DEVELOPMENT OF FIBER OPTIC SENSOR BASED ON
LASER RAMAN SPECTROSCOPY

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Laser Raman Spectroscopy (LRS) has received worldwide acknowledgement as a powerful molecular ‘finger print’ technique. The Raman spectrum of sample contains useful information such as molecular identity, composition, constituent’s concentration ratio etc. These information are manifested in the Raman spectrum in band heights, peak wavelength, band areas etc. The basis of quantitative analysis in Raman spectroscopy lies in the measurement of Raman band intensity, which is linearly dependent upon the sample concentration. On the other hand, Raman spectroscopy can also yield the qualitative information of samples by exhibiting bands corresponding to various chemical constituents in the sample mixture. The potentiality of Raman spectroscopy to perform quantitative as well as qualitative analysis of samples has been exploited in the development of Raman sensors in conjugation with the techniques of fiber optics. The main focus of the presented doctoral work is to realize a fiber optic Raman sensor to
monitor the quality of liquid oxygen (LO$_2$) in a rocket engine feed line. In this research investigation, I have shown how a bulk experimental configuration can be transformed to miniaturized prototype sensor, which is equally capable to determine the ratio of liquid oxygen and liquid nitrogen in their cryogenic mixture. This research was extended to monitor the concentration of oxygen and nitrogen in their gaseous mixture. Further, I have demonstrated that the Raman spectroscopy has the potentiality to measure the temperature of hydrogen in a laboratory environment by monitoring the variation in Raman rotation-vibrational line of hydrogen gas with temperature. Finally, I have experimentally studied the surface enhanced Raman spectroscopy (SERS) of silver colloidal solution, which is another interesting branch of Raman spectroscopy that has transcended the limitation of very low Raman cross-section to offer more insight to the chemical properties of samples.
DEDICATION

I would like to dedicate this research to my grandparents; Ram C. Tiwari, G. Devi, my parents; Radhey S. Tiwari, Priyamvada Tiwari, my brother; Vibhuti B. Tiwari, and my sister in-law; Shilpi Tiwari.
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CHAPTER I

INTRODUCTION

Optical fibers have played a vital role in the evolution of world-wide communication systems that has occurred in the past few decades. While optical fibers were originally designed for transmitting light signal, it was soon found that they had a great potential for sensing applications, which required light to interact with the fiber’s surrounding. Fiber optic sensor (FOS) technology has always been a key beneficiary of the components associated with optoelectronic and communication industry. The development of optical fiber sensors begin in mid-1970s, when researchers started acknowledging its potential for measuring pressure, temperature, strain, torque and several other parameters of interest. Today, optical fiber sensing technology has evolved to the point where one can measure nearly all of physical parameters of interest and a very large number of chemical species as well.

There are different approaches to categorize fiber optic sensors. Some are based on their ability to diagnose a specific parameter (e.g., temperature, pressure, velocity etc.). An alternative approach takes into consideration the type of modulation scheme being used, such as intensity, polarization, wavelength etc. Conventionally, FOS may be broadly classified as direct or indirect sensors. In the first, the fiber simply serves as media for guiding light from the sensing location to monitoring instrumentation and thus measures the optical properties of the analyte under study. In the second (also referred as
optrodes), suitable reagent (label) is immobilized at the fiber tip to react specifically to the analyte. This causes changes in the optical properties of the reagent (e.g. fluorescence or absorption) which gives an estimation of the analyte concentration.5

**Fiber Optics and Spectroscopy**

Fiber optic sensors are well suited for analytical applications. Most optical chemical sensors employ spectroscopic techniques, such as absorption, reflectance, fluorescence, Raman, etc. The basic underlying principle for spectroscopy-based sensors lies in the interaction of light such as laser light with the target analyte.5 The chemical information is contained in the spectral response of the target analyte. In most of the cases, optical fibers serve as guide media for carrying the excitation light from the light source to the sample, and again carrying the optical response of the sample to a detector.5 Spectroscopy-based fiber optic sensors have played an important role in environmental monitoring, biomedical sensing and industrial process control.6,7-9 In many cases, these sensors exploit the specific advantages made available by optical fiber technology. Fiber optic chemical sensors (FOCS) can benefit from, for example, the geometrical versatility, low attenuation and electrical noise immunity of optical fibers.10 Chemical sensing based on optical fibers has several attractive features. The low attenuation of optical fibers enables remote, *in situ* monitoring of species in hazardous locations, e.g., ground water monitoring, monitoring of hydrocarbons in fuel and industrial chemical processing11 determining the quality of cryogenic fuels in liquid propellant rockets and others.12
**Raman Effect**

Absorption and fluorescence are considered as important spectroscopic interrogation techniques. But there are other spectroscopic methods, for example Raman spectroscopy, that yield ‘molecular finger print’ vibrational spectra of chemicals. Raman spectroscopy deals with light scattering phenomena, known as the ‘Raman effect’, which was first experimentally demonstrated by Raman and Krishnan in 1928.\(^{13}\)

The Raman effect can be described as a process in which monochromatic light is scattered by the molecular sample. The scattered light has a wavelength shift that corresponds to energy differences between rotational or vibrational energy levels of the molecule, and is observed in the form of a Raman spectrum. The probability of light being scattered by the molecule is many times less than the probability of light being absorbed or reflected by the molecule. It’s an established fact that only one out of $10^8$ photons undergoes Raman scattering, and therefore this is considered to be a weak process.\(^5,7\) The Raman spectrum is marked by narrow bands that are specific to particular molecular species in a mixture. This feature enables characterization of sample mixtures and therefore Raman spectroscopy is often used as an analytical technique in various chemical and pharmaceutical industries. Since the intensity of Raman peaks is proportional to the concentration of molecules, Raman spectroscopy is widely accepted as a powerful analytical tool.\(^7\)

**Raman Sensor Development**

The key components involved in a ‘Raman Optical Sensor’ are an excitation light source to illuminate the sample, an optical filter to attenuate scattered laser light, and a
detector interfaced to a computer for sensing the Raman signal of the species under study.\textsuperscript{7,9} Currently, laser are widely used as an excitation light source in most of Raman-based spectroscopic studies. Before the discovery of lasers in 1960, Raman instrumentation employed a water-cooled mercury arc lamp as the excitation light source and a small spectrograph equipped with a photographic plate. However, at that times infrared absorption spectroscopy was the much more preferred technique owing to its simplicity and ease of operation.\textsuperscript{7,9} The invention of lasers and photomultiplier tubes completely revolutionized the world of Raman spectroscopy in terms of performance and gave birth to several non-linear Raman techniques such as CARS (coherent anti–Stokes Raman spectroscopy), stimulated Raman spectroscopy etc.\textsuperscript{7,9} High powered lasers with a high degree of monochromaticity have greatly improved the Raman signal by enabling more photons to undergo Raman scattering. Different types of lasers used for Raman spectroscopic studies include helium-neon ion lasers, diode-pumped solid state lasers etc.\textsuperscript{7,9} Another requirement of designing a Raman system is the need to filter the weak Raman signal, thereby rejecting the scattered laser radiation. Various types of optical filters, such as absorption filter, reflective interference filters, Raman edge filters, and holographic notch filters, are employed in Raman systems. Among these, holographic notch filters have became the most popular choice of researchers owing to their ability to reduce laser line intensity by a factor of $\sim 10^8$, thus allowing the transmission of Raman wavelengths of interest.\textsuperscript{7,9}

The Raman signal from the sample is filtered and then send to a detection unit which generally comprises a detector interfaced to a computer. As the Raman scattering
is a weak process, careful selection of a detector has been required. These detectors exploit the phenomena of the ‘photoelectric effect’ and consist of a photocathode and an anode. Silicon CCD (charge coupled device) detectors are now the detectors of the choice for most Raman measurements at wavelengths shorter than about 1000 nm. A CCD detector is actually an array of detector elements, often referred to as pixels, which are photosensitive capacitors that store light in the form of charge. The accumulated charge is measured by moving it to a charge-sensing amplifier. The amplifier output is digitized and stored in a computer. Other kinds of detectors used in Raman spectroscopy include intensified CCD (ICCD) detectors, and near-infrared (NIR) single-element detectors. Each one of these detectors has its own unique importance and use as per experimental requirements.

Introduction of fiber optic probes, during the 1980’s, opened new doors for Raman spectroscopy to be applied to the samples located far away from the Raman instrument. In general, fiber optic probes employ two fibers—excitation and collection fibers. The excitation fiber carries the laser light from the laser to the sample, whereas the collection fiber delivers the Raman scattered light from the sample to the detector. The fiber optic probes are widely used in conjugation with Raman spectroscopy for characterization of chemical species in hazardous environments and in various processing plants.
Analytical Considerations for Applied Raman Spectroscopy

The aim of analytical Raman spectroscopy is to seek information about a sample. The information is related to the sample’s identity, composition, molecular orientation, or crystal form. This information is contained in Raman spectra in the form of intensities, widths, areas, positions and/or shapes of various Raman bands. To further extract this information from Raman spectra, bands corresponding to the analyte(s) are separated from the spectral background. Another important aspect of analytical Raman spectroscopy is interfacing the Raman instrument to the sample. Raman analysis doesn’t usually affect the physical or chemical properties of the sample, requires no or little sample preparation or physical contact with the sample, and therefore has an advantage over various other analytical techniques.9

The fact that the Raman scattering cross section (Raman signal) is linearly proportional to the analyte concentration forms the basis for quantitative analysis in Raman spectroscopy. Apart from quantitative analysis, Raman spectroscopy is also acknowledged as a potential tool for qualitative studies of samples. Raman spectra can be used to distinguish among a large number of samples because of the many well resolved bands possible in a Raman spectrum.9 The doctoral research presented here also exploits the analytical aspect of Raman spectroscopy and demonstrates that Raman spectroscopy has the potential for qualitative as well as quantitative monitoring of constituents in their sample mixtures.
Surface Enhanced Raman Scattering

In 1917, Van Duyne and Jeanmaire demonstrated that the magnitude of the Raman signal can be enhanced by $10^5$-10$^6$ times of pyridine adsorbed on silver electrode. Initially, the idea that the surface effects can play a role in enhancement of the Raman signal was looked upon with skepticism. But in later years, researchers carried out several experiments to validate the existence of ‘enhancement effects’ when molecules are placed in the vicinity of nanostructure materials, such as gold or silver. This phenomenon was named ‘surface-enhanced Raman scattering’ (SERS). The discovery of SERS opened new doors for Raman spectroscopic techniques to be applied to a wide variety of molecules, especially biological species, which are usually weak Raman scatterers. Two important mechanisms are responsible for the enhancement of Raman signal—electromagnetic field enhancement and chemical effects. These will be discussed in details in subsequent chapters.

Dissertation Overview

The author endeavors to present various facets of his doctoral research to the readers of this dissertation. The doctoral dissertation has been divided into six chapters. The second chapter describes the fundamental principles of Raman spectroscopy and surface enhanced Raman spectroscopy (SERS). Further chapters combine various segments of my doctoral research. Each of these chapters begins with a brief introduction of the scientific problem, and the methods adopted by the previous researchers in addressing them. This is followed by my approach towards solving these problems and
then followed by a brief description of the experimental configuration. The experimental results are shown and discussed. Here is summary of the chapters 3 to 6:

The third chapter is related to the development of a spontaneous Raman scattering optical fiber sensor for a specific need of the National Aeronautics and Space Administration (NASA) for long-term detection and monitoring of the purity of liquid oxygen (LO₂) in the oxidizer feed line during ground testing of rocket engines at Stennis Space Center (SSC). Chapter 4 is an extension of the work described in Chapter 3, and deals with monitoring of a gaseous mixture of nitrogen and oxygen in a high pressure sample cell. The work presented in chapter 5 is again motivated by a specific need of NASA/SSC for a sensor that can measure the temperature in a super heated hydrogen (SHH₂) line, which is an important unit in a nuclear thermal rocket (NTR) propulsion system. Chapter 6 is a study of the non-resonance surface enhanced Raman scattering (SERS) effect of silver colloids with different shapes.

Finally, conclusions of each of the above mentioned chapters are given in Chapter 7, followed by an independent section of references.
CHAPTER II
RAMAN SPECTROSCOPY

The underlying principle behind Raman scattering is the Raman effect, which can be described as a process of exchange of energy between incident photons and the scattering molecules. There are two approaches towards understanding Raman spectroscopy (classical and quantum mechanical) which are briefly described below.

Classical Theory of Raman Scattering

The classical theory of the Raman effect is based on the polarizability property of molecules. The polarizability is defined as the degree to which the electrons in the molecule can be displaced relative to the nuclei. The polarizability of a molecule is an anisotropic property, conventionally represented by drawing a polarizability ellipsoid. In general, a polarizability ellipsoid is defined as a three-dimensional surface on which any point has a distance of $\alpha^{-1/2}$ from the electrical center of the molecule, where $\alpha$ is the polarizability in that direction. Similar to a moment of inertia of a molecule, polarizability is a tensor property, and can be expressed as a matrix given by Equation 2.1

$$\alpha = \begin{pmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{pmatrix}$$ (2-1)
When a molecule is put into an oscillating electric field $E$, a dipole moment $\mu$ is induced in the molecule. The induced dipole is proportional to the electric field as\(^\text{19}\)

$$\mu = \alpha E$$  \hspace{1cm} (2-2)

where $E$ and $\mu$ are vector quantities. The polarizability ellipsoid rotates with molecules at a frequency $\nu_{\text{rot}}$ and variation of $\alpha$ with rotation is given by\(^\text{19}\)

$$\alpha = \alpha_{0,r} + \alpha_{1,r} \sin 2\Pi c(2\nu_{\text{rot}})t$$  \hspace{1cm} (2-3)

where $\alpha_{0,r}$ is the average polarizability and $\alpha_{1,r}$ is the amplitude of the change of polarizability during rotation. Also the time dependent electric field $E$ is given by\(^\text{19}\)

$$E = A \sin 2\Pi c \nu t$$  \hspace{1cm} (2-4)

Substituting the equations (2-3) and (2-4) into equation (2-2) gives\(^\text{19}\)

$$\mu = \alpha_{0,r} A \sin 2\Pi c \nu t - \frac{1}{2} \alpha_{1,r} A \cos 2\Pi c(\nu + 2\nu_{\text{rot}})t + \frac{1}{2} \alpha_{1,r} A \cos 2\Pi c(\nu - 2\nu_{\text{rot}})t$$  \hspace{1cm} (2-5)

The three scattering terms in the above equation correspond to Rayleigh, anti-Stokes and Stokes Raman scattering respectively. The classical theory also provides an expression for the dipole moment due to vibrational motion of the molecules, which is similar to that for molecular rotation as shown in Equation (2-6). The expression for the induced dipole moment due to vibrational motion of molecule is given by\(^\text{19}\)

$$\mu = \alpha_{0,v} A \sin 2\Pi c \nu t - \frac{1}{2} \alpha_{1,v} A \cos 2\Pi c(\nu + \omega) t + \frac{1}{2} \alpha_{1,v} A \cos 2\Pi c(\nu - \omega) t$$  \hspace{1cm} (2-6)

where again the scattering terms correspond to Rayleigh, anti-Stokes and Stokes Raman scattering respectively. The classical theory has a limitation in assigning discrete
rotational frequencies to the molecule which is overcome by the quantum mechanical theory of Raman spectroscopy.\textsuperscript{21}

**Quantum Mechanical Theory of Raman Scattering**

According to quantum mechanical theory, Raman scattering is a process resulting from the transition of the molecule from some energy state to a virtual excited state, followed by its return to a higher (or lower) vibrational (or rotational) state with the emission of a photon. The virtual state is an unstable energy state. In one of the process, energy of photon may remain unchanged after the collision (inelastic) with a molecule, and the frequency of scattered photon is same as that of the incident photon. This is termed as Rayleigh scattering. When the energy of photon is transferred to the molecule, the scattered photon has less energy as compared to that of incident photon. This is termed as Raman Stokes scattering. In an another situation, when the molecules is already in excited state, energy from the molecules is transferred to the photon ,and the scattered photon has more energy as compared to that of incident photon. This is termed as Raman anti-Stokes scattering.\textsuperscript{9} Figure 2.1 shows the Raman and Rayleigh scattering processes involving virtual states $V_0$ and $V_1$. The intensities of Rayleigh scattered light and Raman scattered light are proportional to the number of molecules being illuminated.\textsuperscript{9}

Raman scattering is not only due to transitions between the vibrational energy states. Molecular rotations also cause Raman scattering. Rotational Raman bands result from transitions between rotational energy levels within a single vibrational energy level (pure rotational bands), or between different vibrational energy levels (rotation-vibration
Figure 2.1: Examples of Raman and Rayleigh scattering processes involving virtual states $V_0$ and $V_1$.
bands), as shown in Figure 2.2. Figure 2.3 shows pure rotational bands and rotation-vibration bands in an ideal Raman spectrum.

A quantum-mechanical modification to the model for Raman scattering was first used by Placzek\textsuperscript{9,22} to derive an expression for Raman scattering intensity. The Raman scattering intensity, \( I_R \) is given by,

\[
I_R = \frac{2^4 \pi^3}{45 \times 3^2 \times c^4} \times \frac{hI_L N (\nu - \nu_0)^4}{\mu \nu (1 - e^{-h \nu / kT})} \left[ 45(\alpha_a')^2 + 7(\gamma_a')^2 \right]
\]  

(2-7)

where:

- \( c \) = speed of light;
- \( h \) = Planck’s constant;
- \( I_L \) = excitation intensity;
- \( N \) = number of scattering molecules;
- \( \nu \) = molecular vibrational frequency, (in Hertz);
- \( \nu_0 \) = laser excitation frequency, (in Hertz);
- \( \mu \) = reduced mass of the vibrating molecule;
- \( k \) = Boltzmann’s constant;
- \( T \) = absolute temperature (in Kelvin)
- \( \alpha_a' \) = mean value invariant of the polarizability tensor;
- \( \gamma_a' \) = anisotropy invariant of the polarizability tensor.
Figure 2.2 Energy level diagram showing examples of rotation-vibration scattering and pure rotational scattering.

Figure 2.3 Raman spectrum showing both pure rotational bands and rotation-vibration bands.
Equation (2-7) shows that the Raman scattering intensity is proportional to the number of molecules being illuminated. This is the basis for quantitative analysis using Raman spectroscopy. The Raman scattering intensity is proportional to the excitation light intensity, and to \((v_0-v)^4\). The Raman scattering intensity can therefore be increased by increasing the incident light intensity or by using incident light of a higher frequency, \(v_0\) (shorter wavelength).

**Raman Spectra of Diatomic Molecules**

Infrared and Raman spectroscopy are popular methods for determining the molecular ‘finger print’ of molecules on the basis of rotation vibration transition. Raman spectroscopy has great importance for homonuclear diatomic molecules such as \(N_2\), \(O_2\), \(H_2\) etc because their permanent electric dipoles are zero, and therefore have no infrared vibrational spectrum. The rotation vibration selection rule for Raman transitions in diatomic molecules is \(\Delta J=0, +2,\) and \(-2\) giving a Q (\(\Delta J=0\)), an S (\(\Delta J=+2\)) and an O (\(\Delta J=-2\)) branch as shown in Fig.2.4 where \(F(J)\) and \(G(v)\) represent the rotation and vibration term values respectively. Under the assumption that the rotational constants for ground vibrational state \(B_0\) and first excited vibrational state \(B_1\) are approximately same \(B\), the wave numbers \(\tilde{\nu} [S (J)]\), \(\tilde{\nu} [O (J)]\) and \(\tilde{\nu} [Q (J)]\) of the S-, O- and Q-branch lines, respectively are given by

\[
\tilde{\nu} [S (J)] = \omega_0 + B (J+2) (J+3) - BJ (J+1) = \omega_0 + 4BJ + 6B \tag{2.8}
\]

\[
\tilde{\nu} [O (J)] = \omega_0 + B (J-2) (J-1) - BJ (J+1) = \omega_0 - 4BJ + 2B \tag{2.9}
\]

\[
\tilde{\nu} [Q (J)] = \omega_0 \tag{2.10}
\]
Equation (2.10) shows that Q-branch lines are coincident in this approximation. The above equations (2.8-2.10) clearly indicates the separation of the first S-branch line S (0) and the first O-branch line O (2) is 12B and the separation of adjacent S-branch lines and of adjacent O-branch lines is 4B.\textsuperscript{19} Figure 2.4 shows Raman transition for S, Q and O branch.\textsuperscript{21}

**Dependence of Raman Rotation-Vibration Bands on Temperature**

At thermal equilibrium, the Stokes Raman intensity is higher than the anti-Stokes Raman intensity. This is attributed to the fact that number of molecules in a lower rotational/vibrational level is always larger than those in a higher rotational/vibrational level.\textsuperscript{9} The relative intensities of vibration/rotational band is governed mainly by the Boltzmann distribution of population among the initial states, as expressed in Equation (2.11).\textsuperscript{19}

\[
\frac{N_J}{N_0} = (2J''+1) \exp \left( - \frac{h \nu B' (J''+1)}{kT} \right)
\]

When the temperature of the molecule is raised, the concentration of molecules in the higher vibrational or rotational energy levels is increased. As a result, Raman transitions in molecule from higher energy levels become more prominent, as evidenced by the change of relative intensity of the Raman bands. Variation in the relative intensities of Stokes and also anti-Stokes Raman band with change in temperature has been utilized for determining the temperature of species.\textsuperscript{9, 23, 24}
Figure 2.4 Raman transitions for S, Q and O branch
Surfaced Enhanced Raman Spectroscopy (SERS)

The inherently small cross section of Raman scattering (~$10^{-30}$) results in weaker Raman signal, thus limiting the possibility of analyte detection at low concentration levels. The Raman scattering signal can be enhanced by several orders of magnitude ($10^7$) when the analyte is adsorbed on the roughened metal surface or in the presence of metal colloids. This effect is called surface enhanced Raman spectroscopy (SERS). The mechanism involved in the enhancement effect of SERS is still an issue of debate. However, there are two important theories proposed towards understanding SERS, which are based on electromagnetic (EM) and chemical (CHEM) enhancement. Brief descriptions of these theories are as follows.

Electromagnetic Enhancement

The electromagnetic enhancement is based upon the optical properties of the noble metals and their ability to support plasmon resonances in the visible or near infrared (NIR) regions. The basic concept of EM enhancement can be understood by considering the molecule (analyte) in the vicinity (at a distance d) of a nano sized metallic sphere of radius 2r as shown in Figure 2.5. The frequency dependent dielectric constant of the metallic sphere is $\varepsilon$, which has real as well the imaginary parts. The medium surrounding the molecule has the dielectric constant as $\varepsilon_0$. The analyte molecule is under the influence of field $E_M$, which is the combination of the incoming field $E_0$ and the field of an electric dipole $E_{sp}$ induced in the metal sphere. The ratio of the electric field at the point of molecule to the incoming field is termed the field enhancement factor $A(\nu)$ and is expressed as \[ A(\nu) = \frac{E_M}{E_0} \]
Figure 2.5 Schematic diagram for showing electromagnetic enhancement in molecules in the vicinity of spherical nanoparticles

\[ E_M = E_0 + E_{sp} \]

\[ E_{sp} = r^3 \frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0} E_0 \frac{1}{(r + d)^3} \]
\begin{equation}
A(v) = \frac{E_M(v)}{E_0(v)} - \frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0} \left( \frac{r}{r + d} \right)^3
\end{equation}

The condition of resonant excitation of surface plasmons is achieved when the real part of \(\varepsilon(v)\) is equal to \(-2\varepsilon_0\). In the SERS effect, the field enhancement occurs twice. Initially, the field enhancement amplifies the intensity of incident light interrogating the molecule, thus increasing the Raman scattering signal. The Raman scattering signal further gets enhanced by the nano particle surface by the same mechanism as the incident light, resulting in an overall increase in the output Raman signal.\textsuperscript{25} Taking into consideration enhancing effects of the laser and the Raman Stokes field, the electromagnetic enhancement factor for the Raman Stokes signal power \(G_{em}(v_S)\) is given by equation\textsuperscript{25}

\begin{equation}
G_{em}(v_S) = |A(v_L)|^2 |A(v_S)|^2 \sim \left| \frac{\varepsilon(v_L) - \varepsilon_0}{\varepsilon(v_L) + 2\varepsilon_0} \right|^2 \left| \frac{\varepsilon(v_S) - \varepsilon_0}{\varepsilon(v_S) + 2\varepsilon_0} \right|^2 \left( \frac{r}{r + d} \right)^{12}
\end{equation}

The above equation indicates that the enhancement is proportional to the fourth power of the local field of the nano particle. Also, the enhancement is maximum when the scattered and excitation field are in resonance with the surface plasmons. Another interesting point to observe is that for the SERS effect, there is no requirement for the molecule to be in contact with the metal nanostructure. The enhancement effect is inversely proportional to the distance between the metallic structure (for e.g., a sphere) and the molecule as evident in Equation (2.13)\textsuperscript{18,25}
Chemical enhancement

The electromagnetic field enhancement is mainly responsible for strong SERS signals in most molecules, and has been found to be independent of the chemical nature of molecules. However, the experimentally observed enhancement in SERS signal is more (by a factor of $10^2$) than that calculated theoretically for electromagnetic enhancement. It was soon realized that in addition to EM enhancement, a chemical mechanism is also involved and its contribution is responsible for enhancement of the SERS signal. Chemical enhancement results from an electronic resonance-charge transfer between a molecule and a metal surface with atomic-scale roughness features. This results in increasing the polarizability of the molecule and effectively increasing the Raman scattering cross section. An important condition for the occurrence of chemical enhancement is that the molecule must be directly adsorbed to the roughened surface of the substrate (metal).\textsuperscript{18, 25}
CHAPTER III
RAMAN SENSOR FOR CRYOGENIC MIXTURE

The escalating use of liquid phase elements like oxygen and hydrogen as cryogenic fuels and the consequent need for monitoring their quality led to the development of a variety of sensor systems. Several types of electronic sensors such as capacitance based and electrochemical sensors are commercially available but lose their reliability in the supercritical environment of rocket engines, where low temperatures and high pressures severely inhibit their optimal performance.\textsuperscript{26-28} The high flow rate of the oxidizer feed lines pose serious limitations on the accurate measurement of impurity level in the cryogenic oxygen and requires a sensor system with a fast response time. Quantitative detection of impurities in oxygen is critical for this technologically important applications.\textsuperscript{29} Application of fiber optic technology offers an alternative approach to measuring various parameters of interest and addresses several measurement issues associated with characterizing the cryogenic fuels feeding a rocket engine. Today, optical fiber sensing technology has evolved to the point where one can measure nearly all the physical parameters of interest and a very large number of chemical species as well.\textsuperscript{5} Jason et. al. reported the differential absorption sensor applied for liquid oxygen measurements.\textsuperscript{30} A computational-analytical technique for quality maintenance in cryogenic liquid methane at the entrance to the test article tank has been reported.\textsuperscript{31}
This research work is motivated by a specific need of the National Aeronautics and Space Administration (NASA) for detection and monitoring of the quality of liquid oxygen in the delivery line during ground testing of rocket engines.\textsuperscript{32,33} Figure 3.1 shows a schematic of liquid oxygen (LOX) tank, which subjected to high pressure by nitrogen gas, connected to rocket engine via feed line. Online, near real-time characterization of cryogenic fluid mixtures like liquid nitrogen (LN\textsubscript{2}) and liquid oxygen (LO\textsubscript{2}) by optical diagnostics is an area that has not yet been explored to the best of our knowledge. This research deals first phase of development of an all-optical cryogenic fluid sensor based on Raman spectroscopy, in conjunction with fiber optics. The sensor under study can be used to infer the abundance of impurities in a rocket engine fuel feed line.\textsuperscript{34} An attractive design feature of a fiber optic sensor lies in the capability for real-time, \textit{in-situ} qualitative as well as quantitative determination of LO\textsubscript{2} and/or LN\textsubscript{2} from their mixtures through the Raman spectral analysis. Various issues involved in monitoring supercritical fluid mixtures, like sample vaporization/condensation, system optimization, signal/noise ratio, and other safety parameters, have been well addressed and provide a novel vision for encountering challenges involved in process/control of cryogenic fuels.

Optical fiber sensors have certain distinct advantages over conventional sensors, such as remote sensing, multiplexing and distributed sensing, immunity towards EM signals, etc., that make them more advantageous in practical applications. Laser Raman Spectroscopy (LRS) has been known for years as a relatively simple analytical method for identification of molecules in gases, liquids and solids. Raman spectroscopy is based on the Raman effect that results from energy exchange between incident photons and the
Figure 3.1 Liquid oxygen tank subjected to high pressure of nitrogen gas and connected to rocket engine via feed line.
scattered molecules.\textsuperscript{9} The Raman scattered light occurs at frequencies that are shifted from the incident laser light by the change in vibrational, rotational or electronic energies of a molecule. By measuring the frequency and intensity of inelastically scattered light from the sample, the molecules in the sample can be qualitatively and quantitatively characterized. In order to explore various possibilities of employing a low cost, portable optical sensor based on LRS in the harsh environment of a rocket engine, we evaluated three excitation light sources for the sensor. Two frequency doubled 532-nm continuous wavelength (cw) Nd:YAG lasers (Coherent and Milles Griot lasers) were first used as the excitation light source with a fiber optic miniaturized Raman probe. Then a diode laser operating at 670-nm was used as the excitation source in an attempt towards configuring a cost-effective optical sensor, which caters to the needs of various national laboratories and cryogenic industries.

**Experimental Details**

The main focus of this research effort was to develop a real time optical fiber sensor that employs a cw 532-nm laser as an excitation light source for monitoring the concentration of LN\textsubscript{2} in a LN\textsubscript{2} and LO\textsubscript{2} mixtures. In the process of developing a miniaturized and cost effective optical fiber Raman sensor, we have also evaluated a diode laser as an excitation light source. The details of the excitation sources used in this study are given in Table 3.1.

In the initial experiment, an optical fiber Raman sensor is set up using a frequency-doubled 532-nm continuous wavelength (cw) Nd:YAG laser (Coherent DPSS 532) as the excitation light source, with maximum output power of 330 mW. The laser
Table 3.1
DETAILS OF THE EXCITATION SOURCES USED IN THIS STUDY

<table>
<thead>
<tr>
<th>Excitation Source</th>
<th>Wavelength (nm)</th>
<th>Laser Line Width (nm)</th>
<th>Max. Power (mW)</th>
<th>Beam Diameter* (mm)</th>
<th>Transverse Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A. 532-nm laser</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>❖ Coherent</td>
<td>532</td>
<td>0.00047</td>
<td>330</td>
<td>0.70</td>
<td>TEM(_{00})</td>
</tr>
<tr>
<td>❖ Milles Griot</td>
<td>532</td>
<td>0.18</td>
<td>3000</td>
<td>0.24</td>
<td>Multimode</td>
</tr>
<tr>
<td><strong>B. 670-nm diode laser</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Power Technology Inc.</td>
<td>670</td>
<td>0.70</td>
<td>700</td>
<td>1.5</td>
<td>Multimode</td>
</tr>
</tbody>
</table>

*1/e² at waist
output energy was attenuated through use of neutral density filters in order to protect the fiber in the excitation arm of the probe from potential damage by high intensity light. The throughput sample power was ~120mW. This sensor configuration optic employed a modified In Photonics fiber miniaturized Raman probe. The probe consisted of just two parallel optical fibers; one (90-μm core diameter) guided the incident light to a liquid sample mixture enclosed within a dewar, whereas the other (200-μm core diameter) collected the emitted Raman signal and fed it to an Ocean Optics Inc. (OOI) spectrometer (USB 2000). This OOI spectrometer had a 1200 line/mm grating along with a 2048-element charge coupled device (CCD) detector attached to the exit of the spectrograph, and was interfaced with a computer via a USB port. The spectral range of the spectrometer is from 550 nm to 858 nm. A block diagram of the experimental set-up is shown in Fig. 3.2.

Probe performance in terms of Raman signal response and background noise level was improved by incorporating a miniaturized lens at the tip of the probe with a working distance of about 30-mm. The sample mixture was prepared with different concentration ratios of LN₂ and LO₂. Raman spectrum of each set of sample mixture was recorded with an integration time (It) of 300-ms and averaged (Avg) for 10 spectra resulting in a 3-sec (It*Avg) data acquisition time/recording time. The data acquisition parameters (integration time/average) were chosen so as to have a minimum time for recording mixture data while taking into consideration that the phase of the sampling mixture was rapidly changing from liquid to gas. Owing to the low temperature of the liquid mixture,
Figure 3.2 Experimental set-up of Inphotonic Raman probe based optical fiber Raman sensor for monitoring LN$_2$ and LO$_2$ concentration ratios using 532 nm Nd:YAG laser
the greatest challenges of the experiment were minimization of vaporization loss and also
determination of the accuracy with which the weight ratio of the sample constituents
were determined during preparation of the mixtures. In the initial experiment, a cap with
a hole was mounted on the dewar. Though it allowed a clear passage from the probe for
the laser light to focus onto the LN$_2$/LO$_2$ mixture, it could not prevent the vapors from
escaping and condensing onto the tip of the fiber probe. Condensation of vapors onto the
tip of probe, over a prolonged time, would have affected the coating of lens at the tip of
the probe. Therefore, to overcome this problem, two identical quartz windows (1/4")
were introduced into the Dewar cap hole which prevented vapors from reaching the tip of
the probe. Attenuation of the laser light was observed by the introduction of the quartz
windows and increased as the vapors from the sample mixture condensed on the surface
of quartz windows, resulting in an overall reduction of signal-to-noise ratio of the Raman
signal. Laser power was further increased to compensate for the attenuation in the laser
light falling onto the sample mixture. Also, a heat gun was installed in the vicinity of
dewar cap to minimize condensation of vapor on the surface of the quartz window facing
towards the sample mixture. As a result, long-term stable operation of the Raman sensor
could be achieved.

To study the effect of laser properties on the Raman signal, the Raman spectra
produced by a narrow band 532-nm laser (Coherent DPSS 532) and by a high power, and
inexpensive broadband 532-nm laser (Milles Griot GHS 309) were compared. The
experimental configuration was kept same for both lasers except a neutral density filter
was employed to the broadband 532-nm laser output to attenuate the laser power so as the laser power on the sample mixture were about ~ 140 mW.

A prototype Raman sensor based on a 700-mW, cw diode laser (Power Technology Inc.), operating at 670-nm, as an excitation light source and a Y-shaped reflection/backscattering probe (Ocean Optics Inc., R200-REF) was designed and evaluated. Fig. 3.3 shows the schematic diagram of this system. Photographs of prototype Raman system based on a reflection probe using 670 nm diode laser is shown in Fig. 3.4. This Y-shaped probe consists of seven optical fibers, each having 200-µm core diameter and 0.22 numerical aperture with one launching fiber and six surrounding collection fibers. The uniqueness of the prototype sensor lies in its compact design configuration that includes carefully aligned optical components, viz., laser diode, filter holder, long wave pass/cut-off filter (725 nm) and a compact spectrometer (Ocean Optics Inc., USB 2000). The compact spectrometer is similar to the one in Fig. 3.2, but the spectral range is from 695 to 965 nm. Raman spectra of mixtures of LO₂ and LN₂ of different concentration (weight) ratios were recorded with prototype Raman sensor in the same manner as described earlier.

Results and Discussions

The present study was primarily focused on quantitative as well as qualitative analysis of LO₂ and LN₂ mixtures at varied levels of their weight ratio. The mixture sample was prepared by adding LO₂ to LN₂, owing to the fact that the molecular weight of oxygen is higher than nitrogen, and therefore suppressing the rate of vaporization of liquid nitrogen. The Raman spectrum recorded for a 40% LO₂ and 60% LN₂ (LN₂/LO₂
Figure 3.3 Schematic diagram of prototype Raman system based on a reflection probe using 670 nm diode laser.
Figure 3.4 Photographs of prototype Raman system based on a reflection probe using 670 nm diode laser.
~1.5) mixture is shown in the Fig. 3.5. Raman bands for LO₂ (~ 580 nm) and LN₂ (~ 607 nm), corresponding a Raman shift for O₂ of 1556.4 cm⁻¹ and for N₂ of 2330.7 cm⁻¹, are indicated on the spectrum.³⁶ The concentration ratio of LN₂ and LO₂ was varied from 0.01 to 1.00 at normal atmospheric pressure and temperature, while maintaining a total mixture weight of 100 gram. The Raman band intensity corresponding to LN₂ increased as the relative concentration of LN₂ in sample mixture increased against the LO₂ as shown in Fig. 3.6. A narrow band Coherent cw Nd:YAG laser, operating at 532 nm, was used in this experiment. The observed Raman bands of LO₂ and LN₂ were analyzed in terms of spectral band shape, signal-to-noise (S/N) ratio, and peak intensity. Peak intensity ratio corresponding to Raman bands of LN₂ and LO₂, at various concentrations of their weight ratio, was estimated for the calibration curve shown in Fig. 3.7. Sensor response exhibited a linear trend within the LN₂ and LO₂ concentration ratio limit of 0 to 1.5 and was observed to saturate for the concentration ratio range (LN₂/LO₂) of 1.5 to 4. Lower signal response of the sensor at higher concentration ratios of LN₂/LO₂ was attributed to the fact that the vaporization rate of liquid nitrogen increased resulting in the formation of cloud of semi-liquid gaseous phase mixture and thereby affecting the sensor performance. The spectral band area ratios of Raman LN₂ and LO₂ peaks were also calculated. This calculation was performed for all the sets of spectra corresponding to a particular concentration ratio of LN₂ and LO₂ and was averaged to obtain a single data point. As a result, error due to fluctuations of peak intensity was minimized. Finally, a calibration curve was drawn between the averaged spectral band area ratios of Raman LN₂ and LO₂ peaks as a function of the corresponding weight ratios, as shown in Fig. 3.8.
Figure 3.5 Raman Spectrum of 40% LO₂ and 60% LN₂ (LN₂/LO₂ ~1.5) mixture. Laser wavelength: 532nm

Figure 3.6 Sensor response to the LN₂ and LO₂ mixture as a function of LN₂ concentration.
Figure 3.7 The intensity ratio variation of LN$_2$ and LO$_2$ against their weight ratios

Figure 3.8 The area ratio variation of LN$_2$ and LO$_2$ against their weight ratios
The following conclusions have been drawn from above experimental results.

First, the sensor system is capable of successfully monitoring the LN$_2$ concentration in a LN$_2$ and LO$_2$ mixture. Second, Raman peak area follows the same characteristics as the intensity ratio curve. For example, both intensity ratio and area ratio curves exhibit a linear trend within a range of low concentration ratio of LN$_2$ and LO$_2$ (LN$_2$/LO$_2$ below 1.5) but tend to slightly saturate for LN$_2$/LO$_2$ ratios more than ~1.5. This implies that the sensor has high detection sensitivity in the low concentration range and can measure LN$_2$ percentage as low as 1% in a sample mixture. For a typical sample mixture of 60% LN$_2$ and 40% LO$_2$ (LN$_2$/LO$_2$ ~1.5), the limit of detection (LOD) of the sensor was calculated to be ~1%. Also, intensity/area ratio data points fluctuate less as reflected by the error bars on the calibration curves which are barely visible in Fig. 3.7. This signifies not only the long term stable operation of the sensor, but also the reproducibility in the sensor response towards analyte concentration. Although the calibration curve obtained by area ratio method involved statistical averaging of multiple sets of spectra, it did not provide better sensor response. The linear calibration data for the LN$_2$/LO$_2$ ratio indicates that the fiber optic Raman sensor has a great potential for qualitative as well as quantitative monitoring of sample constituents in supercritical LN$_2$ and LO$_2$ mixtures.

To develop a less expensive sensor for this application, the feasibility of using an inexpensive, high power, broadband laser (Melles Griot) operating at 532-nm as an excitation light source was tested. Using the same laser energy as with Coherent laser (~140 mW) and the same experimental setup, spectra were recorded for various
concentration ratios of LO₂ and LN₂ and compared with those obtained using the 532-nm Coherent laser. Since the spectrometers used in this work have low optical resolution (~ 3 nm), the laser beam quality did not play an important role in the observed spectral feature. Comparative analysis of spectra recorded with the two lasers suggest that in both the cases, spectra share common features and depending upon the requirement, either of these could be employed as the excitation light source. The laser line width of the Melles Griot laser (~0.18nm) is wider than that of the Coherent laser (~0.00047nm) and showed slightly higher spectral background in comparison to the Coherent laser. Also, the Melles Griot laser could be operated in the high range of power that is suitable for trace LN₂/LO₂ monitoring.

To develop a prototype sensor using a 670-nm diode laser from Power Technology Inc., the performance of the sensor was first estimated by considering the laser energy and detector response near 532 and near 670 nm. Since the Raman cross-section depends inversely on the fourth power of the laser wavelength (\(\lambda\)), \(^{10}\) the Raman signal is also affected by the excitation wavelength. The various parameters that can affect Raman signal are summarized in Table 3.2. Estimation based on these parameters (the effects of optical response from other optics at these two wavelengths were not included in this calculation) shows that the prototype sensor should provide about 4.4-times lower signal than with the system with the more expensive 532-nm excitation source. This signal level should be good enough for this type of application.

A typical spectrum of 60% LN₂ and 40% LO₂ (LN₂/LO₂ ~1.5) in the sample mixture, recorded with the prototype sensor using the 670nm laser as the excitation light
Table 3.2

ESTIMATION OF THE RAMAN SIGNAL FROM 532-NM AND 670-NM LASER

<table>
<thead>
<tr>
<th></th>
<th>532-nm Laser</th>
<th>670-nm Diode Laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Laser Power on Sample</td>
<td>140 mW</td>
<td>380 mW</td>
</tr>
<tr>
<td>CCD Detector Efficiency</td>
<td>2.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Grating Efficiency</td>
<td>60%</td>
<td>72%</td>
</tr>
<tr>
<td>Relative Raman Cross Section ($\chi^4$ )</td>
<td>12.48</td>
<td>4.96</td>
</tr>
<tr>
<td>Overall Relative Raman signal</td>
<td>4.44</td>
<td>1</td>
</tr>
</tbody>
</table>
source, is shown in Fig. 3.9 (a), where the LN\textsubscript{2} Raman peak corresponds to \(\text{\sim} 795\) nm and the LO\textsubscript{2} peak corresponds to \(\text{\sim} 749\) nm respectively. The limit of detection (LOD) of LN\textsubscript{2} was estimated from the signal-to-noise ratio found from the Raman spectrum of 60% LN\textsubscript{2} and 40% LO\textsubscript{2} (LN\textsubscript{2}/LO\textsubscript{2} \text{\sim} 1.5). The limit of detection (LOD) of LN\textsubscript{2} with the prototype sensor was found to be \text{\sim}20\%, which is much higher than the LOD of LN\textsubscript{2} of \text{\sim}1\% found from the sensor using a 532 nm laser (see Fig. 3.2). The spectrum recorded with the 670-nm laser diode also shows a strong background that severely affects the Raman signal of LO\textsubscript{2}/LN\textsubscript{2}. The overall spectral quality (signal-to-noise ratio) of the prototype sensor using the 670-nm diode laser is not as good as that observed with a 532-nm laser (see Fig. 3.5).

The performance of the sensor systems with different lasers is actually determined by many factors, such as the spectral characteristics of the laser systems, the optics, and also the scattered light. Due to the broadband spectral line width of the 670-nm laser diode, a long wave pass/cut-off filter, centered on 725 nm, is unable to suppress the scattered incident laser light. The scattered light has contributed to part of the strong background observed. The optical fiber can also give rise to a Raman spectral feature and also a fluorescence background signal that is superimposed on the LO\textsubscript{2} and LN\textsubscript{2} spectrum. The current prototype sensor is very compact, but is unable to effectively remove these background features. To suppress the background and to improve the signal/noise ratio of the Raman signal, appropriate combinations of various filters will need to be tested and added to the collection optics of the miniaturized prototype sensor. However, some data processing techniques can be applied to improve the quality of the data. Fig. 3.9 (b) shows the processed Raman LO\textsubscript{2} and LN\textsubscript{2} spectrum of the prototype.
Figure 3.9 Raman spectrum for 60% LN₂ & 40% LO₂ (LN₂/LO₂ ~1.5) with 670nm diode laser (a) raw spectrum (b) background subtracted spectrum
sensor. This spectrum was obtained by subtracting the raw data from the background spectrum (the background spectrum was obtained by fitting with some polynomial functions). Spectral averaging can also be applied to further improve the signal-to-noise ratio. Intensity ratios for a LN₂ and LO₂ weight ratios of 1.5 were calculated to be ~1.4 from background subtracted spectrum obtained from the prototype sensor. The intensity ratios obtained with a 532 nm coherent laser for the same weight ratios of LN₂ and LO₂ is about 1.3.
CHAPTER IV
RAMAN SENSOR FOR GASEOUS MIXTURE

The ultimate objective of my research was to design an integrated Raman sensor for monitoring the concentration ratios of LN$_2$ and LO$_2$ in a cryogenic mixture, as discussed in Chapter 3. However, the initial phase data were taken with pure gaseous nitrogen (GN$_2$) and oxygen (GO$_2$) in a high pressure cell. This chapter is basically an extension of work presented in the chapter 3, and deals with qualitative as well as quantitative monitoring of gaseous mixture of nitrogen and oxygen in a high pressure sample cell.

In the past, researchers have performed spectroscopic studies on various kinds of gaseous mixtures as a function of pressure. In some of these studies, an important consideration was given to the design configuration of the enclosures in which gaseous mixture samples were prepared. Frantz et al. have developed an optical sample cell for Raman spectroscopy studies of supercritical fluids and water, which is relevant for data acquisition in geological process.$^{37}$ They have thoroughly acknowledged the problems associated with sealing optical windows at high-pressure, high-temperature vessels, and focused on developing a nickel alloy-based miniaturized optical cell with diamond as the optical window. Hansen et al. have performed Raman spectroscopic studies of methane-ethane mixtures as a function of pressure.$^{38}$ They have also constructed a high-pressure
sample cell for monitoring the constituents of natural gas, such as methane, oxygen, nitrogen, carbon dioxide, etc.\textsuperscript{39} The sample cell described here shares some of the configuration features described in Ref. 39, including Swagelok fittings, pressure monitoring gauge etc.

In my research, study of gaseous mixture of nitrogen and oxygen was important for realizing an optical sensor for LN\textsubscript{2} and LO\textsubscript{2} due to the following reasons. Firstly, it was intended to test the system components, especially the laser, the In Photonics probe, and the spectrometer for identifying the Raman bands of nitrogen and oxygen. Secondly, the Raman signal of gaseous nitrogen/oxygen is more stable in comparison with that of liquid nitrogen or liquid oxygen which continuously changes their phase at room temperature. Therefore, it allowed me to study the spectrometer response for the Raman signal of nitrogen and oxygen. This part of the study was also important from the sensor application point of view for the actual rocket engine testing environments. Optical access to cryogenic fluids in the feed lines is usually restricted due to high condensation of these fluids, which are also subjected to high pressure. In this situation, a small fraction of cryogenic fluid mixture can be sampled out from the feed line under reduced pressure. During this process, the cryogenic mixture sample changes its phase from liquid to gaseous phase, which can be interrogated with the laser light to extract the constituent information. Hence, a fiber optic spontaneous Raman gas sensor has been developed as an analytical tool for sensitive and rapid interrogation of nitrogen/oxygen gaseous mixture in a high-pressure sample cell.
Experimental Details

High-Pressure Sample Cell

The schematic diagram of the high-pressure cell, which was assembled in the laboratory, is shown in the Fig. 4.1. Type 304L stainless steel seamless tubing from Swagelok formed the main body of the cell with dimensions 3.5”×10.88” and was capable of sustaining a maximum pressure of 1800 psi. A 3/4” national pipe thread (NPT) bull’s eye from Pressure Products Company (PPC) Inc was attached at the top end with the help of a 3/4” NPT-to-1/2” NPT adaptor as shown in the Fig. 4.1. A Swagelok T (1/2”) was connected at the other end of the main pressure cell. A quartz window of diameter ~1” and thickness 3/4” was embedded into the NPT bull’s eye and provided optical access for the laser light to interact with the gaseous mixture. A terminating cap was attached to the other end of the T. The side end of the T was attached to a four way Swagelok (1/4”) connector, which was connected with a safety valve (rated for ~1000psi), and a pressure gauge to monitor experimental parameters. The four-way connector was connected to nitrogen/oxygen cylinder for recording the Raman spectra with different gas mixtures of N₂ and O₂.

Experimental Configuration

An optical fiber Raman sensor is setup using a frequency-doubled, 532 nm continuous wave Nd:YAG laser as the excitation light source, with maximum output
Figure 4.1. Schematic of high pressure sample cell for monitoring gaseous mixture of nitrogen and oxygen.
Figure 4.2 Experimental set-up of optical fiber Raman Sensor for monitoring gaseous nitrogen and oxygen
power of 330 mW. The laser output energy was attenuated through proper neutral density filters (NDF). The sensor configuration, employing In-Photonics fiber optic state-of-the-art miniaturized Raman probe, consisting of just two parallel optical fibers, with one fiber (90μm core diameter) guiding the launched light to the gaseous sample mixture enclosed within high pressure cell, whereas the other fibers (200μm core diameter) collect the emitted Raman signal and feed it to the Ocean Optics spectrometer. This spectrometer has a 1200 1/mm grating (which covers the 555-855nm wavelength region) along with a 2048-element charge coupled device (CCD) detector attached to the exit of the spectrograph, and was interfaced to a computer via a USB port. Probe performance, in terms of Raman signal response and background noise level, was modified by incorporating a miniaturized lens at the tip of the probe at a working distance of about 30 mm. Light was focused onto the nitrogen/oxygen gaseous mixture through an optical quartz window (thickness ~ 3/4 inch and diameter ~ 1 inch) inside the high pressure cell shown in Fig.4.2. The high-pressure cell was simultaneously interfaced to oxygen/nitrogen gas cylinder through a four way Swagelok (1/4”) connector which is further attached to a safety valve and pressure gauge to monitor experimental parameters. Nitrogen pressure was gradually increased against oxygen pressure, while maintaining a constant pressure ~800 psi in the pressure cell over a long period of time. Raman spectra of different gaseous N₂ - O₂ mixtures were recorded on the computer for further analysis.

**Results and Discussions**

The present study primarily focused on qualitative as well as quantitative analysis of the component ratio of N₂/O₂ gaseous mixture at varied levels of their partial pressures.
However, in the first part of the investigation, experiments were carried out to evaluate the performance of the assembled high-pressure cell with pure nitrogen gas to evaluate various safety parameters and also to calibrate/optimize with respect to pressure variation at different stages of the experiment. Fig.4.3 shows the background subtracted Raman spectra of pure N₂ gas at a partial pressure of ~400 psi. A N₂ Raman peak at ~ 607 nm with bandwidth of ~ 3.5nm was clearly observed. The intensity of the nitrogen peak increased linearly as the pressure inside the pressure cell was raised from 100 psi to 800 psi at the constant intervals of 100 psi (see Fig.4.4). A similar experiment was performed by replacing pure N₂ with pure gaseous O₂ and a similar linear trend was observed as in case of N₂ (not shown here). After successful testing/calibration of high-pressure cell, data were recorded with different concentrations of N₂ -O₂ gaseous mixture while maintaining a constant pressure of ~ 800 psi in the pressure cell. These spectra were recorded at full laser power (~300 mW) with an integration time of 500 milliseconds and an averaging of 5 spectra. Throughput sample power was ~120 mW. The partial pressure of N₂ gas was increased gradually from an initial pressure of 100 psi against the O₂ pressure to 700 psi, at regular intervals of 100 psi. The background was recorded with an empty high-pressure cell and was subtracted from the recorded N₂ and O₂ gas mixture spectra. The background-filtered spectra at different partial pressures of N₂/O₂ investigated are shown in Fig.4.5. As spectral multi-component technique based on spectral shape, band intensities, and areas was tested to find the most effective tool
Figure 4.3 Raman spectrum of pure nitrogen gas at 400psi

Figure 4.4 Variation in Raman peak intensity of nitrogen gas with pressure

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Figure 4.5 Variation in the Raman peaks of gaseous nitrogen and oxygen with increase in the partial pressure of nitrogen. Total pressure of gaseous mixture was 800 psi.

Figure 4.6 Raman peak intensity ratio of $N_2$ and $O_2$ increasing with their pressure ratio.
for quantifying the N\textsubscript{2} partial pressure within a gaseous mixture. Polynomials of suitable order were introduced to make a smooth background curve that could be subtracted from the original spectra and further extend the technique to calculate the Raman peak intensity. Fig. 4.6 shows the linear response of Raman peak intensity of N\textsubscript{2} against O\textsubscript{2} with increase in their pressure ratio. A linear response of intensity ratio versus pressure ratio is significant for estimation of nitrogen content in a N\textsubscript{2}-O\textsubscript{2} gaseous mixture at certain levels of their partial pressure ratio. Finally, the correlation between the nitrogen band areas and oxygen band areas was found by the area ratio method, which was further used to determine the nitrogen concentration in the gaseous mixture. At first, areas of the selected bands were determined by means of the peak-fitting module. Spectral band areas of N\textsubscript{2} and O\textsubscript{2}, was plotted against the pressure ratio of N\textsubscript{2} and O\textsubscript{2} shown in Fig.4.7. The following conclusions can be drawn from these results. First, the sensor system is capable of successfully detecting N\textsubscript{2} in a N\textsubscript{2}-O\textsubscript{2} gaseous mixture. Second, peak area follows the same characteristics as the intensity ratio follows. The correlation between the area ratio of N\textsubscript{2} and O\textsubscript{2} (N\textsubscript{2}/O\textsubscript{2}) and their concentration ratios is linear but area ratio is slightly less compared to the intensity ratio curve. One might expect a little shift/change in the Raman linewidth of gaseous nitrogen and oxygen with increase in pressure as reported in some of studies\textsuperscript{38} related to gaseous mixture under high pressure. But in our case, no shift in the Raman peaks of nitrogen and oxygen was observed. This is attributed to the fact that a low resolution spectrometer was used in this study which was not sensitive to change in the band shape or to shift in the wavelength.
Figure 4.7 Raman band area ratio of N$_2$ and O$_2$ increasing with their pressure ratio
CHAPTER V

RAMAN SPECTROSCOPY FOR SHH₂

The use of advanced sensors in aerospace applications has increased significantly in recent years. These sensors are used in developmental, testing, and routine health monitoring applications for engines, airframes, and subsystems. Engine sensing to characterize operating conditions, aerodynamic forcing and structural response are particularly challenging. Non-intrusive sensors for real-time assessment of flow rate, temperature, pressure, rocket engine plume constituents and effluent gas detection are already under operation in propulsion ground test facilities. The aerospace environment poses unique difficulties for sensor access, weight, ruggedness, and data collection. Light weight, immunity to electromagnetic interference (EMI), fire safety, high bandwidth, and high signal fidelity have made photonics in general and fiber optics in particular an attractive alternative to other type of conventional sensors such as catalytic bead sensors, electrochemical sensors, paper tape detectors, etc. Fiber optics in conjugation with laser spectroscopy is allowing increased sensitive detection of species concentration, density measurements, flow speed, temperature, pressure and other parameters of cryogenic interest. There is a renewed interest in hydrogen as an important cryogenic fuel as well as a viable substitute for conventional hydrocarbon fuel with the potential to
alleviate emission problems. Temperature and concentration monitoring of hydrogen is of great importance in a combustion environment and leak detection in aerospace vehicles.

This part of my doctoral research is related to a study of Raman rotational vibrational lines of hydrogen as a function of pressure and temperature in a laboratory environment. Furthermore, a higher resolution spectrometer was employed for resolving the Raman bands of hydrogen in the visible region. In the past, ultraviolet (UV) Raman spectroscopy was applied for studying the dependence of Raman hydrogen line width on temperature by David et al. 46

Our research can be extended to fulfil a specific requirement of NASA/SSC for a sensor that can measure the temperature in a superheated hydrogen (SHH₂) line—an important unit in a Nuclear Thermal Rocket (NTR) propulsion system.47 The schematic of a conceptual design of a nuclear reactor with superheated hydrogen (SHH₂) is shown in Fig. 5.1. For various short primary propulsion maneuvers, a large quantity of thermal power is produced in the NTR. Thermal energy is removed by flowing liquid hydrogen (LH₂) around the core of the nuclear reactor cooling the LH₂ to undergo a phase transition from liquid to gas, resulting in superheated hydrogen (SHH₂) coming out the engine’s nozzle to generate high thrust. Although the main focus of my research was to study the response of hydrogen (H₂) Raman vibrational-rotational bands to temperature variation, I have also investigated the effect of varying pressure on these bands at room temperature. Pressure monitoring of hydrogen is significant owing to the relationship of
Figure 5.1 Schematic of the conceptual design of the nuclear reactor and super heated hydrogen (SHH$_2$).
pressure with temperature, and for indirect estimation of propellant (SHH$_2$) temperature and thrust to ensure effective propellant usage.

**Experimental Details**

In the initial phase of this investigation, temperature-sensitive Raman rotational and ro-vibrational lines of hydrogen were identified, and the effect of varying pressure on these lines was studied. An optical fiber Raman sensor was setup employing a frequency-doubled 532-nm continuous wave (CW) Nd: YAG laser (Coherent, DPSS-532) as the excitation light source, and an InPhotonic Probe for signal collection. This probe consisted of just two parallel optical fibers: one (90-μm core diameter) to guide the launched light to the hydrogen gas enclosed within a high-pressure cell, and the others (200-μm core diameter) to collect the emitted Raman signal and feed it to a high-resolution spectrometer. For clear resolution and a high signal to noise ratio of temperature-sensitive hydrogen Raman lines, a 0.5m high resolution spectrometer (Jobin-Yvon-SPEX HR460) equipped with 1200 and 2400 line/mm gratings was used. This spectrometer was coupled with an intensified charge coupled detector (Princeton Instruments ITE/CCD-1024). A pulse generator (Princeton Instruments, PG-200) was interfaced to the ICCD detector through a controller for applying a suitable voltage to the detector intensifier. The experimental setup is shown in Fig. 5.2. The detection system was optimized with respect to various parameters such as grating, slit width, MCP (micro channel plate) voltage, detector temperature, etc. to achieve the best signal-to-noise ratios of the H$_2$ Raman signals. This system was used to record H$_2$ spectra at different pressures in a high-pressure cell.
Figure 5.2. Experimental set-up for monitoring pressure of hydrogen gas in high pressure cell. IF: neutral density filter, L: lens
In the next phase of the investigation, we focused on studying the effect of temperature on the hydrogen Raman lines. An effort was made to assemble the various parts of the system which include a laser, a detection unit, a hydrogen sample cell, temperature-controlled furnace, and a vacuum pump. The choice of optical components as well as their proper alignment is of utmost importance for realizing a good signal to noise ratio of H$_2$ Raman signals, especially at low pressure. The optical design of the Raman system is shown in Figure 5.3. The second harmonic (λ=532 nm, 200 mJ, 9-mm diameter) of a pulsed Nd: YAG laser (Big Sky Model CFR 400) is turned 90° with a 532-1064-nm harmonic separator (CVI Laser) and sent to a 532-nm dichroic mirror (CVI Laser), which is also a part of the collecting optics train. The laser beam reflected by the dichroic mirror is focused by a UV grade-fused silica plano-convex lens (f=50cm) into the inside of the ceramic sample cell. The scattered Raman signal is collected by the same focusing lens, sent back through the dichroic mirror, and then focused with another quartz lens (f = 20 cm) onto the input (1.0 mm diameter) of a quartz optical fiber bundle. The Mie and Rayleigh scattering at 532 nm are reduced by the dichroic mirror and a notch filter placed in front of the optical fiber bundle. This optical configuration with coaxial backscattering collection has good efficiency, and it is very insensitive to misalignment of the optics.

Choice of material for the sample cell of hydrogen was critical. The greatest challenge in designing the cell was to prevent leakage of hydrogen gas under high temperature, thereby minimizing the risk of fire or an explosion during the experiment.
Figure 5.3 Schematic of the optical design for hot hydrogen measurements
Initially, the alumina ceramic tube sample cell was mounted through the hot zone of an automatic temperature-controlled high-temperature furnace. But the leak rate of hydrogen in ceramic tube was a few torr per hour, which was not an acceptable situation for long-term safe operation of the test bed. Various properties such as porosity and durability at higher temperature of the ceramic as a sample cell material were examined and compared with other materials, especially stainless steel, used in similar applications. A sample cell made of Type 316 stainless steel was tested and found no significant leaks. Therefore, I had used this tested stainless steel sample cell for the high-temperature measurements. Since the furnace available in our laboratory was suitable for vertical operation, efforts were made to mount the furnace in a vertical position. To achieve this, a rugged stainless steel bar (inverted T-shaped) was designed for holding the high temperature furnace in a vertical position. The sample cell was symmetrically placed inside the furnace and clamped to the furnace support as shown in Figure 5.4. A sapphire window was attached to one end of the stainless steel tube to provide optical access for laser light to interact with the hydrogen gas. A photograph of the furnace with the hydrogen sample cell is shown in Fig.5.5.
Figure 5.4 Schematic of stainless steel based sample cell experimental setup
Figure 5.5 Photograph of furnace and hydrogen sample cell along with Raman system
Results and Discussions

To observe the effect of varying pressure on the Raman hydrogen lines, a frequency-doubled 532-nm continuous wave (CW) Nd: YAG laser (Coherent, DPSS-532) was used as the excitation light source, along with an In Photonic Probe for signal collection. The potential Raman bands of hydrogen for temperature measurement are listed in Table 5.1. The spectrometer grating position was centered at the wavelength of ~680nm to observe the Raman lines of hydrogen as shown in Figure 5.6. The peaks corresponding to wavelength positions of ~683nm and ~682nm were identified as the temperature-sensitive rotational-vibrational Raman lines $Q (1)$ and $Q (3)$ of hydrogen, respectively. Some other peaks were also observed in the vicinity of 683nm and 682nm, but they were not well resolved and strong enough to study further. A calibration curve was obtained for the peak intensity corresponding to the most prominent [i.e. $Q (1)$] rotational-vibrational line with varying levels of pressure in the sample cell and is shown in Figure 5.7. The rotational-vibrational peak intensity at 683 nm increases almost linearly with increase in pressure.

The hot hydrogen temperature can be inferred from either pure rotational transitions (i.e. $v_i = v_f, \Delta J = \pm 2$) or rotational-vibrational transitions (i.e. $|v_f - v_i| = 1, \Delta J = 0, \pm 2$) using integrated line ratios, line peak ratios, or by fitting the calculated Raman spectrum to the experimental spectrum. For hydrogen Raman measurements at elevated temperature, I performed a leak check at the beginning of each run and conducted a complete heat test using nitrogen to ensure there were no abnormalities or malfunctions.
### Table 5.1

THE POTENTIAL HYDROGEN RAMAN TRANSITIONS FOR TEMPERATURE MEASUREMENT

<table>
<thead>
<tr>
<th>J</th>
<th>Vibrational Q Branch (cm⁻¹)</th>
<th>Wavelength* (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4161.18</td>
<td>683.25</td>
</tr>
<tr>
<td>1</td>
<td>4155.26</td>
<td>682.98</td>
</tr>
<tr>
<td>2</td>
<td>4143.47</td>
<td>682.43</td>
</tr>
<tr>
<td>3</td>
<td>4125.89</td>
<td>681.61</td>
</tr>
</tbody>
</table>

*Wavelength with respect to excitation wavelength: 532 nm*
Figure 5.6 Rotation-vibrational Raman spectrum of hydrogen at the pressure of 700psi using 0.5m spectrometer.

Figure 5.7 Intensity variation of the Raman ro-vibrational Q(1) line of hydrogen with pressure using 0.5m spectrometer.
Since the sample cell used in this experiment is made of Type 316 stainless steel and has less than 1/10\(^{th}\) the strength at high temperatures than it has at room temperature, we decided to limit our measurements to 600\(^{0}\) C. For safety reasons, we used hydrogen and nitrogen mixtures in this experiment. The sample cell was filled with 129 torr of hydrogen and 129 torr of nitrogen at room temperature. The gas pressure reached near one atm at 600\(^{0}\)C, according to the ideal gas law. Due to temperature and pressure gradients in the sample cell, the actual gas temperature in the cell has lower than 600\(^{0}\) C, and the gas pressure was lower than one atm. To reduce the background from blackbody radiation, we also used a frequency-doubled, pulsed Big Sky Nd:YAG laser and a 0.5 m spectrometer (Jobin-Yvon-SPEX HR460) with an intensified charge coupled detector. The detector was operated in the gated mode to eliminate the unwanted continuous background in this experiment. The Raman spectra of hydrogen recorded at different furnace temperatures are shown in Figure 5.7. The intensity ratio of hydrogen Q (3)/Q (1), at different gas temperatures is shown in Figure 5.8. It depicts a linear response of the Raman peak intensity ratio of these two H\(_2\) ro-vibrational lines with the furnace temperature. The temperature variation was restricted within a range of 600\(^{0}\) C in order to comply with the lab safety issues. The fluctuations in error bars as shown in Fig. 5.8 signify the presence of temperature gradient within the sample cell. More accuracy in the measurements could be achieved by collecting the data over a long period of time and averaging of spectral data.
Figure 5.7 Hydrogen Raman spectra at different furnace temperatures
Figure 5.8 The intensity ratio of hydrogen Q(3)/Q(1) at various gas temperatures.
CHAPTER VI
SERS ON COLLOIDAL SILVER NANO PARTICLES

Shape-controlled synthesis of metal nanostructures has opened many new possibilities to design ideal building blocks for future nanodevices. Surface-enhanced Raman scattering (SERS) has demonstrated potential as a sensitive, vibrationally specific probe for chemical and bioanalytical sensing and imaging applications. The possibility of observing Raman signals, which are normally very weak, with enhancements of the order of $10^6$-$10^9$ has interesting applications, in particular in analytical chemistry. The most significant progress that should be mentioned is single-molecule detection observed by Nie et al.\textsuperscript{53} and Kneipp et al.\textsuperscript{54} The enhancement factor can be as high as $10^{14}$-$10^{15}$ on a single Ag nanoparticle. The SERS phenomenon is often described by traditional enhancement mechanisms: electromagnetic (EM) and chemical (CHEM) enhancement.\textsuperscript{17, 25} The EM mechanism is based upon the optical properties of noble metals and their ability to support plasmon resonances at visible wavelengths. Chemical enhancement results from an electronic resonance–charge transfer between a molecule and a metal surface with atomic-scale roughness features, ultimately increasing the polarizability of the molecule and effectively increasing the Raman scattering cross section. Most reports describe SERS on primarily aggregated nanoparticles where determining the dependence of SERS on nanoparticle optical properties is difficult. In
order to determine EM and CHEM contributions to SERS from the substrate optical properties alone, one would have to use a more homogeneous experimental system: for example, dilute colloidal solutions or well dispersed on planar substrates. In this research, we describe how the non-resonance SERS enhancement factor depends on concentration, size and shape of the silver colloids. In order to understand the mechanism of enhancement for molecules adsorbed on silver nanosurfaces and to deconvolute plasmon coupling from particle aggregation and plasmon resonance effects, SERS experiments have been performed in aqueous solutions under dilute conditions. This is essential since nanoparticle aggregation effects on the SERS intensity give rise to surface enhancement factors of up to $\sim 10^{14}$ and would greatly outweigh the nanosystem size and shape effects I hope to investigate. To improve understanding of the effect, particularly for practical applications in analysis, a study was carried out with a silver colloidal suspension under as simple and reliable conditions as possible

The largest Raman scattering enhancements, even single-molecule SERS, 53-54 have been described for molecules residing in the fractal space between aggregated colloidal nanoparticles. This is attributed to plasmonic coupling between nanoparticles in close proximity, which results in huge local electromagnetic field enhancements in these confined junctions or SERS “hot spots”. While the use of colloidal SERS substrates is widespread, studies of substrates with different morphologies are limited, despite their shape-dependent optical properties 55-57 that support well defined plasmon resonances whose frequencies can be controlled by judicious modification of the geometry of the nanoparticle. Each of these nanostructure geometries offers its own unique near-field
properties: plasmon resonant frequency, spatial distribution of the near-field amplitude across the surface of the nanostructure, orientation dependence on polarization of the incident light wave, and spatial extent of the near field. For example, in addition to having transverse plasmon absorption of silver nanorods, they also have longitudinal plasmon bands that can be tuned from the visible to the near-infrared region by varying the nanorod aspect ratio. Then Raman scattering enhancements from these materials can be maximized by plasmon resonance with the excitation source, effectively optimizing contributions from the EM enhancement mechanism for a given aspect ratio. In this part of my doctoral research, I have performed a comparative study of SERS spectra of nanosphere, nanorods and nanoprisms in colloidal solution. The optical properties of these nanocrystals have been tailored to have a variable degree of plasmon overlap with the excitation source. As a result, the EM contribution to the overall enhancement should vary as we move from nanosphere to nanop prism to nanorod.

**Materials, Synthesis and Characterization**

Silver nitrate (AgNO$_3$), sodium borohydride(NaBH$_4$), ascorbic acid, 4-mercaptopyridine, cetyltrimethylammonium bromide (CTAB) and sodium hydroxide (NaOH) were purchased from Aldrich. Cetyltrimethylammonium bromide (CTAB) and Rhodamine 6G (Rh 6G) were purchased from Sigma.

**Preparation of Silver Nano spherical particles**

Silver spheres 30 ± 6 nm in diameter were prepared according to conventional citrate reduction method.$^{58}$ 18 mg of AgNO$_3$ was diluted in 100 ml of deionized water
and the resulting solution was heated with magnetic stirring until it began to boil. Then 7 ml of 1% sodium citrate solution in water was quickly added to the vigorously stirred AgNO₃ solution. The heating was continued until the color changed to yellow and afterward to dark brown green. The solution was removed from heating and stirred until it cooled to room temperature. The absorption spectra of silver nanospheres shows only one principal plasmon band at 420 nm and the TEM images (as shown in Fig.6.1 (a) and Fig.6.1 (b)) show the spherical particle size is about 30 nm.

**Preparation of Silver Nano Rod Particles**

Silver nanorods were prepared via the seed-mediated techniques in aqueous surfactants described previously. Silver seed of 4 nm average diameter were prepared by chemical reduction of AgNO₃ by NaBH₄ in the presence of trisodium citrate. To make a nanorod of aspect ratio 3.5 with length 40 nm and width 12 nm, AgNO₃ was reduced by ascorbic acid in the presence of seed, CTAB and NaOH. Nanorods were separated from spherical nanoparticles by centrifugation. Silver nanorods with a 3.5 aspect ratio show both a transverse plasmon band, also observed at 420 nm, and a longitudinal plasmon bands at 615 nm, respectively shown in Fig.6.1 (b). TEM images (shown in Figure 6.2(b)) confirm the nanoparticle length of 40 nm and width of 12 nm.

**Preparation of Silver Nano Prism Particles**

We have used the photoinduced method for converting silver nanospheres into triangular nanoprisms as reported in the literature. 3 x 10⁻⁴ M sodium citrate was added to 1 x 10⁻⁴ M aqueous silver nitrate solution of with rapid stirring. Then a freshly prepared 5
Figure 6.1 Absorption spectrum of (a) silver nanospheres (b) silver nano rod.
Figure 6.2 (a) Transmission electron microscopy images of silver nanoparticle (b) SEM images of silver nanorod (c) Change of absorption spectra during nanoprinism formation with time (d) TEM images of silver colloids during nanoprinism formation at different times (D1) 0 h, (D2) 3h, (D3) 8h (D4) 12 h, (D5) 20 h.
$10^{-5}$ M sodium borohydride solution was added by drop-wise addition to the mixture under vigorous stirring. The solution changed to yellow color immediately. After stirring for 30 s, the reaction solution was irradiated with sunset CPS + Atlas lamp. I followed the photo-process by time-dependent ultraviolet-visible spectroscopy and transmission electron microscopy, as shown in Figure 6.2(c) and 6.2(d). We observed a decrease in intensity of the characteristic surface plasmon band in the ultraviolet-visible (UV-Vis) spectroscopy for the spherical particles at $\lambda_{\text{max}} = 400\text{nm}$ with a concomitant growth of the new band at $\lambda_{\text{max}}=600$ nm. This allowed us to observe several key intermediates in and characteristics of the conversion process. The reaction is initiated by light and therefore the conversion does not take place in the dark. Therefore, the reaction, which results in nanoprisms, can be selectively turned on or off simply by controlling the exposure of the colloid to light of the appropriate wavelength. The small nanoprisms (10- to 20-nm edge lengths) observed herein form concurrently with the formation of these small clusters. Silver nanoprisms then act as seeds and grow as the small spherical crystals are digested. Once the spherical particles and small nanoclusters are consumed, the reaction terminates. The photo induced conversion of silver particles into small clusters makes the use of light an efficient way to control the growth of the silver nanoprisms.

**Experimental Details**

The experimental configuration involved a portable mini Raman spectrometer (B&W TEK, Inc. shown in Fig. 6.3) with 785 nm as an excitation wavelength and a maximum output power $\sim 350$ mW. I have used 785 nm excitation source to avoid
Figure 6.3 Photograph of mini Raman spectrometer (B&W TEK, Inc.) with 785 nm as an excitation wavelength (Courtesy: B&W TEK, Inc.)
resonance and to eliminate fluorescence background. This also avoids possible melting of nanoparticles which may take place due to interaction of visible light and surface plasmons.\textsuperscript{60} The Raman shift spectral response range of the mini Raman spectrometer is 225-3100 cm\textsuperscript{-1}, equipped with thermo electric (TE) cooled 2048-pixel CCD, and interfaced to computer via a USB port.

**Results and Discussion**

In order to understand the mechanism of enhancement for molecules adsorbed to these silver colloids and to deconvolute plasmon coupling from particle aggregation and plasmon resonance effects, SERS experiments were performed in aqueous solutions under dilute conditions. This is essential since nanospheres aggregation effects on the SERS intensity give rise to surface enhancement factors of up to \( \sim 10^{14} \) and would greatly outweigh the nanorod aspect ratio effects we hope to investigate. It is important to note that in aqueous solution nanospheres, nanorods and nanoprisms are randomly oriented and these SERS spectra are representative of all possible orientations averaged over the entire acquisition time. The ideal geometry would be to fix the nanorod and nanoprism orientation with the long axis parallel to the excitation source polarization, in order to have maximum longitudinal plasmon overlap. However, colloidal solution samples are used to eliminate nanoparticle aggregation effects.

The SERS spectrum of Rhodamine 6G adsorbed on silver nanosphere surfaces is quite analogous to the Raman spectra (RS) spectral pattern of Rhodamine 6G in ethanol solution (as shown in figure 6.4). Only a SERS band at 235 cm\textsuperscript{-1} has no corresponding
Figure 6.4 Raman spectra of Rhodamine 6G with and without silver nano sphere
peak in the RS spectrum. Nine Raman bands with strong scattering intensities are centered around 613, 775, 1130, 1278, 1364, 1389, 1512, 1577, and 1651 cm\(^{-1}\), which mainly correspond to the vibrational modes.

The concentration dependence of SERS spectra is shown in Figure 6.5. It has been observed that SERS signal changes very strongly as the concentration is changed from \(5 \times 10^{-6}\) to \(5 \times 10^{-5}\) M and then started decreasing as the concentration is increased above \(10^{-4}\) M. At extremely low concentration, the metal surface coverage by the adsorbates is submonolayer and in the absence of sufficient scattering molecules, the SERS signal is weak. With an increase in concentration, as the surface coverage increases, the SERS increases and attains maximum intensity with monomer coverage where both EM and CT contributions reach their maximum. With further increase of concentration of the adsorbates, multilayers are formed and the SERS signal decreases in intensity. Hence, the enhancement factor is generally considered as the ratio of the intensities of SERS and the corresponding Raman bands observed in a reference aqueous solution. However, this ratio represents only an "apparent value" of the enhancement factor. The SERS spectra are closely dependent on the coverage of the colloidal surface. Thus no correlation is possible with the enhancement of the Raman signal without knowing the amount of Rhodamine 6G really adsorbed onto the metal substrate. Figure 6.6 shows the SERS spectra of Rhodamine 6G adsorbed on silver nanosphere, nanorods and silver nanoprisms. The experimental results indicates that Raman enhancement of silver nanoprisms is much higher than that of silver nanorods and silver nanosphere, and
Figure 6.5 SERS spectra of Rhodamine 6G adsorbed on silver nano sphere at different concentration.
Figure 6.6 SERS spectra of Rhodamine 6G adsorbed on silver nanosphere, nanorod and nanoprism
silver nanospheres are the least enhanced. As shown \(^{48-52}\) in literature by many reports, the SERS enhancement is the result of a combination of an electromagnetic effect and a chemical effect, but the chemical effect is generally thought to contribute only a factor of \(10^{-10^2}\), compared to factors of \(10^4-10^7\) for the electromagnetic effect. In the present study, the SERS enhancement of our samples must also come from both an electromagnetic effect and a chemical effect. The CHEM effect is also important due to the appearance of Ag-N stretching vibrations at \(\sim235\) cm\(^{-1}\) which confirms that the Rhodamine 6G molecule is coordinated to the Ag surface through the nonbonding electrons of the nitrogen atom in ethylamino group. The fluorescence energy of Rhodamine 6G is transferred from the molecules to the metal surface which leads to the reduction of the fluorescence intensity and an amplification of the Raman enhancement factors. But the EM mechanism, contributing a large part to the overall enhancement factor (EF) and based on the amplified electromagnetic field generated upon optical excitation of surface plasma resonance of nanoscale surface roughness features, is believed to produce the dominant contribution to the SERS activity of silver nanoprisms.

Silver spheres show only one principal plasmon band at 420 nm. Silver nanoprisms show a weak transversal out-of-plane (410 nm) dipole band and a very intense in-plane (660 nm) dipole band. Since our excitation source (785 nm) is closer to 660 nm than to 420 nm, we expect the EM effect should be much higher in the case of nanoprisms than that of nanospheres. Because of high anisotropy in their dimensions, the optical properties of silver nanoprisms are richer and more complicated than those of normal spherical nanoparticles. In agreement with the "rough surface" electromagnetic
enhancement, they can act as "hot sites" for surface plasmons. Differing from spherical
nanoparticle SERS substrates that rely on interparticle coupling or agglomerations, these
unconventional nanostructures are considered as independent substrates that enhance the
local scattering field. From the above analysis of morphologies and surface optical
properties, it is understandable that these Ag nanoprisms should have very different
SERS activities with organic molecules than do the corresponding silver nanospheres.

But the same phenomena cannot explain very low SERS enhancement for silver
nanorods compare to nanospheres. The silver nanorods with a 3.5 aspect ratio have both a
transverse plasmon band, also observed at 420 nm, and longitudinal plasmon bands at
615 nm. If the EM effect is mainly responsible for SERS enhancement, then one expects
silver nanorods should exhibit a higher SERS signal than do silver nanospheres. But the
experimental data presented here shows an opposite trend. So the CHEM effect should be
paid more attention here. As we know, Ag substrates expose different crystal
plates with corresponding well-defined nanostructures. Ag nanorods mainly expose
{111} and {100} plates, whereas nanosphere particles exposed nearly all the crystal faces
of face centered cubic (FCC) silver. Furthermore just as in heterogeneous catalysis, the
enhanced Raman vibration spectra of an organic molecule absorbed at a noble metal (Ag
colloid, Ag electrode, gold nanoparticle aggregates, etc) are a surface interaction
process. As previously reported, the {110} planes are confirmed to be more active
than the {111} and {100} plates in heterogeneous catalysis, which is consistent with the
order of free energies associated with these crystallographic planes: \( \gamma_{[110]} > \gamma_{[100]} > \gamma_{[111]} \). In this work, the sequence of Raman enhancement quality is Ag nanoprisms > Ag
nanosphere > Ag nanorod. This is partly due to the exposure of all possible FCC crystal faces in nanoparticles, \{111\} planes in nanorods that have higher free energies and silver nanoprisms are highly oriented single crystals with (111) planes as the basal plane. The results presented here indicate that besides the size effect, the morphology effect is also great for SERS enhancement.
CHAPTER VII

CONCLUSIONS

In this dissertation, practical applications of Laser Raman Spectroscopy for development of optical sensors for NASA applications were described. Also, experimental demonstration of surface enhanced Raman scattering (SERS) on Rhodamine 6G molecules in presence of various size and shape silver nanoparticles has been discussed in the dissertation. An independent conclusion of research described in chapter 3 through 5 is summarized below.

Chapter III

The research described in Chapter 3 was related to development of an optical fiber Raman sensor suitable for cryogenic applications and the evaluation of the sensor performance with different excitation light sources. The sensor performance with two different 532-nm lasers and an In Photonic probe was demonstrated. Efficient light collection optics and good signal-to-noise ratio of the Raman LN₂/LO₂ signal make these laser based sensor systems an effective tool for rapid as well as sensitive monitoring of LN₂/LO₂ during the testing of a rocket engine. To design a low-cost, reliable sensor for this type of application, I have also tested with a compact, inexpensive diode laser. Although this miniaturized prototype sensor system yielded a low signal-to-noise ratio of the Raman LN₂/LO₂ signal, with appropriate data processing techniques the extracted
intensity ratio of the Raman signals of LN$_2$ and LO$_2$ is close to that obtained with the more expensive 532-nm excitation systems. This miniaturized diode laser sensor system offers a great deal of flexibility and provides a cost-effective solution for measuring the quality as well as quantity of cryogenic fluids. However, due to the relatively poor signal-to-noise ratio and background problem, the performance of the current diode laser sensor system is not suitable for real time monitoring. On the other hand, the system using the high power 532-nm laser can offer good quality LN$_2$/LO$_2$ spectra with a reasonable response time, and therefore it is more suitable for real-time applications. Future research will focus on improving the performance of the sensor for cryogenic liquids under high pressure.

**Chapter IV**

The research described in Chapter 4 can be considered as the extension of sensor development work for monitoring the ratios of liquid nitrogen and liquid oxygen. The liquid mixtures of nitrogen and oxygen in the cryogenic environment may exist as a gaseous mixture. In that situation, it would be advantageous to have a sensor system (similar to those described in chapter 3 and 4) that can extract the sample constituent from the gas/liquid mixture. The results of this work demonstrate that Raman spectroscopy, in conjugation with fiber optics can be exploited to fabricate a sensitive as well as reliable optical gas sensor to identify and quantify components of a gas mixture at partial pressures upto 100psi.
Chapter V

Chapter 5 describes the experimental study of pressure and temperature measurement of hydrogen by exploiting the technique of Raman spectroscopy in conjunction with fiber optics. A high-resolution spectrometer was employed in this work to monitor the rotational and vibrational Raman lines of hydrogen as function of pressure and temperature. The problem associated with sealing hydrogen gas in a sample tube was also described. The designed instrumentation based on Raman spectroscopy can be modified to measure the temperature in other high temperature industrial applications. This can be further used for hydrogen fuel technology, the generation of liquefied gases, ethanol manufacturing plant, and other chemical industrial processes.

Chapter VI

Chapter 6 describes an experimental study on SERS of Rhodamine 6G in the presence of various shaped silver nanoparticles such as spheres, rods and prisms. I have investigated SERS spectra of Rhodamine 6G with different kinds of Ag substrates that have correspondingly particular morphologies and crystal planes. Silver nanostructures are containers for surface plasmons - the collective oscillation of conduction electrons in phase with incident light. By controlling the shape of the container, one can control the ways in which electrons oscillate, and in turn how the nanostructure scatters light, absorbs light, and enhances local electric fields. The intensity of the SERS signal was the smallest for the gold nanorod, and the nanoprism gave the strongest SERS signals. Our results indicate that besides the size effect, the morphology effect is also great for SERS enhancement. The great differences of the SERS spectra for different shape Ag colloids
confirmed that like electromagnetic enhancement, chemical enhancement also plays a very important role in SERS signal enhancement. This is an exciting time to work with plasmonic nanostructures, because the field is truly in its infancy. The majority of well-defined silver nanostructures have been produced in the past five years, and the work of characterizing their optical properties has only just begun. Finding ways to predictably assemble plasmonic nanostructures onto a surface will not only facilitate their characterization, but also enable high-throughput, solution-phase production of nanostructure arrays for sensing, spectroscopy, and the guiding of light at the nanoscale level.
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