

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

Anonymous Referee #1

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 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.

We added a section on the implications at the end of the conclusion. See comments below.

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.

We added the paragraph: *This spans the temperature range where NPF might occur in southern latitudes (25°C), high-latitude boreal regions (5°C) and free troposphere (-25°). For example, NPF events were reported to occur in an Australian Eucalypt forest (Suni, T. et al., Atmos. Chem. Phys., 8, 129-139, 10.5194/acp-8-129-2008, 2008) and at the boreal station in Hyytiälä (Kulmala, M et al, Science, 339, 943–946, 2013). New particle formation by organic vapors was also observed at a high mountain station (Bianchi et al. 2016). Moreover, high aerosol particle concentrations were measured in the upper troposphere over the Amazon Basin and attributed to the oxidation of biogenic volatile organic compounds.*

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?

“Before the start of the experiments” refers to the start of the campaign. This has been clarified.

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.

Yes, our calibration was a mass calibration only. We agree with the referee that a sensitivity calibration would have been interesting. However, this is difficult to achieve and needs specialized equipment. This needs to deliver a well-defined concentration of ions of different m/z . Since our measurements are inherently qualitative and not quantitative (i.e. concentrations) we did not perform a sensitivity calibration. We do expect ion rates to be consistent across experiments since the settings used during the whole campaign were the same; therefore the relative transmission of ions was kept constant. The transmission is the fraction of ions reaching the detector out of those entering the inlet. The transmission varies with m/z , see Junninen et al. (AMT, 3, 1039–1053, 2010) and Heinritzi et al. (AMT, 9, 1449-1460, 2016).

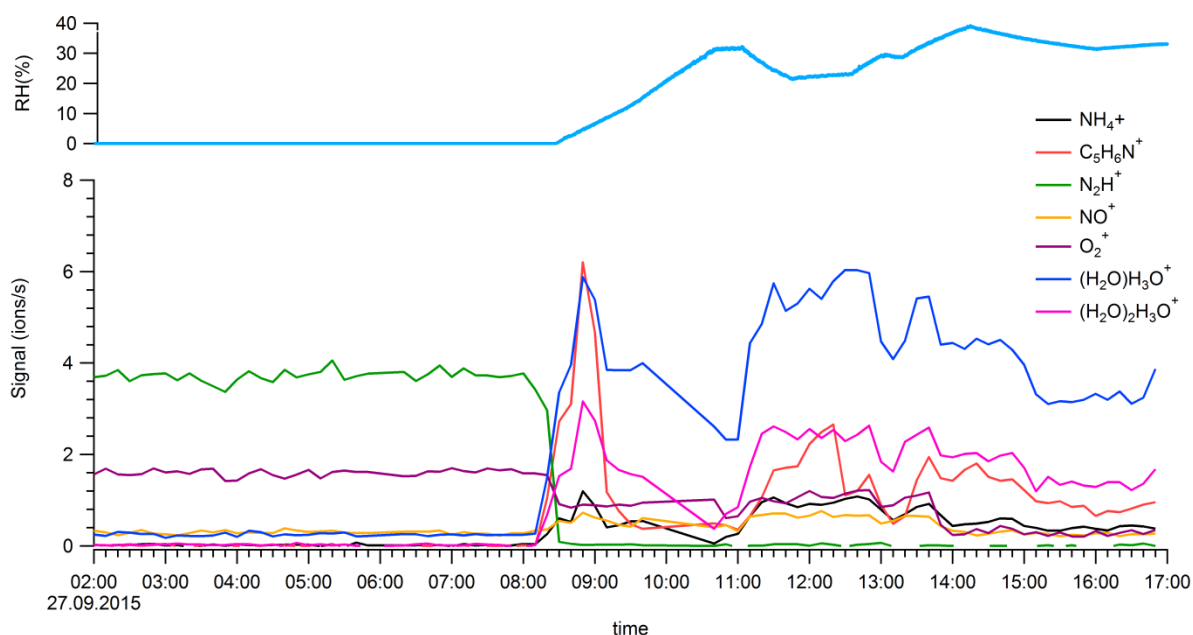
In theory you can reach a closure between a decrease of compounds and increase of others (Heinritzi et al., 2016). However, you would need to know the ionization and clustering energies of all the compounds to calculate their relative ion distribution. GCR or the π^+ beam generates a certain amount of ions in the chamber, which are then distributed among all the compounds, clusters and particles. Thus, due to lack of information on clustering energies it is not possible to determine the ion distribution.

We added a short paragraph on the characteristics of the measurements, which reads:

There is no direct chemical ionization in front of the instrument. The APi-TOF measures the positive or negative ions and cluster ions as they are present in the ambient atmosphere. As described above in the CLOUD chamber ions are formed by GCR or deliberately by a π^+ beam, leading to ion concentrations of a few hundred to thousands per cm^3 , respectively. In our chamber the ionizing species are NH_4^+ and NO_3^- (see below). These ions mainly form clusters with the organic molecules, which process is driven by the cluster energies. Therefore, the signals obtained do not provide a quantitative measure of the concentrations of the compounds. The higher the cluster energy with certain compounds the higher the ion cluster concentration will be.

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.

This paragraph has been clarified. By “relative dry” we meant 0% RH. For the referee information we show below a plot with the increasing RH described in the paragraph and the appearance of N_2H^+ and O_2^+ and the water clusters. This was only with GCR, without the π^+ beam.



P. 8, I. 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.

Indeed, the type and prevalence of the cluster ion depends on the type and degree of contamination. In a perfectly (100.0%) clean humid chamber the ionizing ions would be H_3O^+ and O_2^- . However, this is impossible to achieve. In a freshly cleaned chamber the levels of NH_3 and HNO_3 are expected to be way below 1 ppt. Despite these trace level concentrations, they become the main carriers of charge as also found in the real, relatively clean atmosphere (Frege et al. 2017; Ehn et al. 2010). In the ambient, most of the negative cluster ions are composed of an organic molecule clustered with NO_3^- or HSO_4^- . In the positive mode, the ions are found as clusters with NH_4^+ or amines.

P. 10, I. 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.

Indeed, there are also other factors explaining the fact that nocturnal events are not frequently observed in Hyytiälä. Using the data of CLOUD (Kirkby et al., 2016), which also includes this data, Gordon et al. (2016) did not find any nocturnal new particle formation at Hyytiälä in his model calculations. This is attributed mainly to the low terpene concentrations during night time. In addition, differences in condensation sink between this forested site and the CLOUD chamber may

also potentially contribute to the suppression of nocturnal nucleation. It has also to be considered that new particle formation rates smaller than $0.1 \text{ cm}^{-3}\text{s}^{-1}$ are hardly detected as such under ambient conditions, while they are measured in the CLOUD chamber. The concentrations of α -pinene used in this publication (258-618 ppt, see Table 1) are rather high for nocturnal concentrations in Hyytiälä (see Kontkanen et al., Atmos. Chem. Phys., 16, 13291–13307, 2016). What we show in Figure 2 is that the main HOMs components formed by α -pinene ozonolysis in the CLOUD chamber are also observed in Hyytiälä during night time. We do not consider here variations in relative intensities, which result from differences in i) concentrations; ii) temperature; iii) condensation sink. Presently, more experiments at the CLOUD chamber and more detailed analyses of measurements in Hyytiälä are underway to better understand the new particle formation mechanism. We therefore decided to delete this sentence and to set any speculation aside here as new particle formation is not addressed in this paper.

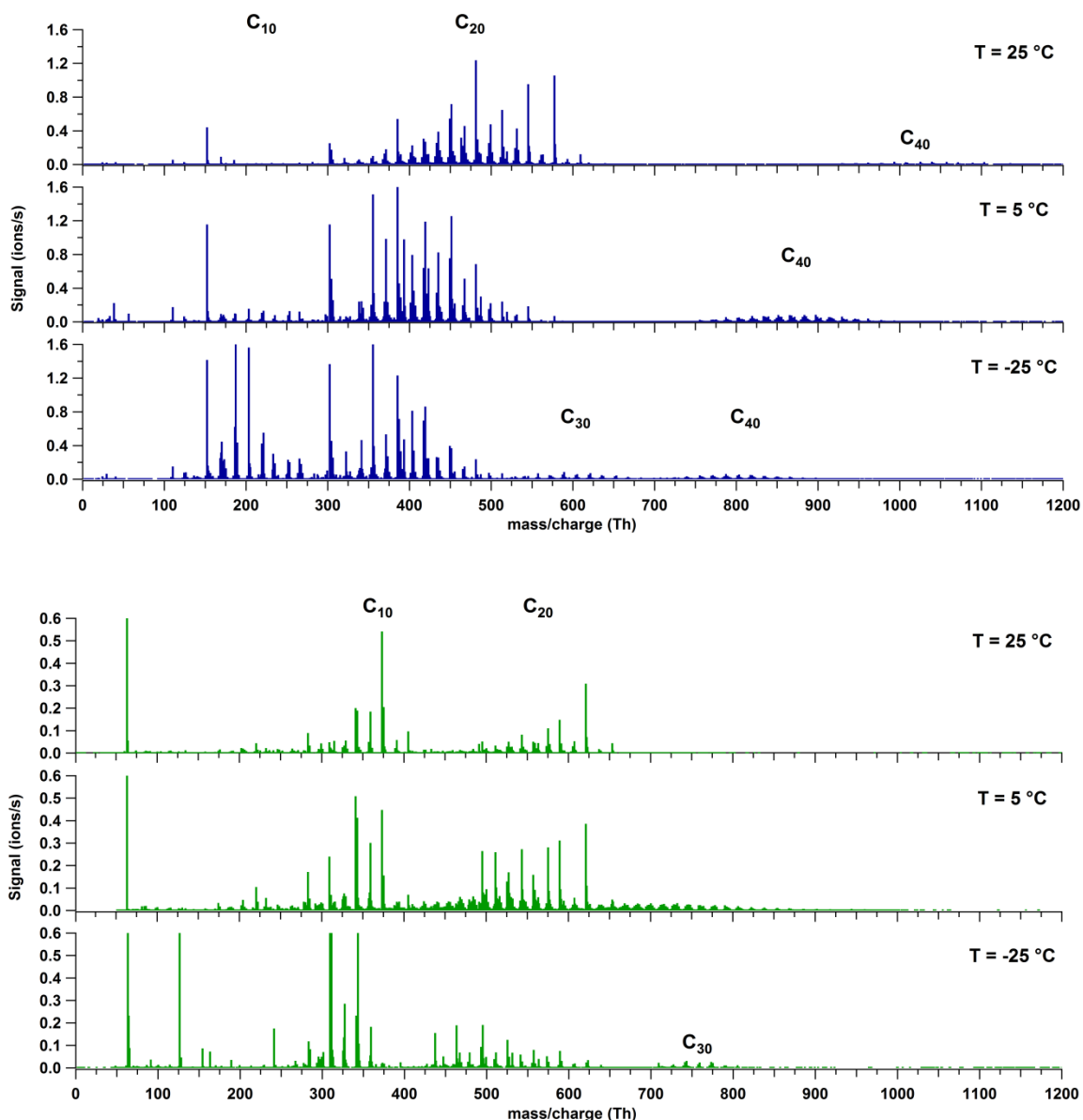
P. 11, l. 276 – 278: Do you have an explanation for this observation? Could differences in NH_3 + mixing ratios for the different temperatures play a role?

NH_3 was present in the chamber as a contaminant and its level should not have changed over the course of the experiments. The gas phase concentration might be lower at lower temperatures as more NH_3 might condense to the walls. However, we did not see a change in the clustering of NH_4^+ . Even at the lowest temperature, NH_4^+ -clusters contributed more than 90% to the signal intensity. As written we observe the same features/trends for positive and negative mode spectra as seen from the C_{20} band. However, in the positive mass spectrometer we can see a well separated C_{40} band, which clearly shows the decrease in O/C with decreasing temperature. We would not expect a decrease in signal intensity of high O/C compounds if not due to a decrease in concentration because the clustering energy is highest for these. In the negative mass spectrometer the signal of the C_{40} band is too noisy. This might have to do with lower sensitivity of the instrument at higher m/z or lower concentrations of C_{40} clusters.

We changed the text as following: *Although the observations described in the following are valid for both polarities, the trends at the three temperatures are better seen in the positive mass spectra due to a higher sensitivity at high m/z .*

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

We agree with the referee; however it was difficult to plot in a single Figure both polarities, at the three temperatures and show the signals (y-axis) of quite different intensities depending on the band. All the intensities are seen in Figure 4. Please find below another version of the plot with the y-axis beyond 0.2. In this presentation, the higher bands cannot be seen anymore. The full scale of intensities at 5°C can be seen in Figures 1B and 2. We refer to these now. We would like to keep the figure as it is.



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.

Yes, the measurements were done before and during nucleation time. If wall loss rate influenced the concentration ratio of dimer to monomer, we should see the opposite trend. At lower temperature the monomers would stick better to the walls than at higher temperatures and their concentrations should decrease. As a matter of fact, most HOMs (C_{10} and C_{20}) condense with the highest possible rate to the walls similarly as sulfuric acid. Thus, wall loss does not influence this shift.

Dimers are only a small fraction of the monomers. The reason, that the dimer signal is still larger than the monomer signal at higher temperatures is due to the higher cluster formation energies for dimers as seen in Table 3. The reviewer suggests that an increase of monomer formation could also

lead to this trend. The two processes are coupled. If less RO₂ radicals are formed that can combine to dimers, they end up as monomers. Thus, the monomer concentration increases while the dimer concentration decreases. Because dimers are only a small fraction of monomers the increase in monomer concentration is small. Thus, the strongest influence on the signal is caused by a decrease of dimers. Another reason for a shift in signal intensity could be a stronger stabilization of monomer NH₄⁺ clusters at lower temperatures than of dimer clusters. Although the QC calculations given in Table 3 do not point in this direction, we cannot rule it out for other compounds than those used in the calculations.

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-axes labels would suggest otherwise, but it is hard to see.

Yes, we mean the better agreement between the simulated and measured mass spectrum of tetramers. We have reformulated this sentence to *“The better agreement of the modeled mass spectrum of the tetramer band in the later case with the measured one suggests that only the molecules with O/C ≥ 0.4 are able to form the tetramer cluster.”*

We do not understand the question on ion rate closure. We show here which combinations of dimers could lead to the tetramer pattern. We cannot predict the intensity distribution well, as this depends on the clustering energies of the NH₄⁺ with the organic cluster. We assume here that it represents somewhat the actual concentration distribution of dimers and tetramers. This premise has been added now: *“One has to note that the comparison of modeled and measured spectrum relies on the assumption that the charge distribution of dimers is also reflected in the tetramers”*.

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

No. Ion clusters are more stable at all temperatures compared to neutral clusters. Therefore, ion clusters evaporate at lower rates and can grow faster. We slightly modified the sentence: *Finally, a comparison of the ΔG values as presented in Table 3 confirms the expected higher stability of charged clusters compared to neutral clusters, decreasing the evaporation rate of the nucleating clusters and enhancing new particle formation.*

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.

Thank you for this comment. We added the following sentences: Nucleation and early growth is driven by the extremely low volatility compounds, i.e. dimers and monomers of high O:C ratios (Tröstl et al., 2016). Here, we observe a reduction of the autoxidation rate leading to oxidation products with lower O:C ratios with decreasing temperature. We expect that this is accompanied by a reduction of nucleation rates. However, a lower temperature reduces evaporation rates of clusters and thereby supports nucleation. The relative magnitude of these compensating effects will be subject of further investigations.

Technical corrections

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

We added a reference to Figure 1A. We agree with the referee and increased the size of the axis and labels as much as possible.

P. 14, l. 329: Dot is missing

This was corrected.

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

Thank you for the observation, this has been corrected

References

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