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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The role of ions in new-particle formation in the CLOUD chamber" *by* Robert Wagner et al.

Anonymous Referee #2

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The authors reported results from experiments at CLOUD 5 on four systems of different chemical compositions involving monoterpenes, sulfuric acid, nitrogen oxides, and ammonia. With instrument setup consisting of two nano-particle counters, one of them equipped with an ion filter, the authors were able to investigate the effect of ions on nucleation and measure the progressive neutralization due to ion-ion recombination as clusters grow. The measurements indicate that ions enhance the nucleation process when the charge is necessary to stabilize newly formed clusters, and a large fraction of the clusters carried a charge at 1.2 nm diameter but most of these charged clusters were largely neutralized before they grew to 2.2 nm. The authors also compared CLOUD measurements to atmospheric observations at SMEAR II, Hyytiälä, Finland.

The measurements and data analysis presented in this manuscript are important to

better understand the role of ions in new particle formation under different conditions. The manuscript is well within the scope of ACP. Some clarifications and additional details are needed to further improve the manuscript. I recommend the publication of this manuscript in ACP after the following comments are addressed.

Main comments

1. Figures 3-6. These figures present neutral fraction of particle formation rates versus [MT] or [MT] combined with other parameters ([H2SO4], [NO], [Cluster ions]). It is established that HOMs (from the oxidation of MT) are involved in the nucleation and/or growth of clusters. Since [HOMs] are measured (page 7) and it appears that [HOMs] are affected by other parameters such as temperature (lines 7-9, page 10), I think that the results will be more straightforward and easier to understand if [MT] in x-axis is replaced with measured [HOMs] and the figures are replotted.

2. Uncertainty and effect of detection thresholds of PSMs.

(1) The neutral nucleation fractions are derived at 1.2 nm, 1.7 nm, and 2.2 nm threshold. It appears that these values are cluster mobility diameters. Please provide corresponding mass diameters and rough numbers of HOM and H2SO4 molecules in the clusters.

(2) Page 9, line 11. "... we accounted for this by increasing the detection thresholds by 0.3 nm above their calibration values". What do you mean here? So the given 1.2 nm threshold is actually 1.5 nm?

(3) Page 9, line 15. "...should be noted that the reported diameters could be systematically underestimated by up to 0.5 nm." So the given 1.2 nm threshold could actually be 1.7 nm? The actual sizes are important as charged fractions decrease quickly with cluster sizes. Please more specific so readers can better understand the results.

(4) Page 9, line 18. "... the cut-off diameter for ions can be up to 0.5 nm smaller than for neutral particles". Does this imply that the results for 1.7 nm could actually be those

for 1.2 nm?

This manuscript focuses on the results for clusters of 1.2 nm, 1.7 nm, and 2.2 nm. It appears the uncertainty in the cluster sizes detected could be up to 1 nm (see above comments), comparable to the size range of clusters analyzed here (1.2 nm - 2.2 nm). The authors need provide a more in-depth discussion on how this uncertainty might influence the results presented and their conclusions.

3. Based on results given in the manuscript (Figures 2-9), the role of ions in nucleation depends on multiple parameters. To help interested readers to better understand the results presented in various Figures which focus on the dependence of neutral fractions on certain parameter(s), I strongly suggest that the authors provide a table to list all controlling parameters measured (T, [cluster ions], [HOM], [H2SO4], [NO], [NH3], [MT], PS beam intensity) as well as derived Jn, Jiin, Jrec, and Jtot (Fig. 1) at the three thresholds for all data points (or cases) presented in Figure 2. The table can be provided as supplementary material. Such a table will also fulfill the ACP requirement with regard to the availability of underlying data (https://www.atmospheric-chemistry-and-physics.net/about/data_policy.html):

“Authors are required to provide a statement on how their underlying research data can be accessed. This must be placed as the section "Data availability" at the end of the manuscript before the acknowledgements. Please see the manuscript composition for the correct sequence. If the data are not publicly accessible, a detailed explanation of why this is the case is required.

The best way to provide access to data is by depositing them (as well as related metadata) in reliable public data repositories, assigning digital object identifiers, and properly citing data sets as individual contributions. If different data sets are deposited in different repositories, this needs to be indicated in the data availability section.”

4. Page 10, lines 8-9. How much can the lower temperature affect the HOMs production rate? Also see comment 1 above.

5. Page 10, line 22. What are the possible reasons that NO affects neutral fraction?

6. It appears that [NH3] in System IV ranged from 178 ppt to 1971 ppt (Table 2). Did you observe any effects of [NH3] on neutral fraction? How does the effect of [NH3] compare to that of [NO]?

7. Page 11, lines 17-19: “We compared the 1.2 nm formation rates in CLOUD with the nucleation rates of 1.5 nm particles (Kulmala et al., 2013), and the recombination rates of 1.5–1.7 nm particles (Kontkanen et al., 2013). In addition, we compared the formation rates of 1.7 nm particles in CLOUD with the formation rates at 2 nm from Manninen et al. (2009).” If you compared the 1.7 nm formation rates in CLOUD with the nucleation rates of 1.5 nm particles (Kulmala et al., 2013) and the formation rates of 2.2 nm particles in CLOUD with the formation rates at 2 nm from Manninen et al. (2009), would the conclusion change? How the possible uncertainty the PSM thresholds (see comment 2 above) may affect the comparisons and conclusions?

Minor comments

1. Page 7, lines 10-11. A factor of two error: Please provide the possible sources of errors and relevant references.

2. Page 7, line 17. NH3 detection limit: Any reference?

3. Figure 1. Which system in Table 1 does this example case correspond to? If system III or IV, what was the concentrations of NO and/or NH3?

4. Per ACP Data Policy (https://www.atmospheric-chemistry-and-physics.net/about/data_policy.html), please provide a "Statement on the availability of underlying data" (also see main comment #3).

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