Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Ion Collision Cross Section Analyses in Quadrupole Ion Traps Using Filter Diagonalization Method: A Theoretical Study

Supplementary Information

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Generation of the theoretical ion trajectory in Figure 1:

The theoretical time-domain signal was generated as the following equation:

$$y = A\cos(\varphi)$$

where A is the amplitude of the time-domain signal described as

$$A = \frac{3\, a_0\, \pi}{3\, \pi + 4\, a_0\ \delta_2\, \omega_0\, t}$$

$$\varphi = \frac{24\, \pi\, \varphi_0 + 24\, \pi\ \omega_0\, t + 9\, {a_0}^2 \pi\, \varepsilon_3\, \omega_0\, t\ + 32\, a_0\, \delta_2\, \varphi_0\, \omega_0\ t\ + 32 a_0\, \delta_2\, {\omega_0}^2\, t^2}{8\, (3\, \pi + 4\, a_0\ \delta_2\, \omega_0\, t)};$$

where a_0 is the initial displacement of the ions ;angiotensin I (m/z = 432) was used as model ions; Helium was used as the buffer gas (1mTorr); $\delta_2 = \sigma_{hard-sphere}\frac{p\quad M}{TkM + m}$ is the hard-sphere damping coefficient. $\sigma_{hard-sphere} = \pi\, {r_0}^2$ is the ion collision cross section, where r_0 is the effective radius of the ion; φ_0 is the initial phase ; ω_0 is the ion secular motion frequency.

Space charge effects on ion motion frequency:

Space charge effects on ion motion frequency can be calculated using a method we developed earlier[1] and characterized by ion motion amplitudes (*z*), ion numbers (*N*), and q_x values. In the calculation, a group of ions was placed in the linear ion trap.[1] With the presence of 10^3 ions in the linear ion trap, Figure S1a plots the frequency shifts of the ion at different q_x values. Ion motion frequency shifts furthermore at lower q_x values with small ion motion amplitudes, and the frequency shifts are less than 6 Hz at q_x = 0.39. Denser ion clouds will induce stronger space charge effects. Figure S1b plots the frequency shifts of the ion with different number of ions. When the number of the ions reaches 10^5, the frequency shifts will be close to

0.6 kHz. Such frequency shifts will influence the extraction of ion collision cross sections.

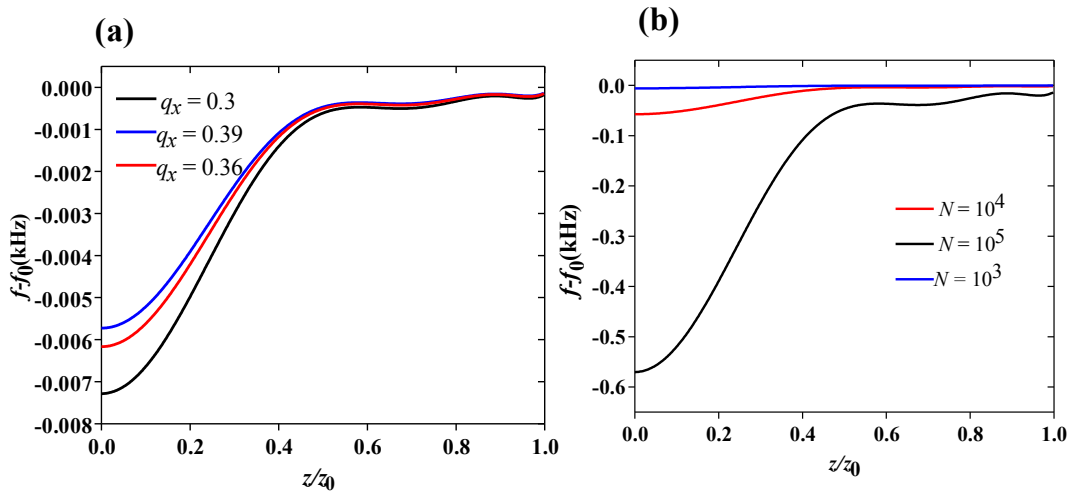

Figure S1 Space charge induced ion secular frequency shifts at different ion motion amplitudes. (a) Different q_x values with 10^3 ion number. (b) Different ion numbers at q_x = 0.39. T = 300 K, r_0 = 5 mm, q = 3 × e , m/z = 432 Da, helium pressure 1 mTorr.

Resolving ubiquitin isomer ions (+7) simultaneously:

Time-frequency curves in Figure 5a were obtained by simulating ubiquitin isomers individually. However, it is still possible to differentiate ubiquitin isomers when they were placed in the ion trap simultaneously. Although their trajectories add on top of each other, FDM could effectively identify two ion motion frequencies as their motion frequencies separate from each other due to their different ion-neutral collision rates (> ~100 Hz). Figure S2 plots the time-frequency curves of ubiquitin isomer mixtures (+7, 1000 ions of each type), whose physical sizes are 15.81 nm^2 and 13.61 nm^2 respectively. Two ion CCSs, 19.31 nm^2 and 16.32 nm^2, could then be

extracted after fitting these two curves. Results agree with those obtained by simulating each type of ions individually as shown in Figure 5a.

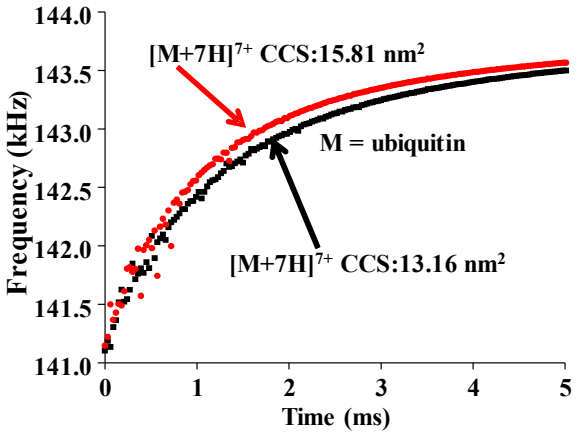

Figure S2 Simulated time-frequency curves of ubiquitin (+7) isomer ions, when these isomer ions were placed simultaneously in the ion trap.

Ion CCS extraction and line fitting:

Eqn. (7) described in a previous work[2] was modified as follows,

$$f(t) = a\sqrt{1 + b\left(\frac{1}{(c + d\,a)e^{f\,t} - a\,d}\right)^2}$$

and used to fit the time-frequency profiles, where a, b, c, d, f are unknown parameters . The calculated fitting parameters and R^2 are shown in Table S1.

Table S1 Fitting parameters using the mixed ion-neutral collision model at pressure $5*10^{-4}$ and $1*10^{-3}$ Torr, respectively.

$5*10^{-4}$ Torr

A4	a	b	c	d	f	R^2
-0.01	131300	-3620	479	0.1725	7.917	0.9996
-0.02	131300	-5132	407.8	0.003267	32.1	0.9987
-0.03	131300	-6036	359.1	0.009908	80.45	0.9944

$1*10^{-3}$ Torr

A4	a	b	c	d	f	R^2
-0.01	131300	-3723	486.6	0.6238	4.523	0.9998
-0.02	131300	-5058	398.5	0.2831	8.245	0.9996
-0.03	131300	-6044	361.7	0.04015	47.42	0.9994
-0.04	131300	-6548	332.4	0.01499	102.5	0.9979
-0.05	131200	-7149	302.7	0.0155	109	0.9766

References

1. D. Guo, Y. Wang, X. Xiong, H. Zhang, X. Zhang, T. Yuan, X. Fang and W. Xu, *Journal of the American Society for Mass Spectrometry*, 2014, 25, 498-508.
2. M. He, D. Guo, Y. Chen, X. Xiong, X. Fang and W. Xu, *Analyst*, 2014, 139, 6144-6153.