Ion dynamics simulation: Space charge effects in a fourier transform 3D-ion trap (FT-ion trap)

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Introduction

The coulombic interaction between charged particles, generally known as "space charge", is of pivotal role for the characteristics of diverse technological systems, including ion trap mass analyzers. The electric interaction between ions induces complex couplings between ion densities, ion motion and the electric field generated by an ion population. This complicates the mathematical and numerical modeling of such systems when considering space charge. A numerical Monte-Carlo model of an ion population with fast approximate space-charge calculation using a Barnes-Hut tree method [1] is one approach to address this problem type.

We developed such a model and applied it to theoretically investigate space charge effects in a modern 3D quadrupolar ion trap mass analyzer [2], which detects the mirror charge signal induced by ions oscillating in the trap on detector plates. Subsequent Fourier transform (FT) yields the corresponding mass signals.

Methods

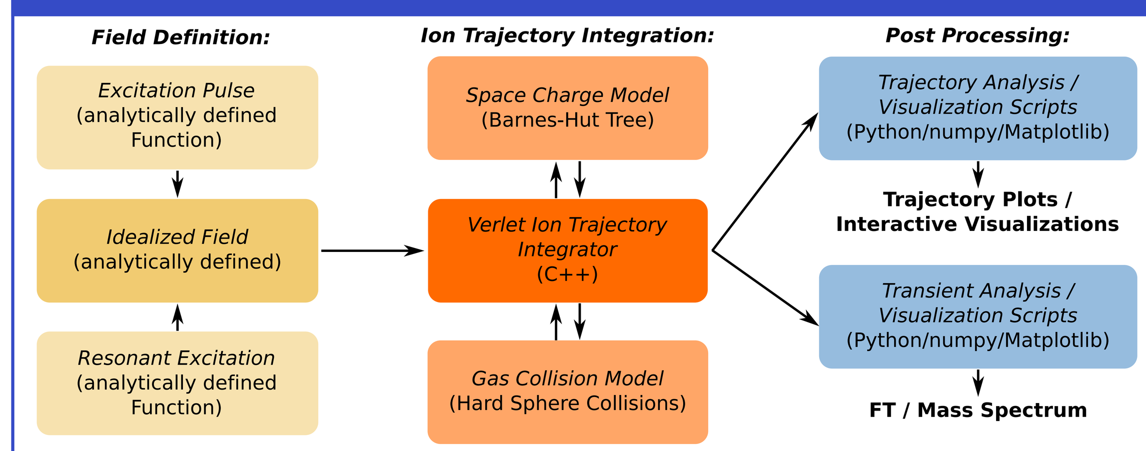
Ion Trajectory Simulation:

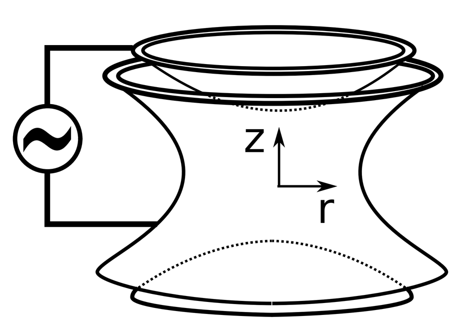
- Custom Verlet ion trajectory integrator
- Idealized trapping field, defined as analytical functions, resonant and non resonant excitation of ions via excitation potential in z-direction
- Background gas collisions are modeled with a hard sphere scattering model

Post Processing:

- Ion trajectories and the time resolved averaged center of the ion cloud is exported from the simulation
- Inverse Fourier transform of the average ion position transient yields the simulated frequency / mass spectrum

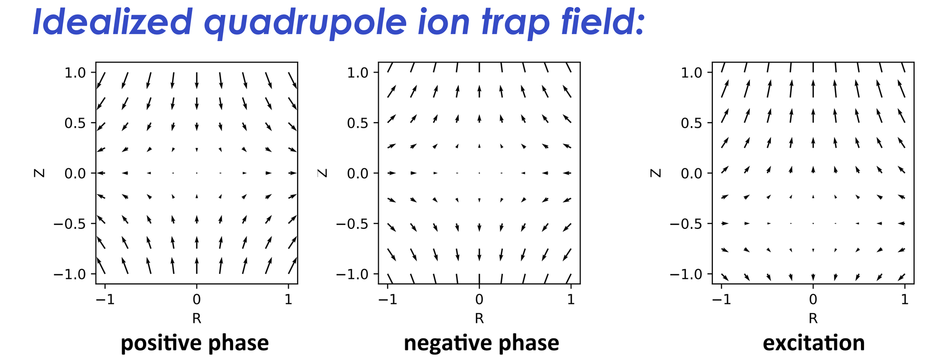
Simulation Setup Overview





Scheme of a quadrupole / 3D ion trap.

Idealized quadrupole ion trap field:



Idealized quadrupolar field in the positive and negative phase of the trapping field

Excitation potential is applied in Z direction

Space Charge Effects: Peak Coalescence / Peak Shifts

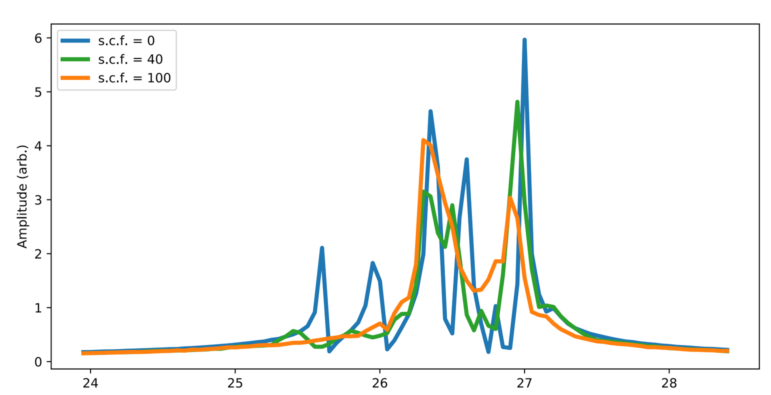
The FT-ion trap mass separation principle is based on the mass dependent secular oscillation frequency of trapped ions. Space charge interferes with the secular oscillation: Ion species of different mass interact with each other, the oscillation of a species becomes dependent on other ions present in the trap. This potentially leads to frequency shifts in the observed ion signals.

In extreme cases, multiple close mass signals can become indistinguishable and fuse to a single signal, which is generally known as "peak coalescence" [3,4].

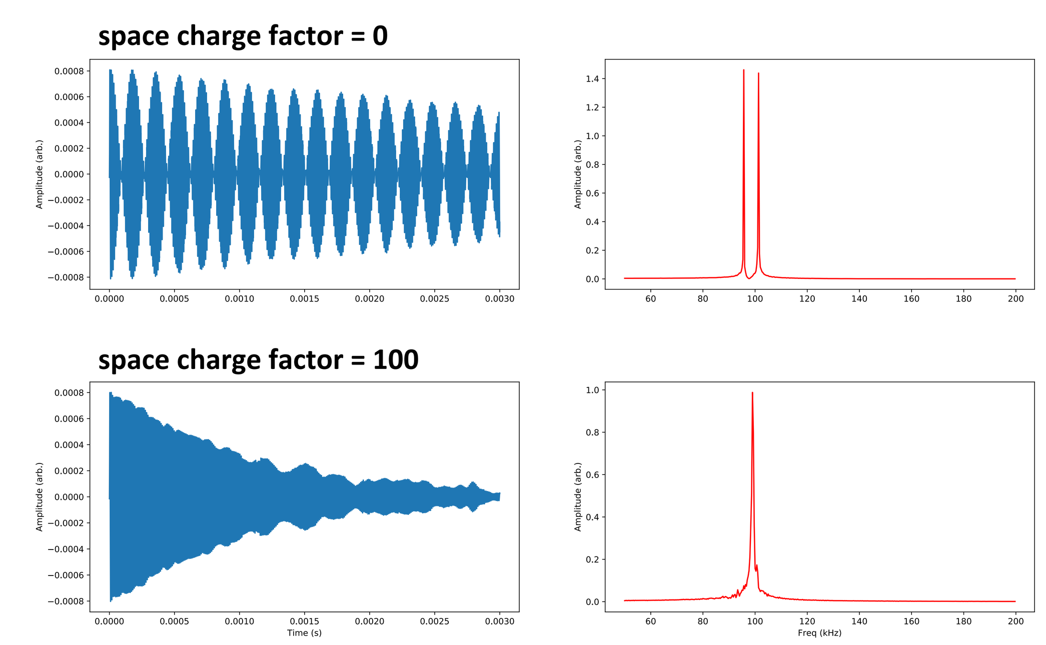
We have performed simulations with Chlorine and Xenon isotopes to assess the effects of space charge on simulated spectra of these species in an idealized 3D FT-Ion Trap.

Xenon Isotopes:
Complex Peak Coalescence

Similarly to the results with Chlorine isotopes, the more complex Xenon isotope pattern shows peak coalescence to two remaining signals. At lower extent of space charge, the less abundant signals (at 25.5 kHz and 25.8 kHz corres-ponding to m/z=135.9 and 133.9) vanish, while the other signals show complex amplitude modulation.



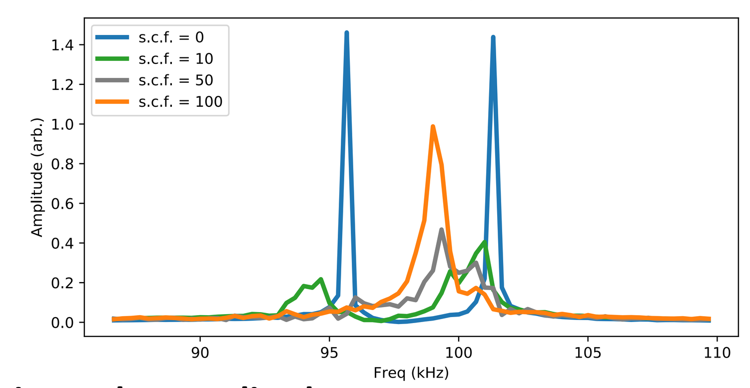
Chlorine Isotopes:
Space charge effect: Peak Coalescence



left:
Simulated transients of Chlorine isotopes (m/z=35 and 37, 500 particles per species, background gas pressure 0.001 Pa) and resulting FT-spectrum, without space charge (space charge factor, s.c.f = 0) and with a charge weight of 100 elementary charges per simulated ion in the space charge calculation (s.c.f. = 100).

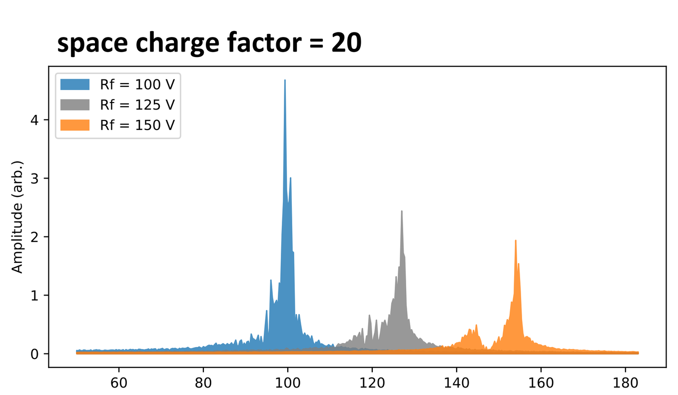
The transient amplitude quickly decreases with the high charge weight and total peak coalescence is observed.

bottom:
FT-spectra of Chlorine isotopes for different space charge factors in comparison: The resolved signals without space charge show complex amplitude modulation and position shifts until they become indistinguishable at a s.c.f. of 100.



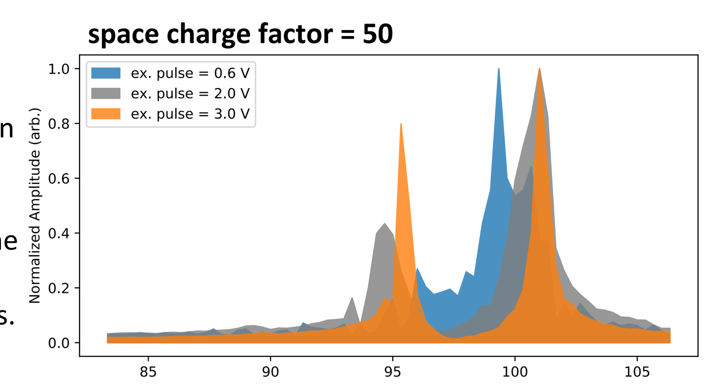
Trap RF field amplitude:

Increasing the amplitude of the trapping RF, which also shifts the secular frequencies upwards, resolves the mass signals of Chlorine isotopes despite the relatively high space charge factor.



Excitation pulse amplitude:

Ions are detected upon applying an excitation pulse in the FT-trap. Increasing the excitation and thus the oscillation amplitude of the ions, the mass signals become resolved even at high space charge conditions.



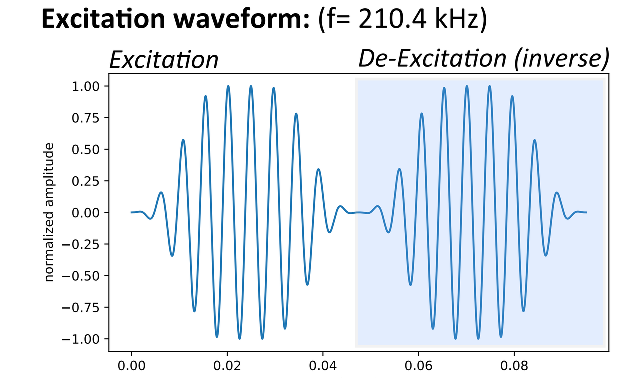
Resonant Ion Excitation

Model Case:
O_2^+ Excitation with pure sine waveform

Resonant excitation of ions in an ion trap allows to selectively manipulate and excite individual ion species (Stored Waveform Inverse Fourier Transform, *SWIFT*, [6]), which enables many interesting analytical operation modes. To study space charge coupling effects with resonant ion excitation, a simple model case was simulated: Excitation of O_2^+ ions in the presence of N_2^+ ions with a pure sine wave excitation waveform.

right: Excitation waveform for the simulated model case.

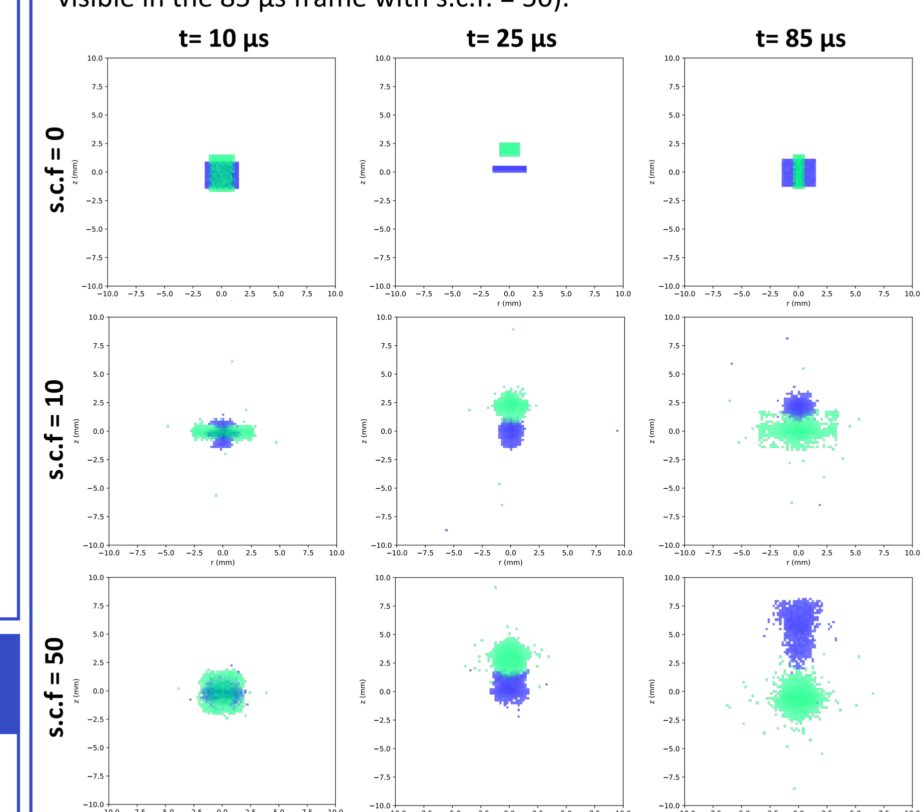
Excitation waveform: (f= 210.4 kHz)



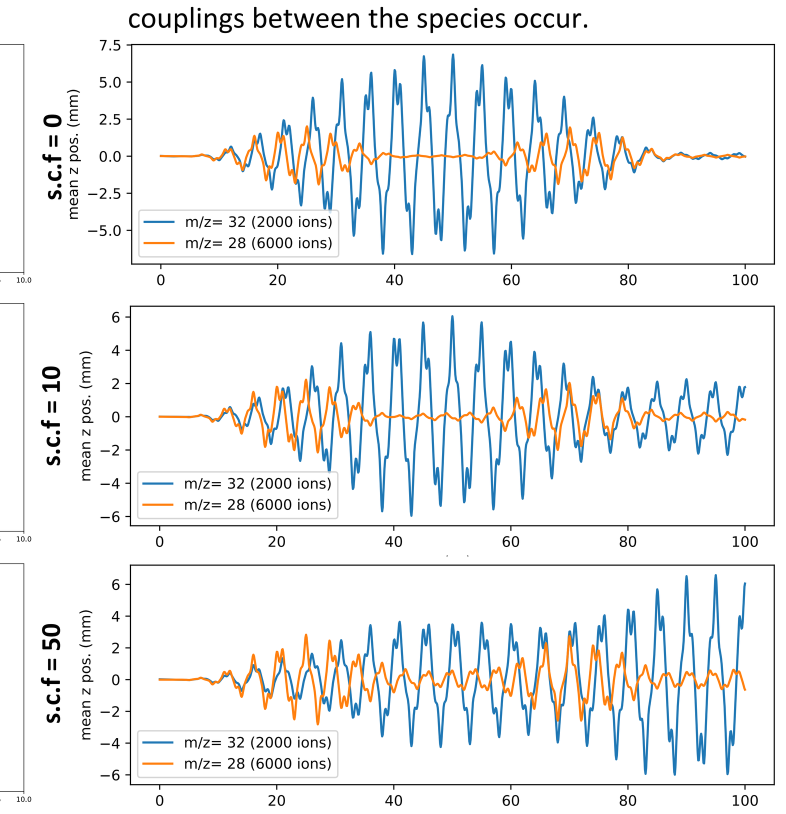
Effect of Space Charge:

below:
Ion density plots (r-z projection) for simulations with resonant excitation of O_2^+ (dark blue, m/z=32) and N_2^+ (light blue, m/z=28). The space charge interactions lead to de-correlation of the individual ion clouds and to intense interactions between them (particularly visible in the 85 µs frame with s.c.f. = 50).

below:
Averaged secular motion of the ion species in the simulations shown below-left. Without space charge, O_2^+ can be resonantly excited and de-excited by the applied waveform. With increasing space charge factor, intensive couplings between the species occur.



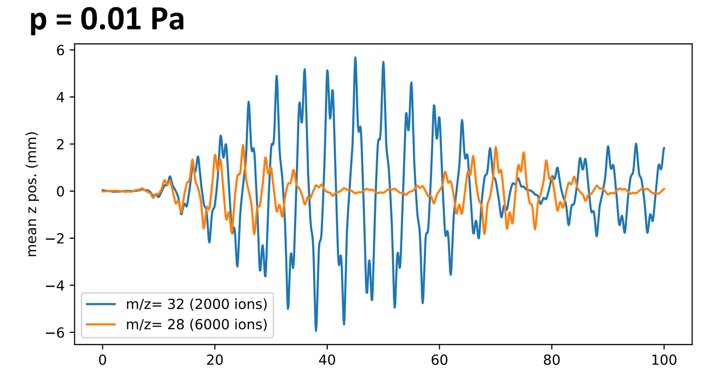
(simulations without background gas)



Effect of Background Pressure:

Collisions with background gas lead to effects, which are comparable to space charge induced interactions: The de-excitation of the O_2^+ remains incomplete similarly to the result with a space charge factor 10 shown above.

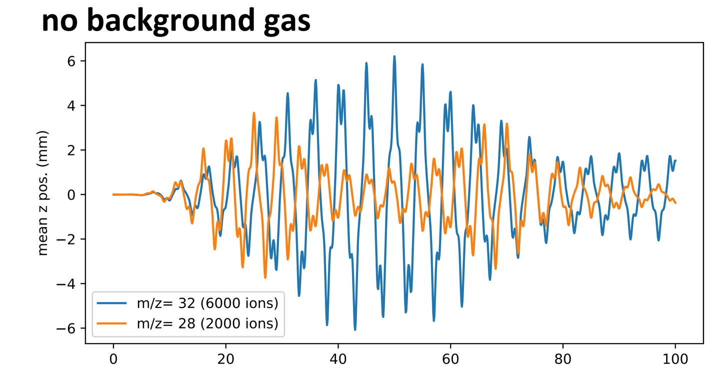
p = 0.01 Pa



Effect of Ion Concentrations:

Reversing the amounts of simulated particles in the simulation leads to differences to the result shown above: More abundant O_2^+ ions affect now the N_2^+ ions more intensively. In addition, the strong increase in secular oscillation in the last 20 µs of the simulation visible above is much less pronounced.

no background gas



Space Charge Effects: Background Gas and Background Ions

Background Ions:

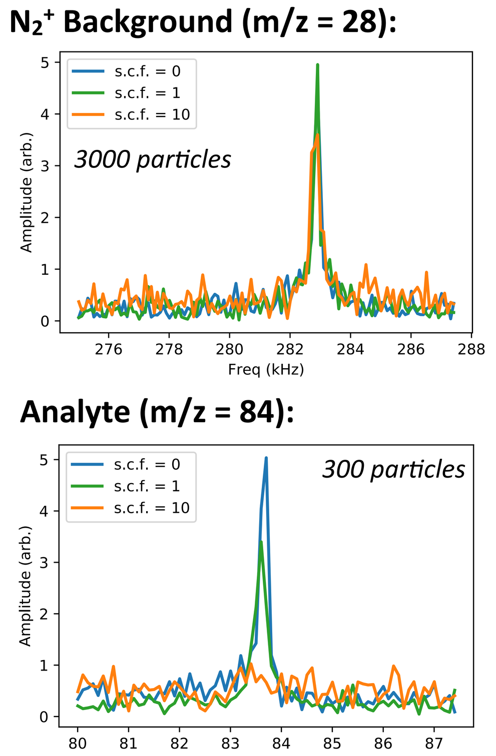
In-trap electron ionization [5] may lead to significant amounts of background gas ions. These background ions potentially affect the oscillation of analyte ions and thus their mass signals by space charge interactions.

Analyte Signal Loss:

In extreme cases this scenario leads to quantitative losses of analyte signals, as shown on the right:

With increasing space charge factor the signal of an analyte vanishes, while the signal of the N_2^+ background ions remains mostly unaffected.

N_2^+ Background (m/z = 28):

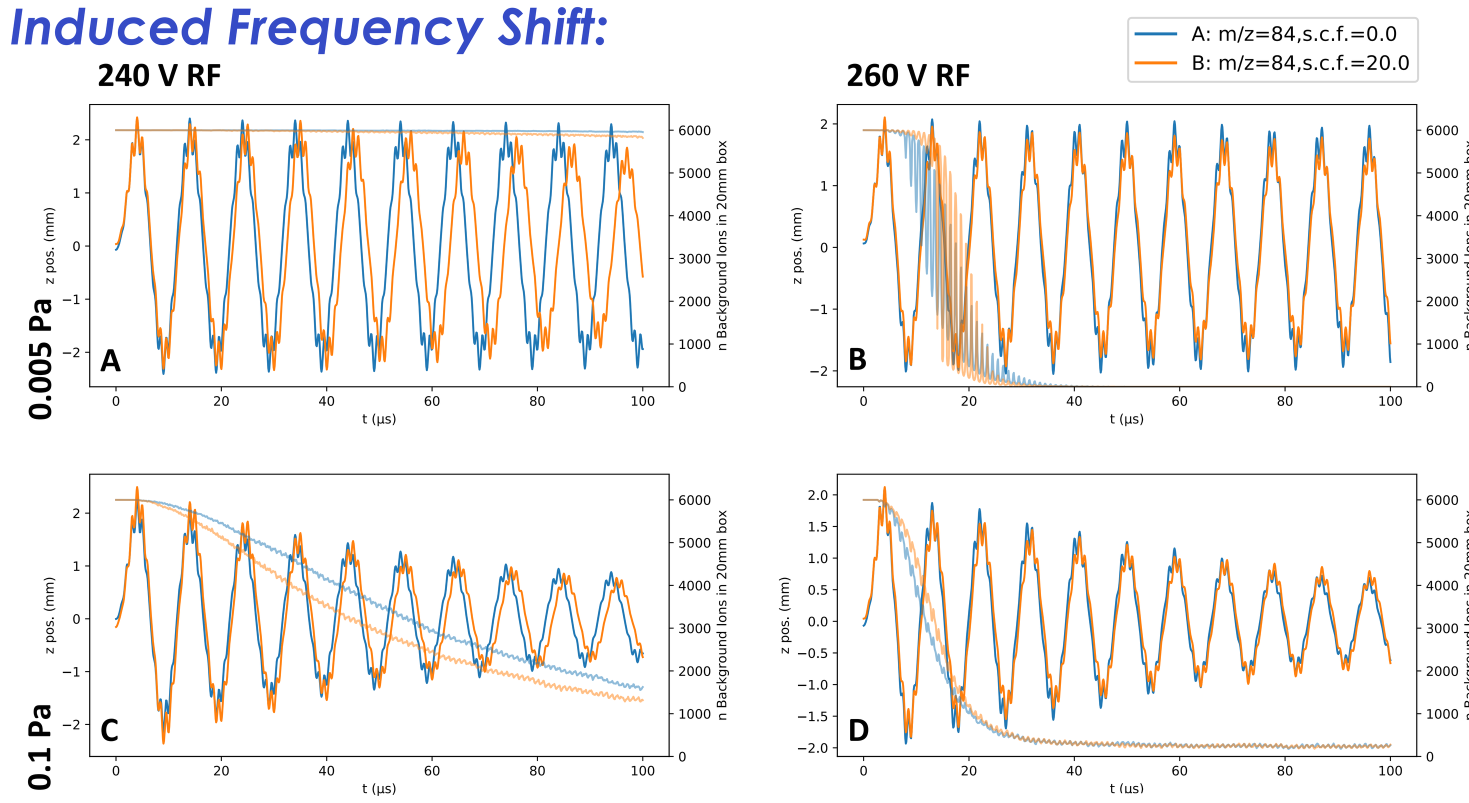


Background Ion Induced Frequency Shift:

The frequency shift of an analyte signal in the presence of background ions is directly dependent on their concentration in the ion trap:

With a high amount of N_2^+ background ions, a significant shift of the secular oscillation of an analyte is observed when space charge is considered (A).

The frequency shift vanishes when the background ions are removed from the trap, either making them unstable by an increased trap RF (B), higher gas pressure (C) or both (D).



Outlook

The presented simulations mark a first step towards the detailed investigation of ion dynamics in 3D-FT-ion traps.

Future work includes:

- Optimizations of the simulation code and integration of other space charge approximation methods (e.g. fast multipole methods) to increase the number of simulated particles
- Consideration of chemical ion-neutral and ion-ion interactions and charge transfer reactions
- Detailed simulation of in-trap ionization methods
- Consideration of ion temperature and internal states of molecular ions

Conclusions

- A new code for the simulation of ion trajectories with a Barnes-Hut tree approach for calculating coulombic particle-particle interactions was developed
- First simulation results show general applicability for the simulation of ion dynamics in a 3D-FT ion trap
- Well-known space charge effects, particularly peak coalescence, peak shifts and signal losses, are reproduced by the simulations
- The simulations allow to estimate the tolerable amount of ions present in an ion trap device, which in turn enables the design of charge control techniques in analytical 3D-FT ion traps.

Literature

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Acknowledgement

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