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(2+2) Resonance-Enhanced Multiphoton Ionization (REMPI) and Photoacoustic (PA) Spectroscopic Detection of Nitric Oxide (NO) and Nitrogen Dioxide (NO_2) Near 454 nm

by R. C. Sausa
and R. L. Pastel

ARL-TR-1418 July 1997

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ARL-TR-1418 **July 1997**

(2+2) Resonance-Enhanced Multiphoton Ionization (REMPI) and Photoacoustic (PA) Spectroscopic Detection of Nitric Oxide (NO) and Nitrogen Dioxide (NO_2) Near 454 nm

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Abstract

Trace concentrations of NO and NO_2 are detected with a dye laser operating near 454 nm. NO is detected by a (2 + 2) resonance-enhanced multiphoton ionization process by means of NO A $^2\Sigma^+$–X $^2\Pi(0, 0)$ transitions with miniature electrodes, and NO_2 is detected by a one-photon absorption photoacoustic process by means of NO_2 $\tilde{A}'\ ^2B_1(0, 8, 0)$ – $\tilde{X}\ ^2A_1(0, 0, 0)$ transitions with a miniature microphone. Rotationally resolved excitation spectra show that the spectral resolution is sufficiently high to identify these species at 1 atm. The technique's analytical merits are evaluated as functions of concentration, pressure, and laser intensities. Low laser intensities favor NO_2 photoacoustic detection whereas high laser intensities favor NO ionization. Limits of detection (signal-to-noise ratio 3) of 160 parts in 10^9 for NO and 400 parts in 10^9 for NO_2 are determined at 1 atm for a 10-s integration time. Signal response and noise analyses show that three decades of NO/NO_2 mixtures can be measured with a computational relative error in concentration that is three times the relative error in measuring the NO and NO_2 signals.

ACKNOWLEDGMENTS

This work was supported by the U.S. Army Research Laboratory Director's Research Initiative (ARL-DRI) and the Strategic Environmental Research and Development Program (SERDP) on cleanup, ARMY-713-94 and ARMY-729-94. Purchase of equipment through the Productivity Capital Investment Program (R. C. Sausa) and the ARL-SCEEE Postdoctoral Research Fellowship Program (R. L. Pastel) is gratefully acknowledged.

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1. INTRODUCTION

There is a growing interest in laser-based analytical techniques for remote or *in situ* trace detection of nitric oxide (NO) and nitrogen dioxide (NO_2) [1, 3]. Much of this interest stems from concerns related to public heath and the environment. These compounds play key roles in catalytic ozone destruction and in acid rain and photochemical smog formation. NO and NO_2 are hazardous pollutants emitted predominantly from motor vehicle exhaust and stationary sources, such as electric utilities and industrial boilers. The U.S. Federal Environmental Protection Agency (EPA) has established a 25-ppm National Ambient Air Quality Standard (NAAQS) threshold limit for NO with concentrated exposures not to exceed 100 ppm for 15 min [4]. NO_2 is estimated to be 30 times more toxic than NO [4]. The detection of NO and NO_2 is also important to laser photofragmentation/fragment detection techniques being developed for the chemical analysis of propellants and explosives because they are generated in the photolysis of many energetic materials [5–7].

Laser photoacoustic (PA) and resonance-enhanced multiphoton ionization (REMPI) spectroscopy are sensitive techniques for NO and NO_2 trace detection. PA detection is based on sensing the pressure wave generated by the heat released from an excited analyte caused by collisional deactivation. PA detection is particularly effective at high pressures for weak fluorescers or species that predissociate with laser absorption. High sensitivity and selectivity can be achieved using a narrow band, high-power pulsed laser. REMPI detection is based on sensing the ion signal following excitation of the analyte. The ionization process is enhanced if there are electronic states resonant with the energy of one or more of the photons. Ion detection can be accomplished using a mass spectrometer or a pair of miniature electrodes. With electrode-based detection, the bulky mass spectrometer is no longer needed. However, species selectivity is then based solely on excitation wavelength. In both PA and REMPI detection, using a laser frequently increases the response without increasing the noise.

The analytical application of PA for NO_2 detection using visible laser radiation has been reported. Fried measured the 488-nm PA detection limit of NO_2 in NO, N_2, H_2O and O_2

matrices with identical sensitivities of 5 ppb (S/N=1) in all matrix gases except O_2 [8]. Oxygen decreased the NO_2 signal by 20% because of electronic energy transfer between the two molecules. From low-resolution excitation NO_2 spectra recorded in the range 480–625 nm, Claspy et al. [9] estimated a 4-ppb sensitivity (S/N=1) at 600 nm for a laser power of 1 W [9]; Terhune and Anderson measured NO_2 sensitivities better than 0.1 ppb using a 514.5-nm Ar^+ ion laser [10]; and Angus et al. estimated a 10-ppb NO_2 detection limit from low-resolution cw dye laser excitation scans over the range of 580-610 nm [11].

Recently, we have studied NO and NO_2 detection by ultraviolet (UV) laser spectroscopy [12, 3]. NO was detected by (1+1) REMPI via its $A^2\Sigma^+$-$X^2\Pi$ (0,0) transitions near 226 nm, while NO_2 was detected by laser photofragmentation with subsequent fragment NO ionization also using 226-nm radiation. The NO and NO_2 limits of detection (LOD) at 100 Torr were 1 and 22 ppb, respectively, for a S/N=3, a laser energy of 10 μJ, and 10-s integration time [12]. The two species could not be differentiated, however, because only the total NO ion signal was measured.

The detection and discrimination of NO and NO_2 by a single, laser-based apparatus are important analytical challenges. Part of the challenge stems from NO and NO_2 absorbing in different spectral regions. NO_2 absorbs in the visible; whereas, NO absorbs in the UV. NO_2 predissociates at wavelengths less than 400 nm making ionization and PA detection difficult. Although both NO and NO_2 absorb in the infrared, few lasers can be tuned in the region where both species absorb. Also, H_2O is a major spectral interferant in the infrared.

In the present study we employ a single laser operating near 454 nm to detect trace NO and NO_2 concentrations in N_2 at atmospheric pressure by (2+2) REMPI and PA spectroscopy. Rotationally resolved excitation spectra are recorded and characterized. To the best of our knowledge, this is the first time that a high-resolution NO_2 visible PA spectrum has been reported. The effects of laser energy, pressure, and species concentration on the REMPI and PA signals are determined and discussed. A single laser coupled to a pair of miniature electrodes and a

microphone minimizes the instrumental complexity and makes the technique attractive for NO and NO_2 detection.

2. EXPERIMENTAL

The experimental schematic is depicted in Figure 1. An excimer-pumped dye laser (Lumonics, HYPER EX-400, and HYPER DYE-300) operating at 10 Hz with a line width of ~0.07 cm^{-1} was used to excite NO or NO_2 around 454 nm. The energy per pulse was typically 15 mJ with better than 10% shot-to-shot variation, and the pulse duration was ~20 ns (FWHM). A calorimeter (Scientech) and Joulemeter (Molectron Detector, J4-05) monitored the laser energy. The laser beam diameter was 3 mm. Two 5-cm-diameter quartz lenses with focal lengths of 12 and 50 cm focused the laser beam for REMPI detection. The laser beam was not focused for PA detection.

The sample cell was a six-arm (4-cm diameter) stainless steel cross. Opposing arms with quartz Brewster windows provided optical access to the sample. Two other arms provided access for a pair of laboratory-constructed stainless steel electrodes and a directional electret condenser microphone (Radio Shack 270-090), both mounted on separate vacuum feedthrough flanges. A mechanical pump drew the sample gas through the cell, and a needle valve upstream of the cell regulated the flow rate. The sample gas pressure was varied to 1 atm and monitored with a capacitance manometer (Edwards 600A-1000T-R16-H21X). Various concentration of NO and NO_2 were prepared by serial dilution of 0.1% NO in N_2 or 500-ppm NO_2 in N_2 with N_2 buffer gas. All the gases were obtained from Matheson with a purity of >99.999%. The NO measurements were recorded using N_2 as a diluent instead of air to eliminate reduction of NO by the $2NO + O_2 \rightarrow 2NO_2$ three-body reaction. At room temperature, 50% of NO (100 ppm) oxidizes to NO_2 in 40 min, the time required for a typical experimental run. The NO_2 measurements were also recorded using N_2 buffer gas for experimental consistency. Samples were flowed through the cell to prevent accumulation of photolysis products.

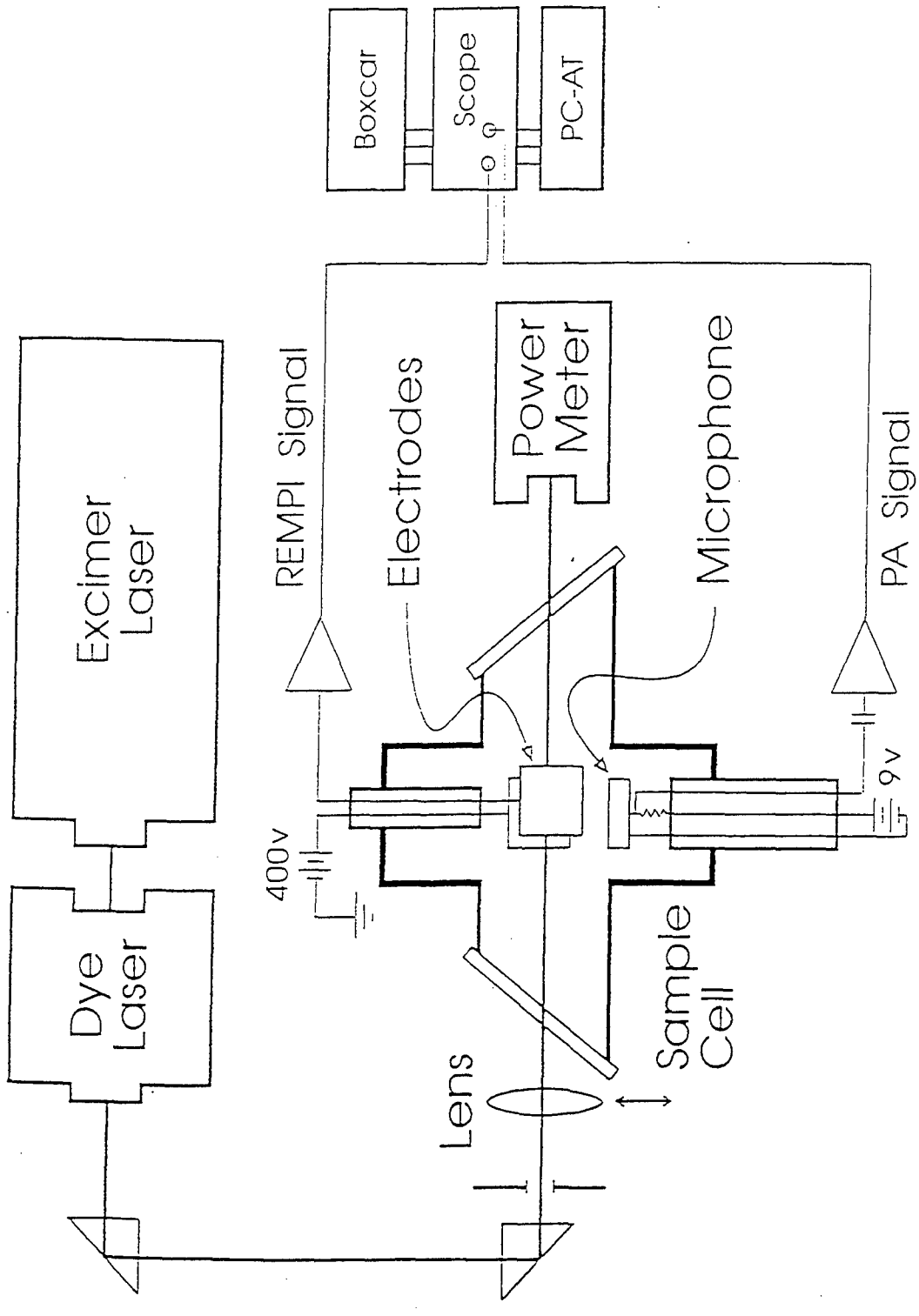

Figure 1. Schematic of the experimental apparatus.

For REMPI detection, the laser beam was focused at the center of two square electrodes (1.25 × 1.25 cm) separated by 3 mm. The collection voltage was 400 V for all measurements. The ion signal was amplified by a current amplifier (Keithly 427, gain 10^5–10^6 V/A, time constant 0.01 ms) and displayed on a 125-MHZ digital oscilloscope (LeCroy 9400). For PA detection, the electrodes were removed from the laser-interaction region and a small microphone was positioned 2–3 mm from the laser beam. The focusing lens was also removed from the beam path. The microphone was encased in a small cylinder (9-mm diameter by 6 mm long) and had a 3-mm^2 active area. Its frequency response was flat from 20 to 1500 Hz. A 9-V battery and 1-kΩ resistor biased the microphone, and a 3.3-μF capacitor coupled the signal to the current amplifier. Signals from the amplifier were then directed to the digital oscilloscope. A PC-AT computer interfaced to a gated integrator (Stanford Research Systems SR250) with 3-shot averaging recorded and stored the spectra. The sensitivity signals were integrated for 10 s at 10 Hz for 100-shot averaging and read from the oscilloscope. The background noise was measured with the laser operating at the excitation frequencies and N_2 flowing through the sample cell. Twenty independent measurements of the noise with 100-shot averaging were made. The limiting noise in this study is due to fluctuations in background ionization and laser energy for the photoionization detection and window vibrations for the PA detection.

3. RESULTS AND DISCUSSION

A potential-energy diagram that shows the physical processes in NO_2 PA and NO (2+2) REMPI detection is presented in Figure 2. In PA detection, 454-nm radiation excites NO_2 into the $\tilde{A}'$ ($^2B_1$) or $\tilde{A}$ ($^2B_2$) states. Radiationless deactivation of excited NO_2 by inter- and intra-molecular interactions causes heat release inducing a pressure wave that generates the PA signal. Loss mechanisms for PA detection include ionization, dissociation, energy transfer, and fluorescence. PA detection is favored over ionization or dissociation at low laser intensities. At low pressures, fluorescence competes effectively with PA detection. The 454-nm laser excitation of NO_2 results in both discrete fluorescence and continuum emission [13–15]. The continuum emission is prompt (<100 ns) and decays by intramolecular radiationless transitions [14]. Longer time-scale quenching mechanisms include intermolecular and buffer gas radiationless collisions.

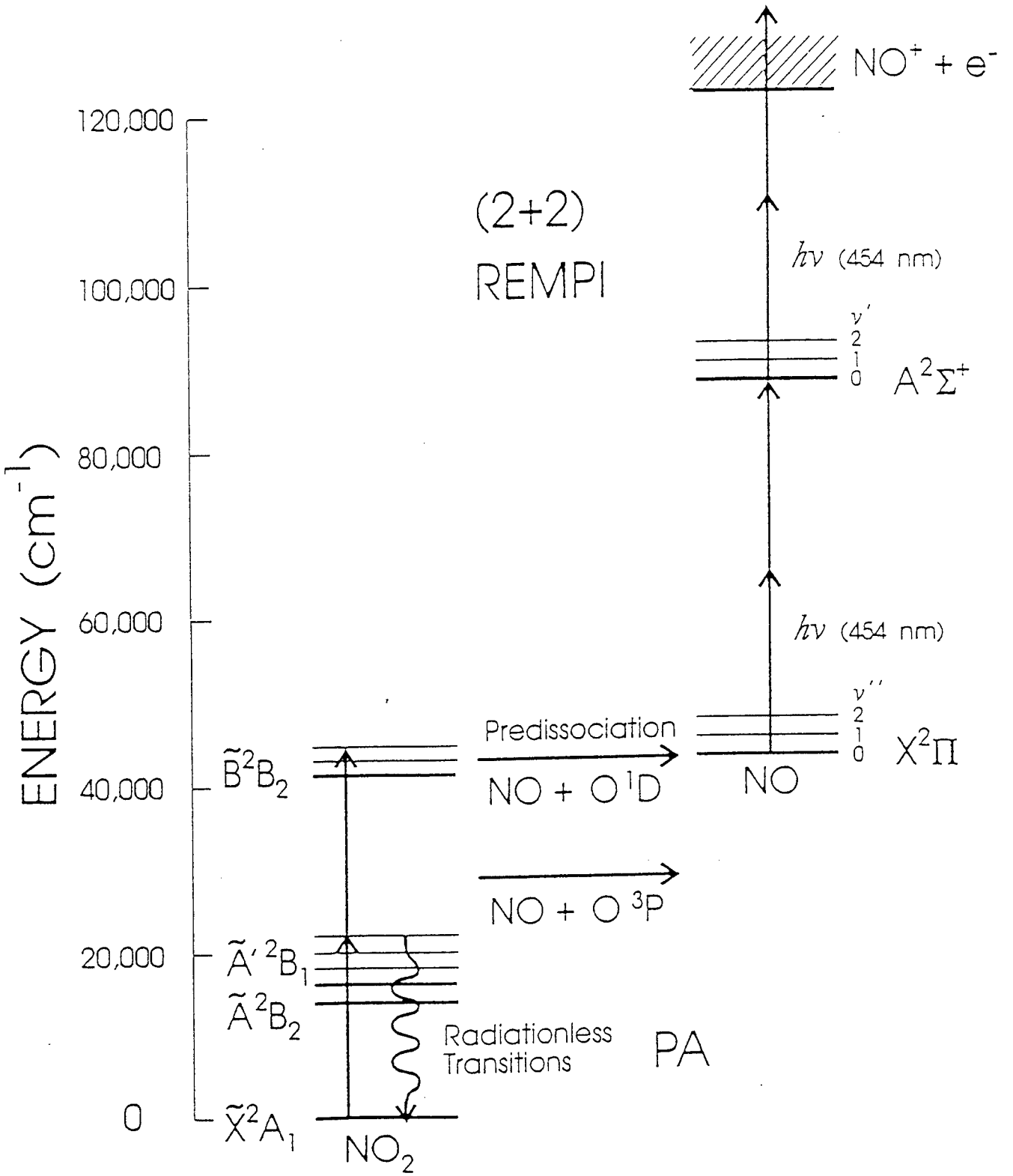

Figure 2. Partial potential energy diagram of NO and NO_2.

In the visible and at low laser intensities, NO has a small absorption coefficient, hence, no PA response. At high laser intensities, NO is ionized by 4-photon absorption, (2+2) REMPI. The ionization process is enhanced at 454 nm by 2-photon resonance with the $A^2\Sigma^+$ state. At high laser intensities NO_2 also contributes to the "ambient" NO REMPI signal because it photodissociates. As shown in Figure 2, two 454-nm photons excite NO_2 into the $\tilde{B}(^2B_2)$ state. Electronically excited NO_2 then quickly [16] (<40 psec) predissociates [17] into NO $X^2\Pi + O\ (^3P)$ and NO $X^2\Pi + O\ (^1D)$. For the NO $X^2\Pi + O(^1D)$ dissociation pathway, NO is predominantly formed in the $\upsilon''=0$ and 1 vibrational levels because of intramolecular relaxation in the intermediate $\tilde{A}'$ and $\tilde{A}$ states that are resonant with the energy of one 454-nm photon [18]. As a result, the nascent NO ($\upsilon''=0$) from NO_2 photoionizes just like ambient NO ($\upsilon''=0$).

NO (2+2) REMPI and NO_2 PA laser excitation spectra were recorded between 440–470 nm at various concentrations and pressures. Presented in Figure 3 are typical NO_2 PA and NO REMPI spectra recorded in the 453.5–454.5-nm region. The laser was focused for NO REMPI detection, but not for NO_2 PA detection. The concentrations of NO and NO_2 in N_2 were 95 and 65 ppm, respectively, and the cell pressure was approximately 1 atm. The prominent features of spectrum A are attributed to the $P_{22}+O_{12}$, $P_{12}+O_{22}$, and O_{12} branches of the $A^2\Sigma^+$-$X^2\Pi$ (0,0) band. These features are the result of 2-photon selection rules governing the (2+2) NO REMPI by means of the resonant $A^2\Sigma^+$ state. Thus, the visible REMPI spectrum exhibits strong, main O and S branches ($\Delta J=\pm2$) in addition to the P, Q, and R branches ($\Delta J=0,\pm1$) observed in 226-nm (1+1) NO REMPI. An enhancement of the rotational lines of the O_{12} branch (e.g., J = 10.5) that is due to double resonance processes is not observed as in low-pressure environments since these processes are quenched at 1 atm. The O and S branches enhance the NO REMPI selectivity because they contribute additional "fingerprints" for NO identification. In addition, the O_{12} branch is red-shifted from all the other congested branches and exhibits a larger rotational energy spacing. These features are particularly attractive for NO detection at atmospheric conditions because collisions degrade the spectral resolution.

The visible spectrum of NO_2 is complex due to Coriolis and Renner-Teller rovibronic interactions. Imasaka et al. characterized the vibrational levels of NO_2 $^2B_1$ and $^2B_2$ states by

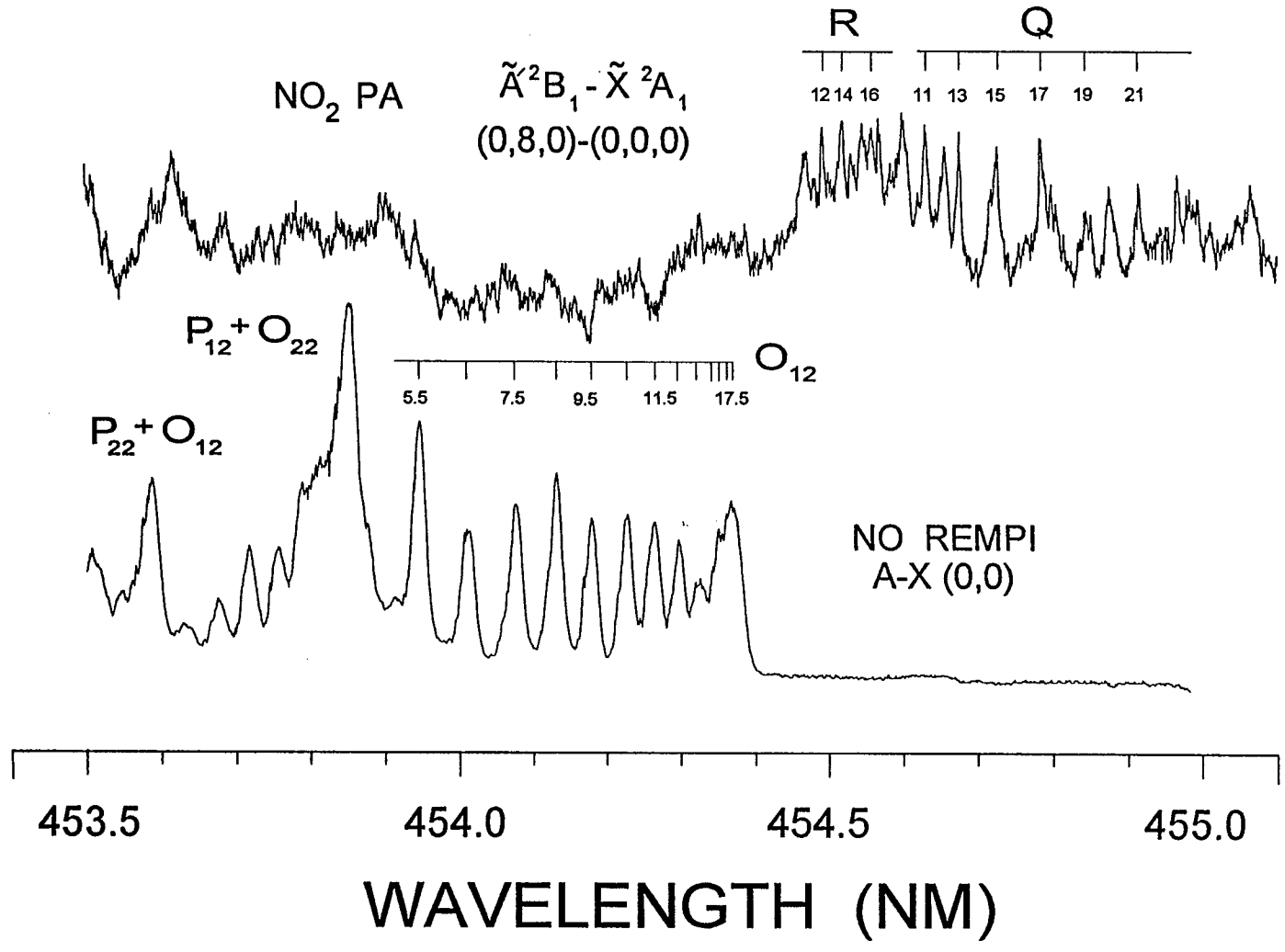

Figure 3. Laser excitation spectra of NO and NO_2 obtained by (2+2) REMPI and PA spectroscopy, respectively, near 454 nm.

time-resolved spectroscopy [19]. Based on their work, and the works of Hardwick [20] and Douglas and Huber [21], we assign the sharp features of the NO_2 to P and Q rotational lines of the $\tilde{A}'\,^2B_1$-$X\,^2A_1$ [(0,8,0)-(0,0,0)] band. Other vibrational bands with higher intensities were observed, but the (0,8,0) band was studied because of its proximity to the NO O_{12} branch. As shown in Figure 3, the rotational resolution at 1 atm is sufficiently high to discriminate NO and NO_2 by laser wavelength excitation.

Presented in Figure 4 is the laser energy dependence of NO_2 PA, NO REMPI, and NO from NO_2 REMPI signals with 12- and 50-cm lenses. Fitting the data to powers of the laser energy yields powers of 1 for NO_2 PA, 3.9 for NO REMPI when a 50-cm lens is used, and 1.9 and 3.0 for NO and NO_2 REMPI, respectively, when a 12-cm lens is used. The NO_2 PA signal response is approximately linear with laser energy and suggests an unsaturated 1-photon absorption process, as expected for PA detection. The NO (2+2) REMPI quartic dependence indicates a 4-photon process at low laser intensity; whereas, the near quadratic dependence indicates saturation from the intermediate $A^2\Sigma^+$ state into the ionization continuum subsequent to 2-photon absorption. A geometric effect caused by strong conical focusing of the laser beam is ruled out, as it would yield a 3/2-power dependence [22]. The REMPI response using the 12-cm lens was 100 times greater than that using the 50-cm lens. Thus, the 12-cm lens was used for the pressure and LOD studies. Also, the laser beam was not focused for the NO_2 PA studies because focusing enhanced multiphoton dissociation and decreased the signal.

Figure 5(a) shows the N_2 buffer gas pressure dependence on NO_2 PA and NO REMPI signals at a fixed NO or NO_2 density. The NO_2 PA signal increases until around 400 Torr and then levels off. The PA signal is proportional to kM/(kM+A), where A is the spontaneous transition rate, k is the quenching rate constant, and M is the density of the buffer gas [23]. Thus, a leveling off occurs when the radiationless quenching rate, kM, is greater than radiation rate, A. For NO REMPI, the signal increases to a maximum near 100 Torr and then decreases nonexponentially. The increase is due to charge amplification by N_2; whereas, the decrease is due to NO $A^2\Sigma^+$ quenching by N_2 and three-body recombination of NO^+, N_2, and electrons.

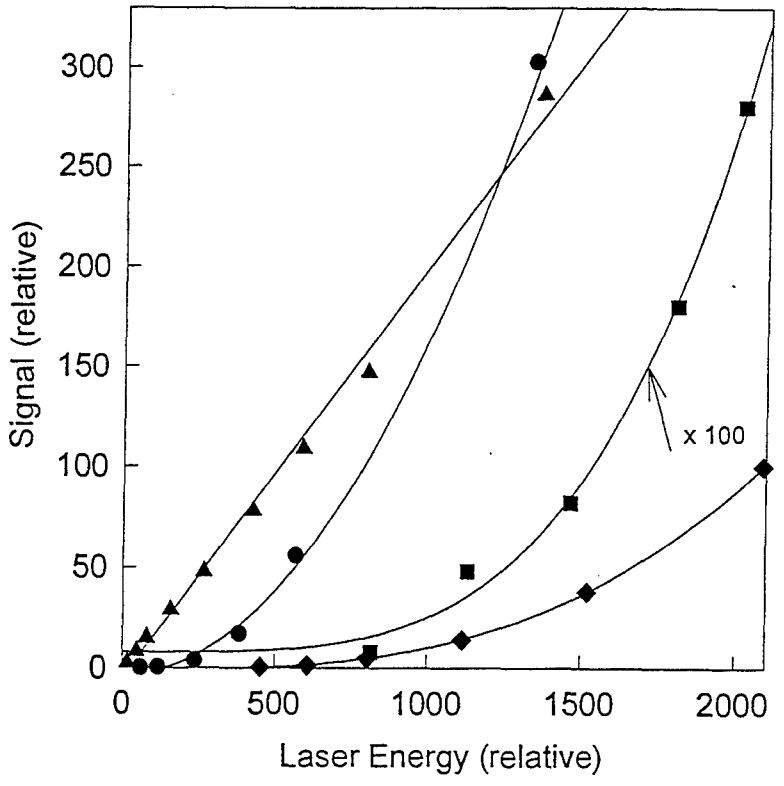

Figure 4. Signal dependence on laser intensity for 147-ppm NO_2 PA (▲) without lens, 86-ppm NO REMPI (●), 78-ppm NO_2 REMPI (♦) using a 12-cm lens, and 333-ppm NO REMPI using a 50-cm lens (■).

Presented in Figure 5(b) is the PA and REMPI signal dependence on pressure for 86-ppm NO and 147-ppm NO_2. As the density of NO or NO_2 increases with the pressure, these plots represent the combined pressure and density effects. The NO_2 PA signal has a 0.7 power dependence with pressure. This tendency to saturate is due to the pressure saturation observed in Figure 5(a). The NO REMPI response is approximately linear with pressure and suggests that the pressure effects at fixed density, illustrated in Figure 5(a), are small compared to the NO REMPI response from increased density.

Figures 6(a) and 6(b) show sensitivity plots of the NO_2 and NO PA and NO and NO_2 REMPI, respectively, at 453.856 nm. Measurements were made under flowing conditions at ~1 atm by serial dilution of NO or NO_2 with N_2. The ionization signals were measured at the peak ion signal; whereas, the PA signals were measured as the difference between the first maximum and

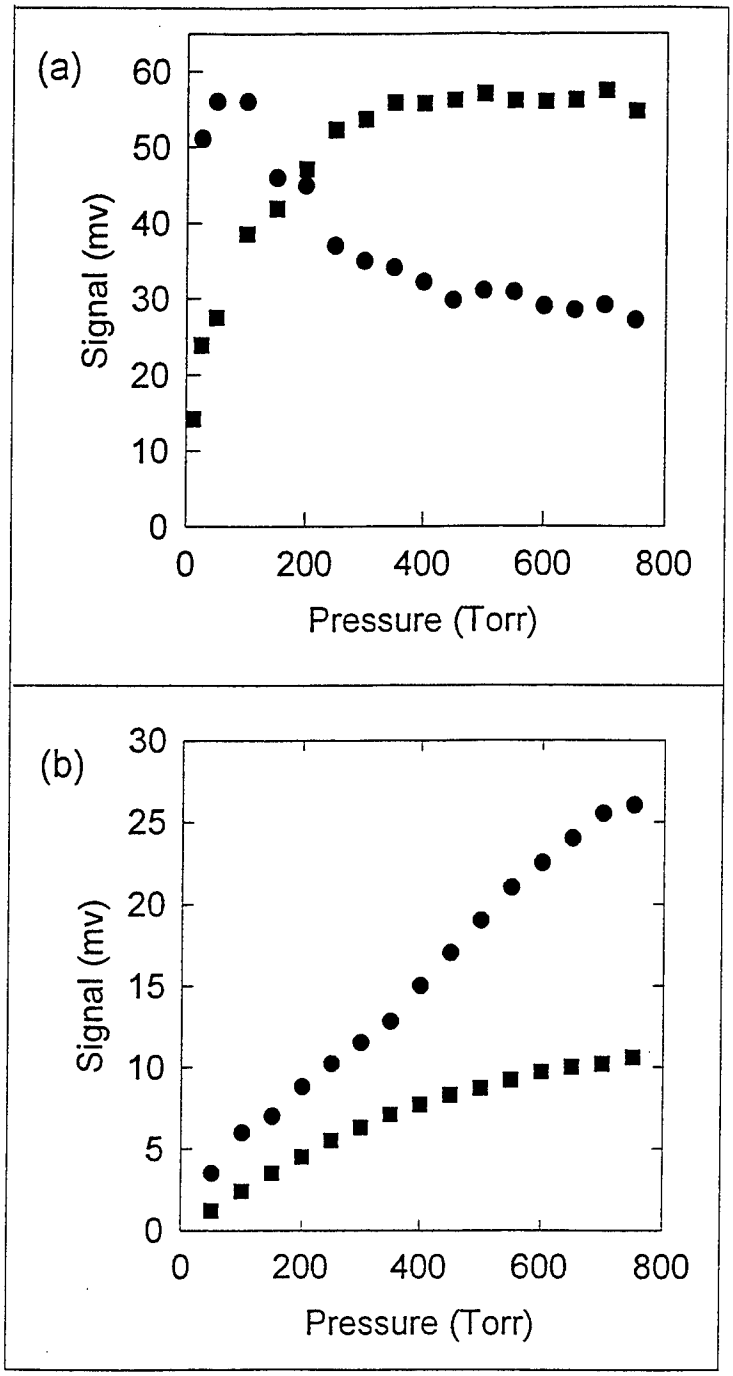

Figure 5. Plots of NO REMPI and NO_2 PA signals as a function of N_2 pressure at (a) constant density and (b) constant mixture. For (a), the densities are $[NO_2] = 3.7 \times 10^{14}$ cm^{-3} (■) and $[NO] = 1.5 \times 10^{15}$ cm^{-3} (●). For (b), the mixtures are 86-ppm NO in N_2 (●) 147-ppm NO_2 in N_2 (■).

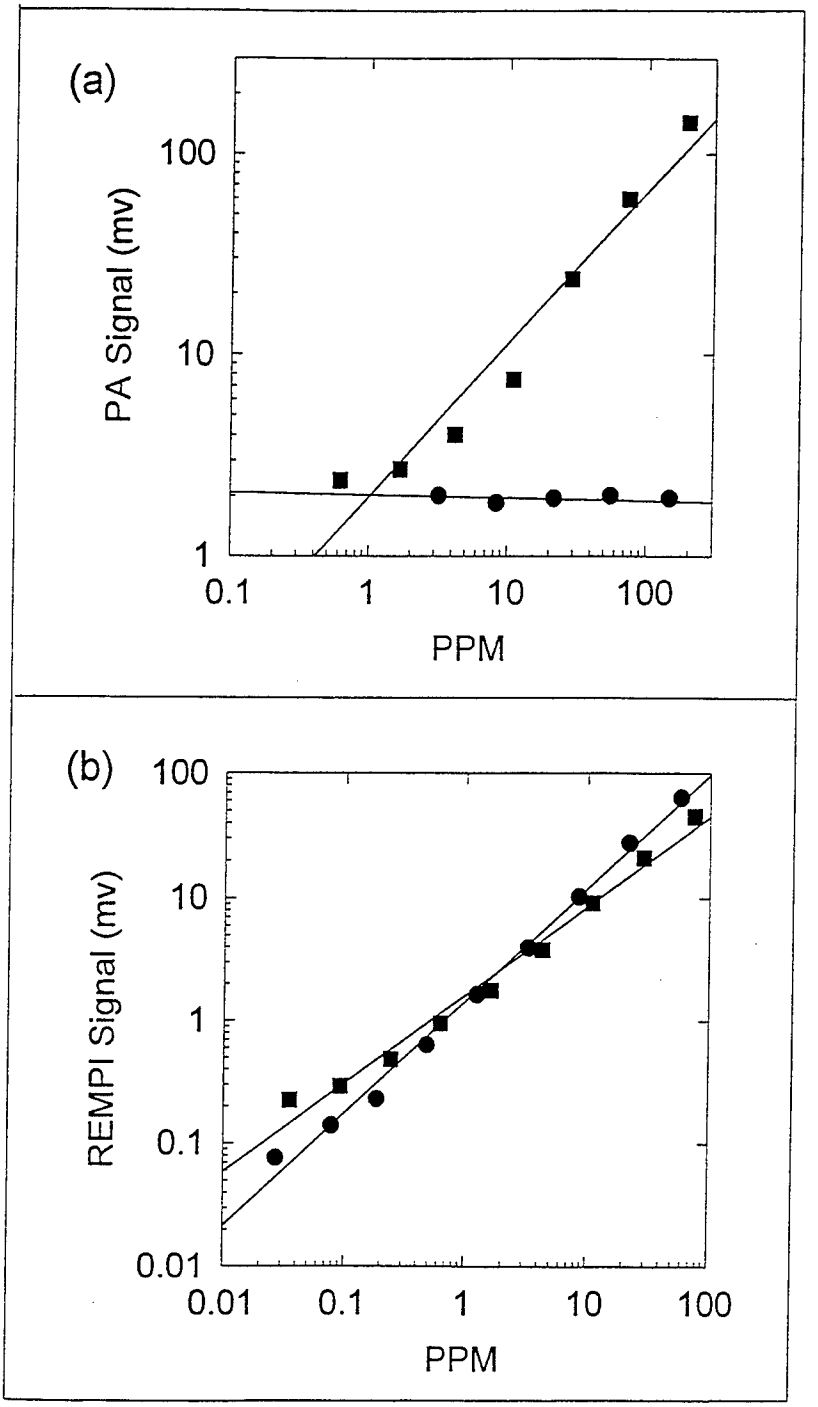

Figure 6. Sensitivity plots of (a) NO PA (●) and NO_2 PA (■), and (b) NO REMPI (●) and NO_2 REMPI (■), at 453.856 nm. The data are plotted on log scales.

minimum of the pressure wave. The slope of the sensitivity plot is the response (millivolts/parts per million [mV/ppm]). Responses for NO and NO_2 PA and REMPI are listed in Table 1 for both 453.856-nm and 454.348-nm laser excitation. The NO_2 PA signals are linear to 400 ppb, whereas the NO and NO_2 REMPI signals are linear to 20 ppb. The NO PA responses were below the sensitivity of the apparatus and are listed as zero.

Table 1. NO and NO_2 Responses by REMPI and PA Detection at Laser Wavelengths of 453.856 and 454.348 nm.

	453.856 nm		454.348 nm	
	NO	NO_2	NO	NO_2
PA	0.0	0.74	0.0	0.71
REMPI	1.12	0.61	0.33	0.18

In this study, the LOD is defined as the concentration that produces a signal equaling three times the standard deviation of the noise. The standard deviation of the noise was determined from 20 independent 100-shot averages with only N_2 flowing through the sample cell. Table 2 shows the LOD for NO and NO_2 in N_2 by REMPI and PA detection at the two-laser-excitation wavelengths. The NO_2 PA LOD would be approximately 5% less in air [8] compared with N_2; whereas, the NO and NO_2 REMPI LODs would not change [12]. The NO REMPI LOD at 453.856 nm is approximately a factor of 3 less than that measured at 454.348 nm. This difference is due to the difference in signals, apparent in the NO REMPI spectrum, because the noise is same for both laser wavelengths. The NO_2 PA LODs are similar for both wavelengths. We project higher NO_2 PA sensitivities by using the P and Q transitions near 454.7 mm or other vibrational bands that are more intense than the (0, 8 ,0) band.

An upper bound of the relative response error due to computing the relative concentration error of the mixtures is determined by numerical analysis. The combined PA and REMPI signals can be expressed by two simultaneous linear equations, whose matrix representation is:

$$\begin{bmatrix} R_{PA}(NO) & R_{PA}(NO_2) \\ R_{REMPI}(NO) & R_{REMPI}(NO_2) \end{bmatrix} \begin{bmatrix} [NO] \\ [NO_2] \end{bmatrix} = \begin{bmatrix} S_{PA} \\ S_{REMPI} \end{bmatrix} \quad (1)$$

Table 2. NO and NO_2 LOD (ppm) by REMPI and PA Detection at Laser Wavelengths of 453.856 and 454.348 nm

	PA		(2+2) REMPI	
Laser Wavelength	NO	NO_2	NO	NO_2
453.856 nm	—	0.41	0.18	0.34
454.348 nm	—	0.42	0.63	1.10

Equation 1 can be rewritten in vector notation as, **Rx** = **s**, where the elements of the response matrix, **R**, are the NO and NO_2 responses to PA and REMPI detection; the elements of the signal vector, **s**, are the total PA and REMPI signals from a NO-NO_2 mixture; and the elements of unknown vector, **x**, are the NO and NO_2 concentrations. The condition number of the response matrix [24], $K = \|\mathbf{R}\|\|\mathbf{R}^{-1}\|$, where $\|\mathbf{R}\|$ is the norm of **R**, scales the relative signal error, $\|\Delta\mathbf{s}\|/\|\mathbf{s}\|$, to the relative concentration error, $\|\Delta\mathbf{x}\|/\|\mathbf{x}\|$. The condition numbers for the 453.856- and 454.348-nm PA and REMPI detection systems are 2.8 and 2.7, respectively, using the values presented in Table 1 and row norm. Thus, the relative error in calculating the NO and NO_2 concentrations will be no more than 2.8 times the relative signal error.

The range of NO-NO_2 mixtures that can be accurately measured by REMPI is determined by the noise in the signals while measuring the NO and NO_2 responses. The signal noise is $N_s = n(\Delta E/E)m^{-1/2}$, where n is the power of the signal dependence on laser energy (see Figure 4), $\Delta E/E$ is the variation in laser energy, and m is the number of laser pulses. The signal noises for NO and NO_2 are 0.02 and 0.03, respectively, for 10% (shot-to-shot) laser energy variation and 100-shot averaging. Requiring the ratio of signals from NO and NO_2 to be greater then three times the relative signal noise yields,

$$3N_s\left(\frac{R_{REMPI}(NO_2)}{R_{REMPI}(NO)}\right) \leq \frac{[NO]}{[NO_2]} \leq \left(\frac{1}{3N_s}\right)\left(\frac{R_{REMPI}(NO_2)}{R_{REMPI}(NO)}\right) \quad (2)$$

Thus, nearly three decades of NO-NO_2 mixtures centered around $[NO]/[NO_2]=½$ can be accurately measured using our present apparatus.

4. CONCLUSION

The analytical utility of a combined PA and REMPI technique has been demonstrated for the trace detection of NO and NO_2 in N_2 at atmospheric pressure using a narrow-band tunable dye-laser operating near 454 nm. Rotationally resolved spectra of the NO $A^2\Sigma^+$-$X^2\Pi$ (0,0) and NO_2 $\tilde{A}'^2B_1$(0,8,0)-$X\,^2A_1$(0,0,0) bands suggest that the technique is highly selective based on excitation wavelength. The sensitivity of the technique is also high with LODs (S/N=3) of 100 and 400 ppb for (2+2) NO REMPI and NO_2 PA, respectively, for 10-s integration time. Higher sensitivities are projected with an increase in laser energy, different excitation schemes, and an improved apparatus. The results reveal that the technique enables a simple instrument design to be used for the sensitive measurement of these compounds and NO/NO_2 mixtures.

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	July 1997	Final, Jan 96 - Jan 97

4. TITLE AND SUBTITLE
(2+2) Resonance-Enhanced Multiphoton Ionization (REMPI) and Photoacoustic (PA) Spectroscopic Detection of Nitric Oxide (NO) and Nitrogen Dioxide (NO_2) Near 454 nm

5. FUNDING NUMBERS
PR: 1L161102AH43

6. AUTHOR(S)
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13. ABSTRACT *(Maximum 200 words)*

Trace concentrations of NO and NO_2 are detected with a dye laser operating near 454 nm. NO is detected by a (2 + 2) resonance-enhanced multiphoton ionization process by means of NO $A\,^2\Sigma^+ - X\,^2\Pi(0,0)$ transitions with miniature electrodes, and NO_2 is detected by a one-photon absorption photoacoustic process by means of NO_2 $\tilde{A}'\,^2B_1(0, 8, 0) - \tilde{X}\,^2A_1(0, 0, 0)$ transitions with a miniature microphone. Rotationally resolved excitation spectra show that the spectral resolution is sufficiently high to identify these species at 1 atm. The technique's analytical merits are evaluated as functions of concentration, pressure, and laser intensities. Low laser intensities favor NO_2 photoacoustic detection whereas high laser intensities favor NO ionization. Limits of detection (signal-to-noise ratio 3) of 160 parts in 10^9 for NO and 400 parts in 10^9 for NO_2 are determined at 1 atm for a 10-s integration time. Signal response and noise analyses show that three decades of NO/NO_2 mixtures can be measured with a computational relative error in concentration that is three times the relative error in measuring the NO and NO_2 signals.

14. SUBJECT TERMS
photoacoustic spectroscopy, resonance-enhanced multiphoton ionization, nitric oxide, nitrogen dioxide, visible radiation, laser

15. NUMBER OF PAGES
31

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