

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

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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

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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 (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.

Response: We thank Referee #2 for the comments and suggestions on our manuscript. As you said, some papers have reported the exchange reactions of ammonium. We also highlighted these work in our manuscript (page 167, line 30, and page 168, lines 1-10). The newest results (Chan and Chan, 2012) were also added in our revised paper as follows. “Recently, Chan and Chan (2012) also confirmed the displacement reaction between triethylamine (TEA) and $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 , NH_4NO_3 , NH_4Cl and $(\text{NH}_4)_2\text{CO}_3$ using in situ Raman spectroscopy”. However, our paper is mainly focused on the difference in reactivity of MA on ammonium salts. We established a structure-reactivity relationship for the reaction between MA and ammonium salts. This is the first time to investigate this issue. It is also the first time to report the uptake coefficients of MA on NH_4NO_3 , NH_4HSO_4 , and NH_4Cl . In our manuscript (page 168, Lines 10-11), we have pointed out that at present date, it is not clear yet that how the property of inorganic ammonium salts affects the reactivity for this reaction. This might be not so strong. As you suggested, we further addressed this issue more clearly in our revised manuscript as follows: “At present date, the reported uptake coefficients showed a discrepancy among different ammonium salts. However, it is hard to directly compare these results because of the difference in reaction conditions, such as the particle size, the type of amines and ammonium salts, and the reaction temperature used in experiments and so on. On the other hand, the relatively few kinetic data is available for one kind of amine. For example, for MA, only one paper (Qiu et al., 2011) reported its uptake coefficient on $(\text{NH}_4)_2\text{SO}_4$. The uptake coefficients of MA on other salts are unknown. Thus, it is not clear yet that how the property of inorganic ammonium salts affects the reactivity for this reaction. In this study, we investigated the heterogeneous uptake of MA on NH_4HSO_4 , $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 and NH_4Cl to understand the effect of ammonium salts on their reactivity with MA.

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We established for the first time the structure-reactivity relationship between MA and ammonium salts.”

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?

Response: Thank you. Knudsen cell reactor is a low pressure reactor. Thus, the effect of water on the heterogeneous reaction can not be considered in this study and our work was conducted under dry condition. Recently, Chan and Chan (2012) found that aqueous salts of $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 and NH_4Cl show higher degree of exchange reaction to TEA. It implies the uptake coefficients of MA on these salts might also be larger under ambient RH than these measured under dry conditions. In ambient environments, however, low RH conditions may also induce potential crystallization of these ammonium salts (Clegg et al., 1998). Thus, as the low limits for uptake coefficient of MA onto ammonium salts, the measurements in this study at least suggest that amines uptake onto pre-existing ammonium salts even under dry conditions may contribute, under particular circumstances, as high concentrations of ammonium salts and low concentration of acidic gas species, to the atmospheric source of particulate amines. This paragraph was also added in our revised manuscript. Of course, the uptake coefficients of MA under higher RH need to be measured using other instruments such as flow tube reactor in the future. Chan and Chan (2012) also found enhanced amine uptake by amorphous NH_4NO_3 over crystalline NH_4NO_3 . In order to compare the difference in reactivity of ammonium salts with MA, crystalline salts with the similar specific surface area was used in this study to simplify the influencing factors.

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.

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Response: Thanks. According to your suggestion, we further measured the uptake of amines on some other samples. As shown in Fig. 1R, linear dependent relationship was not observed for DMA on both NH_4Cl and NH_4NO_3 and TMA on NH_4NO_3 , while it was observed for MA, DMA, TMA on humic acid (this will be discussed in another paper).

Fig. 1R. LMD relationship between $\gamma(\text{obs})$ and sample mass.

In Knudsen cell reactor, the diffusion of reactive molecules from gas-phase to particle surface is eliminated because molecular flow regime is realized under low pressure in the reactor. However, the diffusion of reactive molecules in the particle beds might happen. Several papers have discussed this question (Keyser et al., 1991; Underwood et al., 2001; Grassian, 2002) and also put forward several solutions such as KML model (Keyser et al., 1991), LMD model (Underwood et al., 2001; Grassian, 2002) and FPL model (Hoffman, et al., 2003). Based on KML model, Underwood et al. (2001) developed a linear mass dependent (LMD) model, which is widely used in Knudsen cell experiments. That's,

$$\gamma(\text{obs}) = \gamma(\text{t}) * m(\text{eff}) * S(\text{BET}) / A(\text{g}) \quad (1)$$

where, $\gamma(\text{obs})$ and $\gamma(\text{t})$ are the observed uptake coefficient and the true uptake coefficient; $m(\text{eff})$ is the effective sample mass; $S(\text{BET})$ is the specific surface area of sample; $A(\text{g})$ is the geometric area of the sample holder. Thus, the $\gamma(\text{t})$ can be determined by measuring the $m(\text{eff})$ or probe depth of reactive molecules in multilayer powder sample. The probe depth can be measured by response of the $\gamma(\text{obs})$ with sample mass if the powder sample can evenly cover the sample holder. The probe depth is a function of several parameters including density, pore size and particle size of powder sample, diffusion constant (D_f) of reactive molecules and the $\gamma(\text{t})$ of reactive molecules on powder sample. For a given sample, the probe depth is determined by D_f and $\gamma(\text{t})$ (Underwood et al., 2001). If the $\gamma(\text{t})$ is small, and the D_f is large enough, a linear mass dependent relationship between

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gamma(obs) and sample mass should be observed. As discussed in our manuscript (page 177, lines 6-10), many reaction system showed this linear relationship. However, if the gamma(t) is large enough with a small Df, uptake of reactive molecules should be confined on the surface and diffusion of reactive molecules into the underlayers can not be detected. We also measured the response of gamma(obs) to sample mass in this study. However, gamma(obs) did not change with sample mass for MA on these salts. Qiu et al. (2012) also found that gamma(obs) did not change with sample mass for uptake of MA, DMA, and TMA on (NH₄)₂SO₄. As discussed above, the probe depth is determined by Df and gamma(t) for a given particle sample. Both of these two parameters are determined by the interaction between the particle sample and the reactive gas molecule. Therefore, we think the response of gamma(obs) to sample mass just reflects the relative value of Df and gamma(t) for a given reaction system and it is reasonable to postulate that a large gamma(t) of MA on these salts.

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?

Response: At present, only one paper reported the uptake coefficient of MA on (NH₄)₂SO₄ to be 2.6×10^{-2} - 3.4×10^{-2} using a flow tube reactor (Qiu et al., 2011). It is about four times as much as ours. We think the main reason for this difference might be resulted from the discrepancy in particle sizes or morphology of salt sample. Recently, Chan and Chan (2012) found that amorphous NH₄NO₃ and NH₄HSO₄ showed higher degree of exchange reaction to TEA than that of crystalline NH₄NO₃ and NH₄HSO₄. Qiu et al. (2011) used amorphous (NH₄)₂SO₄, while we used crystalline (NH₄)₂SO₄ in this work. In our manuscript (page 177, line 22 - page 178, line 4), we compared our data with them. In our revised manuscript, we also further discussed this question in detail as follows. The uptake coefficients of MA onto (NH₄)₂SO₄, NH₄Cl and NH₄NO₃ measured in this work are comparable to that of TMA on NH₄NO₃ ($2 \pm 2 \times 10^{-3}$) reported by Lloyd et al. (2009), while they are two orders of magnitude lower

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than the values for DMA and TMA uptake on clusters of NH₄HSO₄ and NH₄NO₃ reported by Bzdek et al. (2010a, b). The uptake coefficient of MA onto NH₄HSO₄ is comparable to that on sulfuric acid (Wang et al., 2010a). As for the uptake of MA on (NH₄)₂SO₄, uptake coefficients were slightly lower than the value (2.6×10^{-2} - 3.4×10^{-2}) reported by Qiu et al. (2011). Recently, Chan and Chan (2012) found that amorphous NH₄NO₃ and NH₄HSO₄ showed higher degree of exchange reaction to TEA than that of crystalline NH₄NO₃ and NH₄HSO₄. Thus, the difference in the uptake coefficient may be ascribed to different reaction systems, different samples with different particle sizes or morphology. In the studies by Bzdek et al (2010a, b), for example, 1-2 nm clusters of bisulfate or nitrate were used, and amorphous (NH₄)₂SO₄ was used by Qiu et al. (2011); while crystal samples were used in the present study. In ambient environments, however, low RH conditions may also induce potential crystallization of these ammonium salts (Clegg et al., 1998). Thus, the uptake coefficients reported here should represent the low limits for uptake of MA on ammonium salts.

Other comments: 1) Line 219, the authors have concluded that CH₃NH₃(NH₄)SO₄ was formed after the reaction. Is CH₃NH₃(NH₄)SO₄ a stable salt? How would CH₃NH₃(NH₄)SO₄ be differentiated from a mixture of (NH₄)₂SO₄/(CH₃NH₃)₂SO₄ using Raman?

Response: As shown in Fig. 3, no desorption of MA and NH₃ was observed at 298 K from MA treated (NH₄)₂SO₄ and NH₄HSO₄ samples. On the other hand, release of NH₃ was not observed during uptake of MA by NH₄HSO₄ in Fig. 1, while it does for the reaction between MA and (NH₄)₂SO₄. Thus, we conclude that CH₃NH₃(NH₄)SO₄ was formed on NH₄HSO₄ and CH₃NH₃(NH₄)SO₄ or (CH₃NH₃)₂SO₄ might be formed on (NH₄)₂SO₄. Based on these results we can also concluded that CH₃NH₃(NH₄)SO₄ or (CH₃NH₃)₂SO₄ is stable even under high vacuum condition. This was discussed in section 3.2. Using Raman, it is difficult to differentiate CH₃NH₃(NH₄)SO₄ from a mixture of (NH₄)₂SO₄/(CH₃NH₃)₂SO₄ because of their high similarity in groups. On the other hand, the degree of exchange reaction

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was very low (<1% in Knudsen cell reactor) in our experiment. Thus, Raman spectra should reflect the information from both the unreacted salts and surface products. Fig. 2R comprised the Raman spectra for MA exchanged (NH₄)₂SO₄ (black line) and NH₄H₂SO₄ (red line), and pure (NH₄)₂SO₄ (black dot line) and NH₄H₂SO₄ (red dot line). Apart from the peaks at 1008 (C-N) and 1470 cm⁻¹ (CH₃ deformation) in MA exchanged NH₄H₂SO₄, the main difference between MA exchanged (NH₄)₂SO₄ and MA exchanged NH₄H₂SO₄ was originated from the difference between (NH₄)₂SO₄ and NH₄H₂SO₄. So, it is very difficult to discern the subtlety of the distinctions between CH₃NH₃(NH₄)SO₄ and (NH₄)₂SO₄/(CH₃NH₃)₂SO₄.

Fig. 2R. Comparison of Raman spectra for MA exchanged (NH₄)₂SO₄ (black line) and NH₄H₂SO₄ (red line), and pure (NH₄)₂SO₄ (black dot line) and NH₄H₂SO₄ (red dot line).

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and γ -Al₂O₃. *Atmos. Environ.*, 42, 960-969, 2008.

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Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/12/C1213/2012/acpd-12-C1213-2012-supplement.pdf>

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

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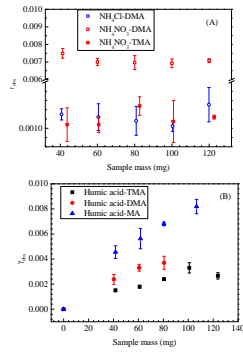


Fig.1R

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Fig. 1.

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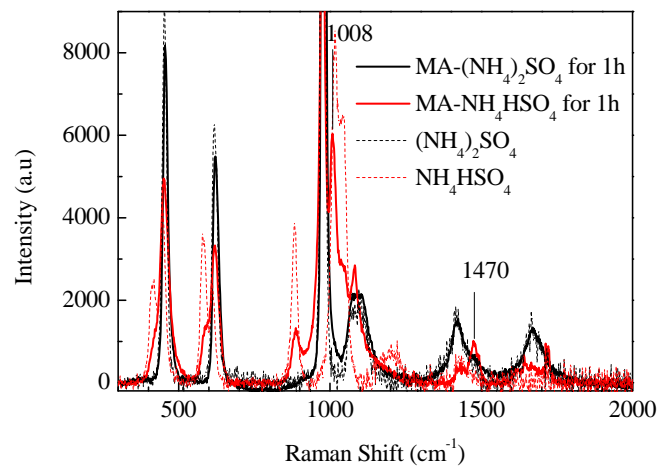


Fig.2R

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