Correlated Molecular Plasmas

by

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Abstract

Ultracold neutral plasmas (UNPs) are highly correlated, charged-particle systems studied in standard atomic-molecular optical physics laboratories. Advances in ultracold physics techniques have led to the development of magneto-optical traps that permit the localization of micro-Kelvin temperature atomic samples \((10^8 \text{ - } 10^{10} \text{ cm}^{-3})\) that can be photoionized with a defined excess laser energy.

Magneto-optical trapping of molecules proves difficult, and to date, lags in reaching conditions attainable for atoms. Molecules possess additional degrees of freedom where energy can flow during laser trapping and cooling. Alternatively, elastic collisions with inert gases offer another route to low temperatures. Super-sonic expansions of target molecules seeded in a noble gas can reduced the translational temperature to values as low as 0.1 K.

Here I report on the formation of a molecular ultracold plasma in a molecular beam of nitric oxide seeded in an inert gas. Our method does not directly form a plasma, but instead, I create a Rydberg gas that spontaneously evolves to a plasma. I have verified the transition to a collective plasma state by applying pulsed-fields to the field-free flight region, and observe a signal that persists well beyond classical field amplitudes required to ionize individual Rydberg states. Electric field screening is a collective effect occurring over a characteristic distance, quantified by the Debye length, \(\lambda_D\). Molecular ultracold plasmas described here exhibit Debye lengths smaller than the overall size, \(\lambda_D << \sigma\).

Plasmas of this nature offer an exotic environment for which to study fundamental phenomena. While plasmas are generally thought of as hot, UNPs exist at low enough
temperatures that electrostatic interaction energy between particles is greater than their kinetic energy. At this point, charged particles begin to find themselves in local potential energy minima. Over the entire sample this translates to long-range order, or correlation. It is of great interest for researchers studying UNPs to maximize particle correlation, which requires UNPs to remain very cold, and dense through their lifetime.
Preface

Below is a list of published articles reporting results from research work completed during this thesis.


  Conducted experiments and collected data published within this article.


  Performed experiments and collected data published within this article.


  Contributed to experiments and model calculations.

Constructed simulation code and generated results published within. Contributed to analysis and manuscript.


Contributed to calculations, analysis, and manuscript.
Table of Contents

Abstract ................................................................................. ii

Preface .................................................................................. iv

Table of Contents ................................................................. vi

List of Tables .......................................................................... xi

List of Figures ........................................................................... xiii

List of Abbreviations ............................................................. xxiv

List of Symbols .......................................................................... xxv

Acknowledgements ................................................................ xxvii

Dedication ................................................................................ xxviii

1 Introduction ............................................................................. 1
  1.1 Plasmas as a State of Matter ........................................... 1
  1.2 Ultracold Neutral Atomic Plasmas ................................. 4
  1.3 Ultracold Neutral Molecular Plasmas ............................. 6

2 Experimental Details ............................................................ 8
  2.1 Overview .......................................................................... 8
  2.2 Experimental Details .................................................... 10
2.3 Gas Supply and Molecular Beam .......................... 14
2.4 Electrostatic Grid Arrays: ZEKE and Moveable-Grid Profiles  .... 15
  2.4.1 Static-Grid Assembly .................................. 15
  2.4.2 Moving-Grid Assembly ................................ 18
2.5 Electron Detection ........................................ 19
2.6 Pulsed-Field Experiments .................................. 21
2.7 Data Acquisition ......................................... 24
2.8 Summary ................................................. 25

3 Molecular Beam Gas Dynamics .................................. 26
  3.1 Overview ................................................. 26
  3.2 Molecular Beam Introduction ................................ 27
  3.3 Experimental Gas Properties ............................... 27
  3.4 Free-Jet Structure ........................................ 30
  3.5 Kinetic Theory and Method of Moments .................... 31
    3.5.1 Flow Properties from an Ideal Thermodynamic Analysis .... 34
  3.6 Speed Ratio .............................................. 38
  3.7 Intramolecular Energy Relaxation .......................... 41
    3.7.1 Rotational and Vibrational Temperature ................ 41
    3.7.2 Resonance-Enhanced Multi-Photon Ionization (REMPI) for the Determination of Rotational Temperature .... 42
  3.8 Molecular Beam Intensity ................................ 45
  3.9 Nitric Oxide Spectroscopy ................................ 48
  3.10 Summary ................................................. 52

4 Rydberg Molecules ............................................ 53
  4.1 Theoretical Description .................................. 53
  4.2 Rydberg-Rydberg Ionization (Penning Ionization) .......... 57
### 4.2.1 Erlang Distribution Model for Penning Ionization

59

### 4.3 Charged Particle Collisions with Rydberg Molecules

60

### 4.4 Pulsed Field Ionization (PFI) of Rydberg Molecules

62

#### 5 Evolution from a Molecular Rydberg Gas to an Ultracold Plasma in a Seeded Supersonic Expansion of NO

5.1 Introduction and Experimental

66

5.2 Pulse Field Experiments

72

5.3 Summary

76

#### 6 Very Slow Expansion of an Ultracold Plasma Formed in a Seeded Supersonic Molecular Beam of NO

6.1 Introduction

77

6.1.1 Plasma Expansion

77

6.2 Expansion Results

78

6.2.1 Seeding in Heavier Carrier Gas

78

6.2.2 Moveable Grid Expansion

79

6.3 Discussion

80

6.4 Summary

91

#### 7 Classical Scaling and the Correspondence Between the Coupled Rate Equation and Molecular Dynamics Models for the Evolution of UNPs

7.1 Introduction

92

7.2 Models

96

7.2.1 Molecular Dynamics

96

7.2.2 Coupled Rate Equations

96

7.2.3 Results: Classical Scaling of Rate Equations

97

7.3 Discussion

102
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.3.1</td>
<td>$n_{\text{min}}$ and Soft-Core Comparison</td>
<td>103</td>
</tr>
<tr>
<td>7.4</td>
<td>Summary</td>
<td>107</td>
</tr>
<tr>
<td>8</td>
<td>Recombinative Dissociation and the Evolution of a Molecular Ultracold Plasma</td>
<td>108</td>
</tr>
<tr>
<td>8.1</td>
<td>Introduction</td>
<td>108</td>
</tr>
<tr>
<td>8.1.1</td>
<td>Kinetic Rate Processes in a Molecular Ultracold Plasma</td>
<td>109</td>
</tr>
<tr>
<td>8.1.2</td>
<td>Simulation Models for Ultracold Plasma Relaxation</td>
<td>111</td>
</tr>
<tr>
<td>8.1.3</td>
<td>Simulation Models Incorporating Dissociation</td>
<td>112</td>
</tr>
<tr>
<td>8.2</td>
<td>Rate Properties of Atomic Ultracold Plasmas</td>
<td>114</td>
</tr>
<tr>
<td>8.2.1</td>
<td>Direct Photoionization and the Validation of Simulation Models</td>
<td>114</td>
</tr>
<tr>
<td>8.2.2</td>
<td>Plasma Created by Penning Ionization</td>
<td>116</td>
</tr>
<tr>
<td>8.3</td>
<td>Molecular Features</td>
<td>121</td>
</tr>
<tr>
<td>8.3.1</td>
<td>Predissociation</td>
<td>121</td>
</tr>
<tr>
<td>8.3.2</td>
<td>Dissociative Recombination</td>
<td>123</td>
</tr>
<tr>
<td>8.3.3</td>
<td>Steady-State Kinetics of Predissociation</td>
<td>124</td>
</tr>
<tr>
<td>8.4</td>
<td>Summary</td>
<td>126</td>
</tr>
<tr>
<td>9</td>
<td>Conclusions</td>
<td>128</td>
</tr>
<tr>
<td></td>
<td>Bibliography</td>
<td>130</td>
</tr>
<tr>
<td>Appendix A</td>
<td>Plasma Properties: Derivations</td>
<td>141</td>
</tr>
<tr>
<td>A.1</td>
<td>Debye Screening Length</td>
<td>141</td>
</tr>
<tr>
<td>A.2</td>
<td>Plasma Frequency</td>
<td>143</td>
</tr>
<tr>
<td>A.3</td>
<td>Electric Potential from Vlasov Equations</td>
<td>144</td>
</tr>
<tr>
<td>A.4</td>
<td>Plasma Collisional Terms for Local Thermodynamic Equilibrium (LTE)</td>
<td>146</td>
</tr>
<tr>
<td>Appendix B</td>
<td>Rate Equation Simulation Code</td>
<td>150</td>
</tr>
</tbody>
</table>
# List of Tables

1. Parameters for laboratory and natural plasmas ........................................... 2

2.1 Longitudinal and radial dimensions of the back-flange mounted grid assembly. The last two entries, rchamber and Rchamber, are the diameters for the inner shielding and outer shielding of the grid assembly, respectively. 18

2.2 Here are listed typical voltage values for standard experimental extraction and detection. Anode and detector voltages can be adjusted to smaller values depending on the strength of the electron signal. Ranges indicate that applied voltages are optimized for experimental conditions. 21

2.3 Load capacitance and rise-times ............................................................ 23

4. Selected Rydberg atom properties and scaling with principal quantum number. The last column on the right-side provides values for a nitric oxide $51f$ state. ................................................................. 55

4.2 Distance and time for 90% ionization events between two Rydberg atoms 59

6.1 Arrival times, estimated velocities, and widths obtained by Gaussian fits to spatial waveforms of Fig. 6.1 ................................................................. 80
8.1 Fraction of the initial Rydberg gas density converted by Penning ionization to form ions and free electrons with an initial average energy described by $T_e(0)$. Penning fraction determined as 0.9 times the number of nearest neighbour pairs separated by 1.8 times the orbital diameter at $n_0$, as a fraction of the total gas density.
List of Figures

1.1 Summary of neutral plasmas in temperature-density space. Equilibrated plasmas exhibit a uniform temperature for all components. Ultracold plasmas are non-equilibrated, and plotted here is the temperature for the ion-component. Diagonal white lines are constant values of the Coulomb coupling parameter, $\Gamma$, from Eq. (1.1), with values indicated. ........................................ 3

2.1 An overview of the standard experimental arrangement. Laser systems begin with pulsed (10 Hz) Nd:YAG pump lasers at wavelengths 532 nm and 355 nm for $\omega_2$ and $\omega_1$, respectively. Dye lasers then convert pump laser light into wavelengths of $\approx 655$ and $\approx 452$ nm followed by frequency doubling (halving the wavelengths) by Inrad Autotrackers. Finally beams travel to the experimental vacuum chamber where they intersect the molecular beam in a counter-propagating manner. ........................................ 11

2.2 An example of an optimized timing scheme generated by the BNC pulse generator. Channels are in blue circles and A and B trigger the $\omega_1$-laser flashlamp and Q-switch, respectively, while C and D trigger $\omega_2$-laser flashlamp and Q-switch, respectively. Channel D is referenced to the instrument’s internal frequency, $t_0$, while all other channels are referenced to D with the exception of B, which is referenced to A. Timing values shown are all relative to D, i.e. $B_{\text{trig}} = D_{\text{trig}} + 90$ ns. Channel H is the molecular beam pulse driver trigger. All times are in $\mu$s unless otherwise indicated. ........................................ 12
2.3 (a) Photodiode intensity (arb. units) as a function of razor-blade position on the left. Data is fit to error function and the corresponding Gaussian beam profile is displayed on the right. 2.3 (b) Laser beam polarizations starting from the pump laser to a final polarization along the horizontal, all in reference to the laboratory frame.

2.4 Illustration representing the gas manifold used to supply the experimental vacuum chambers with nitric oxide sources. Valves are indicated by numbered circles, and regulators by lower case lettered circles. For instance: NO-He experiments will have valves 1, 2, and 6 will open for gas supply. All tanks are outfitted with gas regulators. Home-made gas mixtures were connected to the manifold as 'mix tank' in the figure. The line pump clears any residual nitric oxide gas that could oxidize between experiments.

2.5 An exploded view drawing of the nozzle assembly taken from [6]. A driving current pulse drives the poppet-capped armature magnet in and out, thereby opening and closing the nozzle orifice allowing for the pulsed passage of reservoir gas into the vacuum chamber.

2.6 Shown is the original, static grid-array apparatus. Originally built as a ZEKE spectrometer, the interaction region is defined by the intersection of the blue line, representing the laser beam, with the centre beam axis of the chamber. The wall-mounted skimmer resides in the expansion compartment. Along with the skimmer are mounted four alignment rods designed to point the gas nozzle directly along the chamber’s z-axis. This assembly has a set of static extraction grids, with the detection stack mounted on the back flange. Labels are associated with distances shown in Table 2.1.
2.7 Static grid assembly dimensions. Most relevant for experiments is the distance between Zex1 and Zex2 which determines the electric field strength when applying a voltage to Zex1. Similarly, the distance between Zex2 and Zfcyl along with the voltage applied at Zfcyl determines extraction field strength. Dimensions are listed in Table 2.1.

2.8 Shown here is the moveable-grid assembly where the entire detection carriage can be translated along the z-axis of the chamber, which varies the distance between G1 and G2, and ultimately varying the plasma flight-time. FMP1 and FMP2 represent front-mounting plate 1 and 2, respectively. The detection assembly is analogous to the ZEKE system and will be discussed further below.

2.9 2D cartoon of moving grid cross-section showing detector carriage mobility along the z-direction. The green object on the right-hand side represents the mounting plate, FMP1 in Fig. 2.8.

2.10 An exploded view drawing of the 18 mm micro-channel plate detection system. Voltages are applied to the labelled grids according to Fig. 2.11. The bare detection anode is visible as the inverted cone-shaped protrusion.

2.11 Electronic circuit diagram detailing the voltage division for the detector stack and anode. Also shown is the capacitively coupled signal output.

2.12 Circuit diagram for the experiment’s grid assembly electrical properties. C1 and R1 represent the intrinsic chamber impedance and along with the load capacitance, CL, across G1 and G2, the total impedance can be determined. CV is a trim capacitor that can be varied to match the impedance as CL changes with grid distance. RS is an optional resistor suggested by Behlke Electronic GMBH to reduce ringing.
A typical plot generated by integrating the electron signal intensity of the plasma peak as a function of $\omega_2$ laser energy, which shows intensity maximum at specific Rydberg energy levels. The false-colour image on the top is the original two-dimensional data with the arrow representing the time dimension.

3.1 Two dimensional rendering of the experimental chamber. To the left side of the wall is the source chamber, and to the right side is the plasma chamber. The distance of nozzle to skimmer (2.5 cm) and nozzle to laser interaction region (10.5 cm) are shown. Excluded in this simple picture are distances to the detector which is not important for molecular beam expansion calculations.

3.2 Illustration of a super-sonic expansion (in 2D $y, z$-plane) from a high-pressure gas source showing quitting surface model along with definitions of parallel ($T_\parallel$) and perpendicular ($T_\perp$) temperatures. Representative streamlines are labelled as three rays and provide a perspective on how the expansion can be approximated in the free-molecular flow region. Three dimensional coordinate system is defined in the upper right portion of this figure, and will be used throughout this thesis unless otherwise stated. For clarity, axes $y$ and $z$ are in the plane of the page, and $x$ points out of the page.

3.3 Fluid dynamics commonly makes use of a coordinate transformation from cartesian to natural streamlines illustrated in the plot on the left by $s_1$ and $s_2$. Unit vectors for streamlines are $\hat{s}$ (parallel to streamline flow) and $\hat{n}$ (perpendicular to flow). The plot on the right shows how streamlines become essentially linear and appear to radiate in the free-molecular flow region of the expansion from a point source at the nozzle. Here, the velocity components, $v_\parallel$ and $v_\perp$, first introduced in Eq. (3.6), can be defined as components of the overall streamline velocity.
3.4 Isentropic thermodynamic values given by Eq. (3.11)-(3.14) are plotted against reduced distance from the nozzle, \( z/d \). Temperature (blue dashed) and density (blue dash-dot) are normalized to reservoir conditions, \( T_0 \) and \( n_0 \), respectively and follow the left \( y \)-axis. Beam velocity (red solid) is in units of m/s, and follows the right \( y \)-axis. Note the early rise to the terminal beam velocity, \( u_\infty \), in terms of expansion distance. 38

3.5 Collision frequency \((\text{cm}^{-1})\) as a function of distance along the expansion axis \(\hat{z}\) using a two-body hard sphere approximation of He-He collisions. Collisions drop off to \(\approx 1/\text{cm}\), 0.5 cm from the nozzle, as indicated by the dashed line. Laser interaction occurs 10 cm from the nozzle. 39

3.6 Plots showing experimental REMPI data (top) and simulations. In the graphs, electron signal intensity (arb. units) is plotted against the \(\omega_1\) wavelength. Accompanying each simulation plot is the rotational temperature used to acquire the simulation results. 43

3.7 Applicable Hund’s cases for angular momentum coupling of different electronic states of nitric oxide used in our \((1+1')\) multiphoton excitation. \( J \) is the total angular momentum, given as \( J = N + L + S \), where \( N \) is the rotational angular momentum of the molecule, \( L \) is the total electron orbital angular momentum, \( L = \Sigma_i \ell_i \), and \( S \) is the total electron spin angular momentum, \( S = \Sigma_i s_i \). Projections of \( L \) and \( S \) onto the internuclear axis are given as \( \Lambda \) and \( \Sigma \), respectively. The total electronic momentum projection is expressed as \( \Omega = \Lambda + \Sigma \). For Hund’s case (b) and (d), \( K \) is the total angular momentum apart from spin. 49

3.8 Two-photon excitation of nitric oxide form the ground state to Rydberg states converging to the lowest ionization potential 51
4.1 Illustration showing the effect of a field pulse on the nuclear potential felt by an electron .......................................... 63

5.1 Resonant 1+1' ionization spectrum of the $X^2\Pi(v''=0)$ to the $A^2\Sigma^+(v'=0)$ transition in NO seeded 1:10 in a supersonic beam of He. This ratio of intensities fits a ground-state population distribution corresponding to a rotational temperature, $T_R^\infty = 2.5$ K. ........................................ 69

5.2 Schematic diagram showing the molecular beam flight path from a differentially pumped source chamber through a skimmer to enter a system of three grids ending in a flight tube capped by a microchannel plate detector. The interaction region is defined as the region between G1 and G2, and the extraction region including the flight-tube is defined as the region beyond G2. 70

5.3 Oscilloscope trace showing the arrival time of electrons produced following two-color production of NO molecules in the 52$f(2)$ Rydberg state with -250 mV applied to G1 and 60 V applied to G3. ................................. 71

5.4 Resonances in the late signal observed by scanning $\omega_2$ for the plasma formed from NO seeded in He. Spectrum assigned to the lines in the $n\ell$ Rydberg series converging to the rotational level $N^+ = 2$ in the vibrational ground state of NO$^+X^1\Sigma^+$. Ionization fitted to 30 534.5 cm$^{-1}$. .................. 72

5.5 High-Rydberg excitation spectra of the plasma signal under conditions in which 1 $\mu$s positive pulses at voltages producing the electrostatic fields indicated are applied starting 500 ns after $\omega_2$. The y-axis is the magnitude of the electric field in V/cm, and the x-axis is the energy of the second photon, $\omega_2$. Diamonds show the adiabatic field-ionization threshold for the principal quantum numbers from 40 to 110, and align with the peaks of the spectra. Both axes are linear. ................................. 73
5.6 Voltage pulse stepping towards laser arrival time ($t_0$) illustrated in 5.6(a) and the integrated plasma signal as a function of pulse arrival time 5.6(b) for $n = 60$ (cyan) and $n = 50$ (red). The initial slope of Signal/Time is much higher for $n = 60$ suggesting formation dynamics occurring on a faster timescale due to larger orbital size.

6.1 Electron signal waveforms appearing at $G_2$ following the substantial promotion of NO molecules to the 52$f(2)$ Rydberg state in seeded supersonic expansions of - in order top to bottom - Kr, Ar, Ne, and He using the experimental flight path outlined in Section ??.

6.2 Late electron-signal temporal waveforms from Fig. 6.1 transformed to yield spatial plasma distributions, displayed according to peak arrival time at $G_2$. Solid curves show Gaussian fits with residuals below. The bottom figure is derived from the measurement of laser width, above which are plotted the data for He, Ne, Ar, and Kr carrier gases. An initial $t = 0$ width is defined by the laser width, and subsequent width measurements from noble gases determine rate of expansion.

6.3 Fitted plasma width as a function of the arrival time of the peak of the Gaussian plasma signal at $G_2$. The solid line through the data represents a fit to Eq. (6.8) with $T_e(0) + T_i(0) = 5$ K.

6.4 Waveforms captured by the MCP detector for different positions of the moving carriage. The large peak represents the signal of electrons as the plasma volume passes through $G_2$. Signal passing through $G_3$ produces a small residual signal most noticeable at small laser-interaction-$G_2$ distances.
6.5 Plot of plasma FWHM at G2 as a function of flight time, compared with width predicted after 10 µs for ambipolar expansion at $T_e = 40$ K (red dot) and Vlasov expansion of a spherical Gaussian plasma for $T_e(0) = 40$ K (bold line). The line through the data represents a Vlasov fit for $T_e(0) = 6.8$ K. Error bars reflect the experimental uncertainty in the measured flight distance to G2, which exceeds the error introduced by using velocity averages to transform time to distance.

7.1 Output of rate equation calculations describing the variation in scaled temperature ($\Gamma^{-1}$) with scaled time ($t\omega_{pe}$) for neutral plasmas initialized to contain frozen ions and free electrons with scaled temperature of $\Gamma_e^{-1} = 2.0$, at an initial particle density of $10^9$ cm$^{-6}$ (blue curves), for Rydberg $n_{max} = 153$ with values of $n_{min}$ of 25 (blue dashed line) and 10 (blue solid line), and density of $10^{11}$ cm$^{-3}$ (red curves), for Rydberg $n_{max} = 71$ with values of $n_{min}$ of 25 (red dashed line) and 10 (red solid line).

7.2 Output of rate equation calculations describing the variation in scaled temperature ($\Gamma^{-1}$) with scaled time ($t\omega_{pe}$) for neutral plasmas initialized to contain frozen ions and free electrons at particle densities of $10^9$ (blue) and $10^{11}$ (red) cm$^{-3}$ at a scaled temperature of $\Gamma_e^{-1}(0) = 2.0$, $n_{min} = 10$. Values of Rydberg $n_{max}$ defined by $\sqrt{0.1a_{WS}/a_0}$ (bottom), $\sqrt{0.2a_{WS}/a_0}$ (middle) and $\sqrt{0.3a_{WS}/a_0}$ (top). Dashed curves show similar variations for $\Gamma_e^{-1}(0) = 2.0$, $n_{min} = 10$, with dynamically defined $n_{max} = \sqrt{R/k_B T_e}$, for particle densities of $10^9$ (blue) and $10^{11}$ cm$^{-3}$. 
7.3 Reduced temperature, $\Gamma_e^{-1}$, versus reduced time, $t\omega_{pe}$, obtained from molecular dynamics calculations with soft-core parameter $C = 0.02$ (blue) and 0.01 (red) for initial $T_e = 3, 4, 5, 10, 15$ and 20 K, and particle densities of $10^9$ cm$^{-3}$, together with the output of corresponding rate equation calculations for which $n_{\text{max}} = \sqrt{0.2a_{WS}/a_0}$. Pairs of curves compare results for $n_{\text{min}} = 10$ (solid) with $n_{\text{min}} = 55, 57, 60, 70, 75$ and 75 (dashed). Divergence between solid and dashed curves, measured by the ratio of slopes at $\tau = 500$, increases as 2.5, 2.6, 3.2, 16, 130 and 450.

7.4 Evolution of level population densities in scaled time for initial charged-particle densities of $10^9$ cm$^{-3}$ and electron temperature of $T_e = 4$ K (left), and $10^{11}$ cm$^{-3}$ and 18.57 K (right), as determined by coupled rate equations for fixed $n_{\text{max}} = 153$ and 71, respectively. For top set, $n_{\text{min}} = 25$. For bottom set, $n_{\text{min}} = 10$. In all cases, $\Gamma_e(0) = 1.495$. Starting with early times, the uppermost line traces the population of $n_{\text{max}}$. The lowest line describes the population of $n_{\text{min}}$. In the upper right, note how a relaxation truncated at $n_{\text{min}} = 25$ for $\rho_e = 10^{11}$ cm$^{-3}$ creates a gap in population (and energy release) that is absent for $\rho_e = 10^9$ cm$^{-3}$ in the upper left, invalidating scaling.

7.5 Soft-core electron-ion potentials, Eq. (7.10) for $C = 0.03$ (purple), 0.02 (green), and 0.01 (red) with reference to a pure Coulomb potential (blue) and the energies of the hydrogenic Rydberg levels indicated.
8.1 Output of rate-equation calculations describing the variation in scaled electron temperature (Γ−1) with scaled time (tωe) for neutral plasmas consisting of frozen (T_i = 0 K) atomic ions and free electrons initiated with an initial scaled temperature of Γ−1(0) = 2.5, at an initial particle density of 10^9 and 10^{12} cm^{-3}. Dashed lines compare the evolution in scaled coordinates for a fixed n_{max} = \sqrt{0.2a_{WS}/a_0}. Solid lines show the evolution in scaled temperature using a dynamic n_{max} = \sqrt{R/k_BT_e}. Curves for higher density track below those obtained in each case for the lower density.

8.2 Output of rate-equation calculations predicting the time variation of temperature (left) and electron density (right) for a neutral plasma formed by the evolution of a gas of Rydberg atoms of initial density 10^{12} cm^{-3} and principal quantum number, n_0=50 (solid line), compared with the similar evolution of a fully ionized plasma prepared to have the same initial particle density and an electron temperature of 21 K (dashed line) as determined by Penning ionization from n_0 = 50. Note that the timescale on the right is expanded by a factor of 10.

8.3 Output of rate-equation calculations showing the time dependence of electron temperature (left) and density (right) for plasmas evolving from atomic Rydberg gases of initial quantum number, n_0 = 30, 35, 40, 50 and 60 (referring to curves at t = 40 ns reading from low right to upper left) at an initial particle density of 10^{12} cm^{-3}.

8.4 Output of rate-equation calculations comparing the variation in electron temperature and density for a neutral plasma formed by a gas of predissociating Rydberg molecules excited to n_0=50 at an initial particle density of 10^{12} cm^{-3} (solid line) compared with that for a gas of the same initial conditions without predissociation (dashed line). The dot-dashed line show the effect of including dissociative recombination with predissociation.
8.5 Output of rate-equation calculations detailing the density of products as a function of time formed by the predissociation of Rydberg levels $n$ for levels from $n = 22$ to 10 (left) and $n = 22$ to 42 (right), in each case reading from top to bottom. Flattening of its time dependence at high $n$ occurs as the thermal ionization threshold falls below the energy of a level with increasing electron temperature.

A.1 Langmuir oscillations represent the periodic motion of electrons about an equilibrium position, $r_0$. 

A.2 Illustration and definition of parameters for Coulomb collision involving two charged particles.
# List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCP</td>
<td>Ultracold Plasma</td>
</tr>
<tr>
<td>UNP</td>
<td>Ultracold Neutral Plasma</td>
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<tr>
<td>SCP</td>
<td>Strongly Coupled Plasma</td>
</tr>
<tr>
<td>MOT</td>
<td>Magneto-Optical Trap</td>
</tr>
<tr>
<td>DIH</td>
<td>Disorder-Induced Heating</td>
</tr>
<tr>
<td>TOF</td>
<td>Time-of-Flight</td>
</tr>
<tr>
<td>SHG</td>
<td>Second Harmonic Generation</td>
</tr>
<tr>
<td>ZEKE</td>
<td>Zero Electron Kinetic Energy</td>
</tr>
<tr>
<td>REMPI</td>
<td>Resonance Enhanced Multi-Photon Ionization</td>
</tr>
<tr>
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<td>Direct Current</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>MCP</td>
<td>Micro-channel Plate</td>
</tr>
<tr>
<td>TBR</td>
<td>Three-body recombination</td>
</tr>
<tr>
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<td>Dissociative recombination</td>
</tr>
<tr>
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<td>Predissociation</td>
</tr>
<tr>
<td>PI</td>
<td>Photo-ionization</td>
</tr>
<tr>
<td>KE</td>
<td>Kinetic energy</td>
</tr>
<tr>
<td>PE</td>
<td>Potential energy</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular dynamics</td>
</tr>
</tbody>
</table>
# List of Symbols

In the following definitions subscript $\alpha$ stands for ions ($\alpha = i$) or electrons ($\alpha = e$) when dealing with plasmas.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e$</td>
<td>elementary charge</td>
</tr>
<tr>
<td>$\epsilon_0$</td>
<td>permittivity of vacuum</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$\mathcal{R}$</td>
<td>Rydberg constant</td>
</tr>
<tr>
<td>$\hbar$</td>
<td>Planck’s constant/2$\pi$</td>
</tr>
<tr>
<td>$K$</td>
<td>degrees Kelvin</td>
</tr>
<tr>
<td>$T_\alpha$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$P$</td>
<td>Pressure</td>
</tr>
<tr>
<td>$m_\alpha$</td>
<td>mass</td>
</tr>
<tr>
<td>$\rho_\alpha$</td>
<td>number density</td>
</tr>
<tr>
<td>$M$</td>
<td>Mach Number</td>
</tr>
<tr>
<td>$u$</td>
<td>Flow velocity</td>
</tr>
<tr>
<td>$H$</td>
<td>Enthalpy</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Heat capacity at constant pressure</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas constant</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Solid angle (steradians sr)</td>
</tr>
<tr>
<td>$\Gamma_\alpha$</td>
<td>Coulomb coupling parameter (Correlation Value)</td>
</tr>
<tr>
<td>$a_{WS}$</td>
<td>Wigner-Seitz radius</td>
</tr>
<tr>
<td>$n$</td>
<td>Principal quantum number</td>
</tr>
<tr>
<td>$\ell$</td>
<td>Electron angular momentum quantum number</td>
</tr>
</tbody>
</table>

xxv
$m_\ell$  Projection $\ell$ onto inter-nuclear axis

$J$  Total angular momentum quantum number

$N$  Molecular rotation angular momentum number

$K$  Total angular momentum dis-regarding spin

$\omega_{p\alpha}$  Plasma frequency

$\lambda_D$  Debye screening length

$\mathcal{F}$  Gaussian distribution full-width at half-maximum
I would like to extend my gratitude to my thesis supervisor, Prof. Ed Grant, whose unbounded scientific passion and leadership has made this thesis possible.

I would like to acknowledge the people who I have had the privilege to call colleagues and friends over the years. A special thanks to previous post doctoral fellows, Dr. Chris Rennick and Dr. Nicolas Saquet. Thanks to Markus Schulz-Weiling, Hossein Sadeghi, Zhiwen Chen, and Jaime Ortega-Arroyo. I also appreciate the many informative discussions with Prof. Roman Krems over the years.

A big thanks to my parents, Ken and Chris Morrison, who were always willing to entertain me when I took an infrequent break from work.

Finally, I would like to thank my girlfriend, Amanda Zimmerman, who fuelled my efforts with her delicious treats and provided much needed motivation through the final stretch. Thanks babe.
Dedication

I would like to dedicate this thesis to my wonderful parents, Dr. Ken and Chris Morrison.
Chapter 1

Introduction

1.1 Plasmas as a State of Matter

Plasmas can be broadly defined as conducting gases of charged particles existing in nature over a wide range of conditions: From temperatures of millions of kelvin in the sun’s core to hundreds of kelvin in Earth’s ionosphere, and densities as high as $10^{30}$ cm$^{-3}$ in white dwarf stars to values of 1 cm$^{-3}$ in interstellar space [7]. To properly qualify as a plasma a system must exhibit collective phenomena [8]. For example, despite their charged nature, plasmas are incredibly resistant to external electric fields since mobile charges have the ability to screen the electric fields over short distances. This particular type of collective response fundamentally underlies the more formal plasma definition that the screening length, quantified by the Debye length, $\lambda_D = \sqrt{\epsilon_0 k_B T/\rho e^2}$, must be much smaller than the plasma size. Here, $T$ is the temperature of the singly-charged particle of density $\rho$.

Plasma oscillations represent another fundamental type of collective effect and oscillations can occur over a wide range of modes and frequencies [9–12]. A thorough introduction to theory of waves in plasmas can be found in [13]. The most rudimentary oscillation is the Langmuir oscillation, which was the first observed plasma wave phenomena and arises when an oscillating electric field couples to the electron motion, thereby providing energy to electrons and displacing them from the equilibrium position at the plasma electron frequency, $\omega_{pe} = \sqrt{\rho_e e^2/m_e \epsilon_0}$, with $\rho_e$ being the electron density. Plasma oscillations can be monitored by Langmuir probes, which exploit electron wave behaviour in order to directly measure many important plasma properties such as electron temperature and density by
making contact with a hot plasma using one or more electrodes. Certain types of exotic laboratory plasmas [14] created in high vacuum environments must avoid direct contact with probe-electrodes and instead monitor oscillations through non-invasive measurements, such as charged-particle detection.

At equilibrium, plasmas actually exhibit low charged-particle fractions since ionization requires large amounts of kinetic energy. For example, the ionization equilibrium of helium, $\text{He} \rightleftharpoons \text{He}^+ + e^-$, requires a temperature of 12 000 K in order to sustain a 0.1% charged-particle fraction at 1 atm. Table 1.1 provides some examples of the parameter space for both laboratory and natural plasmas and the densities of electrons, $\rho_e$, and neutral atoms, $\rho_a$.

<table>
<thead>
<tr>
<th>Type of Plasma</th>
<th>$\rho_e$ (cm$^{-3}$)</th>
<th>$\rho_a$ (cm$^{-3}$)</th>
<th>$T_e$ (K)</th>
<th>$T_a$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sun’s photosphere</td>
<td>$10^{13}$</td>
<td>$10^{17}$</td>
<td>6000</td>
<td>6000</td>
</tr>
<tr>
<td>Ionosphere E-layer</td>
<td>$10^5$</td>
<td>$10^{13}$</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>He-Ne laser</td>
<td>$3 \times 10^{11}$</td>
<td>$2 \times 10^{16}$</td>
<td>$3 \times 10^4$</td>
<td>400</td>
</tr>
<tr>
<td>Argon laser</td>
<td>$10^{13}$</td>
<td>$10^{14}$</td>
<td>$10^5$</td>
<td>$10^3$</td>
</tr>
<tr>
<td>Ultracold Neutral Plasma</td>
<td>$10^8$-$10^{12}$</td>
<td>$10^7$-$10^{11}$</td>
<td>$1$-$10^3$</td>
<td>$10^{-6}$-$10^{-3}$</td>
</tr>
</tbody>
</table>

Charged-particle constituents can include a positive cationic component and a neutralizing negative electron component in the case of a two-component plasma, or just one charged species usually stabilized by a magnetic field, typical of a one-component plasma. Two- and multi-component plasmas can be further defined as *equilibrium* or *non-equilibrium*. In an *equilibrium* plasma all species must posses the same kinetic energy. In a *non-equilibrated* plasma an apparent temperature discrepancy exists between plasma components. Common examples of *equilibrium* plasmas include lightning, flames, and magneto-hydrodynamics generators. *Non-equilibrium* plasmas are found in He-Ne, and
argon lasers. Evidently, plasmas exist over a range of different physical environments, and in contrast to neutral rarefied gases, can be manipulated by electric and magnetic fields.

Figure 1.1: Summary of neutral plasmas in temperature-density space. Equilibrated plasmas exhibit a uniform temperature for all components. Ultracold plasmas are non-equilibrated, and plotted here is the temperature for the ion-component. Diagonal white lines are constant values of the Coulomb coupling parameter, $\Gamma$, from Eq. (1.1), with values indicated.

In addition to their energy equilibration characteristics, plasmas are further distinguished by the ratio of electrostatic to thermal kinetic energies. At high kinetic energies, electrostatic interactions between charged particles are comparatively small and have little effect on individual particle motion. The distinction between ideal, high temperature plasmas and those where Coulombic forces begin to have an effect is quantified by the Coulomb coupling parameter $[15]$. 
\[ \Gamma = \frac{e^2}{4\pi\varepsilon_0 a_{WS} k_B T}. \] (1.1)

When densities are high, the Wigner-Seitz radius, \( a_{WS} = \left[\frac{3}{(4\pi\rho)}\right]^{1/3} \), describing the average particle distance at density \( \rho \), is shorter and enhances the correlation at a constant temperature, \( T \). Figure 1.1 illustrates some examples of common plasmas found in nature and in laboratories. As can be seen, the parameter space occupied by ultracold neutral plasmas (UNPs) is an exotic region of the plasma \( T - \rho \) space, previously unexplored, yet rich in fundamental, many-body physics accessible in experiments conducted at standard atomic-molecular optical physics research labs.

### 1.2 Ultracold Neutral Atomic Plasmas

Traditional plasma studies have focused on regions of ideality where \( \Gamma < 1 \) and consequently a great deal of theoretical understanding has been established for these systems. When \( \Gamma > 1 \) charged particles begin to align and exhibit liquid-like behaviour for \( \Gamma \approx 10 \), and can form crystalline phases when \( \Gamma > 200 \) [16]. Correlation values of this magnitude are exclusive to the ion component, however, since a variety of heating effects will restrict the much lighter electron correlation to \( \Gamma_e \approx 0.5 \). Plasmas of this kind are referred to as strongly coupled plasmas (SCPs). SCPs can be found in interstellar matter and the interior of Jovian planets [17], and are of interest for understanding compressed material [18, 19], as well as processes involving inertial confinement fusion [20, 21]. Laser-irradiation experiments of clusters have provided experimental access to strongly coupled systems [22–24] by ionizing matter with intense, femtosecond laser pulses. These types of studies present a limited ability to probe the system, however, since the charged particle density can exceed \( 10^{24} \text{ cm}^{-3} \) and electron temperatures approach 80 eV. Conditions of this magnitude requires experimental access to timescales on the order of the inverse plasma frequency, \( \omega_p^{-1} = \sqrt{m\varepsilon_0/(e^2\rho)} \), which can approach femtoseconds for ions and attoseconds.
for electrons.

Magneto-optical traps (MOTs) [25] provide a method for creating strongly coupled plasmas. UNPs created in standard atomic physics laboratories have been shown to exhibit strong ion correlation [26, 27], but at much lower densities and temperatures than high-energy laser pulse experiments, thereby expanding the observation window to the nano- to micro- second timescale. UNPs are readily created at densities of $\rho \approx 10^8-10^{10} \text{ cm}^{-3}$ and initial ion and electron temperatures $T_i \approx 1-10^3 \mu\text{K}$ and $T_e \approx 1-1000 \text{ K}$, respectively.

From a theoretical standpoint, UNPs are convenient systems for study since they can be simulated simply using classical forces. For instance, quantum effects in plasmas become significant when the Brückner parameter, $r_s = (4\pi \rho / 3)^{-1/3} e^2 m / \hbar^2$, is less than 1, and the average inter-particle spacing is on the order of the Bohr radius, $a_0$. At these close distances the interaction potential is not strictly represented by the Coulomb interaction, and wave function overlap needs to be considered. Quantum effects also play a more significant role as the electron temperature approaches the Fermi energy, $E_F$. For a degenerate electron gas at zero temperature, the Fermi energy can be defined as the highest occupied quantum state. When the average electron kinetic energy is well above the Fermi energy, energy levels are better represented as a classical continuum. Standard conditions found in UNPs yield values of $r_s \approx 10^4$ and electron temperatures well above Fermi energies, justifying a purely classical physical treatment and providing an excellent environment to study plasma phenomena such as thermalization and collective properties. Classical scaling permits the extension to more extreme conditions.

Extending the plasma parameter space to the that of UNPs raises the question of whether these systems still adhere to the standard definition. UNP experiments did indeed reveal electron oscillations [11, 28, 29] and ion waves [30], confirming that in fact these types of systems are plasmas and behave collectively. To determine if they are strongly coupled requires the measurement of the temperature of both ions and electrons. Absorption spectroscopy has revealed Doppler broadening of the ions, providing a thermometer from
which an ion temperature on the order of a few Kelvin - orders of magnitude higher than the precursor neutral atoms - is determined [26]. The rise in temperature is attributed to an ionic energy conservation process called disorder-induced heating (DIH). Immediately following ionization, the newly formed ions are in an uncorrelated regime and experience strong Coulombic repulsion for closely spaced partners. To reduce the energy of interaction for near-neighbours requires the conversion of electrostatic potential energy to kinetic energy, thereby raising the temperature. If there are no additional ion cooling mechanisms to compensate for DIH, correlation is limited to values on the order of 10.

Measuring electron temperature has proven more elusive. UNPs are created in a non-equilibrium state and evolve by adiabatically expanding into vacuum. Ion temperature reflects the average ion kinetic energy, and since initial $T_i(0)$ values are so low, expansion energy is determined by the electron temperature. In the simplest picture, the radial electron pressure - in an idealized spherical symmetric picture - pulls on the heavier ions and accelerates them outward. Recording the plasma width at different times during the process produces a data set that exhibits characteristic ambipolar expansion features and provides a method by which to extract an initial electron temperature.

1.3 Ultracold Neutral Molecular Plasmas

Discussion thus far has focused on atomic UNPs formed in MOTs. This thesis reports on findings of a molecular UNP created by an entirely different technique [1, 31]. One may ask if the different preparation methods lead to comparable plasma environments. Indeed, experiments reveal molecular UNPs exhibit comparable properties to atomic systems, particularly in terms of expansion dynamics [2]. Expansion is monitored through charged-particle detection of both atomic and molecular UNPs, but experimental similarities do not extend further.

MOTs provide a cold, localized atomic gas sample in vacuum, while the molecular
beam technique - which will be discussed in Chapter 3 - provides a cold gas sample moving at a high velocity along the detection axis of the vacuum chamber. Optically probing a molecular plasma is more difficult since the entire volume is moving through space. This is a drawback to the technique. An advantage is that the choice of plasma particle is not limited by its spectroscopy: While MOTs require the trapped atom to have a strong transition in a convenient laser colour, molecular beams can cool any type of atom or molecule. More importantly, the center-line particle densities found in molecular beams can exceed atomic densities of MOTs by orders of magnitude. Hence, following laser excitation, molecular beams will evolve to form plasmas of higher densities than those formed in a MOT. Since correlation is proportional to density ($\Gamma \propto \rho^{1/3}/T$), a plasma formed in a molecular beam (and of a singly charged species) will be more correlated than one formed in a MOT, as long as the temperatures remain comparable.

Another distinguishing feature of molecular UNPs are the added energetic degrees of freedom. Atomic UNPs mediate kinetic energy through particle translation; molecular UNPs undergo dissociative dissipation, as well as rotational and vibrational motion which can both act as energy channels. Reflecting on the fact that correlation is inversely proportional to temperature, one can surmise that molecules are able to mitigate high temperature spikes through the use of molecular energy sinks, and exhibit higher correlation.

Results presented in this thesis are gauged to observations made on atomic UNP experiments. Comparative discussions address the differentiating features of a molecular UNP, as a consequence of both preparation technique and intrinsic molecular properties. Identifying the role these properties play in forming a highly correlated environment is of main concern, since the underlying motivation for UNP research is to continuously increase the correlated plasma state. The next few chapters will detail the pertinent aspects of the experiment and will include the molecular beam expansion, experimental infrastructure, and Rydberg molecules before diving into experimental and computational studies of molecular UNPs.
Chapter 2

Experimental Details

2.1 Overview

This chapter presents experimental details in hopes of providing a novice researcher a thorough technical resource for various types of measurements made in this research. The physical chemistry lab can be - and indeed was for this author - a daunting environment for those without prior experience. It helps to have a roadmap.

The experiment operates at 10 Hz, dictated by the frequency at which lasers fire, and the rate at which gas is introduced into the experimental vacuum chamber. Thus the experiment has two critical prerequisites: Light from the lasers and matter from the molecular beam. I will provide a brief account of both on a separate basis, up to the point of plasma formation. From there I’ll proceed with the plasma’s journey, ending the experimental walk-through with electron detection.

Exciting molecular nitric oxide to Rydberg levels is achieved through a double-resonant process, at laser frequencies $\omega_1$ and $\omega_2$. These two frequencies correspond to light generated from two independent laser systems, each consisting of a pump and dye laser. Pump light is produced in Nd:YAG laser cavities at 1064 nm, and Q-switched to pulse at 10 Hz. Pump light for the $\omega_1$ beam exits the pump laser at 355 nm following third-harmonic generation, while pump light for the $\omega_2$ beam exits at 532 nm following second-harmonic generation. These pump beams proceed respectively to enter dye-laser systems outputting precursor laser light for $\omega_1$ and $\omega_2$ at $\approx 452$ and $\approx 655$ nm, respectively, which then undergo frequency doubling. The final UV wavelengths of $\omega_1 \approx 226$ and $\omega_2 \approx$
$327 \text{ nm}$, are independently directed to the vacuum chamber, where they enter through windows on opposite sides, and intersect the molecular beam at $90^\circ$ in a counter-propagating fashion. This description is illustrated in Fig. 2.1.

Matter is introduced by way of a molecular beam expansion. A gas mixture consisting of 10% NO and 90% helium is stored in a tank at a pressure of 5 atm, and is connected to the vacuum chamber by a gas-line. The gas-line enters the pulsed-nozzle compartment, which is inside the vacuum chamber, through a vacuum feed-through coupler. When the nozzle is closed, gas pressure inside the pulsed-nozzle compartment is the same as that of the reservoir tank. Every 0.1 seconds, a small teflon poppet is retracted from the nozzle orifice, offering a direct path for the gas to enter the two-stage vacuum chamber. A pressure differential accelerates the gas through the orifice, and after a brief, turbulent fluid-like environment, the gas forms a molecular beam with a flow velocity of 1392 m/s along the $z$-axis. A skimmer mounted on a wall separating the two-stage chamber selects the coldest, densest, centre portion of the beam. Following the skimming process, the beam travels along its axis until laser intersection, approximately 11 cm from the nozzle. The region of laser intersection is flanked by two metal electrodes perpendicular to the beam axis, and held at a ground potential during excitation.

For the purposes of this experimental overview, we can exclude the particular details of plasma formation, and simply conclude that following laser excitation, the nitric oxide evolves to a plasma. Helium plays no role once the plasma has formed: its utility is found exclusively in the super-sonic expansion process. The newly formed plasma created between the two parallel electrodes travels away from the electrode closest to the nozzle, and towards the electrode closest to the detector assembly. All the while, the potential is held fixed at ground, and the plasma travels at a velocity determined by the precursor neutral, molecular beam. In the region beyond the far electrode a static electric field environment of 100 V/cm is maintained. Once the plasma reaches the far electrode, this static field extracts electrons and accelerates them to a micro-channel plate detector assembly. Following
amplification by the micro-channel plates, the electron current then strikes a bare metal anode, capacitively coupled to an oscilloscope. A representative waveform of the time-dependent anode current is displayed on the oscilloscope every 0.1 seconds corresponding to one cycle of the entire aforementioned process. The actual electron signal from a single cycle extends from $t = 0$, defined by laser-excitation, to times as long as 50 µs, defined by the time it takes the plasma volume to travel through space to the extraction grid (this grid can be translated along the beam-axis, thereby extending the flight time). Experimental details will be elaborated upon in the following sections of this chapter.

2.2 Experimental Details

The laboratory layout is provided in Figure 2.1 and displays an top-down view of the experimental setup. Action happens every tenth of a second or at a 10 Hz frequency. Lasers are Q-switched pulsed and the molecular beam valve is driven at 10 Hz. Laser output is diverted into the chamber in a co-propagating fashion with alignment achieved through two optical diaphragms. The diaphragm apertures can be adjusted to vary the beam diameter (hence excitation volume).

Laser systems consist of two Continuum Nd:YAG pump lasers, models Powerlite 8000 and Surelite. Both pump lasers are Q-switched and operate at 10 Hz. The Surelite supplies 355 nm light to a Lumonics HyperDye300 dye laser, circulating with a Coumarin 460 (Radiant Dyes) dye solution (0.26 g/L in methanol) which generates $\sim$452 nm output. We refer to this laser source frequency as $\omega_1$. The Powerlite 8000 supplies 532 nm light to a Continuum ND6000 dye laser circulating DCM (Radiant Dyes) dye solution (0.1 g/L for the oscillator cell, 0.033 g/L for the amplifier. Both dyes are dissolved in methanol) and outputs an $\omega_2$ beam with a wavelength of $\approx 655$ nm. Second harmonic generation (SHG) by BBO crystals in Inrad Autotrackers frequency-doubles each dye-laser output which results in the final wavelengths $\omega_1 \approx 226$ nm and $\omega_2 \approx 355$ nm.
Figure 2.1: An overview of the standard experimental arrangement. Laser systems begin with pulsed (10 Hz) Nd:YAG pump lasers at wavelengths 532 nm and 355 nm for $\omega_2$ and $\omega_1$, respectively. Dye lasers then convert pump laser light into wavelengths of $\approx 655$ and $\approx 452$ nm followed by frequency doubling (halving the wavelengths) by Inrad Autotrackers. Finally beams travel to the experimental vacuum chamber where they intersect the molecular beam in a counter-propagating manner.

All elements of the signal generation and data acquisition must be synchronized to optimize experimental measurements. To control timing we use an 8-channel Berkeley Nucleonics 575 Series Pulse Generator with 250 picosecond delay and width resolution. An
An optimized timing scheme is shown in Figure 2.2 and includes instrument output channels A, B, C, D, and H. The figure includes an explicit description but most important here is that timing is referenced to channel D, the $\omega_2$ Q-switch trigger. Also, channel B - $\omega_1$ Q-switch trigger - is referenced to channel A - $\omega_1$ flashlamp trigger - so that experiments that monitor the decay of NO transition state population can be performed by adjusting the time between the first and second excitation events, without affecting the rest of the experiment.

![Figure 2.2: An example of an optimized timing scheme generated by the BNC pulse generator. Channels are in blue circles and A and B trigger the $\omega_1$-laser flashlamp and Q-switch, respectively, while C and D trigger $\omega_2$-laser flashlamp and Q-switch, respectively. Channel D is referenced to the instrument’s internal frequency, $t_0$, while all other channels are referenced to D with the exception of B, which is referenced to A. Timing values shown are all relative to D, i.e. $B_{\text{trig}} = D_{\text{trig}} + 90$ ns. Channel H is the molecular beam pulse driver trigger. All times are in $\mu$s unless otherwise indicated.](image)

The vacuum chamber consists of two compartments separated by a partition wall mounted with an Ni electroformed skimmer. Each compartment is outfitted with a Pfeiffer TMU 520 turbomolecular drag pump with a helium pumping capacity of 500 litres/second, connected to a fore-line pumped by a Welch 1397 Duo-Seal roughing pump. Operating pressures are higher in the expansion-compartment with values on the order of $10^{-4}$ torr. The second compartment, where the plasma is created and detected, maintains a much lower operating pressure on the order of $10^{-8}$ torr.

A very important aspect of the laser excitation volume is the spatial distribution of photons in the $\omega_1$ beam which determines the overall plasma shape. If we define the molecular beam axis as the laboratory $z$-axis, and the laser axis, which intersects the beam
Figure 2.3: 2.3(a) Photodiode intensity (arb. units) as a function of razor-blade position on the left. Data is fit to error function and the corresponding Gaussian beam profile is displayed on the right. 2.3(b) Laser beam polarizations starting from the pump laser to a final polarization along the horizontal, all in reference to the laboratory frame.

at $90^\circ$, as the $x$-axis, we can determine the beam cross section in the $y, z$-plane in order to map the initial size and shape of Rydberg excitation volume. Measurements of this profile were obtained by placing a photodiode along the beam path, and stepping a razor blade across the beam and measuring intensity. Signal intensity versus razor-blade position are fitted to an error function,

$$\text{Erf}(z) = \frac{2}{\pi} \int_{\Delta z} \exp[-z^2/(2\sigma^2)]dz,$$

(2.1)

where $z$ is in the laboratory frame, and $\Delta z$ is the range over which the photodiode signal is obtained. We assume the laser beam has cylindrical symmetry. This approximation has not been verified experimentally, but simulations that mimic charged-particle extraction by a planar grid show that as long as the plasma distribution is Gaussian in the $z$-axis, the recorded signal will not deviate far from this distribution. As well, the temporal width of the gaussian beam packet is $\approx 9$ ns, making it’s spatial width on the order of meters and so, in comparison, the variation in density along the $x$-axis is negligible. A Gaussian profile obtained by this method is shown in Figure 2.3(a) For beam conditions for the analysis shown here, an $\omega_1$ FWHM was measured to be around 750 $\mu$m.
2.3 Gas Supply and Molecular Beam

This thesis reports on experiments that use nitric oxide exclusively as the plasma constituent. Super-sonic expansion of a NO/He gas mixture forms a cold sample of nitric oxide suitable for the experiment. Initial studies employed home-made NO/He mixtures formed in the mix tank, illustrated in Figure 2.4, by quantitatively adding from pure He and nitric oxide tanks. Experience has shown a 10% NO-helium mixture is optimal for plasma formation and the later experiments used a commercially available supply (Prax-air). Studies using heavier inert gases were performed by home-made 10% NO-inert gas mixtures, all at backing pressures of 5 atm.

Figure 2.4: Illustration representing the gas manifold used to supply the experimental vacuum chambers with nitric oxide sources. Valves are indicated by numbered circles, and regulators by lower case lettered circles. For instance: NO-He experiments will have valves 1, 2, and 6 will open for gas supply. All tanks are outfitted with gas regulators. Home-made gas mixtures were connected to the manifold as ‘mix tank’ in the figure. The line pump clears any residual nitric oxide gas that could oxidize between experiments.

Along with the gas supply, another critical element of the molecular beam apparatus is the pulsed nozzle. The main components include a General Valve pulsed-valve body and Iota One pulse driver. Figure 2.5 provides an exploded drawing of the valve body including

14
the poppet (Teflon, General Valve). The poppet is retracted from the nozzle by a +5 volt TTL pulse operating at 10 Hz, triggered externally by the BNC pulse generator.

Replacement of the poppet is the most frequently encountered maintenance procedure. A pulsed value operating properly ensures a well expanded, cold molecular beam. The following is a brief outline of the procedure and reference can be made to Figure 2.5. First, the chamber is brought to atmospheric pressure. Removal of the top-flange of the expansion chamber provides access to the valve mount assembly. From here, the pulsed-valve mount can be slid off the alignment rods and brought outside the chamber. Once outside the chamber, removal of the top-plate of the valve provides access to the armature. Removing the armature from the coil assembly permits the replacement of the poppet, and this is followed by reassembly. Further adjustment to the tension in the buffer spring can be done with the pulsed nozzle back in place by loosening or tightening the gas supply feed. Experience has revealed that running a new teflon poppet for a few hours with helium gas allows the poppet to cold-flow to an equilibrium shape conforming to the valve seat.

2.4 Electrostatic Grid Arrays: ZEKE and Moveable-Grid Profiles

2.4.1 Static-Grid Assembly

Extraction and detection of electrons for experiments reported in this thesis was accomplished using two different grid-array apparatus. By virtue of the fact the apparatus is mounted on the back flange of the chamber, they could be interchanged with minimal effort. The original ZEKE setup shown in Figure 2.6 clearly illustrates the laser interaction region, extraction and detection grids. The extraction grid, G2, is the first grid to the left of the blue laser line, and while G2 is typically set to ground, the electric field beyond this plate is $\approx 100 \text{ V/cm}$ and accelerates electrons to the detection assembly mounted on the
Figure 2.5: An exploded view drawing of the nozzle assembly taken from [6]. A driving current pulse drives the poppet-capped armature magnet in and out, thereby opening and closing the nozzle orifice allowing for the pulsed passage of reservoir gas into the vacuum chamber.

back flange. The entire electron-lensing array of grids were never fully exploited for plasma experiments, and were held at the field required to direct electrons to the detector.

Values for electrode plate spacing along the $z$-axis are provided in Table 2.1 with reference to Figure 2.7 for the position and name of each plate in the assembly.
Figure 2.6: Shown is the original, static grid-array apparatus. Originally built as a ZEKE spectrometer, the interaction region is defined by the intersection of the blue line, representing the laser beam, with the centre beam axis of the chamber. The wall-mounted skimmer resides in the expansion compartment. Along with the skimmer are mounted four alignment rods designed to point the gas nozzle directly along the chamber’s $z$-axis. This assembly has a set of static extraction grids, with the detection stack mounted on the back flange. Labels are associated with distances shown in Table 2.1.

Figure 2.7: Static grid assembly dimensions. Most relevant for experiments is the distance between Zex1 and Zex2 which determines the electric field strength when applying a voltage to Zex1. Similarly, the distance between Zex2 and Zfcyl along with the voltage applied at Zfcyl determines extraction field strength. Dimensions are listed in Table 2.1.
Table 2.1: Longitudinal and radial dimensions of the back-flange mounted grid assembly. The last two entries, rchamber and Rchamber, are the diameters for the inner shielding and outer shielding of the grid assembly, respectively.

<table>
<thead>
<tr>
<th>Label</th>
<th>Position (mm)</th>
<th>Diameter (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zex1</td>
<td>0</td>
<td>38</td>
</tr>
<tr>
<td>Zex2</td>
<td>21.2</td>
<td>38</td>
</tr>
<tr>
<td>Zfcyl</td>
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</tr>
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<td>Zlens1</td>
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<td>17.72</td>
</tr>
<tr>
<td>Zlens2</td>
<td>82.86</td>
<td>17.72</td>
</tr>
<tr>
<td>Zlens3</td>
<td>108.86</td>
<td>17.72</td>
</tr>
<tr>
<td>Zlensend</td>
<td>211.16</td>
<td>38</td>
</tr>
<tr>
<td>Zcyclend</td>
<td>301.16</td>
<td>38</td>
</tr>
<tr>
<td>Zend</td>
<td>314</td>
<td>-</td>
</tr>
<tr>
<td>rchamber</td>
<td>-</td>
<td>76.1</td>
</tr>
<tr>
<td>Rchamber</td>
<td>-</td>
<td>150</td>
</tr>
</tbody>
</table>

2.4.2 Moving-Grid Assembly

A significant experimental enhancement was brought about by the fabrication of a translatable extraction and detection grid carriage. The entire carriage design was guided by a past post-doctoral fellow, Dr. Chris Rennick. The assembly is well visualized by Figures 2.8 and 2.9. This system is mounted on the chamber’s back flange in the same way as the ZEKE instrument, with the important difference that the entire detection system can be translated along three 1/2 inch mounting rods via linear bearings. For instance, a range-of-motion of 10 cm extends the nitric oxide seeded in helium experimental observation window out to 70 $\mu$s or more (i.e. 10 cm / 1392 $\mu$m/$\mu$s (distance/beam velocity)). The relative position of the assembly is controlled by a bellows-isolated linear actuator driven by an animatics integrated SM23165D Smart Motor at a resolution of 10
µm. The grid-position is measured by a set of precision calipers mechanically coupled to the linear actuator on the outside of the chamber.

Figure 2.8: Shown here is the moveable-grid assembly where the entire detection carriage can be translated along the $z$-axis of the chamber, which varies the distance between G1 and G2, and ultimately varying the plasma flight-time. FMP1 and FMP2 represent front-mounting plate 1 and 2, respectively. The detection assembly is analogous to the ZEKE system and will be discussed further below.

2.5 Electron Detection

Inclusive to both grid systems is a 18 mm micro-channel plate detector (Jordan TOF Products, Inc.) outfitted with microchannel plates (Photonis), that amplify electron signal with a $1 \times 10^7$ gain. An exploded assembly is shown in Figure 2.10 and clearly labelled is G (input grid), the channel plate stack assembly D1, D2, D3, and the bare detection anode. Signal amplification is produced by the stack assembly with 1000 V across each plate.
Figure 2.9: 2D cartoon of moving grid cross-section showing detector carriage mobility along the z-direction. The green object on the right-hand side represents the mounting plate, FMP1 in Fig. 2.8.

Figure 2.10: An exploded view drawing of the 18 mm micro-channel plate detection system. Voltages are applied to the labelled grids according to Fig. 2.11. The bare detection anode is visible as the inverted cone-shaped protrusion.

Table 2.2 provides standard operating voltages for the UCP experimental electrodes. Extraction and repelling is performed by the G-electrodes, and detection by the D-electrodes.
Table 2.2: Here are listed typical voltage values for standard experimental extraction and detection. Anode and detector voltages can be adjusted to smaller values depending on the strength of the electron signal. Ranges indicate that applied voltages are optimized for experimental conditions.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Applied Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>Variable</td>
</tr>
<tr>
<td>G2</td>
<td>Ground</td>
</tr>
<tr>
<td>G3</td>
<td>60-150</td>
</tr>
<tr>
<td>Flight Tube*</td>
<td>60-150</td>
</tr>
<tr>
<td>Input Grid</td>
<td>D3 Voltage</td>
</tr>
<tr>
<td>Detector Front Plate (D1)</td>
<td>200</td>
</tr>
<tr>
<td>Detector Middle Plate (D2)</td>
<td>1200</td>
</tr>
<tr>
<td>Detector Back Plate (D3)</td>
<td>2200</td>
</tr>
<tr>
<td>Anode</td>
<td>2400</td>
</tr>
</tbody>
</table>

* Flight Tube includes electrostatic lenses

The detection anode is capacitively coupled to the anode in order to isolate the high voltage from the signal output which forms a high-pass filter.

Figure 2.11 provides the electronic circuitry for the detection stack.

2.6 Pulsed-Field Experiments

Impedance matching of electrical networks allows for the optimal flow of power across a circuit. Mis-matched impedance can generate reflections that can interfere with signal detection. Electrical components found in our experiments are generally rated to 50 Ω. However, the grid components in the chamber are not rated at 50 Ω, and monitoring rise-forms of voltage pulses applied to grid G1 can reveal significant deviations from the ideal value. In particular, the rise-time can lengthen to unwanted values when performing time-sensitive pulsing experiments (< 50 ns resolution), and parasitic ringing can occur at both the rising and falling edges.
A quality fast high voltage solid-state switch can minimize many of the pulse-shape problems. When a high voltage pulse is generated, it can be envisaged as leaving a source and transmitting through a wire to the load. Current from ground will compensate voltage change along the wire as this pulse is transmitted and lead to unwanted ringing and reflections. Properly designed circuits can minimize this. Pulses for our experiments are generated by a Behlke HV push-pull switching unit, model GHTS 60 which has gate-controlled MOSFETs giving excellent switching performance. Table 2.3 provides the manufacturer’s rise-time values.
Table 2.3: Load capacitance and rise-times

<table>
<thead>
<tr>
<th>Load Capacitance ($C_L$) pF</th>
<th>Rise-Time ($t_{r(ON)}$) ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>15</td>
</tr>
<tr>
<td>100</td>
<td>38</td>
</tr>
<tr>
<td>500</td>
<td>105</td>
</tr>
</tbody>
</table>

On the static grid assembly, the impedance contribution from the load capacitance ($C_L$) is constant, i.e. the distance between G1 and G2 does not change. In contrast, the moving grid has a G1-G2 separation distance that is constantly changing. Hence, to perform short time-resolved experiments requires variable impedance matching as $C_L$ changes. Figure 2.12 provides a simple electric circuit intended to represent the experiment.

![Figure 2.12: Circuit diagram for the experiment’s grid assembly electrical properties. C1 and R1 represent the intrinsic chamber impedance and along with the load capacitance, $C_L$, across G1 and G2, the total impedance can be determined. CV is a trim capacitor that can be varied to match the impedance as $C_L$ changes with grid distance. RS is an optional resistor suggested by Behlke Electronic GMBH to reduce ringing.

By monitoring the pulse-shape in real-time, the trim capacitor, CV, can be adjusted to obtain the cleanest rise-time. Resistor RS has been suggested by Behlke to improve impedance matching which would smooth rising and falling edges of the pulse. Suggested values are between 10 and 100 $\Omega$. 

23
2.7 Data Acquisition

Electron signal from the anode is digitized and displayed by a 500 MHz bandwidth, Agilent DSO5052A oscilloscope sampling at 4 GSa/s. Raw waveform data is sent to the computer at 10 Hz, or every laser shot. A 10-shot average is calculated by the computer and saved to disk. The experiment is controlled using a suite of home-built LabVIEW programs interfaced to control the lasers and acquire data from the oscilloscope. Recorded data is composed of two ASCII files: a .wf file providing a complete waveform description from the oscilloscope, and a .wl file containing data arrays (i.e. time, signal or wavelength, signal). A third .raw file saves the data in binary format and is required for experiments that scan over a dependent variable such as laser wavelength or G2 position. It is composed of oscilloscope time traces taken at each particular variable step. Post-processing of the data is performed by a file-reading LabVIEW program. To process raw data, an time-range is chosen for each oscilloscope trace, and the range is then integrated to generate plots of integrated signal versus experimental variable (i.e. laser wavelength, moving-grid position, etc.). In this manner, we can obtain characteristic Rydberg spectra as seen, for example, in Figure 5.4.
2.8 Summary

This chapter provides details of the equipment used for experiments that create and analyze ultracold molecular plasmas. Of particular importance to the experiment is the molecular beam nozzle which was introduced in Section 2.3 since it generates the cold, dense molecular sample required for plasma formation. For this reason, the next chapter will focus on the molecular beam gas expansion and ultimately provide estimations for temperature and density of nitric oxide gas at the point of laser excitation.
Chapter 3

Molecular Beam Gas Dynamics

3.1 Overview

Initial conditions encountered in the atomic MOT experiments are well defined considering the gas sample is localized, essentially stationary, with starting densities primarily dependent on atomic absorption efficiencies. A variety of experiments have been performed that verify initial conditions. Molecular beams, although well studied, span a broad range of starting conditions depending on the choice of parameter such as reservoir pressure, nozzle diameter, and gas mixture. A reliable estimate of the density and temperature at the point of laser-excitation is needed to estimate initial plasma conditions, and this requires an understanding of the super-sonic expansion. Near the nozzle source is a highly turbulent, chaotic environment. Fortunately, the chaos is rapidly reduced as the expansion proceeds and the flow becomes directed along the experimental $z$-axis. It is in the directed-flow regime that theoretical models apply to the highest accuracy. It is important to know the beam conditions at the point of laser-illumination because UNP formation depends on having high enough densities and low enough temperatures, and the molecular beam requires optimization to provide these conditions. This chapter will go through free-jet molecular beam expansion as it applies to our experiment.
3.2 Molecular Beam Introduction

Free-jet molecular beams are usually composed of a seeded fraction \((X_S)\) entrained in a two-component supersonic expansion, where the carrier gas fraction \((X_C)\) is typically a low weight noble gas used to evaporate the kinetic energy of the seeded fraction. A reservoir containing the gases \(X_S\) and \(X_C\) at temperature and pressure of \(P_0\) and \(T_0\), provides the high-pressure gas source that expands through a small nozzle into a low pressure, ambient background. The expansion converts the random thermal motion in the reservoir into directed flow in the experimental chamber, thereby reducing the translational temperature about the molecular beam flow velocity, \(u\).

Molecular beams are an indispensable tool used ubiquitously by spectroscopists since the technique is highly robust and reproducible for generating cold molecular samples. There are a wide range of parameters to consider when predicting flow-field properties and a full-blown analytic solution to beam dynamics is intractable, but thankfully, theory and experiment have shown that under the right conditions, certain expansion models can simplify the calculation of the more important beam values. In particular, we are interested in downstream values for center-line number density and temperature at the point where the molecular beam intersects the lasers. We can then use these values to extrapolate initial, \(t = 0\), plasma conditions.

3.3 Experimental Gas Properties

The gas source is a pre-mixed, commercial supply of 10% nitric oxide in 90% helium. Experiments performed using different noble buffer gases have used home-made mixtures with the same proportion of NO.

A gas line connects the reservoir canister to the nozzle chamber. The backing pressure, \(P_0\), is set to 510 kPa (60 psi), and is maintained throughout the line to the nozzle. Reservoir temperature, \(T_0\), is simply the laboratory temperature, 293 K.
Expansion occurs into a differentially-pumped vacuum chamber, separated from the experimental chamber by a wall mounted with a skimmer through which the beam passes. Figure 3.1 shows the distance from the nozzle - defined as \( z = 0 \) - to the skimmer and laser interaction region. The fore chamber, where the expansion occurs, is termed the \textit{source} chamber, and the aft chamber, where laser excitation occurs, is termed the \textit{plasma} chamber. At a pulsing rate of 10 Hz, and pulse width of \( \approx 150 \, \mu s \), the source chamber pressure is typically \( \sim 0.013 \, \text{Pa} \), while the plasma chamber pressure is \( 1.3 \times 10^{-4} \, \text{Pa} \) owing to the much lower gas intake. Setting the pulse duration to 150 \( \mu s \) permits the continuous steady-state approximation for the molecular beam since the beam package will be large enough - \( \Delta z = u \Delta t \approx 21 \, \text{cm} \) - to neglect any effects inherent to pulsed beams of shorter duration \[32\].
Explicitly treating each gas component in the expansion dynamics would make solutions intractable. The collision frequency is dominated by seed-carrier (SC) and carrier-carrier (CC) events, $\omega_{SS} \ll \omega_{SC} \sim \omega_{CC}$, which allows for an accurate description of the dynamics by assuming equilibration between carrier and seed gases, and adopting molar average molecular weight, $\bar{m}$, and molar average molecular heat capacity, $\bar{C}_p$. At 293 K, NO has a heat capacity of $C_{p}^{\text{NO}} = 29.88 \text{ J mol}^{-1}\text{K}^{-1}$ and deviates significantly from this value only below the characteristic rotational temperature, $\Theta_R = 2.4 \text{ K}$, when only the lowest rotational level is thermally accessible. Thermal vibrational up-population requires temperatures higher than 300 K, so throughout the experiment NO remains in the ground vibrational state. Hence, it is safe to approximate a constant $C_{p}^{\text{NO}}$ over our experimental conditions. Helium has a constant heat capacity of $C_{p}^{\text{He}} = 20.8 \text{ J mol}^{-1}\text{K}^{-1}$.

For the standard He-NO mixture, the molar average properties are calculated as:

\[
\bar{m} = \sum_i X_i m_i = 0.9 \cdot m_{\text{He}} + 0.1 \cdot m_{\text{NO}}
\]

\[
= (0.9 \cdot 4.0026 + 0.1 \cdot 30.006) = 6.603 \text{ g mol}^{-1} \tag{3.1}
\]

\[
\bar{C}_p = \sum_i X_i C_{p}^{\text{mol}} = 21.7 \text{ J mol}^{-1}\text{K}^{-1} \tag{3.2}
\]

\[
\bar{\gamma} = (1 - R/\bar{C}_p)^{-1} = 1.62 \tag{3.3}
\]

where $\bar{\gamma}$ is the mean heat capacity ratio, $X_i$ is the molar fraction, and $R$ is the gas constant.
3.4 Free-Jet Structure

The nozzle used in the free-jet expansion is a pinhole type, with a diameter of 0.05 cm. The gas is initially in a stagnation state \((P_0, T_0)\) that changes once the nozzle-poppet opens by the pressure difference, \(P_0 - P_b\), accelerating the gas through the orifice. The term supersonic implies velocities faster than the local sound speed. This is quantified by Mach number, \(M = u/a\), where \(a = \sqrt{\gamma RT/m}\) is the local speed of sound and \(u\) is the average beam velocity.

Supersonic beams are unable to respond to the surroundings since beam propagation is faster than information received from chamber walls or background pressure. As a result, a thin, high density layer forms on the outer parts of the expanding beam, which represents a thin, non-isentropic region having high gradients of pressure, temperature and density that force a deflection of particles. If the deflection is insufficient to reduce the flow velocity to subsonic values, shock waves develop in order to change flow direction and slow the beam in order to meet boundary conditions. The Mach disk is a shock wave that forms perpendicular to the flow direction, and encloses the high velocity \((M >> 1)\) core. Beyond the Mach disk, flow slows to a value \(M < 1\), which can introduce extreme turbulence. At the pressures we operate our expansion, the Mach disk location is \(\sim 210\) cm downstream from the nozzle - well beyond the entire chamber length. The core of the expansion is left to expand freely without boundary restrictions.

Equilibration of the center beam region requires a sufficient number of collisions between particles. The early part of the expansion has a high collision frequency and completely equilibrates translational energy. It is referred to as the continuum flow region. However, collision frequency falls off rapidly and beyond a certain point the rate is low enough that the mean-free path approaches the beam packet size, and the expansion becomes frozen-in. This is the free-molecular flow region. Figure 3.2 provides an illustrative description of these two regions. The dotted semi-circle in Figure 3.2 represents the quit-
ting surface, which is a virtual boundary between continuum and non-continuum flow. It is virtual because in reality, the transition between the two flow regions does not occur at a distinct coordinate, but instead happens over a range. For some expansions the quitting surface may need to be considered in the design of the chamber, but for our expansion, the quitting surface is close to the nozzle and need not be considered.

Flow directly out of the nozzle is incredibly turbulent and chaotic. However, after only a short distance (in terms of nozzle diameters \(d\)) - in the case of monatomic ideal gas, 0.075\(d\) [32] - expansion begins to exhibit spherical symmetry. This simplifies the quantitative analysis and theoretical models commonly express solutions to the dynamics along radial streamlines originating from the source. Accordingly, the center streamline is most relevant for characterizing the thermodynamic properties at the point of laser excitation.

3.5 Kinetic Theory and Method of Moments

Of greatest interest to researchers operating super-sonic expansions are downstream, center-line parameters for temperature and density. Obtaining equations that detail the relaxation of these parameters requires a kinetic theoretical treatment. It is beyond the scope of this chapter to perform a complete quantitative analysis, and in practice, unnecessary for well behaved expansions. However, frequently used beam expansion terminology (i.e. parameters) can be clarified by framing the relevant aspects of the model used to solve the Boltzmann equation. An illustration of the model for the expansion process is provided in Fig. 3.2, along with a definition of the cartesian and spherical coordinate systems as they apply here, and throughout the remainder of this thesis. The two regions labelled continuum flow and free-molecular (non-continuum) flow were introduced in the previous section, and since the continuum flow region exists over such a small distance from the nozzle, kinetic theory deals with the more relevant free-molecular region.
Simplification of the expansion is required. For instance, the seeded molecular gas fraction is neglected, and instead calculations are limited to treatment of a purely monatomic gas process, with molar average properties as discussed in section 3.3. Also, the spherical expansion is treated as axisymmetric with no angular dependence, having variation only in the radial direction. The radially dependent Boltzmann equation for the particle distribution function, \( f = f(r, \theta, \phi, v) \) can be expressed as,

\[
v_r \frac{\partial f}{\partial r} + \frac{(v_\theta^2 + v_\phi^2)}{r} \frac{\partial f}{\partial v_r} = \left( \frac{\delta f}{\delta t} \right)_{\text{collisions}}
\]

where the term, \( \left( \frac{\delta f}{\delta t} \right)_{\text{collisions}} \), accounts for collisions and will not be discussed in any further detail. Velocity components are defined in terms of spherical coordinates, \((r, \theta, \phi)\). The spherical, axisymmetric approximation is a good one for our conditions, especially for center-line thermodynamic values at distances \( z > 25 \text{ mm} \) [32] from the nozzle.
Conventionally, fluid dynamics makes use of a coordinate transformation to characterize flow in a more natural direction along streamlines. Theoretical analysis of molecular beams perform the same type of transformations by switching from cartesian or spherical unit vectors to unit vectors $\hat{s}$ and $\hat{n}$, where $\hat{s}$ is the direction along a particular streamline, and $\hat{n}$ is perpendicular to $\hat{s}$. The basic definition of streamlines is illustrated in Fig. 3.3 in the left plot, while the right plot shows how streamlines adopt a radiating nature in the free-molecular flow region of the expansion, and $v_{\parallel}$ and $v_{\perp}$ can then be regarded as component vectors for the two-dimensional planar expansion.

![Diagram showing streamlines and velocity components](image)

Figure 3.3: Fluid dynamics commonly makes use of a coordinate transformation from cartesian to natural streamlines illustrated in the plot on the left by $s_1$ and $s_2$. Unit vectors for streamlines are $\hat{s}$ (parallel to streamline flow) and $\hat{n}$ (perpendicular to flow). The plot on the right shows how streamlines become essentially linear and appear to radiate in the free-molecular flow region of the expansion from a point source at the nozzle. Here, the velocity components, $v_{\parallel}$ and $v_{\perp}$, first introduced in Eq. (3.6), can be defined as components of the overall streamline velocity.

Replacing spherical velocity components, with the parallel velocity component, dependant on the radial coordinate, $v_{\parallel} = v_r$, and the perpendicular velocity component, dependent on angular coordinates, $v_{\perp} = (v_\theta^2 + v_\phi^2)^{1/2}$ simplifies the Boltzmann equation (Eq. 3.4) to,

$$v_{\parallel} \frac{\partial f}{\partial r} + \frac{v_{\perp}^2}{r} \frac{\partial f}{\partial v_{\parallel}} = \left( \frac{\delta f}{\delta t} \right)_{\text{collisions}}. \quad (3.5)$$

The most commonly used velocity distribution function is Maxwellian [33], and can be expressed in terms of streamline velocity components, and mass flow velocity, $u$, along a
streamline as,

$$f(v) = \rho(r) \left( \frac{m}{2\pi k_B T_{\parallel}} \right)^{1/2} \left( \frac{m}{2\pi k_B T_{\perp}} \right)^{1/2} \exp \left[ -\frac{m}{2k_B T_{\parallel}} (v_{\parallel} - u)^2 - \frac{m}{2k_B T_{\perp}} v_{\perp}^2 \right]. \quad (3.6)$$

Here, $\rho(r)$ is the density. Eq. 3.6 can be substituted into the Boltzmann equation (Eq. 3.5) to generate four moment equations for the parameters $\rho$, $u$, $T_{\parallel}$, and $T_{\perp}$, which are then solved to provide the relaxation dynamics. Since the distributions are gaussian, $\rho$, $u$, $T_{\parallel}$ and $T_{\perp}$ correspond to the zeroth, first, and second moments of Eq. 3.5.

The explicit details of the method of moments has been neglected here. Instead, the parallel and perpendicular velocity components have be defined through a brief explanation of the frequently used kinetic model. Furthermore, $T_{\parallel}$ naturally arises by assuming a Gaussian velocity distribution along a streamline, and will be referred to throughout the remaining of the thesis, since its value best represents the average particle translational kinetic energy in a molecular beam. Parameters displaying the $\infty$-superscript, i.e. $T_{\parallel}^\infty$, refer to final, asymptotic values for that particular parameter, except asymptotic flow velocity, $u_\infty$, which uses the subscript. In the next section, a simpler thermodynamic approach will be explored that provides analytic equations for the relaxation of the important parameters.

### 3.5.1 Flow Properties from an Ideal Thermodynamic Analysis

Deriving the relevant properties of the molecular beam begins with the first law of thermodynamics, which equates the enthalpy per unit mass, $H_m$, and velocity, $u$, to the stagnation enthalpy per unit mass, $H_m^0$. Under the assumptions that viscous and heat conduction effects can be neglected, flow is isentropic, and heat capacity $\hat{C}_p$ is constant, so the energy balance can be written,
\[ H_m^0 = H_m + \frac{u^2}{2} \]  

(3.7)

which holds for a particular streamline originating at the virtual nozzle source. At the source reservoir, \( H_m^0 = H_m \), and \( H_m^0 \) is constant for the expansion. As the gas expands, it adiabatically cools, enthalpy decreases, and the mean velocity increases. Assuming the gas is ideal, \( dH_m = \bar{C}_p dt \), and \( \bar{C}_p = \left(\frac{\gamma}{\gamma} - 1\right)\left(R/\bar{m}\right) \) is the constant heat capacity with a gas of molar average molecular weight of \( \bar{m} \), and \( \bar{\gamma} = 1.62 \) from (3.3), we can then write,

\[ u^2 = 2(H_m^0 - H_m) = 2 \int_T^{T_0} \bar{C}_p dT \]  

(3.8)

\[ u = \sqrt{2\bar{C}_p(T_0 - T)} \]  

(3.9)

where (3.9) takes into account the constant heat capacity over the temperature range of interest. Further replacement of \( \bar{C}_p = \left(\frac{\bar{\gamma}}{\bar{\gamma}} - 1\right)\left(R/\bar{m}\right) \) leads to an equation for the terminal beam velocity,

\[ u_{\infty} = \sqrt{\frac{2R}{\bar{m}} \left(\frac{\bar{\gamma}}{\bar{\gamma} - 1}\right) T_0} \]  

(3.10)

for a constant \( \bar{\gamma} \), Eq. (3.10) depends inversely on the molar average molecular weight:

Seeding nitric oxide in a heavier carrier gas slows down the beam.

Rearranging (3.9) and substituting for \( \bar{C}_p \) and \( u = M \cdot a \), one can obtain relations for thermodynamic variables \((T, u, P, \rho)\) upon a particular expansion streamline in terms of stagnation conditions \((T_0, u_0, P_0, \rho_0)\),
\[
\frac{T}{T_0} = \left(1 + \frac{\tilde{\gamma} - 1}{2} M^2\right)^{-1}
\]  
(3.11)

\[
\frac{P}{P_0} = \left(1 + \frac{\tilde{\gamma} - 1}{2} M^2\right)^{-\tilde{\gamma}/(\tilde{\gamma} - 1)}
\]  
(3.12)

\[
\frac{\rho}{\rho_0} = \left(1 + \frac{\tilde{\gamma} - 1}{2} M^2\right)^{-1/(\tilde{\gamma} - 1)}
\]  
and,
(3.13)

\[
u = M \sqrt{\tilde{\gamma} R T_0 / m} \left(1 + \frac{\tilde{\gamma} - 1}{2} M^2\right)^{-1/2}
\]  
(3.14)

Equations (3.11)-(3.14) all depend on Mach number, \( M \), and having an analytical expression for the Mach number would simplify the calculation of flow-field properties.

Obtaining an expression for Mach number requires solving the steady-state conservation equations of mass, momentum and energy (analogous to the technique described in the last section):

\[
\nabla \cdot \rho \mathbf{u} = 0
\]  
(3.15)

\[
\rho \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla P
\]  
(3.16)

\[
\mathbf{u} \cdot \nabla H_0 = 0
\]  
(3.17)

along with the equations of state,
\[ P = \rho \frac{R}{m} T \]  
(3.18)

\[ dh = \bar{C}_p dT \]  
(3.19)

Solutions to this complete set of fluid mechanics equations are obtained by changing from cartesian to streamline coordinates, which converts the partial differential equations to ordinary differential equations that can be numerically integrated to obtain values of \( M \) [32]. Integration results are fitted to an analytical formula for Mach number as a function of scaled distance from the nozzle, \( z/d \), along the center streamline (i.e. along the laboratory axis of electron detection), and can be expressed as [34],

\[ M = 3.26 \left( \frac{z - z_0}{d} \right)^{\gamma^{-1}} - \frac{1}{3.26} \left( \frac{z + 1}{\gamma - 1} \right)^{\gamma^{-1}}. \]  
(3.20)

For an axisymmetric expansion from a circular source nozzle, Eq. (3.20) holds well for \( z/d > 2.5 \), and streamlines appear to radiate from a virtual source point that is a reduced distance, \( z_0/d \), downstream form the real nozzle. For conditions used in the experiment, the virtual source has a value of \( z_0/d = 0.075 \). Laser interaction occurs hundreds of nozzle diameters downstream, and so the virtual source phenomena has negligible effect on the calculations and can be ignored.

We can compute reliable thermodynamic values for an expansion from typical reservoir conditions of \( P_0 = 60 \) psi, \( T_0 = 295 \) K, through a nozzle of diameter 0.05 cm by substituting Eq. (3.20) into Equations (3.11)-(3.14). The evolution of temperature, \( T \), and density, \( n \), normalized to stagnation values \( T_0 \) and \( n_0 \), respectively, and as a function of reduced distance, \( z/d \), is plotted in Figure 3.4, along with the absolute beam velocity, \( u \).
3.6 Speed Ratio

In the continuum regime, the high collision rate equilibrates all degrees of freedom, and flow field properties of Eqs. (3.11)-(3.14) are accurately expressed in terms of Mach number, $M$. As rarefaction increases into the free-molecular region, flow is more commonly characterized by the speed ratio. The speed ratio is defined as the ratio of mass transportation velocity, $u$, to the velocity spread in the parallel direction,

$$ S = \frac{u}{\sqrt{\frac{2k_BT}{mW}}} $$

and describes the velocity resolution without using the sound speed, $a$. Plotting the colli-

Figure 3.4: Isentropic thermodynamic values given by Eq. (3.11)-(3.14) are plotted against reduced distance from the nozzle, $z/d$. Temperature (blue dashed) and density (blue dash-dot) are normalized to reservoir conditions, $T_0$ and $n_0$, respectively and follow the left $y$-axis. Beam velocity (red solid) is in units of m/s, and follows the right $y$-axis. Note the early rise to the terminal beam velocity, $u_\infty$, in terms of expansion distance.
sion frequency against distance for a simple 2-body hard sphere collision (Fig. 3.5) shows that at an interaction distance of 0.5 cm from the nozzle ($z/d \approx 10$), there is less than one collision per centimeter. This is a suitable criterion for transition from continuum to free molecular flow regime.

![Graph showing collision frequency against distance](image)

Figure 3.5: Collision frequency (cm$^{-1}$) as a function of distance along the expansion axis ($\hat{z}$) using a two-body hard sphere approximation of He-He collisions. Collisions drop off to $\approx 1$/cm, 0.5 cm from the nozzle, as indicated by the dashed line. Laser interaction occurs 10 cm from the nozzle.

Speed ratios are commonly used to characterize nozzle beams in fluid dynamics since they provide a dimensionless gauge to quantify the extent of cooling. A large speed ratio refers to a narrow distribution of velocities about $u$ and a low temperature. For speed ratios greater than 10 the temperature of a monatomic gas ($\gamma = 5/3$) in the moving frame is well described by the simple relation [35]:

$$T/T_0 \approx 2.5/S^2$$  \hspace{1cm} (3.22)
Thus a knowledge of the speed ratio as a function of experimental parameters provides a
gauge that can be used to maximize the cooling in the expansion. Standard conditions
found in our experiment predict a final asymptotic speed ratio value of $S_\infty = 79$ which
supports the use of Eq. (3.22) to give a final $T_\infty = 120 \text{ mK}$. 
3.7 Intramolecular Energy Relaxation

3.7.1 Rotational and Vibrational Temperature

In previous sections the discussion was limited to the approximation of an expanding monatomic gas in order to simplify the kinetic theory. Nitric oxide has internal degrees of freedom that can store energy. Temperature relaxation for rotational ($T_R$) and vibrational ($T_{vib}$) motion does not follow the same relaxation pattern as translational counterparts ($T_\parallel$ and $T_\perp$). Indeed, vibrational modes for simple diatomics do not even participate in the expansion process since their relaxation requires in excess of $10^4$ collisions, while the total number of binary collisions experienced by a molecule during the expansion is typically on the order of $10^2$-$10^3$. Furthermore, for nitric oxide it is safe to assume that nearly all of the population is in the ground vibrational state, since, for the lowest $^2\Pi_{1/2}$ electronic state, the characteristic vibrational temperature, $\Theta_{vib}$, is 2719 K \cite{36} which we use to approximate the fraction of population in vibrational levels other than $v = 0$ to be $f_{v>0} = e^{-\Theta_{vib}/T_0} \approx 9 \times 10^{-5}$ at a reservoir temperature of $T_0 = 293$ K (expansion cooling would only enhance this value).

Rotational modes, on the other hand, are separated energetically on a scale orders of magnitude smaller than vibrational modes, and participate in the cooling process of the expansion, albeit to a lesser degree than translational energy. Because the collisional cross section for rotational cooling is smaller than that for translation, the rotational temperature reaches a final, asymptotic value earlier in the expansion. Incorporating rotational motion into the kinetic model for expansion adds a much higher level of complexity to the monatomic gas treatment; rotational temperature can be obtained experimentally by performing a spectroscopic technique called resonant-enhanced multi-photon ionization. In this way, we are able to obtain a value for final rotational temperature, $T_R^\infty$, in our supersonic beam expansion.
3.7.2 Resonance-Enhanced Multi-Photon Ionization (REMPI) for the Determination of Rotational Temperature

Rotational temperature is measured by two-photon resonance-enhanced ionization. First, we find a suitable nitric oxide resonance that provides a strong \((1 + 1)\) ionization signal by which to tune \(\omega_1\) laser power. Glan-Taylor polarizers are carefully adjusted so that the photon flux is low enough in order to extinguish the \((1 + 1)\) two-photon ionization \((< 500 \mu J)\). The ionization laser frequency, \(\omega_2\), is tuned well above threshold. We scan the \(\omega_1\) laser from \(\approx 44150 \text{ cm}^{-1}\) to \(44210 \text{ cm}^{-1}\) thereby exciting NO electrons from the ground \(X^2\Pi_{1/2}\) \((v'' = 0, K'' = 1, J'' = 1/2(-)\) ) state to intermediate levels before final ionization. The top trace of Figure 3.6 is the acquired electron signal as a function of \(\omega_1\) wavelength.

Rotational temperature is measured by comparing the spectra to simulations. We use PGOPHER\(^1\) to simulate the nitric oxide \((v'' = 0)\) absorption. Below the experimental spectrum are simulation spectra for temperatures of 2.5, 5, and 10 K. Comparing peak intensity ratios provides a reliable method by which to determine the rotational temperature of nitric oxide at the point of laser excitation, since variation of the intensity of lines in a rotational band, as a function of rotational quantum number provides the thermal distribution of these levels. The simulation spectrum that best represents the experimental spectrum of Fig. 3.6 is for a rotational temperature, \(T_R^\infty\), of 2.5 K.

With a rotational temperature we are now able to determine the population of the nitric oxide electronic ground state from which we excite electrons to high Rydberg levels. The fraction of population for a particular rotational level, \(p(N_i)\), can be calculated from the Boltzmann distribution as,

\[
p(N_i) = \frac{2(2N_i + 1) \exp\left(-E_{\text{Rot}}(N_i)/k_B T\right)}{\sum_0^N 2(2N_i + 1) \exp\left(-E_{\text{Rot}}(N_i)/k_B T\right)}
\]

\(^1\)PGOPHER, A program for Simulating Rotational Structure, C.M. Western, University of Bristol, http://pgopher.chm.bris.ac.uk
Figure 3.6: Plots showing experimental REMPI data (top) and simulations. In the graphs, electron signal intensity (arb. units) is plotted against the $\omega_1$ wavelength. Accompanying each simulation plot is the rotational temperature used to acquire the simulation results.

where $E_{Rot}(N_i) = h c F_{Rot}(N_i) = h c B_v N_i (N_i + 1) - D_v N_i^2 (N_i + 1)^2$ [36] is the truncated rotational energy of level $N_i$, where $T$ is the temperature, and for nitric oxide, $B_v = 1.67$ cm$^{-1}$ and $D_v = 0.45 \times 10^{-6}$ cm$^{-1}$ represent the rotational and mean rotational constant,
respectively. If we assume that the dominate term in the equipartition theorem for the supersonic expansion is rotational energy, setting the temperature to $T_R^\infty = 2.5$ K, the ground $X^2\Pi_{1/2}$ level has a 90% occupancy, which is further reduced by Λ-splitting to make (-) and (+) states, which leads to a $X^2\Pi_{1/2}(-)$ fraction of 0.45.
3.8 Molecular Beam Intensity

Intensity is defined as the center-line ($z$-axis) particle flux per steradian. It is needed to calculate the density at the point where the lasers intersect the molecular beam. For this calculation skimmer effects are neglected: Current electroformed Ni skimmer design prevents particles with high perpendicular velocity from recoiling off the skimmer surface and back into the center-line beam. This calculation also assumes our molecular beam is sufficiently dilute that the properties are dominated by the carrier gas. It is then straightforward to calculate the expected neutral NO density at the laser interaction region.

Supersonic expansions can be well described using the number density and velocity components parallel and perpendicular to streamlines. However, when analyzing gas dynamics it is preferential to use parameters independent of the point of observation. For a point-source approximation, the ideal center-line beam can be expressed as the differential luminosity element of total flow rate $\dot{\phi}$ (molecules·s$^{-1}$) [37],

$$\frac{d\dot{\phi}}{d\Omega} = I(0)f(x,y)p(v)d^2\Omega dx dy dv$$  \hspace{1cm} (3.24)

where $I(0)$ is the center-line intensity (molecules·s$^{-1}$·sr$^{-1}$), $p(v)$ is the normalized parallel velocity distribution of the beam flux, and $d^2\Omega$ is the solid angle element. The function $f(x,y)$ is the normalized distribution function of the beam flux in the source $x,y$-plane in units of m$^{-2}$, and has the value $f(x,y) = 4/(\pi d_0^2)$ for $x^2 + y^2 \leq d_0^2$, and zero everywhere else. The nozzle diameter is given as $d_0$. Luminosity describes the flux per solid angle, per unit area, per unit time.

Instead of using angular intensity distribution $I(\theta)$, the beam source is characterized by the peaking factor [37], $\kappa$.

$$\kappa = \frac{\dot{\phi}}{\pi I(0)}.$$  \hspace{1cm} (3.25)
For the center-line of a monatomic gas expanding from a nozzle, $\kappa = 2$.

Equation 3.24 can be integrated at the source nozzle to describe the flow rate, $\dot{\phi}$, through the source plane as

$$\dot{\phi} = f(\gamma)\rho_0 u_0 (\pi d_0^2 / 4)$$

(3.26)

where $f(\gamma)$ is a function of heat capacities,

$$f(\gamma) = (\gamma / (\gamma + 1))^{1/2} (2 / (\gamma + 1))^{1/(\gamma - 1)}.$$

(3.27)

Here, $u_0 = \sqrt{2k_B T_0 \bar{m}}$ is the most probable molecular speed in the reservoir at temperature $T_0$, $\bar{m}$ is the weighted mass, $\rho_0$ is the reservoir density, and $f(5/3) = 0.513$.

In order to obtain a downstream value for the on-axis number density, we can manipulate (3.25) for $I(0)$ and equate this to (3.26),

$$I(0) = \frac{\dot{\phi}}{\kappa \pi} = f(5/3)\rho_0 u_0 (\pi d_0^2 / 4).$$

(3.28)

To get downstream flux value, we multiply (3.28) by solid angle per area, $A$,

$$\frac{\Omega}{A} = \frac{1}{z^2}$$

(3.29)

where $z$ is the standard distance along the beam axis. Using the terminal, most-probable velocity, $u_\infty$, we can obtain an expression for center-line number density, $\rho_{CL}$,

$$\rho_{CL} = \frac{I(0)}{u_\infty z^2}$$

(3.30)

This isentropic centre-line density formalism holds for the continuum and non-continuum region of expansion, because density falls as $1/z^2$ in both regions (Eq. 3.30), and the velocity asymptotically approaches $u_\infty$ early in the expansion. Evidently, high intensity beams
rely on a high nozzle flow rate, which requires a large pressure gradient and small nozzle diameter - conditions typical for our experiment. Introducing our experimental values for absolute number yields a center-line nitric oxide number density at $z = 10.5$ cm of $1.4 \times 10^{14}$ cm$^{-3}$. 
3.9 Nitric Oxide Spectroscopy

This section will provide a basic summary of the standard photo-excitation scheme used to generate Rydberg states. It is not intended to be a rigorous review of the extensive nitric oxide spectroscopic literature but instead provide the important details of the (1+1’) two-photon excitation common to all plasma experiments reported in this thesis.

Nitric oxide is a favourable plasma substrate for our purposes, largely due to the accessibility of the upper manifold by two-photon excitation through a fully assigned A-state, and the closed-shell NO⁺ core. The occupation of molecular orbitals for the lowest electronic nitric oxide state is given by,

\[
(\sigma 1s)^2(\sigma 1s)^2(\sigma 2s)^2(\sigma 2s)^2(\sigma 2p)^2(\pi 2p)^4 \pi 2p
\]

where \(\sigma\) and \(\pi\) refer to bonding orbitals on the internuclear axis and perpendicular to it, respectively. This formalism also details the predominant atomic orbital (\(ns, np, nd,\) etc) types contributing to the molecular orbit.

In order to properly describe photo absorption-induced transitions in a molecule, careful consideration must be made when labelling the many possible quantum mechanical angular momentum states. Depending on magnitudes of the values, different scenarios exist for the coupling of angular momentum: these scenarios are traditionally classified as Hund’s cases (a), (b), (c) or (d). The two-photon nitric oxide excitation used in our experiment involves an initial \(A^2\Sigma^+ \leftarrow X^2\Pi\) transition, followed by a subsequent excitation to Rydberg states converging to the lowest rotational level of the NO⁺ ion. The nitric oxide rovibronic states addressed in our experiments always involve the vibrational ground state, \(v = 0\).

The \(X\)-ground state of nitric oxide contains a closed inner shell with a single radical electron. The coupling follows a Hund’s case (a) (Fig. 3.7 (a)) and the electron orbital
Figure 3.7: Applicable Hund’s cases for angular momentum coupling of different electronic states of nitric oxide used in our (1+1′) multiphoton excitation. $J$ is the total angular momentum, given as $J = N + L + S$, where $N$ is the rotational angular momentum of the molecule, $L$ is the total electron orbital angular momentum, $L = \sum_i \ell_i$, and $S$ is the total electron spin angular momentum, $S = \sum_i s_i$. Projections of $L$ and $S$ onto the internuclear axis are given as $\Lambda$ and $\Sigma$, respectively. The total electronic momentum projection is expressed as $\Omega = \Lambda + \Sigma$. For Hund’s case (b) and (d), $K$ is the total angular momentum apart from spin.

angular momentum is weakly coupled to core rotation, but is very strongly coupled to the internuclear axis making its projection, $\Lambda$, a good quantum number. Since there is a only a single un-paired electron, the total projection of momentum onto the internuclear axis, $\Omega$, becomes $\Lambda \pm \frac{1}{2}$ and for the $X \Pi$-state, $\Lambda = 1$, which leads to two configurations: $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$. The splitting between these two states is large enough ($\approx 124$ cm$^{-1}$) that at low temperatures, the majority of the population is in the $^2\Pi_{1/2}$-state. When $\Lambda \neq 0$ symmetric tops have two linearly independent, degenerate rotational eigenfunctions for symmetric and anti-symmetric reflections about the origin and are designated by (+) or (−). This arises from the invariance of the Hamiltonian upon reflection of the value of $\Lambda$ through a $\sigma_v$ plane perpendicular to inter-nuclear axis. The ground state is given by $X^2\Pi_{1/2}$ ($v'' = 0$, $K'' = 1$, $J'' = \frac{1}{2}$) ($-$).

A single photon ($\approx 226$ nm) promotes the ground state population to the $A^2\Sigma^+$-state which is a mixture of Hund’s case (a) and (b) (Fig. 3.7 (a)and (b)). Hund’s case (b)
introduces the value $K$ which is a combination of $\Lambda$ and $N$. $K$ can take values $\Lambda, \Lambda+1, \Lambda+2, \ldots$ and if $\Lambda = 0$, $K$ is identical to $N$. Electron spin, $S$, is decoupled from the internuclear axis for this model. The $3s\sigma$ molecular orbital contains mostly (94% [38]) $s$-character, and the specific $Q_{11}$ transition we select a final state with no rotational angular momentum ($N' = 0$), and so $J = 1/2$. The complete description for this level is $A^2\Sigma^+ (\nu' = 0, K' = 0, J' = \frac{1}{2}(+))$.

This is a convenient route to high-lying Rydberg states because dipole selection rules confine the final Rydberg states to those only with $|N| = 1$. Rydberg states follow Hund’s case (d) (Fig. 3.7 (c)) where the coupling between $L$ and the axis of rotation is stronger than $L$ coupling with the internuclear axis. This is easily understood considering highly excited Rydberg state wave functions spend the majority of their time away from the core. Angular momentum of nuclear rotation is given as $R$ for this case (instead of $N$), and $K$ has the standard definition.

More explicitly, if $N = N^+ + \ell$ (ignoring spin), where $N^+$ and $\ell$ are the NO$^+$ core rotation and electron orbital angular momentum, respectively, it can be seen that for Rydberg states converging to $N^+ = 0$, $\ell$ must be equal to 1, for the $N^+ = 1$ series, $0 \leq \ell \leq 2$, and Rydberg states approaching $N^+ = 2$ requires that $1 \leq \ell \leq 3$. This follows the vector addition of angular momenta producing values $|N| = (N^+ + \ell), (N^+ + \ell - 1), \ldots, |N^+ - \ell|$. Thus, $np$ Rydberg series accessible from the NO $A^2\Sigma^+ N' = 0$ state must converge to the $N^+ = 0$ ionization threshold, while the accessible $nf$-series from the $A$ state must converge to the $N^+ = 2$ ionization threshold.

Our integrated plasma signals fit best to the expected quantum defect of the $nf$-series. Quantum defect values account for deviations from the Rydberg formula when calculating the energy of a particular Rydberg level. While transitions to certain $ns$ and $np$ series are allowed by angular momentum selection rules, these states appear to decay before the Rydberg gas can evolve to plasma. At intervals in the spectrum where $ns$ or $np$ states overlap with $nf$ states, lifetimes may be lengthened by $\ell$-mixing and we do observe
additional features.

Figure 3.8: Two-photon excitation of nitric oxide form the ground state to Rydberg states converging to the lowest ionization potential
3.10 Summary

This chapter has provided some background theory for the technique of super-sonic expansion. It is a valuable tool for generating very cold (≈ 0.1K), high density (10^{14} \text{ cm}^{-3}) nitric oxide beams that can be photo-excited from the ground-state. Personal experience has shown that achieving optimal conditions requires art along with science for this type of apparatus. Determining thermodynamic properties downstream of the nozzle is accomplished by comparing calculations based on an isentropic flow model that yields values agreeing well with experimental observations (i.e. terminal beam velocity measurement calculated from the time required for neutral plasma to traverse 1 cm. See Fig. 5.3 on page 71). The ability to slow the beam by using heavier carrier gases will be shown to be a convenient tool for extending the observation window after the initial laser illumination.

Nitric oxide spectroscopy was also discussed with focus on the specific double-resonant transition commonly used to excite electrons to high-lying Rydberg states. The spectroscopic discussion naturally lead to the REMPI technique we use to determine nitric oxide rotational temperature.
Chapter 4

Rydberg Molecules

We photo-excite cold, ground-state, nitric oxide molecules prepared in a supersonic expansion to states with very high principal quantum number ($n > 30$). When a bound electronic state is well described using the classical Bohr model of an atomic orbital, it can be referred to as a Rydberg state. This is an important aspect of the experiment: Our plasma is created when an ensemble of Rydberg states - all energetically below the lowest ionization threshold of nitric oxide - interact to ionize and form a plasma. Indeed, the strong nature of Rydberg-Rydberg interactions make them particularly suitable for our purposes. To that end, a description of Rydberg states will be provided, along with important Rydberg properties that apply to our experiment.

4.1 Theoretical Description

Rydberg molecules conform to a type of molecular quantum state where the wave-function of a highly excited electron ranges so far from the nucleus that the potential interaction approaches a limit where it can be sufficiently described by a Coulombic field. A large electron-core separation, increasing with $n$, greatly simplifies the Hamiltonian, which, for low principal quantum number, requires the inclusion of multi-body interactions with core electrons. To a first order approximation this situation is analogous to that of a hydrogen atom, whose Schrödinger equation in atomic units is,

$$\hat{H}\Psi = E\Psi$$

(4.1)
\[
\left(-\nabla^2/2 - \frac{1}{r}\right)\Psi = E\Psi
\]  

(4.2)

and \(\nabla\) is the gradient operator in spherical coordinates with \(r\) being the Rydberg electron radial distance from the nucleus. Without any external fields, Eq. (4.2) is best described using spherical symmetry, and a detailed solution can be found in [39]. Solutions to the hydrogen wave function are well known, and the familiar equation for allowed energy levels is,

\[
E_H = -\frac{R}{n^2}
\]  

(4.3)

where \(R\) is the Rydberg constant, \(n\) is the principal quantum number, and at infinite electron-ion separation, the potential is zero. For larger atoms and molecules, the hydrogen model for Rydberg states remains valid for high \(n\) and high angular momentum, \(\ell\), when the Rydberg electron closely follows a Bohr orbit. However, when the electron is in low-angular momentum states it can both polarize and penetrate the shell of ion-core valence electrons. Because the wave function of the penetrating Rydberg electron has a finite probability of being within the ion-core valence shell, it experiences a greater overall positive charge. The inner electrons do not fully shield the nucleus. This tends to increase the binding energy and decrease the overall energy of the Rydberg electron.

To account for the deviation from hydrogen energy levels, a parameter called the quantum defect, \(\delta_\ell\), is introduced to define an effective principal quantum number, \(\nu = n - \delta_\ell\). Quantum defects depend on orbital angular momentum. For NO, \(\delta_\ell\) can range from \(\delta_{ns} = 1.21\) to \(\delta_{nf} = 0.01\) [40]. For atoms and molecules other than hydrogen, the Rydberg equation becomes

\[
E_{Ryd} = E_{IP} - \frac{R}{(n - \delta_\ell)^2}
\]  

(4.4)
where $E_{IP}$ is the particular ionization threshold the Rydberg series is converging to and for high-$\ell$, $\delta_\ell \to 0$.

By their nature Rydberg states possess many exploitable features that scale strongly with principal quantum number. Table 4.1 summarizes key properties of Rydberg states and how they scale with $n$, along with accompanying numerical values for a common plasma gateway state - NO(51f).

Table 4.1: Selected Rydberg atom properties and scaling with principal quantum number. The last column on the right-side provides values for a nitric oxide 51f state.

<table>
<thead>
<tr>
<th>Property</th>
<th>Formula</th>
<th>$n$-Scaling</th>
<th>NO(51f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binding Energy ($E_n$)</td>
<td>$IP_{v^+,N^+} - \frac{R}{n^2}$</td>
<td>$n^{-2}$</td>
<td>42 cm$^{-1}$*</td>
</tr>
<tr>
<td>Energy Spacing</td>
<td>$</td>
<td>E_n - E_{n\pm1}</td>
<td>$</td>
</tr>
<tr>
<td>Orbital Radius $\langle r \rangle$</td>
<td>$\frac{1}{2}(3n^2 - \ell(\ell + 1))$</td>
<td>$n^2$</td>
<td>3896$a_0$</td>
</tr>
<tr>
<td>Geometric Cross-section</td>
<td>$\pi \langle r \rangle^2$</td>
<td>$n^4$</td>
<td>$4.8 \times 10^7 a_0^2$</td>
</tr>
<tr>
<td>Dipole Moment</td>
<td>$\langle n\ell</td>
<td>e\mathbf{r}</td>
<td>n\ell + 1 \rangle$</td>
</tr>
<tr>
<td>Predissociation Lifetime</td>
<td>$\tau_\ell = \left[ k_{\ell} \cdot 4.16 \times 10^{16} \right]^{-1}$</td>
<td>$n^3$</td>
<td>17 ns</td>
</tr>
</tbody>
</table>

* ($v^+ = 0$, $N^+ = 2$)

The orbital diameter scales as $n^2$ (area $\propto n^4$) so at large $n$ the electron spends most of its time at large distances from the core which leads to a very diffuse wave function that is particularly susceptible to long-range interactions. Long range forces offer a doorway to ionization which will be discussed in the next section.

Rydberg state lifetimes can be predicted considering the predominant decay channel. Atoms and molecules both decay either radiatively or by autoionization. Molecules can also decay through intramolecular couplings such as internal conversion and predissociation. Both processes rely on the intramolecular coupling of a particular Rydberg electron with a decay channel. Internal conversion alters the vibrational state of the core molecule and is restricted to large molecules, while predissociation leads to the production of two neutral fractions from the breaking of a bond. Nitric oxide decays primarily through
predissociation. Zero-electron kinetic energy (ZEKE) experiments performed by Reiser et al. [41] showed a significant lifetime enhancement for a $n \approx 200$ $p$-state of nitric oxide from a theoretical value of 200 ns to an observed lifetime of at least 1.2 $\mu$s. Further work by Bixon and Jortner [40] determined that specific photo-excited Rydberg doorway states are significantly $\ell$-mixed even in weak DC fields. $\ell$-mixing can be represented by,

$$M^{**}(n, \ell) + A^+ \rightarrow M^{**}(n, \ell') + A^+$$  \hspace{1cm} (4.5)$$

where $M^{**}$ represents a neutral Rydberg molecule with initial principal quantum number, $n$, and initial angular momentum, $\ell$, undergoing an angular momentum changing process to final state $\ell'$, while $A^+$ represent the colliding ion. The change in angular momentum is due to the Rydberg electron slowly precessing around a weak electric field either externally applied, or due to the Coulombic field of a grazing ion collision. Precession imposes directionality that, over an entire distribution of randomly oriented molecules, results in a statistically $\ell$-mixed manifold. This process is a very weak type of interaction without any energy transfer. Mixing greatly dilutes the low-$\ell$ core-penetrating wave functions and enhances lifetimes by orders of magnitude. Particularly relevant to our experiment was the study of NO Rydberg states in the range $nf = 40 - 95$ converging to the $N^+ = 2$ ionization threshold. It was reported that strong mixing (SM) occurs for stray fields of $\approx 0.3$ V/cm. As a result, the lifetime is increased according to the equation,

$$\langle \tau_{SM} \rangle = \frac{n^4 \hbar}{\Gamma_0^{\text{Total}}}$$  \hspace{1cm} (4.6)$$

where $\Gamma_0^{\text{Total}} = \sum_\ell \Gamma_0(\ell)$ is the decay width constant and takes the value of 3200 ($\pm$ 500)cm$^{-1}$ for NO. State-mixing increases the principal quantum number scaling to an $n^4$ dependence.
4.2 Rydberg-Rydberg Ionization (Penning Ionization)

The spontaneous evolution of a Rydberg gas to plasma was first observed some time ago by Haroche and coworkers in an effusive beam of Cs [42]. This phenomenon has also been seen in a MOT where ultracold atoms were photo-excited to Rydberg states that went on to form a plasma [43, 44]. Mechanistically, this spontaneous evolution results from high density (> $10^{10}$ cm$^{-3}$) Rydberg ensembles interacting through dipole-dipole forces [44–46]. Penning ionization is defined as the outcome of such interactions. It it symbolically represented by the interaction of two Rydberg particles, $M^{**}$, leading to the formation of an ion, $M^+$, Rydberg state, $M^*$, and free electron. It can be expressed as,

$$M^{**}(n, \ell) + M^{**}(n, \ell) \rightarrow M^+ + M^*(n', \ell') + e^-$$  \hspace{1cm} (4.7)

where $(n, \ell)$ and $(n', \ell')$ represent principal quantum number and angular momentum for initial and final states, respectively. Penning ionization occurs when the total electronic energy of the colliding pair overcomes the ionization potential of one of the atoms. Collisions are initiated by attractive dipole-dipole couplings. Rydberg atoms have large dipole moments that scale as $n^2$. We can write the Hamiltonian for this interaction as $H = H_0 + V$. $H_0 = H_{M1} + H_{M2}$ represents the non-interacting Hamiltonian of the individual molecules. The dipole-dipole interaction potential is,

$$V_{dipole} = \frac{\mu_1 \cdot \mu_2}{d^3} - \frac{3(\mu_1 \cdot d)(\mu_2 \cdot d)}{d^5}$$  \hspace{1cm} (4.8)

where $\mu$ is the dipole moment vector and $d$ is distance vector between interacting Rydberg atoms. Over an entire ensemble of a dense sample of Rydberg atoms, dipole moments will be randomly oriented. If two states are oriented on an attractive potential, they will accelerate towards one another and induce ionization in one of the atoms. Stray fields,
along with Rydberg collisions with thermal electrons, effectively mix all $\ell$ states in our experiment. $\ell$-mixing can be understood as the transfer of population from an initial $\ell_0$ state to all other nearly degenerate $\ell$ states of the same $n$ \cite{39}. Penning ionization can then be ascribed the classical picture for a particular $n$, and relies on the large polarizability of the Rydberg atom as reported in \cite{47}. A study assuming complete $\ell$-mixing will therefore be discussed.

Penning ionization must conserve energy, and assuming the Rydberg molecules are essentially frozen, the kinetic energy of the newly ionized electron plus its initial binding energy must equal the binding energy gained by the de-excited Rydberg molecule as it relaxes to a more deeply bound state. A theoretical study by Robicheaux \cite{48} investigated the phenomenon of ionization induced by two interacting Rydberg molecules. In this work, classical trajectory Monte Carlo simulations were used to determine the rate of free electron production caused by Penning ionization. These simulations employed a classical Hamiltonian to propagate each initially bound electron, with appropriate length and time parameters to identify an electron that has reached the continuum. The study employed atoms, with negligible kinetic energy, and dynamics were governed by the asymptotic form of the dipole-dipole interaction: $V_{\text{asym}} = -\mu^2/d^3$, where $\mu \propto n^2$, is roughly the dipole moment of the Rydberg atom, and $d$ is the separation between atoms. When atoms are translationally cold, it is suitable to use this as the dominant force term since for typical densities of $10^{12}$ cm$^{-3}$, $d \approx 620$ nm, and the ratio $k_B T/(\mu^2/r^3) < 1$ at a starting level of $n = 60$, and temperature of 120 mK. The simulation was launched with a random distributions of $\ell, m$ states according to the fully mixed $\ell$-manifold.

The results of these simulations showed the distribution of de-excited $n$-level population (the right side of Eq. (4.7)) followed a $n^5$ distribution up to the maximum of $n_0/\sqrt{2}$. Final bound state must have at least twice the initial binding energy. The average energy of the ejected electron follows,
\[ KE_e^- = 2 \times \left( \frac{1}{2n_0^2} \right) + \frac{\mathcal{R}}{n'^2} \]  

(4.9)

where \( n' \) represents the lower and \( n_0 \) the initially populated Rydberg levels, respectively.

Table 4.2 provides the ionization criteria obtained from results of simulations performed in [48]. Results are reported for three different Rydberg atom separation distances and the corresponding time in terms of Rydberg electron orbit periods for the ionization event to occur.

Table 4.2: Distance and time for 90% ionization events between two Rydberg atoms

<table>
<thead>
<tr>
<th>Maximum Separation</th>
<th>Rydberg Periods</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1.6 \times 2n^2a_0 )</td>
<td>400</td>
</tr>
<tr>
<td>( 1.8 \times 2n^2a_0 )</td>
<td>800</td>
</tr>
<tr>
<td>( 2.1 \times 2n^2a_0 )</td>
<td>1200</td>
</tr>
</tbody>
</table>

### 4.2.1 Erlang Distribution Model for Penning Ionization

In order to apply the results of Robicheaux’s model, we must first ask: what fraction of particles are within the distances given in Table 4.2? The answer to this question requires the determination of the first nearest-neighbour distribution function, \( P_{NN}(r) \), which we calculate following the results reported in [49]. Assuming a uniform density, \( P_{NN}(r) \) can be expressed as,

\[ P_{NN}(r) = \rho \frac{dv_D(r)}{dr} \exp[-\rho v_D(r)] \]  

(4.10)

where \( v_3(r) = \frac{4}{3} \pi r^3 \) is the sphere volume for a distribution in three dimensions \( (D = 3) \), and \( \rho \) is the particle density. Each particle center is assumed to follow a random Poisson distribution. Replacing the density term with \( \rho = 1/(4/3 \pi a_{WS}^3) \), and differentiating the
sphere volume gives,

$$dP_{NN}(r) = 3 \frac{r^2}{a_{WS}^3} \exp\left[\left(-\frac{r^3}{a_{WS}^3}\right)\right]dr.$$  \hspace{1cm} (4.11)

By substituting $r = C \cdot 2n_0^2a_0$, where $n_0$ is the initial principal quantum number, the fraction of Rydberg molecules undergoing Penning ionization can then be determined.

### 4.3 Charged Particle Collisions with Rydberg Molecules

Large cross-sections, $\propto n^4$, and low binding energies, $\propto n^{-2}$, make Rydberg molecules good collisional targets. In particular, we can describe the collision of a Rydberg molecule with an ion or electron as a dipole-charged particle interaction which scales as $1/d_{Ryd-e}^2$. This long-range potential gives rise to very large collisional cross sections for elastic and inelastic collisions.

Ion-Rydberg atom collisions lead to charge exchange at low ion velocities. When the colliding ion velocity is less than or comparable to the Rydberg electron velocity, $v_{\text{ion}}/v_{\text{e-Ryd}} \leq 1$, there is a strong likelihood that the Rydberg electron will transfer to the ion, since Rydberg states are much 'stickier' than regular ground-state molecules. The charge-exchange process can be represented as

$$A(n, \ell) + M^+ \rightarrow A^+ + M(n', \ell') \hspace{1cm} (4.12)$$

where the colliding ion, $M^+$, can form a Rydberg quantum state, $M(n', \ell')$, different from the initial Rydberg molecule, $A(n, \ell)$. Principal quantum number and angular momentum quantum number are given as $n$ and $\ell$, respectively.

Charge-exchange of sodium Rydberg atoms and ions was verified experimentally by MacAdam et al. [50], and the cross-section, $\sigma_{CX}$, was shown to depend strongly on the
reduced velocity in experiments performed by Hansen et al. [51]. Both studies measured the exchange cross sections by field ionization of the Rydberg atom formed by electron exchange. Subsequent studies [52] investigating the principal quantum number distributions observed exchanged Rydberg states in a fairly narrow range peaked at the principal quantum number of the original Rydberg state. Ultracold molecular plasmas undoubtedly will undergo charge-exchange considering the very low ion temperatures.

Rydberg collisions with electrons represent an important class of interactions that determine many ultracold plasma properties. They are similar to ion-Rydberg atom collisions in that they are long-range, but differ in several respects. Most notably, charge exchange is not possible since the colliding charged particle is an electron and not an ion. This leaves electron impact ionization,

\[ A(n, \ell) + e^- \rightarrow A^+ + e^- + e^- \]  

(4.13)

and state-changing events,

\[ A(n, \ell) + e^- \rightarrow A(n', \ell') + e^- \]  

(4.14)

A full quantum mechanical account of the impact event has proven non-trivial but has seen much progress since the advent of super-computers. Gregor et al. have provided a comprehensive review [53] of the difficult three-body problem as it pertains to a two-electron atom when described fully by quantum mechanics. Monte Carlo (MC) classical trajectory simulations have provided a successful alternative approach. Rate formulas giving the frequency of collisions for a three-body classical model representing an ion-electron Rydberg atom and a colliding electron were first determined more than 40 years ago. Improved rate formulas based on early work by Mansbach and Keck [54] were obtained by Pohl et al. [55] and are discussed in more detail in later chapters. Explicit formulas fitted to the numerical MC data found in [55] are given as,
\[ k(n_i, n_f) = k_0 \frac{\varepsilon_i^{5/2} \varepsilon_f^{3/2}}{\max(\varepsilon_i, \varepsilon_f)^{5/2}} e^{-(\varepsilon_i - \min(\varepsilon_i, \varepsilon_f))} \left[ \frac{22}{(\max(\varepsilon_i, \varepsilon_f) + 0.9)^{7/3}} + \frac{9/2}{\max(\varepsilon_i, \varepsilon_f)^{5/2} \Delta \varepsilon} \right] \]  

(4.15)

for inelastic collisions from principal quantum number \( n_i \) to \( n_f \), \( \varepsilon_{i(f)} = R/n_{i(f)} k_B T_e \) is the binding energy normalized to the electron temperature, \( T_e \), \( \Delta \varepsilon = |\varepsilon_f - \varepsilon_i| \), and \( k_0 = e^4/(4\pi\varepsilon_0)^2(k_B T_e \sqrt{m_e R}) \). Ionization from level \( n_i \) proceeds with a bimolecular rate constant,

\[ k_{\text{ion}}(n_i) = \frac{11}{\varepsilon_i^{7/3}} \frac{\sqrt{(R/k_B T_e)} k_0 e^{-\varepsilon_i}}{4.38\varepsilon_i^{1.72} + 1.32\varepsilon_i}. \]  

(4.16)

Quantitatively, inelastic collision rates following Penning ionization from \( n_0 = 51 \), which will result in an initial electron temperature of \( \approx (1/3) R/n^2 = 34.3 \) K, will be for ionization, \( k_{\text{ion}}(51) = 4.4 \times 10^{-5} \) cm\(^3\)/s, and for Rydberg-electron inelastic collisions, \( k(51, 52) = 3.6 \times 10^{-3} \), and \( k(51, 50) = 3.5 \times 10^{-3} \) cm\(^3\)/s.

Since more energy is gained by the electron bath for down-pumping collisions - \( \Delta E(51, 52) < \Delta E(51, 50) \) - the closeness in value of the rate constants implies an early-time feedback that quickly raises the electron temperature and induces an avalanche ionization over a nano-second timescale. Rate equation calculations that use Eqs. 4.15 and 4.16 show this effect, and will be discussed further in Chapter 8.

### 4.4 Pulsed Field Ionization (PFI) of Rydberg Molecules

Another important feature of Rydberg molecules is their susceptibility to field ionization. High resolution zero-kinetic energy (ZEKE) spectroscopy is an example of a technique that exploits the loosely bound nature of Rydberg molecules. Selective ionization occurs when a delayed pulsed electrostatic field \( (F) \) lowers the potential barrier enough to release
a bound, highly excited electron. Because Rydberg states are close to the ionization potential, the fields required are generally not more than a couple hundred volts per centimeter for deeply bound states and offers enhanced resolution over optical techniques for weakly bound, high-$n$ states when laser bandwidth is comparable to level separation.

Figure 4.1: Illustration showing the effect of a field pulse on the nuclear potential felt by an electron

A good approximation for PFI begins with the hydrogenic model for a pulse rising to the final field $F = F \hat{z}$. The field will create a saddle point in the $\hat{z}$ direction and the total potential along that axis will be,

$$V(z) = -\frac{1}{|z|} + Fz$$

(4.17)

where the saddle point is calculated by differentiating (4.17) and setting $dV/dz$ equal to zero. This leads to a lowering of the potential to a value $V_{sp}(z_{sp}) = -\sqrt{F}$ and a principal quantum state with binding energy, $E_n$, greater than this value will ionize. Neglecting any Stark effects, and for $m = 0$ states, a general expression for the classical ionization limit with electric field, $F$, as a function of Rydberg binding energy, $E_n = -\frac{1}{2n^2}$, becomes

$$F = \frac{E_n^2}{4} = \frac{1}{16n^4}.$$  

(4.18)

The well known classical expression for adiabatic lowering of the ionization threshold of hydrogen-like Rydberg states is [39, 56]

$$E_{FI} = -6.12\sqrt{F}$$

(4.19)
with electric field unit of $V/cm$ and $E_{FI}$ in $cm^{-1}$. A centrifugal barrier prevents states with $m \neq 0$ from aligning along the $z$-axis where the saddle point forms, and so an additional $\Delta E/E = |m|/2n$ relative to the $m = 0$ ionization field is required to ionize these states.

Non-hydrogenic PFI deviates from the classical ionization description due to Rydberg electron interactions with the core. This is manifested in the way the Rydberg electron-wavefunction traverses a crossing. Under the assumption that before the pulse all the degenerate levels are equally populated, the Stark effect caused by the electric field will create red and blue states that will be shifted to higher and lower energies, respectively. Realistically, most of the low-$\ell$ states will undergo predissociation or autoionization well before the pulse and simplify the Stark map due to the high quantum defect of these states. Curve-crossing can be described using Landau-Zener theory and a useful equation to calculate the probability that the crossing will be adiabatic from state $i$ to $j$ is given by [56],

$$P_{ij}^{A} = 1 - \exp \left[ -2\pi \frac{|\langle i|V|j\rangle|^2}{\hbar(d\Delta E_{ij}/dt)} \right]$$

where the coupling element $|\langle i|V|j\rangle|$ diverges for increasing $n$, and $(d\Delta E_{ij}/dt) = d(E_i - E_j)/dF\cdot(dF/dt)$ is the rate of change between level energies and is dependent on the voltage slew rate $dF/dt$. The diabatic probability, $1 - P_{ij}^{A}$, will approach 1 if the principal quantum number is high and the pulse rise-time remains short. Slew rates of 0.8-7 Vcm$^{-1}$/ns$^{-1}$ and $n >> 50$, typical for our experiment, ensure that ionization is predominately diabatic. The advantage of diabatic ionization is that it simplifies the mechanism to the hydrogenic model. Since our experiments are performed at relatively high principal quantum number ($n >> 50$) the statistical weighting of low-angular momentum states is small, and the hydrogenic wavefunction approximation is valid.

Lowering of the ionization threshold in experiments was calculated using the adiabatic mechanism given by Eq. (4.19), when in fact a more likely scenario would be that of the
diabatic pulsed field ionization value $-4\sqrt{F}$ [57]. The pre-factor is small enough, however, that conclusions drawn in subsequent chapters by applying the adiabatic threshold to pulsed field ionization experiments remain valid. But more care must be taken to discern the ionization mechanism if the resolution of results is within the difference in the pre-factor.
Chapter 5

Evolution from a Molecular Rydberg Gas to an Ultracold Plasma in a Seeded Supersonic Expansion of NO

5.1 Introduction and Experimental

Neutral plasmas conventionally exist as a gas of charged particles, maintaining high charged particle densities through ionizing collisions. Considering the ionization potential lies on the order of 1 eV, plasmas typically exhibit high particle temperatures of thousands of kelvin. At these high temperatures, thermal motion dominates electrostatic forces and spatial correlations from Coulombic repulsion can be safely neglected. This is commonly quantified by the coupling parameter, $\Gamma = q^2/4\pi\epsilon_0akT$, defined as the ratio between Coulombic repulsion of charges $q$ at a distance $a_{WS} = (3/4\pi\rho)$, where $\rho$ is particle density, to the thermal energy, $k_BT$, and for high temperature plasma is below 1. As the temperature is reduced, particles tend to organize their spatial positions in order to minimize energy, and $\Gamma$ rises to values greater than 1. Increased correlation can lead to liquid-like behaviour and even crystallization at values of 174 [58].

Correlation values of $\Gamma > 1$ in an ultracold atomic plasma was first achieved using laser cooling and magnetic trapping techniques developed at the University of Colorado [25]. In a magneto-optical trap (MOT) a sample of neutral atoms can be localized to $\mu$K temperatures and densities of $10^9$ cm$^{-3}$. Subsequent photoionization creates a plasma with
an initial electron temperatures, $k_B T_e(0) \approx (\hbar \nu - E_{IP})$. Killian et al. were the first to experimentally observe an ultracold plasma \[59\] by trapping and then ionizing a gas of Xenon atoms.

Molecules have a much richer intra-particle environment that prevents them from being laser-cooled. In particular, rotational cycling offers a degree of freedom that poses a significant impediment to the standard light-friction slowing technique. For this reason, up until \[1\], molecular ultracold plasmas had not been realized.

Dense molecular samples cooled to temperatures of 1 K and less can routinely be produced in a super-sonic beam expansion. Although this temperature is orders of magnitude higher than initial plasma conditions in a MOT, substantial excursions in energy occur in atomic MOTs as a result of disorder-induced heating and three-body recombination that quickly brings the MOT plasma to temperatures around 1 K. For this reason, plasmas created in a supersonic beam can achieve the exotic regimes seen in MOT plasmas, if not to a higher degree.

In comparison, charged-particle densities of $10^{12}$ cm$^{-3}$ along with electron and ion temperatures of 50 and 1 K, respectively, exhibit correlation values approaching $\Gamma_e = 0.5$, while cation correlation, $\Gamma_i$, could exceed 15. The realization of a cold molecular plasma under such conditions would represent a significant development, opening the door for the many different molecular candidates that can be seeded in a beam. Some time ago Haroche and coworkers showed that Rydberg gases of alkali atoms form warm plasmas under the conditions of an effusive beam source \[60\].

We have established that an excited gas of NO in photoselected Rydberg states lying more than 80 cm$^{-1}$ below the lowest ionization threshold can interact in a supersonic beam to produce a cold plasma that is long lived and highly resistant to perturbation by an external field. The preparation of this plasma begins with the double-resonant excitation of NO, seeded at 10% in pulsed jet of helium at a backing pressure of 5 atm. An electroformed Ni skimmer selects a 1 mm diameter center-line beam from the expansion
of this gas mixture through a 0.5 mm nozzle. This beam then travels another 8 cm before being intersecting by counter-propagating lasers.

Beam dynamics calculations predict a center-line density at the interaction region of $4.8 \times 10^{14}$ cm$^{-3}$, with a translational temperature of $< 1$ K [61]. Rotational relaxation occurs with a smaller collision cross section, yielding a terminal molecular beam rotational temperature, $T_R^\infty$, higher than the terminal parallel temperature, $T_{\parallel}^\infty$, owing to incomplete equilibration by the time free-molecular flow is reached. We calculate the absolute density of excited-state molecules by scaling the center-line beam density to the seeding ratio (0.1), then accounting for the rotational fraction in $J'' = \frac{1}{2}(-)$ at 3 K (0.44), and finally multiplying by 0.25 to recognize two saturated steps of $\omega_1$ and $\omega_2$ excitation. This treatment yields an upper limit density of high-Rydberg NO molecules of $5 \times 10^{12}$ cm$^{-3}$. Saturation of the photo-excitation transitions has been validated experimentally by observing the effect of ionization signal intensity as laser power is changed. We adjust the polarizer to obtain an intensity as close as possible to the plateau of the signal (indicative of saturation) without observing $(1 + 1)$ photo-electrons.

To excite the entrained NO molecules, the sequential application of two unfocused 5 ns laser pulses, $\omega_1$ and $\omega_2$ from independent frequency-doubled Nd:YAG-pumped dye lasers are used. A first 226 nm photon, $\omega_1$, transfers population to the $A^2\Pi^+$-state. A wavelength scan of $\omega_1$ with $\omega_2$ tuned above the ionizing potential produces a resonant spectrum by a $(1+1')$ ionization method to determine $T_R^\infty$. Relative line intensities from the resonant-enhanced multiphoton ionization (REMPI) provide a gauge for rotational temperature, once fitted to simulation spectra. Fig. 5.1 shows a typical REMPI scan that fits to simulated rotational spectra having a $T_R^\infty$ of 2.5 K.

From the $A^2\Sigma^+$ state, excitation by $\omega_2$ then populates high-lying Rydberg states over the range from 30 400 to 30 530 cm$^{-1}$ converging to the lowest ionization threshold of NO. Careful consideration is taken at this point to maintain $\omega_1$ pulse energies below 500 $\mu$J to completely quench any $(1+1)$ double ionization which would seed the Rydberg sample.
Figure 5.1: Resonant 1+1’ ionization spectrum of the $X^2\Pi(v''=0)$ to the $A^2\Sigma^+ (v'=0)$ transition in NO seeded 1:10 in a supersonic beam of He. This ratio of intensities fits a ground-state population distribution corresponding to a rotational temperature, $T_R^\infty = 2.5$ K.

with high-energy, free electrons. Rydberg molecules formed in this manner move with the jet velocity through a nominally field-free region to reach an exit grid, G2, illustrated in Fig. 5.2.

At certain frequencies of $\omega_2$ well below the ionization threshold, the double excitation produces a characteristic oscilloscope trace of the time-resolved electron signal integrated over the laboratory $(x,y)$-plane as the plasma traverses G2, and is shown in Fig. 5.3.

The signal trace displays a prompt burst of electrons, which arrive at the micro-channel plates within 200 ns of $\omega_2$ excitation, followed by a broader gaussian electron packet, that for this particular G2 position, arrives $7.5 \mu s$ later. Prompt electron signal is sensitive to small dc fields: applying an increasingly positive voltage (0 to 400 mV) to G1 will delay and eventually eliminate the prompt signal while leaving the late-gaussian unaffected. A negative voltage (0 to -400 mV) sharpens the signal and accelerates electrons
Figure 5.2: Schematic diagram showing the molecular beam flight path from a differentially pumped source chamber through a skimmer to enter a system of three grids ending in a flight tube capped by a microchannel plate detector. The interaction region is defined as the region between G1 and G2, and the extraction region including the flight-tube is defined as the region beyond G2.

towards the detector. The late signal remains unaffected by small dc fields. If the detector is biased to operate as a time-of-flight mass spectrometer, the late-peak waveform conforms to the flight-time of a cation with NO$^+$ mass.

Late-peak amplitude depends on the magnitude of the dc-voltage applied to flight-tube entrance grid, G3: this setting determines the field in the flight tube past G2 which rises from zero with no gradient between G2 and G3, to late-peak amplitudes that plateau at gradients of 100 V/cm and higher. The delayed signal amplitude shows no dependence on the principal quantum number of the initially prepared Rydberg state, even if the flight-tube field is higher than the $-6\sqrt{F}$ magnitude required to ionize Rydberg state $n$. This indicates that Rydberg molecules prepared by $\omega_1+\omega_2$ excitation have evolved to form a plasma that flies along at supersonic beam velocity until it reaches the G2 grid 7.5 $\mu$s later. From beam dynamics calculations our initial conditions predict a final mass average velocity, $u_\infty$, of 1358 m/s and considering the distance from the laser interaction region to G2 is 10 mm, the 7.5 microsecond flight time corresponds to an observed velocity of 1350 m/s. Kinetic theory detailing the expansion of a monatomic gas appears to be a good approximation by comparison of the predicted and experimentally observed velocity.

Integration of the late-peak over a wavelength scan of $\omega_2$ produces a spectrum of the
Figure 5.3: Oscilloscope trace showing the arrival time of electrons produced following two-color production of NO molecules in the 52\,f(2) Rydberg state with -250 mV applied to G1 and 60 V applied to G3.

Rydberg series populated by second-photon absorption, shown in Fig. 5.4, that can readily be assigned to the \( nf \) Rydberg series converging to the \( v^+ = 0, N^+ = 2 \) state of \( ^1\Sigma \) NO\(^+\). The fact that the plasma signal tracks Rydberg resonances indicates plasma formation depends on excitation to these states.

Interspersed within the prominent \( nf \)-series are some lines of the \( np \)-series converging to the \( N^+ = 0 \) rotational level of the cation ground state. Predissociation lifetimes vary significantly going from low orbital angular momentum, \( \ell \), levels to higher ones, and scale with principal quantum number as \( n^{-3} \). For low \( \ell \), the electron wavefunction has greater interaction with the nucleus and so lifetimes of the \( np \)-series of NO at \( n \) less than 70 fall below 1 ns. For the \( nf \)-series, lifetimes from \( n=40 \) to 70 can range from 10 to 30 ns. However, as previously discussed, plasma microfields as well as stray electric fields readily mix \( \ell \) and \( m_\ell \) levels and appreciably extend lifetimes when accidental resonance conditions are satisfied.
Figure 5.4: Resonances in the late signal observed by scanning $\omega_2$ for the plasma formed from NO seeded in He. Spectrum assigned to the lines in the $n f$ Rydberg series converging to the rotational level $N^+ = 2$ in the vibrational ground state of NO$^+X^1\Sigma^+$. Ionization fitted to 30 534.5 cm$^{-1}$.

5.2 Pulse Field Experiments

Applying a square wave voltage pulse to the G1 grid, and varying the pulse arrival-time, $t_{\text{pulse}}$, pulse voltage, $V_{\text{pulse}}$, and pulse width, $\Delta t_{\text{pulse}}$, we can gain much information on the plasma properties. For a standard pulse experiment ($t_{\text{pulse}} = 500$ ns, $V_{\text{pulse}} = 30$ V/cm, $\Delta t_{\text{pulse}} = 1$ $\mu$s) with a negative polarity, the primary response is an instantaneous electron signal from extracted electrons accelerated towards the detector, and a delayed plasma peak that is essentially unaffected. Reversing the bias of the pulse similarly has little effect on late peak. As a matter of fact, pulses with amplitudes as high as $V_{\text{pulse}} = 150$ V/cm leave the peak electron signal produced as the illuminated volume passes G2 undiminished,
even though such a voltage exceeds the field ionization threshold of Rydberg states in this range of \( n \). Results of such an experiment are detailed in Fig. 5.5 which shows a series of integrated late-peak signals as a function of \( \omega_2 \) laser energy taken with pulsed-fields varying in amplitude from 5 to 125 V/cm.

![Figure 5.5: High-Rydberg excitation spectra of the plasma signal under conditions in which 1 \( \mu \)s positive pulses at voltages producing the electrostatic fields indicated are applied starting 500 ns after \( \omega_2 \). The y-axis is the magnitude of the electric field in V/cm, and the x-axis is the energy of the second photon, \( \omega_2 \). Diamonds show the adiabatic field-ionization threshold for the principal quantum numbers from 40 to 110, and align with the peaks of the spectra. Both axes are linear. Overlayed on this plot are the principal quantum number field ionization thresholds according to the adiabatic \(-6\sqrt{F(n)}\) dependence. This result provides further evidence that the active volume has converted to a cold plasma able to shield external electrostatic fields. In particular, comparing spectra of 50 V/cm and voltage gradients twice that shows a resilience manifested in a practically undiminished signal for select Rydberg states. We can interpret this as a plasma property called Debye shielding. Assuming half the initial Rydberg molecules are Penning ionized, and for the 500 ns before the pulse, recombination...
and ionization reduce the electron density to $\approx 1 \times 10^{12}$ cm$^{-3}$, at an electron temperature of 50 K we calculate a Debye screening length, $\lambda_D = \sqrt{\epsilon_0 k T_e / q_e^2 \rho_e}$, of about 0.5 $\mu$m - far smaller than the width of the active volume. Hence, before the electric field is able to penetrate the high density-core region of the plasma, electrons are able to mobilize and shield the interior region indicating the onset of collective effects. Isolated Rydberg states will not exhibit collective effects and will be ionized according to the adiabatic threshold shown as diamonds in Fig. 5.5, in accordance with the offset of each plot. At 100 V/cm, the plot shows that the ionization threshold lies between $n = 43$ and $n = 44$, yet there is still signal from higher principal quantum numbers indicating a transition of the initial Rydberg ensemble to a plasma.

While this significant result provides evidence for plasma formation, it begs the following question: How does transmission through G2, where the plasma encounters field gradients no more than 100 V/cm, produce an electron signal, despite this remarkably robust resistance to fields of hundreds of volts per centimeter? This electron signal very likely depends on the fact that the active volume physically transverses a fine-mesh grid (99.5% transmittance) that imposes mechanical ionization effects along with strong microfields created by very small grid dimensions.

Even though the plasma shows great durability to pulses at 0.5 $\mu$s after excitation, applying pulses much lower in amplitude coincident with $\omega_2(t = 0)$ completely extinguishes that plasma signal. Increasing the time between laser excitation and the arrival of the pulse allows for increasing formation time. Integrating the plasma signal as the pulse arrival time is increased reveals a rise-time plot (Fig. 5.6(b)) that grows in intensity until it reaches a field-free maximum amplitude at 200 ns. This simple rise-time result provides a window into the early-time dynamics of plasma formation that involves Penning and subsequent avalanche ionization followed by inelastic electron-mediated collisions.

This chapter has provided experimental evidence a plasma forms from Rydberg states in a supersonic gas expansion, but not yet discussed are the conditions where no plasma
Figure 5.6: Voltage pulse stepping towards laser arrival time ($t_0$) illustrated in 5.6(a) and the integrated plasma signal as a function of pulse arrival time 5.6(b) for $n = 60$ (cyan) and $n = 50$ (red). The initial slope of Signal/Time is much higher for $n = 60$ suggesting formation dynamics occurring on a faster timescale due to larger orbital size.
formation is observed. For instance, initial Rydberg density has a critical effect on all early-time processes that combine to form a durable plasma. This can be seen by regulating the delay between $\omega_1$ and $\omega_2$ which allows for $A^2\Sigma^+$-state decay over a lifetime of 210 ns [62]. If the density is too low, no plasma forms. Terminal rotational molecular beam temperature also has an affect: at high rotational temperatures we do not observe plasma formation. Temperature in the molecular beam can have a two-fold effect: A high $T_R^{\infty}$ reduces ground-state population since the distribution will have sufficient energy to access higher energy levels not involved in the double-resonant excitation process. In addition, it is likely that attractive intermolecular interactions drive disproportionating Rydberg-Rydberg electronic energy transfer in NO, analogous to the dipole-dipole coupling that ignites ultracold plasmas in cold atomic Rydberg gases [44]. The rate constant for interactions in an attractive potential generally depends inversely on the temperature, thus a higher $T_R^{\infty}$ inhibits plasma formation by decreasing the likelihood of dipole-dipole interactions.

5.3 Summary

A dense gas of Rydberg molecules can spontaneously evolve to form an ultracold plasma - under the right conditions. The lifetime of the plasma begins with excitation to Rydberg states and ends when plasma electrons are extracted at G2. Over this lifetime we can investigate the system with pulsed electric fields. We observe a collective electron response to the applied pulse that opposes the field and prevents electron extraction. Molecular features such as predissociation and dissociative recombination are two types of dissociative channels that can reduce the overall charged-particle density and shorten the lifetime, and have not yet been considered but will be discussed in later chapters.
Chapter 6

Very Slow Expansion of an Ultracold Plasma Formed in a Seeded Supersonic Molecular Beam of NO

6.1 Introduction

6.1.1 Plasma Expansion

The free expansion of an ultracold plasma offers an important diagnostic. Measuring the rate of this expansion allows a determination of the initial electron energy. With the static grid system, we were able to increase the observation window by seeding NO in neon, argon, or krypton instead of helium, reducing the molecular beam velocity (refer to Eq. (3.10)) and substantially increasing the flight time required for the volume to reach G2. By measuring the arrival time of the plasma for each particular gas, and knowing the initial illumination size, we were able to extract an expansion rate considerably slower than conventional MOT UCPs that conforms with a Vlasov fit of $T_e(0) \sim 7$ K.
Figure 6.1: Electron signal waveforms appearing at $G_2$ following the substantial promotion of NO molecules to the $52f(2)$ Rydberg state in seeded supersonic expansions of - in order top to bottom - Kr, Ar, Ne, and He using the experimental flight path outlined in Section ??.

6.2 Expansion Results

6.2.1 Seeding in Heavier Carrier Gas

Waveforms obtained for fixed-grid electron detection appear in Fig. 6.1. They display the typical pattern observed for experiments using He as the buffer gas, with the notable exception $G_2$ arrival times increase with increasing mass of buffer gas. The widths of these waveforms represent the plasma density distribution as it expands in the spatial dimensions transverse to the laser illumination axis. They can be well represented by measuring the $z$-axis distance in terms of a two-dimensional Gaussian distribution:

$$n_i(y, z, t) = \frac{N_i}{\sigma(t) \sqrt{2\pi}} \exp \left[ -\frac{(y^2 + z^2)}{2\sigma^2(t)} \right]$$  (6.1)
and from the time-varying standard deviation, $\sigma(t)$, the full width at half-maximum, $\mathcal{F}$, can be calculated with the formula $\mathcal{F} = 2\sqrt{2\ln 2} \sigma(t)$. We fit spatially-transformed Gaussian peaks from Fig. 6.1 to the 2D Gaussian distribution of Eq. (6.1) for the different carrier gases. The results are tabulated in Table 6.1 and shown in Fig. 6.2.

![Figure 6.2: Late electron-signal temporal waveforms from Fig. 6.1 transformed to yield spatial plasma distributions, displayed according to peak arrival time at G2. Solid curves show Gaussian fits with residuals below. The bottom figure is derived from the measurement of laser width, above which are plotted the data for He, Ne, Ar, and Kr carrier gases. An initial $t = 0$ width is defined by the laser width, and subsequent width measurements from noble gases determine rate of expansion.](image)

Along with expansion results, Fig. 6.2 also displays the initial ($t = 0$) plasma size as determined by the experimentally determined laser profile of $\omega_1$.

### 6.2.2 Moveable Grid Expansion

We use the specially designed moveable-grid detection carriage outlined in ?? to increase the distance between the laser interaction region and G2 - and consequently the
Table 6.1: Arrival times, estimated velocities, and widths obtained by Gaussian fits to spatial waveforms of Fig. 6.1

<table>
<thead>
<tr>
<th>Carrier gas</th>
<th>Arrival time ((\mu s))</th>
<th>Velocity ((m/s))</th>
<th>(\sigma(t)) ((\mu s))</th>
<th>Width ((\mu s))</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>9.0</td>
<td>1358</td>
<td>364</td>
<td>856</td>
</tr>
<tr>
<td>Ne</td>
<td>15.8</td>
<td>758</td>
<td>446</td>
<td>1050</td>
</tr>
<tr>
<td>Ar</td>
<td>20.1</td>
<td>560</td>
<td>548</td>
<td>1291</td>
</tr>
<tr>
<td>Kr</td>
<td>28.7</td>
<td>394</td>
<td>686</td>
<td>1617</td>
</tr>
</tbody>
</table>

expansion time - to produce the set of waveforms in Figure 6.4. We have selected the 50\(f(N^+ = 2)\) principal quantum number as the initial gateway state for this particular experiment. Successive waveforms show electron signal amplitude as a function of time for increasing G2 displacements. Each waveform arrival time corresponds to the neutral molecular beam flight-time corresponding to the advancing grid position. We are able to position the grid immediately adjacent to the laser excitation volume which provides high fidelity expansion data for times < 5\(\mu s\), that - by the nature of the experiment - was unattainable in the Seeding in Heavier Carrier Gas. Expansion broadens the plasma signal width, and each late peak signal can be fit to a Gaussian function in order to extract a values for \(\mathcal{F}\), and arrival time. The Vlasov expansion plot from the fitted data can be seen in Fig. 6.3 with error bars reflecting one standard deviation of the Gaussian fit to the data.

### 6.3 Discussion

The ultracold plasma expansion rate depends primarily on the thermal energy of the electrons. A number of published studies have worked to accurately describe electron temperature over the evolution of the plasma [29, 63–65] and to relate \(T_e(t)\) to observed rates of expansion. Plasmas prepared by photoionization have an initial electron temperature
Figure 6.3: Fitted plasma width as a function of the arrival time of the peak of the Gaussian plasma signal at G2. The solid line through the data represents a fit to Eq. (6.8) with $T_e(0) + T_i(0) = 5$ K.

quantified by the excess energy of the photoionizing laser, as long as this energy exceeds $\approx 30$ cm$^{-1}$. Below this threshold, heating mechanisms, predominately driven by three-body recombination (TBR), scaling as $T_e^{-9/2}$, quickly raise the electron temperature. An excess laser energy of 35 K appears to inhibit this process.

Plasmas formed both by direct photoionization and from Rydberg states undergo elevation of ion temperature, $T_i$, from that of the neutral precursor. Momentum transfer from electrons is inherently slow owing to the large mass difference between the two particles. Ionic heating is primarily due to the fact that plasmas are formed with a random energy landscape that has some ions sitting on large electrostatic potential energy hills. This energy converts to thermal motion. This disorder-induced heating (DIH) constitutes the primary ion-heating mechanism [66]. Molecular dynamics simulations [67] predict an
Figure 6.4: Waveforms captured by the MCP detector for different positions of the moving carriage. The large peak represents the signal of electrons as the plasma volume passes through G2. Signal passing through G3 produces a small residual signal most noticeable at small laser-interaction-G2 distances.

The equilibrium ion temperature according to,

$$ T_i = \frac{2}{3} \frac{e^2}{4\pi\varepsilon_0 a_{WS} k_B} \left| \frac{\tilde{u}}{\Gamma_i} + \frac{\kappa}{2} \right| $$

where $\tilde{u}/\Gamma_i$ is the electrostatic potential energy per particle in units of average ion-ion repulsion energy. Screened Coulomb interactions used in these simulations treat ion interaction through a linear-electron screened Yukawa potential, $\phi(r) = \frac{e^2}{4\pi\varepsilon_0 r} \exp(-r/\lambda_D)$, where $\lambda_D = \sqrt{T_e/4\pi\rho e^2}$ is the electron Debye screening length. Equation 6.2 includes electron screening effects by virtue of $\kappa$, the ratio of Wigner-Seitz radius, $a_{WS}$, to the Debye length. This quantity combined with $\tilde{u}/\Gamma_i$, provides the excess correlation energy.
available to heat the ions. It can be seen from the dependence on $a_{WS}$ that denser systems will have higher final temperatures independent of the initial temperature. Under typical MOT conditions, $\kappa$ falls in the range of 0.5, $u/\Gamma_i \approx -0.7$, and DIH leads to an equilibrated ion temperature between 1 and 2 K [26, 68].

Molecular beam conditions produce initial conditions of $5 \times 10^{12}$ cm$^{-3}$ Rydberg molecules at temperatures of about 1 K in the moving frame. Assuming an avalanche ionization with complete efficiency, the plasma would have an initial Wigner-Seitz radius of 360 nm - an order of magnitude smaller than that typical of a MOT plasma. Such a small distance would suggest significant DIH heating form Eq. (6.2) upon equilibration, but the high charge densities causes Debye shielding to occur over a length $\lambda_D = 82$ nm, leading to a $\kappa$ of 4.4. Simulation results [67] predict for initial $\Gamma_i = 46$ a reduced correlation energy $\ddot{u}/\Gamma_i = -2.29$ and an equilibrated ion temperature due to disorder-induced heating of only 2 K.

Ambipolar expansion occurs on timescales longer than ion equilibration, but can still provide valuable information on electron temperatures. Electrons formed during early times expand much faster than their heavier ion counterparts. As electron expansion progresses, however, charge imbalance develops which requires work to be done on the heavier ions to reduce charge separation, thereby reducing the overall expansion to ionic timescales. Coupling of energy through the Coulombic interaction can be generalized to ion expansion velocity, $v_i$, as:

$$\frac{1}{2} m_i v_i^2 = \frac{1}{2} k_B T_e$$ (6.3)

For an initial plasma volume diameter of $\sigma(0) = 758 \mu$m, equation (6.3) predicts a $m_{NO^+}$ expansion rate of 100 $\mu$m/µs at an electron temperature of 40 K. This is shown in Fig. 6.5 by the red dot at 10 $\mu$s. Evidently, the plasma size predicted from ambipolar expansion at $T_e(0) = 40$ K substantially exceeds the data points from observations. This
can be expected, however, by considering the work required to overcome the ion inertia and initiate expansion draws from the electron energy and electron temperature should fall with time.

Figure 6.5: Plot of plasma FWHM at G2 as a function of flight time, compared with width predicted after 10 µs for ambipolar expansion at $T_e = 40$ K (red dot) and Vlasov expansion of a spherical Gaussian plasma for $T_e(0) = 40$ K (bold line). The line through the data represents a Vlasov fit for $T_e(0) = 6.8$ K. Error bars reflect the experimental uncertainty in the measured flight distance to G2, which exceeds the error introduced by using velocity averages to transform time to distance.

A more complete account of the expansion necessitates the inclusion of the phase-space distribution function changing in time, described by the Vlasov equation for vector quantities of coordinates, $\vec{r} = (r_x \hat{x}, r_y \hat{y}, r_z \hat{z})$ and velocity, $\vec{v} = (v_x \hat{x}, v_y \hat{y}, v_z \hat{z})$,

$$\frac{\partial f_\alpha}{\partial t} + \vec{v}_\alpha \frac{\partial f_\alpha}{\partial \vec{r}_\alpha} - m_\alpha^{-1} \frac{\partial f_\alpha}{\partial \vec{v}_\alpha} q_\alpha \frac{\partial \Phi(\vec{r}_\alpha)}{\partial \vec{r}_\alpha} = 0 \quad (6.4)$$

where $\alpha = e, i$ for electrons and ions, respectively, $m_\alpha$ and $q_\alpha$ are the mass and charge
of species $\alpha$, and $\Phi(\vec{r})$ is the mean field potential from the Poisson equation, $\Delta \Phi = e(\rho_e - \rho_i)/\epsilon_0$. The phase-space distribution, $f_e(\vec{r}, \vec{v}, t)$, of typical MOT plasmas as well as dimensions of analysis for molecular beam plasmas can be described by a Gaussian distribution,

$$f_e(\vec{r}, \vec{v}, t) \propto \exp \left( -\frac{\vec{r}^2}{2\sigma^2(t)} \right) \exp \left( -\frac{m_e v^2}{2k_B T_e(t)} \right)$$  \hspace{1cm} (6.5)$$

which assumes the small electron mass permits an adiabatic approximation to the ion dynamics.

Substituting Eq. (6.5) along with quasineutrality ($\rho_e \approx \rho_i$) results in an equation for the mean-field potential in terms of the ion density, which together with the ionic Vlasov Eq. (6.4), forms a closed-set of equations for the ionic phase-space distribution. The mean-field potential solution (described in more detail in Appendix Electric Potential from Vlasov Equations),

$$e \frac{\partial \Phi}{\partial \vec{r}} = k_B T_e \rho_i^{-1} \frac{\partial \rho_i}{\partial \vec{r}}$$  \hspace{1cm} (6.6)$$
along with a Gaussian spatial plasma density leads to the ansatz for the ion distribution,

$$f_i \propto \exp \left( -\sum_j \frac{r_j^2}{2\sigma_j^2} \right) \exp \left( -\sum_j \frac{m_i(v_j - \gamma_j r_j)^2}{2k_B T_{j,i}} \right)$$  \hspace{1cm} (6.7)$$
giving the self-similar solution of the ion kinetic equation. Indices $j = x, y, z$ accounts for the three cartesian coordinates, $\sigma$ is the rms-radius, and $\gamma$ is a parameter determining the local mean of the velocity distribution.

To arrive at analytic expressions for macroscopic plasma parameters, $\sigma$, $\gamma$, $T_i$, and $T_e$, the plasma is assumed to be spherically symmetric and substituting Eq. (6.7) into Eq. (6.4) leads to,
\[ \sigma^2(t) = \sigma^2(0)(1 + t^2/\tau_{\text{exp}}^2), \]  
\[ \gamma(t) = \frac{t}{1 + t^2/\tau_{\text{exp}}^2}, \]  
\[ T_i(t) = \frac{T_i(0)}{1 + t^2/\tau_{\text{exp}}^2}, \]  
\[ T_e(t) = \frac{T_e(0)}{1 + t^2/\tau_{\text{exp}}^2}, \]  
\[ \tau_{\text{exp}}^2 = \frac{m_i \sigma^2(0)}{k_B[T_e(0) + T_i(0)]}. \]  

Fitting the expansion data in Figures 6.5 and 6.4 to Eq. (6.8) leads to very good agreement of the Vlasov description of plasma expansion to experimental data points. For comparison, the solid line in Figure 6.5 represents a similar NO\textsuperscript{+} expansion for \( T_e(0) = 40 \) K and \( T_i(0) = 2 \) K, and shows a significant overestimation for the rate at which our plasma expands. The solutions of Equations (6.12) are valid for a self-similar expansion of a gaussian ion distribution. Physically speaking, this feature of the expansion is maintained by the quasineutrality assumption which produces an electric field that is dependent on the density gradient. For instance, no expansion occurs at the center of the plasma where the electric field is zero.

Driving the plasma expansion is the density gradient. Using the Vlasov equation requires equilibrium conditions. Obviously this condition is not met over the entire plasma ensemble, but local thermodynamic equilibrium (LTE) is a condition that is well met. Charged particle interactions occur over a distance corresponding to the Debye screening length, so it would seem logical to define that distance as an upper limit for LTE. Appendix A.4 goes through a derivation for scattering off a Yukawa potential. The result
is an equation for electron-electron $\approx$ electron-ion collision times, $\tau_{ee} \approx \tau_{ei}$ which will determine if the LTE approximation is applicable in regards to the expansion timescale. In the equation for $\tau_{ee}$, the Coulomb logarithm, $\ln \Lambda = \ln b_{\text{max}}/b_{\text{min}}$, is calculated for a maximum impact parameter $b_{\text{max}} = \lambda_D$ and a minimum $b_{\text{min}} = e^2/(k_B T_e)$. At densities of $5 \times 10^{12}$ cm$^{-3}$ and electron temperatures less than 100 K, collision times (seconds) are on the order of $\approx 2$ picoseconds. Hence, within the local approximation, equilibration is a good approximation.

Properly accounting for our expansion based on analytic formulas derived for spherically symmetric volumes requires some discussion since the co-propagating laser excitation scheme produces a prolate ellipsoid plasma volume, as opposed to the assumed Gaussian sphere. However, beam profiles taken with razor-blade tomography reveal a Gaussian $(y,z)$-plane laser intensity distribution. Electron signal measurements of consecutive planar projections over the molecular beam $z$-axis display Gaussian profiles. This suggests that a Gaussian distribution accurately describes the plasma in the $(y,z)$-plane.

This hypothesis is confirmed by previous work on an ellipsoidal plasma of comparable aspect ratio performed by Cummings et al. [27]. Here they determined the equitorial expansion rate of a Ca$^+$ plasma by modelling the time-dependent laser-induced fluorescence signal. It was determined that despite the difference in geometry between experimental ellipsoid and spherical symmetric volumes, the expansion rate determined by Cummings et al. almost exactly matched previous experiments of spherically symmetric expanding plasmas [63] when matched for initial electron energy and accounting for ion mass discrepancies. This result suggest that by extension, the spherical formalism can be used for expansion of an ellipsoidal geometry in the equitorial plane and provide a gauge for electron temperature.

The line through the data points on Fig. 6.5 fits with a $T_e(0) = 6.8$ K with an assumed ion temperature of $T_i(0) = 2$ K. The fit tracks the equitorial-plane expansion from 0 to 30 $\mu$s remarkably well. At longer times, adiabatic expansion lowers the electron
The temperature is lowered to 1.4 K, while doubling the Wigner-Seitz radius. Using these parameters, electron correlation is calculated to be $\Gamma_e \approx 10$.

The line through the data point on Fig. 6.3 tracks the expansion out to 40 $\mu$s and fits to a combined $T_e(0) + T_i(0) = 5$ K. Compared to the noble gas expansion, the moving grid experiment was able to generate many more data points that fit to the Vlasov formula for $\sigma(t)$, but in all respects yields a complementary validation to the measurement of low electron temperature.

Formation of an ultracold plasma from Rydberg molecules begins with Penning ionization collisions that initiate an avalanche of charge particle creation. Electrons with high energy quickly leave the volume until a small charge imbalance (less than 1%) develops, trapping the remaining electrons. At this point, inelastic collisions reshuffle the flow of energy on the timescale (100 picoseconds for $n_e = 10^{12}$ cm$^{-3}$) determined by the inverse electron plasma frequency, $\omega_{pe}^{-1}$, and is led predominately at low temperatures by three-body recombination (TBR) which scales as $T_e^{-9/2}$. Cross sections of electron-driven inelastic collisions are strongly dependent on the electron temperature, and MOT experiments appear to show that the properties of atomic ultracold plasmas vary continuously with excitation energy tuned across the ionization threshold [27]. By the same argument, starting from a negative electron energy is expected to lead to a lower initial electron temperature that is expected to greatly enhance the recombination heating.

What mechanism inhibits heating by three-body recombination? A simple classical picture of TBR begins by defining the Thomson radius, $r_T$, as the largest bound orbital radius [69] available to a free electron approaching an ion, during which time a secondary electron collision removes the binding energy. This mechanism requires any ion-electron collision resonance be bound by the energy that electrons collisionally thermalize and so the electron temperature determines the largest orbital radius stabilized by three-body recombination as,
\[
\frac{3}{2} k_B T_e = \frac{e^2}{4\pi \epsilon_0 r_T}.
\]

(6.13)

This highest bound orbital dominates the recombination channel since cross sections for electron capture and collisional thermalization scales as \( r^2 \) which agrees with the strong low-temperature scaling which will define a higher \( r_T \) where bound states have the highest number density. Various collision theory formulations developed to model three-body recombination consistently yield third-order rate constants that scale with temperature as \( T_e^{-4.5} \) [54, 69, 70]. For this reason, it is difficult to form a plasma with an electron temperature less than 25 K [71].

However, conventional derivations of the three-body recombination rate neglect the effect of plasma density on the accessible values of \( r_T \) or \( n_{\text{max}} \). For instance, at an electron temperature of \( T_e = 2 \)K, the Thomson radius is calculated to be 560 nm, which at typical MOT densities of \( 3 \times 10^{15} \) m\(^{-3} \) lies well within the Wigner-Seitz radius of 4 \( \mu \)m. Comparatively, our upper-limit estimate of an ion density of \( 5 \times 10^{18} \) m\(^{-3} \) results in a much smaller Wigner-Seitz radius of 360 nm. A smaller Wigner-Seitz radius distorts the isolated ion picture by changing the local electric field environment of the recombining electron. Models that include the ion-density for high-\( n \) recombination yield rate coefficients that scale as \( T_e^{-1} \), greatly reducing the recombination rate and thus electron heating [72, 73]. It then appears by this argument molecular beam conditions are able to suppress three-body recombination and its subsequent heating effects, thereby reducing the electron temperature and overall expansion.

More recently, calculations performed by Bannasch and Pohl [74] revealed that electron correlation has a direct effect on recombination rate. Molecular dynamics (MD) simulations of both one-component and two-component plasmas suggest that the divergence of recombination as \( T_e \) goes to zero disappears at correlation values greater than \( \Gamma_e \approx 2 \). Instead the rate approaches a constant value of \( \approx 0.03 \omega_{pe} \). Thus we might ex-
pect that any electron correlation suppresses recombination and reduces electron heating, thereby diminishing the rate of plasma expansion compared with atomic systems prepared in MOTs.
6.4 Summary

We have shown that by slowing the terminal velocity of a molecular beam with heavier carrier gases, the observation time is increased. Complimentary expansion information is obtained by implementing a translating detector carriage designed specifically for this type of experiment. By extracting spatial widths of the plasma in the $(y, z)$-plane as a function of arrival time at G2, the expansion rate can be fit to the analytical solutions of the Vlasov equation for a self-similar phase-space particle distribution. Driving the overall adiabatic expansion is the initial electron energy which has fitted values reported here of $T_e(0) = 6.8$ and $\approx 5$ K. This is considerably lower than electron temperatures observed for plasmas created in MOTs, and suggests interesting physics at work.
Chapter 7

Classical Scaling and the Correspondence Between the Coupled Rate Equation and Molecular Dynamics Models for the Evolution of UNPs

7.1 Introduction

The formation and evolution of an ultracold plasma is governed by classical electrostatic interactions and collisions between electrons, ions, and neutral Rydberg particles. Simulation models that accurately represent this physical environment have added a great deal to the understanding of ultracold plasmas. In particular, classical trajectory calculations [54, 75] and molecular dynamics (MD) simulations [48, 55, 76] have played crucial roles in uncovering the important physics that govern the evolution and dissipation of UCPs [77].

Molecular dynamics methods numerically integrate the equations of motion for charged particles in an electrostatic field. The capacity of present-day computers limits the discrete electron-ion scattering dynamics to short-times on the order of 1000 plasma periods or less. Results of these simulations generally exhibit an immediate increase in electron
temperature caused by the release of correlation energy \[70, 78\], followed by a cascade of inelastic collisions until the plasma evolves to a quasi-equilibrium between free electrons, ions, and bound neutral particles.

Longer time simulations treat the electrons as a thermalized fluid to properly account for discretized ion motion, and represent transformations associated with electron-ion collisions in terms of coupled rate processes. Rate coefficients, originally determined by calculating equilibrium transition probabilities for reaction rates by deriving the appropriate probability integrals to sample in Monte Carlo trajectory calculations \[54\], and further refined by Pohl, Vriceanu, and Sadeghour (PVS) to include small energy transfers \[55\] that can properly describe the formation of a steady-state distribution of Rydberg level population in a recombining plasma with an accompanying elevation in electron temperature.

Both molecular dynamics simulations and rate equation calculations take a classical approach to three-body electron-electron-cation scattering processes, detailed by recombination to Rydberg atoms

\[
M^+ + e^- + e^- \xrightarrow{k_{	ext{thr}}} M_n + e^-
\]

(7.1)

collision ionization,

\[
M_n + e^- \xrightarrow{k_{	ext{ion}}} M^+ + e^- + e^-
\]

(7.2)

and Rydberg-Rydberg energy transfer

\[
M_n + e^- \xrightarrow{k_{nj}} M_j + e^-.
\]

(7.3)

To define a Rydberg electron in molecular dynamics calculations requires spatial and temporal thresholds by which to determine that a discrete electron is close enough to an ion and remains so for multiple orbital periods. Introducing a soft-core factor to the
Coulombic interaction at short electron-ion distances prevents singularities. Rate equations define an energy scale in terms of discrete Rydberg levels over which a population evolves. Dynamics in both cases proceed as the mass-action rate processes of charged particles interacting classically.

Simple equations of motion regulate the behaviour of electrons and ions represented exactly by molecular dynamics simulations, or approximately by rate laws derived from phase-space probabilities. These equations of motion for a particle \(j\) at position \(\vec{R}_j\), velocity \(\vec{V}_j\) and time \(t\) scale with the Wigner-Seitz radius \(a_{\text{WS}} = (3/4\pi \rho_e)^{1/3}\), and the plasma frequency, \(\omega_{\text{pe}} = \sqrt{\rho_e e^2/\epsilon_0 m_e}\) to become functions of the dimensionless quantities, \(\vec{r}_j, \vec{v}_j; \tau\):

\[
\vec{R}_j = a_{\text{WS}} \vec{r}_j \quad \vec{V}_j = a_{\text{WS}} \omega_{\text{pe}} \vec{v}_j \quad t = \tau / \omega_{\text{pe}}.
\]

The equations of motion for any particle \(j\) is

\[
m_j \frac{d\vec{V}_j}{dt} = \sum_{j' \neq j} \frac{e^2 Z_j Z_{j'}}{4\pi \epsilon_0} \frac{\vec{R}_j - \vec{R}_{j'}}{|\vec{R}_j - \vec{R}_{j'}|^3} \quad \frac{d\vec{R}_j}{dt} = \vec{V}_j
\]

where \(Q_j = eZ_j\) is the charge of particle \(j\) having mass \(m_j\). Substituting the dimensionless quantities (7.4) in the equations of motion (7.5) yields

\[
a_{\text{WS}} \omega_{\text{pe}} m_j \frac{d\vec{r}_j}{d\tau} = \left[ \sum_{j' \neq j} \frac{e^2 Z_j Z_{j'}}{4\pi \epsilon} \frac{\vec{r}_j - \vec{r}_{j'}}{|\vec{r}_j - \vec{r}_{j'}|^3} \right] \frac{1}{a_{\text{WS}}^2} \quad \frac{d\vec{r}_j}{d\tau} = a_{\text{WS}} \omega_{\text{pe}} \vec{u}_j. \ (7.6)
\]

Using the fact that \(\frac{e^2}{4\pi \epsilon_0} \frac{1}{a_{\text{WS}}^2 \omega_{\text{pe}}^3} = \frac{m_e}{3}\), equation (7.6) becomes

\[
\frac{d\vec{u}_j}{d\tau} = \frac{m_e}{3m_j} \sum_{j' \neq j} \frac{Z_j Z_{j'} (\vec{r}_j - \vec{r}_{j'})}{|\vec{r}_j - \vec{r}_{j'}|^3} \quad (7.8)
\]
and (7.7) becomes

\[ \frac{d\vec{r}_j}{d\tau} = \vec{u}_j \]  

(7.9)

Scaling fundamental variables in this way provides a density independent description of the particle ensemble. Accordingly, in scaled coordinates, any choice of initial $\vec{R}_j; \vec{V}_j$, for which the scaled values $\vec{r}_j; \vec{v}_j$ are the same, evolves identically. In particular, scaled temperature, defined by $\Gamma^{-1}(\tau) = k_B T_e(\tau) 4\pi \epsilon_0 a_{WS}/e^2$, evolves the same in scaled time, $\tau$, for any system initialized to start with the same $\Gamma^{-1}(0)$. This property of classical Coulomb systems serves usefully to validate simulation models, particularly for the purpose of comparing rate equation simulations with molecular dynamics calculations.

This chapter reports on results from such a comparison. A coupled rate equation model for the evolution of a system of atomic ions and electrons to a state of quasi-equilibrium with recombined Rydberg atoms, shows how the initial specifications of the Rydberg domain sensitively affects the predicted evolution in plasma properties. A strong dependence on the dynamics of relaxation in Rydberg manifold requires a self-consistent procedure for the selection of minimum and maximum principal quantum number to define a range in which the simulated evolution in scaled electron temperature, $\Gamma^{-1}$, varies self-consistently in scaled time. To validate the scaling of the rate-equation simulations a comparison with plasma evolution dynamics predicted by classical molecular dynamics is useful. Results of such a comparison reveal the effect of soft-core modifications made to the Coulomb potential in terms of constraints governing the relaxation of Rydberg levels in rate equation simulations.
7.2 Models

7.2.1 Molecular Dynamics

Classic Monte Carlo molecular dynamics calculations were performed by Robicheaux and co-workers [79, 80] using standard methods for ultracold plasma simulations [65, 70, 78]. The interaction force between particles was described by a modified Coulomb potential

\[ PE_{ij} = \frac{q_i q_j}{4 \pi \epsilon_0 \sqrt{R_{ij}^2 + (Ca_{WS})^2}} \]  

(7.10)

where \( R_{ij} \) is the distance between charges \( q_i \) and \( q_j \), and the product \( Ca_{WS} \) scales the Wigner-Seitz radius to moderate the potential for small \( R_{ij} \). Soft-core parameters, \( C \), for this work are 0.01 and 0.02. To initiate simulations, starting conditions select particle positions and electron thermal energies of 3, 4, 5, 10, 15 or 20 K at densities of \( 1 \times 10^9 \) cm\(^{-3} \). The system is set to evolve for 300 ns, avoiding boundary singularities by using periodic boundary conditions, and temperature is determined from the average kinetic energy of all electrons with a distance greater than \( R_{\text{max}} = 0.2 a_{WS} \) from an ion-core.

7.2.2 Coupled Rate Equations

Simulations based on rates derived from a statistical perspective are constructed with the set of coupled equations

\[ \frac{d\rho_n}{dt} = - \sum_j k_{nj} \rho_e \rho_n + \sum_j k_{jn} \rho_e \rho_j - k_{\text{ion}}^n \rho_e \rho_n + k_{tbr}^n \rho_e^3 \]  

(7.11)

\[ \frac{d\rho_e}{dt} = \sum_n k_{\text{ion}} \rho_e \rho_n - \sum_n k_{tbr}^n \rho_e^3 \]  

(7.12)

with the PVS rate formulas for coefficients \( k_{nj} \), for electron impact transitions from Ry-
dberg state $n$ to $j$, $k_{\text{ion}}^n$ for collisional ionization from state $n$ and $k_{\text{ibr}}^n$ for three-body recombination to state $n$. Implicit in this analysis is a quasi-neutral approximation of equal electron, $\rho_e$, and ion, $\rho_n$, densities and is valid considering $< 1\%$ of the electrons leave in the prompt evaporative loss, and any charge imbalance that does exist will be at the outer edges of the plasma. The Rydberg manifold ranges from a lower $n_{\text{min}}$ value of $n$ to an upper $n_{\text{max}}$ of $j$. Energy is conserved by summing populated Rydberg states and free-electron of energy $T_e(t)$:

$$E_{\text{tot}} = \frac{3}{2} k_B T_e(t) \rho_e(t) - R \sum_n \frac{\rho_n(t)}{n^2}$$  \hspace{1cm} (7.13)

In this study, calculations began with a completely photo-ionized plasma having a thermal electron energy, $T_e(0)$, and a zero-energy ionic background that remains constant over the time-scale of the relaxation to steady-state. Selection of $n_{\text{max}}$ is determined by the molecular dynamics criteria of scaled distance, while $n_{\text{min}}$ is chosen to produce results that scale.

### 7.2.3 Results: Classical Scaling of Rate Equations

To verify classical scaling of the coupled rate equation model, scaled electron temperature, $\Gamma_e^{-1}$, is plotted versus scaled time, $\tau = t \omega_{pe}$, for plasmas evolving from charged-particle densities of $10^9$ and $10^{11}$ cm$^{-3}$. All results point to a constantly increasing $\Gamma_e^{-1}(\tau)$ as ions and electrons recombine, forming Rydberg states that release energy in super-elastic collisions with free electrons.

Molecular dynamics simulations partition energy between bound and free electrons energies based on a scaled distance criteria, $r_{\text{max}} = R_{\text{max}}/a_{\text{WS}}$, which for the current study uses $r_{\text{max}} = 0.2$ unless indicated otherwise. We echo this distinction in the rate equation model by converting $R_{\text{max}}$ to a value of $n_{\text{max}}$ using $r_{\text{max}} a_{\text{WS}} = n_{\text{max}}^2 a_0$, where $a_0$ is the Bohr radius.
Electron temperature is also strongly influenced by the choice of minimum Rydberg size. MD simulations define this by choice of the soft-core parameter, $C$. Variations in $C$ lead to a change in $\Gamma_e^{-1}(\tau)$ but scale for any choice of $C$ as long as this parameter is defined by the density. Analogously, rate equations employ a $n_{min}$ which has been verified for a $n = 25$ by Pohl and coworkers using MD simulations, but is shown to viably extend even lower in the study.

Figure 7.1: Output of rate equation calculations describing the variation in scaled temperature ($\Gamma_e^{-1}$) with scaled time ($t\omega_{pe}$) for neutral plasmas initialized to contain frozen ions and free electrons with scaled temperature of $\Gamma_e^{-1} = 2.0$, at an initial particle density of $10^9$ cm$^{-6}$ (blue curves), for Rydberg $n_{max} = 153$ with values of $n_{min}$ of 25 (blue dashed line) and 10 (blue solid line), and density of $10^{11}$ cm$^{-3}$ (red curves), for Rydberg $n_{max} = 71$ with values of $n_{min}$ of 25 (red dashed line) and 10 (red solid line).

Figure 7.1 shows the behaviour of rate equation calculations of $10^9$ (blue curves) and $10^{11}$ (red curves) when $n_{min}$ is set to 25 (dashed line) and 10 (solid line), respectively. For all results, $n_{max}$ conforms to the MD value, $r_{max} = 0.2$. It is apparent that at a higher $n_{min}$, scaling is not observed, yet with $n_{min}$=10 there is strong overlap in $\Gamma_e^{-1}(\tau)$ indicative
of classical scaling.

To compare different $r_{\text{max}}$, Figure 7.2 illustrates the effect of changing $n_{\text{max}}$ while maintaining $n_{\text{min}}$ at 10. There is an obvious difference in the evolution of $\Gamma_e^{-1}(\tau)$ as $r_{\text{max}}$ changes, yet the curves superimpose for the same $r_{\text{max}}$ and differing densities. Defining $r_{\text{max}}$ defines the highest bound Rydberg level and since rate equation simulations can not smoothly transition into the continuum, a lower limit for the upper-bound Rydberg level is required. With a quick look at Figure 7.2 it is apparent that choosing an $n_{\text{max}}$ of at least $\sqrt{0.2a_{\text{WS}}/a_0}$ converges to a final inverse correlation that agrees with larger limits.

The highest stable recombination state can also be defined dynamically by the relation $n_{\text{max}} = \sqrt{k_B T_e/a_0}$[55] with the argument the electron thermal bath will not support a bound state that is less than at least $T_e$ below the ionization potential. To support this argument we introduce the Saha equilibrium,

$$\rho_{eq}(n) = n^2 \rho_e^2 \left( \frac{2\pi \hbar^2}{m_e k_B T_e} \right)^{3/2} \exp \left[ \frac{\mathcal{R}}{n^2 k_B T_e} \right]$$

which defines the equilibrium density, $\rho_{eq}(n)$, for Rydberg level $n$. As temperature increases, the population at a particular $n$ will decrease since ionizing collisions with the electron bath will have, on average, enough energy to ionize. Furthermore, an equilibrium exists between free electrons and ions and Rydberg states bound with an energy on par with the electron temperature. A dynamical lower limit for the equilibrium in Eq. (7.14) is referred to as the bottleneck which arises as a result of the propensity of the system to increasingly populate lower $n$, and the loss in degeneracy scaling as $n^2$.

Implementing a dynamic thermal threshold on $n_{\text{max}}$ can affect the early-time recombination dynamics, but after 400 plasma periods the effect is reduced.

It is instructive to compare rate equation calculations to molecular dynamics results in order to relate parameters between each model formalism. More specifically, results of molecular dynamics simulations for a uniform distribution of ions and electrons over
Figure 7.2: Output of rate equation calculations describing the variation in scaled temperature ($\Gamma^{-1}$) with scaled time ($t_{\omega_{pe}}$) for neutral plasmas initialized to contain frozen ions and free electrons at particle densities of $10^9$ (blue) and $10^{11}$ (red) cm$^{-3}$ at a scaled temperature of $\Gamma^{-1}_e(0) = 2.0$, $n_{\text{min}}=10$. Values of Rydberg $n_{\text{max}}$ defined by $\sqrt{0.1a_{WS}/a_0}$ (bottom), $\sqrt{0.2a_{WS}/a_0}$ (middle) and $\sqrt{0.3a_{WS}/a_0}$ (top). Dashed curves show similar variations for $\Gamma^{-1}_e(0) = 2.0$, $n_{\text{min}} = 10$, with dynamically defined $n_{\text{max}} = \sqrt{R/k_B T_e}$, for particle densities of $10^9$ (blue) and $10^{11}$ cm$^{-3}$.

Time intervals of 500 plasma periods were reproduced with rate equations by replication of starting conditions. It was necessary to compensate for a $\Gamma^{-1}_e(\tau)$ transient from $\tau = 0$ to 40 implicit in the method of launching MD simulations. The rising portion of this transient has been associated with correlation-induced heating of electrons [70, 78, 79]. In order to compare with molecular dynamics simulations beyond this transient, we select an initial electron temperature, $T_e(0)$, for rate equation calculations, to match molecular dynamics $\Gamma^{-1}_e$ at 100 plasma periods. Scaling is maintained by setting $n_{\text{min}} = 10$.

Figure 7.3 shows scaled temperature, $\Gamma^{-1}_e$, as a function of scaled time, $\tau_{\omega_{pe}}$, obtained from coupled rate equation simulations, compared to molecular dynamics calculations for
Figure 7.3: Reduced temperature, Γ_e^{-1}, versus reduced time, t_{\omega pe}, obtained from molecular dynamics calculations with soft-core parameter \( C = 0.02 \) (blue) and 0.01 (red) for initial \( T_e = 3, 4, 5, 10, 15 \) and 20 K, and particle densities of \( 10^9 \) cm\(^{-3} \), together with the output of corresponding rate equation calculations for which \( n_{\text{max}} = \sqrt{0.2a_{\text{WS}}/a_0} \). Pairs of curves compare results for \( n_{\text{min}} = 10 \) (solid) with \( n_{\text{min}} = 55, 57, 60, 70, 75 \) and 75 (dashed). Divergence between solid and dashed curves, measured by the ratio of slopes at \( \tau = 500 \), increases as 2.5, 2.6, 3.2, 16, 130 and 450.

two different soft-core radii, 0.02a_{\text{WS}} and 0.01a_{\text{WS}}, and an initial density of \( 10^9 \) cm\(^{-3} \) for a series starting temperatures. Beyond the initial transient, rate equation simulations conform with molecular dynamics calculations for the first 150 plasma periods, as quasi-equilibria is reached with free-electron fractions of around 0.85. Beyond this point, the curves begin to diverge. The divergence is due to a faster temperature increase in the coupled rate equation model that observed by molecular dynamics for either value of \( C \). The difference grows with the size of the soft-core and increases with initial electron tem-
temperature. For $T_e(0) = 3$ K, a MD simulation using a soft-core parameter of 0.01 nearly agrees with a rate equation calculation that scales. But higher temperatures cause greater divergence between rate equations and molecular dynamics. At $T_e = 20$ K MD values using parameters of $C = 0.01$ and 0.02 and rate equations with $n_{\min} = 10$ deviate to the same degree and exhibit little temperature change beyond the early transient. A similar steady-state can be seen by setting $n_{\min}$ to a higher value in rate equation calculations.

In fact, when we set $n_{\min}$ to 50, the coupled rate simulation for $T_e(0) = 3$ K agrees very well with the corresponding molecular dynamics calculations using $C = 0.02$. For higher $T_e(0)$, the strategy of adjusting $n_{\min}$ to superimpose results is quite successful and as initial temperature is increased a corresponding increase in $n_{\min}$ is necessary.

## 7.3 Discussion

Figure 7.2 shows that the value selected for $n_{\max}$ in the rate equation simulation of an ultracold plasma affects the electron temperature evolution, but classical scaling can still be observed if the criterion that defines $n_{\max}$ scales. Thereby the MD distance criteria $r_{\max} = 0.2$ defines values of $n_{\max}$ of 153 and 71 for densities of $10^9$ and $10^{11}$ cm$^{-3}$, respectively, by means of the relation $n_{\max} = \sqrt{r_{\max}a_{WS}/a_0}$. Choosing $r_{\max} = 0.1$ similarly defines $n_{\max}$ values of 108 and 50. Evident in Figure 7.2 is the identical suppression of $\Gamma^{-1}_e(\tau)$ for both densities at lower $n_{\max}$ values.

The specification of $n_{\max}$ regulates the highest orbital populated by three-body recombination. Decreasing $n_{\max}$ to a value smaller than the thermal threshold $\sqrt{R/k_B T_e}$ alters the relaxation dynamics by suppressing three-body recombination and slowing the rise in $\Gamma^{-1}_e$. Choosing $n_{\max}$ greater than $\sqrt{R/k_B T_e}$ increases the range of principal quantum numbers available for recombination, thereby accelerating a rise in $\Gamma^{-1}_e(\tau)$ during the early evolution times. However, this effect is diminished as the bottleneck, or Saha equilibrium threshold, moves towards lower values as the evolution progresses. This is seen in
Figure 7.2 by the convergence of results for $r_{\text{max}} = 0.2$ and 0.3 at $\tau = 1000$. Even with a thermal threshold for $n_{\text{max}}$, rate equation simulations agree reasonably well with results for $r_{\text{max}} = 0.2$, when initial $\Gamma_e^{-1} = 2.0$ ($T_e(0) = 5.4$ or 25 K for $10^9$ or $10^{11}$, respectively). Ignoring the transient MD effect, Figure 7.3 shows that rate equation results using a $n_{\text{max}}$ defined by $r_{\text{max}} = 0.2$ fit very well with a soft-core parameter $C = 0.02$.

In molecular dynamics simulations, the choice of $r_{\text{max}}$ has no effect on the dynamics since it is a post-processing parameter that decides the partitioning of electron energy for the purposes of determining electron temperature. For instance, a small value of $r_{\text{max}}$ produces a slightly faster rise in $\Gamma_e^{-1}(\tau)$ by adding more fast electrons to the population that determines $T_e$. The effect is not as pronounced as results observed for the analogous variation in $n_{\text{max}}$ for rate equations.

To achieve a meaningful comparison between the output of molecular dynamics simulations with the predictions of rate equation calculations, one must choose the appropriate criteria for designating the largest bound electron-ion distance and the largest stable principal quantum number. It was found that rate equation calculations best correspond with molecular dynamics simulations for $n_{\text{max}} \approx \sqrt{R/k_BT_e}$. As a consequence, the consistently optimum criteria should allocate $r_{\text{max}}$ to fit with thermally limited $n_{\text{max}}$ by specifying $r_{\text{max}} = \Gamma_e/2$.

### 7.3.1 $n_{\text{min}}$ and Soft-Core Comparison

Electron temperature evolution depends on the choice of $n_{\text{min}}$. Truncating the relaxation at a higher minimum value of $n$ retards electron heating in such a way that the properties of the system do not scale with charged particle density required from classical mechanics. Variation in $\Gamma_e^{-1}(\tau)$ with choice of $n_{\text{min}}$ can be explained by examining comparative plots of Rydberg level populations as a function of reduced time. Figure 7.4 shows the evolution of number densities in Rydberg levels populated by three-body recombination at charged-particle densities of $10^9$ and $10^{11}$ cm$^{-3}$, corresponding to the conditions of the
rate equation simulation results displayed in Figure 7.1.

Figure 7.4: Evolution of level population densities in scaled time for initial charged-particle densities of $10^9$ cm$^{-3}$ and electron temperature of $T_e = 4$ K (left), and $10^{11}$ cm$^{-3}$ and 18.57 K (right), as determined by coupled rate equations for fixed $n_{\text{max}} = 153$ and 71, respectively. For top set, $n_{\text{min}} = 25$. For bottom set, $n_{\text{min}} = 10$. In all cases, $\Gamma_e(0) = 1.495$. Starting with early times, the uppermost line traces the population of $n_{\text{max}}$. The lowest line describes the population of $n_{\text{min}}$. In the upper right, note how a relaxation truncated at $n_{\text{min}} = 25$ for $\rho_e = 10^{11}$ cm$^{-3}$ creates a gap in population (and energy release) that is absent for $\rho_e = 10^9$ cm$^{-3}$ in the upper left, invalidating scaling.

Population density begins to grow in $n_{\text{max}}$ and then dissipates to lower levels at the same rates, in scaled time. Conformance in scaled temperature is due to the isomorphism in Rydberg levels that arises from the scaling of level density with $n^2$, and the binding energy scaling as $1/n^2$. Evidently, scaling is prevented when the number of available Rydberg levels is insufficient in order to preserve the isomorphism between bound population and
energy, as seen in Fig. 7.4 where the top-right plot of Rydberg level density versus scaled time exhibits a gap below the lowest, $n_{\text{min}} = 25$, level. This gap coincides with the point in scaled time at which the $\Gamma^{-1}_e(\tau)$ diverges. Population tends to build up at the lowest level at high initial densities, but if the simulation is repeated for $n_{\text{min}} = 10$, the lowest levels dilute the downward-pumped Rydberg states and temperature scaling is observed.

Molecular dynamics show a similar relationship between smallest electron-ion distance and classical scaling: relaxation slows dynamical evolution of $\Gamma^{-1}_e(\tau)$ when, for instance, a simulation is performed with a smaller soft-core parameter (Fig. 7.3, blue curves). When $n_{\text{min}}$ is set to 55, rate equations successfully track the molecular dynamics evolution of $\Gamma^{-1}_e(\tau)$ for $C = 0.02$ at a density of $10^9$ cm$^{-3}$ and initial temperature, $T_e = 3$ K ($\Gamma^{-1}_e(0) = 2.1$ for the purpose of rate equation simulation). As initial temperature is increased up to 20 K, MD results become increasingly depressed when compared to rate equation results for $n_{\text{min}} = 10$. However, by systematically increasing $n_{\text{min}}$ from 55 to 75, $\Gamma^{-1}_e(\tau)$ from rate equations converges with molecular dynamics results, after the initial transient.

The definition of the soft-core potential contains no reference to the thermal energy of the system. Disagreement between the two models that both scale with density suggests that by using a potential that inherently scales with density ($C = 0.2a_{\text{WS}}$) neglects important physics at small ion-electron distances. Limitations of attenuated potentials have been previously addressed in molecular dynamics studies of ultracold plasmas [70, 78]. In the study performed by Niffenegger et al. [79] the effect of varying the soft-core parameter from $C = 0.01$ to 0.03 was negligible on the timescale of 100 plasma periods.

However, at longer times recombination to Rydberg states has a profound effect on the evolution to the extent that, at 500 plasma periods, rate equations need to set $n_{\text{min}}$ to a substantially higher value to reflect the soft-core effect in molecular dynamics. Two factors combine to this.

In Figure 7.5 it is evident that the soft-core potential gives a poor representation
Figure 7.5: Soft-core electron-ion potentials, Eq. (7.10) for $C = 0.03$ (purple), 0.02(green), and 0.01(red) with reference to a pure Coulomb potential (blue) and the energies of the hydrogenic Rydberg levels indicated.

of semi-classical states derived from the hydrogenic potential. The limitations of the soft-core potential become more serious under conditions where the relaxing population samples states of deeper binding energy. Quasi-equilibrium is established between Rydberg states and free electrons above the bottleneck principal quantum number $\sqrt{R/4k_BT_e}$[55]. Over a temperature range from 3 to 20 K, the corresponding bottleneck changes from 115 to 44, respectively. Starting with an electron temperature of 20 K, molecular dynamics simulations will resort to an orbital-radii sampling range restricted to the soft-core potential. This visibly inhibits the relaxation dynamics and is made apparent by the accompanying rate equation results (Figure 7.5) that require an elevated $n_{\text{min}}$ to mimic conditions.
7.4 Summary

We have compared rate equation simulations based on phase-space theory models for the three-body electron-electron-ion scattering dynamics associated with ultracold plasma evolution with the results of molecular dynamics calculations. Our results establish that the predictions of rate equation models scale with density in accord with the classical mechanics of a Coulomb system, provided that the simulation spans a range of Rydberg levels that extends to a sufficiently low value of minimum principal quantum number, \( n_{\text{min}} \). Intuitively, \( n_{\text{min}} = 0 \) would seem like the best choice for a lower limit, but is not appropriate for this model which neglects any radiative decay. Results from simulations using \( n_{\text{min}} = 0 \) show a very strong temperature divergence most likely due to the kinetic energy gained by the electron bath from low-\( n \) transitions.

We explain scaling behaviour for \( n_{\text{min}} = 10 \) in a semi-classical limit in terms of a Rydberg level isomorphism in which the Rydberg state density and binding energy both vary as \( n^2 \). We show that the choice of \( n_{\text{max}} \), the maximum principal number populated by three-body recombination, does not affect scaling, so long as the criterion that defines this quantity scales with density. Rate equation calculations agree best with molecular dynamics simulations for \( n_{\text{max}} \) and \( R_{\text{max}} = r_{\text{max}} a_{\text{WS}} \) consistently defined with respect to a thermal limit by selecting \( r_{\text{max}} = \Gamma_e / 2 \). Rate equation simulations thus serve as a gauge for validating molecular dynamics models for the evolution of an ultracold plasma.
Chapter 8

Recombinative Dissociation and the Evolution of a Molecular Ultracold Plasma

8.1 Introduction

Ultracold plasmas offer a novel regime in which to study the collision physics of Coulomb systems in or near states of charged particle correlation [81]. Collisional processes involving electrons play a particularly important role in the dynamics of such systems. Electrons recombine with ions and undergo energy transfer collisions with Rydberg neutrals, in kinetic sequences that redistribute population and regulate the electron temperature [70, 82, 83].

The frequency of electron-ion collisions governs the evolution of a laser-prepared plasma to quasi equilibrium. In the approach to equilibrium, intrinsic properties of the plasma, such as its ambipolar expansion and radiative decay, pace collisional phenomena that include three-body recombination, electron-impact ionization and the heating of free electrons associated with the cascade deactivation of Rydberg neutrals.

At high charge densities, such as those encountered in the ultracold plasma formed in a molecular beam [1–3], collisional processes alone determine the development of a steady state. For such a plasma, produced to contain molecular ions, the ability to dissociate adds an important dissipative channel [84]. This dissipation can alter plasma evolution by the
introduction of additional collisional (dissociative recombination) or intrinsic (predissocia-
tion) rate processes, or both.

Even under ultracold conditions, the molecular plasma represents a complex kinetic
system. Here we develop a mechanistic simulation for the rate processes associated with
the short-time evolution of a molecular ultracold plasma at high charge density with a
particular view to exploring how the dissociative loss of neutral excited states in channels
of cascade relaxation affects the mass and energy balance of the plasma steady state.

8.1.1 Kinetic Rate Processes in a Molecular Ultracold Plasma

A molecular beam plasma differs from the ultracold plasma formed by exciting atoms
in a MOT by virtue of its density and by the fact that here molecular NO$^+$ cations carry
the positive charge. Upon recombination with electrons these cations can dissociate to
form neutral N and O atoms.

This dissociation proceeds via one of two paths: (8.1) dissociative recombination
(DR) of NO$^+$ with an electron produces N + O in a binary, single collision,

\[
\text{NO}^+ + e^- \overset{k_{\text{DR}}}{\longrightarrow} \text{N} + \text{O}
\]

(8.2) NO molecules in Rydberg states formed in quasi equilibrium with NO$^+$ undergo
predissociation (PD).

\[
\text{NO}^* + e^- \overset{k_{\text{TBR}}}{\underset{k_{\text{ion}}}{\rightleftharpoons}} \text{NO}^* + e^-
\]

\[
\text{NO}^* \overset{k_{\text{PD}}}{\longrightarrow} \text{N} + \text{O}
\]
Under steady-state conditions – and in a limit for which the effective first-order rate constant for collisional ionization, $k_{\text{ion}}\rho_e$, exceeds that for unimolecular decay, $k_{\text{PD}}$ – mechanism (8.2) consumes NO$^+$ ions and electrons at a rate that varies in second order with charged particle density, with an effective rate constant, $k_{qe}$, viz:

$$\frac{d[\text{NO}^+]}{dt} = \frac{k_{\text{TBR}}}{k_{\text{ion}}} k_{\text{PD}} \rho_e^2 = k_{qe} \rho_e^2$$  \hspace{1cm} (8.3)

where the cation concentration, $[\text{NO}^+]$, equals the electron density, $\rho_e$, under conditions of quasi neutrality.

In another study [84], we have used a phase-space theory formulation of electron-electron-ion collisional rate processes [54, 55], together with experimental and theoretical determinations of $k_{\text{PD}}$ [85–87] to estimate $k_{qe}$ as a function of Rydberg principal quantum number, $n$. The Rydberg states in quasi equilibrium with free ions and electrons populate a range of integers, $n$, that extends from the bottleneck [88] at $n_b \approx \sqrt{\mathcal{R}/4k_B T_e}$ to a thermal upper limit for Rydberg binding, $n_{\text{max}} \approx \sqrt{\mathcal{R}/k_B T_e}$, where $T_e$ is the electron temperature and $\mathcal{R}$ is the Rydberg constant [82, 83]. Between these limits, we calculate a $k_{qe}$ that is substantially smaller than $k_{\text{DR}}$ for all but the lowest electron temperatures [89]. Our experimental measurements of long-term plasma dissipation suggest a small role for steady-state predissociation, which appears to grow in importance with decreasing charge density [84].

The predissociation rate of NO Rydberg states substantially increases with decreasing $n$ [85–87]. While not in quasi equilibrium with ions and electrons, cascade relaxation populates states below $n_b$, and the dissociation of these states surely contributes to the flux from ions to neutrals. The irreversible loss of low-$n$ Rydberg population affects the evolving energy balance of the plasma. Steady-state kinetics cannot describe this. Instead, to completely characterize the important effects of low-$n$ Rydberg state decay, both on plasma dissipation and energetics, we must turn to simulations that fully model the coupled
dynamics of plasma relaxation and dissociation as the system evolves.

8.1.2 Simulation Models for Ultracold Plasma Relaxation

Ultracold plasma dynamics are well represented in a classical limit by molecular dynamics (MD) simulations [90, 91], and by coupled differential rate equations [71, 92]. Both approaches consider the elementary dynamics of three-body electron-electron-ion collisions leading to electron impact ionization and electron-ion recombination, such as (8.2), in combination with Rydberg energy level redistribution:

\[ \text{NO}^*(n_i) + e^- \rightarrow \text{NO}^*(n_j) + e^- \quad (8.4) \]

Molecular dynamics calculations treat electron-electron-ion collisions discretely, and serve well to describe the early time dynamics of plasma evolution. However, the small time steps necessary to accommodate electron motion make it impractical to extend such simulations for timescales over which ions move appreciably.

Rate equation simulations follow the evolution of electron, ion and Rydberg state populations and energies as fluxes in phase space [54, 55]. We can construct a set of differential equations in much the same way as before (see Chapter 7 page 96), which can be written out explicitly, including molecular dissociation channels, as,

\[
\frac{d\rho_i}{dt} = -\sum_j k_{ij} \rho_e \rho_i + \sum_j k_{ji} \rho_e \rho_j - k_{\text{ion}} \rho_e \rho_i + k_{\text{tbr}} \rho_e^3 - k_{\text{PD}}(n_i) \rho_i \quad (8.5)
\]

\[
\frac{d\rho_e}{dt} = \sum_i k_{\text{ion}} \rho_e \rho_i - \sum_i k_{\text{tbr}} \rho_e^3 - k_{\text{DR}}(T_e) \rho_e^2 \quad (8.6)
\]

and in comparison to the purely atomic set previously reported, we have included rate constants for temperature-dependent dissociative recombination, \( k_{\text{DR}}(T_e) \), and level-dependent
predissociation, $k_{PD}(n_i)$ in this model. The system of differential equations can be integrated for times corresponding to the full dissipation of the plasma to describe evolving particle densities, and determine $T_e$ as a function of time according to:

$$\frac{3}{2} k_B T_e(t) \rho_e(t) - R \sum_i \frac{\rho_i(t)}{n_i^2} - E_{tot}(t) = 0,$$

where $\rho_e(t)$ is the electron density and $\rho_i(t)$ is the density in Rydberg level, $n_i$, at time $t$, and $E_{tot}(t)$ is the potential energy of the plasma Rydbergs together with the thermal energy of its free electrons.

In the limit of simple pairwise Coulomb interactions, equations of motion formulated in either representation scale with the Wigner Seitz radius, $a_{WS} = (3/4\pi \rho_e)^{1/3}$ and the plasma frequency, $\omega_e = \sqrt{\rho_e e^2 / \varepsilon_0 m_e}$ [70, 93]. Described in scaled coordinates, a system with an initial scaled temperature $\Gamma^{-1} = 4\pi \varepsilon_0 a_{WS} k_B T_e / e^2$ evolves in scaled time, $\tau = t \omega_e$, in a manner that is independent of its density.

### 8.1.3 Simulation Models Incorporating Dissociation

NO$^+$ ions in a molecular ultracold plasma can decay by direct dissociative recombination and by the predissociation of Rydberg states formed by three-body recombination [84]. These channels, which serve to distinguish the molecular ultracold plasma from its atomic counterpart, have important implications for the properties of the plasma state, both as it forms and as it evolves.

Dissociative recombination occurs over a long timescale and affects relaxation dynamics by reducing electron and ion density. Predissociation occurs in the manifold of relaxing Rydberg states, where it significantly alters the collisional flow of energy from molecules to free electrons. Both processes remove energy associated with the loss in population. In the simulation, $E_{tot}(t) = E_{tot}(0) - \sum_0^t E_{loss}(t)$, where we define the energy lost in time step $t$ by:
\[ E_{\text{loss}}(t) = \frac{3}{2} k_B T_e(t) \rho_e^{DR}(t) - R \sum_i \frac{\rho_i^{PD}(t)}{n_i^2}, \] (8.8)

in which \( \rho_e^{DR}(t) \) refers to the instantaneous electron density lost to dissociative recombination and \( \rho_i^{PD}(t) \) similarly accounts for the loss of Rydberg population density in level \( i \) to predissociation.

The aim of the work in this chapter was to isolate properties that most distinguish the molecular ultracold plasma, and use simulation models to explore how evolution dynamics vary as a result. To this end, we present a series of rate equation calculations detailing the flow of population and energy in model atomic and molecular plasmas. We use a hierarchal approach, starting with the simulation of a fully ionized atomic plasma to demonstrate conformance with classical scaling and examine criteria that define an upper bound on principal quantum number. Photoionized plasmas are then compared with plasmas formed from state-selected Rydberg gases, and finally the molecular properties of Rydberg predissociation and electron-cation dissociative recombination are introduced.

For all models, we consider a plasma of uniform density, and follow the evolution of particle populations over time intervals long enough for significant Rydberg relaxation and predissociation, but not so long that the distribution of charged particles undergoes a meaningful degree of expansion. Calculations focus particularly on the plasma that forms in a dense Rydberg gas following Penning ionization. We investigate the influence of the initial Rydberg principal quantum number, \( n_0 \), on the evolution of the plasma, and compare the molecular plasma with plasmas formed by the ionization of atoms, showing in particular both how dissociative recombination and predissociation affect the time dependence of ion density and the evolution of electron temperature.
8.2 Rate Properties of Atomic Ultracold Plasmas

8.2.1 Direct Photoionization and the Validation of Simulation Models

For the most part, experimental and theoretical work on ultracold plasmas has focused on charged particle distributions formed by photoionization. Under such conditions, evolution to a state of quasi equilibrium begins with an ensemble of ions and electrons, formed at a density approaching that of the initial gas, and an electron temperature determined by the photon energy in excess of the ionization threshold.

In the previous chapter, we chose such a model system for the purpose of comparing rate equation calculations with predictions drawn from molecular dynamics simulations [4]. For Rydberg manifolds chosen to conform with the range of electron binding energies sampled by molecular dynamics calculations, the results show how the lower bound for such a manifold ($n_{\text{min}}$) constrains electron temperature evolution. Choosing too high a value of $n_{\text{min}}$ prevents the scaling of rate equation simulations.

Both rate equation and molecular dynamics simulations must also define an upper limit for electron binding ($n_{\text{max}}$). Molecular dynamics calculations typically set an implicit value of $n_{\text{max}}$ geometrically by defining a maximum orbital radius for bound electrons as a quantity scaled by the Wigner-Seitz radius, $R_{\text{max}} = r_{\text{max}}a_{\text{WS}}$, which in semi-classical terms of the Bohr radius, $a_0$, yields $n_{\text{max}} = \sqrt{r_{\text{max}}a_{\text{WS}}/a_0}$. We used this convention for the purpose of comparing rate equation calculations with molecular dynamics simulations for which $r_{\text{max}} = 0.1$, 0.2 and 0.3 [4].

As an alternative, it seems natural to set $n_{\text{max}}$ by a thermal criterion, such as $n_{\text{max}} = \sqrt{R/k_B T_e}$, reasoning that the evolving thermal energy of the electrons provides a more comprehensive gauge of the smallest stable binding energy [55, 82, 83]. Simply equating these expressions for $n_{\text{max}}$ shows that the geometric criterion conforms with the thermal
one for the condition, \( r_{\text{max}} = \Gamma_e / 2 \).

Figure 8.1: Output of rate-equation calculations describing the variation in scaled electron temperature \( (\Gamma_e^{-1}) \) with scaled time \( (t\omega_e) \) for neutral plasmas consisting of frozen \( (T_i = 0 \text{ K}) \) atomic ions and free electrons initiated with an initial scaled temperature of \( \Gamma_e^{-1}(0) = 2.5 \), at an initial particle density of \( 10^9 \) and \( 10^{12} \text{ cm}^{-3} \). Dashed lines compare the evolution in scaled coordinates for a fixed \( n_{\text{max}} = \sqrt{0.2a_{\text{WS}}/a_0} \). Solid lines show the evolution in scaled temperature using a dynamic \( n_{\text{max}} = \sqrt{R/k_B T_e} \). Curves for higher density track below those obtained in each case for the lower density.

Here we compare these \( n_{\text{max}} \) criteria for the simplest case of an atomic plasma produced by direct ionization. Figure 8.1 shows the evolution of scaled temperature, \( \Gamma_e^{-1} \) with scaled time, \( \tau = t\omega_e \) obtained by rate equation simulations using MD-validated rate coefficients for three-body recombination, collisional ionization and Rydberg energy level redistribution developed by Pohl and coworkers [55]. For charged-particle densities of \( 10^9 \) and \( 10^{12} \text{ cm}^{-3} \), simulations using a dynamic thermal upper limit scale well for 500 plasma periods. Simulations using a fixed value of \( n_{\text{max}} \) scale a little less well. The slightly higher temperature track for simulations with a fixed threshold arises as a consequence of three-body recombination into levels that are suppressed by a dynamic thermal threshold.

Classical scaling begins to break down in simulations with a dynamical threshold for scaled times longer than 1000 plasma periods because simulations at high density pile up
population in $n_{\text{min}}$. Thus, for higher densities, a Rydberg manifold that extends from thermal ionization threshold down to $n_{\text{min}} = 10$ is too narrow to support quantitative scaling beyond $\tau = 1000$. Calculations described below use the evolving electron temperature to determine $n_{\text{max}}$ dynamically by applying the thermal criterion, and remain mindful of the apparent importance of levels of low principal quantum number to accurately characterize the relaxation of systems at higher density and temperature.

### 8.2.2 Plasma Created by Penning Ionization

As first shown in earlier chapters, a cold gas excited to form a sufficient initial density of Rydberg atoms in a state $n_0$ evolves to form an ultracold plasma with properties comparable to plasmas formed by direct photoionization. Strong dipole-dipole interactions initiate this process by causing Penning ionization to occur for pairs of excited atoms with nearest neighbour distances within a few orbital diameters [48].

\[
A^{**}(n_0) + A^{**}(n_0) \rightarrow A^*(n^' < n_0) + A^+ + e^- (8.9)
\]

To briefly reiterated the important points, Penning ionization (8.9) produces a distribution of companion particles in lower-energy Rydberg states and energy conservation requires the neutral products of this process to exist in states of principal quantum number no higher than $n_0/\sqrt{2}$. The distribution of final states over $n$ directly reflects the distribution of Penning electron kinetic energies, and thus the temperature of the Penning electrons.

As discussed by Robicheaux [48], this long-range Coulomb interaction favours the production of threshold electrons, and in a classical Monte Carlo model for Penning ionization, he finds that $n$ declines from its maximum value as $n_0^{5}$. The mean kinetic energy $k_B T_e'$ of the Penning electrons relates accordingly to the initial Rydberg binding energy: $(3/2)k_B T_e' \approx \mathcal{R}/2n_0^2$. For the purposes of rate equation simulations, we apply this model
to estimate initial electron temperatures following Penning ionization that range from 58 K for \( n_0 = 30 \) to 8 K for \( n_0 = 80 \).

Figure 8.2: Output of rate-equation calculations predicting the time variation of temperature (left) and electron density (right) for a neutral plasma formed by the evolution of a gas of Rydberg atoms of initial density \( 10^{12} \text{ cm}^{-3} \) and principal quantum number, \( n_0 = 50 \) (solid line), compared with the similar evolution of a fully ionized plasma prepared to have the same initial particle density and an electron temperature of 21 K (dashed line) as determined by Penning ionization from \( n_0 = 50 \). Note that the timescale on the right is expanded by a factor of 10.

It is interesting to compare the evolution of electron temperature and density for simple atomic plasmas prepared by direct ionization and from a Rydberg gas by Penning ionization followed by electron-impact avalanche. Figure 8.2 plots the results of a rate equation calculation that simulates the evolution of an initial Rydberg gas of density \( \rho_R = 10^{12} \text{ cm}^{-3} \) and principal quantum number \( n_0 = 50 \). At \( t = 0 \), applying the Robicheaux model, we assume the system to have instantaneously formed a gas of Penning electrons at a density of \( \rho_e = 10^{11} \text{ cm}^{-3} \) and initial temperature, \( T_e = 21 \text{ K} \). For comparison, this figure shows the temperature and electron density evolution for a fully ionized plasma of the same particle density with the same initial electron temperature.

Starting from these initial conditions, collisions with Penning electrons redistribute population in the manifold of Rydberg states by an avalanche of up-pumping and ionizing collisions. An effect of this appears in the right-hand frame of Figure 8.2 as a 10 ns rise...
of free electron density in the plasma formed by the Rydberg gas. On a timescale about 50 times shorter than this, the free electron density of the fully ionized plasma falls, owing to the formation of high Rydberg states by three-body recombination. After these initial transients, the electron densities in both systems relax with comparable rates to Saha quasi equilibria in which $k_{\text{ion}}$ balances $k_{\text{TBR}}$.

In the left frame of Figure 8.2, the temperature of the electron gas created by avalanche from $n_0 = 50$ shows a short induction, but then rises faster to overshoot the temperature of the evolving photoionized plasma. We can understand the initial spike in electron energization as a consequence of the collisional relaxation of Rydberg states downward from $n_0 = 50$. As the two systems settle to quasi equilibrium, the electron temperature of the plasma formed by avalanche from Rydberg states falls to a lower value. This simply reflects the fact that a population of neutral molecules prepared with $n_0 = 50$ starts with less total energy than a comparable sample of ions and free electrons.

The early-time evolution of the state-selected Rydberg gas to plasma depends to some degree on its initial quantum number. The value of $n_0$ determines the orbital radius, which governs the fraction of molecules with nearest neighbour distances small enough to permit rapid Penning ionization. $n_0$ also determines the initial binding energy, which, as noted above, regulates the initial energy of the Penning electrons.

In order to model these dynamics, we gauge Robicheaux’s critical distance for Penning ionization in units of orbital diameter, against the Erlang distribution of nearest-neighbour distances [94]. Table 8.1 summarizes the Penning fractions and electron temperatures we determine for various values of $n_0$ for use in rate equation models to simulate this initial phase of plasma formation. The Robicheaux model predicts that both the Penning fraction and the initial electron temperature vary strongly with the initial principal quantum number of the Rydberg gas.

Figure 8.3 shows how these strongly varying starting conditions affect the growth of charged particle density and electron temperature as an atomic Rydberg gas evolves
Table 8.1: Fraction of the initial Rydberg gas density converted by Penning ionization to form ions and free electrons with an initial average energy described by $T_e(0)$. Penning fraction determined as 0.9 times the number of nearest neighbour pairs separated by 1.8 times the orbital diameter at $n_0$, as a fraction of the total gas density.

<table>
<thead>
<tr>
<th>$n_0$</th>
<th>Penning fraction</th>
<th>$T_e(0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.007</td>
<td>58</td>
</tr>
<tr>
<td>35</td>
<td>0.016</td>
<td>43</td>
</tr>
<tr>
<td>40</td>
<td>0.036</td>
<td>33</td>
</tr>
<tr>
<td>50</td>
<td>0.12</td>
<td>21</td>
</tr>
<tr>
<td>60</td>
<td>0.28</td>
<td>15</td>
</tr>
</tbody>
</table>

Remarkably, we see very little difference in the properties of the plasma that forms.

For $n_0 = 30$, Penning ionization produces a very small number of electrons. This population drives a slow collisional process that spreads population to principal quantum numbers above and below this initial level. The very first transitions down release more energy than is absorbed by the first step up. This causes a small initial increase...
in the temperature of the free electrons. Thereafter, the Penning electrons serve simply as a medium to transfer energy from down-pumping collisions to drive transitions up the Rydberg manifold, and the electron temperature remains relatively constant for a time.

This phase ends with the appearance of electrons released by collisional ionization. The rising population of high-$n$ Rydberg states relaxes to quasi equilibrium with free electrons, and the energy released by relaxing low-$n$ levels begins to heat those electrons. The electron temperature increases rapidly until the downward-moving Rydberg population reaches a level of principal quantum number for which the collisional deactivation cross section becomes insignificant.

Selecting a higher value of $n_0$, creates many more Penning electrons, and the initial collisional redistribution of the Rydberg level population remaining in $n_0$ proceeds at a much faster rate. Initially, the downward cascade of Rydberg level population releases far more energy than that consumed by collisional ionization, and, with less Rydberg excitation required, a rapid rise in electron density and temperature begins sooner. The $T_e$ curves for lower values of $n_0$ overshoot those for higher $n_0$ because the relaxation of population to low-$n$ transfers energy to a lagging density of free electrons.

However, three-body recombination soon creates a quasi equilibrium, and the population redistributed over the manifold of higher Rydberg states exhibits a similar partition between free charges and excited neutrals regardless of $n_0$. Curves cross as relaxation gives rise to a steady-state population distribution and electron temperature regulated by the total energy of excitation above the ground state, which, in relative terms, varies only slightly with $n_0$ over this range.

The kinetic model, as developed thus far, describes fast relaxation to quasi equilibrium as it might occur in the spatially homogeneous core of a particularly dense atomic plasma. It predicts steady states of relatively high electron temperature. The collisional deactivation of low-$n$ Rydberg states have the greatest heating effect. The relaxation of, as few as one-percent of the excited atoms to the neutral ground state releases enough
energy to raise the electron temperature to more than 1,000 K. Thus, low-$n$ inelastic cross sections play an important role in the energy balance.

Also important, even for the simplest atomic systems, are dissipative effects that have so far been neglected. For example, at low electron density, low-$n$ radiative emission competes with collisional deactivation, and this depletes the total energy of the plasma. A molecule can radiate as well. But, in a system like NO, predissociation occurs faster than photon emission, and it is important to consider the effect of such a dissipation channel on ultracold plasma evolution dynamics. The next section turns to simulations that examine this question.

8.3 Molecular Features

8.3.1 Predissociation

Predissociation of NO$^*$($n$) occurs when the bound Rydberg electron collides with the many-electron molecular ion core. In any such close-coupled collision, the Coulomb energy available to drive internuclear separation exceeds that of a typical chemical bond by a factor of three or more. The predissociation rate depends on frequency of such collisions [95], or the close-coupled electron probability density, which scales with $n$ as the Bohr frequency, $\nu = 2R\hbar^{-1}n^{-3}$. Orbital angular momentum matters too: Angular momentum barriers exclude small radial distances for larger values of $\ell$, and so dilution of the low-$\ell$ subspace further reduces the predissociation rate with increasing $n$.

We incorporate these characteristics of Rydberg-valence coupling in a simple predissociation model for NO. In this model, we assume that inelastic electron-Rydberg collisions populate states at each $n$ statistically. Only low-$\ell$ states decay with appreciable rates. We take these rates from the model developed by Gallagher and coworkers [87], patterned on the work of Bixon and Jortner [40]. Thus, for a given $n$, we calculate a $k_{PD}(n)$ from
the statistically-weighted sum of \( \ell \)-dependent rate constants, \( k_\ell = 0.014, 0.046, 0.029 \) and 0.0012 in atomic units for \( \ell \) from 0 to 3, and 0.00003 for \( \ell \geq 4 \), scaled by \( n^{-3} \):

\[
k_{PD}(n) = \frac{\sum_\ell (2\ell + 1)k_\ell}{n^2} \frac{4.13 \times 10^{16} \text{s}^{-1}}{2\pi n^3}
\]

This elementary algorithm predicts a predissociation rate constant at \( n = 10 \) of \( 2 \times 10^{10} \) s\(^{-1} \), and decay times for levels near \( n = 50 \) of about 200 ns, in accord with observations for NO states in this range, when prepared by broad-band excitation in the presence of an \( \ell \)-mixing electric field \([40, 85, 86]\).

Figure 8.4: Output of rate-equation calculations comparing the variation in electron temperature and density for a neutral plasma formed by a gas of predissociating Rydberg molecules excited to \( n_0=50 \) at an initial particle density of \( 10^{12} \text{ cm}^{-3} \) (solid line) compared with that for a gas of the same initial conditions without predissociation (dashed line). The dot-dashed line show the effect of including dissociative recombination with predissociation.

We add a unimolecular decay term, \( k_{PD}(n_i) \), to the rate expression for each Rydberg level, \( n_i \), as shown in Eqs.8.6. N–O bond scission removes both population and potential energy from the relaxing distribution of ions, electrons and NO Rydberg molecules.

Figure 8.4 shows results comparing the time dependence of the electron temperature and density for systems with, and without predissociation. At a density of \( 10^{12} \text{ cm}^{-3} \) the avalanche to ions and electrons (c.f. Figure 8.3) occurs on a timescale faster than
predissociation for all but the lowest values of \( n \). So, initially, the two systems evolve the same. However, as the predissociating plasma approaches quasi equilibrium, the Rydberg population descends to lower-\( n \). Here, predissociation rates are faster. The deactivation of these low-\( n \) states represents a large source of energy for the electron gas, so their predissociation at first retards the rate of electron heating.

As time proceeds, the plasma without predissociation quickly reaches a condition of quasi equilibrium, while the predissociating plasma continues to heat. The removal of population from lower levels by predissociation pulls a compensating flux of population downward, and with time this pumps energy to the electrons. Thus, the simple addition of predissociation to the matrix of rate equations leads ultimately to further plasma heating. We can expect other intrinsic bound-state rate processes, such as radiative emission, to have a similar effect.

### 8.3.2 Dissociative Recombination

Dissociative recombination of cations with electrons simply reduces the charged-particle density. This has no direct effect on electron temperature. However, much like the predissociative loss of low-\( n \) molecules draws population down the Rydberg ladder, dissociative recombination, diminishes the number of ions and electrons in quasi equilibrium with high-\( n \) levels at the top of the Rydberg manifold. This pulls population up the Rydberg ladder, and, as a result, decreases the flow of energy to the electrons.

Experiments and theory provide a reliable estimate of \( k_{\text{DR}} \) as a function of electron temperature \([89]\), and it is straightforward to incorporate direct dissociative recombination as an additional loss channel for ions and electrons in a coupled rate equation calculation. We obtain an expression for the dissociative recombination rate constant as a function of temperature for this purpose by fitting the theoretical results of Schneider et al. as:

\[
k_{\text{DR}} = 6.91 \times 10^{-6} (T_e)^{-0.5146}
\]

(8.11)
Figure 8.4 includes curves showing the effect of opening a channel for dissociative recombination in our non-expanding model plasma. Evidently, the addition of DR serves to suppresses the temperature increase associated with the adjustment of the quasi equilibrium to predissociation.

8.3.3 Steady-State Kinetics of Predissociation

The electron-Rydberg avalanche and subsequent relaxation to plasma quasi equilibrium form a complex sequence of coupled reactions. Plasma decay to neutral products occurs both by direct dissociative recombination and by the predissociation of molecules in collisionally coupled Rydberg states. The dissociative recombination rate in a real system continuously adjusts to the local charged-particle density. Kinetic fits to experimental results show that in practice expansion quickly quenches the DR channel, while predissociation continues as long as Rydberg states are present.

To isolate the steady-state effect of predissociation on plasma dissipation, we run rate equation calculations without dissociative recombination. Figure 8.5 details the formation of N- and O-atom predissociation products as a function of $n$ for Rydberg levels from $n = 10$ ($n_{\text{min}}$) to 42.

Early in the approach to steady state, lower levels gain population at the inelastic collision rate. This fast process determines the initial rate of neutral atom production; N and O atoms appear at the rate with which dissociating levels fill. As the system nears quasi equilibrium, products form through a system of strongly coupled parallel reactions. Under these conditions, the decay rate in all channels is determined by the overall rate at which the total dissociation consumes neutral molecules.

Figure 8.4 displays this overall rate as seen in the time-variation of electron density. The electron density decay clearly matches the rise in neutral atoms produced by individual Rydberg levels in steady state. The initial rate of this decay yields a second-order quasi-equilibrium rate constant, $k_{qe} = 1.4 \times 10^{-7}$ cm$^3$ s$^{-1}$, which is about an order of magnitude
Figure 8.5: Output of rate-equation calculations detailing the density of products as a function of time formed by the predissociation of Rydberg levels $n$ for levels from $n = 22$ to 10 (left) and $n = 22$ to 42 (right), in each case reading from top to bottom. Flattening of its time dependence at high $n$ occurs as the thermal ionization threshold falls below the energy of a level with increasing electron temperature.

smaller than the rate constant for direct dissociative recombination, as determined by theory for this range of electron temperature [89]. Previous published work not recounted in this thesis has argued based on representative values for $k_{\text{TBR}}$, $k_{\text{ion}}$ and $k_{\text{PD}}$, that $k_{\text{qe}}$ lags $k_{\text{DR}}$ in the NO ultracold plasma [84]. Present simulations confirm this assessment.

As noted above, decreasing charged-particle density in a realistic, expanding plasma can be expected to quickly suppress the direct dissociative recombination channel, while molecular Rydberg states formed by three-body recombination continue to predissociate. Interestingly, we note that, beyond 1 $\mu$s, the time dependence of the electron density in this simulation exhibits a first order decay with a rate constant of $6 \times 10^4$ s$^{-1}$.

Molecular NO ultracold plasmas produced experimentally show a very similar first-order decay, which has been attributed to electron evaporation [84]. Work in this chapter suggests instead that this behaviour is quite consistent with steady-state predissociation. The time constant predicted by simulations for the present predissociation model agree well with the dissipation observed experimentally.

A complete model for the kinetic properties of a molecular ultracold plasma could
include additional channels of energy redistribution and dissipation. But, we have yet to find a process that alters the basic conclusions that can be drawn from the present results.

For example, collisions of electrons with NO Rydberg molecules could give rise to perturbations that facilitate Rydberg-valence internal conversion and accelerate predissociation. Simulations show that such processes suppress the avalanche production of free electrons and retard electron heating, initially. The system, however, then simply behaves as a reduced-density plasma, in which the pull of dissipative reaction channels at lower principal quantum numbers sustains relaxation and drives further electron heating on a longer timescale.

It is also possible that the large amount of energy transferred to an electron by a low-$n$ super-elastic collision causes it to escape the plasma before thermalizing with the free-electron bath. However, a simple calculation of the electrostatic potential as a function of excess charge for a $1 \text{ mm}^3$ plasma volume shows that even the most energetic such electron cannot escape a plasma with only a small fraction of one-percent charge excess.

This of course changes somewhat with plasma expansion, and this inevitable reduction in density can also cause other collisional processes affecting the plasma steady state to freeze out. With dissociation, the early stage of molecular plasma evolution could proceed under conditions of ion and even electron correlation, and collisional properties associated with this could affect ionization and recombination rates in ways that shift the quasi equilibrium electron density and temperature.

8.4 Summary

Coupled rate-equation simulations show that a kinetic model accounting for state-detailed rate processes in the evolution of a molecular Rydberg gas to plasma accords with a steady-state picture of Rydberg predissociation and its contribution to plasma dissipation. Unimolecular decay rates in this steady state are relatively slow. For this reason, direct
dissociative recombination can be expected to dominate the early stage of plasma decay, giving way to a pseudo first-order decomposition under the reduced density conditions of an expanded plasma.

Experiments exhibit charged-particle decay patterns that support this decomposition hierarchy. Less in keeping with experiment, model electron temperatures range substantially above 100 K. In simulations, super-elastic collisions with low-\( n \) Rydberg states drive this heating. Dissociation depletes the relaxing population of these molecules. This retards heating in the early approach to quasi equilibrium, but redistribution to fill this hole in the collisionally coupled Rydberg level system ultimately promotes heating. It remains to be seen whether the effects of expansion on these collisional kinetics, perhaps in concert with the effects of charged-particle correlation on three-body recombination and collisional ionization, can act to sustain a lower-temperature quasi equilibrium.
Chapter 9

Conclusions

We have described the formation of an ultracold molecular plasma. We have validated our findings with a combination of pulsed-field ionization and field-free expansion experiments. Expansion of the plasma has been observed by two different experiments: slowing the molecular beam velocity by seeding with heavier noble gases, and translation of the detector stack along the axis of observation, using the moveable-grid assembly. The anomalous expansion of this plasma into vacuum suggests considerably lower electron energies and higher ion correlation than atomic plasmas created in MOTs when fitted to solutions to the Vlasov equation.

The entropic favourability of the plasma state drives the spontaneous conversion from a dense Rydberg gas. Simulation models have shown that little memory remains of the initial gateway state following early-time collision dynamics. However, more recent experiments reveal a select range of $\approx 20$ principal quantum numbers that form the most durable plasma system. Evidently, the plasma formation mechanism acts to minimize plasma degradation through loss channels during the early-time energy redistribution. Molecular properties undoubtedly play a pivotal role in this effect; verifying the molecular beam method for the formation of an atomic UCP will answer some questions as to exactly what role molecules play.

Exploring a novel physical state such as this one provides both rich discovery and challenging obstacles. Our toolbox used to interpret experimental results has grown exponentially. That is to say, early experiments that exhausted ideas on our current perspective of ultracold plasmas at the time generated extensive data sets that remain uninterpreted.
I will address some of the more pertinent experiments that aim to substantially enhance our understanding.

**Radio frequency absorption.** Progress in experiments observing the radio-frequency absorption of our plasma is expected to be underway shortly. Preliminary studies have suggested the plasma absorbs radiation over the MHz range of frequencies by heating resonant electrons at the Langmuir frequency. The original ZEKE-chamber setup restricted the \( \mathbf{k} \)-vector of the radiation to point cylindrically outward in a \( \mathbf{\bar{r}} = x\hat{x} + y\hat{y} \) direction, coupling the electric field to the detection axis. New electrodes aim to resolve this problem by rotating the electric field vector by 90°. Reliable RF-absorption measurements will provide more conclusive evidence for the extent of correlation and particle densities.

**Atomic UCPs formed in a supersonic expansion.** At the time of writing this thesis, experiments were underway that examined the potential for forming UCPs from a supersonic expansion of xenon. If it is observed that plasmas do indeed form by this method would provide an immediate bridge to the atomic MOT field. Direct comparison between experimental results could then be more readily applied.

**Two-dimensional plasma imaging.** A 2D imaging device consisting of a phosphor screen and CCD imaging camera is currently being built in the TOF chamber. Once completed, it will provide important information pertaining to the spatial distribution of plasma particles. To a first approximation, spherical symmetry is usually applied throughout the analysis found in this thesis, when, in fact, the shape of the plasma created experimentally is more ellipsoidal. The extent to which spherical symmetry applies depends on the aspect ratio of the ellipse, as well as plasma dynamics occurring in the fringes. 2D images will thus determine if our analysis requires more geometric fine-tuning. As well, it will give insight into molecular decay rates through dissociative recombination and the density effect this decay has on the overall evolution.
rydberg gas to an ultracold plasma in a seeded supersonic expansion of NO. *Phys.

plasma formed in a seeded supersonic molecular beam of NO. *Phys. Rev. A*, 79:062706,
Jun 2009.

E. R. Grant. On the formation and decay of a molecular ultracold plasma. *Journal

between the coupled rate equation and molecular dynamics models for the evolution
of ultracold neutral plasma. *Journal of Physics B: Atomic, Molecular and Optical

evolution of a molecular ultracold plasma. *Journal of Physics B: Atomic, Molecular


Appendix A

Plasma Properties: Derivations

A.1 Debye Screening Length

Plasmas have the ability to screen external fields since they are composed of mobile, charged particles that can redistribute themselves to dissipate the field over a characteristic length called the Debye screening length.

Deriving this important parameter begins with the Poisson equation

$$\nabla \cdot \mathbf{E} = -\nabla^2 \Phi = 4\pi e (\rho_i - \rho_e) \quad (A.1)$$

where the gradient ($\nabla$) of the potential $\phi$ provides the electric field as $\mathbf{E} = -\nabla \Phi$, and number density of electrons and single-charged ions is given by $n_e$ and $n_i$, respectively. Assuming thermodynamic equilibration, the electron and ion number densities will follow the Boltzmann equation,

$$\rho_{\alpha} = \rho_{0\alpha} \exp\left(-e_{\alpha} \Phi(r)/k_B T_{\alpha}\right) \quad (A.2)$$

for the plasma particle $\alpha$ with an average number density $\rho_{0\alpha}$ and temperature $T_{\alpha}$. Substituting A.2 into A.1 and expanding the exponential terms in Taylor series and keeping the only the first few terms the Poisson equation can be written

$$\nabla^2 \Phi = \frac{4\pi e^2}{\epsilon k_B} \left[ \frac{1}{T_i} + \frac{1}{T_e} \right] \Phi. \quad (A.3)$$

Placing a test charge in a plasma and defining its position to be the origin, the resulting
potential can be obtained form the the solution of A.3 and is called the Yukawa potential:

\[
\Phi(r) = \frac{e}{4\pi \epsilon_0 r} \exp \left( -\frac{r}{\lambda_D} \right)
\]  

(A.4)

for a distance \( r \). Here \( \lambda_D \) defines the distance over which the charge will be screened, explicitly given as \( \lambda_D = \sqrt{\frac{4\pi e^2}{\epsilon_0 k_B} \left[ \frac{1}{T_i} + \frac{1}{T_e} \right]} \).
A.2 Plasma Frequency

Langmuir oscillations are fundamental plasma collective modes caused by the periodic displacement of electrons in 1D about some equilibrium position, described by $\Delta r$ and $r_0$, respectively, in Fig. A.1, when perturbed by an external field, $E$.

Figure A.1: Langmuir oscillations represent the periodic motion of electrons about an equilibrium position, $r_0$.

The equation of motion for an individual electron becomes,

$$m_e \frac{d^2 (r + \Delta r)}{dt^2} = -eE$$

(A.5)

and the electric field strength corresponds to the Poisson equation for an infinite plasma volume with a quasineutral, uniform density,

$$\frac{dE}{dx} = 4\pi e(\rho_i - \rho_e)$$

(A.6)

which can be integrated over $r_f - r_i = \Delta r$ and combined with Eq. A.5 to give,

$$\frac{d^2 \Delta r}{dt} = -\omega_{pe}^2 \Delta r.$$  

(A.7)

Here, the electron plasma frequency is defined as $\omega_{pe} = \sqrt{4\pi \rho_0 e^2 / m_e}$ and $\rho_0$ is the average charged particle number density. The derivation is analogous for the ion component, leading to $\omega_{pi} = \sqrt{4\pi \rho_0 e^2 / m_i}$. Plasma electron frequency is commonly used to reduce the time-coordinate to values characteristic of average electron plasma motion.
A.3 Electric Potential from Vlasov Equations

Electric potential is most commonly determined by solving the Poisson equation. In the quasineutral approximation finding another formula for the potential is necessary. Starting from the Vlasov equation, I provide a recount of the derivation that follows [? ].

The one-particle phase-space density, \( f_\alpha(\vec{r}_\alpha, \vec{v}_\alpha, t) \), can be determined by the Vlasov equation,

\[
\frac{\partial f_\alpha}{\partial t} + \vec{v}_\alpha \frac{\partial f_\alpha}{\partial \vec{r}_\alpha} + \frac{q_\alpha}{m_\alpha} \frac{\partial f_\alpha}{\partial \vec{v}_\alpha} \frac{\partial \Phi(\vec{r})}{\partial \vec{r}_\alpha} = 0 \tag{A.8}
\]

which describes the the evolution for electrons, \( \alpha = e \), and ions, \( \alpha = i \), in a collisionless plasma. Particle charge and mass are given by \( q_\alpha \) and \( m_\alpha \), respectively. Each component is therefore coupled through the electric field term which can be written as the gradient of the potential, \( -\nabla \Phi(\vec{r}) \). To arrive at analytical solutions describing the time-evolution of macroscopic plasma parameters adhering to Eq. A.8 requires the condition of quasineutrality, \( \rho_i \approx \rho_e \). To apply this approximation in a meaningful way requires another equation for the electric field instead of Equation A.1, which would reduce to the Laplace equation. A new form can be obtained by multiplying Eq. A.8 by particle velocity, \( \vec{v}_\alpha \), and integrating over velocities which gives the first moment of Vlasov equation. Here we introduce a macroscopic plasma property, the hydrodynamic flow,

\[
\vec{u}_\alpha n_\alpha = \int \vec{v}_\alpha f_\alpha(\vec{r}, \vec{v}, t) d\vec{v}_\alpha \tag{A.9}
\]

which includes the density, \( n_\alpha = \int f_\alpha d\vec{v}_\alpha \). The two first moment equations for ions and electrons are then subtracted from each other and leads to an equation for the electric field,

\[
\frac{\epsilon}{c} \frac{\partial \Phi}{\partial \vec{r}} = \left( \frac{1}{\rho_e/m_e + \rho_i/m_i} \right) \left[ \rho_e \left( \frac{\partial \vec{u}_e}{\partial t} + \vec{u}_e \frac{\partial \vec{u}_e}{\partial \vec{r}} \right) - \rho_i \left( \frac{\partial \vec{u}_i}{\partial t} + \vec{u}_i \frac{\partial \vec{u}_i}{\partial \vec{r}} \right) + \frac{\partial}{\partial \vec{r}} \left( \frac{P_e}{m_e} - \frac{P_i}{m_i} \right) \right] \tag{A.10}
\]
and applying the quasineutrality condition equates the first two terms in the square bracket and removes them from the equation. $\mathcal{P}_\alpha$ is the pressure tensor which reduces to the scalar field, $\mathcal{P}_\alpha = k_B T_\alpha n_\alpha$, for isotropic thermal velocity distributions. The potential can then be written,

$$
\rho_e \frac{\partial \Phi}{\partial \vec{r}} \approx k_B T_e \frac{1}{\rho_e} \frac{\partial \rho_e}{\partial \vec{r}} \approx k_B T_e \frac{1}{\rho_i} \frac{\partial \rho_i}{\partial \vec{r}} \quad (A.11)
$$

where the electron distribution responds instantaneously to ion dynamics in the adiabatic approximation.
A.4 Plasma Collisional Terms for Local Thermodynamic Equilibrium (LTE)

Figure A.2 illustrates the collision event defined by a charged particle of mass $m_1$ colliding with stationary particle of mass $m_2$, taken in the center-of-mass frame, $m_r = \mathbf{r}_1m_1 + \mathbf{r}_2m_2$, at impact parameter $b$. 

![Diagram of Coulomb collision](image)

Figure A.2: Illustration and definition of parameters for Coulomb collision involving two charged particles.

At this point we can introduce the collision parameter called the Landau length which is the distance where the potential energy equals the kinetic energy for two single-charged ($q = e$) particles:

$$
\lambda_L = \frac{e^2}{4\pi\epsilon_0 k_B T} 
$$

and describes the typical scale for Coulomb collisions. Backscattering collisions occur with a cross-section,

$$
\sigma_{90^\circ} = \pi \lambda_L^2.
$$
In the semi-classical approach\(^2\) scattering can be described for an incident particle with wavefunction,

\[
\varphi_{\text{inc}}(k, \vec{r}) = \varphi_0 \exp(i k \cdot \vec{r}) \tag{A.14}
\]
as having a probability flux \(j_{\text{inc}} = \left(\frac{\hbar}{2\pi m}\right)k\) and a scattered probability flux \(j_{\text{scat}} = \left(\frac{\hbar}{2\pi m}\right)\frac{|f(k', k)|^2}{r^2} k \hat{r}\) where \(|f(k', k)|^2\) is a function that provides the differential cross-section for particles with incident momentum \(h\vec{k}\) to be scatter into states within solid angle element \(d\Omega\) around the momentum vector \(h\vec{k}'\). Therefore, we can write the number of particles scattered per unit time into \(d\Omega\), divided by the incident flux as,

\[
\frac{d\sigma}{d\Omega} = |f(k', k)|^2 \tag{A.15}
\]

Assuming only collisions where total energy is conserved, a Debye screening Coulomb potential as in Eq. (A.4), and employing an adiabatic approximation for the scattered wave function that approximates it to the incident wavefunction, we can write:

\[
f(k', k) = -\frac{m_r}{2\pi \hbar^2} \int \exp[i(k - k') \cdot \vec{r}'] \Phi(\vec{r}') d^3 \vec{r}' \tag{A.16}
\]

where \(m\) is the scattering particle mass. Substituting the wave-vector \(\kappa \equiv k - k'\) and assuming spherical symmetry about the scattering event, Eq.(A.16) becomes,

\[
f(k', k) = -\frac{m_r}{2\pi \hbar^2} \int \int \int \exp[i \kappa r' \cos \theta] \Phi(\vec{r}') r'^2 d\theta d\phi \tag{A.17}
\]

and can be evaluated to yield,

\[
f(k', k) = -\frac{m_r}{2\pi \hbar^2} \int_0^\infty r' \Phi(r') \sin(\kappa r') dr'. \tag{A.18}
\]

\(^2\)Remarkably, quantum mechanical treatment will yield the same result as the classical derivation for a Coulomb scattering event as a consequence of the \(1/r^2\) scaling of the force.
It can be shown that

$$\kappa \equiv |k - k'| = 2k \sin(\chi/2) \quad (A.19)$$

where $\chi$ is the scattering angle as defined in Fig. A.2. Substituting Eq. (A.4) for $\Phi(r')$ into Eq. (A.18) and using the integration,

$$\int_0^\infty \exp[-r'/\lambda_D] \sin(\kappa r')dr' = \frac{\kappa}{\lambda_D^2 + \kappa^2} \quad (A.20)$$

leads to the differential scattering cross-section by a Yukawa potential,

$$\frac{d\sigma}{d\Omega} = \left[ \frac{e^2/4\pi\epsilon_0}{\hbar^2/(2m_r\lambda_D^2) + 2m_rv^2\sin^2(\chi/2)} \right]^2 \quad (A.21)$$

which replaced the wavenumber by $\hbar k = |p| = |m_r \vec{v}|$.

The cumulative of many small angle collision events dominates the contribution to the effective total cross section,

$$\sigma_{eff} = \int_{\Omega} \frac{d\sigma}{d\Omega} d\Omega = \sigma_{90^\circ} \cdot \ln \Lambda \quad (A.22)$$

which introduces the Coulomb logarithm $\ln \lambda \equiv \ln(b_{\text{max}}/b_{\text{min}})$.

The total Coulomb collision cross section can be written as,

$$\sigma_{eff} = \sigma_{tot} = \pi \ln \Lambda \left( \frac{e^2}{4\pi\epsilon_0 k_B T} \right)^2 \quad (A.23)$$

for a particle of density $\rho$ and temperature $T$. The Coulomb logarithm for a Yukawa potential can be written,

$$\ln \Lambda \cong \ln \frac{b_{\text{max}}}{b_{\text{min}}} \cong \ln \frac{\lambda_D}{e^2/k_B T} \quad (A.24)$$

which says the largest effective impact parameter for a small angle collision will be the
distance over which the particle field has a significant magnitude, while the smallest impact parameter will be the distance of closest approach of a thermal particle with temperature \( T \). Under the assumption the scattering particle is incident upon a stationary thermal bath of particles, the reduced mass \( m_r \) can be written as \( m_\alpha \).

Collision times can then be calculated from \( \tau = 1/(\sigma \rho v_{\text{thermal}}) \), with \( v_{\text{thermal}} = (3k_B T/m)^{1/2} \). This leads to the formula:

\[
\tau_{ee} \equiv \tau_{ei} \simeq \frac{16\pi e_0^2 m_e^{1/2} (k_B T_e)^{3/2}}{\sqrt{3} \rho_e e^4 \ln \Lambda}.
\] (A.25)
Appendix B

Rate Equation Simulation Code

B.1 Summary

Provided below is the complete code for ordinary differential equation integration tracking electron and Rydberg densities in time. Within the class `PlasmaSimExp.SetRateFunctions` is the option to call a non-expanding (`mkDrhoDtPINum`) or expanding plasma with ion correlation (`DNumberDtexp_corr`) or without (`DNumberDtexp`). All text in italics is comment-code, while all the red coloured text is C-language code passed to a gcc compiler through the `weave` module native to SciPy. Since Python is a pre-compiled language, the option to add compiled code greatly enhances the performance of demanding calculations (i.e. hours to seconds).

B.1.1 `mkDrhoDtPINum`

This class module calculates the derivative of the set of coupled rate equations tracking the electron and Rydberg level density of an infinite, non-expanding plasma. Chapter 7 provides a detailed explanation.

B.1.2 `mkDrhoDtexp_corr`

Here, a collisional, expanding plasma including ion correlation is considered. The theoretical description for this model can be found in [96? ]. Basically, it solves for the time evolution of macroscopic plasma parameters for a self-similar plasma expansion
derived from kinetic equations starting from the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy. Equations solved by this module include:

\[
\frac{d\sigma^2}{dt} = 2\gamma\sigma^2, \tag{B.1}
\]

\[
\frac{d\gamma}{dt} = \frac{N_i}{N_i + N_{\text{bound}}} \frac{k_B T_e + k_B T_i + (1/3)U_{ii}}{m_i \sigma^2} - \gamma^2, \tag{B.2}
\]

\[
\frac{d(k_B T_i)}{dt} = -2\gamma k_B T_i - \frac{2}{3} \gamma U_{ii} - \frac{2}{3} \frac{dU_{ii}}{dt}, \tag{B.3}
\]

\[
\frac{dN_A(n)}{dt} = -\sum_j k_{Aj} N_e N_A(n) + \sum_j k_{jn} N_e N_j - k_{\text{ion}}^n N_e N_A(n) + k_{\text{thr}}^n N_e^3 - k_{PD}(n) N_A(n), \tag{B.4}
\]

\[
\frac{dN_e}{dt} = \frac{dN_i}{dt} = \sum_n k_{\text{ion}} N_e N_A(n) - \sum_n k_{\text{thr}}^n N_e^3 - k_{DR} N_e^2, \tag{B.5}
\]

and electron temperature is calculated at each time step using the energy conservation,

\[
E_{\text{tot}}(t) = E_{\text{tot}}(0) = 3 \frac{k_B}{2} N_e(t) [T_e(t) + T_i(t) + m_i \gamma(t)^2 \sigma(t)^2] \tag{B.7}
\]

\[
= \sum_n N_A(n, t) \frac{R}{n^2} - \frac{3}{2} k_B T_e(t) N_e^{DR}(t) + \sum_n \frac{R N_A^{PD}(n, t)}{n^2}. \tag{B.8}
\]

\(N_A(n)\) is the Rydberg molecule particle number at principal quantum number \(n\), and \(N_e = N_i\) are the electron and ion particle numbers in the quasineutral approximation. The ion-ion correlation energy is represented by \(U_{ii}\) the correlation-time approximation, with a time derivative given by,
\[
\frac{dU_{ii}}{dt} \approx -\frac{U_{ii}(t) - U_{ii}^{eq}}{\omega_{\pi i}^{-1}}
\]  
(B.9)

\[U_{ii}^{eq} = k_B T_i \Gamma_i \left( \tilde{u} + \frac{\kappa}{2} \right)\]  
(B.10)

this is where \(U_{ii}^{eq}\) is the equilibrium correlation value. Eq. B.9 approximates the ion-ion correlation time derivative as the relaxation towards equilibrium correlation of a one-component plasma in the thermodynamic equilibrium. Relaxation time is scaled to the inverse ion plasma frequency, \(\omega_{\pi i}^{-1}\). Eq. B.10 is used to calculate the equilibrium correlation value and is dependent on the parameters \(\kappa = a_{WS}/\lambda_D\) and \(\tilde{u}\), where \(\tilde{u}\) is obtained from tables from molecular dynamics simulations.

The inclusion of molecular predissociation and dissociative recombination into the model above differentiates it from the atomic model for which the theory was derived as originally reported in ??.

### B.1.3 \textit{mkDrhoDtexp}

This module considers expansion of a collisional plasma neglecting ion-ion correlation. Results from this simulation show early time dynamics that are similar to an expansionless plasma driven by inelastic collisions that turn off as the ions move and the density is reduced. Hence, it appears the Vlasov approximation for plasma expansion is quite adequate for times on the order of microseconds.
B.2  PlasmaSimExp.py

from scipy import weave
from scipy.weave import converters
from scipy.integrate import odeint,ode
from numpy import empty, where, array, zeros, vstack, append,
arange, linspace, savetxt, ones, shape,
isnan, concatenate
from math import exp, fabs, sqrt, pi, log
import doThings as dTh
from time import localtime, strftime
import cProfile
from scipy.special import erf
import doData as dD
import corr_uhat as corru
from constants_um import*

""
For initial popluation of just electrons:
1) must set TeInit!
2) nToStart = 0.
3) the second term in temp_elec should be zero if no
initial Rydberg population

To set include all pqn’s:
1) in mkDrhoDt function comment out ’try’ statement to find self.ncrit
2) set ’index’ equal to ’Number’ or number of pqn’s being used
3) ’tempCalc’ already sums over all pqn’s regardless

With no DR:
1) y[1] = 0

With DR:
1) remove comment line in DrhoDt for rho[1]
2) calcTemp() can be used for DR
3) use mkDrhoDtPI()
4) final temperature calculation should be calcTemp()

With DR/PD:
1) set y0 = MAKEynot(pennInd, 1) with 1 for appended PD-products
2) change ’odeint’ call to use mkDrhoDtPDDR()
3) change final temperature calculation to calcTempPDDR()""
To sum the Rydberg levels as a function of time, make and output array like:
rydbergs = ynew[extraNs:-1][::-1]
rydsum = rydbergs.sum(axis=0)
will rydsum(rydberg total population as function of time)

VERIFY

```python
if m3units == 1:
    rateFile = '<NumberRates.h>'
    FWHM = 400e-6 #meters

if um3units == 1:
    rateFile = '<NumberRates_um.h>'
    FWHM = 400 #micrometers
```

### Parameters
DensInit = 5.0e12 #cm^-3
nToStart = 50.0
NumofLevels = 110
#Robicheaux Numbers: 1e9: 101 + 28(n_max = 153) 163(n_max=187);
#1e11: 47(n_max = 71) 62(n_max=61)

#t = arange(1e-11, 4.02e-9, 2e-11)
tvec = linspace(0., 1e-7, num=6000)

TeInit = (1./3.)*Rydhc/(nToStart**2.*kB)  # 3/2 * kB * Te = Ryd/n^2 * 1/2

### reduced TBR rate factors
red1 = (echg**2.)/(4*pi*epsilon*kB)**(1.5)*(3.8e-3/0.019)
#linear part of curve \( \propto w_{pe} \Gamma^{-3} \)
red2 = (echg**2.)/(4*pi*epsilon*kB)**(4.5)*(0.03/0.019)
#constant rate of 0.03*wpe

nPenning = 0. #declaration NOT option: needed for purely electron/ion plasma
if nToStart:
    nPenning = round(nToStart/sqrt(2.))  #populate lower \( n' \) i.e.
    #\[ n + n \rightarrow n' + \text{NO}^+ + \text{e}^{-} \]
the range specified below is for principal quantum numbers that undergo higher rate of decay.
  i.e. incorporates some favourable decay coupling

```
range1 = 49.0
range2 = 65.0
```

tcritical = array((3.87443494731e-06, 3.98280389204e-06))
#array used to troubleshoot integration problems

laughs

########SWITCHES#########

pi_switch = 0
 correlation_switch = 1
 # set aijswitch to '0' or int(1) since it passes into C++ code
aijswitch = 0  # int(1)

laughs

Minimum: (2) 1 (electrons) + 1 (DR products)
Expansion with N and correlation: (7) 1 (electrons)
  + 1 (DR products) + 1 (sigma) + 1 (gamma) + 1 (Ti) + 1 (Te) + 1 (Uii)

if pi_switch:
    extraNs = 2
elif correlation_switch:
    extraNs = 7

laughs

####Parameters for Expansion####

sigma_0 = FWHM/(2.*sqrt(2.*log(2.)))  #meters

laughs

########Some Function Calls######
nPop0, ePop0 = dTh.pennFrac(nToStart, DensInit)
n_lst = dTh.nlistMK(10., NumofLevels)
pennInd = dTh.findncrit(n_lst, nPenning)
index1 = int(where(n_lst==range1)[0][0])
index2 = int(where(n_lst==range2)[0][0])

laughs

####Initialized Arrays######
#dPdrt = zeros( NumofLevels)
#newTemp = 0.
#eps_i = (1/n_lst[:])**2
#eps_f = eps_i
#knn = empty((NumofLevels,NumofLevels))

########################################################################
#Functions
########################################################################
def printTime():
    print strftime("%a, %d %b %Y %H:%M:%S", localtime())

def redok0(Temp):
    return float( echg**4./(kB*Temp*sqrt(emass*Rydhc))*
                   (1./(4.*pi*epsilon)**2.) )
    #’Rydhc’ is in J’s, 1e6 is converting m^-3 --> cm^-3

########################################################################
#Main Class
########################################################################
class SetRateFunctions:
    ""
    this class is used to take a particular density
    (rhoelectron,rhoelec) with a corresponding quantum
    number (unless it is rho_elec, or rho_DR) and to calculate
    the rates for it. Also trying to implement as much of ‘weave.inline()’
    as possible.
    ""

def __init__(self, kpdlist = None):
    ""
    Function to generate y-vector for scipy.odeint
    which represents y[0] being electron density,
    and the remaining y corresponding to density of
    quantum level ‘n’. **Amendment - rho_hat[1] is the DR loss**
    First unpackage parameters and then determine
    rates for each y[j]
    Number: number of quantum levels
    Te0: initial electron Temperature
    y00: initial density of free electrons
    (accounting for any initial population)
    nStart: initial quantum level (if any) having population
    init_Pop: initial density of nStart
    rho: density of particular level
    n: quantum number of level
#Switches

self.correlation = correlationswitch
self.nlist = n_lst
self.Number = NumofLevels
self.Te0 = TeInit
self.Te_t = TeInit
self.nStart = nToStart

#########Units########
if cm3units == 1:
    self.init_pop = nPop0  # initial n=nToStart density in cm^-3
    self.y00 = ePop0  # initial electron density in cm^-3
if m3units == 1:
    self.init_pop = nPop0*1e6
    self.y00 = ePop0*1e6
if um3units == 1:
    self.init_pop = nPop0*1e-12  # convert to um^-3
    self.y00 = ePop0*1e-12  # convert to um^-3

try:
    self.penn_ind = int(pennInd)
except TypeError:
    self.penn_ind = 0

if kpdlist.any():
    self.kpdarray = array(kpdlist)
    self.ncrit = round(sqrt(Rydhc/(kB*self.Te0)))
    self.temperatureArr = array(TeInit)
    self.tt = 0.0

####Conversions for Pohl 2011 paper from Gamma-ratios########
self.redTBRc1 = (4*pi*epsilon*kB)**1.5*0.195/(0.019*echg**3.)
#linear part of curve
self.redTBRc2 = (4.*pi*epsilon*kB/echg**2.)**(9./2.)*(0.03/0.019)
#--------------------------------------------------------------------------------
self.ncritch = self.ncrit

#Parameters for ion-ion correlation
self.Ti0 = 0.7
self.Ti_t = 0.0
self.Te_t = 0.0
self.Gammai = 0.0
self.Gammae = 0.0
self.IonDensity = 0.0
self.debye = 0.0
self.debye0 = 1./sqrt( echg**2.*self.y00/(epsilon*kB)*1./
    (self.Ti0+self.Te0) )
self.Gammai0 = echg**2./self.wigner_seitz(self.y00)*
    (4.*pi*epsilon)*kB*self.Ti0
self.sigma0 = sigma_0  # currently rho[2] = sigma^2
self.length = self.sigma0*5.  # cylinder length
self.Volume0 = self.Volume(sigma_0)
#self.Volume0 = self.VolumeCyl(sigma_0)
self.Uii0 = 0.0  # kB*sigma.Ti0*corru.what2(self.Gammai0)
#self.Uii0 = kB*sigma.Ti0*sigma.Gammai0*
#    (what(self.wigner_seitz(sigma.y00*1e6),
#    self.Gammai0) + self.wigner_seitz(sigma.y00*1e6)/
#    (2.*self.debye0))

self.rho0 = self.make_y0()
self.rydPenn,self.ryd0 = 0.0,0.0
if self.penn_ind:
    self.rydPenn = float(sum(self.rho0[extraNs :]
        self.penn_ind + extraNs]/
        n_lst[:self.penn_ind]**2.))
    self.ryd0 = float(self.Volume0*self.init_pop/self.nStart**2.)

def findncrit(self, ncritical, i = None):
    # i = start - 1
    try:
        i = where(n_lst == ncritical)[0][0]
    except IndexError:
        i = self.Number  # set the index in mkDrhoDt
        # equal to the number of
        # n-levels, if the critical
        # 'n' not available
        # (assumes it is too high)

    return i

def Volume(self,sig):
    ""
    calculate spherical volume
    FWHM = 2*sqrt(2*ln(2))*sig
    r = FWHM/2
    ""
    return (4./3.)*pi*( sig*sqrt(2.*log(2.)) )**3.

158
def VolumeCyl(self, sig):
    
    calculate cylindrical volume
    remember to multiply self.length by 1e-4
    to convert to cm

    return pi*sig**2.*self.length

def wigner_seitz(self, density):

    find the average inter-particle spacing from a
given density

    return (3./(4.*pi*density))**(1./3.)

def newNumber(self, yy, Cyl=None):

    returns array of particle numbers
    i.e. array should be able to address only pgn’s
    yy[2] is always ’sigma’

    if Cyl==None:
        yy[0] = yy[0]*self.Volume(yy[2])
        yy[extraNs:] = yy[extraNs:]*self.Volume(yy[2])
    else:
        yy[0] = yy[0]*self.VolumeCyl(yy[2])
        yy[extraNs:] = yy[extraNs:]*self.VolumeCyl(yy[2])

    return yy

def newDensity(self, yy):

    ’yy’ should be array of particle numbers

    yy[0] = yy[0]/self.Volume(yy[2])
    yy[extraNs:] = yy[extraNs:]/self.Volume(yy[2])

    return yy

def newGammai(self):
    self.Gammai = echg**2./( self.wigner_seitz(self.IonDensity)*
                          (4.*pi*epsilon)*kB*self.Ti_t )

def newGammae(self):
    self.Gammae = echg**2./( self.wigner_seitz(self.IonDensity)*
                          (4.*pi*epsilon)*kB*self.Ti_t )
\[(4. \cdot \pi \cdot \epsilon_0) \cdot k_B \cdot \text{self}. \cdot \text{Te}_t \]

```python
def w_pe(self):
    """
    \( w_{pe} = \sqrt{n_e \cdot e^2 / m_e \cdot \epsilon_0} / 2 \cdot \pi \text{ Hz} \)
    """
    self.wpe = 8.9787e9*sqrt(self.IonDensity)

def w_pi(self):
    """
    \( w_{pi} = \sqrt{n_i \cdot e^2 / m_{NO} \cdot \epsilon_0} / 2 \cdot \pi \text{ Hz} \)
    """
    self.wpi = 3.8401e7*sqrt(self.IonDensity)

def newDebye(self,density,Te_t):
    try:
        self.debye = 1./sqrt(echg**2.*density/(epsilon*kB)*
                          1./(self.Ti_t+Te_t))
    except ValueError:
        print 'ValueError for newDebye'

def make_y0(self):
    """
    initial \( y_0 \) vector has \( n^5 \) population dependence for
    lower \( n \)-populations after Penning \( \text{penn\_ind} \) here
    represents the upper limit for \( n_{\text{penning}} \)
    """
    if self.correlation == 1:
        ypp = zeros(2*NumofLevels + extraNs)
        #construct array of \( n \)-levels + rho(electrons) + rho(DR products) +
        #\( N \cdot \rho (PD \text{ products}) \)
    else:
        ypp = zeros(NumofLevels + extraNs)
    ypp[0] = self.y00
    if self.nStart:
        ypp[where(n_lst == self.nStart)[0][0] + extraNs] = self.init_pop
    if self.penn_ind:
        #Total Population to lower Penning Population
        nIndex = where(n_lst == round(nToStart/sqrt(2.)))[0][0]
        ypp[extraNs : self.penn_ind + extraNs] = self.y00*
        n_lst[:self.penn_ind]**5./
        self.nStart**5.
    #This initial array should be in absolute number of
```
if self.correlation == 1:
    ypp[2] = self.sigma0
    ypp[3] = 0.0
    ypp[4] = self.Ti0
    ypp[5] = 0.0
    ypp[6] = self.Uii0
    ypp = self.newNumber(ypp)
self.electronArr = array(ypp[0])
return ypp

def ncritical(self, Temperature):
    try:
        n_crit = round( sqrt(Rydhc/(kB*Temperature)) )
        if abs(n_crit - self.ncrit) > 5:
            self.ncrit = n_crit
            self.index = int(self.findncrit(self.ncrit))
    else:
        pass
except ValueError:
    print 'ValueError with ncritical calculation'

def ncritical2(self, Temperature, Density):
    n_critT = round( sqrt(Rydhc/(kB*Temperature)) )
    n_critD = round( sqrt(0.5*self.wigner_seitz(Density)/a0 ) )
    n_crit = min(n_critT, n_critD)
    if abs(int(n_crit - self.ncrit) ) > 3:
        self.ncrit = n_crit
        self.index = int(self.findncrit(self.ncrit))
    else:
        pass

def uhat_select(self, kappa):
    return float(corru.uhat_select(kappa,self.Gammai))

def uhat2(self):
    """
    use analytic expression for u_ii
    """
    A1 = -0.9052
    A2 = 0.6322
    A3 = -sqrt(3.)/2. - A1/sqrt(A2)
    + A3/(1.+self.Gammai))
def calcTemp(self, rho):
    """
    E_tot = 3/2 \* kB \* Te(0) \* rho0(0) - \sum(Rydhc*rho(n_0)/n_0**2) =
            3/2 \* kB \* Te(t) \* rho0(t) - \sum(Rydhc*rho(n)/n**2)
    Te(t) = Te(0) \* (rho0(0)/rho0(t)) - 2/3 \* 1/kB \* 1/rho0(t) *
            \sum(Rydhc*rhon(0)/n**2) + 2/3 \* 1/kB \* 1/rho0(t) *
            \sum(Rydhc*rhon(n)/n**2)
    Added DR-products which should be 0.0 for pure PI-plasma
    """
    temp_elec = self.y00*self.Te0/(rho[0] + rho[1])
                - ( Rydhc*2./( kB*3.* (rho[0] + rho[1] ) ) )
                ( ryd0 + rydPenn )
    newTemp = sum( rho[extraNs:]* (1. / n_lst[:]**2. ) )
    return newTemp*( 2.*Rydhc/( 3.*kB*(rho[0] + rho[1])) ) + temp_elec

def tempCalcExpNum(self, rho):
    """
    E_tot = 3/2*(kB*Te0+kB*Ti0)*Ne(0) - \sum(Ryd*N_n(0)/n^2) -
            \left(-\sum(Ryd*N_nPD(t)/n^2)\right)
    = 3/2*N(kB*Te(t)+kB*Ti(t))*Ne(t) +3/2*M_i*gamma^2*sigma^2*Ne(t)
    + Uii*Ne(t) - \sum(Ryd*N_n(t)/n^2)
    Te(t) = Te(0) \* (rho0(0)/rho0(t)) - 2/3 \* 1/kB \* 1/rho0(t) *
            \sum(Rydhc*rhon(0)/n**2) + 2/3 \* 1/kB \* 1/rho0(t) *
            \sum(Rydhc*rhon(n)/n**2) - M_i*gamma**2*sigma**2 - T_i
    Added DR-products which should be 0.0 for pure PI-plasma; Also
    added the ion expansion term!
    """
    temp_elec = self.rho0[0]*(self.Te0 + self.Ti0) - ( Rydhc*2./( kB*3. ))*
                ( self.ryd0 + self.rydPenn )
                - rho[4]*(rho[0] + rho[1])
                - (2./3.)*rho[0]*rho[6]/kB
                - (NOmass/kB)*(rho[3]*rho[2])**2.*rho[0]
    newTemp = sum( rho[extraNs:NumofLevels + extraNs:]* (1. / n_lst[:]**2. ) )
                + sum( rho[extraNs + NumofLevels:]* (1. / n_lst[:]**2. ) )
    return (newTemp*( 2.*Rydhc/(3.*kB)) ) + temp_elec)/(rho[0]+rho[1])

def mkDrhoDtPINum(self, rho):
    Number = int(self.Number)
Temp = self.calcTemp(rho)
drhodt = zeros(len(rho))
self.ncritical(Temp)
index = self.index

# print n_lst[index]
direct = ['/Users/jmorri23/Desktop/Dropbox/trunk',
    '<iostream>',
    '<cmath>',
    '<algorithm>',
    '<blitz/array.h>']

heads = ['<ratesCdub.h>',
    '<iostream>',
    '<cmath>',
    '<algorithm>',
    '<blitz/array.h>']

support = "using namespace std;"

code = """"""""""""""""""""""""""""""""""""""""""""
""""""""""""""""""""""""""""""""""""""""""""""""
//RECOMPILE command here
blitz::Array<double,1> ktbrlst(Number);
blitz::Array<double,1> kionlst(Number);
blitz::Array<double,2> knp_n(Number,Number);
blitz::Array<double,2> kn_np(Number,Number);
blitz::Array<double,1> kn_npION(Number);

ktbrlst = 0.;
kionlst = 0.;

for (int jj = 0; jj < Number; jj++) {
    kionlst(jj) = kION(n_lst(jj), Temp)*rho(jj + extraNs);
    for (int kk = 0; kk < Number; kk++){
        kn_np(jj,kk) = knTOnprme( n_lst(jj), n_lst(kk), Temp );
    }
}

for (int qq = 0; qq < index ; qq++) {
    //if ( n_lst(qq) < 10 )
    //    ktbrlst(qq) = 0.;
    //else
    ktbrlst(qq) = kTBR( n_lst(qq), Temp);
    for (int pp = 0; pp < Number ; pp++) {
        knp_n(qq,pp) = kn_np(pp,qq)*rho(pp + extraNs);
    }
}

if (index != Number){
for (int gg = 0; gg < index; gg++){
    for (int bb = index; bb < Number; bb++){
        kn_npION(gg) += kn_np(gg, bb)*rho(gg + extraNs);
    }
}

kn_np(blitz::Range::all(), blitz::Range(index, Number-1)) = 0.0;

// P-I plasma:

drhodt(0) = sum(kionlst)*rho(0) -
sum(ktbrlst)*pow(rho(0), 3.);
// + sum(kn_npION)*rho(0); // - kDR(Temp)*pow(rho(0), 2.);

drhodt(1) = 0.; // kDR(Temp)*pow(rho(0), 2.);
for (int pp = 0; pp < Number; pp++){
    cout « (pp + extraNs) « endl;
    drhodt(pp + extraNs) = ktbrlst(pp)*pow(rho(0), 3.) -
        kionlst(pp)*rho(0) -
        sum( kn_np(pp, blitz::Range::all()) )*
        rho(pp + extraNs)*rho(0) +
        sum(knp_n(pp, blitz::Range::all()) )*
        rho(0); // - kn_npION(pp)*rho(0);
}

weave.inline(code, ['Number', 'index', 'Temp', 'n_lst',
    'rho', 'drhodt', 'extraNs'],
    verbose = 1, support_code = support,
    type_converters = converters.blitz, headers = heads,
    include_dirs = direct)

return drhodt

def DNumberDtexp(self, rho, tt):
    
    Rate equations for change in Number of particles with
    change in volume
    adjusted to include expansion and
    PD and DR
    Used for solving equations of motion for collisional
    plasma, i.e. with expansion by maintaining constant volume,
    and changing density
    returns 'drhodt':
    drhodt(0) = electron density
    drhodt(1) = dissociated product density
    drhodt(2) = sigma
drhodt(3) = gamma
drhodt(4) = Ti
drhodt(5: Number of Levels) = density of pqns
drhodt(Number of Levels: end) = predissociation products

Expansion using collisional Boltzmann

self.sigma = rho[2]
self.gamma = rho[3]
self.Ti_t = rho[4]

Number = int(self.Number)
index = Number  #comment out for P-I plasma
Temp = self.tempCalcExpNum(rho)
drhodt = zeros(len(rho))
kpd = self.kpdarray
#self.ncritical(Temp, rho[0])
#index = self.index
#ncrit = round( sqrt(Rydhc/Temp) )
#index = int(self.findncrit(ncrit))

Volume = float(self.Volume(rho[2]))
dVdt = float(Volume*3.*rho[3])

direct = ['/Users/jmorri23/Dropbox/Plasma-project']
heads = ['<ratesCdub.h>',
  '<iostream>',
  '<cmath>',
  '<algorithm>',
  '<blitz/array.h>
]
support = "using namespace std;"
code = """
kionlst = 0.;
knp_n = 0.;
kn_np = 0.;

for (int jj = 0; jj < Number; jj++) {
    kionlst(jj) = kION(n_lst(jj), Temp)*rho(jj + extraNs);
    for (int kk = 0; kk < Number; kk++)
        kn_np(jj,kk) = knTOnprme( n_lst(jj), n_lst(kk), Temp );
}

for (int qq = 0; qq < index; qq++) {
    ktbrlst(qq) = kTBR( n_lst(qq), Temp);
    for (int pp = 0; pp < Number; pp++) {
        knp_n(qq,pp) = kn_np(pp,qq)*rho(pp + extraNs);
    }
}

for (int gg = 0; gg < index; gg++){
    for (int bb = index; bb < Number; bb++){
        kn_npION(gg) += kn_np(gg,bb)*rho(gg + extraNs);
    }
}

if (index != Number){
    for (int gg = 0; gg < index; gg++){
        for (int bb = index; bb < Number; bb++)
            kn_npION(gg) += kn_np(gg,bb)*rho(gg + extraNs);
    };

kn_np(blitz::Range::all(),blitz::Range(index,Number-1)) = 0.;

//Dissociate Recombination Plasma:

  drhodt(0) = sum(kionlst)*rho(0)/Volume - sum(ktbrlst)*
        pow(rho(0), 3.)/pow(Volume, 2.)
        + rho(0)*dVdt/Volume
        - kDR(Temp, Volume)*pow(rho(0),2.);
    // + sum(kn_npION)*rho(0)

  drhodt(1) = kDR(Temp)*pow(rho(0), 2.);

  //PD Plasma:
  for (int pp = 0; pp < Number; pp++){
      //Add to list for PD’d n’s for Temperature Calc
      drhodt(pp + extraNs) = ktbrlst(pp)*pow(rho(0), 3./
\[ \text{pow}(\text{Volume}, 2.) \] 
\[ - \text{knIonList}(\text{pp})/\text{Volume} \] 
\[ - \text{sum}( \text{kn_np}(\text{pp}, \text{blitz::Range::all()})* \text{rho( pp + extraNs )}/\text{Volume} + \text{sum} (\text{knp_n}(\text{pp}, \text{blitz::Range::all()}))* \text{rho(0)}/\text{Volume} + \text{rho( pp + extraNs )*} \text{dVdt}/\text{Volume}; \] 
\[ // - kpd(\text{pp})*\text{rho( pp + extraNs )} - \text{kn_npION}(\text{pp})*\text{rho(0)}; \]
\[ \text{drhodt}(\text{pp + Number + extraNs}) = 0.; \] 
\[ //kpd(\text{pp})*\text{rho( pp + extraNs )}; \] 
\[ //\text{Add to rho vector for particle number conservation} \}

"""
weave.inline(code, ['Number','index','Temp','n_lst','rho','drhodt', 'extraNs', 'kpd','Volume','dVdt'],
verbose = 1, support_code = support,
type_converters = converters.blitz,
headers = heads, include_dirs = direct)

\[ \text{drhodt}[2] = \text{rho}[3]\times\text{rho}[2] \]
\[ \text{drhodt}[3] = \text{rho}[0]/(\text{rho}[0] + \text{sum}(\text{rho}[\text{extraNs:extraNs+NumofLevels}]))*\]
\[ (\text{kB}*\text{Temp} + \text{kB} \times \text{rho}[4])/(\text{NOmass} \times \text{rho}[2]**2.) - \text{rho}[3]**2. \]
\[ \text{drhodt}[4] = -2*\text{rho}[3]\times\text{rho}[4] \]

return drhodt

def DNumberDtexp_corr(self, rho, tt):
    ""
    Rate equations for change in Number of particles with
    change in volume
    adjusted to include expansion and
    PD and DR
    Used for solving equations of motion for collisional
    plasma, i.e. with expansion by maintaining constant volume,
    and changing density
    returns 'drhodt':
    drhodt(0) = electron number
    drhodt(1) = dissociated product number
    drhodt(2) = sigma
    drhodt(3) = gamma
    drhodt(4) = Ti
    drhodt(5) = Te
    """


drhodt(6) = \frac{Uii}{kB}
drhodt(7: \text{Number of Levels}) = \text{number of qns}
drhodt(\text{Number of Levels: end}) = \text{predissociation products/sink}

Expansion using collisional Boltzmann
Although full derivative has ‘\(\rho\cdot dV/dt/volume\)’ term, adding that here prevents particle conservation – microconical(N,V,E)

self.Ti_t = rho[4]
Number = int(NumofLevels)
#index = Number #comment out for P-I plasma
self.Te_t = float(self.tempCalcExpNum(rho))
Temp = self.Te_t
drhodt = zeros(len(rho))
kpd = self.kpdarray
self.temperatureArr = append(self.temperatureArr,Temp)
#self.electronArr = append(self.electronArr,rho[0])

#self.ncritical(Temp)
index = self.index

### Volume and dVdt Values###

Volume can be cylinder or sphere!

#Volume = float(self.Volume(rho[2]))
Volume = float(self.VolumeCyl(rho[2]))

Dynamics n_crit####

self.ncritical(Temp)
index = self.index

### Correlation Energy###

self.IonDensity = rho[0]/Volume
self.newGammai() #refreshes self.Gammai
self.newDebye(self.IonDensity,Temp) #refreshes self.debye
self.w_pi()
self.newGammae()
#kappa = self.wigner_seitz(self.IonDensity)/self.debye
tau_i = float(1./self.wpi)
#uhat = self.uhat_select(kappa)
uhat = float(self.uhat2())
gamma_i = float(self.Gammai)
acoeff = (1. - erf((self.nlist-self.ncrit)/3.))/2.

###Reduced TBR Params###
#self.w_pe()
#wpe = float(self.wpe)
gammae = float(self.Gammae)

Zpartit = sum(n_lst[:self.index]**2.*numpexp(-Rydhc/(n_lst[:self.index]**2.*kB*self.Te_t)))/2.

# print 1./self.Gammae

###Step T_e and t_(n-1) forward a value###
self.ncritch = self.ncrit
self.tt = tt

direct = ['/Users/jmorri23/Desktop/Dropbox/trunk/']
heads = [rateFile,
    '<iostream>',
    '<cmath>',
    '<algorithm>',
    '<blitz/array.h>',
    '<typeinfo>
    ]
support = "using namespace std;"
code = ""

//RECOMPILe here
/* Rates in 'NumberRates_um.h' are scaled
for micro-meter length scale and also include
the appropriate volume denominator to make
them accurate for number-calculations
Array<int,1> A(7);
A = 0, 1, 2, 3, 4, 5, 6;
cout << A(Range::all()) << endl // [ 0 1 2 3 4 5 6 ]
<< A(Range(3,5)) << endl // [ 3 4 5 ]
<< A(Range(3,toEnd)) << endl // [ 3 4 5 6 ]
<< A(Range(fromStart,3)) << endl // [ 0 1 2 3 ]
<< A(Range(1,5,2)) << endl // [ 1 3 5 ]
<< A(Range(5,1,-2)) << endl // [ 5 3 1 ]
<< A(Range(fromStart,toEnd,2)) << endl; // [ 0 2 4 6 ] */

blitz::Array<double,1> ktbrlst(Number);
blitz::Array<double,1> kionlst(Number);
blitz::Array<double,2> knp_n(Number,Number);
blitz::Array<double,2> kn_np(Number,Number);
//blitz::Array<double,1> kn_npION(Number);
blitz::Array<double,2> kan_np(Number,Number);
blitz::Array<double,2> kanp_n(Number,Number);
blitz::Array<double,2> kan_npsink(Number,Number);
blitz::Array<double,2> kanp_nsink(Number,Number);
blitz::Array<double,1> a_ij(Number);
a_ij = 0.0;
kan_np = 0.0;
kanp_n = 0.0;
kan_npsink = 0.0;
kanp_nsink = 0.0;
//kn_npION = 0.0;
ktbrlst = 0.0;
kionlst = 0.0;
knp_n = 0.0;
kn_np = 0.0;
double gammaei = 1./gammae;
double e_dens = rho(0)/Volume;
double wignerseitz = pow((3./(4.*PI*e_dens)),1./3.);

/* whatever n_crit is - rates go up to (n_crit - 1) */
//#################################################################
for (int jj = 0; jj < Number; jj++) {
    kionlst(jj) = kION(n_lst(jj), Temp, Volume)*
                 rho(jj + extraNs);
    for (int kk = 0; kk < Number; kk++){
        knp_n(jj,kk) =
            knTOnprme( n_lst(jj), n_lst(kk), Temp, Volume );
    }
}
//#################################################################
/* The 'qq' in this loop goes to
'index' if no acoeff below */
//CURRENTLY OFFLINE
/*for (int qq = 0; qq < index ; qq++) {
    //ktbrlst(qq) = kTBR( n_lst(qq), Temp, Volume)*
    //                   2.7*exp(-4.5*gammai);
    ktbrlst(qq) = kTBR( n_lst(qq), Temp, Volume);
    cout << ktbrlst(qq) << endl;
    for (int pp = 0; pp < Number ; pp++) {
        knp_n(qq,pp) = kn_np(pp,qq)*rho(pp + extraNs);
    }
} */
//ACTIVE TBR
//#################################################################
if (gammaei > 2.5){
    for (int qq = 0; qq < index ; qq++) {
        ktbrlst(qq) = kTBR( n_lst(qq), Temp, Volume);
    }
}
for (int pp = 0; pp < Number; pp++) {
    knp_n(qq, pp) = kn_np(pp, qq) * rho(pp + extraNs);
}

else if (gammaei < 2.5 && gammaei > 0.5) {
    for (int qq = 0; qq < index; qq++) {
        kbrlst(qq) = kTBR(n_lst(qq), Temp, Volume) * 
                    pow((wignerseitz * Temp), -1.5) * red1;
        for (int pp = 0; pp < Number; pp++) {
            knp_n(qq, pp) = kn_np(pp, qq) * rho(pp + extraNs);
        }
    }
}
else {
    for (int qq = 0; qq < index; qq++) {
        kbrlst(qq) = kTBR(n_lst(qq), Temp, Volume) * 
                    pow((wignerseitz * Temp), -4.5) * red2 * 
                    Zfactor(n_lst(qq), Temp, Zpartit);
        for (int pp = 0; pp < Number; pp++) {
            knp_n(qq, pp) = kn_np(pp, qq) * rho(pp + extraNs);
        }
    }
}

//#######################################################
//#######################################################
//knp( blitz::Range::all(), blitz::Range(index,blitz::toEnd) ) = 0.0;
//########################################################
/*if (index != Number){
    for (int gg = 0; gg < Number; gg++){
        kbrlst(gg) = kbrlst(gg)*acoeff(gg);
        for (int ll = 0; ll < Number; ll++){
            knp_n(gg, ll) = knp_n(gg, ll)*acoeff(ll);
            knp_n(gg, ll) = knp_n(gg, ll)*acoeff(gg);
        }
    }
}*/

//Electrons,DR and Macro Variables:
/*##############*/
drhodt(0) = blitz::sum(kionlst)*rho(0) - 
            blitz::sum(kbrlst)*pow(rho(0), 3.) - 
            kDR(Temp, Volume)*pow(rho(0), 2.); 
            // + rho(0)*dVdt/Volume;

drhodt(2) = rho(3)*rho(2);

drhodt(3) = (k_b*Temp + k_b*rho(4) + rho(6)/3.) / 
            (NOmass*pow(rho(2),2.)) 
            - pow(rho(3),2.);

drhodt(4) = -2.*rho(3)*rho(4) - (2./3.)*(rho(3)*rho(6) 
            - (rho(6) - uhat*rho(4)*k_b)/taui)/k_b;
\begin{verbatim}
drhodt(5) = 0.0;
drhodt(6) = -(rho(6) - k_b*uhat*rho(4))/taui;
/*###############*/
//Rydberg levels and Sink:
/*###############*/
if (aijswitch == 1)
{
    /* Create adjusted rates based on fraction array 'a_ij(n)' for both regular rates and sink rates*/
    for (int jj = index1; jj < index2; jj++){
        a_ij(jj) = aIJfunc(n_lst(jj),n_lst(index1));
    }
    for (int gg = 0; gg < Number; gg++){
        for (int bb = 0; bb < Number; bb++){
            kan_np(gg,bb) = (1.-a_ij(gg))*kn_np(gg,bb);
            kanp_n(gg,bb) = (1.-a_ij(bb))*knp_n(gg,bb);
            kan_npsink(gg,bb) = (a_ij(gg))*kn_np(gg,bb);
            kanp_nsink(gg,bb) = (a_ij(bb))*knp_n(gg,bb);
        }
    }
    for (int pp = 0; pp < Number; pp++){
        /*Calculate appropriate DrhoDt for Rydberg levels and sink levels WITH collisional channeling*/
        /*################*/
        drhodt(pp + extraNs) = ktbrlst(pp)*pow(rho(0),3.)
            - kionlst(pp)*rho(0)
            - blitz::sum( kan_np(pp, blitz::Range::all() ) )*rho( pp + extraNs )*rho(0)
            - blitz::sum( kan_npsink(pp, blitz::Range::all() ) )*rho( pp+extraNs )*rho(0)
            + blitz::sum(kanp_n(pp, blitz::Range::all() ) )*rho(0)
            - kpd(pp)*rho( pp + extraNs );
        //+ rho( pp + extraNs )*dVdt/Volume;// - kn_npION(pp)*rho(0);
        /*################*/
        drhodt(pp + Number + extraNs) = kpd(pp)*rho( pp + extraNs )
            + blitz::sum(kan_npsink(pp,blitz::Range::all() ) )*rho(pp+extraNs)*rho(0);
        //+ blitz::sum(kanp_nsink(pp, blitz::Range::all() ) )*rho(0);
    }
}
else
{
    
}
\end{verbatim}
for (int pp = 0; pp < Number; pp++){
    drhodt(pp + extraNs) = ktbrlst(pp)*pow(rho(0), 3.)
        - kionlst(pp)*rho(0)
        - blitz::sum( kn_np(pp, blitz::Range::all() ) )*
            rho( pp + extraNs )*rho(0)
        + blitz::sum(knp_n(pp, blitz::Range::all() ) )*
            rho(0)
        - kpd(pp)*rho( pp + extraNs );
    //+ rho( pp + extraNs )*dVdt/Volume;
    //-- kn_npION(pp)*rho(0);
    drhodt(pp + Number + extraNs) = kpd(pp)*rho( pp + extraNs );
    //Add to rho vector for particle number conservation
}

return drhodt

class kRates2:
    ""
    Deprecated Class
    ""
    def __init__(self, TforK, k000):
        self.Tk = TforK
        self.knot = k000
        self.epsfactor = Rydhc/(kB*self.Tk)
        self.lmbd = sqrt(h**2/(2.*pi*emass*kB*self.Tk))*1e2
    ""
thermal de Broglie wavelength quantifying average
gas particle wavelength:
\[ \lambda \ll a, \text{ classical M-B gas: IN cm's !!!!} \]

```python
def k_ion(self, ni):
    # rate constant for A + e \rightarrow A^+ + e with A at QN n
    eps_i = self.epsfactor*(1./ni[:])**2.
    try:
        tempion = 11.*sqrt(Rydhc/(kB*self.Tk))*self.knot*numpexp(-eps_i[:])/
            (eps_i[:]**(2.33) + 4.38*eps_i[:]**1.72 + 1.32*eps_i[:])
    except OverflowError:
        print eps_i, self.Tk, self.knot
    return tempion
```

```python
def k_tbr(self, ni):
    # rate constant for A^+ + e^- + e^- \rightarrow A + e^- (prop. to k_ion)
    eps_i = self.epsfactor*(1./ni[:])**2. #h*c*Ryd/(ni**2*kB*self.Tk)
    try:
        temtbr = float(self.k_ion(ni)*ni[:]**2.)*(self.lmbd**3.)*
            numpexp(eps_i[:])
    except OverflowError:
        print eps_i,self.Tk,self.knot
    return float(self.k_ion(ni)*ni**2*(self.lmbd**3)*exp(eps_i))
```

```python
def kntonprime(self, ni, nf):
    # left off here - compose knnp matrix
    if ni == nf:
        knn = 0.
    else:
        eps_i = self.epsfactor*(1/ni**2) #h*c*Ryd/(ni**2*kB*self.Tk)
        eps_f = self.epsfactor*(1/nf**2) #h*c*Ryd/(nf**2*kB*self.Tk)
        knn = self.knot*( (eps_i**(5./2.)*eps_f**(3./2.))/
            (max(eps_f,eps_i)**(5./2.))*exp( -(eps_i - min(eps_f,eps_i)) )*
                ( (22./((max(eps_f,eps_i)+0.9)**(7./3.))) + ((9./2.)/
                    (max(eps_f,eps_i)**(5./2.)*(fabs(eps_f-eps_i))**(4./3.))))
        return float(knn)
```

```python
def kDR(self):
    return 9.1e-5*self.Tk**(-0.54) #From Schneider et al,
    # Fig. 7: 9.1e-6*Te**(-0.54)
```

```python
def kPD(self, ni):
    au = 1./(2.42e-17) #s
    #tau = ones(5)*0.0006
```
tau = array([0.014, 0.046, 0.029, 0.0012, 0.00003])
extendtau = 0.00003*ones(ni-len(tau))
#extendtau = zeros(ni-len(tau))
tau = append(tau, extendtau)
llist = arange(float(ni))
gsum = ni**2.
gvalue = array((2.*llist[:]+1.)*tau[:])
return (sum(gvalue)/gsum)*(1./(2.*float(ni)**3.))*au

#################################################################
krate = kRates2(TeInit, redok0(TeInit))
#kpdarr = zeros(len(n_lst))
#kpdarr[:where(n_lst==49.][0]] = 1e11
kpdarr = array([krate.kPD(nn) for nn in n_lst])
KK = SetRateFunctions(kpdarr)

#################################################################

###ODEINT Functions###
def func(y, t):
    
    mkDrhoDtPI: Simple photo-ionized atomic case with the option for DR
    DNumberDtexp: Number Expansion but without PD/DR
    DNumberDtexp_corr: Expansion, and PD/DR using absolute Number of particles
    
    #StateDensityArray = KK.mkDrhoDtPI(y)
    #StateDensityArray = KK.DNumberDtexp(y)
    StateDensityArray = KK.DNumberDtexp_corr(y, t)
    return StateDensityArray

#function for integrate.ode
def f(t, y):
    StateDensityArray = KK.DNumberDtexp_corr(y, t)
    return StateDensityArray

#################################################################

"""atol array for odeint: sets absolute tolerance for integration according to:
max-norm of ( e(i)/ewt(i) ) <= 1
where
ewt = (ewt(i)) is a vector of positive error weights"""
according to:

<table>
<thead>
<tr>
<th>itol</th>
<th>rtol</th>
<th>atol</th>
<th>ewt(i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>scalar</td>
<td>scalar</td>
<td>rtol*abs(y(i)) + atol</td>
</tr>
<tr>
<td>2</td>
<td>scalar</td>
<td>array</td>
<td>rtol*abs(y(i)) + atol(i)</td>
</tr>
<tr>
<td>3</td>
<td>array</td>
<td>scalar</td>
<td>rtol(i)*abs(y(i)) + atol</td>
</tr>
<tr>
<td>4</td>
<td>array</td>
<td>array</td>
<td>rtol(i)*abs(y(i)) + atol(i)</td>
</tr>
</tbody>
</table>

```
atoler = zeros(len(KK.rho0))
atoler[0] = 1e-5  # 10^-6
atoler[1] = 1e-5  # 10^-6
atoler[2] = 1e-7  # 10^-2
atoler[4] = 1e-9  # 10^-1
atoler[5] = 1e-5  # 10^-6
atoler[6] = 1e-20 # 10^-10
atoler[7:] = 1e-5  # 10^-6
```

rtoler = zeros(len(KK.rho0))
rtoler[0] = 1e-8
rtoler[1] = 1e-8
rtoler[2] = 1e-10
rtoler[3] = 1e-8
rtoler[4] = 1e-10
rtoler[5] = 1e-10
rtoler[6] = 1e-20
rtoler[7:] = 1e-8

#atoler=atoler*1e0
#rtoler=rtoler*1e3

```
if __name__=="__main__":
    printTime()
```

```
scipy.integrate.odeint(func, y0, t, args=(), Dfun=None, col_deriv=0,
                       full_output=0, ml=None, mu=None, rtol=None,
                       atol=None, tcrit=None, h0=0.0, hmax=0.0,
                       hmin=0.0, ixpr=0, mxstep=0, mxhnil=0,
                       mxordn=12, mxords=5, printmessg=0)
```

`ml, mu : integer`

*If either of these are not-None or non-negative, then the*
Jacobian is assumed to be banded. These give the number of lower and upper non-zero diagonals in this banded matrix.

For the banded case, Dfun should return a matrix whose columns contain the non-zero bands (starting with the lowest diagonal).

Thus, the return matrix from Dfun should have shape:

\[
\text{len}(y0) \times (ml + mu + 1) \text{ when } ml \geq 0 \text{ or } mu \geq 0
\]

rtol, atol : float.
The input parameters rtol and atol determine the error control performed by the solver. The solver will control the vector, e, of estimated local errors in y, according to an inequality of the form max-norm of (e / ewt) <= 1, where ewt is a vector of positive error weights computed as: ewt = rtol * abs(y) + atol - rtol and atol can be either vectors the same length as y or scalars. Defaults to 1.49012e-8.

tcrit : array
Vector of critical points (e.g. singularities) where integration care should be taken.

h0 : float, (0: solver-determined)
The step size to be attempted on the first step.

hmax : float, (0: solver-determined)
The maximum absolute step size allowed.

hmin : float, (0: solver-determined)
The minimum absolute step size allowed.

ixpr : boolean
Whether to generate extra printing at method switches.

mxstep : integer, (0: solver-determined)
Maximum number of (internally defined) steps allowed for each integration point in t.

mxhnil : integer, (0: solver-determined)
Maximum number of messages printed.

mxordn : integer, (0: solver-determined)
Maximum order to be allowed for the nonstiff (Adams) method.

mxords : integer, (0: solver-determined)
Maximum order to be allowed for the stiff (BDF) method.

?hu?
vector of step sizes successfully used for each time step.

?tcur?
vector with the value of t reached for each time step.
(will always be at least as large as the input times).

?toisf?
vector of tolerance scale factors, greater than 1.0, computed when a request for too much accuracy was detected.

?tsw?
value of t at the time of the last method switch.
(given for each time step)

?nst?
cumulative number of time steps

?nfe?
cumulative number of function evaluations for each time step

?nje?
cumulative number of jacobian evaluations for each time step

?nqu?
a vector of method orders for each successful step.

?imxer?
index of the component of largest magnitude in the weighted
local error vector

(e / ewt) on an error return, -1 otherwise.

?lenrw?
the length of the double work array required.

?leniw?
the length of integer work array required.

?mused?
a vector of method indicators for each successful
time step: 1: adams (nonstiff),
2: bdf (stiff)

""

yout, youtdict = odeint(func, KK.rho0, tvec, atol=atoler,
full_output=True, mxords=3, printmessg = True)

""

Attempted to implement an alternative integrator.

""

##########ODE Integrator#############

""

Option for RK4 stiff integrator

""

#r = ode(f).set_integrator('vode')
#r.set_initial_value(KK.rho0, 0.0)
#t1 = 10e-6
#dt = 5e-9
#tvec = array(0)
#yout = KK.rho0
#
#while r.successful() and r.t < t1:
#    r.integrate(r.t+dt, step=True)
#    yout = vstack((yout, r.y))
# tvec = append(tvec,r.t)
printTime()
print 't', len(yout[0]), 't', NumofLevels+extraNs
timestamp = strftime("%Y-%m-%d-%H:%M:%S-", localtime()) + 'Te0_'
        + str(TeInit)
        + 'ddens0' + str(ePop0)
newy = empty((len(yout),len(yout[0]) + 1))
for ii in range(len(yout)):
    if correlationswitch:
        newy[ii] = append(yout[ii],KK.tempCalcExpNum(yout[ii]))
    elif piswitch:
        newy[ii] = append(yout[ii],KK.calcTemp(yout[ii]))
output_vec = array(dD.make2list(newy))
timestamp = strftime("%Y-%m-%d-%H:%M:%S-", localtime())
        + 'Te0_' + str(TeInit)
        + 'ddens0' + str(ePop0)
f2 = open('/Users/jmorri23/Desktop/ModelOutput/' + timestamp +
        'PopulData' + '.txt', 'w')
savetxt(f2, newy)
f2.close()
B.3 penningCalc.py

```python
from math import pi, sqrt, exp
import numpy as np
from matplotlib import pyplot as plt
from matplotlib import ticker as tck
from constants import *

""
This file contains the class 'PennFrac' which generates
the fraction of particles undergoing penning ionization, based
on principal quantum number.
""

nmin = 30
nmax = 80
q = 1.602e-19
eps = 8.854e-12
elecC = q**2/(4*pi*eps)
R2J = 4.359744e-18
J2K = 7.243e22
NRydb = 1.1e9
NOmass = 4.98e-26
amu = 1.66057e-27 #kg
a0 = 5.29177e-11 #m

# Constants
#kB = 1.3806504e-23 #m2 kg s-2 K-1; J K-1; 8.62e-5 #eV K-1,
#Ryd = 10973731.6 #m-1 #13.6 #eV ,
#NOmass = 4.98e-26 #kg
#emass = 9.1093822e-31 #kg
#echg = 1.6021765e-19 #C
#h = 6.6260690e-34; #m2 kg / s 4.13e-15 #eV s
#hbar = h/pi
#epsilon = 8.854187817e-12 #C2 J-1 cm-1
#c = 3.e8 #m s-1
#Rydhc = 2.179872e-18 #J: Ryd [cm-1] --> [J]

rho = 5e18 #m-3
centTOmicro = 1e-12
```
fwhm = 500.

nlist = np.arange(float(nmin), float(nmax))

def gaussian(sigma):
    r = np.arange(0., 900.) #0 to 900 micrometers
    return np.exp(-np.square(r)/(2*sigma**2))

class PennFrac:
    def __init__(self, dens):
        self.rho = dens*1e6  #*centTOmicro
        self.alpha = 200e-6  #variance in m
        self.mass = NOmass#/amu
        self.nlist = nlist  #only for local use -
        #not used when called from PlasmaSim.py
        self.r = np.linspace(0., 5.*self.alpha, num=500)

    """Initialization class. 'rho' is density. 'alpha' is
    Gaussian variance. 'mass' is NO mass. 'nlist' is
    the list of principal quantum numbers. 'r' is
    the maximum distance for calculations using Gaussian
distribution."
    ""

    def WSrad(self):
        """Wigner-Seitz radius calculation
        ""
        return (3./(4.*pi*self.rho))**(1./3.)

    def gaussian(self):
        """gaussian list for a typical plasma with
        variance of 320x10^-6 m
        ""
        return self.rho*np.exp(-np.power(self.r, 2.)/(2.*self.alpha**2.))

    def particle_dist(self, gauss=None):
        """for uniform density plasma density distribution
        should be step-function"""
if gauss==None:
    return self.rho*(np.ones(len(self.r)))
else:
    return self.gaussian()

def Tcome2geth(self):
    ""
    returns the time it takes for two Rydberg molecules to
    approach each other
    ""
    return 20e-6*np.sqrt(self.mass*self.WSrad()**5)/
            np.square(self.nlist*a0)

def Tperiod(self):
    ""
    Rydberg period
    ""
    return 2.*pi*np.power(self.nlist,3)*2.419e-17

def ionize90(self):
    ""
    Gives maximum separation distance for which
    90% of trajectories leads to ionization
    ""
    T400 = 1.6*2.*np.power(self.nlist,2.)*a0
    T800 = 1.8*2.*np.power(self.nlist,2.)*a0
    T1200 = 2.1*2.*np.power(self.nlist,2.)*a0
    return T400

def erlangCDF(self, n):
    ""
    Erlang has the form:
    \[
    P(r) = \left(\frac{4\pi r}{k!}\right)^2 \left(\frac{3}{4\pi}\right) \exp\left(-\left(\frac{r}{R_0}\right)^3\right)
    \]
    where 'r' is the distance (orbital diameter),
    kth nearest neighbour, and
    \(R_0 = \left(\frac{4\pi n_{\text{ryd}}}{3}\right)^{1/3}\)
    ""
    Rmax = 1.6*2.*n**2.*a0  #T400 - 400 Rydberg periods
    #Rmax = 1.8*2.*n**2.*a0  #T800 - 800 Rydberg periods
    erlcdf = 1. - np.exp(-self.particle_dist()*Rmax**3.*(4./3.)*pi)
0.5 of the interacting pairs undergoes ionization. Of the 0.5 of interacting pairs, 90% of the distribution will end up getting ionized

```python
return 0.5*0.9*np.average(erlcdf)
```

def NNdist(self):
    
    Nearest-neighbour distribution calculation
    
    rholst = np.power(self.nlist, 2.)*a0
    #*hbar**2*4.*pi*eps/(echg**2*emass)
    #list of radii for each ‘n’
    rmax = self.ionize90()  #list for ‘n’
    nulst = np.power(rholst, 3.)*pi*self.rho*(4./3.0)  #list for ‘n’
    cdfNN = np.array([self.erlangCDF(n) for n in self.nlist])
    return cdfNN

def plots(self):
    t400arr = self.ionize90()
    fig = plt.figure()
    plt.plot(self.nlist, self.NNdist(), 'b.', linewidth=15)
    ax = fig.add_subplot(111)
    formatter = tck.FormatStrFormatter('%1.2f')
    ax.yaxis.set_major_formatter(formatter)
B.4 NumberRates_um.h

//##########Constants##########
const double kB = 1.3806504e-11;  //#um2 kg s-2 K-1; J K-1; 8.62e-5 #eV K-1,
const double Ryd = 109737.316;  //#um-1 #13.6 #eV ,
const double NOmass = 4.98e-26;  //#kg
const double emass = 9.1093822e-31;  //#kg
const double echg = 1.6021765e-19;  //#C
const double h = 6.6260690e-22;  //#um2 kg / s 4.13e-15 #eV s
const double epsilon = 8.854187817e-30;  //#C2 J-1 um-1
const double cee = 3.0e8;  //#m s-1
const double Rydhc = 2.179872e-6;  //# Ryd [cm-1] --> [J in kg*um^-2 s^-2]
const double PI = 3.14159265;
//#############################
# include <vector>
using namespace std;

/* Volume factor used to compute the accurate rates for dNumber/dt
instead of dDensity/dt*/

//RECOMPILE Here
double kNOT (double T)
{
    return pow(echg,4.)/(kB*T*sqrt(emass*Rydhc)*pow(4.*PI*epsilon,2.));
}

double kION (double n, double T, double volume)
{
    double epsi = Rydhc/(pow(n,2.)*kB*T);
    return (11.*sqrt(Rydhc/(kB*T))*kNOT(T)*exp(-epsi))/(pow(epsi,(7./3.))
        + 4.38*pow(epsi,1.72) + 1.32*epsi)/volume;
}

double kTBR (double n, double T, double volume)
//rate constant for A+ + e- + e- --> A + e- (prop. to k_ion)
{
    double epsi = Rydhc/(pow(n, 2.)*kB*T);
    double lmbd = h/sqrt(2.*PI*emass*kB*T); //thermal de Broglie
        //wavelength quantifying average
        //gas particle wavelength:
        //lmbd << a, classical M-B gas
    return kION(n, T, volume)*pow(n, 2.)*pow(lmbd, 3.)*exp(epsi)/volume;
double Zfactor (double n, double T, double Z)
{
    double epsi = Rydhc/(pow(n, 2.)*kB*T);
    return pow(n,2.)*exp(-epsi)/Z;
}

double knTOnprme (double ni, double nf, double T, double volume)
{
    double knn;
    if (ni == nf)
    {
        knn = 0.;
    }
    else
    {
        double eppsi = Rydhc/(pow(ni,2.)*kB*T);
        double epsf = Rydhc/(pow(nf,2.)*kB*T);
        knn = (kNOT(T)*pow(eppsi,(5./2.))*pow(epsf, (3./2.))/
              pow( max(epsf,eppsi), (5./2.)) )*  
              exp( -(eppsi - min(epsf,eppsi)) )*  
              ( (22./
                ( pow( (max(epsf,eppsi) + 0.9), (7./3.) ) ) ) + ((9./2.)/
                (pow( max(epsf,eppsi), (5./2.)) )*  
                ( pow( fabs(epsf-eppsi), (4./3.)))) )/volume;
    }
    return knn;
}

double kDR (double T, double volume)
{
    return 1e12*9e-6*pow(T, -0.528)/volume;  //5.623e-6*
}

double kPD (double ni, double T)
{
    double au = 1./(2.42e-17);
    vector<double> tau (int(ni), 0.00003);
    double gvalue = 0.;
    double gsum = 0.;
    tau[0] = 0.014;
tau[1] = 0.046;
tau[2] = 0.029;
tau[3] = 0.0012;
for (int kk = 0; kk < int(ni); kk++)
{
gsum += (2.0*double(kk) + 1.0);
}
for (int ii = 0; ii < int(ni); ii++)
{
gvalue += (2.0*double(ii) + 1.0)*tau[ii];
}
return gvalue*(1./gsum)*(1./2.*PI*pow(ni,3.))*au;

double aIJfunc (double ni, double nf)
{
    return pow(nf,2.)/pow(ni,2.);
}
double smoothTBR ( double ni, double n0, double alpha )
{
    return exp( pow(( 1./pow(n0,2.) - 1./pow(ni,2.) ),2.)/pow(alpha,2. ) );
}
import numpy as np
import time
from scipy.optimize import leastsq

# Constants

#k_b = float(1.3806504e-23) #m2 kg s-2 K-1; J K-1; 8.62e-5 #eV K-1
kB = float(1.3806504e-23) #m2 kg s-2 K-1; J K-1; 8.62e-5 #eV K-1,
Ryd = 10973731.6 #m-1 #13.6 #eV ,
NOmass = 4.98e-26 #kg
emass = 9.1093822e-31 #kg
echg = 1.6021765e-19 #C
h = 6.6260690e-34; #m2 kg / s 4.13e-15 #eV s
epsilon = 8.854187817e-12 #C2 J-1 m-1
c = 3.8 e8 # m s-1
Rydhc = 2.179872e-18 #J: Ryd [cm-1] --> [J]
a0 = 52.9177e-12 #m

This file contains many useful function scripts used within PlasmaSimExp and otherwise.

---

def make2list(lst):
    """
    function to transpose python list
    """
    newlst = []
    for i in range(len(lst[0])):
        tmplst = [lst[j][i] for j in range(len(lst))]
        newlst.append(tmplst)
    return newlst

def npArr2Lst(npArr):
    """
    function to convert numpy array to python list
    """
    newlst = []
    for value in npArr:
        newlst.append(value)
    return newlst
def saveTofile(y, Te0):
    """
    function to save data file with unique
    name given by data/time stamp.
    'y' is data array to save
    """
    timestamp = time.strftime("%Y-%m-%d-%H:%M:%S-",
                            time.localtime())+'Te0_' + str(Te0)
    f2 = np.open('/Users/jmorri23/Desktop/output/
                 + timestamp + 'PopulData' + '.txt', 'w')
    np.savetxt(f2, y)
    f2.close()

def reduce(tArr, temperature, density,inverse=None):
    """
    tArr: time array
    temperature: temperature array
    density: density array
    inverse: 1/Gamma

    function to calculate 1/Gamma which is reduced
temperature as well as t*omega which is reduced
time in plasma frequencies.
    convenient value for scaling studies.

    returns: reduced time, reduced temperature
    """
    density = density*1e6
    temperature = np.array(temperature)
    tArr = np.array(tArr)
    tred = tArr*np.sqrt(density*echg**2./(emass*epsilon))
    #tred = tArr[:]*(1./(2.*pi))*np.sqrt(dens*echg**2./(emass*epsilon))
    if inverse != None:
        rhored = 1./(3./(4.*pi*density)**(1./3.))**1./(kB*temperature)*echg**2./(4*pi*epsilon)
    else:
        rhored = temperature[:]*( (4.*pi*kB*epsilon/echg**2.)*
                                  (3./(4.*pi*density))**(1./3.))
    return tred, rhored

def reduce1(temp,density):
    """
    same calculation as previous function but
    will perform for only one value
    """
if density > 1e14:
    density = density
else:
    density = density*1e6
return temp*( (4.*pi*kB*epsilon/echg**2.)*(3./(4.*pi*density))**(1./3.))


def gamma2temp(gamm,dens):
    ""
    converts correlation parameter into a temperature
    ""
    return echg**2./(4.*pi*epsilon*kB*gamm)*(4.*pi*dens*1e6/3.)**(1./3.)

def gammai2temp(gammi,dens):
    ""
    converts inverse correlation parameter into a temperature
    density in cm^-3
    ""
    return echg**2./(4.*pi*epsilon*kB)*(4.*pi*dens*1e6/3.)**(1./3.)*gammi

def tTOred(time,density):
    ""
    converts real time to reduced time
    ""
    #density in cm^-3
    #return time*(1./(2.*pi))*sqrt(density*1e6*echg**2./(emass*epsilon))
    return time*sqrt(density*1e6*echg**2./(emass*epsilon))

def redTOt(reduced_t,density):
    ""
    returns real time from reduced time (plasma periods)
    ""
    #density in cm^-3
    #return reduced_t*2.*pi/(sqrt(density*1e6*echg**2./(emass*epsilon)))
    return reduced_t/(sqrt(density*1e6*echg**2./(emass*epsilon))

def Tpe(density):
    return 2*pi*sqrt(epsilon*emass/(density*echg**2.))
def fitting(x, y, fitexp = None):
    x = np.array(x)
    y = np.array(y)
    if fitexp == None:
        errfunc = lambda p, x, y: fitfunc(p, x) - y
        p0 = [1., 1., 1., 1., 1., 1.]
    else:
        fitfunc = lambda p, x: p[0]*np.exp(x/p[1])
        errfunc = lambda p, x, y: fitfunc(p, x) - y
        p0 = [-.2, -1.]
    p1, success = leastsq(errfunc, p0[:], args=(x, y))
    return p1, success

def rydEnergy(time, rydarr, nlist):
    """
    time: index for specific time to analyze
    rydarr: full time list of rydberg state densities
    nlist: self-explanatory
    """
    if len(rydarr) == len(nlist):
        sumE = sum(rydarr[:,time]*Rydhc/nlist[:]**2.)
    else:
        print "Your rydberg levels and number of pqs does not agree!"
        sumE = 0.
    return sumE

def rydPop(time, rydarr, nlist):
    """
    time: time vector
    rydarr: rydberg levels or really any array with same number as nlist
    """
    rydPoparray=np.zeros(len(time))
    if len(rydarr[:,0])==len(nlist):
        for i in range(len(time)):
            rydPoparray[i] = sum(rydarr[:,i])
    else:
        print "Your rydberg levels and number of pqs does not agree!"
    return rydPoparray

def aws(dens):
### Code Examples

**Function Definitions**

```python
def rad_lifetime(pqns, Z):
    
    """
    Radiative lifetime of Rydberg atom as a function of principal quantum number.
    \[ T(n) = C_0 \left(\frac{n^{5/2}Z^4}{2n^2}e^{\frac{1}{2n}}\right) \]
    \[ C_0 = 92e-12 \text{ s for normal atom; for exotic atom, } C_0 \]
    \[ \text{must be divided by the reduced mass in electron mass units} \]
    """
    return 92e-12*(pqns**5./(2.*Z**4.))*1./(np.log(2.*pqns-1.) - 0.365)

def bottleneck(Temp,nlist,extras):
    
    """
    Calculates bottleneck returns the integer position for 'nlist'
    """
    bottl_neck = np.rint(np.sqrt(Rydhc/(4.*kB*Temp)))
    bK_array = np.where(bottl_neck==nlist)
    return bK_array.ravel() + extras

def reduceArray(array1,array2):
    
    """
    array1 is time array
    array2 is the bottleneck array (as an index for dDensity array)
    returns:
    array22: index for dDensity array of bottleneck only when bottleneck changes
    array12: corresponding time values for the position of bottleneck change
    """
    count = len(array1)
    array12 = np.array( [array1[0]] )
    array22 = np.array( [int(round(array2[0]))] )
    indexarr = np.array((0.))
    temp = int(round(array2[0]))
    for i in range(count):
        if int(round(array2[i])) == temp:
            pass
        else:
```

---

The above code defines functions for calculating properties of Rydberg atoms, such as their radiative lifetimes and bottleneck effects in thermal environments. The functions are designed to handle different aspects of quantum state transitions in Rydberg atoms, which are important in research fields like plasma physics and quantum computing.
array22 = np.append(array22, int(round(array2[i])))
array12 = np.append(array12, array1[i])
indexarr = np.append(indexarr, i)
temp = int(round(array2[i]))
return array12, array22, indexarr

def plotBK(dvec, bkindex, tindex):
    a = np.array(())
    b = np.array(())
    i = 0
    for index in tindex:
        a = np.append(a, dvec[index][bkindex[i]])
        i = i+1
    return a

def Conservation(array1):
    arrayout = np.zeros(len(array1[0]))
    rows = array1.shape[0]  # level array
    cols = array1.shape[1]  # time
    for j in range(cols):
        for i in range(rows):
            arrayout[j] += array1[i][j]
    return np.array(arrayout)