Enhanced Gas Phase Raman Spectroscopy by means of Multipass Laser Excitation

W. M. Doyle, Hellma Axiom, Inc.

This technical note describes an approach to the spectroscopic analysis of organic vapors which employs multiple passes of the exciting laser radiation through the sample so as to achieve more than an order of magnitude enhancement of the detected Raman shifted optical spectrum and the resultant analytical sensitivity.

Introduction

Raman scattering is a rare event. It is only the extreme brightness of a focused laser radiation that makes Raman spectroscopy practical. Thus, since the laser beam is not materially affected by the interaction, it should be possible to pass the same laser beam through a sample multiple times with little attenuation of the laser power. We have accomplished this by means of a probe design in which a laser beam is reflected multiple times between a reflector behind the sample and a reflecting optical filter within the body of the probe.[1] Using this approach, we have been able to demonstrate more than an order of magnitude signal enhancement for optically clear samples.[2] This advance has a range of potential applications. For example, it provides the possibility of reducing the cost of some Raman installations by allowing the use of less sensitive detectors and less powerful lasers. At the other extreme, when used with high performance instruments, it may allow Raman spectroscopy to be applied in completely new areas - such as the replacement of Gas Chromatographs in applications requiring routine operation and low cost of ownership.

In an earlier paper, we employed a prototype design to demonstrate the application of the multipass approach to providing an order of magnitude sensitivity enhancement in the analysis of clear liquids.[3] The present paper reports on the performance of a fully refined commercial probe designed for vapor phase analysis.

Probe Design

Figure 1 illustrates the probe design used in our studies. A key element of this design is the use of a small fused silica rhomboid to inject the laser excitation beam on a path parallel to the axis of the collection optics but displaced to one side. The objective lens serves to both focus the laser beam at the surface of a reflector in the sample region and to collect the Raman scattered radiation emanating from the focal region. After being reflected, the laser beam is recollimated by the objective lens and returned on a parallel path to the optical head where it passes the tip of the rhomboid and strikes the laser blocking filter. (This can be either a long pass or a notch filter.) Since this filter is a very good reflector at the laser wavelength, it reflects the beam back to the objective lens where it is again focused at the reflector. By appropriate adjustment of the probe optics, we can arrange to have the laser beam returned to sample region multiple times, resulting in a significant enhancement of the collected Raman scattering.

It should be noted that simply placing a mirror behind the sample can result in a signal enhancement of up to four times with almost any Raman probe. This enhancement is due to two factors, the collection of both the forward and back scattered Raman radiation and the doubling of the laser power in the sample region. The difference with our design is due to the use of the blocking filter to further multiply the effective enhancement.

Figure 1: RFP-465 Optical layout.
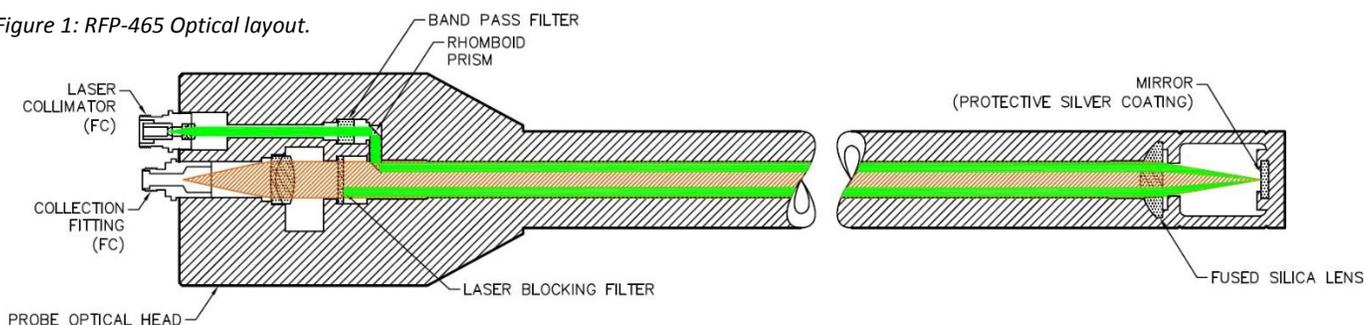
Enhancement of Atmospheric Spectra

Figure 2 shows the O_2 spectral bands of normal room air obtained with the multipass probe (Model RFP-465) and with a conventional single pass probe (Model RFP-410). Both spectra have been offset to a zero baseline for comparison. The peak height of the multipass spectrum is almost thirty times higher than that of the single pass spectrum and the rotational sidebands are clearly discernable.
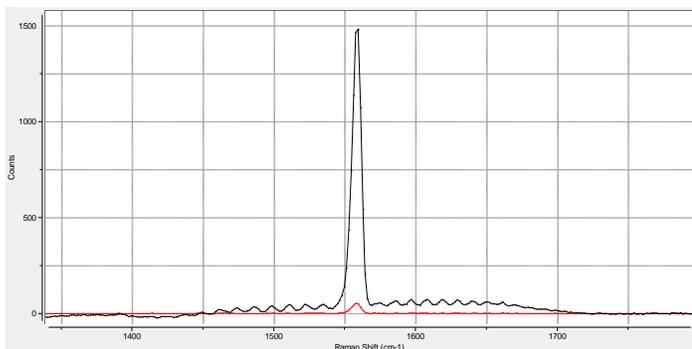

Figure 2: Single pass (red) and multipass (black) spectra of atmospheric oxygen obtained using a Tornado Spectral Systems U1 Raman spectrometer with 532 nm excitation and 20 second data acquisition.

Figure 3 shows the same two spectra with the single pass spectrum scaled up by a factor of 27.4 to allow comparison of the analytical sensitivity. Although the multipass effect enhances the Raman signal by a large factor in this case, it also increases the noise level due to increased shot noise. As a result, for these particular experimental conditions, the signal-to-noise enhancement is limited to a factor of approximately six.
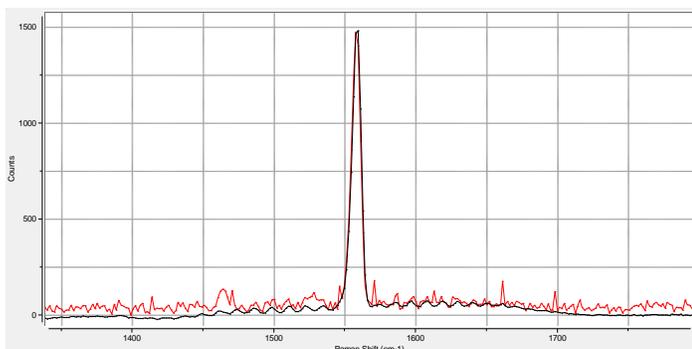

Figure 3: The data of Figure 2 with the single pass spectrum scaled up by a factor of 27.4 to match the intensity of the multipass spectrum.

Noise Considerations

The performance of a spectroscopic system employing a multipass probe depends both on the characteristic signal enhancement of the probe and on the nature of the relevant noise sources. These can be separated into two general categories: signal dependent shot noise and instrument

background noise. With modern high performance Raman spectrometers employing cooled detector arrays, the

instrument noise can be quite low, and shot noise will often dominate. The latter is characteristic of both the Raman signal generated by the sample being studied and of any spurious signals generated by the components within the sampling probe.

The RFP-465 multipass probe used for our tests includes two types of background radiation, Raman scattering and fluorescence. The Raman scattering component is primarily the fused silica Raman spectrum characteristic of the bulk optical materials of the probe. We would expect this component to be independent of excitation wavelength. The fluorescence component may be due to both impurities in the fused silica and the materials used for the filter coatings. This component will vary depending on the excitation wavelength. In particular, it should be possible to reduce fluorescence by using a different excitation wavelength than the 532 nm used for our tests. Both background components are magnified by the enhancement effect.

As long as shot noise is dominant, we would expect the signal-to-noise enhancement to be proportional to the square root of the signal enhancement. However, if we were to use a spectrometer system employing a lower power laser or a non-cooled detector array, both of which might be desirable in a process environment, we could easily operate in a region where additive instrument noise is important. In this case, the signal-to-noise enhancement will approach the signal enhancement.

To test the above assumption, we reduced the system performance by attenuating the received signal. To do this, we simply coupled a 100 micron core optical fiber in series with the 300 micron core fiber normally used for collection. This resulted in approximately an order of magnitude signal reduction. The result is shown in Figure 4.
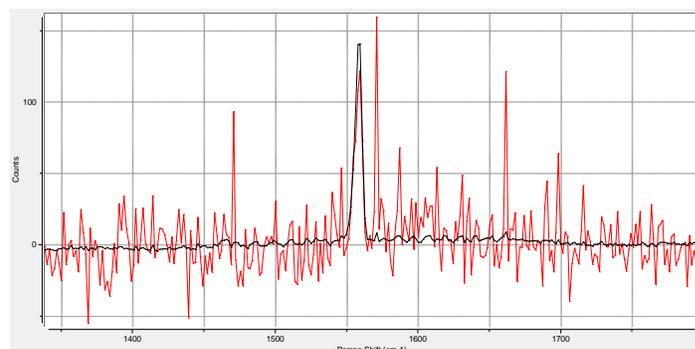

Figure 4: Single pass (red) and multipass (black) spectra of atmospheric oxygen acquired under the same conditions as Figures 2 and 3 but with a 10 X attenuation of the collected signal. The single pass spectrum has been scaled up by a factor of 30. This scale factor was determined by matching the stronger N2 band for the two spectra.

To compare the noise levels, we first acquired two spectra under each condition. Using Symbion DX software, we took the difference between the two spectra in each pair and then calculated the RMS noise levels for various spectral regions. The results are shown in Table I.

Table I: Signal-to-noise enhancement under the full signal and reduced signal conditions.

Spectral Region	S/N Enhancement (Full Signal)	S/N Enhancement (Reduced Signal)
300 – 500 cm^{-1}	3.3 X	8.8 X
600 – 900 cm^{-1}	5.1 X	17.1 X
1000 – 2500 cm^{-1} (Av.)	6.0 X	18.3 X

For each condition, the signal-to-noise was roughly constant over the 1000 – 2500 cm-1 range. The reduced enhancement at lower Raman shifts is due to the presence of the strong fused silica background in this region.

Probe Background Spectral Effects

Figure 5 includes two spectra obtained with the multipass probe inserted into a sealed vapor test fixture. The blue spectrum shows and ambient air spectrum as well as the fused silica Raman spectrum and a broad fluorescence background. For the red spectrum, we put a drop of toluene in the fixture and allowed the head space vapor to come to equilibrium. (At 20 ºC, the vapor pressure of toluene is approximately 0.029 bar.)
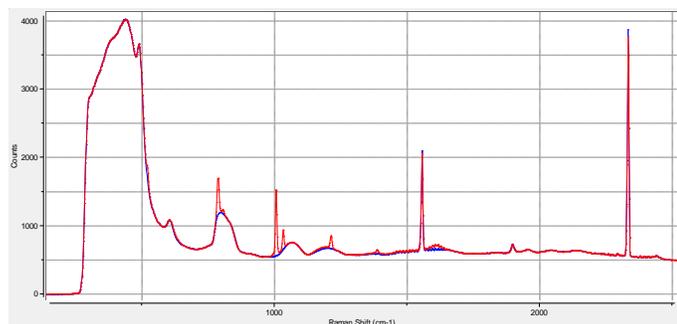

Figure 5: Raw spectra of ambient air (blue) and of Toluene vapor (vapor pressure = 0.029 bar) in ambient air (red). Note the strong O2 and N2 bands centered at approximately 1559 cm^{-1} and 2336 cm^{-1} as well as the fused silica background spectrum.

To determine the degree to which the probe background spectrum can be subtracted from a measured sample difference between the two spectra.

The result is given in Figure 6. As can be seen the background can be subtracted out to within the noise level, or roughly 2 counts out of 4000 in the low frequency region.
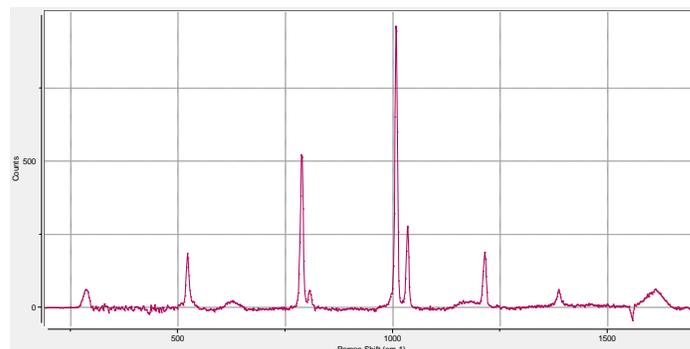

Figure 6: Toluene vapor spectrum of Figure 4 after subtracting the ambient air spectrum. Note that the subtraction effectively removes the fused silica features. The negative peak at 1559 cm^{-1} is due to the reduced oxygen level in the presence of the toluene vapor. The increased noise level between 250 cm^{-1} and 600 cm^{-1} is the result of the increase shot noise caused by the strong fused silica Raman band in this region.

Conclusion

We have demonstrated that, when used to analyze clear gasses, the RFP-465 multipass Raman probe can provide a signal enhancement of between twenty and thirty times compared to a conventional probe. The signal-to-noise enhancement will depend on the nature of the noise sources in the overall system. It can range from typically six times in the case where signal dependent short noise is dominant to values approaching the signal enhancement factor of twenty to thirty when additive noise is dominant.

References:

1. US Patent 6,795,177 B2

2. "Enhanced Raman spectroscopy by means of multiple pass laser excitation", IFPAC-2008, Paper I-062.

3. "New Developments in Probes and Systems for High Sensitivity Molecular Spectroscopy", IFPAC-2012, Paper I-071

Hellma® Axiom
Analytical Technology