Assessment Of Surface-Catalyzed Reaction Products From High Temperature Materials In Plasmas

Luke Daniel Allen
University of Vermont

Follow this and additional works at: https://scholarworks.uvm.edu/graddis
Part of the Aerospace Engineering Commons, and the Mechanical Engineering Commons

Recommended Citation
https://scholarworks.uvm.edu/graddis/655

This Thesis is brought to you for free and open access by the Dissertations and Theses at ScholarWorks @ UVM. It has been accepted for inclusion in Graduate College Dissertations and Theses by an authorized administrator of ScholarWorks @ UVM. For more information, please contact donna.omalley@uvm.edu.
Assessment Of Surface-Catalyzed Reaction Products From High Temperature Materials In Plasmas

A Thesis Presented

by

Luke Daniel Allen

to

The Faculty of the Graduate College

of

The University of Vermont

In Partial Fulfillment of the Requirements for the Degree of Master of Science Specializing in Mechanical Engineering

October, 2016

Defense Date: August 26th, 2016

Thesis Examination Committee:

Douglas G. Fletcher, Ph.D., Advisor
Yves Dubief, Ph.D.
Britt A. Holmén, Ph.D., Chairperson
Cynthia J. Forehand, Ph.D., Dean of Graduate College
Abstract

Current simulations of atmospheric entry into both Mars and Earth atmospheres for the design of thermal protections systems (TPS) typically invoke conservative assumptions regarding surface-catalyzed recombination and the amount of energy deposited on the surface. The need to invoke such assumptions derives in part from lack of adequate experimental data on gas-surface interactions at trajectory relevant conditions. Addressing this issue, the University of Vermont’s Plasma Test and Diagnostics Laboratory has done extensive work to measure atomic specie consumption by measuring the concentration gradient over various material surfaces. This thesis extends this work by attempting to directly diagnose molecular species production in air plasmas. A series of spectral models for the A-X and B-X systems of nitric oxide (NO), and the B-X system of boron monoxide (BO) have been developed. These models aim to predict line positions and strengths for the respective molecules in a way that is best suited for the diagnostic needs of the UVM facility. From the NO models, laser induced fluorescence strategies have been adapted with the intent of characterizing the relative quantity and thermodynamic state of NO produced by surface-catalyzed recombination, while the BO model adds a diagnostic tool for the testing of diboride-based TPS materials.

Boundary layer surveys of atomic nitrogen and NO have been carried out over water-cooled copper and nickel surfaces in air/argon plasmas. Translation temperatures and relative number densities throughout the boundary layer are reported. Additional tests were also conducted over a water-cooled copper surface to detect evidence of highly non-equilibrium effects in the form of excess population in elevated vibrational levels of the A-X system of NO. The tests showed that near the sample surface there is a much greater population in the $v'' = 1$ ground state than is predicted by a Boltzmann distribution.
ACKNOWLEDGEMENTS

I want to thank everyone on the UVM Plasma and Laser Diagnostics team for their immense help. Doug Fletcher, Jason Meyers, Corey Tillson, Andrew Lutz, Nick Martin and Roland Herrmann-Stanzel, thank you for everything you have done.

To my family, especially my wife Anna, and my parents Anne and Don Allen, thank you for your continued support and encouragement during this endeavor.

This work has been supported by the Air Force Office of Scientific Research (FA9550-11-1-0201, Dr. Ali Sayir, Technical Monitor) and the National Aeronautics and Space Administration (Grant NNX11AR69G, Dr. Anthony Calomino, Technical Monitor)
# Table of Contents

Acknowledgements ................................................................. ii

1 Introduction ........................................................................... 1
  1.1 Overview ............................................................................ 1
  1.2 Surface Recombination of NO ............................................. 3
  1.3 Boron Monoxide ................................................................. 5

2 Experimental Setup ............................................................... 7
  2.1 30 kW Inductively Coupled Plasma Torch ............................ 7
    2.1.1 30 kW Power Supply .................................................. 9
    2.1.2 Gas Injection System and Test Chamber ....................... 11
  2.2 Laser Configuration ......................................................... 13

3 Laser Induced Fluorescence ................................................. 16
  3.1 Overview ............................................................................ 16
  3.2 TALIF Experimental Strategy ............................................. 17
    3.2.1 Atomic Nitrogen ......................................................... 17
    3.2.2 Atomic Oxygen ......................................................... 20
  3.3 Single-Photon LIF Strategy ................................................ 22
    3.3.1 Nitric Oxide .............................................................. 22
    3.3.2 Boron Oxide ............................................................. 23
  3.4 Assessing Surface Location ............................................... 24
  3.5 Fluorescence Lifetime Measurements in the Boundary Layer ... 26
  3.6 Species Temperature and Relative Number Density ................ 27
  3.7 Absorption ......................................................................... 32

4 Spectral Modelling ............................................................... 35
  4.1 Nitric Oxide ........................................................................ 35
    4.1.1 Calculation of Transition Frequencies ............................ 36
    4.1.2 Calculation of Line Strengths ...................................... 42
    4.1.3 Line Shape ............................................................... 46
    4.1.4 Model Validation ....................................................... 52
4.2 Boron Monoxide ........................................... 53
  4.2.1 BO Transition Frequencies ........................ 54
  4.2.2 BO Line Strengths ................................. 55

5 Results and Discussion .................................... 59
  5.1 N atom TALIF Measurements ........................... 59
  5.2 NO LIF Measurements .................................. 61
    5.2.1 Finding suitable NO transitions ................. 61
    5.2.2 NO Boundary Layer Survey Results ............... 63
    5.2.3 Vibrationally Excited NO ......................... 65

6 Summary .................................................. 71

Bibliography ............................................... 73

A Frank-Condon Factors of NO ............................... 78
## List of Figures

1.1 Potential energy vs. internuclear distance for NO molecule showing recombination (dissociation) energy as well as some arbitrary energy at which molecules leave the material surface.  
2.1 Illustration of boundary layer formation during atmospheric entry along side the simulated conditions in the ICP facility. The non-equilibrium boundary layer is represented in each case by a dashed line labeled NEQBL.  
2.2 Schematic of ICP Torch facility [32].  
2.3 Injection block and quartz tube assembly.  
2.4 Schematic of laser system arrangement.  
2.5 Illustration showing beam focus relative to the plasma jet.  
3.1 LIF excitation schemes for N and O atoms. Solid arrows indicate absorption of a photon at the stated wavelength, while wavy, red arrows indicate emission of a photon.  
3.2 Comparison plots of the different accessible N atom transitions. The upper left is the 207 nm transition, and the others are three of the four quartet transitions near 211 nm ($J' = 3/2, 5/2, 7/2$).  
3.3 Plot showing NO absorption (top) and N atom LIF (bottom) at 207 nm (621 nm dye fundamental wavelength) during a single scan. The rotational transitions assignments of NO are also indicated.  
3.4 Plot showing the hyperfine structure of the O atom $J'' = 2$ electronic transition.  
3.5 Schematic view of LIF strategies used for NO A-X and B-X.  
3.6 Energy level diagram for the B-X system of BO.  
3.7 Typical laser pulse energy ratio data record through a boundary layer scan to assess surface location. Values are normalized such that they are near unity well away from the surface (> 1 mm).  
3.8 Weighted centroid of beam during clipping.  
3.9 Sample TALIF scan of the N atom $J' = 7/2$ feature at 211 nm over copper in an air plasma.
3.10 Nitric oxide total partition sum from HITRAN 2004 database. 31
3.11 Illustration of the ICP test chamber during the absorption process. 33
3.12 A: absorption detected by ICP energy meter. The lower, blue trace shows energy trend in MDFR during same scan. B: transitions clipped from the experimental transmission signal for baseline curve fit, $I_0$. C: transmission signal, $I$, plotted with baseline fit, $I_0$. D: calculated absorption signal. 34

4.1 NO B-X simulation centered near the N atom 207 nm transition (621 nm dye fundamental). Relative intensities for the (3-0), (5-1) and (7-2) bands are shown. $T = 1000$ K 45
4.2 Comparison plot showing normalized Gaussian, Lorentzian and Voigt distributions with equal FWHM. 46
4.3 Ratio of collisional and Doppler broadening contributions at low (room) temperature and $p = 0.5$ torr. 50
4.4 Ratio of collisional and Doppler broadening contributions at high temperature and $p = 160$ torr. 51
4.5 Calculated NO B-X (2-0) band head vs. the LIFBASE simulation in the negative scale for validation at $T = 300$ K. 52
4.6 Calculated NO A-X (0-0) band head vs. the LIFBASE simulation in the negative scale for validation at $T = 300$ K. 53
4.7 Plot of NO B-X (2-0) model vs. experimental data at $T = 297$ K. The experimental data are comprised of several 0.1 nm (dye fundamental) scans stitched together. 54
4.8 Plot of NO A-X (0-0) model vs. experimental data at $T = 297$ K. Data are comprised of a single long range scan. Line positions are accurate to within ±0.005 nm at the dye fundamental wavelength (±0.0017 nm frequency tripled). 55
4.9 Plot of BO B-X (0,0) model. $T = 300$ K, $\Delta \nu_{laser} = 0.1$ cm$^{-1}$. 56

5.1 N atom TALIF boundary layer survey of temperature (top) and integrated area (bottom) above water-cooled Cu and Ni. 61
5.2 Simulated spectrum showing the selected scan region for probing NO. The x-axis represents the theoretical dye fundamental wavelength in a vacuum. Transitions A and B are the target high- and low-temperature transitions, respectively. 62
5.3 Typical LIF scan containing both MDFR and ICP data. This scan represents NO over Ni at $x = 0.737$ mm. 63
5.4 NO LIF boundary layer survey of temperature (top) and temperature-corrected integrated area (bottom) above cooled Cu and Ni. 64
5.5 Previous experimental O atom temperature data over cooled Cu used for NO integrated area correction. Test ID: Cu20130426.

5.6 Plots of vibrationally excited NO at \( x \approx 0.06 \) mm (top) and \( x \approx 0.56 \) mm (bottom). Vertical dashed lines the transitions used to calculate area ratios.

5.7 Plots of vibrationally excited NO at \( x = -0.20 \) mm (top, beam clipped), \( x = 0.18 \) mm (middle) and \( x = 0.56 \) mm (bottom).
# List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>UVM 30 kW Test Parameters</td>
<td>9</td>
</tr>
<tr>
<td>4.1</td>
<td>Spectral constants for the X, A and B electronic states of NO. All units are given in cm$^{-1}$</td>
<td>37</td>
</tr>
<tr>
<td>4.2</td>
<td>Hönl-London factors for doublet transitions with $\Delta \Lambda = 0$ where both states are intermediates of Hund’s case (a) and (b)</td>
<td>57</td>
</tr>
<tr>
<td>4.3</td>
<td>Hönl-London factors for doublet transitions with $\Delta \Lambda = \pm 1$. Branch assignments are for $^2\Sigma - ^2\Pi$.</td>
<td>57</td>
</tr>
<tr>
<td>4.4</td>
<td>Spectral constants for the X and B electronic states of BO. All units are given in cm$^{-1}$</td>
<td>58</td>
</tr>
<tr>
<td>4.5</td>
<td>Hönl-London factors for $^2\Sigma - ^2\Sigma$ transitions with Hund’s case (b) coupling.</td>
<td>58</td>
</tr>
<tr>
<td>5.1</td>
<td>Relevant LIF tests in air plasmas.</td>
<td>59</td>
</tr>
<tr>
<td>5.2</td>
<td>NO LIF tests for excited vibrational levels.</td>
<td>67</td>
</tr>
<tr>
<td>A.1</td>
<td>Frank-Condon factors for the A-X system of NO.</td>
<td>79</td>
</tr>
<tr>
<td>A.2</td>
<td>Frank-Condon factors for the B-X system of NO.</td>
<td>79</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 OVERVIEW

Planetary atmospheric entry presents a variety of challenging engineering problems. Among these problems is the intense heat produced as a large amount of kinetic energy is converted into thermal energy. At hypersonic speeds the bow shock produces enough thermal energy to dissociate many of the molecular gas species of the atmosphere. The resulting post-shock environment is a mixture of molecules, atoms, ions and electrons. This harsh, chemically reacting environment has motivated the development of advanced materials to act as thermal protection systems (TPS). As the gases continue toward the vehicle they tend to relax toward local thermodynamic equilibrium. At the TPS surface, further reactions occur. The speed and likelihood of the surface reactions largely depends on the material properties of the TPS. These material properties dictate both the chemical products which form via processes such as oxidation, as well as surface recombination of dissociated atmospheric molecules. Strongly catalytic materials promote exothermic surface reactions which can greatly
increase the heating experienced by the vehicle. The current lack of reliable data for material testing in atmospheric entry conditions means that accurate physical-chemical models for catalytic efficiency are unavailable. Because these efficiencies are not well understood, the current technique is to assume that the TPS material is highly efficient at recombining atomic species. This conservative assumption results in TPS which may be oversized and thus adds unnecessary mass, limiting mission capabilities [45]. The development of better models and better materials heavily relies on the characterization of this behavior.

To address the issue of insufficient experimental data, boundary layer studies of oxidation products and surface catalyzed reactions in air plasmas are being conducted using laser spectroscopic techniques in a 30 kW Inductively Coupled Plasma (ICP) Torch Facility. An ICP facility has two key advantages over arc-jet facilities: 1) the plasma is generated by coupling with a magnetic field, rather than electrodes, and is therefore contaminant free; and 2) test gas composition can be easily adjusted during testing. Though ICP facilities generally operate in the subsonic regime, the boundary layer flow is very similar to flight conditions provided that the specified total enthalpy, post-shock total pressure, and stagnation point velocity gradient can be reproduced. Additionally, because both types of facilities must match the same post-shock test conditions, results for stagnation point heat flux can readily be scaled from one to the other [13].

This thesis intends to better characterize the surface catalyzed reactions in air plasmas by measuring the spatial variation of major species present in the boundary layer. Later sections will also include initial work on the assessment of oxidation products attributed to TPS chemistry, namely BO. The development of optical tech-
niques for these assessments will expand the diagnostic capabilities of the ICP Facility at UVM and will help produce more accurate models of the gas-surface interactions taking place.

1.2 Surface Recombination of NO

For Earth atmospheric entry, the bow shock of a vehicle is strong enough to highly dissociate the impinging gas, leaving atomic nitrogen and atomic oxygen as the primary species in the post-shock environment. Uncertainty in numerical models can be partially attributed to uncertainty in the surface production of NO. Many simulations include only the homonuclear recombination pathways:

\[
O + O + [s] \rightarrow O_2 + [s] \quad (1.1)
\]

\[
N + N + [s] \rightarrow N_2 + [s] \quad (1.2)
\]

Here, \([s]\) represents a surface site, indicating that the reaction is taking place on the material surface. The heteronuclear recombination reaction is often neglected:

\[
N + O + [s] \rightarrow NO + [s] \quad (1.3)
\]

Neglecting the heteronuclear recombination reduces the boundary layer complexity, but is most commonly left out because the pathway is poorly understood. However, work has been done experimentally which shows that surface recombined NO exists and cannot be safely ignored [7, 22]. Data from experiments like this one prompted development of new models which do account for NO production, provid-
ing better agreement with flight data [18]. Additional work was done showing that agreement could be further improved between simulation and experiment by including the NO surface recombination in the surface boundary condition [38]. This same group went on to demonstrate the production of NO at lower enthalpy ranges with surface temperatures between 300 K and 1200 K [37].

In addition to the heteronuclear surface reaction, it is also of interest to look at competing reactions which can take place after NO formation. Of particular interest is the fast reaction:

\[ N + NO \rightarrow N_2 + O \]  \hspace{1cm} (1.4)

This secondary reaction can account for the decreasing N-atom population, but relatively constant O-atom population approaching the material surface, as seen experimentally [27, 29]. Assessing the thermodynamic state of NO leaving the surface will provide insight to this problem. By looking at a representative diagram of potential energy versus the internuclear spacing of an NO molecule, one can see that when

![Figure 1.1: Potential energy vs. internuclear distance for NO molecule showing recombination (dissociation) energy as well as some arbitrary energy at which molecules leave the material surface.](image)

\[ E_{surf} \]
\[ E_{NO} \]
atoms recombine, they do so at a very high vibrational level as shown in Figure 1.1. This recombination energy is equal to the dissociation energy, $D$, of the molecule. The newly formed molecule leaves the surface with a somewhat lower energy, $E_{NO}$, after having deposited some presently unknown energy, $E_{surf}$, onto the material surface. The ratio of the energy deposited on the surface to the recombination energy is defined as the energy accommodation, $\beta$. An energy accommodation near unity indicates that the molecules are approximately in equilibrium, while smaller values could indicate the presence of NO molecules in higher vibrational states, which are thus capable of further reactions. Adding experimental data by direct detection of NO produced in air plasmas at relevant flight conditions will provide a better understanding of what is taking place and will help drive the development of better models.

1.3 **Boron Monoxide**

Ultra-high temperature ceramics have emerged as leading candidates for thermal protection materials for leading-edge and control surface applications for atmospheric entry [12,14,15,23]. Diboride-based materials such as ZrB$_2$ and HfB$_2$ are particularly well suited for the extreme heating rates that these surfaces experience, with melting points of 3245 and 3380 °C, respectively [11], and thermal conductivities of 80 ± 40 W·m$^{-1}$·K$^{-1}$ [16,47]. The oxidation of the diboride materials at high temperature leads to the production of electronically excited BO in the boundary layer [36]. Recognizing the importance that BO has in the boundary layer chemistry then led to the development of optical diagnostics including single-photon laser induced fluorescence
(LIF) techniques for the $A^2\Pi - X^2\Sigma^+$ [6] and $B^2\Sigma^+ - X^2\Sigma^+$ [44] electronic systems.

This thesis lays the groundwork for implementing BO diagnostics using LIF by developing a high-resolution spectral model of the (0-0) vibrational band of the B-X system. LIF excitation of this transition occurs in a region which is very close to transitions already being probed by the UVM laser system. Details of which will be presented in the following chapters. Development of this model, and implementation of a BO LIF scheme will add a valuable diagnostic tool for future material testing.
Chapter 2

Experimental Setup

2.1 30 kW Inductively Coupled Plasma Torch

The 30 kW ICP Torch was built at the University of Vermont to test and analyze the performance of advanced aerospace materials. The primary focus is characterizing the key gas-surface interactions for candidate atmospheric-entry TPS materials [33]. The facility is capable of producing high-enthalpy flow that can replicate the post shock chemical composition and heating experienced by the TPS during planetary entry, as illustrated in Figure 2.1.

The torch is comprised of three main systems: the radio frequency (RF) power supply, the gas injection system, and the test chamber. A general overview of the three systems will be given here, with more detailed descriptions given in the following subsections. Cold gases are fed from pressurized cylinders into the injector block. They are then channeled upward through a quartz tube surrounded by a water cooled,
copper induction coil. The coil is connected to the 30 kW power supply and is subject to alternating current operating at frequencies from 2.5 to 4 MHz. The oscillating current induces a RF magnetic field within the quartz tube, which couples to the flowing gas, rapidly heating and ionizing the flow to create plasma. The plasma then exits the quartz tube and enters the test chamber. Pressure inside the chamber is regulated using a vacuum pump exhausted to the roof of the building. Figure 2.2 illustrates the general layout of the facility.

Torch startup is initiated using a start gas (argon) at relatively low mass flow rate and low test chamber pressure (< 1 torr). Once the flow is coupled and plasma is being generated within the quartz tube the gas flow rate, chamber pressure and power are gradually increased to a standard condition. At this time, the start gas is removed and the test gas introduced and increased to target flow rate. Table 2.1 describes some of the operating parameters inside the plasma torch.
Figure 2.2: Schematic of ICP Torch facility [32].

Table 2.1: UVM 30 kW Test Parameters

<table>
<thead>
<tr>
<th>Test Gas</th>
<th>air, Ar, N₂, CO₂, O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inductive Heating Power</td>
<td>30 kW (max) @ 4 MHz</td>
</tr>
<tr>
<td>Normal Operating Pressure</td>
<td>100 to 200 torr (13 to 26 [kPa])</td>
</tr>
<tr>
<td>Stagnation Heat Flux</td>
<td>10 to 200 W/cm²</td>
</tr>
<tr>
<td>Mach Range</td>
<td>&lt; 0.3 and &gt;1.0 [-]</td>
</tr>
<tr>
<td>Plasma Jet Diameter</td>
<td>36 mm</td>
</tr>
<tr>
<td>Operating Frequency</td>
<td>2 to 3 MHz</td>
</tr>
</tbody>
</table>

2.1.1 30 kW Power Supply

The plasma torch power supply is a Lepel Model T-30-3-MC5-J-TL1 induction heating generator. The unit was originally designed to power a heater for the production of fiber optics and has been re-purposed to meet the needs of the ICP facility. Within the power supply, standard 3 phase alternating current is converted to high DC volt-
age. By varying the DC voltage it is possible to vary the output power of the power supply.

The power supply features a tank circuit and an oscillator. These systems work to automatically match the source frequency to the tank circuit resonant frequency, which changes based on test conditions. Similarly, the source current is adjusted based on the impedance of the tank circuit. Some tuning is required to adjust for varying power and frequency, this is done with a tunable grid. The oscillator is maintained at resonant frequency by the grid current loop, which takes a small amount of power from the tank circuit and feeds it back to the oscillator.

The tank circuit is comprised of a bank of capacitors and a load, or induction, coil. This circuit is what actually couples the incoming test gas to the power supply to create and sustain the plasma. The load coil is a multi-turn helical coil made from 6 mm copper tubing with de-ionized water flowing through it for cooling. This coil surrounds a quartz confinement tube containing the flowing gas, and concentrates the magnetic field created by the current in the tank circuit. During operation, a large current oscillates between the tank capacitors and the load coil. With each oscillation, some of the energy is dissipated into the plasma. The dissipated energy is then replaced by the tuned oscillator. In theory, efficiency is maximized when the plasma flow and the load coil are the same diameter. However, due to physical limitations, this is not possible and the coil and confinement tube are designed to optimize efficiency without the danger of electrical arcing either from coil to plasma, or between turns in the coil itself.
2.1.2 Gas Injection System and Test Chamber

Test gasses are contained in large pressurized cylinders plumbed into a bank of mass flow controllers. Each gas has a dedicated MKS Instruments flow controller calibrated to deliver each specific gas at rates up to 50 slm. The controllers are connected to a central computer which manages and monitors all gas flow rates, as well as several other parameters.

The cold gas now travels into the gas injection block. The injection block is based on a design by Playez [35] and is illustrated in Figure 2.3a. The block is located beneath the test chamber and the induction coil and serves the purpose of mixing the incoming gas into a more uniform flow before it enters the quartz tube. The gas continues through the injection block and is delivered from below into the quartz tube through a thin annulus at the wall of the tube. At low velocity, conduction within the gas is enough to keep the plasma confined to a constant location. However, at higher velocities it is necessary to introduce recirculation into the flow. Centered within the tube is a brass insert which extends upward to the bottom of the induction coil. The end of the brass insert creates a low pressure region and recirculation in the area surrounded by the induction coil. The recirculating gas remains coupled with the power supply and sustains the plasma ball (Figure 2.3b). New gas entering the tube flows around the plasma ball and is rapidly heated and ionized before finally entering the test chamber as a jet.

Fused quartz was chosen as the material for the confinement tube due to its relatively high melting point and high electrical resistance, 2,000 K and $10^6$ ohms.
Figure 2.3: Injection block and quartz tube assembly.

respectively [32]. The walls of the quartz tube are protected from intense heat of the plasma ball, which can reach temperatures on the order of 10,000 K, by the new gas entering the tube at the wall. This method of cooling has proven to be sufficient to prevent failure of the quartz and provides additional advantages over water cooling. Key advantages include the added efficiency due to heat being carried away by the test gas rather than being lost to the cooling water, thus keeping more energy in the flow. By not water cooling it is also possible to observe the plasma inside the quartz tube. To reach conditions which require higher power levels, compressed air jets are directed at the outer surface of the quartz tube to provide additional convective cooling.
2.2 Laser Configuration

The 30 kW ICP Torch test chamber was designed to include several fused silica windows located on orthogonal flanges (see Figure 2.2) that provide optical access for a variety of spectroscopic techniques. Primary thought was given to the use of LIF as a means of probing atomic and molecular species in the plasma flow. The UVM system relies on a frequency-doubled Nd:YAG (neodymium-doped yttrium aluminum garnet) laser producing 532 nm radiation which pumps a dye laser to produce tunable radiation from 600 to 700 nm, depending on the dye used. The visible light is then frequency doubled by second harmonic generation in the first of two Inrad Autotrackers. The doubled light and the residual red light are then sum frequency mixed in the second Autotracker to produce the 200 to 233 nm UV radiation required for probing target species via single- or two-photon LIF excitation. The UV light is then separated from the residual beams using a harmonic separator.

A beam splitter is used to direct 20% of the laser beam into a microwave discharge flow reactor (MDFR). The MDFR is used to calibrate LIF measurements acquired in the ICP Torch. This is accomplished by creating a population of the target species at known temperature and pressure inside the MDFR and using these values to determine laser performance characteristics, namely the laser line width. The remainder of the laser energy is directed toward the ICP Torch test chamber. In both locations, LIF signal is collected by a gated photomultiplier tube (PMT) and the laser pulse energy is measured by a Molectron energy meter. Thus, for each LIF measurement, four signals are acquired: 1) LIF signal in the ICP, 2) laser pulse energy in the ICP, 3) LIF signal in the MDFR, and 4) laser pulse energy in the MDFR. A schematic of
the laser system is shown in Figure 2.4.

Figure 2.4: Schematic of laser system arrangement.

An intrinsic problem with diagnosing a brightly radiating system is that light in the target wavelength can be radiated from sources other than the LIF process. Narrow band filters centered around the emission wavelength are used to minimize undesired light, however the passage of some ambient radiation is unavoidable. Thus, a background signal is captured in the ICP just prior to the laser pulse arrival, allowing for background signal subtraction in post processing.

A series of beam steering and shaping optics direct the laser beam through the ICP test chamber. These optics focus the beam to a point between the plasma jet and the wall of the chamber, as shown in the illustration in Figure 2.5. Having the focal point in the center of the jet would increase spatial resolution, however
the high concentration of energy is enough to introduce undesired effects, such as three-photon ionization. Placing the focal point beyond the jet avoids this problem while also maintaining a high degree of spatial resolution. The steering optics and PMT for the ICP are mounted on translating stages, which are moved in unison to capture gradients above the sample surface. Current capabilities provide spatial resolution of 0.125 mm. Experiments are designed so that measurements are taken starting from the sample surface and moving outward through the entire boundary layer, approximately 4 mm.

**Figure 2.5**: Illustration showing beam focus relative to the plasma jet.
Chapter 3

Laser Induced Fluorescence

3.1 Overview

Laser Induced Fluorescence (LIF) is described as an absorption of one or more photons by an atom or molecule, followed after some finite time by spontaneous emission from the excited state [9]. This emission can occur at many frequencies; however, to avoid capturing the laser pulse itself, it is usually necessary to view shifted fluorescence. That is, emission that occurs at a wavelength that is different from the excitation wavelength. Additionally, it is required that the emission spectrum of the target species be known. For many species this is made possible by using an available software [20, 26]. The present study depends on these models but also requires a tailor-made simulation capable of fitting experimental data for the extraction of thermodynamic properties. To this end, a physics-based spectral model for multiple electronic systems of NO has been developed and is presented in Chapter 4.

This chapter outlines the LIF strategies and procedures used during this study. The following sections will elaborate on the different methods used to target individual
species, as well as address the issues associated with using them.

\section*{3.2 TALIF Experimental Strategy}

Due to the large energy spacing between the electronic states of many atom species it is often not possible to excite particular transitions using a single photon from a commercially available laser system. This prompted the development of multi-photon techniques including two-photon absorption laser induced fluorescence (TALIF) \cite{3}. As the name implies, this strategy relies on the simultaneous absorption of two separate photons by the atom. Figure 3.1 shows the excitation schemes chosen for atomic nitrogen and oxygen measurements. Care must be taken when selecting which transitions to probe. In general, one wants to work with a transition that is highly populated at the given thermodynamic conditions, thus maximizing the available signal. However, there are several other factors that need be considered. Some of these factors include: accessibility by the UVM laser system; proximity to transitions from other species that may cause interference; and ability to identify the transition (more difficult for molecules). Transition selection requirements and additional considerations are broken down by specie in the following sections.

\subsection*{3.2.1 Atomic Nitrogen}

There are several electronic transitions of atomic nitrogen that are readily accessible by UVM’s laser system by TALIF. These are the: $2p^3 \, ^4S^o \leftarrow 2p23p \, ^4D^o$ two-photon transition near 211 nm with subsequent $2p23p \, ^4D^o \leftarrow 2p23p \, ^4P$ emission at 869 nm; and the $2p^3 \, ^4S^o \leftarrow 2p23p \, ^4S^o$ two-photon transition near 207 nm \cite{42}. These elec-
Figure 3.1: LIF excitation schemes for N and O atoms. Solid arrows indicate absorption of a photon at the stated wavelength, while wavy, red arrows indicate emission of a photon. Additionally, the 211 nm transition has a quartet upper state, where $J' = 1/2, 3/2, 5/2, 7/2$. This provides additional measurement locations to examine. To determine the usefulness of these transitions, a survey of their relative strengths was done. By sequentially visiting and scanning over each transition using the MDFR, and assuming constant laser performance, a direct comparison was made. Results of this survey are shown in Figure 3.2, where wavelengths are given in terms of the dye laser fundamental, $\lambda_f$, and the intensity is the normalized LIF signal, $S_{LIF}$. For the case of two-photon excitation, normalization refers to dividing the raw LIF signal by the square of the laser pulse energy. Note that the $J' = 1/2$ transition is not shown owing to its relative weakness.
Figure 3.2: Comparison plots of the different accessible N atom transitions. The upper left is the 207 nm transition, and the others are three of the four quartet transitions near 211 nm (J′=3/2, 5/2, 7/2).

In terms of signal strength, the 207 nm transition is the strongest, and indeed this transition works very well for measurements taken in N\textsubscript{2} plasmas. However, when scanning this location in an air plasma, there is significant interference from absorption in the NO B-X band (see Figure 3.3). The NO P2(6) NO transition overlaps the N atom feature, precluding meaningful N atom results in the ICP. The absorption occurs at low temperature and is a result of NO recirculation within the ICP test chamber. This phenomenon is unavoidable in the current facility configuration, thus eliminating the 207 nm N atom transition as a viable option when probing in air. Instead, the 211 nm J′=7/2 transition should be used, as it is the next strongest and is unaffected by interference from absorption. A brief explanation of absorption in the UVM facility is given later in this chapter.
**3.2.2 Atomic Oxygen**

LIF measurements of atomic oxygen make use of the $2s^22p^33p \, ^3P \leftarrow 2s^22p^4 \, ^3P \, (J''=2)$ two-photon transition near 226 nm with subsequent $2s^22p^33s \, ^3S \leftarrow 2s^22p^33p \, ^3P$ emission near 845 nm. The $J'' = 2$ transition is selected because it is the lowest in energy, thus containing the greatest population and maximizing signal. Unlike nitrogen, both the excited and ground electronic states of oxygen are triplets. The ground state $J'' = 0, 1, 2$ levels are fairly widely spaced, while the upper state $J' = 0, 1, 2$ levels are very close to one another. The result is a set of three lines, each made up of three tightly overlapping transitions. An example plot showing the hyperfine structure of the $J'' = 2$ transition is shown in Figure 3.4. Curve fitting routines are adapted to account for this structure.
Figure 3.4: Plot showing the hyperfine structure of the O atom $J'' = 2$ electronic transition.
3.3 Single-Photon LIF Strategy

3.3.1 Nitric Oxide

Following the successful LIF scans of the NO B-X (2-0) band in the MDFR, attempts were made to find suitable transitions for conditions in the ICP. Scans were carried out in close proximity to the N atom 211 nm transition to aid in feature identification. These scans yielded few usable results due to low signal levels, overlapping of several vibrational bands, and the relatively broad band UG-11 filter used for the PMT. For these reasons, transitions in NO A-X near the O atom transition at 226 nm were used instead. Excitation strategies for each case are shown in Figure 3.5. The O atom transition falls in a relatively sparse (at room temperature) region of the NO spectrum. The NO features in this region are easily identifiable through modeling. Aside from being identifiable, it has been previously shown that it is important that there be a high temperature transition that is separated from any low temperature transitions, but still near enough to be captured in the same scan [29]. This is because the recirculating gas inside the test chamber, but not near the plasma flow, contains NO at low temperature (∼ 400 K). The recirculating NO absorbs a portion, or all, of the laser light along its path length. The absorbed energy causes a loss in both the PMT and pulse energy signals, resulting in poor normalization and misleading results.
3.3.2 Boron Oxide

The B-X system of BO was selected as the best candidate for LIF diagnostics. This decision was based on literature [44], modelling, and the capabilities of the laser system. The (0-0) vibrational band of this system lies at 233.2 nm (699.6 nm dye fundamental), with subsequent emission in the UV. The location of the absorption wavelength falls well within the reach of the dye laser operating with the same dye used for O atom, making this a convenient test, requiring only new filters. The strategy uses a band-pass filter centered at 265 nm in series with a neutral density filter. Care is taken to ensure that the filter is narrow enough that it blocks laser excitation wavelengths below 240 nm.
3.4 Assessing Surface Location

One key aspect of the investigation of the boundary layer is the accurate determination of the surface location with respect to the incident laser beam and data collection location. The procedure for determining the surface is carried out by first calculating the ratio of laser pulse energies in the flow reactor and the ICP, and second by observing the drop in the energy ratio as the beam is clipped by the sample surface. The energy ratio, $\varepsilon_r$, is equal to $E_{p,ICP}/E_{p,FR}$, where $E_{p,ICP}$ and $E_{p,FR}$ are the laser pulse energies measured at the ICP and MDFR, respectively. The ratio is normalized such that the value well away from the surface is unity. Near the surface, the energy ratio drops off linearly to zero, indicating a fully clipped beam. The data are interpolated to find the distance measurement for which the energy ratio is 0.5. This is taken...
Figure 3.7: Typical laser pulse energy ratio data record through a boundary layer scan to assess surface location. Values are normalized such that they are near unity well away from the surface (> 1 mm).

to be the sample surface and position data is shifted to bring the surface to 0 mm.

Figure 3.7 shows a typical plot used for surface assessment where the y-axis is the normalized energy ratio, \( \varepsilon_r \), and the x-axis is the distance above the sample surface, \( x \). The dashed line indicates the onset of clipping and the shaded region is the sample surface. The beam diameter is taken to be twice the distance from clipping onset to the sample surface, which in this case is approximately 0.3 mm.

Data points which fall to the left of the dashed line are considered less reliable since it is currently unclear how much of the beam reflects back into the collection optics of the PMT. For this reason, only points to the right of the dashed line are studied thoroughly. Additionally, some of the points appear to reside within the sample material. This is due to the width of the beam, and the fact that a weighted centroid of the beam shape and its energy distribution has not been implemented. Figure 3.8 clearly illustrates this issue. Once clipping occurs, the translation measurement from the beam steering optics no longer represent the true measurement point. The measurement point now lies at the beam centroid of the unclipped portion, as shown in B and C.
3.5 Fluorescence Lifetime Measurements in the Boundary Layer

An additional factor affecting detected fluorescence signal is the fluorescence lifetime of the transition being probed. When a particle becomes excited by absorbing a photon, it remains in that state only for a finite amount of time, typically on the order of nanoseconds. In the absence of competing mechanisms, the decay from upper state to lower state is caused only by spontaneous emission. The spontaneous emission rate from state 2, to state 1 is the Einstein A coefficient, $A_{21}$. Taking the inverse of the spontaneous emission rate gives the radiative lifetime of the upper state: $\tau_{rad} = 1/A_{21}$. In reality, one must take into account other mechanisms which can shorten the effective upper state lifetime. The most commonly encountered mechanism is collisional quenching, and the quenching rate, $Q$, describes the rate of collisional de-excitation. In the given test conditions, the primary quenching mechanism is through the collisions of fluorescing particles with other particles in the flow. The observed lifetime can then be calculated by:

$$\tau_{obs} = \frac{1}{A_{21} + Q} \quad (3.1)$$
Fortunately, the fluorescence lifetime can be directly measured by observing the excitation and decay of the fluorescence signal on an oscilloscope. Traces of the fluorescence signal with time are recorded and averaged and the resulting data are fit with an exponential function of the form:

\[ I = I_0 e^{-t/\tau} \]  

The measured lifetime is then the time for the fluorescence to decay to \(1/e\) of its peak value. The experimental arrangement is the same as for LIF experiments, making this a relatively simple measurement to acquire. However, instead of scanning the laser through an absorption feature, it is positioned at the transition peak. The laser beam and collection optics are then translated through the boundary layer, collecting fluorescence lifetime data at each point along the way.

### 3.6 Species Temperature and Relative Number Density

At each measurement location the laser is tuned over a narrow wavelength band centered around the energy transition of interest. The data acquisition system records both the laser pulse energy, \(E_p\), and the PMT signal, \(S_{PMT}\), while the laser is tuned over the wavelength range. The normalized LIF signal, \(S_{LIF}\), is determined by dividing the PMT signal by the pulse energy for single-photon strategies, or by the pulse energy squared for two-photon strategies. A typical, normalized, laser scan of atomic nitrogen is shown in Figure 3.9. The broad, lower trace represents LIF in the ICP,
while the narrow, upper trace represents the MDFR. A smooth Gaussian curve is fit to both sets of data.

**Figure 3.9:** Sample TALIF scan of the N atom $J' = 7/2$ feature at 211 nm over copper in an air plasma.

The widths, expressed as full width at half maximum (FWHM), of the two lines are assumed to come only from Doppler (thermal) and laser linewidth broadening. This is due to the very low pressure in the MDFR ($\sim$0.55 torr at 300 K) and the high temperature in the ICP (2000 to 7000 K at 160 torr). Linewidth contributions are discussed in greater detail in Chapter 4. The relationships between the total, Doppler and laser linewidths are given by:

\[
(\Delta \nu_{\text{tot,ICP}})^2 = (\Delta \nu_{D,\text{ICP}})^2 + \alpha(\Delta \nu_{\text{laser}})^2
\]  

(3.3)

\[
(\Delta \nu_{\text{tot,FR}})^2 = (\Delta \nu_{D,\text{FR}})^2 + \alpha(\Delta \nu_{\text{laser}})^2
\]  

(3.4)

The subscripts FR and ICP, indicate values for the flow reactor and plasma torch,
respectively, while the tot and $D$ subscripts indicate whether the value is the total or Doppler width. The laser linewidth, $\Delta \hat{\nu}_{\text{laser}}$, is the same for both measurement locations. The $\alpha$ term is a constant, where $\alpha = 1$ for single-photon processes and $\alpha = 2$ for two-photon processes.

Because the temperature inside the flow reactor is known (equal to the measured room temperature), the Doppler width $\Delta \hat{\nu}_{D,\text{FR}}$ can be determined by:

$$\Delta \hat{\nu}_{D,\text{FR}} = \frac{\hat{\nu}_0}{c} \sqrt{\frac{2k_b T_{\text{FR}}}{M}} = \hat{\nu}_0 \cdot 7.162 \times 10^{-7} \sqrt{\frac{T_{\text{FR}}}{M}}$$

where the expression on the right is used for units of cm$^{-1}$. The broadening depends on the center wavelength, $\hat{\nu}_0$, the mass of the atom or molecule, $M$, and the temperature, $T$. Eq. (3.4) can now be solved for the laser linewidth, $\Delta \hat{\nu}_{\text{laser}}$.

With the laser linewidth now known, Eq. (3.3) is solved for the ICP temperature by:

$$T_{\text{ICP}} = \frac{M}{(\hat{\nu}_0 \cdot 7.162 \times 10^{-7})^2} \left[ (\Delta \hat{\nu}_{\text{tot,ICP}})^2 - (\Delta \hat{\nu}_{\text{laser}})^2 \right]$$

(3.6)

For determining the relative number density of individual species, the simplest case of those discussed here is for nitrogen atom. For this case, the number density, $n_N$, is directly proportional to the integrated LIF signal when normalized by the laser pulse energy squared:

$$n_N \propto \int \frac{S_{\text{PMT}}}{E_p^2} (\lambda) \, d\lambda$$

(3.7)

where $S_{\text{PMT}}$ is the signal detected by the PMT, $E_p$ is the laser pulse energy, and $\lambda$ is the wavelength range of the integration. The approaches for O and NO are similar.
to that of N, but require the multiplication by an additional factor relating to the population distribution in the lower state, $f(T)$. Additionally for the case of NO, because it is a single-photon process, the signal is normalized by the first power of the pulse energy rather than the pulse energy squared. The correction term accounts for the temperature dependence of the lower state of the transition, and is assumed to follow a Boltzmann distribution [43]. The equations for the relative number densities of O and NO are:

$$n_O \propto \int \frac{S_{PMT}}{E_p^2} (\lambda) \, d\lambda \times f_O(T)^{-1} \quad (3.8)$$

$$n_{NO} \propto \int \frac{S_{PMT}}{E_p} (\lambda) \, d\lambda \times f_{NO}(T)^{-1} \quad (3.9)$$

Oxygen, unlike nitrogen, has a ground state that is a triplet, with $J'' = 0, 1, 2$. The temperature correction term for the $J'' = 2$ substate (which is the strongest) is:

$$f_O = \frac{5}{5 + 3e^{-228.75/T} + e^{-326.59/T}} \quad (3.10)$$

NO molecules have a far greater number of available energy levels due to the addition of vibrational and rotational modes. The correction term is derived from a Boltzmann distribution approximation for the rotational-vibrational level and is included below:

$$f_{NO} = \frac{2(2J'' + 1)e^{(-\nu''\theta_v-J''(J''+1)\theta_r)/T}}{Q_{tot}(T)} \quad (3.11)$$

In this expression, $\theta_v$ and $\theta_r$ are the characteristic vibrational and rotational tempera-
tures (2740 K and 2.5 K, respectively for NO [43]). The temperature dependent total partition sum, $Q_{tot}(T)$, is derived from a fit to experimental data from the HITRAN 2004 database [40]. A 3rd-order polynomial fit was used, resulting in the following expression:

$$Q_{tot}(T) = -41.817 + 3.648T + 0.00116T^2 + 1.1396 \times 10^{-7}T^3$$  \hspace{1cm} (3.12)

Note that the HITRAN 2004 data used for the fit only spans from 100 K to 3000 K and is shown in Figure 3.10. This model was extrapolated for cases up to 7000 K.

![Figure 3.10: Nitric oxide total partition sum from HITRAN 2004 database.](image_url)
3.7 Absorption

Occasionally during the LIF experimental process, transitions from non-target atoms or molecules can be encountered. As the hot gas is injected into the chamber, it quickly expands to fill the low pressure environment before being expelled by the exhaust system. The expanding gas rapidly cools, resulting in an area of relatively low temperature gas ($T \approx 400$ K) surrounding the hot plasma in the center of the chamber. Figure 3.11 illustrates this as well as the long path length along the direction of laser propagation through the recirculation region. This means that if the laser frequency is tuned over a low temperature transition of any of the species existing in the recirculating gas, many of the photons will be absorbed, and the result will be a decrease in the laser pulse energy as measured by the energy meter. As more photons are absorbed, the signal level measured by the PMT is also decreased. Additionally, as the pulse energy approaches zero, the noise of the signal rapidly increases. This happens because the signal is normalized by dividing by the laser energy, resulting in division by a very small number.

An example of the laser energy dropout is shown in Figure 3.12A, where low temperature nitric oxide transitions were found to interfere with N atom measurements near 207 nm (621 nm dye fundamental). Clearly, the drop in laser energy will have adverse effects on the LIF signal being collected. However, some useful data may still be extracted. The technique for calculating absorption proceeds as follows: first, the transition features are clipped from the transmission signal (Figure 3.12B); next, a curve is fit to the remaining points, establishing the estimated baseline transmission (Figure 3.12C); and finally, the absorption is calculated using Eq. (3.13) (Figure
\[ \text{Absorption} = -\ln \left( \frac{I}{I_0} \right) \] (3.13)

While absorption is certainly a valid measurement technique, one loses a degree of spatial resolution when compared to LIF. This is due to the signal being dependent on the entire path length of the laser beam, rather than at just one point, as illustrated in 3.11. In general, absorption is avoided by selecting scan regions which do not contain overlapping high and low temperature transitions.
Figure 3.12:  A: absorption detected by ICP energy meter. The lower, blue trace shows energy trend in MDFR during same scan.  B: transitions clipped from the experimental transmission signal for baseline curve fit, $I_0$.  C: transmission signal, $I$, plotted with baseline fit, $I_0$.  D: calculated absorption signal.
Chapter 4

Spectral Modelling

Determining which regions of a molecular spectrum to use in a LIF scheme is challenging due to their high complexity and many overlapping features. The additional degrees of freedom of even a diatomic molecule drastically increase the difficulty of identifying features compared to atomic spectra. This process is complicated further by the limitations of the laser system being used. The UVM laser is capable of only short scans (0.05 to 0.1 nm dye laser fundamental or 0.0167 to 0.333 nm frequency tripled). While longer scans are possible, the process introduces greater error. For these reasons it is imperative that an accurate spectral model for the desired molecular species be developed.

4.1 Nitric Oxide

Nitric oxide is an important species in the study of air plasmas. Thus, its characterization and the ability for the UVM lab to diagnose NO in the plasma flow is a primary objective. There are two electronic transitions of interest for NO due to the
wavelengths at which they occur being near identifiable atomic transitions. They are also well within the capabilities of the UVM laser system. These are the $B^2\Pi \leftarrow X^2\Pi_r$ and $A^2\Sigma^+ \leftarrow X^2\Pi_r$ electronic transitions, known also as the NO B-X (beta) and NO A-X (gamma) bands, respectively. A model for NO beta was developed first due to its proximity to the N atom 207 and 211 nm two-photon transitions which were already being probed. Following that, the model for NO gamma was developed for use near the triplet O atom transition around 226 nm. The two simulations are calculated in a similar fashion. The process is outlined in detail in the following sections and generally follows the steps of: 1) importing and defining spectroscopic constants, 2) calculation of line center locations, 3) calculation of line strengths, 4) calculation of line shape.

Most of the basic spectral constants are taken from published literature. The ground state, X, constants are from Amiot [1] via Laux [21], gamma constants are from Huber and Herzberg [17], and beta constants are from Engleman and Rouse [10]. Constants are shown in Table 4.1.

4.1.1 Calculation of Transition Frequencies

Molecular energy levels are divided into electronic, vibrational and rotational levels. Transitions will occur between each pair of these levels, provided that the transition is allowed by a set of selection rules. The total internal energy of a given state is given by:

$$T_{evJ} = T_e + G(v) + F(J)$$  (4.1)
Table 4.1: Spectral constants for the X, A and B electronic states of NO. All units are given in cm⁻¹.

<table>
<thead>
<tr>
<th>State</th>
<th>X</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tₑ</td>
<td>0.0</td>
<td>43965.7</td>
<td>45868.53</td>
</tr>
<tr>
<td>ωₑ</td>
<td>1904.1346</td>
<td>1037.449</td>
<td>2374.31</td>
</tr>
<tr>
<td>-ωₑₓₑ</td>
<td>-14.0884</td>
<td>-16.106</td>
<td>-7.4724</td>
</tr>
<tr>
<td>ωₑʸₑ</td>
<td>0.0100467</td>
<td>-0.0465</td>
<td>0.07253</td>
</tr>
<tr>
<td>ωₑᶻₑ</td>
<td>-1.5331(-4)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Bₑ</td>
<td>1.70488847</td>
<td>1.1250</td>
<td>1.9965</td>
</tr>
<tr>
<td>-αₑ</td>
<td>-0.0175416</td>
<td>-0.013482</td>
<td>-0.01915</td>
</tr>
<tr>
<td>γₑ</td>
<td>-1.4886(-5)</td>
<td>0.000125</td>
<td>0</td>
</tr>
<tr>
<td>Dₑ</td>
<td>5.46616(-6)</td>
<td>5.6(-6)</td>
<td>5.2(-6)</td>
</tr>
<tr>
<td>βₑ</td>
<td>1.7032(-8)</td>
<td>2.0(-8)</td>
<td>1.4(-8)</td>
</tr>
<tr>
<td>Aₑ</td>
<td>123.26</td>
<td>31.32</td>
<td>0</td>
</tr>
<tr>
<td>Aₐ</td>
<td>-0.1906</td>
<td>1.152</td>
<td>0</td>
</tr>
<tr>
<td>A₋</td>
<td>-0.0108</td>
<td>0.0448</td>
<td>0</td>
</tr>
</tbody>
</table>

Sources: [1, 10, 17, 21]

where Tₑ, G(ν) and F(J) are the electronic, vibrational and rotational energies respectively. The values of Tₑ for NO are tabulated for all electronic systems of interest [21], while the values of G(ν) and F(J) are to be calculated from other available constants and quantum numbers. The vibrational energy, G(ν), is a function of the vibrational quantum number, ν, and is calculated using the expression:

\[ G(ν) = \omegaₑ \left( ν + \frac{1}{2} \right) - \omegaₑₓₑ \left( ν + \frac{1}{2} \right)^2 + \omegaₑʸₑ \left( ν + \frac{1}{2} \right)^3 + \omegaₑᶻₑ \left( ν + \frac{1}{2} \right)^4 \]  (4.2)

Rotational energy levels are calculated according to the representation by Zare [46], with corrections suggested by Paul [34] for the case of NO A-X. The methods are summarized in the following two sections.
NO B-X Rotational Energy

For NO B-X, the upper and lower state energy levels are calculated in the same manner. Constants from Table 4.1 are used to evaluate the spin-splitting and coupling constants as in Eqs. (4.3) and (4.4), respectively.

\[ A_v = A_e + A_a (v + \frac{1}{2}) + A_b (v + \frac{1}{2})^2 \] (4.3)

\[ B_v = B_e - \alpha_e (v + \frac{1}{2}) + \gamma_e (v + \frac{1}{2})^2 \] (4.4)

Following Zare’s formalism [46], two additional parameters, \( Y_v \) and \( X_v \), are now defined. \( Y_v \) is a constant for each vibrational band and is given by \( Y_v = A_v / B_v \). The parameter \( X_v \) is a function of \( J \) and is defined as:

\[ X_v(J) = \left[ 4 \left( J + \frac{1}{2} \right)^2 + Y_v (Y_v - 4) \right]^{\frac{1}{2}} \] (4.5)

where \( J = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \text{ etc.} \). Finally, the spin-split rotational energy levels are calculated as:

\[ F(J) = B_v \left[ \left( J - \frac{1}{2} \right) \left( J + \frac{3}{2} \right) \pm \frac{X(J)}{2} \right]. \] (4.6)

The resulting terms are labeled \( F_1 \) and \( F_2 \). By convention, \( F_1 > F_2 \).

NO A-X Rotational Energy

For NO A-X, a modified expression for the rotational energies of both the upper and lower levels is described by Paul [1997]. Unfortunately, because it was derived from
Zare, some notation is very similar to the method described above and care must be
taken to ensure proper bookkeeping. The constants $A_v$, $B_v$ and $Y_v$ are defined the
same way as before. Additional terms are the spin orbit parameter, $A_{Dv}$, which is
taken from Amiot [2] via Paul for $v \leq 8$ (Amiot reports values up to $v = 22$), and
the centrifugal distortion parameter $D_v$, defined as:

$$D_v = D_e + \beta_e \left(v + \frac{1}{2}\right)$$

(4.7)

For the ground state of NO, Paul [1997] defines the rotational energy as $F \equiv F_{\Lambda,s}(v, J)$,
where $F_{\Lambda,s}$ is now the energy for the two spin-split ($s = 1/2$ and $3/2$) and the two
lambda-doubled ($\Lambda = e$ and $f$) components. Now, following the notation from Paul
[1997], let $x \equiv J + 1/2$ and define the following expressions:

$$T_{\Lambda}(x) \equiv -\frac{A_v}{2} + (B_v - A_{Dv})x^2 - D_v(x^4 + x^2 - 1) + \frac{1}{2} \left(p_v + q_v(1 \pm x)\right)$$

(4.8a)

$$T_i(x) \equiv \frac{A_v}{2} + (B_v + A_{Dv})(x^2 - 2) - D_v((x^2 - 2)^2 + x^2 - 1) + \frac{q_v}{2}(x^2 - 1)$$

(4.8b)

$$H_{\Lambda}(x) \equiv 2D_v(x^2 - 1)^{3/2} - \left(B_v + \frac{p_v}{4} + \frac{q_v}{2}(1 \pm x)\right)(x^2 - 1)^{1/2}$$

(4.8c)

The $\pm$ symbols in Eqs. (4.8a) and (4.8c) take the values of ‘+’ and ‘−’ for the $e$ and
$f$ sublevels, respectively. Finally, the ground state spin-split energy levels are defined
using the above expressions as:
For the present study, lambda-doubling is considered negligible \((p_v = q_v = 0)\), allowing the terms to simplify.

For the upper state, A, let rotational energy, \(F\), be defined as \(F = F_s(v, J)\). For the \(2\Sigma\) state \(s = \pm 1/2\). The spin-split energy levels are defined as:

\[
F_{-1/2}(x) = B_v x (x - 1) - D_v x^2 (x - 1)^2 - \frac{\gamma_v}{2} (1 - x) \tag{4.10a}
\]
\[
F_{1/2}(x) = B_v x (x + 1) - D_v x^2 (x + 1)^2 - \frac{\gamma_v}{2} (1 + x) \tag{4.10b}
\]

Once the rotational levels are determined, the process merges again for both the B-X and A-X cases. The rest of this section is identical for both A-x and B-X systems of NO.

**Calculation of Excitation Wavelength**

Absorption of a photon can result when the energy of the impinging photon is equal to the difference in energy between two allowed states. Determining the absorption energies, and thus the required laser wavelength (recall \(E = h\nu\)), for each transition requires looping through all possible pairs of energy levels and determining the difference in energy between them. This is done for each of the allowed rotational branches of the vibrational level. The allowed rotational transitions are
\[ \Delta J = -1, 0, +1, \] which are termed \( P \), \( Q \) and \( R \) branches, respectively [9]. Moreover, transitions in which the spin does not change (i.e. \( s' = s'' \)) make up the six main branches (\( P_1, Q_1, R_1, P_2, Q_2 \) and \( R_2 \)), while transitions involving a change in spin make up the six satellite branches (\( P_{12}, Q_{12}, R_{12}, P_{21}, Q_{21} \) and \( R_{21} \)). The relationship between energy difference and the vacuum wavenumber is given below.

\[ \hat{\nu}_{\text{ev},J} = \Delta T_e + \Delta G(v) + \Delta F(J). \] (4.11)

The hat over the frequency variable, \( \nu \), denotes that units of \( \text{cm}^{-1} \) are being used. This value of the wavenumber is useful, but since all observations in this study are done in air rather than a vacuum, it is helpful to convert by the refractive index. For the refractive index of air, Ciddor’s Formula is used [5]. This first requires conversion of the vacuum wavenumber to wavelength in \( \mu \text{m} \) by

\[ \lambda = 1 \times 10^4 / \hat{\nu}. \]

The wavelength is then modified using Ciddor’s Formula, before being converted back to wavenumber.

\[ \lambda_{\text{air}} = \left[ 1 + \frac{0.05792105}{238.0185 - (\lambda_{\text{vac}})^{-2}} + \frac{0.00167917}{57.362 - (\lambda_{\text{vac}})^{-2}} \right] \lambda_{\text{vac}} \] (4.12)

It is worth noting that this method differs from the method used in the LIFBASE [26] simulations which were used to help with validation. LIFBASE uses the Edlen Formula, which results in a small shift in the final wavelength compared to the model presented here. Ciddor’s Formula was chosen because it is considered to be more accurate than Edlen’s Formula over a broader range of wavelengths [5,41]. A linear correction is all that is needed to bring the two into agreement.
4.1.2 Calculation of Line Strengths

The intensity of lines depends on two main factors, the population of molecules in each rotational level; and the probability of transitions occurring between the upper and lower levels. These transition probabilities can also be divided into two factors, one being the band strength; and the second being the relative distribution of molecules among the different rotational branches within a band, known as Hönl-London factors [9]. Accurate determination of Hönl-London factors varies considerably for different electronic transitions. The methods used for the B-X and A-X systems are detailed below.

NO B-X Hönl-London Factors

Transitions in the NO B-X band are intermediates between Hund’s case (a) and case (b) [4]. Hönl-London factors for the intermediate case, $\Delta \Lambda = 0$ transitions are calculated according to Bennet [4] with the general expressions provided in Table 4.2. Note that for NO B-X, both upper and lower states are $^2\Pi$ and thus $\Lambda = 1$. Bennet includes several abbreviations in his expressions, which are provided in Eq. (4.13) and are simplified according to work by Kováks.

\[
Z = Y_v - 2 \\ U = \frac{1}{X_v(J)} \\ A(\xi) = \left[ (2\xi + 1)^2 - 4 \right] \left[ (2J + 1)^2 - 4 \right] \\ D(\xi) = (2\xi + 1)(2J + 1) - 4
\]
and $X_v(J)$ are the same as defined in the previous section. The use of $A$ and $D$ as additional terms is unfortunate, but not to be confused with Eqs. (4.3) and (4.7). The $\xi$ term is simply a dummy variable.

**NO A-X Hönl-London Factors**

Hönl-London factors for the NO A-X band are calculated according to Paul [34]. Paul includes higher order effects in his calculations than were included for NO B-X. To do this he defines a polynomial correction term, $\varphi_v$. For the simplified case of negligible lambda-doubling, this expression is approximated as:

$$\varphi_v \approx 1 - \frac{2D_v}{B_v} + 2 \left( \frac{AD_v + 2D_v}{A_v - 2B_v} + \frac{D_v}{B_v} \right) x^2$$

(4.14)

Recall from Paul’s calculation of rotational energy levels that $x = J + 1/2$. Paul then redefines Eq. (4.5) to include this correction (shown below), and presents the modified expressions for the Hönl-London factors, which are presented here in Table 4.3.

$$X_v^{(PP)} = \left( 4(x^2 - 1) + (Y_v - 2)^2 \varphi_v^2 \right)^{1/2}$$

(4.15)

**Overall Relative Line Strengths**

With Hönl-London factors now calculated, the two models again merge and the remaining steps are the same for both cases. To determine the relative population distribution within each rotational branch, the appropriate set of Hönl-London factors is multiplied by the rotational partition function, as shown in Eq. (4.16). The
energy term, $F''$, in the partition function exponent is equal to that of the rotational energy of the lower state of the transition.

$$I_J \propto S_i(J) \frac{\theta_{rot}}{T} \exp \left( -\frac{F'' h c}{k_b T} \right)$$  \hspace{1cm} (4.16)

$I_J$ is the intensity of the rotational transition and is proportional to the Hönl-London factor, $S_i(J)$, multiplied by the Boltzmann expression, which is given as everything to the right of $S_i(J)$. $\theta_{rot}$ is the characteristic rotational temperature, $h$ is Plank’s constant, $c$ is the speed of light, $k_b$ is Boltzmann’s constant, and $T$ is the absolute temperature.

Often, it is required to simulate several vibrational bands simultaneously. Up to this point, all of the calculations have been done within a single band. Plotting the bands at the same time requires knowledge of the population fractions and of the transition probability. The vibrational transition probability is known as the Frank-Condon factor, $q_{v'v''}$, values for which are taken from Laux [21]. Values of the Frank-Condon factors for NO A-X and B-X are provided in Appendix A. It is assumed that the population fraction follows a Boltzmann distribution and is calculated by:

$$f_{v''}(T) = \frac{n_{v''}}{n_{total}} = \frac{e^{-v'' \theta_v / T}}{\left( \frac{1}{1-e^{-\theta_v / T}} \right)}$$  \hspace{1cm} (4.17)

where $\theta_v$ is the characteristic vibrational temperature and $v''$ is the vibrational quantum number of the lower state. The term in the denominator is the vibrational partition function, $Q_{vib}$, and is derived from:

$$Q_{vib} = \sum_{v''=0}^{\infty} e^{-v'' \theta_v / T}$$  \hspace{1cm} (4.18)
The overall intensity of the lines is then proportional to the product of the population fraction and the Frank-Condon factor for the vibrational band:

\[ I_{v'v''} \propto f_{v''}(T) \cdot q_{v''} \]

(4.19)

An example plot showing several vibrational bands of NO B-X superimposed onto one plot is shown in Figure 4.1. This illustrates the relative intensities of the three bands at moderate temperature in the region near the N atom 207 nm transition. Note that the wavelength is given in terms of the dye fundamental output, which is three times larger than the absorption wavelength.

![Figure 4.1](image)

**Figure 4.1:** NO B-X simulation centered near the N atom 207 nm transition (621 nm dye fundamental). Relative intensities for the (3-0), (5-1) and (7-2) bands are shown. \( T = 1000 \) K
4.1.3 **Line Shape**

An individual atom or molecule transitioning between energy states emits a single photon with a well defined, and predictable, energy and wavelength. However, the profiles of real spectral lines are not infinitely sharp. Instead they have some population distribution centered at, or near, the idealized line frequency location. The shape of this distribution depends on the broadening mechanism. For example, natural broadening and collisional broadening effects contribute to a Lorentz distribution, while thermal broadening and laser line width effects are Gaussian in shape [9]. On occasions where both Lorentzian and Gaussian broadening exist, the two distributions can be convolved using a Voigt profile. The three distribution profiles are shown in Figure 4.2. While many types of broadening exist, only the effects of natural, collisional, thermal and laser broadening will be considered here.

![Figure 4.2: Comparisson plot showing normalized Gaussian, Lorentzian and Voigt distributions with equal FWHM.](image)
A laser beam is not perfectly monochromatic. This is especially true for short duration pulsed lasers. This results in a broadening of spectral features, and needs to be accounted for by the LIF simulation. Laser broadening follows a Gaussian profile and for the purpose of the simulation, the full width at half maximum (FWHM) is a user input and is typically $\sim 0.1 \text{ cm}^{-1}$. During an experiment, the laser line width is determined independently for each scan and is used to extract temperature and number density information in the ICP, as described in Chapter 3.

Thermal broadening is the result of the small variations in the absorbed frequency due to the Doppler effect (Doppler broadening). Particles moving with some velocity parallel to the line of sight of the observer will appear to absorb at a slightly different frequency. The FWHM of the line due to thermal effects is called the Doppler width and is given in Eq. (3.5), and is reproduced here for convenience:

$$\Delta \hat{\nu}_D = \frac{\hat{\nu}_0}{c} \sqrt{\frac{2k_bT}{M}} = \hat{\nu}_0 \cdot 7.162 \times 10^{-7} \sqrt{\frac{T}{M}}$$

where $\hat{\nu}_0$ is the center frequency of the transition and $M$ is the molar mass of the molecule. The laser line width and Doppler width are often combined into a single term, with the total line width calculated as:

$$\Delta \hat{\nu}_{\text{tot}} = \sqrt{\Delta \hat{\nu}_D^2 + \Delta \hat{\nu}_{\text{laser}}^2}$$

As previously stated, thermal broadening follows a Gaussian profile. Inserting the total line width from Eq. (4.21) into the Gaussian profile function, and normalizing such that $\int_{-\infty}^{\infty} \phi_G(\hat{\nu})d\hat{\nu} = 1$ yields the total Gaussian line shape function:
The natural linewidth of a transition is due to the uncertainty in the energy levels themselves. Heisenberg’s Uncertainty Principle states that energy levels have a width, $\Delta E$, and that $\Delta E \tau \geq h/2\pi$, where $\tau$ is the particle lifetime. Energy can also be defined in terms of wavenumber, $E = \hbar \hat{\nu}$, and thus $\Delta E = \hbar \Delta \hat{\nu}$. This then yields an expression for the natural linewidth, $\Delta \hat{\nu} \geq 1/2\pi \tau$. By this relationship, the more stable a particular energy level is (i.e. large $\tau$), the narrower the spectral line will be. For the purpose of this spectral simulation, the effects of natural broadening are considered negligible, and are not included. However, it is worth mentioning because it helps explain other competing broadening mechanisms.

Collisional broadening is caused by the interference of other atoms and molecules with the emission process. These collisions cause small shifts in the energy levels of both states that are joined by the absorption process, and this effect becomes more important as the collision frequency increases at higher densities. Similar to natural broadening, the change in $\Delta E$ causes a change in $\Delta \hat{\nu}$. If the collisional line width, $\Delta \hat{\nu}_C$, is known, it follows a Lorentzian profile calculated by:

$$\phi_L(\hat{\nu}) = \frac{1}{2\pi} \frac{\Delta \hat{\nu}_C}{(\hat{\nu} - \hat{\nu}_0)^2 + (\Delta \hat{\nu}_C/2)^2}$$  \hspace{1cm} (4.23)

Again, the line shape function is normalized such that the integral over all frequencies is unity. The collisional line width is determined by the system pressure and the temperature dependent broadening coefficient, $\gamma$, by:
\[ \Delta \nu_C = \gamma(T)p \] (4.24)

The broadening coefficient can be determined by scaling from existing data at some reference temperature, \( T_0 \), by:

\[ \gamma(T) = \gamma(T_0) \left( \frac{T_0}{T} \right)^n \] (4.25)

The \( n \) term is the temperature-broadening exponent for collisional broadening and usually has a value between 0.5 and 1.0 [28]. More accurate determination of \( n \) is done experimentally. In the case of multiple chemical species, \( \Delta \nu_C \) becomes a summation of the effects of each specie, \( i \):

\[ \Delta \nu_C = p \sum_i X_i \gamma_i(T_0) \left( \frac{T_0}{T} \right)^{n_i} \] (4.26)

where \( X_i \) is the specie mole fraction. For the simplified case of determining the relative contribution of collisional broadening, only self-broadening is considered (\( X = 1, i = 1 \)).

Due to the higher computation cost associated with Voigt profiles, it is advantageous to assume that a distribution is either purely Gaussian or purely Lorentzian. Throughout this work, it is assumed that the Doppler and laser broadening mechanisms dominate other forms of broadening, resulting in a purely Gaussian profile. To verify this assumption, a study of the ratios of collisional to Doppler broadening was done for conditions in the ICP and in the Flow Reactor. Values used for the broadening coefficient, \( \gamma(T_0) \), come from published literature. These values are 0.119 cm\(^{-1}\)/atm for the MDFR [24] and 0.265 cm\(^{-1}\)/atm for the ICP [25]. For each
case the temperature-broadening exponent, $n$, takes on the extreme values of 0.5 and 1.0.

Results for the low-temperature, low-pressure (room temperature, $p = 0.5$ torr) case corresponding to the MDFR is shown in Figure 4.3. The ratio of collisional to Doppler broadening is calculated for the two values of $n$ in a range of temperatures. This provides confidence that the true behavior lies somewhere within these two limits. At room temperature and low pressure, the ratio $\Delta \hat{\nu}_C / \Delta \hat{\nu}_D$ is on the order of $10^{-3}$, indicating that Doppler broadening is several orders of magnitude greater than the collisional contribution. Thus, collisional broadening is safely ignored.

![Figure 4.3: Ratio of collisional and Doppler broadening contributions at low (room) temperature and $p = 0.5$ torr.](image)

For the high-temperature, high-pressure ($T = 1000$ to $3000$ K, $p = 160$ torr) test case corresponding to the ICP, the contribution from collisional broadening is expected to be higher, but still negligible. The temperature range was chosen to be consistent with the range reported by Di Rosa and Hanson for the case of broadening
Figure 4.4: Ratio of collisional and Doppler broadening contributions at high temperature and $p = 160$ torr.

of NO by $N_2$ [25]. It was also assumed that the broadening term would not vary greatly with rotational quantum number. For the purpose of this simulation, it was decided that a broadening ratio that is less than 0.1 is sufficient for the assumption of negligible collisional broadening to hold. Results for this case are shown in Figure 4.4. For $n = 1.0$, it still apparent that Doppler broadening dominated for the temperature range chosen, and that the trend will hold true for higher temperatures as well. In the extreme case of $n = 0.5$, the assumption loses some of its validity for $T \leq 1650$ K. The real temperature range of validity will depend on the actual values of $\gamma(T_0)$ and $n$. For conditions inside the ICP, these results are still thought to be good enough to support the assumption of negligible collisional broadening, since temperatures are more often between 3000 and 6000 K.
4.1.4 Model Validation

To determine whether the proposed model is valid, results were compared at different temperatures to simulations performed for the same conditions in LIFBASE [26], as well as experimental data obtained in the MDFR. Figures 4.5 and 4.6 show models of the NO B-X (2-0) and A-X (0-0) vibrational band heads, respectively. Simulations are at room temperature and compared to the LIFBASE simulation for the same conditions in the negative axes. The model shows excellent agreement in line spacing and location. However, minor discrepancies exist in the strengths of lines. These result from different computation methods used for the Hönl-London Factors. Figures 4.7 and 4.8 show the two simulations matched to experimental results from the MDFR. Again, strong agreement in line positions is shown.

**Figure 4.5:** Calculated NO B-X (2-0) band head vs. the LIFBASE simulation in the negative scale for validation at $T = 300$ K.
Figure 4.6: Calculated NO A-X (0-0) band head vs. the LIFBASE simulation in the negative scale for validation at $T = 300$ K.

### 4.2 Boron Monoxide

Boron monoxide, BO, is another molecule of interest for diagnostics. Spectrally, the (0-0) band of the B-X system of BO lies close to the O atom $J'' = 2$ transition discussed previously, with its band head at 233.2 nm (699.6 nm dye fundamental). Moreover, BO is an important product which appears on the boundary layer of high-enthalpy flows over boron containing TPS materials [36]. Targeting BO molecules will add a diagnostic tool for future testing in the ICP facility. A scheme for probing this transition was first developed and described by White et. al [44]. White also notes the presence of the $^{10}$BO isotope B-X (0,0) band head, which lies 7.6 cm$^{-1}$ to the red of the $^{11}$BO band head. However, the natural isotope ratio of $^{11}$BO to $^{10}$BO is about 4:1 [39], and $^{11}$BO is expected to dominate the spectra. Though interference from $^{10}$BO is not expected, it is worth being aware of, and potentially adding to future
molecular constants provided in Table 4.4 and are taken from the NIST database [17] via contributions from Mulliken [31] and Lagerqvist et. al [19].

4.2.1 BO Transition Frequencies

Calculation of line positions for BO is done in the same way as for NO with the exception of the equation used to calculate the rotational energies. In its most general form, which includes rotational-vibrational coupling, the equation can be written as:

$$F(J) = B_v J(J+1) - D_v J^2 (J+1)^2$$

(4.27)

Note that BO is a $^2\Sigma - ^2\Sigma$ transition and that, just as for NO, both the upper and lower states are doublets, allowing for spin-splitting into $F_1$ and $F_2$ substates. Moreover, since $\Delta \Lambda = 0$ and $\Lambda = 0$ for both states, the spectrum is simplified.
Figure 4.8: Plot of NO A-X (0-0) model vs. experimental data at $T = 297$ K. Data are comprised of a single long range scan. Line positions are accurate to within $\pm 0.005$ nm at the dye fundamental wavelength ($\pm 0.0017$ nm frequency tripled).

somewhat compared to NO. The upper $B \, ^2\Sigma^+$ state follows Hund’s case (b) coupling and thus the selection rules dictate that $\Delta J = \pm 1$. In other words, the main $Q$ branches ($\Delta J = \Delta N = 0$) do not appear. There is a small contribution from the satellite $Q_{12}$ and $Q_{21}$ branches ($\Delta J = 0$, $\Delta N \neq 0$), however they quickly become negligible as rotational number increases, as will be shown later.

4.2.2 BO LINE STRENGTHS

The line intensity calculation also follows a familiar pattern. Hönl-London factors are calculated according to work by Mulliken [30], which describes in detail the band structure for $^2\Sigma-^2\Sigma$ transitions. He goes on to specify the line intensities for Hund’s case (b) coupling specifically. He notes the approximate symmetry between intensities of the $P$ and $R$ branches, with the $P$ branch being slightly stronger due to the
Boltzmann factor. The equations used to calculate the Hönl-London factors are shown in Table 4.5 both as functions of $N$ and $J$, where $J = N \pm 1/2$. In this formulation, $N$ and $J$ take on the larger of either $N'$ and $N''$, or $J'$ and $J''$.

Once the Hönl-London factors are calculated, the overall intensity, as well as the line shapes are computed in the same way as for NO (Eqs. (4.16)-(4.19),(4.22)). A plot of the simulated B-X (0,0) band at 300 K is shown in Figure 4.9. The structure is theoretically comprised of two identifiable bands of triplet transitions. However, except at low $J$ as mentioned above, the contributions from the $Q_{12}$ and $Q_{21}$ branches can be considered negligible, resulting in what are effectively two bands of doublet transitions corresponding to $R_1 + R_2$ and $P_1 + P_2$.

![Figure 4.9](image)

**Figure 4.9**: Plot of BO B-X (0,0) model. $T = 300$ K, $\Delta \hat{\nu}_{\text{laser}} = 0.1$ cm$^{-1}$.  

56
Table 4.2: Hönl-London factors for doublet transitions with $\Delta \Lambda = 0$ where both states are intermediates of Hund’s case (a) and (b).

<table>
<thead>
<tr>
<th>Branch</th>
<th>$S(J)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R1$</td>
<td>$\frac{1}{8(J+1)} [D(J+1) + 4A^2Z U' + 4A^2Z'' U'' + [A^2Z' Z'' D(J+1) + A(J+1) U' U'']$</td>
</tr>
<tr>
<td>$Q1$</td>
<td>$\frac{1}{8(J+1)} [1 + 4A^2 - 4A^2Z U' - 4A^2Z'' U'' + [A^2 (4A^2 + 1) Z' Z'' - A(0)] U' U'']$</td>
</tr>
<tr>
<td>$P1$</td>
<td>$\frac{1}{8(J+1)} [D(J-1) + 4A^2Z U' + 4A^2Z'' U'' + [A^2Z' Z'' D(J-1) + A(J-1) U' U'']$</td>
</tr>
<tr>
<td>$R12$</td>
<td>$\frac{1}{8(J+1)} [D(J+1) + 4A^2Z U' - 4A^2Z'' U'' - [A^2Z' Z'' D(J+1) + A(J+1) U' U'']$</td>
</tr>
<tr>
<td>$Q12$</td>
<td>$\frac{1}{8(J+1)} [1 + 4A^2 - 4A^2Z U' + 4A^2Z'' U'' - [A^2 (4A^2 + 1) Z' Z'' - A(0)] U' U'']$</td>
</tr>
<tr>
<td>$P12$</td>
<td>$\frac{1}{8(J+1)} [D(J-1) + 4A^2Z U' - 4A^2Z'' U'' - [A^2Z' Z'' D(J-1) + A(J-1) U' U'']$</td>
</tr>
<tr>
<td>$R21$</td>
<td>$\frac{1}{8(J+1)} [D(J+1) - 4A^2Z U' + 4A^2Z'' U'' - [A^2Z' Z'' D(J+1) + A(J+1) U' U'']$</td>
</tr>
<tr>
<td>$Q21$</td>
<td>$\frac{1}{8(J+1)} [1 + 4A^2 - 4A^2Z U' + 4A^2Z'' U'' - [A^2 (4A^2 + 1) Z' Z'' - A(0)] U' U'']$</td>
</tr>
<tr>
<td>$P2$</td>
<td>$\frac{1}{8(J+1)} [D(J-1) - 4A^2Z U' - 4A^2Z'' U'' + [A^2 (4A^2 + 1) Z' Z'' - A(0)] U' U'']$</td>
</tr>
</tbody>
</table>

*Primed values denote upper state, double primed values denote lower state.

Source: [4]

Table 4.3: Hönl-London factors for doublet transitions with $\Delta \Lambda = \pm 1$. Branch assignments are for $^2\Sigma^- \rightarrow ^2\Pi$.

<table>
<thead>
<tr>
<th>Branch</th>
<th>$S(x)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R1$</td>
<td>$x[x + (2x^2 - 1) + (Y_v - 2)\varphi_v]/X_v^{(PP)}]/(2x + 1)$</td>
</tr>
<tr>
<td>$Q1$</td>
<td>$2x[(2x^2 - 1) + (4x(x^2 - 1) + (Y_v - 2)\varphi_v)/X_v^{(PP)}]/(4x^2 - 1)$</td>
</tr>
<tr>
<td>$P1$</td>
<td>$x[x + (2x^2 - 1) - (Y_v - 2)\varphi_v]/X_v^{(PP)}]/(2x - 1)$</td>
</tr>
<tr>
<td>$R12$</td>
<td>$x[x - (2x^2 - 1) + (Y_v - 2)\varphi_v]/X_v^{(PP)}]/(2x + 1)$</td>
</tr>
<tr>
<td>$Q12$</td>
<td>$2x[(2x^2 - 1) - (4x(x^2 - 1) + (Y_v - 2)\varphi_v)/X_v^{(PP)}]/(4x^2 - 1)$</td>
</tr>
<tr>
<td>$P12$</td>
<td>$x[x - (2x^2 - 1) - (Y_v - 2)\varphi_v]/X_v^{(PP)}]/(2x - 1)$</td>
</tr>
<tr>
<td>$R21$</td>
<td>$x[x - (2x^2 - 1) - (Y_v - 2)\varphi_v]/X_v^{(PP)}]/(2x + 1)$</td>
</tr>
<tr>
<td>$Q21$</td>
<td>$2x[(2x^2 - 1) - (4x(x^2 - 1) - (Y_v - 2)\varphi_v)/X_v^{(PP)}]/(4x^2 - 1)$</td>
</tr>
<tr>
<td>$P21$</td>
<td>$x[x - (2x^2 - 1) + (Y_v - 2)\varphi_v]/X_v^{(PP)}]/(2x - 1)$</td>
</tr>
<tr>
<td>$R2$</td>
<td>$x[x + (2x^2 - 1) - (Y_v - 2)\varphi_v]/X_v^{(PP)}]/(2x + 1)$</td>
</tr>
<tr>
<td>$Q2$</td>
<td>$2x[(2x^2 - 1) + (4x(x^2 - 1) - (Y_v - 2)\varphi_v)/X_v^{(PP)}]/(4x^2 - 1)$</td>
</tr>
<tr>
<td>$P2$</td>
<td>$x[x + (2x^2 - 1) + (Y_v - 2)\varphi_v]/X_v^{(PP)}]/(2x - 1)$</td>
</tr>
</tbody>
</table>

Source: [34]
Table 4.4: Spectral constants for the X and B electronic states of BO. All units are given in cm\(^{-1}\).

<table>
<thead>
<tr>
<th>State</th>
<th>X</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_e)</td>
<td>0.0</td>
<td>43174.05</td>
</tr>
<tr>
<td>(\omega_e)</td>
<td>1885.69</td>
<td>1281.69</td>
</tr>
<tr>
<td>(-\omega_e x_e)</td>
<td>-11.81</td>
<td>-10.66</td>
</tr>
<tr>
<td>(B_e)</td>
<td>1.7820</td>
<td>1.5171</td>
</tr>
<tr>
<td>(-\alpha_e)</td>
<td>-0.0166</td>
<td>-0.0210</td>
</tr>
<tr>
<td>(D_e)</td>
<td>6.32(-6)</td>
<td>8.8(-6)</td>
</tr>
<tr>
<td>(\beta_e)</td>
<td>2.0(-8)</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Sources: [17,19,31]

Table 4.5: Hönl-London factors for \(^2\Sigma\rightarrow\Sigma\) transitions with Hund’s case (b) coupling.

<table>
<thead>
<tr>
<th>Branch</th>
<th>(S(N))</th>
<th>(S(J))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R1) and (P1)</td>
<td>(2N(N + 1)/(2N + 1))</td>
<td>((J^2 - 1/4)/J)</td>
</tr>
<tr>
<td>(R2) and (P2)</td>
<td>(2N(N - 1)/(2N - 1))</td>
<td>((J^2 - 1/4)/J)</td>
</tr>
<tr>
<td>(Q12) and (Q21)</td>
<td>(2N/(4N^2 - 1))</td>
<td>((2J + 1)/(4J(J + 1)))</td>
</tr>
</tbody>
</table>

Source: [30]
Chapter 5

Results and Discussion

5.1 N atom TALIF Measurements

N atom TALIF measurements were performed in a predominantly air plasma above water-cooled copper and water-cooled nickel surfaces (see Table 5.1). Note that the test over copper was done in pure air, while the test over nickel was done in a buffered air/Ar mixture. This does not appear to affect temperature trends and was done initially for facility performance and stability reasons. All subsequent tests of N and NO were performed in the same buffered air/Ar plasma. Figure 5.1 represents the reduced temperature and normalized integrated area data from those tests versus the

<table>
<thead>
<tr>
<th>Specie</th>
<th>Sample Material</th>
<th>Test ID</th>
<th>Test Gas [SLPM]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N atom</td>
<td>Copper</td>
<td>20160222</td>
<td>air [40]</td>
</tr>
<tr>
<td>NO</td>
<td>Copper</td>
<td>20160512</td>
<td>air [30] + Ar [10]</td>
</tr>
</tbody>
</table>
distance above the sample surface, \( x \). Copper data to the left of the dashed vertical line yielded results below the system detection limit and produced erroneous values, for this reason the points have been artificially forced to zero. In the case of nickel, the test was done from the boundary layer edge and stepping inward until the signal was depleted, thus avoiding false values near the surface. Because the data points do not extend to \( x = 0 \), a separate test was done at the time of the experiment to precisely determine the surface location, as described above. Temperature data between the two tests agree reasonably well, showing a value of \( \sim 5500 \) K near the boundary layer edge, and appearing to roll off to around 4000 K approaching the detection limit. It is expected that the temperature continues to fall to the surface temperature (\( \sim 900 \) K) as it nears the sample. The integrated area data has been normalized such that it is equal to unity well away from the sample (\( x > 3.5 \) mm) in each test case. Since the integrated area is proportional to the relative number density by Eq. (3.7), it is shown that both materials are highly catalytic in air, with almost total depletion of N atoms when \( x \leq 0.6 \) mm. This result agrees with previous data taken over copper [29].

While copper and nickel were expected to behave similarly (because they are both metals and were tested at similar temperatures), these are the first measurements of this kind done over nickel. It is also worth noting that while the copper samples were able to be polished to a virgin surface between each test, the nickel samples were not. This is because the nickel samples are made from brass which has been coated in a thin layer of pure nickel, and repeated polishing of this surface would reveal the brass underneath. This is important because, over time, a layer of oxidized nickel (NiO) was formed on the front face of the sample. During this time, no significant change in material behavior was observed.
5.2 NO LIF MEASUREMENTS

5.2.1 FINDING SUITABLE NO TRANSITIONS

Following the successful LIF scans of the NO beta (2-0) band in the MDFR, attempts were made find suitable transitions conditions in the ICP. Scans were carried out in close proximity to the N atom 211 nm transition in order to aid in feature identification. These scans yielded few usable results due to low signal levels, overlapping of several vibrational bands, and the relatively broad band UG-11 filter used for the PMT. For these reasons, transitions in NO gamma near the O atom transition at 226 nm were used instead. The O atom transition falls in a sparse (at room temperature) region of the NO spectrum. The NO features in this region are easily identifiable through modeling. Aside from being identifiable, it has been previously shown that
it is important that there be a high temperature transition that is separated from any low temperature transitions, but still near enough to be captured in the same scan [29]. This is because the gas recirculating inside the test chamber, but not near the plasma flow, contains some amount of NO at low temperature (∼400 K). The recirculating NO absorbs a portion, or all, of the laser light along its path length. The absorbed energy causes a loss in both the PMT and pulse energy signals, resulting in poor normalization and misleading results. Figure 5.2 shows the scan region of interest, containing both a low and high temperature transition with adequate separation. This range represents a 0.1 nm (dye fundamental) scan commonly done in this facility. The high temperature transition, A, is a quartet made up of P2(39)+P12(39) in the (0-0) vibrational band, with contributions from Q1(61)+Q21(61) in the (2-3) vibrational band increasing with temperature. At sufficiently high temperatures (T ≥ 4000 K) the transition becomes asymmetric, and must be dealt with accordingly.

**Figure 5.2:** Simulated spectrum showing the selected scan region for probing NO. The x-axis represents the theoretical dye fundamental wavelength in a vacuum. Transitions A and B are the target high- and low-temperature transitions, respectively.
A routine has been implemented which utilizes the calculated line position differences and relative strengths when fitting the data. The low temperature transition, B, is the singlet R21(17). Figure 5.3 shows a typical scan over the chosen region.

Figure 5.3: Typical LIF scan containing both MDFR and ICP data. This scan represents NO over Ni at \( x = 0.737 \) mm.

## 5.2.2 NO Boundary Layer Survey Results

NO LIF measurements were carried out in air/Ar plasmas above cooled copper and nickel surfaces. The transitions highlighted as A and B in Figure 5.2, with a representative scan shown in Figure 5.3, were probed starting from the sample surface and moving axially outward to \( x \approx 1.5 \) mm. Unlike with N atom, NO population spikes up near the surface and depletes away from the surface. Continuing to probe at greater distances is unnecessary and would not provide reliable temperatures. Figure 5.4 shows the results from these tests. In the top plot of the extracted translational temperature, points to the left of the vertical, dashed lines indicate temperature val-
ues that are in line with, though higher than, expected values. Between the two lines, NO signal was approaching the signal detection limit. Poor curve fitting of these data result in higher than expected temperatures. Data which fall to the right of the dashed lines are below the current system detection limit for temperature and are artificially forced to zero. The bottom plot represents the temperature-corrected integrated area, or relative NO number density. Because the temperatures obtained in this experiment are unreliable, number density information was calculated using temperature data from a previous experiment of O atom that is considered reliable, shown in Figure 5.5 [29]. Integrated areas are normalized such that they are equal to unity in the free stream.

Figure 5.4: NO LIF boundary layer survey of temperature (top) and temperature-corrected integrated area (bottom) above cooled Cu and Ni.
5.2.3 **Vibrationally Excited NO**

Additional were carried out to begin to quantify the thermodynamic state of NO molecules leaving the sample surface. These tests aimed to detect NO from lower state vibrational levels which contain a greater population than would be predicted if molecules were allowed to reach equilibrium. Recall from Figure 1.1 that molecules recombine at high vibrational energy, some of which is deposited on the material surface, and some of which is carried away by the molecule. At present, it is unknown whether the molecules relax to vibrational equilibrium before leaving the surface.

NO LIF tests were performed at several locations in the thermal boundary layer. Spectral modeling was used to locate regions containing transitions from vibrational levels which would not normally be populated at conditions in the ICP. As before, it is also important to capture a low-temperature transition in the MDFR. The region
chosen contains several transitions of interest from \( v'' = 1, 2 \) and 4. Results showed a significantly larger population in \( v'' = 1 \) than was expected. Additionally, there is evidence of a smaller contribution from \( v'' = 4 \), though the low signal and relatively high noise make it difficult to say for certain. Some resulting plots from \( x = 0.06 \) mm and \( x = 0.56 \) mm are shown in Figure 5.6 along with their equivalent simulations in the negative axis. Note that some regions are clipped from the experimental data due to interference from a low-temperature absorption feature.

To quantify the non-equilibrium effects, the area ratio between two transitions of
different vibrational number was calculated for both the simulated spectrum and a fit to the experimental data. The transitions used for the area ratio are the $P1(34)$ transition from $v'' = 0$ and the $R1(76) + R21(76)$ doublet transition from $v'' = 1$, labeled Transition 1 and Transition 2, respectively. Temperatures for the simulations are estimated to be similar to Figure 5.5. For measurements very near the surface, a temperature of 1000 K is assumed, representing the higher end of allowed surface temperatures since the samples are not melting. For measurements further from the surface, a value of 3500 K is assumed, representing a reasonable temperature estimate between $x = 0.5$ mm and $x = 1.0$ mm. Results are given for 20160608b and 20160608d in Table 5.2. The area ratios are converted to number density ratios using the following expression derived from a Boltzmann distribution:

$$\frac{n_2}{n_1} = \frac{A_2 (2J_1 + 1)e^{\left[-v_1\theta_v - J_1(J_1+1)\theta_r\right]/T}}{A_1 (2J_2 + 1)e^{\left[-v_2\theta_v - J_2(J_2+1)\theta_r\right]/T}}$$

(5.1)

<table>
<thead>
<tr>
<th>Test ID</th>
<th>$x$ [mm]</th>
<th>$T_{est}$ [K]</th>
<th>$n_2/n_1$ [-] (simulation)</th>
<th>$n_2/n_1$ [-] (experimental)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20160608b</td>
<td>0.06</td>
<td>1000</td>
<td>0.0</td>
<td>$1.72 \times 10^5$</td>
</tr>
<tr>
<td>20160608d</td>
<td>0.56</td>
<td>3500</td>
<td>0.76</td>
<td>18.85</td>
</tr>
<tr>
<td>20160609c</td>
<td>-0.20</td>
<td>1000</td>
<td>0.0</td>
<td>$4.11 \times 10^5$</td>
</tr>
<tr>
<td>20160609b</td>
<td>0.18</td>
<td>1000</td>
<td>0.0</td>
<td>$2.51 \times 10^5$</td>
</tr>
<tr>
<td>20160609e</td>
<td>0.56</td>
<td>3500</td>
<td>0.0053</td>
<td>45.16</td>
</tr>
</tbody>
</table>

It is apparent that in both cases, the number density ratio, $n_2/n_1$, is considerably larger than expected. This is especially true at lower temperatures near the sample surface, where the simulation shows zero population in the $v'' > 0$ states, however the experimental data show definite LIF signal coming from the $v'' = 1$ transition. Due to the high rotational number associated with this transition, this modest LIF signal could indicate a very large nonequilibrium population in the $v'' = 1$ state.
What is interesting about the results is that, because the simulation predicts zero population very near the surface, seeing any population at all (i.e. if $n_2/n_1 > 0$) in the experiment supports the conclusion of severe nonequilibrium, regardless of the assumed temperature. In fact, there only begins to be a population in $v'' > 0$ in the simulation when $T$ exceeds the melting point of copper, which is not physical.

Moving away from the surface and to higher temperatures, the number density ratio drops significantly; however, it still remains an order of magnitude larger than the predicted value. Moreover, overall signal levels for all of the transitions dropped appreciably, due to the sharp decline in NO population. The combination of diminishing signal and high noise levels make it difficult to draw any conclusions from this limited data set.

A follow up test was performed in an attempt to increase the spectral resolution on the key features in the wavelength range above. Figure 5.7 shows two representative scans from these tests. In addition to the simulation data and simulated spectrum, these plots also show the $R1(19) + R21(19)$ low-temperature transition as the green traces, captured in the MDFR for reference. The plots show data from $x = -0.20$ mm (top), $x = 0.18$ mm (middle) and $x = 0.56$ mm (bottom), again for estimated temperatures of 1000 and 3500 K. The negative value of $x$ for the top plot indicates that the majority of the beam was cut off by the sample, however because the scan is not being used for quantitative diagnostics, it is still usable and shows an interesting trend. The other transitions identified are $O12(45)$ from $v'' = 0$, $R1(76)$ from $v'' = 1$ (Transition 2 from previous test) and the $Q2(46) + Q12(46)$ doublet from $v'' = 4$.

Table 5.2 also reports the relative density ratios for this follow up test. This time the lower state transition used to calculate $A_1$ was the $O12(45)$ transition from $v'' = 0$
while the excited state transition for $A_2$ is the same as the previous test ($R1(76)$ from $v'' = 1$). Equation (5.1) is then used once again to compute the ratios. As with the previous test, the calculated density ratios for the experimental and simulated spectra differ by a considerable amount, with extremely dissimilar values very close to the sample surface. Though it is somewhat difficult to ascertain the whole cause, this could be evidence of severe nonequilibrium, and suggests a large excess population of NO in the $v'' = 1$ state.

The results reported here are preliminary. The quality of the curve fits used to get relative number density information could be improved considerably with greater signal and less noise. However, given the reflectivity of metallic samples, and the need to use transitions of high rotational number due to the density of the spectrum, these improvements are difficult to make. Nonetheless, these tests represent a step toward understanding the energy exchange between molecule and sample surface.
Figure 5.7: Plots of vibrationally excited NO at $x = -0.20$ mm (top, beam clipped), $x = 0.18$ mm (middle) and $x = 0.56$ mm (bottom).
CHAPTER 6

SUMMARY

This thesis begins by presenting the history and importance of surface recombined NO as a key specie for Earth entry simulations, it emphasizes the need to characterize the thermodynamic state of NO molecules leaving the TPS surface, and establishes a case for BO LIF as a useful and accessible diagnostic. Additionally, it details the experimental arrangement of the 30 kW ICP Torch facility at the University of Vermont, including the pulsed laser system. It then describes LIF and the species selective diagnostic methods used. Following that, it presents a thorough description of the development of LIF excitation models for the A-X and B-X systems of NO and the B-X system of BO, providing high resolution spectra for identification of potentially useful transitions.

Results for the boundary layer LIF surveys of N and NO over water-cooled copper and nickel test surfaces in air/argon plasmas are presented. Also reported are tests of NO in the same conditions identifying an excess ground state population with $v'' = 1$. These results represent the first steps toward quantifying the thermodynamic state of surface-combined NO molecules leaving the material face, and toward quantifying the
energy accommodation of the material. Though still early, these tests seem to show
that NO molecules are leaving the surface in a vibrationally excited state, i.e. before
relaxing to thermodynamic equilibrium. This means that molecules are carrying
energy away with them, and that less of the molecule’s energy is transferred to the
TPS material than is currently predicted.

Future work shall include performing O atom TALIF boundary layer scans over
copper and nickel to complete the data set for air plasmas. Additional NO scans will
also be performed to refine the data showing vibrationally excited molecules in the
ground state of NO. To accompany the work with NO, tests will be done to measure
the fluorescence lifetimes at points throughout the boundary layer. The last step
in characterizing NO will be to take additional measurements necessary to convert
the relative number densities, presented here, to absolute number densities. Finally,
scans of BO will be performed in the MDFR and the ICP in order to validate the
spectral model developed in this thesis, and to partially diagnose boron oxidation
from diboride based TPS materials.
Bibliography


[2] Amiot C., Bacis R. and Guelachvili G., “Infrared Study of the $X^2\Pi v = 0, 1, 2$ levels of $^{14}\text{N}^{16}\text{O}$. Preliminary Results on the $v = 0, 1$ Levels of $^{14}\text{N}^{17}\text{O}$, $^{14}\text{N}^{18}\text{O}$ and $^{15}\text{N}^{16}\text{O}$.” *Canadian Journal of Physics* Vol. 56 No. 2 (1978): 251-265.


Appendix A

Frank-Condon Factors of NO
Table A.1: Frank-Condon factors for the A-X system of NO.

<table>
<thead>
<tr>
<th>v&quot;</th>
<th>v'=0</th>
<th>v'=1</th>
<th>v'=2</th>
<th>v'=3</th>
<th>v'=4</th>
<th>v'=5</th>
<th>v'=6</th>
<th>v'=7</th>
<th>v'=8</th>
<th>v'=9</th>
<th>v'=10</th>
</tr>
</thead>
<tbody>
<tr>
<td>v=8</td>
<td>8.129e-6</td>
<td>8.217e-4</td>
<td>1.991e-1</td>
<td>1.366e-1</td>
<td>2.013e-1</td>
<td>7.969e-4</td>
<td>1.094e-1</td>
<td>8.183e-3</td>
<td>4.233e-2</td>
<td>6.456e-2</td>
<td>1.037e-2</td>
</tr>
</tbody>
</table>

Source: Laux [21]

Table A.2: Frank-Condon factors for the B-X system of NO.

<table>
<thead>
<tr>
<th>v&quot;</th>
<th>v'=0</th>
<th>v'=1</th>
<th>v'=2</th>
<th>v'=3</th>
<th>v'=4</th>
<th>v'=5</th>
<th>v'=6</th>
<th>v'=7</th>
<th>v'=8</th>
<th>v'=9</th>
<th>v'=10</th>
</tr>
</thead>
<tbody>
<tr>
<td>v=0</td>
<td>1.646e-5</td>
<td>2.426e-4</td>
<td>1.693e-3</td>
<td>4.444e-4</td>
<td>2.153e-2</td>
<td>5.417e-2</td>
<td>9.909e-2</td>
<td>1.452e-1</td>
<td>1.734e-1</td>
<td>1.704e-1</td>
<td>1.389e-1</td>
</tr>
<tr>
<td>v=1</td>
<td>1.292e-4</td>
<td>1.590e-3</td>
<td>8.949e-3</td>
<td>3.037e-2</td>
<td>6.062e-2</td>
<td>1.067e-1</td>
<td>1.119e-1</td>
<td>7.046e-2</td>
<td>1.586e-2</td>
<td>2.595e-3</td>
<td>4.768e-2</td>
</tr>
<tr>
<td>v=5</td>
<td>6.782e-3</td>
<td>3.757e-2</td>
<td>7.386e-2</td>
<td>5.269e-2</td>
<td>2.870e-3</td>
<td>2.267e-2</td>
<td>5.206e-2</td>
<td>1.264e-2</td>
<td>1.005e-2</td>
<td>5.004e-2</td>
<td>2.156e-2</td>
</tr>
</tbody>
</table>

Source: Laux [21]