Response to the editor

We thank the editor for the time and the helpful comments on our manuscript. We have addressed all the comments. According to these comments, we have revised our manuscript. As follows, please find our one-by-one responses to these comments. The original comments are shown in italics and the revised texts are highlighted.

Comments to the Author:

dear authors

I acknowledge that the reaction studied in this manuscript, NO$_2$ + SO$_2$, in absence of O$_2$, is important enough to merit publication as a separate manuscript. The formation of sulfate from S(IV) in aerosol particles especially under heavy pollution conditions has been suggested to operate with NO$_2$ being the oxidant. Even though this study has not covered the atmospherically relevant NO$_2$ partial pressure range and also has not looked at the effect of pH or especially high pH values for which the reaction NO$_2$ + SO$_2$ has been suggested to contribute most to the formation of sulfate, it provides valuable insight into the mechanism of this reaction at low pH (relevant for most atmospheric conditions). It is important to document the low reaction rates resulting from this reaction.

Response:

We thank the editor for the supportive remarks on the scientific significance of our study.

To make sure that these aspects are well documented and explained I am asking for a few minor additional revisions in the relevant sections of the manuscript:

abstract, line 17: please also mention that it is not important also in comparison to the other aqueous phase pathways, such as reaction with O$_2$, w/o transition metals, or H$_2$O$_2$.

Response:

Accepted. In the revised manuscript, we have revised the sentence as follows:

“We estimate that the direct multiphase oxidation of SO$_2$ by NO$_2$ is not an important source of sulfate in the ambient atmosphere compared with the SO$_2$ oxidation by OH in the gas phase and is not as important as other aqueous phase pathways, such as the reactions of SO$_2$ with H$_2$O$_2$, O$_3$, and O$_2$, with or without transition metals.”

line 38: replace 'liquid water' by aqueous solution. Strictly speaking, 'liquid water' refers to pure water only. please check the usage of the term 'liquid water' also in the remainder of the manuscript.

Response:

Accepted. In the revised manuscript, we have replaced “liquid water” with “aqueous solution” here and checked its usage throughout the manuscript. In some parts, we have replaced it with “water in aqueous solution”.

line 63: ionic strength (not ion strength)

Response:
Accepted. In the revised manuscript, we have corrected it.

*line 67 and 78: mention the contribution of this reaction to sulfate formation in the Cheng/Wang/Xue studies in comparison to that involving O₂ (if they looked at it). For the Cheng et al. reference: explicitly mention that they considered this reaction (not with O₂) being the most important pathway.*

**Response:**

Accepted.

The studies of Cheng et al., 2016/Wang et al., 2016/Xue et al., 2016 all focus on the contribution of the direct oxidation of SO₂ by NO₂ to sulfate formation. The reaction involving O₂ was only investigated in Wang et al., (2016) and was found to be negligible in sulfate formation. In the revised manuscript, we have mentioned this. We have also explicitly mentioned that the study of Cheng et al. (2016) considered the direct oxidation of SO₂ by NO₂ to be the most important sulfate formation pathway. The revised text is as follows:

“In this study, we present [the finding that the multiphase reaction of SO₂ directly with NO₂ is not an important source of sulfate in the atmosphere, in the absence of other oxidants such as O₂. The direct oxidation of SO₂ by NO₂ pathway was proposed in a number of recent studies to be potentially important for sulfate formation (Cheng et al., 2016; Wang et al., 2016; Xue et al., 2016). For example, Cheng et al. (2016) considered the direct oxidation of SO₂ by NO₂ to be the most important pathway to explain the missing sulfate source during the haze events in Beijing. Wang et al. (2016) also proposed that the direct oxidation of SO₂ by NO₂ is key to efficient sulfate formation in the presence of high relative humidity and NH₃ and showed that in their laboratory study sulfate formation is mainly contributed by the direct oxidation by NO₂ and the role of O₂ is negligible.]”

*line 114: maybe explain why the majority of experiments were not performed with Ca(NO₃)₂ directly. I don't think that reaction of CaCO₃ with NO₂ is the main source of Ca(NO₃)₂ in the atmosphere. I guess HNO₃ is doing this mostly.*

**Response:**

Accepted.

Most of the experiments in this study were conducted using CaCO₃ rather than directly using Ca(NO₃)₂ because CaCO₃ is an important component of mineral aerosols, especially in China as mentioned in the introduction and often used as a surrogate of mineral aerosols. Moreover, using CaCO₃ particles can better simulate the reaction on internally-mixed CaCO₃(solid)-Ca(NO₃)₂(aqueous) particles, which is widely observed in the ambient atmosphere and laboratory (Laskin et al., 2005; Zhang et al., 2003; Li and Shao, 2009; Sullivan et al., 2007; Li et al., 2010; Liu et al., 2008), and is formed via the reaction of CaCO₃ with acidic gases such as HNO₃ and NO₂ due to its alkalinity. Ca(NO₃)₂ is usually believed to be mainly formed by the reaction of CaCO₃ with HNO₃. The reaction of CaCO₃ with NO₂ also contributes to the formation of Ca(NO₃)₂, especially at high NO₂ and at high RH (Li...
et al., 2010). Regardless of the source of Ca(NO$_3$)$_2$, Ca(NO$_3$)$_2$ droplet or Ca(NO$_3$)$_2$ aqueous layer on CaCO$_3$ particles can provide a site for the multiphase oxidation of SO$_2$ by NO$_2$.

In the revised manuscript, we have revised the text as follows.

"Most experiments were conducted using CaCO$_3$ particles rather than directly using Ca(NO$_3$)$_2$ particles. CaCO$_3$ was selected because it is an important component of mineral aerosols, especially in China as mentioned in the introduction and often used as a surrogate of mineral aerosols. Moreover, using CaCO$_3$ particles can better simulate the reaction on internally-mixed CaCO$_3$(solid)-Ca(NO$_3$)$_2$(aqueous) particles, which is widely observed in the ambient atmosphere and laboratory (Laskin et al., 2005; Zhang et al., 2003; Li and Shao, 2009; Sullivan et al., 2007; Li et al., 2010; Liu et al., 2008), and is formed via the reaction of CaCO$_3$ with acidic gases such as HNO$_3$ and NO$_2$ due to its alkalinity."

line 160: of H$_2$O in aqueous solution.

Response: Accepted. In the revised manuscript, we have changed “liquid water” to “water in aqueous solution”.

line 364: add a caveat here that this study did not look at the pH dependence, and especially not at high pH, for which recent studies have claimed this reaction to be important. Also please mention that more likely other oxidation pathways, such as with H$_2$O$_2$, O$_3$ and O$_2$ as oxidants, and w/o transition metals, must be more important.

Response: Accepted.

In the revised manuscript, we have added the following discussion as the editor suggested.

“It is worth mentioning that this study did not investigate the dependence of the reactive uptake coefficient due to the direct oxidation of SO$_2$ by NO$_2$ on pH, especially not under high pH conditions, for which recent studies have claimed this reaction to be important (Cheng et al., 2016; Wang et al., 2016). Because of the important role of multiphase/heterogeneous reactions in SO$_2$ oxidation found in the atmosphere and the low reaction rate of the direct multiphase oxidation of SO$_2$ by NO$_2$, it is more likely that the aqueous reactions of SO$_2$ with other oxidants, such as the reactions with H$_2$O$_2$, O$_3$, and O$_2$, with or without transition metals, could be important pathways for sulfate formation in the atmosphere.”

lines around 370: I think the statements about the mixing state of CaSO$_4$ with nitrate are ok, but this is independent of the oxidation mechanism; but the source of nitrate is more likely HNO$_3$ and N$_2$O$_5$, and rather not NO$_2$ under atmospheric conditions.

Response: Accepted.

We agree that the formation of internally-mixed CaSO$_4$/Ca(NO$_3$)$_2$ particles is independent of the oxidation mechanism of SO$_2$ once Ca(NO$_3$)$_2$ aqueous layer is formed via the reaction with either HNO$_3$, N$_2$O$_5$, or NO$_2$, although the reaction of SO$_2$ with NO$_2$ is shown to contribute to the formation of these
internally-mixed particles in this study. In the revised manuscript, we decide to delete this paragraph.

References
Multiphase Oxidation of SO$_2$ by NO$_2$ on CaCO$_3$ Particles

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Abstract. Heterogeneous/multiphase oxidation of SO$_2$ by 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, in order to assess the importance of the direct oxidation of SO$_2$ by NO$_2$ we investigated the heterogeneous/multiphase reaction of SO$_2$ with NO$_2$ on individual CaCO$_3$ particles in N$_2$ using Micro-Raman spectroscopy. In the 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 NO$_2$ and the deliquescence of Ca(NO$_3$)$_2$, and then NO$_2$ oxidized 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 SO$_2$ by NO$_2$. The precipitation of CaSO$_4$ from the droplet solution promoted sulfate formation. The reactive uptake coefficient of 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 SO$_2$ by NO$_2$ is not an important source of sulfate in the ambient atmosphere compared with the SO$_2$ oxidation by OH in the gas phase and is not as important as other aqueous phase pathways, such as the reactions of SO$_2$ with H$_2$O$_2$, O$_3$, and O$_2$, with or without transition metals.
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 SO$_2$ (Seinfeld and Pandis, 2006). In the continent, the main source of sulfate is the oxidation of SO$_2$, an important air pollutant from fossil fuel combustion. SO$_2$ can be oxidized in the gas phase, mainly by OH, or in the particle phase such as by H$_2$O$_2$, O$_3$, or O$_2$ catalyzed by transition metal ions in cloud or fog water (Seinfeld and Pandis, 2006; Finlayson-Pitts and Pitts Jr., 1999) or by O$_3$ 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 SO$_2$ oxidation are identified, the source of sulfate and relative importance of various pathways of SO$_2$ 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 SO$_2$ 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; 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; Cheng et al., 2016; Wang et al., 2016). 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 aqueous solution. In particular, several recent studies propose that the multiphase oxidation of SO$_2$ by NO$_2$, another important air pollutant, on liquid particles may be a major pathway of sulfate formation (Wang et al., 2016; Xue et al., 2016; Xie et al., 2015; Cheng et al., 2016). Both SO$_2$ and NO$_2$ 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 SO$_2$ in sulfate formation, laboratory studies are needed to understand the reaction process and obtain kinetic parameters for modeling such as uptake coefficients of SO$_2$. Among many studies investigating the heterogeneous reactions of SO$_2$ 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 SO$_2$ in the presence of NO$_2$ (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 NO$_2$ can promote sulfate formation from SO$_2$ 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 SO$_2$ due to the reaction with NO$_2$. Importantly, most of these studies focused on the gas-solid reactions on particles. Very few laboratory studies have investigated the multiphase reaction of SO$_2$ with NO$_2$ 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 ($\text{H}_2\text{SO}_3$, $\text{HSO}_3^-$, $\text{SO}_3^{2-}$) 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 Gracic, 2001) relevant to the conditions in cloud water. However, in aqueous aerosol particles, the reaction rate and process may be substantially different from those in bulk solution due to high ionic 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 present the finding that the multiphase reaction of SO$_2$ directly with NO$_2$ is not an important source of sulfate in the atmosphere, in the absence of other oxidants such as O$_2$. The direct oxidation of SO$_2$ by NO$_2$ pathway was proposed in a number of recent studies to be potentially important for sulfate formation (Cheng et al., 2016; Wang et al., 2016; Xue et al., 2016). For example, Cheng et al. (2016) considered the direct oxidation of SO$_2$ by NO$_2$ to be the most important pathway to explain the missing sulfate source during the haze events in Beijing. Wang et al. (2016) also proposed that the direct oxidation of SO$_2$ by NO$_2$ is key to efficient sulfate formation in the presence of high relative humidity and NH$_3$ and showed that in their laboratory study sulfate formation is mainly contributed by the direct oxidation by NO$_2$ and the role of O$_2$ is negligible.

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. N$_2$ was used as carrier gas in order to avoid confounding effects of other oxidants including O$_2$ in SO$_2$ oxidation. 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 oxidation of SO$_2$ by NO$_2$ in the atmosphere.

### 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$_3$, and 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. Most experiments were conducted using CaCO$_3$ particles rather than directly using Ca(NO$_3$)$_2$ particles. CaCO$_3$ was selected because it is an important component of mineral aerosols especially in China as mentioned in the introduction and often used as a surrogate of mineral aerosols. Moreover, using CaCO$_3$ particles can better simulate the reaction on internally-mixed CaCO$_3$(solid)-Ca(NO$_3$)$_2$(aqueous) particles, which is widely observed in the ambient atmosphere and laboratory (Laskin et al., 2005; Zhang et al., 2003; Li and Shao, 2009; Sullivan et al., 2007; Li et al., 2010; Liu et al., 2008), and is formed via the reaction of CaCO$_3$ with acidic gases such as HNO$_3$ and NO$_2$ due to its alkalinity.

CaCO$_3$ (98%, Sigma) with diameters about 7-10 μm on average, Ca(NO$_3$)$_2$·4H$_2$O (ACS, 99-103%; Riedel-de Haén), 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):

$$I(\nu) = I_0 \cdot A(\nu) \cdot J(\nu) \cdot \nu^4 \cdot D \cdot K$$  \hspace{1cm} (1)

where $I_0$ is the intensity of incident laser, $A(\nu)$ is the collection efficiency function of a 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 as an internal standard (Zhao et al., 2011; Liu et al., 2008). However, in this study, one product (CaSO₄, 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 CaSO₄ 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 μm 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 of 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 SO₂. The reactive uptake coefficient $\gamma$ of SO₂ 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 ($Z$),

$$\gamma = \frac{d\{SO_4^{2-}\}}{dt} \cdot \frac{1}{Z}.$$ \hspace{1cm} (2)

$$Z = \frac{\frac{1}{2} c A_s [SO_2]}{},$$ \hspace{1cm} (3)

$$c = \frac{R T}{\sqrt{\pi M_{SO_2}}}.$$ \hspace{1cm} (4)

where $R$ is the gas constant, $T$ is temperature, $M_{SO_2}$ is the molecular weight of SO₂, and $c$ is the mean molecular velocity of SO₂, $A_s$ is the surface area of an individual particle. $Z$ is the collision rate between SO₂ and a particle. $\{SO_4^{2-}\}$ indicates the amount of sulfate on the particle phase in mole, and $[SO_2]$ indicates the concentration of SO₂ 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(NO₃)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 of a 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 CaCO₃ particle during the reaction with SO₂ and NO₂. The peak at 1087 cm⁻¹ is assigned to the symmetric stretching mode of carbonate (ν₁) (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 (ν₁). This demonstrates that calcium nitrate (Ca(NO₃)₂) was produced during the reaction. A broad band at 2800-3800 cm⁻¹ was also observed together with the formation of Ca(NO₃)₂. It is assigned to –OH stretching of water in aqueous solution. The formation of aqueous solution is attributed to the deliquescence of Ca(NO₃)₂, which is very hygroscopic and can deliquesce at ~10% 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 (ν₁) in anhydrite (CaSO₄) (Sarma et al., 1998). This peak clearly demonstrates that sulfate was formed. CaSO₄ 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 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 water or water in aqueous solution, 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. HNO$_2$ could evaporate into the gas phase due to the continuous flushing of reactant gases during the experiments and acidity of the droplet (see below). The reaction equations are as follows:

$$\text{NO}_2(g) \leftrightarrow \text{NO}_2(aq) \quad (R1)$$

$$2\text{NO}_2(aq) + \text{H}_2\text{O}(aq) \rightarrow \text{HNO}_3(aq) + \text{HNO}_2(aq) \quad (R2)$$

$$\text{HNO}_3(aq) \rightarrow \text{H}^+(aq) + \text{NO}_3^-(aq) \quad (R3)$$

$$\text{CaCO}_3(s) + \text{H}^+(aq) \rightarrow \text{Ca}^+(aq) + \text{HCO}_3^-(aq) \quad (R4)$$

$$\text{HCO}_3^-(aq) + \text{H}^+(aq) \rightarrow \text{H}_2\text{O}(aq) + \text{CO}_2(g) \quad (R5)$$

$$\text{HNO}_2(aq) \leftrightarrow \text{HNO}_2(g) \quad (R6)$$

The detailed mechanism of the formation of Ca(NO$_3$)$_2$ in the reaction CaCO$_3$ with NO$_2$ have been studied by Li et al. (2010).

The second process was the formation of CaSO$_4$ through the oxidation of SO$_2$ by NO$_2$. CaSO$_4$ was mainly produced after CaCO$_3$ was completely reacted and increased steadily as the reaction proceeded. The amount of Ca(NO$_3$)$_2$ as the product of NO$_2$ uptake was overwhelmingly higher than that of CaSO$_4$ as the product of the reaction SO$_2$ with NO$_2$, which only reached detection limit after the complete conversion of CaCO$_3$. This indicates that the reaction of SO$_2$ with NO$_2$ did not contribute significantly to NO$_2$ uptake before CaCO$_3$ completely converted to Ca(NO$_3$)$_2$. Afterwards, the reaction of SO$_2$ with NO$_2$ promoted the reactive uptake of NO$_2$ by Ca(NO$_3$)$_2$ droplet.

### 3.3 Reaction mechanism

#### 3.3.1 Mechanism of sulfate formation

Based on the results above, we found that a series of reactions of SO$_2$ and NO$_2$ on a CaCO$_3$ particle led to sulfate formation. Almost the entire sulfate was produced after a CaCO$_3$ particle was converted to a Ca(NO$_3$)$_2$ droplet (Fig. 4), although in some experiments a trace amount of sulfate could be observed when a small amount of CaCO$_3$ was still left in the Ca(NO$_3$)$_2$ droplet. The absence or low amount of sulfate before CaCO$_3$ was completely reacted might be due to the competition between the reaction of aqueous NO$_2$ with CaCO$_3$ and the reaction with SO$_2$. This result suggests that forming a Ca(NO$_3$)$_2$ droplet was key to the formation of sulfate.

This finding is further supported by the results of the reaction of SO$_2$ with NO$_2$ on a Ca(NO$_3$)$_2$ droplet (Fig. 5 and Table 1). Using a Ca(NO$_3$)$_2$ droplet as the reactant, the reaction with SO$_2$/NO$_2$ at the same condition still produced CaSO$_4$, confirming CaCO$_3$ was not necessary for sulfate formation. The reaction with Ca(NO$_3$)$_2$ produced similar amount of sulfate to the reaction with CaCO$_3$ based on Raman spectra and microscopic images (Fig. 5), which indicates that Ca(NO$_3$)$_2$ droplet was important for sulfate formation. Therefore, we conclude that SO$_2$ was mainly oxidized via the multiphase reaction on the Ca(NO$_3$)$_2$ droplet while CaCO$_3$ mainly worked as a precursor of the Ca(NO$_3$)$_2$ droplet.

The oxidant of SO$_2$ can be NO$_3^-$ or NO$_2$ in the Ca(NO$_3$)$_2$ droplet here. In a reaction between Ca(NO$_3$)$_2$ droplets and SO$_2$ (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 NO$_3^-$ was not the oxidant for SO$_2$ in our study, which was also consistent with a previous study (Martin et al., 1981). Therefore, we conclude that SO$_2$ was oxidized by NO$_2$ in the Ca(NO$_3$)$_2$ droplet.

According to previous studies, NO$_2$ 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 reaction equation was described to be (Clifton et al., 1988):

\[
2\text{NO}_2(\text{aq}) + \text{SO}_3^{2-}(\text{aq}) + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + 2\text{NO}_2^-(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \quad (R7)
\]

\[
2\text{NO}_2(\text{aq}) + \text{HSO}_3^-(\text{aq}) + \text{H}_2\text{O} \rightarrow 3\text{H}^+ + 2\text{NO}_2^-(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \quad (R8)
\]

Under the experimental conditions of our study, water uptake of Ca(NO$_3$)$_2$ led to condensation of water, which provided a site for aqueous oxidation of S(IV) by NO$_2$. 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 SO$_2$ in this study and estimated to be ~3. The characteristic time to reach the equilibrium in the gas-particle interface (~10$^{-5}$ s) was estimated to be much less than the characteristic time for the aqueous phase reaction of SO$_2$ with NO$_2$ (10$^{-2}$-10$^{-1}$ s) (Supplement S2). Therefore, aqueous S(IV) species can be considered to be in equilibrium with SO$_2$ in the gas phase. The concentrations of HSO$_3^-$, H$_2$SO$_3$, and SO$_3^{2-}$ were estimate 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) (HSO$_2$=1.23 mol L$^{-1}$ atm$^{-1}$, $K_1$=1.3×10$^{-2}$ mol L$^{-1}$, $K_2$=6.6×10$^{-8}$ mol L$^{-1}$) and thus the main S(IV) species was HSO$_3^-$. Then SO$_4^{2-}$ from S(IV) oxidation can react with Ca$^{2+}$ forming CaSO$_4$ precipitation as observed in Raman spectra due to the low value of $K_{sp}$ for CaSO$_4$ (Lide, 2009):

\[
\text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightleftharpoons \text{CaSO}_4(\text{s}) \quad (R9)
\]

Some previous studies have shown that SO$_2$ can react with CaCO$_3$ to produce calcium sulfite (CaSO$_3$) (Li et al., 2006; Prince et al., 2007b; Ma et al., 2013a), and CaSO$_3$ can be oxidized to CaSO$_4$ by NO$_2$ (Rosenberg and Grotta, 1980; Ma et al., 2013a). In our study, we investigated the reaction between CaCO$_3$ and SO$_2$ (150 ppm) at 72% RH. We found that both sulfate and sulfite were lower than the detection limit of our Raman spectrometer (~5×10$^{-14}$ mol for sulfate at a signal to noise ratio of 2 and ~3×10$^{-14}$ mol for sulfite according to the relative Raman scattering cross-section of sulfate and sulfite (Meyer et al., 1980)) even after 300 min of the reaction. This indicates that forming CaSO$_3$ was not the main pathway in CaSO$_4$ formation in our study and CaCO$_3$ did not directly contribute to the formation of CaSO$_4$.

### 3.3.2 Effects of cations in sulfate formation

Since sulfate was observed to precipitate as CaSO$_4$, we further analyzed the effect of precipitation reaction and cations on the aqueous oxidation of SO$_2$ by NO$_2$. In order to test effects of cations, we replaced Ca$^{2+}$ with Na$^+$ or NH$_4^+$. 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, either as aqueous ion (at 984 cm$^{-1}$ and 979 cm$^{-1}$ for (NH$_4$)$_2$SO$_4$ and Na$_2$SO$_4$, respectively) or as in CaSO$_4$ crystal, 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). Considering that the Raman scattering cross-section of sulfate in (NH$_4$)$_2$SO$_4$ aqueous aerosol particle is even higher than sulfate in CaSO$_4$ (Wright, 1973; Stafford et al., 1976), it can be concluded that 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 two possible reasons. The first possible reason may be due to the change of Gibbs energy. The spontaneity of the SO$_2$ oxidation by NO$_2$ for Reaction (R8) can be analyzed using the reaction Gibbs energy as follows:

$$\Delta_r G = \Delta_r G^\theta + RT \ln \frac{a_{H^+}a_{SO_3^-}a_{NO_2}^{a_s}}{a_{NO_2(aq)}^{a_s}a_{HSO_3^-}}$$  

(5)

where $\Delta_r G$ is the reaction Gibbs energy, $\Delta_r G^\theta$ is the standard reaction Gibbs energy, $R$ is the gas constant, $T$ is temperature, and $a$ is the activity of various species.

$\Delta_r G$ 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$_4$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$_2$NO$_3$ 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. The second possible reason is that sulfate may crowd the reaction environment and suppress the colliding probability of S(IV) species with NO$_2$ in aqueous phase and the uptake coefficient of SO$_2$ or NO$_2$ on the droplet. Precipitation of sulfate as CaSO$_4$ can cancel such suppressions and thus promote the reaction. Regardless of the reasons behind, we can conclude that the precipitation of less soluble CaSO$_4$ promoted sulfate formation.

### 3.4 Reactive uptake coefficient of SO$_2$

The reactive uptake coefficients of SO$_2$ ($\gamma$) 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 water in aqueous solution plays an important role in the formation of CaSO$_4$. At 17% RH, the reaction between CaCO$_3$ and NO$_2$ (the first process of the whole reaction) proceeded very slowly, and the amount of water in aqueous solution formed due to the water uptake of Ca(NO$_3$)$_2$ was very low. As a result, we did not observe the formation of CaSO$_4$ (the second process of the whole reaction) after 1000 min of the reaction and even at higher SO$_2$ and NO$_2$ concentrations (200 ppm SO$_2$, 200 ppm NO$_2$). 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 CaCO$_3$ and NO$_2$ proceeded quickly and CaCO$_3$ was completely converted to a Ca(NO$_3$)$_2$ droplet within 100 min after the reaction. In the presence of enough water in aqueous solution, 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$_2$ (($2.10\pm0.08)\times10^{-6}$) determined by Park and Jang (2016). $\gamma$ here is also much lower than the $\gamma$ 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 water in aqueous solution played a key role.

The $\gamma$ 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 $\gamma$ 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 $1.4 \times 10^7$ 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 $\gamma$ 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 $10^{-6}$-$10^{-3}$ mol Kg$^{-1}$), which may also influence the reaction rate.

In the ambient atmosphere, the reactive uptake coefficient of SO$_2$ due to the multiphase oxidation by NO$_2$ is influenced by various factors such as RH, NO$_2$ concentration, pH, sulfate concentration, and the presence of other ions in aerosol particles. For example, NO$_2$ concentrations in the atmosphere are much lower than those used in this study. At lower NO$_2$ concentrations, the uptake coefficient of SO$_2$ decreases, because the oxidation rate of SO$_2$ in aqueous phase decreases with decreasing 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 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 $\Delta G$ (as shown in Eq. 5) and reduce the colliding probability of S(IV) species with NO$_2$ in the aqueous phase as discussed above and thus suppress the reaction of SO$_2$ and NO$_2$. This can reduce the uptake coefficient of SO$_2$. Therefore,
the reactive uptake coefficient of SO\(_2\) obtained in this study (10\(^{-8}\) at 46-72% RH and 75 ppm NO\(_2\)) can be regarded as an upper limit of the reactive uptake coefficient of SO\(_2\) due to the multiphase reaction with NO\(_2\) in the ambient atmosphere.

4 Conclusion and implications

We investigated the heterogeneous reaction of SO\(_2\) directly with 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 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 SO\(_2\) with NO\(_2\). The sulfate formation was observed only during the multiphase oxidation by 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 SO\(_2\) for sulfate formation in the multiphase reaction with NO\(_2\) is on the order of 10\(^{-8}\) under the experimental conditions of this study (RH: 46-72%, NO\(_2\): 75 ppm). The reactive uptake coefficient of SO\(_2\) was found to be enhanced at higher RH.

In order to assess the importance of the multiphase reaction of SO\(_2\) directly oxidized by NO\(_2\) to sulfate in the atmosphere, we compare the lifetime of SO\(_2\) due to the multiphase oxidation of SO\(_2\) by NO\(_2\) with the lifetime due to the gas phase oxidation of SO\(_2\) by OH. Using a daytime OH concentration of 1\times10^6 molecule cm\(^{-3}\) (Lelieveld et al., 2016; Prinn et al., 2005), the lifetime of SO\(_2\) in the atmosphere due to gas phase OH oxidation is around 12 days. The life time of SO\(_2\) due to the multiphase oxidation by NO\(_2\) is around 7000 days using the uptake coefficient of SO\(_2\) from this study (3.22\times10^{-8}) and a typical particle surface area concentration for mineral aerosols in winter in Beijing (6.3\times10^{-6} cm\(^2\) cm\(^{-3}\)) (Huang et al., 2015). Using an annual average particle surface area concentration of PM\(_{10}\) in Beijing (1.4\times10^{-5} cm\(^2\) cm\(^{-3}\)) (Wehner et al., 2008) results in a SO\(_2\) life time of 3300 days due to the multiphase oxidation by NO\(_2\). In the atmosphere, the lifetime of SO\(_2\) due to the multiphase oxidation by NO\(_2\) should be even longer than these values because the uptake coefficient of SO\(_2\) used here (3.22\times10^{-8}) is an upper limit of the uptake coefficient of SO\(_2\) in the ambient atmosphere as discussed above. This comparison indicates that the direct multiphase oxidation of SO\(_2\) by NO\(_2\) is unlikely to be an important sink of SO\(_2\) and source of sulfate compared with the oxidation of SO\(_2\) by OH.

It is worth mentioning that this study did not investigate the dependence of the reactive uptake coefficient due to the direct oxidation of SO\(_2\) by NO\(_2\) on pH, especially not under high pH conditions, for which recent studies have claimed this reaction to be important (Cheng et al., 2016; Wang et al., 2016). Because of the important role of multiphase/heterogeneous reactions in SO\(_2\) oxidation found in the atmosphere and the low reaction rate of the direct multiphase oxidation of SO\(_2\) by NO\(_2\), it is more likely that the aqueous reactions of SO\(_2\) with other oxidants, such as the reactions with H\(_2\)O\(_2\), O\(_3\), and O\(_2\), with or without transition metals, could be important pathways for sulfate formation in the atmosphere.

Acknowledgements

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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>CaCO$_3$</td>
<td>SO$_2$(75 ppm)+NO$_2$(75 ppm)</td>
<td>72</td>
<td>Yes</td>
</tr>
<tr>
<td>Ca(NO$_3$)$_2$ droplet</td>
<td>SO$_2$(75 ppm)+NO$_2$(75 ppm)</td>
<td>72</td>
<td>Yes</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>SO$_2$ (150 ppm)</td>
<td>72</td>
<td>No</td>
</tr>
<tr>
<td>Ca(NO$_3$)$_2$ droplet</td>
<td>SO$_2$ (150 ppm))</td>
<td>72</td>
<td>No</td>
</tr>
<tr>
<td>NaNO$_3$ droplet</td>
<td>SO$_2$(75 ppm)+NO$_2$(75 ppm)</td>
<td>72</td>
<td>No</td>
</tr>
<tr>
<td>NH$_4$NO$_3$ droplet</td>
<td>SO$_2$(75 ppm)+NO$_2$(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$^b$</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.

$^b$: The uncertainties are the standard deviations of $\gamma$ from duplicate experiments.
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 CaCO₃ particle (same as in Fig. 2) reacting with NO₂ (75 ppm) and SO₂ (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(NO₃)₂ droplet reacting with NO₂ (75 ppm) and SO₂ (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 CaSO₄ was formed in this reaction.
Fig. 6. Raman spectra of a NH$_4$NO$_3$ (a) and NaNO$_3$ (b) droplet reacting with NO$_2$ (75 ppm) and SO$_2$ (75 ppm) at 72% RH at the reaction time of 300 min.
Supplement of

Multiphase Oxidation of SO₂ by NO₂ on CaCO₃ Particles

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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).

\[
\frac{1}{\gamma} = \frac{1}{\Gamma_{\text{diff}}} + \frac{1}{\Gamma_{\text{sat}}} + \frac{1}{\Gamma_{\text{rxn}}} 
\]  
(S1)

where \( \Gamma_{\text{diff}} \) is the transport coefficient in the gas phase, \( 1/\Gamma_{\text{diff}} \) is the resistance due to the diffusion in the gas phase. Similarly, \( 1/\Gamma_{\text{sat}} \) and \( 1/\Gamma_{\text{rxn}} \) are the resistance due to liquid phase saturation and liquid phase reaction, respectively. \( \alpha \) is the mass accommodation coefficient of SO2.

\( 1/\Gamma_{\text{diff}} \) can be derived using the following equation:

\[
\frac{1}{\Gamma_{\text{diff}}} = \frac{0.75+0.238\text{Kn}}{\text{Kn}(1+\text{Kn})} 
\]  
(S2)

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

\[
\text{Kn} = \frac{\lambda}{a} 
\]  
(S3)

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

\[
\lambda = \frac{3D_g}{c} 
\]  
(S4)

where \( D_g \) is the diffusion coefficient in the gas phase and \( c \) is the mean molecular velocity.

\( c \) is derived from

\[
c = \sqrt{\frac{8RT}{\pi M}} 
\]  
(S5)

where \( R \) is the gas constant, \( T \) is temperature, and \( M \) is the molecular mass of SO2.

\( 1/\Gamma_{\text{sat}} \) can be derived from

\[
\frac{1}{\Gamma_{\text{sat}}} = \frac{c}{4\text{HRT}} \sqrt{\frac{\pi}{D_l}} 
\]  
(S6)

where \( H \) is the Henry constant of SO2, \( t \) is time, and \( D_l \) is the diffusion coefficient of SO2 in the liquid phase.

\( 1/\Gamma_{\text{rxn}} \) can be derived from

\[
\frac{1}{\Gamma_{\text{rxn}}} = \frac{c}{4\text{HRT}} \sqrt{\frac{1}{k_{\text{rxn}}D_l}} 
\]  
(S7)

where \( k_{\text{rxn}} \) is the first order rate constant of the reaction in the liquid phase.

\[
k_{\text{rxn}} = k[\text{NO}_2(\text{aq})] 
\]  
(S8)

where \( k \) is the second order rate constant of the reaction of S(IV) with NO2 and \([\text{NO}_2(\text{aq})]\) is the NO2 concentration in the liquid phase.

\[
[\text{NO}_2(\text{aq})] = H_{\text{NO}_2}\text{P}_{\text{NO}_2} 
\]  
(S9)

where \( H_{\text{NO}_2} \) is the Henry constant of NO2 and \( P_{\text{NO}_2} \) is the concentration of NO2 in the gas phase.
S2. Characteristic time for aqueous reaction and gas-particle equilibrium

The characteristic time to achieve the equilibrium in the gas-particle interface and for aqueous reaction of SO$_2$ with NO$_2$ were derived using the method in Seinfeld and Pandis (2006).

\[
\tau_p \cong \frac{a H^* \sqrt{2\pi MRT}}{3 \alpha} \quad (S10)
\]

\[
\tau_{ra} = \frac{1}{k_{rxn}} \quad (S11)
\]

$\tau_p$ is the radius of the particle, $H^*$ is the effective Henry constant, $M$ is the molecular weight, $R$ is the gas constant, $T$ is temperature, $\alpha$ is the mass accommodation coefficient of SO$_2$, $k_{rxn}$ is the first-order rate constant of the reaction in the liquid phase (see Equation S8). The values of the constants are shown in Table S1.

The characteristic time to achieve the equilibrium in the gas-particle interface is around $4 \times 10^{-5}$ s. The characteristic time for aqueous reaction is 0.5 and 0.08 s using the reaction rate constant of $2 \times 10^6$ mol$^{-1}$ L s$^{-1}$ (Lee and Schwartz, 1983) and $1.24 \times 10^7$ mol$^{-1}$ L s$^{-1}$ (Clifton et al., 1988), respectively.


<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D_g) (m² 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_{SO2}) (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) (m² s⁻¹)</td>
<td>(8.3 \times 10^{-12a})</td>
<td>Mahiuddin and Ismail (1983)</td>
</tr>
<tr>
<td>(H_{SO2}) (mol L⁻¹ atm⁻¹)</td>
<td>1.23</td>
<td>Seinfeld and Pandis (2006)</td>
</tr>
<tr>
<td>(H_{NO2}) (mol L⁻¹ atm⁻¹)</td>
<td>(1 \times 10^{-2})</td>
<td>Seinfeld and Pandis (2006)</td>
</tr>
<tr>
<td>(k) (mol⁻¹ L s⁻¹)</td>
<td>(2 \times 10^6)</td>
<td>Lee and Schwartz (1983); Clifton et al. (1988)</td>
</tr>
</tbody>
</table>

\(^a\)The aqueous phase diffusion coefficient was derived from the viscosity of Ca(NO₃)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 \(10^{-9}\) m² s⁻¹.
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.