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Pulsed cavity ring-down spectroscopy of NO and NO₂ in the exhaust of a diesel engine

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ABSTRACT The application of pulsed cavity ring-down spectroscopy has been demonstrated for the in situ quantitative determination of NO and NO₂ in the exhaust of a diesel engine. NO absorption has been monitored at the transition from the $X^2\Pi$ ground state to the $A^2\Sigma^+$ state at 226 nm. For NO₂, absorption bands in the spectral region from 438 nm to 450 nm were used. At the selected engine conditions, concentrations of 212 ± 22 ppm and 29 ± 4 ppm have been measured for NO and NO₂, respectively, in good agreement with separate chemical exhaust gas analysis. The method is sensitive enough to meet the European Euro V standard directive on NO_x emissions. This communication discusses the relatively simple setup needed for this type of measurement, the problems encountered, as well as the prospects for single-stroke, simultaneous measurements of both NO and NO₂ at the sub-ppm level.

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1 Introduction

Emissions of pollutants like NO and NO₂ from diesel engines present a serious health and environmental hazard. For example, NO and NO₂, collectively called NO_x, play an important role in the destruction of ozone [1]. Therefore, in combustion science, a lot of effort is put into the correct prediction of NO_x formation [2]. Different routes for NO formation and destruction have been identified. Depending on temperature, pressure and flame stoichiometry, thermal and prompt NO formation are normally the most important, but not yet fully quantitatively understood, pathways.

Nitric oxide can be detected easily by fluorescence-based techniques, e.g. through excitation out of the $X^2\Pi$ ground state to the $D^2\Sigma^+$ state at 193 nm or to the $A^2\Sigma^+$ state around 226 nm. Using these techniques, NO can be identified even under harsh conditions,

like in the combustion chamber of a diesel engine [3,4]. Atmospheric nitrogen dioxide can be studied by means of laser spectroscopy as well. The NO₂ absorption spectrum in the range from 430 nm to 450 nm is the result of two electronic transitions, $^2B_2 \leftarrow ^2A_1$ and $^2B_1 \leftarrow ^2A_1$ [5]. The ro-vibrational bands of these transitions overlap, resulting in a complex absorption spectrum [6]. Collisional quenching and vibrational energy transfer appear to limit the application of laser-induced fluorescence (LIF) for the detection of NO₂ to sub-atmospheric pressures [7]. For different applications at low pressures, a number of direct and indirect detection schemes have been developed with sensitivities down to the ppt range [8]. However, the quantitative interpretation of the LIF signal is difficult. Therefore, a straightforward analysis by a simple but sensitive absorption technique may be preferable for potential applications.

Cavity ring-down absorption spectroscopy (CRDS) has been shown to be a powerful technique for trace-gas detection. Since 1988, numerous papers have shown the potential of the technique (see [9] for a review), both for trace-gas detection [10] and in harsh environments like combustion processes [11]. CRDS measurements of NO₂ have been demonstrated down to concentrations of 16 ppb in ambient air in the 425–460-nm range at a resolution of 1 cm^{-1} [12]. Romanini et al. have shown the application of cw diode lasers in CRDS by recording a high-resolution spectrum around 785 nm and 796 nm of NO₂ cooled in a supersonic jet [13, 14]. Recently, a paper was published on the catalytic degradation and diffusion processes of NO₂ at 612.9 nm investigated by CRDS [15].

In this communication, we show the potential of the in situ application of pulsed cavity ring-down spectroscopy to the exhaust of a diesel engine [4] as opposed to off-line, discontinuous or (pretreated) sample-handling methods. The experimental setup enables the on-line monitoring of both NO₂ and NO in the exhaust gas.

2 Experimental

The basic CRDS setup is similar to those described elsewhere [10]. Two different sets of mirrors were used (HR_{max} at 226 nm and HR_{max} at 430 nm, $R = -250$ mm from Laser Optik). The mirrors were connected with bellows to glass rods as a shield to the surroundings and enabling a continuous, small, homogenous flow of nitrogen to flush the mirrors. The distance between the mirrors was $d = 450$ mm. A tun-

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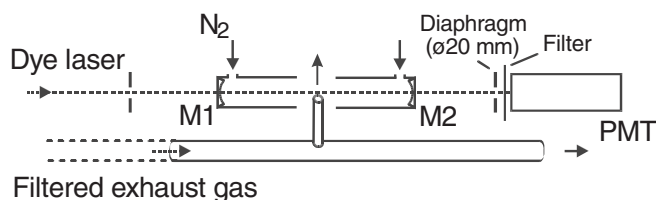


FIGURE 1 Experimental scheme of the CRDS experiment on the exhaust gas of a diesel engine

able dye laser (Lambda Physik Scanmate 2E, dye coumarine 47, bandwidth 0.18 cm^{-1}), pumped by the third harmonic of a Nd:YAG laser (Continuum Powerlite 9010) was used to generate radiation in the blue (for NO_2) and, after frequency doubling, in the UV (for NO) spectral range. The beam is spatially filtered by a pinhole (1.0 mm) before it is coupled into the cavity. The light transmitted through the cavity was detected by a fast photomultiplier tube (PMT) (Thorn-EMI 9814QB) placed behind the end mirror and a diaphragm and a band-pass filter ($460 \pm 80 \text{ nm}$) for NO_2 detection to reduce background signals. In the case of NO detection at 226 nm, the PMT was placed at 90 degrees to the cavity and light was detected via a $225 \pm 10\text{-nm}$ mirror at 45 degrees to decrease background scatter. The signals were recorded on an 8-bit, 300-MHz, 2.5-GS/s digital oscilloscope (LeCroy 9361); 30 traces were added and read out using a PC.

The exhaust gases of a test engine, a DAF six-cylinder, 11.6-l, direct-injection WS diesel engine with an early injection of 15° before TDC, instead of 12° before TDC, were studied. During operation of the engine, the exhaust gases of three cylinders were led through a fiberglass soot-particle filter (Unikat E, separation $> 95\%$ $0.4\text{-}\mu\text{m}$ particles). In order to prevent saturation effects, part of the flow in the exhaust pipe (100-mm i.d.) was diverted through a small sampling tube (12.0-mm i.d.) positioned inside the exhaust pipe, probing the middle of the gas stream (path length 95 mm to tube exit), as is shown in Fig. 1. The distance between the laser beam and the exit of the tube was varied between 2.0 mm and 6.2 mm, but this did not affect the results. Therefore, the absorption path lengths were assumed to be constant and equal to the exit diameter of the tube. The temperature and density distributions were assumed constant over the complete absorption path length above the exit of the tube.

3 Results

The time behavior of the light intensity transmitted through the rear mirror follows a single exponential decay function if a pulsed laser source with a small bandwidth is used. The exponential time constant $\tau(\lambda)$, the cavity ring-down time, is given by the equation

$$\tau(\lambda) = \frac{d}{c[|\ln R(\lambda)| + \sum_i \sigma_i(\lambda) N_i l]} \quad (1)$$

where d is the cavity length, c the speed of light, $R(\lambda)$ the mirror reflectivity, $\sigma_i(\lambda)$ the combined absorption and Mie/Rayleigh scattering cross sections at wavelength λ for the species i present inside the cavity, l the absorption path length and N_i the density of particles or molecules in the energy state from which the absorption takes place. Obviously, τ is not dependent on the laser-beam intensity and the sensitivity is limited only by the mirror reflectivity, the absorption cross section and the ratio d/l . Given the absorption cross section of a chemical species, the ring-down time as a function of wavelength provides quantitative information on the density of that species.

Figure 1 shows the current experimental scheme. In earlier attempts, molecular absorption was often obscured by the occurrence of larger or smaller soot particles. This problem has now been eliminated by the introduction of a soot-particle filter. Secondly, the absorption path length is decreased to 12 mm, in order to reduce the total absorption and to prevent saturation of the CRDS system. In addition, the current setup allows flushing the cavity mirrors

with nitrogen to avoid fouling of the mirrors.

The results obtained in the exhaust gas of the diesel engine at 1360 rpm and a load of 30 (NO) and 35 (NO_2) Nm are shown in Table 1. They are the results of an average over three spectral scans for each species, which takes ~ 7 min per scan. Measurements were started after a 10-min warm-up period and a stable baseline was obtained. The temperature of the exhaust gas taken at the exit of the sampling tube is included as well.

In Fig. 2a the absorption cross section of NO_2 as a function of wavelength as determined in calibration measurements preformed in a cell is shown as a reference [16]. Figure 2b shows an example of the CRDS spectrum recorded with the current setup during operation of the engine at 1360 rpm, 30-Nm load and 398 K. From the relation $\alpha = \sigma N_{\text{tot}}$ the total concentration N_{tot} of NO_2 has been calculated to be 29 ± 4 ppm. With the calibrated absorption data, structureless broadband background absorption, possibly caused by soot, is accounted for. From the previously performed measurements and literature, it is known that the influence of temperature on the NO_2 absorption spectrum is small at the current temperatures and resolution [17].

Figure 3 shows a part of the experimental $A^2\Sigma^+ \leftarrow X^2\Pi$ CRD spectrum of NO at 1360 rpm, 30-Nm load and an exhaust-gas temperature of 408 K at the tube exit. To calculate accurate NO densities, weak absorption lines were selected to avoid saturation effects [18]. From the coinciding $Q_1(19.5)$ and $P_{21}(19.5)$ lines, the absorption cross section obtained from the Einstein A coefficients given by Luque and Crosley [19] and the Boltzmann distribution at 408 K, the concentration of NO could be calculated as given in Table 1. The errors are determined by the experimental noise and the accuracies of the values used for the absorption cross sections. For NO, a 3% error in

Species	Speed (rpm)	Load (Nm)	Temperature (K)	Concentration (ppm)
NO_2	1360	35	398	29 ± 4
NO	1360	30	408	212 ± 22

TABLE 1 Concentration as a function of engine conditions

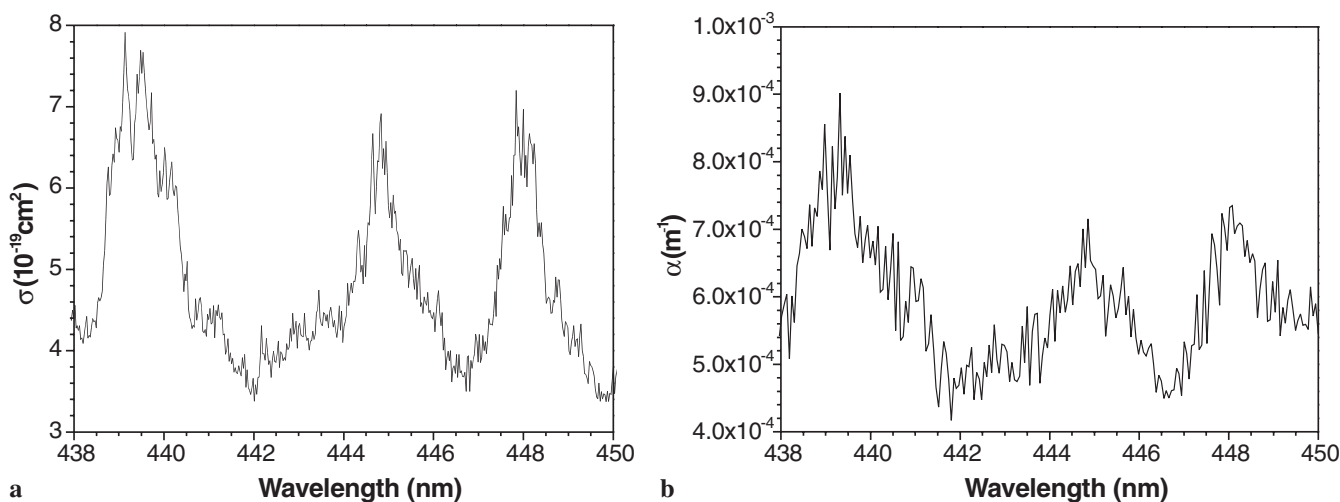


FIGURE 2 **a** NO₂ reference spectrum measured in a cell at atmospheric pressure and room temperature. **b** NO₂ CRD spectrum measured in the exhaust gas of a diesel engine at 1360 rpm, 35 Nm and 398 K

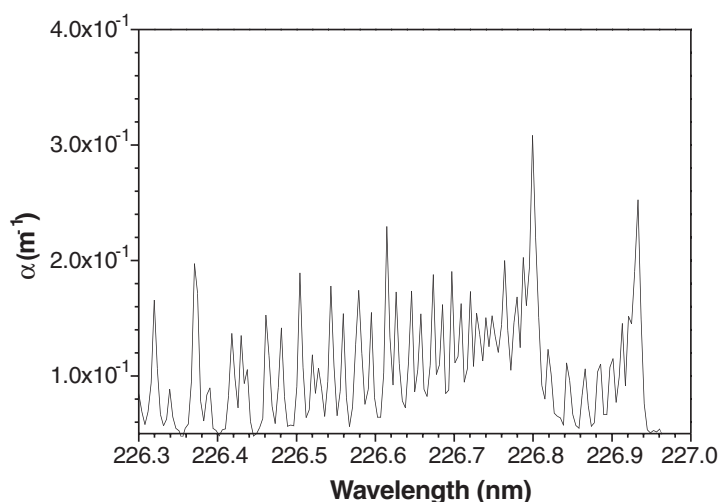


FIGURE 3 Part of the NO $A^2\Sigma^+ - X^2\Pi$ CRD spectrum measured in the exhaust gas of a diesel engine at 1360 rpm, 30-Nm load and 408 K

the absorption cross section has been added.

In addition, measurements with a chemical gas analyzer (Signal Instruments, Camberley, UK, calibrated with a 800 ppm NO in N₂ gas mixture) was performed to enable a comparison of the data. At an engine speed of 1360 rpm and 30-Nm load this resulted in a total NO_x level of 290 ppm.

Surprisingly, removal of the soot filter during the NO measurements did not result in a significant change of the experimental spectrum. Therefore, the production of large soot particles in this engine under the current operation conditions is apparently low enough not to disturb the CRDS measurements. To study the influence of engine running conditions on the production of NO_x, several different measurements were

made. Results will be presented elsewhere [20].

4 Discussion and outlook

The densities measured during the experiment at the outlet of the sampling tube must be correlated with the densities inside the exhaust pipe. The air intake of the three unmodified cylinders of the engine is 70 g/s, resulting in a maximum gas-flow speed of 11 m/s at the sampling point. This is still below the incompressibility limit of Mach 0.3 [21]. Therefore, the exhaust-gas flow can be considered incompressible and the species densities in the gas mixture, including NO₂ and NO, are independent of the flow speed. Consequently, the densities inside the main exhaust pipe and just outside the sampling

tube can be assumed to be equal, and the data are directly representative of the concentrations inside the main exhaust-gas flow.

The experimental results show the detection of the broadband NO₂ spectrum at 430 nm and NO at 226 nm in the exhaust gases of a diesel engine using a simple experimental setup. A sensitivity of 3 ppm and 25 ppm for a 12-mm absorption path length could be easily obtained for NO₂ and NO, respectively. If necessary, sensitivities down to the low-ppb range may be reached by using the full absorption path length, mirrors with a higher reflectivity and by selecting the more intense R-branch for NO, provided interfering absorptions are not the limiting factor.

At the applied engine conditions an experimental NO_x level of 241 ± 26 ppm was found. Measurements with the gas analyzer at an engine speed of 1360 rpm and 30-Nm load resulted in a total NO_x level of 290 ppm, in reasonable agreement with the CRDS results. Examination of the experimental values and sensitivities shows that with this method the maximum emission levels of NO_x required by the European Euro V standard directive on the emission of NO_x (2008) can be easily determined.

The precision of the experimental method can be further increased by reducing the spectral range (to only two or three lines in the case of NO) to increase the number of spectral scans. A substantial reduction of the acquisition time can be attained by recording only the

on- and off-resonance ring-down times. This will enable single-cylinder, single-stroke measurements, which is important for a detailed study of the combustion process in internal-combustion engines. Techniques based on gas analysis generally have a long response time and are unable to achieve this. The current method may provide a direct optical approach to measure both time-averaged NO_x -emission levels as well as stroke-to-stroke fluctuations. Furthermore, since the wavelength for detection of NO is half the wavelength of NO_2 absorption, it may be possible to monitor both species during the same experimental run using both the fundamental and the second harmonic of the laser source. A further improvement of the method can be the application of more sensitive, but slightly more complex, continuous wave absorption techniques (cw CRDS or CEA (cavity enhanced absorption spectroscopy)), increasing the sensitivity by a factor of 10 to 100 [9]. In addition, cw and diode-laser systems are also smaller, which makes a more compact, portable experi-

mental setup possible that can be used in the field.

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