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Raman Gas Species Measurements in Hydrocarbon-Fueled Rocket Engine Injector Flows

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Abstract

Rocket engine propellant injector development at NASA-Marshall includes experimental analysis using optical techniques, such as Raman, fluorescence, or Mie scattering. For the application of spontaneous Raman scattering to hydrocarbon-fueled flows a technique needs to be developed to remove the interfering polycyclic aromatic hydrocarbon fluorescence from the relatively weak Raman signals. A current application of such a technique is to the analysis of the mixing and combustion performance of multijet, impinging-jet candidate fuel injectors for the baseline Mars ascent engine, which will burn methane and liquid oxygen produced in-situ on Mars to reduce the propellant mass transported to Mars for future manned Mars missions. The Raman technique takes advantage of the strongly polarized nature of Raman scattering. It is shown to be discernable from unpolarized fluorescence interference by subtracting one polarized image from another. Both of these polarized images are obtained from a single laser pulse by using a polarization-separating calcite rhomb mounted in the imaging spectrograph. A demonstration in a propane-air flame is presented, as well as a high pressure demonstration in the NASA-Marshall Modular Combustion Test Artice, using the liquid methane-liquid oxygen propellant system.

Introduction

Technology development associated with advanced space transportation propulsion systems includes design and analysis of new types of propellant injectors. An effort exists at NASA-Marshall to include experimentally-obtained reactant/product mixing/combustion information as part of the injector analysis.

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Hardware associated with this effort includes an optically-accessible high pressure combustion chamber sized for single-element fuel injectors (Unielement Test Article) and a newer, larger Modular Combustion Test Article (MCTA) that can accommodate multi-element fuel injector configurations and that is also optically-accessible. Optical accessibility allows laser-based methods, such as laser Mie scattering, fluorescence, and spontaneous Raman scattering, to be applied. Raman spectroscopy has been used to analyze an oxygen-rich gaseous hydrogen/liquid oxygen (GH$_2$/LOx) injector flow in the unielement test article (1) and most recently is being considered for use in the MCTA to analyze the mixing and combustion performance of multijet, impinging-jet candidate fuel injectors for the baseline Mars ascent engine (2). This engine will burn methane (CH$_4$) and LOx produced in-situ on Mars to reduce the propellant mass transported to Mars for future manned Mars missions (3).

Application of Raman spectroscopy to hydrocarbon-fueled combustion brings the issue of interference of the weak Raman scattering light signals with strong laser-induced fluorescence. The fluorescence interference can be from polycyclic aromatic hydrocarbons (PAH's) which are excited and fluoresce across the ultraviolet and visible spectrum (4) and when using ultraviolet lasers can be due to the hydroxyl radical (OH) and to vibrationally-excited O$_2$, both of which are present in combustion reaction zones (5). By taking advantage of the polarization properties of Raman scattering, it is possible to discriminate the Raman signal from interfering fluorescence interference and hence apply Raman scattering to the analysis of hydrocarbon-fueled combustion. This can be done by obtaining two Raman images, one using a vertically polarized laser and one using a horizontally-polarized laser, and then subtracting the intensity of one image from another to obtain a net Raman signal (6). A second method that lends itself to single-pulse (and hence instantaneous) measurements is to obtain two simultaneous Raman images created from the same laser pulse. One of these images is the vertically-polarized signal and one is for the horizontally-polarized signal. The difference between these images

provides the net Raman signal, free of fluorescence interference. This technique has been demonstrated for a time-averaged application (7) and this paper describes a single-pulse application of the technique.

Single-Pulse Polarized UV Raman Measurements

While visible lasers may be best at providing interference-free Raman data for steady, laminar flames, it may still be desirable to use a UV laser, when probing turbulent flames, in order to obtain sufficient signal strength for single-pulse measurements. By exploiting the differences in polarization properties between Raman and PAH fluorescence, it is possible to obtain UV Raman signals in PAH-ridden environments.

In addition to laser wavelength, the signal strength of Raman scattering depends on two molecular invariants, the square of the mean polarizability $(a')^2$ and the square of the anisotropic polarizability $(\gamma')^2$. These are used to determine a constant Φ, which can be considered as the Raman scattering cross section for a single molecule, not including the laser wavelength contribution. The value of Φ also depends on the polarization of the incident laser beam, the polarization of the detected Raman signal, and the angle of detected Raman signal with respect to incoming laser beam. For a 90° collection angle and for the Raman and laser beams both in a horizontal plane, the value of Φ for vertically polarized Raman scattering is:[22]

$$\Phi = (a')^2 + 1/45 \, (\gamma')^2$$

and for horizontally polarized Raman scattering Φ is:

$$\Phi = 1/60 \, (\gamma')^2$$

Usually a'^2 and γ'^2 are similar in magnitude and the vertically polarized light is almost two orders of magnitude greater than the horizontally polarized light. Thus the Raman scattering signal essentially retains the polarization of the incoming laser beam. However a fluorescence light emission process does not retain the laser polarization because of the relatively long time the molecule exists in the excited state before fluorescing. During this time the molecule rotates, eliminating any correlation between the polarization of absorbed and emitted photons.

By providing two laser pulses, one horizontally polarized and the other vertically polarized, two signal spectra can be obtained, with one containing both Raman and fluorescence and one containing essentially only fluorescence. This method has been used to obtain fluorescence-free, time-averaged UV Raman measurements in hydrocarbon flames.[8,23] Single-pulse, polarization-resolved,

fluorescence-free UV Raman measurements have been obtained in an iso-octane fueled engine[24] by placing a Glan prism at the focal plane of the imaging spectrograph, and then refocusing the two polarized spectra onto two separate ICCD cameras. Another method uses a calcite rhomb located at the spectrograph entrance slit to displace the horizontally-polarized light from the vertically polarized light and has been used to obtain time-averaged PAH fluorescence-free UV Raman spectra in C_3H_8-fueled flames.[25] This latter method is described here, and single-pulse UV Raman images in a C_3H_8-air flame are presented.

Figure 14 shows the UV Raman system used for polarization-resolved measurements. It represents a typical UV Raman system except for one unique feature: a calcite rhomb inserted just behind the entrance slit of the spectrograph. This optical element displaces the horizontally polarized Raman image about 5 mm from the vertically polarized Raman image, which travels directly straight through the rhomb. The length of the entrance slit is limited to 4 mm to keep the two polarized images from overlapping. Figure 15 shows a typical single-pulse image obtained from the experimental system, and this image shows the relative strength of vertically polarized signal compared to horizontally polarized signal. The H_2O Raman signal (from air humidity) is almost completely polarized, while the N_2 signal is slightly depolarized and the O_2 signal is more depolarized than N_2. This corresponds to others' experimental observations.[8,26]

Spatially-integrated single-pulse Raman spectra are shown in Fig. 16, obtained from a slightly premixed C_3H_8-air bunsen flame. One of these spectra is the vertically polarized Raman-fluorescence signal. The horizontally polarized signal shows essentially only the fluorescence signal, that has two contributions. A broadband component is caused by PAH fluorescence, extending from below 255 nm to above 275 nm. A second contribution to the fluorescence background is the OH fluorescence from about 265 to 270 nm, caused by tuning the laser slightly onto a strong OH transition. This is done to demonstrate the ability of the technique to simultaneously measure Raman spectra and OH fluorescence. Before subtracting the horizontally polarized signal from the vertical it is first multiplied by a factor of 2.22 to account for the ratio in transmission efficiency (for the spectrometer/calcite rhomb) between the vertically and horizontally polarized signals. The net signal shows a fluorescence-free Raman spectrum that reveals the simultaneous occurrence of CO_2 and H_2O (products of combustion), CO and H_2 (intermediate products), and unburned C_3H_8. Information about the spatial structure of the flame can be revealed in the single-pulse image

of Fig. 17. This image shows unburned C_3H_8 occurring near the 0 mm position. The cooler, denser unburned gas mixture also provides a stronger N_2 Raman signal near that location. At ~1.5 mm the C_3H_8 pyrolizes into other hydrocarbons, including PAH's that cause a strip of broadband fluorescence to appear at this location. Farther into the flame chemical reactions involving oxidation take place, creating the OH intermediate. This shows up in Fig. 17 by the replacement of PAH fluorescence with OH fluorescence at flame positions greater than ~2.5 mm. By subtracting the scaled upper part of Fig. 17 (horizontally polarized fluorescence signal) from the bottom part (vertically polarized signal), and by summing the net Raman signal for each location (wavelength integration) a qualitative picture of the structure of the flame can be discerned, as in Fig. 18. This figure shows the drop in C_3H_8 signal and the concurrent increase in H_2O signal, showing the formation of that product occurring close to the fuel zone. In the same region the H_2 and CO signals are generally higher than in the fuel zone or in the OH reaction zone past 2.5 mm.

Hot-fire tests from Modular Combustion Test Article (MCTA) burning liquid CH_4 & O_2

The polarization-resolved UV Raman spectroscopy system has been applied to the analysis of liquid-CH_4/LOx combustion in the modular combustion test article (MCTA) at Test Stand 115 of NASA-Marshall..

Three hot fire tests were performed that involved use of the Raman system. Of these three, only one provided Raman data in conjunction with a hot fire test. One test resulted in an early cut and thus never provided main stage operation. One test was a successful run of the MCTA, but the Raman system laser beam did not enter the test article during the test because a mirror directing the beam into the test article was wrongly oriented. However the images obtained during this test did provide some useful information, as mentioned below.

Figures 2 and 3 show selected Raman images from the successful test. These images are taken from a group of 100, which were obtained at 5 Hz over a total time of 20 sec. The Raman images were initiated at the beginning of the test, however the Raman images can be correlated to the known events occurring during the test sequence. The first Raman image at time 0 sec (an arbitrary reference time) shows the N_2 purge as the only gas present just before ignition. The next image in Fig. 2, at 0.6 sec., shows combustion of H_2 and O_2 occurring as the igniter becomes operational. This is shown by the presence of their Raman signals in addition to the purge Raman signal. Next in the

operational sequence is to introduce CH_4 without O_2. This shows as a strong CH_4 Raman signal occurring in the image for 1.8 sec. After injection of CH_4 comes injection of O_2 to commence main stage combustion. The images obtained during this part of the sequence are all similar to the lower right one in Fig. 2 in that there is significant broadband emission occurring across most of the spectrum, and the Raman signals for the reactants and products have all diminished because of the increased temperature and reduced density during main stage combustion.

The question as to whether the broadband emission is caused by laser-induced fluorescence, by direct flame emission, or by a combination was answered by the results of one of the other tests, the one wich did not have a laser beam entering the combustion chamber. The images obtained during that test had about one half of the emission intensity as from Test 25, indicating that constant flame emission contributes about half of the interference background. The exposure time used for the camera was 200 nsec and could be reduced down to 20 nsec, the time span of the laser pulse. Doing so would reduce the detected flame luminosity by a factor of ten.

Other parts of the hot fire test sequence are shown in the remaining images of Fig. 3. These are for the following events: LOx valve closing, LOx valve completely off, and both propellents off with only the N_2 purge remaining at the end of the test.

The utility of the polarization resolved imaging becomes important when trying to detect Raman signals among the unpolarized interference background. However when the vertical polarized imaged is scaled (to account for transmission efficiency differences in the spectrograph and calcite crystal) and subtracted from the horizontally polarized imaged, no net Raman signal is left for the main stage images, one of which is shown in Fig. 4. The problem occurs because there is approximately the same amount of Raman signal occurring in the vertically polarized image as for the horizontally polarized image, for both N_2 and for CH_4, and probably for the other species' Raman signals. This is completely unexpected, since the Raman images of Ref. 1, and Raman theory, both show that significantly less Raman signal should exist at one polarization compared to the other.

The absence of a net Raman signal for the main stage Raman images is a result of at least two problems that must be surmounted. The first one involves the presence of Raman signals in both polarization images. This problem must be solved because the fundamental way that Raman signals are

extracted from interfering background is by their highly polarized characteristics. The second problem is that the Raman signals are weak compared to the background. Raman signal strength must be improved relative to background interference during a hot fire test. One way to do this is to reduce the exposure time of the camera down to the laser pulse length, which has already been mentioned. Also these tests were all performed with an unfocused laser beam, which has a cross section of 1 cm by 2 cm. The beam was left unfocused to eliminate the possibility of laser damage to the MCTA optical windows, which was a problem when the Raman system was applied to the Unielement Test Article (Ref. 1). By lightly focusing down to, say a cross section of 2 mm x 1 mm, the Raman signal strength will be improved relative to the background by a significant amount, at least a factor of ten because the Raman signal will occur over a narrow band of wavelengths instead of a broad wavelength region. The Raman detection system can also be placed closer to the MCTA optical window to increase it light gathering power. This should result in about a factor of four increase in signal since it was approximately 20 inches away and the lens system is designed for a minimum distance of 10 inches between the sample volume and the first light collection lens.

Conclusions and Future Work

The critical issue still unresolved, after the first application of polarization-resolved UV Raman to high pressure combustion, is the polarization of the Raman signal. Do the polarization characteristics of Raman scattering change as pressure is increased? In order to determine the effects of pressure on Raman scattering polarization, a high pressure sample cell is being constructed that can be used to both determine the influence of gas pressure and glass properties upon detected Raman signal polarization.

References

1. Wehrmeyer, J. A., J. M. Cramer, R. H. Eskridge, C. C. Dobson. 1997. UV Raman Diagnostics for Rocket Engine Injector Development. AIAA Paper 97-2843 presented at the AIAA 33rd Joint Propulsion Conference, Seattle, WA, July 6-9

2. Wehrmeyer, J. A., and H. P. Trinh. 1999. Raman Spectroscopy for Instantaneous Multipoint, Multispecies Gas Concentration and Temperature Measurements in Rocket Engine Propellent Injector Flows. Paper presented at the 10th Thermal and Fluids Analysis Workshop, sponsored by NASA-Marshall Space Flight Center, Huntsville, AL, Sept. 13-17.

3. Nandula, S. P., Brown, T. M., Pitz, R. W., and DeBarber, P. A., "Single-Pulse, Simultaneous Multipoint Multispecies Raman Measurements in Turbulent Nonpremixed Jet Flames," *Optics Letters*, Vol. 19, No. 6, 1994, pp. 414-416.

4. Reckers, W., Hüwel, L., Grünefeld, G., and Andresen, P., "Spatially Resolved Multispecies and Temperature Analysis in Hydrogen Flames," *Applied Optics*, Vol. 32, No. 6, 1993, pp. 907-918.

5. Chen, Y.-C., and Mansour, M. S., "Measurements of the Detailed Flame Structure in Turbulent H_2-Air Jet Diffusion Flames with Line-Raman/Rayleigh/LIPF-OH Technique," *Twenty-Sixth Symposium (International) on Combustion*, Combustion Inst., Pittsburgh, PA, 1996, pp. 97-103.

6. Tacke, M. M., Cheng, T. C., Hassel, E. P., and Janicka, J., "Study of Swirling Recirculating Hydrogen Diffusion Flame Using UV Raman Spectroscopy," *Twenty-Sixth Symposium (International) on Combustion*, Combustion Inst., Pittsburgh, PA, 1996, pp. 169-175.

7. Frank, J. H., Lyons, K. M., Marran, D. F., Long, M. B., Stårner, S. H., and Bilger, R. W., "Mixture Fraction Imaging in Turbulent Nonpremixed Hydrocarbon Flames," *Twenty-Fifth Symposium (International) on Combustion*, Combustion Inst., Pittsburgh, PA, 1995, pp. 1159-1164.

8. Schefer, R. W., Namazian, M., and Kelley, J., "CH, OH, and CH_4 Concentration Measurements in a Lifted Turbulent-Jet Flame," *Twenty-Third Symposium (International) on Combustion*, Combustion Inst., Pittsburgh, PA, 1990, pp. 669-676.

9. Yeralan, S., Pal, S., and Santoro, R. J., "Major Species and Temperature Profiles of LOx/GH_2 Combustion," AIAA paper 97-2940, 1997.

10. Grünefeld, G., Beuhausen, V., and Andresen, P., "Interference-Free UV-Laser-Induced Raman and Rayleigh Measurements in Hydrocarbon Combustion Using Polarization Properties," *Applied Physics B*, Vol. 61, 1995, pp. 473-478.

11. Masri, A. R., Bilger, R. W., and Dibble, R. W., "Fluorescence' Interference with Raman Measurements in Nonpremixed Flames of Methane," *Combustion and Flame*, Vol. 68, 1987, pp. 109-119.

12. Rabenstein, F., and Leipertz, A., "One-Dimensional, Time-Resolved Raman Measurements in a Sooting Flame Made with 355-

nm Excitation," *Applied Optics*, Vol. 37, No. 21, 1998, pp. 4937-4943.

13. Takagi, Y., "A New Era in Spark-Ignition Engines Featuring High-Pressure Direct Injection," *Twenty-Seventh Symposium (International) on Combustion*, Combustion Inst., Pittsburgh, PA, 1998, pp. 2055-2068.

14. Kee, R. J., Rupley, F. M., Miller, J. A., Coltrin, M. E., Grcar, J. F., Meeks, E., Moffat, H. K., Lutz, A. E., Dixon-Lewis, G., Smooke, M. D., Warnatz, J., Evans, G. H., Larson, R. S., Mitchell, R. E., Petzold, L. R., Reynolds, W. C., Caracotsios, M., Stewart, W. E., and Glarborg, P., "CHEMKIN Collection," Release 3.5, Reaction Design, Inc., San Diego, CA, 1999.

15. Osborne, R. J., "Application of Ultraviolet Raman Spectroscopy to Methane-Air vs. Air Counterflow Flames," Master's Thesis, Department of Mechanical Engineering, Vanderbilt University, 1999.

16. Tanoff, M. A., Smooke, M. D., Osborne, R. J., Brown, T. M., and Pitz, R. W., "The Sensitive Structure of Partially Premixed Methane-Air vs. Air Counterflow Flames," *Twenty-Sixth Symposium (International) on Combustion*, Combustion Inst., Pittsburgh, PA, 1996, pp. 1121-1128.

17. Petarca, L., and Marconi, F., "Fluorescence Spectra and Polycyclic Aromatic Species in a *N*-Heptane Diffusion Flame," *Combustion and Flame* Vol. 78, 1989, pp. 308-325.

18. Beretta, F., Cincotti, V., D'Alessio, A., and Menna, P., "Ultraviolet and Visible Fluorescence in the Fuel Pyrolysis Regions of Gaseous Diffusion Flames," *Combustion and Flame* Vol. 61, 1985, pp. 211-218.

19. Miller, J. H., Mallard, W. G., and Smyth, K. C., "The Observation of Laser-Induced Visible Fluorescence in Sooting Diffusion Flames," *Combustion and Flame* Vol. 47, 1982, pp. 205-214.

20. Vander Wal, R. L., and Weiland, K. J., "Laser-Induced Incandescence: Development and Characterization Towards a Measurement of Soot-Volume Fraction," *Applied Physics B*, Vol. 59, 1994, pp. 1994.

21. Will, S., Schraml, S., and Leipertz, A., "Two-Dimensional Soot-Particle Sizing by Time-Resolved Laser Induced Incandescence," *Optics Letters*, Vol. 20, 1995, pp. 2342-2344.

22. Wehrmeyer, J. A., Yeralan, S., and Tecu, K. S., "Multispecies Raman Imaging in Flames by Use of an Unintensified Charge-Couple Device," *Optics Letters*, Vol. 20, No. 8, 1995, pp. 934-936.

23. Miles, P. C., "Raman Line Imaging for Spatially and Temporally Resolved Mole Fraction Measurements in Internal Combustion Engines," *Applied Optics*, Vol. 38, No. 9, 1999, pp. 1714-1732.

24. Long, D. A., "*Raman Spectroscopy*," McGraw-Hill: New York, 1977.

25. Grünefeld, G., Beushausen, V., Andresen, P., and Hentschel, W., "Spatially Resolved Raman Scattering for Multi-Species and Temperature Analysis in Technically Applied Combustion Systems: Spray Flame and Four-Cylinder In-Line Engine," *Applied Physics B*, Vol. 58, No. 4, 1994, pp. 333-342.

26. Knapp, M., Luczak, A., Beuhausen, V., Hentschel, W., Manz, P., and Andresen, P., "Polarization Separated Spatially Resolved Single Laser Shot Multispecies Analysis in the Combustion Chamber of a Realistic SI Engine with a Tunable KrF Excimer Laser," *Twenty-Sixth Symposium (International) on Combustion*, Combustion Inst., Pittsburgh, PA, 1996, pp. 2589-2596.

27. Hartfield, R., Dobson, C., Eskridge, R., and Wehrmeyer, J., "Development of a Technique for Separating Raman Scattering Signals from Background Emission with Single-Shot Measurement Potential," AIAA Paper 97-3357, 1997.

28. Penney, C. M., Goldman, L. M., and Lapp, M., "Raman Scattering Cross Sections," *Nature Physical Science*, Vol. 235, 1971, pp. 110-112.

TO COMPUTER

DIGITAL CAMERA WITH
GATED INTENSIFIER

0.3 m IMAGING
SPECTROGRAPH

TRIGGER FOR
LASER AND
CAMERA
INTENSIFIER

50 mm DIA., 250 mm
FOCAL LENGTH
QUARTZ DOUBLET
LENSES

2 mm   4 mm

BEAM
DUMP

CALCITE
RHOMB

0.25 mm DIA.
BEAM WAIST

PROPANE-AIR FLAME

0.5 m FOCAL LENGTH LENS

PULSED UV LASER
400 mJ/PULSE
NARROWBAND: 0.001 nm
TUNABLE: 248 to 249 nm

CALCITE RHOMB

WAVELENGTH
SENSITIVE
DISPLACEMENT
5 mm @ 270 nm

38 mm

16 mm

8 mm

HORIZONTALLY
POLARIZED SIGNAL

VERTICALLY
POLARIZED SIGNAL

4

mm

0

4

mm

0

255   WAVELENGTH, nm   277

VERTICALLY | HORIZONTALLY
POLARIZED SIGNAL | POLARIZED SIGNAL

4
mm
0

4
mm
0

PAH   PAH   OH   PAH

CO₂   CO   N₂ C₂H₂   H₂O H₂

255   WAVELENGTH, nm   277

WAVELENGTH INTEGRATED RAMAN SIG., arb. units

90000
70000
50000
30000
10000
-10000

C₂H₂

N₂

CO₂

H₂O

CO

H₂

0   1   2   3   4
POSITION, mm

7000
6000
5000
4000
3000
2000
1000
0
-1000

VERTICALLY POLARIZED SIGNAL
(RAMAN + FLUORESCENCE)

HORIZONTALLY POLARIZED SIGNAL
(FLUORESCENCE)

VERTICALLY - HORIZONTALLY
POLARIZED SIGNAL (RAMAN)

PAH
FLUOR.

PAH
FLUOR.

OH

CO₂   CO   N₂   C₂H₂   H₂O   H₂

SIGNAL, arb. units

255   260   265   270   275
WAVELENGTH, nm