Multiphase oxidation of SO₂ by NO₂ on CaCO₃ particles

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Abstract. Heterogeneous/multiphase oxidation of SO₂ by NO₂ 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 SO₂ by NO₂, we investigated the heterogeneous/multiphase reaction of SO₂ with NO₂ on individual CaCO₃ particles in N₂ using Micro-Raman spectroscopy. In the SO₂ / NO₂ / H₂O / N₂ gas mixture, the CaCO₃ solid particle was first converted to the Ca(NO₃)₂ droplet by the reaction with NO₂ and the deliquescence of Ca(NO₃)₂, and then NO₂ oxidized SO₂ in the Ca(NO₃)₂ droplet forming CaSO₄, which appeared as needle-shaped crystals. Sulfate was mainly formed after the complete conversion of CaCO₃ to Ca(NO₃)₂, that is, during the multiphase oxidation of SO₂ by NO₂. The precipitation of CaSO₄ from the droplet solution promoted sulfate formation. The reactive uptake coefficient of SO₂ for sulfate formation is on the order of 10⁻⁸, and RH enhanced the uptake coefficient. We estimate that the direct multiphase oxidation of SO₂ by NO₂ is not an important source of sulfate in the ambient atmosphere compared with the SO₂ oxidation by OH in the gas phase and is not as important as other aqueous-phase pathways, such as the reactions of SO₂ with H₂O₂, O₃, and O₂, with or without transition metals.

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 either comes from primary sources, such as sea spray, or from secondary sources, i.e., from the oxidation of reduced sulfur compounds such as dimethyl sulfide (DMS), carbonyl sulfur (COS), and SO₂ (Seinfeld and Pandis, 2006). In the continental atmosphere, 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 the particle surface (Zhu et al., 2011; Li et al., 2006, 2007, 2011; Shang et al., 2010).

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; Y. S. Wang et al., 2014; G. J. Zheng et al., 2015; Guo et al., 2014). The relative contribution of regional transport versus local formation and the 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 as 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; B. Zheng et al., 2015; X. Y. Wang et al., 2016, 2014, 2016; He et al., 2014; Ju et al., 2016; Xie et al., 2015; Cheng et al., 2016). During haze episodes, relative humidity (RH) is often high (Zhang et al., 2014; Wang et al., 2016; G. J. Zheng et al., 2015), and particles or some components of particles can deliquesce, forming aqueous solutions. 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 sul-
fate 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, 2004, 2006; Shang et al., 2010; Huang et al., 2015, 2016; Zhou et al., 2014; Kong et al., 2014; Passananti et al., 2016; Cui et al., 2008; Chu et al., 2016; Zhao et al., 2015; Wu et al., 2011, 2013, 2015 He et al., 2014; Liu et al., 2012; Ma et al., 2008; Park and Jang, 2016; Ullerstam et al., 2002, 2003; Sorimachi et al., 2001), 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, 2017; Park and Jang, 2016; Ullerstam et al., 2003). 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 coefficients 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 (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 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 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 that the role of O$_2$ is negligible.

We investigated the heterogeneous reaction of SO$_2$ with NO$_2$ on CaCO$_3$ particles at 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, 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$_3$, the 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 a Micro-Raman spectrometer with a flow reaction system. N$_2$ was used as a 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 the 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 the 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 an-
nealed 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 have been 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 CaCO₃ particles reacting with NO₂ (75–200 ppm) and SO₂ (75–200 ppm) mixing gas diluted with N₂ were conducted under certain RH (17–72 %). All the measurements were carried out at 25 ± 0.5 °C. Each reaction was repeated three times.

In this study, the size of CaCO₃ 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 a new aqueous phase or solid phase, and particles may grow. Because particles are larger than the laser spot (~1.5 µm), the 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 obtain the chemical information of the whole particle. The mapping area is a rectangle slightly larger than the particle, and mapping steps are 1 × 1 µm. Raman spectra in the range 800–3900 cm⁻¹ were acquired with an exposure time of 1 s for each mapping point. During each mapping period (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 the 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 calculate the peak area for the whole particle.

Besides the reaction of CaCO₃ with SO₂ and NO₂, other reaction systems including the reaction on Ca(NO₃)₂, NaNO₃, and NH₄NO₃ particles with SO₂ or SO₂ and NO₂ mixing gas (summarized in Table 1) were also studied in order to elucidate the reaction mechanism. Most experiments were conducted using CaCO₃ particles rather than directly using Ca(NO₃)₂ particles. CaCO₃ was selected because it is an important component of mineral aerosols, especially in China as mentioned in the Introduction, and it is 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 it is formed via the reaction of CaCO₃ with acidic gases such as HNO₃ and NO₂ due to its alkalinity.

CaCO₃ (98 %, Sigma) with diameters about 7–10 µm on average, Ca(NO₃)₂·4H₂O (ACS, 99–103 %; Riedel-de Haén), NH₄NO₃ (AR, Beijing Chemical Works), and NaNO₃ (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 in Eq. (1):

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

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 in a 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 number 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 \(z\) dimensions, respectively. The volume of each particle was calculated based on 3-D profiles of the particles using 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 in the Supplement).
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>

2.3 Determination of reactive uptake coefficient

In this study, sulfate was produced from the oxidation of SO₂. The reactive uptake coefficient γ of SO₂ on individual particles was estimated from sulfate formation. γ is derived as the rate of sulfate formation \( \left( \frac{d\{SO_4^{2-}\}}{dt} \right) \) divided by the rate of surface collisions with an individual particle \( (Z) \):

\[
\gamma = \frac{d\{SO_4^{2-}\}}{Z},
\]  

\[
Z = \frac{1}{4}cA_s[SO_2],
\]

\[
c = \frac{8RT}{\pi M_{SO_2}},
\]

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 in the particle phase in moles, 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 a 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 obtain 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 (Q. X. Ma et al., 2013). Afterwards, no other Raman peaks than those of CaCO₃, Ca(NO₃)₂, and CaSO₄ were detected until 1050 min after the reaction.
Concomitantly with the formation of Ca(NO$_3$)$_2$ and CaSO$_4$, the microscopic morphology of the particle changed significantly. The initial CaCO$_3$ particle was a crystal close to a rhombohedron of about 9–10 µm (Fig. 3a). After reacting with NO$_2$/SO$_2$, 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 revealed that the outer liquid layer consisted of Ca(NO$_3$)$_2$ and water. As the reaction proceeded, the solid CaCO$_3$ core diminished gradually, and finally CaCO$_3$ completely disappeared and a Ca(NO$_3$)$_2$ 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(NO$_3$)$_2$ 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 CaSO$_4$. The amount of CaSO$_4$ 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(NO$_3$)$_2$, CaSO$_4$, and CaCO$_3$, 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(NO$_3$)$_2$ was produced before CaSO$_4$. Nitrate was detected immediately after the reaction started, and it 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(NO$_3$)$_2$, which was accompanied by the decline of CaCO$_3$ (Fig. 4), indicating that Ca(NO$_3$)$_2$ was produced due to the reaction of CaCO$_3$ with NO$_2$. 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 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 mechanisms 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 of 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 the 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$_2$ in the same conditions still produced CaSO$_4$, confirming CaCO$_3$ was not necessary for sulfate formation. The reaction with Ca(NO$_3$)$_2$ produced a similar amount of sulfate to the reaction with CaCO$_3$ based on Raman spectra and microscopic images (Fig. 5), which indicates that the 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 images 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 sulfitie and bisulfite ions into sulfate ions in the aqueous phase (Ellison and Eckert, 1984; Shen and Rochelle, 1998; Littlejohn et al., 1993). The overall reaction equation was described to be as follows (Clifton et al., 1988):

\[
2\text{NO}_2 (aq) + \text{SO}_3^{2-} (aq) + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + 2\text{NO}_2^- (aq) + \text{SO}_4^{2-} (aq) \tag{R7}
\]
\[
2\text{NO}_2 (aq) + \text{HSO}_3^- (aq) + \text{H}_2\text{O} \rightarrow 3\text{H}^+ + 2\text{NO}_2^- (aq) + \text{SO}_4^{2-} (aq). \tag{R8}
\]

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 was estimated to be $\sim$ 3. The characteristic time to reach the equilibrium in the gas–particle interface ($\sim 10^{-5}$ 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) (Sect. S2 in the

Figure 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$_4$ formed in this reaction.
Supplement). Therefore, aqueous S(IV) species can be considered to be in equilibrium with SO₂ in the gas phase. The concentrations of HSO₄⁻, H₂SO₃, and SO₃²⁻ were estimated to be \( \sim 1.1 \times 10^{-3}, 9.2 \times 10^{-5}, \) and \( 6.6 \times 10^{-8} \text{ mol L}^{-1} \), respectively, using the equilibrium constants in Seinfeld and Pandis (2006) \((\text{H}_2\text{SO}_3 = 1.23 \text{ mol L}^{-1} \text{ atm}^{-1}, K_1 = 1.3 \times 10^{-2} \text{ mol L}^{-1}, K_2 = 6.6 \times 10^{-8} \text{ mol L}^{-1})\), and thus the main S(IV) species was HSO₄⁻. Then SO₃²⁻ from S(IV) oxidation can react with Ca²⁺, forming CaSO₄ precipitation, as observed in Raman spectra due to the low value of \( K_{sp} \) for CaSO₄ (Lide, 2009):

\[
\text{Ca}^{2+} (\text{aq}) + \text{SO}_4^{2-} (\text{aq}) \rightarrow \text{CaSO}_4 (s).
\]

(R9)

Some previous studies have shown that SO₂ can react with CaCO₃ to produce calcium sulfite \((\text{CaSO}_3)\) (Li et al., 2006; Prince et al., 2007b; Q. Ma et al., 2013), and CaSO₃ can be oxidized to CaSO₄ by NO₂ (Rosenberg and Grotta, 1980; Q. Ma et al., 2013). In our study, we investigated the reaction between CaCO₃ and SO₂ \((150 \text{ ppm})\) at 72 % RH. We found that both sulfate and sulfite were lower than the detection limit of our Raman spectrometer \((\sim 5 \times 10^{-14} \text{ mol for sulfate at a signal-to-noise ratio of 2 and } \sim 3 \times 10^{-14} \text{ 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 CaSO₄ was not the main pathway in CaSO₄ formation in our study and that 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 an NaNO₃ or an NH₄NO₃ droplet with NO₂ / SO₂, sulfate, either as aqueous ions (at 984 and 979 cm⁻¹ for \((\text{NH}_4)_2\text{SO}_4\) and \(\text{Na}_2\text{SO}_4\), respectively) or as CaSO₄ crystals, was below the detection limit after 300 min in the same reaction conditions as Ca(NO₃)₂ and CaCO₃ (Fig. 6 and Table 1). Considering that the Raman scattering cross-section of sulfate in \((\text{NH}_4)_2\text{SO}_4\) aqueous aerosol particles is even higher than sulfate in CaSO₄ (Wright, 1973; Stafford et al., 1976), it can be concluded that the sulfate production rate was larger in the presence of Ca²⁺ compared to that in the presence of Na⁺ or NH₄⁺. 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 SO₂ oxidation by NO₂ for Reaction (R8) can be analyzed using the reaction Gibbs energy as follows:

\[
\Delta_r G = \Delta_r G^\circ + RT \ln \frac{\alpha_{\text{H}^+} \cdot \alpha_{\text{SO}_2^2} \cdot \alpha_{\text{NO}_2^2}^2}{\alpha_{\text{SO}_2^{\text{aq}}}^2 \cdot \alpha_{\text{HSO}_3}^2},
\]

where \(\Delta_r G\) is the reaction Gibbs energy, \(\Delta_r G^\circ\) is the standard reaction Gibbs energy, \(R\) is the gas constant, \(T\) is temperature, and \(\alpha\) is the activity of various species.

\(\Delta_r G\) increases with increasing sulfate concentration. According to the different results between the reaction on the Ca(NO₃)₂ droplet and the reaction on NaNO₃ and NH₄NO₃ droplets, 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 droplets, once sulfate concentration reached a certain level, the reaction may stop due to the increase of \(\Delta_r G\). For Ca(NO₃)₂ droplets, the precipitation of CaSO₄ can substantially decrease the activity of SO₄²⁻ and thus decrease \(\Delta_r G\) and promote the oxidation of SO₂ 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 NO₂ in the aqueous phase and the uptake coefficient of SO₂ or NO₂ on the droplets. The precipitation of sulfate as CaSO₄ can cancel such suppression and thus promote the reaction. Regardless
of the reasons behind it, 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 (γ) for sulfate formation under different conditions are shown in Table 2. Each reaction was repeated three times, during which three particles with different sizes were selected. γ was higher at higher relative humidity, suggesting again that water in the aqueous solution 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 water in the aqueous solution 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 differences for γ 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 of the reaction. In the presence of enough water in the aqueous solution, RH no longer seemed to be a limiting factor. In such conditions, an increase of NO₂ concentration (from 75 to 200 ppm at 72% RH) promoted the reactive uptake of SO₂.

The reactive uptake coefficient of SO₂ 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 the islands of Cabo Verde (the main contents being potassium feldspars and quartz) obtained by Ullerstam et al. (2003) using NO₂ / SO₂ mixing gas and the diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) technique. But the uptake coefficient in this study is lower than the uptake coefficient of SO₂ on Arizona test dust (ATD) particles in the presence of NO₂ ((2.10 ± 0.08) × 10⁻⁶) determined by Park and Jang (2016). γ here is also much lower than the γ of SO₂ on oxalic acid particles in the presence of NO₂ and NH₃ (10⁻⁶–10⁻⁸) 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 in the 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 the aqueous solution played a key role.

The γ of SO₂ was further compared with the reaction rate constants of the aqueous reaction of NO₂ with sulfite and bisulfite in bulk solution in the literature by deriving γ from rate constants using the method in Davidson et al. (2006). Details of this method can be referred to in Sect. S1. Lee and Schwartz (1983) determined the rate constant of the reaction of NO₂ with bisulfite to be 2 × 10⁷ mol⁻¹ L s⁻¹ at pH 5.8 and 6.4. Clifton et al. (1988) determined the rate constant of the reaction of NO₂ with sulfite/bisulfite to be (1.24–2.95) × 10⁷ mol⁻¹ L s⁻¹ at pH 5.6–13 and further reported a rate constant of 1.4 × 10⁸ 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 of determining the reaction rate by Clifton et al. (1988). Clifton et al. (1988) determined the reaction rate from the consumption rate of the reactant, NO₂, which corresponds to the first reaction step of NO₂ with S(IV). However, Lee and Schwartz (1983) determined the reaction rate from the production rate of products (their conductivity), which is expected to be much slower than NO₂ consumption since the formation of products needs more steps. In this study, we determined γ using the sulfate production rate, and thus our data are comparable to the study of Lee and Schwartz (1983). However, 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 × 10⁸ mol⁻¹ L s⁻¹ at pH 5 corresponds to the uptake coefficient of 4.3 × 10⁻⁷, which is around 1 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 the bulk aqueous reaction, and the different concentrations of each S(IV) species since the different species may have a different reactivity with NO₂. The reaction rate of S(IV) has been found to decrease with decreasing pH, and the reactivity of sulfite with NO₂ seems to be higher than bisulfite (Lee and Schwartz, 1983; Clifton et al., 1988; Takeuchi et al., 1977). In addition, the ionic strength in the droplet of this study (15–55 mol kg⁻¹) was much higher than that in the bulk solution in previous stud-

### Table 2. Reactive uptake coefficient of SO₂ for sulfate formation (γ) during the reaction of SO₂ with NO₂ on individual CaCO₃ particles under different conditions at 298 K.

<table>
<thead>
<tr>
<th>[SO₂] (ppm)</th>
<th>[NO₂] (ppm)</th>
<th>RH</th>
<th>γ (× 10⁻⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>75</td>
<td>72</td>
<td>3.22 ± 1.08b</td>
</tr>
<tr>
<td>75</td>
<td>200</td>
<td>72</td>
<td>16.0 ± 3.12</td>
</tr>
<tr>
<td>75</td>
<td>46</td>
<td>72</td>
<td>3.22 ± 0.90</td>
</tr>
<tr>
<td>75</td>
<td>75</td>
<td>46</td>
<td>0a</td>
</tr>
<tr>
<td>200</td>
<td>200</td>
<td>17</td>
<td>0a</td>
</tr>
</tbody>
</table>

* Sulfate was below the detection limit.

** The uncertainties are the standard deviations of γ from duplicate experiments.
ies (on the order of $10^{-6}$–$10^{-1}$ 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 the 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 (Sect. 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 $\Delta_r G$ (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 deliquescent of Ca(NO$_3$)$_2$, and then it 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 a 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 $1 \times 10^9$ 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 lifetime 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 × 10$^{-8}$) and a typical particle surface area concentration for mineral aerosols in winter in Beijing (6.3 × 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 × 10$^{-5}$ cm$^2$ cm$^{-3}$) (Wehner et al., 2008) results in a SO$_2$ lifetime 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 × 10$^{-8}$) 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.

Data availability. The data in the figures in both the main text and the supplement are available upon request to the corresponding author (tzh@pku.edu.cn).

The Supplement related to this article is available online at https://doi.org/10.5194/acp-18-2481-2018-supplement.

Competing interests. The authors declare that they have no conflict of interest.

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