

Observations of nitrous acid and its relative humidity dependence in Shanghai

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Abstract: Nitrous acid, HNO₂, is an important precursor of OH radicals in the troposphere. Measurements of HNO₂ and NO₂, using differential optical absorption spectroscopy (DOAS), were performed in Shanghai, China for a period from October 22, 2004 to January 4, 2005. The mean (and median) hourly concentrations of HNO₂ and NO₂ during this period were 1.1 (0.7) ppb and 24 (21.4) ppb respectively. A correlation between HNO₂/NO₂ and PM₁₀ mass concentrations was obtained. This correlation suggests that significant heterogeneous chemical production of HNO₂ may occur through NO₂ reactions on aerosol surfaces. This hypothesis was further supported by detailed analysis of selected pollution episodes in this study. At the same time, the water dependence of HNO₂ formation was studied by analysis of relative humidity (RH). It showed that the maximum HNO₂/NO₂ ratio was increased along with RH below 70% and inhibited at RH>70%.

Keywords: DOAS; heterogeneous formation; nitrous acid; PM₁₀ aerosol; relative humidity

Introduction

Nitrous acid, an important component of NO_x in polluted atmosphere, is considered to play a significant role in atmospheric chemistry because it is a source of OH radicals through photolysis. Recent study showed that up to 30% of the total OH is produced by HNO₂ photolysis in a 24-h period (Alicke *et al.*, 2003; Stutz *et al.*, 2002). Moreover, HNO₂ constitutes a possible public health problem because it is a potential carcinogenic agent (Pitts *et al.*, 1978). However, the mechanisms of producing HNO₂ are not well established. The investigation showed that the numbers of motor vehicles in Shanghai were increased 23% annually since 1992, and now exceeded 2.0 million. The emissions of nitrogen oxide are increased rapidly due to the increasing number of motor vehicles. Therefore, it is necessary to measure the HNO₂ concentrations of Shanghai for the NO_x monitoring and HNO₂ producing research.

Nitrous acid was first detected in the atmosphere by differential optical absorption spectroscopy (DOAS) (Perner and Platt, 1979; Platt *et al.*, 1980), since then many atmospheric measurements at various sites had been reported (Lammel and Cape, 1996). Nevertheless, the production processes of HNO₂ are still not well understood. Generally, sources of HNO₂ include direct emission, homogeneous reactions and heterogeneous reactions (formation on a surface). Homogeneous reactions, clarified by many laboratory studies, are too slow to explain the observed HNO₂ concentrations. In addition, direct emission can only partly explain atmospheric HNO₂ level (Kurtenbach *et al.*, 2001). In recent years, the assumption of heterogeneous reactions on wet surfaces like aerosols, buildings or the ground has been suggested and

confirmed by several researchers (Notholt *et al.*, 1992; Calvert *et al.*, 1994; Harrison and Kitto, 1994; Harrison *et al.*, 1996; Ammann *et al.*, 1998; Aumont *et al.*, 1999; Reisinger, 2000; Seung *et al.*, 2004).

One of the main uncertainties in heterogeneous reactions is the role of aerosols playing in the formations of HNO₂. Various types of aerosol particles such as soot aerosol particles, different carbonaceous surfaces and secondary organic aerosols were identified as possible substrates for HNO₂ formations (Grassian, 2001). However, Harrison *et al.* (1996) was able to model ambient HNO₂ concentrations with the solid grounds as the only reactions surface. Kleffmann *et al.* (2003) suggested that the HNO₂ formation was dominated by process on ground surface, not on particle surface.

Stutz *et al.* (2004) believed that water played an important role in the HNO₂ formation, but until now only a few investigations have been conducted on this role. Kalberer *et al.* (1999) stated that for a reaction time of 20 s the amount of HNO₂ (formed on the soot aerosol particles) increased with increasing of relative humidity (RH) up to 30%, but decreased when it exceeded 40%.

This paper reports measurements of ambient HNO₂, NO₂ by DOAS system, PM₁₀, and relative humidity over Shanghai, China. The heterogeneous formation of HNO₂ on aerosol surface and the impact of water were studied in our measurement campaigns. To the author's knowledge these measurements represent the first research on the origin of HNO₂ in China.

1 Experiment setup

DOAS is based on detecting narrow absorption features of different molecules that absorb light

following the Lambert-Beer's law (Platt, 1994). Fig.1 shows the setup of the DOAS system developed by our laboratory. This DOAS system, described in detail by Zhou *et al.* (2002) and Yu *et al.* (2004), was developed under the cooperation between German and Chinese researchers ("ChinaSky" project). It consists: a 150-W high pressure xenon lamp as light source; a co-axial telescope with transmitting and receiving optics combined in one device; retroreflectors; fiber; spectrometer; a photodiode array with 1024 pixels as detector; and a software package, DOASIS for data collection and spectra analysis. The light from the source is collimated by the telescope into a parallel beam and transmitted into an array of retroreflectors at the other end of the light path which is 200 to 10000 m apart from telescope. After reflected by the retroreflectors, the light is collected by the telescope and focused onto a quartz fiber, which transports the light to the spectrometer, at the outlet of the spectrometer. The spectrum is recorded by the detector and stored in a computer.

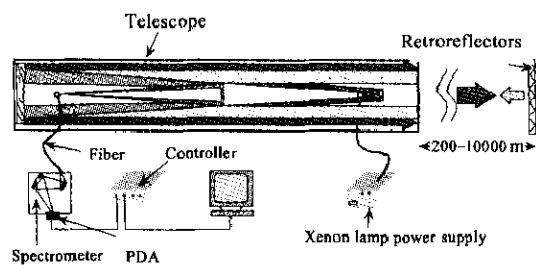


Fig.1 Setup of DOAS instrument

Measurements of HNO₂ and NO₂ were made by DOAS in the northwestern part of Shanghai City from October 22, 2004 to January 4, 2005. As shown in Fig. 2, the transmitting and receiving telescopes were installed at the 11th monitoring station of Shanghai, on the top of a 7-story building (about 20 m above

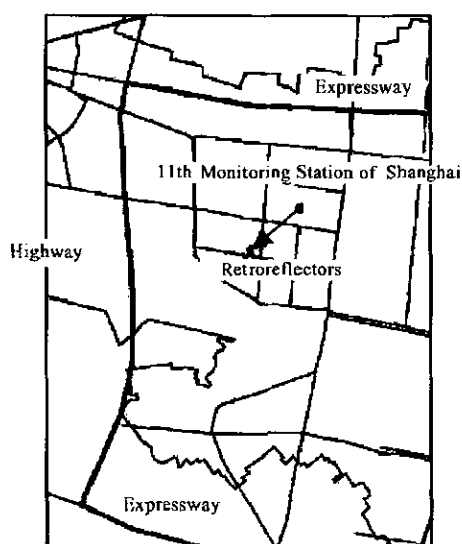


Fig.2 A map of measurement sites

ground), and retroreflectors were located at the top of a 8-story building (25 m above ground). The distance between the two places was 507 m, yielding a total optical path of 1014 m. Hourly PM₁₀ mass was measured simultaneously by TEOM series 1400a monitor (Rupprecht & Patnshnick Co., Inc.). Meteorological data with 1 h resolution, including temperature, relative humidity, wind direction, and speed, were collected at the same sites. For identification of HNO₂ and NO₂ the spectral range used for analysis was 340–375 nm. The detection limits of HNO₂ and NO₂ are 0.3 ppb and 0.9 ppb. The integration time of per spectrum was about 5 min. Average concentrations of HNO₂ and NO₂ in the light path were determined using a non-linear least-squares fitting algorithm (Stutz and Platt, 1996).

2 Result and discussion

2.1 Measurement of HNO₂, NO₂ and PM₁₀

Table 1 shows that HNO₂ concentrations ranged between below the detection limit (200 ppt) and a maximum of 6.8 ppb. These concentrations are in good agreement with measurements obtained by other workers under moderately polluted urban conditions (Lammel and Cape, 1996). Comparing daytime (07:00–17:00) with nighttime (18:00–06:00) levels of HNO₂, the nighttime HNO₂ concentrations (average value of 1.4 ppb) were higher than the daytime concentrations (average value of 0.7 ppb). As shown in Fig.3, the mixing ratios of HNO₂ indicate a pronounced diurnal cycle. The concentrations of HNO₂ increased in the afternoon between 15:00 and 16:00 and remained the high level after midnight. However, after sunrise, a rapid decrease is occurred because of photolysis. The minimum concentrations were obtained between 11:00 and 14:00.

Table 1 Mean, median, and concentration range of HNO₂, NO₂, and PM₁₀

Item	Mean	Median	Minimum	Maximum
HNO ₂ , ppb	1.1(1.0)	0.7	below the detection limit	6.8
NO ₂ , ppb	24(11.7)	21.4	5.5	75.4
PM ₁₀ , mg/m ³	0.14(0.08)	0.096	0.003	0.94

Note: One standard deviation is given in the parentheses

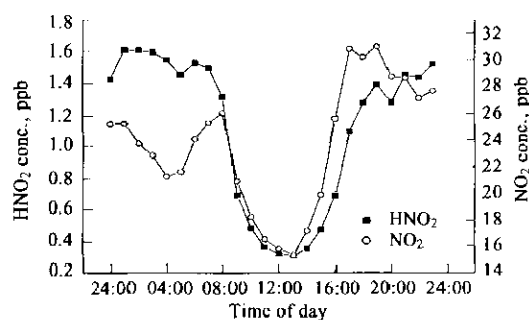


Fig.3 Diurnal patterns of HNO₂ and NO₂

NO₂ concentrations were in the range of 5.5–75.4 ppb. Two concentration peaks occurred during the morning from 7:00 to 9:00 and during the afternoon from 16:00 to 20:00. This strong diurnal variation of NO₂ and HNO₂ has three likely main reasons. Firstly, it was caused by increased emission of NO_x from motor vehicles in rush-hour. Secondly, photochemistry forces a diurnal trend anti-correlated to solar irradiation. Finally, the boundary layer height has also an impact on the concentrations of NO₂ and HNO₂. An interesting point is that the NO₂ concentrations remain high level from 20:00 to midnight. The reason is that the measurement site locates at a logistics center, where few decrease of vehicle flows occurred after 20:00. The high level of NO₂ before midnight also led to the difference of HNO₂ concentration variation in the night between our study and other sites (Reisinger, 2000) where a significant HNO₂ peak existed from 18:00 to 23:00. The concentrations of HNO₂ and NO₂ are found to be highly linear correlated ($R=0.8$), as shown in Fig 4. This relationship is consistent with the assumption that NO₂ is an important precursor species in the heterogeneous formation of HNO₂. Moreover, when NO₂ concentration was below 10 ppb, the HNO₂ concentration was small even below the detection limit. Therefore, the linear fit line does not pass the grid origin.

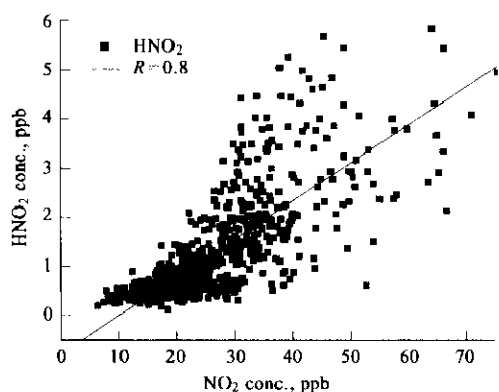


Fig.4 Correlation between HNO₂ and NO₂, and linear fit to data

Total average hourly PM₁₀ mass concentration was 0.14 mg/m³ during all the measurement period and the highest PM₁₀ concentration was found to be 0.94 mg/m³. The PM₁₀ concentrations in our study were higher than other sites (Park *et al.*, 2004). Moreover, our hourly data of PM₁₀ were time consistent to the data of HNO₂ and NO₂, which can help us to research the HNO₂ formation through NO₂ heterogeneous reactions on the aerosol surfaces.

2.2 Evidence of HNO₂ formation on aerosol surface

It was reported that aerosols could be an importance source of HNO₂ by combining HNO₂ and

aerosol surfaces observations (Lammel and Pernel, 1988; Notholt *et al.*, 1992; Andres-Hernandez *et al.*, 1996; Reisinger, 2000). Park *et al.* (2004) measured HNO₂ and PM₁₀ simultaneously at South Korea with 6 h time resolution. As we known, aerosol mass concentration can be used as a comparison index for the total surface of aerosols (μm²/cm³). In our study, the average HNO₂/NO₂ ratio was 0.04, within the wide range between 0.005 and 0.05 of other sites (Reisinger, 2000). To eliminate the influence of photolysis, only the nighttime data (from 18:00 to 06:00 next day) were used. The HNO₂/NO₂ ratio, which lies in the range 0.005–0.14, shows a clear positive correlation with the PM₁₀ mass with a correlation coefficient of 0.63. This explains that particular matter loading in the ambient air plays an important role in the heterogeneous formation of HNO₂. However, Lammel and Cape (1996) and Reisinger (2000) stated that HNO₂ and NO₂ had different chemical reaction time scales, and hence NO₂ was increased near the top of the inversion layer, leading to a decrease of HNO₂/NO₂, when the aerosol and HNO₂ were reduced through dispersion. To eliminate the influence of this situation, two individual episodes, where HNO₂ increased along with NO₂ decreased or remain constant, will be reported in the following section.

2.3 Case studies of pollution episodes

Fig.5 illustrates the variations of concentrations of HNO₂, NO₂ and PM₁₀ mass during the night on November 21 and 22 in 2004 along with the HNO₂/NO₂ ratio and the relative humidity. NO₂ concentrations increased from 16:00 to 20:00 were likely caused by the emission of vehicles or the formation of strong inversion layer. Then they remained high until about 24:00, then declined to about 5:00 in the morning. In contrast to NO₂, the concentrations of HNO₂ always increased from 16:00 to 23:00 and then remained the high levels, except for a few spikes. The HNO₂/NO₂ ratio is in good agreement with the PM₁₀ mass concentrations during this period. This striking correspondence between the HNO₂/NO₂ ratio and PM₁₀ mass concentrations may indicate that the heterogeneous formation of HNO₂ on aerosol surface occurred. Especially the constant of NO₂ from 20:00 to 23:00, while HNO₂ increased along with PM₁₀, contradicts the assumption that HNO₂/NO₂ ratio is decreased along with aerosol because of the increase of NO₂ mentioned in last paragraph. At the same time, the relative humidity remained constant from 20:00 to 23:00, excluding its impact of heterogeneous formations of HNO₂ on aerosol surfaces. After midnight, HNO₂ remain the high levels along with the PM₁₀, although NO₂ decreased from 40 ppb to 28 ppb. This phenomenon is attributed to the relative humidity increased from 24:00 according to

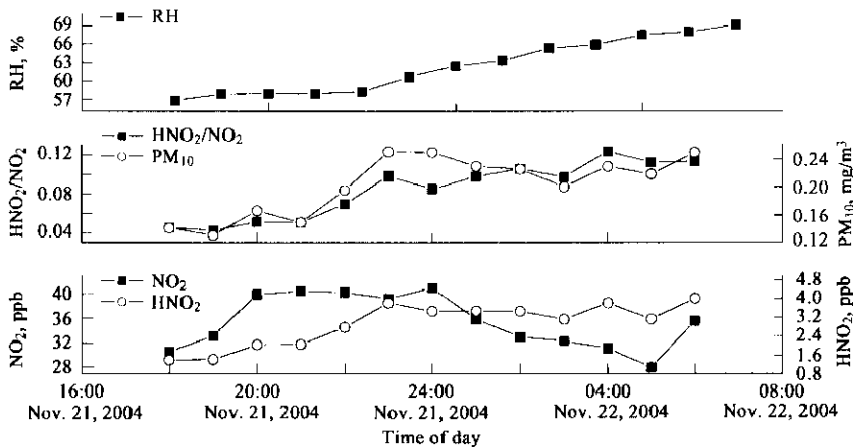


Fig.5 Time-series plots of HNO₂, NO₂, PM₁₀ mass, relative humidity (RH) and HNO₂/NO₂ ratio

the conclusion of Stutz *et al.* (2004). The influence of the relative humidity to HNO₂/NO₂ ratio will be discussed in the next section.

To better understand the important role of aerosol in the heterogeneous formation of HNO₂, we compared the results of two nights (December 24–25 and December 25–26) which have the similar NO₂ concentrations. As shown in Fig.6, the higher PM₁₀ mass concentration of Dec. 25–26, while two nights have the similar NO₂ concentration and relative humidity, lead to the higher HNO₂ concentration and HNO₂/NO₂ ratio. The difference of boundary layer

height in two nights maybe weaken our conclusion, so the data of boundary layer height of Shanghai (with 6 h time resolution) in these two nights are compared (from FNL stability time-series of ZSSS-code of Shanghai Hongqiao at <http://www.arl.noaa.gov/eady/amet.html>) in Fig.6. We found that the boundary layer heights of two nights were not different enough to explain the difference of HNO₂/NO₂ ratio. This episode can prove the conclusion that the formation of HNO₂ is occurred through reactions of NO₂ on aerosol surface.

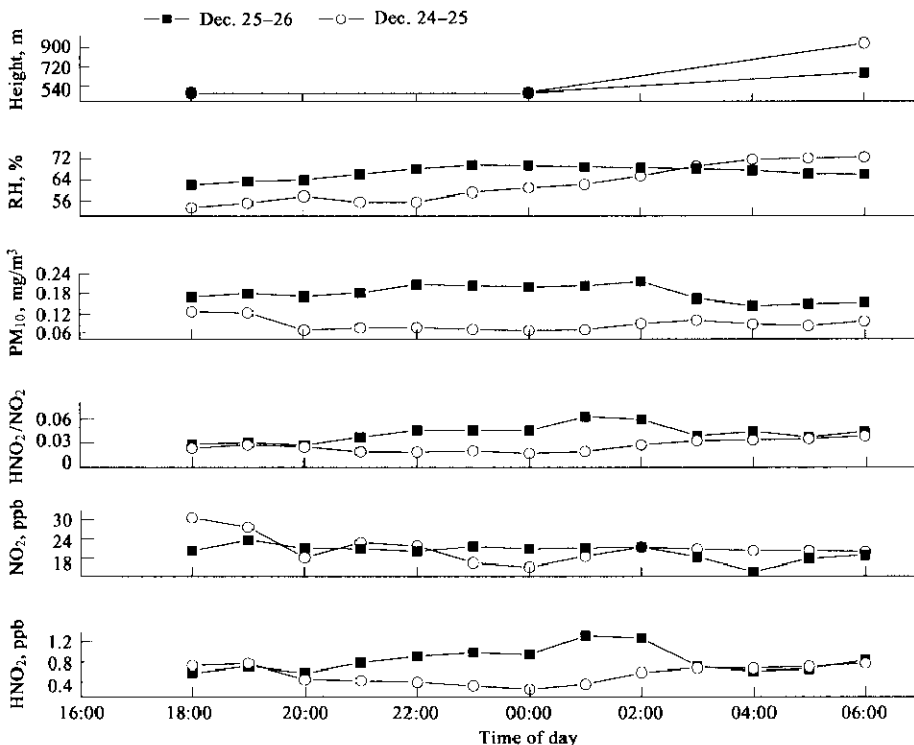


Fig.6 Comparison of results obtained in two nights have the similar NO₂ concentrations and meteorological data

2.4 Relative humidity dependence of HNO₂ formation

Water, most likely in its surface adsorbed form, can have an influence on the HNO₂ formation (Stutz *et al.*, 2004). To prove the role of water on the HNO₂

formation, the relationship of HNO₂/NO₂ ratio and relative humidity was discussed in the paper. Fig.7 shows that the correlation coefficient ($R=0.7$) between HNO₂/NO₂ and $PM_{10} \times RH$ is higher than correlation coefficient of HNO₂/NO₂ and PM_{10} ($R=0.63$). It

indicates that water did play a role on the formation of HNO_2 . More details about the role of water will be studied in the following part.

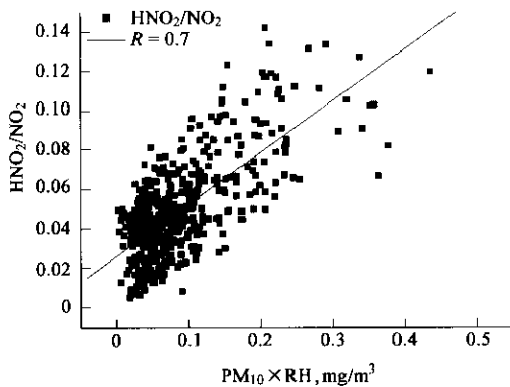


Fig.7 Correlation between HNO_2/NO_2 ratio and $\text{PM}_{10} \times \text{RH}$ (relative humidity), and linear fit to data

Fig.8 plots all the nocturnal HNO_2/NO_2 ratios observed in our experiments against their respective humidities. The average of the five highest HNO_2/NO_2 values in RH intervals of 10%, which can eliminate much of the uncertainty connected with the influence of other parameters (Stutz *et al.*, 2004), were calculated. These average maxima are shown in Fig.8 as black horizontal bars, where the lengths of the bars indicate the RH interval. As shown in Fig. 8, the maximum values of HNO_2/NO_2 in the 40%—50% RH interval are in the range between 0.06—0.07, while they reach 0.13—0.14 at RH between 60% and 70%. On the basis of these results one might speculate that a higher RH value (below 70%) leads to that heterogeneous formation of HNO_2 on the aerosol surface is easier to occur. But when the RH values exceed 70%, the heterogeneous reactions are inhibited. This idea is supported by the theory as follows: The newly formed particles are hydrophobic and they are not in favor of the reactions occurrence because H_2O is either directly involved in the chemical reaction of NO_2 to HNO_2 or builds up a precursor (e.g., by hydrolysis) that is the reaction partner for NO_2 . Therefore, when the RH values increased at the beginning under some value, the heterogeneous reactions were occurred easier for more adsorbed water on the surfaces. However, at the high humidity the increasing amount of adsorbed water makes the reactive surface less accessible or less reactive for NO_2 . As we known, the wetting of surfaces occurs as a function of humidity, because they take up liquid water above the humidity of deliquescence of the predominant salt components. The growth of curve of ambient aerosol rises steeply above 70%—75% RH and this situation will result in the inhibition of HNO_2 formation on aerosol surfaces (Lammel and Cape, 1996).

Care must be taken, however, not to over-

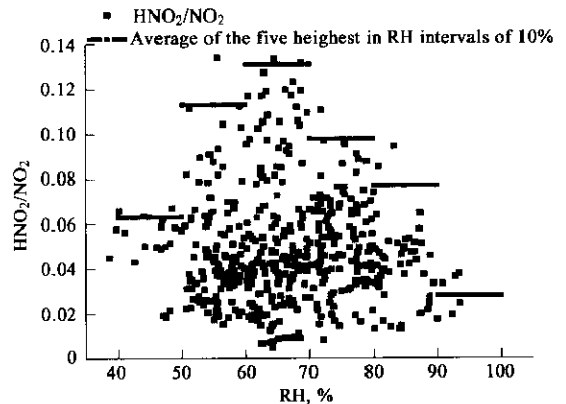


Fig.8 HNO_2/NO_2 ratio versus RH in our experiment

interpret the relationship between the HNO_2/NO_2 ratio and RH value of ambient atmosphere, since many other parameters influence the heterogeneous formation of HNO_2 on aerosol surface and lack of $\text{RH} < 40\%$ data. As shown in Table 2, average of all HNO_2/NO_2 ratio has no significant relationship to the RH and most data are in the range of RH 50%—80% during the experiment. The reason is that aerosol surface and other meteorological parameters also play the important roles in the heterogeneous formations of HNO_2 on aerosol surfaces. The value of HNO_2/NO_2 ratio is the result determined by aerosol mass concentration, relative humidity of ambient atmosphere and boundary layer height.

Table 2 Average values of HNO_2/NO_2 ratio in varied relative humidity ranges

RH range, %	Avg.	Num.
40—50	0.049 ± 0.004	17
50—60	0.047 ± 0.002	124
60—70	0.052 ± 0.002	182
70—80	0.052 ± 0.0018	151
80—90	0.041 ± 0.002	70
90—100	0.028 ± 0.003	6

3 Conclusions

Simultaneous measurements of HNO_2 , NO_2 by DOAS system and PM_{10} were made from fall to winter in Shanghai, China, to investigate the source of HNO_2 -heterogeneous reactions on aerosol surfaces. The close correlation between the HNO_2/NO_2 ratio and the PM_{10} mass concentrations, both in all measurement periods and during individual pollution episodes, suggested that HNO_2 formation maybe occur on aerosol surfaces. Especially, the impact of boundary layer height, which was thought to result in the coincidence of above high correlation, was eliminated in the above two case studies.

The higher correlation between the HNO_2/NO_2

ratio and the PM_{10} mass concentrations multiply the relative humidity of ambient atmosphere indicated that surface adsorbed water play an important role in the heterogeneous formations of HNO_2 . The highest data in the RH interval were compared in our study. It can be concluded that the RH are in a positive correlation to the HNO_2/NO_2 ratio under 70%, while the ratio decreased along with the $RH > 70\%$. Some theories prove our observations about the relationship between the RH and HNO_2/NO_2 ratio. But the evidence is limited for the lack of $RH < 40\%$ data in our experiment. Moreover, RH is one of the impact factors of heterogeneous formation of HNO_2 on aerosol surfaces. The investigation about the water dependence of HNO_2 formation in the atmosphere will be continued in our group.

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