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Detection of NOx Compounds by Laser-Induced Photofragmentation/ Photoionization Spectrometry

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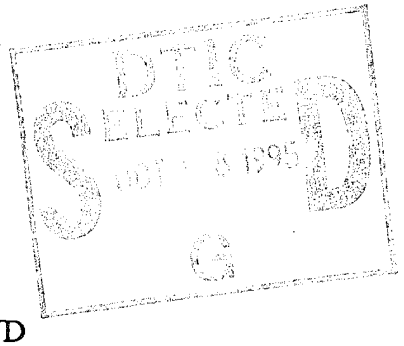

ARL-TR-873 September 1995

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	September 1995	Final, Apr 94–Jan 95

4. TITLE AND SUBTITLE

Detection of NOx Compounds by Laser-Induced Photofragmentation/ Photoionization Spectrometry

5. FUNDING NUMBERS

PR: 1L161102AH43

6. AUTHOR(S)

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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ATTN: AMSRL-WT-PC
Aberdeen Proving Ground, MD 21005-5066

8. PERFORMING ORGANIZATION REPORT NUMBER

ARL-TR-873

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Laser-induced photofragmentation/photoionization (PF/PI) spectrometry has been used to detect trace ambient concentrations of NO, NO_2, HNO_3, and CH_3NO_2. The method uses a single laser operating near 226 nm to both fragment the parent molecule and photoionize the resultant NO fragment by a 1+1 resonance-enhanced multiphoton ionization (REMPI) process via its $A^2\Sigma^+ \leftarrow X^2\Pi$ (0,0) band. Ion detection is accomplished by using a pair of miniature electrodes. Use of a single laser and optogalvanic ion detection greatly simplifies the instrumental requirements of the method and allows for real-time, *in situ* monitoring of the above-mentioned compound under ambient conditions. Analytical merits of the technique have been evaluated as a function of the sampling pressure and detection electrode voltage. Limits of detection (LODs) determined for NO, NO_2, HNO_3, and CH_3NO_2 are 1 ppbv, 22 ppbv, 5 ppbv, and 220 ppbv, respectively, using 10 μJ of pulse energy and an integration time of 10 s. Results of the study indicate that PF/PI spectrometry enables a simple instrument design to be used for sensitive measurements of these compounds. The high sensitivity is a reflection of the high efficiency of each of the PF and PI processes employed. The ability to use low fluences has the added benefit of suppressing nonresonant multiphoton ionization background signals. Sensitivities demonstrated for species in this study suggest the technique has excellent potential for measurements of NO_x ($NO + NO_2$) and NO_y, the concentration of total reactive odd nitrogen compounds.

14. SUBJECT TERMS

photofragment spectroscopy, lasers, NOx detection, Resonance-Enhanced Multiphoto Ionization (REMPI)

15. NUMBER OF PAGES
28

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

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ACKNOWLEDGMENTS

This work was supported by the U.S. Army Research Laboratory Director's Research Initiative Program, Strategic Environmental Research and Development Program (SERDP) on Cleanup, Army-713-94, and by the U.S. Army Corps of Engineers at the Waterways Experiment Station, SERDP: Cleanup, Army-729-94. Purchase of equipment through the Productivity Capital Investment Program (R. C. Sausa) and support from the National Research Council (NRC) Postdoctoral Research Program (J. B. Simeonsson and G. W. Lemire) is gratefully acknowledged.

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1. INTRODUCTION

The development of real-time, laser-based sensitive monitors of pollutants in the atmosphere (e.g., automobile exhaust, waste products of incineration) has been of great interest in recent years. For a partial list of representative studies, see references [1–7] and references cited therein. Of importance is the detection and monitoring of atmospheric nitrogen oxide compounds because of their key roles in atmospheric reaction cycles, such as the production of acid rain, photochemical smog, and regulation of species such as OH and ozone in the atmosphere [8–10]. Precise measurements of NO_x (NO, NO_2) and NO_y, the sum concentration of NO, NO_2, HNO_3, HNO_2, NO_3, N_2O_5, HO_2NO_2, organic nitrates (e.g., PAN, PPN) and other nitrocompounds, are crucial if a comprehensive understanding of the processes that determine the tropospheric levels of these compounds is to be achieved.

Presently, the measurement of NO, NO_2, and other nitrogen oxide compounds at background and polluted levels (pptv to ppbv) remains an important analytical challenge [11,12]. For NO, the most common method of detection is by chemiluminescent (CL) reaction with O_3. The reaction produces electronically excited NO_2^* whose emission intensity is proportional to the initial concentration of NO. Other measurement methods include absorption spectroscopy such as Light Detection and Ranging (LIDAR) and Differential Absorption LIDAR (DIAL) [13]. For NO_2, the Environmental Protection Agency (EPA) standard method for measurement is also by CL with ozone; however, prior to measurement, NO_2 must be quantitatively converted to NO by catalytic or photolytic means [11]. An alternative method is based on a different chemiluminescence reaction in which NO_2 reacts directly with a luminol solution (CL-luminol) at a wetted surface [11]. Other methods include tunable diode laser absorption spectrometry (TDLAS) [14], differential optical absorption spectrometry (DOAS) [15], opto-acoustic spectrometry [16], denuder methods, and wet chemical methods. Methods for detecting HNO_3 are generally limited to filtration techniques employing wet chemical and chromatographic detection of the filtrate [11,17], denuder techniques, and optical absorption spectrometries. The sensitivity of the previously mentioned methods for detecting nitrogen oxide compounds in the atmosphere usually requires that the signal be integrated over time or distance, resulting in a loss of temporal or spatial resolution. Furthermore, the selectivity of these methods is often insufficient to prevent interference effects for low level determinations.

Laser photoionization (LPI) spectroscopy was proposed as a method for detecting atmospheric pollutants as early as 1979. Briefly, the results of selected representative studies are as follows. Brophy

and Rettner first demonstrated the feasibility of the approach by using two-photon ionization to detect trace levels (ppmv) of aniline in air [18]. High sensitivity was also demonstrated by Frueholz, Wessel, and Wheatley who used two-photon ionization to detect naphthalene vapor at densities less than $10^7/cm^3$ [19]. Cool and Williams [3] have recently demonstrated the detection of chlorinated ethylenes using resonance-enhanced multiphoton ionization (REMPI) with time-of-flight mass spectrometry (TOFMS) [3,20,21]. Using this technique, they detected C_2Cl_4 at the 240 ppb level in a mixture prepared from automobile exhaust and a set of chlorinated hydrocarbons chosen as potential interferences. Recent studies by Lubman and coworkers [6] reveal that a resonance two-photon ionization (R2PI) at 266 nm can be used to detect trace levels (ppb) of substituted nitrobenzenes at atmospheric pressures by soft ionization with a minimum amount of fragmentation.

REMPI with TOFMS has also been employed by Syage and coworkers for the sensitive detection of atmospheric constituents [7]. The studies were conducted using air expansions for a variety of organophosphonates and organosulfides. Detection limits as low as 300 ppt were reported for dimethylsulfide using (2 + 1) REMPI near 391 nm corresponding to a resonance enhancement through the vibrationless level of the 3p Rydberg state at 195.31 nm. More recent studies in our laboratory have shown that molecular beam sampling with TOF spectrometry can be used to detect NO (8 ppb) at atmospheric pressures by (1 + 1) REMPI via its $A^2\Sigma^+ \leftarrow X^2\Pi$ (0,0) band near 226 nm [1]. The previously mentioned examples reveal that the sensitivity of LPI is high, and that it can be employed for detecting trace pollutants in various environments. However, a potential problem of LPI is that moderate to high laser intensities are required for the method to be analytically useful. This can result in the generation of intolerable background signals due to nonresonant ionization processes.

An alternate method to LPI for monitoring trace atmospheric constituents is laser photofragmentation (PF) with subsequent fragment detection. This method is particularly useful for fragile molecules such as NO_2 and HNO_3, which easily dissociate upon the absorption of UV-visible radiation or for molecules which lack absorption features in the UV-visible. Recently, a laser photofragmentation-fluorescence (LPFF) technique has been used to determine atmospheric levels of HNO_3 *in situ* [22,23]. An ArF laser served as the excitation/photolysis source while emission of the excited $OH(A^2\Sigma^+)$ fragment was monitored near 308 nm. By simultaneously measuring the HNO_3 with LPFF and conventional filter methods, an intercomparison of the two approaches demonstrated that LPFF provides good agreement with the filter methods. It has nearly the same sensitivity, yet allows significantly faster response times (nominal 75% reduction in integration times). Sandholm and coworkers have reported on a photofragmentation/laser-

induced fluorescence (PF/LIF) technique using a two-color excitation scheme for the detection of NO_2 [24] and NO [24,25]. The measurement of NO_2 was accomplished by the PF of NO_2 at 355 nm via an XeF excimer laser, and the resultant NO fragment was then quantitatively detected using two-photon LIF via the $A^2\Sigma^+ \leftarrow X^2\Pi$ (0,0) and $D^2\Sigma^+ \leftarrow A^2\Sigma^+$ (0,0) bands near 226 nm and 1.1 μ, respectively. The fluorescence signal resulting from $D^2\Sigma^+ \rightarrow X^2\Pi$ transitions was monitored in the 187–220 nm region. Limits of detection (S/N = 2) of 10 pptv for NO_2 (6 min of integration time) and 3.5 pptv for NO (2 min of integration time) were reported.

Recent studies in our laboratory have shown that an approach which combines laser-induced PF with LPI, photofragmentation/photoionization (PF/PI), can be used to detect NO and nitro-containing vapors with both high sensitivity and selectivity [1,2]. In one study, a single laser was employed to both fragment the parent molecule and photoionize the resultant characteristic NO fragment by a (1 + 1) REMPI process via its $A^2\Sigma^+ \leftarrow X^2\Pi$ (0,0) band near 226 nm [1]. The technique employed molecular beam sampling with time-of-flight mass spectrometric detection of the ions. At 226 nm, NO^+ ions were generated from a variety of nitrocompounds and were produced almost to the exclusion of any other ions such that the use of mass spectrometric detection was virtually unnecessary. By virtue of the selectivity and efficiency of the PF/PI mechanism employed, it was possible to achieve high sensitivities with relatively low laser pulse energies (< 100 μJ). For this reason, it was believed that the PF approach could be extended and applied equally to detecting trace levels of NO_x and NO_y at atmospheric pressures with nonselective ion detection. More recently, we have reported results of studies employing a PF/PI approach with nonselective ion detection for measuring ambient NO, NO_2 and HNO_3 under atmospheric conditions [26]. Similar studies of NO/NO_2 have been performed by Ledingham and coworkers [27].

In this report, we report further studies of a PF/PI spectrometry technique used to measure trace levels of NO, NO_2, HNO_3, and CH_3NO_2 under ambient conditions. Measurements are performed at pressures ranging from 5 to 760 torr with total (integrated) optogalvanic ion detection. The technique employs one laser to both photofragment the precursor molecule and ionize the characteristic NO fragment by a (1 + 1) REMPI process via its $A^2\Sigma^+ \leftarrow X^2\Pi$ (0,0) transition near 226 nm. Due to the high efficiency of PF and PI processes at 226 nm, only 10 μJ of pulse energies are required to achieve high-sensitivity measurements for the compound studied. The use of total ion detection and a single laser in the PF/PI approach minimizes complexity of the instrumentation and makes the current approach a feasible alternative to conventional methods. Evaluations of the sensitivity, selectivity, and signal-to-noise characteristics have

been performed. Results of this study are compared to those reported previously using similar PF/LIF techniques.

2. EXPERIMENTAL

Figure 1 is a diagram of the experimental apparatus used to perform the PF/PI studies. An excimer-pumped dye laser system with frequency doubling (Lumonics, HYPER EX-400, HYPER DYE-300, and HYPER TRAK-1000) was used to provide tunable UV radiation in the region of 224–228 nm (coumarin 450). The line width for wavelengths obtained by frequency doubling is approximately 0.11 cm^{-1} (fwhm). The pulse energies were nominally 10–100 μJ, and were monitored between measurements using a Joulemeter (Molectron Detector Inc., J4-05). The laser was operated at 10 Hz, and the output was directed using prisms to the photolysis/ionization sampling cell. Focusing of the laser was accomplished using a 250-mm lens (suprasil) external to the cell.

The photolysis cell consisted of a six-arm stainless steel cross with arm diameters of 4 cm. Quartz windows mounted on the cell provided optical access to the center of the cell where two planar electrodes served as ion/electron detectors. The electrodes were laboratory constructed from stainless steel square sheets, each approximately 1.5 cm^2 in area, and were separated by 0.63 cm. Collection voltages ranged from 0 to 800 V. The laser beam passed between the electrodes and was focused in the center of the electrode length to optimize ion/electron collection. The beam waist in the focal region is estimated to be 90 μm in diameter resulting in a maximum fluence of $10^8 W/cm^2$. An estimation of the effective volume probed by the laser is approximately $10^{-5} cm^3$ (equal to 2-mm path length and $6 \times 10^{-5} cm^2$ focal area).

NO and NO_2 samples were prepared by serial dilution of NO or NO_2 in air or N_2 (Matheson, > 99.999%). Nitromethane (Mallinckrodt, spectroscopic grade) and nitric acid, 70 weight-percent aqueous solution (Fisher, ASC grade), were sampled at their room temperature vapor pressures as trace species in buffer gases (air, N_2). HNO_3 comprises approximately 42% of the total vapor pressure above such a solution [28]. Samples were flowed through the photolysis cell to prevent build-up of photolysis products. Sample flows were nominally 500 cm^3/min. The photolysis cell volume was estimated to be 350 cm^3.

Signals from the detection electrodes were amplified using a current amplifier (Keithley 427, gain 10^5–10^7 V/A, time constant 0.01 ms) and then sampled by a boxcar averager with a gate of 15 μs. The

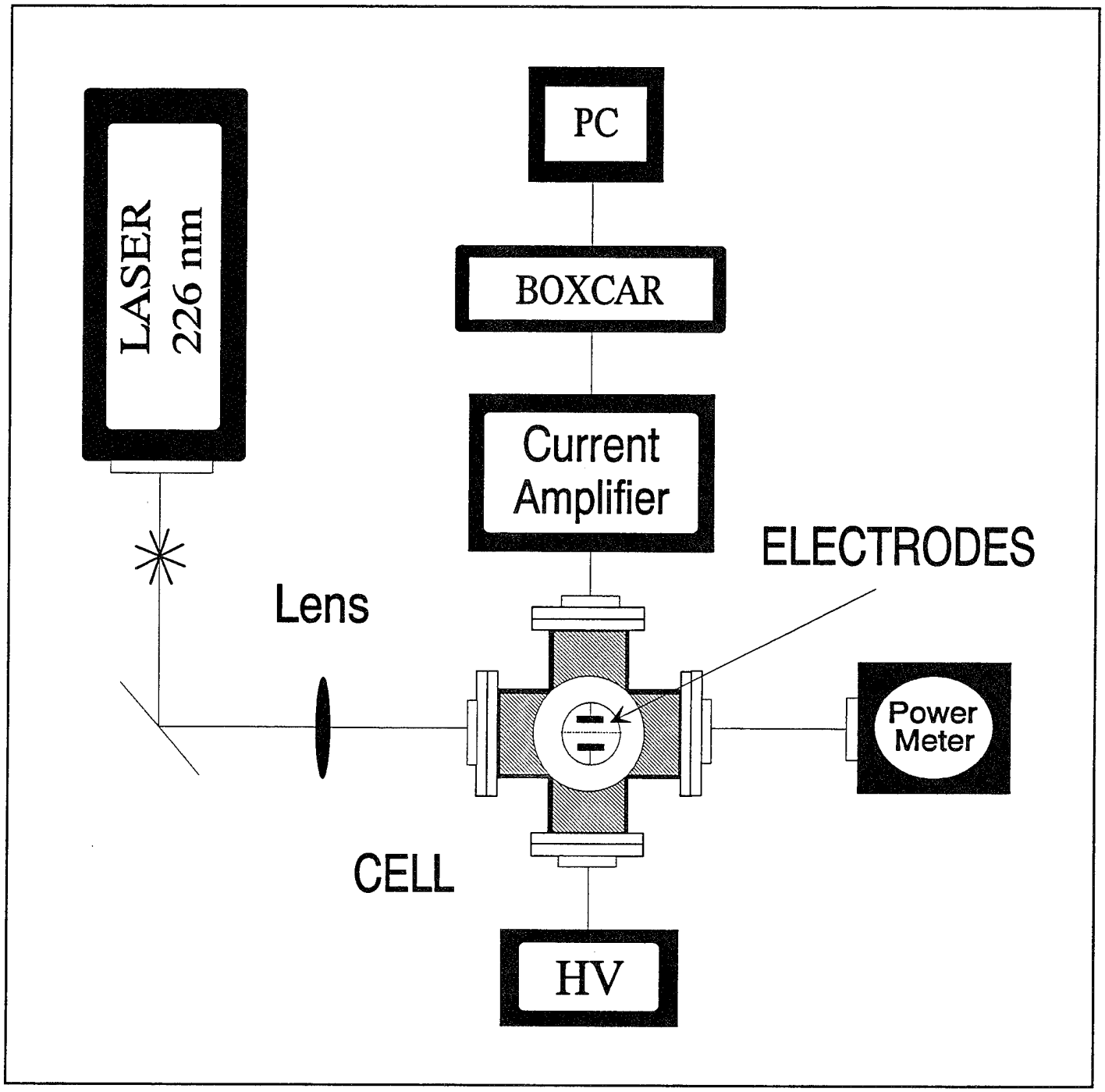

Figure 1. Diagram of experimental apparatus.

amplifier was connected as close as possible to the collection electrode output to minimize radio-frequency pickup along the signal cable. The signals were viewed in real-time on a 125 MHz digital oscilloscope (LeCroy 9400). The boxcar output was acquired by a personal computer for storage and subsequent data analysis. Signals were integrated for 10 s at 10 Hz with 100 shot averaging. The background noise was evaluated off resonance at 224.17 nm and was taken to be the standard deviation (σ) of 16 independent measurements. The minimum noise measured was 150 μV (referred to the boxcar input) which corresponds to 15 pA or approximately 1,400 electrons per pulse for a 15 μs gate width and 10^7 gain on the current-to-voltage amplifier. The limiting noise in this study is due to fluctuations in the nonresonant ionization background present in all the measurements.

3. RESULTS AND DISCUSSIONS

To optimize the experimental conditions and assess the analytical utility of the PF/PI technique, parametric studies of the signal-to-noise ratio (SNR) were performed. The measurement of cell pressure is an important experimental parameter which was studied for the following reasons: (1) the collisional dynamics affect the PF efficiency yielding ground state NO, (2) collisional ionization processes may determine both the production of electrons and NO ions, and (3) collisional broadening of the spectral features degrades the spectral resolution. Spectral resolution is improved at lower pressures, but, only at the cost of a corresponding reduction in sample density.

Figure 2 shows a plot of the SNR for NO and NO_2 (both approximately 6 ppmv) as a function of the cell pressure. It is important to note that the sample density changes with respect to the pressure; thus the plot represents the SNR for a fixed mixing ratio of gases (initially at 1 atm) over the pressure range indicated. Experimental conditions for these measurements were laser pulse energies of 10 μJ at 226 nm and a collection electrode voltage of 150 V. The plot shows that the optimum pressure is approximately 100 Torr for both NO and NO_2. It appears that at this pressure the favorable effects of reduced collisions and a lower background signal are balanced by dilution of the sample and loss of signal with further decreases in the pressure.

Figure 3 shows the ionization spectra for NO at 100 Torr, and NO_2 at 100 Torr and 760 Torr, respectively. The concentrations of NO and NO_2 are approximately 6 ppmv, and the collection electrode voltage is 150 V. A comparison of the ionization spectra for NO and NO_2 at 100 Torr shows that the spectral features are very similar and, in fact, correspond directly to the $A^2\Sigma^+ \leftarrow X^2\Pi$ (0,0) band of NO.

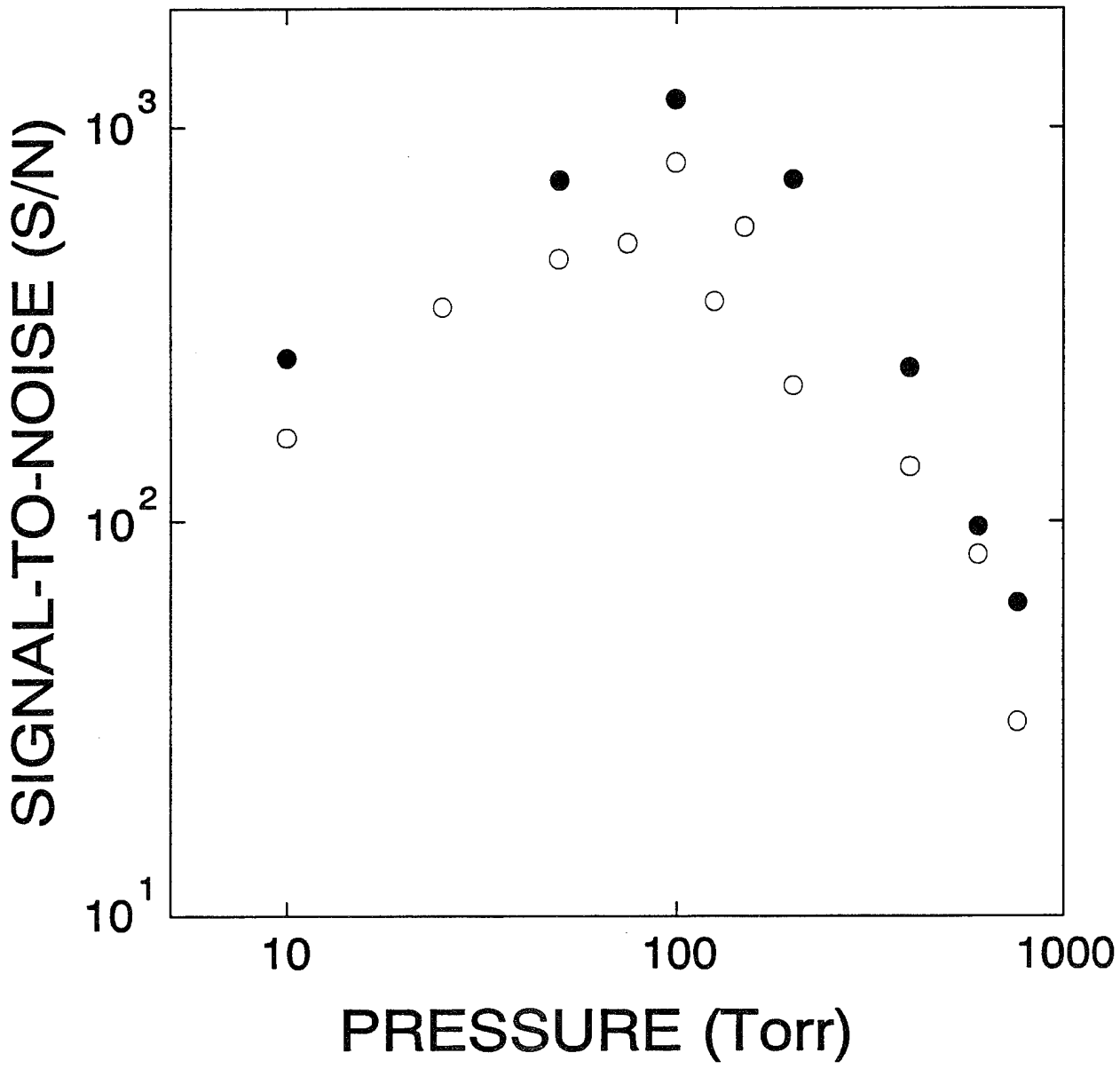

Figure 2. Plot of the signal-to-noise ratio (SNR) as a function of the measurement cell pressure for NO (filled circles) and NO_2 (open circles). Experimental conditions given in text.

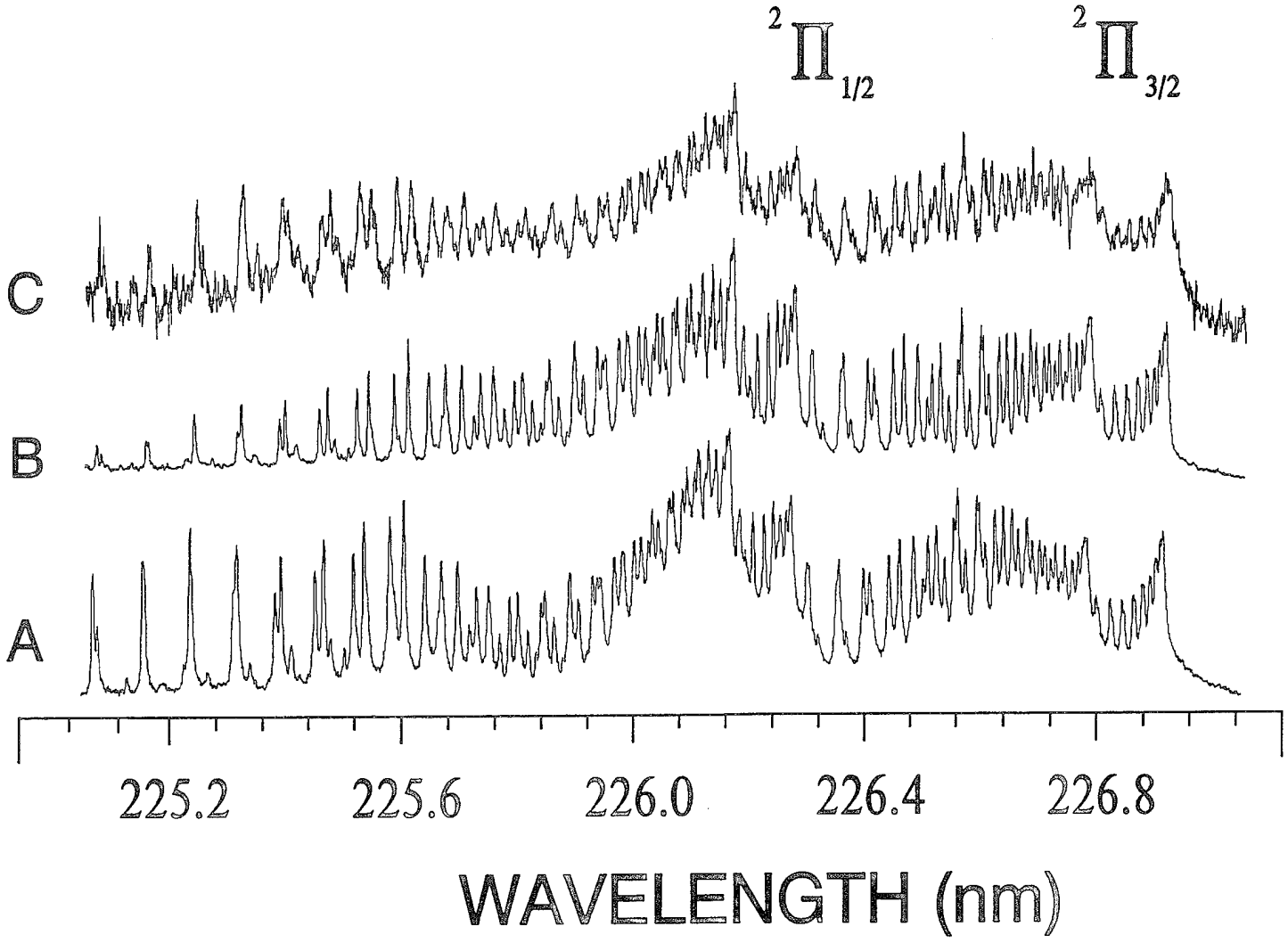

Figure 3. Ionization spectrum of 6 ppmv of NO at 100 Torr (a). Ionization spectra of NO produced by the 226-nm photolysis of 6 ppm of NO_2 at 100 Torr (b) and 760 Torr (c).

The two bandheads displayed in the spectra arise from the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ spin-orbit components of the NO ground electronic state. The NO_2 spectrum demonstrates the utility of the PF/PI approach for detecting NO_2 by monitoring the ionization of the NO photofragment. It is observed that the spectral resolution at 100 Torr is sufficient to differentiate individual rotational lines in the spectra. Ionization spectra for other nitrocompounds such as nitromethane and HNO_3 exhibit nearly identical spectral features in the region of 225–227.25 nm, as illustrated in Figure 4 which shows the spectrum for HNO_3.

The analytical selectivity of the present technique is solely reliant on the spectral selectivity of the laser, as ion detection in the approach is nonselective. Therefore, it is crucial that the technique possess sufficient spectral resolution such that characteristic spectral features of the NO fragment can be identified unequivocally. As shown in Figures 3 and 4, the vast majority of the rotational features are resolved to the baseline, confirming their identification. An ionization spectrum of air over the same region shows minimal background ionization above the noise. The ionization spectra collectively demonstrate both the spectral selectivity and the feasibility of the PF/PI approach for ambient measurements. The selectivity is demonstrated by the (1) the high spectral resolution available in the $A^2\Sigma^+ \leftarrow X^2\Pi$ (0,0) band at 100 Torr and (2) the high efficiency of the PF/PI approach at only modest pulse energies (10 μJ), which minimizes nonresonant multiphoton ionization interferences. Nonspecific ionization interferences resulting from broad absorptions are possible, but are unlikely for atmospheric constituents at these wavelengths. Moreover, if they exist, they will not exhibit the rotational structure observed for NO. Most ionization interferences can thus be accounted for simply by scanning the laser wavelength and measuring the signal on and off resonance.

Another study was performed to determine the relationship of the SNR to the collection electrode voltage. At a given pressure, the measured noise was little affected by changes in the voltage, and the SNR was primarily determined by the signal magnitude. The SNR as a function of the electrode voltage (0 to 800 V) was measured for NO at 5, 100, and 760 Torr, and NO_2 at 100 Torr using laser pulse energies of 10 μJ near 226 nm. At low voltages (0 to 250 V), the SNR increases linearly to a maximum value at 400 V, beyond which no improvement is realized. The plateau is indicative of saturation in the charge collection. Although the trend is the same at 5 Torr, it was not possible to raise the electrode voltage above 270 V due to instabilities and potential breakdown between the electrodes. It is noted that optimum conditions (i.e., voltage, pressure) determined in this study depend on experimental parameters characteristic of the instrumentation and conditions utilized. Due to the multiphoton nature of the PF/PI approach, it is anticipated that changes in the experimental parameters (e.g., laser pulse energy, laser focusing characteristics, or electrode spacing) could result in different optimum conditions.

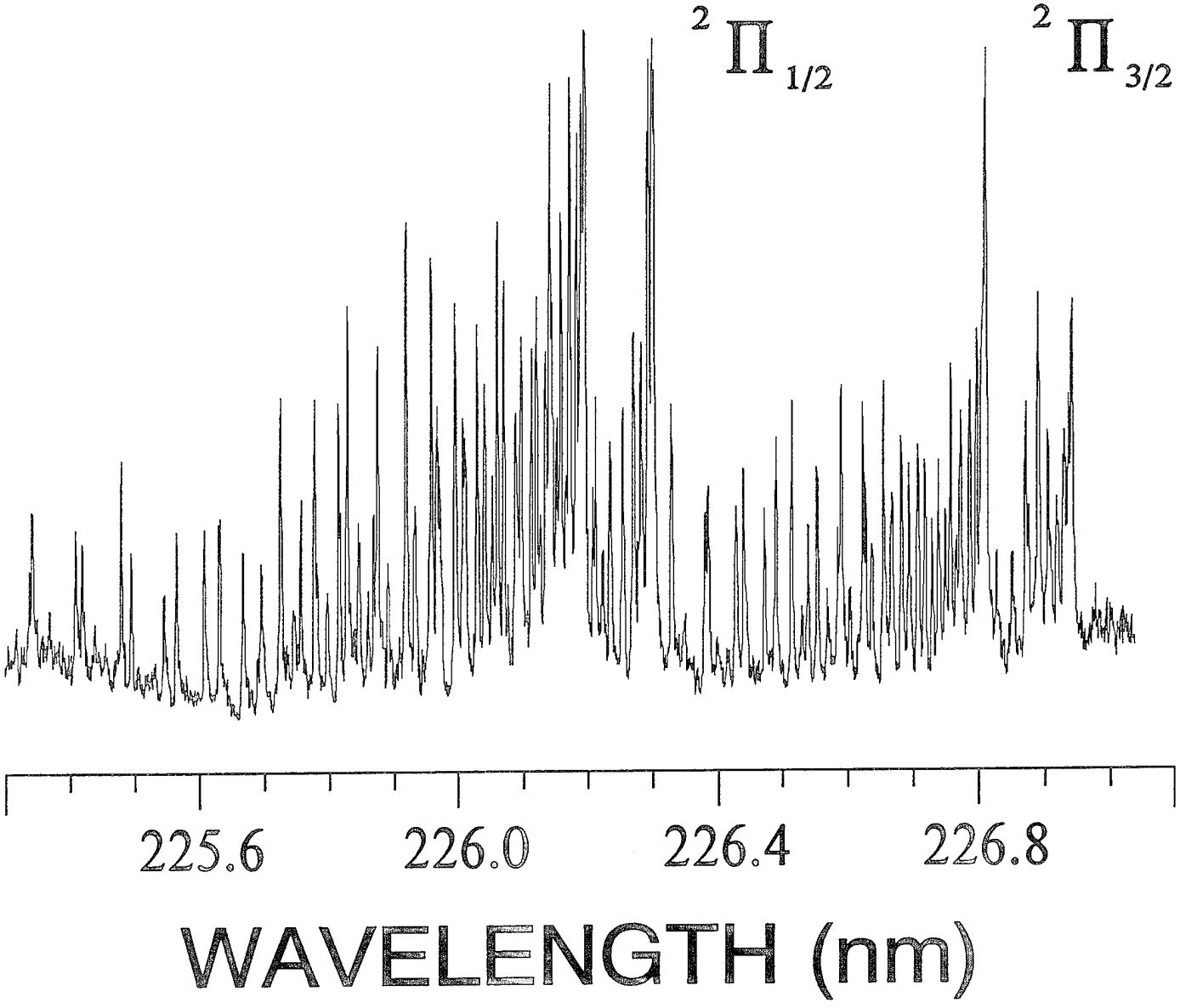

Figure 4. Ionization spectrum of NO generated by the photolysis of trace HNO_3 at 100 Torr.

Once the optimum conditions were established, analytical sensitivities were determined for NO, NO_2, HNO_3, and CH_3NO_2. Conditions for these determinations were 10 μJ of laser pulse energy at 226.29 nm (P_{11} branch, J" = 9.5–11.5), 100 Torr total pressure and 400 V on the detection electrodes. Limits of detection (LODs), reported as the concentration equivalent to 3σ, are given in Table 1 for the previously mentioned compounds. In addition to the current PF/PI results, LODs are given for the same compounds using the PF/PI technique with molecular beam sampling and TOFMS ion detection (MB/PF/PI) from Lemire, Simeonsson, and Sausa [1], and for a variety of PF/LIF techniques. Also shown in Table 1 are values (given in parentheses) corresponding to the number of analyte molecules estimated to be in the laser probe volume at the LOD. Comparison of concentration LODs as well as absolute numbers of molecules detected gives an indication of the detection capability of the PF/PI technique relative to the PF/LIF techniques. Using $10^{-5}cm^3$ as an estimate of the probe volume, a LOD of 1 ppbv for NO corresponds to 3×10^9 molecules per cm^3 or 30,000 NO molecules probed by the laser per pulse. Assuming 100% ionization and detection efficiency of the probed molecules, a detection limit of 1 ppbv is within one order of magnitude of the detection limit determined by the noise (15 pA equal to 1,400 electrons per pulse). This estimate of the absolute number of molecules detected is also within an order of magnitude of the minimum detectable concentration predicted using expressions given by Winefordner and Rutledge [29]. The linear dynamic range (LDR) of the technique extends from the LOD up to 10 ppmv for NO.

A comparison of the PF/PI results in Table 1 with MB/PF/PI indicates a nearly one order of magnitude increase in sensitivity. Although the sample density is much higher in the PF/PI measurement cell than in the molecular beam, collisional effects reduce the efficiency of signal production. Consequently, only a moderate increase in overall sensitivity is realized. The PF/PI apparatus does represent a considerable improvement over the molecular beam system, however, in terms of instrumental complexity and expense.

Shown in the last column of Table 1 are LODs for PF/LIF measurements of NO, NO_2, HNO_3, and CH_3NO_2. The PF/LIF measurements of NO and NO_2 both employ laser excitation of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of NO at 226 nm as the first excitation step [24,25,30], the same as is employed in the present studies. The HNO_3 measurements were performed using an ArF laser as the excitation/photolysis source [22,23]. Emission of the photolysis product OH is observed near 308 nm corresponding to the $A^2\Sigma^+ \rightarrow X^2\Pi_i$ transition and used to quantitate the HNO_3. Measurements of CH_3NO_2 were also performed using an ArF excimer laser as the excitation source with CH photofragment emission ($A^2\Delta \rightarrow X^2\Pi$) observed at 431 nm [31]. As seen in Table 1, the LODs for the various PF/LIF techniques are well into the pptv for NO, NO_2, and HNO_3 while the PF/PI results are in the low ppbv. The higher sensitivities for

Table 1. Limits of Detection (in ppbv) and Absolute Number of Molecules Detected for Signal-to-Noise of 3

	PF/PI[a]	MB/PF/PI[b]	PF/LIF
NO	1 (3.3E4)	8 (2,000)	0.05[c]/0.005[d] (6.9E9/1E8)
NO_2	22 (7.3E5)	240 (6E4)	0.015[e] (3.1E8)
HNO_3	5 (1.2E5)	—	0.03[f] (7.5E8)
CH_3NO_2	220 (7.3E6)	1,000 (2.5E5)	2.0[g,h] (1.6E8)

[a] This work; assuming $V = 10^{-5}$ cm^3.
[b] Reference [1]; assume $V = 5 \times 10^{-5}$ cm^3.
[c] Reference [29]; $V = 0.18$ cm^3.
[d] Reference [25]; $V = 1.2$ cm^3.
[e] Reference [24]; $V = 1.2$ cm^3.
[f] Reference [23]; $V = 0.45$ cm^3.
[g] Reference [30]; $V = 0.0375$ cm^3.
[h] Not sampled from atmosphere; equivalent mixing ratio assuming measurement at 100 Torr, final density of 4.2×10^9/cm^3 and S/N = 3.

PF/LIF are probably a consequence of longer integration times, which range from minutes for NO and NO_2 to one hour for HNO_3. Longer integration periods enhance the ultimate sensitivity of the PF/LIF method, although the relationship of the enhancement to the integration period cannot be accounted for directly. The integration time for each of the PF/PI results in the present work is 10 s.

3.1 NO and NO_2. Two different LODs are shown in Table 1 for the PF/LIF detection of NO. The first LOD corresponds to one-color excited fluorescence of NO [30], while the second corresponds to two-color excited fluorescence (first at 226 nm followed by 1.1 μm) [24,25]. Two-color excitation followed by emission detection at 187 nm results in at least an order of magnitude improvement relative to the one-color result. Both results are reported here for completeness; however, it is most appropriate in this study to compare the one-color PF/LIF to the PF/PI as the PF/PI only employs one-color excitation. A direct comparison of the two results indicates that the sensitivities are nearly within an order of magnitude despite a considerable difference in integration periods. For similar integration times, the sensitivities are likely to be more similar.

Due to the similarity of the approaches, it is worthwhile to compare the relative merits of PF/LIF and PF/PI for NO and NO_2. Both methods are capable of high sensitivity (ppbv to sub-ppbv) and both have high spectral selectivity, although the selectivity of the PF/LIF approach is somewhat higher as the detection step provides an additional degree of selectivity. Since the PF/PI technique employs total ion detection, analyte selectivity is determined solely by the laser excitation/ionization processes.

As presented in this study, the PF/PI technique is more simple to implement than comparable PF/LIF techniques as it only requires a single laser for simultaneous measurement of NO, NO_2 and other nitrocompounds. By comparison, the PF/LIF techniques of references [24] and [25] require two and three lasers for measurements of NO and NO_2, respectively. Furthermore, the arrangement of the PF/PI laser beam and detection apparatus (i.e., focusing the laser between two electrodes) is considerably less complex than the alignment of two spatially and temporally coincident laser beams in the viewing region of multiple photomultiplier tubes, as is required for PF/LIF. In short, instrumental cost and simplicity are important advantages of the current PF/PI technique.

An important fundamental distinction between PF/LIF and PF/PI methods is the difference in detection efficiencies. First, it is possible in ionization methods to collect practically 100% of the produced charges with each laser pulse (i.e., detection efficiencies approaching 1). This is demonstrated by the measured signals which are consistent with near unity collection/detection efficiency using an estimated probe volume of $10^{-5}cm^3$. In LIF, the fluorescence photons are emitted isotropically and detection efficiencies are nominally 10^{-4}. The difference in detection efficiencies of the two approaches is clearly evident when comparing the absolute numbers of molecules detected at the LOD (see Table 1). Approximately 10^4 NO molecules are required for the PF/PI technique, whereas 10^8 NO molecules are required for the two-color (PF/LIF) technique, a difference of about four orders of magnitude. Normalized to the same concentration, the difference is approximately six orders of magnitude. Furthermore, collional quenching and/or reactions of electronically excited NO with atmospheric gases is more prominent in LIF than ionization methods. The radiative lifetime of $NO(A^2\Sigma^+)$, approximately 200 ns, is much longer than the time required for photon absorption of this state leading to ionization, typically picoseconds. Thus, the electronically excited state of NO is preserved until ionization. Above the ionization threshold, ionization occurs typically in the subpicosecond time scale. For these reasons, it is believed that the PF/PI approach has great analytical potential and could prove to be superior to PF/LIF for rapid measurements of nitrogen oxides at the pptv level.

Presently, the NO and NO_2 PF/LIF techniques possess an important advantage over the PF/PI approach. By employing two-step excitation and fluorescence detection at 187 nm, Bradshaw and coworkers have reportedly achieved signal limited (SL) measurement conditions in their determinations of NO and NO_2 for measurement times of up to 5 min [24,25]. In essence, SL operation means that there are so few (or no) background counts over the measurement period such that the sensitivity is limited by the photon statistics of signal counts. This is an attribute which enhances the ultimate sensitivity of the method, since under SL conditions the LOD improves linearly with the integration period. Under more typical shot noise limited conditions, the LOD improves with only the square root of the integration period. The present PF/PI technique is not signal limited due to detectable background ionization signals. A more careful study of the limiting noises is required to determine whether SL conditions are achievable by the PF/PI method.

3.2 HNO_3. Using PF/PI, the LOD for HNO_3 is 5 ppbv. This compares favorably with those of NO and NO_2 at 1 ppbv and 22 ppbv, respectively. These results indicate that the 226-nm photolysis of HNO_3 yielding ground state NO is more efficient than that of NO_2. The excitation of NO_2 at 226 nm corresponding to the $B(^2B_2) \leftarrow X(^2A_1)$ transition results in predissociation into $NO(X^2\Pi)$ and $O(^1D)$ (see reference [1] and references cited therein). For HNO_3, the UV photolysis is generally understood to occur by way of the following reaction,

$$HNO_3 \xrightarrow{h\nu} NO_2 + OH \qquad (1)$$

with a quantum efficiency approaching one in the wavelength range of 200–315 nm [32]. Subsequent photodissociation of ground state NO_2 at 226 nm would then yield $NO(X^2\Pi)$. However, this two-step mechanism is not consistent with our results, which show that the sensitivity for HNO_3 is significantly higher than that for NO_2. If this mechanism was responsible for the production of NO, then the sensitivity of HNO_3 would be at best equal or less than that for NO_2.

In a recent study on the 248-nm photolysis of HNO_3 in a flow tube using flash kinetic spectroscopy, Schiffman, Nelson, and Nesbitt [33] have concluded that other photodissociative pathways are energetically possible for wavelengths less than 250 nm in addition to reaction [1]. These pathways are represented by the following reactions:

$$HNO_3 \xrightarrow[<239\ nm]{h\nu} NO(X\,^2\Pi) + OH(X\,^2\Pi) + O(^3P) \quad (2)$$

$$HNO_3 \xrightarrow[<245\ nm]{h\nu} HONO + O(^1D) \quad (3)$$

The HONO intermediate has absorption features in the range of 195–270 nm and can further fragment to yield NO and OH. Kenner et al. have invoked reaction (3) to explain the production of $NO(X^2\Pi)$ and $OH(A^2\Sigma^+)$ for the 193-nm photolysis of HNO_3 by way of the HONO intermediate [34]. Energetically, reaction (2) and the two-photon mechanism proposed by Kenner et al. are accessible with 226-nm radiation via the 260-nm band of HNO_3 [35] assigned as a n-π^* transition localized on the nitro group [36]. This suggests that the high sensitivity of the PF/PI approach may be due to the direct formation of NO via reaction (2) and/or the production and subsequent photolysis of the HONO intermediate, rather than reactions (1) followed by the predissociation of NO_2. These two mechanisms are consistent with our results. However, other mechanisms, particularly those that involve electronically excited species, cannot be ruled out.

3.3 $\underline{NO_y}$. The concentration of total reactive odd nitrogen, NO_y, is a quantity that is necessary to establish primary contributors to the total atmospheric nitrogen budget of a given region [37]. NO_y measurements are currently performed using a chemiluminescence (CL) instrument as is used to measure NO or NO_2 [11,37]. The PF/PI method is an excellent candidate for NO_y determinations as it is highly sensitive to NO and can photolytically generate NO from a variety of NO_y. Furthermore, it is not sensitive to the chemical interferents (i.e., NH_3, HCN, sulfur and chlorine species) that are problematic when using catalytic converters with CL detection [11]. Unlike CL, zeroing in the PF/PI method is accomplished easily by tuning the laser to a nonresonance wavelength. With refinement of the current technique, it is projected that PF/PI (possibly combined with a photolytic converter) would be capable of detecting NO_y at the pptv level with rapid (s) response times.

3.4 $\underline{N_2O}$. Nitrous oxide (N_2O), which is not a constituent of NO_y, is the most abundant nitrogen oxide compound in the troposphere and is an important greenhouse gas. Although it is relatively inert in

the troposphere, N_2O is readily photolyzed in the stratosphere and becomes a major source of NO_x [8]. It was therefore of interest whether the PF/PI technique employing 226-nm radiation is sensitive to N_2O, as this would present a major chemical interference for trace detection of NO_x and NO_y. While N_2O absorbs at 226 nm, absorption in this region primarily results in the products N_2 + O [38,39], with much lesser production of NO + N. Attempts in this study to detect NO^+ ions from even highly concentrated samples of N_2O in air were unsuccessful using the PF/PI approach, indicating that N_2O will not be an interference at typical tropospheric levels.

4. CONCLUSIONS

The analytical utility of the PF/PI technique has been demonstrated for trace level determinations of NO, NO_2, HNO_3, and nitromethane in air. The technique employs direct atmospheric sampling and total ion detection in a simple cell. By using a single laser operating at 226 nm, successive PFs and a (1 + 1) PI process can be performed with only 10 μJ of laser pulse energy due to the highly favorable nature of the individual processes at this wavelength. Limits of detection in the low parts-per-billion by volume range have been achieved for all four compounds with instrumental response times of 10 s, making the PF/PI method competitive with standard methods of NO/NO_2 detection (i.e., CL methods). It is anticipated that sub-ppbv sensitivities can readily be attained with refinements to the current apparatus. The PF/PI technique is ideally suited to determinations of NO_x. It is also projected that the technique can be adapted for rapid and sensitive determinations of NO_y. With steady improvements in the size, cost, and performance of tunable lasers (especially solid-state), the PF/PI approach is certain to become an attractive alternative to CL and other standard methods presently used for measurements of nitrogen oxides.

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