Simplification of RELIEF Velocimetry Using Pico-Second Tagging and Broad Band
Interrogation

Thesis

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By

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Abstract

This work demonstrates the potential for a simplified portable “RELIEF” velocity apparatus, employing the use of a compact, relatively low cost, ~150 pico-second duration Nd:YAG laser to vibrationally excite molecular oxygen in a stimulated Raman scattering, tagging step. The tagged oxygen molecules are interrogated by Laser Induced Fluorescence, utilizing a low cost broadband ArF laser, as a replacement for the injection – seeded ArF laser which has been traditionally employed. The Stokes beam required in the tagging step is generated in both a single and multi-pass Raman Shifting Cell, with the corresponding Raman shift conversion efficiencies reported herein.

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Chapter 1

Introduction to the RELIEF Method

Introduction

The RELIEF method was developed by the Miles¹ group at Princeton University in 1987 to determine the velocity of high speed air flows. A laser is employed to pump a Stimulated Raman scattering cell and the output in-turn “tags” or vibrationally excites molecular oxygen naturally present in the flow. After some delay, during which time the “tagged” molecules convect with the flow, the displacement pattern of vibrationally excited oxygen molecules is “interrogated” by employing an argon fluoride (ArF) excimer laser which selectively electronically excites molecules in $v''=1$. From the electronically excited state the molecules fluoresce and the location of the tagged molecules is ascertained by an ICCD camera. Further details of the RELIEF method will be found in subsequent sections. Historically this work has employed a nano-second Nd:YAG laser to pump the Raman cell in the tagging process, but we have demonstrated the use of a pico-second laser in addition to the use of a multi-pass Raman cell. We have also employed a simple broadband ArF excimer laser to interrogate the tagged molecules, in place of the previously employed narrow linewidth injection locked ArF laser (Chapter 2).

1.1 Anemometry

Velocity measurement of air flows, or anemometry, has been studied since the 1600's when the first anemometers were used to measure wind velocity. Anemometry has continued to gain importance with the development of the wind tunnel and subsequently modern flight.

Early aeronautical engineers employed what is known as a Pitot tube². Originally developed for water flows the Pitot tube is actually a pair of tubes, one, of which is bent at an angle with an open end directed into the flow to measure the stagnation pressure. The second tube is oriented perpendicular to the flow and measures the static pressure. The stagnation pressure reaches a maximum when the flow stagnates at the face of the Pitot tube ($V_2=0$). Airspeed can be determined using Bernoulli's equation

$$p_1 + \frac{1}{2}\rho V_1^2 = p_2 + \frac{1}{2}\rho V_2^2 \quad 1.1$$

However, as the flow velocity nears the speed of sound (Mach ~ 1) shock waves will begin to form in front of the Pitot tube, causing significant changes in the flow properties behind the shock, including pressure, so that equation 1.1 becomes invalid when $M \geq 1$. A further drawback of a Pitot tube is that it will only yield velocity data at discrete points and must be physically inserted into the flow. While there are systems that allow for either multiple Pitot tubes, or the ability to move the tube within the flow, these are still unable to characterize more than a few points in the flow at any given instant. Additionally, when used in wind tunnels, Pitot tubes significantly disrupt the flow, particularly if the flow is supersonic.

The invention of the laser has made the development of modern optical velocity measuring techniques possible. There are, in general, three categories of common optically-based laser velocimetry techniques; Doppler shifted Velocimetry, Particle Imaging Velocimetry (PIV), and Molecular Tagging Velocimetry (MTV).

The use of the Doppler shift of the frequency of light scattered by particles in a flow was first developed by Cummins et al.³, and Yeh and Cummins⁴. This led to a variety of Doppler shifted velocimetry techniques, one of the most common being Planar Doppler Velocimetry (PDV), shown schematically in figure 1.1. In its most general form the Doppler shift of scattered light, Δf_d , is given by

$$\Delta f_d = \left[\frac{\vec{s} - \vec{o}}{\lambda} \right] \cdot \vec{V} \quad 1.2$$

where $\vec{s}$ and $\vec{o}$ are unit vectors pointing along the propagation direction of the scattered and incident radiation respectively, λ is the wavelength of the incident light and $\vec{V}$ is the flow velocity vector. For PDV⁵, the incident laser is tuned such that its frequency is, in general at the midpoint between the maximum absorption and maximum transmission of a molecular filter that is positioned in front of a camera. The incident laser beam is focused into a plane, illuminating particles in the flow. The Doppler shifted scattered light, typically from very small particles or clusters, is then split into two paths using a beam splitter. The light from one path is imaged onto a reference camera, while the light from the second camera is passed through a molecular filter before being imaged onto a signal camera. In this way one component of velocity is determined at every point on the sheet, simultaneously. It is possible to obtain a 3-dimensional velocity but it requires

Figure 1.1 Schematic of a Planar Doppler Velocimetry experiment. Incident Laser light $\mathbf{o}$ is focused into a plane. A fraction of the scattered light is captured and split. Half of the captured light is directed into an iodine filter, then imaged on half the CCD chip of a camera, while the other half of the scattered light is imaged unfiltered. This can also be done by employing two cameras. By filtering half of the signal a Doppler shift can be measured and therefore a velocity determined. Figure taken from Samimy and Warnet⁵.

either 3 intersecting incident beams, or more commonly 3 pairs of cameras. PDV has the advantage that the velocity can be characterized either from a single laser pulse, or time averaged. However, because of the complexity of the optical setup, PDV measurements can be difficult to obtain and the data analysis can be cumbersome. Additionally, the costs can be prohibitive especially in 3-D PDV.

Particle Imaging Velocity (PIV) is another important velocimetry technique that has become quite commonly employed over the last ten years. Like PDV the incident laser is focused into a plane to illuminate particles in the flow. However, the particles are

Figure 1.2 Schematic of a typical PIV setup. A laser is focused into a sheet and directed into a flow that has been seeded with tracer particles. PIV is a time of flight technique so two images are obtained such as those in the bottom left corner of figure 1.2. The velocity is determined by tracking the relative position of individual molecules. Figure taken from Raffell et al.¹⁸

significantly larger such that they can be individually resolved. In this case, the laser acts as a photograph flash for a camera, and the particles in the flow scatter the light. A schematic diagram of the PIV technique is shown in figure 1.2. PIV is a time-of-flight technique, meaning the velocity is determined by comparing the relative position of individual particles between two (or more) images taken in quick succession. In Practice, correlation-based image processing algorithms are use to identify large numbers of “particle pairs”, with the relative displacement providing a spatially resolved map of velocity in a plane.

Scattering in both PDV and PIV generally requires that particles be inserted into the flow, a process known as seeding, which is often undesirable and difficult to accomplish. Although PDV and PIV both require seeding, PDV generally employs a

large number and therefore high density of small particles, or clusters, ($\sim 50\text{nm}$), while PIV employs fewer large particles ($\sim \text{microns}$) that must be evenly distributed and track with the flow. PIV particle size is selected such that particles are approximately 2 pixel widths on the imaging camera. In this way individual particles are tracked. However, the large discrepancies in the relative inertia of the particles to the molecules in a flow with strong velocity gradients can make it difficult for the particles to track the flow. The resulting particle lag limits the accuracy of particle tracking techniques, particularly at supersonic speeds. Additionally, uniform seeding can be difficult to maintain especially in turbulent flow structures, such as vortexes, or in large flow facilities.

Molecular Tagging Velocimetry (MTV) was designed to overcome the issues that PDV and PIV have faced with seeding. MTV is similar to PIV in that it is a time-of-flight technique, although instead of seeding a flow with large particles, trace molecules are “tagged” and allowed to convect with the flow. This is accomplished by employing a pulsed, spherically focused laser to “write” a line in the flow, either by inducing a chemical reaction that generates a new chemical species or excites the internal energy of a molecule that already exists. Once tagged, the molecule’s location must be interrogated after a specified time period. Koochesfahani and Nocera⁶ describe the four basic mechanisms utilized by various MTV techniques to interrogate tagged molecules. Visualization of the tagged molecule is dependent on both the technique and the tracer molecule, however, fluorescence and phosphoresce are the dominant mechanisms.

Figure 1.3 An energy level diagram, depicting the RELIEF method. Ground State oxygen molecules are excited from the $v''=0$ to the $v'=1$ vibrational state. After a delay of 1-10 μ sec the vibrationally excited $v'=1$ oxygen molecules are electronically excited to the $v'=7$ vibrational level of the $B^3 \Sigma_u^-$ excited electronic state. From the excited electronic state the oxygen molecules fluoresce back to the ground electronic state. (Diagram taken from Miles et. al.¹⁴)

1.2 Overview of RELIEF

The RELIEF method is an MTV technique. It is an acronym based on the names of the two optical processes that are used in this method, Stimulated **R**aman **E**xcitation + **L**aser **I**nduced **E**lectronic **F**luorescence, as shown in figure 1.3. Molecular oxygen in an airflow is vibrationally excited by Raman Excitation, and the oxygen convects in the flow and is subsequently interrogated by Laser Induced Electronic Fluorescence (LIF). The inclusion of the term *electronic* fluorescence indicates that the LIF process is a transition between electronic states.

1.2.1 Stimulated Raman Scattering

Stimulated Raman Scattering is a non-linear optical effect based on Spontaneous Raman Scattering. When light is incident to a Raman active medium a portion of the light is inelastically scattered, with the (Stokes/anti-Stokes) frequency shift corresponding to the Raman active molecular vibrations or rotations. For the purpose of this work only vibrational Raman Scattering will be discussed. Additionally, only the Q branch will be considered. While O and S branches have been observed⁷, their optical gain is typically much lower. Stimulated Raman Scattering occurs when the intensity of the incident light is increased by employing a sufficiently high intensity laser beam. The resulting scatter is coherent and differs from the spontaneous phenomenon by producing a high intensity, small divergence angle, beam of scattered light.

A schematic of the vibrational Stokes Raman process is shown in figure 1.4a and will be discussed in more detail in chapter 3. The Raman process⁸ is an inelastic scattering process which can be conceptualized in two steps. First, a laser field at the “pump” frequency (ω_l), “pumps” a molecule in the ground state to a linear combination of time-independent states (the so called “virtual state”). This state then decays back to a single time independent state by emission of a photon at its resonant frequency, $\omega_l - \omega_v$ (where ω_v is the vibrational frequency of the molecule), also known as the Stokes frequency, ω_s . While it can be conceptualized as a two-step process, these events occur simultaneously. Rayleigh Scattering occurs when $\Delta\omega=0$, whereas Raman Scattering occurs when $\Delta\omega\neq 0$. The emitted photon propagates in the same direction and with the

Figure 1.4 Energy level diagrams depicting a.) Stokes scattering where the laser frequency is ω_l . A Stokes photon is created with frequency $\omega_l - \omega_v$, and the molecule is vibrationally excited one vibrational quantum. b.) Anti-Stokes scattering, where the laser photon at ω_l and the vibrational quantum ω_v are absorbed, and a photon at $\omega_l + \omega_v$ is created. (Figure taken from Yariv⁸.)

same phase as the incident photon. Therefore, as the beam propagates through the Raman medium the Stokes beam grows exponentially and the incident beam is depleted.

In the absence of other competing effects, the intensity (I_s) of the Stokes wave generated by stimulated Raman scattering grows according to⁸:

$$\frac{dI_{Stokes}}{dz} = g \cdot I_{Stokes} \cdot I_{Pump} \quad 1.3$$

where g is the Raman gain factor. If the degree of depletion of the pump is small, then I_{pump} can be considered constant, so that there is no absorption, and the Stokes intensity, for a given path length, L , is given by

$$I_{Stokes}(z) = I_{Stokes}(0) \cdot e^{g \cdot I_{Pump} \cdot L} \quad 1.4$$

Anti-Stokes Raman scattering competes with the stimulated Raman Scattering and is depicted in figure 1.4b. Once a molecule is in a vibrationally excited state it can absorb a second pump photon ω_l exciting the molecule to another imaginary state but decaying back to the ground vibrational level $v''=0$, such that the anti-Stokes frequency, ω_{AS} , is $\omega_l + \omega_v$ is generated. Additionally, the first Stokes beam that is generated can act as a pump beam and excite a second Stokes scattering process generating the second Stokes beam, $\omega_l - 2\omega_v$. Stimulated Brillouin Scattering also competes with the Stokes frequency and will be described in detail in chapter 3.

1.2.2 Laser Induced Fluorescence

In the Laser Induced Fluorescence (LIF) process, the laser is tuned such that the photon energy matches the difference in energy between the ground and excited state. If the single photon transition is allowed at least a portion of the ground state population is excited. Once in the excited state the molecule may relax via spontaneous emission to any of the lower states, emitting a photon. The relative probability of decaying to a particular lower-state vibrational level from a given upper-state vibrational level, varies as $q_{v',v''} \cdot \nu_{v',v''}^3$ where $q_{v',v''}$ is the Frank-Condon factor and $\nu_{v',v''}$ is the frequency of the emitted photon. Generally this probability has a broad maximum with respect to v' , signifying that the LIF signal consists of many vibrational bands over a relatively broad stretch of wavelengths as can be seen in the RELIEF diagram in figure 1.3. In addition to spontaneous emission, the excited species may decay by dissociation, or collisional quenching, or be ionized by absorption of additional photons.

Figure 1.5 Energy transfer paths for laser induced excitation and fluorescence of molecular oxygen, where W_{21} is the spontaneous emission, W_L is the laser excitation, W_c is collisional redistribution, W_D is pre-dissociation and W_f is the total spontaneous emission. Figure taken from Laufer et al.¹⁰

The RELIEF method relies on the Schumann-Runge bands of oxygen which couple the ground electronic state ($^3X \Sigma_g^-$) with the $B^3 \Sigma_u^-$ excited electronic state. Oxygen molecules which have been previously excited to the $v''=1$ vibrational level of the ground state are electronically excited to the $v'=7$ level of the $B^3 \Sigma_u^-$ excited state. The change in the population of the upper ro-vibrational state can be seen in figure 1.5 and is expressed by¹⁰

$$\frac{dN_2}{dt} = N_1 W_L - N_2 (W_D + W_f + W_{21} + W_c) \quad 1.5$$

where W_L is the laser excitation rate, defined as $W_L = I_L \sigma_{l2} / h\nu$, I_L is the laser intensity,

σ_{12} is an effective absorption cross section, W_D is the pre-dissociation rate, W_f is the total spontaneous emission rate of the upper state including transitions to all the accessible levels in the ground electronic state except the absorbing state, W_{21} is the spontaneous emission rate for the specific transition from the upper state to the initial state, W_c is the collisional redistribution rate for the rotational levels in the upper vibronic state. The $O_2 B^3\Sigma_u^-$ state rapidly pre-dissociates due to strong interactions with several repulsive states. Pre-dissociation occurs via⁹

This occurs on a time scale that is significantly faster than the relevant optical processes. The time for pre-dissociation is on the order of 10 pico-seconds, whereas collisional quenching occurs on the order of hundreds of pico-seconds, and radiative decay, which is dependent of ν' , is on the order of tens of nanoseconds. Thus, Equation 1.5 becomes

$$\frac{dN_u}{dt} = W_L N_1 - W_D N_u \quad 1.7$$

1.3 Applications of RELIEF

To date, there have been relatively few applications of the RELIEF method. It has been predominately employed by the Miles group at Princeton University. They have demonstrated the RELIEF technique in many small scale circular nozzles¹¹. Additionally, they have taken turbulence quality measurements^{12, 13} as well as free stream velocity measurements in an 8" by 8" Mach 3 wind tunnel¹⁴. Other instances of the RELIEF method include a system at NASA Langley Research Center used to study fuel-air mixing and verify computational fluid dynamic codes and another system assembled

at Arnold Engineering Development Center by M. L. Energia to non-intrusively test high performance engines¹⁵.

One of the largest drawbacks to greater application of the RELIEF method has been its cost and complexity. Tunable excimer lasers are expensive and difficult to operate. This work has reduced the complexity of the system by incorporating a simple tabletop excimer laser as this will be discussed further in chapter 2. Other complications arise with the presence of water in the air flow. Water has a near-resonate energy transfer mechanism between the ν_2 bending mode of H_2O and the $\nu=1$ level of O_2 . Thus the tagged oxygen molecule will lose its tag upon collision with a water molecule, and because the process is nearly iso-energetic, the probability is high, thus decreasing the lifetime of the tagged molecule. Additionally, there has been interest in doing these measurements in combustion environments, however, at flame temperatures (800C) the vibrational levels of the ground electronic state are elevated making it difficult to efficiently tag molecules.

The remainder of this work is outlined as follows. Chapter 2 will discuss the experimental techniques and the apparatus employed to obtain RELIEF images. Chapter 3 is a discussion of stimulated Raman scattering conversion efficiency and the effects of stimulated Brillouin scattering on stimulated Raman conversion efficiency. Additionally chapter 3 will discuss the use of a cylindrically focused multi-pass Raman pumping cell employed to improve conversion efficiency. Chapter 4 will discuss fitting parameters to obtain velocity measurements from RELIEF images. Chapter 5 will discuss conclusions and possible future work.

Chapter 2

Experimental Techniques and Apparatus

Introduction

This work can be divided into two distinct portions. The first section describes the generation of a Stokes beam via stimulated Raman scattering, while the second describes the actual velocity measurements via the RELIEF method.

2.1 Stokes Generation

In the RELIEF method a line is written into an unseeded airflow by Stimulated Raman Excitation. This requires a pair of high intensity beams, termed the “Pump” and “Stokes” that must overlap in time and space. In addition to being temporally and spatially overlapped the difference in frequency between the Pump and Stokes beams ($\omega_p - \omega_s$) must be ω_v , the resonant vibrational frequency of oxygen. Most previously reported RELIEF measurements have employed the second harmonic of a “Q-switched” Nd:YAG laser at 532nm with a pulse duration on the order of 10 nano-seconds to create the pump beam^{1,12,15}. However, in this work we have demonstrated the use of the second harmonic of a simplified pico-second Nd:YAG laser (Ekspla SL 333). The Ekspla SL 333 has a small master oscillator cavity and generates a single mode 2 nano-second pulse that is subsequently pulse compressed to approximately 150 pico-seconds in a stimulated

Brillouin scattering (SBS) cell containing carbon tetrachloride. It has a maximum output pulse energy of 120 milli-Joules at 532 nm.

This work generates the Stokes beam using stimulated Raman scattering (SRS). However, previous work has demonstrated the use of an Nd:YAG pumped tunable dye lasers to generate the Stokes beam, but stimulated Raman scattering has the advantage that the pump and Stokes beams are automatically overlapped in time, space, and frequency. Stokes generation and the stimulated Raman scattering process will be discussed further in Chapter 3. The stimulated Raman process is essentially an intensity driven phenomenon where intensity, I , is

$$I = \frac{P}{\pi w_0^2/2} \quad 2.1$$

P is the power and w_0 is the focused beam waist ($1/e^2$ radius). Therefore the shorter duration of the 150 pico-second laser provides the high intensity needed to drive the stimulated Raman Scattering at lower pulse energy and/or less tight focusing.

The “Stokes” beam at 581nm is generated via stimulated Raman scattering in a pressurized cell. We have employed two Raman pumping cells, a traditional single pass spherically focused Raman cell and a cylindrically focused multi-pass Raman cell, also known as a Herriot cell.

Figure 2.1 is a schematic of the apparatus used to generate the pump/Stokes beam pair, and to characterize the efficiency of the Stokes generation via the stimulated Raman scattering process. The pump beam is focused into the single pass Raman Cell by a 1500 mm focal- length lens in to a 2.5m Raman shifting cell, equipped with 2.54cm diameter

Figure 2.1 (Left) A schematic diagram of the experimental setup used to determine the Raman conversion efficiency.

Figure 2.2 (Above) A picture depicting the transmitted output after being beam, second and third Stokes as well as first and second Anti-Stokes beams are present.

by 1.27cm thick optical windows and filled with a 1:1 mixture of oxygen and helium pressurized to 1000psi (70 bar). The transmitted output is re-collimated using a second 1500mm focal length lens, and the pump and Stokes beams are separated using a triangular dispersing prism. The conversion efficiency is determined by measuring the power of each of the various Stokes beams using a Scientech Astral thermopile calorimeter. Figure 2.2, shows an image of the dispersed beams.

It has been shown previously that heating the cell will induce convective cooling between laser pulses, providing a fresh slug of gas for each laser pulse. However, due to the low pulse energy of the pico-second laser this was found to not be necessary. In addition previous studies have¹⁹⁻²² seeded the Raman cell at the first Stokes frequency,

using a simple broadband dye laser, to increase the conversion efficiency. In an attempt to reduce the system complexity the Raman cells in this work have not been seeded.

As previously stated the greatest losses for the Raman process and the Stokes beam generation is stimulated Brillouin scattering. To help offset these losses we have utilized a multi-pass Raman Cell. The “Stokes” beam grows exponentially, in the forward direction, while stimulated Brillouin scattering grows linearly in the backwards direction. Because stimulated Brillouin scattering is a back scattering process, the scattering generated at each focal point is out of phase with the scattering generated at previous focal points, minimizing the losses due to Brillouin scattering. Stimulated Brillouin scattering will be discussed in more detail in chapter 3.

The multi-pass stimulated Raman scattering cell is shown in figure 2.3. Unlike the traditional single pass Raman pumping cell all of the optics are on the inside of the multi-pass Raman pumping cell. The beam is directed through a 300mm focal length plano-convex cylindrical lens, and onto a pair of plano-concave cylindrically focused mirrors. These are then adjusted such that the beams are refocused, as shown in figure 2.3. The curvature in the mirrors in figure 2.3 is actually in the perpendicular plane to what is shown, but it is depicted this way to remind the reader that the mirrors are cylindrically focused. The laser beam can be aligned such that there are between 5 and 11 passes, after which the transmitted output is re-collimated using a second plano convex cylindrical lens. As with the traditional single pass Raman cell, the pump and Stokes beams are separated, although a Pellin-Broca prism is used rather than a triangular dispersing prism. The conversion efficiency was determined at several helium: oxygen

Figure 2.3 A schematic of the multi-pass Raman cell. All of the optics shown are inside of the cell, complicating the alignment. Five passes are shown however, most of this work had eleven passes.

ratios, and with varying numbers of passes in the Raman cell, using a Scientech Astral thermopile calorimeter. As with the single pass Raman pumping cell, the multi-pass Raman pumping cell is not seeded. It was, however, heated in an attempt to induce conductive cooling, but had little effect in the conversion efficiency. The results of these measurements will be discussed in detail in chapter 3.

2.2 Making Relief Measurements

The Stokes and Pump beams are focused using a 250mm, 400mm, or 500mm, spherical lens into a high speed airflow. Stimulated Raman excitation occurs causing a fraction of the oxygen molecules to be excited from the ground ($v''=0$) to the first excited ($v'=1$) vibrational level, of the ground electronic state ($X^3\Sigma_g^-$). This effectively writes a

line in the flow. The short pulse duration of the pico-second laser has the advantage that it is able to provide the high intensity necessary to drive the non-linear stimulated Raman scattering but with lower pulse energy and less tight focusing allowing for longer tagging lines to be written. Once a line is written in the flow, the vibrationally excited molecules are allowed to convect with the flow for between 1 and 10 micro-seconds. The displacement in this time interval is subsequently “interrogated” by Planar Laser Induced Fluorescence (PLIF). In the PLIF process, a fraction of the vibrationally excited molecules are electronically excited from the $v''=1$ vibrational level of the ground electronic state ($X^3\Sigma_g^-$) to the $v'=7$ vibrational level of the $B^3\Sigma_g^-$ excited electronic state via the Schumann-Runge band. This occurs when the output of an appropriate UV laser beam is cylindrically focused into a plane containing the co-linear pump and Stokes beams as well as the flow. The molecules in the $B^3\Sigma_g^-$ excited electronic state fluoresce, and the fluorescence is captured on an ICCD camera.

Previous works have employed an injection seeded Argon Fluoride laser^{1, 16, 17} for the interrogation step. The narrow bandwidth of the injection seeded laser has the advantage that the laser can be spectrally tuned to selectively interrogate the “tagged” vibrationally excited oxygen molecules. It has the disadvantage, however, of high cost (~\$300K), large size (6.5' x 2.5' x 4.5') and rather difficult and unreliable operation. For this work we have demonstrated the use of a compact broadband ArF excimer laser (MPB Technologies model MSX-250) centered at 193nm as the interrogation source. A schematic of the system is shown in figure 2.4. The tagging portion is essentially the same as the set-up shown in figure 2.1, with the dispersion prisms removed. The

Figure 2.4. A schematic of the experimental set-up to perform RELIEF measurements.

pump/Stokes beam pair is focused into a line with, BK7 plano convex lenses with focal lengths ranging from 250-500mm. To interrogate the tagged molecules, the output from the broadband excimer laser is focused in to a plane parallel to the flow, and containing the pump/Stokes beam pair, using a UV fused silica plano convex cylindrically focusing lens with a 500mm focal length. The resulting fluorescence is captured on a Princeton Instruments PI-MAX UV Gen.II ICCD camera. In addition, a 1cm cell containing 0.7M urea was used as a filter to separate the Rayleigh scattering from the oxygen Schumann-Runge fluorescence¹⁷.

The compact broadband laser has many advantages including, being significantly less expensive (\$30,000 vs. ~\$300,000), being air cooled, being simple to operate (requires only routine gas refilling), and a much smaller footprint occupying only approximately 20" x 30" of the optical table as opposed to 8' x 6' of floor space.

The broadband interrogation does have the drawback that there is some interrogation of non-tagged oxygen molecules. Molecules in the $v''=0$ vibrational level of the ground electronic state can be electronically excited to the $v'=4$ vibrational level of the $B^3\Sigma_g^-$ excited electronic state (non-tagged). This problem could have been solved by putting a cell containing oxygen in the excimer lasers beam path prior to the interrogation of the tagged oxygen, effectively depleting the gain at the wavelength of the transition. However, in order to maintain system simplicity, we have overcome this dilemma by fitting the single slice grey scale intensity, output from the ICCD camera to a sum of two Lorentzians accounting for both the UV sheet and the line written in the flow. Fitting will be discussed in more detail in chapter 4.

Chapter 3

Conversion Efficiency of the Raman Shifting Cell

Introduction

There are two scattering processes that play a significant role in the RELIEF velocimetry method, stimulated Raman scattering or pumping, and stimulated Brillouin scattering. The RELIEF method relies on stimulated Raman pumping to tag oxygen molecules by inducing a transition from the $v''=0$ to the $v'=1$ vibrational level of ground state oxygen molecules. To achieve efficient stimulated Raman pumping two high intensity beams are required, one at the laser frequency, ω_l , and one at the Stokes frequency, ω_s . The Stokes beam is generated in a high pressure Raman pumping, or shifting, cell by stimulated Raman scattering. Unfortunately, because oxygen has a very low Raman gain, stimulated Brillouin scattering will compete significantly with the stimulated Raman scattering, decreasing the intensity of the Stokes beam and thus the stimulated Raman pumping achieved in the measurement section. The remainder of the chapter consists of a description and discussion of these competing effects, including a discussion of the multi-pass Raman Cell that was employed to reduce the effects of stimulated Brillouin gain.

3.1 Stimulated Raman Scattering

Raman scattering was first described by C. V. Raman as “Molecular Diffraction of Light” in 1922²³. Early Raman spectroscopy experiments were performed with the sun as the light source, with subsequent experiments employing arc lamps. Raman spectroscopy progressed further with the development of the laser, and thus a monochromatic, high intensity light source. In 1962, shortly after the development of laser technology, while experimenting with Q-switched lasers, Woodbury and Ng discovered accidentally that with a sufficiently high intensity light source, Raman scattering could be stimulated²⁵. These experiments were the beginning of many developments in Raman scattering and spectroscopy, and they enabled techniques like RELIEF velocimetry.

Scattering occurs whenever a photon flux is incident on a medium (figure 3.1a). Most of the scattered light has essentially the same frequency as the incident light, indicated as ω_l in figure 3.1. This phenomenon is known as elastic scattering (or often Rayleigh scattering). However, a small fraction of the scattered light may also consist of radiation at $\omega_l \pm \omega_m$, where the frequency ω_m corresponds to transitions between internal rotational, vibrational and electronic quantum levels. This scattering process is known as Raman scattering. There are two types of Raman shifts, a downward shift in frequency, to $\omega_l - \omega_m$, known as Stokes shift, or Stokes band (shown on the left of figure 3.1b), and an upward shift in frequency to $\omega_l + \omega_m$, known as the Anti-Stokes shift or band (shown on the right in figure 3.1b). Brillouin scattering, which results from collective density

Figure 3.1. (a) When light with intensity I_L and frequency ω_l is incident on a Raman medium a fraction of the light is scattered. (b) Most of the light is scattered at the frequency of the incident light. This is known as Rayleigh scattering. A small fraction of the scattered light is shifted in frequency. A shift in frequency by ω_m is known as Raman scattering. Brillouin scattering is also shown. Brillouin scattering is an intensity driven scattering process that occurs in the backward s direction. Figure taken from Boyd²⁴.

fluctuations in the medium, and produces spectral side bands as shown in 3.1b, will be discussed in section 3.2

As described in chapter one, Raman scattering⁸ is a two photon inelastic scattering process which can be conceptualized as occurring in two steps, as depicted in the energy level diagram of figure 3.2a. First, a photon at the “pump” frequency (ω_l) “collides” with a molecule, annihilating the pump photon and “pumping” the molecule in the ground state to a linear combination of time-independent quantum states (the so called “virtual state” indicated by a dotted line in figure 3.2a). This state then “decays”

Figure 3.2 Energy level diagrams depicting a.) Stokes scattering where the laser frequency is ω_l . A stokes photon is created with frequency $\omega_l - \omega_v$, and the molecule is vibrationally excited one vibrational quantum. b.) Anti-Stokes scattering, where the laser photon at ω_l and the vibrational quantum ω_v are absorbed, and a photon at $\omega_l + \omega_v$ is created. (Figure taken from Yariv⁸.)

back to a single time independent state by emission of a photon at the shifted frequency, $\omega_l - \omega_m$, also known as the Stokes frequency, ω_s . Note that while figure 3.2a depicts an energy level diagram for a vibrational transition, so ω_m is represented as ω_v , although it could equally well depict a rotational transition. Raman scattering can be conceptualized as a two-step process, however, these events occur simultaneously. For ordinary, or spontaneous Raman scattering, the shifted radiation is emitted in all directions (subject to polarization constraints). However, the Raman scattering process can become stimulated if a sufficiently high intensity pump light source is used. In this case the emitted photon propagates in the same direction and with the same phase as the incident photon. As the shifted beam propagates through the Raman medium the Stokes beam grows exponentially (similar to a laser), and the incident pump beam is depleted. For the purpose of this work, only vibrational Raman Scattering will be discussed. Additionally,

only the Q branch will be considered. While O and S branches have been observed,⁷ their optical gain is typically much lower.

Quantum mechanical and classical electromagnetic descriptions of both the spontaneous and stimulated Raman scattering processes have been previously published^{24, 8, 27}. These lengthy derivations can be derived using tensor calculus however the derivations are beyond the scope of this work and will not be reported here. It is worthwhile to note that a quantum mechanical treatment of Raman scattering, is of limited usefulness because the matrix elements are often unknown and in most practical cases too difficult to calculate⁸. This work will focus on the gain of the Raman scattering processes as it relates to the gain of the Brillouin scattering process.

As was pointed out in chapter 1, for a high intensity pump laser beam the Stokes intensity will grow according to the plane wave equation, $I_s(z) = I_s(0)e^{gI_p z}$ (Eq.1.4), which can be derived in terms of the number density of Raman scatterer's. Starting from scattering theory it is known that the number of photon per unit length in the Stokes “beam” is given by^{24, 16}

$$\frac{dn_s}{dz} = \frac{1}{c/n} D n_p (n_s + 1) \quad 3.1$$

where n_s is the mean number of photons in the Stokes mode, z is the beam propagation direction, c/n is the speed of light in the medium, n_p is the mean number of incident photons per mode in the incident pump radiation, and D is a proportionality constant that is dependent on the physical properties of the medium. In C.V Raman's original Raman experiments employing the sun or subsequently an arc lamp as a light source, there were

very few scattered photons per mode ($n_s \ll 1$), and only spontaneous Raman scattering was observed. However, when an intense laser light source is applied, a large number of scattered photons are generated ($n_s \gg 1$). From Eq. (3.1) with $n_s \gg 1$ we obtain exponential light amplification

$$n_s(z) = n_s(0)e^{gI_p L} \quad 3.2$$

or

$$I_s(z) = I_s(0)e^{gI_p L} \quad 1.4$$

where I_p is the intensity of the incident or “pump” beam, L is the length of the gain medium and g is the Raman gain intensity factor for individual scattering processes given by³⁴

$$g = \frac{16\pi^2 c^2 \Delta N}{\hbar n^2 \omega_s^3 \Gamma} \left(\frac{d\sigma}{d\Omega} \right) \quad 3.3$$

where ΔN is the population difference between levels $v''=0$ and $v'=1$ (for the case of vibrational Stokes scattering), ω_s is the Stokes frequency, Γ is the Raman linewidth (FWHM), and $d\sigma/d\Omega$ is the spontaneous Raman scattering cross section. Table 3.1 compares the cross sections for a select few materials. Notice how large the gain factor is for liquid O_2 and N_2 when compared with the gaseous counterparts. Many fundamental experiments have been performed using both H_2 and CH_4 because of their relatively large gain factors. In addition it can be seen that the gain factor for gaseous O_2 is 2 orders of magnitude smaller than gaseous H_2 , and 3 orders of magnitude lower than liquid O_2 . Since from Eq 1.4, the growth of the Stokes beam depends exponentially upon the gain factor, g , this is an enormous factor and explains why virtually all gas phase Raman shifting is preformed in H_2 (or D_2) or CH_4 .

Substance	Frequency Shift ν_0 (cm ⁻¹)	Linewidth $\Delta\nu$ (cm ⁻¹)	Cross Section $(\partial\sigma/\partial\Omega)$ (10 ⁻³⁰ cm ² sr ⁻¹)	Gain Factor g/I_1 (cm/GW)
Liquid O ₂	1552	0.117	.250	14.5
Liquid N ₂	2326.5	0.067	0.185	16
H ₂	4155	0.2	0.943	1.5
CH ₄	2916	~0.5	2.6	0.66
N ₂	2326	~1	0.46	0.071
O ₂	1555	~1	0.47	0.016

Table 3.1. Gain factors for Stimulated Raman scattering for several substances. Notice how large the gain factor is for Liquid O₂, N₂, and CS₂ when compared with the gaseous counterparts. Many fundamental experiments have been performed using both H₂ and CH₄ because of their relatively large Gain Factors. It is shown that the gain factor for gaseous O₂ is 2 orders of magnitude lower than H₂, and 3 orders of magnitude lower than liquid O₂^{24, 35, 36}.

In the case of the focused Gaussian beam, I_s , in Eq. 3.3 is a function of position z . Therefore the cumulative gain factor G , is more appropriate to describe the Raman gain accumulation. It has been shown by Zhang¹⁶ that the single pass Raman gain when a spherically focused pump beam traverses a medium with cumulative gain coefficient G , is given by

$$G_s = \frac{4gP}{\lambda_p + \lambda_s} \tan^{-1}(L/b) \quad 3.4$$

where λ_l is the laser wavelength, P is the pump power given by

$$P = I_p w_0^2 \pi \quad 3.5$$

and b is the pump beam confocal parameter given by

$$b = \frac{4\pi w_0^2}{\lambda_p + \lambda_s} \quad 3.6$$

where, w_0 is the beam waist. Because the pump and Stokes beams have different

Figure 3.3 Plot of $\arctan(L/b)$. It can be seen that the arctangent approaches $\pi/2$ asymptotically, when $L \gg b$.

confocal beam parameters and therefore different beam waists the approximation

$\lambda = \frac{\lambda_p + \lambda_s}{2}$ has been used in equations 3.4 and 3.6. The confocal beam parameter for this

work is approximately 30cm, so L/b is approximately 8. As can be seen from figure 3.3 as L/b increases, arctangent (L/b) approaches $\pi/2$ asymptotically, so that in the case when the confocal beam parameter is much longer than the length of the gain medium, $b \gg L$ the gain coefficient reduces to

$$G_s = gI_p L \quad 3.7$$

The preceding discussion of Raman gain has assumed a pulse duration that is much longer than the dephasing time for the induced polarization, T_2 (also known as the photon lifetime). This is an invalid assumption for this work, which is performed in the

transient stimulated Raman regime, because the pulse duration (150ps) is of the same order as the dephasing time. The transient stimulated Raman regime occurs when the non-linear polarization in the medium cannot be completely established during the pump pulse, because the medium cannot respond quickly enough. According to Wang²⁸ and Zhang¹⁶, the stimulated scattering time-dependant Stokes intensity can be expressed as

$$I_s(t) \propto \exp \left[2 \sqrt{\frac{gI_p L t}{T_2}} - \frac{t}{T_2} \right] \quad 3.8$$

Recall that g is the gain coefficient, I_p is the pump intensity, L is the interaction length, t is time, and T_2 is the polarization lifetime. The polarization lifetime is defined as the inverse of the linewidth of the Raman transition ($T_2 = \Gamma^{-1}$). Making the assumption that the intensity and power of the pump remains uniform (the plane wave approximation) and that the confocal beam parameter is much longer than the gain medium Eq. 3.8 can be simplified by inserting Eq. 3.7 such that

$$I_s(t) \propto \exp \left[2 \sqrt{\frac{Gt}{T_2}} - \frac{t}{T_2} \right] \quad 3.9$$

where G is the gain factor for either spherically focused G_s , (Eq. 3.4), or cylindrically focused G_c , (to be defined in section 3.4) schemes. If we allow $t = GT_2$ then Eq. 3.9 simplifies to $I_s(t) \propto \exp[G]$ which is the steady-state Raman equation. Therefore, GT_2 differentiates between the transient and the steady-state Raman processes. Consequently, the transient regime is dependent on the pump power P in addition to the photon lifetime, T_2 . Additionally, as will be discussed in the next section, Brillouin scattering competes with Raman scattering reducing the gain, G , of the Raman process and thus reducing the

Figure 3.4 Schematic of the stimulated Brillouin scattering process. An intense beam with frequency ω_L is scattered from the refractive index variations in the scattering medium produced by a sound wave of frequency Ω traveling away from the incident beam. The Brillouin scattering is generated at $\omega_B = \omega_L - \Omega$. Figure reproduced from Boyd²⁴.

time required to reach steady-state, t_{ss} . Generally speaking the time to reach steady-state conditions, t_{ss} , is at least one order of magnitude greater than T_2 although it is often three or more orders of magnitude greater¹⁶. It is interesting to note however that “high” Raman gain gases, such as H_2 , D_2 , and CH_4 have high gain precisely because the Raman linewidth, Γ , is small. Recall the Raman width is in the denominator of the gain expression (Eq. 3.3). For this reason, while the steady-state gain is high, transient effects are worse. For example, for typical operating conditions T_2 is 16 psec for CH_4 and 208 psec for H_2 .

3.2 Stimulated Brillouin Scattering

Stimulated Brillouin scattering is the backward scattering of incident light due to induced spatially correlated density variations in the scattering medium. This is shown schematically in figure 3.4 where an incident beam with frequency ω_L is scattered from the variations in the refractive index generated from a sound wave with frequency Ω_B . The scattered light is shifted downward in frequency because the acoustic wave fronts are moving away from the incident beam and Brillouin scattered light is generated at

$\omega_B = \omega_L - \Omega_B$. There are two physical mechanisms whereby the acoustic wave can be driven. The first is thermal stimulated Brillouin scattering. Heat is produced in regions of high optical intensity causing expansion in those regions, and generating density variations that excite acoustic disturbances. The second and more common mechanism for acoustic wave generation is electrostrictive stimulated Brillouin scattering. Electrostriction is the tendency of materials to become compressed in the presence of an electric field²⁴.

The intensity of Stimulated Brillouin scattering for a single component gas or liquid grows according to

$$I_B(z) = I_B(0) \exp[(g_0 I_p - \alpha)(L - z)] \quad 3.10$$

where I_p is the pump intensity, α is the absorption coefficient which corrects for depletion of the pump beam, L is length of the medium, z is the length of propagation into the medium, and g_0 is the steady-state electrostrictive stimulated Brillouin scattering gain coefficient is given by

$$g_0 = \frac{\gamma_e^2 \omega_B^2}{n v c^3 \rho \Gamma_B} \quad 3.11$$

where ω_B is the frequency of the Brillouin scattered light, v is the velocity of sound, ρ is the gas mass density, γ_e is the electrostrictive constant given by

$$\gamma_e = \rho \left(\frac{\partial \varepsilon}{\partial \rho} \right) \quad 3.12$$

where ε is the dielectric constant, and Γ_B is the Brillouin linewidth given by²⁹

$$\Gamma_B = \frac{k^2}{2} \left[\frac{\frac{4}{3} \eta_s + \eta_v}{\rho} + \frac{\kappa}{\rho C_p} (\gamma - 1) \right] \quad 3.13$$

The magnitude of the acoustic wave vector is given by

$$k = \frac{\omega_B}{v} \quad 3.14$$

where the Brillouin frequency is

$$\omega_B = \frac{4\pi n}{\lambda_p} v \quad 3.15$$

λ_p is the wavelength of the pump beam, and v is the sound velocity. In equation 3.13 η_s and η_v are the sheer and volume viscosities respectively, κ is the thermal conductivity, γ is the ratio of specific heats, and C_p is the specific heat. The first term in the brackets represents acoustic attenuation from viscous effects that tend to dissipate the density variations that constitute the acoustic wave. The second term accounts for losses due to thermal conduction of hotter, denser regions to cooler, less dense regions.

For a given Brillouin medium and a given pump wavelength the gain is dependent on the density, the electrostrictive constant γ_e , and the Brillouin linewidth, Γ_B .

Furthermore, both the electrostrictive constant and the Brillouin linewidth are explicitly dependent on the density. However, according to Eq. 3.13 increasing the kinematic viscosity, η/ρ , or the thermal diffusivity, $\kappa/\rho C_p$ will also increase the Brillouin linewidth, and therefore decreasing the Brillouin gain. This can be accomplished by the addition of a buffer gas such as Helium. Mountain and Duetch³⁰ have shown that the Brillouin line width for monatomic gases in a binary mixture to be

$$\Gamma_B = \frac{k^2}{2} \left[\frac{\frac{4}{3}\eta_s + \eta_v}{\rho} + \frac{\kappa}{\rho C_p} (\gamma - 1) + \frac{Dv^2}{\rho^2 \left(\frac{\partial \mu}{\partial c'}\right)} \left[\left(\frac{\partial \rho}{\partial c'}\right)_{p,T} + \frac{k_T}{C_p} \left(\frac{\partial \rho}{\partial T}\right)_{p,c'} \left(\frac{\partial \mu}{\partial c'}\right)_{p,T} \right]^2 \right] \quad 3.16$$

where D is the diffusion coefficient, c' is the concentration of the Brillouin active

medium in the mixture, μ is the chemical potential, and k_T is the thermal diffusion ration of the binary mixture. It is important to note that in the binary mixture there is an extra damping term due to concentration fluctuations³¹ which are dependent on $(\partial\rho/\partial c')_{p,T}$. When there is a large difference in the masses of the individual components, there is significant suppression of the sound wave, and therefore the Brillouin threshold. Brillouin scattering in a binary gas mixture is also dependent on diffusion effects which exist in concentration and temperature gradients, both of which occur in sound waves. Although Mountain and Duetch's model is specific to monatomic gasses, it provides useful physical insight and several studies have shown that Eq. 3.16 remains effective for small molecules. The thermal conduction effect resulting from the addition of Helium buffer gas will be demonstrated below (figure 3.8) where it is shown that stimulated Raman gain increases at higher concentrations of Helium, up to approximately 70% He.

Control of the coherence length of the pump beam can also lead to significant Brillouin scattering suppression (depicted in figure 3.5). The stimulated Brillouin process is suppressed when the confocal beam parameter is much longer than the coherence length. Zhang has shown in a 2m Raman pumping cell similar to that used in this work, that an un-seeded Nd:YAG laser, with a coherence length of approximately 1cm, exhibited virtually no stimulated Brillouin scattering, but when a seeded Q-switched Nd:YAG was employed with a coherence length of approximately 3m stimulated Brillouin scattering dominated over stimulated Raman scattering.

Figure 3.5 Depiction of long and short coherence length. Brillouin Scattering is suppressed with shorter focal lengths because backward scattered photons are not in phase with each other.

3.3 Conversion Efficiency Results in a Spherically Focused Single Pass Raman Pumping Cell.

The first and second Stokes Raman conversion efficiencies for a single pass 2.5m Raman pumping cell pressurized to 1000psi with a 50:50 mixture of O₂:He, are shown in figure 3.6a. The conversion efficiency is corrected for “Fresnel” losses which occur at each of the uncoated shifting cell windows (~ 7% per window). The conversion efficiency is determined by relating the input power, to the power of the individual components of the output beam according to

$$Conversion\ Efficiency\ (x) = \frac{P_x}{P_{Input}} \quad 3.17$$

where x signifies the component of the output beam (i.e. 1st Stokes, 2nd Stokes, etc.). It can be seen in figure 3.6a that the maximum utilizable first Stokes conversion efficiency is approximately 14%. It is noteworthy to observe that the threshold for stimulated Raman Scattering in this work is very low, only 1-3mJ compared with 10-30mJ per pulse

using 10ns pulses in a similar work by Zhang¹⁶. Figure 3.6b is a plot of the losses in the Raman pumping cell, defined as $1 - \frac{E_{out}}{E_{in}}$, plotted against input energy. It can be seen that at low input energy there is very little loss, but as the pump power is increased Brillouin scattering begins to dominate and as much as 60% of the input energy is lost.

3.6a

3.6b

Figure 3.6 a) Plot of the first and second Stokes conversion efficiency of the 2.5m single pass Raman cell pressurized to 1000psi with a 50:50 mixture of O_2 :He. This is the corrected conversion efficiency assuming a 7% loss from each surface, for a maximum corrected Raman conversion of approximately 12%. b.) A plot of the losses within the Raman Cell. The largest contributor being stimulated Brillouin scattering with as much as 60% of the energy lost with a pump energy of 40mJ.

Figure 3.7 A schematic of the multi-pass Raman cell. All of the optics shown are inside of the cell, complicating the alignment. Five passes are shown however, most of this work had eleven passes.

3.3 Multi-Pass Raman cell

In an attempt to reduce the influence of Brillouin scattering, and thus increase the Raman conversion, this work has also employed the use of cylindrically focused multi-pass Raman cell (or Herriott cell) shown schematically in figure 3.7. The advantages to cylindrically focused Raman pumping is the Raman Stokes shifted beam is generated in the first pass through the Raman pumping cell and amplified exponentially in each subsequent pass. However, the cylindrically focused per pass Raman gain is much lower than the spherical Raman gain, necessitating multiple passes. Even after 5 passes in the Raman pumping cell the Raman Stokes beam is not intense enough to measure or even visualize. Brillouin scattering is also generated in each pass. The scattering is generated

in the backwards direction, so that the Brillouin scatter generated at each focal point is out of phase with the Brillouin scattering at the previous focal point(s). This prevents exponential growth of the stimulated Brillouin scattering signal, and with a sufficient number of passes will greatly increase the stimulated Raman scattered conversion.

As in the spherically focused Raman pumping scheme the intensity grows according to Eq 1.4, which can be written as

$$I_s = I_s(0)e^{G_c} \quad 3.18$$

Zhang¹⁶ calculated the cumulative cylindrical Raman gain coefficient to be

$$G_c = \frac{4gP}{\lambda_L + \lambda_P} \sqrt{\frac{b_x}{b_y}} F \left[\left(\sqrt{1 - \left(\frac{b_x}{b_y} \right)^2} \right), \tan^{-1} \left(\frac{L}{b_x} \right) \right] \quad 3.19$$

where b_x, b_y are the confocal beam parameters in the x and y directions, and F is an elliptic integral.

The first Stokes Raman conversion efficiencies for a multi-pass 1m Raman pumping cell pressurized to 500psi with varying mixtures of O₂:He, is shown in figure 3.8. It can be seen that the maximum useable Raman conversion efficiency was approximately 14% and occurred at a 350:150 ratio of He:O₂. The uncorrected single pass conversion efficiency in the 2.5m Raman pumping cell pressurized to 1000psi with a 50:50 ration of He:O₂ is also shown (light blue). The uncorrected conversion efficiency in the multi-pass cell is shown to be almost 2.5 times higher than in the single pass Raman pumping cell. The yellow line in figure 3.8 is the second Stoke conversion

efficiency with a 50:50 mixture of He:O₂. The cavity mirrors are less reflective to the second Stoke at 640nm and thus the second Stokes beam is only weakly amplified.

Figure 3.8 First Stokes conversion efficiencies in a cylindrically focused multi-pass Raman pumping cell at varying concentrations of He:O₂. It can be seen that the maximum useable Raman conversion efficiency was approximately 14% and occurred at a 350:150 ratio of He:O₂. The yellow line is the second Stokes conversion efficiency with a 50:50 mixture of He:O₂. The cavity mirrors are less reflective to the second Stoke at 640nm and thus the second Stokes beam is only weakly amplified. The uncorrected single pass conversion efficiency in the 2.5m Raman pumping cell pressurized to 1000psi with a 50:50 ratio of He:O₂ is also shown (light blue).

In a similar experiment employing a 10 nano-second Q-switched Nd:YAG laser, Zhang found that in high density oxygen, a steady state non-uniform distribution of the intensity appears due primarily to the temperature gradient generated from the previous laser pulse. Oxygen molecules have a slow vibrational to translational relaxation rate and at the high pressures of the Raman pumping cell the energy is turned into heat which creates a temperature gradient and therefore an index of refraction non-uniformity. Zhang found that by gently heating the Raman cell they could induce enough convection such that each laser pulse was focused into a fresh slug of gas. Zhang found this to significantly increase the beam quality.

In an attempt to improve beam quality the multi-pass Raman cell was heated to approximately 40°C. In this work heating the Raman cell resulted in essentially no change in Raman conversion efficiency as can be seen in figure 3.9. This is because a given energy the 150 pico-second laser employed in this work generates a pulse that has an intensity two orders of magnitude larger than the pulse generated by the 10 nano-second counterpart employed by Zhang¹⁶. Because stimulated Raman scattering is intensity driven, the 150 pico-second laser is able to generate the first Raman stokes beam at much lower energy, thereby reducing heating of the cell.

Figure 3.9 Zhang found that heating the Raman pumping cell induced convection in the cell, such that each laser pulse was focused into a fresh slug of gas, improving conversion efficiency and beam special quality. In an attempt to improve beam quality the cylindrically focused multi-pass Raman cell was heated to approximately 40°C. The results are shown above. The 150 pico-second laser used in this work generates pulses that are ~100 times more intense, than the 10 nano-second counterpart used in previus works. Because stimulated Raman scattering is intensity driven, the 150 pico-second laser is able to generate the first Raman stokes beam at much lower energy, thereby reducing heating of the cell

Chapter 4

Determining Velocity with Pico-Second RELIEF

After the first Raman Stokes beam is generated in the stimulated Raman pumping cell the collinear Stokes and pump beams are spherically focused into the experimental test section, inducing further stimulated Raman scattering and effectively “writing” a line in the flow. As was described in the previous section, the ground vibrational state, $v''=0$, oxygen molecules are vibrationally excited to the $v'=1$ excited vibrational state through this process. After some delay, in which the tagged molecules were allowed to convect

Figure 4.1 Tagged Oxygen Molecules are electronically excited via an ArF excimer laser from the $v''=1$ vibrational level in the ground state ($^3X \Sigma_g^-$) to the $v'=7$ level of the $B^3 \Sigma_u^-$ excited electronic state. The excited molecules then fluoresce back to the ground State emitting photons.

with the flow, the tagged molecules are “interrogated”. As was described previously, the RELIEF method relies on the Schumann-Runge bands of oxygen which couple the ground electronic state ($^3X \Sigma_g^-$) with the $B^3 \Sigma_u^-$ excited electronic state. Oxygen molecules which have been previously excited to the $v''=1$ vibrational level of the ground state are electronically excited to the $v'=7$ level of the $B^3 \Sigma_u^-$ excited state. Once in the excited state the molecule may relax via spontaneous emission to any of the lower states, emitting a photon. The relative probability of decaying to a particular lower-state vibrational level from a given upper-state vibrational level, varies as $q_{v',v''} \cdot \nu_{v',v''}^3$ where $q_{v',v''}$ is the Frank-Condon factor and $\nu_{v',v''}$ is the frequency of the emitted photon. Generally this probability has a broad maximum with respect to v' , signifying that the LIF signal consists of many vibrational bands over a relatively broad stretch of wavelengths as can be seen in the RELIEF diagram in figure 4.1

The photons emitted in the LIF process are imaged on a UV ICCD camera as shown in the image in figure 4.2. Due to the broad spectral linewidth of the compact broadband ArF excimer laser ($\sim 75 \text{ cm}^{-1}$), there is some interrogation of ground state oxygen molecules via the $v''=0 \rightarrow v'=4$ absorption of the O_2 Schumann-Runge band system. This generates the thick “background” UV sheet visible in figure 4.2, (indicated loosely with two red lines), and reduces the contrast between the background and LIF signal from the tagged oxygen molecules. However, the absorption to the $v'=4$ level (dictated by the Franck-Condon factor) and the subsequent fluorescence quantum yield (dictated by non-radiative “pre-dissociation”) from that level are significantly weaker than the corresponding $v''=1 \rightarrow v'=7$ strategy employed for RELIEF interrogation^{32, 33}.

Figure 4.2 A typical RELIEF image is shown. The thin bright horizontal line is the fluorescence interrogation from the tagged $v''=0$ oxygen molecules. A thick horizontal UV sheet due to the inadvertent excitation of untagged $v''=0$ ground state oxygen molecules can also be seen (~between the red lines). The single vertical slice of grayscale intensity is fit to Eq 4.1 to determine the pixel position of the tagged molecules.

4.1 Fitting to a Lorentzian Distribution

RELIEF images obtained with the broadband compact ArF excimer laser will require some additional processing to account for the $v''=0 \rightarrow v'=4$ background signal. Because the excited molecules all have an equal probability of decaying back to the ground state they are said to be homogeneously broadened, and are therefore fit to a Lorentzian distribution, as opposed to in-homogeneous broadening which is fit to a Gaussian distribution. Once the image is obtained a single slice of the grayscale intensity

is extracted and both the UV sheet and the line of tagged molecules “written” in to the flow is least squares fit to the following sum of two Lorentzians profile distributions (in this case with SigmaPlot software),

$$f = y_0 + \frac{a_1}{\left(1 + \left(\frac{x - x_0^{(1)}}{b_1}\right)^2\right)} + \frac{a_2}{\left(1 + \left(\frac{x - x_0^{(2)}}{b_2}\right)^2\right)} \quad 4.1$$

where x is the position, y_0 is the intensity of the background noise, $x_0^{(1)}$, $x_0^{(2)}$ are the positions corresponding to peak intensity, a_1 , a_2 are the peak intensities and b_1 , b_2 are scale parameters specifying the half width at half max (HWHM).

4.2 RELIEF velocimetry in a Static Cell

Initial RELIEF images were taken in a static cell, containing dry air at room pressure. Figure 4.3 shows a collage of three cropped RELIEF images where the horizontal field of view is 2.5cm and the tagged lines are approximately 1.5cm long. The “tagging”, “pump” and Stokes beam pair was focused with a 250mm spherical lens and the UV sheet was generated with a 500mm focal length cylindrically focusing lens. The delay between pump and probe was 5 μ s. Figures 4.3a,b,c are single shot, 10 shot average (1sec), and 50 shot average (5sec) images respectively. Figures 4.4 are the single vertical “slices” of grayscale intensity data (filled circles) along with a least squares fit to a sum of two Lorentzian functions (line). One of the Lorentzians is quite sharp and corresponds to the “tagged” oxygen molecules, while the other is quite broad (~200 pixels) and corresponds to the untagged background signal which results from the broad spectral linewidth ArF interrogation laser. The images on the right in figures 4.4 are expanded on the “pixel” (spatial) axis in the range 300 – 400 pixels. Despite the

Figure 4.3 RELIEF images obtained where the pump and Stokes beam pair is focused with a 250mm focal length spherical lens, and the UV sheet was generated with 5 μ s delay and a 500mm focal length cylindrical lens. Images 4.3a, 4.3b, and 4.3c are single shot, 10 shot average (1 sec.), and 50 shot average (5 sec.) respectively.

relatively low signal to noise ratio of the raw data, the statistical uncertainty in the center position of the narrow component, which is determined by the least squares procedure, is ~ 0.08 pixels (2σ) for figure 4.3a. It can be seen that the signal to noise ratio of the raw data is increased in figures 4.3b (10 shot/1sec. average) and 4.3c (50 shot/5sec. average). Correspondingly the uncertainties in the center line position of the narrow peaks in both figures 4.3 b and c are decreased to 0.6 pixels (2σ), resulting in an estimated uncertainty in the velocity of ~ 0.35 m/sec.

Figure 4.4: (left) Single slice of grey scale intensity data from the images in figures 4.3 (right) Pixel axis expansion of data given on left. a) single shot b) 10 shot average and c) 50 shot average

Figure 4.5 five second averaged RELIEF image obtained under conditions identical to that of fig. 4.3, except that a 400 mm focal length tagging lens is utilized resulting in a longer 2.5cm RELIEF line (as opposed to 1.5cm in fig. 4.3.)

Figure 4.5 is a 50 shot averaged (5sec.) RELIEF image where the tagging, beams are focused with a 400mm focal length spherical lens instead of the 250mm lens employed for the images in figure 4.3. All other conditions, including the interrogation beam energy and focusing, and the image capture solid collection efficiency and field-of-view remained unchanged. Employing a 400mm lens increased the length of the tagged line from 1.5cm to ~2.5cm. The longer RELIEF lines expand the viewable area, but with a slight decrease in resolution. Figures 4.6 are similar to those in 4.4 but correspond to RELIEF images taken with a 400mm lens. It can clearly be seen that the signal to noise ratio is much lower than the analogous images in figure 4.4. However, the approximate statistical uncertainties are still quite good at 0.8, 0.5 and 0.5 m/ sec corresponding to the single shot, 10 shot (1sec) and 50 shot (5sec) averages respectively. RELIEF images were also taken with a 500mm focal length tagging lens although it gave very similar result to the 400mm focal length lens. Velocity uncertainty results obtained to date using the

Figure 4.4: (left) Single slice of grey scale intensity data from the images in figures 4.3 (right) Pixel axis expansion of data given on left. a) single shot b) 10 shot average and c) 50 shot average

Tagging Lens Focal Length (mm)	$2\sigma_v$ (m/sec) single shot	$2\sigma_v$ (m/sec) 1 second	$2\sigma_v$ (m/sec) 5 second	line length (cm)
250	0.8	0.6	0.6	~1.5
400	1.5	1.0	0.6	~2.5
500	1.2	1.0	1.5	~2.5

Table 4.1 Velocity uncertainty results obtained to date using the portable RELIEF system are summarized in Table 4.1 (assumes a $10\mu\text{s}$ delay between pump and interrogation), along with approximate lengths of the observed RELIEF lines. The data for the 5 second averaged, 500mm focal length lens appears to have suffered from some sort of misalignment which resulted in an uncertainty that is most likely in error.

portable RELIEF system are summarized in Table 4.1, along with approximate lengths of the observed RELIEF lines. The data for the 5 second averaged, 500mm focal length lens appears to have suffered from some sort of misalignment which resulted in an uncertainty that is most likely in error.

4.3 RELIEF Velocimetry in a Jet

As proof of concept Relief images were taken in 2 simple sonic orifice air “Jets”, driven by bottled dry air and vented into the ambient laboratory environment. The RELIEF image in figure 4.7 employed a circular 1mm I.D. nozzle, while the image in figure 4.8 employed a circular 4.5mm I.D. nozzle. Both of these images are 50 shot averages and were taken with a $2\mu\text{s}$ delay between the tagging and interrogation beams. In figures 4.7 and 4.8 there are two vertical lines labeled “a” and “b”. These vertical lines are representative of the position where the single slice of grayscale intensity was analyzed. The corresponding plots of the grayscale intensity (filled circles), including the

least squares fit to the sum of Lorentzians (red line) are shown below figures 4.7 and 4.8. For figure 4.7 the best fit of the center line position of the tagged molecules of the “a” and “b” slices are separated by 14.9 pixels with statistical uncertainties of 0.2 and 0.06 pixels respectively corresponding to a velocity of 358 ± 5 m/s. For figure 4.8 the best fit of the center line position of the tagged molecules of the “a” and “b” slices are separated by 9.63 pixels, with statistical uncertainties of 0.11 and 0.5 pixels respectively, corresponding to a velocity of 243 ± 3 m/s. Note that the uncertainty estimate in this case is higher than that given in table 4.1 due to a combination of two factors. First, the relatively weak intensity ambient flow region of the RELIEF image (position “a”) was used to obtain the zero time delay location of the fluid. As noted above, the uncertainty from this line is approximately double that from the jet centerline. Second, due to some unsteadiness in this very simple jet, a relatively short time delay (2 μ sec) was used, rather than the 10 μ sec assumed for the estimates in Table I. Nonetheless, despite this non-optimal configuration, the velocity error, relative to the centerline velocity, is approximately 1%.

Figure 4.7 RELIEF velocimetry image taken with a 1mm cylindrical nozzle, expanded into a laboratory environment. The lines “a” and “b” represent the single vertical slice of grayscale intensity are shown in their respective plots above, along with the least squares fit to two Lorentzians. The best fit of the center line position of the tagged molecules of the “a” and “b” slices are separated by 14.9 pixels with statistical uncertainties of 0.2 and 0.06 pixels respectively corresponding to a velocity of 358 ± 5 m/s.

Figure 4.8 RELIEF velocimetry image taken with a 4.5mm cylindrical nozzle, expanded into a laboratory environment. The lines “a” and “b” represent the single vertical slice of grayscale intensity are shown in their respective plots above, along with the least squares fit to two Lorentzians. The best fit of the center line position of the tagged molecules of the “a” and “b” slices are separated by 9.63 pixels with statistical uncertainties of 0.11 and 0.5 pixels respectively corresponding to a velocity of 243 ± 3 m/s.

4.4 Multi-Pass Raman Pumped RELIEF Velocimetry

An example of a RELIEF image obtained by using a multi-pass Raman cell is shown in figure 4.9 where the best fit of the center line position of the tagged molecules of the “a” and “b” slices are separated by 20.7 pixels, with statistical uncertainties of 0.2 and 0.12 pixels respectively, corresponding to a velocity of 215 ± 2 m/s. From the plots of the grayscale intensity shown in figure 4.9a,b it can be seen that the signal to noise ratio is much lower than in the corresponding images obtained with the single-pass spherically focused Raman Cell. This is primarily due to the poor beam quality of the tagging beam pair. This prevented tight focusing into the experimental section, reducing intensity and therefore reducing stimulated Raman excitation.

Figure 4.9 RELIEF velocimetry image taken with a 4.5mm cylindrical nozzle, expanded into a laboratory environment. The lines “a” and “b” represent the single vertical slice of grayscale intensity are shown in their respective plots above, along with the least squares fit to two Lorentzians. The best fit of the center line position of the tagged molecules of the “a” and “b” slices are separated by 20.7 pixels, with statistical uncertainties of 0.2 and 0.12 pixels respectively, corresponding to a velocity of 215 ± 2 m/s. From the plots of the grayscale intensity shown in figure 4.9a,b it can be seen that the signal to noise ratio is much lower than in the corresponding images obtained with the single-pass spherically focused Raman Cell.

Chapter 5

Conclusions and Future Work

Conclusions

It has been demonstrated that RELIEF velocimetry images can be produced with a simple, and relatively low cost RELEIF system utilizing a 150 pico-second Nd:YAG laser and a broadband compact ArF excimer laser. This work has demonstrated oxygen stimulated Raman corrected conversion efficiencies of ~12% in the single pass Raman pumping cell. Relief images with 2.5cm tagging lines and a potential precision of ~ 1 m/sec are demonstrated for single shot images, and sub- m/sec for time averaged images.

The two most critical goals were met, specifically the successful demonstration of the compact, broad-band ArF excimer laser as a viable interrogation source, and the ability to utilize a modestly priced, SBS compressed, 150 pico-second Nd:YAG laser as a Raman pump source. In this regard it should be noted that while the high intensity of the 150 pico-second Nd:YAG laser might imply that its use for stimulated Raman scattering would be obvious, the inherently narrow spectral linewidth, $\sim 0.1 \text{ cm}^{-1}$, results in a coherence length which is approximately 10 times longer than the broad band Nd:YAG laser previously used by the miles group¹. The impact of this on stimulated Brillouin scattering completion was considered a major concern prior to the initiation of this

research. In addition, as shown by Diskin¹⁷, where ~ 10 micro-second pump/stokes beams are used for the vibrational pumping step, there is not insignificant collisional refilling of the $J''=7(+9)$ levels, which are excited to $v'=1$. In other words, a larger fraction of the rotational manifold is potentially available for vibrational pumping when nano-second sources are used, as compared to pico-second sources.

However, the third goal, to demonstrate the utility of the cylindrically focused multi-pass Raman pumping cell for stimulated Raman scattering excitation was not met. The uncorrected conversion efficiencies of the multi-pass cell were much higher ($\sim 14\%$) than the conversion efficiency in the single pass Raman cell however, due to poor beam quality the RELIEF images that were obtained are of lower quality than the corresponding spherically focused RELIEF images. The implication is that while the cylindrical multi-pass cell clearly improves the Raman conversion efficiency for low gain gases, the spatial quality of the output needs to be improved in order to be utilized for non-linear experiments.

Future Work

The initial goal of this work was to construct a compact and mobile RELIEF velocimetry system that would be of lower cost and could be easily moved to different facilities. The beam quality of the current multi-pass Raman pumping cell setup is too degraded to get good results. One approach which might improve the beam quality, would be to move the focusing optics out of the Raman pumping cell as shown in figure 5.1. This would allow adjustments to the alignment after the cell has been pressurized.

Additionally, because the optics don't have to fit inside the cell, a smaller cell could be used. A smaller diameter is advantageous because the cell could also be pressurized to higher pressures which would increase the stimulated Raman conversion. Zhang employed a Raman pumping cell similar to that shown in figure 5.1, in which the optical access constrained the Raman pumping to a maximum of 5 passes. He achieved similar gain in 5 passes and 70 bar as he did with 9 passes and 30 bar.

Figure 5.1 A schematic of a multi-pass Raman cell, in which the Raman pumping cell is between the optics rather than the optics inside the Raman cell. External optics would allow for a more precise alignment, something that is very problematic with internal optics.

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