Raman Scattering at 532 and 355 nm in Rich Flames, Including Effects from Liquid Fuel Droplets

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INTRODUCTION

Raman scattering is a powerful tool for the simultaneous detection of major species and temperature in flames, with good spatial and temporal resolution [1,2]. It is of interest because it can provide a spatially and temporally resolved, simultaneous measurement of N₂, O₂, CO₂, CO, H₂ and H₂O [3]. Fluorescence from hydrocarbons, OH, NO, carbon and other species can produce a strong background emission that makes Raman detection very difficult in certain spectral locations, when specific laser wavelengths are used. In sooting flames, particle incandescence can potentially interfere as well. These interferences can often be avoided, however, by suitable choice of excitation wavelength and detection schemes.

Our interest is to apply Raman scattering to the gas-phase flow inside a diesel simulator [4]. Liquid fuels will be injected into this simulator and they will very likely introduce strong interferences that may render impossible Raman detection during portions of the transient spray event. This is not the first time that Raman scattering has been applied to this environment, and much of the data has indeed been discarded due to interferences [2,5]. The goal in this work is to explore these problems further, in order to evaluate options and to optimize the measurement.

BACKGROUND

The optical system required for a Raman scattering measurement is straightforward. One arbitrary wavelength laser can be used (see e.g. Fig. 1). The beam is focused into the flow field of interest and the scattered light is typically collected at 90º to the beam. The collected optical signal is usually dispersed and analyzed using a spectrometer. The Raman signal is shifted in wavelength from the laser wavelength, and it is very weak relative to the Rayleigh scattered laser light. A filter that blocks scattered light at the laser wavelength is thus placed in front of the spectrometer.

The second harmonic of Nd:YAG is the most common laser wavelength for Raman studies, because the available power level is quite high (up to the J/pulse regime), and it can be used in its entirety when a pulse stretcher is implemented to avoid laser breakdown in the sample volume. Use of 532 nm, however, has several potential problems. Interference by soot incandescence near 500 nm, and the well-known C₂ interference, can both prove problematic. The C₂ interference can be caused by direct laser induced fluorescence of naturally occurring C₂, or the laser pulse can create C₂ via fragmentation of soot (even nascent soot) and then this laser-created C₂ will fluoresce. The propensity for laser breakdown is also higher in the

Figure 1. Basic layout for a Raman measurement.
presence of a droplet mist. Additional problems associated with the use of liquid fuels like dodecane or diesel have not been explored in detail. It would therefore be worthwhile to consider alternatives to 532 nm excitation.

The Raman cross section for a molecule is dependent upon the inverse of the wavelength to the fourth power (e.g. $1/\lambda^4$). The third harmonic of YAG (355 nm) is worthy of consideration despite reduced pulse energy, based upon this increase in the cross section. This wavelength is too long for many UV-induced fluorescence interferences and somewhat short for soot incandescence (which peaks at above 500 nm) [6,7].

In the work presented here we evaluate both 532 and 355 nm wavelengths in fuel rich propane flames, and we observe the effect of liquid fuel sprays and droplets on Raman signatures at atmospheric pressure.

EXPERIMENTS

Figure 1 contains a schematic diagram of the experiment described here. The same type of laser was used for both wavelengths; a Quanta-Ray GCR16 (10 Hz, 10 ns pulsewidth in the fundamental) in the second and third harmonics. Various pulse energy levels were investigated. The beam was focused past the measurement zone, using a 1 M focal length lens. The beam in the sample volume (diameter of about 1.3 mm for 532 nm and about 650 µm for 355 nm) was thus converging slightly. The Raman signal was collected by $f\#=4.8$ optics and focused into a spectrometer entrance slit that was set at 300 µm for all experiments. The spectrometer was an $f\#=4.0$ Acton Research SpectraPro-300, fitted with a Roper Scientific ICCD-1024MG-E intensified array. The spectral resolution was 1.6 nm.

Two burners were used in this study. For purely gas-phase flames, a standard McKenna premixed burner producing stable, rich flames with a nitrogen shroud flow was used. The second burner was a Perkin-Elmer aspirating burner body fitted with a water-cooled, Meeker style burner head using a stainless steel honeycomb flame stabilizer and a nitrogen shroud flow. The Perkin-Elmer burner was used primarily to study the effect on Raman spectra of mixed flames burning vaporizing liquid fuel (dodecane or commercially available diesel) with propane and air. Gas flows for both flames were supplied by frequently calibrated Brooks mass flow meters. The various flames investigated are described in Table 1. Some soot was usually observed in the measurement volume. Most Raman measurements were performed in the post flame region (15 mm above the flame front), to avoid questions about interpretation of signals from within the flame front (which is difficult to probe in these burners at 1 atmosphere anyway). The effects of pulse energy, intensifier gate width, gate delay (to observe decay of the background signal), and polarization state were investigated.

<table>
<thead>
<tr>
<th>Flame No.</th>
<th>burner</th>
<th>φ(propane/air)</th>
<th>φ(propane/air + dodecane)</th>
<th>φ(propane/air + diesel)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>McKenna</td>
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<td>none added</td>
<td>none added</td>
</tr>
<tr>
<td>2</td>
<td>Perk.-Ell.</td>
<td>2.3</td>
<td>2.7</td>
<td>2.9</td>
</tr>
<tr>
<td>3</td>
<td>Perk.-Ell.</td>
<td>3.2</td>
<td>3.8</td>
<td>3.4</td>
</tr>
<tr>
<td>4</td>
<td>Perk.-Ell.</td>
<td>2.3</td>
<td>none added</td>
<td>none added</td>
</tr>
<tr>
<td>5</td>
<td>Perk.-Ell.</td>
<td>5.9</td>
<td>none added</td>
<td>none added</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

In order to compare our results to those of Meier and Keck [7], we acquired one data set with a long intensifier gate width of 100 ns, and we fixed our pulse energy at 175 mJ. Figure 2 contains the various Raman spectra from Flame 1, using a 532 nm laser beam under these conditions. In this case we have also investigated the effect of a polarizer in the collection optics. The spectrum that used no polarizer has been scaled to match the background-
subtracted N$_2$ Raman peak of the case where the polarizer passed the Raman, because the polarizer we used attenuates the light. Two polarization states were examined here: one that maximizes the Raman signal and one that minimizes it. Both are depicted in the figure. Because the polarizer is a sheet device, it does not have the rejection ratio of a calcite polarizer, but there is a clear loss of most of the Raman signal at the orientation that minimizes the Raman signatures. In addition, the LIF is clearly depolarized, and the polarizer orientation that passes the Raman signature improves the strength of the Raman signal relative to LIF. This effect is most pronounced just to the red of the N$_2$ Raman peak, where two C$_2$ vibrational bands can be found. Figure 2 also contains a spectrum that was acquired asynchronous with the laser pulse. CO$_2$, CO, N$_2$, H$_2$O and H$_2$ features are Raman, C$_2$ is fluorescence.

Next, Raman spectra were taken at laser pulse energy levels ranging from 50 to 250 mJ, triggered synchronously with the laser. Flame 1 was used again with the 532 nm laser beam. The intensifier gate width was set to 20 ns, for better background rejection. The acquired spectra were marginally improved relative to Figure 2, but the signal-to-background ratio clearly improved with energy. No obvious soot incandescence was observed. The nitrogen data were then converted into a signal-to-background ratio and then plotted as a function of laser energy in Figure 3a.

The Raman spectrum acquired at 355 nm, using 145 mJ per pulse with a beam diameter of 650 µm in Flame 1, was similar to Figure 2. The asynchronous signal was lower than the synchronous signal by a greater margin than for the 532 nm case. It is clear, however, from the polarizer results that there is a significant laser-generated background embedded within the 355 nm Raman spectra at the synchronous gate time. Synchronous Raman spectra were then taken at laser pulse energy levels ranging from 30 to 147 mJ, with the same experimental settings. As with the 532 nm results, the signal rises much faster than the background. The nitrogen data were then converted into a signal-to-background ratio and then plotted as a function of laser energy in Figure 3b. The 355 nm signal-to-background ratios we achieve are better than those found by Meier and Keck [7], even at the same pulse energy level they used.
The Perkin-Elmer burner (Flames 2 - 5) measurements were performed without a polarizer. Otherwise the Raman experimental setup was unchanged. First, Raman spectra were acquired synchronous with the 532 nm laser pulse in Flame 2 using a 20ns gate and energy of 175 mJ per pulse. The spectra were what one would expect from gas-phase fueled flames at the same equivalence ratios. The asynchronous results were also predictable. This occurred because the fuel droplets evaporated fully before the flame front. The 355 nm data (145 mJ/pulse) for Flame 2 were also unsurprising. Clearly, if liquid phase fuels have evaporated and reacted, they pose no additional problem to Raman measurements. For Flame 3, two neutral density filters of OD 3 and 1 were required to reduce the signal below the detector array saturation threshold, because there was a good deal of laser breakdown at droplets that survived into the sample zone. The combined problems of droplet-related breakdown and high levels of interference at both wavelengths render this region of a spray flame impossible for Raman detection.

In order to evaluate the contribution of CH$_2$O and PAH, the laser was fixed at 355 nm (a wavelength known to have this problem) and no polarizer was used. Figure 4 presents spectra with gate widths of 1000 ns, taken just inside Flame 4. Here, one can see the nitrogen Raman feature, together with a structured spectrum clearly arising from formaldehyde fluorescence and several small Raman features from flame products. Spectra taken just inside Flame 5 are similar to Figure 4 but less structured. The entire spectrum is dominated by laser induced fluorescence from formaldehyde and PAH species. The nitrogen Raman line is in evidence, but no other distinguishing Raman features can be found. The 355 nm case could be used, however, for line imaging; to acquire formaldehyde fluorescence signatures near flame zones while clean Raman signatures would be observed in the post flame zone. Appearance of PAH signatures above the formaldehyde spectrum in specific locations could also prove useful, because they appear at higher equivalence ratios.

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