Width-Increased Dual-Pump Enhanced Coherent Anti-Stokes Raman Spectroscopy (WIDECARS)

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WIDECARS is a dual-pump coherent anti-Stokes Raman Spectroscopy technique that is capable of simultaneously measuring temperature and species mole fractions of N_2, O_2, H_2, C_2H_4, CO, and CO_2. WIDECARS is designed for measurements of all the major species (except water) in supersonic combustion flows fueled with hydrogen and hydrogen/ethylene mixtures. The two lowest rotational energy levels of hydrogen detectable by WIDECARS are H_2 S(3) and H_2 S(4). The detection of these lines gives the system the capability to measure temperature and species concentrations in regions of the flow containing pure hydrogen fuel at room temperature.

I. Introduction

The design of air-breathing supersonic combustion engines is currently being facilitated by creating computational fluid dynamic (CFD) models of turbulent supersonic combustion flow[1]. To create and verify CFD models, time-resolved fundamental properties of turbulent supersonic combustion need to be measured. Coherent anti-Stokes Raman spectroscopy (CARS)[2,3] is a nonintrusive laser-based measurement technique that can measure space- and time-resolved temperature and species concentrations. Studies of hydrogen-fueled supersonic combustion flows were measured with a CARS system design by O'Byrne *et al.*[4]. The CARS system developed by O'Byrne *et al*. can measure temperature and species mole fractions of nitrogen, oxygen, and hydrogen. Typically, CARS systems can only measure relative species concentrations, but because all the major species present in the combustion flow (except water, which is found by difference) were measured, absolute concentration measurements could be made as discussed in Ref. 4.

Future studies are planned to revisit supersonic combustion flow with hydrogen fuel and a mixture of ethylene and hydrogen fuel. To fully characterize these flows, it is desirable to make measurements of as many properties as possible for the full range of conditions within the flow. In these flows, pure, room-temperature fuel is injected into the flow; therefore some regions of the flow will contain only room temperature fuel (hydrogen and/or ethylene). The O'Byrne *et al.* CARS system is incapable of making measurements in pure, room temperature hydrogen as discussed in Ref. 5. The O'Byrne *et al.* system is not ideal for measuring combustion of an ethylene-hydrogen fuel mixture because it does not have the capability to measure any of the carbon species present in the flow (CO_2, C_2H_4, and CO).

Others have designed CARS systems that are closer to the desired measurement attributes for these flows. The dual-pump CARS systems designed by Kearney *et al.* [6] and Beyrau *et al.* [7] have measured many of the major species present in ethylene- and hydrogen-fueled combustion. Additionally, the Kearney *et al.* system is capable of the needed dynamic temperature range in pure hydrogen. Flores[8] designed a single pump CARS system that can measure all major species in ethylene and hydrogen combustion except water and that can also measure pure hydrogen from room temperature to flame temperatures. In the present work, a new CARS system called Width Increased Dual-pump Enhanced CARS (WIDECARS) has been designed to improve on the Flores system by using the dual-pump CARS technique[9]. The dual-pump CARS technique simultaneously probes two spectral regions and produces a spectrally overlapped signal. As a result, WIDECARS improves on the Flores system by increasing the possible spectral resolution and the efficiency of phase matching, while maintaining the same spectral coverage and

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similar signal intensity. A more detailed discussion of all these above-mentioned systems and their comparison to WIDECARS will be included in the following section.

WIDECARS is a dual-pump CARS method that employs a broadband dye laser with a full width half maximum (FWHM) of ~18 nm. This spectral range is twice as wide as a typical CARS broadband dye laser with a gain medium of Rhodamine dyes [4,6,7,9,10,11]. With WIDECARS, all probed species (N_2, O_2, H_2, C_2H_4, CO, and CO_2) are measured simultaneously. This allows for a more complete characterization of the flow. Because WIDECARS measures all the major species (besides water) present in hydrogen-ethylene combustion, absolute species mole fractions can be measured, as demonstrated by O'Byrne *et al*.

To demonstrate the measurement potential of WIDECARS, measurements were made of gas mixtures containing the species WIDECARS was designed to measure. This article includes a discussion of the design of WIDECARS, a comparison of the system's capabilities to those of the other existing CARS systems mentioned above, a description of the experimental setup of WIDECARS, the results of measurements made with a WIDECARS system in various gas mixtures, and the results of spectral fits to the experimental data.

II. The Design of WIDECARS

This section discusses how and why WIDECARS was designed. To better understand the capabilities and limitations of WIDECARS, comparisons are made with other similar CARS systems. WIDECARS has been designed to measure mole fractions of all the major species (besides water) of supersonic combustion fueled with either pure hydrogen or hydrogen mixed with ethylene. This design allows WIDECARS to make absolute mole fraction measurements in these types of flows. The major species present in these flows are nitrogen, oxygen, water, hydrogen, ethylene, carbon monoxide, and carbon dioxide. Additionally, the system has been designed to be capable of making these measurements at all conditions expected in the flow.

Traditionally, the CARS technique is performed with two pump lasers of the same frequency and a third probing (Stokes) laser of a different frequency. This is sometimes called *single-pump* CARS. The spectral region that CARS probes is determined by the difference between the pump and probe frequencies. If the Stokes laser is broadband, then a range of frequencies are probed. The *dual-pump* technique[9] uses lasers of three different frequencies. This allows for two frequency combinations of pump and probe. Therefore, dual-pump CARS simultaneously probes two spectral regions. This design doubles the spectral range probed as compared to a single-pump system. WIDECARS is a simple extension of the dual-pump CARS technique in which the bandwidth of the Stokes laser is increased in order to expand the spectral coverage. More complicated CARS techniques exist such as triple-pump CARS[11], dual-pump dual-broadband CARS[12], and others[13,14]. These techniques could possibly reach the design requirements of WIDECARS. But the design of WIDECARS avoids the complexity of a fourth laser beam and/or an additional or complicated detection system as required in these CARS techniques.

Figure 1 shows the spectral region probed by WIDECARS (red solid and dashed lines) and compares it to other similar CARS systems. The solid lines show the spectral region probed by the broadband dye (Stokes) laser and Nd:YAG (pump) laser frequency combination. For dual-pump techniques, the dashed lines represent the regions probed by the broadband dye laser (Stokes) and narrowband dye laser (pump) frequency combination. The Flores system, shown in black (circles), is not a dual-pump system, and therefore only has one excitation region. The probed regions are drawn in the shape of the spectral profile of the broadband dye laser from each CARS system and are plotted as normalized probing energy verses wavenumber (Raman shift). The

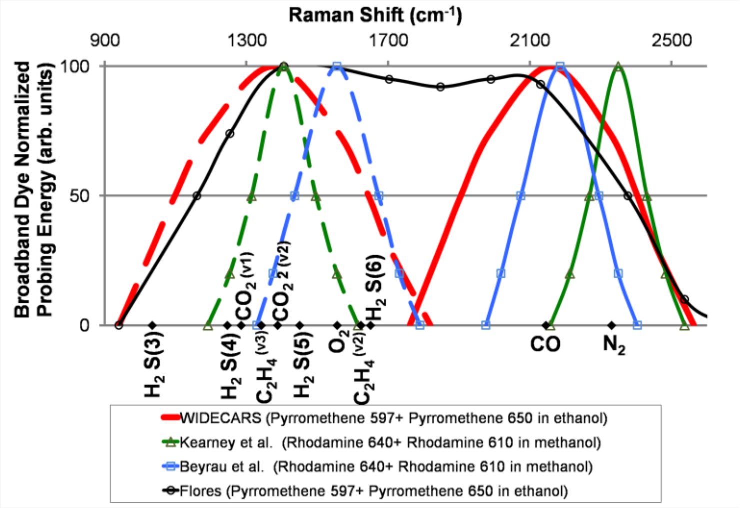

Figure 1: Other CARS techniques spectral probing regions compared to WIDECARS. *The solid lines show the spectral region probed by the broadband dye (Stokes) laser and Nd:YAG (pump) laser frequency combination. For dual-pump techniques, the dashed lines represent the regions probed by the broadband dye laser (Stokes) and narrowband dye laser (pump) frequency combination. Flores did not use dual-pump CARS.*

broadband dye laser spectrum for each system was created using the dye solutions indicated in the legend of Fig. 1 as the oscillator gain medium. Shown in Fig. 1 by green solid and dashed lines (triangles), the CARS system used by Kearney *et al.* could have probed the same species as WIDECARS except carbon monoxide. Although the C_2H_4 v(3) band is in the detection range of the Kearney *et al*. system, it cannot be accurately measured due to interference from the N_2 line. As seen in Fig. 1, the relevant transitions of C_2H_4 v(3) and N_2 are associated with different Raman shifts. However, the frequency of the signal associated with a given probed transition is a function of both this Raman shift and the third laser's frequency. For the Kearney *et al*. system, these frequency combinations result in spectrally overlapped signals for these two transitions.

The blue solid and dashed lines with squares in Fig. 1 show the regions probed by the CARS dual-pump system of Beyrau *et al*. While the Beyrau *et al*. system can simultaneously detect all the same species as WIDECARS, it only detects half as many of the vibrational spectral lines of carbon dioxide. Like the Kearney *et al*. system for the C_2H_4 v(3) line, in the Beyrau *et al*. system the signal from the C_2H_4 v(2) band is directly overlapped with the signal from the lowest energy nitrogen vibrational band and therefore cannot be measured accurately.

The O'Byrne *et al.* dual-pump system probes the same region as the Kearney *et al.* system depicted in Fig. 1 by the solid green curve with triangles. This region is probed by the frequency combination of the Stokes laser and the Nd:YAG pump laser. However, its probing region formed by the combination of the Stokes laser and the narrowband dye pump laser frequencies is the same as the Beyrau *et al*. system (dashed blue with squares).

In fuel-injected flows which WIDECARS is designed to measure, parts of the flow contain pure fuel (hydrogen or a mixture of hydrogen and ethylene). These fuels are injected at room temperature and therefore the system must be able to measure in pure fuels at room temperature. In Fig. 2, the square root of the theoretical CARS signal peak heights (signal strengths) of H_2 S(3), H_2 S(4), H_2 S(5) and H_2 S(6) in pure hydrogen are plotted as a function of temperature (where the number in parentheses is the rotational quantum number). The signal strengths of these S-branch lines were computed in a CARSFT code[15] that was modified as described in Ref. 4. These S-branch spectral lines are the most populated in the probing region of WIDECARS (shown in Fig. 1) for the temperature range in which measurements will be made. Below ~450 K, as the hydrogen gas temperature decreases towards room temperature, all these rotational energy levels become less and less populated. This is indicated in Fig. 2 by a decrease in the signal strength below ~450 K.

As the populations of the H_2 rotational energy states decrease, the CARS signal decreases and will eventually fall below the measurement limit of the CARS system. This *measurement limit* is the level of signal below which the data analysis software (CARSFT) cannot distinguish the signal from the noise. The measurement limit for different CARS systems will vary with the amount of energy used to probe spectral lines and with other attributes of each system such as detector sensitivity and noise, data analysis method, etc. When the O'Byrne *et al*. system was used to make measurements in supersonic combustion flow[5], it showed a measurement limit lower bound of peak height of 3 (square root of the theoretical signal in CARSFT). Square root of the theoretical signal is used in CARSFT because species mole fractions typically scale with the square root of the CARS signal. Using this measurement limit, the corresponding lower bound of temperature of the H_2 S(6) line is indicated by a vertical black dashed line in Fig. 2. The H_2 S(6) line is not populated enough to measure a CARS signal at temperatures lower than 500 K.

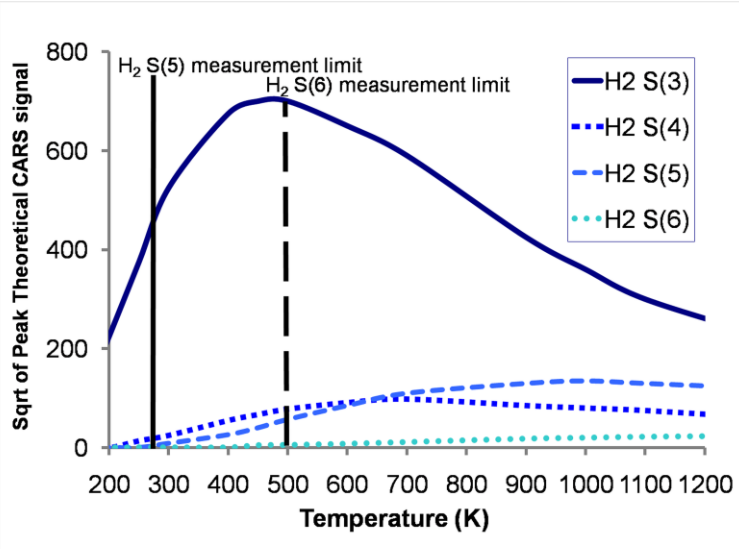

Figure 2*:* Plot of the square root of the theoretical CARS signal peak height of rotational S-branch H_2 lines as a function of temperature. *The square root of the theoretical CARS signal peak heights were calculated in CARSFT with 100% hydrogen. The vertical black lines indicate the lowest temperature at which the H_2 S(5) and H_2 S(6) lines can be detected.*

Because of this lack of CARS signal at low temperatures, the O'Byrne *et al.*-design system was unable in Ref. [0] to measure mole fractions or temperature in regions of the flow containing nearly pure hydrogen fuel injected at around room temperature. The lowest rotational lines detected by the O'Byrne *et al.* system are H_2 S(5) and H_2

S(6). In the regions of the flow below 500 K, the one detected spectral line of H_2 S(5) was not enough for the CARS signal analysis software (a modified CARSFT code)[4,15] to distinguish between temperature and concentration. Therefore, to make measurements of temperature and mole fraction in pure hydrogen, a CARS spectrum must contain signal from two H_2 rotational spectral lines. In gas mixtures that contain more than just hydrogen, the minimum requirements for measurements of temperature and mole fraction of hydrogen are: signal from one H_2 rotational spectral line and a vibrational spectral band from at least one other species.

The Beyrau *et al.* system has the same measurement limitation as the O'Byrne *et al*. system: its two lowest energy H_2 S branch lines detected are also H_2 S(5) and H_2 S(6). The lowest energy rotational H_2 lines detected by Kearney *et al*. are H_2 S(4) and H_2 S(5), which allows for measurements in pure hydrogen down to ~275 K (below room temperature). This is shown in Fig. 2 by the vertical solid black line indicating the lower bound temperature measurement limit of the H_2 S(5) line. However, with this scheme at room temperature, measurements are just above the measurement limit, which may result in noisy data.

The two lowest energy rotational hydrogen lines probed with WIDECARS are H_2 S(3) and H_2 S(4). The inclusion of H_2 S(3) and H_2 S(4) lines guarantees concentration and temperature measurements down to room temperature in pure hydrogen. It also allows for hydrogen detection in mixes of room temperature hydrogen and ethylene fuel. In Fig. 3, the square root of theoretical CARS signal peak height at room temperature of hydrogen S branch lines are plotted against hydrogen mole fraction where the balance species is ethylene. The peak heights were calculated in CARSFT, using hydrogen as the only resonant species and ethylene as the nonresonant background[16]. Estimating the same lower bound measurement limit from the O'Byrne et al. system (i.e. square root of the theoretical signal of 3), a black horizontal line is used to indicate the measurement limit in Fig. 3. This estimate does not account for any changes in noise or other effects that may raise or lower the measurement limit. The H_2 S(4) line height is below the measurement limit for mole fractions less than 0.50. Therefore, H_2 S(3) is included in the WIDECARS probing region to allow measurement of hydrogen concentrations down to 0.03 mole fraction in ethylene at room temperature.

A spectral or empirical model of the vibrational C_2H_4 v(3) band has not yet been developed for the CARSFT code to be used to analyze spectra measured with WIDECARS. Because of the lack of an ethylene model it is possible that, in regions of the flow containing room temperature fuel mix, the hydrogen rotational lines will be needed to determine temperature. As shown in Fig. 3, the H_2 S(3), H_2 S(4) line combination will be needed to measure temperature for mole fractions of hydrogen below 0.95. This line combination is predicted to work as a temperature gauge down to hydrogen mole fractions of 0.50 in ethylene.

Shown in black (circles) in Fig. 1 is the probing region of the Flores system. This system has the capability to detect the same spectral lines as WIDECARS. The Flores system uses a ~40 nm FWHM dual-dye single-Stokes laser to cover the desired spectral region. The Flores system does not use the dual-pump technique and therefore the spectral range of the CARS signal is the same as that of the probed region. A feature of dual-pump CARS is that signals originating from probing two spectral ranges are overlapped on the CCD camera, resulting in wide spectral coverage simultaneous with higher resolution. A disadvantage of this feature is that spectral lines can overlap, in which case the difficulty of data analysis may be increased. If the same collection setup used for WIDECARS were used for the Flores system, a grating with half the dispersion would be required to disperse the full spectral range of the CARS signal on the CCD. Therefore WIDECARS would have twice the spectral resolution as the Flores system. On the other hand, WIDECARS' increased broadband dye spectral range would mean a decrease in its spectral resolution compared to the other dual-pump systems in Fig. 1. Higher spectral resolution allows for increased accuracy of temperature measurements at temperatures for which only the first energy level of the nitrogen

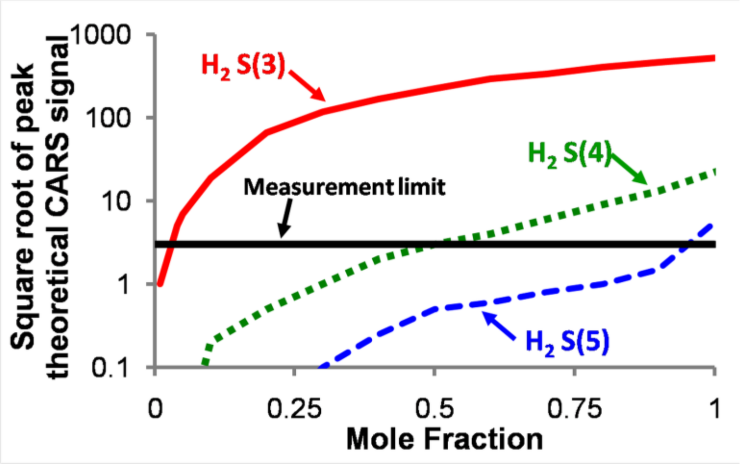

Figure 3*:* **The square root of theoretical CARS signal peak height from CARSFT plotted as a function of the hydrogen mole fraction.** *This relationship is plotted for H_2 S-branch lines at room temperature with a balance gas of ethylene. The measurement limit is a lower bound on the detectable peak height and was obtained from the application of the O'Byrne et al. system in a hydrogen fueled supersonic combustion flow.*

vibrational spectrum is populated.

Another limitation of the Flores system is the broadness of the spectral region covered by the dual-dye single-Stokes laser, which reduces the efficiency of phase matching for its full spectral probing region[8]. If phase matching is optimized for the center wavelength of the broadband dye laser, then the efficiency of CARS signal generation decreases with increasing difference from the center wavelength. Therefore, the maximum losses of CARS signal occur for the spectra probed with the wavelengths farthest from the center wavelength of the broadband dye laser. The largest losses of the spectra probed by the Flores system are 21% for H_2 S(3) and 14% for N_2 . These losses were calculated using the proportionality of the CARS signal intensity to,

$$\left(\frac{\sin\frac{\Delta kl}{2}}{\frac{\Delta kl}{2}}\right)^2 \tag{1}$$

as defined in Ref [2], where Δk is the phase mismatch and l is the length of the probe volume (assumed to be 1.5 mm). The WIDECARS Stokes beam has half the spectral width and therefore increases the efficiency of phase matching compared to the Flores system. The maximum losses of signal due to phase mismatch for the spectra probed by WIDECARS are 4.5% for H_2 S(3) and 3% for O_2, about 5x lower than for the Flores system. In comparison to the other dual-pump systems in Fig. 1, WIDECARS has a larger spectral width; however, its phase matching efficiency at FWHM of the Stokes laser is only ~2 % less.

Because WIDECARS uses the dual-pump technique, its potential signal strength is decreased by a factor of four compared to the Flores system. But WIDECARS reduces the spectral range of the broadband dye laser in comparison to the Flores system; therefore, the energy available for probing each line is increased. Using the same reasoning, the increased spectral range of WIDECARS over the other dual-pump systems decreases its available probing energy by the ratio of the Stokes beams' bandwidths. So overall, WIDECARS has a similar signal strength potential as the Flores system and less than the other dual-pump systems.

In summary, compared to the other dual-pump techniques featured in Fig. 1, WIDECARS has the potential capability to more fully characterize hydrogen and ethylene fueled supersonic combustion flows. This capability is achieved by increasing the width of the broadband dye laser to include the measurement of all the desired species concentrations and to increase the dynamic temperature range, enabling measurements in room temperature fuel. However, the doubled spectral range of WIDECARS reduces the possible resolution, the phase matching efficiency, and the overall signal strength when compared to typical dual-pump systems. Compared to Flores' single-pump CARS system, WIDECARS has the same spectral coverage and similar signal strength, but offers increased spectral resolution and improved phase matching efficiency. Other more complicated CARS techniques[11-14] are available that could possibly measure the same spectral lines as WIDECARS. WIDECARS offers an advantage over these systems by maintaining a simpler optical setup. In conclusion, WIDECARS is a relatively simple system that overcomes the limited spectral coverage offered by typical dual-pump systems and the disadvantages of the Flores system.

III. Experimental Setup

A. Lasers

The experimental setup of WIDECARS consists of a frequency doubled Nd:YAG laser (Spectra Physics DCR-4) (532 nm), a narrowband dye laser (Spectra Physics PDL-2), and an in-house built broadband dye laser. The Nd:YAG (green) laser serves as the pump energy for the narrowband dye and the broadband dye laser. The Nd:YAG laser used for measurements presented in this paper has a 10 Hz repetition rate and produces 10 ns pulses with an output of 370 mJ. The narrowband dye laser is centered at 556.8 nm (yellow) with a FWHM of 0.07 cm^{-1}.

B. Broadband Dye Laser Details

A diagram of the optical setup of the broadband dye laser is shown in Fig. 4. The oscillator cell is side pumped (excited) by a frequency doubled Nd:YAG laser (532 nm) pulsed for 10 ns at a 10 Hz repetition rate. The average maximum input energy to the oscillator cell is 37.9 ± 0.4 mJ. To maximize the conversion efficiency from the pump laser to the emitted laser, the pump laser is expanded in the horizontal direction to use the full length of the dye cell. This expansion is done with a 5.08 cm diameter concave cylindrical lens of -12 cm focal length, placed 21±.5 cm from the front face of oscillator cell. In the vertical direction the excitation light is focused with a 5.08 cm

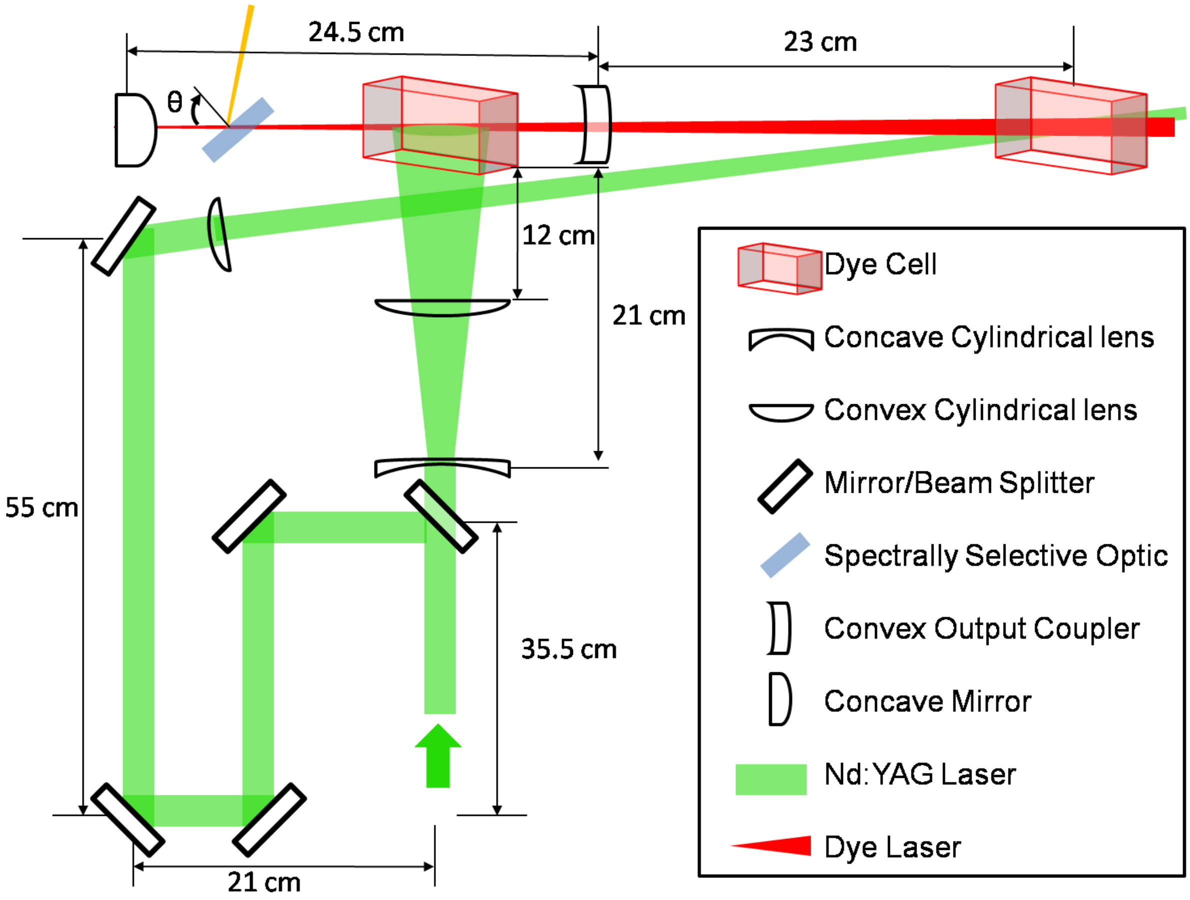

Figure 4: Drawing of optical setup of the laser. *All distances measured with an accuracy of ±0.5 cm.*

diameter, convex cylindrical lens of focal length 15 cm, placed 12±0.5 cm from the oscillator cell. This vertical focus increases the energy density overlap of the pump and oscillator laser beams. Increasing this overlap increases the energy conversion efficiency. The convex lens is mounted on a rotation mount so that the pump beam can be aligned with the path of the oscillator beam. The cross section of the pump beam on the front face of the oscillator cell is 22±1 mm by 4±1 mm.

The oscillator cavity is formed by a concave mirror and a convex output coupler. This gives the oscillator cavity inherent stability for laser beam creation, allowing for easy alignment. This design outputs a divergent beam. Therefore, the laser created by this cavity design never reaches its focus which would be located outside the cavity beyond the back mirror. This reduces the energy density within the cavity and therefore the likelihood of burning optics. The cavity is constructed with a 0.5 m radius convex back mirror and a 0.75 m radius concave output coupler, both with a diameter of 2.54 cm. The distance between the mirrors are 24.5±0.5 cm. The output coupler's coating is 50% reflective and is centered at 589 nm. The back mirror has a coating centered at 600 nm with a manufacturer reported reflectivity of greater than 99% for a 68 nm range. The oscillator dye cell is placed between the mirrors nearer to the output coupler. This is where the diameter of the oscillator beam is the largest allowing for a larger volume of the gain medium to be used, therefore increasing the intensity output of the laser. The dye cell dimensions are ~ 1.5 cm × 2 cm × 5 cm with its longest dimension perpendicular with the pump beam and parallel to the oscillator beam. The dye cell's walls are at Brewster's angle with respect to the propagation direction of the oscillator beam.

A spectrally-selective optic is placed within the oscillator, between the back mirror and the oscillator dye cell. Depending on the type of optic used, mirror or filter, this optic rejects or absorbs light of undesired wavelengths, respectively. The spectral region of light that this optic rejects or absorbs suppresses the gain of the laser in that region. This suppression allows increased gain in other spectral regions of the laser's frequency output operating on the same principle as tunable narrowband dye lasers. Just like narrowband dye lasers, the frequency selective optic channels all the stored energy into a narrower range of emission with low loss in power.

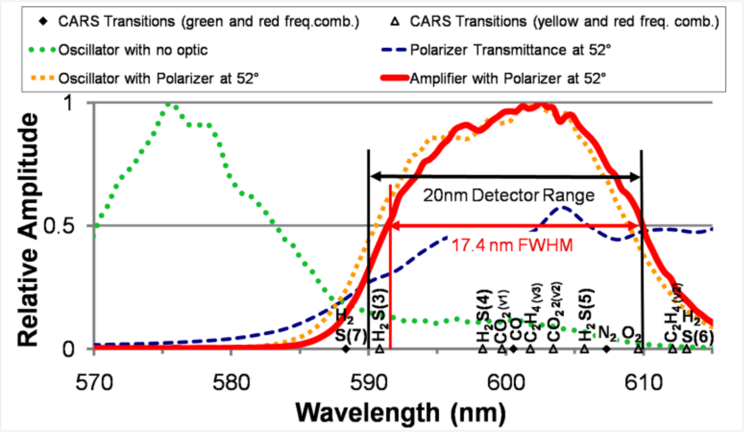

Figure 5: The normalized amplitude of laser output versus wavelength. *The green circle dotted line shows the spectral output of the oscillator of the broadband dye laser with no polarizer in the oscillator cavity. The orange square dotted line is the spectral output of the oscillator cavity containing the polarizer. The red solid line shows the spectral output of the broadband laser after amplification. The polarizer transmittance of unpolarized white light is shown in with a dashed blue line.*

The laser light from the oscillator cavity is passed through an amplifier cell 25.4±0.5 cm away from the output coupler. The amplifier cell's dimensions are ~ 1 cm × 3 cm × 6 cm. It is oriented at Brewster's angle with respect to the propagation of the laser light. The laser is amplified in the cell with a mixture of Rhodamine dyes dissolved in methanol and pumped by light from the Nd:YAG laser. The beams are crossed in the cell at the smallest angle geometrically possible to maximize the overlap length in the cell and therefore increase the energy conversion efficiency. The maximum energy of the amplifier pump beam is 169 ± 1 mJ. To maximize the energy conversion, the cross sections of the beams are matched using a 2.54 cm diameter cylindrical lens with a 2 m focal length in the amplifier pump beam, placed 53±.5 cm from the amplifier cell. The cross sections of the beams are approximately 1 cm^2 as they enter the cell. So that the time overlap of the pump and broadband laser beam in the amplifier dye cell is optimum for energy conversion, the pump beam is delayed with a path 71±0.5 cm longer than the broadband.

WIDECARS system requires a broadband dye laser with a full-width half-maximum (FWHM) of ~18 nm, from 592 to 610 nm. The broadband dye laser spectrum, shown by a red solid line in Fig. 5, is centered at 602.3 ± 0.1 nm (red) and has a FWHM of 17.4 ± 0.1 nm with a range (10%-10% of maximum) of 26.6 ± 0.1 nm as measured with a spectrometer with a resolution of 0.48 nm. The spectrum of the broadband dye laser is produced by using a mixture of Pyrromethene dyes as oscillator gain medium, a mixture of Rhodamine dyes as the amplifier gain medium, and a spectrally selective optic (thin film polarizer) within the oscillator cavity. In the oscillator gain medium, the concentrations of Pyrromethene dyes dissolved in ethanol are 49.08 mg/L PM 597 and 4.60 mg/L PM 650. This dye mixture produces a spectrum that is shown in green circles in Fig. 5. A thin film polarizer (part TP2607K060 from Rocky Mountain Instruments) placed inside the oscillator cavity creates a spectrum of the desired shape, shown in orange squares in Fig. 4. The polarizer is positioned between the back mirror and the gain medium at an angle of incidence of 53 degrees. The thin film polarizer coating is centered at 600 nm. Its transmission curve of unpolarized white light at 53 degrees is shown as a dashed blue line in Fig 5. The polarizer not only helps to shape the spectral output of the laser to the desired spectrum but also rejects the unwanted polarization. The rectangular oscillator dye cell is side pumped by the Nd:YAG laser with a fluence of 0.41 mJ/mm^2. The energy efficiency of the oscillator cavity is 21% with total output of ~8 mJ. The amplifier gain medium is a mixture of Rhodamine dyes with concentrations of 21.7 mg/L R610 and 8.4 mg/L R640 dissolved in methanol. The amplifier shifts the spectral output of the oscillator ~1 nm to the red producing the spectrum shown as a red solid line in Fig. 5. When the rectangular amplifier dye cell is pumped longitudinally, with fluence of 1.6 mJ/mm^2, the overall energy efficiency of the laser is 8% with total output of ~17 mJ.

The spectral attributes of the WIDECARS laser were not the only goals when designing this laser for a practical application of CARS. Other goals of the WIDECARS laser were achieved such as simple construction, safety, and ease of maintenance. The laser has almost the same construction as a typical broadband dye laser, only adding a selective optic in the cavity. The dye lasers offers no more safety hazard than a typical broadband dye laser made with only Rhodamine dyes because Pyrromethene dyes have similar safety guidelines. The PM 650 dye showed a noticeable photodegradation rate over a testing day creating a change in the spectral profile during the day. The rate of this change is similar to a broadband dye Rhodamine dye laser. The spectral output of the laser changes by < 1 nm in shape and location during a testing day (~8 hours). The spectral output from the PM 650 in the dye mixture slowly decreases after several days whether or not the mixture is exposed to pump light. To maintain the spectral output shown in red in Fig. 5, a small amount of PM 650 concentrate is added to the oscillator solution at the beginning of each testing day. A possible solution to make the photodegradation rate slower is to deoxygenate the solution; this was not tested and could be pursued further. The other components of the laser are identical to previously-used broadband dye lasers and therefore will have similar maintenance requirements.

C. CARS Signal Generation and Collection in a Glass Cell Demonstration

The three lasers are crossed in folded BOXCARS phase matching regime[2] to create the CARS signal. The energies of the lasers, measured directly before the 400 mm focal length beam-crossing lens, are 34 mJ from the Nd:YAG, 12 mJ from the narrowband dye, and 17 mJ from the broadband dye. To demonstrate the detection range of WIDECARS, a glass cell 100 mm in length and 1 inch in diameter was centered at the measurement volume. Through the glass cell, room temperature gas mixtures (with known concentrations) were flowed at 0.1 slpm flow rate. These commercially purchased gas mixtures were chosen to contain as many of the species measurable by WIDECARS as possible. The concentrations of the species in the mixtures where chosen to test the predicted measurement limits. The concentrations in the mixtures were certified to 1% of their measured value to verify the accuracy of the CARS system.

The CARS signal, generated in the glass cell, is reduced by a neutral density filter of appropriate strength to prevent saturation on the CCD camera. Then the signal is dispersed by a ¾ m spectrometer with an 1800 line/mm grating. The CARS signal is then collected on to a 1 inch PixelVision (1100 × 300 pixel) CCD, producing a detector range of ~20 nm or ~600 cm^{-1}. This range is shown in Fig. 4 by vertical black lines. Black diamonds in Fig. 4 show the frequencies of the broadband dye laser that will excite resonant CARS transitions (spectral lines) when combined with the green laser frequency. Black triangles in Fig. 5 represent the frequencies of the broadband dye laser that will probe resonant CARS transitions when combined with the yellow frequency laser. The detector range allows for collection of the species probed from O_2 to H_2 S(3), but excludes the probed C_2H_4 v(2), H_2 S(6), and H_2 S(7) lines. All species collected are within the FWHM of the broadband dye laser profile except H_2 S(3), which is placed at 40% of the maximum. Spectral lines are probed within the FWHM so that the probing intensities are larger than the shot-to-shot spectral shape fluctuations of the laser. These spectral shape fluctuations contribute to noise in the collected CARS spectra, keeping the probing intensity large, in relation, increases the signal to noise ratio.

The H_2 S(3) spectral line is placed slightly outside the FWHM as a strategy to increase the dynamic range of WIDECARS. The H_2 S(3) spectral line has a much larger signal intensity than all other probed the spectral lines, especially at cold fuel conditions. Probing the H_2 S(3) line with less intensity reduces its signal intensity, which will reduce the conditions at which this line will saturate the CCD. Also, this probing intensity reduction will allow the other species to be collected with higher signal intensities, increasing their signal-to-noise ratio. Because H_2 S(3) has such a large signal intensity, the slightly increased noise from probing it at 40% of the Stokes laser profile is predicted to be minimal.

D. Data Analysis

The spectra presented in the results have been processed by the following steps. After collection on the CCD, the background is then subtracted from the signal. Then it is divided by an averaged nonresonant spectrum, collected with argon gas in the glass cell. This removes the spectral profile of the broadband dye laser from the CARS signal. The square root of the data is taken, which makes the scale of the spectral lines approximately proportional to their mole fraction. The spectra are then fit in a new code and methodology developed by Cutler *et al.*[17]. The new code uses a library of theoretical CARS spectra calculated in CARSFT. The fitting mode of CARSFT was not used because it converges to results that are dependent on the initial conditions when fitting for more than three species. The Cutler *et al*. code has demonstrated the capability to fit four species at once. The ethylene spectral line is not fitted because, as previously mentioned, a Raman spectral model for ethylene does not exist. In these fits, the ethylene spectral line has been blocked and an estimated value of the nonresonant background susceptibility was used from Ref. 16. The addition of an empirical model of ethylene to this code may be conducted in future work.

IV. Results and Discussion

A demonstration of the species detection capability of WIDECARS was performed by taking measurements of gases slowly flowing through a glass cell. Sample results from the demonstration are shown in Fig. 6 and Fig. 7. All measurements for this demonstration were taken at room temperature.

The gas measured in Fig. 6 has a composition of 40% hydrogen, 1% carbon dioxide, 1% carbon monoxide, 1% ethylene, and 57% nitrogen. The spectral lines visible in Fig. 5 from left to right are: H_2 S(3), H_2 S(4), CO_2 v(1), CO, C_2H_4 v(3), CO_2 2 v(2) and N_2. This spectrum is a single-shot sample from a series of ~100 spectra. The fitted compositions for this single-shot spectrum are 28% hydrogen, 1.7% carbon dioxide, 1.4% carbon monoxide, and 67% nitrogen. Note that the ethylene composition cannot be fit because of the lack of a theoretical model and so the ethylene resonant part of the spectrum is omitted from the fitting. The mean value fitted results for a series of ~100 shots are 321±23 K, 30±6% hydrogen, 1.4±0.3% carbon dioxide, 1.1±0.6% carbon monoxide, and 66±5% nitrogen. The uncertainties quoted with the means are the standard deviations, given as a representation of the single-shot uncertainty in the instrument. The mean composition fit to hydrogen is 25% low because of the same modeling error as reported in Ref. 4. Because the species mole fractions to add to one (including nonresonant species), the error in the hydrogen model creates errors in the concentration fits of all the species. This is most notable in the species with the largest concentration (nitrogen) which has a mean that is high by 14%. The standard deviation of the mole fraction of hydrogen (6%) is larger than those reported in Ref. 4 of the O'Byrne *et al.* system (~3%). This could be a result of noise from large variations of the broadband dye laser intensity when probing the H_2 S(3) line. As discussed in the previous section, the H_2 S(3) line is placed slightly outside the FWHM of the broadband dye laser. Just as the hydrogen mean fit affects the means of the other species, it is expected to affect their standard deviations, explaining the high nitrogen standard deviation of 5%.

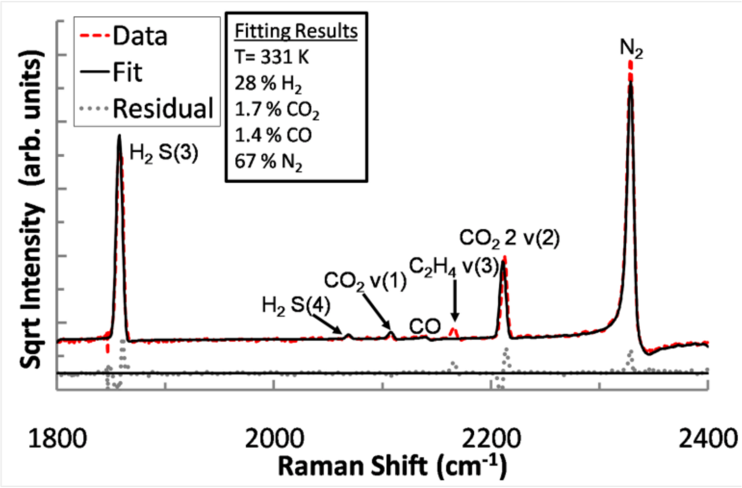

Figure 6*: * **Single-shot CARS spectrum of gas mixture** *40% H_2, 1% CO_2, 1% CO, 1% C_2H_4, and 57% N_2 at room temperature. The fit does not include C_2H_4.*

In the CARS spectra, the nitrogen spectral line has the maximum intensity, which was just below saturation when a neutral density filter of 47% intensity reduction was used. This single-shot spectrum shows that H_2 S(4) is detectable at 0.40 mole fraction, which is slightly lower than the theoretical measurement limit of 0.50 mole fraction predicted in Fig. 3. This spectrum also demonstrates that at room temperature, ethylene will be detectable down to a 0.01 mole fraction.

In Fig. 7, another single-shot WIDECARS spectrum is shown measured in a gas mixture with a composition of 3% hydrogen, 20% carbon dioxide, 8% carbon monoxide, 10% ethylene, and 59% nitrogen. The spectral lines visible in Fig. 6 from left to right are: H_2 S(3), CO_2 v(1), CO, C_2H_4 v(3), CO_2 2 v(2), and N_2. When a neutral density filter with 1% transmittance was used to reduce the CARS signal, the CO_2 2 v(2) spectral line was just below saturation. The fitted concentration results for this single-shot spectrum are 2.9% hydrogen, 21% carbon dioxide, 8.6% carbon monoxide, and 59% nitrogen. The fitted mean temperature from a series of ~100 shots is 276±34 K. The mean values of the fitted concentrations are 1.8±3% hydrogen, 19±2% carbon dioxide, 9.4±1% carbon monoxide, and 61±3% nitrogen. Because of the low concentration of hydrogen in this gas mixture, the inaccuracy of the hydrogen mole fraction model has

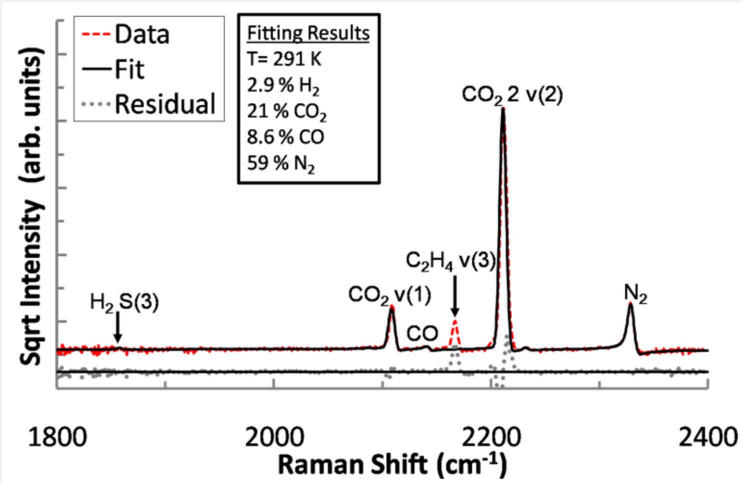

Figure 7*: * **Single-shot CARS spectrum of gas mixture** *3% H_2, 20% CO_2, 8% CO, 10% C_2H_4, and 59% N_2 at room temperature. The fit does not include C_2H_4.*

less effect on the other species than in the previous gas mixture. Therefore, the mean values fitted for this gas mixture are more accurate than the previous gas mixture presented. The mole fraction standard deviations representing the single-shot uncertainties are comparable (near 3%) to those reported in Ref. 4 of the O'Byrne *et al.* system.

This gas mixture contains a concentration of hydrogen at the previously predicted measurement limit of H_2 S(3) in Fig. 3. This measurement limit appears to be accurate: Fig. 7 indicates that the H_2 S(3) is almost indistinguishable from the noise. But the measurement limit may actually be at a lower mole fraction, because the hydrogen mole fraction fits to a value greater than a gas containing no hydrogen. Whether the hydrogen mole fraction fit is to noise or to signal is difficult to assess. To further verify the measurement limit, gases containing decreasing amounts of hydrogen mole fractions could be measured and fit.

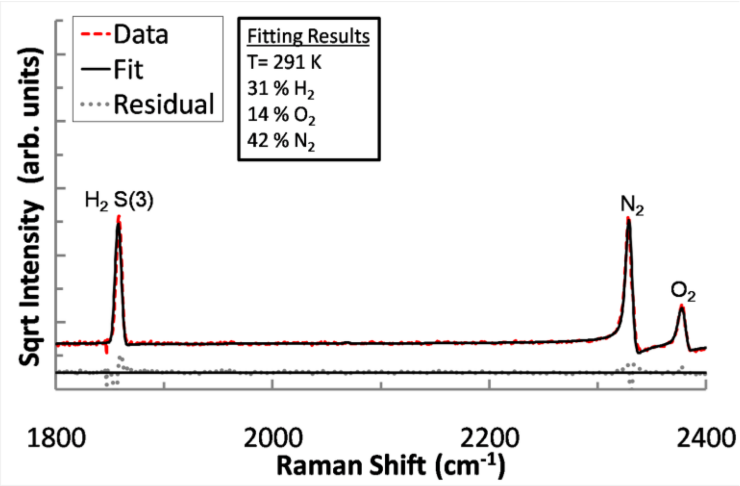

Figure 8*:* Single-shot CARS spectrum of unlit water welder gases mixing in air, concentrations unknown.

Figure 8 shows a single-shot measurement made at room temperature in a jet of hydrogen and oxygen produced by a unlit water welder mixing with ambient air; detected are the spectral lines H_2 S(3), N_2 , and O_2 . To prevent an explosion, the measurements of the water welder gases were made in the open air and not in the glass cell. Because these measurements were made in open air, the concentrations of the shown spectrum are unknown. The fitted results are 291 K for temperature and concentrations of 14% for oxygen 42% for nitrogen, and 31% for hydrogen. Figures 6, 7, and 8 in combination show all the species detectable with WIDECARS: nitrogen, oxygen, hydrogen, ethylene, carbon monoxide, and carbon dioxide.

Higher temperature spectra of these gas mixtures were not collected because of ventilation limitations of the laboratory in which this testing was performed. At higher temperatures, there are other spectral lines that WIDECARS can detect that are not shown in these results. These lines include H_2 S(5) and higher energy lines from vibrational bands of the other molecules. As the temperature of the gas species increases, higher energy levels of the molecules will become increasingly populated.

Because the species' spectra are tightly spaced, when the higher energy levels become more populated, spectra of some species will become overlapped. Most species combinations that have the potential to overlap, such as N_2 and O_2, C_2H_4 and CO, do not coexist at high temperatures in combustion flows. N_2 and CO_2 2 (v2) spectra coexist at high temperatures and therefore can have spectral overlap of their higher energy levels. This overlap of spectra has the potential to increase the difficulty for a fitting code to distinguish between the different species' spectra. But Refs. 11,18, and 19 mention no difficulties in fitting this spectral overlap, perhaps because the spectral shapes of N_2 and CO_2 2 (v2) differ vastly.

If fits of higher temperature measurements with WIDECARS show that the conflict of the N_2 and CO_2 2 (v2) spectra at higher temperatures is a problem, then a possible solution is to change the placement of N_2 and CO_2 2 (v2) spectra. This can be done by tuning the narrowband dye and the broadband dye to a different combination of wavelengths that will place the N_2 spectra in-between H_2 S(3) and H_2 S(4). This alternative spectral arrangement places the CO spectra at the edge of the broadband dye spectrum and may cause the loss of the capability to measure carbon monoxide.

Another potential problem with the current wavelength combination is the possible interference between the spectral response of the C_2 Swan band and N_2 as seen in Ref. 20-22. Soot can be present in ethylene combustion. If soot is present in significant quantities, a signal from the C_2 Swan band will interfere with the nitrogen vibrational signal. This will cause incorrect temperature fitting as shown in Ref. 22. If significant amounts of soot are present in the flow, this problem could be mitigated by using the same previously mentioned alternative spectral arrangement. Unfortunately, the soot signal is probed by the same frequency combination as oxygen. So while this alternative arrangement would avoid overlap of the soot signal for all other spectra, oxygen measurement would be confounded.

V. Conclusion

WIDECARS can detect all major species in ethylene and hydrogen combustion except water, which can be inferred by difference. This allows for absolute measurement of species concentrations in these types of flows. WIDECARS's inclusion of H_2 S(3) and H_2 S(4) allows temperature measurement in pure hydrogen for the full temperature range (room to flame temperature) and detection of hydrogen at room temperature for hydrogen mole fractions as low as ~0.03. This allows for temperature and concentration measurement in fuel injection zones. The measurement limits of WIDECARS for hydrogen have currently only been approximated using theoretical signal levels from CARSFT and the measurement limit from the O'Byrne *et al.* CARS system. The slowly flowing glass cell measurements did not fully verify the lower bound limit of the system's ability to measure hydrogen concentration at room temperature. The actual measurement limits need to be assessed using more gas mixtures with known small concentrations of hydrogen and fitting the measured spectra. For WIDECARS to make absolute measurements in ethylene combustion, a theoretical or empirical model for ethylene must be developed and incorporated into the fitting code.

WIDECARS has currently only been tested on room temperature gases. Next, WIDECARS must be tested for the full range of temperatures in a calibration flame (e. g. a Hencken burner). If the spectral overlap of nitrogen and carbon dioxide causes poor fitting at high temperatures or signal from soot causes interference with the nitrogen signal, a slightly different arrangement of wavelengths of the lasers may be advantageous. WIDECARS has been demonstrated to have the capability to detect nitrogen, oxygen, hydrogen, ethylene, carbon monoxide, and carbon dioxide simultaneously; therefore, this system has the potential to be very useful for measurements of supersonic ethylene and hydrogen combustion flows.

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References

[1] Keistler, P. and Hassan, H. A., "Simulation of Supersonic Combustion Involving H_2/Air and C_2H_4/Air", *47th AIAA Aerospace Sciences Meeting*, AIAA-2009-28, Orlando, Florida, Jan. 5-8, 2009.

[2] Eckbreth, A. C., *Laser Diagnostics for Combustion Temperature and Species*, Gordon & Breach, Amsterdam, Nederland, 1996.

[3] Roy, S., Gord, J. R., and Patnaik, A. K., "Recent advances in coherent anti-Stokes Raman scattering spectroscopy: Fundamental developments and applications in reacting flows," *Progress in Energy and Combustion Science*, doi:10.1016/j.pecs.2009.11.001, 2009.

[4] O'Byrne, S., Danehy, P. M., Cutler, A. D., and Tedder, S. A., "Dual-Pump Coherent Anti-Stokes Raman Scattering Measurements in a Supersonic Combustor " AIAA J. Vol. 45, 2007, pp. 922-933.

[5] Tedder, S. A., Bivolaru, D., Danehy, P. M., Weikl, M. C., Beyrau, F., Seeger, T., and Cutler, A. D., "Characterization of a Combined CARS and Interferometric Rayleigh Scattering System" *45th AIAA Aerospace Sciences Meeting and Exhibit*, AIAA-2007-871, Reno, Nevada, Jan. 8-11, 2007.

[6] Kearney, S. P., Frederickson, K., and Grasser, T. W., "Dual-pump coherent anti-Stokes Raman scattering thermometry in a sooting turbulent pool fire" *Proceedings of the Combustion Institute,* Vol. 32, 2009, pp. 871-878.

[7] Beyrau, F., Datta, A., Seeger, T., and Leipertz, A., "Dual-pump CARS for the simultaneous detection of N_2, O_2 and CO in CH_4 flames", *J. of Raman Spec*. Vol. 33, 2002. pp. 919-924.

[8] Flores, D. V., "Analysis of Lean Premixed Turbulent Combustion Using Coherent Anti-Stokes Raman Spectroscopy Temperature Measurements" PhD dissertation, Chemical Engineering Department, Brigham Young University, 2003.

[9] Lucht, R. P., "Three-laser coherent anti-Stokes Raman scattering measurements of two species" *Opt. Lett*. Vol. 12, 1987, pp. 78-80.

[10] Yueh, F. Y. and Beiting, E. J., "Simultaneous N_2, CO, and H_2 multiplex CARS measurements in combustion environments using a signal dye laser", *Applied Optics*. Vol. 27, 1988. pp. 3233-3243.

[11] Roy, S.,. Brown, M. S, Velur, V. N., Lucht, R. P., and Gord, J. R., "Triple-pump coherent anti-Stokes Raman scattering (CARS): temperature and multiple-species concentration measurements in reacting flows" *Opt. Comm.,* Vol. 224, 2003, pp. 131-137.

[12] Weikl, M. C., "Development of a simplified dual-pump dual-broadband coherent anti-Raman scattering system" Applied Optics. Vol. 48, 2008, pp. 43-50.

[13] Anderson, T. J. and Eckbreth, A. C., "Simultaneous Coherent Anti-Stokes Raman Spectroscopy Measurements in Hydrogen-Fueled Supersonic Combustion", *J. Propulsion*. Vol. 8, 1992, pp. 7-15.

[14] Eckbreth, A. C., Anderson, T. J., and Dobbs, G. M., "Multi-Color CARS for Hydrogen-Fueled Scramjet Applications", *Applied Physics B.*, Vol. 45, 1988. pp. 215-223.

[15] Palmer, R. E., "The CARSFT computer code for calculating coherent anti-Stokes Raman spectra: user and programmer information", Report SAND89-8206, Sandia National Laboratories, Livermore, CA, 1989.

[16] Snelling, D. R., Sawchuck, A. A., and Parameswaran, T., "Measurements of the total third-order nonresonant susceptibilities of C_3H_8, CO_2, and C_2H_4, and their application to N2 CARS thermometry", *Applied Optics*, Vol. 32, 1993. pp. 7546-7550.

[17] Cutler, A. D. and Magnotti, G., "CARS Spectral Fitting of Multiple Resonant Species Using Sparse Libraries", *48th AIAA Aerospace Sciences Meeting Including the New Horizons Forum and Aerospace Exposition*, Orlando, Florida, Jan. 4-7, 2010.

[18] Roy, S., Meyer, T. R., Lucht, R. P., Belovich, V. M., Corporan, E., and Gord, J. R., "Temperature and CO_2 concentration measurements in the exhaust stream of a liquid-fueled combustor using dual-pump coherent anti-Stokes Raman scattering (CARS) spectroscopy", *Combustion and Flame*. Vol. 138, 2004, pp. 273-274.

[19] Meyer, T. R., Roy, S., Lucht, R. P., and Gord, J. R., "Dual-pump dual-broadband CARS for exhaust-gas and CO_2-O_2-N_2 mole-fraction measurements in model gas-turbine combustors", *Combustion and Flame*. Vol. 142**,** 2005, pp. 52-61.

[20] Kearney, S. and Jackson, M. N., "Dual-Pump Coherent Anti-Stokes Raman Scattering Thermometry in Heavily Sooting Flames", *AIAA Journal*. Vol. 45, 2007, pp. 2947-2956.

[21] Brackmann, C., Bood, J., Bengtsson, P., Seeger, T., Schenk, M., and Leipertz, A., "Simultaneous vibrational and pure rotational coherent anti-Stokes Raman spectroscopy for temperature and multispecies concentration measurements demonstrated in sooting flames", *Applied Optics*, Vol. 41, 2002, pp. 564-572.

[22] Malarski, A., Beyrau, F., and Leipertz, A. "Interference effects of C_2-radicals in nitrogen vibrational CARS thermometry using a frequency-doubled Nd:YAG laser", *J. Raman Spectrosc.*, Vol. 36, 2005, pp. 102-108.