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Insight into the resonance ejection process during mass analysis through simulations for improved linear quadrupole ion trap mass spectrometer performance

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ABSTRACT

A methodology for the simulation of mass analysis of ions in RF ion traps is described and demonstrated. This methodology utilizes the very high computational throughput capabilities of a GPU to accelerate ion trajectory modeling by ~10,000 fold over simple CPU based systems. This capability enables modeling of ion trajectories for realistic numbers of ions in realistic ion trap devices (defined by electrode structures and applied electrode voltages) and provides simulated mass spectral peaks as an end product. Comprehensive characterization of the effects on peak shape and resolution of electrode features such as slots or particular profiles, as well as critical operating parameters such as the amplitude and phase of the auxiliary voltages, is demonstrated. The simulated dependence of observed m/z peak resolution on auxiliary voltage phase and amplitude corresponds well with the results from a real commercial linear ion trap instrument. It is further confirmed via simulation that the extent of radial electrode displacement (stretch) for our commercial device corresponds to the minimum electrode displacement necessary to optimize m/z resolution. The results of a simulation study involving a set of 15 different ion trap configurations incorporating various trapping field compositions, electrode geometries, and applied voltages are presented. Several of the modeled trap configurations indicate the promise for improved m/z resolution.

1. Introduction

Quadrupole ion trap (QIT) technology has a rich history of development, and its commercial availability as a mass spectrometer has had a significant impact on the field, and applications of mass spectrometry. Among other qualities, the unique ability to perform multiple-stages of mass spectrometry (MS^n) in a single analyzer, as well as being highly sensitive for full scan mass analyses makes them a powerful, yet cost effective mass analyzer [1].

The capabilities of RF quadrupole ion trap (QIT) based mass spectrometers have steadily progressed in the past 30 years since their commercial introduction [2–8]. All aspects of performance including sensitivity, ion capacity (dynamic range), spectral scan speed, resolution, and dissociation capabilities have improved dramatically. There is a long history of mathematical modeling and computer simulations of ion motion in RF quadrupole ion traps in support of this advancement. Although analytical modeling approaches have been, and still are, useful [9–13], numerical simulations are required when the scope of the study includes stochastic ion-neutral collisions, space charge effects, scanning of fields, and realistic ion trap electrode geometries.

Many simulations studies have been performed of both the 3D [14–22] and 2D (linear) QIT [23–26] with all components of the basic RF QIT functionality including ion injection [21], ion isolation, ion activation [15,26,27], and mass-to-charge (m/z) analysis [19,28,29] being investigated. One of the principle areas of study has been the effect of non-linear (non-quadrupolar) components of the RF trapping potential introduced to enhance QIT performance [16,22,30], by simplification in the electrode shapes for fabrication purposes and by the apertures or slots in the electrodes [18,19]. Aside from the important function of letting ions out to the external detector, the holes and slots have been shown to predominantly have a negative influence on QIT performance as an m/z analyzer and m/z selector [4,31]. Various electrode geometry modifications have been utilized to compensate for the influence of such apertures and even improve on the performance relative to that theoretically anticipated for a pure (albeit physically unrealizable) quadrupole trapping potential. In

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particular, superposition of higher order multipole field perturbations such as even ordered nonlinear fields [10], and the associated introduction of odd [22,30] and even [16] ordered nonlinear resonances have been reported to enhance m/z resolution.

Computing power has steadily improved over the past 30 years as well, and with the widespread adoption of ion optics software packages such as SIMION [32], very powerful tools for state-of-the-art numerical simulation are available to a wide range of researchers. The simulation of mass analysis for a single ion in a QIT in which the effects of collisions are included and with modeled fields that represent the non-ideality of physically realizable electrode structures still takes on the order of 10 s of CPU (central processing unit) computing time for a contemporary (ca. 2014) personal computer. Answering questions that require simulating the trajectories of ensembles of ions is thus extremely time consuming. For example, to generate a single spectrum using realistic conditions can take hours. Therefore exploring the effect of instrumental parameters on peak shape is quite challenging. However, in 2006 the computational power of the personal computer received a tremendous boost with NVIDIA's introduction of the compute unified device architecture (CUDA) platform of highly programmable graphics processing units (GPU) [29,33]. In concert with the traditional host CPU, the GPU allows parallelizable problems like matrix multiplication, fast Fourier transforms, sorting, reductions, and particle trajectory calculations to be easily mapped onto its hundreds of cores which execute in parallel, giving speed increases over CPU-only operation that can exceed several orders of magnitude. In a particular example, Xiong et al. have demonstrated the application of GPU computing to ion trap trajectory simulations in idealized fields, for an investigation into space charge effects using realistic numbers of ions [29]. This important work demonstrated a 390× increase in simulation speed over single core CPU-only computations and thereby allowed the simulation of ion cloud distributions as well as the effects of the number of ions on boundary ejection m/z analysis.

In this paper we demonstrate the concept of employing modern techniques for high end parallel processing in the context of ion trap simulations and geometry optimization. We have developed a simulation tool which takes advantage of this new computational capability to enable rapid large scale simulations involving realistic ion numbers, collisions and realistic field configurations. The results of such simulations have the capacity to directly provide new insights into the fundamental behavior of ions in RF ion traps and therefore can be utilized to inspire new ideas and approaches to improve QIT performance. Here we focus on the mass selective resonance ejection process during m/z analysis with the objective of developing insight that will allow us to enhance this aspect of performance of the linear QITs we design.

2. Methods

2.1. Field and ion trajectory simulations

Numerical simulations of ion trajectories were performed using a custom CUDA/C++ program (called ThermoSIM), using the NVIDIA CUDA 4.2 toolkit, running on a Xeon x5550 2.67 GHz CPU, with 24 GB RAM and a Tesla Fermi c2050 graphics card. A 4th order Runge–Kutta numerical integration method [34] with a fixed 35 ns time step was used to integrate the equations of motion. Accuracy of the numerical integration with a 35 ns integration step size was assessed in two ways, first by monitoring the accumulation of errors in the computed trajectories of ions in both a 1200 kHz harmonic oscillator and in a pure quadrupolar trapping field, and second, by monitoring the shift in m/z peak ejection times as the integration step size was increased. The number of ions used for most simulations was 10,240, with 128 ions assigned to each CUDA thread block. With the ThermoSim CUDA/C++ program, a simulation of the m/z analysis of a 50 Th window at a rate of 33 Th/ms for 10,240 ions can be simulated in about 12 s (35 ns/ion/time step for these conditions). In contrast, using SIMON running on the same computer, an identical simulation for only a single ion takes 12 s to compute. Although not directly compared to a CPU based implementation of our software, we estimate that the results would be at least 50× slower than our current GPU based version, by considering that approximately 700 floating point operations/electrode/ion/time step are required on the 2.67 GHz CPU.

For simulations involving ions within "realistic" trap electrode geometries, SIMION 8.1 was first used to separately calculate the reference potential arrays for each electrode of the ion trap, using a finite-difference relaxation technique [32]. Each electrode reference potential array corresponded to the case where the particular electrode was maintained at a potential of 1 and all of the other electrodes are maintained at 0. These output potential array (pa) files were subsequently used as input to the ThermoSIM program. During the trajectory simulations the magnitude of the grid potentials were rescaled according to the magnitude of the applied voltages for each electrode in the set $\varepsilon = \{x^+, x^-, y^+, y^-, d\}$, where x^+, x^-, y^+, y^-, d indicate the trap rod electrodes and d the high energy conversion dynodes (a single reference potential was used for both dynodes). The electric fields $E_x^{\varepsilon}(x,y)$ and $E_y^{\varepsilon}(x,y)$ associated with the respective reference potential at a given position during the ion trajectory simulation were computed via linear interpolation of the grid potentials [33]. The equations of motion between collisions were thus:

$$\frac{d^2x}{dt^2} - \frac{e}{(m/z)}\left[\sum_{\varepsilon} V_{\varepsilon}(t) E_x^{\varepsilon}(x,y)\right] = 0$$

$$\frac{d^2y}{dt^2} - \frac{e}{(m/z)}\left[\sum_{\varepsilon} V_{\varepsilon}(t) E_y^{\varepsilon}(x,y)\right] = 0$$

$$\frac{d^2z}{dt^2} = 0$$

where

$$V_{x+}(t) = (1+\alpha)V_T\cos(\omega_T t) + V_{aux}\cos(\omega_{aux} t + \phi)$$

$$V_{x-}(t) = (1-\alpha)V_T\cos(\omega_T t) - V_{aux}\cos(\omega_{aux} t + \phi)$$

$$V_{y+}(t) = -V_T\cos(\omega_T t)$$

$$V_{y-}(t) = -V_T\cos(\omega_T t)$$

$$V_d = -15{,}000\text{volts} \quad (1)$$

Here, the quantity (m/z) is the specific mass (mass per elemental charge) of the ion and e is the elemental electric charge. The quantities V_T and V_{aux} are the nominal magnitudes and ω_T and ω_{aux} are the corresponding angular frequencies of the RF trapping and auxiliary voltages applied to the QIT electrodes. The quantity α allows a deviation in scaling from this nominal magnitude for the voltages applied to the x^+ and x^- electrodes. As described below, $\alpha = 0$ for all simulated trap voltage configurations except those referred to as unbalanced(see below). Here the initial phase of the trapping field was zero. The initial phase of the auxiliary field is given as φ . Since in all of the simulations described herein, $\omega_T = 3\omega_{aux}$ ($\omega_T/2\pi = 1200$ kHz and $\omega_{aux}/2\pi = 400$ kHz), the initial phase of the auxiliary field established a fixed phase relationship