Compensated FT-ICR Ion Trapping Cell Performance at High Magnetic Field

Errol W. Robinson[1]; Aleksey Tolmachev[2]; Si Wu[1]; Christian Berg[3]; Donald F. Smith[1]; Shawna M. Hengel[1]; Rosalie Chu[1]; Thomas L. Fillmore[1]; Gordon A. Anderson[2]; Richard D. Smith[2], and Ljiljana Paša-Tolić[1]
[1]Environmental Molecular Sciences Laboratory and [2]Biological Sciences Division, Pacific Northwest National Laboratory, Richland, WA; [3]Bruker Daltonics, Billerica, MA

EMSL at Pacific Northwest National Laboratory

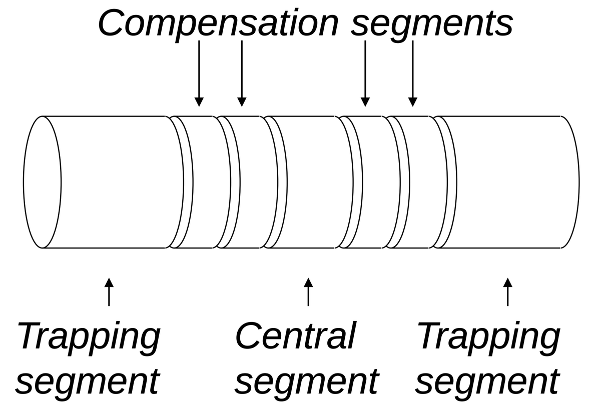
Overview

- Design FTICR cells with improved performance at higher ion excitation radii
- Experimentally validate theoretical models predicting FTICR cell performance based on the measurement of calibration coefficients as a function of post-excitation radius
- Theoretical and experimental study of two recently introduced FTICR cell designs
- Explore radial electric field divided by radius (E_r/r) as a criterion for FTICR cell design

Introduction

- FTICR MS applications at PNNL include top-down proteomics, MS imaging, analysis of complex biological systems such as microbial communities
- These applications require increased MMA, dynamic range, and sensitivity
- Optimizing FTICR ion trapping cell design to maximize performance, minimize deleterious effects
- Maximize MMA by minimizing variations in the radial electric field per radius (E_r/r)
- Maximize sensitivity by exciting ion packets closer to the detection electrodes
- Maximize dynamic range by reducing Columbic interactions by utilizing a larger cell volume, increased excitation
- New FTICR cell designs use additional compensation electrodes with the intent to improve cell performance
  - Open cylindrical 7 segment (OC-7S) compensated cell design [1-2]
  - Leaf cell, or paracell [3-4]
- Evaluate cell performance using both experiment and theoretical models
- Evaluation of cell performance based on calibration function [5-6] results from theoretical models

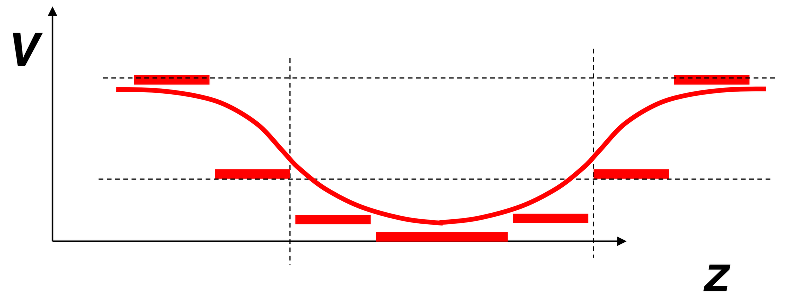
OC-7S compensation configuration



Methods

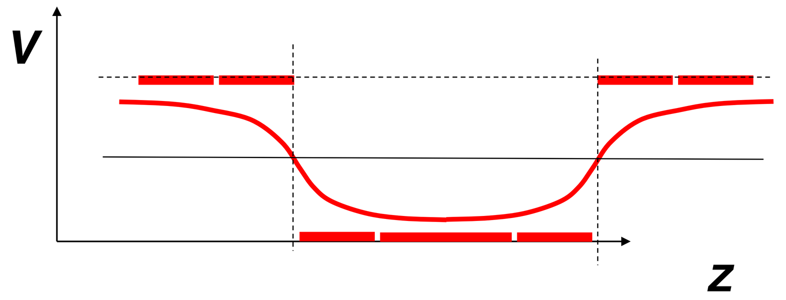
- Mass Spectra were acquired of a peptide mixture and ubiquitin using a series of excitation values, trapping potentials, and ion population on a 12T FTICR MS
- In-house software internally calibrated each spectra and calculated B_F, resolution, and MMA
- Datasets were acquired with the OC-7S cell in two configurations

Compensated cell configuration



Relative potentials for each cell segment
1, 0.3167, 0.1333, 0, 0.1333, 0.3167, 1

Open cell configuration



Relative potentials for each cell segment
1, 1, 0, 0, 0, 1, 1

- E_r/r was calculated using Laplace equations for each FTICR cell geometry
- Key properties of the Laplace equations (linear superposition, boundary condition effects, and the scale rule) simplified the modeling and design process
- The frequency shift in the cyclotron frequency due to the electric field was then calculated from the models
- Calibration coefficients based on Francl's [5] and Ledford's [6] calibration functions were then determined
- This enabled the comparison of theoretical and experimental cell performance. Plots of Fancl's second term, B_F, are shown as an example.

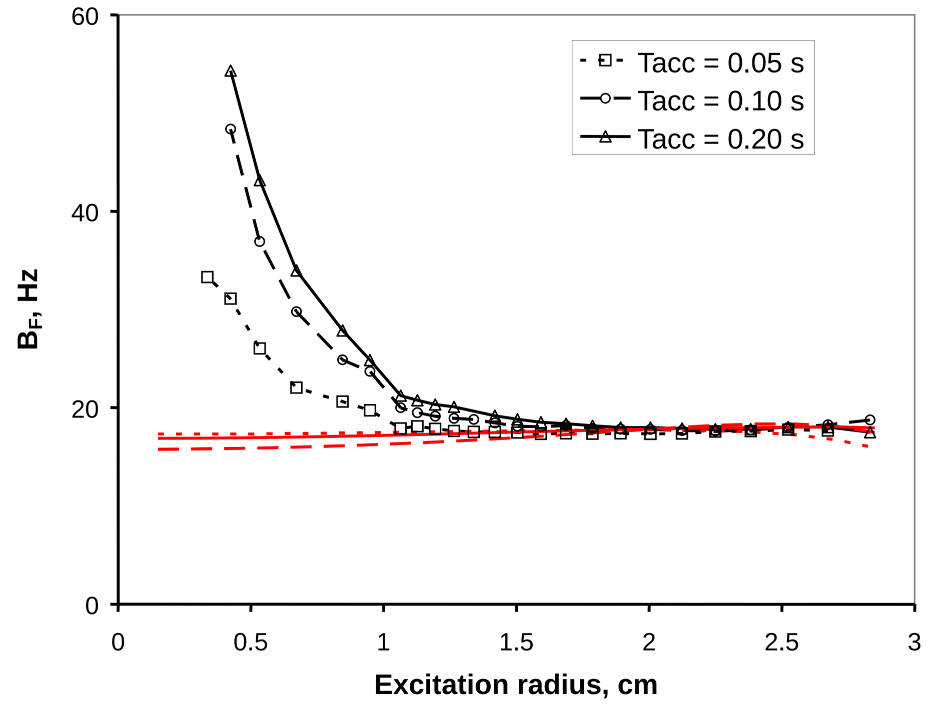
$$B_F = -\Delta f_E = -\frac{1}{2\pi B_z}\cdot\frac{E_r}{r}$$

with the frequency shift Δf_E, produced by electric fields equal to the inverse of B_z (the magnetic field inside of the ion trapping cell) times the radial electric field per radius.

Results

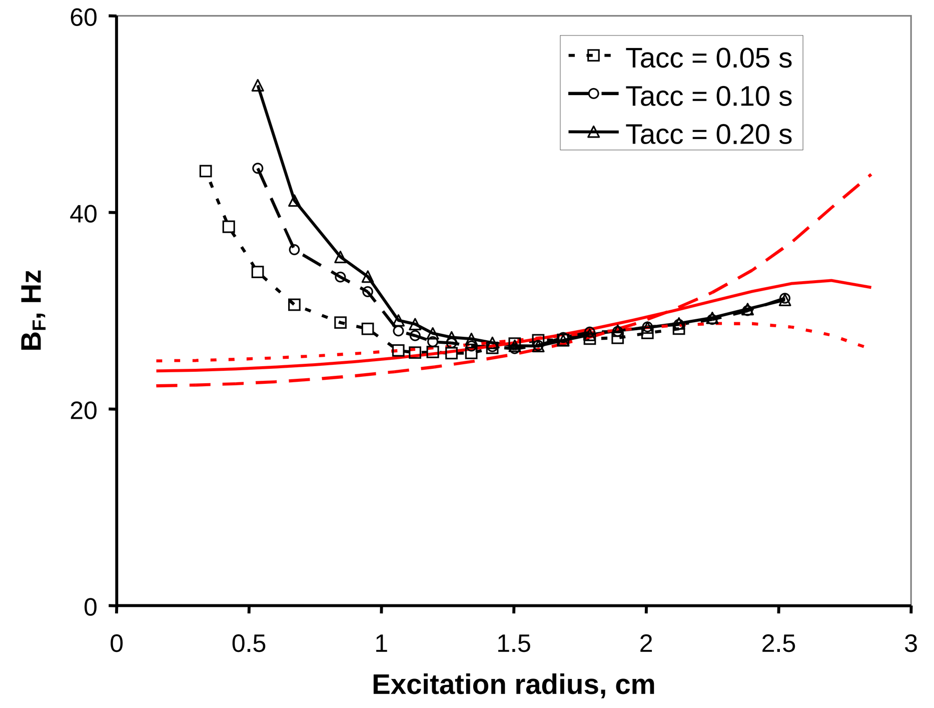
Comparing measured and predicted electric field related frequency shifts

Compensated cell configuration



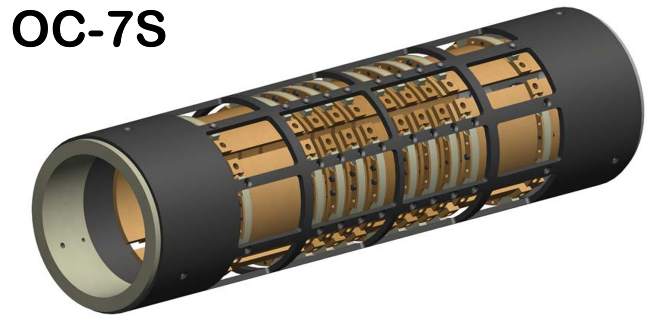
- B_F calculated from internally calibrated spectra of a 9 peptide mixture from a range of excitation powers
- 3 different ion populations corresponding to external accumulation times (Tacc) of 0.05 s (squares), 0.10 s (circles) and 0.20 s (triangles).
- Red curves: B_F coefficient calculated using the radial electric field obtained from potential calculations
- 3 curves are shown corresponding axial kinetic energy of 0.5 eV (dotted), 0.8 eV (solid) and 1.2 eV (dashed)

Open cell configuration

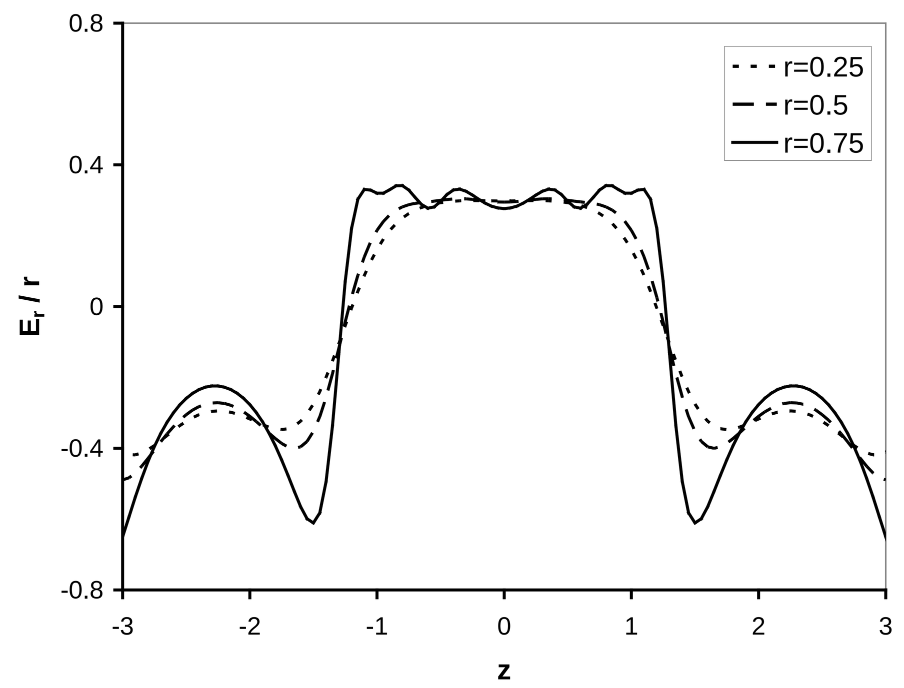


E_r/r models for the OC-7S and Leaf cells

OC-7S

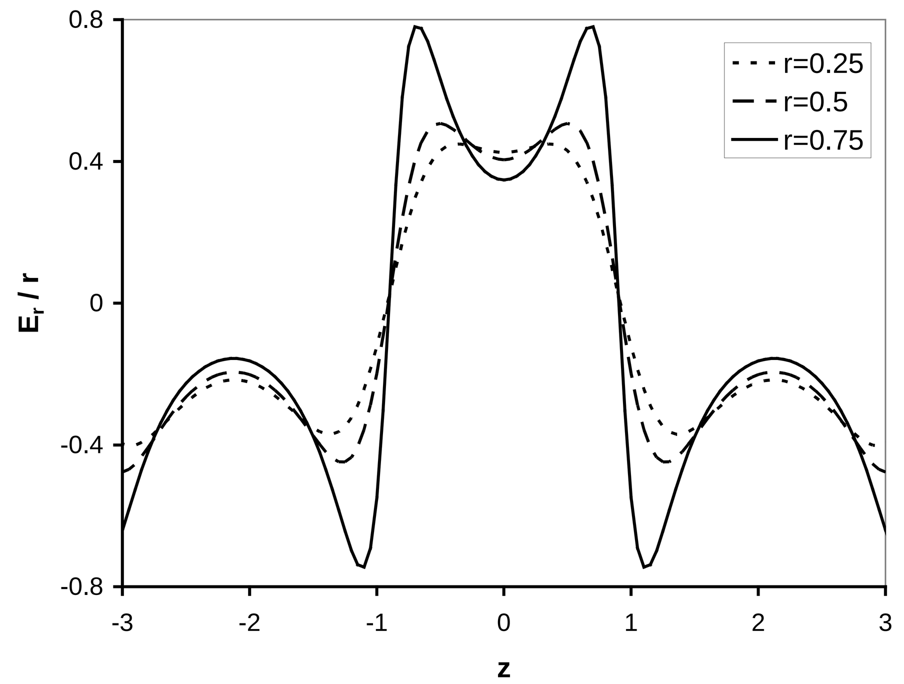


OC-7S axial E_r/r profiles

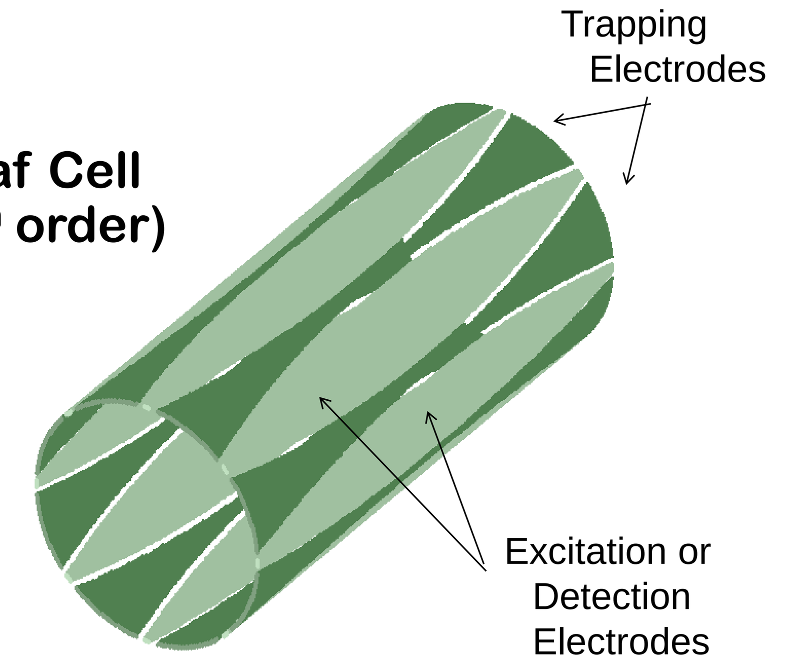


- The effect of compensation was more pronounced in E_r/r profiles, where deviations of the open cell configuration (below) were significantly larger than those of the compensated cell (above) relative to Er plots (far left)
- The improved spatial uniformity of E_r/r for the compensated cell was the target of cell configuration optimization.

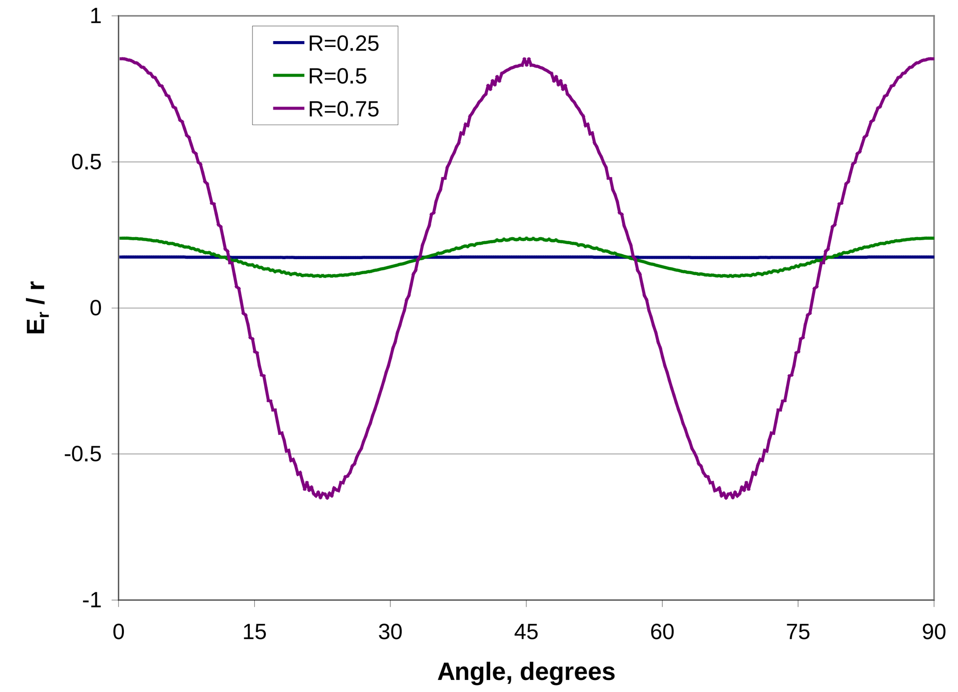
Open cylindrical cell axial E_r/r profiles



Leaf Cell (8[th] order)

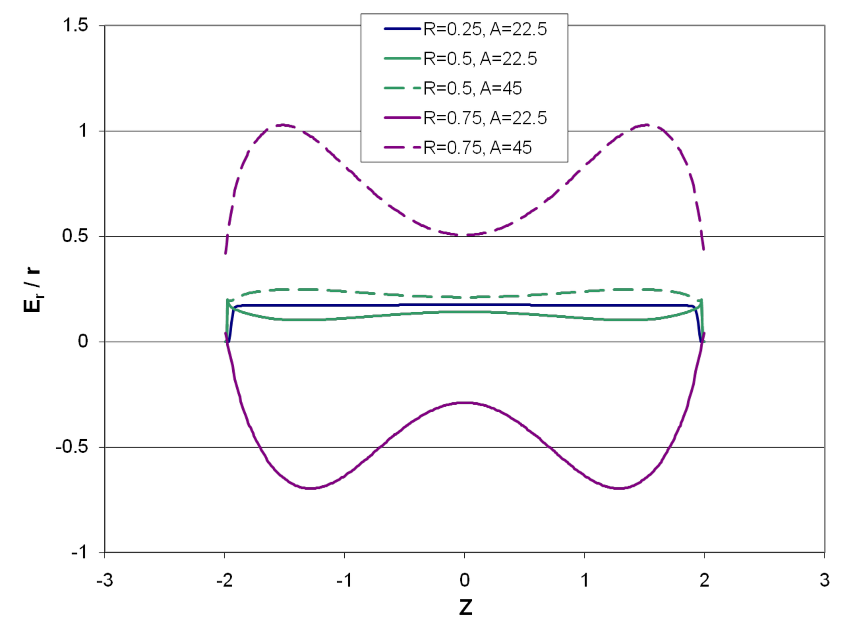


E_r/r angular dependence



E_r/r values calculated halfway between cell center and cell entrance (above) and at two polar angles, corresponding to a minimum and a maximum of the angular dependence. (below)

Leaf Cell axial E_r/r profiles



Conclusions

- Francl's calibration coefficient B_F was calculated independently from theoretical models and experimental measurements
- Using B_F as a link between theory and experiment, models based on radial electric field per radius (E_r/r) were experimentally demonstrated to accurately predict FTICR cell performance at higher cell excitation radii
- Modeling was successfully extended to asymmetric cell designs, e.g. the Leaf Cell
- E_r/r modeling predicts the Leaf Cell to perform well at low ion excitation (some uncertainty at higher excitation values).

Acknowledgements

We thank James Ewing, Brian LaMarche, and Adam Flory for their assistance. This work was funded in part by the American Recovery and Reinvestment Act of 2009, and portions of the research were performed using EMSL, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory in Richland, Washington.

References

1. A. V. Tolmachev, E. W. Robinson, S. Wu, H. Kang, N. M. Lourette, L. Paša-Tolić and R. D. Smith, Trapped-ion cell with improved DC potential harmonicity for FT-ICR MS. *J. Am. Soc. Mass Spectrom.* **2008**, *19*, 586-597.
2. A. V. Tolmachev, E. W. Robinson, S. Wu, L. Paša-Tolić and R. D. Smith, FT-ICR MS optimization for the analysis of intact proteins. *Int. J. Mass Spectrom.* **2009**, *287*, 32-38.
3. E. N. Nikolaev, I. A. Boldin, R. Jertz, and G. Baykut, Initial Experimental Characterization of a New Ultra-High Resolution FTICR Cell with Dynamic Harmonization. *Rapid Com. Mass Spectrom.* **2011**, *25*, 122-126.
4. I. A. Boldin and E. N. Nikolaev, Fourier transform ion cyclotron resonance cell with dynamic harmonization of the electric field in the whole volume by shaping of the excitation and detection electrode assembly. *J. Am. Soc. Mass Spectrom.* **2011**, http://dx.doi.org/10.1007/s13361-011-0125-9.
5. T. J. Francl, M. G. Sherman, R. L. Hunter, M. J. Locke, W. D. Bowers and R. T. McIver, Experimental-determination of the effects of space-charge on ion-cyclotron resonance frequencies. *Int. J. Mass Spectrom. Ion Process.* **1983**, *54*, 189-199.
6. E. B. Ledford, D. L. Rempel and M. L. Gross, Space-charge effects in Fourier-transform mass-spectrometry - mass calibration. *Anal. Chem.* **1984**, *56*, 2744-2748.

CONTACT: Robby Robinson, Ph.D.
Environmental Molecular Sciences Laboratory
Pacific Northwest National Laboratory
P.O. Box 999, Richland, WA 99352
E-mail: errol.robinson@pnnl.gov