Examining Space-Charge Effects in FTICR Mass Spectrometry With Multiparticle Simulations of Ion Motion

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Tin tribromide isotopic fine structure
FTICR circa 1983, 3 tesla, cubic cell

The Simplicity of FTICR-MS

\[ \omega_c = \frac{qB}{m} \]

Fourier Transform Ion Cyclotron Resonance: 
The Basic Experiment

$\omega_c = xxxxxxx.x$

$m/z = xxx.xxxx$

$\frac{m/z}{\omega_c} = \frac{B}{\omega_c}$

99.99% accurate

Electric field (applied and intrinsic) shift observed frequency by 10’s of ppm

Calibration

Graphics by Steve Hofstadler
Complexity Enters

\[ \omega_{\text{eff}} = \frac{qB}{m} - \frac{2\alpha V_T}{\alpha^2 B} - \frac{q\rho G_i}{\varepsilon_0 B} \]

Unperturbed Cyclotron Frequency (accurate to 99.99%)

Reduction Due to Trapping Electric Field (Magnetron Frequency, Causes shifts of 10-100 ppm)

Reduction Due to Space Charge, Shifts of 10's ppm

Ion Motion Can be Calculated by Numerical Integration of:

\[ \vec{F} = m\vec{a} = q\vec{E} + q\vec{v} \times \vec{B} \]
Charged particle simulation and its sub-problems

- Charge deposition on the mesh
  - Particle in a cell [Mitchell, Smith 1997]

- Solving Poisson equation
  - Potential interpolation back to the mesh
    - Advancing particles in the mesh
      - SIMD, MIMD, MISD

Mathematical expressions:

\[
V^2 u(r) = -\frac{\rho(r)}{\varepsilon}
\]

- Cartesian
- Cylindrical in Cartesian
- "true" cylindrical

- Capacitance calculation
- Planning
- Almost done
- done
9 Peptide Simulation
52,000 ions
Space-Charge Effects on Mass Accuracy

The observed frequency shifts with changes in the number of ions that are trapped in the analyzer cell. The frequency shift, $\omega_{eff}$, is given by the equation:

$$\omega_{eff} = \frac{qB}{m} - \frac{2\alpha V_T}{a^2 B} - \frac{q\rho G_i}{\epsilon_0 B}$$

$\rho$ is the ion density, $G_i$ is a geometric factor for the ion cloud spatial distribution, and $\epsilon_0$ is the vacuum permittivity of free space.

1) Space charge frequency shift is independent of mass.
2) All ions undergo the same space-charge induced shift.
3) Internal calibration is immune from space-charge effects on mass accuracy.
4) External calibration requires correction of space-charge shift when analyte and calibrant total ion intensities differ.
Single m/z Frequency Shifts

Simulation Parameters

- 7.0 T magnetic field
- m/z 133 (Cs⁺)
- Ion number - 100 – 750,000
- Dimensions -2.0”x2.0”x2.0”
- PIC Grid - 32x32x32
- Cubic and Penning Trapping Potentials
- Trapping Voltage - 1V
- Burst excitation - 1V - 5V
- Coulombic interactions enabled
Excite Radius Dependent Frequency Shift
Ion-Image Charge Interaction

Experiment: Effect of Orbital Radius
larger radius = lower ion density

Simulation: Two masses present (m/z 133, 150)
One mass value (m/z 133) versus two mass values (m/z 133 and 150)

Slope Ratio = 7.0

Image-Charge Induced Frequency Shift


Harmonic Inversion – FDM
Filter Diagonalization Method

Simulation Parameters

• 1M data points @ ~10 MHz
• Transient ~10 ms
• Total of 30k ion used in each simulation (Sub P)
  – “A” = 30k
  – “A”/ “A+1” = 15k each
  – “A”/ “A+2” = 15k each
  – “A”/ “A+1”/ “A+2” = 10k each
• B = 7.0 T
• 2” cubic cell
• Idealized quadrupolar trapping potential
Simulation of a Single Isotope SubP, “A” ion - 30,000 ions

- FDM of 25,000 pts, stepped 10,000 pts each time across 1M data pts
- 10 micro-Hertz variation in simulated frequency
- Frequency stability is 1 part in $10^{10}$ for a pure quadrupolar trapping field
Simulation of “A” and “A+1”

- 30,000 ions total, 15K of “A”, 15K of “A+1”
- FDM of 15,000 pts, stepped 10,000 pts across 1M pts
- Beat is ~ 170,000 pts
Simulation of “A” and “A+2”

- 30,000 ions
- FDM of 15,000 pts, stepped 10,000 pts across 1M data pts
- Beat is ~ 80000 pts
Projection of Cyclotron Motion
Substance P, “A” / “A+1”

Image Current

A Peak X Position

A+1 Peak X Position
Conclusions

- PIC Simulations effectively replicate FTICR-MS phenomena (theoretical and experimental)
- Harmonic Inversion (FDM) of Simulated Transients provides insight into dynamic space charge frequency shifts
- Insights into the range of charge-induced frequency shifts should lead to better calibration and ppb or sub-ppb mass accuracy
Acknowledgements

• Franklin Leach
• Ron Heeren
• Andriy Kharchenko
• Eugene Nikolaev
• Kostya Aizikov
• Pete O’Connor

NSF - MSPIRE