Response

Response to referee:

We are grateful to Referee #1 for the comments and the constructive suggestions to improve our manuscript. Our response to the comments and changes to the manuscript are included below. We repeat the specific points raised by the reviewer in bold font, followed by our response in italic font. The pages numbers and lines mentioned below are consistent with those in the Atmospheric Chemistry and Physics Discussions (ACPD) paper.

Mineral dust and sulfate are common components in atmospheric particulate maters (PMs), and their coagulation in the atmosphere can form new types of PMs whose physical and chemical characters will be altered, thus affecting on atmospheric physical and chemical processes. Because only few studies investigated the heterogeneous reactions under complex conditions, there is still large gap to explain many phenomena of field measurements by using the current knowledge of atmospheric chemistry. The new finding in this study about the heterogeneous reactions of NO_2 on the surface of $CaCO_3$-$(NH_4)_2SO_4$ mixtures provided important information, that is, the heterogeneous reactions in the atmosphere may play important role on formation of nitrate, $CaSO_4 \cdot 0.5H_2O$ (bassanite), $CaSO_4 \cdot 2H_2O$ (gypsum) and $(NH_4)_2Ca(SO_4)_2 \cdot H_2O$ (koktaite). This reviewer recommends the manuscript be published in the journal after considering the following one specific: The formation rates of nitrate based on the integrated absorbance of the IR peak area between 1390 and 1250 cm -1 are inconsistent with the final concentrations of nitrate measured by IC. The intensity of the IR absorbance in the DRIFTS can only reveal the surface concentration of nitrate, whereas the nitrate concentrations measured by IC are the bulk concentrations in the PMs. The surface nitrate formed through the heterogeneous reactions was suspected to easily diffuse into inner layer of the PMs under high RH conditions. The authors should present the explanations.

Reply: *Thanks for the reviewer's comment. We agree with the reviewer's point that the infrared beam primarily interrogates the upper portion of the particulate samples and IR absorbance in the DRIFTS reveals the surface concentration of nitrate. The infrared beam is, however, not restricted solely to the top few particle layers (Vogt and Finlaysonpitts, 1994). In fact, DRIFTS has been applied extensively to study the kinetics and mechanisms of gas-solid reactions (Ullerstam et al., 2002, 2003; Li et al., 2007; Li et al., 2010; Tong et al. 2010), where the kinetics of the reactions are followed using the integrated absorbance-reaction time behavior and the reactive uptake coefficient (γ) is determined from the infrared absorbance, that calibrated by ion chromatography (IC).*

Vogt et al. (1994) investigated the depth of the pellet from which the infrared signal generated. They mixed homogeneous $NaNO_3$ *or NaCl mixture with an additional 0.2-0.5mm layers of neat NaCl powder on top and found that significant signals could still be observed. Also they reported that the absorbance integrated over the* v_3 *region was linearly dependent on the amount of nitrate determined by IC in the reaction of solid NaCl with gaseous* NO_2 *and* HNO_3*. In this study, as indicated in Figure S3 that over a large concentration range the integrated nitrate absorbance over the* v_3 *region (1390 to 1250* cm^{-1}*) was proportional to the nitrate ions concentration detected by IC. In another word, the reacted particles were within the depth that infrared signal generated and the nitrate formed during the reaction could be presented by the integrated absorbance over the* v_3 *region.*

Li et al. (2010) investigated the heterogeneous reaction of $CaCO_3$ *with* NO_2 *using a DRIFTS reactor and found that there was a linear relationship between absorbance integrated over the* v_1 *region (1013-1073* cm^{-1}*) and the number of nitrate ions determined by IC. They reported that the conversion factor f (in the equation of the nitrate ions* $\{NO_3^-\}$ = *(integrated absorbance* I_A*)* × *f) was found to be independent of reaction time and* NO_2 *concentration as long as the experiment was completed at a stage when the absorption of the nitrate band was still growing. In this research, we found that the integrated nitrate absorbance over the* v_1 *region (1013-1073* cm^{-1}*) and the* v_3 *region (1250-1390* cm^{-1}*) could well overlap after the former multiplied by a* *constant (see in Figure S2). And all the experiments in our study were completed as the integrated nitrate absorptions were still growing (Figure 3).*

Therefore the nitrate formation rates based on the integrated absorbance of the IR peak area between 1390-1250 were well consistent with the nitrate concentrations measured by IC.

Following the referee's suggestion, we added a series of experiments that stopped the heterogeneous reactions of NO_2 *with* $CaCO_3$ *and* $CaCO_3$*-*$(NH_4)_2SO_4$ *mixtures at the initial stage (e.g. 20min, 30min, and 40min) under wet and dry conditions. The results indicated that the integrated absorbance of nitrate has a linear relationship with the amount of nitrate determined by ion chromatography during all the reaction periods. Some modifications have been made in Figure S3 after some data added to the calibration plot. Figure S2 was added to illustrate that the integrated nitrate absorbance over the* v_1 *region (1013-1073* cm^{-1}*) and the* v_3 *region (1250-1390* cm^{-1}*) could well overlap after the former multiplied by a constant.*

Related changes included in the revised manuscript:

Page 10 line 24, after the sentence "... interruption of the absorptions of sulfates" we added "The integrated nitrate absorbance over the v_1 *region (1013-1073* cm^{-1}*) and the* v_3 *region (1250-1390* cm^{-1}*) could well overlap after the former multiplied by a constant (Figure S2)."*

*Page 11 line 12, we revised "*Fig. S2*" in the sentence "*... at 60%, 40% RH and dry condition (see Fig. S2).*" to Fig S3.*

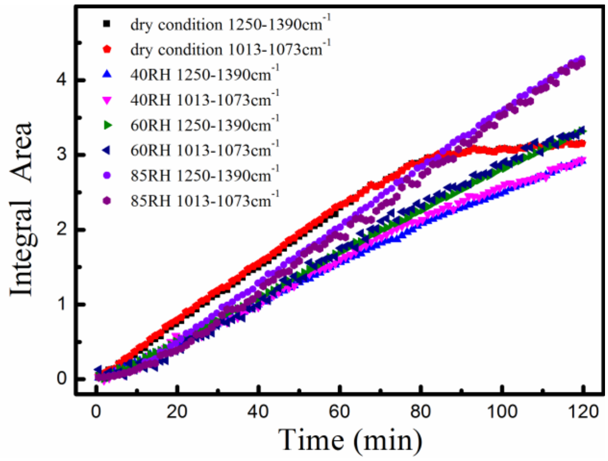

Figure S2: *The integrated nitrate absorbance over the v_1 region (1013-1073 cm^{-1}) and the v_3 region (1250-1390 cm^{-1}) after the v_1 region multiplied by 3, 7, 10, 12 under dry condition, 40% RH, 60% RH, and 85% RH, respectively, for the reaction of NO_2 with $CaCO_3$ particles.*

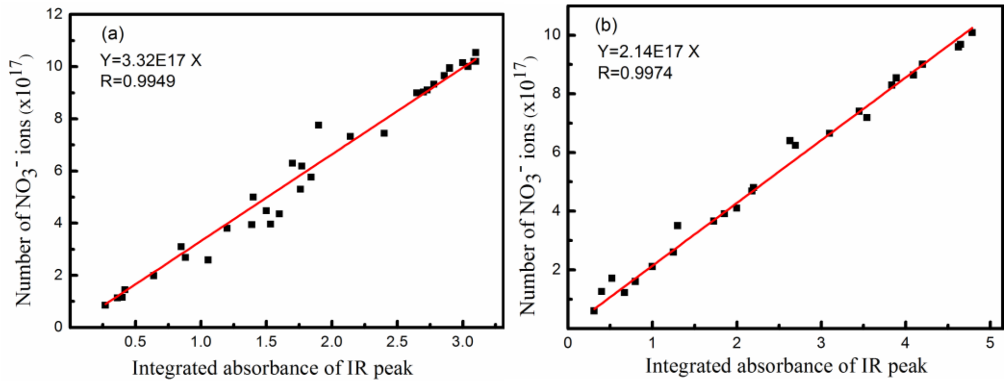

Figure S3. *The number of NO_3^- ions detected by IC as a function of integrated absorbance of IR peak between 1390 and 1250 cm^{-1} at (a) dry condition, 40% RH, and 60% RH, (b) 85% RH.*

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