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Dual-Pump CARS Probing of Meter-Scale Turbulent Pool Fires

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Presented here are broadband, dual-pump CARS measurements which were performed in a 2-meter diameter methanol pool fire. Single-shot temperature and relative mole fractions were obtained simultaneously. The temperatures were compared to traditional thermocouple measurements in the pool fire. It was found that the CARS mean temperatures agree to within 4% of the thermocouple measurements, while the RMS temperatures were an order of magnitude less for the thermocouple. The accuracy and precision of the single-shot temperature measurements were characterized by comparison to a laboratory standard. It was determined that between 500-1400 K the CARS instrument was accurate to better than 4% and the measurements were reproducible to within 6%.

I. Introduction

FIRE remains one of the dominant risks not only to personal safety but to commercial and military assets as well. More effective risk-management requires a greater understanding of the fundamental physics of fire. As predictive modeling tools become more highly developed, a more sophisticated experimental approach is required, which can measure the properties of interest on the scale demanded by simulation. For this reason, optical diagnostics have become a vital tool in the field of combustion research[1,2]. Traditionally, fire testing has employed physical-probe measurements, but the spatial and temporal scales of turbulent flames are such that probe measurements often cannot provide the necessary resolution. Additionally, physical sensors, such as thermocouples, are prone to bias errors, resulting from sensor intrusion, thermal lag, lead conduction, soot deposition and radiative heat loss. At high temperatures these errors can reach 40%[3]. In place of traditional, physical probes, the fire community has turned to implementing optically-based techniques for investigating fire environments. Recent applications of optical diagnostics for fire experiments include particle-image velocimetry and scalar imaging with planar laser-induced fluorescence[4,5], tunable diode laser absorption spectroscopy for species detection[6], and thermometry using IR emission[7], and *in situ* pyrometric probes[6-8].

A popular optical technique for probing combustion environments is coherent anti-Stokes Raman spectroscopy (CARS). This technique has many advantages over other optical techniques. By employing a broadband Stokes laser, a complete spectral profile may be obtained on a single-shot basis for the species of interest. Using the dual-pump approach provides flexibility in probing multiple species simultaneously and the capability of tuning the wavelength of the signal. Additionally, the CARS technique minimizes line-of-sight averaging, which can be more severe for other optical techniques, such as absorption or emission. Of primary importance, however, is the ability of CARS to cope with particulate/soot laden flames. At heavy soot loading, other techniques succumb to optical interference from soot scattering, emission, and absorption much more readily than CARS. This consideration alone makes CARS the technique of choice for investigating particle/soot laden flames, which are commonly encountered in fire testing.

In this study, temperature and relative mole fraction results will be presented, demonstrating the effectiveness of the broadband, dual-pump CARS approach. The optical thermometry measurements will be compared to traditional thermocouple measurements, which will show the superior temporal resolution of the CARS instrument. Additionally, relative mole fraction data will be presented indicating the advantage offered by utilizing the dual-

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pump configuration. Lastly, the accuracy and precision of the CARS temperature data, obtained from fitting of the N_2 *Q*-branch signature, will be characterized by comparison to a laboratory standard.

II. Experimental

The physics of the dual-pump CARS approach were first demonstrated by Lucht[10]. In order for a molecular species to exhibit a resonance in the degenerate-pump CARS process, Eq. (1) must be satisfied, where ω corresponds to frequencies of the pump and Stokes beams and the Raman frequency of the species of interest.

$$\omega_{Pump} - \omega_{Stokes} = \omega_{v,J} \qquad (1)$$

In dual-pump CARS, two pumps of different frequency are used, and each pump/Stokes combination accesses the Raman resonance for different species. For example, N_2 and O_2 can be probed simultaneously if the pump 1, pump 2, and Stokes wavelengths are 532 nm, 556 nm and 607 nm, respectively. The pump-1/Stokes combination will access the Raman frequency of N_2 and the pump-2/Stokes pair will access the Raman frequency of O_2. The resulting CARS signal frequencies will be given by Eq. (2) and Eq. (3),

$$(\omega_1 - \omega_S) + \omega_2 = \omega_{CARS1} \qquad (2)$$

$$(\omega_2 - \omega_S) + \omega_1 = \omega_{CARS2} \qquad (3)$$

such that the signals from the two species of interest are in close spectral proximity and can be placed on the same detector. Additionally, the position of the N_2 Raman *Q*-branch signature used for thermometry may be spectrally tune away from electronic and Raman-resonant interferences from the C_2 molecule which is produced by laser ablation of soot particles, enabling measurements in sooting flames commonly encountered in fire testing. [11,12]

The facility and apparatus used to perform this work has been covered in depth previously and will only be reviewed here[9]. This work was performed in the FLAME (Fire Laboratory for Accreditation of Models and Experiments) facility located within the Thermal Test Complex at Sandia National Laboratories. The facility test bay is 18.3 m in diameter with a ceiling height of 12.2 m. A 2-m-diameter pan with 50 mm depth is located at the center of the facility floor and is recessed so that the lip of the pan is flush with the steel-grated floor. Air is drawn in through the basement of the facility via a ring of balanced and conditioned air ducts by the natural draft of the fire, and excess air and combustion products are exhausted through the facility chimney to an electrostatic precipitator and vented to the atmosphere through a smokestack. The walls of the test bay are water cooled to provide a controlled, ambient-temperature radiative boundary condition. A schematic depicting the layout of the facility is shown in Figure 1. The duration of a typical test is 15-20 minutes and, while the facility is capable of handling many types of liquid and gaseous fuels, only data acquired from methanol fires will be presented here.

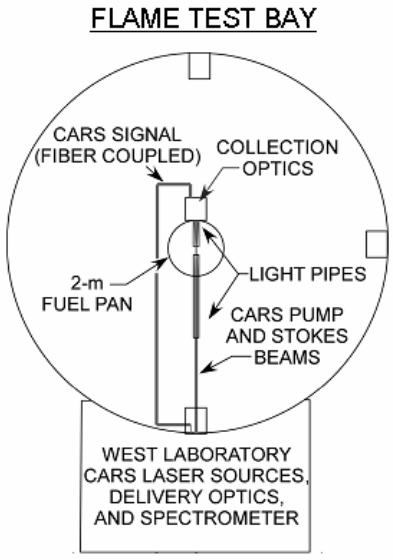

Figure 1. Schematic of the test bay.

Adjacent to the test bay are three laboratory spaces which were designed to facilitate laser-diagnostic measurements of the combustion environment. The west laser lab houses the CARS instrumentation. A depiction of the optical layout is shown in Figure 2. This CARS system is nearly identical to the degenerate-pump CARS system used by Kearney and Grasser[9]. The only substantive difference between the two systems being the inclusion of a narrowband dye laser to replace one of the degenerate pump beams used previously.

In this system, the beam from an injection-seeded, frequency doubled, Q-switched Nd:YAG laser with 8-ns pulse width, 0.003-cm^{-1} linewidth and ≈1.7 J/pulse is divided into three optical paths. The first path is to be used as a CARS pump beam. The second path pumps the broadband Stokes dye laser; and the last path pumps the narrowband dye laser, which acts as the second pump beam for the CARS process. The Stokes dye laser is operated multimode and uses a mixture of Rhodamine 610 and Rhodamine 640 in methanol. The output is optimized for CARS probing of N_2, with a line center of approximately 607 nm and a linewidth of approximately 225 cm^{-1}. The tunable

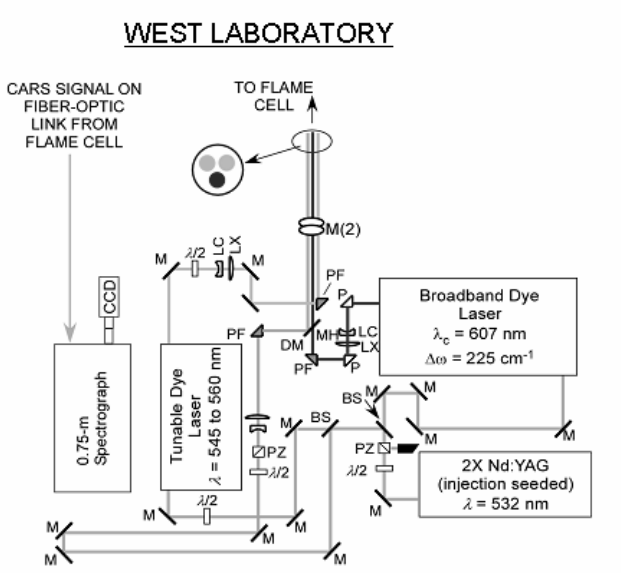

Figure 2. Optical layout of the CARS instrument. Legend is as follows: (BS) beam-splitter; (M) dielectric turning mirror; (M2) mirror periscope; (LC) concave lens; (LX) convex lens; (P) turning prism; (PF) turning prism on fine-adjust mount; (PZ) polarizer; (λ/2) half-wave rotator.

narrowband dye laser (Continuum ND6000) uses Rhodamine 590 dye in methanol, has a manufacturer-specified linewidth of 0.08 cm^{-1}, and is tuned to approximately 556.4nm, which results in a CARS signal near 493 nm. For the methanol pool-fire data presented here, the energies are 60, 70 and 28mJ/pulse for the pump-1, pump-2 and Stokes beams, respectively. The pump-2 and Stokes beams are expanded using telescopes to match the diameter and focus of pump 1. The beams are oriented in the folded BOXCARS configuration prior to entering the test bay.

Inside the test bay, the beams are directed toward a set of enclosed optical rails which shield the focusing and collecting optics from the fire. The ends of the optical rails protrude above the pan, reducing the path length through the fire to approximately 0.67 m, minimizing beam steering. Within the focusing optical housing a 1000-mm-focal-length lens crosses and focuses the beams approximately 1 m above the center of the pan, where a 50-100-μm diameter × ~10-mm long CARS measurement volume is formed. The beams are aligned through a 100-μm-diameter pinhole which is placed at the focus. In the collecting optical housing, a 1000-mm lens collimates the pumps, Stokes and CARS-signal beams. A series of four dichroic mirrors is used to separate the signal from the pump and Stokes beams. After separation, a 100-mm focal-length lens couples the signal into a 100-μm-diameter, 30-m-long optical fiber. An interference filter (%T>90% at 493nm) inserted between the lens and fiber removes any remaining pump or Stokes energy. The 30-m optical fiber couples the signal to the slits of the spectrometer in the west laser lab. The slits are open to 50 μm and the 0.75-m spectrometer utilizes a 1200 l/mm grating. The dispersed signal is relayed to the CCD detector by a lens pair with a magnification of 3.75. At the CARS signal wavelength, the back-illuminated CCD has a quantum efficiency of 93%. The spectral resolution of the instrument, estimated from the FWHM of an emission line from a xenon lamp is ≈1.8 cm^{-1}. In room-temperature air, the peak intensity of the resulting single-shot signal averaged ≈3 million photoelectrons/shot, while the intensity ranged from 1-7 million photoelectrons/shot. As many as three orders of magnitude are lost in the peak signal intensity at the highest temperatures exhibited by the methanol pool fire. In a typical acquisition several thousand single-shot spectra may be recorded in 15-20 minutes. For comparison purposes, three thermocouples (diameters 1.016 mm, 1.5875 mm, 3.175 mm) were inserted into the fire ≈76 mm from the CARS probe volume. A tube furnace with 25.4-mm bore and maximum temperature of 1400 K was used as a laboratory standard to characterize the accuracy and precision of the dual-pump CARS temperature measurement.

III. Results and Discussion

A. Dual-Pump CARS Thermometry

The dual-pump CARS apparatus described was used to acquire spectra from two 2-m-diameter methanol pool fires, with the CARS probe volume fixed at the center of the fire plume and 1 m above the surface of the fuel pool. The raw spectra are background subtracted and normalized with respect to the average Stokes-laser profile, obtained from nonresonant CARS spectra of argon. Nonlinear least-squares fits were performed using the Sandia CARSFT code[13]. Modifications of CARSFT to accommodate dual-pump CARS were performed and summarized by Hancock *et al.*[14] and we refer the reader to their work for a more detailed description of the dual-pump CARS equations used in CARSFT. The parameters in the fitting routine include a vertical shift to account for shot-to-shot variation in the optical background correction, the temperature, and the mole fractions of N_2, O_2 and H_2. An example of typical single-shot spectra and the corresponding best-fits are shown in Figures 3 and 4. From the fits to the single-shot spectra the temperature and the relative mole fractions (O_2/N_2, H_2/N_2) data may be extracted. Since the nonresonant susceptibility of the bath-gas is uncertain in the dynamic, turbulent pool-fire environment, only relative mole fractions may be extracted. The main source of noise in the spectra is due to mode-amplitude fluctuations in the

Stokes laser spectral profile. This is especially apparent in the $T = 1723$ K spectrum in Figure 4, where the jagged nature of the spectral envelope of the N_2 Q-branch signature relative to the theory is quite obvious. Additionally, these sample spectra show the ability of CARSFT to handle multiple species (N_2, O_2 and H_2 in this case). Analysis of the quantitative accuracy of the mole-fraction data is ongoing, however, some qualitative statements may be made regarding the state of the gas based on the temperature and species present. For example, in Figure 3 the spectrum at $T = 1257$ K reveals the presence of H_2 with N_2 in the absence of oxygen reveals that product gas is present in the measurement volume. At $T = 662$ K, the spectrum shows all three species are present; in this case, the measured values of O_2/N_2 and H_2/N_2 suggest that hydrogen combustion would occur under these conditions if molecular mixing has occurred, and the presence of both H_2 fuel and oxidizer in the spectrum suggests a concentration gradient in the CARS measurement volume.

Shown in Figure 5 are the temperature histograms for the two methanol pool fires investigated. The mean temperatures determined for these fires are 1161 and 1215 K with standard deviations of 407 and 405 K, respectively, which illustrates the repeatability of the canonical wind-free fire plumes generated in the FLAME facility. The CARS results can be compared to thermocouple measurements shown in Figure 6. The mean temperatures (≈ 1166-1209 K depending on probe diameter) exhibited by the thermocouple data are in good agreement with the mean temperature of the CARS measurement, exhibiting a maximum deviation of approximately 4%. However, it is also apparent that the thermocouples lack the temporal resolution to probe the fire; the thermocouple-measured rms temperatures (≈17-35 K depending on probe diameter) are an order of magnitude smaller than the CARS-measured rms temperature fluctuation, which should be expected given the thermal lag of the physical probes.

The accuracy and precision of the CARS temperature measurements were characterized using a tube furnace as the temperature standard. The air temperature was determined by fitting the N_2-containing portion of the CARS spectra. Shown in Figure 7 are sample single-shot spectra from the tube furnace and corresponding theoretical fits to the data. Figure 8 depicts the tube-furnace temperatures determined by the CARS instrument and a thermocouple. Each data point represents the mean of 100 single-shot temperatures acquired with the CARS instrument. The error bars show the standard deviation in the CARS single-shot temperatures. With the exception of the lowest two temperatures, the agreement between the CARS instrument and the thermocouple is excellent. The low-temperature deviation may be caused by uncertainty in the resolution/instrument function of the spectrometer/CCD detection system. In the 500-1400K temperature range, the mean of the CARS single-shot temperatures is within 0.25-3.7% of the thermocouple temperature. The error bars indicate the standard deviation in the CARS single-shot temperatures, which ranges from 3.5-6%. It is important to note that for these methanol pool fires approximately 66% of the single-shot temperatures determined from the CARS measurement fall in the range covered by the tube furnace.

B. Species Mole-Fraction Measurements

The CARS instrument not only performs high-fidelity thermometry, but demonstrates the ability to simultaneously measure mole fractions relative to the N_2 molecule as well. Scatter plots of temperature and the relative mole fractions O_2/N_2 and H_2/N_2 are displayed in Figure 9. The temperature/oxygen correlation displays the behavior on the fuel-lean side of the mixture-fraction space in the pool fire. At 300 K, the O_2/N_2 ratio approached 0.25-0.26, near the expected value of 0.266 for atmospheric air. The temperature rises as oxygen is consumed near the flame fronts in the fire and peaks with a mean value near 1600-1700 K and ±300-400 K scatter at low oxygen levels.

The temperature-hydrogen correlation reveals some information on the fuel-rich side of the mixture-fraction space. In general, H_2 was observed in a much lower fraction of the single-shot CARS spectra than was O_2. Additionally, only a very small fraction of the spectra show the presence of both H_2 and O_2, such as at $T = 662$ K in Figure 3. This should be expected as any mixing of H_2 and O_2 would typically result in combustion, and spectra which exhibit both species results from a mixture which is too lean to burn, which is unlikely given the broad flammability limits of H_2, or from a concentration gradient along the axis of the CARS probe volume. While the general relationship between temperature and O_2/N_2 is relatively clear, more data are required to determine the correlation between temperature and H_2/N_2. The mapping of relative mole fraction vs. temperature shows promise as a method for at least estimating the mixture fraction in our turbulent pool-fire experiments. The ratio O_2/N_2 is an obvious indicator of fuel-lean mixture fraction, whereas the presence of measurable H_2/N_2 in the absence of O_2 indicates a rich-side mixture fraction. Future work will focus on acquiring mole fraction data for other combustion products, primarily CO_2 and efforts will be made to estimate the mixture fraction. This will require comparison of all mole-fraction measurements against calibrated standards or well-understood flame environments, and may require some modification of CARSFT, as recent results by O'Byrne *et al.*[15] suggest a low-mole-fraction bias in

their dual-pump CARS measurements of H_2 in the Hencken burner, which was attributed to insufficient modeling of H_2 in CARSFT.

IV. Summary and Conclusions

Single-shot temperature measurements were acquired with a broadband, dual-pump CARS instrument constructed for full-scale fire testing at Sandia National Laboratories. Temperature and relative mole fractions of O_2/N_2 and H_2/N_2 were extracted from the CARS spectra. For the methanol pool fire, the agreement between the mean of the single-shot CARS temperature and mean thermocouple temperatures is quite good, with a maximum deviation of approximately 4%. However, there is an order of magnitude difference in the temperature standard deviations of the CARS and thermocouple measurements, which indicates that the ruggedized sheathed thermocouple probes commonly used for fire testing cannot resolve the temperature fluctuations found within turbulent fires. The combination of temperature and relative mole fraction data offered by dual-pump CARS shows promise as a method to infer the mixture fraction within the fire.

The CARS thermometry measurement was characterized by comparison to a tube-furnace standard. At temperatures between 500-1400 K, the CARS temperature measurements were accurate to within 3.7%, with a low-temperature bias observed for temperatures below 500 K, which may result from uncertainty in the resolution/instrument function of our optical detection system. Characterization of the instrument performance with respect to relative mole fractions must be performed if the mixture fraction is to be estimated. Future work will focus on acquiring CO_2 mole fractions, inferring the mixture fraction and investigating more heavily sooting flames.

Acknowledgments

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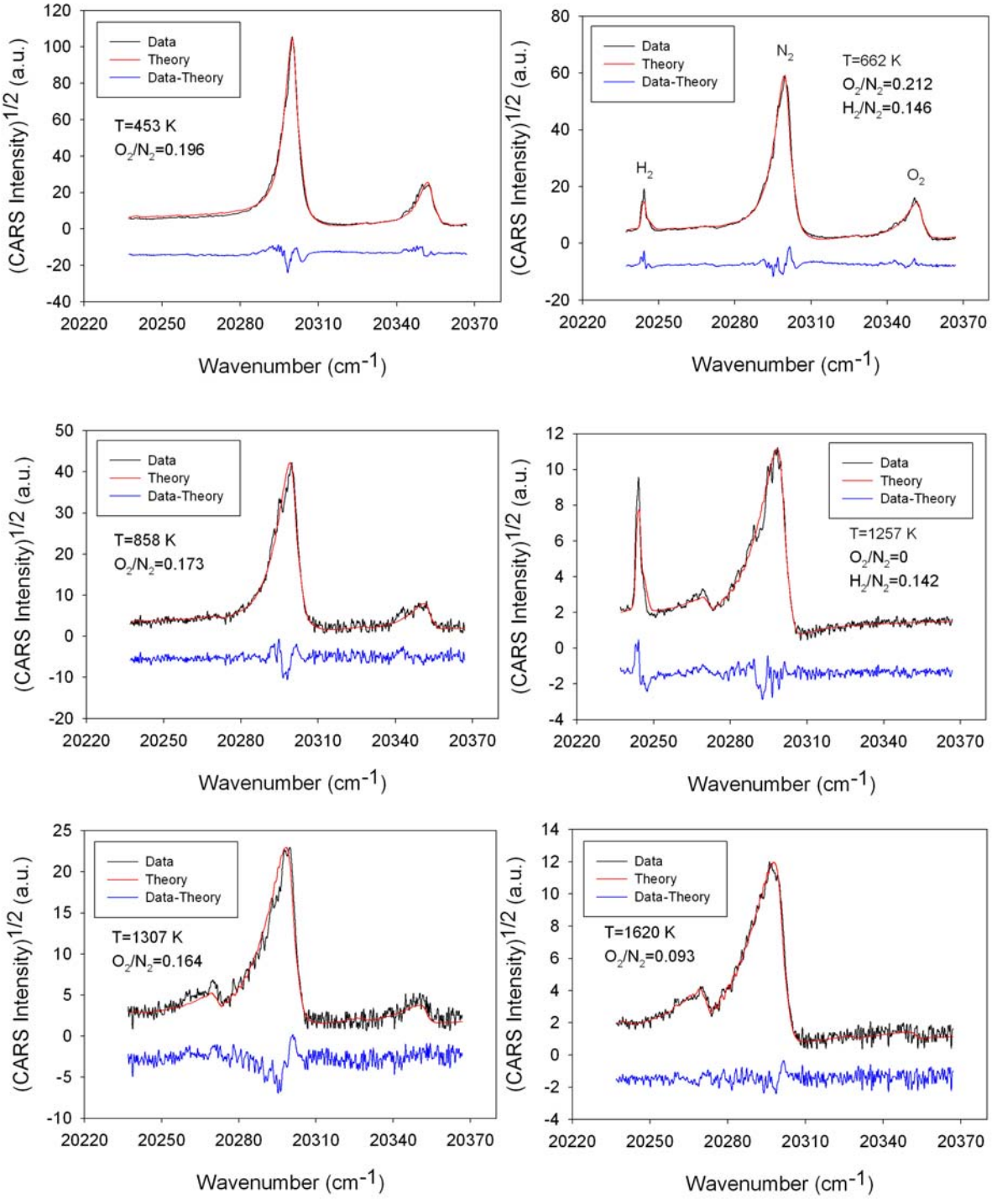

Figure 3. Sample fits of CARS spectra from the first methanol pool-fire experiment.

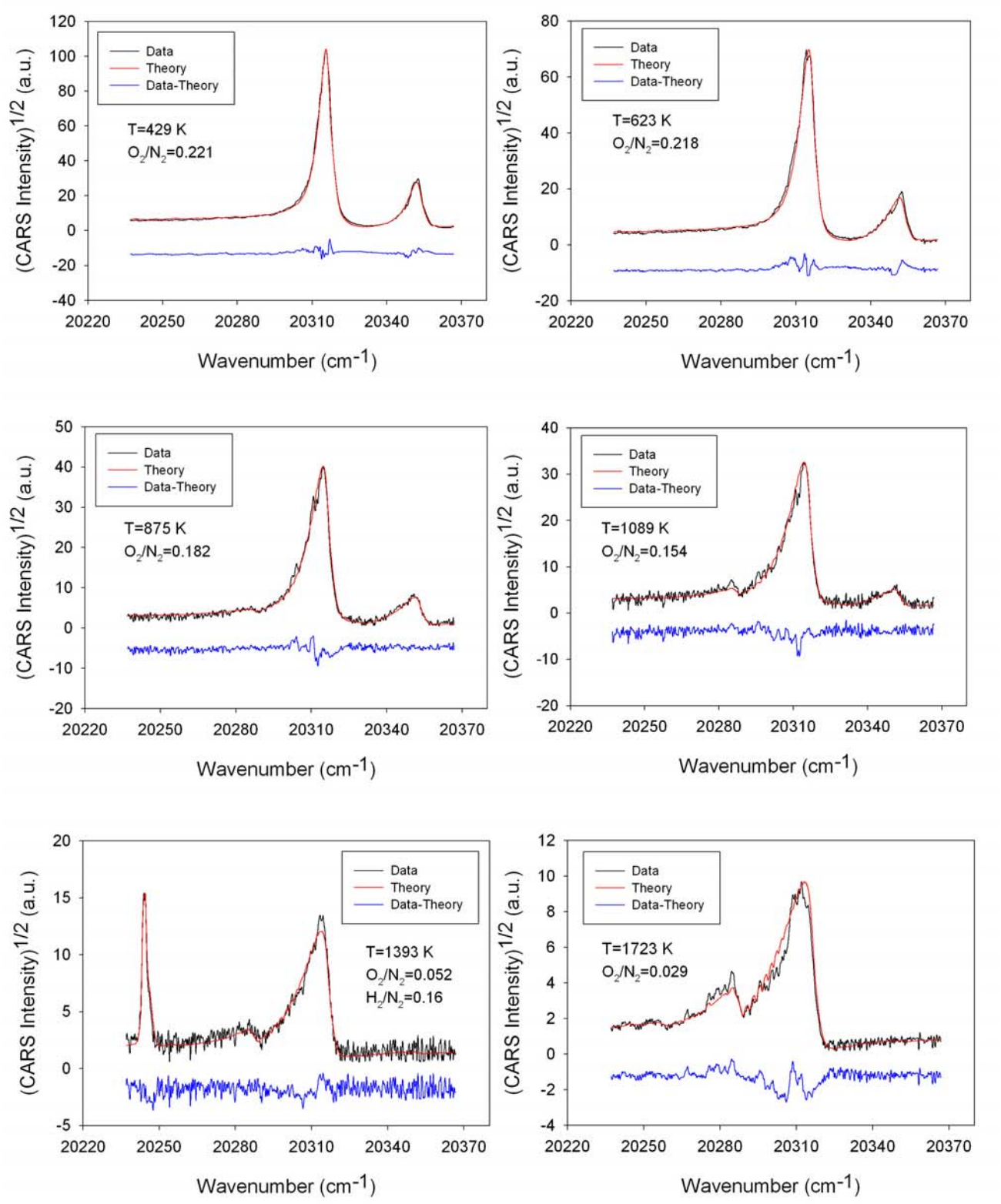

Figure 4. Sample fits of spectra from the second methanol pool-fire experiment.

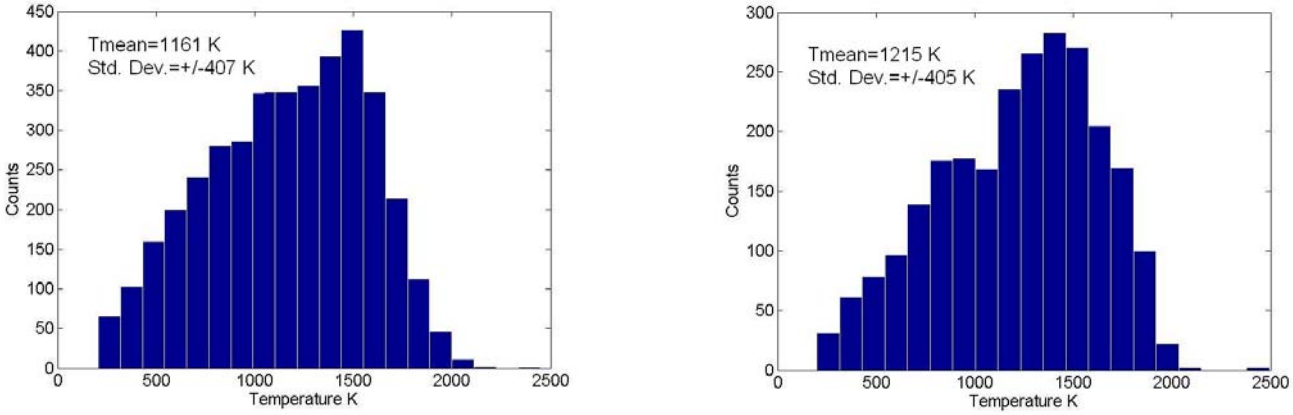

Figure 5. Temperature histograms for two consecutive methanol pool-fire burns

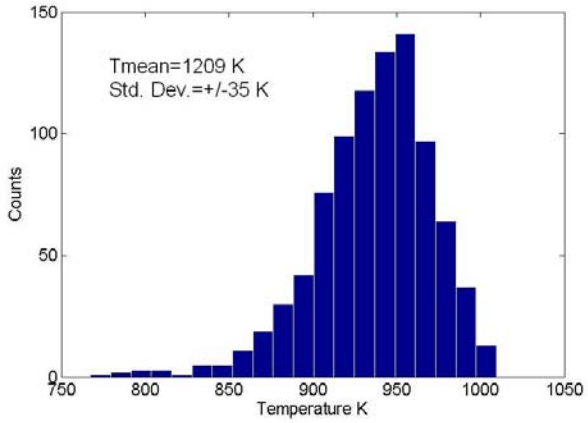

Figure 6. Sample histogram of methanol pool fire measured with 1.016mm diameter thermocouple.

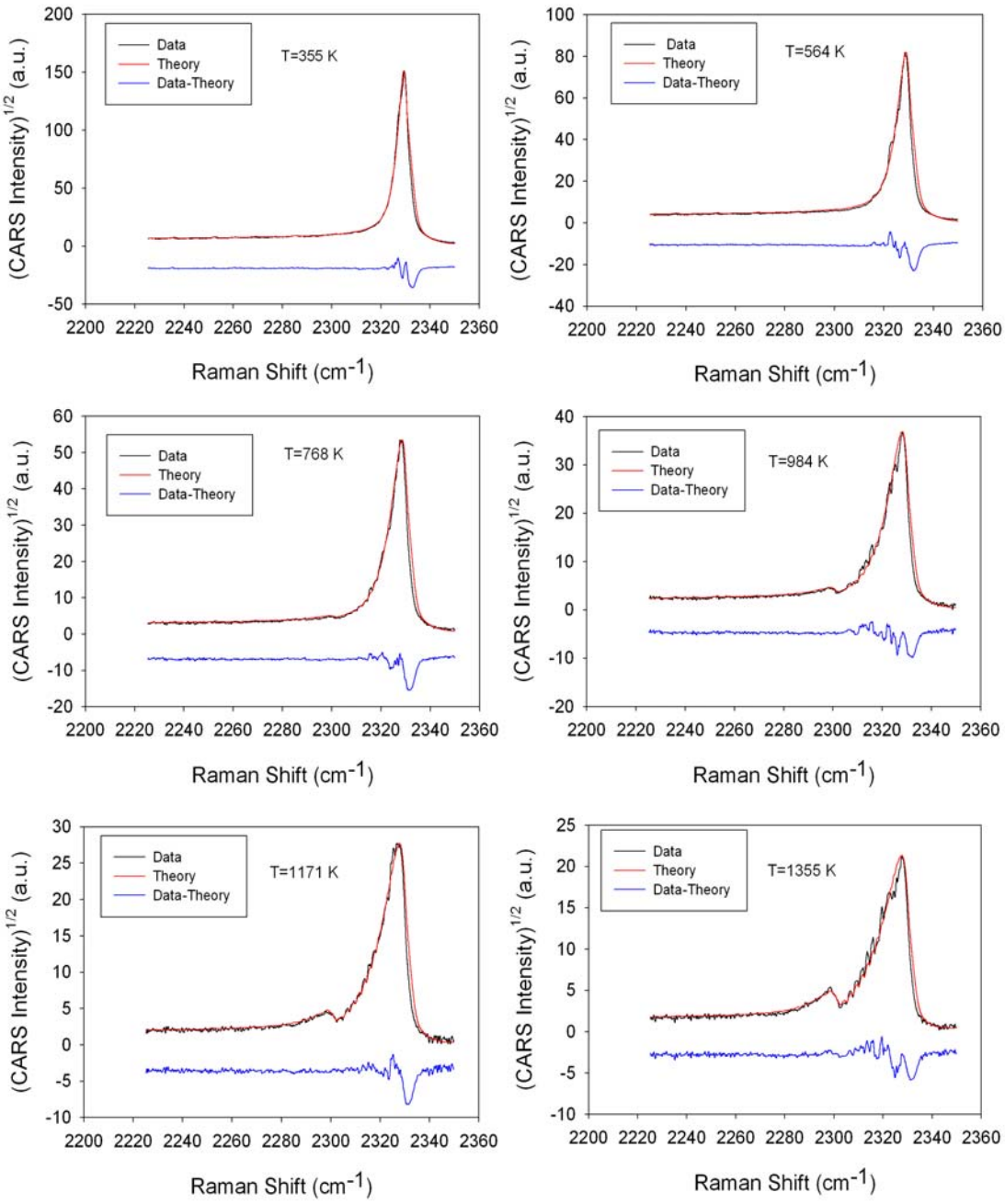

Figure 7. Single-shot N_2 *Q*-branch spectra and theoretical fits from CARS measurements in a tube furnace.

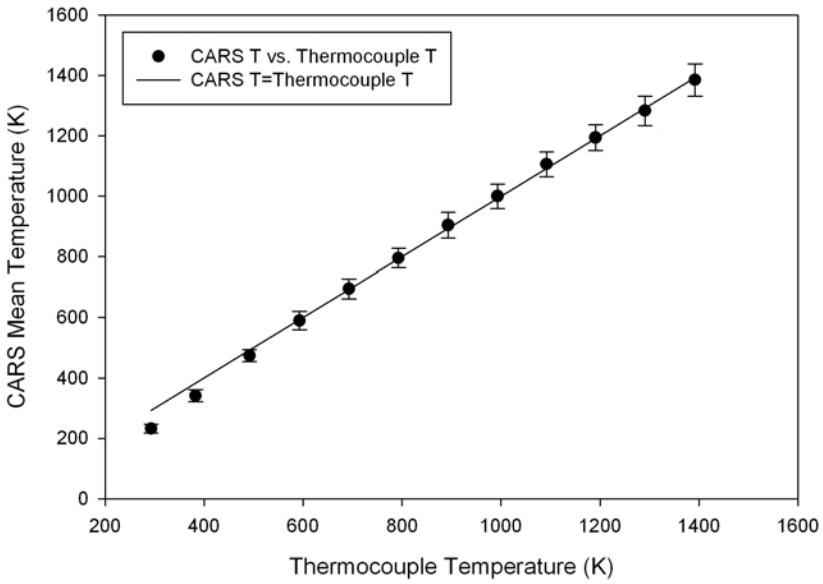

Figure 8. Temperatures of tube furnace determined by CARS and thermocouple measurement.

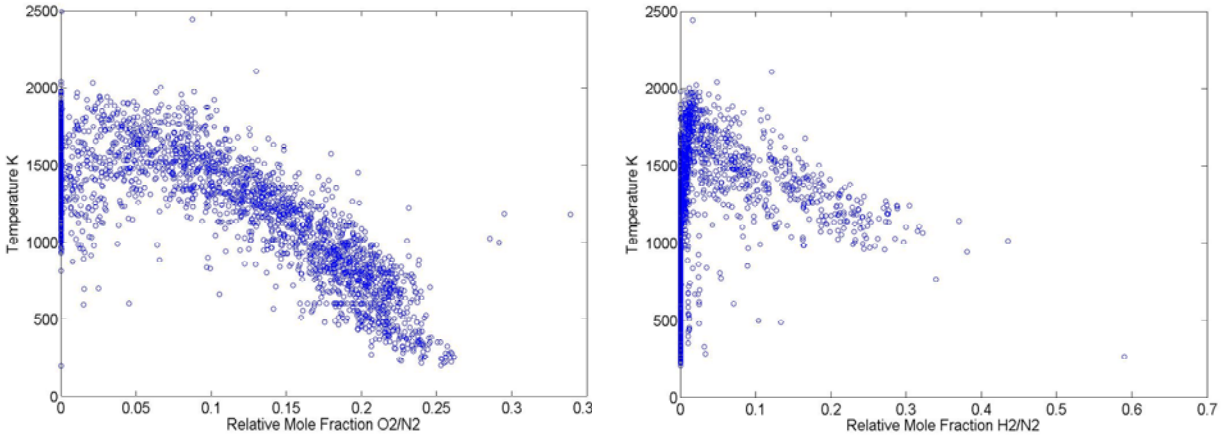

Figure 9. Scatter plots of temperature and the relative mole fractions O_2/N_2 and H_2/N_2.