Experimental Evidence of Ion Cyclotron Resonance Frequency Modulations Induced by Inhomogeneities of the Trapping Electric Field

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Inhomogeneities of the electric field encountered by ion packets in the FTICRMS are among the major contributing factors for ion cloud de-phasing, magnetron motion expansion, and instabilities of the resonant frequencies, which results in reduction of mass accuracy, resolution, and sensitivity.

The Filter Diagonalization Method (FDM) is useful for studying the rapid frequency shifts caused by electric field inhomogeneities because it provides excellent frequency resolution and precision on millisecond time frames. This work presents an application of FDM in the analysis of the frequency modulations induced by inhomogeneities of the trapping field.

Experimental data was acquired on a custom built ESI-FTMS with 7 T Cryomagnetics® magnet. All chemicals and samples used in the study were purchased from Sigma Chemical Co. Upon injection ions were transferred to the open cylindrical ICR cell via a quadrupole and a pair of hexapoles, where they were excited using an RF sweep. The induced image current was amplified using a low noise amplifier and sampled with a 12 bit ADC. The acquisition rate was set at 2 or 4 MHz. Data analysis was performed on the Boston University Data Analysis (BUDA) system with embedded in-house implementation of the FFT square window FDM.

In order to avoid interference of adjacent isotopes, and the resulting “beat pattern” space-charge induced modulation, a single Cesium Iodide cluster at 392.7 Da was selected for the transient frequency modulation analysis. A number of spectra acquired at identical experimental conditions were signal-averaged and analyzed with the FDM for resonant frequency modulations. The resulting signal was analyzed with the FFT to identify the modulating frequencies (Fig. 1).

The analysis revealed two general regions in the frequency domain where modulations were stable and systematic. The major peak was roughly at that of the axial frequency (Fig. 1.a). The minor peak was centered at the reduced ICR frequency (Fig. 1.b).

As was expected, the axial frequency modulations were quite significant due to the fact that ions oscillating in the Z direction experience substantial inhomogeneities of the instantaneous electric field. Hence the effective reduced cyclotron frequency modulates as a function of the electric field with the frequency roughly twice that of the Z-motion.

The second peak, much weaker in comparison with the previous, is positioned at the effective ICR frequency. This modulation can only be explained as resulting from radial inhomogeneities in the trapping field. Clearly, in order for this behavior to be observed, both cyclotron and magnetron radii should be substantial and, more importantly, the inhomogeneities of the field within the cyclotron motion diameter is sufficient to cause significant frequency modulation.

Previously reported space-charge and image charge induced frequency shifts are known to have an adverse effect on the mass accuracy, resolution, and sensitivity of FTICRMS instruments. This work presents evidence of the modulations caused primarily by radial and axial electric field inhomogeneities, which, being comparable in magnitude and similar in manifestation, are the second major cause of ion packets dephasing and diocotron instability in ICR cells.

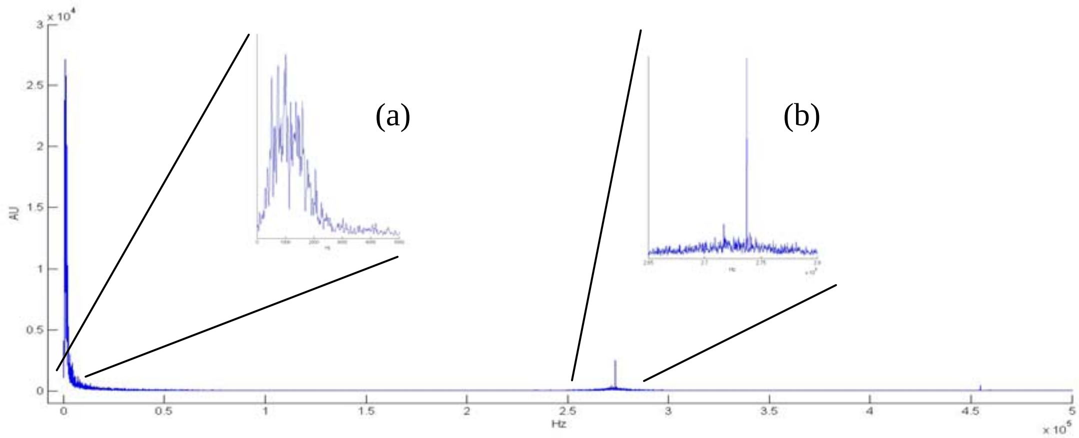

Figure 1: The Fourier Transform of the result of the frequency shift calculations conducted on the ScI transients.

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