Dear Reviewer,

We appreciate your careful consideration of our manuscript. We have carefully responded to all of your point-by-point comments and issues and have revised the manuscript accordingly. These revisions are described in detail below.

Reviewer 1#

The dominant formation pathway of sulfate aerosols under haze conditions is still under debate. Liu et al. investigated the formation mechanism of particulate sulfate based on a statistical analysis of long-term observations in Shijiazhuang and Beijing supported with flow tube experiments. They found that the uptake of SO_2 is the rate-determining step of sulfate formation. Ammonium nitrate plays an important role in sulfate formation by impacting the aerosol liquid water content and the phase state of particles. Overall, the paper is well written and the findings have important implications for understanding the sulfate chemistry under haze conditions and improving the air quality in urban environments. However, I have some concerns regarding methods and data analysis that must be addressed before the paper can be considered for publication.

Response: Thank you for your positive comments.

General comments:

Uptake kinetics of SO_2: the authors stated that the RDS of sulfate formation should be the uptake of SO_2 because the dependence of sulfate formation rate on RH is opposite to the dependences of SOR and γ_{SO2} on RH. Did the uptake of SO_2 refer to the mass transfer of SO_2 to aerosol particles? If yes, the rates of mass transfer of SO_2 and aqueous oxidation of S(IV) can be calculated using a resistance model (Cheng et al. 2016). According to Cheng et al. (2016), the mass transfer of SO_2 is not the rate-determining step.

Response: Thank you for your good comments and suggestion. Yes, the uptake of SO_2 refers to the mass transfer of SO_2 to aerosol particles. Fig. R1 shows the probability weighted production rate of sulfate through mass transfer (uptake) and aqueous phase oxidation of SO_2 in Shijiazhuang. The mass transfer of SO_2 to aerosol particles is the

RDS, in particular, when RH is lower than 70%. We added the production rate of sulfate through mass transfer in Fig. 4 in the revised manuscript.

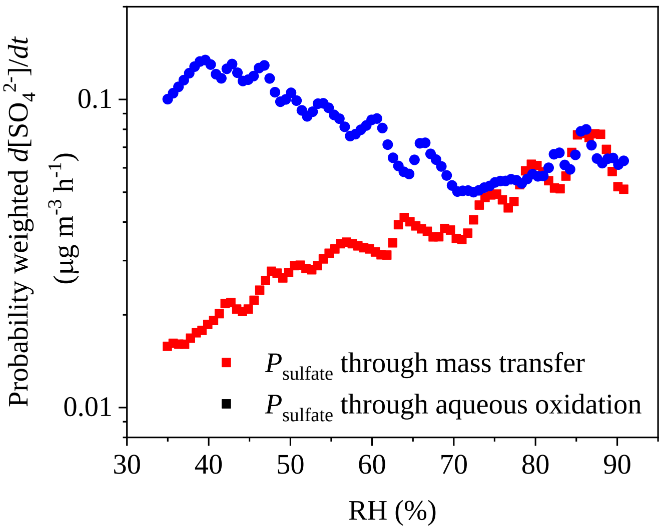

Fig. R1. Dependence of the probability weighted production rate of sulfate through mass transfer and aqueous oxidation of S(IV) in Shijiazhuang.

Using a resistance model, Cheng et al (2016) proposed out that the mass transfer of SO_2 is not the RDS. It should be noted that a large mass accommodation coefficient of SO_2 ($\alpha = 0.11$) was used in their calculations (Cheng et al., 2016). According to the relationship between the mass accommodation coefficient (α) and the uptake coefficient (γ) of SO_2 (Kulmala and Wagner, 2001), the α_{SO2} on particles is on the same order of the γ_{SO2} (Fig. R2). This means that the mass accommodation of SO_2 on particles should be much lower than the value used by Cheng et al (2016) according to the measured uptake coefficient of SO_2 in this work. Therefore, the mass transfer rate coefficient (k_{MT}) is much lower than their value. We added a paragraph "We further calculated the production rate of sulfate through uptake of SO_2 (mass transfer to aerosol particles) according to,

$$\frac{d[SO_4^{2-}]}{dt} = 3600 \cdot \frac{96}{64} \cdot \frac{\gamma_{SO_2} A_s \omega c_{SO_2}}{4} \qquad (8)$$

where, A_s is the surface area concentration of $PM_{2.5}$, ω is the mean molecular velocity of SO_2 and c_{SO2} is the mass concentration of SO_2. As shown in Fig. 4C, the probability weighted production rate of sulfate through uptake of SO_2 (the grey line) is lower than that through aqueous oxidation of S(IV), in particular, when RH is lower than 70%. It should be noted the mass transfer of SO_2 was not thought as the RDS using a large mass accommodation coefficient of SO_2 ($\alpha = 0.11$) (Cheng et al., 2016). According to the relationship between the mass accommodation coefficient (α) and the uptake coefficient (γ) of SO_2 (Kulmala and Wagner, 2001), the α_{SO2} on particles is on the same order of the γ_{SO2}. This means that mass transfer rate might be greatly overestimated by Cheng et al. (2016)" in lines 432-444 in the revised manuscript.

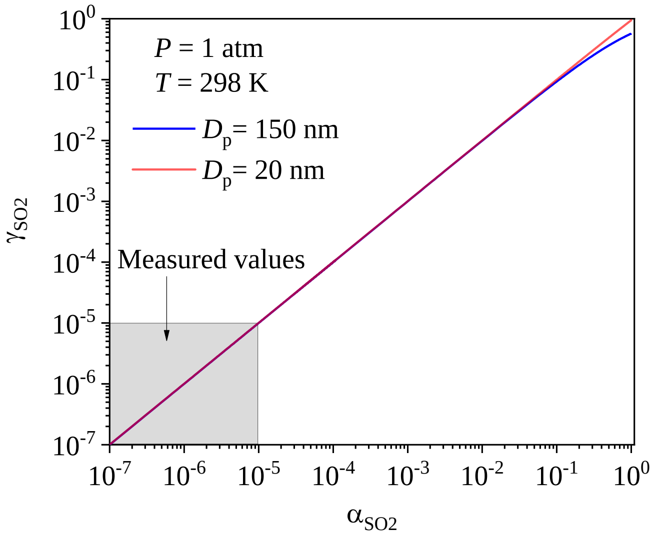

Fig. R2. The relationship between the mass accommodation coefficient (α) and the uptake coefficient (γ) of SO_2 for 20 nm and 150 nm particles at 1 atm and 298 K.

Flow tube experiments: (1) The wall loss of SO_2 on the inner surface of the outside tube and the outside surface of the sample holder was subtracted. However, the wall loss of SO_2 in the presence of NH_3 and/or NO_2 would be larger even in the absence of seed aerosols (Ge et al., 2019), which may lead to an overestimation of γ_{SO2} in the presence of NH_3 and/or NO_2. Did the authors measure the γ_{SO2} in the presence of NH_3 and/or NO_2 without the presence of seed aerosols?

Response: Thank you. We agree with you that the wall loss of SO_2 in the presence of NH_3 and/or NO_2 would be larger in the absence of seed aerosols. The γ_{SO2} was 2×10^{-7} in the presence of NH_3 and NO_2 and in the absence of seed particles. This value is significantly lower than that in the presence of particles ($\sim1\times10^{-5}$). On the other hand, the c_0 and c of SO_2 are required when we calculating the uptake coefficient. Figure R3A shows the configuration of the flow tube reactor for measuring the c_0, and Figure R3B shows that for measuring the c. Because all the inner surface of the sample tube is covered by particles, the contribution of the wall loss of SO_2 to the drop of the c is limited (less than 3%). We added a short paragraph "It should be noted that the wall loss of SO_2 in the presence of NH_3 and/or NO_2 would be larger in the absence of seed aerosols. Additional control experiments in the presence of NO_2 and NH_3 demonstrate that the contribution of wall loss of SO_2 should be less than 3 % to the measured γ" in lines 211-214 in the revised manuscript.

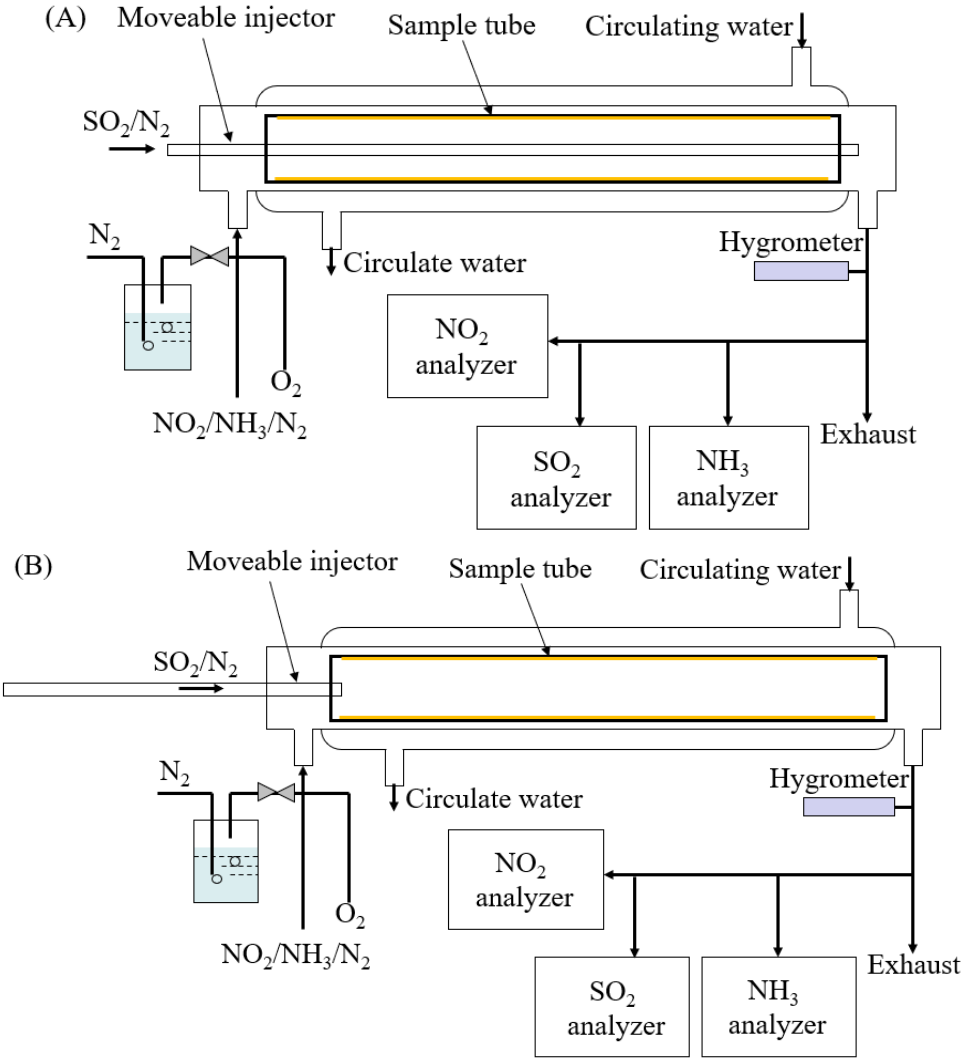

Fig. R3. The configuration of the flow tube for measuring the c_0 and c of SO_2.

(2) Can 100 ppb of NO_2 oxidize 190 ppb of SO_2 at a detectable rate in around 1 min?

The comparable γ_{SO2} in the absence and presence of NO_2 may not demonstrate that NO_2 is not an important oxidant of SO_2 if the enhanced uptake of SO_2 in the presence of NO_2 is too low under the experimental conditions of the paper.

Response: Thank you so much for your good comment. The γ_{SO2} at 80% RH was $1.7\pm0.3\times10^{-6}$ on the mixture of dust and NH_4NO_3 in the absence of NH_3 and NO_2 (Fig. R4 and Fig. 3). It increased to $3.7\pm0.2\times10^{-6}$ in the presence of NO_2 at the same RH. This means that NO_2 can promote SO_2 uptake at high RH in the absence of NH_3. Thus, the short reaction time should not be a problem. However, in the presence of NH_3, the γ_{SO2} showed no difference between with and without NO_2. This means that the promotion effect of NO_2 on SO_2 uptake might be too low to be detected in the presence of NH_3. Because NH_3 is abundant in North China, we think the promotion effect of NO_2 alone to SO_2 uptake should be limited in the atmosphere. In the revised manuscript, we added a paragraph "It should be pointed out that the γ_{SO2} at 80% RH was $1.7\pm0.3\times10^{-6}$ on the mixture of dust and NH_4NO_3 in the absence of NH_3 and NO_2 (Fig. 3). It increased to $3.7\pm0.2\times10^{-6}$ in the presence of NO_2. This is consistent with the promotion effect of NO_2 for converting SO_2 to sulfate in the absence of NH_3 as observed in both a smog chamber (Wang et al., 2016) and a bubbling reactor (Chen et al., 2019d). However, the enhanced uptake of SO_2 induced by NO_2 might be too low to be measured in the presence of NH_3. Therefore, the weak promotion effect by NO_2 alone cannot explain the negative correlation between the SOR and the concentration of NO_2 in Fig. 6F" in lines 607-615 in the revised manuscript.

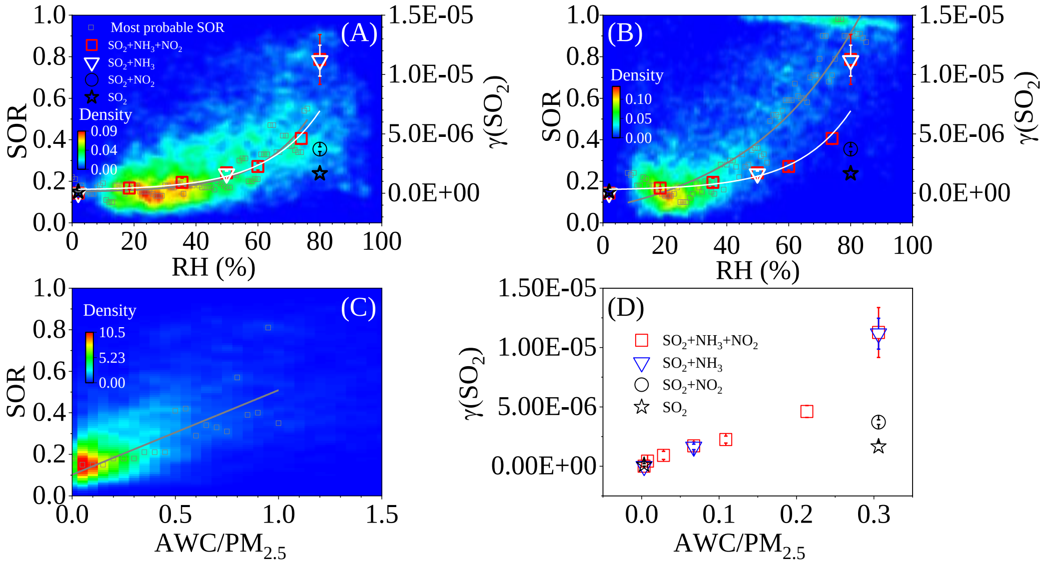

Fig. R4. Relationship between SOR and $\gamma_{SO2,BET}$ on dust internally mixed with NH_4NO_3 (2:1) and RH in (A) Shijiazhuang and (B) Beijing, and the correlation of (C) SOR in Shijiazhuang and (D) $\gamma_{SO2,BET}$ with AWC/$PM_{2.5}$. The initial concentrations of SO_2, NO_2 and/or NH_3 in the flow tube reactor were 190 ± 2.5, 100 ± 2.5 and/or 50 ± 2.5 ppb, respectively. The grey lines are the fitting curves for the most probable SOR and the white lines are the fitting curves for the $\gamma_{SO2,BET}$.

Specific comments:

Lines 191-192: Did the control experiments run in the presence of NH_3 and NO_2?

Response: Thank you. Yes, it has been done. We added a short paragraph "It should be noted that the wall loss of SO_2 in the presence of NH_3 and/or NO_2 would be larger in the absence of seed aerosols. Additional control experiments in the presence of NO_2 and NH_3 demonstrate that the contribution of wall loss of SO_2 should be less than 3 % to the measured γ" in lines 211-214 in the revised manuscript.

Lines 368-372: The oxidation of SO_2 by O_2 on the aqueous microdroplets has been found to occur under acidic conditions (pH <3). What is the aerosol pH of the mixture of ammonium nitrate and dust?

Response: Thank you so much for your comment. We cannot calculate or measure the pH of the mixture of NH_4NO_3 and dust. The pH of deliquesced NH_4NO_3 is around 4.2

calculated using the ISORROPIA II model. This value is close to the literature value ($pH<3.5$) (Hung et al., 2018). We revised the paragraph "Another study also observed a quick formation of sulfate on the surface of aqueous microdroplets under acidic conditions ($pH < 3.5$) without the addition of other oxidants, which was explained by the direct interfacial electron transfer from SO_2 to O_2 on the aqueous microdroplets (Hung et al., 2018). The pH of deliquesced NH_4NO_3 is 4.2 calculated using the ISORROPIA II model" in lines 398-403 in the revised manuscript.

Fig 5C: The AWC was attributed to individual components using E-AIM model. Are the concentrations of the total AWC consistent with the ISORROPIA model? At RH of 60%-80%, only ammonium nitrate aerosols contributed to the AWC. Does this indicate that ammonium sulfate aerosols are effloresced and phase-separated with ammonium nitrate aerosols? Please explain why ammonium sulfate aerosols and ammonium nitrate aerosols are not in the same liquid phase.

Response: Thank you for your good comments. The AWC attributed to the individual salt cannot be separated from that of $PM_{2.5}$ using the ISORROPIA model. Thus, it was estimated using the reconstructed mass concentration of the salts and the growth factors. In Fig. R5 (Fig. 5C in the revised manuscript), we compared the total AWC of $PM_{2.5}$ calculated using the ISORROPIA model with the sum of the AWC attributed to the individual salt using the E-AIM model. Overall, the latter one underestimates around 13% of the AWC. This should be related to the difference in the mixing state between these two calculation methods. NH_4NO_3 dominates the AWC at RH of range 60-80%. However, we don't think this means $(NH_4)_2SO_4$ aerosols are effloresced and phase-separated with NH_4NO_3. As shown in Fig. R5, NH_4NO_3 explained ~70% of the AWC of $PM_{2.5}$. Thus, we think it is reasonable to draw a conclusion that NH_4NO_3 is the dominant contributor to AWC in the RH range of 60-80%. In the revised manuscript, we added a new paragraph "As shown in Fig. 5C, the sum of the AWC of individual salts overall underestimated around 13 % of that calculated using the ISORROPIA II model (the gray line) because the mixing state was not considered in the former method. However, we can still draw a conclusion that NH_4NO_3 and $(NH_4)_2SO_4$ are the major contributors to the AWC" in lines 511-515 in the revised manuscript.

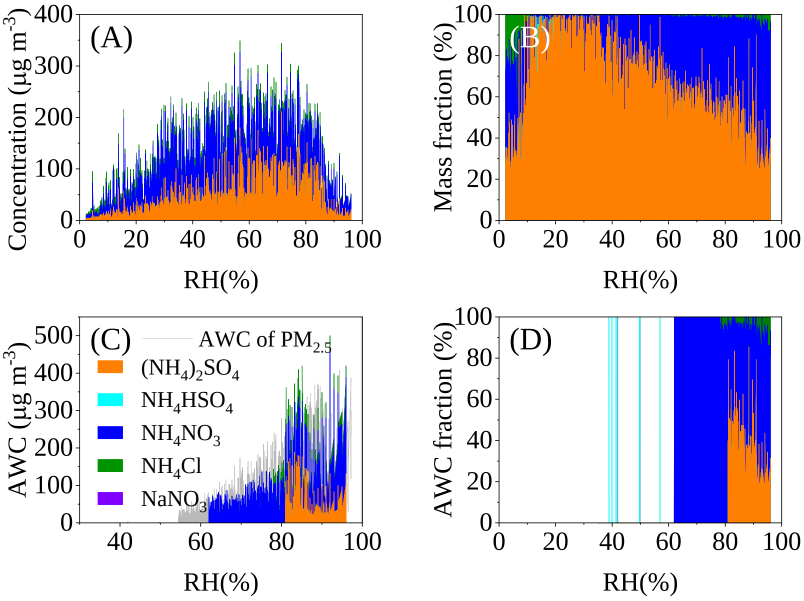

Fig. R5. Variations of (A) concentrations and (B) fractions of molecular composition of water-soluble ions, and (C) and (D) the corresponding contributions to AWC with RH in Shijiazhuang.

Lines 545-551: The authors should rule out the possibility that the enhanced uptake of SO_2 induced by NO_2 in the reaction time scale of the flow tube experiments is too low to be measured. Previous smog chamber experiments with longer reaction times have demonstrated that NO_2 can promote sulfate formation (Wang et al., 2016; Chen et al., 2019).

Response: Thank you for your suggestion. We added a paragraph as "It should be pointed out that the γ_{SO2} at 80% RH was $1.7\pm0.3\times10^{-6}$ on the mixture of dust and NH_4NO_3 in the absence of NH_3 and NO_2 (Fig. 3). It increased to $3.7\pm0.2\times10^{-6}$ in the presence of NO_2. This is consistent with the promotion effect of NO_2 for converting SO_2 to sulfate in the absence of NH_3 as observed in both a smog chamber (Wang et al., 2016) and a bubbling reactor (Chen et al., 2019d). However, the enhanced uptake of SO_2 induced by NO_2 might be too low to be measured in the presence of NH_3. Therefore, the weak promotion effect by NO_2 alone cannot explain the negative correlation between the SOR and the concentration of NO_2 in Fig. 6F" in lines 607-615 in the revised manuscript.

Technical comments:

Line 28: Write out “SOR”.

Response: Thank you. It has been defined as “sulfur oxidation ratio” in line 28 in the revised manuscript.

Fig 5: Variations of (A) concentrations…

Response: Thank you. We revised the caption as “Variations of (A) the mass concentrations and (B) the mass fractions of molecular composition in $PM_{2.5}$, (C) the estimated AWC attributed to different composition and (D) the corresponding AWC fraction as a function of RH in Shijiazhuang” in the revised manuscript.

References:

Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., Gao, M., Zhang, Q., He, K., Carmichael, G., Poschl, U., and Su, H.: Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China, Sci. Adv., 2, https://doi.org/10.1126/sciadv.1601530, 2016.

Hung, H.-M., Hsu, M.-N., and Hoffmann, M. R.: Quantification of SO_2 oxidation on interfacial surfaces of acidic micro-droplets: Implication for ambient sulfate formation, Environ. Sci. Technol., 52, https://doi.org/9079-9086, 10.1021/acs.est.8b01391, 2018.

Kulmala, M., and Wagner, P. E.: Mass accommodation and uptake coefficients — a quantitative comparison, J. Aerosol Sci., 32, 833-841, https://doi.org/10.1016/S0021-8502(00)00116-6, 2001.