EXPERIMENTAL AND THEORETICAL INVESTIGATIONS OF
COHERENT ANTI-STOKES RAMAN SCATTERING AS A
NONINTRUSIVE DIAGNOSTIC FOR GAS-PHASE SYSTEMS

BY

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THESIS

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Abstract

In this study, two coherent anti-Stokes Raman scattering (CARS) diagnostic techniques were investigated. The first study involved the experimental examination of high-resolution $N_2$ CARS measurements using a modeless dye laser as the Stokes beam source to reduce the presence of mode noise. A new spectra-fitting procedure was developed to avoid starting-point bias in the least-squares fitting results. Time-averaged and single-shot measurements of pressure were made in a static pressure vessel over the range from 0.1 to 4.0 atm to test the pressure sensitivity of the technique. In addition, the precision of these single-shot measurements is indicative of the baseline pressure-fluctuation detection limit. The precision uncertainty of the measurements was studied to investigate the possibility of making property fluctuation measurements in high-speed flows. Centerline measurements of pressure and temperature in an underexpanded jet ($M_j = 1.85$) were obtained to determine the performance of the technique in a compressible flowfield. Improvements in accuracy for time-averaged and single-shot mean measurements and increased precision were found for pressure levels above 1.0 atm. For subatmospheric pressure levels, the results indicated that the method is incapable of making fluctuation measurements due to limited precision. Nevertheless, the increased precision above 1.0 atm indicates that fluctuation measurements may be possible with further modifications.

The second portion of the work concerned the development of a theoretical model for electronic-resonance-enhanced CARS (ERE CARS) spectra of nitric oxide. This model incorporates the effects of the Raman resonance in conjunction with an electronic resonance to provide the first known theoretical predictions for NO. To determine the model’s accuracy
and effectiveness, predictions were compared to previously obtained experimental data. The comparisons displayed close agreement between spectral peak locations and relative intensities. Experimental linewidths were larger than predicted by the theory, which is attributed to saturation or Stark effects in the experiment. The model also allowed for the correct assignment of the molecular constants for the split ground states. This model can be used for investigations of NO formation in hypersonic flow and combustion and can be extended to other species for rapid detection of air pollutants and toxins.
To my Grandfather, the greatest teacher to ever grace this earth.
Acknowledgments

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# Contents

Nomenclature \hspace{1cm} xii

1 Background \hspace{1cm} 1

1.1 Introduction \hspace{1cm} 1

1.2 CARS Overview \hspace{1cm} 3

1.2.1 Background Theory \hspace{1cm} 3

1.2.2 Advantages of CARS \hspace{1cm} 5

1.2.3 Obtaining Temperature, Pressure, Density, and Velocity \hspace{1cm} 7

1.2.4 Noise Characteristics of the CARS Process \hspace{1cm} 15

1.2.5 Previous N₂ CARS Pressure, Temperature, and Density Results \hspace{1cm} 21

1.2.6 Alternative Techniques to CARS \hspace{1cm} 23

1.2.7 Underexpanded Jet Flowfield for CARS Measurements \hspace{1cm} 28

1.3 ERE CARS Overview \hspace{1cm} 35

1.3.1 Background Theory \hspace{1cm} 37

1.3.2 Advantages of ERE CARS \hspace{1cm} 39

1.3.3 Previous ERE CARS Studies \hspace{1cm} 40

1.3.4 NO Molecular Structure and Spectral Constants \hspace{1cm} 41

1.3.5 Previous NO Absorption, Raman, and CARS Measurements \hspace{1cm} 42

1.3.6 Alternative Techniques to ERE CARS \hspace{1cm} 46

1.4 Objectives \hspace{1cm} 51
2 Equipment and Facilities

2.1 MDL CARS System ........................................ 53
2.2 ERE CARS System ....................................... 56
2.3 Gas Cell ................................................. 59
2.4 Underexpanded Jet ..................................... 60

3 Modeless Dye Laser N₂ CARS Investigation ..... 62

3.1 Introduction ............................................. 62
3.2 Spectra-Fitting Procedure ............................ 63
3.3 Pressure Vessel Results ............................... 68
3.4 Underexpanded Jet Results ........................... 80
3.5 Summary ................................................. 88

4 ERE CARS Modeling Results ..... 92

4.1 Introduction ............................................. 92
4.2 Model Development ..................................... 92
4.3 Enhancement Factor ................................... 98
4.4 UV Scan Results ....................................... 99
4.5 Stokes Scan Results .................................. 103
4.6 Summary ................................................. 111

5 Conclusions and Recommendations 114

5.1 Conclusions from the MDL CARS Investigation .......... 114
5.2 Recommendations for the MDL CARS Investigation .......... 115
## Nomenclature

### English Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>Einstein spontaneous emission coefficient</td>
</tr>
<tr>
<td>$a$</td>
<td>pressure coefficient in collisional broadening model, speed of sound</td>
</tr>
<tr>
<td>$E$</td>
<td>energy</td>
</tr>
<tr>
<td>$g$</td>
<td>degeneracy</td>
</tr>
<tr>
<td>$h$</td>
<td>enthalpy</td>
</tr>
<tr>
<td>$I$</td>
<td>intensity</td>
</tr>
<tr>
<td>$J$</td>
<td>rotational quantum number</td>
</tr>
<tr>
<td>$K$</td>
<td>line strength</td>
</tr>
<tr>
<td>$\tilde{k}$</td>
<td>wave vector</td>
</tr>
<tr>
<td>$L$</td>
<td>length of oscillator cavity; total electron angular momentum</td>
</tr>
<tr>
<td>$\ell$</td>
<td>length of probe volume</td>
</tr>
<tr>
<td>$M$</td>
<td>Mach number</td>
</tr>
<tr>
<td>$m$</td>
<td>molecular mass</td>
</tr>
<tr>
<td>$N$</td>
<td>molecular number density; nuclear rotation</td>
</tr>
<tr>
<td>$n$</td>
<td>index of refraction</td>
</tr>
<tr>
<td>$P$</td>
<td>pressure</td>
</tr>
<tr>
<td>$\tilde{p}$</td>
<td>photon momentum</td>
</tr>
<tr>
<td>$R$</td>
<td>molecular specific gas constant</td>
</tr>
<tr>
<td>$S$</td>
<td>total electron spin</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
</tbody>
</table>
$U$  velocity
$\mathbf{V}$  average velocity magnitude
$v$  vibrational quantum number
$Z$  partition function

**Greek Symbols**

$\alpha$  probe volume crossing angle
$(\frac{\partial \alpha}{\partial \Omega})_J$  Raman cross section
$\Gamma$  transition linewidth
$\gamma$  damping constant
$\Delta$  fractional population distribution
$\Delta \vec{k}$  phase mismatch
$\Delta \omega$  axial mode spacing
$\Delta \omega_J$  detuning parameter
$\varepsilon$  energy associated with the electronic energy level
$\Lambda$  axial component of electron momentum
$\mu$  dipole matrix element
$\nu$  frequency in cm$^{-1}$
$\rho$  density; fractional population density; depolarization ratio
$\Sigma$  relative Raman cross section
$\chi$  nonlinear, third-order polarization susceptibility
$\omega$  angular frequency in rad/s
Superscripts

elec characteristic of the electronic quantum state

Subscripts

1 freestream 1
2 freestream 2
∞ ambient
a ambient; energy level
b energy level
c collisional; convective; energy level
d energy level
CARS CARS beam
CFD computational fluid dynamics
D Doppler
e exit
elec characteristic of the electronic quantum state
i energy level
J rotational quantum number
j fully expanded; jet; energy level
l electronic quantum number
m molecule specific
NR nonresonant
n natural
o  stagnation; ground electronic quantum state

p1  first pump beam

p2  second pump beam

ref  reference case

rot  characteristic of the rotational quantum state

rot, nuc  characteristic of the rotational-nuclear quantum state

S  Stokes beam

TRAN  transducer

v  vibrational quantum number

vib  characteristic of the vibrational quantum state

**Physical Constants**

c  speed of light in a vacuum, \(2.99792458 \times 10^8\) m/s

\(\varepsilon_o\)  permittivity of free space, \(8.854187817 \times 10^{-12}\) F/m

\(h\)  Planck’s constant, \(6.6260755 \times 10^{-34}\) J·s

\(\hbar\)  Planck’s constant, \(\hbar / (2\pi)\), \(1.0545727 \times 10^{-34}\) J·s

\(k\)  Boltzmann’s constant, \(1.380658 \times 10^{-23}\) J/K

**Abbreviations**

CARS  coherent anti-Stokes Raman scattering

CBDL  conventional broadband dye laser

CCD  charge-coupled device

CFD  computational fluid dynamics
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>cw</td>
<td>continuous-wave</td>
</tr>
<tr>
<td>DFWM</td>
<td>degenerative four-wave mixing</td>
</tr>
<tr>
<td>DNS</td>
<td>direct numerical simulation</td>
</tr>
<tr>
<td>ERE CARS</td>
<td>electronic-resonance-enhanced coherent anti-Stokes Raman scattering</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>HORSES</td>
<td>higher-order Raman spectral excitation studies</td>
</tr>
<tr>
<td>LDV</td>
<td>laser Doppler velocimetry</td>
</tr>
<tr>
<td>LIF</td>
<td>laser-induced fluorescence</td>
</tr>
<tr>
<td>LIF/R</td>
<td>laser-induced fluorescence in conjunction with Raman scattering</td>
</tr>
<tr>
<td>MDL</td>
<td>modeless dye laser</td>
</tr>
<tr>
<td>MOC</td>
<td>method of characteristics</td>
</tr>
<tr>
<td>MTV</td>
<td>molecular tagging velocimetry</td>
</tr>
<tr>
<td>NPR</td>
<td>nozzle pressure ratio</td>
</tr>
<tr>
<td>PLIF</td>
<td>planar laser-induced fluorescence</td>
</tr>
<tr>
<td>PMT</td>
<td>photomultiplier tube</td>
</tr>
<tr>
<td>PS</td>
<td>polarization spectroscopy</td>
</tr>
<tr>
<td>RECARS</td>
<td>resonance enhanced coherent anti-Stokes Raman scattering</td>
</tr>
<tr>
<td>RELIEF</td>
<td>Raman excitation plus laser-induced electronic fluorescence</td>
</tr>
<tr>
<td>SNR</td>
<td>signal-to-noise ratio</td>
</tr>
<tr>
<td>STOVL</td>
<td>short take-off and vertical landing</td>
</tr>
<tr>
<td>TEM</td>
<td>transverse electromagnetic mode</td>
</tr>
</tbody>
</table>
1 Background

1.1 Introduction

As the demand for improved performance of high-speed missiles, projectiles, and aircraft increases, so does the requirement for extensive knowledge of the thermodynamic and kinematic properties of compressible flowfields. For the projectile and missile designer, the base drag\(^1\) and infrared plume signature\(^2\) are important design criteria that are dependent on near-wake properties. Similarly, in aircraft design, structural fatigue due to acoustic fluctuations presents one of many issues to be dealt with.\(^3\) In addition, other important practical applications, such as supersonic combustion, gas dynamic lasers, and metal deposition, depend on an in-depth understanding of compressible flows.\(^4\) Beyond these flowfields, the hypersonic regime presents unique challenges for measurement techniques due to the short length scales and high temperature levels. The accurate numerical simulation of hypersonic flowfields requires extensive knowledge of NO formation at the extreme temperature levels generated behind strong shock waves and in the boundary layer.\(^5\) Due to compressibility effects in supersonic and hypersonic flows, probe-based measurements are limited in their accuracy by interference effects. Additionally, these probes may not survive exposure to harsh hypersonic environments. Therefore, advances in and applications of nonintrusive, laser-based diagnostics are required to assist in the design and implementation of the applications discussed above.

This thesis presents two methods intended to fulfill the need for new diagnostic techniques in these flows. The first study involves the experimental development and investigation of an innovative, broadband coherent anti-Stokes Raman scattering (CARS) technique
for diatomic nitrogen that may have the capability to obtain mean and fluctuating pressure, temperature, density, and velocity measurements in a compressible flow. Past methods have shown the ability of making mean measurements; the first experiment described herein details attempts at extending the capabilities of a CARS technique to making reliable fluctuation measurements at low-temperature and low-pressure, supersonic conditions by applying a known improvement for combustion diagnostic methods. The second portion of this thesis entails the theoretical development of the first application of electronic-resonance-enhanced CARS (ERE CARS) to nitric oxide. The ERE CARS technique has been experimentally demonstrated in previous work, probing concentrations of nitric oxide of the order of 1000 ppm in N\textsubscript{2}. In this work, a numerical model is developed to calculate theoretical spectra for comparison with the previously obtained experimental data.

In the following section, a brief overview of the CARS process employed in the above experiments and its applications are presented. Included in this overview is a description of the noise characteristics of the CARS method relevant to the objectives of the first experiment. A survey of previous results with the current CARS system, along with a comparison to similar techniques, is then discussed. With an understanding of the CARS process and its capabilities at hand, the challenges to be faced in the application of CARS to an underexpanded jet flowfield are then presented. Previous experimental and numerical studies of underexpanded jet flows are reviewed, with particular attention given to the regions of interest in this study.

Building on the discussion of CARS, the background of ERE CARS is then discussed, followed by a review of previous ERE CARS studies. Previous measurements of NO are
presented, and the previous CARS studies of NO are described. The ERE CARS review is completed with a comparison of alternative techniques.

1.2 CARS Overview

The development and use of CARS as a diagnostic technique has been ongoing for nearly three decades. Therefore, a substantial amount of theory has been developed and a large number of experimental results have been reported. The critical points of the theory and experimentation applicable to this study will be presented, whereas a more thorough review of the theory can be found in the extensive reviews of CARS that exist in the literature.8–11

1.2.1 Background Theory

It is well known that the electron cloud of a molecule will be displaced from its equilibrium position when irradiated by oscillating electromagnetic radiation, such as a laser beam. This displacement of the electron cloud, more commonly known as polarizability, is the basis for the CARS process. In this process, the molecule is irradiated or probed by three laser beams: two pump beams and one Stokes beam. The input frequencies can be narrowband, broadband, or a combination, depending on the experimental needs,8 which will be discussed further in the following section. In order for a CARS signal to be generated by the polarization of the molecule by these beams, three requirements must be satisfied. First, the frequency difference between one pump beam and the Stokes beam must be equal to a transition frequency, \( \nu_m \), of a Raman-active resonance of the molecule. This requirement can be realized as:

\[
\nu_m = \nu_{p1} - \nu_S
\]  

(1.1)
where in this case, \( \nu_m \) is referred to as the Raman shift, and \( \nu_{p1} \) and \( \nu_S \) are the frequencies in cm\(^{-1}\) of the first pump and Stokes beams, respectively. The Raman shift is not only dependent on the molecule, but also on the initial ground state it resides in and the excited state it is scattered from. The second constraint lies in the conservation of energy. Because the molecular transition is parametric, \( i.e., \) the molecule returns to its initial state, the transfer of energy in the three incident beams must be accounted for by the signal generated:

\[
\nu_{CARS} = \nu_{p1} + \nu_{p2} - \nu_S
\] 

(1.2)

Note that here the energy of a photon is related to its frequency by \( E_i = h\nu_i \), where \( h \) is Planck’s constant, and \( c \) is the speed of light in a vacuum. In a similar fashion as before, \( \nu_{p2} \) and \( \nu_{CARS} \) are the frequencies of the second pump and CARS beams, respectively.

The final requirement is derived from the conservation of momentum. This requirement is referred to as phase matching, and is written as:

\[
\vec{k}_{CARS} + \vec{k}_S = \vec{k}_{p1} + \vec{k}_{p2}
\] 

(1.3)

where \( \vec{k}_i \) is the wave vector of beam \( i \), with magnitude equal to \( \nu_i \), and is related to the photon momentum by \( \vec{p} = h\vec{k} \). This relation defines the crossing angle and interaction length of the three input beams. The interaction region of the three beams is referred to as the probe volume. The geometry of the resulting wave vectors that form the probe volume is termed the phase-matching geometry.

To demonstrate these concepts, the current study investigating diatomic nitrogen is given as an example. In order to excite the nitrogen Q-branch, which corresponds to the vibrational Raman transition \( \nu = 0 \to 1 \), the Raman shift used in Equation 1.1 is approximately equal
to 2330 cm\(^{-1}\). Both pump beams are at the same frequency, 18794 cm\(^{-1}\) (532 nm), which requires the broadband Stokes frequency to be centered around 16464 cm\(^{-1}\) (607 nm). An energy level diagram for this process, governed by Equation 1.2, can be seen in Figure 1.1. In this diagram, the purple band represents the broadband nature of the Stokes beam employed in this study. It is important to note that in this case the upper levels in Figure 1.1 are represented by dashed lines, indicating that these excited states are virtual states, a fact that will become important later. The folded-BOXCARS phase-matching geometry\(^8\) utilized in this CARS technique is displayed in Figure 1.2.

1.2.2 Advantages of CARS

The constraints above do not imply limitations to the application of CARS. In fact, these constraints outline the major advantages of employing CARS. Equation 1.1 shows that the

![Figure 1.1: CARS energy-level diagram](image-url)
process is molecule-specific, and therefore, so are the properties obtained. Because each molecule has a unique spectral signature, this allows for relative concentration studies to be performed. It can be seen then that Equation 1.1 also represents the species selection criterion for CARS. Equation 1.2 infers that the signal obtained will be at a unique frequency different from those of the input beams; thus, the signal can be spectrally separated. According to Equation 1.3, the signal will exist at a specific spatial location, and in addition, the signal will be coherent in nature. This provides spatial separation of the CARS signal beam from the input beams. The coherent nature of the signal eliminates the need for large, solid-angle, signal collection optics, such as used in fluorescence techniques, thus increasing the signal-to-noise ratio (SNR). Depending on the choice of phase-matching geometry, the size of the probe volume can be controlled, providing for well-defined spatial resolution.

![Figure 1.2: Folded-BOXCARS phase-matching geometry](image)

Figure 1.2: Folded-BOXCARS phase-matching geometry
Additional benefits of the CARS process make the technique very attractive. With the use of pulsed lasers, the CARS signal is formed on a time scale of the order of nanoseconds. Therefore, along with the aforementioned spatial resolution, the CARS process provides excellent temporal resolution. Due to the relatively high SNR, the CARS process also provides the ability to probe areas of low molecular number density. The above benefits outweigh the complex implementation of the CARS method in many cases.

1.2.3 Obtaining Temperature, Pressure, Density, and Velocity

In order to obtain thermodynamic and kinematic properties from the resulting CARS signal, it is necessary to recall the theory for a volume of molecules and investigate its effects on the spectral behavior of the CARS signal. Consider the molecules present at the probe volume of the CARS system. The population will be distributed over various electronic, vibrational, and rotational states based on the aggregate temperature of the volume. Assuming that the population is in thermal equilibrium before the CARS process occurs, the distribution of molecules is given by Boltzmann statistics. Further, assuming that the population is composed entirely of homonuclear diatomic molecules such as diatomic nitrogen, the distribution is given as:

\[ \frac{N_l}{N} = \frac{g_l e^{-e_{l,\text{elec}}/kT}}{Z_{\text{elec}}} \] (1.4)

\[ \frac{N_{vl}}{N_l} = 1 - e^{-T_{\text{vib}}/T} \frac{Z_{\text{vib}}}{Z_{\text{elec}}} \] (1.5)

\[ \frac{N_{Jvl}}{N_{vl}} = \begin{cases} \frac{g_o(g_o+1)(2J+1)}{2Z_{\text{rot,nuc}}} e^{-J(J+1)(T_{\text{rot}}/T)} & \text{if } J \text{ is odd} \\ \frac{g_o(g_o-1)(2J+1)}{2Z_{\text{rot,nuc}}} e^{-J(J+1)(T_{\text{rot}}/T)} & \text{if } J \text{ is even} \end{cases} \] (1.6)

where the alternating strengths in the rotational distribution are due to the modulation induced by the coupling of the nuclear spin and the nuclear rotation in a homonuclear
molecule. If the diatomic molecule under consideration is heteronuclear, then the rotational
distribution is given as:\textsuperscript{12}

\[
\frac{N_{Jvl}}{N_{vl}} = \frac{(2J + 1)e^{-J(J+1)(T_{rot}/T)}}{Z_{rot}}
\]  

(1.7)

This rotational distribution will involve additional considerations for a specific molecule and
will be discussed for NO in Section 1.3.4. The above relations are comprised of molecular
constants, quantum state identifiers, the aggregate temperature of the volume, \( T \), and the
Boltzmann constant, \( k \). The population in level \( i \) is given by \( N_i \), and \( N \) is the total molecular
number density. The degeneracy of level \( i \) is \( g_i \); \( T_{rot} \) and \( T_{vib} \) are the characteristic temper-
ature of the rotational and vibrational states of the molecule, respectively, and \( \varepsilon_{l}^{elec} \) is the
energy associated with the electronic level \( l \). The partition function for the energy-storage
mode under consideration is given by \( Z_i \), and \( J \) and \( v \) are the rotational and vibrational
quantum numbers, respectively.

To understand why this distribution is important, it is necessary to determine the factors
that affect the CARS signal. The CARS signal intensity can be written as:\textsuperscript{8}

\[
I_{CARS} = \frac{\omega_{CARS}^2}{n_1 n_2 n_S n_{CARS} \varepsilon_0^2} I_1 I_2 I_S |\chi_{CARS}|^2 \left( \frac{\sin(\Delta \tilde{k} \ell/2)}{\Delta \tilde{k} \ell/2} \right)^2
\]  

(1.8)

where \( I_i \) is the intensity of laser beam \( i \) at angular frequency \( \omega_i \), \( n_i \) is the index of refraction
of the medium at \( \omega_i \), \( \varepsilon_0 \) is the permittivity of free space, \( \chi_{CARS} \) is the nonlinear, third-order,
polarization susceptibility of the medium, \( \ell \) is the length of the probe volume, and \( \Delta \tilde{k} \) is
the phase mismatch defined as \( \tilde{k}_{p1} + \tilde{k}_{p2} - \tilde{k}_S - \tilde{k}_{CARS} \). Note that in this section, angular
frequency is now referred to, which can be related to the previously discussed frequency by
\( \omega_i = 2 \pi c \nu_i \).
The factor of spectroscopic interest in Equation 1.8 is the polarization susceptibility, \( \chi_{CARS} \), which represents the polarizability concept discussed in Section 1.2.1. For the case shown in Figure 1.1, where the upper states are virtual, the susceptibility can be written as:

\[
\chi_{CARS}(\omega_{CARS} : \omega_{p1}, -\omega_{S}, \omega_{p2}) = \sum_j \left( \frac{K_J}{2\Delta \omega_J - i\Gamma_J} \right) + \chi_{NR} \tag{1.9}
\]

where \( K_J \) is the line strength, which for this case can be written:

\[
K_J = \frac{4\pi^2 n_{p1} \varepsilon_0 c^4 N \Delta_J}{n_S h \omega_S^4} \left( \frac{\partial \alpha}{\partial \Omega} \right)_J \tag{1.10}
\]

where \( \Delta_J \) is the fractional population difference between the first excited and ground vibrational states, \( \Gamma_J \) is the transition linewidth, \( (\partial \alpha/\partial \Omega)_J \) is the Raman cross section, and \( \Delta \omega_J \) is the detuning parameter derived from Equation 1.1, \( \Delta \omega_J = \omega_J - (\omega_{p1} - \omega_S) \). The last term in the equation, \( \chi_{NR} \), is the nonresonant portion of the susceptibility that arises from contributions from distant Raman resonances and electron cloud distortions of other molecules.

From Equations 1.8 and 1.9, it can be seen that the CARS signal intensity is proportional to the square of the population density at the initial probed state. This fact can then be used to deduce the effects that the population distribution has on the spectral behavior of the CARS signal. In order to avoid referencing an absolute intensity value for a single transition, the temperature can be derived from the relative intensities of two or more transitions through Equations 1.4 - 1.7. To obtain this resulting intensity distribution, Equation 1.1 then requires that there must be a series of different laser frequencies employed as the pump or Stokes beams. If two narrowband frequencies are chosen for the input beams, then one laser (typically the Stokes beam) must be scanned in frequency across two or more Raman
transitions of the probed molecule. Otherwise, as in the CARS study here, a broadband frequency must be used for the Stokes beam. This second choice allows all transitions investigated to be probed on a single laser pulse, providing another benefit of the CARS method: the ability to acquire instantaneous, single-shot measurements.

While temperature can be extracted primarily from Boltzmann statistics, pressure must be acquired through knowledge of the transition linewidth and lineshape. In this work, linewidth will refer to the full width at half maximum (FWHM) of the transition. The natural linewidth of emitted radiation from an excited diatomic molecule, considered to be in isolation, can be derived from the classical model of the damped harmonic oscillator.\textsuperscript{13} The resulting lineshape is a Lorentzian profile with linewidth:

\[ \Gamma_{j,n} = \gamma \]  \hspace{1cm} (1.11)

where \( n \) is used to denote that this is the natural linewidth, and \( \gamma \) is the damping constant of the oscillator. The damping constant can be shown to be equal to the spontaneous emission probability \( A_{ij} \), one of the Einstein coefficients. This natural lineshape, however, is rarely observed, due to the effects of random molecular motion and intermolecular collisions. Thus, these effects must be taken into account when generating theoretical spectra.

When considering a volume of molecules at low pressure (\( P < 0.1 \text{ atm} \)), the linewidth of a transition is Doppler broadened by the velocity of the molecules themselves. Assuming that the molecules follow a Maxwellian velocity distribution, the lineshape of the transition becomes Gaussian in nature, and the linewidth is given as:\textsuperscript{13}

\[ \Gamma_{j,D} = \omega_{\text{CARS}} \sqrt{\frac{8kT \ln 2}{mc^2}} \]  \hspace{1cm} (1.12)
where $\omega_{CARS}$ is the center frequency of the transition of interest, $m$ is the mass of the molecule under consideration, and $T$ is the translational temperature. Note that Doppler broadening is inhomogeneous, i.e., its effects are not uniform for all molecules. The center of the lineshape represents molecules moving at lower speeds, and the wings represent the molecules traveling at the higher prescribed rates. Because this lineshape dominates at low pressure, where there is a relatively low collision rate, there is very little intermolecular transfer of energy. Therefore, for a laser tuned to the line center, saturation will affect the slower moving molecules before affecting the higher velocity molecules.

As pressure rises above 0.1 atm, the intermolecular collision rate will begin to affect the lineshape. This phenomenon is termed collisional or pressure broadening. Assuming inelastic collisions, the linewidth will be broadened without any effect on the center frequency of the transition. The lineshape becomes Lorentzian, and the linewidth is now:

$$\Gamma_{J,c} = \gamma + aP$$

(1.13)

where $\gamma$ is again the natural linewidth of the molecule in isolation, and the second term represents the broadening due to collisions. The coefficient $a$ is molecule-dependent, and $P$ is the pressure of the medium. This form of broadening is homogeneous, due to the transfer of energy through intermolecular collisions. Before collisional broadening becomes completely dominant, though, a process known as collisional or Dicke narrowing will occur. If the mean free path of the molecules is shorter than the wavelength of the transition, and the Doppler width is still larger than the collisional width at the given pressure, the linewidth of the transition will narrow.
Thus, there are three simultaneously competing molecular mechanisms that affect the lineshape and linewidth. Additional contributions to the linewidth and lineshape can arise from saturation\textsuperscript{15} and Stark\textsuperscript{16} effects. Because the lines in the nitrogen Q-branch are not completely isolated, interference effects from neighboring transitions can be very significant. Additionally, because the CARS signal intensity depends on the square of the polarization susceptibility, the nonresonant portion of the susceptibility must also come into consideration. It would be difficult to analytically account for these effects in Equation 1.9; therefore, significant work has been performed in modeling CARS spectral behavior. Many spectral models have been developed throughout the last twenty years\textsuperscript{17} but the dominant model that has emerged is the modified exponential gap model\textsuperscript{18}. This model considers the transition between collisional narrowing and collisional broadening and includes the ability to predict the changing lineshape of the transitions. The data-reduction process employed in the CARS portion of this study utilizes the modified exponential gap model when generating the theoretical spectra.

With the understanding of the CARS signal spectral behavior, the two steps necessary in determining pressure and temperature from the CARS signal can be covered. First, the discussion above implies that the CARS signal must be spectrally resolved. This allows an observation of the relative intensities, linewidths, and lineshapes of all transitions probed. Then, these experimental spectra must be compared to theoretically modeled spectra to obtain the pressure and temperature. Note that since interference effects will modify the intensities of each transition, the model used to reproduce these effects will predict the relative intensity distribution seen in the experimental CARS signal better than the unmodified
Boltzmann distribution. Therefore, an accurate model will not only increase the accuracy of pressure predictions but will also provide more accurate temperature predictions. The comparison process is typically done using a least-squares fitting method as follows: pressure and temperature are estimated for a given experimental spectrum, then a theoretically modeled spectrum is generated for comparison based on these estimations, and finally the residual between the two spectra is determined. The estimated values of pressure and temperature are varied until the residual between the theoretical and experimental spectra is minimized, using a chi-square goodness-of-fit test. For this study, software known as CARSFIT, developed at Sandia National Laboratories, is employed to perform the least-squares fitting process.

To acquire CARS signal spectra, typically a charge-coupled device (CCD) is exposed to the spectrally resolved signal intensity. There are two methods of exposure that can be performed. Referred to as time-averaged, the CCD can be exposed to the CARS signal intensity for a given number of laser shots before the resulting accumulated intensities are recorded. In a sense, this method averages the instantaneous intensity of each CARS signal involved. Because this masks the instantaneous behavior, the method is usually only used when a medium with steady-state properties such as laminar flow is probed. For the other method, referred to as instantaneous or single-shot, the CCD is only exposed to a single laser shot. Therefore, shot-to-shot fluctuations can be observed, and turbulent media can be probed. For both methods, mean values of properties can be reported, but meaningful property fluctuations can only be inferred from the \( \text{rms} \) values of the instantaneous CARS signal behavior.
Under the conditions typically encountered in compressible flow, the diatomic nitrogen molecule being probed will obey the ideal gas law. Therefore, once pressure and temperature have been determined through the least-squares fitting process, density can be determined as follows:

\[
\rho = \frac{P}{RT}
\] (1.14)

where \(R\) is the gas constant for the probed molecules, and \(\rho\) is the density.

The CARS system could be designed to provide the velocity component in the direction of the CARS signal wave vector, \(\vec{k}_{CARS}\). This manipulation of the system relies on a sharp crossing angle between the two pump beams, which in turn, severely limits the maximum CARS signal intensity. This limitation can be seen by recalling Equation 1.8. The CARS signal intensity is directly proportional to the length of the probe volume squared. It can be shown that this length is inversely proportional to the crossing angle, \(\alpha\):

\[
\ell \propto \frac{1}{\sin \alpha}
\] (1.15)

Thus, as the crossing angle is increased to obtain the velocity, the signal level drops drastically. Fortunately, for internal compressible flows, it is possible to calculate velocity magnitude from the pressure and temperature determined from the spectral profile of the CARS signal. If the flow is steady and adiabatic, with negligible work and elevation changes, and it originates from a uniform reservoir, the flow can be assumed to be homenergetic. This allows the velocity to be related to enthalpy by:

\[
h_o = h + \frac{V^2}{2} = \text{constant}
\] (1.16)
where $V$ represents the mean velocity of the molecules at the probe volume, $h$ is the enthalpy, and $h_o$ is the stagnation enthalpy. With pressure and temperature known at the measurement location, enthalpy is a measurable quantity. The stagnation enthalpy can be determined through knowledge of the temperature and pressure in the stagnation chamber of a blowdown wind tunnel, allowing for velocity magnitude to be calculated.

1.2.4 Noise Characteristics of the CARS Process

It is without question that with all the benefits of the CARS process, there must be limitations of the technique. The foremost problem is the noise characteristics that are inherent to the system itself.\textsuperscript{21,22} As seen in the previous section, the use of a broadband Stokes beam allows for instantaneous measurements to be made. The accuracy of this measurement, however, relies on the quality of the broadband spectral profile of the Stokes beam. As discussed with reference to Equation 1.8, the intensity of all four beams involved is dependent on the frequency at which the beam is lasing. The frequency dependence of the CARS signal strength should be based solely on the Boltzmann population distribution and linewidth effects. Assuming that the pump beams are supplied by a well-behaved, single-longitudinal-mode source, as is typical of commercially available Q-switched lasers with injection seeding, the remaining source of noise in the CARS signal intensity lies in the Stokes beam. Ideally, the Stokes beam should provide a uniform intensity at every frequency at which it lases, so that each transition is probed equally. This spectral profile is depicted in Figure 1.3(a). As in previous work,\textsuperscript{6} the source for the Stokes beam is typically derived from a conventional broadband dye laser (CBDL), which utilizes commercially available organic dye. As with any other excitable source, organic dye absorbs and emits light with uneven
spectral intensity, referred to as its gain curve. This gain curve presents the first drawback to using a CBDL. While dye concentrations can be manipulated to provide a relatively flat spectral profile in the region of interest, nonuniformities still exist. An exaggeration of this phenomenon is shown in Figure 1.3(b), where the gain curve is shown as a Gaussian curve. Actual gain curves are not as well behaved.\textsuperscript{23}

The second drawback to the CBDL is inherent in its design. As seen in Figure 1.4, the CBDL employs the use of an oscillator cavity, which is nothing more than a Fabry-Perot

Figure 1.3: Examples of the spectral profile of a CBDL: (a) ideal output, (b) gain curve, (c) mode structure, and (d) final random structure
etalon, and as such, exhibits the same performance qualities. One characteristic of the oscillator cavity is the requirement that a given frequency can only oscillate if it forms a standing wave in the cavity. Therefore, only certain frequencies, or axial modes, within the range of the gain curve can oscillate and eventually contribute to the spectral profile of the CBDL. This effect can be seen in Figure 1.3(c); note that the mode spacing is greatly exaggerated to clarify the effect. The quantum dynamical nature of an axial mode is governed by the quantum statistics of the spontaneous emission at that mode. As this process is statistically determined, there will be no well-defined, shot-to-shot axial mode structure. Further complicating the structure is the fact that certain axial modes will absorb the energy of others, and these “parasitic” modes will then dominate the spectral profile. Unfortunately, there is no simple method to predict which axial modes will dominate on a given laser pulse; thus,
the random start to the mode structure is then randomly manipulated. This final result is shown in Figure 1.3(d).

While the axial modes are typically spaced closer in frequency than any two molecular transitions, their random shot-to-shot behavior still presents a problem termed mode noise. First, on a single laser pulse, not all transitions will be pumped uniformly. Second, each individual transition will be pumped nonuniformly on consecutive laser shots. These effects will introduce artificial fluctuations into the instantaneous measurements that could be mistaken for property fluctuations in the flowfield being investigated.

Aside from referencing a simultaneous nonresonant signal, there is little recourse for the nonuniformities in the gain curve. While this nonuniformity presents a problem, it is not as severe as mode noise and is typically accounted for using an average broadband dye laser spectral profile. Therefore, there have been numerous studies aimed at modeling, diminishing, or eliminating mode noise. The relevant investigations of reducing or eliminating mode noise will be discussed here, while the reader is referred to the work of Kröll and Sandell for a discussion of modeling mode noise. In this review, CARS system noise levels are based on standard deviations of a quantity, i.e., signal intensity or temperature, when all conditions at the probe volume are held constant.

In an attempt to diminish mode noise, Greenhalgh and Whittley modified the CBDL in two ways. First, they decreased the axial mode spacing by increasing the oscillator cavity length, $L$; this method is referred to as axial mode packing. The axial mode spacing, $\Delta \omega$, is defined as:

$$\Delta \omega = \frac{1}{2L}$$ (1.17)
Decreasing the axial mode spacing brings the spectral profile of the CBDL closer to a smooth, continuous curve. Observing the change in CBDL and CARS spectral profiles, Greenhalgh and Whittley report a decrease in percentage $rms$ mode noise of $\sim 42\%$ for the CBDL and $\sim 33\%$ for the CARS signal for an increase of $\sim 45$ cm (300%) in cavity length. Their collected data follow a noise reduction based on an $L^{-1/2}$ dependence. In a second, separate attempt to reduce mode noise, they replaced the rear oscillator cavity mirror with a corner cube prism. This replacement modifies the transverse mode distribution, and in effect removes the lowest order transverse mode. By doing so, they report a reduction in noise of $\sim 30\%$ for the CBDL, as well as similar results for inserting a $\sim 1$ mm square aperture in the oscillator cavity, proposing that it has the same effect as the corner cube prism.

Another possible method for reducing the effects of mode noise is to replace the longitudinally pumped oscillator dye cell, as shown in Figure 1.4, with a transversely pumped dye cell. This change promotes more uniform pumping of the organic dye, which provides a more uniform spatial intensity profile. While this does not alter the existence of mode noise when used in an oscillator cavity, the uniformity of the distribution of axial and transverse modes is increased, which is still beneficial to CARS signal generation and noise statistics.

A less attractive, but practically viable technique is to obtain a nonresonant signal on every laser pulse for which a CARS signal is obtained. Because it is difficult to obtain a resolution sufficient to fully resolve the mode spacing, this solution is limited in scope. This method has been shown to reduce the effects of mode noise only marginally.

Obviously, rather than attempt to reduce mode noise, it would be far more beneficial to eliminate it altogether. As presented above, the source for mode noise derives from the use
of an oscillator cavity. While the cavity provides an efficient method for creating a coherent source of light, it maintains undesirable characteristics when a broadband spectral profile is desired. Therefore, an attractive option would be to employ a broadband dye laser that eliminates the need for an oscillator cavity. Due to the lack of oscillation, a reduction in conversion efficiency from input pump power is to be expected, although the benefits can be shown to outweigh this loss.

Two unique designs of “oscillatorless” broadband dye lasers are currently used in the literature, and are referred to as modeless dye lasers (MDLs). These two designs have been used almost exclusively at combustion temperature levels, with no thorough investigations being performed at low temperature to the author’s knowledge. The first design was presented by Ewart,28 for which stimulated emission is amplified in four stages without oscillation. Since its inception, this MDL has been utilized in a few CARS investigations, two of which are reviewed here. Snowdon et al.29 report a reduction in the standard deviation of noise of single-shot CARS spectra from ∼13% for a CBDL to ∼5% for an MDL. Included in their study was the improved precision of single-shot temperature measurements. The use of the MDL provided for a reduction from ∼5% to ∼1.25% in standard deviation of temperature at a mean of 1200 K. The second investigation performed a systematic evaluation of different styles of dye lasers.30 The evaluation revealed a reduction from ∼22% to ∼6% standard deviation of CARS signal noise when switching from a CBDL to an MDL. The investigation also displayed increased precision of single-shot temperature measurements, as standard deviations dropped from ∼3.5% to ∼1.5% at a mean temperature of 1600 K.
The second MDL design, introduced by Hahn et al., makes use of Bethune dye cells. The same report includes an evaluation of the abilities of the MDL design. While percent standard deviation of CARS signal noise was not reported, reduction in percent standard deviation of temperature measurements was. The use of this MDL reduced temperature fluctuations from $\sim 5\%$ to $\sim 2\%$ at 1200 K. This MDL was also employed in a separate investigation. Lucht et al. utilized the benefits of this MDL design in the measurement of temperature and CO$_2$ concentration. No comparison was given to experiments using a CBDL, but the percent standard deviation of temperature was reported at $\sim 2\%$ at a mean temperature of 2000 K. These four MDL studies solidify the benefits of using an MDL over a CBDL, as reductions in noise levels in CARS signal intensity and resulting temperature measurements are consistent among the investigations.

1.2.5 Previous N$_2$ CARS Pressure, Temperature, and Density Results

The development of CARS for measurements in high-speed flows has been ongoing at the University of Illinois for several years. The work started with dual-pump CARS measurements of pressure and temperature. This method probed the vibrational and pure rotational transitions of diatomic nitrogen in a stagnant gas cell and along the centerline of an underexpanded jet. The technique provided accurate time-averaged pressure results above 1 atm, as well as accurate mean and instantaneous temperature results throughout the range of 100 – 300 K. Unfortunately, the method performed poorly for time-averaged pressure measurements below 1 atm and for instantaneous pressure measurements below 3 atm. For instantaneous pressure measurements, the standard deviation was reported at approximately 10% of the mean for 3 atm, dropping to 4% at 18 atm. This baseline noise level
prohibits the technique’s use for obtaining meaningful pressure fluctuation measurements in many applications.

In light of these results, modifications to the dual-pump CARS technique were made in order to increase pressure sensitivity at lower pressure and to investigate the ability of the method to obtain accurate, instantaneous, single-shot measurements.\(^6\) Instead of probing both pure rotational and vibrational resonances of diatomic nitrogen, the modified technique focused on vibrational resonances. Whereas in the previous study the CARS signal spanned a range between 40 and 100 cm\(^{-1}\), the modified CARS measurements only spanned 10 cm\(^{-1}\). Using a relay lens system to magnify the CARS signal spectrally, this new, high-resolution technique was able to resolve the CARS signal to within 0.10 cm\(^{-1}\), allowing pressure and temperature sensitivity of the diatomic nitrogen Q-branch (\(v = 0 \rightarrow 1\)) to be investigated. As before, the method was tested in a stagnant gas cell and throughout the flowfield of an underexpanded jet. The results from the gas cell revealed that only below 2 atm was the method capable of making accurate time-averaged and ensemble-averaged single-shot measurements of mean pressure, therefore displaying the opposite pressure sensitivity as compared to the previous dual-pump method. The high-resolution technique also provided accurate mean pressure and temperature measurements in the underexpanded jet flowfield. Most notably, the method displayed the ability to generate usable single-shot signal levels at high spatial resolution even at low molecular number density.

One goal of the modified technique was to provide the ability to measure fluctuating thermodynamic properties in compressible shear flows.\(^{36}\) While the technique could provide single-shot measurements with accurate mean values, the ensemble-averaged fluctuations
were not accurate. From the gas-cell experiment, the baseline noise level over the 0.1 to 5.0 atm range examined was approximately 12% of the mean pressure value on average. These artificial fluctuations (precision uncertainty), which dominated the results, were attributed to mode-noise contributions from the CBDL that was used as the source for the Stokes beam.\textsuperscript{37}

1.2.6 Alternative Techniques to CARS

While CARS provides numerous attractive qualities as a diagnostic technique, its implementation is still relatively complex. Therefore, other, more easily applied techniques for obtaining thermodynamic properties have been investigated. Absorption, laser-induced fluorescence (LIF), alone and in combination with Raman scattering, and Rayleigh scattering, among many others, have appeared in the literature as viable alternatives. The current survey of these studies will be viewed in the light of making mean and fluctuating property measurements.

Davidson \textit{et al.}\textsuperscript{38} reported measurements of velocity, temperature, pressure, density, and mass flux using a continuous-wave (cw), dual line-of-sight absorption technique in a shock tube. By rapidly scanning across the $R_1(7)$ and $R_1(11)$ line pair ($A^2\Sigma^+ \leftarrow X^2\Pi (0,0)$) of OH, the absorption profile could be recorded by a photomultiplier tube. Because two laser beams were passed through the test section, one normal to the flow and one at 60°, the Doppler shift between the two resulting profiles could be used to determine the velocity magnitude.\textsuperscript{39} The relative intensities of the line pair were used to calculate temperature. From the magnitude of absorption and the calculated temperature, partial pressure and density of OH were calculated via a chemical kinetic model. An alternative method allowed
pressure and density to be calculated from the linewidth of the collisionally broadened lines. Mass flux was then determined by the density and velocity magnitude. In all cases, the resulting mean measurements agreed well with one-dimensional shock calculations, especially for the first method of obtaining pressure and density. This technique suffered most in regions of low temperature, due to the low molecular number density of OH in the flow. Without seeding the flow with additional OH, the study depended on the dissociation of water molecules as the only source of OH.

Chang et al.\textsuperscript{40} reported additional results with a similar absorption experiment when probing the line pairs in the $A \leftrightarrow X (0,0)$ band of NO. The increased complication of overlapping transitions in this band was offset by the increased stability of the NO mole fraction in the shock tube. The results confirmed the stability of the NO molecule, as the mean thermodynamic properties displayed increased accuracy over the earlier investigation. While measurement accuracy was highlighted at low temperature, the method unfortunately displayed poor characteristics at higher temperature, where the signal showed decreased temperature sensitivity.

The first major disadvantage of these absorption techniques is the inability to extend the method to provide instantaneous measurements, as the peak-to-peak scanning rate of the line pairs was 35 $\mu$s. A fixed frequency method was briefly investigated\textsuperscript{38} for velocity and pressure, but instantaneous results were not promising. Three other important disadvantages also exist. The line-of-sight nature of the technique provides poor spatial resolution, and the method is only applicable in one or two-dimensional flows. In addition, to obtain accurate measurements, the flow must be seeded with tracer particles.
Similar in nature and complexity to absorption, LIF can be employed to provide thermo-
dynamic and kinematic properties. DiRosa et al.\textsuperscript{41} performed cw LIF measurements along
the centerline of an underexpanded jet seeded with NO. In a method very similar to the
absorption technique of Chang et al.,\textsuperscript{40} broadband fluorescence was acquired from excited
NO molecules. By passing the laser beam through the flowfield at angles of 60° and 120°
to the centerline, the Doppler-shifted fluorescence provided a means for measuring velocity
when referenced to a stagnant gas cell signal. Using the relative intensities and linewidths of
the two probed transitions, the pressure and temperature were determined. Standard devi-
ations from the mean temperature were estimated at 6 K, and constant for all temperature
levels. For pressure, the standard deviations were reported at 8% of the measured value in
the range of 0.02 to 0.18 atm. Velocity standard deviations were estimated at 35 m/s for
all measured values. For similar reasons as the absorption techniques discussed above, this
method cannot provide instantaneous measurements. Also detracting from this technique
is the requirement for large, solid-angle, signal collection optics, as LIF is not a coherent
technique. This increases the chances for interference scattering from particulates and flow
boundaries, thus reducing the SNR.

Although more complex in nature, LIF can be implemented in a different manner than
above to obtain fluctuation properties. By employing two dye lasers, Gross et al.\textsuperscript{42} reported
mean and fluctuation measurements of pressure, temperature, and density in a Mach 2
boundary layer flow. Separating dye laser pulses by 125 ns, two separate transitions of NO
can be excited almost simultaneously, providing a means for the measurements. By detun-
ing both laser frequencies away from peak resonance, density can be interpreted through
the signal strength, and temperature is inferred through the relative transition intensities. Pressure is then calculated from an equation of state. Referencing the LIF signal to one generated in a stagnant gas cell to account for laser power fluctuations, the authors reported an instrument noise level of 1% for temperature and density measurements, and 2% for pressure measurements. Mean measurements showed excellent comparison with pitot-static data. Temperature and density fluctuation amplitudes were shown to rise between 4 and 6% throughout the boundary layer, whereas pressure fluctuation amplitudes only reached a level of 3%. While the acquisition of fluctuation measurements with this technique is promising, there are some underlying drawbacks. First, as above, LIF requires large, solid-angle, signal collection optics, increasing the chance for interference scattering and reducing the SNR. Second, without a reference cell, meaningful fluctuation measurements would not be possible. Third, the flow must be seeded with a tracer molecule. Finally, the measurements are referred to as instantaneous, although they span a time frame of 125 ns, which is over an order of magnitude longer than the current CARS method.

In order to remove the need for tracer seeding, LIF of diatomic oxygen in conjunction with Raman scattering of diatomic oxygen and nitrogen (LIF/R) has been explored in the same facility as described in the previous experiment. Since the integrated Raman scattering intensity is temperature independent under 500 K, density is directly proportional to this integrated value. Temperature can then be determined by observing only a single O₂ fluorescence transition. Again, a reference cell was used to eliminate the effects of laser power fluctuations. Due to the multiple transitions being probed simultaneously, the signal must be spectrally resolved. The low signal level requires the use of an intensifier for the
imaging array, providing an instrument noise level of 4% for density and 3% for temperature. Mean and fluctuating pressure were not reported in this study. While these instrument noise levels are significantly higher than in the previous LIF study,\textsuperscript{42} fluctuation results still agree well between the two investigations. In this case, though, the maximum fluctuations in both quantities barely exceed the quoted noise levels. Thus, it becomes difficult to refer to these and previous\textsuperscript{42} fluctuation measurements as meaningful. This fact notwithstanding, the LIF/R technique is instantaneous in nature, as the laser pulse is only 15 ns long. Unfortunately, the low signal level and SNR inherent in this technique obviously plague the measurements.

Rayleigh scattering has recently received increased attention for measuring thermodynamic and kinematic properties. Molecular-based\textsuperscript{44} and Fabry-Perot etalon\textsuperscript{45} filters have been used to reduce or separate Mie scattered light from the signal. When the flow is absent of particulates or condensate, no filtering may be necessary.\textsuperscript{46} Elliott and Samimi\textsuperscript{44} report the ability to simultaneously measure temperature, density, and velocity using a gaseous iodine filter to absorb Mie scattered light. Temperature and density are reported to within a 7% uncertainty, while velocity is reported at an uncertainty of 11%.

By obtaining only unfiltered Rayleigh scattered light, Panda and Seasholtz\textsuperscript{46} were able to measure density and its fluctuations in an underexpanded jet. The investigation employed a \textit{cw} laser, so that time-trace measurements could be obtained. The uncertainty in the measurements was reported to be within 1%; thus, fluctuations above this level were attributed to actual property fluctuations. Mean density was provided along the centerline and for radial traverses of an underexpanded jet for a range of the fully expanded jet Mach number,
$M_j$. The density fluctuations were found to be modulated at the screech frequency of the jet. By simultaneously measuring screech tones, the density was not only time-averaged, but also phase-averaged at the screech frequency. Coherent $rms$ density fluctuations around the phase-averaged density were presented. Fluctuations peaked at $\sim 7\%$ in the shear layer of the jet between two and three jet diameters downstream for $M_j = 1.19$, and at $\sim 10\%$ at about five jet diameters downstream for $M_j = 1.42$. This study represents the first measurements of a meaningful thermodynamic property fluctuation in a compressible flow known to the author. While this achievement is of obvious import, there are disadvantages to using Rayleigh scattering. First, in order to avoid referencing, the flow must be free of particulates and condensate. This was easily achieved in this study for the air supplied to the jet, but the entrained room air had to be constantly filtered. In addition, without adding a signal filter of some sort, the technique cannot provide temperature or pressure measurements simultaneously.

1.2.7 Underexpanded Jet Flowfield for CARS Measurements

The investigation of compressible flows has been hindered by restrictions on applicable experimental methods. The compressible nature of the flow prohibits the application of probe-based measurement techniques without accounting for interference effects. As a result, many compressible flowfields of practical importance lack in-depth experimental investigation. Thus, the advent of laser diagnostics as a viable alternative to probes such as hot-wires and pitot tubes has advanced the knowledge base in areas never before achievable. Additionally, the technological advances in computational power have only recently allowed for useful numerical work to be performed for these flows.
One specific compressible flow found in a large range of practical engineering applications and experimental investigations is the compressible shear layer. As a result, there has been a great deal of research into understanding the effects of compressibility on turbulence. Notably, the most distinct effect of compressibility is the reduced growth rate or mixing rate of supersonic shear layers when compared to their incompressible counterparts. Thus, investigations into enhancing the mixing rate have been performed in applications such as supersonic combustion, metal deposition, ejectors, noise suppression, and base flows. For extensive reviews on the effects of compressibility and mixing enhancement, the reader is referred to the works of Dutton\textsuperscript{47} and Gutmark \textit{et al.}\textsuperscript{4}

Although there is an extensive amount of data already accumulated, understanding of the characteristics of most practical compressible flows is still not complete. Evidenced by this is the vast amount of ongoing work for the underexpanded jet flowfield. The current study involves experiments in this flowfield and will therefore be detailed in this section.

The characteristics of the underexpanded jet flowfield govern the dynamics of numerous practical flows. Short take-off and vertical landing (STOVL) aircraft suffer from a phenomenon known as “lift loss” that is due to the entrainment of flow by the lifting jets.\textsuperscript{3} Supersonic jets also provide increased noise levels that are of concern for sonic fatigue of structural elements near the jet exit.\textsuperscript{3} Therefore, future aircraft involving underexpanded jets, such as the Joint Strike Fighter, would benefit from an increased knowledge base of acoustic and flowfield structures, thermodynamic property distributions, and shear layer mixing rates.
Before reviewing past studies of the underexpanded jet, a description of the supersonic flowfield issuing from a nozzle is required. Figure 1.5 displays the relevant features to be discussed. For a jet to be underexpanded, the exit pressure of the nozzle must be greater than that of the ambient surroundings. This mismatch causes a Prandtl-Meyer expansion fan to form at the lip of the nozzle. These expansion waves propagate across the flow and reflect from the constant-pressure jet boundary as compression waves, which in turn coalesce to form the intercepting shock (sometimes called the “barrel shock”) that is attached to the nozzle lip. The flow is accelerated to supersonic speeds by the expansion fan and travels downstream to a point where the intercepting shock would cross the centerline. Here, the flow will be recompressed. If the exit pressure is great enough ($P_e/P_a \geq 3$), the simple crossing (i.e., regular reflection) of the intercepting shock along the centerline will no longer provide sufficient pressure rise, and a minimally curved, normal shock, or Mach disk, forms. Instead

![Figure 1.5: Underexpanded jet flowfield](image-url)
of crossing (reflecting) at the centerline, the intercepting shock intersects the edge of the Mach disk, where the reflecting shock forms and propagates downstream to the constant-pressure boundary. The triple point is the intersection of the intercepting shock, reflecting shock, and Mach disk, and is the starting point for the slip line or inner shear layer. The inner shear layer complements the outer shear layer, which resides along the constant-pressure boundary. As the reflecting shock reflects from the outer shear layer, a new series of expansion waves form. The expansion waves are the start of a semi-duplication of the first series of flow features that result in a new shock cell. The shock train that forms from this repeating shock cell pattern exists downstream until the pressure mismatch is dissipated by viscosity. As in the subsonic case, the outer and inner shear layers will grow until they close off the jet core region and the jet becomes fully turbulent.

The underexpanded jet flowfield is typically characterized by one of three parameters: the nozzle pressure ratio, NPR = $P_o/P_a$, the Mach number the jet would attain if it was perfectly expanded, also known as the fully expanded jet Mach number, $M_j$, and the convective Mach number, $M_c$. The convective Mach number is the primary parameter that quantifies the effects of compressibility. Defined as the Mach number of the freestream relative to the large-scale structures in the shear layer, the convective Mach number for a homogeneous shear layer can be written as:

$$M_c = \frac{U_1 - U_2}{a_1 + a_2} \quad (1.18)$$

where $U_i$ is the velocity and $a_i$ is the speed of sound of freestream $i$, and 1 and 2 refer to the two different freestreams. For a jet, the flow expands into quiescent room air, and thus the
above relation can be simplified to:

\[ M_c = \frac{U_j}{\sqrt{a_j + a_\infty}} \] (1.19)

where the subscript \( j \) refers to properties of the jet at the measurement location, and \( \infty \) refers to ambient conditions.

Early in the study of underexpanded jets, the method of characteristics (MOC) was applied to investigate the centerline pressure and Mach number distributions.\textsuperscript{49} Furthering this research, Adamson and Nicholls\textsuperscript{50} present an approximation for the standoff distance of the first Mach disk from the jet exit and the jet boundary location. Further work on standoff distance, including extensions to Mach disk diameter, were later performed.\textsuperscript{51-53} Addy\textsuperscript{53} determined that the Mach disk standoff distance and diameter are proportional to the square root of the NPR, confirming earlier results.

The above investigations into flow structure were augmented by laser Doppler velocimetry (LDV)\textsuperscript{54} measurements made in various regions of the underexpanded jet. Centerline and radially distributed measurements of mean velocity were obtained by Eggins and Jackson.\textsuperscript{55} Included in the study is a discussion of particle response justifying the application of LDV near the Mach disk. DeOtte \textit{et al.}\textsuperscript{56} also report mean velocity measurements along the centerline and over numerous radial traverses. Included in this report is a contour plot of axial turbulence intensity. A more recent investigation at two different values of NPR was presented by Nouri and Whitelaw.\textsuperscript{57}

Additional velocity measurements were made by Miles \textit{et al.}\textsuperscript{58} with a molecular flow tagging technique termed molecular tagging velocimetry (MTV). By employing Raman excitation plus laser-induced electronic fluorescence (RELIEF), diatomic oxygen is marked in
the flowfield and then observed. A time-of-flight methodology is applied to successive images
to determine the velocity. A line is marked perpendicular to the centerline, and these im-
ages are employed to present velocity versus radial distance. Mean velocity and turbulence
intensity just upstream and downstream of the first Mach disk were determined.

Beyond the flowfield structure, the distribution of thermodynamic properties in an un-
derexpanded jet is also of great interest. As discussed in Section 1.2.5, Woodmansee et al.6,37
employed CARS to obtain mean pressure, temperature, and density measurements along the
centerline and on radial traverses from the nozzle exit to beyond the first Mach disk. This
work represents the most detailed experimental data of this kind. Comparable centerline
dual-pump CARS measurements can be found in the work of Foglesong et al.35 Additional
reports of mean pressure and temperature, along with velocity, using LIF have also been
made.41 Hiller and Hanson59 provide planar mean measurements of velocity and pressure
using planar LIF (PLIF).

Panda and Seasholtz46 have provided mean and fluctuating density measurements through-
out the jet flowfield using Rayleigh scattering, as discussed in Section 1.2.6. Highlighting
this study was the first presentation of meaningful density fluctuations showing peaks well
downstream of the first Mach disk.

In addition to the above reports, investigations of shear layer instability have been per-
formed in part to study the noise characteristics of the underexpanded jet. There are two
dominant regimes of instability present in the underexpanded jet. First, the streamline
curvature found in the outer shear layer forms Taylor-Görtler instabilities. These instabil-
ities can amplify the disturbances created by nozzle wall roughness.60 The combination of
the instabilities and disturbances can cause streamwise vortices to form. The presence of streamwise vorticity greatly increases the shear layer growth rate, but it is not attributed to being a source of noise. In addition to these results, other detailed investigations into this phenomenon have been performed.

Second, Kelvin-Helmholtz instability waves formed in the outer shear layer can impart circumferential vortical structures. The inner shear layer formed at the triple point also provides a region for circumferential vorticity to exist. The circumferential vorticity in the outer shear layer interacts with the existing shock cell structure and is the source for screech tones. The sound waves emitted from this interaction propagate upstream in the subsonic portion of the outer shear layer and the ambient region and excite the shear layer at the nozzle lip, forming a self-sustaining feedback loop. Streamwise and circumferential vorticity are not independent, especially when considering the formation of screech tones. While streamwise vorticity was noted above as not being a source for screech tones, the increased shear layer thickness resulting from its presence has a damping effect on the feedback loop. Additional work on screech tones has been performed in attempts to predict and control its formation.

The importance of measuring thermodynamic property fluctuations in the inner and outer shear layers is clear, as the results can help delineate the complicated vortical structures that affect the noise and shear layer growth rate in underexpanded jets. The density fluctuation results presented by Panda and Seasholtz provide the first known experimental insight into this region with respect to screech tone formation.
Further insight was provided into the thermodynamic property fluctuations with respect to growth rate by means of direct numerical simulation (DNS) of an annular mixing layer. Previous to this work, it was suggested that reduced pressure fluctuations in the shear layer were the cause of the reduced growth rate. Freund et al. confirmed this by demonstrating the relation between the reduced growth rate and the decline of the pressure-strain rate correlation. As reported in this study, reduced pressure fluctuations were the primary cause for the decrease in the pressure-strain rate correlation, whereas reduced strain rate fluctuations display a smaller contribution.

1.3 ERE CARS Overview

Even though CARS provides characteristically strong signal levels, experimental circumstances exist for which increased signal level is required. Beyond this concern, while the CARS signal frequency is molecule-specific per Equation 1.1, additional species selection criteria can be advantageous. With the increased attention on combustion emission and pollutant formation and the need for tracer molecules in flowfield mixing studies, the need has arisen for a diagnostic technique capable of probing low molecular number density levels (∼ 100 ppm) of radical species such as NO. Additionally, there is strong interest in studying thermally generated NO in hypersonic flowfields. Knowledge of NO concentration at elevated temperature levels would provide insight into the reaction rates for NO, which are required for modeling these flowfields. Beyond the effects on the flowfield, NO formation has recently been shown to be an excellent flowfield tracer that was used to measure the flowfield properties of a hypersonic flow over a cone and in the separated base flow region.
While other techniques discussed below have proven useful for these types of investigations, the application of CARS to such species suffers from two major issues. First, the inherent nonresonant background from major species, such as $N_2$, or nonresonant species, such as Ar, dominates the real portion of the polarization susceptibility, Equation 1.9, when the probed species is at low concentrations. This problem is magnified by the fact that species such as NO suffer from small Raman cross sections, resulting in an additional reduction in signal level as compared to nitrogen. The second concern arises from the number of species typically present in a combustion or plasma environment. At elevated temperatures, the vibrational CARS spectrum of different species can overlap, resulting in uncertainty as to which species is being probed. This is especially a concern for CARS measurements of small hydrocarbon molecules in the C-H bond stretch region of 3000 cm$^{-1}$.

Therefore, over the past two and a half decades, investigations into the capabilities of resonance CARS have been performed. The term resonance is used to indicate that the method not only probes a Raman resonance, but also that one or both pump beam frequencies is tuned such that the Stokes or the CARS frequency is in resonance with an electronic transition or the dissociative continuum of the molecule. These additional resonances not only increase the signal level, but also enhance greatly the species selectivity of the measurement. This study will focus on using additional resonances with electronic transitions, and therefore the technique is termed “electronic-resonance-enhanced” CARS (ERE CARS). In the literature, the technique is also referred to as resonance CARS or resonance-enhanced
CARS (RECARS). In the following section, the relevant background theory and the advantages of ERE CARS will be presented. For a more detailed and comprehensive discussion of ERE CARS, the review of Attal-Trétout et al.\textsuperscript{79} is recommended.

1.3.1 Background Theory

As with CARS, ERE CARS involves the interaction of three input beams under the same conditions as described by Equations 1.1-1.3. In order for the method to probe electronic transitions, additional restrictions on the three frequencies must be applied. To understand the origin of these restrictions, a more detailed theoretical analysis of the polarization susceptibility must be considered in contrast to that presented in Equation 1.9. This analysis begins by focusing on a more general energy level diagram of the CARS process than that presented in Figure 1.1. Figure 1.6 displays this energy level diagram for a generic diatomic molecule. Note that the virtual states in Figure 1.1 are now replaced by actual energy levels of the molecule. For this diagram, Equation 1.1 can be recast as:

\[
\omega_{ba} = \frac{E_b - E_a}{\hbar} = \nu_m \omega_c = \omega_{p1} - \omega_S
\]  

(1.20)

As seen in absorption and stimulated emission processes, there are now resonances to be considered between levels c and b and levels d and a. Eesley,\textsuperscript{80} among others, has developed the full form of the third-order, nonlinear polarization susceptibility for coherent Raman studies using Hellwarth diagrams. This form of the susceptibility consists of twenty-four terms representing all of the possible interactions of the laser beams with the four energy levels during the CARS process. Of these twenty-four terms, only two account for a Raman resonance between levels a and b as governed by Equation 1.20. Therefore, the terms that
come into consideration for this study are: \(^7^9\)

\[
\chi_{\text{CARS}}(\omega_{\text{CARS}} : \omega_{p1}, -\omega_S, \omega_{p2}) = \frac{N}{\hbar} \sum_{a,b,c,d} \left\{ \frac{1}{\omega_{ba} - (\omega_{p1} - \omega_S) - i\Gamma_{ba}} \right\} \left\{ \frac{1}{\omega_{da} - \omega_{\text{CARS}} - i\Gamma_{da}} \right\} \cdot
\sum_{a,b,c,d} \left\{ \frac{1}{\omega_{ca} - \omega_{p1} - i\Gamma_{ca}} \right\} \left\{ \frac{1}{\omega_{cb} - \omega_S - i\Gamma_{cb}} \right\} + \chi_{\text{NR}} \right\}
\]

(1.21)

where \(\mu_{k,ij}\) is as follows:

\[
\mu_{k,ij} = \hat{e}_k \cdot \vec{\mu}_{ij}
\]

(1.22)

where \(\vec{\mu}_{ij}\) is the dipole matrix element for the transition \(i \rightarrow j\), \(\hat{e}_k\) is the polarization angle of laser beam \(k\), and \(\rho_{ii}^{(0)}\) is the fractional population of the rotational state \(i\). The linewidth considerations discussed in Section 1.2.3 will also apply to the linewidths \(\Gamma_{ca}\) and \(\Gamma_{cb}\) of

---

**Figure 1.6: CARS energy-level diagram including electronic resonances**

---

38
the electronic resonances. Note that the twenty remaining terms are small in magnitude and relatively frequency-independent as compared to the above four terms and therefore are accounted for in $\chi^{NR}$. As can be seen from Equation 1.2, the CARS frequency is determined by the frequencies of the three input beams. Therefore, if $\omega_{p1}$ is tuned to $\sim \omega_{ca}$, $\omega_S$ must be tuned to ensure resonance with the Raman transition, forcing $\omega_S \sim \omega_{cb}$. This leads to the requirement that $\omega_{p2}$ be tuned such that $\omega_{CARS}$ is in resonance with $\omega_{da}$. When all three resonances occur simultaneously, the process is termed triple resonance, whereas if only the Raman resonance and one electronic resonance is met, the process is termed double resonance. Note that this new form of the polarization susceptibility now includes the line strengths in terms of the dipole matrix elements, more common to one-photon spectroscopy terminology, rather than the previous form, Equation 1.10, which involved line strengths in terms of Raman spectroscopic terminology. The relation between these two forms of line strengths will be discussed in Chapter 4.

1.3.2 Advantages of ERE CARS

Due to the similarities between ERE CARS and CARS, it is clear that ERE CARS will possess all of the advantages discussed in Section 1.2.2, and is therefore a useful technique. Although the use of nondegenerate pump frequencies (i.e., $\omega_{p1} \neq \omega_{p2}$) in ERE CARS adds another dimension of complexity to the experimental setup, there are distinct advantages that arise from this addition. As stated previously, the addition of the electronic resonances will increase the signal level. This can now be seen from Equation 1.21. A peak in the CARS signal occurs when $\omega_{p1} - \omega_S \sim \omega_{ba}$, and this peak is magnified whenever $\omega_S \sim \omega_{cb}$ or $\omega_{CARS} \sim \omega_{da}$. This enhancement can allow for the weak Raman transitions of molecules
such as NO or OH to be probed, even at low concentrations. Improvements in detection limits on the order of \(10^2\) to \(10^8\) can be expected.\(^{81}\)

The extra resonance contributions also include additional species selectivity criteria. These criteria begin with Equation 1.20, and are completed with:

\[ \omega_{cb} = \omega_S \]  
(1.23)

\[ \omega_{da} = \omega_{p1} - \omega_S + \omega_{p2} \]  
(1.24)

This can alleviate the confusion of overlapping spectra of molecules such as the \(A \leftarrow X(0, 0)\) fluorescence band of NO with the Schumann-Runge system of \(O_2\)\(^{78}\) or the pure rotational Raman bands of \(N_2\) and \(O_2\).\(^{82}\) Even in the case of double-resonance ERE CARS, the extra selection criterion will provide a distinction between the species. These two additional advantages, above and beyond those found for CARS, make this diagnostic method applicable to many diverse environments that require investigation.

### 1.3.3 Previous ERE CARS Studies

Originally, ERE CARS was observed in liquids and was referred to as higher-order Raman spectral excitation studies (HORSES).\(^{83,84}\) Since then, ERE CARS has been experimentally applied and theoretically investigated for many species of practical interest. It was first applied to the gas phase in 1978 by Attal \textit{et al.}\(^{85}\) in \(I_2\) vapor in air at a temperature of 308 K and a partial pressure of 0.001 atm. ERE CARS has since been employed in studies of gaseous \(OH\),\(^{86,87}\) \(C_2\),\(^{88,89}\) \(CH\),\(^{90,91}\) \(NO_2\),\(^{92,93}\) \(NaH\),\(^{94,95}\) and \(s\)-tetrazine vapor.\(^{96}\) To the knowledge of the author, ERE CARS has never been experimentally applied to NO, nor has any theoretical analysis of the resulting spectrum been performed.
As mentioned above, intensive theoretical studies of the form of the polarization susceptibility have been performed and tested. Eesley employed Hellwarth diagrams as a basis for the derivation. Druet et al. also used a time-ordered diagrammatic approach. Bloembergen et al. and Oudar and Shen both performed a perturbation expansion of the density matrix for the system. A review of these and other works of interest is found in Attal et al. Theoretical consideration of the lineshape is investigated by Bloembergen et al. for varying cases of damping. Doppler broadening and the resulting lineshape has been investigated by Druet et al. Experimental investigations of the effects of laser linewidth on the spectra of I₂ were performed by Aben et al. Line strengths of OH, C₂, and CH have been theoretically treated, covering Hund’s cases (a) and (b) and the intermediate case between them. Aben et al. have derived the theoretical expressions for the line strengths including the polarization effects for I₂, covering Hund’s case (c). While significant work has been done to model the aforementioned molecular species, applying these models to NO requires additional considerations given the difference in molecular structure of NO. In particular, the satellite branches in the absorption spectrum of NO are much stronger for higher values of the rotational quantum number, J, than for species such as OH, as NO is closer to a pure Hund’s case (a). This introduces new transitions into the resulting spectrum, which must be accounted for in the model.

1.3.4 NO Molecular Structure and Spectral Constants

Compared to a diatomic molecule such as N₂, the molecular electronic structure of NO introduces additional features that can complicate the resulting spectrum. These features arise from the interactions of the nuclear and electron motions in the molecule. There are
three important interactions for NO. The first is in reference to the ground electronic state, which due to the presence of a non-zero projection of the orbital angular momentum of the electrons on the internuclear axis, \( \Lambda \), is classified as \( ^2\Pi \). For NO, this \( ^2\Pi \) state belongs to an intermediate form of Hund’s coupling cases (a) and (b),\(^{103}\) for which there is a strong coupling between the combined axial components of electron angular momentum and spin, \( \Lambda + S \), and the nuclear rotation, \( N \). This causes a splitting of the ground state into \( ^2\Pi_{1/2} \) and \( ^2\Pi_{3/2} \) states, the former having an electronic energy greater by \( \sim 124 \text{ cm}^{-1} \).\(^{104}\)

The second phenomenon of interest arises from the energy difference of the total electron angular momentum, \( L \), and \( N \), which occurs depending on the orientation of \( \Lambda \) on the internuclear axis. This leads to a splitting of the individual rotational levels in the \( ^2\Pi \) ground states. This splitting doubles the number of rotational levels, and is referred to as \( \Lambda \)-doubling. Finally, the first excited electronic state of NO is a \( ^2\Sigma \) state, i.e., \( \Lambda = 0 \), which belongs to Hund’s coupling case (b). For this state, there is a strong interaction between the combination of \( \Lambda + N \) and \( S \). This does not split the electronic state, such as is the case for the ground state; rather, it introduces a splitting of the rotational levels. The results of these interactions are seen in Figure 1.7. Note that the spacing between energy levels displayed in Figure 1.7 is exaggerated and is not scaled to actual energy values for the molecule.

### 1.3.5 Previous NO Absorption, Raman, and CARS Measurements

In order to model the ERE CARS spectrum of NO, certain molecular constants must be known. In particular, the relative Raman cross section and the depolarization ratio are necessary to determine the amplitude of the Raman transitions. Values according to Schwiesow\(^{105}\) were used in the current study because both quantities were measured in the
same experiment. These values are in general agreement with the rest of the literature and are as follows:

\[
\Sigma_j = \left( \frac{\partial \sigma / \partial \Omega}{\partial \sigma / \partial \Omega} \right)_{zz,Q,j} \frac{(\nu_{p1} - 2331)^4}{(\nu_{p1} - \nu_m)^4} (1 - e^{-\frac{\hbar \nu_{p1}}{kT}}) = 0.45
\]  

(1.25)

\[
\rho = 0.11
\]  

(1.26)

In an early study of NO CARS, the relative Raman cross sections for both ground states of NO were determined to be the same.\(^{106}\) Additionally, the Raman linewidths, \(\Gamma_{ba}\), were taken from the work of Doerk et al.\(^{107}\)

\[
\Gamma_{ba} = 0.06 \left( \frac{T_{\text{ref}}}{T} \right) \left( \frac{P}{P_{\text{ref}}} \right) \text{ cm}^{-1}
\]  

(1.27)

where \(T_{\text{ref}} = 298\) K, and \(P_{\text{ref}} = 1\) atm.

![Energy-level diagram of the \(A^2\Sigma \leftarrow X^2\Pi\) transition of NO](image)

Figure 1.7: Energy-level diagram of the \(A^2\Sigma \leftarrow X^2\Pi\) transition of NO
In order to calculate the Raman shift and the relative population distributions, additional molecular constants are necessary. The values for $\omega_x$, $\omega_y$, $\omega_z$, $\alpha_x$, and $D_e$ were taken from Huber and Herzberg. The rotational constant, $B_e$, was obtained from Laane and Kiefer. The values and their use will be discussed in further detail in Chapter 4.

The properties necessary to model the electronic resonance portion of the ERE CARS spectrum were found using the program LIFBASE. These values include the line positions, $\omega_{bd}$ and $\omega_{da}$, and the spontaneous emission coefficients, $A_{bd}$ and $A_{da}$, for the two electronic transitions of interest.

Beyond the above molecular and spectroscopic constants, it is insightful to review the CARS studies of NO to provide a perspective on the applicability of CARS to NO. The first known report of NO CARS was a theoretical study in 1980 involving the interference effects of the rotational lines as dependent on the transition linewidths. The first experimental spectra were reported in 1981 by Beckmann et al. The investigation probed pure NO at pressure levels from 0.13 to 2.27 atm. The study employed a scanning CARS technique, which provided a resolution of 0.05 cm$^{-1}$. The spectra obtained at 0.13 atm displayed the effects of the split ground state on the CARS spectra, as line splitting was evident for the Q(11.5) through Q(17.5) lines. Using cw-stimulated Raman spectroscopy, Lempert et al. studied the effects of collisional narrowing on the NO spectrum in the range of 0.17 to 1.0 atm. These measurements were used in the development of the linewidths reported above.

Following these measurements, the first NO CARS combustion investigation was performed in solid propellant flames to study the decomposition process of NO. In this study,
NO concentration levels below 10000 ppm could not be detected throughout the measured temperature range of 2000 to 2500 K. In the reported spectra, the NO Raman signature is noticeable, but the intensity is not significant compared to the background. During the study, a pure rotational transition of H$_2$ interfered with the first hot band of NO. Brüggemann et al.\textsuperscript{112} then reported average spectra of NO in Ar at temperature levels up to 1200 K and concentration levels of 1 to 100%. Experimental spectra were reported with theoretical comparisons, for which there was good agreement in line positions, but less accuracy in intensity distributions. The first extensive study of NO CARS was performed by Doerk \textit{et al.}\textsuperscript{107} The investigation probed a pressure vessel filled with NO mixed with N$_2$ at temperature levels of 300 to 800 K. The detection limit at atmospheric pressure was determined to be 2500 ppm. Excellent agreement between experimental and theoretical spectra was displayed for measurements obtained near 300 K for pure NO. In an attempt to lower the detection limit, a polarization CARS setup was applied, but it did not alter the detection limit in a significant manner. This study was therefore followed by additional attempts with polarization CARS.\textsuperscript{113} This setup was used to study NO decomposition in a microwave-generated nitrogen plasma. With the new setup, the detection limit was lowered to 200 ppm, although the CARS spectrum was barely discernible at this level.

From this review it can be seen that, in order to probe combustion environments for which NO concentrations are on the order of 100 ppm or less, a modified CARS technique is necessary.\textsuperscript{8} Additionally, as seen in the work of Kurtz and Giesen,\textsuperscript{111} conditions exist for which increased species selection criteria, such as Equations 1.23 and 1.24, would eliminate interference from Raman lines from different species, such as H$_2$. 

45
1.3.6 Alternative Techniques to ERE CARS

Aside from ERE CARS, a number of other techniques have been investigated that have the potential for performing similar measurements to the ones under consideration. Some of these techniques include LIF, degenerate four-wave mixing (DFWM), and polarization spectroscopy (PS). This section will compare these techniques to ERE CARS, focusing on applications to NO and the corresponding detection limits when possible.

LIF is a well-developed technique that is often applied in combustion environments to probe minor species such as NO. Meier et al.\textsuperscript{74} performed single-shot NO LIF concentration measurements in an H\textsubscript{2}/N\textsubscript{2}/air diffusion flame. LIF was used to probe the $A \leftrightarrow X$ transition of NO in conjunction with Raman scattering for major species concentration and temperature measurements. The temperature level ranged from 500 to 2000 K. A calibration method was developed by doping known levels of NO in the N\textsubscript{2} flow, and included corrections for laser power fluctuations. The technique was capable of detecting 15 ppm of NO in a mixture of 60\% N\textsubscript{2} and 40\% H\textsubscript{2}. Concentration measurements of NO were performed in multiple flame chemistries at an accuracy level determined to be 10 to 15\%. Meier et al.\textsuperscript{74} report mean and $rms$ temperature and NO concentration levels for radial distributions at different centerline locations and discuss the mechanism of NO formation.

While LIF provides low detection limits, as seen in the study above, the technique can suffer from its dependence on collisional quenching. In order to interpret the experimental spectrum for concentration measurements, not only must the temperature be known, but the collision partners must also be identified.\textsuperscript{74} In particular for NO, O\textsubscript{2} rapidly quenches the signal, on a time scale two orders of magnitude faster than spontaneous emission, whereas
N₂ does not significantly affect the signal at all.\textsuperscript{74} In an attempt to enhance the accuracy of NO LIF measurements, numerous studies have been performed for different species to determine these quenching rates.\textsuperscript{114}

Beyond this major issue, LIF can also suffer from interference effects from scattered light because it is an incoherent technique. This multiplies the confusion arising from overlapping spectral lines from other species, as mentioned previously. Doerk \textit{et al.}\textsuperscript{91} performed a comparative study of LIF and ERE CARS for CH radicals formed in a microwave-excited Ar/H₂/CH\textsubscript{4} plasma. Both techniques probed the $A^2\Delta \leftarrow X^2\Pi$, electronic transition of CH. The study measured rotational and vibrational temperature levels for comparison. Using a calibration scheme, the detection limits of the methods were determined to be $4 \cdot 10^{15} \text{m}^{-3}$ for ERE CARS and $5 \cdot 10^{15} \text{m}^{-3}$ for LIF. Therefore, the techniques performed nearly equally. Beyond the sensitivity of the LIF method, ERE CARS was also capable of detecting the small population density of the $v = 1$ state.

A similar study comparing LIF and ERE CARS was also performed by Kohse-Höinghaus \textit{et al.}\textsuperscript{115} with measurements in CH\textsubscript{4}/air flames burning at pressure levels from 1.0 to 9.6 bar. Temperature and OH concentration levels were gathered from LIF measurements of the $A^2\Sigma^+ \leftarrow X^2\Pi(1,0)$ band, and these results were compared to the ERE CARS work of Attal-Trétout \textit{et al.}\textsuperscript{79} Overall, both techniques exhibited similar SNR, although ERE CARS was applicable at any pressure level, whereas quenching reduced the effectiveness of LIF at higher pressure levels, where it is harder to saturate transitions. The report concluded that neither technique was comprehensively superior, and that each technique had unique areas of application.
With the issues arising from the incoherent nature of LIF and quenching correction issues, other coherent techniques such as DFWM have been explored to reduce signal dependence on quenching rates. DFWM is very similar to ERE CARS in that it depends on the nonlinear, third-order polarization susceptibility, although in DFWM, all three input beams are of the same frequency and are usually in resonance with an electronic transition of the molecule. Danehy et al.\textsuperscript{116} have studied the effects of quenching rates on DFWM for the $A \leftarrow X$ band of NO using N$_2$ and CO$_2$ as buffer gases. The phase-conjugate geometry, with counterpropagating pump beams, was employed. The results indicate that even when not performed in saturation, \textit{i.e.}, $I/I_{\text{sat}} = 0.02$, DFWM is not as susceptible to quenching as LIF. For studies that are closer to full saturation, \textit{e.g.}, $I/I_{\text{sat}} > 0.5$, DFWM is nearly independent of the quenching rate. This study confirmed the earlier results of Dreier and Rakestraw,\textsuperscript{117} who investigated DFWM in the phase-conjugate geometry for OH in premixed propane/air flames. Without corrections for quenching rates, the temperature extracted from the DFWM signal was in excellent agreement with previous measurements by CARS.

Vander Wal et al.\textsuperscript{118} have performed high-resolution, phase-conjugate geometry, DFWM measurements of NO in the $A \leftarrow X$ band. The investigation probed a controlled mixture of He and NO over a range of pressure levels to study the effects of Doppler and collisional broadening. Of importance in this study was the confirmation of the rapid decrease in DFWM signal with increasing pressure by a foreign gas, albeit slower than theoretically predicted. When the technique was performed in saturation, this pressure dependence was found to diminish but was not eliminated. Through the use of absorption measurements in the controlled mixture, the detection limit of DFWM for NO was estimated to be of the
order of 10 ppm. The study also included DFWM and LIF measurements in an H₂/O₂/N₂ diffusion flame, in which thermal generation of NO occurred. It was determined that the SNR and total intensity of both techniques were very similar, although the LIF spectrum reportedly displayed increased interference.

Krüger et al. investigated DFWM applied in the strong-field regime to the NO (A ← X) band. The experiment was performed in an H₂/air premixed flame at atmospheric pressure with 1% NO in N₂ added to the air. It was estimated that these flame conditions corresponded to an NO concentration of ∼ 400 ppm. The investigation studied the effects of temperature and pressure, which govern collisional broadening, on the DFWM signal in the saturated regime using a BOXCARS, or forward, geometry. From these measurements, Krüger et al. were able to measure the saturation intensity for NO. Intermediate saturation was found to occur at \( I_{\text{total}} = 48 \, \mu J \). The experimental spectra, acquired at an SNR of 2000 : 1, displayed excellent agreement with the theory developed during the study. For both of the previous studies, the O₂ (\( B^3\Sigma_u^- \leftarrow X^3\Sigma_g^- \)) Schumann-Runge band appeared in the NO DFWM spectra, complicating the data analysis and reduction. This interference arises because DFWM has only one species selection criterion.

A detailed comparison of the capabilities of DFWM and ERE CARS was performed by Bervas et al. The OH A ← X band in a high-pressure CH₄/air premixed flame was probed by DFWM in the phase-conjugate geometry. The detection limit was determined to be \( 7 \cdot 10^{13} \, \text{mol/cm}^3 \), comparable to the detection limit for ERE CARS found in the work of Attal-Trétout et al. The study also discusses the species selectivity for each technique,
concluding that DFWM is more susceptible to overlapping spectral signatures. The investigation concluded that ERE CARS was more sensitive for pressure levels above 1 bar, but that DFWM could be performed at these levels.

The experiment was later extended by performing it in the forward BOXCARS geometry. Using this geometry led to the detection of Doppler broadening in the resulting spectra, but was also shown to reduce the amount of background light scatter in the detection scheme. Through the two DFWM studies, Bervas et al. were able to determine that DFWM was more sensitive than ERE CARS to dye laser fluctuations, such as those discussed in Section 1.2.4. With the detection limits of ERE CARS and DFWM being similar, the advantage of ERE CARS comes from the fact that the signal frequency is shifted away from the input beams, making the detection easier and with less background light scatter. Additionally, as discussed above, ERE CARS has at least two species selection criteria, whereas DFWM, which only probes one electronic resonance, has only one. Finally, DFWM suffers from a reduction in signal level proportional to the pressure level being probed, which limits its application at high pressure levels.

While DFWM requires a less complex experimental setup, using only one frequency for all three input beams, PS goes one step further by only employing two input beams. In contrast to ERE CARS and DFWM, PS is not a signal-generating technique, but rather a modulation technique. The first known investigation of NO by PS was a concentration study performed simultaneously with measurement of OH concentration. The investigation was performed in a premixed H2/N2O flame. Both species were detectable at the same time by employing two different laser frequencies. One principal frequency at 225 nm was generated for probing
NO. The residual frequency from this generation process was at 285 nm which is in resonance for OH. Probing both species simultaneously increases the detection limits, as the power levels in the two input beams are highly coupled, forcing a compromise between detection of each species. The detection limit for NO was determined to be $10^{-15}$ mol/cm$^3$. This study was followed by one in which only NO was measured in the same flame environment. In this subsequent study, the NO detection limit was lowered to $10^{14}$ mol/cm$^3$. While the experimental setup for PS is less complex than ERE CARS, PS can be affected by collision rate in a manner similar to DFWM. Löffstedt et al. intend to study this dependence of intensity on pressure. Also, as with DFWM, PS has only one species selection criterion, allowing for extra species interference in the resulting signal.

1.4 Objectives

With the preceding review of the pertinent literature providing a perspective, the objectives of this thesis can now be presented. The first objective of these investigations was to improve the performance of a previously developed CARS method to allow for flow-property fluctuation measurements to be made. This was to be accomplished by replacing the CBDL with an MDL. The measurement accuracy and precision uncertainty of the new method were investigated in a pressure vessel and an underexpanded jet flowfield. The results of these experiments, which represent the first thorough attempt to lower the noise of a CARS method in a low-pressure, low-temperature environment, can be found in Chapter 3.

The second objective was to develop a theoretical model for ERE CARS spectra of NO. The details of this treatment and the comparison with the previously acquired data can be found in Chapter 4. This new model forms the basis for the first generation of ERE CARS
theoretical spectra of NO, allowing for new applications of ERE CARS to combustion events and hypersonic flowfields.
2 Equipment and Facilities

The facilities and equipment described herein are located in the Gas Dynamics Laboratory at the University of Illinois at Urbana-Champaign, with the exception of the ERE CARS experiments which were performed at Texas A&M University. A review of the CARS system is presented, including the traversing capabilities. An overview of the Texas A&M ERE CARS system is then given. Afterwards, the flowfields to be investigated are discussed. The compressor and air storage facilities that supply high-pressure air to the underexpanded jet are detailed in the thesis of Shaw.125

2.1 MDL CARS System

A top view of the MDL CARS system is shown in Figure 2.1. On the right side of the figure is the Q-switched, injection-seeded, Nd:YAG laser (Continuum Powerlite 8010). The
Nd:YAG laser has a maximum pulse energy of approximately 800 mJ at a wavelength of 532 nm and a repetition rate of 10 Hz. The beam is turned such that it passes through a quarter wave plate and a Glan polarizer; these two optics comprise the power attenuation control for the rest of the CARS system. Following this, the beam is directed around the translation system, which will be discussed later. A beamsplitter separates 20% of the beam to provide the pump beams in the CARS process ($\nu_{p1}$ and $\nu_{p2}$ in Figure 1.1). The pump beam is directed through a delay line so that it arrives at the probe volume coincident in time with the Stokes beam. This is the reason for the winding path in the upper left-hand corner of the figure. Shortly before the beam is directed to the probe volume, it is split equally using a 50% beamsplitter to form the two necessary pump beams.

The remaining 80% of the initial 532-nm beam is used to pump the MDL. The MDL is derived from the Ewart design, modified to include an additional amplification stage. Rhodamine 640 perchlorate dissolved in methanol provides the organic dye solution used as the gain medium. Dye concentration studies were performed that resulted in a solution of 17 mg and 30 mg, respectively, in 400 ml of methanol used in the “oscillator” and amplifier. The MDL emits coherent light in the range of 607 nm at approximately 25 mJ of energy per pulse. The MDL beam is the source for the Stokes beam in the CARS process ($\nu_S$ in Figure 1.1). The Stokes beam is then directed into the probe volume. Note that the last turn made by each of the three input beams is performed by fixing a prism to a high-precision mirror mount (Newport 610 Series) to allow for fine tuning of the probe volume alignment. The timing of the three input beams is checked at this point in the system using a fast
photodiode and oscilloscope to ensure that all beams reach the probe volume within 1 ns of each other.

The path of the beams through the traversing system is shown in Figure 2.2. The traversing system is based on an earlier, successful design, and has a position repeatability under 5 µm in each direction. In order to maintain beam alignment during translation, movement must occur along the path of beam propagation. For example, considering the beam propagation into the translation system as shown in Figure 2.1, the first stage (Parker Hannifin 424012) is required to move left-to-right. Returning attention to Figure 2.2, all three beams are turned 90° using one large prism attached to the first stage and directed towards the next stage (Parker Hannifin 412012). The beams are then projected upwards to the initial vertical stage (Parker Hannifin 404300) with a prism attached to the second stage. Once on the initial vertical stage, the beams are focused at the probe volume (see

![Figure 2.2: Translation system for CARS probe volume](image-url)
Figure 1.2) using a 250-mm focal length lens. The beams, including the newly generated CARS signal, are collimated using another 250-mm lens attached to an identical second vertical stage. Using two vertical stages allows for a test section to be placed between them. Once the system is aligned, the motion of the two vertical stages is coupled so that they move simultaneously. The three input beams are now directed into beam dumps to reduce scattered light in the CARS signal channel. The CARS signal follows a path similar to the input beams as it leaves the translation system. Specially designed mirrors (CVI TLM2-475) are substituted for the prisms in the CARS signal channel.

Returning to Figure 2.1, the CARS signal is then directed to the 1.25-m spectrometer (SPEX 1250M). A 100-mm lens focuses the CARS signal onto the entrance slit. The spectrometer design is based on a single-pass Czerny-Turner configuration\textsuperscript{127} using a 3600-groove/mm holographic grating. This configuration provides a theoretical resolution of $\Delta \omega \approx 0.09 \text{ cm}^{-1}$. At the exit of the spectrometer, a relay lens pair disperses the signal onto the CCD (Roper Scientific NTE/2500PB). The CCD is a 2500 x 600 pixel, 16 bit array that provides on average one count for every 3.5 incident photons. The relay lens pair consists of 28-mm and 210-mm focal length Nikon camera lenses focused at infinity, resulting in a magnification factor of 7.5. The image of the CARS signal is captured and binned on the CCD chip to provide the CARS spectra that will be analyzed, as discussed in Section 1.2.3.

2.2 ERE CARS System

A schematic of the Texas A&M ERE CARS system is displayed in Figure 2.3. The system begins with two Q-switched Nd:YAG lasers (Continuum 8010, 9010), with output characteristics similar to that described above in the CARS setup. The lasers are externally
triggered by a delay generator (Stanford Research Systems DG535). The Nd:YAG laser at the bottom of the figure is configured to output a frequency tripled beam at 355 nm, which is used to pump the first narrowband dye laser (Continuum ND6000). Using LD490 laser dye, this laser converts the 355-nm beam into a 472-nm beam with an approximate linewidth of 0.1 cm⁻¹. The output from this laser is then frequency doubled to 236 nm using a β-BBO crystal in an INRAD AutoTracker III, providing the second or UV pump beam with a linewidth of ∼ 0.3 cm⁻¹ for the ERE CARS process. The output from the second Nd:YAG, which lases at 532 nm, is split into two beams using a 30% beamsplitter. The transmitted beam is used to pump the second narrowband dye laser (Continuum ND6000), which employs R610 laser dye. This results in the Stokes beam centered at 591 nm with a linewidth of 0.08 cm⁻¹. The remaining portion of the 532-nm beam is directed into the

Figure 2.3: Top view of the ERE CARS system
phase-matching geometry as the first pump beam. All three input beams pass through half-wave plates, and the first pump beam and the Stokes beam pass through polarizers. This provides the polarization scheme shown in Figure 2.4, which was utilized to suppress the effects of the nonresonant background. The length of the Stokes beam in Figure 2.4 differs from the other beams only to avoid confusion with the overlap of the identical first pump beam polarization. The three input beams are focused at the probe volume using a 300-mm focal length lens. The probe volume is formed near the rear window of a static gas cell filled with a mixture of NO and N₂. The input beams, along with the newly formed ERE CARS signal beam, are recollimated using another 300-mm lens. Because they are no longer needed, the Stokes and the first pump beam are directed into beam dumps, and the UV pump beam is directed into an energy meter to monitor the shot-to-shot power fluctuations. The ERE CARS signal, formed at 226 nm, is passed through an α-BBO polarizer oriented

Figure 2.4: Polarization scheme for the suppression of the nonresonant background
as shown in Figure 2.4, to reject the nonresonant portion of the signal. Following this, the
beam is then passed through an aperture and a set of filters (70% T 226 nm, 1% T 236 nm)
to reduce the effects of scattered light. These filters are 45° full reflectors at 213 nm (CVI)
and are used here at 0° incidence. Finally, the signal beam is focused onto the slit of a
0.5-m SPEX spectrometer using a 100-mm focal length lens. The spectrometer is used to
reduce scattered light into the detector. The ERE CARS signal intensity is detected with
a solar-blind photomultiplier tube (PMT) (Hamamatsu R166), and the resulting voltage is
acquired by employing gated integrators (Stanford Research System SR240). This voltage
is then recorded using a PC.

2.3 Gas Cell

An optically-accessible gas chamber was modified for use in this study. As seen in Fig-
ure 2.5, air, argon, and propane can fill the gas cell. Air is used to provide the constant
pressure levels in benchmarking the CARS technique. Because they contain no resonant
transitions in the frequency range being probed, argon and propane are used to obtain non-
resonant signals. Argon is also employed in the propane line as a nonoxidizing purge gas.
While a combustible mixture of air and propane is never intended to occupy the gas cell,
safety features have been installed in the event that such a mixture occurs. Breakdown at
the probe volume due to high laser power can provide the energy to ignite a combustible
mixture. Therefore, a routine safety procedure for switching between air and propane has
been established. Furthermore, flashback arrestors were placed in the air and propane lines,
and a pressure snubber is inline to the vent. The vent is connected to the building exhaust.
To avoid surpassing the maximum operating pressure of the chamber (estimated at 250 psi),
a 100 psi check valve was installed. In addition to pressurizing the test gases, the cell can be evacuated using a vacuum pump. This allows subatmospheric pressure levels to be investigated with the CARS system. Pressure is monitored using digital pressure transducers: a 1000 torr absolute transducer (MKS 722A13TCE2FK) for subatmospheric studies, and a 5000 torr absolute transducer (MKS 722A53TCE2FK) for above-atmospheric studies. Both transducers are accurate to 0.5% of the pressure reading.

### 2.4 Underexpanded Jet

The underexpanded jet facility can be seen in Figure 2.6. It is similar in design to that used in previous investigations.\(^{35,37}\) Dry, high-pressure air is supplied to the horizontally mounted inlet pipe at approximately 120 psig. A 4-in. control valve (Fisher EK-14/40) mounted far upstream and a 1-in. ball valve at the start of the inlet pipe are employed.

![Diagram of gas cell facility](image)

**Figure 2.5: Gas cell facility**
to control the stagnation pressure. The stagnation pressure and temperature are monitored using the 5000-torr transducer described earlier and a hermetically sealed thermistor (Omega ON-920-4007), respectively. The nozzle exit is 10 mm in diameter, and contracts linearly from the inner pipe diameter of 19.3 mm. The area reduction, which occurs over 101.6 mm, results in an angle of contraction of 2.61°. The jet can be operated over a range of $M_j$ up to $\sim 2$ and $M_c$ up to $\sim 0.86$.

![Figure 2.6: Underexpanded jet facility](image)
3 Modeless Dye Laser \(N_2\) CARS Investigation

3.1 Introduction

This study examines modifications of the high-resolution \(N_2\) CARS method developed by Woodmansee et al.\(^6\) (see Section 1.2.5) to extend its capabilities to measure mean and fluctuating thermodynamic properties. To reduce the effects of mode noise, an MDL, based on the design of Ewart,\(^{28}\) has been implemented as the new source for the Stokes beam. While the results in the literature indicate that the inclusion of the MDL should improve the single-shot precision of the method,\(^{29–31,33}\) these studies were performed at combustion temperature levels and not at the thermodynamic conditions considered in this study. As noted in Section 1.2.4, these studies showed a decrease in percentage standard deviation of temperature down to as low as 1.25%.\(^{29}\) While these types of percentage standard deviations are low enough to resolve a typical probability density function (pdf) in a turbulent combustion environment,\(^8\) this precision may not be enough for measurements in a turbulent, supersonic flowfield. It should be noted that the above percentage standard deviation corresponds to an absolute standard deviation of 15 K, which is a significant level for a typical supersonic flow where mean temperature levels of the order of 100 K occur. Since there is no indication as to whether the above success in noise reduction will scale in an absolute or percentage sense, an estimate for how the MDL will perform at supersonic conditions cannot be made. This is due to the fact that there are no investigations in the literature known to the author that have employed an MDL in a CARS experiment focused on measurements.
in a low-pressure, low-temperature, supersonic environment. In addition to this, there is no manner of correlating the above decrease in standard deviation of temperature to one for pressure, which is of the most interest in this study. Therefore, the following results represent a unique perspective on the performance of an MDL CARS system in a non-combustion environment. The capabilities of the method were benchmarked in two well-defined experiments. First, the capability of making fluctuating pressure measurements were assessed in a gas cell. Then, measurements were obtained along the centerline of an underexpanded jet flowfield. The results of these investigations were compared to previous work and used to determine the measurement accuracy and precision of the new CARS method.

3.2 Spectra-Fitting Procedure

When analyzing data for the pressure vessel, the final answer is known a priori from the transducer measurements. However, in flowfield investigations, the pressure and temperature measured are not known before the spectra are fit. This can present a problem, as CARSFIT requires an initial value for all variables. If an individual spectrum is of poor quality or the specified initial values of the fit are too far from the true conditions, CARSFIT may return the initial values as an indication that a fit could not be made. Therefore, a procedure was developed to determine if the returned values were an accurate prediction of pressure and temperature or if the spectrum should be discarded. This helps to eliminate the effects of a starting-point bias. The procedure was tested on sample pressure vessel data to determine its effectiveness.

The process begins by initially discarding any spectra that exhibited a saturated CCD pixel or contained a low integrated signal intensity ($I_{int} < 55$ counts $\cdot$ cm$^{-1}$). The remaining
spectra are fit starting from three unique points. If two of the three fitting results are within a set percentage of each other, the spectrum with the lowest chi-squared, goodness-of-fit value is kept, regardless of the prediction of temperature or pressure. However, if all three fitting results are separated by more than this set percentage, the spectrum is discarded. For the pressure vessel, for which only pressure is allowed to float, each spectrum was started at 70%, 100%, and 130% of the transducer-measured pressure and was retained if two of the results were within 10% of each other. In the case of a flowfield where both pressure and temperature are allowed to float, the pressure and temperature are started at the three different starting points, based on either theoretically estimated values or data extracted from computational results, and must simultaneously meet the same criterion for both pressure and temperature for the spectrum to be kept.

To demonstrate how the spectra-fitting process works, an example is shown in Figure 3.1. Because CARSFIT compares the square root of intensity in the least-squares fitting process, these and all subsequent spectra will be plotted as such. Two time-averaged spectra are shown with the corresponding results from the fits starting from the three different starting points. Note that pressure is reported to three decimal places for demonstration purposes only, this is not an implied statement of accuracy, and all further reports of pressure will be given only to two decimal places. The results for Spectrum 1 are shown in Figures 3.1(a), (c), and (e), with the results for Spectrum 2 in Figures 3.1(b), (d), and (f). It is somewhat difficult to discern the differences between these experimental spectra, as the only noticeable differences between Spectra 1 and 2 are found surrounding the Q(2) peak in the bandhead, which is labeled in Figure 3.1(a). As seen in Figure 3.1(a), there is a small shoulder on the
Figure 3.1: Comparison of the spectra-fitting results for two spectra from three starting points (a) Spectrum 1, 70%, (b) Spectrum 2, 70%, (c) Spectrum 1, 100%, (d) Spectrum 2, 100%, (e) Spectrum 1, 130%, and (f) Spectrum 2, 130%
right side of Q(2) and an extra peak, perhaps Q(3), between Q(2) and Q(4), also labeled in Figure 3.1(a). While these differences may seem slight to the observer, they result in significantly different results in predicted pressure. Notice that for Spectrum 1, the predicted pressure levels resulting from the three starting points differ by more than 10%, and therefore Spectrum 1 is discarded. However, there is excellent agreement between the results for Spectrum 2 when the fits were started at 100% and 130% of the true condition. Therefore, Spectrum 2 is kept, and the results from the 100% starting point, $P_{CARS} = 0.910$ atm, will be used, as the corresponding chi-squared value$^{19}$ is the lowest.

Using 70% and 130% starting points for comparison considerably relaxes the required accuracy in estimating the conditions at the probe volume for use as initial values in the spectra-fitting procedure. However, this advantage in turn brought about the concern that CARSFIT may not be capable of starting this far from the true condition and still be able to return an accurate prediction. Hence, a test was performed on a small set of time-averaged pressure vessel spectra, which were selected because of their excellent quality. Each pressure level is represented by 100 spectra, and these ensembles were fit with 70% and 130% starting points, as well as 90% and 110% starting points for comparison. As seen in Figure 3.2, the ensemble-averaged pressure levels resulting from both sets of starting values are in excellent agreement over the pressure range investigated. In addition, Figure 3.3 shows the relatively good agreement between the standard deviations of the time-averaged ensembles for each case. These results verify the integrity of the newly developed spectra-fitting procedure and lend considerable confidence to measurements obtained with this method.
Figure 3.2: Comparison of the mean spectra-fitting procedure results for different starting points.

Figure 3.3: Comparison of the standard deviation of the spectra-fitting procedure results for different starting points.
3.3 Pressure Vessel Results

The current results represent 100 time-averaged (1 sec exposure, 10 laser shots) and 500 single-shot measurements acquired in the gas cell at 25 pressure levels in the range from 0.1 to 4.0 atm. Figure 3.4 displays time-averaged CARS spectra obtained in the gas cell at 0.1, 0.5, 1.0, 2.0, 3.0, and 4.0 atm and 292 K along with the theoretical results from CARSFIT. For reference, each spectrum is labeled with the transducer pressure, $P_{TRAN}$, and the predicted CARSFIT pressure, $P_{CARS}$.

All spectra in Figure 3.4 display excellent agreement between data and theory. Not only are the peak intensities of each transition generally well matched by the theory, but the linewidth and lineshape are as well. Of importance is the fact that these, and all theoretical spectra presented herein, were generated at a resolution of 0.10 cm$^{-1}$, reinforcing the high-resolution nature of the experimental spectra. Notice that the linewidths of the transitions broaden and interfere as pressure increases, denoting the competing effects of collisional broadening and collisional narrowing. It is these features that give the technique its pressure sensitivity. This sensitivity is evident, as all the spectra produced accurate predictions of the transducer pressure.

The low signal level seen in Figure 3.4(a) for 0.1 atm is a cause for concern, as the intensity will drop to approximately one-tenth of this value for single-shot spectra. Because the experimental setup closely resembles a previous setup$^6$ in all ways aside from the MDL, which is used in place of a CBDL, the MDL is considered the most probable cause for this low signal level. While the total average power out of the MDL is 30% lower than previous experiments with the CBDL$^6$, this does not completely account for the drop in
Figure 3.4: Comparison of time-averaged experimental CARS and theoretical CARSFIT spectra from the pressure vessel for (a) 0.1 atm, (b) 0.5 atm, (c) 1.0 atm, (d) 2.0 atm, (e) 3.0 atm, and (f) 4.0 atm.
signal level. The low signal level is most likely attributed to the decrease in spatial beam quality and transverse electromagnetic mode (TEM) structure provided by the MDL as compared to the previous CBDL, which employed an oscillator cavity. While it is known that the CBDL typically does not lase in the lowest order TEM mode, TEM\textsubscript{00}, which typically provides the strongest CARS signal, and even though the TEM modes are nonuniformly distributed throughout the spatial cross-section of the CBDL beam\textsuperscript{24}, the CBDL still provides a better transverse mode structure and spatial beam quality than the MDL. Note that these transverse modes are a separate, but not necessarily independent, phenomenon from the axial modes that cause axial mode noise. This further decline in overall beam quality from the CBDL to the MDL lowers the efficiency at which the CARS signal is generated in the nonlinear wave-mixing process. It was hoped during this study that this decrease in signal strength would be more than offset by the reduction of mode noise in single-shot spectra.

A comparison of the time-averaged CARS-predicted pressure and transducer pressure over the entire range is shown in Figure 3.5(a), with Figure 3.5(b) focusing on the subatmospheric portion of the results. Included in this figure are the results of a previous study\textsuperscript{36}, which is used as a comparison for the current technique. Here, and in all plots, the uncertainty bars denote the standard deviation of the pressure levels obtained from the ensembles of spectra at each pressure level. Above 1.0 atm, the current results compare very well with the transducer values with an accuracy slightly better than for the previous study. The deviation between the CARS and transducer values seen at 3.4 atm is considered to be an isolated incident associated with a temporary loss in single-mode operation of the Nd:YAG laser that was not immediately noticed. As is seen in Figure 3.5(b), the accuracy of the
Figure 3.5: Comparison of time-averaged pressure vessel results to transducer values and results of Woodmansee\textsuperscript{36} (a) full range and (b) low-pressure subset
technique decreases for pressure levels below 1.0 atm, with CARS values that are consistently below the transducer values. Because the transducer pressure for the subatmospheric region was monitored with different transducers and the results were similar, it is unlikely that this loss of accuracy is due to a zero offset with the transducer. In addition, the issue is not attributable to an inaccurate spectral instrument function, as the one employed in the convolution of the theoretical spectra was varied to provide the best comparison between experimental and theoretical spectra and the most accurate mean results. The decrease in accuracy is therefore most likely the indirect result of the decrease in signal level at these lower molecular number density levels. This discrepancy is unfortunate, as the results for pressure levels above 1.0 atm indicate that the inclusion of the MDL in the system improves the accuracy of the technique.

As a preliminary study of the precision of the technique, the standard deviations presented as uncertainty bars in the previous figure are plotted in Figure 3.6 over the entire pressure range and compared to previous results. The standard deviation normalized by the mean pressure is also presented in Figure 3.7. Because these are standard deviations of time-averaged spectra, they cannot be considered as an indication of the precision uncertainty of the method. However, it is promising that the modified method with the MDL produces similar standard deviation results for pressure levels above 1.0 atm. Once again, the data point at 3.4 atm is considered anomalous, and its increased standard deviation is not indicative of the method’s performance. The increase in standard deviation below 1.0 atm compared to the previous results is not unexpected, since the decrease in signal
strength degrades current system performance at low pressure. Additionally, it is believed that the previous measurements were affected by the starting-point bias discussed earlier.

Figure 3.8 presents the number of spectra that were kept at each pressure level using the new spectra-fitting procedure described earlier. The dropoff seen at low and high pressure levels is expected. At low pressure, the low signal strength produces spectra that cannot be fit by CARSFIT. The effects of collisional broadening at high pressure reduce the sensitivity of the technique to changes in pressure, and this difference in spectral behavior also reduces the number of spectra that can be fit. Aside from those effects and the obvious problem discussed previously at 3.4 atm, nearly all of the time-averaged spectra obtained were successfully fit from at least two different starting points with best-fit pressure values falling within a prescribed tolerance. Not only were these spectra fit successfully, but in addition, each data

![Graph](image)

Figure 3.6: Comparison of time-averaged standard deviation results from the pressure vessel to those of Woodmansee\textsuperscript{36}
Figure 3.7: Comparison of time-averaged normalized standard deviation results from the pressure vessel to those of Woodmansee\textsuperscript{36}

Figure 3.8: Number of time-averaged pressure vessel spectra kept out of 100 in each data set
set provided accurate mean values, as seen in Figure 3.5. This result confirms the ability of the technique to provide accurate predictions when the actual conditions at the probe volume are not known.

Example spectra from the single-shot measurements in the pressure vessel are shown in Figure 3.9 at the same pressure levels as in Figure 3.4. As expected from the time-averaged spectra at 0.1 atm, low signal levels are evident in Figure 3.9(a). Even with the low signal strength, the single-shot spectra generally match closely with the best-fit theoretical spectra from CARSFIT, except at the lowest pressure level of 0.1 atm.

The mean pressure results from the single-shot spectra are presented in Figure 3.10. For comparison, the results of the previous study are again included. As seen with the mean time-averaged results, the accuracy of the technique is improved compared to the previous experiments for pressure levels above 1.0 atm. Figure 3.10(b) focuses on the subatmospheric pressure levels, where the trend for the time-averaged measurements is again exhibited by the single-shot results. In particular, the accuracy of the mean single-shot measurements is generally poorer than that of the previous experiments with most of the CARS pressure levels falling below the transducer values. As discussed above, the current technique suffers from low signal levels in this region, which is the probable cause of the errors in predicted pressure.

Figure 3.11 displays the precision of the technique by plotting the standard deviations of the single-shot measurements for the corresponding pressure level. This plot is accompanied by Figure 3.12, where the normalized standard deviations are shown. In comparison to the previous study, the increased accuracy of the technique above 1.0 atm is complemented by
Figure 3.9: Comparison of single-shot experimental CARS and theoretical CARSFIT spectra from the pressure vessel for (a) 0.1 atm, (b) 0.5 atm, (c) 1.0 atm, (d) 2.0 atm, (e) 3.0 atm, and (f) 4.0 atm
Figure 3.10: Comparison of mean single-shot pressure vessel results to transducer values and results of Woodmansee\textsuperscript{36} (a) full range and (b) low-pressure subset
Figure 3.11: Comparison of single-shot standard deviation results from the pressure vessel to those of Woodmansee\textsuperscript{36}

Figure 3.12: Comparison of single-shot normalized standard deviation results from the pressure vessel to those of Woodmansee\textsuperscript{36}
a small but discernible increase in precision as well. The subatmospheric trend seen in the standard deviations of the time-averaged results is also duplicated by the single-shot data. While the previous technique displayed better precision in this region, it is believed that those results may have been influenced by starting-point bias, as reported above.

As a final note, the number of spectra kept from the ensemble of 500 single-shot spectra at each pressure level is presented in Figure 3.13. Because the technique loses pressure sensitivity as pressure increases, there is a dropoff in the number of spectra kept above 2.0 atm, similar to the trend seen in the time-averaged measurements. Still, the large number of spectra kept confirms the ability of the technique to provide spectra that can be fit independently of the initial value for the least-squares fitting process.

Figure 3.13: Number of single-shot pressure vessel spectra kept out of 500 in each data set
Regardless of the reason for decreased precision of the single-shot measurements below 1.0 atm, these results indicate that meaningful fluctuation measurements may not be obtainable in a supersonic flowfield with this technique due to low signal strength at low molecular number density. In typical supersonic flowfields, regions of low pressure are often accompanied by low to moderate temperature. While this may correspond to low molecular number density depending on the specific combination of pressure and temperature, previous experiments have shown improved performance of the CARS technique at the low temperature levels encountered in an underexpanded jet. This improved performance is due to the increased signal strength encountered at low temperature levels. This experience provides the motivation to attempt the underexpanded jet measurements described in the following section.

3.4 Underexpanded Jet Results

In this investigation, 50 time-averaged (1 sec exposure, 10 laser shots) and 250 single-shot spectra were obtained at nine locations along the centerline from the jet exit to just beyond the Mach disk. Figure 3.14 displays time-averaged spectra at centerline positions corresponding to the jet exit, halfway to the Mach disk, just upstream of, and just downstream of the Mach disk ($z/d_j = 0.019, 0.870, 1.508, \text{ and } 1.579$) along with the fitted theoretical spectra. Included in the plots are the CARSFIT ($P_{CARS}$ and $T_{CARS}$) and CFD ($P_{CFD}$ and $T_{CFD}$) predictions of pressure and temperature for comparison. As with the pressure vessel results, the experimental spectra exhibit the same spectral behavior as the theoretical spectra. Special attention is drawn to the differences between Figures 3.14(c) and 3.14(d), where the large differences in thermodynamic conditions upstream and downstream of the Mach disk
are readily apparent in the spectra. These spectra display the sensitivity of the technique to these differing thermodynamic conditions. Moreover, for all of the spectra, there is a close correlation between the CFD calculations and experimental measurements of temperature and pressure. In general, the CFD calculations and experimental measurements of pressure are in closer agreement than is the case for temperature. The increased discrepancy in temperature and pressure predictions seen in Figures 3.14(c) and 3.14(d) can be accounted

![Data vs Theory Graphs](image)

Figure 3.14: Comparison of time-averaged experimental CARS and theoretical CARSFIT spectra along the centerline of the underexpanded jet at $z/d_j$ = (a) 0.019, (b) 0.870, (c) 1.508, and (d) 1.579
for by considering the unsteady position of the Mach disk, which will add to experimental uncertainty at these locations, along with the inability of the CFD to accurately capture the shock location.

The mean results from the time-averaged spectra at all centerline locations examined are compared to previous measurements\textsuperscript{36} and the CFD results\textsuperscript{128} in Figure 3.15. For these results to be meaningful, the flow must be in rotational equilibrium at all measurement locations. Calculations show that for the worst case, \textit{i.e.}, the rapid temperature change across the Mach disk, a molecule will undergo over 400 collisions as it proceeds through the compression, ensuring equilibrium. It is clearly seen in Figure 3.15 that there is a substantial improvement in agreement between the current CARS measurements and CFD results for pressure levels above 1.0 atm. This result is expected from the pressure vessel measurements. There is a small but consistent discrepancy between the CFD and experimental mean temperature results upstream of the Mach disk, with the CARS results always being slightly lower. There are two possible reasons for this offset. First, the stagnation temperature in the current experiment (290 K) was slightly lower than for the previous study (296 K). Second, the previous nozzle used a contraction angle of 4.1°, almost twice the current angle, thus providing slightly different flow conditions at the jet exit. Overall, though, the current time-averaged measurements match well with the CFD predictions from the jet exit through the Mach disk.

The standard deviation of the time-averaged measurements is shown in Figure 3.16, along with those from the comparison study.\textsuperscript{36} There is a noticeable increase in standard deviation in both pressure and temperature as compared to the previous work. The most plausible
Figure 3.15: Comparison of time-averaged centerline results to those of Woodmansee\textsuperscript{36} and CFD results (a) pressure and (b) temperature
Figure 3.16: Comparison of time-averaged standard deviation centerline results to those of Woodmansee\textsuperscript{36} (a) pressure and (b) temperature
explanation for this increase is due to the low signal strength of the current technique and the possibility of a starting-point bias in the previous work. Adding another variable to the least-squares fitting process further exposes the low signal strength problem of this method. This is again demonstrated in Figure 3.17, where the number of spectra kept drops severely in the region of low molecular number density just upstream of the Mach disk. Note that the number of spectra fit is included in this plot, as some of the spectra were discarded before fitting because of saturated pixels or low signal conditions.

Turning to the single-shot centerline results, Figure 3.18 shows sample spectra at the same locations as in Figure 3.14 for the time-averaged measurements. Aside from a slight increase in noise level, all the spectra exhibit the same excellent agreement between data and theory that was seen in the time-averaged spectra. In addition, the predicted pressure and temperature levels agree relatively well with the CFD values, with the discrepancy in

![Figure 3.17: Number of time-averaged centerline spectra fit and kept](image-url)
temperature predictions in Figures 3.18(c) and 3.18(d) likely occurring for the same reasons as discussed with respect to the time-averaged spectra in Figure 3.14.

Ensemble-averaged pressure and temperature values from the single-shot data set at all centerline locations examined are presented in Figure 3.19, which includes the previous results and CFD predictions for comparison. The current technique again displays better accuracy at high pressure and good agreement with the CFD results through the first Mach

![Figure 3.18: Comparison of single-shot experimental CARS and theoretical CARSFIT spectra along the centerline of the underexpanded jet at $z/d_j = (a) 0.019$, (b) 0.870, (c) 1.508, and (d) 1.579](image-url)

86
Figure 3.19: Comparison of mean single-shot centerline results to those of Woodmansee\textsuperscript{36} and CFD results (a) pressure and (b) temperature
disk. For temperature, a similar slight offset of the CARS measurements below the CFD predictions as was seen in the time-averaged results exists.

The standard deviation of the current and previous\textsuperscript{36} single-shot measurements, which is representative of the precision of the method, is plotted in Figure 3.20. Because there is low turbulence intensity along the centerline of the jet before the Mach disk, the standard deviation results here should represent the baseline detection limit of fluctuations nearly exactly. As expected from the time-averaged results, the technique displays an increase in standard deviation as compared to the previous technique, most likely due to the decreased signal strength of the current method. This result is confirmed in Figure 3.21, since approximately half of the experimental spectra were discarded at each location using the spectra-fitting procedure described earlier. As with the time-averaged spectra results, this demonstrates that the method has difficulty producing high signal strength, high quality spectra that can be fit from multiple starting points.

### 3.5 Summary

Reviewing the comparison between the previous and current work, several conclusions can be drawn. While for some conditions, the new method outperforms the previous one, the new method is hindered greatly by a drop in signal strength at other conditions. In particular, the new method provides increased accuracy and improved precision uncertainty above 1 atm, as compared to the previous work. Turning to the subatmospheric portion of the pressure vessel results, though, the new method demonstrates decreased accuracy and increased precision uncertainty. For a representation of the new technique’s capabilities at thermodynamic conditions typical of supersonic flows, the underexpanded jet results display the current
Figure 3.20: Comparison of single-shot standard deviation centerline results to those of Woodmansee\textsuperscript{36} (a) pressure and (b) temperature
method’s ability to generate ensembles of experimental spectra with accurate mean values. Similar to the subatmospheric pressure vessel results, the measurements indicate an increased estimate of precision uncertainty for these thermodynamic conditions.

As many supersonic flowfields involve thermodynamic conditions similar to those found in the underexpanded jet, these results infer that the best technique for measurements therein would be the previously developed method with the CBDL. This conclusion does not detract from the results of the current investigation. As shown in Figure 3.11, the precision uncertainty of this method can be lowered, particularly at pressure levels above 1 atm, confirming that the MDL does have a beneficial effect on the noise level of the technique. Therefore, as outlined in Chapter 5, further investigations that examine different sources for the Stokes beam should be performed. If a Stokes-beam source can be found that provides an increased

![Figure 3.21: Number of single-shot centerline spectra fit and kept](image)
CARS signal level, the success shown in the current results above 1 atm might be extended throughout the entire range of interest.
4 ERE CARS Modeling Results

4.1 Introduction

The following results represent the first known development of a theoretical model for NO ERE CARS spectra. The model was incorporated into the framework of CARSFIT, a reliable and widely accepted spectral modeling program. Two different forms of the model were programmed to provide means of fitting the two types of experimental data that have been obtained. During the laboratory investigation, either the Stokes or the second (UV) pump frequency was scanned to produce a CARS spectrum. Only one of these frequencies was scanned at a time, therefore generating two unique forms of spectra that must be modeled. These types of spectra will be distinguished as “Stokes scans” or “UV scans” to indicate which frequency was varied. All data presented herein were obtained by Hanna et al. at Texas A&M University.

Once the development of the model was completed, it was applied to both forms of the spectra. The results of these comparisons provides insight into the physics of the ERE CARS process and into the potential of the technique for trace species measurements. The accuracy of the assignment of spectral constants discussed in Section 1.3.4 can also be confirmed.

4.2 Model Development

In order to discuss the finer details of the numerical model and the resulting spectra, it is first necessary to review the energy-level diagram that represents the spectroscopy of the ERE CARS experiments. This diagram is shown in Figure 4.1 for the $X^2\Pi_{1/2}$ state of NO. Only the Raman Q-branch was probed during the study; therefore, the S- and O-branches are not included in the diagram. In accordance with the selection rules for Raman
transitions, there are two distinct Raman Q-branch transitions that can occur, corresponding to the different parity of the lower rotational levels. To distinguish between parity levels, the transitions that couple negative parity levels are shown with solid lines, whereas those that couple positive parity levels are shown with dashed lines. Note that the Raman transition

Figure 4.1: Energy-level diagram of the ERE CARS process for the $X^2\Pi_{1/2}$ ground electronic state of NO
occurs through a virtual state, as only the UV pump beam is in electronic resonance. Once the molecule is excited to the first vibrational state, there are three electronic transitions for each parity that will excite the molecule to the $A^2\Sigma$ state. Finalizing the process, each of these electronic transitions is matched with corresponding electronic transitions returning the molecule to the ground electronic and ground vibrational state where it began. A similar schematic could be shown for the $X^2\Pi_{3/2}$ state. The dual-pump scheme shown in Figure 4.1 is in contrast to most previous experimental work in the literature, in which both pump beams are in the UV and the process is in or near triple resonance. In this case, the Raman resonance process and the electronic resonance process are separated completely, allowing for the enhancement to be distinguished during the CARS process. This also significantly simplifies the theoretical model, as discussed below.

To distinguish each transition, a notation is introduced here that is similar to that seen in the ERE CARS literature. The notation will begin by listing the Raman transition, which in this case is always a Q-branch, with a subscript to denote which ground $\Pi$ state that the molecule is in. This will be followed by listing the final electronic transition that occurs based on the notation of Mavrodineanu and Boiteux. After the transition notation, the value of J in the ground state will be listed in parentheses. Therefore, the processes involving the rightmost and second-to-rightmost transition in Figure 4.1 would be denoted by $Q_{1/2}R_{2}(1.5)$ and $Q_{1/2}P_{Q12}(1.5)$, respectively.

Each of the above twelve processes can now be accounted for in the model according to Equation 1.21, which is reproduced here for convenience:
\[
\chi_{\text{CARS}}(\omega_{\text{CARS}} : \omega_{p1}, -\omega_S, \omega_{p2}) = \frac{N}{\hbar^2} \mu_{p1,ac}\mu_{S,cb}\mu_{p2,bd}\mu_{\text{CARS,da}} \cdot \\
\sum_{a,b,c,d} \left\{ \left( \frac{1}{\omega_{ba} - (\omega_{p1} - \omega_S) - i\Gamma_{ba}} \right) \left( \frac{1}{\omega_{da} - \omega_{\text{CARS}} - i\Gamma_{da}} \right) \right\} \cdot \\
\left[ \left( \frac{(\rho_{aa}^{(0)} - \rho_{cc}^{(0)})}{\omega_{ca} - \omega_{p1} - i\Gamma_{ca}} \right) - \left( \frac{(\rho_{bb}^{(0)} - \rho_{cc}^{(0)})}{\omega_{cb} - \omega_S - i\Gamma_{cb}} \right) \right] + \chi_{\text{NR}} \\
\right)
\]

(1.21)

As stated above, \(\omega_S \neq \omega_{cb}\), as the molecule passes through a virtual state during the Raman transition. Therefore, without an actual state \(c\), the line strengths \(\mu_{p1,ac}\) and \(\mu_{S,cb}\) can be dealt with in a different manner. In fact, because the first pump frequency and the Stokes frequencies are similar to the CARS experiment discussed in Chapter 3, this type of transition can be described using the formulation seen in Equation 1.10. Thus \(\mu_{p1,ac}\mu_{S,cb}\) is replaced by \(K_J\), or in this notation, \(K_{ab}\). Because \(\omega_S \neq \omega_{cb}\), the part of the denominator concerning this resonance in Equation 1.21 can be considered frequency-independent, and the term can be absorbed into the nonresonant background.\(^{81}\)

The effects of the resonance between \(\omega_{\text{CARS}}\) and \(\omega_{da}\) can then be considered using the dipole matrix element line strengths \(\mu_{p2,bd}\) and \(\mu_{\text{CARS,da}}\). Neglecting the Zeeman effect, these quantities can be related to the spontaneous emission coefficient as:\(^{130}\)

\[
\mu = \sqrt{\frac{3\epsilon_0\hbar \lambda^2 \lambda_{ji}^2 A_{ji}}{8\pi^2 G(J_j, J_i)}} \\
\]

(4.1)

where state \(j\) refers to the upper, excited state, and \(i\) refers to the lower, ground state, and \(G\) is the following function:\(^{130}\)
Using the above relations, Equation 1.21 can be now be rewritten as:

\[
\chi_{\text{CARS}}(\omega_{\text{CARS}} : \omega_p1, -\omega_S, \omega_p2) = \sum_{a,b,d} \frac{K_{ab\mu_p2,bd\mu_{\text{CARS}},da}}{(\omega_{ba} - (\omega_p1 - \omega_S) - i\Gamma_{ba})(\omega_{da} - \omega_{\text{CARS}} - i\Gamma_{da})} + \chi_{\text{NR}}
\]  

(4.3)

The remaining elements of Equation 4.3 that must be defined are the Raman shift \(\omega_{ba}\), and the linewidth \(\Gamma_{da}\). Recall that \(\Gamma_{ba}\) is given by Equation 1.27, and \(\omega_{da}\) is determined from LIFBASE as discussed in Section 1.3.5. The Raman shift can be calculated according to Equation 1.20, which can be recast using the standard notation:

\[
\omega_{ba} = \frac{E_b - E_a}{\hbar} = (G(v') + F_{v'}(J')) - (G(v'') + F_{v''}(J''))
\]

(4.4)

where the terms \(G(v)\) and \(F_v(J)\) can be written as:

\[
G(v) = \omega_e(v + \frac{1}{2}) - \omega_x^e(v + \frac{1}{2})^2 + \omega_y^e(v + \frac{1}{2})^3 + \cdots
\]

(4.5)

\[
F_v(J) = (B_e - \alpha_e(v + \frac{1}{2}) + \cdots)J(J + 1) - (D_e + \cdots)J^2(J + 1)^2 + \cdots
\]

(4.6)

Note that the above forms are abbreviated to only represent the molecular constants known for NO. The molecular constants used in the above relations were obtained as discussed in Section 1.3.5 and are listed in Table 4.1. It is important to note that the values listed in Table 4.1 for each \(\Pi\) state were interchanged from their designation in the source. This convention is also the reverse of the assignment stated elsewhere in the literature.\(^{104,109}\) It was found that the reassignment of the molecular constants to the opposite state was the only configuration that provided line positions in the theoretical ERE CARS spectra that
matched the data. By only performing studies with one species selection criterion, it would be difficult for the previous studies to discern which state is which. With the absolute dependence on the extra species selection criterion in ERE CARS, it is believed that the assignment of the ground states employed here is an accurate description, and that those in the literature are, in fact, reversed. In other words, the ERE CARS process employed here uses the electronic resonance to probe in detail the vibrational Raman spectrum.

The absorption linewidth, $\Gamma_{da}$, was calculated from the combination of the Doppler and collisional widths. The collisional width was approximated as:

$$\Gamma_{da,c} = 0.6P \tag{4.7}$$

where $\Gamma_{da,c}$ has units of cm$^{-1}$ and $P$ has units of atm. The above relation is an approximation to the work of Chang et al.\textsuperscript{131} and is in agreement with other studies in the literature.\textsuperscript{116,132}

The Doppler width for the electronic resonance transitions is $\Gamma_{da,D} = 0.1$ cm$^{-1}$.\textsuperscript{132} The total

<table>
<thead>
<tr>
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<th>$\Pi_{1/2}$</th>
<th>$\Pi_{3/2}$</th>
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<tbody>
<tr>
<td>$\omega_e$</td>
<td>1904.040</td>
<td>1904.204</td>
</tr>
<tr>
<td>$\omega_e \alpha_e$</td>
<td>14.100</td>
<td>14.075</td>
</tr>
<tr>
<td>$\omega_e \beta_e$</td>
<td>0.0110</td>
<td>0.0077</td>
</tr>
<tr>
<td>$B_e$</td>
<td>1.7201377</td>
<td>1.6720433</td>
</tr>
<tr>
<td>$\alpha_e$</td>
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<td>0.0182</td>
</tr>
<tr>
<td>$D_e$</td>
<td>0.000000054</td>
<td>0.00001023</td>
</tr>
</tbody>
</table>

Table 4.1: Molecular constants for NO; all values are in cm$^{-1}$
linewidth was then calculated as:

\[ \Gamma_{da} = \sqrt{\Gamma_{da,c}^2 + \Gamma_{da,D}^2} \quad (4.8) \]

Because the line strengths in Equation 4.3 are not of the same order of magnitude, specifically \( K_{ba} \gg \mu_{p2,bd} \mu_{CARS,da} \), a correction is necessary to alleviate potential problems during the convolution of the spectra. This was accomplished by considering the fact that Equation 4.3 should hold even when \( \omega_{CARS} \neq \omega_{da} \). Therefore, the equation was referenced to the case of degenerate pump beam frequencies, which is the case that Equation 1.9 is typically used for. This results in the final form of the polarization susceptibility used in the model:

\[
\chi_{CARS}^{\text{norm}}(\omega_{CARS}) = \frac{\sum_{a,b,d} \left( \frac{K_{ab} \mu_{p2,bd} \mu_{CARS,da}}{(\omega_{ba} - (\omega_{p2} - \omega_S) - \Pi_{ba})(\omega_{da} - \omega_{CARS} - \Pi_{da})} \right)}{\sum_{a,b,d} (\mu_{p2,bd} \mu_{CARS,da})} + \chi_{NR} \quad (4.9)
\]

where \( \omega_{ref} = \omega_{532} + \omega_{ba} \) represents the degenerate pump beam case, and \( \omega_{532} \) correlates to \( \lambda_{p2} = 532 \text{ nm} \).

These values and equations were then added as two new models to CARSFIT, one for Stokes scans and one for UV scans. Both models were based on an isolated line model, as opposed to the modified exponential gap model used in the CARS experiments. This method not only simplifies the calculations, but it also avoids the issue of generating exponential gap parameters for NO. The effects of the polarization scheme used in the experiments, shown in Figure 2.4, were not accounted for in the model to simplify the initial development.

### 4.3 Enhancement Factor

Because a primary advantage of employing ERE CARS over CARS is the increase in signal level, a parameter that quantifies this increase was developed as part of the study.
The concept relates the magnitude of Equation 4.9 when it is in electronic resonance to the case when $\omega_{CARS} = \omega_{ref}$. Therefore, the enhancement factor, $\beta(\omega_{CARS}, \omega_{ref})$, can be defined as:

$$
\beta(\omega_{CARS}, \omega_{ref}) = \frac{\chi_{CARS}^{\text{norm}}(\omega_{CARS} : \omega_{p1}, -\omega_{S}, \omega_{p2})}{\chi_{CARS}^{\text{norm}}(\omega_{ref} : \omega_{p1}, -\omega_{S}, \omega_{p1})}
$$

(4.10)

The enhancement factor can then be used to evaluate the gain from achieving electronic resonance against the added complexity of requiring a UV pump beam. Because it is an important parameter, the enhancement factor $\beta$ will be presented along with the theoretical spectral results in the following two sections.

4.4 UV Scan Results

The theoretical and experimental results for the case in which the Stokes frequency is held fixed and the UV pump frequency is scanned is discussed in this section. The theory will be compared to six experimentally acquired spectra. For each of these scans, the UV pump frequency was tuned over the approximate range of 42190 to 42400 cm$^{-1}$. The results will encompass fixed Stokes frequencies that correlate to Raman shifts between 1874.35 and 1876.06 cm$^{-1}$. Figure 4.2 shows the comparison between the theoretical and experimental spectra. The data were acquired at a pressure of 0.13 atm and a temperature of 292 K. The mixture in the gas cell was composed of 99.9% N$_2$ and 0.1% NO, i.e., 1000 ppm NO. The values listed in Figure 4.2 for the Stokes wavelength and Raman shift were the values used to generate the theoretical spectra and not the values recorded during the experiment. The discrepancy is most likely due to the fact that the Stokes wavelength was not measured external to the dye laser, but rather was obtained from the prediction of the dye laser software. The correction is of little concern, as it only amounted to a shift in wavelength of
Figure 4.2: Comparison of theoretical and experimental ERE CARS spectra for Stokes wavelengths of (a) 591.01 nm, (b) 591.02 nm, (c) 591.03 nm, (d) 591.04 nm, (e) 591.06 nm, and (f) 591.07 nm
approximately 0.05 nm. Of great importance is the fact that the shift was constant for each spectrum analyzed, thus reaffirming that the dye laser wavelength reading from the computer was simply offset from the true value. Additionally, the recorded UV pump wavelength had to be shifted by a consistent value of 0.01 nm, which is most likely attributable to the same cause as for the Stokes wavelength shift. It is noted that Figure 4.2(c) represents a higher-resolution scan than the others, which accounts for the increased number of data points shown.

As seen in Figure 4.2, there is excellent agreement between the theoretical and experimental spectra for all Raman shifts. The outstanding correlation of line positions confirms the reassignment of the molecular constants described in Section 4.2 to the opposite Π states of those in the literature. While there is generally a good match in linewidths, the theoretical spectra were generated using Stokes and UV pump linewidths of 0.2 cm$^{-1}$ and 6.0 cm$^{-1}$, respectively. These are wider than the estimated laser linewidths discussed in Section 2.2, especially for the UV pump beam. The need for these increased linewidths possibly indicates that a significant amount of saturation$^{15}$ or Stark broadening$^{16}$ occurred for both the Raman process $a \rightarrow b$ and the electronic process $b \rightarrow c$ (see Figure 1.6). Nevertheless, these results confirm that the model is capable of calculating theoretical spectra that are in good agreement with experimental spectra, and more importantly that the essential physics of the ERE CARS process are captured by the model.

The amplitude variation of the spectra seen in Figure 4.2 occurs because $\omega_{p1} - \omega_S$ is in resonance with different Raman Q-branch transitions. Table 4.2 lists the specific Raman resonances that are predominant in each spectrum. The Π$^{1/2}$ transitions correspond to the
peaks on the lefthand side of each spectrum, and the $\Pi_{3/2}$ transitions occur on the righthand side. As an example, the peaks in Figure 4.2(a) correspond to the following transitions from left to right: $Q_{1/2}P_{2}(8.5) + Q_{1/2}P_{12}(8.5)$, $Q_{1/2}Q_{2}(8.5) + Q_{1/2}R_{12}(8.5)$, $Q_{1/2}R_{2}(8.5)$, $Q_{3/2}P_{1}(9.5)$, $Q_{3/2}Q_{1}(9.5) + Q_{3/2}Q_{21}(9.5)$, and $Q_{3/2}R_{1}(9.5) + Q_{3/2}R_{21}(9.5)$. The last row in Table 4.2 shows that, in the case of Figure 4.2(f), the Raman shift is only in resonance with the $\Pi_{3/2}$ state. Therefore, there should only be transitions on the right side of the spectrum, as seen in the figure. The predicted relative intensities between the $\Pi$ states, i.e., right and left sides of the spectra, are not in perfect agreement. This is principally due to the decrease in the UV pump beam power during the scan, which is due to the short lifetime of the LD490 laser dye. The experimental spectra were normalized by dividing by the measured UV pump beam power, but this may not be an accurate normalization technique if the electronic resonance is saturated. The multimode character of both the Stokes and UV pump beams also induces significant noise in the ERE CARS spectrum. Additionally, the

<table>
<thead>
<tr>
<th>Figure</th>
<th>$Q_{1/2}$</th>
<th>$Q_{3/2}$</th>
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<tr>
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</tr>
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<td>4.2(b)</td>
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</tr>
<tr>
<td>4.2(c)</td>
<td>6.5</td>
<td>7.5</td>
</tr>
<tr>
<td>4.2(d)</td>
<td>5.5</td>
<td>6.5</td>
</tr>
<tr>
<td>4.2(e)</td>
<td>2.5</td>
<td>3.5</td>
</tr>
<tr>
<td>4.2(f)</td>
<td>-</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 4.2: Values of J for Q-branch transitions in resonance in Figure 4.2
discrepancy could be due to a slight error in the Raman shift used to generate the spectra or to discrepancies in the relative population distributions between the states. There is a minor energy difference between the ground electronic states, approximately 124 cm$^{-1}$, that was not accounted for in the population calculation. This energy difference will alter the distribution between the two states, and in turn, the relative intensity distributions. For the most part, the relative intensities within a given $\Pi$ state are predicted with good accuracy.

The enhancement factor associated with each spectrum in Figure 4.2 is shown in Figure 4.3. Due to the isolated electronic resonances that dominate the spectra, the spectral behavior of the enhancement factor is very similar to the corresponding spectrum. As Figure 4.3 displays, the enhancement due to electronic resonance in the ERE CARS process is a factor of up to $\sim 3500$ as compared to CARS. This increase is significant even though the experiment was most likely performed in saturation. If the laser linewidths used in generating the spectra resemble those achievable in the experiment, the enhancement factor can increase by another order of magnitude, as seen in Figure 4.4. Therefore, there is an obvious benefit in signal strength for the ERE CARS method, and a significant motivation for studying saturation in the ERE CARS process.

4.5 Stokes Scan Results

Figure 4.5 shows ten theoretical ERE CARS spectra compared to the available experimental data. The experimental spectra were acquired by scanning the Stokes frequency between 1872.5 and 1877.5 cm$^{-1}$. The fixed UV pump beam frequency spanned the range of $\sim 42319.8$ to $\sim 42344.9$ cm$^{-1}$. The experimental spectra were obtained for the same thermodynamic conditions as the UV scan spectra, and the theoretical spectra were generated
Figure 4.3: Theoretical enhancement factor for Stokes wavelengths of (a) 591.01 nm, (b) 591.02 nm, (c) 591.03 nm, (d) 591.04 nm, (e) 591.06 nm, and (f) 591.07 nm
using the same laser linewidths. In addition, the same frequency offset corrections applied to the recorded Stokes and UV pump frequencies for the UV scans were also employed here.

As seen in the previous section, the theoretical spectra in Figure 4.5 match closely with the experimental results. As compared to the UV scan spectra, the Stokes scans display an increase in the number of transitions with significant intensity and a greater amount of interference between lines. These effects arise because the Stokes frequency is tuned over almost the entire Raman Q-branch of NO. Therefore, almost all the NO molecules can start the ERE CARS process, as opposed to the UV scans, for which only one or two Raman Q-branch transitions were probed. Because there are three possible electronic transitions for each Raman transition (see Figure 4.1), there is a chance that the fixed UV pump frequency will come into or be near resonance for a number of the Raman Q-branch transitions. This results in numerous ERE CARS transitions appearing in the spectra, which increases the

![Figure 4.4: Theoretical enhancement factor for optimal linewidth case](image.png)
Figure 4.5: Comparison of theoretical and experimental ERE CARS spectra for UV pump wavelengths of (a) 236.30 nm, (b) 236.28 nm, (c) 236.26 nm, (d) 236.24 nm, (e) 236.22 nm, and (f) 236.20 nm
Figure 4.5(cont’d): Comparison of theoretical and experimental ERE CARS spectra for UV pump wavelengths of (g) 236.18 nm, (h) 236.16 nm, (i) 236.14 nm, and (j) 236.12 nm complexity of the modeling procedure. It is no surprise, then, that the theoretical Stokes scan spectra do not agree as well with the experiment as is the case for the UV scan spectra, which can comprise at most eight transitions. As is seen when the entire Raman Q-branch of a molecule is probed, the close-lying rotational features interfere with each other.\textsuperscript{109} Because the ERE CARS model does not account for the collisional effects, \textit{i.e.}, it uses an isolated line approach, there will typically be a larger gap between transitions than seen in the experiment. This effect is clearly seen in Figure 4.5(e) through 4.5(j), even though the Stokes linewidth
used in the convolution is twice as large as the true linewidth. Even with these challenges and discrepancies, the theoretical model still provides spectra of excellent quality that are comparable to the experimental spectra.

The increased number of transitions that contribute to the Stokes scan spectra is more easily seen in Figure 4.6, in which the enhancement factor is presented for the same conditions as in Figure 4.5. The behavior of the Stokes scan spectra and enhancement factor can be explained by considering the transitions that are probed as the UV pump frequency is changed for each Stokes scan. Because there are so many transitions occurring here, it is not practical to list them, as was possible for the UV scans. Therefore, a discussion of the transitions in general is more appropriate. Starting with Figure 4.6(a), the ERE CARS process is in strong resonance with the $Q_{3/2}Q_1$ and the $Q_{3/2}^Q P_{21}$ transitions for $J = 1.5-6.5$, corresponding to the features on the righthand side of the spectrum. As the UV pump beam is scanned to higher frequencies, these resonances move to higher values of $J$, and the dominant peaks shift to the left (see Figures 4.6(b) and 4.6(c)). As this is occurring, a new set of resonances starts to appear on the righthand side of the spectra, Figure 4.6(c), and then become just as dominant, 4.6(d). These new resonances correspond to $Q_{3/2}R_1$ and $Q_{3/2}^R Q_{21}$ for $J = 1.5-3.5$. The two sets of resonances continue to move left as the UV pump frequency continues to rise, Figures 4.6(e) through 4.6(g). The splitting between the main and satellite electronic transitions becomes noticeable for the first set of resonances as $J$ increases, Figures 4.6(e) and 4.6(f). As this first set of resonances moves left, another resonance begins to contribute from the $\Pi_{1/2}$ state, which is the $Q_{1/2}R_2$ transition for $J$ near 13.5. This is the only $\Pi_{1/2}$ transition that appears in these Stokes scan spectra.
Figure 4.6: Theoretical enhancement factor for UV pump wavelengths of (a) 236.30 nm, (b) 236.28 nm, (c) 236.26 nm, (d) 236.24 nm, (e) 236.22 nm, and (f) 236.20 nm
As the UV pump frequency reaches its maximum value in this data set, a final resonance, $Q_{3/2}^S R_{21}$, appears on the righthand side of the spectra and begins the leftward progression, Figures 4.6(h) through 4.6(j). Similar to the case for the UV scans, the enhancement factor is of the order of 5000 for the Stokes scans. This can be almost doubled using linewidths closer to the actual values, as seen in Figure 4.7.

Figure 4.6(cont’d): Theoretical enhancement factor for UV pump wavelengths of (g) 236.18 nm, (h) 236.16 nm, (i) 236.14 nm, and (j) 236.12 nm
4.6 Summary

The excellent agreement between the experimental and theoretical spectra for both the UV and Stokes ERE CARS scans highlights the capabilities of the theoretical model developed herein. It also demonstrates that, with additional model adjustments to be discussed in Chapter 5, thermodynamic data could be extracted from the experimental spectra, as is performed for the nitrogen spectra presented in Chapter 3. The accuracy of the predicted line positions confirms the assignment of the molecular constants to the two Π ground electronic states. The fact that the corrections applied to the Stokes and UV pump frequencies could be used consistently for all spectral comparisons indicates that they are simply corrections to the calibration of the actual frequencies and not model parameters that need to be adjusted for each spectrum. This validates the use of these corrections.

![Figure 4.7: Theoretical enhancement factor for optimal linewidth case](image-url)
With the additional development of the enhancement factor concept, the signal strength benefits of ERE CARS can be explored. Even under the linewidth considerations presented above, the increase in signal strength is significant. This prompts the need for future investigations in which UV pump and Stokes beam laser powers are adjusted to avoid what could be saturation and Stark effects. While lower laser power should result in a lower signal level, the theoretical increase in enhancement factor at these conditions has the possibility of overcoming the loss.

Another advantage of ERE CARS is the increased species selectivity. This feature can be realized from the results presented for both the UV and Stokes scans. As shown in Figure 4.2, only a few transitions occur for each configuration of UV and Stokes frequencies. Even though there is an increased number of transitions occurring for the Stokes scan spectra (Figure 4.5), it is clear in both cases that not all of the Raman Q-branch transitions can be probed and enhanced simultaneously. Therefore, if the entire range of transitions for one molecule can not be satisfied completely, it is very unlikely that the UV and Stokes frequencies chosen will satisfy the selection criteria for a different molecule. This benefit of ERE CARS is of the same order of magnitude as the increase in signal strength, because a strong signal arising from multiple species can be just as useless as a weak, indiscernible signal.

Therefore, the development of the theoretical model in this study has many uses. The model provides a means of predicting experimental results and the future possibility of extracting thermodynamic measurements from the data. Additionally, the signal strength
benefits can be demonstrated with the enhancement factor. Finally, the increased species selection criterion is evident in the theoretical spectra already presented herein.
5 Conclusions and Recommendations

With a thorough review of the results in hand, conclusions based on the results can be drawn. In addition, recommendations for future experiments and theoretical developments are discussed as appropriate. Because the results of this investigation fall into two parts, the conclusions and recommendations will be discussed separately.

5.1 Conclusions from the MDL CARS Investigation

Reviewing the pressure vessel results from Chapter 3, an improvement in accuracy of time-averaged and single-shot mean measurements was shown as compared to previous work for pressure levels above 1.0 atm. This result demonstrates the benefit of employing the MDL. Decreased performance for subatmospheric pressure levels was attributed mainly to the low signal strength at these conditions. Standard deviations of the time-averaged results were similar to previous results above 1.0 atm, and marginally higher below this level. A decrease in standard deviations for the single-shot spectra was shown above atmospheric pressure, representing improved precision resulting from the use of the MDL. Below 1.0 atm, the single-shot standard deviations increased as compared to previous results. Both time-averaged and single-shot CARS spectra displayed excellent spectral behavior, allowing for good agreement between theoretical and experimental spectra.

Time-averaged and mean single-shot results from the centerline traverse of an underexpanded jet displayed excellent agreement with CFD results, especially for pressure levels above 1.0 atm. Slight offsets in mean temperature were observed and explained. Experimental spectra from the centerline traverse provided good predictions of pressure, with a slight decrease in agreement in temperature as compared to previous results. Increases in
standard deviations for both temperature and pressure occurred in the time-averaged and single-shot measurements, which is most likely indicative of low signal strength that results from using the MDL.

The possibility of fluctuation measurements using high-resolution N₂ CARS was displayed. The small increase in precision for pressure vessel measurements above 1.0 atm confirms that the baseline fluctuation detection limit of the technique can be lowered. Unfortunately, this increased precision falls outside the thermodynamic property range that a majority of compressible flows operate in. The decrease in signal strength at lower pressure levels (more representative of compressible flows) degrades system measurement precision from that seen in the previous experiment. Nevertheless, this experiment provides a significant contribution as the first demonstration of the effects of an MDL on pressure measurements and the overall MDL CARS system performance at supersonic conditions.

5.2 Recommendations for the MDL CARS Investigation

In order to improve the performance of the current technique, a new source for the Stokes beam should be explored. A promising source would be a modeless dye laser based upon the design of Hahn et al. This laser employs Bethune dye cells as opposed to the transversely pumped dye cells in the current MDL, with a single, concentrated pass through the “oscillator” dye cell rather than four, distributed passes. Bethune dye cells provide better spatial beam quality, with a more uniform intensity distribution over the cross-section of the beam. This increase in beam quality could provide stronger CARS signal levels than seen in the current experiment, as the beam will have an improved focus
at the probe volume. As seen in a previous experiment,\textsuperscript{33} this dye laser provides low standard deviations in temperature measurements in a steady laminar flame.

Another possible solution would be to incorporate two single-mode, solid-state, tunable sources into the system: one to replace the Stokes source and one to replace a pump beam, in a dual-pump CARS technique.\textsuperscript{34} With the correct choice of wavelengths for these two sources, two transitions of the nitrogen Q-branch could be probed simultaneously. This second option is less attractive, as it involves a potential decrease in pressure sensitivity by not probing the entire linewidth of both transitions, and it is also more expensive to implement. Nevertheless, using all single-mode sources for the pump and Stokes beams would provide excellent beam quality and TEM mode structure and would eliminate the possibility of mode noise.

If the above two modifications to the system are not possible, modifications to the current CBDL are available that should provide decreased mode noise levels. These modifications are outlined in the work of Greenhalgh and Whittley\textsuperscript{24} and discussed in Section 1.2.4. Specifically, because there is ample power generated in the CBDL, the oscillator cavity should be lengthened to explore the effects of axial mode packing. While the increased oscillator length will lower the total output power of the CBDL, the increased system performance might offset this loss.

Beyond finding a new source for the Stokes beam, there is a more basic diagnostic that could be applied to any system that should improve results. Monitoring the laser power in each beam on a shot-to-shot basis would provide a means of normalization for the CARS signal intensity. While this would not correct for the spectral nonuniformities of the Stokes
beam, the ability to monitor the power and correlate it with the behavior of the CARS signal should prove beneficial.

While more challenging, sophisticated beam analysis equipment could be employed to diagnose the output state of the Stokes beam. Such equipment can be used to monitor the spatial beam quality and compare it to a Gaussian intensity distribution. In particular, a BeamStar system from Ophir Optronics, Inc. would provide this type of diagnostic capability. Additionally, the use of a Hartmann wavefront analyzer would allow for measurement of the spatial beam profile and knowledge of how the beam will propagate and focus. Spiricon, Inc., is planning to make such a system available commercially. This equipment would refine the alignment procedures of the Stokes beam laser to provide the best spatial beam quality possible. In turn, the better the Stokes beam focuses, the better the efficiency of the CARS signal generation. In addition, a tighter, more well-defined focus will put more of the Stokes beam energy into the region where the two pump beams focus, again providing for an increase in CARS signal strength.

While rudimentary, an effective solution for better system performance would be to install a climate control system in the laboratory that would control the temperature and humidity more consistently than the current system. Temperature stability provides better performance from the Nd:YAG laser, the MDL, and the overall system. Since the entire system is constructed of various metals, temperature shifts cause misalignment, as there are varying coefficients of expansion across the length of the setup. This is most severely recognizable in the performance of the Nd:YAG laser. Additionally, the gain curve of the organic dye used in the MDL is temperature-dependent. Finally, the performance of the injection
Seeder in the Nd:YAG laser is highly temperature-dependent, and swings in temperature or shifts in internal laser alignment cause degraded seeding performance.

Outside of the experimental setup, there is a need for an investigation into the spectral modeling used in the least-squares fitting process. While widely used and accepted, the modified exponential gap law does not model the spectral behavior of the CARS signal exactly; this is especially noticeable in the relative intensities in the bandhead of the nitrogen Q-branch. Large discrepancies in lineshape are also noticeable between experimental and theoretical spectra. While the lineshape discrepancies can be accounted for, often the experimental spectra are still misrepresented by the modified exponential gap law, especially at low pressure levels of 1 atm and below. As this and most models for nitrogen spectra were developed for combustion temperature and pressure levels, modifications of the older models or new models should be developed. In addition to these modifications, an modern optimization scheme for the least-squares fitting process should be investigated. Not only could this scheme increase the data processing rate, but it could also eliminate the need for the spectra-fitting procedure.

5.3 Conclusions from the ERE CARS Modeling Investigation

The results from Chapter 4 represent the first known theoretical predictions of ERE CARS spectra of NO. This provides an important contribution to the literature as the separation of the Raman and electronic resonances during the CARS process allows for the enhancement to be distinguished. The results display outstanding agreement between theory and experiment, thus validating the model. The predicted line positions match closely with the transitions seen in the data. The UV scans display approximately six isolated transitions,
corresponding to at most two Raman Q-branch transitions. While relative line intensities did not compare as well across an entire spectrum, the relative intensities corresponding to each Π state were approximately correct. Modifications to the population distributions discussed in the next section could help account for this.

The Stokes scans involve an increased number of transitions in each spectrum. Even with this added complication, the model was able to provide theoretical spectra that compared well with the experimental spectra. Due to the increased number of transitions, a significant amount of interference between lines is evident. The outstanding predictions of the model for the Stokes scans complement the exceptional results found in the UV scans.

In addition to the capabilities of the model, the enhancement factor concept was introduced. This parameter enables an experimentalist to calculate the increased signal strength due to the ERE CARS method and to weigh this advantage of increased detection sensitivity against the increased complexity of the experimental setup. With the use of the model and the enhancement factor, it is possible to study the effects of the added electronic resonance on the CARS process. This provides a perspective on how selective the process is to molecular properties.

5.4 Recommendations for the ERE CARS Modeling Investigation

While the theoretical spectra presented in Chapter 4 display excellent agreement with the experimental spectra, improvements to the model can be made. Because the ground state of NO is a split Π state, there is a slight difference in the electronic contribution to the energy of the molecule. In specific, the Π \(_{1/2}\) state lies \(\sim 124 \text{ cm}^{-1}\) above the Π \(_{3/2}\) state.\(^{104}\) This will affect the relative population distributions in between the two states, therefore reducing the
peak intensities of the $\Pi_{1/2}$ state relative to the $\Pi_{3/2}$ state. In addition to this, CARSFIT was developed for species with integral values of $J$ and for homonuclear molecules. Therefore, while the population distribution calculations were modified to include half-integral $J$ values, the calculations should be modified for a more general case in which effects such as lambda-doubling are accounted for in the event that they become significant.

Beyond the population distributions, the line strength calculations for $K_{ab}$, see Equation 1.10, in CARSFIT were developed for $^1\Sigma$ ground states, and therefore an alternative calculation for $\Pi$ ground states should be considered. Rather than using the $K_{ab}$ formulation for line strengths, which are more relevant to Raman spectroscopy, line strengths based on the dipole matrix elements, $\mu_{ij}$, would provide a more accurate description of the ERE CARS process. These types of calculations are similar to those of Attal-Trétout et al. and would require the numerical solution of the time-dependent density-matrix equations. This new model could then incorporate the more general case of triple resonance.

In order to make the current model more accurate, saturation and Stark effect considerations should be included in the calculations. While a model for saturation in cw CARS is already available in CARSFIT, there is no applicable model for pulsed measurements. With these corrections, the actual laser linewidths could be used in the generation of the spectra along with saturation or Stark parameters. The effects of the polarization scheme employed in the experiments also should be accounted for in the model, similar to the work of Aben et al.

On the experimental side of the ERE CARS investigation, it would be advantageous to monitor the frequencies of the Stokes and UV pump lasers. This could possibly alleviate
the need for the frequency offset corrections applied in this work. This would also allow for the linewidths of both beams to be estimated, as well. While these issues were not of great importance in the development of the current model, solidifying these values would add validation to the capabilities of this and future models. Instead of monitoring the linewidths of the lasers, it would be even more beneficial to employ single-mode sources for the Stokes and UV pump lasers. Not only would this eliminate the linewidth-monitoring equipment, the reduction in mode structure would greatly benefit the convolution process in the model and simplify the experimental spectra.

Finally, it would be beneficial to acquire experimental ERE CARS spectra of other molecules, such as OH, I$_2$, or C$_2$H$_2$, in order to test the model further. These species represent different molecular structures than NO, and therefore these spectra would also test the capabilities of the model to predict new spectral behavior. Beyond just different species, ERE CARS spectra obtained in a mixture of one or more species that have overlapping Raman transitions would demonstrate the ability of the technique to select one species over the other and would provide a unique and challenging scenario for the model.
References


Vita

Joel Paul Kuehner was born on October 7, 1975 in Poughkeepsie, NY to Eileen and Paul Kuehner. Along with his sister, Elizabeth, he grew up in rural Pennsylvania. In May of 1993, Joel graduated from Parkland High School, and that fall, he began working on his B.S. degree in Mechanical Engineering at the Pennsylvania State University. During his junior year, Joel was initiated into Pi Tau Sigma and was awarded the Member of the Year honor in the local chapter of the American Society of Mechanical Engineers. He also spent many hours working on the Sea Lion Project, a human-powered submarine, helping to take the craft to its first competition. In his senior year, Joel was elected Vice-President of Pi Tau Sigma. During his time in office, he enacted group tutoring sessions for the Mechanical Engineering Department. Along with these accomplishments, Joel was honored with membership in Tau Beta Pi. Joel graduated with distinction from the Pennsylvania State University in May of 1997.

Immediately following his graduation, Joel enrolled at the University of Illinois, where he started his graduate work. Under the guidance of Professors J. Craig Dutton and Robert P. Lucht, Joel performed research on coherent anti-Stokes Raman scattering using counter-propagating pump beams for his M.S. thesis. He was awarded his M.S. degree in January of 2000, and began working on his doctoral research. During his graduate work, Joel became a member of Phi Kappa Phi, and was awarded a University and Shell Grant Foundation Fellowship. Beyond his research, Joel was a teaching assistant for the undergraduate fluid dynamics laboratory and was named to the Incomplete List of Teachers Ranked as Excellent by Their Students for his work in that course. In addition, Joel received the General
Electric Teaching Incentive Grant. It was also during his graduate work that Joel met his wife, Elizabeth Denton. They were happily married in September of 2001.