Supporting Information:

Ion Emission from 1–10 MDa Salt Clusters: Individual Charge State Resolution with Charge Detection Mass Spectrometry

Matthew S. McPartlan, Conner C. Harper, Emeline Hanozin, and Evan R. Williams*

Department of Chemistry, University of California, Berkeley, California, 94720-1460, United States

For submission to *Analyst*

*Address correspondence to this author.

Email: erw@berkeley.edu

Telephone: (510) 643-7161

Supporting Information

Effects of STFT Segment Length on Time and Frequency Resolution. The ion trace data shown in Figure 1a was generated using a 25 ms STFT segment length. The fission event shown in **IV** appears to occur over several ms. However, this a result of the 25 ms STFT segment length used which limits the time resolution. Shorter STFT segment lengths improve time resolution, but this occurs at the expense of frequency resolution. The frequency peak width is 80 Hz when a 25 ms segment is used, which produces a smoothing effect when combined with the overlapping 5 ms step size selected for this analysis. It also makes it appear that the frequency before and after the ion emission event cannot be clearly resolved. Figure S1 shows the same data in Figure 1a but processed with a 100 ms STFT segment. This longer segment length reduces the frequency width of these peaks and clearly shows that the frequencies before and after ion emission for ion **IV** are distinct and can be clearly resolved.

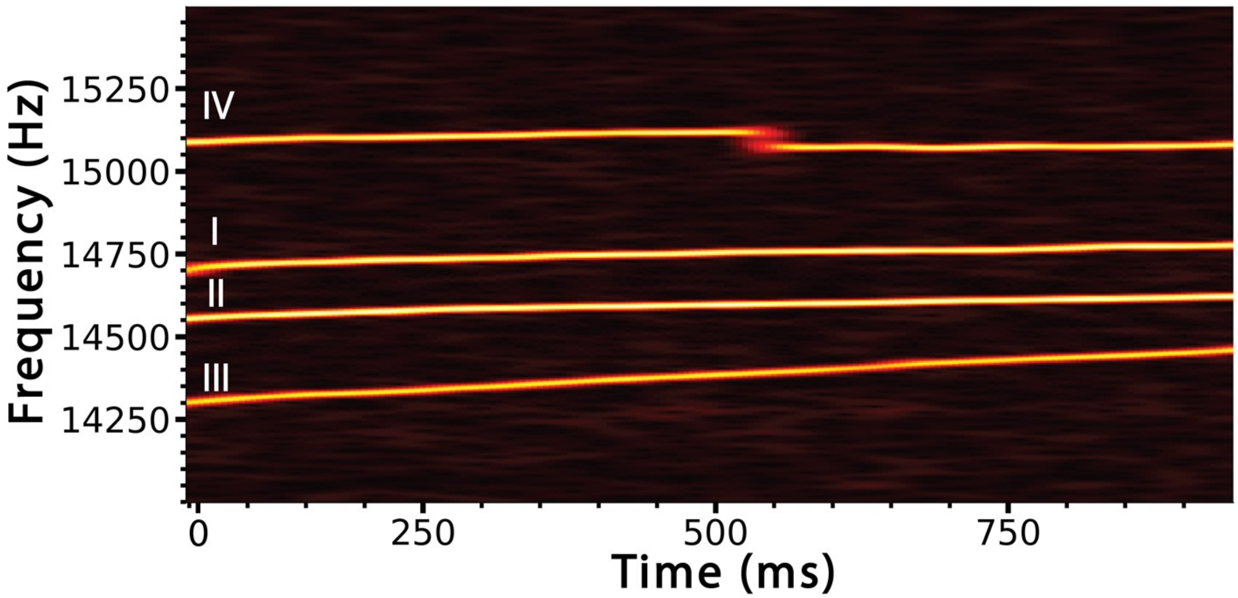

Figure S1. Data for the same four (of ten total) ions shown in Figure 1a but processed with a longer STFT segment length (100 ms instead of 25 ms). This leads to lower time resolution for the ion emission event but higher frequency resolution so that the frequencies of ion **IV** before and after ion emission are clearly resolved.

Calculation of Dynamic Frequency Threshold for Charge Emission Events. Due to the nonlinear relationship between ion energy and frequency, charge emission events corresponding to the loss of the exact same charge will lead to different magnitudes of frequency drops that occur upon ion emission for ions that have different frequencies of ion motion. The frequency drop for a high frequency ion is larger than that for a low frequency ion with an identical number of charges that are lost through ion emission. The frequency changes associated with charge emission events are typically larger than frequency changes due to the interferences that can occur between two traces, but distinguishing the two based on the frequency change alone is challenging. With a fixed threshold, it would not be possible to simultaneously identify emission events from low frequency traces and exclude minor perturbations in oscillation frequency from higher frequency traces. Instead, a quadratic threshold function that takes the initial trace frequency into account was used. This function is given in eq S1.

$$f_{threshold} = \left(\frac{f_{trace}}{6000} - 1\right)^2 + 15 \tag{S1}$$

A 15 Hz minimum threshold is used for the lowest frequency ions. With increasing $f_{trace}{}^2$, this threshold increases so that the highest frequency ions must exhibit a larger frequency change in order for an emission event to be detected. Within the frequency range of 8,000 – 40,000 Hz for the ions investigated here, the threshold ranges from 15 Hz at the lowest frequency to ~31 Hz for the highest frequency. Implementing this thresholding method significantly improves the reliability of the automated charge emission analysis.

Frequency of Zero, One and Multiple Ion Emission Events for Single Ions. The vast majority of ions only undergo either no charge emission or a single charge emission event. However, hundreds of ions also have multiple ion emission events over the course of the 1 s trapping period. Ion frequency traces where multiple fission events were observed were counted by requiring a minimum separation of 250 ms between ion emission events to ensure that these are independent events. This leads to a slight undercounting of ions that undergo two or more emission events, but the data for different ions are directly comparable. The data showing the number of ion emission events for each detected ion is shown for $CaCl_2$ and $LaCl_3$ in Figure S2. KCl did not undergo ion fission events.

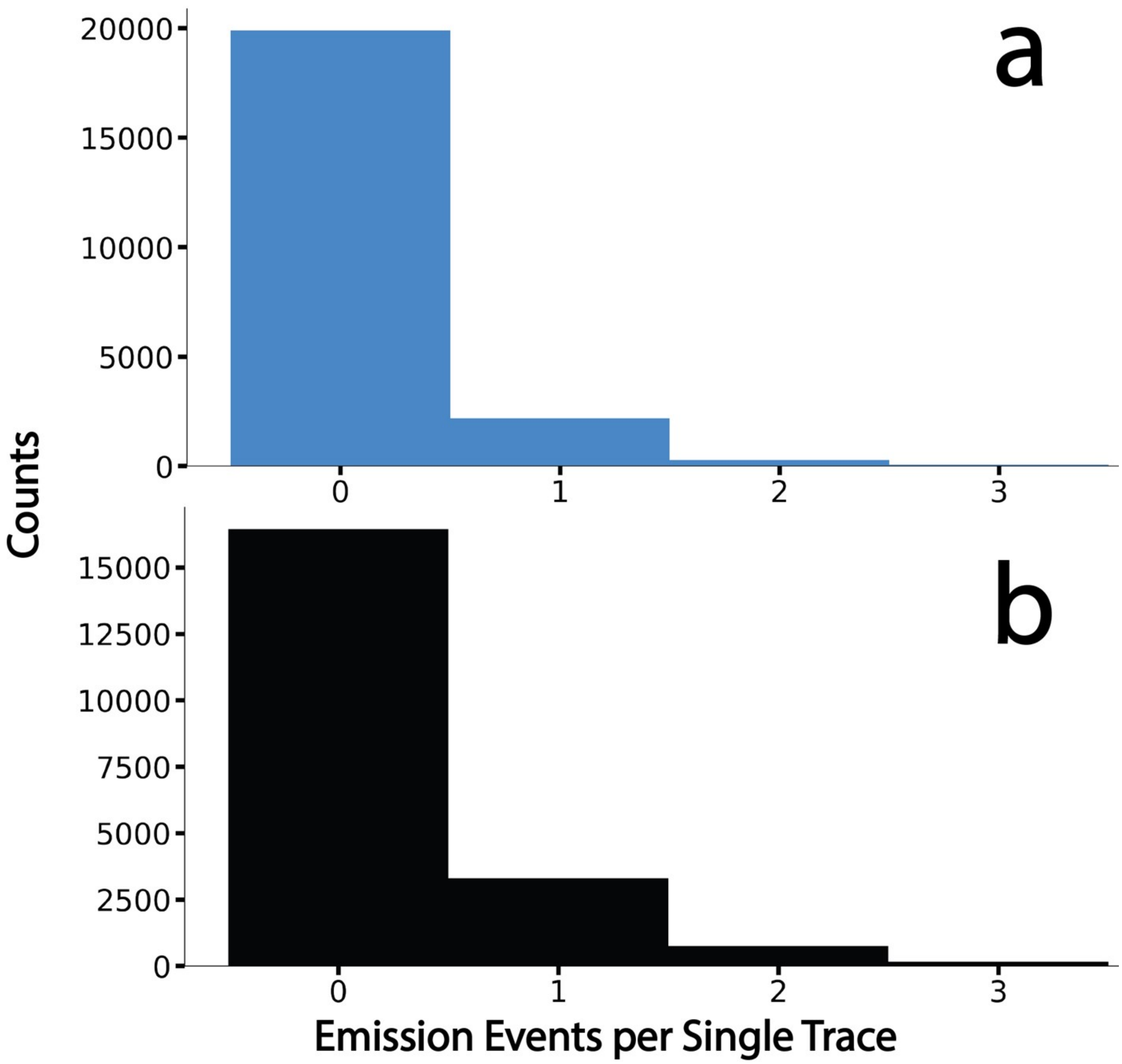

Figure S2. The frequency of ion emission events for clusters of **(a)** $CaCl_2$ and **(b)** $LaCl_3$ showing a higher number of multiple emission events for single $LaCl_3$ clusters compared to $CaCl_2$ clusters.