

Unprecedented Ambient Sulfur Trioxide (SO₃) Detection: Possible Formation Mechanism and Atmospheric Implications

Lei Yao, Xiaolong Fan, Chao Yan, Theo Kurtén, Kaspar R. Daellenbach, Chang Li, Yonghong Wang, Yishuo Guo, Lubna Dada, Matti P. Rissanen, Jing Cai, Yee Jun Tham, Qiaozhi Zha, Shaojun Zhang, Wei Du, Miao Yu, Feixue Zheng, Ying Zhou, Jenni Kontkanen, Tommy Chan, Jiali Shen, Joni T. Kujansuu, Juha Kangasluoma, Jingkun Jiang, Lin Wang, Douglas R. Worsnop, Tuukka Petäjä, Veli-Matti Kerminen, Yongchun Liu, Biwu Chu, Hong He,* Markku Kulmala,* and Federico Bianchi*



Cite This: *Environ. Sci. Technol. Lett.* 2020, 7, 809–818



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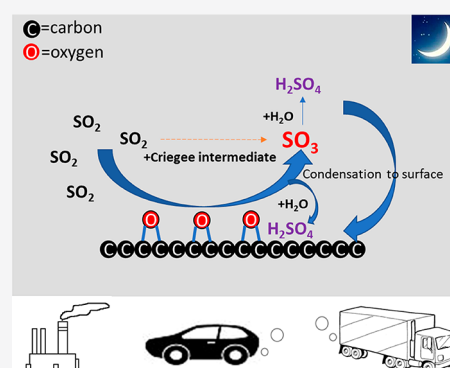


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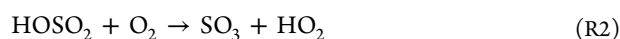
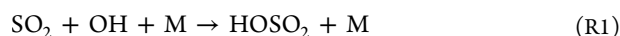
Supporting Information

ABSTRACT: Sulfur trioxide (SO₃) is a crucial compound for atmospheric sulfuric acid (H₂SO₄) formation, acid rain formation, and other atmospheric physicochemical processes. During the daytime, SO₃ is mainly produced from the photo-oxidation of SO₂ by OH radicals. However, the sources of SO₃ during the early morning and night, when OH radicals are scarce, are not fully understood. We report results from two field measurements in urban Beijing during winter and summer 2019, using a nitrate-CI-API-LTOF (chemical ionization-atmospheric pressure interface-long-time-of-flight) mass spectrometer to detect atmospheric SO₃ and H₂SO₄. Our results show the level of SO₃ was higher during the winter than during the summer, with high SO₃ levels observed especially during the early morning (~05:00 to ~08:30) and night (~18:00 to ~05:00 the next day). On the basis of analysis of SO₂, NO_x, black carbon, traffic flow, and atmospheric ions, we suggest SO₃ could be formed from the catalytic oxidation of SO₂ on the surface of traffic-related black carbon. This previously unidentified SO₃ source results in significant H₂SO₄ formation in the early morning and thus promotes sub-2.5 nm particle formation. These findings will help in understanding urban SO₃ and formulating policies to mitigate secondary particle formation in Chinese megacities.

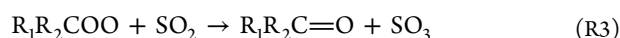


INTRODUCTION

Atmospheric SO₃ is a vital intermediate in gaseous H₂SO₄ formation, which in turn is a crucial compound in acid rain formation, new particle formation, secondary aerosol formation, and other atmospheric physicochemical processes.^{1–8} During the daytime, when the intensity of UVB (ultraviolet radiation B) radiation that leads to the formation of OH radicals is high, SO₃ is mainly formed by atmospheric photo-oxidation of SO₂ by OH radicals. The mechanism of formation of SO₃ from photo-oxidation can be written as



However, during the early morning and at night, when OH radicals are scarce, the sources of atmospheric SO₃ remain unclear. Stabilized Criegee intermediates (sCI; general formula of R₁R₂COO) generated from the ozonolysis of alkenes have been found to be an important gas-phase oxidant for SO₂ in addition to OH (eq R3):^{9,10}



Besides gas-phase oxidation of SO₂ by OH radicals and sCI, SO₃ may also be formed from the heterogeneous oxidation of SO₂ on oxygen-functionalized graphene and soot surfaces.^{11–13} He et al. have proposed that SO₂ molecules can react with surface epoxide groups of carbonaceous (or soot) aerosols, leading to SO₃ formation. These surface epoxy groups are considerably enhanced by atmospheric aging of soot particles in the presence of O₂.^{12,14} Additionally, a recent theoretical study revealed high atmospheric water content could promote the oxidation of SO₂ to SO₃ by O₂ on carbonaceous aerosol surfaces.¹⁵ Although extensive laboratory studies have reported that persistent particulate H₂SO₄ and sulfate can be formed from catalytic heterogeneous reaction between SO₂ and carbon (soot) particles in the presence of O₂, O₃, NO_x, NH₃, and water,^{16–19} the

Received: August 7, 2020

Revised: September 24, 2020

Accepted: September 25, 2020

Published: September 25, 2020



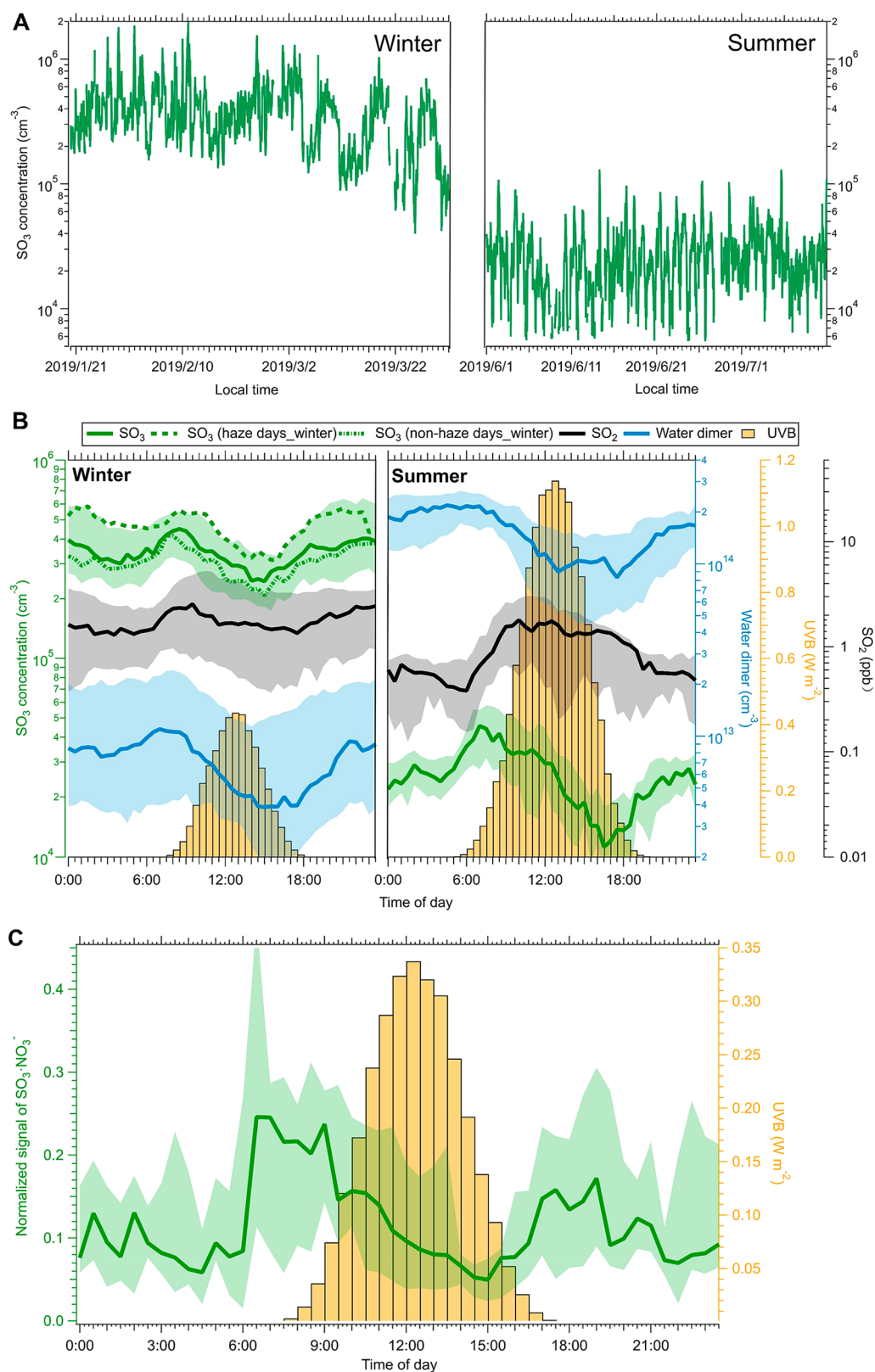


Figure 1. (A) Time series of SO_3 during the winter (January 20 to March 31, 2019) and summer (June 1 to July 10, 2019), (B) median diurnal patterns of SO_3 , UVB, and atmospheric water dimer concentrations during the winter and summer, and (C) median normalized intensities of the atmospheric ion $\text{SO}_3 \cdot \text{NO}_3^-$. Rainy and snowy days were excluded. The shadows show the values from the 25th to 75th percentile. In panel B, the dashed lines show diurnal variations of SO_3 during haze and nonhaze days. The water dimer concentration was calculated on the basis of temperature and relative humidity.^{26,39} In panel C, the signals of atmospheric ion $\text{SO}_3 \cdot \text{NO}_3^-$ were normalized by the sum of NO_3^- and $\text{HNO}_3 \cdot \text{NO}_3^-$ that are dominant natural charged ions in urban Beijing (Figure S7).

intermediate precursors of particulate sulfate, and the molecular-level details of this process, remain unclear. In addition to atmospheric formation of SO₃ via the oxidation of SO₂, a large amount of SO₃ can also be emitted to the air from coal-fired power plants and other industrial processes related to coal combustion and then be rapidly converted to H₂SO₄.^{20–22}

In the atmosphere, the water-catalyzed hydration of SO₃ plays an essential role in H₂SO₄ formation (eq R4).



In reaction R4, the second water molecule acts as a catalyst and significantly reduces the energy barrier of SO₃ hydration.^{23,24} The rate coefficient of the reaction of SO₃ with the water dimer [(H₂O)₂], or H₂O-catalyzed hydrolysis, is between 10⁻¹² and 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹, resulting in a very short lifetime (<1 s) of SO₃.^{23–26} In the atmosphere, besides water-catalyzed hydration, ammonia, sulfuric acid, formic acid, nitric acid, and oxalic acid (among others) can also act as catalysts for the SO₃ hydration process and thus facilitate H₂SO₄ formation.^{25,27–29}

The detection of SO₃ is challenging owing to its high reactivity with water in ambient air. Various measurement technologies have been utilized for SO₃ detection in flue gases, including the controlled condensation method, absorption by isopropyl alcohol, selective reaction method with calcium oxalate, and spectroscopy and mass spectrometry methods.^{22,30} The detection limits of these methods are unfortunately too high to measure trace-level SO₃ in ambient air. In some laboratory studies, the ions SiF₅⁻, SF₆⁻, NO₃⁻·HNO₃, and *n*-C₃H₇NH₃⁺ have been used as reagent ions to detect SO₃.^{31–35}

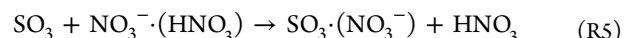
In this study, we deployed a nitrate-chemical ionization-atmospheric pressure interface-long-time-of-flight (nitrate-CI-APi-LTOF) mass spectrometer in two field measurements for atmospheric SO₃ and H₂SO₄ during the winter from January 20 to March 31 and during the summer from June 1 to July 10, 2019, in urban Beijing. This paper presents, for the first time, the trace-level measurement of gaseous SO₃ by a nitrate-CI-APi-LTOF mass spectrometer in an urban atmosphere. Additionally, atmospheric naturally charged ions were also measured from November 9 to 22, 2018. Combining the SO₃ measurements with data on trace gases, black carbon (BC), traffic flow, and atmospheric ions, we suggest a possible mechanism of formation of SO₃ in urban Beijing. We also probe the effects of SO₃ on atmospheric H₂SO₄ and sub-2.5 nm particle formation.

MATERIALS AND METHODS

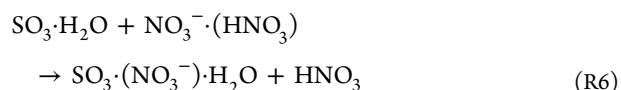
Detection of SO₃ and H₂SO₄ by a Nitrate-CI-APi-LTOF Mass Spectrometer. The working principle of the nitrate-CI-APi-LTOF mass spectrometer is described in Text S2 and many other studies.^{5,36} The high-resolution peak fit of SO₃·(NO₃⁻) and its isotope peak [³⁴SO₃·(NO₃⁻)] are depicted in Figure S1. The nitrate-CI-APi-LTOF mass spectrometer was calibrated by in situ-generated SO₃ and H₂SO₄³⁷ (Text S4). The calibration coefficients for SO₃ and H₂SO₄ are determined to be 1.7 × 10¹⁰ and 6.1 × 10⁹ cm⁻³, respectively (Figure S4). The ratio between the calibration coefficients of SO₃ and H₂SO₄ is 2.8, which is consistent with the theoretical prediction of a difference of a factor of 3 in the charging efficiency (Text S5). On the basis of repeat

experiments, the 1σ of the SO₃ calibration coefficient was ±10%.

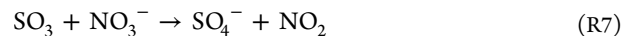
According to our quantum chemical calculation for the binding thermodynamics of SO₃·(NO₃⁻) and HNO₃·(NO₃⁻) ion–molecule clusters, the electronic binding energy of SO₃·(NO₃⁻) is -44.4 kcal/mol, which is substantially higher than that of HNO₃·(NO₃⁻) (-29.2 kcal/mol) (Texts S6 and S7 and Table S1). Thus, SO₃ molecules can be efficiently charged by nitrate ions. The highly favorable ligand exchange reaction between neutral SO₃ molecules and nitrate ions can be written as



Furthermore, on the basis of the quantum chemical calculation, reaction R6 is exothermic by 8.7 kcal/mol in free energy (Text S6). The lowest-free energy structure for SO₃·(NO₃⁻)·H₂O is depicted in Figure S6. Therefore, the hydrate complex intermediate (SO₃·H₂O) also can be detected as SO₃·(NO₃⁻).



Besides the ligand exchange reaction, the reaction between SO₃ and NO₃⁻ can also lead to SO₄⁻ formation (eq R7).³² However, SO₄⁻ can also be produced by the reaction of SO₂ with O₂⁻·(H₂O)_{*n*}.^{34,38} From our ambient data, the averaged ratios of SO₄⁻ to SO₃·(NO₃⁻) were 0.26 ± 0.07 (winter) and 2.51 ± 2.60 (summer). During the summer, a large abundance of O₂⁻·(H₂O)_{*n*} favored SO₄⁻ formation. Hence, only the signal of SO₃·(NO₃⁻) was taken into account in the SO₃ quantification, and it could cause a slight underestimation of SO₃ concentrations.



Atmospheric ions were also measured with the CI-APi-LTOF mass spectrometer by turning off the chemical ionization unit. Details of other auxiliary measuring instruments for trace gases, BC, meteorological parameters, and sub-3 nm particles can be found in Texts S8 and S9. Also, the calculation of condensation sink (CS) and quantification of SO₃ and H₂SO₄ were introduced in Texts S10 and S3.

RESULTS AND DISCUSSION

Abundance and Diurnal Behavior of SO₃ in the Winter and Summer. As shown in Figure 1A, the abundance of SO₃ was significantly higher in the winter than in the summer. During the winter, the mixing ratios of SO₃ varied from ~4.0 × 10⁴ to 1.9 × 10⁶ molecules cm⁻³. In comparison, during the summer, SO₃ concentrations ranged from ~5.0 × 10³ to 1.4 × 10⁵ molecules cm⁻³. Under 298 K and 1 atm, the atmospheric SO₃ concentration has been proposed to reach 10⁵ molecules cm⁻³ around noon.²⁵ In this study, because the influence of ambient ions (i.e., SO₃·NO₃⁻) was not excluded and the hydrate complex intermediate (SO₃·H₂O) also could be detected as SO₃·NO₃⁻ (eq R6), SO₃ concentrations could be overestimated. Median diurnal variations of SO₃ and SO₂ concentrations, water dimer concentrations [(H₂O)₂; computed from the relative humidity and temperature],^{26,39} and intensities of UVB (280–315 nm) on all measurement days during the winter and summer are illustrated in Figure 1B. The water dimer

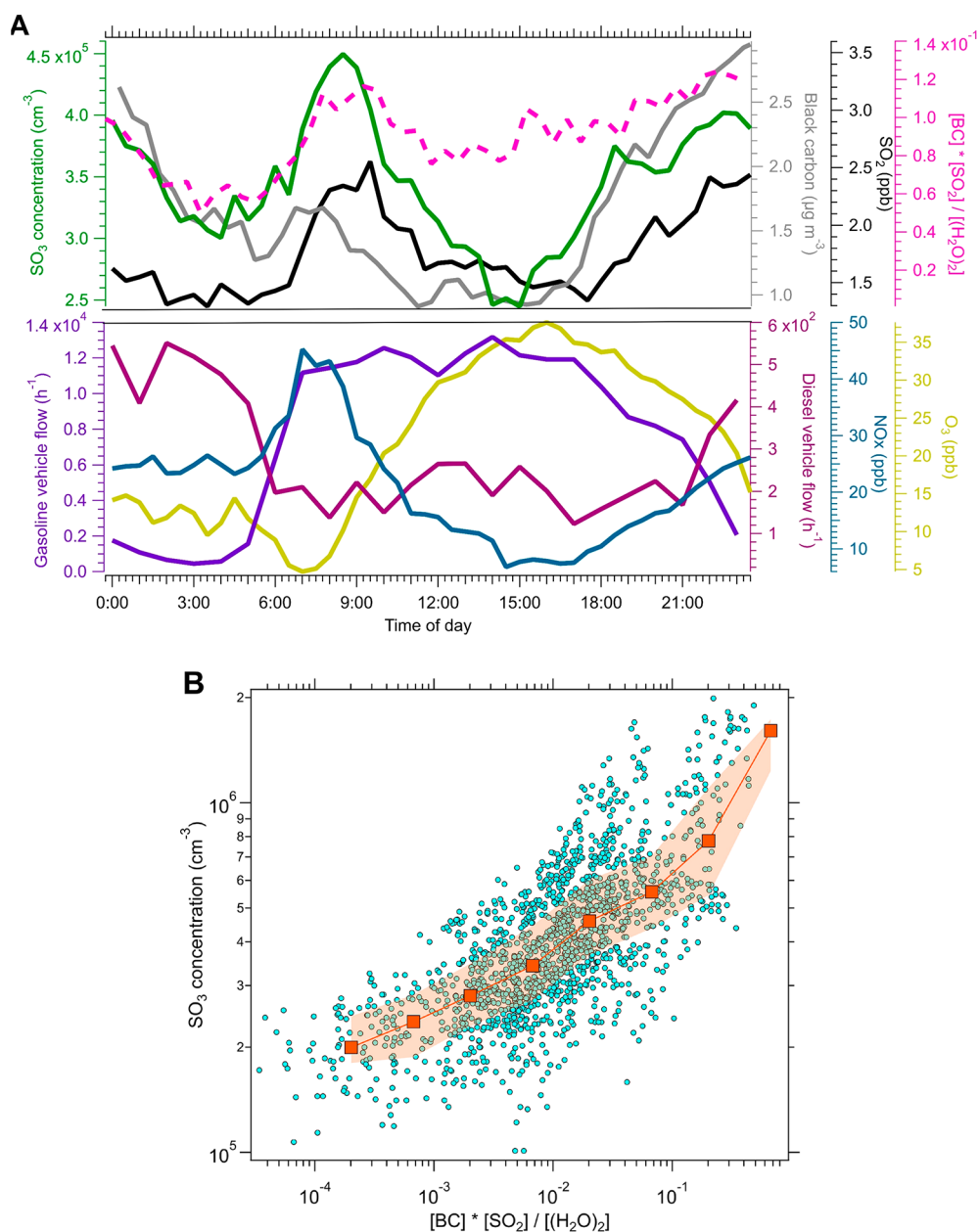


Figure 2. (A) Median diurnal variations in the concentrations of SO_3 , SO_2 , black carbon (BC), NO_x , the approximate abundance term $\{([\text{BC}][\text{SO}_2])/[(\text{H}_2\text{O})_2]\}$ of SO_3 , and gasoline and diesel vehicle flow of the “West Third Ring Road”, which was ~ 550 m to the west of the sampling station in 2017,⁴¹ and (B) correlation between the SO_3 concentration and its approximate abundance term during the night and the early morning (from 18:00 to 08:00 the next day) for the whole field measurement during the winter. In panel A, the units of BC, SO_2 , and water dimer $[(\text{H}_2\text{O})_2]$ in approximate source terms were micrograms per cubic meter, molecules per cubic meter, and molecules per cubic meter, respectively. In panel B, the SO_3 concentrations were divided into logarithmic bins, and the median values in each bin are shown as squares. The orange shadow represents the values from the 25th to 75th percentile.

concentration during the summer was notably higher than during the winter. In contrast, the mixing ratio of SO_2 during the summer was lower than that during the winter. In the atmosphere, due to the large abundance of water, it is generally accepted that hydration to H_2SO_4 is the main fate of SO_3 .²⁴ As a second water molecule is needed to lower the barrier of the SO_3 hydration reaction, the reaction rate effectively depends on the water dimer concentration.^{23,40} Therefore, the low SO_3 concentrations during the summer likely result from the large abundance of the water dimer and low SO_2 concentration.

During the winter and summer, SO_3 showed similar diurnal patterns (Figure 1B). During the winter, SO_3 levels increased from $\sim 05:00$ and reached their peak at $\sim 08:30$. The abundance of SO_3 was higher during the early morning from $\sim 06:00$ to $\sim 09:00$ and night from $\sim 18:00$ to $\sim 03:00$ (the next day) than around noon. Similarly, during the summer, SO_3 concentrations increased from $\sim 4:00$ and reached their peak values at $\sim 07:00$. A peak of SO_3 in the early morning ($\sim 04:00$ to $\sim 08:00$) was also observed. During both the winter and the summer, lower SO_3 concentrations were observed around noon when the water dimer concentration reached its minimum level (Figure 1B).

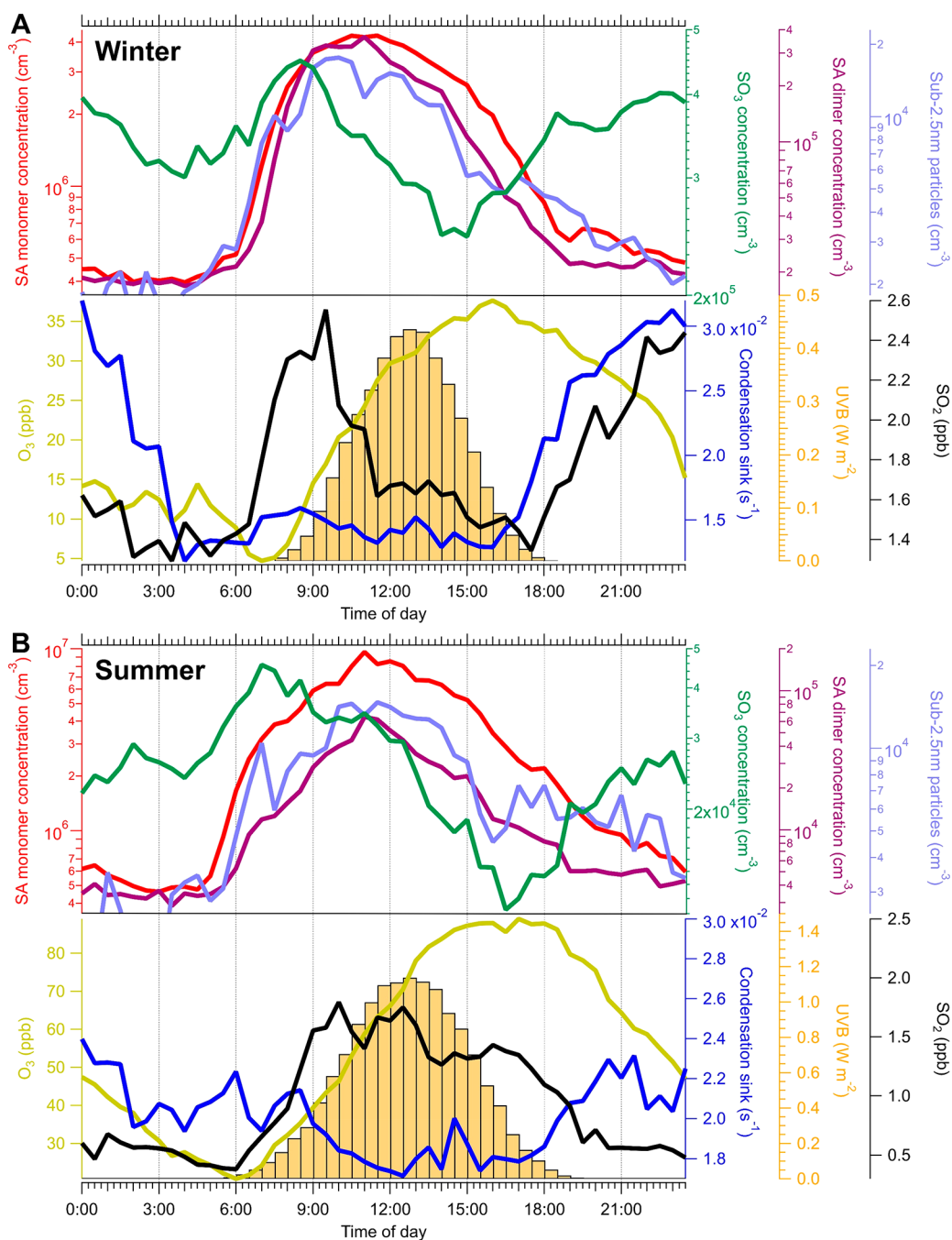


Figure 3. Median diurnal variations in the concentrations and intensities of SO₃, the sulfuric acid (SA) monomer (H₂SO₄) and dimer, sub-2.5 nm particles, SO₂, O₃, UVB, and condensation sink (CS) during the (A) winter and (B) summer.

Besides water-catalyzed hydration, around noon, a large abundance of other atmospheric components (e.g., H₂SO₄, HCOOH, HNO₃, and oxalic acid) also promoted the conversion of SO₃, leading to relatively short lifetimes. In addition, diel patterns of SO₃ on nonhaze and haze days in winter are also shown in Figure 1B. The abundance of SO₃ exhibited a similar daily pattern during both haze and nonhaze days (Text S8), though the actual values were higher on haze days.

The averaged mass spectra of atmospheric naturally charged ions for a day are shown in Figure S7. The dominant anions in urban Beijing are nitrate ions (NO₃⁻ and HNO₃·NO₃⁻), similar to the case in Shanghai.⁵ Therefore,

the normalized intensity of SO₃·NO₃⁻ by the sum of nitrate ions also can represent the abundance of SO₃ in the air. Figure 1C shows the diel variation of the normalized signals of SO₃·NO₃⁻ in November 2018. The normalized signals also exhibited two peaks, in the early morning (~6:00 to ~9:00) and at night (~17:00 to ~20:00).

Potential Source Identification for SO₃. To investigate the possible sources of SO₃ molecules during the early morning and night, we monitored other trace gases (SO₂ and NO_x), BC, and traffic flow of the main road nearby.⁴¹ During the summer, the average SO₃ concentration was 2.9×10^4 molecules cm^{-3} , which is likely close to the detection limit of the instrument. Hence, the possible source identification for

SO₃ was focused on winter data. During the winter, the median concentrations of SO₂, NO_x, and BC in PM_{2.5} exhibited diurnal trends similar to those of SO₃ (Figure 2A). On the basis of previous studies of SO₂ and together with stable weather conditions (low wind speeds and shallow mixing layer) (Text S11 and Figure S8), the elevated SO₂ concentration during the early morning could mainly be attributed to local emissions (e.g., residential and industry emission) and transportation.^{42–50} BC concentrations were tightly linked with traffic emission dominated by diesel vehicles (Figure 2A).

During the early morning, the UVB intensity was low, which meant that OH radical concentrations from photochemistry were also low, because of the linear correlation between OH concentrations and the ozone photolysis frequency [*j*(O1D)] in Beijing during daytime.⁵¹ During a summer night in the suburban area of Beijing, OH radical concentrations from ~0.5 to 3 × 10⁶ cm⁻³ still can be observed.^{52,53} Nevertheless, during the winter in suburban Beijing, the mean observed OH concentrations were <3 × 10⁵ cm⁻³ at night and <1 × 10⁶ cm⁻³ in the early morning (06:00–09:00).^{54,55} Hence, the oxidation of SO₂ by OH radicals was not the main source for SO₃ during the early morning and night. In addition, during the early morning, the median ozone concentration was only ~5 ppb, which was low in comparison to the values during the rest of the day, resulting in a minor contribution to SO₃ production from the reaction between sCI and SO₂. Although SO₃ molecules can also be co-emitted with SO₂,^{20–22,56,57} transportation is not feasible for SO₃ owing to its short lifetime (<1s) in the air. Previous studies based on quantum chemical calculations have suggested that the heterogeneous reaction between SO₂ and soot can lead to SO₃ formation.^{11,12} If this mechanism were to dominate SO₃ formation, and further assuming that the SO₃ is removed by reaction with the water dimer, the concentration of SO₃ would be proportional to ([BC]·[SO₂])/[(H₂O)₂]. Figure 2A shows that during the early morning (06:00–09:00) and night (from 18:00 to 6:00 the next day), the median diurnal variations of SO₃ and ([BC][SO₂])/[(H₂O)₂] were consistent with each other. Also, for the whole measurement period during the winter from 18:00 to 08:00 the next day, the correlation between SO₃ and this approximate abundance term was positive [*r* = 0.7; *P* < 0.0001 (Figure 2B)]. Furthermore, on nonhaze days, SO₃ was tightly linked to particulate sulfate, implying SO₃ may originate from heterogeneous reaction (Figure S9). Therefore, our results together suggested the heterogeneous reaction between SO₂ and BC could be the possible source of SO₃ during the early morning and at night. However, other formation mechanisms (e.g., Criegee intermediate and SO₂) may also contribute.⁹

Enhancement of Sulfuric Acid and Sub-2.5 nm Particle Formation. Median diurnal variations of the concentrations or intensities of H₂SO₄, the sulfuric acid dimer (H₂SO₄·HSO₄⁻), SO₃, sub-2.5 nm particles, CS, SO₂, ozone, and UVB during the winter and summer are shown in panels A and B of Figure 3A and B, respectively. During the winter and summer, elevated levels of SO₃ and H₂SO₄ were simultaneously observed in the early morning. During the winter, the median concentrations of H₂SO₄ during the early morning were comparable with that around noon. In addition, it showed a good correlation (*r* = 0.7) between atmospheric ions of HSO₄⁻ and SO₃·NO₃⁻ during the early

morning (5:00–8:00) and night (from 18:00 to 5:00 the following day) (Figure S10). Thus, the SO₃ formed from nonphotochemical processes enhanced H₂SO₄ formation during the early morning and night. In a recent study in urban Beijing, under clean conditions, oxidation of SO₂ by oxidants produced in the ozonolysis of alkenes (i.e., sCI and “dark” OH) was suggested as a source of H₂SO₄ during the night.⁵⁸ This study also pointed out that, under polluted conditions, additional sources of H₂SO₄ exist. Hence, during the night in urban Beijing, H₂SO₄ can be enhanced both by SO₃ molecules produced by the heterogeneous reaction between BC and SO₂ and by the oxidation of SO₂ by oxidants from ozonolysis of alkenes.

As shown in Figure 3, during the winter or summer, the median concentrations of H₂SO₄, H₂SO₄·HSO₄⁻, and sub-2.5 nm particles followed the same diurnal behavior. The concentrations of H₂SO₄·HSO₄⁻ and sub-2.5 nm particles started to increase at ~5:00. During the early morning during the winter, the median concentrations of H₂SO₄·HSO₄⁻ and sub-2.5 nm particles were comparable with that around noon. On the basis of the studies in urban Shanghai, if atmospheric bases were abundant, the sulfuric acid dimer could be treated as an indicator of nanocluster formation.^{5,59} In urban Beijing, the concentrations of atmospheric bases (e.g., amines and ammonia) may also be sufficient for efficient clustering. Thus, the increased level of formation of SO₃, possibly produced by the oxidation of SO₂ on top of soot particles, can intensify the production of secondary particles and enhance gas to particle conversion during the early morning and night. We note that the contribution to nanoclusters of traffic, or the reaction of SO₃ with ammonia/methanol, cannot be wholly excluded.^{25,60–62} Our results together point toward the need to control the emission of SO₂ and soot to mitigate secondary aerosol formation in urban Beijing.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.estlett.0c00615>.

Description of the sampling site (Text S1), the nitrate-CI-API-LTOF mass spectrometer (Text S2), detection of sulfuric acid with nitrate reagent ions (Text S3), detailed calibration experiment for SO₃ (Text S4), quantum chemical calculations (Text S6), computational details (Text S7), PM_{2.5}, black carbon, particulate sulfate, trace gases, meteorological parameters, and UVB measurements (Text S8), sub-3 nm particle measurements (Text S9), calculation of condensation sink (Text S10), source identification of SO₂ during the winter (Text S11), high-resolution peak fitting of the ³²SO₃·NO₃⁻ peak and its ³⁴SO₃·NO₃⁻ main isotope peak (Figure S1), schematic of the calibration experiment setup (Figure S2), time series of normalized signals of H₂SO₄ and SO₃, and [H₂O] in the calibration experiment (Figure S3), correlation between normalized SO₃ signals measured by the CI-API-LTOF mass spectrometer and SO₃ concentrations formed by photo-oxidation of SO₂ by OH radicals (Figure S4), optimized structure of the SO₃·(NO₃⁻) cluster (Figure S5), lowest-free energy (at 298 K) structure found for SO₃·(NO₃⁻)·H₂O (Figure S6), averaged mass spectra of atmospheric naturally charged ions for one whole

day (November 10, 2018) (Figure S7), median diurnal variation of the concentrations of SO_3 and SO_2 , the mixing layer heights (MLH), intensities of UVB, and wind speeds during the winter (Figure S8), time profile of the SO_3 concentration and mass concentration of sulfate in $\text{PM}_{2.5}$ and median diel variation of SO_3 and sulfate for all nonhaze days during the winter measurement period (Figure S9), relationship between the atmospheric ion signals of HSO_4^- and $\text{SO}_3 \cdot \text{NO}_3^-$ during the night (from 18:00 to 5:00 next day) and early morning (5:00–8:00) from November 9 to 22, 2018 (Figure S10), and comparison of the binding thermodynamics of $\text{HNO}_3 \cdot (\text{NO}_3^-)$ and $\text{SO}_3 \cdot (\text{NO}_3^-)$ ion–molecule clusters (Table S1) (PDF)

AUTHOR INFORMATION

Corresponding Authors

Federico Bianchi – Aerosol and Haze Laboratory, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100089, China; Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, Helsinki 00560, Finland; orcid.org/0000-0003-2996-3604; Email: federico.bianchi@helsinki.fi

Markku Kulmala – Aerosol and Haze Laboratory, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100089, China; Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, Helsinki 00560, Finland; Joint International Research Laboratory of Atmospheric and Earth System Sciences (JrLATEST), Nanjing University, Nanjing 210023, China; Email: markku.kulmala@helsinki.fi

Hong He – State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences and Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Beijing 100085, China; Email: honghe@cees.ac.cn

Authors

Lei Yao – Aerosol and Haze Laboratory, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100089, China; Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, Helsinki 00560, Finland; orcid.org/0000-0002-2680-1629

Xiaolong Fan – Aerosol and Haze Laboratory, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100089, China

Chao Yan – Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, Helsinki 00560, Finland

Theo Kurtén – Department of Chemistry, University of Helsinki, Helsinki 00014, Finland; orcid.org/0000-0002-6416-4931

Kaspar R. Daellenbach – Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, Helsinki 00560, Finland

Chang Li – Aerosol and Haze Laboratory, Beijing Advanced Innovation Center for Soft Matter Science and Engineering,

Beijing University of Chemical Technology, Beijing 100089, China

Yonghong Wang – Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, Helsinki 00560, Finland

Yishuo Guo – Aerosol and Haze Laboratory, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100089, China

Lubna Dada – Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, Helsinki 00560, Finland

Matti P. Rissanen – Aerosol Physics Laboratory, Physics Unit, Tampere University, Tampere 33100, Finland; orcid.org/0000-0003-0463-8098

Jing Cai – Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, Helsinki 00560, Finland

Yee Jun Tham – Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, Helsinki 00560, Finland

Qiaozhi Zha – Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, Helsinki 00560, Finland

Shaojun Zhang – State Key Joint Laboratory of Environment Simulation and Pollution Control, State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex, School of Environment, Tsinghua University, Beijing 100084, China; orcid.org/0000-0002-2176-6174

Wei Du – Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, Helsinki 00560, Finland

Miao Yu – Institute of Urban Meteorology, China Meteorological Administration, Beijing 100081, China

Feixue Zheng – Aerosol and Haze Laboratory, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100089, China

Ying Zhou – Aerosol and Haze Laboratory, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100089, China

Jenni Kontkanen – Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, Helsinki 00560, Finland

Tommy Chan – Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, Helsinki 00560, Finland

Jiali Shen – Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, Helsinki 00560, Finland

Joni T. Kujansuu – Aerosol and Haze Laboratory, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100089, China; Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, Helsinki 00560, Finland

Juha Kangasluoma – Aerosol and Haze Laboratory, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100089, China; Institute for Atmospheric and Earth System

Research/Physics, Faculty of Science, University of Helsinki, Helsinki 00560, Finland; orcid.org/0000-0002-1639-1187

Jingkun Jiang – State Key Joint Laboratory of Environment Simulation and Pollution Control, State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex, School of Environment, Tsinghua University, Beijing 100084, China

Lin Wang – Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP3), Department of Environmental Science & Engineering, Fudan University, Shanghai 200438, China; orcid.org/0000-0002-4905-3432

Douglas R. Worsnop – Aerodyne Research Inc., Billerica, Massachusetts 01821, United States

Tuukka Petäjä – Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, Helsinki 00560, Finland

Veli-Matti Kerminen – Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, Helsinki 00560, Finland

Yongchun Liu – Aerosol and Haze Laboratory, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100089, China; orcid.org/0000-0002-9055-970X

Biwu Chu – Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, Helsinki 00560, Finland; State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences and Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Beijing 100085, China; orcid.org/0000-0002-7548-5669

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.estlett.0c00615>

Author Contributions

L.Y. and X.F. contributed equally to this work. L.Y. and F.B. designed the research and analyzed the data. L.Y., C.Y., Y.G., C.L., X.F., Y.Z., K.R.D., F.Z., Y.W., and T.C. performed the measurements for this study. T.K. provided quantum calculation results. L.Y., X.F., B.C., F.B., T.P., M.P.R., L.W., Y.L., J.J., D.R.W., V.-M.K., T.K., and M.K. interpreted the results and revised the manuscript. M.K., F.B., and H.H. supported and supervised this research. L.Y. wrote the manuscript with contributions from all co-authors.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The work is supported by Academy of Finland (Center of Excellence in Atmospheric Sciences, project no. 307331, and PROF13 funding, 311932), the European Research Council via ATM-GTP (742206) and via CHAPAs (850614) and the EMME-CARE project which has received funding from the European Union's Horizon 2020 Research and Innovation Programme, under Grant Agreement No. 856612.

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