Supplementary Information:

Greatly Increasing Trapped Ion Populations for Mobility Separations Using Traveling Waves in Structures for Lossless Ion Manipulations

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Space Charge Effects on Ion Accumulation.

Here we present a short and qualitative discussion related to space charge effects in FF when excessive charge is accumulated. The space charge effects occur strongly depending on sample solutions (i.e. the m/z's, mobilities, and relative abundances of charged species) as well as the experimental conditions applied including TW amplitudes and speeds, RF pseudopotential, DC guard and the accumulation time, *etc*., this combined effects are possible resulting in m/z or mobility based bias, caused by ion activation, ion dissociation or ion loss, and spatial redistribution. As discussed in Figure S-1B and Figure S-2, increasing TW1 amplitude will significantly reduce the accumulated ions in the trapping region, low and high m/z ions can be discriminated against, indicating that higher TW1 amplitude will reduce ion rollover frequency during ion filling, most ions will be pushed to the end of the trapping region in a limited space, and the charge density will be increased with accumulation time. Increasingly excessive ion populations produce stronger and stronger space charge effects that can include: causing low and high m/z ions to 'fall over' into adjacent TW bins, be pushed into regions where significant RF heating can occur, or be lost due to insufficient lateral guard confinement.

In the case where roll-over into adjacent bins is the preferred route for the dissipation of excessive space charge, the ions will be expanded in the trapping region and redistributed in an m/z dependent manner, and in such cases 'peak tailing' may be observed, as discussed in the text, in cases where ions are released from different positions in trapping region and move through different path lengths in 'funnel' region and then refocused in the end of this region. The more abundant species (e.g., higher abundant ion m/z 622 in Figure 3 and Figure S-6) will thus be more spread out in trapping region during ion filling and as space charge drive more ions into adjacent TW bins and causing longer tailing in 'funnel' section during ion transmission after ion release. However, in case where the charge limit of the trapping region is reached with increasing the accumulation time, and roll-over into adjacent TW bins cannot efficiently alleviate the space charge, other alternatives apply. In this case low and high m/z ions can be driven into regions that have higher DC and RF potentials. If there is insufficient DC guard potential, this may result in a lateral loss of ions. With sufficiently high guard DC high m/z ions can be preferentially driven to close to the RF electrodes, and potentially activated (or dissociated) and also lost. As discussed in Figure 2A, both low and high m/z ion cutoffs are observed for long accumulation times (e.g., 1782 ms).

In conclusion, the space charge effects play an important role in ion accumulation, it can cause that we believe primarily include: lateral ion loss under lower guard potentials, roll-over into adjacent TW bins, and expansion into the region near RF electrodes leading to ion heating, dissociation and other artifacts. Such effects are complex and remain to be studied in detail. However, selecting and optimizing conditions avoiding such phenomena is feasible.

Figure S-1. Number of charges measured at the quadrupole with various parameters (A) TW1 speed (TW1 amplitude was 10 V and sequence was 11110000; Guard 1 was set to 15 V); (B) TW1 Amplitude (TW1 speed was 82 m/s, TW1 sequence was 11110000; Guard 1 was set to 15 V); (C) TW1 sequence (TW1 speed was 82 m/s, TW1 amplitude was 10 V; Guard 1 was set to 15 V) and (D) Guard1 (TW1 speed was 82 m/s, TW1 amplitude was 10 V, TW1 sequence was 11110000). Other conditions were: TW2 speed was 82 m/s, TW2 amplitude was 30 V, TW2 sequence was 11110000; TW3 speed was 123 m/s, TW3 amplitude was 30 V, TW3 sequence was 11110000; Guard 2 was set to 15 V; G1 was 15 V and G2 was 50 V; RF amplitude was 320 V_{pp} at a frequency of 950 kHz; Fill time was 486 ms and release time was set to 8 ms; Gap was 3.15 mm and at 3.00 Torr pressure.

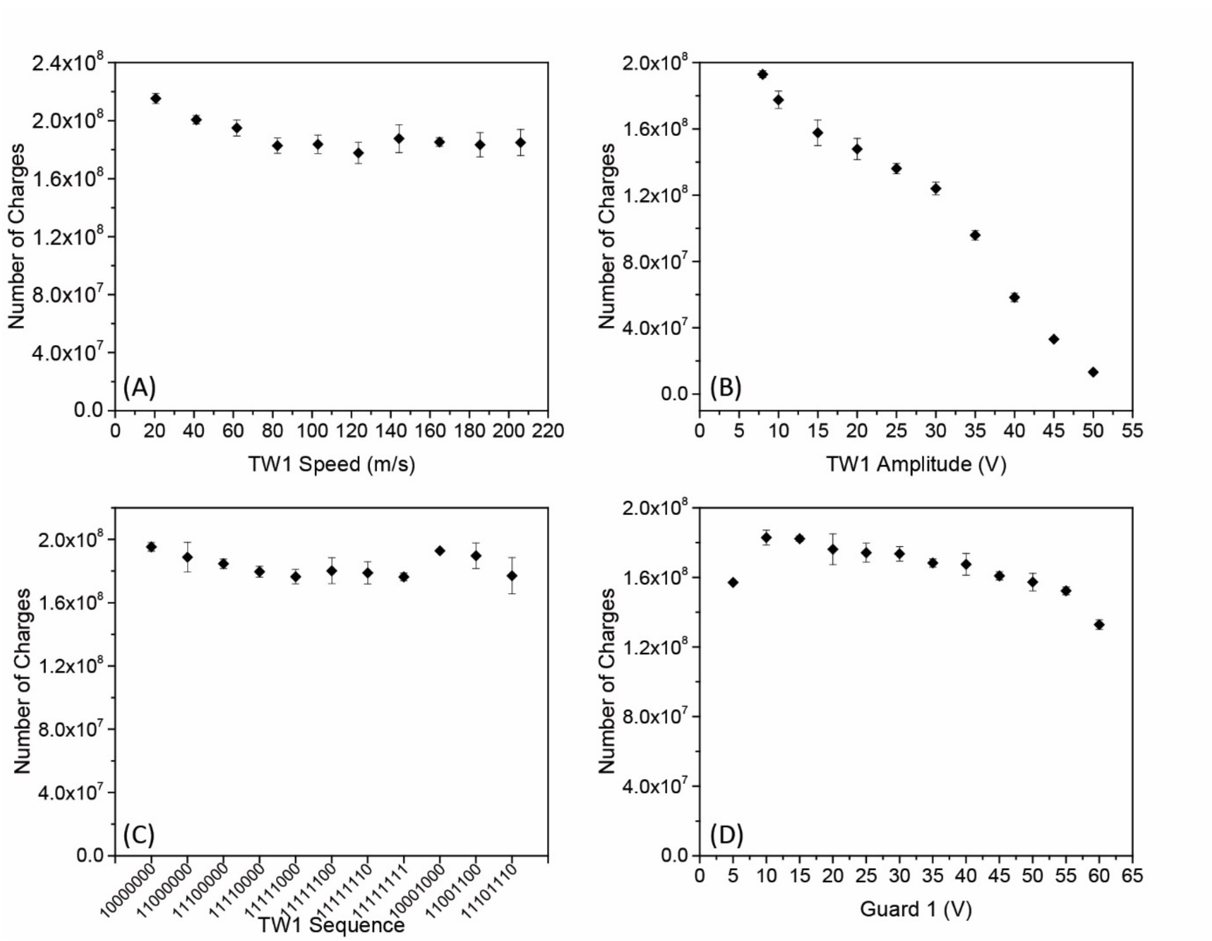

Figure S-2. Ion current pulse measurements at the quadrupole for ESI of the low concentration Agilent tuning mix solution with various TW1 amplitudes. The following conditions were used: TW1 speed was 82 m/s, TW1 sequence was 11110000; TW2 speed was 82 m/s, TW2 amplitude was 30 V, TW2 sequence: 11110000; TW3 speed was 123 m/s, TW3 amplitude was 30 V, TW3 sequence was 11110000; Guard1 and guard 2 were set to 15 V; G1 was 15 V and G2 was 50 V; RF frequency was 950 kHz and RF amplitude was 320 V_{pp}; Fill time was set to 486 ms; Release time was set to 8 ms; Gap was 3.15 mm and at 3.00 Torr pressure.

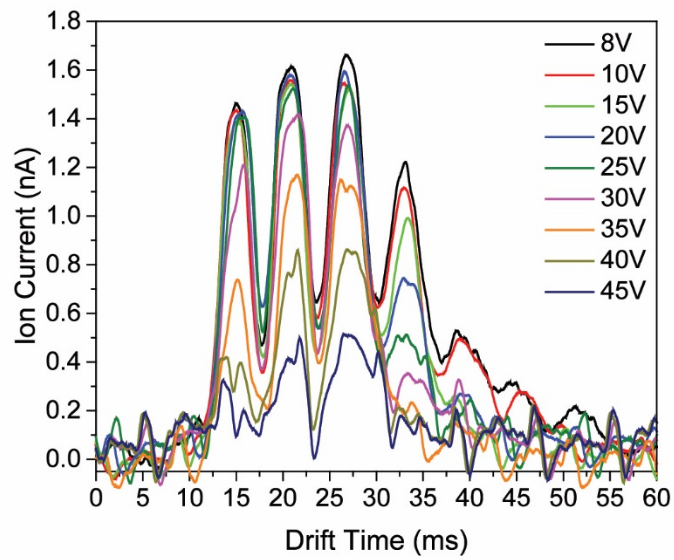

Figure S-3. Number of charges measured at the quadruple with various parameters (A) Gate2 (TW2 amplitude and sequence was 30 V and 11110000; RF amplitude was 320 V_{pp}); (B) RF amplitude (TW2 amplitude and sequence was 30 V and 11110000; G2 was set to 50 V); (C) TW2 amplitude (TW2 sequence was 11110000; RF amplitude was 320 V_{pp}; G2 was set to 50 V); and (D) TW2 sequence (TW2 amplitude was 30 V; RF amplitude was 320 V_{pp}; G2 was set to 50 V). Other conditions were: TW1 speed was 82 m/s, TW1 amplitude was 10 V, TW1 sequence was 11110000; TW2 speed was 82 m/s, TW3 speed was 123 m/s, TW3 amplitude was 30 V, TW3 sequence was 11110000; Guard 1 and guard 2 was set to 15 V; G1 was 15 V; RF frequency was 950 kHz; Fill time was 486 ms and release time was set to 8 ms; Gap was 3.15 mm and at 3.00 Torr pressure.

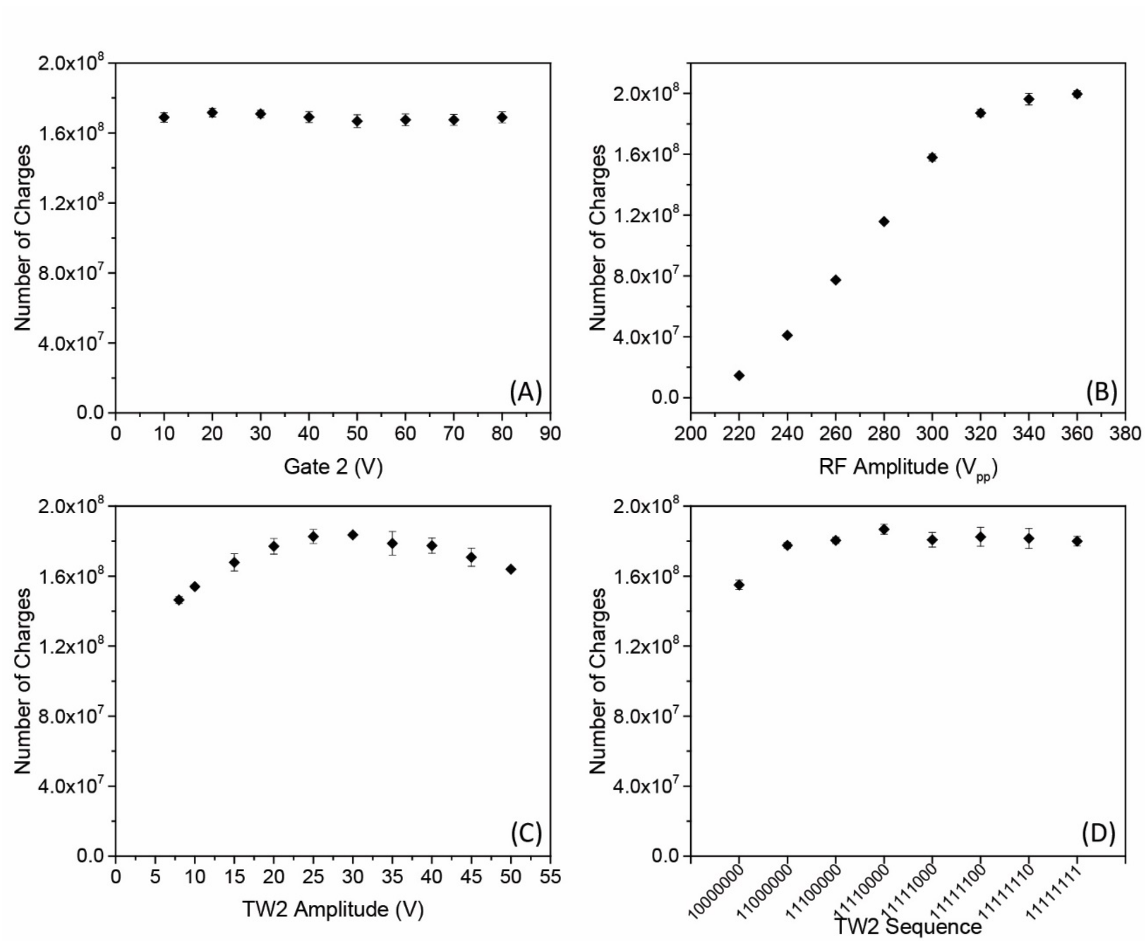

Figure S-4. Number of charges measured at the quadruple with various parameters (A) TW3 speed (TW3 amplitude was 30 V and sequence was 11110000; Guard 2 was set to 15 V); (B) TW3 Amplitude (TW3 speed was 82 m/s, TW3 sequence was 11110000; Guard 2 was set to 15 V); (C) TW3 sequence (TW3 speed was 82 m/s, TW3 amplitude was 30 V; Guard 2 was set to 15 V) and (D) Guard2 (TW3 speed was 82 m/s, TW3 amplitude was 30 V, TW3 sequence was 11110000). Other conditions were: TW1 speed was 82 m/s, TW1 amplitude was 10 V, TW1 sequence was 11110000; TW2 speed was 82 m/s, TW2 amplitude was 30 V, TW2 sequence was 11110000; TW3 speed was 123 m/s, TW3 amplitude was 30 V, TW3 sequence was 11110000; Guard 1 and guard 2 was set to 15 V; G1 was 15 V and G2 was 50 V; RF frequency was 950 kHz and RF amplitude was 320 V_{pp}; Fill time was 486 ms and release time was set to 8 ms; Gap was 3.15 mm and at 3.00 Torr pressure.

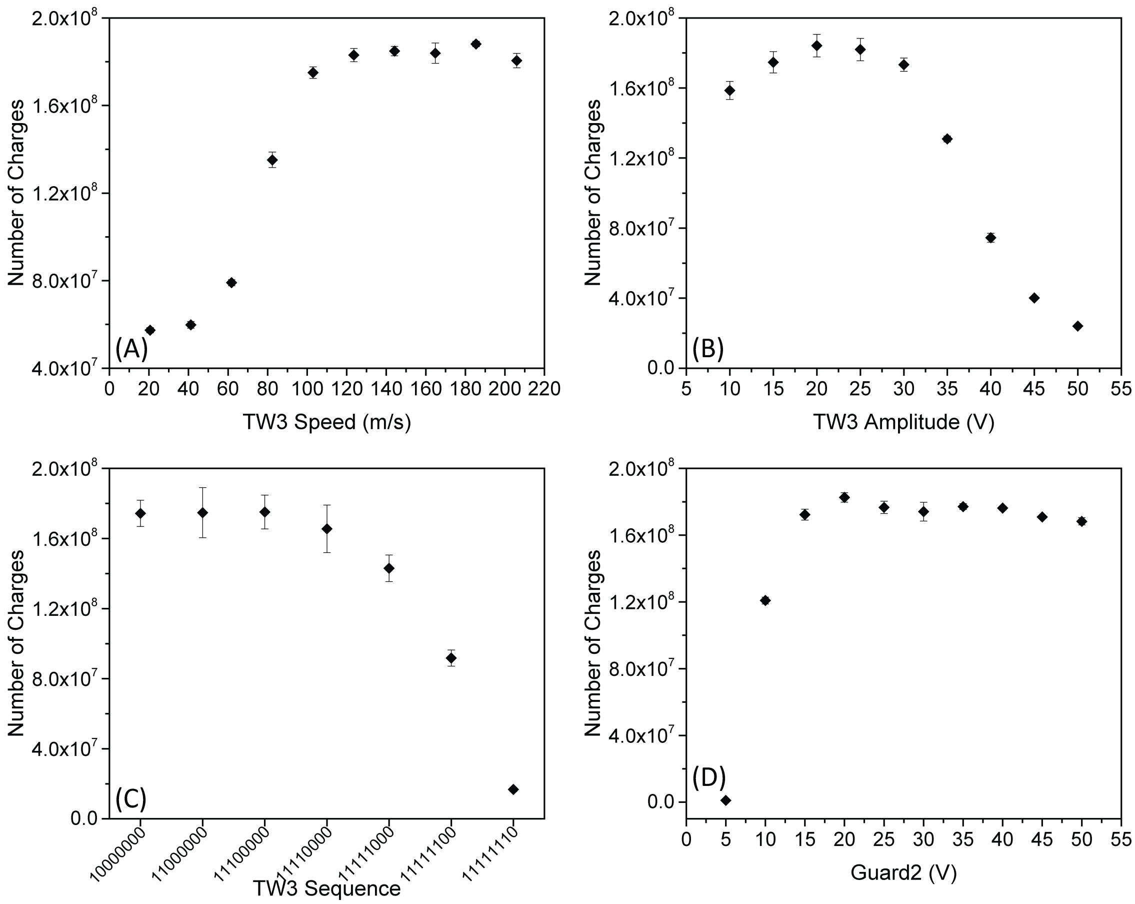

Figure S-5. (A) Number of charges measured at the quadrupole from ESI of low concentration Agilent tuning mix as a function of the release time at four TW2 speeds. The following conditions were used: TW1 speed was 82 m/s, TW1 amplitude was 10 V, TW1 sequence was 11110000; TW2 speed was 82 m/s, TW2 amplitude was 30 V, TW2 sequence: 11110000; TW3 speed was 123 m/s, TW3 amplitude was 30 V, TW3 sequence was 11110000; Guard1 and guard 2 were set to 15 V; G1 was 15 V and G2 was 50 V; RF frequency was 950 kHz and RF amplitude was 320 V_{pp}; Fill time was set to 486 ms; Gap was 3.15 mm and at 3.00 Torr pressure.

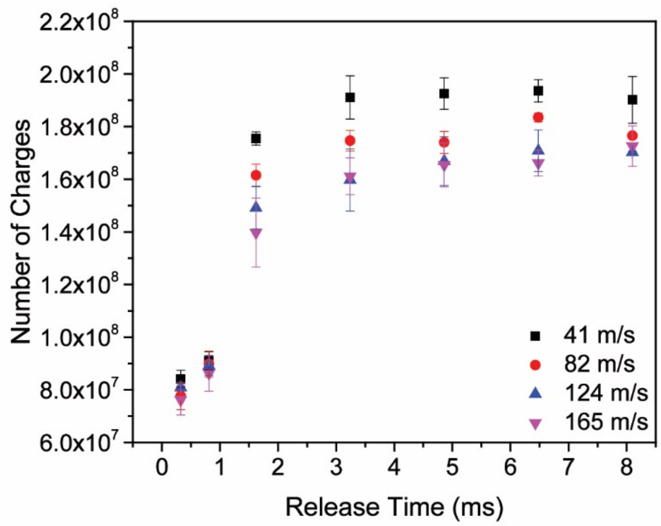

Figure S-6. The extracted ion mobility spectra of different ions for ESI of low concentration Agilent tuning mix was obtained by TW SLIM FF at the optimum conditions: TW1 speed was 82 m/s, TW1 amplitude was 10 V, TW1 sequence was 11110000; TW2 speed was 82 m/s, TW2 amplitude was 30 V, TW2 sequence: 11110000; TW3 speed was 123 m/s, TW3 amplitude was 30 V, TW3 sequence was 11110000; Guard1 and guard 2 were set to 15 V; G1 was 15 V and G2 was 50 V; RF frequency was 950 kHz and RF amplitude was 320 V_{pp}; Fill time was 81 ms and release time was set to 1.62 ms; Gap was 3.15 mm and at 3.00 Torr pressure.

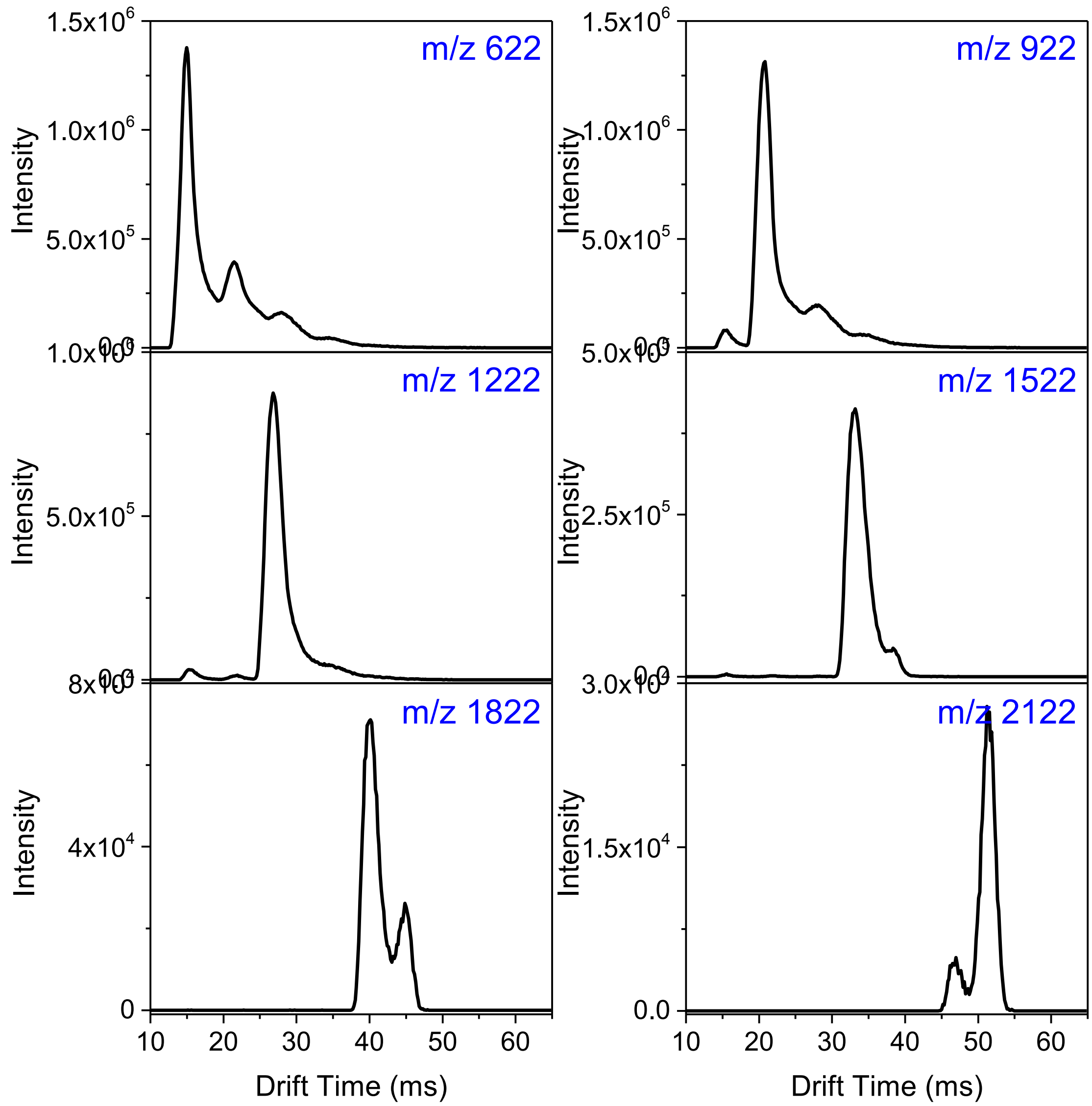

Table S-1: All TW, RF, and DC parameters as well as the fill time and release time of TW SLIM FF, the characterization range, the optimum condition for all parameters and some notes are listed.

Parameters	Characterization Range	Optimum Conditions	
TW1 Speed (m/s)	20-200	<100	
TW1 Amplitude (V)	5-50	<20V	Insufficient confinement from guard (>20V)
TW1 Sequence	10000000-11111111	All	
TW2 Speed (m/s)	20-200	<100	Equal to TW1 Speed
TW2 Amplitude (V)	5-50	25-35	
TW2 Sequence	10000000-11111111	11000000-11111111	
Guard1 (V)	5-60	10-30	
TW3 Speed (m/s)	20-200	>100	
TW3 Amplitude (V)	5-50	10-30	
TW3 Sequence	10000000-11111111	10000000-11110000	
Guard2 (V)	5-50	>15	
RF Amplitude (V_{pp})	220-360	>320	Higher RF amplitude gives better confinement
G2 (V)	10-80	All	G1 was set to 15V in this work
Fill Time (ms)	10-1800	<162	
Release Time (ms)	0.324-8.1	>1.62	