Response to Anonymous Referee #2

We thank the referee for providing helpful comments. We respond to these comments **in bold** below.

1. Some of the introduction has to do with nucleation in the troposphere which is mostly through non-ion processes (some might call them neutral) which seems to be addressed by this research only indirectly: if not addressable directly, these parts can be pared down significantly. In place, please add some experimental details.

   We feel that the introduction section needs to briefly review two topics: 1) what is known about amine-ammonia chemistry in the early stages of particle formation and growth; 2) how can ambient clusters be chemically characterized. These are the driving forces for our study – nucleation is the atmospheric process we ultimately want to elucidate, and chemical characterization of ambient clusters by mass spectrometry requires detection of ions. Therefore, we believe the organization and content of the introduction section is appropriate.

2. The terminology of neutralized and un-neutralized to described the ratio of base to acid is a little confusing when trying to understand ions of different polarities and also in trying to make some statements about non-ion clusters (neutral.)

   In the revised manuscript, we will ensure that each reference to neutralization is clearly linked to bisulfate (e.g. "neutralized to bisulfate"). We will adjust accordingly any wording that could be considered ambiguous.

3. Please expand on the following experimental topics to help the reader. At least summarize briefly if explained in detail elsewhere.
   a. How accurately is the concentration of amine/ammonia known? How was it determined? Uncertainties are 1 sigma? Precision? Accuracy?

      We measure the pressure by an ionization gauge in the ion cyclotron resonance (ICR) cell. However, due to effects associated with the external magnetic field and the polarizability of the gas being measured, the pressure reading from the ionization gauge does not correspond exactly to the absolute pressure. We therefore use a correction factor that is described in detail in Bzdek et al. (2010a). Uncertainties in the pressure arise from uncertainties in 1) the ionization gauge precision and 2) polarizability of the measured gas. Propagation of these uncertainties results in a total uncertainty of about 20% (one sigma), which we assign to all pressure reading values reported in the text. In the revised manuscript, we will add a sentence to indicate where this information can be found.

b. The conditions inside the ICFTR are not representative of the atmosphere.

The reviewer is correct in noting that the conditions inside the ICR are not representative of the atmosphere. Specifically, temperature is not well-defined in this experiment and RH is zero. However, we feel the presence of vacuum does not significantly alter our conclusions. With regard to temperature / internal energy, we performed an experiment in our previous work where we held positively-charged ions in the ICR cell and exposed them to a low pressure of unreactive argon gas or to no gas whatsoever (Bzdek et al., 2010a). Exposure time was varied in order to investigate the time-dependent stability of these clusters. Cluster distributions did not change with increasing residence time in the ICR cell, indicating that the ions initially trapped in the ICR cell are sufficiently stable that they do not undergo ancillary reactions in addition to those due to exposure to a reactive gas. We discuss the role of water in our response to comment 3d. In the revised manuscript, we will add an additional paragraph at the end of Section 4 (Atmospheric implications) to address the limitations of this work in terms of atmospheric relevance. Additionally, in the revised manuscript we will add a paragraph at the end of Section 3.1 (Electrospray of ammonium sulfate and dimethylammonium sulfate solutions) to address the potential effects on cluster composition due to the presence of vacuum.

c. What about high pressure limits? The addition steps are likely to be influenced by a bath gas.

Because these experiments were performed in a vacuum, the temperature is not as well defined as it would be at the high pressure (e.g. 1 atm) of a bath gas. Since the addition reactions occur at reasonable rates, they are likely to be thermodynamically favorable. The energy released from these reactions is not likely to affect the results. In previous work (Bzdek et al., 2011) and in this work, we examined the effect of internal energy and cluster decomposition on the measured rate constants. These models indicated that measured rate constants were larger than the actual rate constants because of cluster decomposition upon reaction, but that the difference was relatively small and therefore would not significantly impact the conclusions of our work. Additionally, with regard to internal energy, we performed an experiment in our previous work (Bzdek et al., 2010a) where we held positively-charged ions in the ICR cell and

exposed them to a low pressure of unreactive argon gas or to no gas whatsoever (see response to comment 3b, above).

d. In the atmosphere, many ions will be heavily hydrated. It is likely that rates will be affected but also perhaps thermodynamics. Please address this here.

   The effect of water is an important topic that merits study. However, our experimental method did not permit us to address this topic. Amine substitution for ammonia in these clusters is driven by the large difference in gas phase basicity between the two molecules (Bzdek et al., 2010a). Solvation and cation-anion binding effects also play a role but the magnitude is much smaller. Therefore, it is unlikely that the presence of water in the cluster will make substitution less efficient. Addressing the role of water will require different experimental methods. In the revised manuscript, we will include a paragraph at the end of Section 4 (Atmospheric implications) to address the limitations of this work.

4. The laboratory work on sulfuric clusters of Curtius, Lovejoy and Froyd and its application to atmospheric clusters (Eisele et al. JGR 2006) should be compared to these results. Their results can help guide the discussion in this paper. The paper would be improved by having a more focused and quantitive statements about how the results apply to the atmosphere. With detection of ambient ions, can you make any quantitative statements? Are your results consistent with observations? Are there perhaps direct (but maybe qualitative) cautions this work implies for these type of measurements?

   We agree that some of the work from these groups merits addition to the paper. In the revised manuscript, we will add references to Hanson and Eisele (2002) in the discussion of the electrospray ionization mass spectra (Section 3.1) and in the discussion of the reactivity of negatively-charged ammonium bisulfate clusters (Section 3.2). Additionally, we will compare our results to those of Eisele et al. (2006) (Section 4). What we can say quantitatively about ambient ions is how quickly and in what manners they will transform upon collision with amine molecules in the atmosphere. The results of this work, combined with those of our previous experiments on positive ions (Bzdek et al., 2010a, b;Bzdek et al., 2011), indicate that ammonium salt clusters in the 1-2 nm size range would be expected to quickly react with amine to form aminium salts upon atmospheric collision of the ammonium salt with the gas-phase amine. Based on the addition kinetics, we can infer that when ambient concentrations of ammonia and amine are comparable, amine chemistry will likely compete favorably with ammonia chemistry.

5. Then, separate from this, how they might apply to measurements of neutral clusters (as in Zhao et al.) in the atmosphere. For example, you might want to give an example of a neutral cluster of 4 H2SO4 and 4 NH3 (the waters of hydration can be stated to be assumed to act as bystanders.) Once ionized, what happens to it? How would with this vary with ion exposure time to amines? Some of the laboratory cluster work of Eisele and Hanson circa 2001 has some information about species loss upon ionization. How much better (or worse) would the amines remain on the ion? Would positive work better than negative, to retain the base content?

    From these experiments, we do not learn directly about neutral cluster composition. Specifically, this work does not inform about what transformations would occur upon ionization of a neutral cluster, as the clusters ultimately trapped in the ICR cell result from larger metastable charged clusters that dissociate as they travel into and through the mass spectrometer (Bzdek et al., 2010b). However, once these clusters are ionized, the charged clusters would continue to react according to the kinetics discussed in this work. In the revised manuscript, we will include a paragraph at the end of Section 4 (Atmospheric implications) to discuss the limitations of this work in terms of neutral clusters.

References:

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