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Development of an ambient pressure laser-induced fluorescence instrument for nitrogen dioxide

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Concerns about the health effects of nitrogen dioxide (NO2) and its role in forming deleterious atmospheric species have made it desirable to have low-cost, sensitive ambient measurements of NO2. We have developed a continuous-wave laser-diode laser-induced fluorescence (LIF) system for NO2 that operates at ambient pressure, thereby eliminating the need for an expensive pumping system. The current prototype system has achieved sensitivity several orders of magnitude beyond previous efforts at ambient pressure (limit of detection of 2 ppb, 60 s averaging time). Ambient measurements of NO2 were made in Portland, Oregon using both the standard NO2 chemiluminescence method and the LIF instrument and showed good agreement (r2 = 0.92). © 2009 Optical Society of America

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1. Introduction

Nitrogen dioxide (NO2) is an important chemical species in the atmosphere and in combustion processes. Concerns about the health effects of NO2 and its role in forming deleterious atmospheric species have made it desirable to have sensitive ambient measurements of NO2. Although many direct and indirect measurement techniques exist [1–6], laser-induced fluorescence (LIF) has the advantage of being both a direct and sensitive measure of NO2. Several research groups have successfully implemented LIF for in situ atmospheric measurements of NO2 using the fluorescence assay with gas-expansion (FAGE) technique and have achieved excellent sensitivity at short averaging times [5,7–11]. Although laser diodes have dramatically reduced the cost and energy requirements of NO2 LIF [10], the low-pressure regime of these systems adds significant cost, energy use, and bulk via their pumping systems. We describe here a continuous-wave laser-diode LIF-based approach for NO2 that operates at ambient pressure, thereby obviating the need for a high-volume pumping system. The current system has achieved sensitivity several orders of magnitude beyond previous efforts [12,13], and with further equipment improvements it promises to be a sensitive, portable, and relatively low-cost NO2 monitoring system. As with low-pressure NO2 LIF, this system could also potentially serve as a “backend” to NO2 systems [6,14,15].

2. Instrument Description

Low-pressure LIF, as implemented in the FAGE technique developed by Hard et al. [16], involves the rapid expansion of sample gas, drawn through an orifice, to subambient conditions and requires a pumping system that is able to accomplish this while maintaining a substantial flow rate [8]. Because low pressure extends the fluorescence lifetime of the excited NO2, time-gated electronics can be employed to discriminate against the scattered laser photons. Sensitivities down to 15 ppt (10 s averaging time) have been reported using this technique [5]. Table 1...
The goal for this research was the development of a LIF instrument for operation at atmospheric pressure in order to reduce instrument complexity, cost, and energy consumption. In the current system the pressure dependence of the fluorescence signal was calculated using the governing equations for a LIF signal (system values follow parameters in parenthesis), $S_{NO_2}$, which is equal to the product of the excitation rate ($E_{NO_2}$), the fluorescence efficiency ($\Phi_{NO_2}$), and the collection efficiency ($C_{NO_2}$) of the detection system:

$$S_{NO_2} = C_{NO_2} \times E_{NO_2} \times \Phi_{NO_2}. \tag{3}$$

While excited $NO_2$ emits light over a wide spectrum (>1000 nm), only a fraction of that light falls within the spectral window of a typical detector (200–900 nm). $C_{NO_2}$ represents the efficiency involved with collecting the fluorescence signal:

$$C_{NO_2} = \Omega \times F \times T, \tag{4}$$

where $\Omega$ (0.038) is the solid angle intercepted by the collection optics for a typical off-axis design, $F$ (0.7) is the fraction of fluorescence occurring within the spectral window of the detector, and $T$ (0.8) is the fraction of transmitted fluorescence through the optics (lens and filters).

$E_{NO_2}$ is the rate at which $NO_2$ is excited with units of molecules s$^{-1}$, and can be expressed by

$$E_{NO_2} = ct \int \varphi(v)\sigma(v, \text{temp, pressure})dv, \tag{5}$$

where $c$ is the number density of $NO_2$ (molecules cm$^{-3}$), $l$/1 cm is the length through which laser light interacts with the gas that is within the detector’s view, $\varphi$ (3 × 10$^{15}$ photons s$^{-1}$ cm$^{-2}$) is the laser flux, and $\sigma$ (≈ 6 × 10$^{-18}$ cm$^2$ molecule$^{-1}$) is the absorption cross section of $NO_2$ at $\lambda = 406.3$ nm.

$\Phi_{NO_2}$ is a function radiative rate constant for electronically excited $NO_2$ and the quenching rates

### Table 1. Various LIF Instrumentation for NO$_2$, Excitation Wavelength $\lambda$, Radiative Lifetime for the Transition, Operational Cell Pressure, and Limit of Detection for a 1 min Averaging Interval

<table>
<thead>
<tr>
<th>LIF Instrumentation</th>
<th>Reference</th>
<th>Excitation $\lambda$(nm)</th>
<th>Radiative Lifetime ($\mu$s)</th>
<th>Cell Pressure (Torr)</th>
<th>LOD (ppt min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Low Pressure</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>George and O’Brien (1991)</td>
<td>[11]</td>
<td>532</td>
<td>140</td>
<td>0.26</td>
<td>600</td>
</tr>
<tr>
<td>Fong and Brune (1997)</td>
<td>[8]</td>
<td>565</td>
<td>140</td>
<td>7.5</td>
<td>460</td>
</tr>
<tr>
<td>Thornton et al. (2000)</td>
<td>[5]</td>
<td>585</td>
<td>100</td>
<td>0.35</td>
<td>5</td>
</tr>
<tr>
<td>Matsumoto et al. (2001)</td>
<td>[9]</td>
<td>523.5</td>
<td>82</td>
<td>0.7</td>
<td>125</td>
</tr>
<tr>
<td>Cleary et al. (2002)</td>
<td>[7]</td>
<td>640.2</td>
<td>330</td>
<td>0.2</td>
<td>145</td>
</tr>
<tr>
<td>Takentani et al. (2007)</td>
<td>[10]</td>
<td>473</td>
<td>108</td>
<td>0.5</td>
<td>140</td>
</tr>
<tr>
<td>Takentani et al. (2007)</td>
<td>[10]</td>
<td>410</td>
<td>39.9$^a$</td>
<td>0.5</td>
<td>390</td>
</tr>
<tr>
<td><strong>High Pressure</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Barnes and Kircher (1978)</td>
<td>[13]</td>
<td>450–470</td>
<td>~100</td>
<td>1–760</td>
<td>&gt; 100 000</td>
</tr>
<tr>
<td>Mann et al. (1995)</td>
<td>[12]</td>
<td>450–480</td>
<td>~100</td>
<td>760</td>
<td>&gt; 100 000</td>
</tr>
<tr>
<td>This Work</td>
<td></td>
<td>406.3</td>
<td>39$^a$</td>
<td>760</td>
<td>2000</td>
</tr>
</tbody>
</table>

$^a$Sivakumaran et al. [18] (2001).
For high pressures (\(\sum k_{qi}M_i \gg k_r\)) Eq. (6) simplifies to Eq. (7), where \(K_Q\) is a weighted average of the quenching rates, which for dry air is \(\sim 6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) \cite{10} and \(M\) is the total number density of air molecules (molecules cm\(^{-3}\)). The radiative rate constant for the fluorescence transition at \(\lambda_{\text{excitation}} = 406.3\) nm is \(k_r = 2.6 \times 10^4 \text{ s}^{-1}\) so that approximation in Eq. (7) can be made for pressures >10 Torr (\(M > 3.26 \times 10^{17}\) molecules cm\(^{-3}\)):

\[
\Phi_{\text{NO}_2} = \frac{k_r}{k_r + \sum k_{qi}M_i^i},
\]

\[
\Phi_{\text{NO}_2} = \frac{k_r}{K_QM},
\]

\[
E_{\text{NO}_2} \times \Phi_{\text{NO}_2} = \frac{k_r}{K_Q} \times X \times l \int \phi(\nu)\sigma(\nu, \text{temp, pressure})d\nu.
\]

The \(\text{NO}_2\) number density, \(c\), and the total number density of air, \(M\), combine to yield the result that the fluorescence is proportional to the mixing ratio of \(\text{NO}_2, X\), and does not depend on the absolute number density of \(\text{NO}_2\) at high pressures. Figure 1 shows the calculated lifetime and modeled fluorescence signal as a function of pressure with \(\lambda_{\text{excitation}} = 406.3\) nm. The analysis above indicates that the fluorescence yield is higher at atmospheric pressure, is pressure independent, and the yield is even higher for transitions that have short lifetimes. Low-pressure LIF succeeds by using temporal gating to discriminate against laser photons and reduce background. In this design, discrimination is achieved through optical filters. Based on Eq. (4), the expected fluorescence signal is \(\sim 40 \text{ counts s}^{-1} \text{ ppb}^{-1}\). To achieve a LOD of 1 ppb \(\text{NO}_2\) for a 60 s averaging time and a SNR = 2, the background should be less than 24,000 counts s\(^{-1}\) [Eq. (1)]. Background reduction (\(S_{\text{bg}} = 10000 \text{ counts s}^{-1}\)) was achieved through the use of high-quality long-pass filters (optical density >5 for \(\lambda = 300-431 \text{ nm}\) and \(\%T > 90\) for \(\lambda = 448-900 \text{ nm}\)). The instrumental design used in the current study is typical of low-pressure LIF instrumentation, which consists of a compact excitation laser system, long-pass filters, and a photomultiplier and signal processing system but without a high-volume pumping system (Fig. 2).

A. Laser Choice

The zero-pressure fluorescence lifetime, \(\tau^0\), and the radiative rate constant are reciprocal so that Eq. (7) may be rewritten as

\[
\Phi_{\text{NO}_2} = \frac{1}{\tau_{\text{NO}_2}^0 \times K_QM}.
\]

Therefore a fluorescence transition with a shorter lifetime would yield a greater fluorescence signal.

\[\text{Fig. 1. (Color online) Modeled lifetime [Eq. (2)] and fluorescence signal [Eqs. (3)-(6)] dependence on cell pressure. The parameters used to model our system with \(\text{NO}_2\) excitation at } \lambda=406.3\text{ nm were the detection solid angle (} \Omega = 0.038\text{), the fraction of fluorescence in the PMT spectral window (} \Phi = 0.7\text{), the transmission of the optics (} 0.8\text{), the path length (} l = 1\text{ cm), the absorption cross section (} \sigma = 6 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}\text{), the radiative rate constant (} k_r = 1/\tau^0 = 2.6 \times 10^4 \text{ s}^{-1}\text{), and the quenching constant (} Q = 6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\text{).}\]

\[\text{Fig. 2. (Color online) Schematic of ambient pressure LIF monitor. For calibration the dilution system with } \text{NO}_2\text{ standard and zero air inputs is used to deliver various concentrations of } \text{NO}_2\text{. When monitoring ambient } \text{NO}_2\text{ the digital valve is switched to deliver the air sample through the FeSO}_4 \text{ filter for background measurements.}\]
in other LIF instrumentation (Table 1), thereby gaining a factor of 2 by exciting in the blue. It was advantageous to choose a wavelength further into the blue that would allow more of the red-shifted fluorescence to be within the spectral window of the detector this system used (200–900 nm). A temperature- and current-controlled 35 mW continuous-wave GaN semiconductor laser diode centered on 405 nm (Sanyo, DL 5146-152) was used for the current design. The compact and relatively inexpensive laser diode is capable of being tuned over the range of 395–415 nm. Taketani et al. also employed a GaN laser diode tuned to 410 nm and, using the FAGE technique, they were able to achieve a LOD of 390 ppt for a 60 s average time [10]. The typical lifetime for a laser diode operating near room temperature is ~100,000 h. In this work, a greater SNR was achieved by tuning the diode to 406.3 nm, where the absorption cross section of NO₂ is ~6 × 10⁻¹⁹ cm² molecule⁻¹ [20, 21] at ambient pressure and temperature.

B. Fluorescence Cell

Although this system does not require a vacuum-tight fluorescence cell to make measurements, a cell was constructed to reject ambient light and facilitate gas sampling for calibration and ambient measurements. The fluorescence chamber is an airtight cell consisting of a cubic portion (4 cm × 4 cm × 4 cm) and two side arms ending with windows held at Brewster's angle, through which the laser beam is directed. The fluorescence signal is then detected orthogonal to the laser beam. In the two faces orthogonal to the detector and laser beam there are 0.25 in. (0.63 cm) stainless steel gas ports (Swagelok) to which 0.25 in. (0.63 cm) polytetrafluoroethylene tubing is connected for gas delivery and removal.

Ambient measurements were made by connecting a diaphragm pump (Rietschel Thomas, Model 2107, capable of 46.1 pm at 760 torr) to one of the gas ports while gas was drawn through the second gas port from an ambient roof-top intake manifold. Prior to entering the LIF chamber the gas passed through a Teflon filter (SKC, 47 mm) with a 2 µm pore size to remove light-scattering particles. Background measurements (ambient air minus NO₂) were made by passing the sample through ferrous sulfate (FeSO₄) which reduces NO₂ to NO. A digitally controlled Teflon valve switched between ambient air and background.

C. Signal Acquisition

Two 25 mm achromatic lenses with antireflection coating and 30 mm focal length (Edmunds Optics, ACH 25 × 30 VIS-NIR) were used to collect and focus the fluorescence signal onto the detector. In between the two lenses, four long-pass filters with cut-on wavelengths at 440 nm were employed (Chroma Tech, HQ440LP) to reject scattered laser photons and transmit fluorescence photons. These filters each achieve an optical density of 5 for wavelengths shorter than 431 nm and a transmittance greater than 90% for wavelengths in the range of 448–900 nm. The focal length of the first lens intercepts the laser beam so that the fluorescence signal travels parallel through the long-pass filters, passes through the second lens, and is focused onto the active surface of the detector. Fluorescence photons were detected by a photomultiplier tube (PMT) with quantum efficiency above 10% to 900 nm (Burle electron tubes, C31034). The PMT was kept at ~25 °C in a thermoelectric cooler (EMI Gencom, FACT 50 MKIII). The signal from the PMT was fed into a discriminator (Phillips, Model 704) with a pulse-pair resolution of 3.3 ns. Pulses from the discriminator were counted by a 100 MHz counter (Tennelec, TC531); the BCD output of the counter was read by a digital input/output module (Measurement Computing USB-DIO96/H) and then imported to a microcomputer via the USB bus. Data acquisition software written in-house using LabView simultaneously recorded photon (counts s⁻¹) and analog signals from the laser controlling system (i.e., power, temperature). For ambient measurements a chemiluminescence NOx analyzer (Thermo Environ. Inc., Model 42c) and an ozone monitor (Daisibi Environ. Corp., Model 1003AH) sampled ambient air from the same manifold as the LIF instrument. The data was collected by an analog-to-digital converter (Measurement Computing, USB-1408FS) and imported to the data acquisition software.

D. Possible Interferences

A potential source of interference for LIF NO₂ systems is the photolysis of ambient NO₃ to NO₂ during the time that it crosses the laser beam and the subsequent excitation to fluorescence of the produced NO₂ [11]. For wavelengths shorter than 585 nm the quantum yield of NO₂ from this reaction is near unity. The absorption cross section of NO₃ at 406.3 nm is 0.2 × 10⁻¹⁹ cm molecule⁻¹. Based on numerical simulations, the kinetics of photodissociation, laser excitation, and fluorescence, with the flow rate and photon flux of this system, the production of NO₃ from NO₂ will be negligibly low even when [NO₃] is orders of magnitude greater than [NO₂]. By operating in continuous-wave mode, this system has the advantage of very low photon density, thereby significantly reducing the likelihood of two photon inferences. Other species which can photodissociate to NO₂ include HNO₃, N₂O₅, HNO₄, peroxyacetyl nitrate, and CINO₂ but, with absorption cross sections 10–100,000 times smaller than that of NO₂, they will not interfere significantly at concentrations typically found in the atmosphere. The quenching rate constant for water is 6 times greater than for air [17], resulting in a LIF signal reduction of ~14% for 3% vol./vol. H₂O (approximately 100% relative humidity at 298 K) [10]. Simultaneous measurement of relative humidity and temperature can be used to correct for this when needed.
3. Results

A. Calibration

Calibration of the LIF instrument was performed for 0–350 ppb NO\textsubscript{2} concentrations. A standard of 46 ± 5\% ppm NO\textsubscript{2} in N\textsubscript{2} (Matheson Tri-Gas) was diluted with clean air using a multigas dilution system (Dasibi Model 5008). Clean air was produced from compressed ambient air passed through a laboratory constructed Purafil/Drierite/activated charcoal/molecular sieve filtration pack. The resulting air is ozone free, NO\textsubscript{x} < 1 ppb, total volatile hydrocarbons <1 ppb, dew point −0.6 C. Finally, the purified air is passed through a FeSO\textsubscript{4} cartridge in order to convert residual higher oxides of nitrogen to nitric oxide. A collocated chemiluminescence NO\textsubscript{x} (CL NO\textsubscript{x}) (calibrated with NIST standard gases at the Oregon Department of Environmental Quality), with a stated LOD of 0.4 ppb was used for calibrating our LIF instrument. Both instruments were allowed to stabilize at a given concentration for at least 30 min before using the point for calibration. The two methods are in good agreement ($r^2 = 0.998$) as shown in Fig. 3.

The slope of this plot is $16 ± 0.04$ counts s\textsuperscript{-1} ppb\textsuperscript{-1}, the standard error in $y$ is equivalent to 2.0 ppb and the intercept is equivalent to 0.4 ± 1.6 ppb NO\textsubscript{2}. This sets the LOD for our instrument at 2 ppb (1 min averaging time), and is the lowest reported concentration LIF measurement of NO\textsubscript{2} at atmospheric pressure. Actual operating system parameters, such as actual optical collection efficiency, filter transmission, and overlap of fluorescence to PMT quantum efficiency, are likely to be the causes of the discrepancy between expected and achieved sensitivities. These also provide a good starting place for improving the sensitivity of our instrument, such as increasing the solid angle ($\Omega$) collected by adding a curved mirror opposite of the collection lens.

B. Ambient Measurements

Ambient measurements of NO\textsubscript{2}, NO, and O\textsubscript{3} were made 10 through 14 February 2009 at Science Building 2 on Portland State University’s campus (Portland, Oregon) at a 1 min average interval. Air was drawn through a 10 m long intake manifold (15 cm diameter) from the rooftop, approximately 40 m above street level (the top of the intake is 2 m above the roof surface). The I-405 expressway runs 200 m west and south of the building. Our LIF instrument and CL NO\textsubscript{2} and ozone analyzers sampled from this manifold via 0.25 in. (0.63 cm

![Fig. 3. (Color online) Calibration of the LIF NO\textsubscript{2} signal (counts s\textsuperscript{-1}) against a standard chemiluminescence analyzer (CL NO\textsubscript{2} parts per billion).](image)

![Fig. 4. (Color online) Ambient measurements of ozone, NO, CL NO\textsubscript{2}, and LIF NO\textsubscript{2} made 10 through 14 February 2009 at the Portland State University campus Science Building 2 near the I-405 expressway.](image)
perfluoroalkoxy tubing. A Teflon filter with a pore size of 2 μm (SKC, 47 mm) was used in front of the LIF sampling tube (the same as the one integrated into the CL–NO₂ system). A background measurement was made once every half-hour for 5 min by passing the sample through a filter of FeSO₄ to convert NO₃ to NO.

The ambient data is presented with a 1 min averaging time for all instruments. Figure 4 shows the good agreement between the two NO₃ methods (r² = 0.92, slope = 0.98, intercept = 0.7 ppb). It is notable that the relatively high frequency changes in NO₂ levels are reproduced by both instruments. The wind direction during this period is generally from the East with an average temperature of ~5 °C; these winds originate from the Columbia River Gorge [22]. Nitrogen oxide and ozone anticorrelation is evident during this period. The high NO period on 12 February 2009 is attributable to the accumulation of NO emissions into the airshed during a low ventilation period (high-pressure system with very low wind speed). Since very little photochemistry is occurring during the overcast days of this period, oxidation of NO to NO₂ is limited to ozone titration.

4. Conclusion

We have described a continuous-wave laser-diode LIF-based approach for NO₂ that can be operated at atmospheric pressure. The use of high-quality optical filters has facilitated low-concentration detection of NO₂ using atmospheric pressure LIF by providing substantial discrimination against scattered laser photons without the use of time-gated electronics, which add complexity and cost to the LIF instrumentation. This improvement allows operation at atmospheric pressure with a low-cost diaphragm sampling pump.

Although chemiluminescence detection of NO₂ has known and potentially significant interferences, it is the most common method for in situ ambient regulatory monitoring of NO₂. LIF offers a direct and sensitive method for ambient NO₂, but current systems are complex and costly to operate. By operating at higher pressures this system lowers the cost and complexity of LIF for in situ ambient detection of NO₂. This system can be utilized as a “backend” detector of an NO₂ ambient monitor. Since this NO₂ system does not require an expensive high-capacity pump, separate cells for each constituent of NO can be employed, thereby eliminating the complexity and potential chemical artifacts associated with switching between NO₂ modes.

In summary, we have developed a LIF instrument for NO₂ detection which may operate at atmospheric pressure and has a limit of detection of 2 ppb (SNR = 2) with an averaging interval of 60 s. With improvements in the optical train, it is expected that this system will easily achieve sub-parts-per-billion detection limits, making it suitable for ambient measurements of NO₂. Tuning of the laser on-off the NO₂ absorption peak (currently not possible with our system) will eliminate the need for FeSO₄ for background measurements. This system also has potential application for other fields where direct and nonintrusive measurements of NO₂ are needed, such as flame, combustion, and surface chemistry.

References

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