Evaluation of Space Charge Effects in Scanning- vs. Fourier Transform (FT)-Quadrupole Ion Traps (QITs)

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Introduction

The significance of coulombic interactions between charged particles ("space charge") is one of the primary challenges for the design of ion traps and similar devices [1]. Quadrupole Ion Traps (QITs), while still being commonly used in commercial mass spectrometers, are particularly sensitive to such space charge effects [2].

The established operation mode of QITs is to eject ions sequentially from the trap in dependence of their mass [1]. The ejected ions are detected with an ion detector outside of the ion trap volume. Alternatively, ions can be trapped and excited by an electric stimulus, which leads to a mass dependent coherent oscillation of the trapped ions [3,4,5,6]. This ion oscillation can then be detected by dedicated electrodes and Fourier transformed to a mass spectrum, similarly to techniques used in FT-ICR or Orbitraps.

We have used numerical simulations of ion dynamics in an idealized QIT to investigate the characteristics of different detection modes in terms of sensitivity to space charge effects, to estimate feasible operation boundaries for instruments based on the individual detection principles.

Ion Trajectory Simulation

- Custom simulation framework [7]
- Background gas collisions are modeled with hard sphere scattering
- Idealized potentials of trapping field, defined as analytical functions [8]:

$$\Phi_{\mathrm{total}} = \Phi_0 + \Phi_0\left(A_1\Phi_1 + A_2\Phi_2 + A_3\Phi_3 + A_4\Phi_4 + \dots\right)$$

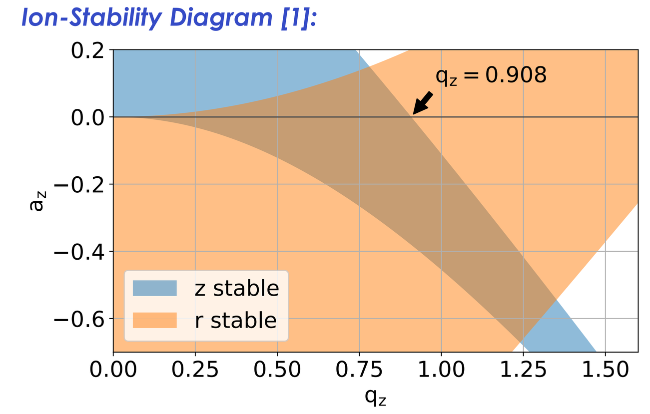
$$\Phi_0 = \frac{U + V\cos(\Omega t)}{2} \qquad \Phi_2 = \frac{r^2 - 2z^2}{r_0^2}$$

$$A_i = \text{field order coefficient}, \quad \Omega = \text{trap RF Frequency}, \quad U = \text{trap DC Voltage}, \quad V = \text{trap RF Voltage } (U_{\mathrm{rf}}), \quad t = \text{time}$$

$$\Phi_3 = \frac{2z^3 - 3zr^2}{r_0^3} \qquad \Phi_4 = \frac{8z^4 - 24z^2r^2 + 3z^4}{r_0^4}$$

Detection Modes / Ion Stability

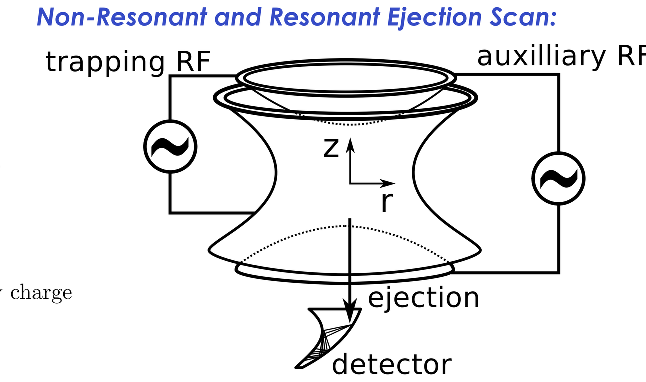
Ion-Stability Diagram [1]:



Ions have to be z- and r-stable to be trapped, which is indicated by the area where both regions overlap in the stability diagram.
Commonly, QITs operate with an stability parameter a_z=0, in this case ions remain stable with an $q_z < 0.908$.
The mass dependent stability parameter q_z is given by:

$$q_z = \frac{8eV}{m(r_0^2 + 2z_0^2)\Omega^2} \qquad r_0 = \text{radial trap size} \quad e = \text{elementary charge} \quad z_0 = \text{trap height} \quad m = \text{ion mass}$$

Non-Resonant and Resonant Ejection Scan:

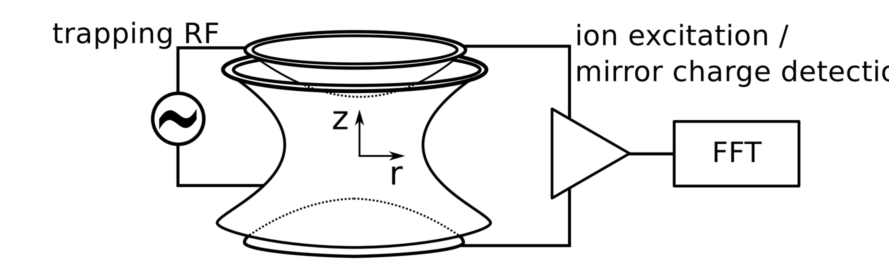


A mass scan in a QIT can be performed by sequentially ejecting ions from the trap.

A basic ejection technique is increasing the trap-RF voltage, which takes ions to the stability boundary at $q_z < 0.908$ (non-resonant ejection).

Most commercial instruments apply an additional auxiliary RF voltage with an integer ratio (e.g. 1/3) to the main trap RF to the cap electrodes. This leads to *resonant* ejection from the trap with a q_z<0.908.

Fourier-Transform-Scan:



Alternatively, a mass spectrum can be acquired without ejecting ions from the trap[5,6]: Trapped ions are coherently excited by a signal applied to the cap electrodes. The oscillation frequency of the excited ions is mass dependent and can be measured by detecting the mirror charge of the ions on the cap-electrodes.

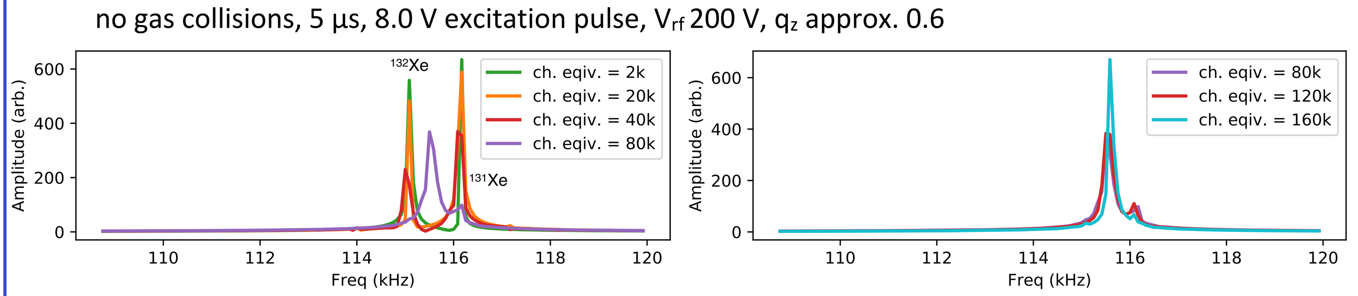
Space Charge Induced Peak Fusion

Xe^+ Isotopes, f_t = 500 kHz

Two Xe Isotopes (m/z = 131, 132 Th, 21 % and 27 % relative abundance) were simulated with all three ejection methods. The total number of simulated particles was 2000 in all cases. The charge weight in the space charge simulation is varied to generate higher charge densities.

Fourier Transform Detection:

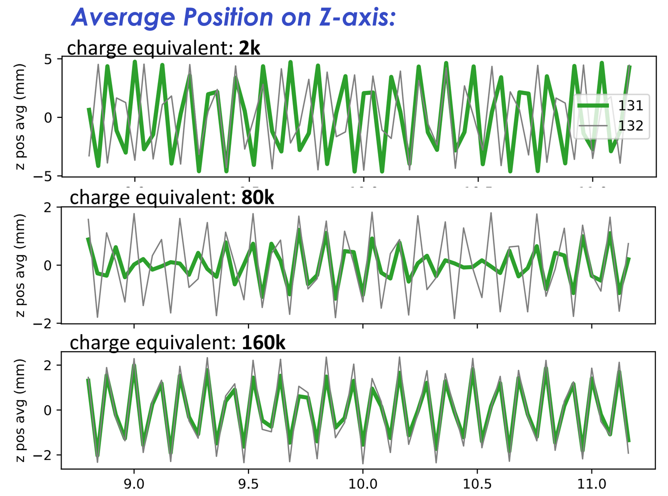
no gas collisions, 5 µs, 8.0 V excitation pulse, V_{rf} 200 V, q_z approx. 0.6



top / top-right:
Secular frequency spectra with different space charge weights. The signal of ^{131}Xe disappears nearly quantitatively with a charge equivalent of 80k charges in the trap. With higher charge densities, the peak fusion intensifies further.

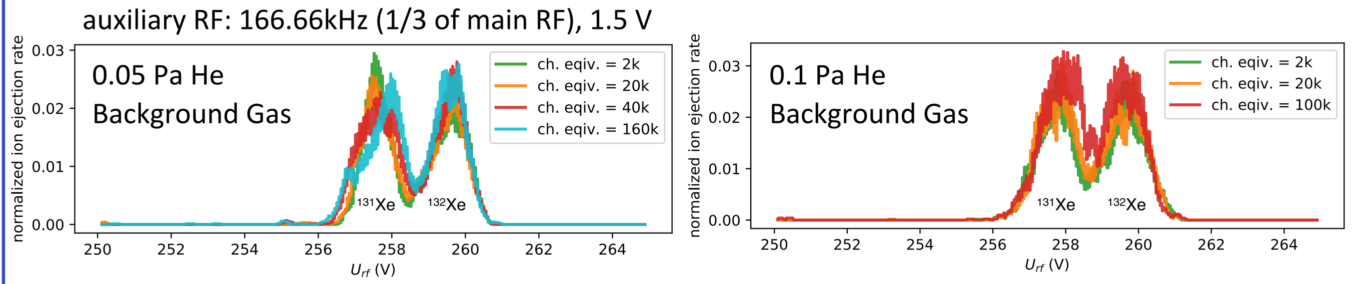
right:
Averaged positions of the individual ion ensembles on the z-axis (the primary mirror charge detection axis): Severe space charge interaction is visible with an equivalent of 80k elementary charges, while total oscillation synchronization occurs at 160k elementary charges equivalent.

Average Position on Z-axis:



Resonant Ejection Detection:

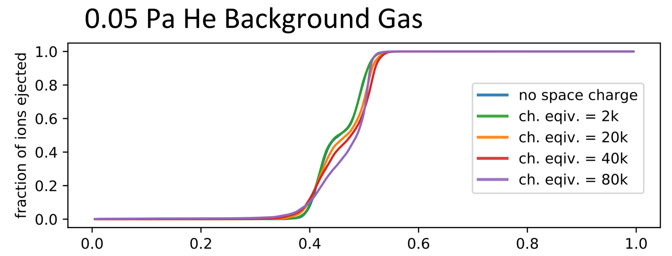
auxiliary RF: 166.66kHz (1/3 of main RF), 1.5 V

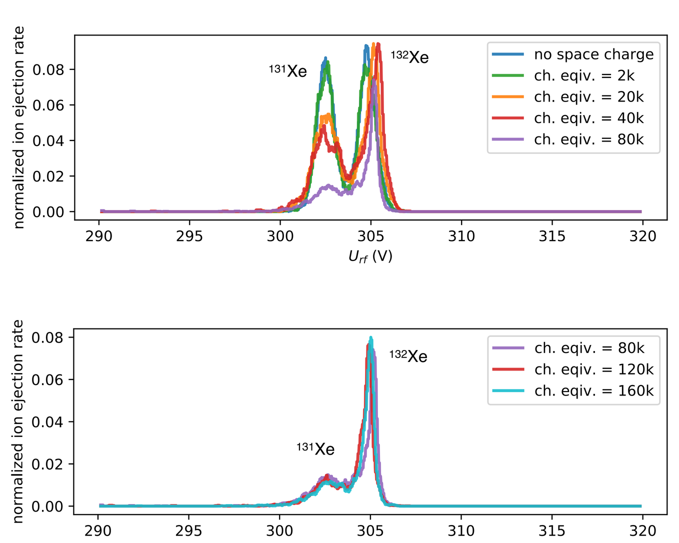


top:
Resonant ejection spectra for two gas pressures and different space charge weights. In contrast to FT-detection, the mass signals are partly resolved even with a charge equivalent of 160k charges in the trap.

Non Resonant Ejection (instability at q=0.908) Detection:

0.05 Pa He Background Gas





top:
Non resonant ejection of ions from the trap volume during the trajectory simulation. The numerical derivative yields the ejection spectrum (*top-right*)

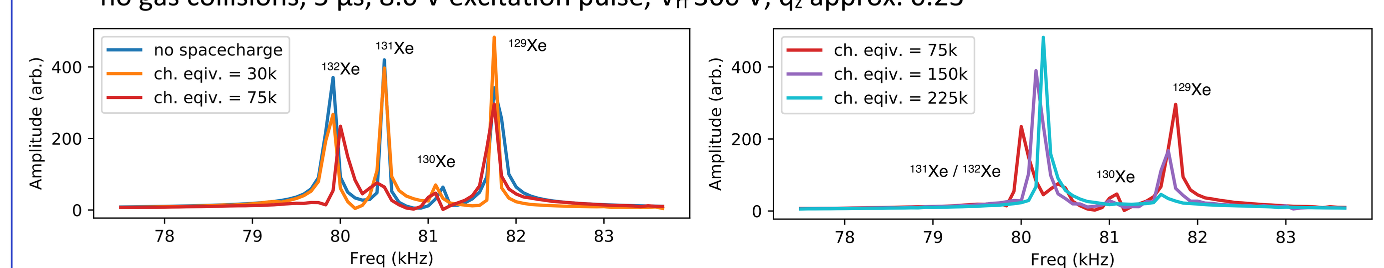
top-right / right:
Non resonant ejection spectra. Note that the decrease of charge density in the trap is clearly visible in the signal of ^{132}Xe with high space charge weights.

Xe^+ Isotopes, f_t = 1 MHz

Xe Isotopes (m/z = 129, 130, 131, 132 Th, 26 %, 4 %, 21 %, 27 % relative isotope ratio) were simulated with all three ejection methods. The total number of simulated particles was 3066 in all cases. The charge weight in the space charge simulation is varied to generate higher charge densities.

Fourier Transform Detection:

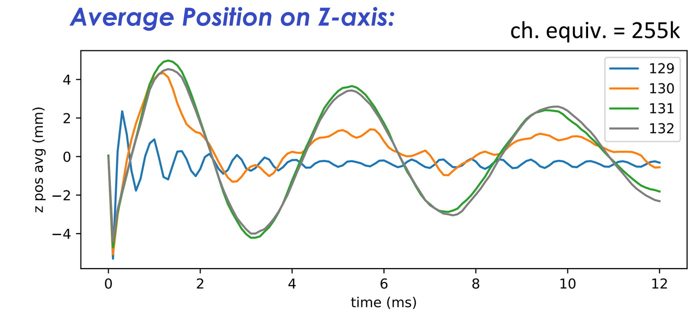
no gas collisions, 5 µs, 8.0 V excitation pulse, V_{rf} 300 V, q_z approx. 0.23



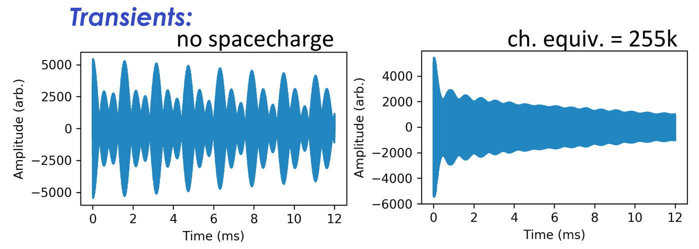
top / top-right:
Secular frequency spectra with different space charge weights. The signals quickly fuse to two main signals with 75k elementary charges in the trap and ultimately fuse to one signal at an equivalent 225k elementary charges in the trap.

right:
Averaged positions of the individual ion ensembles on the z-axis and two example transients. Synchronization of all species is visible at 255k charges, which also leads to a quickly decreasing transient signal in the time domain.
(note that the low oscillation frequency in the averaged z-position plot is due to aliasing effects with the low frequency of exported full trajectory frames)

Average Position on Z-axis:

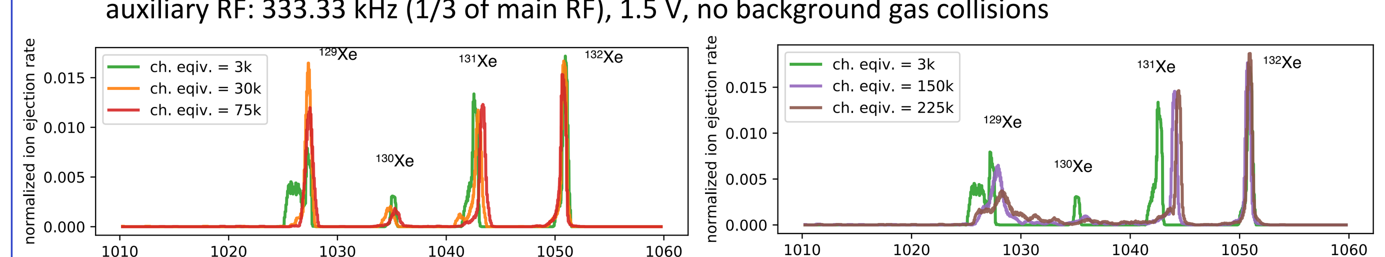


Transients:



Resonant Ejection Detection:

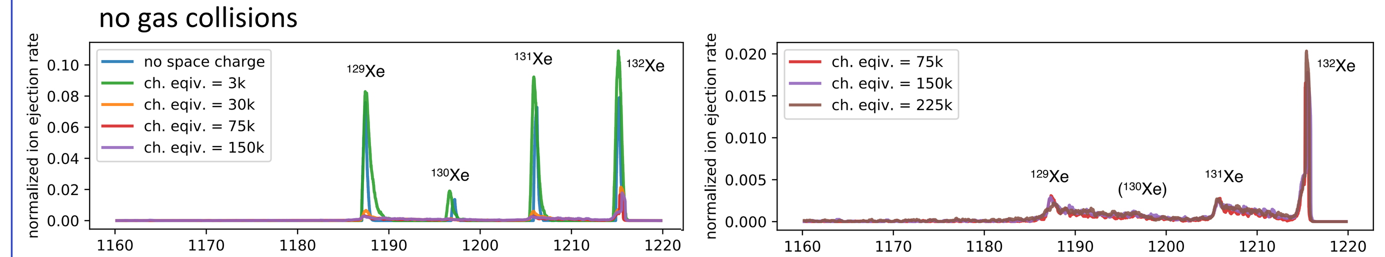
auxiliary RF: 333.33 kHz (1/3 of main RF), 1.5 V, no background gas collisions



top:
Resonant ejection spectra without background gas collisions. Mass signals shift and change shape, but even with a charge equivalent of 225k charges, the main signals remain clearly separated.

Non Resonant Ejection (instability at q=0.908) Detection:

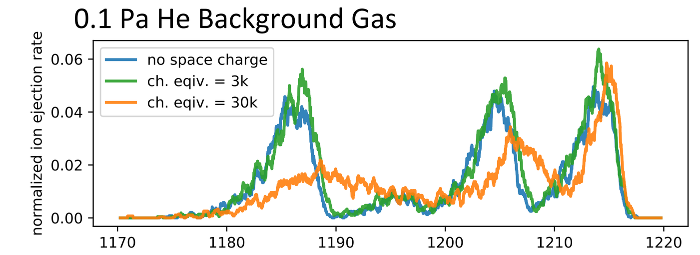
no gas collisions



top / top-right:
Non resonant ejection spectra for different space charge weights without background gas collisions. Note that the decrease of charge density in the trap is clearly visible in the signal of ^{132}Xe.

right:
Non resonant ejection spectra at 0.1 Pa He in the background, the mass signals become significantly wider due to the background gas collisions.

0.1 Pa He Background Gas

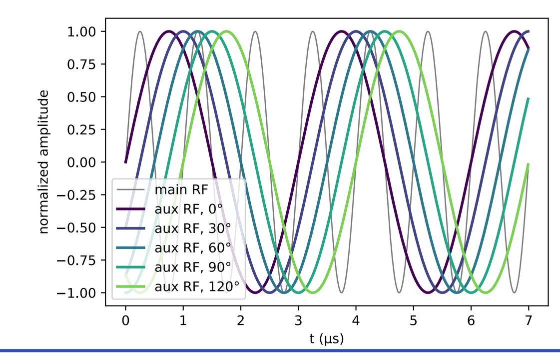


Resonant Ion Ejection: Auxiliary RF Phase

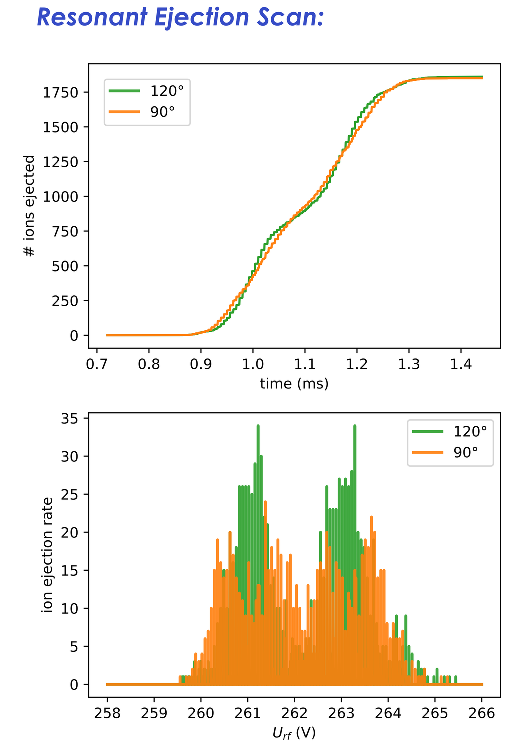
The phase between the auxiliary RF waveform and the main trap RF is another adjustable parameter of the resonant ion ejection mode.

right:
Significant peak widening and the formation of double peak structures is visible with 90° phase between aux. RF and main RF in contrast to 120° phase difference.

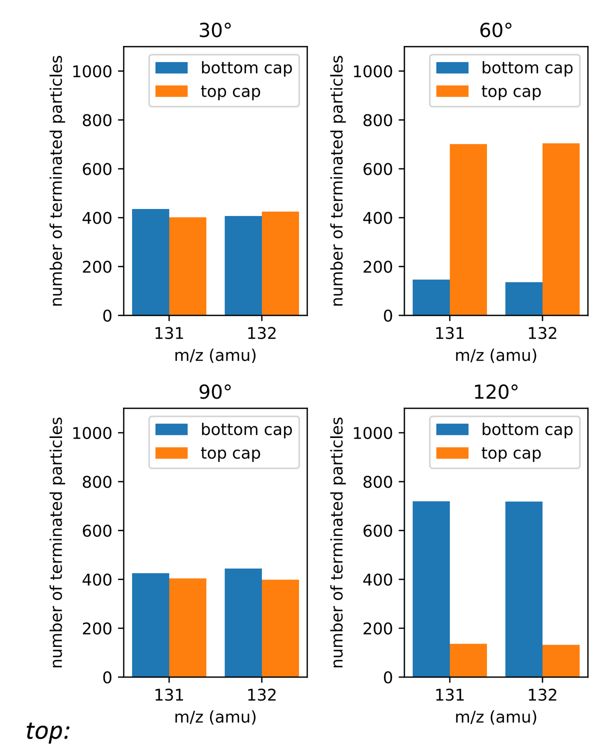
bottom:
Auxiliary RF signal applied to the cap electrodes with phase differences relative to the main trap RF



Resonant Ejection Scan:



Ion Termination Positions:



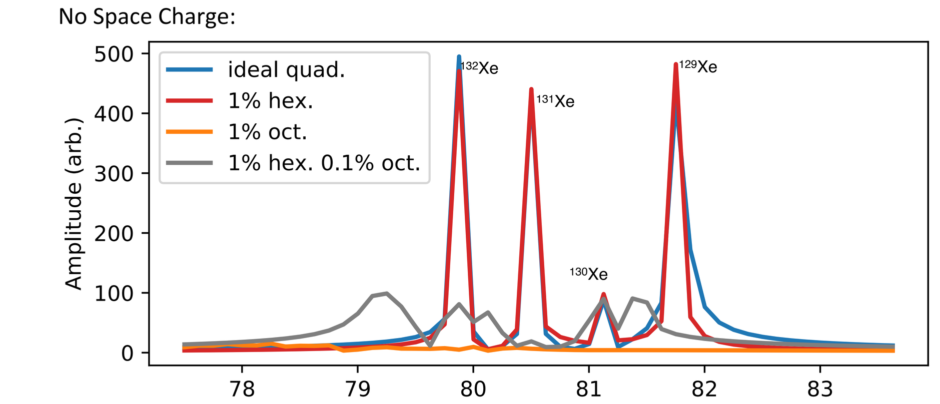
top:
The ejection direction depends significantly on the auxiliary RF phase

Higher Field Orders: Non ideal trap field

The occurrence of higher order distortions of the ideal quadrupolar trapping field can result from non-ideal trap geometries. To investigate the effects of higher field orders on the individual detection modes, simulations with small fractions of hexapolar (Φ_3) and octapolar (Φ_4) orders were performed with Xe Isotopes (m/z = 129, 130, 131, 132 Th) at 1 MHz trap RF frequency.

FT-Detection:

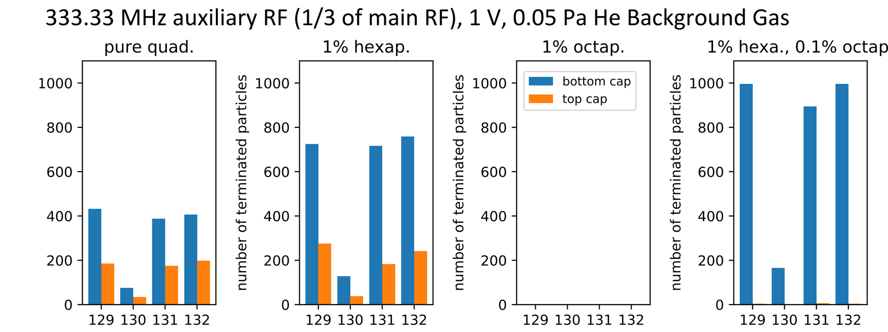
No Space Charge:



top:
General effects of hexa- and octapolar field components on FT-QIT spectra without background gas interaction. Octapolar field components have a pronounced effect on the simulated mass signals.

Resonant Ejection Scan:

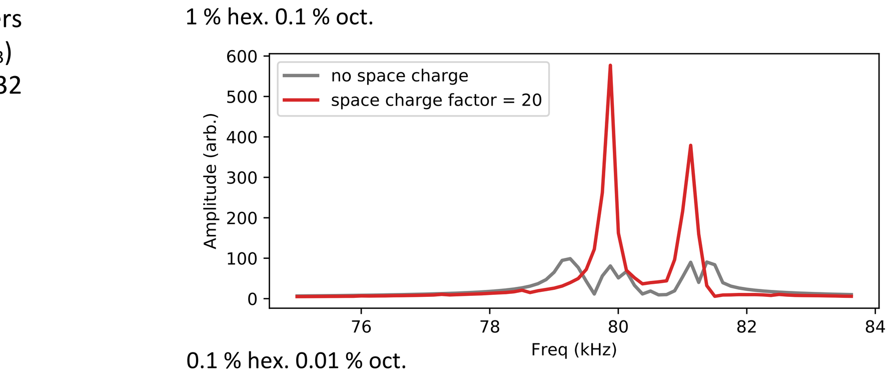
333.33 MHz auxiliary RF (1/3 of main RF), 1 V, 0.05 Pa He Background Gas



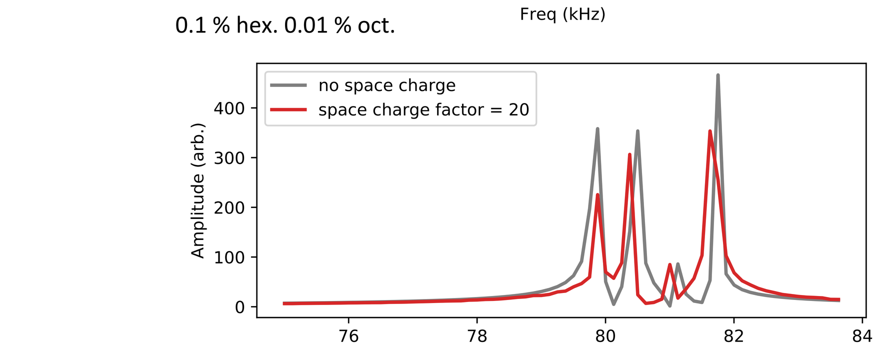
top:
Ejection directions with higher field order components present. Note the pronounced effect of the octapolar field component.

Space Charge Variation:

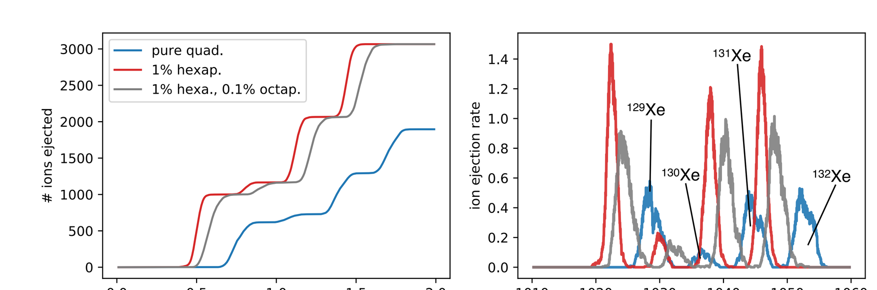
1 % hex. 0.1 % oct.



0.1 % hex. 0.01 % oct.



top / top-right:
Effects of space charge on FT-QIT results with higher order field components present. Note that in the upper case, the consideration of space charge lead to a re-occurrence of two main mass signals.



top:
Exemplary resonant ejection spectra in correspondence to changing field components

Conclusions

- The direct comparison between resonant and non-resonant ejection and FT-detection shows:
  - Total peak fusion with synchronized oscillation of the individual ion species for the FT mode
  - Ejection scan modes are less sensitive to total peak fusion compared to FT detection
  - Particularly resonant ejection techniques are very robust against space charge induced peak fusion in comparison to the other detection modes
  - Space charge effects vanish with decreasing charge density in the trap during an ejection scan
- The variation of the auxiliary RF phase relative to the main trap RF reveal interesting consequences of the phase difference:
  - Peak widening and the formation of double peaks
  - Asymmetric ejection behavior towards one cap electrode
- Consideration of hexa- and octapolar field components also show interesting effects on the trapped ions and the operation modes:
  - Shifts of the simulated mass signals in FT and resonant ejection modes
  - Significant change of the ion stability in resonant ejection mode

Literature

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