Responses to Referee # 1

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.

General comments

The paper presents the results on multiphase reaction of SO$_2$ with NO$_2$ on individual CaCO$_3$ particles in N$_2$ at RH between 17 and 72% using Micro-Raman spectrometer with a flow reaction system. The reaction process was systematically investigated and found that CaCO$_3$ converts first to Ca(NO$_3$)$_2$ (by the reaction with NO$_2$) and its deliquescence to droplet, where further SO$_2$ oxidizes with NO$_2$ forming CaSO$_4$. The reactive uptake coefficient $\gamma$ of SO$_2$ was determined on the basis of sulfate formation rate.

Although many studies concerning SO$_2$ oxidation in the atmosphere were performed in late 1980s and 1990s, mainly due to much higher pollution with SO$_2$ all over the world at that time, and various pathways of oxidation were identified, the questions concerning sulfate formation have not yet been fully resolved. As shown e.g., that high concentrations of sulfate during heavily polluted episodes under haze conditions in China could not be explained on the basis of known pathways only. In addition, due to the progress and development of techniques, nowadays there are more possibilities to study processes also on the micro level as shown in this paper.

Thus, I found the paper of sufficient atmospheric interest to merit publication after revision; in “specific comments” some questions and/or comments are listed which should be considered.

However, I would strongly recommend showing also the results for the system SO$_2$/NO$_2$/H$_2$O/O$_2$ together with those presented here and not in the next paper as said in line 80. Experimental conditions will be closer to atmospheric, and as mentioned on p.9 (lines 301-303) it is expected that the reactions under O$_2$ are faster and could be more important source of sulfate.

Response:

We thank the reviewer for the supporting remarks.

As to the recommendation “showing also the results for the system SO$_2$/NO$_2$/H$_2$O/O$_2$ together with those presented here and not in the next paper as said in line 80”, we realized that our phrasing in the some texts of the manuscript was not precise and clear enough to express our primary motivation. We have modified these texts (e.g. lines 80-83, lines 350-357) in the revised manuscript to clearly state our motivation, i.e., to address the multiphase reaction of SO$_2$ directly with NO$_2$ and evaluate the
importance of this reaction pathway in sulfate formation in the real atmosphere, which was proposed by a number of recent studies (Cheng et al., 2016; Wang et al., 2016; Xue et al., 2016) but remains unclear. In order to exclude potential confounding reactions from other compounds, we used inert N₂ as a carrier gas. For this motivation, the direct reaction of SO₂ with NO₂ has ambient relevance no matter whether O₂ is present or not.

The reason that we did not include the multiphase reaction of SO₂ with O₂/NO₂ in this paper is because we found that in this reaction SO₂ was actually oxidized by O₂, not by NO₂. It is distinct from the reaction of SO₂ directly with NO₂ with markedly different mechanisms, products, and atmospheric implications, as we will show (Yu et al., 2017). O₂ was the main oxidant of SO₂ and NO₂ only acted as an initiator of chain reactions. The atmospheric implications are significantly different from the direct reaction of SO₂ with NO₂ because not only the oxidation of SO₂ by O₂ leads to much faster sulfate oxidation but also the reaction is not linked to reactive nitrogen chemistry in the atmosphere. Therefore, we address this reaction in a separate companion manuscript (Yu et al., 2017).

In addition, in order to reflect the distinction of these two studies more precisely, we have revised the title of our manuscript as follows:

“Multiphase Reaction of SO₂ on CaCO₃ Particles. 1. Oxidation of SO₂ by NO₂”.

Accordingly, we plan to change the title of our companion manuscript to:

“Multiphase Reaction of SO₂ on CaCO₃ Particles. 2. NO₂-initiated Oxidation of SO₂ by O₂”.

Specific comments

Introduction:  (1)  P.3, lines 59-62: It would be worth to mention also the studies from 2001 (Turšič et al., 2001, Atmos. Environ.).

Response: Accepted.

Experimental: (2) The experimental approach (Raman mapping analysis) where you can follow the changes during the reaction course (as can be seen in Fig. S2) is intriguing.

Response: We thank the reviewer for the supporting remark.

Results and discussion: (3) Fig. 2 nicely shows how the peak for CO₃²⁻ decreases and disappears after certain time of reaction; the change can be seen also in Fig. 3. What happens to it (releases as CO₂)? (4) It is not correct to explain its “disappearance” as “completely consumed” (line 171).
Response:

CO$_3^{2-}$ was converted to CO$_2$ by the reaction with H$^+$, which was released into the gas phase. In the revised manuscript, we have briefly discussed this process.

“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.”

In the revised manuscript, we have rephrased the “completely consumed” to “completely reacted”.

(5) Line 186: “the consumption of CaCO$_3$” is not appropriate

Response: Accepted.

In the revised manuscript, we have changed it to “the decline of CaCO$_3$”.

(6) Lines 186-187: If Ca(NO$_3$)$_2$ is formed in the reaction between CaCO$_3$ and NO$_2$, NO$_2$ should first disproportionate to NO$_3^-$ and NO$_2^-$, which is possible in the presence of water. How is then Ca(NO$_3$)$_2$ first formed from CaCO$_3$, and only then converts into droplet in the presence of water? The authors should explain the reactions also for the first step, i.e. the conversion of CaCO$_3$ to Ca(NO$_3$)$_2$ although the reference is given (line 188). I suggest that the complete mechanism is written.

Response:

The details of the mechanism of the reaction of CaCO$_3$ with NO$_2$ are reported in our previous paper (Li et al., 2010). In the revised manuscript, we have added the following texts and reaction equations:

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., 2017). 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:

\[
\begin{align*}
\text{NO}_2(g) & \leftrightarrow \text{NO}_2(aq) \quad (R1) \\
2\text{NO}_2(aq) + H_2O(aq) & \rightarrow \text{HNO}_3(aq) + \text{HNO}_2(aq) \quad (R2) \\
\text{HNO}_3(aq) & \rightarrow H^+(aq) + \text{NO}_3^-(aq) \quad (R3) \\
\text{CaCO}_3(s) + H^+(aq) & \rightarrow \text{Ca}^+(aq) + \text{HCO}_3^-(aq) \quad (R4) \\
\text{HCO}_3^-(aq) + H^+(aq) & \rightarrow H_2O(aq) + \text{CO}_2(g) \quad (R5)
\end{align*}
\]

(7) The authors may want to add a reference of Tan et al., 2016, ACP.

Response: Accepted.
In the revised manuscript, we have added Tan et al. (2016) as a reference.

(8) It is concluded that aqueous phase plays a key role in SO₂ oxidation by NO₂, which is also known from previous studies. Line 219: pH is estimated to be around 3. What would be the concentrations of reactive species in Ca(NO₃)₂ droplet?

Response:

We suppose that the reviewer referred to the concentrations of S(IV) species. The concentrations of HSO₃⁻, H₂SO₃, and SO₃²⁻ were estimated to be ~1.1×10⁻³, 9.2×10⁻⁵, and 6.6×10⁻⁸ mol L⁻¹, respectively, using the equilibrium constants in Seinfeld and Pandis (2006).

We have added these values in the revised manuscript.

“The concentrations of HSO₃⁻, H₂SO₃, and SO₃²⁻ were estimated to be ~1.1×10⁻³, 9.2×10⁻⁵, and 6.6×10⁻⁸ mol L⁻¹, respectively, using the equilibrium constants in Seinfeld and Pandis (2006) and thus the main S(IV) species was HSO₃⁻.”

(9) Lines 236-241: This part is not well understandable. It is concluded that precipitation of CaSO₄ formed in/on Ca(NO₃)₂ droplet promotes sulfate formation. On the other hand, when NaNO₃ or NH₄NO₃ droplet is used instead of Ca(NO₃)₂, no sulfate was formed after 300 min. If aqueous phase is a key factor for the oxidation of SO₂ with NO₂, then this should happen also in these droplets, although the reaction is most probably much slower. Why the reaction was not carried out at longer times?

Response:

The purpose of the comparison between the reaction of NaNO₃ and NH₄NO₃ and the reaction of Ca(NO₃)₂ was to qualitatively examine the effect of cations on sulfate formation rate. At 300 min, sulfate was readily detectable in the reaction of Ca(NO₃)₂ while it was below the detection limit in the reaction of NaNO₃ and NH₄NO₃ (Fig. 5, Fig. 6). Although sulfate may have been formed, the absence of sulfate at 300 min shows that the sulfate production was extremely slow. The difference by 300 min has clearly indicated that the sulfate formation in the reaction of Ca(NO₃)₂ was much faster than that in the reaction the NaNO₃ and NH₄NO₃ and Ca²⁺ promoted sulfate formation, which likely resulted from CaSO₄ precipitation. Therefore, the reaction was not continued for longer times.

In the revised manuscript, we have made some changes to improve the clarity of the discussion. Now it reads:
“Based on Raman spectra, we found that in the reaction of a NaNO$_3$ or a NH$_4$NO$_3$ droplet with NO$_2$/SO$_2$ sulfate was below the detection limit after 300 min in the same reaction conditions as Ca(NO$_3$)$_2$ and CaCO$_3$ (Fig. 6 and Table 1). Accordingly, no sulfate solid particles were observed in these droplets. Clearly, the sulfate production rate was larger in the presence of Ca$^{2+}$ compared to those in the presence of Na$^+$ or NH$_4^+$. The difference can be explained by the change of Gibbs energy.”

“$\Delta rG$ 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$_4$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. For NaNO$_3$ and NH$_4$NO$_3$ droplet, once sulfate concentration reached certain level, the reaction may stop due to the increase of $\Delta rG$. For Ca(NO$_3$)$_2$ droplet, the precipitation of CaSO$_4$ can substantially decrease the activity of SO$_4^{2-}$, and thus decrease $\Delta rG$ and promote the oxidation of SO$_2$ and sulfate formation.”

(10) Line 240: In droplets of NaNO$_3$ or NH$_4$NO$_3$, CaSO$_4$ cannot be formed.

Response:

Accepted. In the revised manuscript, we have changed “CaSO$_4$” to “sulfate”.

(11) Line 250: Is it correct that at RH of 46% the conditions for a complete conversion into a Ca(NO$_3$)$_2$ droplet are achieved?

Response:

Yes. We observed that a complete conversion from CaCO$_3$ particle to Ca(NO$_3$)$_2$ droplet occurred at 46% RH and then sulfate was observed.

(12) Line 259: Write what is DRIFTS technique (it was not mentioned before).

Response:

Accepted. In the revised manuscript, we have provided the full name of DRIFTS as “Diffuse Reflectance Infrared Fourier Transform Spectroscopy”.

(13) Line 206: ATD particles?

Response:

In the revised manuscript, we have provided the full name of ATD as “Arizona Test Dust”.

5
(14) Lines 273-275: Is this statement correct? Higher concentrations of aqueous sulfate may suppress the reaction between SO$_2$ and NO$_2$, while CaSO$_4$ precipitation can promote it.

Response:

As we found on the effect of cations (Section 3.3.2), reduced sulfate concentration by CaSO$_4$ precipitation likely led to the enhanced sulfate production rate in the reaction of SO$_2$ on Ca(NO$_3$)$_2$. According to Eq. 5, higher sulfate concentration could increase the reaction Gibbs energy $\Delta rG$ and thus suppress the reaction of SO$_2$ and NO$_2$.

In the revised manuscript, we have further explained this statement.

“According to the effect of cations (Section 3.3.2), while reduced sulfate concentration by CaSO$_4$ precipitation likely led to the enhanced sulfate production rate in the reaction of SO$_2$ on Ca(NO$_3$)$_2$, higher sulfate concentration could increase the reaction Gibbs energy $\Delta rG$ (as shown in Eq. 5) and thus suppress the reaction of SO$_2$ and NO$_2$. This can reduce the uptake coefficient of SO$_2$."

References


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 $> 2 \times 10^6$"
mol$^{-1}$ L s$^{-1}$ at pH 5.8 and 6.4. Clifton et al. (1988) determined the rate constant of the reaction of NO$_2$ with sulfite/bisulfite to be $1.24-2.95 \times 10^7$ mol$^{-1}$ L s$^{-1}$ at pH 5.6-13 and further reported a rate constant of $1.4 \times 10^5$ 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 of 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 $\gamma$ 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 $1.4 \times 10^5$ mol$^{-1}$ L s$^{-1}$ at pH 5 corresponds to the uptake coefficient of $4.3 \times 10^{-7}$, 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:
“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 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(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:

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

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 NO₂ with SO₂ and sulfate as the reaction product of SO₂ was essentially only observed after CaCO₃ was completely converted to Ca(NO₃)₂ droplet by NO₂. Therefore, the influence of SO₂ on NO₂ uptake was not significant.

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

“The much faster Ca(NO₃)₂ formation due to the NO₂ uptake on CaCO₃ particle compared with the reaction of SO₂ with NO₂ and sulfate appearing only after the complete conversion of CaCO₃ indicate that the reaction of SO₂ with NO₂ does not contributed significantly to NO₂ uptake.”

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

Response:

By 118 min, CaCO₃ was completely converted to Ca(NO₃)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


Multiphase Reaction of $\text{SO}_2$ on CaCO$_3$ Particles. 1. Oxidation of $\text{SO}_2$ by $\text{NO}_2$

Defeng Zhao*, Xiaojuan Song*, Tong Zhu, Zefeng Zhang, Yingjun Liu

BIC-ESAT and SKL-ESPC, College of Environmental Sciences and Engineering, Peking University, Beijing, 100871, China

*These authors contributed equally to this work.

Correspondence to: Tong Zhu (tzhu@pku.edu.cn)

Abstract. Heterogeneous/multiphase reaction of $\text{SO}_2$ with $\text{NO}_2$ on solid or aqueous particles is thought to be a potentially important source of sulfate in the atmosphere, for example, during heavily polluted episodes (haze), but the reaction mechanism and rate are uncertain. In this study, we investigated the heterogeneous/multiphase reaction of $\text{SO}_2$ with $\text{NO}_2$ on individual CaCO$_3$ particles in N$_2$ using Micro-Raman spectroscopy in order to assess the importance of the direct oxidation of $\text{SO}_2$ by $\text{NO}_2$. In the $\text{SO}_2$/NO$_2$/H$_2$O/N$_2$ gas mixture, the CaCO$_3$ solid particle was first converted to the Ca(NO$_3$)$_2$ droplet by the reaction with $\text{NO}_2$ and the deliquescence of Ca(NO$_3$)$_2$, and then NO$_2$ oxidized $\text{SO}_2$ in the Ca(NO$_3$)$_2$ droplet forming CaSO$_4$, which appeared as needle-shaped crystals. Sulfate was mainly formed after the complete conversion of CaCO$_3$ to Ca(NO$_3$)$_2$, that is, during the multiphase oxidation of $\text{SO}_2$ by $\text{NO}_2$. The precipitation of CaSO$_4$ from the droplet solution promoted sulfate formation. The reactive uptake coefficient of $\text{SO}_2$ for sulfate formation is on the order of $10^{-8}$, and RH enhanced the uptake coefficient. We estimate that the direct multiphase oxidation of $\text{SO}_2$ by $\text{NO}_2$ is not an important source of sulfate in the ambient atmosphere compared with the $\text{SO}_2$ oxidation by $\text{OH}$ in the gas phase.
1 Introduction

Sulfate is a major component of atmospheric particulate matter. It contributes to a large fraction of atmospheric aerosol particles in both urban and rural areas (Seinfeld and Pandis, 2006; Zhang et al., 2007). Sulfate is either from primary source, such as sea spray, or from secondary source, i.e., by the oxidation of reduced sulfur compounds such as dimethyl sulfide (DMS), carbonyl sulfur (COS), and SO₂ (Seinfeld and Pandis, 2006). In the continent, the main source of sulfate is the oxidation of SO₂, an important air pollutant from fossil fuel combustion. SO₂ can be oxidized in the gas phase, mainly by OH, or in the particle phase such as by H₂O₂, O₃, or O₂ catalyzed by transition metal ions in cloud or fog water (Seinfeld and Pandis, 2006; Finlayson-Pitts and Pitts Jr., 1999) or by O₃ or photochemical reactions on particle surface (Zhu et al., 2011; Li et al., 2006; Li et al., 2007; Shang et al., 2010; Li et al., 2011).

Although various pathways of SO₂ oxidation are identified, the source of sulfate and relative importance of various pathways of SO₂ oxidation forming sulfate in the atmosphere still remain uncertain. For example, during heavily polluted episodes (haze) in China in recent years, high concentrations of sulfate were observed, but the source of sulfate is elusive (Wang et al., 2016; Wang et al., 2014a; Zheng et al., 2015b; Guo et al., 2014). The relative contribution of regional transport versus local formation and physical and chemical mechanisms responsible for sulfate formation are still not clear. Recent studies have highlighted heterogeneous reactions of SO₂ on solid or liquid particles to be a possibly important source of sulfate based on model, field and laboratory studies (Huang et al., 2014; Zhu et al., 2011; Cheng et al., 2016a; Gao et al., 2016; Zheng et al., 2015a; Wang et al., 2014b; He et al., 2014; Fu et al., 2016; Xue et al., 2016; Xie et al., 2015). During haze episodes, relative humidity (RH) is often high (Zhang et al., 2014; Wang et al., 2016; Zheng et al., 2015b) and particles or some components of particles can deliquesce forming liquid water. In particular, several recent studies propose that the multiphase oxidation of SO₂ by NO₂, another important air pollutant, on liquid particles may be a major pathway of sulfate formation (Cheng et al., 2016a; Wang et al., 2016; Xue et al., 2016; Xie et al., 2015). Both SO₂ and NO₂ are from fossil fuel combustion and both concentrations are often high during haze episodes, and their reaction may significantly contribute to sulfate formation.

In order to assess and quantify the role of the heterogeneous reactions of SO₂ in sulfate formation, laboratory studies are needed to understand the reaction process and obtain kinetic parameters for modeling such as uptake coefficients of SO₂. Among many studies investigating the heterogeneous reactions of SO₂ on various particles (Goodman et al., 2001; Li et al., 2011; Shang et al., 2010; Huang et al., 2015; Huang et al., 2016; Zhou et al., 2014; Li et al., 2004; Kong et al., 2014; Passananti et al., 2016; Cui et al., 2008; Chu et al., 2016; Zhao et al., 2015; Li et al., 2006; Wu et al., 2011; He et al., 2014; Liu et al., 2012; Ma et al., 2008; Park and Jang, 2016; Ullerstam et al., 2002; Sorimachi et al., 2001; Ullerstam et al., 2003; Wu et al., 2013; Wu et al., 2015), only a few have investigated the heterogeneous reaction of SO₃ in the presence of NO₂ (He et al., 2014; Liu et al., 2012; Ma et al., 2008; Park and Jang, 2016; Ullerstam et al., 2003; Ma et al., 2017). These studies found that NO₂ can promote sulfate formation from SO₂ oxidation (He et al., 2014; Liu et al., 2012; Ma et al., 2008; Park and Jang, 2016; Ullerstam et al., 2003). However, the mechanism of this effect is still not clear and only few studies reported kinetic parameters such as uptake coefficient of SO₂ in the presence of NO₂. Importantly, most of these studies focused on the gas-solid reactions on particles. Very few laboratory studies have investigated the multiphase reaction of SO₂ with NO₂ on atmospheric aqueous particles or solid-aqueous mixed phase aerosol
particles, and the uptake coefficient of SO$_2$ on atmospheric aqueous particles due to the reaction with NO$_2$ is largely unknown. From several decades ago until now, a number of studies have investigated the aqueous reaction of soluble S(IV) species (H$_2$SO$_3$, HSO$_3^-$, SO$_3^{2-}$) with NO$_2$ in dilute bulk solution (Lee and Schwartz, 1983; Clifton et al., 1988; Littlejohn et al., 1993; Takeuchi et al., 1977; Nash, 1979; Ellison and Eckert, 1984; Shen and Rochelle, 1998; Tursic and Grgic, 2001) relevant to the conditions in cloud water. However, in aqueous aerosol particles, the reaction rate and process may be substantially different from in bulk solution due to high ion strength resulted from high concentrations of solutes, potential interactions of sulfate with other ions, and low water activity in aerosol particles.

In this study, we investigated the heterogeneous reaction of SO$_2$ with NO$_2$ on CaCO$_3$ particles at the ambient RH. CaCO$_3$ is an important component of mineral aerosols, especially in East Asia (Cao et al., 2005; Song et al., 2005; Okada et al., 2005) and it is a very reactive component (Krueger et al., 2004; Li et al., 2010; Li et al., 2006; Prince et al., 2007a). It is also one of the few alkaline particles in the atmosphere, especially in northern China, which can neutralize acids on particles and increase the pH of aerosol water, thus promoting the apparent solubility and uptake of SO$_2$. The reaction of SO$_2$ with NO$_2$ on CaCO$_3$ has been suggested by field observations, which showed internal mixing of CaCO$_3$, CaSO$_4$, and Ca(NO$_3$)$_2$ in particles (Hwang and Ro, 2006; Li and Shao, 2009; Zhang et al., 2000). More importantly, as shown below, during the reaction on CaCO$_3$, aqueous phase can be formed, which allows us to investigate the multiphase reaction of SO$_2$ with NO$_2$. We studied the reaction of SO$_2$ and NO$_2$ on individual CaCO$_3$ particles in N$_2$ using Micro-Raman spectrometer with a flow reaction system.

Combining the chemical and optical information from Micro-Raman spectrometer, we systematically investigated the reaction process and quantified the reactive uptake coefficient of SO$_2$ due to the oxidation by NO$_2$ based on sulfate production rate. We further assessed the importance of the multiphase reaction of SO$_2$ with NO$_2$ in the atmosphere. In this study, we present the findings of the multiphase reaction of SO$_2$ directly with NO$_2$, a reaction pathway proposed in a number of recent studies to be potentially important for sulfate formation (Cheng et al., 2016b; Wang et al., 2016; Xue et al., 2016). In a companion paper, we shall report another study of the multiphase reaction of SO$_2$ with O$_2$ initiated by NO$_2$.

2 Experimental

2.1 Apparatus and procedures

The experimental setup used in this study is illustrated in Fig. 1. The details of the setup have been described previously (Liu et al., 2008; Zhao et al., 2011). NO$_2$ and SO$_2$ of certain concentrations were prepared by adjusting the flow rates of standard gases of specified concentrations (NO$_2$: 1000 ppm in N$_2$, Messer, Germany; SO$_2$: 2000 ppm in N$_2$, National Institute of Metrology P.R.China) and high-purity nitrogen (99.999%, Beijing Haikeyuanchang Corp.). We used N$_2$ as a carrier gas to exclude the potential inference from other compounds in SO$_2$ oxidation such as O$_2$, which is key to investigate the direct oxidation of SO$_2$ by NO$_2$. RH was regulated by adjusting the flow rates of humidified N$_2$ and of dry N$_2$ and other dry gases. Humidified N$_2$ was prepared by bubbling N$_2$ through fritted glass in water. Flow rates of the gases were controlled by mass flow controllers (FC-260, Tylan, Germany). Mixed gases reacted with CaCO$_3$ particles in a stainless steel reaction cell. Individual CaCO$_3$ particles were deposited on a Teflon FEP film substrate annealed to a silicon wafer. The substrate was
then placed in the reaction cell, which has a glass cover on top of the center. Through this top window, a Micro-Raman spectrometer (LabRam HR800, HORIBA Jobin Yvon) was used to acquire the Raman spectra of particles. A 514 nm excitation laser was focused onto selected particles and back scattering Raman signals were detected. The details of the instrument are described in previous studies (Liu et al., 2008; Zhao et al., 2011).

The RH and temperature of the outflow gas from the reaction cell were measured by a hygrometer (HMT100, Vaisala). Experiments of individual CaCO\(_3\) particles reacting with NO\(_2\) (75-200 ppm) and SO\(_2\) (75-200 ppm) mixing gas diluted with N\(_2\) were conducted under certain RH (17-72%). All the measurements were carried out at 25±0.5 °C. Each reaction was repeated for three times.

In this study, the size of CaCO\(_3\) particles was around 7-10 μm. During a reaction, components of an individual particle may distribute unevenly within the particle due to the formation of new aqueous phase or solid phase, and particles may grow. Because particles are larger than the laser spot (~1.5 μm), Raman spectrum from one point does not represent the chemical composition of the whole particle. Therefore Raman mapping was used to obtain the spectra on different points of a particle in order to get the chemical information of the whole particle. The mapping area is a rectangular slightly larger than the particle and mapping steps are 1×1 μm. Raman spectra in the range 800-3900 cm\(^{-1}\) were acquired with exposure time of 1 s for each mapping point. During each mapping (7-10 min, depending on the mapping area), no noticeable change in composition was detected. The mean time of a mapping period was used as reaction time. During the reaction, microscopic images of particles were also recorded. Raman spectra were analyzed using Labspec 5 software (HORIBA Jobin Yvon). Raman peaks were fit to Gaussian-Lorentzian functions to obtain peak positions and peak areas on different points of the particle. The peak areas were then added up to get the peak area for the whole particle.

Besides the reaction of CaCO\(_3\) with SO\(_2\) and NO\(_2\), other reaction systems including the reaction on Ca(NO\(_3\))\(_2\), NaNO\(_3\), NH\(_4\)NO\(_3\) particles with SO\(_2\) or SO\(_2\) and NO\(_2\) mixing gas (summarized in Table 1) were also studied in order to elucidate the reaction mechanism.

CaCO\(_3\) (98%, Sigma) with diameters about 7-10 μm on average, Ca(NO\(_3\))\(_2\)·4H\(_2\)O (ACS, 99-103%; Riedel-de Haën), NH\(_4\)NO\(_3\) (AR, Beijing Chemical Works), and NaNO\(_3\) (AR, Beijing Chemical Works) were used without further purification.

### 2.2 Quantification of reaction products on the particle phase

The Raman intensity of a sample is described as Equation (1):

\[
I(\nu) = I_0 \cdot A(\nu) \cdot J(\nu) \cdot \nu^4 \cdot D \cdot K
\]

(1)

where \(I_0\) is the intensity of incident laser, \(A(\nu)\) is the collection efficiency function of Raman spectrometer, \(J(\nu)\cdot\nu^4\) is the Raman scattering section of the sample, \(D\) is the number density of the sample, and \(K\) is the effective depth of the sample. Raman intensity is not only determined by the amount of the sample molecules, but also by the configuration of the instrument, whose influence cannot be eliminated unless internal standards are used. For soluble compounds, water can be used an internal standard (Zhao et al., 2011; Liu et al., 2008).

However, in this study, one product (CaSO\(_4\), see below) appeared as solid state. For solid particles of micro-scale, it is hard to add internal standards into the system. Therefore it is difficult to establish the relationship between Raman intensity and the amount of sample molecules, which makes the quantification very challenging.
In this study, we chose seven individual CaSO\(_4\) particles varying in size as the standard for solid products. The profile of each particle can be obtained by scanning the particle using Raman mapping with steps of 1, 1, and 2 \(\mu\)m for \(x\), \(y\), and \(z\) dimension, respectively. The volume of each particle was calculated based on 3D profiles of the particles using a CAD software (AutoDesk). In order to minimize the influence variations of incident laser on Raman intensity, these seven particles were measured before each experiment, which produced a calibration curve for each experiment (Fig. S1).

### 2.3 Determination of reactive uptake coefficient

In this study, sulfate was produced from the oxidation of SO\(_2\). The reactive uptake coefficient \(\gamma\) of SO\(_2\) on individual particles was estimated from sulfate formation. \(\gamma\) is derived as the rate of sulfate formation \((d\{SO_4^{2-}\}/dt)\) divided by the rate of surface collisions with an individual particle \((Z)\),

\[
\gamma = \frac{d\{SO_4^{2-}\}}{dt} \cdot \frac{1}{Z}.
\]

\[(2)\]

\[
Z = \frac{\gamma cA_s[SO_2]},
\]

\[(3)\]

\[
c = \frac{BR}{\sqrt{\pi M_{SO_2}}},
\]

\[(4)\]

where \(R\) is the gas constant, \(T\) is temperature, \(M_{SO_2}\) is the molecular weight of SO\(_2\), and \(c\) is the mean molecular velocity of SO\(_2\), \(A_s\) is the surface area of an individual particle. \(Z\) is the collision rate between SO\(_2\) and a particle. \(\{SO_4^{2-}\}\) indicates the amount of sulfate on the particle phase in mole, and \([SO_2]\) indicates the concentration of SO\(_2\) in the gas phase. \(\{SO_4^{2-}\}\) was determined by a calibration curve as stated above. In this study, since sulfate was mainly formed after the formation of Ca(NO\(_3\))\(_2\) droplet as shown below, \(A_s\) was calculated by estimating the diameter of the droplet according to its microscopic image and using a shape of spherical segment defined by the contact angle water droplet on Teflon (Good and Koo, 1979). For each experiment, at least three particles with different diameters were measured to get an average reactive uptake coefficient.

### 3 Results and discussion

#### 3.1 Reaction products and particle morphology changes

Figure 2 shows typical Raman spectra of a CaCO\(_3\) particle during the reaction with SO\(_2\) and NO\(_2\). The peak at 1087 cm\(^{-1}\) is assigned to the symmetric stretching mode of carbonate \((v_1)\) (Nakamoto, 1997), which could be detected during the initial stage of the reaction. Shortly after the reaction started, a peak at 1050 cm\(^{-1}\) was observed, which is attributed to the symmetric stretching mode of nitrate \((v_1)\). This demonstrates that calcium nitrate (Ca(NO\(_3\))\(_2\)) was produced during the reaction. A broad band at 2800-3800 cm\(^{-1}\) was also observed together with the formation of Ca(NO\(_3\))\(_2\). It is assigned to –OH stretching of liquid water. The formation of liquid water is attributed to the deliquescence of Ca(NO\(_3\))\(_2\), which is very hygroscopic and can deliquesce at \(\sim10\%\) RH (Liu et al., 2008; Al-Abadleh et al., 2003; Tang and Fung, 1997). After about 82 min, a new peak at 1013 cm\(^{-1}\) was observed, which is attributed to the symmetric stretching mode of sulfate \((v_1)\) in anhydrite (CaSO\(_4\)) (Sarma et al., 1998). This peak clearly demonstrates that sulfate was formed. CaSO\(_4\) as a reaction product has also been found in the
reaction of CaCO₃ with SO₂ and NO₂ in a previous study (Ma et al., 2013b). Afterwards, no other Raman peaks than those of CaCO₃, Ca(NO₃)₂, and CaSO₄ were detected until 1050 min after the reaction.

Concomitant with the formation of Ca(NO₃)₂ and CaSO₄, the microscopic morphology of the particle changed significantly. The initial CaCO₃ particle was a crystal close to a rhombohedron of about 9-10 μm (Fig. 3a). After reacting with NO₂/SO₂, the surface of the particle became smoother, and then a liquid layer formed surrounding the solid particle core (Fig. 3c). Raman spectra of the particle reveal that the outer liquid layer consisted of Ca(NO₃)₂ and water. As the reaction proceeded, the solid CaCO₃ core diminished gradually and finally CaCO₃ completely disappeared and a Ca(NO₃)₂ spherical droplet was formed (Fig. 3d). The whole particle became larger due to the growth of the outer liquid layer. The diameter of the Ca(NO₃)₂ droplet reached ~16 μm, and the droplet did not change much in the subsequent period of the reaction. Despite the invariant droplet diameter, a new solid phase of needle-shaped crystals was formed as the reaction proceeded, which distributed unevenly in the droplet. The Raman spectra of the new solid phase and Raman mapping (Fig. S2) reveal that this solid matter was CaSO₄. The amount of CaSO₄ increased gradually during the reaction, and its Raman peak could be observed more clearly at 1050 min.

3.2 Reaction process

In order to learn about the reaction process and mechanism, the amounts of Ca(NO₃)₂, CaSO₄, and CaCO₃, represented by the peak area at 1050, 1013, and 1087 cm⁻¹ in Raman spectra, respectively, were investigated as a function of reaction time. As shown in Fig. 4, Ca(NO₃)₂ was produced before CaSO₄. Nitrate was detected immediately after the reaction started, and reached a maximum at ~50 min whereas sulfate did not reach the detection limit until 82 min of the reaction. Sulfate increased slowly in the reaction and we did not observe it leveling off even after 1050 min.

According to the time series of carbonate, nitrate, and sulfate, this reaction consisted of two successive processes. The first process was the formation of Ca(NO₃)₂, which was accompanied with the decline of CaCO₃ (Fig. 4), indicating that Ca(NO₃)₂ was produced due to the reaction of CaCO₃ with NO₂. Ca(NO₃)₂ has been observed in the reaction of CaCO₃ with NO₂ in previous studies (Li et al., 2010; Tan et al., 2017). 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:

\[ \text{NO}_2(g) \leftrightarrow \text{NO}_2(aq) \]  \hspace{1cm} (R1)

\[ 2\text{NO}_2(aq) + \text{H}_2\text{O}(aq) \rightarrow \text{HNO}_3(aq) + \text{HNO}_2(aq) \]  \hspace{1cm} (R2)

\[ \text{HNO}_3(aq) \rightarrow \text{H}^+(aq) + \text{NO}_3^-(aq) \]  \hspace{1cm} (R3)

\[ \text{CaCO}_3(s) + \text{H}^+(aq) \rightarrow \text{Ca}^+(aq) + \text{HCO}_3^-(aq) \]  \hspace{1cm} (R4)

\[ \text{HCO}_3^-(aq) + \text{H}^+(aq) \rightarrow \text{H}_2\text{O}(aq) + \text{CO}_2(g) \]  \hspace{1cm} (R5)

The detailed mechanism of the formation of Ca(NO₃)₂ in the reaction CaCO₃ with NO₂ have been studied by Li et al. (2010). The second process was the formation of CaSO₄ through the oxidation of SO₂. CaSO₄ was mainly produced after CaCO₃ was completely reacted and increased steadily as the reaction proceeded. The much faster Ca(NO₃)₂ formation due to the NO₂ uptake on CaCO₃ particle compared with the reaction of SO₂ with NO₂ and
sulfate appearing only after the complete conversion of CaCO₃ indicate that the reaction of SO₂ with NO₂ does not contributed significantly to NO₂ uptake.

3.3 Reaction mechanism

3.3.1 Mechanism of sulfate formation

Based on the results above, we found that a series of reactions of SO₂ and NO₂ on a CaCO₃ particle led to sulfate formation. Almost the entire sulfate was produced after a CaCO₃ particle was converted to a Ca(NO₃)₂ droplet (Fig. 4), although in some experiments a trace amount of sulfate could be observed when a small amount of CaCO₃ was still left in the Ca(NO₃)₂ droplet. The absence or low amount of sulfate before CaCO₃ was completely reacted might be due to the competition between the reaction of aqueous NO₂ with CaCO₃ and the reaction with SO₂. This result suggests that forming a Ca(NO₃)₂ droplet was key to the formation of sulfate.

This finding is further supported by the results of the reaction of SO₂ with NO₂ on a Ca(NO₃)₂ droplet (Fig. 5 and Table 1). Using a Ca(NO₃)₂ droplet as the reactant, the reaction with SO₂/NO₂ at the same condition still produced CaSO₄ confirming CaCO₃ was not necessary for sulfate formation. The reaction with Ca(NO₃)₂ produced similar amount of sulfate to the reaction with CaCO₃ based on Raman spectra and microscopic images (Fig. 5), which indicates that Ca(NO₃)₂ droplet was important for sulfate formation. Therefore, we conclude that SO₂ was mainly oxidized via the multiphase reaction on the Ca(NO₃)₂ droplet while CaCO₃ mainly worked as a precursor of the Ca(NO₃)₂ droplet.

The oxidant of SO₂ can be NO₃⁻ or NO₂ in the Ca(NO₃)₂ droplet here. In a reaction between Ca(NO₃)₂ droplets and SO₂ (150 ppm) under 72% RH, we did not observe any sulfate formation on the basis of the Raman spectra and microscopic image after 5 h of reaction. This indicates that NO₃⁻ was not the oxidant for SO₂ in our study, which was also consistent with a previous study (Martin et al., 1981). Therefore, we conclude that SO₂ was oxidized by NO₂ in the Ca(NO₃)₂ droplet.

According to previous studies, NO₂ can oxidize sulfite and bisulfite ions into sulfate ion in aqueous phase (Ellison and Eckert, 1984; Shen and Rochelle, 1998; Littlejohn et al., 1993). The overall mechanism was described to be (Clifton et al., 1988):

\[
\begin{align*}
2\text{NO}_2(aq) + \text{SO}_3^{2-}(aq) + \text{H}_2\text{O} & \rightarrow 2\text{H}^+ + 2\text{NO}_2^-(aq) + \text{SO}_4^{2-}(aq) \quad (R6) \\
2\text{NO}_2(aq) + \text{HSO}_3^-(aq) + \text{H}_2\text{O} & \rightarrow 3\text{H}^+ + 2\text{NO}_2^-(aq) + \text{SO}_4^{2-}(aq) \quad (R7)
\end{align*}
\]

Under the experimental conditions of our study, water uptake of Ca(NO₃)₂ led to condensation of liquid water, which provided a site for aqueous oxidation of S(IV) by NO₂. The relative fractions of the three S(IV) species depend on pH and the equilibrium between them is fast (Seinfeld and Pandis, 2006). The pH of the droplet was mainly determined by the gas-aqueous equilibrium of SO₂ in this study and estimated to be ~3. The concentrations of HSO₃⁻, H₂SO₄, and SO₄²⁻ were estimate to be ~1.1×10⁻³, 9.2×10⁻⁵, and 6.6×10⁻⁴ mol L⁻¹, respectively, using the equilibrium constants in Seinfeld and Pandis (2006) and thus the main S(IV) species was HSO₃⁻. Then SO₄²⁻ from S(IV) oxidation can react with Ca²⁺ forming CaSO₄ precipitation as observed in Raman spectra due to the low value of Kₛ_p for CaSO₄ (Lide, 2009):

\[
\text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq) \rightarrow \text{CaSO}_4(s) \quad (R8)
\]
Some previous studies have shown that SO₂ can react with CaCO₃ to produce calcium sulfite (CaSO₃) (Li et al., 2006; Prince et al., 2007b; Ma et al., 2013a), and CaSO₃ can be oxidized to CaSO₄ by NO₂ (Rosenberg and Grotta, 1980; Ma et al., 2013a). In our study, we investigated the reaction between CaCO₃ and SO₂ (150 ppm) at 72% RH. We found that both sulfate and sulfite were lower than the detection limit of our Raman spectrometer even after 300 min of the reaction. This indicates that forming CaSO₃ was not the main pathway in CaSO₄ formation in our study and CaCO₃ did not directly contribute to the formation of CaSO₄.

### 3.3.2 Effects of cations in sulfate formation

Since sulfate was observed to precipitate as CaSO₄, we further analyzed the effect of precipitation reaction and cations on the aqueous oxidation of SO₂ by NO₂. In order to test effects of cations, we replaced Ca²⁺ with Na⁺ or NH₄⁺. Based on Raman spectra, we found that in the reaction of a NaNO₃ or a NH₄NO₃ droplet with NO₂/SO₂, sulfate was below the detection limit after 300 min in the same reaction conditions as Ca(NO₃)₂ and CaCO₃ (Fig. 6 and Table 1). Accordingly, no sulfate solid particles were observed in these droplets. Clearly, the sulfate production rate was larger in the presence of Ca²⁺ compared to those in the presence of Na⁺ or NH₄⁺. The difference can be explained by the change of Gibbs energy. The spontaneity of the SO₂ oxidation by NO₂ for Reaction (R2) can be analyzed using the reaction Gibbs energy as follows:

\[
\Delta_rG = \Delta_rG^\theta + RT \ln \frac{a_{H^+}^{a_{SO_3}^{aq}} \cdot a_{NO_2}^{aq}}{a_{HNO_2}^{aq} \cdot a_{HSO_3}^{aq}}
\]

where \(\Delta_rG\) is the reaction Gibbs energy, \(\Delta_rG^\theta\) is the standard reaction Gibbs energy, \(R\) is the gas constant, \(T\) is temperature, and \(a\) is the activity of various species. \(\Delta_rG\) 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 \(\Delta_rG\). For Ca(NO₃)₂ droplet, the precipitation of CaSO₄ can substantially decrease the activity of SO₄²⁻, and thus decrease \(\Delta_rG\) and promote the oxidation of SO₂ and sulfate formation. Therefore, we can conclude that the precipitation of less soluble CaSO₄ promoted sulfate formation.

### 3.4 Reactive uptake coefficient of SO₂

The reactive uptake coefficients of SO₂ (\(\gamma\)) for sulfate formation under different conditions are shown in Table 2. Each reaction was repeated for three times, during which, three particles with different size were selected. \(\gamma\) was higher at higher relative humidity, suggesting again that liquid water plays an important role in the formation of CaSO₄. At 17% RH, the reaction between CaCO₃ and NO₂ (the first process of the whole reaction) proceeded very slowly, and the amount of liquid water formed due to the water uptake of Ca(NO₃)₂ was very low. As a result, we did not observe the formation of CaSO₄ (the second process of the whole reaction) after 1000 min of the reaction and even at higher SO₂ and NO₂ concentrations (200 ppm SO₂, 200 ppm NO₂). Under higher relative humidity (46% and 72% RH), sulfate was observed soon after the reaction. It is interesting to note that there were no significant difference for \(\gamma\) between 46% and 72% RH. In either case, the reaction between CaCO₃ and NO₂ proceeded quickly and CaCO₃ was completely converted to a Ca(NO₃)₂ droplet within 100 min.
after the reaction. In the presence of enough liquid water, RH seemed to be no longer a limiting factor. In such conditions, an increase of NO$_2$ concentration (from 75 ppm to 200 ppm at 72% RH) promoted the reactive uptake of SO$_2$.

The reactive uptake coefficient of SO$_2$ for sulfate formation was determined to be on the order of $10^{-8}$ at 46% and 72% RH. This value is higher than the uptake coefficient ($10^{-10}$) on mineral particles sampled from Cape Verde Islands (the main contents being potassium feldspars and quartz) obtained by Ullerstam et al. (2003) using NO$_2$/SO$_2$ mixing gas and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) technique. But the uptake coefficient in this study is lower than the uptake coefficient of SO$_2$ on Arizona Test Dust (ATD) particles in the presence of NO$_2$ ((2.10±0.08)×$10^{-6}$) determined by Park and Jang (2016). γ here is also much lower than the γ of SO$_2$ on oxalic acid particles in the presence of NO$_2$ and NH$_3$ ($10^{-6}$–$10^{-4}$) determined at varying RH reported by Wang et al. (2016). The difference in these uptake coefficients is attributed to the different chemical composition of particles, reaction mechanism, reaction conditions, and the ways that the particle surface is determined. It is worth noting that in the studies of Ullerstam et al. (2003) and Park and Jang (2016), particles exist as solid state and sulfate formation is via gas-solid heterogeneous reaction, and in the study of Wang et al. (2016) sulfate formation is stated to be via aqueous reaction. In this study sulfate formation was via gas-liquid-solid multiphase reaction and liquid water played a key role.

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×$10^6$ mol$^{-1}$ L s$^{-1}$ at pH 5.8 and 6.4. Clifton et al. (1988) determined the rate constant of the reaction of NO$_2$ with sulfite/bisulfite to be (1.24-2.95)×$10^7$ mol$^{-1}$ L s$^{-1}$ at pH 5.6-13 and further reported a rate constant of 1.4×$10^6$ 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, 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 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$^{-4}$ mol Kg$^{-1}$), which may also influence the reaction rate.
In the ambient atmosphere, the reactive uptake coefficient of $\text{SO}_2$ due to the multiphase oxidation by $\text{NO}_2$ is influenced by various factors such as RH, $\text{NO}_2$ concentration, pH, sulfate concentration, and the presence of other ions in aerosol particles. For example, $\text{NO}_2$ concentrations in the atmosphere are much lower than those used in this study. At lower $\text{NO}_2$ concentrations, the uptake coefficient of $\text{SO}_2$ decreases, because the oxidation rate of $\text{SO}_2$ in aqueous phase decreases with decreasing $\text{NO}_2$ concentration. In addition, aqueous sulfate concentrations in aerosol particles in the atmosphere are often high. According to the effect of cations (Section 3.3.2), while reduced sulfate concentration by CaSO4 precipitation likely led to the enhanced sulfate production rate in the reaction of $\text{SO}_2$ on Ca(NO3)$_2$, higher sulfate concentration could increase the reaction Gibbs energy $\Delta G$ (as shown in Eq. 5) and thus suppress the reaction of $\text{SO}_2$ and $\text{NO}_2$. This can reduce the uptake coefficient of $\text{SO}_2$.

Therefore, the reactive uptake coefficient of $\text{SO}_2$ obtained in this study ($10^{-8}$ at 46-72% RH and 75 ppm $\text{NO}_2$) can be regarded as an upper limit of the reactive uptake coefficient of $\text{SO}_2$ due to the multiphase reaction with $\text{NO}_2$ in the ambient atmosphere.

4 Conclusion and implications

We investigated the heterogeneous reaction of $\text{SO}_2$ directly with $\text{NO}_2$ on individual CaCO$_3$ particles in N$_2$ using Micro-Raman spectrometry. The reaction first converted the CaCO$_3$ particle to the Ca(NO$_3$)$_2$ droplet via the reaction with $\text{NO}_2$ in the SO$_2$/NO$_2$/H$_2$O/N$_2$ gas mixture and the deliquescence of Ca(NO$_3$)$_2$, and then formed needle-shaped CaSO$_4$ crystals in the Ca(NO$_3$)$_2$ droplet via the multiphase reaction of $\text{SO}_2$ with $\text{NO}_2$. The sulfate formation was observed only during the multiphase oxidation by $\text{NO}_2$, that is, after the complete conversion of CaCO$_3$ to Ca(NO$_3$)$_2$ droplet. The precipitation of CaSO$_4$ from solution promoted sulfate formation. The reactive uptake coefficient of $\text{SO}_2$ for sulfate formation in the multiphase reaction with $\text{NO}_2$ is on the order of $10^{-8}$ under the experimental conditions of this study (RH: 46-72%, $\text{NO}_2$: 75 ppm). The reactive uptake coefficient of $\text{SO}_2$ was found to be enhanced at higher RH.

In order to assess the importance of the multiphase reaction of $\text{SO}_2$ directly oxidized by $\text{NO}_2$ to sulfate in the atmosphere, we compare the lifetime of $\text{SO}_2$ due to the multiphase oxidation of $\text{SO}_2$ by $\text{NO}_2$ with the lifetime due to the gas phase oxidation of $\text{SO}_2$ by OH. Using a daytime OH concentration of $1 \times 10^6$ molecule cm$^{-3}$ (Lelieveld et al., 2016; Prinn et al., 2005), the lifetime of $\text{SO}_2$ in the atmosphere due to gas phase OH oxidation is around 12 days. The life time of $\text{SO}_2$ due to the multiphase oxidation by $\text{NO}_2$ is around 7000 days using the uptake coefficient of $\text{SO}_2$ from this study ($3.22 \times 10^{-8}$) and a typical particle surface area concentration for mineral aerosols in winter in Beijing ($6.3 \times 10^{-6}$ cm$^2$ cm$^{-3}$) (Huang et al., 2015). Using an annual average particle surface area concentration of PM$_{10}$ in Beijing ($1.4 \times 10^{-5}$ cm$^2$ cm$^{-3}$)(Wehner et al., 2008) results in a $\text{SO}_2$ life time of 3300 days due to the multiphase oxidation by $\text{NO}_2$. In the atmosphere, the lifetime of $\text{SO}_2$ due to the multiphase oxidation by $\text{NO}_2$ should be even longer than these values because the uptake coefficient of $\text{SO}_2$ used here ($3.22 \times 10^{-8}$) is an upper limit of the uptake coefficient of $\text{SO}_2$ in the ambient atmosphere as discussed above. This comparison indicates that the direct multiphase oxidation of $\text{SO}_2$ by $\text{NO}_2$ is unlikely to be an important sink of $\text{SO}_2$ and source of sulfate compared with the oxidation of $\text{SO}_2$ by OH.

In this study, we investigated the multiphase oxidation of $\text{SO}_2$ directly by $\text{NO}_2$ via using inert N$_2$ as a carrier gas and assessed the importance of this reaction in the atmosphere. Although the oxidation of $\text{SO}_2$ by $\text{NO}_2$ alone
unlikely contributes significantly to sulfate formation, NO₂ may facilitate the oxidation of SO₂ by other oxidants. For example, in the ambient atmosphere, O₂ is abundantly present and previous studies have suggested that O₂ can oxidize sulfite in the presence of NO₂ in bulk aqueous solution (Littlejohn et al., 1993). Therefore, the potential synergy of NO₂ and other multiphase oxidation pathways of SO₂ on aqueous aerosol particles warrants further studies. We will address the synergy of NO₂ and the multiphase oxidation of SO₂ by O₂ in a companion paper.

Despite the less important role in sulfate formation, the multiphase oxidation of SO₂ by NO₂ on CaCO₃ particles helps interpreting the findings from field studies. For example, internally mixed CaCO₃ with Ca(NO₃)₂ and CaSO₄ particles with varying reacted fractions of CaCO₃ were observed in the field (Hwang and Ro, 2006; Li and Shao, 2009), but how the internally mixed particles are formed is not clear. In this study we showed that CaSO₄ can be formed inside the Ca(NO₃)₂ droplet after the deliquescence of initially produced Ca(NO₃)₂ through the reaction of SO₂ with NO₂. In this way, internally mixed CaCO₃ with Ca(NO₃)₂ and CaSO₄ particles can be formed. Moreover, Hwang and Ro (2006) found that CaSO₄-containing particles were observed to be almost always internally mixed with nitrate. The multiphase reaction process of SO₂ with NO₂ on CaCO₃ particles found in this study can also explain this finding.

Acknowledgements

This work was supported by Natural Science Foundation Committee of China (41421064, 21190051, 40490265) and Ministry of Science and Technology (Grant No. 2002CB410802).
References


Table 1 Summary of the results obtained in different reaction systems

<table>
<thead>
<tr>
<th>Particle</th>
<th>Gases</th>
<th>RH (%)</th>
<th>Whether sulfate was detected</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃</td>
<td>SO₂(75 ppm)+NO₂(75 ppm)</td>
<td>72</td>
<td>Yes</td>
</tr>
<tr>
<td>Ca(NO₃)₂ droplet</td>
<td>SO₂(75 ppm)+NO₂(75 ppm)</td>
<td>72</td>
<td>Yes</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>SO₂ (150 ppm)</td>
<td>72</td>
<td>No</td>
</tr>
<tr>
<td>Ca(NO₃)₂ droplet</td>
<td>SO₂ (150 ppm)</td>
<td>72</td>
<td>No</td>
</tr>
<tr>
<td>NaNO₃ droplet</td>
<td>SO₂(75 ppm)+NO₂(75 ppm)</td>
<td>72</td>
<td>No</td>
</tr>
<tr>
<td>NH₄NO₃ droplet</td>
<td>SO₂(75 ppm)+NO₂(75 ppm)</td>
<td>72</td>
<td>No</td>
</tr>
</tbody>
</table>
Table 2. Reactive uptake coefficient of SO$_2$ for sulfate formation ($\gamma$) during the reaction of SO$_2$ with NO$_2$ on individual CaCO$_3$ particles under different conditions at 298 K.

<table>
<thead>
<tr>
<th>[SO$_2$] (ppm)</th>
<th>[NO$_2$] (ppm)</th>
<th>RH (%)</th>
<th>$\gamma \times 10^{-8}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>75</td>
<td>72</td>
<td>3.22±1.08</td>
</tr>
<tr>
<td>75</td>
<td>200</td>
<td>72</td>
<td>16.0±3.12</td>
</tr>
<tr>
<td>75</td>
<td>75</td>
<td>46</td>
<td>3.22±0.90</td>
</tr>
<tr>
<td>75</td>
<td>75</td>
<td>17</td>
<td>0$^a$</td>
</tr>
<tr>
<td>200</td>
<td>200</td>
<td>17</td>
<td>0$^a$</td>
</tr>
</tbody>
</table>

$^a$: Sulfate was below the detection limit.
Fig. 1. Schematic diagram of the experimental setup. MFC: mass flow controller.
Fig. 2. Raman spectra of an individual CaCO$_3$ particle during the reaction with NO$_2$ (75 ppm) and SO$_2$ (75 ppm) at 72% RH at the reaction time of 0, 8, 30, 95, and 1050 min.
Fig. 3. Microscopic images of an individual CaCO$_3$ particle (same as in Fig. 2) reacting with NO$_2$ (75 ppm) and SO$_2$ (75 ppm) at 72% RH. a-f corresponds to the reaction time of 0, 6, 29, 37, 94, and 1050 min, respectively.
Fig. 4. Raman peak intensity of carbonate, nitrate (left axis), and sulfate (right axis) as a function of time during the reaction of an individual CaCO$_3$ particle with NO$_2$ (75ppm) and SO$_2$ (75ppm) at 72% RH (same as in Fig. 2 and 3). Note that the scales of the left axis and right axis are different. The intensity of NO$_3^-$, SO$_4^{2-}$, and CO$_3^{2-}$ show the peak area at 1050, 1013, and 1087 cm$^{-1}$, respectively, in Raman spectra obtained by Raman mapping. 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.
Fig. 5. Raman spectra (a) and microscopic image (b) of a Ca(NO$_3$)$_2$ droplet reacting with NO$_2$ (75 ppm) and SO$_2$ (75 ppm) at 72% RH at a reaction time of 300 min. The peak at 1014 cm$^{-1}$ in Raman spectra and crystals from the microscopic image indicate CaSO$_4$ was formed in this reaction.
Fig. 6. Raman spectra of a NH₄NO₃ (a) and NaNO₃ (b) droplet reacting with NO₂ (75 ppm) and SO₂ (75 ppm) at 72% RH at the reaction time of 300 min.
Supplement of
Multiphase Reaction of SO₂ on CaCO₃ Particles. 1. Oxidation of SO₂ by NO₂

Defeng Zhao*, Xiaojuan Song*, Tong Zhu, Zefeng Zhang, Yingjun Liu

BIC-ESAT and SKL-ESPC, College of Environmental Sciences and Engineering, Peking University, Beijing, 100871, China

*These authors contributed equally to this work.

Correspondence to: Tong Zhu (tzhu@pku.edu.cn)
S1. Deriving the reactive uptake coefficient from aqueous reaction rate constant

The reaction rate constant in the literature was used to derive the reactive uptake coefficient to particles under the same conditions as in this study using the method in Davidovits et al. (2006).

\[ \frac{1}{\gamma} = \frac{1}{\Gamma_{diff}} + \frac{1}{\alpha} + \frac{1}{\Gamma_{sat} + \Gamma_{rxn}} \]  

(1)

where $\Gamma_{diff}$ is the transport coefficient in the gas phase, $1/\Gamma_{diff}$ is the resistance due to the diffusion in the gas phase. Similarly, $1/\Gamma_{sat}$ and $1/\Gamma_{rxn}$ are the resistance due to liquid phase saturation and liquid phase reaction, respectively. $\alpha$ is the mass accommodation coefficient of SO$_2$.

$1/\Gamma_{diff}$ can be derived using the following equation:

\[ \frac{1}{\Gamma_{diff}} = \frac{0.75 + 0.238Kn}{Kn(1 + Kn)} \]  

(2)

where $Kn$ is the Knudsen number. Knudsen number is defined as

\[ Kn = \frac{\lambda}{a} \]  

(3)

where $\lambda$ is the mean free path of molecule in the gas phase and $a$ is the radius of the particle.

$\lambda$ can be derived from

\[ \lambda = \frac{2D_g}{c} \]  

(4)

where $D_g$ is the diffusion coefficient in the gas phase and $c$ is the mean molecular velocity.

$c$ is derived from

\[ c = \frac{3RT}{\pi M} \]  

(5)

where $R$ is the gas constant, $T$ is temperature, and $M$ is the molecular mass of SO$_2$.

$1/\Gamma_{sat}$ can be derived from

\[ \frac{1}{\Gamma_{sat}} = \frac{c}{4HRT} \sqrt{\frac{\pi}{D_1}} \]  

(6)

where $H$ is the Henry constant of SO$_2$, $t$ is time, and $D_1$ is the diffusion coefficient of SO$_2$ in the liquid phase.

$1/\Gamma_{rxn}$ can be derived from

\[ \frac{1}{\Gamma_{rxn}} = \frac{c}{4HRT} \sqrt{\frac{1}{k_{rxn}D_1}} \]  

(7)

where $k_{rxn}$ is the first order rate constant of the reaction in the liquid phase.

$k_{rxn} = k[\text{NO}_2(\text{aq})]$  

(8)

where $k$ is the second order rate constant of the reaction of S(IV) with NO$_2$ and $[\text{NO}_2(\text{aq})]$ is the NO$_2$ concentration in the liquid phase.

$[\text{NO}_2(\text{aq})] = H_{\text{NO}_2}P_{\text{NO}_2}$  

(9)

where $H_{\text{NO}_2}$ is the Henry constant of NO$_2$ and $P_{\text{NO}_2}$ is the concentration of NO$_2$ in the gas phase.
References


<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_g$ (m$^2$ s$^{-1}$)</td>
<td>$10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>$a$ (m)</td>
<td>$8.3 \times 10^{-6}$</td>
<td></td>
</tr>
<tr>
<td>$R$ (J mol$^{-1}$ K$^{-1}$)</td>
<td>8.314</td>
<td></td>
</tr>
<tr>
<td>$T$ (K)</td>
<td>298</td>
<td></td>
</tr>
<tr>
<td>$M_{SO_2}$ (Kg mol$^{-1}$)</td>
<td>$6.4 \times 10^2$</td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.35</td>
<td>Davidovits et al. (2006)</td>
</tr>
<tr>
<td>$D_l$ (m$^2$ s$^{-1}$)</td>
<td>$8.3 \times 10^{-12}$a</td>
<td>Mahiuddin and Ismail (1983)</td>
</tr>
<tr>
<td>$H_{SO_2}$ (mol L$^{-1}$ atm$^{-1}$)</td>
<td>1.23</td>
<td>Seinfeld and Pandis (2006)</td>
</tr>
<tr>
<td>$H_{NO_2}$ (mol L$^{-1}$ atm$^{-1}$)</td>
<td>$1 \times 10^{-7}$</td>
<td>Seinfeld and Pandis (2006)</td>
</tr>
</tbody>
</table>

$a$ The aqueous phase diffusion coefficient was derived from the viscosity of Ca(NO$_3$)$_2$ solution providing that diffusion coefficient is inversely proportional to viscosity according to the Stokes–Einstein equation (Bones et al., 2012) and assuming that the diffusion coefficient in water is $10^{-9}$ m$^2$ s$^{-1}$.  

4
Figure S1. Calibration curve for sulfate showing the peak area of sulfate at 1016 cm$^{-1}$ in Raman spectra versus the amount of CaSO$_4$. 
Figure S2. Raman mapping analysis of a CaCO₃ particle during the reaction with NO₂ (75 ppm) and SO₂ (75 ppm) at 72% RH at the reaction time of 0, 8, 26, 40, 97, and 1053 min. Blue, red, and green indicate the Raman peak intensity of carbonate, nitrate, and sulfate at 1087, 1050, and 1013 cm⁻¹, respectively.