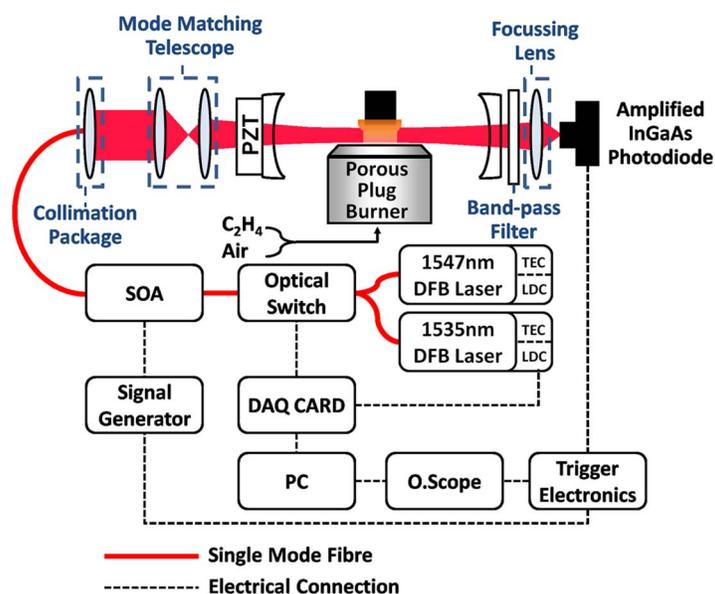


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Application of Continuous-Wave Cavity Ring-Down Spectroscopy to Laminar Flames

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Abstract: In this paper, we describe the application of diode-laser continuous-wave cavity ring-down spectroscopy (cw-CRDS) to in-situ flame diagnostics. Spectra of the P17e acetylene feature at 1535.4 nm were recorded in a premixed laminar ethylene/air flame. The overall absorption of the feature was measured to be $\approx 1.5 \times 10^{-4} \text{ cm}^{-1}$, which is a short distance above the reaction zone for a flame fuel equivalence ratio of 1.66, and the minimum detection limit (3σ) of the system was calculated to be $1.2 \times 10^{-5} \text{ cm}^{-1}$. This demonstrates the potential of the technique for the measurement of weakly absorbing species in flames. Finally, we discuss the advantages and limitations of the cw-CRDS technique for flame measurements.

Index Terms: Continuous-wave cavity ring-down spectroscopy (cw-CRDS), combustion, cavity ring-down, diode laser.

1. Introduction

In-situ optical sensing techniques are the preferred method for measuring species concentration in high-temperature reacting flows, such as flames. This is because optical sensing techniques, such as tunable diode laser absorption spectroscopy, produce little to no perturbation in the combustion process as it is non-intrusive and measurements can be made in-situ. However, standard single-pass absorption spectroscopy often lacks the required sensitivity for species concentration measurements in flames. This can be due to a combination of the low concentration or the low absorption cross-section of the target species, a short interaction length, and the intense background emission from the flame [1]. Even with specialized correction techniques and extensive averaging, direct absorption typically has a minimum detectable absorbance on the order of 10^{-4} , and this performance is generally poorer under combustion conditions [2]. Recently, Wagner *et al.* [3] used direct diode laser absorption spectroscopy to probe the P17e transition of acetylene to measure acetylene concentration in methane/air flames, stabilized on a Wolfhard-Parker slot burner and in a Tsuji counter flow burner [4].

To improve the sensitivity of diode laser absorption spectroscopy in flames a number of strategies are available; these are all essentially based on increasing the overall absorption by

increasing the laser-gas interaction length [2] or reducing the noise by introducing modulation techniques such as wavelength modulation spectroscopy (WMS) [5]. Recently, calibration-free techniques for WMS have proven to be ideal for gas concentration and system temperature measurements in harsh environments [6], [7]. These applications of WMS have achieved extremely high sensitivities in such environments and have been fully developed into commercially available measurement systems. However, technique can be limited by the complexity of the signal processing and by spectral broadening that results from the high modulation amplitude. In particular, the broadened derivative-like signals make it difficult to interpret spectra, especially in environments where a number of unidentified features are present. Thus this can limit its application in multi-species, high-temperature environments such as flames, particularly when targeting near-infrared ro-vibrational transitions.

In this paper we develop an alternative technique based on increasing the laser-gas interaction length using cavity ring-down spectroscopy (CRDS) [8]. Cavity ring-down spectroscopy has previously been performed in flames using pulsed dye lasers for measurements of species such as OH, CH and $^1\text{CH}_2$ [9]–[11]. The related technique of continuous-wave cavity ring-down spectroscopy (cw-CRDS) [12] allows the use of compact, low-power diode lasers [13], [14] but has received little attention for in-situ flame measurements. Here, we report on the novel application of diode laser cw-CRDS to flames involving the development of an instrument for detection of acetylene.

The performance of the cw-CRDS system is demonstrated using a premixed laminar ethylene/air flame stabilized on a porous plug burner. We discuss how features of its performance compare with previous cavity ring-down studies performed in similar flames using pulsed laser sources.

2. Cavity Ring-Down Spectroscopy

CRDS is a cavity based spectroscopic technique which improves the sensitivity of absorption measurements by increasing the effective path-length of the laser light through the absorbing medium. This is achieved by coupling light into a high finesse optical cavity (typical mirror reflectivity is greater than 99.99%). When the input light into the cavity is terminated the intensity of light leaving the cavity through the output mirror decays exponentially. If no absorbing medium is present, the rate of decay should ideally only be due to mirror transmission/scattering losses. When an absorbing species is present this rate of decay is significantly increased due to the absorption losses in the optical cavity. Theoretically, following the termination of input light, the intensity of light $I(t)$ remaining within the cavity at a time t is described according to the equation [15]

$$I(t) = I_0 \exp\left(-\frac{t}{\tau}\right) \quad (1)$$

where I_0 is the intensity of the light at the moment the input light was terminated, and the decay constant τ is the cavity ring-down time described as

$$\tau = \frac{L_c}{c[(1 - R) + \alpha(\lambda)d + X]} \quad (2)$$

where c is the speed of light, R is the mirror reflectivity, $\alpha(\lambda)$ is the absorption coefficient at a wavelength λ , d the path length through the absorbing medium, and L_c is the cavity length. X describes the proportion of light lost per pass in the cavity from sources other than the narrow-band absorption, for example thermo-optic effects, and losses due to the presence of an particulates intra-cavity [16].

The application of cw-CRDS in flames using diode lasers is a challenging objective for several reasons. In a low-power cw-CRDS set-up it is necessary to accurately mode-match a single transverse mode, which will allow enough optical power to build up within the resonant cavity to provide a detectable signal. This necessity for optical mode-matching in a cw-CRDS setup presents difficulties when an optically perturbing medium, such as a flame, is located within the cavity. For example, thermo-optical effects inherent to flame measurements, such as beam

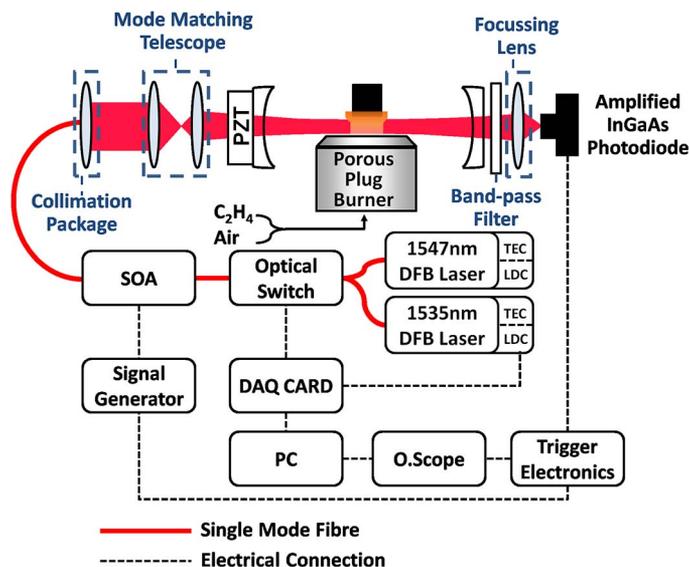


Fig. 1. Cw-CRDS Experimental Setup: SOA, Semiconductor Optical Amplifier; DAQ Card, Data Acquisition Card; TEC, Thermoelectric Controller; LDC, Laser Diode Controller.

steering, can divert light into higher order transverse modes on each pass, reducing the intensity of light within the resonant, fundamental TEM_{00} mode and reducing the cavity ring-down time. Miller *et al.* [17] encountered this difficulty, and only report data obtained by extractive sampling of gas from the flame. Lamoureux *et al.* [18] also preformed cw-CRDS on gas samples extracted from flames.

The only cavity-based diode laser measurements that have been conducted in flames were based on the cavity enhanced absorption spectroscopy (CEAS) technique [19], where the averaged intensity of the light transmitted through the cavity over a scan of several periodically excited modes is measured, instead of measuring the cavity ring-down time. Peeters *et al.* [19] used diode laser CEAS to make measurements of OH radicals in laminar flames. However, these were relative measurements since CEAS is a technique that requires calibration, unlike CRDS which provides an absolute measure of optical losses from the cavity.

Until now the application of cw-CRDS for species detection in flames has therefore been limited to extractive sampling using a probe [20] with in-situ measurements being conducted using the pulsed CRDS technique [18]. In this paper we describe in-situ cw-CRDS measurements of optical absorption due to acetylene in a flame with a higher overall SNR than can be achieved using standard single-pass absorption or WMS.

3. Spectrometer Design

A detailed diagram of the spectrometer is shown in Fig. 1, presenting the key components in this new cw-CRDS approach to in-flame optical absorption measurements. Two diode sources are shown; the first is used to interrogate a targeted gas spectrum, in this case acetylene, and the second laser is used for signal normalization.

The interrogation laser is a 15 mW, 1535 nm distributed feedback (DFB) diode laser, selected to probe the P17e transition of acetylene. The normalization laser is a 20 mW DFB at 1547 nm, and is used to quantify the optical losses caused by thermal gradients in the flame and alignment drift over time. The final active optical source is a C-band semiconductor optical amplifier (SOA) (manufacturer: Kamelian), that has a maximum output power of 20 mW and is current controlled using an arbitrary function generator (manufacturer: Agilent Technologies). This SOA is used in place of the more common acousto-optic modulator (AOM) to interrupt the input laser light to the cavity and initiate ring-down. The SOA also has the further advantage of being able

to amplify the optical output of the laser. This increase in power can help to compensate for the loss in the on-resonance transmission encountered during combustion measurements (shown in Section 4), providing better signal to noise in the raw ring-down trace and was originally tested for cw-CRDS applications by Huang *et al.* [21].

The output from the SOA is collimated into the bulk optics section of the spectrometer using a fiber coupled aspheric lens collimation package, which produces a beam with a measured diameter of 2.7 mm. The optical cavity is constructed using two concave ultra-high reflectivity mirrors (ROC: 1 m, $R = 0.9999$ at 1550 nm, manufacturer: CRD Optics) which are spaced 500 mm apart, with the burner located in the centre of the cavity. The input mirror is mounted on a three actuator piezoelectric (PZT) mount (manufacturer: ThorLabs) that provides the fine variation of the cavity length, required to periodically bring a single longitudinal mode into resonance.

Mode-matching to the TEM_{00} mode is achieved using two biconvex positive spherical lenses (focal lengths 60 mm and 30 mm, respectively) arranged in a basic Keplerian telescope format. The mode-matching optics reduce the beam diameter to 0.93 mm ($1/e^2$) at the center of the cavity, matching both the diameter and waist position of the TEM_{00} transverse mode. The light that exits the cavity, by transmission through the output mirror, is initially passed through an optical band pass filter (FWHM 40 nm, centre wavelength: 1550 nm), which reduces the intensity of the flame emission transmitted through the output mirror, before being focused onto an amplified InGaAs photodiode. The photodiode output voltage is fed into a simple comparator circuit which outputs a TTL pulse when the cavity transmission exceeds a preset level. This TTL pulse triggers the signal generator to rapidly switch off the SOA drive current (edge time ≈ 5 ns), allowing the cavity to ring-down. The total time delay from the cavity transmission exceeding the preset threshold until termination of input light to the cavity is ≈ 40 ns. Ring-down signals are recorded using a NI LabView controlled, 1 GS/s, digital oscilloscope (manufacturer: Tektronix).

A premixed flame of ethylene and air was stabilized on a 33 mm diameter porous-plug burner at atmospheric pressure [22]. This resulted in one-dimensional laminar flames, with conditions such as temperature, species concentration, and soot volume fraction varying only with height above the burner surface. The flame produced by the burner is stabilized using a 38 mm diameter steel cylinder mounted 21 mm above the burner surface. The flow-rates of air and ethylene (supplied at ambient temperature) are controlled using rotameters. The flame conditions have been described in detail previously [22]. The burner is mounted on an adjustable stage which allows it to be vertically translated with respect to the spectrometer. The zero-point for the translation is taken to be the point at which the surface of the burner is at the same vertical position as the center of the TEM_{00} transverse mode.

The spatial resolution of the spectrometer in the flame can be determined from the diameter of the beam waist of the TEM_{00} mode, which varies very little through the flame (Rayleigh distance = 434.5 mm). There is potential for improving the spatial resolution of the system by using mirrors with a smaller radius of curvature.

Initially, an in-flame CRD spectrum of the normalization DFB laser was obtained, to ensure that a suitable region free of significant absorption features was available, as shown in Fig. 2. In this case, the optical switch and the interrogation DFB laser were removed from the system. The 1547 nm laser was wavelength tuned by controlling the applied current using a laser diode controller (Manufacturer: ThorLabs Model: LDC 210C), whose output current can be varied via an applied input voltage, with a conversion rate of 100 mA/V. The control voltage was obtained from the analogue output (AO) of a 16 bit data acquisition (DAQ) board (manufacturer: National Instruments, Model: PCI 6120). The wavelength was varied through a 0.285 nm range around 1547.89 nm by tuning the drive current at 0.25 mA intervals. At each current increment, 32 ring-down signals were recorded and averaged on the oscilloscope and the data was recorded on the control PC.

The region of maximum ring down time in Fig. 2 is highlighted using an arrow. This value has been assumed to be free of gas absorption and is therefore used to quantify the broadband optical losses in the cavity and thus provides a baseline for the gas absorption measurements.

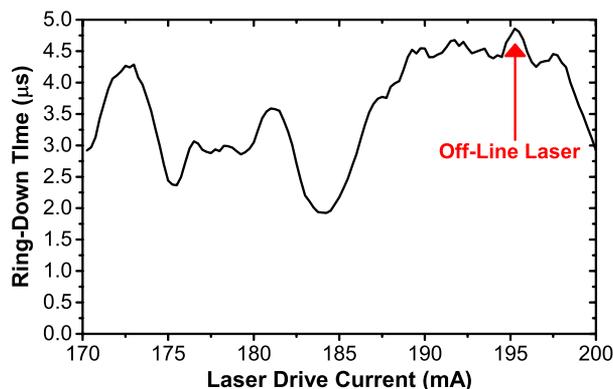


Fig. 2. Spectrum recorded using the 1547 nm DFB Laser. The point to which the laser is tuned to quantify broadband optical losses is shown using an arrow. Recorded 3 mm above the burner in a 1.54 equivalence ratio flame.

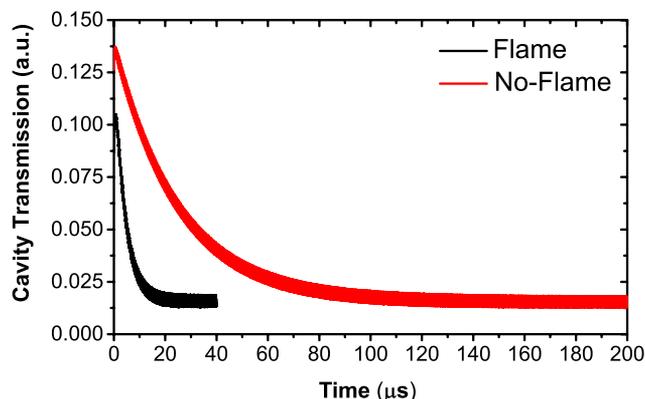


Fig. 3. Average ring-down traces recorded 3 mm above the burner surface. In absence of the flame (red) and with an equivalence ratio flame of 1.54.

To carry out normalized in-flame CRDS measurements of gas spectra, the optical switch and the interrogation DFB laser are re-introduced. In this case, the interrogation DFB laser is current tuned using the DAQ board. Between each wavelength increment of the interrogation DFB laser, a LabView program triggers the optical switch to shift to the normalization laser. Once a CRD signal of the normalization laser is recorded the LabView program switches the optical switch back to the interrogation laser output and changes the drive current to tune the laser wavelength by one increment. The process is then repeated until a spectrum has been recorded over the desired wavelength range. The tuning characteristics of the interrogation laser are measured using a fiber ring resonator (FSR: 475 MHz) [23], which allows the relative wavelength scale of the scan to be determined. Although the wavelength relationship with laser drive current is not linear the average wavelength change achieved using this tuning method is ≈ 0.0145 nm per mA.

4. Spectrometer Performance

The presence of a flame in the centre of an optical cavity significantly reduces its optical coupling efficiency, due to perturbation of the excited cavity mode. This results in a reduction in the cavity ring-down time and the resonant cavity transmission when the flame is ignited. Fig. 3 highlights this effect at the off-line wavelength of the 1547 nm normalization laser. This figure shows a comparison of a ring-down measurement in the absence of the flame and a ring-down

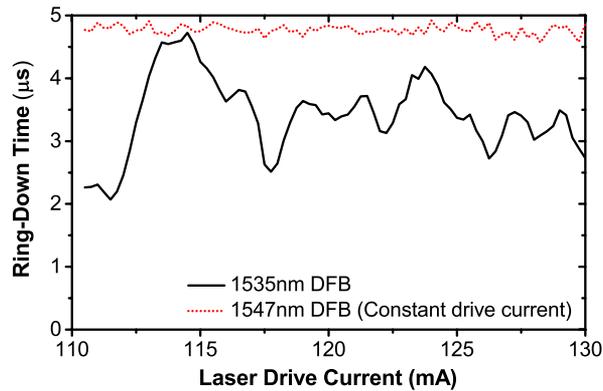


Fig. 4. Ring-down times acquired 3 mm above the burner in a 1.42 equivalence ratio flame.

measurement for a 1.54 fuel equivalence ratio flame where the centre of the TEM_{00} mode is positioned 3 mm above the burner surface. The trigger voltage level has been reduced for the in-flame signal to achieve comparable measurement repetition rates.

The ring-down time for the optical cavity without the presence of the flame is $25.00 \mu\text{s}$. The increase in optical loss in the ignited flame leads to a ring-down time of $4.74 \mu\text{s}$, implying an increase in the fractional cavity loss, X , of 2.85×10^{-4} , calculated using (2). This reduction in coupling efficiency is due to the thermal effects of the flame causing beam steering and thermal lensing of the light into transverse modes other than the TEM_{00} transverse cavity mode. Although the loss in overall cavity transmission indicates that light is being lost from the TEM_{00} mode, it remains the primary excited mode and setting a sufficiently high trigger threshold ensures that the ring-down events recorded are from the TEM_{00} mode only.

Implementing the experimental measurement procedure described in Section 3, Fig. 4 shows a typical raw spectrum recovered at 3 mm above the burner surface in a 1.42 fuel equivalence ratio flame. In this case, the 1535 nm interrogation laser wavelength has been scanned from 1535.3 nm to 1535.55 nm in average increments of 3.6 pm. Averages of 32 ring-down events were taken for each wavelength increment of the 1535 nm laser and also for the 1547 nm measurements. The standard deviation of the 32 individual ring-down traces has been measured to be $0.132 \mu\text{s}$. For the 1547 nm laser, which is equivalent to 3% of its average ring-down time. As stated in Section 2, the drive current for the normalization laser was held constant at the point on the spectrum free of any strong absorption features, providing the dotted [red online] background trace in Fig. 4. The recorded ring-down signals were fitted using a least squares exponential fit algorithm in Matlab. The overall data acquisition time for this spectrum was ≈ 470 s and, as can be seen from Fig. 4, the background ring-down measurement does drift a little over this timescale, meaning that the use of the normalization laser improves the quality of the resulting measurements. The overall drift in ring-down time has been estimated to be $\approx 1 \times 10^{-4} \mu\text{s/s}$ in this case. The source of this drift is thought to be due to a combination of optical alignment drift and fouling of the dielectric mirror coating.

The large number of interfering features presents some difficulty in assigning each one to a specific species. However, the assignment of the main P17e acetylene peak is clear, as shown in the higher resolution spectrum in Fig. 5, which provides a comparison of experimental data taken at wavelength increments of 1.45 pm, between 1535.36 nm and 1535.65 nm, and a modeled and scaled spectrum of acetylene, calculated for a temperature of 1600 K using the HITRAN 2008 database. The measurements were taken at a height of 3 mm above the surface of the burner in a 1.66 equivalence ratio flame. The overall acquisition time for this spectrum was ≈ 3700 s and the ring-down time of the 1547 nm laser was reduced by $0.154 \mu\text{s}$ over this time-scale.

It is also possible to assign some of the stronger peaks as high temperature water vapor transitions using the HITRAN 2010 database [25]. However, the majority of the weaker measured

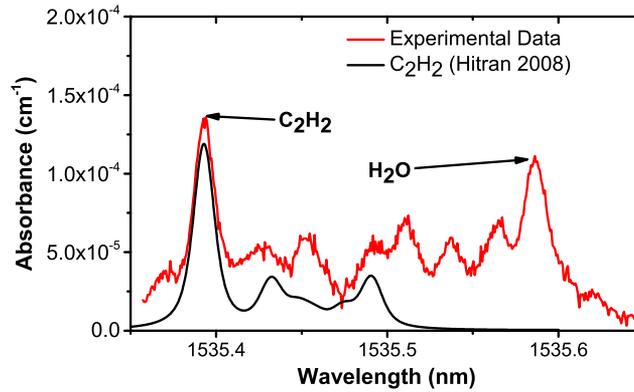


Fig. 5. Higher resolution spectrum acquired 3 mm above the burner in the 1.66 equivalence ratio flame. Also shown is a model spectrum of C_2H_2 from the Hitran 2008 Database [24]. The p17e acetylene transition and H_2O transition are identified.

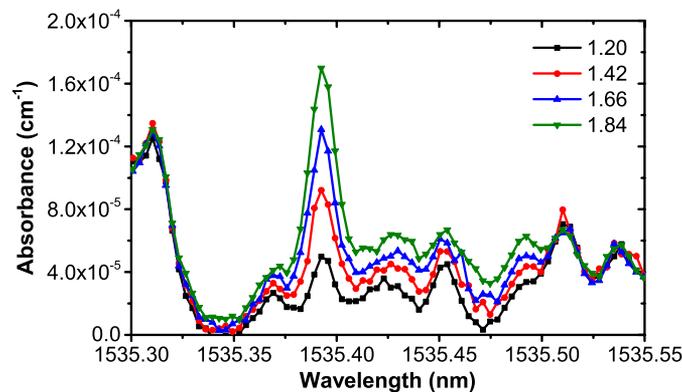


Fig. 6. Lower resolution spectra acquired 3 mm above the burner surface for a range of fuel equivalence ratios (1.20–1.84).

absorption features remain un-assigned in this paper. The SNR for the P17e absorption peak has been calculated to be 32 for this spectrum, by measuring the standard deviation for the 1547 nm reference laser ring-down time and comparing it with the reduction in ring-down time due to the acetylene absorption. The measured absorbance of the P17e feature is $1.3 \times 10^{-4} \text{ cm}^{-1}$ for the above flame conditions, leading to an overall minimum absorption measurement sensitivity (3σ) of $1.2 \times 10^{-5} \text{ cm}^{-1}$.

Finally, Fig. 6 highlights the variation in optical absorption from acetylene as a function of the fuel equivalence ratio, implying an increase in acetylene concentration. This is expected to increase due to the progressively more reducing conditions as the equivalence ratio is increased. Interestingly, the variation in absorbance as a function of equivalence ratio is limited to the region in which acetylene has a contribution, as shown in Fig. 5. It appears that the spectral features for which absorbance is roughly invariant with equivalence ratio may be associated with species, perhaps water vapor, whose concentration at this location in the flame is fairly constant over the range of conditions studied.

5. Discussion

In introducing the application of cw-CRDS for in-situ flame diagnostics, it is worth considering how this method compares to the use of pulsed lasers (typically dye lasers) to perform CRDS in flames. CRDS using pulsed laser sources has been applied to the in-situ measurement of

weakly absorbing species in flames [9]–[11], [26]–[28], achieving sensitivities as low as 10^{-6} fractional absorption. It is therefore necessary to discuss the advantages and disadvantages of both cw-CRDS and pulsed-CRDS in both a thermally homogenous cavity and with an intra-cavity flame.

Typically, in a homogenous environment cavity ring-down spectrometers can achieve sensitivities on the order of 10^{-9} cm^{-1} [2], and this sensitivity is directly related to the gas-laser interaction length. It is therefore essential to contain the light within the cavity for as long as possible, i.e., achieve the longest possible ring-down time.

In a cw-CRDS system light is coupled into a single transverse cavity mode, typically the TEM_{00} , thus requiring accurately designed mode matching optics. To initiate a ring-down the light being coupled into the cavity is switched off, and during the ring-down process it is desirable that all the coupled light not being transmitted through the output mirror continues to resonate in the TEM_{00} mode [29]. In some circumstances the sensitivity of cw-CRDS can be enhanced by improving the mechanical stability of the cavity or by increasing the coupled optical power into the cavity through locking the laser to a single longitudinal cavity mode [30].

Pulsed-CRD systems involve lasers that are much more bulky and expensive than the fiber-coupled diode lasers used for cw-CRDS. On the other hand, the high peak powers of pulsed dye lasers ($\approx \text{MW}$) and the large line-widths ($\approx \text{GHz}$), makes optical coupling into the cavity simpler. It is not necessary to temporarily attenuate the incoming light as the pulse duration of the coupled light is typically shorter than the cavity round-trip time. The implication of this is that there is very little overlap of the coherent field in the cavity, which results in no build up in intensity over time. Therefore, the maximum power that can be coupled into the cavity is just the proportion of light that is transmitted through the high reflectivity input mirror. As the peak pulse power is typically on the order of MW even this small fraction of transmitted light is enough to be detected. In contrast, due to the much lower output power of the laser sources used, cw-CRDS is entirely dependent on the coherent field replicating itself and building up over time to a much higher intra-cavity power.

A further contrast between the approaches becomes apparent when a flame is present within the optical cavity. As resonant effects are minimal in the pulsed regime it follows that any disturbance to the transverse mode structure of the cavity, caused by thermal gradients of the flame, will produce a lesser reduction in the cavity ring-down time. This is not the case for a cw-CRD system, where all the light needs to remain within the TEM_{00} mode. We have previously used CRDS with a pulsed dye laser, with a pulse power of 6 mJ and a line-width of 0.1 cm^{-1} , to undertake studies on singlet methylene and HCO in the same porous plug burner [31]. During these measurements a reduction of $\approx 50\%$ in the ring-down time was observed due to the thermal disturbance of the optical field, which is much less than the $\approx 80\%$ reduction seen in the cw-CRDS setup presented in Section 3. In the cw-CRDS system described in this work the most significant cause for de-coupling from the TEM_{00} mode is therefore the introduction of the flame into the cavity. Any improvements to the mechanical stability of the cavity would have a negligible effect on the overall sensitivity of the flame measurements since thermal losses are dominant.

There are, however, a number of reasons for using a cw-CRDS approach for the quantification of species concentrations in flames, in addition to the considerable practical advantages of diode lasers over dye lasers. Typically, at atmospheric pressure spectral features have line-widths of a few GHz, which is similar to the line-width of a high power pulsed laser source. The resulting output spectrum is therefore a convolution of the spectral feature and the laser line-width. For isolated spectral lines, for example electronic transitions in the visible region, the convolved spectral output will not cause many difficulties in species identification and concentration measurement. However, at wavelength regions with densely populated spectral features, the convolved output from a typical pulsed source makes spectral identification difficult, if not impossible. This is particularly true in the near and mid-infrared regions where the ro-vibrational transitions of vibrationally active molecules are targeted. In this work, we have used DFB lasers with line-widths on the order of megahertz to generate spectra that are a true representation of the physical characteristics of the molecule and its environment. This has allowed us to identify the

acetylene features of interest and show regions where spectral features assumed to be water vapor are present. Furthermore, by working in the near-infrared all vibrationally active species can be targeted. The use of a reference laser in the near-IR at a wavelength where no significant optical absorption occurs allows a very simple, real-time calibration technique that provides absolute measurements of absorbance, even when the cavity alignment may be drifting or the mirrors become fouled over time.

CRDS, whether pulsed or cw is inherently a path-integrated technique, as are all other optical absorption measurements. They are therefore most suited to relatively stable, laminar flames. If spatially resolved concentration measurements were required a tomographic approach would need to be developed. The use of laminar flames also improves the overall sensitivity of cw-CRD as the average of a number of ring-down measurements can be taken. Indeed, the inhomogeneous conditions and complex flame fronts produced by dynamic turbulent flames would cause a greater and more random disturbance to the transverse mode structure of the cavity. In the worst case this could potentially prevent resonance from occurring. The cw-CRDS approach we have taken does, however, show significant potential for the study of trace intermediates in suitable flames, which can be used for the validation of flame chemistry models.

6. Conclusion

We have demonstrated what is, to the best of our knowledge, the first applications of cw-CRDS to conduct in-situ flame measurements. Although there is a significant loss in sensitivity due to thermo-optic effects we still achieved an absorption sensitivity limit (3σ) of $1.2 \times 10^{-5} \text{ cm}^{-1}$ which is a significant improvement on single pass techniques. The spectrometer is immune to noise caused by flame emission and produces a direct measurement of absorption without the complex calibration required by some other cavity based techniques.

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