The Spontaneous Loss of Coherence Catastrophe in FTMS

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Space-charge effect is the major contributor to mass error in FTMS, but due to its transient nature, it remains poorly studied. The Filter Diagonalization Method (FDM), a new computational techniques in Mass Spectrometry, is useful for studying space-charge because it provides excellent resolution and precision on short transients.[1] The Spontaneous Loss of Coherence Catastrophe (SLCC), also called the "nipple effect", is a space-charge induced phenomenon often observed in overloaded ICR cells, manifesting itself in deviation from exponential decay of the transient and rapid (~50 ms) collapse down to base-line noise level. This work presents an application of FDM in an analysis of the SLCC and an attempt to explain the phenomenon from the ion cloud dynamics in the ICR cell.

One simulated (noiseless) transient[2] (fig.1) and two real transients (fig. 2) were analyzed for frequency shifts through the SLCC. The analysis of the simulated and experimental signals of SLCC shows that they are fundamentally the same, but with slight differences are primarily due to the presence of multiple ion species and the inherent noise in the real signal, both of which result in a somewhat less pronounced nipple in the real data.

In the frequency domain (with the exception of the isotope beat pattern) the data generally agree as well. There is a general positive frequency drift prior to the collapse, erratic frequency behavior at the nipple, followed by dramatic alteration of the frequency shifts. The general positive drift in frequency domain is due to a general reduction of the ion density in the cell and reduction of the induced image charge[3, 4], which increases the observed cyclotron frequency.

The real data is somewhat complicated by the isotopic beat pattern. However, this frequency beat pattern prior to the nipple is consistent with the expectations as well. The observed cyclotron frequency spikes up at the point of the smallest space-charge. However at the nipple, the frequency shift changes direction and spikes down instead. This finding can be only explained by a dramatic magnetron expansion.

As the magnetron orbit expands, the ions reach the point where they rapidly switch between the approximately hyperbolic central trap potentials and the decidedly non-hyperbolic trap potentials near the edge of the cell (fig. 3). This rapid switch causes uncorrelated frequency shift, an indication of the cloud de-phasing. In addition, rapid magnetron expansion can carry ions to the cell walls where they are neutralized.

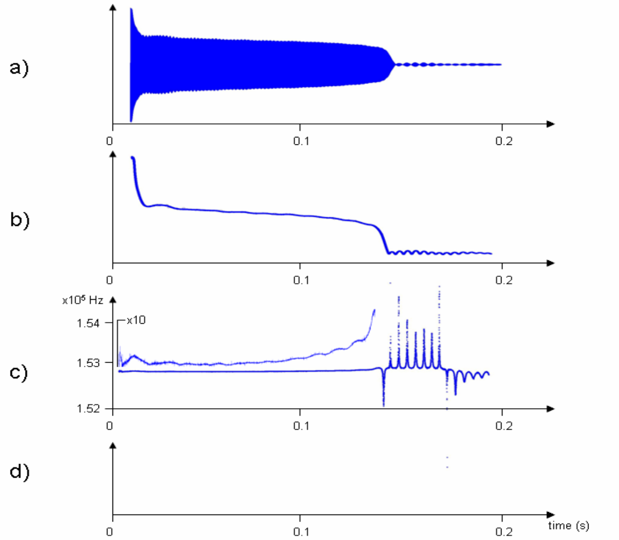

Figure 1: The results of the frequency shift calculations conducted on the simulated SLCC, where a) is the transient subjected to the analysis, b) its temporal amplitude, c) frequency, and d) damping.

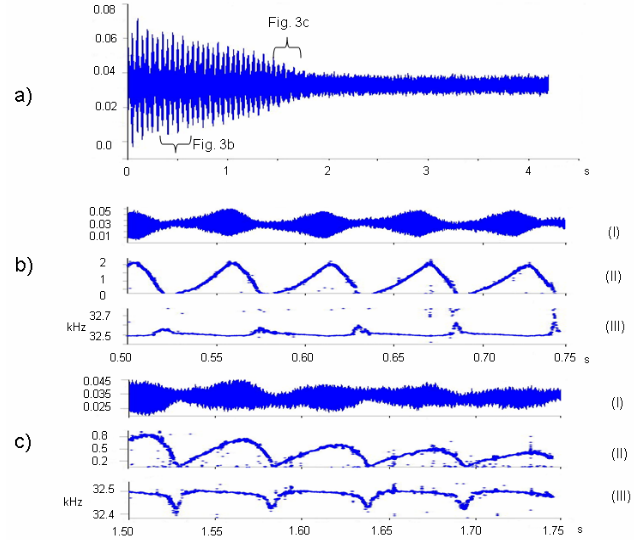

Figure 2: The results of the frequency shift calculations conducted on the experimental SLCCs a), where the characteristic flip from frequency spikes to dives occur b) prior to, and c) right at the nipple. (I) is the magnification of the region of the transient signal under investigation, (II) its amplitude, and (III) frequency temporal behaviors.

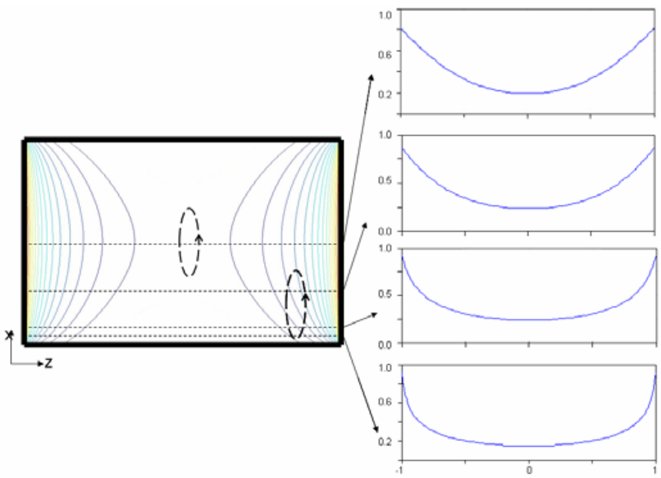

Figure 3: An illustration of the inhomogeneities in the electric field experienced by a trapped ion packet in the Penning trap. When the ions follow the cyclotron orbit close to the middle of the cell, they are subjected to nearly hyperbolic electric potential. As the z and magnetron components start to contribute ions travel through highly inhomogeneous electric field, which perturbs the motion further increasing the magnetron component.

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