

Sequential two-photon-laser-induced fluorescence: a new method for detecting atmospheric trace levels of NO

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Received January 13, 1982

Sequential two-photon-laser-induced fluorescence (TP-LIF) in NO has been achieved by using 226-nm radiation to excite the $X^2\Pi \rightarrow A^2\Sigma$ transition followed by excitation of the $A^2\Sigma \rightarrow D^2\Sigma$ transition using the fundamental output of a Nd:YAG laser at 1064 nm. The resulting fluorescence was monitored at wavelengths as low as 187 nm ($D^2\Sigma \rightarrow X^2\Pi$ transition), thus permitting major discrimination against conventional noise sources as encountered in single-photon-laser-induced fluorescence (SP-LIF) systems. Also, since the 226-nm radiation used in the TP-LIF method is generated in the same manner as in the SP-LIF technique (i.e., the sum-frequency mixing of 288- with 1064-nm radiation), the two-photon sequential-pumping scheme requires no major extra optical hardware. Although the final optimization of the TP-LIF NO method has not yet been completed, extrapolations based on currently measured signal and noise levels suggest a detection sensitivity level of 3 parts in 10^{13} (0.3 pptv) under atmospheric conditions. This would represent approximately a 25-fold increase in sensitivity over the SP-LIF NO technique.

Earlier laser efforts at detecting NO under atmospheric conditions of composition and pressure have involved single-photon excitation of NO with the monitoring of fluorescence at wavelengths that are red shifted relative to the excitation wavelength.¹ The sequential two-photon-laser-induced fluorescence (TP-LIF) technique being reported on here has potentially far greater sensitivity than the single-photon method because the resulting fluorescence is blue shifted relative to the shortest laser wavelength used to pump NO optically.

The relevant energy levels employed in the two-photon excitation of NO are shown in Fig. 1. (Data on the natural radiative lifetime of NO and the appropriate quenching rates for different electronic states are given in Table 1.) For this system, it can be seen that a significant fraction of the fluorescence, monitored at λ_3 , occurs at a lower wavelength than both the λ_1 and λ_2 laser excitation wavelengths. As is shown in Fig. 2, this scheme thus permits discrimination against all Rayleigh- and Stokes-shifted Raman noise sources and white fluorescence from aerosols and chamber walls as well as fluorescence from other trace gases, such as that from SO₂. The dominant noise sources in the TP-LIF method now appear to be anti-Stokes Raman scatter, resulting from N₂ and O₂, and weak multiphoton-absorption processes by unidentified gas-phase impurities. Evaluation of the magnitude of this real photon noise (relative to the signal) is easily achieved by simply tuning the dye laser (in actual fact the 226-frequency-mixed wavelength) ~ 0.02 nm off the NO absorption line.² Although noise tests have not yet been completed on the NO system by using fast-collection optics, based on other two-photon systems in our laboratory also involving blue-shifted fluorescence,⁴ the real photon noise from the TP-LIF NO system is predicted to be 10^5 to 10^6 times lower than that observed in the single-photon-laser-induced fluorescence (SP-LIF) NO system—both being normalized to the same input energy at 226 nm

and for the same transmission in collection optics. Thus, unlike SP-LIF systems, all of which tend to be signal-to-noise limited under realistic atmospheric sampling conditions, the TP-LIF system is expected to be a signal-limited system under typical sampling conditions.

The TP-LIF signal strength D_{λ_3} (e.g., detected signal photons per laser shot) can be expressed in terms of several convenient efficiency terms, namely,

$$D = E_{\lambda_1} \times E_{\lambda_2} \times E_f \times E_d \times E_e \times V \times [\text{NO}]. \quad (1)$$

Each of these terms can be assigned physical significance as follows:

$$E_{\lambda_1} = \left(\begin{array}{c} \text{optical pumping} \\ \text{efficiency} \\ \text{at } \lambda_1 \end{array} \right) = \left[1 - \exp - \left(\frac{P_{\lambda_1} \sigma_{\lambda_1}}{a_{\lambda_1}} \right) \right] \times f_i \times S_{\lambda_1}, \quad (2)$$

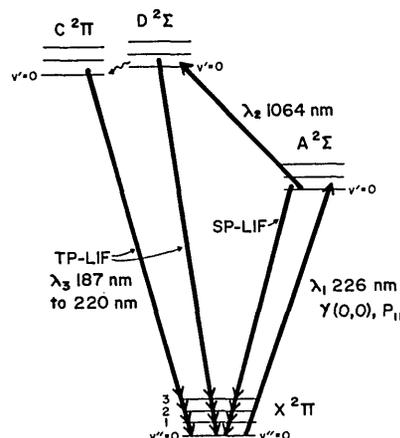


Fig. 1. NO energy-level diagram showing those transitions involved in the sequential two-photon-laser-induced fluorescence detection scheme.

Table 1. Spontaneous Emission and Quenching Frequency Factors in One Atmosphere of Air^a

Upper State	$A^2\Sigma$	$C^2\Sigma$ (sec ⁻¹)	$D^2\Sigma$ (sec ⁻¹)
k_f to $X^2\Pi$	5×10^6 sec ^{-1b}	5×10^{7b}	4×10^{7b}
k_f to $A^2\Sigma$	–	3.5×10^{7b}	9.5×10^{6b}
k_d ($v' < 1$)	No predissociation for $v' < 4^b$	1.7×10^{9b}	$< 8 \times 10^{6b}$
$k_q[M]$	1×10^9 sec ^{-1c}	4×10^{10b}	$\sim 2 \times 10^{9d}$

^a The composition has been taken to be 590-Torr N₂, 150-Torr O₂, and 10-Torr H₂O.

^b Taken from Ref. 5.

^c Taken from an average of data in Refs. 6 and 7.

^d Taken from Ref. 8.

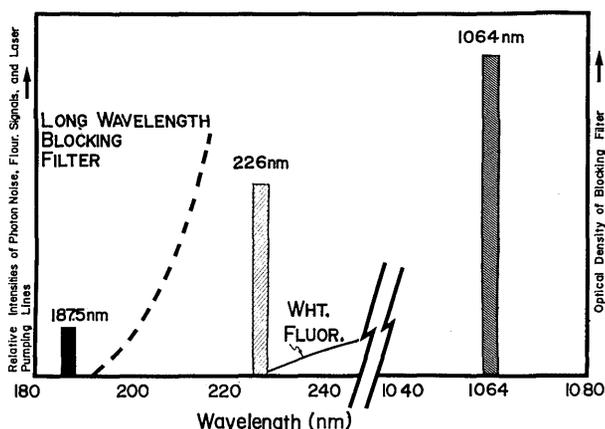


Fig. 2. Qualitative presentation of the two-photon-laser-induced detection scheme showing the spectral location of the laser pumping lines, the monitored fluorescence, white-noise fluorescence, and the cutoff characteristics of a future long-wavelength cutoff filter. It is not intended that absolute photon fluxes be estimated from this graph.

$$E_{\lambda_2} = \left(\begin{array}{c} \text{optical pumping} \\ \text{efficiency} \\ \text{at } \lambda_2 \end{array} \right) = \left[1 - \exp - \left(\frac{P_{\lambda_2} \sigma_{\lambda_2}}{a_{\lambda_1}} \right) \right] \times \frac{a_{\lambda_1}}{a_{\lambda_2}} \times R \times S_{\lambda_2}, \quad (3)$$

$$E_f = \left(\begin{array}{c} \text{fluorescence} \\ \text{efficiency} \end{array} \right) = \frac{k_f}{k_f + k_d + k_q[M]}, \quad (4)$$

$$E_d = \left(\begin{array}{c} \text{optical} \\ \text{detection} \\ \text{efficiency} \end{array} \right) = \gamma_{\lambda_3} \times Y_{\lambda_3} \times Z_{\lambda_3} \times \phi_{\lambda_3}, \quad (5)$$

$$E_e = \left(\begin{array}{c} \text{electronic} \\ \text{detection} \\ \text{efficiency} \end{array} \right) = \frac{\text{PMT signal pulses counted}}{\text{PMT signal pulses emitted}}, \quad (6)$$

$$V = \left(\begin{array}{c} \text{volume of} \\ \text{sampling} \\ \text{region} \end{array} \right) = a_{\lambda_1} \times l \text{ for } a_{\lambda_1} < a_{\lambda_2}. \quad (7)$$

Here P_{λ_1} and P_{λ_2} represent the number of laser photons per laser shot at λ_1 and λ_2 , respectively; σ_{λ_1} and σ_{λ_2} are the effective absorption cross sections for NO at λ_1 and λ_2 ; f_i is the fraction of the total NO population in quantum states that can be pumped at 226 nm with a laser linewidth $\Delta\lambda$; k_f is the reciprocal of the natural lifetime; k_d is the first-order rate constant for dissociation; k_q is the biomolecular electronic-quenching-rate constant; $[M]$ is the concentration of the quenching species; γ_{λ_3} is the fraction of total fluorescence falling within the optical-transmission window; Y_{λ_3} is the optical-collection efficiency; Z_{λ_3} is the optical-filter transmission factor; ϕ_{λ_3} is the quantum efficiency of the photomultiplier tube (PMT) at λ_3 ; and a_{λ_1} and a_{λ_2} are the cross-sectional areas of the λ_1 and λ_2 laser beams. S_{λ_1} and S_{λ_2} are saturation parameters, which can be taken to be unity under low laser-energy-density conditions and/or with small cross sections for the absorbing species. Bradshaw *et al.*¹ have demonstrated this to be the case for S_{λ_1} for 226-nm laser energies up to 1 mJ involving a 5-mm-diameter beam. S_{λ_2} has not been quantitatively assessed, but it appears that the cross section for the $A^2\Sigma \rightarrow D^2\Sigma$ transition, when 1064-nm radiation is used, is quite small; thus the value of S_{λ_2} is likely to be close to unity. This assumption, however, will need to be verified. The quantity R in the expression for E_{λ_2} defines the fraction of NO molecules that have been pumped into the $A^2\Sigma$ state that survives quenching by N₂ and O₂ and therefore is excited into the $D^2\Sigma$ state. This quantity cannot be evaluated directly at this time because of the absence of a known cross section for 1064-nm absorption from the $A^2\Sigma$ state. Thus the term E_{λ_2} has here been evaluated by experimentally determining the quantities D_{λ_3} , V , $[\text{NO}]$, E_d , and E_e and using calculated values for E_{λ_1} and E_f .

The TP-IF system used in this study is shown in Fig. 3. In this system, the Nd:YAG laser type was an ILS NT-572, whereas the pulsed dye laser was designed and built by Quanta Ray. The latter dye-laser unit was operated in an oscillator-end-pumped-amplifier configuration and was flied with R610 dye.

An evaluation of each of the efficiency terms in Eq. (1), for the experimental system shown in Fig. 1, gave $E_{\lambda_1} = 0.013$, $E_{\lambda_2} = 0.0052$, $E_f = 0.020$, $E_d = 3 \times 10^{-7}$, $E_e = 0.9$, $V = 0.04$ cm³. The signal strength D_{λ_3} for an NO concentration of 2.5×10^{12} molecules cm⁻³ (100 ppbv) is calculated to be

$$D_{\lambda_3} = 220 \text{ photons/6000 laser shots.}$$

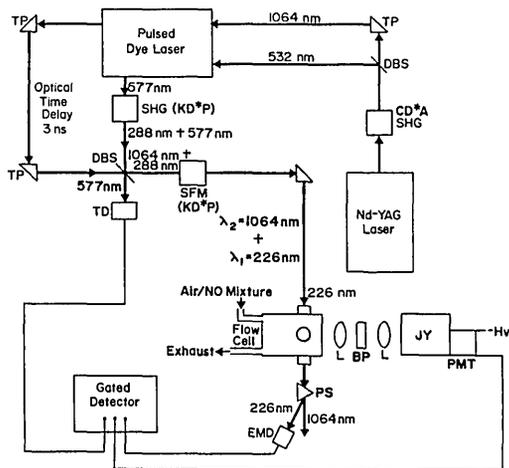


Fig. 3. Sequential two-photon-laser-induced fluorescence experimental setup: BP, bandpass filter; DBS, dichroic beam splitter; EMD, energy-monitor diode; L, lens; PMT, photomultiplier tube; PS, 60° prism separator; SFM, sum-frequency-mixing crystal; SHG, second-harmonic-generating crystal; TD, trigger diode; TP, turning prism; JY, Jobin-Yvon double monochromator.

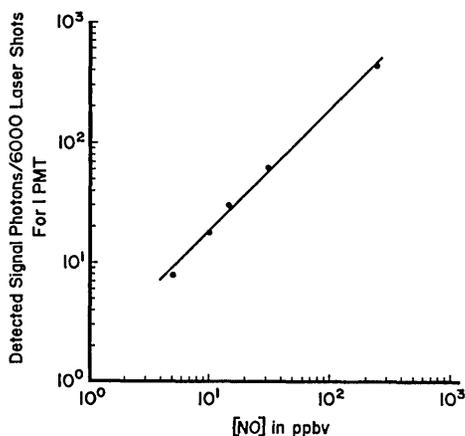


Fig. 4. Two photon-laser-induced fluorescence calibration curve for NO: $\lambda_1 = 650 \mu\text{J}$ (226 nm), $\lambda_2 = 75 \text{ mJ}$ (1064 nm). Signals are reported for a 1-atm-pressure air mixture.

An experimental calibration curve showing the linearity of the TP-LIF NO system over 2 orders of magnitude in NO concentration is shown in Fig. 4. These data were recorded under atmospheric conditions of pressure and composition. The signal-limited nature inherent in the TP-LIF technique permits linear gains in detection sensitivity with increases in the efficiency of the collection optics, laser energy, etc., compared with the square-root gain in detection sensitivity inherent in signal-to-noise-limited methods. By a judicious choice of hardware, namely, a fast far-UV solar-blind PMT, high-transmission chemical-solution filters, high-speed-collection optics, and a somewhat higher laser energy at 226 nm (i.e., 1.2 versus 0.65 mJ), we expect to achieve the following values for each of the above efficiency terms: $E_{\lambda_1} = 0.024$, $E_{\lambda_2} = 0.0052$, $E = 0.020$, $E_d = 1.3 \times 10^{-5}$, $E_o = 0.9$, $V = 0.25 \text{ cm}^3$, where the change in the value of V reflects the improvement in the frac-

tion of the laser beam (length and width) from which fluorescence is to be sampled rather than a change in the laser-beam diameter. The increase in the value of E_d , on the other hand, reflects the calculated improvement in the efficiency with which fluorescence from a given volume/element in the laser beam will be sampled using $f:1$ collection optics in conjunction with chemical filters rather than the J-Y double-monochromator system. In the above improved experimental system (currently under development in our laboratory), we would calculate a signal strength for an NO concentration of 100 ppbv of

$$D_{\lambda_3} = 1.1 \times 10^5 \text{ photons/6000 laser shots.}$$

This represents an improvement of ~ 500 -fold over the system used here initially to assess the TP-LIF technique. In addition, if six PMT's are utilized rather than one (for purposes of airborne field sampling), the improvement in sensitivity would be ~ 3000 -fold, again assuming that we are operating in a signal-limited NO-concentration range. Thus we now estimate that the detection limit for NO by the sequential TP-LIF method (utilizing technology currently available or under development in our laboratory) will be ~ 0.3 pptv for an integration time of 20 min.

In conclusion, it now appears that the sequential TP-LIF technique has the potential for detecting atmospheric NO levels as much as a factor of 25 times lower than that possible by using the SP-LIF detection method. In addition, this new technique's inherent ability to overcome conventional noise sources, e.g., Rayleigh and Stokes-Raman scatter and white-background fluorescence, suggests that it may be applicable to environments heretofore inaccessible to the SP-LIF technique as well as to other nonlaser techniques. This might involve using the TP-LIF system to measure NO in high aerosol environments, such as in clouds.

References

1. J. D. Bradshaw, M. O. Rodgers, and D. D. Davis "Single photon/laser-induced fluorescence detection of NO and SO₂ under conditions of atmospheric composition and pressure" Appl. Opt. (to be published).
2. In actual fact, several NO lines are excited at the P_{11} bandhead, the average J value being 15/2.
3. M. O. Rodgers, K. Asai, and D. D. Davis, "Photofragmentation-laser-induced fluorescence: a new method for detecting atmospheric trace gases," Appl. Opt. **19**, 3597 (1980).
4. D. D. Davis, M. O. Rodgers, K. Liu, and J. D. Bradshaw, "Photofragmentation/laser-induced fluorescence detection of NO₂ under conditions of atmospheric composition and pressure" Appl. Opt. (to be published).
5. S. Cieslik and M. Nicolet, "The aeronomic dissociation of nitric oxide," Planet. Space Sci. **21**, 925 (1973).
6. L. A. Melton and W. Klemperer, "Quenching of NO $A^2\Sigma^+$ by O₂ $X^2\Sigma_g^-$," Planet. Space Sci. **20**, 157 (1972).
7. I. S. McDerimid and J. B. Laudenslager, "Radiative lifetimes and electronic quenching rate constants for single-photon-excited rotational levels of NO ($A^2\Sigma^+$, $v' = 0$)," J. Quant. Spectrosc. Radiat. Transfer (to be published).
8. Y. Haas and M. Asscher, "Photosensitive chemistry," *Advances in Chemical Physics*, Vol. XLVII, J. Jortner, R. D. Levine, and S. A. Rice, eds. (Wiley, New York, 1981).