

Supplementary Material for

Fast sulfate formation from oxidation of SO₂ by NO₂ and HONO observed in

Beijing haze

Junfeng Wang^{1, 2†}, Jingyi Li^{1†}, Jianhuai Ye^{2†}, Jian Zhao³, Yangzhou Wu^{1,4}, Jianlin Hu¹, Dantong Liu⁴, Dongyang Nie^{1,10}, Fuzhen Shen¹, Xiangpeng Huang¹, Dan Dan Huang⁵, Dongsheng Ji³, Xu Sun⁷, Weiqi Xu³, Jianping Guo⁸, Shaojie Song², Yiming Qin², Pengfei Liu², Jay R. Turner⁹, Hyun Chul Lee¹¹, Sungwoo Hwang¹¹, Hong Liao¹, Scot T. Martin², Qi Zhang⁶, Mindong Chen¹, Yele Sun³, Xinlei Ge^{1*}, and Daniel J. Jacob^{2*}

¹Harvard-NUIST Joint Laboratory for Air Quality and Climate, Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, School of Environmental Science and Engineering, Nanjing University of Information Science and Technology, Nanjing 210044, China

²John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138

³State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100191, China

⁴Department of Atmospheric Sciences, School of Earth Sciences, Zhejiang University, Hangzhou 310007, China

⁵State Environmental Protection Key Laboratory of Formation and Prevention of Urban Air Pollution Complex, Shanghai Academy of Environmental Sciences, Shanghai 200233, China

⁶Department of Environmental Toxicology, University of California Davis, Davis, CA 95616, USA

⁷State Key Laboratory of Urban and Regional Ecology Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

⁸State Key Laboratory of Severe Weather, Chinese Academy of Meteorological Sciences, Beijing 100081, China

⁹Department of Energy, Environmental and Chemical Engineering, Washington University in Saint Louis, St. Louis, MO 63130, USA

¹⁰School of Atmospheric Sciences, Nanjing University, Nanjing 210023, China

¹¹Samsung Advanced Institute of Technology, Suwon-si, Gyeonggi-do, 16678, Republic of Korea

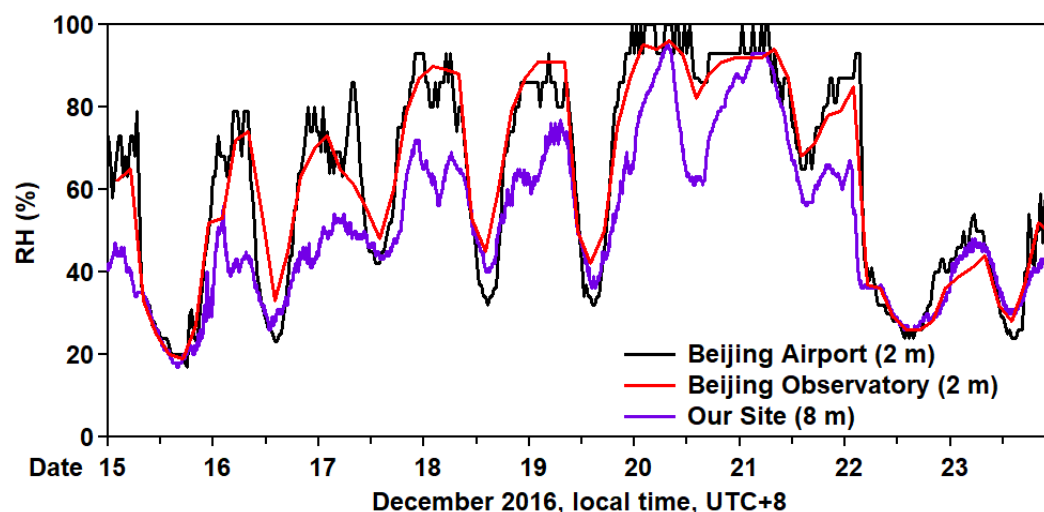
[†]These authors contributed equally to the work.

*Corresponding authors: Xinlei Ge (Email: caxinra@163.com); Daniel J. Jacob (Email: djacob@fas.harvard.edu)

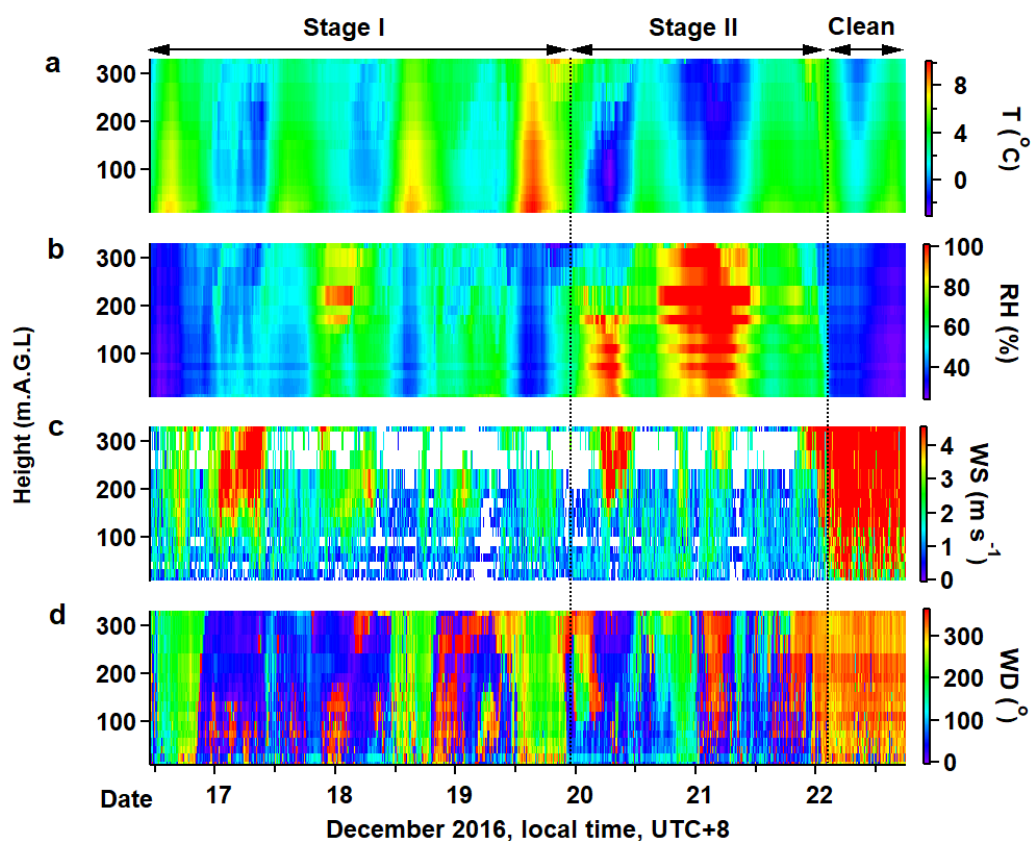
Supplementary Table 1: Henry's law and acid dissociation constants^a

Equilibrium	Equilibrium constant at 271 K
$\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$	$1.0 \times 10^{-15} \text{ M}$
$\text{CO}_2(\text{g}) + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 \cdot \text{H}_2\text{O}$	$7.7 \times 10^{-2} \text{ M atm}^{-1}$
$\text{CO}_2 \cdot \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HCO}_3^-$	$5.9 \times 10^{-7} \text{ M}$
$\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$	$8.5 \times 10^{-11} \text{ M}$
$\text{SO}_2(\text{g}) + \text{H}_2\text{O} \leftrightarrow \text{SO}_2 \cdot \text{H}_2\text{O}$	3.3 M atm^{-1}
$\text{SO}_2 \cdot \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HSO}_3^-$	$2.5 \times 10^{-2} \text{ M}$
$\text{HSO}_3^- \leftrightarrow \text{H}^+ + \text{SO}_3^{2-}$	$1.1 \times 10^{-7} \text{ M}$
$\text{NH}_3(\text{g}) + \text{H}_2\text{O} \leftrightarrow \text{NH}_3 \cdot \text{H}_2\text{O}$	$2.5 \times 10^2 \text{ M atm}^{-1}$
$\text{NH}_3 \cdot \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^-$	$4.0 \times 10^{-5} \text{ M}$
$\text{NO}_2(\text{g}) + \text{H}_2\text{O} \leftrightarrow \text{NO}_2 \cdot \text{H}_2\text{O}$	$2.3 \times 10^{-2} \text{ M atm}^{-1}$
$\text{HONO}(\text{g}) \leftrightarrow \text{HONO} \cdot \text{H}_2\text{O}$	$2.4 \times 10^2 \text{ M atm}^{-1}$
$\text{HONO} \cdot \text{H}_2\text{O} \leftrightarrow \text{NO}_2^- + \text{H}^+$	$3.4 \times 10^{-4} \text{ M}$

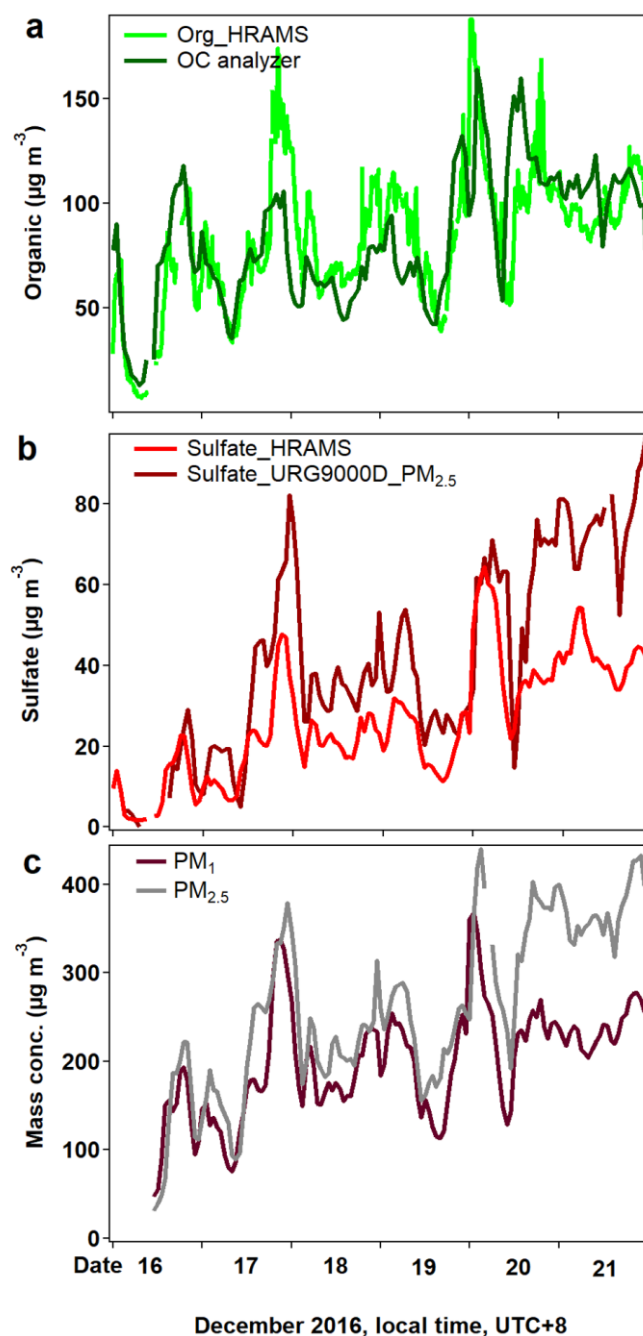
^a Equilibrium constants as given by Seinfeld and Pandis¹ and adjusted to 271 K using the van't Hoff equation.



Supplementary Figure 1: Relative humidity during the haze event. Observed relative humidity (RH) at Beijing International Airport, Beijing Observatory Meteorological Station, and our sampling site during the December 16-22, 2016 haze event. UTC+8 refers to Coordinated Universal Time + 8 hours and indicates the local solar time in hours.



Supplementary Figure 2: Meteorological profiles above the sampling site. Vertical profiles above ground level (AGL) of (a) temperature (T), (b) relative humidity (RH), (c) wind speed (WS) and (d) wind direction (WD) measured at the IAP 325-m meteorological tower during the December 16-22, 2016 haze event.



Supplementary Figure 3: Differences between PM₁ and PM_{2.5}. The plots compare PM₁ and PM_{2.5} (a) organic, (b) sulfate and (c) total mass concentrations during the December 16-22, 2016 haze event. PM₁ organic and sulfate mass concentrations were measured by HR-AMS. PM_{2.5} sulfate mass concentrations were measured with a URG-9000D Ambient Ion Monitor. PM_{2.5} organic carbon (OC) mass concentrations were measured by a thermo-optical ECOC analyzer (Sunset Laboratory Inc., Tigard, Oregon). We assumed an organic mass to organic carbon ratio of 1.9² to convert the OC measurement to total organic mass. PM₁ is the total particulate mass concentration inferred from the HR-AMS data. PM_{2.5} was measured 4 km to the northeast of the IAP site.

Supplementary References

- 1 Seinfeld, J. & Pandis, S. in *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, 3rd Edition* Ch. 26, 1152 (2016).
- 2 Turpin, B. J. & Lim, H.-J. Species Contributions to PM_{2.5} Mass Concentrations: Revisiting Common Assumptions for Estimating Organic Mass. *Aerosol Sci Tech* **35**, 602-610, doi:10.1080/02786820119445 (2001).