Reply on RC2
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Thank you very much for your comments and questions. Below are the answers for each question individually.

1. We believe that since 1B is a highly stable ion, neutral evaporation or fragmentation in M1B→ M+1B (M is an arbitrary cluster) is the reason for such horizontal lines appearing in the 2D plot. In general, we can observe this phenomena when evaporation or fragmentation leads to formation of highly stable ions or clusters. This will be included in the explanation of the figure.

   We will change the text as reported below.

   From line 102 ‘If a cluster entering the APi-TOF fragments, multiple signals are seen at the same voltage but at different mass/charge ratios. In Fig. 2, an example of a cluster and its fragment are shown (circled by dashed red lines). Moreover, many clusters upon entering the APi-TOF MS undergo neutral evaporation or fragmentation, especially when the produced cluster or ion is a highly stable one. This could result in a continuous horizontal line as seen in Fig.2 for the 1B ion where M1B→ M+1B (M is an arbitrary cluster).’

2. The probability of fragmentation before the next collision is given at the end by two parameters: the collision rate and the fragmentation rate. Precisely, the probability to fragment before the next collision occurs is given by k/(k+c), where fragmentation rate is “k” and collision rate is “c”. If k<<c, then we can exclude that a fragmentation would occur before the collision, because the probability is practically zero. The collision rate is approximately $10^7$ 1/s in the first chamber and $10^5$ 1/s in the second chamber, and we set the threshold for the fragmentation rate at 1000 1/s (which is about three orders of magnitude lower than the typical collision rate) because using this value we can safely assume that the cluster will not fragment before the next collision (the probability of fragmentation is $\sim 0.1\%$). The threshold value has been chosen arbitrarily, considering 0.1% a reasonable probability limit for neglecting fragmentation. Of course, there’s no precise value for the threshold, one could decide to set it at a lower value to have an even smaller probability of fragmentation.
We will add the following sentence in the supporting information.

SI from line 47 ‘... internal energy of the clusters. We set the threshold for the fragmentation rate at $10^3$ s$^{-1}$ (which is about three orders of magnitude lower than the typical collision rate) because using this value we can safely assume that the cluster will not fragment before the next collision (the probability of fragmentation is $\sim 0.1\%$). Table S1 lists all....’

3. At the moment, it is not possible to measure the degree of fragmentation in a setup of API-TOF MS only without the use of a differential mobility analyzer and an electrometer at the inlet of the system. It is, however, possible to calculate the degree of fragmentation in the API-TOF using our statistical model. The degree of fragmentation depends on a lot of variables, mainly including the type of clusters being measured, the pressure inside the API-TOF MS, the voltages across the different API chambers, and the radio frequencies of the quadrupoles, etc.. We can assume that the degree of fragmentation for a specific cluster will be the same in an API-TOF with the same voltage configuration and the same pressures (in the API chambers) as used in our experiments. In case the API-TOF is run with different voltage configuration and pressures it is possible to estimate the cluster fragmentation using our statistical model. Indeed, the input data of our model are the pressures in the API chambers, the voltage configuration and the quantum chemistry data (energy levels and vibrational frequencies) of the studied cluster. We can also use inverse mathematics and/or machine learning to back calculate the original cluster distribution from the detected one once the model has been validated against experiments.

In general, the lack of comprehensive studies on the quantification of fragmentation of different ambient clusters being measured is a major setback for retrieving realistic concentrations of clusters in air samples. It would be good to collect a large set of fragmentation data to be used as reference for common atmospheric clusters.