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On the Feasibility of CO LIF Applied to Automotive Diesel Engines

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Carbon monoxide (CO) is not only an important intermediate species in hydrocarbon combustion, but also a crucial pollutant species emitted from automotive engines. To better understand the physical processes impacting CO emissions, the development of measurement techniques that can be applied to measure in-cylinder CO distributions is desirable. Among these techniques, laser-induced fluorescence (LIF) is a sensitive, species-selective detection technique capable of good spatial resolution. However, due to the need for deep UV two-photon excitation, the severe pressure dependency of the LIF signal, and the potential interference from other species, CO LIF is not easily applied to severe combustion environments with elevated pressures, elevated turbulence levels and large numbers of intermediate species. The present study investigates the feasibility of CO LIF in a direct-injection diesel engine operating at typical pressures and temperatures and burning conventional diesel fuels. Spectroscopic analysis shows that the CO fluorescence signal can be separated from C_2 Swan band emissions when the signal is collected near 483 nm while broadband interference from other sources is small at lower pressures. The signal-to-noise ratio of CO LIF deteriorates rapidly as pressure is increased, closely following the theoretical $p^{-1.4}$ signal pressure dependency.

1. Introduction

In automotive engines, carbon monoxide (CO) is not only an important intermediate species in the combustion process, but also a toxic pollutant under increasingly stringent government regulation. CO is the last major intermediate species preceding the complete carbon combustion product, namely carbon dioxide (CO_2), and significant chemical energy is released through the chemical oxidation of CO to CO_2. Consequently, increased CO emissions indicate incomplete combustion and increased fuel consumption. Global regulations for CO emission, in addition to NOx, hydrocarbons and soot, are becoming increasingly stringent for the reasons of environmental safety and human health.

Direct measurements of the temporal and spatial distribution of CO during combustion in the automotive engines will lead to a better understanding of the physical and chemical processes impacting these emissions. The use of laser-based optical measurements have become widely used to investigate the complicated combustion processes present in automotive engines; however, the current development of laser-based measurement techniques that can be applied to measure in-cylinder CO distributions is lacking. Among the possible techniques for CO, laser-induced fluorescence (LIF) is a sensitive, species-selective detection technique capable of good spatial resolution. However, due to the need for deep UV two-photon excitation, the severe pressure dependency of the LIF signal, and the potential interference from other species, application of CO LIF to an internal combustion engine is difficult.

Despite the limited research involving the CO LIF technique applied to internal combustion engines, a significant amount of work exist chronicling CO excitation chemistry. Following initial, fundamental research investigating excited electronic states of CO [1], many studies focused on obtaining qualitative and quantitative CO spatial distribution measurements in premixed and diffusion flames [2-8]. These studies were mainly conducted under low-pressure conditions, using simple hydrocarbon fuels such as methane.

Figure 1 shows a schematic energy level diagram depicting the CO LIF excitation and emission processes employed in these studies. Some intermediate species of combustion, including CO, have very short resonant wavelengths, so that a vacuum-UV photon is needed to excite the orbital electrons of these species. Instead, excitation can also be achieved by the simultaneous absorption of two photons [9]. For CO, excitation from the ground state ($X^1\Sigma^+$) to the excited state ($B^1\Sigma^+$) is possible using two-photon excitations at wavelengths near 230 nm. Subsequently, spontaneous emission occurs during transition from the excited state to a lower energy level ($A^1\Pi$), resulting in the emission of fluorescent photons with wavelengths between 450–660 nm.

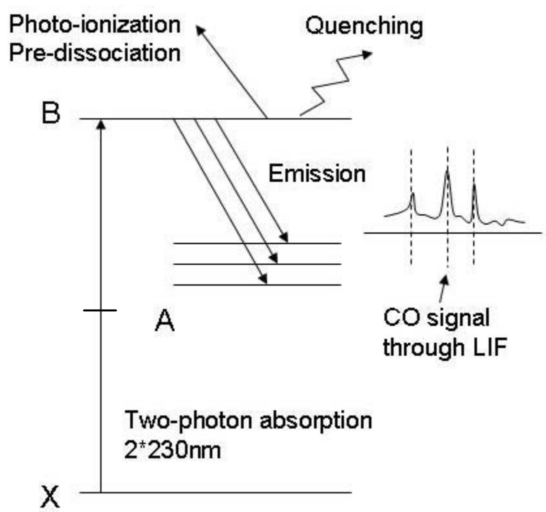


Figure 1: Schematic energy level diagram showing the two-photon CO-LIF process (redrawn from the Figure in Ref. [4]).

Several issues must be resolved prior to the application of CO LIF to automotive engines. The probability that CO will be successfully excited via the two-photon process is very low, which is a problem exacerbated at high pressures. Furthermore, not all excited molecules emit fluorescence, as much of the energy is lost through photo-ionization, pre-dissociation, and most importantly, quenching via collisions with other molecules. High laser power at 230 nm wavelength is therefore required, as well as the ability to transmit this into the cylinder without damaging optical windows. Additionally, fluorescent emissions from other species can arise, decreasing the signal-to-noise ratio.

Recently, the work by Richter et al. successfully obtained planar images of CO LIF in a specially-modified combustion chamber of a spark-ignition engine [10]. However, several issues relevant to application of CO LIF to diesel engines were not addressed — particularly those related to signal interferences and the anticipated signal loss at the elevated pressures characteristic of diesel engines.

Therefore, the study is intended to investigate those issues applying CO LIF technique to diesel engine operated under LTC regime [11]. To investigate the pressure dependence of the CO LIF intensity, the technique was applied to an optically-accessible automotive diesel engine operating at a motored condition (no fuel injection), wherein CO was added to the intake stream. Potential sources of interferences from C_2 Swan bands and broadband PAH fluorescence were subsequently investigated under fired operation using a conventional diesel fuel.

2. Experimental setup

The experimental setup was designed to permit identification of the excitation wavelength yielding the maximum CO LIF signal, to characterize the pressure dependence of the signal, and to allow investigation of signal interferences under a typical diesel operating condition. Figure 2 depicts a schematic of the setup employed.

The excitation wavelength is identified by removing mirror A, such that the laser beam passes over a laminar, burner-stabilized, rich methane/air flame (Figure 2(a)). The beam is supplied by an Nd:YAG laser source (Spectra-Physics, Quanta-Ray PRO 270) coupled to an optical parametric oscillator (Spectra-Physics, Quanta-Ray MOPO 730) equipped with an integral frequency doubler (Spectra-Physics, Quanta-Ray FDO-970). The system provided approximately 4–5 mJ of excitation radiation over an excitation scan ranging from approximately 229.9 to 230.1 nm, with an estimated linewidth of less than 0.3 cm^{-1}. A beam splitter sends 10% of the beam energy to a pyroelectric detector (Coherent, J4-09) which provides a measure of the energy in each laser pulse. For each excitation wavelength, fluorescent emissions from CO generated in the flame are collected, spectrally-filtered and imaged onto the photocathode of a photo-multiplier tube (PMT, Hamamatsu H6780-06). The optical band-pass filter employed was characterized by a center wavelength of 486.1 nm, and a FWHM of 10 nm. The PMT signal is gated and integrated over a period of approximately 50 ns using a boxcar integrator (Stanford Research Systems, SR-250).

For investigations of the signal pressure dependence and interferences, Mirror A is replaced and the excitation beam is provided to the cylinder of an optically-accessible engine (Figure 2(b)). The beam is focused by a spherical lens to an estimated waist size of approximately 0.028 mm, and traverses the cylinder approximately 10 mm below the head. Quartz windows in the upper cylinder liner allow for beam access and collection of the resulting fluorescence. The laser is set to the excitation wavelength providing the maximum LIF signal identified in the burner excitation scans. Fluorescence excited from a portion of the beam is collected and focused onto the entrance slit of an imaging spectrograph (SPEX 270M) with an intensified CCD camera (Princeton Instruments ICCD-576-E) mounted in the exit plane. The entrance slit width of 8 mm both determines the length of the measurement volume and the spectral resolution in the exit plane of the spectrograph (≈ 6 nm/mm). The spectrograph grating is held fixed, such that the fluorescent emission spectrum is measured over a wavelength range from 440–540 nm.

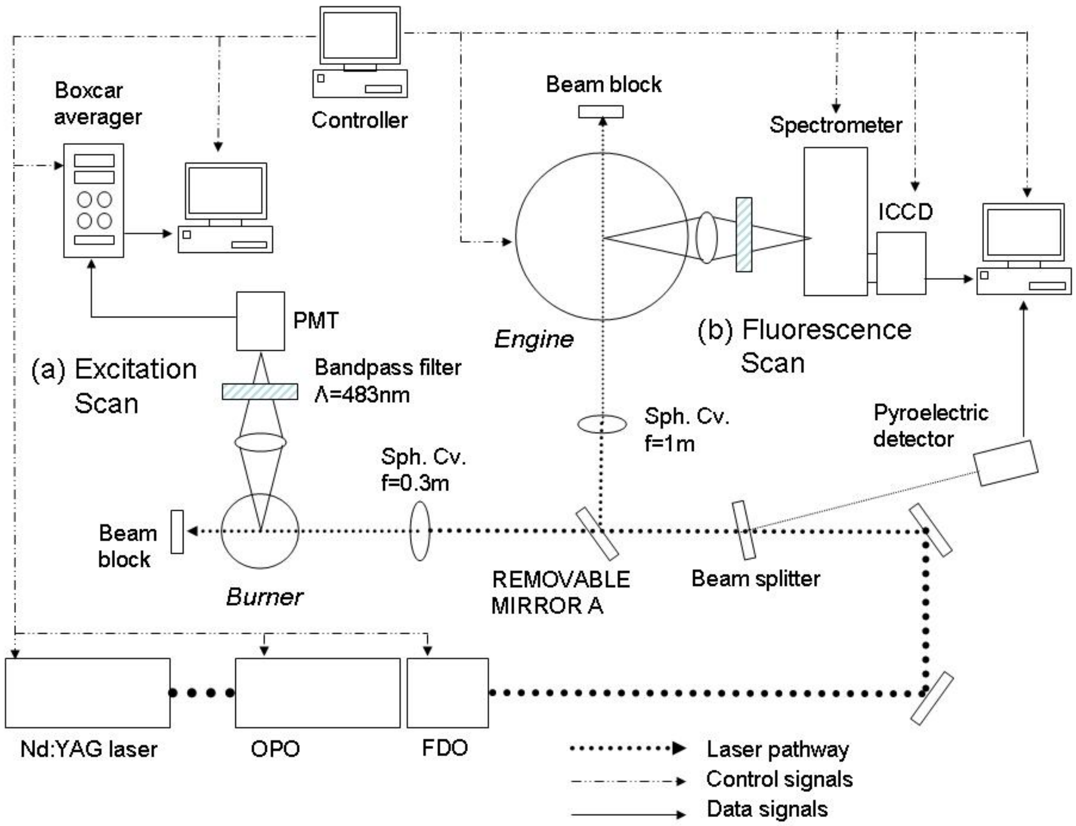


Figure 2. Schematic diagram of (a) the experimental setup used to perform excitation scans, and (b) the set-up used to investigate the emissions spectra and the signal pressure dependence.

Investigations of the signal pressure dependency are conducted with CO seeded into the intake flow at a concentration of 3000 ppm under motored engine condition. The engine is instrumented with a piezoelectric pressure transducer, such that the cylinder pressure is known at the crank angle of the LIF measurements. LIF signals are captured at crank angles corresponding to cylinder pressures ranging from 150–1000 kPa. Interferences are studied with the engine operated skip-fired, with fuel injection occurring on one of every 4 cycles. At a load of 3 bar IMEP and an O_2 mole fraction of 10%, the CO mole fraction in the engine exhaust is approximately 1%. Summarized specifications of the engine and fuel injection equipment are provided in Table 1, while the operating conditions are summarized in Table 2. Intake flowrate is equivalent to the conditions of part load operation with 75% EGR under LTC regime [11].

Table 1. Specifications of test engine

Geometry			
Bore			82.0 [mm]
Stroke			90.4 [mm]
Displacement volume			447 [cm^3]
Geometric CR			16.7
Squish height			0.78 [mm]
Swirl ratio			2.2
Valve events			
IVO	ATDC 1	EVO	BBDC 48
IVC	ABDC 28	EVC	BTDC 0
Fuel injector			
Number of holes			7
Included angle			149^o
Sac volume			0.12 [mm^3]
Nozzle hole diameter			0.14 [mm]
Injection pressure			860 [bar]
Bosch flow number			440 cm^3/30 s @ 100 bar
fuel			#2 Diesel

Table 2. Experimental conditions

Operating conditions					
Engine speed					1500 [rpm]
Intake temperature					97.1 [^oC]
Intake pressure					1.5 [bar]
IMEP (When fired)					3 [bar]
Intake gas flowrate [g/s]					
Air	4.113	N_2	3.588	CO_2	1.235
CO supply in motored cycles					3000 [ppm]
Injection timing in fired cycles					BTDC 26.6

3. Results and discussions

Figure 3 shows the experimental results of an excitation scan. The LIF signal, laser power and the ratio of signal-to-laser power are plotted against excitation wavelength. The average laser energy was 4.1 mJ with a standard deviation of 0.2 mJ. Hence, the power varied little over the investigated wavelength range as well as the LIF signal was normalized by the laser power. For wavelengths less than 230 nm the LIF signal remained almost zero, and began a rapid increase at 230.00 nm to a maximum at 230.041 nm. As the wavelength increased further, the signal decreased rapidly and was nearly zero again at 230.05 nm. LIF signals in the engine were therefore measured with the wavelength tuned to 230.041 nm ("on-line" measurements), while background emissions were measured by tuning the laser to a wavelength of 229.991 nm ("off-line" measurements).

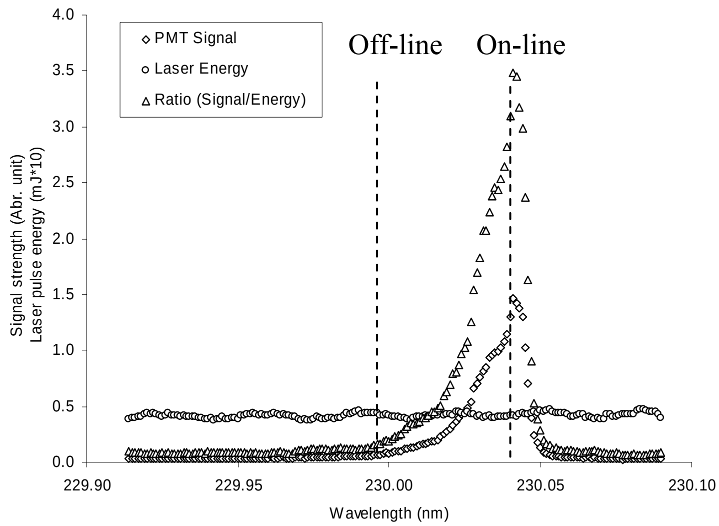


Figure 3. Excitation scan: Fluorescence signal strength variation with wavelength

Figure 4 indicates the fluorescence emission spectra measured under on-line and off-line conditions at a cylinder pressure of 150 kPa. When offline excitation was applied the background intensity was very low over the full wavelength range investigated, except near 470 nm and 515 nm. As will be seen below, these wavelengths correspond to prominent features in the C_2 emission spectrum. For on-line excitation, three additional strong features were observed at wavelengths of 450 nm, 483 nm and 518 nm. The latter two features exhibit the greatest signal level. As will be seen below, the CO LIF signal near 483 nm was advantageous for avoiding C_2 interferences, and was thus selected for evaluating the impact of pressure in the signal level.

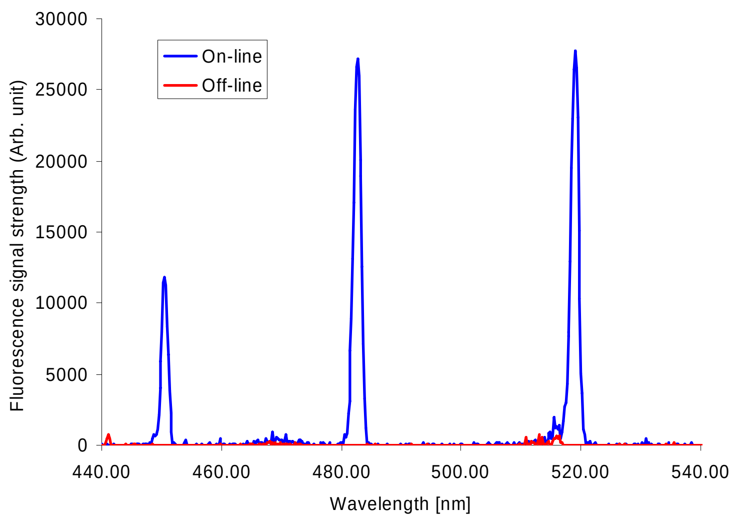


Figure 4. CO fluorescence spectrum from on-line and off-line excitation wavelength under motored, lower cylinder pressure (150kPa) conditions

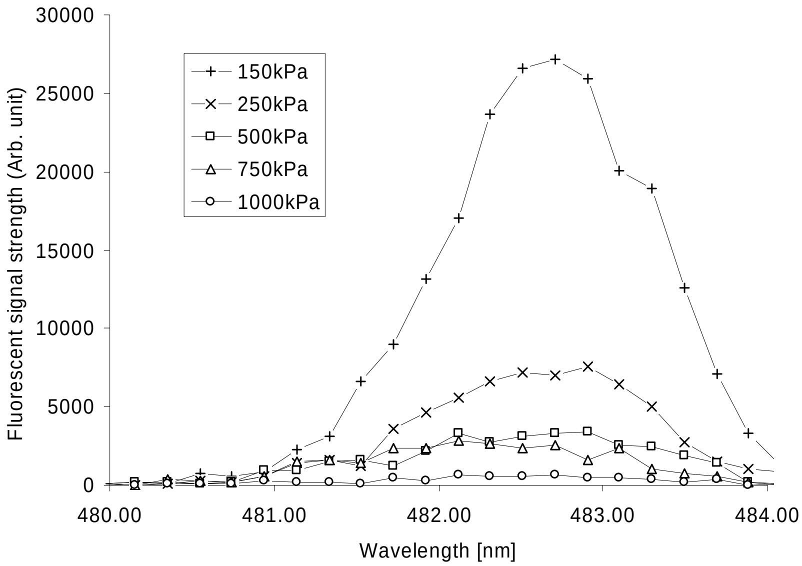


Figure 5. On-line CO fluorescence spectra obtained near 483.0 nm under motored, various cylinder pressure conditions

Figure 5 depicts the fluorescent signal strength near 483 nm for various ambient pressures. An increase in pressure results in a significant reduction in signal strength. The various factors that influence the pressure dependency of the LIF signal are discussed extensively in [9], and are summarized in the following discussion.

The fluorescent signal strength is proportional to the number density of chemical species (N_1^0), excitation rate constant (W_{12}) and fluorescence efficiency (η_F).

$$F \propto \eta_F \times W_{12} \times N_1^0 \tag{1}$$

For two-photon LIF, the excitation rate constant is written as

$$W_{12} \propto \frac{\alpha_{12}}{h\nu}\left[I_\nu^0 \int_\nu L(\nu) g(\nu) d\nu \right]^2 \tag{2}$$

where α_{12} represents the two-photon absorption cross-section, h is Planck's constant, and ν is the excitation wavelength. The normalized laser irradiance I_ν^0 is moderated by an integral characterizing the overlap of the laser lineshape *L(ν)* and the pressure broadening lineshape function *g(ν)*. Effect of pressure on the integral is calculated under assumptions that *L(ν)* has Gaussian distribution and *g(ν)* has Lorentzian distribution [9].

$$g(\nu) = \frac{\Delta\nu_c}{2\pi} \frac{1}{(\nu - \nu_0)^2 + (\Delta\nu_c/2)^2} . \tag{3}$$

Figure 6(a) shows that the calculated integral value is proportional to $P^{-0.7}$. Due to the I_ν^2 dependence of W_{12}, changes in the magnitude of this overlap integral can greatly affect the excitation rate. Therefore, the effect of pressure on W_{12} is estimated as $W_{12} \propto P^{-1.4}$.

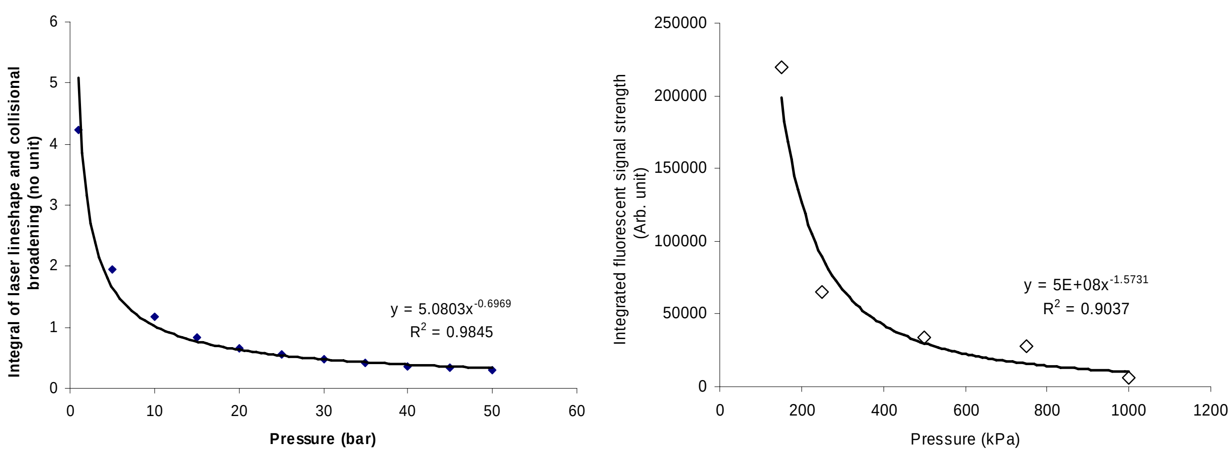
The fluorescence efficiency η_F is the ratio of the number of fluorescent molecules (A) to the total number of excited molecules. An excited molecule fails to emit fluorescence mainly due to the energy loss from collisional quenching. The number of quenched molecules Q is generally much greater than A, and is directly proportional to the number density N_i of the quenching partner. Thus, at fixed composition, the fluorescence efficiency is inversely related to the total molecular number density N and hence pressure:

$$\eta_F \propto \frac{A}{A+Q} \approx \frac{1}{Q} \propto \frac{1}{N} \propto \frac{1}{P} \tag{4}$$

Finally, if it is assumed that the ground state number density of the species being detected is proportional to pressure, the LIF signal strength can be expected to decrease strongly with pressure:

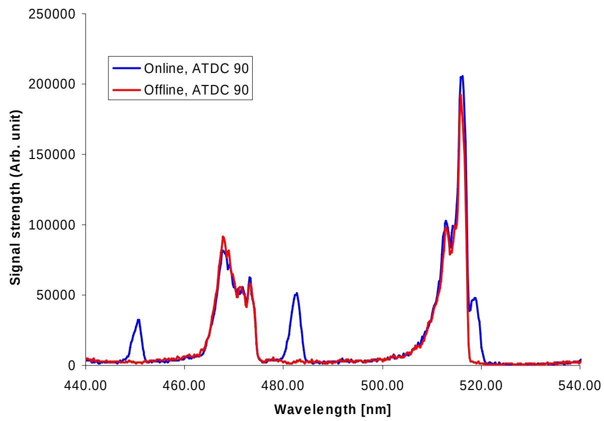
$$F \propto P^{-1.4} \tag{5}$$

Figure 6 (b) indicates the integrated signal strength from Figure 5 for various pressures. A curve fit calculation showed that the signal strength is proportional to $P^{-1.57}$. The higher than expected pressure dependency is due primarily to the high-pressure limit employed to approximate the pressure dependency of the overlap integral. Despite this difference, the simple model described is useful to understand how pressure affects the LIF signal magnitude. Our future work will evaluate the pressure dependency more quantitatively, as well as the temperature and composition dependency introduced by the various possible quenching partners. With this knowledge the potential for obtaining quantitative CO measurements can be assessed.

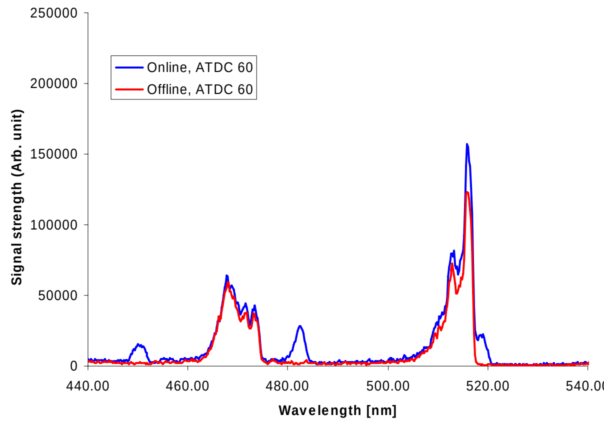


(a) Theoretical : $\int_{\nu} L(\nu)g(\nu)d\nu \propto P^{-0.7}$ (b) Experimental : $F \propto P^{-1.57}$

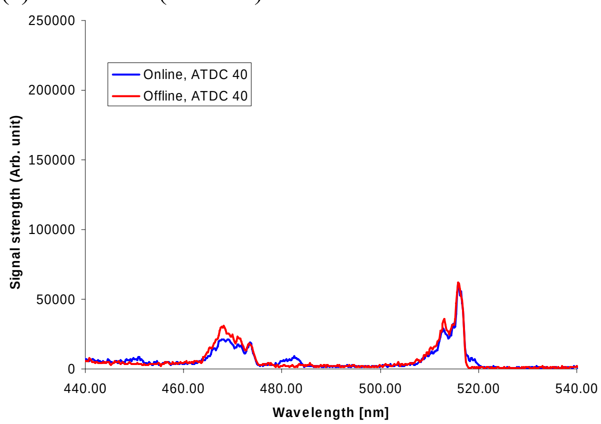
Figure 6. Relation between LIF signal strength and cylinder pressure



(a) ATDC 90^o (4.18 bar)



(b) ATDC 60^o (8.47 bar)



(c) ATDC 40^o (17.45 bar)

Figure 7. CO fluorescence spectrum from on-line and off-line excitation under fired conditions

Signal interferences are investigated by examining the fluorescent emission spectra obtained in a fired mode. Figure 7 depicts on-line and off-line spectra for crank angles of 90^o, 60^o and 40^o after top dead center (ATDC) during fired cycles. Measured pressure at each crank angle was 4.18, 8.47 and 17.45 bar, respectively. With fuel injection and combustion, both fuel molecules and intermediate species affect the fluorescent spectra. Figure 7 shows two strong signal bands from 464–476 nm and 500–520 nm which are due to C_2 Swan band emissions [1]. These spectral features were also presented in Figure 4. It is also noticeable that a very weak broadband signal exists in both the on-line and off-line spectra, likely due in part to broadband emissions from PAHs. Note that the three CO LIF spectral features seen in Figure 4 can also be clearly identified in Figure 7. Despite the strong magnitude of the feature near 518 nm, significant C_2 interference exists in this spectral range. Although the CO signal near 450 nm is free of C_2 interference, its strength is less than the signal near 483 nm. Therefore, fluorescence from 483 nm spectral band will be a good candidate for measuring CO without interference of signals from other species. The same pressure dependency of signal strength observed in Figure 6 can also be derived from Figure 7, though spatial variations in CO mole fraction that may occur in the fired mode make this evaluation less quantitative.

4. Concluding Remarks

This study focuses on the feasibility of applying the CO LIF technique to an automotive diesel engine operating under high pressure conditions. The major findings of this study are summarized as follows:

- Direct measurement of CO LIF in a direct-injection diesel engine operating at typical pressures and temperatures with conventional diesel fuels has been proven feasible. Measurements of CO fluorescence were possible under pressurized in-cylinder conditions and the interference from Swan band or broadband PAH emission was avoided with appropriate filtering.

- Excitation scans using a methane/air burner was helpful to determine critical excitation wavelength of CO.

- The LIF signal was strongly dependent on ambient pressure. A simplified model indicated that the LIF signal would be proportional to $P^{-1.4}$, with experiments showing $F \propto P^{-1.57}$. The development of specified model is expected to be helpful for analyses of CO concentration or distribution with CO LIF under high pressure operating conditions.

- CO fluorescence was detected near wavelengths of 450nm, 483nm, and 518nm, with the signal near 483nm being identified as the critical fluorescence wavelength at which interference from other species could be avoided under fired operation of a direct-injection diesel engine.

Acknowledgments

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