

Fluorescence Detection of Ion Frequencies in a Quadrupole Ion Trap

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OVERVIEW

- First demonstration of optical, nondestructive detection of ion frequencies within a quadrupole ion trap
- Can detect ion micromotion related to rf trapping field and ion secular motion yielding a mass spectrum
 - FT based technique providing multiplex advantage
 - Large m/z range can be analyzed using SWIFT excitation
- Trap dynamics and fundamentals can be studied

INTRODUCTION

- Fluctuations in the fluorescence are introduced by density non-uniformities in the cloud of ion trajectories which traverse the laser beamwidth
 - Observed photons are accurately recorded to allow FT processing for extraction of frequency information
 - Purely optical method: rf voltage does not interfere as in induction based FT detection techniques [2,3]
 - Nondestructive provided laser fluence is lower than the thermal dissociation threshold
- Ion secular motion is driven by sideband excitation
 - Detection of secular motion yields mass spectrum
- Relies on ion containing a fluorophore
- Capable of interrogating trap dynamics and fundamentals of operation

EXPERIMENTAL

Analytes

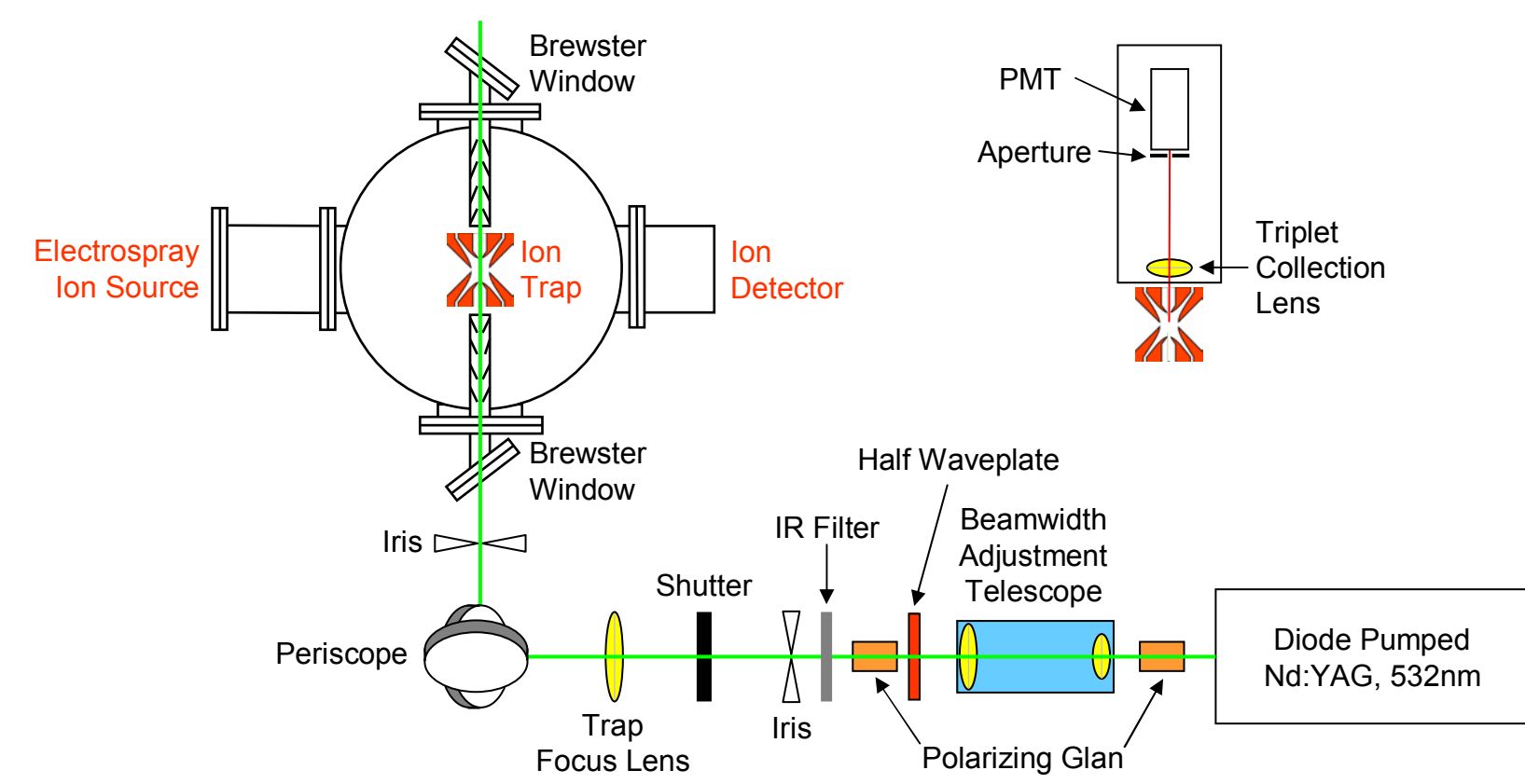
- 1 μM Rhodamine 640 in MeOH (for technique characterization)
- 15 μM TMR-T13G in 70/20/10 Methanol/Water/Trifluoroethanol

Mass Spectrometry

- Custom-built quadrupole ion trap ($\Omega = 600$ kHz) with nESI source [1]

Fluorescence

- CW Nd:YAG laser (Spectra Physics)
 - 30-300 mW through the vacuum system
- Photomultiplier tube detector (Hamamatsu)
 - Operating in pulse counting mode
- FWHM of beam is varied with telescope beam expander
 - Range of 60 to 300 μm FWHM
 - Laser spot imaged with a CCD camera to measure FWHM
- Photon counts are recorded with NI PCI-6602 counter board operating with 50 nsec (20MHz clock) resolution



EXPERIMENTAL

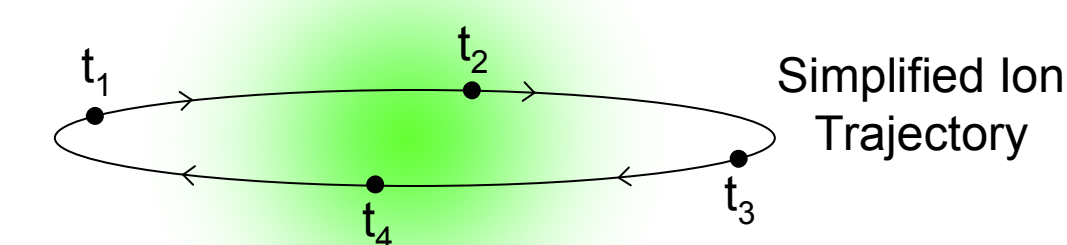
Secular Motion Excitation Schemes

- 1) **Single frequency** \rightarrow single m/z value
 - 2) **SWIFT waveform** \rightarrow m/z range \rightarrow fluorescence mass spectrum
- All signals applied to both endcap electrodes, 180° out of phase
 - Excitation is applied **during** fluorescence detection
 - **Excite** at a sideband of the ion frequency = $f_{\text{rf drive}} - f_{\text{secular}}$
 - **Detect** f_{secular} (characteristic of ion m/z)

Origin of Fluorescence Signal

- Gaussian laser beam partially overlaps the ion trajectory
- When ion is in the beam it can fluoresce (times t_2 and t_4 below)

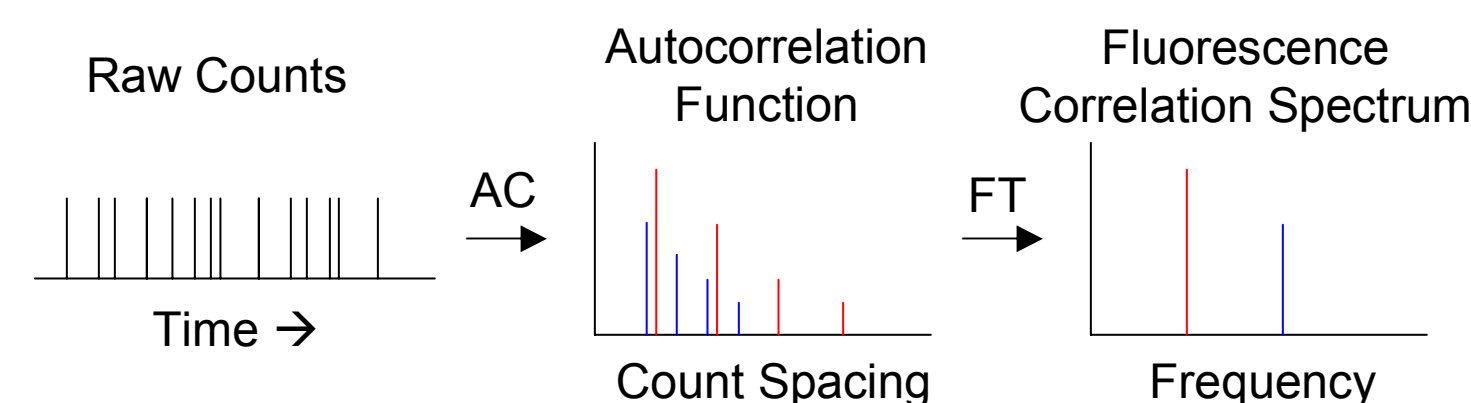
Laser Beam Focus Within Ion Trap



- Time duration between photon emission will characterize frequency of ion motion

Processing Photon Data

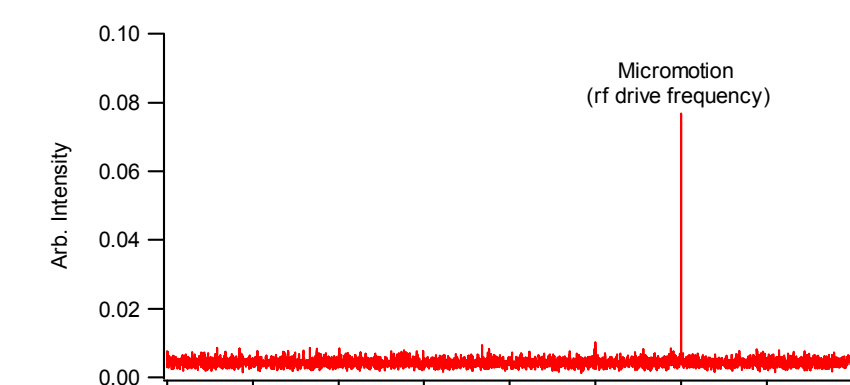
- Time spacing between counts binned to form autocorrelation signal
- Fourier transform of autocorrelation yields frequency components



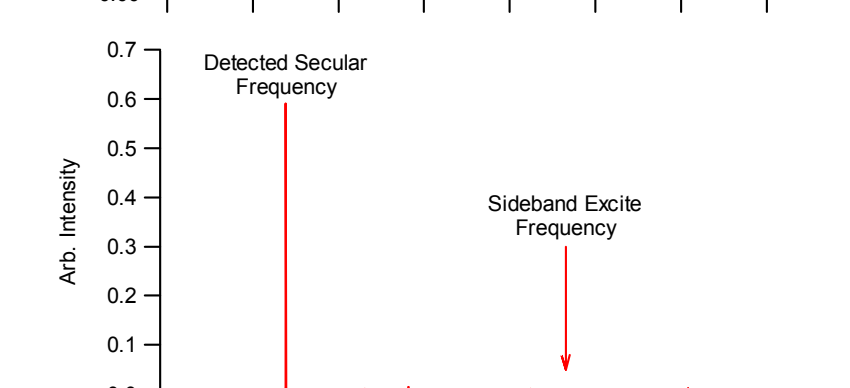
- Custom LabVIEW program collects and processes photon data in real time to yield fluorescence correlation spectrum

EXAMPLE FLUORESCENCE CORRELATION SPECTRA

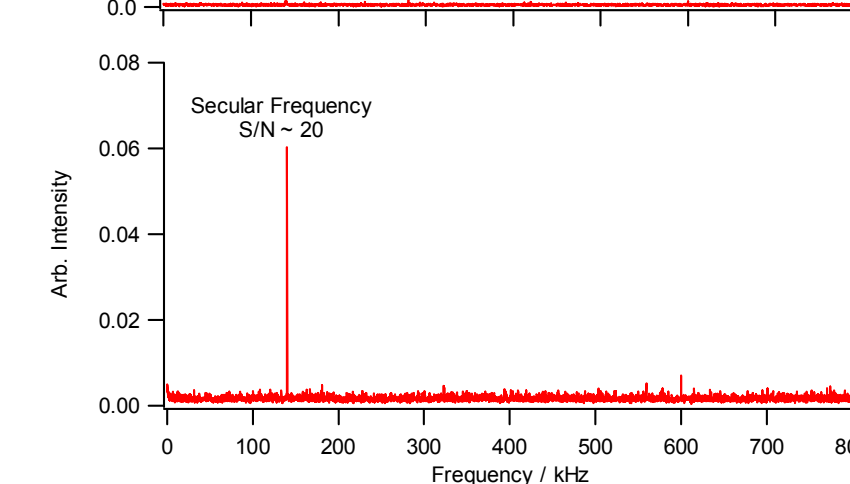
- No excitation signal applied
 - Only ion micromotion due to the rf drive frequency is observed



- Excite at 460 kHz sideband
 - Detect secular frequency at 140kHz (600kHz - 460kHz)
 - 100 msec of photon data
 - Micromotion almost completely suppressed



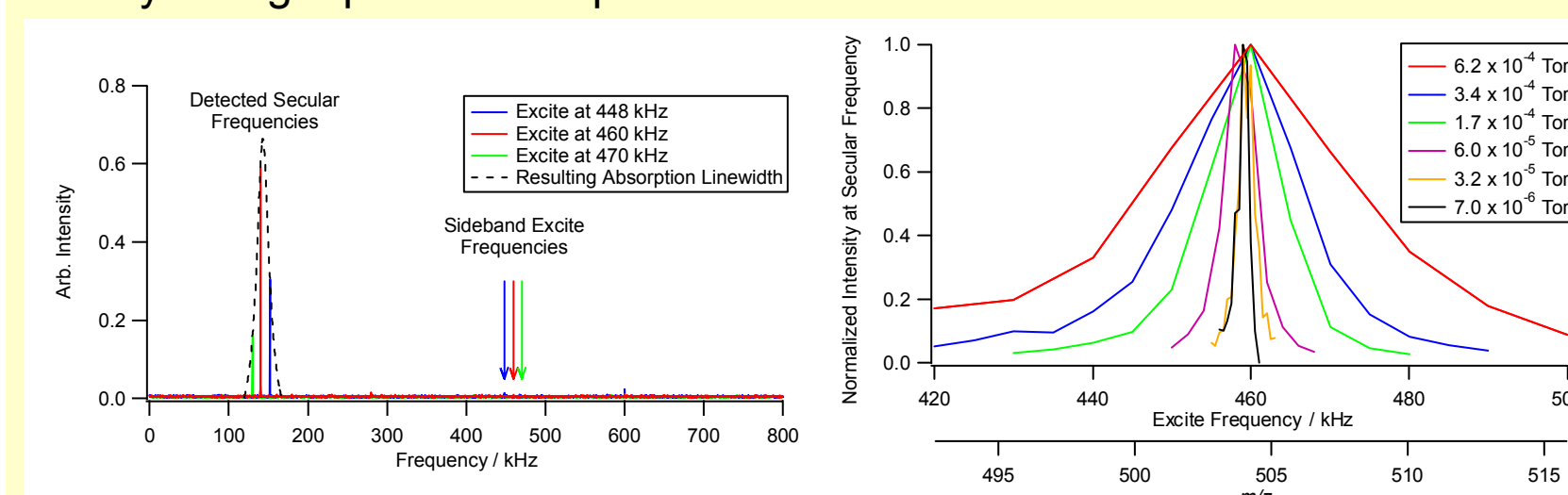
- Excite at 460 kHz sideband
 - **10 msec** of photon data
 - High S/N easily achievable with short acquisition times



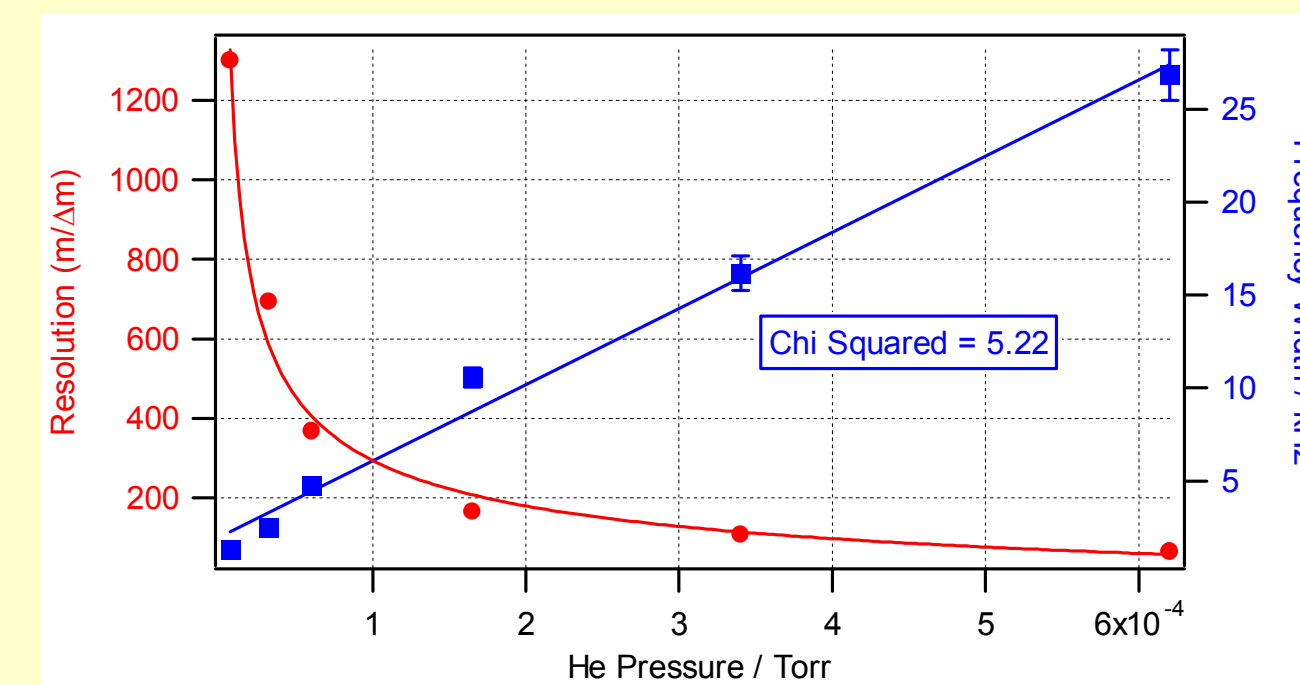
RESULTS

Mass Resolution as f(He Pressure)

- Measured secular frequency shifts with the applied sideband frequency yielding a power absorption linewidth

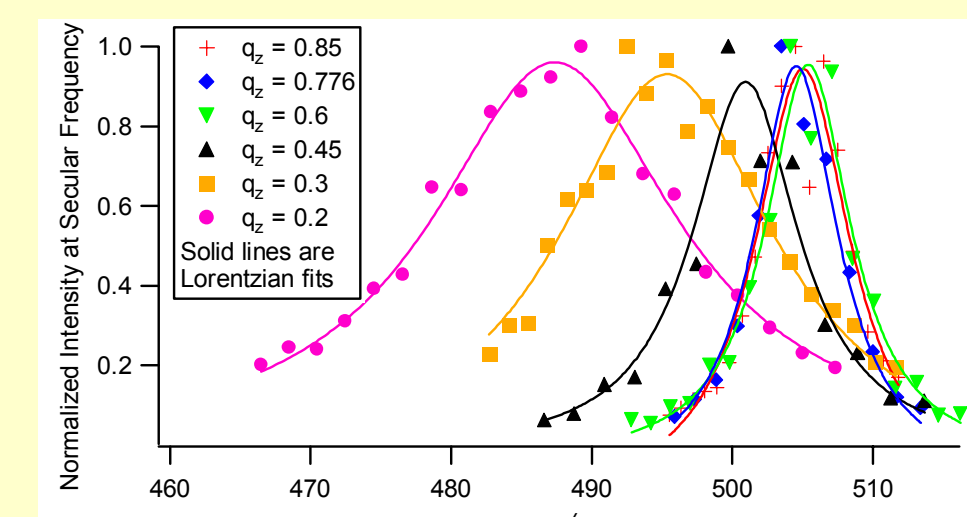


- Frequency and associated mass widths increase linearly with He pressure
- At $< 10^{-5}$ Torr He, absorption becomes very narrow producing resolutions greater than 1300

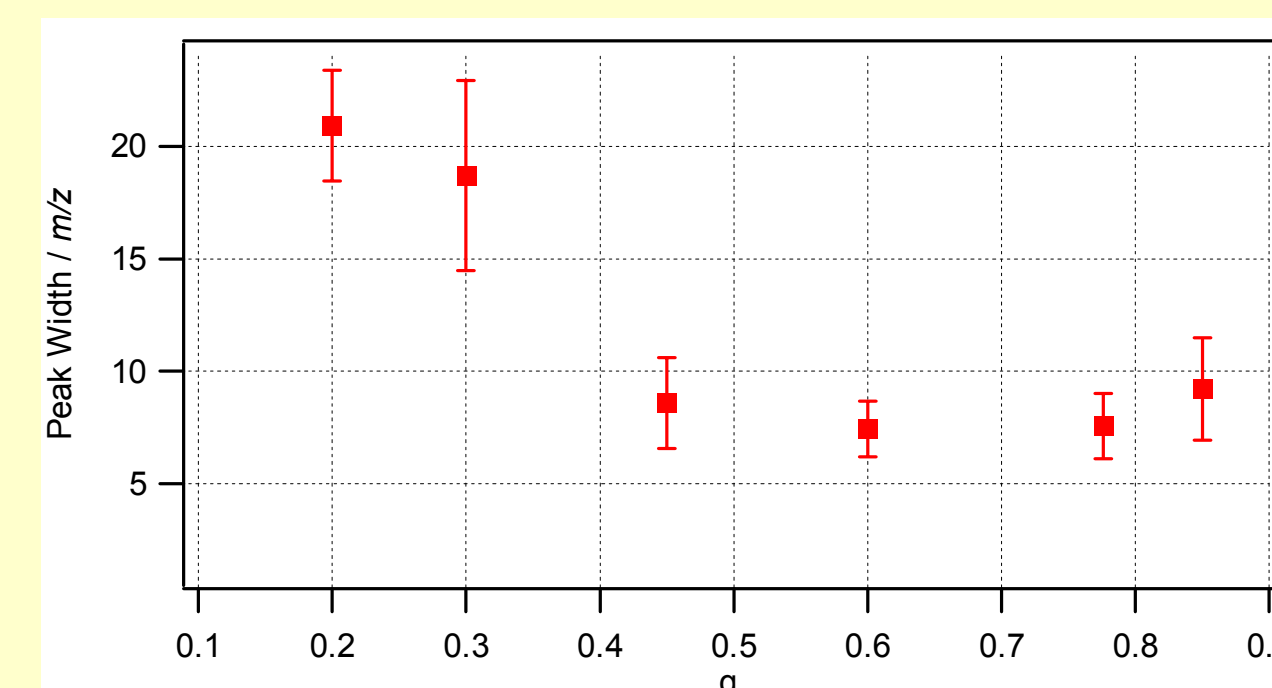


Mass Resolution as a f(qz)

- Absorption linewidth depends on ion q_z during fluorescence observation

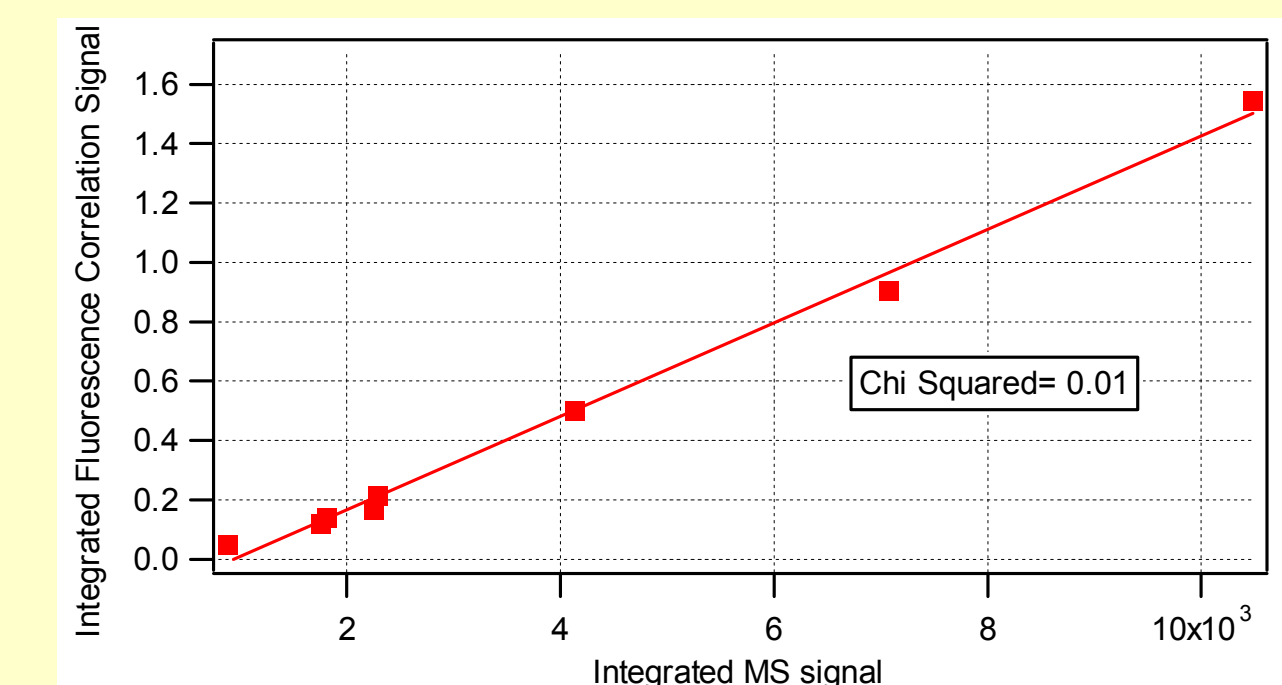


- Mass widths increase below $q_z \sim 0.4$
- Absorption widths may be pressure limited above $q_z = 0.5$
 - Operating pressure for all q_z experiments = 3.2×10^{-5} Torr He



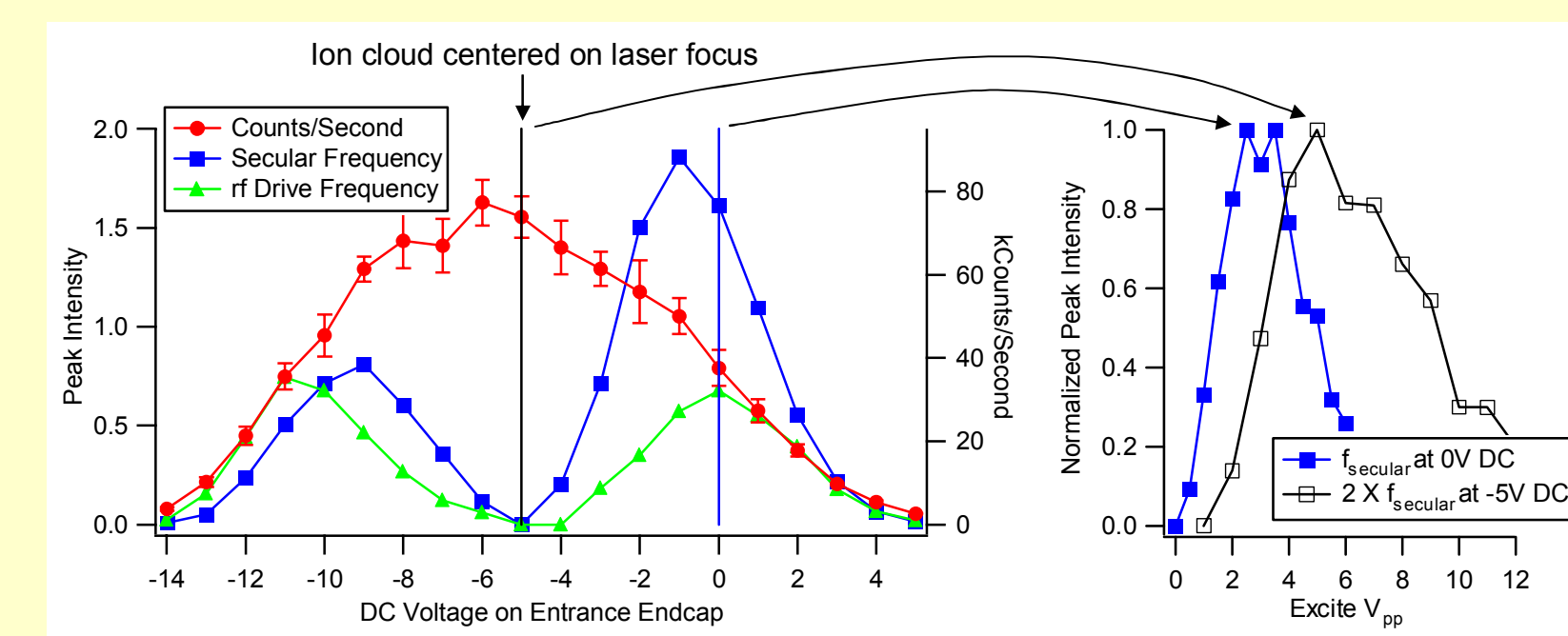
Quantitative Performance

- Fluorescence correlation peak area is linear with mass spectral peak area for greater than one order of magnitude change in trapped ion number



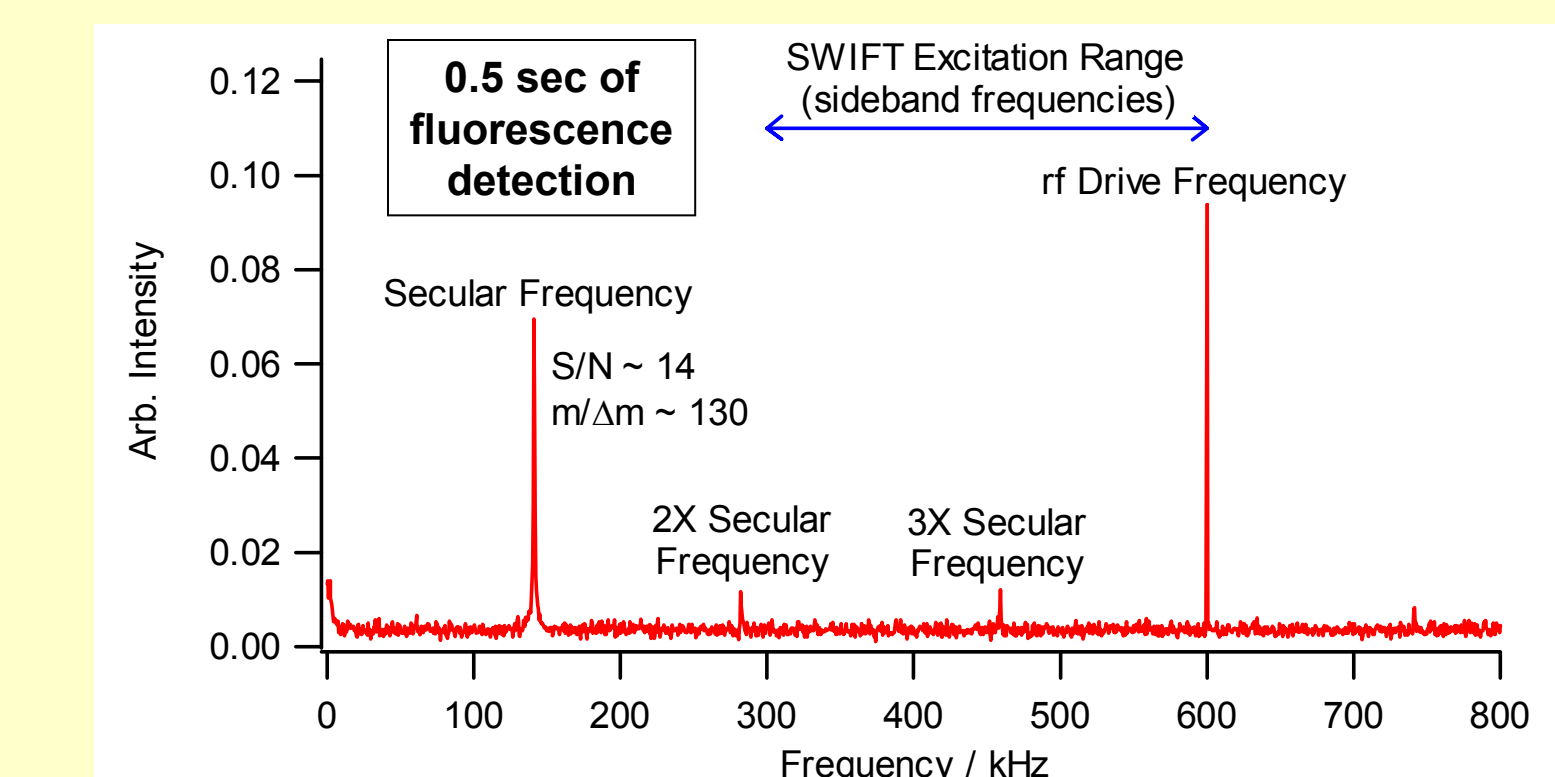
Laser Position Relative to Ion Cloud

- Ion cloud moved horizontally in the ion trap with a DC voltage applied to the entrance endcap (1V represents a displacement of ~ 75 μm)
- Position of the laser overlap with the ion cloud has large effects on the observed frequencies in the correlation spectrum
- Laser focus **centered** on ion cloud
 - No secular or rf drive frequency observed
 - 2X the secular frequency observed at high excitation amplitudes
- Laser focus **on edge** of ion cloud
 - Yields largest secular frequency correlation signal



SWIFT Excitation – Broadband

- Broadband SWIFT pulses applied continuously during fluorescence detection
 - Frequency range covers all stable m/z values



DISCUSSION

- Excitation of secular motion is required for detection
- Two secular excitation schemes proposed and demonstrated
 - Single frequency
 - Highest mass resolutions are obtained at lowest He pressures
 - Multiple separated frequencies could be used to detect multiple m/z species
 - SWIFT
 - Moderate S/N and resolution are obtained in 0.5 sec
 - Future work will further demonstrate and optimize the utility of collecting mass spectra of many m/z values
- Simple study of ion trap fundamentals is possible
 - Pressure broadening is found to be completely linear with He pressure
 - Operating at low q_z values broadens the resonant secular frequency as expected due to the shallower pseudopotential well depths
- An optimum position exists within the ion cloud to observe the secular frequency correlation
 - **Small** density fluctuations in the **center** of the ion cloud \rightarrow only 2X the secular frequency observed and only at high excitation amplitudes when ions traverse the entire laser beam
 - **Large** density fluctuations at the **edges** of the ion cloud \rightarrow greatest response at the secular frequency which can dominate the spectrum such that no micromotion is observed

SUMMARY

- Ion secular motion and ion micromotion can be directly detected with fluorescence
 - Mass resolutions of 1300 have been obtained
 - S/N > 10 obtained in 10 msec for single m/z values
 - Nondestructive
 - Pressure broadening of the secular frequency is directly observed
- Correlation signal can be used for direct quantitation
 - Response is linear with mass spectral intensity
- Optimum performance depends on optimizing the laser overlap of the ion cloud
- Broadband excitation with a SWIFT waveform is possible
 - S/N of 14 and resolution of 130 have been obtained
 - Range of m/z values can be excited and simultaneously detected yielding the possibility to perform mass spectrometry using only the fluorescence correlation spectrum

REFERENCES

- [1] Khoury, J. T.; Rodriguez-Cruz, S. E.; Parks, J. H. *J. Am. Soc. Mass Spectrom.* **2002**, *13*, 696-708.
- [2] Soni, M.; Frankevich, V.; Nappi, M.; Santini, R. E.; Amy, J. W.; Cooks, R. G. *Anal. Chem.* **1996**, *68*, 3314-3320.
- [3] Nappi, M.; Frankevich, V.; Soni, M.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1998**, *177*, 91-104.