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Simultaneous detection of CO_2 and CO in engine exhaust using multi-mode absorption spectroscopy, MUMAS

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ABSTRACT

Multi-mode absorption spectroscopy, MUMAS has been employed for the simultaneous detection of CO_2 and CO. MUMAS signatures were recorded using a diode-pumped Er:Yb:glass microlaser emitting a multi-mode spectrum in the region of 1.57 μm. The ratio of CO_2:CO concentrations in a calibration gas was measured to within the manufacturers uncertainty of ±1.4%. Both gases were also detected and the ratio of their concentrations measured in the exhaust gas of a SI internal combustion engine under varying conditions of fuel/air ratio and compared with measurements using a commercial gas analyser. Standard errors on the mean for the measurements were in the range 0.4–0.8%. The detection limit for CO partial pressure was determined to be 0.15 mbar in 100 mbar total pressure.

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1. Introduction

The detection of gas species for monitoring or control purposes has been greatly facilitated by the use of tuneable diode laser absorption spectroscopy, TDLAS, in a variety of forms [1–3]. The control of combustion or industrial processes involving gas-phase reactions, however, often requires simultaneous detection of multiple species and parameters [4–6]. In many cases the absorption lines of the different species may be separated by a frequency range beyond the tuning range of a single single-mode laser and so some kind of multiplexing and de-multiplexing is required to combine beams from a number of separate lasers, each tuned to a resonance line in a specific species [7,8]. Wide tuneability is available from VCSEL devices and their ability to directly scan a single mode over a wide range gives these devices a particular advantage in detecting absorption lines at elevated pressures where collisional broadening becomes an issue. However, they are not readily available in all spectral regions and generally have lower power and broader linewidths, than other single-mode devices. Alternative approaches to multi-species detection have included spectroscopic techniques employing broad-band light sources such as super-luminescent light emitting diodes [9], super-continua from optical fibres [10], or wide bandwidth frequency combs from femto-second laser systems [11] with some method of spectral dispersion and detection. The requirement for spectral dispersion and resolution is obviated by gas correlation spectroscopy, COSPEC, which uses temporal correlations in signals from the sample under test and reference gas cells containing specific target species [12]. The use of multi-mode diode lasers for COSPEC has also allowed multi-species detection [13].

Recently an alternative method, also using multi-mode lasers, has been introduced – Multi-mode Absorption Spectroscopy, MUMAS. The technique detects absorption of any of the longitudinal modes in the laser spectrum when it is resonant with a molecular transition by the consequent reduction in the total transmitted light. The technique offers wide spectral coverage together with high spectral resolution and has been applied to multi-species and multi-parameter sensing [14,15]. The primary advantage over TDLAS is that multiple species can be detected using only a single laser and a single detector. MUMAS avoids the complexity and expense of methods requiring multiple or complex laser systems, additional spectral dispersion or reference cells for each target species and can be carried out, in principle, with any kind of multi-mode laser and so is not restricted to a limited number of spectral regions.

In this paper we report the use of MUMAS to detect simultaneously CO and CO_2 as a demonstration, or test case, of detection of two species by MUMAS that can act as a monitor of an important industrial process and which, in principle, could provide a signal for control purposes, or for environmental monitoring.

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The ratio of CO_2 to CO is well known as an indicator of the completeness of combustion and measurement of both gases in the atmosphere or in technical combustion devices has received considerable attention since the introduction of TDLAS. The ratio is also used as an atmospheric indicator of the origin of carbon emissions since the completeness of combustion, and hence the relative amount of CO, varies for different combustion devices and fuels [16]. The ready availability of single-mode diode lasers for telecommunications in the spectral region of 1.3 μm motivated their application as sensors for both CO_2 and CO with the potential for process control [17]. Detection of both these gases was achieved using a multi-mode laser emitting at 1.58 μm but, interestingly, the lasers were forced into single-mode operation by coupling to an external cavity [18]. This allowed a single one of the multiple modes to be tuned in a controlled way across the absorption lines of interest and so only one of the species was detected at a given time. Detection of CO using the stronger absorption features around 2.35 μm was demonstrated by TDLAS employing a GaInSbAs/GaSb multiple quantum well device [19]. CO had previously been detected in, and the temperature measured of, a methane/air flame using a Pb-salt laser at this wavelength [20]. Detection of both CO and CO_2 was achieved by scanning successively over individual lines in the region of 1.55 μm [21]. Using a commercial external cavity diode laser ECDL a near coincidence of transitions in both CO and CO_2 near 1.57 μm was exploited to measure both species essentially simultaneously [22]. Such simultaneous recording of CO and CO_2 absorptions was also demonstrated using a DFB diode laser at the same wavelength region [23]. An alternative technology based on a specially fabricated multi-section InGaAsP diode laser was demonstrated for multi-species detection by recording absorption spectra of CO, CO_2, OH and H_2O in room temperature and combustion gases over a total range of 100 nm [24]. The wide single-mode tuneability of VCSEL devices has been exploited using a MEMS-device to detect CO and CO_2 in spectral ranges of the order of 100 cm^{-1} [25]. The detection of CO_2 using COSPEC employing a multi-mode diode laser has been reported recently [26].

The aim of the present work is to demonstrate that MUMAS has the potential to allow simultaneous monitoring of two (or more) species whose relative concentrations can be used for process control. Many of the TDLAS schemes allow significant improvements in detection sensitivity by the use of signal-to-noise enhancement techniques such as Balanced Ratiometric Detection, Wavelength Modulation Spectroscopy, WMS, Frequency Modulation Spectroscopy, FMS, Cavity Enhancement Absorption Spectroscopy, CEAS and Optical Feedback Cavity Enhanced Absorption Spectroscopy, OF-CEAS. Increase in sensitivity however is often at the cost of detection bandwidth. A quantitative comparison of the present work with all the varieties of TDLAS schemes and *S*/*N* enhancement methods is beyond the scope of the present paper. In general, however, *S*/*N* improvements use methods to increase the signal e.g. by extending the absorption path in cavity-based methods, or reducing the noise on the signal by modulating and detecting within a narrow band of frequencies centred at a frequency well above that of most noise interferences. For process control applications the detection bandwidth is an important issue with detection rates in the kHz range typically required corresponding to signal averaging times in the 10^{-3} s range. Bandwidths in this range are easily achieved using noise cancellation by balancing methods and bandwidths up to MHz rates are achievable [27]. Recently a new method, auto-digital gain balancing, has been introduced and applied to CO and CO_2 detection in the 10–100 ppm range at 1.58 μm [28]. A Noise Equivalent Sensitivity of 3.6×10^{-6} was reported comparable to the best figures by Balanced Ratiometric Detection but with higher bandwidth in the kHz range.

An indicator of the potential of the present work is indicated by noting that a recent demonstration of WMS-enhanced TDLAS measured CO and CO_2 concentrations in controlled stable cell environments with a detection limit of 250 ppm m and 280 ppm m respectively [29]. The present work, as will be shown, achieved by direct absorption, a detection limit of the order of 2000 ppm m in a relatively unfavourable environment of exhaust gas sampled from a running IC engine. It is conceivable that by applying WMS, or similar enhancement methods, the detection limit could be improved and made comparable to that achieved in the cell-based measurements. Rather than comparing the performance of MUMAS in a non-ideal environment with more favourable cell-based measurements, the results obtained here are compared instead with that of a commercial gas analyser in order to demonstrate its ability to provide quantitative measurements in agreement with conventional detectors. Of perhaps more significance for process control is the present work's ability to measure the ratio of the two gases with good precision and accuracy.

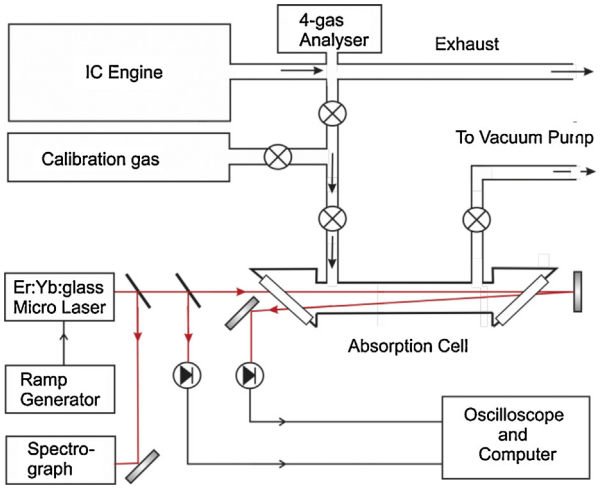

Fig. 1. Diagrammatic representation of the experimental arrangement for MUMAS of exhaust gas emission from the internal combustion (IC) engine. The water vapour trap on the line from the engine exhaust to the absorption cell is not shown.

2. Experimental apparatus and method

The experimental arrangement for absorption spectroscopy using MUMAS is shown schematically in Fig. 1. The absorption cell consisted of a stainless steel tube, of length 0.8 m, fitted with Brewster angled windows and an externally mounted retro-reflecting mirror. Gas samples were admitted to the cell via stainless steel valves and either held, or drawn through, at a pressure of 0.1 bar. In initial tests a sample of gas containing a mixture of CO and CO_2 at a fixed concentration ratio was provided for calibration purposes. For measurements on emissions from the spark ignition (SI) engine, gas was extracted from the exhaust pipe and drawn first through an ice trap to remove water vapour. This avoided issues arising from condensation of water in the valves or on cell windows which adversely affected the control of the cell pressure. The laser intensity incident on the cell, and that transmitted after a double pass through the cell, was detected using photo-diodes (Thorlabs DET10C/M) and recorded on a digital oscilloscope (Handy Scope HS4) before storing on a computer. During recording of MUMAS data to determine the CO and CO_2 concentrations the exhaust gas was simultaneously analysed by a four-gas analyser (Pickavant 324200SP) having a read-out accuracy of 5%.

The multi-mode laser used in the present work, and the procedure for obtaining a MUMAS spectrum, is similar to that employed in previous experiments to demonstrate multi-species detection and details can be found in reference [15]. The overall bandwidth of the laser was determined by the gain profile of the Er:Yb:glass

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