Electronic Supplementary Material (ESI) for Analyst.

Measurement of the effective electric field radius on Digital ion trap spectrometer

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1. Related parameters of the digital ion trap mass spectrometer

Table S1. Relationship among n, β and q

n	6	5.75	5.375	5	4.625	4.375
β	0.3333	0.3478	0.3721	0.4000	0.4324	0.4571
q	0.3522	0.3661	0.3890	0.4147	0.4435	0.4647

Table S2. Working parameters of the digital ion trap mass spectrometer

Parameters	values	Parameters	values
RF $V_{0\text{-}p}$, V	300	CID time, ms	40
Buffer gas	Helium	Ionization mode	Positive
AC $V_{0\text{-}p}$, V	2	Detector Voltage, kV	-1.2
Ion cooling time, ms	10	Ion isolation time, ms	30
RF scan time, ms	150	ESI voltage, kV	4.0

2. Measurement of the effective electric field radius through experiments for cRITs with x0×y0= 6.5 mm×5.0 mm and x0×y0= 7.0 mm×5.0 mm when q was fixed at 0.3522

The maximum fragmentation efficiencies for $x_0 \times y_0$=6.50 mm×5.00 mm and 7.00 mm×5.00 mm had reached and their corresponding optimum trapping waveform frequency f for the maximum CID efficiency were at 641.02 kHz and 606.06 kHz respectively when q was setting at 0.3522. Figure S1-a and Figure S1-b had presented the experimental mass spectra where the precursor m/z=609 ion is indiscernible from the background while the main fragmental ion peaks m/z=448, 397and 365 could be found. According to above experiments, the ion dipolar excitation frequencies were found when the maximum CID efficiency were obtained for different RITs at certain q value.

Figure S1-c and S1-d shows the linear relationship between q and T^2 for $x_0 \times y_0$=6.50 mm×5.0 mm and 7.00 mm×5.00 mm ion trap analyzers which had been listed in the table 2. The linear equation from least squares best-fit could be used to calculate the optimum trapping waveform frequency f for the maximum CID efficiency, besides, for any mass selected ion in this ion trap using DIT, the effective electric field radius could be calculated according to beforementioned equation (4). In this case, the effective electric field radius of these four rectangular ion traps were to 4.89, 5.15, 5.79 and 6.10 mm for $x_0 \times y_0$=5.00 mm×5.00 mm, 5.50 mm×5.00 mm, 6.50 mm×5.00 mm and 7.00 mm×5.00 mm respectively, and it is very close to their geometrical radius.

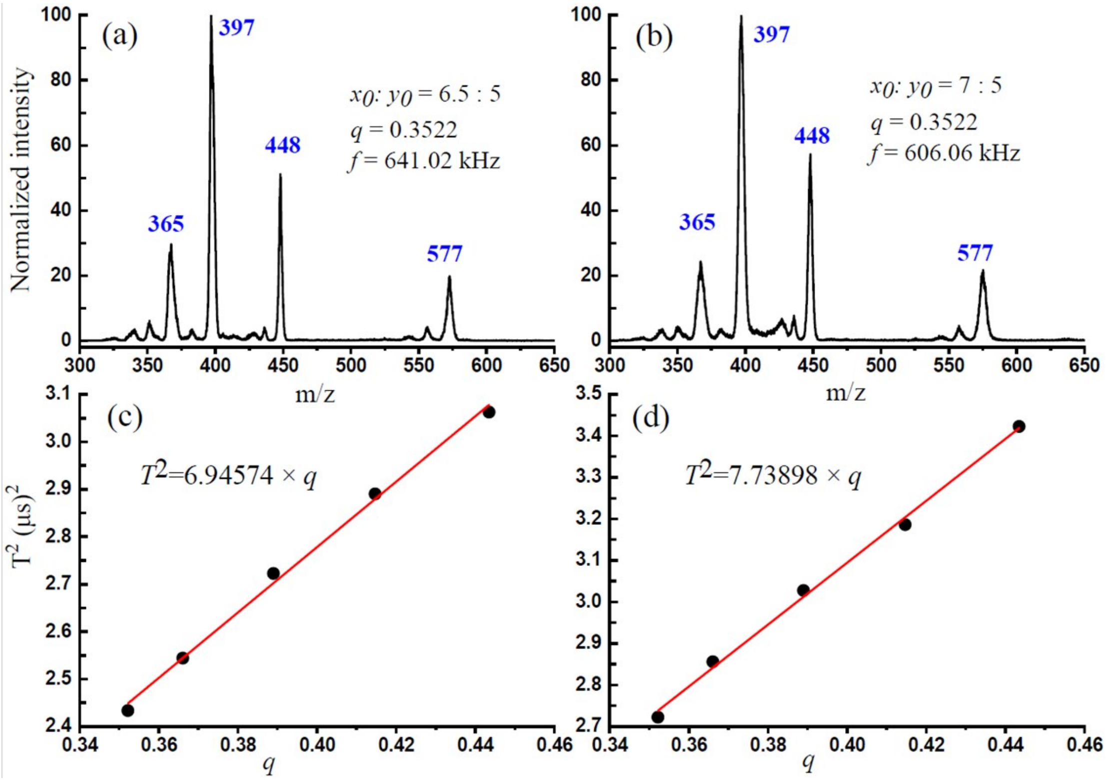

Figure S1. (a) The CID mass spectra of Reserpine ion (*m/e* =609) for cRIT with $x_0 \times y_0$=6.5 mm×5.0 mm when q was fixed at 0.3522. (b) The CID mass spectra of Reserpine ion (*m/e* =609) for cRIT with $x_0 \times y_0$= 7.0 mm×5.0 mm when q was fixed at 0.3522. (c) Relationship between q and the optimum trapping waveform frequency f for the maximum CID efficiency of $x_0 \times y_0$=6.5 mm×5.0 mm (d) Relationship between q and the optimum trapping waveform frequency f for the maximum CID efficiency of $x_0 \times y_0$=7.0 mm×5.0 mm

3. Introduction to the Simulation process with Axsim

3.1 Simulation Parameters

The rectangular ion trap with x0 × y0 =5.0 mm × 5.0 mm was chosen as the object showing the detail process of simulation and calculation. The simulative related parameters were shown in table S3, and we could perceive three kinds of signal in the ion trap, including RF voltage, 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 S2 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 S3 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)	300	1.2	30
Frequency(MHz)	0.754	simulation	--
TimeStart(μs)	0	0	0
Offset(V)	0	0	0
VoltageScan	None	None	None

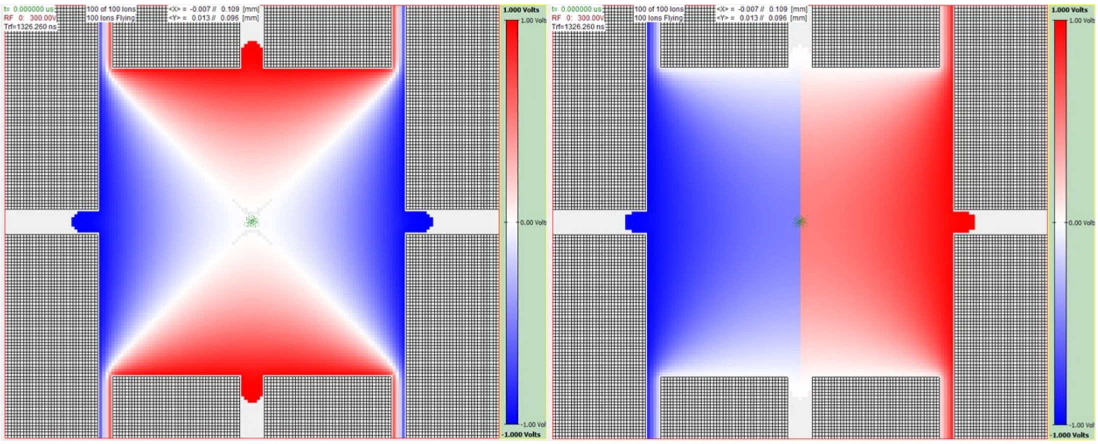

Figure S2 Normalized electric field distribution of RF and AC in the ion trap on the x-y plane

3.2 Signal Preview

Figure S3 preview the setting signal applied on the RF and AC respectively in the AXSIM. The digital square wave has a constant amplitude of 300 $V_{p\text{-}0}$ for RF, and the AC has a constant amplitude of 1.2 $V_{p\text{-}0}$ for AC. Since the dipolar excitation waveform was derived digitally by dividing down the frequency of the trapping waveform with a factor of n, and the f can be obtained when the ion CID process was found in the experiment.

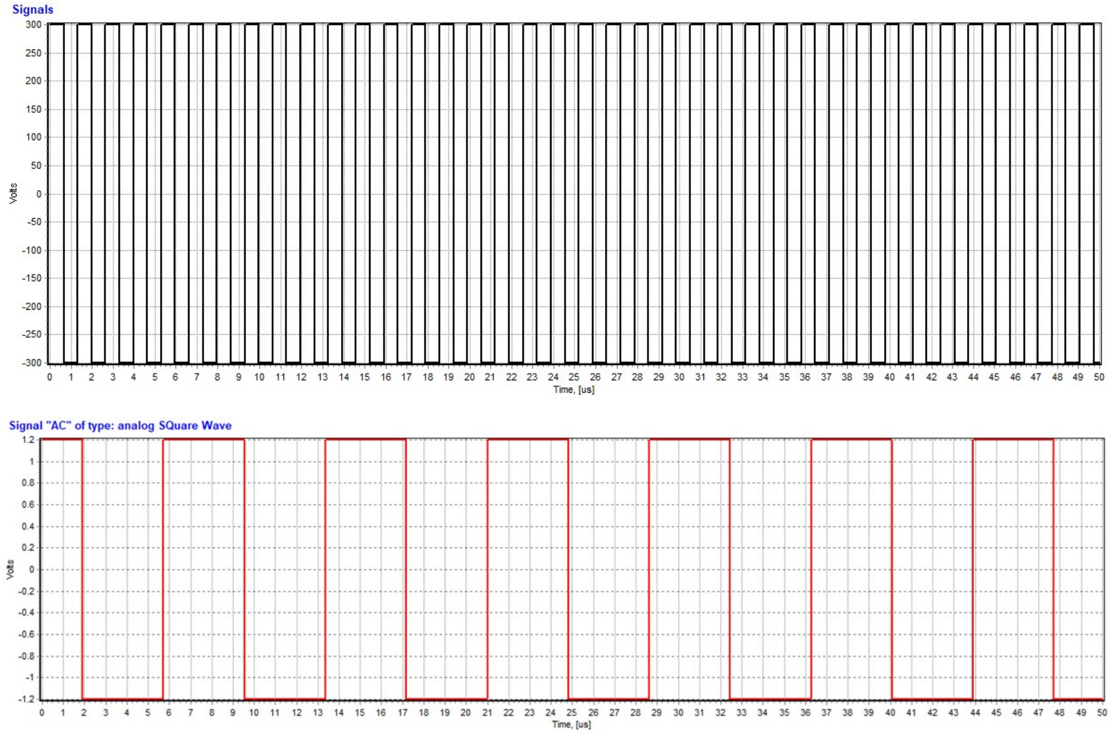

Figure S3 Preview Signal of RF and AC voltage

3.3 Exploring the simulative dipole AC frequency in the ion trap through AXSIM

The simulating ion trajectory of resonance excitation in the cRIT with x0 × y0 =5.5 mm × 5.0 mm using DIT in the ion trap on the x direction were presented in Figure S4-a. The simulative frequency spectra for ion trajectory on the x direction when there is no AC were presented in the Figure S4-b, and the responding simulative AC frequency ω_s on the x direction is 0.132. Figure S4-d is the simulative frequency spectra for ion trajectory on the x direction when there is a dipole AC, and it could be found that the resonance frequency ω_s disappeared and a very strong peak arises at in the left of the x axis.

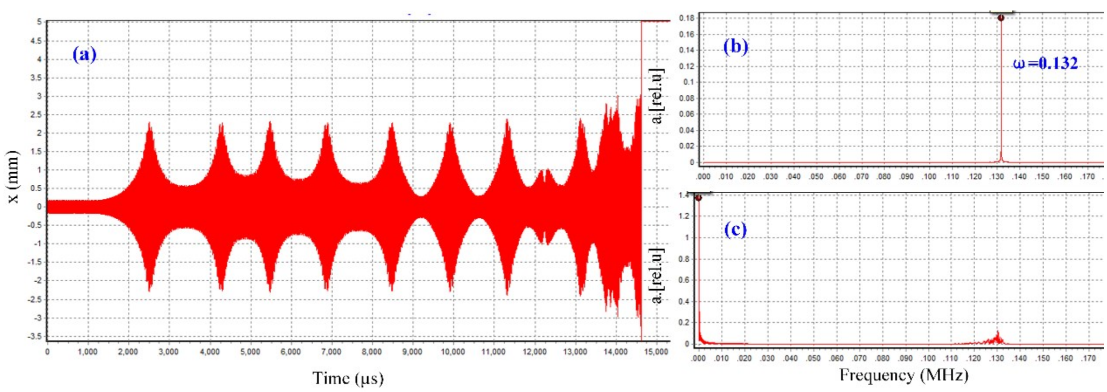

Figure S4 (a) The simulative ion trajectory of resonance excitation in the cRIT using DIT, (b) The simulative frequency spectra of reserpine in the cRIT when there is no AC, (c) The simulative frequency spectra of reserpine in the cRIT when there is a AC.

3.4 Calculation the simulative radius of the ion trap

The ω_x had been obtained when the ion CID process was found in the experiment, then the β_x could be calculated through the equation S-1, and the q_x could calculated through the equation S-2. Finally, the simulative radius of the ion trap was calculated through the equation S-3. The detail calculation process for cRITs with different size had be presented on the Table S4 to Table S7. Figure S-4 shows the linear relationship between simulative q and T^2. The least squares best-fit linear curve based on the experimental simulative data from table S4 to table S7. Figure S-4 shows the linear relationship between simulative q values and T^2. The least squares best-fit linear curve based on the simulative data from table S-2 to table S-5.

$$\omega_x = \frac{\beta_x \Omega}{2} \qquad S-1$$

$$\beta_x = \frac{1}{\pi} arccos[\cos\left(\pi\sqrt{\frac{q_x}{2}}\right)\cosh\left(\pi\sqrt{\frac{q_x}{2}}\right)] \qquad S-2$$

$$r = T\sqrt{(\frac{m}{e})^{-1}\frac{V}{q\pi^2}} \qquad S-3$$

Table S4 The Calculation Process for cRIT with x0 × y0 =5.00 mm × 5.00 mm

RF (kHz)	T^2 (μs)^2	ω_x (MH$_z$)	β	q	$r_{simulation}$(mm)
754.72	1.7556	0.131	0.3471	0.3655	4.81
740.74	1.8225	0.134	0.3622	0.3798	4.81
719.42	1.9321	0.140	0.3894	0.4050	4.80
696.86	2.0592	0.146	0.4195	0.4322	4.80
675.68	2.1904	0.152	0.4504	0.4590	4.80
The average radius/ mm					4.804

Table S5 The Calculation Process for cRIT with x0 × y0 =5.5 mm × 5.0 mm

RF (kHz)	T^2 (μs)^2	ω_x (MH$_z$)	β	q	$r_{simulation}$(mm)
716.85	1.9460	0.126	0.3520	0.3701	5.04
706.71	2.0022	0.127	0.3598	0.3775	5.06
684.93	2.1316	0.133	0.3884	0.4041	5.04
662.25	2.2801	0.138	0.4168	0.4298	5.05

641.03	2.4336	0.145	0.4524	0.4607	5.04
The average radius/ mm					5.046

Table S6 The Calculation Process for cRIT with x0 × y0 =6.5 mm × 5.0 mm

RF (kHz)	T^2 $(\mu s)^2$	ω (MH_z)	β	q	$r_{simulation}$(mm)
641.02	2.4336	0.114	0.3557	0.3736	5.60
626.96	2.5440	0.118	0.3764	0.3930	5.58
606.06	2.7225	0.123	0.4095	0.4232	5.57
588.24	2.8900	0.127	0.4318	0.4430	5.61
571.43	3.0625	0.131	0.4585	0.4659	5.63
The average radius/ mm					5.598

Table S7 The Calculation Process for cRIT with x0 × y0 =7.0 mm × 5.0 mm

RF (kHz)	T^2 $(\mu s)^2$	ω_s (MH_z)	β	q	$r_{simulation}$(mm)
606.06	2.7225	0.109	0.3597	0.3774	5.89
591.72	2.8561	0.113	0.3819	0.3981	5.88
574.71	3.0276	0.117	0.4072	0.4212	5.88
560.22	3.1863	0.119	0.4248	0.4368	5.90
540.54	3.4225	0.126	0.4662	0.4724	5.90
The average radius/ mm					5.890

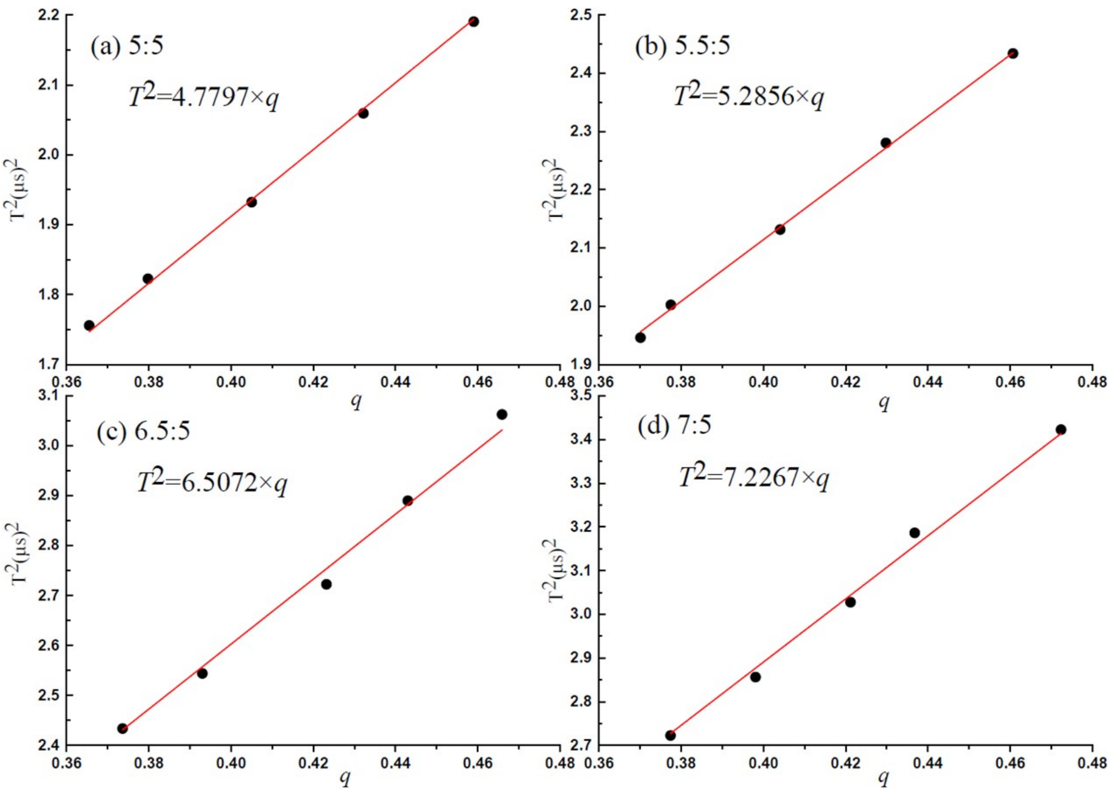

Figure S5 Simulated Relationship between q and f of different cRITs