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Detection of Ambient NO by Laser-Induced Photoacoustic Spectroscopy Using $A^2\Sigma^+$-$X^2\Pi$ (0,0) Transitions Near 226 nm

by R. C. Sausa, C. K. Williamson,
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Abstract

Trace concentrations of NO are detected under ambient conditions by laser-induced photoacoustic spectroscopy. NO is excited via its $A^2\Sigma^+$-$X^2\Pi$ (0,0) band with radiation near 226 nm, and the subsequent heat released is monitored by a microphone. Rotationally resolved photoacoustic spectra are recorded and fit using a multiparameter computer simulation based on a Boltzmann distribution. Transition probabilities and rotational energies are used as input parameters. The effect of buffer gas pressure, buffer gas, laser energy, and NO concentration on PA signal is investigated both experimentally and by model calculations. Limits of detection of 1.2, 2.8, and 4.9 ppm are obtained for NO in Ar, N_2, and air, respectively. The ultimate sensitivity of this approach is greater with LODs projected in the low parts per billion by utilizing higher laser energies and an improved system design. The results are compared with previous studies using complementary laser-based spectroscopic techniques.

Acknowledgments

We thank Dr. A. Kotlar of the U.S. Army Research Laboratory (ARL) for providing us with his absorption/fluorescence fitter and a program used to calculate line positions and transition probabilities. We also thank Drs. W. Anderson and S. Modiano of ARL for many helpful discussions. Support from the National Research Council (NRC) and American Society of Engineers (ASE) Postdoctoral Program is gratefully acknowledged. This work was supported by the ARL Director's Initiative Research Program, Strategic Environmental Research and Development Program (SERDP) Program on Cleanup, and the U.S. Army Corps of Engineers' Waterways Experiment Station's (WES) Site Characterization and Analysis Penetrometer System (SCAPS) Program. Purchase of equipment was made available through the Productivity Capital Investment Program.

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1. Introduction

The detection of NO is of interest due to its function in atmospheric chemistry (acid rain, smog, ozone reduction) and formation in the photochemistry of energetic compounds [1, 2]. Conventional methods for determining ambient concentrations of NO include chemiluminescence and passive collection with subsequent wet chemical analysis. Laser-based methods are, however, being implemented more frequently since they offer fast and real-time monitoring capabilities with excellent sensitivity. These methods include laser-induced florescence (LIF) [3, 4] resonance-enhanced multiphoton ionization (REMPI) [1, 2, 5] and laser photoacoustic spectroscopy (PA) [6–12].

The analytical application of LIF for the detection of ambient NO has been reported [3, 4]. Bradshaw et al. [3] have investigated the analytical application of NO detection by one-photon LIF for atmospheric conditions. NO was excited via the $A^2\Sigma^+$-$X^2\Pi$ (0,0) γ-band using 226-nm radiation, and the fluorescence emitted from the (0,2) band was detected at 247.5 nm. A limit of detection (LOD) of 0.5 ppb was reported. In later work by the same group, Sandholm et al. reported even higher levels of NO sensitivity using a two-color LIF excitation scheme [4]. With a more complex experimental apparatus, trace concentrations of tropospheric NO were measured from an aircraft platform. NO was excited by two lasers simultaneously. One laser was tuned to the NO $A^2\Sigma^+$-$X^2\Pi$ (0,0) band near 226 nm, while the other was tuned to the NO $D^2\Sigma^+$-$A^2\Sigma^+$ (0,0) band near 1.1 μm. Fluorescence detection was accomplished by monitoring the $D^2\Sigma^+$-$X^2\Pi$ transitions in the 187–220-nm region. Since the fluorescence occurs at a higher frequency than either of the excitations, the laser contribution to the observed background is essentially zero and the measurements are effectively signal limited. A LOD (signal-to-noise [S/N] = 2) of 3.5 pptv for integration time of 2 min was reported.

Recent studies in our laboratory that centered on detecting nitrocompounds by laser photofragmentation/fragment ionization have shown that ambient concentrations of NO can be measured with high sensitivity and selectivity by molecular beam, time-of-flight mass spectrometry

[1, 2]. In one study, a LOD (S/N = 3) of 8 ppb was attained by using a 226-nm tunable laser to ionize NO by a (1 + 1) REMPI processes via its NO $A^2\Sigma^+$-$X^2\Pi$ (0,0) band [1]. In a subsequent study, NO ionization was accomplished with an ArF laser operating at 193 nm by (1 + 1) REMPI processes via the NO $A^2\Sigma^+$-$X^2\Pi$ (3,0) and/or $B^2\Pi$ -$X^2\Pi$ (7,0) transitions at 193 nm [2]. A LOD (S/N = 3) of 1.2 ppm was reported. The difference in sensitivities between the two REMPI techniques was attributed to (1) a more favorable Franck-Condon overlap for the 226-nm transitions compared with the 193-nm transitions following supersonic cooling, and (2) a reduced spectral energy density of the ArF laser compared to the 226-nm tunable laser (approximately a factor of 60). More recently, it has also been demonstrated in our laboratory that NO can be detected at atmospheric pressure with the use of the same (1 + 1) ionization scheme at 226 nm without ion selection by using a pair of miniature electrodes [5]. With this technique, a LOD (S/N = 3) of 1 ppb was determined using 10 μJ of pulse energy and an integration time of 10 s.

Although both LIF and REMPI techniques offer high sensitivity under many conditions, there are situations where these techniques are less suitable. In particular, both LIF and, to some extent, REMPI suffer from collisional quenching at atmospheric pressures. REMPI also suffers from nonresonant background ionization and requires relatively high laser fluences because of the multiphoton processes involved. Detection of NO by laser PA can circumvent some of these problems. The PA technique is primarily calorimetric in nature and is based on conversion of photo to acoustic energy by collisional quenching of laser excited NO. The quenching results in a local temperature increase followed by a pressure rise that generates the photoacoustic signal. PA spectrometry is thus complementary to LIF and REMPI, since the mechanism involves a competing process to fluorescence and ionization. Higher diluent gas pressures increase the rate of collisional deactivation and improve performance. Unlike REMPI, the PA technique does not require large laser intensities and has the benefit of remote detection through the implementation of a tube between the detector and the sample or system of interest. For REMPI detection, the electrodes must be in contact with the sample and in proximity to the laser beam. The PA transducer (e.g., electret microphone) is also compact, simple to implement, and significantly inexpensive, compared with high-voltage sources necessary for REMPI and LIF and the photomultiplier/monochromator required for LIF.

Laser photoacoustic detection of NO has been demonstrated with both its fundamental absorption band in the infrared (IR) and γ-band in the ultraviolet (UV). Kreuzer and Patel first reported the application of the PA technique in the IR to measure concentrations of NO in N_2, laboratory room air, field air, and automobile exhaust [6]. A continuously tunable spin-flip Raman (SFR) laser pumped by a CO laser was used to excite NO in the region of 1814–1825 cm^{-1}. All of the NO lines excited were not observed, because water vapor also has strong absorptions in this region. Using the NO($\Pi_{3/2}$) $P_{16.5}$ and NO($\Pi_{1/2}$) $P_{17.5}$ lines, which correspond to frequencies 1818.74 and 1816.56 cm^{-1}, respectively, these authors estimated a detection limit of 0.01 ppm for 4-s integration time. Patel also employed a similar experimental apparatus for NO temporal measurements near 1,888 cm^{-1} in the stratosphere using a balloon-born system [7]. The measured NO concentrations, which ranged from $<1.5 \times 10^8 - 22 \times 10^8$ molecules cm^{-3}, correspond to volumetric mixing ratios of approximately 0.2 and 4.2 ppb, respectively. A disadvantage of this system is the complexity of the equipment and bulk of the apparatus. The apparatus could be simplified by replacing the SFR laser with a step-tunable CO laser. Kreuzer, Kenyon, and Patel [8] measured the line strengths of NO absorption resonant with the output from a CO laser near 5.3 μ. They estimated that atmospheric mixtures of NO can be measured in the presence of 10–100% water vapor with sensitivities in the 0.01–0.1-ppm range.

Patel and Kerl [9]; Patel, Kerl, and Burkhardt [10]; and Patel [11] applied the PA technique using a two-color excitation scheme for probing NO with vibrational excitation in its ground electronic state. In the study by Patel and Kerl, the ^{14}NO isotope was excited by a fixed-frequency CO laser at 1917.86 cm^{-1} to produce excited $^{14}NO(\upsilon'' = 1)$ [9]. This state was then probed with tunable IR radiation obtained from an SFR laser pumped with another CO laser operating at 1891.65 cm^{-1}. As the SRL was scanned, high-resolution Zeeman spectra of $\upsilon'' = 1 \rightarrow \upsilon'' = 2$ ro-vibrational transitions of the $^{14}NO(^2\Pi_{1/2})$ and $(^2\Pi_{3/2})$ states were obtained. In subsequent work, Patel, Kerl, and Burkhardt studied the molecular energy transfer of $^{14}NO(\upsilon'' = 1)$ to $^{15}NO(\upsilon'' = 1)$ [10, 11]. Irradiation of a 1:1 mixture of the two NO isotopes by a fixed-frequency CO laser caused only the ^{14}NO molecules to be excited to their first vibrational state. Vibrational energy transfer then allowed for probing the $^{15}NO(\upsilon'' = 1)$ state using tunable SFR laser radiation resonant with $^{15}NO(\upsilon'' = 1) \rightarrow {}^{15}NO(\upsilon'' = 2)$ transitions.

NO is a suitable molecule for PA detection in the UV. First, it has a relatively strong absorption coefficient at 226 nm [12], ($\sigma_{226\,nm} = 6.6 \times 10^{-18}$ cm^{-2}). Second, its energy release during collisional deactivation is greater in the UV than IR on a per photon basis. Last, there is minimal spectral interference from H_2O and other pollutants at 226 nm compared to 1,890 cm^{-1}. Experimental precaution must be taken in the UV, however, since the PA signal intensity can be reduced due to competing fluorescence and ionization processes. The work of Stenberg, Hernberg, and Vattulainen is the only account in the literature that reported laser PA detection of NO in the UV [13]. Various pollutants, such as NH_3, H_2S, N_2O, and NO produced in a combustion environment, were monitored using a microphone probe mounted at the end of a sound-transmitting tube. A broad band near 226 nm was ascribed to NO, and LODs (S/N = 1) of 0.6 ppm and 3 ppm were determined for NO in a low-noise reactor and bubbling-bed reactor, respectively.

In this report, the detection of ambient NO by laser PA via the $A^2\Sigma^+$-$X^2\Pi$ (0,0) band near 226 nm is reported. Rotationally resolved spectra are recorded and fit using a multivariable computer spectral program. The analytical merits of the technique are evaluated as a function of buffer gas, pressure, laser energy, and NO concentration. LODs are determined for NO in Ar, N_2, and air. The results of this study are explained using a simple model and are compared to those reported using other laser-based techniques.

2. Experimental

The experimental apparatus used in this study has been described previously [5]. Briefly, a photoacoustic probe was used in place of a REMPI probe. The radiation source used was an excimer pumped dye laser (Lumonics, HyperEx 400/Hyper Dye 300) with a second harmonic generator (Lumonics, HYPER TRAK-1000). The laser was operated at 10 Hz with Coumarin 450 dye and beta baruim borate (BBO) crystal to produce wavelengths in the range 224–228 nm. The laser linewidth was estimated to be 0.11 cm^{-1} at 226 nm from the 0.076 cm^{-1} value specified for the fundamental (Lumonics). Typical pulse energies were 10–50 μJ with duration of approximately 20 ns. The energy was monitored between measurements using a Joulemeter (Molectron Detector Inc.,

J4-05). The laser beam has a diameter of approximately 2 mm and was not focussed for routine data collection. For experiments in which the laser beam was focused, dielectric breakdown was not observed.

The PA cell consisted of a standard six-way, stainless steel cross with internal arm diameters of 3.6 cm. The cell volume was estimated as 350 cm^3. MgF_2 windows were mounted on opposing arms for transmitting the laser radiation. A vacuum feed through flange, containing an omni directional electret condenser microphone (Radio Shack 270-090), was mounted on the third arm. The flange provided excellent electrical shielding and allowed horizontal translation of the microphone. The microphone was positioned approximately 2–3 mm normal to the laser beam for maximum signal response. At this distance scatter radiation contacting the microphone was minimal.

The microphone was encased in a small cylinder of 9-mm diameter and 6-mm length. It had an active area of approximately 3 mm^2 and exhibited a relatively flat sensitivity response of 65 ± 4 dB in the frequency range of 20–1500 Hz. It was powered with a 9-V battery. The output of the microphone was dropped across a capacitor and amplified with a current amplifier (Keithley, model 427, time constant 0.01 ms). Signals from the microphone were sampled with a boxcar averager (Stanford Research Systems) using a gate width of 100 μs or with a 125-MHz digital oscilloscope (LeCroy 9000). In both cases, the first peak of the PA waveform was sampled, since it corresponds to the pressure fluctuation from the focal volume and is thus directly proportional to the heat produced [14, 15]. For routine data analysis, 3 or 10 shot averaging was employed. Spectral recording was accomplished with both a boxcar interfaced to a PC and a strip chart recorder.

Serial dilutions of NO (Matheson, >99.9%) or 0.1% NO/Ar (Union Carbide) were prepared in the sample cell using air (Matheson, 99.9%), N_2 (Potamic Gases, O_2 free), or argon (Spectra Gases, 99.999%). Cell pressures were monitored with a barocel pressure sensor interfaced to a recorder (Edwards-Datametrics 600A-1000T, 1500) and ranged from 1–850 torr. Measurements were made under static conditions.

3. Spectral Simulation

A computer program based on absorption or fluorescence was used to fit the NO photoacoustic data [16]. The signal, S_{pa}, is proportional to the energy absorbed over a certain pathlength of the laser beam. Using Beer-Lambert's absorption law and assuming the pathlength to be optically thin, S_{pa} can be expressed as,

$$S_{pa} = S\left[E(\nu_0,\ell_1) - E(\nu_0,\ell_2)\right], \tag{1}$$

where S is the scaling factor that includes system response, and E (ν_0, ℓ) is the transmitted laser energy with frequency ν_0 and traveling a distance ℓ. For a system described by a Boltzmann distribution, E (ν_0, ℓ) is adapted from Vanderhoff and Kotlar [16] as

$$E(\nu_0,\ell) = \int E_{\nu,0}(\nu_0)\, e^{(-h\nu\ell/c)[N_T/Q(T)]\sum_j P_j B_j g_j e^{-E_j/kT}} d\nu, \tag{2}$$

where h is Planck's constant; c is the speed of light; N_T is the total population of ground electronic state NO ($X^2\Pi$); Q (T) is the partition function; g_j is the degeneracy of the jth sublevel and E_j, its energy; k is the Boltzmann constant; T is the temperature; and P_j is the Voigt transition lineshape. E (ν_0, ℓ) was evaluated by numerical integration over ν. The limits of integration were chosen to include more than 99% of the laser profile.

The photoacoustic spectrum is generated by evaluating equation (1) for each datum (ν_0) and is fit to the observed spectrum using a multiparameter, nonlinear weighed least-squares-fitting routine. Parameters include, the laser lineshape, Doppler and collisional broadening, the number density, temperature, absolute frequency values, relative frequency values for the data, and parameters associated with experimental conditions. The standard deviation of each parameter, as statistically determined from the fit, is obtained from the computed variance/covariance matrix, once convergence is achieved.

4. Results

A typical PA spectrum of NO normalized with respect to the laser energy is presented in Figure 1(a). The concentration of NO in Ar was 213 ppm, and the total cell pressure was 1 atm. The spectrum was recorded at 10 Hz with a scan speed of 0.005 nm/s and 3 shot averaging. Presented in Figure 1(b) is a graphical simulation generated by fitting the observed data using our multivariable computer program. The program utilized over 600 transition probabilities for various rotational levels as input data. The data were generated with spectroscopic constants reported in Herzberg [17]. Evident from Figures 1a and 1b are the spectral features due to the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ spin-orbit components of the NO ground electronic state. The unique features of the spectrum and rotational resolution at one atmosphere indicate that the PA technique can be highly selective on the basis of excitation wavelength for NO detection. A PA spectrum of air over the same region shows little, if any, PA signal above the noise.

A plot of PA signal intensity as a function of laser energy is presented in Figure 2. The plot is linear and indicative of a one-photon process. The energies employed ranged from approximately 10–50 μJ and were so sufficiently low that saturation of the signal was not observed. Focusing the laser beam reduced the signal. The intensity of the focused beam was calculated as 10^8 W/cm^2 using an estimated value of 90 μ for the beam diameter. At this intensity, (1 + 1) NO REMPI processes compete favorably with collisional de-excitation [1, 5], and a reduction in the PA signal is observed. The possibility that a focused beam excites a smaller cross section of the sample in proximity to the microphone should also be considered. Simultaneous measurements of PA and optogalvanic signals in discharges have been used to ascertain mechanisms of current production [18, 19].

Presented in Figure 3 is a plot of measured signal intensity as a function of Ar pressure. A similar trend was observed with N_2. The position of the boxcar gate or oscilloscope cursors was optimized for maximum signal with each measurement since the shape of the PA waveform varied with pressure as described by Chin et al. [20]. The first peak drifted in time relative to the pressure;

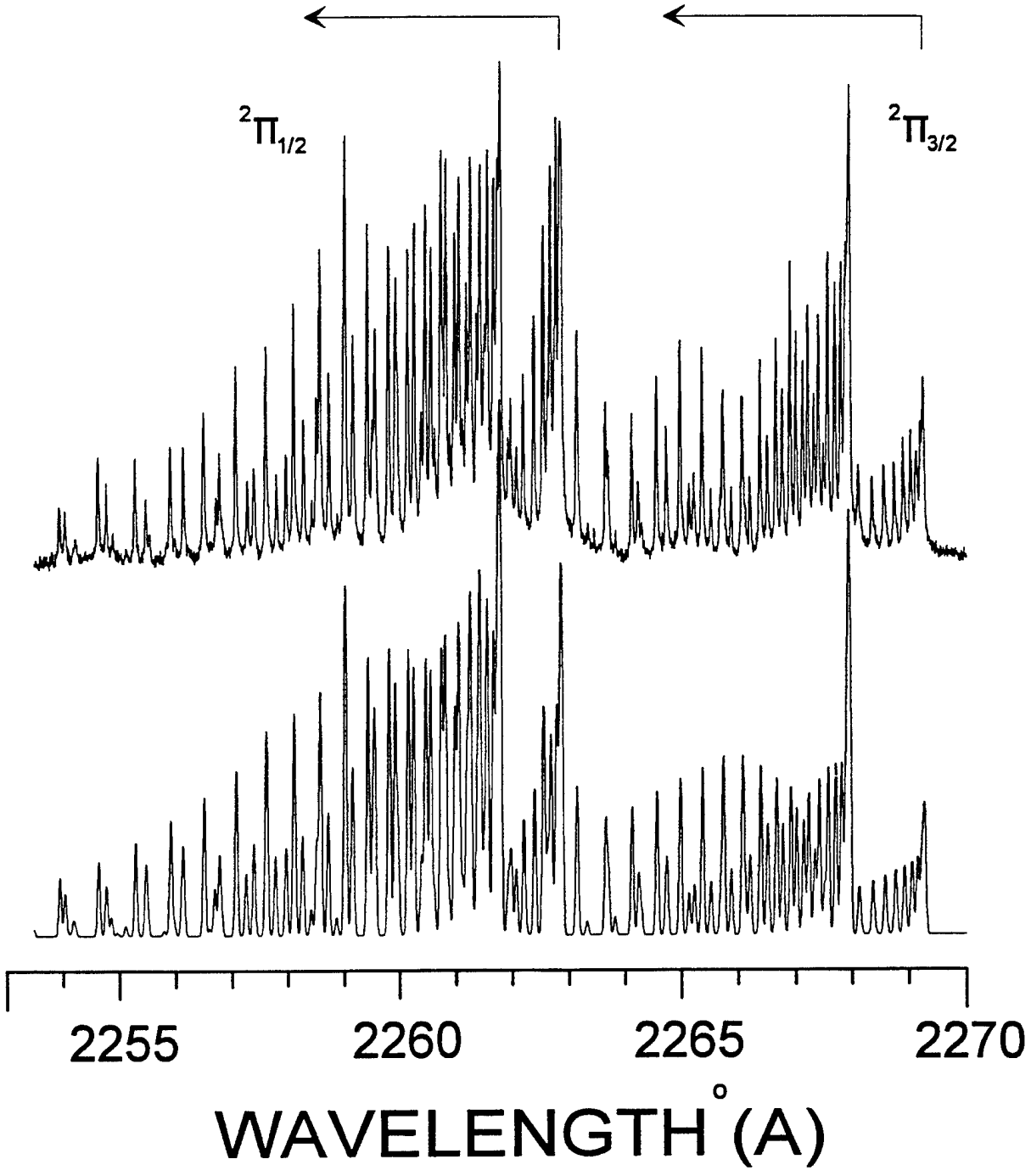

Figure 1. Experimental (a) and Simulated (b) PA Spectra of NO in the Region of 226 nm. The Simulation Is a Best Fit of the Data and Yields a Boltzmann Rotational Temperature of 305 ± 5 K. The Two Spectra Are Offset in Signal Intensity for Clarity.

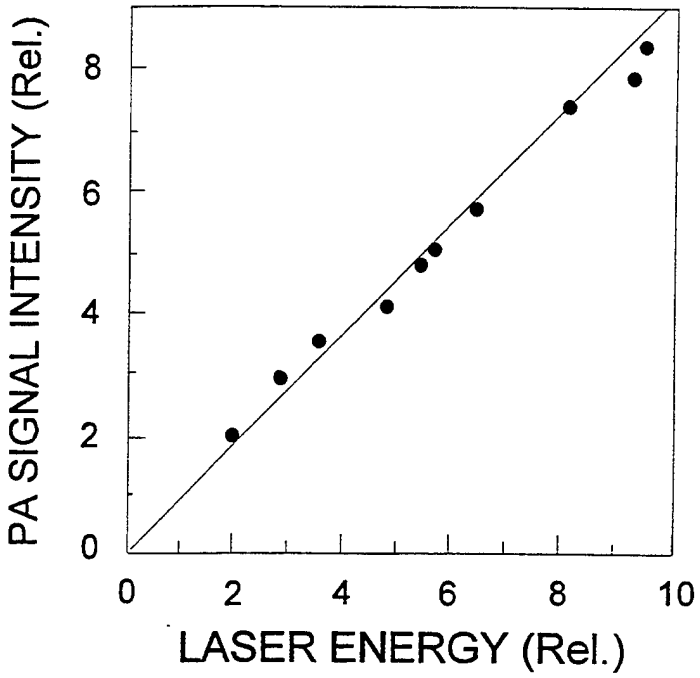

Figure 2. Dependence of PA Signal on Laser Energy. The Laser Was Tuned to 226.29 nm, and the Maximum Energy Was Approximately 50 μJ/pulse.

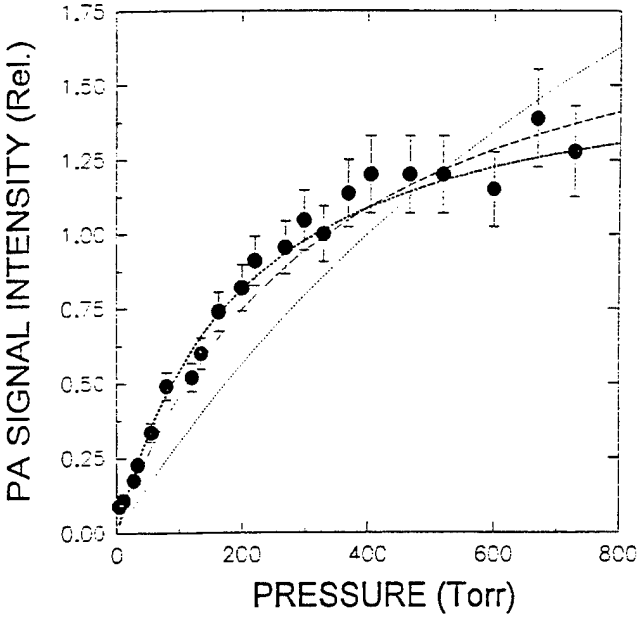

Figure 3. Plots of PA Signal as a Function of Ar Buffer Pressure Using Laser Radiation Tuned to 226.29 nm. The Experimental Data Is Represented by the Symbol (●), Fitted Curve by (−), and Computed Curves by (...) and (---) Obtained by Using Electronic Quenching Rate Constants $k = 1.0 \times 10^{-13}$ and 3.9×10^{-13} cm^3/molecule-s, Respectively.

a decrease in the delay time was observed with increasing pressure. The various curves shown in Figure 3 were generated using equation $S_{pa} = K\ [kM/(A + kM)]$, where K is a proportionality constant that includes NO concentration, laser energy, and system response, k is the NO ($A^2\Sigma^+$) electronic quenching rate, and A is the NO($A^2\Sigma^+$) spontaneous decay rate. The nature of this equation will be discussed in detail in the following section of this report. The dashed curves were generated using a value of $A = 4.6 \times 10^6\ s^{-1}$, determined form the well-known NO ($A^2\Sigma^+$) radiative lifetime [21, 22]; reported values of $k_{Ar} = 3.9$ and 1.0×10^{-13} cm^3/molecule-s by McDermid and Laundenslager [21] and Callear [23], respectively; and varying K. Both reported values of k_{Ar} were obtained by LIF using Stern-Volmer analyses. As can be seen from Figure 3, the curve generated using $k_{Ar} = 3.9 \times 10^{-13}$ cm^3/molecule-s agrees with our data reasonably well. The best fit to our data that is given by the solid curve yields $k_{Ar} = 6.9 \pm 1.0 \times 10^{-13}$ cm^3/molecule-s and K = 1.6. Although the PA technique has been used for measuring vibrational relaxation rates [24, 25], it has not been routinely implemented for determining electronic quenching rates. As an alternative to LIF, the technique may be potentially useful for measuring electronic quenching rates, particularly for species that are weak fluorophores. However, the specie's radiative lifetime must be measured or calculated.

Presented in Figure 4 are sensitivity plots for NO in 1 atm of Ar, N_2, and air. The plots are linear for the shown concentration. Not shown is a leveling off of the signal at concentrations greater than 350 ppm. At these concentrations NO strongly absorbs the laser energy, and the PA signal saturates. The slope of the plot in the linear region yields a sensitivity value for Ar of 0.343 mV/ppm. Using a background noise of 0.398-mV yields a value of 1.2 ppm for the LOD, reported as the concentration equivalent to 3σ. The background noise was evaluated in the absence of NO from 20 independent measurements, each the average of 10 laser pulses, and was found to be independent of buffer gas. Absorption of radiation by the windows and scattered light contacting the microphone contributed to the most of the noise. Measurements using N_2 and air as diluents produced LODs of 2.8 and 4.9, respectively.

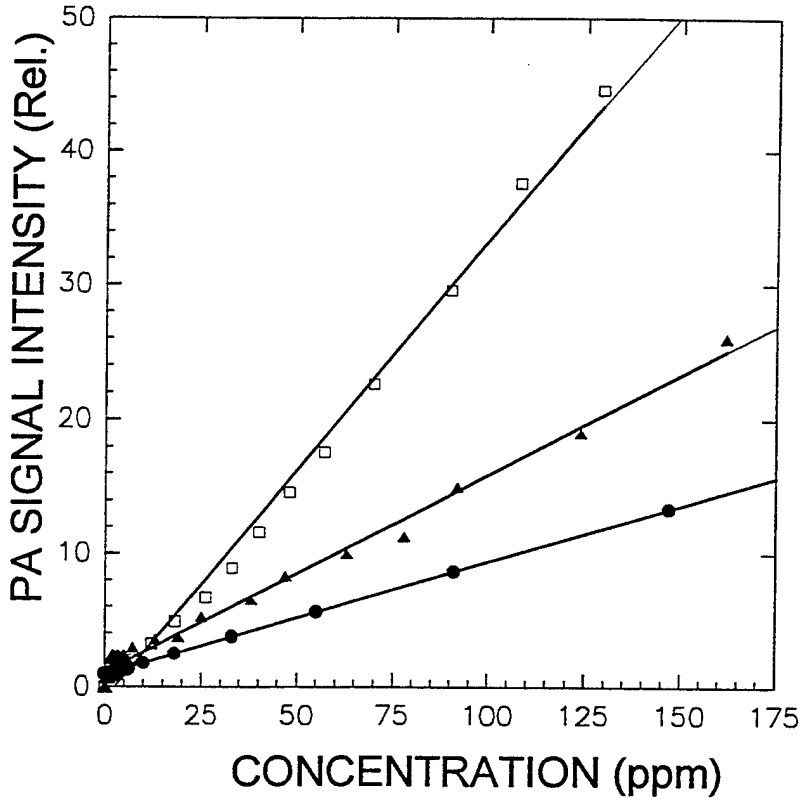

Figure 4. PA Signal Intensity as a Function of NO Concentration Using Ar (□), N_2 (△), and Air (●) as Buffer Gases. The Laser Was Tuned to 226.29 nm.

5. Discussion

A first-order model is used to explain the effect of pressure, buffer gas, laser energy, and NO concentration on the PA signal. Once NO is electronically excited by the laer pulse, it decays either radiatively by spontaneous transition or by collisional quenching with diluents. For a two-level electronic system, the rate equation for the decay of excited NO ($A^2\Sigma^+$), N^*, is expressed as,

$$\frac{dN^*}{dt} = -AN^* - kN^* M, \qquad (3)$$

where A is the spontaneous transition rate, k is the quenching rate constant, and M is the density of the diluent. This equation assumes that all other loss processes, such as those involving energy

transfer, ionization, and reactions, are negligible. If each collisional quenching of NO generates heat, the rate equation for the heat density, Q, can be expressed as

$$\frac{dQ}{dt} = k N^* M h\nu. \tag{4}$$

Integrating equations (3) and (4) yields the total heat gained:

$$Q = N_0^* h\nu \frac{kM}{A + kM}, \tag{5}$$

where N_0^* is the initial excited NO density following the laser absorption.

For a system at constant volume, the change in pressure is proportional to the total heat gained divided by the heat capacity, $\Delta P \sim \Delta T = QV/C_v$, where V is the volume. If we ignore the thermodynamic work, $P\Delta V$, produced in generating the pressure wave, the photoacoustic signal is

$$S_{pa} \sim \frac{N_0 E \sigma \ell}{C_v} \left[\frac{kM}{kM + A}\right], \tag{6}$$

where we have used Beer-Lambert's Law, $N_0^* = N_0 \sigma \ell E/h\nu$.

As can be seen from equation (6), the photoacoustic signal is proportional to the number density of ground electronic state NO and laser energy, as was observed experimentally. The PA signal also depends on the buffer gas pressure, heat capacity of the buffer gas, as well as, the k and A rate constants. For $kM >> A$, the PA signal is independent of pressure and makes it ideal for analytical applications in high-pressure environments. Overall, the model agrees with our experimental data. The model can be improved, however, by including shock wave relaxation effects at higher pressure, work required to produce the pressure wave, and transport properties of the buffer gases.

The LODs of NO in Ar, N_2, and air were determined as 1.2, 2.8, and 4.9 ppm, respectively. The higher values in N_2 and air compared to Ar are due to the decrease in signal intensities, since the noise levels are approximately the same for all three diluent gases. As expected, the signal of NO

in N_2 at 1 atm is less than Ar since N_2 has a smaller heat capacity and quenching rate constant. Quantitatively, the $(S_{Ar}/S_{N_2})_{1\ atm}$ ratio of 2.3 determined from the experimental values agrees reasonably well with the value of 3.7, calculated using equation (6) with reported k_{Ar} and k_{N_2} values of 3.9×10^{-13} and 9.1×10^{-14} cm^3/molecule-s, respectively [21]. For air, one would predict *a priori* that the signal level of NO would be larger than in N_2 given that their heat capacities are approximately equal and that k_{air} is greater than k_{N_2} because of the contribution of k_{O_2}, 1.41×10^{-13} cm^3/molecule-s [21]. However, the reverse is true. Possible explanations as to why the observed NO signal is smaller in air than N_2 are as follows: (1) reaction of NO ($X^2\Pi$) with O_2, (2) energy transfer between NO ($A^2\Sigma^+$) and O_2, and (3) reaction of NO($A^2\Sigma^+$) with O_2. The first explanation is ruled out since the oxidation of NO by O_2 by the slow, third-order reaction $2NO + O_2 = 2NO_2$, $k = 2 \times 10^{-38}$ cm^6/molecule^2-s is negligible given the concentrations used in this study and the time required in order to perform the experiment. The possibility that the presence of O_2 has an effect on the energy transfer of the analyte was investigated by Fried [26]. He observed a 34.5% decrease in NO_2 signal when N_2 was replaced with O_2. This was interpreted as energy transfer between electronically excited NO_2^* (λ = 488 nm) and O_2 ($^3\Sigma_g$), yielding ground electronic state NO_2 and metastable $O_2(^1\Delta_g)$. A modulation frequency of 250 Hz was used in his experiments; thus, the energy released by the $^1\Delta_g$ state of O_2 (collisional relaxation lifetime of 23 ms at 600 Torr) was effectively trapped or lost. In our case, the energy transfer process could involve O_2 ($B\ ^3\Sigma_u^-$). However, this mechanism seems unlikely, given the energy difference of approximately 5,100 cm^{-1} between the NO (A-X) (0,0) band and the O_2(B-X) Schuman-Runge band centered at 49,363 cm^{-1} [17]. Thus, we favor the plausible mechanism involving reactions of NO ($A^2\Sigma^+$) with O_2. Verification of this mechanism would require experimental and theoretical reaction kinetic studies.

The LODs of NO obtained in this study are comparable to the low-ppm values obtained by Stenberg, Hernberg, and Vattulainen [13] in a combustion environment using PA with UV laser excitation. However, they are 2 to 3 orders of magnitude greater than those obtained by REMPI, one-color LIF, and infrared laser PA. This difference is not a fundamental limitation of the technique, but is related to the system used. Instrument performance can be improved to enhance PA signal in the UV. First, significant improvements in the sensitivity can be expected with higher

laser energies. The energy required to saturate the transition, E_{sat}, is estimated using the relationship, $E_{sat} = hvA/2\sigma$, where A is the area of the laser beam. Using a value of 1 mm for the beam radius and a value of $\sigma_{226\ nm} = 6.6 \times 10\text{-}18\ cm^2$ [12], yields a value of approximately 4 mJ. This value is approximately 2 orders of magnitude more than that employed in this study. Second, an improvement in the signal can be realized by using a miniature PA cell with cylindrical microphones having built-in preamplifiers. Patel and Kerl have reported an improvement of a factor of ~10 with the use of new geometry and microphones [9]. Third, a reduction in noise will also result in lower LOD. Most of the PA noise is due to absorption or scattering of laser radiation from the widows, particularly if a thin film of absorbing material is deposited on the window. One solution to this problem is to use a windowless PA cell, as did Gerlach and Amer for monitoring in ambient conditions [27]. With an improved system design and employing higher laser energies, LODs of NO in the low-ppb are thus projected.

6. Conclusion

PA is complementary to LIF and REMPI methods and is particularly useful for environments requiring high-pressure and low laser intensities. The analytical utility of PA has been demonstrated for the detection of NO in Ar, N_2, and air using single-photon absorption corresponding to NO $A^2\Sigma^+$-$X^2\Pi$ (0,0) transitions near 226 nm. Characteristic features of the spectra and the relatively high rotational resolution at one atmosphere indicate that PA technique can be highly selective on the basis of excitation wavelength. The results show that the method enables a simple instrument design for the detection of NO in the low-ppm at atmospheric pressure using only 10–20 μJ of laser energy. LODs in the low-ppb range are projected with modifications of the experimental apparatus. For a given NO concentration and laser energy, the diluent gas influences the LOD. This influence is due to a difference in signal intensities rather than noise. The differences in signal intensities result from variations in heat capacities and collisional quenching rate constants. For air, the possibility of reactions involving electronically excited NO with O_2 must also be considered.

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Trace concentrations of NO are detected under ambient conditions by laser-induced photoacoustic spectroscopy. NO is excited via its $A^2\Sigma^+$-$X^2\Pi$ (0,0) band with radiation near 226 nm, and the subsequent heat released is monitored by a microphone. Rotationally resolved photoacoustic spectra are recorded and fit using a multiparameter computer simulation based on a Boltzmann distribution. Transition probabilities and rotational energies are used as input parameters. The effect of buffer gas pressure, buffer gas, laser energy, and NO concentration on PA signal is investigated both experimentally and by model calculations. Limits of detection of 1.2, 2.8, and 4.9 ppm are obtained for NO in Ar, N_2, and air, respectively. The ultimate sensitivity of this approach is greater with LODs projected in the low parts per billion by utilizing higher laser energies and an improved system design. The results are compared with previous studies using complementary laser-based spectroscopic techniques.

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