

Interactive comment on “Influence of temperature on the molecular composition of ions and charged clusters during pure biogenic nucleation” by Carla Frege et al.

Anonymous Referee #1

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General comments

The manuscript presents data from pure α -pinene ozonolysis nucleation experiments performed at three different temperatures at the CERN CLOUD chamber. Organic ions were measured with an APi-ToF. The authors discuss differences in positive and negative ion mass spectra, as well as ion binding energies for the different temperature conditions. This is a very well written paper. It presents information on atmospheric particle nucleation at a range of tropospheric temperatures, and thus is of high atmospheric relevance. There are a few aspects that could profit from further clarification, and the manuscript leaves the reader somewhat in the dark of the implications of the

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results. A paragraph discussing the importance of the observed differences in ion composition for atmospheric new particle formation is missing. I suggest publication after these aspects and the specific comments have been addressed.

Specific comments

P. 4, l. 120 – 122: It would be informative to give a rough idea of the actual tropospheric altitudes these temperatures correspond to, in regions where and seasons when α -pinene emissions are important.

P. 5, l. 136 – 139: Does “before the start of the experiments” refer to each experiment, or a series of experiments/an entire campaign? Please clarify. If you mean a series of experiments - how do backgrounds evolve during their course?

P. 6, l. 158 – 174: Your description of calibrations refers to mass calibration only. Are there no sensitivity calibrations? Throughout the manuscript, instrument transmission is mentioned a few times, but not discussed specifically. See also comments further down – can you expect ion rates to be consistent across experiments with similar precursor concentrations? Can you expect the instrument to be able to measure potential closure between (simplified) e.g. a decrease in monomer rate due to an increase in dimer formation? A short paragraph on instrument limitations would help the reader put your ion rates into perspective.

P. 7, l. 197 - 205: Presumably this paragraph describes the chamber background before increasing RH or adding precursor gases. This could be stated more clearly. Was ionization already on? Please clarify. What does “relatively dry” mean. If possible replace by RH percentage.

P. 8, l. 207: In your spectra the majority of ions is in the form of clusters with NH_4^+ or NO_3^- , or in other words, contaminants. Does this mean your results depend on contamination of the chamber, and in a perfectly clean chamber you would miss a large fraction of your APi-ToF spectra? Please clarify.

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P. 10, l. 262 – 264: Are differences in condensation sink the only possible explanation for the “missing” nocturnal new particle formation in Hyytiälä? How do precursor concentrations compare? Have you done similar experiments in the CLOUD chamber, but with condensation sink? Please elaborate shortly on the meaning of similarity in observed spectra/ion composition between field and laboratory, but difference in new particle formation rates.

P. 11, l. 276 – 278: Do you have an explanation for this observation? Could differences in NH₃+ mixing ratios for the different temperatures play a role?

P. 11, l.279 – 280: This would be easier to see if y-axis ranges were expanded to beyond 0.2

P. 11, l. 279 – 288: Presumably these measurements are during nucleation/before the onset of particle growth, but can you rule out influence of condensation to the walls in this shift? And related, it is not well discernible from the figure that the rate of dimer formation at -25 °C is reduced, there could also simply be an increase in monomer formation rate. Please clarify.

P. 15, l. 368 - p. 16, l. 379: What exactly is meant by “better consistency”? Overlapping of ion masses? Can one expect ion rate closure? Y-axis labels would suggest otherwise, but it is hard to see.

P. 22, l. 513: Shouldn't the sentence finish with “with lower temperature”?

P. 23, l. 544: You mention O:C ratio in a subclause. O:C ratios are being discussed as a determining factor in many processes related to atmospheric new particle number or mass formation. Your results imply temperature to be just as important. Please elaborate further on such an important implication.

Technical corrections

P. 8, l. 221 No reference to Figure 1A Figure 4 would profit from larger axis labels

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P. 14, l. 329: Dot is missing

P. 22, l. 491: Delta is not printed properly

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