Final response

The authors wish to thank both referees for their comments, which have helped make the manuscript clearer and more thorough. Overall, we have corrected some typographical errors, as well as some rounding errors in the listed evaporation rates. In addition we have made changes according to the referees' comments. Responses to each individual comment are presented below.

Best regards, Kai Ruusuvuori

Anonymous Referee #1

P11013, "Since electric fields can be used to manipulate the trajectories of ions, which makes charged particles easier to detect than neutral ones, sample air is often charged." To the best of my knowledge, this is not the main reason why sample air needs to be charged. Rather it must be charged because the detector can only probe ions and it cannot detect (neutral) molecules.

The referee is correct in pointing out that charging is also needed for detection, but especially in time of flight mass spectrometry the ions are focused and have to travel specific trajectory before hitting the detector. So, charging is also needed for guiding the ions. However, if talking about atmospheric pressure applications and detection with electrometers the main reason for charging is indeed the detection like the referee pointed out. We have revised the text to make it clearer and more accurate.

P11014, "The disadvantages are that if there are bases in the sample with an even higher proton affinity than the molecule species we wish to detect, these molecules may end up receiving most of the charge." Charge distribution depends not only on properties of the detected molecules (e.g., proton affinity if the ion molecule reactions follow proton transfer), but also on the amounts (or concentrations) of the molecules presented in the sample.

We agree with referee. The text has been changed to:

"The disadvantage is that if there are high enough concentrations of bases in the sample with an even higher proton affinity than the molecule species we wish to detect, these molecules may end up receiving most of the charge."

P11014, "CI is not the only measurement technique that takes advantage of different proton affinities. For example, a similar approach to charging is used also in ion mobility spectrometry (IMS) with doped gases (Puton et al., 2008)." That is still chemical ionization. What make it special is that the species involving in chemical ionization affect the ionization scheme but in principal it is still CI.

We agree with referee. The sentence has been changed to:

"CI mass spectrometry is not the …"

P11014, the second paragraph talks about ion molecule reactions that include two types: proton transfer reaction vs association reaction. The association reaction rate constant would be more complicated than the proton transfer one which was related to proton affinity. The association reactions might also involve three body reactions. This paragraph is quite confused in the current presentation.

The chapter tries to describe the inadequacy of proton affinity in describing the interactions between molecules. We have attempted to clarify the chapter. Our main argument is that all the proton transfer reactions start by an association reaction, after which the proton may transfer, and finally the cluster will evaporate if it is not stable.

P11018, the first paragraph, even for a simple system composed of sulfuric acid, dimethyl amine, and water, before ionization, how accurate the molecule/cluster distribution is? Also, it seems that the quantity of fraction of DMA bound to sulfuric acid or its clusters does not give any useful information because when DMA concentration is very high, the limiting species for bounding is sulfuric acid not DMA so that the fraction will be inevitable small.

The chapter describes a simulated cluster distribution. The simulations in general contain approximations and simplifications used in calculating the quantum chemical free energies of the clusters. However, the calculated changes in free energies are expected to be accurate to within a couple of kcal/mol for the simulated clusters. This can lead to some quantitative error, but qualitative results are expected to be correct. In addition, the simulated system does not contain water molecules, since the necessary quantum chemical data related to all the relevant clusters is not yet available. Based on the results by Henschel et al. (2014), the sulfuric acid monomers and $(SA)_1(DMA)_1$ clusters would on average have less than two water molecules even at relative humidity (RH) of 90%, and less than one water molecule at RH 15%. Dimethylamine monomers on the other hand will not get hydrated (Olenius et al., 2014). Since we were interested mainly in how the DMA would be charged, and since no water was seen in the experiments, possible hydration was assumed to have little importance for the qualitative results.

The referee is correct in pointing out that the amount of sulfuric acid compared to the amount of DMA affects the relative concentrations. We agree that fraction of DMA bound to sulfuric acid – only sulfuric acid, not sulfuric acid clusters – tells little more than that the initial distribution consists of mostly monomers even with the lowest DMA concentration combined with the highest SA concentration. However, we feel that in the name of completeness, the initial conditions should be described as accurately as they have been.

Some slight clarifications and additions have been made to the text in this chapter.

It is strongly urged that the authors attach all the reaction schemes including all possible neutral and ion reactions in the supplementary material so that the readers can have better understanding how the ion- or neutral products are produced in the *model simulation. In the text, it seems that a lot of ion molecule reactions and the evaporation reactions are speculative and the authors seem to make an impression that those speculations favor the modeling results.*

Even with our limited system size, the simulation contains 21 species of molecules and clusters. Collisions are allowed between all molecules and clusters, leading to 210 possible cluster formation reactions. Some of these will result in clusters that are larger than the allowed size and these are treated as is described in the manuscript. The clusters that are within the allowed cluster size may, in turn, evaporate into smaller clusters and/or monomers in several different ways. We thus feel that listing all possible reaction schemes explicitly in the supplementary would result in an overwhelming amount of reactions and thus not have the desired effect. We do agree, however, that the manuscript could be clearer on how the dominant reactions have been identified – namely, the ACDC code allows us to look at the fluxes to and from different cluster sizes during the simulation, which is what we have done. We have made small changes in the text regarding the dominant reactions related to the formation of the obtained cluster types, and added an explanation of where these are obtained from in Chapter 2. We have also added evaporation rates for all clusters and their evaporation reactions in Table 2 (instead of only the ones listed in Figure 5). In addition, we have added a table containing the delta E, delta H, delta G and delta S for all allowed clusters as well as a table containing the dipole moments and polarizabilities of the allowed neutral clusters and monomers in the supplementary. The supplementary material also contains Cartesian coordinates for the most stable structure of each cluster, optimized at the B3LYP/CBSB7 level.

P11024, "there is no way of knowing if the detector does not count an ion that hits it." The authors appear to be lack of knowledge how the detector works in the mass spectrometer. The counting rate itself is an average parameter, no matter how short the time used for collecting the counts. The actual concentration of an ion cannot be only determined by the counting rate. An overall transmission efficiency must be known in order to calculate the ion concentration. The concentration of the corresponding neutral species can be estimated from ratio of counting rate of the ion to that of the reagent ion, provided that the transmission efficiencies of both ions are known.

The sentence in brackets is not very clear. The referee is correct with regard to how the detector works. We know that the overall transmission of the ions is 0.5-1% (the method is described in Junninen et al., 2010) and the concentrations of the neutral molecule are calculated as described by the referee. However, no conversion from counts per second to concentrations has been performed in the manuscript. The sentence mentioned by the referee has been removed from the paper and the text has been further clarified with regard to the format of the data.

P11025-28, about charging efficiency. No matter what advanced technology is used, the charging efficiencies for molecules and clusters will remain low. It is impossible that all of them can be charged, that is, charging efficiencies are far below 1. So in the sample flow, the corresponding neutral components are still the majorities. In *fact, in Fig. 2, a charging efficiency for DMA can be estimated based on the modeled concentration and the initial concentration introduced.*

We agree that the charging efficiency is not unity. None of the simulations led to a situation, where all of the molecules were charged and only the effect of SA concentration on the charging efficiency was discussed. It is thus unclear to us which changes, if any, the referee would like to see in the manuscript.

The experimental section, regarding the reagent ion (or the total ion) concentration. In the dynamic simulation, an arbitrary upper concentration can be used, for example, up to 10ˆ12 cmˆ-3. However, in reality, it is very difficult to obtain such high ion concentration. Depending on the ionization technique used, it is usually below 10ˆ8 cm-3.

We agree with the referee, the charger ion concentration of 10^{12} cm^{-3} is not realistic and is included purely as a hypothetical test case. The text has been clarified on this.

As shown in the paper, there are several discrepancies between results from the cluster dynamic simulation and those from the experiment: 1) The presence of different major ions in the simulations and in the experiments; 2) The depletion of primary ions. The reasons for those discrepancies are unknown and the authors speculate that they might partially arise from the steric effects so that a sub-collision rate is proposed for the ion molecule reactions, and that the CI-APi-TOF might be subject to some fragmentation. I would have my reservation to those explanations. The discrepancies would indicate that the mechanism of the ion chemistry shown from the experiments is not the same as proposed in the modeling simulations. One possible reason would be: the presence of major $H^+AC{\cdot}DMA$ *ion implies existence of a dominant ion molecule reaction* $H^+(AC)_2 + DMA \rightarrow H^+(AC){\cdot}DMA + AC$ *and also the reaction rate constant of this reaction would be far smaller than the corresponding collision rate, as the reagent ions are not depleted in the experiment and are depleted from the modeled results. Then the minor* H^+DMA *can be easily explained from the evaporation of one AC from the ion* $H^+AC{\cdot}DMA$ *in the vacuum chamber.*

We agree that there may be other reasons for the discrepancies than those listed in the manuscript. Some room for speculation would remain even in the case that the simulation results and experimental results would match. Since the measurement data itself had unexpected features - as described in the manuscript - it is our view that a thorough test of the various possible sources for the discrepancies is beyond the scope of this, mainly theoretical paper due to the amount of experimental work needed. Instead, the manuscript should be seen as a first step in the attempt to qualitatively model the chemical ionization process within a measurement device. We are hoping that future work by us and other groups will further our understanding of the mechanisms involved and their importance.

Anonymous Referee #2

1) The authors claimed that a previous work (Yu and Lee., 2012) with ethanol ion chemistry may suffer artifacts due to the less selective nature. As Yu and Lee (2012) used a quadrupole system, the ToF system, the authors utilized should provide much higher mass resolution in the level of the enough separation of potential artifacts. At least the authors should present convincing arguments or specific examples why more selective ion chemistry is required to properly quantity atmospheric amines even with the ToF system by sacrificing sensitivity.

We have not made any claims concerning possible artifacts in the work of Yu and Lee. Furthermore, the choice between reagent ions is complex and a universally correct answer does not exist. The referee is right in pointing out, that the usage of a TOF instead of a quadrupole mass spectrometer helps reliably identify measured ions and avoid counting overlapping peaks as the product ions. However, if interfering compounds have similar elemental compositions as the molecule of interest, the higher mass separation of TOF does not help anymore. Here the more selective ionization scheme becomes important. There is also a practical reason to consider when choosing an ionization reagent: acetone is an easier chemical to purchase than ethanol. Purchasing ethanol involves getting permissions and doing paperwork (the complexity varies from country to country).

2) The experimental method is very poorly described in two fronts. First, More thorough descriptions on calibration techniques (e.g. calibration curve) and the lower detection limit should be presented. Especially, for sticky compounds like amine, the authors should thoroughly describe how they prevent and characterize the wall loss. It is also unclear how the DMA standard permeation rate is characterized.

The scope of the paper is to investigate the charging of DMA using acetone. The emphases are on theoretical and computational investigation of the charging mechanism inside the CI-inlet. The referee is correct in pointing out that the instrument description with calibration, sensitivity and limit of detection is not discussed thoroughly, but the paper does not include any ambient data and concentrations are not reported, only average ion counts per second. This makes the discussion on sampling and calibration artifacts largely irrelevant considering the topic of the paper. The methods chapter in the paper has been changed to clarify the fact that ambient concentrations of DMA are not used.

The DMA standard permeation rate was obtained from manufacturer of the permeation tubes (VICI, rate: 12ng/min +/- 50% at 40C). For permeation we used commercially available gas calibrator (Ansyco Sycos Kt-PM2) that consist of permeation oven with temperature control and gas dilution system with mass flow controllers. The resulted known DMA standard gas was further diluted using ambient air. This information is added to the paper.

3) The more extensive field observational dataset should be presented. In the same context as pointed out in 2), the authors should describe how an inlet was configured for the field observations. It is also highly unclear the time frame and duration of the presented observational data points. Therefore, It is impossible to determine the statistical validity and representativeness of the presented observational data points.

Related to the comment above the paper does not contain ambient data and is focused on theoretical investigation on charging mechanism. As stated in the response to the previous comment, the methods chapter in the paper has been changed to clarify the fact that ambient concentrations of DMA are not used.

References:

Henschel, H., Acosta Navarro, J. C., Yli-Juuti, T., Kupiainen-Määttä, O., Olenius, T., Ortega, I. K., Clegg, S. L., Kurtén, T., Riipinen, I., and Vehkamäki, H., The Journal of Physical Chemistry A, 118, 14, 2599-2611, 2014.

Olenius, T., Kurtén, T., Kupiainen-Määttä, O., Henschel, H., Ortega, I. K., and Vehkamäki, H., Aerosol Science and Technology, 48, 6, 593-603, 2014.