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CARS in an Inductively Coupled Plasma Torch, Part 2: Temperature and Carbon-Monoxide Measurements in the Reaction Layer of a Graphite Ablator

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We demonstrate coherent anti-Stokes Raman scattering (CARS) detection of the CO and N_2 molecules in the reaction layer of a graphite material sample exposed to the 5000-6000 K plume of an inductively-coupled plasma torch operating on air. CO is a dominant product in the surface oxidative reaction of graphite and lighter weight carbon-based thermal-protection-system materials. A standard nanosecond CARS approach using Nd:YAG and a single broadband dye laser with ~200 cm^{-1} spectral width is employed for demonstration measurements, with the CARS volume located less than 1-mm from an ablating graphite sample. Quantitative measurements of both temperature and the CO/N_2 ratio are obtained from model fits to CARS spectra that have been averaged for 5 laser shots. The results indicate that CARS can be used for space- and time-resolved detection of CO in high-temperature ablation tests near atmospheric pressure.

I. Introduction

Hypersonics R&D is experiencing significant and renewed interest. As new vehicle designs are considered, requirements for innovative thermal protection systems (TPS) to perform across a range of new environments have emerged. Any new TPS design must be qualified in extreme temperature environments, where gas temperatures reach 5000–10,000 K or higher, and complex finite-rate chemical processes must be considered for effective TPS design. Noninvasive laser-based diagnostics offer both multi-parameter temperature/species measurements and can be applied in the harsh hypersonic test environment, where physical sensors cause severe flow perturbations and may not survive the extreme thermochemical environment. Methods used in combustion studies, including Raman/Rayleigh scattering [1], laser induced fluorescence (LIF) [2], absorption/emission spectroscopies [3], and coherent anti-Stokes Raman scattering (CARS) [4] can play a significant role in facilities such as high-temperature shock tubes [5], reflected shock

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tunnels [6], and arc jets [7]—all of which can present reacting flow conditions at temperatures much higher than hydrocarbon combustion. In this study, we report initial proof-of-concept experiments, which assess the applicability of CARS for simultaneous thermometry and carbon-monoxide detection at atmospheric pressure and reaction-layer temperatures as high as T = 3500 K, in the 50-kW Inductively-Coupled Plasma (ICP) Torch at The University of Texas at Austin [8]. CARS offers significant advantages for the ICP torch environment, including efficient background rejection of high torch luminosity, high spatial resolution, outstanding signal strength, and the potential for very high-fidelity thermometry with simultaneous detection of multiple gas-phase chemical species [9]. We demonstrate high-fidelity N_2 CARS thermometry at temperatures in excess of T = 6000 K in a companion paper [10]. The emphasis in this article is our ability to measure CO concentration at very high temperatures in the vicinity of a graphite ablator inserted into the ICP torch environment. CO is a particularly important species, as it is a dominant product of carbon oxidation in the TPS environment [11]. CO has been reliably measured in flames using similar nanosecond-laser-based CARS arrangements to the instrument described here [9, 12]. The present study extends CARS detection of CO to significantly higher temperature.

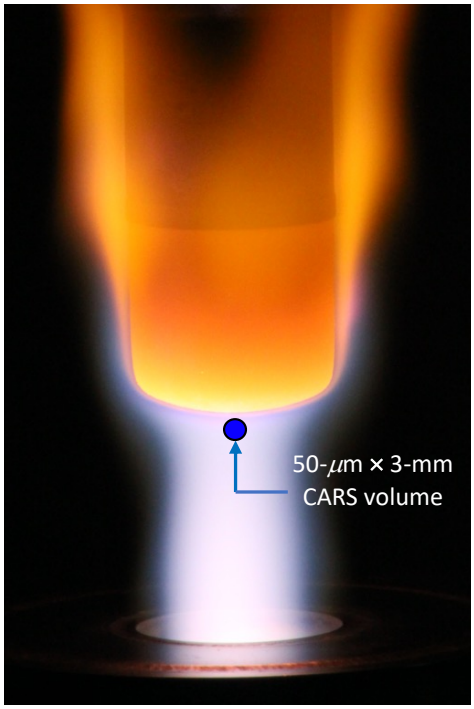

Figure 1. Photograph of the 30-mm graphite sample inserted into the air plasma torch plume with approximate location of the CARS measurement volume indicated.

II. Experiment

Our CARS instrument utilizes ~10-ns pulses from a Q-switched, frequency-doubled Nd:YAG laser, operating at 10-Hz repetition rate. The 1-J/pulse laser output is sufficient to pump a broadband Stokes dye laser and provide two 532-nm CARS pump beams with 30-mJ nominal pulse energies each. The Stokes source has been described previously by Rock *et al.* [12], and utilizes a unique oscillator design that contains two dye cuvettes, each containing a different dye mixture, to maximize Stokes bandwidth. The dye laser is operated in both a conventional laser cavity arrangement and with the output coupler removed for modeless operation. Nominal Stokes pulse energy is ~25–30 mJ/pulse. The laser beams are crossed with a f = 500-mm spherical lens to achieve a ~3-mm long beam overlap region, in which 90% of the CARS radiation is generated. CARS signal from the N_2 and CO Raman Q branches near 473 and 478 nm, respectively, is dispersed at 1-cm^{-1} resolution by a 0.75-m grating spectrograph and detected using an intensified CCD camera. A 20-ns gate is centered on the arrival of the CARS pulse to provide efficient rejection of particularly intense ICP-torch background emission. The intensifier was operated near minimum gain, as significant CARS signal strength was attained, even in the extreme temperature environment of the ICP torch.

The 50-kW ICP torch is described in detail elsewhere [8]. Air is utilized as the working fluid and the torch exhausts into room-air at atmospheric pressure. Centerline temperature near the torch exit plane is measured to be in excess of T = 7000 K, based on N_2 CARS measurements in [10]. A 30-mm-diameter graphite sample plug was inserted into the torch plume, with the sample face positioned ~30 mm from the torch exit plane. The CARS measurement volume is centered on the torch axis and positioned nominally 500 μm from the graphite surface, as shown in Figure 1. Upon insertion into the torch plume, the sample is moved toward the CARS volume at a rate of 21 μm/sec until detectable CARS signal from the CO Q branch is observed, at which time the sample motion is halted and CARS spectra are recorded as 5-laser-shot accumulations, while the sample ablates away from the measurement region.

Measured CARS spectra are fitted using a Matlab implementation of well-known frequency-domain expressions for the CARS susceptibility [13] in the isolated-line approximation. The CARS susceptibility is convolved with a Gaussian instrument function. The pump laser convolution is neglected, as the pump pulses are assumed to be Fourier-transform limited. Purely collision-broadened linewidths are employed—an assumption which should be checked at very high plasma torch temperatures, where Doppler broadening may become non-negligible. Molecular parameters and Raman cross sections for N_2 and CO are obtained from the Sandia CARSFT code [14]. Self-broadened N_2 [15] and CO [16] collisional linewidths are calculated using the modified-exponential-gap (MEG) formulation. The MEG constants in [15, 16] were determined from measurements at maximum temperatures of 2400 K and 1500 K,

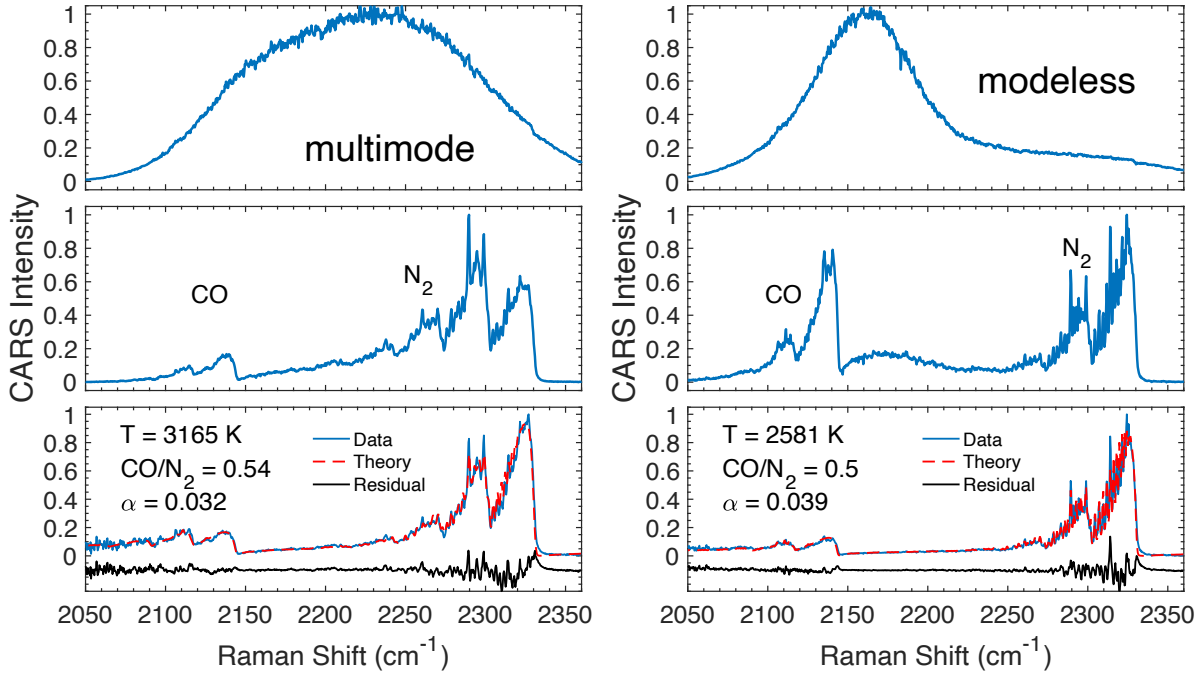

Figure 2. Representative data from the ICP-torch experiments. Results obtained with the Stokes dye laser in a multimode configuration are shown at left, and data obtained with modeless Stokes-laser operation at right. (Top panels) Nonresonant CARS spectra obtained in argon and averaged for several hundred laser shots; (middle panels) five-shot-average spectra acquired near an ablating graphite sample inserted into the ICP torch, presented without correction for the Stokes laser profile; (lower panels); the same spectra, when normalized by the corrections at top (blue) and fit to a CARS spectral model with indicated temperature, relative CO concentration, and nonresonant scaling parameter, α.

respectively; the MEG model form is used to extrapolate Raman linewidth data to much higher temperatures encountered in the ICP torch environment.

III. Results and Discussion

Nonresonant CARS spectra recorded by flooding the measurement volume with argon are shown for the multimode (left) and modeless (right) dye-laser configurations in the top-most panels of Figure 2. These nonresonant CARS spectra have been averaged for several hundred laser shots. Conventional multimode Stokes laser operation results in a wideband laser spectrum with ~200 cm^{-1} FWHM spectral width. The modeless dye-laser configuration results in a more narrow ~80 cm^{-1} main peak, centered near 2160 cm^{-1}, and a broad region where the intensity is approximately 15–20% of the main peak from 2240–2320 cm^{-1}. The shape of the modeless dye laser profile results in much larger corrections to CARS spectra acquired from the torch prior to least-squares fitting. However, the proximity of the main peak in the modeless dye-laser spectrum to the CO bandhead at ~2140 cm^{-1} has the effect of increasing the CO signal strength relative to the much more intense N_2 Q-branch spectrum—thereby increasing the sensitivity of the CARS instrument to CO. Five-shot-averaged CARS spectra, uncorrected for the shape of the Stokes laser spectrum, are shown in the middle panels of Figure 2. These two spectra have been selected because the CARS-determined CO/N_2 ratio is similar, thereby facilitating a comparison of the raw CO signals. The uncorrected spectrum obtained with the modeless dye laser, and shown in the right middle panel, exhibits a CO signal that is almost 80% of the peak N_2 spectrum and is ~4× higher than the CO contribution obtained with the multimode dye laser at left. Quantitative measurements are obtained by normalizing each of the spectra in the middle row of Figure 2 by the respective nonresonant corrections and fitting with a least-squares optimization routine in which temperature, CO/N_2 mole-fraction ratio, and the strength of the nonresonant background contribution, α, were fit parameters in the model. The resulting fits are shown in red, with the measured CARS signals in blue and the fit residual in black.

Temperature and CO/N_2 data obtained over the duration of graphite sample insertions with multimode (left) and modeless (right) Stokes laser operation are shown in Figure 3. The data are plotted vs. a "realization number", which simply reflects the number of five-laser-shot average spectra acquired over the course of each experiment. Moving from left to right, the sample is approached, and the temperature drops by ~1000 K as the cooler sample surface moves closer to the CARS measurement volume. When CO is detected, the sample motion is halted; temperature changes generally limited to a ± 200 K band; and CO concentration rises steadily to almost 60% of the local N_2 mole fraction as a result of high rates of carbon ablation. The CO level rises throughout each experiment, suggesting that the initially cold graphite sample has not yet achieved thermal equilibrium before removing it from the torch plume. Temperatures recorded with the Stokes laser in multimode operation (Figure 3, left) are generally 500–1000 K higher than the demonstration with modeless dye-laser operation (Figure 3, right). The differences are likely a result of high levels of uncertainty in the relative position of the CARS measurement volume and the graphite surface, which was not well characterized in these proof-of-concept measurements. The level of scatter in the CO/N_2 ratio appears higher than in the temperature data; this is very likely a result of both finite measurement precision and real changes in CO levels, as the fluid dynamics of the open-air torch plume are dominated by unsteady buoyant fluctuations.

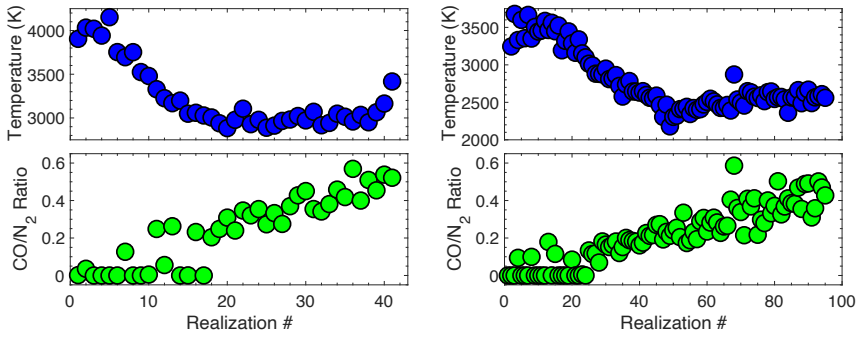

Figure 3. Measured temperature and CO histories obtained during the graphite sample insertion. Results obtained with the multimode Stokes-laser configuration are shown at left, with modeless configuration results shown at right.

IV. Summary, Conclusions, and Future Work

We have demonstrated simultaneous measurement of temperature and relative CO/N_2 mole-fraction ratio in the reaction layer of a graphite material sample exposed to the 5000-6000 K plume of an inductively-coupled plasma torch operating on air, During graphite sample insertion, CO was detected in high concentrations, ranging from ~10–60% of the local N_2 mole fraction, at temperatures of T = 2250–3500 K. CO mole fraction was determined by fitting the CARS intensity spectrum, which is often difficult because the CO Raman intensity is weak relative to N_2. Nevertheless, strong CO CARS signals, as high as 80% of the peak N_2 Q-branch contribution, were observed in our CARS spectra. This enhanced level of detectivity was made possible by both the very high CO concentrations near the ablating graphite sample, and, in some cases, by tailoring the Stokes dye laser profile to favor CO relative to N_2 in the CARS process. Future work will focus on more systematic evaluation of the temperature and CO profiles using image-based determination of the sample surface location and, potentially, a 1D line CARS configuration [17]. We will also quantify CO detection limits at high temperatures and evaluate fitting procedures which enhance sensitivity to CO concentration, such as objective functions weighted toward the CO-containing portion of the spectrum. Single-shot CO/temperature measurements also appear to be feasible, as peak detector counts for 5-laser-shot accumulations in the ICP torch environment reached 30- to 60-thousand at minimal detector gain.

Acknowledgments

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References

1. Barlow, R. S. "Laser diagnotics and their interplay with computations to understand turbulent combustion," *Proceedings of the Combustion Institute* Vol. 31, 2002, pp. 49-75.
2. Juddoo, M., and Masri, A. R. "High-speed OH-PLIF imaging of extinction and re-ignition in non-premixed flames with various levels of oxygenation," *Combustion and Flame* Vol. 158, 2011, pp. 902-914.
3. Murphy, J. J., and Shaddix, C. R. "Soot property measurements in a two-meter diameter JP-8 pool fire," *Combustion Science and Technology* Vol. 178, 2006, pp. 865-894.
4. 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* Vol. 36, 2010, pp. 280-306.
5. Winters, C., Haller, T., Kearney, S., Varghese, P., Lynch, K., Daniel, K., and Wagner, J. "Pulse-burst spontaneous Raman thermometry of unsteady wave phenonmena in a shock tube," *Optics Letters* Vol. 46, No. 9, 2021, pp. 2160-2163.
6. Sharma, S. P., Ruffin, S. M., Gillespie, W. D., and Meyer, S. A. "Vibrational relaxation measurements in an expanding flow using spontaneous Raman scattering," *Journal of Thermophysics and Heat Transfer* Vol. 7, No. 7, 1993, pp. 697-703.
7. Bamford, D. J., O'Keefe, A., Babikan, D. S., Stewart, D. A., and Strawa, A. W. "Characterization of arcjet flows using laser-induced fluorescence," *Journal of Thermophysics and Heat Transfer* Vol. 9, No. 1, 1995, pp. 26-33.
8. Greene, B. R., Clemens, N. T., Varghese, P. L., Bouslog, S. A., and Papa, S. V. D. "Characterization of a 50-kW inductively coupled plasma torch for testing of ablative thermal protection materials," AIAA2017-0394, *AIAA SciTech Forum*. Grapevine, TX, 2017.
9. Cutler, A. D., Gallo, E. C. A., and Cantu, L. M. L. "WIDECARS spectra fitting in a premixed ethylene-air flame," *Journal of Raman Spectroscopy* Vol. 47, 2016, pp. 416-424.
10. Fries, D., Murray, J. S., Stark, S. T., Clemens, N. T., Varghese, P. L., Bhakta, R. B., Jans, E. R., and Kearney, S. P. "CARS in an inductively coupled plasma torch, Part 1: High-temperature nitrogen thermometry," *AIAA SciTech Forum*. National Harbor, MD, 2023.
11. Prata, K. S., Schwartzentruber, T. E., and Minton, T. K. "Air-carbon ablation model for hypersonic flight from molecular beam data," *AIAA Journal* Vol. 60, No. 2, 2022, pp. 627-640.
12. Rock, N., Hsu, P. S., Lauriola, D. K., Rahman, N., Estevadeordal, J., Grib, S. W., Jiang, N., Kearney, S. P., and Wrzesinski, P. "WIDECARS multi-parameter measurements in premixed ethylene-air flames using a wavelength stable ultrabroadband dye laser," *Applied Optics* Vol. 59, No. 8, 2020, pp. 2649-2655.
13. Eckbreth, A. C. *Laser Diagnostics for Combustion Temperature and Species*: Gordon and Breach, 1996.
14. Palmer, R. E. "The CARSFT Computer Code for Calculating Coherent Anti-Stokes Raman Spectra: User and Programmer Information." SAND89-8206, Sandia National Laboratories, Livermore, CA, 1989.
15. Lavorel, B., Guillot, L., Bonamy, J., and Robert, D. "Collisional Raman linewidths of nitrogen at high temperature (1700-2400 K)," *Optics Letters* Vol. 20, No. 10, 1995, pp. 1189-1191.
16. Rosasco, G. J., Rahn, L. A., Hurst, W. S., Palmer, R. E., and Dohne, S. M. "Measurement and prediction of Raman *Q*-branch line self-broadening coefficients for CO from 400 to 1500 K," *The Journal of Chemical Physics* Vol. 90, No. 8, 1989, pp. 4059-4068.
17. Jonuscheit, J., Thumann, A., Schenk, M., Seeger, T., and Leipertz, A. "Accuracy and precision of single-pulse one-dimensional vibrational coherent anti-Stokes Raman-scattering temperature measurements," *Applied Optics* Vol. 36, No. 15, 1997, pp. 3253-3260.