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Chaotic motion of single ions in a toroidal ion trap mass analyzer

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ABSTRACT

Although widely used in mass spectrometry, radiofrequency ion traps involve complex electric field shape and correspondingly complex ion motion. In addition, numerous variations of electrode geometry have been developed to address or benefit from different aspects of ion motion and the resulting effects on performance as a mass analyzer. We report on SIMION simulations that show classical chaotic behavior of ions in the toroidal ion trap. The chaotic motion is a result of the non-linear components of the electric fields as established by the trap electrodes, and not by Coulombic interaction from other ions. The chaotic behavior was observed specifically in the ejection direction of ions located in non-linear resonance bands within and adjacent to the region of stable trapping. The non-linear bands crossing through the stability regions correspond to hexapole resonance conditions, while the chaotic ejection observed at the boundary of the stable trapping region represents a "fuzzy" ejection boundary. Fractal-like patterns were obtained in a series of zoomed-in regions of the stability diagram.

1. Introduction

Ion trap mass spectrometers are widely used for identifying and quantifying compounds and analyzing mixtures in fields of study as diverse as biochemistry [1], environmental monitoring [2], forensics [3], petrology [4] and planetary science [5,6]. In a 3-D quadrupole ion trap, a radiofrequency (RF) waveform and three hyperboloidal electrodes—two end-caps and one ring electrode—create the quadratically varying electric potential needed to trap and mass-analyze ions [7,8]. Similarly, the quadrupole mass filter employs four hyperbolic rods, trapping ions in two dimensions and allowing a subset of ions to pass through the length of the device [9]. Many geometrical variants have been designed to facilitate miniaturization or otherwise modify some aspect of trap performance. For instance, the cylindrical ion trap (CIT) utilizes cylindrical electrodes, which are simpler to manufacture and miniaturize than those of the quadrupole ion trap [10,11]. The linear ion trap (LIT) is derived from the quadrupole mass filter but with added axial trapping [12,13]. The LIT has the advantage that ions are not confined to a small volume at the trap center, but rather are confined along a line, allowing more ions to be trapped for a given frequency and RF amplitude [12–14]. The rectilinear ion trap is derived from the LIT, but with flat-rectangular electrodes [15,16]. In 2001, Lammert et al. created the toroidal ion trap, in which the cross section of a quadrupole ion trap is rotated along an axis located outside of the trapping region. The toroidal ion trap consists of a central electrode, an outer ring electrode, and two end-caps, all based on hyperbolic surfaces of revolution. Analogous to the LIT, the toroidal trap exhibits a larger trapping capacity—ions are trapped in a torus or ring and ejected through slits in the endcap electrodes [17,18]. A miniaturized version of this toroidal ion trap is currently used in a commercial, portable GC–MS instrument [19]. Taylor and Austin presented a simplified electrode geometry in which the toroidal trapping region is made using cylindrical electrodes and ions are ejected radially to a detector located at the center [20].

Although the electrode geometry may be simplified, the ion motion in all RF trapping devices is rather complex. Ion motion consists of several components, including micromotion (small-amplitude motion at the same frequency and phase as the applied RF) and secular motion (large-amplitude, harmonic motion with frequencies corresponding to the position of the ion as plotted on a stability diagram) [21]. Secular motion consists of several frequencies, with the dominant frequency typically a fraction of the frequency of the driving RF. Secular motion is often resonantly excited by a supplementary applied signal for ion excitation, fragmentation, isolation, or ejection [22–26].

The complex motion of trapped ions is commonly studied using a combination of mathematical models and computer simulations. These studies seek to optimize ion trap design and performance or to understand specific observations. For instance, Berkeland et al. discussed the ion micromotion in a quadrupole ion trap, and described three methods to detect and minimize adverse micromotion [27]. Londry et al. discussed mass selective axial ion ejection from a linear quadrupole ion trap via studying the ion motion to obtain optimal electric fields [26]. Higgs et al. studied the ion motion in three different types of toroidal ion traps [28]. Huo et al. presented a SIMION simulation study of the

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slit impact on the miniature rectilinear ion trap in which the trap performance was optimized via adjusting the slit geometry [29]. Yang et al. optimized the performance of a toroidal ion trap with triangular electrode geometry via SIMION simulation [30]. Wu et al. studied the electrode misalignment of the planar linear ion trap via simulating the electric field and ion trapping [31]. Blain et al. discussed design considerations for a micrometer-scaled cylindrical ion trap relying on SIMION simulations of ion motion [32].

The motion of trapped ions is due primarily to the shape and magnitude of the time-varying electric potentials and fields within the trap. The electric potential distribution within a perfect quadrupole ion trap is purely quadratic, and the resulting field perfectly linear, but in practice this cannot be achieved due to electrode truncation, slits and/or holes, and imperfections in electrode fabrication and positioning. These factors lead to distortions of the potential distribution. For distortions with the same symmetry as the trap itself, the distortions are conveniently modelled using higher-order solutions to the Laplace equation. For instance, small amounts of hexapole, octopole, decapole, dodecapole, and other higher-order terms superimpose onto the dominant quadrupole and make the resulting electric field non-linear. Even small contributions of these nonlinear terms can have a significant effect on the ion motion. The nonlinear field is either detrimental or in some cases beneficial to ion excitation and ejection. Non-linear fields can cause undesirable and unexpected ion ejection (black holes or black canyons) that make ions eject at undesirable times, but can also be used to contain ions during excitation and improve ion ejection and mass analysis [33–37]. Numerous studies have focused on optimizing trap performance via adjusting the higher order field terms. For instance, the original Finnigan quadrupole ion trap was stretched by 10.8% in the ejection direction, improving mass accuracy and resolution [12]. Other groups including Wu et al., Ouyang et al. and Bruker-Franzen instruments also optimized higher order fields in ion traps by modifying the geometric structures [11,15,38]. A "−10% compensation rule" was presented for field optimization, suggesting that an optimal field for a boundary or linear resonance ejection mass scan should contain a sum of −10% of the relative strengths of octopole and dodecapole [39].

Compared to the electric fields in other ion traps, the electric field in the toroidal ion trap has additional complexities due to the curvature of the trapping region. Lammert et al. demonstrated that a pure quadrupole field cannot be achieved in the toroidal ion trap due to the radius of curvature of the trapping region [17]. Wang also noted that, for the same reason, none of the conventional higher-order multipoles are strictly applicable to this device [40]. The trapping center of a toroidal trap is not co-located with the rotational axis, so electric potentials increasing with any polynomial form from the trapping center will of necessity have a "cusp" or discontinuity at the rotational axis. While they may be useful to first order, they do not completely describe the potentials or the ion behavior in the device. Kotana and Mohanty have developed mathematical models to describe the potential distribution in the toroidal ion trap [41]. They also presented a computation method on the stability diagram in the toroidal ion trap and observed features similar to what we observed [42].

Higgs et al. conducted SIMION simulations exploring motion of ions in toroidal ion traps [28], and also in a potential representing a mathematically pure, quadrupole-like toroidal harmonic [43]. Among other findings is that a centripetal effect shifts the center of ion motion outward from the saddle-point of the trapping potential. In addition, the pure toroidal harmonic shows a strong, fairly broad chasm or black canyon running through the stability region. We subsequently conducted simulations on these toroidal systems to understand mass analysis through boundary ejection, including characterizing the direction of ion ejection under different conditions. In doing so we have observed an interesting and unusual behavior. On many portions of the stability diagram, including black canyons and expected non-linear resonance lines, the direction of ion ejection shows fractal-like behavior. The direction of ion ejection is extremely sensitive to initial conditions of the simulation, and zooming in to a specific feature shows finer details with similar pattern. In other words, the ion ejection demonstrates classical chaotic behavior.

Classical chaotic motion is a deterministic but unpredictable long-term state in a nonlinear dynamic system that is highly sensitive to initial conditions. A common example is the double pendulum (a pendulum is attached to the bottom of another pendulum). The motions of the pendula do not follow simple, predictable patterns. Using appropriate equations of motion, it is possible to calculate any future state, but the calculation must be done iteratively—calculation of a given future state requires knowing the immediately preceding state [44,45]. The motion of chaotic systems is generally represented by a set of nonlinear equations of motion. Because of the nonlinearity, it is impossible to calculate the $(n)^{th}$ step state without knowing the information of the $(n\text{-}1)^{th}$ step. Therefore, it is unpredictable in the long-term, but deterministic. Small differences in the initial state will cause diverse results. A chaotic system contains many "decision" points where small differences in the current state lead to different paths. In some cases rounding errors in calculations can have a similar effect.

Chaotic motion of ions in traps has been studied from the standpoint of the two-ion effect, which is different from what is reported in the present study. With two ions in a trap, the position and charge of one ion affect the motion of the other ion, analogous to the effect one pendulum has on the other in the double pendulum example. Blümel showed that two or more ions in a quadrupole ion trap demonstrate chaotic motion due to Coulombic repulsion, and argued that this chaotic motion is responsible for RF heating of trapped ions [46]. Baumann et al. also studied the regular and chaotic motion of two ions in a quadrupole ion trap, and provided integrals of ion motion and critical parameters that can cause chaotic behaviors [47]. Hoffnagle et al. investigated an order-chaos transition of two ions in a quadrupole ion trap, and presented the Mathieu-Coulomb equations to interpret a boundary transition [48]. Hasegawa et al. demonstrated the nonlinear equations of two-ion motion in a quadrupole ion trap using a discrete Fourier expansion method that predicts a bistability between the regular and chaotic state [49]. In each case, the motion of a given ion is perturbed by the other ion.

Trapped ions also exhibit chaotic behavior in a quantum mechanical context, including transitions of excited states. These quantum effects have been widely studied, but are of a fundamentally different nature than the chaotic behavior in the present study. For instance, Walther characterized quantum chaos-order transitions of single ions in a quadrupole ion trap using polarization gradient laser cooling, and obtained relevant parameters for phase transitions [50]. Berman et al. introduced a quantum model for a single-ion transition to quantum chaos in a linear ion trap, and compared with the classical dynamic system in different dimensionless driving forces [51].

In our simulations of toroidal ion traps, we have observed that individual ions exhibit chaotic motion due entirely to the trapping fields and the resulting simulations of motion. This paper focuses on chaotic behavior of single ion ejection in the cylindrical toroidal ion trap. We present the stability diagram for this device. Fractal-like patterns appear in a series of zoomed-in regions of the stability diagram, including nonlinear resonance lines. We also discuss the implications for other ion trap geometries and the effect on mass analysis.

2. Methods

Ion trajectory simulations using SIMION 8.1 (Scientific Instrument Services, Inc., Ringoes, NJ) were carried out on the toroidal ion trap composed of cylindrical electrodes [20]. Fig. 1 shows the design of this ion trap. The SIMION model contains a 2-D array rotated about an axis. The dimensions as published and as used in these simulations are $R = 36.15$ mm, $r_0 = 5.91$ mm, $z_0 = 5.81$ mm, slit width = 1.6 mm with a reported hexapole component of −2.3%, octopole of +0.8%, and decapole of −3.6%. The size of the SIMION potential array was