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 s⁻¹ at pH 5.8 and 6.4. Clifton et al. (1988) determined the rate constant of the reaction of NO₂ with sulfite/bisulfite to be (1.24-2.95)×10⁷ mol⁻¹ L s⁻¹ at pH 5.6-13 and further reported a rate constant of 1.4×10⁵ mol⁻¹ L 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, NO₂, which corresponds to the first reaction step of NO₂ 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 NO₂ 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 1.4×10⁵ mol⁻¹ L 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 NO₂. The reaction rate of S(IV) has been found to decrease with decreasing pH and the reactivity of sulfite with NO₂ 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 SO₂ by NO₂ (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(NO₃)₂ droplet and the reaction on NaNO₃ and NH₄NO₃ droplet, there might be a backward reaction of SO₂ 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(NO₃)₂ droplet and the reaction on NaNO₃ and NH₄NO₃ droplet.

In the revised manuscript, we have modified the discussion:
ΔrG increases with increasing sulfate concentration. According to the different results between the reaction on Ca(NO₃)₂ droplet and the reaction on NaNO₃ and NH₄NO₃ droplet, there might be a backward reaction of SO₂ oxidation which consumed sulfate, although the detailed mechanism of the backward reaction is unknown at the moment. For NaNO₃ and NH₄NO₃ droplet, once sulfate concentration reached certain level, the reaction may stop due to the increase of ΔrG. For Ca(NO₃)₂ droplet, the precipitation of CaSO₄ can substantially decrease the activity of SO₄²⁻, and thus decrease ΔrG and promote the oxidation of SO2 and sulfate formation.

Other comments:

Page 5 line 133, half sentence?

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(NO₃)₂ formation.

Response:

Accepted. In the revised, we have briefly described the reaction mechanism of Ca(NO₃)₂ formation and provided a brief mechanism of the reaction of CaCO₃ with NO₂. Now it reads:

“Ca(NO₃)₂ has been observed in the reaction of CaCO₃ with NO₂ in previous studies (Li et al., 2010; Tan et al., 2016). The formation of Ca(NO₃)₂ started with the reaction of NO₂ with adsorbed or liquid water, forming HNO₃ and HNO₂. Then HNO₃ reacted with CaCO₃ forming Ca(NO₃)₂ as well as CO₂, which was released to the gas phase. The reaction equations are as follows:

\[
\begin{align*}
\text{NO}_2(g) & \leftrightarrow \text{NO}_2(aq) \quad \text{(R1)} \\
2\text{NO}_2(aq) + \text{H}_2\text{O}(aq) & \rightarrow \text{HNO}_3(aq) + \text{HNO}_2(aq) \quad \text{(R2)} \\
\text{HNO}_3(aq) & \rightarrow \text{H}^+(aq) + \text{NO}_3^-(aq) \quad \text{(R3)} \\
\text{CaCO}_3(s) + \text{H}^+(aq) & \rightarrow \text{Ca}^+(aq) + \text{HCO}_3^-(aq) \quad \text{(R4)} \\
\text{HCO}_3^-(aq) + \text{H}^+(aq) & \rightarrow \text{H}_2\text{O}(aq) + \text{CO}_2(g) \quad \text{(R5)}
\end{align*}
\]

Will the present of SO₂ influence the uptake of NO₂?

Response:

In principle, the presence of SO₂ should enhance NO₂ uptake due to its reaction with NO₂. However, as we observed in our study, the reactive uptake of NO₂ on CaCO₃ 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


