Attenuation corrections for in-cylinder NO LIF measurements in a heavy-duty Diesel engine

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ABSTRACT Quantification of the nitric oxide (NO) concentration inside the cylinder of a Diesel engine by means of laser-induced fluorescence (LIF) measurements requires, amongst others, knowledge of the attenuation of the ultraviolet radiation involved. We present a number of laser diagnostic techniques to assess this attenuation, enabling a correction for laser intensity and detection efficiency of the raw NO LIF data. Methods discussed include overall laser beam transmission, bidirectional laser scattering (bidirectional LIF), spectrally resolved fluorescence imaging, and Raman scattering by N\textsubscript{2}. A combination of techniques is necessary to obtain the complete attenuation of laser beam and NO fluorescence. The overall laser beam transmission measurements and bidirectional LIF measurements (the latter yielding spatially resolved transmission) provide evidence of a non-uniform attenuation distribution, with predominant attenuation within or near the piston bowl. Fluorescence imaging of multiple vibrational bands through a spectograph is shown to be a powerful method for obtaining spatially resolved data on the transmission losses of fluorescence. Special attention is paid to the role of CO\textsubscript{2} and O\textsubscript{2} as UV light absorbers, and the consequences to different excitation-detection schemes for NO.

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1 Introduction

In order to improve the exhaust emissions of oxides of nitrogen (NO\textsubscript{x}) from Diesel engines, it is of great importance to study the formation processes involved. The laser-induced fluorescence (LIF) technique has been widely employed for in-cylinder visualisation of nitric oxide (NO) in Diesel engines [1–6] and SI engines [7–13], offering robust and non-intrusive diagnostics, high spatial and temporal resolution, and species selectivity, even under extreme combustion conditions of high pressures and temperatures.

This work focusses on in-cylinder NO LIF measurements in a Diesel engine by A–X(0,0) excitation at 226 nm and detecting the fluorescence bands around 237, 248, 259, and 271 nm. Absolute NO densities can be obtained from the raw LIF intensity, after processing the data for several effects, among which temperature and pressure dependence of the excitation efficiency, collisional quenching, and overlap of the excitation line with the spectral profile of the laser. Interference by O\textsubscript{2} LIF must carefully be investigated as well. All these issues have been extensively studied (see e.g. [5, 14–17]).

More elusive, but equally important, are the necessary corrections for non-uniform excitation laser intensity and fluorescence attenuation. Previous in-cylinder measurements of NO, conducted in our engine, suggest that both the laser beam and the induced NO fluorescence are strongly attenuated by the cylinder contents during a large fraction of the combustion stroke [5, 18]. Such attenuation is usually attributed to absorption and scattering by fuel (droplets and/or vapour) [19–22], soot particles [2, 23], absorption by aromatic fuel compounds [24, 25], and absorption by combustion products such as CO\textsubscript{2} and H\textsubscript{2}O [26, 27]. In addition, the numerous and closely-spaced vibronic transitions of the Schumann–Runge system of O\textsubscript{2} cause UV absorption that may become significant at combustion temperatures [28]. Since the spatial distribution of all these agents is mostly unknown, it is difficult to predict the in-cylinder attenuation of the laser beam and the NO fluorescence.

In this paper, we present a number of experimental techniques to quantitatively assess this attenuation, focussing on: (1) the local attenuation of the laser beam, (2) the attenuation of the fluorescence on its way to the detection window, and (3) losses due to soiled windows. Each technique assesses one or more of these items, as is illustrated in Table 1. They will be introduced in the next section. Generally, combinations of techniques are needed for a complete picture of all

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<thead>
<tr>
<th>method</th>
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<tbody>
<tr>
<td>CO\textsubscript{2} and O\textsubscript{2} absorption spectroscopy</td>
<td>fluorescence attenuation (by CO\textsubscript{2} and O\textsubscript{2} only)</td>
<td>1 and 2</td>
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<tr>
<td>bidirectional laser scattering</td>
<td>local laser beam attenuation</td>
<td>1</td>
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<tr>
<td>N\textsubscript{2} Raman scattering</td>
<td>soot-based attenuation of laser beam and fluorescence</td>
<td>2</td>
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TABLE 1 Measurement techniques for attenuation corrections of laser-induced fluorescence

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attenuation factors; the three techniques in Table 1 constitute two combinations that assess the total attenuation. Quantitative in-cylinder NO measurements, based on the attenuation corrections discussed in this paper, will be presented elsewhere [29].

## 2 Laser diagnostics

### 2.1 Fluorescence attenuation: absorption by hot CO₂ and O₂

Since the laser probe volume is a distance \( d = 37 \) mm away from the detection window, the induced NO fluorescence can be significantly attenuated before it reaches the detector. A major part of this fluorescence attenuation turns out to be caused by absorption by CO₂ and O₂. Schulz et al. have demonstrated that CO₂ and, to a lesser extent, H₂O are potential UV absorbers (\( \lambda \leq 300 \) nm) at combustion temperatures (\( T \geq 1000 \) K) [26]. Both species feature broad-band absorption in the wavelength range of NO LIF, the cross section increasing with decreasing wavelengths, and with increasing temperature. It can be parameterised by a function of the form [26]

\[
\sigma_{\text{CO}_2} = \exp(a(T) + b(T) \lambda). \tag{1}
\]

In most practical cases, the H₂O absorption cross section is at least one order of magnitude smaller than that of CO₂ [27]. Since UV absorption by H₂O is generally negligible in combustion engines [30], it is not taken into account here.

In addition to CO₂, O₂ can lead to significant attenuation [28], especially at high temperatures. The many closely-spaced absorption lines in the O₂ transmission spectrum are (to some extent) averaged by the spectrally broader emission bands of NO. As a result, the O₂ absorption cross section can be approximated by a smooth absorption function, similar to (1). This approximation is by no means valid in general, but in our experiments it leads to deviations of < 5% compared to detailed calculations based on simulated high-resolution O₂ absorption and NO emission spectra.

Detection of NO LIF through a spectrograph gives the opportunity to simultaneously measure the intensities of a number of vibronic bands. The relative intensities of these bands are governed by Franck–Condon factors and spectral efficiency of the detection system, and are therefore constant. Thus, any deviations of the observed LIF spectrum from the theoretical spectrum are caused by wavelength-dependent absorption of the fluorescence. A discrete transmission spectrum can be obtained by dividing the observed (relative) LIF peak intensities by their theoretical values, as was demonstrated by Hildenbrand and Schulz (albeit with O₂ LIF instead of NO LIF) [30]. Subsequently, the transmission spectrum of CO₂ and O₂ can be fitted to this spectrum, using the temperature dependent absorption cross sections from [26] and [28], respectively (NO self absorption is negligible; < 5% for the band at 237 nm and less for the others). This fit yields both the effective fluorescence absorption by CO₂ and O₂, as well as an effective temperature of the absorbing volume.

Unfortunately, this method only yields the wavelength dependent attenuation of the NO fluorescence; attenuation by soot (which can be significant but has only a very weak wavelength dependence compared to the molecular absorbers) cannot be retrieved. It can be measured with Raman scattering by N₂, however, as will be presented in Sect. 2.3.

### 2.2 Laser beam attenuation: bidirectional LIF

Although it is straightforward to measure the transmission of the laser beam over its entire traversal of the measurement cylinder (and thus the average extinction), this is a line-of-sight measurement and spatial information (along the laser beam) is lacking. Spatially resolved laser beam transmission measurements can be realised with a technique called bidirectional laser scattering [20, 31–33], involving two laser pulses traversing the same trajectory through the cylinder (quasi) simultaneously, but in opposite directions (see Fig. 1). Both pulses will be scattered by the same medium but have a different “history” in terms of integrated extinction. The (in-) elastically scattered light from each laser pulse is recorded separately on a CCD camera. From the two intensity profiles, the local extinction coefficient can be reconstructed.

Stoffels et al. [33] applied this technique to correct for laser beam extinction in a Diesel engine. Corrections for laser beam extinction in fuel sprays have also been reported [19–21].

In this work, spatial profiles of NO fluorescence were measured for both laser beam propagation directions (i.e. top-down and bottom-up). The analysis is slightly different to that by Stoffels et al., in order to handle the strong noise amplification that is inherent to this technique [20, 33].

In general, the detected NO LIF signal \( S(z) \) can be written as:

\[
S(z) = CA(z)n_{\text{NO}}(z)\sigma_{\text{NO}}(z)I_{\text{laser}}(z), \tag{2}
\]

in which \( z \) is the location within the combustion chamber, measured from the top of the detection window, as is indicated in Fig. 1. \( C \) is a proportionality constant accounting for e.g. detection efficiency, \( A(z) \) the collection efficiency (including fluorescence transmission on its way to the detector), \( n_{\text{NO}} \) the NO number density, \( \sigma_{\text{NO}} \) the NO fluorescence cross section, and \( I_{\text{laser}}(z) \) the local laser intensity. For clarity the temperature and pressure dependence of \( \sigma_{\text{NO}} \) are not written explicitly.

![FIGURE 1 Geometry of bidirectional laser scattering in the measurement cylinder (vertical cross-section). The laser beams propagate along the vertical axis \( z \). The slot on the right of the piston bowl ensures optical access throughout the cycle](image)
The intensities of the downward and upward laser beams $I_{\text{down}}$ and $I_{\text{up}}$ are given by:

$$I_{\text{down}}(z) = I_{\text{down}}(0) \exp \left\{ - \int_0^z \alpha(z') \, dz' \right\},$$

and

$$I_{\text{up}}(z) = I_{\text{up}}(L) \exp \left\{ - \int_z^L \alpha(z') \, dz' \right\},$$

where $I_{\text{down}}(0)$ is the intensity of the downward laser beam before it enters the cylinder, $I_{\text{up}}(L)$ is the intensity of the upward laser beam at the bottom of the field of view (i.e. at $z = L$; $L$ increases with increasing crank angle until the detection window is no longer partially blocked by the piston, see Fig. 1), and $\alpha(z)$ is the effective local extinction coefficient encountered by both laser beams.

Combining (2), (3), and (4), we see that in the quotient of $S_{\text{down}}$ and $S_{\text{up}}$, the NO densities and $A(z)$ cancel, and the laser beam attenuation is left as the only $z$-dependent term:

$$\frac{S_{\text{down}}(z)}{S_{\text{up}}(z)} = \frac{C_{\text{down}}}{C_{\text{up}}} \frac{I_{\text{down}}(0)}{I_{\text{up}}(L)} \times \exp \left\{ -2 \int_0^z \alpha(z') \, dz' + \int_0^L \alpha(z') \, dz' \right\},$$

(5)

This can be rewritten to express the local attenuation coefficient in terms of $S_{\text{up}}$ and $S_{\text{down}}$:

$$\alpha(z) = \frac{1}{2} \frac{d}{dz} \ln \left[ \frac{S_{\text{down}}(z)}{S_{\text{up}}(z)} \right],$$

which is identical to the equation presented by Stoffels et al. [33], and may be used to directly calculate the laser beam transmission along the beam path. Unfortunately, the mathematical operations in (6) cause severe noise amplification, which limits its use to cases with very good signal-to-noise ratios. Therefore, we return to (5) and note that the square root of $S_{\text{down}}/S_{\text{up}}$ is proportional to the integrated laser beam extinction:

$$S_q(z) = \sqrt{\frac{S_{\text{down}}(z)}{S_{\text{up}}(z)}} \propto \exp \left\{ - \int_0^z \alpha(z') \, dz' \right\}.$$

(7)

In practice, $S_q$ is a gradually varying function of the location $z$. Rather than taking the logarithm and derivative, the function $f(z) = p_1 \exp \left\{ -(p_2 z + p_3 z^2 + p_4 z^3) \right\}$

(8)

is fitted to $S_q$, immediately yielding the local laser beam transmission after setting parameter $p_1$ equal to 100%. A third degree polynomial fits our data within the uncertainty of the observed laser beam transmission profiles; for this reason no higher degrees were included.

### 2.3 Combined laser beam and fluorescence attenuation: N$_2$ Raman scattering

Similar to NO LIF, the intensity of the Raman-scattered light by N$_2$ is not only proportional to the N$_2$ density, but is also affected by attenuation of both the laser beam and the Raman-scattered light. Since the amount of N$_2$ is constant during the combustion, and density variations due to temperature inhomogeneities can be estimated (e.g. using the temperature obtained from the fitted UV absorption spectra, see previous section), the variation of the N$_2$ Raman scattering intensity is a direct measure of the relative attenuation by the cylinder contents. This attenuation includes both laser beam and fluorescence attenuation. The relatively low Raman scattering efficiency can be compensated by high laser intensities and – especially early in the stroke – the high N$_2$ density, yielding good signal-to-noise levels.

If the Raman wavelengths are beyond the CO$_2$ and O$_2$ absorption range (as is the case here), the derived transmission mainly reflects soot-based attenuation. In order to extrapolate to NO LIF wavelengths, the additional absorption by CO$_2$ and O$_2$ (as discussed in Sect. 2.1) needs to be included. Additionally, the marginal wavelength dependence of scattering and absorption properties of soot particles may need to be taken into account as well (see Appendix I). Finally, the Raman scattering cross section varies up to 30% over the temperature range of interest here [34], which needs to be accounted for.

### 2.4 Losses caused by window fouling

After each fuel injection, some of the in-cylinder soot will deposit on the windows. Fouling of the entrance window for the laser beam and of the detection window will cause the (detected) fluorescence intensity to decrease during a measurement session. The average effect of window fouling can be derived by monitoring the LIF intensity at a certain (fixed) crank angle as a function of the number of fuel injections. Except for random variations due to cycle-to-cycle fluctuations, the generally decreasing trend can be attributed to increasing window opacity.

### 3 Experiment

#### 3.1 The engine

All measurements have been performed on a heavy-duty, six-cylinder truck engine (DAF 1160 series block, cylinder head WS268L). One cylinder is fitted with the cylinder head of the modern DAF 95XF type engine and is used for in situ measurements. Apart from changes providing optical access, it has been kept as realistic as possible. Five quartz windows are mounted in the cylinder, see Figs. 1 and 2. One of the exhaust valves was replaced by a cylindrical window, referred to as the top window. Additionally, there are three 48 × 23 mm$^2$ windows in the cylinder wall ("side windows"), giving a view of the uppermost part of the combustion chamber. Finally, a 70 mm diameter window in the piston (flat surfaces to prevent image distortion) enables an upward view into almost the complete chamber. An example image of the combusting sprays, as seen through the piston window, is shown in Fig. 2b. The cam-driven, eight-hole fuel injector is mounted in the centre of the cylinder head. It can be rotated, allowing
measurements at different positions relative to the fuel sprays without repositioning the laser beam. In this work, the laser probe volume is 35 mm downstream of the fuel injector, either along the fuel spray path (“through spray”), or with the injector rotated by 22.5° (“between sprays”).

A slot machined into the piston crown provides optical access through one of the side windows even at Top Dead Centre (TDC). Because of this slot and the flat windows in the cylinder wall and in the piston, the compression ratio is reduced from 16 to 15. The resulting lower TDC temperature is partly compensated by preheating the inlet air. No lubricants are used since they would absorb the UV (laser) radiation and contribute to soot formation; to avoid overheating the measurement cylinder is skip-fired (1:35). Steady-state conditions are mimicked by (pre-) heating the cooling water to operational temperatures.

All measurements presented here were conducted at an engine speed of 1430 rpm and 25% load. The latter corresponds to injection of 60 mg of low-sulfur diesel between 5° before TDC (bTDC) and 6° after TDC (aTDC), with a boost pressure of 130 kPa (absolute). With these settings, a TDC temperature of 688 K, and a gross indicated mean effective pressure (gIMEP) of around 500 kPa were calculated from the cylinder pressure data [35].

3.2 NO LIF measurements

NO is detected by means of laser-induced fluorescence (LIF), exciting the molecules from the electronic ground state $X^2\Pi(v' = 0)$ to the $A^2\Sigma(v' = 0)$ state. The coinciding $P_1(23.5)$, $Q_1 + P_2(14.5)$, and $Q_2 + R_2(20.5)$ transitions are induced by laser radiation at 226.035 nm. This excitation wavelength was suggested by DiRosa et al. for its high sensitivity and minimal O$_2$ LIF interference even at elevated pressures [36].

Laser radiation is produced by either a frequency-doubled dye laser (Lambda Physik ScanMate 3 using Coumarin 47) pumped by a Nd:YAG laser (Continuum PowerLite 9010), or a frequency-mixed dye laser (Radiant Narrowscan D, using Rhodamin 101) pumped by a Nd:YAG laser (Continuum Powerlite Precision II 8010). The unfocused laser beam (4 mm diameter) of circa 2.5–5 mJ/pulse traverses the combustion chamber nearly parallel to the cylinder axis, entering through the top window, and leaving it through the piston window (Fig. 2). For the bidirectional LIF experiments, measurements were also performed with a reversed laser beam direction.

Laser-induced fluorescence is detected through a side window closest to the probe volume by an intensified CCD camera (Roper Scientific, ICCD 512T, 512$^2$ pixels, 16 bits) mounted behind a spectrograph (ARC SpectraPro 500i, 600 grooves/mm) that is equipped with a Nikkor UV 105 mm objective. The spectrograph allows spatially and spectrally resolved simultaneous detection of the $\Delta - \bar{X}$ (0,1), (0,2), (0,3), and (0,4) fluorescence bands around respectively 237, 248, 259, and 271 nm. Its entrance slit is parallel to the laser beam and fully open (3 mm) to maximise signal strength. The probe volume is determined by the diameter of the incident laser beam (4 mm), and the height of the side window (23 mm), or, early in the stroke, by the slot in the piston crown. Since the laser beam immediately enters the field of view, the effect of laser beam extinction is minimised. The in-cylinder fluorescence path length is 37 mm. Background combustion luminosity is reduced by short camera gating (∼60 ns).

3.3 Transmission measurements

During the NO LIF measurements, the transmission of the laser beam over its trajectory through the cylinder is recorded simultaneously. After exiting the cylinder

![FIGURE 2](image_url)

**FIGURE 2** (a) Schematic representation of the setup (top view). The laser beam propagation is out of plane, nearly parallel to the cylinder axis, either top-down or – for the bidirectional measurements – bottom-up. NO fluorescence is detected by an imaging grating spectrograph through the nearest side window. (b) 100 ns snapshot of the combusting fuel sprays (left), together with a contour plot (right) of the same image, indicating the two laser probe positions and the spray axes (solid grey lines). Circle: “through spray”; dot: “between sprays”.

![FIGURE 3](image_url)

**FIGURE 3** Laser beam transmission over its complete trajectory through the cylinder (averages of 15 cycles, error bars denote the standard error). The lines are added to guide the eye; the solid grey line shows the cylinder pressure. Top: shadowgraphs of the fuel spray at TDC, 1°, and 2° aTDC. The top window is uniformly and continuously illuminated, while the shadow is recorded through the piston window (window contours indicated by dashed white circles). The camera gate width is 60 μs, which corresponds to 0.5 crank angle degree.
through the piston window, the laser beam is deflected by a 45° dichroic mirror onto a quartz diffuser plate where it is scattered and detected by a second intensified CCD camera (Princeton Instruments ICCD 512T; 16 bits, 512^2 pixels, Nikkor UV 105 mm objective). Background combustion light is suppressed by the dichroic 45° mirror; any remainder is smeared out by the diffuser plate and contributes to a uniform background. This background is eliminated by fitting a Gaussian curve through a cross section of the laser spot, yielding not only the transmitted laser intensity (the area under the curve), but also information on beam steering and divergence.

The gradually increasing effect of window fouling during a measurement session is excluded by normalising the transmission at each crank angle by a reference measurement at the same crank angle during a previous, non-fired cycle. Here it is assumed that soot deposition is a gradual process, without dramatic changes between individual cycles. Musculus et al. give an extensive discussion of laser-extinction-based measurements of fuel jet soot and window soot in a Diesel engine [37].

### 3.4 O_2 LIF measurements

The experimental configuration for the O_2 LIF measurements is identical to the one used for NO LIF, except the laser radiation being provided by a tunable pulsed ArF excimer laser (Lambda-Physik, Compex 350T). Fluorescence of O_2 was induced by laser radiation at 193.221 nm, corresponding to the combined P1 + P2 + P3(15) and R2 + R3(17) lines in the B^3Σ_u^+ (v' = 10) ← X^3Σ_g^- (v'' = 2) transition in the Schumann–Runge system. Since the O_2 excitation spectrum contains many, closely-spaced, lines involving transitions to and from various vibrational energy levels [38], emission spectra from more than one vibrational state cannot be avoided. This transition was chosen because it is relatively strong, and because 193.221 nm is minimally absorbed by cold oxygen in the ambient air (the laser beam travels over 5 m before it reaches the measurement cylinder). The spectrograph was set to detect O_2 fluorescence bands around 225, 233, 240, 248, 255, and 265 nm, corresponding to the v' = 10 → v'' = 7 − 12 transitions respectively.

### 3.5 N_2 Raman scattering measurements

Raman measurements have been performed in a setup similar to that for NO LIF detection, using the unfocused 355 nm radiation of a frequency-tripled Nd:YAG laser (Spectron Lasers, SL 8354 YDA) at about 210 mJ pulse energy, and an ARC SpectraPro 300i spectrograph with a 1200 grooves/mm grating. The grating was oriented such that Raman scattering by O_2 (376 nm) and N_2 (387 nm) could be observed simultaneously.

### 4 Results and discussion

#### 4.1 Transmission measurements

Figure 3 shows averaged laser beam transmission curves at 226 nm for the two probe locations. Early in the stroke, the laser beam transmission decreases drastically to approximately 1% for both locations. The earlier decrease for the “through spray” position may be explained by the fuel spray hitting the laser beam between 1° and (at least) 7° aTDC, as confirmed by shadowgraphy experiments (top of Fig. 3).

At the “between sprays” position, the transmission decreases shortly after the start of combustion, as can be seen from the pressure rise around 3° aTDC (the first combustion spots are visible through the piston window at 3° aTDC). Likely attenuators are soot, hot CO_2, and hot O_2. Around 20° aTDC, both curves start to increase asymptotically to about 55% (and reach 100% in the subsequent non-fired stroke).

#### 4.2 NO fluorescence absorption by hot CO_2 and O_2

Figure 4 displays two NO LIF images as recorded through the spectrograph at 20° aTDC and 130° aTDC. In both images the laser beam enters from the top and is directed through a fuel spray. The (0,1), (0,2), (0,3), and (0,4) emission bands are visible as “sub-images” (indicated by dashed grey contours). Along the vertical axis, these sub-images contain spatial information; the horizontal axis is a convolution of space and the (rovibronic) emission spectrum. There is no sign of O_2 fluorescence in either image. Despite the slot in the piston crown, the side window is still partly blocked at 20° aTDC, resulting in shorter sub-images.
As was mentioned in Sect. 2.1, CO₂ and O₂ are the most likely candidates for wavelength dependent attenuation of the NO fluorescence. This attenuation depending strongly on the CO₂ and O₂ densities and on temperature, the fluorescence transmission will vary during the combustion stroke. This can be seen in Fig. 4c: at 20° aTDC, the (0,1) and (0,2) bands are much weaker compared to the spectrum at 130° aTDC. At 130° aTDC, the average gas temperature (calculated from the cylinder pressure trace [35]) is around 800 K, which is too low for significant CO₂ and O₂ absorption.

The relative transmission of the NO fluorescence is calculated by dividing the intensities of the four detected fluorescence bands by those at the end of the stroke (i.e. 130° aTDC). These intensity ratios (still in arbitrary units) are normalised at 271 nm, so that they represent the fluorescence transmission relative to that at 271 nm. An example is given in Fig. 4d. By dividing the spectra, wavelength dependent detector response is eliminated as well.

Subsequently, these relative transmission spectra are fitted by CO₂ and O₂ spectra (Fig. 4d) using the absorption cross-sections from [26] and [28]. Free fitting parameters are temperature (assumed uniform over the path length) and CO₂ number density. The O₂ density is not treated as a variable, but instead determined from the local O₂/N₂ ratio [28] measured by Raman scattering.

By fitting CO₂ and O₂ transmission spectra for a number of crank angles, one obtains transmission values during the combustion stroke for each NO fluorescence band. Extrapolation to e.g. 226 nm is possible, too. This is demonstrated in Fig. 5 showing considerable attenuation of the shorter wavelengths, especially at 10–40° aTDC. As the cylinder volume expands (and the temperature decreases) absorption by CO₂ and O₂ decreases. By 80° aTDC, it is negligible. The fitted temperature agrees with the values reported by Flynn et al. [39], reaching values of 2400 K between 20° and 30° aTDC. Later in the stroke, it approaches the average gas temperature. The obtained CO₂ number densities are realistic as well: e.g. at 40° aTDC, n_CO₂ = 3.4 × 10¹⁸ cm⁻³, whereas complete combustion of the injected 60 mg of Diesel fuel would yield n_CO₂ = 6.2 × 10¹⁸ cm⁻³, assuming uniformly distributed CO₂, and taking C₁₆H₃₄ as a Diesel representative.

For comparison, fluorescence transmission data based on the same analysis but using O₂ LIF instead of NO LIF are included in Fig. 5 as smaller symbols. Both experiments were performed under identical engine conditions, and in the same probe volume. Within the experimental accuracy and cyclic variations, the two independent results match well, proving the consistency of this method.

### 4.3 Bidirectional LIF

For the bidirectional LIF measurements, NO LIF images like those in Fig. 4 have been recorded separately for the two opposite directions of the excitation laser beam. Vertical NO LIF profiles are constructed by summing the intensities of the pixel rows (horizontal direction in Fig. 4) in all NO subimages and plotting this sum as a function of the vertical distance z (see also Fig. 1). Two vertical LIF profiles recorded at 16° aTDC are presented in panel a of Fig. 6. At 16° aTDC, only the uppermost 13 mm of the combustion chamber are visible. The two profiles have not been recorded simultaneously for practical reasons; average profiles of ten shots (20 for bottom-up propagation where the signal is weaker) are presented here instead. A similar example is given in panel b for 40° aTDC.

Panels c and d show S_q (defined in (7)) for 16° and 40° aTDC, respectively, together with a fit of the exponentially decaying curve described in (8). This fit follows the data very well, indicating that a third degree polynomial is indeed sufficient to describe the extinction coefficient. The 95% confidence limits are based on numerical simulations, and show the highest uncertainty around z = 0 and z = L (where the signal-to-noise ratio of S_q is lowest). This affects the accuracy of the overall constant p₁, and as a consequence the 95% confidence intervals for the transmission curves (panels e and f) are considerably larger than those for the fit of S_q. A more detailed description of the noise sensitivity of this method is presented in Appendix II.

At 40° aTDC the laser beam attenuation is not as strong as at 16° aTDC. Additionally, the NO signal is much stronger, increasing the signal-to-noise ratio of S_q. The results for 40° aTDC show a 30% attenuation of the laser beam, even though the two NO LIF profiles have similar shapes by eye judgement, which would suggest negligible extinction [18]. This apparent inconsistency stresses the importance of a quantitative analysis.

### 4.4 Raman scattering by N₂

Raman spectra, recorded in the engine, are shown in Fig. 7. They are obtained by summing the intensities of all (relevant) pixel rows of an iCCD image similar to the example in the upper left corner. These spectra have been recorded during the first 40 crank angle degrees of the combustion stroke. Later in the stroke the signal becomes weaker due to decreasing density.
Already at 2° aTDC is the spectrum dominated by broadband radiation, caused by (laser-induced) incandescence (LII) of soot, and/or laser-induced fluorescence of aromatic fuel components [40, 41]. The actual Raman intensities are obtained by fitting a set of Gaussians to the spectra, including a broad one to account for the background. An additional feature at a Raman shift of $\sim 3000 \text{ cm}^{-1}$, corresponding to the C–H stretch and attributed to fuel, can be observed at 397 nm between 2° and 6° aTDC.

The possible presence of LII raises the question if the laser beam is not simply burning soot away, thus measuring too low extinction. Vander Wal and Jensen [42] observed that 1064 nm laser beam transmission through a sooting flame suddenly improved for fluences above 0.5 $\text{J/cm}^2$. Above this threshold intensity, the initial part of the laser pulse causes soot to evaporate, improving the transmission of the later part. They estimated that this threshold scales with wavelength,
leading to 0.2 J/cm² for 355 nm radiation. In order to compensate for the relatively weak Raman scattering, the laser fluence was kept at 1.0 J/cm² in our experiments, clearly exceeding the threshold of 0.2 J/cm². Yet, for a Gaussian laser beam profile (as in our measurements) the intensity threshold is somewhat higher [43] (Vander Wal and Jensen used a top-hat beam profile). Moreover, C₂ fluorescence, indicative of soot particle fragmentation, was not observed in our experiments.

The curves in Fig. 7 nicely demonstrate the effect of attenuation: at 10° aTDC hardly any N₂ signal is visible, and even the broadband background is less compared to 2° aTDC. The broadband luminosity never disappears completely; the strong attenuation (as reflected in the N₂ signal) is possibly partly compensated by increased emission due to increased soot volume fraction (if the signal is due to LII) or increased fuel density (if it is fuel LIF). Both soot and fuel droplets do attenuate the N₂ Raman intensity, of course. By 24° aTDC, there is a clear N₂ peak again, indicating that the transmission has already increased.

The N₂ signal can be interpreted as the product of the laser beam transmission and the transmission of the Raman-scattered light. To this end, the crank angle dependence of the local N₂ density is calculated from (1) the cylinder volume and (2) the ratio of the local temperature (estimated from the fitted absorption spectra) and the average gas temperature (calculated from the cylinder pressure trace [35]). Additionally, the N₂ Raman scattering cross section depends on temperature [34], and can be calculated using the estimated local temperature. Furthermore, the scattering and absorption properties of soot particles depend on wavelength, particle size, and the refractive index of soot (itself also a function of wavelength). As a result, the extinction observed at the Raman wavelengths is slightly different than for NO LIF wavelengths. This effect is discussed in the Appendix I. Finally, the corrected curves (still in arbitrary units) are scaled to 100% transmission at crank angles before the start of injection. They will be addressed in Sect. 5.3.

4.5 Window fouling

Figure 8 shows the normalised NO LIF intensity (at constant crank angles) during a measurement session. The decreasing trend is attributed to window fouling (the error bars are due to cycle-to-cycle variations [29]). The fouling rate for the “through spray” probe location is significantly higher than for the other position, in agreement with visual inspection of the detection window after a measurement session. This is explained by the different orientation of the fuel injector: for the “through spray” measurements the fuel jet is directed towards the slot in the piston crown, causing more soot to deposit on the detection window. The curves show that window fouling effects are respectively ≤ 4% and ≤ 1% for the “through spray” and “between sprays” locations, for the measurement order in our experiments ¹. This is negligible compared to the cyclic fluctuations (typically 25%–30%).

5 Discussion: complete attenuation correction requires a combination of techniques

5.1 Bidirectional LIF versus laser beam extinction

From Fig. 6 it follows that laser beam extinction is not at all uniform, not even over the relatively small field of view of 23 mm (compared to the stroke of 146 mm). As a consequence, overall laser beam transmission measurements (Fig. 3) are not suitable for accurate attenuation correction. This is illustrated in Fig. 9, displaying the field-of-view averaged laser beam transmission ² as derived from both the bidirectional LIF results and the overall transmission data, assuming uniform attenuation for the latter (the CO₂ absorption curve is discussed below). Until about 40° aTDC, the laser beam transmission measurements greatly underestimate the local laser intensity. This leads us to the conclusion that

¹ The NO LIF measurements are repeated in sequences of increasing crank angle, each sequence consisting of 15 crank angles.

² The field-of-view averaged transmission is obtained by averaging the transmission curve between z = 0 and z = L. It thus is a measure for the average laser beam intensity in the probe volume.
the major laser beam attenuation takes place below the field-of-view, most likely within the piston bowl. This is also reflected in the window fouling; after a measurement session, the piston window is generally more opaque than the detection window.

5.2 CO$_2$ and O$_2$ absorption in relation to the total attenuation

The extrapolation of the fluorescence transmission to 226 nm in Fig. 5 suggests that the laser beam, too, may be strongly absorbed by hot CO$_2$. O$_2$ absorption, on the other hand, is negligible for the laser beam as its frequency is carefully chosen to avoid O$_2$ excitation. According to the conceptual model proposed by Flynn et al. [39], hot CO$_2$ is concentrated around the diffusion flame. As a consequence, the laser beam and the NO fluorescence would traverse similar regions with high temperature and high CO$_2$ density, and it is reasonable to expect similar CO$_2$ absorption for the two.

It is illustrative to compare the (field-of-view averaged) laser beam transmission through hot CO$_2$ with the transmission obtained from the bidirectional LIF results, the latter reflecting all contributions to laser beam attenuation. The laser beam attenuation by CO$_2$ can be calculated from the fit parameters from Fig. 5, accounting for the shorter path length (23 mm against 37 mm). It is included in Fig. 9. During the first 40 crank angle degrees, CO$_2$ absorption accounts for 30% of the total extinction. The remaining laser beam attenuation, most likely absorption and scattering by soot particles, is readily calculated. It has been used to estimate the soot-based attenuation of the NO fluorescence.

5.3 Combined transmission of laser beam and fluorescence

The product of laser beam transmission and fluorescence transmission can be obtained by combining the bidirectional LIF data yielding the local laser beam transmission (the middle curve in Fig. 9) and the CO$_2$ and O$_2$ transmission curves of the fluorescence radiation (Fig. 5). The remaining fluorescence attenuation by soot can be estimated from Fig. 9 (Sect. 5.2).

Alternatively, the N$_2$ Raman scattering data already encompass the combined laser beam and fluorescence transmission, albeit without the effect of absorption by CO$_2$ and O$_2$ (the Raman wavelengths are beyond the absorption range of CO$_2$ and O$_2$). This absorption, however, is easily included taking the data in Fig. 5.

This brings us two combinations of techniques to assess the combined transmission:

1. bidirectional LIF combined with CO$_2$ and O$_2$ absorption spectra, and
2. N$_2$ Raman scattering, also combined with CO$_2$ and O$_2$ absorption spectra

The two resulting curves are shown in Fig. 10, and show good agreement. This demonstrates the reliability and accuracy of either combination. The relative accuracy is generally around 20%, except at very low transmission (2%), when it reaches 50%--60%. Yet, attenuation correction of NO LIF signals is possible at all crank angles of interest.

6 Discussion: comparison of excitation-detection schemes for NO LIF

The combined laser beam and fluorescence losses depend on the wavelengths used for excitation and detection. Bessler et al. have discussed several excitation-detection schemes for NO measurements in high-pressure combustion [16]. One of the discussion points is the effect of CO$_2$ absorption on these excitation-detection schemes in terms of laser beam and fluorescence losses in piston engines. For their particular experimental geometry (laser beam entering through cylinder window, travelling 40 mm; LIF detected through piston window, travelling 10 mm), absorption losses were found to be minimal for A= 2(0,2) excitation of NO at 248 nm [16]. In our setup, the fluorescence path is considerably longer than that of the laser beam, necessitating a new analysis.

The transmission curves in Fig. 5 allow us to predict the field-of-view averaged laser beam transmission for other NO excitation wavelengths, again assuming similar absorption by CO$_2$ and O$_2$ for the laser beam and the fluorescence. This way, the transmission losses can be calculated for each excitation laser wavelength and for each detected fluorescence band, allowing several excitation-detection schemes for NO LIF to be compared. The individual fluorescence transmission curves are averaged using the appropriate Franck-Condon factors as weight factors. Additional losses by soot are not included, but since these are almost equal for all schemes, they do not affect our conclusions (the weak wavelength dependence of soot-based attenuation is neglected). Figure 11 shows the product of laser beam and fluorescence transmission curves (i.e. combined transmission) for the following excitation-detection schemes:

1. excitation at 226 nm and detecting red-shifted fluorescence at 237, 248, 259, and 272 nm;
2. excitation at 237 nm and detecting red-shifted\(^3\) fluorescence at 248, 259, and 272 nm;
3. excitation at 248 nm and detecting blue-shifted\(^4\) fluorescence at 226 and 237 nm.

With a spectrograph, simultaneous detection of blue- and red-shifted fluorescence is possible, whereas bandpass filters limit the choice of detection wavelengths to either red- or blue-shifted fluorescence. The above mentioned schemes can be, and have been, implemented using band-pass filters (see e.g. [2, 9, 12]), but we advocate the use of a spectrograph as it provides an on-line monitoring of spurious fluorescence interference. Figure 11 shows that, in terms of attenuation, 237 nm excitation would clearly be advantageous in our setup, with a combined transmission of at least 59% compared to 44% and 23% for 226 nm and 248 nm excitation, respectively. The apparent discrepancies with the calculations by Bessler et al. [16] are caused by differences in experimental geometry, detection wavelengths (in the case of 226 nm excitation), temperature, and column densities of CO\(_2\) and O\(_2\), showing that the “optimal” (i.e. least affected by absorption) scheme for NO detection indeed depends strongly on the experimental configuration.

Besides attenuation effects, absolute signal strength is an important selection criterion for excitation-detection schemes. The signal strength varies from one scheme to the other, additionally depending on the available laser power, population(s) of the laser-excited state(s), transition strength, spectral sensitivity of the detection system, and the number of detected fluorescence bands. In Fig. 12 we predict the signal strength in our engine for the above-mentioned schemes, taking into account the effects of (vibrational) energy level population (using the temperature from the fits in Fig. 5), transition probabilities (i.e. Einstein absorption and emission coefficients), quenching, and, of course, attenuation (Fig. 11). As a consequence, these curves may be interpreted as LIF intensities per NO molecule per laser pulse energy unit. Detector sensitivity is not included. It is obvious that 226 nm excitation yields the strongest signal throughout the combustion stroke (note the logarithmic ordinate).

7 Summary and conclusions

We have demonstrated three laser diagnostic techniques for assessment of (fractions of) the attenuation involved in in-cylinder NO LIF experiments. Complete attenuation corrections require a combination of techniques, combining CO\(_2\) and O\(_2\) absorption spectroscopy with (1) bidirectional LIF or (2) N\(_2\) Raman scattering. When a spectrograph is used, the fluorescence absorption by CO\(_2\) and O\(_2\) can be retrieved from the NO LIF spectra themselves, and only one additional measurement is required, being either the second, reversed laser pulse for bi-LIF, or N\(_2\) Raman scattering. All methods can in principle be used on a single-shot basis, although this requires extensive equipment, and averaging may be a good alternative. In our experiments, signal-to-noise levels did not allow a single-shot approach. The bidirectional LIF combination yields slightly better signal-to-noise ratios (as is reflected in the error bars in Fig. 10). The accuracy of the Raman-based transmission measurements can be reduced by selecting an excitation wavelength that is closer to 226 nm (Appendix I).

The bidirectional LIF results indicate that laser beam attenuation is far from uniform, being mainly localised in the piston bowl. This implies that (overall) laser beam transmission measurements cannot be used to accurately determine the local laser beam intensity.

UV absorption by CO\(_2\) and O\(_2\) leads to significant attenuation. Up to 40° aTDC, CO\(_2\) causes one third of the laser beam attenuation, the remaining part being attributed to soot (scattering and absorption). Later in the stroke, absorption by CO\(_2\) and O\(_2\) is less prominent due to the lower temperatures. If the local O\(_2\) density is not known, the transmission of the NO fluorescence could be estimated by fitting only the CO\(_2\) absorption

\(^3\) Detection of blue-shifted fluorescence at 226 nm is possible, but yields a lower signal than the combined (0,2) and (0,3) bands [44].
\(^4\) Detection of red-shifted fluorescence is not recommended due to lower signal and increased interference by O\(_2\) LIF [16].
cross-section. In our case, this yields fits of equal quality, deviating by ~ 10% from those in Fig. 5. The fitted CO₂ density is then overestimated by about 60% [28].

The wavelength dependence of the absorption by CO₂ and O₂ should be kept in mind when selecting an appropriate excitation-detection scheme for NO LIF measurements. The actual effect of such absorption on some commonly used schemes strongly depends on the experimental geometry. In our setup, \( A-X(0,1) \) excitation with red-shifted detection is least affected by CO₂ and O₂ absorption, although attenuation up to 40% is still predicted. In terms of absolute signal strength, \( A-X(0,0) \) excitation is clearly advantageous, yielding the strongest NO signal per laser pulse energy throughout the entire combustion stroke.

Despite the short path lengths in our experimental configuration, the laser beam and the NO fluorescence are heavily attenuated, reaching (combined) transmission levels as low as 2%. Later in the stroke, it increases to 85%. Since even the lowest observed transmission can be measured reasonably accurately (50%–60% relative error), correction of NO LIF for attenuation effects is now possible at all relevant crank angles. Applications of these findings for quantitative in-cylinder NO measurements will be published soon [29].

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Appendix I: Wavelength-dependence of extinction by soot particles

Many studies of the optical properties of soot have been reported, showing a considerable variety in extinction spectra and the derived refractive index. Here, we refer to UV-visible extinction spectra measured in the exhaust of a Diesel engine [23, 45, 46]. These experiments (soot primary particle diameter \( d_p = 20–25 \text{ nm} \)) show a wavelength dependence of the extinction coefficient \( K_{\text{ext}} \) that is very close to that in the Rayleigh approximation (valid for \( d_p < 0.1 \lambda \)), i.e. \( K_{\text{ext}} \propto \lambda^{-1} \). Despite coagulation of particles into chain-like structures, the observed extinction and scattering spectra can be attributed to the primary particle size [23]. Schnaiter et al. reported that, above a certain aggregate size, coagulation hardly influences the extinction spectra [46]. Furthermore, the extinction scales with \( \lambda^{-D_1} \), where \( D_1 \) is the fractal dimension of the aggregate (\( D_1 = 1 \) for a chain of primary particles).

Time-resolved laser-induced incandescence measurements in our engine indicate primary particles around 50 nm [47]. Although this is in the order of the Rayleigh limit, we will use the ratio 355/226 to scale the soot-based attenuation obtained with N₂ Raman scattering to 226 nm, with an estimated relative error of 20%. (This value is in agreement with more detailed calculations, extending the valid range to \( d_p < 0.25 \lambda \) by taking higher order terms of the Mie theory expansion into account.)

Appendix II: Noise analysis of the bidirectional LIF method

The sensitivity of the bidirectional LIF method to noise on the input signals \( S_{\text{down}} \) and \( S_{\text{up}} \) has been studied with numerical simulations. In these simulations, the spatial resolution, the extinction and scattering distributions, and signal strength were kept identical to the data in Fig. 6, but different amounts of noise were added. The noise characteristic of the iCCD cameras was modelled assuming Poisson statistics [48]. For each given noise level, the \( S_{\text{up}} \) and \( S_{\text{down}} \) signals were generated 100 times, and the resulting laser beam transmission was calculated for each generation.

The relative uncertainty of the (field-of-view averaged) laser beam transmission as a function of the noise on the \( S_{\text{down}} \) and \( S_{\text{up}} \) signals is shown in Fig. 13 (the curve for 41% transmission). This analysis was repeated for different extinction values (multiplying the extinction distribution by a factor of 0.25, 0.5, or 2), covering the range observed in the combustion stroke. The noise dependence behaves linearly, except for higher extinction values or high noise levels (both leading to low signal-to-noise ratios). Judging from the graph in Fig. 13, noise levels of 15%–20% (i.e. signal-to-noise ratios of 6–5) are still accepted by the algorithm.

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