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Detection of NO in a spark-ignition research engine using degenerate four-wave mixing

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ABSTRACT We report the first application of degenerate four-wave mixing (DFWM) to combustion diagnostics in a methane-fuelled internal combustion research engine. Combustion-generated NO in the spark-ignited engine was detected using scanning narrowband DFWM in a modified forward folded BOXCARS geometry. The resulting spectra of the $X^2\Pi - A^2\Sigma^+(0, 0)$ band at 226 nm display an excellent signal-to-noise ratio. Extension of the technique to different engine operating conditions and to time-resolved multiplex DFWM is discussed.

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1 Introduction

Laser techniques are now widely used for the study of combustion in both laboratory flames and engineering devices [1]. Such optical studies of combustion are valuable as they can provide, for example, in situ monitoring of pollutant formation. Linear techniques such as absorption spectroscopy and laser-induced fluorescence (LIF) are frequently used. LIF allows 2-dimensional imaging and has been successfully applied in engines. Planar laser-induced fluorescence, PLIF, of OH was used to image the flame front in a firing internal combustion engine [2] and yields valuable qualitative information on species distributions. LIF and PLIF have been widely applied in engines [3] although interpretation of the signal is often complicated by collisional quenching. Interference from hydrocarbon fluorescence can also significantly reduce the signal-to-noise ratio. Non-linear techniques offer particular advantages in such situations, owing to the coherent nature of the generated signal. Coherent anti-Stokes Raman scattering (CARS) has been applied to thermometry and concentration measurements in a variety of situations, including internal combustion (IC) engines. Unfortunately, only major species such N_2 and CO_2 can be probed using CARS. Degenerate four-wave mixing (DFWM) has the sensitivity to detect trace combustion species, such as OH [4] and NO [5], owing to the resonant nature of the interaction. The advantages of DFWM, particularly its sensitivity and the coherent nature of the generated signal, have so far not been exploited for the study of practical combustion devices. In this paper we report what, to our knowledge, is the first practical demonstration of DFWM in a research IC engine.

We have chosen to demonstrate the practical application of DFWM in a research engine by detecting the environmentally important NO molecule. NO is directly responsible for the generation of ground-level ozone and, in combination with hydrocarbon emissions, the formation of a photochemical summer smog [6]. Although the chemical mechanism of NO generation in a spark-ignition IC engine is well understood, predictions of in-cylinder NO concentrations depend on the accuracy of the combustion model [7]. Monitoring the formation of NO as a function of engine operating parameters, fuel composition and engine design may lead to an improved understanding of the combustion cycle and subsequent reductions in emissions level.

Traditionally, in-cylinder NO has been monitored either by chemiluminescence techniques or by gas sampling [7]. Previous laser-based studies of NO in IC engines have been based on planar laser-induced fluorescence, PLIF, excited by a variety of laser sources. Initial measurements of in-cylinder NO distributions utilised excitation by ArF excimer lasers at 193 nm. This allowed detection in a spark-ignition (SI) engine [8], in both a directly-injected [9] and in an indirectly-injected Diesel engine [10]. Excitation of NO at 226 nm by frequency-doubled tunable dye lasers enabled measurements to be made in a single-cylinder square-piston engine [11] and in a directly injected Diesel engine [12]. NO has also been studied in a SI engine using PLIF with excitation at 248 nm from a KrF excimer laser [13]. More recent work has extended the study of NO formation in Diesel engines under realistic operating conditions [14, 15].

In general, collisional quenching complicates the interpretation of LIF signals [16]. This is particularly true for images produced by PLIF. When properly post-processed [17], such images can be used qualitatively to find areas of maximum average NO concentration [18] or to study cycle-by-cycle variations in NO spatial distributions [13]. A simplified quenching correction has been attempted [19], but such approaches yield results of questionable accuracy owing to the poorly characterised nature of the combustion process.

As well as having a sensitivity comparable to LIF in combustion environments [20], DFWM can be made much less sensitive to collisional quenching by operating under saturat-

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ing conditions [21]. Flame-generated NO has been detected using DFWM [5] although the signal needs to be carefully distinguished from scattering off laser-induced thermal gratings which arise from collision-induced relaxation effects [22]. DFWM signals can also be analysed to yield absolute species concentrations in well-characterised flames [23]. As with CARS, DFWM can be operated in the broadband mode, yielding single-shot thermometry of flames [24, 25]. This facility for time-resolved measurements is a potential advantage in engine applications.

2 Engine system

A single-cylinder research engine, based on the four-stroke Rover K4 SI automotive engine, was modified for optical access by replacing the upper part of the cylinder with an alloy annulus of identical diameter. A plane fused silica window (diameter = 25 mm, thickness = 15 mm) was mounted at each quadrant of the annulus, allowing optical access along two orthogonal axes. The piston blocked optical access through the cylinder from 60° bTDC (before top dead centre) to 60° aTDC (after top dead centre). The piston was sealed with four reduced-friction synthetic rings to eliminate the need for lubrication, thus preventing an undesirable oily film from accumulating on the windows. The engine had a bore of 80 mm, a stroke of 89 mm, a compression ratio of 10 and was fuelled with a methane-air mixture to provide relatively clean combustion. The mixture was adjusted to be slightly lean of stoichiometric ($\lambda \approx 1.1$), thus ensuring maximum in-cylinder NO concentrations [7].

Cylinder pressure was monitored by means of a piezoelectric pressure transducer (AVL QL32D) mounted in the pent roof of the cylinder head; pressure traces were logged on a PC with an analogue-to-digital converter. NO_x levels in the exhaust gas were monitored with a chemiluminescence analyser (Thermoelectron Model 10A).

In all the measurements presented here, the engine speed was fixed at 1200 rpm to ensure that the Nd:YAG pump laser was triggered at its optimal 10 Hz repetition rate. All experimental timing was derived from the engine. The laser and data acquisition system could be triggered at any point in the engine cycle by means of adjustable delays. The jitter in the laser timing was estimated to be less than one degree of crank angle.

Thermal distortion of the windows under continuous engine firing led to severe beam wander, resulting in the DFWM signal beam drifting off the detector. To avoid such effects the engine was skip fired. Skip firing is common during laser-based measurements, especially where Diesel or other heavily sooting fuels are used. A skip-fire ratio of 1:8 (fire 1, skip 8 cycles) was sufficient to eliminate thermal effects in the windows. Residual beam steering effects arising from thermally inhomogeneous burnt gas in the cylinder were also observed but proved to be insignificant in the particular optical layout used.

3 Optical layout

The experimental layout is shown in Fig. 1. The output of the Nd:YAG laser (Continuum PowerLite 8000 Series) was frequency tripled, giving 7 ns pulses at 355 nm with an energy of 250 mJ, in order to pump a Littrow-grating type tunable dye laser (Spectra Physics PDL-3) operating with Coumarin 460 dye. The output of the dye laser at 452 nm was frequency doubled in a BBO crystal (Photox Optical Crystals) to give 300 µJ pulses at 226 nm with a linewidth of approximately 0.2 cm^{-1}. The collinear UV and remaining blue light were completely separated by an arrangement of four Pellin Broca prisms arranged at the four corners of a rectangle. The

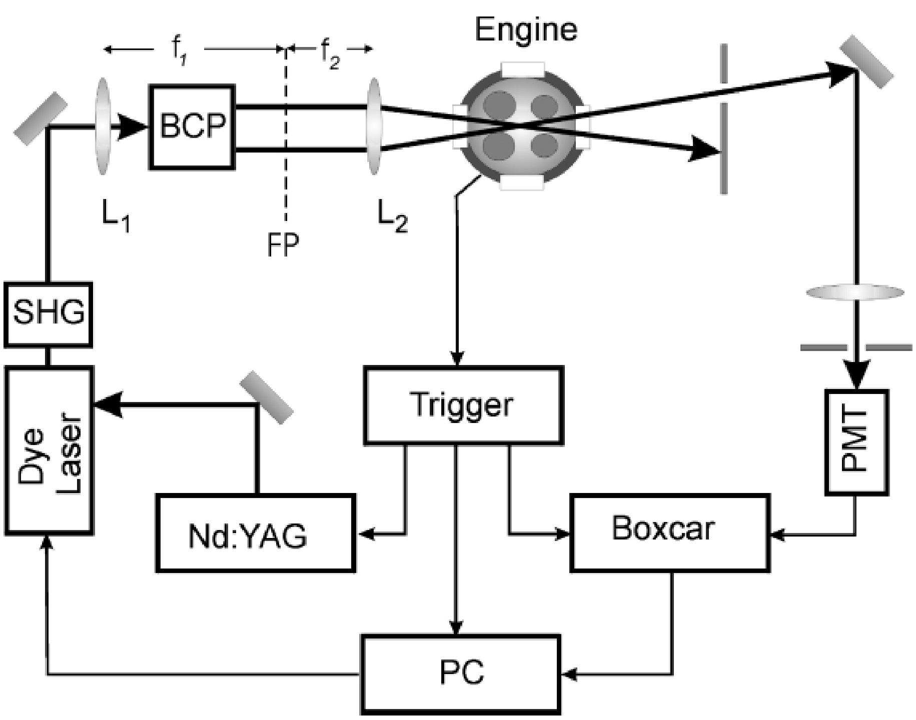

FIGURE 1 Schematic representation of the experimental layout for DFWM in the engine. *Thick lines* represent laser and signal beams and the *thin lines* indicate electrical connections. The trigger for laser firing and data acquisition is derived from the engine to ensure that the signal detected by the photomultiplier, PMT, coincides with the skip-fired cycle, processed by the boxcar averager and stored on the computer, PC. SHG represents the second harmonic generating crystal. The defocussed forward folded BOXCARS geometry is achieved using the BOXCARS plate assembly, BCP, with lenses L_1 and L_2 having focal lengths f_1 and f_2 respectively. The *dotted line* indicates the common focal plane, FP, of the lenses L_1 and L_2

incident beam axis coincided with one side of this rectangle, such that the input UV beam emerged along its original direction after traversing the other three sides of the rectangle. The fundamental beam at 452 nm emerged at an angle to this direction and was collected in a beam dump. This arrangement ensured that the beam direction was stable as the laser was tuned, as the deviation in the first two prisms was cancelled for the UV beam by the second two prisms. The wavelength of the dye laser was scanned under computer control, enabling post-averaging of the data at each wavelength step to reduce shot-to-shot signal fluctuations. These fluctuations are larger when conducting DFWM in the non-saturated regime due to the increased dependency of the signal on input beam intensity. The frequency-doubling crystal was rotated slowly by means of a micrometer-controlled rotational stage to ensure optimal phase matching as the dye laser was tuned.

The forward folded BOXCARS geometry was chosen to generate the DFWM signals since it minimises the effect of beam steering due to thermally-induced refractive index gradients. This geometry also ensures that the signal beam is spatially separated from the more intense input beams. Four parallel propagating beams of approximately equal intensity can be conveniently produced by a pair of coated parallel-sided optical plates, termed the BOXCARS plates (BCP). Transmission and reflection at the front and back faces of the first plate produces two parallel beams. Similar transmission and reflection at the orthogonally oriented second plate results in four emerging parallel beams. Two of the beams act as the pumps, a third as the probe beam and the fourth is used as an alignment beam. When the four beams pass through a converging lens propagating parallel to and displaced symmetrically about the axis of the lens, they come to a common focus and form the diagonals of a rectangular box. A simple wave-vector analysis shows that the DFWM process is then automatically phase matched. The signal beam is constrained by the phase-matching condition to follow the path of the alignment beam. In the conventional forward folded BOXCARS geometry, a lens is used to collimate the diverging signal beam. However, this collimating lens also collects light scattered from the windows, with the result that the signal-to-noise ratio is substantially reduced. Noise arising from scattered light therefore constitutes the major limitation to detecting trace concentrations of in-cylinder species.

To avoid the problem of collecting scattered light, we adopted the novel defocussed BOXCARS geometry [26]. In this arrangement, the original 226 nm laser beam is focussed by a spherical lens L_1 ($f = 1000$ mm) before entering the BCP. On exiting the BCP, the four beams are therefore focussed at each corner of a 14 mm square in the back focal plane of lens L_1. A second lens L_2, placed at its focal distance ($f = 250$ mm) from the back focal plane of L_1, collimates each of the four beams and causes them to intersect on the axis of the system in the back focal plane of L_2. Lenses L_1 and L_2 form a near-confocal telescope. The input beams are therefore crossed in the interaction region without focussing. The resulting signal beam has a very low divergence and a collimating lens is therefore not necessary. The amount of scattered light directed towards and detected by the PMT is therefore substantially reduced.

The interaction region was positioned on the central axis of the cylinder, directly below the spark plug where the hottest burnt gas and therefore the largest NO concentrations can be found [7]. An aperture was used to select a uniform section of the frequency-doubled beam at 226 nm, before it entered the BCP. The combination of lenses L_1 and L_2 reduced the beam diameter by a factor of four, resulting in a diameter of 0.8 mm in the interaction region. The beam diameter and crossing angle set by the BCP and lens L_2 provided an interaction length of approximately 14 mm. The consequent loss in spatial resolution is not a serious issue in the present work as the NO concentration is expected to be fairly uniform at the point in the cycle when the medium is probed (just after bottom dead centre). In practice, a compromise will have to be sought between spatial resolution and signal strength since the signal intensity scales with the square of the interaction length.

After propagating approximately 8 m, the signal passed through a spatial filter assembly and was detected by a PMT (Thorn EMI 9783B). The long propagation distance and the spatial filter help to further discriminate against scattered light. The output from the PMT was pre-amplified (EG & G Ortec VT120) and recorded by a boxcar averager (Stanford Research Systems SR250). A PC was used both to control the scanning of the dye laser and to collect data from the boxcar averager. The wavelength was scanned in steps of approximately 0.001 nm and six shots were acquired at each wavelength for post averaging. At a skip-fire ratio of 1:8, a spectrum was recorded in approximately 30 min.

4 Results

Initially, the DFWM signal generated from 1200 ppm NO in Argon seeded into the cylinder was used to optimise the experimental alignment. The engine was then purged, fuelled with methane and operated under conditions where the NO concentration was expected to be approximately 2000 ppm.

DFWM spectra were then recorded under different engine conditions by altering the ignition timing. All spectra were recorded at BDC in the expansion stroke where the exhaust valves were fully opened. At this point the in-cylinder pressure is approximately atmospheric and so interference from laser-induced thermal gratings is minimised [22]. The light scattered off a thermal grating follows the same direction as the DFWM signal and cannot easily be distinguished from it. This laser-induced thermal grating LITG signal, increases with increasing pressure owing to an increasing rate of collisional quenching and may eventually exceed the DFWM signal in intensity. In general it is difficult to determine the relative contributions to the detected signal from DFWM and LITGS. Previous studies have shown that at atmospheric pressure, and with the laser pulses of the duration used in the present experiments, the detected signal will be dominated by DFWM [22]. Figure 2 shows a DFWM spectrum of NO in the burnt gas for an ignition timing of 40° bTDC. For wavelengths greater than the point on the spectrum indicated by the arrow, the probe beam was blocked to eliminate the signal and reveal the very small level of background noise. The figure shows the excellent signal-to-noise ratio that has been

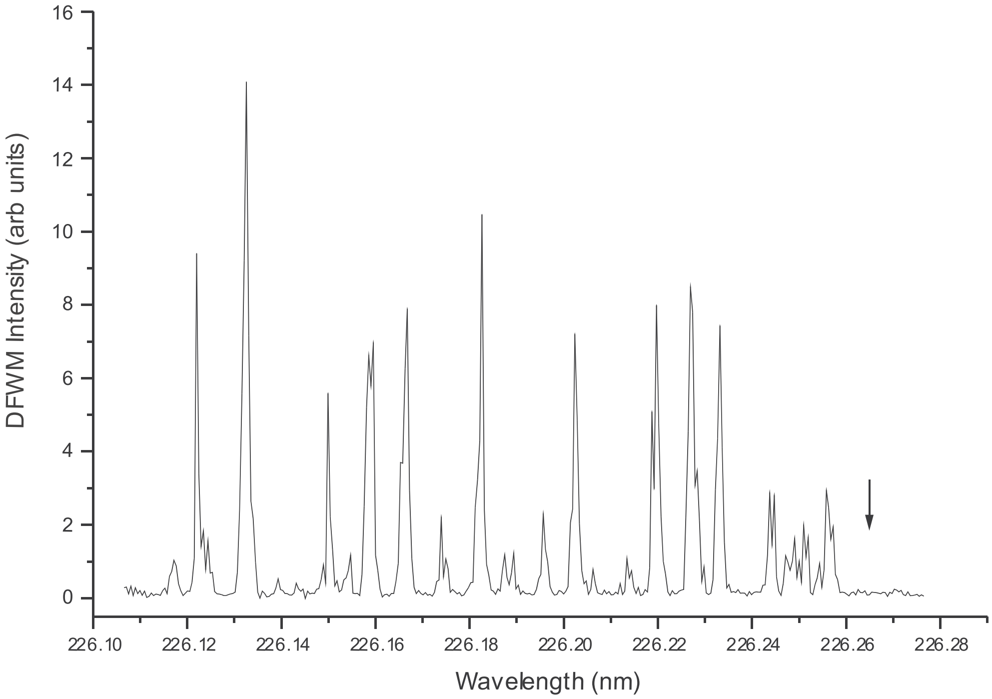

FIGURE 2 DFWM spectrum of NO recorded in the cylinder for an ignition timing of 40° bTDC. The spectrum to the right of the arrow at 226.265 nm was recorded with the probe beam blocked and indicates the level of background noise from scattered light

achieved using the defocussed forward BOXCARS geometry. Figure 3 shows a DFWM spectrum recorded when the ignition timing was changed to 30° bTDC showing differences in the relative intensity of the spectral lines. Such differences may be accounted for by a change in the in-cylinder temperature arising from the altered ignition conditions.

In principle it is possible to derive the temperature from DFWM spectra of NO. However this is not possible with the present data for several reasons. Firstly, absorption effects can distort the spectral intensities and lead to substantial errors in derived temperatures [27]. Unsaturated DFWM spectra are particularly subject to effects of absorption and unless the spectra are recorded under optically thin conditions, complex regression procedures are required to account for the systematic shift in the temperature derived from such spectra [28]. Figure 3 shows also an absorption spectrum recorded under similar engine firing conditions as obtained in the production of the DFWM spectra of Figs. 2 and 3. The line-centre absorption levels are seen to be around 20%–30% and render it difficult to derive accurate temperatures from the DFWM spectra. Secondly, cycle-by-cycle variations in both the burnt gas temperature and NO concentration prevent a meaning-

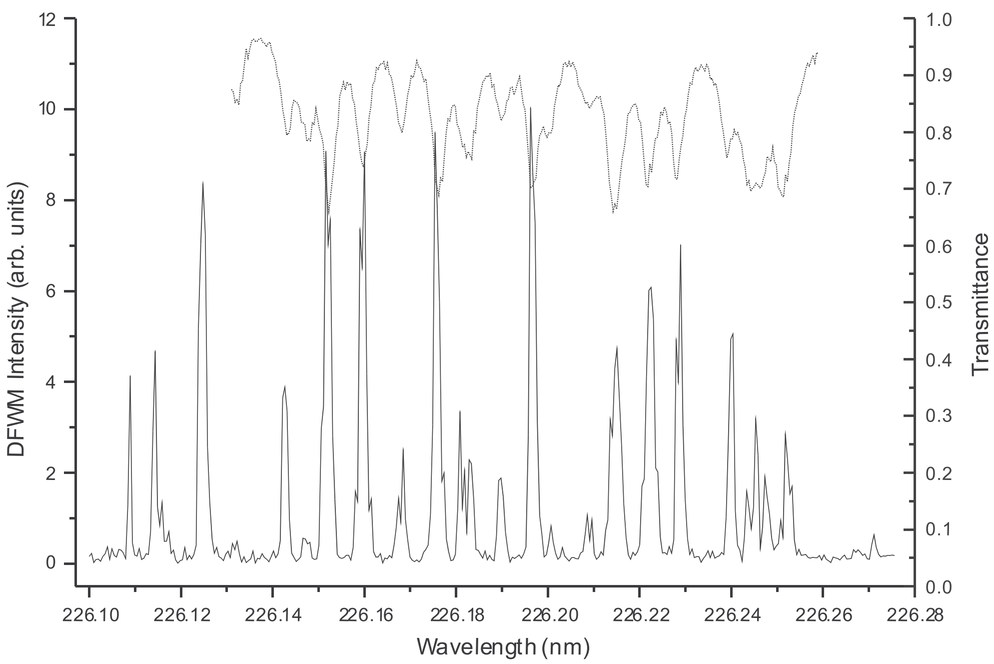

FIGURE 3 DFWM spectrum of NO recorded in the cylinder for an ignition timing of 30° bTDC. The change in relative spectral intensity of the lines from that shown in Fig. 2 indicates mostly the change in temperature arising from the changed ignition conditions. The upper trace (*dotted line*) shows an absorption spectrum recorded under similar engine conditions using an attenuated probe beam. Peak absorptions of 25% are evident at line-centres. Note the higher resolution of the DFWM spectrum relative to that recorded by absorption

ful temperature from being derived, especially considering that the spectra shown in Figs. 2 and 3 represents approximately 20,000 engine cycles. Finally, long-term drifts in laser intensity and experimental alignment further complicate the interpretation of these spectra.

The signal levels and excellent signal-to-noise ratios observed in the present work suggest that broadband DFWM could also be a viable technique. Broadband DFWM spectra provide single-shot spectra from which instantaneous temperatures can be derived. Alternatively, if the temperature is known, or relatively temperature-insensitive spectral lines are analysed, measurements of spectral intensity could yield information on cycle-by-cycle variations in relative NO concentration. In principle it may be possible ultimately to measure absolute concentrations. It is worth noting that since the spectrum of NO is more dense than that of OH, temperatures could be derived from spectra covering a smaller spectral width than is necessary in the case of OH. Thus the limitation to the bandwidth that can be generated by critically phase-matched frequency doubling is not anticipated to be a significant problem. In addition, it has been shown that the effects of absorption on broadband DFWM spectra can be minimised by operating with saturating beam intensities [29]. Thus saturated broadband DFWM of NO is a viable avenue of exploration for temporally and spatially resolved NO concentration and temperature measurements in IC engines.

Analysis of DFWM signals at points in the engine cycle where the pressure is above atmospheric will be complicated by scattering from thermal gratings which arise from collisional quenching of population gratings. It can be difficult to disentangle the relative contributions to the recorded signal from population and laser-induced thermal gratings [22]. Thermal gratings can, however, be eliminated by using orthogonally polarized pump and probe beams and such an arrangement can also help to reduce noise from scattered pump light. Calculations have shown that the loss in signal incurred by cross-polarizing the input beams may be recovered by using higher input intensity since the saturation intensity is also increased by crossing the polarization [23]. When the thermal grating signal dominates the DFWM signal it can be used to derive useful information. Previous work has shown that laser-induced thermal grating spectroscopy (LITGS) allows simultaneous single-shot measurements of temperature and pressure in high-pressure flames [30]. The present work suggests that LITGS could also be applied to in-cylinder measurements of minor species.

5 Conclusion

We have demonstrated that DFWM is a viable technique for the in-cylinder detection of combustion products in a SI engine. It should be noted, however, that in this demonstration of principle, the conditions deviate from those typical of usual engine operation. Principally, gaseous fuel (methane) has been used, resulting in less interference from soot; detection was demonstrated only at a point in the cycle where the pressure was at atmospheric level to minimize thermal grating interference and skip firing has been required to avoid thermal distortion of the optical access windows. Nonetheless we have shown how the use of the defocussed forward folded BOXCARS geometry has overcome a major limitation to DFWM arising from scattering near the interaction region.

The low signal-to-noise ratio of the recorded spectra demonstrates that useful information on NO concentrations could be obtained in a firing engine. By monitoring the intensity of a temperature-insensitive line, with the laser tuned to the line-centre, data could be obtained without the need for spectral scanning. For example, it could then be possible to investigate relative changes in NO levels as a function of engine operating conditions, residual NO levels in the engine cycle subsequent to firing, as well as cycle-by-cycle variations in NO concentration. It has been shown that residual levels can rise to 20% of the initial concentrations. [31] The technique should therefore have the sensitivity to detect residual NO under typical engine operating conditions. Future work could also investigate applications involving liquid fuels such as iso-octane/n-heptane mixtures, which more closely approximate commercial gasoline. The excellent signal-to-noise ratios obtained using DFWM will be advantageous in discriminating against background fluorescence induced in hydrocarbon species produced by these more complex fuels.

Furthermore, this demonstration of narrowband DFWM suggests that broadband DFWM techniques could also be viable for the study of trace species in IC engines. Such single-shot measurements would be useful for the study of cycle-by-cycle variations in both temperature and concentration of trace species. The optical arrangement applied in the present work will also assist in improving signal-to-noise ratio of LITG signals from engine environments. Experiments to detect LITG signals from the engine are under development in our laboratory and aim to extend the range of pressures over which NO can be detected during the cycle.

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