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Interactive comment on "Experimental study of H_2SO_4 aerosol nucleation at high ionization levels" *by* Maja Tomicic et al.

Anonymous Referee #1

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The manuscript by Tomicic et al. reports on chamber experiments investigating the effect of ions on new particle formation (NPF). The chemical system investigated is the (nominally) binary system of sulfuric acid and water, although high levels of contamination by ammonia (1200 pptv) are required to explain the high NPF rates, i.e., the relevant chemical system is rather ternary (H2SO4-H2O-NH3 with ions) than binary. The novelty of the study is that high ionization rates (up to 560 ion pairs cm-3 s-1) were investigated by irradiating the chamber with gamma ray sources. The high ionization rates cause ion concentrations that could be representative of atmospheric levels due to a nearby supernova explosion. Regarding the high ion concentrations (1700 to 1.9e+04 cm-3) the present study expands a previous one by Dunne et al. (2016), where the maximum ionization rate was ∼75 ion pairs cm-3 s-1. In principle, the results by Tomicic should be eventually published; however, currently the manuscript contains too many technical flaws and needs some major revisions.

Main comments:

(1) Currently it is stated that the parametrization from Dunne et al. (2016) is expanded to lower sulfuric acid concentrations and higher ion concentrations. This is an overstatement since Dunne et al. explored new particle formation for a wide range of sulfuric acid, ammonia, temperature and ion concentrations. However, the present study examined NPF at only one temperature (295 K) and one ammonia mixing ratio (1200 pptv). For these conditions, the sulfuric acid and ion concentrations were varied. Given the fact that the authors did not resolve the chemistry of the nucleating clusters, it is also speculative that NH3 is the only possibility of explaining the high NPF rates at low sulfuric acid. In principle, other contaminants (e.g. organics or amines) could probably also explain the data. Therefore, without having identified the chemistry of the nucleating clusters the statements about the chemical parameter space that the current study explores need to be re-formulated.

(2) The results presented in figure 6 are not in agreement with previous studies. At 2e+07 cm-3 of sulfuric acid, the contribution from binary neutral nucleation to the total neutral nucleation rate is as high as the contribution from the other channels (binary ion-induced, ternary neutral and ternary ion-induced). For this warm temperature, it is impossible that binary neutral nucleation yields a formation rate of ∼0.04 cm-3 s-1 (at sulfuric acid of 2e+07 cm-3) since the clusters evaporate too rapidly (see, e.g., Hanson and Lovejoy, 2006; Ehrhart et al., 2016; Duplissy et al., 2016). At these conditions, binary neutral nucleation should be completely negligible and even the binary ion-induced component should be negligible compared to the ternary channels (Ehrhart et al., 2016; Duplissy et al., 2016). Therefore, a re-evaluation of the different nucleation channels is necessary as well as a more thorough inter-comparison to previous studies. Given the presented results and the results from previous studies it seems very likely that the nucleation rates presented are by far dominated by the ternary channel.

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(3) Regarding the identification of the relevant nucleation scheme, one possibility would be to use the CI-APi-TOF as an APi-TOF. This should indicate what fraction of sulfuric acid cluster ions contains ammonia molecules (or any other contaminants); based on Schobesberger et al. (2015) it might also be possible to derive an estimate of the ammonia contaminant level. Given the fact that the experiments were made at high ion concentrations, the APi-TOF should yield strong signals, which would shine a light on the nucleation pathway.

(4) The data evaluation process needs to be explained in more detail. Especially, an additional figure should be added that shows the time development of particle concentration, UV light intensity, H2SO4 concentration, temperature, etc. Based on that figure it should be explained over what period the data for the derivation of J were averaged.

Specific comments:

p. 1, l. 10/11 (abstract): the parameter space is only extended for one NH3 concentration and one temperature (1.2 ppbv and 295 K, see Fig. 4)

p. 2, l. 1: further references regarding the influence of organics on NPF should be added (e.g., Zhang et al., 2004; Ehn et al., 2014; Kirkby et al., 2016)

p. 2, l. 9: add “The” at the beginning of the sentence

p. 2, l. 10: replace “outlet” with “emissions”

p.2, l. 31/32: Where did the air originate from? Was it from gas bottles, from a dewar or was an (ambient) air purification system used? If a gas purification system was used, what measures were taken to clean the gas? Later in the paper it is concluded that the contamination of ammonia was quite high (1.2 ppbv); therefore, it would be good to know if and how it was attempted to minimize the ammonia contamination.

p. 3, l. 5: Temperature has a strong influence on NPF (see e.g. Ehrhart et al., 2016). How was the temperature held constant at 295 K? Was there any increase in temperature when the UV light was turned on? If yes, by how much did the temperature increase?

p. 4, l. 7: “irradiation” instead of “radiation”

p. 5, Figure 2: What is meant by “average ionization” for the left panel of the figure? What is the unit?

p. 5, l. 9 ff. (section 2.2): The authors need to add a figure that shows the time development of [H2SO4], particle concentration, UV light and temperature; based on that figure the experimental run sequence should be explained.

p. 6, l. 21: please mention the detection limit for the sulfuric acid measurements

p. 6, l. 3 (something is wrong with the line numbering): “drifts” instead of “drift”

p. 7, l. 18: The reference to Hansen (2016) refers to a bachelor’s thesis, which I couldn’t find on the internet. The authors need to summarize how the mentioned corrections were made. In addition, it is not clear why the H2SO4 was not derived from the signal related to the exact mass of HSO4-. The CI-APi-TOF has a mass resolving power that is high enough to discriminate HSO4- from most other isobaric signals. The commonly used data evaluation tools for CI-APi-TOF data (Toftools and Tofware) also allow the subtraction of noise. Therefore, it is not clear why this software has not been used.

p. 7, l. 4: The retrieval of the “mean peak concentration” should be demonstrated in a figure. The whole data evaluation process needs to be described in more detail.

p. 7, l. 20/21: The GRs are indeed very high given the rather low sulfuric acid concentrations. The theoretical approach from Nieminen et al. (2010) indicates that a sulfuric acid concentration of 1.5e+07 cm-3 results in a GR of ∼1 nm/h (with GR being linearly dependent on H2SO4) for the binary system. This relationship has been found to be consistent with measured data (Lehtipalo et al., 2016). Therefore, the expected GR for the sulfuric acid range relevant for this study would be 0.5 to 2 nm/h, i.e., a factor of ∼20 lower than what has been measured.

p. 8, l. 22/23: The authors attribute the fast growth of the particles to the presence of highly oxidized molecules. However, if these compounds dominate the GR (see previous comment) a fraction of them should also be capable of enhancing the particle formation rates (see Kirkby et al., 2016). Discussion about the possibility of explaining the high formation rates due to organics should be added.

p. 8, l. 27-29: Again, it would be good to show a figure that indicates the range over which the gradient dN/dt was calculated. In addition, the equation for determining the particle formation rates neglects some potential corrections: In the calculation, all particles larger than the cut-off diameter of 1.4 nm are considered. However, the particles beyond that size are subject to loss processes such as wall loss, dilution and coagulation. These processes lower the measured particle number density to some degree (see Kulmala et al., 2012). In fact, the authors write that the majority or particles is lost during their growth from 1.4 to 4 nm (p. 6, l. 22); in this case the loss terms definitely need to be taken into account in the calculation of J. In addition, a mobility diameter of 1.4 nm is quite small. The results from Duplissy et al. (2016) indicate that the critical size can be significantly larger at warm temperature. Are the authors sure, that 1.4 nm is at or above the critical size?

p. 8, l. 32: The systematic uncertainty of 5% for the H2SO4 measurements is quite low. How was this value derived?

p. 10, l. 9: The experimental data were fitted to functions representing binary nucleation (neutral and ion-induced, eq. (4) and (5)). However, from Dunne et al. (2016) it can be concluded that nucleation is almost entirely dominated by the ternary nucleation terms (J_tn and J_ti) at 295 K (sulfuric acid between 7e+06 and 3e+07, [ion] = 1700 cm-3) if ammonia is present at 1.2 ppbv. Therefore, the use of binary nucleation to represent and fit the data (Fig. 5) is not justified (see also comment above). In addition, the parameters provided by Dunne et al. (2016) do not have high enough precision in order to replicate their measured data; therefore, the higher precision values provided by Gordon et al. (2017) should be used for calculating the individual components of the nucleation channels.

p. 10, l. 15: “n_” instead of “N”?

p. 11, Fig. 5: something seems to be wrong with the fit curves, e.g., the yellow line separates the yellow symbols such that 2 points are above the line and 9 points are below the line. For the blue curve, the situation is similar, which should not be the case if all points are weighted equally.

p. 12, l. 26: “suggests”

p. 12, l. 27: “were”

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