

Nighttime measurements of ambient N_2O_5 , NO_2 , NO and O_3 in a sub-urban area, Toyokawa, Japan

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Abstract

We report on the development of a highly sensitive instrument for measuring ambient N_2O_5 molecules and its application to nighttime measurements of N_2O_5 in a sub-urban area, Toyokawa, Japan, during February 2006. The mixing ratio of N_2O_5 was quantified by cavity ring-down spectroscopy detection of NO_3 at 662 nm, in which the NO_3 radicals were produced by thermal decomposition of the N_2O_5 molecules. The minimum detection limit (1σ) for N_2O_5 was estimated to be 2.2 pptv in a 100 s averaging time. The mixing ratios of ambient NO_2 , NO and O_3 were simultaneously measured along with N_2O_5 . The ambient N_2O_5 mixing ratios range from below the detection limit (2.2 pptv) to 20 pptv during nighttime. By applying the steady-state approximation on the data of 27–28 February when the surface wind field was characterized by northerly wind associated with winter monsoon surges over Japan, the heterogeneous loss rate of N_2O_5 was estimated. Based on the mixing ratios and the loss rate of N_2O_5 , the nocturnal loss rate of NO_x was evaluated as 0.5 ppbv per night for that night. In addition, the temporal variation of N_2O_5 concentration during several hours after the local sunset on that night was calculated using the time-dependent box model. By comparing the results with the observed data, significant contributions of gas-phase loss processes of NO_3 were inferred.

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1. Introduction

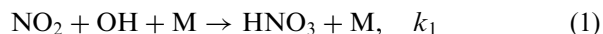
Nitrogen oxides, NO_x ($= \text{NO} + \text{NO}_2$), play an important role in the photochemistry of the atmo-

sphere, controlling ozone production and hence hydroxyl radical (OH) and other radical concentrations. The budget for the emissions of NO_x and its rate of removal from the atmosphere are of substantial current interest. NO_x is removed from the atmosphere primarily by its conversion to nitric acid (HNO_3), which is removed via wet deposition to the surface or rainout. There are two pathways of

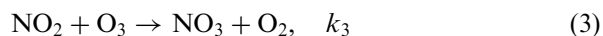
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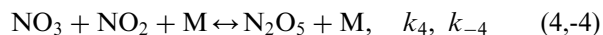
conversion of NO_x to HNO_3 . One is the daytime reaction of NO_2 with OH:



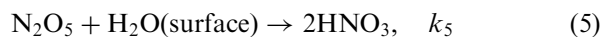
The other is formation of nitrate radical (NO_3), and dinitrogen pentoxide (N_2O_5). The NO_3 radical is primarily formed via the oxidation of NO_x by O_3 :



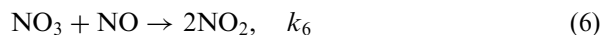
Subsequently, NO_3 can react with NO_2 to form N_2O_5 reversibly:



N_2O_5 may then be hydrolyzed on surfaces to form HNO_3 :



Because NO_3 is photolyzed efficiently during daytime, this pathway is believed to be especially important during nighttime. As a sink of NO_3 , the rapid reaction with NO is also important:



Field observations of NO_3 in the troposphere have been performed using differential optical absorption spectroscopy (DOAS) in a long path through the atmosphere (e.g., Platt and Perner, 1980; Noxon et al., 1980; Geyer et al., 2001). Recently, new spectroscopic techniques including cavity ring-down spectroscopy (CRDS) (King et al., 1999; Brown et al., 2001, 2002; Ball et al., 2001; Simpson, 2003) and laser-induced fluorescence (LIF) (Wood et al., 2003; Matsumoto et al., 2005a) have been developed for real-time *in-situ* measurement of both NO_3 and N_2O_5 .

With the aim of forming a detailed understanding of the chemistry involving NO_3 and N_2O_5 , the simultaneous observation of NO_3 and/or N_2O_5 with related compounds have been performed by several

groups using CRDS or LIF techniques. Brown and co-workers reported the measurements of NO_3 and N_2O_5 with NO , NO_2 , O_3 , NO_y , HNO_3 , dimethyl sulfide (DMS), volatile organic carbons (VOCs), and/or aerosols at various fields including near Boulder in Colorado in the fall of 2001 (Brown et al., 2003a, b, 2004, 2007), on board NOAA research vessel in the marine boundary layer along the United States' east coast in the summer of 2002 and 2004 (Brown et al., 2004; Aldener et al., 2006; Osthoff et al., 2006), and from an aircraft platform in the east parts of the United States in the summer of 2004 (Brown et al., 2005, 2006). Wood et al. (2005) reported the measurements of N_2O_5 with NO_2 and O_3 at Contra Costa County near San Francisco Bay in California during January 2004. Matsumoto et al. reported the measurements of NO_3 and N_2O_5 with NO , NO_2 , and O_3 in the west of central Tokyo during December 2003 (Matsumoto et al., 2005b) and at Izu-Oshima Island, Japan during June 2004 (Matsumoto et al., 2006). Ayer and Simpson (2006) reported the measurements of N_2O_5 with CO and O_3 at the sub-arctic site near Fairbanks, Alaska, in the winters of 2002 and 2004.

In this study, we performed *in-situ* measurements of N_2O_5 with NO , NO_2 , and O_3 in a sub-urban area, Toyokawa, Japan, during February 2006. A newly developed instrument based on pulsed CRDS at 662 nm with a thermal converter was used for the observation of N_2O_5 . Applying the steady-state approximation, the heterogeneous loss rate of N_2O_5 on the aerosol surfaces and the nocturnal NO_x losses are evaluated.

2. Experimental

2.1. N_2O_5 measurement system

The techniques used in the present study to observe N_2O_5 , NO , NO_2 , and O_3 are summarized in Table 1. The *in-situ* measurements of ambient N_2O_5

Table 1
Equipments used in the present study

Method	Detection limit ^a	Average time (s)	Instruments
Pulsed-CRDS (N_2O_5)	2.2 ^b pptv	100	This work
LIF (NO_2)	0.17 ppbv	10	Taketani et al. (2007)
Chemiluminescence (NO)	0.2 ppbv	10	This work
UV absorption (O_3)	0.2 ppbv	10	Thermo-Electron model 49C

^aNoise equivalent detection limit for the average time listed above.

^bThe minimum detection limit is 1.5 and 2.2 pptv for NO_3 and N_2O_5 , respectively.

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