

Nitric Oxide Measurements in the Core of Diesel Jets Using a Biofuel Blend

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ABSTRACT

Maintaining low NO_x emissions over the operating range of diesel engines continues to be a major issue. However, optical measurements of nitric oxide (NO) are lacking particularly in the core of diesel jets, i.e. in the region of premixed combustion close to the spray axis. This is basically caused by severe attenuation of both the laser light and fluorescent emission in laser-induced fluorescence (LIF) applications. Light extinction is reduced by keeping absorption path lengths relatively short in this work, by investigating diesel jets in a combustion vessel instead of an engine. Furthermore, the NO-detection threshold is improved by conducting 1-d line measurements instead of 2-d imaging. The NO-LIF data are corrected for light attenuation by combined LIF and spontaneous Raman scattering. The quantified maximum light attenuation is significantly lower than in comparable previous works, and its wavelength dependence is surprisingly weak.

Thereby, NO is reliably detected in the jet core. It can be attributed to premixed combustion.

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INTRODUCTION

Spatially and temporally resolved measurements of in-cylinder NO are generally quite challenging in internal combustion engines. For instance, NO is much less accessible than soot and its precursors, as concluded in a recent review [1]. LIF applications suffer from fluorescence quenching at high pressure [2]. In addition, attenuation of both the laser output and the fluorescent emission can be a severe problem, even in soot-free and droplet-free combustion gases [3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17]. In the hot post-flame gases, where most of the NO was previously found, the extinction of UV light was basically attributed to absorption by CO₂ [7, 8, 9, 10, 11, 12, 13, 14, 17]. Minor contributions may arise from H₂O, O₂, and combustion intermediates such as polycyclic aromatic hydrocarbons, PAHs, e.g. [10, 11, 17]. Severe absorption of UV light was also observed in the cool-flame gases produced by a reacting iso-octane/n-heptane mixture in an engine [5]. This was likely caused by combustion intermediates. According to [3, 4, 5, 6, 7, 8, 9, 11, 12, 13, 14], the discussed absorption decreases generally with increasing wavelength in the concerning UV range. For instance, according to [5], the absorbance was found to be a factor of ≈10 higher at 226 nm compared to 248 nm during high-temperature combustion of the iso-octane/n-heptane blend. The corresponding factor was reported to be somewhat lower in the cool flame. Most previous NO measurements were conducted by using laser wavelengths at ≈226 nm [10, 11, 12, 13, 14, 15, 16, 18, 19]. However, the excitation wavelength of ≈248 nm was also applied to spark ignition (SI) [3, 4, 6, 8] and diesel [7] engines. Since radiation at ≈248 nm can be produced by tunable KrF* excimer lasers, higher laser-pulse energy is

available at this wavelength than at ≈226 nm generated by most commercial lasers [20]. For these reasons, a KrF* excimer laser is used in the present work.

Excitation of NO by significantly longer laser wavelengths can only be achieved via a two-photon process [17]. However, low LIF signal intensities were found in this case.

The quantitative analysis in [11] indicated that NO-LIF signals can be dramatically attenuated in diesel engines. For instance, transmission levels as low as 1-2% were observed for measurements relatively early in the combustion event, using a laser at ≈226 nm [11]. Note that this was partly caused by the absorption of the fluorescence. Thus, the absorption path length of both the laser beam and the fluorescence should be as short as possible for reliable NO measurements in the jet core. This is achieved in the present work by conducting the measurements in a high-pressure combustion vessel [21] instead of an engine. In the vessel, the investigated diesel jet is not surrounded by absorbing combustion gases, so that absorption is only caused by the jet itself. Window fouling is also generally lower in the vessel than in an engine and the jet is more easily accessible.

The generally increasing absorption with decreasing wavelength indicates that fluorescence-detection wavelengths should be as long as possible. However, this is often hindered by spectroscopic constraints, e.g. [11]. Thus, the feasibility of NO-LIF detection at different wavelengths is also investigated in the current study.



For the discussed reasons, NO-LIF measurements are particularly challenging in the jet core, i.e. in the region of premixed combustion close to the jet axis and the position of flame lift-off [11, 12, 13, 16]. This is the aim of the current work.

There is one prior study in which a KrF* laser was applied to NO measurements by LIF in a diesel engine, but the jet core was not probed in that work [7].

Since NO-LIF signal intensities are expected to be low in the jet core [11, 12, 13, 14, 15, 16, 18, 19], 1-d spatially and spectrally resolving measurements are conducted in the present work instead of 2-d imaging. First, higher laser-power density is therefore available in the probe volume. Second, interfering emissions can be identified more accurately, based on the spectral resolution of the detector [2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 20, 22, 23]. Thereby, suitable detection and data-reduction strategies can be developed to cope with the interfering emissions. Under the current conditions, major interfering emissions arise from O₂-LIPF (laser-induced predissociative fluorescence), LIF from combustion intermediates and potential fuel impurities, and SRS (spontaneous Raman scattering) from O₂, N₂, and HCs (hydrocarbons). In order to suppress the broadband portion of the laser radiation and the resulting interfering LI(P)F emissions, the commercial KrF* laser is modified as described in [20, 24]. Briefly, the Cassegrain mirrors of the amplifier are removed and the oscillator beam is intensified and expanded by using an aperture with a vertical slit at the oscillator output and beam-expanding optics to match the amplifier's discharge volume. Thereby, locking efficiency, beam profile and polarization are improved and the overall output energy is essentially maintained. Potentially interfering LIPF from OH is completely avoided and LIPF from O₂ is significantly reduced when the laser is tuned between the excitation lines. In this configuration of the laser, vanishing off-resonant O₂-LIPF is currently observed in an open atmospheric flame and tolerable interfering O₂-LIPF is found in the diesel jets. Note also that the high degree of polarization of the laser output is employed to reduce unwanted SRS emissions in some of the measurements.

It is also important to note that the current 1-d detection set-up can also be used to acquire valuable additional data on light attenuation, other species, and the temperature. Basically by changing only the laser's wavelength and/or polarization, different LI(P)F and SRS signals from a number of species, such as O₂, N₂, CO₂, H₂O, PAHs, CO, and OH, can be probed with tolerable interferences [20]. In the present study, this is particularly used to quantify light attenuation. Absolute total light extinction at the laser wavelength, caused by the entire illuminated jet plume, is measured by using N₂-SRS. The relative wavelength dependence of the extinction is determined via O₂-LIPF emission spectra [4, 7, 11]. The combination of both techniques yields quantitative data on light attenuation in the concerning wavelength range. For instance, NO-LIF signals can be approximately corrected in terms of attenuation by absorption in this way.

It is also noteworthy, that a very similar experimental set-up was previously used to measure air/fuel ratio and temperature prior to the second stage of ignition in diesel-like jets in the authors' lab [22, 25,

26, 27, 28]. Different fuels and nozzles were investigated in those studies, but such measurements may be repeated by using the current set-up for the present jets in a future experiment.

Furthermore, the current 1-d set-up is combined with 2-d shadowgraphy to visualize the overall shape of the combusting jets simultaneously.

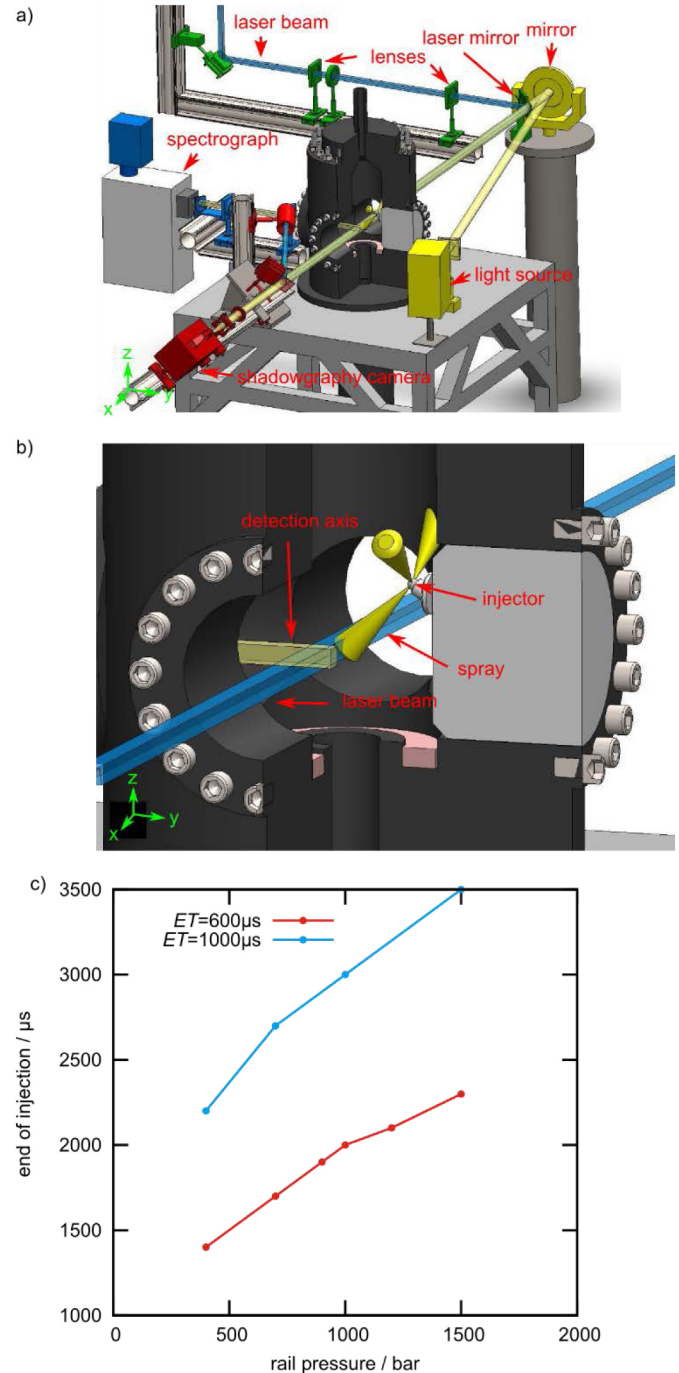


Figure 1. Experimental set-up (a); combustion vessel (b); end of injection in terms of time after energizing the injector (t_{aci}) (c). Injection always starts at $t_{aci}=0,2$ ms. Energizing time (ET) equals 1000 μs and 600 μs, respectively. In panel a), the light beam of laser and lamp passing through the combustion vessel appears to be greenish gray because of the overlap of the beams of both sources (blue: laser, yellow: lamp).

The current fuel blend consists of 50% 1-octanol and 50% (by volume) di-n-butylether (DNBE). These two species are isomers ($C_8H_{18}O$) and they are interesting biofuel candidates [21, 29, 30, 31]. They were separately used as single-component fuels in those previous studies. As shown in Table 1, both reactivity (cetane rating) and volatility are relatively low for 1-octanol, whereas both properties are relatively high for DNBE. Thus, intermediate auto-ignition and vaporization characteristics are expected for the currently used blend. Therefore, the spray and combustion characteristics of the current blend are expected to be between the corresponding values for the separately used single-component fuels presented in [21, 29, 30, 31], since essentially the same fuel injection system is employed in the current work. The operating conditions of the combustion vessel and the injection system also correspond to some of these previous results, as discussed in more detail in the following section.

Table 1. Properties of fuels investigated at 20°C.

		1-octanol	DNBE
Boiling temperature	°C	195	141
Heating Value	MJ/kg	38.4	38.4
Density	kg/m ³	830	770
Cetane number (derived)	-	≈34	≈115
Oxygen content	% m/m	12.3	12.3
Vapor pressure	mbar	0.125	6.4
Surface tension	mN/m	27.5	22.2
Dynamic viscosity	mPa s	7.3	0.64
Enthalpy of vaporization	kJ/kg	562	341

EXPERIMENTAL

Laser Diagnostics

The experimental set-up is illustrated in Figure 1. The output of a tunable KrF* excimer laser (LPX 250T, Lambda Physik) is formed into a rectangular beam, which is approximately parallel in the probe volume. It has a width (y direction, according to Figure 1) of ≈3 mm and a height (z direction) of ≈6 mm in the probe volume.

The laser provides a pulse energy of ≈150 mJ at the NO detection wavelength of 247.94 nm. However, it is reduced by an aperture so that it is ≈50 mJ in the probe volume, in order to avoid window damage. The laser-pulse energy is further reduced in some of the measurements, which are not shown here for brevity, in order to investigate the power dependence of the NO-LIF in the diesel jet. They indicate that the measurements presented in the following section are conducted in the linear LIF regime. The height of the probe volume, which is determined by the detector, is 1.2 mm. Since it is much smaller than the height of the laser beam (6 mm), the influence of beam steering by density gradients in the vessel on signal throughput is greatly reduced.

A 30 mm long section of the laser beam in the vessel is imaged onto the entrance slit (width=0.5 mm) of an imaging spectrograph (Acton Research, grating: 1200 grooves per mm, resolution: 0.1 nm,

aperture: $f/4$) by two spherical lenses ($f_1=500$ mm, $f_2=200$ mm). The laser-induced emission passes one or two stray-light filters (Laseroptik HR 248 nm/45°) in front of the spectrograph, depending on the intensity of stray light. In the exit plane of the spectrograph, an image-intensified charge-coupled device (ICCD) camera (LaVision, Dynamight) is installed. The same combination of laser and camera was recently used for 1-d SRS measurements in an engine [32]. More details are given therein.

The spatial resolution in the direction of observation, y, is limited by the 3 mm width of the laser beam. The spatial resolution along the laser beam axis, x, is essentially limited by the data averaging by software, which is given in the following section. Data averaging is necessary due to relatively low signal intensities. However, the resolution in the x direction is still better than the one in the y direction. The resolution in the z direction corresponds to the vertical extension of the probe volume of 1.2 mm given above.

Two types of measurements are basically presented in this article. First, NO-LIF and SRS measurements are conducted simultaneously. In particular, N_2 -SRS yields the total light attenuation, as noted previously. Second, O_2 -LIPF measurements are presented, in which SRS is suppressed, so that the O_2 -LIPF is nearly interference free. This is achieved by exploiting the different polarization properties of SRS and LI(P)F [20, 33]. For this purpose, the polarization of the laser beam is rotated by 90°, using a half-wave plate (248 nm) between the oscillator and the amplifier of the laser. Similarly, a half-wave plate is installed in front of the spectrograph to rotate the polarization of laser-induced emissions by 90°, since the efficiency of the grating depends on the polarization. For SRS measurements, this also leads to discrimination of SRS against broadband PAH-LIF, because it acts as a polarizer.

Both NO and O_2 on-resonance measurements are conducted by tuning the laser to selected excitation lines shortly before the diesel jets are actually probed, so that laser detuning is negligible. This is achieved by using an atmospheric flame in a separate experiment, in which the species are identified via excitation-emission spectra [20].

Various rotational levels of $v''=2$ of the electronic ground state of NO can be probed by laser wavelengths smaller than 248.0 nm [8, 20]. Within the tuning range of the KrF* laser, these levels are excited to $v'=0$ in the A state. Since an excited vibrational level is probed, LIF emissions can not only be observed on the Stokes (red-shifted) side of the spectrum but also on the anti-Stokes (blue-shifted) side. On one hand, anti-Stokes emissions are generally less affected by LIF interferences, in particular from PAHs, O_2 , CO_2 and fuel components [8, 20]. On the other hand, light attenuation is expected to be less important on the Stokes side, as noted in the previous section. Since the optimal detection scheme depends on the actual combustion regime, two promising emission lines on both the Stokes and the anti-Stokes sides are recorded simultaneously in some of the measurements in this work at ≈237 nm and ≈272 nm, respectively.

In principle, the NO emission at ≈272 nm can also be affected by H_2O -SRS, e.g. [20]. However, this is a minor interference in the present study, because measurements are conducted in a relatively early stage of high-temperature combustion, in which the H_2O concentration is still

very low, as indicated by the concerning SRS. For the same reason, CO_2 -LIF is also a minor source of error in this work. Note also that NO-LIF at ≈ 272 nm may be discriminated against H_2O -SRS in future applications, because of the particularly strong polarization dependence of H_2O -SRS [33]. However, this is not done in the present study, because the feasibility of simultaneous NO-LIF and N_2 -SRS measurements is investigated. Potentially, N_2 -SRS yields information on both light attenuation and temperature. This would be an important step towards quantification of the NO data.

Quantification is discussed in more detail in [2, 4, 6, 7, 8, 10, 11, 12, 13, 14]. For instance, the NO signal intensity increases by a factor of about five with increasing temperature in the range from 1000 to 2000 K for constant NO mole fraction at an ambient pressure of 50 bar [8], when an excitation wavelength of 247.94 nm is used [3, 6, 20]. These temperatures, pressure, and the laser wavelength are highly relevant in the present work. Presumably, light attenuation and temperature are the most important varying input parameters for quantification of the current NO data. Due to quenching, NO-LIF signals also depend on the local gas composition, e.g. [6]. The latter may be inferred from SRS measurements. This is another reason why simultaneous NO-LIF and SRS data are acquired in this work. Combined LI(P)F and SRS measurements in diesel jets were also discussed in [22].

Hot O_2 can be readily probed via LIPF (B-X transitions) with a tunable KrF* laser, e.g. [20]. Since vibrationally excited O_2 ($v''=6, 7$) is accessible, the signals are highly temperature dependent, so that this yields additional temperature information. However, O_2 -LIPF is primarily used to quantify the wavelength dependence of light attenuation, as noted previously. For this purpose, four emission lines at about 232, 240, 257 and 267 nm are recorded simultaneously. The Franck-Condon pattern is well known. Since broadband light absorption varies generally smoothly in the concerning wavelength range, the relevant absorption at the interesting NO-LIF emission at 237 nm can be determined by interpolation of values obtained from the adjacent O_2 -LIPF bands. The attenuation is calibrated by using O_2 -LIPF measurements in the weakly absorbing trail of the diesel flame and it is quantified by the total, absolute absorption at 248 nm determined by N_2 -SRS.

Measurement Geometry

As shown in Figures 1 and 2, the laser beam intersects the centerline of the investigated jet at right angles. The observation axis of the detector, which is parallel to the y axis, also crosses the laser beam perpendicularly, so that the jet axis is in the center of the probe volume. The angle between the jet axis and the y axis is 45° . The distance between the nozzle-hole exit of the investigated jet and the probe volume on the jet-axis is denoted the nozzle distance (ND). In this work, measurements are conducted at $\text{ND}=40$ mm and 55 mm, respectively. The locations and extensions of these probe volumes in the plane of the shadowgraphy measurements are shown in the images in Figure 2. This demonstrated that the spatial resolution of the 1-d line imaging is significantly smaller than the extension of the established jet plume in the y and z directions. This also holds for the resolution in the x direction, because it is not longer than in the other directions as noted previously. Thus, the jet core can be investigated selectively.

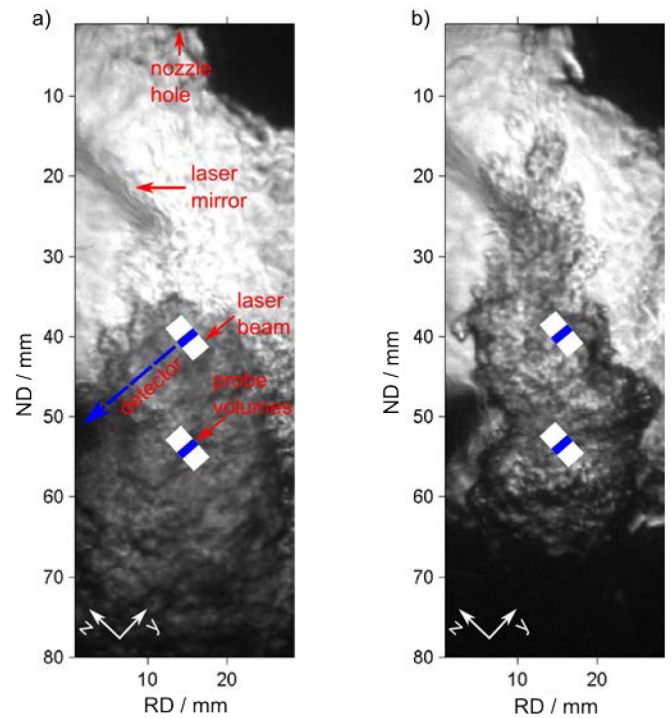


Figure 2. Typical shadowgraph images acquired at $t_{aei}=4600$ μs for $p_{\text{rail}}=1500$ bar (a) and 400 bar (b). Fixed parameters: $ET=1000$ μs , $p_a=50$ bar, $T_a=800$ K. Probe volumes for 1-d line imaging are also shown as the blue rectangles. The white rectangles denote the laser beam. RD: radial distance; ND: nozzle distance.

Test-Bench

The nitric oxide measurement experiments have been conducted at the high pressure test-bench (HPC) at RWTH Aachen University. During operation, the HPC is scavenged by a continuous air volume flow of $50 \text{ m}^3/\text{h}$, which enters the HPC at the bottom side and is heated by electrical cartridges in the lower test-bench section. As a result, steady-state boundary conditions in the combustion vessel of a maximum ambient pressure $p_{\text{max,a}}=140$ bar and a maximum ambient temperature $T_{\text{max,a}}=1000$ K, which are representative of a common passenger-car diesel engine in part- and full-load operation, can be generated within the measurement volume. In the present measurements the conditions in the combustion vessel are an ambient pressure of $p_a=50$ bar and an ambient temperature of $T_a=800$ K. These conditions are representative of part-load of a reference passenger car diesel engine (engine speed 1500 min^{-1} , mean effective pressure $=6.8$ bar) which is running at RWTH Aachen University [21].

The combustion volume of the high pressure-test bench is accessible from all four horizontal sides. Three sides of the volume can be equipped with circular windows (diameter $=127$ mm), which allows the application of various optical measurement techniques.

At the fourth side, a series production piezo-injector is mounted in a tailor-made holding device. High pressure of the fuel up to 2200 bar is generated by a high pressure pump. In order to avoid optical overlay of neighbouring spray cones in side-wise perspective and needle tilting, the injector is equipped with an equiangular 3-hole nozzle (diameter of holes $=109$ μm). The injector holder is designed to direct the investigated spray diagonally through the measurement volume [34].

Shadowgraphy

To clarify the mixture formation and ignition stability simultaneously to the nitric oxide measurements, shadowgraphic high speed visualization is installed. This set-up consists of a continuously operated light source, a concave mirror, and a high-speed camera. Within the measurement volume, the light beams are deflected in direction by passing the contact surface of two transparent media of different density (in non-perpendicular direction). The acquisition of the partly deflected light, which exits the measurement volume at the opposite side, allows the discrimination of the mixture against the background of ambient air [34].

RESULTS

The typical, quasi-instantaneous shadowgraph images in Figure 2 correspond to 1-d LIF/SRS measurements depicted in Figure 3. The liquid-fuel jets are not observed in Figure 2, because the images are acquired after the end of injection at a time after energizing the injector (t_{aei}) of 4600 μ s. This is demonstrated by the image sequences in the Appendix. The end of fuel injection in terms of t_{aei} is given in Figure 1c) for all investigated operating conditions. The current measurements are typically conducted after the end of injection, basically because of the chosen short injection durations.

Figure 2a) shows that the probe volumes of the 1-d line measurements are located in the upstream section of the reaction zone, i.e. the combusting jet plume. By contrast, they are located closer to the center of the reaction zone in Figure 2b). This difference is caused by the varied fuel-rail pressure (p_{rail}) which is 1500 bar in Figure 2a) and 400 bar in Figure 2b), respectively. Accordingly, it was demonstrated previously that the lift-off length (LOL) is shorter at lower p_{rail} shortly after the end of injection [35]. The LOL is not exactly known in the current work, but the shadowgraph images indicate that it is generally relatively close to the 1-d probe volumes at the investigated t_{aei} values.

Figure 3 shows typical 1-d imaging ICCD frames acquired at t_{aei} =4600 μ s and ND =55 mm. Other experimental parameters are given in the caption. Since the frames in Figure 3c)/d) and the shadowgraph images in Figure 2a)/b) are recorded simultaneously, it can be stated that these 1-d line measurements are conducted in the established combusting jet plume relatively close to the LOL. There are signs of heat release downstream from ND = 34 mm and 15 mm in Figure 2a) and b), respectively. The situation observed in these single-shot results is similar to the one of the ensemble-averaged frames in Figure 3a)/b), because shot-to-shot variations of the jet are relatively small under the chosen conditions.

In Figure 3, the horizontal axis of the images corresponds to the x axis of the probe volume. (The coordinate system is shown in Figures 1 and 2). The vertical axis of these frames in Figure 3 corresponds to the spectral resolution of the detector. The emission-wavelength range illustrated in Figure 3 is used for most of the current measurements, because it contains NO-LIF at $\approx$ 237 nm, N_2 -SRS at $\approx$ 263 nm, and four emission bands of O_2 -LIPF, as described in the experimental section. In the measurements of Figure 3, the laser is tuned to 247.94 nm to excite NO.

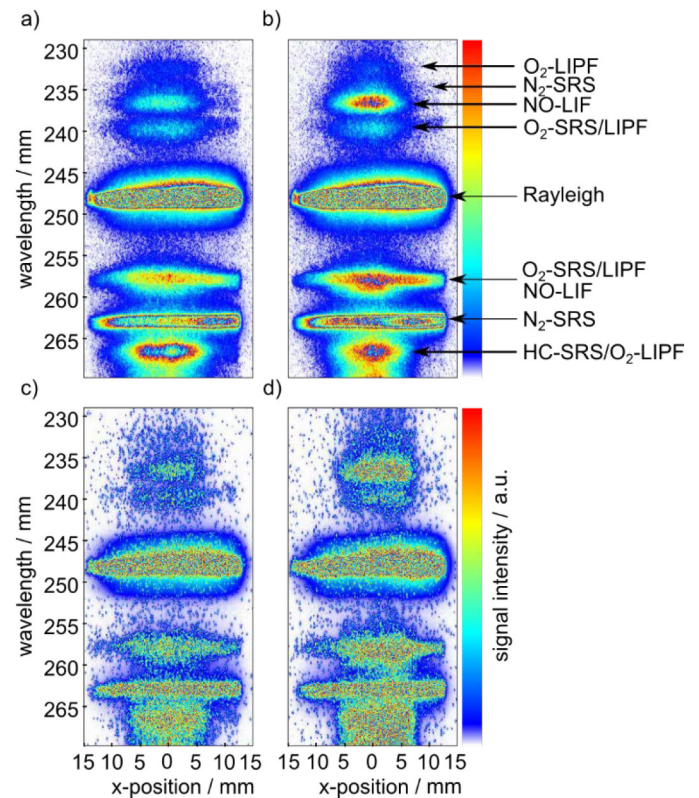


Figure 3. Typical raw line-imaging frames acquired at t_{aei} =4600 μ s for p_{rail} =1500 bar (a, c) and 400 bar (b, d). Fixed parameters: ET =1000 μ s, p_a =50 bar, T_a =800 K, ND =55 mm. Frames (a) and (b) are averaged over 20 laser shots. Frames (c) and (d) are single-shot results. False-color representation of intensities is shown on the right (palette wrapping is used for proper presentation).

In Figure 3, the jet plume and the neat ambient air on both sides of it are recognized. In the ambient air, essentially only O_2 - and N_2 -SRS are detected on the Stokes side of the spectra and elastically scattered laser light is also found. (The latter is basically attributed to Rayleigh scattering, as demonstrated by polarization analysis not shown here for brevity.) By contrast, additional emissions appear in the flame zone, which are basically caused by NO-LIF ($\approx$ 237, $\approx$ 259 nm), O_2 -LIPF ($\approx$ 232, $\approx$ 240, $\approx$ 257, $\approx$ 267 nm), potentially HC-SRS ($\approx$ 267 nm), and broadband LIF presumably from PAHs particularly on the Stokes side. This is also demonstrated by the emission spectra depicted in Figure 4, which are vertical profiles of the images in Figure 3 at x =(0 $\pm$ 1.5) mm. They show the spectroscopic situation in the jet core in more detail.

Figures 3 and 4 reveal that the NO-LIF line at $\approx$ 237 nm is not interference free. Weak anti-Stokes N_2 -SRS at $\approx$ 234 nm and broadband LIF are observed near or at the pressure-broadened NO line, respectively. Based on the spectroscopic data, these interferences can be accurately taken into account in the NO-data reduction.

It is interesting to note that NO was only found in a shell-like structure on the periphery of the jet during injection in LIF-measurements in [15, 16, 18, 19]. In general, the detected NO distribution is strikingly different in the current measurements, as shown in Figure 3 and the radial NO profiles presented below. The NO distributions spread throughout almost the entire jet plume and the strongest LIF signals are generally found close to the jet