Responses to Referee # 2

We thank the reviewer for carefully reviewing our manuscript. The comments and suggestions are greatly appreciated. All the comments have been addressed. In the following, please find our responses to the comments one by one and corresponding revisions made to the manuscript. The original comments are shown in italics. The revised parts of the manuscript are highlighted.

This study investigated the heterogeneous reaction of SO_2 with NO_2 on individual $CaCO_3$ particles in N_2 using Micro-Raman spectroscopy. The results show that $CaCO_3$ was first converted to $Ca(NO_3)_2$ forming a droplet and promoting the oxidation of SO_2 by NO_2. The precipitation of $CaSO_4$ was suggested as a key step accelerating the sulfate formation. Based on the uptake coefficient determined, the authors concluded that the $SO_2 + NO_2$ reaction was not important compared to the oxidation of SO_2 by OH radicals. The experiment was well designed and the paper was well written.

But I do have concerns about the role of $CaSO_4$ precipitation and I would also suggest the authors to compare their results with literature data before making strong statement on the role of NO_2+SO_2 chemistry.

Major concern:

1. The authors generalized the results of their $CaCO_3$ experiments to assess the role of NO_2+SO_2 chemistry. I am not sure if such generalization is correct because according to early studies of Lee and Schwartz,1983 and Clifton et al.,1988, this reaction can be important under polluted and less acidic conditions in contrary to the authors' statement. The authors used deposited super-micro particles in their experiments. But I don't expect much difference between such a system and bulk experiments because large particles are not subject to strong Kelvin effect and particles contacted with substrates would not become supersaturated solution of high ionic strength due to nucleation. Thus before generalizing results for ambient aerosols, I would suggest the authors to discuss their difference with those early studies.

Response:

We thank the reviewer for this comment and suggestion.

In the revised manuscript, we have added the following paragraph to discuss the comparison of our study with previous studies using bulk solution.

"The γ of SO_2 was further compared with the reaction rate constants of the aqueous reaction of NO_2 with sulfite and bisulfite in bulk solution in the literature by deriving γ from rate constants using the method in Davidovits et al. (2006). The detailed method can be referred to the supplement S1. Lee and Schwartz (1983) determined the rate constant of the reaction of NO_2 with bisulfite to be $>2\times10^6$

mol^{-1} L^{-1} s^{-1} at pH 5.8 and 6.4. Clifton et al. (1988) determined the rate constant of the reaction of NO$_2$ with sulfite/bisulfite to be (1.24-2.95)×10^7 mol^{-1} L^{-1} s^{-1} at pH 5.6-13 and further reported a rate constant of 1.4×10^5 mol^{-1} L^{-1} s^{-1} at pH 5 from the study of Lee and Schwartz (1983). The different rate constants were attributed to the different approaches to determine the reaction rate by Clifton et al. (1988). Clifton et al. (1988) determined the reaction rate from the consumption rate the reactant, NO$_2$, which corresponds to the first reaction step of NO$_2$ with S(IV). Yet, Lee and Schwartz (1983) determined the reaction rate from the production rate of products (their conductivity), which is expected to be much slower than NO$_2$ consumption since formation of products needs more steps. In this study, we determined γ using sulfate production rate, and thus our data are comparable to the study of Lee and Schwartz (1983). Yet, the study of Lee and Schwartz (1983) only covers a pH range of 5-6.4 and has no overlap with the pH (~3) in our study, therefore uptake coefficients from both studies are not directly comparable. Nevertheless, the reaction rate of 1.4×10^5 mol^{-1} L^{-1} s^{-1} at pH 5 corresponds to the uptake coefficient of 4.3×10^{-7}, which is around one order of magnitude higher than the uptake coefficient in our study determined at pH ~3 for the droplet. The difference may be due to the different pH between these two studies, the different mechanisms between the multiphase reaction on particles and bulk aqueous reaction, and the different concentrations of each S(IV) species since the different species may have different reactivity with NO$_2$. The reaction rate of S(IV) has been found to decrease with decreasing pH and the reactivity of sulfite with NO$_2$ seems to be higher than bisulfite (Lee and Schwartz, 1983; Clifton et al., 1988; Takeuchi et al., 1977). In addition, the ionic strength in the droplet of this study (15-55 mol Kg^{-1}) was much higher than that in the bulk solution in previous studies (on the order of 10^{-6}-10^{-1} mol Kg^{-1}), which may also influence the reaction rate."

2. Based on Equation (5), the authors concluded that the precipitation-induced reduction of sulfate will promote the oxidation of SO$_2$ by NO$_2$ (reaction 2). I don't know if it is correct to use Eq. (5) in this way. Because Equation (5) is valid for reversible reactions and removing/adding products of non-reversible reactions will not change the reaction rate much.

Response:

Using the change of Gibbs energy to express the spontaneity of a reaction is applicable to all reactions. Moreover, in theory, all chemical reactions are reversible, to some extent (Keeler and Wothers, 2008; de Nevers, 2012). According to the different results between the reaction on Ca(NO$_3$)$_2$ droplet and the reaction on NaNO$_3$ and NH$_4$NO$_3$ droplet, there might be a backward reaction of SO$_2$ oxidation which consumed sulfate, although the detailed mechanism of the backward reaction is unknown at the moment. Therefore, we used Equation (5) to explain the difference between the reaction on Ca(NO$_3$)$_2$ droplet and the reaction on NaNO$_3$ and NH$_4$NO$_3$ droplet.

In the revised manuscript, we have modified the discussion:

"$\Delta_r G$ increases with increasing sulfate concentration. According to the different results between the reaction on $Ca(NO_3)_2$ droplet and the reaction on $NaNO_3$ and NH_4NO_3 droplet, there might be a backward reaction of SO_2 oxidation which consumed sulfate, although the detailed mechanism of the backward reaction is unknown at the moment. For $NaNO_3$ and NH_4NO_3 droplet, once sulfate concentration reached certain level, the reaction may stop due to the increase of $\Delta_r G$. For $Ca(NO_3)_2$ droplet, the precipitation of $CaSO_4$ can substantially decrease the activity of SO_4^{2-}, and thus decrease $\Delta_r G$ and promote the oxidation of SO_2 and sulfate formation."

Other comments:

Page 5 line 133, half sentene?

Response:

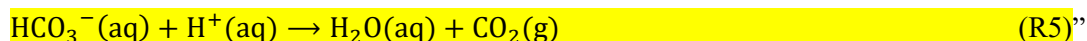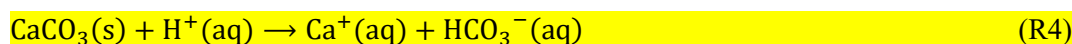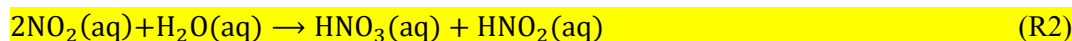Accepted. In the revised manuscript, we have fixed this sentence. Now it reads:

"In order to minimize the influence variations of incident laser on Raman intensity, these seven particles were measured before each experiment..."

Page 6 line 187, I would suggest to briefly describe the mechanism of $Ca(NO_3)_2$ formation.

Response:

Accepted. In the revised, we have briefly described the reaction mechanism of $Ca(NO_3)_2$ formation and provided a brief mechanism of the reaction of $CaCO_3$ with NO_2. Now it reads:

"$Ca(NO_3)_2$ has been observed in the reaction of $CaCO_3$ with NO_2 in previous studies (Li et al., 2010; Tan et al., 2016). The formation of $Ca(NO_3)_2$ started with the reaction of NO_2 with adsorbed or liquid water, forming HNO_3 and HNO_2. Then HNO_3 reacted with $CaCO_3$ forming $Ca(NO_3)_2$ as well as CO_2, which was released to the gas phase. The reaction equations are as follows:

$$NO_2(g) \leftrightarrow NO_2(aq) \tag{R1}$$

$$2NO_2(aq) + H_2O(aq) \rightarrow HNO_3(aq) + HNO_2(aq) \tag{R2}$$

$$HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq) \tag{R3}$$

$$CaCO_3(s) + H^+(aq) \rightarrow Ca^+(aq) + HCO_3^-(aq) \tag{R4}$$

$$HCO_3^-(aq) + H^+(aq) \rightarrow H_2O(aq) + CO_2(g) \tag{R5}$$"

Will the present of SO_2 influence the uptake of NO_2?

Response:

In principle, the presence of SO_2 should enhance NO_2 uptake due to its reaction with NO_2. However, as we observed in our study, the reactive uptake of NO_2 on $CaCO_3$ particles was much faster than the

reaction of NO_2 with SO_2 and sulfate as the reaction product of SO_2 was essentially only observed after $CaCO_3$ was completely converted to $Ca(NO_3)_2$ droplet by NO_2. Therefore, the influence of SO_2 on NO_2 uptake was not significant.

In the revised manuscript, we have added one sentence to discuss this point.

"The much faster $Ca(NO_3)_2$ formation due to the NO_2 uptake on $CaCO_3$ particle compared with the reaction of SO_2 with NO_2 and sulfate appearing only after the complete conversion of $CaCO_3$ indicate that the reaction of SO_2 with NO_2 does not contributed significantly to NO_2 uptake."

Fig. 4, no data for nitrate and carbonate after 120 min, why?

Response:

By 118 min, $CaCO_3$ was completely converted to $Ca(NO_3)_2$. Carbonate had decreased to zero and nitrate had reached a plateau. Therefore no further data of carbonate and nitrate were shown. In the revised manuscript, we have explained this in the caption of Fig. 4.

References

Clifton, C. L., Altstein, N., and Huie, R. E.: Rate-constant for the reaction of NO_2 with sulfur(IV) over the pH range 5.3-13, Environ. Sci. Technol., 22, 586-589, 10.1021/es00170a018, 1988.

Davidovits, P., Kolb, C. E., Williams, L. R., Jayne, J. T., and Worsnop, D. R.: Mass accommodation and chemical reactions at gas-liquid interfaces, Chem. Rev., 106, 1323-1354, 10.1021/cr040366k, 2006.

de Nevers, N.: Physical and Chemical Equilibrium for Chemical Engineers, 2nd ed., John Wiley & Sons, Inc., Hoboken, New Jersey, 348 pp., 2012.

Keeler, J., and Wothers, P.: Chemical Structure and Reactivity: An Integrated Approach, 1st ed., Oxford University Press, Oxford, 924 pp., 2008.

Lee, Y.-N., and Schwartz, S. E.: Kinetics of oxidation of aqueous sulfur (IV) by nitrogen dioxide, in: Precipitation Scavenging, Dry Deposition and Resuspension, edited by: Pruppacher, H. R., Semonin, R. G., and Slinn, W. G. N., Elsevier, New York, 453-466, 1983.

Li, H. J., Zhu, T., Zhao, D. F., Zhang, Z. F., and Chen, Z. M.: Kinetics and mechanisms of heterogeneous reaction of NO_2 on $CaCO_3$ surfaces under dry and wet conditions, Atmos. Chem. Phys., 10, 463-474, 2010.

Takeuchi, H., Ando, M., and Kizawa, N.: Absorption of Nitrogen Oxides in Aqueous Sodium Sulfite and Bisulfite Solutions, Industrial & Engineering Chemistry Process Design and Development, 16, 303-308, 10.1021/i260063a010, 1977.

Tan, F., Tong, S. R., Jing, B., Hou, S. Q., Liu, Q. F., Li, K., Zhang, Y., and Ge, M. F.: Heterogeneous reactions of NO_2 with $CaCO_3$-$(NH_4)(2)SO_4$ mixtures at different relative humidities, Atmos. Chem. Phys., 16, 8081-8093, 10.5194/acp-16-8081-2016, 2016.