

Design and Testing of a Modular Raman Cell and Air Sampling System for Hydrogen Gas Detection

Honors Thesis

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By

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ABSTRACT

Hydrogen is emerging as a potential energy carrier and low-carbon alternative to fossil fuels. As hydrogen infrastructure grows, detecting hydrogen emissions will become increasingly important for reasons including safety monitoring, quantifying product loss, and setting greenhouse gas inventories. Laser diagnostic methods such as coherent anti-Stokes Raman spectroscopy (CARS) and photoacoustic Raman spectroscopy (PARS) can provide reliable detection of trace hydrogen gas concentrations but have primarily been demonstrated in laboratory environments. This study investigates the design of more compact system components and flow sampling hardware to enable practical field deployment of CARS or PARS for the development of a portable hydrogen gas sensing instrument. A modular Raman shifter cell was designed and tested at multiple lengths ranging from 0.5 to 2 meters. Testing involved maintaining a constant input laser energy while varying cell pressure to characterize Raman scattering conversion for a given cell configuration. In addition, a flow-through gas sampling system was designed to enable gas flow through CARS or PARS sample cells to support development of the instrument's air sampling system. Results show that reducing Raman cell length decreases the stimulated Raman scattering (SRS) conversion which can be supplemented through an increase in gas pressure within the cell. Additionally, flow-through testing with nitrogen demonstrated that flow-induced acoustic noise is a limiting factor for PARS measurements, with higher flow rates producing increased acoustic noise that can interfere with detection sensitivity. The results demonstrate that compact Raman cell configurations and controlled flow sampling systems are viable for supporting development of a portable hydrogen sensing instrument capable of active ambient air sampling in field and industrial environments.

Keywords: Raman scattering, Raman shifter cell, coherent anti-Stokes Raman spectroscopy (CARS), photoacoustic Raman spectroscopy (PARS), air sampling, hydrogen detection

Word Count: 2,599

INTRODUCTION

Hydrogen continues to be developed as an energy carrier and low-carbon alternative to fossil fuels. As hydrogen usage increases with the push toward renewable energy sources, understanding the emissions and leakage of hydrogen becomes increasingly important for several reasons. A major reason is that hydrogen is an indirect greenhouse gas, meaning it can preserve lifetimes of atmospheric greenhouse gases, particularly methane [1]. With production costs ranging from \$2-4 per kg, understanding hydrogen leakage rates is important for quantifying financial losses as well [2]. Additionally, with the lower flammable limit (LFL) of hydrogen being 4% in air, monitoring hydrogen concentrations in ambient conditions is important for maintaining safe environments [3].

Historically, portable sensor platforms for hydrogen gas detection focus on using electrochemical, metal oxide, and chemical film detectors. While sensitive, these detection methods are often affected by environmental effects such as humidity and temperature [3].

Optical detection methods are advantageous because they are non-intrusive, sensitive, and can support versatile and compact detection instruments [4]. Many optical detection methods rely on detecting molecules by observing the amount of light absorbed by those molecules [5]. Molecular hydrogen does not absorb light in the ultraviolet, visible, or infrared, making its optical detection challenging [3], [6].

Hydrogen Detection Via CARS and PARS

Coherent anti-Stokes Raman spectroscopy (CARS) is a laser diagnostic method well suited for trace species measurements due to its strong coherent signal generation. CARS generates a detectable light signal using stimulated Raman scattering (SRS), a nonlinear interaction in which photons at frequency ω_1 inelastically scatter into a Stokes photon at ω_2 , and an anti-Stokes photon at ω_3 . SRS strength increases when the difference $\omega_1 - \omega_2$ is near the Raman active molecular vibration resonant frequency ω_v [7-16].

Photoacoustic Raman spectroscopy (PARS) is closely related and utilizes the same inelastic scattering interaction as CARS but generates a pressure wave which can be detected by a microphone [6], [17-20].

CARS and PARS have a high signal-to-noise ratio (SNR) and the ability to measure specific chemicals. Both detection methods have sensitivities capable of reaching down to approximately 2-30 ppm [6]. In addition, both methods are well suited for the detection of hydrogen gas due to its large frequency shift and low optical dispersion. These properties allow for strong signal generation and signal quality, allowing for hydrogen to be detected reliably with these methods [21].

Raman Shifter Cells

One way to generate the pair of laser beams required for CARS or PARS at frequencies ω_1 and ω_2 is the use of two lasers. Another way is the use of a single laser paired with a Raman shifter cell to generate the second laser beam via SRS, shown in Figure 1. The strength of the SRS through the Raman shifter cell is related to the number of molecules in the cell such that increasing either the interaction length, or the pressure within the cell, increases the strength of the SRS process [21-23].

Many sources support the use of Raman cells at 2 meters in length. This length allows the stimulated Raman scattering process to build upon itself over the length of the Raman shifter cell, generating a Stokes beam of higher energy, while depleting more of the initial pump beam [21].

Previous research has investigated the effects of more compact Raman cells, introducing tradeoffs between conversion efficiency and cell length. Research on compact Raman cells down to 15 cm shows major limitations in reduced SRS conversion as well as increased probability of optical break-down when pressure of the gain medium is increased. Optical breakdown occurs due to gas ionizing and forming plasma caused by high intensity of a laser beam [21]. The Stokes intensity (I_s) grows exponentially as shown in Equation 1:

$$I_s(l) = I_s(0) \exp(rI_p l) \quad (1)$$

This introduces a tradeoff between length (l) and the product of the Raman gain coefficient and the intensity of the pump beam [21]. The Raman gain coefficient (r) is directly proportional to the gas density within the Raman cell, meaning that increased pressure within the cell could partially account for lost intensity due to changes in cell length [21], [24]-[26].

MATERIALS AND METHODS

Raman Cell Experimental Setup

The Raman cell originally used in the current laboratory setup is 2 meters in length and is used to support detection of hydrogen gas via either CARS or PARS. To enable the development of a portable trace hydrogen gas instrument using PARS, a more compact Raman cell is desirable.

To demonstrate Raman scattering conversion for various Raman cell lengths, a modular design for the Raman cell was adopted, as shown in Figure 1. The cell was divided into two 0.25 meter

end sections and interchangeable middle sections of either 0.5 or 1.0 meters in length. These are attached using one-inch Swagelok fittings and adapters, allowing the cell to be assembled to lengths of 0.5, 1, 1.5, or the original 2 meter length.

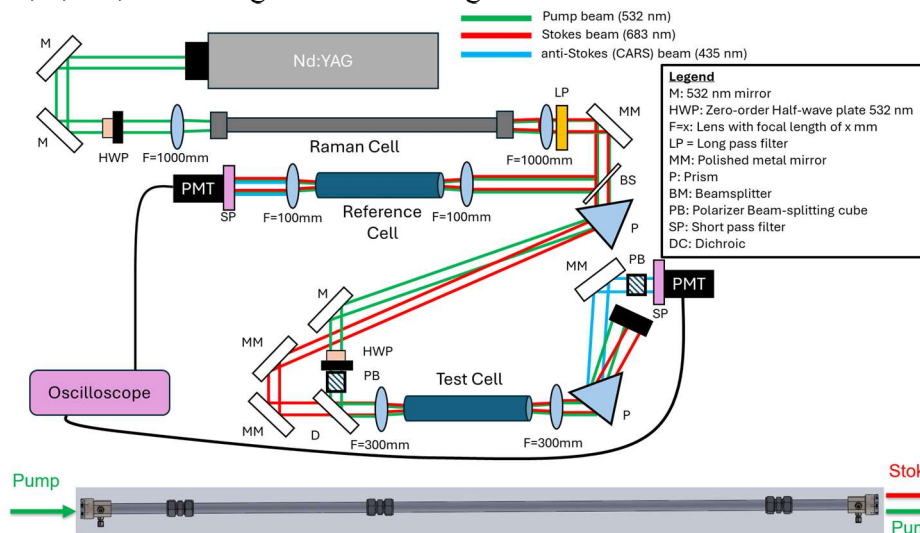


Figure 1: Schematic of current CARS Laboratory Setup [27] (top) and Modular Raman Cell (bottom).

The experimental methodology used for testing each length of the Raman cell was to hold the input pump laser energy constant, while varying the pressure within the cell to determine the pressure dependence of Raman scattering conversion. The remaining green (pump) and generated red (Stokes) laser beams are then separated using a prism, and their energies are measured using a power meter.

Flow-Through Test Cell Experimental Setup

In addition to developing compact hardware for a field deployable instrument, the ability to continuously draw air or gas samples through the PARS or CARS sample cell is a crucial step towards a final instrument.

Similar photoacoustic and laser-based detection methods used for active gas detection direct air flow-through particulate filters and desiccant dryers to limit interference to measurements introduced by humidity and particulates [4], [28].

A flow-through system was designed to enable the active flow of pure gas samples to allow for calibration, residence time observations, and to observe the performance of the filtration and drying components needed for active air sampling.

The designed system is shown in the piping and instrumentation diagram (P&ID) in Figure 2. Active flow is driven by upstream pressure delivered from regulated gas cylinders and controlled using critical orifices to cause choked flow, maintaining a controlled flow rate through downstream components. A single line can be used, or a second branch can be added, to allow for the dilution of gas samples to achieve intermediate concentrations as desired. The flow is then directed through the chosen particulate filter and desiccant dryer to observe the pressure drop/back pressure across those combined components using a pressure transducer. The sample then flows through the PARS sample cell and is safely vented to an exhaust vent.

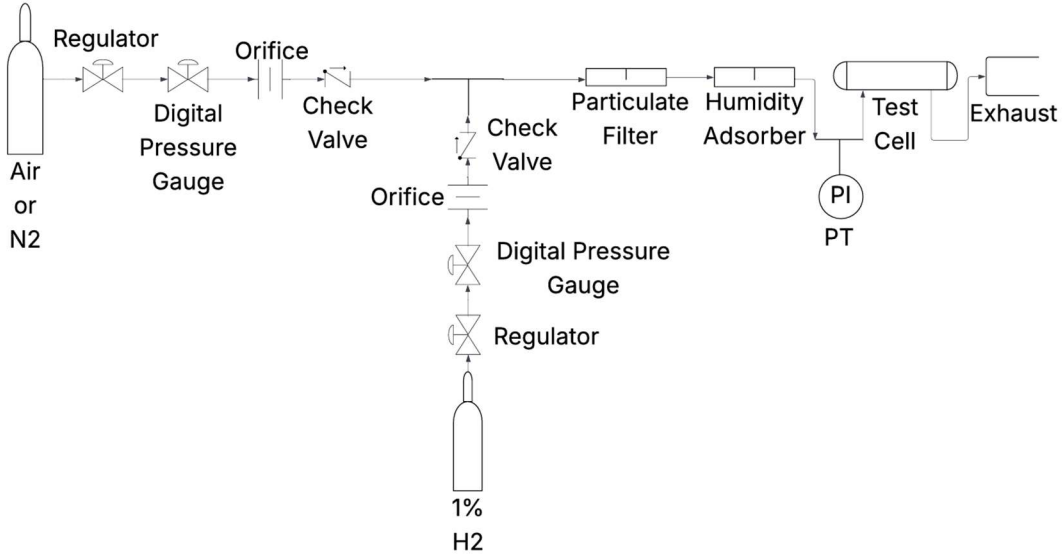


Figure 2: Flow Through Test Cell Experimental Setup.

RESULTS

Raman Cell Length Characterization Results

Raman cell testing was initially performed at the full two meter length to characterize SRS conversion at multiple pressures. The input laser energy was maintained at a constant 115 mJ, the same laser input energy typically used for performing CARS. This was used to determine the effects of changing cell pressure for a given input energy shown in Figure 3.

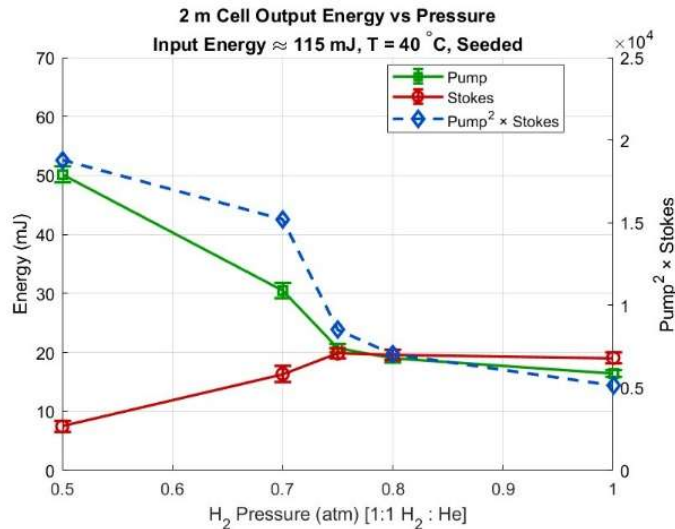


Figure 3: Full Length Raman Cell Baseline.

The right axis displays an important parameter used to determine the balance of pump and Stokes beam energies used for CARS. The signal generated in CARS is in the form of a third blue beam referred to as the anti-Stokes beam. The intensity of the anti-Stokes beam (I_{as}) is proportional to the intensities of the pump (I_p) and Stokes (I_s) beams as shown in Equation 2 [6], [8].

$$I_{as} \propto I_p^2 I_s \quad (2)$$

The cell length was then decreased to 1.5 meters. A small reduction in SRS conversion was observed, with the remaining pump beam energies approximately 10 mJ higher than those produced with the full length cell, while the generated Stokes beam energies are approximately 10 mJ lower, both for a given pressure, shown in Figure 4.

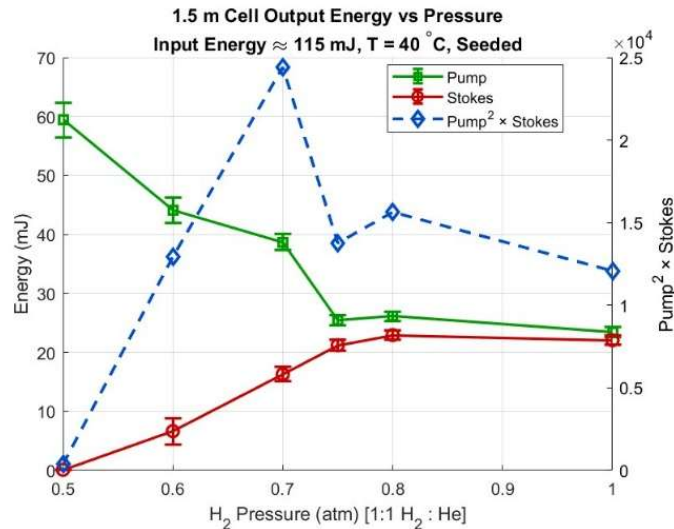


Figure 4: 1.5 meter Raman Cell Results.

Following successful testing of the 1.5 meter Raman cell, the cell length was further reduced to 1 meter. The focusing lens at the input of the Raman cell was then changed from 1000 mm to 500 mm to prevent damage to the fused silica windows used on the Raman cell due to being placed closer to the focal point of the laser beam. The cell pressure was then increased to achieve SRS conversion, shown below in Figure 5.

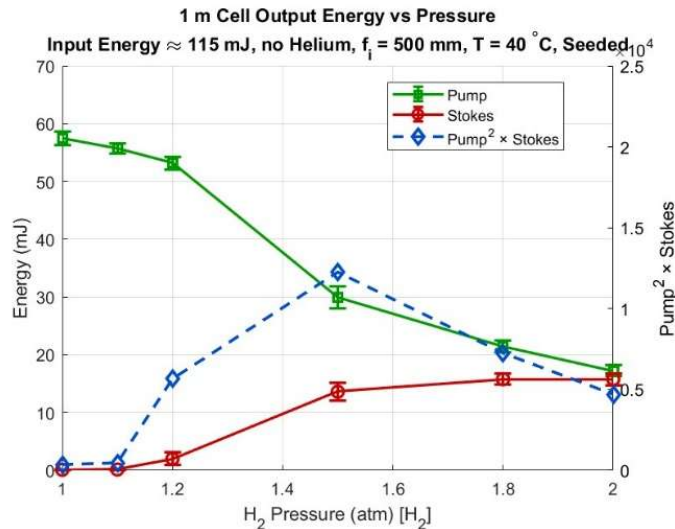


Figure 5: 1 meter Raman Cell Results.

Following successful testing of the 1 meter Raman cell, the cell length was further reduced to 0.5 meters. The same focal length lens of 500 mm used for the 1 meter cell was used for the 0.5 meter cell. The observed SRS conversion was achieved through an increase in pressure, notably

nearly twice the cell pressure used for the 2 meter cell, as well as a slight increase from the 1 meter configuration, shown in Figure 6.

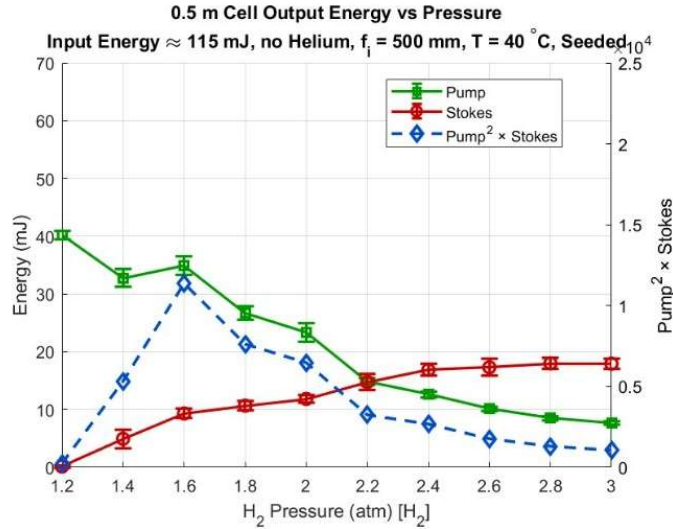


Figure 6: 0.5 meter Raman Cell Results.

Laser Beam Profile Improvements

An important consideration for the generated Stokes beam is its beam quality. Due to the non-linear nature of SRS, the Stokes beam generated was observed to have a degraded beam quality compared to the pump beam. Laser beam profiles were measured with a charge-coupled device (CCD) beam profiling camera.

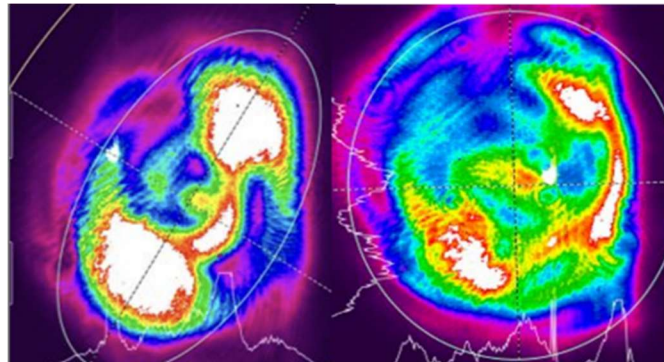


Figure 7: Stokes Beam Profile Without (left) and With (right) Addition of Heat and Helium.

The addition of helium buffer gas and heat tape along the bottom of the Raman cell was found to improve the Stokes beam quality, shown in Figure 7, while having a negligible effect on SRS conversion. The heat tape introduces a temperature gradient to induce convection within the cell, while the addition of helium increases the thermal conductivity of the gas mixture. These combined effects help to minimize local temperature gradients or hot spots [29]. Ideal conditions were found at a temperature of 40°C with a 1:1 ratio of hydrogen and helium in the Raman cell, with both present at 0.7 atm for a total cell pressure of 1.4 atm.

Acoustic Flow Cell Noise Results

The flow through system shown in Figure 2 was successfully tested with nitrogen at flow rates of 100, 860, 1000, and 1260 standard mL/min. The variation in flow rate was chosen to determine the impact of various flow rates on the back pressure observed through filtration and drying components, as well as acoustic noise generated by active flow over the microphone mounted in the sample cell for PARS measurements.

A back pressure increase of approximately 0.03-0.06 psi was observed due to the particulate filter and desiccant dryer used. The acoustic noise generated was significant for the higher flow rates tested, and negligible for the lowest flow rate of 100 standard mL/min. The noise level was found to be approximately equivalent to that produced by a 1% hydrogen concentration measurement using PARS.

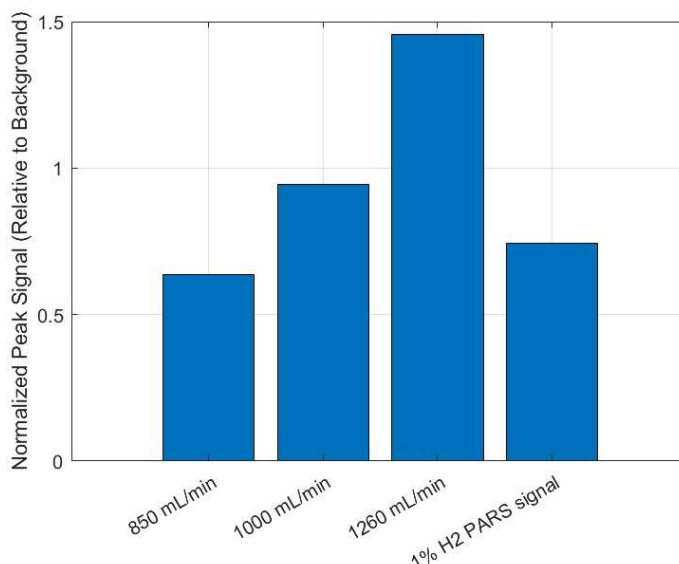


Figure 8: Acoustic Noise Normalized by Background Noise.

This was obtained by observing the acoustic signal measured by the microphone used for PARS during active flow as well as ambient background noise using an oscilloscope. The signal level was then normalized using the background signal and compared to PARS measurements taken under similar conditions, shown in Figure 8.

DISCUSSION

The reduction in Raman shifter cell length was observed to reduce the amount of SRS conversion through the cell, depleting the energies of pump and Stokes beams used for the detection of hydrogen gas via CARS or PARS. The reduction in conversion efficiency was determined to have been caused by a reduction in interaction length between the incoming pump beam and hydrogen gas within the cell as the cell length was reduced.

As the Raman cell length was reduced from 2 meters to 1.5 meters, the observed pump energy increased and Stokes energy decreased, both by approximately 10 mJ. Following further reductions to 1 and 0.5 meter configurations, a shorter focal length lens was used in addition to the shorter cell length, causing a significant reduction in Raman conversion.

The Raman conversion in the 1 and 0.5 meter cell configurations was then improved by increasing the total hydrogen pressure within the cell. The pressure increased by nearly a factor of two to achieve pump and Stokes energies comparable to those generated with the longer cell configurations.

The reduction in Raman shifter cell length, and ability to achieve the desired output laser beam energies due to an increase in cell pressure demonstrates the ability to adopt shorter Raman cell configurations for use with CARS and PARS detection methods.

The flow testing performed with the photoacoustic cell used in PARS was observed to have significant impact on the signal level detected by the microphone. This effect is likely caused by the flow of gases passing directly over the microphone, which is situated a short distance between the input and output lines of the sample cell. In addition, as the flow rate was increased, this flow noise was observed to increase, as expected. For this reason, lower flow rates on the order of 100-800 standard mL/min will likely be desirable for reducing flow-induced noise as well as maintaining an appropriate residence time of gases within the sample cell.

CONCLUSION

In conclusion, this work successfully demonstrated the reduction in length of the Raman shifter cell used for generating laser beams for CARS and PARS detection methods, supporting the development of a portable hydrogen detection instrument. Raman scattering conversion was observed to decrease with a reduction in both Raman cell length, as well as focal length. The reduction was mitigated by increasing the hydrogen pressure within the Raman cell. An increase in pressure increases the number density of hydrogen molecules present, supplementing a reduction in interaction length associated with reduced cell length.

Flow-through testing of the PARS photoacoustic sample cell determined that interference imparted by flowing gases over the detection microphone used is a significant limiting factor for maintaining low detection limits. Future work will focus on the development of flow noise reduction hardware and techniques, as well as improved flow systems to support air sampling in a portable hydrogen detection system.

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