linked to changes in
major geometry features (e.g. ring thickness and electrode spacing). Based on the published
characteristics of the lower-order multipoles and their prominence among the geometries that were experimentally evaluated in the present study, it is reasonable to limit the correlation analysis in this chapter to these terms.

As stated previously, after the quadrupole only the lowest-order multipoles typically have a strong presence in the center of the trap, where ions are located most of the time during mass analysis. The polynomial terms of the higher-order multipoles involve high exponential powers, so that their actual contribution to the field is only significant at large displacements from the center of the trap. As an example, the components of the electric field in the axial dimension ($E_z$ along $z$-axis from 0 to $z_0$) of Figure 4.2c can be plotted for the individual multipole terms, as done in Figure 4.3. It can be seen that the linear quadrupole field ($A_2$ coefficient) has near exclusive control over the first quarter of the axial dimension, with the octopole ($A_4$) and dodecapole ($A_6$) becoming substantial around the halfway point. It is only in the last quarter of $z$ that the highest-order terms become dominant among the nonlinear fields (terms near $A_{30}$ are likely grossly inaccurate due to the regression limitations covered in the previous section). The fields of all the traps from the high-pressure geometry optimization study have a similar arrangement, as compared in Figure 4.4 for the $A_4$, $A_6$, and $A_8$ terms, where again the octopole is strongest, followed by the dodecapole and then the hexadecapole. The octopole field is positive in all cases (increasing the strength of the quadrupole) while the dodecapole fields are all negative, suggesting that some degree of compensation between these terms is possible. Given that the dodecapole field strength does not vary as much as the octopole, and that the hexadecapole and higher fields are generally far removed from the trap center, it can be surmised that the octopole will have the biggest effect on
performance. These inferences are examined later in the chapter with respect to various interpretations of multipole activity.

The coefficient values for the octopole, dodecapole and hexadecapole fields (relative to the quadrupole) of mesh-endcap CITs are shown as surface plots in Figure 4.5 across a broad range of parameter space (as described in § 4.1.2). Although the $A_6$ and $A_8$ coefficients have an appreciably inverse relationship, the different spatial distributions of their electric fields only leads to strong compensatory interaction far from the center of the trap (as Figure 4.4 shows). The hexadecapole is included in the correlation analysis for better contrast with the octopole and because its status as a midrange field has less determinate consequences for performance based on the aforementioned assumptions. This vast array of geometries was reduced to a smaller subset (bounded by the gray box in the figure) for the purposes of experimental testing through the selection process covered in § 3.1.1, which included practical considerations such as trap capacitance and ejection voltage limitations. The coefficient values and trends from this subset are shown as contour plots in Figure 4.6. Negative octopole contributions are known to be deleterious to performance (as confirmed in the preliminary low-pressure geometry study), hence the lack of experimental data points (round markers) in the gray region of Figure 4.6a. Conversely, the dodecapole coefficients in panel (b) are all negative, in accordance with the fields of Figure 4.4, while the hexadecapole in panel (c) has a single negative coefficient. The wider contour line spacing of the dodecapole and hexadecapole coefficients shows that they do not vary as much as the octopole for these geometries. Since these coefficients are mapped in the same geometry space as the contour plots of experimental performance in Chapter 3, it is interesting to note that the trend direction of the octopole contour lines in panel (a) is very similar to those in Figures 3.23, 3.24, and 3.25, portending the outcome of a correlational
analysis. This also applies to panel (d) where the $A_4$ and $A_6$ values are added together based on the model used by Wu et al., which is explored in §4.3.1. The fact that none of the coefficient values in Figure 4.6 have abrupt deviations with changes in geometry, but instead vary smoothly, supports the assertion in §3.4.2 that local extrema are unlikely for interpolated peak width values in the contour plots.

Ideally, all ion traps could be designed without any geometric constraints on the trapping fields. Trap geometry optimization is an indirect means of changing the multipole distribution and performance. Simplified electrode shapes are among the least-suitable options for fundamental studies, wherein it is both difficult to ascertain the influences of multipoles on an individual basis and to optimize the beneficial ones while minimizing those with harmful effects. A possible alternative to defining the trapping fields strictly via geometry is to employ arrays of independent electrodes, such as with the planar Paul trap in which two opposing plates are segmented into many concentric rings. A high degree of control has been demonstrated over the lower-order multipoles using this electrode system, with the ability to freely tune them during experiments by simply adjusting the ring voltages. However, the higher-order multipole contributions (e.g. $A_{10}$ and $A_{12}$) are extremely large for these devices, exacerbating the problem of knowing if and how these terms are interfering. Although the selection range of multipoles is far more limited with the CIT, there is not as much uncertainty regarding performance. Moreover, the CIT is highly practical and already capable of providing good selectivity and sensitivity. Even if the exact ion dynamics are not understood, the results of an empirical mapping approach are still applicable. Correlating performance with multipole components is useful for more conclusively identifying optimization endpoints as well as simplifying the optimization process for traps that require different geometric parameters.
4.2 Individual Multipole Effects on Mass Analysis

Due to the complex and nonlinear relationship between mass spectral performance and the strengths of higher-order fields, as well as possible multipole interdependencies and the necessary high-pressure collisional damping considerations, there does not yet exist a realistic model that ties them together. Thus, quantitative multidimensional correlations would not be particularly meaningful at this stage. Instead, the results in this section are again presented as qualitative correlations by way of 2D contour plots that can be readily surveyed. By separating the coefficients on two independent axes, concurrent influences can be observed without making any assumptions about multipole interactions.

4.2.1 Spectral Resolution

Given that most of the experimental results were obtained in the double-resonance ejection mode utilizing the octopolar nonlinear resonance near $\beta_z = 0.70$, the contour plots were constructed to always show trends with the $A_4$ coefficient compared to one of the other terms ($A_6$ or $A_8$), relative to the strength of the quadrupole ($A_2$). At the very least, changes in the octopole field strength should affect its own resonances. The peak width results from the high-pressure geometry optimization study (same as the data presented in Figure 3.23 and discussed in §3.4.2) are replotted versus the coefficient values of $A_6$ and $A_4$ in Figure 4.7 and versus $A_8$ and $A_4$ in Figure 4.8. As before, the interpolated contour values are lightly smoothed, while the colors of the overlaid round markers correspond to the exact peak widths obtained with the tested geometries. In both cases, a clear trend is seen with the octopole coefficient at all background pressures. At 20 mTorr, values of $A_4$ around 6−9% gave the best resolution. With greater damping, the minimum peak widths shifted to geometries possessing stronger octopole fields: by 400 mTorr the resolution was best with
$A_4$ around 10–12%, while at 700 mTorr the ideal range was approximately 14–16%. The octopole is strengthened when $z_0$ is increased via either the ring thickness or electrode spacing, as illustrated by the additional traces in panel (h) of each figure. The $A_6$ coefficient appears to have much less of an effect on resolution in Figure 4.7, but this is due in part to its smaller range of values compared to the octopole. In general, resolution improved with more positive $A_6$ values, as evident by the tilted contour lines. At some of the pressures (panels b–f) the contour lines are closed, indicating a possible minimum with dodecapolar strength. However, considering an estimated experimental uncertainty of at least one contour line (0.025 Th) and the wrap-around edge effects caused by interpolation near the data boundary, this minimum is not considered significant. These edge effects also make it difficult to discern if the hexadecapole has a real effect on resolution in Figure 4.8, where the data boundaries are even closer together. Within this fixed system of CIT parameters, the covariation of the multipole coefficients with one another diminishes the significance of their correlation with performance. Consistent trends with other performance aspects would help to establish more definitive links.

An examination of the rates at which peak widths increased versus pressure with respect to the lower-order coefficients shows a similar trend as before. The data from Figure 3.24 is replotted versus $A_6$ and $A_4$ in Figure 4.9a and versus $A_8$ and $A_4$ in Figure 4.9b. Again, there is a clear trend with the octopole field: the rate consistently decreased with larger $A_4$ coefficients, from a maximum of ca. 1.2 Th/Torr around 2–3% to an eventual inversion to a value of ca. −0.1 Th/Torr near 20%. As discussed in §3.4.2, this change in rate corresponds to peak widths measured above 250 mTorr in an effort to only characterize the linear portion of the curves from Figure 3.19, and the change in rate is likely due to an extension of the typical low-pressure nonlinearity to higher pressures for the geometries.
with large octopole contributions. It is expected that at high enough background pressures, the peak width broadening rate would be the same for all geometries. The dodecapolar coefficient in (a) appears to affect the rate as well, with the overall contour gradient showing a decrease in rate with more positive $A_6$ values. The hexadecapole coefficient in (b), on the other hand, does not seem to be correlated with the rate.

The results presented in this section so far were obtained in the double-resonance ejection mode, such that the octopole resonance $\beta_r + \beta_z = 1$ could directly exert influence on performance. In the boundary ejection mode the multipoles have a less direct role, but they are no less important. The boundary ejection results collected at 20 mTorr (see Figure 3.25) are replotted versus the lower-order coefficients ($A_6$ and $A_4$ in Figure 4.10a and against $A_8$ and $A_4$ in Figure 4.10b). Compared to the double-resonance mode peak widths in Figure 4.7a, the trends with the $A_4$ and $A_6$ terms are nearly identical: there is a clear minimum with octopole strengths between 6–9%, and the peak width is slightly narrower with more positive $A_6$ values. Due to the lack of any real correlation with the $A_8$ term yet again, it can be relegated fairly conclusively to the same status as all the other higher-order fields. That is not to say that it is inconsequential, but as a first approach to optimizing CIT fields it can be safely discounted in favor of the more active octopolar and dodecapolar terms.

### 4.2.2 Supplementary Dipole Strength

The supplementary dipole requirements for double-resonance ejection are interesting to examine because they provide useful hints about ion dynamics and the ejection process. However, this data set is just another piece of the puzzle in understanding the performance trends seen with nonlinear fields and does not explain things by itself. The
purpose of a supplementary dipole field in performing double-resonance ejection is covered in § 1.3.4. When tuning the supplementary dipole field strength, the typical value of interest is where the peak width is minimized. However, since the minimum occurs over a range that broadens with damping (see § 3.3.2), it is simpler to report the field strengths at which resonant ejection first begins (this point can be precisely determined without requiring extensive peak fitting).

The supplementary dipole field strengths required to start ejecting ions via double-resonance ejection near $\beta_z = 0.70$ are given in Figure 4.11 as a function of helium background pressure and the octopolar and dodecapolar coefficients. The field strength values are based on an assumed ideal electric dipole established between the endcaps, such as with infinite parallel plates, and was computed as the quotient of the supplementary RF amplitude (applied in bipolar mode to each endcap) and the $z_0$ of each trap. The trends are noticeably different than those seen for peak width. There is a maximum in field strength that does not coincide with the position of the peak width minimums in Figures 4.7 and 4.9, and the field strength requirements appear to be strongly affected by both the $A_4$ and $A_6$ coefficients. The dodecapolar trends are consistent with the supplementary dipole requirement changes observed with aperture-endcap versus mesh-endcap traps: for a geometry where all other parameters are fixed, a switch from mesh to aperture endcaps induces a more negative dodecapole which is accompanied by the need for lower dipole field strengths. Simulation work performed by Franzen showed that a stronger dipole field is necessary to resonantly eject ions from a trap that has a small octopole superposition (2%) compared to a purely quadrupolar trap, caused by the formation of a stabilizing beat frequency. While this same increase in dipole strength is seen for the CITs here, there is an unexpected drop in dipole field strength for octopole coefficients above ca. 12% at
20 mTorr, suggesting a major change in ion motion. With higher pressures, however, the
dipole field strength is increasingly spread out. This supports the view that as nonlinear
resonances are damped out at high pressure, thus precluding double-resonance, the
different trap geometries have a more uniform ejection process via the standard
supplementary dipole resonance mode.

4.2.3 Field Linearity

It is appropriate to revisit field linearity, which is the central construct for mass
analysis with ion traps. Its variation with geometry, as discussed in § 4.1.1, showed that
both the double-resonance and boundary ejection modes benefit from a more linear central
trapping field, while some nonlinearity improved resolution at high background pressure.
Strong performance trends were demonstrated for the octopole in § 4.2.1, and to confirm
that it is also connected to axial field linearity, the $R^2$ values used in Figure 4.1 can be
converted from geometry parameter space to the $A_4$ and $A_6$ components, as done in
Figure 4.12. A familiar trend can be seen within the white data boundaries. The field
linearity is greatest in the octopole coefficient range of about 6 to 10%, which is also where
the best resolution was observed at 20 mTorr. Outside of this range, the field linearity
continuously decreases. It is interesting to note that for a given octopole strength, a weaker
dodecapole field corresponds with increased nonlinearity. This indicates that without the
negative dodecapole field, CITs with strong octopole superpositions (ca. 8%) would not be
as linear as they are. From another perspective, if the negative dodecapole was not present
in CITs, it is likely that the best performance would be found with weaker octopole
contributions, just as QIT devices typically only have weak octopole fields added to
enhance performance. The interrelation of these fields is investigated in the next section to determine the merits of simpler rules for optimal geometry selection.

4.3 Simplification of Analysis

Although correlation alone is insufficient to establish causality, any argument against the predominant influence of the octopole and dodecapole fields on CIT performance would have to be built on one or more of the other multipoles instead, for which there is less evidence. To avoid ambiguity, this statement should not be read as a dismissal of the effects of higher-order multipoles, only that they appear to be secondary in CITs. This is not a new position, but one already well-considered in the literature. However, a full explanation of the mechanics behind the octopole and dodecapole has not yet been developed. To aid in this endeavor, the relationship between them can be explored more explicitly.

4.3.1 Field Compensation

As done earlier with field linearity, this discussion assumes that characterizing the electric field along the trap z-axis is a reasonable model for the overall conditions that ions experience throughout their trajectories. Although the octopole and dodecapole have different numbers of electric poles that vary across r-z space, they are aligned and have maximum overlap along the axis of symmetry. For CITs, the magnitude of the $A_6$ coefficient is typically larger than $A_4$, but this does not necessarily mean the dodecapole field is stronger. Rather, as dictated by their polynomials, toward the center of the trap the octopole will be stronger even if the dodecapole coefficient is much larger. Figure 4.13 provides an example of their relative strengths in pure form. When the coefficients are the same, the octopole is stronger until the last 30% of the axial dimension, and when the
The dodecapole coefficient is twice as large, the octopole is still stronger through the halfway point. The two fields have the same sign in this case, but the dodecapole is negative for all practical CIT geometries. Although their shapes are not the same (the octopole field increases as $z^3$ and the dodecapole as $z^5$), they are similar enough that there is approximate compensation. Wu et al. have taken advantage of this by disregarding the polynomial differences in order to simplify the CIT trapping field to a single variable composed of the sum of the coefficients relative to the quadrupole ($A_4/A_2 + A_6/A_2$). An alternative to this is to use the ratio $A_4/A_6$, which makes no assumptions about field shape but fails to take into account the absolute strength of the terms.

It is instructive to examine how these simplifications describe the superimposed field shapes. In Figure 4.14 the axial electric field due to just the octopole and dodecapole is computed using the coefficients of the geometries from the high-pressure optimization study (see Table B.2), producing a wide range of field strengths. The field trace colors are set by their value according to the simplified coefficient models, with the coefficient sum applied in (a) and the ratio in (b). The summation predicts the field strength order reasonably well but with a few obvious deviations, especially on the lower end of the scale (under $-10\%$), while the ratio sorts them almost exactly. In both sets, the classification far from the center of the trap is less and less accurate as the polynomial functions diverge. Although most of the summation values are negative, the field strength near the center of the trap is always positive because the octopole is stronger there. Thus, the $A_4 + A_6$ scale is somewhat ad hoc and only the relative differences have meaning. If the field shapes were identical then a coefficient sum of 0\% would result in perfect cancellation. Likewise, despite the efficacy of the ratio for these particular geometries, it only applies because the
coefficients have similar magnitudes. The same ratios can be obtained with much weaker or stronger fields, but the performance would surely be different.

The total axial electric field for each of the geometries from the high-pressure study is given in Figure 4.15, as well as the nonlinear contribution to that field (total electric field minus the quadrupolar portion). These are the same fields for which linear fitting was performed in sections 4.1.1 and 4.2.3 (except for the normalization), and it can be seen here that all the traps are highly linear for the first 20% of \( z \), with significant stratification by 50% (which was the arbitrarily chosen fitting limit). The trace colors correspond to the coefficient sum values to show that this simple model is reasonably suited to predict the relative field strength through the midrange section. Ideally, it would be possible to accurately translate all the field details into a single value that could be correlated with spectral performance, and the summation model is a good first approach.

4.3.2 Interpretations

The treatment of the octopole and dodecapole coefficients as a summed value to distinguish trap geometries originated in previous CIT optimization work by Wu et al.\textsuperscript{111} It is based on a field linearity model by Plass et al. that explains chemical mass shifts in QITs, wherein unwanted ion ejection delay is attributed to a decrease in field strength near the endcap electrodes due to holes.\textsuperscript{96} Consequently, in considering the effects of the octopole and dodecapole fields on CIT performance, Wu et al. emphasized their interaction and compensation in the regions adjacent to the endcaps. However, there is evidence to suggest that the field linearity closer to the center of the trap is more important for CITs.

As shown earlier in Figure 4.3, the fringing fields are dominated by higher order multipoles. Therefore, a discussion of field linearity near the endcaps should not rely on
just the lower order terms (i.e. the sum of the octopole and dodecapole coefficients). For instance, the investigation by Plass et al. found that terms on the order of $z^{22}$ are necessary to account for endcap holes. Since spectral performance in CITs is adequately described without invoking such high-order terms, they are probably less important. The issue of endcap apertures is often substantial with CITs because the hole size is disproportionately larger to improve ion transfer efficiency. Nevertheless, it has been observed that even dramatic changes in field strength close to the endcaps due to aperture size does not necessarily affect performance. As an example, the axial field strength for a CIT with three different endcaps is shown in Figure 4.16. A change from solid/mesh endcaps (blue curve) to those with apertures leads to a considerable drop in field strength beyond $z/z_0 = 0.6$, yet these specific traps were found to give equivalent resolution in numerous experiments. This is also true of the hybrid-endcap traps used in the alignment experiments (compare a1 to b1 in Figure 3.8), where switching the detector-side endcap from mesh to an aperture had an insignificant effect on resolution. This is not the case for all trap geometries, but the lack of consistency indicates that it is necessary to look at other field aspects as well.

As discussed in §4.2.3, the intermediate field linearity appears to be critical for performance in both the boundary and double-resonance ejection modes at low pressure. Ions that are stored in a more linear field have better coherency, leading to tighter distributions. In the double-resonance mode, these coherent ion packets can be excited onto a nonlinear resonance for rapid ejection from the trap, thereby minimizing interferences at the extremities. In the boundary ejection mode, the coherency of the ions is subject to greater disruption by higher-order fields during the more gradual increase in amplitude, hampering resolution to a wider extent.
Regardless of the true nature behind the interplay of the octopole and dodecapole fields, the experimental results from the present study are in good agreement with the empirical rule of Wu et al. that a value of $A_4/A_2 + A_6/A_2$ around $-10\%$ provides optimal resolution for both the boundary and octopolar double-resonance ejection modes at low pressure. To see how the simplified designation compares to the independent 2D correlation of the coefficients, they can be plotted together. This is done in the context of boundary ejection performance at 20 mTorr in Figure 4.17. The light gray traces demarcate constant summation values in (a) and constant ratio values in (b). In both cases, the overlaid coefficient traces are approximately parallel to the contour lines, so that the trend in peak width follows the coefficient relations. However, the ratio follows the trend much more consistently, with the best resolution found close to the $-50\%$ line; with the summation, the best resolution lies in the range of $-10\%$ to $-8\%$. Despite the better fit of the ratio, it is less likely to be applicable outside these specific parameters. For example, a ratio of $-50\%$ could be achieved with $A_4/A_6$ values of $+8/-16$, $-8/+16$, and $+50/-100$, all of which are very different fields. Therefore, the ratio should not be applied for traps with fields far beyond the typical CIT range.

4.4 Combined Multipole Parameters

In this section, various performance trends of the double-resonance mode utilizing the octopole (near $\beta_z = 0.70$) are examined with respect to the sum and ratio of the $A_4$ and $A_6$ coefficients, as well as $A_4$ alone. By directly comparing these functions and their assumptions, the combined influence of the octopole and dodecapole is further demonstrated. The experimental results are also presented in a different plot format for a more detailed view.
4.4.1 Spectral Resolution

The peak widths obtained at 20, 250, and 500 mTorr of helium background pressure, as well as the rates at which they increased with pressure, are shown as a function of $A_4/A_2 + A_6/A_2$ in Figure 4.18, as a function of $A_4/A_6$ in Figure 4.19, and as a function of $A_4/A_2$ in Figure 4.20. The data points are color-coded according to ring thickness, and larger values on the abscissa for each ring are due to wider electrode spacing in these three plots. The trends are the same in all cases. As with the contour plots in § 4.2.1, there is a peak width minimum that shifts as the background pressure increases. For the coefficient summation in Figure 4.18b, the best resolution at 20 mTorr is approximately in the range of $-10\%$ to $-7\%$, which is also where it was best for the boundary ejection mode, and is consistent with Wu et al.\textsuperscript{111} At 250 mTorr the minimum occurs over ca. $-6\%$ to $-4\%$, and then extends to $-1.5\%$ by 500 mTorr. As shown in panel (a), the peak widths at the positive end of the scale broaden the slowest, even decreasing for sums around $+7\%$, but are coincident with a large increase in peak width at 20 mTorr. Below $-5\%$ the rate of increase is practically the same. The values over which these features occur with the coefficient ratio and the strength of $A_4$ are not enumerated here, but are evident in the respective figures.

Given that all of the trends in peak width and their rate of increase are observed with the octopole coefficient alone in Figure 4.20, it is clearly the main driver of performance for these CITs. However, by accounting for the strength of the dodecapole field, deviations in the curves are reduced. This is particularly true when the coefficients are treated as a ratio in Figure 4.19, where the curves are dramatically smoother. By itself, this could be misinterpreted as an indication that the relative strength of the octopole and dodecapole is instead the main factor for resolution, when in fact this ratio simply happens
to be strongly correlated with the strength of the octopole, as shown in Figure 4.21a. This stems from the intrinsic properties of the CIT geometry whereby the multipoles do not vary independently, and partly from the smaller range of $A_6$ values (if the dodecapole strength was fixed, then any change in $A_4/A_6$ would be due to the octopole only). Thus, the ratio is tied to performance due to the correlation with the octopole strength, and the trend is smooth because the ratio also relates the octopole and dodecapole without making any assumptions about how they interact. The summation necessarily assumes that the fields have the same shape—when plotted versus the ratio, as done in Figure 4.21b, it is evident that the biggest discrepancies occur when the octopole is relatively weak compared to the dodecapole (sums below ca. −8%, where the octopole-to-dodecapole ratio is less than half). This is also where the curves in Figure 4.18b are the most irregular.

Based on the observation that the greatest peak width fluctuations occur at high pressure when the strength of the dodecapole is not taken into account (in comparing the 20 mTorr curve to 250 and 500 mTorr in Figure 4.20b), it appears that the dodecapole has a stronger effect under high damping conditions. It is believed that at low pressure, resolution is primarily contingent on the quality of the octopolar nonlinear resonance, which is not disturbed much by the dodecapole (and even less by higher terms). However, at high pressure the nonlinear resonances are damped out, and the octopole improves performance by increasing the restoration force on the ions, which is known to stabilize them (see § 1.3.2). In this case, the negative dodecapole behaves counter to the positive octopole by decreasing the restoration force, which is an aggregate of all the fields.

A stronger octopole field does not continually improve resolution, but has an optimum value that varies with damping. The principles of nonlinear resonance (§ 1.3.3) were derived for weak superpositions of higher-order terms, and Wang et al. noted that
excessively strong multipole fields may lead to chaos and unexpected effects. Some of the experimentally evaluated geometries have octopole weights near 20%, which is perhaps too high for standard consideration under the existing perturbation theory. Ultimately, resolution depends on the coherence of the ion secular frequencies, and it is not yet understood how the dynamics of the octopole and dodecapole change with pressure to narrow the frequency distribution.

4.4.2 Supplementary Dipole Strength

Changes in the supplementary dipole field strength requirements can be used to indicate variation in the trapping field due to higher-order multipoles, especially since excitation energies for double-resonance ejection are affected by more than just the pseudopotential well depth. As discussed in § 4.2.2, the supplementary dipole does not follow the same trends as peak width; therefore, it offers another method of comparing the octopole and dodecapole coefficient relations.

The supplementary dipole field strengths (as needed to start ejecting ions via double-resonant ejection near $\beta_z = 0.70$) from Figure 4.11 at pressures of 20, 250 and 500 mTorr are replotted as a function of $A_4/A_2 + A_6/A_2$ in Figure 4.22a, as a function of $A_4/A_6$ in Figure 4.22b, and as a function of $A_4/A_2$ in Figure 4.22c. Once again, as with peak width, the trends seen with the coefficient sum and ratio are identical to those seen with just the octopole coefficient. Using the coefficient summation in plot (a) as an example, the dipole field strength at 20 mTorr is observed to increase nonlinearly with sums up to approximately $-4\%$, after which it quickly decreases. However, at higher pressures the trend becomes more continuous, so that by 500 mTorr the dipole field strength appears to increase linearly with the coefficient sum, suggesting a change in the mechanism by which
ions are ejected. Recalling Figure 4.18b, at low pressure (20 mTorr) the minimum peak widths occur between about −10% to −7%, which is on the rising edge of the maximum dipole strength in Figure 4.22a; at more positive coefficient sums the peak width increases without any apparent deviations concurrent with the drop in dipole strength. The fact that the supplementary dipole strength needs to be increased with the octopole field is consistent with the view that greater energy is required to excite an ion from the center of a trap with a deeper well depth, but the subsequent decrease in strength indicates that there is more at play.

The greatest deviations in the supplementary dipole trend are seen in Figure 4.22c, where only the octopole coefficient is considered. Trap geometries with different ring thicknesses can have the same octopole field strength with an adjustment in electrode spacing, but the dodecapole coefficients (and other multipoles) will be different, and this leads to the shifts between the curves of different rings in the plot. When the dodecapole field strength is accounted for by either the coefficient sum in plot (a) or ratio in plot (b), the trend in dipole strength becomes better defined, particularly at 20 mTorr. The curves with the coefficient sum are not as spread out as the ratio, however, since the sum also evaluates the multipole strengths relative to the quadrupole.

For a more complete picture of supplementary dipole changes, the field strengths required for optimal resolution at 20 mTorr, as well as the strengths at which the entire ion population is transitioned from boundary ejection to double-resonant ejection near $\beta_z = 0.70$ (see §3.3.2), are given in Figure 4.23 as a function of the octopole and dodecapole summation. For trap geometries with coefficient sums below −8%, the dipole field strength for optimal resolution was coincident with the cessation of boundary ejection. At sums above ca. −4%, though, the differences between the curves drastically increases, again
underscoring a major change in resonant dynamics. Additionally, the dipole field strength needed for optimal resolution increased linearly with background pressure for all of the geometries with sums below −4%, but was generally independent of pressure (in the experimentally tested range) for geometries that were more positive (data not shown).

4.4.3 Survey of Geometry Optimization Results

The ability to categorize CIT geometries by their fields using simplified multipole coefficient relations facilitates a comprehensive overview of performance. For instance, the curves showing peak width variation with background pressure in Figure 3.19 are difficult to compare because the trends are not apparent in geometry parameter space. Since this plot provides details that are not as obvious on the smoothed contour plots from §4.2.1, it is recreated in Figure 4.24, this time with the curves colored according to the sum of the octopole and dodecapole coefficients of each geometry. The curve belonging to the trap with a 0.700 mm thick ring and 0.175 mm electrode spacing and a coefficient sum of −6.6% (dashed line) is used as a benchmark: geometries with more negative sums are plotted in panel (a), and those with more positive sums are plotted in (b). The −6.6% geometry is not the absolute best at either low or high pressure (although the slight gains in resolution from other geometries are likely to be inconsequential), but it was optimal in the midrange of 150 to 500 mTorr. Thus, it is ideal for applications with variable background pressures, and it approximately outlines the lowest attainable peak widths (within the limits of the present study).

The peak widths in panel (a) are not widely dispersed at low pressure (which is better seen in quantified form with the 20 mTorr curves in Figure 4.18b), but the damping of the octopole resonance through the range up to 250 mTorr causes a nonlinear increase in
peak width such that the curves maintain a spread of about 0.4 Th at all higher pressures, as confirmed by their near-constant slopes in Figure 4.18a. Above 250 mTorr the curves are shifted to lower peak widths (indicated by arrow) as the coefficient sum becomes more positive, reaching a minimum with the −6.6% geometry. As the coefficient sum becomes even more positive for the traps in panel (b), the low-pressure end of the curves steadily increases in peak width (indicated by arced arrow), becoming nearly level by +3.9% and declined by +6.7%. However, these curves do not have a fixed ‘pivot’ point; instead, they intersect the −6.6% curve at successively higher pressures, after which the slopes change to approximately match the slope of the −6.6% curve. This change is observed to start occurring for the −1.4% curve between 500 to 600 mTorr and the +3.9% curve between 600 to 800 mTorr, with the +6.7% curve expected to follow suit at higher pressures. For this reason, the geometries with very positive sums (>3%) are unlikely to offer much better high-pressure (>1 Torr) performance than the other geometries in panel (b). This merging behavior suggests that the −6.6% curve does in fact approximately define the lower limit for peak width above 150 mTorr for CITs with these geometry parameters. It should be noted that the coefficient sum model predicts that the −6.5% geometry should have very similar performance to the −6.6% geometry, and while this is true below 200 mTorr they are substantially different at higher pressures. Assuming that this is not due to experimental error, it shows the weakness of treating the multipoles as a sum.

The optimization results are best summarized as a contour plot of Figure 4.24, as shown in Figure 4.25a; the peak widths are also given as a function of the coefficient ratio in (b) and versus the octopole coefficient alone in (c). Smoothing was applied to the contours, which masks the discrepancies in each case, but the original data points (round markers) are overlaid without smoothing to reveal the differences. As before, the major
trends can be attributed to the octopole field—the contours in (c) indicate optimal resolution at 20 mTorr with $A_4$ between 6% to 9%, with incremental shifts to stronger fields as the pressure increases, consistent with the contour plots in Figure 4.7. Presenting the results in this smoothed format is inaccurate because it might appear that the coefficient sum in (a) and the ratio in (b) offer no advantage to simply using the octopole to describe geometries and predict performance. Hence, they are suited for an overall view of performance trends, but the contour plots in Figures 4.7 and 3.23 should be used in selecting optimal multipole and geometry parameters based on the conditions of the intended application.

4.5 Characteristics of Double-Resonance Ejection

Most of the trap geometries from the optimization study had an active octopolar nonlinear resonance near $\beta_z = 0.70$ (from the $\beta_r + \beta_z = 1$ condition) that greatly improved resolution at low background pressures. Although it was not always the best mode of mass analysis for higher pressures, the resonance ejection operating point was fixed at $\beta_z = 0.70$ for consistent comparison among the different geometries. As noted in § 3.4.1, there are cases where the dodecapole resonances were competitive with the octopole at lower pressures (below ca. 300 mTorr), and at high enough pressures boundary ejection appears to become the best choice for all traps (above ca. 1 Torr). However, at intermediate pressures most trap geometries had slightly narrower peak widths under standard resonance ejection at $\beta_z$ points not associated with specific nonlinear resonances. To demonstrate this transformation, peak widths were measured in the resonance ejection mode across a broad range of $\beta_z$ values by scanning the supplementary dipole frequency at a fixed amplitude. The results from several pressures are given for a typical CIT (0.650 mm
thick ring, 0.250 mm electrode spacing) in Figure 4.26. At low pressure (20 and 50 mTorr) the curves show clear enhancement in resolution for the $\beta_z = 0.70$ nonlinear resonance, leading to ion ejection via the double-resonance mode. The resonance $Q$ factor is high, providing sharp mass spectral peaks over a narrow frequency range, while peak widths off resonance are significantly higher. As damping increases beyond 75 mTorr the $Q$ factor drops and the resonance bandwidth quickly increases, leading to a broad frequency response such that the octopole nonlinear resonance becomes indistinguishable from the surrounding $\beta_z$ operating points in terms of peak width. At 300 mTorr and above, a lower peak width is possible at higher $\beta_z$ values (ca. 0.75 to 0.80) for this trap. With the nonlinear resonance quenched and offering no further advantage, higher $\beta_z$ values help counter resolution loss due to damping by raising the secular frequency, as covered in § 1.4.3.

Higher drive frequencies will keep the nonlinear resonance active at higher pressures, but at 9 MHz the critical damping point appears to be rather low. However, even without nonlinear resonances, the ion secular frequency coherence is benefited at higher pressures by the presence of the positive octopole field, as results in earlier sections show.

In addition to damping, the nonlinear resonance width is affected by amplitude-dependent frequency shifting of the ions, causing beat frequencies and self-quenching behavior. The strength of the octopole field appears to be the main factor behind this for the $\beta_z = 0.70$ resonance. In this study, spectral peak width was observed to cease improving under double-resonance ejection for large octopole coefficients, with the transition occurring between 14% to 17%. The peak widths from $\beta_z$ scans in the resonance ejection mode of a trap with $A_4/A_2 = 17.8\%$ (0.750 mm thick ring, 0.250 mm electrode spacing) are shown in Figure 4.27. At 50 mTorr there is a conspicuous lack of peak width enhancement at the position of the octopole nonlinear resonance ($\beta_z = 0.704$). Notably, the dodecapole
resonances at $\beta_z = 0.404$ and 0.522 are severely detrimental to resolution in this case. The best resolution with this trap was obtained in the $\beta_z$ range of ca. 0.55 to 0.65, where it is practically constant (unlike the trap in Figure 4.26). With a pressure increase to 200 mTorr the peak widths at apparent nonlinear resonance positions fluctuate considerably, but in all other regions they merely rise a little. Although this CIT and others with strong octopole fields perform slightly better at $\beta_z$ values lower than the octopole nonlinear resonance, this becomes less true as damping increases. This is not evident in Figure 4.27 since the pressure only extends to 200 mTorr, but the peak widths measured at $\beta_z = 0.60$ and 0.70 are compared up to 800 mTorr in Figure 4.28. The difference between the two curves decreases with pressure until they are equal around 700 mTorr—with yet greater damping the higher secular frequency afforded by $\beta_z = 0.70$ is expected to be more favorable. Likewise, boundary ejection at $\beta_z = 1.0$ is presumed to ultimately yield the best resolution if drive frequency compensation against damping is not implemented.

4.6 Hexapole Field Superposition

Due to the symmetry of the CITs from the high-pressure geometry study, odd-order multipoles are expected to be negligible. However, given the widespread commercial application of the hexapole to enhance ion trap performance, an attempt was made to include it in the geometry study. In order to control the strength of the hexapole field through asymmetrical adjustments in electrode spacing, an impractical number of experiments would have been required. Instead, field asymmetry was induced electrically as described in §2.1.3. Perfect in-phase field cancellation was assumed so that the odd multipole coefficients could be determined through the superposition of static terms after independently fitting the multipole contributions from each electrode (using the same
procedure as in § 4.1.2, with the added step of reversing the potential of the ring electrode with one of the endcaps).

Unfortunately, the field-cancellation circuitry caused amplitude instability in the drive RF that was not resolved satisfactorily enough for a systematic study. Nevertheless, with careful monitoring of the RF voltage, several trap geometries were tested in the double-resonance ejection mode using the hexapolar nonlinear resonance located at $\beta_z = 2/3$ and compared to the octopolar nonlinear resonance at $\beta_z = 0.70$. In general, the hexapole resonance became noticeably active at strengths ($A_3/A_2$) near 3% and had optimal resolution near 7%. Example spectra are provided in Figure 4.29 for a CIT that has good resolution at 20 mTorr with the $\beta_z = 0.70$ resonance (red peaks). With no electrical asymmetry, the hexapole resonance was inactive and resonance ejection at $\beta_z = 0.65$ (gray peaks) was only slightly better than boundary ejection (green peaks). When a hexapole field was induced with a strength of about 7%, double-resonance ejection was able to be performed at $\beta_z = 0.65$ and the resolution became significantly better (blue peaks). The lower supplementary dipole frequency (excitation at $\beta_z = 0.65$ versus the mathematical pole at 0.67) is normal for double-resonance ejection (see § 1.3.4). Interestingly, the octopole resonance was found to be superior to the hexapole in all cases, even for geometries with strong octopole fields (>15%) that have degraded low-pressure resolution at $\beta_z = 0.70$. Thus, although the hexapole can be tuned independently of the even-order multipoles, the $\beta_z = 2/3$ resonance does not have consistent performance with all traps. This is not surprising since the octopole and hexapole are known to have a combined effect on ion motion.$^{69}$
4.7 Octopole Effects on Ion Storage Capacity

In the previous chapter, §3.4.3, the ion storage capacity of CITs was demonstrated to decrease with larger $z_0$ dimensions, which is opposite of the prediction from QIT theory. This is because nonlinear fields are not considered in the pseudopotential well model, where a perfect quadrupole is assumed. Among the higher-order multipoles, the octopole appears to have the most influence on the ability of traps to contain charge. The space-charge-limited ion storage capacity results from Figure 3.27 are replotted as a function of the octopole strength in Figure 4.30. The dashed curve was not fitted to the data but sketched to show the estimated trend. The data points are distributed fairly broadly for the experimental reasons discussed previously, but overall the signal seems to decrease exponentially with a stronger octopole. An interpretation for this change can be found by examining the trapping field in the radial dimension. A positive even multipole is defined as increasing the electric field strength of the quadrupole in the axial dimension when their coefficients have the same sign. A comparison of the potential surfaces of $A_2$ and $A_4$ in Figure 1.4a,c shows that while they augment each other along $z$, they diverge along $r$. Consequently, a positive octopole actually weakens the radial quadrupolar field. This is illustrated in Figure 4.31 as surface plots of the magnitude of the electric field from the superposition of a quadrupole with a positive octopole. A pure quadrupole is shown in (a), which has a linear increase in electric field strength in all directions from the center. In (b) an octopole field with a 10% coefficient weight ($A_4/A_2$) is added, while (c) and (d) have weights of 25% and 50%, respectively. This causes the field strength in the $z$ dimension to increase compared to (a), but decrease in the $r$ dimension. Since the octopole is weak in the center of the trap, a portion of the field always remains linear, but this region decreases in size. The radial potential well depth of a pure quadrupolar field is already about half that of
the axial well (depending on \( r \) and \( z \) dimensions), and with a superimposed octopole the disparity is even greater. With weaker radial containment the ions are more likely to hit the ring electrode. An analysis with just the octopole is an oversimplification of the total electric field in CITs, but the plausibility of ion losses in the radial dimension remains. Although the exact nature of ion storage in CITs may be far more complex, it is clear that trap geometry affects charge capacity in addition to mass resolution, leading to possible tradeoffs in figures of merit. Whether the spectral space charge limit follows the same trend as total charge capacity is uncertain, but the spectral quality was generally observed to degrade at lower signal levels with traps that held fewer ions at the space-charge limit.

4.8 Conclusions

While the electric field of the CIT is composed of many different multipolar terms, the central region of typical traps is relatively undisturbed and remains linear. An extension of this linearity towards the endcaps is possible by using positive multipoles to compensate for decreased field strength due to the presence of negative multipoles, with the octopole and dodecapole having the greatest influence due to their proximity to the center. This was found to be correlated with improved mass resolution at low pressure in both the boundary and double-resonance ejection modes of mass analysis, consistent with prior work. Changes in performance with CIT geometry were found to be predominantly driven by the octopole field, with an appreciable impact from the dodecapole. In addition to affecting field linearity, the strength of the octopole changed the dynamics of its nonlinear resonance at \( \beta_z = 0.70 \), with strong self-quenching observed as \( A_4/A_2 \) approached 20%. Although this led to significant peak width broadening at low pressure, in the course of transitioning to high damping conditions the best resolution was observed with traps that
had increasingly stronger octopole fields, whereby the overall field was more than linear at intermediate axial displacements. Below ca. 250 mTorr the peak width minimum occurred over a narrow range of octopole strengths that shifted with pressure, reaching an apparent stopping point near $A_4/A_2 = 10\%$. Since the peak widths are less spread out among the geometries at lower pressures, consideration of the dodecapole strength is particularly helpful for fine-tuning resolution in these cases. At all higher pressures, the peak widths of traps with stronger octopole components broadened at a lower rate until they approximately matched those of the 10\% geometries. Hence, between ca. 250 to 1000 mTorr (beyond which boundary ejection supersedes the resonant ejection mode), an octopole strength of roughly 10\% is expected to be optimal. The exact performance was mapped in terms of the multipole coefficients so that these results can be used for traps with alternative geometries, at least as a first approach. Without the benefit of simulation studies, it is presumed from the demonstrated trends that multipoles of order greater than $n = 6$ are of secondary concern for symmetric traps that have nonlinear field distributions similar to the CIT (i.e. comparable coefficient sign and weight).
4.9 Figures

Figure 4.1 Axial electric field linearity for trap geometries from the high-pressure optimization study in terms of the ring thickness and electrode spacing parameters. The color scale values are the coefficients of determination ($R^2$) for linear fitting of one dimension of the electric field between the trap center and halfway along $z_0$ for each geometry. Light smoothing was applied to the contours, as with the plots in Chapter 3 (with total points increase factor of 50 and smoothing parameter set to 0.005). The 20 large data markers of the overlaid scatter plot correspond to the experimentally evaluated traps, while the smaller markers were added to ensure accurate interpolation and to extend the trend beyond the white data boundary.
Figure 4.2  Qualitative view of fitting accuracy relative to number of terms included in multipole expansion equation. Each contour plot shows magnitude of static electric field in a typical CIT (0.650 mm thick ring and 0.250 mm spacing) with the endcaps grounded and 1 V applied to ring electrode. (a) Electric field cross-section as solved by SIMION. (b) Electric field as calculated from coefficients obtained through fitting the potential of (a) with eq 1.33 using terms through $A_{24}$ with the boundary extending 95% along $r$ and $z$ from trap center. (c) Same as (b) except using fitting coefficients through $A_{30}$ and a 100% fitting boundary.
Figure 4.3  Individual multipole components of the axial electric field $E_z$ for a typical CIT (0.650 mm thick ring set to 1 V, separated by 0.250 mm from grounded solid endcaps) as calculated from the same coefficients determined in Figure 4.2c. The field strength curves are labeled with the multipole order.
**Figure 4.4** Axial electric field strength of the octopole \( (A_4) \), dodecapole \( (A_6) \), and hexadecapole \( (A_8) \) for all 20 of the geometries evaluated in the high-pressure optimization study. The electric field of each trace is normalized relative to the maximum quadrupole strength for that geometry \( (2VA_2z_0/r_0^2) \), while the axial dimension is normalized by the \( z_0 \) value, in the manner of Plass et al.\textsuperscript{96}
Figure 4.5  Surface plots of coefficient values for the octopole ($A_4$), dodecapole ($A_6$), and hexadecapole ($A_8$) fields relative to the quadrupolar term ($A_2$) across a broad range of ring thickness and electrode spacing parameters for an $r_0 = 0.500$ mm CIT with mesh endcaps. The mesh was approximated with solid electrode surfaces to compute the electric field; see §4.1.2 for fitting details. The data points for each surface were computed with a 0.025 mm interval for each parameter. Geometry optimization was focused within the gray boundaries of the inner box.
Figure 4.6  Expanded view of coefficient values (given as %$A_j$) in contour plot format, taken from the gray inner box of Figure 4.5. The coefficients shown in each panel are (a) octopole, $A_4$; (b) dodecapole, $A_6$; (c) hexadecapole, $A_8$; and (d) $A_4 + A_6$. Coefficient values are color-coded based on sign: negative values are gray (blue within the data boundaries) and positive values are white (red within the data boundaries). The large round markers represent geometries evaluated in the high-pressure optimization study.
Figure 4.7  Contour plots of peak width (FWHM) variation for CITs with different octopole and dodecapole compositions. Mass analysis was performed in the double-resonance ejection mode near $\beta_z = 0.70$ at increasing helium background pressures (labeled). The contour line increment is 0.025 Th. The traces in panel (h) delineate changes in $A_4$ and $A_6$ due to adjustments in ring thickness (labeled in mm) and electrode spacing (not labeled).
Figure 4.8  Contour plots with same peak width data and format as those in Figure 4.7, except showing variation with the hexadecapole coefficient values of the CITs on the vertical axis.
Figure 4.9  Contour plots of slopes of the curves in Figure 3.19 at pressures above ca. 250 mTorr. Both panels show trends with $A_4$ coefficient on abscissa, with $A_6$ on ordinate of (a) and $A_8$ on ordinate of (b). The trend interruptions around $A_4$ values of 2–8% are not statistically significant (margin of error spans at least 1 contour line, which are incremented 0.05 Th/Torr). The individual curves show variation in coefficient values with ring thickness (labeled in mm) and electrode spacing (not labeled, but increases left to right).
Figure 4.10 Contour plots of peak widths (FWHM) obtained in the boundary ejection mode at 20 mTorr. The octopole coefficient values lie on the abscissa of both panels; the ordinate of (a) shows trends with the dodecapole, while the hexadecapole values are given in (b). The contour lines are incremented by 0.05 Th. The overlaid black traces with small round markers show variation in coefficient values with ring thickness (labeled in mm) and electrode spacing (not labeled, but increases left to right).
Figure 4.11 Contour plots of required supplementary dipole field strengths ($V_{pp}$/mm) to start resonantly ejecting ions near $\beta_z = 0.70$ (the octopolar nonlinear resonance) at different helium background pressures, as a function of the octopole and dodecapole coefficient values. The field strength was calculated by normalizing the supplementary RF amplitude (bipolar application to endcaps) by the $z_0$ value of each trap geometry.
Figure 4.12 Axial electric field linearity as a function of the octopole and dodecapole field strengths. The linearity values are the same as in Figure 4.1, and are evaluated as the coefficients of determination ($R^2$) for a linear fit between 0 to 0.5$z_0$ along the $z$-axis of each trap. The black curves show the variation of $A_4$ and $A_6$ with ring thickness and electrode spacing. The 20 large round markers represent the traps from the high-pressure optimization study, and the geometries represented by the smaller colored markers were added for more accurate interpolation of the contours.
Figure 4.13  Calculated axial electric field strengths for pure quadrupole ($A_2$), octopole ($A_4$), and dodecapole ($A_6$) terms, with different coefficient weights applied to the dodecapole. All fields are positive to show spatial overlap. The fields are normalized relative to the quadrupole.
Figure 4.14 Axial electric field strengths of superimposed octopole and dodecapole terms as calculated from the coefficients determined for the traps from the high-pressure geometry optimization study. The curves are colored according to the summation model in (a) and by the field coefficient ratios in (b). The fields are separately normalized by the maximum quadrupolar strength of each trap ($2VA_2 z_0/r_0^2$).
Figure 4.15 Axial electric fields of the CITs from the high-pressure geometry study compared to the ideal linear quadrupole field (QIT). The colors are set according to the octopole and dodecapole coefficient sums. The curves for the total field ($E_{z,\text{total}}$) at the top were solved using SIMION. The lower curves (magnified by a factor of 5) show only the nonlinear contribution to the total field, calculated by subtracting the quadrupole component from the total field. The fields are separately normalized by the maximum quadrupolar strength of each trap ($2VA_2z_0/r_0^2$). The offset from 0 of some of the lower curves (noticeable near origin) is due to a grid unit rounding error in data processing.
Figure 4.16 Variation of axial electric field strength with endcap (EC) aperture size in a CIT, compared to the linear field of an ideal quadrupole. The trap geometry was fixed at $r_0 = 0.500$ mm, ring thickness of 0.635 mm, electrode spacing of 0.250 mm, and endcap thickness of 0.250 mm, with a single concentric aperture in both endcaps. The fields are normalized by the quadrupole ($2VA_z z_0/r_0^2$).
Figure 4.17 Two methods of relating the octopole and dodecapole field strengths for the purposes of identifying conditions for best performance. The contour plots show peak widths obtained in the boundary ejection mode at 20 mTorr, same as Figure 4.1a. The gray lines in (a) demarcate constant $A_4/A_2 + A_6/A_2$ while in (b) they follow constant $A_4/A_6$ values. The black traces show variation of $A_4$ and $A_6$ due to ring thickness (labeled) and electrode spacing.
Figure 4.18 Trends in peak width from the high-pressure geometry optimization study as a function of the sum of the octopole and dodecapole coefficients (relative to the quadrupole) of the respective CITs. The rates of peak width increase versus helium pressure are given in (a), as determined through linear fitting of the curves in Figure 3.19 for data points above 250 mTorr. Panel (b) shows peak widths obtained at three different background pressures.
Figure 4.19 Same as Figure 4.18 except showing peak width trends versus the ratio of the octopole and dodecapole coefficients. The absolute values of the ratios are used to orient the trend in the same direction (the original values are all negative since the $A_4$ coefficient is positive and $A_6$ is negative for these geometries).
Figure 4.20  Same as Figure 4.18 except showing peak width trends versus the strength of the octopole field relative to the quadrupole.
Correlations of the octopole-to-dodecapole coefficient ratio to (a) the strength of the octopole relative to the quadrupole and (b) the sum of the octopole and dodecapole coefficients. The coefficient values shown are for mesh/solid-endcap CITs with variable ring thicknesses and electrode spacings. The red markers are traps that were experimentally evaluated in the high-pressure optimization study. Since the dodecapole fields are negative for all these geometries, the negative ratios on the abscissa are due to positive octopoles and vice versa.
Figure 4.22  Continued on next page
Figure 4.22 Correlation of supplementary dipole field strength that is required to start ejecting ions via the octopolar nonlinear resonance ($\beta_z = 0.70$) with combined weights of octopole and dodecapole coefficients, with the abscissa in (a) showing their sum, (b) showing their ratio (absolute value), and (c) showing the octopole strength alone (relative to the quadrupole). The individual curves are for different ring thicknesses, with data points set by electrode spacing; the curves are grouped by the labeled helium background pressures. The field strength was calculated by normalizing the supplementary RF amplitude (bipolar application to endcaps) by the $z_0$ value of each trap geometry.
Figure 4.23 Comparison of supplementary dipole field strength requirements at 20 mTorr for various mass spectral set points under octopolar double-resonance ejection ($\beta_z = 0.70$), including the first detectable signal of resonantly ejected ions (green), the end of boundary ejection, so that all ions are resonantly ejected (blue), and minimum peak width (red). Since the peak width minimum occurs over a range of dipole field strengths, there is more experimental uncertainty in those values, hence the focus on the resonant ejection starting point.
Figure 4.24 Peak width variation with helium background pressure, with the curve colors set according to the sum of the respective trap octopole and dodecapole coefficients to show trends based on the electric field composition. The curves are separated into two plots for clarity: those in panel (a) have sums lower than $-6.6\%$, and those in panel (b) have sums greater than $-6.6\%$ (the $-6.6\%$ curve appears in both). The experimental conditions are the same as for Figure 3.19.
Figure 4.25  Continued on next page
Figure 4.25 Contour plots of peak width data from Figure 4.24 showing trends versus background pressure and (a) the sum of the octopole and dodecapole coefficients, (b) the octopole-to-dodecapole ratio, and (c) the weight of the octopole field alone. The pressure range is limited to 20–500 mTorr, for which results were obtained from all 20 traps from the geometry optimization study. The contours are smoothed to provide a general overview, but the original data points are included as round markers with no smoothing to indicate deviations that are otherwise obscured.
Figure 4.26  Plot of resonance activity as measured through mass spectral peak width in the resonance ejection mode over a range of $\beta_z$ ejection points. The $\beta_z$ value was varied by scanning the supplementary dipole frequency (bipolar application) with a 20 kHz increment at a fixed amplitude (varied with helium pressure for maximum resolution at $\beta_z = 0.70$). The CIT had a ring thickness of 0.650 mm and electrode spacing of 0.250 mm ($A_1/A_2 = 9.0\%$). The drive frequency was 9.0 MHz, and analysis was performed on the 108 Th peak of anisole. The mass scan rate was calibrated to 20 Th/ms at $\beta_z = 0.70$ and was allowed to vary uncorrected at all other points, skewing the curves to a degree. The smaller random fluctuations in peak width should not be considered as significant due to the use of a relatively imprecise peak fitting procedure (for faster semi-automated processing).
Figure 4.27  Plot of resonance activity obtained in the same manner as Figure 4.26, except using a CIT with a ring thickness of 0.750 mm and electrode spacing of 0.250 mm that has an octopole field strength of 17.8% relative to the quadrupole.
Figure 4.28 Plot of peak width versus helium background pressure in the resonance ejection mode at two different $\beta_z$ ejection points (labeled) for the CIT from Figure 4.27 that has a ring thickness of 0.750 mm and electrode spacing of 0.250 mm. The light gray curves are included for reference to the peak widths of other geometries at $\beta_z = 0.70$ and are the same as those in Figure 4.24b.
Figure 4.29 Mass spectra obtained under different modes of mass analysis to demonstrate the effect of the hexapole field on resolution. Except for changes in supplementary dipole frequency to shift the $\beta_z$ ejection point (labeled), the spectra (averaged) were obtained under constant experimental conditions: 20 mTorr helium using anisole as analyte, 9 MHz drive RF, $r_0 = 0.500$ mm CIT with 0.650 mm thick ring and 0.250 mm electrode spacing. The supplementary dipole amplitude was 1.05 V_{pp} for ejection at $\beta_z = 0.70$ (bipolar application) and 1.10 V_{pp} for ejection at $\beta_z = 0.65$ (unipolar application to ionization-side endcap). Both endcaps were grounded for boundary ejection.
Figure 4.30  Space-charge-limited ion storage capacity of CITs as a function of the strength of the octopole field relative to the quadrupole. The data and experimental conditions are the same as in Figure 3.27. The markers are colored according to ring thickness, and larger $A_4$ values were obtained with wider electrode spacings.
Figure 4.31 Surface plots (with projected contour lines) of magnitude of electric field from the superposition of a pure quadrupole with a pure positive octopole of variable strength. The fields were computed with a constant ring potential and $A_2 = 1.00$, with the weight of the $A_4$ coefficient varying as: (a) 0.00, (b) 0.10, (c) 0.25, and (d) 0.50. The fields are normalized for $r_0 = 0.500$ mm, and the $z$-scale (not shown) is fixed to allow a direct comparison of relative total field strength.
CHAPTER 5
CONCLUSIONS AND FUTURE DIRECTIONS

Although CITs are significantly removed from the ideal concepts of quadrupolar devices, their utility for portable applications does not necessarily come with a large compromise in analytical performance. This is especially likely in the face of harsh damping conditions under the HPMS strategy, where ion trap operation and development are still in the nascent stage. Given that the preceding decades of research have focused on relatively low-pressure systems, the classic features of the QIT may not be the most desirable for high background pressures, where stabilization by higher-order fields seems to provide a large advantage. Moreover, the behavior of ions during mass analysis with intense collisional damping is not fully described by existing theory. Therefore, without the ability to predict CIT performance, an empirical approach to optimization was undertaken through systematic exploration of the electrode geometry.

Ultimately, the scope of the project was limited to the basic geometric parameters of the CIT, despite the more general treatment of performance in terms of multipole fields in Chapter 4 to dissociate it from specific electrode shapes. Although the simplified electrodes do not allow for arbitrary control over the electric field composition, thus inhibiting performance somewhat, they can be fabricated at much smaller scales using readily available technology. This, in turn, makes it possible to scale up the drive frequency at practical voltages to counteract the otherwise severe loss of resolution due to damping. The primary asset of HPMS in reaching operating pressures around 1 Torr is frequency
compensation, while geometry optimization is most useful at lower damping factors where resonances are more active (that is, when the ion secular frequency coherence is sufficiently maintained by the drive RF, either at high pressure with high drive frequencies or vice versa).

Prior to evaluating performance, the CIT geometry parameter range was narrowed by practical experimental considerations. With all else fixed, the $z_0$ dimension was varied via the ring electrode thickness and the electrode spacing. An upper limit on $z_0$ exists based on ion ejection voltage and mass range, and there is a lower limit on electrode spacing due to trap capacitance; between these bounds the RF power requirements are minimized. For the remaining pool of geometries, mesh endcaps were employed to avoid electrode alignment concerns. There are a few challenges with using mesh endcaps, but they seem to offer resolution that is as good as or better than what is achievable with aperture endcaps in CITs. However, further trap scaling below $r_0 = 0.500$ mm will make the mesh more difficult to implement.

An analysis of the higher order field content with respect to mass spectral performance supports the consensus that the first few multipolar terms above the quadrupole are the most important for typical symmetrical traps. Although strong links were found for the octopole and dodecapole through comparative qualitative correlations, establishing causality will require greater insight into the complex dynamics behind ion ejection, which is best suited for simulations. At this point, there appear to be at least three aspects of the electric field that affect mass resolution at different pressures: linearity, nonlinear resonances, and stabilization against collisions by more-than-linear restoration forces. For the CITs in the present study, these effects are predominantly associated with
the octopole and can be characterized as having either direct or indirect influence on resolution.

All of the multipoles indirectly affect performance through their aggregate impact on trapping field linearity and the restoration force on ions. The proximity of the typically positive octopole and negative dodecapole to the center of the trap means that they can be counterbalanced to extend the linearity of the quadrupole further towards the endcaps, thereby prolonging simple harmonic ion motion and helping sustain narrow secular frequency distributions. This is advantageous for all mass analysis modes at low pressure, as indicated by the fact that the best resolution was obtained with the most linear traps in both the boundary and double-resonance modes. However, while field linearity is a significant factor, it cannot be improved sufficiently enough with CITs to give better resolution with boundary ejection than what is offered by the double-resonance ejection mode.

Unlike a QIT, the maximum field linearity achieved with CITs is coincident with the presence of a strong intrinsic octopole, which is one of the few multipoles that generates a nonlinear resonance ($\beta_r + \beta_z = 1$) that is directly beneficial for mass analysis. It is naturally the first choice among the many available nonlinear resonances and does not require any further geometric modifications to implement, unlike the hexapole. At underdamped conditions (equivalent to pressures near 20 mTorr at 9 MHz drive RF) the primary benefit of the octopole is rapid ejection via this nonlinear resonance near $\beta_z = 0.70$, which improves resolution by transporting ions from the linear quadrupolar region to beyond the endcaps with minimal interaction time with the other nonlinear fields. Normal boundary ejection leads to a more gradual increase in ion amplitude, subjecting them to greater ejection delays and the resultant temporal peak broadening. At low pressure, then, one of the main
focuses of geometry optimization is tuning the octopole field for fast nonlinear resonance ejection. To this end, the results of the present study are consistent with prior work, following the ‘−10% rule’ of Wu et al. closely. More specifically, peak widths were minimized in the boundary and double-resonance modes with octopole strengths between ca. +7% to +9% relative to the quadrupole ($A_4/A_2$) and ca. −50% relative to the dodecapole ($A_4/A_6$). For applications where the trap geometry will be very similar to the parameters utilized here, an exemplary set includes a ring thickness of 0.650 mm (1.30 $r_0$) and electrode spacing between 0.225 to 0.250 mm (0.45 to 0.50 of $r_0$). As noted previously, the nominal electrode spacing values do not account for the mesh thickness, which decreases it slightly.

At higher pressures the nonlinear resonances become overly damped and offer no advantage over standard resonance ejection via the supplementary dipole field. The octopole remains beneficial to resolution, but in a different capacity that is believed to be related to its known stabilizing properties. With greater damping, resolution is indirectly improved by stronger octopole contributions and overall field strengths that increase more than linearly beyond the center of the trap. Negative multipole superpositions act against the field strength, and a consideration of the dodecapole with the octopole establishes a clearer relationship to performance. This transition to a different operating regime is marked by an initial nonlinear broadening of peak width at lower pressures as the nonlinear resonances are damped out, followed by a constant rate of increase at all higher pressures. Since the octopole nonlinear resonance was specifically examined, its dynamics were also observed to change with octopole strength, exhibiting strong self-quenching behavior as $A_4/A_2$ approached +20%. While this was highly deleterious to low-pressure resolution, it also expanded the nonlinear peak width broadening zone such that the rate did not become linear until increasingly higher pressures. This was measured as a decrease
in the peak width broadening rate in the tested pressure range. It is expected that at high-enough pressures, the broadening rate becomes the same for all geometries in a given mass analysis mode. Additionally, in line with theory, at high damping factors the boundary ejection mode becomes superior for resolution, whereby the secular frequency is maximized by operation at $\beta_z = 1$ and outweighs the benefits of resonance excitation.

Since higher pressures are better served by a stronger octopole, the optimum trap geometries are not the same as for low pressure and are less specifically defined. It appears that all traps with $A_4/A_2$ greater than ca. $+10\%$ eventually have equivalent resolution when damping is sufficiently great ($>800$ mTorr in this case). This includes CITs that have very poor resolution at low pressure due to an excessively strong octopole (approaching $+20\%$). However, limiting the octopole to around $+10\%$ is desirable to avoid unnecessarily decreasing the charge capacity. Furthermore, this limit maximizes resolving power over the widest possible pressure range. Among the tested geometries, one trap was particularly favorable for use in applications with variable background pressures, consisting of a $0.700$ mm thick ring ($1.40r_0$) and electrode spacing of $0.175$ mm ($0.35r_0$).

Although this study empirically demonstrated that CIT performance can be significantly improved at both high and low pressure through geometry optimization, there are still many questions remaining about the fundamental processes involved. Unfortunately, trends in performance with static multipole coefficient values do not reveal much about the underlying ion dynamics—a better understanding would help narrow the scope of any future optimizations of alternative trap geometries, which may further improve performance without adding too much complexity. Rather than try to statistically decouple the perturbations of all the multipole fields, it would be ideal to study the terms on an individual basis with the pure quadrupole so as to conclusively separate the
beneficial fields from those with detrimental effects. This knowledge might then be applied towards designing specific optimization functions and thus decrease reliance on time-consuming systematic exploration. New simulation tools are being developed\textsuperscript{116} so that realistic ion trajectory modeling can be performed at high pressures on reasonable time frames, wherein the trapping field can be defined arbitrarily to aid more basic investigations. For HPMS, the influence of nonlinear fields on ion secular frequency distributions at high pressure is especially interesting. Given that the presented results were all obtained with helium, the consequences of greater scattering forces from a heavier background gas such as nitrogen are also still uncertain. Other prospects include the long-standing intricacies behind the interplay of the octopole and dodecapole, and whether odd multipoles have any useful properties at high pressure.
APPENDIX A: STABILITY PARAMETER APPROXIMATIONS

Although $\beta_u$ and the stability parameters can be accurately calculated from one another using the full continued-fraction formula given in eq 1.28, it is convenient to have algebraic approximations that can be quickly solved for many different values, such as when tracing nonlinear resonance lines on the stability diagram. A closed-form expression for $\beta_u$ in terms of $q_u$ and $a_u$ is given by Carrico as

$$\beta_u \approx \left( a_u - \frac{(a_u - 1)q_u^2}{2(a_u - 1)^2 - q_u^2} - \frac{(5a_u + 7)q_u^4}{32(a_u - 1)^3(a_u - 4)} - \frac{(9a_u^2 + 58a_u + 29)q_u^6}{64(a_u - 1)^5(a_u - 4)(a_u - 9)} \right)^{1/2}$$ (A.1)

which is accurate for $q_u < 0.8$, as shown by March et al.\textsuperscript{128,129} Conversely, $q_u$ can be solved for in terms of $\beta_u$ and $a_u$ using an abbreviated form of the continued-fraction equation:

$$\beta_u^2 = a_u + \frac{q_u^2}{(\beta_u + 2)^2 - a_u - \frac{q_u^2}{(\beta_u + 4)^2 - a_u}} + \frac{q_u^2}{(\beta_u - 2)^2 - a_u - \frac{q_u^2}{(\beta_u - 4)^2 - a_u}}$$ (A.2)

Using the standard ‘solve’ command provided in Mathematica v9.0 on eq A.2, the following solution was obtained:

$$q_u \approx \left( \frac{x - y}{3\beta_u^2 - 3a_u + 32} \right)^{1/2}$$ (A.3a)

where

$$x = 2(\beta_u^2 - a_u + 8)(\beta_u^4 - 2a_u\beta_u^2 + a_u^2 + 4\beta_u^2 - 20a_u + 64)$$

$$y = (\beta_u^{12} + 184\beta_u^{10} + 1040\beta_u^8 + a_u^6 + 4096\beta_u^6 - 6(\beta_u^2 + 12)a_u^5 + (15\beta_u^4 + 472\beta_u^2 + 2064)a_u^4 + 155648\beta_u^3 - 4(5\beta_u^6 + 292\beta_u^4 + 2320\beta_u^2 + 7424)a_u^3 + (15\beta_u^8 + 1392\beta_u^6 + 13408\beta_u^4 + 79872\beta_u^2 + 221184)a_u^2 + 262144\beta_u^2 - 2(3\beta_u^{10} + 404\beta_u^8 + 3616\beta_u^6 + 27136\beta_u^4 + 155648\beta_u^2 + 393216)a_u + 1048576)^{1/2}$$ (A.3b)
In the case that \( a_u = 0 \), the expression can be simplified to

\[
q_u \approx [2 \beta_u^6 + 24 \beta_u^4 + 192 \beta_u^2 + 1024 - (\beta_u^{12} + 184 \beta_u^{10} + 1040 \beta_u^8 + 4096 \beta_u^6 \\
+ 155648 \beta_u^4 + 262144 \beta_u^2 + 1048576)^{1/2} / (3 \beta_u^2 + 32)]^{1/2}
\]  

(A.4)

At the stability boundary \( \beta = 1 \), eq A.4 gives a value for \( q_u \) of 0.908187, whereas an iterative calculation using eq 1.28 extended to the 14th recursion level returns 0.908046, which amounts to an error of +0.015%.
### APPENDIX B: MULTIPOLe COEFFICIENTS FOR EVALUATED CIT GEOMETRIES

Table B.1 Raw values of multipole expansion coefficients for mesh-endcap CIT geometries tested at high pressure

<table>
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<th>Thickness (mm)</th>
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**Note:** These coefficients correspond to the multipole terms and sign conventions described in § 1.3.1, and were determined through a least-squares fit as described in § 4.1.2. The actual trap dimensions differ from the nominal values above according to aforementioned tolerances and \( z_0 \) decrease due to mesh thickness.
Table B.2 Relative multipole expansion coefficient values for mesh-endcap CIT geometries tested at high pressure

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<th>Thickness (mm)</th>
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Note: Multipole coefficient strengths are referred to throughout the dissertation relative to the quadrupole term, as given above, so that comparisons can be made among different CIT geometries. The sum and ratio of the octopole and dodecapole terms are provided as well, which are correlated to trap performance in Chapter 4.
REFERENCES


(120) OriginLab Online Documentation: Creating Contour Graphs


(125) OriginLab Online Documentation: Interpreting Regression Results


