

Interactive comment on “The charging of neutral dimethylamine and dimethylamine-sulphuric acid clusters using protonated acetone” by K. Ruusuvuori et al.

Anonymous Referee #1

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This paper uses quantum chemical calculations and cluster dynamic codes to investigate the charging process of a base compound, dimethylamine, and its sulfuric acid clusters, although a small portion of the manuscript is devoted to experimental examination for comparison. While base compounds were recently found to greatly enhance atmospheric particle formation, their atmospheric concentrations and distributions need to be better known. Currently several in-situ measurement techniques have been developed including chemical ionization mass spectrometry (CIMS) for measurements of amines/ammonia. The CIMS method employs several different reagents (e.g., water, acetone, ethanol etc) for different targeted amines. This study focuses on the

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charging process involving protonated acetone as the reagent. While the study itself is interesting to the reader of atmospheric particle formation, it might also cause confusion and misleading if the authors are lack of basic understanding of experimental ion chemistry, which is indeed reflected in the manuscript presentation. Attempting to fully explain observations using quantum chemical calculations and cluster dynamic modeling based on quantum calculations is not realistic, not even convincing if the theory has large uncertainties/errors. The presentation has a lot of misunderstanding of the ion chemistry and instrumentation when describing the detailed experimental processes. The authors ought to rewrite those descriptions. Below are detailed comments:

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.

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.

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.

P11014, the second paragraph talks about ion molecule reactions that include two types: proton transfer reaction vs association reaction. The association reaction rate

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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.

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.

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.

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.

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

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fact, in Fig. 2, a charging efficiency for DMA can be estimated based on the modeled concentration and the initial concentration introduced.

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 10^{12} cm^{-3} . However, in reality, it is very difficult to obtain such high ion concentration. Depending on the ionization technique used, it is usually below 10^8 cm^{-3} .

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 $\text{H}^+\cdot\text{AC}\cdot\text{DMA}$ ion implies existence of a dominant ion molecule reaction $\text{H}^+\cdot(\text{AC})_2 + \text{DMA} \rightarrow \text{H}^+\cdot(\text{AC})\cdot\text{DMA} + \text{AC}$ 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 $\text{H}^+\cdot\text{DMA}$ can be easily explained from the evaporation of one AC from the ion $\text{H}^+\cdot\text{AC}\cdot\text{DMA}$ in the vacuum chamber.

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