Quadrupole Excitation of Ions in Linear Quadrupole Ion Traps with Added Octopole Fields

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Modeling and experimental studies of quadrupole excitation of ions in linear quadrupole traps with added octopole fields are described. An approximate solution to the equations of motion of ions trapped in a quadrupole with added octopole and dodecapole fields, with quadrupole excitation and damping is given. The solutions give the steady-state or stationary amplitudes of oscillation with different excitation frequencies. Trajectory calculations of the oscillation amplitudes are also presented. The calculations show that there can be large changes in the amplitude of ion oscillation with small changes in excitation frequency, on both the low and high-frequency sides of a resonance. Results of experiments with quadrupole excitation of reserpine ions in linear quadrupole traps with 2.0%, 2.6%, and 4.0% added octopole fields are given. It is found that as the excitation frequency is changed, two resonances are generally observed, which are attributed to the motion in the x and y directions. The two resonances can have quite different intensities. Sudden jumps or sharp sided resonances are not observed, although in some cases asymmetric resonances are seen. The calculated frequency differences between the two resonances are in approximate agreement with the experiments. (J Am Soc Mass Spectrom 2008, 19, 510–519) © 2008 American Society for Mass Spectrometry

Linear quadrupole ion traps are finding widespread applications in mass spectrometry [1]. For tandem mass spectrometry, where ions are excited at their resonant frequencies in the presence of a collision gas to induce fragmentation, the addition of field distortions, described by the addition of higher multipoles to the potential, can increase the fragmentation efficiency, particularly at low pressures [2, 3]. The spatial part of the potential in a linear quadrupole with field distortions can be written as a superposition of multipoles

$$\Phi(x_r, y_r) = \text{Re} \left[\sum_{N=0}^{\infty} A_N \left(\frac{x_r + iy_r}{r_0} \right)^N \right] \quad (1)$$

where $\text{Re}[func]$ is the real part of the complex function $func$ and A_N is the dimensionless amplitude of a $2N$ -pole field. If no dc voltages are applied between the rods, the time-dependent potential is

$$V(x_r, y_r, t_r) = \Phi(x_r, y_r) V_{rf} \cos(\Omega t_r) \quad (2)$$

where V_{rf} is the zero to peak rf voltage pole to ground, r_0 the field radius, x_r, y_r are Cartesian coordinates, and t_r time. The addition of higher multipoles can lead to nonlinear dynamics, giving sudden changes in the

amplitude of ion oscillation with small changes in excitation frequency. These effects have been described in detail for dipole excitation of ions in a linear quadrupole trap with a 4% added octopole field [2a].

Trapped ions can also be excited by quadrupole excitation, sometimes called parametric excitation [4]. With quadrupole excitation, the excitation electric field strength is proportional to the distance off axis. In a pure quadrupole field, ions are excited when the excitation angular frequency ω_{ex} is

$$\omega_{ex} = |n + \beta| \frac{\Omega}{K} \quad (3)$$

where $n = 0, \pm 1, \pm 2, \dots, K = 1, 2, 3, \dots$, Ω is the angular frequency of the trapping radiofrequency field, and β is a function of the Mathieu parameter q given by

$$q = \frac{4zeV_{rf}}{m\Omega^2 r_0^2} \quad (4)$$

with e the charge of an electron, and z the number of charges on an ion. The effects of nonlinear dynamics can also be seen with quadrupole excitation. Werth and coworkers have reported large changes in oscillation amplitude and strongly asymmetric resonances with parametric excitation of ions in 3D Paul traps [5–7] and electrons in Penning traps [8, 9]. These effects were attributed to the higher order fields of the traps.

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Table 1. Rod dimensions and calculated harmonic amplitudes, $R_x = r_0$. The rod sets used in the experiments here have $r_0 = 4.5$ mm

Nominal % octopole	R_y/R_x	A_0	A_2	A_4	A_6	A_8	A_{10}
2.0	1.220	−0.02029	0.9994	0.01961	0.003281	0.0008604	−0.002345
2.6	1.300	−0.02638	1.0014	0.02567	0.001286	0.0009514	−0.002358
4.0	1.516	−0.0403	1.0056	0.03980	−0.002990	0.0008702	−0.002319

Here we describe modeling and experimental studies of quadrupole excitation of ions in linear quadrupole traps with added octopole fields. We give an approximate solution to the equations of motion of ions trapped in a quadrupole with added octopole and dodecapole fields with quadrupole excitation and damping. The solutions give the steady-state or stationary amplitudes of oscillation with different excitation frequencies. Trajectory calculations of the oscillation amplitudes are also presented. The results show that there can be large changes in the amplitude of ion oscillation with small changes in excitation frequency. These large changes appear on both the low and high-frequency sides of a resonance, and thus might be used to produce high-resolution in isolating ions [2a, 10], the main motivation for this work. We then describe an experimental investigation of quadrupole excitation of ions in linear quadrupole traps with 2.0%, 2.6%, and 4.0% added octopole fields. Protonated ions of reserpine are trapped at pressures of 1.0 and 0.2 mTorr of nitrogen and excited at the resonances with $K = 1$ and 2. Our principal finding is that as the excitation frequency is scanned, two resonances are generally observed, which we attribute to the motion in the x and y directions. The two resonances can have quite different intensities. Sudden jumps or sharp sided resonances are not observed, although in some cases asymmetric resonances are seen. The calculated frequency differences between the two resonances are in approximate agreement with the experiments.

Theoretical Treatment

An octopole field can be added to a round rod quadrupole by making the radius of the y rods, R_y , greater than the radius of the x rods, R_x [11]. All rods are equally spaced a distance r_0 from the quadrupole axis. The ratio R_y/R_x determines the magnitude of the added octopole field. Smaller amounts of higher even multipoles are also added. The ratios R_y/R_x and multipole amplitudes, A_N , of the rod sets modeled and used in the experiments here are shown in Table 1. Note the rod sets have an axis potential $A_0 V_{rf}$ where $A_0 \approx -A_4$.

The equations of motion of an ion in the potential of eq 2 cannot be solved analytically. To gain some insight into the ion motion, we use a perturbation method to calculate the stationary oscillation amplitudes of an ion in the pseudo- or effective potential arising from the time-dependent potential of eq 2 with quadrupole excitation and damping.

The effective potential, $V_{eff}(x_r, y_r)$ is determined by the electric fields arising from the potential of eq 2 and is given by [12],

$$\begin{aligned}
 V_{eff}(x_r, y_r) &= \frac{ze\tilde{E}^2}{4m\Omega^2} \\
 &= \frac{ze}{4m\Omega^2} \left[\left(\frac{\partial \Phi(x_r, y_r)}{\partial x_r} \right)^2 + \left(\frac{\partial \Phi(x_r, y_r)}{\partial y_r} \right)^2 \right] \\
 &= \frac{zeV_{rf}^2}{4m\Omega^2 r_0^2} \left[4A_2^2 \frac{x_r^2 + y_r^2}{r_0^2} + 16A_2A_4 \frac{x_r^4 - y_r^4}{r_0^4} \right. \\
 &\quad \left. + (16A_4^2 + 24A_2A_6) \frac{x_r^6 + y_r^6}{r_0^6} + \dots \right] \quad (5)
 \end{aligned}$$

The equation of motion of an ion in this effective potential with quadrupole excitation and collisional damping is

$$m \frac{d^2 \tilde{r}}{dt_r^2} = -ze \nabla V_{eff} - ze \nabla \Phi_{ex} - \Gamma \frac{d\tilde{r}}{dt_r} \quad (6)$$

where $\tilde{r} = x_r \hat{i} + y_r \hat{j}$ is the position vector, and $\hat{i}$ and $\hat{j}$ are unit vectors in the x and y directions. The quadrupole excitation potential Φ_{ex} is

$$\Phi_{ex}(x_r, y_r, t_r) = \Phi(x_r, y_r) V_{ex} \cos(\omega_{ex} t_r) \quad (7)$$

where $\omega_{ex} = 2\pi f_{ex}$ is the angular frequency of the quadrupole excitation. The damping coefficient Γ due to ion collisions with the background gas is [2a].

$$\Gamma = \frac{3.01 \sigma n m_2 \sqrt{2k_B T / m_2}}{2} = \frac{3.01 P \sigma \sqrt{2m_2 / (k_B T)}}{2} \quad (8)$$

where n is the background gas number density, m_2 is the mass of the background gas, P is the background gas pressure, σ is the collision cross section, k_B is Boltzmann's constant, and T is the gas temperature.

In general, the ion motions in the x and y directions are coupled by the higher multipole fields. However, motions along the x axis (i.e., x_r when $y_r = 0$) and along the y axis (y_r when $x_r = 0$) are uncoupled. Including the nonlinear terms up to x^5 and y^5 but retaining only the quadrupole excitation terms, the equations of motion are

$$\frac{d^2 x}{dt^2} + \lambda \frac{dx}{dt} + [1 - \gamma \cos(\omega t)]x + B_3 x^3 + B_5 x^5 = 0 \quad (9)$$

$$\frac{d^2y}{dt^2} + \lambda \frac{dy}{dt} + [1 + \gamma \cos(\omega t)]y - B_3y^3 + B_5y^5 = 0 \quad (10)$$

Here we have introduced the dimensionless variables x , y , t , ω , λ , γ , B_3 , and B_5 .

The dimensionless coordinates, time, and excitation frequency are defined as

$$x = \frac{x_r}{r_0}; y = \frac{y_r}{r_0}; t = \omega_0 t_r; \omega = \frac{\omega_{ex}}{\omega_0} \quad (11)$$

where

$$\omega_0 = 2\pi f_0 = \frac{qA_2}{\sqrt{8}}\Omega \quad (12)$$

is the secular frequency of ion oscillation in a quadrupole potential. With these definitions, the calculated angular frequencies and angular frequency shifts are in units of the secular frequency ω_0 , and the positions of ions and the ion oscillation amplitudes are in units of the field radius r_0 . The dimensionless damping and driving coefficients, λ and γ are defined as

$$\lambda = \frac{\Gamma}{m\omega_0} = \frac{3.01P\sigma\sqrt{2m_2/(k_B T)}}{m\omega_0} \quad (13)$$

$$\gamma = \frac{2zeV_{ex}}{m\omega_0^2 r_0^2} \quad (14)$$

The dimensionless constants B_3 and B_5 are determined by the multipole components of the field. Keeping multipoles up to $N = 6$,

$$B_3 = \frac{8A_4}{A_2} \quad (15)$$

$$B_5 = \frac{12A_4^2 + 18A_2A_6}{A_2^2} \quad (16)$$

Equations 9 and 10 are essentially the same, except for the different signs in front of γ and B_3 . Therefore, we solve eq 9, for the x motion, and simply state the solution for the y motion.

A perturbation method is necessary to solve eq 9. To properly order the terms, we first calculate the coefficients for the conditions of the experiments described below. These are listed in Table 2. The two nonlinear terms contribute in the same (first) order of perturbation theory. Based on the magnitudes of the coefficients, eq 9 can be rewritten as

$$\frac{d^2x}{dt^2} + \epsilon\lambda \frac{dx}{dt} + [1 - \epsilon\gamma \cos(\omega t)]x + \epsilon B_3x^3 + \epsilon B_5x^5 = 0 \quad (17)$$

where ϵ denotes the order of the terms and has no

Table 2. Coefficients in eq 9 calculated for an ion of m/z 609.28, a quadrupole with an added 4% octopole field and zero to peak excitation amplitudes of 0.30 V and 0.35 V for excitation at pressures of 0.2 mTorr and 1 mTorr, respectively

Pressure	λ	γ	B_3	B_5
0.2 mTorr	0.00154376	0.0396614	0.318042	-0.0354884
1 mTorr	0.00771878	0.0462716	0.318042	-0.0354884

physical meaning. Equation 17 describes a damped and parametrically driven nearly harmonic oscillator with odd orders of nonlinear distortions to the force. The method of multiple time scales (MMS) [13] is used to find an approximate solution. In this method, independently varying time scales are assumed. The fast time scale, T_0 , is the normal time scale, and the first-order slower time scale $T_1 = \epsilon T_0$. Keeping only these two time scales we seek an approximate solution of the form

$$x(T_0, T_1) = x_0(T_0, T_1) + \epsilon x_1(T_0, T_1) + o(\epsilon^2) \quad (18)$$

where $o(\epsilon^2)$ denotes terms equal to or smaller than the second-order. With these two time scales, the time derivatives are

$$\frac{d}{dt} = D_0 + \epsilon D_1 \quad (19)$$

$$\frac{d^2}{dt^2} = D_0^2 + \epsilon 2D_0D_1 + o(\epsilon^2) \quad (20)$$

Where $D_0 = d/dT_0$ and $D_1 = d/dT_1$ are the derivative operators with respect to the times T_0 and T_1 . Inserting eqs 18, 19, and 20 into eq 17 and equating like terms according to the orders of ϵ yields

$$\epsilon^0: D_0^2x_0 + x_0 = 0 \quad (21)$$

$$\epsilon^1: D_0^2x_1 + x_1 = -2D_0D_1x_0 - \lambda D_0x_0 + \gamma \cos(\omega t)x_0 - B_3x_0^3 - B_5x_0^5 \quad (22)$$

Equation 21 is that of a simple harmonic oscillator. We write the solution in complex form

$$x_0(T_0, T_1) = A(T_1)e^{iT_0} + A^*(T_1)e^{-iT_0} \quad (23)$$

where $A^*(T_1)$ is the complex conjugate of $A(T_1)$, which is a function of the slow time scale T_1 . The function $A(T_1)$ is determined to ensure there are no secular terms in eq 22. Substituting eq 23 into the right side of eq 22 yields

$$\begin{aligned}
D_0^2 x_1 + x_1 = & \left(-i \frac{dA}{dT_1} - i\lambda A - 3B_3 A^2 A^* \right. \\
& \left. - 10B_5 A^3 (A^*)^2 \right) e^{iT_0} \\
& + \frac{\gamma}{2} [A e^{i(\omega+1)t} + A^* e^{i(\omega-1)t}] - B_3 A^3 e^{i3T_0} - B_5 (A^5 e^{i5T_0} \\
& + 5A^4 A^* e^{i3T_0}) + C.C.
\end{aligned} \quad (24)$$

where C.C. stands for the complex conjugate of all the preceding terms. We consider the case where the excitation frequency is about twice that of the secular frequency ($n = 0$, $K = 1$ in eq 3). In this case, write the excitation frequency as

$$\omega = 2 + \epsilon \cdot \Delta\omega \quad (25)$$

where $\Delta\omega$ is the excitation frequency detuning from the primary resonant frequency, 2 (in units of ω_0). Substituting eq 25 into eq 24 and removing the secular terms by equating the coefficient of term e^{iT_0} to zero, a differential equation for $A(T_1)$ is obtained:

$$\begin{aligned}
-i2 \frac{dA}{dT_1} - i\lambda A - 3B_3 A^2 A^* - 10B_5 A^3 (A^*)^2 + \frac{\gamma}{2} A^* e^{i\Delta\omega T_1} \\
= 0
\end{aligned} \quad (26)$$

Recall $A(T_1)$ is a complex function of T_1 . Writing $A(T_1) = a(T_1)e^{i\phi(T_1)}$ and splitting eq 26 into real and imaginary parts gives

$$\text{Real: } \frac{d\phi}{dT_1} - \frac{3}{8}B_3 a^2 - \frac{5}{16}B_5 a^4 + \frac{\gamma}{4}a \cdot \cos(\Delta\omega \cdot T_1 - 2\phi) = 0 \quad (27)$$

$$\text{Imaginary: } -\frac{da}{dT_1} - \frac{\lambda}{2}a + \frac{\gamma}{4}a \cdot \sin(\Delta\omega \cdot T_1 - 2\phi) = 0 \quad (28)$$

To eliminate T_1 a variable replacement of $\Psi = \Delta\omega \cdot T_1 - 2\phi$ changes eqs 27 and 28 into

$$\frac{d\Psi}{dT_1} = \Delta\omega - \frac{3}{4}B_3 a^2 - \frac{5}{8}B_5 a^4 + \frac{\gamma}{2}\cos\Psi \quad (29)$$

$$\frac{da}{dT_1} = -\frac{\lambda}{2}a + \frac{\gamma}{4}a \cdot \sin\Psi \quad (30)$$

We now seek the stationary solutions to eqs 29 and 30. Letting $d\Psi/dT_1 = 0$ and $da/dT_1 = 0$ and solving for Ψ and a , one finds two possible sets of solutions. The first set of solutions is

$$\begin{aligned}
a = 0 \\
\Psi = \cos^{-1}\left(\frac{2 \cdot \Delta\omega}{\gamma}\right)
\end{aligned} \quad (31)$$

and the second set satisfies

$$\begin{aligned}
\frac{3}{4}B_3 a^2 + \frac{5}{8}B_5 a^4 = \frac{\gamma}{2}\cos\Psi + \Delta\omega \\
\Psi = \sin^{-1}\left(\frac{2\lambda}{\gamma}\right)
\end{aligned} \quad (32)$$

One of the most interesting things one can deduce from eq 32 is the dependence of the ion oscillation amplitudes on the excitation frequency

$$\omega_{\pm}^x = 2 \pm \sqrt{\frac{\gamma^2}{4} - \lambda^2 + \frac{3}{4}B_3 a_{\pm}^2 + \frac{5}{8}B_5 a_{\pm}^4} \quad (33)$$

$$\omega_{\pm}^y = 2 \pm \sqrt{\frac{\gamma^2}{4} - \lambda^2 - \frac{3}{4}B_3 a_{\pm}^2 + \frac{5}{8}B_5 a_{\pm}^4} \quad (34)$$

The superscripts x and y denote the frequencies for the x and y directions, respectively. A simple comparison of eq 10 to eq 9 gives eq 34 for ω^y . For a given set of driving and damping parameters, there are two branches labeled by the $+$ and $-$ subscripts, which correspond to the $+$ and $-$ signs in front of $\sqrt{\gamma^2/4 - \lambda^2}$, respectively. The stability of these solutions can be analyzed by considering the Jacobian matrix of eqs 29 and 30 for each of the solutions [14]. Specifically, when the eigenvalues of the matrix have a positive (negative) real part, that solution is unstable (stable).

It should also be noticed from eqs 33 and 34, in the presence of damping, there is a threshold for the excitation force to produce a resonance given by

$$\gamma_{\min} = 2\lambda \quad (35)$$

Thus the minimum excitation voltage required for resonance is

$$(V_{ex})_{\min} = \frac{\omega_0 r_0^2 \Gamma}{ze} \quad (36)$$

The threshold for excitation of a damped harmonic oscillator with parametric excitation has been described previously [15].

Figure 1a and b show the stationary amplitudes calculated from eqs 33 and 34 for a quadrupole ion trap with a 4.0% octopole field, ions excited at $q = 0.2$, $P = 1$ mTorr (N_2) (1 mTorr = 0.133 Pa), and an excitation amplitude $V_{ex} = 0.40 V_{0-p}$. For Figure 1a the multipoles with amplitudes A_2 , A_4 , and A_6 (Table 1) are included in the calculation. Both the stable (solid lines) and unstable (dashed lines) solutions near the primary resonant

Figure 1. Oscillation amplitudes for a linear quadrupole with a 4.0% added octopole field, at a pressure $P = 1$ mTorr of N_2 , $q = 0.2$, $V_{ex} = 0.40 V_{0-p}$, $\Omega = 2\pi \cdot 768.107 \times 10^3 s^{-1}$, $m/z = 609.28$, gas temperature $T = 295$ K, collision cross section $280 \text{ \AA}^2$. (a) Stationary amplitude versus excitation frequency for the x and y motions with A_2 , A_4 , and A_6 included in the calculation. (b) Stationary amplitude versus excitation frequency for the x and y motions with different combinations of the multipoles included. (c) Stationary amplitudes from ion trajectories versus quadrupole excitation frequency for the x and y motions. The solid triangles are for initial positions of $x_0 = 0.1, y_0 = 0.1$; the open structure stars are for simulations with initial positions of $x_0 = 0.3, y_0 = 0.3$.

frequency, for motion in the x (labeled $a^x_\pm$) and y directions ($a^y_\pm$), are shown. For convenience two frequencies, f_L and f_R are defined as illustrated in Figure 1a. For frequencies $f_{ex} < f_L$ there are two stable branches for the y direction, a^y_+ and $a^y_- = 0$. The solution a^y_- is unstable. In this region there are no resonant frequencies for the x motion. Conversely for frequencies $f_{ex} > f_R$ there are two stable branches for the x direction, a^x_+ and $a^x_- = 0$; in this region there are no resonant frequencies for the y motion. The solution a^x_- is unstable. For frequencies $f_L < f < f_R$, both the x and y directions have stable resonant solutions, a^x_- and a^y_+ . In the regions $f_{ex} < f_L$ and $f_{ex} > f_R$ where there are two stable solutions for the y and x motions respectively, bistable behavior is possible. For a given stationary amplitude, a_m , the difference in frequency in the x and y directions for the two stable branches can be derived from eqs 33 and 34:

$$2\pi \cdot \Delta f = \left| 2 \sqrt{\frac{\gamma^2}{4} - \lambda^2 - \frac{3}{2} B_3 a_m^2} \right| \quad (37)$$

Figure 1b demonstrates how the higher order multipoles influence the dependence of the stationary amplitude on the excitation frequency. Only stable solutions are shown. Between the two dotted vertical lines are the resonant frequencies for the given parameters for a pure quadrupole field (A_2 only). There are infinitely large stationary amplitudes for these frequencies. This is characteristic of parametrically excited motion; the amplitudes increase exponentially with time at resonance. The curved thicker lines are for the case where only A_2 and A_4 are considered. The existence of the octopole term A_4 has the effect of limiting the stationary amplitudes to finite values. The amplitudes with A_2 , A_4 , and A_6 included in the calculation (the same amplitudes as in Figure 1a) are shown by the symbols. The small term A_6 , (about 0.3% of the quadrupole field), makes a negligible change to the amplitudes under these conditions. The stationary amplitudes for the x and y directions are approximately symmetric about the frequency ω_0 .

Trajectory Calculations

When the ion motion with quadrupole excitation is considered in the exact potential, rather than the pseudopotential, the equation of motion can be written as

$$m \frac{d^2 \vec{r}}{dt^2} = -ze \nabla V(x_r, y_r, t_r) - ze \nabla \Phi_{ex}(x_r, y_r, t_r) - \Gamma \frac{d\vec{r}}{dt} \quad (38)$$

Where $V(x_r, y_r, t_r)$ and $\Phi(x_r, y_r, t_r)$ are given by eqs 2 and 7, respectively. Trajectory calculations were used to determine the stationary oscillation amplitudes from eq 38. Only the quadrupole and octopole terms were included in the potential. The initial radial velocities were zero. The initial x and y positions (x_0, y_0) were varied. Trajectories were calculated for 5000 cycles of the trap-

ping rf. For each excitation frequency, after initial transients, a trajectory reaches a stationary oscillation amplitude. Figure 1c shows results of these calculations for the x and y motions at different excitation frequencies. Also plotted in Figure 1c is the stable stationary amplitude response to the excitation frequency calculated from eqs 33 and 34 for the same parameters. There is reasonable agreement with the trajectory calculations. The analytical calculation somewhat underestimates the amplitudes. The trajectory calculations show that there are sudden changes in the amplitudes of oscillation in both the x and y directions with very small changes in excitation frequency. With $x_0 = 0.1$, $y_0 = 0.1$, the amplitude of oscillation in x decreases from a maximum at 110.934 kHz to zero at 110.937 kHz. The y oscillation amplitude decreases from a maximum and 107.969 kHz to zero at 107.968 kHz. In these trajectory calculations, the frequencies of the “jumps” depend on the initial conditions. When the initial positions are changed to $x_0 = 0.3$ and $y_0 = 0.3$, the “jumps” in oscillation amplitude change to 106.883 and 111.593 kHz for the y and x motions, respectively. The frequencies of the jumps also change with the initial x and y velocities (data not shown). These sudden large changes in oscillation amplitude with small changes in frequency, manifestations of bistable behavior, motivated us to investigate experimentally quadrupole excitation with linear quadrupole traps that have added octopole fields of 2.0%, 2.6%, and 4.0%.

Experimental Methods

A linear trap time-of-flight (TOF) system described in detail previously [2a] was used. Ions formed by electrospray pass through a dry nitrogen curtain gas, a 0.25 mm diameter orifice, into a region with a background pressure of 1.0 Torr, and then through a skimmer with a 0.75 mm diameter orifice. Ions then pass through a quadrupole ion guide Q0, (length 30 cm, field radius 4.5 mm) pumped to a pressure of about 3.5 mTorr, pass through an “entrance” lens with a 2.0 mm diameter aperture, and enter a linear quadrupole ion trap, Q1 (operating frequency 768 kHz) pumped to a base pressure of 3.3×10^{-6} Torr. The pressure in the trap can be increased above the base pressure by adding nitrogen (99.999% stated purity, Praxair Canada Inc.) to the chamber through a needle valve. The trap pressure was measured with an ion gauge for pressures below 1×10^{-4} Torr and a 0.1 Torr capacitance manometer for pressures above 1×10^{-4} Torr. The quadrupole rod sets, Q1, have nominal added octopole fields of 2.0, 2.6, and 4.0% (Table 1).

Positive ions of reserpine, m/z 609, are injected into the linear trap (30–100 ms fill time), confined in Q1 by applying trapping potentials to the entrance and exit apertures, cooled for 20 ms, and are then excited for 100 ms at a given frequency. Ions are then cooled for 20 ms before mass analysis and detection in the TOF system. Finally, Q0 and Q1 are drained for 50 ms. Table 3 shows

Table 3. Operating voltages

Sprayer	4000 V
Curtain plate	1.2 kV
Orifice	180 V
Skimmer	25 V
Q0 rod offset	15 V
Entrance lens	+5 V or +30 V
Q1 trap rod offset	0 V
Exit lens	−7 V or +43 V

the voltages applied to various elements. To inject ions into Q1, the entrance lens was set to +1 to +5 V (dependent on the pressure in Q1) and to trap ions, to +30 V. The exit lens was set to +43 V to trap ions and to −7 V to allow ions to drain into the TOF analyzer.

For a given excitation amplitude, reserpine ions are excited at a given frequency. At each frequency, spectra from 100 cycles of filling the trap, exciting ions, and mass analysis were summed to determine the intensities of precursor and fragment ions. The quadrupole excitation voltage was generated by an arbitrary waveform generator (Agilent 33120m; Agilent Santa Clara, CA) and applied to the rods with a circuit described previously [4b]. All excitation voltages are reported as volts zero to peak (V_{0-p}) pole to ground. The excitation circuit has capacitors between the quadrupole power supply and rod set. These form a capacitive voltage divider, so the rf voltage applied to the rods is less than the voltage set on the power supply. The q values of the trapped ions were calculated from the resonant frequencies of the ions. The trapping q of reserpine ions was chosen to be ca. 0.20 to confine both reserpine and fragment ions. All experiments were done with no dc applied between the rod pairs so the Mathieu parameter “ a ” was zero.

Precursor ions were not isolated. At resonance, reserpine ions are depleted by fragmentation (see below). Plots of the intensity of reserpine ions and fragment ions versus excitation frequency are used to investigate the ion motion. The intensities are normalized to 1.0 for the maximum sum of all ions (precursor and fragments). This method does not directly probe the stationary amplitude response to the excitation frequency, as fragmentation is not related to oscillation amplitude in any simple way [2a, 16]. Nonetheless it gives insight into the ion motion.

Reserpine (Sigma, St. Louis, MO) was 50 μ M in MeOH (HPLC Grade; Fisher Scientific, Nepean, ON, Canada): H₂O (deionized) 50:50 mixture with 0.02% acetic acid and was infused into the source at 1 μ L min^{−1}.

Results and Discussion

Figure 2 shows the intensities of reserpine ions and the sum of fragment ions versus quadrupole excitation frequency for the rod sets with 2.0% (Figure 2a and b), 2.6% (Figure 2c and d), and 4.0% (Figure 2e and f), added octopole fields excited at the $K = 1$ and $K = 2$ resonances. (In some experiments, resonances with

Figure 2. Ion intensities versus excitation frequency at $P = 0.2$ mTorr, $q \approx 0.20$. (a) $A_4 = 0.020$, $K = 1$, $V_{ex} = 0.20$ V; (b) $A_4 = 0.020$, $K = 2$, $V_{ex} = 2.0$ V; (c) $A_4 = 0.026$, $K = 1$, $V_{ex} = 0.30$ V; (d) $A_4 = 0.026$, $K = 2$, $V_{ex} = 2.25$ V; (e) $A_4 = 0.040$, $K = 1$, $V_{ex} = 0.40$ V; (f) $A_4 = 0.040$, $K = 2$, $V_{ex} = 2.75$ V. Filled square: m/z 609 intensity, open triangle: sum of all fragment ions.

higher values of K were investigated. However no new phenomena were found.) The trap pressure was 0.20 mTorr. The excitation voltages were chosen to give approximately equal depletions of reserpine ions in each case. The most abundant fragment ions had m/z values of 581, 448, 438, 397, 365, and 195, with abundances that changed with operating conditions. The maximum intensities of the sum of fragment ions exceeded the initial reserpine ion intensities most likely because of mass discrimination effects in transferring the ions into and through the TOF analyzer. The $K = 1$ resonances are at twice the frequency of the $K = 2$ resonances, and higher voltages are required to excite the $K = 2$ resonances, as expected [4b]. Our principal observation is that there are two resonances for depletion of reserpine ions, each accompanied by the forma-

tion of fragment ions. In general the two resonances do not have the same strengths. The frequency differences between the two resonances increase with increasing amplitude of the octopole field.

Assuming the maximum ion depletion occurs at frequencies corresponding to the maximum stationary amplitudes, a_m , can be estimated through eq 37 for the measured frequency difference Δf_m . These values are listed in Table 4. In all cases $a_m \approx 2.3$ mm, significantly less than r_0 . This, along with the observation of abundant fragment ions indicates the reserpine ions are removed mostly by dissociation and not by ejection.

With ions trapped at $q = 0.20$, the fundamental frequency of oscillation is $f_0 = 54.695$ kHz. Thus, the $K = 2$ and $K = 1$ resonances are expected to occur near 54.695 and 109.39 kHz, respectively. These frequencies

Table 4. Comparison of calculated $f_R - f_L$ with the measured difference in frequency Δf of the two resonances for linear quadrupole ion traps with 2.0%, 2.6%, and 4.0% added octopole fields for the $K = 1$ resonances, and the amplitude, a_m , calculated from eq 37, corresponding to the measured Δf_m

Quadrupole	Pressure P (mTorr)	Excitation V_{ex} (V)	Calculated $f_R - f_L$ (kHz)	Measured Δf_m (kHz)	a_m from Δf_m (mm)
2.0% Octopole	0.2	0.20	1.436	1.95	2.31
	1.0	0.25	1.598	1.90	2.35
2.6% Octopole	0.2	0.30	2.163	2.55	2.37
	1.0	0.35	2.386	2.50	2.41
4.0% Octopole	0.2	0.40	2.887	3.75	2.27
	1.0	0.40	2.766	4.00	2.30

Figure 3. Ion intensities versus excitation frequency at $P = 1.0$ mTorr, $q \approx 0.20$. (a) $A_4 = 0.020$, $K = 1$, $V_{ex} = 0.25$ V; (b) $A_4 = 0.020$, $K = 2$, $V_{ex} = 2.0$ V; (c) $A_4 = 0.026$, $K = 1$, $V_{ex} = 0.35$ V; (d) $A_4 = 0.026$, $K = 2$, $V_{ex} = 2.25$ V; (e) $A_4 = 0.040$, $K = 1$, $V_{ex} = 0.40$ V; (f) $A_4 = 0.040$, $K = 2$, $V_{ex} = 2.85$ V. Filled square: m/z 609 intensity, open triangle: sum of fragment ions.

might be expected to be the center frequencies between the two resonances. In fact the center frequencies are a few percent less, indicating that the q value is slightly less than 0.20 (typically 0.195), and changes slightly (ca. $\pm 1\%$) between experiments done on different days, limited by the reproducibility of the electronics.

The trajectory calculations show that in some cases the maximum oscillation amplitudes occur near f_R and f_L . Table 4 lists the measured differences in frequency between the two $K = 1$ resonances and the calculated $f_R - f_L$. The measured frequency differences (Δf_m) are somewhat greater than $f_R - f_L$. We assign the low and high-frequency resonances to excitation of motion in the y and x directions respectively. Equation 37 shows the frequency difference is determined by two terms. When the amplitude of oscillation is zero, the frequency difference is $2\sqrt{\gamma^2/4 - \lambda^2}$, and is determined by the excitation strength and damping, but not the magnitude of the octopole field. When the amplitude of oscillation increases, the frequency difference between x and y initially decreases, but then increases. This can be seen in Figure 1a where the curves for a_y^+ and a_x^- first approach each other, cross, and then separate. The measured frequency differences are greater than $f_R - f_L$, indicating the ions have somewhat greater amplitudes of oscillation than those corresponding to f_R and f_L .

At different pressures and with different operating conditions, other behavior can be seen. Figure 3 shows ion intensities versus excitation amplitude when the trap is operated at a higher pressure, 1.0 mTorr (N_2). The $K = 1$ and $K = 2$ resonances are shown for rod sets with 2.0%, 2.6%, and 4.0% added octopole fields. In most cases, two resonances are seen. The frequency differences between the two peaks are very similar to those at 0.2 mTorr, implying the oscillation amplitudes leading to depletion and fragmentation at these two pressures are similar.

From Figure 3, clearly the low-frequency resonance can be substantially greater in intensity than the high-frequency resonance. This can also be seen somewhat in Figure 2. In some cases, e.g., Figure 3b, the higher frequency resonance is not seen. Simple arguments based on the potential given in eq 1 when retaining the amplitudes A_2 and A_4 only, suggest the high-frequency resonance, corresponding to the x motion, should have the greater depletion. First, the electric field in the x direction is greater than in the y direction. Second, the effective potential well depth is greater in the x direction than in the y direction. Collings [17] has shown that at $q \approx 0.2$, small increases in well depth can give relatively large increases in fragmentation efficiency (at least at ca. 3×10^{-5} Torr). However our

Figure 4. Ion intensities versus excitation frequency with a quadrupole with 4.0% added octopole field, $P = 1.0$ mTorr, $q \approx 0.2$, $K = 1$, excitation amplitudes of (a) 0.30 V, (b) 0.40 V, (c) 0.50 V.

observations cannot be explained by either of these effects.

The excitation amplitude partially controls whether two resonances are seen. Figure 4 shows the effect of changing the excitation amplitude on the $K = 1$ resonances at 1.0 mTorr. With 0.30 V amplitude, only the low-frequency resonance at 105.5 kHz is significant, although a trace of the higher frequency resonance can

be seen in the fragment yield. At 0.40 V the higher frequency resonance has increased in intensity and both peaks can be seen. At 0.5 V both peaks have grown in intensity such that the region between the peaks is filled in, and two resonances can just be seen. This is simply a saturation effect. Trajectory calculations show that under these conditions the ion oscillation amplitudes remain significantly less than r_0 . A broader range of excitation frequencies give sufficient ion fragmentation to cause depletion of reserpine ions. Similar effects are seen with the rod sets with 2.0% and 2.6% added octopole fields. At higher amplitudes (data not shown) the region between the peaks fills in nearly completely and only one broad resonance is seen. Observation of the two resonances then requires a judicious choice of operating conditions.

As described, our initial motivation was to find depletion peaks that are sharp on the low-frequency side and sharp on the high-frequency side as suggested by Figure 1. We found neither. The peaks in Figures 2, 3, and 4 are fairly symmetric, although in some case some small asymmetry is seen. With dipole excitation between the large rods of a quadrupole with 4% octopole field, an asymmetric peak sharper on the low-frequency side is seen [2a]. However with excitation between the smaller, x, rods, no asymmetry is seen. The frequencies at which jumps occur will depend on the initial conditions of the ions. Because the ensemble of ions has a distribution of initial positions and velocities, our experiments may contain an average over jumps at many different frequencies. Chu et al. [7] saw sharp changes in oscillation amplitude with small changes of frequency for the collective motion of the entire ion cloud in a 3D trap. However under the same conditions, the resonance for the incoherent motion of the individual ions showed only a smooth broadened resonance with no jumps and little asymmetry. Possibly, if the ions are prepared with different initial conditions, with methods such as laser cooling [18], the resonances might show asymmetries with sharp sides. From a practical point of view, quadrupole excitation of ions in these rod sets does not offer a method of producing high-resolution ion isolation, at least with the operating conditions described here.

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