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Sensitive multi-photon nonlinear laser spectroscopic methods for isotope analysis in atmospheric and environmental applications

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Sensitive Multi-Photon Nonlinear Laser Spectroscopic Methods for Isotope Analysis
in Atmospheric and Environmental Applications

A dissertation submitted in partial satisfaction of the requirements for the degree
Doctor of Philosophy

in
Chemistry

by
Wendy Jean Lyons

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2009
The Dissertation of Wendy Jean Lyons is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

Chair

University of California, San Diego
San Diego State University
2009
DEDICATION

To my mother and father, who always supported me in whichever direction I decided to travel.
Felix, qui potuit rerum cognoscere causas

Virgil
# TABLE OF CONTENTS

Signature Page........................................................................................................................................ iii
Dedication................................................................................................................................................ iv
Epigraph................................................................................................................................................... v
Table of Contents..................................................................................................................................... vi
List of Figures.......................................................................................................................................... ix
List of Tables........................................................................................................................................... xiii
Acknowledgments...................................................................................................................................... xiv
Vita........................................................................................................................................................... xvi
Abstract.................................................................................................................................................... xviii

Chapter 1 Introduction to Laser Spectroscopy................................................................. 1
  1.1 Introduction................................................................................................................................... 1
  1.2 Laser Spectroscopy ....................................................................................................................... 2
  1.3 Atomic Spectroscopy..................................................................................................................... 4
  1.3.1 Atomic Line and Hyperfine Splitting ...................................................................................... 6
  1.4 Molecular Spectroscopy............................................................................................................... 6
  1.5 Narrow Bandwidth Laser Sources.............................................................................................. 7
  1.5.1 Semiconductor Diode Lasers ................................................................................................. 7
  1.5.2 Quantum Cascade Lasers ....................................................................................................... 8
  1.6 Gas-Phase Atomizers ................................................................................................................... 10
  1.7 Dissertation Outline ..................................................................................................................... 11
  1.8 References.................................................................................................................................... 13

Chapter 2 Introduction to Isotope and Hyperfine Analyses............................................. 14
  2.1 Atomic Spectra ............................................................................................................................ 14
  2.2 Linewidths................................................................................................................................... 15
  2.2.1 Natural Linewidth .................................................................................................................. 15
  2.2.2 Doppler Broadening ................................................................................................................ 17
  2.2.3 Pressure Broadening .............................................................................................................. 18
  2.2.4 Power Broadening .................................................................................................................. 19
  2.3 Atomic Line Splitting .................................................................................................................... 20
  2.3.1 Fine Splitting .......................................................................................................................... 20
  2.3.2 Hyperfine Splitting ................................................................................................................ 23
  2.4 Isotope Shifts ............................................................................................................................... 25
7.3 Results and Discussion

7.3.1 Mid-IR Laser Absorption Measurement

7.3.1.1 Acetone

7.3.1.2 Freon 113

7.3.2 Mid-IR Multi-Photon Wave-Mixing Detection

7.3.2.1 Freon 113

7.3.2.2 Nitrous Oxide

7.4 Conclusions

7.5 References

Appendix A

Appendix B
LIST OF FIGURES

Figure 1.1 A model of a simple two-level resonant transition................................. 3
Figure 1.2 Schematic of a standard atomic absorption experiment............................. 5
Figure 1.3 Frequency range of currently available quantum cascade lasers............... 9
Figure 2.1 Energy level diagram for oxygen.............................................................. 16
Figure 2.2 Fine splitting diagram for the $^4$D atomic chlorine transition.................... 22
Figure 2.3 Molecular isotope shift of SO$_2$ at 1,351 cm$^{-1}$........................................ 26
Figure 2.4 Carbon and chlorine isotope ratios in detergent for select manufacturing companies........................................................................................................... 28
Figure 3.1 Formation of a grating by two intersecting waves with spatially modulated population differences........................................................................................................... 34
Figure 3.2 Backward-scattering phase-matching geometry....................................... 37
Figure 3.3 Out-of-plane backward-scattering optical arrangement............................ 40
Figure 3.4 Forward-scattering phase-matched optical arrangements......................... 41
Figure 3.5 Simultaneous backward-scattering and forward-scattering wave-mixing geometry....................................................................................................................... 42
Figure 3.6 Typical gas-phase wave-mixing optical setup........................................... 44
Figure 4.1 Schematic diagram of the plasma torch and relative positions of the regions probed......................................................................................................................... 53
Figure 4.2 Experimental setup for dual forward-and-backward wave mixing.............. 55
Figure 4.3 Experimental data with temperature fit profile of 3,400 K............................. 58
Figure 4.4 Theoretical fitting of experimental data of both wave-mixing geometries. The fits result in a temperature of 8,100 K................................................................. 59
Figure 4.5 Plot of measured temperatures across the radius of the torch using 1.25 mm increments from the center and 3 mm and 5 mm above the bonnet.................. 62
Figure 4.6 Plot of calculated temperatures across the radius of the torch at 8 mm and 10 mm above the bonnet ................................................................. 63

Figure 4.7 Contour plot of calculated temperatures in the analytical zone of the torch .......................................................................................................................... 64

Figure 4.8 Contour plot of the calculated electron density (given in units of $10^{15} \text{ cm}^{-3}$) in the analytical zone of the torch ............................................................... 65

Figure 5.1 Excited oxygen atomic energy levels ............................................................................................................................................................................. 72

Figure 5.2 Fine and hyperfine splitting of oxygen near 777 nm ........................................ 73

Figure 5.3 The demountable hollow-cathode lamp (HCL) atomizer .................................. 77

Figure 5.4 DFWM signal intensity variation with change in discharge current ...... 81

Figure 5.5 Comparison of copper and stainless-steel signal strengths ..................... 83

Figure 5.6 Mapping atomic density in the plasma .......................................................... 84

Figure 5.7 Signal intensity dependence on analyte flow rate ....................................... 85

Figure 5.8 Oxygen 50 ppmv peak with a S/N of 40 ...................................................... 87

Figure 5.9 Fine structure of atomic oxygen at 777 nm ................................................. 90

Figure 5.10 Effect of laser power on analytical peak shape and width .................... 91

Figure 5.11 Theoretical fitting of atomic oxygen profile ............................................. 93

Figure 5.12 Surface map of least squared fitting procedure used to determine experimental temperature and Doppler width values ........................................ 94

Figure 5.13 Simulated hyperfine spectrum for enriched oxygen in the cathode discharge (50:40:10 mixture of oxygen 16, 17 and 18 isotopes) ....................... 95

Figure 6.1 Fine and hyperfine splitting of atomic chlorine ........................................ 102

Figure 6.2 Isotope and hyperfine splitting model of atomic chlorine ....................... 103

Figure 6.3 Wave-Mixing signal verification by blocking each of the three input beams .............................................................................................................. 105
Figure 6.4  Wave-mixing signal dependence on discharge current
Figure 6.5  Wave-mixing signal dependence on discharge cell pressure
Figure 6.6  Wave-mixing signal dependence on modulation frequency
Figure 6.7  Raw wavelength scan of solid sodium chloride
Figure 6.8  Wave-mixing signal for 62 ppmv chlorofluorocarbon Freon 113
Figure 6.9  Power saturation effects at different laser power levels
Figure 6.10  Experimental profile of atomic chlorine with calculated isotope and hyperfine lines
Figure 6.11  Experimental profile of atomic chlorine with calculated overall hyperfine profile
Figure 7.1  Relative amount of anthropogenic greenhouse gases released in the United States in 2007
Figure 7.2  Simulated isotope splitting of N₂O absorption spectrum at 1,290 cm⁻¹
Figure 7.3  Gas analyte cells with CaF₂ windows for use in mid-IR optical Setups
Figure 7.4  Typical mid-IR laser absorption optical setup
Figure 7.5  Mid-IR absorption spectrum of acetone
Figure 7.6  Mid-IR absorption spectrum of 3 pptv acetone
Figure 7.7  Mid-IR absorption spectrum of 2,000 ppmv chlorofluorocarbon Freon 113. (a) FT-IR, (b) absorption
Figure 7.8  Mid-IR absorption spectrum of 5 ppmv CFC Freon 113 (the two main features are apparent at this low concentration level)
Figure 7.9  Different absorption spectral features of three different gas analytes in the wavelength tuning range of the 8.4 µm quantum cascade laser
Figure 7.10  Typical forward-scattering wave-mixing optical setup
Figure 7.11  Wave-mixing signal verification for 500 ppmv CFC Freon 113
Figure 7.12  Cubic wave-mixing signal dependence on laser power......................... 141

Figure 7.13  Comparison of 500 ppmv CFC Freon 113 signal with that of an argon blank.............................................................................................................................................. 143

Figure 7.14  Wave-mixing spectrum of CFC Freon 113........................................... 145

Figure 7.15  Cubic dependence of wave-mixing signal on laser power.................... 146

Figure 7.16  Mid-IR wave-mixing spectrum of 1,000 ppmv N$_2$O compared with FT-IR reference spectrum (15 mW QCL at 100 kHz)................................................................. 147
LIST OF TABLES

Table 2.1 Line broadening sources............................................................................ 21
Table 4.1 Results obtained from dual forward-and-backward wave-mixing setup... 60
Table 5.1 Naturally occurring isotopes of oxygen..................................................... 70
Table 5.2 Comparison of reported limits of detection (LOD) for oxygen............... 88
Table 6.1 Estimated global chlorine content............................................................. 100
Table 6.2 Comparison of previously reported methods and detection limits for atomic chlorine........................................................................................................... 113
Table 7.1 Comparison of previously reported detection methods for acetone........ 131
Table 7.2 Cubic dependence of wave-mixing signal on laser power......................... 142
Table A4.1 Switch settings for common diode laser configurations......................... 157
Table B.1 Analyte loss processes in the hollow-cathode discharge cell............... 160
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Studies in Nonlinear Wave-mixing Spectroscopy
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ABSTRACT OF THE DISSERTATION

Sensitive Multi-Photon Nonlinear Laser Spectroscopic Methods for Isotope Analysis in Atmospheric and Environmental Applications

by

Wendy Jean Lyons

Doctor of Philosophy in Chemistry

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San Diego State University, 2009

Professor William G. Tong, Chair

Multi-photon nonlinear laser wave-mixing spectroscopy is presented as a sensitive optical detection method for environmentally hazardous gases with isotope-level spectral resolution. When compared to other detection techniques, degenerate four-wave mixing offers unique advantages including high spatial resolution, excellent sensitivity and small laser probe volumes that are suitable for diagnostic studies. Unlike those in conventional optical methods, the wave-mixing signal is a coherent laser-like beam, and as such, it can be spatially and optically modulated to enhance
signal-to-noise ratios. This signal also has a quadratic dependence on analyte concentration, making it a powerful tool for detecting small changes in analyte properties. In addition, the nonlinear signal has a cubic dependence on laser power, which provides excellent detection sensitivity as well as the ability to use low-power laser sources such as portable solid-state laser diodes.

Four-wave mixing is demonstrated as a powerful tool for in-situ diagnostics. This novel optical setup allows simultaneous collection of signals from two distinct wave-mixing geometries in a common analytical atomizer (radio-frequency inductively coupled plasma torch). Experimental data fit well to those calculated based on an iterative perturbation model, resulting in reliable determination of temperature and electron density levels for the analytical zone of the ICP atomizer. Three dimensional mapping yields temperature levels ranging from 3,500 to 14,000 K ± 150 K and electron density levels from 6.1 (± 0.3) x 10^{15} cm^{-3} to 10.1 (± 0.3) x 10^{15} cm^{-3} with 5 % uncertainty.

Nonlinear wave mixing is also used for sensitive detection of atomic oxygen and chlorine with isotope or hyperfine spectral resolution. Preliminary mass detection limits of 3.48 picograms and 2.2 picograms are reported for oxygen and chlorine, respectively. Isotope and hyperfine splittings for chlorine-35 and chlorine-37 are obtained from a sample of the environmental contaminant, Freon 113.

Mid-infrared laser absorption techniques are applied to molecular detection of environmental pollutants using an 8 mm quantum cascade laser. Nitrous oxide and CFC Freon 113 are detected in their native forms at room temperature and room
pressure. A preliminary concentration detection limit of 3 pptv (parts per trillion by volume) is determined for gas-phase acetone analytes.
Chapter 1

Introduction to Laser Spectroscopy

1.1 Introduction

Our society today requires cheaper, faster, and more accurate analytical techniques to help fill an ever-increasing need for chemical solutions to global issues. Recent discussions over the causes of global warming and their repercussions have put more pressure on scientists to explore new and emerging disciplines in the study of global climate. These studies demand not only the utmost accuracy, but also the ability to be transported onto unmanned vehicles as well as stratospheric airplanes. Additionally, the heightened attention to security threats since 9/11 has spawned a new field of interest in the detection of biological and radiological weapons. A review of biosensors for detection of biological warfare agents noted, “Biological agents are many times deadlier than chemical agents”\(^1\) and that environmental security is a “fundamental requirement” of human society and yet it remains a major global challenge.\(^2\) Furthermore, U.S. troops serving overseas constantly demand the best detection systems for explosives and other harmful materials, ideally those capable of detecting chemical agents at a distance to minimize casualties. Often, only minute amounts of sample are available for research, requiring new methods to maximize detection sensitivity, selectivity, efficiency, and speed at an affordable price. One such innovative method that has achieved success in these areas is nonlinear laser spectroscopy.
1.2 Laser Spectroscopy

Since its invention, the laser has found a myriad of uses in analytical chemistry. Its characteristic monochromatic light is particularly useful in molecular and atomic spectroscopy. Spectroscopy is the study of interaction of electromagnetic radiation and matter. Radiation impinging on different phases of matter can be absorbed, scattered, or transmitted through the medium. The spectrum associated with each medium is unique to that particular substance, much like a fingerprint is unique to an individual. Thus, spectroscopy is often used for the identification of substances based on the characteristic spectrum emitted or absorbed by that substance. Laser spectroscopy is simply the utilization of the electromagnetic radiation emitted from a laser to probe the discrete energy levels of a particular substance. Figure 1.1 depicts a typical atomic energy level diagram of a two-level system. The levels shown here can be illustrative of electronic, vibrational, or rotational states, depending upon the absorbing medium.
Figure 1.1 A model of a simple two-level resonant transition.
1.3 Atomic Spectroscopy

Each element in the periodic table has its own unique set of energy levels. By measuring these characteristics, the identity of a species can be determined. This method is known as atomic spectroscopy and can be further categorized by what is measured, e.g., absorption, emission, or fluorescence. Characteristic energy level diagrams and wavelength tables have been published for many of the elements in the periodic table, allowing for quick and efficient identification.3

In order to develop a sensitive technique for atomic studies, one must address the many challenges atomic spectroscopy presents. A typical optical setup consists of a radiation source, an atomization source, and a detector as shown in Figure 1.2. Some of the most popular radiation sources include thermal sources such as incandescent wires, tungsten lamps and hollow-cathode discharge lamps. These thermal sources suffer from poor resolution and low power density levels, especially as compared to the high power density levels and narrow bandwidths available from lasers. Excellent spatial and temporal coherence properties of a laser allow convenient alignment and focusing of multiple input beams into a sample. The narrow linewidth of the light also allows researchers to resolve fine and hyperfine spectra. There are a number of laser sources available today that offer a variety of characteristics useful for specific applications. For atomic or isotope resolution, a tunable narrow bandwidth laser is required. Possible sources include semiconductor diode lasers and dye lasers, and more recently, quantum cascade lasers for the infrared wavelength range.
Figure 1.2 Schematic of a standard atomic absorption experiment
1.3.1 Atomic Line and Hyperfine Splitting

Within each atom, an electron has particular discrete energy levels it may occupy. Angular momentum, spin-orbit coupling and nuclear angular momentum each play a role in splitting these principal energy levels that an electron may occupy. Combinations of these characteristics contribute to the unique spectrum exhibited by each atom. With improvements in detection resolution, scientists have been able to take advantage of the distinctive spectra of different elements as a powerful tool to identify atoms and their isotopes.

Three of the most visible types of splitting are fine, hyperfine, and isotope splittings. Fine structures in atomic spectra result from spin-orbit interactions and are typically on the order of $10^{-3}$ eV. Hyperfine splitting is more closely spaced (on the order of $10^{-4}$ eV) and results from interactions between the nuclear spin angular momentum and the total electronic angular momentum. Analytes with different isotopes can not only have different splittings from numerous nuclear spin possibilities, but they also experience a shift in the transition of absorbed radiation due to mass and volume differences referred to as isotope shifts. This can lead to a very complex spectrum that is unique to each element and can be used as a fingerprint for selective detection.

1.4 Molecular Spectroscopy
The spectra for molecules can be much more complicated as compared to those of simple atoms. The range of molecular sizes and shapes creates the possibility of endless varieties of spectra. Additionally, similar combinations of atoms within different molecules cause molecular spectra to more closely resemble each other than those in atomic spectroscopy, making it difficult to distinguish molecular spectra. These challenges are slowly being improved by emerging technologies that increase the resolution and wavelength tunability of lasers.

1.5 Narrow Bandwidth Laser Sources

1.5.1 Semiconductor Diode Lasers

Solid-state diode lasers offer a low-cost high-resolution alternative to more elaborate pulsed dye lasers and optical parametric oscillators (OPO). Laser diodes can often be purchased for as little as $30 (without power supply, housing, etc.) and they are more rugged and much smaller than other tunable laser sources. Unfortunately, standard diode laser systems are prone to mode hopping, which produces gaps in their wavelength tuning ranges. These gaps can be mitigated to some degree by altering the current and temperature regimes (sometimes referred to as blue- or red-shifting). Alternatively, an external cavity grating can be used to minimize mode hopping and produce very narrow linewidths (kHz). However, these instruments have much lower power output levels and are orders of magnitude more expensive than conventional diode lasers. Another drawback of using a diode laser is the limited wavelength ranges currently available, which lie mostly in the visible range. Nevertheless,
wavelength ranges are continually expanding as commercial ventures find new uses for these tools, such as CD readers and new HD-DVD readers that use 400 nm light sources. Additionally, research into nonlinear materials for frequency doubling or tripling has yielded wavelengths in the blue and UV regions where many atoms have their strongest optical absorption lines. Unfortunately, to date, these methods have only produced limited power density levels and poor conversion efficiencies resulting in microwatt power output levels.

1.5.2 Quantum Cascade Lasers

One of the newest lasers available to researchers is the quantum cascade laser. These lasers allow one to probe analytes using the mid-IR wavelength range (between 4 and 12 micrometer) that is useful for molecular vibrational spectroscopy (Figure 1.3). These lasers come in a variety of configurations including a pulsed version with a large tuning range of up to 100 cm\(^{-1}\) and a relatively broad 1 cm\(^{-1}\) bandwidth, and a continuous-wave mode-hop-free (CW-MHF) version with a much narrower tuning range, but very sharp bandwidths (0.001 cm\(^{-1}\)). These lasers are small and compact with some versions running solely on battery power. At this point, the cost of these light sources is still relatively high ($60k), but as the technology evolves, the price will likely drop as the UV diode laser prices did in 2005. The development of turnkey systems in the mid-IR wavelength range allows researchers to incorporate remote sensing into their plans and place these instruments on unmanned aerial vehicles for
Figure 1.3 Frequency range of currently available quantum cascade lasers
atmospheric testing. It is clear that this technology will greatly expand the tools that environmental sensing has at its disposal.

1.6 Gas-Phase Atomizers

The atomization source is one of the most important components in an atomic spectroscopic setup. It can pose some difficulty if not chosen and calibrated properly in accordance with individual experimental needs. The purpose of the atomizer is to provide an atomic vapor and generate free atoms from liquid- and solid-phase samples. This needs to be done efficiently and consistently. The atomizer can also be used as an energy source when probing non-ground state levels. The two most common atomizers used in atomic absorption spectroscopy are analytical flames and electrothermal atomizers. Graphite furnace atomizers offer minimal background noise levels and good detection limits; however, the pulsed release of free atom population with 2-second atomization cycles leads to relatively long data acquisition times that can be frustrating when processing wide spectra. Analytical flames have been used for years and they are inexpensive, but background effects, sample waste, and limited sensitivity levels\(^7\) led to the development of more complex atomization sources.

Plasma-based atomizers have become more common as scientists discover their unique advantages in specific studies. Using excited argon atoms contained in a radio-frequency field, the inductively coupled plasma (ICP) can reach up to 16,000 K. This continuously firing atomizer utilizes a flowing liquid analyte, which is nebulized into the argon gas flow, and hence, it allows faster data sampling rates. A much
simpler and lower temperature plasma alternative to the ICP is the hollow-cathode discharge cell. This cell incorporates a low-pressure gas discharge induced by two electrodes. This provides for the introduction of solid, liquid and gas analytes, though only gases can be analyzed in a continuous mode. The lower pressure environment reduces pressure broadening in atomic spectral lines. Taking advantage of faster data sampling rates, reduced pressure broadening and flexible sample introduction options, we will use the inductively coupled plasma (ICP) and the hollow-cathode discharge atomizers.

1.7 Dissertation Outline

The purpose of this research is to develop a new sensitive analytical technique based on nonlinear spectroscopy for the detection of environmental gases. Degenerate four-wave mixing (DFWM) is a high resolution optical technique that is capable of not only differentiating absorbing analytes of different species, but also distinguishing absorbing isotopes of the same species while requiring only picoliter sample volumes. Chapter 2 describes an introduction to atomic hyperfine and isotope analyses, followed by a brief discussion of the DFWM theory in Chapter 3. Chapter 4 describes nonlinear spectroscopy as an innovative technique to map the temperature in a turbulent environment using simultaneous measurements of two distinct wave-mixing geometries. An introduction to atomic absorption spectroscopy in a hollow-cathode discharge cell is presented in Chapter 5 along with experimental results for the detection of atomic oxygen with isotopic resolution. This technique will be further
explored in Chapter 6 with the study of isotopic spectra of atomic chlorine with its two naturally occurring isotopes. Both of these isotopes exhibit hyperfine splitting. These results are partially obtained using real-world samples of EPA-monitored Freon 113, an ozone-depleting gas. Finally, we present a study of Freon 113 and the greenhouse gas nitrous oxide (N₂O), both in their native form, using a mid-infrared quantum cascade laser to probe molecular vibrational transitions.
1.8 References


2.1 Atomic Spectra

Atomic optical absorption spectra consist of many lines that are specific to each particular element due to the finite number of energy levels that an atom can assume. The complexity of an atomic spectrum can serve as a type of fingerprint for each element and allows for specific identification of elements. Absorption of a photon with the same energy as the allowed transition is one method by which a ground-state electron can be excited to an upper energy level or excited state. Energy level diagrams, sometimes referred to as Grotrian diagrams, contain information on the ground state configuration and allowed transitions for an atom. Figure 2.1 is an example of the Grotrian diagram for atomic oxygen.

The absorption process can be modeled with a simple two-level system as described in Chapter 1. Normally the energy gap between the two states is large enough that thermal energy available to the atom is insufficient to overcome this gap. Thus, the population of atoms in the ground state is much higher than the population found in the excited state. Relative population levels of the ground and excited states are described using the Boltzmann expression for thermal equilibrium between two states:¹

$$\frac{N_2}{N_1} = \exp\left(\frac{E_2 - E_1}{kT}\right)$$  \hspace{1cm} (2.1)
where $N_1$ is the number of atoms that are in the ground state and $N_2$ is the number of atoms in the excited state. $E_1$ is the ground state energy, $E_2$ is the excited state energy, $T$ is the thermodynamic temperature of the group of atoms and $k$ is Boltzmann’s constant ($1.38 \times 10^{-23} \text{ J/K}$).

There are three different photon-atom interactions that can alter this equilibrium and redistribute population levels. These interactions are absorption, spontaneous emission and stimulated emission. Nonlinear degenerate four-wave mixing takes advantage of absorption, which originates from the presence of radiation exactly matching the difference in energy between the ground state and the excited state.

### 2.2 Linewidths

Atomic absorption lines are normally sharp, but can be influenced by a few different factors. The most significant factors are the natural linewidth, Doppler broadening and pressure broadening. If line-broadening mechanisms are minimized, very narrow and precise spectra can be resolved, allowing for unambiguous identification of individual elements.

#### 2.2.1 Natural Linewidth

The natural linewidth is determined by the lifetime of the excited state. When an atom absorbs a photon, the system becomes unstable and the absorbed energy is lost through decay processes. The absorption process may be extremely fast, on the
Figure 2.1 Energy level diagram for oxygen.
Partial energy diagram (Grotrian) for atomic oxygen indicating the complexity of the atomic spectra.
order of $10^{15}$ s, when compared to the lifetime of the excited state, which is typically on the order of $10^9$ s. Heisenberg Uncertainty Principle states that one cannot know both the time of a system and the energy exactly or simultaneously, even when dealing with these short time frames. This principle holds true for the atomic systems studied here and gives rise to natural linewidth. The uncertainty in the wavenumber for the transition becomes $\Delta \nu$, such that:

$$\Delta \nu = \frac{1}{2\pi c \tau}$$

(2.1)

where $c$ is the speed of light and $\tau$ is the lifetime of the excited state. The excited state lifetime is unique to each electronic transition, and thus, each spectral line has a different natural linewidth. It should be noted that these linewidth contributions are small, in most cases less than $10^{-3}$ cm$^{-1}$, when compared to other line-broadening contributions such as Doppler broadening and pressure broadening.

2.2.2 Doppler Broadening

For atomic absorption spectra in the visible and UV wavelength ranges, the limit on resolution is often set by Doppler broadening. Doppler broadening is caused by the random thermal motion of atoms. The motion of an atom relative to the source of radiation shifts the frequency of radiation absorbed during a transition. This is called the “Doppler Shift.” The motion of an atom toward or away from the laser probe volume will cause a spread in the observed spectral linewidth. The width of a spectral line due to Doppler broadening can be described as:
\[ \lambda_{\frac{1}{2}} = \lambda \frac{2}{c} \sqrt{\frac{2RT}{m}} \]  

(2.2)

where \( \lambda \) is the transition line center, \( c \) is the speed of light, \( R \) is the gas law constant, \( m \) is the mass of the absorbing atom in kg and \( T \) is the absolute temperature. This equation is simplified by replacing the known constants, which yields:

\[ \lambda_{\frac{1}{2}} = 7.16 \times 10^{-7} \sqrt{\frac{T}{m}} \]  

(2.3)

Doppler widths can be on the order of \( 10^{-2} \) cm\(^{-1} \) and increase significantly as temperature increases. This inhomogeneous broadening is extremely important as it can mask much of the atomic fingerprint characteristics useful in hyperfine and isotope spectral analyses. A few techniques can be used to minimize Doppler broadening. One such technique makes use of an atomic beam where all the atoms are traveling in the same direction with a restricted range of velocities. Alternatively, Doppler-free or sub-Doppler laser techniques with two counter-propagating beams sample only one velocity group of atoms, and therefore, minimize Doppler broadening. One such technique, degenerate four-wave mixing, is discussed in detail in Chapter 3.

### 2.2.3 Pressure Broadening

In an analyte cell, interactions with the environment can cause the excited atoms to lose energy through collisional processes. This relaxation process occurs when an atom collides with other atoms, molecules or even cell walls. As a result of these interactions, spectral line broadening occurs. In addition, collisions can cause
distortions in the energy levels allowing coupling between the atom and photons that are slightly off the transition line center. A significantly strong collision causes the oscillating dipole of an atom or molecule to be randomly altered. Since each atom experiences the same number of collisions on average, this process is considered homogeneous broadening. Further discussion of collisional theory with consideration given to temperature and pressure is presented in Chapter 4.

2.2.4 Power Broadening

Another effect on linewidth can occur when input laser power levels are too high. Power saturation limits can be estimated by:

\[
I_{sat} = \frac{\varepsilon c \left( \frac{h}{2\pi} \right)^2}{2T^2 \mu^2}
\]  

(2.4)

where \(\varepsilon\) is the permittivity in a vacuum, \(c\) is the speed of light, \(h\) is Planck’s constant, \(T\) is the total radiative lifetime and \(\mu\) is the dipole moment operator described as:

\[
\mu = \sqrt{\frac{A3h\lambda^3 g 4\varepsilon}{64\pi^4}}
\]  

(2.5)

In equation 2.5, \(A\) is the transition probability, \(\lambda\) is the wavelength and \(g\) is the degeneracy of the transition. This broadening effect is not usually seen when using lower-power laser sources, yet it has been observed with as little as 10 mW of laser power and should be seriously considered when using pulsed laser systems where temporal factors create high power density levels. Similar broadening can result from
high concentration levels in samples. Several sources of line broadening are illustrated in Table 2.1.

### 2.3 Atomic Line Splitting

#### 2.3.1 Fine Splitting

As shown in Figure 2.1, for each atomic transition, there are a number of possible allowed transitions. A less complicated atomic transition diagram is shown in Figure 2.2 for chlorine. Recall that the $s$, $p$, $d$ and $f$ orbitals within a shell have the same principle quantum number $n$, but not the same energy due to electron-electron interactions for multi-electron atoms. The value of $l$ for $s$, $p$, $d$ and $f$ orbitals are 0, 1, 2 and 3, respectively. The selection rule of $\Delta l = \pm 1$, where $l$ is the angular momentum quantum number, prohibits transitions between all energy levels. The complexity of the electronic structure increases with the number of valence electrons and becomes particularly complex for transition metals with a large number of partly-filled shells.

The electronic state can be written more specifically by indicating the spin of the valence electrons, which can assume a spin “up” $\uparrow$ or a spin “down” $\downarrow$ configuration. The two cases are a result of spin-orbital coupling that causes an energy difference between the two levels. Using a chlorine atomic transition line as an example, Figure 2.2 shows how the two upper levels can be distinguished. This energy level difference is referred to as *fine* splitting.
Table 2.1 Line broadening sources.

<table>
<thead>
<tr>
<th>Method</th>
<th>Type</th>
<th>FWHM (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural linewidth</td>
<td>Homogeneous</td>
<td>( \Delta \nu = \frac{1}{2\pi c \tau} )</td>
</tr>
<tr>
<td>Doppler broadening</td>
<td>Inhomogeneous</td>
<td>( \lambda_{1/2} = 7.16 \times 10^{-7} \sqrt{\frac{T}{m}} )</td>
</tr>
<tr>
<td>Lorentzian broadening (pressure)</td>
<td>Homogeneous</td>
<td>( \Delta_{\nu, L} = 2 \times N_A \sigma^2 P \left( \frac{2}{\pi R T} \right) \left( \frac{1}{A} + \frac{1}{M} \right) )</td>
</tr>
<tr>
<td>Power broadening</td>
<td>Homogeneous</td>
<td>( \Delta_{\nu, P} = \frac{P_{12} E}{\hbar} )</td>
</tr>
</tbody>
</table>

\( N_A = \text{Avogadro’s number} \), \( \sigma = \text{collisonal cross section} \), \( P = \text{pressure} \), \( A = \text{atomic weight} \), \( M = \text{molecular weight} \)

\( P_{12} = \text{transition dipole moment} \), \( E = \text{strength of laser field} \), \( \hbar = \text{Planck’s constant} \)
Figure 2.2 Fine splitting diagram for the $^4D$ atomic chlorine transition.
2.3.2 Hyperfine Splitting

The use of high-resolution techniques to examine individual multiplets will reveal further splitting of electronic transitions. Each element has an intrinsic nuclear spin magnetic moment associated with it. When this nuclear spin magnetic moment interacts with the electronic spin and the total angular momentum, hyperfine splitting is observed. Hyperfine splitting depends on the total angular momentum of the electrons, depicted by \( J \), and the spin angular momentum of the nucleus, \( I \). The two combine to form the new quantum number, \( F \), which is defined as:

\[
F = J + I
\]  
(2.6)

where \( F \) is the total angular momentum of the atom and can have allowed values from \( F = I + J \) to \( F = I - J \).

Not every transition between different energy levels is allowed. Selection rules are applied to determine which transitions are permissible. These rules are dictated by the theory that states that absorption of light must be accompanied by a change in dipole moment. If there is no net change, the transition cannot occur, or is considered “forbidden”. The dipole moment operator, based on the wave function of the atom, can be solved to determine the change in dipole moment:

\[
P_{uL} = \int \psi_u P \psi_L d\tau
\]  
(2.7)

where \( P \) is the dipole moment operator and \( u \) and \( L \) denote the upper and lower states, respectively. When \( P \) is non-zero, the transition is allowed according to three basic
selection rules, which state $\Delta L = \pm 1$, $\Delta J = 0$, $\pm 1$ and $\Delta F = 0$, $\pm 1$. The relative position of the hyperfine component can be determined from the Casimir formula described as: $^6$

$$ W_F = A\left(\frac{K}{2}\right) + B\left[ \frac{3/4}{I(2I-1) 2J(2J-1)} K(K+1) - I(I+1) J(J+1) \right] $$

(2.8)

where $A$ and $B$ are the magnetic dipole and electric quadrapole hyperfine splitting constants, and $I$ is the nuclear spin. $K$ is defined as:

$$ K = F(F+1) - J(J+1) - I(I+1) $$

(2.9)

where $J$ and $I$ are their respective quantum numbers and $F$ is the hyperfine sublevel. Additionally, individual hyperfine contributions to each peak can be determined using

$$ K_{F-F'} = (2F+1)(2F'+1)\left[ \frac{F}{J} \frac{1}{I} \frac{F'}{J} \right] $$

(2.10)

where $F$ and $F'$ represent the quantum numbers obtained when the nuclear spin magnetic moment, the electronic spin and total orbital angular momentum are coupled for the lower and upper states. These calculations can be solved for all allowed transitions or found in published tables. $^7,^8$

Hyperfine splitting is significantly smaller than the fine splitting previously described. Hyperfine splittings can continue further if a magnetic field is applied to the system. Measuring this degeneracy in each of the $F$ levels is the basis for Zeeman spectroscopy.
2.4 Isotope Shifts

In addition to the signature resulting from previously discussed fine and hyperfine splittings for atomic transitions, the presence of multiple isotopes further increases the complexity of the spectrum. Most elements consist of atoms of different masses referred to as isotopes. Experimental observations of isotopes in optical transitions go back almost a century. Bohr’s atomic theory developed in 1913 suggests that spectra of different isotopes should be mass dependent. While fine and hyperfine splitting are limited to atomic transitions, isotope shifts can be found in both atomic and molecular absorption spectra. Isotope shifts are determined by combination of the volume shift, the normal mass shift and the specific mass shift. The volume shift results from a variation in mean squared nuclear charge radius between different isotopes of an element. It is the movement of the nucleus that causes the normal mass shift, while the specific mass shift originates from outer electron interactions. Generally, the mass effects dominate the shifts of lighter elements (< 30 amu) while heavier elements with atomic masses larger than 50 amu are dominated by the volume shift. Elements in between these masses receive contributions from both the volume and the mass effects. This dual contribution can result in a net cancellation of effects leading to very small isotope shifts. The fact that these shifts are small, coupled with large Doppler linewidths, makes accurate measurements by conventional optical spectroscopic methods difficult. Figure 2.3 is a simulation of the isotope shift in the infrared wavelength spectrum of the industrial pollutant SO$_2$.13
Figure 2.3 Molecular isotope shift of SO$_2$ at 1,351 cm$^{-1}$. This spectrum simulates the shift of SO$_2$ molecular vibrational transitions containing three different sulfur isotopes at natural abundance levels.
A need for isotope-level precision in optical spectroscopy has found widespread significance in recent years. New technology has allowed scientists to develop novel methods to detect diseases, track biohazardous pollutants in trace amounts and replace costly clinical methods with safer less complicated alternatives. Environmental forensics is a term given to a wide classification of chemical analyses used in various levels of law enforcement. Isotope ratio measurements form the basis for several applications in this relatively new field of study. Biological weapons detection, explosives characterization and illicit drug tracking are just a few examples of such applications.\textsuperscript{14,15} The effluent from manufacturing and refining companies often have unique isotope signatures\textsuperscript{16} as shown in Figure 2.4. Hence, isotope ratio measurements can help track down pollutant sources for remediation.

There is a growing need for sensors that can be used out in the field to accurately and quickly determine the nature of a pollutant. Complex fingerprints resulting from both hyperfine and isotope splittings and the continuing development of new laser sources, make the use of high-resolution spectroscopy an attractive choice for these applications.
Figure 2.4 Chlorine isotope ratios in detergent for select manufacturing companies.
2.5 References


Chapter 3

Introduction to Nonlinear Spectroscopy and Degenerate Four-Wave Mixing

3.1 Nonlinear Spectroscopy

Nonlinear processes occur when the effects of a perturbation become large enough such that the response to the perturbation no longer follows the magnitude of the perturbation. As discussed in Chapter 1, a conventional optical technique such as absorption spectroscopy relies on linear absorption of light that yields signal intensity levels according to Beer’s law defined as:

\[ A = \epsilon b C \]  \hspace{1cm} (3.1)

Equation 3.1 shows that the intensity of the absorption signal is directly proportional to the intensity of light absorbed. However, when using a nonlinear optical method, the intensity level varies as a function of the incident light intensity. When considering interaction of light with matter, polarization of the electric fields relate according to the function:

\[ P = a_1 E + \frac{1}{2} a_2 E^2 + \frac{1}{6} a_3 E^3 + ... \]  \hspace{1cm} (3.2)

where \( P \) is the polarization, \( E \) is the strength of the applied optical field, \( a_1, a_2, \) and \( a_3 \) represent the first, second and third order derivatives of \( P \) with respect to \( E \) at \( E = 0 \). Here, \( a_1 = \epsilon_0 \chi \) and the first term is linear. At small values of \( E \), this first term dominates the series. Conversely, as the applied electric field increases, the second and third order terms become more significant. These coefficients are characteristic of
the medium and, for most materials, a center of inversion only permits odd powers of $P$. Realizing this, Equation 3.2 can be rewritten as:

$$P = \varepsilon_0 \chi E + 4 \chi^{(3)} E^3$$

where $\chi^{(3)}$ is the third-order susceptibility that characterizes the medium. Again, the first term in the series is linear and the third term gives rise to the nonlinear component and nonlinear optical phenomena. This nonlinear term is a single quantity that considers all nonlinear interactions of the grating generation and detection processes. It is this term, $\chi^{(3)}$, that is the root of analytical nonlinear spectroscopic methods including second and third harmonic generation, coherent anti-Stokes Raman spectroscopy (CARS), the Kerr effect, and multi-photon nonlinear absorption methods such as degenerate four-wave mixing.

### 3.1.1 Degenerate Four-Wave Mixing

Degenerate four-wave mixing (DFWM) is one of the most versatile nonlinear optical methods. This nonlinear optical process has received attention for its potential as an ultrasensitive detection technique\(^2,3\) due to its many attractive and unique features. First, as an absorption technique, it does not require the sample to fluoresce in order to collect strong signals. Second, DFWM is a spatially precise method with a small overlap volume, i.e., detection probe volume, formed by the input laser beams. Third, it is a resonant optical technique, and hence, it is very sensitive to small analyte concentration changes. Finally, sub-Doppler linewidths obtained in a counter-propagating wave-mixing setup offer hyperfine-level spectral resolution.
A typical wave-mixing optical setup consists of two input beams from a single laser source mixed inside a medium and a third input beam that scatters off this medium. The result is the creation of an output signal beam with an intensity level proportional to those of the input beams. Two intersecting waves can interfere to generate a spatially sinusoidal intensity pattern in an absorbing medium. These spatially modulated absorption and dispersion perturbations generate an optical grating as shown in Figure 3.1. The third input beam diffracts off the grating at an angle determined by phase matching, generating the signal beam. Since all four of the beams have the same frequency, it is termed degenerate four-wave mixing. The spatial period of the grating, $\Lambda$, is a function of the laser wavelength, $\lambda$, and the angle between the input beams, $\theta$, as shown below:

$$\Lambda = \frac{\lambda}{2 \sin \frac{\theta}{2}}$$  \hspace{1cm} (3.4)

Various mechanisms contribute to the formation of the laser-induced gratings and the diffraction of light from these gratings. The dominant mechanism in gas-phase analytes involves the perturbation of population levels of absorbing molecules or atoms. Due to constructive and destructive interferences formed by the input beams, the molecules or atoms resonant with the laser frequency form a spatially modulated population grating. This coherence difference between ground-state and excited-state species conforms into an interference pattern generated by the overlapping input beams as shown in Figure 3.1. The third resonant beam probes this grating created by the absorptive and refractive contributions of the absorbing species.
Figure 3.1 Formation of a grating by two intersecting waves with spatially modulated population differences.
The intensity of the signal beam is given by: \(^4\)

\[
I_{\text{signal}} = \alpha^2 L^2 I_{\text{probe}} \frac{4 \left( \frac{I_{\text{pump}}}{I_{\text{sat}}} \right)^2}{\left( 1 + \frac{4 I_{\text{pump}}}{I_{\text{sat}}} \right)^3}
\]

(3.5)

where \(L\) is the interaction path length, \(I_{\text{probe}}\) is the probe beam intensity, \(I_{\text{pump}}\) is the pump beam intensity, and \(I_{\text{sat}}\) is the frequency dependent saturation intensity. \(^5\) The parameter \(\alpha\) is the line center coefficient given by:

\[
\alpha = \omega \frac{\Delta N |\mu_{1,2}|^2 T_2}{2 c \hbar \varepsilon_0}
\]

(3.7)

where \(\omega\) is the line-center frequency, \(\Delta N\) is the population difference in the absence of an applied field, \(\mu_{1,2}\) is the line-center transitional dipole moment, \(T_2\) is the coherent dephasing time, \(c\) is the speed of light, \(\hbar\) is Plank’s constant, and \(\varepsilon_0\) is the permittivity of vacuum.

Input laser power saturation causes the DFWM signal to deviate from expected behavior and this limit is termed the saturation intensity, \(I_{\text{sat}}\), such that:

\[
I_{\text{sat}} = \frac{\varepsilon_0 c \hbar^2}{2 T_1 T_2 |\mu_{1,2}|^2}
\]

(3.6)
where \( \varepsilon_0 \) is the permittivity of vacuum, \( c \) is the speed of light, \( h \) is Plank’s constant, \( \mu_{1,2} \) is the line-center transitional dipole moment, \( T_1 \) is the population decay time and \( T_2 \) is the coherent dephasing time.

Equation 3.5 is significant in several aspects. First, unlike conventional optical absorption signals, the wave-mixing signal has a quadratic dependence on analyte concentration as described by the \( \alpha^2 \) term. This greater sensitivity to small changes in concentration is a powerful diagnostic tool for trace-concentration environmental and biomedical applications where tiny changes must be monitored in natural ambient levels. Second, for small values of \( I_{pump}/I_{sat} \) where no power saturation is present, there is a cubic dependence on laser intensity. This cubic response to changes in laser power allows the use of relatively low power lasers to effectively generate large nonlinear signal levels. This allows design and development of small, portable detection systems that are in high demand. These advantages make degenerate four-wave mixing well suited for a range of applications including trace-concentration measurements, isotope-ratio determinations and diagnostics in harsh environments. Several of these applications are explored in this work.

3.1.1.1 Optical Configurations for Laser Wave Mixing

There are three types of four-wave mixing optical geometries used in the projects described in this dissertation. Figure 3.2 shows the wave-vector arrangement for what is referred to as the backward-scattering phase-matching geometry. When the phase-matching requirement is satisfied, light scattered from the grating
Figure 3.2 Backward-scattering phase-matching geometry.
propagates in phase, thus amplifying the nonlinear process. Phase matching can be described using the wave-vector mismatch:

\[ \Delta \vec{k} = \vec{k}_f + \vec{k}_b - \vec{k}_p - \vec{k}_s \]  \hspace{1cm} (3.8)

The subscripts \( f \), \( b \), \( p \), and \( s \) denote the forward, backward, probe and signal beams, respectively. The maximum signal occurs when \( \Delta \vec{k} = 0 \) and the experimental geometries must follow this relationship.

In the backward-scattering phase-matching geometry, the wave-vector arrangement can be given by \( \vec{k}_f + \vec{k}_b = 0 \) and the signal beam is generated as the phase conjugate of the probe beam, such that \( \vec{k}_p = -\vec{k}_s \). The area where all three beams intersect is often referred to as the probe volume. The experimental geometry used here is an out-of-plane arrangement where the vectors are still phase matched and the pump beams are nearly collinear while \( \theta \) is small (less than 2°). By moving the input beams slightly out of plane, the phase-conjugate signal beam is removed from the path of the probe beam while still maintaining most of the original intensity and line shape. This allows 100% optical collection efficiency for the signal beam and minimal background optical interference.

The laser output is split into three beams by a 30/70 % R/T beam splitter and a 70/30 % R/T beam splitter to produce the first, \( E_b \), second, \( E_p \), and third, \( E_f \) beams. The forward pump, \( E_f \), the backward pump, \( E_b \), and the probe beam, \( E_p \), are aligned through templates to ensure accurate collection of the generated signal beam. Because the beams are counter propagating, Doppler broadening is greatly reduced. An optical
arrangement of this out-of-plane geometry is shown in Figure 3.3. This particular arrangement is used for experiments described in Chapters 5 and 6.

In the forward-scattering wave-mixing optical arrangement, both pump beams and the probe beam travel in the same general direction. Figure 3.4(a) shows the phase-matching orientation for the wave vectors. This three-input-beam arrangement is non-planar. With no counter-propagating beam, this geometry yields Doppler-broadened signals.

Another experimental setup described in Chapter 4 couples the backward-scattering geometry with the forward-scattering phase-matched geometry. In order to arrange the backward and forward setups simultaneously, the backward pump is reflected back onto itself using the alignment templates, forming the probe beam for the forward phase-matched geometry. Care must be taken when reflecting the beam toward its source in order to avoid potential mode hopping or multi-moding problems. In this work, spatial filters are incorporated to diminish these effects. The combination of backward and forward geometries is shown in Figure 3.5. The use of an out-of-plane alignment allows collection of the signal beams without interference from either setup.

When Doppler broadening is not an issue as for condensed-phase analytes, it is helpful to use a two-beam forward-scattering wave-mixing optical setup. This alignment as illustrated in Figure 3.4(b) is relatively simple to assemble. The two input beams interact to form a grating and a second photon from either beam is diffracted off the grating. The phase-matching relationship remains satisfied in this
Figure 3.3 Out-of-plane backward-scattering optical arrangement.
Figure 3.4  Forward-scattering phase-matched optical arrangements. (a) Three-beam out-of-plane phase-matching geometry, (b) simplified two-beam forward-scattering geometry.
Figure 3.5 Simultaneous backward-scattering and forward-scattering wave-mixing geometry.
arrangement. The two input beams are split from a single laser source using a 30/70% R/T dielectric beam splitter. All other alignment procedures are similar to those previously discussed.

Figure 3.6 illustrates a typical wave-mixing optical setup for gas-phase analytes where the sample cell or atomizer is positioned between the templates at the intersection of all input beams. A reference beam can be aligned through the templates to ensure correct placement of all signal collection optics. Unless otherwise stated, an optical chopper (Stanford Research Systems, Sunnyvale, CA, Model SR540) is used in conjunction with a lock-in amplifier (Stanford Research Systems, Sunnyvale, CA, Model SR810) to enhance signal-to-noise ratios and minimize background interference.
Figure 3.6 Typical gas-phase wave-mixing optical setup.
3.2 References


Chapter 4

Spatially-Resolved Four-Wave Mixing as a Diagnostic Tool to Measure Kinetic Temperature and Electron Density in an Inductively Coupled Plasma Atomizer

4.1 Introduction

An inductively coupled plasma (ICP) atomizer, an argon-gas plasma sustained by a RF field, has a very high electron density and can reach temperatures over 16,000 K. Because of these high energy levels, an ICP is often used as an excitation source or an atomization system in optical instruments or in conjunction with mass spectrometers. These versatile energy sources are also used in materials processing, non-equilibrium physics and radiative heat transfer studies. The temperature of the gases in the observation region of the ICP torch is of critical interest to the use and modeling of these plasmas. Several different methods have been investigated previously to measure the temperature of an ICP torch including emission spectroscopy.\textsuperscript{1,2} However, emission spectroscopy is not spatially precise since it is a line-of-sight measurement method, resulting in erroneous assumptions of symmetry. To determine an electronic temperature, emission spectroscopy often makes use of several different spectral lines to determine the mean distribution of the electron populations in the excited electronic states of an analyte. Additional information about the plasma can be obtained by measuring spectral line broadening. For example, the kinetic temperature can be derived from Doppler broadening and the
Stark broadening. This temperature can then be used to infer the electron number density.

Diagnostic studies of plasmas have also been carried out by linear absorption techniques. In 2002, Wang et al.\textsuperscript{3} applied cavity ring down spectroscopy on argon in a plasma torch. Moreover, both Baer\textsuperscript{4} and De Regt\textsuperscript{5} used tunable diode lasers for line-of-sight absorption measurements in atmospheric pressure plasma. However, none of these techniques are spatially precise.

In addition, laser-induced fluorescence has been used to effectively measure temperatures in a plasma.\textsuperscript{6} Laser-induced fluorescence (LIF) is a spatially precise technique with the measurement location defined by the intersection of the laser beam and the detection system. Hence, there is no assumption of symmetry. However, the laser-induced fluorescence signal is scattered isotropically. Collecting this signal in such a luminous environment is time consuming since the weak LIF signal must be discriminated from strong ambient emission background levels. De Regt et al.\textsuperscript{7} compared Thomson and Raleigh scatterings using a 100 MHz argon ICP. However, both of these processes are relatively weak and have similar problems as those associated with LIF. One method that has been used effectively in combustion research for temperature and species density measurements is degenerate four-wave mixing (DFWM).\textsuperscript{8} Green et al.\textsuperscript{10} used pulsed DFWM to probe a RF-ICP torch and measured the vibrational temperature of CH and the CH concentration of multiple CH vibrational levels. Musiol et al.\textsuperscript{11} made assumptions about the local thermodynamic state of the plasma to obtain an approximate electronic temperature of argon, based
only on the intensity of a single spectroscopic line. This nonlinear optical method offers some advantages over other techniques in that it is a spatially precise technique with the measurement location defined by the overlap volume of three distinct input laser beams. Wave mixing offers two significant advantages over laser-induced fluorescence. First, the wave-mixing signal is relatively insensitive to quenching collisions, and hence, the signal relates more directly to species density (or state population in the case that an excited state is probed). Second, the wave-mixing signal is a coherent laser-like beam, therefore, spatial filtering can be used very effectively to improve the signal-to-noise ratio, allowing the use of small, low-power diode lasers.

In this study, we use DFWM to measure the kinetic temperature of argon atoms by simultaneously detecting the forward- and backward-scattering DFWM spectra. Previous wave-mixing measurements used the backward-scattering phase-conjugate geometry that yields sub-Doppler or Doppler-free spectra in the limit of small beam crossing angles. More recently, the forward geometry has been investigated and different groups reported that forward DFWM spectra are Doppler broadened. In this study, we use DFWM to measure the kinetic temperature of argon atoms by simultaneously monitoring the forward- and backward-scattering DFWM spectra. Danehy et al. obtained forward-geometry spectra of nitric oxide in a gas cell. They later obtained backward-geometry spectra under the same conditions, yet with a different optical setup. By sequentially fitting both spectra using perturbation theory, Danehy et al. were able to determine both the Doppler
broadening and the homogeneous broadening. The gas pressure and temperature values were determined from these broadening parameters.

The present study substantially extends this capability in three ways. Most importantly, the forward- and backward-scattering spectra are obtained simultaneously using a novel beam alignment to ensure consistent broadening parameters across both spectra. The spectra are subsequently processed to yield temperature and electron number density. Additionaly, the technique is applied to a continuously flowing, highly luminous inductively coupled plasma torch using argon. Lastly, a compact low-power high-resolution tunable diode laser is used.

4.2 Theory

In 1978, Abrams and Lind presented a model for DFWM in an absorbing, homogeneously broadened two-level medium. However, this model does not take into account atomic motion. To address the effects of atomic motion, Nilsen and Yariv presented a perturbative framework for predicting DFWM spectra and intensities for any phase-matching geometry. Abrams et al. simplified these expressions for the case of phase-conjugate phase-matched wave mixing. In 1995, Danehy evaluated the perturbation-theory solution for the case of the forward phase-matching geometry. The resulting expressions assumed that the three input beams are collinear. This is a valid assumption when the beam crossing angle is small. This analysis includes (1) inter-molecular collisions, which lead to pressure (homogeneous)
broadening, and (2) molecular motion, which results in Doppler (inhomogeneous) broadening.

The phase-conjugate geometry is often called the backward phase-matching geometry. In this experiment, we use a non-planar counter-propagating beam geometry. In the limit of small $\theta$, where $\theta < 2\gamma/k\nu_0$, then the normalized wave vectors are:

$$\hat{n}_f = \hat{n}_p = -\hat{n}_b = -\hat{n}_s$$

(4.1)

In the forward geometry, if $\theta < 2\gamma/k\nu_0$, then all four beams have effectively identical normalized wave vectors:

$$\hat{n}_f = \hat{n}_p = \hat{n}_b = \hat{n}_s$$

(4.2)

Unlike the backward phase-conjugate geometry, the forward geometry spectrum is Doppler broadened significantly, even at small-crossing angles. Isolating Doppler broadening of the argon spectral line allows one to measure the kinetic temperature.

An iterative method is used to increase accuracy since the sub-Doppler line width is slightly dependent on temperature. Initially, an estimate is made ($T_1$) and the backward-scattering geometry spectrum is fitted using the phase-conjugate perturbation theory. This results in a preliminary estimate of the homogeneous broadening ($\Delta \nu_{\text{homog}}$). This broadening parameter is then used in fitting the forward-geometry spectrum with perturbation theory to determine a secondary temperature estimate ($T_2$), which then replaces $T_1$ in the process to produce a more accurate
estimate of $\Delta t_{\text{homog}}$. This iteration is continued until $T_1$ and $T_2$ agree with the desired precision.

The homogenous broadening effects of spectral lines are used to calculate the electron density. These effects can result from collisions with other particles. Van der Waals broadening refers to collisional broadening resulting from collisions of the absorbing particle with neutral particles. This type of broadening can be ignore for argon since it is approximately 0.1 % of the total homogeneous width.\(^\text{19}\) Resonance broadening refers to collisions with particles of the same species. This is noteworthy when the initial state is coupled with the atomic ground state and is not significant for the argon metastable state probed here.\(^\text{19}\)

An electric dipole can be induced when an external field is applied to the atomic system. When this dipole moment interacts with the external field, it will shift the atomic energy levels. This shift is proportional to the square of the field strength. The external field can result from charged particles or particles with permanent dipole moments, and the resulting shift is referred to as the Stark shift. The influence of many colliding partners causes the Stark effect to result in an overall broadening of the spectral line referred to as Stark broadening.

Homogeneous broadening and shift of spectral lines can be related to electron density and temperature through theoretical Stark parameters. The Stark parameters for the 4s $^3P_2 \rightarrow 4p ~^3D_3$ argon transition can be found in Griem.\(^\text{20}\) The Stark effect results in a full width half maximum (FWHM) $w_{\text{th}}$ of:\(^\text{19}\)

$$w_{\text{th}} = 2\left[1 + 1.75 \times 10^{-4} \left(1 - 0.068 \frac{n_e^{1/6}}{T_e^{-1/2}}\right)\right]^{1/2} 10^{-16} \text{wn}_e$$

(4.3)
where $n_e$ is the electron density, $\alpha$ is the ion-broadening parameter, $T_e$ is the electron temperature, and $w$ is the electron impact parameter. Non-equilibrium calculations suggest that the gas and electron kinetic temperatures should be identical.\textsuperscript{3} Hence, all species are assumed to be at the atomic kinetic temperature. Electron density is then solved by matching the previously measured temperature and collisional width to Equation 4.3.

4.3 Experimental

In this work, a 27 MHz radio-frequency inductively coupled plasma (Varian, Inc., custom unit) operating at 1 kW incident power is used. The plasma torch, as shown in Figure 4.1, consists of a series of three concentric quartz tubes that carry argon at different flow velocities through the RF coil region. The outer argon flow (typically 5 - 15 L/min) serves to sustain the plasma and to carry the heat of the plasma away from the quartz glass walls of the torch. The intermediate tube gas flow (typically 0.5 - 2.0 L/min) serves to lift the plasma a few millimeters from the RF coils. Upon igniting the torch, the intermediate or “auxiliary” flow is made electrically conductive by a Tesla spark before it passes through the RF coil. A RF power of approximately 0.5 - 2 kW is transferred using a coil wrapped around the torch. The RF field inductively heats and subsequently ionizes the formed plasma to temperatures exceeding 5,000 K. The entire process of forming and stabilizing an ICP takes several milliseconds.
Figure 4.1 Schematic diagram of the plasma torch and relative positions of the regions probed. The origin of the coordinates is shown at the top of the glass bonnet above the nebulizer.
The centrally located gas flow or nebulizer flow (typically 0.3 – 1.5 L/min) is used to introduce analyte into the existing plasma. While passing through the induction region, the aerosol is desolvated, dissociated, atomized and excited. Only deionized water is used in the present experiment. The ICP is mounted on a 2D translational stage to accurately probe the analytical region from 3 to 10 mm above the ICP bonnet.

As discussed in Chapter 3, the optical setup is a combination of the backward phase-conjugate geometry and the forward phase-matched geometry. The $E_b$ beam from the backward-scattering geometry is reflected back along the original path to create one of the forward-scattering pump beams as shown in Figure 4.2. The light source is a laser diode (Optima Precision, Model Sharp LT016MD) operated at 36.6 °C and wavelength tuned by changing the diode current. The diode laser system used consists of a low-noise current source (ILX Lightwave Corp., Model LDX-3320), a thermoelectric temperature controller (ILX Lightwave Corp., Model LDX-5525) and a laser diode mount (ILX Lightwave Corp., Model LDM-5910B). The diode has an average power of 25 mW. A small fraction of the laser is directed into a high-resolution wavemeter (Burleigh Instruments, Model WA-1500) to verify the wavelength in real time during a frequency scan.

The laser output beam is split into three input beams. A 50/50 % R/T beam splitter is used to create the backward input beam, $E_b$. A second 70/30 % R/T beam splitter is used to produce the probe $E_p$ and the forward $E_f$ input beams. The three beams are easily aligned using our custom-made alignment templates. The beams are
Figure 4.2  Experimental Setup for dual forward-and-backward wave mixing
left collimated as they pass through the torch (i.e., no additional focusing lens is used). The crossing angle between the input beams is 1.25 degrees, resulting in a spatial resolution of 5 mm in the long dimension of the probe volume and an order of magnitude smaller in width. The length of the probe volume was determined by observing the crossing of the beams with an infrared card.

Signal from each wave-mixing setup is collected by a simple photodiode (Thorlabs, Inc., Model PDA55) and the signal is processed by a lock-in amplifier (Stanford Research Systems, Inc., Model SR810DSP). To improve signal-to-noise ratio, the forward pump beam is optically modulated at 1,500 Hz by a mechanical chopper (Stanford Research Systems, Inc., Model SR540). The lock-in amplifier output is digitized by a custom-built data acquisition system. The perturbation theory program, written in Fortran, is used to fit the measured spectra. Temperature and collisional widths are determined from the theoretical fit of both forward and backward data. Each frequency scan at a desired position takes approximately 3 minutes to acquire. The probe volume is relatively small (13 µL) and the longest dimension is oriented along azimuthally, so that the probe volume does not span steep into temperature gradients.

4.4 Results and Discussion

Several experimental parameters affect the intensity of the wave-mixing signal. For instance, a small difference in RF power creates a hotter or cooler torch, changing the available population of the probed state, which in turn can change the signal
intensity level. From a DFWM signal perspective, the optimal RF range depends on the energy required to disassociate molecules or to populate any non-resonant states. The DFWM signal intensity drops off at RF power levels lower than about 1,000 W due to the lack of energy to sufficiently excite the atoms to this level. An RF power level sufficient to populate the probed state is used in all experiments in this study.

In order to measure temperature levels in the torch, the diode laser is scanned to obtain spectral profiles for both wave-mixing geometries simultaneously. The spectra are imported into the fitting program described previously and iteratively fitted with temperature and collisional width as variables. An example of perturbation theory fitted to phase-conjugate experimental data is shown in Figure 4.3. Figure 4.4 illustrates a comparison of spectra collected simultaneously from forward and backward geometries.

Reproducibility of our experimental data is tested by comparing the line-shape fitting procedures for a set of multiple scans. The results for fitting each data set are listed in Table 4.1, along with the residual (chi-squared error). The measured temperatures differ by less than 50 K (less than 1% of the measured temperature). To test the error in the fitting program starting with the estimate of T1, the initial T1 is varied by up to 5,000 K, while fitting the same set of spectra. This process results in temperature and linewidth uncertainties of ±10 K and ± 0.0001 cm\(^{-1}\), respectively.

The variability introduced into the fitting program by the sampling rate is also tested. Cutting the effective sampling rate down by 30 % introduces ± 150 K and ± 0.005 cm\(^{-1}\) variability in the results of the same set of data. This variability is
Figure 4.3  Experimental data with temperature fit profile of 3,400 K.
Figure 4.4 Theoretical fitting to experimental data of both wave-mixing geometries. The fits result in a temperature of 8,100 K.
Table 4.1  Results obtained from dual forward-and-backward wave-mixing setup.

<table>
<thead>
<tr>
<th>Run</th>
<th>Temperature Measured</th>
<th>Collision Width Measured</th>
<th>Residual (Chi Sqr) Forward</th>
<th>Residual (Chi Sqr) Backward</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8618.4</td>
<td>0.10608</td>
<td>$2.3 \times 10^{-3}$</td>
<td>$3.1 \times 10^{-3}$</td>
</tr>
<tr>
<td>2</td>
<td>8567.4</td>
<td>0.10966</td>
<td>$4.0 \times 10^{-3}$</td>
<td>$2.3 \times 10^{-3}$</td>
</tr>
<tr>
<td>3</td>
<td>8599.4</td>
<td>0.10790</td>
<td>$3.1 \times 10^{-3}$</td>
<td>$3.0 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
extremely small when compared to the temperature gradients in the torch, and thus, it does not affect the calculated temperature levels. Hence, we estimate that the overall uncertainty in the measured temperature and line width from a single measurement is approximately ±150 K and ± 0.005 cm⁻¹. This line width uncertainty corresponds to an uncertainty of ± 0.3 x 10¹⁵ cm⁻³ in electron number density calculations.

To make a complete scan of the torch, radial measurements are collected at several different heights above the bonnet. These intensities are then fitted to produce calculated temperatures laterally across the torch (Figures 4.5 and 4.6). Using a standard power level of 1,048 W, the maximum temperature is determined to be 14,000 ± 150 K at 3 mm above the bonnet. Figure 4.7 combines the radial profiles to create a topographical map of the entire sampled region of the torch.

Using the homogenous broadening and temperature measured at each spot, one can calculate the electron number density based on the Stark broadening width (w_th) expressed in Equation 4.3. A contour map of the calculated electron densities is shown in Figure 4.8. The electron density is found to range from 6.1 (± 0.3) x10¹⁵ cm⁻³ to 10.1 (± 0.3) x10¹⁵ cm⁻³. These results compare favorably with the results reported by De Regt et al.⁷ using a diode laser-based absorption technique.

4.5 Conclusions

This work presents degenerate four-wave mixing as a spatially precise tool for measuring temperature and electron density levels with the ability to map highly luminous and turbulent environments. A novel wave-mixing optical setup is used to
Figure 4.5  Plot of measured temperatures across the radius of the torch using 1.25 mm increments from the center and 3 mm and 5 mm above the bonnet.
Figure 4.6 Plot of measured temperatures across the radius of the torch using 1.25 mm increments from the center and 8 mm and 10 mm above the bonnet.
Figure 4.7 Contour plot of calculated temperatures in the analytical zone of the torch.
Figure 4.8 Contour plot of calculated electron density (given in units of $10^{15}$ cm$^{-3}$) in the analytical zone of the torch.
collect both the forward- and the backward-geometry wave-mixing spectra simultaneously in an atmospheric radio-frequency inductively coupled plasma (RF-ICP) torch operating with argon. The atomic argon transition at 811.754 nm is probed using an inexpensive low-power diode laser. This non-intrusive technique yields spectra that are subsequently processed to determine temperature and homogeneous broadening values. A three dimensional contour map of the torch is obtained yielding a temperature range of 3,500 to 14,000 K ± 150 K. The uncertainty in the measurements and calculations is found to be less then 5%. Electron density levels measured range from 6.1 (± 0.3) x 10^{15} \text{ cm}^{-3} to 10.1 (± 0.3) x 10^{15} \text{ cm}^{-3}. 
4.6 References


5.1 Background

Environmental and atmospheric reaction studies as well as biological applications demand accurate isotope and concentration measurements. Oxygen plays a vital part in many of these chemical processes in the atmosphere and environment due to the high natural abundance of this element. Additionally, stable isotope ratio chemistry of nonmetals is frequently used for insight into these processes.\(^1\) Natural materials such as biomatter, rocks and water preserve the isotopic signatures in O\(_3\), H\(_2\)O\(_2\), CO\(_2\), and other oxygen containing species. Yet, equilibrium processes such as evaporation, condensation, isotopic exchange and diffusion will change the composition of the molecular species present. Thus, these signatures are able to offer a geological record of occurrences in ancient environments or past climactic conditions. These signatures can also be used to deconvolute surface environments and reaction processes. Rare isotopes of oxygen can be used to monitor anthropogenic activity, track greenhouse gas production, understand biosphere productivity and processes involving the sulfur cycle, as well as to reconstruct the paleoclimate.\(^1,2\) Table 5.1 shows naturally occurring isotopic data for oxygen. Oxygen has three stable isotopes, however, oxygen-16 is by far the most abundant (99.8%).
Table 5.1 Naturally occurring isotopes of oxygen.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Nuclear Spin (I)</th>
<th>% Natural Abundance</th>
<th>Mass(^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{16}\text{O})</td>
<td>0</td>
<td>99.757</td>
<td>15.994915</td>
</tr>
<tr>
<td>(^{17}\text{O})</td>
<td>5/2</td>
<td>0.038</td>
<td>16.999131</td>
</tr>
<tr>
<td>(^{18}\text{O})</td>
<td>1</td>
<td>0.205</td>
<td>17.999160</td>
</tr>
</tbody>
</table>

\(^{1}\) CRC Handbook of Chemistry and Physics, 75\(^{th}\) ed. (1995)
An energy level diagram for atomic transitions in neutral oxygen is shown in Figure 5.1. The metastable $^5S_2$ state is 9.15 eV above the $^3P$ ground state of atomic oxygen. This metastable state couples with the $^5P_3$ level allowing absorption at 777.407 nm. The probability of atomic transition at the $^5S_2$ level is enhanced by a lifetime of 180 $\mu$s. Fine structures are expected to be seen from this triplet state with three closely spaced transitions at 777.4 nm, 777.6 and 777.75 nm. Oxygen-17, with a non-zero nuclear spin, is the only natural isotope expected to show hyperfine splitting. Figure 5.2 shows the expected fine structures for the 777 nm transition, including the hyperfine splitting for oxygen-17. Hyperfine component contributions are shown in parentheses.

Measuring nonmetal elements using optical methods can be challenging since the strongest resonance transitions occur in the ultraviolet region. For instance, resonant absorption of atomic oxygen occurs at 113 nm. Currently available tunable light sources with narrow linewidths are not widely available at deep UV wavelength ranges. However, using VUV pulsed dye lasers, some success has been achieved by two-photon excitation of oxygen at 226 nm. Unfortunately, in-situ and routine use of these experimental arrangements is limited due to the cost and complexity involved. Hyperfine and isotope analysis measurements are also difficult with these lasers due to linewidth limitations. Investigating strong excited-state transitions in the near-IR with compact diode lasers offers an alternative to bulky, expensive, and complicated UV sources for the detection of nonmetals. Semiconductor diode lasers have many advantages including narrow linewidths and short-range wavelength tunability suitable
Figure 5.1  Excited oxygen atomic energy levels.
Figure 5.2 Fine and hyperfine splitting of oxygen near 777 nm.
for probing entire isotope and hyperfine profiles. External cavity diode lasers improve upon these advantages by offering MHz linewidths and mode-hop-free tuning.

At room temperature, the energy available is not enough to populate the excited-state energy level of atomic oxygen. Even with typical atomization temperatures of 3,000K, Boltzmann distribution estimates the upper-state population to be $10^{-14}$%. This can make using optical absorption techniques difficult.

Optical techniques such as emission spectroscopy, atomic absorption spectrometry (AAS), laser-induced fluorescence (LIF), saturation absorption spectroscopy (SAS), and two-photon degenerate four-wave mixing (TP-D4WM) spectroscopy have been investigated for use in oxygen detection. Mass spectrometry is currently the most commonly used technique for measurement of isotopes. Yet, measuring oxygen by this technique requires a specialized and expensive instrument incapable of multi-element analysis.

For the detection of atomic oxygen, there are several atomization sources to consider. The inductively coupled plasma, commonly used with mass spectrometers, is able to atomize more difficult samples that require higher amounts of energy when compared to spark sources, flames and graphite furnace atomizers. The ICP atomizers will effectively populate the excited-state energy levels of atomic oxygen, however, they have some important limitations. For instance, sample contamination can be an issue since it is important to eliminate large background oxygen levels present in room air when using an atmospheric atomizer. Also, the inductively coupled plasma can be cost-prohibitive and cumbersome. A direct-current (DC) discharge atomizer,
however, is especially effective in minimizing atmospheric and room-air oxygen interferences and is relatively inexpensive and portable.

### 5.2 Demountable Hollow-Cathode Discharge Cell

The hollow-cathode discharge cell is a low-pressure, low-temperature plasma. Direct-current electrical power is delivered through two electrodes, which in turn excite a noble gas buffer. The energy in this plasma dissociates the molecular oxygen and provides the 9 eV energy required for the excitation of atomic oxygen. It was proposed by Sasso, et al.\textsuperscript{11} that Penning collisions with metastable noble gas atoms (X) produce molecular oxygen ions. Dissociative recombination then follows this reaction, forming excited oxygen atoms such that:

\[
X^* + O_2 \rightarrow O_2^+ + e^- + X
\]

\[
O_2^+ + e^- \rightarrow O^* + O
\]

Loss of excited oxygen occurs by collisional quenching.

\[
O_2 + O^* \rightarrow 3 \text{ O}
\]

The smaller excitation energy of some noble gases does not allow them to partake in Penning ionization, so the mechanism was revised to consider a quasi-molecule followed by dissociation.

\[
Ar^* + O_2 \rightarrow [ArO_2]
\]

\[
[ArO_2] \rightarrow Ar + O (2^1S_0 \text{ and } 2^1D_2) + O (2^3P) + \Delta E
\]

Electron collision then transfers the energy of these products to the \(2p^3 3s \, {}^5S_2\) level. Direct population of the metastable level is also possible from radiative decay
of excited argon. Additionally, collisional energy between argon and oxygen is quite high due to the abundance of argon in the cell. This can lead to higher effective temperatures when optical thermal measurements yield lower temperatures near 800 K.

Experimental parameters such as buffer gas properties, discharge cell dimensions, electrode geometry, electrode properties and discharge currents affect the efficiency of the discharge to dissociate and excite the analyte. Additionally, loss of excited species can occur by processes including loss to cell walls and electrodes, molecular recombination, and radiative and nonradiative relaxations. Optimizing these parameters can maximize the population of the non-resonant transition, allowing the use of near-IR diode lasers for oxygen detection.

5.3 Experimental

5.3.1 Discharge Cell

Figure 5.3 shows a diagram of the demountable hollow-cathode discharge. This custom-built Pyrex cell is eleven inches long. At the ends, quartz windows are attached at an angle to reduce scatter from incident laser beams. Side arms are fashioned both above and below the main Pyrex chamber to allow electrodes to be inserted, mounted and sealed. The two side arms are offset to ensure a small separation between the anode and the cathode. This gap can be varied from 6 mm to 20 mm by adjusting either electrode. For this experiment, the gap is usually set at 9 mm. The anode is composed of a standard commercial $1 \frac{1}{16}$ x 2-inch tungsten welding
Figure 5.3 The demountable hollow-cathode lamp (HCL) atomizer.
rod (Bestweld, San Diego Welder’s Supply, San Diego, CA). A 1/2-inch diameter Cajon Ultra-Torr fitting is used to mount the anode to one of the arms of the cell. The cathode is a ¾ inch x 1 inch stainless-steel tube threaded onto a stainless-steel support rod. This is also mounted to the cell using a 1-inch diameter Cajon Ultra-Torr fitting. Various other metals such as copper, aluminum or tungsten can be used for the cathode tube.\textsuperscript{13,14} A high-voltage power supply (Kepco, Inc., Flushing, NY, Model BHK 2000-0.1 M) serves as the direct-current power source. To increase the current above the operating range of 100 mA, a second power supply (Kepco, Inc., Flushing, NY, Model BOP 1000M) is added to increase the current level to 140 mA. Both electrodes are shielded by glass sleeves to prevent unnecessary electrical arcing at high current levels. Samples are introduced by two 1/4-inch diameter side arms attached to the main chamber. Inlet and outlet gas lines are connected to the Pyrex cell using 1/4-inch diameter Teflon Cajon Ultra-Torr unions.

5.3.2 Optical Setup

The backward-scattering phase-matched geometry, as described in Chapter 3, is used with some modifications as stated below. The diode laser (Sharp Electronics, Nara, Japan, Model LT024MD0) has an average output power of 26 mW when scanned within the operating wavelength range of 777 nm to 780 nm. A peak laser power level of 34.5 mW is used at the analyte line center for detection limit studies. When smoother wavelength tuning is required, an external cavity diode laser (ECDL) (New Focus, Inc., Santa Clara, CA, Model 6300) with 10mW output power is used.
This laser has an extremely narrow bandwidth (MHz) and can be precisely controlled by a computer.

A translational XYZ stage is used to precisely adjust the position of the discharge cell in the probe volume where all three beams intersect. Real-time monitoring of the wavelength is accomplished by directing a small fraction of the laser output into a wavemeter with sub-picometer resolution (Burleigh Instruments, Fishers, NY, Model WA-1500VIS). Since the signal is a coherent laser-like beam, spatial filters can be effectively used to minimize background optical noise before it is collected by a simple photodetector (Thorlabs, Inc., Newton, NJ, Model PDA-55).

Internal chamber pressure is monitored by a pressure transducer (MKS Instruments, Andover, MA, Model 222BA-00100) and the flow rate is monitored by a mass flow meter (Hastings, Inc., Hampton, VA, Model 200L). The flow rate and pressure levels are controlled by micrometer valves attached to premixed analyte tanks and a vacuum pump (Trivac, Inc., Model D4A).

Gas samples are prepared from 10 % O$_2$ (San Diego Welders Supply, San Diego, CA), 1.25 % oxygen (Praxair, Los Angeles, CA), or 192 ppm pre-mixed oxygen in high-purity argon tanks (Praxair, Los Angeles, CA). A custom-designed dilution setup allows preparation of different concentration levels from these original gas cylinders. The cell is cleaned before each run with deionized water and acetone/ethanol. The electrodes are soaked in nitric acid to remove any residual buildup. The cell is reassembled and completely evacuated to less than 0.5 Torr three times in order to remove any remaining oxygen. A stable discharge is then maintained.
while the current is ramped to 80 mA for 10 minutes to burn off any other contaminants such as organics.

5.4 Results and Discussion

5.4.1 Signal Optimization

The small cathode region concentrates the collisional energy of the excited argon to provide a dense area of excited state oxygen. But this effect can be increased by optimizing the parameters of the discharge. Figure 5.4 illustrates the effect of discharge current on signal intensity. This parameter has the most significant effect on the population inside the cathode, and thus, the signal intensity. As expected, the signal intensity increases as the current is ramped from 20 to 100 mA. It should be noted that at the highest current levels, the discharge becomes difficult to maintain, and therefore, an average current of 80 mA is normally used.

The effect different cathode materials have on signal intensity is also investigated. Materials tested include, copper, aluminum and stainless steel. Copper cathodes yield the highest signal intensities, but sputtering of the actual cathode material results in damaged or contaminated gas cells and windows. Aluminum cathodes perform poorly due to excessive electrical arcing resulting in unstable plasma atomization for any reliable length of time. The stainless-steel cathodes produce reliable and strong signal intensity levels for sustained periods with minimal breakdown or deposition. Because of these advantages, stainless-steel cathodes are
Figure 5.4 DFWM signal intensity variation with change in discharge current.
used for all subsequent runs. A comparison of signal intensities collected with copper and stainless-steel hollow cathode compositions is shown in Figure 5.5.

Chapter 4 describes the use of a small laser probe volume to map the topography of a turbulent ICP atomizer environment. In the hollow-cathode cell, the laser probe volume is considerably smaller than that used for the ICP since the cathode plasma zone is much smaller. Hence, the position of the probe volume inside the cathode cell is an important experimental parameter. The discharge cell is mounted on an XYZ translational stage, which allows the laser probe to be located anywhere inside the cathode tube and up to 20 mm outside the cathode tube. Signal intensity is recorded as the cell is slowly moved in all three directions to collect a topographical map of signal levels in all regions of the cathode. The results of these scans are shown in Figure 5.6. As expected, the maximum signal intensity is found at the center of the 10 mm cathode tube and this location is used for all subsequent spectral scans.

Lastly, the flow rate of the analyte of interest is investigated. Signal intensity is found to increase with flow rate (up to 4 sccm), as expected. After this, the plasma becomes unstable, resulting in lower signal intensity levels. Figure 5.7 shows an increase in signal intensity when the analyte gas flow rate is increased.

Figure 5.8 shows a typical signal peak from a 50 ppmv oxygen analyte in argon. A preliminary concentration detection limit of 11 ppmv (S/N 2) is determined for oxygen. A preliminary mass detection limit of 3.48 pg is estimated for oxygen, assuming that the density of oxygen atoms in the cell is $1.03 \times 10^{13}$ atoms cm$^{-3}$ and the laser probe volume, determined by AutoCAD simulations, is 12.73 mm$^3$. 
Figure 5.5  Comparison of copper and stainless-steel signal strengths.
Figure 5.6 Mapping atomic density in the plasma. As expected, the highest intensity levels are observed at the center of the hollow-cathode discharge tube and at the location between the cathode and the anode.
Figure 5.7 Signal intensity dependence on analyte flow rate.
Detection of a reactive species like atomic oxygen from a non-resonant metastable state is affected by analyte depletion through various losses through collisional quenching with walls and other species. It is also be affected by atomization and excitation efficiencies. Appendix B shows a summary of these processes applicable to a hollow-cathode discharge cell used to detect free oxygen atoms. Based on the preliminary mass detection limit of 3.48 pg and the average values of the mechanisms listed in Table B.1, an effective mass detection limit of \( 2.5 \times 10^{-17} \) g, 25 attogram or 14 attomole is determined for atomic oxygen. The use of a small amount of impurity, such as N\(_2\), could significantly enhance signal intensity by minimizing the loss of free atomic oxygen to the cell walls and electrodes (i.e., surface recombination).\(^{16}\) However, this may not be as important in a design where the probe volume in the cathode is some distance from the walls of the cell.

Table 5.2 lists previously reported detection limits from different detection methods for this element. It should be noted that some of the methods reported in this table require significant pre-concentration steps and others used unrealistic extrapolation schemes such as S/N of 1 or extrapolated the detection limits from much higher concentration levels (e.g. room air). Moreover, some methods report detection of other species such as O\(_2\) or O\(^-\) rather than atomic oxygen. Since most of the oxygen in the upper atmosphere is dissociated, it is important that one can directly detect atomic oxygen species when studying atmospheric processes.
Figure 5.8  Oxygen 50 ppmV peak with a S/N of 40. An effective mass detection limit of $2.5 \times 10^{-17}$ g, 25 attogram or 14 attomole is determined for atomic oxygen.
Table 5.2  Comparison of reported limits of detection (LOD) for oxygen.

<table>
<thead>
<tr>
<th>Method</th>
<th>Density (atom/cm$^3$)</th>
<th>Actual Injected Concentration</th>
<th>Reported LOD</th>
<th>Species Detected</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diode Laser AAS</td>
<td>--</td>
<td>21,000 ppm</td>
<td>170 ppm</td>
<td>$O_2$</td>
<td>17</td>
</tr>
<tr>
<td>Secondary Ion Mass Spec.</td>
<td>$2 \times 10^{15}$</td>
<td>13.3 ppm</td>
<td>53 ppb</td>
<td>$O^-$</td>
<td>7</td>
</tr>
<tr>
<td>Diode Laser AAS</td>
<td>--</td>
<td>21,000 ppm</td>
<td>20 ppm</td>
<td>$O_2$</td>
<td>18</td>
</tr>
<tr>
<td>Dual beam Laser AAS</td>
<td>--</td>
<td>35 ppm</td>
<td>7.6 ppm</td>
<td>$O_2$</td>
<td>19</td>
</tr>
<tr>
<td>Two-Photon LIF (Flame)</td>
<td>--</td>
<td>21,000 ppm</td>
<td>200 ppm</td>
<td>O</td>
<td>20</td>
</tr>
<tr>
<td>Two-Photon-D4WM (Flame)</td>
<td>--</td>
<td>21,000 ppm</td>
<td>30 ppm</td>
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<td>20</td>
</tr>
<tr>
<td>Two Photon-D4WM (R.F. Discharge)</td>
<td>$1 \times 10^{16}$</td>
<td>1,000 – 10,000 ppm</td>
<td>260 ppb</td>
<td>O</td>
<td>4</td>
</tr>
<tr>
<td>Laser Optogalvanic/D C Discharge</td>
<td>--</td>
<td>--</td>
<td>100 ppm</td>
<td>O</td>
<td>21</td>
</tr>
<tr>
<td>Two-Photon-D4WM (Microwave Discharge)</td>
<td>$1 \times 10^{14}$</td>
<td>95,000 ppm</td>
<td>32 ppb</td>
<td>O</td>
<td>5</td>
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<tr>
<td>Diode Laser/Laser Ablation AAS</td>
<td>$\sim 5 \times 10^{13}$</td>
<td>21,000 ppm</td>
<td>2.7 ppb</td>
<td>O</td>
<td>22</td>
</tr>
<tr>
<td>Dye Laser AAS (Flame)</td>
<td>$6 \times 10^{14}$</td>
<td>21,000 ppm</td>
<td>15.9 ppb</td>
<td>O</td>
<td>23</td>
</tr>
<tr>
<td>Two-Photon LIF</td>
<td>$1.2 \times 10^{13}$</td>
<td>--</td>
<td>1000 ppm</td>
<td>O</td>
<td>24</td>
</tr>
<tr>
<td>Two-Photon LIF</td>
<td>$4 \times 10^{14}$</td>
<td>--</td>
<td>--</td>
<td>O</td>
<td>25</td>
</tr>
<tr>
<td>GC/ ICP-AES</td>
<td>--</td>
<td>--</td>
<td>25 ng</td>
<td>O</td>
<td>26</td>
</tr>
<tr>
<td>ICP-AES</td>
<td>--</td>
<td>21,000 ppm</td>
<td>0.5 µg</td>
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<td>8</td>
</tr>
<tr>
<td>Laser Wave Mixing</td>
<td>$1.03 \times 10^{13}$</td>
<td>50 ppm</td>
<td>11 ppm (25 ag)</td>
<td>O</td>
<td><strong>This work</strong></td>
</tr>
</tbody>
</table>
5.4.2 Isotope and Hyperfine Spectra

As mentioned above, the 777 nm transition is expected to show both fine and hyperfine structures. Oxygen isotope spectra have been reported by others using a variety of methods.\textsuperscript{3,9,11,12} Figure 5.9 shows a wave-mixing spectrum for atomic oxygen from 777.4 nm to 777.8 nm. The three fine structures resulting from the triplet state are clearly resolved. All peaks show a laser power saturation dip in the middle of their line profiles. When the laser power is reduced, these power saturation dips as expected, along with power broadening. Figure 5.10 shows obvious changes in linewidth and saturation dip as the power is reduced from 8 mW to 1 mW. Without power saturation, the wave-mixing analyte linewidth is very narrow since it is Doppler cancelled. Our wave-mixing linewidth for oxygen-16 at 5 Torr is 99.26 MHz or 0.0033 cm\textsuperscript{-1}. This linewidth is comparable to the results reported by de Angelis in a low-pressure cell using multi-photon laser saturation spectroscopy with counter propagating input beams.\textsuperscript{3} Figure 5.11 shows the experimental data fitted to theoretical spectrum using a temperature of 950 K and 15\% residual Doppler broadening\textsuperscript{17} (due to imperfect positioning of counter propagating beams). The temperature and Doppler width values are determined by least square fitting of theoretical and experimental spectral profiles. Figure 5.12 shows a surface plot of deviations using the entire range of temperature and Doppler values with a minimal point indicating the best fit.

Oxygen-17 and oxygen-18 naturally occur in relatively small amounts, but they serve as very important environmental indicators. Figure 5.13 shows a simulated
Figure 5.9 Fine structure of atomic oxygen at 777 nm. Spectral dips in the center result from laser power saturation effects.
Figure 5.10 Effect of laser power on analytical peak shape and width.
spectrum for a sample with 10% $^{18}$O, 40% $^{17}$O, and 50% $^{16}$O based on the discharge parameters used in this study. Individual peaks for oxygen-16 and oxygen-18 flank the hyperfine splitting profile of oxygen-17. These hyperfine features could be resolved by taking advantage of unique properties of high-resolution laser wave mixing spectroscopy.

5.5 Conclusions

Nonlinear wave mixing with sub-Doppler spectral resolution is demonstrated as a sensitive, high-resolution method for the detection of atomic oxygen in a direct-current hollow-cathode discharge atomizer. A preliminary concentration detection limit of 11 ppmv is reported using a low-cost, low-power, compact diode laser. A preliminary mass detection limit of 25 attograms is determined, assuming a 13 µL laser probe volume and a typical analyte transport loss rate. Laser wave mixing offers unique advantages including isotope and hyperfine spectral resolution, little or no sample preparation steps and portability that is suitable for in-situ field analysis.
Figure 5.11 Theoretical fitting of atomic oxygen profile. Dashed line, experimental profile; solid line, theoretical profile.
Figure 5.12 Surface map of the least squared fitting procedure used to determine experimental temperature and Doppler width values.
Figure 5.13  Simulated hyperfine spectrum for enriched oxygen in the cathode discharge (50:40:10 mixture of oxygen 16, 17 and 18 isotopes).
5.6 References


Chapter 6

Laser Wave Mixing-Based Hyperfine and Isotope Measurements of Atomic Chlorine Using a Low-Pressure Discharge Atomizer

6.1 Introduction

Chlorine plays an important role in catalytic ozone depletion in the upper atmosphere since chlorine containing molecules make their way into the upper atmosphere where they dissociate on polar stratospheric clouds. This dissociation produces the chlorine radicals responsible for ozone destruction. Due to the long lifetime of chlorine containing molecules, a single radical is able to catalytically destroy several thousand ozone molecules before forming ClO$^\bullet$. The ability to measure small amounts of chlorine is essential in the determination of minor components in these reactions. Moreover, a detection technique that could simultaneously monitor chlorine and oxygen would prove incredibly useful when reconstructing reaction mechanisms involving ozone destruction.

Monitoring stratospheric reaction mechanisms presents some unique challenges for conventional analytical methods. One such difficulty is the need to make measurements in-situ in real time. This requires a field-portable detection system that can be mounted on a small aircraft or an unmanned aerial vehicle (UAV). Current detection methods require gas analytes to be collected, transported to the laboratory, stored, and kept isolated from ground-level contaminants. In addition, the required complex pre-treatment steps further hinder analysis of these gas analytes.
Nonlinear laser wave mixing is ideally suited to in-situ studies in real time since it offers portability, excellent sensitivity and minimal interference problems. Using low-power diode lasers, a compact optical setup could be developed for simultaneous detection of oxygen, chorine and several other atmospherically significant compounds.

Chlorine has two naturally occurring isotopes, chlorine-35 and chlorine-37. The ratio of these two isotopes is characteristic to the origin of the chlorine analyte due to natural processes that fractionate the molecules. These ratios can then be used as tracer signatures for a variety of applications. Temperature reconstruction in ice cores, isotope ratio dating, industrial semiconductor gas purity measurements, and determination of chlorine-36 as an indicator of nuclear fallout are a few applications that have used detection of chlorine isotope signatures. Pollutant source determination and environmental reclamation studies have also used simultaneous detection of chlorine and carbon to characterize chlorofluorocarbons (CFCs) and track detergent in effluent streams. Table 6.1 lists the average estimated abundance of chlorine in different zones of the earth. Potential biological applications include identification of drug metabolites and pharmaceutical differentiation based on the atomic signatures.

The last decade has seen much concern over the use and storage of chemical weapons. Even with current international bans, there are still tons of materials stored throughout the world. Chlorine and chlorine-containing molecules are the main component of chemical weapons such as mustard gas and neurotoxins. These chemicals are at the heart of much legislation including the U. S. Chemical Weapons
Table 6.1 Estimated global chlorine content.

<table>
<thead>
<tr>
<th>Location</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Topsoil</td>
<td>100 ppmw</td>
</tr>
<tr>
<td>Rivers</td>
<td>5.8 ppmv</td>
</tr>
<tr>
<td>Groundwater</td>
<td>40 ppmv</td>
</tr>
<tr>
<td>Troposphere</td>
<td></td>
</tr>
<tr>
<td>Remote areas</td>
<td>700 pptv</td>
</tr>
<tr>
<td>Urban areas</td>
<td>up to 3500 pptv</td>
</tr>
</tbody>
</table>
Convention. Hence, it is important to be able to detect these substances reliably in a variety of media including soil, plants and water.

Chlorine has several atomic transitions in the near-IR wavelength range. The strongest of these are centered at 837.827 nm, 833.560 nm and 843.059 nm. An energy level diagram for the 837.827 nm absorption transition is shown in Figure 6.1 with relative intensity levels for expected hyperfine lines. Environmental chlorine has two naturally occurring isotopes, chlorine-35 and chlorine-37, with abundances of 75.48 % and 24.22 %, respectively. Since both of these isotopes have a nuclear spin of 3/2, additional hyperfine splitting is expected. With both isotope and hyperfine contributions, the spectrum of atomic chlorine is very complicated with 15 distinct spectral lines. A theoretical model of this complex spectrum is shown in Figure 6.2. In this near infrared wavelength range, there are additional interferences from background components in the air. Hence, a sensitive high-resolution optical method is needed to measure chlorine spectra. The chlorine transition mentioned above offers well-spaced hyperfine splitting and the two isotopes have reasonably high abundance levels, making it an ideal transition for chlorine isotope ratio measurements. Laser wave mixing offers unique advantages for hyperfine measurements including excellent detection sensitivity, sub-Doppler spectral resolution and ease of use.
Figure 6.1 Fine and hyperfine splittings of atomic chlorine.
Figure 6.2 Isotope and hyperfine splitting model of atomic chlorine.
6.2 Experimental

The experimental optical setup is similar to that used for atomic oxygen studies in a hollow-cathode discharge cell. Initially, a solid sodium chloride (NaCl) sample is used to generate gas-phase atomic chlorine. This sample is deposited directly in the hollow cathode. An 830 nm line filter is placed in front of the detector to block the strong sodium emission. Once the discharge is stable, it can be operated until all the solid analytes are consumed. The cell is then disassembled and cleaned with acetone and deionized water. The cathode assembly is soaked in a nitric acid bath to remove all residual deposits. The cell is then reassembled and flushed with argon gas for 5 minutes. The plasma is then allowed to burn off residual contaminants for 10 minutes. A solid-state diode laser (Hitachi, Chula Vista, CA, Model HL8325G) with a 33.6 mW total output power is used to probe the near infrared transition.

6.3 Results and Discussion

Figure 6.3 shows a typical wave-mixing signal. Since generation of the nonlinear signal is dependent on the interaction of all three input beams, the signal is verified by blocking each of the input beams in turn. Figure 6.3 shows expected loss of signal intensity levels when each input beam is blocked. In this optical setup, the probe beam \( E_p \) is modulated, resulting in a lower baseline when compared to blocking either of the two other beams.

Many experimental parameters affect the wave-mixing signal level and one of the most important parameters is the available analyte population level. The hollow-
Figure 6.3  Wave-mixing signal verification by blocking each of the three input beams.
cathode discharge provides the collisional energy to not only atomize the sample, but to also populate the non-resonant metastable $^4P_{5/2}$ level from the ground state. Increasing the current delivered to the discharge generates a more energetic plasma plume, and thus, increasing the analyte population. Figure 6.4 illustrates the effect of discharge current on signal intensity with the expected trend of increasing signal with increasing current resulting from a rise in the number of dissociated and excited chlorine atoms. Unfortunately, the solid NaCl sample only allows a maximum current of 60 mA before the plasma becomes unstable as the cathode surface is coated by broken down salt crystals.

Decreasing the cell pressure also results in a more energetic discharge plume, and hence, larger signals, as illustrated in Figure 6.5. The wave-mixing signal intensity shows a marked increase as the pressure is reduced to 2.2 Torr. However, the discharge no longer has enough buffer gas to maintain a stable plasma below 1.6 Torr, resulting in a total loss of signal.

Figure 6.6 shows signal dependence on amplitude modulation frequency. As expected, the signal-to-noise ratio, if not the noise level, is higher at higher modulation frequency values. The diode laser wavelength is tuned by adjusting the current driving the laser diode. As shown in Figure 6.7, one can collect an entire spectrum by tuning the current across the entire wavelength range. It is apparent that many different individual components make up the overall spectrum. The spectral resolution and peak widths depend on the laser linewidth and the potential
Figure 6.4 Wave-mixing signal dependence on discharge current.
Figure 6.5 Wave-mixing signal dependence on discharge cell pressure.
Figure 6.6 Wave-mixing signal dependence on modulation frequency.
Figure 6.7 Raw wavelength scan of solid sodium chloride.
concentration- and power-saturation levels. All three factors contribute to line broadening that can mask peak characteristics.

For our high-resolution spectral measurements, gas cylinders are prepared from 2,000 ppmv chlorofluorocarbon Freon 113 in argon (Praxair, Los Angeles, CA) and diluted as needed in a custom gas dilution setup. An external cavity diode laser (ECDL) (New Focus, Santa Clara, CA, Model 6226) with 10 mW output power is used. This laser has more stable tuning capabilities and a much narrower linewidth as compared to the solid-state diode laser. Figure 6.8 shows a typical wave-mixing signal for 62 ppmv Freon 113 (7.18 pg of chlorine). A preliminary concentration detection limit of 19 ppmv (S/N 2) and a preliminary mass detection limit of 2.2 picograms are determined for chlorine.

Table 6.2 lists previously reported detection methods and their detection limits for atomic chlorine. Our preliminary detection limits could be improved by using higher probe laser power levels and by using wavelength or polarization modulation techniques as demonstrated in our other wave-mixing setups. Furthermore, microwave discharge cells offer enhanced sensitivity levels as compared to DC discharge atomizers.\(^\text{18}\)

The power level of the external cavity diode laser is varied to study the effects of power saturation on analyte spectra. Figure 6.9 shows less peak broadening as the laser power is reduced from 10 mW to 1.13 mW, as expected. New spectral features previously masked are also visible when power broadening is minimized.
Figure 6.8  Wave-mixing signal for 62 ppmv chlorofluorocarbon Freon 113.
Table 6.2  Comparison of previously reported methods and detection limits for atomic chlorine.

<table>
<thead>
<tr>
<th>Method</th>
<th>Injected Concentration</th>
<th>Reported LOD</th>
<th>Species Detected</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>LA-MIP-DLAAS</td>
<td>1000 ppm</td>
<td>85 ppm</td>
<td>Cl</td>
<td>18</td>
</tr>
<tr>
<td>WM-LAAS-MMIP</td>
<td>400 pptv</td>
<td>60 pptv</td>
<td>Cl</td>
<td>19</td>
</tr>
<tr>
<td>GC-WM-LAAS-MIP</td>
<td>250 ppb</td>
<td>2.5 ppb</td>
<td>Cl</td>
<td>19</td>
</tr>
<tr>
<td>He MIP-AES</td>
<td>80 ppb</td>
<td>6.8 ppb</td>
<td>Cl</td>
<td>20</td>
</tr>
<tr>
<td>LIBS</td>
<td>50 ppmv</td>
<td>2 ppm</td>
<td>Cl</td>
<td>14</td>
</tr>
<tr>
<td>Particle-Induced X-ray Emission</td>
<td>500 ppm</td>
<td>1 ppm</td>
<td>Cl</td>
<td>21</td>
</tr>
<tr>
<td>Cyclic Voltammetry</td>
<td>0.1 mg L(^{-1}) (ppm)</td>
<td>8.3 ug L(^{-1}) (ppb)</td>
<td>Cl</td>
<td>22</td>
</tr>
<tr>
<td>Laser Wave Mixing</td>
<td>62 ppm</td>
<td>19 ppm (2.2pg)</td>
<td>Cl</td>
<td>This work</td>
</tr>
</tbody>
</table>
Figure 6.9  Power saturation effects at different laser power levels.
Experimental spectra are fitted to a theoretical model based on previously published hyperfine splitting and intensity calculations.\textsuperscript{13} As previously discussed, hyperfine and isotope splittings contribute over 13 individual peaks. Figure 6.10 shows comparison of experimental data plotted against individual isotope and hyperfine peaks, with 5 lines from hyperfine splitting of chlorine-35 and two from major hyperfine transitions of chlorine-37. Figure 6.11 shows comparison of experimental data plotted against the overall convoluted hyperfine profile. Experimental data and the theoretical profiles match reasonably well, especially for the major hyperfine peaks.

\textbf{6.4 Conclusions}

Cathode discharge-based laser wave mixing is presented as a viable method for high-resolution fingerprinting of atomic chlorine. Using a low-power compact diode laser, a preliminary concentration detection limit of 19 ppmv (parts-per-million by volume) and a preliminary mass detection limit of 2.2 picograms are determined. Wave mixing offers advantages over mass spectrometry including faster sample preparation steps, no need for pre-concentration steps, in-situ analysis, and field portability suitable for environmental and atmospheric applications.
Figure 6.10 Experimental profile of atomic chlorine with calculated isotope and hyperfine lines. Experimental data is circles (calculations ignore residual pressure contributions, and hence, slight deviations).
Figure 6.11 Experimental profile of atomic chlorine with calculated overall hyperfine profile (calculations ignore residual power saturation, and hence, slight deviations).
6.5 References


Chapter 7
Detection of Chlorofluorocarbon Freon 113 and Nitrous Oxide Using Mid-infrared Nonlinear Laser Wave Mixing

7.1 Introduction

Sensitive monitoring of environmental pollutants in soil, water and air is very important to ensure overall safety and security of humans, animals and plants. Environmental security is one of the fundamental requirements of human wellbeing, yet it remains a major global challenge. While highly sensitive and selective, traditional chromatographic and conventional spectroscopic techniques are time consuming, expensive, bulky, and usually not field portable. Hence, there is a need for simple, rapid, selective, sensitive and portable methods for analyzing environmental pollutants.

Chlorofluorocarbons (CFCs) were developed in the early 1930s and are used in a variety of industrial, commercial and household products. They are non-toxic, non-flammable, non-reactive, and they have stable thermodynamic properties, making them ideal for use in various products including coolants for commercial and home refrigeration, aerosol propellants, electronic cleaning solvents and blowing agents. Unfortunately, CFCs, along with other chlorine- and bromine-containing compounds, have been implicated in the accelerated depletion of ozone in the stratosphere. CFCs are carried into the stratosphere where they can undergo hundreds of catalytic cycles involving ozone before being scavenged by other chemical species. From the mid-
1930s to the mid-1980s, production and use of chlorofluorocarbons experienced nearly uninterrupted growth as demand for products requiring their use continued to rise. In 1973, chlorine was determined to be a catalytic agent in ozone destruction. Announcement of polar ozone depletion over Antarctica\(^1\) in March 1985 prompted calls to freeze or diminish production of chlorinated fluorocarbons. Despite the rapid phase-out of CFCs, ozone levels are expected to be lower than pre-depletion levels for several decades due to long tropospheric lifetimes of CFCs.

Greenhouse gases, such as carbon dioxide that trap heat in the atmosphere, occur naturally and are emitted into the atmosphere both through natural processes and human activities. The principal greenhouse gases that enter the atmosphere from human activities are carbon dioxide (CO\(_2\)), methane (CH\(_4\)), nitrous oxide (N\(_2\)O) and fluorinated gases such as hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs), and sulfur hexafluoride (SF\(_6\)), which are sometimes used as replacements for the ozone-depleting substances chlorofluorocarbons (CFCs).\(^2\) Figure 7.1 shows the relative amount of anthropogenic greenhouse gases released into the environment in the U.S. for 2007.

Nitrous oxide is a greenhouse gas with a capacity to trap heat in the atmosphere more than two orders of magnitude larger than that of CO\(_2\).\(^3,4\) The N\(_2\)O infrared absorption band fills the gap between the H\(_2\)O and CO\(_2\) absorption bands. N\(_2\)O also participates in the stratospheric ozone cycle.\(^5\) The concentration of N\(_2\)O in the atmosphere is increasing at a rate of 0.25% per year, mostly due to agricultural soil management and fuel combustion processes. The atmospheric residence time of N\(_2\)O
Figure 7.1  Relative amount of anthropogenic greenhouse gases released in the United States in 2007. High-GWP gases are HFCs, PFCs, and SF₆. (Energy Information Administration, Emissions of Greenhouse Gases Report, http://www.eia.doe.gov/oiaf/1605/ggrpt/index.html).
is about 150 years and it is destroyed through photolysis and photooxidation.\textsuperscript{6} Despite numerous studies in the last 20 years, the global N\textsubscript{2}O budget and mechanisms of formation and decay for N\textsubscript{2}O are still not well understood. A powerful tool for identification of its sources and sinks is the isotopic characterization of nitrous oxide collected from different locations across the globe. High-resolution laser spectroscopic methods promise effective determination of the actual intramolecular position of each nitrogen isotope. Figure 7.2 shows simulated isotope splitting of N\textsubscript{2}O with positions of the respective isotopomers based on previous condensed-phase FT-IR experiments.\textsuperscript{7} Mass spectrometric methods still face some challenges for this type of isotope-specific analyses since they are still relatively bulky and not very portable.\textsuperscript{8} Compact laser-based sensitive detection methods offer inherent advantages in trace-concentration measurements of gases needed to characterize global climate change due to anthropogenic and biogenic effects.\textsuperscript{9-12} Currently available laboratory procedures and methods for field samples require constant attention to avoid surface reactions or contamination with CO\textsubscript{2}. Hence, portable laser-based systems that allow in-situ measurements offer important advantages.

Various laser-based methods have been developed for sensitive gas-phase measurements including direct absorption spectroscopy using long-path multi-pass cells,\textsuperscript{13} wavelength-modulation spectroscopy,\textsuperscript{14-15} cavity ring down spectroscopy,\textsuperscript{16} and modified off-axis integrated cavity output spectroscopy.\textsuperscript{17} Degenerate four-wave mixing (DFWM) has been shown to be a sensitive method for hyperfine and isotope
Figure 7.2. Simulated isotope splitting of N₂O absorption spectrum at 1,290 cm⁻¹.
analyses.\textsuperscript{18,19} In this report, we present mid-IR laser wave mixing as an effective detection tool for important gases in their native form.

The advent of quantum cascade lasers (QCL) allows one to use these compact tunable mid-IR sources instead of lead chalcogenide lasers or other bulky mid-IR lasers that require liquid nitrogen-based cooling systems and big power supplies. Quantum cascade lasers offer many advantages for field use since they are more rugged, power efficient and they do not require cryogenic cooling. Moreover, QCLs generally offer narrow linewidths, excellent mode stability and wavelength reproducibility levels, and “turn-key” ease of use. Newly available thermoelectrically (TE) cooled detectors also offer greater sensitivity levels in the mid-IR wavelength range.

\section*{7.2 Experimental}

The laser source is a mid-IR pulsed 8.4 $\mu$m quantum cascade laser (Daylight Solutions, Poway, CA, Model TLS 11084/11078) with an average output power of 15 mW and a wavelength tuning range of 70 cm\textsuperscript{-1} operating at 100 kHz. This laser is driven by a simple 120-V controller (Daylight Solutions, Poway, CA, Model 1001-TLC). A thermoelectrically cooled HgCdZnTe photovoltaic detector designed for mid-infrared detection (Daylight Solutions, Poway, CA, Model RT, amplified MCT detector, MCT-10001) is used to acquire both optical absorption and nonlinear wave-mixing signals. All mirrors are infrared coated and our mid-IR lenses have calcium fluoride substrate.
Figure 7.3 shows the two custom-built analyte cells with calcium fluoride windows (Curtis Technologies, Inc., Sorrento Valley, CA). The smaller cell measures 2.5 cm x 5.08 cm and has windows attached at a slight angle (1 degree) in order to minimize background optical noise levels. Two ¼ inch diameter arms are attached to the main body on alternate sides to allow analyte introduction and evacuation. The larger cell measures 10 cm x 2.54 cm and has three inlets/outlets to allow introduction of gas, liquid and solid analytes. All FT-IR spectra, unless otherwise indicated, are obtained using these analyte cells and a Nicolet Nexus 760 Series FT-IR spectrophotometer with a 50-pass absorption mode. These spectra are then referenced to those published by the National Institute of Standards and Technology (NIST) for validity.

7.3 Results and Discussion

7.3.1 Mid-IR Laser Absorption Measurement

7.3.1.1 Acetone

Due to the complex nature and possible problems associated with using a light source in the mid-infrared wavelength range, a simple linear mid-IR laser absorption optical setup is used first to troubleshoot and optimize optical parameters and signal-to-noise ratios. A typical mid-IR laser absorption optical setup is shown in Figure 7.4. The lock-in amplifier (Stanford Research Systems, Sunnyvale, CA, Model SR810) is referenced to the laser repetition rate instead of the optical chopper normally used in continuous-wave laser experiments. The input laser power is kept below 2 mW to
Figure 7.3 Gas analyte cells with CaF₂ windows for use in mid-IR optical setups.
Figure 7.4 Typical mid-IR laser absorption optical setup.
reduce background levels and at 1 mW for detection limit studies. Acetone is chosen as the initial test analyte using its characteristic absorption band at 8.4 µm. Since the optical absorption signal is linearly dependent on the path length, the large analyte gas cell shown in Figure 7.3 with a 10 cm optical path length is used. A small amount of acetone analyte (5 ml) is introduced by pipette through the ½ inch opening and then allowed to evaporate in the sealed analyte gas cell. All three inlet/outlet arms of the analyte cell are sealed using Cajon Ultra-Torr fittings with end caps.

Figure 7.5 shows the mid-IR laser absorption spectrum at 8.4 mm for a 30 pptv acetone analyte as compared to that from a reference FT-IR spectrum (2,000 ppmv, 4 cm⁻¹ resolution). The spectrum matches the reference reasonably well, considering that the spectra were collected under different experimental parameters (concentration, hardware, physical conditions, etc.). A preliminary concentration detection limit of 3 pptv is determined for acetone (S/N of 2) at room pressure and room temperature as shown in Figure 7.6. As shown in Table 7.1, this concentration detection limit compares favorably with other reported detection limits for acetone in the infrared wavelength region.

Sensitive detectors for acetone in its native form offer many potential applications. Normal human breath contains hundreds of volatile organic compounds, some of which have been identified as biomarkers for disease.²³,²⁴ Acetone is formed during ketosis in the body and patients with diabetes show a rise in breath acetone concentration levels.²³ Acetone has recently received much attention for its non-invasive diagnostic potential for diabetes and for patients on ketogenic diets.²⁵
Figure 7.5 Mid-IR absorption spectrum of acetone.
(a) FT-IR (2000 ppmv), (b) absorption (30pptv).
Table 7.1 Comparison of previously reported detection methods for acetone.

<table>
<thead>
<tr>
<th>Method</th>
<th>Injected Limit of Detection (LOD)</th>
<th>Calculated LOD</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photoacoustic spectroscopy, 7.3 mm QCL</td>
<td>30 ppb</td>
<td>3 ppb</td>
<td>20</td>
</tr>
<tr>
<td>Photoacoustic spectroscopy</td>
<td>-</td>
<td>4 ppb</td>
<td>21</td>
</tr>
<tr>
<td>LED-based photometric detection using a liquid-core waveguide (465 nm)</td>
<td>159 ppb</td>
<td>14 ppb</td>
<td>22</td>
</tr>
<tr>
<td>Nano-sized Fe$_2$O$_3$ sensor</td>
<td>1 ppm</td>
<td>200 ppb</td>
<td>23</td>
</tr>
<tr>
<td>Cavity ringdown spectroscopy (266 nm laser)</td>
<td>4 ppm</td>
<td>500 ppb</td>
<td>24</td>
</tr>
<tr>
<td>Multi-pass absorption difference-frequency generation (DFG)</td>
<td>1,665 ppm</td>
<td>760 ppb</td>
<td>25</td>
</tr>
<tr>
<td><strong>Single-pass mid-IR absorption, 8.4 mm QCL</strong></td>
<td>3 ppt</td>
<td>3 ppt</td>
<td><strong>This work</strong></td>
</tr>
</tbody>
</table>
Figure 7.6  Mid-IR absorption spectrum of 3 pptv acetone.
Moreover, it has been suggested that breath acetone may be more effective than urine samples for monitoring ketonemia in insulin-dependent diabetic patients with high ketone levels. The overall mean concentration in healthy breath is generally accepted to be about 0.49 ppmv, though different studies report values spanning the range of 0.35 - 0.85 ppmv. Several studies have been conducted to develop mid-infrared detection of breath acetone. As shown in Table 7.1, our gas-phase acetone detection limit is already better than those of other methods while using a relatively short optical absorption path length. Our mid-IR laser detection sensitivity levels could be further enhanced by up to a factor of 10,000 with the use of multi-pass absorption cells as in other absorption methods. Thus, our simple compact mid-IR quantum cascade laser-based absorption detector promises a wide range of applications including breath acetone monitoring for biomedical applications.

7.3.1.2 Freon 113

The same gas analyte cell and the detection parameters described above are used for the detection of Freon 113 chlorofluorocarbon analytes. Figure 7.7 shows the mid-IR laser absorption spectrum of a 2,000 ppmv Freon 113 analyte using our short path length gas analyte cell, and it has the same expected absorption characteristics of those in the FT-IR reference spectrum. Figure 7.8 shows a mid-IR laser absorption spectrum of a 5 ppmv Freon 113 analyte and the general characteristics of the reference spectrum are still observed at this much lower concentration level using a relatively short gas cell in a single-pass detection mode. Hence, it is promising that our preliminary detection limits could be significantly enhanced by using well
Figure 7.7 Mid-IR absorption spectrum of 2,000 ppmv chlorofluorocarbon Freon 113. (a) FT-IR, (b) absorption.
Figure 7.8  Mid-IR absorption spectrum of 5 ppmv CFC Freon 113 (the two main features are apparent at this low concentration level).
established wavelength modulation detection modes, multi-pass sample cells, multi-pass spectral averaging as in our laser absorption spectroscopic methods. Figure 7.9 illustrates chemical/spectral selectivity and specificity levels of our mid-IR laser absorption method for the wavelength tuning range available for our particular quantum cascade laser. Even with a mixture of compounds, the individual fingerprints allow one to differentiate different analytes present.

7.3.2 Mid-IR Multi-Photon Wave-Mixing Detection

7.3.2.1 Freon 113

After optimizing optical parameters of our single-pass mid-IR laser absorption setup, a multi-photon mid-IR wave-mixing setup is assembled to take advantage of the unique nonlinear properties. A simplified forward-scattering wave-mixing optical configuration is used since relatively broad molecular peaks and a relatively broad QCL linewidth of 1 cm$^{-1}$ make cancellation of Doppler broadening unnecessary. Figure 7.10 shows our simplified L-shaped wave-mixing setup with two input beams mixing at a very small angle inside the analyte gas cell. All other optical components remain the same as described above for the mid-IR laser absorption studies.

The wave-mixing signal is verified by blocking each of the input laser beams and observing expected loss of signal as shown in Figure 7.11 for a Freon 113 analyte. A small amount of background noise level results from each input beam because both input beams are modulated at the same frequency (i.e., the 100 kHz rep rate of the pulsed quantum cascade laser). This background noise level would be lower if only one of the input beams could be amplitude modulated as in other wave-mixing setups.
Figure 7.9  Different absorption spectral features of three different gas analytes in the wavelength tuning range of the 8.4 μm quantum cascade laser.
Figure 7.10  Typical forward-scattering wave-mixing optical setup.
Figure 7.11 Wave-mixing signal verification for 500 ppmv CFC Freon 113.
using continuous-wave lasers. Further confirmation of the wave-mixing signal is observed by plotting the wave-mixing signal intensity vs. the laser input power level. Figure 7.12 shows a log-log plot of the data with a slope of 2.87, i.e., cubic power dependence as predicted by Equation 3.5 ($R^2$ is 0.9475). Table 7.2 shows reproducibility results of this cubic dependency test from different experiments. It also shows the expected linear dependence (slope of 1) for the optical background noise monitored at an off-peak non-resonant wavelength position. The laser input power level is measured in real time by a thermal power meter (Coherent, Inc., Santa Clara, CA, Model PS10) after splitting a fraction of the input laser beam using a CaF$_2$ window. Slightly higher dependency levels in Table 7.2 are due to a ratio of 1.0:1.2 when comparing the measured power of the split-off beam to directly measured output of the laser head. As shown in Table 7.2, cubic dependence of signal on laser power confirms the nonlinear analytical signal level and distinguishes the wave-mixing signal from any linear optical background noise levels that may be present. Table 7.2 also confirms that wave mixing allows efficient use of low power levels available from compact mid-IR lasers as demonstrated in other wave-mixing experiments using low-power UV and visible solid-state lasers.$^{32}$ A preliminary concentration detection limit of 500 ppmv is determined for Freon 113 as shown in Figure 7.13 where the analyte signal is compared to that from a blank (argon gas).

To obtain full spectral fingerprinting, mid-IR wavelength scans are performed by slowly tuning the laser controller either in manual or automatic scan mode. As shown in Figure 7.14, the wave-mixing spectrum for chlorofluorocarbon Freon 113
Figure 7.12 Cubic wave-mixing signal dependence on laser power.
Table 7.2  Cubic dependence of wave-mixing signal on laser power.

<table>
<thead>
<tr>
<th>Trial</th>
<th>On-Peak (Resonant) Dependence 1,204 cm(^{-1})</th>
<th>On-Peak Linear Fit (R(^2))</th>
<th>Off-Peak (Non-Resonant) Dependence 1,160 cm(^{-1})</th>
<th>Off-Peak Linear Fit (R(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.1</td>
<td>0.99</td>
<td>0.5</td>
<td>0.84</td>
</tr>
<tr>
<td>2</td>
<td>3.4</td>
<td>0.99</td>
<td>0.85</td>
<td>0.88</td>
</tr>
<tr>
<td>3</td>
<td>3.2</td>
<td>0.99</td>
<td>0.89</td>
<td>0.93</td>
</tr>
<tr>
<td>4</td>
<td>3.4</td>
<td>0.98</td>
<td>1.1</td>
<td>0.89</td>
</tr>
<tr>
<td>5</td>
<td>3.5</td>
<td>0.99</td>
<td>1.0</td>
<td>0.93</td>
</tr>
<tr>
<td>6</td>
<td>3.5</td>
<td>0.99</td>
<td>1.0</td>
<td>0.96</td>
</tr>
<tr>
<td>7</td>
<td>3.4</td>
<td>0.99</td>
<td>0.98</td>
<td>0.94</td>
</tr>
<tr>
<td>8</td>
<td>3.4</td>
<td>0.99</td>
<td>1.1</td>
<td>0.96</td>
</tr>
</tbody>
</table>
Figure 7.13 Comparison of 500 ppmv CFC Freon 113 signal with that of an argon blank.
contains the major features along with a minor feature near 1,168 cm\(^{-1}\). The second major feature at 1,215 cm\(^{-1}\) is limited in intensity due to the QCL power loss near the end of the laser tuning range. This QCL power loss is typically more pronounced at the higher wavelength end than at the lower end of the tuning range, and it could be compensated for in the future with the use of a balanced detector.

### 7.3.2.2 Nitrous Oxide

Laser wave-mixing spectra are also obtained for nitrous oxide analytes and confirmed by plotting signal intensity vs. laser input power. Figure 7.15 shows nonlinear cubic dependence on laser power as expected with a significant increase in signal resulting from a modest increase in laser power. The cubic power dependence also verifies that power levels are within saturation parameters, ensuring minimal power broadening in the collected spectrum.

Figure 7.16 compares a mid-IR wave-mixing molecular spectrum of a 1,000 ppmv N\(_2\)O analyte to a FT-IR reference spectrum. The wavelength tuning range of our quantum cascade laser is not wide enough to cover all the major absorption features, however, it is apparent that the wave-mixing spectrum agrees reasonably well with both the peak width and the peak position shown in the reference FT-IR spectrum. Moreover, this transition is approximately a factor of 16 and 52 weaker than the commonly used major transitions at 1,300 cm\(^{-1}\) and 2,240 cm\(^{-1}\), respectively. Consequently, our wave-mixing detection sensitivity levels could be much better when using a mid-IR laser source with more appropriate excitation wavelengths.
Figure 7.14  Wave-mixing spectrum of CFC Freon 113. Major features match previously acquired FT-IR spectrum, however, QCL power drift problems at the end of wavelength tuning ranges result in some deviations. (a) FT-IR, (b) wave-mixing.
Figure 7.15 Cubic dependence of wave-mixing signal on laser power.
Figure 7.16  Mid-IR wave-mixing spectrum of 1,000 ppmv N₂O compared with FT-IR reference spectrum (15 mW QCL at 100 kHz).
7.4. Conclusions

Wave-mixing detection limits and spectral resolution levels collected with this particular quantum cascade laser are severely limited by etaloning problems, drifting QCL power levels, limited wavelength tuning levels, and background scattering levels. Continuous-wave mode-hop-free quantum cascade lasers (available to our lab soon) with 1,000 times narrower linewidths (i.e., 0.001 cm\(^{-1}\)) will offer more stable power levels and much higher spectral resolution that is suitable for fine rotational and vibrational lines and for isotope-specific spectra. Nevertheless, we have demonstrated that mid-IR quantum cascade laser-based absorption and wave-mixing detection methods are sensitive and robust for detection of environmental gas-phase analytes in their native form at room temperature and room pressure. Using a low-power compact quantum cascade laser, a preliminary concentration detection limit of 3 pptv (parts-per-trillion by volume) is determined for acetone. Molecular vibrational spectra are obtained in minutes using a relatively compact optical setup. Hence, mid-IR wave mixing promises compact field-portable detection systems capable of in-situ analysis for environmental and atmospheric applications.
7.5 References


Appendix A

Standard Operating Procedures (SOP) for Lasers, Atomizers and Optoelectronics

A.1 SOP for the Inductively Coupled Plasma (ICP) Atomizer

*Turn ON the ICP*

1. Make sure the sample solution is ready to be pumped through the RABBIT pump.

2. Turn on the cooling water (under the table or behind the tabletop ICP module).

3. Turn on the argon gas (near the door).

4. Turn on the square white POWER ON switch on the AMNPS-1 module (i.e., the tabletop unit).

5. Turn on the AUX and the PLASMA gas flows and let them run for a few minutes.

6. Switch TUNING to MANUAL and adjust it to about 59 using the two white square buttons.

7. **Pull the big golf-ball size RED EMERGENCY BUTTON out**

8. Turn on the WHITE SQUARE button on the ICP-16 RF POWER SUPPLY (under the optical table).

9. Set RF to about 1048 Watts on the RF POWER SUPPLY.

10. Turn on the NEBULIZER gas flow and set it just under 30 psi (i.e., flush it out before ignition).

11. Turn off the NEBULIZER gas flow.

12. Quickly follow the following three steps in the correct order:
    - Turn ON the RF-ON/OFF button (i.e., the red button on the ICP-16 RF POWER SUPPLY under the table).
    - Push the ICP IGNITE button.
    - Flip the TUNING SWITCH to AUTO. If the ICP does not light or there is crackling, then press the RF-OFF button.
    - Repeat Step 10.

13. Turn on the NEBULIZER gas flow.
14. Turn on the RABBIT sample pump.

**Turn OFF the ICP**

1. Turn off the RABBIT sampler pump.
2. Turn off the NEBULIZER gas flow.
3. Turn off the RF power supply (i.e., the button on the tabletop unit).
4. Turn off the PLASMA and the AUX gas flows.
5. Turn off the ICP-16 Power Supply (i.e., the WHITE SQUARE button on the ICP-RF POWER SUPPLY under the table).
6. Turn off the argon gas and water supply.
A.2 SOP for the Nd:YAG Laser

Turn ON the Nd:YAG Laser

1. Check all cables and connections for loose fittings or water leaks.

2. Turn key to on, you will hear the water pump begin to circulate and several beeping sounds as the laser goes through a diagnostic. The flash lamp count will be displayed for a few seconds.

3. Cycle to appropriate repetition rate using the select button and the up and down arrows.

4. Block the output port with a beam blocker.

5. Press start/stop button. The flashlamp will start to fire.

6. When all safety precautions are in place, press the shutter button to release the laser beam from the main cavity.

Turn OFF the Nd:YAG Laser

1. Block all beams.

2. Depress shutter button to contain the laser beam inside the main cavity.

3. Depress the start/stop button to disengage the flashlamp.

4. Turn key to standby.

5. Check the main power unit for any leaks or unusual presence of water.
A.3 SOP for Lambda Physik Dye Laser

To Turn ON the Dye Laser

1. Read the manuals.

2. Watch the laser alignment videos.

3. Wear safety goggles and make sure everyone else in the room is aware that both Nd:YAG and dye lasers are ON.

4. Turn on cooling water for the dye laser located under the table (labeled “dye laser”).

5. Turn on black power switch (for the dye laser computer) on the left side of the laser box. If the red pump power switch is off, then turn it on as well (located on the front left of the box).

6. After the computer turns on, make sure the reference wavelength displayed matches the wavelength printed in the grating box assembly, i.e., 1051.327 nm.

7. Using the keyboard, set the laser to the desired wavelength. You will need to press enter and “e” (for “execute”) after typing in the numbers.

8. Make sure the pump-beam entrance hole to the dye laser is blocked.


10. Turn Nd:YAG laser up to the desired power by increasing the timing of the Q switch (no more than 188).

11. Unblock the input hole to allow the Nd:YAG laser beam to come into the dye laser box.

12. Open the exit hole on the right side of the dye laser box to set your laser beam free and off to your experimental setup.

To Turn OFF the Dye Laser

1. Turn OFF the Nd:YAG laser (see the SOP for the Nd:YAG laser).

2. Block the input hole to the dye laser.
3. Turn OFF the dye laser power switch.

4. Turn OFF the cooling water switch.

Under no circumstances should you open the grating assembly box located on the far left of the inside on the dye laser box. You should also not mess with any mirrors or switches on the inside of the orange dye laser box. Minor adjustments can be made with the yellow and green knobs, but only if you know what you are doing and you have another experienced user watching you.
A.4 Standard Operating Procedure for MOUNTING LASER DIODES
(e.g., LDM-4407 Mount)

**CAUTION!**
Laser diodes are extremely susceptible to damage caused by electrostatic discharge and surge currents. Make sure worker and work benches are grounded at all times (using gloves and an anti-static wristlet). In addition, the mount (e.g., LDM-4407) should be grounded to the workbench, and tools should always be grounded (using dc screw on the receptacle) before utilization.

**Laser Diode Mounting**

1. Remove front cover by loosening the two button head screws.

2. Remove the two socket-head cap screws from the laser clamp with the 1.5 mm hex key wrench and remove the clamp.

3. Insert the laser, with the indexing notch up, through the hole in the laser plate, and into the test socket. Ensure that the laser pins uniformly engage the socket.

4. Replace the laser clamp over the laser package. Make sure that the clamp is parallel to the laser plate. Firmly secure the mounting screws and re-check the laser position. Re-adjust if necessary.

**Note:** The laser plate does not have an electrically insulating surface. Therefore, the possibility of shorting the laser pins exists. Although the possibility of this occurring with a carefully installed laser is very remote, take every precaution. It is recommended that insulating tubing be placed over the laser leads before installing a laser into the plate. The tubing should have a thin wall and should not be more than 3.2 mm (1/8”) long.

**Note:** For maximum thermal performance, it is highly recommended that a thermal compound be used at the interface between the laser and the laser plate. This will maximize heat transfer from the package and reduce the temperature gradient produced by the metal-to-metal interface. This is especially important for higher-power 9-mm packages which must dissipate a large amount of thermal energy. A thermal pad/material may also be used, but this is not recommended because of the lower thermal transfer characteristics of this material.

5. Finally, replace front cover.
Changing the PCB switches

1. Remove the four connector studs at the back of the mount with a 3/16” nut driver.

2. Slide the rear cover straight off the back of the mount, clearing the PCB board connectors.

3. Table A4.1 indicates the pin-outs for common laser configurations. Compare these to the pin assignment information given on the data sheet of the particular laser diode you are using. If the pin-outs are identical to a laser listed, you may reconfigure the mount using the switch settings for that laser.

Table A4.1  Switch settings for common diode laser configurations

<table>
<thead>
<tr>
<th>Pin Configuration</th>
<th>Switch Settings (Positions listed are On)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>LC</td>
<td>LA/PC</td>
</tr>
<tr>
<td>LA</td>
<td>LC/PC</td>
</tr>
<tr>
<td>PA</td>
<td>LA/PC</td>
</tr>
<tr>
<td>LC</td>
<td>PA</td>
</tr>
<tr>
<td>LA</td>
<td>LC/PA</td>
</tr>
<tr>
<td>LC</td>
<td>LA</td>
</tr>
<tr>
<td>LC</td>
<td>PC</td>
</tr>
<tr>
<td>LA</td>
<td>PC</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
</tr>
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<td>1,4</td>
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<tr>
<td>3</td>
<td>1,4</td>
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<td>3</td>
</tr>
<tr>
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<td>2,3</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
</tr>
</tbody>
</table>

LA = Laser Anode (Position 1 on each DIP switch)
LC = Laser Cathode (Position 2 on each DIP switch)
PA = Photodiode Anode (Position 3 on each DIP switch)
PC = Photodiode Cathode (Position 4 on each DIP switch)

Amongst manufacturers, there is no standard procedure for numbering of the laser pins. Therefore, we have adopted a somewhat generic scheme which coincides with most packages:

• View the laser package from the rear or leaded side.
• Pin 1 is identified as the left pin when the package is orientated with the indexing notch up.
• Pin 2 is the topmost pin and pin 3 and pin 4 are numbered in clockwise order.

4. When you are finished, replace the back of the mount. You can now reconnect the controllers and operate the laser.
A.5 SOP for alignment of the New Focus External Cavity Diode Laser

1. Do not use this SOP without an experienced supervisor watching you. Use PD detector with voltmeter to monitor power output. You may need several density filters to make sure detector is not saturated and voltmeter is responding quickly to slight adjustments.

2. Set current at threshold or a little above. Check PD to make sure operating properly and quick response.

3. Use a 0.035 hex to remove the set screw in the back of housing under silver label.

4. Slide a 1/16th hex driver into hole and feel for adjustment screw.

5. Adjust screw until output is optimized. You may have to turn several times (screw is about 12 turns from end to end).

6. If this does not fix the problem or screw is almost at the end of threads (12 turns), proceed to remove housing:
   - Unscrew bottom
   - Unscrew red layer
   - Replace 2 bottom screws for stability
   - Uncover optics in main housing
   - Center previous adjustment screw (using 1/16th)

   Use bent hemostats to turn screw under brass ring/platform beneath main silver base that holds prism. It is on the left side when facing beam propagation direction. Use VERY SLIGHT adjustments! Carefully watch power output on voltmeter. Look for peak in power. (Also could be harmonic of diode, be careful.) Check to see if the threshold is close to specs.

   You will not know if this has stabilized the diode until you align into the wavemeter.
A6. SOP for Mapping Diode Laser Modes

1. Make sure all beams are safely contained.

2. Using a quartz window, align a fraction of the main beam into the Burleigh wavemeter. Align the reference HeNe beam back along the original path until the display registers a signal.

3. Start Temperature controller set at 10° C and set the current controller to the threshold current found on the laser diode spec sheet (this is normally around 45 mA).

4. Record the laser wavelength

5. Increase the current by 10 mA, record the wavelength.

6. Repeat step 5 until the maximum operating current is reached (this is normally around 100 mA)

**BE CAREFUL NOT TO GO OVER THIS RATING AS IT WILL CAUSE DAMAGE TO THE DIODE!!**

7. Reduce the current to the threshold current.

8. Increase the temperature of the diode by 10° C.

9. Repeat steps 5-8 until the upper operating temperature is reached (this is normally about 50° C)
Appendix B

Reaction Processes in the Direct Current Hollow-Cathode Discharge Cell

Table B.1  Analyte loss processes in the hollow-cathode discharge cell

<table>
<thead>
<tr>
<th>% Analyte Remaining</th>
<th>Process</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%</td>
<td>% analyte dissociated</td>
<td>1-4</td>
</tr>
<tr>
<td>3%</td>
<td>% of atoms excited to metastable state</td>
<td>3</td>
</tr>
<tr>
<td>28%</td>
<td>Loss to atomic collisions with particles</td>
<td>5, 6</td>
</tr>
<tr>
<td>5%</td>
<td>Loss to reaction with cell walls</td>
<td>2, 4, 7</td>
</tr>
<tr>
<td>13%</td>
<td>% of excited atoms that absorb 777 nm radiation</td>
<td>8</td>
</tr>
<tr>
<td>0.005%</td>
<td>Total % of analyte that participates in nonresonant transition</td>
<td></td>
</tr>
</tbody>
</table>

References


