TEMPERATURE MEASUREMENTS BY SPONTANEOUS RAMAN SCATTERING IN A MESO–SCALE COMBUSTOR

L. CARATTI, F. COZZI

Abstract
The actual technological trend shows an increasing interest in system miniaturization. This, in turn, requires the development of compact, energetically dense supply devices: actual Li – ion batteries have a limit around 1.2 MJ/m$^3$, while the emerging sector of small scale, hydrocarbon - fueled combustors shows the possibility to increase this limit above 2 MJ/m$^3$ even at very low efficiencies. This paper describes the development of a Spontaneous Raman Scattering system for the measurement of temperature inside a meso – scale combustor (i.e. a combustor which dimensions are of the same order of magnitude of flame characteristic scales). Preliminary measurements on the simplified case of a free hot air jet have been performed in order to obtain an estimate of the system signal – to – noise ratio, and important issues relative to the application of the system to small volumes have been pointed out.

Theoretical review
Spontaneous Raman scattering is an phenomenon by which incident radiation (such as that of a laser) is diffused by the particles (atoms or molecule) of a medium. The light is anelastically scattered, this meaning that the Raman radiation is different from that of the incident light: in particular two distinct Raman lines exists, Stokes (shifted towards the red range of the spectrum) and anti – Stokes (shifted towards the blue range). Quantum mechanics shows that Stokes Raman signal is produced when a photon interacts with a ground state electron: the electron reach a virtual excited state and instantaneously returns to an acceptable energy level which is different from the original one. The emitted photon is less energetic than the incident one, and the associated wavelength is lower. On the contrary, anti – Stokes Raman is associated with the interaction of a photon and an excited electron: in this case, the electron reach a virtual level and return to an acceptable state which is less energetic than its original one, thus the wavelength of the scattered radiation is higher than that of the incident light.

Raman shift (i.e. the distance of Stokes and anti – Stokes lines from the incident radiation wavelength) depends upon the chemical species that is actually diffusing, therefore contributions from each single species can be analyzed separately. Table 1 shows Raman lines for some substances. Additionally, the ratio between Stokes and anti – Stokes Raman intensity is a function of temperature. However, Raman signal is characterized by an extremely low intensity due to the fact that Raman cross section (a measurement of the probability of producing a “Raman photon” for each incident photon) is on the order of $10^{-30}$. 
### Experimental set – up

System was tested and analyzed for a simplified case of a free air jet. The second harmonic (532 nm) of an Nd:YAG pulsed laser (max. energy per pulse: 200 mJ), previously used for P.I.V. measurements. Both pulses were used for each acquired shot. An half-waveplate was used for fine adjustment of the polarization plane (Raman scattered light is polarized) and a 500 mm focal length lens was used for focusing the laser in the probe volume, which was inside a free air jet. An electrical heater was available, which permitted to heat the air flow up to ~250 °C.

Scattered light was collected using a 50 mm lens; in order to achieve an attenuation of the noise from Mie and Rayleigh scattering, a notch filter was used. The filter allowed for a 1:10^6 reduction at 532 nm, with a transmittance above 90% at Nitrogen Stokes and anti – Stokes lines. Collected radiation was sent to a monochromator, and then to a Photomultiplier tube (PMT). Estimated signal – to – noise ratio of the PMT was ~60, with a Quantum Efficiency of 9.5% at Nitrogen Stokes line and 18.8% at Nitrogen anti – Stokes line. Monochromator spectral resolution was 4 nm with the selected 1 mm wide slit, while the global spatial resolution of the system was 1 mm.

PMT signal was integrated using a boxcar integrator, and then acquired using a National Instruments acquisition board.

A major issue relating the use of Spontaneous Raman Scattering for temperature measurement is the necessity of converting scattered light intensity to an information on the medium temperature. As it has been pointed out by other authors [2][3], it is possible to acquire both Stokes and anti – Stokes signal for a single species (typically Nitrogen) and then evaluate temperature from the ratio of the two. This procedure requires the acquisition of two spectrum lines. However, different behaviour of the system at different wavelengths poses the necessity of calibration, and since with a single monochromator + PMT line we can examine only one wavelength at a time, no instantaneous measurements will be feasible.

From the performances of the selected hardware, a rough estimate of Raman signal – to – noise ratio was performed following eqn. 1, which states that the number $N_R$ of Raman photons contributing to the signal is proportional to the number $N_{las}$ of photons which pass through the probe volume. The proportionality constant depends upon a “conversion energy” which is a measure of how many Raman photons are generated for every incident light photon (the estimate shows that, although about $10^{17}$ photons are contained in each pulse, Raman photons are on the order of $10^3$); the transmittance of the collection optics estimated to be around 30%; and the PMT quantum efficiency. Finally, considering that the PMT output signal follows Poisson statistics [4], an estimated S/N ratio of 5.5 was obtained.

$$N_R = \eta_{conv} \eta_{opt} \eta_{QE} N_{las}$$

### Table 1: Examples of Raman shift form some chemical substances

<table>
<thead>
<tr>
<th>Chemical Species</th>
<th>Raman Shift [cm^{-1}]</th>
<th>Stokes line [nm]</th>
<th>Anti – Stokes line [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>2330.7</td>
<td>607.3</td>
<td>473.0</td>
</tr>
<tr>
<td>Oxygen</td>
<td>1556.0</td>
<td>491.3</td>
<td>580.0</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4169.2</td>
<td>683.2</td>
<td>435.6</td>
</tr>
</tbody>
</table>
Preliminary results

A first analysis of the effective system performances was obtained for an air jet at ambient pressure and temperature (P = 1 atm, T = 15 °C). Scattered light intensity was obtained by first acquiring system noise (a shutter was placed in front of the collecting lens), the mean of which was then subtracted from the resulting signal of 5000 shots without the shutter. Figure 1 shows the mean scattered light intensity at different wavelengths: the peaks of Oxygen and Nitrogen Stokes Raman lines (at 580 and 608 nm respectively) are clearly visible. Figure 2 shows the probability density function (PDF) of light intensity at N\textsubscript{2} Stokes line (607 nm): for a large number of occurrences, the system output doesn't differ from random noise; also, when a Raman signal is detected, its dispersion is much wider than expected, resulting in a measured S/N ratio of the order of 1.

Possible explanations of the difference between the predicted S/N ratio and the expected one include:

● an optimistic estimate of collection optic efficiency: no data on monochromator transmittance at different wavelength was obtained, thus the estimated global value of 30% could be higher than the effective value;
● an effect of laser point instability: system's Depth of Field (DoF) was estimated to be around 40 \(\mu\)m, while uncertainty about laser position was about 60 \(\mu\)m. Thus, considering that laser diameter is 30 \(\mu\)m in the probe volume, a rough estimate shows that, due to laser point instability, up to 50% variation in the energy flux in the probe volume are possible.

Main issues related to the micro – burner

A first problem related to the application of Spontaneous Raman Scattering to a micro – burner is the necessity to provide optical access to the combustion chamber: this issue was resolved by opening a small, 0.6 mm wide rectangular opening on the burner side, thus permitting temperature measurements along the burner axis. Every access is sealed using a quartz window: preliminary tests showed that focused laser radiation could damage these windows. This issue results in an
upper limit to pulse energy, and therefore of the achievable S/N ratio.

A second issue is related to the high temperatures inside the combustion chamber: preliminary measurements conducted in a heated air jet shows an inverse proportionality of Raman signal with temperature (see Fig. 3), as predicted by theory [4]. This imply that signal intensity in the micro-burner will be much lower than that in non-reacting conditions, and therefore S/N ratio will be adversely affected.

![Fig. 2: Raman N\textsubscript{2} Stokes line PDF compared with noise PDF](image)

![Fig. 3: Raman N\textsubscript{2} Stokes line intensity at different temperatures of an hot air jet.](image)
Concluding remarks
A Spontaneous Raman thermometry system has been tested and analyzed in a simple configuration of a free air jet. The necessity of acquiring both Stokes and anti – Stokes Raman signal poses the necessity of a calibration of the system; moreover, using a single monochromator + PMT acquisition line only mean measurements will be possible.

System measured signal – to – noise ratio has been found to be lower than the expected one, and some possible explanations have been proposed: these include an optimistic estimate of optics efficiency and the effect of laser point instability.

Some preliminary issues related to the application of Raman thermometry to a micro – burner were pointed out, including the effect of temperature on signal intensity and windows damage threshold.

Future developments of the activity will necessarily include ways to increase S/N ratio:
- optics with a higher f - number could increase DoF and reduce the effect of laser point instability, but they would also reduce the portion of collected scattered light, thus a balance between positive and negative effects must be performed;
- a pulse stretcher would permit to use the same laser intensity: since Raman signal is related to incident light energy, increasing pulse transit time while not changing the overall pulse energy would not adversely affect signal intensity;
- in literature, it has been found a proposal related to the use of Nd:YAG third harmonic [1]: this would allow us to operate in a spectrum region where PMT quantum efficiency is higher, while increasing Raman cross section (which is proportional to $\lambda^{-4}$). However, this solution is not feasible at this time due to costs and potential LIF interference.

More generically, the next step of the activity will be the application of the system to the micro – burner. At first, non reacting conditions will be considered (i.e. injection of hot air); successively, reacting conditions will be considered, examining the necessity of a calibration.

Acknowledgements
The authors of this paper wish to thank Dr. G.Zizak, Dr. S. De Iuliis, Dr. A. Olivani and Mr. L. Pelagatti.

This work is supported by the Italian Ministry for University and Research (MIUR) under contract n° 2006094334_002.

Bibliography