An IH-QCL based gas sensor for simultaneous detection of methane and acetylene

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Abstract

Extended wavelength tuning of an IH-QCL (integrated heater quantum cascade laser) is exploited for simultaneous detection of methane and acetylene using direct absorption spectroscopy. The integrated heater, placed within few microns of the laser active region, enables wider wavelength tuning than would be possible with a conventional DFB (distributed feedback) QCL. In this work, the laser current and heater resistor current are modulated simultaneously at 25 kHz to tune the laser over $1279.6 - 1280.1 \text{ cm}^{-1}$, covering absorption transitions of methane and acetylene. The laser is characterized extensively to understand the dependence of wavelength tuning on modulation frequency, modulation amplitude and phase difference between laser / heater modulation. Thereafter, the designed sensor is validated in room-temperature static cell experiments. Finally, the sensor is applied for simultaneous detection of methane and acetylene during the high-temperature pyrolysis of iso-octane behind reflected shock waves.

Keywords: QCL; Shock tube; Methane; Acetylene; Absorption spectroscopy

1. Introduction

As a virtually ideal coherent source in the mid-infrared wavelength range, quantum cascade laser (QCL) has become increasingly popular for gas sensing in a variety of fields such as environmental monitoring [1-3], industrial process control [4, 5], biomedical devices [6, 7] and combustion diagnostics [8, 9]. A QCL emits radiation by using inter-subband transitions through a stack of quantum wells [10], which are realized by burying quantum heterostructures into the laser structure. To obtain stable single mode emission, a distributed feedback (DFB) grating is usually integrated in the buried heterostructure, which forms a DFB QCL. Usually, this DFB QCL has limited electrical tunability, typically $\sim 0.1 - 0.2\%$ of the central frequency. Although the tuning range can be a few times wider by changing the substrate temperature of the laser, the tuning speed is limited to Hz range when changing the substrate temperature in contrast to tens of kHz tuning rate with electrical tuning. To achieve a wide tuning range as well as a high tuning speed, Bismuto et al. [11] placed an integrated heater (IH) very close (within a few microns) to the laser active region (AR). This arrangement allowed the control of AR temperature much faster by changing the current injected into the IH. Bismuto et al. [11] demonstrated wider tuning capability of the IH-QCL concept at wavelengths near $7.8\ \mu\text{m}$ and $4.9\ \mu\text{m}$, and achieved frequency tuning up to 0.5% of the central frequency. Such a device presents new opportunities for molecular spectroscopy in the mid-IR region to achieve broader tuning for detecting many species simultaneously or for broadband absorbers.

Although, commercial external-cavity QCLs can provide relatively large wavelength access in the mid-IR region, the tuning is achieved by mechanical movement of a grating which limits the tuning speed to $\sim 350\ \text{Hz}$ [12]. Another widely tuning source is a super-continuum laser but such lasers are not yet available in the mid-IR beyond $\sim 4.2\ \mu\text{m}$ [13] and measurements carried out with super-continuum sources typically require significant averaging to suppress intensity fluctuations.

65 In this work, we utilize the new IH-QCL technology to develop a gas sensor for combustion applications.
66 We chose an IH-QCL, emitting near 7.8 μm , which was readily available at Alpes Lasers and its
67 performance had been verified in reference [11]. The wavelength range accessible by this laser has
68 absorption features of nitrous oxide (N_2O), methane (CH_4) and acetylene (C_2H_2). Here, we selected
69 methane and acetylene as target molecules, mainly because these are very important intermediate species
70 formed during the pyrolysis and oxidation of hydrocarbon fuels. Simultaneous detection of these two
71 species with high accuracy can help validate the chemical kinetic models and constrain the rate constants
72 of critical reaction steps.

73 Previously, methane sensing based on QCL absorption spectroscopy has been demonstrated in
74 atmospheric and plasma applications [14, 15]. Acetylene detection in the mid-IR with QCL absorption
75 spectroscopy is quite scarce [16]. Sajid et al. [17, 18] demonstrated highly time-resolved measurements
76 of methane and acetylene at high temperatures by using an external cavity quantum cascade laser (EC-
77 QCL). However, due to the slow wavelength-scanning speed of the EC-QCL, they were unable to measure
78 CH_4 and C_2H_2 simultaneously; the EC-QCL had to be operated separately at two different wavelengths
79 for CH_4 and C_2H_2 measurements. Here, we use the IH-QCL to realize simultaneous, time-resolved
80 measurements of CH_4 and C_2H_2 during the high-temperature pyrolysis of iso-octane in a shock tube. To
81 our knowledge, this is the first application of an IH-QCL architecture for combustion diagnostics.

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2. Measurement principles

The sensor presented in this work is based on direct absorption spectroscopy which is described by the Beer-Lambert law. The absorbance α_{ij} of a spectroscopic transition i for a species j is given by,

$$-\ln\left(\frac{I_t}{I_0}\right) \equiv \alpha_{ij}(\nu_i, T, P) = \frac{P \cdot L}{R \cdot T} \cdot X_j \cdot \sigma_{ij}(\nu_i, T, P) \quad (1)$$

where I_t is the transmitted laser intensity, I_0 the zero-absorption laser intensity, ν_i the wavenumber (cm^{-1}), T the temperature (K), P the total pressure (bar), L the absorption path length (m), R the gas constant ($= 8.3144598 \text{ m}^3 \cdot \text{bar} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$), X_j the mole fraction of species j , σ_{ij} the absorption cross-section (m^2/mol) at frequency ν_i .

The IH-QCL used in this work is able to access 1276 cm^{-1} to 1284 cm^{-1} region, which contains several absorption transitions of methane and acetylene. In order to select suitable detection wavelengths, homogeneous-reactor chemical kinetic simulations were carried out for the pyrolysis of is-octane, a primary reference fuel, by using the detailed kinetic mechanism of Mehl et al. [19] in Chemkin-Pro [20]. A representative simulation result is shown in Fig. S1 (Supplementary Material). It may be observed that the primary products of iso-octane pyrolysis are CH_4 , C_2H_2 , H_2 , C_2H_4 , C_3H_6 , C_2H_6 , and C_4H_8 . Among the product species, H_2 is not infrared active. Spectroscopic simulations for other major species were carried out over 1276 cm^{-1} to 1284 cm^{-1} using the spectral parameters given in the HITRAN [21] and PNNL [22] spectral database (see Fig. S2). It was found that C_2H_4 , C_2H_6 and C_3H_6 have negligible absorption in the target wavelength region. Iso-butene (C_4H_8) has broadband spectra in this region; however, the combination of relatively small production of iso-butene (Fig. S1) and its relatively smaller absorption cross-section (Fig. S2) would limit interference absorption by iso-butene. Secondly, the interference by any broadband absorber can easily be mitigated by the ‘differential absorption strategy’ which is straightforward to implement here due to the scanned-wavelength approach adopted here. Therefore, this wavelength region ($1276 - 1284 \text{ cm}^{-1}$) is quite suitable for the detection of methane and acetylene during

hydrocarbon pyrolysis. A representative spectroscopic simulation is plotted in Fig. 1, which shows that the target species (CH_4 and C_2H_2) have resolved spectra in this wavelength window. Three simple criteria were used for selecting detection wavelengths: i) maximum peak absorption, ii) minimum interference absorption, iii) minimum wavelength separation between the two species. This process resulted in selecting two detection wavelengths, 1279.67 cm^{-1} and 1280.01 cm^{-1} , for simultaneous sensing of CH_4 and C_2H_2 , respectively. Figure 1 shows that the 1279.67 cm^{-1} (labelled p_1) wavelength has some interference absorption by C_2H_2 . On the other hand, the acetylene detection wavelength, 1280.01 cm^{-1} (labelled p_2), has negligible interference from methane. Negligible interference by methane at 1280.01 cm^{-1} was verified by carrying out high-temperature shock tube experiments (not reported here) with 3% CH_4/Ar mixture, and measuring absorption at p_2 .

Fig.1. Simulated spectra for a 2.5% CH_4 , 1.5% C_2H_2 , balance air mixture. $T = 1800 \text{ K}$, $P = 1 \text{ atm}$, $L = 14 \text{ cm}$.

Absorbance at the two selected peaks may be described as:

$$\begin{cases} \alpha_{p_1} = \frac{P \cdot L}{R \cdot T} \cdot (X_{\text{CH}_4} \cdot \sigma_{\text{CH}_4}^{p_1} + X_{\text{C}_2\text{H}_2} \cdot \sigma_{\text{C}_2\text{H}_2}^{p_1}) \\ \alpha_{p_2} = \frac{P \cdot L}{R \cdot T} \cdot X_{\text{C}_2\text{H}_2} \cdot \sigma_{\text{C}_2\text{H}_2}^{p_2} \end{cases} \quad (2)$$

where X_{CH_4} , $X_{\text{C}_2\text{H}_2}$ are the unknowns, i.e., the mole fractions of methane and acetylene, respectively; $\sigma_{\text{C}_2\text{H}_2}^{p_1}$, $\sigma_{\text{C}_2\text{H}_2}^{p_2}$ are the cross-section of C_2H_2 at the two peaks, and $\sigma_{\text{CH}_4}^{p_1}$ is the cross-section of CH_4 at p_1 . The mole

fractions of CH₄ and C₂H₂ can be determined by solving Eq. (2). It should be noted that the absorption cross-sections are generally a function of temperature, pressure and mixture composition.

3. Experimental details

The IH-QCL (integrated heater – quantum cascade laser) used here was provided by Alpes Lasers in a high-heat load (HHL) packaging. The substrate temperature of the laser was controlled by a thermoelectric cooler (TEC) over -15 to 50 C. Some operating conditions required the HHL to be kept below room temperature; therefore, the laser was mounted on a copper plate which was cooled by a recirculating chiller (ThermoCube 400). The current injected into the laser was controlled by two current controllers (ILX Lightwave LDX-3232); one for the AR (active region) current, and the other for IH (integrated heater) current. The maximum allowable AR and IH currents were 225 mA and 600 mA, respectively. The maximum output power of the laser was ~ 80 mW. A function generator (LeCroy 2052) was used to drive the two current controllers with waveforms of desired shape, frequency, amplitude and phase difference (between the two waveforms).

Optical setup used for shock tube experiments is shown in Fig. 2. The shock tube facility has been described in detail previously [23-25]. The laser was divided in two beams by a beam splitter (Thorlabs BSW710). One beam was aligned to a wavelength-meter (Bristol Instruments 621-XIR) for absolute frequency measurement or to a Germanium etalon (FSR = 0.0164 cm⁻¹) for monitoring the wavelength tuning. The second beam was propagated through the shock tube via ZnSe optical windows, installed at 2 cm from the shock tube end-wall. A plano-convex lens (CaF₂, focal length of 200 mm) and an iris, upstream of the shock tube, were used to minimize beam steering effects caused by density gradients during high-temperature experiments. A second iris, downstream of the shock tube, was used to reduce the undesired broadband thermal emission caused by hot gases. A concave mirror (focal length of 5 mm)

was utilized to focus the laser beam onto a photo-detector (Vigo Systems PVI-2TE-10.6 2mm × 2mm). A data acquisition system, PicoScope 5444B, sampled the detector and shock tube pressure (Kistler 6031B) signals at a sampling rate of 62.5 MHz with a 15-bit resolution.

Fig. 2. Optical schematic of the experimental setup.

4. Laser characterization

In order to make simultaneous measurements of methane and acetylene at the selected peaks, the IH-QCL is to be scanned $\sim 0.5 \text{ cm}^{-1}$ at a high time resolution (few tens of kHz), which meets the requirement of kinetic measurements in a shock tube. Therefore, the laser was characterized to understand how the tuning range is affected by relevant parameters, such as AR/IH tuning, modulation frequency of the injected currents, type of modulation wave, and phase difference between the respective modulation waves for IH (integrated heater) tuning and AR (active region) tuning. The first two factors were examined by operating the laser at various modulation frequencies in three different tuning manners, AR tuning, IH tuning and simultaneous AR/IH tuning. The tuning range was measured by using the Ge etalon, as described in Section 3. Figure 3 shows that the tuning range is larger when both AR and IH current are modulated simultaneously, although the incremental tuning achieved by AR + IH modulation decreases at faster modulation speeds. The tuning range was characterized at different substrate temperatures and with

167 various waveform shapes, such as ramp signal with varying duty cycles, triangular wave, and sinusoidal
 168 wave. Among these, a sinusoidal wave provided maximum tuning range, followed by a triangular
 169 waveform.

170

171 *Fig. 3. Wavelength tuning range of the IH-QCL at different modulation frequencies in three different tuning*
 172 *manners. The substrate temperature of the laser was set at 5 °C, and the chiller was set at 15°C. Ramp signal*
 173 *(90:10) was used as the modulation wave. For simultaneous AR and IH tuning, the phase difference between the*
 174 *two waveforms was 0°.*

175 Since simultaneous AR and IH tuning leads to increased wavelength tuning, the differences in phase and
 176 the frequency of two modulation waves were investigated to see their effects on laser performance. It was
 177 found that when the two waves were not modulated at the same frequency, the laser intensity was not
 178 stable. Yet, a stable laser intensity signal is necessary for direct absorption experiments, therefore, the
 179 same modulation frequency was used for the two waves. For the phase difference investigation, the phase
 180 in IH current wave was fixed at 0° while the phase in AR current wave was changed from 0° to 360°. The
 181 results are shown in Fig. 4. It may be observed that maximum tuning range was achieved when the two
 182 waves were in phase. The tuning range decreased steadily as the phase difference increased, reaching a
 183 minimum when the two waves were out of phase. Moreover, as the modulation frequency increased, the
 184 minima moved from phase difference of $\sim 180^\circ$ to $\sim 130^\circ$. This shift may be attributed to the fact that
 185 wavelength tuning is thermal in nature, which depends on local values of the thermal resistance and heat
 186 expansion as well as chip geometry, and increased modulation frequencies perhaps lead to varying thermal
 187 behavior from the two tuning modes (AR and IH). Based on the above laser characterization and required

188 tuning range of $\sim 0.5 \text{ cm}^{-1}$, the AR and IH currents were both modulated at 25 kHz with a phase difference
 189 of zero in the experiments presented in Section 5 and Section 6.

190

191 *Fig. 4. Wavelength tuning range as a function of phase difference between AR and IH tuning waves. Sinusoidal*
 192 *waveforms were used for both tuning modes at 1 kHz, 10 kHz and 25 kHz. The substrate temperature of the laser*
 193 *was set at 5 °C, and the chiller was set at 15°C. The AR dc current was set to 160 mA while IH dc current was 300*
 194 *mA.*

195 Additionally, the intensity modulation response of the laser with IH and AR tuning was investigated. The
 196 laser was modulated with IH and AR tuning modes separately, and the amplitude of the respective input
 197 waveform was adjusted to achieve maximum wavelength tuning response at each modulation frequency.
 198 Figure 5 shows that the intensity amplitude decreased steadily for AR modulation as the modulation
 199 frequency increased from 1 to 100 kHz, while the amplitude remained stable at frequencies higher than
 200 20 kHz for IH modulation. Moreover, the intensity amplitude of IH tuning was much lower than that of
 201 AR tuning at the same modulation frequency and approximately same wavelength tuning range. The
 202 reduced intensity modulation response can be a very desirable feature for a number of applications. For
 203 example, the use of IH modulation for wavelength modulation spectroscopy (WMS) can be quite useful
 204 for minimizing the undesired residual amplitude modulation signal [26].

Fig. 5. Modulation amplitude with AR tuning and IH tuning separately. The substrate temperature of the laser was set at 5 °C. Ramp signal (90:10) was used as the modulation wave. Input IH waveform amplitude: 2.9 Vp-p; input AR waveform amplitude: 0.65 Vp-p. The chiller was set to 15 °C. The AR dc current was set to 160 mA while IH dc current was 300 mA.

5. Static cell measurements

To verify the methodology of simultaneously sensing CH₄ and C₂H₂, we performed room-temperature (294 K) experiments in a 14 cm long static cell. The static cell was first vacuumed to get the zero-absorption signal (I_0). Then it was filled up to various pressures with a mixture of 1.4% CH₄, 0.77% C₂H₂ and balance N₂. The transmitted laser signal (I_t), with simultaneous AR and IH modulation, was then recorded to obtain the absorbance profile. A representative absorbance profile is shown in Fig. S3 (Supplementary Material). Measured mole fractions of methane and acetylene were calculated by using Eq. (2) with the absorption cross-section values taken from the HITRAN database. For a specific experiment carried out at a total pressure of 102 Torr, the laser measurement gave CH₄ mole fraction of 1.38% and C₂H₂ mole fraction of 0.79%. These results are in excellent agreement with the manometrically recorded mole fractions. Uncertainty in the measured values comes primarily from uncertainties in the HITRAN spectral parameters, pressure measurement, mixture preparation and minor variations in laser intensity.

225

226 **6. Shock tube measurements**

227 Shock tube experiments are generally performed with argon as the bath gas, since the use of nitrogen bath
 228 gas can lead to boundary layer separation and shock bifurcation [27]. The HITRAN database can be used
 229 to calculate absorption cross-section values for air (or nitrogen) bath gas but not for argon bath gas.
 230 Therefore, for the high-temperature detection of methane and acetylene in the shock tube, the respective
 231 absorption cross-sections must be measured experimentally. Methane cross-section measurements were
 232 carried out over 1300 – 1750 K using 3% CH₄/Ar mixture, and acetylene cross-sections were measured
 233 over 1300 – 1700 K using 5% C₂H₂/Ar mixture. Fixed-wavelength absorption strategy was employed to
 234 achieve high temporal resolution, and the measured absorbance signals were averaged over 1 ms after the
 235 reflected shock wave. A representative laser transmission signal is shown in Fig. S4 (Supplementary
 236 Material), which depicts high signal-to-noise ratio achieved in these experiments. It should be noted that
 237 methane and acetylene may start to undergo pyrolysis at high temperatures (> 1700 K); absorbance signal
 238 at time zero (arrival of reflected shock wave) was used in such cases to determine absorption cross-section.
 239 The measured cross-sections are plotted in Fig. 6, and the best fit values (shown as solid red line) are
 240 described by Eq. (3). The scatter in measured values results mainly from the relatively large dependence
 241 of cross-sections on pressure for these narrow absorption lines. The uncertainty in cross-section comes
 242 from uncertainties of pressure (< 1%) and temperature (< 1%) of the reflected shock, path-length in the
 243 shock tube (~1.4%), mole fraction of methane or acetylene (~0.2%) and the noise in measured absorption
 244 signal (~3%). Gathering all these factors in a root-sum-squared method, uncertainties in measured cross-
 245 sections range ~3 – 7%, and are shown as error bars in Fig. 6.

$$246 \quad \begin{cases} \sigma_{CH_4}^{p_1} = 2 \times 10^7 \cdot T^{-2.08} \cdot P^{-0.56}; & (1300-1750 \text{ K}), (0.97-1.3 \text{ atm}) \\ \sigma_{C_2H_2}^{p_1} = 59 \cdot T^{-0.44} \cdot P^{-0.077}; & (1300-1700 \text{ K}), (0.97-1.3 \text{ atm}) \\ \sigma_{C_2H_2}^{p_2} = 3.6 \times 10^5 \cdot T^{-1.50} \cdot P^{-0.46}; & (1300-1700 \text{ K}), (0.97-1.3 \text{ atm}) \end{cases} \quad (3)$$

248

249 *Fig. 6. Measured absorption cross-sections of methane and acetylene at the two selected peaks by using 3% CH₄ /*
 250 *Ar and 5% C₂H₂ / Ar mixtures. The black circles are the measured data, while the red solid lines represent the fitted*
 251 *results normalized at 1.1 atm. Error bars indicate measurement uncertainty.*

252 Thereafter, shock tube experiments were carried out with mixtures of methane and acetylene to verify the
 253 sensing methodology and measured absorption cross-sections. Two different nominal mixtures were used:
 254 3% CH₄ / 5% C₂H₂ / Ar and 2% CH₄ / 3% C₂H₂ / Ar. In these experiments, the laser was modulated at 25
 255 kHz using simultaneous AR and IH tuning to scan over the intended absorption transitions of methane
 256 and acetylene. A representative laser transmission signal and its absorbance profile are shown in Fig. S5
 257 (Supplementary Material). The experiments scanned temperature range of $\sim 1300 - 1700$ K and pressures
 258 near 1 atm. Representative measured time-history results are shown in Fig. 7 which have an average
 259 absolute deviation of $\sim 6\%$ compared to the manometrically measured mole fraction values. Since methane
 260 undergoes pyrolysis at temperatures > 1600 K, those results are not included here. The uncertainty in C₂H₂
 261 mole-fraction comes from the uncertainty of temperature ($< 1\%$), pressure ($< 1\%$), path-length ($\sim 1.4\%$),
 262 the absorbance peak near p_2 (α_{p_2} , $\sim 2-4\%$) and the C₂H₂ cross-section near p_2 ($\sigma_{\text{C}_2\text{H}_2}^{p_2}$, $\sim 3-5\%$). Combining
 263 the above factors in a root-sum-squared method, the uncertainty in measured C₂H₂ mole-fraction is
 264 estimated to be $< 7\%$. Three additional factors, i.e., the uncertainty of absorbance peak near p_1 (α_{p_1} , $\sim 2-$
 265 4%), C₂H₂ cross-section near p_1 ($\sigma_{\text{C}_2\text{H}_2}^{p_1}$, $\sim 4-5\%$) and the CH₄ cross-section near p_1 ($\sigma_{\text{CH}_4}^{p_1}$, $\sim 3-7\%$), are used
 266 to calculate the uncertainty in CH₄ mole-fraction, which is estimated to be $< 12\%$.

Fig. 7. Measured mole-fraction time-histories for 3.1% CH₄ / 4.9% C₂H₂ / Ar mixture. The two black dash lines are the manometric mole fractions while the colorful scatters are the measured results by the sensor.

Finally, the sensor was applied to make simultaneous measurements of methane and acetylene during the pyrolysis of 2% iso-octane in argon. The pyrolysis process is endothermic and results in a temperature drop after the reflected shock wave. Temperature time-history was obtained from chemical kinetic simulation in Chemkin-Pro [20] by using constant-volume assumption and the detailed kinetic model of Mehl et al. [19]. Previous works [18] have discussed the suitability of using constant-volume or constant-pressure constraints in calculating temperature time-histories for shock tube pyrolysis experiments. The simulated temperature time-history was used to calculate time-varying temperature-dependent absorption cross-sections using Eq. (3). Finally, the mole fractions of methane and acetylene were calculated using Eq. (2). A representative absorbance profile is shown in Fig. S6 (Supplementary Material). Two representative results are presented in Fig. 8 and compared with the predictions of Mehl et al. [19] model. To achieve faster time resolution for these kinetic measurements, absorption profiles in both upward and downward scan of sinusoidal wave were used, which resulted in an effective time resolution of 20 μ s. Measured and simulated profiles show that the production of methane and acetylene increases with temperature. The measured mole fractions are generally higher than the predicted ones, which may either be due to deficiencies in the chemical kinetic model for pyrolytic reactions at these conditions or due to some contribution by broadband absorbing species (e.g., iso-butene). The latter effect can be easily

286 removed by analyzing the data with differential absorption strategy. For the 1965 K case in Fig. 8, the
 287 measured CH_4 mole-fraction exhibits a downward trend between 0.4 and 0.8 ms, which may be caused by
 288 some measurement noise, such as beam steering or laser intensity fluctuation. Nevertheless, these results
 289 show the potential of this new laser sensor for multi-species measurements in shock tube chemical kinetics
 290 experiments.

291

292 *Fig. 8. Mole fraction results of methane and acetylene for two reflected-shock experiments at 1616 K, 1.20 bar*
 293 *and 1965 K, 1.01 bar. The dash lines are simulated results from Mehl et al. model [19].*

294

295 Using a minimum detectable absorbance of 0.1%, a path-length of 14 cm and the measured absorption
 296 cross-sections, the detection limit of this sensor, at 1300 K and 1 atm, will be ~75 ppm for CH_4 and ~101
 297 ppm for C_2H_2 . Detection limits for methane and acetylene as a function of temperature are summarized in
 298 Fig. S7 (Supplementary Material).

299

300 7. Conclusions

301 A new laser sensor, based on scanned-wavelength direct absorption spectroscopy, was developed by
 302 employing a novel IH-QCL (integrated heater – quantum cascade laser). The IH-QCL allows faster control
 303 of the AR (active region) temperature and a wider tuning capability compared to conventional DFB lasers.
 304 The IH-QCL exhibits some very interesting features that could be quite useful for various absorption

spectroscopy applications. When the IH and AR currents are modulated in phase, the laser provides wider wavelength tuning than would be possible with the typical AR current modulation. When the two modulations are out of phase, the wavelength tuning is suppressed and this may be of use for experiments which seek to maximize intensity modulation with minimal wavelength tuning. On the other hand, the laser intensity modulation amplitude is reduced significantly with IH modulation alone, which could be taken advantage of in wavelength modulation spectroscopy to minimize residual amplitude modulation. To demonstrate the potential of this laser architecture for combustion applications, the laser was used to make simultaneous measurements of methane and acetylene in a shock tube with a time resolution of 20 – 40 μ s. Measurements carried out during the high-temperature pyrolysis of iso-octane showed the high potential of multi-species detection in shock tube chemical kinetics experiments. Future work will be aimed at exploiting the capabilities of this laser for high-pressure measurements and for sensing species with broadband spectral features.

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369 **List of figure captions:**

Figure No.	Caption
Fig. 1	Simulated spectra for a 2.5% CH ₄ , 1.5% C ₂ H ₂ , balance air mixture.
Fig. 2	Optical schematic of the experimental setup.
Fig. 3	Wavelength tuning range of the IH-QCL at different modulation frequencies in three different tuning manners.
Fig. 4	Wavelength tuning range as a function of phase difference between AR and IH tuning waves.
Fig. 5	Modulation amplitude with AR tuning and IH tuning separately.

Fig. 6	Measured absorption cross-sections of methane and acetylene at the two selected peaks by using 3% CH ₄ / Ar and 5% C ₂ H ₂ / Ar mixtures.
Fig. 7	Measured mole-fraction time-histories for 3.1% CH ₄ / 4.9% C ₂ H ₂ / Ar mixture.
Fig. 8	Mole fraction results of methane and acetylene for two reflected-shock experiments at 1616 K, 1.20 bar and 1965 K, 1.01 bar.

List of supplementary material:

Supplementary materials	Caption
Fig. S1	Chemkin simulation results of the pyrolysis of 2% iso-octane/Ar mixture at an initial temperature of 1800 K and pressure of 1 atm.
Fig. S2	Absorbance of the species shown in Fig. S1. These are calculated using the PNNL database with a mole fraction of 1 ppm and a path-length of 1 m at a temperature of 25 C and a pressure of 1 atm.
Fig. S3	Experimental absorbance profile for a mixture of 1.4% CH ₄ , 0.77% C ₂ H ₂ and balance N ₂ at room temperature (294K), pressure of 102 torr and effective path-length of 14 cm.
Fig. S4	Representative laser signal for cross-section measurement of methane.
Fig. S5	A typical one-cycle laser transmitted signal (left) and its absorption profile (right) for the reflected shock of 1388 K and 1.07 atm.
Fig. S6	Measured absorption profiles of 38 cycles for (a) the reflected shock of 1616 K and 1.2 atm and (b) the reflected shock of 1965 K and 1.0 atm.
Fig. S7	Detection limits in methane and acetylene at different temperatures from 1300 K to 1700 K and a pressure of 1 atm.