Cavity-Enhanced Absorption Sensor for Carbon Monoxide in a Rapid Compression Machine

Ehson F. Nasir[1], Aamir Farooq*[1]

[1] King Abdullah University of Science and Technology, Clean Combustion Research Center, Physical Sciences and Engineering Division, Thuwal, 23955-6900, Saudi Arabia

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*Corresponding Author: aamir.farooq@kaust.edu.sa

Clean Combustion Research Center

King Abdullah University of Science and Technology (KAUST)

Thuwal, 23955-6900, Saudi Arabia

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Abstract

A sensor based on cavity-enhanced absorption spectroscopy (CEAS) was implemented for the first time in a rapid compression machine (RCM) for carbon monoxide concentration measurements. The sensor consisted of a pulsed quantum cascade laser (QCL) coupled to a low-finesse cavity in the RCM using an off-axis alignment. The QCL was tuned near 4.89 μm to probe the P(23) ro-vibrational line of CO. The pulsed mode operation resulted in rapid frequency down-chirp (6.52 $cm^{-1}/\mu s$) within the pulse as well as a high time resolution (10 μs). The combination of rapid frequency down-chirp and off-axis cavity alignment enabled a near complete suppression of the cavity coupling noise. A CEAS gain factor of 133 was demonstrated in experiments, resulting in a much lower noise-equivalent detection limit than a single-pass arrangement. The sensor thus presents many opportunities for measuring CO formation at low temperatures and for studying kinetics using dilute reactive environments; one such application is demonstrated in this work using dilute n-heptane/air mixtures in the RCM. The formation of CO during first-stage ignition of n-heptane was measured over 802 – 899 K at a nominal pressure of 10 bar. These conditions correspond to the NTC region of n-heptane and such results provide useful metrics to test and compare the predictions of low-temperature heat release by different kinetic models.

Keywords: *Rapid compression machine; Cavity-enhanced absorption spectroscopy; Carbon monoxide; Low-temperature heat release; n-heptane.*

1. Introduction

The auto-ignition behavior of hydrocarbon fuels is determined by chemical processes that are temperature-specific. For the intermediate temperature range (700 – 900 K), certain classes of hydrocarbons, such as paraffins, exhibit two stages of heat release during their oxidation, with the first stage often referred to as low-temperature heat release (LTHR). Several previous works have shown that LTHR is primarily sensitive to reactions involving fuel radicals and is thus fuel-specific. Consequently, low-temperature oxidation is more challenging to model than high-temperature chemistry which is controlled by smaller radical species [1, 2]. Moreover, LTHR can influence overall ignition and this property can be leveraged to increase knock resistance in SI engines [3] or to control the heat release rate in HCCI engines [4].

Rapid compression machines (RCM) have been important tools in studying LTHR and the kinetics of low-temperature ignition [5]. RCMs offer an operating range of temperatures that cover both the low and intermediate temperature range (600 – 900 K) as well as high pressures encountered in practical combustion systems (10 – 40 bar). RCMs also provide much longer test times than shock tubes (5 – 100 ms) and, therefore, ignition delay times, measured using pressure traces in RCMs, are typically used for validating low-temperature kinetic models. However, ignition delay times provide a global view of the overall ignition process; time-resolved laser diagnostics can offer a much deeper insight into the kinetics through measured species concentration and/or temperature profiles.

Semiconductor lasers, particularly quantum cascade lasers (QCLs) in the mid-infrared wavelength region, have been successfully used for sensitive, time-resolved species concentration measurements, based on laser absorption spectroscopy, in transient reactors such as shock tubes [6, 7]. In RCMs, however, limited studies exist in the literature on applications of semiconductor laser absorption diagnostics. Early

applications were demonstrated by Sung and co-workers [8, 9] for measuring H_2O concentration using a mid-infrared QCL, though their sensor lacked sufficient time resolution. A previous publication by the authors of the current work made use of intrapulse absorption with pulsed QCLs for time-resolved temperature measurements in an RCM [10]. The intrapulse technique offered significant benefits over previous QCL implementations in terms of both high time resolution and large spectral tuning range. More recently, Werblinski et al. have demonstrated high time-resolution (50 – 100 μs) measurements of H_2O concentration in an RCM using a near-infrared supercontinuum laser source [11, 12].

Laser absorption measurements are path-averaged in nature and, therefore, work best in homogeneous gas environments. Reactor configurations for creating ideal constant volume conditions, such as shock tubes and RCMs, are designed to achieve homogeneous environments in order to reduce sensitivity of chemical processes to transport phenomena. RCMs attempt to suppress thermal boundary layer mixing with the core gas via the use of crevices, though thermal gradients can still arise due to first-stage ignition [13] or due to certain conditions promoting pre-ignition [14]. The use of highly dilute reactive mixtures can greatly reduce heat release and ensure a homogeneous temperature field is maintained. Such mixtures require sensors of higher sensitivity than conventional laser absorption diagnostics. One method of increasing the sensitivity of laser absorption spectroscopy has been to increase the path length of measurement via cavity enhancement. A specific cavity technique, known as cavity-enhanced absorption spectroscopy (CEAS), has been successfully demonstrated by Hanson and co-workers in recent shock tube studies for several species [15, 16].

In this work, we have demonstrated the use of a sensor based on CEAS for measuring CO concentration in the RCM. The CEAS sensor enabled us to achieve a much lower detection limit than would have been possible with a conventional single-pass technique using the same absorption transition. The improved

sensitivity allowed for the investigation of first-stage ignition kinetics of n-heptane using diluted reactant mixtures. The dilution of fuel suppressed first-stage heat release and thus the adiabatic core assumption remained valid after the first-stage ignition. This is the first reported application of the CEAS technique in an RCM and the results highlight the potential of the technique in other RCM experiments involving highly dilute reactant mixtures and for measuring radicals / trace species.

2. CEAS principles

For conventional laser absorption spectroscopy, absorption of spectrally narrow light is related to gas properties *via* the Beer-Lambert relation:

$$\ln (I_0 / I_t) = A_{SP} = (SPXL\Phi_v) \quad (1)$$

In this relation, A_{SP} is the absorbance for a single-pass arrangement which is directly proportional to the mole fraction X of the absorbing species. The goal of any absorption experiment is to maximize the absorption signal (I_0 / I_t) for a given X. The line-strength S and line-shape function Φ_v are specific to a particular molecular absorption transition and, therefore, for a given absorption transition and experimental gas conditions (T, P, X), the only possibility for increasing the absorption signal is to increase the path length L. An optical cavity, made of two parallel concave mirrors, accomplishes this through multiple reflections. In such a cavity, the absorbance will be defined as A_{CEAS}, where:

$$\ln (I_0 / I_t) = A_{CEAS} = \ln (1 + GA_{SP}) \quad (2)$$

provided that $A_{SP} << 1$ [16, 17]. The term G refers to the gain factor of the cavity and is related to the reflectivity R of the mirrors through the following relation:

$$G = 1/(1 - R) \quad (3)$$

While the cavity gain only depends on the mirror reflectivity, the signal-to-noise ratio (SNR) is also dependent on how well the laser beam couples with the resonant modes of the cavity. For an optical cavity, the free spectral range (FSR) determines the spectral spacing between resonant cavity modes:

$$\mathrm{FSR} = 1 / 2nL \text{ (in cm}^{-1}\text{ units)} \quad (4)$$

where n is the refractive index of the medium. Effective coupling requires matching the laser emission mode with at least one cavity mode. If the laser line-width is narrower than the cavity FSR, spurious mode-matching can be achieved through off-axis alignment, as described by Engel et al. [18]. Off-axis alignment results in a Lissajous spot pattern on the cavity mirrors [19] and the effective cavity FSR is reduced by the number of non-overlapping spots, thus increasing the likelihood of resonance between cavity modes and a narrow line-width laser. A necessary requirement for off-axis alignment is to use a cavity made of concave mirrors such that the cavity length is much smaller than the focal length of the mirrors. Additionally, Sun et al. [16] showed that the cavity noise can be suppressed further by a rapid scan of the laser frequency, further increasing the likelihood of spurious mode-matching.

3. Sensor implementation

The measurement target of the CEAS sensor in this work is carbon monoxide due its relevance to LTHR, as described by Tekawade et al. [20]. A pulsed distributed feedback (DFB) QCL system sourced from Alpes Lasers, was used to probe the P(23) ro-vibrational transition of CO near 2046.28 cm^{-1} (4.887 μm). A detailed description of the laser system can be found in a previous publication [10]. Relevant spectroscopic parameters needed to convert the single-pass absorbance to mole fraction were taken from the HITRAN 2016 database [21].

In this work, the CEAS technique was implemented on the KAUST RCM facility. While relevant details are mentioned here, further information about the facility can be found elsewhere [10, 22, 23]. The optical cavity was formed by installing highly reflective concave mirrors (sourced from Rocky Mountain Instrument Co.) on the centrally located ports of the RCM combustion chamber. The RCM has an internal diameter of 5.08 cm, which serves as the single-pass path length, resulting in a cavity FSR of 0.0984 cm^{-}

[1]. The cavity mirrors had a manufacturer-specified reflectivity of 99.5 ± 0.2% at 4.887 μm and a radius of curvature of -1 m. The QCL was aligned in an off-axis arrangement to produce a small ellipsoidal spot pattern on the cavity mirrors. The light was collected on the receiving end using an aspheric ZnSe lens (focal length 12.7 mm), as shown in Fig. 1, and focused on a high bandwidth (500 MHz) HgCdTe detector from Vigo System (1 mm^2 active area). The detector signal was acquired by an oscilloscope at 100 MHz sampling rate.

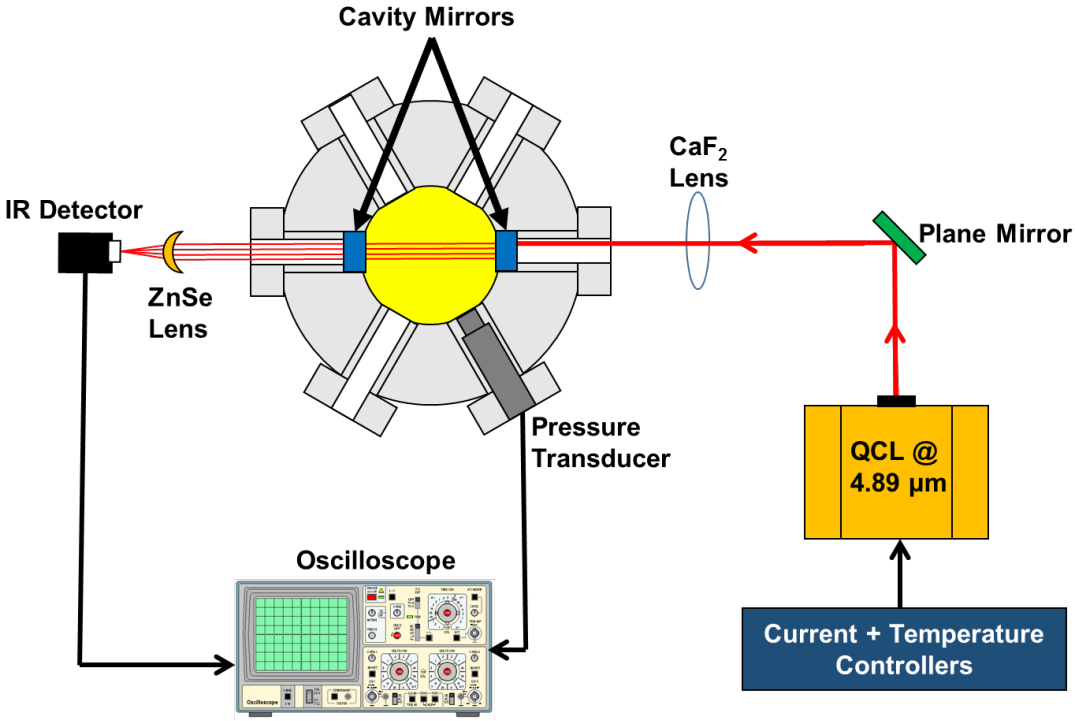

Fig. 1. Schematic of the laser sensor aligned through the cross-section of the RCM combustion chamber.

The QCL was operated in pulsed mode with a pulse repetition frequency of 100 kHz and a pulse duration of 500 ns, resulting in an effective time resolution of 10 μs. Upon examination with a Germanium etalon, the intrapulse spectral tuning range was found to be 3.26 cm^{-1}. The average frequency scan rate of 6.52 $cm^{-1}/\mu s$ in this case is two orders of magnitude higher than that reported by Sun et al. [16] using injection current scanning with a cw-QCL. The extremely rapid scan rate combined with an off-axis alignment resulted in an almost complete suppression of cavity coupling noise, as illustrated in Fig. 2.

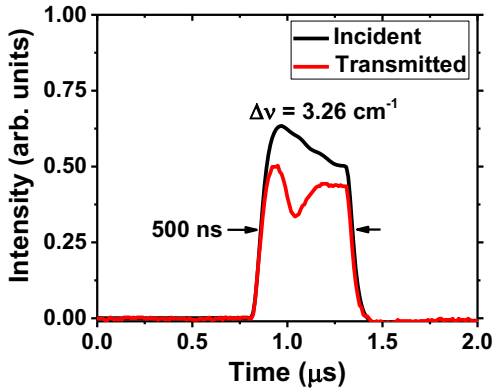

Fig. 2. Representative laser intensity signal showing absorption by CO in the transmitted trace. Conditions: 100 ppm CO/N_2, 796 K, 10.5 bar.

The uncertainty specified by the manufacturer on the mirror reflectivity (± 0.2%) can translate into a large uncertainty in the gain factor (143 – 333). Significant deviations from the manufacturer-specified reflectivity can occur [17]. Therefore, to determine the actual mirror reflectivity and to reduce the uncertainty, the CEAS sensor was tested against known mixtures of CO/N_2 at high pressures (> 5 bar) for both ambient temperature as well as higher temperature conditions in the RCM. Using the measured peak CEAS absorbance (A_{CEAS}) and the calculated peak single-pass absorbance (A_{SP}) using HITRAN parameters, the reflectivity can be ascertained through Eqs. 2 and 3. The mirror reflectivity from these experiments was found to be 99.25 ± 0.04%, which translates to a gain factor of 133 ± 8. The gain was not found to be significantly affected by the compression process despite low-frequency intensity fluctuations in the laser signal due to mechanical vibrations. Measurement of mirror reflectivity results in a factor of five reduction in the uncertainty compared to the manufacturer specification. The gain factor can then be used to establish a new detection limit for CO measurements based on a fixed absorbance. Figure 3 shows a comparison between the detection limit offered by a single-pass arrangement and that provided by a CEAS arrangement for typical RCM operating conditions (10 bar, 700 – 900 K). It is clear that the CEAS technique provides a substantial improvement in detection limit and hence SNR. As an

example, at 800 K the CEAS detection limit (2.4 ppm) is 63 times lower than the single-pass detection limit (151 ppm).

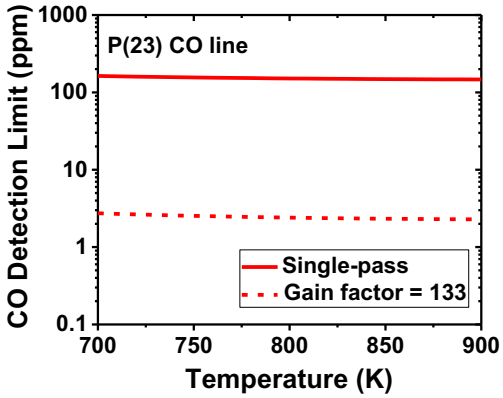

Fig. 3. Comparison of detection limit for single-pass and CEAS (with gain factor of 133). Calculated with HITRAN parameters [21] at 10 bar total pressure and assuming minimum-detectable-absorbance of 0.01.

4. RCM experiments with n-heptane

The CEAS sensor was applied to RCM experiments involving the oxidation of lean n-heptane/air mixtures. n-Heptane is a highly reactive fuel, defined to have zero octane number, and therefore ignition delay studies of n-heptane in an RCM require tailored experimental conditions such that the ignition delay time is in a measurable range. For RCM experiments on fuels depicting two-stage ignition behavior, it is preferable to have at least a 5 ms delay between the end-of-compression (EOC) and first-stage ignition to avoid significant chemical activity during the compression phase. Moreover, Mittal et al. [13] showed that in the event of significant LTHR, the increasingly energetic core gas could compress the cold boundary layer and expand into the crevice region, resulting in a lower post-ignition temperature than predicted using the adiabatic core assumption. This was recently confirmed through *in situ* laser-based temperature measurements in the KAUST RCM [10]. In light of these considerations, experimental conditions were chosen such that LTHR would be significantly reduced and first-stage ignition delay would be lengthened beyond 5 ms. A mixture of n-heptane, oxygen and nitrogen at equivalence ratio of 0.5 was used, where

187 the n-heptane mole fraction was kept at 0.2% as opposed to nearly 1% for an undiluted mixture. A
188 temperature range of ~ 800 – 900 K was covered at a nominal pressure of 10 bar; these conditions
189 correspond to the NTC region of n-heptane.

190 Figure 4 shows experimental results for a specific n-heptane oxidation case at 802 K and 10.4 bar. The
191 large rise in CO absorbance near 13 ms marks first-stage ignition, while second-stage ignition is not
192 observed for this highly dilute reactive mixture. The measured pressure trace in Fig. 4 provides no
193 indication of a pressure rise associated with LTHR near 13 ms (a comparison with non-reactive pressure
194 profiles is provided in Figs. S1 and S2), in contrast with our previous work with undiluted n-pentane
195 mixtures in which the onset of 1st stage ignition was clearly discerned from the pressure rise [10]. Thus,
196 in these diluted n-heptane experiments, heat release (LTHR) at the onset of first-stage ignition is negligibly
197 small and the gas mixture can be considered isentropic up to, and beyond, EOC. Based on the adiabatic
198 core assumption [5], the temperature in RCM experiments is normally inferred from the measured pressure
199 trace by using the isentropic relation:

200 $$\int_{T_I}^{T} \frac{\gamma}{\gamma-1} \frac{\mathrm{d}T}{T} = \ln\left(\frac{P}{P_I}\right) \tag{5}$$

201 The subscript *I* in this relation refers to the initial conditions prior to compression. Given the dilute fuel
202 concentration in our case as well as the observation that the mixture does not reach 2nd stage ignition (an
203 indication that most of the initial fuel remains unconsumed), for the purpose of calculating thermodynamic
204 parameters for Eq. 5, the initial reactant mixture composition (dominated by nitrogen) is used for the
205 temperature profile beyond EOC. For experiments in this work, temperature profile calculated from Eq. 5
206 was used for spectroscopic parameters in the Beer-Lambert relation.

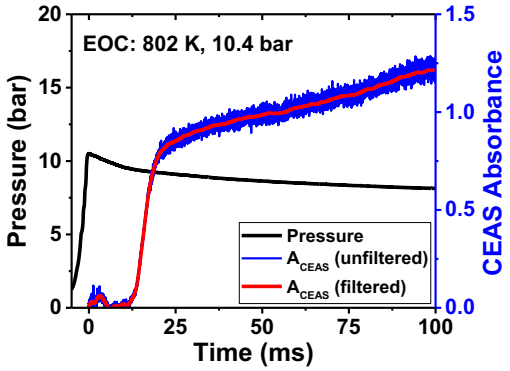

Fig. 4. Representative measured CEAS absorbance and pressure traces. EOC conditions: 802 K, 10.4 bar. Initial composition: 0.2% n-heptane/4.4% O_2/95.4% N_2 (ϕ = 0.5).

For the purpose of determining CO mole fraction, only the peak CEAS absorbance was used for each laser pulse. Using the measured CEAS absorbance and gain factor, the single pass absorbance can be determined from Eq. 2, which in turn is used in Eq. 1 for computing the CO mole fraction. The unfiltered CEAS absorbance plot in Fig. 4 exhibits high-frequency noise that can be attributed to a combination of sampling bit noise and pulse-to-pulse intensity variation. The filtered trace in Fig. 4 is a result of applying a 2 kHz low-pass filter during post-processing. A small deviation in the laser signal (beam steering) occurs near EOC due to the effect of mechanical vibration on the laser alignment. The CEAS absorbance plot presented here has been corrected for a small background (interference) absorption by n-heptane. This background was determined by the average absorbance between EOC and first-stage ignition. The background was found to be similar for various conditions and since complete fuel conversion is not expected to occur at such dilute conditions, the background can be assumed to remain nearly constant during the experiment.

Figure 5 shows measured carbon monoxide mole fraction traces, calculated from the filtered CEAS absorbance profiles, at four different EOC temperatures. The rise of CO formation in all cases denotes the onset of LTHR. Since these conditions lie in the NTC region of n-heptane, the first-stage ignition delay is

expected to increase with temperature, which is substantiated by an observed decrease in measured CO formation rate with increasing temperature. Despite the potential for beam steering effects from flow or mechanical perturbations over a time window of ~ 100 ms, the CEAS sensor successfully captures time-resolved, quantitative species information that can serve as validation target for kinetic models.

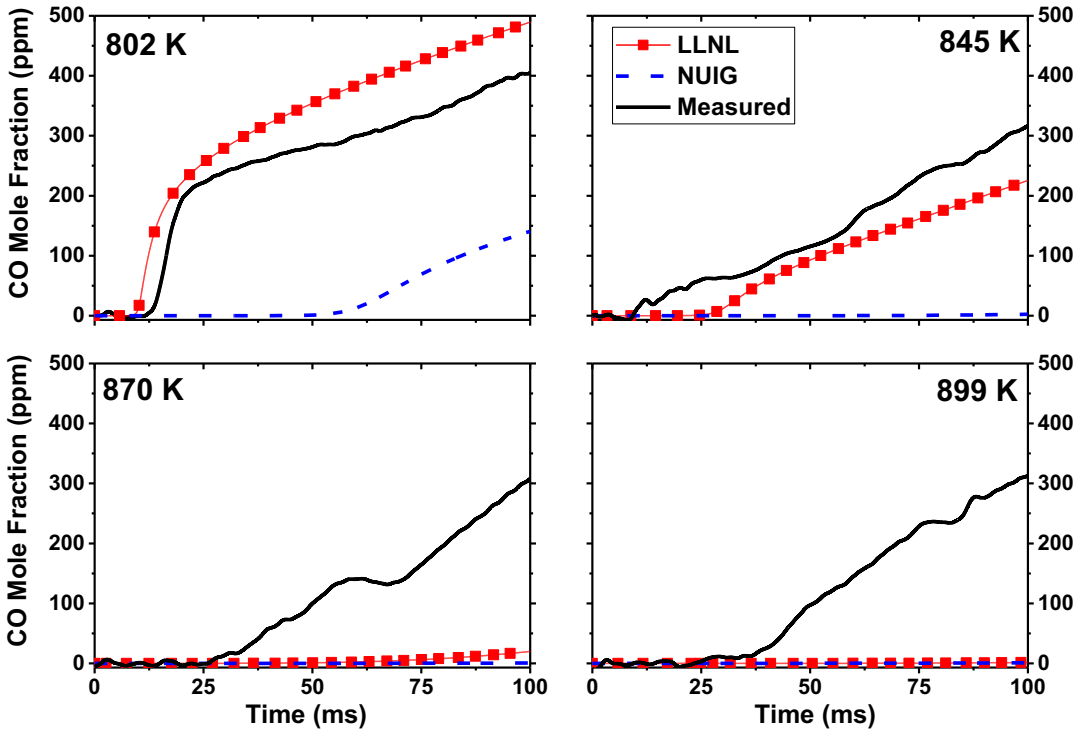

Fig. 5. Measured CO mole fraction overlaid with simulation results from LLNL and NUIG n-heptane mechanisms. Initial composition: 0.2% n-heptane/4.4% O_2/95.4% N_2. Nominal EOC pressure is 10 bar.

Included in Fig. 5 are simulation results obtained using the n-heptane mechanisms developed at LLNL [24] and NUI Galway [25] (a further comparison of simulated temperature profiles is provided in Fig. S3). The simulations were performed in Chemkin-Pro software package using isentropic volume profiles to model the compression phase as well as post-compression heat loss. These volume profiles were generated from pressure traces measured in non-reactive experiments carried out at EOC conditions similar to the respective reactive experiments. Although both LLNL and NUIG models show an increasing trend for first-stage ignition delay, the increase in ignition delay time with respect to temperature is significantly

242 higher than that observed in experiments. The LLNL model is in approximate agreement with the
243 experimental data at 802 and 845 K but deviates significantly at higher temperatures. By contrast, the
244 NUIG model predicts much higher ignition delay (by factor of 4) at 802 K than the experiment, while for
245 higher temperatures the predicted rise in CO formation is no longer within the 100 ms window. In a
246 previous study, a comparison of predictions of total ignition delay between the NUIG and LLNL models
247 showed that, for undiluted conditions, the NUIG model does indeed predict longer ignition delays (refer
248 to Fig. 8a in [25]). However, the magnitude of the discrepancy between the LLNL and NUIG models
249 (factor of 1.5) was found to be significantly less than what has been observed here for diluted conditions.
250 The controlling factors for ignition delay times at these conditions are the addition of O_2 to the fuel alkyl
251 radical as well as the decomposition or isomerization of the resultant alkylperoxy radical. Due to the
252 dependence of the overall reactivity on the alkyl radical, fuel concentration plays a significant role in
253 determining the timing of LTHR. Diluted fuel/air mixtures thus greatly exaggerate differences in ignition
254 delay between the two kinetic models and allow for a much clearer comparison with experimental data.

255

256 **5. Measurement uncertainty**

257 Equations 1 and 2, which are used to compute CO mole fraction, include factors that contribute to
258 the overall uncertainty in the measured mole fraction. These factors are: the gain factor *G,* line-strength *S*
259 and the line-shape function Φ_v. The latter two are determined from the HITRAN database and are
260 temperature-dependent. Thus the uncertainties in the HITRAN values as well as the uncertainty in
261 temperature need to be propagated to the mole fraction uncertainty. The error codes within the HITRAN
262 data files provide uncertainties for line-strength, as well as for air-broadening coefficient and the
263 temperature exponent of broadening which are used to calculate the line-shape function.

264

As mentioned earlier, tests with CO/N_2 mixtures in the RCM yielded an uncertainty of 6.02% in the gain factor (G). This uncertainty resulted from measurement errors due to pulse-to-pulse intensity variation as well as mechanical perturbations affecting the laser signal. The RCM used in this work has creviced piston heads to prevent mixing of the thermal boundary with the core gas, thus establishing a homogeneous temperature field at the end of compression phase. Nevertheless, after EOC, the thermal boundary layer is expected to grow due to heat loss, especially in the measurement time window of 100 ms used in this work. Mittal et al. [26] showed that the influence of the boundary layer on the core gas is inversely related to the piston stroke length. For an EOC pressure of 10 bar, their simulation results showed a 1% change in average core gas temperature for a piston stroke length of 17.78 cm. For our RCM facility, the stroke length is 16.9 cm [10] and, therefore, the result from Mittal et al. can serve as a reasonable estimate for the uncertainty in temperature. Moreover, the measured laser absorption is a sum of absorption in the core gas as well as the absorption in the boundary layer. Assuming that the boundary layer thickness increases with thermal diffusivity and time ($\delta \sim \sqrt{\alpha t}$), the thickness is expected to be about 15% of the total path length at 100 ms. The effective temperature in the boundary layer is assumed to be an average of the core gas and wall temperature, which, coupled with the boundary layer thickness, translates to an uncertainty of 4.05% in the absorbance. This represents an upper limit for the uncertainty estimate since the boundary layer thickness will be much smaller at the early (< 100 ms) measurement times.

Each of the aforementioned parameters was perturbed to its uncertainty limits and the resultant effect on the value of the CO mole fraction was calculated. The effect from each parameter is shown in Table 1. The total uncertainty in the CO mole fraction is calculated as the root-sum-square of the individual contributions, and is found to be 8.51% at a nominal condition of 850 K and 10 bar. It may be seen in Fig. 3 that for the temperature range of interest in RCMs, i.e. 700 – 900 K, the minimum detection limit of CO for the P(23) transition has very weak temperature dependence. Thus, the CEAS measurements are

289 expected to be largely unaffected by any temperature changes in this temperature range. The uncertainty
290 in measurements due to pressure would increase significantly at lower pressures as the laser line-width
291 becomes comparable with the molecular collisional width. Thus, as in the previous study [10], the
292 diagnostic was applied to high-pressure (10 bar) measurements to avoid this issue. At higher pressures (>
293 20 bar), the collisional broadening would become large enough to cause interference of the P(23) line with
294 other CO as well as non-CO lines in spectral proximity.

295 Table 1. Uncertainty contributions to CO mole fraction measurements. Conditions: 850 K, 10 bar, $A_{CEAS} = 0.5$.

Parameter	**% Uncertainty**	**% Effect on X_{CO}**
Temperature	1.00	0.25
Boundary layer absorption	4.05	5.16
Gain Factor	6.02	6.06
Line-strength	1.00	1.01
Broadening coefficient	1.50	1.47
Temperature exponent	3.50	2.43
Total Uncertainty in CO mole fraction		**8.51%**

296

297 ## 6. Conclusions

298 A highly sensitive CEAS (cavity-enhanced absorption spectroscopy) sensor for quantitative and
299 sensitive measurements of carbon monoxide has been demonstrated for investigating LTHR (low-
300 temperature heat release) of dilute n-heptane mixtures in a rapid compression machine. The sensor was
301 based on a pulsed QCL which provided excellent suppression of cavity coupling noise through rapid
302 intrapulse frequency tuning. A significant reduction in the minimum detection limit for CO was achieved
303 and this holds great potential for applications in ignition studies that use diluted fuel/air mixtures. The

effect of dilution was shown to minimize thermal effects on the kinetic behavior as well as illuminate differences between experiments and modelling results more clearly. Improved sensitivity in species concentration measurements, as achieved with CEAS, would prove useful in detecting trace intermediate combustion species formed at low temperature conditions such as H_2O_2, HO_2 and CH_2O. New sensing strategies, such as the one demonstrated here, are likely to become important in expanding the measurement capabilities of RCM facilities.

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List of Figure and Table Captions

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