



# Enhancement of aqueous sulfate formation by the coexistence of NO<sub>2</sub>/NH<sub>3</sub> under high ionic strengths in aerosol water<sup>\*</sup>

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## ABSTRACT

Current air quality models usually underestimate the concentration of ambient air sulfate, but the cause of this underestimation remains unclear. One reason for the underestimation is that the sulfate formation mechanism in the models is incomplete, and does not adequately consider the impact of the synergistic effects of high concentrations of multiple pollutants on sulfate formation. In this work, the roles of gaseous NO<sub>2</sub>, NH<sub>3</sub> and solution ionic strength in the formation of sulfate in the aqueous phase were quantitatively investigated using a glass reactor and a 30 m<sup>3</sup> smog chamber, separately. The results showed that sulfate formation was enhanced to different degrees in the presence of gas-phase NO<sub>2</sub>, NH<sub>3</sub> and their coexistence as solutes in both liquid solution and aerosol water. NH<sub>3</sub> enhances the aqueous oxidation of SO<sub>2</sub> by NO<sub>2</sub> mainly by accelerating the uptake of SO<sub>2</sub> through increased solubility. More importantly, we found that high ionic strength in aerosol water could significantly accelerate the aqueous oxidation of SO<sub>2</sub>, resulting in unexpectedly high S(VI) formation rates. We estimate that under severe haze conditions, heterogeneous oxidation of SO<sub>2</sub> by NO<sub>2</sub> on aerosols may be much shorter than that through gas phase oxidation by OH, aided by high ionic strengths in aerosols. Considering the existence of complex air pollution conditions with high concentrations of NO<sub>2</sub>, NH<sub>3</sub> and aerosol water, as expected in typical urban and suburban settings, the sulfate formation mechanisms revealed in the present work should be incorporated into air quality models to improve the prediction of sulfate concentrations.

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## 1. Introduction

In recent years, along with rapid social and economic development, many areas in China have suffered from frequent haze events (Li et al., 2017b; Shen et al., 2015; Sun et al., 2006; Tan et al., 2009). Similar air quality issues are also encountered in other rapidly growing countries (Fedorova et al., 2013; Pachauri et al., 2013). During such events, high concentrations (up to 100 ppb) of SO<sub>2</sub>, NO<sub>x</sub> and NH<sub>3</sub> have been observed (Fu et al., 2015; Ianniello et al., 2010; Liu et al., 2013; Meng et al., 2011; Yang et al., 2009), and

these gaseous precursors contributed to high concentrations of secondary species in PM<sub>2.5</sub> (Yang et al., 2011; Ye et al., 2011; Zhang et al., 2015b; Zhao et al., 2013). Sulfate (SO<sub>4</sub><sup>2-</sup>) is a dominant component in PM<sub>2.5</sub> during these haze events and plays a significant role in haze formation under high relative humidity (RH) conditions (Guo et al., 2014; He et al., 2001; Pathak et al., 2009; Wang et al., 2005; Zhang et al., 2011).

Sulfate is primarily generated from the homogeneous oxidation of SO<sub>2</sub>, mainly by OH radicals and Criegee intermediates (Mauldin III et al., 2012; Welz et al., 2012) in the gas phase, heterogeneous oxidation of SO<sub>2</sub> on particle surfaces (He et al., 2014; Liu et al., 2012; Ma et al., 2008), and aqueous oxidation of dissolved S(IV) (the sum of SO<sub>2</sub>·H<sub>2</sub>O, HSO<sub>3</sub><sup>-</sup>, and SO<sub>3</sub><sup>2-</sup>) by dissolved oxidants (e.g., H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, NO<sub>2</sub>) and transition metals (e.g., Fe(III), Mn(II)) in cloud/fog droplets (Hung and Hoffmann, 2015; Li et al., 2017a; Quan et al., 2015; Seinfeld and Pandis, 2016; Xue et al., 2016). Both OH oxidation in

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the gas phase and most aqueous oxidation reactions have been included in the Weather Research and Forecasting-Community Multiscale Air Quality (WRF-CMAQ) model system and most other air quality models, but simulation results have usually underestimated sulfate concentrations, especially under heavy haze pollution conditions (Cheng et al., 2016). Previous studies have demonstrated qualitative mechanisms for rapid sulfate growth under complex pollution conditions (Cheng et al., 2016; He et al., 2014; Li et al., 2018; Liu et al., 2012; Ma et al., 2008; Wang et al., 2016; Yang et al., 2016). For example, sulfate formation can be promoted by the coexistence of  $\text{NO}_x$  on the surface of mineral oxides (He et al., 2014; Liu et al., 2012; Ma et al., 2008; Xie et al., 2015). Synergistic effects were found between  $\text{NH}_3$  and  $\text{SO}_2$  on typical mineral dust particles;  $\text{NH}_3$  increases the surface alkalinity and leads to water film on the surface of mineral dust, which enhances  $\text{SO}_2$  adsorption on the surface and increases its oxidation to sulfate (Yang et al., 2016). However, the aqueous-phase oxidation of S(IV) by  $\text{NO}_2$  was ignored in the description of the mechanism because of the low solubility of  $\text{NO}_2$  under typical atmospheric conditions.

Due to the large discrepancies in the model-predicted pH of fine particles (Cheng et al., 2016; Guo et al., 2017; Liu et al., 2017; Wang et al., 2018; Wang et al., 2016), which might result from differences in model assumptions and inputs in those related studies (Song et al., 2018), the importance of the  $\text{NO}_2$  pathway for sulfate formation in the aqueous phase remains unresolved. The aqueous-phase oxidation pathway of S(IV) by  $\text{NO}_2$  has recently been shown to be a key mechanism in the formation of sulfate under fog/cloud conditions with high  $\text{NO}_2$  concentration levels (Cheng et al., 2016; Li et al., 2018; Wang et al., 2016). Wang et al. (2016) also indicated that the neutralization of  $\text{NH}_3$  could enhance sulfate formation from the reaction of S(IV) with  $\text{NO}_2$  under aerosol water or cloud conditions, implying that this reaction was greatly influenced by the pH values of the aqueous phase (Clifton et al., 1988; Huie, 1994; Nash, 1979; Spindler et al., 2003). Previous studies have shown that with increases in pH, the aqueous-phase equilibrium concentration of S(IV) increased, clearly caused by the increased solubility of  $\text{SO}_2$  (McVay and Ervens, 2017; Seinfeld and Pandis, 2016). Meanwhile, the reaction rate constant of S(IV) oxidation by dissolved  $\text{NO}_2$  also increased significantly (Littlejohn et al., 1993). Studies also found that the rate and efficiency of  $\text{NO}_2$  absorption could be enhanced during the process of simultaneous removal of  $\text{SO}_2$  and  $\text{NO}_2$  gases in alkaline solutions (Hu et al., 2010; Kameoka and Pigford, 1977; Takeuchi et al., 1977). The increased absorption of both  $\text{SO}_2$  and  $\text{NO}_2$  in alkaline solutions further enhanced the oxidation of sulfite (Shen and Rochelle, 1998). However, quantitative estimation of the increased absorption and oxidation rates in the presence of  $\text{NO}_2$  and  $\text{NH}_3$ , for inclusion in a mechanism in air quality models to predict the sulfate concentration, is still lacking. This is one of the main subjects of this study.

In addition, ionic species significantly affect the ionic strength of the reaction media and result in different reaction media for the aqueous oxidation of  $\text{SO}_2$  in bulk solutions (cloud droplets, fog) and aerosol water. Previous experimental studies have indicated that the ionic strength ( $I$ ) of solutions could lead to changes in the rate constants ( $k$ ) (Herrmann et al., 2015) for reactions leading to sulfate formation in the aqueous phase, such as S(IV) oxidation by  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ , and  $\text{NO}_2$ . Studies have shown that an increase in solution ionic strength could increase the rate of oxidation of S(IV) by  $\text{O}_3$  (Maahs, 1983) and by  $\text{H}_2\text{O}_2$  in aqueous solutions (Ali et al., 2014; Maaß et al., 1999). However, with respect to the oxidation of S(IV) by  $\text{NO}_2$ , there has been no report on the relationship of  $k$  and  $I$ , except for some plausible estimation (Cheng et al., 2016). The effects of ionic strength may be crucial for evaluating the importance of the aqueous-phase reactions, and need further investigation.

Hence, studying the synergistic effects among  $\text{SO}_2$ ,  $\text{NO}_x$  and  $\text{NH}_3$  in sulfate formation is important to reveal the formation mechanisms of sulfate in aerosol water, especially during severe haze events with high levels of  $\text{NO}_x$  and  $\text{NH}_3$ . There is a need to evaluate the effects of the coexistence of  $\text{NH}_3$  and high ionic strength on the solubility and aqueous-phase oxidation of S(IV) by  $\text{NO}_2$  in different reaction environments. The present work was carried out to address this need and to determine the significance of these effects.

## 2. Experimental section

### 2.1. Simulation of aqueous-phase reaction in a glass reactor

Simulation of aqueous sulfate formation was carried out in a glass reactor as shown in Fig. S1 (Volume = 600 mL, see in Supporting Information (SI)). The specifications of the gases used are as follows:  $\text{SO}_2$  (100 ppm in  $\text{N}_2$ , Beijing Huayuan),  $\text{NO}_2$  (100 ppm in  $\text{N}_2$ , Beijing Huayuan), carrier gas  $\text{N}_2$  (99.999% purity, Beijing Huayuan). 6 mL ultrapure water (18.2 M $\Omega$ , Millipore Milli-Q) or 0.02 wt%  $\text{NH}_3$  solution (Sinopharm Chemical Reagent Co., Ltd, Guaranteed reagent) were firstly added at the bottom of the glass reactor. Then, steady concentrations of  $\text{SO}_2$  or/and  $\text{NO}_2$  carried by high purity  $\text{N}_2$  were introduced into the glass reactor at a flow rate of 2.0 L  $\text{min}^{-1}$  with Peclet number ~580, which indicated that the gas phase species were not transported to the interface of flow tube, so a mixing tube was used (see Fig. S1A, marked in red) to make sure the reaction gases were evenly mixed. As the reaction gases ( $\text{SO}_2$  or/and  $\text{NO}_2$ ) swept over the liquid surface, they would dissolve in the water, and aqueous-phase reaction would occur. After flowing the reaction gas for 10 min, the reaction cell was purged with 2.0 L  $\text{min}^{-1}$  of high purity  $\text{N}_2$  for 5 min. All the simulations were carried out under dark conditions and at constant temperature (~298 K). Four different reaction systems, namely  $\text{SO}_2$ ,  $\text{SO}_2/\text{NH}_3(\text{aq})$ ,  $\text{SO}_2/\text{NO}_2$  and  $\text{SO}_2/\text{NO}_2/\text{NH}_3(\text{aq})$  were designed, marked as GR- $\text{SO}_2$ , GR- $\text{SO}_2/\text{NH}_3(\text{aq})$ , GR- $\text{SO}_2/\text{NO}_2$  and GR- $\text{SO}_2/\text{NO}_2/\text{NH}_3(\text{aq})$ , respectively. The concentrations of  $\text{SO}_2$  or/and  $\text{NO}_2$  were controlled at about 300 ppb and 300 ppb, which were monitored with an interval of 1 min by a  $\text{SO}_2$  analyzer (Model 43i, Thermo Fisher Scientific, Inc. USA) and  $\text{NO}_x$  analyzer (Model 42i-TL, Thermo Fisher Scientific, Inc. USA), respectively. The detailed conditions of the experiments are listed in Table 1. Additional parallel experiments in oxalic acid solution (Table S1) were also conducted. For each system, the simulation was repeated three times to understand the distribution due to experimental error, and the relative standard deviation (RSD) was also calculated to be less than 5%.

After reaction, the liquid samples were transferred to 5 mL vials (PolyVials™, Thermo Scientific, Inc. USA). 1 wt % formaldehyde (Sigma-Aldrich, ACS reagent, 37 wt % in  $\text{H}_2\text{O}$ ) was added in order to suppress sulfite oxidation and avoid overestimating sulfate (Kong et al., 2014). Then the samples were analyzed by ion chromatography (IC, Model DIONEX ICS-2100 and ICS-1100, Thermo Scientific, Inc. USA) to determine the concentrations of water-soluble ions (e.g.,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ) (SI, Section S1). Meanwhile, the pH of the solution at the end of the reaction was determined by a pH meter (FE28-Standard, Mettler-Toledo Instruments Co., Ltd).

### 2.2. Simulation of aqueous-phase reaction in the smog chamber

We also performed experiments by exposing oxalic acid seed aerosols to gaseous  $\text{SO}_2$ ,  $\text{SO}_2/\text{NH}_3$ ,  $\text{SO}_2/\text{NO}_2$  and  $\text{SO}_2/\text{NO}_2/\text{NH}_3$ , respectively under dark and high relative humidity (RH =  $98 \pm 1.5$  %) conditions in a 30 m<sup>3</sup> smog chamber (SI, Section S2), these four experimental systems were marked as SC- $\text{SO}_2$ , SC- $\text{SO}_2/\text{NH}_3$ , SC- $\text{SO}_2/\text{NO}_2$  and SC- $\text{SO}_2/\text{NO}_2/\text{NH}_3$ , respectively.  $\text{SO}_2$  and  $\text{NO}_x$  were also monitored using a  $\text{SO}_2$  analyzer and a  $\text{NO}_x$  analyzer mentioned

**Table 1**  
Experimental conditions in different reaction systems.

Exp. <sup>a</sup>	Gaseous SO <sub>2</sub> (ppb)	Gaseous NO <sub>2</sub> (ppb)	Gaseous NH <sub>3</sub> (ppb) <sup>b</sup>	Aqueous conditions
GR-SO <sub>2</sub>	300	–	–	Ultrapure water
GR-SO <sub>2</sub> /NO <sub>2</sub>	310	312	–	Ultrapure water
GR-SO <sub>2</sub> /NH <sub>3</sub> (aq)	302	–	–	0.02 wt %NH <sub>3</sub> solution
GR-SO <sub>2</sub> /NO <sub>2</sub> /NH <sub>3</sub> (aq)	300	310	–	0.02 wt %NH <sub>3</sub> solution
SC-SO <sub>2</sub>	298	–	–	Aerosol water of oxalic acid (RH = (98 ± 1.5) %)
SC-SO <sub>2</sub> /NO <sub>2</sub>	288	307	–	Aerosol water of oxalic acid (RH = (98 ± 1.5) %)
SC-SO <sub>2</sub> /NH <sub>3</sub>	288	–	~300	Aerosol water of oxalic acid (RH = (98 ± 1.5) %)
SC-SO <sub>2</sub> /NO <sub>2</sub> /NH <sub>3</sub>	284	317	~300	Aerosol water of oxalic acid (RH = (98 ± 1.5) %)

<sup>a</sup> GR represents the experiments performed in the glass reactor; SC represents the experiments performed in the 30 m<sup>3</sup> smog chamber.

<sup>b</sup> NH<sub>3</sub> concentration is estimated by the amount of NH<sub>3</sub> added and the volume of the smog chamber.

above. For the concentration of NH<sub>3</sub>, it was estimated according to the amount of NH<sub>3</sub> introduced and the volume of the chamber reactor. Aerosol particle size distributions and number concentrations were measured using a custom-built Scanning Mobility Particle Sizer (SMPS, TSI) with a 5-min cycle, which consists of a differential mobility analyzer (DMA, 3080 Classifier, TSI, Inc., USA) coupled with a Condensation Particle Counter (CPC, 3776, TSI, Inc., USA). Also, the mass concentrations of sulfate, nitrate and ammonium were measured using a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Inc. USA). The wall loss of pollutants were measured in several specialized experiments at the beginning and the end of chamber experimental study. The deposition rate of the pollutants in these experiments turned out to be quite similar. The wall loss rates of gaseous NO<sub>2</sub> and SO<sub>2</sub> were  $(1.67 \pm 0.25) \times 10^{-4}$  and  $(3.32 \pm 0.21) \times 10^{-4}$ , respectively. The wall loss rate ( $k_{\text{dep}}$ ) of particles was in accordance with  $k_{\text{dep}} = 4.15 \times 10^{-7} \times D_p^{1.89} + 1.39 \times D_p^{-0.88}$  ( $D_p$  is the particle diameter (nm)), which is used to correct the wall loss of aerosol particles similarly as Takekawa et al. (2003). T and RH were monitored using a hydro-thermometer (Vaisala HMP110).

Prior to each experiment, the Teflon chamber was flushed with purified and dry zero air for about 24 h at a flow rate of 100 L min<sup>-1</sup> until there was almost no residual NO<sub>x</sub>, SO<sub>2</sub>, or NH<sub>3</sub>, and the particle number concentration was <10 cm<sup>-3</sup>. Before the experiments, the Teflon chamber was humidified to the expected RH by passing purified air through ultra-pure water (18.2 MΩ, Millipore Milli-Q). Then the oxalic acid seed aerosols were injected into the Teflon chamber by atomizing 0.02 M oxalic acid solution and passed through a diffusion dryer before entering the chamber. These seeds would absorb water and even become deliquescent under high RH conditions (Peng et al., 2001), and formed a liquid reaction environment on their surface. SO<sub>2</sub>, NO<sub>2</sub>, and NH<sub>3</sub> were then injected into the chamber in purified dry zero air. The concentrations of the gases were continuously monitored at a measurement point in the reactor. The initial concentration of gaseous NH<sub>3</sub> was approximately 300 ppb, as shown in Table 1, and the concentrations of SO<sub>2</sub> and NO<sub>2</sub> were similar to those in the simulation carried out in the glass reactor.

At the end of the experiments, filter samples were collected onto 47 mm pure quartz filters (0.3 μm pore size, Staplex Air Sampler Division, USA) by use of a vacuum pump with a flow rate of 10 L min<sup>-1</sup> during the first 6 h of the cleaning process. The sampling port for the filters was located in the middle of the south side, and the cleaning air inlet was located in the middle of the east side of the smog chamber. After that, the collected filter samples were extracted in 12 mL of ultra-pure water in an amber sample vial (Strg Vial Kit, Agilent Technologies, USA) by sonication (Ultrasonic Cleanser, KQ-300DE) for 30 min, and then samples were analyzed by the IC system as mentioned above for the concentration of water-soluble inorganic ions, including SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>. The trend of the SO<sub>4</sub><sup>2-</sup> concentration of the filter samples determined by IC was consistent with the AMS results (Fig. S2).

### 2.3. Determination of reaction kinetics

In order to calculate the reaction kinetics of heterogeneous reactions, the mass transport in different media needs to be taken into account (Cheng et al., 2016). Considering the mass transport, a standard resistance model was adopted to describe the relationship between the aqueous-phase reaction rate and the overall reaction rate (Cheng et al., 2016; Seinfeld and Pandis, 2016):

$$\frac{1}{R_{aq}} = \frac{1}{R_{H,aq}} + \frac{1}{J_{aq,lim}} \quad (1)$$

where  $R_{aq}$  is the aqueous-phase reaction rate,  $R_{H,aq}$  is the overall reaction rate, and  $J_{aq,lim}$  is the limiting mass transfer rate.

$R_{H,aq}$  could be derived by Eq. (2) using the experimental results:

$$R_{H,aq} = \frac{\Delta[SO_4^{2-}]}{\Delta t} \quad (2)$$

in which  $\Delta[SO_4^{2-}]$  is the concentration of sulfate determined by IC or HR-ToF-AMS, and  $\Delta t$  is the reaction time.

Correspondingly, the aqueous-phase reaction rate  $R_{aq}$  could be estimated by Eq. (3):

$$R_{aq} = k[S(IV)][NO_2] \quad (3)$$

where  $k$  is the reaction rate coefficient of the oxidation reaction,  $[S(IV)]$  and  $[NO_2]$  are the concentrations of  $S(IV)$  and  $NO_2$  in the aqueous phase, respectively, and  $[NO_2]$  was determined by Henry's law:

$$[NO_2] = p(NO_2) \cdot H^*(NO_2) \quad (4)$$

where  $p(NO_2)$  and  $H^*(NO_2)$  are the partial pressure of NO<sub>2</sub> in the gas phase and the effective Henry's constant with  $1.00 \times 10^{-2}$  M atm<sup>-1</sup> at 298K, respectively.

Meanwhile,  $J_{aq,lim}$  could be determined via Eq. (5) and Eq. (6) as follows:

$$J_{aq,lim} = \min\{J_{aq}(SO_2), J_{aq}(NO_2)\} \quad (5)$$

$$J_{aq}(X) = k_{MT}(X) \cdot p(X) \cdot H^*(X) \quad (6)$$

in which X refers to SO<sub>2</sub> or NO<sub>2</sub>, and  $k_{MT}(X)$  is the mass transfer rate coefficient of species X, which could be calculated by Eq. (7):

$$k_{MT}(X) = \left( \frac{R_p^2}{3D_g} + \frac{4R_p}{3\alpha v} \right)^{-1} \quad (7)$$

where  $R_p$  is the aerosol radius,  $D_g$  is the gas-phase molecular diffusion coefficient,  $\alpha$  is the mass accommodation coefficient of

species X on the aqueous surface, with 0.11 (Seinfeld and Pandis, 2016) and  $2.00 \times 10^{-4}$  (Jacob, 2000) for SO<sub>2</sub> and NO<sub>2</sub>, respectively.  $v$  is the mean molecular speed of species X.

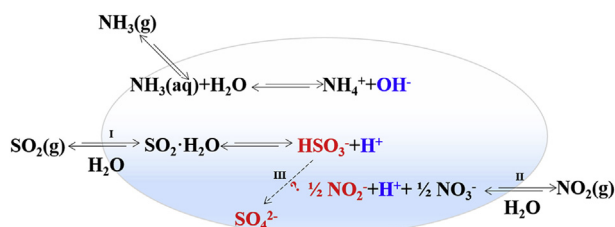
### 3. Results and discussion

#### 3.1. Description of the reaction process in different reaction systems

A simplified conceptual model of sulfate (S(VI)) species will be mainly SO<sub>4</sub><sup>2-</sup> under the pH conditions in GR reactions, while SO<sub>4</sub><sup>2-</sup> and HSO<sub>4</sub><sup>-</sup> may both exist under the pH conditions in SC reactions in this study. SO<sub>4</sub><sup>2-</sup> formation in the aqueous phase as investigated in this study is shown in Fig. 1, which includes the solubility of SO<sub>2</sub> and NO<sub>2</sub> (process I and II) and aqueous-phase oxidation (process III). SO<sub>4</sub><sup>2-</sup> formation was determined in both a glass reactor with a water solution and in a smog chamber with aerosol water associated with oxalic acid seed aerosols. The experimental conditions for the reactions in the glass reactor (GR) and reactions in the smog chamber (SC) are summarized in Table 1. In the experiments GR-SO<sub>2</sub> and GR-SO<sub>2</sub>/NH<sub>3</sub>(aq), dissolved SO<sub>2</sub> (mainly HSO<sub>3</sub><sup>-</sup>) was oxidized by background oxidants in the water (e.g., dissolved oxygen), while in the experiments GR-SO<sub>2</sub>/NO<sub>2</sub> and GR-SO<sub>2</sub>/NO<sub>2</sub>/NH<sub>3</sub>(aq), dissolved NO<sub>2</sub> (i.e., NO<sub>2</sub><sup>-</sup>) also contributed to the oxidation of dissolved SO<sub>2</sub>. Similar processes occurred in the aerosol water of the oxalic acid seed aerosols. The presence of NH<sub>3</sub> (in solution or in the gas phase) is expected to increase the alkalinity of the aqueous phase and influence both SO<sub>2</sub>/NO<sub>2</sub> solubility and the oxidation rate of HSO<sub>3</sub><sup>-</sup> by NO<sub>2</sub><sup>-</sup>, which could be generated in the fast hydrolytic disproportionation of NO<sub>2</sub> (Li et al., 2018).

#### 3.2. The role of NO<sub>2</sub> for SO<sub>4</sub><sup>2-</sup> formation in the aqueous-phase oxidation

Fig. 2A summarizes the SO<sub>4</sub><sup>2-</sup> concentrations resulting from reactions in the GR system. Ten minutes after the start of reaction in the experiment GR-SO<sub>2</sub>, the concentration of SO<sub>4</sub><sup>2-</sup>, which came from the oxidation of dissolved SO<sub>2</sub> (mainly HSO<sub>3</sub><sup>-</sup>) by background oxidants in the solution, was  $0.005 \pm 0.002 \mu\text{g mL}^{-1}$ . In the experiment GR-SO<sub>2</sub>/NO<sub>2</sub>, the SO<sub>4</sub><sup>2-</sup> generated was  $0.041 \pm 0.001 \mu\text{g mL}^{-1}$ , which was increased by a factor of about 8 compared to GR-SO<sub>2</sub>, suggesting a significant contribution of NO<sub>2</sub> to the oxidation of SO<sub>2</sub> in the water solution. The apparent reaction rate constant for the aqueous-phase oxidation of dissolved S(IV) by NO<sub>2</sub>(aq) was calculated to be  $1.31 \times 10^6 \pm 2.86 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . The rate constant reported by Lee and Schwartz (1983) was  $1.40 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  when pH < 5.0 and  $2.00 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  when pH > 5.8, while Clifton et al. (1988) calculated the rate constant to be  $1.24 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  and  $1.67 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  at pH of 5.3 and 8.7, respectively. In the present study, the pH of the solution was 4.1 at the end of the reaction. Considering the uncertainty in pH, our experimental results for the reactions in water solution using the glass reactor are in the range



**Fig. 1.** A simplified conceptual model of SO<sub>4</sub><sup>2-</sup> formation in the aqueous phase. Process I and II represent the dissolution of SO<sub>2</sub> and NO<sub>2</sub> into the aqueous phase, respectively, and process III represents SO<sub>4</sub><sup>2-</sup> formation by NO<sub>2</sub> oxidation.

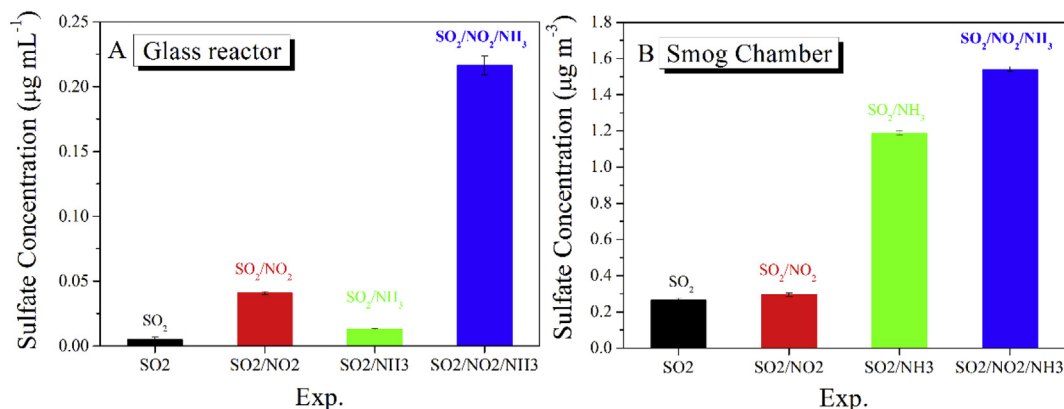
of results from previous studies (Clifton et al., 1988; Huie and Neta, 1986; Lee and Schwartz, 1983).

In the SC experiments using oxalic acid seed aerosols, there was also similar enhancement of the SO<sub>4</sub><sup>2-</sup> formation from the oxidation of SO<sub>2</sub> by NO<sub>2</sub> (Fig. 2B). The time series of SO<sub>2</sub>, NO<sub>2</sub>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> during each SC experiment were shown in Fig. S3. Normalizing SO<sub>4</sub><sup>2-</sup> formation with the initial SO<sub>2</sub> concentration, SO<sub>4</sub><sup>2-</sup> formation increased by 15.2% in the presence of NO<sub>2</sub>. As shown in Fig. 3, the consumption rate of gaseous SO<sub>2</sub> (after correction for wall loss) was  $5.26 \times 10^{-4} \text{ min}^{-1}$  in the experiment SC-SO<sub>2</sub>/NO<sub>2</sub>, which is higher than in SC-SO<sub>2</sub> ( $4.33 \times 10^{-4} \text{ min}^{-1}$ ). Meanwhile, the size distributions for different SC experiments were also given in Fig. S4. Compared with SC-SO<sub>2</sub>, the slightly larger particle size were observed in the SC-SO<sub>2</sub>/NO<sub>2</sub> (~250 nm, Figs. S4A and S4B). Meanwhile, the reaction rate constant was calculated to be  $1.56 \times 10^8 \pm 4.67 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  (Table 2), which is two orders of magnitude higher than that in the GR system. This was probably caused by the different reaction environments (e.g. the concentration of ionic species in the aqueous phase), and this influence will be discussed in detail later in this paper. Meanwhile, based on the concentrations of chemical species measured by HR-ToF-AMS, the molarity based pH (i.e., pH<sub>c</sub>) of the aerosol water was estimated using the extended aerosol inorganics model (E-AIM, Model II) (Clegg et al., 1998; Wexler and Clegg, 2002; Jia et al., 2018). In the SC experiments, the gas-phase NH<sub>3</sub> concentration was estimated by considering the amount of NH<sub>3</sub> added and the volume of the smog chamber. Considering the uncertainty of the NH<sub>3</sub> concentration due to its strong stickiness with walls and other surfaces, and the presence of oxalic acid aerosols, which was not considered in the E-AIM model, the predicted pH of the aerosol by E-AIM model might have some uncertainty. In addition, recent studies have reported that organic compounds had an effect on pH (Guo et al., 2015; Jia et al., 2018; Pye et al., 2018). Therefore, the estimated pH<sub>c</sub> was for reference only and was not used in the analysis of the results.

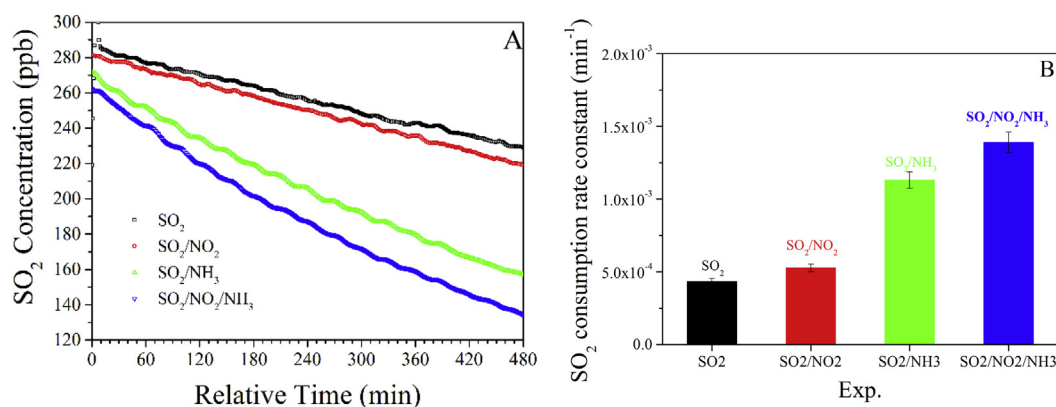
#### 3.3. The role of NH<sub>3</sub> in SO<sub>4</sub><sup>2-</sup> formation in the aqueous-phase reaction

Similarly, we studied the role of NH<sub>3</sub> in the aqueous-phase oxidation of SO<sub>2</sub>. With the presence of NH<sub>3</sub> in the aqueous-phase reaction, the formation of SO<sub>4</sub><sup>2-</sup> was enhanced to varying degrees (Fig. 2). In the GR system,  $0.013 \pm 0.006 \mu\text{g mL}^{-1}$  of SO<sub>4</sub><sup>2-</sup> was formed in the experiment GR-SO<sub>2</sub>/NH<sub>3</sub>(aq), more than two times that in GR-SO<sub>2</sub>. We attributed this increase in SO<sub>4</sub><sup>2-</sup> formation to increased SO<sub>2</sub> dissolution due to the increase in the alkalinity of the reaction solution. In the experiment GR-SO<sub>2</sub>/NO<sub>2</sub>/NH<sub>3</sub>(aq), SO<sub>4</sub><sup>2-</sup> formation was promoted further by the presence of gaseous NO<sub>2</sub> and NH<sub>3</sub>, and its concentration ( $0.22 \pm 0.009 \mu\text{g mL}^{-1}$ ) was about 44.0 times and 5.4 times that in the experiments GR-SO<sub>2</sub> and GR-SO<sub>2</sub>/NO<sub>2</sub>, respectively. These results are consistent with a previous study (Turšič et al., 2004) showing that the presence of NH<sub>3</sub> could promote SO<sub>4</sub><sup>2-</sup> formation by a factor of 23 under aqueous droplet conditions. For the SC experiments, the presence of NH<sub>3</sub> in the experiment SC-SO<sub>2</sub>/NH<sub>3</sub> enhanced the SO<sub>4</sub><sup>2-</sup> formation by a factor of 4.4 compared to SC-SO<sub>2</sub> ( $1.19 \mu\text{g m}^{-3}$  vs  $0.27 \mu\text{g m}^{-3}$ , respectively). The promotion of SO<sub>4</sub><sup>2-</sup> formation due to NH<sub>3</sub> is more significant in the SC experiments than that in the GR experiments. One possible reason is that the presence of NH<sub>3</sub> in the SC experiments also increased the volume of aerosol water, while this effect did not exist in the GR experiments. This could be supported by the size distribution observed in SC-SO<sub>2</sub>/NH<sub>3</sub> and SC-SO<sub>2</sub>, in which the former had the larger particle size (Figs. S4A and S4C). Meanwhile, in another separate SC experiment, NH<sub>3</sub> was injected into the chamber with similar RH and quantity of oxalic acid seed aerosol. The seed aerosol volume rose 23% after the injection of NH<sub>3</sub> into the chamber ( $24.0 \mu\text{m}^3 \text{ cm}^{-3}$  vs  $29.6 \mu\text{m}^3 \text{ cm}^{-3}$ ,





**Fig. 2.** The generated concentration of  $\text{SO}_4^{2-}$  (A) in GR under different experimental conditions, i.e., 300 ppb  $\text{SO}_2$ , 310 ppb  $\text{SO}_2/312$  ppb  $\text{NO}_2$ , 302 ppb  $\text{SO}_2/\text{NH}_3(\text{aq})$ , and 300 ppb  $\text{SO}_2/310$  ppb  $\text{NO}_2/\text{NH}_3(\text{aq})$ , and (B) in SC under analogous experimental conditions, i.e., 298 ppb  $\text{SO}_2$ , 288 ppb  $\text{SO}_2/307$  ppb  $\text{NO}_2$ , 288 ppb  $\text{SO}_2/\text{NH}_3$  (~300 ppb), and 284 ppb  $\text{SO}_2/317$  ppb  $\text{NO}_2/\text{NH}_3$  (~300 ppb). The error bars represent the standard deviations.



**Fig. 3.** (A) Time-resolved concentration and (B) consumption rate constant of  $\text{SO}_2$  in the SC experiments under different conditions.

**Table 2**

Summary of reaction rate constants derived from different studies.

Exp.	Reaction rate constant ( $\text{M}^{-1} \text{s}^{-1}$ )			
This study	GR- $\text{SO}_2/\text{NO}_2$	GR- $\text{SO}_2/\text{NO}_2/\text{NH}_3(\text{aq})$	SC- $\text{SO}_2/\text{NO}_2$	SC- $\text{SO}_2/\text{NO}_2/\text{NH}_3$
	$1.31 \times 10^6 \pm 2.86 \times 10^4$ (pH>4.1)	$1.63 \times 10^6 \pm 2.29 \times 10^5$ (pH>5.3)	$1.56 \times 10^8 \pm 4.67 \times 10^6$ (pH~0.5)	$5.98 \times 10^8 \pm 5.44 \times 10^6$ (pH~1.6)
Lee and Schwartz, 1983	$1.40 \times 10^5$ (pH<5.0)	$2.00 \times 10^6$ (pH>5.8)		
Clifton et al., 1988	$1.24 \times 10^7$ (pH=5.3)	$1.67 \times 10^7$ (pH=8.7)		

respectively), indicating that the aerosol water was increased in the presence of  $\text{NH}_3$  (Chu et al., 2016). The reaction rate constants between  $\text{NO}_2$  and  $\text{S}(\text{IV})$  in the experiments GR- $\text{SO}_2/\text{NO}_2/\text{NH}_3(\text{aq})$  and SC- $\text{SO}_2/\text{NO}_2/\text{NH}_3$  were calculated to be  $1.63 \times 10^6 \pm 2.29 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  and  $5.98 \times 10^8 \pm 5.44 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. These values are 1.2-fold and 3.8-fold those in the experiments GR- $\text{SO}_2/\text{NO}_2$  ( $1.31 \times 10^6 \pm 2.86 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ) and SC- $\text{SO}_2/\text{NO}_2$  ( $1.56 \times 10^8 \pm 4.67 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ), respectively, indicating an important role of  $\text{NH}_3$  in accelerating the aqueous-phase oxidation of  $\text{SO}_2$  by  $\text{NO}_2$ .

As shown in Fig. 1,  $\text{SO}_4^{2-}$  formation in the aqueous phase is dependent on solubility of  $\text{SO}_2$  and  $\text{NO}_2$  (process I and II) and aqueous-phase oxidation (process III). Therefore, the increased ratio of  $\text{SO}_4^{2-}$  concentration ( $R[\text{SO}_4^{2-}]$ ) should be equal to the increase ratio of  $\text{SO}_2$  dissolution ( $R[\text{S}(\text{IV})]$ ) multiplied by the increase ratio of  $\text{NO}_2$  dissolution ( $R[\text{NO}_2(\text{aq})]$ ), then multiplied by the increase ratio of the reaction rate constant ( $R_k$ ), i.e.,  $R[\text{SO}_4^{2-}] = R[\text{S}(\text{IV})] \times R$

$[\text{NO}_2(\text{aq})] \times R_k$ . Gas-phase  $\text{NH}_3$  increases all these processes mentioned in Fig. 1, leading to increased  $\text{SO}_4^{2-}$  formation. The effects of  $\text{NH}_3$  on the three processes were evaluated separately in this study. First, the influence of  $\text{NH}_3$  on the dissolution of  $\text{SO}_2$  was studied in the experiments GR- $\text{SO}_2/\text{H}_2\text{O}_2(\text{aq})$  and GR- $\text{SO}_2/\text{NH}_3/\text{H}_2\text{O}_2(\text{aq})$  (SI, Table S1). Considering that the reaction rate constant between  $\text{SO}_2$  and  $\text{H}_2\text{O}_2$  ( $k = 7.45 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) is constant when the solution pH is > 2.5 (Seinfeld and Pandis, 2016), the increased  $\text{SO}_4^{2-}$  formation in the experiment GR- $\text{SO}_2/\text{NH}_3/\text{H}_2\text{O}_2(\text{aq})$  compared with that in GR- $\text{SO}_2/\text{H}_2\text{O}_2(\text{aq})$  can be attributed to the increased solubility of  $\text{SO}_2$  in the presence of  $\text{NH}_3$ . Based on the production of  $\text{SO}_4^{2-}$ , we estimated that  $\text{SO}_2$  dissolution was increased by a factor of 3.2 with the coexistence of  $\text{NH}_3$ . This factor was assumed to be similar in the experiment GR- $\text{SO}_2/\text{NO}_2/\text{NH}_3(\text{aq})$  compared to GR- $\text{SO}_2/\text{NO}_2$ . Similarly, we compared the concentration of nitrate in the experiments GR- $\text{SO}_2/\text{NO}_2/\text{NH}_3(\text{aq})$  and GR- $\text{SO}_2/\text{NO}_2$ , and estimated that  $\text{NO}_2$  dissolution was increased by a factor of 1.5 in the presence

of  $\text{NH}_3$ . These two ratios in processes I and II could not fully explain the 5.3-fold higher  $\text{SO}_4^{2-}$  formation in the experiment GR- $\text{SO}_2/\text{NO}_2/\text{NH}_3(\text{aq})$  compared to GR- $\text{SO}_2/\text{NO}_2$ . The remaining increase was attributed to the promotion of the oxidation rate constant, namely process III in Fig. 1. An increase of 12% in the oxidation rate constant with the coexistence of  $\text{NH}_3$  was needed to match the total increase of  $\text{SO}_4^{2-}$  formation. This slight increase in the oxidation rate constant might be attributed to the change in the pH of the aqueous solution. In summary, our estimation showed that the enhancement effects of  $\text{NH}_3$  on the solubility of  $\text{SO}_2$  and  $\text{NO}_2$  were the main factors in promoting  $\text{SO}_4^{2-}$  formation in the aqueous-phase reaction.

### 3.4. Influence of ionic strength on aqueous-phase reactions

The electrolyte (i.e., hygroscopic oxalic acid) concentrations were higher in the aerosols in the SC experiments than those in the solution in the GR experiments. Previous studies have shown that electrolyte concentrations can alter the rate constant for a reaction involving a neutral species (e.g., the reactions of nitrogen trioxide ( $\text{NO}_3$ )) by about one order of magnitude (Herrmann and Zellner, 1998). For the H-abstraction reactions of chlorine radical anion ( $\text{Cl}_2^-$ ) with formaldehyde and formic acid, higher rate constants were observed with increasing ionic strength (Jacobi et al., 1999). Therefore, it is reasonable to attribute the higher reaction rate constant derived from the SC experiments compared to that from the GR experiments to the higher ionic strength (Herrmann et al., 2015) in the aerosol water, where the products and pre-existing electrolyte were highly concentrated.

The ionic strength ( $I$ ) of a solution is defined as:

$$I = \frac{1}{2} \sum_{i=1}^n c_i z_i^2 \quad (8)$$

where  $c_i$  is the concentration of species  $i$  and  $Z_i$  is the ionic charge of species  $i$  in aqueous solution.

For a reaction  $A + B \rightarrow [A-B]^\ddagger \rightarrow P$ , where reactants A and B form an intermediate product  $[A-B]^\ddagger$ , which then quickly converts into the final product P, the relationship between reaction rate constant ( $k$ ) and ionic strength ( $I$ ) can be described by the following equation (Herrmann, 2003):

$$\log \frac{k}{k(I=0)} = \log \gamma_A + \log \gamma_B - \log \gamma_{(AB)} \quad (9)$$

where  $\gamma_i$  is the activity coefficient of species  $i$ , and  $k(I=0)$  is the kinetic rate constant at the infinite dilution condition, namely  $I=0$  M.

According to the previous reported mechanisms for the reaction of  $\text{NO}_2$  with S(IV) (Clifton et al., 1988; Huie, 1994; Nash, 1979; Spindler et al., 2003), the rate-controlling step of this oxidation process involves an ion (i.e.,  $\text{HSO}_3^-$ ,  $\text{SO}_3^{2-}$ ) reacting with a neutral molecule (i.e.,  $\text{NO}_2$ ). For the neutral species, the expression for the activity coefficient  $\gamma_i$  can be described by equation (10), which indicates that  $\gamma_i$  of the neutral species could be positively influenced by  $I$  via the ion-pair interaction (Herrmann, 2003).

$$\log \gamma_i = bI \quad (10)$$

where  $b$  is the kinetic salting coefficient.

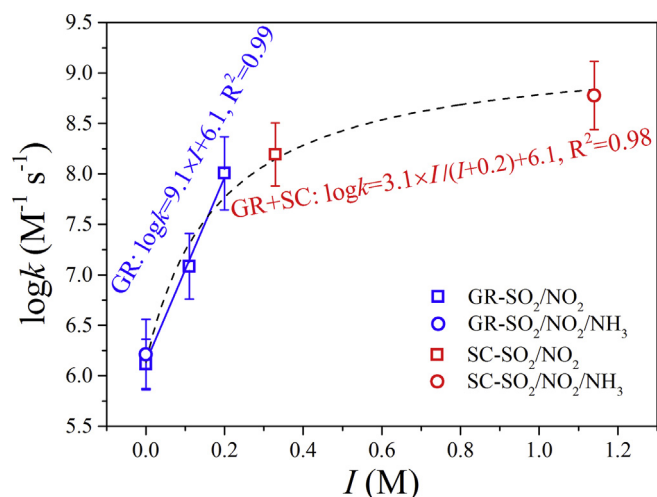
As a result, the relationship between  $k$  and  $I$  for the reaction of  $\text{NO}_2$  with S(IV) should be expressed as:

$$\log \frac{k}{k(I=0)} = bI \quad (11)$$

In the light of previous studies (Kameoka and Pigford, 1977),  $b$  should be a positive value. Therefore, the reaction rate constant  $k$  increases with increases in the ionic strength  $I$  of the solution.

Based on the concentrations of water-soluble ions (mainly  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ) (SI, Table S2), the ionic strength of the reaction systems was low ( $I = 2.40 \times 10^{-6}$  M and  $7.20 \times 10^{-6}$  M for GR- $\text{SO}_2/\text{NO}_2$  and GR- $\text{SO}_2/\text{NO}_2/\text{NH}_3(\text{aq})$ , respectively) in the GR experiments. In a previous study conducted by Lee et al. (Lee and Schwartz, 1983), the initial reaction solution concentration ( $[\text{HSO}_3^-]_0 = 1.3 \times 10^{-6}$  M) was also low. Hence, it is reasonable that the reaction rate constants derived from the GR experiments in our study are comparable to the results by Lee et al. (Lee and Schwartz, 1983). On the other hand, under a higher S(IV) concentration ( $[\text{S(IV)}] = 5 \times 10^{-4} - 2 \times 10^{-3}$  M) condition, Clifton et al. (1988) derived higher rate constants compared to Lee et al. (Lee and Schwartz, 1983) and this study (Table 2). The comparison suggests that higher concentrations of solutes, namely higher ionic strengths in the solution can result in higher rate constants. To test this hypothesis, we performed experiments on the oxidation of  $\text{SO}_2$  by  $\text{NO}_2$  in solutions with different concentrations of oxalic acid (Table S1). Higher  $\text{SO}_4^{2-}$  concentrations (Table S2), resulting from higher formation rate constants, were indeed observed for higher concentrations of oxalic acid in solution. A linear relationship between  $\log k$  and  $I$  ( $R^2 = 0.99$ , blue solid line, Fig. 4) was obtained, which is consistent with equation (11) and thus confirms the hypothesis.

Meanwhile, for the SC experiments SC- $\text{SO}_2/\text{NO}_2$  and SC- $\text{SO}_2/\text{NO}_2/\text{NH}_3$ , the oxalic acid seeds were deliquescent under the experimental conditions of  $\text{RH} = (98 \pm 1.5)\%$  (Peng et al., 2001), providing an aerosol water reaction medium in which the reactions occurred. Using similar methods as in Guo et al. (2015) (SI, Section S3), the volume of aerosol water was estimated, allowing the concentrations of water-soluble ions (mainly  $\text{HC}_2\text{O}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$ ) in this aerosol water (SI, Table S3) and the ionic strength of the solution to be calculated. The ionic strength was much higher ( $I = 3.29 \times 10^{-1}$  M and 1.14 M for the experiments SC- $\text{SO}_2/\text{NO}_2$  and SC- $\text{SO}_2/\text{NO}_2/\text{NH}_3$ , respectively) in the SC experiments than that in the GR experiments. The higher ionic strengths can explain the high reaction rate constants for  $\text{SO}_4^{2-}$  formation in the aerosol water. Together with the GR experiments with further reduced ionic strength (i.e., in total 5 experimental data points), an empirical



**Fig. 4.** Relationship between reaction rate constant ( $k$ ) and ionic strength ( $I$ ). Each data point refers to an experiment listed in Table 1 and Table S1, and the  $\log k$ - $I$  data corresponding to the all points are given in Table S4. A linear relationship  $\log k = 9.1 \times I + 6.1$  was obtained for GR experiments, while an empirical relationship  $\log k = 3.1 \times I / (I + 0.2) + 6.1$  was obtained when combining GR and SC experiments.

relationship between  $\log k$  and  $I$  could also be obtained ( $R^2 = 0.98$ , black dashed line, Fig. 4). According to this empirical relationship, the reaction rate constant may increase linearly with the increase of ionic strength in aerosol water, but the increase progressively diminish. Although there is no scientific explanation for this phenomenon yet, it is supported by previous studies investigating the salt effect in reactions between ions and dipolar molecules (Amis and Jaffe, 1942; Castanedaagullo et al., 1961). These empirical relationships in Fig. 4 might provide a parameterized solution to the air quality models for simulation of  $\text{SO}_4^{2-}$  formation in cloud/fog droplets and aerosol water.

#### 4. Conclusions and atmospheric implications

As the major inorganic constituent of atmospheric particle matter (PM),  $\text{SO}_4^{2-}$  plays an important role in haze pollution not only over North China (Guo et al., 2014; Sun et al., 2016), but also other rapidly developing countries (Gordon, 2003). Based on the present understanding of  $\text{SO}_4^{2-}$  formation mechanisms, the observed  $\text{SO}_4^{2-}$  levels cannot be accurately simulated in air quality models, which indicates the presence of reactions and factors in addition to the current formation mechanisms (Gao et al., 2016a; Zheng et al., 2015a). In the present study, the chemical reaction kinetics of aqueous oxidation of  $\text{SO}_2$  by  $\text{NO}_2$  under different atmospheric conditions were quantitatively evaluated. The GR experimental results, in which we found that  $\text{SO}_2$  oxidation by  $\text{NO}_2$  contributed significantly to  $\text{SO}_4^{2-}$  formation, may be applicable to  $\text{SO}_4^{2-}$  formation in fog and clouds. Meanwhile, the coexistence of  $\text{NH}_3$  would mainly enhance the dissolution of  $\text{SO}_2$  and  $\text{NO}_2$  and subsequently promote  $\text{SO}_4^{2-}$  formation. The SC experimental results may be applied to  $\text{SO}_4^{2-}$  formation in aerosol water. Unexpectedly high reaction rate constants for the oxidation of S(IV) by  $\text{NO}_2$  were observed in aerosol water, which was attributed to the high ionic strength in the aerosol water.

In severe haze episodes (Gao et al., 2016b), ground-level photochemical reactivity can be weak due to radiative attenuation and the ozone concentration can be low (Zheng et al., 2015b). Gas-phase oxidation of  $\text{SO}_2$  by OH and aqueous-phase oxidation of dissolved  $\text{SO}_2$  by  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  can be suppressed to a great extent because of the low oxidant levels. Under these situations, the oxidation of S(IV) by  $\text{NO}_2$  in the liquid phase may become an essential pathway of  $\text{SO}_4^{2-}$  formation when RH,  $\text{NO}_2$  and  $\text{NH}_3$  levels are all high. Such conditions exist in the winter season in cities such as Beijing (Zhang et al., 2015a) and Shanghai (Ye et al., 2011), China, where haze episodes were frequently observed but oxidant levels represented by  $\text{O}_3$  were low, yet  $\text{SO}_4^{2-}$  was high (He et al., 2014; Wang et al., 2016). Using observed  $\text{NO}_2$ ,  $\text{NH}_3$  and PM concentrations in such haze episodes (Cheng et al., 2016), the atmospheric lifetime of  $\text{SO}_2$  due to oxidation by  $\text{NO}_2$  in aerosol water is estimated to be approximately 24 h based on the present laboratory study results (SI, Section S4), which is shorter by an average factor of about 2 than the atmospheric lifetime of  $\text{SO}_2$  due to OH oxidation by assuming an daytime average OH concentration of  $5.2 \times 10^6$  molecules  $\text{cm}^{-3}$  (Lu et al., 2013). Atmospheric OH concentrations varied a lot ( $<1 \times 10^6$ – $1.7 \times 10^7$  molecules  $\text{cm}^{-3}$ ) in different seasons and at different altitudes and latitudes (Lu et al., 2013; Seinfeld and Pandis, 2016; Wang et al., 2016; Yang et al., 2017), while ranged from  $2.4 \times 10^6$  molecules  $\text{cm}^{-3}$  to  $3.6 \times 10^6$  molecules  $\text{cm}^{-3}$  in Beijing winter (Tan et al., 2018). The atmospheric lifetime of  $\text{SO}_2$  due to OH oxidation will increase with decreasing OH concentration in winter time during haze episodes. These  $\text{SO}_2$  lifetime analyses suggest that heterogeneous oxidation of  $\text{SO}_2$  by  $\text{NO}_2$  in aerosol water, especially with the coexistence of  $\text{NH}_3$ , high concentrations of PM and high RH, is a major pathway for  $\text{SO}_4^{2-}$  formation in the atmosphere in severe haze episodes. Such a high oxidation rate was

clearly promoted by high ionic strengths in aerosol water. High aerosol ionic strengths have been observed in typical haze events in Beijing (Guo et al., 2017), at 12 times higher than that under our experimental conditions. Given the finding of the already large impact under the ionic strength conditions of our laboratory study, the impact of  $I$  under real-world haze conditions should be even stronger, and hence should be considered in air quality models to improve simulations of haze formation process.

There have been questions about the importance of the oxidation of  $\text{SO}_2$  to  $\text{SO}_4^{2-}$  by  $\text{NO}_2$  based on low pH value predictions for aerosols (Cheng et al., 2016; Guo et al., 2017; Liu et al., 2017; Song et al., 2018; Wang et al., 2018; Wang et al., 2016). Our results indicated that  $\text{SO}_4^{2-}$  formation by  $\text{NO}_2$  oxidation can still be significant in acidic aerosol water under high ionic strength conditions (Table 2). Expanding and continuing the present work to include more atmospherically relevant conditions may provide more accurate kinetic parameters for simulation of  $\text{SO}_4^{2-}$  formation in air quality models.

#### Competing financial interests

The authors declare no competing financial interest.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2019.05.119>.

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