Supporting Information

Investigation of the effect of octopole electric field on the linear ion trap and an Asymmetric Semi-Circular Linear ion trap Analyzer

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[#] The author contribution equal to the article

Introduction to the Simulation process

1. Multipole Distribution calculation

The internal field distribution was calculated using software named PAN33, which was developed based on the potential array of SIMION. During the calculation of multipole components in AsC-LITs, one pair of electrodes was kept at a positive unit voltage of +1, and another pair of electrodes was kept at a negative unit voltage of −1. The multipole coefficients computed in this method and those reported by Sudakov *et al.* were compared and are in very good agreement.

2. Axsim parameters

The simulation work bench contained a cylindrical symmetrical field region for the rotational symmetric field structure of AsC-LIT and a 3D field region. The simulative related parameters were shown in table S-1, and we could perceive three kinds of signal in the ion trap, including digital RF voltage, digital dipole AC voltage and Front&Endcap voltage. These three kinds of signal were used to trap the ion of interest in the trap for a while. Figure S1 presented the normalized electric field distribution of RF and AC in the ion trap on the x-y plane, and balanced RF waveforms with the same amplitude but in opposite phase were applied to the x and y electrode pairs. The dipolar excitation waveform was derived digitally by dividing down the frequency of the trapping waveform, and coupling with the trapping power similar to conventional RF mode, which was applied on the x axis with opposite phase.

Table S1 The simulative related parameters

Signals / Parameters	RF (Radio frequency) voltage	AC (Alternating Current) voltage	Front&End cap
Signal Type	DigitalSQWave	SquareWave	Direct current
Amplitude (V)	250	1.2	30
Frequency (MHz)	1	0.333	--
TimeStart (μs)	0	0	0
Offset (V)	0	0	0
PeriodStep (ns)	0.6	None	None

Axsim could be used for simulating of the frequency spectrum, ion trajectory and mass spectra. The software allows reproduction of all the details of ion motion in ion traps with a square wave supply and frequency scanning. The hard sphere collision model was used in the simulation. Collision conditions were a pressure of 0.06 mTorr with helium as a buffer gas and a temperature of 300 K. Mass spectra for *m/z*=175, 176, 177 and *m*/*z*=609, 610, 611 were simulated using dipolar resonance ejection. For each *m*/*z*, 100 ions were traced to ejection to the detector without considering space charge effects. The ions initially had a Gaussian distribution from the center of the ion traps (x=y=z=0) with a 0.1-mm standard deviation in the x- and y-directions. The main RF power supply provided square wave pulses with a duty cycle of 0.5 and pulse amplitude of 250 $V_{0\text{-}p}$. The initial repetition period of pulses was T-start = 1.0 μs, the period was increased by T-step =0.6 ns every N waves = 20 RF cycles. Resonance excitation was also applied in the reverse phase to the opposite rods in the x-direction. Such excitation caused the ejection of ions when the secular frequency was 1/3 of the RF frequency $\omega_s = \Omega/3$ or $\beta = 2/3$. The amplitude of the excitation signal was also optimized to achieve the best resolution, while the scan speed was kept at approximately 1200 Da/s. The simulations were performed for ion ejection from either the larger semi-circular electrodes or the smaller semi-circular electrodes for comparison.

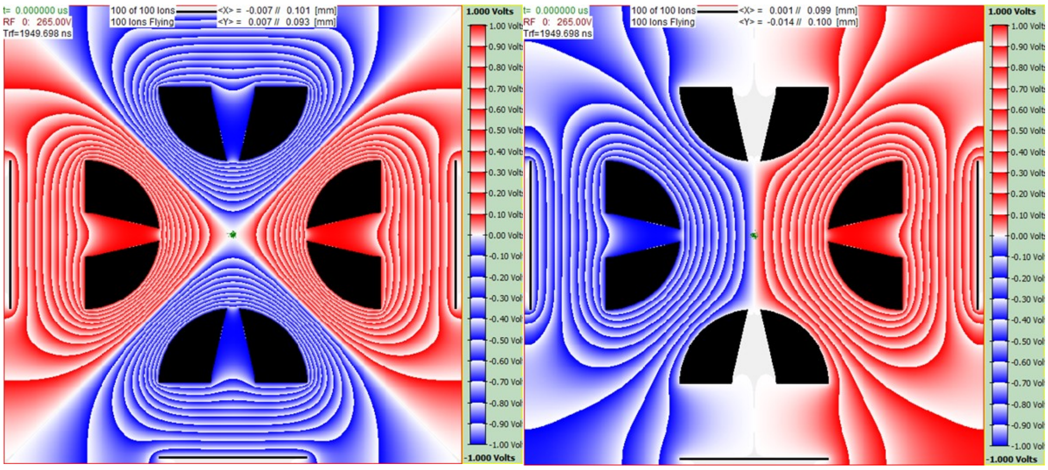

Figure S1 Normalized field distribution of RF (left) and AC (right) in the ion trap on the x-y plane

Frequency spectrum and ion trajectory simulation

The frequency spectrum of aimed ion is the fourier transform of the ion trajectories. The main RF power supply provided square wave pulses with a duty cycle of 0.5 and pulse amplitude of 250 $V_{0\text{-}p}$. The initial repetition period of pulses was T-start = 1.0 μs, the period remains unchanged. Resonance excitation was not applied for simulating the resonant ejection because at this point the secular frequency of aimed ions reach to resonant frequency of AC.

The simulated frequency spectrum of reserpine ion at the same trapping RF condition in the x direction had been shown in the Figure S2a. Specifically, the trapping RF frequency was setting as 512 kHz for simulating the resonant ejection because at this point the secular frequency of reserpine reaches to resonant frequency of AC at 0.18 MHz. There are two secular frequencies in the frequency spectrum where the spectral lines are around at the 180 kHz and 330 kHz, and these two frequencies present regular excursion when adding the octopole component. The low main spectral line nearby 180 kHz is increasing with adding octopole component and it is the main secular frequency ω_x of arginine ion, while the high spectral line is decreasing with adding the octople component, and it should be the sideband frequency Ω-ω_x of resperine ion. Obviously, the sum of the main secular frequency and the sideband frequency is equals to the trapping RF frequency. Therefore, when the high spectral line is decreasing with adding the octople component, the low spectral line should increase for compensation.

The simulated ion trajectory of reserpine ion at same scanning RF condition and same AC condition in the x direction had been shown in the Figure S2b. The initial repetition period of pulses was T-start = 1.0 μs, the period was increased by T-step =0.6 ns every N waves = 20 RF cycles. Resonance excitation was also applied in the reverse phase to the opposite rods in the *x*-direction. Such excitation caused the ejection of ions when the secular frequency was 1/3 of the RF frequency $\omega_s = \Omega/3$ or $\beta = 2/3$. The amplitude of the excitation signal was also optimized to achieve the best resolution, while the scan speed was kept at approximately 1200 Da/s. The amplitude of the excitation signal was also kept the same condition.

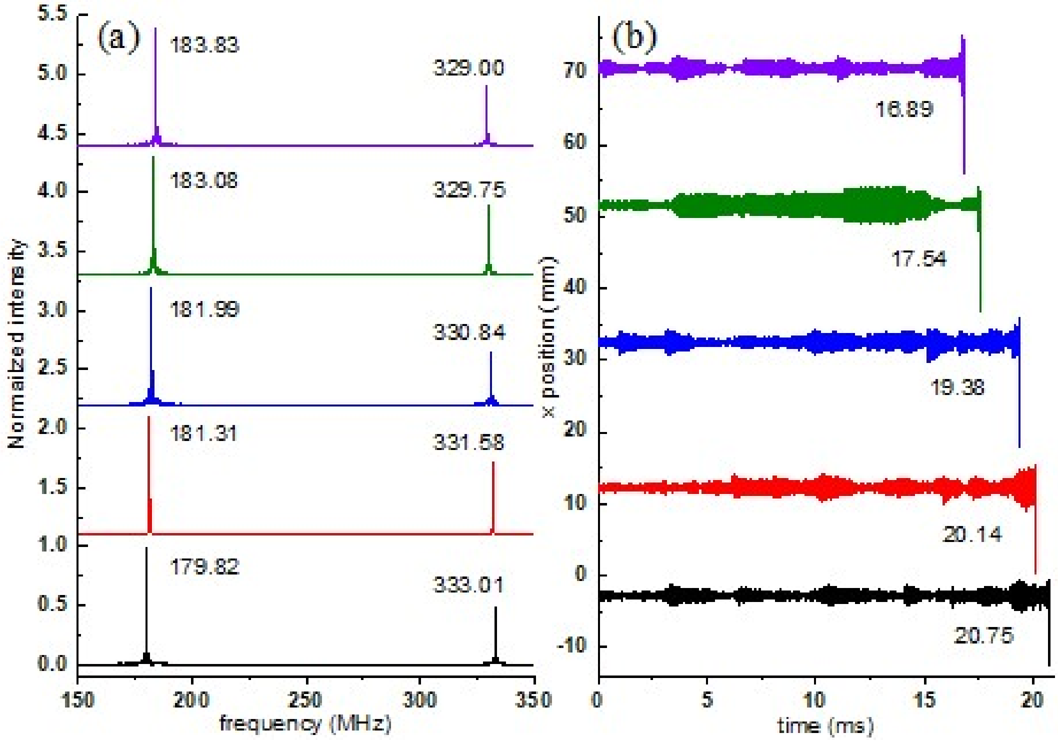

Figure S2. (a) The simulated frequency spectrum of reserpine ion at the same trapping RF condition in the x direction; (b) The simulated ion trajectories in x direction with adding octopole components (1) A_4/A_2=0 %, black line (2) A_4/A_2=0.95 %, red line (3) A_4/A_2=1.80 %, blue line (4) A_4/A_2=2.56 %, green line and (5) A_4/A_2=3.24 %, purple line

Mass spectrum comparison between simulation and experiments

In accordance with the above field calculations, representative simulated mass spectra and experimental mass spectrum for these configurations are shown in Figures S3 and S4. Figure S3-a, c, e, and g display the m/z = 609, 610 and 611 ions being ejected from the smaller electrodes, while Figure S3-b, d, f and h show the ions being ejected from the larger electrodes. Figure S4 shows typical experimental mass spectra for protonated reserpine ions through configuration which are used to test the effect of the octopole component (A_4/A_2) on the mass resolution (m/Δm, FWHM). It can be observed that the mass resolution gradually improved as A_4 was increased from A_4=0 to A_4/A_2=2.56 %, but then decreased when A_4/A_2=3.24 %. Negative A_4 component was also added to the when the ions were ejected from the y direction from AsC-LIT, and the mass resolution is seriously degraded consequently. The more the negative A_4, the lower the mass resolution is. The main reason that the mass resolution decrease at A_4/A_2=3.24 % might attribute to the large edge effects introduced. These experimental results are in good agreement with the simulation mass spectra in Figure S3.

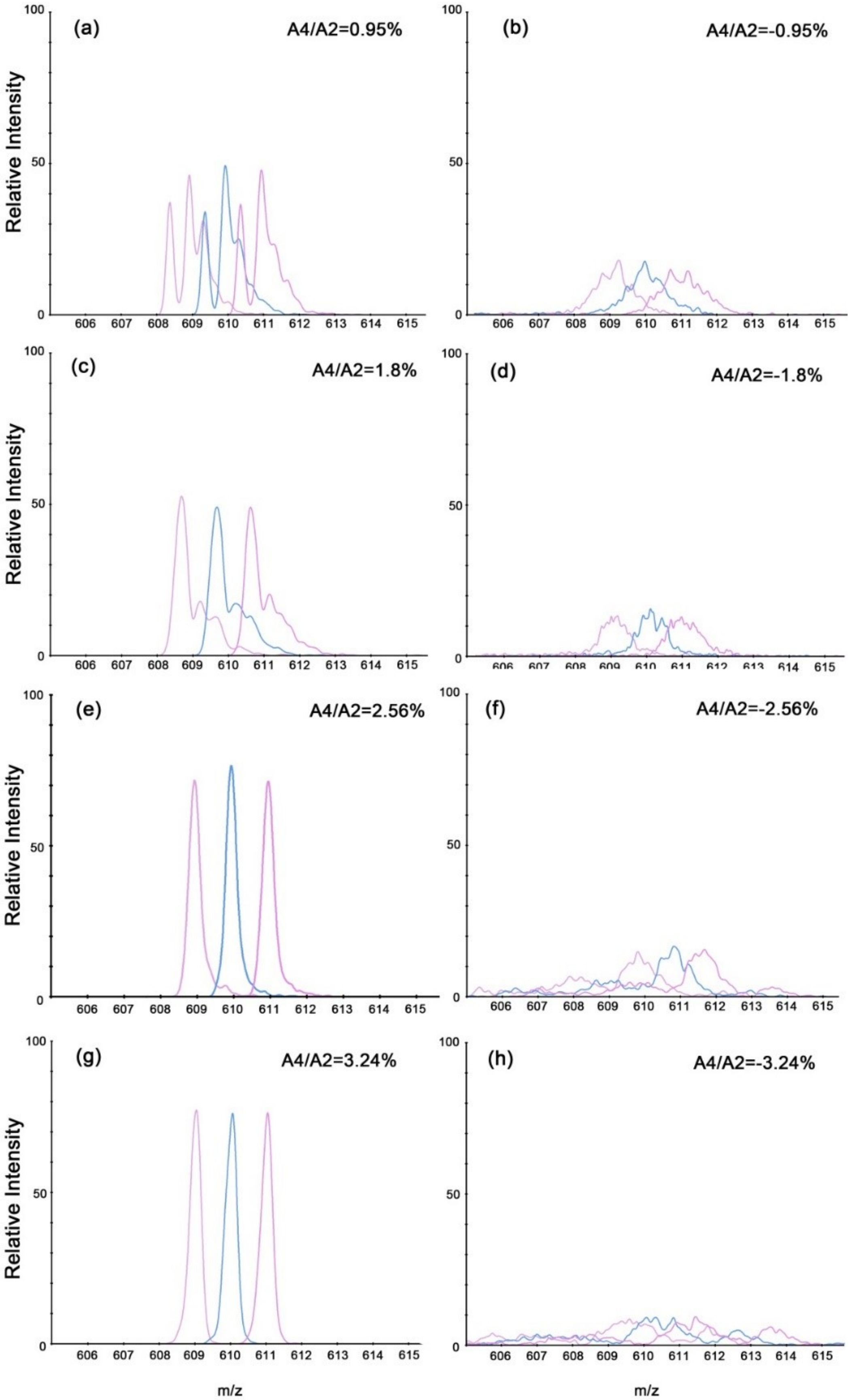

Figure S3. Simulated mass spectra for m/z= 609, 610, and 611 with the addition of positive or negative octopole components

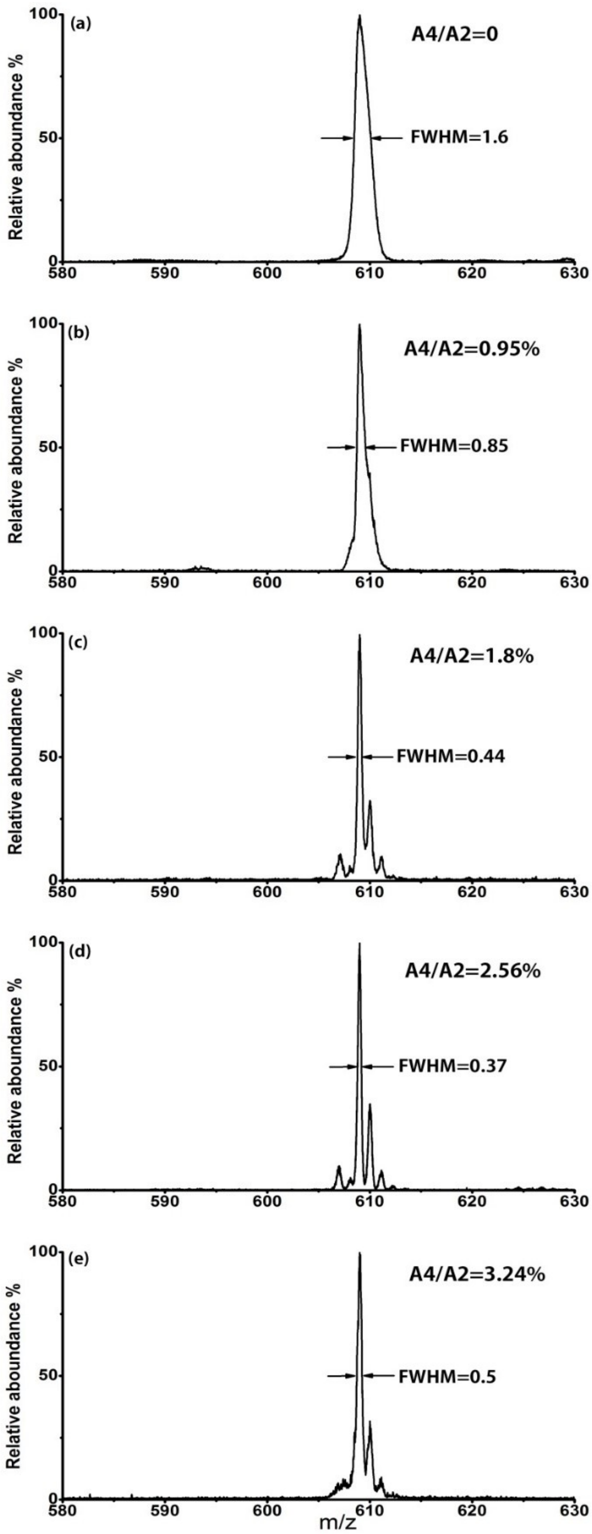

Figure S4 Mass spectra of protonated reserpine when ions were ejected from the smaller rod side (a) A_4/A_2=0, (b) A_4/A_2=0.95%, (c) A_4/A_2=1.80%, (d) A_4/A_2=2.56%, and (e) A_4/A_2=3.24%

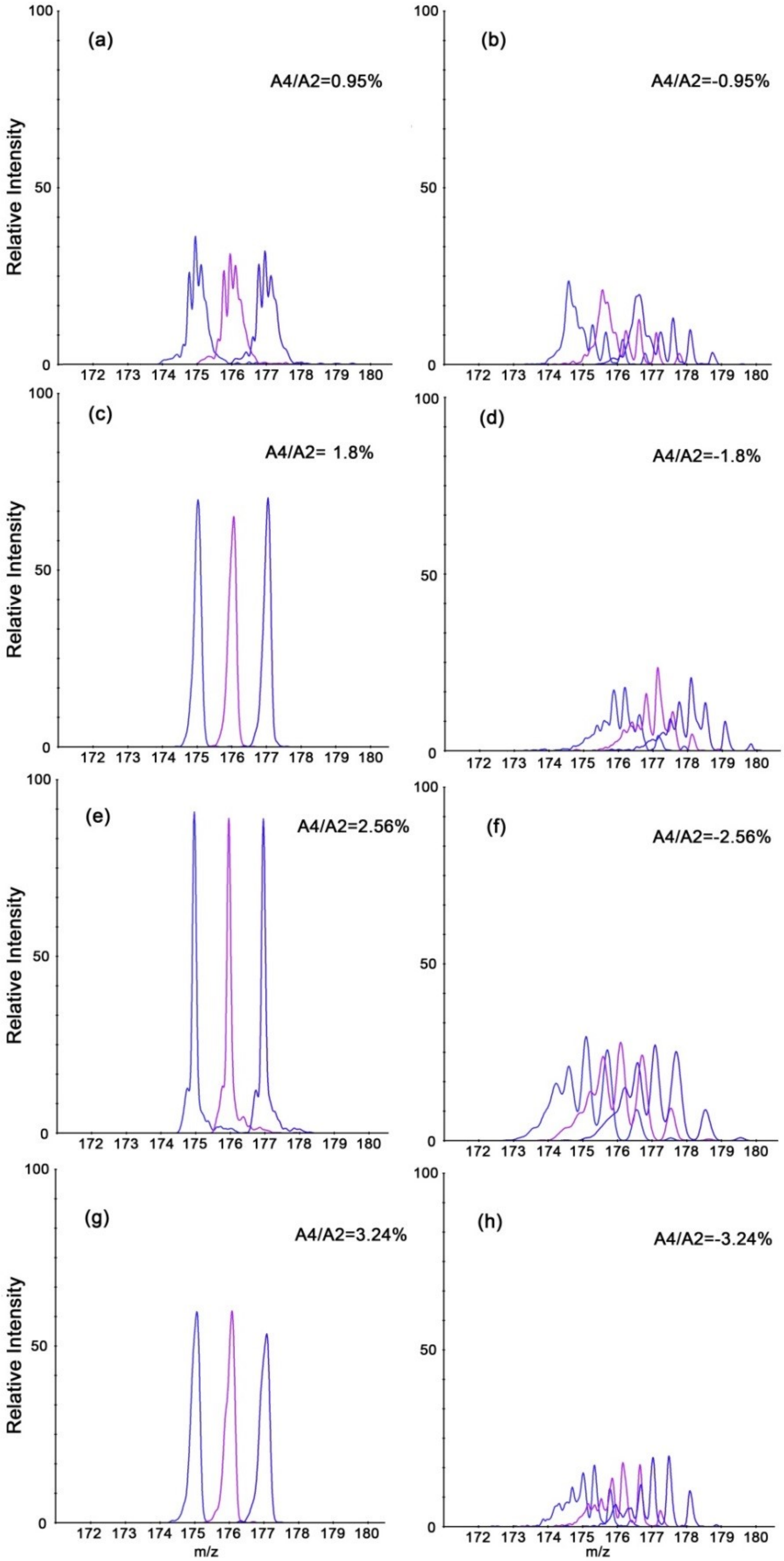

Figure S5. Simulated mass spectra for m/z=175, 176, and 177 ions with the addition of positive or negative octopole components