New Application of Old Methods for Phase-Locking Reduction in FTMS

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One might say that, as a general rule, FTMS fails at the task of high performance mass analysis. This is because it is too easy to produce a mass spectrum in which isobaric peaks have been coalesced into one peak giving no clues as to the real number of peaks. This phenomenon was first explained by Mitchell and Smith as phase locking, whereby two ensembles of ions of similar mass magnetron around each other because of mutual electrostatic repulsion even as they cyclotron in the trap. One possible solution is to eliminate many of the ions from the trap as Marshall [1998] has done.

Experimental evidence taken by examining the behavior of molecular ions of cyclohexane and perdeuterated benzene in a 2.54-cm cubic trap in a 1.2 Tesla magnetic induction suggest two solutions. The masses of the two species differ by about 118 ppm. Phase locking is easily produced under conditions often described a desirable for detection of high mass-to-charge-ratio ions, ie., when the ions have been focused to the origin of the trap by QE or the RF-only-mode. Both solutions work by reducing the charge density for a given number of ions by making use of noncyclotron modes.

The first solution involves exciting the z-mode amplitudes of initially centered ions to approximately 60% of the trap size before the normal cyclotron excitation is applied in an uncompensated cubic trap. This strategy exploits the fact that in the normal cubic trap, the high resolving power peak is formed by ions that have a z-mode amplitude close to 60% of the trap size. The exercise of exciting the z-mode of centered ions to improve performance in a cubic trap has been done at least once before in an asymmetric trapping well event.[1] By varying the ionization time, the ion number threshold in increased by a factor of at least 4.3 over the ion number required to completely phase lock centered ions in a compensated trap.

The second solution makes use of a 0.5-s $2x10^{-5}$-Torr He gas pulse to radially diffuse the initially centered ions to fill the enlarged magnetron acceptance range of the compensated cubic trap. By varying the ionization time, the ion number threshold in increased by a factor of at least 4.5 over the ion number required to completely phase lock centered ions in a compensated trap that have not experienced the He gas pulse.

Because the frequency as a function of magnetron- and z-mode amplitudes in a cubic trap forms a saddle for z-mode amplitudes in the range of 60% of the trap size, some increase in the magnetron-mode amplitudes can be expected to be accommodated without degradation in performance. Thus, the combination of z-mode excitation and He gas pulse in the uncompensated trap should provide an additional increase in the threshold for phase lock over the individual solutions. Again by varying the ionization time, the ion number threshold for phase lock with the combined solution (see Fig. 1A) is increased by a factor of at least 4.8 over the ion number threshold for centered ions in a compensated trap that have not experienced the He gas pulse (see Fig. 1B).

Theoretical evidence suggests another phase locking reduction method whereby a symmetric ion cloud, initially centered at the origin of the trap, is parametrically excited by superimposing the excitation waveform on the trapping plate potential. The mean square of the cloud radius is detected by amplifying the image current obtained from the non-trapping plates. This mode of operation has been used before. See reference 2 and citations therein. The behavior of a model system represented by a reduced set of nonlinear equations describing two superimposed uniform symmetrical ion clouds, infinite in the z direction and parametrically coupled, indicate that phase-locking behavior is difficult to achieve. Indeed, the separation of the peaks for two distinct masses in the model system increases when the ion number is increased. While the two clouds most likely still phase lock by the mechanism described above, this behavior is no longer relevant because the centroids of the clouds are no longer involved in the detection. Experimental evidence taken from a compensated cubic trap indicate that this mode of operation becomes more feasible when the outer segments of the trapping plates are operated as high as 1.6 V_{dc} while the disk segments are operated at 0.56. For normal cubic trap operation, only 0.95 V on the outer segments is needed.

1. D. L. Rempel, C. L. Holliman, C. B. Jacoby, R. Ramanathan and M. L. Gross; Compensation and RF-only-mode for the improvement of high mass in a superconducting solenoid FTMS; Proceedings of the 45th ASMS Conference on Mass Spectrometry and Allied Topics, Palm Springs, California, June 1-5, 1997.

2. D. L Rempel, E. B. Ledford, S. K. Huang and M. L. Gross; Parametric mode operation of a hyperbolic penning trap for Fourier transform Mass Spectrometry, Anal. Chem., 1987, *59*, 2527-2532.

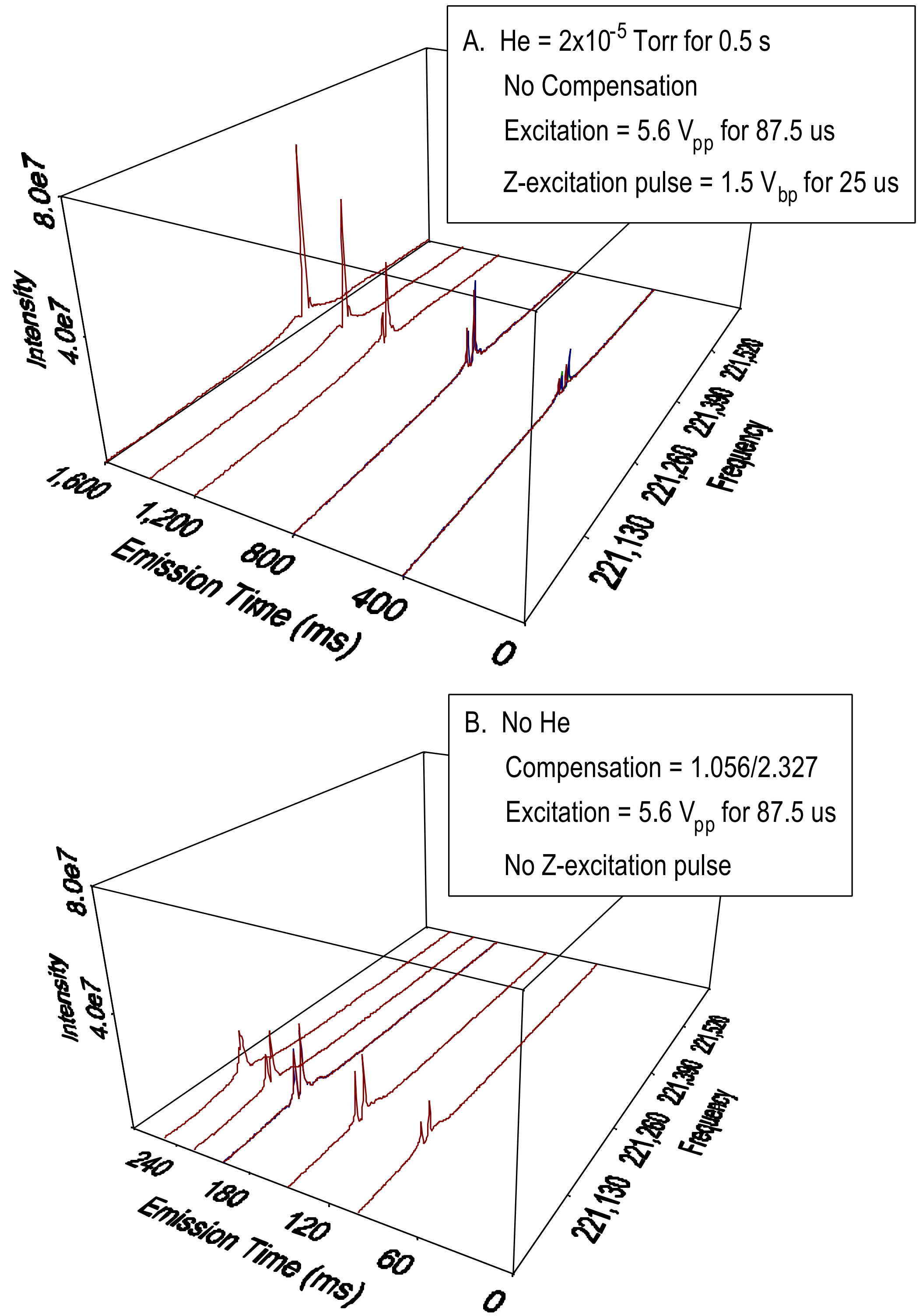

Figure 1. Increased threshold for phase locking obtained by both exciting the z-mode and collisionally expanding the magnetron-mode distribution.