High-sensitivity detection of NO in a flame using a tunable ArF laser

A. M. Wodtke, L. Huwel, H. Schluter, G. Meijer, and P. Andersen

Max-Planck-Institut für Strömungsforschung, Bunsenstrasse 10, D-3400 Göttingen, Federal Republic of Germany

H. Voges

Laser Laboratorium Göttingen e.V., Tamannstrasse 6, D-3400 Göttingen, Federal Republic of Germany

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A tunable, narrow-band ArF laser has been used for laser-induced fluorescence detection of NO in natural abundance in a flame experiment. Probing rotational states of the D $^{3}Σ$ v′ = 0 ← $^{3}Π_{3/2,1/2}$ v″ = 1 transition was observed in a relatively long fluorescence lifetime of 20 nsec, quenching is less severe than in the A state. Dispersed-fluorescence experiments show that trace NO can be selectively detected with the narrow-band laser. Therefore use of a high-transmission broadband filter and high-efficiency collection optics should yield a single-shot detection limit at or below 1 part in 10⁸ (ppb).

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we would say that $8 \times 10^{-6}$ T

Neglecting fluorescence quenching the concentration of NO increased by $2.5 \times 10^4$ over the same magnitude of the signal was estimated that the observed concentration of NO is of the order of 100 ppm, consistent with other observations. The absence of the $B \rightarrow X$ transition in the flame is explained by a calculation similar to that just described, which predicts a detection limit of 50–100 ppm.

The 1-ppm detection limit observed for the $D \rightarrow X$ transition can be greatly improved, as discussed below. The greatest loss in experimental sensitivity is due to the use of a monochromator, which collects only $10^{-3}$ of the fluorescence and has a transmission efficiency of 0.1. The selective detection of flame species often requires the use of dispersed-fluorescence techniques, because in the complex environment of a flame there are many possible absorbers and fluorescers other than the molecule of interest. This is especially true when one is detecting minority species at the ppm level. If the molecule of interest can be selectively excited by the laser, a large increase in detection sensitivity can be achieved.

In particular, with an ArF laser there is a problem because of the numerous O$_2$ transitions that are observed with strong LIF signals despite the fast predissociation of the excited electronic state. This can be clearly seen from Fig. 3(a), which shows the dispersed-fluorescence spectrum observed when a broadband ArF laser is employed. O$_2$ accounts for more than 50% of the fluorescence. Without the use of a monochromator, NO cannot be distinguished from O$_2$ with the broadband laser.

Figure 3(b) shows the dispersed-fluorescence spectrum observed when the $R_1(26.5)$ transition is excited with a narrow-band ArF laser. Two progressions are observed, one from the D state ($v' = 0 \rightarrow v'' = 2–5$) and one due to rapid quenching of the D state to the C state and subsequent fluorescence ($v' = 0 \rightarrow v'' = 1–4$). The C-state progression is shifted 919 cm$^{-1}$ to the red and has the same Franck-Condon factor pattern as the D state, an expected result owing to the similarity of the D and C states. Laser excitation spectra at an emission wavelength of 221.2 nm yield the same $D \rightarrow X$ spectra as in Fig. 1, confirming that quenching of the D state is responsible for the C-state emission and that no direct excitation of the C state is observed.

The resolution of the monochromator was set high enough to observe the single P, R line pair emission, expected if O$_2$ were excited by an accidental coincidence with the narrow-band component of the laser output. Since this is not observed, any O$_2$ fluorescence can be excited only by the broadband component of the laser, which is at least 10 times smaller in

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\includegraphics[width=\textwidth]{Fig. 1. NO D $^2\Sigma$ $v' = 0 \rightarrow X^3\Pi_{3/2,1/2} v'' = 1$ transitions observed with an unfocused tunable ArF laser in a propane-O$_2$ flame. The concentration of NO is estimated to be 100 ppm. Emission from $v' = 0$ to $v'' = 3$ was monitored at 208.0 nm with a 0.6-nm monochromator resolution.
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\includegraphics[width=\textwidth]{Fig. 2. NO D $^2\Sigma$ $v' = 0 \rightarrow X^3\Pi_{3/2,1/2} v'' = 1$ (asterisks) and $B^2\Pi$ $v' = 7 \rightarrow X^3\Pi v'' = 0$ transitions measured in a cell at 2 Torr pressure and 300 K. Monochromator conditions are the same as for Fig. 1.
\end{center}
compared with what is possible with the monochromator. It is anticipated that, with such an experimental arrangement, NO will be detectable with single laser shots at or below the 1-ppb level in a real combustion system. NO LIF imaging without doping should also be achievable with single laser shots.

LIF detection of NO in natural abundance in a flame has been observed with a high signal-to-noise ratio by using a narrow-band tunable ArF laser, an ideal tool for combustion analysis. A detection limit of 1 ppm was obtained with a monochromator-based dispersed-fluorescence detection method, in which only $10^{-4}$ of the fluorescence light is observed by the photomultiplier. Selective excitation of NO with the narrow-band laser yields a clean NO emission spectrum over a large spectral range and presents the possibility of using high-transmission filters with high-efficiency collection optics to bring the detection limit to the 1-ppb level. Two-dimensional imaging of NO without seeding should also be possible.

References