

# Improvement of the New NO Detection Method Using Laser-Induced Two-Photon Ionization with a TOF Mass Spectrometer

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We have developed a new method to detect low concentrations of tropospheric NO, using laser induced two-photon ionization (Lee, S.-H.; Hirokawa, J.; Yoshizumi, Y.; Akimoto, H. *Rev. Sci. Instrum.* **1997**, *68*, 2891). This method uses a frequency-doubled pulsed-dye laser operating near 226 nm to photoionize NO by resonance enhanced two-photon ionization via its  $A^2X^2(0,0)$  band. This work reports our recent results regarding the improvement of the overall instrumental performance obtained by applying a time-of-flight (TOF) mass spectrometer and further discusses the water vapor influence in this method. NO ion signals were discriminated efficiently from the other ions generated by impurities in the ionization cell by using a TOF mass spectrometer. The obtained sensitivity of this method was 10 pptv ( $S/N = 2$ ), at a laser power of 44  $\mu$ J and an integration time of 1 min. Also, the background signal was decreased from 5 to 0.25 Hz as compared to the previous study, indicating that a nearly signal-limited condition was obtained, which enables NO detection free from background noise. In our laser ionization instrument, the uncertainty in NO ion intensity caused by the fluctuation of laser power was deviated less than 3% from a long-term average. Moreover, by comparison with the ozone-chemiluminescence method, water vapor influence has been investigated by introducing humid sampling gases into the molecular beam. As the relative humidity in the sampling gases varied from 0 to 85% at room temperature, no significant change in the NO detection efficiency was observed. This demonstrates an important advantage over the ozone-chemiluminescence method, although further field intercomparisons are required to certify the applicability of this new NO ionization method into the atmospheric study.

## Introduction

The most critical factor controlling the photochemical production of ozone in troposphere is the availability of NO (2). With increase of tropospheric ozone buildup caused by the increasing emission of anthropogenic pollutants (2–6), the determination of NO concentrations has become a crucial issue in atmospheric chemistry. The most common method

used for the detection of tropospheric NO is the ozone-chemiluminescence (7–10), and the two-photon laser-induced fluorescence has also been put to practical use in aircraft (11–13). Development of new detection methods employing different techniques is valuable, since it adds credibility to the measurement of low levels of tropospheric species and provides increased confidence in new and existing instruments by intercomparisons (14).

In previous work, we developed a new detection method for NO by using a pulsed-dye laser operating at near 226 nm to photoionize NO by (1+1) resonance enhanced two photon ionization via its  $A^2X^2(0,0)$  band (1). In this method, a pulsed nozzle was used to expand sampling gases into the ionization cell and to obtain high selectivity against other nitrogen oxides; it was shown that this NO detection technique has a selectivity of 45 for NO against  $NO_2$ , with a laser power of 44  $\mu$ J. A detection limit of 16 pptv ( $S/N = 2$ ) was estimated by using the total ion counting method, with an integration time of 1 min, a pulse energy of 44  $\mu$ J, and a voltage of 3.2 kV for the electron multiplier.

It is well-known that laser ionization has a significant advantage over laser-induced fluorescence in the detection efficiency (15). The laser ionization technique has been proposed by Simeonsson et al. (16) for nonselective measurements of NO,  $NO_2$ ,  $HNO_3$  and nitromethane. They used a 226-nm light to photodissociate the parent molecules and also to photoionize the resultant NO fragment by a (1+1) resonance-enhanced multiphoton ionization process via its  $A^2X^2(0,0)$  band. A detection limit of 1 ppbv was reported with an integration time of 10 s. In contrast to such nonselective detection for all those nitrogen compounds, we used the laser ionization method for the selective measurement of low NO concentrations in the atmosphere.

In this study, a time-of-flight (TOF) mass spectrometer was applied to fully discriminate NO ions from the other ion signals generated by impurities in the ionization cell and to further improve the sensitivity for NO measurement. TOF mass spectroscopy is one of the most efficient detection techniques used for laser ionization (17) and, hence, has received special attention for many years. Plate voltages, timing, and physical dimensions of a TOF mass spectrometer with improved sensitivity have been described by Willey et al. (18) and by Adams and Read (19, 20). Water vapor influence was also investigated for this laser ionization NO detection method, since the collision free condition in the super sonic jet beam may offer a medium for the species to form van der Waals (vdW) dimers or larger complexes (17).

## Experimental Section

The instrumental schematic is shown in Figure 1. The experimental setup consists of three parts: a laser excitation system, an ionization cell in which a super sonic pulsed nozzle was attached, and an ion detection system. The ion detection system, realized in our previous work as an electron multiplier to directly collect total ions (1), was replaced with a TOF mass spectrometer. Laser radiation was provided by a tunable dye laser (Scanmate, Lambda Physik, 0.1  $cm^{-1}$  resolution) optically pumped by a Nd:YAG laser (LPY 150, Lambda Physik, 20 Hz frequency). The dye laser output was frequency doubled with a BBO I crystal (wavelength range between 225 and 227 nm), providing a laser power of 100  $\mu$ J. For every laser pulse, the power was monitored in real time with a photodiode, and the measured digital signals were further averaged over 1 min.

The TOF flight tube attached to the ionization cell was differentially pumped by a 300 L/s turbo-molecular pump

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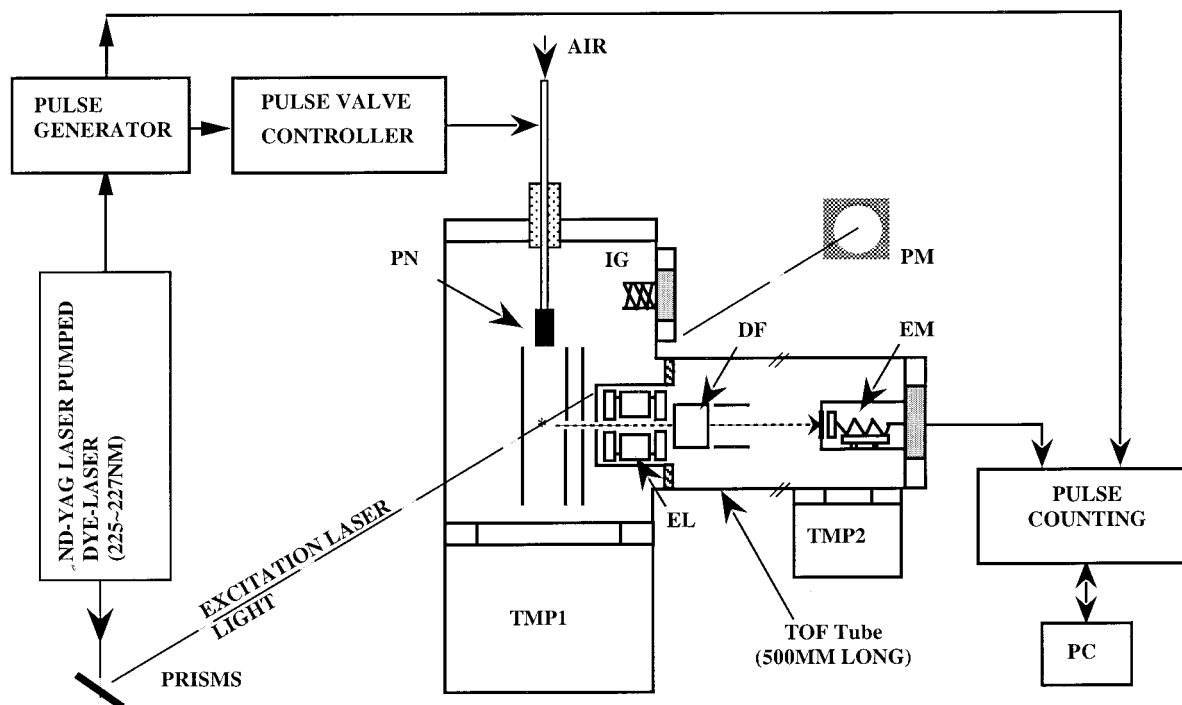


FIGURE 1. Schematic of the NO laser ionization instrument: TMP, turbo-molecular pump; PM, laser power monitor; PN, pulsed nozzle; DF, deflector; EL, Einzel lenses; IG, ionization gauge; EM, electron multiplier. A TOF mass spectrometer was used for selective ion detection instead of an electron multiplier that was used in the previous work to further improve instrumental sensitivity.

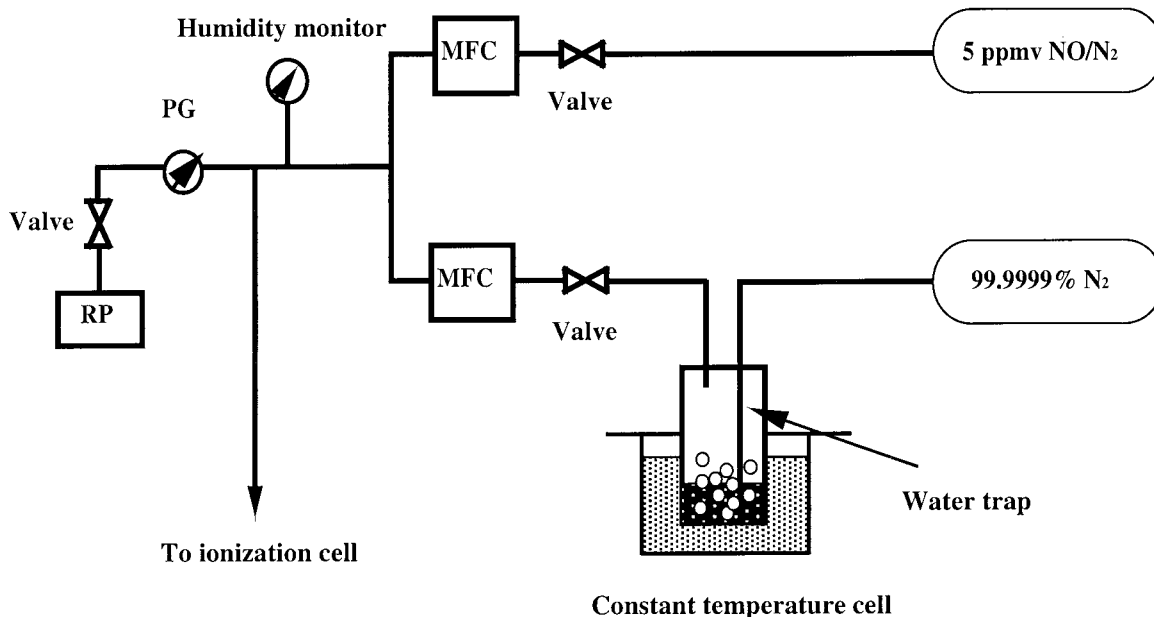


FIGURE 2. Gas supply system used for the investigation of water vapor influence: MFC, mass flow controller; RP, rotary pump; PG, pressure gauge.

(PT-300, Mitsubishi) to keep a pressure of  $1 \times 10^{-8}$  Torr, while the ionization cell was pumped by a 450 L/s turbo-molecular pump (TP 550, Varian). Gases were injected with a pulsed nozzle (Universal System, 0.5 mm diameter) at a duration time of 300  $\mu$ s. NO ions formed in the ionization region were accelerated and allowed to drift down the 500 mm long TOF flight tube to an electron multiplier (Ceratron, Murata Seisakujo). To obtain a high resolution, a double-fielded acceleration, an Einzel lens, and a deflector were also equipped in the TOF mass spectrometer.

A gas line system was used to provide sampling gases with high humidity, as illustrated in Figure 2. Water vapor was generated by bubbling pure nitrogen gases in water,

and the temperature of the water trap was controlled by a constant temperature oven to obtain high stability in the degree of the humidity. A semiconductor humidity sensor (Tomas Kagaku, 0.1% of sensitivity) was placed inside the gas line to monitor the humidity of the gases before being introduced into the ionization cell.

## Results and Discussion

Figure 3a shows a typical TOF mass spectrum taken as the laser wavelength was tuned for a NO resonance; 100 ppbv NO/N<sub>2</sub> gases and a laser power of 40  $\mu$ J were used. The most intense peak appeared at 13  $\mu$ s was assigned to be NO<sup>+</sup> ( $m/e = 30$ ) ion signals, since its wavelength dependence was very

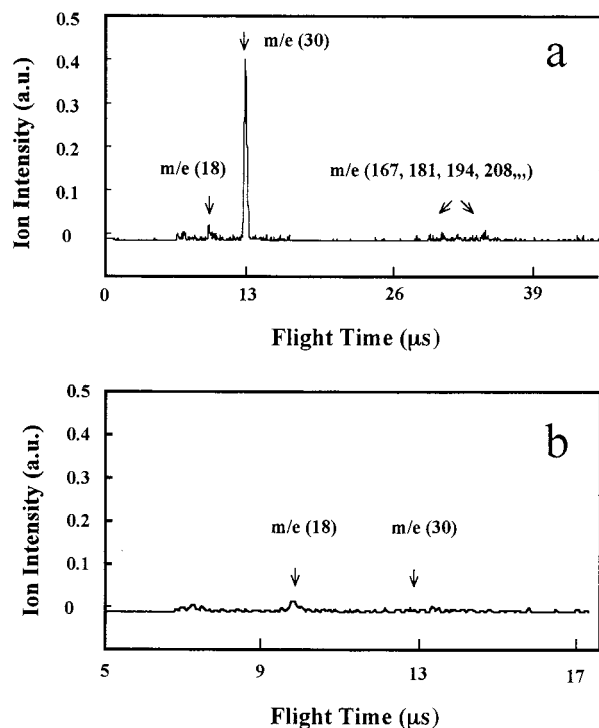


FIGURE 3. (a) Typical TOF mass spectrum recorded by expanding 100 ppbv NO/N<sub>2</sub> gases at the wavelength favorable for NO two-photon resonance ionization. Laser power, 40 μJ. (b) Typical TOF mass spectrum as the wavelength was tuned for off-resonance for NO ionization, using the same experimental conditions as in panel a. The ion signals were not averaged at both of the spectra. Note panels a and b have different x-axis ranges. a.u. in y-axis indicates arbitrary units.

similar to a typical 1 + 1 resonance-enhanced multiphoton ionization (REMPI) spectrum for NO shown in our previous work (1). Figure 3b shows a TOF mass spectrum recorded as the wavelength was shifted to a off-resonance ionization. The same experimental conditions as in Figure 3a were used, and there was no peak as observed at the flight time of 13 μs.

Except for NO ion signals, other peaks also appeared at the flight time of about 10 μs and in the region from 30 to 40 μs (Figure 3a). Mass-to-charge ratio (*m/e*) of each of these peaks can be calculated from

$$m_1/m_2 = t_1^2/t_2^2 \quad (1)$$

where *t*<sub>1</sub> corresponds to the time of arrival of an ion with mass *m*<sub>1</sub>, and *t*<sub>2</sub> to the time of arrival of an ion with mass *m*<sub>2</sub> in the TOF mass spectrometer (18–20). The peak corresponding to the *m/e* of 18 appeared at 10 μs was assigned to water ions. And peaks with calculated *m/e* values of 167–221 at 30–40 μs were estimated to be large unknown organic ions, since the interval between these peaks has the mass-to-charge ratio of 13 or 14. In contrast to NO ion signals, all these extra peaks did not show any wavelength dependence; they appeared with the UV radiation at any wavelengths even as no gases were introduced into the ionization cell. The ion strength increased with increasing pressure of the ionization cell and also with an increase of laser power. Therefore, these water ions and unknown organic ions can be characterized as secondary ions generated from impurities in the ionization region by absorbing UV scattering on the wall inside of the ionization cell. However, we still do not fully understand the feature of these impurity organic compounds.

The TOF mass spectra indicate that selective ion detection can be obtained by using a TOF mass spectrometer, since

TABLE 1. Comparison of the Detection Limits Obtained in Our Previous Instrument (7)<sup>a</sup> and in This Study<sup>b</sup>

	instrumental sensitivity ( <i>C</i> ) (Hz/ppbv)	background signal ( <i>S</i> <sub>bg</sub> ) (Hz)	[NO] limit ( <i>t</i> = 1 min) (pptv)
total ion counting (7)	26	5	16
TOFMS (this work)	9	0.25	10

<sup>a</sup> The ions are collected totally by an electron multiplier. <sup>b</sup> A TOF mass spectrometer is used for selective NO ion detection. <sup>c</sup> Laser power, 44 μJ; voltage for the electron multiplier, 3.2 kV; and *X/D* = 45 (*X* is the distance between the pulsed nozzle and the ionization region; *D* is the diameter of the orifice of the pulsed nozzle).

the NO ions are effectively discriminated from the other background signals. Table 1 shows a comparison of the detection limits for NO obtained in this study with the detection limit obtained in the previous study. The detection limit for NO determination was estimated with (21)

$$[\text{NO}]_{\text{limit}} = (S/N)(2S_{\text{bg}})^{1/2} C^{-1} t^{-1/2} \quad (2)$$

where *S*<sub>bg</sub>, *C*, and *t* correspond to the background signal intensity, the instrumental sensitivity, and the integration time, respectively. A detection limit of 16 pptv (*S/N* = 2) was estimated with total ion counting method, as an integration time of 1 min, and a pulse energy of 44 μJ and a voltage of 3.2 KV for the electron multiplier were used (1). However, this detection limit was strongly dependent on a high level of the nonresonant background ionization signals (5 Hz) that were caused by the impurity ions as shown in Figure 3a. In the present study, the detection limit was estimated to be 10 pptv (*S/N* = 2), with an integration time of 1 min and a laser power of 44 μJ. Although the instrumental sensitivity was only decreased to one-third as compared to that in the total ion counting method, the background signal intensity was decreased from 5 to 0.25 Hz since the NO ions and the other impurity ions were discriminated effectively by using the TOF mass spectrometer. Consequently, the detection limit was almost ion signal limited rather than background noise limited. This nearly negligible background signal significantly enhances ultimate sensitivity since the detection limit can be improved linearly with integration time. The two-photon laser-induced fluorescence method, which achieved a low detection limit of sub pptv levels, also attained a signal-limited measurement condition due to the fact that the fluorescence signal near 193 nm is free from the laser (226 nm) scattering-generated background signal (12).

NO ionization is characterized by the two-photon process, which is more sensitive to laser power variations as compared to the one-photon process. In fact, the laser power dependence of the NO ion signal was measured to be *S* ∝ *P*<sup>1.75</sup>, where *S* and *P* represent NO ion signal intensity and the laser power, respectively (1). Therefore, a large apparent fluctuation in NO ion intensity can be caused by fluctuations of laser power in the laser ionization method. The standard deviation of laser fluctuation was measured to be as low as 1.8% over time range of about 40 min at typical experimental conditions. Also, the correlated uncertainty in NO ion intensity was also within 3% of standard deviation. From this results, it can be seen that the fluctuation of NO ionization intensity caused by laser power fluctuations is negligible in our ionization instrument.

Interference of water vapor on NO detection was investigated by introducing water vapor into the vacuum ionization cell. Water vapor interference can be problematic, when a pulsed nozzle is used to inject air gases possibly due to the formation of NO–H<sub>2</sub>O van der Waals (vdW) clusters. vdW clusters are not stable in normal gas or liquid phases since

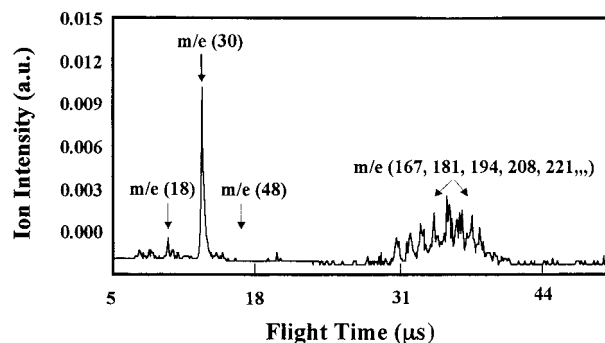


FIGURE 4. TOF mass spectrometer taken by expanding 100 ppbv NO in  $N_2$  gases with a relative humidity of 39.2% at room temperature. As the wavelength of the UV laser varied from 225 to 227 nm, no significant peak was observed at 16.44  $\mu s$ , which corresponds to the flight time of NO–H<sub>2</sub>O cluster ions. a.u. in y-axis ( $I$ ) indicates arbitrary units.

their binding energies, usually less than 1 kcal/mol, are usually much lower than thermal energy at room temperature (22). However, at extremely low temperatures attained in a supersonic beam, even such weakly bounded NO–H<sub>2</sub>O clusters can be stable. Also, the open shell molecule of NO is considered as an attractive vdW partner (23, 24). Obviously, if NO formed vdW complexes with H<sub>2</sub>O in the nozzle, it would decrease the signal strength due to nonresonant excitation and loss of mass identification.

Figure 4 shows a TOF mass spectrum recorded with 100 ppbv NO/ $N_2$  gases containing a relative humidity of 39.7% at room temperature. From the flight time of 13  $\mu s$  for NO ions, the flight time of NO–H<sub>2</sub>O ions ( $m/e = 48$ ) was calculated to be 16.44  $\mu s$  with eq 1. As UV radiation was scanned from 225 to 227 nm, no significant peak corresponding to NO–H<sub>2</sub>O ions was observed, even when the integration time or the laser power was increased. Shift of the  $\rho$ -vibrational levels of A–X transition of NO–X clusters could also be expected due to the difference of the vdW forces between the ground (X) and excited (A) state (23, 24). However, the laser ionization spectra of NO taken from such highly humid NO gases did not show any shift of excitation frequency by comparison with the spectra of the humidity free NO gases.

For NO molecules photodissociated from NO–Ar clusters, broad Doppler widths appeared in the LIF spectra for the photodissociated NO, and a relatively high rotational temperature of 165 K for  $v = 0$  was attained (22). However, we did not observe any such broadening resulted from the large kinetic energy of NO fragmentation even at relative humidity of 39.2% at room temperature. Moreover, the rotational temperatures calculated from the NO ionization spectra recorded at various humidity conditions, as shown in Figure 5, are all about 30 K while the relative humidity is increased up to 85.2%. Therefore, it seems that NO does not form NO–H<sub>2</sub>O or any clusters at our experimental conditions. Furthermore, NO ion intensities for 100 ppbv NO/ $N_2$  gases appear almost constant at various relative humidities that range from 0 to 85.2% (Figure 5). This result shows that water vapor hardly affects overall NO ion detection efficiency in the NO laser ionization instrument. By careful selection of carrier gas, expansion nozzle temperature, and backing pressure, clustering in the jet beam arising from vdW complexes can usually be avoided.

Efficient supersonic molecular cooling provides a high selectivity for NO against other nitrogen compounds (1) and demonstrates the lack of water molecules for humid atmospheric air expansions, thereby attesting to the applicability to the technique of molecular beam/REMPI/TOF mass spectroscopy (MB/REMPI/TOFMS) for atmospheric moni-

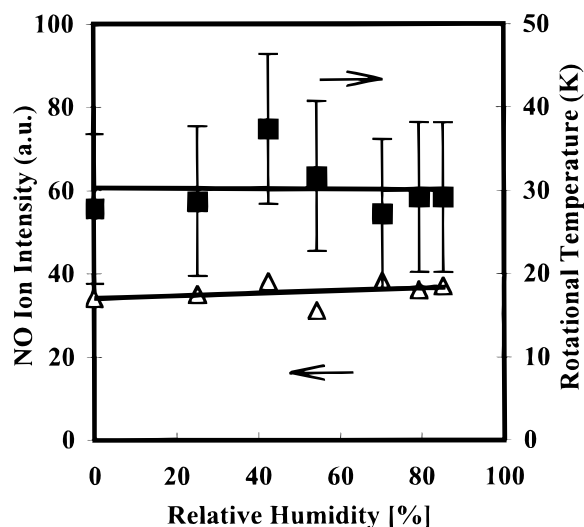


FIGURE 5. Variation in NO ion intensity (triangle) and in the rotational temperature for NO (rectangle) were plotted as a function of the relative humidity in the 100 ppbv NO/ $N_2$  sampling gases.

toring. These results also demonstrate that our NO detection technique possesses an important advantage over the ozone-chemiluminescence method. In the chemiluminescence method, detection efficiency is influenced by water vapor, since water vapor acts as a quencher of the excited NO<sub>2</sub>\* and also causes background variability (25). To further test the instrumental capabilities, intercomparison between the NO laser ionization instrument and the chemiluminescence instrument is required.

## Summary

(i) Improvements for the new NO laser ionization instrument have been achieved in order to obtain high sensitivity for NO measurement, by applying a TOF mass spectrometer. This modification allows to discriminate NO ions effectively from the background impurity signals. As a result, the detection limit for NO determination was estimated to be as low as 10 pptv ( $S/N = 2$ ), at a laser power of 44  $\mu J$  and with an integration time of 1 min. A signal limited detection condition was obtained with a low background signal of 0.25 Hz. It should be noted that we have estimated this detection limit from the data obtained at NO concentrations higher than 10 pptv.

(ii) No significant variation in NO ion intensity was observed due to the laser power fluctuations for this two-photon laser ionization method.

(iii) By measuring NO laser ionization spectra and calculating the rotational temperature of NO molecules with injection of the highly humid sampling gases and by comparing NO ion intensities at various relative humidities, it was found that no NO–H<sub>2</sub>O clusters were formed in our laser ionization instrument. Such little interference of water vapor shows an advantage over the ozone-chemiluminescence technique and a successful application of the laser ionization method into the atmospheric NO measurement.

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