RADICAL-MOLECULE REACTION DYNAMICS STUDIED USING A PULSED SUPersonic LAVAL NOZZLE FLOW REACTOR BETWEEN 53 AND 188 KELVIN

By

Christopher Mullen

A Dissertation Submitted to the Faculty of the

DEPARTMENT OF CHEMISTRY

In Partial Fulfillment of the Requirements
For the Degree of

DOCTOR OF PHILOSOPHY

In the Graduate College

THE UNIVERSITY OF ARIZONA

2004
INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.
As members of the Final Examination Committee, we certify that we have read the
dissertation prepared by Christopher Mullen
entitled Radical-Molecule Reaction Dynamics Studied Using a Pulsed
    Supersonic Laval Nozzle Flow Reactor

and recommend that it be accepted as fulfilling the dissertation requirement for the
Degree of Doctor of Philosophy

20 Aug 2001
Dr. Mark A. Smith
date

16 Aug 2004
Andrei Sanov
date

16 Aug 2004
Dr. Steve Kukolich
date

8 Oct 2001
Scott Saavedra
date

16 Aug 2001
Dr. Jeanne Pemberton
date

Final approval and acceptance of this dissertation is contingent upon the
candidate's submission of the final copies of the dissertation to the Graduate College.
I hereby certify that I have read this dissertation prepared under my direction and
recommend that it be accepted as fulfilling the dissertation requirement.

26 Aug 2001
Dissertation Director: Dr. Mark A. Smith
date
STATEMENT BY AUTHOR

This dissertation has been submitted in partial fulfillment of requirements for an advanced degree at The University of Arizona and is deposited in the University Library to be made available to borrowers under rules of the Library.

Brief quotations from this dissertation are allowable without special permission, provided that accurate acknowledgement of source is made. Requests for permission for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the head of the major department of the Dean of the Graduate College when in his or her judgment the proposed use of the material is in the interest of scholarship. In all other instances, however, permission must be obtained from the author.

SIGNED:  

______________________________
ACKNOWLEDGMENTS

There are a number of people who deserve recognition for the impact they have made on my life, and for the sake of brevity I will include only the positive here. First and foremost I would like to thank my dissertation advisor Dr. Mark A. Smith for providing his scientific insight and continual support throughout the duration of time it took to obtain this degree. For this I am truly grateful. I would also like to thank the past group members and visiting scientists for their help throughout the years. In particular I would like to single out Dr. Andrey E. Belikov. His dedication to his work and passion for sport is unparalleled. I would also like to acknowledge the members of the machine shop, electronics shop, and glass shop; Ron Clayton, Bob Smith, Ted Weight, Larry Cook, and Charly Amling for their friendship and help during this time. I have learned more from these individuals than I ever would have imagined.

On a more personal level I would like to thank my friends and family for their support and guidance. My father, in a roundabout way, instilled in me the virtue of a hard work ethic and knowledge of the mechanical world that were instrumental to the completion of this degree, although I am not sure either of us realized it at the time. My mother has always been supportive of my endeavors which I believe would have pushed most people over the edge. She has always been just a phone call away and was, and still is, always willing to lend an ear. I know for certain that I would have ordered caller ID a long time ago in her situation. Liz, what can I say, you get plenty of recognition so I’ll omit any here. Wally Doherty, I really enjoyed our thirst quenching collaborations. Cheers! And finally, Phil Sheridan and Rob Kevwitch, I’ll simply state your names.
# Table of Contents

LIST OF ILLUSTRATIONS ........................................................................................................... 7

LIST OF TABLES ........................................................................................................................ 12

ABSTRACT .................................................................................................................................. 13

CHAPTER 1. INTRODUCTION ................................................................................................... 15

CHAPTER 2. EXPERIMENTAL .................................................................................................. 29
  2.1. Laval Nozzle Principles .................................................................................................. 29
  2.2. Description of the Pulsed Supersonic Laval Nozzle Flow Reactor .............................. 48
  2.3. Nozzle Flow Characterization ....................................................................................... 62

CHAPTER 3. IMPLEMENTATION OF A TUNABLE VACUUM AND EXTREME ULTRAVIOLET FREQUENCY LIGHT SOURCE FOR THE STUDY OF H ATOM CHEMISTRY AT LOW TEMPERATURES ......................................................... 77
  3.1. Background .................................................................................................................... 77
  3.2. Non-Linear Frequency Mixing ....................................................................................... 78
  3.3. Implementation of the Frequency Source ....................................................................... 88

CHAPTER 4. TEMPERATURE DEPENDENCE AND KINETIC ISOTOPE EFFECTS FOR THE OH + HBr AND H/D ISOTOPIC VARIANTS AT LOW TEMPERATURE .................................................................................. 128
  4.1. Abstract .......................................................................................................................... 128
  4.2. Introduction ...................................................................................................................... 129
  4.3. Experimental .................................................................................................................... 134
  4.4. Results .............................................................................................................................. 139
  4.5. Discussion ......................................................................................................................... 152
  4.6. Conclusion ......................................................................................................................... 159

CHAPTER 5. LOW TEMPERATURE NH (X ^3Σ^-) RADICAL REACTIONS WITH NO, SATURATED AND UNSATURATED HYDROCARBONS BETWEEN 53 AND 188 KELVIN ......................................................................................... 161
  5.1 Abstract ............................................................................................................................. 161
  5.2. Introduction ...................................................................................................................... 162
TABLE OF CONTENTS - Continued

5.3. Experimental ................................................................. 166
5.4. Results .............................................................................. 180
5.5. Discussion ......................................................................... 189
  5.5a. NH + NO ................................................................. 189
  5.5b. NH + Unsaturated hydrocarbons ............................... 192
5.6. Conclusion ........................................................................ 202

CHAPTER 6. CONCLUSION ......................................................... 203

REFERENCES ........................................................................... 209
LIST OF ILLUSTRATIONS

Figure 2.1. An illustration of the key aspects of the Laval nozzle.......................... 35
Figure 2.2. Divergent section of the Laval nozzle divided into the three parts necessary to achieve uniform flow. ................................................................. 35
Figure 2.3a. Illustration of the Prandlt-Meyer turning angle. The effect of a corner in a flow system causes an expansion of the fluid and a corresponding acceleration, described by the angles \( \alpha \) and \( \Psi \), where \( \alpha \) is the Mach angle and \( \Psi \) is the expansion angle. Adapted from Crown, 1948 [66]................................................................. 38
Figure 2.3b. Formalism for expressing the change in Mach number due to a corner for an arbitrary initial Mach number. \( \delta \) equals the change in expansion angle \( \Psi_2 - \Psi_1 \). Adapted from Crown, 1948 [66]................................................................. 38
Figure 2.4. Illustration of the result of the crossing of two expansion waves as a result of the two corners present in the system. The flow streamline experiences changes in flow direction and Mach number as a result of crossing both expansion waves. \( \theta_1 \) and \( \theta_2 \) are the corresponding changes in angle of the flow streamline. Adapted from Crown, 1948 [66]................................................................. 40
Figure 2.5. Treatment for the reflection of an expansion wave due to a surface. The surface is treated using the mirror image concept which allows the problem to be reduced to the intersection of two expansion waves. \( \theta \) is the incident angle of the expansion wave with the surface, \( \phi \) the angle for the reflected wave to the surface, and \( \delta \) the change in flow streamline. Adapted from Crown, 1948 [66]................................................................. 42
Figure 2.6. Cancellation of an expansion wave by a surface. Cancellation is accomplished by changing the angle of the surface with respect to the expansion wave, such that a compression wave of equal yet opposite strength is created due to the concave corner in the system. Adapted from Crown, 1948 [66]................................................................. 43
Figure 2.7. Treatment of the boundary layer. The effect is an addition to the nozzle contour of a displacement thickness \( \delta^* \) normal to the wall coordinate. ......................... 46
Figure 2.8. Schematic of the pulsed supersonic Laval nozzle flow reactor. Shown are the essential components of the reactor minus the pulse generating and signal processing electronics. ................................................................. 50
Figure 2.9. Circuit diagram of the pulsed valve driver ........................................ 52
Figure 2.10. Schematic of the gas mixing rack and flow delivery lines ................. 54
Figure 2.11. Timing diagram for the OH and NH radical studies. All times are referenced to \( T_0 \) ................................................................. 55
Figure 2.12. Block diagram of the electronic components used to conduct experiments. Arrows indicate the direction of information travel. ................................. 56
LIST OF ILLUSTRATIONS - Continued

Figure 2.13. Transducer output circuitry drift during warm up. Stable output voltage is critical for proper transducer calibration. The transducers were always allowed to warm up for at least an hour before measurements were made......................... 66

Figure 2.14. Calibration curves for the stagnation and pitot transducers. The pressure for these experiments was measured using an MKS differential capacitance manometer. .......................................................... 67

Figure 2.15. Laval nozzle pulsed valves response to the trigger. The trigger pulse is designed to rapidly open the pulse valve with a high voltage leading edge, followed by maintenance of the open condition requiring 12 Volts................................. 69

Figure 2.16. OD LIF A $^2\Pi \leftarrow X ^2\Sigma (v' = 1 \leftarrow v'' = 0) S_{21}(N)$ branch spectrum taken at 135 K using the N$_2$M33e16 nozzle................................................................. 74

Figure 2.17. OD Boltzmann plot used to extract the rotational temperature from the flow. The plot is the natural log of the normalized population ($N_i/g_i$) versus the rotational energy of the state. Here $N_i$ is the population and $g_i$ is the degeneracy of the rotational state................................................................. 75

Figure 2.18. Temperature profile of the N$_2$M33e16 nozzle as a function of distance from the nozzle exit. Filled squares are the temperatures derived from the LIF spectra. Open circles are the temperatures derived from the pitot impact measurements. .... 76

Figure 3.1. Energy level diagram indicating the states used in non-resonant third harmonic generation. The input frequency $\omega_1$ is tripled producing an output frequency $\omega_{VUV} = 3\omega_1$................................................................. 83

Figure 3.2. Energy level diagram indicating the states used in the four wave mixing process. The input frequencies $\omega_1$ and $\omega_2$ are combined producing an output frequency $\omega_{DFM} = 2\omega_1 - \omega_2$ for difference frequency mixing and $\omega_{SFM} = 2\omega_1 - \omega_2$ for sum frequency mixing................................................................. 86

Figure 3.3. Schematic of the setup used in the four wave frequency mixing experiments. ........................................................................................................................................................................... 90

Figure 3.4. Timing diagram of the pulse delay sequence used to conduct the four wave mixing experiments. All times quoted are with respect to $T_0$. Delays A through D are generated using the SRS DG-535 digital delay generator................................. 91

Figure 3.5. Oscilloscope trace of Xe pulsed valve response to external trigger. The ordinate time scale is 1 ms/div. Lower trace is the external trigger of duration 180 $\mu$sec. Upper trace is pressure transducer signal................................................................. 93
LIST OF ILLUSTRATIONS - Continued

Figure 3.6. Oscilloscope trace of the xenon two photon optogalvanic signal. The time scale for the x-axis is 0.5 μsec/div. The upper trace represents a 150 laser shot average of the Xe signal, while the lower trace shows the boxcar gate used to collect the two photon optogalvanic spectrum. ................................................................. 102

Figure 3.7. Xenon two photon optogalvanic spectrum of the 6p[3]K ← 5p6 1S0 series. 103

Figure 3.8. NO B' 2Δ1 ← X 2Π1/2 (v' = 1 ← v'' = 0) LIF spectrum in the VUV .......... 106

Figure 3.9. Optimization of the xenon pulsed valve delay as a function of pressure observed by monitoring the NO LIF signal on the boxcar. ............................................. 108

Figure 3.10. NO LIF signal as a function of xenon pulsed valve duration taken at two backing pressures. ............................................................................................................. 109

Figure 3.11. NO LIF signal as a function of ultraviolet laser power obtained by varying the NY61-10 Q-Switch delay .......................................................... 111

Figure 3.12. NO LIF signal as a function of visible laser power obtained by varying the NY 660 Q-Switch delay ................................................................. 112

Figure 3.13. Lyman band B 1Σu+ ← X 1Σg+ (v' = 6 ← v'' = 0) spectrum of H2 taken with the solar blind PMT. Shown are the first few transitions of the R(J) and P(J) branches. ..................................................................................................................... 115

Figure 3.14. H atom LIF spectrum taken in the ArM32e17 nozzle resulting from the Lyman β pump (3p 2p ← 1s 2S), Balmer α (3p 2p → 2s 2S) fluorescence collected at 656 nm ................................................................. 117

Figure 3.15. H atom fluorescence decay profile. The oscilloscope conditions are 50 ns/div, and 0.1 V/div, for the x and y axis respectively. The trace represents a 100 laser shot average, and is 781 mV in amplitude. The lifetime measured at FWHM equals 22.5 ns. .............................................................................................................. 118

Figure 3.16. Optimized delay required between the two laser pulses (as set on the DG 535 digital delay generator) versus time (over a 4 hour period) to achieve maximum LIF signal. The fluctuation is most likely due to fluctuations in the Q-switch response, and changes in pulse shape and duration throughout the course of the day. ....... 121

Figure 3.17. H atom LIF signal versus delay between laser pulses obtained by changing the channel A delay on the SRS DG-535 ......................................................... 123
LIST OF ILLUSTRATIONS - Continued

Figure 4.1. Pseudo 1st order decays for the reaction of OH + HBr at 53 K taken in the post ArM32e16 nozzle flow. The normalized OH signal is plotted as a function of reaction time and the pseudo 1st order decay rates (sec\(^{-1}\)) are extracted using a linear least squares fitting routine. The process is repeated a number of times under different concentrations of HBr reactant......................................................... 137

Figure 4.2. Graph of k' vs. [HBr] used to extract the bimolecular rate coefficient (molecules·cm\(^3\)·sec\(^{-1}\)) for the OH + HBr reaction at 53 K in the post ArM32e16 nozzle flow. The slope is equal to the bimolecular rate coefficient and is obtained from a linear least squares best fit to the data.............................................. 138

Figure 4.3a. Plot of the rate coefficient versus temperature for the OH + HBr reaction.141

Figure 4.3b. Plot of the rate coefficient versus temperature for the OD + HBr reaction.142

Figure 4.3c. Plot of the rate coefficient versus temperature for the OH + DBr reaction.143

Figure 4.3d. Plot of the rate coefficient versus temperature for the OD + DBr reaction.144

Figure 4.4. Comparison of Jaramillo and Smith 2001 [32] data before and after revision for the OH + HBr and H/D isotopic variant reactions.............................................. 146

Figure 4.5. OH + HBr global fit to the temperature dependent rate data over the 23 – 360 K window........................................................................................................ 147

Figure 4.6. Primary and secondary KIE’s plotted versus temperature. k\(_1\) and k\(_3\) share the common reactant OH, while k\(_1\) and k\(_2\) share the common reactant HBr............. 150

Figure 4.7. Primary and secondary KIE’s plotted versus temperature. k\(_2\) and k\(_4\) share the common reactant OD, while k\(_3\) and k\(_4\) share the common reactant DBr.............. 151

Figure 5.1. Nitrogen chemistry on Titan........................................................................ 164

Figure 5.2. NH radical A \( ^3\Pi \leftarrow X \ ^3\Sigma^- \ (v' = 1 \leftarrow v'' = 0) \) LIF spectrum taken at 188 K using the N\(_2\)M21e17 nozzle......................................................... 168

Figure 5.3. Hund’s case b coupling scheme as applied to the NH radical..................... 170

Figure 5.4. Energy level diagram and transition nomenclature for the NH radical. The splittings in the ground and excited state have been greatly exaggerated for clarity. ........................................................................................................ 171

Figure 5.5. Expanded view of the A \( \leftarrow X \ (v' = 2 \leftarrow v'' = 1) \) band transition. Transitions from the \((v' = 1 \leftarrow v'' = 0)\) band are labeled \((1 - 0)\). .............................................. 174

Figure 5.6. Graph of the branch (P, Q, R) transition assignments vs. their literature value used to ensure correct spectral assignment. Literature values were taken from Brazier et al., 1986 [146]......................................................... 175
LIST OF ILLUSTRATIONS - Continued

Figure 5.7. Boltzmann plot used to extract the flow temperature in the N$_2$M21e17 nozzle using the NH radical spectrum................................................................. 179

Figure 5.8. Pseudo 1$^{st}$ order decays of the NH LIF signal for the reaction of NH + NO in the post N$_2$M33e16 nozzle flow................................................................. 182

Figure 5.9. $k'$ vs. [NO] for the NH + NO reaction in the post N$_2$M33e16 flow used to extract the bimolecular rate coefficient.................................................. 183

Figure 5.10. Plot of the rate coefficient versus temperature for the NH + NO reaction. 185

Figure 5.11. Plot of the rate coefficient versus temperature for the NH + hydrocarbon reactions................................................................. 187

Figure 5.12. Plot of the rate coefficient versus temperature for the NH + hydrocarbon reactions including the high temperature data from Rohrig et al. Closed symbols – this work. Open symbols – Rohrig et al. [133, 134]........................................ 188
LIST OF TABLES

Table 2.1. Laval Nozzle Calibrated Flow Parameters. .............................................73
Table 4.1. Temperature Dependent Rate Data for the OH + HBr and H/D Isotopic
Variants. ..................................................................................................................140
Table 4.2. Best Fit Parameters Obtained for the OH + HBr and H/D Isotopic Variant
Reactions to the Functional Form: $k_{fit}(T) = A \times (T/298)^n$. .................................140
Table 4.3. OH + HBr Rate Data Used to Obtain the Temperature Dependent Global Fit
of Figure 4.5. ...........................................................................................................148
Table 5.1. Temperature Dependent Rate Data for the Reaction of NH Radical
with NO, Saturated, and Unsaturated Hydrocarbons. .............................................184
Table 5.2. Best Fit Parameters Obtained for the NH + Unsaturated Hydrocarbon
Reactions to the Functional Form: $k_{fit}(T) = A \times (T/298)^n$. .................................186
Table 5.3. NH Radical Abstraction Reaction Thermochemistry with Saturated and
Unsaturated Hydrocarbons. ..................................................................................195
Table 5.4. Thermochemistry of Potential Exothermic Reaction Routes for NH Radical
with Unsaturated Hydrocarbons Initiated by the Initial Addition of NH
into the $\pi$ Bond. ....................................................................................................195
ABSTRACT

A pulsed supersonic Laval nozzle flow reactor has been employed to investigate a variety of neutral-radical reaction processes at temperatures between 53 and 188 Kelvin. These supersonic flows simulate the conditions found in the Earth's upper atmosphere as well as certain environments in the interstellar medium and outer planetary atmospheres and thus provide direct information on the chemistry and physical processes occurring in those environments. Studies of this type, in the limit of 0 Kelvin, coupled with modern astronomical observations of planetary atmospheres and dense molecular clouds provide for a global understanding of chemistry in cold environments. With this in mind, the flow reactor was used to conduct fundamental studies involving the reactivity of hydroxyl (OH) and imidogen (NH) radical species with a variety of partners.

More specifically, the reactions of OH + HBr and all of the H/D isotopic variants were explored between 53 and 135 K, with the goal of elucidating the kinetic isotope effects, both primary and secondary, for a reaction system occurring over a potential energy surface without an appreciable barrier, that demonstrates inverse temperature dependence. While not of direct astronomical importance, the reaction of OH + HBr does affect the partitioning of Br in the Earth's atmosphere, and knowledge of kinetic isotope effects helps one understand the chemistry leading to H/D fractionation observed in a variety of interstellar environments.

The reactions of NH radical with NO, saturated, and unsaturated hydrocarbons were also studied between 53 and 188 Kelvin in the Laval nozzle flow reactor. These
species were chosen as most are important constituents in the atmosphere of Titan, which is known to possess a rich organic chemistry. The reactions of NH with the unsaturated hydrocarbons are found to display negative temperature dependence over the window investigated, and are thought to proceed through an addition mechanism.

Finally, the flow reactor was also coupled to a tunable vacuum and extreme ultraviolet frequency source based on four wave frequency mixing to allow for studies of radical species with their first electronic transitions in this frequency range. A discussion of the development, implementation, and future directions is included.
CHAPTER 1. INTRODUCTION

The study of low temperature gas phase chemistry is by no means in its infancy. Experiments designed to extract kinetic information on a number of systems, including ion-molecule and neutral-radical reactions have found acceptance in the scientific community. While these techniques vary in the way they create the low temperature environment, they all provide essential information on the dynamics of chemical processes at low temperatures. Information of this sort is fundamental to the understanding of chemical processes occurring under a diverse set of circumstances and is necessary to accurately represent a number of naturally occurring low temperature environments including planetary atmospheres and the interstellar medium (ISM) where temperatures can range from a few Kelvin to approximately 250 K. The subject of this dissertation is the study of neutral-neutral reactions studied at low temperature (53 to 188 K), with the specific goal of providing accurate experimental data necessary for understanding complex low temperature environments. The data from individual experiments or sets of experiments by no means provides a complete picture. Support from a variety of efforts including *ab initio* calculations of reaction potential energy surfaces, calculation of reaction rates from semi classical, quantum, and transition state theories, and accurate modeling based on a large chemical networks, are required to build a construct in which complex chemical situations are understood.

As early as the 1900’s experimental evidence was starting to surface indicating that chemical processes could in fact be efficient at low temperatures, contradictory to the
Arrhenius picture, where the activation energy \((E_a)\) for a process, effectively inhibits reactivity at low temperature due to the exponential dependence of the rate coefficient on the activation energy, \(k = A \times \exp\left[\frac{E_a}{k_BT}\right]\). These early works, conducted using cryogenically cooled solid matrices, reviewed by Goldanskii,\(^1\) may very well have stimulated research in the field of low temperature chemistry, due to the anticipation of the breakdown in the Arrhenius picture of reactivity. The low temperature gas phase community would have to wait a number of years for the advancement of technology to a state where experiments could be conducted that directly probe chemical reactivity in low temperature environments. Major efforts to understand exothermic gas phase radical-molecule reactions including those pertinent to stratospheric chemistry were first conducted in the 1950's and 60's due to the invention of the discharge flow and flash photolysis techniques, which were capable of monitoring individual reactions. Processes relevant to the stratosphere was and still are ideal candidates for study due to the pressure (1-100 Torr) and temperature (~200-300 K) range encountered, and their importance to our everyday life. The early results and the techniques used to obtain them are reviewed by Kaufman,\(^2\) and more comprehensively by DeMore et al.\(^3\) and Atkinson et al.\(^4\) Inspection of these documents will reveal that very few studies of radical-molecule reactions have been carried out at temperatures lower than 200 Kelvin. This is due mainly to problems involving reactant vapor pressure encountered when cryogenically cooling reaction vessels.

The first truly low temperature gas phase rate measurements were reported for the three-body recombination reaction of hydrogen and deuterium atoms down to 77 K
measured in a flow system,\textsuperscript{5,6} and the isotopic exchange reaction \( \text{D} + \text{H}_2 \rightarrow \text{DH} + \text{H} \)
measured between 167 – 346 K.\textsuperscript{7} These studies were accomplished because the problems
normally encountered at low temperatures using flow tubes could be circumvented due to
the high vapor pressure of hydrogen under the experimental conditions. However, future
measurements on a wide variety of low temperature radical-molecule reactions using a
more universal technique would have to wait another two decades for the development of
the CRESU (Cinétique de Réactions en Ecoulement Supersonique Uniforme). The
controlled supersonic expansions created using a carefully calculated Laval nozzle design
were initially tested and applied to the study of fundamental ion-molecule reactions
between 20 and 160 Kelvin.\textsuperscript{8,9} The first neutral-neutral reaction studied was done in 1992
on the \( \text{CN} + \text{O}_2 \) system down to 26 K, employing \text{N}_2 and \text{Ar} buffers.\textsuperscript{10} These studies were
motivated by earlier the earlier work of Sims and Smith,\textsuperscript{11} who studied the reaction down
to 99 K using a cryogenically cooled cell and found an inverse temperature dependence
of the rate coefficient over the temperature range (99 – 761 K) explored. Subsequent
experiments extended the temperature dependence of the above reaction down to 13 K.\textsuperscript{12}
While this behavior was not the first of its type to be observed, the results were
nonetheless exciting, for the CRESU flows promised to be capable of surmounting the
difficulties previously associated with low temperature flow tube studies, while at the
same time being amenable to a variety of studies. Further, and most importantly, it was
realized that the new temperature regime available would allow researchers to study
reactions important to the chemistry of lower temperature environments, such as the
interstellar medium and planetary atmospheres.
These results came at a time when there were some 120 or so known interstellar molecules, as determined by ground based radio frequency telescopes, and also insufficient information regarding the dynamics of a variety of reactive systems. The early efforts to synthesize interstellar chemistry, by Herbst and Klemper, focused on ion-molecule chemistry, as their rates were known to remain high at low temperature. There were also reasonable models based on capture theory by which rates for unknown reactions could be estimated, contrary to the case for neutral-neutral reactions. Dense molecular clouds are not the only cold environment of interest. Planetary scientists have long been focused on the atmosphere of Titan (one of Saturn’s moons) due to the presence of nitrogen, hydrocarbons, and haze layers in its environment. By as early as 1984 Yung et al. were working on photochemical models of Titan’s atmosphere based on the data provided by the Voyager mission, which passed by Saturn in 1981. They realized the necessity of accurate rate data at temperatures pertinent to Titan, and it is to this effect that experiments employing supersonic expansion can contribute to the field. More on the species and conditions found on Titan are mentioned later in this chapter.

Since the introduction of the CRESU in Meudon, France in 1984 five other supersonic flow reactors have been employed to study neutral-neutral processes, and the next few paragraphs are dedicated to reviewing the individual contributions made by the research groups involved. While this is not an exhaustive review it is intended highlight the progress made in the field of low temperature neutral chemistry and illustrate the progression of knowledge on fundamental processes in the low temperature regime.
The groups of Bertrand Rowe and Ian R. Sims and Ian W. Smith, at The University of Rennes, Rennes Cedex, France, and the University of Birmingham, Edgbaston, Birmingham, U.K., respectively, have worked in close collaboration over the years, and are thus treated together here. These first versions of the CRESU employ continuous flow nozzles capable of attaining 15 K flow temperatures without pre-chilling the stagnation reservoir. Achievement of this remarkable ultra-low temperature by other techniques has in most cases been accomplished for ion-molecule studies using trapping techniques\textsuperscript{16,17} and free jet expansions,\textsuperscript{18} although the free jet has been adapted to study neutral relaxation processes.\textsuperscript{19} Aside from the study of the CN + O\textsubscript{2} methysis reaction the groups have studied the reactions of OH radicals with the butenes,\textsuperscript{20} the association reaction with NO,\textsuperscript{21} and the abstraction reaction with HBr.\textsuperscript{22} These early works were the first to provide experimental evidence of inverse temperature dependence of neutral reactions at low temperature and provided the impetus for continued studies on systems directly applicable to interstellar environments. Further, these studies provided data against which reaction theories could be compared and formation mechanisms could be tested. In addition, studies of CN radical with the saturated and unsaturated hydrocarbons CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{2}, and C\textsubscript{3}H\textsubscript{6},\textsuperscript{23} demonstrated the efficiency of addition/elimination reactions, and of H atom abstraction (for the case of ethane) through the indirect collision.

The discovery of a rich organic chemistry in many interstellar environments has shifted the efforts of low temperature experimentalists to species directly applicable to the ISM and planetary atmospheres. In this respect questions regarding the formation mechanisms of complex highly unsaturated carbon chains found in the ISM, and nitriles
and haze particles detected in Titan’s atmosphere can be more directly addressed.

Ensuing work by Rowe, Sims and Smith has indeed focused on these problems. Studies of CH radical with methane, ethane, ethylene, acetylene, and but-1-ene demonstrated that C-H insertion followed by elimination is the most likely mechanism for the CH + methane and ethane reactions, while addition followed by elimination is most likely for the unsaturated hydrocarbons, with both processes remaining fast at low temperatures. These reactions potentially provide synthetic routes to increasing molecular complexity in molecular clouds under the correct circumstances, i.e. low photon flux, and fractional ionization. These reactions also provide mechanisms to molecular formation that do not involve ion-molecule chemistry or radiative association and helped to establish the feasibility of neutral processes in chemical formation.

In a similar fashion the reactions of C₂H radical with O₂, C₂H₂, C₂H₄, and C₃H₆, and C(3P) with O₂, C₂H₂, C₂H₄, C₃H₆, methylacetylene (CH₃CCH) and allene (H₂CCCH₂) have also been investigated, and while their temperature dependencies differ, their rates remain fast at low temperatures and provide another set of reagents through which complex chemistry can emerge from rudimentary precursors under low temperature conditions.

The group of Mark A. Smith at the University of Arizona has also made significant contributions to the field of low temperature neutral chemistry, the most significant of which was the conversion of the CRESU to a pulsed format. These advantages are discussed in detail in Chapter 2 of this dissertation, but for now it is enough to say that the pulsed version allowed for the study of low temperature chemical
processes in an affordable fashion. Verification of this statement is reflected in the number of times a version of the pulsed Laval flow reactor has been employed in other laboratories. The pulsed DC discharge supersonic Laval nozzle flow reactor was initially capable of generating flows between 222 to 90 K employing a variety of N₂ nozzles and was first used to study the termolecular association of OH with NO. A portion of this dissertation focuses on the extension of the attainable temperature window down to 53 K using an argon flow, and is covered in Chapter 2. The flow reactor has also been applied to the study of the OH + HBr system and all of the isotopic variants, with the goal of providing rate data in a window applicable to the terrestrial atmosphere and also to gain insights into the kinetic isotope effects for a reacting system occurring over a potential energy surface without a barrier.

More recently the group of Stephen R. Leone at the University of California, Berkeley, has constructed a pulsed Laval nozzle apparatus to study the reactions of C₂H and OH radicals at low temperatures. This group has made a number of measurements on the kinetics of C₂H radicals with various reaction partners using transient infrared laser absorption spectroscopy in flow cells from 154 – 361 K. Their version of the pulsed Laval nozzle instrument initially employed laser photolysis for the creation of radical reactants followed by laser ionization time of flight mass spectroscopy for detection of reactants and products, but has been more recently been used in conjunction with laser induced fluorescence (LIF) detection for OH radicals, and chemiluminescent detection of C₂H species. The temperatures employed for these experiments range from 90 to 295 K, with the 295 K measurements being made at a chamber pressure
significant enough to cause sonic flow conditions. Again, the radicals and reactant species were chosen to demonstrate the feasibility of low temperature radical-neutral processes applicable to particular atmospheres. Vakhtin et al. point out that OH radicals are one of the most important transient species in Saturn's atmosphere, and that their reactions with unsaturated species, such as the additions studied with propene and 1-butene, may be responsible for production of species containing C-O bonds. Similarly, the reactions of C2H with acetylene, O2, methylacetylene, and allene, with ethane, propene, and 1-butene, with ethane, propane, and n-butane, and with hydrocarbons and nitriles, show promise as a subset of the candidates responsible for the formation of the complex chemical species found in the atmosphere of Titan.

The most recent incarnation of the pulsed Laval nozzle flow reactor resides in Göttingen, Germany in the group of Bernd Abel. It employs laser photolysis and LIF detection of hydroxyl radicals over at temperature window of 58 to 300 K, and will be dedicated to the study of processes important to low temperature environments. An initial investigation of the reactions of OH with propene and isoprene has been conducted and was used to calibrate their results with those previously available at low temperature.

One can easily understand the reason for the dedication of these instruments to the context of interstellar chemistry and the understanding of fundamental reaction processes with the wealth of information already obtained, and that to be obtained in the near future from space exploration. In particular the Cassini-Huygens probe, equipped with a GC mass spectrometer, aerosol collector, and surface science package, will acquire data on the atmospheric and surface composition of Saturn and Titan. Titan is of particular
importance to astronomers and planetary scientists because of its atmospheric composition. Voyager 1 directly observed molecular and atomic nitrogen in the upper atmosphere, while the dominance of N$_2$ in the atmosphere was determined through a measurement of the mean molecular mass. While N$_2$ is present in a 90 – 99% mixing ratio, the other major species are methane and H$_2$ in parts per thousand concentration, ethane, acetylene, propane and ethylene in the parts per million concentration range, with ethane the largest of the four. Other species in lower concentration have been detected and include propylene, diacetylene, hydrogen cyanide, cyanoacetylene, acetonitrile, carbon dioxide, and carbon monoxide. Water has been detected in the infrared by the infrared space observatory (ISO), and argon is speculated to be present in the atmosphere, although not currently detected.

The temperature of the atmosphere and thermal structure varies from approximately 70 K at the troposphere to approximately 190 K high up in the thermosphere. More interestingly though are the haze layers observed to form extensively throughout the entire atmosphere. They are comparable to a photochemical smog, and the mechanism for their formation is most likely initiated by the photo-dissociation of N$_2$ and CH$_4$, the products of which can then participate in chemistries leading to more complex molecules that are capable of form aerosol particles and condensates due to the temperature of the atmosphere. From this rather cursory treatment of Titans atmosphere it is easy to see that there must exist a rich set of chemistries leading to diversity of species and haze observed in the atmosphere.
A sense of the importance of fundamental chemical and physical processes to the atmosphere can be attained by examining the types of questions currently being posed with regards to Titan’s atmosphere. These ideas are taken from a review by Lunine et al.54 and are grouped into three categories. First, the composition of Titan’s atmosphere, previously described, can be used to deduce its origin. Chemical abundances and D/H ratios in specific molecules help to locate the origins of the atmospheric materials and might allow researchers to decide whether the origin of the material is Saturnian or cometary. Second, the long term stability of Titan’s atmosphere is an active concern and is thought to be dictated by photochemical processes of the hydrocarbons. More specifically, the absorption of photons by methane at specific levels in the atmosphere influences the heating and cooling processes in these regions, and is thus the reason that climate change can partially be attributed to photochemical hydrocarbon processes. Finally, Titan serves as a remote laboratory for studying the evolution of a pre-biotic environment, similar to what may have been present on Earth, and a chance to glimpse the transition between simple organic chemistry to biology. While rigorous answers to these questions may seem like lofty goals they highlight the need for continued development of experimental and theoretical investigations.

Lara et al.55 use 37 photodissociation processes and 122 chemical reactions to model the neutral constituents of Titan’s atmosphere. There is one photodissociation reaction involving the formation of OH radicals, six reactions of OH with various species, and six reactions of the NH radical. Of the NH reactions, all involve radical-radical chemistry. Chapter 5 of this dissertation treats the chemistry of the imidogen radical with
some of the neutral species found in the atmosphere. It is easy to understand the difficulty in modeling an atmospheric environment, considering the number of processes that need to be taken into account. These include the reaction network, the mixing ratios and knowledge of condensation and diffusion processes, for which the vertical profile, the ultimate goal of which is to reproduce, is sensitive to.

Difficulties often arise in accurately reproducing the chemical profiles found in these environments due to the availability, or lack thereof, of rate data for the species present. It is oftentimes not the rate data that is incorrect, rather temperature range in which it was taken. Outside of the chemistry measured in Laval nozzle expansions, most rate coefficients have been measured at room temperature and above, due to the difficulty of obtaining reliable data at low temperature with conventional flow methods. While this is generally not problematic, there are a number of examples where extrapolation of the rate of reaction to low temperatures, pertinent to the ISM and planetary atmospheres, from high temperature data results in gross error. In these cases it is either the nature of the potential energy surface or a change in reaction mechanism at low temperature that accounts for this discrepancy. An example of each case is given below involving the chemistry of the OH radical.

The H atom abstraction reaction of OH + HBr has been studied in detail both experimentally and theoretically, due to its importance in the partitioning of Br atoms in the atmosphere. The low temperature gas phase experiments revealed an onset to reactivity occurring near 200 K, resulting in a $T^{-0.9}$ dependence of the rate on temperature in the low temperature regime.\textsuperscript{31,33,56} Above 200 K the rate is at best weakly dependent on
temperature, and has a value of approximately \(1 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}\). The value measured at 23 K by Sims et al. is \((10.7 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}\), an order of magnitude higher than would have been anticipated from the high temperature data. The reason for the increase in reactivity is discussed in detail in Chapter 4, but is attributed to the orientational dependence of the collision necessary for a successful reactive event. As the temperature is lowered, and the rotational energy is removed, the collision complex has more time to access the correct orientation, and thus increase the reaction efficiency.\(^{60,61}\)

Hydroxyl radical chemistry with unsaturated hydrocarbons also has surprises. In particular the reaction of OH with propene, demonstrates Arrhenius behavior above 700 K attributed to H atom abstraction from the \(-\text{CH}_3\) substituent group, while at temperatures below 467 K the reaction proceeds via addition into the double bond.\(^{62}\) The low temperature work of Vakhtin et al.\(^{41}\) corroborate these ideas. Again, the low temperature work reveals not only increased reaction efficiency, but a change in mechanism leading to very different reaction products due to the influence of the collision complex. If the reaction products participate in subsequent chemistry, the partitioning of chemical species is dependent on correct knowledge of reaction products and branching ratios where multiple pathways are available.

These two examples, while certainly not exhaustive, serve to exemplify the importance of accurate chemical rate measurements in the temperature regime in which they occur. For the ISM and planetary atmospheres this corresponds to a few Kelvin upwards to approximately 200 K, a regime naturally suited to the supersonic expansions
created by the Laval nozzle. With this in mind, the purpose of this dissertation research has been to provide rate data between 53 and 188 K on a number of systems.

Chapter 2 is the experimental section of this report and is dedicated to the description of the theory behind supersonic Laval nozzle expansions and the methods (LIF and pitot tube) of characterization used to ensure that equilibrated supersonic flows suitable for kinetic measurements were established. It further details the experimental setup and compares it with the other instruments found worldwide.

Chapter 3 is dedicated to the description of the efforts undertaken to incorporate a tunable vacuum and extreme ultraviolet source to the flow reactor, for the LIF detection of atomic and molecular species with their first electronic transition in this frequency range. Specifics pertaining to the theory of frequency mixing, the experimental conditions, and the detection of hydrogen atoms with an off resonance detection scheme are included.

Chapter 4 details the low temperature kinetic measurements on the OH + HBr and H/D isotopic variants system, including an analysis of the kinetic isotope effects found. A fundamental understating of kinetic isotope effects whether primary (PKIE) or secondary (SKIE) in nature provides insights into the reaction potential energy surface, the important features along the surface, such as the transition state, and the influence of the ratio of the number of states and state densities in the reactants and transition state on the outcome of the collision. Further, experimental KIE ratios help, as well as challenge, theoretical efforts to reproduce the potential energy surface where oftentimes reduced
dimensionality has to be used. The discussion includes experimental and theoretical examples that establish the validity of the results.

Chapter 5 represents a new direction for the Smith laboratory and describes the measurements of the rate coefficients for the reaction of the ground state NH radical with a variety of reaction partners. These include NO, methane, ethane, ethylene, acetylene, propene, and diacetylene. NO was chosen as a calibration for the Laval technique, since high temperature data was available for comparison, and these are the first measurements on this radical species in Laval flows. LIF experiments were also conducted on the NH radical as a cross check and are described. The rest of the reaction partners were chosen for the applicability to the atmosphere of Titan, and are species which are currently not attributed with the chemistry of the imidogen radical. The mechanisms of NH radical reactions are discussed in context with previous experimental findings, along with speculation as to the importance of these reactions to the complex chemistry of Titan.

Chapter 6 concludes the dissertation and summarizes the findings on these studies, as well as highlights the future contributions that might be made with this technique to the development of an understating of low temperature chemistry.
CHAPTER 2. EXPERIMENTAL

2.1. Laval Nozzle Principles

The central component in the uniform supersonic pulsed flow reactor used to study collision and reaction dynamics in this laboratory is the Laval nozzle. These nozzles derive their heritage from working wind tunnels, and aerospace and rocket technology. Indeed large amounts of research have been conducted in the field of propulsion technology aimed at understanding the underlying fundamental principles of fluid flow that allow for such things as the development of hypersonic propulsion systems that provide enough thrust for the successful deployment of interplanetary spacecraft or an aerospace plane. While the requirements are quite different for each individual goal, the study of gas phase chemical reactions versus the propulsion of a payload through space, the fundamental physics behind the nozzle contour and design are actually quite similar. It is the intention then to provide an adequate description of the methodology used to create uniform supersonic expansions in a cohesive manner with emphasis on a physical rather than the mathematical picture. Several excellent accounts of the design of supersonic nozzles are used to present this methodology. In addition, the thesis chapter on Laval nozzle design Chapter 2, by Dean Atkinson, is an excellent resource for an in depth discussion of the salient principles of fluid dynamics required to design these nozzles. As a result, only a highlight of the most important features drawn from these resources in conjunction with material which helps to further clarify the
fundamentals and methodology employed in axisymmetric Laval nozzle design is presented in this chapter.

The fundamental objective of a supersonic nozzle is to take a fluid at rest and accelerate it in a known and controllable fashion to a terminal well defined supersonic velocity, with non-turbulent streamlines. Further, it is desirable to create these circumstances such that the flow post nozzle, often times referred to as the test section of flow, is equilibrated, the flow streamlines are parallelized and the density and temperature remain constant for many nozzle diameters allowing for enough time in which to conduct a kinetic measurement. While these might at first seem to be lofty goals, they are indeed realistic. Supersonic expansions exploit the first and second laws of thermodynamics, which state that for any process the total energy of the system is conserved, including the internal and kinetic energy, and that those that occur naturally are those for which the entropy remains constant or increases, respectively. As gas molecules are forced through a tube they respond to their environment by either expanding or compressing depending on the geometry of the tube. Changes to the gas density can be accomplished in either a reversible or irreversible manner. In the reversible case, gradual changes to the environment such as compression and expansion, allow the flow to return to the original state. In this case the reversibility implies a constant value of entropy, or an isentropic flow. Irreversible changes occur when supersonic flows are turned abruptly and compression occurs, causing shock waves to form, and are for obvious reasons undesirable. Crucial to the understanding of the isentropic flow is the concept of the Mach number. As defined, the Mach number is the
ratio of the hydrodynamic velocity of the flow to the local speed of sound, as represented in Equation 2.1

\[ M = \frac{v}{a} \quad (2.1) \]

where \( a \) is the speed of sound

\[ a = \sqrt{\gamma RT} \quad (2.2) \]

and \( \gamma \) = the heat capacity ratio \( \frac{C_p}{C_v} \) of the gas, \( R \) is the ideal gas constant divided by the molecular weight of the gas, and \( T \) is the temperature. This parameter, \( M \), is a measure of the amount of energy converted into directed flow motion at a cost to inter-particle relative velocity according to the conservation of energy. The pressure and density of an isentropic flow are related according to Equation 2.3:

\[ \frac{P}{\rho^\gamma} = c \quad (2.3) \]

Defining the pressure and density at which the flow is brought to rest isentropically allows one to define the constant (\( c \), not to be confused with \( C_p \), the constant pressure heat capacity) in Equation 2.3 through:
Substitution of the equation of state into Equation 2.4 allows one to define some useful expansion relationships in terms of the flow Mach number:

\[
\frac{P}{\rho^\gamma} = c = \frac{P_\infty}{\rho_\infty^\gamma}
\]  

(2.4)

At this point it is now possible, with the introduction of a few definitions, to define the one-dimensional isentropic expansion relationships. The one dimensional relationships relate all of the adjustable flow parameters, temperature, pressure, and density, to the Mach number of the flow, and are thus their utility in designing specific flow conditions in the laboratory.

The enthalpy of a system is defined as the constant pressure heat capacity \(C_p\) times the temperature \(T\) according to Equation 2.6:

\[
H = C_p \times T
\]  

(2.6)

Further, the total enthalpy of a flow system is defined as
\[ H_T = H + \frac{\nu^2}{2} \]  \hspace{1cm} (2.7)

where \( H_T \) is the total enthalpy and \( C_p \) is the gram heat capacity (\( \text{JK}^{-1}\text{kg}^{-1} \)). Substituting Equation 2.2 into Equation 2.1, rearranging for \( \nu \), and squaring both sides yields:

\[ \nu^2 = M^2 \gamma RT \]  \hspace{1cm} (2.8)

Substitution of Equations 2.8 and 2.6 into Equation 2.7 yields:

\[ C_p T_T = C_p T + \frac{M^2 \gamma RT}{2} \]  \hspace{1cm} (2.9)

Division of Equation 2.9 by \( C_p \) and rearrangement yields the one dimensional isentropic expansion relationship in terms of temperature

\[ \frac{T}{T_0} = \left(1 + \frac{\gamma - 1}{2} M^2 \right)^{-1} \]  \hspace{1cm} (2.10)

where \( T_T \) has been substituted for the more traditionally used \( T_0 \). Similarly substitution of Equation 2.5 into 2.10 allows for the other two one-dimensional relationships to be obtained, Equations 2.11 and 2.12:
The utility of the Mach number is now easily seen. One can see that the final flow parameters are defined solely in terms of the Mach number of the flow and the starting conditions, denoted by $P_0$, $\rho_0$, and $T_0$.

With knowledge of the isentropic flow behavior it is instructive to know how the flow properties respond to changes in the system, in particular the shape of the nozzle. Laval nozzles consist of three sections, as can be seen in Figure 2.1. The first section is a short convergent section that begins to accelerate the flow from its near zero net hydrodynamic velocity. A necessary requirement for this acceleration is that a large enough pressure gradient across the nozzle from the stagnation region to the nozzle exit is established and maintained according to Equation 2.11. For a Mach 2 nitrogen flow the ratio $P/P_0 = 7.82$. The stagnation region is coupled to the throat region of the nozzle, where the nozzle area is at a minimum. At this point the Mach number of the flow equals 1, because the highest velocity attainable by a purely contracting flow is that of the local speed of sound. Further increases in the flow velocity are obtainable only with subsequent expansion of the flow. The divergent section serves that purpose, with the following goals in mind. It should accelerate the flow to the desired velocity in the test
Figure 2.1. An illustration of the key aspects of the Laval nozzle.

Figure 2.2. Divergent section of the Laval nozzle divided into the three parts necessary to achieve uniform flow.
section, it should parallelize the flow streamlines (a flow streamline runs in the direction of the flow at all points, with its tangent everywhere having the direction of the flow velocity vector), as well as remove any expansion waves that are generated in the acceleration process, such that the test section is disturbance free and complies to the desired final flow parameters in T, P, and ρ.

In order to accomplish these goals the divergent section is divided into three parts, according to Figure 2.2. Part one serves to rapidly expand the gas to near the desired terminal Mach number. The second region is the source flow region where the flow streamlines are linear and appear to originate from a source point, while the third section serves to remove the effects of expansion waves propagated from the first region, parallelize the flow streamlines, and accelerate the flow to the terminal velocity.

A brief digression into supersonic fluid dynamics is most instructive at this point, as it will provide the basic understanding of the nozzle contour, which can then be calculated by any number of methods available in the literature. The most illuminating way to consider forming a parallelized supersonic expansion is to consider the response of a unidirectional supersonic flow over a curved surface. An analytical expression for the flow field resulting from a convex corner formed by two intersecting lines has been treated by Prandtl and Meyer, with the result being that the change in Mach number of the flow streamline is a function of the angle of the corner, i.e. the change in direction experienced by the streamline, according to Equations 2.13-2.15 and Figure 2.3a.
\[ \psi = \kappa \tan^{-1} \left( \frac{\cot \alpha}{\kappa} \right) - (90^\circ - \alpha) \]  
(2.13)

\[ \alpha = \sin^{-1} \frac{1}{M} \]  
(2.14)

\[ \kappa = \sqrt{\frac{\gamma + 1}{\gamma - 1}} \]  
(2.15)

where \( \psi \) is the expansion angle, \( M \) is the Mach number, and \( \alpha \) is the corresponding Mach angle.

In addition, it is often convenient to represent the perturbations to flow conditions between two curved surfaces, as a series of changes due to an infinite or large number of line segments with discreet yet definable length. The reason being, that the solution for supersonic flow about a corner is known, which reduces the solution complexity of flow about a surface to that of flow around a number of consecutive corners. The utility of the formalism presented in Equations 2.13–2.15 is realized when considering changes in acceleration between two arbitrary Mach numbers, Figure 2.3b, as the streamline traverses region I through III. It can be shown that

\[ \delta = \psi_2 - \psi_1 \]  
(2.16)
Figure 2.3a. Illustration of the Prandtl-Meyer turning angle. The effect of a corner in a flow system causes an expansion of the fluid and a corresponding acceleration, described by the angles $\alpha$ and $\Psi$, where $\alpha$ is the Mach angle and $\Psi$ is the expansion angle. Adapted from Crown, 1948 [66].

Figure 2.3b. Formalism for expressing the change in Mach number due to a corner for an arbitrary initial Mach number. $\delta$ equals the change in expansion angle $\Psi_2 - \Psi_1$. Adapted from Crown, 1948 [66].
or, equivalently that the change in expansion angle is equal to the change in stream deflection due to a single corner. It is therefore possible to predict the flow streamline properties referenced to Mach numbers other than 1, and thus judge the changes to the flow based on a series of these single corner scenarios. The creation of an expansion or shock wave results from the finite change in Mach number and area of the flow due to a corner, and this propagating disturbance needs to be properly treated. One can envision a series of these waves interacting with the flow, emanating from the series of corners used to approximate the nozzle wall contour, thus rendering a proper understanding of their constructive and destructive interferences necessary.

It is necessary at this time to introduce the idea of a characteristic, as the downstream boundary of an expansion wave. It can be seen from Figure 2.1 that for axisymmetric Laval nozzles used in these experiments the symmetry of the nozzle implies that for any point on the nozzle wall creating an expansion wave, there is an equal yet opposite point also contributing an expansion wave. At some point in the flow their characteristics must cross, the net result being the linear sum of the two, such that the streamline impinging on the two has been deflected by some angle (+θ₁) due to the first expansion wave, and deflected in the opposite direction (-θ₂) due to the second expansion wave which emanated from the opposing wall, with the net result (θ₁ - θ₂) in the flow direction and change in Mach number, see Figure 2.4.

Two other problems need to be understood before adiabatic core nozzle design can be accomplished and they are the treatment of the reflection of expansion waves by a wall and the neutralization of expansion waves. The treatment of the reflection of an
Figure 2.4. Illustration of the result of the crossing of two expansion waves as a result of the two corners present in the system. The flow streamline experiences changes in flow direction and Mach number as a result of crossing both expansion waves. $\theta_1$ and $\theta_2$ are the corresponding changes in angle of the flow streamline. Adapted from Crown, 1948 [66].
expansion wave by a surface is understood by invoking a mirror image concept. Within this framework the physical wall is replaced by a fictitious flow streamline containing the original flow and an image of the flow field, Figure 2.5. The mirror image concept reduces the problem of the intersection of an expansion wave and a surface to that of the intersection of two expansion waves that has previously been treated. The angles \( \theta \), the incident expansion wave-surface angle, and \( \phi \), the exit expansion wave-surface angle, of Figure 2.5 are not equal due to the fact that the expansion angle \( \psi \) (Equation 2.13) has been altered twice due to the flow streamline interacting with the two expansion waves. The net result is a new expansion angle of \( \psi + 2\delta \), with an unaltered flow stream angle relative to some reference line in the flow.

It is desirable in Laval nozzle design to neutralize the expansion waves created from the nozzle surface, such that they do not interact with the flow streamlines. This can be accomplished by changing the angle of the wall with respect to the expansion wave, as shown in Figure 2.6. The expansion wave originating from point \( a \) in the flow and propagating downstream to some point \( b \), can be neutralized at that point by creating a compression wave of equal strength. The compression is easily created by a deflection in a concave corner. Remember that the expansion wave arose from the interaction of the supersonic flow streamline with a convex corner in the nozzle wall. The net result of the interaction of the expansion and compression waves of equal, yet opposite strength, is to cancel the incoming expansion wave. Therefore, the expansion angle remains unchanged while the stream angle is altered by an amount equal to the angle necessary to produce the compression wave.
Figure 2.5. Treatment for the reflection of an expansion wave due to a surface. The surface is treated using the mirror image concept which allows the problem to be reduced to the intersection of two expansion waves. \( \theta \) is the incident angle of the expansion wave with the surface, \( \phi \) the angle for the reflected wave to the surface, and \( \delta \) the change in flow streamline. Adapted from Crown, 1948 [66]
Figure 2.6. Cancellation of an expansion wave by a surface. Cancellation is accomplished by changing the angle of the surface with respect to the expansion wave, such that a compression wave of equal yet opposite strength is created due to the concave corner in the system. Adapted from Crown, 1948 [66].
With the fundamentals necessary to construct the Laval nozzle contours presented it is now possible to understand the three specific regions of the divergent section of the nozzle wall in terms of the curvature with respect to the nozzle axis. The actual calculation of the nozzle shape is broken into two parts, in order to greatly simplify the calculation. The methodology is as follows. The nozzle flow is first treated as being isentropic with respect to the nozzle walls, implying that the effects of heat transfer and viscous forces are negligible. While this is obviously not the case, a separate treatment of these effects is considered, as an inclusion of a displacement thickness to the wall shape calculated in the isentropic assumption, which can be numerically computed using the known flow properties from the isentropic solution. The displacement thickness necessary to shield the isentropic core from effects of heat transfer and viscous forces arises due to the well known boundary layer that forms as molecules of a viscous fluid interact with the surface over which they flow. The “sticky” interaction causes disturbances near the surface that result in a lowering of the stream velocity. From the standpoint of the conservation of mass in three dimensions, the lowering of the stream velocity in one dimension implies that a change in velocity in the other two directions results. These off stream components serve to displace the flow above it. The effect is reduced the farther removed a stream is from the surface, due to the fewer collisions with molecules affected by the surface. The displacement thickness required to remove these turbulent forces depends on the Reynolds number, $Re = \frac{vl}{\mu}$, a function of the flow velocity $v$, the density $\rho$, the characteristic length $l$, and the viscosity coefficient $\mu$. It can be either laminar or turbulent depending on the flow regime, but it’s effect once properly
treated is to displace the wall of the nozzle by a certain amount \( \delta^* \), such that the new wall produces the same mass flow, as in the idealized isentropic flow case, Figure 2.7.

The method of characteristics of Moger and Ramsey\(^{67}\) is the one chosen to design the axisymmetric Laval nozzles employed in these experiments. The method was apparently chosen over others available as the numerical integrations necessary to calculate the nozzle geometry were easily performed by digital computer. As mentioned previously, the details of the method have been carefully and eloquently described by Atkinson, Chapter 2,\(^{63}\) and thus only a brief description is included here. The ordinary differential equations governing the method of characteristics for a axisymmetric supersonic flow in cylindrical coordinates are

\[
\frac{dr}{dz} = \tan(\theta \alpha) \quad (2.17)
\]

\[
d\theta \pm \frac{\cot(\alpha)}{W} \frac{dW}{\sin(\theta) \sin(\alpha)} \frac{dr}{r} = 0 \quad (2.18)
\]

where \( z \) is the distance along the nozzle axis, \( r \) is the radial distance, \( \theta \) is the flow angle with respect to the nozzle axis, \( \alpha \) is the Mach angle (Equation 2.14), \( W \) is the speed ratio (Equation 2.19), and the \( \pm \) symbol refers to an individual characteristics slope:

\[
W^2 = \left( \frac{V}{V_{\text{max}}} \right)^2 = \frac{\gamma - 1}{2} M^2 \left( 1 + \frac{\gamma - 1}{2} M^2 \right)^{-1} \quad (2.19)
\]
Figure 2.7. Treatment of the boundary layer. The effect is an addition to the nozzle contour of a displacement thickness $\delta^*$ normal to the wall coordinate.
The speed ratio is the ratio of the flow velocity to the maximum velocity attainable at infinite Mach number. $V_{\text{max}}$ is given by the following expression

$$V_{\text{max}} = \left( \frac{2\gamma k T_0}{\gamma - 1} \frac{m}{V} \right)^{1/2}$$

(2.20)

where $k$ is Boltzmann's constant and $m$ is the molecular mass of the flow. Equations 2.17 – 2.20 are used to follow the flow properties along the characteristics, for a sufficient number of characteristics required to attain the desired flow properties. Once these conditions have been satisfied in an iterative manner, the wall coordinates are located by mass flux integration along the characteristics.

With the isentropic core calculated and the preliminary wall coordinates $(z,r)$ obtained, it is then necessary to locate the actual nozzle wall by inclusion of the boundary layer. This has been accomplished in accord with the method of Cohen and Reshotko$^{68,69}$ reported by Potter and Carden.$^{70}$ The boundary layer acts as an insulating layer to the isentropic core and shields it from the effects of heat transfer and viscous effects. The boundary layer displacement thickness ($\delta^*$), calculated in the laminar flow regime, is applied normal to the isentropic core coordinates, locating the physical nozzle wall. With this calculation complete, it is then possible to take the $(z, r)$ coordinates, plot them using graphical software, fit the curve to a high order polynomial, and use the fit to machine the physical nozzle. A help file for use of the `nozzle.exe` code is available in the lab, which
discusses the relevant input file parameters, and provides a step by step methodology for running the nozzle code that includes actual screen shots produced during various stages of the nozzle calculation. Again, the information contained in the help file is intended to be complimentary to the information found in Appendix A: Specific Application Notes and Source Code Listing For Nozzle Design Computer Program, of the Atkinson thesis, and it is therefore recommended that both are used in conjunction when constructing new Laval nozzles.

2.2. Description of the Pulsed Supersonic Laval Nozzle Flow Reactor

The pulsed supersonic Laval nozzle flow reactor housed in Tucson is one of five in the world, at the time of this writing, employing the Laval nozzle technology for the study of atomic and molecular reaction dynamics. While this is quite a broad field many of the measurements made to date have focused on bimolecular and termolecular collisions and have provided information of reactive processes including spin-orbit relaxation, association, abstraction, and addition reaction mechanisms. More recently the equilibrated supersonic flows have been used to study cluster formation and nucleation dynamics.

It is the focus of this subsection to provide a detailed description of the Tucson flow reactor and also to compare and contrast it with the others available throughout the world. Once an adequate description has been provided it will then be the goal to present
the methods of characterization used on these flows to obtain the accurate flow properties necessary for conducting kinetic experiments.

A schematic diagram of the instrument is shown in Figure 2.8, and provides a good starting point for discussion of the instrument. The Laval nozzle resides in a vacuum chamber connected in series to a roots pump (Leybold WS-501, 300 cfm) and mechanical pump (Kinney KC-46, 46 cfm). The pumping system is chosen such that it can handle the moderately high pumping speed required by the gas consumption rate of the Laval nozzle (approximately 5 sLmin\(^{-1}\) which varies from nozzle to nozzle), and still provide the moderately low pressures (0.1 – 10 Torr) required to attain collimated supersonic flows for a number of nozzle diameters past the nozzle exit. The second requirement arises from the criteria that the chamber pressure equals the flow pressure for optimal performance. Matching this criteria ensures that the collimated flow does not experience expansive forces upon exiting the nozzle body, and allows for the perpetuation of the supersonic flow for a much longer duration than would be possible if these forces were present.

The nozzles are a two piece design both machined from aluminum. For the experiments described here the short convergent region is permanently affixed to the divergent section, to ensure a more reproducible flow system. Misalignment between the two regions can introduce perturbations into the flow such as differing boundary layers, and undesirable shock structure, in effect creating optimal flow conditions that can change as a function of the convergent/divergent sections alignment. The nozzle is attached to a brass body through a series of threads that serves a number of functions.
Figure 2.8. Schematic of the pulsed supersonic Laval nozzle flow reactor. Shown are the essential components of the reactor minus the pulse generating and signal processing electronics.
The first function of the brass body is to provide a small stagnation region volume (approximately 1 cm$^3$) where pre-expansion thermalized flow conditions can be established. The stagnation region for pulsed experiments is ideally kept small so that the stagnation pressure can rapidly raise to ideal flow conditions in the shortest time possible upon opening of the pulsed valves. The stagnation volume also serves to pre-mix the gases introduced by the pulse valves before they enter the nozzle region. At flow rates typical to these experiments (500 – 2000 sccm), the residence time in the stagnation region is calculated to be between approximately 5 and 25 μsec. Taking into account the flow velocity in the stagnation region ($\approx 5 \times 10^4$ cm/sec) and the residence time, the distance traveled by a molecule under these conditions is estimated to be between 0.3 to 1 cm, while the mean free path, $\lambda = 1/\rho \sigma$, where $\rho$ is the density (molecules/cm$^3$) and $\sigma$ is the cross section (assumed to be $5 \times 10^{-15}$ cm$^2$ for N$_2$) is around 6 μm, allowing for a number of collisions to occur.

Two pulsed valves, General Valve Series 9, are attached to the brass body and are used to introduce gases into the stagnation volume in a pulsed fashion, and are triggered by the circuit in Figure 2.9. The nozzles are operated at 10 Hz, for durations of 5 ms. In this mode of operation a reduction of the duty cycle of the experiment is achieved resulting in lower gas consumption rates by the nozzle and a reduction in the necessary pumping speed required to successfully conduct an experiment. Each pulsed valve is attached to a separate reactant/carrier gas line, which are connected to mass flow controllers (MKS). The reason for this arrangement is so that reactive gases can be separated from each other prior to the Laval nozzle, and thus their pre-flow concentration
FET Trigger IRFBC20

Pulse In

G

100 Ω

1.5 Ω

PIN160 (3)

Current Monitor

1N4007

General Valve Pulse Valve

R = 110 Ω

V_{Source} (300 V)

0.22 μF

R_{Load} 100 Ω

Figure 2.9. Circuit diagram of the pulsed valve driver.
be accurately known. A schematic of the gas mixing rack and delivery line is shown in Figure 2.10.

Also attached to the brass body are a pulsed cold cathode DC discharge and a stagnation pressure transducer (Omega Model PX-170). The pulsed DC discharge is used to create radical species in the stagnation volume from small amounts of precursors mixed into reactant/carrier gas lines. For the NH radical studies N₂ and H₂ were used, for OH radical H₂O was used, and for the detection of H atoms H₂ was used. The DC discharge electrode is a Champion small engine spark plug (model 810° - RA8HC). The gap was set to 0.010 – 0.012" for ideal performance, but could be operated at gaps up to about 0.025" before erratic behavior was observed. The plugs side electrode derives its ground from the brass body, which in turn is connected to an external ground through the translation arm. The discharge is driven by a Borg-Warner 12 Volt coil (model E-30) that is triggered through a homebuilt circuit. It is triggered for a duration of 1 ms during the initial time that the pulse valves are open, while the laser that is used to probe the experiment is fired 1 ms after the discharge trigger has been shut off. Figure 2.11 represents a detailed pulse timing diagram for the experiment. A block diagram of all the electronic components required to conduct the experiments is shown in Figure 2.12. The arrows indicate the direction of information flow, whether it be a trigger pulse, computer command, or signal.
Figure 2.10. Schematic of the gas mixing rack and flow delivery lines.
Figure 2.11. Timing diagram for the OH and NH radical studies. All times are referenced to $T_0$. 

- $C = T_0 + 4.1$ ms
- $D = C + 286$ µsec
- $T_0 + 2.9$ ms
- $3.5$ msec
- Laval Nozzle Pulse Valves
- $1$ ms
- Flash Lamp (Nd:YAG)
- Q-Switch (Nd:YAG)
- Discharge
Figure 2.12. Block diagram of the electronic components used to conduct experiments. Arrows indicate the direction of information travel.
Affixed to the brass body and the nozzle are a set of 0.25" copper tubing coils, which are connected to a VWR scientific model 1156 programmable heated/refrigerated circulator, in order to achieve precise temperature control of the nozzle and stagnation volume. The circulator was operated with a 50/50 mixture of water and ethylene glycol, and with this mixture is theoretically capable of attaining temperatures between -30 to 90 °C, although only temperatures between -10 and 25 °C were used for experiments, as these were found to be the stagnation temperatures that created the desired final flow temperatures. As can be seen in Equation 2.10, the final flow temperature is a function of the stagnation temperature $T_0$, and it was therefore desirable to ensure that the nozzle body remained at a constant temperature throughout the duration of a kinetic run such that changes in the flow conditions were minimized. The circulator also served to pre-chill the nozzle so that colder final flow temperatures could be achieved.

The whole assembly is attached to the translation arm, which allows for a translation of the nozzle in the Z direction, of 30 cm. The translation is necessary in these experiments because the nozzle to laser distance defines the reaction time, a necessary parameter for extraction of kinetic data. A detailed description follows later in the chapter. The absolute distance and the change in distance are measured on a ruler, mounted on the vacuum chamber wall. Typically the distance was changed over approximately 20 cm, in 1 cm intervals during the kinetic runs of most experiments, except for those that employed the Mach 2 nozzle, where much shorter overall distances were employed due to the flow characteristics.
In order to extract kinetic information from the flows one must be able to monitor the time dependent concentration of one of the species participating in reaction, whether it be reactants or products. Of the available techniques, we have chosen to employ laser induced fluorescence (LIF) for the non-destructive probing of the reactant radical relative concentration. LIF is advantageous in the respect that the detection limits are quite low, about $10^7$-$10^8$ species/cm$^3$, and that the radiation frequencies necessary for detection of most atomic and diatomic radical species are easily generated in the laboratory using commercially available laser systems. The LIF technique is also advantageous in the respect that under the appropriate conditions it can be used to extract information on the radical population in a state specific manner. Knowledge of the population in conjunction with the rotational line strength factors allows for the determination of the rotational temperature of the radical species in the flow, and serves as a method of flow characterization. More on LIF temperatures follows in the next section.

A laser induced fluorescence scheme has been used to detect the following radicals: NH, OH, and H atom. The specifics of each scheme are discussed separately elsewhere, but LIF is accomplished with either or both of the pulsed Nd:YAG laser available in the laboratory. Both Nd:YAG lasers, Continuum model YG660 and NY61-10, have similar specs and produce 300 mJ of 532 nm or 170 mJ of 355nm radiation in 6-8 ns duration pulses. Both are used to pump dye lasers, the YG660 a homebuilt model based on a grazing incidence Littman configuration, the NY61-10 a Moya-type oscillator cavity dye laser Continuum Model ND60. The ND60 is attached to a non-linear frequency generation stage (Continuum UVX/UVT) which allows for frequency doubling,
mixing after doubling and mixing with the YAG fundamental. The homebuilt dye laser is capable only of frequency doubling with harmonic crystals such as KD\textsuperscript{+}P or BBO. However, the dye lasers allow for the creation of pulsed tunable laser frequencies in the ultraviolet, visible, and infra-red portion of the electromagnetic spectrum, from 483-844 nm in the fundamental, 292-378 nm in doubling mode using KD\textsuperscript{+}P crystals, 241-295 nm using a BBO crystal, 369-442 nm in the mixing mode using KD\textsuperscript{+}P crystals, and 219-279 nm in the mixing after doubling mode, again using KD\textsuperscript{+}P crystals. The Continuum UVX and UVT operation manual can be referenced for proper choice of dye and crystal at a particular wavelength. The dye laser radiation is used to state specifically promote radical population in a ground ro-vibrational state to an excited state, and is introduced into the vacuum chamber via a Brewster’s window. The excited state created by the laser induced absorption event undergoes subsequent decays processes, one of which is fluorescence to the ground state. The laser induced fluorescence is then collected on a photomultiplier tube (PMT) (Hamamatsu R3896) positioned orthogonal to the plane defined by the intersection of the flow with the laser beam, and amplified using either a 10 or 100 times 100 MHz preamplifier (Phillips Scientific 6931). The signal is either averaged on a boxcar averager (Stanford Research SR 250) or sent to an oscilloscope (LeCroy 9310, 300 MHz) for manipulation. The PMT uses a set of filters in front of the photocathode to block unwanted light, both laser scattered light, and wavelengths outside of the band desired for the experiment. The laser radiation also exits the vacuum chamber via a second Brewster’s window and the beam energy is monitored with a power meter (Scientech 361) to ensure laser stability throughout the duration of the experiment. The
experiments were conducted in the linear fluorescence regime, and it was therefore very important to ensure the stability of the laser power to within the spec of ± 5%.

The Tucson instrument differs from the four other instruments in two main ways. The others available are in the laboratory of Bertrand Rowe in the Département de Physique Atomique et Moléculaire, at the Université de Rennes in France (continuous duty, pulsed laser photolysis), in the laboratory of Ian R. Sims in the School of Chemistry, at the University of Birmingham, in the UK (continuous duty, pulsed laser photolysis), in the laboratory of Stephen R. Leone in the Departments of Chemistry and Physics, and Lawrence Berkeley National Laboratory, at the University of California Berkeley (pulsed duty, pulsed laser photolysis), and in the laboratory of Bernd Abel in the Institute for Physical Chemistry, at the University of Göttingen, in Germany. All four share the common characteristic that they use laser photolysis for the generation of radical species, followed by LIF for radical detection and concentration, although the Leone apparatus has been adapted to chemiluminescent detection more recently. In this respect the experiments differ in the way they define the reaction time. For the pulsed DC discharge reactor here in Tucson, the reaction time is attributed to the difference in distance from the nozzle exit to the LIF image point. The difference can be used to determine a reaction time through knowledge of the flow velocity. The useful thing about the Laval expansions is that they produce a uniform flow in velocity, temperature, and density all of which can be accurately measured. As far as the flow velocity is concerned it can be determined independently through either of two methods. Using LIF to extract the flow temperature and Equation 2.10, the flow Mach number is obtained. Remembering that the
Mach number is a ratio of the flow velocity to the local speed of sound, according to Equation 2.1, the flow velocity can then be determined. Further, the Raleigh-Pitot formula, Equation 2.21, also relates the Mach number of a flow to the impact pressure produced on a Pitot tube placed in the flow path

\[ \frac{P_i}{P_0} = \left( \frac{\gamma + 1}{2} M^2 \right)^{\gamma-1} \left( \frac{\gamma + 1}{2\gamma M^2 - (\gamma - 1)} \right)^{\gamma-1} \]  

(2.21)

where \( P_i \) is the impact pressure and \( P_0 \) is the static pressure. Again, knowledge of the Mach number allows for determination of the flow velocity. Finally, the reaction time is obtained by dividing the distance between the nozzle exit and the LIF image point, by the flow velocity. Typical reaction times are on the order of a few hundred microseconds for the nozzles and distances employed in these experiments.

The photolysis experiments define the reaction time as the difference in time between the photolysis laser pulse and the LIF laser pulse, which is easily adjusted with the use of a suitable delay generator. Both laser beams copropagate through the flow, instead of intersecting it at right angles, as in the case of our experiment, and they image the resulting fluorescence at a fixed point, rather than by translation.

The second difference between the Tucson apparatus and the two found in France and the UK, is the pulsed nature of the experiment in Tucson. As hinted earlier, the reduction in duty cycle gained by going pulsed (approximately 20) allows for the flow experiments to be conducted at reasonable pumping speeds, such as those attained by a
single moderately sized roots pump. Indeed the continuous machines require multiple pumping stages for the remarkably high consumption rates of their nozzles run in a continuous mode. It is emphasized that there is no apparent down side to running these instruments in a pulsed fashion, as long as the chamber size and pumping speed are sufficient to make $dP/dt \approx 0$, so that shock structure and perturbations to the flow are not introduced. At 1 Torr chamber pressure and a flow rate of 2 standard liters per minute, a typical pulse adds approximately 15.2 liters of gas to the chamber, while the roots pump at 300 cfm, is capable of removing 1.1 liters in this same time duration. At an estimated chamber volume of 560 liters, the calculated change in chamber pressure is 2.5% during the duration of the pulse. A typical experiment is conducted in 200 - 300 μsec in the middle of a 5 ms pulse, which effectively looks continuous to the time duration of the experiment. In fact, the pulsed experiments are regarded with a much lower cost of operation, not only in the equipment necessary for operation, but also in the cost of reactant and buffer gases employed. At a typical cost of a few hundred dollars per liter for reactant purity and isotopically labeled gases, the low consumption rate is quickly appreciated.

2.3. Nozzle Flow Characterization

Section 2.1 presented the fundamental principles applicable to nozzle design and implementation, and introduced the idea of the one dimensional relationships, Equations 2.9 – 2.11, which demonstrated that the ratio of the flow properties are related solely to
the Mach number and the heat capacity ratio $\gamma$. While these are theoretically achievable, it is also desirable to have methods of flow characterization available to the experimentalist to ensure that indeed the flow parameters predicted from the isentropic relationships are being established. Further, establishment of equilibrated flows at well defined temperatures and pressures is essential to the researchers interested in studying chemical processes that are sensitive to both of these parameters. Two methods of flow characterization have been employed, the pitot method for extraction of the flow Mach number and uniformity as a function of distance from the nozzle exit, and LIF for rotational temperature measurement, and are discussed below.

Pitot measurements have traditionally been used to measure the speed of an aircraft but are adapted here to measure the speed of the Laval flow. Briefly, a pitot tube is a device capable of measuring the difference in strain experienced by a differential pressure transducer exposed to two different environments. In the case of an airplane one side of the transducer is connected to a tube that is pointed in the direction of travel of the aircraft, while the other side is connected perpendicular to the direction of travel. In this geometry the transducer is able to measure the dynamic pressure exerted on the tube connected in the direction of the aircraft travel, and the static pressure of the environment by the perpendicular tube. The reason for doing so comes from Bernoulli’s Equation, which states that the total pressure is the sum of the dynamic pressure and the static pressure. Further, the dynamic pressure is defined as
where $P_d$ is the dynamic pressure, $\rho$ is the density, and $v$ is the velocity. From the expression for the total pressure

$$P_t = P_s + P_d$$

(2.23)

the velocity can be obtained, and is equal to:

$$v = \sqrt{\frac{2(P_t - P_s)}{\rho}}$$

(2.24)

Therefore, a measurement of the total pressure, static + dynamic for the parallel tube, and the static pressure by the perpendicular tube allows for a determination of the velocity. When the flow velocity gets high enough, in the supersonic regime, a shock forms at the front of the tube and the assumptions inherent in Bernoulli’s equation are violated, and corrections need to be made. However, if the flow is assumed to be isentropic, and the probe measures the total pressure along the flow, then the supersonic Rayleigh-Pitot equation can be used to derive the Mach number, Equation 2.21. The pulsed nature of the supersonic expansion provides an obstacle to the measurement of Mach numbers, due to the fact that the transducer sees only the total pressure including the supersonic
component, for a fraction of the time when the nozzle is operating. As a result, the response time of the transducer must be faster than the duration of the nozzle pulse, in order to accurately sample the conditions found in the supersonic portion of the flow, and discriminate between the static pressure during the times when the nozzle is off. These experiments employ a differential pressure transducer produced by Omega (PX-170) with a response time of 1 ms, which produces an output voltage proportional to the differential pressure applied. They are based on an active-four-element piezoresistive bridge, and include a thermistor to reduce temperature drift. The voltage is amplified using a homebuilt amplification circuit with gain equal to 8x or 80x. There is an inherent drift in the output voltage of the amplification circuit as a function of time after the device is turned on, Figure 2.13. The drift becomes important when calibrating the pressure transducers, and as a result, the amplifiers were always allowed to warm up for at least an hour before making measurements with them. Further, the stability of the output voltage was verified using an oscilloscope. Calibration curves for the pitot and stagnation transducers are shown in Figure 2.14. The calibrations were accomplished by connecting the reference side (P2) of the transducer to vacuum, and applying known pressures to the active side (P1) of the transducer. At each pressure the output voltage was recorded. This was done for pressures up to 40 Torr. In all cases the pressure on the active side was measured with a differential capacitance manometer, (MKS Baratron 220CD).

Once successful calibration of the transducers was accomplished they were used as measurement tools to derive the flow properties for the Laval nozzles available in the laboratory. The stagnation transducer was used to derive the time evolution of the Laval
Figure 2.13. Transducer output circuitry drift during warm up. Stable output voltage is critical for proper transducer calibration. The transducers were always allowed to warm up for at least an hour before measurements were made.
Figure 2.14. Calibration curves for the stagnation and pitot transducers. The pressure for these experiments was measured using an MKS differential capacitance manometer.

\[
\text{Pitot Fit- Out (mV)} = [7.34 \times \text{Pressure (Torr)}] - 0.62
\]

\[
\text{Stagnation Fit- Out (mV)} = [7.87 \times \text{Pressure (Torr)}] - 0.31
\]
pulse in the stagnation region relative to the trigger pulse, Figure 2.15. The trigger pulse shown is the current through the coil measured at the current monitor indicated in Figure 2.9. The figure reveals a 1 ms lag time due to the mechanical properties associated with the valve opening, followed by a sharp rise to a 4 ms plateau. It is the plateau region that is used for experiments. The pitot transducer is mounted to an optical rail inside the vacuum chamber that allows for its placement in the center streamline of the Laval flow at a distance of approximately 2 cm below the axis of the laser beam. The alignment of the pitot transducer and the Laval flow was accomplished using an alignment jig. The jig was turned on a lathe from nylon material so that its inner diameter matched that of the Laval nozzles outer diameter. A hole was drilled in the center, while still mounted in the lathe, through which an alignment rod of 20 cm in length was attached. The alignment rod was ground to a fine point on one side. The device could then be attached to the nozzle with a set screw and used to align the centers of the nozzle and the transducer at variable nozzle to transducer distances. The advantage of permanently attaching the pitot mount to the optical rail at a distance lower than the laser axis is that the transducer could be left in place during kinetic runs, and therefore be used in real time to ensure flow uniformity.

The pitot transducer was used in conjunction with the Rayleigh-Pitot equation, Equation 2.21, to find the best conditions leading to uniform flows for the longest amount of time, i.e. farthest distance from the nozzle exit. It was found in general that the best nozzle performance corresponded to the perpetuation of supersonic flow for the longest distance (20 cm for the Mach 3 nozzles, and 7 cm for the Mach 2 nozzle).
Figure 2.15. Laval nozzle pulsed valves response to the trigger. The trigger pulse is designed to rapidly open the pulse valve with a high voltage leading edge, followed by maintenance of the open condition requiring 12 Volts.
While conditions could be found that generated reasonable flow for a few centimeters past the nozzle exit, they were generally not the conditions anticipated from the isentropic relationships, and therefore conditions were sought that best satisfied the anticipated conditions. The best conditions were found in an iterative fashion by adjusting either the flow rate into the nozzle and thus the stagnation pressure, or by varying the chamber pressure, and scanning the flow in either 0.5 or 1 cm increments, until the flow parameters (temperature and mach number) were found to be constant to within ± 10% for the largest amount of distance.

Once the best flow parameters were found using the pitot transducer, and the flow temperature derived from the Rayleigh-Pitot equation, the LIF method was employed as an independent measurement of the rotational temperature, and thus the flow temperature, as all degrees of freedom in the flow are equilibrated. The LIF technique allows for extraction of the rotational temperature because the area under the absorbing peak is proportional to the population in that state. With knowledge of the fluorescence regime and the rotational line strength factors for each individual transition and use of the Boltzmann equation the rotational temperature can be obtained. Rotational temperatures were obtained by scanning the excitation laser frequency through a number of rotational transitions in the ground state of the OH or OD radical. A preference for OD was found as the smaller rotational constant (10.02 cm\(^{-1}\) vs. 18.91 cm\(^{-1}\) for OH\(^7\)) allows for greater population in higher rotational states at a given temperature, and thus more data points for curve fitting and error analysis. The fluorescence signal intensity \(I_i\) obtained when
excitation occurs from a specific ro-vibrational level \( i \) in the ground state to a level \( f \) in the excited state is

\[
I_i = G \Phi_f B_i N_i
\]  

(2.25)

where \( G \) is a constant accounting for the light collection efficiency, \( B_i \) is the excitation line strength factor for the respective rotational transition, \( N_i \) is the population in the ground state rotational level, and \( \Phi_f \) is the fluorescence quantum yield. \( \Phi_f \) can vary greatly depending on the environment in which the probed species resides and also on the transition that was pumped. It is defined as

\[
\Phi_f = \frac{A_f}{A_f + Q + k_p}
\]  

(2.26)

where \( A_f \) is the Einstein A coefficient for spontaneous emission of a photon, \( Q \) is the total collisional quenching rate which will be pressure dependent, and \( k_p \) is the predissociation rate. Within a rotational band the \( \Phi_f \) is assumed to be constant, and the peak areas are converted to a population using the appropriate \( B_i \) value. All of the measurements were made in the linear fluorescence regime, and the laser power was continuously monitored and recorded throughout the duration of the scans. It was also used to normalize the signal intensity. The population for a number of states, usually between 3 and 5, was then used to extract the rotational temperature through the Boltzmann equation:
The distribution for molecules in particular rotational levels is given by

\[
\frac{N_i}{N_j} = \frac{g_i e^{-\frac{(E_i - E_j)}{kT}}}{q}
\]  

(2.27)

where \( N_i \) and \( N_j \), \( g_i \) and \( g_j \), and \( E_i \) and \( E_j \) represent the population, degeneracy, and energy of the \( i \)th and \( j \)th states, respectively. Since the collection efficiency is not known, relative intensities are used to extract the flow temperature, and Equation 2.25 can be expressed as

\[
\frac{I_i}{I_j} = \frac{B_{\beta i} N_i}{B_{\beta j} N_j}
\]  

(2.29)

assuming that the collection efficiency and fluorescence quantum yield are the same.

Substitution of Equation 2.28 into Equation 2.29 yields

\[
\frac{I_i}{I_j} = \frac{B_{\beta i} g_i e^{-\frac{(E_i - E_j)}{kT}}}{B_{\beta j} g_j}
\]  

(2.30)
and from this equation it is realized that a plot of the \( \ln(I_i/g_iB^E) \) vs. \( E_i/k \), or similarly \( \ln(N_i/g_i) \) vs. \( E_i/k \), where \( E_i \) is the energy of the rotational state, \( k \) is Boltzmann’s constant, and \( g_i \) is the degeneracy of that state, yields a linear plot with a slope equal to \(-1/T\).

Linear least squares analysis gave the error associated with each measurement. LIF spectra were taken at various positions in the flow and the temperatures obtained were compared to the temperature obtained from the pitot measurements. A representative LIF spectrum, Boltzmann plot, and obtained temperature plot from both characterization methods are shown in Figures 2.16, 2.17, and 2.18 respectively. Agreement between the two methods is observed for all of the nozzles characterized in these studies. Table 2.1 summarizes the characterization results. The flow conditions quoted are those that were found to give the best flow.

<table>
<thead>
<tr>
<th>Nozzle</th>
<th>Mach #a</th>
<th>Stagnation Temp (K)</th>
<th>( T_{\text{flow LIF}} ) (K)</th>
<th>( T_{\text{flow Impact}} ) (K)</th>
<th>Flow Density (10^{10} cm^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>ArM32e16</td>
<td>3.5</td>
<td>263</td>
<td>53 ± 4</td>
<td>53 ± 3</td>
<td>3.2 ± .2</td>
</tr>
<tr>
<td>N2M32e16</td>
<td>3.2</td>
<td>273</td>
<td>83 ± 3</td>
<td>89 ± 5</td>
<td>1.7 ± .2</td>
</tr>
<tr>
<td>N2M33e16</td>
<td>2.5</td>
<td>300</td>
<td>135 ± 11</td>
<td>132 ± 6</td>
<td>4.5 ± .5</td>
</tr>
<tr>
<td>N2M21e17</td>
<td>1.7</td>
<td>300</td>
<td>188 ± 7</td>
<td>183 ± 4</td>
<td>14.1 ± .6</td>
</tr>
</tbody>
</table>

a Mach number derived from LIF temperatures
Figure 2.16. OD LIF A $^{2}\Pi \leftarrow X \: ^{2}\Sigma (\nu' = 1 \leftarrow \nu'' = 0) \: S_{21}(N)$ branch spectrum taken at 135 K using the N$_2$M33e16 nozzle.
Figure 2.17. OD Boltzmann plot used to extract the rotational temperature from the flow. The plot is the natural log of the normalized population (N_i/g_i) versus the rotational energy of the state. Here N_i is the population and g_i is the degeneracy of the rotational state.
Figure 2.18. Temperature profile of the N₂M33e16 nozzle as a function of distance from the nozzle exit. Filled squares are the temperatures derived from the LIF spectra. Open circles are the temperatures derived from the pitot impact measurements.

\[ T_{\text{flow LIF}} = (135 \pm 11) \text{ K} \]
\[ T_{\text{flow Pitot}} = (132 \pm 6) \text{ K} \]
CHAPTER 3. IMPLEMENTATION OF A TUNABLE VACUUM AND EXTREME ULTRAVIOLET FREQUENCY LIGHT SOURCE FOR THE STUDY OF H ATOM CHEMISTRY AT LOW TEMPERATURES

3.1. Background

Laser based studies of radicals and atoms are generally limited by two factors: knowledge of their electronic spectroscopy and ease by which radiation of the appropriate frequency can be generated in the laboratory. For most diatomic radicals the first excited state lies in the UV making them readily accessible for study using conventional pulsed laser systems which can easily create tunable coherent radiation in this region of the electromagnetic spectrum using doubling crystals. However, for species with the first transition in the vacuum ultraviolet (VUV), or for spectroscopic studies in a higher frequency range, such as the extreme ultraviolet (XUV), other methods must be used to probe these transitions. These can be either single or multiphoton processes, with preference for the first due to the higher transition moment and conversion efficiencies normally found. Of course, all of these hurdles are easily overcome with the use of synchrotron radiation. Unfortunately, the limited access to these instruments makes them an inconvenient tool for most researchers. As a result other methodologies are sought that produce tunable radiation in the frequency range of interest with spectral characteristics suitable for the study of radical processes.
Described herein is the design and implementation of a tunable VUV and XUV radiation source based on four wave sum and difference frequency mixing, coupled to the pulsed supersonic Laval nozzle reactor, for the purpose of studying atomic radical processes in the flows. The theory of non-linear frequency mixing is presented, the spectral characteristics of the source are compared to other sources, and the application of the technique is demonstrated for the LIF detection of H atoms through the single photon Lyman $\beta$ transition at 102.5 nm.

3.2. Non-Linear Frequency Mixing

The reason for the lack of broadly tunable laser sources operating in VUV and XUV stems from a fundamental limitation in the emission process between two states. Laser action requires the establishment of a population inversion between two states, such that the gain realized from stimulated emission from the excited state exceeds the losses per round trip in a cavity due to a number of processes including spontaneous emission, scattering, reflectivity and absorptive losses. The threshold condition for lasing, Equation 3.1, states that if the inverted population difference $\Delta N$ of the active medium is larger than the threshold losses, the wave that is reflected back and forth in the cavity will be amplified, and is initiated by spontaneous emission

$$\Delta N = N_2 \left( \frac{g_1}{g_2} \right) - N_1 > \Delta N_{thr} = \frac{\gamma}{2\sigma(v)L}$$  \hspace{1cm} (3.1)
where \( g_1 \) and \( g_2 \) are the degeneracy of the ground and excited state, respectively, \( N_2 \) and \( N_1 \) are the population in the state, \( \gamma \) is a constant accounting for the intensity losses, \( \sigma(\nu) \) is the cross section for the transition \((E_1 \rightarrow E_2)\), and \( L \) is the length of the active medium. The probability that a molecule will be in a specific state due to the interaction of a radiation field with a two level system, is expressed by the following relations

\[
\frac{d}{dt} P_{12} = B_{12} \rho(\nu) \tag{3.2}
\]

\[
\frac{d}{dt} P_{21} = B_{21} \rho(\nu) + A_{21} \tag{3.3}
\]

where \( \frac{dP_{ij}}{dt} \) represents the probability per unit time that a molecule will absorb or emit a photon, \( B_{ij} \) is the Einstein coefficient of induced absorption (Equation 3.2) or emission (Equation 3.3), \( \rho(\nu) \) is the spectral energy density of the radiation field, and \( A_{ij} \) is the Einstein coefficient of spontaneous emission. Relationships between the three coefficients can be obtained by considering the distribution of the total number of molecules in specific energy levels \( E_i \). In thermal equilibrium the population distribution is dictated by the Boltzmann equation. Further, in a stationary field the total absorption rate has to equal the emission rate, so that the spectral energy density remains constant. Under these conditions one obtains for the spectral energy density \( \rho(\nu) \), the following expression
where \( \nu \) represents the frequency and \( k \) is Boltzmann’s constant. Realizing that the spectral energy density in a thermal radiation field derived from Planck’s law equals

\[
\rho(\nu) = \frac{A_{21}}{B_{21}} \left( \frac{g_1}{B_{12}} \right) \exp \left( \frac{\hbar \nu}{k_B T} \right) - 1
\]

(3.4)

where \( c \) is the speed of light, allows one to obtain the following fundamental relationships:

\[
\rho(\nu) d\nu = \frac{8\pi \nu^2}{c^3} \frac{\hbar \nu}{\exp \left( \frac{\hbar \nu}{k_B T} \right) - 1} d\nu
\]

(3.5)

It can immediately be realized from Equation 3.7 that as the frequency of the transition is increased, or alternatively as the wavelength is decreased, the ratio of stimulated to spontaneous emission drops rapidly. As a result it becomes increasingly harder to
maintain the population inversion necessary for lasing. Therefore, alternative methods are sought that produce tunable VUV and XUV radiation with characteristics similar to that of the more common UV and visible laser pulses.

One of the methods designed to circumvent the above problem is the use of non-linear frequency mixing techniques. They use the high energy available from the output pulse of dye lasers, in conjunction with a non-linear medium, to upconvert the input frequencies, in a manner that retains the properties of the input beams, i.e. coherence and polarization. The theory behind the generation of tunable VUV and XUV radiation by frequency mixing techniques is described in two excellent reviews by John W. Hepburn and Robert H. Lipson and is summarized below.

The nonlinear response of a medium to an applied external field, under moderate laser intensities, can be expressed by a Taylor expansion of the induced polarization \( P(\omega) \), as a result of the applied oscillating electric filed \( E(\omega) \)

\[
P(\omega) = N(\chi^{(1)} \cdot E(\omega) + \chi^{(2)} \cdot E(\omega) \cdot E(\omega) + \cdots)
\]  (3.8)

where \( N \) is the number density of the medium, \( \chi^{(i)} \) is the \( n^{th} \) order nonlinear susceptibility tensor of the medium, and \( E(\omega_{i,k}) \) can either be the same or different frequencies. \( \chi^{(1)} \) is the linear term responsible for traditional effects such as the absorption effects of a material, while the higher order terms \( \chi^{(i)}, i \geq 2, \) are responsible for nonlinear harmonic frequency generation, due to the oscillating induced polarization generated by the strong field. \( \chi^{(2)} \) is responsible for second harmonic generation crystals, commonly used to
double input laser light, and remains non-zero only for systems possessing a center of
symmetry, such as crystalline media. The main repercussion resulting from the
requirement that the nonlinear susceptibility must not vanish, in the case of frequency
doubling, is that most crystals become opaque in the VUV and XUV, and thus create a
limiting frequency that can be generated by solid media. This limit currently resides at
189 nm for BBO. In addition, shorter wavelength generation is then dominated by the
third order susceptibility tensor in isotropic gaseous media, where the second order term
is zero. Interestingly, third harmonic output generation can occur at a number of
frequencies due to the fact that the susceptibility tensor is dependent on three oscillating
electric fields which need not be equal in frequency, with \( \omega_{\text{Out}} = \omega_1 \pm \omega_2 \pm \omega_3 \). The term
four wave mixing arises due to the fact that there are four oscillating fields present in the
medium, three input and one output. Three distinct possibilities arise from these
circumstances; non-resonant tripling (THG) where \( \omega_{\text{Out}} = 3\omega_1 \), four wave sum frequency
mixing where \( \omega_{\text{Out}} = 2\omega_1 + \omega_2 \), and four wave difference frequency mixing where \( \omega_{\text{Out}} = 2\omega_1 - \omega_2 \). Each of the three cases is discussed as they were all utilized at some point
during the implementation of VUV generation.

Non-resonant tripling is best described by the energy level diagram of Figure 3.1.
The VUV output at \( 3\omega_1 \) arises when a two photon resonance to a Rydberg state of the
medium is approached. In addition the third photon must be of sufficient energy to access
Figure 3.1. Energy level diagram indicating the states used in non-resonant third harmonic generation. The input frequency $\omega_1$ is tripled producing an output frequency $\omega_{\text{UV}} = 3\omega_1$. 
the ionization continuum. Two restrictions on THG severely limit the frequency range in which this technique can be applied. First, the necessity that $2\omega_1$ be near a Rydberg resonance greatly limits the tunability of this technique, and secondly the phase matching requirement that the medium be negatively dispersive forbids THG whenever the refractive index at $3\omega$ is higher than at $\omega$. Typically these negatively dispersive regions are found to the blue of resonance lines, and can produce tunable radiation, albeit at varying intensities, for a few nanometers, before a gap arises. While narrow tunability at first seems like an inherent limitation for the technique, there are a number of rare gas atoms that produce THG, allowing for THG over a wide range of frequencies by carefully selecting the tripling medium. Commonly used gases are Xe, Kr, Ar, and Hg.

The output intensity at $3\omega$ for THG is expressed as

$$I_{3\omega} = N^2|\chi^{(3)}(3\omega)|^2 I_\omega F(b\Delta k)$$

(3.9)

where $I_\omega$ is the intensity at the fundamental wavelength, $N$ is the number density of the medium, $\chi^{(3)}$ is the third order susceptibility tensor, and $F(b\Delta k)$ is the phase matching function which places restrictions on the refractive index of the medium, $b$ is the path length of the medium, and $\Delta k$ is the wave vector mismatch function that is wavelength dependent. Typical conversion efficiencies for the THG process are $10^{-3}$-$10^{-6}$, leading to approximately $10^9$ photons per pulse when created with millijoule pulses from conventional dye lasers.
Significant gains in tuning ability and conversion efficiency can be realized by exploiting the resonant nature of the two photon resonance, and led to the development of four wave sum and difference frequency mixing. An energy level diagram for the sum and difference frequency mixing schemes is shown in Figure 3.2. It differs from THG in the respect that it is a two laser process, and derives tunability from the fact that one laser supplying two photons of frequency $\omega_1$ is tuned to the two photon resonance, denoted state (b), while the other laser, supplying frequency $\omega_2$ is tunable, with an output frequency equal to $\omega_{\text{UV}} = 2\omega_1 + \omega_2$ for sum frequency mixing and $\omega_{\text{UV}} = 2\omega_1 + \omega_2$ for difference frequency mixing. The output intensity is now proportional to two input intensities

$$I_{\text{UV}} = N^2 \left| \chi^{(3)}(2\omega_1 \pm \omega_2) \right|^2 I_{\omega_1} I_{\omega_2} F(b\Delta k)$$

and the phase matching conditions now depend on three frequencies, rather than the two in THG. The expression for the $\chi^{(3)}$ term responsible for the four wave mixing phenomena perhaps best illustrates the situation:

$$\chi^{(3)}(2\omega_1 \pm \omega_2; \omega_1, \omega_1 \pm \omega_2) = \frac{1}{\hbar^2} \sum \frac{\langle g | e_4 \mu | a \rangle \langle a | e_1 \mu | b \rangle \langle b | e_2 \mu | c \rangle \langle c | e_3 \mu | g \rangle}{(\Omega_{ge} - \omega_1)(\Omega_{ge} - 2\omega_1)(\Omega_{ge} - 2\omega_1 \pm \omega_2)}$$

The summation in the numerator contains the dipole transition moment matrix elements, where $e_i$ is the unit vector denoting the polarization of the wavevector $i$, and $\mu$ is the
Figure 3.2. Energy level diagram indicating the states used in the four wave mixing process. The input frequencies $\omega_1$ and $\omega_2$ are combined producing an output frequency $\omega_{DFM} = 2\omega_1 - \omega_2$ for difference frequency mixing and $\omega_{SFM} = 2\omega_1 - \omega_2$ for sum frequency mixing.
electric dipole moment operator. They are non-vanishing when the selection rules for two photon rules are obeyed. The numerator describes the resonant enhancement terms available to the process, where $\Omega_{jk}$ is the complex frequency for the specified transition and contains a linewidth contribution, Equation 3.12

$$\Omega_{jk} = \omega_{jr} - i \frac{\Gamma_j}{2}$$

(3.12)

where $\omega$ represents the energy between the two states, and $\Gamma_j$ is the linewidth of the $j^{th}$ level. The first term in the denominator ($\Omega_{ag} - \omega_1$) represents a linear absorption for the medium and thus a loss process for the frequency mixing scheme and is undesirable. Gains in the conversion efficiency due to resonance enhancements in $\chi^{(3)}$ are due to the second and third terms in the denominator of Equation 3.11, $(\Omega_{bg} - 2\omega_1)$ and $(\Omega_{cg} - 2\omega_1 \pm \omega_2)$. The former the two photon transition to the intermediate state, the latter represents a gain when the generated $\omega_{VUV}$ is resonant with a transition in the medium.

Tunability for the four wave sum and difference frequency mixing schemes are much better than those of the non-resonant case, however it must be realized that the phase matching conditions often limit the usable wavelength region. Nevertheless, nearly all of the VUV and XUV region can be covered by employing resonant enhanced four wave mixing in Kr, Xe, Hg, and Mg media. The specific regions for each atom are as follows: Kr 94 to 70 nm and 125 to 224 nm, Xe from 108 to 78 nm and 152 to 328 nm, Hg from 129 to 102 nm and 250 to 164 nm, and Mg from 174 to 140 nm, with conversion
efficiencies as high as 5% in some cases, corresponding to greater than $10^{11}$ photons per pulse. The linewidth for the produced VUV/XUV radiation generally follows the linewidth of the input sources and can be made as small as 0.008 cm$^{-1}$, in the 10 – 17 eV (124 – 73 nm) range,$^7_5$ and more recently less than 0.2 cm$^{-1}$ for frequencies up to 20 eV (62 nm),$^7_6$ allowing researchers to conduct elegant experiments in the field of high resolution photoelectron spectroscopy. One can see that these numbers compare nicely to the 5 – 30 eV output of the Chemical Reaction Dynamics Beamline at bend 9.02 of the Advanced Light Source (ALS), with intensity of $10^{11}$ photons/sec/0.01% Bandwidth.

Further, although the repetition rate attainable by the laser based method of VUV creation is much smaller than the ALS, approximately 20 Hz to 500 MHz, the power consumption of a table top laser falls much lower than that required to accelerate a 400 mA electron beam to 1.9 GeV.

3.3. Implementation of the Frequency Source

The approach used in these experiments for the detection of H atoms is the use of four wave sum frequency mixing in a xenon medium, for the production of coherent Lyman $\beta$ radiation at 102.57 nm. The LIF scheme originally envisioned was a one photon pump from the ground state $n = 1$ to $n = 3$, followed by collection of the subsequent Balmer $\alpha$ fluorescence at 656 nm. Generation of wavelengths shorter than 104 nm requires the use of a windowless environment, as the available window materials become opaque below this value. As a result, it is necessary to generate the four wave sum
frequency radiation in the same vacuum chamber as the experiment is being conducted in. Further since the medium used to generate the VUV radiation is lost to the vacuum chamber, and is quite costly in the case of xenon, it was desirable to pulse the gaseous medium into the chamber for short durations at the same repetition rate as the laser. In doing so the consumption rate of xenon was greatly reduced. In addition the pulse valve (General Valve Series 9, 0.4 mm orifice) was housed in a Tee with a 0.250” through hole that served as a restrictor to the expansion, creating in effect a static like situation that allowed the density of xenon to build up to a high enough level to allow for the efficient creation of the VUV wavelengths. A schematic of the experimental setup is shown in Figure 3.3. It consists of the same elements as those described in the Experimental section 2.2, Figure 2.8, with the addition of an additional laser, beam combining optics, a 30 cm focusing lens, and the xenon pulse valve and housing.

Pulse timing and an understanding of the time evolution of the pulses is absolutely crucial to this experiment to ensure that, for instance, the density in the xenon chamber has reached its optimal value when the laser pulses arrive. A detailed timing diagram is shown in Figure 3.4, and represents the conditions that led to optimal LIF signal. Experiments to reveal the temporal response of the pulse valves to the trigger were first conducted. The Laval pulse valves (General Valve Series 9, large bore) time response has already been shown, Figure 2.15, and one sees upon inspection that a 3.5 ms trigger originating at \( T_0 \) produces a 5 to 6 ms pulse duration, with a mechanical lag of 1 ms, and a rise time of another 1 ms before the steady state pressure is achieved. The pressure for these experiments was measured in the stagnation region with the stagnation
Figure 3.3. Schematic of the setup used in the four wave frequency mixing experiments.
Figure 3.4. Timing diagram of the pulse delay sequence used to conduct the four wave mixing experiments. All times quoted are with respect to \( T_0 \). Delays A through D are generated using the SRS DG-535 digital delay generator.
transducer (Omega PX-170 series, rise time = 1 ms). Similar experiments were conducted on the xenon pulse valve residing in the tee shaped housing. In order to determine the temporal pressure response of the xenon valve, the stagnation pressure transducer was attached to one side of the tee by sealing it to a threaded light baffle which mated to the tee. The pulse valve was backed with 30 psig of helium gas, and the valve was triggered with a 180 μsec duration pulse. The response can be seen in Figure 3.5. Again, a significant mechanical delay is observed, although shorter than in the case of the large bore Laval pulse valves, with a much slower rise time to steady state conditions, most likely due to the much lower conductance through the 0.4 mm orifice, and the open ended tee. While this is not the ideal test to the true nature of the pulse time duration, as the conductance through the tee was cut in half by addition of the stagnation transducer, it served to elucidate the pressure vs. time dependence of the valve to first order and provided a starting point in time for conducting the four wave mixing experiments. In reality, the optimal delay was chosen by adjusting the trigger delay of the xenon pulse valve and monitoring the LIF signal.

The value of 180 μsec Xe pulse valve trigger duration was chosen as it provided enough time for significant pressure build up in the mixing cell, allowed for a resultant actual pulse duration of approximately 2 ms FWHM sufficient to flush residual background gases out the cell at the beginning of the pulse, and is a value typically used by other researchers employing this technique. Longer trigger durations did not result in significant gains in LIF signal observed, while shorter ones, on the order of 100 μsec led to a marked decrease in LIF signal and erratic pulse valve behavior, including failure to
Figure 3.5. Oscilloscope trace of Xe pulsed valve response to external trigger. The ordinate time scale is 1 ms/div. Lower trace is the external trigger of duration 180 μsec. Upper trace is pressure transducer signal.
open. Helium was employed in these tests because stringent efforts to conserve xenon were always made.

With the mechanical response of the individual pulse valves understood, the time of arrival of the lasers was chosen. It was desirable to work in the middle of the Laval pulse, as this is the region least affected by pulse valve instabilities, and an arrival time of approximately 5.7 ms with respect to $T_0$ was chosen. Choice of this time was also justified by the fact that it allowed the other important delays, i.e. the discharge trigger and xenon pulse valve trigger, to be freely varied without reaching limits in their time evolution.

The discharge trigger was set so that it was terminated approximately $450 \mu\text{sec}$ before the arrival of the laser pulses. This time had been found previously to give good radical signal for OH LIF, while simultaneously allowing time for collisional relaxation events to initiate. Therefore the trigger originated at 2.9 ms with respect to $T_0$ for a duration of 2.2 ms.

The difference in the absolute value in timing of the two laser pulses ($A + B = 5.686007$ ms for the YG660, and $C + D = 5.686$ ms for the NY61-10, $\Delta t = 7$ ns) represents the time required for the two laser pulses to arrive at the same point in time and space at the entrance to the vacuum chamber, and was measured with a fast rise time photodiode and a 400 MHz oscilloscope (Tektronics TDS 380). It is important to ensure that the photodiode is not saturated during the measurement, so that the true laser pulse width is measured, and further that the pulse being measured is the actual laser pulse and not merely a reflection off an optical surface that reaches the diode. To this effect the
beams were terminated at various points along their path during the photodiode measurements to ensure that the measured signal vanished. The difference of 7 ns in absolute Q-Switch triggering time accounts for the difference in path the two beams travel in their route to the chamber, as well as the lasers inherently different response to the Q-Switch trigger itself. The Tektronics oscilloscope is capable of collecting 2 GigaSamples/sec, corresponding to a data point every 0.5 ns, thus ensuring that a laser pulse of 4 to 8 ns duration consists of 8 to 16 points. This resolution, while not ideal, is enough to capture the inherent Q-switch time jitter of 1 to 2 ns, as well as mode structure in the laser pulses when it was occurring. The optimal time between the laser pulses leading to maximum LIF signal, and thus maximum conversion efficiency was found to change throughout the course of the day. A detailed account of the H atom signal stability follows later in this chapter.

Spatial alignment of the laser beams is also of utmost importance in laser frequency mixing techniques, as they must co-propagate and focus to the same spot within the pulse valve tee in order to achieve good conversion efficiency for the four wave mixing process. The beams are combined using a KrF series 248 nm Excimer laser calcium fluoride laser mirror from CVI (Part # KrF-1025-45-P). The mirror is designed to reflect p-polarized light off its high damage threshold dielectric coating at 45° incidence with near 100% reflectivity. The UV beam is reflected off the front surface at 45° incidence, while the visible beam is transmitted through the back surface. Spatial verification of the beam overlap was confirmed using an index card at the front surface of the combing optic. In addition, two permanently mounted apertures (Iris diaphragms, ID-
1.0, Newport Corp.) were used in series along the beam path to ensure copropagation of the beams, one placed approximately 8 feet from the combining optic, and the other just before the 30 cm focusing lens. The far distances were chosen as they gave the best alignment resolution. The two beams were also allowed to propagate to the west wall of the lab where they were imaged on a business card, as a final verification of their alignment. Focal alignment was verified as best as possible using one of the Zheng tools available in the lab. The Zheng tool is a thin piece of brass bar stock with a small diameter hole drilled in the center. It is used to verify alignment by placing the hole at the laser focus. On center the focused beam is transmitted through the tool. It is also useful in determining the focal length, as the beam can be heard to snap the brass in the vicinity of the focus. The alignment procedure for the two beams, involved the initial alignment of the visible beam first. Once this beam was centered on all optics and passing thorough the machine in the desired fashion, the UV beam was then adjusted until it overlapped the visible beam. It was often necessary to do so in an iterative manner, as the corrections necessary at the beamsplitter to properly steer the UV beam altered the visible beam path, or cut the beam at the beamsplitter optic holder. Nonetheless, once the alignment was accomplished it could easily be maintained due to the fixed nature of the inline apertures, and by visual inspection at the west wall.

The focusing lens is a 30 cm focal length plano-convex lens made of S1-UV grade fused silica. The particular focal length was chosen to minimize ionization and breakdown processes in the medium that reduces conversion efficiency due to the large field intensity at the waist, while at the same time still allowing enough intensity for
efficient four wave mixing to occur. Typically focal lengths of 6 to 50 cm’s are used in laser based frequency mixing techniques. For a fixed wavelength experiment an achromatic lens may prove to be a better focusing tool, as the calculated difference in focal length for a 30 cm lens focusing a 252 nm beam and a 548 nm beam is 2.87 cm, or a 9% difference, however this was never verified and the VUV generation was never problematic for the experiments.

Absolute calibration of the laser wavelengths was accomplished using optogalvanic spectroscopic methods. Both lasers were calibrated using an iron hollow cathode lamp, by fitting the observed transitions to the well know atomic transition frequencies of neon and iron. However, due to the number of (or lack thereof) lines in a given optogalvanic spectrum and the number of theoretically available lines, it is sometimes possible to obtain two entirely different, although similarly attractive fits, producing a systematic error in the laser wavelength calibration. While this is generally not a problem, because one can scan in wavelength space until the appropriate molecular LIF lines are found and calibrate versus those, say the P, Q, or R branch of hydroxyl radical, a situation was envisioned in the four wave mixing scheme, where great amounts of time could be lost attempting to find signal due to improper laser calibration or laser frequency drift that naturally occurs. This was deemed to be most important for the UV laser that is tuned to the two photon resonance of the medium, because of the enhancement in VUV generation due to the resonance nature of the process. As a result a method was sought that would allow quick, accurate calibration of the UV laser, and would preferably employ the same two photon resonances used in the four wave mixing
scheme. There are a total of three two photon resonances in xenon that are used in four wave sum and difference frequency mixing. They are the $5p^6 1S_0 \rightarrow 6p[5/2]_2$ at 256.0 nm, the $5p^6 1S_0 \rightarrow 6p[3/2]_2$ at 252.5 nm, and $5p^6 1S_0 \rightarrow 6p[1/2]_0$ at 249.6 nm. The excited state levels are commonly designated by the $j\ell K$-coupling scheme. In this scheme, the $j$ of the core electrons, $j = 3/2, j = 1/2$ is coupled with the orbital angular momentum of the excited electron, $\ell$, to give the $K$ quantum number. $K$ then couples with the excited electron spin to give the resultant $J$ and the levels are designated as $[K]_J$. Excitation of one of the $5p^6$ electrons leaves behind a $5p^5$ core, and the Rydberg series spectroscopy is found to converge to the $5p^5 (^2P_{3/2})$ and $5p^5 (^2P_{1/2})$ series ion limits. The selection rules for a two photon transition are $\Delta J = 0, \pm 2$, allowing for population of even parity states in promotion of a single electron from the ground state.

Two photon optogalvanic spectroscopy of Xe has been conducted before in low pressure discharge cells by Piracha et al. and Hanif et al. Both authors describe the construction and operational characteristics of their low pressure discharge cell, and one was constructed in the laboratory using their specifications as a guide. The cell is constructed out of 1.25" OD quartz tubing. The overall cell length is 8.5", with 0.125" thick UV grade quartz windows affixed at each end at the Brewster’s angle to minimize reflections. The windows are affixed with Torr seal, so that a high vacuum could be obtained within the cell. The cell is attached to a Nupro SS-4BG bellows sealed valve through a glass to metal seal. The two electrodes are made from high purity nickel (Goodfellow, 99.5%, 8.4 mm OD) cylindrical rod and are affixed to glass vacuum electrical feedthroughs with silver solder. They reside in the center of the cell at an inner
electrode separation of 15 mm. The anode is connected to a DC power supply (Glassman High Voltage Inc., Model # PS/EQ006R200-22, 0-6 kV, 0-200 mA, reversible polarity) in series with a 60 kΩ ballast resistor. The optogalvanic signal is monitored through a 0.1 μF capacitor (600 V breakdown potential) through the boxcar and the oscilloscope terminated at 50 Ω. Optogalvanic signals arise as changes to the discharge impedance when the dye laser radiation is in resonance with an atomic transition. The signal can be either positive or negative in nature depending on the nature of the photoelectric process leading to the optogalvanic signal. If the laser radiation absorbed produces states which are more easily ionized by electron impact the discharge voltage will drop since the electron temperature required to maintain the discharge decreases. If on the other hand, the radiation is causing stimulated population transfer from excited states downward, the reduction in metastable states decreases and the discharge voltage conversely increases in order to maintain the discharge. The discharge operated here produces negative signals indicating the dominant discharge process is the population of metastable states by the laser wavelength.

The procedure for operating the discharge cell is as follows. The cell is connected to the flight tube vent valve on the free jet apparatus. This allows for the cell to be roughed out with the mechanical pump as well as evacuated to a high vacuum (10⁻⁶ Torr) with the diffusion pumps. The cell was attached via a stainless steel Swagelok cross so that it could simultaneously be connected to a thermocouple, the vent valve, and a tank of Research Grade Xe. The cell and the Xe tank regulator were first roughed out with the mechanical pump to the milliTorr range through the free jet chamber. Once this was
accomplished the cell apparatus was closed off from the free jet pumping system using the vent valve, and the free jet’s 10” diffusion pump was opened, and allowed to operate long enough to bring the baseline pressure in the chamber down to 10^-6 Torr. Once the baseline pressure was established the vent valve was slowly opened, ensuring that the foreline pressure didn’t rise appreciably high to where the diffusion pump would stall. The cell and regulator were pumped down to 10^-6 Torr, usually overnight while baking on the cell and the connected stainless tubing with heating tapes. After the final ultimate pressure was achieved and there was no further evidence of outgassing, the cell was filled with Xe. To do so, the free jet vent valve and the other valve were closed. The diffusion pump was also closed as an additional safety measure. The regulator valve was closed while the tank of xenon was opened, with the regulator set at the lowest setting possible, to ensure that overpressure of the cell didn’t occur. The cell was filled by cracking the regulator valve, and slowly adjusting the flow rate using the needle valve, until the desired pressure was reached (50 – 200 mTorr), as determined by the thermocouple gauge. At this point the cell valve was closed, followed by the regulator valve and tank valve, and the cell was removed from the vacuum line and was ready for use.

In order to conduct the two photon spectroscopy the cell was connected to the oscilloscope and boxcar averager. It was placed in the UV laser beam path with the aide of a labjack, such that the focus of the beam was centered in the anode. The discharge was first struck using the power supply. Typically 400 Volts were required to initiate the discharge, which was the dropped to 250 Volts for operation. Under these conditions the discharge current was typically 4 mA. The breakdown potential on the coupling capacitor
is 600 Volts and as a result the discharge was initiated before the cell was connected to the oscilloscope and boxcar to ensure their safety (their maximum input voltages are much below the 600 Volt breakdown value).

Once the cell was in place and the discharge stabilized, the dye laser was scanned over the wavelength region of interest, and the resulting spectrum collected. The two photon signal is shown in the oscilloscope trace of Figure 3.6, along with the boxcar gate used in that particular experiment. The resulting two photon Xe spectrum is shown in Figure 3.7. All three resonances are observed. For the four wave mixing experiment the UV laser was set 1 cm$^{-1}$ to the blue of the 6p[3/2]$_2$ resonance at 252.48 nm, as this value was found to produce the most signal.

The xenon two photon lamp produced discharge characteristics suitable for spectroscopy for approximately two weeks, depending on the amount of usage. The discharge encompassed the anode and would focus into the cathode, the overall shape dependent on the potential applied to the lamp, with colors ranging from yellow at the anode to a blue/purple color at the cathode, most likely reflective of the different processes occurring at each electrode. Poisoning of the discharge became evident as the voltage necessary to sustain the discharge increased. When the voltage approached 500 Volts, the cell was evacuated and refilled, according to the above procedure.

The YG660 laser, coupled to the homebuilt laser was used to produce the visible beam, and was calibrated solely with optogalvanic spectroscopy employing the hollow cathode lamp. It was necessary to scan the frequency of this laser daily to the resonance wavelength to attain maximum signal. Typically 2 mJ of light were used for experiments,
Figure 3.6. Oscilloscope trace of the xenon two photon optogalvanic signal. The time scale for the x-axis is 0.5 μsec/div. The upper trace represents a 150 laser shot average of the Xe signal, while the lower trace shows the boxcar gate used to collect the two photon optogalvanic spectrum.
Figure 3.7. Xenon two photon optogalvanic spectrum of the $6p[J]_K \leftarrow 5p^6 \, ^1S_0$ series.
although usually 50 to 60 mJ were available. The value of 2 mJ was found to be sufficient to saturate the one photon requirements for the four wave mixing while at the same time producing a minimal amount of scattered light for the experiment. Minimization of scattered light is of utmost importance to the H atom experiment, because it directly affects the signal to noise, due to the fact that the H atom fluorescence lifetime is relatively short in comparison to the laser pulse duration. Under these conditions it is difficult to gate out the scattered portion of the signal using the boxcar or by visual inspection using the oscilloscope.

Tune up of the four wave mixing process was accomplished stepwise using test systems that systematically reduced the complexity of the experiment, so that the variables affecting the generation of the VUV wavelengths could be isolated. Of particular concern at the time was the ability to produce densities of H atoms high enough to exceed their detection limit, and the feasibility of the fluorescence scheme. As a result a search was conducted for stable molecules that could be easily delivered into the machine that had spectroscopic transitions near the wavelength we were interested in for H atoms, 102.5 nm. The best transition according to our calculations was the nitric oxide (NO) B' \( ^2\Delta_i \leftarrow X^2\Pi_{1/2} \) transition with Te = 60364.2 cm\(^{-1}\) (165.66 nm).\(^{72}\) The excited B' state is inverted with the \( ^2\Delta_{5/2} \) state lying 2.4 cm\(^{-1}\) lower in energy than the \( ^2\Delta_{3/2} \) state. The P and R branch transitions for the \( v'' = 0 \) to \( v' =1 \) band were calculated to lie within the interval 61,093 \( \rightarrow \) 61,203 cm\(^{-1}\) (163.68 \( \rightarrow \) 163.39 nm) for \( J'' \) up to 13.5 using the constants in Huber and Herzberg. This interval lies within the wavelength tuning region for difference frequency mixing (\( \omega_{\text{VUV}} = 2\omega_{\text{UV}} - \omega_{\text{VIS}} \)) using the xenon 6p[3/2]\( _2 \)
resonance at 252.48 nm, in conjunction with visible wavelengths near 554.75 nm created using Fluorescein 548 laser dye. Further, it uses the same dyes required to do the sum frequency mixing for the H atom LIF scheme.

The NO experiments were conducted with simplicity in mind. The Laval nozzle and brass body were removed from the translation arm, and were replaced by a 3/8” ID Teflon tube, connected to a microwave discharge cavity. The tube was firmly attached to the translation arm using zip ties, such that translations in Z of the arm, did not affect the tubes x-y coordinate. The reasons for the discharge cavity will be evident later, and are unrelated to this experiment. The discharge cavity is coupled to the vacuum chamber through one of the available KF-40 feedthroughs on the chambers top flange. The cavity in return is connected to the mixing and delivery rack, described in the experimental, such that known, regulated flow rates of NO could be delivered to the chamber. The experiment was arranged such that lasers were aligned on center, 0.5 cm below the exit of the Teflon tube, to provide interaction of the laser beams with the resultant effusive beam of NO emanating from the tubes exit. The photomultiplier tube used was a solar blind model (Hamamatsu R1259) sensitive between 115 – 195 nm.

Two goals were desired of these experiments. The first was to verify the existence of VUV light generation through LIF on the NO molecule, and the second, assuming the first was accomplished, was to find the conditions that optimized the VUV generation. A spectrum of the (NO) B’ 2Δi ← X2Π1/2 (v’ = 1 ← v” = 0) band is shown in Figure 3.8. It shows the signal to noise level of approximately 50, and demonstrates the linewidth of the technique of about 0.9 cm⁻¹ FWHM. Optimal conditions for VUV generation were
Figure 3.8. NO B' ^2Δ_i ← X ^2Π_{1/2} (v' = 1 ← v'' = 0) LIF spectrum in the VUV.
found by tuning to the resonance at 163.42 nm, and systematically adjusting the experimental parameters. First the optimal xenon pulse valve delay for a variety of backing pressures was found by varying the leading edge of the trigger pulse with respect to $T_0$, while holding the pulse duration constant at 160 μsec. Figure 3.9 shows the results.

A number of comments can be made regarding the data in this graph. First, the optimal delay appears between 0.9 and 1.6 ms. This is most likely due to the time dependence of gas density in the pulse which effects the phase matching requirement ($F(bΔK)$) of the four wave mixing process. Further, the time window within which the four wave mixing process occurs widens as a function of the backing pressure on the pulse valve. Again, this can be attributed to the time evolution of the density of the gas pulse, where at higher backing pressure, the density in the mixing tee rises faster than for the lower backing pressures due to the gradient established by the vacuum. Thirdly, the increase in the NO LIF signal as a function of backing pressure, appears fairly constant, within the scatter of the data set, for pressures greater than 12 psig, which can be understood in terms of the absolute number density in the tee, and the dependence of the phase matching requirement on density. Consideration of the results in Figure 3.9, led us to conclude that a pulse valve backing pressure of 12 psig would allow for efficient conversion efficiency while at the same time provide reasonable consumption rates for xenon throughout the duration of the experiment.

The NO LIF signal dependence was then investigated as a function of the pulse duration of the xenon valve at two pressures, 12.5 and 30 psig, at a constant delay of 1.48 ms with respect to $T_0$. The results are displayed in Figure 3.10. No signal is observed at
Figure 3.9. Optimization of the xenon pulsed valve delay as a function of pressure observed by monitoring the NO LIF signal on the boxcar.
Figure 3.10. NO LIF signal as a function of xenon pulsed valve duration taken at two backing pressures.
durations shorter than 100 μsec and is attributed to a lack of opening of the pulse valve. Both pressures investigated lead to a rise in the observed NO LIF signal as a function of the pulse valve duration, with saturation apparent for the 30 psig case at durations greater than about 350 μsec. At 12.5 psig, no saturation of the signal is observed and it may be that under these conditions the valve is not able to achieve a high enough flow rate to efficiently flush out the pulse valve tee and provide the optimal density of xenon.

The final signal characterization involved the dependence on both of the laser powers. The LIF signal was examined by varying the time between the flash lamp fire signal and the Q-Switch fire signal, while holding the other laser conditions constant. In order to do so, and retain good temporal overlap between the two laser pulses, the delay of the flash lamp fire pulse had to be moved with respect to T₀, by the corresponding amount of time that the Q-Switch had been adjusted. Figures 3.10 and 3.11 show the results for the power dependence on the UV and the visible lasers, respectively. For the powers employed in Figure 3.11, 0 to 550 μJ, no saturation of the signal is present. This was typical for all experiments, even those employing higher powers up to about 1 mJ. Producing UV powers at 252 nm in the range of 2 mJ, was possible, with fresh laser dye, but the stability with time was poor, as the power often rapidly decayed as the laser dye degraded. For these reasons, it was much more desirable to work with a dye mixture that was a day or two old, but not older than a few weeks, where it would reliably produce modest, stable power. Contrary to the signal dependence on the UV laser, the visible laser dependence does show saturation effects, Figure 3.12. As was mentioned previously, the visible laser contributed significantly to the amount of scattered light in the system, even
Figure 3.11. NO LIF signal as a function of ultraviolet laser power obtained by varying the NY61-10 Q-Switch delay.
Figure 3.12. NO LIF signal as a function of visible laser power obtained by varying the NY 660 Q-Switch delay.
when the most stringent attempts at light baffling and restriction were employed. As a result, the laser was operated in the linear signal regime, in order to balance the signal to noise. However, at a few mJ, it was still possible to attain approximately 75% of the total signal available.

With the signal dependence understood, the search for H atom LIF signal was undertaken. The first attempts employed a microwave discharge, rather than the Laval nozzle with pulsed DC discharge. Microwave discharges have been proven to deliver extremely high neutral densities for a number of species, due to their ability to efficiently couple large amounts of radiation into a cavity producing intense plasmas. Concentrations of H atoms in the $1 \times 10^{12}$ cm$^{-3}$ range are easily generated by discharging commercial grade Ar or He, and can be increased by poisoning the discharge walls with phosphoric acid. Further, quite high percent dissociations, up to 75%, have been observed for H$_2$ plasmas incorporating surface wave discharges. For these reasons, it was determined to be advantageous to tune up the H atom signal first with a microwave discharge. The discharge used is based on an Optos MPG-4M 100 Watt microwave source operating at 2.45 GHz coupled to a brass tunable resonant frequency Evenson cavity, by means of a coaxial waveguiding cable (RG-393/U). The design characteristics and operational performance of the cavity is described in a report by Fehsenfeld et al. The cavity couples the radiation into a 13 mm OD quartz tube, through which the plasma gases flow. The quartz discharge tube is connected to the chamber through a Cajon fitting mounted to a KF-40 flange. Mixtures of 2 to 3 percent H$_2$ in helium were discharged in this manner at a total discharge pressure of 6 Torr.
The first experiments conducted were done with the solar blind PMT, because the machine was already setup in that configuration. Four wave sum frequency mixing was employed to produce 102.57 nm photons, resonant with the H atom Lyman β transition. Creation of this wavelength requires the use of the xenon 6p [3/2]₂ resonance at 252.48 nm, in conjunction with a 547.09 nm photon. To do so the ND60 dye laser was blue 355 nm pumped by the NY61-10 and operated with Coumarin 503 laser dye. The fundamental out of the dye laser was doubled in a Type I BBO crystal. The fundamental from the second homebuilt dye laser was created by 532 nm pumping Fluorescein 548 dye with the YG660, and was used without further modification. The initial scans revealed the presence of 5 transitions in the Lyman series of H₂. These are the R(0), R(1), R(2), P(1), and P(2) lines of the B \( ^1\Sigma_u^+ \leftarrow X \ ^1\Sigma_g^+ \) \((ν' = 6 \leftarrow ν'' = 0)\), occurring at 68736.57, 68729.85, 68677.80, 68613.71, and 68485.32 cm\(^{-1}\) respectively. Figure 3.13. They are mentioned here, because they serve to demonstrate the utility of the tunability of the four wave mixing technique and also because they are a nice VUV calibrant in the region where the H atom resonance lies. The R(1) and P(1) lines bracket the region of wavelength space between the H atom resonance. They could be easily tuned to in the course of experiments to verify and optimize the production of VUV radiation.

H atom LIF signal was observed on both the solar blind and the visible PMT as a result of the Lyman β pump using the microwave discharge. In the case of the visible PMT the fluorescence detected was the Balmer α transition at 656 nm. Balmer α is the only fluorescence available that falls within the bandpass of the PMT and filter set. The
Figure 3.13. Lyman band $B \leftarrow X \; ^1\Sigma^+ \leftarrow X \; ^1\Sigma^+ \; (v' = 6 \leftarrow v'' = 0)$ spectrum of H$_2$ taken with the solar blind PMT. Shown are the first few transitions of the R(J) and P(J) branches.
filters used were a 656 nm bandpass filter in conjunction with a redpass color glass filter (Corning 2-61). The situation differs for the solar blind PMT. Due to the wavelength sensitivity of 118 – 195 nm, the fluorescence collected must be from Lyman α, which could only result from the relaxation of the initially prepared n = 3 state, to n = 2, followed by subsequent fluorescence at 121 nm to the ground state. In addition, one might argue that the fluorescence collected was actually Lyman β, occurring at the pump wavelength, however, the photocathode of the PMT resides behind a LiF window. LiF material becomes opaque below 104 nm, making it unlikely that the signal results from this transition.

With all the signal characterization and optimization conducted, the hydrogen atom LIF was attempted in the Laval flow incorporating the pulsed DC cold cathode discharge, as this is the scheme that would be used to conduct kinetic experiments. Figure 3.14 shows the 656 nm detection of H atom in an ArM32e17 flow, and represents one of the best attainable scans. Conditions for the scan were as follows. The total signal on the oscilloscope was approximately 1 Volt, with the visible PMT set to 700 Volts. The UV laser power was 300 μJ, the visible was set to 2 mJ by adjusting to the appropriate Q-Switch delay. The boxcar was set to a sensitivity of 1 Volt full scale and the gate width was set at 15 ns. The xenon pulse valve was backed with 12 psig, and the duration was set to 175 μsec. An oscilloscope trace of the amplified PMT signal is shown in Figure 3.15. The oscilloscope settings were 50 ns/div, 0.1 Volts/div, and the signal shown is the average of 100 laser shots, with a total intensity of 781 mV. The width of the fluorescence decay equals 22.5 ns FWHM, and is most likely accurate to within ± 10 ns,
Figure 3.14. H atom LIF spectrum taken in the ArM32e17 nozzle resulting from the Lyman β pump (3p $^2P \leftarrow 1s\, ^2S$), Balmer α (3p $^2P \rightarrow 2s\, ^2S$) fluorescence collected at 656 nm.
Figure 3.15. H atom fluorescence decay profile. The oscilloscope conditions are 50 ns/div, and 0.1 V/div, for the x and y axis respectively. The trace represents a 100 laser shot average, and is 781 mV in amplitude. The lifetime measured at FWHM equals 22.5 ns.
due to limitations in the scopes resolution. At 100 MegaSamples/sec, the scope is taking a
data point every 10 ns, and therefore the peak corresponds to only a few points. The
transition probability for spontaneous fluorescence ($\Lambda_{ik}$) for the $n = 3 \to n = 2$ transition
is reported to be $4.410 \times 10^7$ sec$^{-1}$, while that of $n = 3 \to n = 1$ is $5.575 \times 10^7$ sec$^{-1}$, corresponding to a lifetime ($\tau = 1/\Sigma \Lambda_{3i}$) of 10.02 ns. This value neglects collisional quenching, but is in reasonable agreement with the observed lifetime, especially with the scope resolution taken into consideration.

Following the successful detection of H atoms employing the Lyman $\beta$ pump,
Balmer $\alpha$ fluorescence via production in the DC discharge of the Laval nozzle, kinetic experiments were conducted with the goal of studying the temperature dependent addition of H and D atoms into unsaturated hydrocarbons. Results of this nature are of extreme importance to researchers interested in modeling interstellar environments, as $\text{H}_2$ and H atoms generally compose a large proportion of the gas in molecular clouds. Further, previous studies on these systems have shown that the barrier to reaction decreases with increasing reactant molecular complexity, in going from the series ethylene, acetylene, propene, and the butenes. Inverse temperature dependent reaction rates have been shown to occur in a number of cases now, making this class of reactions particularly attractive for study, as they could lead not only to the incorporation of H atoms into unsaturated hydrocarbons, but also are potentially a viable mechanism by which isotopic fractionation in ultracold environments could occur.

Unfortunately, instabilities in the H atom signal disallowed the extraction of kinetic information for any of the systems attempted. A brief discussion of the sources of
instability and future solutions to these problems is addressed below. The inherent limitation to the successful completion of these experiments stemmed from the inability to reproducibly overlap the laser pulses. The dye laser pulse durations of 4 to 6 ns are only a few times larger than the jitter associated with the individual laser pulses. Continuum specifies a pulse to pulse jitter of ± 0.5 ns, but this number is extremely sensitive to the Marx bank performance. Realistically jitter of ± 1 to 5 ns was observed. One could imagine then that bimodal jitter on two timed laser pulses could result in a number of scenarios ranging from complete pulse overlap, to nearly complete separation. Remembering that the four wave mixing process is sensitive to the square and first power of the input laser intensities, it becomes evident that the efficiency of the process will depend on the amount of overlap of the pulses. Had this been the only problem it may have been overcome by signal averaging for an appropriate amount of time, however, other complications arose. It seems that the optimum delay set between the laser pulses varied randomly as a function of time as well. Figure 3.16 shows the optimum delay required to achieve maximum signal as a function of time. The experiment was conducted by moving only delay on channel A of the SRS DG-535, corresponding to the time in which the YG660 laser fires, but without affecting the Q-Switch time. It was desirable to keep the Q-Switch constant so that effects due to the Q-Switching process were not introduced. Figure 3.16 clearly demonstrates that the maximum signal is obtained randomly over a 6 ns interval with time. Further the time interval between changes is sometimes smaller than the time required to take a kinetic measurement. Approximately
Figure 3.16. Optimized delay required between the two laser pulses (as set on the DG 535 digital delay generator) versus time (over a 4 hour period) to achieve maximum LIF signal. The fluctuation is most likely due to fluctuations in the Q-switch response, and changes in pulse shape and duration throughout the course of the day.
5 to 15 minutes for a single decay, and a number of hours or days to complete a full kinetic run.

Optimizing the delay between the lasers is quite important because the signal strength is very sensitive to the delay, Figure 3.17. The H atom LIF signal decays by a factor of three over a 6 ns interval, to a level that was sufficiently difficult to work with for kinetics, because the addition of a reactive reagent reduces the signal even further. The results for Figure 3.17 were obtained in a similar fashion to those of Figure 3.16, where only the delay on channel A of the SRS DG-535 was varied.

The source of the random jitter was vehemently sought after. It was first thought to occur in the SRS DG-535 digital delay generator, since the delays on channel A and C were set to 5.189 and 5.400 ms, respectively. However, the specified maximum jitter in time between two trigger pulses with respect to T₀ for the generator is 60 ps + (delay/10⁸), equal to 600 ps for the delays used here, still 10 times less than the observed delay necessary to re-optimize the signal. As a cross check, a separate experiment was conducted to try to isolate the contribution of jitter from the delay generator. Instead of using just the SRS DG-535, which required delays in the vicinity of 5 ms, a second delay generator (California Avionics Laboratories, Model IIIAR) was used in series with the SRS delay generator. In this respect, the bulk of the delay necessary, 5 ms, could be supplied by the Cal Av. generator, and used to trigger the SRS unit. In doing so the delays necessary for the SRS unit were reduced from 5 ms, to 500 μsec, shifting the specified jitter to 110 ps. Similar performance was observed, indicating that the source of the random jitter originated in the lasers, not the delay generator.
Figure 3.17. H atom LIF signal versus delay between laser pulses obtained by changing the channel A delay on the SRS DG-535.
The most likely source of jitter in the experiments is due to the time response of the lasers Q-Switch to the trigger, and also the duration and shape of the individual laser pulses. Laser pulse shape and duration were found to change throughout the duration of the day and is thought to be attributable to temperature fluctuations in the lab. These fluctuations may cause changes in electrical response of some of the components or may cause critical alignments to change. For instance, the laser pulse shape and duration out of the oscillator cavity is dependent on the alignment of the beam onto the Gaussian output coupler. Misalignment has been verified to cause increases in the Q-Switch reduction time, as well as a broadening of the pulse. Proper alignment of the cavity can reduce the Q-Switch reduction time by tens of nanoseconds, a number comparable to the drift between laser pulses throughout the day. In addition, part of the pulse broadening shows up as mode structure, complicating the overlap of the two laser pulses. Problems with mode structure can theoretically be eliminated in the NY61-10 laser through use of the seeding option; however, the seeder is also extremely sensitive to temperature swings in the laboratory. It may also be that there is some amount of damage to the diode laser used to seed, resulting in a low output power that contributes to the laser going into and out of seeding. The YG600, without a seeding option, has to be used as is.

Recommendations for kinetic experiments using this instrumentation in the future are the following, and are twofold. Use of the current setup could possibly be improved with rigorous characterization of the laser pulses. Methods need to be devised to ensure proper laser performance, and the method needs to be such that the performance can be continuously monitored. Such a system might encompass the placement of photodiodes
into the YAG housing that are sensitive to the oscillator pulses. In doing so the photodiodes could be coupled to a fast data acquisition system that monitors the pulse duration and pulse arrival, and plots them in real time so that the experimental conditions could be instantly known. Further, incessant tuning and continuous maintenance of the lasers is required for their operation within the Continuum specifications. Here again, a system that allowed for real time monitoring would be beneficial in realizing the above goal.

Use of a single high power pulsed YAG laser to pump both dye lasers would eliminate all of the pulse jitter problems associated with 2 pulsed laser experiments, and is the typical setup used by most, if not all researchers in the field employing non-linear four wave frequency mixing techniques. These setups employ a Nd:YAG capable of 1 Joule/pulse at 1.064 microns, with pulse durations near 4 ns, yielding approximately 10 mJ out of each dye laser. A few prototypical examples are referenced here, but realize that many others exist.\textsuperscript{100-102} In these arrangements the time jitter is removed because the same source beam is used to pump both dye lasers. If only one color pump is required a beamsplitter can be employed, otherwise both colors can be brought out of the YAG and used separately. Temporal alignment of the laser pulses is accomplished by increasing the path length of the short time pulse. Consideration of a setup such as the one described was considered, however, there proved to be a few obstacles. Both the NY61-10 and the YG660 Nd:YAG lasers are capable of 650 mJ/pulse at 1.064 microns. It is thought that while this energy is quite low compared to the 1 J/pulse typically employed, that there might be enough energy from a single YAG to sufficiently pump both dye lasers, thus
eliminating the jitter problem. In order to test this hypothesis, knowledge of the energy of the first and second YAG harmonic was needed. Measurements of the YAG energies were conducted on the NY61-10, due to its better overall performance and ability to be seeded. The ND60 dye laser was separated from the YAG body, and the shutter that normally blocks the remaining 1064 and 532 nm radiation after the third harmonic generation crystal was opened so that the beam could be further manipulated. The 532 was separated from the 1064 nm beam with use of a dichroic beamsplitter and the energy was measured. 65 mJ of 532 nm light were recovered, under conditions when the 355 nm energy was 145 mJ. Normal pump powers for the dye lasers are 300 mJ of 532 nm light when operating with green pumped dyes such as F548. Of this 300 mJ, 5 to 10% (15 to 30 mJ) is used to pump the oscillator cavity, depending on the dye laser, while the rest is used in the amplifier. It is not clear whether the 65 mJ is enough to fully pump both the oscillator and amplifier of the other dye laser, and tests need to be done. Conversion efficiencies of 20% are readily realized when green pumping F548 laser dye on the homebuilt system. However, if it is not clear whether that efficiency applies to low pump powers. If it turns out to not be enough to produce the 2 mJ of dye laser radiation required for the experiment, it may be possible to use the correct portion of the 65 mJ to pump only the homebuilt oscillator cavity. The YG660 could then be used to pump the homebuilt amplifier only. Again, it is thought that the time jitter is reduced in this configuration because the critical timing comes from the oscillator pulse, which emanates from the same pump pulse as the one used for the other dye laser. Since the dye laser pulse duration is typically shorter than the YAG, the jitter associated with the second
YAG pulse could be reduced. However, no conclusions are drawn as to the effectiveness of
the proposed method. It may turn out that pulse intensity problems arise in the
configuration where the YG660 pumps the homebuilt dye laser amplifier.

Described herein are the methods by which tunable, coherent VUV radiation can
be created and used in conjunction with a supersonic Laval nozzle flow reactor. The
tunability of the method in the region between 102 to 163 nm has been demonstrated on a
number of atoms and molecules including H atom, H₂ and NO. The four wave sum and
difference frequency method opens the opportunity for study of many of the first row
atoms, and molecules which have transitions in the VUV region. As far as the hydrogen
atom is concerned it is the first time, to the best of our knowledge, that the Lyman β
pump, Balmer α LIF scheme has been demonstrated, and its utility in the future will
hopefully be exploited. Characterization of the signal as well as sources of instability
were described, as well as experimental setups that would allow for successful
completion of low temperature kinetic experiments with H atoms in Laval flows.
CHAPTER 4. TEMPERATURE DEPENDENCE AND KINETIC ISOTOPE EFFECTS FOR THE OH + HBr AND H/D ISOTOPIC VARIANTS AT LOW TEMPERATURE

4.1. Abstract

The reactions of OH + HBr and all isotopic variants have been measured in a pulsed supersonic Laval nozzle flow reactor between 53 and 135 K, using a pulsed DC discharge to create the radical species, and laser induced fluorescence on the A $^2\Sigma \leftarrow X$ $^2\Pi (v' = 1 \leftarrow v'' = 0)$ transition. All reactions are found to possess an inverse temperature dependence, in accord with previous work, and are fit to the form $k = A \times (T/298)^n$, with $k_1$ (OH + HBr) = $(10.84 \pm 0.31) \times 10^{-12} \times (T/298)^{(-0.67 \pm 0.02)} \text{cm}^3/\text{sec}$, $k_2$ (OD + HBr) = $(6.43 \pm 2.60) \times 10^{-12} \times (T/298)^{(-1.19 \pm 0.26)} \text{cm}^3/\text{sec}$, $k_3$ (OH + DBr) = $(5.89 \pm 1.93) \times 10^{-12} \times (T/298)^{(-0.76 \pm 0.22)} \text{cm}^3/\text{sec}$, and $k_4$ (OD + DBr) = $(4.71 \pm 1.56) \times 10^{-12} \times (T/298)^{(-1.09 \pm 0.21)} \text{cm}^3/\text{sec}$. A global fit of $k$ vs. $T$ over the temperature range 23 – 360 K, including the new OH + HBr data, yields $k(T) = (1.06 \pm 0.02) \times 10^{-11} \times (T/298)^{(-0.90 \pm 0.11)} \text{cm}^3/\text{sec}$, and (0.96 $\pm 0.02) \times 10^{-11} \times (T/298)^{(-0.90 \pm 0.03)} \times \exp((2.88 \pm 1.82)K/T) \text{cm}^3/\text{sec}$, in accord with previous fits. In addition the primary and secondary kinetic isotope effects are found to be independent of temperature within experimental error over the range investigated and take on the value of $(k_H/k_D)_{\text{AVG}} = 1.64$ for the primary effect, and $(k_H/k_D)_{\text{AVG}} = 0.87$ for the secondary effect. These results are discussed within the context of current experimental and theoretical work.
4.2. Introduction

The reaction of OH + HBr → H₂O + Br and the isotopic variants has been studied both experimentally and theoretically in the past by a number of different research groups.

\[
\begin{align*}
\text{OH} + \text{HBr} & \stackrel{k_1}{\longrightarrow} \text{H}_2\text{O} + \text{Br} & \text{R1} \\
\text{OD} + \text{HBr} & \stackrel{k_2}{\longrightarrow} \text{HOD} + \text{Br} & \text{R2} \\
\text{OH} + \text{DBr} & \stackrel{k_3}{\longrightarrow} \text{DOH} + \text{Br} & \text{R3} \\
\text{OD} + \text{DBr} & \stackrel{k_4}{\longrightarrow} \text{D}_2\text{O} + \text{Br} & \text{R4}
\end{align*}
\]

Motivation for doing so has been twofold. First, the reaction affects the Br partitioning in the middle to lower stratosphere of earth’s atmosphere. Bromine has been implemented as a species known to oxidize ozone creating BrO and O₂, and therefore a rigorous understanding of the reaction network surrounding Br creation and destruction has been sought. In addition, the kinetics of the reaction of OH with HBr has been experimentally found to show strong inverse temperature dependence below approximately 200 K, i.e. temperatures pertinent to the upper atmosphere and stratosphere. To date experiments on the OH + HBr system have been carried out in the temperature range from 23 to 416 K. Ravishankara et al. conducted the first temperature dependent study between 249 and 416 K using the technique of laser flash photolysis-resonance fluorescence and found the rate to be independent of temperature over the temperature window investigated, with a rate of \((1.19 \pm 0.14) \times 10^{-11} \text{ cm}^3 \text{sec}^{-1}\). This study was motivated by earlier measurements of \(k_1\).
at temperatures of 298 K and 1925 K, by Takacs and Glass, Smith and Zellner, and Wilson et al., who found the rate to be $(5.1 \pm 1.0) \times 10^{12} \text{ cm}^3\text{sec}^{-1}$, $(4.5 \pm 1.0) \times 10^{12} \text{ cm}^3\text{sec}^{-1}$, and $2.56 \times 10^{11} \text{ cm}^3\text{sec}^{-1}$, respectively. Following these studies, additional measurements near room temperature were also made using a variety of techniques. I.R. Sims et al. applied the pulsed laser photolysis-laser induced fluorescence technique to the ultra-cold gas phase environment created in the Cinétique de Réactions en Ecoulement Supersonique Uniforme (CRESU) to study the reaction over the temperature range of 23 – 295 K, and found the inverse temperature onset below 295 K. Atkinson et al. also studied the temperature dependence of the kinetics of R1 using a pulsed supersonic Laval nozzle flow reactor over the temperature range 76 – 242 K, and similarly found inverse temperature dependence, although with a later onset around 200 K. The rate coefficient has been found to be pressure independent, consistent with a bimolecular reaction mechanism.

More recently, a joint experimental effort was conducted between the Rowe and M. Smith groups in Rennes, and Tucson, with the aim of reconciling the low temperature data for the OH + HBr reaction, and included new measurements between 48 – 224 K. The study produced temperature dependent fits to the available data between 23 – 416 K of

$$k(T) = 1.11 \times 10^{-11} \times \left( \frac{T}{298} \right)^{-0.91} \text{ cm}^3\text{sec}^{-1}$$  \hspace{1cm} (4.1)
and

\[ k(T) = 1.06 \times 10^{-11} \times \left( \frac{T}{298} \right)^{-0.91} \times \exp\left( \frac{-10.5K}{T} \right) \text{ cm}^3 \text{ sec}^{-1} \]  \hspace{1cm} (4.2)

which were deemed to accurately model the data below 350 K. These fits were also found to be in accord with the previous recommendations of the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, and that of JPL, of

\[ k(T) = 1.1 \times 10^{-11} \times \left( \frac{T}{298} \right)^{-0.8} \text{ cm}^3 \text{ sec}^{-1} \]  \hspace{1cm} (4.3)

and

\[ k(T) = 1.1 \times 10^{-11} \times \exp\left( \frac{0 \pm 250K}{T} \right) \text{ cm}^3 \text{ sec}^{-1} \]  \hspace{1cm} (4.4)

respectively.

The dependence of reactivity on isotopomer for a chemical system is also of great importance. Deuterium enrichment found throughout the interstellar medium is well known, and efforts to understand the origins of these effects have been conducted. The enrichment arises due to differences in zero point energies between the deuterated and non-deuterated species and is initiated via isotopic exchange chemistry, primarily in
ion-molecule reactions involving $H_3^+$, $CH_3^+$, and $C_2H_2^+$ with HD.\textsuperscript{112,113} Once the deuterated ions are formed they participate in a variety of subsequent chemistries, including dissociative recombination, to pass on their deuterium content. In cold clouds the exothermic $D + OH \rightarrow H + OD$ ($\Delta H_{\text{rxn}} = 810$ K) is speculated to influence the local D/H ratio,\textsuperscript{114} and this chemistry is included in the modeling of such environments.\textsuperscript{115} In addition, Lunine et al. point out that the D/H ratio in methane might provide a complimentary chemical test to the origin of Titan's atmosphere\textsuperscript{54} and therefore knowledge of the subsequent chemistry for molecules of interstellar importance is crucial for a complete physiochemical description of the environment. Knowledge of the H/D atom abstraction reactions of OH/OD with HBr/DBr, while not of astrophysical relevance at the time, provides information on the dynamics of a neutral-radical abstraction reaction occurring over a potential energy surface without an apparent barrier. Efficient neutral-radical reactions are now well known,\textsuperscript{98} and the low temperature measurement of their reaction rates will further help modeling efforts of low temperature environments.

Two other studies have significantly contributed to the temperature dependent knowledge on not only the OH + HBr system, but the isotopomers as well. The study of Bedjanian et al. used a mass spectrometric discharge-flow reactor to make measurements between 230 – 360 K, on the reactions R1 through R4.\textsuperscript{57} Further, Jaramillo and Smith, used the pulsed supersonic Laval nozzle flow reactor to study the kinetics of reactions R1 through R4.\textsuperscript{32} These studies will be discussed in detail later, but for now it is prudent to say that knowledge of the kinetic isotope effect (KIE), whether they be primary or
secondary in nature, help to provide constraints to important regions of the reaction potential energy surface.

Theoretical efforts have also been conducted aimed at describing the potential energy surface and the inverse temperature dependence found from experiments. They are mentioned here, and discussed further in context of the current results. Clary et al. performed quantum scattering calculations using the rotating bond approximation (RBA) on a LEPS potential energy surface and found good qualitative agreement between the temperature dependence predicted from the calculations and that experimentally observed, as well as qualitative agreement in magnitude with the rates.\textsuperscript{50} Nizamov et al.\textsuperscript{61} extended the understanding of this reaction with calculations using variational transition state theory on a modified LEPS potential energy surface, with the goal of understanding the nature of the kinetic isotope effects and the fraction of vibrational energy transferred to the departing H\textsubscript{2}O, HDO, and D\textsubscript{2}O molecules found from infrared chemiluminescence measurements by Butkovskaya and Setser.\textsuperscript{116} In addition, a more recent direct \textit{ab initio} dynamics calculation by Liu et al. has found a hydrogen bonded complex intermediate on the reactant side of the potential energy surface at energies lower than that of reactants, and the rate coefficients over a broad temperature range were calculated with improved canonical variational transition state theory with a small-curvature tunneling correction.\textsuperscript{117}

The kinetic isotope effects measured by Bedjanian et al.\textsuperscript{57} and Jaramillo and Smith\textsuperscript{32} are extended in this study to lower temperatures between 53 and 135 K using the pulsed supersonic Laval nozzle flow reactor, in an effort to further understand the nature
of the reaction PES, the temperature dependent KIE’s observed in the two previous studies, and also to provide additional data necessary for the theoretical chemists to accurately describe the reaction mechanism, the entrance channel, and transition state dependence on the reactivity.

4.3. Experimental

A detailed description of our pulsed uniform supersonic expansion flow reactor is presented in Chapter 2, and thus only the details pertinent to the OH experiments are given here. The kinetics of reactions R1 through R4 was studied by co-expanding known quantities of reagent and buffer gases through a supersonic pulsed Laval nozzle. An equilibrated flow ensues for a number of nozzle diameters past the nozzle exit (15 – 20 cm), at a well defined hydrodynamic velocity and density, allowing for enough time (approximately 300 μsec) to perform kinetic measurements. The experiments were conducted such that the concentration of reagent [R], R = HBr or DBr, was much greater than that of the OH radical, ensuring that pseudo-first order conditions were established. OH or OD radicals were created from water or deuterium oxide (Cambridge Isotopes Laboratories, Inc., 99.9 %) precursors, using a pulsed DC discharge in the stagnation volume. The H₂O/D₂O was entrained in the gas phase using a bubbler running with either N₂ (83 and 135 K) or Ar (53 K) depending on the buffer gas used for the experiment. In this manner, a mixture containing the partial pressure of H₂O divided by the total bubbler
backing pressure (30 psig) could be delivered to the nozzle, in concentrations high enough to provide sufficient signal for the kinetic experiments.

The time dependent OH/OD signal was monitored using laser induced fluorescence (LIF). Both OH and OD radicals were excited using the $\text{A} \leftarrow \text{X} (^2\Sigma \leftarrow ^2\Pi_{3/2}, v' = 1 \leftarrow v'' = 0)$ transition, using a pulsed dye laser (Continuum model ND-60) pumped by a Nd:YAG operating on the second harmonic (Continuum model NY61). In both cases, kinetic experiments were conducted by monitoring the $S_{21}(1)$ line. For OH this occurs near 280.6 nm, while for OD at 286.9 nm. These wavelengths were created by doubling the output from the dye laser operating with Rhodamine 590 and a Rhodamine 590/610 mixture, respectively, in a KD*P crystal. The laser frequency was calibrated using the optogalvanic lines of Fe and Ne. The resulting (0,0) and (1,1) fluorescence was collected with a photomultiplier tube (Hamamatsu R3896) perpendicular to the flow, in conjunction with a 310 ± 10 nm bandpass filter and red pass filter (Schott WG29). The LIF signal was amplified and sent to either a boxcar averager (SRS 250) or oscilloscope (LeCroy 9400) and averaged for 200 to 500 shots. The gases used for these studies are as follows: N$_2$, US Airweld 99.99%, Ar, US Airweld, UHP, 99.999%, HBr, Matheson C.P. Grade 99.8% DBr, Cambridge Isotope Laboratories, Inc. 99%. The HBr and DBr gases were each treated to three freeze, degas, thaw cycles with liquid nitrogen to remove the H$_2$ impurities. The rest were used without further modification.

Kinetic experiments are conducted after the flow exits the nozzle, by following the relative OH(OD) concentration as a function of distance in the flow. The reaction time is extracted from the distance between the probe laser and nozzle exit, and is
determined through knowledge of the flow velocity. This in turn is known from the flow Mach number obtained from impact and LIF measurements. The OH(OD) signal follows a single exponential decay, as evidenced by the linearity of the natural log of the normalized signal vs. reaction time plot, Figure 4.1, indicating that pseudo-first order conditions have indeed been satisfied. The bimolecular rate coefficient is extracted from a plot of the pseudo-first order decay constant versus the concentration of reactant under which it was obtained, Figure 4.2. The three nozzles used for this study are the ArM32e16, N2M32e16, and the N2M33e16 nozzles. Their flow characteristics have already been described in Chapter 2, and the reader is referred to Table 2.1 for details.
Figure 4.1. Pseudo 1st order decays for the reaction of OH + HBr at 53 K taken in the post ArM32e16 nozzle flow. The normalized OH signal is plotted as a function of reaction time and the pseudo 1st order decay rates (sec⁻¹) are extracted using a linear least squares fitting routine. The process is repeated a number of times under different concentrations of HBr reactant.
Figure 4.2. Graph of $k'$ vs. [HBr] used to extract the bimolecular rate coefficient ($\text{molecules-cm}^{-3}\cdot\text{sec}^{-1}$) for the OH + HBr reaction at 53 K in the post ArM32e16 nozzle flow. The slope is equal to the bimolecular rate coefficient and is obtained from a linear least squares best fit to the data.
4.4. Results

The rates of reactions R1 through R4 were measured at three temperatures 53, 83, and 135 K under pseudo first order conditions. Table 4.1 shows the temperature dependent results. The errors reported in Table 4.1 are those at the 95% confidence limit. The value and error in each rate represents a weighted average and corresponding error in the mean with unequal uncertainties from a number of measurements. Graphs of $k$ vs. $T$ for R1 through R4 can be seen in Figures 4.3a through 4.3d, respectively. Two fits to the functional form $k(T) = A \times (T/298)^{-n}$ are shown on each graph. They represent a fit to the low temperature data set only, for this work, solid line, and the work of Jaramillo and Smith, dashed line, extrapolated to higher temperatures so that the data could be compared to that of Bedjanian et al. Figure 4.3a also depicts the data of Atkinson et al. It can be seen for all cases, except for OD + HBr, good agreement between the measurements of this work and of Bedjanian et al. is realized. For the case of OD + HBr, Figure 4.3b, it appears that the steepness of the inverse temperature dependence in the region from 53 to 135 K, causes the rate calculated from the fit of the low temperature data only, to be underestimated in comparison to the measurement of Bedjanian et al. However, this underestimation can easily be overcome with a fit to both data sets, but was not done here, as the goal was to illustrate the difference or similarity in the three data sets. Table 4.2 lists the best fit parameters obtained from fitting the data of this work to the power law form.
Table 4.1. Temperature Dependent Rate Data for the OH + HBr and H/D Isotopic Variants

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Temp (K)</th>
<th>[R] (10^{13} \text{ cm}^{-3})</th>
<th>k (10^{-11} \text{ cm}^3\text{ molecule}^{-1}\text{sec}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH + HBr</td>
<td>53</td>
<td>8.5</td>
<td>3.46 ± 0.15</td>
</tr>
<tr>
<td>OH + HBr</td>
<td>83</td>
<td>6.2</td>
<td>2.53 ± 0.21</td>
</tr>
<tr>
<td>OH + HBr</td>
<td>135</td>
<td>9.0</td>
<td>1.86 ± 0.21</td>
</tr>
<tr>
<td>OD + HBr</td>
<td>53</td>
<td>9.5</td>
<td>5.11 ± 0.29</td>
</tr>
<tr>
<td>OD + HBr</td>
<td>83</td>
<td>6.2</td>
<td>2.61 ± 0.16</td>
</tr>
<tr>
<td>OD + HBr</td>
<td>135</td>
<td>6.5</td>
<td>1.93 ± 0.25</td>
</tr>
<tr>
<td>OH + DBr</td>
<td>53</td>
<td>7.2</td>
<td>2.25 ± 0.14</td>
</tr>
<tr>
<td>OH + DBr</td>
<td>83</td>
<td>5.8</td>
<td>1.39 ± 0.12</td>
</tr>
<tr>
<td>OH + DBr</td>
<td>135</td>
<td>11.9</td>
<td>1.19 ± 0.13</td>
</tr>
<tr>
<td>OD + DBr</td>
<td>53</td>
<td>7.5</td>
<td>3.04 ± 0.16</td>
</tr>
<tr>
<td>OD + DBr</td>
<td>83</td>
<td>5.5</td>
<td>2.08 ± 0.17</td>
</tr>
<tr>
<td>OD + DBr</td>
<td>135</td>
<td>12.1</td>
<td>0.97 ± 0.15</td>
</tr>
</tbody>
</table>

Errors quoted are 2σ.

[R] is the maximum concentration of HBr or DBr used in the experiment to extract the bimolecular rate coefficient.

Table 4.2. Best Fit Parameters Obtained for the OH + HBr and H/D Isotopic Variant Reactions to the Functional Form: \(k_B(T) = A \times (T/298)^n\)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A (10^{-12} \text{ cm}^3\text{ sec}^{-1})</th>
<th>-n</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH + HBr</td>
<td>10.84 ± 0.31</td>
<td>0.67 ± 0.02</td>
</tr>
<tr>
<td>OD + HBr</td>
<td>6.43 ± 2.60</td>
<td>1.19 ± 0.26</td>
</tr>
<tr>
<td>OH + DBr</td>
<td>5.89 ± 1.93</td>
<td>0.76 ± 0.22</td>
</tr>
<tr>
<td>OD + DBr</td>
<td>4.71 ± 1.56</td>
<td>1.09 ± 0.21</td>
</tr>
</tbody>
</table>
OH + HBr

$k_{fit}$ to form $k = A(T/298)^n$

Mullen $A=(10.84\pm0.31)$, $n=(0.670\pm0.019)$
Jaramillo and Smith $A=(8.64\pm0.033)$, $n=(1.449\pm0.0048)$
Jaramillo et al. $A=11.1$, $n=0.91$

This Work
Jaramillo and Smith
Atkinson et al.
Bedjanian et al.

Figure 4.3a. Plot of the rate coefficient versus temperature for the OH + HBr reaction.
Figure 4.3b. Plot of the rate coefficient versus temperature for the OD + HBr reaction.
$\text{OH} + \text{DBr}$

$k_{\text{fit}}$ to form $k = A^*(T/298)^n$

This Work $A=(5.89 \pm 1.93)$, $n=(0.761 \pm 0.217)$

Jaramillo and Smith $A=(2.07 \pm 0.73)$, $n=(2.982 \pm 0.416)$

- ■ This Work
- ● Jaramillo and Smith
- ○ Bedjanian et al.
- --- This Work $k_{\text{fit}}$
- --- Jaramillo and Smith $k_{\text{fit}}$

Figure 4.3c. Plot of the rate coefficient versus temperature for the OH + DBr reaction.
Figure 4.3d. Plot of the rate coefficient versus temperature for the OD + DBr reaction.
The data of Jaramillo and Smith\textsuperscript{32} is seen to be markedly steep in all cases, and as a result a re-evaluation of the data was conducted. The errors reported in the original publication for the data measurements were the standard error and the final results (i.e. \( k(T)'s \)) represent the average of the measurements and standard deviation calculated as the square root of the sum of the squares of the individual standard errors divided by the number of measurements, as would be anticipated for a normal error probability function for a large number of measurements. However, in cases where the number of measurements is small, \( N < 20 \), it is desirable to use a statistical treatment of random errors to place a confidence limit on the mean, through use of the Student t distribution which takes into account the joint probability that \( N \) observations fall within a certain range and the number of degrees of freedom in the system.\textsuperscript{119} In this fashion, the raw data was re-plotted and a linear least squares regression analysis was used to extract the individual rates and errors in the rates at the 2\( \sigma \) (95\%) confidence level. The weighted average and error in the average was then calculated in the same fashion as the numbers reported for this study so that a direct comparison of the data could be made. Figure 4.4 shows the difference in the data before and after being treated in this way, for reactions R1 through R4. The revised data is used throughout the rest of this report. The change in the rate and the error associated with it is reflective of the quality of the data.

As mentioned in the introduction, great interest in the temperature dependence of reaction R1 stems from its important role in the atmospheric chemistry of the Br atom. A new temperature dependent fit of the global data set including this work has been done, and can be seen in Figure 4.5. All of the data used for this graph is included in Table 4.3.
Figure 4.4. Comparison of Jaramillo and Smith 2001 [32] data before and after revision for the OH + HBr and H/D isotopic variant reactions.
Figure 4.5. OH + HBr global fit to the temperature dependent rate data over the 23 – 360 K window.
Table 4.3. OH + HBr Rate Data Used to Obtain the Temperature Dependent Global Fit of Figure 4.5.

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Temp (K)</th>
<th>Rate ($10^{-11}$ cm$^3$/sec)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jaramillo and Smith</td>
<td>120</td>
<td>3.15</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>140.8</td>
<td>2.53</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>185</td>
<td>0.936</td>
<td>0.274</td>
</tr>
<tr>
<td></td>
<td>224</td>
<td>1.01</td>
<td>0.15</td>
</tr>
<tr>
<td>Bedjanian et al.</td>
<td>230</td>
<td>1.46</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>243</td>
<td>1.2</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>1.12</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>278</td>
<td>1.2</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>1.11</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>1.05</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>0.97</td>
<td>0.14</td>
</tr>
<tr>
<td>Ravishankara et al.</td>
<td>249</td>
<td>1.31</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>273</td>
<td>1.22</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>1.11</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>326</td>
<td>1.18</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>369</td>
<td>1.12</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>416</td>
<td>1.21</td>
<td>0.1</td>
</tr>
<tr>
<td>Sims et al.</td>
<td>23</td>
<td>10.7</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>30.5</td>
<td>8.78</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>44</td>
<td>7.87</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>52.1</td>
<td>5.54</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>52.3</td>
<td>5.46</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>4.83</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>2.97</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>295</td>
<td>1.16</td>
<td>0.04</td>
</tr>
<tr>
<td>Jaramillo et al.</td>
<td>48</td>
<td>5.67</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>97</td>
<td>3.21</td>
<td>0.18</td>
</tr>
<tr>
<td>Atkinson et al.</td>
<td>242</td>
<td>1.1</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>222</td>
<td>1.3</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>194</td>
<td>1</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>194</td>
<td>1.5</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>173</td>
<td>0.8</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>169</td>
<td>1.5</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>147</td>
<td>1.4</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>133</td>
<td>1.6</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>107</td>
<td>2</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>92</td>
<td>3</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>76</td>
<td>2.9</td>
<td>0.9</td>
</tr>
<tr>
<td>This work</td>
<td>53</td>
<td>3.46</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>83</td>
<td>2.53</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>135</td>
<td>1.86</td>
<td>0.21</td>
</tr>
</tbody>
</table>
A non-linear least squares fitting routine was used to fit the data to a power law and modified Arrhenius functional form, as shown in Figure 4.5. The fitting routine took into consideration the individual error bars associated with each data point, and minimized the sum of the squares deviation. The shaded area represents the 95% confidence limit interval of the modified Arrhenius fit. The best fit parameters over the temperature range 23 – 360 K are found to be \( k(T) = (1.06 \pm 0.02) \times 10^{-11} \times (T/298)^{(-0.90 \pm 0.11)} \text{cm}^3/\text{sec}, \) and \( (0.96 \pm 0.02) \times 10^{-11} \times (T/298)^{(-0.90 \pm 0.03)} \times \exp^{(-2.88 \pm 1.82 K/T)} \text{cm}^3/\text{sec}. \)

The data of Table 4.1 from this work was used in conjunction with the revised data of Jaramillo and Smith and Bedjanian et al. to examine the kinetic isotope effects as a function of temperature over the region 53 to 360 K. The results for the primary kinetic isotope effect (PKIE) for common reactant OH and secondary kinetic isotope effect (SKIE) for common reactant HBr can be seen in Figure 4.6. Similarly, the results for the PKIE with common reactant OD and SKIE with common reactant DBr can be seen in Figure 4.7. The plots are presented in this fashion because they compare reactions that create similar products. In the case of Figure 4.6, HOD vs. HOH, while for Figure 4.7, HOD vs. DOD. Due to the scatter of the data, it was desirable to include a temperature dependent fit to the data, to help guide the eye. The fits seen in Figures 4.6 and 4.7, were made by fitting the data of this work and that of Bedjanian et al. (Figures 4.3a-d) to the power law form, and using the appropriate ratio of the fits to predict the KIE’s, in this manner reducing the statistical fluctuations in the data. Including the data of Jaramillo and Smith caused the fits to shift off the data sets, and this data was not included for this reason.
Figure 4.6. Primary and secondary KIE's plotted versus temperature. $k_1$ and $k_3$ share the common reactant OH, while $k_1$ and $k_2$ share the common reactant HBr.
Figure 4.7. Primary and secondary KIE's plotted versus temperature. $k_2$ and $k_4$ share the common reactant OD, while $k_3$ and $k_4$ share the common reactant DBr.
The fits to the KIE data show only weak temperature dependence and yield values of $k_1/k_2 = (0.93 + 0.13, -0.21)$, $k_1/k_3 = (1.75 + 0.09, -0.16)$, $k_2/k_4 = (1.69 + 0.06, -0.11)$, and $k_3/k_4 = (0.90 + 0.11, -0.19)$, where the (+) and (−) indicate the range with respect to the average value. It can be seen that the fitting procedure provides reasonable agreement with the data except in the case of the 120 and 141 K PKIE ($k_2/k_4$) data of Jaramillo and Smith.

4.5. Discussion

Reactions displaying inverse temperature dependence for a wide variety of systems are now widely known. These include the addition reactions of OH radicals with unsaturated hydrocarbons, CN radical reactions, various carbon atom reactions, $^{10,23}$ and C$_2$H radical with a variety of species. $^{25,44,46-48}$ While the manifestation of inverse temperature dependence is becoming commonplace, measurements of temperature dependent KIE ratios remain sparse. The systems that have been studied to date are discussed below to create a framework within which the current results can be understood.

Battin-Leclerc et al. have studied the temperature dependent KIE ratios for the OH + HCl and all isotopic variants using a pulsed laser photolysis-laser induced fluorescence flow reactor between 200 to 400 K. $^{122}$ They find a normal temperature dependent PKIE ($k_3/k_4$ and $k_1/k_2$, using their nomenclature) that varies from approximately 2 to 6.5 over the temperature window of their experiment, and indicate
that H atom tunneling becomes significant at lower temperatures. They also conducted effective barrier calculations which indicate that the barrier decreases from 12.22 kcal/mol to 9.71 kcal/mol in the series \( \text{OH} + \text{HCl} > \text{OH} + \text{DCl} > \text{OD} + \text{HCl} > \text{OD} + \text{DCl} \), with the reduction in barrier height due to OD because of the zero point energy difference and the lower frequency modes in the transition state. While the primary KIE for \( \text{OH} + \text{HCl} \) gets quite high at low temperatures, qualitative agreement is seen between the portion of the PKIE not attributed to tunneling in the \( \text{OH} + \text{HCl} \) case, and the PKIE’s of this work for \( \text{OH} + \text{HBr} \), \( \frac{k_1}{k_3} \)\(_{\text{Avg}} \), \( \frac{k_2}{k_4} \)\(_{\text{Avg}} \) = 1.64, and the PKIE for \( \text{OH} + \text{HBr} \) of Bedjanian et al. \( \frac{k_1}{k_4} \approx \frac{k_3}{k_5} \approx 1.7 \). But it should be noted the \( \text{OH} + \text{HCl} \) system demonstrates a positive activation energy at all temperatures while the \( \text{OH} + \text{HBr} \) reaction shows no indication of a positive barrier. It is not clear how to directly compare the kinetic isotope effects for reactions occurring over seemingly quite different potential energy surfaces.

The SKIE’s for \( \text{OH} + \text{HCl} \) observed in Battin-Leclerc et al.\(^{122} \) are inverse in nature and vary from approximately 0.83 to 0.95, with the \( \frac{k_1}{k_3} \) (common HCl) ratio showing stronger temperature dependence than that of \( \frac{k_2}{k_4} \) (common DCl). Again, these ratios are in accord with those observed in this study, \( \frac{k_1}{k_2} \)\(_{\text{Avg}} \) = 0.87 and \( \frac{k_3}{k_4} \)\(_{\text{Avg}} \) = 0.88 for \( \text{OH} + \text{HBr} \). Similarly, Bedjanian et al. receive SKIE ratios of \( \frac{k_1}{k_3} \approx \frac{k_4}{k_5} \approx 1 \) for \( \text{OH} + \text{HBr} \).\(^{57} \) The results of the three studies seem to indicate that the secondary kinetic isotope effect is most sensitive to the transition state for these two reactions, even though both occur over different potential energy surfaces. The creation of the lower frequency vibrational modes due to the spectator nature of the OD bond appears to have a greater
influence on the dynamics than it does from the changes in number of states in the reactant manifold due to zero point effects.

More recently Nizamov and Leone have investigated the reactions of C$_2$H with NH$_3$ and ND$_3$ in a pulsed Laval nozzle apparatus, at three temperatures of 104 ± 5 K, 165 ± 15 K, and 296 ± 2 K. They find that in accord with theoretical predictions, the reaction proceeds via the exothermic ($\Delta H^\circ_{298K} = -121$ kJ/mol) hydrogen abstraction mechanism without a barrier, demonstrated by the strong negative temperature dependence observed. In addition, and relevant to the OH + HBr system, they observe a rather large PKIE of (2.0 ± 0.2) independent of temperature over the range investigated. While they acknowledge that precise knowledge of the observed KIE cannot be judged without accurate calculations, the authors suggest the origin of the large KIE could be contributions from tunneling. Alternately, from a statistical standpoint, the KIE could be due to an increase in the reactant rotational density of states upon deuteration, without significant effects on the activated complex, leading to a temperature independent kinetic isotope effect. Further, they argue that explanation of the kinetic isotope effect based solely on changes in zero point energies is inconsistent with the temperature independence of the KIE. This is due to the $\exp(-\Delta E^*/kT)$ factor that is obtained when the $k_H/k_D$ ratio is derived from classical transition state theory, but they also mention that application of classical transition state theory may be too simplistic for reaction systems occurring over potential energy surfaces without a barrier. It is also interesting that the temperature dependence observed for the NH$_3$ + C$_2$H system $T^{(-0.90±0.15)}$, in accord with the temperature dependence observed in this study for OH + HBr and all the isotopic
variants, within the errors quoted. It seems these two abstraction reactions, while differing in the number of degrees of freedom, share similar characteristics due to the large exothermicity involved and the lack of a barrier.

A number of theoretical efforts have also been conducted aimed at understanding the negative temperature dependence, the vibrational energy distribution imparted to the exiting H₂O molecule, and the kinetic isotope effects observed for OH + HBr and isotopic variants. The observed temperature dependence of reaction R1 is best fit by a T⁻⁰.⁹⁰ functional form, and this dependence is consistent with that calculated using quantum scattering calculations with the rotating bond approximation using a LEPS surface.⁶⁰ Nizamov et al.⁶¹ performed quasiclassical trajectory calculations (QCT) to explore the dynamics of reactions R1 and R2 using the Clary potential and a modified form adjusted to match the fraction of H₂O vibrational energy dispersal experimentally measured by Butkovskaya and Setser.¹¹⁶ They also employed variational transition state theory to obtain rate constants that could be compared to the QCT and experimental values. They find the transition state to lie at a classical energy of ~-1.75 kcal/mol with respect to reactants, and with harmonic zero point adjustment the barrier shifts to -0.12, +0.06, and -0.23 kcal/mol, for the Clary OH + HBr PES, the modified OH + HBr PES, and the modified OD + HBr PES, respectively. Due to the fact that the zero point adjusted barrier was lower for OD + HBr by 0.29 kcal/mol, than for OH + HBr, an inverse SKIE (k₁/k₂) was predicted, and attributed to the difference in DOH vs. HOH bending frequencies in the transition state. At 300 K the VTST rates calculated on the modified potential predict
a SKIE of 0.76. While a bit low, the SKIE value predicted by the VTST calculation is in qualitative agreement with the measurements of this work and Bedjanian et al.\textsuperscript{57}

An inverse PKIE ($k_1/k_3$) of 0.72 is also calculated in the Nizamov et al. study\textsuperscript{61} which is similar in magnitude to the SKIE calculated at 300 K using the modified potential. Again, the PKIE arises due to a lowering of the zero point energy adjusted barrier for OH + DBr relative to OH + HBr. However, the authors note that large $k_{1H}/k_{1D}$ values are difficult to explain by any transition state model, when the transition state is located early in the entrance channel. The lack of agreement between the PKIE experimentally measured at 300 K ($k_{1H}/k_{1D} \approx 1.7$)\textsuperscript{57} and calculated using the semiempirical surface is therefore not terribly surprising.

Direct \textit{ab initio} dynamics calculations of the reaction rates for the OH + HBr reaction have also been conducted.\textsuperscript{117} The goal of using this approach was to obtain dynamical information on an accurate potential energy surface obtained from accurate \textit{ab initio} electronic structure calculations. The study finds that on the reactant side of the potential energy surface there is a hydrogen bonded complex (HBC) lower in energy than reactants by -1.71 kcal/mol, that looks similar in geometry to the transition states calculated in the quantum scattering\textsuperscript{60} and QCT calculations.\textsuperscript{61} The reaction is found to pass through a reactant-like transition state with an energy slightly higher in energy than that of the reactants (0.89 kcal/mol) in going from the HBC to products. Further, the rates of reaction are calculated using improved canonical variational transition state theory (ICVT) and with a small curvature tunneling correction (ICVT/SCT). Qualitative agreement is found between the rates calculated and those found experimentally, but the
ratio of the rate coefficients calculated ([ICVT/SCT]/ICVT) is found to be dependent on temperature, with the ICVT/SCT gaining importance as the temperature is reduced, indicating the importance of tunneling to the reaction at low temperatures.

It seems reasonable to suggest that the KIE ratios are constant over the temperature range explored in this study and that of Bedjanian et al.\(^5^7\) Locating the origin of the effect, however, is a bit more difficult. From a transition state theory perspective the KIE ratio arises due to differences in zero point energies and the rotational, vibrational, and translational partition functions according to Equation 4.5

\[
\frac{k_H}{k_D} = \left( \frac{Q_{\text{Trans}}^{\text{HOHBr}}}{Q_{\text{Trans}}^{\text{DOHBr}}} \right) \times \left( \frac{Q_{\text{Vib}}^{\text{HOHBr}}}{Q_{\text{Vib}}^{\text{DOHBr}}} \right) \times \exp \left( \frac{E_{\text{trans}} - E_{\text{trans}}}{k_b T} \right)
\]

where \(Q_{\text{Trans}}\), \(Q_{\text{Vib}}\), and \(Q_{\text{Rot}}\) represent the translational, vibrational, and rotational partition functions, respectively, \(Q_{\text{inter}}\) represents the partition function associated with motion along the reaction coordinate, the exponential term is the difference in activation energy at the transition state, \(k_b\) is Boltzmann’s constant, with the reactant partition function indicated by the subscript OH(D) and the transition state partition function by the subscript H(D)OHBr. Equation 4.5 represents the situation for the SKIE. The expression for the PKIE is similar, with HBr and DBr substituted into the reactants and transition state. Deuteration of either of the reactants leads to changes in the reactant partition functions of \(Q_{\text{Vib}}\), \(Q_{\text{Rot}}\), and \(Q_{\text{Trans}}\) which can be estimated, but it is the
transition state partition functions and energetics that make assessment of the origin of the observed KIE's difficult, due to the necessity of an accurate potential energy surface. Even with an assumed transition state geometry, state sums and densities are difficult to assess due to anharmonic effects, as pointed out by Nizamov et al.\textsuperscript{61} Further, the difference in zero point energy of the transition state for the deuterated vs. non-deuterated case should introduce a temperature dependence to the KIE, although it is not clear at this time to what extent. As previously mentioned, Nizamov et al. attributes the PKIE ($k_1/k_3$) and SKIE ($k_1/k_2$) to a lowering of the zero point adjusted barriers for the deuterated reactions. At 300 K the inverse SKIE observed experimentally is reasonably well reproduced by theory, but the PKIE is not. A temperature dependent expression for the inverse PKIE of Nizamov et al. is provided in that study, which indicates an increased reaction efficiency of $k_D$ vs. $k_H$ as the temperature is lowered. Since neither the absolute value of the PKIE nor the temperature dependence of the PKIE calculated appear to be observed experimentally, it is unclear whether it is a limitation in transition state theory to accurately predict KIE's, as suggested by Nizamov et al., or whether it is another offsetting factor, such as tunneling, as suggested by the calculations of Liu et al.\textsuperscript{117} that leads to the discrepancy.

Questions naturally arise regarding the difference in the data measured using the pulsed supersonic Laval nozzle flow reactor in Tucson. The scatter in the data of Jaramillo and Smith\textsuperscript{32} is thought to reflect statistical or systematic errors in the data obtained in those studies. Oftentimes rates were extracted from $k'$ vs. $[R]$ plots containing four of five data points with considerable deviation from linearity. In addition the plots of
the normalized signal vs. distance used to extract $k'$ showed markedly different decay rates for like concentration of reagent [R]. Therefore the error bars most likely under represent the true error associated with the measurements. Part of the scatter could have been introduced by the method by which the HBr and DBr concentrations were calculated. These concentrations were calculated from a measurement of the absorption cross section at 220 nm (near the minimum in value), so that the absorbance measured in the reactant delivery line, in conjunction with the flow rate and line pressure could be converted into an absolute concentration in the flow. It is difficult to determine whether these measurements suffered from systematic errors due to baseline drift in the absorption spectrometer, or from adsorption of HBr and DBr molecules onto window surfaces. Other sources of error such as improper nozzle calibration leading to un-equilibrated flow and non-uniform flow are also candidates. In the present study care was taken to ensure that the flow was continually monitored to ensure reliable flow conditions and the HBr and DBr concentrations were calculated solely from the gas flow rate, so that errors associated with the absorption measurement could be minimized.

4.6. Conclusion

The rates of reaction for the OH + HBr and H/D isotopic variants have been measured between 53 and 135 K using a pulsed supersonic Laval nozzle flow reactor. For the OH + HBr system, the new low temperature results are found to be in accord with the measurements of Atkinson et al., but systematically lower than the studies of Jaramillo
and Smith, Jaramillo et al., and Sims et al., however this data does not alter our understanding of the temperature dependence of reaction R1. It most likely highlights the difficulty of working with HBr at low temperatures.

The KIE’s were also investigated and found to be independent of temperature between 53 and 135 K. These results seem to be in accord with the study of Bedjanian et al. However, a theoretical study capable of accurately treating the nature of the electronic surface and the zero point energy adjusted barriers would surely lend insight into the dynamics leading to the kinetic isotope effects measured for reactions R1 through R4.
CHAPTER 5. LOW TEMPERATURE NH (X^3\Sigma^-) RADICAL REACTIONS WITH NO, SATURATED AND UNSATURATED HYDROCARBONS BETWEEN 53 AND 188 KELVIN

5.1 Abstract

The reactions of ground state imidogen radicals (NH X^3\Sigma^-) with NO and select saturated and unsaturated hydrocarbons have been measured in a pulsed supersonic expansion Laval nozzle flow reactor in the temperature range of 53 to 188 K. The rate coefficients for the NH + NO system displays negative temperature dependence in the temperature regime currently investigated and a global temperature dependent fit is best represented in a modified power law functional form, with $k_1$ (NH + NO) = $(4.2 \pm 0.3) \times 10^{-11} \times (T/298)^{(-0.31 \pm 0.17)} \times \exp^{(76 \pm 20)/1} \text{cm}^3/\text{sec}$. The reactions of NH with ethylene, acetylene, propene, and diacetylene were measured over the temperature range of 53 – 135 K. In addition the reactions of NH with methane and ethane were also measured at 53 K, for reasons discussed later. The temperature dependence of the reactions of NH with the unsaturated hydrocarbons are fit using power law expressions, $k(T) = A(T/298)^n$, and are as follows: $k_4 = (2.3 \pm 1.2) \times 10^{-12} \times (T/298)^{(-1.08 \pm 0.33)} \text{cm}^3/\text{sec}$, $k_5 = (4.5 \pm 0.3) \times 10^{-12} \times (T/298)^{(-1.07 \pm 0.04)} \text{cm}^3/\text{sec}$, $k_6 = (5.7 \pm 1.9) \times 10^{-12} \times (T/298)^{(-1.23 \pm 0.21)} \text{cm}^3/\text{sec}$, and $k_7 = (7.5 \pm 1.8) \times 10^{-12} \times (T/298)^{(-1.23 \pm 0.15)} \text{cm}^3/\text{sec}$ for ethylene, acetylene, propene, and diacetylene, respectively. The rate for NH + ethane at 53 K is measured to be $k_3 = (6.8 \pm 1.7) \times 10^{-12} \text{cm}^3/\text{sec}$, while that for methane at the same temperature represents an upper
bound of $k_2 = (1.1 \pm 4.3) \times 10^{-12}$ cm$^3$/sec, as this is too slow to be measured with our current technique. The behavior of these systems throughout the temperature range explored indicates that these reactions occur over a potential energy surface without an appreciable barrier through a complex formation mechanism. Implications for chemistry in low temperature environments where these species are found are briefly discussed.

5.2. Introduction

The ground state NH ($X \ 3\Sigma^-$) radical is a chemically interesting species capable of participating in a rich set of chemistries mechanistically ranging from insertion to abstraction to addition. Studies of NH reactions with a variety of partners have been conducted from room temperature up to temperatures relevant to combustion processes. In particular studies of NH with NO have been investigated at high temperatures in shock heated gases, \cite{123,124} in flames, \cite{125,126} and at room temperature and above in order to gain experimental information on mechanism and branching ratio of a relatively simple reactive system. \cite{127-131} In addition, high temperature studies of NH with hydrocarbons have been conducted to investigate the role of abstraction and addition pathways, \cite{132-134} The self reaction \cite{135} and those of NH + OH \cite{126} and NH + O$_2$, \cite{123,136-139} have also been reported, and to the best of our knowledge, no studies below 250 Kelvin with any partner have been conducted.

The chemistry of NH radical on Titan is shown schematically in Figure 5.1. It has been detected in the atmosphere of Titan, and is thought to be formed by reaction of
N(\(^2\)D) with H\(_2\), but is not included in global rate models except with methyl, vinyl, and ethyl radicals.\(^{55}\) Experimental investigations of N(\(^2\)D) + H\(_2\) find this to be a viable formation pathway.\(^{140,141}\) Also explored are the dynamics of the reaction of N(\(^2\)D) atoms with acetylene. The primary reaction product is found to be cyanomethylene (HCCN), and reactions of this type are implicated in the formation of nitriles in the upper atmosphere of Titan.\(^{142}\) Reactions of the CN radical with hydrocarbons found in the atmosphere of Titan are also included in the chemical network, the products of which are also nitriles. Low temperature rate measurements have verified the feasibility of these addition/elimination routes for acetylene, ethylene\(^{23}\) allene, and methyl acetylene,\(^{143}\) as well as an abstraction pathway for CN with ethane.\(^{23}\) NH addition chemistry, although not currently considered in the modeling of planetary atmospheres, is of importance however, as the products of these reactions will similarly lead to the incorporation of nitrogen into carbon containing molecules. Their lack of inclusion in chemical models is probably due to their slow rate of reaction at room temperature and above. However, as presented in the Chapter 1 of this dissertation, a variety of neutral-neutral systems are now found that exhibit non-Arrhenius behavior at low temperature\(^{98}\) due to the effects of long range electrostatic interactions, increased collision complex lifetimes, and reaction surfaces without a potential barrier. Manifestation of these conditions results in appreciable reaction rates as the temperature is decreased, thus requiring accurate rate
Figure 5.1. Nitrogen chemistry on Titan.
data measurements in the temperature regime of interest for the chemical modeling of planetary atmospheres and interstellar environments such as dense molecular clouds.

In the present study we apply the pulsed Laval supersonic flow expansion technique to the study of NH radical reactions at low temperature and elucidate their behavior in a temperature regime important to the interstellar medium and planetary atmospheres such as Titan. The conditions found in Titan’s atmosphere have already been discussed, and thus are omitted here. The rate coefficients for the following reactions have been measured between 53 and 188 Kelvin:

\[
\begin{align*}
\text{NH} + \text{NO} & \quad \xrightarrow{k_1} \text{products} \\
\text{NH} + \text{CH}_4 & \quad \xrightarrow{k_2} \text{products} \\
\text{NH} + \text{C}_2\text{H}_6 & \quad \xrightarrow{k_3} \text{products} \\
\text{NH} + \text{C}_2\text{H}_4 & \quad \xrightarrow{k_4} \text{products} \\
\text{NH} + \text{C}_2\text{H}_2 & \quad \xrightarrow{k_5} \text{products} \\
\text{NH} + \text{C}_3\text{H}_6 & \quad \xrightarrow{k_6} \text{products} \\
\text{NH} + \text{C}_4\text{H}_2 & \quad \xrightarrow{k_7} \text{products}
\end{align*}
\]

Reaction (R1) was chosen as a prototype reaction with which to calibrate the performance of our flow technique, as kinetic data at slightly higher temperature is available. The reactants in (R2) through (R7) were chosen as they are important constituents in the atmosphere of Titan, and their low temperature chemistry with NH was previously unexplored. Reaction (R2) served as a further calibrant for the technique as the heat of reaction for this process is positive and thus the reaction should not be appreciably active at the temperatures employed. The heat of formation of the NH (X $^3\Sigma^-$)
radical leaves some uncertainty in the heat of reaction for reaction (R3), while all others, (R4) through (R7), should possess exothermic product channels.

5.3. Experimental

A detailed description of the pulsed uniform supersonic expansion flow reactor was presented in Chapter 2, and thus only the details pertinent to the NH radical studies will be given here. The kinetics of reactions (R1) – (R7) are studied by co-expanding known quantities of reagent and buffer gasses through a series of supersonic pulsed Laval nozzles. As mentioned previously, the Laval nozzle creates a unique low temperature environment in which the post nozzle flow is in local thermodynamic equilibrium, with a well defined hydrodynamic velocity and density. These conditions can be maintained for a number of centimeters past the exit, typically 20, providing a few hundred microsecond window in which reaction kinetics can be monitored. All kinetic studies were conducted under pseudo first order conditions in which the concentration of the reactant, i.e. [NO] or [hydrocarbon], was in excess of the NH radical. NH radicals are created using a pulsed DC discharge in the stagnation volume, from a mixture of less than 1% H₂ in N₂, for the nitrogen nozzles employed, or mixture of a few percent H₂ and N₂ in Ar, for the 53 K measurements employing an argon buffer. NH radical time dependent evolution was monitored using laser induced fluorescence (LIF). The NH radical A ^3Π ← X ^3Σ^- (v' = 1 ←v'' = 0) transition was excited using a tunable dye laser (Continuum model ND60) operating with Rhodamine 640 dye, which was pumped by a 10 Hz pulsed Nd:YAG laser
The primary dye radiation was doubled in a KD*P crystal producing tunable light near 305 nm. Laser frequency calibration was accomplished using the optogalvanic lines of Fe and Ne pumped with the dye laser fundamental. In all cases the \( R_{P31}(1) \) transition at \( \sim 304.32 \) nm was used for kinetic studies. A 188 K spectrum of the \( A \leftarrow X \) (\( v' = 1 \leftarrow v'' = 0 \)) band taken in the \( \text{N}_2\text{M}21\text{e}17 \) nozzle, is shown in Figure 5.2. The transitions are labeled in \( J'' \). A digression into the labeling of energy levels and the spectroscopy of NH radical is provided to clarify the nomenclature used in Figure 5.2.

The NH radical \( \Lambda^3\Pi \leftarrow X^3\Sigma^- \) system is a good example of a Hund’s case b to case b transition at high \( J \). At low \( J \) a transition to case a behavior in the \( \Lambda \) state is observed. As a result transitions other than those normally allowed from pure case b selection rules become allowed and weak satellite branches are observed. In pure case b each vibrational band has 9 strong transitions \( P_1, P_2, P_3, Q_1, Q_2, Q_3, R_1, R_2, \) and \( R_3 \), the branches being split due to electron spin. There are a total of 18 possible satellite branches allowed, 9 of which have been observed in the LIF spectrum taken in the Laval flow. The important quantum numbers for case b, as well as the coupling scheme follows and is taken from Herzberg. The case b type coupling is generally identified by a weak or zero coupling of the electron spin to the internuclear axis of the molecule. Under these conditions the orbital angular momentum (\( \Lambda \)) when non-zero couples to \( N \), the rotational angular momentum, to form a resultant designated \( K \). The resultant, \( K \), is the total angular momentum neglecting spin, and takes on the values \( K = \Lambda, \Lambda + 1, \Lambda + 2, \ldots \), according to the angular momentum vector addition rules \( \Lambda + N = K \). When \( \Lambda = 0 \), such
Figure 5.2. NH radical $A^3\Pi_i \leftrightarrow X^3\Sigma^-$ ($v' = 1 \leftrightarrow v'' = 0$) LIF spectrum taken at 188 K using the N$_2$M21e17 nozzle.
as in the ground state of the NH radical, \( K = N \) and \( N \) is perpendicular to the internuclear axis, and \( K \) takes on values from 0 on up. The total angular momentum of the system including electron spin is obtained by coupling \( K \) and \( S \) to form \( J \). The possible values of this quantum number are given by: \( J = (K+S), (K+S-1), (K+S-2), \ldots, |K-S| \), and each \( K \) will have \((2S+1)\) components. \( J \) will therefore be integer numbers for an even number of unpaired electrons and half-integer for an odd number of unpaired electrons. A slight splitting of \( J \) levels with equal \( K \) arises due to the magnetic moment caused by the coupling of \( S \) and \( K \) due to molecular rotation, causing each \( N \) component to be split into three \( J \) components in the ground and first excited state of the NH radical. The exception is \( N = 0 \) in the ground state which is singly degenerate. A vector diagram of the coupling in Hund's case b can be seen in Figure 5.3. For the ground state of the NH radical \( X^3\Sigma^- \), two unpaired electrons reside in \( \Pi_x \) and \( \Pi_y \) molecular orbitals leading to the triplet multiplicity. The \((-)\) sign in the term symbol refers to the Kronig symmetry of the orbitals upon reflection through a vertical mirror plane (\( \sigma_v \)). For NH the reflection results in a change in sign for the orbitals in question and is thus of \((-)\) symmetry. The energy level diagram for the \( A \leftarrow X \) system of NH is depicted in Figure 5.4. As can be seen from Figure 5.4 the ground state degeneracy normally observed for the rotational states is removed due to spin-rotation interaction. Each \( N \) state then, except for \( N = 0 \), is split into a triplet. It is standard spectroscopic notation to label the individual fine structure \( J \) states with the \( F \) notation, such that \( F_1 \) represents the state with \( J_{\text{max}} \), i.e. \((N + S)\). The \( \pm \) symbols represent the total parity of the system, with selection rules determined by the transition moment operator, such that only \(+ \leftrightarrow -\) transitions are allowed. The first
Figure 5.3. Hund’s case b coupling scheme as applied to the NH radical.
Figure 5.4. Energy level diagram and transition nomenclature for the NH radical. The splittings in the ground and excited state have been greatly exaggerated for clarity.
excited state A, is $^3\Pi_b$, and is inverted with the degeneracy in this state removed due to
spin-orbit interactions. Additionally the degeneracy of each rotational state is lifted due to
A-doubling, which arises due to spin-spin interactions and perturbations from other states.
The $^1\Sigma$ and $^5\Sigma$ states are the two that have been implicated.\footnote{145} With this in mind the
selection rules for the main branches are $\Delta N = \Delta J = 0, \pm 1$, while the satellite transitions
$\Delta N \neq \Delta J$ occur due to the transition in J from Hund’s case b to case a in the A state.

The nomenclature used for the transitions is similar to that used by Brazier et al.,\footnote{146} with the branch designation referenced to $J''$, i.e. the ground state total angular
momentum. The designations for the individual P, Q, and R branches are as follows,

$A^B_{CD}(J'')$, where A equals the change in N quantum number ($N'' - N'$), B is the change in
the J quantum number ($J'' - J'$), C represents the excited state fine structure component, 1
for $F_1 (^3\Pi_2)$, 2 for $F_2 (^3\Pi_1)$ and 3 for $F_3 (^3\Pi_0)$, D represents the ground state fine structure
level, and $J''$ is the rotational state from which the transition originates. These
designations are all that is necessary to completely define a transition. For the case of the
main branches, P, Q, and R, the A designation is dropped and assumed to follow that of
$\Delta J$, while for the satellite braches it is retained. As an example the $^R{P}_{31}(1)$ transition is R
type in N ($N'' = N' - 1$), P type in J ($J'' = J' + 1$), and is a transition between $F_3$ in the A
state and $F_1$ in the ground state with the ground state $J = 1$. It is this nomenclature that is
used to label the individual transitions of the NH A $\leftrightarrow$ X transition shown in Figure 5.2.
The spectral region of 303 to 308 nm is enough to completely cover the P, Q, R and
satellite branches of the $(v' = 1 \leftrightarrow v'' = 0)$ band, as well as the R and Q branch of the $(v' = 2 \leftrightarrow v'' = 1)$ band. In Figure 5.2 the (2-1) band transitions are labeled with a (2-1)
designation, while in Figure 5.5 (an expanded view of the (2-1) region), the (1-0) transitions are labeled with a (1-0). As can be seen from both spectra the signal to noise is quite high, the Franck-Condon factor for this transition is 0.204.\textsuperscript{147} The specified dye laser linewidth of 0.05 cm\textsuperscript{-1} from Continuum is nearly four times smaller than that observed in the NH radical spectrum (FWHM $^{\text{R}}P_{31}(1)$ transition $\approx$ 0.2 cm\textsuperscript{-1}). The NH spectrum was taken at 900 $\mu$J laser power, as this power was experimentally found to minimize the contribution to the peak width from power broadening. The linewidth observed is thus most likely due to the inherent linewidth at the temperature and pressure of the experiment. Similar linewidths were observed in the spectroscopic studies of Brazier et al. (0.17 – 0.25 cm\textsuperscript{-1}) while slightly larger were obtained in the Crosley study due to the laser linewidth of 0.34 cm\textsuperscript{-1}. The spectral assignment was accomplished with the aid of previous spectroscopic work done on this system. The P, Q, and R main branches used the line positions from Brazier et al.\textsuperscript{146}, while the satellite branch line positions were obtained from Dixon,\textsuperscript{145} and Crosley and Anderson.\textsuperscript{148} A total of 115 lines in all were assigned to the NH (A $\leftrightarrow$ X, 1-0 and 2-1) bands. The remaining are believed to be satellite lines not reported in the spectroscopic literature cited above, and contaminant OH (A $\leftrightarrow$ X, $v' = 0 \leftrightarrow v'' = 0$) fluorescence in the NH (2-1) region which falls within the bandpass of the PMT filters employed in the experiment. Figure 5.6 is a graph of the calibrated laser frequency at which the P, Q, and R spectral lines were assigned vs. that of the line position frequencies for the P, Q, and R branches found by the study of Brazier et al.\textsuperscript{146} The linearity of the plot and the goodness of fit give us confidence in the line assignments made for the spectra in Figures 5.2 and 5.5.
Figure 5.5. Expanded view of the $A \leftrightarrow X (v' = 2 \leftrightarrow v'' = 1)$ band transition. Transitions from the $(v' = 1 \leftrightarrow v'' = 0)$ band are labeled $(1 - 0)$. 

Wavelength (nm)
Figure 5.6. Graph of the branch (P, Q, R) transition assignments vs. their literature value used to ensure correct spectral assignment. Literature values were taken from Brazier et al., 1986 [146].
The resulting NH (1 → 1) fluorescence due to the laser induced absorption event was collected with a photomultiplier tube (Hamamatsu R3896) situated perpendicular to the flow axis employing an appropriate filter set (Schott glass BG-40 and Corning 7-60). This band was chosen to minimize scattered light in the collection system and also to maximize signal, due to the Franck-Condon factors between these two states. The LIF signal was amplified and sent to either a boxcar integrator (SRS 250) or an oscilloscope (LeCroy 9400) and averaged for 200 to 500 shots. The gases used for these studies are as follows: methane, Matheson C.P., 99%, propene, Matheson, Research 99.97%, ethane, Matheson, C.P., 99%, ethylene, Matheson, Research, 99.999%, acetylene, Matheson, Purified, 99.6%, H₂, AirLiquide, 99.95%, N₂, US Airweld, 99.99%, and Ar, US Airweld, UHP, 99.999%. Diacetylene was prepared by the dehydrohalogenation of 1,4-dichloro-2-butyne in DMSO, by gentle heating of the mixture to 75 °C, with dropwise addition of a 20% w/w solution of NaOH over the course of 30 minutes. The diacetylene evolved was dried in a calcium chloride/P₂O₅ trap, and then immediately condensed in a liquid N₂ trap, for storage. This sample was then transferred to a mixing tank and diluted to less than 1% in N₂ and used as such. The purity of the sample was checked via IR absorption, and was found to be in excess of 99%.

While some of the following is a review of the principles and techniques described in Chapter 2, it is included to introduce the independent temperature determination conducted on the NH radical in these studies. As previously mentioned, it is essential to the successful execution of these measurements to obtain precise knowledge of the post nozzle flow conditions where the chemical reaction studies take
place. In particular, one is interested in the distance for which flow uniformity, in both density and temperature, is maintained. The final supersonic flow parameters are linked to the pre-expansion conditions through the Mach number of the flow and the isentropic relationship, Equations 5.1 and 5.2:

\[
\frac{T}{T_0} = \left(1 + \frac{\gamma - 1}{2} M^2 \right)^{-1} \tag{5.1}
\]

\[
\frac{\rho}{\rho_0} = \left(1 + \frac{\gamma - 1}{2} M^2 \right)^{\frac{\gamma}{\gamma - 1}} \tag{5.2}
\]

where \( M \) is the Mach number, \( \rho_0 \) is the chamber pressure, and \( \gamma \) is the heat capacity ratio \( C_p/C_v \). The flow uniformity was verified using an impact pressure transducer, or Pitot probe, placed in the path of the flow, approximately 3 cm below the laser probe beam. The measured impact parameters, \( P_i \), were converted into a Mach number using the Rayleigh-Pitot formula (Equation 5.3)

\[
\frac{P_i}{P_0} = \left(\frac{\gamma + 1}{2} M^2 \right)^{\frac{\gamma}{\gamma - 1}} \left(\frac{\gamma + 1}{2\gamma M^2 \left(\gamma - 1\right)}\right)^{\frac{\gamma}{\gamma - 1}} \tag{5.3}
\]

where \( P_0 \) is the chamber pressure, and the other symbols are the same as defined for the isentropic relationship. The flow Mach number was then used in conjunction with the
isentropic expansion relationship, Equation 5.1, and knowledge of $T_0$, to extract the flow temperature. In addition, the flow temperatures obtained from the impact measurements were compared to the temperatures probed using laser induced fluorescence, by scanning a number of rotational branch transitions and relating the individual fluorescence intensities to the population in that rotational state through the rotational line strengths and the Boltzmann equation. Line intensities were obtained by integrating the individual line profiles. Both methods, pitot and LIF were found to agree within their respective errors, for all nozzles used in this study. The nozzles used were the ArM32e16 ($T = 53 \pm 4$ K), the N$_2$M32e16 ($T = 83 \pm 3$ K), the N$_2$M33e16 ($T = 135 \pm 11$ K), and the N$_2$M21e17 ($T = 188 \pm 7$ K). The temperatures reported above and in Table 2.1 were derived from experiments using the $A ^2\Sigma \leftarrow X ^2\Pi_{3/2} (v' = 1 \leftarrow v'' = 0)$ $S_{21}$ branch transitions of either the OH or OD radical. In addition, it was desirable to verify that the NH radical rotational population was equilibrated in the flows, under conditions used for the kinetic experiments. As a result, the $R_1$, $R_2$, $R_3$, $P_1$, $P_2$, and $P_3$ branch transitions from Figure 5.2 were subjected to a Boltzmann analysis. The flow temperature obtained from the NH lines ($T = 176 \pm 10$ K) was found to agree within experimental error to the temperature derived from OH LIF measurements ($T = 188 \pm 7$ K) and pitot impact measurements ($T = 183 \pm 4$ K) for the N2M21e17 nozzle. Figure 5.7 shows the Boltzmann plot used to obtain the temperature. The rotational line strength factors, $S_{ij}$, and rotational term energies were taken from Lucht et al.$^{150}$ The agreement for the other nozzles, as regards NH equilibration, is assumed.
Figure 5.7. Boltzmann plot used to extract the flow temperature in the N₂M₂1e17 nozzle using the NH radical spectrum.
5.4. Results

Rate coefficients for the reactions of imidogen radical with NO and the hydrocarbons were measured under pseudo first order conditions, such that the concentration of the reactant was much larger than that of the NH concentration. Under these conditions the loss rate of NH can be expressed as

\[
\frac{d[NH]}{dt} = -k[NH][R] = k'[NH] \quad \text{with} \quad k' = k[R]
\]  

(5.4)

where [NH] and [R] represent the concentration of the imidogen radical and reactant in the final supersonic flow, respectively. Rearrangement and integration of equation (4), with the assumption that \( d[R]/dt = 0 \), yields:

\[
\ln \left( \frac{NH(z)}{NH(z_0)} \right) = \frac{k}{u} (Z - Z_0)
\]  

(5.5)

Since the hydrodynamic flow velocity \( u \) is well defined and \( du/dt = 0 \) in the post nozzle Laval flow region, the reaction time \( t \) can be obtained from the relationship \( \Delta t = \Delta Z/u \), where \( \Delta Z \) is the distance between the nozzle exit and the laser probe. The bimolecular rate coefficient \( k \), is extracted by monitoring the distance dependent decay of NH via the LIF method at various positions in the flow, usually between 8 and 10, in the presence of
a known concentration of R. This is repeated for a number of differing concentrations of R, between 5 and 10, while holding the rest of the experimental parameters constant. Flow conditions were constantly monitored throughout the duration of the kinetic runs, using both the stagnation and impact transducers, to ensure uniformity. Plots of the natural logarithm of the normalized signal vs. distance, yield the pseudo first order decay constant k', Figure 5.8. Linear least squares fitting is used to extract k'. The individual k' values are then plotted against the concentration of reactant R, under which they were obtained, Figure 5.9. The slope equals the bimolecular rate coefficient and is extracted in a similar fashion, using linear least squares fitting. The linearity of both plots validates pseudo first order conditions. The non-zero intercept in Figure 5.9, at [R] = 0, is most likely due to reactivity of NH with other species in the flow, and possibly to some extent diffusional loss, but in all cases represents only a small portion of the total NH decay in the presence of reactant.

The temperature dependent rate coefficients determined from these studies, for the reaction partners nitric oxide, methane, ethane, ethylene, acetylene, propene, and diacetylene are summarized in Table 5.1. The inverse temperature dependence of the rate of reaction of NH with NO is illustrated in Figure 5.10, along with previous experimental measurements made by Harrison, et al. in the 250 – 400K window, using a Pyrex photolysis cell. The best fit to the entire data set is found to be k(T) = (4.20 ± 0.31) × 10^{-11} \times (T/298)^{0.31 ± 0.17} \times \exp\left[(76 ± 20)/T\right] \text{cm}^3\text{sec}^{-1}.
Figure 5.8. Pseudo 1st order decays of the NH LIF signal for the reaction of NH + NO in the post N2M33e16 nozzle flow.
Figure 5.9. $k'$ vs. [NO] for the NH + NO reaction in the post N$_2$M33e16 nozzle flow used to extract the bimolecular rate coefficient.
Table 5.1. Temperature Dependent Rate Data for the Reaction of NH Radical with NO, Saturated, and Unsaturated Hydrocarbons.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Nozzle</th>
<th>Temp (K)</th>
<th>[R] (10^{13} \text{ cm}^{-3})</th>
<th>(k(10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>ArM32E16</td>
<td>53</td>
<td>1.3</td>
<td>10.46 ± 0.89</td>
</tr>
<tr>
<td>Methane</td>
<td>ArM32E16</td>
<td>53</td>
<td>1.9</td>
<td>0.105 ± 0.432</td>
</tr>
<tr>
<td>Ethane</td>
<td>ArM32E16</td>
<td>53</td>
<td>4</td>
<td>0.68 ± 0.165</td>
</tr>
<tr>
<td>Ethylene</td>
<td>ArM32E16</td>
<td>53</td>
<td>3.9</td>
<td>1.55 ± 0.16</td>
</tr>
<tr>
<td>Acetylene</td>
<td>ArM32E16</td>
<td>53</td>
<td>1.6</td>
<td>2.88 ± 0.49</td>
</tr>
<tr>
<td>Propene</td>
<td>ArM32E16</td>
<td>53</td>
<td>1.6</td>
<td>4.64 ± 0.7</td>
</tr>
<tr>
<td>Diacetylene</td>
<td>ArM32E16</td>
<td>53</td>
<td>1.1</td>
<td>6.34 ± 0.75</td>
</tr>
<tr>
<td>NO</td>
<td>N2M32E16</td>
<td>83</td>
<td>2.4</td>
<td>7.11 ± 0.35</td>
</tr>
<tr>
<td>Ethylene</td>
<td>N2M32E16</td>
<td>83</td>
<td>3.2</td>
<td>0.786 ± 0.189</td>
</tr>
<tr>
<td>Acetylene</td>
<td>N2M32E16</td>
<td>83</td>
<td>1.9</td>
<td>1.82 ± 0.69</td>
</tr>
<tr>
<td>Propene</td>
<td>N2M32E16</td>
<td>83</td>
<td>1.6</td>
<td>2.97 ± 0.77</td>
</tr>
<tr>
<td>Diacetylene</td>
<td>N2M32E16</td>
<td>83</td>
<td>1</td>
<td>3.37 ± 0.65</td>
</tr>
<tr>
<td>NO</td>
<td>N2M33E16</td>
<td>135</td>
<td>2.4</td>
<td>5.92 ± 1.17</td>
</tr>
<tr>
<td>Ethylene</td>
<td>N2M33E16</td>
<td>135</td>
<td>5.5</td>
<td>0.658 ± 0.123</td>
</tr>
<tr>
<td>Acetylene</td>
<td>N2M33E16</td>
<td>135</td>
<td>4.5</td>
<td>1.03 ± 0.5</td>
</tr>
<tr>
<td>Propene</td>
<td>N2M33E16</td>
<td>135</td>
<td>2.1</td>
<td>1.28 ± 0.28</td>
</tr>
<tr>
<td>Diacetylene</td>
<td>N2M33E16</td>
<td>135</td>
<td>1.9</td>
<td>2.19 ± 0.32</td>
</tr>
<tr>
<td>NO</td>
<td>N2M21E17</td>
<td>188</td>
<td>8.9</td>
<td>5.63 ± 1.57</td>
</tr>
</tbody>
</table>
Figure 5.10. Plot of the rate coefficient versus temperature for the NH + NO reaction.
Figure 5.11 depicts the temperature dependence for the reactions of NH with the unsaturated hydrocarbons ethylene, acetylene, propene, and diacetylene between 53 – 135 K, along with single temperature measurements for methane and ethane at 53 K. Best fits to the power law functional from $A \times (T/298)^n$, are given in Table 5.2. Figure 5.12 includes the data from the studies of Rohrig et al. at temperatures above 1000 K, conducted in incident shock waves in an aluminum shock tube apparatus.\textsuperscript{133,134}

## Table 5.2. Best Fit Parameters Obtained for the NH + Unsaturated Hydrocarbon Reactions to the Functional Form: $k_{fit}(T) = A \times (T/298)^n$

<table>
<thead>
<tr>
<th>Reactant</th>
<th>$A \times 10^{12}$ cm$^3$sec$^{-1}$</th>
<th>-n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>2.3 ± 1.2</td>
<td>1.08 ± 0.33</td>
</tr>
<tr>
<td>Acetylene</td>
<td>4.5 ± 0.3</td>
<td>1.07 ± 0.04</td>
</tr>
<tr>
<td>Propene</td>
<td>5.7 ± 1.9</td>
<td>1.23 ± 0.21</td>
</tr>
<tr>
<td>Diacetylene</td>
<td>7.5 ± 1.8</td>
<td>1.23 ± 0.15</td>
</tr>
</tbody>
</table>
Figure 5.11. Plot of the rate coefficient versus temperature for the NH + hydrocarbon reactions.
Figure 5.12. Plot of the rate coefficient versus temperature for the NH + hydrocarbon reactions including the high temperature data from Rohrig et al. Closed symbols – this work. Open symbols – Rohrig et al. [133, 134].
5.5. Discussion

5.5a. NH + NO

Studies on the NH + NO reaction system were initially conducted for a number of reasons. Past work on this system indicated that the reactivity was fairly constant over the temperature range investigated, and that the reaction proceeded through a complex formation mechanism involving the HNNO species.\textsuperscript{128,151,152} Rates weakly dependent on temperature in a region near room temperature and above are generally indicative of a reaction occurring over an attractive potential energy surface without a barrier, and are ideal candidates for study with the Laval technique, as the onset to their inverse temperature dependence usually occurs around 200 K. Further, it is interesting to note that uncertainty in the branching ratio for two thermodynamically accessible product channels exists. While Lee et al. have had success at determining the products for the reaction of C\textsubscript{2}H radicals with acetylene\textsuperscript{38} and O\textsubscript{2}\textsuperscript{40} using the Laval method, it is by far not universal, and thus presents an interesting challenge to researchers in the field. The two thermodynamically accessible channels are

\begin{align*}
\text{NH} + \text{NO} &\rightarrow \text{Products} \quad \text{(R1)} \\
\text{NH} + \text{NO} &\rightarrow \text{N}_2\text{O} + \text{H} \quad \Delta H_{\text{rxn}} = -146 \text{ kJ/mol} \quad \text{(R1a)} \\
\text{NH} + \text{NO} &\rightarrow \text{N}_2 + \text{OH} \quad \Delta H_{\text{rxn}} = -407 \text{ kJ/mol} \quad \text{(R1b)}
\end{align*}
and both produce species that are potentially traceable in the flow. OH is easily monitored using LIF, while H atoms can be monitored through the chemiluminescent reaction with NO. The reaction is known to produce the HNO* intermediate, which decays by light emission to the red of 600 nm. Harrison et al. fail to see either product species in their experiment, but argue that their OH detection scheme was far from optimal, and are in favor of channel R1b. Yamasaki et al., using a room temperature fluorescence cell with appropriate laser systems for LIF detection of NH and OH were able to measure both channel R1 and R1b independently and conclude that R1b accounts for nearly 100% of the branching. These authors argue the sensibility of their results based on symmetry correlations between the HNNO intermediate $^2A''$ and the OH + N2 products channel. However, Durant measured a branching fraction of $0.8 \pm 0.4$ for channel R1a and supported the result with theoretical calculations implicating the dissociation of the cis-HNNO isomer on the $^2A'$ surface as the responsible species for preferential branching to R1a due to a lower transition state energy. Attempts were made in this study to monitor both of these product species; however complications with both radicals, due to low count rates and high background fluorescence precluded extraction of information regarding their concentration and thus branching ratio for R1.

While most of the interest in R1 has been generated at higher temperature due to its importance to combustion reactions, the low temperature behavior is nonetheless equally as interesting, as it appears that the reaction mechanism remains the same throughout the entire temperature range investigated. Further, observation of the inverse temperature dependence, with an onset near 150 K, provides information on the behavior
of radical-radical reactions occurring at low temperature. While this reaction in particular is not implicated as being responsible for chemistry in chemically interesting environments such as Titan or the ISM, information of this sort is crucial for accurately modeling such situations, especially when considering the difficulty in experimentally obtaining accurate rate data for open shell systems.

The JPL recommendation for reaction R1 is $k_{298} = 4.9 \times 10^{-11}$ cm$^3$ sec$^{-1}$ with a barrier $E_a/R = (0 \pm 300)$ K.$^{154}$ We suggest a global fit to the modified power law form, between 50 – 400 K, of $k(T) = (4.20 \pm 0.31) \times 10^{-11} \times (T/298)^{(0.31 \pm 0.17)} \times \exp^{(176 \pm 20)/T}$ cm$^3$ sec$^{-1}$. This fit is not anticipated to model the temperature dependence outside of this range. Physical interpretation of the parameters $n$ and $E_a$ is somewhat ambiguous, however fits to a power law form $A \times (T/298)^n$, were found to poorly represent both data sets. The $A \times (T/298)^n$ fit to just the low temperature data produces $n = (-0.54 \pm 0.11)$, which is in reasonable accordance with the $T^{-2/3}$ dependence predicted by capture theory based on long range interactions.

The final motivation for conducting experiments on the NH + NO system was to serve as a calibrant for our measurement technique. Previous measurements with OH + HBr were found to be in accord with the available literature;$^{31}$ however, an independent validation was deemed desirable for the NH system. As can be seen in Figure 5.10 the agreement of our data with the available measurements at higher temperature is quite good, and gives us confidence in the results.
5.5b. NH + Unsaturated hydrocarbons

The reactions of NH radical with unsaturated hydrocarbons, as illustrated in Figure 5.11, are also seen to manifest inverse temperature dependence over the temperature range explored. The $A \times (T/298)^n$, best fit parameters reveal a few interesting details. First the temperature dependence for all reaction species, ethylene, acetylene, propene, and diacetylene are the same, within experimental error, and range in value from $n = (1.07 \rightarrow 1.23)$. This is not necessarily anticipated from a simple capture theory model, for two reasons. Capture theory predicts a $T^{1/6}$ temperature dependence for the interaction of a dipole-induced dipole system, and a $T^{2/3}$ dependence for a dipole-dipole interaction, neither of which are observed. The independence of $n$ on reaction partner, dipole-induced dipole for ethylene, acetylene, and diacetylene, and dipole-dipole for propene, and also its nominal value of -1.1 for all systems, indicates that the dynamics of these systems is not described by simple classical capture theory. In addition, the capture theory calculations of $k$ (50 K) predict a rate in the range of $2 \times 10^{-10}$ cm$^3$/sec, for the species in this investigation, nearly a factor of 3 higher than observed for the most reactive partner. However, it is not clear whether this calculation indicates that the reaction is occurring at approximately one-third of the collision frequency, or whether other factors in the capture calculation need to be considered, such as the anisotropy of the potential or inclusion of dipole-quadrupole potential terms. In addition, it has been documented that long range capture theory is not as easily applied to neutral systems as it is to ion-molecule reactions and that detailed *ab initio* calculations on the PES are
necessary. For CN additions into the carbon π system of C₂H₂, ab initio calculations were able to deduce the pertinent features of the PES and found that a barrierless entrance channel, in conjunction with a small exit channel barrier lying below the energy of the reactants, was much better able to reproduce the inverse temperature dependence measured for this system, than was pure capture theory. An exit barrier of this sort prevents the adduct formed from dissociating into products through the effective potential which is the sum of the electronic + centrifugal terms. Therefore, at high temperature and thus high angular momentum, the effective potential slows down the reaction, but its effect at low temperature is reduced as the amount of angular momentum in the system is correspondingly decreased. It seems that similar arguments may apply here, although it is clear that detailed ab initio calculations need to be conducted.

Insights into the reaction mechanism and products formed can be gained by examining the thermochemistry and the trends in reactivity with regards to reactant complexity. NH radicals can potentially participate in either abstraction or addition/elimination chemistry; the addition channel involving either addition into a C-C or C-H bond. Abstraction of an H atom from the C-H bond of the hydrocarbons methane, ethane, ethylene is endothermic, ΔH_rxn(298 K) = 8.2, 3.4, and 14.1 kcal/mol, respectively, and are thus not likely to be occurring in the low temperature environment of the post nozzle flow. The heats of reaction were calculated using the ΔH_f (298 K) values taken from Lias et al. and Chase. Further, significant barriers are found in these cases at high temperature. Table 5.3 lists the thermodynamics and barriers (when experimentally measured) for the reactions of NH radical with hydrocarbons. In contrast,
the thermodynamics of the products formed from an NH addition into the π bond followed by subsequent rearrangement, elimination, or bond cleavage is generally exothermic for the species ethylene, acetylene, propene, and diacetylene, as seen in Table 5.4. Caution should be exercised when viewing Table 5.4 as the products shown generally require a number of rearrangements and/or isomerizations followed by an elimination, bond cleavage, or stabilization event, which may or may not be mechanistically available. The products listed in the table are therefore there to illustrate potential reaction channels and their thermodynamics only.

The slow rates for NH + methane and ethane at 53 K indicate that the endothermic hydrogen atom abstraction channel is not the dominant one. The methane rate is too slow to be measured using the current Laval technique and \((1.1 \pm 4.3) \times 10^{12}\) cm\(^3\)/sec represents an upper bound to the actual rate. In contrast appreciable reactivity is observed at all temperatures investigated for the unsaturated species, with the rate increasing with carbon chain length. Attempts were made to correlate this effect to the ionization potential of the unsaturated species, as the low ionization potential of the unsaturated hydrocarbons has been implicated as facilitating addition reactions involving radical species,\(^{25,159}\) as well as its cross section calculated from a simple geometric model, but correlations were not easily recognized.

Justification for an addition mechanism at low temperature can be gained by examination of other radical plus unsaturated species systems studied under similar conditions. Sims et al. have studied the reactions of CN (X^2Π) with unsaturated
Table 5.3. NH Radical Abstraction Reaction Thermochemistry with Saturated and Unsaturated Hydrocarbons.

<table>
<thead>
<tr>
<th>A</th>
<th>ΔH_{fA}</th>
<th>B</th>
<th>ΔH_{fB}</th>
<th>Prod 1</th>
<th>ΔH_{f1}</th>
<th>Prod 2</th>
<th>ΔH_{f2}</th>
<th>ΔH_{ron}</th>
<th>E_a</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH (^1Σ) 90</td>
<td>CH_4</td>
<td>-17.89</td>
<td>CH_3</td>
<td>34.821</td>
<td>NH_2</td>
<td>45.5</td>
<td>8.211</td>
<td>21 ± 1.2</td>
<td></td>
</tr>
<tr>
<td>NH (^3Σ) 90</td>
<td>C_2H_6</td>
<td>-20.04</td>
<td>C_2H_5</td>
<td>28.4</td>
<td>NH_2</td>
<td>45.5</td>
<td>3.94</td>
<td>16.7 ± 1.2</td>
<td></td>
</tr>
<tr>
<td>NH (^1Σ) 90</td>
<td>C_2H_4</td>
<td>12.54</td>
<td>C_2H_3</td>
<td>71.1</td>
<td>NH_2</td>
<td>45.5</td>
<td>14.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH (^3Σ) 90</td>
<td>C_2H_2</td>
<td>54.19</td>
<td>C_2H</td>
<td>114</td>
<td>NH_2</td>
<td>45.5</td>
<td>15.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH (^1Σ) 90</td>
<td>C_3H_6</td>
<td>4.897</td>
<td>C_3H_5</td>
<td>40.9</td>
<td>NH_2</td>
<td>45.5</td>
<td>-8.497</td>
<td>14.6 ± 1.2</td>
<td></td>
</tr>
<tr>
<td>NH (^3Σ) 90</td>
<td>C_2H_2</td>
<td>111</td>
<td>C_2H</td>
<td>No Data</td>
<td>NH_2</td>
<td>45.5</td>
<td>&gt; 0 ??</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All units are in (kcal/mol)
E_a's taken from Rohrig and Wagner, 1994.

Table 5.4. Thermochemistry of Potential Exothermic Reaction Routes for NH Radical with Unsaturated Hydrocarbons Initiated by the Initial Addition of NH into the π Bond.

<table>
<thead>
<tr>
<th>A</th>
<th>ΔH_{fA}</th>
<th>B</th>
<th>ΔH_{fB}</th>
<th>Prod 1</th>
<th>ΔH_{f1}</th>
<th>Prod 2</th>
<th>ΔH_{f2}</th>
<th>ΔH_{ron}</th>
<th>E_a</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH (^1Σ) 90</td>
<td>C_2H_2</td>
<td>54.19</td>
<td>CH_3CN</td>
<td>17.7</td>
<td>M</td>
<td>0</td>
<td>-126.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH (^3Σ) 90</td>
<td>C_2H_2</td>
<td>12.54</td>
<td>H_2CCN</td>
<td>59</td>
<td>H</td>
<td>52</td>
<td>-33.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH (^1Σ) 90</td>
<td>C_2H_2</td>
<td>54.19</td>
<td>CH_2CN</td>
<td>93</td>
<td>HCN</td>
<td>32.3</td>
<td>-18.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH (^3Σ) 90</td>
<td>C_2H_2</td>
<td>54.19</td>
<td>CH_3</td>
<td>34.8</td>
<td>CN</td>
<td>104</td>
<td>-5.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH (^1Σ) 90</td>
<td>C_2H_4</td>
<td>12.54</td>
<td>H_2CHC=NH</td>
<td>6</td>
<td>M</td>
<td>0</td>
<td>-96.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH (^3Σ) 90</td>
<td>C_2H_4</td>
<td>12.54</td>
<td>H_2C=NCH_3</td>
<td>11</td>
<td>M</td>
<td>0</td>
<td>-91.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH (^1Σ) 90</td>
<td>C_2H_4</td>
<td>12.54</td>
<td>H_2C=CHNH_2</td>
<td>7</td>
<td>M</td>
<td>0</td>
<td>-95.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH (^3Σ) 90</td>
<td>C_2H_4</td>
<td>12.54</td>
<td>C_2H_3N</td>
<td>30.2</td>
<td>M</td>
<td>0</td>
<td>-72.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH (^1Σ) 90</td>
<td>C_2H_4</td>
<td>12.54</td>
<td>CH_3CN</td>
<td>17.7</td>
<td>H_2</td>
<td>0</td>
<td>-84.84</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH (^3Σ) 90</td>
<td>C_2H_4</td>
<td>12.54</td>
<td>CH_2CN</td>
<td>41</td>
<td>H_2</td>
<td>0</td>
<td>-61.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH (^1Σ) 90</td>
<td>C_2H_4</td>
<td>12.54</td>
<td>CH_3NC</td>
<td>??</td>
<td>H_2</td>
<td>0</td>
<td>??</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH (^3Σ) 90</td>
<td>C_2H_4</td>
<td>12.54</td>
<td>CH_3CNH</td>
<td>??</td>
<td>H</td>
<td>52</td>
<td>??</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH (^1Σ) 90</td>
<td>C_2H_4</td>
<td>12.54</td>
<td>CH_3NCH</td>
<td>??</td>
<td>H</td>
<td>52</td>
<td>??</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH (^3Σ) 90</td>
<td>C_3H_6</td>
<td>12.54</td>
<td>CH_4</td>
<td>-17.89</td>
<td>HCN</td>
<td>32.3</td>
<td>-88.13</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All units are in (kcal/mol)
M = 3 Body Stabilization Process
?? = Values for the Heat of Formation not Available
hydrocarbons and speculate that the dominant mechanism is the addition of the radical to
the π bond of the unsaturated hydrocarbon, leading to an exothermic displacement of an
H atom by the CN group. Canosa et al. also speculate that additions of CH radical to
unsaturated hydrocarbons proceeds by a similar mechanism, in which a complex
intermediate is formed and then dissociates producing a radical hydrocarbon and H atom.
Further, they comment that the process is driven at low temperature by the high electron
affinity of the radical and low ionization energy of the hydrocarbon species. Clary et al.,
in a joint theoretical and experimental paper, pay extensive attention to the reaction of
C(3P3) with acetylene. The results from low temperature experimental studies in the
CRESU, crossed molecular beam experiments of integral and differential cross sections
and electronic structure and wave packet calculations show that the mechanism for this
reaction proceeds through an initial addition complex of the C atom to the acetylinic bond.
The addition complex can then access either of two product channels. The first being the
isomerization of the trans form of the cyclic C3H2 intermediate to triplet propargylene
(HCCCH) followed by C-H cleavage to form the C3H + H. The other channel, the more
surprising of the two, involves a facile intersystem crossing from the triplet to the singlet
surface leading to the otherwise spin forbidden C3 and H2 products. The branching ratio
for this channel at room temperature was measured to be 0.53 ± 0.04. In addition
Leone and co workers in a series of studies have investigated the low temperature
reactivity of C2H radical with unsaturated hydrocarbons, and come to the same conclusion
that the mechanism involves an addition intermediate on an attractive potential energy
surface, that leads to elimination of H atom.
A combination of the behavior of similar radical/unsaturated systems at low temperature, in conjunction with the arguments presented based on thermodynamics and the reactivity observed leads us to believe that the mechanism for the reactions involving NH radical and unsaturated hydrocarbons involves the initial formation of an addition complex, via NH addition to the \( \pi \) bond. The complex can then decay via a number of thermodynamically accessible channels, and may involve H atom elimination, \( \text{H}_2 \) elimination (even though it is spin forbidden), or a C-C bond fission to produce a number of products. These could include nitriles, HCN, as well as free amines, although experimental product determinations need to be conducted to corroborate these suggestions. The ratio of these channels would depend on a number of factors including the reaction thermochemistry, and the placement and height of barriers along the reaction potential energy surface.

Figure 5.12 combines the results of this work with previous studies conducted by Rohrig and Wagner\(^{133} \) and Rohrig et al.\(^{134} \) on the same systems at high temperature behind incident shockwaves. They find their data best represented by Arrhenius expressions and are as follows: \( k = (3.0 \pm 0.7) \times 10^{-12} \exp\left(\frac{-6735 \pm 481}{K/T}\right) \text{cm}^3 \text{sec}^{-1} \), \( k = (5.5 \pm 0.2) \times 10^{-11} \exp\left(\frac{-6013 \pm 481}{K/T}\right) \text{cm}^3 \text{sec}^{-1} \), \( k = (8.3 \pm 6.1) \times 10^{-10} \exp\left(\frac{7096 \pm 1082}{K/T}\right) \text{cm}^3 \text{sec}^{-1} \), for ethylene, propene, and acetylene, respectively. A question naturally arises as to the reason for the discrepancy between the two sets of rate data. Normally curvature in Arrhenius plots can be understood in terms of a change in the reaction mechanism. Rohrig and Wagner argue for the addition mechanism, but are unable to rule out contributions from the H atom abstraction channel, due to the limited temperature range.
of their study and their rate extraction method. They indicate that the contribution from abstraction could be as high as 50% for propene. While this might help to resolve some of the discrepancy between the data sets, one might still argue that our study cannot rule out a contribution to the observed decay of NH radicals coming from a three body process, involving stabilization of the adduct formed from the initial collision.

Adduct formation is known to play an important role in the chemistry of hydroxyl radicals with hydrocarbon species, and is perhaps the best comparison to the NH + unsaturated hydrocarbon systems. The OH reactions have been extensively studied for their role in atmospheric chemistry over a wide range of pressure and temperature, and are reviewed by Atkinson. Investigations of the pressure and temperature dependence of the rate coefficient reveal a falloff behavior and a negative temperature dependence of the rates for OH reactions with unsaturated hydrocarbons. Of particular interest to this study are ethylene, propene, and the butenes, where the OH reaction rate coefficient increases from $8.1 \times 10^{-12}$ cm$^3$s$^{-1}$ to approximately $5.5 \times 10^{-11}$ cm$^3$s$^{-1}$ at room temperature, in going from ethylene to different isomers of butene. The pressure at which the bimolecular rate coefficient shows saturation also follows a similar trend decreasing from about 400 Torr of He for ethylene to about 20 Torr for 1-butene. With this information the dependence of the rate on temperature and pressure is understood in terms of a mechanism involving the initial formation of a complex, which can either back dissociate to reactants, proceed to products, or stabilize the OH-alkene radical adduct through third body collisions. It is generally found that the adduct formation process occurs without an activation energy and the negative temperature dependence is associated with the pre-exponential factor.
For the case of OH + ethylene at room temperature the adduct formation is the dominant channel since the energy for production of vinyl alcohol (HOCH=CH₂) + H is approximately 7 kcal/mol endothermic with respect to reactants. Raising the temperature in these studies increases the importance of the thermal decomposition of the adduct and thus reduces the reaction rate. However, at higher temperatures the H atom abstraction pathway becomes accessible and Arrhenius behavior is observed with positive activation energy. This appears to be analogous to the data presented in Figure 5.12, where at low temperature the reaction is likely proceeding via a complex addition intermediate that can either be stabilized by collisions, or react in an elimination or fragmentation process.

Under these circumstances, the data of Rohrig et al. is best understood as participation of NH in addition/elimination chemistry over a portion of the potential energy surface with a barrier to access the elimination product manifold. Moreover the reactions of hydroxyl radical with propene (k₃₀𝐾 = (0.81 ± 0.18) × 10⁻¹⁰ cm³/sec) and 1-butene (k₃₀𝐾 = (1.24 ± 0.27) × 10⁻¹⁰ cm³/sec) have been studied at low temperature in Laval nozzle expansions and their rates are found to be fast and display negative temperature dependence. Vakhtin et al. found that the reactions proceed to produce mainly hydroxyl alkyl radicals, and that these reactions, although conducted at low pressures, are most likely to be near their high pressure limit, due to the number of degrees of freedom in the product radicals and the temperatures of the experiment. More recently Vakhtin et al. have observed U-shaped Arrhenius plots for the reaction of OH with hydrogen peroxide at low temperature and attribute the behavior to a change in
mechanism from abstraction at high temperature to formation of an intermediate complex at low temperature.\textsuperscript{43}

With this in mind it is then interesting to speculate on the nature of the NH reactions studied here at low temperature and pressure. The measured rate for NH + propene at 83 K is $(2.97 \pm 0.77) \times 10^{-11}$ cm$^3$/sec, approximately a factor of two smaller than the OH + propene system at similar temperature and flow conditions measured by Vakhtin et al.\textsuperscript{41} Many possibilities could account for the slower reactivity of NH including the difference in dipole moment of the two diatomic radicals, the electron affinity, the electronic surface over which the reaction takes place, the stability of the radical adduct, and number of product channels accessible.

Rohrig and Wagner\textsuperscript{133} compare their data to the O ($^3P$) + hydrocarbon systems. They find good correlation between the barriers for the NH and O isoelectronic species with homologous reaction partners, and argue that this good correlation is a hint that the chemistries are the same, i.e. both are participating in electrophilic addition. While both O($^3P$) and NH ($^3\Sigma^-$) are isoelectronic, and both form a diradical upon addition, there is most probably a difference in the adduct formation mechanism. It is speculated that the imidogen dipole moment, just like that of hydroxyl, allows for the initial formation of an adduct on an attractive potential, while the O($^3P$) experiences some electronic repulsion upon approach to the $\pi$ system of the unsaturated species leading to a barrier. For the O($^3P$) + unsaturated hydrocarbon systems barriers are common.\textsuperscript{121} Conversely, it may be that at high temperatures the collisions are becoming more direct and accessing a portion
of the potential energy surface with a barrier to elimination chemistry, thus removing the contribution of the adduct.

Finally, Fueno et al. have performed *ab initio* CI calculations, employing the 4-31G basis set, on the NH (X $^3\Sigma^-$) + ethylene reaction and find considerable barriers (in excess of 10 kcal/mol) for the initial addition step to make the triplet diradical, as well as large barriers onto products.$^{161,162}$ Their main focus was the isomerizations on the singlet and triplet surfaces leading to the elimination product CH$_3$CHN + H. They estimate the error in their CI calculations to be about 2.4 kcal/mol, but these results appear inconsistent with the findings of these experiments. The inherent difficulty of calculating open shell energetics and geometries necessary to accurately represent the reacting systems has been emphasized by Villa et al.$^{163}$ In their study the careful examination of the potential energy surface for the OH + C$_2$H$_4$ adduct formation found that the minimum energy path is very sensitive to the level of theory applied. A lowering of the barrier along the minimum energy pathway of 5 kcal/mol was found by removing spin contamination in their calculations. An accurate potential energy surface is clearly needed to resolve the current inconsistencies between experiment and theory. Additionally, knowledge of the potential energy surface would also help to clarify the reaction mechanism over a broad temperature range where experimental data is now available.
5.6. Conclusion

The reactions of NH (X $^3\Sigma^-$) with NO and the hydrocarbons methane, ethane, ethylene, acetylene, propene, and diacetylene have been measure in a pulsed supersonic Laval nozzle flow reactor between 53 → 188 Kelvin. The reactions of NH with NO and the unsaturated hydrocarbons show inverse temperature dependence in the temperature range investigated, and best fits to the data sets have been suggested. For NH + NO good agreement of the data with that available in the literature was observed. The chemistry of the NH + unsaturated hydrocarbon systems is currently understood to occur at low temperature through an addition mechanism, but it is unclear at this time whether the adduct proceeds to products or is stabilized by additional collisions. Further, experiments focusing on the pressure dependence and kinetic isotope effects would help to resolve this issue, as would an accurate potential energy surface. An understanding of the chemistry of these systems will help to determine their importance to the atmospheric chemistry of Saturn's moon Titan, as well as other low temperature environments where these molecules might be found.
CHAPTER 6. CONCLUSION

The utility of low temperature rate measurements to the fields of planetary science and astronomy are easily recognized when one attempts to model individual environments. The research described in this dissertation was aimed at advancing our fundamental knowledge of reactive neutral-radical systems at low temperatures. While not all of the systems studied were directly applicable to interstellar environments, knowledge of neutral-radical reaction processes in general will help to further our understanding of the diverse chemistry occurring in low temperature environments. This is easily witnessed in the progression of species and chemical processes included in today’s rudimentary understanding of the interstellar medium and planetary atmospheres, ranging from ion-molecule, to neutral-neutral, to grain surface chemistry, which will undoubtedly evolve as more experimental and observational information become available.

It also needs to be stressed that our understanding of these environments comes from a multidisciplinary effort involving collaboration among a variety of scientists including experimental chemical kineticians, theoretical chemists and physicists, and astronomers. In this regard the process is an iterative loop in which astronomical observations raise new questions regarding the nature and formation mechanisms of chemical species, while insight into these environments and chemical species is provided by the experimental and theoretical work. Indeed the reverse is also true, as the results of experiment and theory generate new directions in the field of astronomy.
The development of the supersonic Laval nozzle flow reactors and the results obtained on these instruments have for the past twenty years provided valuable information that has increased our understanding of the types of chemical processes that are possible at low temperature. These examples, cited in Chapter 1 of this dissertation, have changed our fundamental understanding of chemical reactivity at low temperatures. Nonetheless, the picture is far from complete. A wealth of information on a number of chemical systems is required before we can begin to predict with accuracy the behavior of neutral chemical systems at low temperature. Certainly an appreciation for the diversity of chemical species found in these environments as well as the physical processes leading to their formation can be gained from this perspective. And, in this regard the research described in the chapters of this dissertation was conducted to provide additional examples of chemical behavior under extreme conditions, such as the low temperature environment provided by the supersonic Laval nozzle flows.

Future contributions to the field can be expected in a variety of areas including the measurement of a number of additional rates at low temperature. However, the biggest contribution is anticipated in the ability to achieve general product detection in the Laval flows. Product detection is essential to the advancement of the technique as it would allow for more concrete conclusions to be drawn regarding the mechanism through which complex chemical reactions occur at low temperature. Currently the disappearance of a reactant radical species in the presence of a reactive partner, in conjunction with arguments based on thermochemistry, and oftentimes theoretical calculations, is used to speculate on the mechanism for the reaction. While these are powerful tools, the ability to
detect the products of reaction would allow for a much more rigorous understating of the influences the important features of the potential energy surface have on the outcome of reactive collisions. A number of schemes may be envisioned to accomplish product detection in these flows including the photoionization of product species followed by mass spectrometric detection, or detection utilizing infrared spectroscopy, and it is hoped that one day these goals are realized.

In summary, the pulsed DC discharge supersonic Laval nozzle flow reactor has been described in detail, including the flow characterization methods. The temperature regime available for study was extended down to 53 K using argon as the buffer gas in conjunction with a pre-chilled stagnation region. Further, implementation of a tunable laser based frequency source using four-wave mixing was described. In light of the shortcomings associated with the pulse jitter inherent in using two Nd:YAG lasers, the utility of four-wave mixing was demonstrated for the detection of hydrogen atoms employing the Lyman β pump at 102.57 nm. With modifications, this technique could be used to study the addition and isotopic fractionation reactions of H and D atoms with unsaturated hydrocarbons at low temperatures as discussed. It could further be used to explore the low temperature chemistry of a variety of atomic species including nitrogen and oxygen, with a variety of reaction partners. While all results are important, studies of \( \text{O}(^3\Pi) \) with unsaturated hydrocarbons would be of particular use to the results documented in Chapter 5 of this dissertation, due to the fact that it is isoelectronic with the \( \text{NH} \ (X^3\Sigma^-) \) species, and they have been predicted to behave similarly. In this respect,
additional insights into the reaction mechanism and potential energy surface for isoelectronic low temperature reactions could be gained.

The reaction of OH + HBr and all the H/D isotopic variants has been studied between 53 and 135 Kelvin using flow reactor. The reaction of OH + HBr is important because it produces a species (Br atom) responsible for the partitioning of ozone in the Earth's atmosphere. The temperature dependent results for the OH + HBr reaction were found to be in accord with the measurements of Atkinson et al., and lower than the studies of Jaramillo and Smith, Jaramillo et al., and Sims et al., although incorporation of the new results into a global temperature dependent fit between 23 and 360 K did not alter the temperature dependence previously understood for the reaction. The new fits, which are important to the atmospheric modeling community are, $k(T) = (1.06 \pm 0.02) \times 10^{-11} \times (T/298)^{(-0.90\pm 0.11)}$ cm$^3$/sec, and $k(T) = (0.96 \pm 0.02) \times 10^{-11} \times (T/298)^{(-0.90\pm 0.03)} \times \exp\left((2.88 \pm 1.82 \text{ K})/T\right)$ cm$^3$/sec.

In addition both the primary and secondary kinetic isotope effects were examined and found to be independent of temperature within experimental error, over the temperature range 53 to 135 K. These results are in accord with the study of Bedjanian et al. The results were discussed within the framework of the current experimental and theoretical studies and highlight the need for accurate potential energy surfaces, before the origin of the normal PKIE and inverse SKIE can be deduced. It is not clear whether the origin of these comes from tunneling effects, anharmonicity in the transition state, differences in barrier heights for the reactions, a combination of these effects, or another
source. Whatever the case may be, knowledge of low temperature kinetic isotope effects provides information on the subsequent chemistry of H/D fractionated species.

The reactions of ground state NH radicals were also investigated with a number of reaction partners including NO, methane, ethane, ethylene, acetylene, propene, and diacetylene between the temperatures of 53 to 188 K. The temperature dependence of the NH + NO reaction was investigated for a number of reasons. First, it was desirable to conduct a product search in the Laval flows; unfortunately, as described in Chapter 5, these attempts were unsuccessful due to low signal count rates. However, these studies allowed us to calibrate our technique by comparing it to experimental data found in the literature. The onset of the inverse temperature dependence was found to occur near 200 K and a temperature dependent fit to the data between 53 and 365 K was found to best represent the following expression: $$k(T)_{\text{NH}+\text{NO}} = (4.2 \pm 0.3) \times 10^{-11} \times (T/298)^{0.31 \pm 0.17} \times \exp[(76 \pm 20 \text{ K})/T] \text{ cm}^3/\text{sec}.$$ 

Interest in the atmospheric chemistry of Titan due to the Voyager and Cassini-Huygens missions motivated the study of the NH radical reactions with saturated and unsaturated hydrocarbons. Both species were chosen for study in an attempt to gain insights into the reaction mechanism. The reactions of NH with methane and ethane were found to be slow at 53 K, while those with ethylene, acetylene, propene, and diacetylene were found to be faster and display inverse temperature dependence. These findings, in conjunction with arguments based on the heat of reaction lead us to speculate that the reaction proceeds through an addition mechanism involving the $\pi$ bond of the unsaturated species. However, without product determination, it is unclear whether the reaction
proceeds though an addition/elimination or adduct stabilization mechanism. Either circumstance, however, leads to efficient neutral-radical chemistry at low temperature resulting in the incorporation of nitrogen into carbon containing species, and a more complex chemical composition. Studies of other isoelectronic species as well as product detection for these reactions would surely be of utility to the understanding of the reaction mechanism presented here.
REFERENCES


(146) Brazier, C. R.; Ram, R. S.; Bernath, P. F. Journal of Molecular Spectroscopy 1986, 120, 381.


