

Interactive comment on “Comparative study on the heterogeneous reaction between methylamine and ammonium salts” by Y. Liu et al.

Anonymous Referee #2

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The authors measured the uptake coefficients of methylamine (MA) by NH_4NO_3 , NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 using a Knudsen cell reactor coupled with a quadrupole mass spectrometer and they also probed the chemical changes in the reacted ammonium salts by in situ Raman spectroscopy. The exchange of ammonium by MA in NH_4NO_3 , NH_4Cl were found to be reversible. On the other hand, irreversible exchange reaction and simple acid-base reaction for MA was found taking place on $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 , respectively. Based on density functional theory, it is proposed that the uptake coefficients of NH_4NO_3 , NH_4Cl and $(\text{NH}_4)_2\text{SO}_4$ were linearly correlated with the electrostatic potentials of ammonium ions in these salts. However, it should be noted that a number of related and similar studies of exchange/displacement of ammonium has been published recently. They include the measurements of uptake coefficients (e.g. Wang 2010 EST 44(7)) and chemical identification of reacted salt

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(e.g. Chan 2012 AST 46(2)). The authors need to clearly address the novelty and impacts of the current work in addition to the literature. Major comments: 1) The current work were conducted at much lower RH compared to the ambient which would limit experiments on “dried” salts only. How would the data of “dry” crystalline salts be useful in explaining the uptake by aqueous and amorphous atmospheric particles? What data treatments are needed?

2) Line 302: The authors may need to conduct further experiments on larger amines such as the di- and tri- methylamines to elucidate the mass transfer limitation in ammonium salts. This may add implication to this work.

3) Line 319: The authors has pointed out that there are differences between the measured uptake coefficients in this work and those in the literature. Would the authors comment on the quality and uncertainty of the data in this work and in the literature?

Other comments: 1) Line 219, the authors have concluded that $\text{CH}_3\text{NH}_3(\text{NH}_4)\text{SO}_4$ was formed after the reaction. Is $\text{CH}_3\text{NH}_3(\text{NH}_4)\text{SO}_4$ a stable salt? How would $\text{CH}_3\text{NH}_3(\text{NH}_4)\text{SO}_4$ be differentiated from a mixture of $(\text{NH}_4)_2\text{SO}_4/(\text{CH}_3\text{NH}_3)_2\text{SO}_4$ using Raman?

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 165, 2012.