Injection of Externally-Generated Low Mass Ions into High Magnetic Field in Q/FT-ICR Instruments: SIMION Simulations and Experimental Observations

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INTRODUCTION

Recently, we showed that externally generated ions with m/z as small as 26 Th can be guided into an ICR cell located within the homogenous section of a 9.4 tesla superconducting magnet of a Fourier transform-ion cyclotron resonance mass spectrometer (FT-ICR MS) by using higher frequency waveforms (*i.e.,* 3 MHz $<f<$10 MHz) and a quadrupole ion guide (QIG) [1]. To better understand and address the challenges associated with guiding small mass ions into a strong magnetic field, we have used SIMION simulations to examine trajectories of small ions (*i.e.,* m/z 28-300) in a QIG (housed in an experimentally measured magnetic field gradient of 9.4 tesla superconducting magnet).

METHODS & SIMULATIONS

Ion trajectory simulation were performed using SIMION 8.0 (Scientific Instrument Services, Inc., NJ) on a 2.5 GHz Pentium 4 PC with 1.25 GB RAM (Dell, Inc., TX, currently upgraded to 3.25 GB). The mass spectrometric system including external ion source, quadrupole ion guide (QIG), and ICR cell was created by writing a single geometry file in SIMION 8.0. For geometry sizes (e.g., quadrupole, ICR cell and external ion source dimensions, *etc*) we used all measured values. For example, the experimentally measured quadrupole length of 39 inches (~99 cm), and all other measured ICR cell and ion source dimensions were used for SIMION simulations with potential array (PA) resolution of 0.01 inches/grid units.

To adjust/apply RF frequency, RF amplitude, DC voltages (on the ion source, QIG, and ICR cell), and gradient magnetic field (defined by an experimentally obtained equation), SIMION 8.0 built-in Lua programming was used. Fast Fourier transform (FFT) of ion trajectory coordinates (*i.e.,* x coordinate) in the quadrupole ion guide was performed using MATLAB 7.0 (The Math Works, Inc., MA). The magnetic field gradient of 9.4 tesla superconducting magnet (Cryomagnetics, Inc., TN) was measured using a F. W. Bell gaussmeter (Model 615, F. W. Bell, Inc., FL). Microsoft Excel (Microsoft® Office Excel 2003) and Origin 7.0 (OriginLab Corporation, MA) were utilized for linear and non-linear curve fittings, respectively. Ion current measurements were performed using a Tektronix multimeter (Tektronix, Inc., OR).

RESULTS and DISCUSSION

(I) Experimentally Measured Magnetic Field Gradient of 9.4 tesla Magnet

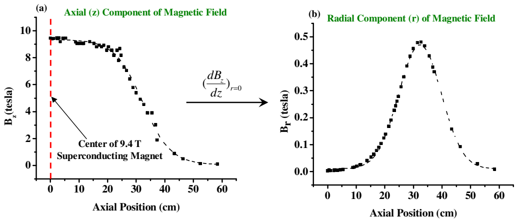


Figure 1. (a) Experimentally measured magnetic field gradient of 9.4 tesla superconducting magnet *vs.* axial distance from the center of the magnet. (b) Radial component of the magnetic field *vs.* axial position obtained using Maxwell equation [2].

Note: The equations obtained from the curve fittings in Figures 1a and 1b were used in SIMION simulations (*viz.,* user programming) to apply the magnetic field on the quadrupole ion guide (QIG) in both axial and radial directions.

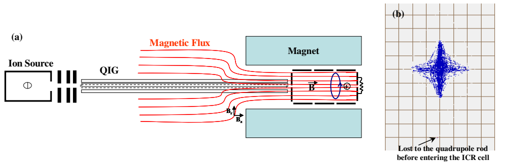
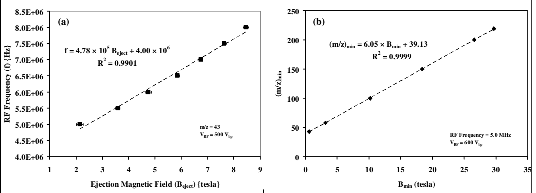


Figure 2. (a) Schematic representation (not drawn to scale) of the home-built external ion source, quadrupole assembly, and the ICR cell used for the SIMION simulations. (b) trajectory of an ion with m/z 43 traveling through the QIG {positioned inside an experimentally measured magnetic field gradient (Figure 1)} with applied RF frequency of 5.0 MHz (600 V_{bp}); note that ion is ejected before entering the ICR cell.

(II) Effect of RF Frequency at Constant Amplitude on Ion Ejection Magnetic Field (B_{min}) inside the QIG



From ICR equation of ion motion [3]:

$$m/z\ 43 \rightarrow \frac{f}{B}=\frac{ze}{2\pi m}=3.5\times10^{5}\ Hz.\ tesla^{-1} \quad but\ slope\ of\ the\ linear\ fit\ is:\sim 4.8\times10^{5}$$

$$\Rightarrow \frac{4.9\times10^{5}(Hz.\ tesla^{-1})}{f/B}\approx\sqrt{2}$$

From Mathieu Equation [4] (B = 0 tesla):

$$q = 1 \rightarrow f_{\min}=\frac{\sqrt{eV_{RF}}}{\sqrt{(m/z)_{\min}}\,\pi r_0}=3.9\times10^{6}\,Hz \quad (\approx \text{intercept of linear fit})$$

$$\omega_{eject}=\frac{\sqrt{2}eB_{eject}}{(m/z)_{\min}}+\frac{eV_{RF}}{(m/z)_{\min}\pi r_0} \qquad \textbf{Equation 1}$$

From ICR equation of ion motion:

$$f = 5.0\times10^{6}\ Hz \Rightarrow \frac{(m/z)}{B}=\frac{e}{2\pi f}=5.1\times10^{-27}\ kg.\ tesla^{-1}$$

$$\Rightarrow or\ 5.1\times10^{-27}\ kg.\ tesla^{-1}\times1000\ g/kg\times N_{Avogadro}\approx3.1\ g.\ mol^{-1}.\ tesla^{-1}$$

$$\Rightarrow but\ slope\ of\ the\ linear\ fit\ is\sim6.1,\ hence: \frac{(m/z)}{B}=\frac{6.1\ (g.\ mol^{-1}.\ tesla^{-1})}{3.1\ (g.\ mol^{-1}.\ tesla^{-1})}\approx2$$

From Mathieu Equation (B = 0 tesla):

$$q = 1 \rightarrow (m/z)_{\min}=\frac{4eV_{RF}}{(2\pi f_{\min} r_0)^2}=33.0\ g.\ mol^{-1} \quad (\approx \text{intercept of linear fit})$$

$$(m/z)_{\min}=\frac{2eB_{eject}}{\omega_{eject}}+\frac{4eV_{RF}}{(\omega_{eject}r_0)^2} \qquad \textbf{Equation 2}$$

Figure 3. (a) Plot of applied RF frequency (500 V_{bp}) on QIG *vs. ion* ejection magnetic field (average of 10 simulations) for m/z 43 and (b) plot of low mass cut-off *vs.* minimum magnetic field (B_{min}) (10 ions for each m/z) required for ion ejection. An RF frequency of 5.0 MHz (600 V_{bp}) was applied on the QIG.

(III) Effect of RF Amplitude on the Ion Loss/Mass Cut-Off in QIG (using experimentally measured B fields as presented in Figure 1)

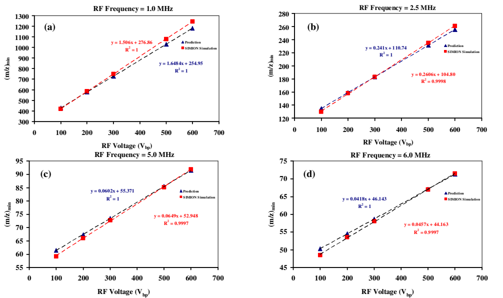


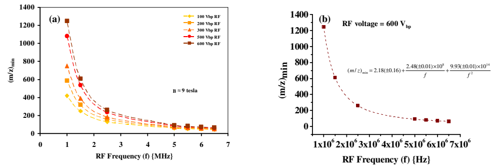
Figure 4. Plots of low mass cut-off *vs.* RF amplitude for QIG at (a) 1.0 MHz, (b) 2.5 MHz, (c) 5.0 MHz, and (d) 6.0 MHz. Data points with symbols "■" and "▲" are from SIMION simulations and prediction (using equation 2 in Figure 3), respectively.

Note: The plots in Figures 4a- 4d suggest that:

(i) lower RF frequencies are associated with lower mass cut-off for ion guiding into the measured gradient magnetic field

(ii) higher RF amplitudes at constant RF frequency increase the low mass cut-off in QIGs

(IV) Effect of RF Frequency on the Ion Loss/Mass Cut-Off in QIG



From equation 2:

$$(m/z)_{\min}=\frac{2eB_{eject}}{\omega_{eject}}+\frac{4eV_{RF}}{(\omega_{eject}r_0)^2}\ ,\ \begin{cases}B_{eject}=9\ \text{tesla}\\ r_0=2.7\times10^{-3}\ \text{m}\\ V_{RF}=600\ V_{bp}\end{cases} \Rightarrow (m/z)_{\min}=\frac{2.8\times10^{8}}{f}+\frac{8.2\times10^{14}}{f^2}$$

Figure 5. (a) Plot of low mass cut-off *vs.* RF frequency {at different RF amplitude (*i.e.,* 100, 200, 300, 500, and 600 V_{bp})} at constant magnetic field of 9 tesla around the QIG. (b) Curve fitting result for RF amplitude of 600 V_{bp} in Figure 5a {the data points were fitted into equation $Y = a + b / X + c / X^2$}.

Note: The results shown in Figure 5 suggest that:

(i) higher RF frequencies are required to guide ions with smaller m/z; conversely, increasing the RF amplitude at constant RF frequency yields ion ejection for low mass ions.

(ii) at higher frequencies (*i.e.,* >6 MHz as shown in Figure 4a), the increase in the RF amplitude does not change the low mass cut-off significantly.

(V) Fourier Transform (FT) Analysis of Ion Trajectories in Quadrupole Ion Guide

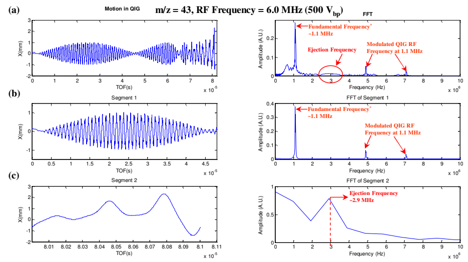


Figure 6. Ion's x-coordinates *vs.* time of flight (TOF) {left hand side} and the corresponding frequency domain FT output {right hand side} for m/z 43 in the QIG when an RF frequency of 6.0 MHz (500 V_{bp}) was applied on the quadrupole rods {(a) whole ion trajectory, (b) the first segment of the ion trajectory before ion ejection, and (c) second segment of the trajectory when the ion oscillation amplitude started to increase}. The inscribed radius (r_0) of the QIG installed on our system is ~2.67 mm. * Fundamental frequencies refer to the oscillation frequencies of the ions within the quadrupole assembly and are not to be confused with mass dependant ICR fundamental frequencies.

Not: FT analyses of ion trajectories for other m/z values (*e.g.,* 28, 58) at 6.0 MHz yield an m/z independent ejection frequency (*viz.,* ~3.0 MHz).

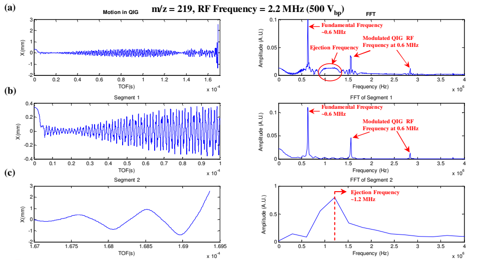


Figure 7. Ion's x-coordinates *vs.* time of flight (TOF) {left hand side} and the corresponding frequency domain FT output {right hand side} for m/z 219 in the QIG when an RF frequency of 2.2 MHz (500 V_{bp}) was applied on the quadrupole rods {(a) whole ion trajectory, (b) the first segment of the ion trajectory before ion ejection, and (c) second segment of the trajectory when the ion oscillation amplitude started to increase}. The inscribed radius (r_0) of the QIG installed on our system is ~2.67 mm. * Fundamental frequencies refer to the oscillation frequencies of the ions within the quadrupole assembly and are not to be confused with mass dependant ICR fundamental frequencies.

Not: FT analyses of ion trajectories for other m/z values (*e.g.,* 264, 502) at 2.2 MHz yield an m/z independent ejection frequency (*viz.,* ~1.2 MHz).

(VI) Experimental Measurement of QIG Ion Transmission Efficiency in the Presence of Magnetic Field

For experimental comparisons, ion currents (from a constant leak of acetone into the external EI ion source) on quadrupole trapping plate (QTP) and filament trapping plate (FTP) of the ICR cell were measured.

With 5.2 MHz RF on QIG, the ion currents were:

a) ~0.0 nA on FTP and ~35 nA on QTP (for ICR cell/QIG positioned outside the 9.4 tesla magnet)

b) ~3.0 nA on FTP and ~0.0 nA on QTP (for ICR cell/QIG positioned inside the 9.4 tesla magnet)

As expected, these measurements suggest that only a small portion of guided ion can be transferred to the ICR cell when a magnetic field is present around QIG. Based on our SIMION simulations, the observed ion loss can be explained by ion oscillation amplitude (*vz.,* ion ejection) in the QIG.

CONCLUSIONS

- ✓ SIMION simulations suggest that the primary cause of ion loss in QIG (in the presence of magnetic field gradient) is the quadrupole ion oscillation amplitude excitation.
- ✓ *The ion trajectory in QIG (in the presence of magnetic field) can be defined by a combination of ICR and Mathieu equations of ion motion.* Potential sources of minor discrepancies between the predicted and simulated values include collisions (presumed to be minor at our experimental conditions) and applied DC offset on the quadrupoles. Equation 2 resembles the previously reported relationship by Steve Beu *et al.* [5]
- ✓ Lower RF frequencies on the QIG allow for smaller ions to be guided into the ICR cell (*e.g.*, at the constant RF amplitude of 100 V_{bp} and experimentally measured magnetic field gradient of 9.4 T magnet, the lower m/z cut-off for applied RF frequencies of 1.0 MHz and 6.5 MHz are 420 and 44 Th, respectively.
- ✓ Higher RF amplitude on QIG increases the low m/z cut-off (*e.g.,* at 5.0 MHz RF frequency, increasing the RF amplitude from 100 V_{bp} to 600 V_{bp} increases the m/z cut-off from ~60 Th to 90 Th).
- ✓ FT analyses of ion trajectories in QIG suggest an ion ejection mechanism in which ions are ejected at half the applied frequencies on the quadrupole ions guide ($\omega_{ejection} = \omega_{applied}/2$).

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