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Haichao Wang

The Chemistry of Nitrate Radical (NO_3) and Dinitrogen Pentoxide (N_2O_5) in Beijing

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The Chemistry of Nitrate Radical (NO_3) and Dinitrogen Pentoxide (N_2O_5) in Beijing

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Author
Dr. Haichao Wang
State Key Joint Laboratory of Environmental Simulation and Pollution Control
College of Environmental Sciences and Engineering
Peking University
Beijing, China

Supervisor
Prof. Keding Lu
State Key Joint Laboratory of Environmental Simulation and Pollution Control
College of Environmental Sciences and Engineering
Peking University
Beijing, China

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Supervisor's Foreword

Nitrate radical (NO_3) and dinitrogen pentoxide (N_2O_5) play a pivotal role in the nocturnal atmosphere. The reaction of NO_3 with VOCs and N_2O_5 heterogeneous uptake broadly impacts the fate of NO_x and VOCs in both the regional and global scales. Over the past decades, many studies are conducted to improve our knowledge of nighttime chemistry. However, there are still many issues that remain poorly understood, especially their atmospheric processes and impacts in China. In this study, Dr. Haichao Wang sets up the first field-deployable instruments in China for the measurement of both NO_3 and N_2O_5 based on cavity-enhanced absorption spectroscopy (CEAS). The main improvements compared to the few available CEAS instruments worldwide include a mechanically aligned non-adjustable optical mounting module and a chemical titration module for determining the zero point. The new improvements also allow the new instruments to be portable, stable, and easy to operate in the field campaigns. Up to now (also after the thesis), the developed instruments have been successfully applied in about ten field campaigns, which provided key supports for the exploration of the nighttime chemistry. Besides, benefit the elucidation of the particulate nitrate formation mechanism in the major cities in China. During the thesis period, four field campaigns were conducted in Beijing with the measurement of N_2O_5 and related parameters. These data covered different seasons and a large variety of ambient conditions. Based on the obtained comprehensive dataset, the features of the ambient behaviors and the budgets of both the NO_3 and N_2O_5 in Beijing were well systematically explored and quantified. Moreover, the N_2O_5 heterogeneous uptake coefficient was determined, the relationship of N_2O_5 uptake coefficient and the particle composition and properties were elaborated, and a new parameterized equation for the N_2O_5 uptake coefficient is proposed. The impacts of NO_3–N_2O_5 chemistry on the atmospheric oxidation and the contribution to particulate nitrate formation were systematically studied and elucidated. These results significantly improved the understanding of the nighttime chemistry in the troposphere and will enlighten the thinking about the role of NO_3–N_2O_5 chemistry in other polluted regions like Beijing. The academic impact of his thesis is very good both in China and the international community. I received excellent explicit comments from Prof. Steven Brown (NOAA) and Prof. Andreas

Wahner (director of IEK-8, FZJ) to his contribution to the nighttime chemistry. The scientists from the Municipality of Milan also contacted me intensively even during the COVID-19 period to ask for help about the particulate nitrate control due to his publications, which I am the corresponding author.

Beijing, China
December 2018

Prof. Keding Lu

Abstract

Nitrate radical (NO_3) and dinitrogen pentoxide (N_2O_5) chemistry are important in the troposphere at night. The quantitative description of them is of great significance for the study of regional air quality and global climate change. This study focuses on NO_3 and N_2O_5 chemistry in Beijing, China. The NO_3 and N_2O_5 field measurement systems are developed based on the cavity-enhanced absorption spectroscopy (CEAS). The detection limits of NO_3 and N_2O_5 are 2.4 pptv and 2.7 pptv for 1 s temporal resolution. The uncertainty of NO_3 and N_2O_5 is 19% and 22–36%, respectively. Compared with other similar measuring systems in the world, there are two significant improvements. (1) The use of high-precision mechanically coupled mirror holders significantly improves the stability of the measurement system and the applicability of the field measurement. (2) The using of chemical titration modules to avoid nonlinear absorption of water vapor interference. The instrument was successfully applied in four comprehensive field campaigns in urban and suburban areas of Beijing, including the Huairou (HR) winter campaign (suburbs), Changping (CP) summer campaign (suburbs), Peking University (PKU) summer campaign (urban), and Peking University winter campaign (urban). High-quality N_2O_5 time series were acquired under four typical environmental conditions. The critical processes in NO_3 and N_2O_5 chemistry were systematically analyzed. The main findings were as follows:

1. The observation shows that the mixing ratio of N_2O_5 is significant in Beijing; the nocturnal maximum over one ppbv was observed frequently; the suburbs are significantly higher than urban areas. Based on the N_2O_5 measurements, the nighttime NO_3 concentration was derived from the thermodynamic equilibrium. The average was between 0.1 and 10 pptv, which was significantly higher in summer than in winter. The average NO_3 production rate (1–2 ppbv h^{-1}) was much higher in summer than in winter (0.1–0.2 ppbv h^{-1}). The difference between urban and suburban areas is mainly affected by the difference in NO_x concentration, and seasonal differences are mainly affected by temperature and ozone concentration.

2. The average NO_3 reactivity (k_{NO3}) for volatile organic compounds (VOCs) in PKU winter, HR winter, and CP summer is 6.6×10^{-3} s^{-1}, 3.7×10^{-3} s^{-1}, and 1.9×10^{-2} s^{-1}, respectively. Biogenic VOCs (monoterpenes) dominated k_{NO3} in CP summer, while anthropogenic VOCs dominated k_{NO3} in winter. The contribution of NO_3 to summer oxidation is significant, especially for BVOCs oxidation. NO_3 dominated more than 90% nocturnal BVOCs degradation, but the NO_3 oxidation capacity in the wintertime is weak.
3. The determined N_2O_5 uptake coefficient, $\gamma(N_2O_5)$, is generally high, ranging from 0.012 to 0.072, with an average value of 0.04 in summer in Beijing. The $\gamma(N_2O_5)$ is generally higher than those reported in Europe and the USA, which may be related to the high water content in aerosols in Beijing. $\gamma(N_2O_5)$ was ranged from 0.001 to 0.017, with an average of 0.005 in the winter suburbs of Beijing, which was much lower than that in summer. In the winter, $\gamma(N_2O_5)$ increased with the increase of relative humidity, and the aerosol liquid water content had a promoting effect on the N_2O_5 uptake, while particulate nitrate had an inhibitory effect. Both the existing organic coating model and inorganic aerosol model are difficult to accurately simulate the $\gamma(N_2O_5)$, which may be related to the underestimation of the inhibition of organic coating.
4. Both the high N_2O_5 concentration and the high aerosol surface area coexist in the $PM_{2.5}$ pollution episode in summer. The higher N_2O_5 uptake coefficient in summer resulted in a significant contribution to particulate nitrate production, with an average daily production of up to 57 μg m^{-3}, which is equivalent to the contribution of the gas-phase oxidation process (OH + NO_2) during the day. The N_2O_5 uptake coefficient was low during the winter pollution episodes, with an average daily nitrate production of 11 μg m^{-3}. The average daily amount of gas-phase oxidation contributed up to 53 μg m^{-3}, indicating that the winter nitrate production was caused by gas-phase oxidation during the daytime. In general, the heterogeneous uptake of N_2O_5 is an essential channel for nitrate production in particulate matter in urban areas. The model simulation results show that $ClNO_2$ formed by the heterogeneous reaction of N_2O_5 during the pollution process in Huairou winter has a vital role in the following daytime chemistry, which can increase the primary source of O_3 and RO_x by 21% and 13%, and become the important daytime source of O_3 and RO_x in wintertime.

Keywords Nitrate radical · Dinitrogen pentoxide · Cavity-enhanced absorption spectroscopy · Field observation · Atmospheric oxidation · Heterogeneous hydrolysis · Particulate nitrate formation

Parts of this thesis have been published in the following journal articles:

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Wang, H. C., Chen, J., and Lu, K*. D.: Development of a portable cavity-enhanced absorption spectrometer for the measurement of ambient NO_3 and N_2O_5: experimental setup, lab characterizations, and field applications in a polluted urban environment, *Atmos Meas Tech*, 10, 1465–1479, https://doi.org/10.5194/amt-10-1465-2017, 2017. (Reproduced with Permission).

Wang, H. C., Lu, K. D. *, Guo, S., Wu, Z. J., Shang, D. J., Tan, Z. F., Wang, Y. J., Le Breton, M., Lou, S. R., Tang, M. J., Wu, Y. S., Zhu, W. F., Zheng, J., Zeng, L. M., Hallquist, M., Hu, M., and Zhang, Y. H.: Efficient N_2O_5 uptake and NO_3 oxidation in the outflow of urban Beijing, *Atmos Chem Phys*, 18, 9705–9721, https://doi.org/10.5194/acp-18-9705-2018, 2018. (Reproduced with Permission).

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