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# Haichao Wang

The Chemistry of Nitrate Radical (NO<sub>3</sub>) and Dinitrogen Pentoxide (N<sub>2</sub>O<sub>5</sub>) in Beijing



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Haichao Wang

# The Chemistry of Nitrate Radical (NO<sub>3</sub>) and Dinitrogen Pentoxide (N<sub>2</sub>O<sub>5</sub>) in Beijing

Doctoral Thesis accepted by College of Environmental Sciences and Engineering, Peking University, Beijing, China



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## **Supervisor's Foreword**

Nitrate radical (NO<sub>3</sub>) and dinitrogen pentoxide ( $N_2O_5$ ) play a pivotal role in the nocturnal atmosphere. The reaction of NO<sub>3</sub> with VOCs and N<sub>2</sub>O<sub>5</sub> heterogeneous uptake broadly impacts the fate of  $NO_{y}$  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<sub>3</sub> 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<sub>2</sub>O<sub>5</sub> 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<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> 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<sub>2</sub>O<sub>5</sub> uptake coefficient is proposed. The impacts of NO<sub>3</sub>-N<sub>2</sub>O<sub>5</sub> 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<sub>3</sub>-N<sub>2</sub>O<sub>5</sub> 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<sub>3</sub>) 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<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> chemistry in Beijing, China. The NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> 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<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> 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<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> 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<sub>3</sub> 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<sub>3</sub> production rate (1–2 ppbv h<sup>-1</sup>) was much higher in summer than in winter (0.1–0.2 ppbv h<sup>-1</sup>). The difference between urban and suburban areas is mainly affected by the difference in NO<sub>x</sub> concentration, and seasonal differences are mainly affected by temperature and ozone concentration.

- 2. The average NO<sub>3</sub> reactivity ( $k_{NO3}$ ) for volatile organic compounds (VOCs) in PKU winter, HR winter, and CP summer is  $6.6 \times 10^{-3} \text{ s}^{-1}$ ,  $3.7 \times 10^{-3} \text{ s}^{-1}$ , and  $1.9 \times 10^{-2} \text{ s}^{-1}$ , respectively. Biogenic VOCs (monoterpenes) dominated  $k_{NO3}$  in CP summer, while anthropogenic VOCs dominated  $k_{NO3}$  in winter. The contribution of NO<sub>3</sub> to summer oxidation is significant, especially for BVOCs oxidation. NO<sub>3</sub> dominated more than 90% nocturnal BVOCs degradation, but the NO<sub>3</sub> oxidation capacity in the wintertime is weak.
- 3. The determined N<sub>2</sub>O<sub>5</sub> 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<sub>2</sub>O<sub>5</sub> 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<sup>-3</sup>, which is equivalent to the contribution of the gas-phase oxidation process (OH + NO<sub>2</sub>) 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<sup>-3</sup>. The average daily amount of gas-phase oxidation contributed up to 53 µg m<sup>-3</sup>, 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<sub>2</sub> 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<sub>3</sub> and RO<sub>x</sub> by 21% and 13%, and become the important daytime source of O<sub>3</sub> and RO<sub>x</sub> 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).

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