In situ vehicle engine exhaust measurements of nitric oxide with a thermoelectrically cooled, cw DFB quantum cascade laser

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Abstract. This paper describes the application of a thermoelectrically cooled, continuous wave (cw), single mode distributed feedback (DFB) quantum cascade laser (QCL) to the real-time, in situ vehicle engine exhaust monitoring of nitric oxide. Experiments have been carried out on a static gasoline engine test bed where the engine operating conditions can be varied in a controlled manner. Results show the response of the nitric oxide concentration to engine conditions. The prospects for further multispecies in situ measurements are discussed.

1. Introduction

Vehicle emissions are an increasing concern and give rise to a range of environmental problems related to air quality. Nitric oxide (NO) is one of the key pollutants emitted from the exhausts of both gasoline and diesel engine vehicles and is generated primarily due to high temperature combustion processes involving air as the oxidant. It is not regarded as toxic but can be rapidly oxidised to nitrogen dioxide, NO₂, which is harmful. Additionally, the NO to NO₂ conversion is involved in the production of photochemical ozone [1]. The ability to measure NO directly in the engine or in the exhaust could link into engine management systems for its control. In situ measurement could also be used to assess the condition of a catalytic converter. The traditional approach to high sensitivity measurement of NO (and NO₂) is chemiluminescence [2] but this involves extraction of the exhaust gases into the measuring unit. Infrared laser absorption spectroscopy has many advantages for this application. Previous work on vehicle exhausts has employed multiplexed near-infrared diode lasers for the detection of CO, CO₂ and CH₄ [3]. These can be made into ruggedised instruments with fibre optic cables for beam transmission. This technique has also been successfully demonstrated over many years on aero-engines by Hansen’s group [4]. However, nitric oxide is only a weak absorber in the near-infrared. A room temperature mid-infrared quantum cascade laser (QCL) is a viable alternative for detection in the fundamental band. Allen’s group has previously employed a pulsed (QCL) for extractive measurements in combustor exhaust flows [5]. Duxbury’s group has also demonstrated the application of a pulsed QCL for extractive measurements in vehicle exhausts [6].
This paper describes the application of a mid-IR spectrometer based on a thermoelectrically-cooled cw single mode quantum cascade laser to the in situ measurement of nitric oxide directly in the exhaust of a static internal combustion engine.

2. Experimental arrangement

2.1. QCL spectrometer

The thermoelectrically cooled cw DFB QCL (Alpes Lasers) operated in the region around 1900 cm\(^{-1}\)(\(\sim 5.263 \mu\text{m}\)) for the detection of nitric oxide in the fundamental band. Figure 1 shows a simulation of the nitric oxide absorption spectrum (10,000 ppm) in this region combined with the absorptions of other relevant combustion species, H\(_2\)O (5%), CO (1%) and CO\(_2\) (1%) for a temperature of 500 K and a pathlength of 23 cm. The QCL spectrometer has been described in detail previously [7] so only the essential details are given here. The main components are shown schematically in figure 2. The QCL laser light was collimated by an uncoated CaF\(_2\). The QCL, the thermoelectric cooler, and the collimating lens were placed in to an aluminum enclosure (QCL head). The QCL current was supplied up to 0.53 A by a current driver (TDL Sensors Ltd) with a current short-term stability of less than 25 \(\mu\text{A}\). The output maximum averaged power of the QCL used in the experiments was measured to be \(\sim 2.5 \text{ mW}\). The wavelength of the QCL was tuned by applying a modulation voltage waveform, generated by a 16-bit data-acquisition (DACQ-TDLS) card (DACQ200, TDL Sensors Ltd) with a scan rate of 952 Hz, to the current driver. The amplified signal of the thermoelectrically cooled photodetector was converted by the 16-bit analogue-to-digital converter of the DACQ-TDLS card, averaged 1000 times and then transferred, by means of a serial data connection, to a computer for further processing and reporting NO concentration. Concentrations were determined in real-time by a non-linear least-squares fitting routine. A minimum detectable optical depth of 0.0018 was estimated at SNR=1 and the NO limit of detection was 8ppm.

![Figure 1. Simulated absorption spectra for NO, H\(_2\)O, CO and CO\(_2\) at 500 K.](image-url)
2.2. Gasoline engine test bed
The engine used in the tests was a Rover K series 1.4 liter 16 valve version with a double overhead cam (DOHC) and a single point fuel injection system (SPi). This is shown in figure 3. The load could be varied by means of a water brake dynamometer and the throttle control could be varied on an arbitrary scale of 0 to 255 with 255 corresponding to throttle wide open. The fuel used as unleaded gasoline with an octane rating of 95.

The mid-infrared QCL beam probed the 2-inch diameter stainless steel exhaust pipe 2.5 m away from the engine. The temperature and pressure of the exhaust gas were monitored just above the measurement point (see figure 2). To allow optical access to the exhaust pipe, a cross-piece was inserted with two wedged sapphire windows mounted 23 cm apart.

Figure 2. Experimental setup for NO measurements on engine exhaust.

Figure 3. Vehicle engine test bed. NO measurements on engine exhaust.
3. Results
Typical raw signals measured in the exhaust are shown in figure 4 for the conditions of engine on and engine off. The 20-point off period at the beginning of the scan was to allow for calibration of the 0% absorption level. The two absorption peaks in the engine on scan are the two nitric oxide absorption lines described above. The difference in intensity of the two signals was due to the attenuation of the beam due to deposits on the cell windows after the engine start.

Figure 4. Typical raw signals within NO measurements on an engine exhaust (2.5 m from the engine).

Figure 5 shows the results obtained for the variation in NO concentration after engine start up. As can be seen there is a steady rise in NO emissions to over 500 ppm over a period of 15 minutes. Additionally, peak levels of up to 2000 ppm are also observed during engine warm up and engine revving. Figure 6 shows the effect on the NO concentration for a step-change in load and throttle settings. The load increased on an arbitrary scale of 40 to 75 and the throttle increased from 61 to 86 resulting in an increase of revs from 2600 to 3460 rpm and an increase in engine temperature from 550 to 650 °C. The effects of the step-change can clearly be seen with a jump in averaged NO levels from around 500 to 1750 ppm with peak concentrations up to 2000 ppm. It is also clear from the results that the NO concentrations vary considerably on a short time scale of a few seconds.

4. Discussion and Conclusions
The results presented here have demonstrated that a room temperature continuous wave (cw) DFB quantum cascade laser can be used for the in situ monitoring of vehicle exhausts. Nitric oxide concentrations have been determined in real-time and clearly respond to changes in engine operating conditions. The increases in NO levels are primarily linked to the increased combustion temperature in the cylinder due to engine startup and primarily to the increasing load on the engine. The rapid sweep integration technique employed here output NO concentrations every second (1000 averages) but this could easily be adapted to produce concentrations on the millisecond timescale. Furthermore, fixed wavelength techniques could also be used for faster measurements.
Figure 5. NO concentration variation after the engine start.

Figure 6. NO concentration variation after the engine start.
For more detailed analysis of NO\textsubscript{x} production under defined engine operating conditions it is planned to simultaneously monitor NO\textsubscript{2} concentrations in the region around 1600 cm\textsuperscript{-1} with another QCL operating in a multiplexed mode. It is also planned to combine the NO\textsubscript{x} measurements with the near-infrared multiplexed spectrometer for simultaneous CO, CO\textsubscript{2} and CH\textsubscript{4} detection [3]. However, for higher sensitivity operation in the mid-infrared is preferable and CO/CO\textsubscript{2} detection can be accomplished with either a QCL or a difference frequency generated laser [7].

In conclusion, the prospects for highly sensitive, simultaneous multispecies, real-time monitoring directly in vehicle engines and exhausts for diagnostic and control purposes based on the latest mid-infrared laser technology appear now to be feasible.

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