Supplemental Information: Precision characterization of three ultrafine condensation particle counters using singly charged salt clusters in the 1-4 nm size range generated by a bipolar electrospray source

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## Adjustment of the settings of the bipolar electrospray source



Figure S1: Example demonstration of the adjustment of the electrospray currents when classifying a large positive THABr cluster at an approximate mobility equivalent diameter of 3.4 nm. Note that these electrospray settings individually depend on the capillary geometry and capillary tip position. In the upper panel, the absolute FCE background when switching from unipolar to bipolar mode is displayed for different ratios of the negative to positive electrospray current. The lower panel shows the counting efficiency measured by the TSI 3777 and Airmodus PSM for each ratio of the currents. At current ratios between approx. 0.5 – 1, the FCE background decreases to zero. The dashed lines mark the value of the counting efficiency curves as shown in Figure 7 (Main Text).

An exemplary demonstration of the procedure for choosing the right settings of the electrospray is given in Figure S1. In the upper panel, the increase in the background measured by the FCE is presented. The FCE background, i.e. a surplus of positive or negative ions behind the DMA, arises when the bipolar electrospray switches from unipolar to bipolar mode. By adjusting the electrospray currents, the background can be reduced to zero. At those settings, the electrospray is assumed to be run at symmetric spray conditions. The counting efficiency of two low cut-off CPCs measured at each electrospray current setting reaches a plateau for high enough current ratios as is display in the lower panel of Figure S1. This behavior is linked to a high enough abundance of counter-ions leading to efficient charge reduction of ions at higher charge states. By the described procedure, the electrospray currents are adjusted prior to each measurement.

## Non size-resolved composition measurement of clusters generated by the bipolar electrospray source



Figure S2: Positive mass spectra of THABr clusters generated from the bipolar electrospray directly installed to the ioniAPi-TOF inlet. The upper panel shows the resulting clusters when operating the electrospray in unipolar (positive) mode, the lower panel the spectrum when having switched to bipolar mode. The ion signal was normalized to the intensity of the monomer peak. The bold text marks the peaks that are assigned to singly charged clusters, z=1, of the form (AB)n(A+)1. The arrow markers show clusters at charge states z=+2, that correspond to the doubly charged species as presented in Fernández de la Mora, Thomson and Gamero-Castaño (2005).

## References

Fernández de la Mora, J., B. A. Thomson, and M. Gamero-Castaño. 2005. Tandem Mobility Mass Spectrometry Study of Electrosprayed Tetraheptyl Ammonium Bromide Clusters. *J. Am. Soc. Mass Spectrom.,* 16(5):717–732.