Review on "Hygroscopicity and CCN potential of DMS derived aerosol particles"

We would like to thank both reviewers for their thorough and constructive comments. We appreciate the input and feel that the comments from the reviewers have helped improve clarity of our manuscript. We have addressed the reviewers' comments in a point-by-point fashion below and revised the manuscript accordingly. Our answers to the comments are given below in blue letters, while the referee comments are given in *black italics*. Additionally, we added the changes we made in the revised manuscript in **blue bold** letters.

Reply to Reviewer: 1

The study by Rosati et al. investigated nucleation, hygroscopicity, and CCN activity of secondary aerosol particles from DMS as a function of temperature and relative humidity. Important findings include reduction in nucleation and particle growth rates at lower temperature (258 K) than that at 293 K. The kappa values for CCN activity were higher for lower temperature. Considering that temperature dependent particle formation from DMS has rarely been conducted, this study will serve as a good starting point for the more detailed studies in the future. The manuscript is well written, although some figures/tables can still be improved. I suggest publication of this manuscript after addressing the following comments.

Major comments:

1) Precursors of ammonium and nitrate:
The experimental procedure (section 2.2) describes that the authors injected H2O2 and DMS. Figure S7 suggests that particles generated in the chamber contained organics, nitrate, and ammonium, in addition to sulfate and MSA. It was not clear to me how ammonia and NOx concentrations were controlled. Ammonia is especially important both for nucleation and hygroscopic processes. So, the concentration of ammonia should clearly be summarized in Table 1. It seems that the authors measured NOx concentration using a NOx analyzer. It would be helpful for readers to understand the paper if the data from the instrument were to be available.

Both NO_x and ammonia are unfortunately always present in air, even after extensive cleaning. Thus, we could not completely avoid them. The NO_x concentration was indeed monitored and the measured concentration range during an experiment is now added to the revised manuscript in Table 1. After acceptance of the manuscript all data and figures produced during the campaigns will be available to all researchers on sciencedata.dk.

We did not have an instrument to monitor the ammonia levels. However, measurements in Tange (56.35°N, 9.58°W; ~50 km from Aarhus; download from http://ebas.nilu.no/) show that ambient NH_3 concentrations were in the range of 1-7 ppb (up to approximately 5 µg/m³ NH_3 as seen in the figure below) at this location during the experiment days. Thus, we expect that we had similar values inside the chamber during the experiments.
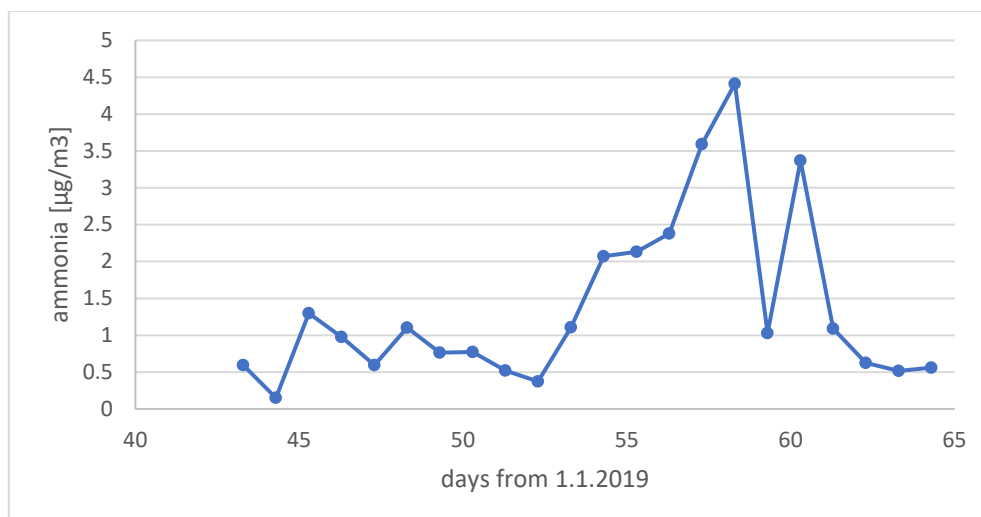
Figure 1: Ammonia concentration at Tange during the time of experiments, downloaded from http://ebas.nilu.no

We have added the following sentence to the revised manuscript:
Ammonia concentrations during the experiments are estimated to be between 1-10 ppb based on data from Tange (56.352222°N, 9.5875°W; ~50 km from Aarhus; http://ebas.nilu.no/).

2) *Formation mechanisms of organic compounds and its influence on hygroscopicity/CCN activity:*

Figure S7 shows that the particles generated by the chamber contained 10 ~30 % of organics. I am wondering how they formed. It will be great if the authors could describe the corresponding formation mechanism. I also wondered if the organics could assist hygroscopic growth of aerosol particles. It would be great to have some additional discussion on this point.

Organics were measured during each experiment and contributed to different % of the overall composition. Absolute concentrations were low in all experiments and organics had similar contributions during all experiments as illustrated in the figure below (Fig. 2). We had seen an approximately constant contribution of organic mass in aerosols derived from the oxidation of DMS by hydroxyl radicals also in our previous work and discussed potential explanations therein (Rosati et al., 2021; Wollesen de Jonge et al., 2021).

In summary, it cannot be entirely excluded that despite careful cleaning the organic signal is due to a contamination in the chamber (e.g. from a previous experiment), it is however also known that the organic fraction as obtained from AMS spectra is susceptible to biases due to the complex fragmentation during ionization, uncertainties arising from the calibration with MSA, previously documented memory effects (e.g. Drewnick et al., 2015; Drewnick et al., 2009; Pieber et al., 2016) and the detection limit of the instrument. The organic signal may thus also be an artefact related to the AMS and the associated data interpretation protocol. Since we do not know the type of organic it is difficult to access its potential impact on hygroscopicity.
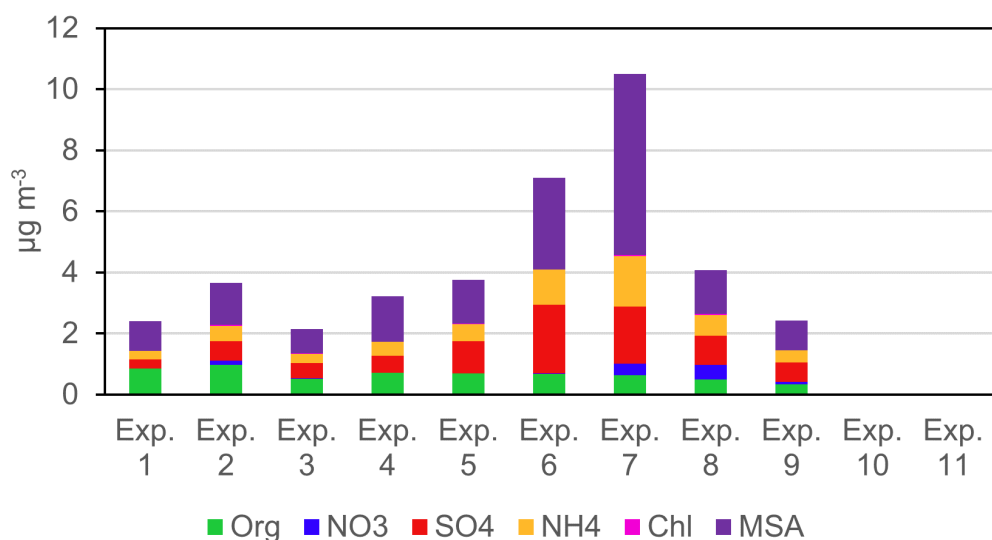
Figure 2: Absolute mass concentrations as measured from the AMS.

The figure above is added to the supplementary of the revised manuscript.

Additionally, we have added the following text to the revised manuscript:
Line 374: **The relative contribution and absolute concentrations of organics, nitrate, sulphate, ammonia, chloride and MSA are illustrated in Fig. S7 (SI) for experiments performed at 273 and 293 K.**

Line 377: **Absolute concentrations show that in general the aerosol mass loading was small and that the organic contribution was comparable during all experiments. As previously discussed in Rosati et al. (2021) and Wollesen de Jonge et al. (2021) we cannot conclude on the exact origin of the organic signal. It cannot be entirely excluded that it is due to contamination from previous experiments. Since we do not know the type of organic it is difficult to access its potential impact on hygroscopicity. It could however also derive from biases due to the complex fragmentation during ionization, uncertainties arising from the calibration with MSA and previously documented memory effects (e.g. Drewnick et al., 2015; Drewnick et al., 2009; Pieber et al., 2016). If this is the case, the organic signal will not influence hygroscopicity.**

Minor comments
Table 1: It is better to show H2O2 concentration by using mixing ratio.

Assuming that the volume of the bag at the start of the experiment was 5 m^3 and that the density of the H_2O_2 solution (30% in H_2O) is 1.11 g ml^{-1} the mixing ratios are:

418 µl	20 °C	65.6 ppm	**1500 µl**	20 °C	235.5 ppm
	0 °C	61.2 ppm		0 °C	219.5 ppm
	-15 °C	57.8 ppm		-15 °C	207.4 ppm

Section 2.2.3: It seems that all the aerosol instruments were operated at room temperature, even though the chamber temperature was cooled down to 258 K. I wonder if potential changes in gas-particle equilibrium could be induced by the temperature change. I also wondered if the change in the equilibrium could influence the nucleation/particle growth rates in addition to chemical composition. It would be ideal to have some discussion about this point in the manuscript.

Indeed, all instrumentation was operated outside the cooling chamber and thus at the standard laboratory temperature of 22°C. Sampling lines for the AMS and SMPS were temperature insolated all the way to the instrument. We cannot fully exclude that some particle properties were affected by the difference in temperature between the bag and the laboratory.

We believe that the reported particle growth rates should not have been affected strongly as their residence time in the tubing before entering the nano or long-SMPS was between 11 – 28 s and growth rates, as illustrated in Fig. 1b, are in the order of nm h^{-1}. The residence time in tubing to the PSM, used to measure the nucleation rates, was approximately 10 s. The fastest nucleation rates were measured during warm conditions and thus conditions where the laboratory and the chamber were comparable (see Fig. 1a). As the measured nucleation rates were slower at the colder temperatures, we expect changes to be slower and thus less affected by the time the particles spent in the warmer laboratory.

We have added the following sentence to the manuscript:
Line 122: **All instruments were operated at the laboratory temperature of 22°C outside the AURA chamber. To limit evaporation in tubing en route to the particle size (SMPS) and chemical composition measurement (AMS), the tubing was insulated.**

Section 2.3.5.: The authors mention that the HTDMA measurement was conducted at RH = 80%. Deliquescence relative humidity of ammonium sulfate is slightly lower than 80%. Considering the chemical composition of the particles, I personally think that it would have been better to conduct the HTDMA measurement at higher RH. Could the authors explain the reason why they selected this condition?

RH=80% was chosen because it could repeatably and stably be set at the laboratory conditions. Particularly in the long-HTDMA higher RH led to quite large fluctuations and thus less stable conditions. We calibrated the HTDMAs with pure ammonium sulfate (see result for long-HTDMA in figure below) and could clearly see that the deliquescence was around 78% and all particles were liquid at RH=80%. We also looked closely at the shape of the humid size distributions to see whether we had some bimodal distributions as often found when too close to the deliquescence (e.g. Biskos et al., 2006) but this was never the case.
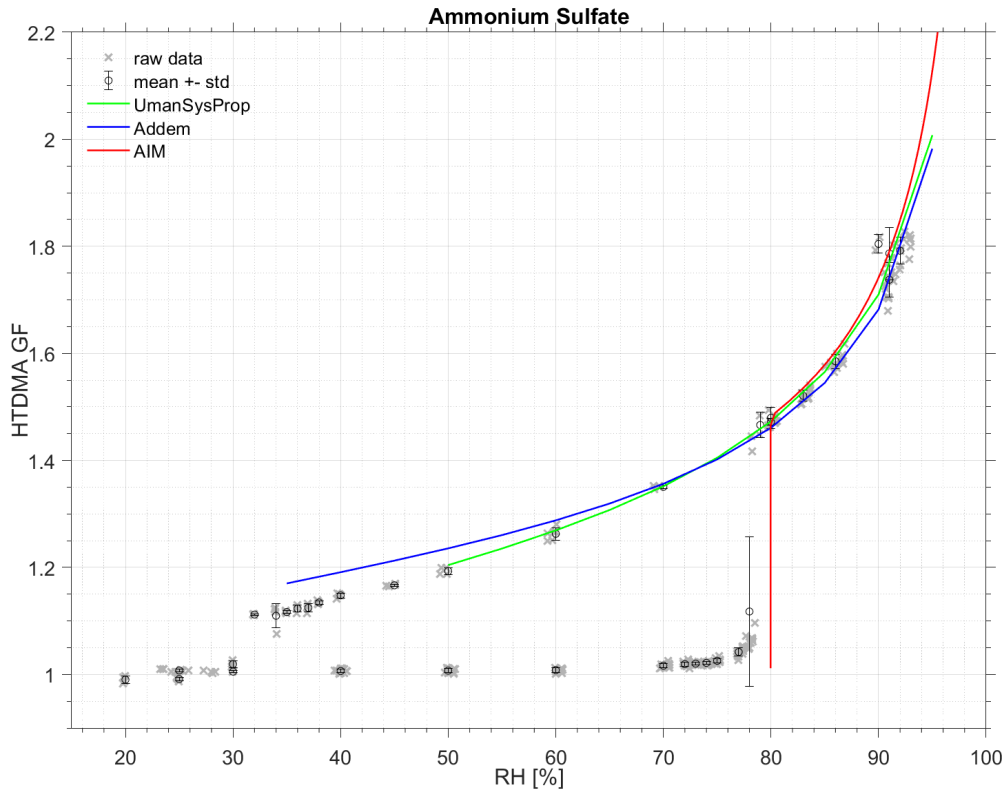
Figure 3: Humidogram for Ammonium Sulfate particles with a dry size of 200 nm.

Figure 1a: There is a cyclic oscillation in the nucleation rate at 273 K. Is it possible to explain the potential cause?

Yes, as stated in the caption of Fig. 1, the fluctuations stem from the fact that the PSM was set to measure in scanning mode after a while. This leads to small changes in the sample flow rate that then induce these fluctuations.

L309 Such a size trend can be expected: I could not understand the reason why it can be expected. Please describe it in more detail.

It is expected from Köhler theory. κ has a size dependence because the water activity at activation depends on the initial dry particle size.

For example: the κ-value for ammonium sulphate varies from 0.51 to 0.63 over the particle size range 20-100 nm (calculated using UManSysprop at 293 K, Topping et al., 2016).

We have reformulated the text to make this clearer:
Line 309 and following: **Such a size trend can be expected from Köhler theory; for comparison the κ-value for ammonium sulphate varies from 0.51 to 0.63 over the particle size range 20-100 nm.**

Figure 2: It requires a lot of efforts and focus to see this figure. I suggest updating the figure so that the readers can easily get the main message of the figure.

We have spent a substantial amount of time discussing other versions of this figure but to our mind this is still the best way to illustrate the data. We have though changed the color-code and increased the size of the text and markers in order to make it easier to read.
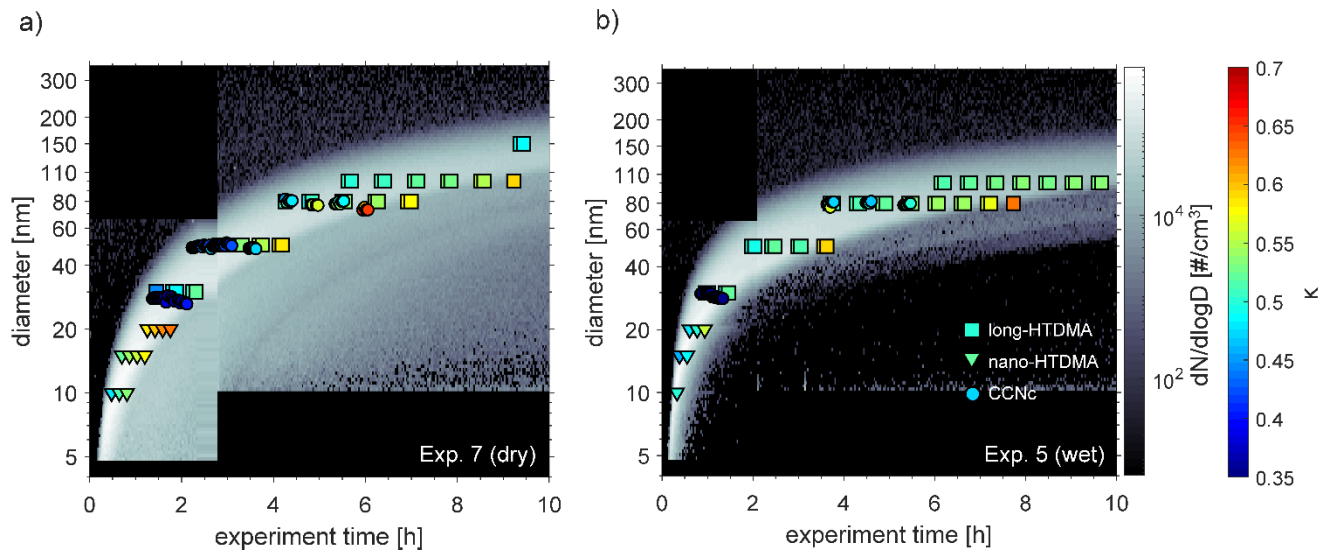

Table 2: The formats of tables 1 and 2 are significantly different. It would be better to have a standardized table format for a manuscript.

The tables were re-formatted to have the same table format in the revised manuscript.

Reply to Reviewer: 2

This work mainly investigated the hygroscopicity and cloud condensation nuclei activity of aerosol particles formed through oxidation of DMS. DMS is emitted by phytoplankton species in the oceans and constitutes the largest fraction of naturally emitted sulphur to the atmosphere. Secondary aerosols formed through oxidation of DMS play significant roles in climate and their hygroscopic properties are key parameters in describing their direct and indirect climate effects. Thus, scientific findings of this study are meaningful and fits well the scope of ACP. The authors have designed comprehensive laboratory chamber experiments and performed very good measurements using a suite of aerosol instruments, especially including synthesized nano-HTDMA, HTDMA, CCN and AMS measurements. In general, experiments are well designed and discussions are insightful. I have one major concern and some minor suggestions as listed below:

Major comment:

As shown in Fig.S7, organic constitutes a non-negligible fraction to formed aerosol mass, but compositions and impacts of organics on hygroscopicity are not even mentioned in the discussions. It seems that authors just neglected this part of aerosol mass, and compared measured aerosol hygroscopicity only with mixed MSA-sulfate system. Authors should explain a little bit their choice in discussions or add more discussions. Also, it would be nice to discuss possible compositions of formed organics.

Fig. S7 shows that the relative contribution of organics can sometimes be as high as 30% but in absolute terms the contribution is actually quite constant throughout the measurement period (see figure below).
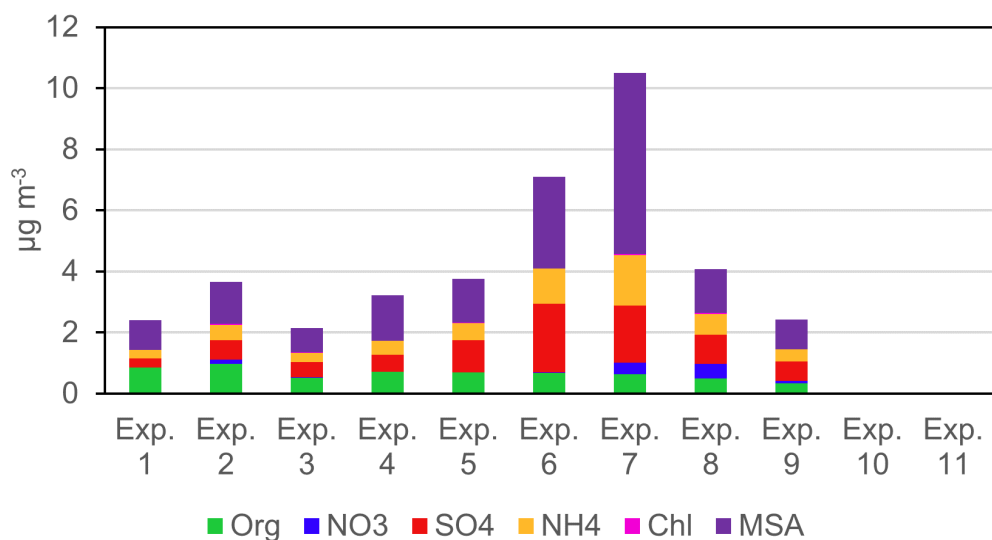
The figure shown above is added to the supplementary material of the revised manuscript.

Organics were measured during each experiment and contributed to different % of the overall composition. Absolute concentrations were low in all experiments and organics had similar contributions during all experiments as illustrated in the figure below (Fig. 2). We had seen an approximately constant contribution of organic mass in aerosols derived from the oxidation of DMS by hydroxyl radicals also in our previous work and discussed potential explanations therein (Rosati et al., 2021; Wollesen de Jonge et al., 2021).

In summary, it cannot be entirely excluded that despite careful cleaning the organic signal is due to a contamination in the chamber (e.g. from a previous experiment), it is however also known that the

organic fraction as obtained from AMS spectra is susceptible to biases due to the complex fragmentation during ionization, uncertainties arising from the calibration with MSA, previously documented memory effects (e.g. Drewnick et al., 2015; Drewnick et al., 2009; Pieber et al., 2016) and the detection limit of the instrument. The organic signal may thus also be an artefact related to the AMS and the associated data interpretation protocol. Since we do not know the type of organic it is difficult to access its potential impact on hygroscopicity.

Additionally, we have added the following text to the revised manuscript:
Line 374: **The relative contribution and absolute concentrations of organics, nitrate, sulphate, ammonia, chloride and MSA are illustrated in Fig. S7 (SI) for experiments performed at 273 and 293 K.**

Line 377: **Absolute concentrations show that in general the aerosol mass loading was small and that the organic contribution was comparable during all experiments. As previously discussed in Rosati et al. (2021) and Wollesen de Jonge et al. (2021) we cannot conclude on the exact origin of the organic signal. It cannot be entirely excluded that it is due to contamination from previous experiments. Since we do not know the type of organic it is difficult to access its potential impact on hygroscopicity. It could however also derive from biases due to the complex fragmentation during ionization, uncertainties arising from the calibration with MSA and previously documented memory effects (e.g. Drewnick et al., 2015; Drewnick et al., 2009; Pieber et al., 2016). If this is the case, the organic signal will not influence hygroscopicity.**

Minor suggestions:
L105: More details about Kappa calculations from CCN measurements should be given

We have added the following sentence to the revised manuscript:
L 101 and following:

To compare water uptake at sub- and supersaturated conditions, the hygroscopicity parameter κ, introduced by Petters and Kreidenweis (2007), was used. The water activity term in Eq. 2 is be described in terms of κ in the following way:
$$\frac{1}{a_w} = 1 + \kappa \frac{V_s}{V_w} \tag{4}$$
where V_s is the volume of the dry particle and V_w the volume of the water in the droplet. By combining Eq. 3, 4 and 5 the semi-empirical κ-Köhler theory can be obtained.

L121: "further"-> "already"?

Yes, that is correct. We changed the wording in the revised version.

Section 2.3.5: set-up of the two HTDMAs are overall similar, introductions of them summarized in one paragraph might be better

We combined the paragraphs with the HTDMA description.

Section 2.4: I suggest present a brief introduction of quantum chemical calculations and needed input parameters before 2.4.1.

We agree that a brief introduction to the quantum chemical calculations should be added. As these are first principal calculations, we do not need other input parameters except the xyz coordinates of

MSA and a water. The cluster structures of the MSA-water clusters are then obtained via geometry optimization. All the necessary information on how the calculations were conducted are contained in section 2.41, 2.42 and the SI.

We have added the following text to introduce the quantum chemical calculations in the manuscript:
To obtain molecular level insight into the hydration free energy of MSA, we carried out highly accurate quantum chemical calculations of the MSA-hydrate cluster structures. These calculations will aid in elucidating to what extent the MSA molecules are hydrated in the gas-phase.

L268: More discussions? Elucidate why it is interesting

Unfortunately, we do not know the reason why different temperature dependences of the rate constant for the reaction of DMS with OH have been reported in the literature and an expanded investigation of the reason is outside the scope of the current work.

We have reformulated the text to read:

The decrease of nucleation and growth rates with decreasing temperature is consistent with a lower observed loss rate of DMS at lower temperatures, see Fig. S4 and Table S1 in SI illustrating an example for each of the temperatures investigated in this study and a comparison between dry and humid experiments (Exp. 1, 2, 8 and 10). Different temperature trends for the rate of the reaction of DMS with OH radicals have been reported in the literature (Albu et al., 2006; Barnes et al., 2006; Hoffmann et al., 2016). Our observed trend is in line with the predicted temperature dependence obtained with the Arrhenius expression used in the Master Chemical Mechanism version 3.3.1 (MCMv3.3.1) and Hoffmann et al. (2016) delineating slower reaction rates at colder temperatures.

L282: "higher absolute concentration", higher-> lower?

We thank the reviewer for spotting this mistake!

We have reformulated the text in the following way:

The absolute water concentration could also have an effect on the observed trends in the nucleation rate as the initial cluster formation in our chamber setup most likely consist of relatively weakly bound sulphuric acid – methane sulfonic acid – ammonia clusters (Rosati et al., 2021). Water has been shown to increase the nucleation rate if the initial cluster is weakly bound such as for sulphuric acid – ammonia clusters (Henschel et al., 2016; Henschel et al., 2014). However, in our studies the absolute concentration of water is lowest at colder temperatures.

References:

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