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Modeling of ion transient response to dipolar AC excitation in a quadrupole ion trap

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ABSTRACT

A theoretical modeling method was explored for characterizing the ion transient response to a dipolar AC excitation in quadrupole ion trap. The ion motion equation was established by applying the pseudo-potential approximation to Mathieu Equation with an ion-molecule collision term included. A step function was introduced to model the transient state of applying a dipolar excitation The Laplace transformation was performed to solve the ion motion equation. The high-frequency ion motion components, typically ignored by the pseudo-potential approximation, have also been included in the modeling. Characterization of ion motions at the excitation frequency, secular frequency and their corresponding high-order harmonic frequencies was achieved using this method. The capability of this theoretical modeling method was validated by applying it for interesting phenomena previously observed, including ion beat motions, frequency broadening at higher pressures, and ion bunching. Numerical simulations were also performed to confirm the results obtained with the theoretical modeling.

1. Introduction

Dipolar excitation has been widely used for mass analysis using quadrupole ion traps. It has been implemented for ion isolation [1–5], collision-induced dissociation (CID) [6,7], resonance ejection [8–10], as well as image current detection [11–17]. When a dipolar excitation is applied, the response of the ion motion could differ significantly at and after the initial transient state. For instance, in response to an AC field applied for CID, the motion amplitude of an ion in resonance increases quickly at the transition state and reaches a steady state when a balance is reached between the AC excitation and the buffer gas cooling. As another example, the transient process can be established by scanning RF voltage to move the ion secular frequency toward the excitation frequency of a dipolar AC signal, which is a typical scenario for the mass-selective instability scan [18]; as well as the scanning of RF frequency and AC frequency at the same time on a digital ion trap for the mass-selective resonance ejection [19]. In these cases, ion motion does not reach a steady state, and ions are ejected out of the ion trap during the transient process.

The excitation of ion motion and its impact upon mass analysis have been studied extensively with numerical simulations and experimental characterizations. Some of the studies include, but are not limited to, ion kinetic energy under dipolar excitations and its impact on mass spectral resolution [20–24], ion motion frequency [25–28] and its relationship with mass shift [8,29], ion-molecule collisions [30–32] and collision-induced fragmentation during Resonance excitation [33–36], space-charge effects [37–39] etc. Most of the efforts have been put into studying the steady state ion motion or the overall effects of the dipolar excitation without differentiating the transient and steady states. Ion motions during the transient state could be much more complicated than those at a steady state, and a direct characterization could be difficult through experimental testing. Previously, the ion ejection with dipolar excitation was studied theoretically with the effects by collisional damping and higher-order field perturbations [40]. The ion motion coherence during resonance ejection has also been studied using theoretical and numerical methods [41]. In this study, we explored a theoretical method to model ion transient responses to dipolar excitations in quadrupole ion traps.

Several theoretical modeling methods have been investigated to explore ion motion within quadrupole ion traps [42,43]. The first approach involves directly solving the ion motion equation (Mathieu equation) [44]. The effects of high-order fields [45–49] and ion-molecule collisions [50] on the stability diagram of quadrupole ion traps have been studied. A different approach to modeling

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ion trajectory utilizes the pseudo-potential approximation [43,51]. Using this method, ion trajectories under dipolar excitations have been calculated to investigate the mass analysis resolution [10,52], high-order field effects [40,53], buffer-gas effects [54], and voltage optimization during dipolar resonance ejection [54]. In each of these methods transient ion motion has been neglected, and characterization of the ion motions at higher frequencies is limited by the pseudo-potential approximation.

In this work, we introduced a step function into the ion motion equation to include the transient process of the dipolar excitation; the Laplace transformation was then performed to obtain the transient responses of the ion motions. Results from the theoretical study provided an insight on a variety of phenomena observed in previous experiments, including the multiple frequencies of the ion motion [26,43,44], ion beat motions under off-resonance excitation [55–57], pressure damping [58,59], peak broadening effects [54,60] and the ion bunching phenomena [41,59,61]. More importantly, ion motion at the excitation frequency and its corresponding high-order harmonic frequency components were observed, which have characteristics significantly different from those of the ion secular motion. Numerical simulations were also performed to confirm the results of the theoretical model.

2. Methods

The primary focus of this study was to include the higher frequency motions to investigate the ion transient response to a dipolar excitation. A 3D ion trap with an ideal geometry was used in this study and the higher-order fields, which typically contribute to less than 10% of the quadrupole field, was not considered for the modeling. A complete derivation of the ion motion equation is given in Supporting Information. The pseudo-potential approximation was applied to calculate the slow motion U (see Eq. (S2) in Supporting Information for details) of an ion trapped in an quadrupole RF field. Helium was used as the buffer gas. Ion–molecule collisions were modeled using a damping term, c (details in Supporting Information) [50,62].

$$U'' + cU' + \omega_0^2 U = P \quad \cos(\omega_{\mathrm{ac}} t) \tag{1}$$

where $P = a(U_{\mathrm{ac}}/u_0)\,(e/m)$ with U_{ac} defined as the amplitude of the applied AC signal, u_0 as the ion trap dimension in the direction of the dipolar AC excitation, e/m as the charge-to-mass ratio of the ion, and a is a constant that accounts for the non-flat electrode geometry ($a = 0.917$, details in Supporting Information). The (aU_{ac}) can be treated as an effective AC voltage applied for the dipolar excitation and is used for the amplitudes for the dipolar excitations in the theoretical calculations discussed below. The value of the damping term c, which depends on the pressure, polarizability of the buffer gas, and the reduced mass of the ion–molecule pair, was calculated based on the Langevin collision theory with the elastic collision model (details in Supporting Information) [50,54]. To study the transient response of an ion to a dipolar excitation, a step function ($g(t)$) was added to the dipolar excitation term,

$$U'' + cU' + \omega_0^2 U = P \quad \cos(\omega_{\mathrm{ac}} t) g(t) \tag{2}$$

Applying the Laplace transformation on Eq. (2):

$$(s^2 + \mathrm{cs} + \omega_0^2) F(U) = \frac{Ps}{s^2 + \omega_{\mathrm{ac}}^2} + (s + c)U(0) + U'(0) \tag{3}$$

where $U(0)$ and $U'(0)$ are the initial position and speed of the ion, respectively. Ion transient response to the dipolar excitation can be derived by applying the inverse Laplace transformation in Eq. (3) (detailed derivation in Supporting Information)

$$\begin{aligned} U(t) = \Bigg(& K_1 e^{-(c/2)t} \quad \cos\left(\sqrt{\omega_0^2 - \frac{c^2}{4}t}\right) + \frac{K_2 - (c/2)K_1}{\sqrt{\omega_0^2 - (c^2/4)}} e^{-(c/2)t} \\ & \times \sin\left(\sqrt{\omega_0^2 - \frac{c^2}{4}t}\right) + K_3 \quad \cos(\omega_{\mathrm{ac}} t) + \frac{K_4}{\omega_{\mathrm{ac}}} \quad \sin(\omega_{\mathrm{ac}} t) \\ & + U(0) e^{-(c/2)t} \quad \cos\left(\sqrt{\omega_0^2 - \frac{c^2}{4}t}\right) \\ & + \frac{U'(0) + (c/2)U(0)}{\sqrt{\omega_0^2 - (c^2/4)}} e^{-(c/2)t} \quad \sin\left(\sqrt{\omega_0^2 - \frac{c^2}{4}t}\right)\Bigg) g(t) \end{aligned} \tag{4}$$

where K_* ($* = 1, 2, 3 \ldots$) are constants and defined as,

$$\begin{aligned} K_1 &= -K_3 = \frac{P(\omega_{\mathrm{ac}}^2 - \omega_0^2)}{(\omega_{\mathrm{ac}}^2 - \omega_0^2)^2 + c^2 \omega_{\mathrm{ac}}^2} \\ K_2 &= -\frac{\omega_0^2}{\omega_{\mathrm{ac}}^2} K_4 = -\frac{cP\omega_0^2}{(\omega_{\mathrm{ac}}^2 - \omega_0^2)^2 + c^2 \omega_{\mathrm{ac}}^2} \end{aligned} \tag{5}$$

The pseudo-potential approximation applied to get Eq. (1) is a first-order approximation, which ignores ion motions at higher frequencies. To fully characterize the ion motions, high-frequency ion motion terms need to be included in the theoretical modeling. With the slow ion motion $U(t)$ expressed in Eq. (4), the total ion motion, $u(t)$ (Eq. (S5) in Supporting Information) can be expressed as (see Supporting Information for details):

$$u(t) = U(t)\left(1 - \frac{q_{\mathrm{u}}}{2} \quad \cos(\Omega t) + O(h)\right) \tag{6}$$

where $O(h)$ represents the omitted higher-order terms, of which the frequencies are 2, 3, 4, ..., n times of the RF frequency [42,44].

Numerical simulations were performed for validating the theoretical model using a home-developed ion trajectory simulation program (details in Supporting Information) [63]. In the simulations, ions were placed in an un-stretched 3D ion trap, with dimensions of $r_0 = 5$ mm and $z_0 = 3.536$ mm. An RF signal at 625 kHz was applied on the ring electrode of the ion trap. Starting at time zero, a dipolar AC excitation signal was applied between the endcaps of the ion trap (in z-direction). Helium was used as the buffer gas. A time step of 80 ns was used for the simulation, corresponding to 20 time steps per RF cycle. Ion trajectories were simulated and recorded for 4.8 ms (otherwise noted); the Fast Fourier Transform (FFT) was performed to obtain the frequency spectra of ion motions.

3. Results and discussion

The introduction of the step excitation and the inclusion of the high-order motion frequencies provided unique capabilities for modeling ion transient responses to dipolar excitations. Ion motions at different frequencies and different pressures were characterized. The results obtained from this theoretical study allowed us to understand the fundamental principles of the interesting phenomena previously observed experimentally.

3.1. Ion motion frequencies

Under a dipolar AC excitation, ion motion inside a quadrupole ion trap has multiple frequency components. Under off-resonance excitation ($f_0 \neq f_{\mathrm{ac}}$), the slow ion motion has a frequency component at the excitation frequency (f_{ac}) and at the ion secular frequency (f_0) (Eq. (4)). According to Eq. (6), a complete set of the ion

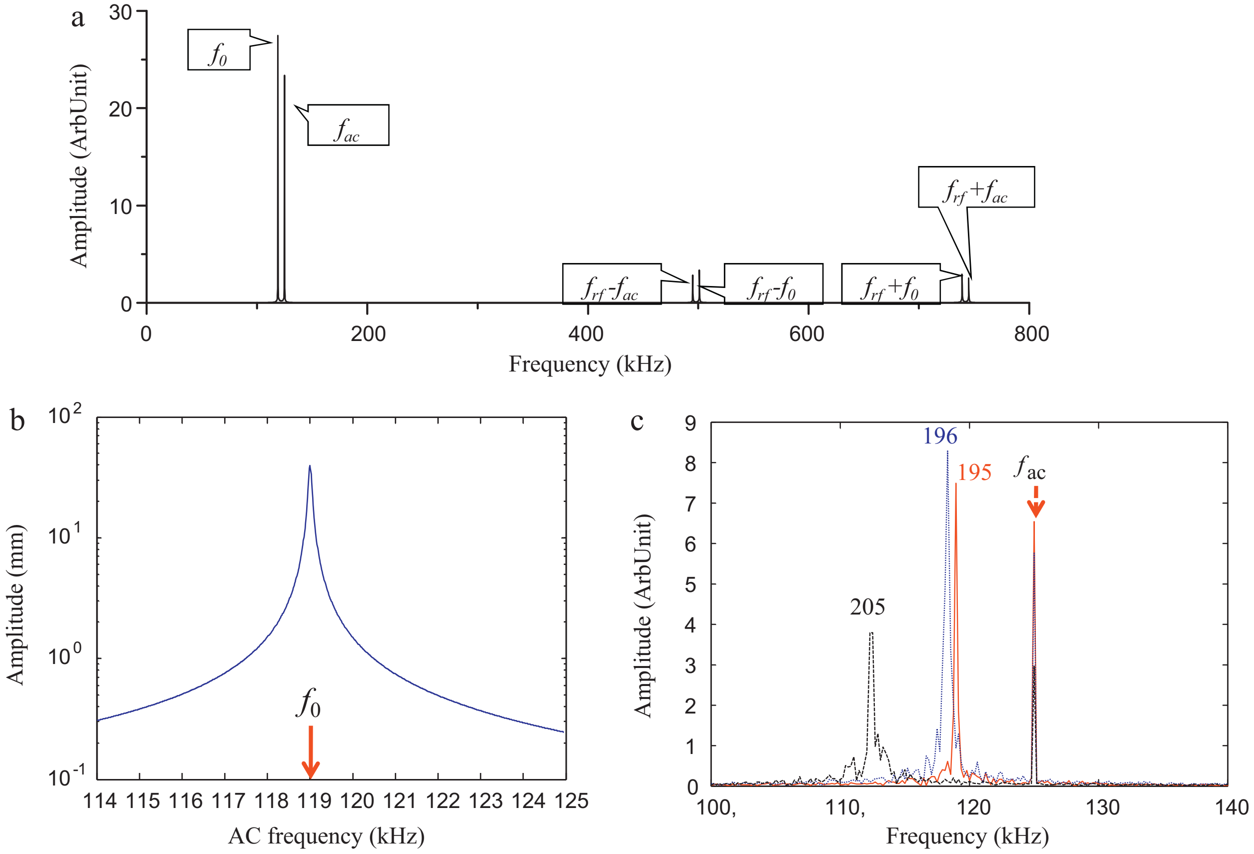

Fig. 1. (a) Ion motion frequency components under off-resonance dipolar excitation (f_0 = 119 kHz and f_{ac} = 125 kHz). (b) Ion motion amplitude after transient state as a function of the dipolar excitation frequency, ion m/z = 195, f_0 = 125 kHz. (c) Ion motion frequencies for ions m/z = 195, 196 and 205, dipolar AC excitation f_{ac} = 125 kHz, f_0 = 119 kHz for ion m/z = 195. Dipolar excitation amplitude V_{ac} = 0.1 V_{0-p}, buffer gas, pressure 1 mTorr.

motion components can be observed at the ion secular frequency f_0, dipolar excitation frequency f_{ac}, and their corresponding higher frequencies ($f_{RF} \pm f_0, f_{RF} \pm f_{ac}$, etc.), as shown in Fig. 1a. Among these frequency components, the ones related to the secular frequency ($f_0, f_{RF} \pm f_0$) decay due to the ion–molecule collisions (see detailed discussion below), which can only be well observed at the transient state of the response. The decay rate is higher at increased pressures. At low q_u values, the slow ion motion ($U(t)$) is dominant, in comparison with high-order motions at ($f_{RF} \pm f_0$) and ($f_{RF} \pm f_{ac}$).

When the frequency of a dipolar AC excitation is close to but not equal to the ion secular motion frequency, ions can still be excited and have increased motion amplitudes. Based on Eqs. (4) and (5), the ion motion amplitude at the excitation frequency ($A_{\omega_{ac}}$) is a function of the difference between the secular and AC frequencies,

$$A_{\omega_{ac}} = \frac{P}{\sqrt{c^2\omega_{ac}^2 + (\omega_{ac}^2 - \omega_0^2)^2}} \qquad (7)$$

which shows that the smaller the frequency difference, the bigger the amplitude of the ion motion. In physics it means that more energy is coupled to a harmonic resonator when the external excitation frequency is closer to the natural resonance frequency of the resonator. The calculated maximum ion motion amplitude $A_{\omega_{ac}}$ was plotted as a function of the excitation frequency in Fig. 1b. A similar situation can be found for the amplitude of the ion secular motion (A_{ω_o}), except that A_{ω_o} also depends on the initial conditions of the ions, $U(0)$ and $U'(0)$ (the last two terms in Eq. (4)).

At a given RF voltage, an ion has motion components at the secular frequency f_0 and the related high-order harmonic frequencies, e.g., ($f_{RF} \pm f_0$). These motions are distinct for each ion with a particular m/z value. However, ions of different m/z values also have motion components at the same excitation frequency, e.g., f_{ac} and ($f_{RF} \pm f_{ac}$). A simulation with three ions trapped in a 3D ion trap, each at m/z 195, 196 and 205, was performed to illustrate this phenomenon. An AC at 125 kHz was applied as the excitation signal. With a 100 V_{0-p} RF voltage applied to the 3D ion trap, the secular frequencies for these ions are 119 kHz, 118.3 kHz and 112.4 kHz, respectively. As shown in Fig. 1c, these three ions all have a motional frequency component at f_{ac} (125 kHz); and their amplitudes are different, which is due to the frequency difference between their secular frequencies and the excitation frequency, ($f_0 - f_{ac}$) (Eq. (7)).

3.2. Pressure effects

According to Eq. (4), the pressure inside an ion trap has two effects on the ion motion at frequencies related to its secular frequency (e.g., f_0, and $f_{RF} \pm f_0$, etc.), (1) the damping effect that is expressed by the exponential decay term ($e^{-c/2t}$) and (2) the broadening effect that is expressed by the term ($\sqrt{\omega_0^2 - c^2/4}$). The damping term ($e^{-c/2t}$) is only included in the secular frequency related terms (f_0, $f_{RF} \pm f_0 \ldots$), but not the AC frequency related terms ($f_{ac}, f_{RF} \pm f_{ac} \ldots$). When a constant excitation signal is applied, an ion can have a stable motion at the excitation frequency (f_{ac}), but a decaying motion at its secular frequency (f_0). Fig. 2a shows the motion amplitudes of an ion m/z 195 at f_0 = 165 kHz and f_{ac} = 170 kHz, in response to a dipolar excitation V_{ac} = 0.32 V, f_{ac} = 170 kHz at a pressure of 1 mTorr ($c \approx 478$). The ion motion is stable at the excitation frequency, while decaying exponentially at the secular frequency. At higher pressures, the motion amplitudes become lower due to the damping effect, as predicted by Eq. (5). Fig. 2b shows the calculated motion amplitudes as functions of

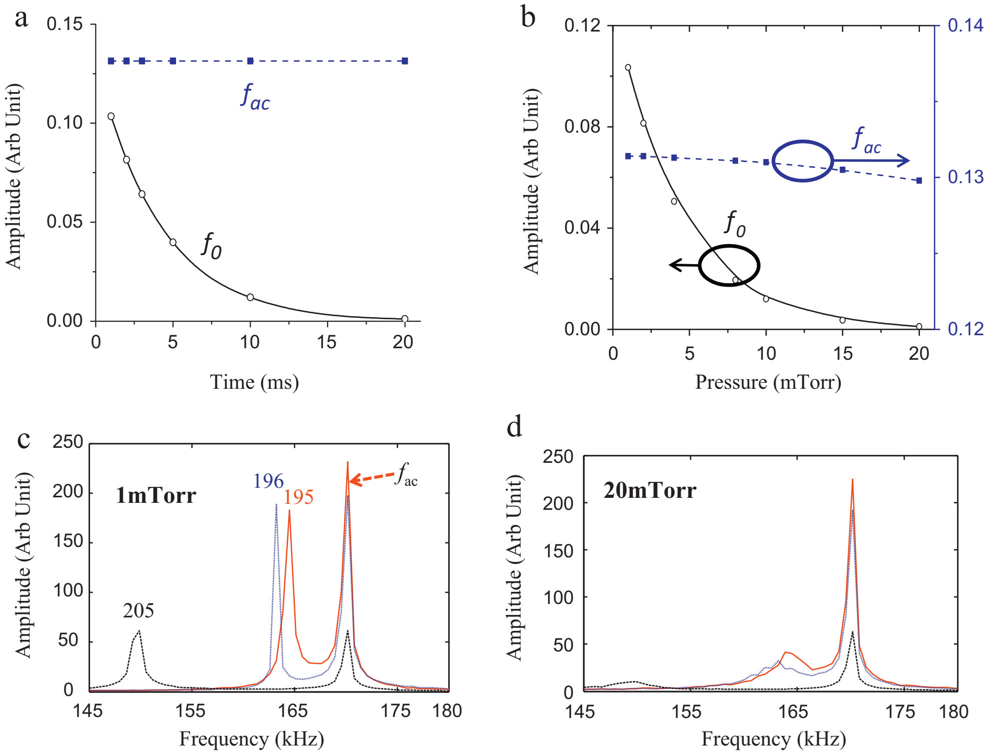

Fig. 2. Calculated ion motion amplitudes at secular and excitation frequencies (a) at different times after applying the excitation (1 mTorr), (b) at different pressures. (At 1 ms after applying the excitation) dipolar excitation $V_{ac} = 0.32\ V_{0-p}$, $f_{ac} = 170$ kHz and $f_0 = 165$ kHz. Simulated frequency spectra for ions $m/z = 195$, 196 and 205 at (c) 1 mTorr and (d) 20 mTorr. RF amplitude 130 V_{0-p}, dipolar excitation $V_{ac} = 0.32\ V_{0-p}$, $f_{ac} = 170$ kHz.

pressure for ion m/z 195 at $f_0 = 165$ kHz and $f_{ac} = 170$ kHz, at 1 ms after applying the dipolar excitation. The amplitude decrease at higher pressures is also much more significant for the ion motions at secular frequencies.

To confirm the predictions by the theoretical modeling, frequency spectra were simulated for three ions m/z 195, 196 and 205 at 1 mTorr (Fig. 2c) and 20 mTorr (Fig. 2d), within 4.8 ms from applying of the dipolar excitation. The ion motion amplitudes at 20 mTorr were slightly lower at the excitation frequency $f_{ac} = 170$ kHz, but much lower at the secular frequencies. The peak broadening effect was also observed for ion motions at the secular frequencies, but not at the excitation frequencies, based on the comparison of the FWHMs of extracted peaks. Although this phenomenon cannot be characterized directly using the theoretical modeling (Eq. (4)), it is consistent with the fact that only the secular frequency terms in Eq. (4), but not the excitation frequency terms, contain the damping term c in the form of $(\sqrt{\omega_0^2 - c^2/4})$, which represents the overall pressure effects in the theoretical modeling.

3.3. Ion beat motion

The characteristics described above for the ion motions in response to an off-resonance dipolar excitation can also be used to explain the ion beat motion. The ion beat motion is described as the amplitude oscillation of the overall ion motion, which has been observed during ion ejection from a linear ion trap [56]. Trajectories of an ion (m/z 195) in response to a dipolar excitation ($V_{ac} = 1\ V_{0-p}$) were calculated for both resonance ($f_{ac} = f_0 = 119$ kHz, Fig. 3a) and off-resonance ($f_{ac} = 125$ kHz, $f_0 = 119$ kHz, Fig. 3b and c) excitations. Pressure inside the ion trap was 2 mTorr ($c \approx 978$). For resonance excitation, the ion motion amplitude increases as a function of $(1 - e^{-c/2t})$ (Eq. (4)). For off-resonance excitation, a fast motion with its amplitude modulated by a slower sinusoidal function was observed during the initial period of the excitation. The frequency for the fast motion was 122 kHz, an average of the secular and excitation frequencies ($(f_{ac} + f_0)/2$); the beat frequency was 6 kHz, which was the difference between the two frequencies ($f_{ac} - f_0$). A simulation was performed, which showed the identical beat motion under the same condition (Fig. 3d). The beat motion can only be well observed during the transient state of the response. Due to the decay of the ion secular motion, the beat motion is suppressed at 10 ms after the applying of the excitation, as shown in Fig. 3c. An interesting phenomenon about ion beat motion is that it allows the ion motion in its initial state to periodically reach amplitudes higher than those at the stable state. During the off-resonance excitation CID [64–70], this helps to rapidly increase the collision energy, while the amplitude oscillation at the lower frequency helps to bring ions back to the center of the trap to avoid to loss of the precursor ions.

3.4. Ion bunching

The bunching effect is critical for ion resonance ejection in quadrupole ion traps [10,18,40]. The best resolution is achieved with the mass selective instability scan when ions of the same m/z value are moving in the same phase and at the same amplitude [18]. In an RF-driven ion trap, ions are cooled to the trap center due to ion–molecule collisions, and the ion cloud has a Gaussian distribution [71]. The speed of an ion in each direction of a Cartesian coordinate also has a Gaussian distribution [71,72]. Without a dipolar excitation, ions are moving in random phases; with a dipolar excitation applied, ions of the same m/z value bunch together and move in the same phase as a group in the direction of the excitation field [61].

With the theoretical model discussed here, the transition of ion motions from random phase to bunched motions can be studied more thoroughly. To better describe this effect, Eq. (4) can be sim-

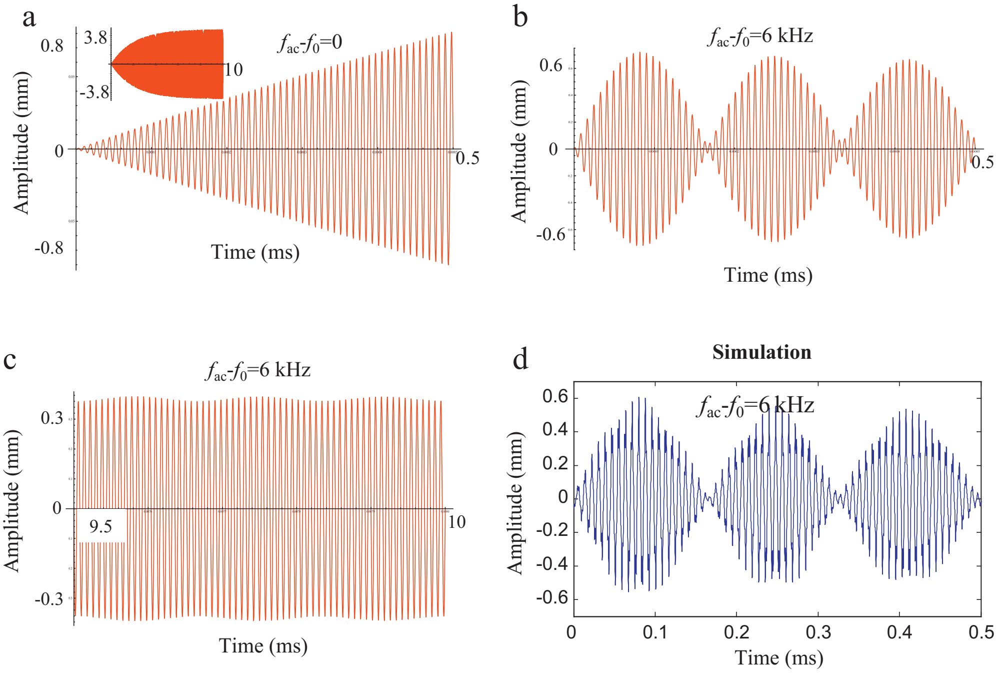

Fig. 3. (a) Calculated ion motion at resonance excitation ($f_0 = f_{ac}$). (b) and (c) Calculated ion motions under off-resonance excitation, with a frequency difference ($f_0 - f_{ac}$) of 6 kHz during 0–0.5 ms and 9.5–10 ms, respectively. (d) Simulated ion motion under off-resonance excitation, $f_0 - f_{ac} = 6$ kHz. $f_0 = 119$ kHz for ion $m/z = 195$, dipolar excitation amplitude $V_{ac} = 0.1\ V_{0-p}$, buffer gas pressure 1 mTorr.

plified as:

$$U(t) = \{Ae^{-(c/2)t} \quad \sin(\omega_0' t + \varphi_0) + B \quad \sin(\omega_{ac} t + \varphi_{ac}) + D\,e^{-(c/2)t} \quad \sin(\omega_0' t + \varphi_1)\}g(t) \tag{8}$$

where the first term in Eq. (8) is equivalent to the first two components in Eq. (4) with $\omega_0' = \sqrt{\omega_0^2 - c^2/4}$ and φ_0 as the phase term; the second term in Eq. (8) is equivalent to the second two components in Eq. (4); the third term in Eq. (8) is equivalent to the last two terms in Eq. (4), with D as a function of the ion initial conditions.

Mathematically, at the beginning of a dipolar AC excitation, the first term and the second term in Eq. (8) cancel each other ($A + B \approx 0$, $\varphi_0 \approx \varphi_{ac}$), since $K_1 + K_3 = 0$, $K_2 + K_4 \approx 0$ (Eq. (5)), when the buffer gas pressure is low ($c < < \omega_{ac}$) and $\omega_{ac} \approx \omega_0$. Therefore, the third term is dominant and related to the ion initial conditions $D\,e^{-(c/2)t} \quad \sin(\omega_0' t + \varphi_1)$. Ion initial position $U(0)$ and speed $U(0)'$ have Gaussian distributions, which result in random ion motions at the beginning of the excitation. As excitation continues, either the ion motion amplitudes ($Ae^{-c/2t}$ vs. B) or the phases $\omega_0' t + \varphi_0$ vs. $\omega_{ac} t + \varphi_1$) at ω_0' and ω_{ac} vary. When the amplitude of one motion is significantly greater than others, or the phases of these motions become coherent, the bunching phenomenon is observed. Examples are given for resonance and off-resonance excitations, as shown in Figs. 4 and 5.

For resonance excitation ($f_0 = f_{ac}$), ion motions at the secular frequency and the excitation frequency are of identical amplitude but different phases. Due to the collisions with buffer gas, ion secular motion decays while the ion motion at excitation frequency is sustained (Fig. 4a). For ions of a same m/z value but different initial conditions, their overall motions eventually have a same phase as their secular motions decay (Fig. 4b). This phenomenon has been confirmed by a simulation of 10 ions (m/z 195) trapped in a spherical volume ($r = 0.03r_0$) of the ion trap, with random initial conditions. The buffer gas pressure was set at 10 mTorr. A 100 V_{0-p} RF at 625 kHz was applied, corresponding to an ion secular frequency of 119 kHz. A 0.06 V_{0-p} AC at 119 kHz was applied for the dipolar excitation. The simulated bunching effect is shown in Fig. 4c.

For off-resonance excitation ($f_0 \neq f_{ac}$, for example, $f_0 = 119$ kHz and $f_{ac} = 124.5$ kHz,) similar trends exist for the ion motion at secular and excitation frequencies (Fig. 5a). However, due to the varying difference in phase (difference between $\omega_0' t + \varphi_0$ and ($\omega_{ac} t + \varphi_1$) in Eq. (8)), ion bunching occurs with a beat frequency

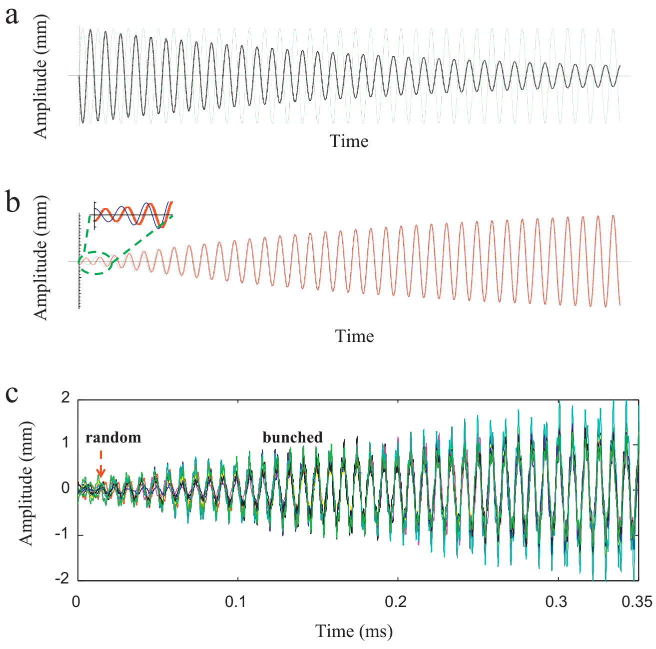

Fig. 4. (a) Calculated motions of ion $m/z = 195$ under resonance excitation ($f_{ac} = f_0 = 119$ kHz) at secular frequency f_0 (black) and excitation frequency f_{ac} (green), each calculated using the first and second term of Eq. (8), respectively. (b) Calculated overall motions of two ions ($m/z = 195$) with different initial conditions; Ion I (blue), $U(0) = 3$ mm, $U(0)' = 1000$ m/s; Ion II (red), $U(0) = -3$ mm, $U(0)' = -1000$ m/s. (c) Simulation of 10 ions with random initial conditions under resonance excitation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

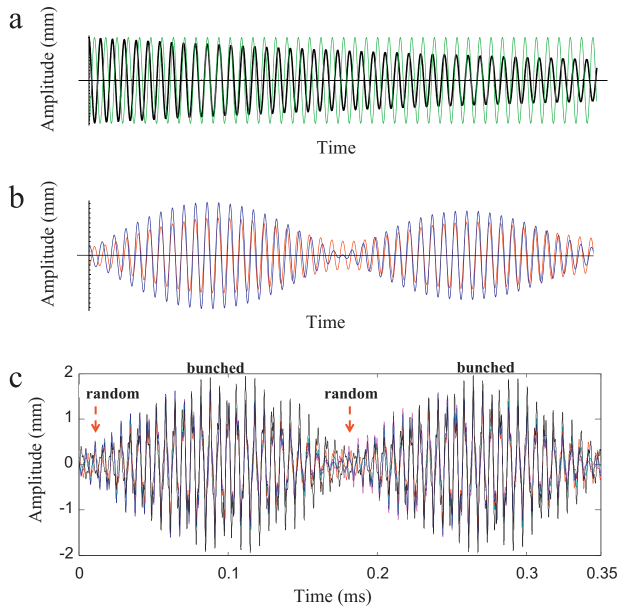

Fig. 5. (a) Calculated motions of ion $m/z = 195$ under off-resonance excitation ($f_0 = 119$ kHz and $f_{ac} = 124.5$ kHz) at secular frequency f_0 (black) and excitation frequency f_{ac} (green). (b) Calculated overall motions of two ions ($m/z = 195$) with different initial conditions; Ion I (blue), ($U(0) = 1$ mm and $U(0)' = 100$ m/s; Ion II (red), $U(0) = -1$ mm and $U(0)' = -100$ m/s. (c) Simulation for 10 ions with random initial conditions under off-resonance excitation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

($(f_{ac} - f_0) = 5.5$ kHz), which can be predicted based on calculations using Eq. (4) (Fig. 5b). A simulation of 10 ions with the same initial conditions as those in Fig. 4c was conducted for off-resonance excitation with $f_0 = 119$ kHz and $f_{ac} = 124.5$ kHz. The observed ion motions were similar to those calculated (Fig. 5c).

4. Conclusion

A theoretical model has been explored to analyze the transient responses of ion motions to dipolar AC excitations inside a quadrupole ion trap. A step function was introduced in the modified Mathieu Equation and the Laplace transformation was performed to solve the ion motion equation. The high-frequency ion motions are included in the theoretical modeling to allow the characterization of ion motions at a secular frequency and its corresponding high-order harmonic frequencies. The theoretical model was used to predict ion motion frequency components and to understand the interesting phenomena related to ion cooling, excitation and mass resolution. The results were used to guide the development of a non-destructive mass analysis method using image current measurement at relatively high pressures [17]. Ion motions under excitation in RF-driven quadrupole ion traps were mainly discussed in this paper; however, similar methods can be applied to ion motions in static field-driven ion traps, such as the Fourier Transform Ion Cyclotron Resonance (FT-ICR) cell and the Orbitrap [58,61,73–75], for which the ion motion in response to the excitation is a key element in the development of instruments and analytical methods.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2011.07.022.

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