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Comment on acp-2021-289

Anonymous Referee #1

Referee comment on "Ammonium nitrate promotes sulfate formation through uptake kinetic regime" by Yongchun Liu et al., Atmos. Chem. Phys. Discuss.,
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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 SO₂ 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.

General comments:

Uptake kinetics of SO₂: the authors stated that the RDS of sulfate formation should be the uptake of SO₂ because the dependence of sulfate formation rate on RH is opposite to the dependences of SOR and γ_{SO_2} on RH. Did the uptake of SO₂ refer to the mass transfer of SO₂ to aerosol particles? If yes, the rates of mass transfer of SO₂ 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 SO₂ is not the rate-determining step.

Flow tube experiments: (1) The wall loss of SO₂ on the inner surface of the outside tube and the outside surface of the sample holder was subtracted. However, the wall loss of SO₂ in the presence of NH₃ and/or NO₂ would be larger even in the absence of seed aerosols (Ge et al., 2019), which may lead to an overestimation of γ_{SO_2} in the presence of NH₃ and/or NO₂. Did the authors measure the γ_{SO_2} in the presence of NH₃ and/or NO₂ without the presence of seed aerosols?

(2) Can 100 ppb of NO_2 oxidize 190 ppb of SO_2 at a detectable rate in around 1 min? The comparable γ_{SO_2} 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.

Specific comments:

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

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

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.

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).

Technical comments:

Line 28: Write out "SOR".

Fig 5: Variations of (A) concentrations...

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