Resonance Shifts in the Excitation of the $n = 0, K = 1$ to 6 Quadrupolar Resonances for Ions Confined in a Linear Ion Trap

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Experiments examining the excitation of the quadrupolar $n = 0, K = 1$ to 6 resonances for the ion reserpine in a linear ion trap have been shown to produce resonance shifts that were dependent upon either or both of the excitation amplitude and trap pressure (Collings, B. A.; Douglas, D. J. *J. Am. Soc. Mass Spectrom.*, **2000**, *11*, 1016–1022). The extent of this dependency was determined by examining the effects of each parameter using an ion trajectory simulator. The simulations indicated that it is the change in excitation amplitude that is mostly responsible for the resonance shifts with a minor dependency upon the trapping pressure. It was found that the higher excitation amplitudes required to observe the higher order resonances resulted in greater shifts relative to the theoretical resonances predicted for an excitation amplitude of zero volts. The nature of these shifts can be understood by examining the equations of motion for an ion trapped in a quadrupolar potential during the excitation process. Rearrangement of the equations of motion lead to a Mathieu stability diagram in which the coordinate and ordinate variables are dependent upon the excitation frequency and amplitude. In such a diagram the resonances occur in the regions of instability. The calculated resonance shifts showed good correlation with the experimental and simulation results. (*J Am Soc Mass Spectrom* 2002, *13*, 577–586) © 2002 American Society for Mass Spectrometry

Recently, higher order quadrupole excitation frequencies ($n = 0, K = 1$ to 6) have been observed experimentally for ions trapped in a linear ion trap (LIT) using moderate excitation amplitudes (≤ 10 V_{0-p}) and trapping pressures ranging from 1.8 to 7.3 mTorr of nitrogen [1]. The resonant frequencies matched, to within a few percent, those predicted theoretically for ions trapped and excited using low excitation amplitudes in a collisionless environment [2]. Although the measured resonant frequencies were shifted slightly from the theoretical values, it was found that the magnitude of the shifts were significant when compared to the full width half maxima (FWHM) of the resonances. This is shown in Table 1 taken from reference [1]. Further investigation revealed that the reso-

nant frequencies were found to depend upon the trapping pressure and/or the excitation amplitude. However, the extent to which the resonant frequencies depended upon each of these variables was difficult to determine experimentally [1]. Indeed, even the possibility of an experimental artifact giving rise to a slight shift in the Mathieu parameter q on the LIT at high excitation amplitudes was given due consideration.

It has been shown, through the use of perturbation theory, that the resonant frequencies can be described by [2].

$$\omega_n^K = \frac{\Omega}{K} |n + \beta|, n = 0, \pm 1, \pm 2, \dots \quad (1)$$

where $K = 1, 2, \dots$ is the order of the resonance, n and β determine the unperturbed oscillation frequencies, and Ω is the angular frequency of the radio frequency

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Table 1. Experimental resonant frequencies for $K = 1$ to 6 and their FWHM as measured in reference [1]. The table also includes the expected resonant frequencies as determined from eq 1 and the difference from experiment when referenced to the $K = 1$ resonance

K	Experimental frequency (kHz)	Expected frequency referenced to $K = 1$ (kHz)	Frequency shift (kHz)	FWHM (kHz)
1	200.0	—	—	1.66
2	100.6	100.0	+0.6	0.62
3	66.38	66.67	−0.29	0.43
4	49.55	50.0	−0.45	0.23
5	39.13	40.0	−0.87	0.17
6	32.43	33.33	−0.90	0.14

(RF) field. However, this equation does not include the damping effects caused by collisions, the effects resulting from the excitation amplitudes used during excitation nor the effects which may be caused by the use of round rods instead of hyperbolic rods.

In the work presented here the effects of collisions, the amplitude of the quadrupolar auxiliary signal, and the rod shape are examined by (a) using an ion trajectory simulator in which these parameters were varied independently while calculating the total kinetic energy lost by ions through collisions and by (b) describing the theoretical effects of the excitation amplitude through the use of the Mathieu stability diagram.

The simulations and the theory are both based upon ions confined by in a 2-D trapping potential while the LIT in fact creates a 3-D trapping potential. The 2-D trapping potential is a valid approximation for those regions which are at least $1.5 r_0$ ($r_0 = 4.171$ mm) away from the ends of the 20 cm long LIT. Near the ends of the LIT the fringing fields cause a distortion in the potential [3]. The blocking potentials, applied to the entrance and exit lenses of the LIT during the trapping and excitation process, move the ions away from the ends of the LIT and into those regions well defined by the 2-D trapping potentials.

The ion trajectory simulations allowed a determination of whether or not the resonant frequencies were dependent upon either the excitation amplitude or pressure, thereby answering the question of whether or not the resonance shifts were the result of an experimental artifact or were in fact real. However, the simulator can only demonstrate the effects of each parameter without answering the question of why each parameter has a particular effect. The question why can only be understood by examining the effects of each parameter theoretically.

The results of the ion trajectory simulations showed that the resonant frequencies were affected to a greater extent by changes in the excitation amplitude than by changes in pressure. The effects of rod shape on the resonant frequency were found to be minimal. Theoretically, the resonant frequencies are shown to relate to the instability regions of the Mathieu stability diagram, induced by the quadrupolar auxiliary signal, and the

stability parameters A and Q , which contain the variables of resonant frequency as a function of K and the amplitude of the auxiliary signal. The effects of pressure on the resonant frequencies is also believed to be minimal.

Methods

Ion Trajectory Simulations

Ion trajectories were modeled for ions confined in the LIT under a variety of trapping conditions [4]. The specific parameters that were examined were rod shape (hyperbolic and round), excitation amplitude, excitation frequency, and trap pressure.

The ion trajectories were calculated incrementally until the terminating boundary condition of time (4 ms) was met. The forces on the ion were calculated by integration of the second order differential equation of motion,

$$\frac{d^2\vec{r}}{dt^2} = \frac{q}{m} \vec{E} \quad (2)$$

where r is the position vector of the ion, q/m is the mass-to-charge ratio, and E is the electric field. Eq 2 is integrated numerically using Richardson extrapolation and the Bulirsch-Stoer method with adaptive step-size and error control [5]. In the case of the round rod simulations for which the electric field was not known analytically, it was obtained by interpolating tabulated numerical solutions to Laplace's equation. The numerical solutions to Laplace's equation were obtained using Maxwell Field Calculators (Ansoft Corporation, Pittsburgh, PA). The Ansoft package includes a CAD system which is used to draw electrodes and define boundary conditions.

The collisions were modelled as inelastic collisions using the hard sphere model and a collision cross section for reserpine with nitrogen of $280 \text{ \AA}^2$ [6]. The initial starting coordinates, initial thermal kinetic energy, time between collisions, scattering angle, and initial rf phase were all selected using a Monte Carlo technique.

When an ion is in or near resonance and a sufficient excitation amplitude is applied, the ion gains kinetic energy and the amount of energy available to be lost in a collision event increases. The resonances were found by measuring the amount of kinetic energy (KE) lost as a function of excitation frequency. The KE loss for an ion is taken as the sum of the KE losses for all collision events during that trajectory.

The resonant frequency was taken as the maximum in a plot of the total kinetic energy loss versus excitation frequency. The maximum was found by fitting the data to a five parameter, modified gaussian (SigmaPlot 2000, SPSS Inc., Chicago, IL).

$$y = y_0 + a \exp\left[-0.5 \frac{(|x - x_0|)^c}{b}\right] \quad (3)$$

where y is the intensity, x_0 is the resonant frequency and a , b , and c are adjustable parameters.

The choice of nitrogen as the collision partner was determined by the experimental conditions in which a base pressure of 1.8 mTorr of nitrogen was always present in the LIT. This base pressure is a result of the nitrogen curtain gas used in the ion source. The use of a collision gas other than nitrogen in the simulations would require the use of an appropriate collision cross-section in addition to an adjustment in the excitation amplitude due to the difference in the center of mass collision energy and the total KE loss.

Theory of High-Order Quadrupole Resonances

The equation of motion for an ion trapped in a pure quadrupolar field and excited with quadrupole excitation (without damping, i.e., no trap gas) can be described by:

$$m \frac{d^2x}{dt^2} + 2 \frac{e}{r_0^2} [U + V \cos \Omega t + V_{ex} \cos(\omega t + \alpha)] \cdot x = 0 \quad (4)$$

where m is the mass of the ion, t is time, r_0 is the field radius, Ω is the trapping radio frequency, U is the dc trapping voltage, V is the RF trapping voltage amplitude (zero to peak), V_{ex} is the excitation voltage amplitude (zero to peak), ω is the excitation frequency, and α is a phase shift. Inserting the dimensionless parameter $\xi = \Omega t/2$ into eq 4 the expression,

$$\frac{d^2x}{d\xi^2} + \frac{4}{m\Omega^2} 2 \frac{e}{r_0^2} [U + V \cos 2\xi + V_{ex} \cos(2\nu\xi + \alpha)] \cdot x = 0 \quad (5)$$

is obtained where $\nu = \omega/\Omega$ is the dimensionless excitation frequency. With the dimensionless parameters,

$$a = \frac{8eU}{m\Omega^2 r_0^2} \quad q = \frac{4eV}{m\Omega^2 r_0^2} \quad q' = \frac{4eV_{ex}}{m\Omega^2 r_0^2} \quad (6)$$

eq 5 simplifies to:

$$\frac{d^2x}{d\xi^2} + [a + 2q \cos 2\xi + 2q' \cos(2\nu\xi + \alpha)] \cdot x = 0 \quad (7)$$

The current experiment deals with $q \approx 0.36$, which is within the range of the effective potential theory [7]. In this range the ion motion can be separated into secular motion and fast RF motion. Experimentally the secular

frequency of the ion is about 100 kHz which is slow in comparison to the micromotion of the ion caused by the 768 kHz drive frequency of the LIT allowing for the separation of the two motions into a fast and a slow component. The secular motion has an isolated frequency spectrum in the low frequency range while the fast RF motion has an isolated frequency spectrum in the high frequency range near the main trapping frequency. In the absence of space charge these motions are correlated. The amplitude of the RF motion is $q/2$ times smaller than the amplitude of the secular motion. If the auxiliary quadrupole excitation is applied, then parametric resonance can occur through interaction of the excitation with both the secular and RF motions. Because of the smaller amplitude, parametric resonance with the RF motion requires a higher excitation threshold. This is why the high order resonance is more likely to couple with the secular motion.

Assuming that RF motion is not in a resonance condition with the quadrupole excitation, we will be interested only in the resonance with the secular motion. The corresponding excitation frequency of the first order resonance is $2\omega_s$, which experimentally is 200 kHz. For the higher order resonances the excitation frequency is even less. This means that the resonance frequencies of interest are in the low frequency regime, well below the frequency of the RF motion. This allows the secular motion theory to be used in describing quadrupole parametric resonances.

Following the methodology of Landau and Lifshitz [8] the ion motion can be separated into its fast and slow components,

$$x = X + h \cos(2\xi) \quad (8)$$

where $h \cos(2\xi)$ is the fast component and X is the slow component (secular motion). While calculating the second derivative of eq 8 we can consider h as a constant and take the derivative of the $\cos(2\xi)$ term only. Substituting this into eq 7 results in the following equation:

$$\frac{d^2X}{d\xi^2} - 4h \cos(2\xi) + [a + 2q \cos(2\xi) + 2q' \cos(2\nu\xi + \alpha)] \cdot [X + h \cos(2\xi)] = 0 \quad (9)$$

Different terms in this equation have different frequencies. The RF motions have a frequency of 2 (in dimensionless units). This part of eq 9 gives the following:

$$-4h \cos(2\xi) + ah \cos(2\xi) + 2q \cos(2\xi) X = 0$$

$$\text{or } h \approx \frac{q}{4-a} X \quad (10)$$

Later, $h = qX/2$ will be used because of the fact that $a \ll 4$ ($a = 0$ when no resolving DC is applied to the quadrupole as is the case for the LIT). It follows then

that the amplitude of the fast motions are decided by the slow motion. The low frequency part of eq 9 describes the secular motion. In order to describe the higher order resonances, it is necessary to consider that the applied excitation and secular motion are in the low frequency range. Keeping the slow terms in eq 9 results in the following equation:

$$\frac{d^2 X}{d\xi^2} + \left[a + \frac{q^2}{2} + 2q' \cos(2\nu\xi + \alpha) \right] \cdot X = 0 \quad (11)$$

This equation describes the interaction of the quadrupole excitation with the secular motion of the ion. Substitution of the dimensionless parameter $\eta = \nu\xi$ into eq 11 gives:

$$\frac{d^2 X}{d\eta^2} + \frac{1}{\nu^2} \left[a + \frac{q^2}{2} + 2q' \cos(2\eta + \alpha) \right] \cdot X = 0 \quad (12)$$

Further substitution of the dimensionless parameters,

$$A = \frac{a + \frac{q^2}{2}}{\nu^2} \quad \text{and} \quad Q = \frac{q'}{\nu^2} \quad (13)$$

into eq 12 produces the Mathieu equation,

$$\frac{d^2 X}{d\eta^2} + [A + 2Q \cos(2\eta + \alpha)] \cdot X = 0 \quad (14)$$

where A and Q define the ordinate and coordinate axis of the Mathieu stability diagram. Substitution of the following approximation for β (for $q < 0.4$) and the expression for the secular frequency, ω_s

$$\beta^2 \approx a + \frac{q^2}{2} \quad \omega_s = \frac{\beta\Omega}{2} \quad (15)$$

along with $\nu = \omega/\Omega$ and q' (eq 6) into the expressions for A and Q (eq 13) yield:

$$A = \frac{\beta^2 \Omega^2}{\omega^2} = 4 \frac{\omega_s^2}{\omega^2} \quad \text{and} \quad Q = \frac{4eV_{ex}}{m\omega^2 r_0^2} = q' \frac{\Omega^2}{\omega^2} \quad (16)$$

These variables, which define the axes of the Mathieu stability diagram, contain the parameters ω and V_{ex} that are of primary interest in this work.

Shown in Figure 1 are the regions of stability and instability as defined by the Mathieu equation. We limit the diagram to the upper right hand quadrant of the full stability diagram due to the symmetric nature of the diagram about the A axis. The diagram is limited to positive values of A because of the fact that $a = 0$ for the LIT (see eq 13). The shaded areas mark the regions of instability and correspond to those values of A and Q that can lead to resonant excitation. At a value of $Q = 0$,

Figure 1. Mathieu stability diagram covering the regions of instability corresponding to the $K = 1$ to 6 quadrupolar resonances. The resonances occur in the regions of instability defined by the shaded regions.

corresponding to $V_{ex} = 0$, the regions of instability intersect the A axis at values of A corresponding to ω_K , as predicted using eq 1. As V_{ex} increases so does Q and, as can be seen in Figure 1, the regions of instability tend to broaden and shift which results in a corresponding broadening and shifting of the resonance.

The K resonances were found by adjusting the excitation frequency while maintaining a constant excitation amplitude over the resonance of interest. In doing so both A and Q were varied simultaneously such that the ratio $A/Q = 4\omega_s^2/q'\Omega^2$ remains a constant. Differentiation of A and Q in eq 16, with respect to ω , shows that the relative change of parameters satisfy the following condition:

$$\frac{dA}{A} = \frac{dQ}{Q} = -2 \frac{d\omega}{\omega} \quad (17)$$

When Q is relatively small we have $A \approx K^2$ for each resonance of order K . This is in accordance with the resonance conditions defined by eq 1. For $Q \ll A$ it follows from eq 17 that an absolute change in Q is considerably less than the corresponding change in A . Hence, the change in Q can be neglected in the following discussion. At a fixed value of Q there are ranges of A , which correspond to the resonance condition. The

Table 2. Analytical expressions for the width and shift of the resonances as derived from the power series for the boundaries of the Mathieu stability diagram. First significant terms are taken into account only. Recall that $Q = 4eV_{ex}/m\omega^2r_0^2$ (eq 16)

K	Width of the unstable band $a_K - b_K$	Shift of the unstable band $K^2 - \frac{a_K + b_K}{2}$	Spectral width of resonance (Hz) $\Delta\omega_K$	Resonance frequency shift (Hz) $\delta\omega_K$
1	$2Q$	$\frac{Q^2}{8}$	$2\omega_s Q$	$\frac{\omega_s}{8}Q^2$
2	$\frac{2Q^2}{4}$	$-\frac{Q^2}{6}$	$\frac{2\omega_s}{32}Q^2$	$-\frac{\omega_s}{48}Q^2$
3	$\frac{2Q^3}{64}$	$-\frac{Q^2}{16}$	$\frac{2\omega_s}{1728}Q^3$	$-\frac{\omega_s}{432}Q^2$
4	$\frac{2Q^4}{2304}$	$-\frac{Q^2}{30}$	$\frac{2\omega_s}{147456}Q^4$	$-\frac{\omega_s}{1920}Q^2$
5	$\frac{2Q^5}{147456}$	$-\frac{Q^2}{48}$	$\frac{2\omega_s}{18432000}Q^5$	$-\frac{\omega_s}{6000}Q^2$
6	$\frac{2Q^6}{14745600}$	$-\frac{Q^2}{70}$	$\frac{2\omega_s}{3185049600}Q^6$	$-\frac{\omega_s}{15120}Q^2$

boundaries of these regions are the boundaries of stability denoted by a_K and b_K . From eq 17 the width of the resonance band, $\Delta\omega_K$, and the shift of resonance frequency, $\delta\omega_K$, may be calculated as follows (taking into account $A = K^2$):

$$\Delta\omega_K = (a_K - b_K) \frac{\omega_K}{2K^2} \quad \delta\omega_K = \left[K^2 - \frac{a_K + b_K}{2} \right] \frac{\omega_K}{2K^2}. \quad (18)$$

where ω_K is the resonance frequency as predicted by eq 1 for $K = 1, 2, \dots$. Substituting $\omega_K = 2\omega_s/K$ into eq 15 results in the width and shifts expressed in terms of the secular frequency,

$$\Delta\omega_K = (a_K - b_K) \frac{\omega_s}{K^3} \quad \delta\omega_K = \left[K^2 - \frac{a_K + b_K}{2} \right] \frac{\omega_s}{K^3}. \quad (19)$$

Analytical expressions, in the form of a power series, can be used to calculate the stability boundaries (a_K and b_K) [9]. Table 2 presents the first significant terms of the expressions which were derived for the width and shift of the resonances using the power series expansions for a_K and b_K and eq 19. The second and third columns of Table 2 show the width and shift of the resonances in units of A while the last two columns are in units of frequency as determined by eq 19.

The expressions in Table 2 do not take into account the fact that the ratio A/Q is experimentally a constant; instead, the expressions assume a constant value of Q . In order to use the experimental ratio of A/Q the resonant frequencies were determined from the stability diagram by first setting V_{ex} constant and then iteratively solving for a value of ω_K which simultaneously satisfied the conditions set by A , Q (eq 16), and

a point located on the lower instability boundary. This process was then repeated to determine a value of ω_K that located a point on the upper instability boundary. The resonant frequency was taken as the midpoint between these two values.

It should be noted that although expressions have been developed for the widths of the resonances, the expressions represent the regions in which there is kinetic energy input into the ions motion. These widths represent an upper limit. Correlation of these widths with the experimental depletion data necessitates the inclusion of a mechanism for fragmentation into the theory to account for the non-linear nature of the fragmentation process with respect to internal energy content. This is beyond the scope of the current paper and is not attempted here.

Results and Discussion

Trajectory Simulations

By simulating ion trajectories it is possible to determine the response of resonant frequency to auxiliary amplitude and pressure independently. Results of these simulations are shown in Figures 2 and 3 for the $K = 1$ and $K = 3$ resonances, respectively. These data were collected using a round rod geometry of infinite length with $r_0 = 4.171$ mm, a drive frequency of 768 kHz, and $q = 0.358549$ ($\beta = 0.260397$) for m/z 609.7. The ions were given random initial coordinates located within a radius of 0.1 mm of the quadrupole axis. The excitation amplitudes and pressures were chosen such that a total energy loss of approximately 200–260 eV was obtained for the maximum total energy loss in each graph. The total energy loss is the average of the results for the 100 trajectories. The trajectories were individually run at each frequency for a period of 4 ms using nitrogen as the collision gas. A comparison of the resonant frequen-

Figure 2. (a) Total energy loss dependence of the $K = 1$ resonance upon the excitation amplitude as a function of excitation frequency. Pressure was 1.8 mTorr of nitrogen. (b) The total energy loss dependence with pressure as a function of excitation frequency. Excitation amplitude was $0.65 V_{0-p}$. Each point is the average of the total energy loss for 100 trajectories. The potential for this simulation was derived using round rods for the quadrupole.

cies, as determined from the fit to the data, for the $K = 1$ resonance for 100 and 500 ion trajectories gave results that were within 2 Hz of each other. This indicated that 100 trajectories were sufficient to obtain valid results to within a precision of a few Hz. This comparison was carried out for hyperbolic electrodes only.

In general, an ion loses KE during a collision event, however, in some cases where the ion's KE is close to thermal energies it can increase slightly leading to a reduction in the total KE loss. This is a result of the inclusion of a thermal energy distribution for the background gas in the trajectory model.

The degree to which an ion absorbs energy from the excitation field is also dependent upon the phase of the ion's motion relative to the excitation field. If the phase difference is favorable, the excitation will lead to an increase in the ion's amplitude of motion and kinetic energy. If the phase difference is unfavorable, the ion's amplitude of motion and kinetic energy can be decreased for a period of time until the ion's phase adjusts to the phase of the excitation frequency [10] and begins to gain in both amplitude and kinetic energy. However, collisions of the ion with the buffer gas serve to randomize the relative phase of the ion's motion and the excitation field causing the ions to be brought into and out of phase with the excitation field. The number of collisions suffered by the ion during a 4 ms simulation period varies from approximately 300 to 800 collisions

Figure 3. (a) Total energy loss dependence of the $K = 3$ resonance upon the excitation amplitude as a function of excitation frequency. Trapping pressure was 1.8 mTorr of nitrogen. (b) The total energy loss dependence with pressure as a function of excitation frequency. Excitation amplitude was $9.3 V_{0-p}$. Each point is the average of the total energy loss for 100 trajectories. The potential for this simulation was derived using round rods for the quadrupole.

(5 to 15 μ s between collisions). These values are dependent upon the excitation amplitude, trap pressure, and whether or not the ion is in resonance. Ions in resonance sustain a higher number of collisions than those off resonance. The time between collisions is sufficiently short that any correlation of the ion's initial phase difference, with respect to the excitation frequency, and the ion's initial velocity and spatial distributions is effectively suppressed within the first few tens of ms of applying the excitation. At too high a pressure the ions are unable to gain in both ion motion amplitude and kinetic energy because of the damping effects of the collisions. This leads to the existence of a minimum excitation amplitude or threshold before either ejection or fragmentation of the ion can be observed [8, 11].

Exciting for extended periods of time at lower gas pressures or higher excitation amplitudes resulted in ions colliding with the electrodes. This produced peaks that were either flat topped or contained a dip in the centre portion of the peak, the result of ion trajectories that did not continue for the full excitation period. That is, if an ion trajectory leads to an impact with an electrode after only a few tenths of a microsecond, it suffers relatively few collisions resulting in a low total energy loss. This situation was avoided in the results presented here through a judicious choice of operating parameters.

It is relevant to examine the relationship between the

Table 3. Resonant frequencies as a function of excitation amplitude, trap pressure, and rod shape as determined from ion trajectory calculated using $\beta = 0.260397$

K	Excitation amplitude (volts)	Pressure (mTorr)	Round Rods		Hyperbolic Rods	
			Resonant frequency (kHz)	Frequency shift (Hz)	Resonant frequency (kHz)	Frequency shift (Hz)
1	0.50	1.8	200 297		199 973	
	0.65	1.8	200 294	–3	199 970	–3
	0.65	3.6	200 294	0	199 964	–6
2	4.5	1.8	99 748		99 598	
	5.1	1.8	99 627	–121	99 476	–122
	5.1	3.6	99 636	+9	99 461	–15
3	8.7	1.8	65 846		65 745	
	9.3	1.8	65 713	–133	65 604	–141
	9.3	3.6	65 700	–13	65 596	–8
4	11.7	1.8	48 838		48 761	
	12.2	1.8	48 718	–120	48 633	–128
	12.2	3.6	48 700	–18	48 629	–4
5	13.6	1.8	38 708		38 642	
	14.2	1.8	38 560	–148	38 492	–150
	14.2	3.6	38 540	–20	38 472	–20
6	15.0	1.8	31 981		31 925	
	15.5	1.8	31 857	–124	31 800	–125
	15.5	3.6	31 857	0	31 793	–7

total kinetic energy loss determined from simulations and the depletion of the reserpine ion observed experimentally. When the dipolar excitation of ions in a Paul trap are modelled on the basis of a forced damped harmonic oscillator [12], the maximum in the power absorption curve as a function of excitation frequency occurs at the resonant frequency and the amount of power absorbed is equal to the average energy lost per collision times the collision frequency [13]. This is the same as the total energy loss, described in the model above, divided by the duration of the exposure. The effective internal temperature of the ion also correlates with the amount of power absorbed, indicating that the ion is at its hottest (highest internal energy content) when on resonance. It is at this frequency, the secular frequency, that the maximum degree of fragmentation occurs.

During the collision event the ion can lose a fraction of its kinetic energy. Ion motion becomes unstable if the energy gain is higher than the energy loss. When this condition occurs the ion trajectory amplitude increases non-linearly until the ion collides with a rod resulting in neutralization of the ion. Neutralization on a rod will correlate with the ions' maximum displacement from the longitudinal axis of the LIT. However, the maximum displacement of an ion does not necessarily occur at the same excitation frequency as the maximum in the power absorption spectrum. In the case of the forced damped harmonic oscillator the maximum displacement is shifted towards lower frequency with increased damping [10]. For example, if the ion reserpine has a secular frequency (ω_0) of 100 kHz and is trapped at a

pressure of 1.8 mTorr of nitrogen, it will have a damping coefficient of 5476 Hz [13]. The frequency at which the maximum displacement occurs for a forced damped harmonic oscillator is determined by:

$$\omega = \omega_0^*(1 - 1/2Q_0^2)^{1/2} \quad (20)$$

where Q_0 is the ratio of the secular frequency to the damping coefficient [10]. This results in the maximum ion ejection occurring at 99,925 Hz, a red shift of 75 Hz from the ion's secular frequency of 100,000 Hz.

The above discussion illustrates that the excitation frequency at which the maximum depletion is measured depends upon the depletion mechanism. With regard to the experimental depletion data reported here, the depletion mechanism occurs primarily through fragmentation. This implies that the experimentally measured resonances should be compared with a model or theory which is based upon the total energy or power absorbed by the ion and not just simply its radial displacement within the LIT.

In order to compare the results of the simulations to the experiment and theory it is necessary to know what the differences are between each. The models that were constructed simulated both hyperbolic and round rod geometries with r_0 constrained to 4.171 mm. The round rod geometry implicitly includes in the trapping potential contributions from higher order multipole components with $N = 6, 10, 14, 18 \dots$ where $2N$ is the number of poles [14, 15]. The presence of the higher order multipole terms will cause a shifting of the ions secular

Figure 4. Expanded views of the instability regions displayed in Figure 1. The intersection of the nearly vertical lines with the a_n and b_n boundaries represent the points at which the values of A and Q give the same excitation frequency at a particular excitation amplitude. The excitation amplitudes used to obtain these intersections are given in Table 4. The resonant frequency was taken as the average value of the frequency obtained at the a_n and b_n intersections. Note the increased Q values with increased K and excitation amplitude.

frequency from that found in a pure quadrupolar field. The contribution of the higher order multipole terms to the overall potential becomes more significant as the amplitude of the ions motion increases [14]. In the case

of the simulations r/r_0 (the ratio of the rod radius to the field radius) was constrained to the value 1.12563 which gives $A_2 = 1.001462$ (quadrupole), $A_6 = 0.001292$ (dodecapole), $A_{10} = -0.002430$, $A_{14} = -0.000297$, and $A_{18} = -0.000024$ [14]. This r/r_0 value is close to the optimum value of 1.12–1.13 [16]. Experimentally, the ratio of r/r_0 was 1.134 giving $A_2 = 1.002023$, $A_6 = 0.000733$, $A_{10} = -0.002439$, $A_{14} = -0.000291$, and $A_{18} = -0.000023$ which are similar to the coefficients for the model. In contrast, the hyperbolic rods produce a quadrupolar potential with $A_2 = 1.0000$ and all other $A_N = 0$. A comparison of the simulation results for the round rod geometry and the hyperbolic rod geometry give some idea of how the resonant frequencies determined from the experimental data (round rods) compare to those determined using a theory based upon a pure quadrupolar potential (hyperbolic shaped rods).

The data for the $K = 1$ resonance, Figure 2, does not show any significant shifts with changes in either the excitation amplitude or gas pressure. However, the data for the $K = 3$ resonance, Figure 3, shows a more definitive shift of approximately 133 Hz towards lower frequency as the excitation amplitude is increased from 8.7 to 9.3 V. The pressure dependence shows a slight shift in the resonant frequency towards lower frequency.

Table 3 shows the resonant frequencies for the $K = 1$ to $K = 6$ resonances as determined from the fits of the data generated from the simulations. This table contains the resonant frequencies as determined for excitation in a round rod quadrupole and for excitation in a quadrupole with hyperbolic rods. Simulations were run using the hyperbolic rod shapes in order to provide a comparison to the theory that was based upon a pure quadrupolar potential.

Examination of the resonant frequencies for $K = 2$ to 6 shows that, over the variation limits of excitation amplitude and pressure, the resonant frequencies are more strongly affected by small changes in excitation amplitude than trap pressure. For example, increases in excitation amplitude of 13 and 3.3% for the $K = 2$ and

Table 4. This table shows a comparison of the resonant frequencies determined from the simulations using the hyperbolic shaped rods, at a pressure of 1.8 mTorr N_2 , to those calculated using the stability diagram, and to those calculated from eq 1. The resonant frequency shifts are also shown for the simulations and as determined from the stability diagram for the stated excitation amplitudes. The shifts are taken relative to the resonant frequencies determined using eq 1. The last column shows the width of the resonances as calculated from the stability diagram at the indicated excitation amplitudes. The resonant frequencies calculated using eq 1 are for zero pressure and zero excitation amplitude. All data is for $\beta = 0.260397$

K	Excitation amplitude (volts)	Resonant frequency (kHz)			Resonant frequency shifts (Hz) from $Q = 0$		Resonance width (Hz)
		Hyperbolic rod model	Stability diagram	Eq 1 ($Q = 0$)	Hyperbolic rod model	Stability diagram	Stability diagram
1	0.65	199 970	199 982	199 985	–15	–3	2997
2	5.1	99 476	99 531	99 992	–516	–461	1380
3	9.3	65 604	65 741	66 662	–1058	–921	841
4	12.2	48 633	48 802	49 996	–1363	–1194	594
5	14.2	38 492	38 690	39 997	–1505	–1307	583
6	15.5	31 793	32 018	33 331	–1538	–1313	491

Table 5. Resonant frequency shifts and widths determined using the eqs of Table 2 with $\omega_s = 99\,992.45$ Hz

K	Excitation amplitude (volts)	Average Q	Spectral width of resonance (Hz) $\Delta\omega_K$	Resonance frequency shift (Hz) $\delta\omega_K$
1	0.65	0.01498	2996	2.8
2	5.1	0.4746	1408	−469.2
3	9.3	1.9838	904	−910.9
4	12.2	4.5773	595	−1091.2
5	14.2	8.3897	451	−1173.0
6	15.5	13.9397	461	−1285.0

$K = 6$ resonances results in frequency shifts of 121 and 123 Hz, respectively, while a 100% increase in trap pressure results in only a shift of +8.3 and −0.8 Hz for the $K = 2$ and $K = 6$ resonances, respectively.

Additionally, the excitation frequencies observed for the hyperbolic rods were on average about 0.2% lower than for the round rods when compared at the same excitation amplitude, frequency, and trap pressure. This indicates that the contributions from the higher order multipoles are minor. Since this difference is well within the experimental FWHM of the measured resonances, as shown in Table 1, there is little justification for the more time consuming round rod calculations.

Stability Diagram Resonances

Figure 4 shows an expanded view of the instability regions that were introduced in Figure 1. These regions are bounded from above and below by the a_n and b_n boundaries. The nearly vertical line in each plot represents the (A, Q) points which exist for the excitation amplitudes 0.65 V, 5.1 V, 9.3 V, 12.2 V, 14.2 V, and 15.5 V for the $K = 1$ –6 resonances, respectively. These amplitudes were chosen so that a direct comparison could be made with the results of the trajectory simulations for the hyperbolic rod shape. From the functional forms of A and Q (eq 16) it can be seen that an increase in excitation frequency results in a decrease in the values of A and Q for a particular excitation amplitude. Experimentally, the excitation amplitude is held constant as the excitation frequency is scanned. However, only one particular combination of excitation

frequency and amplitude will produce a set of A and Q values which lie on an instability boundary.

For the $K = 1$ resonance, the instability boundaries are fairly symmetrical about $A = 1.00$ over the range $Q = 0$ to 0.03. At an excitation amplitude of 0.65 V and $\beta = 0.260397$ the resonance is found at 199,982.1 Hz. This is slightly less than the value of 199,984.9 Hz that is calculated from eq 1, which assumes a value of $Q = 0$. As discussed earlier, the resonant frequency shifts become more pronounced at higher values of K and high excitation amplitudes. This is shown in Table 4 for the resonant frequencies determined from the simulations using the hyperbolic rod model and from the Mathieu stability diagram, Figure 4. Table 5 shows the resonant frequencies and shifts as determined using the average value of Q for each K and the equations of Table 2. With the exception of $K = 1$, the effect is an increasingly larger shift towards lower resonant frequencies. The $K = 1$ shows a slight shift towards higher frequency. This simply illustrates the approximate nature of using an average value of Q instead of solving for the actual values of A and Q . The overall shifts in the resonances towards lower frequencies are the same trend that was observed in the experimental data of reference [1].

The resonance widths as determined from the stability diagram are shown in the last column of Table 4. These widths are based upon maintaining a constant value of A/Q (constant excitation amplitude). The resonance widths determined using the equations of Table 2 and an average Q value are shown in Table 5. The widths are similar for smaller K but tend to deviate

Table 6. A comparison of the experimental resonant frequencies and those determined from the Mathieu stability diagram using the experimental excitation amplitudes and an excitation amplitude of 0.0 V corresponding to eq 1. The $K = 1$ resonant frequency for the theory was adjusted to match the experimental value by using $\beta = 0.260397$

K	Experimental excitation amplitude (volts)	Experimental frequency (kHz)	Theoretical frequency (kHz)	Theory at $V_{0-p} = 0.0$ V
1	0.65	200.0	200.0	200.0
2	2.9	100.6	99.8	100.0
3	6.25	66.38	66.26	66.66
4	7.6	49.55	49.57	50.00
5	9.2	39.13	39.50	40.00
6	9.65	32.43	32.88	33.33

significantly for the higher K values. This simply illustrates that the expressions of Table 2, where an average Q is used, are adequate for small values of Q only. It should be emphasized that these widths are useful for determining an upper bound to the width of the experimentally observed peaks. A direct comparison with experiment requires that the additional factors of trapping pressure, ejection, fragmentation, and peak shape be taken into account.

A comparison of the experimental resonant frequencies to those determined from the Mathieu stability diagram using the experimental excitation amplitudes are shown in Table 6. These values were compared to the resonant frequencies determined using eq 1. In each case, with the exception of the experimental value for $K = 2$, the trend is for a shift towards lower frequencies for each value of K when compared to the frequencies in the last column. It should be noted that although the observed trends and magnitudes of the shifts are reasonably close, an accurate comparison cannot be made at this level of the theory. That is, the theory does not yet include the effects of round rods (contributions from higher order multipoles) or damping on the resonant frequencies. Inclusion of pressure effects would require the addition of a damping term to eq 3 which is beyond the scope of the current paper. However, the effects of pressure are known to enlarge the boundaries of the stable regions or conversely reduce the boundaries of the instability regions where the resonances occur [8, 17]. In light of the results of the ion trajectory calculations, it is not expected that these variations in the boundaries will lead to significant changes in the resonant frequencies.

Conclusions

Ion trajectory simulations have shown that the quadrupolar resonances for $n = 0$ and $K = 2$ to 6 shift significantly to lower frequencies with increased excitation amplitude while pressure changes have been shown to cause only a minor shifting of the resonances. The $K = 1$ resonance showed only a minor shift over the range of the excitation amplitudes examined. A comparison of the resonance shifts obtained from the simulations to those obtained using a theoretical derivation based upon the Mathieu stability diagram have shown good agreement. It has been determined from the theory that the resonant frequencies are dependent upon the excitation amplitude with the shifting of the resonances predominantly towards lower frequencies with increased excitation amplitude (over the range of the experimental amplitudes). It has also been shown that widths of the resonances increase with increasing excitation amplitude.

The results obtained from both the ion trajectory

simulations and the Mathieu stability diagram show a reasonably good correlation with the previously obtained experimental results for the $n = 0$, $K = 1$ to 6 resonances. The theory provides an understanding for the reason why the resonance shifts are excitation amplitude dependent.

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