

Reviewer #2

The manuscript by Zhang and Chan reports an experimental result for reactive uptake of SO₂ and NO₂ by aqueous NaCl droplets using the micro Raman spectroscopy. The experiment was conducted both under dark and irradiation by a Xe lamp. Nitrate formation was observed for droplets both under dark and light-irradiated conditions. Sulfate was observed only when light was available. The experimental result was parameterized using a chemical kinetic model.

Both the experimental technique and result sound. The major conclusion is well supported by the experimental data. The topic is within the scope of the interest of the readers of the journal, although the reviewer wonders if the concentration ranges of chemical species and light intensities are atmospheric relevant. The manuscript is reasonably well written. Revision will be required prior to the publication of this manuscript.

Response:

We thank the reviewer for the valuable comments. We have revised the manuscript according to the questions raised by the reviewer.

Major comments

Comment 1. Atmospheric relevance of the experimental conditions

The concentration ranges for both SO₂ (~6.5 ppm) and NO₂ (~10 ppm) were a few orders higher than that for typical atmospheric conditions. As the authors constructed a chemical kinetic model for reproducing the experimental result, it might be interesting to simulate if the finding of the present study would be important for atmospheric relevant concentration and light intensity ranges.

Response:

We agree that such concentrations are not atmospherically relevant. To our best knowledge, this is probably the first experimental investigation of the mechanisms of nitrate and sulfate formation during the NO₂ and SO₂ uptake into NaCl seed particles under irradiation. In this study, we aimed to have a better understanding of their formation mechanism, especially in the presence of irradiation. Using high concentrations of SO₂ and NO₂ allowed the formation of nitrate and sulfate in a reasonable time to determine their respective formation rate.

Although the derived expression (Equation 1) was from the experimental conditions with co-uptake of NO₂ and SO₂ into NaCl droplets under irradiation at 60%, 70%, and 80% RH, it is based on the nitrate and chloride concentration in the droplets; hence, in principle, it is independent of the SO₂ and NO₂ concentrations and seed particle types.

$$\gamma_{\text{SO}_2} = 0.41 \times P_{\text{NO}_3^-} + 0.34 \times P_{\text{Cl}^-} \quad (\text{Equation 1})$$

To verify it, we performed additional experiments with SO₂ uptake into premixed

NH₄Cl + NH₄NO₃ droplets (4:1 in mole ratio at 75% RH) and pure NH₄Cl droplets under irradiation (Xe lamp), in which no NO₂ gas, but the interaction of nitrate photolysis and chlorine chemistry still can occur in premixed system. Figure Aa shows a higher sulfate production rate in pure NH₄NO₃ droplets, which is likely due to the higher initial nitrate concentration in pure NH₄NO₃ droplets (~8.1M) than in premixed NH₄Cl + NH₄NO₃ droplets (~1.0 M). As reported in our earlier works, nitrate photolysis could also promote sulfate formation. Hence, sulfate concentration is normalized by initial nitrate concentration, as shown in Figure Ab. A significant enhancement in the normalized sulfate production rate was observed in premixed NH₄Cl + NH₄NO₃ droplets, implying that the interplay of nitrate photolysis and chlorine chemistry could also take place.

To evaluate if the equation is applicable to non sea salt system, we compared γ_{SO_2} from the Equation 1 with that from experimental results (i.e., premixed NH₄Cl + NH₄NO₃ system) in Figure Aa. A kinetic model (FACSIMILE software) was used to obtain the fitted nitrate and chloride photolysis rate constants in premixed NH₄Cl + NH₄NO₃ system, which are $1.0 \times 10^{-6} \text{ s}^{-1}$ and $1.6 \times 10^{-6} \text{ s}^{-1}$, respectively. In experiments of premixed NH₄Cl + NH₄NO₃ droplets equilibrated at 75% RH, the initial concentration of nitrate and chloride are 1.0 M and 4.0 M, respectively. Hence, the nitrate photolysis rate, $P_{NO_3^-}$, and chloride photolysis rate, P_{Cl^-} , are the $1.0 \times 10^{-6} \text{ M s}^{-1}$ and $6.5 \times 10^{-6} \text{ M s}^{-1}$, respectively. The calculated γ_{SO_2} (2.6×10^{-6}) agrees well with that from the experiments (3.0×10^{-6}) (Text S2 in Supporting Information). This gives us confidence that the derived expression of uptake coefficient may be useful in ammonium system containing nitrate and chloride too.

Based on our proposed mechanisms and expression for the uptake coefficient, we estimated the sulfate production rate using characteristic data from Beijing reported by Huang et al. (2014). The reported concentrations of nitrate, sulfate, chloride, ammonium, and OM are summarized in Table A. The E-AIM was used to estimate the contribution of all inorganic components to aerosol water content (AWC), $W_{inorganic}$, by assuming RH of 60% during the haze events. The contribution of OM to AWC, W_{org} , was estimated by the same approach of Guo et al. (2015).

$$W_{org} = \frac{OM}{\rho_{org}} \cdot \rho_w \cdot \frac{k_{org}}{\left(\frac{100\%}{RH} - 1\right)} \quad (\text{Equation 2})$$

where OM is the mass concentration of organic matter, ρ_w is the density of water ($\rho_w = 1.0 \times 10^3 \text{ kg m}^{-3}$), ρ_{org} is the density of organics ($\rho_{org} = 1.4 \times 10^3 \text{ kg m}^{-3}$), and k_{org} is the hygroscopicity parameter of organic aerosol composition. We adopted a k_{org} of 0.06 based on previous cloud condensation nuclei measurements in Beijing. Overall, the estimated total AWC ($=W_{inorganic} + W_{org}$) taking into contributions by the inorganics and OM is $\sim 46 \mu\text{g m}^{-3}$.

The sulfate production rate in unit of $\mu\text{g m}^{-3} \text{ h}^{-1}$, $\frac{d[SO_4^{2-}]}{dt}$, can be calculated by:

$$\frac{d[SO_4^{2-}]}{dt} = 3600 \text{ s h}^{-1} \times 10^{-3} \times M(SO_4^{2-}) \times R_{SO_4^{2-}} \times \frac{AWC}{\rho_w} \quad (\text{Equation 3})$$

where $M(\text{SO}_4^{2-})$ is 96.06 g mol^{-1} , AWC ($\sim 46 \text{ } \mu\text{g m}^{-3}$) and ρ_w ($=1 \text{ kg L}^{-1}$) are aerosol water content and water density (Liu et al., 2021), respectively. $R_{\text{SO}_4^{2-}}$ is the sulfate production rate in unit of M s^{-1} , which can be obtained by the uptake coefficient:

$$R_{\text{SO}_4^{2-}} = \frac{1}{4} \omega [\text{SO}_2] \gamma_{\text{SO}_2} A_s \times 10^{-3} \quad (\text{Equation 4})$$

where $[\text{SO}_2]$ (40 ppb) is the gas phase concentration of SO_2 ($\text{mole m}^{-3} \text{ air}$), ω ($= (8RT/\pi M)^{1/2}$) is the mean speed of the molecule, A_s ($=3/r_p$) is the surface area of a particle per volume ($r_p = 0.15 \text{ } \mu\text{m}$) (Cheng et al., 2016).

According to previous studies (Ye et al., 2017, Gen et al., 2019), particulate nitrate photolysis rate constant under $>290 \text{ nm}$ irradiation can achieve $\sim 10^{-5} \text{ s}^{-1}$. The chloride photolysis rate constant is rarely reported in the literature; hence, we used the averaged photolysis rate constant obtained from fitting in our investigation (Table S3 in Supporting Information), which was on the order of $\sim 10^{-7} \text{ s}^{-1}$. Based on these values, we estimated γ_{SO_2} to be $\sim 2.7 \times 10^{-5}$, calculated from Equation 1. Using Equations 3 and 4 with these values, the sulfate production rate is estimated to be $1.1 \text{ } \mu\text{g m}^{-3} \text{ h}^{-1}$, which is comparable to the sulfate production rates from other traditionally reported pathways (e.g., O_3 , TMI, H_2O_2 , and NO_2 pathways) at particle pH of 4-6 during haze events (Liu et al., 2021). Future chemical model simulation of the contribution of proposed mechanisms to sulfate production rate is needed to evaluate its impact in the atmosphere thoroughly.

Table A. The chemical composition of collected $\text{PM}_{2.5}$ during the high pollution events of 5–25 January 2013 at the urban sites of Beijing (Huang et al., 2014).

Component	nitrate	chloride	sulfate	ammonium	Organic compounds (OM)
Mass Concentration ($\mu\text{g m}^{-3} \text{ air}$)	19.0	6.2	25.4	15.5	64.5
Mole Concentration ($\mu\text{mole m}^{-3} \text{ air}$)	0.3	0.17	0.3	0.9	/
Molar concentration (M)	6.5	3.7	6.5	19.6	/
Water content ($\mu\text{g m}^{-3} \text{ air}$)	$W_{\text{inorganic}}: 41.8$				$W_{\text{org}}: 4.1$

Revision in the manuscript (section 4):

In brief, the OH radicals formed from nitrate photolysis can react with chloride ions to promote the formation of chlorine species (e.g., Cl^\bullet and $\text{Cl}_2^{\bullet-}$) and further

enhance sulfate formation. Such effect enhances the γ_{SO_2} by factors of ~ 1.7 , ~ 2.5 , and ~ 2.9 at 80%, 70%, and 60% RH at $0.2 < [\text{NO}_3^-]/[\text{Cl}^-] < 3$, respectively, compared to those from the chloride photolysis (i.e., $\text{NaCl} + \text{SO}_2 + \text{light conditions}$).

To further verify whether our proposed mechanism could apply urban sites, where ammonium salts are the major components of particles, we performed additional experiments with SO_2 uptake into premixed $\text{NH}_4\text{Cl} + \text{NH}_4\text{NO}_3$ (4:1 in mole ratio) droplets and pure NH_4Cl droplets under the same irradiation at 75% RH. Figure S23a shows a higher sulfate production rate in pure NH_4NO_3 droplets, likely due to the higher initial nitrate concentration in pure NH_4NO_3 droplets (~ 8.1 M) than in premixed $\text{NH}_4\text{Cl} + \text{NH}_4\text{NO}_3$ droplets (~ 1.0 M). As reported in our earlier works, nitrate photolysis could also promote sulfate formation. Hence, sulfate concentration is normalized by initial nitrate concentration, as shown in Figure S23b. A significant enhancement in the normalized sulfate production rate was observed in premixed $\text{NH}_4\text{Cl} + \text{NH}_4\text{NO}_3$ droplets, confirming that the interplay of nitrate photolysis and chlorine chemistry could also take place. Note that the uptake coefficient equation ($\gamma_{\text{SO}_2} = 0.41 \times P_{\text{NO}_3^-} + 0.34 \times P_{\text{Cl}^-}$) is based on the experimental results of the co-uptake of NO_2 and SO_2 into NaCl droplets under irradiation at 60%, 70%, and 80% RH. To evaluate if this equation is applicable to non sea salt system, we compared γ_{SO_2} from the equation with that from experimental results (i.e., premixed $\text{NH}_4\text{Cl} + \text{NH}_4\text{NO}_3$ system) in Figure S23a. The calculated γ_{SO_2} (2.6×10^{-6}) agrees well with that from the experiments (3.0×10^{-6}) (Text S2). This gives us confidence that the derived expression of uptake coefficient may be useful in ammonium system containing nitrate and chloride too. In our earlier work, we performed unary uptake of SO_2 into premixed $\text{NH}_4\text{Cl} + \text{NH}_4\text{NO}_3$ droplets under 300-nm irradiation at different $[\text{NO}_3^-]/[\text{Cl}^-]$, in air and N_2 environment (Zhang et al., 2020). Note that the presence of O_2 (air environment) is essential for sulfate formation from reactions of reactive chlorine species with HSO_3^- (Figure 1). The normalized sulfate production rate continuously increases as $[\text{NO}_3^-]/[\text{Cl}^-]$ decreases in air, but no further enhancement of sulfate production rate was observed in N_2 when $[\text{NO}_3^-]/[\text{Cl}^-] < 5$ (Zhang et al., 2020). Such results also support the combined effect of nitrate photolysis and chlorine chemistry in promoting sulfate formation may be applicable in ammonium systems containing nitrate and chloride.

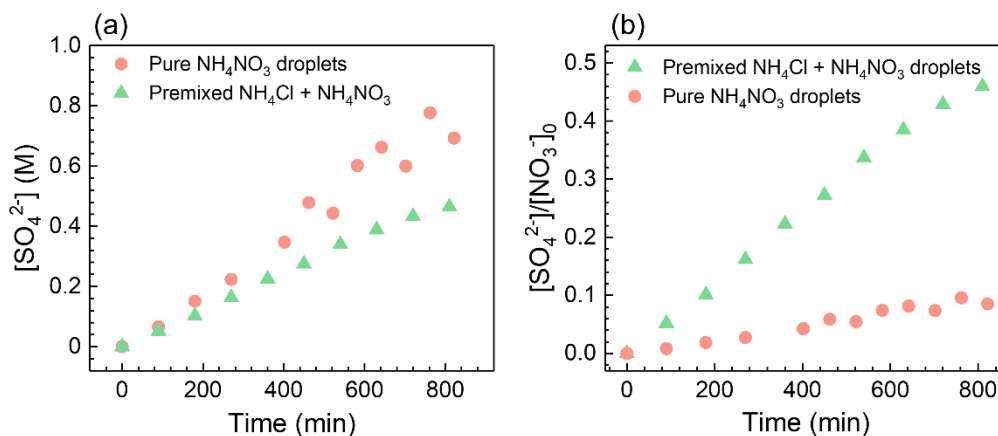


Figure A. (a) Sulfate concentration as a function of time in premixed $NH_4Cl + NH_4NO_3$ (4:1 in mole ratio) and pure NH_4NO_3 droplets under irradiation at 75% RH. (b) Sulfate concentration normalized by the initial nitrate concentration under the same conditions as panel (a).

Reference:

- (1) Zhang, R.; Gen, M.; Huang, D.; Li, Y.; Chan, C. K. Enhanced Sulfate Production by Nitrate Photolysis in the Presence of Halide Ions in Atmospheric Particles. *Environ. Sci. Technol.* **2020**, *54* (7), 3831-3839.
- (2) Cheng, Y.; Zheng, G.; Wei, C.; Mu, Q.; Zheng, B.; Wang, Z.; Gao, M.; Zhang, Q.; He, K.; Carmichael, G.; Pöschl, U.; Su, H., Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China. *Sci. Adv.* **2016**, *2*, (12).e1601530
- (3) Ye, C.; Zhang, N.; Gao, H.; Zhou, X. Photolysis of Particulate Nitrate as a Source of HONO and NOx. *Environ. Sci. Technol.* **2017**, *51* (12), 6849–6856.
- (4) Gen, M.; Zhang, R.; Huang, D. D.; Li, Y.; Chan, C. K. Heterogeneous Oxidation of SO_2 in Sulfate Production during Nitrate Photolysis at 300 nm: Effect of pH, Relative Humidity, Irradiation Intensity, and the Presence of Organic Compounds. *Environ. Sci. Technol.* **2019**, *53* (15), 8757-8766.
- (5) H. Guo, L. Xu, A. Bougiatioti, K. Cerully, S. Capps, J. Hite, A. Carlton, S. Lee, M. Bergin, N. Ng, A. Nenes, R. Weber, Fine-particle water and pH in the southeastern United States. *Atmos. Chem. Phys.* **15**, 5211–5228 (2015).
- (6) Huang, R.-J.; Zhang, Y.; Bozzetti, C.; Ho, K.-F.; Cao, J.-J.; Han, Y.; Daellenbach, K. R.; Slowik, J. G.; Platt, S. M.; Canonaco, F.; Zotter, P.; Wolf, R.; Pieber, S. M.; Brun, E. A.; Crippa, M.; Ciarelli, G.; Piazzalunga, A.; Schwikowski, M.; Abbaszade, G.; Schnelle-Kreis, J.; Zimmermann, R.; An, Z.; Szidat, S.; Baltensperger, U.; Haddad, I. E.; Prévôt, A. S. H. High secondary aerosol contribution to particulate pollution during haze events in China. *Nature* **2014**, *514* (7521), 218-222.

(7) Zhuang, H., Chan, C. K., Fang, M., and Wexler, A. S.: Size distributions of particulate sulfate, nitrate, and ammonium at a coastal site in Hong Kong, *Atmos. Environ.*, 33, 843-853, 1999a.

(8) Zhuang, H., Chan, C. K., Fang, M., and Wexler, A. S.: Formation of nitrate and non-sea-salt sulfate on coarse particles, *Atmos. Environ.*, 33, 4223-4233, 1999b.

Comment 2. Descriptions about the pH measurement

Figure S5 shows change of droplet pH during the experiment. The reviewer wonders how the measurement method of pH was validated. As described in the manuscript, pH is very important for sulfate formation. It would be beneficial to have a detailed description about pH measurement. If it were to be estimated by a thermodynamic model, it should clearly be mentioned with detailed information on how it was calculated.

Response:

Since our droplets are large, we measured their pH directly based on the method reported by Craig et al. (2018). In brief, the reacted droplets were collected on pH indicator paper, and the pH was determined by colorimetric analysis of images collected immediately after sampling. We have tested the accuracy of the such method by generating pure NH_4NO_3 droplets equilibrated at 80% RH (Figure B). The estimated pH value by direct measurement is ~4.2, which is slightly lower than the pH value (~4.4) calculated from the E-AIM model. The error is within 5%. We have added the following text in “Method and Materials” to describe it.

Revision in the manuscript (Section 2.2, Line 100 - 105):

“The reacted droplets were dissolved in ~1 mL ultrapure water, followed by ion chromatograph analysis (IC analysis) with an IonPac AS15 analytical column, an AG15 guard column, and a conductivity detector. **In addition, the droplets pH was measured by colorimetric analysis of images collected immediately after collection on pH indicator paper (Craig et al., 2018).**”

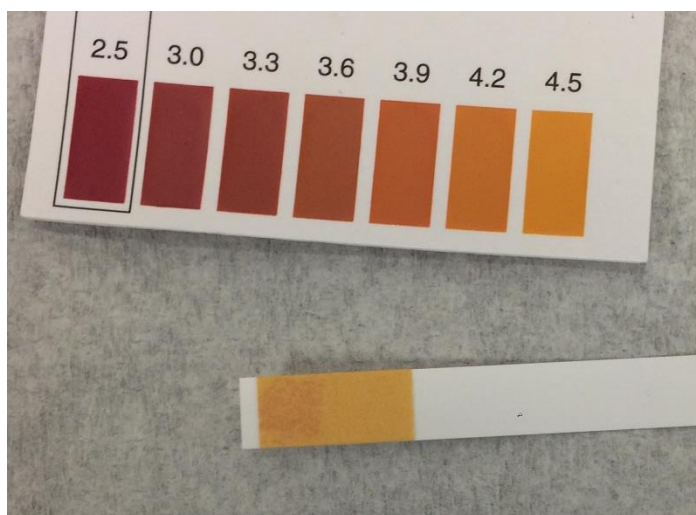


Figure B. The direct measurement of pH of pure NH_4NO_3 droplets equilibrated at 80% RH using pH indicator paper.

Reference:

1. Craig, R. L.; Peterson, P. K.; Nandy, L.; Lei, Z.; Hossain, M. A.; Camarena, S.; Dodson, R. A.; Cook, R. D.; Dutcher, C. S.; Ault, A. P. Direct determination of aerosol pH: size-resolved measurements of submicrometer and supermicrometer aqueous particles. *Anal. Chem.* **2018**, *90* (19), 11232-11239.

Minor comments

Comment 3. *Phase state of NaCl*

Some experiments were conducted at 60%RH, which is lower than the deliquescence RH for NaCl. Did droplets form supersaturated aqueous solution, or did they crystallize?

Response:

The NaCl droplets are supersaturated at 60% RH, but no crystallization was observed. As shown in Figure C, the images were taken at 0 h after equilibrium at 60% RH. We have added the following texts to address this issue.

Revision in the manuscript (Section 3.2, Line 200 - 205):

“As discussed earlier, the direct reaction of NO_2 with S(IV) under dark is not effective in producing sulfate at 80% RH in this study. Also, no sulfate was observed during the unary uptake of SO_2 into NaCl droplets under dark (Figure 2a). The same was found at 60% and 70% RH (Figure 3a). Therefore, we focused on the RH dependence of sulfate production rates in the presence of irradiation. **Note that 60% RH is below the deliquescence point of NaCl particles and the particles existed as supersaturated droplets.**”

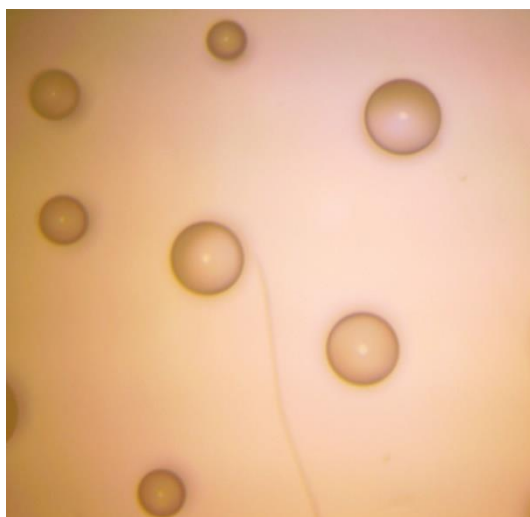


Figure C. The morphology of NaCl droplets equilibrated at 60% RH.

Comment 4. L136: 'However, our open system experiments with a continuous airflow (~ 0.5 L/min) would have removed the formed O₃ efficiently.'

Do the authors have data for O₃ concentration in the gas phase to support this statement?

Response:

Because the number of collected droplets on the hydrophobic substrate is not large enough, it is unable to measure the O₃ concentration due to the technique limitation. The flow cell was used in our experiment with a dimension of 7cm (length) × 7 cm (width) × 1.5 cm (height), hence, we believe 0.5 L/min (close to 7 space volume of the reactor/min) is high enough to remove potentially formed all gas species.