# Peak Formation for an Approximately Tuned FTMS Compensated Cylindrical Trap with a Modest Number of High M/Z Particles

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## Overview

### Purpose

- To obtain a revised understanding of peak formation for single ion species in an approximately tuned compensated trap as obtained from numerical simulation[1].

### Results

- A narrow peak can be formed at low ion number for low z-mode amplitudes (not observed in an uncompensated trap) as well as at high z-mode amplitude.
- The trap electric field inhomogeneity plays an commanding role in the self expression of coulombic effects for a single species.
- Asymmetry in response to inversion of the trap electric field inhomogeneity indicates that some inhomogeneities are better than others.

## Introduction

- We have been making use of a compensated cylindrical trap to improve the detection sensitivity and resolving power of an FTMS instrument.
- The trap design incorporates three compensation ring electrode pairs which theoretically permit electric trap potentials that are quadrupolar to eighth order and constant frequency to third order.
- In the hands of a practitioner, coarse tuning is easily achieved by using the theoretically calculated compensation voltages.
- Practice has shown, however, that fine tuning based on the current understanding of how peaks are formed in uncompensated traps does not work.

## Methods

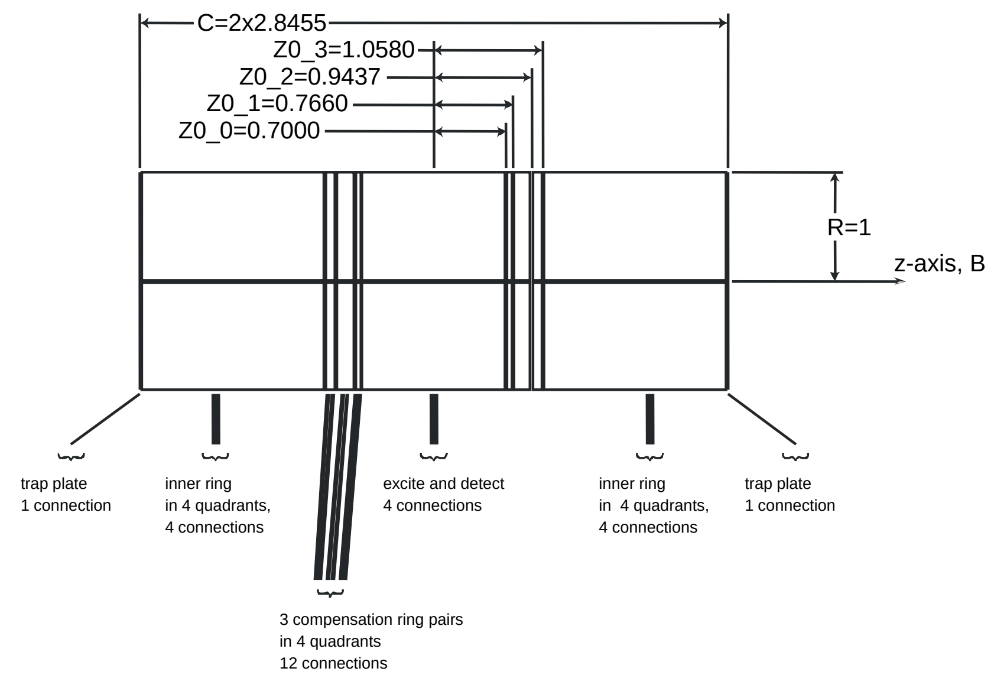
### Simulation

- The time derivative of the state-space vector of velocities and positions of the simulation "super" ions (particles) was expressed using the Lorentz force and straight forward particle-particle coulombic interaction.  Electric trap potential was represented to 8th order.
- The trap electric field was derived from the spherical harmonic expansion of the electric trap potential appropriate for the combination voltages on three auxiliary ring pairs, inner rings and end caps.
- Particles are loaded at the trap origin at random times during the first 1 ms with random velocities characteristic of a temperature (typically 300 K).
- The intra particle coulombic forces where turned on during the first millisecond of each particle's existence.
- A variable order, multistep predictor-corrector method[2] was used to numerically integrate the system of equations.  Relative and absolute error tolerances (control internal step size) where set to obtain reasonable conservation of cloud total energy and angular momentum (except when particles collide with trap walls).
- Ion cloud modeled as 100 particles with charge divided evenly amongst particles.
- Each particle retains an m/z of 15,000.
- Z-mode excitation (if used) is emulated by adding 65% of the maximum trap radius to the z position at 10 ms.
- Cyclotron excitation is emulated by adding 50% of maximum trap radius to the x position and the appropriate velocity to the y velocity at 20 ms.
- Transient data were imported as charge weighted x and y centroids (to emulate quadrature detection) into a Fortran program for calculation of the complex FFT, the subsequent spectra are displayed in magnitude mode.  The spectra are normalized by the initial charge count to facilitate comparison.

### Trap Design

- Trap (Fig. 1) designed in Saint Louis and built in Lake Forest is mounted in a 7.0-T IonSpec ProMALDI FTMS (Lake Forest, CA).
- For this trap[3], the four gaps that separate the auxiliary rings have z-positions at 0.700, 0.766, 0.944, and 1.058 from the center compared to the overall trap length of 5.69, all normalized to the trap inside radius (0.03124 m).
- The ***approximately tuned*** state of the trap was obtained by perturbing the theoretical auxiliary ring voltages 8.602, -8.602 and 8.602 V by the experimentally determined correction voltages 1.187, 0.038 and -1.231 V.  For the ***inverted approximately tuned*** state of the trap, the perturbing voltages are -1.187, -0.038 and 1.231 V.

**Figure 1.  Compensated Cylindrical Trap with End Caps (05aug01)**



## Peak Shape for Theoretically Tuned Trap

Figure 2a.  No Charge vs 1 Charge per Particle at 10s

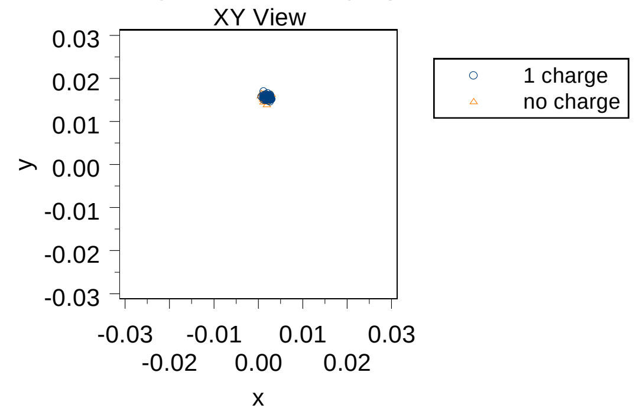


Figure 2b.  No Charge vs 1 Charge per Particle at 10s

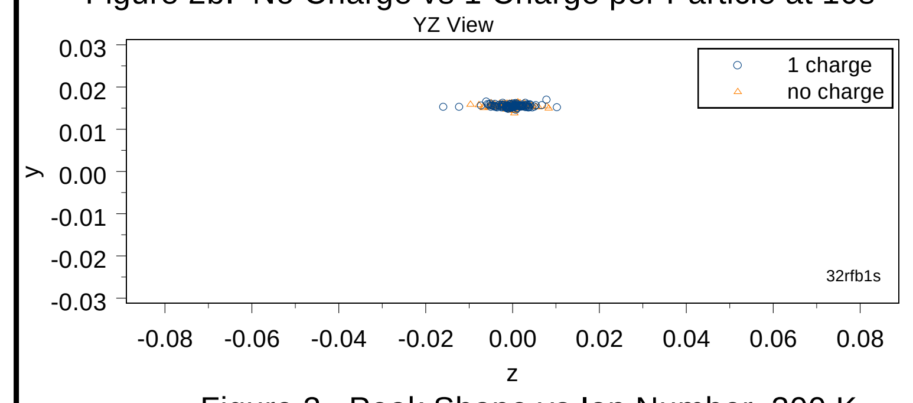
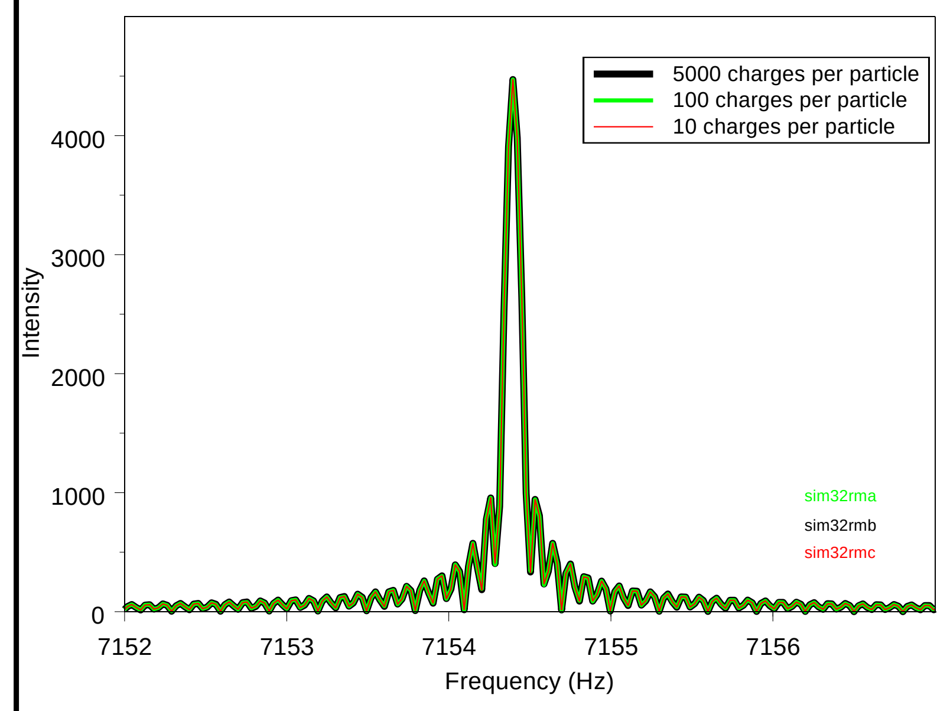


Figure 3.  Peak Shape vs Ion Number, 300 K



- For a cloud of 100 15K m/z, 300 K, 50% radius cyclotron excited ions in the theoretically tuned trap (represented and compensated to 8th order), numerical simulation shows what appears to be a phase-locked cloud (Fig. 2) that produces a transient that extends beyond the 10 s of the computation.
- This suggests that low detection limits for high mass ions should be possible, at least in special experiments.
- There is no apparent difference in centroids for when there is coulombic interaction among particles or not.
- The spectral peaks (Fig. 3) for higher ion number are identical in shape and position.
- These simple points are an illustration of the work of Dehmelt which points out that the ion cloud centroid is unaffected by internal coulombic forces ***if*** the electric trapping potential is quadrupolar[4].
- While this is a desirable goal, a perfectly tuned trap may not be perfectly realizable in practice.

- The ion trajectories are analyzed as curves.  See *Frenet* formulas, for example.
- The frequency at which the trajectory turns is determined from the vector velocity and acceleration at a point time **(0.5 s)**.
- Two accelerations are used to give two frequencies.  One includes the coulombic forces and the other does not.  The frequency difference is the "coulombic frequency shift".
- This analysis "knows" nothing about the magnetron mode.  As a result it reports a higher frequency for ions tat are closer to the trap origin by virtue of a higher magnetron mode orbit.
- In a perfectly tuned trap, this results in the negative slope to the ion pattern for frequencies without coulombic forces as shown by the red triangles in Fig 3b.
- The coulombic frequency shift shows the same kind of pattern to reveal that it adds to the "neutral" behavior of the temporarily uncoupled ions.
- The ion cloud remains a packet at 0.5 s as shown in Fig. 3c and gives a good signal as shown in Fig. 3.

Figure 3b.  Frequency vs Ion Radius, 300 K, 10 charges per particle

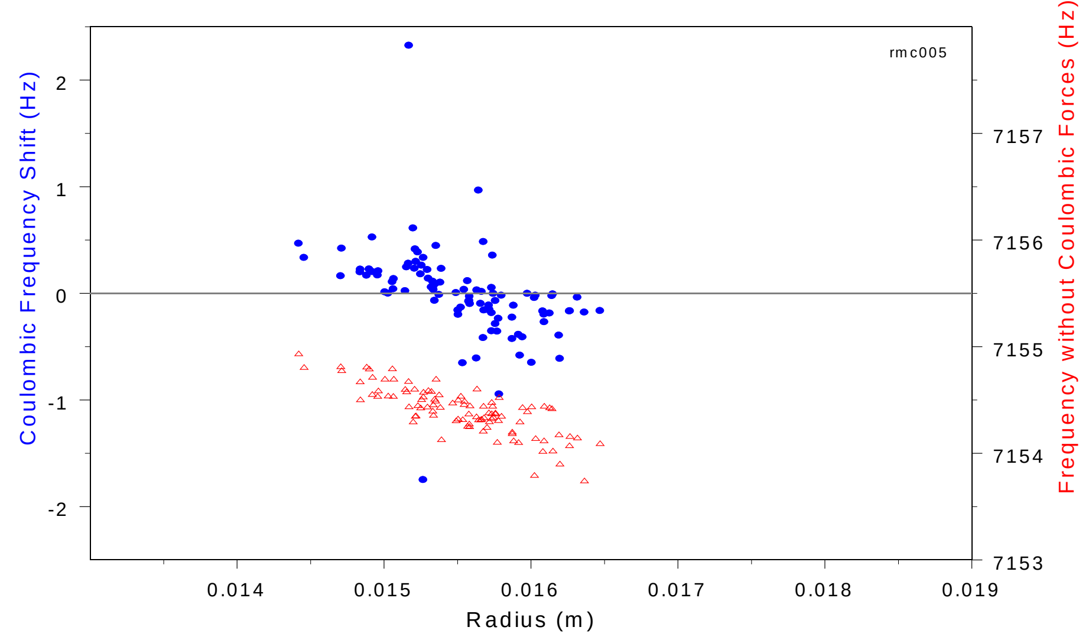
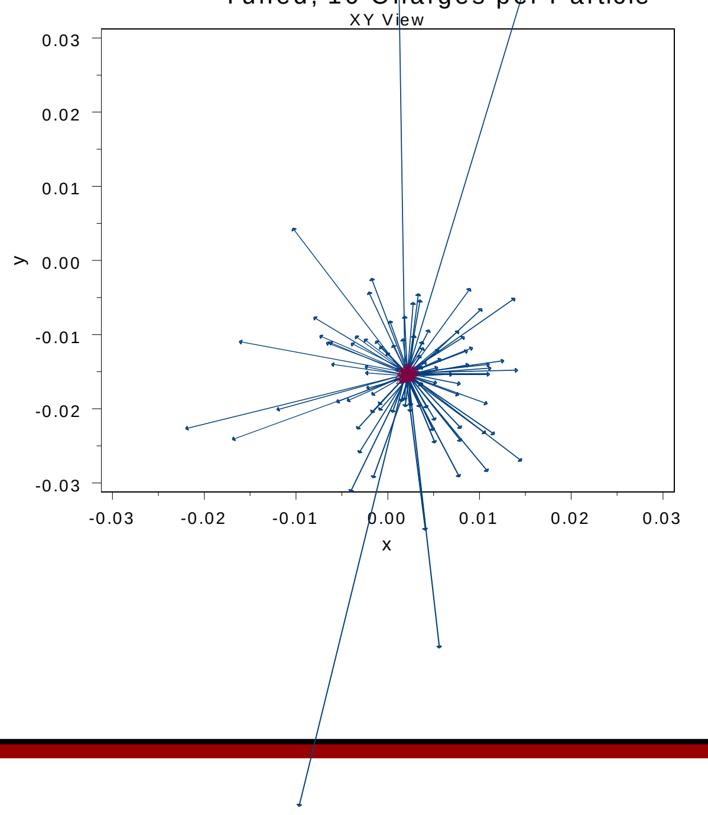
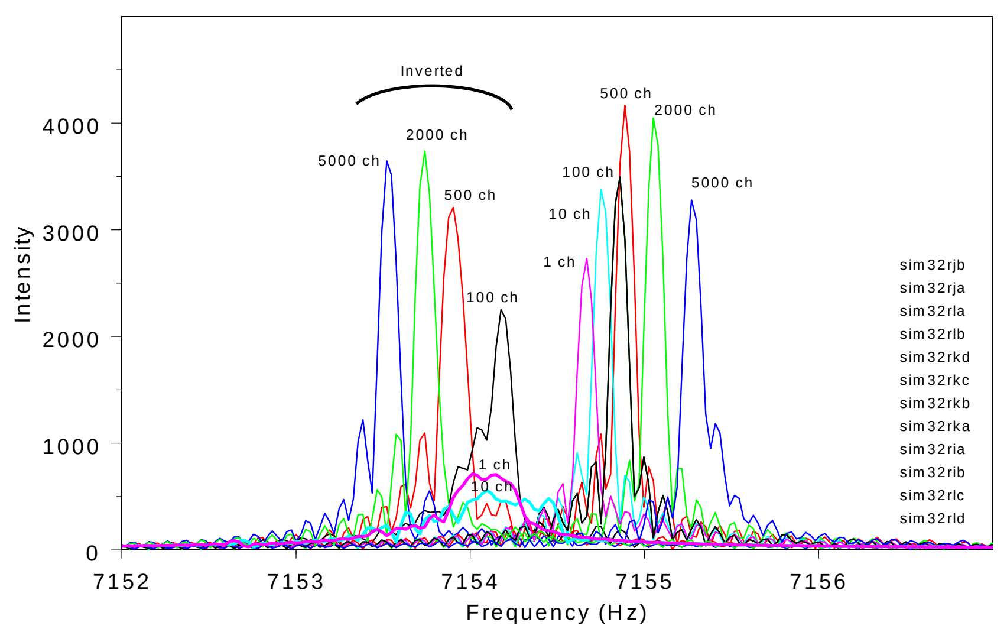


Figure 3c.  Ion Position and Coulombic Forces, Tuned, 10 Charges per Particle



## Cooled Cloud with Approximate Tuning

Figure 4.  Peak Shape vs Ion Number, 300K



- For 50,000 (500 ch) ions a peak is produced (Fig. 4) that is nearly as good as that of the perfectly tuned trap.  Even 100 ions is not so bad.
- This occurs in spite of some variation in the frequency surface for these ions (Fig. 5).
- These ions would normally produce a short transient and low RP peak in an uncompensated trap.
- The peak frequency centroid ***increases*** nonlinearly as ion number is increased.

- If the perturbing correction voltages are negated (inverted), the phase-locking behavior (not shown) and peak performance is degraded.
- The peak for 10,000 ions suffers noticeably.
- The advantage shifts to the inverted case at 500,000 ions, however.
- The peak frequency centroid decreases as ion number is increased.
- Apparently, there are imperfect trap electric fields that work better than others in the context of coulombic effects even though the magnitudes of trapping electric field frequency deviations are the same.

Figure 5.  Normalize Frequency vs Cyclotron and Z-Mode Amplitudes

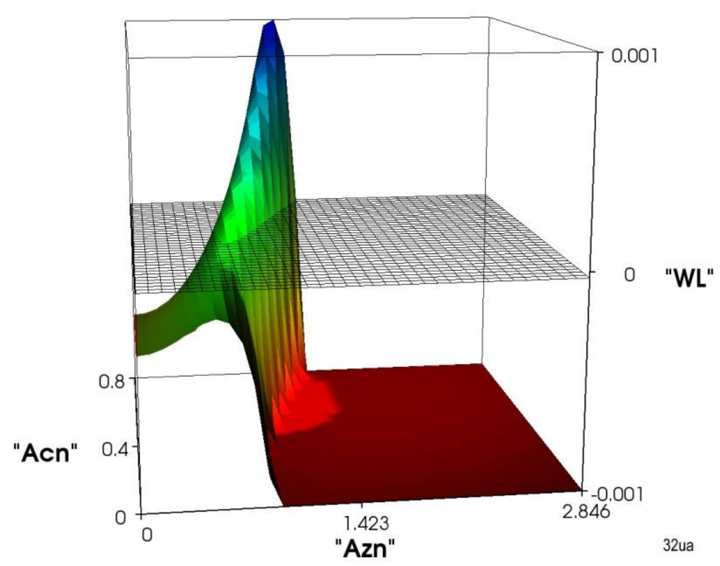
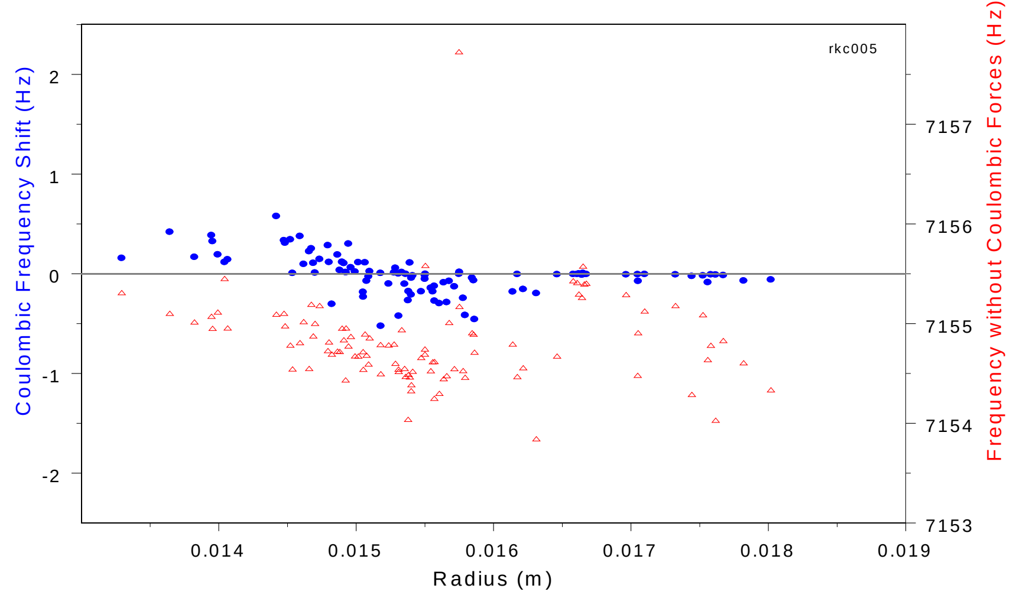


Figure 4b.  Frequency vs Ion Radius, Normal, 10 Charges per Particle



- For the normal approximately tuned trap, a significant portion of the pattern for the frequencies without coulombic forces essentially has a negative slope as shown in Fig 4b.
- The coulombic frequency shift pattern shows the same behavior .
- It is clear that not all ion belong to this pattern.
- Ions with higher z-mode amplitudes have higher cyclotron-mode frequencies (see Fig 5) and lead the packet (see Fig 4c).

Figure 4c.  Ion Position and Coulombic Forces, Normal, 10 Charges per Particle

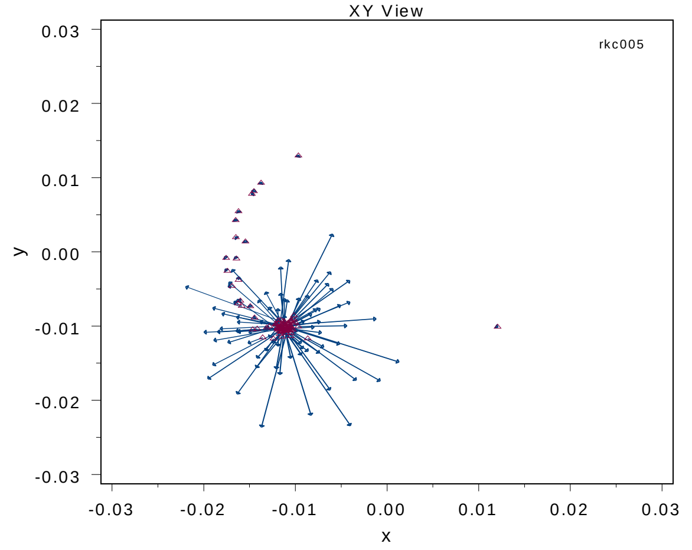
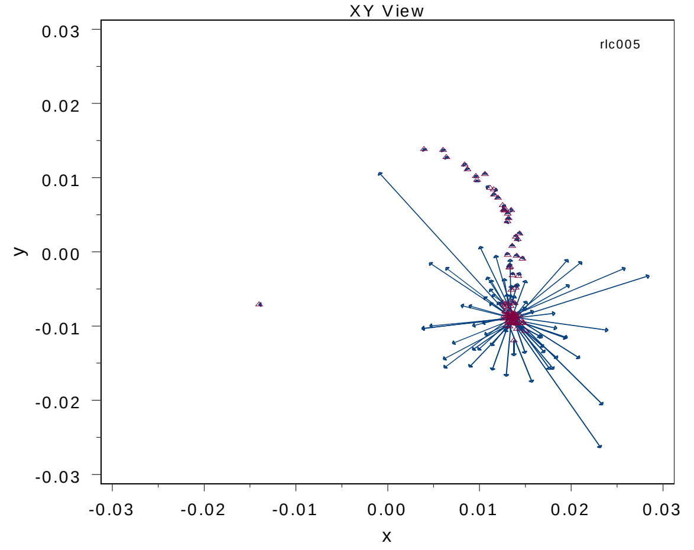


Figure 4d.  Ion Position and Coulombic Forces, Inverted, 10 Charges per Particle



- For the inverted approximately tuned trap, a significant portion of the ions is an exception to the negative-sloping patterns.
- For the frequencies without coulombic forces (red triangles), an essentially positive slope persists as shown in Fig 4e.
- The trapping electric field inhomogeneity works against the action of the coulombic forces perhaps shearing ions off the packet as time goes by.
- A low resolving power signal results (Fig 4) with high z-mode ions trailing the packet (Fig 4d).

Figure 4e.  Frequency vs Ion Radius, Inverted, 10 Charges per Particle

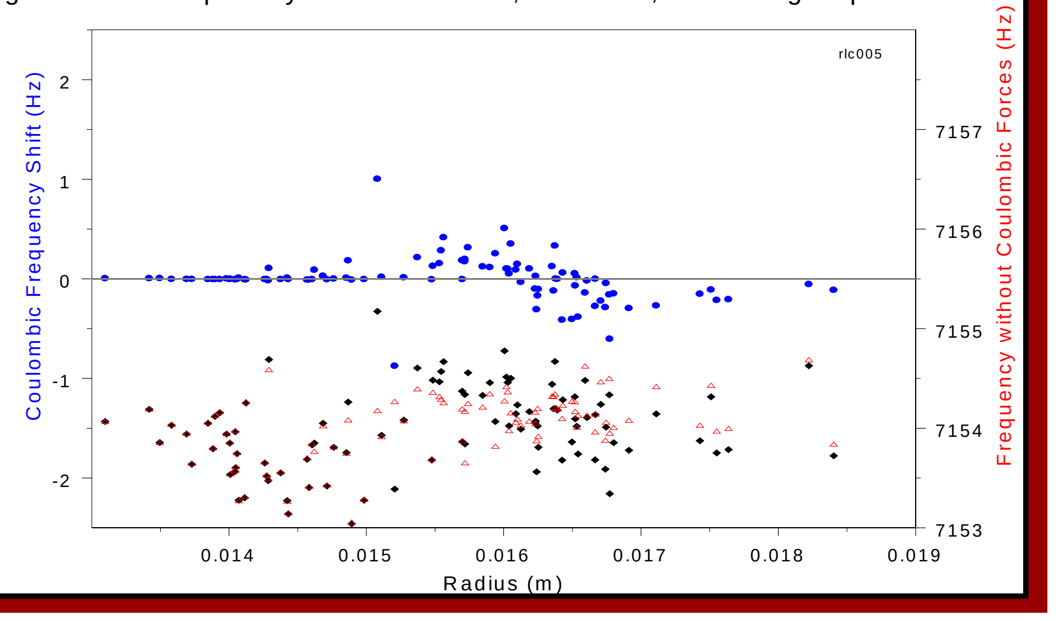


Figure 6a.  5000C Charge vs 1 Charge per Particle at 10s

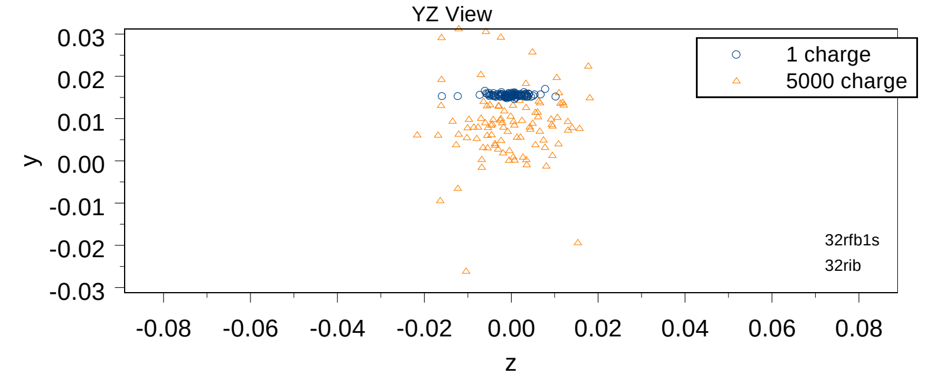
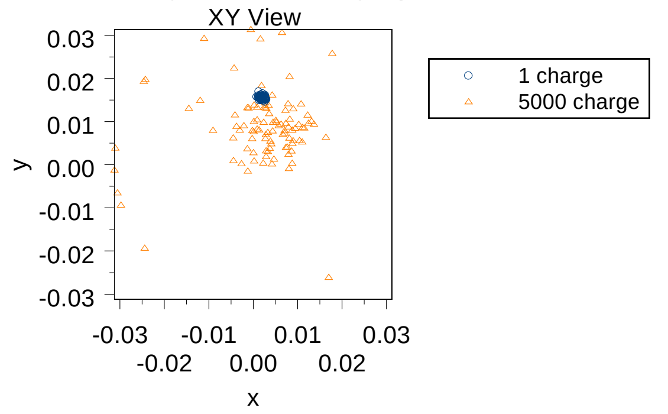
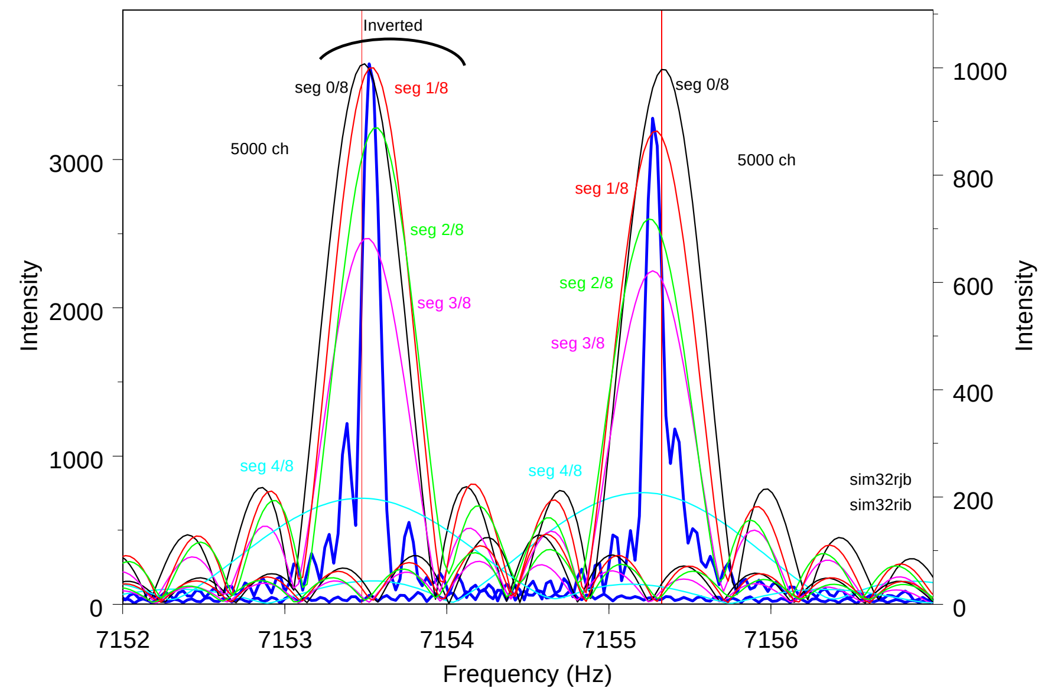


Figure 6b.  5000 Charge vs 1 Charge per Particle at 10s



- Because the direction of frequency shift changes with the inverted perturbation of the trap tuning, the usual rationalizations may not be adequate.
- As the ion number is increased, the ion cloud must occupy more space in the z direction (Fig. 6a).
- The higher z-mode amplitude distribution samples trapping electric fields that produce higher frequencies in the case of the "normal" approximate tuning (Fig. 5).
- The trend will be decreasing frequencies for the inverted tuning because the frequency surface is an upside down version of that shown in Fig. 5.
- As ions are lost on the trap walls or stray from the phase-locked cohort to reduce the space charge density, the cloud could be expected to collapse in the z direction with time.

Figure 6c.  Frequency vs Transient Seqment, 300K

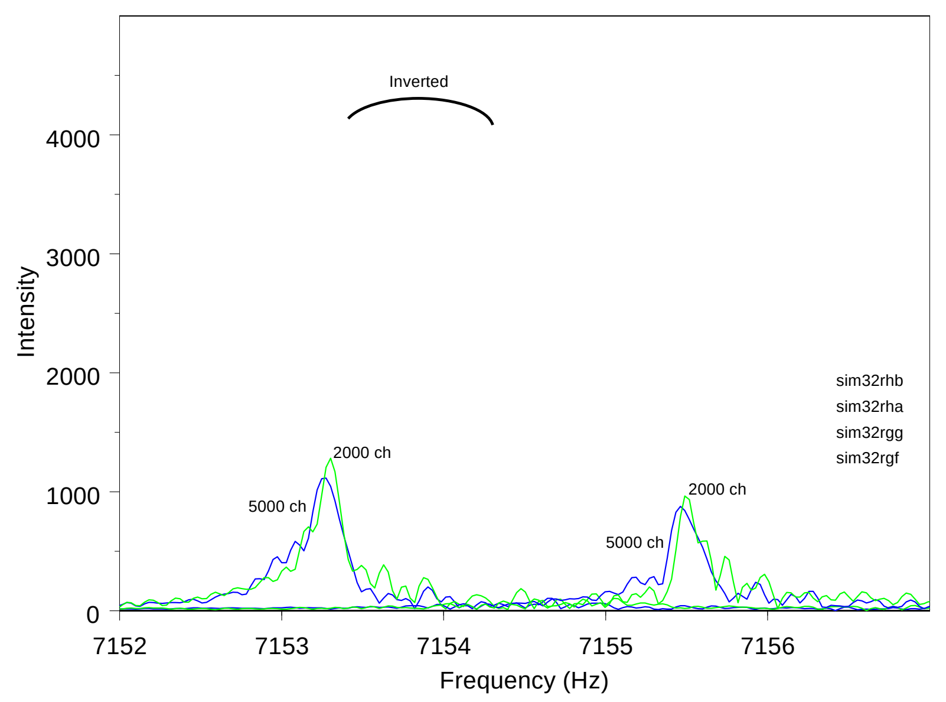


- Thus the frequency should decrease with time for the "normal" approximate tuning.
- The opposite should be true for the inverted tuning.
- This appears to be the case for 500,000 ions (Fig. 6c) although it is not the whole story.
- Note that the frequency shifts are disproportionately fast versus ion number for low ion number in the normal approximately tuned trap (fig 4).

## Z-Mode Excited Cloud with Approximate Tuning

- For a hot cloud (1500 K corresponding to an uncooled cloud from injection) or a z-mode excited cloud, only a fraction of higher z-mode amplitude ions appear to phase lock.
- The fraction of ions that do phase lock may be those that are sampling a local maximum or minimum.  These ions would normally produce the high resolving power peak in an uncompensated trap.
- Increasing ion number decreases the frequency for both normal and inverted tuning (Fig. 7).  The shift is comparatively small.
- The advantage goes to the inverted tuning in this case.

Figure 7.  Peak Shape vs Ion Number, Z-Mode Excited



- Depending on the z-mode amplitude distribution, a narrow peak can appear at one of two frequencies for an approximately tuned trap.
- The sensitivity for a cooled ion cloud is better.

## Acknowledgments

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## References

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