

The study by Jen et al. evaluates the capabilities of two different primary ions (nitrate and acetate) in ionizing clusters composed of sulfuric acid and dimethylamine (DMA), ethylene diamine (EDA), tetramethylethylenediamine (TMEDA), or butanediamine/putrescine (PUT). Such clusters could in principle explain atmospheric new particle formation (NPF) since the produced neutral clusters have low evaporation rates.

The neutral clusters were formed in a flow reactor at ~300 K and at 30% relative humidity. A chemical ionization mass spectrometer (cluster CIMS) was used to detect the clusters after they reacted with nitrate or acetate primary ions used for the chemical ionization. Since the formed neutral clusters can contain equal numbers of acid and base molecules their reduced acidity could make them less susceptible towards ionization by nitrate in comparison to acetate primary ions.

Indeed, the presented results indicate that some clusters can very likely not be ionized efficiently by nitrate (e.g. the sulfuric acid dimer containing two diamines, or the trimer containing DMA or diamines).

In atmospheric studies nitrate chemical ionization is generally used for measuring sulfuric acid and its influence on NPF. If some atmospheric NPF is due to sulfuric acid and amines or diamines its importance could be significantly underestimated because the absence of sulfuric acid clusters would not necessarily indicate that sulfuric acid-amine NPF is not proceeding.

For this reason the manuscript by Jen et al. is a very important contribution and will help the interpretation of the mass spectra obtained in ambient and chamber CIMS measurements. The paper is very well-written and I have no serious comments. I therefore recommend its publication after addressing the points listed in the following:

Line 31: add a space before the bracket and also between the references (after the semicolon, please check the whole manuscript)

Line 145: opening bracket is missing before  $A_m.B_2$

Line 171: “factor of 2 below”, does this mean all concentrations are upper estimates?

Figure 2: By comparing the panels a) and b) for the trimer it is not clear why the trimer in panel b) is >10 times higher for acetate than for nitrate. The trimer signals in panel a) are dominated by the cluster containing 3 acids and 1 base, however these signals seem to be quite similar for acetate and nitrate.

Figure 4: This figure seems to show signals for  $A^-.Put$ , which is surprising given the fact that in the DMA system,  $A^-.DMA$  evaporates very rapidly. It would be good to include some discussion about the presence of  $A^-.Put$ .

Line 249 and SI equation S6: Equation S6 includes the difference between  $k_{21}$  (reaction between  $H_2SO_4$  and  $HSO_4^-$ ) and  $k_1$  (reaction between  $H_2SO_4$  and  $NO_3^-$ ) in the denominator of the equation. It seems that these values are identical ( $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ), therefore this would lead to a zero division. Please clarify.

Line 268 and line 246: two (slightly) different values for the ion-molecule reaction rates are given here. I would recommend to use the same value in the model and in equation 1.

Line 293: please provide the value of the rate constant  $k_{21}$  here; this should be done for all rates by including their values in parentheses

Line 329: “efficiently” instead of “inefficiently”?

Figure 7: The figure caption states a value of  $4 \times 10^9 \text{ cm}^{-3}$  for the initial sulfuric acid concentration. However, in the legends different values for  $[A_1]$  are given. Are these the concentrations after the 3 s reaction time? If so, please mention this in the figure caption.

Line 374: Do these evaporation rates refer to the evaporation of DMA or A?

Line 425: better use “sources of dimer ions” than “dimer ion sources”

Table 3: for the neutral pathway it seems the reaction  $A_3B_2 + B$  is missing

Line 466: do you mean “low” instead of “high”?

References: please use same style for all references, i.e. remove hyperlinks and add page numbers for all references, etc.

SI, Line 39: “ $\text{cm}^{-3}$ ” instead of “ $\text{cm}^3$ ”, also better to use “ $\text{s}^{-1}$ ” instead of “Hz”

SI, Equation S6: see comment above

Table S1: In a previous paper by the same authors (Jen et al., 2016, GRL) it was concluded that diamines are a more potent source of new particles in comparison with DMA. However, from the evaporation rates listed in Table 1 this conclusion does not seem to be supported due to the rather high evaporation rates  $E_1$  for the diamines (50 times higher than for DMA) and the crucial role of  $A_1B_1$  in terms of cluster formation. How can this discrepancy be explained and how does it affect the conclusions from the present paper?