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Simultaneous spatially resolved NO and NO$_2$ measurements using one- and two-photon laser-induced fluorescence

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We demonstrate how spatially resolved distributions of NO and NO$_2$ can be simultaneously detected by using a single laser pulse at 452 nm. The laser-induced fluorescence from NO was achieved by a two-photon transition in the γ band at 226 nm followed by UV detection, whereas NO$_2$ was detected by a one-photon transition followed by Stokes fluorescence.

Laser-induced fluorescence, LIF, is one of the most promising techniques for diagnostics of combustion processes, as described, e.g., in Ref. 1. By tuning a laser wavelength to an absorption line of a molecule or an atom, followed by detection of subsequent fluorescence radiation, it is possible to measure temperatures as well as low number densities for flame radicals, e.g., OH, CH, C$_2$, and CN.

During the past few years two major achievements have been made in the application of LIF to combustion studies. The first of these achievements was a technique yielding spatially resolved measurements, first in one dimension[2] by using a linear diode array, shortly followed by two-dimensional measurements utilizing a vidicon[3] and a diode matrix.[4] The imaging technique was also extended to two-species (C$_2$, OH) detection by using two separate laser systems.[5] The second achievement was the introduction of multiphoton absorption processes, which made it possible to detect atoms and molecules, e.g., O, H, C, and CO, that absorb in the VUV spectral region and therefore are impossible to detect by a one-photon transition because of large molecular absorption at these wavelengths.

Much of the groundwork concerned with the detection of light atoms (O, N) was carried out by Bischel et al.[6] under well-controlled conditions. This work was followed shortly by flame detection of O (Ref. 7) and H.[8,9] The combination of imaging and multiphoton absorption LIF experiments was also recently reported for CO,[10] O,[11] and H (Ref. 12) in a flame environment.

In this Letter we describe the simultaneous detection of NO and NO$_2$ by using one laser pulse at 452 nm. This wavelength induces a two-photon transition in the γ band at 226 nm of NO with subsequent fluorescence in the UV spectral region. NO was previously studied by using either a one-photon transition,[13,14] or a two-photon transition,[15,16] and imaging experiments of NO have been described by Kychakoff et al.[17] NO$_2$ has an absorption band in the blue spectral region, and the fluorescence occurs in the visible region. LIF from NO$_2$ is complicated by the fact that the lifetime is quite long, ~50 μsec, which makes the quenching phe-

nomenon severe. However, Barnes and Kircher[18] have used a laser wavelength between 450 and 470 nm, where the lifetimes are less than 1 μsec,[19] and they were able to observe fluorescence from NO$_2$ in a flame at atmospheric pressure.

With the global interest in NO$_x$ as a major pollutant, we believe that the technique proposed in this Letter is of great value. It would be possible, e.g., to study the spatial conversion of NO into NO$_2$ in flames and turbulent flows. Here the technique is demonstrated in a cell. For a more realistic situation preliminary experiments were performed with a jet of NO in air, where the conversion of NO to NO$_2$ could be seen as a brownish discoloration. However, since we lacked proper ventilation conditions, these experiments were abandoned for reasons of health.

A diagram of the setup used in the measurements is shown in Fig. 1. A Quanta-Ray DCR-1A Nd:YAG laser together with a Quanta-Ray PDL-1 tunable dye laser was used. The dye laser was operated with Coumarin 2 dye (Lambda Physik), yielding an output energy level of about 5 mJ at 452 nm, the wavelength used for the one-photon transition in NO$_2$ and the two-photon transition in NO. Approximately 30% of
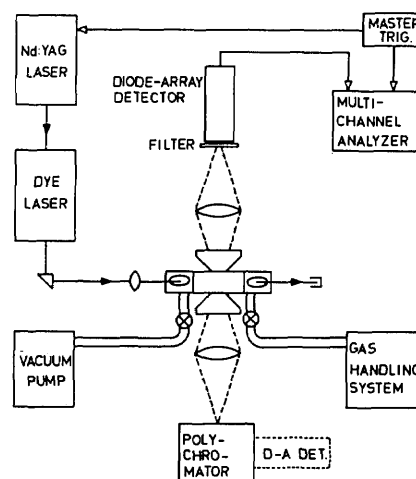

Fig. 1. Experimental setup. D-A DET., diode-array detector.
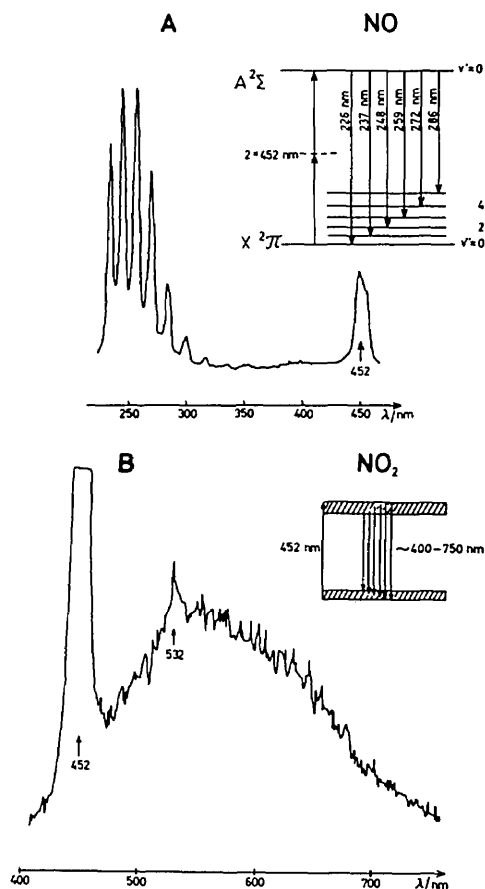
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Fig. 2. LIF spectra of A, NO molecules and B, NO_2 molecules, with an excitation wavelength of about 452 nm. The relevant energy-level diagrams are inserted.

the output power was broadbanded because of amplified spontaneous emission. The dye-laser beam was focused into a cell with a lens (f = 75 mm). The cell, with a volume of 24 cm^3, was made of stainless steel and equipped with windows made of fused silica in order to minimize laser-induced fluorescence. A gas-handling system and a vacuum pump were connected to the cell so that various amounts of pure NO or NO–air/N_2 mixtures could be introduced.

The fluorescence radiation from the NO/NO_2 molecules was collected by a 50-mm-diameter f/1 quartz lens perpendicular to the laser beam. In the spectral measurements the light was focused onto the entrance slit of a Jarrell-Ash MonoSpec 18 that was used as a polychromator with a dispersion of 18 nm/mm (300 grooves/mm, blaze 300 nm). In the focal plane of the polychromator the light was detected by an EG&G PARC Model 1420 intensified diode-array detector.

In the imaging experiments the diode-array detector was placed directly in the image plane, after isolation of the interesting spectral region with optical filters. The diode-array detector was connected to the EG&G PARC Model 1218/1215 detector controller and multichannel analyzer, where the data were finally stored on diskettes. The detector was gated through a PARC Model 1211 high-voltage-pulse generator with a gate width of 1 μsec.

In order for the appropriate filters for the imaging

experiments to be chosen, the spectral emission from NO and NO_2 was identified with the polychromator setup. Figure 2A shows the fluorescence spectrum of NO with an excitation wavelength of 452.16 nm. The fluorescence forms a progression from v' = 0 to v'' = 0–7 in the spectral region between 230 and 320 nm. The peak at 452 nm is due to scattered laser light in optical components. The fluorescence spectrum of NO_2, which is shown in Fig. 2B, lies on the low-energy side of the laser wavelength. The spectrum is broad and extends over the whole visible spectral region. Thus the light can easily be separated from the NO radiation, which is in the UV, with a cutoff filter. We used a Schott OG 590 filter, which also sufficiently suppressed the scattered laser light at 355, 452, and 532 nm. The NO fluorescence could be isolated with a solar-blind interference filter (Corion), which is transparent between 280 and 320 nm. We also used a Schott UG 11 filter, which is transparent for both NO and NO_2 fluorescence but suppresses scattered laser light.

A one-dimensional concentration distribution can be recorded if the laser beam, which gives rise to the fluorescence, is imaged directly onto a diode-array detector. Figure 3A shows a recording from a single pulse in 1000-parts-in-10^6 (ppm) NO in N_2 in the cell at atmospheric pressure. Because of the relatively fast conversion of NO to NO_2, a steady stream of the calibration gas was passed through the cell.

The concentration of NO in the cell is thus uniform. The recording shows the behavior of a two-photon excitation the efficiency being dependent on the intensity squared, which gives rise to a higher signal from the focus of the laser beam. However, a more detailed study of the NO signal strength as a function of laser intensity in the focal point revealed a departure from the squared dependency at high laser power.
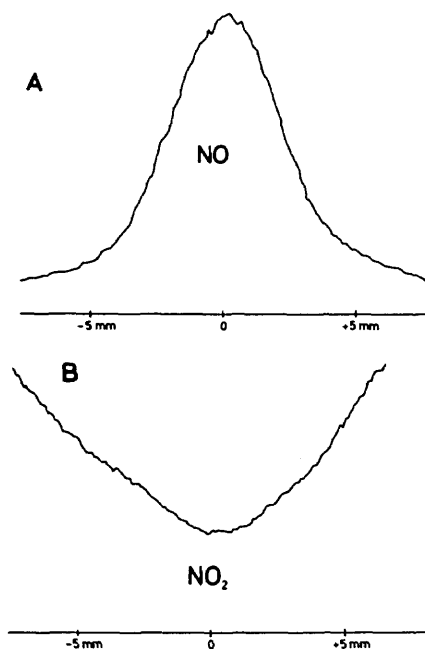

Fig. 3. One-dimensional single-shot image of the fluorescence distribution around the laser-beam focus for NO and NO_2, respectively.
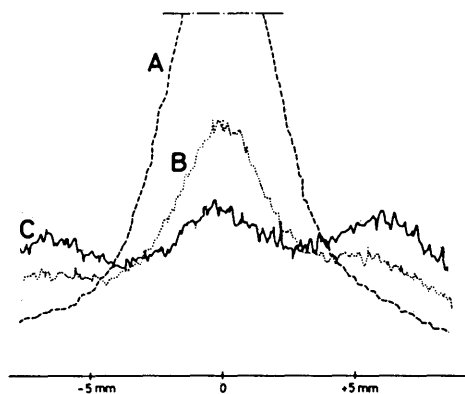
Fig. 4. Overlapping NO and NO_2 fluorescence distributions, captured in a single laser shot. A is a recording taken directly after filling the cell with a small amount of pure NO. B and C were taken with a time delay of 6 and 12 min, respectively.

At this point the signal dependence is closer to linear. According to Ref. 20, this phenomenon is more likely due to resonant Stark broadening than to a pure saturation effect.

In Fig. 3B the laser focus is imaged in the red spectral region with a small amount of NO_2 in the cell. Because of saturation effects the intensity decreases in the focus, although the NO_2 concentration is uniform in the cell. Thus, because of the one- and two-photon excitation, in the first case a greater signal is obtained outside the focus and in the second case most of the signal originates from the focus. These effects can be avoided by using a focusing lens with a longer focal length. In both Figs. 3A and 3B the peak signal intensity was ~1500 counts/pulse.

In order to examine the potential for practical measurements using this two-species approach, preliminary tests were performed yielding detectivity limits. Using the calibration gas with 1000 ppm of NO in N_2 followed by successive dilution, it was possible with the two-photon scheme to detect on the order of 1 ppm of NO at atmospheric pressure. By flowing 2000 ppm of NO_2 in air through the cell, we estimate a detection limit for NO_2 of the order of 100 ppm when using an excitation wavelength at 452 nm and a monochromator followed by a photomultiplier on the detection side. This number may seem surprisingly high since Ref. 18 gives the same detection limit with a laser power ~1000 times lower than ours. However, the use of a different and more favorable excitation wavelength, the saturation effect, and the detection by Barnes and Kircher of a very broadband wavelength distribution are probably the main reasons for the difference.

Figure 4 shows a recording from a single pulse of the somewhat overlapping fluorescence distributions from NO and NO_2 when a UG 11 filter was placed in front of the detector. The recordings were taken sequentially, every 6 min, after the cell was filled with a certain amount of pure NO at low pressure. The apparent transformation of NO to NO_2 is due to a small leakage of air into the cell and also to adsorption of NO on the cell walls followed by catalytic oxidation to NO_2.[21]

As has been demonstrated in this Letter, NO and NO_2 can be detected simultaneously by using only one laser pulse. This can be compared with our previous two-species LIF experiments,[5] in which two completely different laser systems were used. In these experiments the two species (C_2 and OH) were detected separately by using a special mirror arrangement creating two images and different optical filters. This approach would also work in the present NO/NO_2 experiment, since the NO fluorescence occurs in the UV spectral region while the NO_2 fluorescence is found in the visible and toward the red spectral region.

The approach with linear array described here could of course easily be extended to two-dimensional images, as was recently shown by Cattolica.[22]

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