



**Linear and Nonlinear Spectroscopy of
Optically-Thick Argon and Argon-Helium
Plasmas in Radio-Frequency Dielectric-Barrier
Discharges**

DISSERTATION

Ben Eshel

AFIT-ENP-DS-17-J-011

**DEPARTMENT OF THE AIR FORCE
AIR UNIVERSITY**

AIR FORCE INSTITUTE OF TECHNOLOGY

Wright-Patterson Air Force Base, Ohio

DISTRIBUTION STATEMENT A
APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

The views expressed in this document are those of the author and do not reflect the official policy or position of the United States Air Force, the United States Department of Defense or the United States Government. This material is declared a work of the U.S. Government and is not subject to copyright protection in the United States.

AFIT-ENP-DS-17-J-011

LINEAR AND NONLINEAR SPECTROSCOPY OF OPTICALLY-THICK
ARGON AND ARGON-HELIUM PLASMAS IN RADIO-FREQUENCY
DIELECTRIC-BARRIER DISCHARGES

DISSERTATION

Presented to the Faculty
Graduate School of Engineering and Management
Air Force Institute of Technology
Air University
Air Education and Training Command
in Partial Fulfillment of the Requirements for the
Degree of Doctorate of Philosophy in Applied Physics

Ben Eshel, M.S.

May 25, 2017

DISTRIBUTION STATEMENT A
APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

AFIT-ENP-DS-17-J-011

LINEAR AND NONLINEAR SPECTROSCOPY OF OPTICALLY-THICK
ARGON AND ARGON-HELIUM PLASMAS IN RADIO-FREQUENCY
DIELECTRIC-BARRIER DISCHARGES

DISSERTATION

Ben Eshel, M.S.

Committee Membership:

Dr. Glen P. Perram
Chair

Dr. David E. Weeks
Member

Dr. David Dolson
Member

Abstract

The excited states of argon (Ar) in radio-frequency, dielectric barrier discharges have been studied using linear and non-linear techniques. The broadening and shift rates of several Ar (s-p) transitions were measured in 25%, 10%, 5% and 2.5% argon in helium (He) gas mixtures from 10 to 160 Torr. The broadening rates of the 795.036 nm ($1s_3 \rightarrow 2p_4$), 800.836 nm ($1s_4 \rightarrow 2p_6$), and 801.699 nm ($1s_5 \rightarrow 2p_8$) in a 5% Ar in He gas mixture were found to be 20 ± 1.4 , 17 ± 1.1 , and 15.5 ± 0.6 MHz/Torr with corresponding shift rates of 4.0 ± 0.7 , 2.2 ± 0.4 , and 2.0 ± 0.4 MHz/Torr at a temperature of 440 ± 20 K. The phase-changing collision cross sections of the Ar-Ar interaction were shown to have a $T^{-0.2}$ dependence for states terminating on a metastable level, consistent with the prediction of Lindholm-Foley theory and a $T^{-0.4 \pm 0.1}$ dependence for states terminating on a resonance level. Broadening and shift rates of 38.5 ± 1.2 and -1.9 ± 0.2 MHz/Torr for the 842.696 nm ($1s_4 \rightarrow 2p_8$) resonance transition were also measured in a pure Ar discharge from 1.45 to 400 Torr. The low pressure (less than 20 Torr) line shapes showed a systematic residual when fit with a Voigt profile. This residual was reduced when fit with a generalized Rautian-Sobelman profile which accounts for velocity-changing collisions in a hard-collision model and the correlation between the phase-changing and velocity-changing collisions. A systematic residual was still observed due to the failure of the hard-collision model to describe the Ar-Ar collision. The ($1s_4$) density was observed as a function of flow velocity and was found to increase from $1.6\text{--}7.5 \times 10^{10} \text{ cm}^{-3}$ as the flow velocity increased from 90-2400 cm/s. An asymmetric line shape was observed at higher flow rates and is found to linearly correlate with flow velocity.

The saturation behavior of the 811.7542 nm ($1s_5 \rightarrow 2p_9$) transition was studied

using non-linear, sub-Doppler techniques. The observed line shape showed a recess in the core of the line shape, leading to a multi-peak structure which was found to correspond to total absorption of the probe beam. The sub-Doppler line shape was observed as the discharge power was varied from 1 - 40 W and the depth of the recession was found to correlate well with the optical-thickness of the medium. The laser pump and probe power were also varied and it was found that the recession became more shallow as pump power increased from 1.8-17.7 W/cm² due to a spatial increase in the saturation of the transition. A procedure was developed for predicting the line shape in an optically-thick medium using a rate equation formalism for the populations and the laser propagation equation for the spatial dependence of the pump and probe lasers and was shown to qualitatively agree with measurements.

An additional analysis was conducted on the spin-orbit mixing cross-sections of alkali-metal-rare-gas collisions where the interaction was modeled using a time-dependent perturbation theory analysis with an analytic pseudo-potential for the interaction. The full database of alkali-metal-rare-gas cross-sections was well organized by adiabaticity with deviations corresponding to the polarizability of the interaction pair, represented by the C_6 dispersion coefficient. The proposed model was able to reduce the temperature-dependent rate down to a single parameter, the amplitude of the pseudo-potential and was shown to perform equivalently well to the empirical model proposed by *Gallagher*.

To my wife, Mollie, and my daughter, Isabelle.

Acknowledgements

I would like to thank my adviser Dr. Glen Perram for his guidance and patience over the last five years as well as for his financial support that has made obtaining this degree a reality. His experience and knowledge have been invaluable in helping me navigate the complex work and often daunting workload and have molded me into the capable scientist I am today.

I would also like to thank Dr. Chris Rice for his significant support in day-to-day laboratory operations, for teaching me the ins and outs of countless pieces of equipment and for making himself always available to assist in any manner he could. Without his assistance it'd be unlikely that this work would have been completed in a timely manner.

Finally, I would like to thank Dr. David Weeks for our oft long, and occasionally off-topic, discussions about the theoretical intricacies involved in interpreting experimental results. Being able to discuss those theoretical underpinnings helped to greatly improve my understanding of the phenomena studied.

Ben Eshel

Table of Contents

	Page
Abstract	iv
Acknowledgements	vii
List of Figures	x
List of Tables	xv
I. Introduction	1
II. Background and Theory	5
2.1 Notation, Energy Levels and Transitions	5
2.2 Kinetics of Atmospheric Pressure Rare Gas Discharges	9
2.3 Rare Gas Discharges	11
2.4 Plasma Spectroscopy	17
2.4.1 Tunable Laser Absorption Spectroscopy	18
2.5 Doppler-Limited Lineshapes in Plasmas	19
2.6 Saturation Spectroscopy	25
2.6.1 Sub-Doppler lineshapes	28
III. Five-level Ar-He Laser and Plasma Model	31
3.1 Introduction	31
3.2 Mechanisms and Rate Equations	32
3.3 Application to Laser Experiments	39
3.3.1 PSI Microwave-Resonant Strip Discharge	42
3.3.2 AFRL Radio-Frequency Capacitively-Coupled Discharge	44
IV. Pressure broadening and shift rates for Ar (s-p) transitions observed in an Ar-He discharge	51
Abstract	51
4.1 Introduction	51
4.2 Experiment	55
4.3 Results	57
4.4 Discussion	68
4.5 Conclusion	76

	Page
V. Pressure Broadening and Shift Rates of Resonance Transitions in a Pure Ar Discharge	77
5.1 Introduction	77
5.2 Experiment	78
5.3 Results and Discussion	81
5.4 Conclusion	97
VI. Saturation spectroscopy of an optically thick argon plasma	98
6.1 Introduction	98
6.2 Experiment	101
6.3 Results	105
6.4 Discussion	115
6.5 Conclusion	126
VII. Role of adiabaticity in controlling alkali metal fine structure mixing induced by rare gases	128
Abstract	128
7.1 Introduction	128
7.2 Review of fine structure mixing rates	131
7.3 Non-Adiabatic Collision Theory	140
7.4 Discussion	144
7.5 Conclusion	152
VIII. Conclusions	154
8.1 Future Work	158
Appendix A. Ar-He Five-Level Model Rate Table	162
Appendix B. Pressure Broadening and Shift Data	165
B.1 Lineshapes	165
B.2 Number Density, Lorentzian Width, Lorentzian Shift, and Doppler Width	173
Appendix C. Saturation Spectroscopy Data	184
C.1 Laser Absorption Spectroscopy Data	184
C.2 Intermodulated Fluorescence Spectroscopy Data	186
C.3 Saturation Spectroscopy Data	190
Appendix D. Microcathode Structured Array Schematic	198
Bibliography	200

List of Figures

Figure		Page
1.	Grotrian Diagram of Argon	6
2.	Grotrian Diagram of Xe	8
3.	Diagrams of Discharges Tested for RGL.....	12
4.	Comparison of Gaussian, Lorentzian and Voigt Lineshapes	24
5.	Comparison of Doppler-limited and sub-Doppler Saturation Spectra	29
6.	Five-Level Laser Model Energy Levels and Mechanisms	33
7.	Ar* electron temperature dependence.....	36
8.	Ar* electron density dependence	37
9.	Ar* gas temperature dependence.....	38
10.	Influence of Pump Bandwidth on Gain Behavior	41
11.	Five-Level Model - Microdischarge Ar-He cw Laser	43
12.	$1s_5$ and $1s_4$ density as a function of electron temperature	45
13.	$1s_5/1s_4$ and $2p_{10}/2p_9$ ratios as a function of electron density	46
14.	Five-Level Model - Large volume, Capacitively coupled Ar-He discharge	47
15.	Five-Level Model - Optimal Laser Performance	50
16.	Grotrian Diagram of Ar - Transitions Emphasized.....	53
17.	Tuneable Diode Laser Absorption Spectroscopy Apparatus	57
18.	Absorption spectra of 801.699 nm transition from 10 to 160 Torr	59
19.	$1s_5$ Number Density as a function of pressure.....	61

Figure	Page
20.	Doppler Width and Temperature as a function of pressure 63
21.	Lorentzian widths for all three transitions 64
22.	Lorentzian shifts for all three transitions 65
23.	Temperature Dependence of the Pressure Broadening Rate 67
24.	Pressure Broadening rates as a function of Ar mixture 70
25.	Temperature Dependence of the Cross Sections 73
26.	Multiplex Laser Absorption Spectroscopy Diagram 79
27.	Absorption spectra of 842.6963 nm Transition as a function of flow rate..... 83
28.	Pressure gradient as a function of velocity..... 84
29.	Total absorbance of the 842.686 nm transition as a function of velocity 86
30.	Absorption spectra of 842.6963 nm Transition as a function of pressure 88
31.	Absorption spectra of 842.6963 nm transition at low pressure with Voigt and generalized Raution-Sobelman fits 91
32.	Lorentzian Width and Shift as a function of Pressure 92
33.	Doppler width and Temperature as a function of pressure 94
34.	Number density trend for variable pressure, power and flow rate..... 96
35.	Saturated Absorption Spectroscopy Experimental Diagram..... 101
36.	Images of the Ar Discharge at 50 Torr 104
37.	Probe transmission spectra at 5 and 50 Torr..... 106
38.	Absorption spectra of pure Ar at 5 and 50 Torr 107

Figure	Page
39. Inter-modulated fluorescence spectra of pure Ar at 50 Torr	109
40. Probe transmission spectra as a function of pump intensity	111
41. Pump absorption and probe transmission spectra in pure Ar at 1.3 Torr at low and high pump intensity	113
42. Rate Equation Diagram	117
43. Line shape model output	121
44. Line shape model for 5 and 50 Torr vs RF Power	123
45. Lineshape model for 5 and 50 Torr vs Laser Intensity	125
46. Log Cross-Section vs Reduced Temperature	132
47. Natural Log of Probability vs Adiabaticity	136
48. Natural log of Adiabaticity Normalized Cross Section	137
49. Probability vs Adiabaticity with Theoretical Fit	145
50. V0 Parameter vs Polarizability	146
51. Theoretical Potentials vs Calculated Potentials	148
52. Probability vs Adiabaticity with Theoretical Fit - Compare to Lewis' Full Calculations	149
53. Comparison of Rb-He data to Gallagher's empirical model and our semi-classical model	151
54. Absorption spectra of 795.036 nm transition in 2.5 and 5% Ar-He mixtures	166
55. Absorption spectra of 795.036 nm transition in 10 and 25% Ar-He mixtures	167
56. Absorption spectra of 800.836 nm transition in a 2.5% Ar-He mixtures	168
57. Absorption spectra of 800.836 nm transition in a 5% Ar-He mixtures	169

Figure	Page
58. Absorption spectra of 800.836 nm transition in a 10% Ar-He mixtures	170
59. Absorption spectra of 801.699 nm transition in 2.5 and 5% Ar-He mixtures	171
60. Absorption spectra of 801.699 nm transition in 10 and 25% Ar-He mixtures	172
61. Four-Box Plot of 795.036 nm transition in a 2.5% Ar-He mixture	173
62. Four-Box Plot of 795.036 nm transition in a 5% Ar-He mixture	174
63. Four-Box Plot of 795.036 nm transition in a 10% Ar-He mixture	175
64. Four-Box Plot of 795.036 nm transition in a 25% Ar-He mixture	176
65. Four-Box Plot of 800.836 nm transition in a 2.5% Ar-He mixture	177
66. Four-Box Plot of 800.836 nm transition in a 5% Ar-He mixture	178
67. Four-Box Plot of 800.836 nm transition in a 10% Ar-He mixture	179
68. Four-Box Plot of 801.699 nm transition in a 2.5% Ar-He mixture	180
69. Four-Box Plot of 801.699 nm transition in a 5% Ar-He mixture	181
70. Four-Box Plot of 801.699 nm transition in a 10% Ar-He mixture	182
71. Four-Box Plot of 801.699 nm transition in a 25% Ar-He mixture	183
72. Absorption spectra of 811.7542 nm transition in pure Ar at 5 and 10 Torr	184

Figure	Page
73.	Absorption spectra of 811 nm transition in pure Ar at 25 and 50 Torr 185
74.	Intermodulated-fluorescence spectra of 811 nm transition in pure Ar at 5 Torr 186
75.	Intermodulated-fluorescence spectra of 811 nm transition in pure Ar at 10 Torr 187
76.	Intermodulated-fluorescence spectra of 811 nm transition in pure Ar at 25 Torr 188
77.	Intermodulated-fluorescence spectra of 811 nm transition in pure Ar at 50 Torr 189
78.	Saturation and sub-Doppler spectra of 811 nm transition in pure Ar at 1.3 and 3.6 Torr 191
79.	Saturation and sub-Doppler spectra of 811 nm transition in pure Ar at 5 and 10 Torr 192
80.	Saturation and sub-Doppler spectra of 811 nm transition in pure Ar at 25 and 50 Torr 193
81.	High intensity saturation and sub-Doppler spectra of 811 nm transition in pure Ar at 1.3 and 3.6 Torr 194
82.	High intensity saturation and sub-Doppler spectra of 811 nm transition in pure Ar at 5 and 10 Torr 195
83.	Saturation and sub-Doppler spectra of 811 nm transition in pure Ar at 5 as a function of varying probe intensity 196
84.	Saturation and sub-Doppler spectra of 811 nm transition in pure Ar at 5 and 50 Torr as a function of pump intensity 197
85.	Microhollow Cathode Discharge Array Schematic 198
86.	Microcathode Structured Array Design 199

List of Tables

Table		Page
1.	Cavity parameters for three cases of the five-level model results	42
2.	Broadening coefficients for the 801.699 nm, 800.836 nm and 795.036 nm transitions.....	71
3.	Shifting coefficients for the 801.699 nm, 800.836 nm and 795.036 nm transitions	74
4.	Pressure broadening and shift rates of the 842.6963 nm transition	95
5.	Rare Gas Radii	134
6.	Quantum defect cross-sections	135
7.	C_6 Dispersion Coefficients.....	139
8.	Summary of pressure broadening and shift rates	155
9.	Einstein A coefficients for Ar transitions	162
10.	Electron-impact production and spin-orbit mixing mechanisms and rate coefficients	163
11.	Ar-He impact spin-orbit mixing mechanisms and rate coefficients	163
12.	Ar-Ar impact spin-orbit mixing mechanisms and rate coefficients	164

LINEAR AND NONLINEAR SPECTROSCOPY OF OPTICALLY-THICK
ARGON AND ARGON-HELIUM PLASMAS IN RADIO-FREQUENCY
DIELECTRIC-BARRIER DISCHARGES

I. Introduction

Since the inception of the laser in the 1960s, the Department of Defense has had a particular interest in the weaponization of the laser. This drive directly led to the rapid development of chemical lasers in the 1970s culminating in the megawatt class hydrogen-fluoride and deuterium-fluoride (MIRACL, Alpha, THEL) lasers [25]. The goal of a deployable, high-power (1 MW) laser weapons system for strategic engagement of intercontinental ballistic missiles was achieved with the chemical oxygen iodine laser (COIL) on the airborne laser (ABL) platform. This system successfully demonstrated the ability to destroy a missile at range (200 km) but was never realized in the battlespace due to cost and logistical considerations [142]. In parallel to the MW-class chemical lasers was the development of the diode-pumped solid state laser (DPSSL) and fiber laser (FL). DPSSL systems have high wall-plug efficiencies but are limited in their scalability to tens of kW due to thermal issues such as temperature gradients that degrade beam quality and put significant stresses on the gain material eventually leading to their destruction. FLs suffer from similar thermal issues but are also limited by other fiber-specific parasitic processes such as stimulated Brillouin scattering (SBS) [124]. This cap on potential output powers of solid-state systems has led to significant research in coherent and spectral beam combining of lower-power systems to achieve an equivalent high-power laser. Spectral beam combining uses a spectrally dispersive element to spatially combine several smaller lasers that

have slightly different wavelengths. Incoherent beam combining can result in good beam quality of the output laser but the propagation of the incoherently combined beam will suffer from chromatic aberrations and other wavelength-specific effects. Coherent beam combining involves temporally overlapping the electric fields of the laser beam by tuning the phase of each output laser. This leads to a single coherent beam with narrow spectral bandwidth (in contrast to the wider bandwidth of the incoherently combined beams). The feedback loop and adaptive system required to coherently combine beams scales rapidly in complexity with the number of beams and is therefore limited by current phasing techniques and timing of feedback systems. Lockheed-Martin recently demonstrated a 105 kW DPSSL system composed of coherently combined 15 kW DPSSLs [112].

In 2003 William Krupke suggested using the alkali metal vapor as a medium for combining multiple lower power diodes (a few kW) into a single aperture, coherent beam. The diode pumped alkali laser (DPAL) was born and the technology developed rapidly leading to multi-kW demonstrations and high-intensity scaling [100, 177, 119, 26, 85, 150]. The three-level laser consists of the pump transition from the $n^2S_{1/2}$ ground state to the upper fine-structure split $n^2P_{3/2}$ state, collisional mixing between fine-structure levels $n^2P_{3/2} \rightarrow n^2P_{1/2}$, and then lasing back to the ground state. Collisional mixing occurs between an alkali atom and a buffer gas, generally at a much higher pressure. In order to model the gain medium and lasing profiles, the temperature dependence of these rates must be known.

There are several requirements to operate DPAL systems at peak efficiency: the pump laser must be of sufficient intensity to bleach the full length of the gain medium, the pump laser and atomic transition must have sufficient overlap, and the gas pressure must be high enough so that the spin-orbit mixing rate does not bottleneck the laser cycle. The first condition requires laser intensities on the order of kW/cm², the

second requires that the pressure broadening and shift rates of the atomic transition be well known and that the bandwidth of the pump laser is significantly narrowed. The third condition can be satisfied using He at atmospheric pressure in Potassium (K) due to its small spin-orbit splitting but can be used in a rubidium (Rb) DPAL at high pressures (1-20 atm). To operate an atmospheric pressure Rb DPAL or a cesium (Cs) DPAL, hydrocarbons must be used to increase the fine structure mixing rate and prevent bottlenecking. The main issues with the DPAL are the reactivity of the alkali vapor and the requirement to maintain an elevated temperature, the first of which requires special handling of the material and the need for alkali-resistive coatings and flow systems composed completely of metal parts, maintained a slightly elevated temperature over the complete system to prevent condensation of the alkali on cold spots. The reactivity also leads to a short operational lifetime of the gain medium if a hydrocarbon buffer gas is used as the alkali forms alkali halides over time.

One alternative to the DPAL is the diode-pumped rare gas laser (DPRGL), a recently proposed laser system that uses chemically inert rare gas mixtures in a weakly-ionized, low-power electrical discharge as the gain medium for a three- or four-level laser. This system is commonly referred to as a diode-pumped alkali laser (DPAL) analogue since the transition properties (transitions in the NIR, Einstein A Coefficients on the order of 10^7 s^{-1} , favorable degeneracy ratios, small spin-orbit splitting for near gas-kinetic mixing, etc) tend to be similar, the key difference being that the inert gases of the DPRGL do not require any special reactivity handling. The DPRGL was first proposed and demonstrated in 2012 by Heaven, et al, who showed that pulsed lasing was easily achievable in a large-volume (80 cm^3), high-voltage (18 kV), pulsed discharge [74] with any rare gas in combination with helium as a buffer gas (Ne-He, Ar-He, Kr-He, Xe-He) using a 10 ns optical parametric os-

cillator (OPO) as a pump source. Shortly thereafter continuous-wave (cw) laser action was demonstrated in a small volume microwave frequency strip resonator (0.005 cm^3) using a titanium-sapphire (Ti:Saph) ring laser as an optical surrogate to the diode pumps [154]. Pulsed lasing was also demonstrated in a larger-volume (3.2 cm^3) radio-frequency, liquid-cooled, dielectric barrier discharge [68] using a 100 ns Ti:Saph pump source. The highest output laser power achieved is 2.6 W in a 200 kHz, pulsed discharge of medium volume (0.36 cm^3) using Ar-He and pumped by a 30 W volume-Bragg-grating (VBG) narrowed diode source [81]. In the alkali system increasing the laser ground-state density is as simple as increasing the temperature of a melt pool. In the DPRGL the melt pool has been exchanged for the rare gas discharge which must be operated at large volume and high pressure. The development of this discharge is the main issue preventing rapid advancement of the rare gas laser.

The rare gas laser medium is the subject of a majority of this work along with a theoretical effort to predict the temperature dependence of the alkali spin-orbit mixing rates. Pure Ar and Ar-He, radio-frequency discharges with volumes of 0.5 to 2.5 cm^3 are studied using various laser sources, discharge powers and gas pressures. A five-level model of the rare gas laser system and the laser performance dependency on plasma parameters is given in Chapter III. The pressure broadening and shift rates of several transitions have been published in the *Journal of Quantitative Spectroscopy and Radiative Transfer* and is the subject of Chapter IV [57]. The behavior of the rare gas medium under high intensity laser fields using sub-Doppler techniques is presented in Chapter VI and is being prepared for submission to *Physical Review A*. A time-dependent perturbation theory approach to predicting the temperature of the alkali fine-structure mixing rates in collisions with rare gases has been published in *Physical Review A* and is the subject of Chapter VII with the full mathematical treatment provided in the Supplementary Material [56].

II. Background and Theory

2.1 Notation, Energy Levels and Transitions

The energy level structure of the rare gas gain medium differs from that of the alkali vapor in several key ways. The alkali has a single valence electron corresponding to a simple coupling of core and electron angular momenta that is well described by Russell-Saunders (L-S) coupling. Only the ground-state of the rare gas atom is given a L-S coupling term, $^1S_0$. In order to create the laser ground state in the rare gas medium a core electron must be excited. This leads to a more complex coupling scheme between the core, which has a hole, and the valence electron. The energy levels are organized using Racah notation which gives term symbols of the form $nl(^{2S+1}P_j)[K]_J$ where n and l are the electronic and angular momentum quantum numbers of the core, $(^{2S+1}P_j)$ is the Russell-Saunders term for the core with j being the total angular momentum of the core, $K = j + l_e$ is the sum of the core angular momentum and the orbital angular momentum of the valence electron, and $J = K + s_e$ is the sum of the core-coupled angular momentum and the valence electron spin. This rather complex notation organizes the energy levels as shown in Fig. 1, which also provides the simpler and more commonly used Paschen notation. It denotes symbols as l_i where l is alphabetic symbol corresponding to the orbital angular momentum quantum number of the core, and i is an index that decreases with excited state. This is occasionally denoted by al_i where the a in the serves as a surrogate numbering for the excited state manifold to distinguish levels of equivalent quantum numbers. Generally, the levels are denoted by Paschen notation with more clarity provided by the $[K]_J$ piece of the Racah notation. The first excited level would then be referred to as the $1s_5([3/2]_2)$ state.

The Ar-He system is most widely considered where the excited states of the Ar

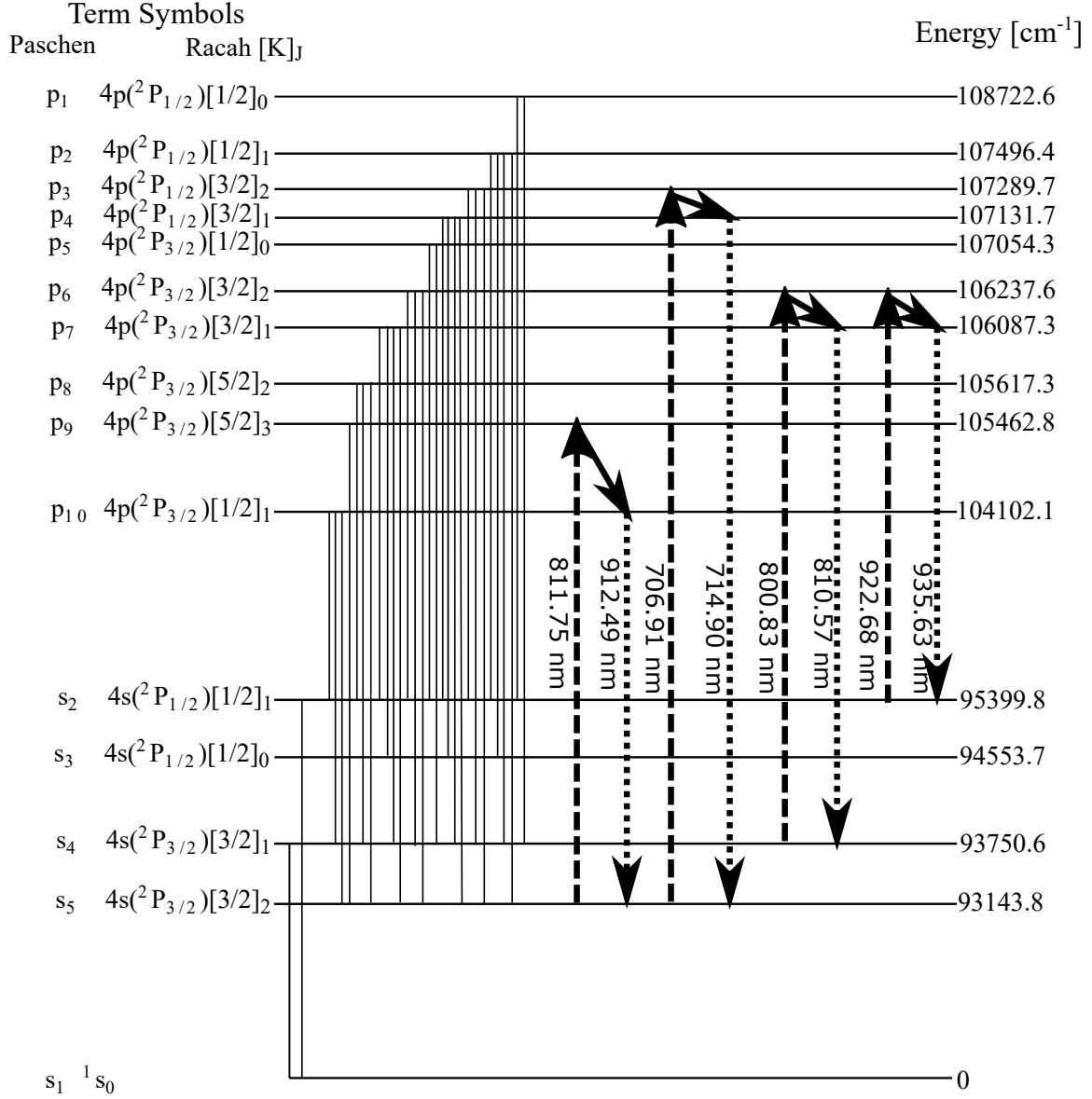


Figure 1. The Grotrian diagram of argon is shown. Line styles correspond to optically allowed transitions (—), pump transitions (---), collisional mixing events (—) and lasing transitions (.....).

atom are used for the lasing cycle and He is used as a buffer gas. Several laser cycles are shown in Fig. 1 with a focus on three-level cycles. Before discussing the laser cycles there are a few noteworthy features of this energy level diagram. The first makes the need for a rare gas discharge obvious as the first excited state is 93143.8 cm^{-1} above the ground state corresponding to a vacuum ultraviolet (VUV) wavelength of 107.361 nm. An electron with a minimum of 11.55 eV is required to transfer enough energy to excite the closed-shell electron up to these states. The thick and thin vertical lines correspond to optically allowed transitions with the resonance transitions ($1s_{2,4} \rightarrow 1s_0$) being defined by the thick lines and corresponding to VUV wavelengths of 104.8 and 106.7 nm, respectively. The $2p$ to $1s$ transitions lie in the range of red-visible to NIR at 696 to 1150 nm. There are a large number of potential three-level laser cycles originating on both metastable and radiatively-trapped resonance levels. The pump transitions ($--$), collisional spin-orbit mixing ($-$), and lasing transitions ($\cdots$) are shown in Fig. 1. The spin-orbit splittings of the upper pump and laser levels are nearly all on the order of a thermal collision (208 cm^{-1}) with the exception of the $p_9 \rightarrow p_{10}$ case. The small splittings lead to quantum efficiencies greater than 0.88 and lasing wavelengths range from 700 to 935 nm. This wavelength range makes Ar a particularly good candidate for diode pumps as well as surrogate Ti:Saph pump sources.

The excited states can be produced in any rare gas medium and the energy level structure gets especially interesting for the xenon system where the inclusion of d states makes cascade lasing transitions possible. Fig. 2 shows the Grotrian diagram for Xe which has complexity absent in the Ar system. Three-level laser cycles are still possible in Xe but lasing wavelengths with good atmospheric transmission properties can be achieved with a cascade lasing scheme. In these schemes a nearby p state is pumped (ex. $s_5 \rightarrow p_5$), a spin-orbit mixing event moves the population over

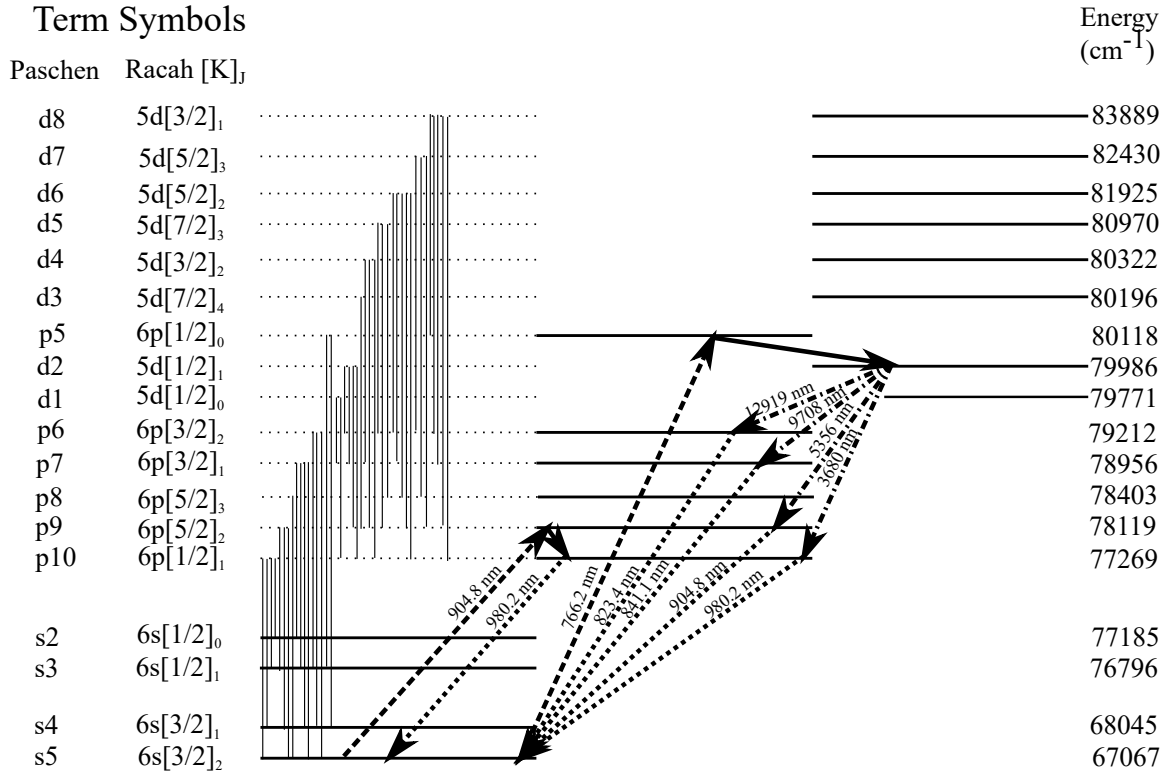


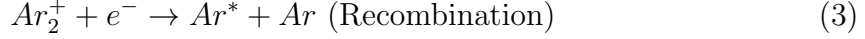
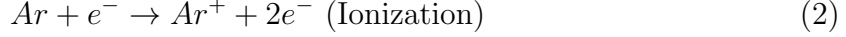
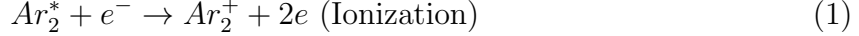
Figure 2. The Grotrian diagram of xenon is shown. Line styles correspond to optically allowed transitions (—), pump transitions (---), collisional mixing events (—), lasing transitions (.....), and cascade lasing transitions (-.-.).

to a nearby d state (ex. $p_5 \rightarrow d_2$) and then that level lases down to a number of different p -states. This level can be tuned using the proper laser cavity and by minimizing losses at a single wavelength using wavelength specific optical elements. From this upper p -state, the system will lase back down to the ground state on an equivalent three-level laser line. The benefits of such a cascade system are the production of a beacon laser and HEL laser at similar powers such that the beacon laser can be used for atmospheric corrections over equivalent distances to the pump laser. Krypton contains an energy level structure similar to that of Xe with nearby d -states allowing for several mid-IR transitions in a cascade lasing scheme. Despite the interesting behavior in Kr and Xe, Ar has been chosen for all of the work covered in this document.

2.2 Kinetics of Atmospheric Pressure Rare Gas Discharges

The kinetics of a rare gas discharge consist of a considerable number of mechanisms. The excited states are produced from the ground-state using electron impact excitation, intra-multiplet (s to s , p to p , d to d) and inter-multiplet (s to p , p to d) mixing is achieved through both neutral-neutral collisions and electron-neutral collisions, and both radiative emission and collisional quenching deplete these excited states. In addition to the excitation mechanisms, maintaining the plasma requires an ionization and recombination equilibrium with ions created both directly by electron impact ionization and through the Ar_2^* excimers and destroyed by recombination of the Ar_2^+ ion. In an Ar-He discharge, the dominant ionization and recombination

mechanisms are



where Eq. (1, 3) are the dominant ionization and recombination mechanisms for a pure Ar discharge as well as for mixtures above 20% Ar in He and Eq. (2, 3) are the dominant mechanisms for discharges with Ar percentages below 20%. A comprehensive listing of all the involved mechanisms for a pure Ar discharge can be found in the collisional radiative model of Zhu, et al [209]. Little modeling of Ar-He discharges has been conducted with many of the Ar-He collisional rates still unmeasured [171].

The first excited state manifold consists of four Paschen s-states, two of which are metastable and two of which are the upper states of resonance transitions. The metastable levels, $1s_5$ ($[3/2]_2$) and $1s_3$ ($[1/2]_0$), consist of optically forbidden transitions to the ground $1s_0$ state with $\Delta J = 2$ and $\Delta J = 0$ with J going from 0 to 0, respectively. The metastable levels have lifetimes in the tens of seconds [91] but are easily quenched by impurities and wall collisions leading to significantly shorter lifetimes on the order of microseconds [145, 192]. The resonance levels, $1s_4$ ($[3/2]_1$) and $1s_2$ ($[1/2]_1$), are optically allowed transitions with $\Delta J = 1$. These resonance transitions have Einstein A Coefficients of 1.18×10^8 and $5.18 \times 10^8 \text{ s}^{-1}$ for the $1s_4$ and $1s_2$ levels, respectively, but are strongly radiation trapped which leads to densities approximately on the order of the metastable levels. The key issue for the development and scaling of the rare gas laser is producing an atmospheric pressure discharge at large volume (greater than 10 cm^3) with a sufficient $1s_5$ density, on the

order of 10^{13} cm^3 .

2.3 Rare Gas Discharges

Towards the goal of large-volume, atmospheric pressure plasmas producing $\text{Ar}(1s_5)$ densities greater than 10^{13} cm^3 , a large number of discharge configurations, presented in chronological order, have been tested with various geometries and plasma production frequencies. Schematic diagrams comparing the geometries and driving frequencies of the various discharges is shown in Fig. 3. These discharges are compared using the metrics of $\text{Ar}(1s_5)$ production, driving reduced electric field (E/N), driving frequency, and plasma volume. It is understood that the driving E/N is not representative of the plasma E/N as the maintaining voltage that exists in the plasma after breakdown is significantly lower, which would be associated with a equivalently lower E/N . It is worth noting that most of the RGL demonstrations have been conducted in Ar-He mixtures which is motivated by several different phenomena. Qualitatively, Ar-He discharges where the fraction of Ar is small (less than 25%) are shown to operate more stably. This stability is thought to be caused by the improved E/N in the plasma corresponding to existence of a larger high-energy electron tail to the distribution function but this is not understood in its entirety.

The original demonstration of the RGL was conducted in a pulsed, direct-current discharge that used the cavity of an Excimer laser by Drs. Michael Heaven and Jiande Han at Emory University [74], shown in Fig. 3(a). The dimensions of the cavity are 80 cm x 2.5 cm with a voltage of 18 kV in a 10 ns pulse operated at 10 Hz. These dimensions correspond to a reduced E-field, at 150 Torr, of 150 Td. The cavity was filled with ultra-high purity (UHP, 99.999%) Ar, Kr and Xe at a partial pressure of 22.5 Torr and was then filled with He to the total pressure ranging from 150 Torr to 1500 Torr. Pure Ar was also investigated. Number densities in excess of 10^{13} cm^{-3}

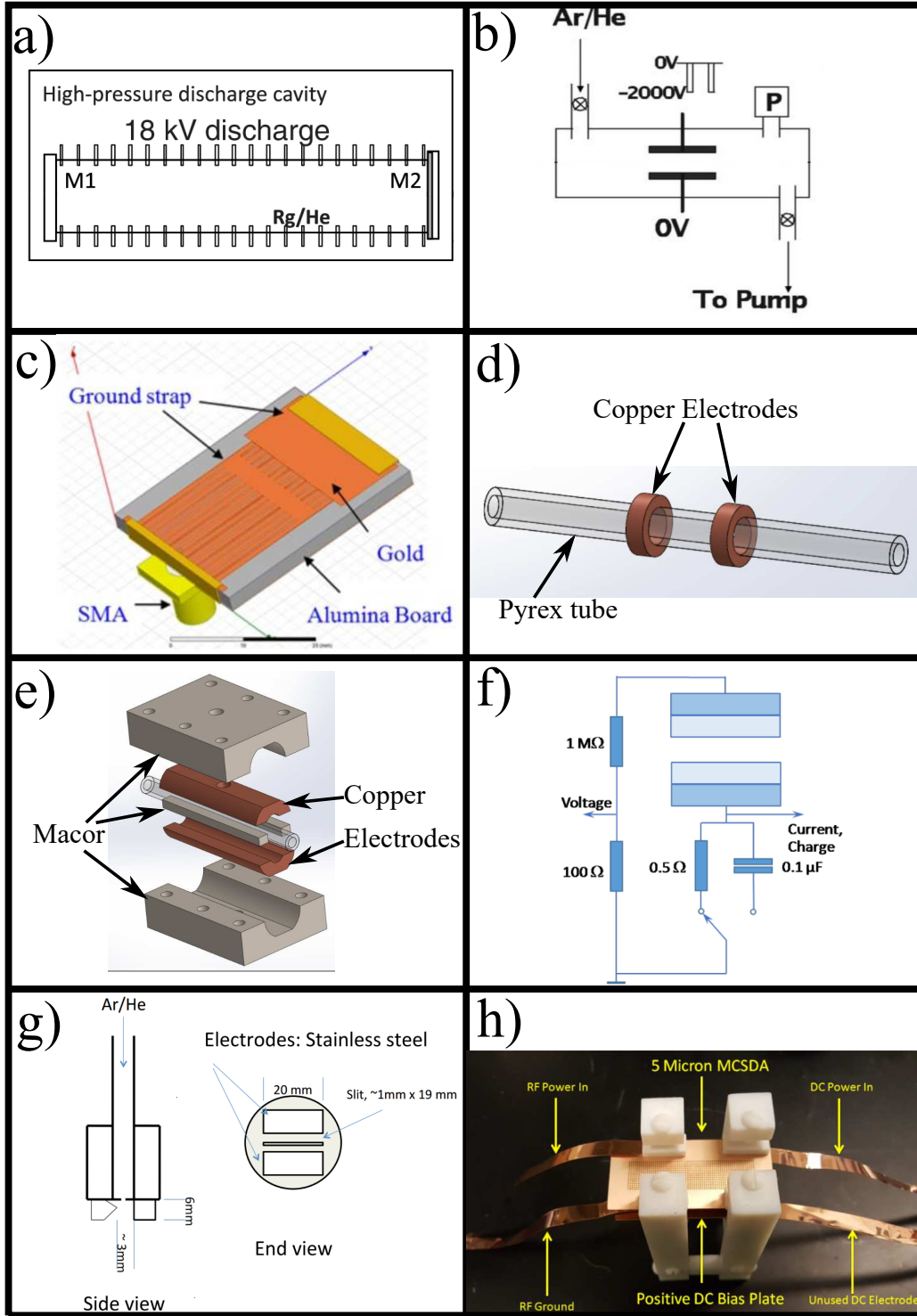


Figure 3. Discharge diagrams are shown for the eight discharges that have been tested: (a) a 10 Hz pulsed discharge [74], (b) a 1 kHz pulsed discharge [73], (c) a linear microwave microstrip resonator array [154], (d) an RF longitudinal DBD [57], (e) an RF transverse DBD, (f) a 20 kHz pulsed DBD [118], (g) a 200 kHz high repetition rate pulsed discharge and (h) a hybrid RF/DC MCSDA.

were produced with projected lifetimes in the microseconds. Absorption of the pump laser was sufficiently high that bleaching of the full volume required waiting for the metastable level to decay sufficiently. Pulsed laser demonstrations were conducted in Ar-He and Kr-He using an optical-parametric-oscillator as a pump source and gain measurements were made with a pulsed tunable dye laser with a 10 GHz linewidth and a 10 ns pulse duration.

The first diode-pumped demonstration was conducted in a pulsed, medium rep-rate (1 kHz) discharge [73], shown in Fig. 3(b). The geometry consisted of two parallel stainless-steel, square plates (2.5 cm) separated by 0.5 cm, corresponding to a plasma volume of 3.125 cm³. The discharge voltage was varied from -1000 to -2000 V and the pulse width was 1 μ s with a peak reduced E-field, at 150 Torr, of 41 to 83 Td. Stable operation was demonstrated at 375 Torr but the exposed electrodes of the discharge lead to stability issues with operation time as optimal performance was observed with freshly cleaned electrodes. This is not uncommon for plasmas where ion bombardment of the electrodes causes sputtering and damage. UHP Ar and He were flowed through the cell. This discharge was recently modeled by Emmons, et al, and it was found that Ar metastable density is peaked in the over-voltage stage of the pulse and then proceeds to decay rapidly to an order-of-magnitude lower density in the quasi-steady-state region [77].

A fully cw demonstration was conducted in Ar-He mixtures in a microwave frequency, linear micro-strip resonator arrays [154], shown in Fig. 3(c). These discharges consist of copper strips placed on an insulating (or dielectric) medium separated from a gold ground plate by 250 μ m gap. With a driving frequency of 920 MHz these discharges produce a high-pressure plasma that is stable both spatially and temporally. The total length along the gap was 1.9 cm with a vertical extent of 200 μ m for a total volume of 9.5×10^{-4} cm³. The electric-field was not monitored so the reduced

electric field could not be calculated for comparison. A 2% Ar-He mixture was flowed at 2 slm over the resonator array. The production of the metastable state is efficient with densities of $4 \times 10^{12} \text{ cm}^{-3}$ at input powers of 9 W and at atmospheric pressure. The density was sufficiently high to conduct a laser demonstration using a Ti:Saph ring-laser as an optical surrogate to a diode. The system was pumped at 4 kW/cm^2 and a gain of 0.7 cm^{-1} was measured. By placing a cavity around the discharge an output power of 22 mW for 40 mW absorbed was demonstrated corresponding to a 55% optical-to-optical efficiency.

Concurrently with the 1 kHz pulsed-discharge and the linear microwave strip-resonator array has been, in the present dissertation project, the development of a radio-frequency, capacitively-coupled dielectric barrier discharge in both longitudinal (concentric ring) and transverse (clamshell) type geometries, shown in Fig. 3(d) and (e), respectively. In both cases the electrodes are placed outside of either an alumina or pyrex tube of 1.27 cm O.D. (0.381 cm I.D.). UHP mixtures of pure Ar and Ar-He are flowed at rates ranging from 5 to 5000 sccm. With the electrodes on the outside of the dielectric material, these discharges are considered electrode-less which prevents sputtering of the electrode material and maintains purity of the gas mixture. For input powers of 10 W, the RMS voltage of these discharges is approximately 500 V with currents about 0.1 A and a phase-angle of 80° . This large phase-angle implies that the plasma has a high impedance and is predominantly an inductive load. The electrode spacing in the longitudinal case is 1.9 cm and is the tube diameter in the transverse case. The reduced electric fields (at 150 Torr) are then 5 and 27 Td, significantly lower than the pulsed system. Accordingly, the metastable Ar number densities produced in these discharges peaks at $1 \times 10^{12} \text{ cm}^{-3}$ at 10 Torr and drops by an order of magnitude at 400 Torr. It is worth noting that while the reduced electric field appears high for the radio-frequency discharges, the significant loss-rate of the

metastable state leads to substantially reduced densities in steady-state as compared to the early-time densities in a high-voltage pulse. Due to these low densities at higher pressure, inversion was not able to be achieved and no lasing demonstration has been conducted to date.

Most recently, a high-repetition rate pulsed dielectric barrier discharge was fabricated and tested [118], shown in Fig. 3(f). This consisted of two electrodes, 1.8 cm in length and 0.635 cm in width, mounted in a glass cell. The gap spacings were 2 and 3 mm leading to volumes of 0.23 and 0.34 cm³. The system was driven at frequencies of 20 kHz with 30 μ s pulse widths. The driving voltage was generally around 300 V with 50 mA of current and power delivered not exceeding 10 W. The reduced electric field (at 150 Torr) is then 31 Td for the 2 mm gap and 20.7 for the 3 mm gap. Ar-He was flowed from 1.65 to 2.2 slm in a 10% mixture. Ar ($1s_5$) densities were observed to be approximately 4×10^{11} cm⁻³ for the 3 mm gap at 250 Torr rising to 1×10^{12} cm⁻³ at 750 Torr. The 2 mm gap showed a rise in the density from 1.1×10^{12} to 1.5×10^{12} cm⁻³ as the pressure is increased from 300 to 700 Torr. Lasing was unable to be achieved in this plasma.

The highest cw output power achieved to date was in a high-repetition rate, pulsed discharge with uncoated stainless steel electrodes [81], shown in Fig. 3(g). One electrode had a square cross-section of 6 mm and the other had a pentagonal structure with the point facing the center of the square electrode. The spacing between the two electrodes was 3 mm. The corresponding volume was approximately 0.36 cm³. The discharge was driven at 200 kHz with a 0.3 μ s pulse of 400 V peak voltage. The Ar density was measured at 1.4×10^{13} cm⁻³. Output lasing intensities as high as 2.6 W were observed when pumped with a 30 W VBG narrowed-diode with slope-efficiency of 36%.

The dominant issue preventing the rapid testing and scaling of the DPRGL lies in

the development of an atmospheric pressure discharge that can operate at pressures ranging from several hundred Torr to two atmospheres that has a low power requirement (less than 1 kW) and can form a homogeneous plasma in a volume of 10 cm^3 . Beyond just the plasma operation and homogeneity this plasma also must produce $\text{Ar}(1s_5)$ densities greater than 10^{13} cm^{-3} for efficient laser operation. If this can be achieved, the pathway to a high-energy laser system becomes clear.

There have been several recent reviews of atmospheric pressure plasmas and micro-discharges [182, 14, 13, 9, 168] and a novel discharge design was designed and fabricated, as a part of the present dissertation project, from an analysis of these works. This novel discharge design consisting of a plasma reactor as a high-energy electron source for a large-volume discharge has recently begun testing. A schematic of this discharge can be found in Appendix D. This system, a micro-cathode structured array, consists of an array of microhollow cathode discharges (MHCD) driven by a DC or RF source and a DC, positively-biased third electrode. The MHCD consists of $100\text{ }\mu\text{m}$ diameter holes laser drilled through a three-layer substrate consisting of a $35.5\text{ }\mu\text{m}$ copper foil, a $256\text{ }\mu\text{m}$ layer of fiberglass-reinforced epoxy and another $35.5\text{ }\mu\text{m}$ copper foil, shown in Fig. 3(h). Other materials and geometries have been tested in large MHCD arrays [139]. If the bias voltage is sufficiently high (several hundred volts), the electrons are pulled from the MHCD and form a plasma jet of divergence angle near 25° on route to the third electrode. The current then flows between the top electrode and third electrode [31]. The expectation is that provided holes that are spaced appropriately (less than 0.5 cm edge-to-edge), the jets will combine to form a homogeneous plasma at a height of 0.5 cm above the bias plate. Modeling of this discharge has shown a homogeneity of the reduced electric field above the bias plate [126]. This system has been demonstrated for a single MCSD in Ar [176, 138]. The appeal of the array application of the MCSD is in its scalability. For a 10 cm^3

volume MCSDA, an active MHCD area of 2 cm x 10 cm would be sufficient with a gap of 0.5 cm.

2.4 Plasma Spectroscopy

Optical analysis of a plasma is commonly done using several different methods, each with their own trade space. Passive techniques are primarily restricted to observation of the fluorescence which can be collected by a fiber and sent to a monochromator to resolve specific transitions. Spatial emission can also be observed using a camera with spectral filters. This passive technique is limited in the resolution of the monochromator used for detection which is ultimately tied to the monochromator length as well as the groove density and blaze of the dispersive grating element. The limited resolution is introduced as a convolution of the spectral lineshape of the plasma emission and that of the instrument which complicates an analysis of narrow atomic features.

Active techniques, primarily laser based, can be used to interrogate a medium without convolving the spectral data with an instrument lineshape. This is done using narrow-band laser sources such as a Ti:Saph ring laser with a 100 kHz line width. The dominant technique is tunable laser absorption spectroscopy, discussed below, where a narrow-band laser is used to tune through an atomic resonance. Using a single laser generally restricts one to collecting Doppler-limited spectra, except for the case of two-photon absorption, where the minimum achievable resolution is defined by the Doppler width of the transition. Doppler-Free techniques require non-linear spectroscopic techniques in order to resolve the atomic transition below the limit of the Doppler width and can be achieved using counter-propagating laser beams. We first discuss the details of tunable laser absorption spectroscopy and Doppler-limited spectra before introducing the invasive technique of saturation spectroscopy and its

application to sub-Doppler spectroscopy and Doppler-free lineshapes.

2.4.1 Tunable Laser Absorption Spectroscopy.

Absorption spectroscopy is an experimental method used to characterize a medium. The basic concept involves tracking the intensities of two laser beams, one which travels through the medium to be analyzed, and one propagated around it. These two beams are designated I and I_0 for the transmitted and incident intensities. The behavior of the transmitted beam depends on the details of the gain medium as well as the laser intensity and spatial distribution. In general, the transmission of a Gaussian laser beam propagating through an absorbing medium follows the differential equation

$$\frac{dI}{dz} = -\alpha(\nu, I)I(r, z) + \frac{dI_p(r, z)}{dz} \quad (4)$$

$$I_p(r, z) = I_0 \left(\frac{w_0}{w(z)} \right)^2 \text{Exp}(-2r^2/w(z)^2) \quad (5)$$

$$w(z) = w_0 \left(1 + \left(M^2 \frac{z}{z_R} \right)^2 \right) \quad (6)$$

where $I_p(r, z)$ is the Gaussian laser beam with evolving beam waist defined by $w(z)$, w_0 is the beam waist at the focus, $z_R = \pi w_0^2/\lambda_{21}$ is the Rayleigh range, or convergence length, of the laser, M^2 is the beam quality metric, and the absorption coefficient is given by

$$\alpha(\nu, I) = \sigma(\nu, I)n_{abs} \quad (7)$$

$$\sigma(\nu, I) = \frac{g_2}{g_1} \frac{A_{21}\lambda_{21}^2}{8\pi n^2} g(\nu, I) \quad (8)$$

where n_{abs} is the number density of absorbers, $\sigma(\nu)$ is the absorption cross section for transitions from state 1 to state 2, $g_{2,1}$ are the degeneracies of the upper and

lower state, respectively, A_{21} is the Einstein A Coefficient of the transition, λ_{21} is the transition wavelength and n is the real index of refraction of the medium (often taken to be 1). We also note that if the beam is collimated then $dI_p/dz = 0$ and $I(r, z) \rightarrow I(z)$. The special case of Eq. (4) is for an absorption coefficient that is independent of intensity, $\alpha(\nu, I) \rightarrow \alpha(\nu)$, and is a collimated beam which occurs when the diagnostic laser is of sufficiently low intensity to not interfere with the medium. In this case the differential equation is easily solved and results in the more common Beer-Lambert law

$$\begin{aligned}\frac{dI}{dz} &= -\alpha(\nu)I \\ I &= I_0 \text{Exp}(-\alpha(\nu)l)\end{aligned}\tag{9}$$

where I and I_0 are the incident and transmitted laser intensities and l is the absorption path length. The lineshape is generally area normalized,

$$\int_{-\infty}^{\infty} g(\nu) d\nu = 1\tag{10}$$

We define the absorbance, in the special case of the Beer-Lambert law, as

$$Abs(\nu) = -\ln\left(\frac{I}{I_0}\right) = \sigma(\nu)n_{abs}l = \frac{g_2}{g_1} \frac{A\lambda^2}{8\pi n^2} n_{abs} l g(\nu)\tag{11}$$

where the integrated absorbance is proportional to the number density of absorbers due to the selection of normalization for the lineshape function.

2.5 Doppler-Limited Lineshapes in Plasmas

The frequency distribution of the cross section, known as the lineshape function, takes different forms depending on the pressure, temperature, state populations and

other conditions of the medium, as well as the incident laser intensity. In the absence of all other perturbations as well as motion relative to the laser beam, an absorbing atom will have a Lorentzian lineshape with width defined by the lifetime of the upper state, or the reciprocal of the Einstein A coefficient, given by

$$g_L(\nu) = \frac{\gamma_N/2\pi}{(\nu - \nu_0)^2 + (\gamma_N/2)^2} \quad (12)$$

where $\gamma_N = 1/(2\pi\tau)$ is called the natural width and ν_0 is the frequency of the transition.

Except for a few very special cases (laser-trapped cold atoms, etc), an absorbing or emitting atom will not be free from perturbations. These perturbations take two main forms: velocity-changing collisions and phase-changing collisions. Generally, velocity-changing collisions will also change the phase. We will briefly address phase changing collisions here and leave velocity changing collisions to the discussion in Chapter VI. When an emitting or absorbing atom interacts with a perturbing atom, the change in the phase of the emission or absorption is related to the molecular potentials of the atom pair. These potentials can be relatively simple, as in the alkali, with the atomic alkali $^2P_{1/2}$ and $^2P_{3/2}$ states become the alkali-rare gas molecular states of $^2\Pi_{1/2}$, $^2\Pi_{3/2}$ and $^2\Sigma_{1/2}$ where the latter two molecular potential energy surfaces correspond to the $^2P_{3/2}$ atomic state in the asymptotic limit. For the rare gas atoms this picture is significantly more complex. Few calculations of the potential energy surfaces have been conducted, mostly focusing on the homo-nuclear Ar-Ar molecular ground state. The excited state potential energy surface calculations that have been conducted show a convoluted set of highly coupled energy levels [53, 54].

These changes in phase lead to broadening and shifting of spectral lines where the temperature dependence of these broadening and shifting rates are sensitive probes of the interaction potential. Fortunately, the lineshape function remains a Lorentzian

where the width and line center frequency take the form

$$\gamma_N \rightarrow \gamma_H = \gamma_N + \gamma_L = \frac{A}{2\pi} + \sum_i \sigma_{\gamma,i} \bar{v}_i n_i \quad (13)$$

$$\nu_0 \rightarrow \nu_0 \pm \beta = \nu_0 \pm \sum_i \sigma_{\beta,i} \bar{v}_i n_i \quad (14)$$

where γ_L is the pressure broadened width, $\sigma_{\gamma,i}$ is the phase-changing collision cross section, $\bar{v}_i = \sqrt{\frac{8k_B T}{\pi \mu_i}}$ is the mean relative velocity with μ_i as the reduced mass of the absorber-perturber interaction, β is the pressure shift, $\sigma_{\beta,i}$ is the phase-shifting collision cross section, and n_i is the density of perturber of species i . The $\pm$ denotes blue and red shifting of the line center frequency. The full width and shift will be given by a sum over the different perturbing species. *Allard and Kielkopf* provide a detailed derivation of the pressure broadening of spectral lines, to include higher-order interaction-potential dependent effects, such as asymmetry and non-linearity in the far wings [5]. We note the subscript H in the width is to designate the homogeneous width as it influences all atoms in the medium in the same manner. It is worth noting that, in general, $\sigma_{\gamma,i}$, $\sigma_{\beta,i}$ are temperature dependent parameters. Broadening rates are generally provided in either MHz/Torr or rad/s/cm³. The temperature dependencies of these broadening rates will differ as the pressure in the former contains an additional temperature dependence given by the ideal gas law. The total temperature dependence of the broadening rates, when Σ_i in Eq. (13) only contains a single term, is given by

$$\gamma_L/n = \sigma_{\gamma}(T) \bar{v} = \sigma_{\gamma}(T) \bar{v}(300 \text{ K}) \sqrt{\frac{T}{300}} \quad (15)$$

$$\gamma_L/P = \gamma/(nk_B T) = \sigma_{\gamma}(T) \bar{v} \frac{1}{k_B T} = \sigma_{\gamma}(T) \bar{v}(300 \text{ K}) \sqrt{\frac{1}{300T}} \quad (16)$$

Assuming the cross section is temperature independent, we see the temperature de-

pendence for the broadening rate has an opposite trend for each case. That is, the broadening rate in terms of pressure is expected to decrease as $T^{-1/2}$ whereas the broadening rate in terms of density is expected to increase as $T^{1/2}$. This is simply due to the relationship between the increasing velocity and decreasing number density, at fixed pressure, for a given rise in temperature. It is also worth noting that the cross sections for phase-changing and shifting collisions are generally temperature dependent and so the full temperature dependent rate can be significantly more complex.

Brownian motion of the atoms in the medium leads to a second type of broadening. Atoms with non-zero axial velocities relative to the incoming laser will experience a Doppler shift of the laser beam frequency. This is considered inhomogeneous broadening as the effect will vary for different atom groups depending on their velocities. With the exception of atomic beams, most gases will be at thermal equilibrium which has a Maxwell-Boltzmann distribution, $f(v) = (m/(2\pi k_b T))^{3/2} \text{Exp}(-mv^2/(2k_b T))$, for the velocities. The frequency is related to the velocity through the Doppler shift by

$$\nu' = \nu_0(1 + \frac{v_z}{c}) \quad (17)$$

where ν' is the Doppler shifted frequency, v_z is the axial velocity, and c is the speed of light. The frequency distribution is then defined by a Gaussian as

$$g_I(\nu) = 2\sqrt{\frac{\ln(2)}{\pi}} \frac{1}{\Delta\nu_D} \text{Exp}\left(-4\ln(2) \left(\frac{\nu - \nu_0}{\Delta\nu_D}\right)^2\right) \quad (18)$$

where $\Delta\nu_D$ is the inhomogeneous width, related to the temperature by

$$\Delta\nu_D = \sqrt{\frac{8k_B T \ln(2)}{mc^2}} \nu_0 \quad (19)$$

For most experimental conditions in this document, the inhomogeneous width and

the homogeneous width are of similar magnitudes. In this case one must consider how the Lorentzian and Gaussian lineshape couple. Each atom in the medium will have a Lorentzian width defined by the pressure and a central frequency defined by the axial velocity and the pressure shifting rate. The Lorentzian is then a velocity dependent function of the form

$$g_L(\nu, v_z) = \frac{\gamma_L/2\pi}{(\nu - \nu_0 - kv_z)^2 + (\gamma_L/2)^2} \quad (20)$$

where $k = 2\pi c/\nu_0$ is the wave vector. The atoms in the medium have axial velocities defined by the Maxwell-Boltzmann distribution and so the lineshape will be given by a velocity-average of these Lorentzian profiles

$$g_V(\nu) = \int_{-\infty}^{\infty} g_L(\nu, v_z) f(v_z) dv_z \quad (21)$$

This is named the Voigt profile and is often expressed in the form:

$$g_V(\nu) = \sqrt{\frac{2\ln(2)}{\pi^3}} \frac{1}{\Delta\nu_D} \int_{-\infty}^{\infty} \frac{\text{Exp}(-(ay - u)^2)}{(y^2 + 1)} dy \quad (22)$$

where $a = \sqrt{\ln(2)}\gamma_H/\Delta\nu_D$, $u = 2\sqrt{\ln(2)}(\nu - \nu_0)/\Delta\nu_D$ and $y = (\nu - \nu')/\gamma_H$ [184].

This integral can be expressed in terms of the complex error function as

$$\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\text{Exp}(-(ay - u)^2)}{(y^2 + 1)} dy = \text{Re}[\text{Exp}(z^2)\text{Erfc}(z)] \quad (23)$$

where $z = a + iu$. This gives us the form of the Voigt profile used in this work

$$g_V(\nu) = \sqrt{\frac{2\ln(2)}{\pi}} \frac{1}{\Delta\nu_D} \text{Re}[\text{Exp}(z^2)\text{Erfc}(z)] \quad (24)$$

The relationship between the Gaussian, Lorentzian and Voigt can be seen in Fig.

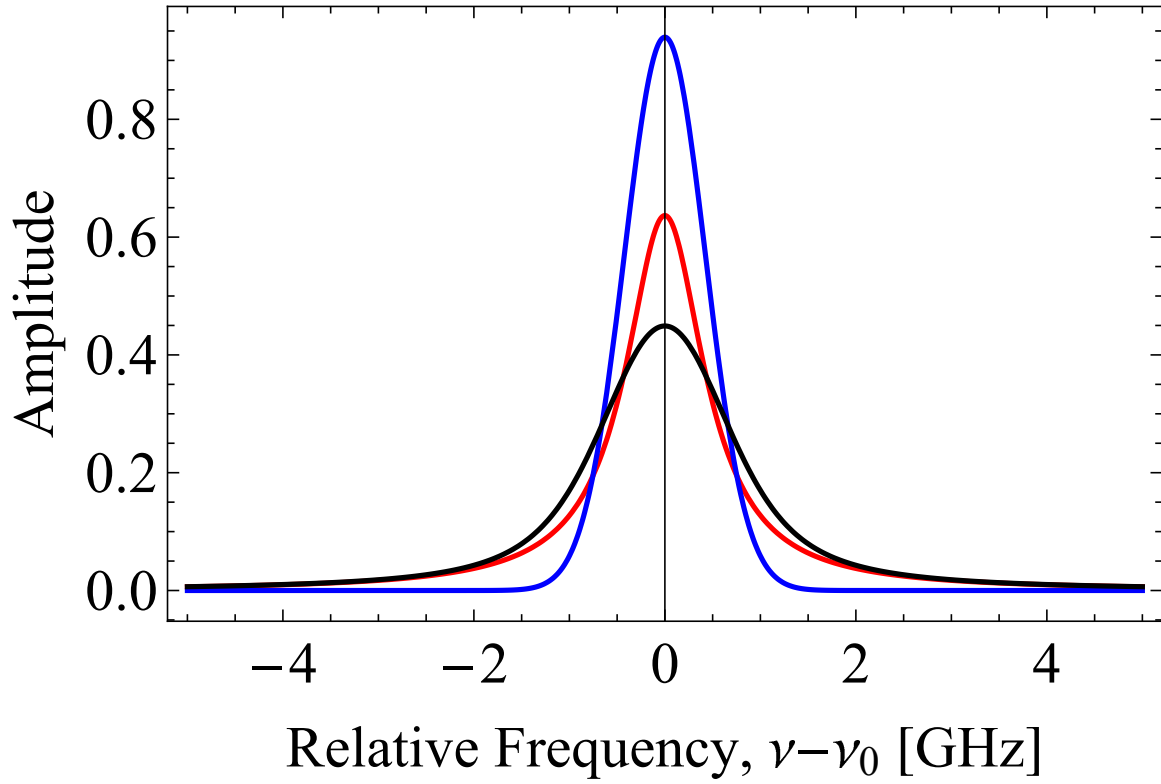


Figure 4. The lineshape functions for a Lorentzian (red), a Gaussian (blue) and the corresponding Voigt (black) are shown. The Lorentzian and Gaussian widths are 1 GHz and all line shapes are area normalized.

4 which shows a Gaussian and Lorentzian lineshape of equal widths and the corresponding Voigt profile.

With the influence of neutral perturbers and motion of the absorbers well described, we briefly introduce the influence of the plasma on the lineshapes. This is a complex study that is the subject of several textbooks [66, 67] and has been a primary focus in the field of astronomy. In weakly-ionized and low-density plasmas, the main contribution to the lineshape comes in the form of electron impact broadening and shift, also known as Stark broadening and shift. This influence can be treated in the impact approximation given a monopole-dipole long-range interaction which results in a Lorentzian lineshape with electron impact broadening and shift rates that are commonly three orders of magnitude larger than neutral-neutral rates. These Stark parameters, the broadening and shift induced by collisions with electrons, are readily available as they have been the subject of several reviews over the last four decades [97, 95, 94, 96, 105]. As the electron density increases it contributes to a local electric field which can cause Stark splitting of the energy levels, called the Dynamic Stark Effect. In highly-ionized plasmas the ion contribution becomes significant and can lead to non-Lorentzian behavior of the spectral line that is dependent on the local ion distribution function, often given by a Holtsmark distribution [66]. The plasmas formed in this work are weakly-ionized and at high pressures where the neutral-neutral effects greatly outweigh the electron-neutral effects.

2.6 Saturation Spectroscopy

When the intensity of the laser is sufficiently high to influence the population then the Beer-Lambert law no longer applies to the absorption of the laser beam along the path. In order to determine the lineshape in these conditions the intensity-dependent absorbance must be derived from either the density-matrix or rate equations. In this

work we use the rate equation approach as any coherence effects that would require the application of the density-matrix are destroyed by collisions at the pressures which we conduct the measurements. The analysis of the saturation of spectral lines in the rate-equation limit are well known for the limiting cases of fully homogeneous or inhomogeneous broadening and low pump intensity, that is, when the Lorentzian width is much larger than the Doppler width or visa versa, corresponding to the high-pressure and low-pressure regimes where the pump intensity leads to small population changes. The intermediate case is generally handled numerically and is the subject of Chapter VI. In the homogeneous limit the saturated absorption coefficient takes the form [47]

$$\alpha_s = \sigma \Delta N = \frac{\alpha^0}{1 + S} \quad (25)$$

where σ is the absorption cross section, ΔN is the population inversion calculated from the rate equations, α^0 is the absorption in the absence of pumping, and S is the saturation parameter given by

$$S = \frac{I}{I_{sat}} = \frac{I\sigma}{h\nu\Gamma} \quad (26)$$

where I is the pump laser intensity, I_{sat} is defined as the saturation intensity, h is Planck's constant, ν is the frequency of the transition, and Γ is the weighted loss-rate of the upper and lower levels. In this work these saturation intensities are generally on the order of 0.1 W/cm², increasing with pressure to the order of 1 W/cm². The saturated absorption coefficient can be written in a more illuminating form as

$$\alpha_s(\nu) = \alpha^0(\nu_0) \frac{\gamma/(2\pi)}{(\nu - \nu_0)^2 + (\gamma_s/2)^2} \quad (27)$$

where ν_0 is the line-center frequency, γ is the homogeneous width and $\gamma_s = \gamma\sqrt{1+S}$ is the saturation broadened width. In the homogeneous limit, the effect of saturation

is then to reduce the total measurable absorbance of the spectral line by broadening the width of the feature.

In the inhomogeneous limit, the velocity dependence of the populations must be taken into account. The pump laser will selectively saturate a particular velocity group that is Doppler-shifted into resonance with the incoming laser beam with a linewidth given by the homogeneously saturated width. The result is

$$\alpha_s(\nu) = \frac{\alpha^0(\nu_0)}{\sqrt{1 + S_0}} \text{Exp} \left(-4 \ln(2) \frac{(\nu - \nu_0)^2}{\Delta \nu_D} \right) \quad (28)$$

where $S_0 = I\sigma(\nu_0)/(h\nu\Gamma)$ and $\Delta \nu_D$ is the Doppler line width [48]. By scanning a single laser over the lineshape we cannot observe any velocity-dependent saturation effects, only the total reduced absorbance given by

$$\alpha_s = \alpha^0 / \sqrt{1 + S_0}. \quad (29)$$

In order to observe the velocity-selective saturation of a spectral line we must use two lasers. There are several schemes for being able to observe this saturation involving either two separate lasers or a single laser split into two beams. In the first case, a single strong beam is tuned to any position within the spectral feature and a second weak laser is tuned over the Voigt profile. The probe (weak) laser will observe the diminished population in a single velocity group contained in the Voigt profile. In the second case the two lasers can either have the same intensity, creating a standing-wave field, or can be divided into a strong pump and weak probe. In either case, the velocity selective saturation will only be observable at line-center where both lasers interact with the zero-velocity group. This is because the Doppler-shifts will be opposite and only the atoms with no axial velocity will be able to interact with both beams. For a weak probe beam counter-propagating against a strong pump beam,

and in the limit of low pump intensity ($S_0 \ll 1$), the lineshape takes the form

$$\alpha_s(\nu) = \alpha^0(\nu) \left(1 - \frac{S_0}{2} \frac{(\gamma_s/2)^2}{(\nu - \nu_0)^2 + (\Gamma_s^*/2)^2} \right) \quad (30)$$

where the width of the hole is given by $\Gamma_s^* = (\gamma + \gamma_s)/2$ [47]. This lineshape does not have an analytic form in the cases of comparable Lorentzian and Doppler widths and for high-pump intensities. Fig. 5 shows the difference in the saturation profiles for varying the Lorentzian width and Gaussian width to reflect the homogeneous and inhomogeneous regimes as well as the sub-Doppler saturation spectrum described in the next section.

2.6.1 Sub-Doppler lineshapes.

Using a single laser restricts us to only being able to detect Doppler-limited spectra. Sub-Doppler techniques require the use of two lasers, as discussed above. Sub-Doppler spectroscopy uses two counter propagating laser beams combined with modulation and phase-sensitive detection in order to systematically subtract out the unsaturated lineshape from the saturated one providing a signal that is given by the velocity-selective saturation only and not a lamb-dip in a Doppler-limited lineshape. The experimental technique involves amplitude modulating the pump beam and measuring the transmitted intensity of the counter-propagating probe at the modulation frequency of the pump. The transmitted signal will then consist of the unsaturated lineshape when the pump is blocked and the saturated lineshape when it is transmitted. The phase-sensitive detection filters out the signal that is not at the modulation frequency (the unsaturated lineshape) and the sub-Doppler lineshape will be of the form

$$\alpha^0 - \alpha_s = \alpha^0 \frac{S_0}{2} \frac{(\gamma_s/2)^2}{(\nu - \nu_0)^2 + (\Gamma_s^*/2)^2} \quad (31)$$

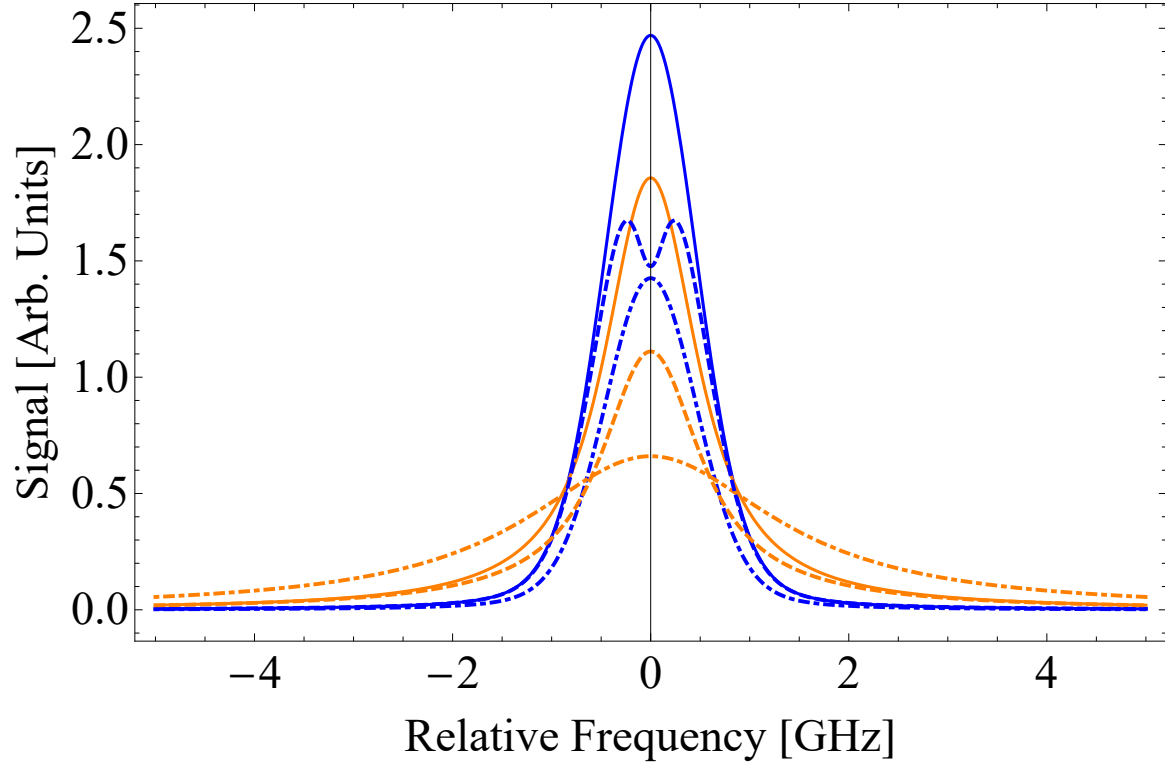


Figure 5. The lineshapes are shown for an inhomogeneous (blue) and homogeneous (orange) profiles with an equivalent Voigt width of 1.1 GHz with Doppler widths of 1 GHz and 0.35 GHz and Lorentzian widths 0.2 GHz and 1 GHz, respectively. Three different profiles are shown for each case: unsaturated (—), saturated (---), sub-Doppler (—·—).

which is just the difference between the unsaturated absorbance α^0 and the saturated absorbance given in equation (30) [48].

A second method for observing the sub-Doppler spectra involves the laser-induced fluorescence of the medium. In this case, the pump and probe are modulated at two different frequencies. The population of the upper state will be increased at the modulation frequency of each laser leading to increased fluorescence. The fluorescence intensity in the presence of both lasers is defined as

$$I_{LIF} = C \left(\Delta N^0(I_1 + I_2) - a\Delta N^0(I_1 + I_2)^2 \right) \quad (32)$$

where C is a constant determined by the Einstein A Coefficient of the transition and the efficiency of the detection scheme, I_1 and I_2 are the pump and probe intensities, respectively [48]. This signal is composed of two linear terms and a quadratic term where each linear term is modulated at the frequency of that particular beam and the quadratic term is modulated at the sum-frequency. Using phase-sensitive detection referenced to the sum-frequency allows us to observe only the signal in the region where atoms are interacting with both laser beams and to subtract out the linear baseline caused by each independent laser signal, leading to a sub-Doppler spectra.

III. Five-level Ar-He Laser and Plasma Model

3.1 Introduction

With the recent laser demonstrations of the DPRGL, there has been a moderate effort to model both the rare gas discharges and the optical physics. These models commonly proceed independent with the plasma model developed to describe the initial population distribution of the excited states and then an optical model applied using those densities. This procedure has the benefit of simplicity in analysis of the optical model but fails to account for any coupling between the plasma dynamics and optical influence. Several models have been recently developed to analyze the rare gas laser medium. An early model was published to examine the lasing behavior of an Ar-He glow discharge where plasma model is done by solving the Boltzmann equation and the optical model is solved independently [49]. A four-level kinetic model was developed by *Rawlins, et al*, to benchmark gain and absorbance measurements in a microwave strip-resonator array and a multi-level model by *Yang, et al* used the *Rawlins, et al* work to benchmark their own model [155, 203]. A model for a novel dual-wavelength pumped Ar laser was developed in order to address the issue of laser cycle bottle-necking due to radiative transmission from the upper laser level $2p_{10}$ to the $1s_4$ resonance level [64]. The most recent models have begun to address different pump schemes for the DPRGL to include transverse pumped systems [63]. All these models only apply an optical/kinetic model for the neutral kinetics and make the assumption that the plasma no longer contributes beyond initial production of the excited states.

In this chapter a five-level laser model, including both plasma production and optical physics, is developed in order to assess the laser performance characteristics of an Ar-He gain medium. This model does not account for ionization-recombination

equilibrium of the medium and so does not account for the influence of the laser on the plasma parameters but does include the influence of those parameters on the pump and lasing behavior. This model is also parametrized by electron temperature and electron density which are used as variable parameters in order to achieve the expected behavior. The electron temperature in particular is important to the discharge model and using a single temperature as a surrogate for the electron energy distribution is an incorrect assumption but sufficient for our purposes. The likely electron energy distribution is non-Maxwellian and contains a high-energy tail, the details of which are dependent on the production mechanism (RF, DC, pulsed, etc) and the gas mixture (a larger tail exists for gas mixtures with significant fractions of He).

3.2 Mechanisms and Rate Equations

Fig. 6 shows a simplified form of the considered kinetics in the five-level model. The five-levels considered in the model consist of the laser and pump ground state, $4s[3/2]_2$ ($1s_5$), the adjacent resonant state, $4s[3/2]_1$ ($1s_4$), the upper laser level, $4p[3/2]_1$ ($2p_{10}$), the upper pump level, $4p[3/2]_3$ ($2p_9$) and a collisionally active adjacent state, $4p[3/2]_2$ ($2p_8$). The main mechanisms considered are electron impact excitation from the $\text{Ar}(1s_0)$ ground state (not considered a level in the model) to all five-levels, electron impact spin-orbit mixing between the five-levels, neutral impact spin-orbit mixing and quenching (caused by both Ar and He), radiative relaxation, and optical excitation and stimulated emission. It is worth noting that ionization, recombination and excitation to higher states are not considered but are important to a full plasma model. The set of mechanisms applied to the model and their corresponding rate coefficients can be found in [209] for the electron-impact and Ar-Ar collisions and for Ar-He rates in [75]. Using these mechanisms and the known rate

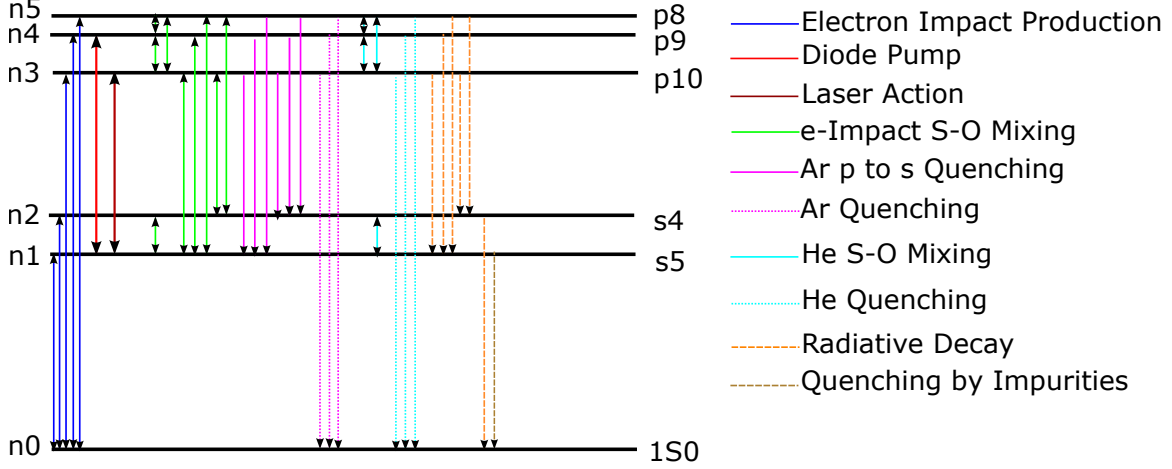


Figure 6. The main interactions are summarized for the five level laser model.

coefficients, a five-level system was developed with rate equations defined as

$$\begin{aligned} \dot{n}_1 = & k_{01}^e n_{Ar} + \frac{\Omega\sigma(\nu)}{h\nu} \left(n_4 - \frac{g_4}{g_1} n_1 \right) \\ & + k_{21}^{He} n_2 + (\Gamma_{31} + k_{31}^{Ar}) n_3 + (\Gamma_{41} + k_{41}^{Ar}) n_4 \\ & + (\Gamma_{51} + k_{51}^{Ar}) n_5 - (k_{10}^e + k_{12}^{He} + k_{13}^{Ar} + k_{14}^{Ar} + k_{15}^{Ar} + k_q, 1) n_1 \end{aligned} \quad (33)$$

$$\begin{aligned} \dot{n}_2 = & k_{02}^e n_{Ar} + k_{12}^{He} n_1 + (\Gamma_{32} + k_{32}^{Ar}) n_3 + k_{42}^{Ar} n_4 + (\Gamma_{52} + k_{52}^{Ar}) n_5 \\ & - (k_{20}^e + \Gamma_{20} + k_{21}^{He} + k_{23}^{Ar} + k_{24}^{Ar} + k_{25}^{Ar}) n_2 \end{aligned} \quad (34)$$

$$\begin{aligned} \dot{n}_3 = & k_{03}^e n_{Ar} + k_{13}^{Ar} n_1 + k_{23}^{Ar} n_2 + (k_{43}^{Ar} + k_{43}^{He}) n_4 + (k_{53}^{Ar} + k_{53}^{He}) n_5 \\ & - (k_{30}^e + \Gamma_{31} + \Gamma_{32} + k_{31}^{Ar} + k_{32}^{Ar} + k_{34}^{Ar} + k_{34}^{He} + k_{35}^{Ar} + k_{35}^{He} - k_{q,3}) n_3 \end{aligned} \quad (35)$$

$$\begin{aligned} \dot{n}_4 = & k_{04}^e n_{Ar} - \frac{\Omega\sigma(\nu)}{h\nu} \left(n_4 - \frac{g_4}{g_1} n_1 \right) + k_{14}^{Ar} n_1 + k_{24}^{Ar} n_2 \\ & + (k_{34}^{Ar} + k_{34}^{He}) n_3 + (k_{54}^{Ar} + k_{54}^{He}) n_5 \\ & - (k_{40}^e + \Gamma_{41} + k_{41}^{Ar} + k_{42}^{Ar} + k_{43}^{Ar} + k_{43}^{He} + k_{45}^{Ar} + k_{45}^{He} + k_{q,4}) n_4 \end{aligned} \quad (36)$$

$$\begin{aligned} \dot{n}_5 = & k_{05}^e n_{Ar} + k_{15}^{Ar} n_1 + k_{25}^{Ar} n_2 + (k_{35}^{Ar} + k_{35}^{He}) n_3 + (k_{45}^{Ar} + k_{45}^{He}) n_4 \\ & - (k_{50}^e + \Gamma_{51} + \Gamma_{52} + k_{51}^{Ar} + k_{52}^{Ar} + k_{53}^{Ar} + k_{53}^{He} + k_{54}^{Ar} + k_{54}^{He} + k_{q,5}) n_5 \end{aligned} \quad (37)$$

$$n_{Ar} = n_0 + n_1 + n_2 + n_3 + n_4 + n_5 \quad (38)$$

where Ω is the longitudinally-averaged pump intensity as defined by *Hager, et al* [70], $\sigma_{ij}(\nu)$ is the stimulated emission cross-section, h is Planck's constant, ν is the frequency of the transition, g_i denotes the degeneracy of level i , Γ_{ij} are the radiative transitions from state i to j , $k_{q,i}$ denotes collisional quenching rate from state i to the ground state, k_{ij}^m denotes the collisional mixing rates that move population from level i to level j where $k_{ij}^m = \gamma_{ij}^m n_m$ with $m = e, Ar, He$ and the inverse rate coefficient γ_{ji}^m is related by detailed balance,

$$\gamma_{ji} = \frac{g_j}{g_i} \gamma_{ij} \exp(-\Delta E_{ij}/k_b T) \quad (39)$$

where ΔE_{ij} is the energy difference between the upper and lower states, k_b is Boltzmann's constant and T is the temperature (gas temperature for neutral rates and electron temperature for electron rates). We note that the electron impact rates (k^e) are parametrized by n_e and T_e , the electron density and temperature, whereas the neutral collisional rates ($k^{Ar,He}$) and the total argon and helium densities (n_{Ar} , n_{He}) are parametrized by p_{Ar} , p_{He} and T , the argon and helium partial pressures and the gas temperature. Attention should also be drawn to the specific dependencies in the model. Neutral rates are measured at a single temperature. The rate coefficient is given by $\gamma = \sigma \bar{v}$ where σ is the cross-section for energy transfer and $\bar{v}$ is the mean relative velocity. The cross-sections are assumed to be temperature independent for the model leaving the relative velocity as the only temperature dependency in the rate coefficient. The form becomes $\gamma(T) = \gamma(T_0)(T/T_0)^{0.5}$ where $\gamma(T_0)$ corresponds to the measured rate coefficient. This functional form is changed for a small subset of the rate coefficients, specifically the $\gamma_{54,53,43}^{He}$ rates. The temperature dependence was taken to follow an Arrhenius form with peak gas-kinetic rate of 3×10^{-10} cm³/s. The motivation for this change is described later on. The electron-Ar collisional rate coefficients have an Arrhenius law dependence on T_e [209].

These equations are solved in steady-state, $d/dt = 0$, and in the absence of the pump laser, $\Omega = 0$, in order to set the zero-order inversion. While the absolute values of the populations require experimental measurements to benchmark, there is significant value in examining how the densities of the five-levels vary with electron temperature, electron density, and gas temperature for a fixed gas pressure. The dependence of the Ar densities on electron temperature is shown in Fig. 7. This was modeled at a fixed electron density of $1.46 \times 10^{15} \text{ cm}^{-3}$, a gas temperature of 650 K, and a gas pressure of 769 Torr. The densities of all the states are strongly dependent on the electron temperature. For a factor of 6 increase in the electron temperature the densities increased by 10 orders of magnitude. This dependence implies that knowledge of the density of a single S or P state can effectively set the electron temperature of the model. The inset to Fig. 7 shows how insensitive the population ratios are to the electron temperature. In this case the largest change occurs for the $2p_{10}/2p_9$ ratio (yellow) which increases by 20% relative to the factor of 6 increase in electron temperature. The population ratios are then not sensitive enough to imply an electron temperature. Fig. 8 shows that the dependence of the populations on electron density is linear for electron densities below 10^{15} cm^{-3} and that they roll off above 10^{17} cm^{-3} . The inset of Fig. 8 shows the dependence of the population ratios on the electron density. The ratios are significantly more sensitive to the electron density with a factor of 17 decrease in the p_{10}/p_9 (orange) ratio for an increase in electron density from 10^{13} cm^{-3} to 10^{16} cm^{-3} . The sensitivity of the population ratio to the electron density implies a particular value for a given measured ratio. The final influence on the populations in the model is given by the gas temperature, shown in Fig. 9. The Ar* density decreases with temperature and trends closely with the expected behavior as defined by the ideal gas law. That is, the temperature and density, for a fixed pressure, are related by $n_1 k_b T_1 = n_2 k_b T_2$ where k_b is Boltzmann's

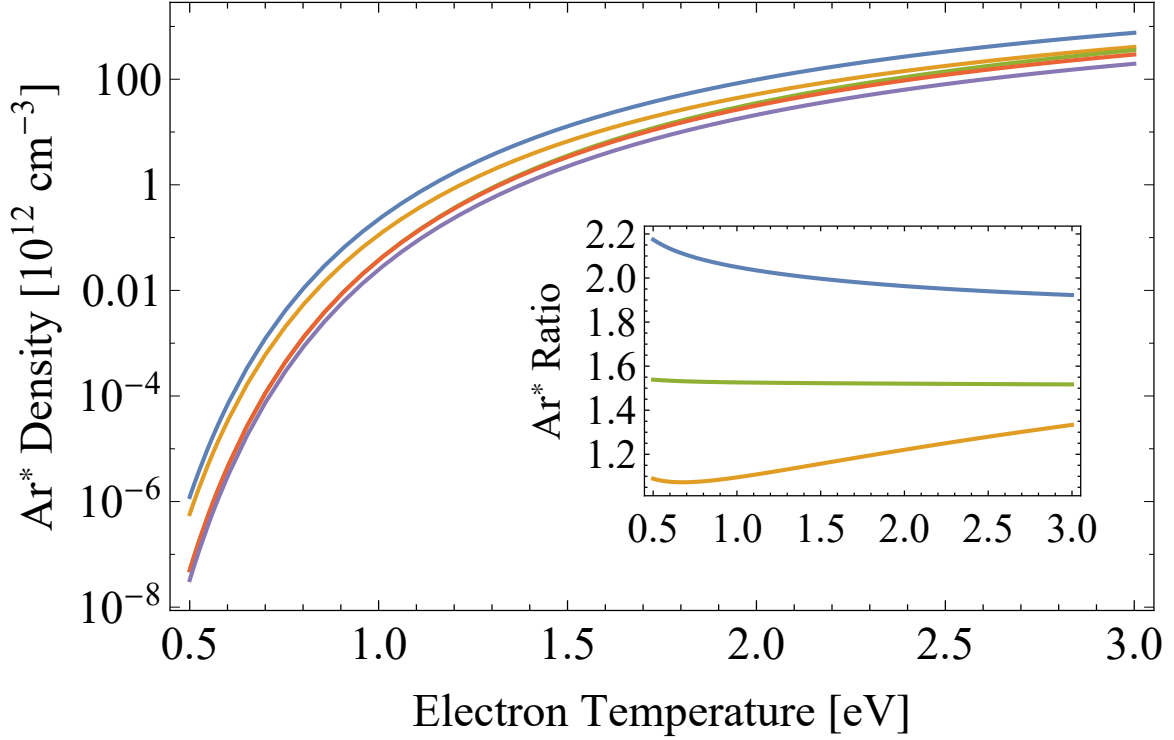


Figure 7. The dependence of the excited states on the electron temperature is shown. The curves correspond to $1s_5$ (—), $1s_4$ (—), $2p_{10}$ (—), $2p_9$ (—), $2p_8$ (—). The densities are highly sensitive to the electron temperature with small changes in temperature corresponding to orders of magnitude changes in density. The inset shows the dependence of the population ratios on the electron density. These curves correspond to $1s_5/1s_4$ (—), $2p_{10}/2p_9$ (—), $2p_9/2p_8$ (—). The population ratios are not sensitive to the electron temperature.

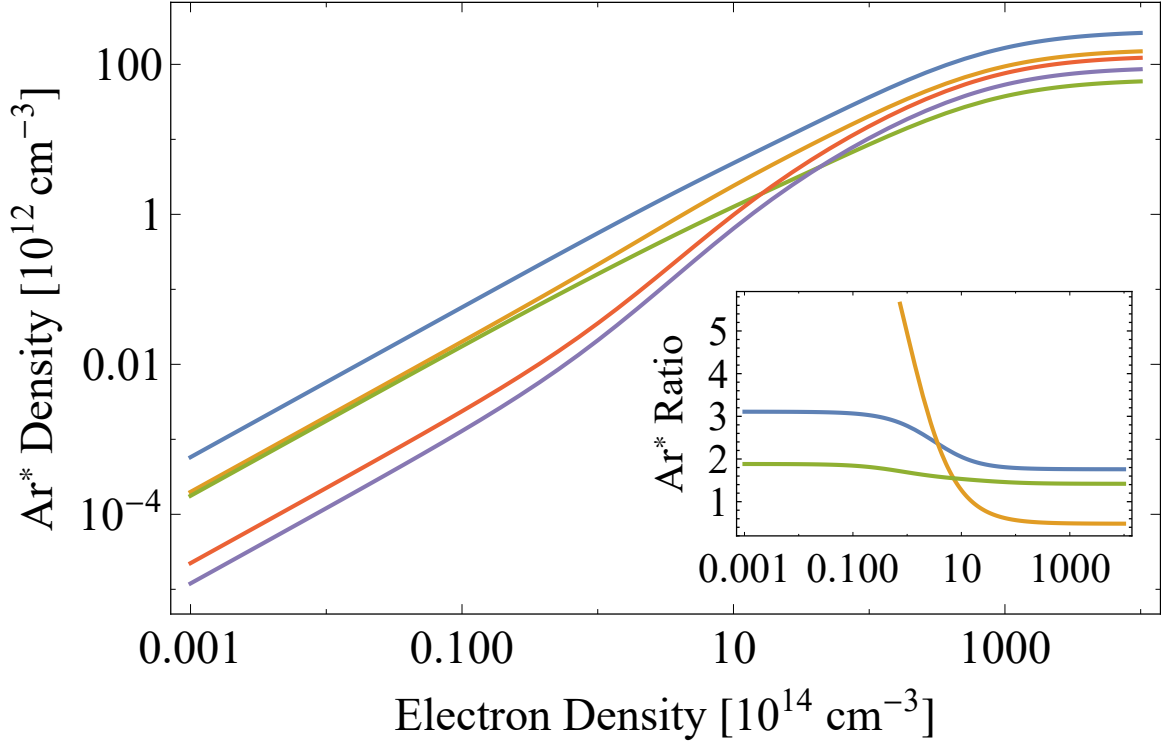


Figure 8. The dependence of the excited states on the electron density is shown. The curves correspond to $1s_5$ (—), $1s_4$ (—), $2p_{10}$ (—), $2p_9$ (—), $2p_8$ (—). The excited state densities are linear for electron densities below 10^{14} cm^{-3} and rolls off as the density rises above 10^{17} cm^{-3} . The inset shows the dependence of the population ratios on the electron density. These curves correspond to $1s_5/1s_4$ (—), $2p_{10}/2p_9$ (—), $2p_9/2p_8$ (—).

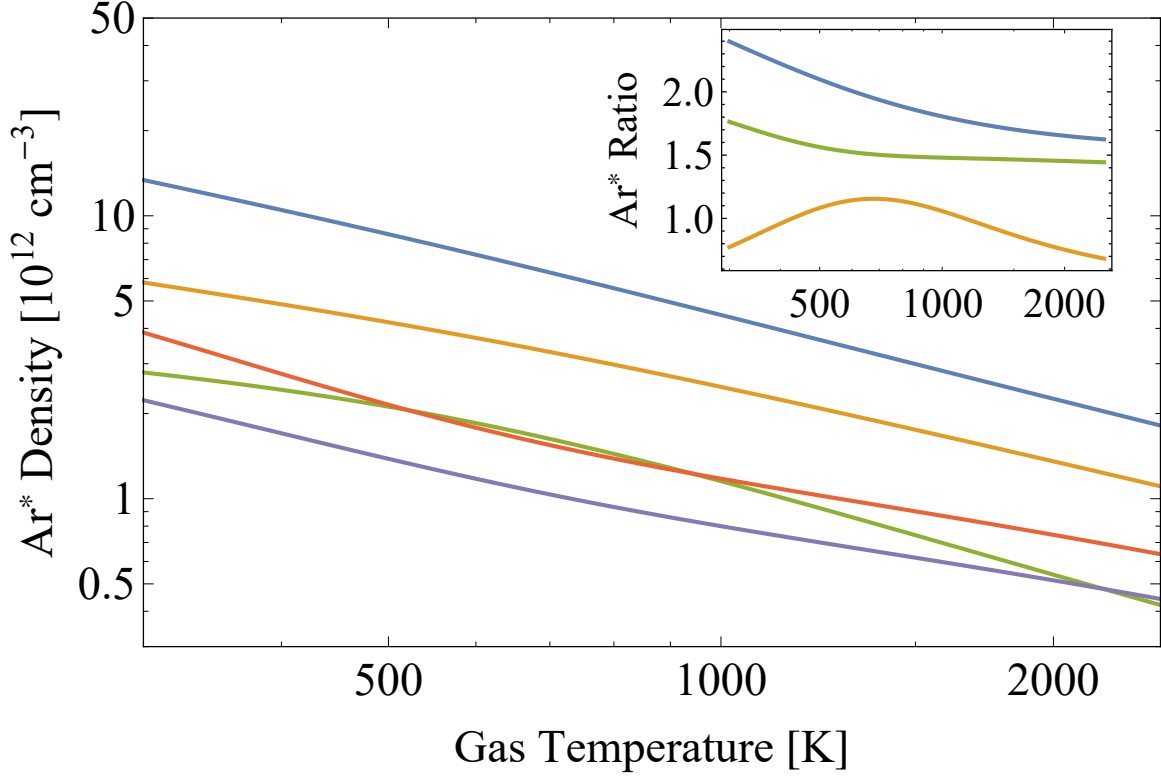


Figure 9. The dependence of the excited states on the gas temperature is shown. The curves correspond to $1s_5$ (—), $1s_4$ (—), $2p_{10}$ (—), $2p_9$ (—), $2p_8$ (—). The densities are sensitive to the electron temperature mostly arising from the relationship between the gas density and temperature given by the ideal gas law. The inset shows the dependence of the population ratios on the electron density. These curves correspond to $1s_5/1s_4$ (—), $2p_{10}/2p_9$ (—), $2p_9/2p_8$ (—).

constant, $n_{1,2}$ are the densities at each temperature, $T_{1,2}$. It is clear from both Fig. 9 and its inset that the population ratios, $1s_5/1s_4$ and $2p_{10}/2p_9$ are sensitive to the gas temperature. The $1s_5/1s_4$ ratio decreases by 25% for a temperature increase from 300 to 1500 K before leveling off. The $2p_{10}/2p_9$ ratio increases by a factor of 2 for a factor of 2 temperature increase from 300 to 600 K and then decreases by 25% as the temperature rises to 1500 K.

The utility of the proposed model is in its ability to leverage a small number of measurements to be able to predict laser performance. By analyzing the trade space of the Ar* densities and their ratios we see that a measurement of the Ar($1s_{5,4}$) densities is sufficient to get the electron temperature, electron density and gas temperature for the model. The choice of these three parameters is improved with fluorescence measurements of the excited P states which provide the estimated population ratios.

3.3 Application to Laser Experiments

In the rate equations the pump laser intensity, Ω , is treated as a single value throughout the medium. This is not the true behavior of the pump laser in the gain medium as the laser will be absorbed as it travels through the medium leading to a lower average intensity. The development of the optical part of the model follows that of Hager, et al, for a pump laser line width much narrower than the pumped atomic transition [70] but can be easily extended to consider wider line width pump lasers where the coupling efficiency is less than 1 [72]. For a broadband pump source, the longitudinally-averaged pump intensity is given by the solutions to the transcendental equation

$$\Omega = \frac{I_{Pin}}{l_g} \left(\int_{-\infty}^{\infty} f_p(\nu) \text{Exp}(\sigma_{31}(\nu) \Delta n_{31}(\Omega) 2l_g) d\nu - 1 \right) \quad (40)$$

which is a function of the incident pump intensity I_{Pin} , the pump laser line shape $f_p(\nu)$ which is taken to be a Gaussian, the stimulated emission cross section $\sigma_{31}(\nu)$,

and the intensity-dependent population inversion $\Delta n_{31}(\Omega)$. This treatment facilitates consideration of two common pump sources: titanium:sapphire (Ti:Saph) ring lasers with narrow line widths, 30 - 100 kHz, and volume Bragg grating narrowed diode lasers with broad line widths, 30 - 50 GHz. These are compared to the atomic line width of ≈ 12 GHz at atmospheric pressure. Fig. 10 shows how the pump line width influences the small-signal gain behavior of the medium. The threshold level is set by the cavity losses which is a function of the gain length, l_g , the window transmission, T_w , and the output coupler reflectivity, r . The threshold is given by

$$g_{th} = \frac{1}{2l_g} \text{Log}(rT_w^4) \quad (41)$$

where $l_g = 3$ cm, $r = 0.2$ and $T_w = 0.9$. The atomic transition is 12 GHz and the pump line widths range from 1 GHz to 100 GHz. There is little deviation between the 1 GHz and 10 GHz cases as they are both less than the atomic line width and the reduced gain on the 10 GHz curve arises from the line shape mismatch between the Gaussian pump beam and Lorentzian atomic transition. As the pump line width increases the rise in gain is diminished because of reduced absorption of the pump due to the spectral mismatch.

Experimental measurements are required in order to define what the electron temperature, electron density and gas temperature are. As will be shown in following sections, the ideal measurement is that of the absorption coefficient and the gain coefficient as a function of the pump intensity but the densities of the $1s_{5,4}$ states combined with fluorescence data of the p_{10} and p_9 states is sufficient for a system characterization. The latter is the only available measurement in the absence of lasing.

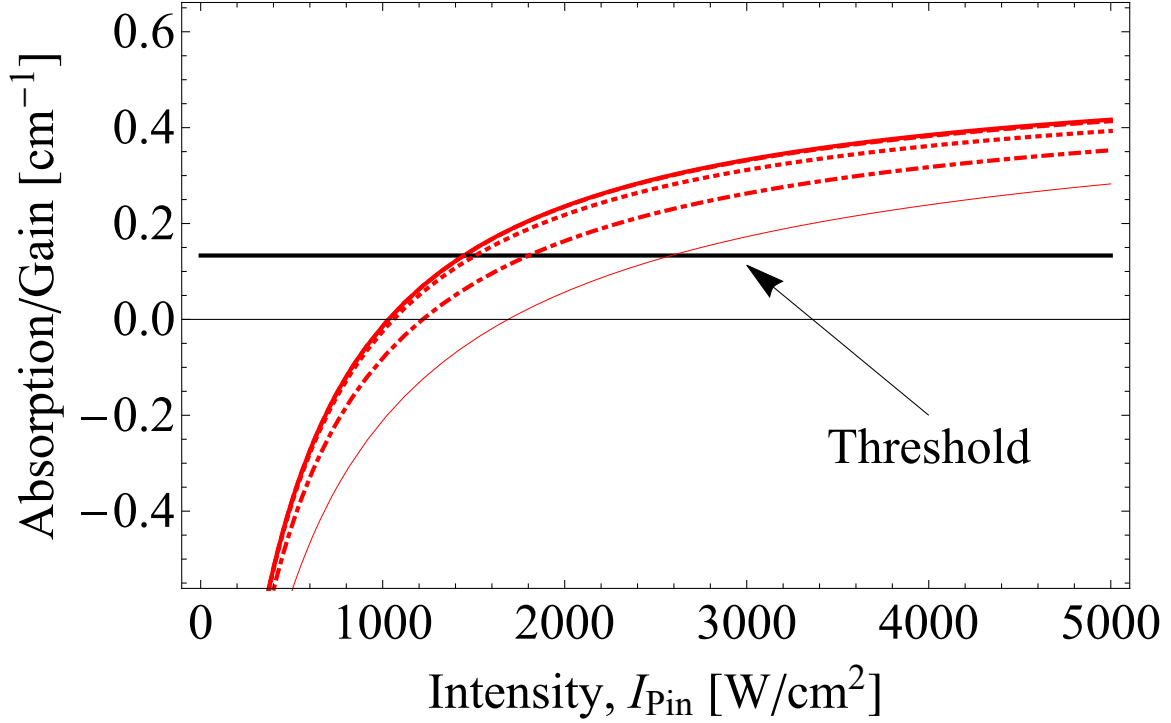


Figure 10. The influence of a spectral mismatch between the pump line width and atomic line width is shown. The atomic line width is 12 GHz and the pump is 1 GHz (—), 10 GHz (---), 25 GHz (.....), 50 GHz (-.-.-), and 100 GHz (—). The black line designates the threshold (losses) above which the system can lase. The 1 and 10 GHz cases are overlaid as both satisfy the narrow bandwidth condition. As the pump line width increases the threshold intensity increases and the gain curve rolls over quicker. This lower efficiency and peak gain is due to the reduced pump absorption outside the width of the atomic feature.

3.3.1 PSI Microwave-Resonant Strip Discharge.

Rawlins, et al, studied an Ar-He gain medium in a micro-discharge array containing 15 microwave-driven strip resonators [154]. They achieved continuous-wave (cw) lasing using a narrow-bandwidth Ti:Saph laser. In this experiment they used a 2% Ar in He mixture, operated at 769 Torr and an assumed temperature of ≈ 600 K. The gas temperature was derived from a Voigt profile fit to the absorbance data. The cavity parameters are summarized in the first column of Tab. 1. In Fig. 10 of their paper the gain and absorbance curves have been given. We note that the absorbance is measured with a probe intensity of 7 W/cm^2 which is large enough to influence the behavior of the populations. They note this phenomena themselves but do not discuss it further. In addition, to match the measured gain profiles using a four-level model, they artificially increase the $1s_4 \rightarrow 1s_5$ and $2p_9 \rightarrow 2p_{10}$ rate coefficients using an Arrhenius law scaling ($k = Ae^{-B/T}$) to 600 K by assuming that A is given by a gas-kinetic rate of $3 \times 10^{-10} \text{ cm}^3/\text{s}$ and solving for B using the rates provided by Heaven, et al [75]. This scaling increases the $1s_4 \rightarrow 1s_5$ rate coefficient by a factor of 20 and the $2p_9 \rightarrow 2p_{10}$ rate coefficient by a factor of 6. We find from our model that increasing these rate coefficients, as well as the $2p_8 \rightarrow 2p_{10}$ rate coefficient, is crucial to matching the observations. Fig. 11 shows the model output for several different combinations of electron temperature, electron density and gas temperature. The modeled absorption coefficient compared to the measurement shows that there is a

Table 1. The cavity parameters of the five-level model for the PSI, AFRL and optimal lasing conditions are given.

Case	Gain Length l_g (cm)	O.C Reflectivity r	Window Transmission T_w	Threshold g_{th} (cm^{-1})
PSI Model	1.9	0.85	0.9	0.151
AFRL Model	7.62	0.2	0.9	0.133
Optimal Model	2	0.2	0.98	0.44

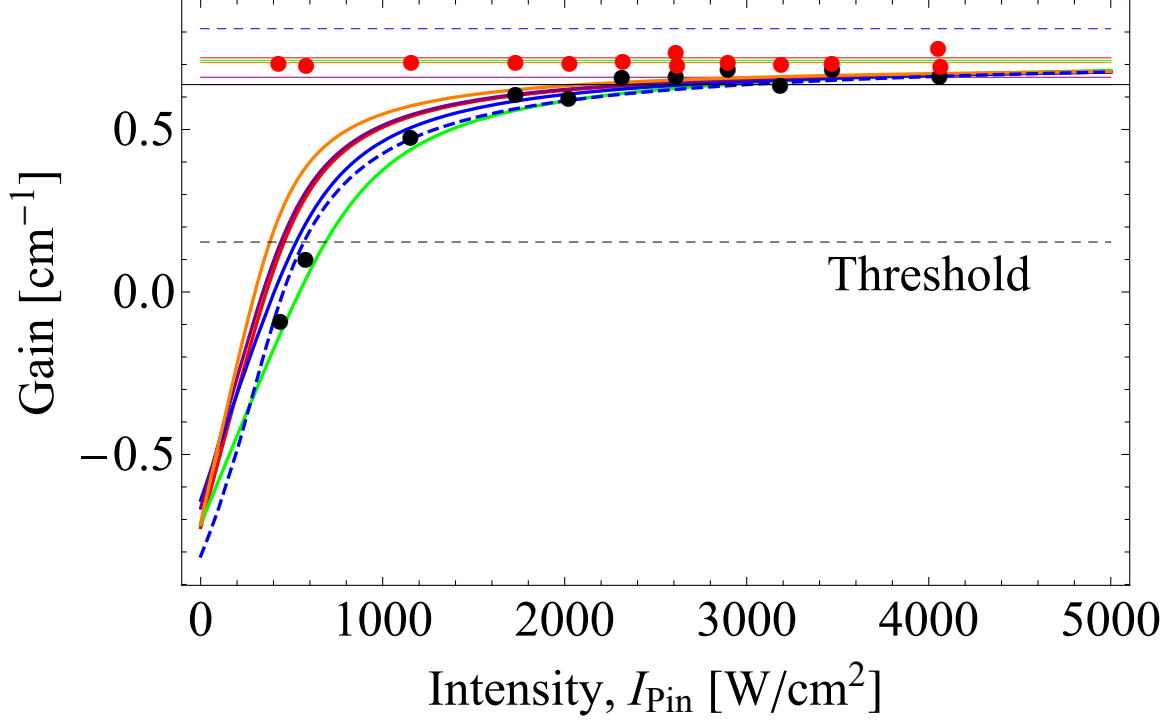


Figure 11. The results are shown for several different electron temperatures, densities and gas temperatures. The red and black markers are the measured absorption and gain [154]. The absorption coefficient alone is not unique in the model and many different combinations of the three parameters can provide the same coefficient. The gain is a significantly more sensitive probe and the two measurements together are matched with an electron density of $1.45 \times 10^{15} \text{ cm}^{-3}$, an electron temperature of 1.39 eV, and a gas temperature of 650 K.

lack of uniqueness in the prediction. For all six combinations of parameters, the same absorption coefficient can be achieved. The uniqueness of the parameters is defined by the measurements of both the gain and absorption coefficients. The parameters which best represent the data are an electron temperature of 1.39 eV, an electron density of $1.46 \times 10^{15} \text{ cm}^{-3}$, and a gas temperature of 650 K, defined by the dashed blue line in the figure.

3.3.2 AFRL Radio-Frequency Capacitively-Coupled Discharge.

Having shown the benefit of the model for a case where cw lasing was achieved, we turn to the case where the test did not result in lasing: a large-volume, capacitively-coupled, dielectric barrier discharge with a liquid dielectric coolant jacket with a 5% Ar in He mixture. In this case, fluorescence is collected from the discharge and absorbance is measured using diode laser absorption spectroscopy. As previously mentioned, the total number density of the $1s_5$ and $1s_4$ levels is sensitive to the electron temperature. Fig. 12 shows the model output for the two s state populations as a function of electron temperature and the corresponding measurement. The intersection occurs at approximately 1 eV. Similarly, the population ratios are sensitive to the electron density. Fig. 13 shows the model prediction for the $1s_5/1s_4$ and $2p_{10}/2p_9$ population ratios and the corresponding measurements. The intersection of the measurements and the model predictions correspond to an electron density of $3 \times 10^{14} \text{ cm}^{-3}$. The temperature was selected as 400 K, consistent with the Doppler widths derived from the Voigt profiles fit to the absorbance data. It is immediately clear that the electron temperature, the main driver of the population densities, is much too low to achieve lasing in this discharge. Fig. 14 shows the results of the modeled gain for the assumed parameters given and a 10% and 25% increase in T_e . The cavity parameters are summarized in the second column of Tab. 1. The VBG diode had a

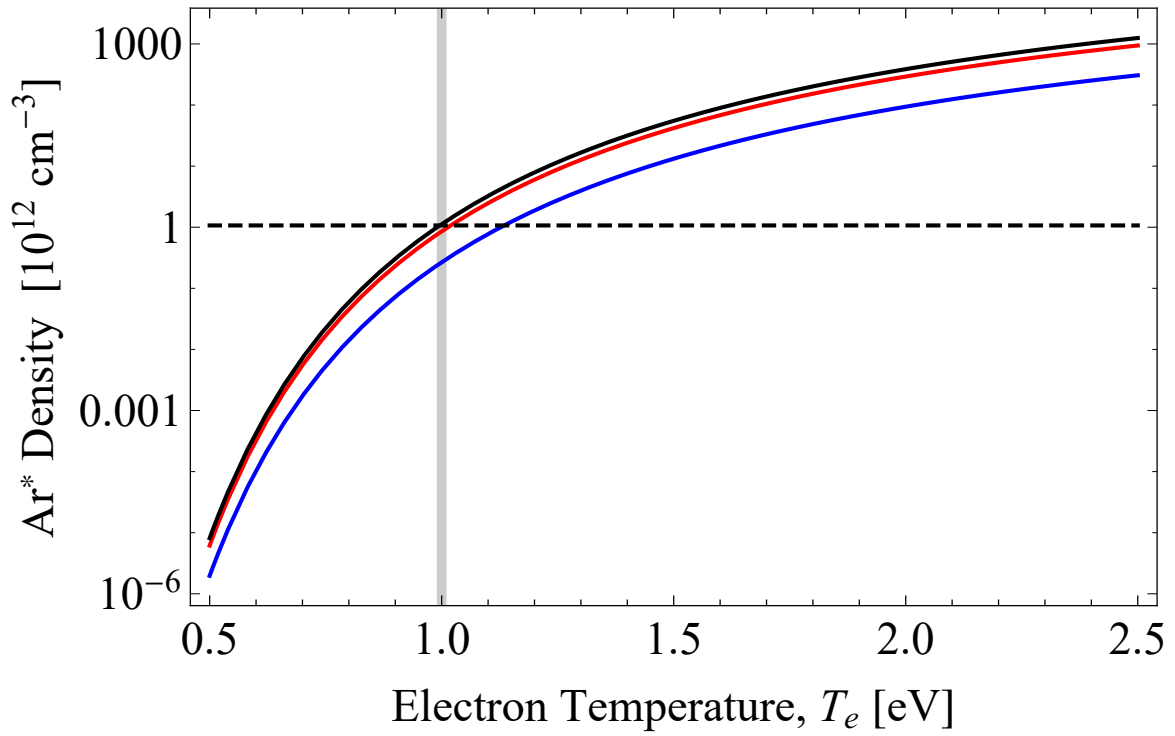


Figure 12. The $1s_5$ (—) and $1s_4$ (—) densities are plotted against electron temperature. The model prediction for the sum, (—), and the measured value, (---), are also shown. The vertical line (—) corresponds to an electron temperature of 1 eV which is the intersection of the two black curves.

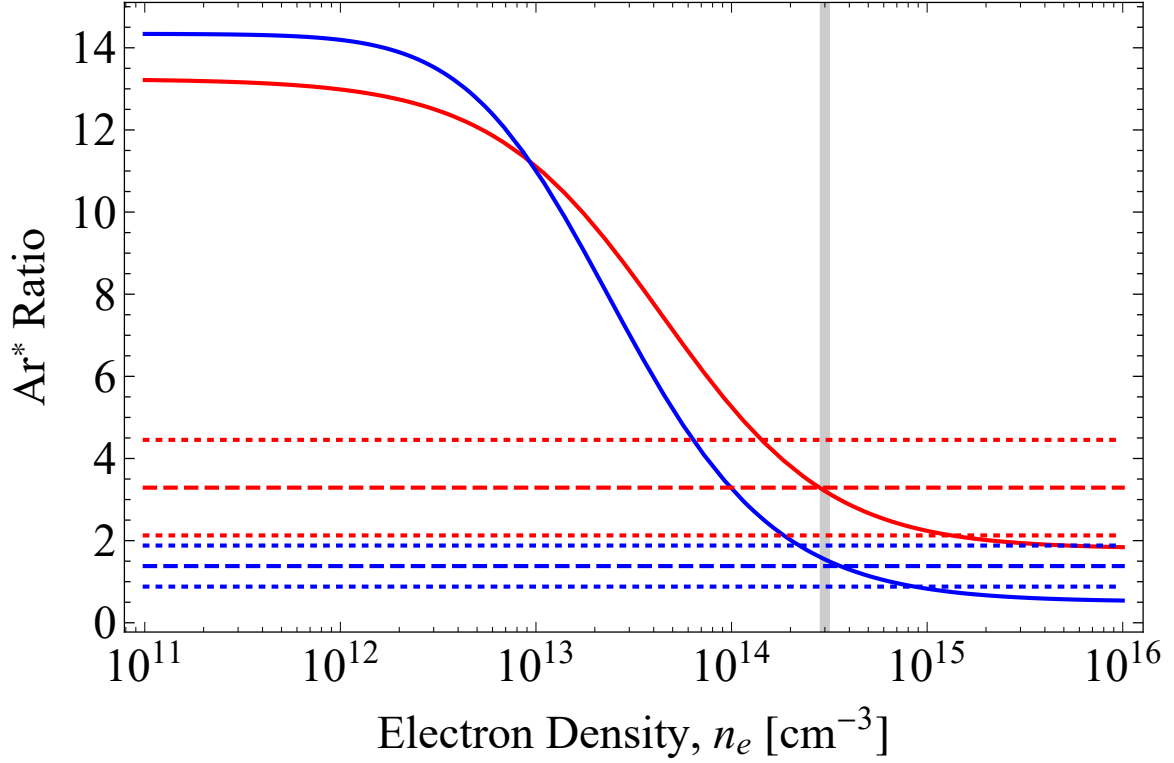


Figure 13. The predicted $1s_5/1s_4$ (—) and $2p_{10}/2p_9$ (—) population ratios are plotted against electron density. The measured ratios are given by (---) and (---) with (.....) and (.....) giving the error bounds for the $1s_5/1s_4$ and $2p_{10}/2p_9$, respectively. The vertical line (—) is at a density of $3 \times 10^{14} \text{ cm}^{-3}$ which is at the intersection of both population ratios and their measured values.

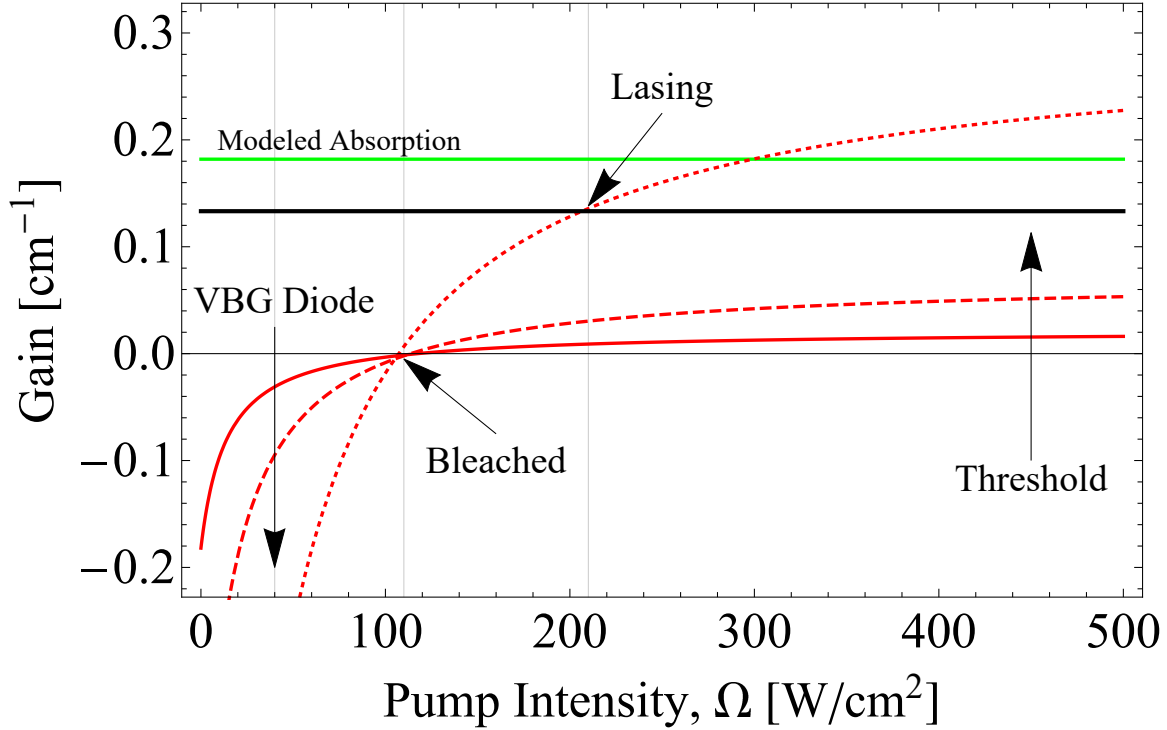


Figure 14. The projected gain curves for an Ar-He, radio-frequency capacitively coupled discharge are shown. The curves correspond to an electron temperature of 1 eV (—), 1.1 eV (---), and 1.25 eV (.....). At an electron density of $3 \times 10^{14} \text{ cm}^{-3}$, an electron temperature of 1 eV, and a gas temperature of 440 K, there is insufficient population to achieve lasing threshold (—). The VBG diode (40 W/cm^2) used to pump the medium is insufficient to bleach the sample, which occurs at 110 W/cm^2 . Lasing is achieved in the high T_e case at intensities greater than 210 W/cm^2 .

maximum intensity of 40 W/cm² due to the discharge configuration and it is clear that this intensity is insufficient to bleach the gain medium. In fact, an intensity of 110 W/cm² is the required intensity to bleach the medium in all three cases. The third, highest T_e , case is the only one capable of achieving lasing at a pump intensity of 210 W/cm². The influence of the mismatched pump and atomic line widths is apparent in these curves as well. Unlike the previous case where the gain increased linearly before rolling over due to maximizing the cycle rate, these curves simply increase slowly to the asymptotic, peak cycle rate values. This behavior arises from the reduced power of the pump laser available for absorption.

With the model bench-marked using two different Ar-He discharges, an investigation of ideal conditions for the gain and lasing profiles can be conducted. In order to do this, the intracavity lasing intensity term, $\Psi_{31}(\nu)\sigma_{31}(nu)/(h\nu_{31}(n_3 - g_3/g_1n_1))$, must be added to the $\dot{n}_1$ rate equation and subtracted from the $\dot{n}_3$ equation. In addition, an equation defining the photon buildup of the intracavity laser intensity must be added [70]

$$\dot{\Psi} = 0 = (rt_w^4 \text{Exp}(\sigma_{31}(n_3 - \frac{g_3}{g_1}n_1)2l_g) - 1) \frac{\Psi}{\tau_{RT}} + \frac{n_3 c^2 \sigma_{31} h \nu_{31}}{l_g} \quad (42)$$

where r is output coupler reflectivity, t_w is the window transmission, l_g is the gain length, τ_{RT} is the cavity round trip time. In Eq. (42) the first term defines the building up of the lasing intensity from stimulated emission and the second term defines the photon buildup associated with spontaneous emission from the upper laser state. In a steady-state treatment we can ignore the second term, as done by Hager, et al [70]. The sixth equation then becomes

$$g_t h = -\frac{\log(rt_w^4)}{2l_g} = \sigma_{31}(n_3 - \frac{g_3}{g_1}n_1) \quad (43)$$

which is the laser threshold condition and states that when lasing is achieved the gain on the lasing transition is fixed to the threshold value. The system can then be analyzed as a function of pump intensity, electron density, electron temperature, gas pressure and gas density and the optimal conditions for a high power laser system can be discovered. Using a pressure of 769 Torr, a gas temperature of 650 K, an electron density of $1.25 \times 10^{15} \text{ cm}^{-3}$ and varying T_e to influence the initial laser-ground state population, the output laser intensity behavior as a function of this density is analyzed. The cavity parameters are summarized in the third column of Tab. 1. Lastly, the pump laser bandwidth is assumed to be narrower than the atomic transition. Fig. 15 shows these curves for $\text{Ar}(1s_5)$ densities ranging from 5×10^{12} to $7.5 \times 10^{13} \text{ cm}^{-3}$. It is clear that as the density rises, so does the linear regime of the lasing intensity curve. The slope efficiency approaches 0.78, 11% less than the quantum efficiency of 0.88.

Examining the output laser intensity from the frame of a high-energy laser system (greater than 100 kW) allows estimation of required gain volumes for these systems. From Fig. 15 the output laser intensity at pump intensities of 10 kW/cm^2 for the $\text{Ar}(1s_5)$ densities 0.5, 1, 2.5, and $5 \times 10^{13} \text{ cm}^{-3}$ are 900, 2640, 5620 and 4020 kW/cm^2 where the reduced output power in the last case is due to the increased lasing threshold. For a 100 kW system at the 2 cm gain length, necessary total gain volumes of 223, 76, 36 and 50 cm^3 are required. Clearly, in order to achieve HEL operation in a suitably small volume, a minimum density of $1 \times 10^{13} \text{ cm}^{-3}$ is required with the volume requirements able to be reduced by a factor of 5 if densities of $5 \times 10^{13} \text{ cm}^{-3}$ can be produced. In a realistic system the diode pump will not be a perfect match for the atomic transition and these output laser powers will be reduced. This will lead to a larger gain volume requirements.

The presented five-level laser model includes both optical and plasma mechanisms.

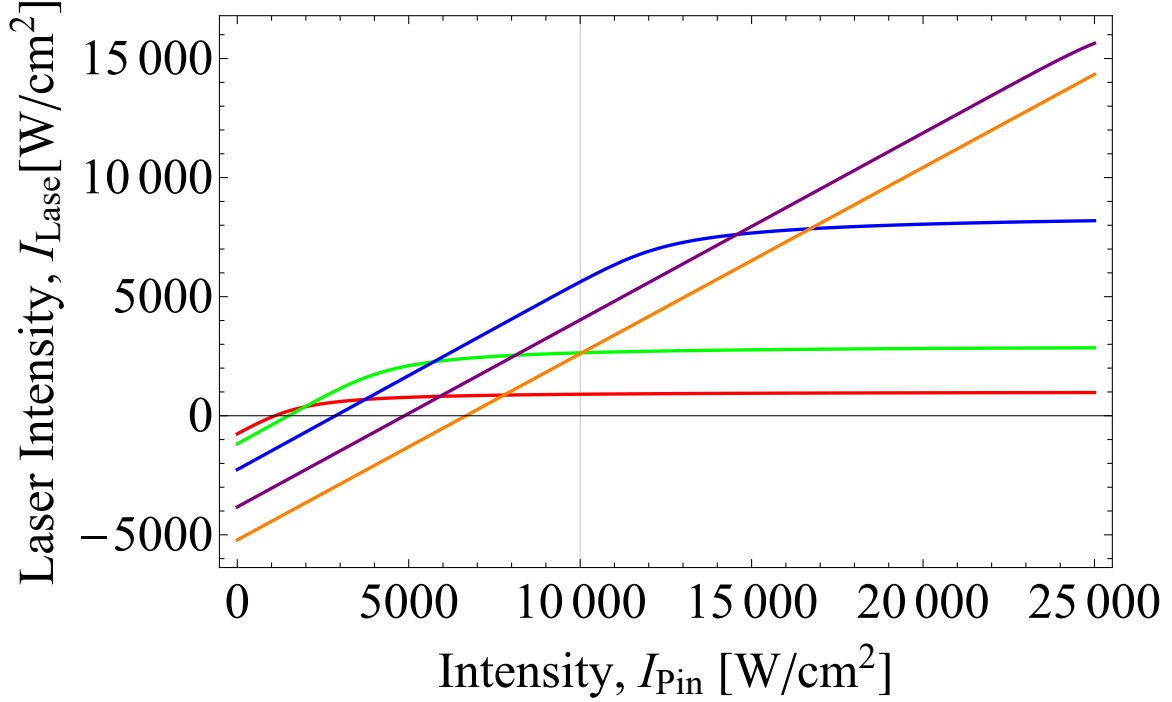


Figure 15. The output laser intensity is shown for various electronic temperatures. The curves correspond to initial $\text{Ar}(1s_5)$ densities of 0.5 (red), 1 (green), 2.5 (blue), 5 (purple), 7.5 (orange) $\times 10^{13} \text{ cm}^{-3}$.

Using measured absorbance of the $\text{Ar}(1s_5)$ level along with either the gain behavior or the $\text{Ar}(1s_4)$ density along with the $2p_{10}/2p_9$ population ratio, the three free parameters, electron density, electron temperature and gas temperature, can be fixed. The model can then be used to investigate the laser performance outside of the regime that was tested, as in the first presented case, or can be used to assess why lasing was not achieved and what the path to lasing is, as in the second case. With the small addition of the lasing equations, the model can also be used to assess what the ideal performance of such a laser system is and, in a more limited sense, what the requirements are for scaling such a system up to HEL levels. The model then allows for a fairly complete analysis of a gain medium in the absence of the pump laser, in the presence of a pump laser with optimal spectral overlap and in the presence of a pump laser with line widths on the order of, or greater than, the atomic transition.

IV. Pressure broadening and shift rates for Ar (s-p) transitions observed in an Ar-He discharge

Abstract

The pressure broadening and shift rates have been measured for the 801.699 nm ($s_5 \rightarrow p_8$), 800.836 nm ($s_4 \rightarrow p_6$) and 795.036 nm ($s_3 \rightarrow p_4$) transitions in argon perturbed by 10 - 200 Torr of helium and argon at a temperature of 440 ± 20 K using a radio-frequency, capacitively coupled discharge. For a 10% Ar in He plasma the pressure broadening and shift rates were measured as 14.18 ± 0.65 and 1.81 ± 0.30 MHz/Torr, 17.85 ± 0.78 and 0.72 ± 0.32 MHz/Torr, and 16.59 ± 1.22 and 2.94 ± 0.48 MHz/Torr for the 801.699 nm, 800.836 nm and 795.036 nm transitions, respectively. The influence of the slightly varying gas temperature on the broadening and shift rates is less than 1%. Stark broadening and shifting by electrons in the discharge are not measurable due to low electron densities and temperatures. Phase-changing collisional cross-sections in the literature decrease with temperature, in good agreement with the Lindholm-Foley $T^{-0.2}$ trend based on the Lennard-Jones potential. Further investigation of the Ar*-Ar and Ar*-He interaction potentials is necessary to understand the behavior of the cross sections.

4.1 Introduction

The Diode Pumped Alkali Laser (DPAL), was introduced in 2003 [100], characterized [208, 211, 177, 205] and scaled to powers as high as 1 kW in 2012 [26]. While the alkali metal vapor is an excellent way to phase together a large number of incoherent or low beam quality (diode) sources, there are engineering issues associated with the reactivity of the alkali metals. An analog to the DPAL system with optical excitation of rare gas metastables has recently been developed to eliminate the alkali

reactivity [74, 73, 75, 154, 68, 155]. A weak rare gas discharge is used to generate population in the excited s states, diode pumping to the lower p states yields lasing with some wavelength agility, as illustrated in Fig. 16. This is a three-level laser and so a high-threshold pump intensity, 0.1 - 1.0 kW/cm², is expected [193, 154].

There has been significant progress in the development of the rare gas laser including pulsed lasing in neon-argon (Ne-Ar), argon-helium (Ar-He), krypton-helium (Kr-He) and xenon-helium (Xe-He) systems using a pulsed discharge [74, 75], the demonstration of a cw pumped Ar-He laser in a pulsed discharge [73], a long-pulse pumped Ar-He laser in a radio-frequency (RF) discharge [68] and a cw Ar-He laser using resonator strip microwave microdischarges [154, 155]. In order to effectively couple the pump radiation into the gain medium the atomic spectral width must be comparable to the diode pump widths of ~ 30 GHz [73, 72]. The central frequency of the atomic transition must be well known as well. In this paper we measure the pressure broadening and shift rates of three transitions; the 801.699 nm ($s_5 \rightarrow p_8$), 800.836 nm ($s_4 \rightarrow p_6$) and the 795.036 nm ($s_3 \rightarrow p_4$) transitions, all at sub-atmospheric pressures.

Collision induced shifts of the resonant frequency to the red or blue depend on whether the interaction potentials are attractive or repulsive on average and the temperature dependence of those rates acts as a sensitive probe of the potentials [151, 148, 106, 71]. The potential energy surfaces for the homogeneous Ar*-Ar interaction have been calculated for the ground Ar-Ar state, the first excited s-state manifold and half of the excited p-state manifold [53]. The surfaces for the heterogeneous Ar*-He interaction have only been calculated for the ground state and the first excited s state manifold [143]. For the Ar*-Ar interaction the s_5 and p_8 states represent the energy levels in the asymptotic limit and divide into 5 and 6 surfaces, respectively. The resulting molecular potential surfaces have strong avoided crossings

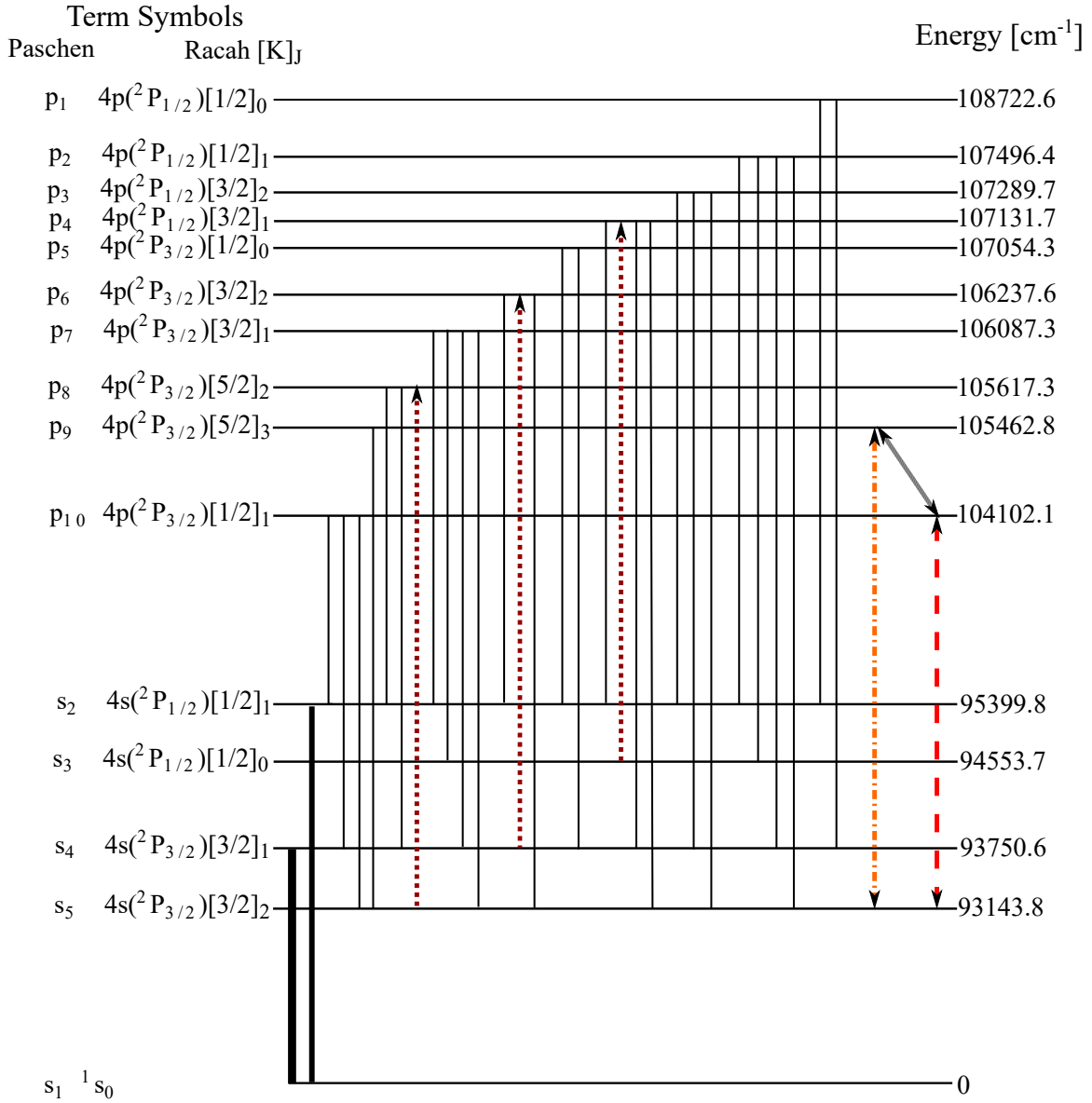


Figure 16. Energy diagram for the first two s and p state manifolds of Ar. The levels are designated by both the Paschen and Racah notation. The solid vertical lines indicate the optically allowed transitions. The 801.699 nm ($s_5 \rightarrow p_8$), 800.836 nm ($s_4 \rightarrow p_6$) and the 795.036 nm ($s_3 \rightarrow p_4$) transitions examined in this paper are shown (...). One lasing scheme involves diode pumping on $s_5 \rightarrow p_9$ (-.-), collisional mixing between the p-states (—) and lasing on the $p_{10} \rightarrow s_5$ transition (- -).

with a significant number of neighboring energy levels, especially for the p_8 state. The s_5 state crosses with s_3 , s_4 and p_{10} and the p_8 state crosses with p_{10} , p_9 , p_7 , p_6 and p_5 where most of the avoided crossings occur around 5 Bohr radii. The avoided crossings represent an interaction mechanism by which fine structure mixing occurs and are one of the defining factors in the strength and range of the fine-structure interaction. These interactions on a large number of potential surfaces must be convolved together in order to predict the line shape which is a complex theoretical task. The measured line shapes, therefore, help test the calculated potential surfaces and the pressure broadening and shift rates along with their temperature dependence serve as a sensitive probe of the interaction. The characterization of potential surfaces using measured line shapes has been conducted for a considerably simpler system, the alkali metals [71].

Previous measurements of the broadening and shifting rates of the excited states of Ar in collisions with Ar, He and Ne have been conducted with most of the measurements being made on the Ar-Ar case. Most published rates for Ar transitions were measured using water-cooled static DC discharges either at high temperature (>1000 K) and high pressure (>1 atm) [37, 36, 190, 125] or at low pressures (0.1 - 100 Torr) [175, 103, 2, 195, 200, 21, 20] where deconvolution of the Doppler, Lorentzian and instrument line shapes becomes difficult. Regardless of the plasma conditions the measurements were made using optical emission spectroscopy (OES) and a monochromator or Fabry-Perot interferometer which limits the fidelity of a fit of the measured absorbance line shape to the resolution of the detection system. Three previous publications have studied the broadening of Ar transitions in collisions with Ar using tunable diode laser absorption spectroscopy (TDLAS). The first, *Tachibana, et al*, measured the broadening and shift rates of 811.5 nm, 810.4 nm and 840.8 nm transitions and found their values to be in good agreement with the OES literature. They

observe a strong broadening and no shift for the 840.8 nm resonance transition, consistent with theory [181]. The second publication, by *Leiweke, et al*, used TDLAS to measure the pressure broadening and shift rates of the 772.376 and 772.4207 nm transitions with the intent of extracting gas temperature from the measured rates using the Lindholm-Foley theory of collisional broadening [104]. The third publication, by *Mikheyev, et al*, used TDLAS to measure the pressure broadening rates of the $s_5 \rightarrow p_9$ transition in Ar-He and Kr-He mixtures. The Ar-Ar rates were found to be in good agreement with the previous literature and the new Ar-He rate is 14% larger [117].

With the use of a single-mode tunable diode laser we measure the broadening and shift rates of Ar-He mixtures at low temperature (≈ 440 K) and pressures of 10 - 200 Torr. This allows us to obtain measurements with higher accuracy than in the past as well as interrogate the combined influence of Ar and He on the broadening and shifts of the excited Ar states.

4.2 Experiment

The Ar excitation is achieved using a radio-frequency (RF) discharge powered by a Dressler Cesar model 1310 1.25 kW, 13.56 MHz, power supply. The discharge apparatus consists of a 1/4" O.D. (0.15" I.D.) alumina tube through which ultra-high purity (99.999%) mixtures of argon and helium are flowed. Two copper rings are connected to the outside of the tube and are separated by 1/2". The reverse power is maintained at <1% of the forward power, matching the plasma load using a Navio Digital matching network. The current and voltage characteristics are measured using a Mangelab CT-D5.0-BNC current transformer. The surfaces of the alumina tubes are cooled with room temperature air delivered to the cell using an opened Swagelok 1/2" connection. RF power was fixed at 10 W to prevent etching of the

alumina near the RF electrode. The pressure was varied from 10 - 200 Torr in 10 Torr steps. Ar/He mixtures are prepared in a mixing tank in mixtures ranging from 2.5% Ar to 25% Ar in He. Gas pressure is controlled using a Matheson 3420A high-purity, brass in-line regulator and measured using an MKS Baratron 690A capacitance manometer connected to a MKS 651C controller. The flow rate is measured using a Sierra Instruments 71797 mass flow controller on the vacuum side. For pressures in the given range, flow rates ranged from 72 to 1,056 sccm.

The pressure broadening and shift rates were measured using tunable diode laser absorption spectroscopy (TDLAS). A diagram of the apparatus can be seen in Fig. 17. The laser source is a New Focus Velocity 6314 diode laser capable of scanning from 792 - 802 nm with a 300 kHz line width and has a maximum power of 8 mW. This allows us to scan over the 795.036 nm ($s_3 \rightarrow p_4$), 800.836 nm ($s_4 \rightarrow p_6$) and 801.699 nm ($s_5 \rightarrow p_8$) transitions in Ar. The laser is sent through a 90/10 beam splitter where the reflected beam is incident on a fiber-coupled Angstrom WSU2 High Finesse Wavemeter referenced to a frequency-stabilized He-Ne laser for absolute frequency calibration to within 10 MHz. The remaining 90% is amplitude modulated using a Stanford Research Systems SR540 mechanical chopper with a 0.17" aperture, 30 slot chopper wheel at 1.8 kHz and is then passed through a Thor Labs BP145B2 45/55 coated pellicle. The intensity of the reflected beam is monitored by a Thor Labs PDA10A 10 ns rise-time photodiode. The remaining fraction is then propagated through the cell and the transmitted intensity is monitored by a second PDA10A photodiode. The two detectors are connected to separate Stanford Research Systems SR850 lock-in amplifiers, both referenced to the chopper frequency. The laser intensity incident on the cell was $< 15 \text{ mW/cm}^2$ which is less than saturation intensity of the 800.8359 nm transition of 55 mW/cm^2 , the lowest of the three lines investigated. A 36 Hz signal was observed in the data and is thought to be induced on the lock-ins by radio-

frequency interference (RFI) caused by the discharge since it only appeared when the RF source was on. A computer with Matlab is used to control instruments and to collect data through a national instruments USB-6251 BNC DAQ unit and an Agilent model 82357B GPIB-to-USB module.

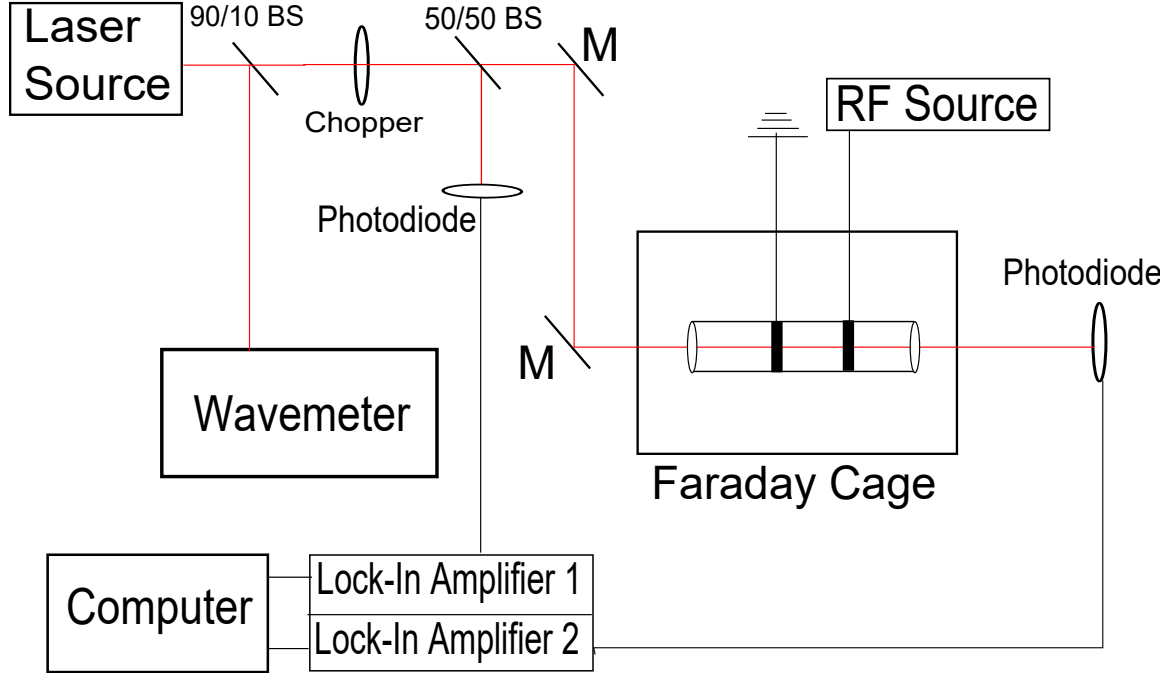


Figure 17. Experimental apparatus used for tunable diode laser absorption spectroscopy measurements.

4.3 Results

Typical absorption spectra for the s_5-p_8 line are provided in Fig. 18. The absorbance is given by, $A = -\ln(I/I_0)$, where I is the transmitted signal and I_0 is the incident signal. There exists a linear baseline in the measurement of the 801.699 nm and 795.036 nm transitions and a quadratic baseline in the 800.836 nm transition. The absorbance can also be defined in terms of the atomic parameters as: $A = \sigma_{lu}nl$ where n is the lower level concentration, l is the absorption path length which ranges from 2.75 to 3.85 cm defined by the discharge fluorescence and decreasing with gas

pressure. $\sigma_{lu} = \frac{g_u}{g_l} \frac{A\lambda^2}{8\pi n^2} g(\nu)$ is the absorption cross-section, where g_u , g_l are the degeneracies of the upper and lower level, A is the Einstein A coefficient, λ is the central wavelength, n is the index of refraction of the medium, taken to be 1, and $g(\nu)$ is the line shape. The Einstein A coefficients for the 795.036 nm ($s_3 \rightarrow p_4$), 800.836 nm ($s_4 \rightarrow p_6$) and 801.699 nm ($s_5 \rightarrow p_8$) transitions are $1.86 \times 10^7 \text{ s}^{-1}$, $4.90 \times 10^6 \text{ s}^{-1}$ and $9.28 \times 10^6 \text{ s}^{-1}$, respectively, with errors that are 25% of the measured values [98]. The cross-sections at line center, assuming a pressure of 150 Torr, a temperature of 440 K and the pressure broadening rates for a 5% Ar mixture measured in this experiment are 2.93×10^{-12} , 5.31×10^{-13} , and $6.48 \times 10^{-13} \text{ cm}^2$, respectively.

In general, the line shape function takes the form of a Voigt profile. This Voigt profile is a convolution of the Lorentzian line shape and the velocity distribution of the absorbing or emitting atoms and is, therefore, a description of the line shape in a regime where neither the pressure (Lorentzian) or temperature (Doppler) is the dominant broadening mechanism. The Voigt profile is given by

$$g(\nu) = \int_{-\infty}^{\infty} dv_z [g_L(\nu - \nu_0 \frac{v_z}{c}) g_D(\nu)] \quad (44)$$

$$= \int_{-\infty}^{\infty} dv_z [(\frac{\Delta\nu_L}{2\pi(\nu - \nu_0 - \nu_0 \frac{v_z}{c})^2 + (\frac{\Delta\nu_L}{2})^2}) \quad (45)$$

$$\times (\frac{M}{2\pi k_b T} \exp(-\frac{M v_z^2}{2 k_b T}))] \quad (46)$$

$$= \int_{-\infty}^{\infty} dv_z [(\frac{\Delta\nu_L}{2\pi(\nu - \nu_0 - \nu_0 \frac{v_z}{c})^2 + (\frac{\Delta\nu_L}{2})^2}) \quad (47)$$

$$\times (\frac{2}{\Delta\nu_D} \sqrt{\frac{\ln(2)}{\pi}} \exp(-(\frac{2\sqrt{\ln(2)}}{\Delta\nu_D} \nu_0 \frac{v_z}{c})^2))] \quad (48)$$

where the integration is over v_z since the projection of the velocity along the laser path is the only contributor to the Doppler broadening, M is the mass of the absorber, c is the speed of light, k_b is the Boltzmann constant, T is the gas temperature, $\Delta\nu_L$

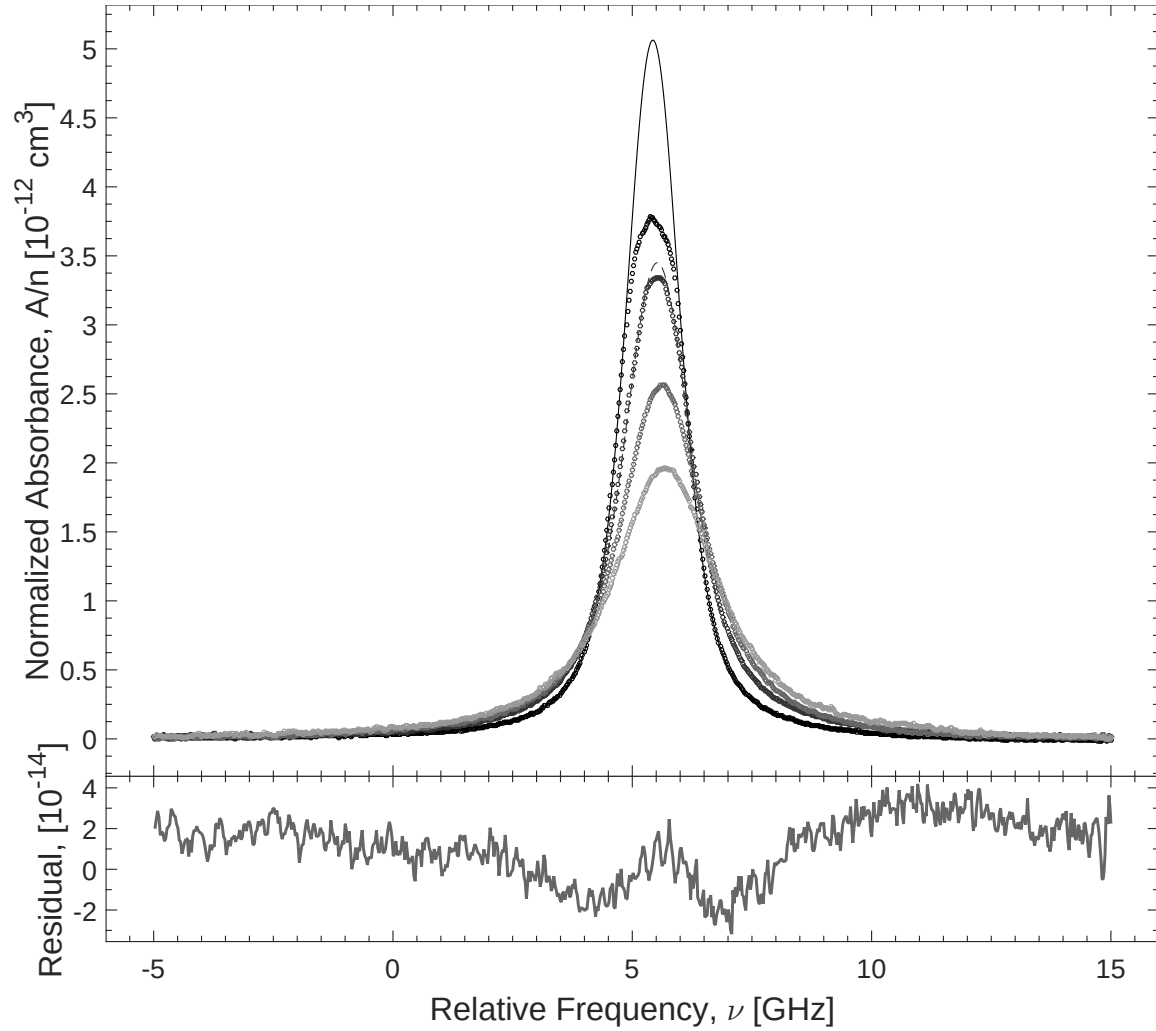


Figure 18. Absorption spectra for the 801.699 nm Ar line for a 5% Ar in He plasma. The data and Voigt fits are shown for total pressures of 40, 60, 80, 100 and 120 Torr colored from light gray to black. The absorbances are normalized to the number density of the $1s_5$ state as summarized in Figure 19. The residuals are shown for the 80 Torr case.

is the Lorentzian width, and

$$\Delta\nu_D = \nu_0 \left(\frac{8k_b T \ln(2)}{Mc^2} \right)^{1/2} \quad (49)$$

is the Doppler width. The Lorentzian width and central frequency can be defined in terms of the pressure broadening and shift rates as:

$$\Delta\nu_L = \sigma \bar{v} n \quad (50)$$

$$= \sigma \bar{v} \frac{P}{k_b T} \quad (51)$$

$$= \gamma P \quad (52)$$

$$\nu_c = \nu_0 + \beta P \quad (53)$$

where γ is the pressure broadening rate, σ is the phase-changing collision cross-section, P is the gas pressure, n is the number density of perturbers, ν_0 is the unperturbed central frequency and β is the pressure shifting rate defined as positive for a blue-shift. At 100 Torr the 801.699 nm transition, in a 5% Ar in He plasma, is composed of a Lorentzian width $\Delta\nu_L = 1879 \pm 2$ MHz, a Doppler width of $\Delta\nu_D = 889$ MHz, the line center is shifted by $\nu_c - \nu_0 = 610.9 \pm 0.6$ MHz and the s_5 concentration is $n_{s5} = 0.74 \times 10^{12} \text{ cm}^{-3}$. The s_5 population decreases with pressure as shown in Fig. 19. The density decreased by a factor of 2 as the pressure increases from 10 to 160 Torr. Combined with the decrease in peak absorbance due to the broadening of the spectral line leads to reduction in the signal-to-noise ratio from 500 to 80 as the pressure increases from 10 to 200 Torr. The lineshapes in Fig. 18 are normalized to the same area to highlight the broadening and shift of the line shapes as a function of pressure without the increased reduction in absorbance due to the decreasing number density with pressure. At the lowest pressures, <100 Torr, the peak absorbance is larger and the sample is nearly opaque. For the strongest s_3 - p_4 transition, the dynamic

range of the absorbance is better, and spectral fitting was limited to $A < 3.2$. For the weakest s_4 - p_6 line, the dynamic range is reduced to $A < 2$.

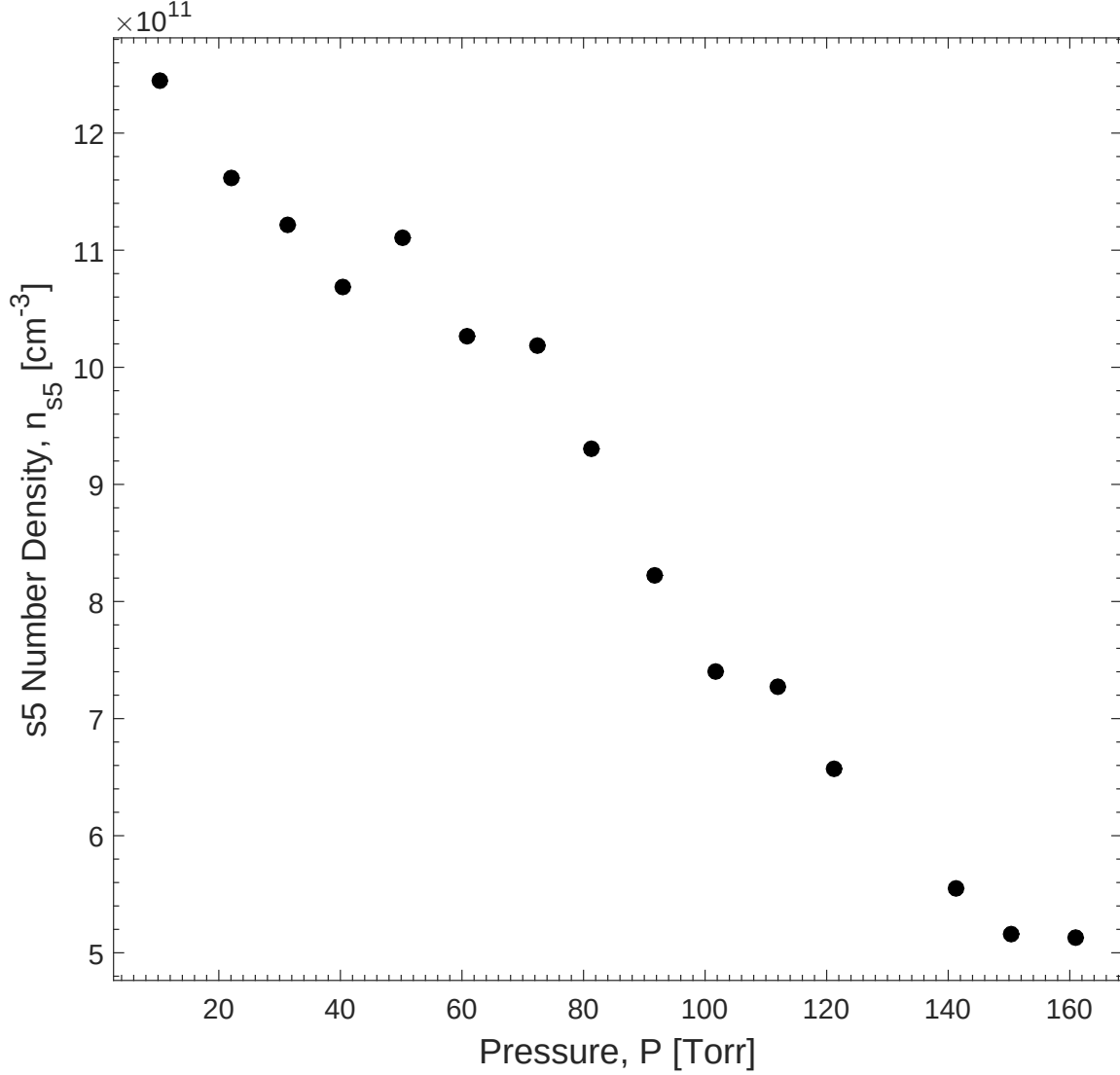


Figure 19. Number density of the s_5 metastable state as a function of the total gas pressure in a 5% Ar in He plasma.

The parameters that are fit from each absorbance profile are the central frequency, the Lorentzian, and Doppler widths. The line shape is fit to a Voigt profile given by the Thompson approximation which is defined in terms of the Faddeeva function [184]. The Lorentzian and Doppler widths are deconvolved using a non-linear least squares fitting routine. The Doppler widths for the 801.699 nm, $s_5 \rightarrow p_8$ transition

for a 25% Ar mixture are shown in Fig. 20. The error in the unconstrained Doppler width increases from 0.1% at 10 Torr to 0.5% at 60 Torr and up to 15% at the highest measured pressure. Two constraints for the Doppler width, a constant and an exponential decrease with pressure, are shown. The constant Doppler width is constrained to the mean value of the temperatures derived from unconstrained fits for pressures below 60 Torr and for all mixtures of the 801.699 nm line for which our signal-to-noise ratio was highest. This mean Doppler width of 888 ± 25 MHz corresponds to a temperature of 440 ± 20 K. It is clear in Fig. 20 that for pressures above 60 Torr we can no longer accurately deconvolve the Doppler and Lorentzian lineshape from the Voigt profile. This critical pressure is consistent with the formulation by *Leiweke, et al* for finding the transition between a collisionally-dominated or Doppler dominated Voigt profile [104].

The second constraint, an exponential decay, was used to investigate the influence of temperature fluctuations on the measured broadening and shift rates. The temperature in the discharge is expected to decrease with pressure due to the influence of the larger heat capacity of the gas along with the decreased residence times in the discharge. As the pressure increases from 10 to 200 Torr the flow rate was observed to increase from 72 to 1,056 sccm (a velocity range of 0.7 to 1.2 m/s) with decreasing residence time in the discharge, from 7.7 to 4.5 ms. This modest temperature drop with pressure is described later in this section. We choose to separate the Lorentzian width from the Voigt width using the constant Doppler width.

The full set of observed line shapes, similar to those presented in Fig. 18, were fit to Voigt profiles from which the pressure broadening and shifting rates are derived. The trend in the Lorentzian widths and shifts for 801.699 nm ($s_5 \rightarrow p_8$), 800.836 nm ($s_4 \rightarrow p_6$) and the 795.036 nm ($s_3 \rightarrow p_4$) transitions are shown in Figures 21 and 22.

Linear fits to the data in Figures 21 and 22 establish the pressure broadening

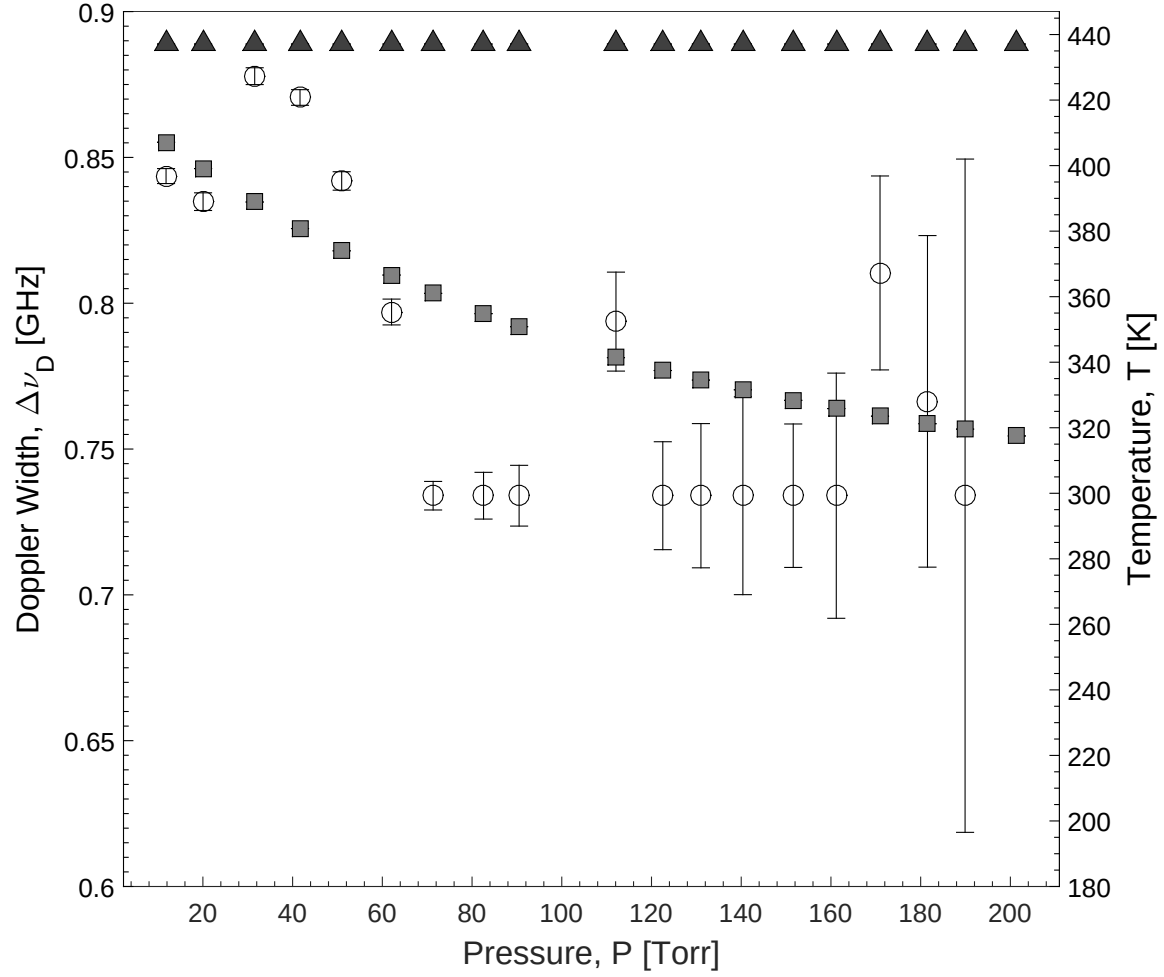


Figure 20. The Doppler widths with corresponding temperatures are shown for the 801.699 nm transition for a 25% Ar in He plasma. The $\circ$ correspond to the Doppler widths in an unbounded Voigt fit and the $\square$ and $\triangle$ correspond to the exponential decay and constant Doppler widths, respectively.

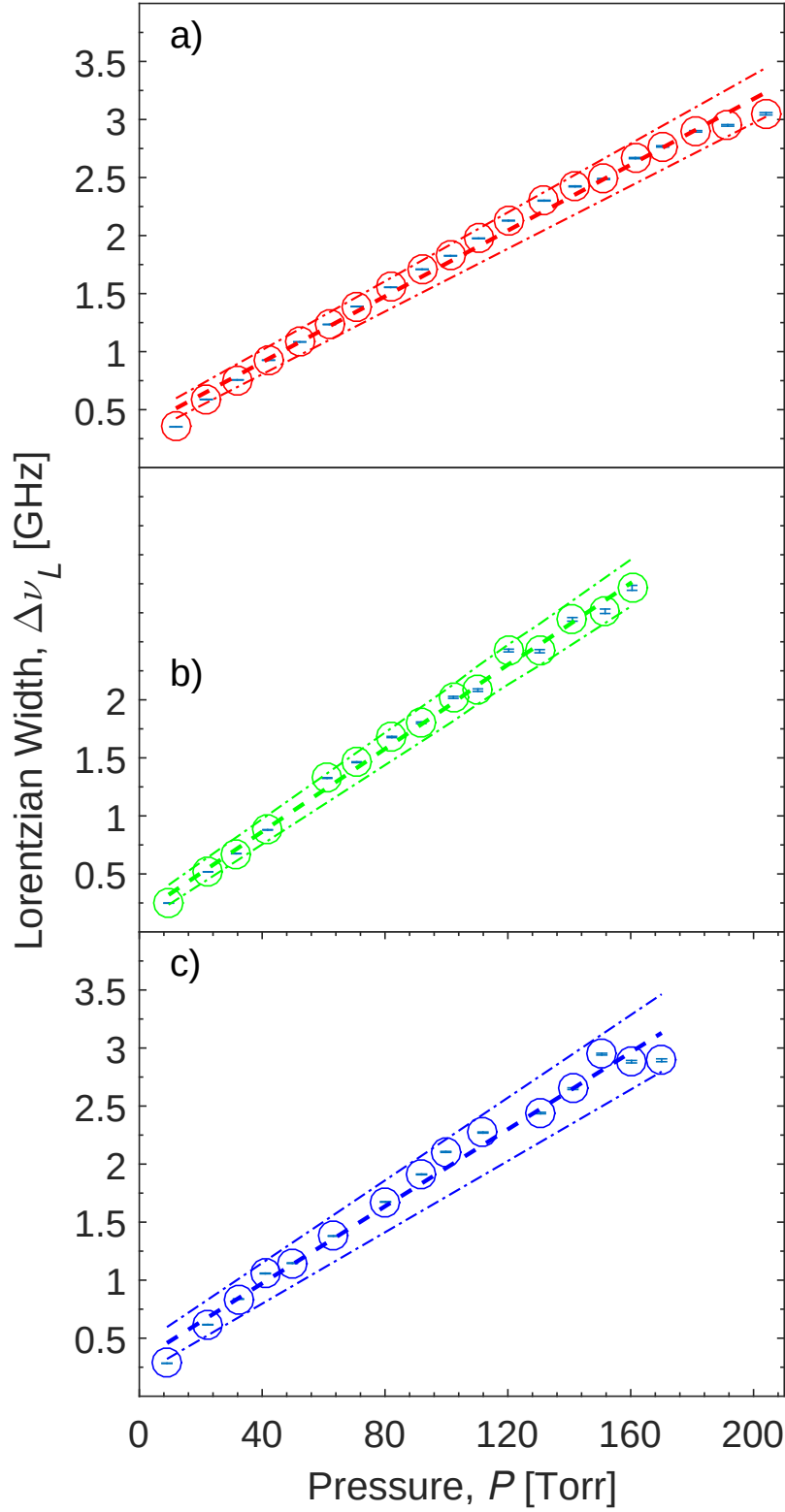


Figure 21. Lorentzian widths for all three measured transitions of the 10% Ar in He plasma. a) The 801.699 nm transition with broadening rate of 14.18 ± 0.65 MHz/Torr, b) the 800.036 nm transition with broadening rate of 17.85 ± 0.78 MHz/Torr and c) the 795.036 nm transition with broadening rate of 16.59 ± 1.22 MHz/Torr.

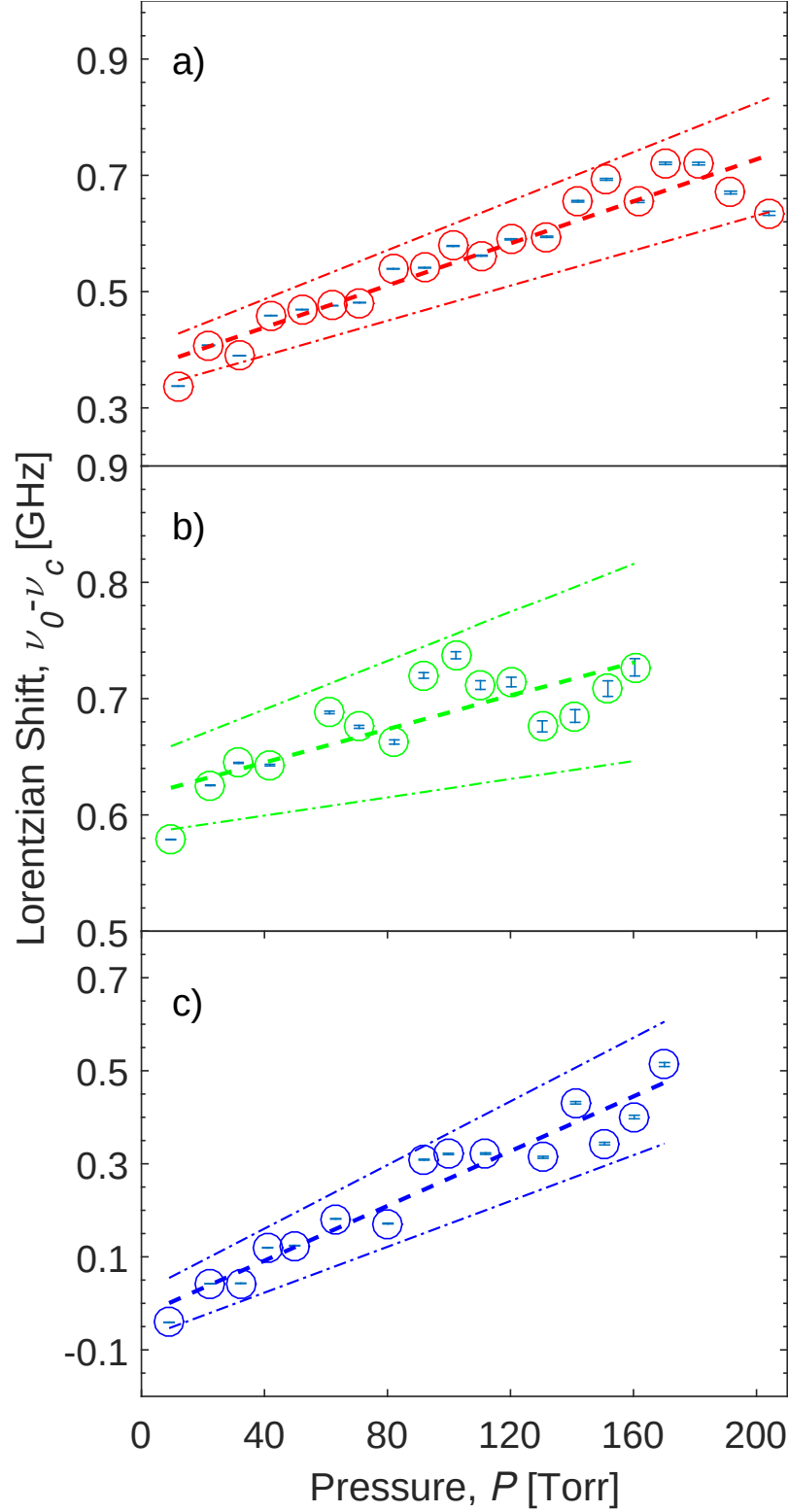


Figure 22. Lorentzian shifts are shown for all three measured transitions of the 10% Ar in He plasma. a) The 801.699 nm transition with shifting rate of 1.81 ± 0.30 MHz/Torr, b) the 800.836 nm transition with shifting rate of 0.72 ± 0.32 MHz/Torr and c) the 795.036 nm transition with shifting rate of 2.94 ± 0.48 MHz/Torr.

and shift rates given in Tables 2 and 3. The errors in the pressure broadening and shift rates are the 95% confidence interval found from fitting the Lorentzian widths with a linear function of pressure. The errors in the pressure broadening rates range from 4% to 9% for the 801.669 and 795.036 nm transitions and gets as high as 26% for the less intense 800.836 nm transition. The shift rates have errors of the same magnitude as the errors of the broadening rates which lead to errors between 15% and 25% and errors get as high as 45%. The errors in the broadening and shift rates are comparable to the uncertainty in the Doppler widths and the unknown temperature in the discharge is a significant driver of the error in the broadening and shift rates.

Two issues may complicate the interpretation of the pressure broadening and shift rates: (1) the broadening and shift rates may be temperature dependent and temperature is varying with pressure, and (2) electrons and ions may influence the line shape. In order to estimate the influence of the temperature dependence on the Lorentzian width we examine three cases. First, we consider a broadening rate that is constant with temperature corresponding to a phase-changing collision cross-section with a positive temperature dependence given by $\sigma(T) = \sigma_0 T^{0.5}$. Second, we consider a cross-section that is temperature independent, $\sigma(T) = \sigma_0$, and last we consider a cross-section with a negative temperature dependence, $\sigma(T) = \sigma_0 T^{-0.2}$, as defined by the Lindholm-Foley theory [60]. Fig. 23 provides the temperature dependence of the cross-section for the 801.699 transition for a 25% Ar mixture using these three assumptions. The residuals of the fits make it apparent that the scatter in the measurement is larger than any deviation caused by the varying temperature.

The second possible contribution to the pressure broadening and shift rates is the influence of electrons and ions in the discharge. Preliminary modeling of the population distributions has shown that the electron density is likely in the 10^{12} to 10^{13} cm^{-3} range and certainly less than 10^{14} cm^{-3} . Based on available Stark broadening and

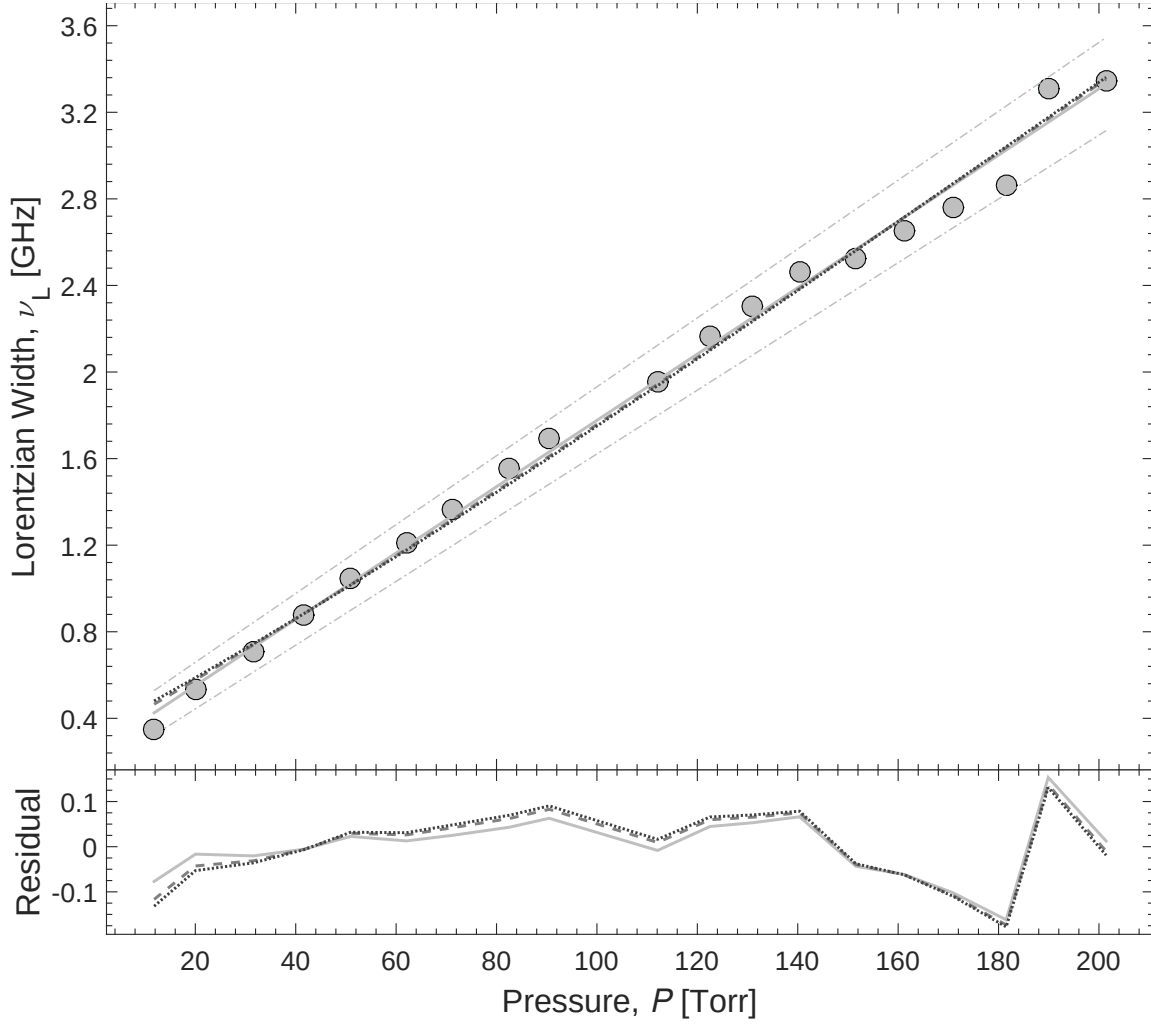


Figure 23. Fits of a temperature dependent broadening rate to the 25% Ar data are shown in the figure above with the Doppler widths fixed to an exponential decay. The three functional forms are compared: a temperature independent rate (—), a $T^{-0.5}$ dependence (---) and a $T^{-0.2}$ dependence (.....) given by the Lindholm-Foley theory.

shifting data we find that the Stark widths and shifts of an electron temperature of ≈ 1 eV or 11600 K are 38.9 and 9.8 MHz, 36.6 and 11.7 MHz, and 46.5 and 21.8 MHz for the 801.699 nm, 800.836 nm and 795.036 nm transitions, respectively, at an electron density of 10^{14} cm $^{-3}$ [96]. The measured zero-pressure width of the 801.699 nm transition are considerably larger and range from 117 ± 44 to 227 ± 33 MHz for Ar mixtures of 2.5% to 25%. Thus, the current observations are not expected to be affected by Stark broadening.

4.4 Discussion

Table 2 shows how the measured broadening rates in this paper compare to the literature. The broadening rates increase slightly with increasing upper state energy. This might be expected as the higher polarizability of the atoms leads to a stronger and longer range interaction. Similarly for the shifting rates, we observe that the higher upper state level shows an increase in the shift rate. The broadening rates (MHz/Torr) in parenthesis represent the rates scaled to 440 K using the Lindholm-Foley $T^{-0.7}$ dependence. In the prior literature optical emission spectroscopy is the method of choice and either a Fabry-Perot interferometer [2, 125] or monochromator [37, 36, 190] is used to measure the line shape. Deconvolution of the instrument line shape in the case of the measurements using a Fabry-Perot interferometer is difficult and leads to large systematic errors, on the order of 10% for Aeschliman [2] and as high as 50% for Moussounda [125]. The deconvolution of the instrument profile of a monochromator and a Voigt is somewhat simpler leading to errors that are <10% for the two Copley measurements [37, 36]. The large error in the broadening rates measured by Vallee are driven by a few different sources. The gas temperature may have a large associated error as the measurement is made invasively using a Joule-heating analysis of a tungsten wire plunged into the plasma. This analysis requires the

assumption that the wire is unaffected by the plasma but the assumed temperature is several hundred degrees above the melting point of tungsten. Because of this the gas temperature must be extrapolated from lower temperatures. Furthermore, the line shape is not deconvolved but rather a calculated convolution is simply compared to the measured profile to find a close match. The uncertainties in the present experiment are 4 - 9%, except for the weaker s_4 to p_6 line where the error bounds are 6 - 26%. The error estimate for the previous experiments are significant, sometimes greater than the published rate itself.

The pressure broadening rates decrease with Ar percentage for the s_5 and s_3 transitions but increase for the s_4 transition as seen in Fig. 24. At these moderate pressures the phase-changing collisions are independent, the total broadening rate may be separable into the individual Ar and He broadening rates using a linear fit of the form: $\gamma = \gamma_{Ar}f_{Ar} + \gamma_{He}(1 - f_{Ar})$. This fit gives an estimate of different influences of Ar and He on the broadening rate and is shown by the trend lines in Fig. 24. The trend lines correspond to Ar-Ar rates of 8, 38 and 12 MHz/Torr and Ar-He rates of 16, 16 and 19 MHz/Torr for the 801.699 nm, 800.836 nm and 795.036 nm transitions, respectively. The 801.699 nm and 795.036 nm transitions have metastable lower levels with Ar-Ar broadening rates that are significantly smaller than the Ar-He rates. The 800.836 nm transition has a resonance lower level and an Ar-Ar broadening rate that is larger than the Ar-He rate. This is expected behavior as the Ar-He interaction is governed by the Van der Waals interaction whereas the Ar-Ar interaction is driven by the much longer range resonance interaction. The Ar-He rate is governed by the $1/R^6$ Van der Waals potential which is why the Ar-He rates for all three transitions are comparable.

We see in Table 2 that the literature for the Ar-Ar and Ar-He broadening rates is sparse. The previously measured Ar-Ar rates show a decreasing trend with tempera-

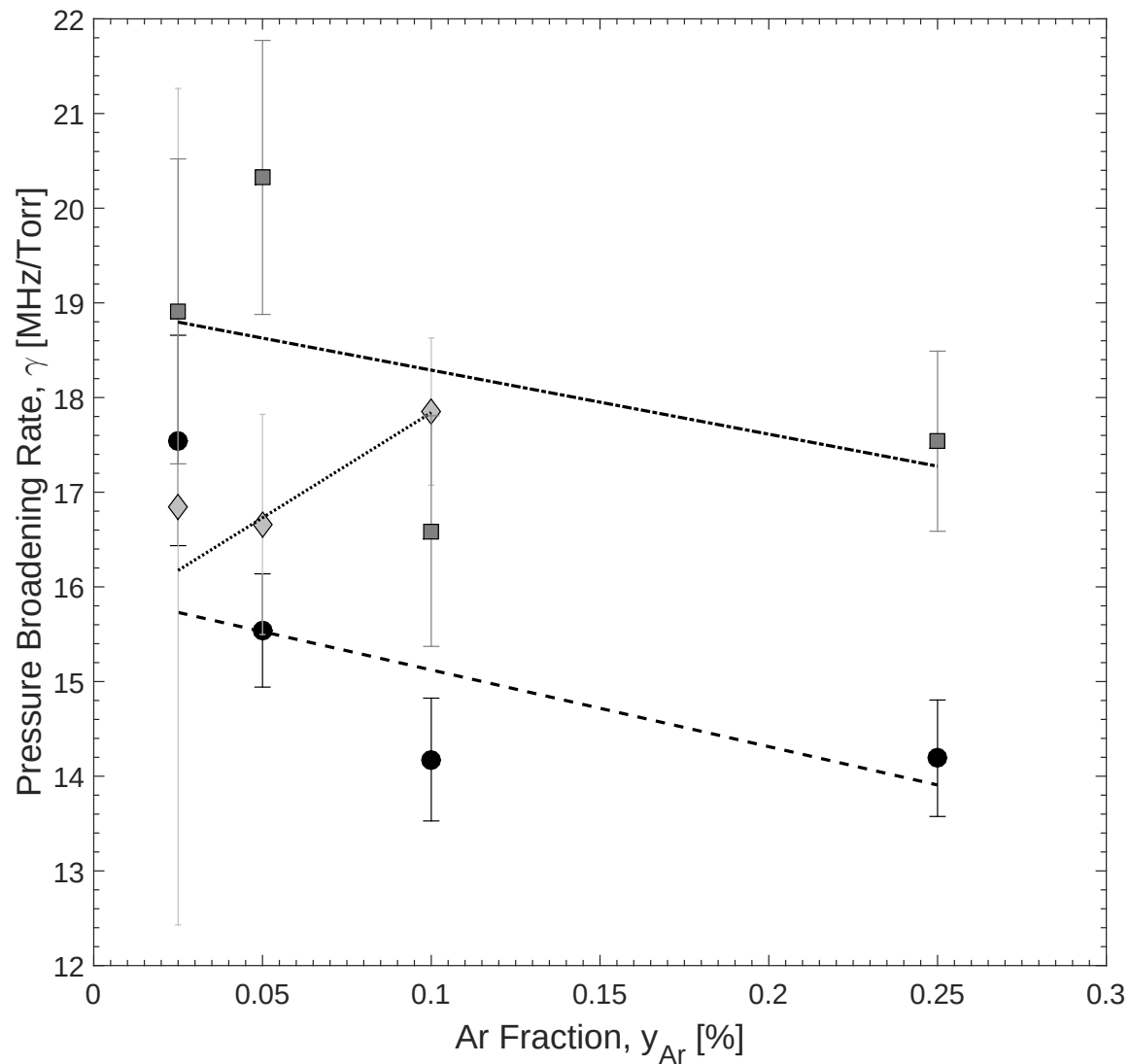


Figure 24. The pressure broadening rates for all three measured transitions as a function of Ar mixture. The 801.699 nm, 800.836 nm and 795.036 nm transitions are given by ○, ◇, and □, respectively. The trend lines represent Ar-Ar rates of 8, 38 and 12 MHz/Torr and Ar-He rates of 16, 16 and 19 MHz/Torr for the 801.699 nm (---), 800.836 nm (.....) and 795.036 nm (-.-) transitions, respectively.

Table 2. Broadening coefficients for the 801.699 nm, 800.836 nm and 795.036 nm transitions as compared to the literature. Rates in parenthesis are scaled to 440 K using the Lindholm-Foley $T^{-0.7}$ dependence.

Pressure Broadening Rate, 2γ [MHz/Torr]						
Mixture (% Ar)	Temperature (K)	Pressures (Torr)	RMS Current (mA)	801.699 nm ($s_5 \rightarrow p_8$)	800.836 nm ($s_4 \rightarrow p_6$)	795.036 nm ($s_3 \rightarrow p_4$)
2.5	440 $\pm$ 20	10 to 160	25	17.55 $\pm$ 1.11	16.85 $\pm$ 4.42	18.91 $\pm$ 1.61
5	440 $\pm$ 20	10 to 160	25	15.54 $\pm$ 0.60	16.66 $\pm$ 1.16	20.32 $\pm$ 1.45
10	440 $\pm$ 20	10 to 160	25	14.18 $\pm$ 0.65	17.85 $\pm$ 0.78	16.59 $\pm$ 1.22
25	440 $\pm$ 20	10 to 160	25	14.19 $\pm$ 0.61	—	17.54 $\pm$ 0.95
Ar-Ar	353	2 to 80		—	29.11 $\pm$ 3.21 (24.95 $\pm$ 2.75)	—
	1130	380 to 1520	0.015	7.45 $\pm$ 0.77 (14.41 $\pm$ 1.49)	10.40 $\pm$ 0.51 (20.13 $\pm$ 0.99)	7.70 $\pm$ 0.77 (14.91 $\pm$ 1.49)
	2250	760 to 1900	0.020	4.59 $\pm$ 1.76 (14.40 $\pm$ 5.51)	—	4.48 $\pm$ 2.84 (14.06 $\pm$ 8.90)
	3900	735 to 2200	250	2.09 $\pm$ 2.34 (9.64 $\pm$ 10.77)	—	2.09 $\pm$ 2.34 (9.64 $\pm$ 10.77)
Ar-He	460	380 to 1520	0.015	16.40 $\pm$ 1.64 (16.04 $\pm$ 1.6)	—	13.88 $\pm$ 1.39 (13.57 $\pm$ 1.36)

ture which appears to be consistent with the the Lindholm-Foley $T^{-0.7}$ temperature-dependence. Furthermore, when corrected using this dependence we find that our approximate separation of Ar-Ar and Ar-He rates are in good-agreement with the database.

The phase-changing collision cross-sections are derived from the measured pressure broadening rates and are shown in Fig. 25. The cross-sections for the 794.036 nm and 801.699 nm transitions appear to trend similarly with temperature as both transitions have metastable lower levels and are governed mainly by the Van der Waals broadening mechanism or a $1/R^6$ potential. These cross-sections are reduced by $\approx 50\%$ from $T = 1100$ to 3900 K which implies a very weak temperature dependence. The trend line shown of $T^{-0.2}$ is consistent with the temperature-dependence as derived from Lindholm-Foley theory. The 800.836 nm transition has the s_4 lower state and is partially Van Der Waals, by both He and Ar, and partially resonance broadened, only by Ar, which generally corresponds to larger cross sections since the resonance interaction is governed by a $1/R^3$ potential [4]. The 800.836 nm transition shows a strong temperature dependence to the cross section of $\approx T^{-0.4}$. This is consistent with an absence of a temperature dependence for the broadening rate given by the resonance theory since the broadening rate would have a temperature dependence of $\approx T^{0.1}$. The resonance transitions are expected to have widths defined by the oscillator strength of the transition and not by the temperature, or speed, of the perturbing interaction [4]. The s_4 lower level of the transition is not entirely resonance broadened, however, since the lower level has a small associated oscillator strength. In addition to the weak influence of the resonance interaction, as temperature increases the perturbing atoms tend to approach closer to the emitting atom and so the $1/R^6$ part of the potential begins to contribute to the cross section. This leads to a partially Van der Waals broadened line and the weak temperature dependence

may arise from that contribution.

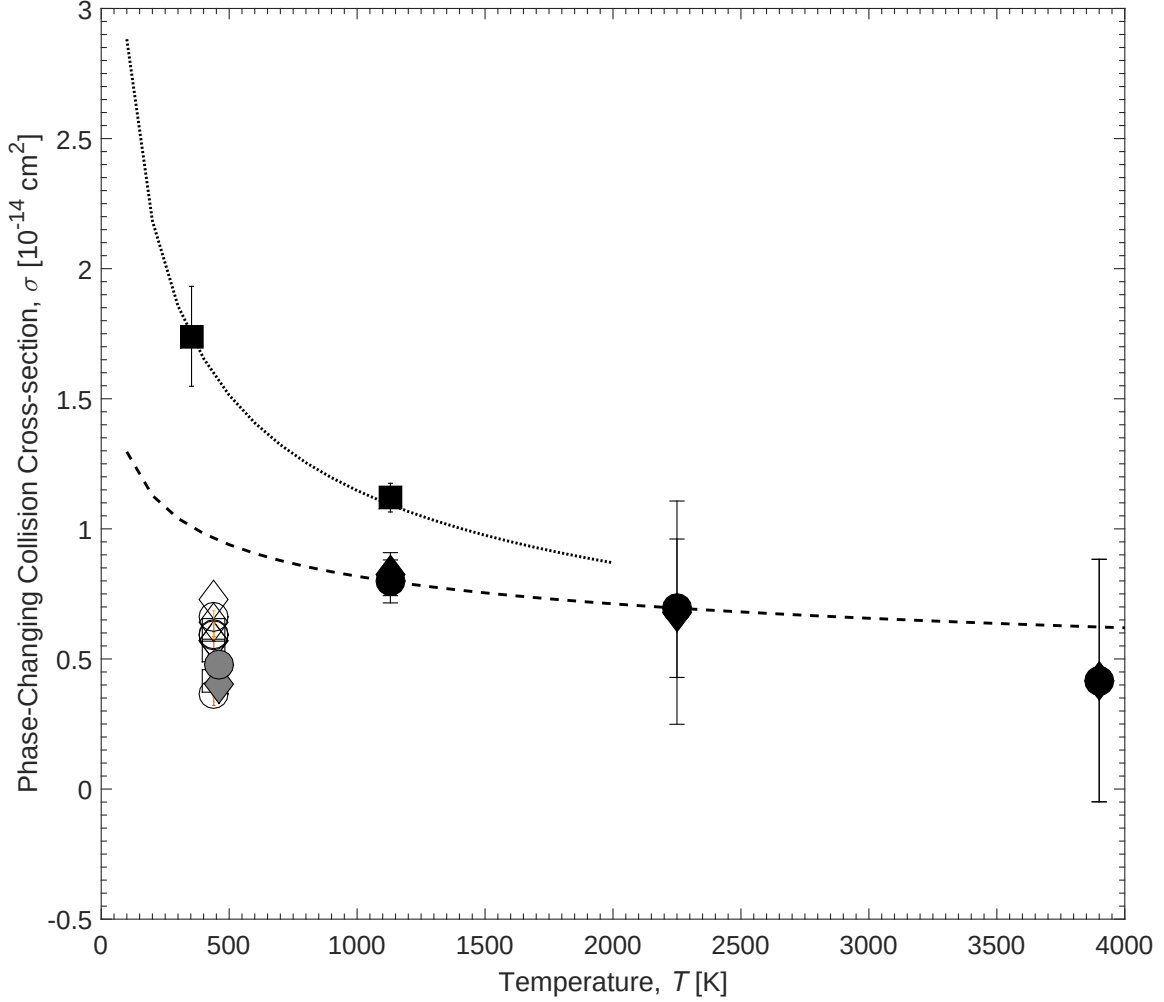


Figure 25. Cross section as a function of temperature. The $\bullet$, $\blacksquare$ and $\blacklozenge$ represent the 801.699 nm, 800.836 nm and 794.036 nm transitions, respectively. The black, gray and empty shapes distinguish the phase-changing collision cross-sections for $\text{Ar}^*\text{-Ar}$, $\text{Ar}^*\text{-He}$ and the mixture of the two, respectively. Trend lines are shown for the $T^{-0.2}$ dependence (---) of the 801.699 nm and 795.036 nm transitions and the $T^{-0.4}$ dependence (.....) of the 800.036 nm transition.

The measured shift rates are shown in Table 3. The previously measured shift rates vary dramatically with temperature with no consistent trend. What is clear is that the Ar-Ar interaction is red-shifted for all three transitions. The red-shift for the 2250 K case is on the order of the broadening rate. The He shifts are strongly to the blue for both observed transitions. The shifts presented in this paper, which

Table 3. Shifting coefficients for the 801.699 nm, 800.836 nm and 795.036 nm transitions as compared to the literature. Negative rates are red-shifts. Rates in parenthesis are scaled to 440 K using the Lindholm-Foley $T^{-0.7}$ dependence.

Pressure Shifting Rate, β [MHz/Torr]						
Mixture (% Ar)	Temperature (K)	Pressures (Torr)	RMS Current (mA)	801.699 nm ($s_5 \rightarrow p_8$)	800.836 nm ($s_4 \rightarrow p_6$)	795.036 nm ($s_3 \rightarrow p_4$)
2.5	440 $\pm$ 20	10 to 160	25	1.55 $\pm$ 0.26	1.99 $\pm$ 0.71	5.38 $\pm$ 0.41
5	440 $\pm$ 20	10 to 160	25	2.04 $\pm$ 0.35	2.18 $\pm$ 0.43	4.04 $\pm$ 0.65
10	440 $\pm$ 20	10 to 160	25	1.81 $\pm$ 0.30	0.72 $\pm$ 0.32	2.94 $\pm$ 0.48
25	440 $\pm$ 20	10 to 160	25	1.67 $\pm$ 0.26	—	4.61 $\pm$ 0.72
Ar-Ar	353	2 to 80	0.015	-8.19 $\pm$ 0.38 (-7.02 $\pm$ 0.32)	-3.04 $\pm$ 0.15 (-2.61 $\pm$ 0.44)	—
	1130	380 to 1520	0.020	-7.45 $\pm$ 0.77 (-14.41 $\pm$ 1.49)	-10.40 $\pm$ 0.51 (-29.30 $\pm$ 1.96)	-7.70 $\pm$ 0.77 (-16.6 $\pm$ 1.51)
	2250	760 to 1900	—	-20.27 $\pm$ 1.15 (-63.54 $\pm$ 3.60)	-15.14 $\pm$ 1.01 (-32.59 $\pm$ 0.48)	-22.64 $\pm$ 1.22 (-24.15 $\pm$ 2.41)
	3900	735 to 2200	250	-6.24 $\pm$ 0.78 (-28.73 $\pm$ 3.59)	—	-8.58 $\pm$ 0.78 (-104.28 $\pm$ 5.60)
Ar-He	460	380 to 1520	0.015	4.91 $\pm$ 0.49 (5.14 $\pm$ 0.51)	—	6.50 $\pm$ 0.65 (6.70 $\pm$ 0.67)

represent a combined influence of Ar and He perturbers, are only slightly blue shifted. It is expected, however, that the 2.5% Ar case should be close to the measured He rate which it is not. The incomplete literature on the high temperature shifting rates for the 800.836 nm transition makes the comparison of resonance and Van der Waals contribution difficult. Furthermore, Anderson-Tallman theory provides a single Lorentzian for the mixture. That is, the resulting Lorentzian is a convolution of the two individual lineshapes. This implies that the shift rates do not add [7]. The 794.036 nm and 801.699 nm transitions appear to trend similarly, however. The cross sections all serve as sensitive probes of the interaction potentials. The similar trends between the two transitions with a metastable lower level implies that the potentials may be governed by the many curve crossings leading to similar off-diagonal matrix elements for the two different transitions. The potential curves for the Ar-Ar interaction have been calculated by *Duplaa, et al.* [53] and the first few excited states of the Ar-He and Ar-Ne interaction have been calculated by *Petsalakis, et al.* [143]. While the Ar-He potential surfaces are significantly less complex than the Ar-Ar interaction, both are overwhelmed with curve-crossings and this makes the interpretation of these shifts and broadenings difficult.

Both the pressure broadening and shift rates are of crucial importance to the rare gas laser system. High power narrow-banded diodes centered at the pump wavelength are currently limited to a spectral width of ≈ 30 GHz [73]. A broadening rate of 20 MHz/Torr implies that in order to achieve a good spectral match between the pump laser and the atomic feature a pressure of 1500 Torr, or 2 atm, is required. The necessary pressure for sufficient spin-orbit relaxation is also approximately 1 atm. At this pressure the diode width of 30 GHz brings us to within 70% of the narrow-band pumping solution [72]. This is significantly smaller than the pressures required for broadening and spin-orbit relaxation in the Rb DPAL, with He as a buffer gas, where

sufficient spin-orbit relaxation requires pressures on the order of 10 atm.

4.5 Conclusion

The pressure broadening and shift rates for Ar-He mixtures ranging from 2.5% to 25% Ar in He have been measured using tunable diode laser absorption spectroscopy in a capacitively-coupled radio-frequency discharge at 10 W. The broadening rates are on the order of 20 MHz/Torr for the 794.036 nm, 800.836 nm and 801.699 nm transitions and decrease as a function of Ar percentage for the 801.699 nm transition but increase for both the 800.836 nm and 795.036 nm transitions. This corresponds to a cross section that decreases as a function of temperature for all three transitions. Compared to the literature these rates are comparable to the He rates, although they are larger and the error bounds are on the order of 5% which is significantly smaller than the previously published rates whose error bounds range from 10% to 100%. The shift rates presented are slightly to the blue with no discernible trend except for the 795.036 nm transition that clearly trends from the He shift rate towards the red, as expected by the increased influence of the attractive Ar-Ar interaction for that state. The previously published Ar-Ar pressure shifting rates do appear to trend with temperature initially increasing and then decreasing beyond 2,250 K. The literature, however, is sparse and more measurements will need to be made to understand the detailed temperature dependence of the cross sections. Updated calculations of the potential surfaces will also be required to assist in this understanding.

V. Pressure Broadening and Shift Rates of Resonance Transitions in a Pure Ar Discharge

5.1 Introduction

The recent development of the diode-pumped rare gas laser (DPRGL) has reignited interest in the spectroscopic details of the excited states of the rare gases. This includes updating the spin-orbit mixing rates [90, 75, 76] and measuring the pressure broadening and shift rates [117, 57]. The main proposed laser cycle, a 3-level DPAL analogue, consists of pumping from the metastable ($1s_5$) level, collisionally relaxing and then lasing back down to the $1s_5$ state. These metastable states have theoretical lifetimes on the order of seconds [91] with measured lifetimes on the order of microseconds due to collisional quenching by impurities and wall collisions as well as super-elastic collisions with other Ar or He atoms [145, 192]. Broadening rates by He collisions for these atoms tend to be approximately 15 MHz/Torr [117, 57] with the rate by Ar being closer to 8 MHz/Torr [36]. Diode lasers generally have line widths on the order of 1000 GHz but can be aggressively narrowed to 100 GHz which is used in large-scale systems. 10 GHz line widths have been achieved in volume-bragg-grating (VBG) narrowed diodes at large expense. The low broadening rates of the Ar-Ar and Ar-He interactions mean that for efficient coupling of the narrowest volume-bragg-grating (VBG) diode, one would have to operate at one atmosphere for Ar-He and two atmospheres for Ar-Ar, a lofty goal for a necessary large-volume discharge with high E/N required to produce the metastable state. Provided that there is enough population, another option exists. Three-level laser cycles that pump and terminate on the resonance $1s_{2,4}$ levels may provide an easier route. While these states are optically allowed transitions to the ground-state, they are also significantly radiation trapped leading to steady state densities that are on the order of the metastable lev-

els, especially for the $1s_4$ state which is only 1000 cm^{-1} higher in energy than the $1s_5$ level. Comparable broadening rates for the $1s_4$ level are on the order of 40 MHz/Torr [175, 36, 190], requiring 750 Torr for spectral matching, and the $1s_2$ level is on the order of 100 MHz/Torr which would only require 300 Torr to effectively couple the diode energy [175, 36, 190].

Our most recent work measured the pressure broadening and shift rates for three argon (Ar) transitions in pure-Ar and Ar-He mixtures using tunable laser absorption spectroscopy (LAS), including one resonance $1s_4$ transition [57]. This work extends those more accurate measurements by adding a second resonance transition, the $842.6963\text{ nm } s_4 \rightarrow p_8$. The broadening and shift rates are compared to previously measured values and the oscillator strength for the transition is derived.

5.2 Experiment

The Ar line shapes were collected using two different tunable laser absorption spectroscopy schemes, both using phase sensitive detection. The first experimental scheme, to include the discharge used, is similar to Ref. [57]. The main change is the shift of laser source from a New Focus diode to a tunable Matisse-TX Titanium:Sapphire (Ti:Saph) ring laser and changing from a single-frequency modulation which requires the use of two detectors to a multi-frequency modulation and a single detector. A diagram of the second experimental scheme is shown in Fig. 26. The probe laser source is a tunable Matisse-TX Ti:Saph ring laser with a 100 kHz line width and horizontal polarization. The laser is scanned over a range of $30\text{-}35\text{ GHz}$. The laser beam is sampled and sent to a High Finesse WSU-2 wavemeter referenced to a frequency-stabilized He-Ne for absolute frequency calibration to within 10 MHz . The primary beam is then sent through a CVI Wedge window with the transmitted intensity incident on a Coherent PM power meter head to track the laser

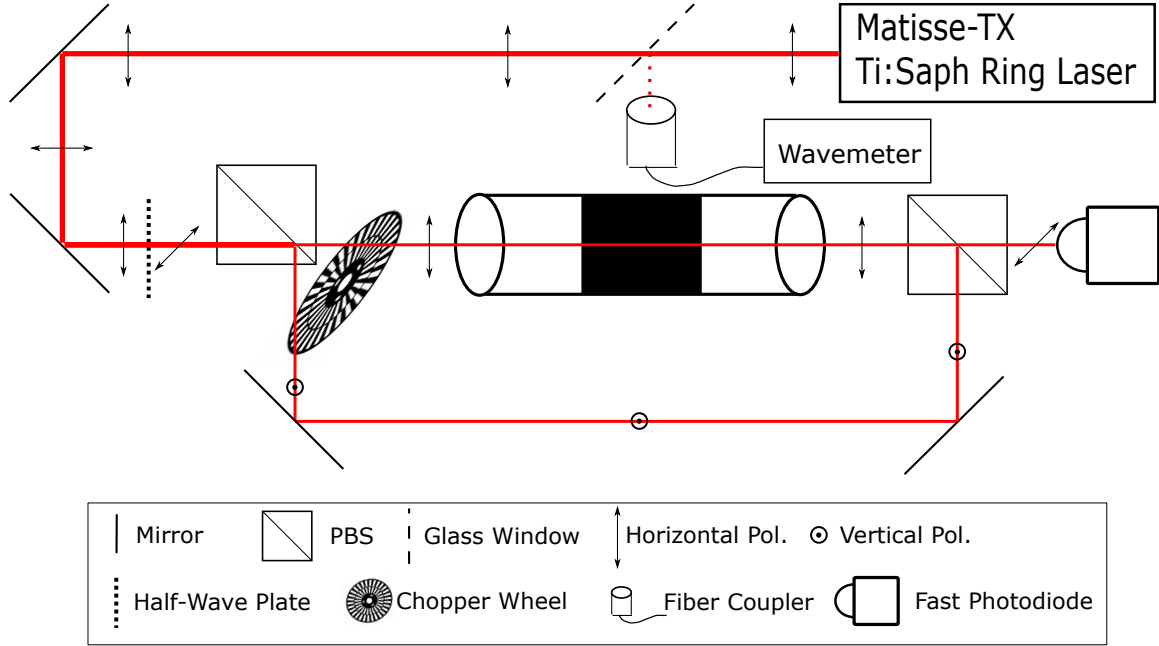


Figure 26. Experimental diagram for the multi-frequency modulation (multiplex) laser absorption spectroscopy experiment. The lock-in amplifiers and computer are not shown.

source performance. The first reflection is sent through a half-wave plate (Thor labs AHWP05M-980) and then to a polarizing beam splitter cube (Thor labs PBS252). This set of optical elements allows for the intensity of each beam split by the PBS to be varied as necessary, set to be equal in this case. Both beams are amplitude modulated at different frequencies using a SR540 Chopper with a 4" diameter, dual-slotted wheel where one beam travels through the inner wheel (0.124" slot spacings) and the other travels through the outer wheel (0.17" slot spacings). These correspond to modulation frequencies of 1.8 kHz for the outer beam and 1.5 kHz for the inner beam for this experiment. One beam, used to track the incident laser intensity I_0 , is sent around the discharge cell using silver mirrors (Thor labs PF10-03-03) and is transmitted through a second PBS to a fast photo-diode (Thor labs PDA100A). The other beam is sent through the discharge cell and is then reflected off the PBS and incident on the same fast photo-diode. The transmitted beam intensity is less than

8 mW/cm² to prevent saturation of the transition. The photo-diode is connected to two SRS850 lock-in amplifiers which are referenced to the two separate modulation frequencies. The lock-in amplifiers are connected to a USB-6251 BNC DAQ and controlled by a PC running Matlab via an Agilent model 82357B GPIB-to-USB module. Matlab is used to collect the data from the DAQ as well as control the instruments.

The multi-frequency detection scheme has improved the signal-to-noise ratio of measurements as compared to our previous work allowing for more accurate determination of the pressure broadening and shift rates. A single-frequency modulation scheme generally requires two separate chopper wheels and photo-diodes leading to different phase jitter, associated with the chopper wheels, as well as varying gain variation and detector noise between the two diodes. The multi-frequency detection scheme minimizes the phase jitter and gain variation by only using a single chopper wheel and photo-diode. The detector noise is also correlated on both channels and can be at least partially removed. These modifications result in a factor of 5 improvement in the noise level. The base noise level in this work is associated with the scanning and locking algorithm of the Matisse-TX source which induces a variation in the laser power. The influence is greater on the I_0 channel which does not travel through the laser cell due to the fact that the I channel floods the cell and is not fully transmitted. This improvement, however, does allow for absorbance as low as 0.1 to be easily detectable.

The flow system is predominantly constructed out of thin-walled 1/4" stainless steel tubing. The gas flow rate is set by two Sierra Instruments C50L flow meters, one for flow rates above 500 sccm and one for flow rates from 25 to 500 sccm. These flow meters were prepared and calibrated for use with room temperature Ar. The pressure is measured upstream and downstream of the discharge cell with the upstream measurement being made by a single 1000 Torr Baratron 690A with 0.12% accuracy and

the downstream pressure measured by a manifold of three Baratron 690A capacitance manometers with full ranges of 1, 100 and 1000 Torr for accurate measurement of the low pressure cases. The pressure in the discharge cell is set by a butterfly valve with a PID controller which references the downstream manifold pressure measurement. A pressure gradient is observed between the upstream and downstream flow. The pressure in the discharge cell in the rest of this work corresponds to the average of the two measurements.

The excited Ar states also were produced in a new discharge. Where the previous work used a longitudinal capacitively-coupled discharge composed of two rings along a tube, the new discharge consists of two electrodes positioned transversely to the tube such that the maximum gap between the electrodes is the tube outer diameter (O.D.). These electrodes were wire EDM cut to fit the Pyrex tubes snugly and leave a 1/8" gap which was filled with a Macor spacer. This is in contrast to the longitudinal discharge which had a variable distance between the electrodes. The new configuration offers increased stability of the discharge at higher pressures although it does not increase the efficiency of production of the Ar states.

5.3 Results and Discussion

Spectra were collected for the 842.6963 nm $s_4 \rightarrow p_8$ resonance line. It has an optically allowed transition to the Ar($^1S_0$) ground state. These spectra were collected for two sets of parameters; flow rates of 25-1000 sccm and pressures of 1.45 to 400 Torr. All of the lineshapes were fit to a Voigt profile of the form

$$g_V(x', y) = C_1 y \text{Re}[w(x', y)] + a_1 + a_2 x + a_3 x^2 \quad (54)$$

where C_1 is a fit parameter that defines the area of the lineshape, a_i are the baseline fit parameters, and $w(x, y)$ is the Faddeeva function with dimensionless parameters defined by

$$w(x', y) = \text{Exp}(-(y + ix')^2) \text{Erfc}(y + ix') \quad (55)$$

$$y = \sqrt{\log(2)} \frac{\gamma_L}{\Delta\nu_D} \quad (56)$$

$$x = 2\sqrt{\log(2)} \frac{\nu - \nu_0}{\Delta\nu_D} \quad (57)$$

$$s = 2\sqrt{\log(2)} \frac{\Delta}{\Delta\nu_D} \quad (58)$$

$$x' = x - s \quad (59)$$

with $\Delta\nu_D$ as the Doppler width, γ_L as the Lorentzian width, Δ as the line shift, ν_0 is the frequency of the line center. The log function above is the natural log with other bases denoted by a subscript corresponding to that base. The results of the variable flow rate experiments will be presented first as they motivate some experimental parameters in the second data set.

The flow rate was varied from 25 to 1000 sccm, corresponding to velocities of 90-2400 cm/s, with the downstream pressure fixed by a butterfly valve to 30 Torr. This pressure was originally chosen to reflect a situation where the Doppler width at room temperature (690 MHz) was expected to be discernible from the Lorentzian width (1.2 GHz) while being at a high enough pressure to allow for a large variation in flow. The flow rate was not expected to have a significant impact on the line shape except for potentially reducing the temperature in the plasma. Fig. 27 shows how the line shape changed as a function of flow rate. Clearly, the assumption of flow rate being an insignificant effect on the line shape was incorrect. Both a broadening of the line shape as well as an increase in the total area (number density) were observed. The explanation for the broadening is simple; the flow system consists of 1/4" tubing

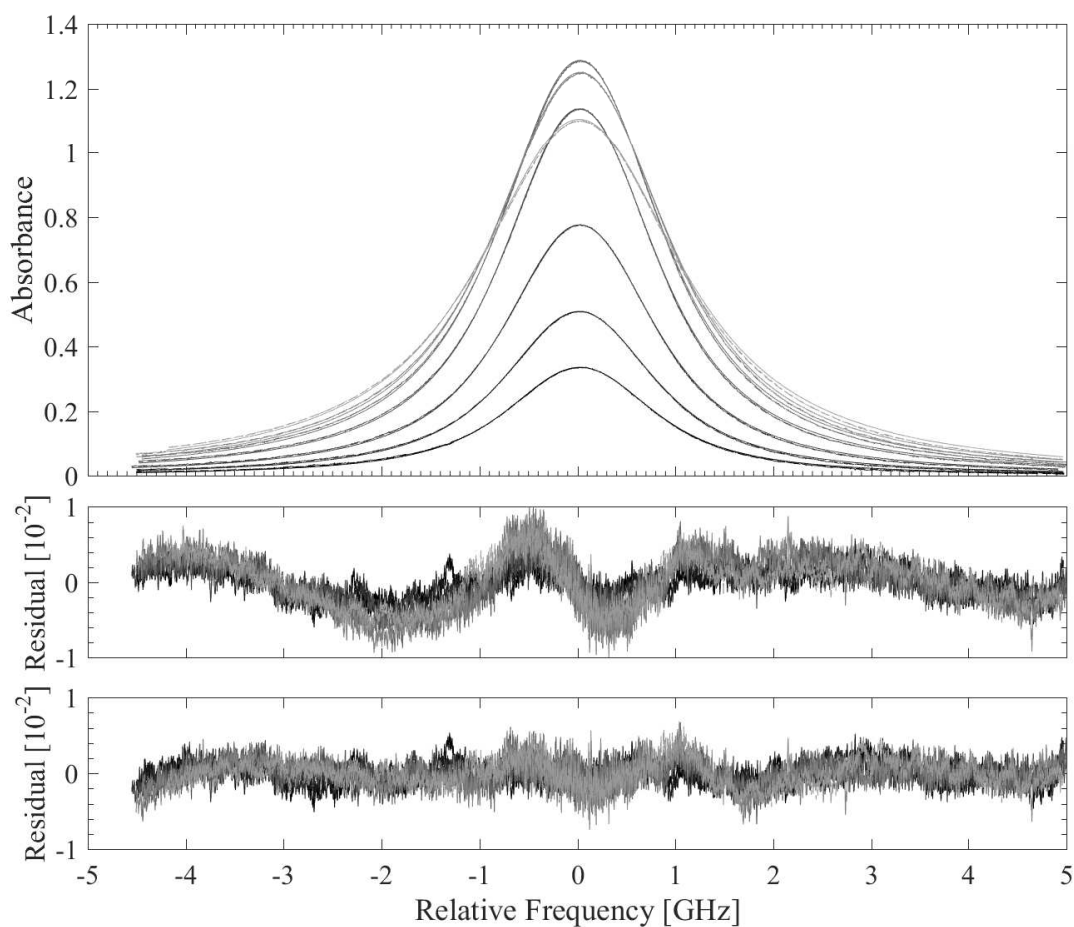


Figure 27. The absorption spectra of the 842.6963 nm transition are shown for flow rates ranging from 25 to 1000 sccm at a pressure of 30 Torr. The first residual shows the results of a Voigt fit to the data. The second residual shows the results of an asymmetric Voigt fit to the data. The asymmetric fit appears to remove some of the systematic residual apparent in the symmetric Voigt fit.

with a free expansion both before and after the Pyrex tube. These free expansions are locations where there will be a pressure drop resulting in a pressure gradient. The

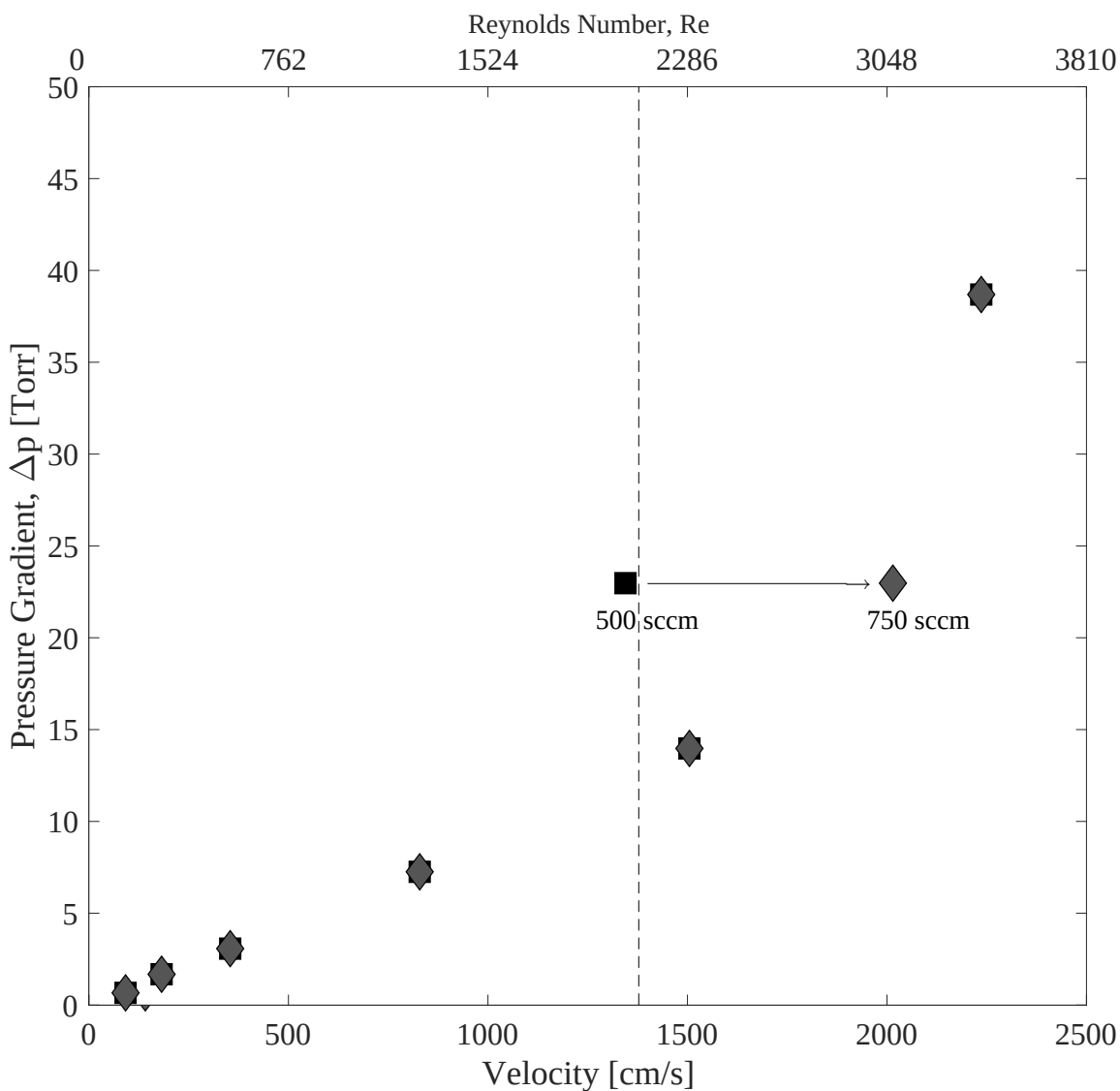


Figure 28. The pressure gradient is shown as a function of velocity. The gradient rises linearly with pressure at low velocities (Reynolds number) and then increases rapidly when the velocity (Reynolds number) is greater than 1350 cm/s (2100), corresponding to the transition from laminar flow to transitional flow.

gradient should be a function of the flow velocity and Fig. 28 shows this expected behavior. Since both flow controllers can reach 500 sccm this measurement was made twice and significant disagreement was observed with the higher range flow meter giving a larger effective flow rate. The shifted marker in Fig. 28 corresponds to what

the real flow rate is projected as in order to agree with the observed trend in the pressure gradient. The vertical line is a Reynolds number of 2100 which corresponds to the boundary between a laminar flow and a turbulent flow, known as a transitional flow, with the gas being characterized as fully turbulent above a Reynolds number of 4000. The Reynolds number is given by

$$Re = \frac{\rho v l}{\mu} \quad (60)$$

where ρ is the gas density, v is the velocity, l is a characteristic length which is taken to be the radius of the tube, and μ is the dynamic viscosity. The relationship between the pressure gradient and the velocity appears linear up to a Reynolds number of 2100 above which the slope appears to change dramatically, consistent with the transition regions of laminar and transitional flow.

The influence of flow rate on the total absorbance is not well understood. The resonance time in the discharge decreases from 56–2.1 ms but no significant changes in current or impedance occurs due to velocity. Regardless of the mechanism that defines the relationship between the flow velocity and the number density, it is clear that increasing flow rate significantly increases number density from $1.6\text{--}7.5 \times 10^{10} \text{ cm}^{-3}$ over this range. The variation of the integrated absorbance as a function of flow velocity is shown in Fig. 29. While the peak absorbance decreases at the highest flow rates, the increase in the width due to the pressure gradient is sufficient so that the area, or total absorbance, continues to increase albeit at a slower pace.

Fig. 27 also shows a systematic deviation from the Voigt profile. A symmetric Voigt fit results in a residual with a derivative-like structure. There are several possible causes for an asymmetry in the line shapes. The two most likely are a correlation between the broadening and shifting parameters and the velocity [191] or a pressure-driven asymmetry that is a result of non-zero intercept in the phase [5]. In either

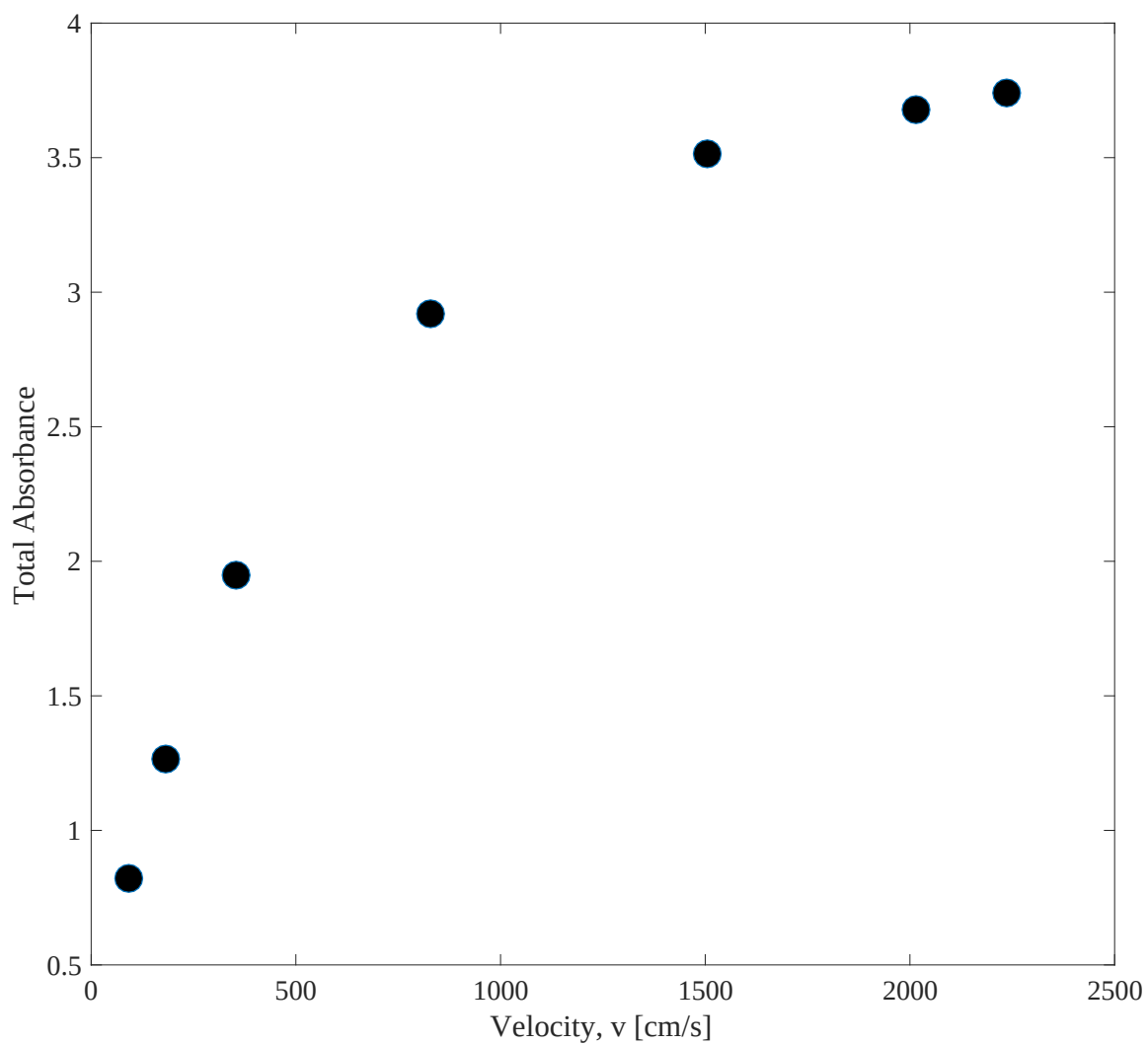


Figure 29. The total integrated absorbance is shown as a function of velocity. The roll over in absorbance is associated with the trade-off between the increasing area due to the pressure gradient and the decreasing peak absorbance.

case, the asymmetric Voigt profile can be represented as

$$g_{VA}(x', y) = y (C_1 \text{Re}[w(x', y)] + C_2 \text{Im}[w(x', y)]) \quad (61)$$

where C_2 is a fit parameter that defines the area of the derivative and $w(z)$ is defined by Eq. 55. The residual of the asymmetric fit is shown in the bottom plot of Fig. 27. The root-mean-square-error (RMSE) of the fits, or the standard deviation of the residual, decreases by a factor of two between the symmetric and asymmetric Voigt fits. The asymmetry increases linearly with flow velocity but not with pressure which is consistent with the mechanism of velocity-dependent correlations and not with deviations from the Lorentzian line width associated with second-order pressure effects and the validity of the impact approximation.

Spectra were similarly collected to examine the pressure broadening and shift rates. While the flow rate analysis only used the second experimental method described above, the measure of the broadening and shift rates used both. Fig. 30 shows the measured spectra for the first (a) and second (b) experimental configurations. The displayed residuals are for pressures of 20 and 200 Torr (a) and 8 and 200 Torr (b). It is clear that there are several distinct trends in the line shapes of each case. Starting with experimental configuration (a) we see that there is a sinusoidal baseline that varies between scans. The sinusoid has a period of 0.4 ns (frequency of 2.5 GHz). Assuming this baseline occurs due to etaloning between two optical elements, the distance between them would have to be approximately 10 cm. This baseline obstructs a clear analysis of the Lorentzian width and shift for this data as the sinusoidal function cannot be clearly separated from the line shape at pressures above 100 Torr. Configuration (b) has removed this sinusoidal baseline experimentally by ensuring optical elements are not perfectly parallel. The residual of (b) has significant structure below 20 Torr but the removal of the sinusoid results in improvement in

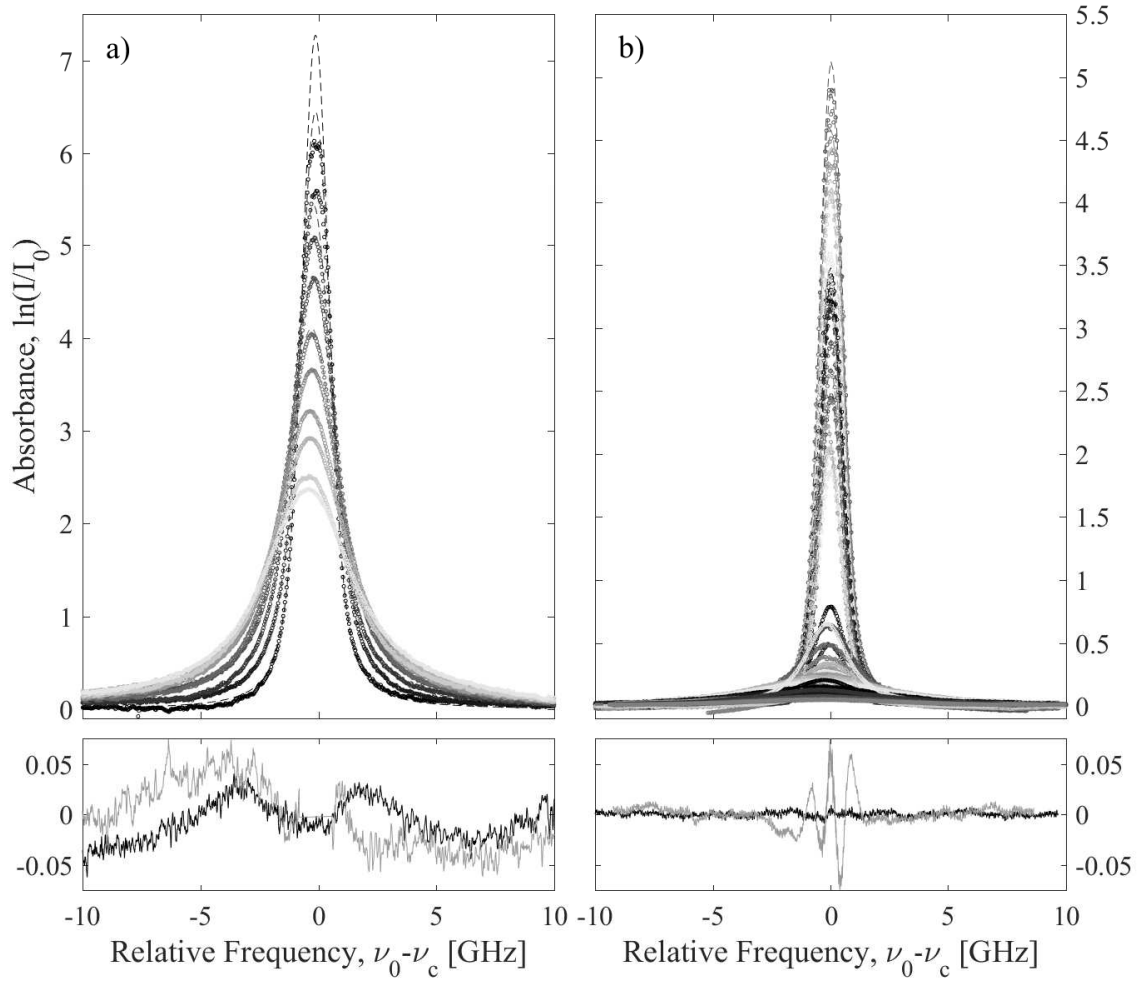


Figure 30. The absorption spectra of the 842.6963 nm transition are shown for pressures of 20 - 400 Torr (a) and 1.45 to 200 Torr (b). The displayed residuals are for the 20 and 200 Torr cases (a) and the 8 and 200 Torr cases (b) with the lighter shading corresponding to the lower pressure. For (a) there is a clear sinusoidal baseline that varies from scan to scan whereas (b) shows a systematic residual at all pressures below and a flat, structureless baseline for all pressures above 20 Torr.

signal-to-noise ratio, especially at higher pressures.

The structure observed in the residual is of the form that results in fitting a Voigt profile to a collisionally-narrowed Galatry or Rautian-Sobelman profile [61, 153, 191]. Collisional narrowing occurs when the absorbing atom experiences velocity-changing-collisions (vcc) during an absorption which causes the corresponding Doppler shift to be reduced. As the collision-frequency (or pressure) rises, the Doppler width will continually narrow until the mean velocity of the atom during an absorption event is zero. This is the limit where the pressure broadening results in a line width that is significantly larger than the Doppler width. Thus the Voigt profile becomes a simple Lorentzian. The difference between the two collisionally-narrowed profiles comes from the treatment of a vcc. The Galatry lineshape, denoted g_G considers a single collision is insufficient to thermalize the absorbing atom and the final velocity is dependent on the initial velocity [61]. This behavior is consistent with atoms of like mass. The Rautian-Sobelman lineshape, denoted g_P , considers a single collision sufficient to thermalize the absorbing atom. This is considered the hard-collision model where the memory of the initial velocity it lost in the collision [153]. Both line shapes assume that these vcc are independent of the phase-changing collisions that lead to broadening and shifting. From the variable flow rate measurements above, we know that the correlations between the velocity and the broadening and shift parameters can be observed. This correlation must then be included in both the Galatry and Rautian-Sobelman lineshapes resulting in generalized lineshapes, denoted g_H and g_Q for the generalized Galatry and generalized Rautian-Sobelman lineshapes [191]. These can all be written in terms of the dimensionless parameters defined for the Voigt, with

the inclusion of two more parameters for the collisional narrowing, as

$$g_G(x', y, z) = \frac{1}{\sqrt{\pi}} \text{Re} \left[\frac{1}{\frac{1}{2z} + y - ix'} M \left(1; 1 + \frac{1}{2z^2} + \frac{y - ix'}{z}; \frac{1}{2z^2} \right) \right] \quad (62)$$

$$g_P(x', y, \xi) = \text{Re} \left[\frac{w(x', y + \xi)}{1 - \sqrt{\pi} \xi w(x', y + \xi)} \right] \quad (63)$$

$$g_H(x', y, Z) = g_G(x', y, Z) \quad (64)$$

$$g_Q(x, y, \xi, s) = \text{Re} \left[\frac{w(x, \xi)}{1 - \sqrt{\pi} (\xi - y - is) w(x, \xi)} \right] \quad (65)$$

$$q' = y + \xi + ix' \quad (66)$$

$$z = 2\sqrt{\log(2)} \frac{\beta}{\Delta\nu_D} \quad (67)$$

$$\xi = 2\sqrt{\log(2)} \frac{\Omega}{\Delta\nu_D} \quad (68)$$

$$Z = z \left(1 - \frac{y}{\xi} \right) - \frac{isz}{\xi} \quad (69)$$

where β is the effective frequency of velocity-changing-collisions and Ω is the total collision frequency for when phase-changing and velocity-changing collisions are correlated. Fig. 31 shows the results of fitting the Voigt, Rautian-Sobelman and generalized Rautian-Sobelman to the measured lineshapes from 1.45 to 20 Torr. The residuals are shown for the 1.45 and 14.8 Torr cases. No sufficient numerical approximation to the Galatry and generalized Galatry profiles could be found or developed and so pressures below 20 Torr are excluded from the fitting routine. It is worth noting, however, that the residual of the generalized Rautian-Sobelman fit is consistent with fitting that functional form to a generalized Galatry [191] which motivates a numerical development of that function. The regular Rautian-Sobelman lineshape does not significantly improve on the Voigt profile but the generalized form does decrease the RMSE by a factor of two. One would expect the generalized Galatry profile to fully capture the measured lineshapes.

As the lowest pressure Lorentzian and Doppler widths and Lorentzian shift can-

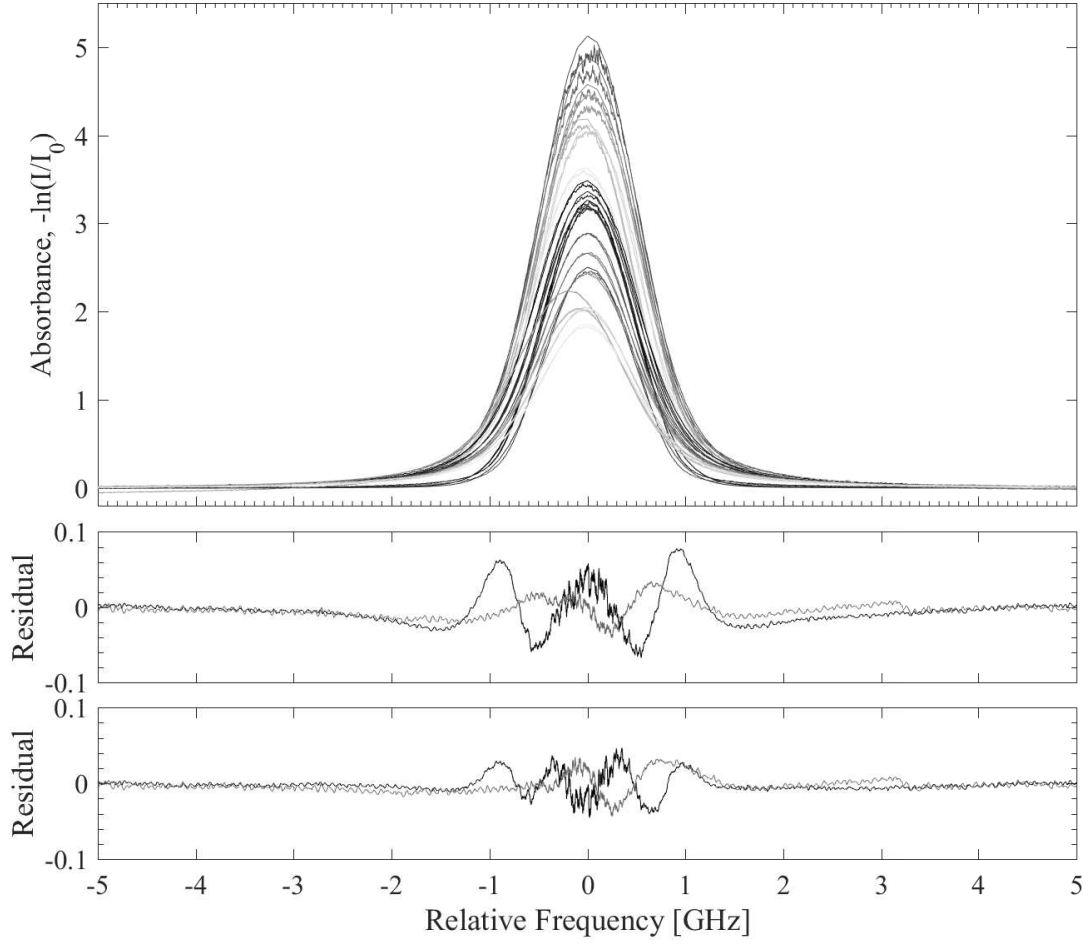


Figure 31. The absorption spectra of the 842.6963 nm transition are shown with a symmetric Voigt and generalized Rautian-Sobelman fit. The residuals displayed are for the 1.45 (black) and 14.8 (gray) Torr cases. The residual for the generalized Rautian-Sobelman (bottom) are a factor of two smaller than that of the symmetric Voigt (top).

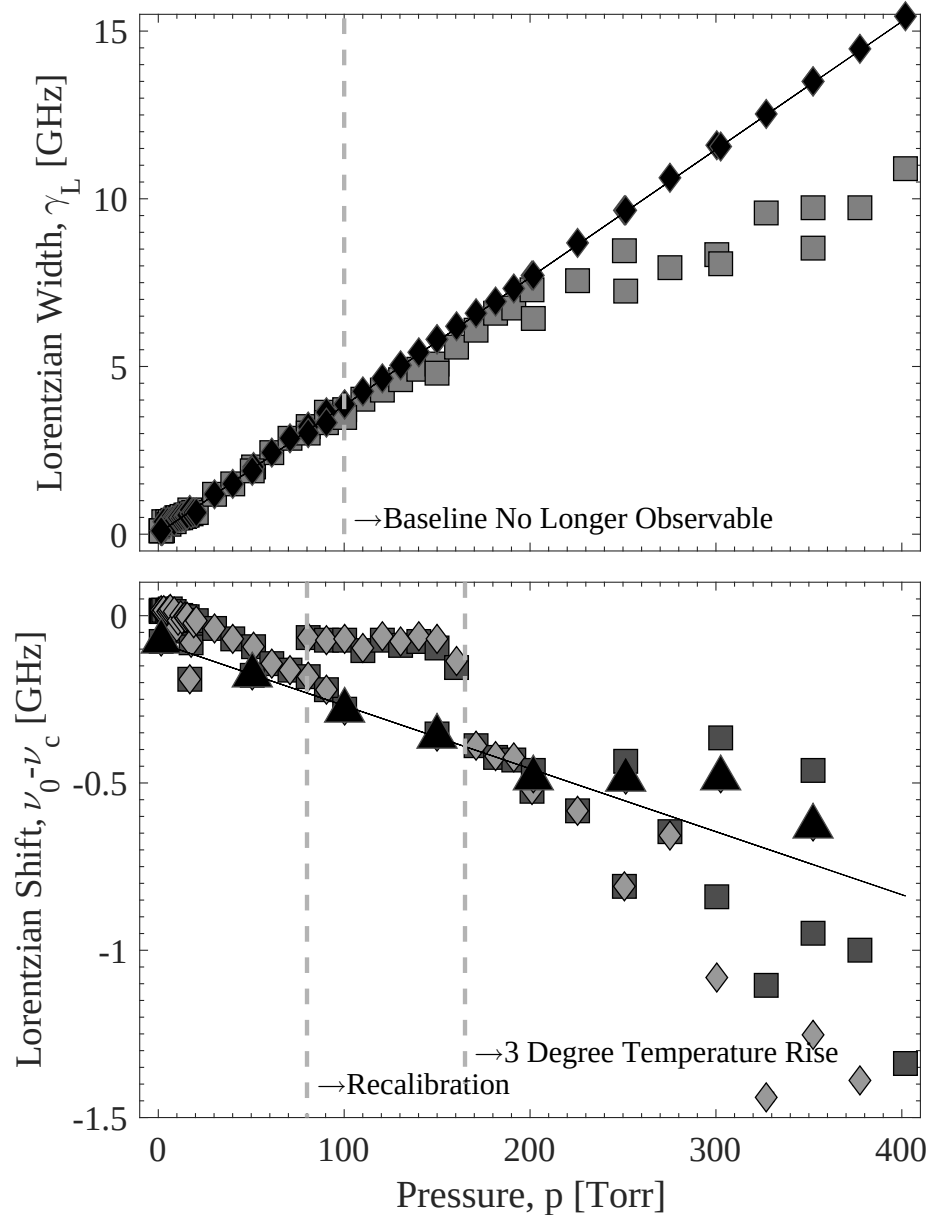


Figure 32. The Lorentzian width (top) and Lorentzian shift (bottom) are shown as a function of the total gas pressure. For the Lorentzian width, the uncorrected data, $\blacksquare$, does not follow a linear trend at higher pressures due to an inability to accurately determine the baseline. The data can be corrected, $\blacklozenge$, using the broadening rate from the 20 to 100 Torr data. The Lorentzian shift is limited by the temperature-dependence of the calibration source. The $\blacksquare$ and $\blacklozenge$ correspond to the uncorrected and corrected width data taken over several days and the $\blacktriangle$ data corresponds to shift measurements made in sequence with a calibration prior to each measurement.

not be determined accurately without the correct lineshape function, they are left out of the measurement of the pressure broadening and shift rates. These are determined from linear fits to the Lorentzian widths and shifts as a function of pressure, represented in Fig. 32 for the Lorentzian width (top) and shift (bottom) by a solid black line. The residuals are minimized at a pressure of 200 Torr. The Lorentzian width is easily distinguishable from the baseline for pressures below 100 Torr. The rollover observed in the data is due to a coupling between the Lorentzian width and the baseline. Above 100 Torr, denoted by the vertical dashed line, the far wings of the Lorentzian are no longer observable and so the full baseline can no longer be measured and removed. In this case, the Lorentzian width is decreased to account for an unknown baseline in the non-linear least squares fitting algorithm, seen in the uncorrected data (■). The widths can be corrected by using the broadening rate measured from 20 to 100 Torr and extrapolating to higher pressure. The error provided is only for the low-pressure fit and does not include the corrected data. This correction neither improves or diminishes the quality of the fit. The zero-pressure intercept was fixed to the natural linewidth of the transition at 22.85 MHz and the measured broadening rate was 38.5 ± 1.2 MHz/Torr.

The observed red-shift rate has significant scatter. This scatter is caused by a temperature-dependent frequency drift in the wavemeter. Laboratory temperatures tended to drift by more than 6 °C over the course of a day and temperature changes as small as 0.1 °C can influence the calibration. Original measurements were calibrated to the nearest alkali line using a low-pressure cell. This calibration could only be done at the start of a scan leading to a drift in frequency with temperature. The uncorrected data (■) and corrected data (◆) both show this significant scatter where a recalibration (first vertical dashed line) significantly changed the measured shift rate. As the temperature rises (second vertical dashed line) the observed shift returns

to the pre-calibrated level. Measurements were retaken with a frequency-stabilized He-Ne source where the calibration of the wavemeter was conducted prior to every measurement, designated by the $\blacktriangle$ symbol. At higher pressures the inability to distinguish the baseline still seriously influences the ability to measure the shift. The shift rate, of -1.9 ± 0.2 MHz/Torr, uses only the data collected from 1 to 200 Torr where the fidelity is high, represented by the solid line in Fig. 32.

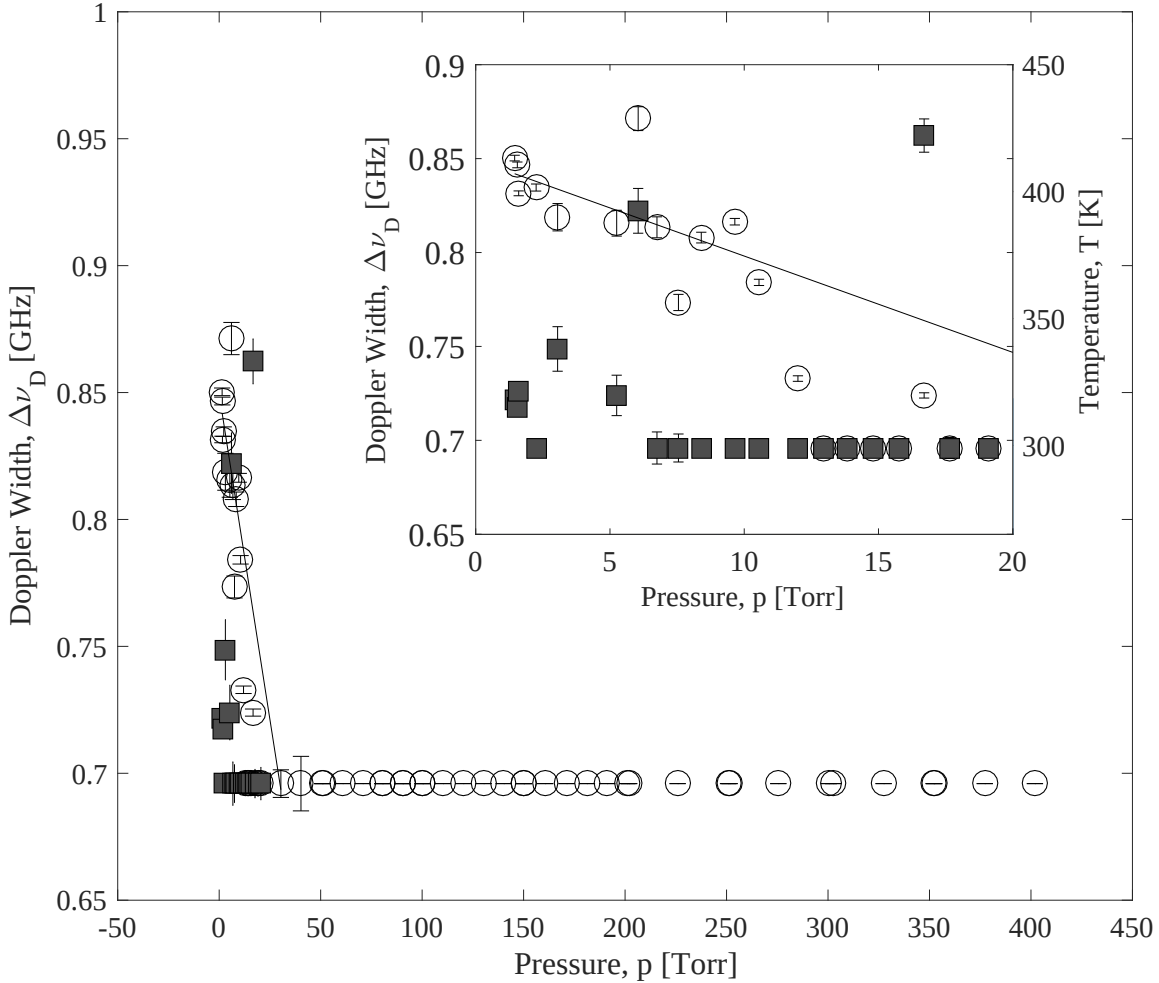


Figure 33. The Doppler width for the Voigt, $\circ$, and generalized Rautian-Sobelman, $\blacksquare$, are shown. The Voigt data implies a peak temperature of 440 K which decreases with pressure in contrast to the generalized Rautian-Sobelman which implies a slightly above room temperature (320 K) at low pressures with no discernible trend.

In order to put our broadening and shift rates in context of the literature, the temperature of the rates must be known. As there is no direct way to measure

temperature using our apparatus, the temperature is deduced from the Doppler width extracted from the fit Voigt profile. There are issues with this approach, the main one being that this temperature is a line-of-sight and spatial average of the real temperature distribution in the discharge. This Doppler width may also be influenced by the varying pressure. Fig. 33 shows the Doppler width as a function of pressure for both the Voigt ($\circ$) and generalized Rautian ($\blacksquare$) fits. The Voigt fit Doppler width implies a peak temperature of 440 K which decreases with pressure to 300 K at 12 Torr. From the generalized Rautian, however, we see that the temperature is more likely just above room temperature, at 320 K, at low pressure and may decrease to 300 K above 10 Torr. As the generalized Rautian provides an improved fit as compared to the Voigt, these broadening and shifting coefficients are expected to be the 300 K rates.

The pressure broadening and shift rates as compared to the literature are given in Tab. 4. The shift rates have been measured by *Vallee, et al* and *Moussanda and Ranson* at temperatures of 3900 and 2000 K [190, 125]. The only other broadening rate measurement that could be found was by *Vallee, et al*, and, when scaled to 300 K, agree well with our measurements.

Lastly, we examine the influence of pressure, flow rate and RF power on the num-

Table 4. Pressure broadening (γ_P) and shift rates (β_P) measured at a temperature of 320 K are given in MHz/Torr. They are compared to measurements made by *Vallee, et al* and *Moussanda and Ranson*. Values in parenthesis have been scaled to 300 K.

Broadening Rate (γ/P) (MHz/Torr)	Shift Rate ($-\beta/P$) (MHz/Torr)	Reference
38.5 ± 1.2	1.9 ± 0.2	This Work
8.97 ± 1.16	1.74 ± 0.29	[190]
(33.86 ± 4.37)		
—	1.43 ± 0.17	[125]

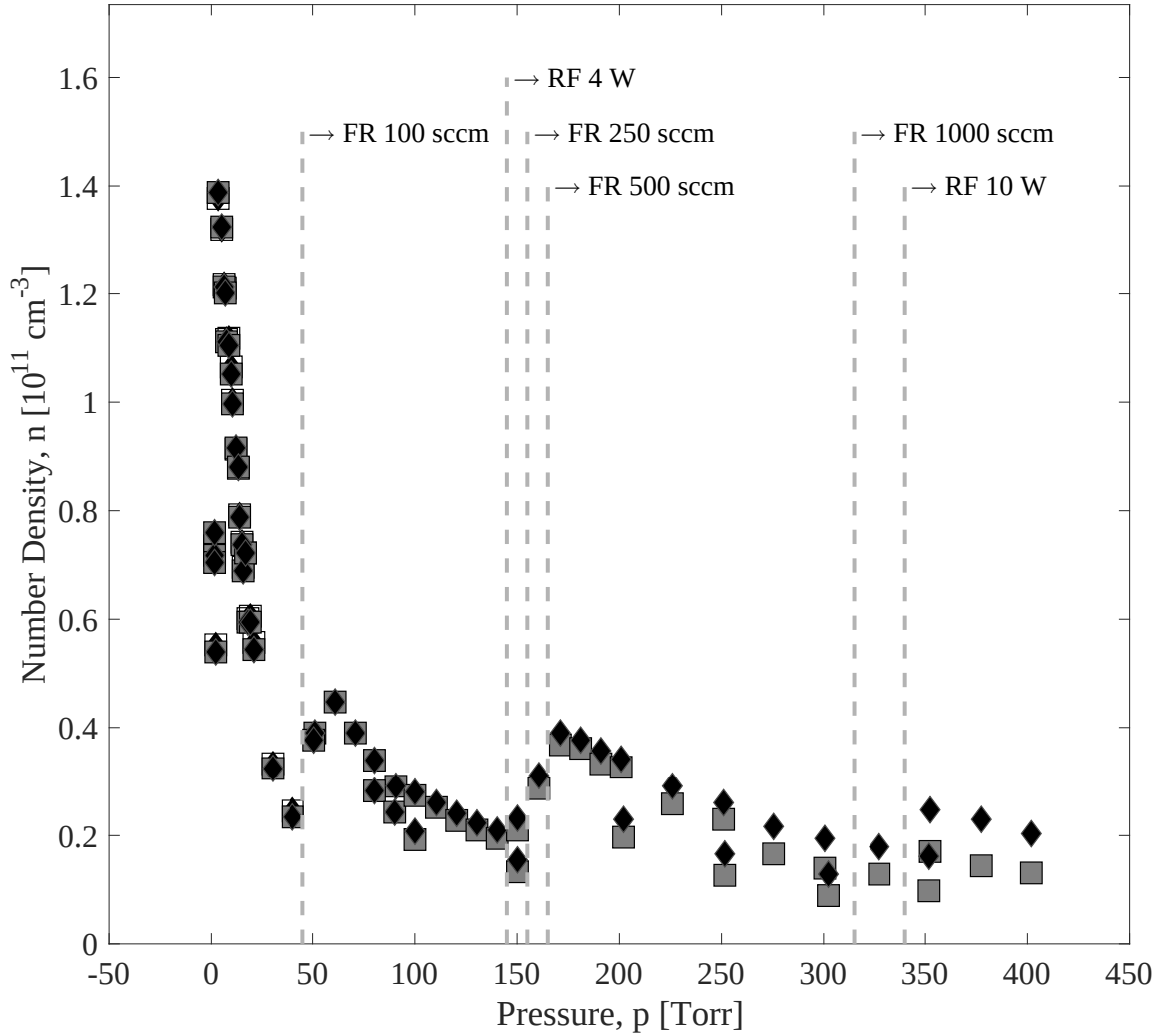


Figure 34. The number density as a function of pressure is shown. The vertical lines correspond to changes in flow rate and RF power but do not significantly change the number density. The $\blacksquare$ and $\blacklozenge$ correspond to the uncorrected and corrected Lorentzian widths.

ber density as it is the most pertinent metric to the development of the DPRGL. From the first presented experiment, one would expect the flow rate to have a significant influence on the number density. This will be particularly true at low pressures where changes in the flow rate correspond to large changes in the velocity and should be mitigated somewhat at higher pressures. Fig. 34 reveals that the change in flow rate only marginally affects the total absorbance, and the increases in RF power even less so. The number density dependence on either flow rate or RF power is insufficient to enable scaling to densities necessary for operation of the DPRGL.

5.4 Conclusion

The pressure broadening and shift rates for the 842.6963 nm $s_4 \rightarrow p_8$ transition have been measured as 38.5 ± 1.2 and -1.9 ± 0.2 MHz/Torr, respectively, at a temperature of 320 ± 20 K. The errors of 3.1% and 10% are an improvement over the literature errors of 12.9% and 11.9%. The Lorentzian line width was shown to be sensitive to the chosen baseline function whereas the shift was sensitive to the laboratory temperature through a temperature-dependent frequency drift induced in the calibration source as well as the difficulty in distinguishing the baseline at higher pressures. The flow rate (velocity) dependence of the line shape was investigated and was shown to have a velocity-dependent asymmetry which is the result of the correlation between the broadening and shifting parameters and the velocity of the interaction. At low pressures the line shape showed a strong collisionally-narrowed line shape that was improved by use of a generalized Rautian-Sobelman line shape where the correlations between the phase-changing and velocity-changing collisions is taken into account in the hard-collision model. A generalized Galatry profile is expected to improve these fits but no high-speed algorithm for calculation of the line shape in the necessary parameter space could be developed.

VI. Saturation spectroscopy of an optically thick argon plasma

6.1 Introduction

The diode pumped rare gas laser (DPRGL) has been recently demonstrated as a viable high-energy laser (HEL) system with three-level laser cycles analogous to the diode-pumped alkali laser (DPAL). Since its inception in 2012, the DPRGL has developed rapidly with pulsed lasing demonstrations conducted in large volume, pulsed discharges [74, 73, 75] as well as CW demonstrations occurring in small-volume atmospheric pressure discharges [154, 155]. Recently, a larger-volume CW demonstration was conducted in a high-rep rate pulsed discharge providing 2.6 W of output power at an estimated optical-to-optical efficiency of 30% [81]. A DPRGL uses helium (He) partnered with another rare gas (Rg), usually neon, argon, krypton or xenon (Ne, Ar, Kr, Xe) in a weakly ionized discharge in order to excite the $1s_5$ ($[3/2]_2$) level which is the lower laser level in a three- or four-level cycle. In order to efficiently operate the DPRGL there must be sufficient spectral matching between the diode pump laser and the atomic transition. For a three-level system using Ar-He and pumped by volume Bragg grating (VBG) narrowed diode bars at 811.7542 nm, this matching generally requires pressures on the order of an atmosphere. At this pressure the atomic transitions are homogeneously broadened and the absorption line shape is expected to be Lorentzian. To achieve high operational powers the gain volume needs to be pumped at intensities of more than 10 kW/cm² making the behavior of these line shapes under high intensity fields important. Furthermore, in the low-pressure regime, hole burning of inhomogeneously broadened transitions is commonly used for frequency stabilization using lamb-dip cells [194, 8, 33, 162]. Studying the behavior of the rare-gas gain medium in the presence of strong pump lasers provides insight

into the complex kinetics that will inevitably influence the operation and efficiency of the DPRGL.

In order to operate these high-gain diode-pumped laser systems efficiently the pressure broadening and shift rates must be well characterized at expected operation conditions of the laser. Because DPRGL systems have high gain, evaluating the active area using traditional spectroscopic methods to make accurate determinations of the number densities is difficult. The typical experiment to measure broadening and shift rates as well as track the population of the lower laser level is a laser absorption measurement. In order to avoid measuring laser transmission through an opaque medium several other techniques can be employed but they generally require more complex experimental methods. The simplest number density diagnostic can be made using transitions that share the same ground state but have significantly smaller absorption cross-sections. This method has been employed to determine the populations in the alkali laser [69]. Other methods involve amplifying the pump signal in a saturation spectroscopy experiment by addition of a second laser source, termed high contrast saturation spectroscopy, [167, 165, 40, 92] or using chirped laser dispersion techniques [131]. While these methods have some utility they do not offer a convenient diagnostic for a gain medium under optically thick conditions as both the collection of the data as well as its analysis require additional equipment.

Saturation spectroscopy of optically thin samples is a commonly used technique to remove the influence of the Doppler component of the line shape allowing for a high-resolution study of the Lorentzian components [79, 18, 137, 183]. The earliest work focused on alkali [6, 80, 134, 202, 3, 44, 45, 170, 135, 35, 185] and excited rare gas [174, 30, 27, 28, 29, 163, 19] transitions but has shifted to molecular-atomic interactions [188, 197, 196]. The work described has focused on determining the influence of velocity-changing collisions on the line shape and to investigate the saturation broad-

ening rate of the Lorentzian core. There is a significant research thread involved in deriving the collisional kernels for a wide variety of atomic and molecular collision partners [17, 16, 80, 187, 186, 115]. Saturation spectroscopy in optically thick samples has been studied less [180, 166, 51, 45] but several models for the line shapes under specific conditions have been suggested [180, 52] with a recent effort to develop analytic line shapes in highly saturated systems [122, 123, 132, 133]. Most of these works have focused on a limited set of measurements, particularly low pressure (less than 10 Torr) with pump intensities kept below the saturation intensities of the transitions. The models have dealt with, at most, radially averaged pump and probe profiles. The influence of velocity-changing collisions on optically thick spectra has not yet been considered in the literature neither experimentally nor theoretically.

In this work we use saturation spectroscopy techniques to measure the sub-Doppler line shape at Ar pressures from 1.3 to 50 Torr, pump intensities from 1.8 to 17.7 W/cm², probe intensities from 0.1 to 1.8 W/cm², and metastable densities, for which RF power is a surrogate varied from 1 to 40 W. The highly saturated, Doppler-limited line shapes are measured simultaneously. The unsaturated line shapes of each transition were also studied, for nearly all the same pressures and RF powers, along with longitudinally resolved inter-modulated fluorescence spectra to corroborate that optically thick conditions are the main driver of the observed line shapes. An absorption coefficient is derived using a rate equation approach for an equivalent two-level system, motivated by a similar derivation in barium conducted by Pappas et al[137], considering velocity-changing collisions in the strong limit [174]. The signal is modeled by propagating the pump and probe beams through the absorbing media, numerically averaging the integrated pump and probe intensities and examining the difference spectra that results in the sub-Doppler line shape. This approach allows us to account fully for the spatial and spectral variation of both the pump and probe

lasers as well as the media.

6.2 Experiment

There are several different configurations used in the analysis of the sub-Doppler spectra but all are modifications of the standard saturation spectroscopy setup. This

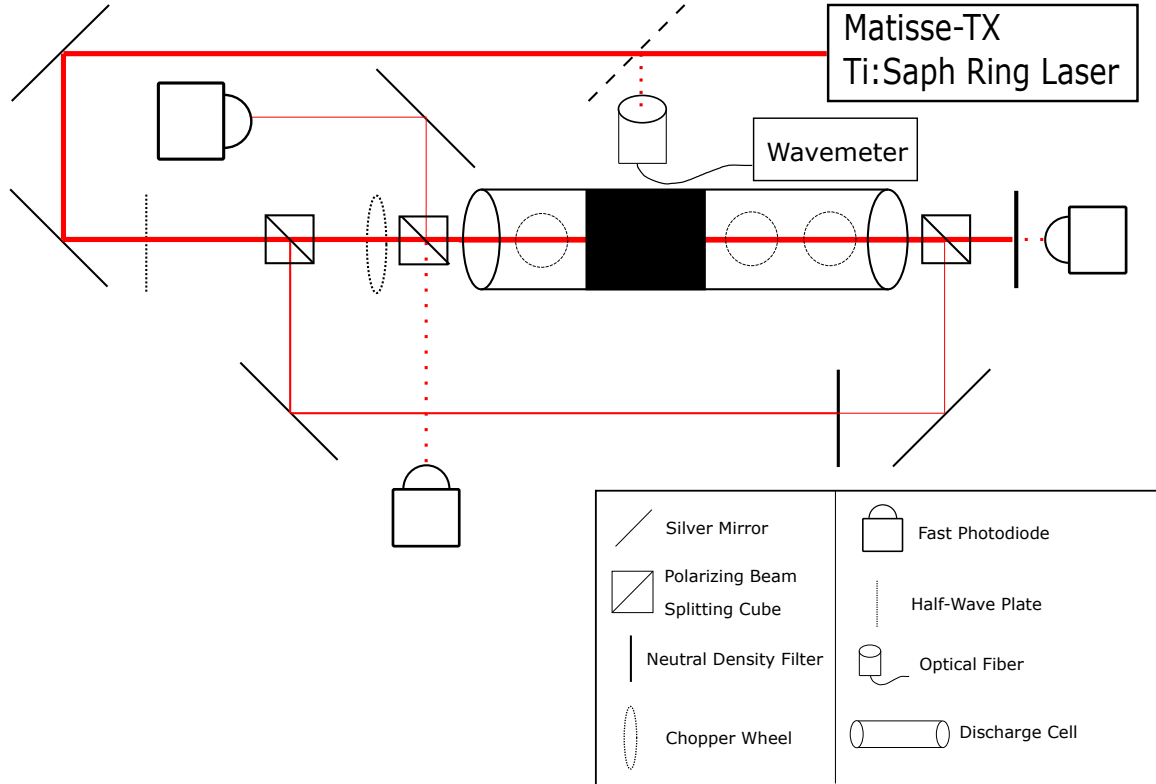


Figure 35. Experimental diagram for the saturation absorption spectroscopy experiment. The lock-in amplifiers and computer are not shown. The second configuration (LAS) rotates the half-wave plate to send most of the optical power to a beam block that is inserted in the path. The third configuration (IFS) replaces the photo-diodes with beam blocks and places them at the locations annotated by dotted circles along the discharge path. In this configuration the chopper is also rotated so that the probe and pump beams are amplitude modulated at different frequencies.

system is shown in Fig. 35. The laser source is a Sirah Matisse-TX Ti:Saph ring laser with peak output power of 3.5 W, a line width of ≈ 100 kHz, with a horizontal polarization. A small fraction of the beam is picked off and fiber-coupled into a WS7 High-Finesse wavemeter for absolute wavelength calibration with error of 60 MHz at

632.8 nm. The laser is tuned over a range of 20 GHz (4.4 Å) centered at the 811.7542 nm $s_5 \rightarrow p_9$ transition in Ar. The beam is propagated through an achromatic half-wave plate (Thor labs AHWP05M-980) and then a polarizing beam splitter (Thorlabs PBS252) in order to split the beam into a pump and probe of varying intensities. The pump is sent through an amplitude modulating chopper wheel (SR540) at 1.8 kHz and is propagated through another PBS where a small fraction is picked off and directed onto a fast photo-diode (Thor labs PDA10A) to track incident pump intensity. The remaining optical power is transmitted through the discharge cell after which it is propagated through another PBS and an ND filter to a second photo-diode to track the transmitted pump intensity. Tracking these two intensities allows us to measure the highly saturated absorbance of the medium. The probe beam is sent around the discharge tube using silver mirrors (Thor labs PF10-03-P01) and is reflected off a PBS into the discharge tube where it is counter-propagating with the pump beam and overlaps the same volume. After exiting the cell, the probe beam is reflected off the PBS and sent to a third photo-diode where the transmitted probe intensity is tracked. All three photo-diodes have a 25 mm focal length lens mounted on a 1" long tube. They are connected to three SR850 lock-in amplifiers for phase-sensitive detection at the chopper frequency. The lock-ins are referenced to the chopping frequency of the pump beam. The signal on the probe detector is from atoms that interact solely with both the pump and probe beam. The lock-ins are connected to a National Instruments USB-6251 BNC DAQ unit and controlled via an Agilent model 82357B GPIB-to-USB module. Matlab is used to collect data with the DAQ as well as control the instruments through the USB-to-GPIB interface.

The second configuration is a laser absorption spectroscopy (LAS) experiment which only slightly modifies the above apparatus. The half-wave plate is rotated from 90 degrees to 0 degrees in order to send most of the laser power down the probe

channel which is then incident on a graphite beam block and not used. The remaining beam, with only ≈ 40 mW of power, is sent through the original pump beam path with both the incident and transmitted intensities tracked by the fast photo-diodes that were used to track the pump beam intensities. The lower power minimizes the influence of saturation broadening expected at intensities greater than 0.25 W/cm^2 . The lock-in amplifiers are referenced to the chopping frequency of the probe beam.

The third configuration is the inter-modulated fluorescence spectroscopy (IFS) experiment which removes the photo-diodes from the original configuration and replaces them all with beam blocks. The photo-diodes are then placed along the glass tube to observe the fluorescence from the discharge at various positions. The 25 mm lenses now serve to collimate the view of the photo-diode which are placed at 2.5 cm, 7.5 cm and 17.5 cm relative to the probe propagation direction. This is annotated on Fig. 35 by the three circles along the discharge cell. The chopper wheel is also shifted so that both the pump and probe beam are chopped at different frequencies (1.8 and 1.5 kHz). In this case, the SR540 chopper controller outputs the sum frequency to which the lock-in amplifiers are referenced. In order for the fluorescence to be at the sum frequency the emitting atoms must be interacting with both beams. This allows the absorption of the pump and probe beam along the path to be investigated.

The Ar metastable state is formed in a radio-frequency dielectric barrier discharge. The gas is Matheson UHP (99.999%) Ar with flow rate set by a Sierra instruments flow controller (C50L) to 25 or 50 sccm. After the controller, the Ar is filtered using an SAES gas purifier (MC200-904FV). The gas then flows to the cell which consists of a $1/4$ " O.D. (0.15" I.D.) Pyrex tube and out to vacuum at the exit. On the outside of the tube there are two copper electrodes that were cut by wire EDM to fit the O.D. of the Pyrex tube. The electrodes were designed so that there would be a $1/8$ " gap between the edges. These electrodes are held together using a custom

Macor mount and the air gaps between them are filled with Macor bars milled to the width of the gaps. Power is fed to the electrodes using an Advanced Energy Cesar 1310 radio-frequency power generator which can output between 1 W and 1.25 kW at 13.56 MHz. The plasma load is impedance matched to the source load using a Vario matching network (VM1000). This system is capable of generating Ar plasmas at pressures as high as 1,000 Torr with sustaining powers in the tens of watts. Fig.

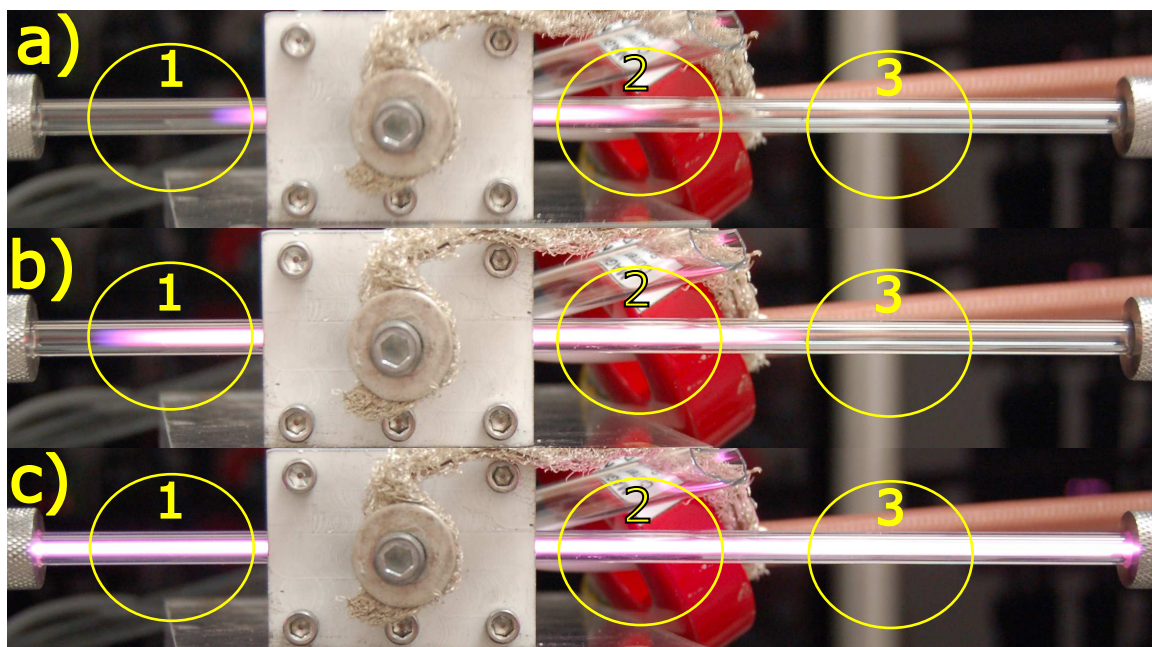


Figure 36. Images of the discharge at 50 Torr of Ar for RF powers of 5 (a), 10 (b) and 25 (c) W. The path length and fluorescence both increase as RF power increases, extending the full 8.4" observable path length above 25 W.

36 shows images of the discharge that were collected at 50 Torr and RF powers of 5, 10 and 25 W. All images were collected using the same exposure time. The images show that as RF power increases, the effective path length and fluorescence intensity increase. These two visual parameters are surrogates for the total absorbance, the longer path lengths increase the total absorption path length, and the fluorescence is correlated with the number density of absorbers. The circles designated by 1-3 are representative of the photo-diode locations discussed in the previous paragraph and in Fig. 35.

6.3 Results

The original goal of this work was to investigate the velocity-changing collision rate of Ar-Ar collisions in an Ar plasma. Based on surveys of the literature, the line shape was expected to be well represented by a Lorentzian core on top of a Doppler pedestal [174, 185]. Towards this end we set up the saturation spectroscopy apparatus and collected data at several different Ar pressures (1.3 to 50 Torr) and RF powers (1 - 40 W). The expectations were that as pressure increases so does the velocity-changing collision rate and therefore the Doppler pedestal should increase in area with a corresponding decrease in the pressure broadened Lorentzian core. Fig. 37 reveals that the measured line shapes did not fulfill these expectations as a multi-peak structure was observed. Focusing first on the 1 W case at 5 Torr, the spectra is nearly represented by a Voigt pedestal in the wings with a Lorentzian core that is inset. As the RF power is increased this dip deepens significantly. In the high pressure case we see a similar behavior except the core only becomes inset at higher RF powers. These line shapes are similar to self-reversed lines observed in optically thick fluorescence experiments [39]. The effect of self-reversal leads the core of the line shape to be removed because of absorption of the pump and probe laser along the path. This is consistent with the observed trend in both pressure and RF power since increasing pressure broadens the original Voigt line shape, lowering the absorption cross-section, which leads to greater transmission. Increasing the RF power has the opposite effect whereby both the absorption path length and number density of absorbers are increased. As expected, higher RF powers creates a significantly more “self-reversed” line.

With absorption of the probe beam (at lower intensity) being a significant contributor to the sub-Doppler line shape, an LAS experiment was conducted to characterize this absorption. Fig. 38 shows the absorbance of a 40 mW probe beam through the

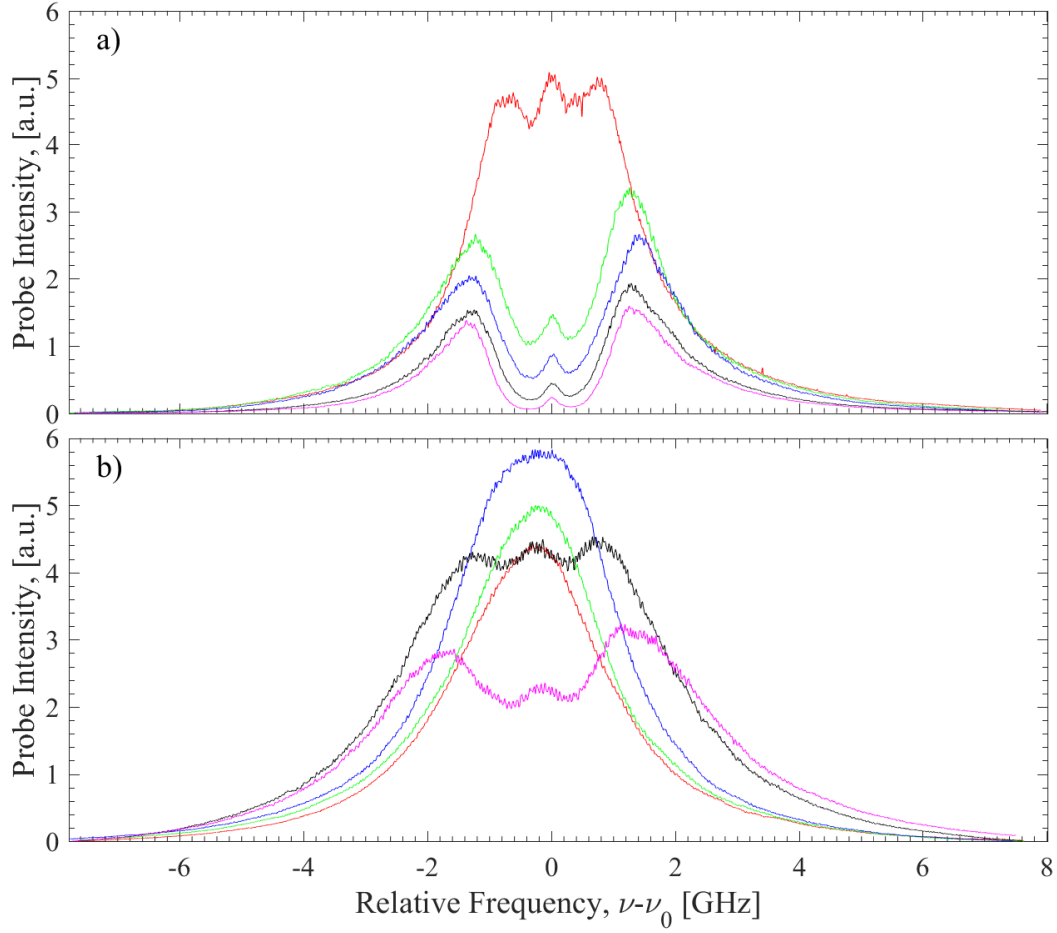


Figure 37. The probe transmission spectra are shown for 5 (a) and 50 (b) Torr where the different RF powers are 1 W (—), 5 W (—), 10 W (—), 25 W (—), 40 W (—). The 5 Torr case shows significant transmission only in the wings and in the Lorentzian core. The 50 Torr case shows absorption in the core about the Lorentzian center only at higher (>25 W) RF Powers. The Lorentzian core in the 50 Torr case shallower and broader than the 5 Torr case, as expected from the pressure broadening of the line.

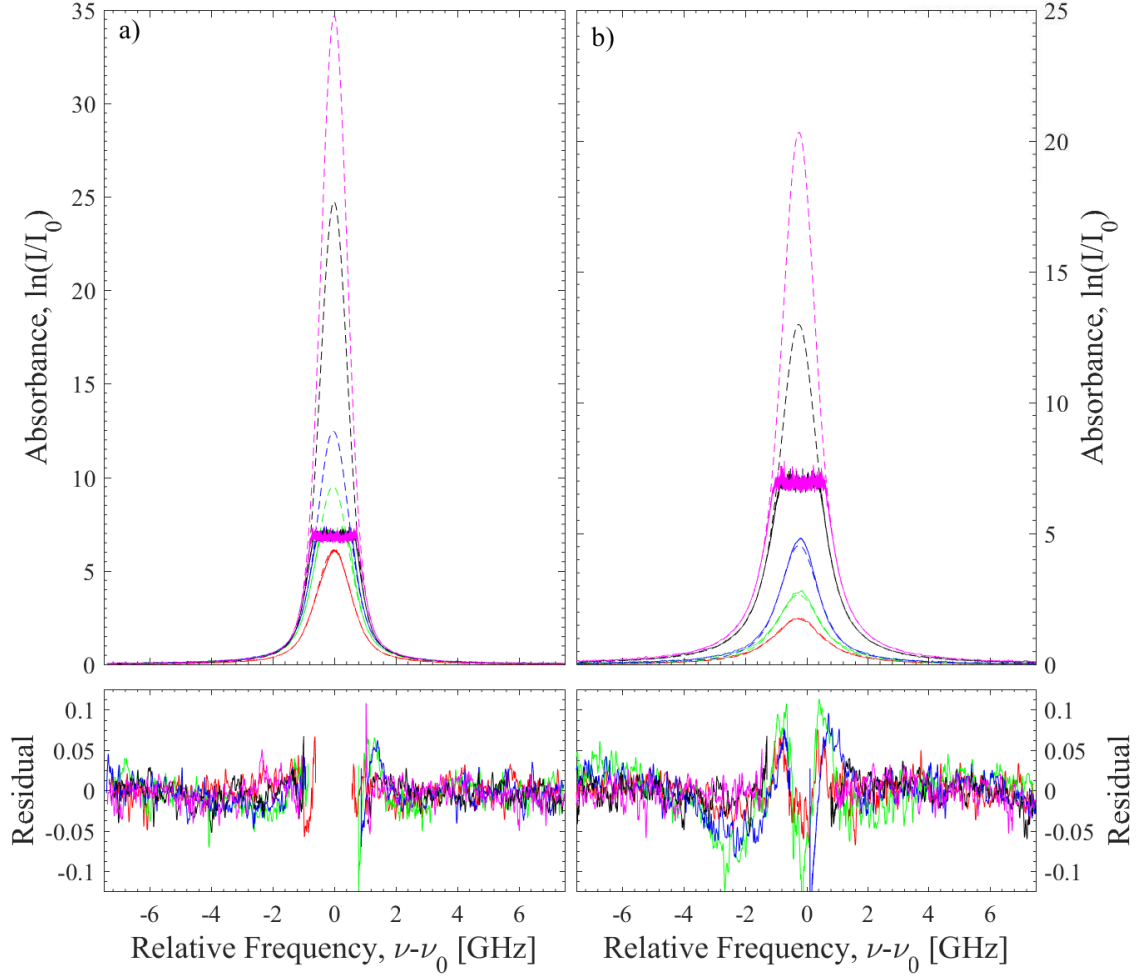


Figure 38. The absorption spectra are shown for the 5 (a) and 50 (b) Torr cases with the RF powers as 1 W (—), 5 W (—), 10 W (—), 25 W (—), 40 W (—). Higher RF powers correspond to the highest absorbances. The maximum measurable absorbance for the experiment is at ≈ 3 and so all data above absorbance 3 is excluded from the fitting routine (as shown in the residuals).

cell for various RF powers at 5 and 50 Torr. The detection limit of this system was absorbance ≈ 3 corresponding to a number densities of 7.6×10^{10} and $1.1 \times 10^{11} \text{ cm}^{-3}$ at 5 and 50 Torr, respectively. It is immediately apparent at 5 Torr the medium is just barely opaque to the probe, even at the lowest RF Power of 1 W. In the higher pressure case the media becomes opaque to the probe at powers above 25 W. This is consistent with the previous observation that the "self-reversed" structure is only apparent at RF powers greater than 25 W in the high pressure case and is a significant influence to the 5 Torr line shape even at a power of 1 W.

It is reasonably clear that opacity is the driver of the observed line shape. Recorded line shapes are a line-of-sight average of the local line shape along the cross-section and length of the cell. In order to observe this longitudinal dependence the experiment was transitioned to configuration three where emission was observed at the sum frequency of the pump and probe, as described earlier. This setup allows us to investigate the contribution of opacity as a function of probe propagation distance through the cell, further cementing the influence of opacity on the observed line shapes. Fig. 36 shows the positioning of the three photo diodes overlaid on images of the discharge cell with RF powers of 5, 10 and 25 W at a pressure of 50 Torr. At 5 W (a) the plasma does not extend to zone 3 and just barely half fills zone 2 whereas at 10 W (b) the plasma fills zones 1 and 2 but does not yet extend to zone 3. At 25 W (c) all three zones are filled with plasma. These three powers offer a good characterization of the absorption as a function of number density and path length. The IFS experiment resulted in the spectra shown in Fig. 39. If we first look at the 5 W (a) case, we see that there is no plasma in zone 3 and very little in zone 2. In fact the spectra in the middle panel appears to be of the expected form with no obvious opacity effects in the core. By zone 1 the plasma has fully absorbed the laser in the core. In the 10 W (b) case we see similar trends except the measured intensity has been reduced, likely due to the

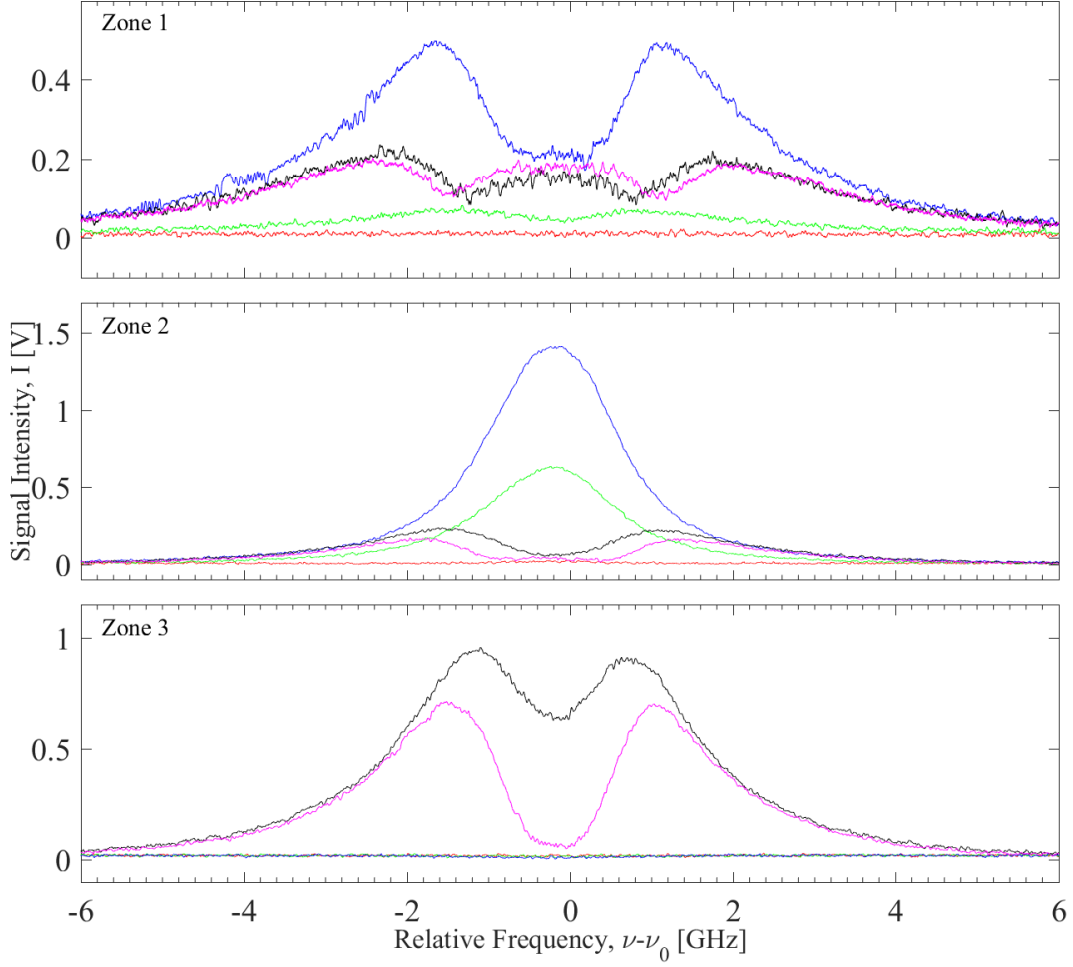


Figure 39. Inter-modulated fluorescence spectra are shown for the 50 Torr case at positions 1 (top), 2 (mid) and 3 (bottom) as shown in Figure 36. The RF powers are given by 1 W (—), 5 W (—), 10 W (—), 25 W (—), 40 W (—). The opacity in the line core as the probe propagates from 3 to 1 is clear.

absorption of the pump beam before reaching zone 2. By the time we reach 25 W (c) there is significant "self-reversal" in the core, even at the shortest path length, with near full absorption of the probe by the time it propagates to zone 1.

With the cause of the line shapes revealed, we chose to investigate the influence of various parameters. The probe and pump intensity were both varied and an optic was introduced only into the pump path and symmetrically into both paths to raise the pump intensity to 15 kW/cm^2 at the focus. It also changes the spatial intensity distribution of the pump and probe. By only focusing the pump laser, the volume overlap between the pump and probe was greatly reduced. This led to significant absorption on the probe beam at radii greater than that of the focused pump resulting in a weaker overall signal in the core of the sub-Doppler feature. Similarly, by putting an optic on both beams but having them cross at a single position in the cell, the probe beam was found to be more attenuated in the core. Increasing the intensity of the probe beam, when the pump was focused, did not significantly change the observed line shape as the absorption in the unsaturated volume was too high. An increase in the intensity of the probe beam by nearly a factor of 10 leads only to a factor of 5 increase in the core transmission.

As these tests did not provide any illuminating information, we instead focus on the influence of the laser intensity in the absence of an optic, on the observed line shape. Fig. 40(a) shows that as laser intensity is increased the opacity in the medium is reduced causing the peak probe transmission to increase from 0.75 to 4 and for the Lorentzian core to increase from absent to an amplitude of 1. This increased transmission is directly due to the pump laser saturating a larger volume of the medium. Furthermore, the Lorentzian core is not significantly broadened by the increased saturation. This may be due to the strong influence of velocity-changing collisions in the larger volume. At the higher pressure of 50 Torr, Fig. 40(b), we

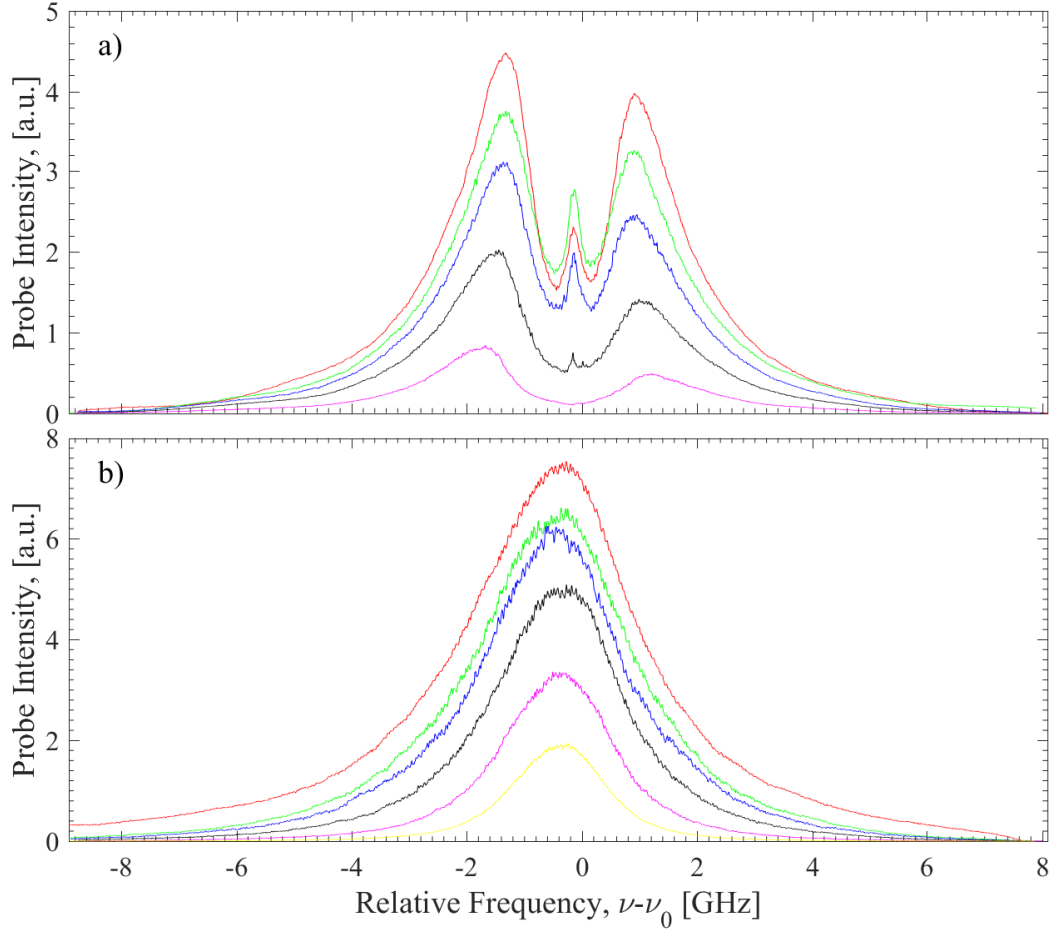


Figure 40. The probe transmission spectra are shown for 5 (a) and 50 (b) Torr and for incident laser intensities of 17.7 (—), 14.1 (—), 10.6 (—), 7.1 (—), 3.5 (—), 1.8 (—) W/cm². As the pump intensity increases the opacity to the probe decreases due to the wings of the atomic feature becoming more saturated. At 5 Torr, the increasing pump intensity leads to a taller core feature and less absorbed core. For the 50 Torr case the probe transmission increases and the line shape broadens slightly with intensity.

see that increasing the intensity of the pump leads to a factor of two increase in probe transmission, for the same reasons as the 5 Torr case, as well as a factor of two increase in width. Due to the pressure-broadened Lorentzian core, it is difficult to see if the resulting broadening is because of saturation in the core or increased width of the pedestal.

At pressures less than five Torr and at the low pump intensity of 17.7 W/cm^2 , significant structure is observed in the line shape that cannot be accounted for by considering only the spatial or spectral variation of the pump or probe lasers. This structure appears in the form of a secondary line shape that is blue-shifted and broadened relative to the main feature. The relative amplitude of the two features as well as the width and shift of the secondary peak show a dependence on the pressure, RF power and pump laser intensity. Fig. 41 shows the RF power and laser intensity dependence. Both the pump absorbance and probe transmission are displayed and separated by a residual that is the result of fitting a sum of Voigt profiles to the measured pump absorbance. Fig. 41 (a) and (b) correspond to the 1.3 Torr case at a pump intensity of 17.7 W/cm^2 and Fig. 41 (c) and (d) are the 15 kW/cm^2 pump intensity for the same pressure. This structure appears to be strongly correlated to the absorption of the pump laser with a larger absorption leading to a more observable influence on the line shape. In the probe transmission spectra the secondary peak appears to shift to the blue with increased pump intensity leading to an asymmetric line shape. The Lorentzian core also appears to be blue-shifted which may correspond to the pump laser saturating the secondary peak at the shifted wavelength.

There are several potential causes of the observed structure. First, we note that there are no other Ar or Ar^+ lines in the vicinity of this transition so this spectral feature must arise from the influences on internal state of the atom. The least likely candidate for this structure lies in the inhomogeneity of the plasma itself. Spatial

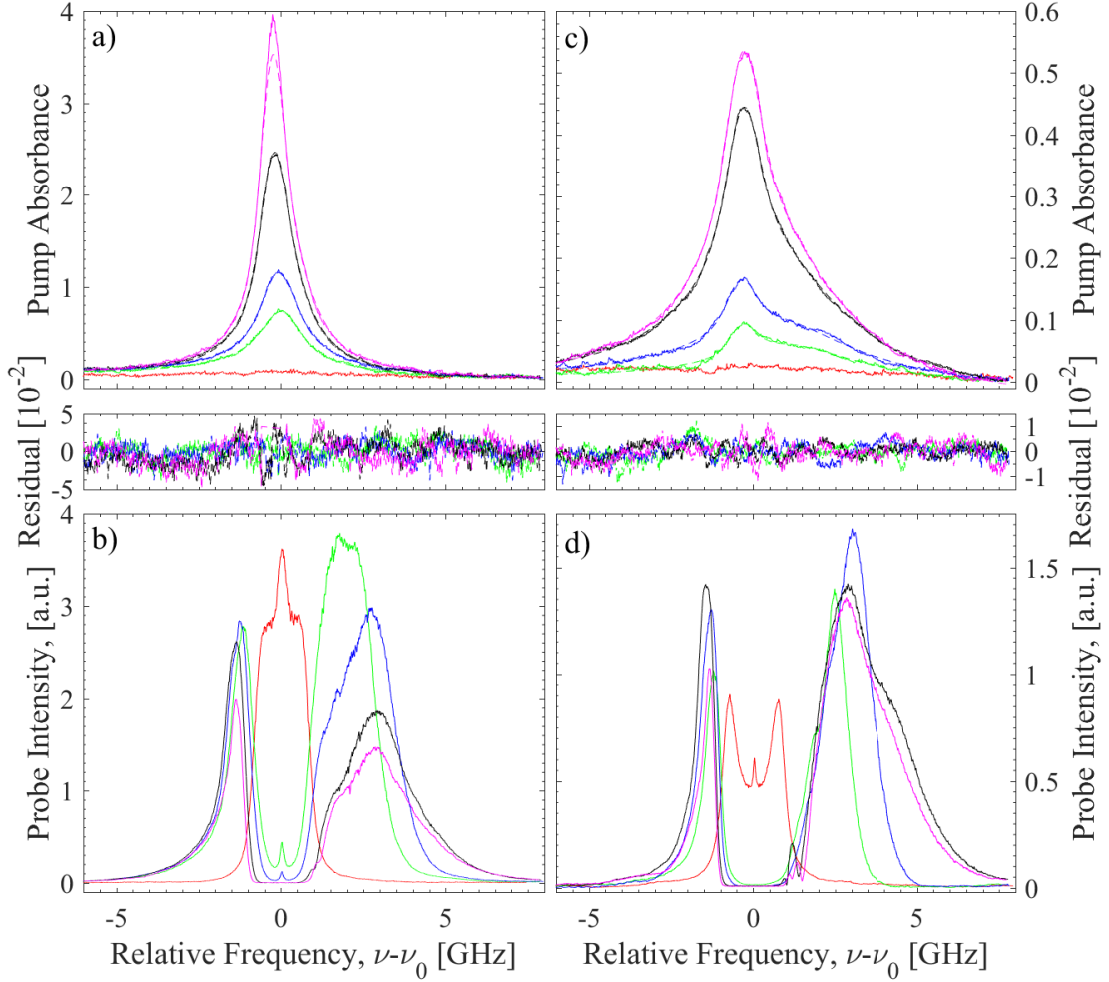


Figure 41. The pump absorbance (a), (c) and probe transmission spectra (b), (d) for the 1.3 Torr case with a pump intensity of 17.7 W/cm^2 (left) and 15 kW/cm^2 (right) are shown. The RF powers are given by 1 W (—), 5 W (—), 10 W (—), 25 W (—), 40 W (—). The pump absorbance shows a clear secondary feature in the blue wing, even at 5 W. The residuals are shown for a dual Voigt fit to the line shape. The probe transmission shows no asymmetry for the 1 W case but even at 5 W there is a clear asymmetry, in both the wings and core feature, that increases with RF power. The behavior is distinct for the low intensity and high intensity cases and appears to be dependent on pump laser absorption.

images show that the peak $\text{Ar}(1s_5)$ number densities exist in the sheath and are significantly diminished towards the center of the plasma. Furthermore, the electron density is increasing in the sheath and is maximized in the central column. The consideration of electrons is important as they significantly broadened and blue-shift spectral features. This stark broadening and shift has been the subject of several reviews [105]. In fact, at the high intensity, 40 W RF Power, the secondary Voigt profile is blue-shifted by 0.7 GHz. The measured Lorentzian width is saturation broadened so it is not useful for this analysis. If we assume the shift is caused purely by electrons then the required density would be approximately $2 \times 10^{15} \text{ cm}^{-3}$ which is somewhat higher than expected densities below 10^{14} cm^{-3} from the model discussed in Ch. III. It is worth noting, however, that these spatial inhomogeneities can cause significant variations in the line shape of a single transition [110]. This is an unlikely candidate because it does not account for the dependence on the pump laser intensity. It also seems unlikely that the change in RF power from 1-40 W would be able to account for the required increase in electron number density as the observed RMS current only increases by about a factor of 3.

The most likely candidate for this structure appears to be coupling between the plasma and the propagating pump laser field where the plasma becomes driven by the field generated in the laser spot and not the RF discharge field. At 5 Torr the 17.7 W/cm² and 15 kW/cm² laser intensities correspond to local reduced electric fields of 72 and 2100 Td which are fields of sufficient strength to rapidly accelerate electrons and ions within the laser spot and could reasonably increase the local ionization rates. The observation of this effect would depend both on the radial intensity of the propagating field and the longitudinal intensity which is absorption, and therefore RF power, dependent. In essence, the laser creates a significant radial gradient in the electron density with peak densities occurring in the spatial core of the pump laser

and decreasing along the path as the pump laser is absorbed. The probe laser then interrogates the complete plasma volume and these gradients would be observable if their influence on the production of the $\text{Ar}(1s_5)$ level and the local electron density was significant enough. Both of these sources of structure amount to speculation at this point and more work is required in order to be able to more definitively state the cause.

6.4 Discussion

A model was developed to give physical insight into the observed optically thick line shapes. We consider the propagation of a laser of arbitrary intensity through an absorbing media. The laser propagation in free-space is well described by a Gaussian propagation

$$I(r, z) = I_0 \left(\frac{w_0}{w(z)} \right)^2 \text{Exp} \left(-\frac{2r^2}{w(z)^2} \right) \quad (70)$$

$$w(z) = w_0 \left(1 + \left(z \frac{M^2}{z_R} \right)^2 \right)^{1/2} \quad (71)$$

where I_0 is the incident laser intensity, w_0 is the beam waist, M^2 is the laser beam quality parameter, $z_R = \frac{\pi w_0^2}{\lambda}$ is the Rayleigh range, or coherence length, of the laser and λ is the laser wavelength. When considering an absorbing media, we must consider the longitudinal (z) variation of the laser intensity. This involves the solution to a differential equation

$$\frac{dI(r, z)}{dz} = -\alpha(\nu, I(r, z))I(r, z) + \frac{2}{w(z)} \frac{dw(z)}{dz} \left(\frac{2r^2}{w(z)^2} - 1 \right) I(r, z) \quad (72)$$

where $\alpha(\nu)$ is the frequency and intensity-dependent absorption coefficient, $I(r, z)$ is the local intensity of the laser. In the absence of absorption Eq. (72) will solve to Eq.

(70). The absorption coefficient is further defined in terms of atomic parameters as

$$\alpha(\nu) = \int_{-\infty}^{\infty} \sigma(\nu, \pm v_z) \Delta n(v_z, I) dv_z \quad (73)$$

where $\Delta n(v_z) = n_2(v_z) - \frac{g_2}{g_1} n_1(v_z)$ is the population inversion of a particular velocity group and is dependent on the laser intensity due to saturation effects and the cross-section is defined as

$$\sigma(\nu, \pm v_z) = \frac{g_2}{g_1} \frac{A \lambda^2}{8 \pi n^2} \frac{\gamma/(2\pi)}{(\nu - \nu_0 \mp k v_z)^2 + (\gamma/2)^2} = \sigma_0 \frac{\gamma/(2\pi)}{(\nu - \nu_0 \mp k v_z)^2 + (\gamma/2)^2} \quad (74)$$

where A is the Einstein A Coefficient for the transition, λ is the vacuum wavelength, n is the non-resonant index of refraction (taken to be 1), γ is the homogeneous width, ν_0 is the central frequency, $k = \nu_0/c$ is the wave-vector and v_z is the axial velocity. We note that the $\pm$ on the LHS of Eq. (74) corresponds to $\mp$ on the RHS and refers to the co-propagating and counter-propagating beams, respectively. The velocity and intensity dependent population inversions are derived from the rate equations for an equivalent two-level system. Fig. 42 shows the energy levels and considered mechanisms. We use the rate equation formalism despite the high pump intensities as the elevated pressures will destroy an coherence effects that would make the use of a density matrix formalism necessary. Henceforth we make the substitution $v_z \rightarrow v$ with the understanding that v refers to the axial velocity. The rate equations for the system are then

$$\dot{n}_1(v) = C_1(v) - \Gamma_1 n_1(v) + \frac{I \sigma(\nu, v)}{h \nu} (n_2(v) - \frac{g_2}{g_1} n_1(v)) - n_1(v) G_1(v) + F_1(v) \quad (75)$$

$$\dot{n}_2(v) = C_2(v) - \Gamma_2 n_2(v) + \frac{I \sigma(\nu, v)}{h \nu} (n_2(v) - \frac{g_2}{g_1} n_1(v)) - n_2(v) G_2(v) + F_2(v) \quad (76)$$

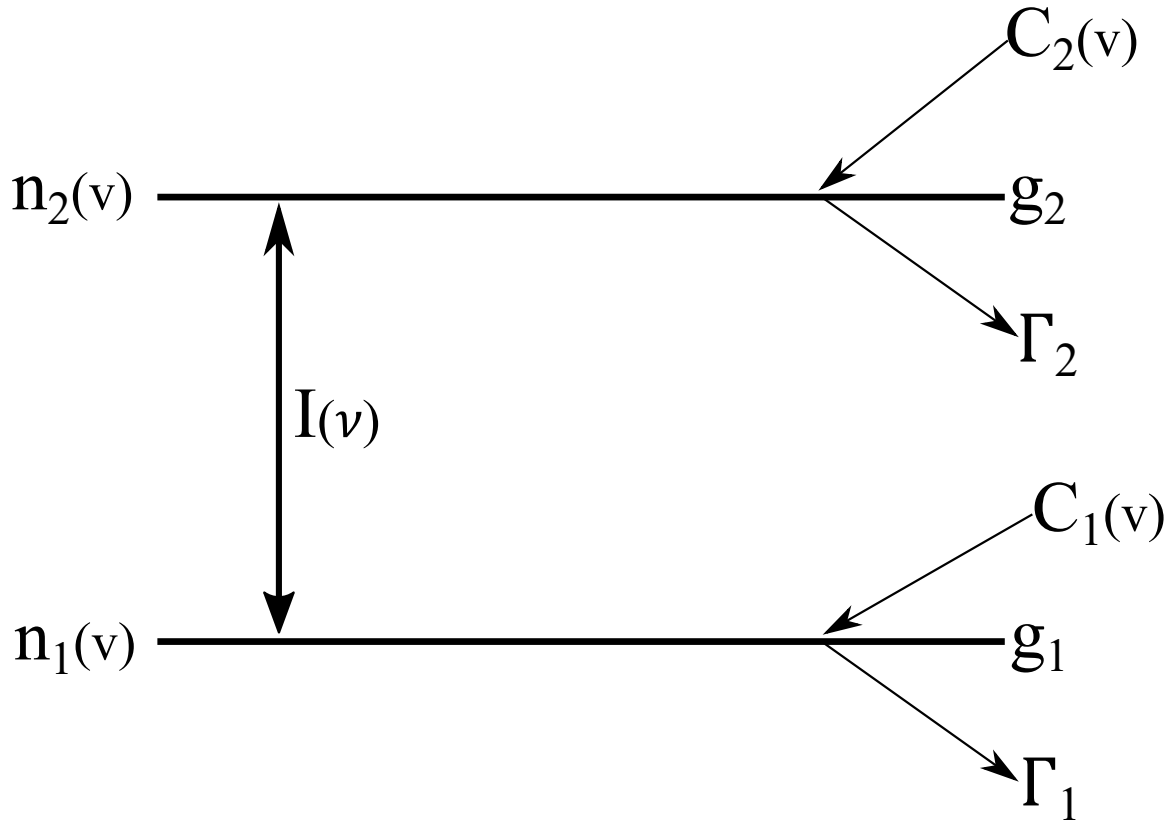


Figure 42. The energy level diagram and corresponding mechanisms, defined in Eq. (75) and (76), are shown. The velocity-changing collisions are internal to each level population and are not displayed.

where $C_i(v) = C_i f(v)$ is the production rate of the i^{th} level, Γ_i is the total loss rate of the i^{th} level, g_2 and g_1 are the degeneracies of the upper and lower level, respectively and $G_i(v)$ and $F_i(v)$ are the production and destruction of a specific velocity group given by the equations

$$G_i(v) = \int_{-\infty}^{\infty} W_i(v \rightarrow v') dv' \quad (77)$$

$$F_i(v) = \int_{-\infty}^{\infty} n_i(v') W_i(v' \rightarrow v) dv' \quad (78)$$

where $W_i(v' \rightarrow v)$ is the velocity changing collision kernel for a change from initial velocity v' to final velocity v . The selection of this collisional kernel has been a source of significant research over the past three decades [17, 16, 80, 187, 186, 115] but the simple strong-collision kernel derived by *Hansch and Smith* [174] will be used later on. The expressions are left in general terms of the collision kernel until the end of the derivation to allow for a straight-forward substitution of another kernel. In the absence of the pump laser, Eq. (75) and (76) yield the initial population inversion

$$\begin{aligned} \Delta n_0(v) &= n_2^0(v) - \frac{g_2}{g_1} n_1^0(v) \\ &= \frac{C_2(v) + F_2(v)}{\Gamma_2 + G_2(v)} - \frac{g_2}{g_1} \frac{C_1(v) + F_1(v)}{\Gamma_1 + G_1(v)} \end{aligned} \quad (79)$$

With a pump laser of arbitrary intensity, the inversion from solving Eq. (75) and (76) is

$$\Delta n(v) = \frac{\Delta n_0(v)}{1 + I/I_{\text{sat}}(\nu, v)} \quad (80)$$

where $I_{\text{sat}}(\nu, v) = \frac{h\nu}{\sigma(\nu, v)} \Gamma^*$ and Γ^* is defined as

$$\Gamma^* = \frac{(\Gamma_1 + G_1(v))(\Gamma_2 + G_2(v))}{(\Gamma_1 + G_1(v) + \frac{g_2}{g_1}(\Gamma_2 + G_2(v)))} \quad (81)$$

In the limit of strong collisions, which should be satisfied for Ar*-Ar collisions, we use the collisional kernel defined by Smith and Hansch [174] as

$$W(v' \rightarrow v) = \Gamma_i^c f(v) \quad (82)$$

where Γ_i^c is the velocity-changing collision rate of the i^{th} level. This collision kernel is equivalent to the statement that all collisions are fully thermalizing collisions and are, therefore, independent of the initial velocity. Using this kernel we find $G_i(v) = \Gamma_i^c$ and $F_i(v) = N_i \Gamma_i^c f(v)$ where $N_i \int_{-\infty}^{\infty} n_i(v') dv'$ is the total population in the i^{th} level. This collisional kernel will result in a zeroth order population inversion and Γ^* defined as

$$\begin{aligned} \Delta n_0(v) &= \frac{C_2(v) + F_2(v)}{\Gamma_2 + G_2(v)} - \frac{g_2}{g_1} \frac{C_1(v) + F_1(v)}{\Gamma_1 + G_1(v)} \\ &= f(v) \left(\frac{C_2 + N_2 \Gamma_2^c}{\Gamma_2 + \Gamma_2^c} - \frac{g_2}{g_1} \frac{C_1 + N_1 \Gamma_1^c}{\Gamma_1 + \Gamma_1^c} \right) \\ &= f(v) \Delta n_0 \end{aligned} \quad (83)$$

$$\Gamma^* = \frac{(\Gamma_1 + \Gamma_1^c)(\Gamma_2 + \Gamma_2^c)}{(\Gamma_1 + \Gamma_1^c + \frac{g_2}{g_1}(\Gamma_2 + \Gamma_2^c))} \quad (84)$$

where we've defined the velocity-independent inversion as Δn_0 . It is clear from Eq. (83) and (84) that the main influence of strong-collisions is to increase the saturation intensity due to increased destruction of a given velocity group. Substituting Eq. (74) and (83) into (73) for the two-cases of a co-propagating and counter-propagating

probe beam we get

$$\alpha_{co}(\nu, I) = \frac{g_2}{g_1} \frac{\sigma_0 \Delta n_0}{(1 + S_0)^{1/2} \sqrt{\pi}} \frac{2\sqrt{\ln(2)}}{\Delta\nu_D} \int_{-\infty}^{\infty} \frac{\text{Exp}[-(a_1 y - u(\nu))^2]}{y^2 + 1} dy \quad (85)$$

$$\alpha_{counter}(\nu, I) = \frac{g_2}{g_1} \frac{\sigma_0 \Delta n_0}{\sqrt{\pi}} \frac{2\sqrt{\ln(2)}}{\Delta\nu_D} \int_{-\infty}^{\infty} \frac{\text{Exp}[-(a_0 y - u(\nu))^2] (y^2 + 1)}{((y - 2u(\nu)/a_0)^2 + 1)(y^2 + 1 + S_0)} dy \quad (86)$$

where $\Delta\nu_D$ is the inhomogeneous (Doppler) width, the line-center saturation parameter is

$$S_0 = I/I_{sat}(\nu_0) = I\sigma(\nu = \nu_0 \pm kv_z)/(h\nu\Gamma^*) \quad (87)$$

and the dimensionless parameters in the integrals are defined as

$$a_0 = \sqrt{\ln(2)} \frac{\gamma}{\Delta\nu_D} \quad (88)$$

$$a_1 = \sqrt{\ln(2)} \frac{\gamma_s}{\Delta\nu_D} \quad (89)$$

$$u(\nu) = 2\sqrt{\ln(2)} \frac{(\nu_0 - \nu)}{\Delta\nu_D} \quad (90)$$

where $\gamma_s = \gamma(1 + S_0)^{1/2}$ is the saturation broadened homogeneous width. The derivation of the sub-Doppler line shape will proceed in three steps, displayed in Fig. 43. First, Eq. (72) is solved for the pump beam with the boundary condition that at $z = 0$ the intensity is equal to the measured incident pump intensity and the absorption coefficient defined by Eq. (85), shown in Fig. 43(a). We then solve Eq. (72) for the probe beam with the same condition but with the boundary condition equal to the incident probe intensity. Since the experimental observations are a line-of-sight average, the observed probe signal will be an integrated average of the simulated probe signal. The solution, $I_{probe}(r, z)$, is then radially-averaged and is shown in Fig.

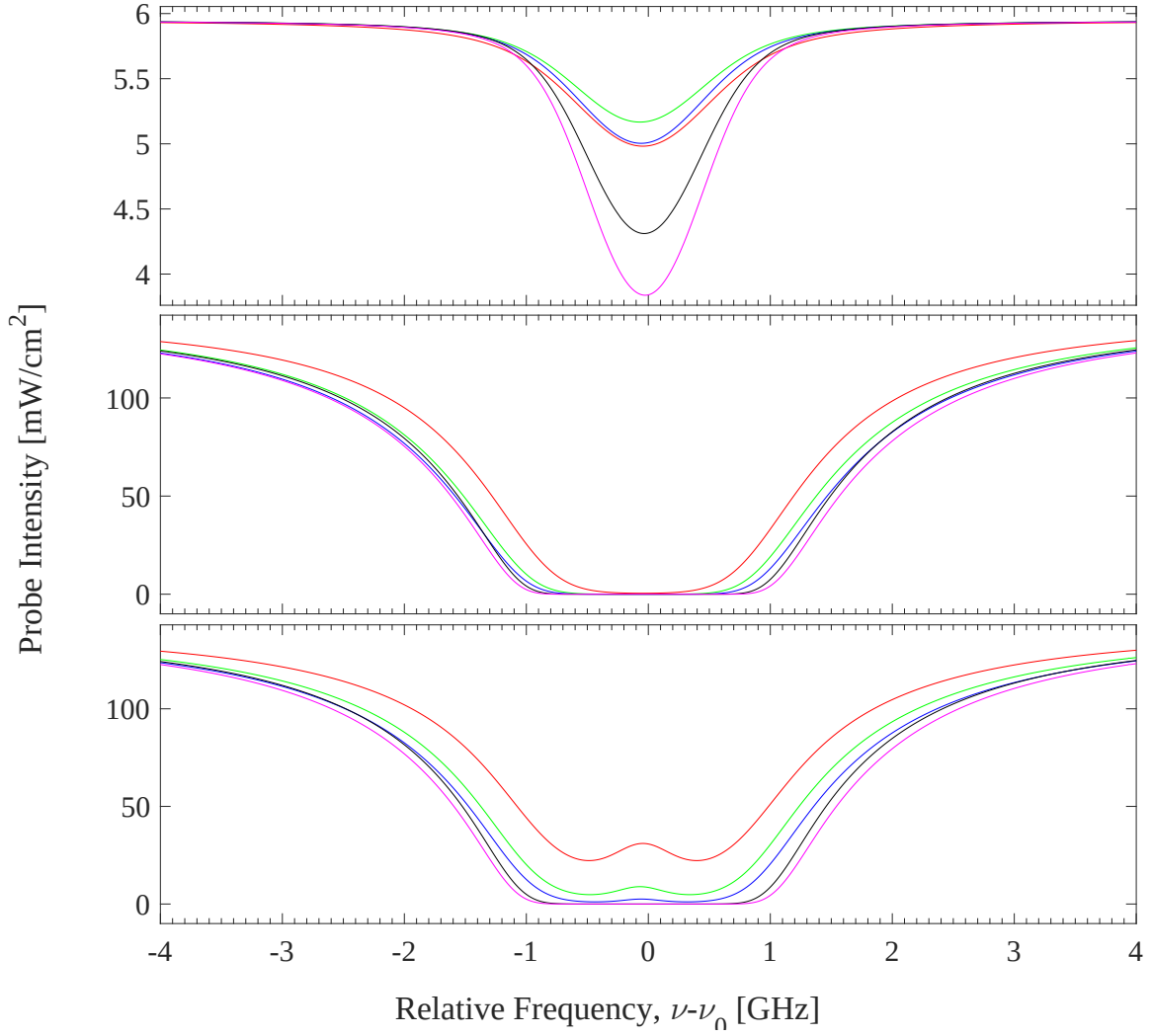


Figure 43. The results of the line shape model is shown for the 5 Torr case and RF powers of 1 W (—), 5 W (—), 10 W (—), 25 W (—), 40 W (—). Figure a) shows the pump transmission intensity at the end of the cell, b) shows the spatially averaged probe transmission in the absence of the pump and c) shows the spatially averaged probe transmission in the presence of the pump.

43(b).

$$I_{probe}(z = L) = \frac{2\pi}{\pi r_{max}^2} = \int_0^{r_{max}} r I_{probe}(r, L) dr \quad (91)$$

where $r_{max} = 2w(L)$ is the point at which the probe beam intensity is down by a factor of 10^4 and is no longer contributing.

Lastly, after solving Eq. (72) for the spatial and spectral dependencies of the pump and probe, the observation of counter-propagating probe beam in the presence of the derived pump intensity is considered. In this case the absorption coefficient is defined by Eq. (86). The I in $\alpha(\nu, I)$ will now be given by the solution to the pump intensity, $I_{pump}(r, L - z)$, and not be defined by the local intensity of the propagating probe. The pump intensity has been flipped along the axial direction to account for the counter-propagating pump, $z \rightarrow L - z$. Equation (86) is substituted into (72) and solve for the intensity of the counter-propagating probe beam in the presence of the pump. This intensity must also be numerically averaged at the final probe position $z = L$ as in (91) and shown in Fig. 43 (c). The sub-Doppler spectra is given by the difference between the probe beam in the absence of the pump and the probe in the presence of the pump. With a working line shape derivation the influence of different parameters on the calculation can be directly compared to the data. In Fig. 37 it was observed that as the RF power increased, the depth of the core increased. This was posited and experimentally verified as being caused by the opacity of the media to the probe laser. It was also observed that the system only became opaque for RF powers >25 W for the 50 Torr case. Fig. 44 verifies these trends. In 44(a) it is clear that as the opacity increases, the core depth feature of the line shape does increase. Additionally, we see in 44 (b) that the 50 Torr case does only become opaque to the probe in the core for RF powers greater than 25 W. In order to calculate these, and the following line shapes, the homogeneous and inhomogeneous widths, γ and $\Delta\nu_D$, the shifted line centers, ν_0 , and the initial inversion, Δn_0 , were pulled from

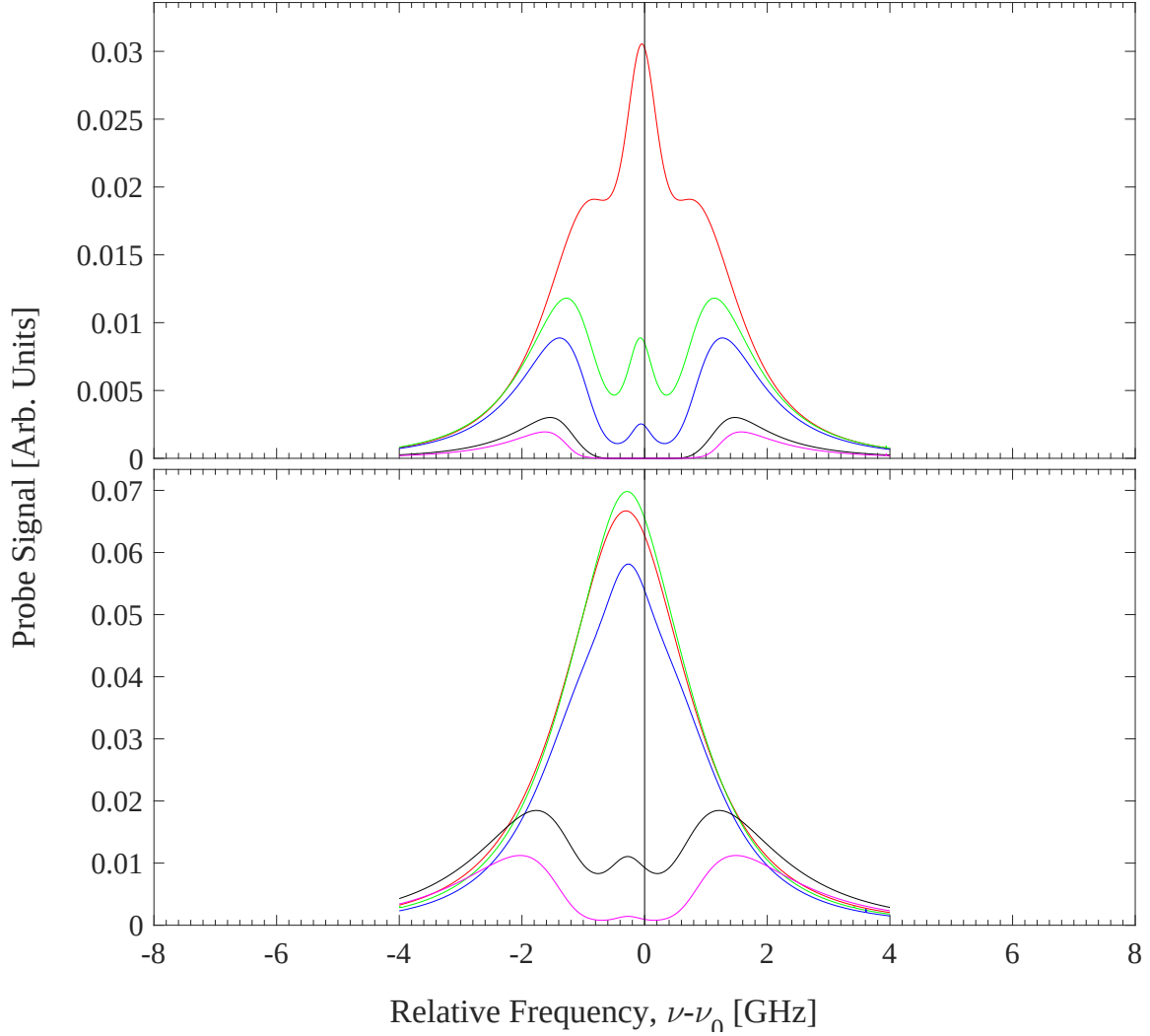


Figure 44. The output of the line shape model is shown for 5 (a) and 50 (b) Torr and for RF powers of 1 W (—), 5 W (—), 10 W (—), 25 W (—), 40 W (—). Increasing the RF power leads to an increased opacity and a line shape that is reduced significantly in the core. Both the 5 and 50 Torr predictions are red-shifted due to pressure effects with a stronger influence of the 50 Torr case, as expected.

Voigt fits to the LAS data for the corresponding pressures and RF powers. There are several deviations of the model from the observations. For the 5 Torr case (top), the Lorentzian feature at the core of the line is emphasized in the model output as compared to the observations. In addition, the opacity of the model is greater at the higher RF powers (25, 40 W) which corresponds to the Lorentzian core being absent from the lineshape; this is not observed in the data where the Lorentzian core persists at the highest RF powers. The 50 Torr case contains a reversed trend as a function of RF power from 1 to 10 W where an increase in probe transmission is observed, in contrast to the model which predicts a decreasing probe transmission. The 50 Torr prediction also displays the same exaggerated influence of opacity at the highest RF powers.

Fig. 40 showed the pump laser intensity dependence on the line shape. The model results for the same parameters are shown in Fig. 45. It is clear that as the laser intensity increases from 1.8 to 17.7 W/cm², the line shape becomes less opaque in the core. The reduced opacity is a direct result of the increased saturation in the wings of the laser profile. As the pump intensity increases, the saturation will increase for the full spatial profile and will lead to a larger volume being saturated. Furthermore, both the model and experimental data show that the width of the Lorentzian core changes minimally with pump intensity, likely due to the redistribution of population by velocity-changing collisions. Similar deviations between the model and observations are observed for the laser intensity predictions. Specifically, at 5 Torr the predicted trend appears to emphasize the Lorentzian core and over emphasize the opacity at line-center at the highest RF powers. At 50 Torr the model shows a factor of eight reduction in the probe transmission in contrast to the factor of four reduction in the observation as the laser intensity decreases 17.7-1.8 W/cm².

A model prediction of the dual Voigt profile shown in Fig. 41 could be treated in

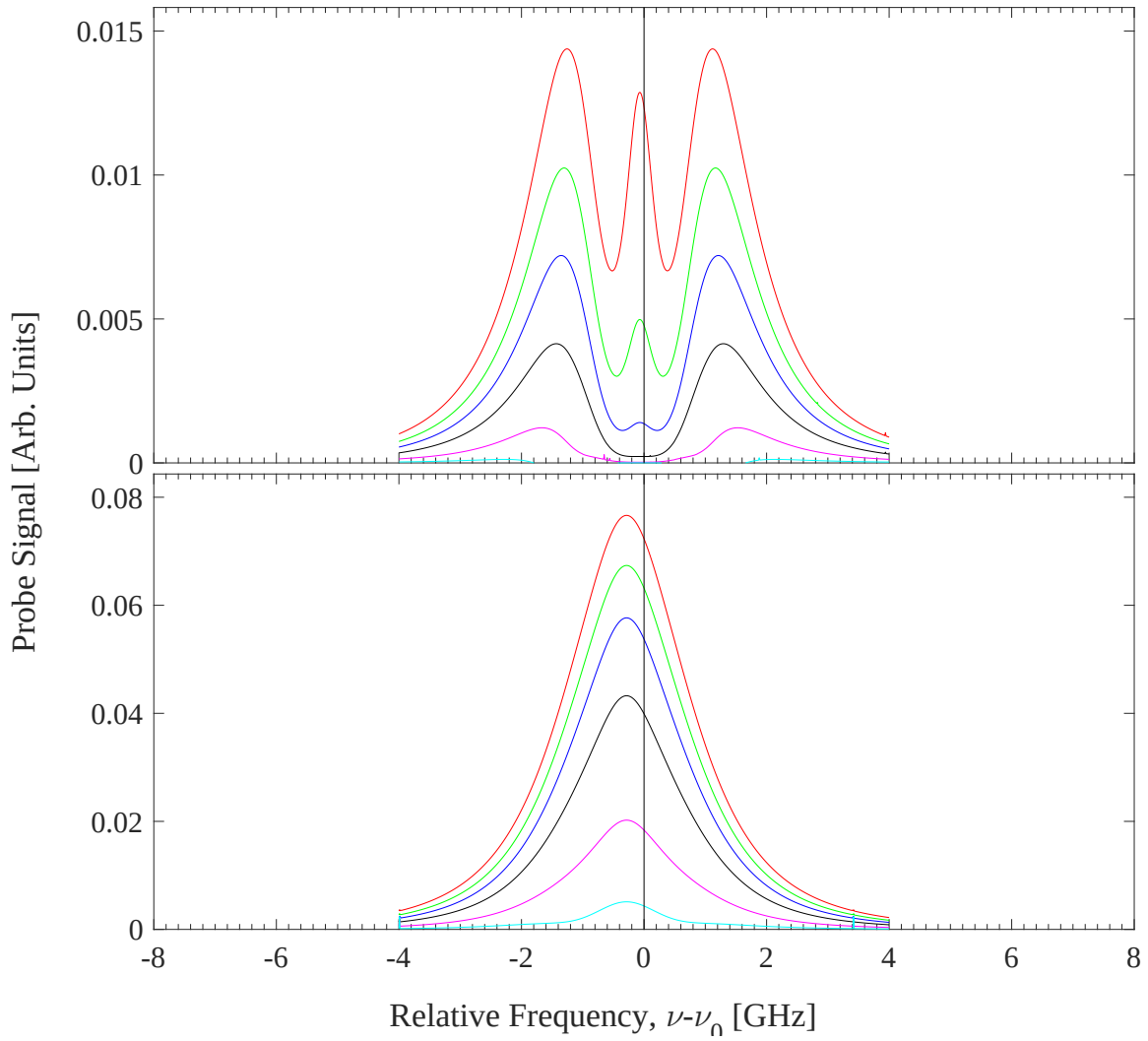


Figure 45. The output of the line shape model is shown for 5 (a) and 50 (b) Torr and for incident laser intensities of 17.7 (—), 14.1 (—), 10.6 (—), 7.1 (—), 3.5 (—), 1.8 (—) W/cm². Increasing the laser intensity leads to a more saturated line shape resulting in less absorption of the probe beam in the core. Both the 5 and 50 Torr predictions are red-shifted due to pressure effects with a stronger influence of the 50 Torr case, as expected.

several ways. Considering the line shape is likely the result of spatial variation in the Ar ($1s_5$) number density as well as the electron density, spatially-dependent number densities and absorption cross-sections could be substituted in place of those given above, which would result in the absorption coefficient being radially or longitudinally dependent. The spatial dependencies of both the Ar ($1s_5$) and electron densities would have to be analyzed, however, using spatially resolved laser absorption spectroscopy. This would require experimentation not conducted in this work and so it is left to a future analysis.

6.5 Conclusion

Saturation spectroscopy was conducted in an optically thick Ar plasma. The expected line shape consisted of a single, narrow Lorentzian centered on a Doppler pedestal, consistent with a sub-Doppler spectrum in the presence of velocity-changing collisions. The observed structure was that of a multi-peak line shape where the Lorentzian core appeared to be centered on a recessed pedestal. The structure was discovered to be due to the plasma opacity relative to the transmitted probe intensity and was characterized using laser absorption spectroscopy and inter-modulated fluorescence spectroscopy. The line shape was observed for Ar pressures of 1.3 to 50 Torr, pump laser intensities of 1.8 to 17.7 W/cm², probe intensities of 0.1 to 1.8 W/cm² and RF powers of 1 to 40 W. Increased laser power was shown to correlate with increased probe transmission, especially about the core of the line shape, reducing the influence of opacity due to more saturation of the pump volume. The opaque line shape was observed at all powers for the low pressure tests but only resulted at RF powers greater than 25 W for the high pressure cases, consistent with the level of opacity measured by the LAS experiment. At the lowest measured pressures (1.3, 3.6 Torr) the Doppler-limited line shape was shown to be non-Voigt-like and well described by

a dual-Voigt profile with a second shifted and broadened peak. The source of this structure may be from the spatial inhomogeneities of the plasma or from coupling of the high-intensity laser field and the ions and free electrons in the plasma.

A line shape model was developed that used the laser propagation equation combined with an absorption coefficient for co- and counter-propagating beams derived from the rate equations for an equivalent two-level system. The resulting line shape was shown to have good qualitative agreement with the observations and can be extended in the future to consider more complex plasma features, such as spatial inhomogeneity.

The high absorbance measured in these spectra is a positive result for the DPRGL. Optically-thick conditions are caused directly by the number density of the ground state which will need to be greater than 10^{13} cm^{-3} for efficient operation and while this work does not reach this order of magnitude, it does display a moderate increasing trend of the number density as a function of the RF power. Most of the complex structure associated with the sub-Doppler spectra is expected to be resolved by the shift away from a Voigt profile to a simple Lorentzian at high pressure. Spatial inhomogeneities in the plasma would result in spatial variations of the output laser intensity leading to a reduced beam quality. Coupling between the electromagnetic field of the laser and the plasma could either be a boon, if it were to cause increased production of the metastable state within the pump beam, or a detractor if increased ionization along the laser path causes laser-induced arcing. In the latter case, this arcing threshold would set an upper bound for the maximum pump intensity of the DPRGL. More research must be conducted on this subject in order to fully understand this phenomena and to discover exactly how it will influence the rare gas laser system.

VII. Role of adiabaticity in controlling alkali metal fine structure mixing induced by rare gases

Abstract

The collision cross-sections for alkali metal-rare gas spin orbit mixing between the $n^2P_{3/2} \rightarrow n^2P_{1/2}$ levels trend strongly with the Massey parameter, or adiabaticity of the collisions. The strength of the interaction, as characterized by the C_6 dispersion coefficient, is a secondary influence on the rates. An analytic expression for the probability of energy-transfer in alkali-rare gas collisions is derived using time-dependent perturbation theory. The model agrees well with a broad literature survey of the observed temperature dependent cross-sections. A simple interaction potential successfully organizes the alkali-rare gas database. The rates become very large for high lying states, as the collisions are quite sudden and the radius of the valence electron is large. In contrast, the highly adiabatic cesium 6^2P mixing rates are 6 to 8 orders of magnitude smaller. The mixing rate for the Rb-He Diode Pumped Alkali Laser (DPAL) system varies from 0.20 to 1.53×10^{-11} cm³/atom-s for $T = 279$ to 893 K.

7.1 Introduction

The diode pumped alkali laser (DPAL) was introduced in 2003 by William Krupke [100] and quickly became a system of great interest for high power applications including laser weapons [142]. Diode laser bars are used to pump the D_2 $^2S_{1/2} \rightarrow ^2P_{3/2}$ transition, and collisional energy transfer to the spin-orbit split $^2P_{1/2}$ state yields lasing on the D_1 $^2P_{1/2} \rightarrow ^2S_{1/2}$ transition in potassium, rubidium or cesium vapor. Multi-kilowatt lasers have been demonstrated [26, 150], the intensity scaled to >7 MW/cm² [85, 177, 119], and performance models developed [70, 72, 10]. Scaling the output power and system efficiency depend critically on pressure broadening

of the pump transition to optimize spectral overlap between the diode pump and atomic transition [120, 148, 160, 151, 159] and rapid collision induced spin-orbit mixing [62, 149, 169, 161] to prevent bottle necking of the laser cycle. Cycle times as short as 74 ps have been achieved in potassium using helium only as the collision partner [85]. The spin-orbit mixing rates induced by rare gases are smaller in Rb, requiring higher pressures, >10 atm [201], and much smaller in cesium requiring hydrocarbons (methane or ethane) [26]. The heat load associated with this fine structure relaxation will likely control the beam quality for the DPAL device. Temperature gradients induced by non-uniform optical excitation, wall effects, and fluid transport impose concentration gradients and thus phase variations across the laser beam profile. A full assessment of the system performance requires temperature dependent rate coefficients for both line broadening and fine structure mixing processes. Our broad objective is to unify the DPAL kinetics via interaction potentials [24, 50], anchored to asymmetric line shape observations [120, 23, 71, 93], capable of predicting the temperature dependent fine structure mixing rates [62, 65]. The maturity of the DPAL kinetic database might then approach that achieved for the HF chemical laser, where well developed interaction potentials are capable of predicting disposition of reaction exothermicity into ro-vibrational population distributions [86] and the Schwartz, Slawsky and Herzfeld (SSH) theory successfully predicts the vibrational-to-translational energy transfer rates [204].

The spin-orbit mixing rates of alkali atoms in collisions with rare gases have been measured in significant number since the early 1960s [62, 169, 12, 41, 34, 89, 99, 146, 147, 144, 140, 55, 84, 127, 116, 199, 210, 178, 179, 15, 111, 87, 109, 22, 65] with a strong effort towards developing a theoretical foundation for predicting the cross-sections of non-adiabatic collisions starting much earlier [102, 101, 206, 164, 128, 129, 43, 83, 157, 113, 42, 114, 152, 130, 136, 156, 59, 141, 158, 46]. More recently, the

experimental focus has shifted to higher lying Rydberg states, the closely spaced n^2D states, and alkali-alkali collisions [108, 198, 87, 38, 22] and quantum scattering calculations [189, 107]. With the dramatic progress in scaling the DPAL power, a resurgence of interest has arisen in the temperature dependence of the fine structure mixing rates for the lowest ^2P states of K, Rb, and Cs. The broadest experimental study of the temperature dependent mixing rates were measured almost 50 years ago [62]. Only recently have ab initio potentials and a full quantum mechanical treatment been used to predict temperature dependence of the cross-sections [107]. However, strong sensitivity to the interaction potential leads to discrepancies with the observations.

Krause described the interaction between an alkali atom and a rare gas perturber qualitatively in terms of the Massey parameter, or adiabaticity [99]. The interactions of lithium, sodium, and potassium with both heavy and light rare gases is expected to be non-adiabatic and cannot be treated with Zener's semi-classical calculation [206]. This is in contrast to the Rb and Cs interactions with heavy rare gases, which can be considered adiabatic due to low relative velocity and large spin-orbit splitting. Krause does not further develop this relationship between the adiabaticity and magnitude of the cross-section. He does observe that the collisional cross-sections do not increase monotonically as might be expected from the polarizability of the rare gas partner, but rather a dip at neon and then a slow increase to Xe. Gallagher followed up on Krause's work by measuring the temperature dependence of spin-orbit mixing rates for the first excited P states of Rb and Cs in interactions with the rare gases [62]. He introduces time-dependent perturbation theory to treat the collision of two atoms but, like Krause, does little to advance this concept further and instead develops an empirical explanation for the trends in the Rb and Cs cross-sections in terms of the reduced mass adjusted temperature [62]. A recent literature review for the

temperature dependence of the Cs-He, Ar mixing rates suggests a different T^2 to $T^{1/2}$ dependence [189].

Utilizing Krause’s idea of adiabaticity [99] along with Nikitin’s physical model [130] and Masnou-Seeuws’ approach [113], this work develops a theoretical expression for the cross-section. We proceed with a development similar to Masnou-Seeuws in that we use a modified interaction potential and a straight-line trajectory in a time-dependent perturbation theory derivation of the energy transfer probability and drive the model using the cross-sections collected from the literature. Organizing the cross-sections using adiabaticity reveals all the behavioral trends observed by Gallagher, Krause and Elward-Berry. The present study provides the theoretical framework for the empirical scaling with adiabaticity we previously reported [58]. Using a single adjustable parameter, the temperature dependence of the fine structure mixing rates for all alkali excited states induced by rare gas collisions is developed.

7.2 Review of fine structure mixing rates

The fine-structure mixing rates have been measured for Li(2p)[55], Na(3p)[89, 147, 140], K(4p)[34, 89, 99, 116], K(5p)[15], Rb(5p)[169, 12, 99, 146], Rb(6p)[172, 127], Rb(7p)[127], Cs(6p)[41, 99], Cs(7p)[127] and Cs(8p)[144] in collisions with all of the rare gases at a fixed temperature. The temperature dependence of the rates has been measured for the Rb(6p)-He, Ne, Ar, Kr, Xe, Cs(6p) - He, Ne and Cs(7p) - He, Ne, Ar, Kr, Xe interactions [62, 169, 173]. We evaluate a total of 203 experimental cross-sections from the literature. Pulsed and cw laser induced fluorescence techniques typically resolve the D_1 and D_2 fluorescence as a function of added buffer gas pressure. Alkali densities are kept below 10^{-5} Torr to prevent self-absorption. Temperature dependent measurements require increasing the gas temperature without dramatically increasing the alkali density. Observed rate coefficients are divided by the mean

relative velocity to provide thermally averaged cross-sections for the inelastic collision. Reported uncertainties typically range from 10-50%. Fig. 46 provides a summary

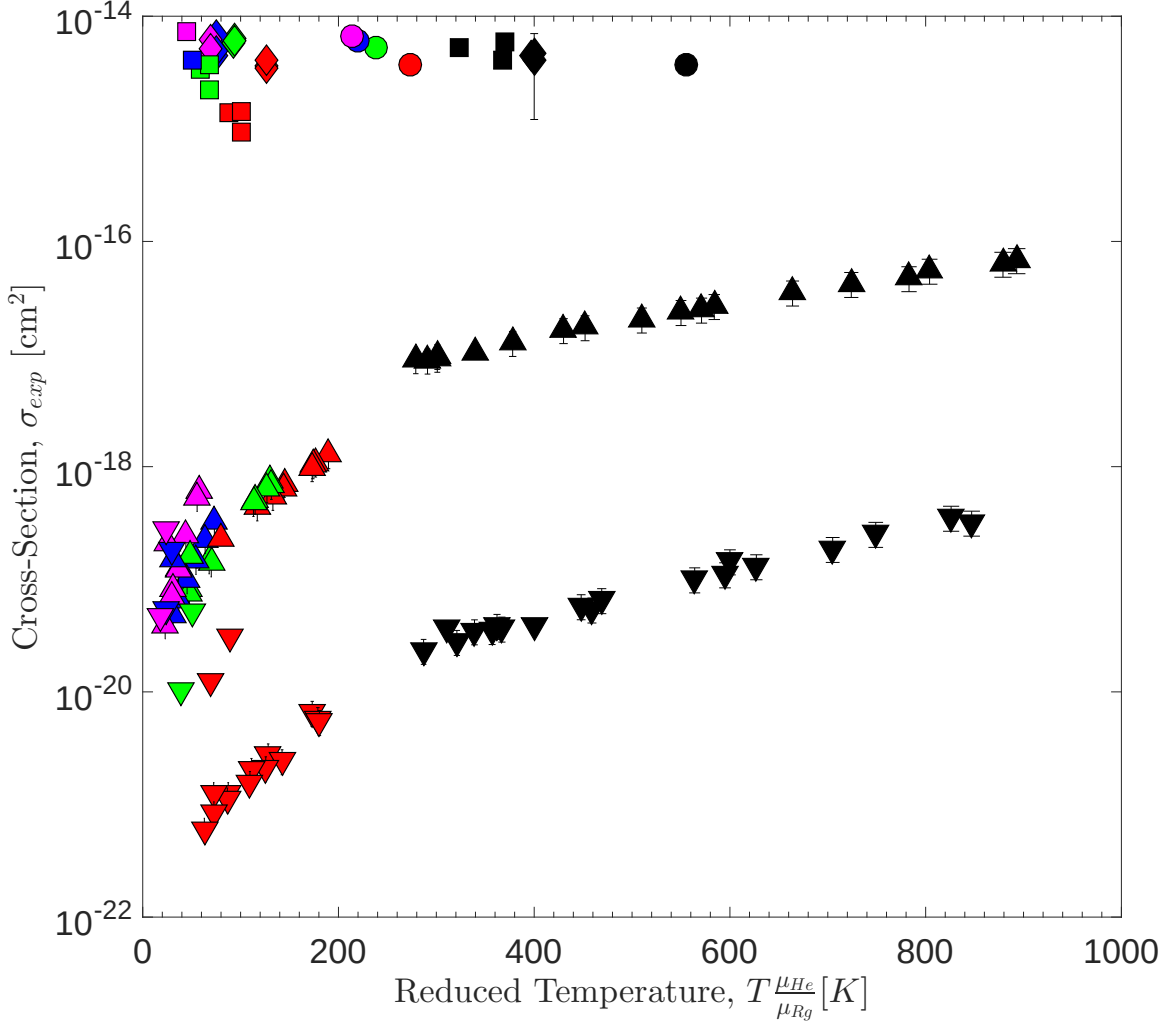


Figure 46. The experimental cross-sections for the fine structure transition between the 1st excited P states are correlated with the reduced temperature. The different alkali are given by $\circ$ - Li, $\diamond$ - Na, $\square$ - K, $\triangle$ - Rb, ∇ - Cs with the colors corresponding to He (black), Ne (red), Ar (green), Kr (blue) and Xe (magenta). The cross-sections have a large decrease as a function of the spin-orbit splitting and a smooth decrease as a function of temperature for a given alkali-rare gas pair.

of the temperature dependent mixing cross-sections for the first excited P states. The temperatures are scaled by the collision pair reduced mass, μ_{Rg} , relative to the reduced mass of the He-alkali pair, μ_{He} , as originally proposed by Gallagher [62]. This reduced temperature accounts for the different relative velocity distributions of the

various rare gas partners and improves the correlation of the observed cross-sections. Several trends are readily identified. First, the cross-section for the heavier alkali-rare gas pairs increases with temperature. Second, Li, Na, and K exhibit much larger, near gas kinetic cross-sections. The fine structure splitting of the first excited P states are 0.34, 17.2, 57.7, 237.6, and 554 cm^{-1} for Li, Na, K, Rb, and Cs, respectively, and the rates decrease dramatically with larger fine structure splitting. Finally, for a given alkali, the cross-sections generally decrease from He to Ne, then increase for the heavier, more polarizable rare gases. While Fig. 46 only shows the values for the first-excited P states for clarity, all measured cross-sections roughly decrease by an order of magnitude as the spin-orbit splitting of the alkali increases from K to Rb to Cs. While the reduced temperature employed in Fig. 46 organizes the cross-sections by alkali it fails to organize the data by alkali-rare gas pairs as the full set of cross-sections do not appear to be correlated by the single variable, reduced temperature.

For a better correlation to the cross-sections, we turn to a modified Massey parameter, or adiabaticity, given by:

$$\xi = \frac{\tau_C}{\tau_N} = \frac{fL}{\bar{v}} \quad (92)$$

where τ_C is the duration of the collision (atom-atom interaction time), $\tau_N = 1/f$ is the oscillation lifetime defined by the spin-orbit splitting, $\Delta E_{fs} = hf$. The duration of the collision, τ_C may be evaluated as the interaction length, L , relative to the mean velocity of the alkali-rare gas collision pair, $\bar{v}$.

In addition to the adiabaticity, we define an energy transfer probability per collision by dividing the experimental cross-section, σ_{exp} , by the quantum-defect cross-section. The quantum-defect cross-section is representative of the hard-sphere cross-section where the size of the alkali atom corresponds to the expectation value of the position of the valence electron, defines as

$$\langle r \rangle = a_0 (n^*)^2 \left(1 + \frac{1}{2} \left(1 - \frac{l(l+1)}{(n^*)^2} \right) \right) \quad (93)$$

where l is the orbital angular momentum quantum number. The alkali state is assumed to be described by hydrogenic wave functions, with a_0 as the Bohr radius. The effective quantum number is then defined as

$$n^* = \sqrt{\frac{E_{Ryd}}{I - E}} \quad (94)$$

where E_{Ryd} is the Rydberg constant and $I - E$ is the energy gap between the level of interest, E , and the ionization potential, I . The quantum-defect cross-section is then given by,

$$\sigma_{QD} = \pi (r_{Rg} + \langle r \rangle)^2 \quad (95)$$

where r_{Rg} is the radius of the rare gas atom as derived from viscosity data [88, 78] and summarized in Table 5. The probability for population transfer from $^2P_{3/2} \rightarrow ^2P_{1/2}$ is then given by

$$P = \frac{\sigma_{exp}}{\sigma_{QD}} = \frac{k_{exp}}{\bar{v}\sigma_{QD}} \quad (96)$$

where k_{exp} is the rate coefficient. The values of σ_{QD} used are given in Table 6. Using

Table 5. Rare gas radii (r_{Rg}), in Bohr, derived from viscosity data [88, 78] and polarizability (α_{Rg}) [5], in atomic units, are provided.

Rare Gas	Radii (r_{Rg}) (Bohr, a_0)	Polarizability (α_{Rg}) (A.U., a_0^3)
He	1.68	1.38
Ne	1.99	2.66
Ar	2.81	11.1
Kr	3.19	16.7
Xe	3.75	27.3

Table 6. Quantum defect cross-sections for alkali-rare gas pairs, $\sigma_{QD}[10^{-15}cm^2]$

	He	Ne	Ar	Kr	Xe
Li (2p)	3.65	4.01	5.04	5.56	6.37
Na (3p)	4.83	5.24	6.41	6.99	7.90
K (4p)	5.88	6.33	7.61	8.25	9.23
K (5p)	24.46	25.38	27.88	29.09	30.91
Rb (5p)	6.46	6.93	8.27	8.93	9.95
Rb (6p)	26.35	27.30	29.90	31.15	33.03
Rb (7p)	73.75	75.33	79.60	81.64	84.67
Cs (6p)	7.20	7.70	9.11	9.80	10.87
Cs (7p)	28.75	29.74	32.44	33.75	35.71
Cs (8p)	79.12	80.76	85.17	87.29	90.42

this probability instead of the experimental cross-section improves the correlation with adiabaticity and allows comparison directly to the results of the time-dependent perturbation theory calculation developed in Section III.

Fig. 47 demonstrates that the probabilities for many collision pairs are neatly organized by adiabaticity. While adiabaticity is clearly the primary parameter that controls the probability, it is not the only one. This is apparent in Fig. 47 as only the He and Ne data, excluding the Cs-Ne data, appear to share the same lower bound curve, regardless of alkali collision partner. This curve is well approximated by a power law for the log probability:

$$\ln(P_\xi) = \ln\left(\frac{\sigma_\xi}{\sigma_{QD}}\right) = a - b\xi^c \quad (97)$$

where we refer to P_ξ as the fine structure mixing probability, σ_ξ as the adiabatic cross-section, and the constants' values are $a = 0.76 \pm 0.74$, $b = 3.34 \pm 0.73$, and $c = 0.7784 \pm 0.1$. These fit parameters are improved from our initial scaling report [58] by removing the Cs-Ne interaction which is enhanced by the Ne polarizability above expected values. This cross-section is independent of polarizability and provides

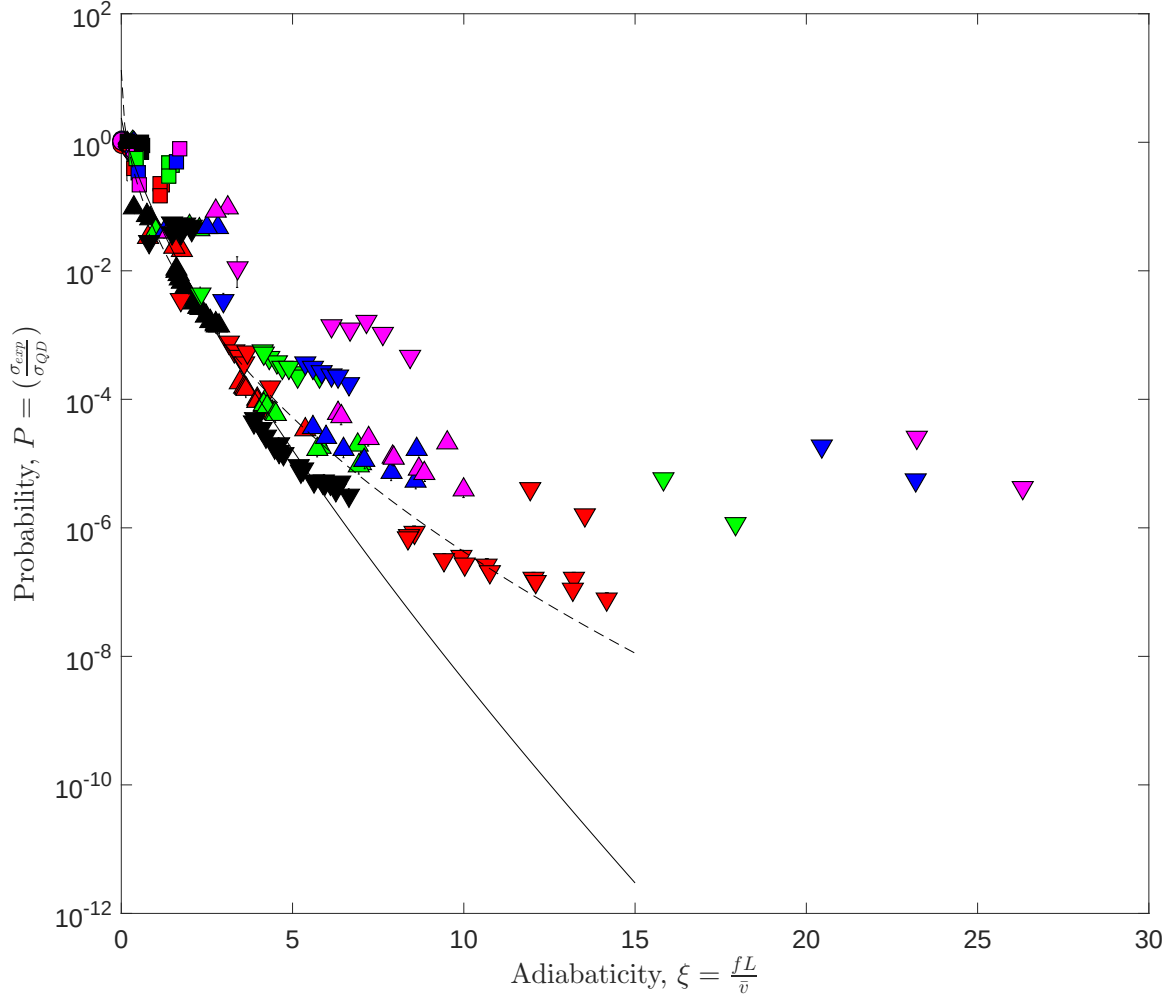


Figure 47. The probabilities are correlated with the adiabaticity with a fixed interaction length, $L = 5\text{\AA}$. The different alkali are given by $\circ$ - Li, $\diamond$ - Na, $\square$ - K, $\triangle$ - Rb, ∇ - Cs with the colors corresponding to He (black), Ne (red), Ar (green), Kr (blue) and Xe (magenta). The solid curve (—) shown is defined by Eq. (97) and the dashed curve (---) is the original empirical fit from [58].

a lower bound for the experimental cross-section, if the interaction was fully governed by adiabaticity.

Some of the probabilities in Fig. 47 are enhanced above the lower bound of Eq. (97). The degree of enhancement increases with both alkali and rare gas polarizability, as shown in Fig. 48. The degree of enhancement is characterized by the ratio of the

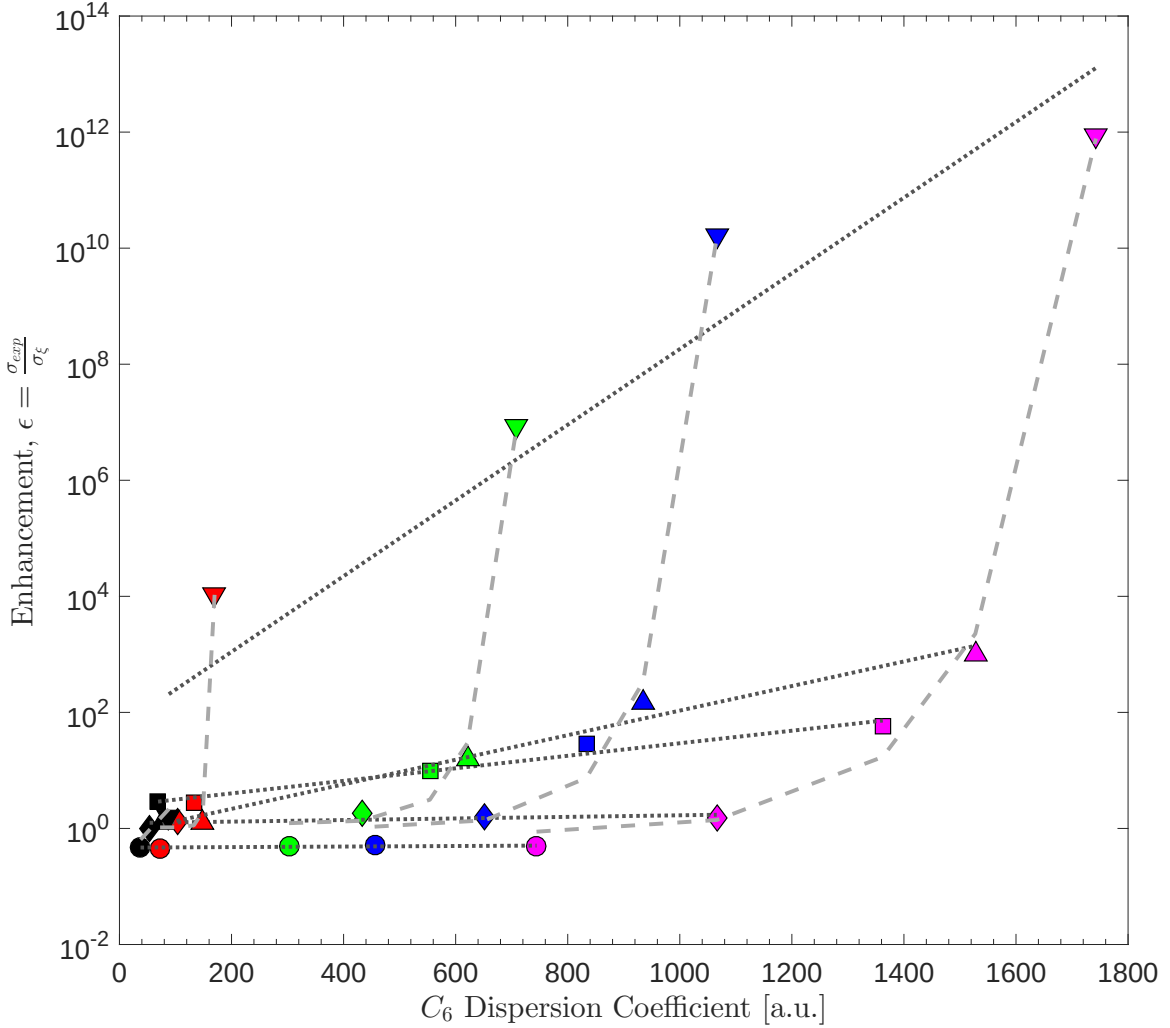


Figure 48. The enhancement is correlated with the C_6 dispersion coefficient. The different alkali are given by $\circ$ - Li, $\diamond$ - Na, $\square$ - K, $\triangle$ - Rb, ∇ - Cs with the rare gases filled with the colors corresponding to He (black), Ne (red), Ar (green), Kr (blue) and Xe (magenta). A linear fit ($\cdots$) for each alkali shows the deviation in cross-section as a function of rare-gas partner. This is in contrast to the exponential fit ($--$) which shows the strong enhancement as a function of alkali partner.

observed cross-section to the empirical lower bound of Eq. (97), $\epsilon = \sigma_{exp}/\sigma_{\xi}$. These

experimental cross-sections vary in temperature for each alkali as measurements at the same temperature do not exist for all alkali-rare gas pairs. The temperatures are: 555 K for Li, 400 K for Na, 323 K for K, 340 K for Rb and 311 K for Cs. The C_6 coefficient determines the strength of the alkali-rare gas interaction potential, $V(r) = C_6/r^6$, at large distances and may be evaluated as [82]:

$$C_6 = -e^2 \langle r^2 \rangle \alpha_{Rg} \quad (98)$$

where e is the electric charge, α_{Rg} is the rare-gas polarizability from Table 5 and $\langle r^2 \rangle$ is the expectation value of the excited state alkali atom radius squared obtained using quantum defect theory together with Eq. (94),

$$\langle r^2 \rangle = \frac{1}{2} (a_0 n^*)^2 [5(n^*)^2 + 1 - 3l(l+1)] \quad (99)$$

A comparison of the empirical C_6 coefficients from the quantum defect theory and recently calculated values for the ground $X^2\Sigma_{1/2}$, and excited $^2\Pi$ potential energy surfaces correlating with the first excited 2^P states [207, 121] are provided in Table 7. The quantum-defect C_6 coefficients, defined in Eq. (98), are chosen for this work. These empirical values are used to correct the long-range behavior of ab initio potentials in order to match observed line broadening and shifting measurements [71]. Furthermore, this development avoids using any calculated potentials or parameters derived from them so that all alkali excited states can be treated identically, an impossible task using ab initio potentials as most calculations focus on the ground and first excited ^2P states. It is worth noting that the quantum defect C_6 coefficients are within 25% of the mean of the coefficients for the excited $B^2\Sigma_{1/2}$ and $^2\Pi_{3/2}$ potential energy surfaces. The probability may be further influenced by the positions and depths of shorter-range wells, location and magnitude of avoided crossings, and

Table 7. Calculated C_6 coefficients, in atomic units, for the ground state, Σ and Π excited states [207, 121] are compared to the quantum-defect coefficients given by equation (98).

Alkali-Rare Gas Pair	$^2S_{1/2}$		$^2P_{3/2}$		
	Calc	Quantum Defect	Calc (Σ)	Calc (Π)	Quantum Defect
Li-He	22.51	23.7	50.71	28.27	37.6
Li-Ne	43.79	45.8	98.22	54.92	72.6
Li-Ar	174	190	401.1	220.1	302
Li-Kr	259.6	287	604.9	329.6	456
Li-Xe	410.7	469	972.8	524.4	744
Na-He	25.76	26	76.94	43.74	53.9
Na-Ne	50.41	50.1	149.2	85.11	104
Na-Ar	196.8	209	608.8	341.3	433
Na-Kr	292.7	315	918.7	512	653
Na-Xe	460.9	514	1479	816.7	1070
K-He	39.49	36	103.3	60.85	68.9
K-Ne	77.44	69.6	200.6	118.7	133
K-Ar	299.3	289	812.7	471.7	553
K-Kr	444.1	437	1223	706	835
K-Xe	697.9	713	1964	1123	1360
Rb-He	44.68	38.8	117.8	70.56	77.2
Rb-Ne	88	75	229	137.9	149
Rb-Ar	336.4	312	924.1	545.1	620
Rb-Kr	498	471	1390	815	936
Rb-Xe	780.1	768	2229	1295	1530

by interaction length, which is not captured by the correlation in Fig. 48.

The enhancement above the adiabatic cross-section increases with both alkali and rare gas. The enhancement is modest, $\varepsilon < 100$, except for Rb and Cs, where the rates are indeed very slow. This enhancement is most significant for a given rare gas and weaker for a given alkali, implying that the influence of the alkali polarizability is larger than that of the associated rare gas. As with the adiabaticity, if the C_6 coefficient were the only factor we would expect Fig. 48 to show all the data correlated to a single curve dependent on the coefficient. As this is not the case, no empirical scaling law can be formed to correct the adiabatic cross-section for the observed increases. Instead, we resort to a time-dependent perturbation theory approach to obtain a theoretical expression for the probability that will be dependent on the interaction potential magnitude, V_0 , and the interaction length, L .

7.3 Non-Adiabatic Collision Theory

The ground $X^2\Sigma_{1/2}^+$ potential energy surface for the alkali-rare gas collision pair correlates to the alkali ground $^2S_{1/2}$ state and the rare gas ground $^1S_0$ state. The first excited alkali $^2P_{1/2}$ state and rare gas $^1S_0$ state yields the $A^2\Pi_{1/2}$ potential energy surface, and the $^2P_{3/2}$ separated atom yields the two potential energy surfaces, $A^2\Pi_{3/2}$ and $B^2\Sigma_{1/2}$. Collision induced transitions between the fine structure split $^2P_{1/2,3/2}$ atomic states occurs primarily due to radial coupling between the $B^2\Sigma_{1/2}$ and $A^2\Pi_{1/2}$ potential energy surfaces. We develop an expression for this fine structure mixing rate by approximating the collisional dynamics as a straight-line trajectory. Position along the trajectory is expressed as a function of time and used to convert the diabatic coupling potential between the $B^2\Sigma_{1/2}$ and $A^2\Pi_{1/2}$ potential energy surfaces to a time dependent perturbation. A detailed description of the interaction Hamiltonian and theoretical development may be found in reference [32]. First order perturbation the-

ory is then used to determine the probability per collision for transferring population from the alkali metal atomic $^2P_{3/2}$ state to the $^2P_{1/2}$ state:

$$P(b, v) = \left| \frac{-i}{\hbar} \int_{-\infty}^{\infty} V(R(t; b, v)) e^{-i\Omega t} dt' \right|^2 \quad (100)$$

where the angular frequency Ω is defined by the fine structure energy difference, $\Omega = 2\pi f = E_{fs}/\hbar$. The collision trajectory $R(t)$ depends on the initial energy and angular momentum, or impact parameter, b , and relative speed, v . The interaction potential, $V(R)$, is defined by the off-diagonal diabatic potential energy surface matrix elements that couples electronic states in the $^2P_{3/2}$ manifold with electronic states in the $^2P_{1/2}$ manifold [32], but will be approximated by an analytic function developed below. When $V(R(t))$ changes more rapidly than the oscillation represented by $\exp(i\Omega t)$, the collision is sudden and the probability is enhanced. If $V(R(t))$ evolves more slowly, the collision is more adiabatic and the integrand averages to near zero.

The predicted rate coefficient is obtained by the sum over all impact parameters and average over relative speeds:

$$k(T) = 2\pi \int_0^{\infty} b db \left[4\pi \left(\frac{\mu}{2\pi k_b T} \right)^{3/2} \int_0^{\infty} dv \left[v^3 e^{-\frac{\mu v^2}{2k_b T}} P(b, v) \right] \right] \quad (101)$$

where k_b is Boltzmann's constant, μ is the reduced mass of the collision pair and T is the temperature. The predicted rate coefficient, $k(T)$, can be compared with the experimentally observed, thermally averaged rate coefficient $k_{exp}(T) = \sigma_{exp}(T)\bar{v}$, where $\bar{v}$ is the average relative speed.

To calculate the probability we must further develop the radial interaction potential $V(R(t; b, v))$. An approximate form for $V(R(t))$ is taken to be a Rectangular-Gaussian; a flat-top function with Gaussian onset. The potential evolves during the

interaction:

$$V_{RG}(t) = \begin{cases} V_0 e^{-\frac{(t+\tau)^2}{2s^2}} & t < -\tau \\ V_0 & -\tau < t < \tau \\ V_0 e^{-\frac{(t-\tau)^2}{2s^2}} & t > \tau \end{cases} \quad (102)$$

with three parameters: the magnitude of the interaction potential, V_0 , the temporal period over which the potential is rapidly changing, s , and the period during which the interaction potential is constant, τ . We assume a straight-line trajectory to relate the interaction length, L , to the interaction period, τ :

$$L^2 = b^2 + v^2 \tau^2 \rightarrow \tau = \pm \left[\frac{(L^2 - b^2)}{v^2} \right]^{\frac{1}{2}} \quad (103)$$

Grazing collisions with $b > L$ yield imaginary τ and are neglected. We note the assumption that s is not a function of velocity and is approximated as $s = \frac{w}{v}$ where w is the length scale for the rapidly changing region of the interaction potential. This is consistent with the idea that nearly head-on collisions are the biggest contributors to the probability. A similar approximation is made in the SSH development for vibrational energy transfer [204]. The utility of this approach to modeling the interaction potential is that V_0 , L , and w can be estimated from available properties such as polarizability, or a single fine structure transition rate measurement performed at a single temperature. As a result, fine structure mixing can be modeled over a wide range of temperatures without explicit knowledge of the ab initio potentials. Also, using this approach, the full set of observations is organized by a few parameters, and temperature dependent rates are predicted from the resulting theory. Validity of the approximate interaction potential will be tested by comparison to the extensive database.

Using Eq. (102,103) for $V(t)$ we can arrive at an analytic form for the fine structure mixing rate, the details of which are only summarized here. See Supplemental

Material at [56] for the full mathematical derivation. The probability for fine structure mixing is evaluated from Eq. (101), using Eq. (102) and (103) to obtain:

$$P(b, v) = \left(\frac{2V_0}{\hbar\Omega} \right)^2 (A^2 \cos^2(\Omega\tau) + 2AB \cos(\Omega\tau) \sin(\Omega\tau) + B^2 \sin^2(\Omega\tau)) \quad (104)$$

where

$$\begin{aligned} A &= \pi^{\frac{1}{2}} \chi e^{-\chi^2} \\ B &= 1 - \pi^{\frac{1}{2}} \chi e^{-\chi^2} \text{Erfi}(\chi) \\ \chi &= \frac{\Omega s}{2^{\frac{1}{2}}} \end{aligned} \quad (105)$$

We define χ in terms of the adiabaticity

$$\chi = \frac{s\Omega}{\sqrt{2}} = \frac{(2\pi)fw}{\sqrt{2}\bar{v}} = \sqrt{2}\pi \frac{w}{L} \xi \quad (106)$$

and integrate the probability over the velocity distribution to yield the analytic expression:

$$\begin{aligned} P(b, T)\bar{v} &= 4\pi \left(\frac{\mu}{2\pi kT} \right)^{\frac{3}{2}} \left(\frac{2V_0}{\hbar\Omega} \right)^2 \left(\frac{kT}{\mu} \right)^2 \times \\ &\times \left[(A^2 + B^2) + (A^2 - B^2)x^2 \sqrt{\pi} G_1(x) + 2AB \sqrt{\pi} \left(x^{\frac{1}{2}} H_1(x) + \frac{2}{3} \sqrt{\pi} x^2 H_2(x) \right) \right] \end{aligned} \quad (107)$$

where $x = \frac{\Omega(L^2 - b^2)\mu}{2kT}$ and G_1 , H_1 and H_2 are the Meijer G and Generalized Hypergeometric functions. The Meijer G function is a further generalization of the Generalized Hypergeometric functions and is a generator for most special functions [11]. We further simplify the above expression by noting that both $(A^2 - B^2)x^2 \sqrt{\pi} G_1(x)$ and $2AB \sqrt{\pi} \left(x^{\frac{1}{2}} H_1(x) + \frac{2}{3} \sqrt{\pi} x^2 H_2(x) \right)$ rapidly approach zero for values of $\xi > 1$. As

most of the alkali adiabaticities are well above this threshold, we proceed by omitting these two terms.

The final step in the calculation is to integrate this probability over the impact parameter. We note that the upper limit to the integral over the impact parameter is reduced to L and as such our perturbation does not account for grazing collisions ($b > L$). This yields the rate

$$\begin{aligned} k(T) &= 8\pi^2 \left(\frac{\mu}{2\pi kT} \right)^{3/2} \left(\frac{2V_0}{\hbar\Omega} \right)^2 \left(\frac{kT}{\mu} \right)^2 (A^2 + B^2) \int_0^L b db \\ &= \left(\frac{8\pi^{1/2}}{2^{1/2}\hbar^2} \right) \left(\frac{V_0^2 L^2}{\Omega^2} \right) \left(\frac{kT}{\mu} \right)^{1/2} (A^2 + B^2) \end{aligned} \quad (108)$$

The rate can then be simplified into the concise form dependent on V_0 , L , ξ and w as

$$k(T) = \frac{V_0^2 L^4}{2\pi\hbar^2\bar{v}} \xi^{-2} (A^2 + B^2) \quad (109)$$

where $A^2 + B^2$ can be written in terms of the Dawson integral, $\mathcal{F}(x) = \frac{1}{2}e^{-x^2}\text{Erfi}(x)$ [1],

$$A^2 + B^2 = 2e^{-4\pi^2(\frac{w}{L})^2} \xi^2 \pi^3 \left(\frac{w}{L} \right)^2 \xi^2 + \left(1 - 2\sqrt{2}\pi \frac{w}{L} \xi \mathcal{F}\left(\sqrt{2}\pi \frac{w}{L} \xi\right) \right)^2 \quad (110)$$

All of the temperature dependence is contained in the expression $\frac{\xi^{-2}}{\bar{v}}(A^2 + B^2)$. The rest of the term establishes the magnitude of this temperature dependence which implies that V_0 and L predominantly act as scale factors for the probability whereas ξ , through $\bar{v}$, and w define most of the temperature dependence.

7.4 Discussion

Fig. 49 shows the results of fitting Eq. (109) to the reviewed literature. These fits were accomplished using a fixed interaction length, L , of 5Å, a fixed onset width,

w , of $3\text{\AA}$, and an interaction potential magnitude, V_0 , left as the only free parameter. The V_0 terms range from 1.3×10^{-5} H for Li(2p)-He to 6.2×10^{-3} H for Rb(5p)-Xe. The expression for the probability effectively captures the observed temperature

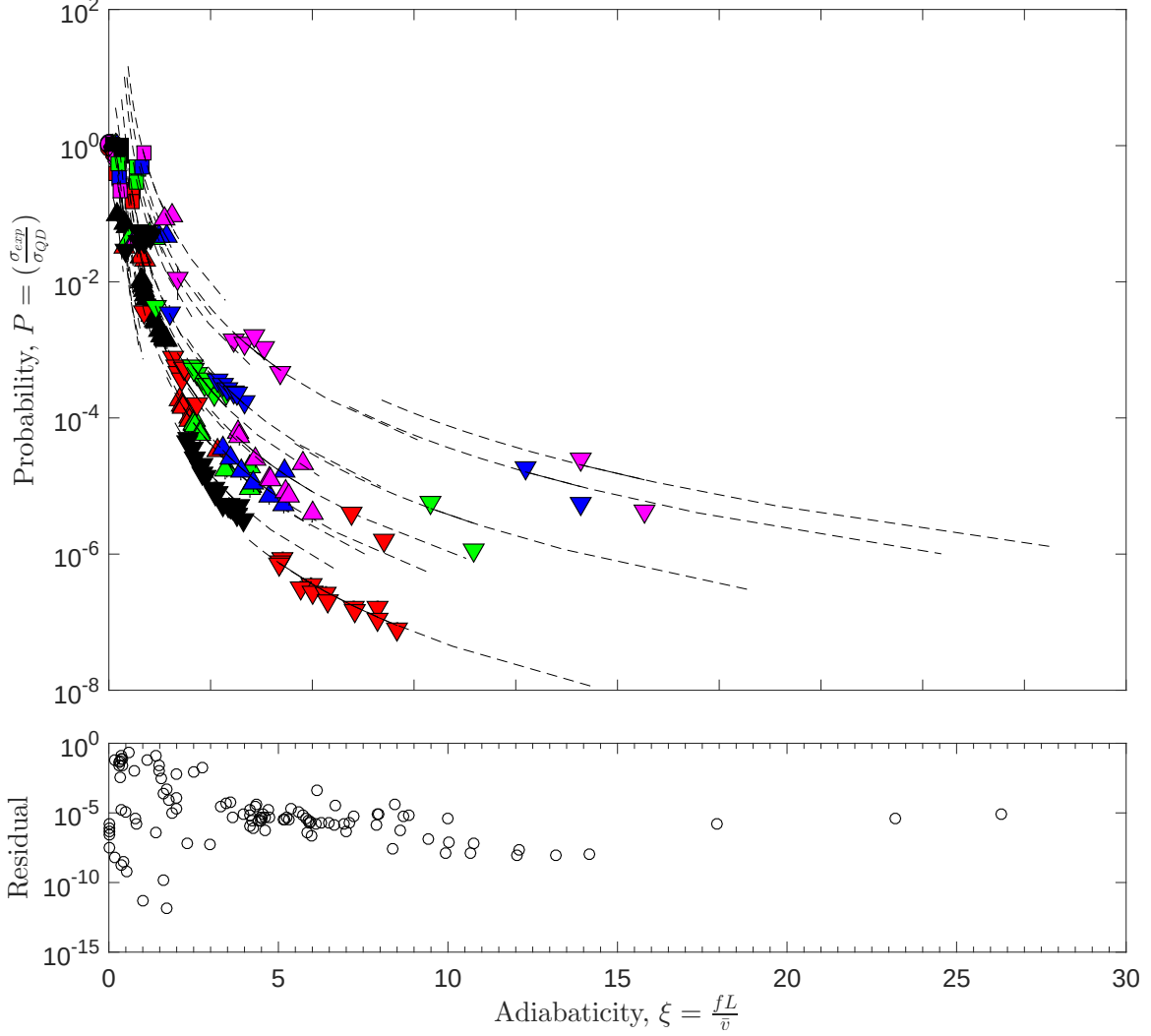


Figure 49. The experimentally measured cross-sections normalized to the quantum defect cross-section are shown as a function of adiabaticity where $\circ$ - Li, $\diamond$ - Na, $\square$ - K, $\triangle$ - Rb, ∇ - Cs with the colors corresponding to He (black), Ne (red), Ar (green), Kr (blue) and Xe (magenta). Residuals of 0.5 correspond to errors of 65%. The symbols are defined by Eq. (96) and the dashed line (--) represents the theoretical prediction, $P(T) = k(T)/(\sigma_{QD}\bar{v})$ where $k(T)$ is given by Eq. (109). The displayed prediction corresponds to a temperature range of 100 to 1000 K. V_0 values range from 1.3×10^{-5} H for Li(2p)-He to 6.2×10^{-3} H for Rb(5p)-Xe.

dependence of the probabilities in spite of the fixed parameters for all the alkali-rare gas pairs. The mean error is $\approx 65\%$, close to the maximum experimental errors of

50% but less than the scatter between distinct measurements of nearly 100%. Given a single measurement for an alkali-rare gas pair to fix V_0 , Eq. (109) has the ability to predict the temperature dependence for that pair to within a factor of two of the measurement error. If the C_6 coefficient is a sufficient surrogate for V_0 then one

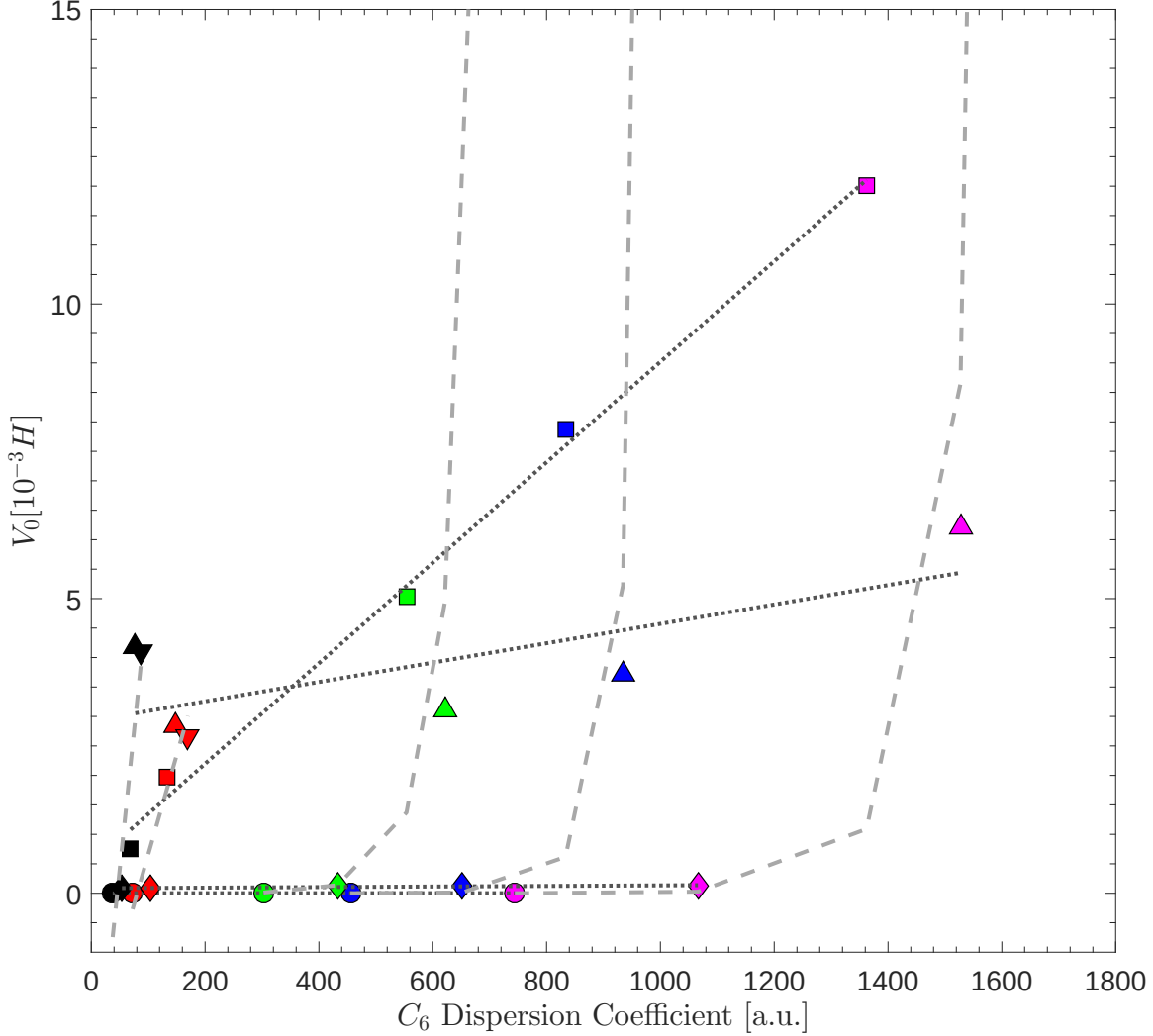


Figure 50. V_0 are plotted against the quantum-defect C_6 coefficients. The different alkali are given by $\circ$ - Li, $\diamond$ - Na, $\square$ - K, $\triangle$ - Rb, ∇ - Cs with the colors corresponding to He(black), Ne(red), Ar(green), Kr(blue) and Xe(magenta). A linear fit ($\cdots$) for each alkali shows the deviation in cross-section as a function of rare-gas partner. This is in contrast to the exponential fit ($---$) which shows the strong deviation as a function of Alkali partner.

might expect the two to be closely correlated. We see in Fig. 50 that this is not necessarily true. In fact, V_0 trends similarly to the enhancement probability shown

in Fig. 48. This is expected as V_0 is the free parameter designed to account for just that dependence. There is one significant deviation between the dependencies of V_0 and the enhancement probability on the C_6 coefficient. The predicted V_0 for the Cs-Ar, Kr, and Xe interactions are anomalously high and have been excluded from Fig. 50. These cross-sections are significantly higher than expected, likely due to a mechanism beyond a simple binary collision modeled in this work. A thorough discussion on the sources of measurement error associated with the Cs-rare gas cross-sections are provided in a recent review of Cs energy transfer measurements [189]. Ignoring the scale of the Cs-Ar, Kr, Xe data, we see that both V_0 and the enhancement probability show the same exponential dependence on alkali polarizability for a given rare gas as well as a linear dependence on rare gas polarizability for a given alkali.

The potentials for the alkali-rare gas interaction have been calculated at the spin-orbit multi-reference configuration interaction level by Blank et al for K, Rb, Cs in collisions with He, Ne and Ar [24]. Fig. 51 shows the calculated diabatic potential energy surfaces compared to the current model predicted potentials. The long-range (> 10 Bohr) form of the model and the calculated potentials are remarkably similar with the predicted potentials decreasing slower due to the large onset width, w . One major deviation between the ab initio potentials and the current modeled forms exist for the Cs-Ar case where the modeled potential is significantly higher in energy, likely driven by the aforementioned three-body effects. In the short range (< 10 Bohr), the ab initio potential vary more drastically from their modeled counterparts. This is driven by the complex interaction of the alkali-rare gas that is overly simplified by our proposed potential structure designed to maintain an analytic form. The current predicted mixing rates are similar to the probabilities computed using a time-dependent wave packet approach [107], as seen in Fig. 52. These calculated quantum mechanical probabilities for the K and Rb cases agree with the predicted

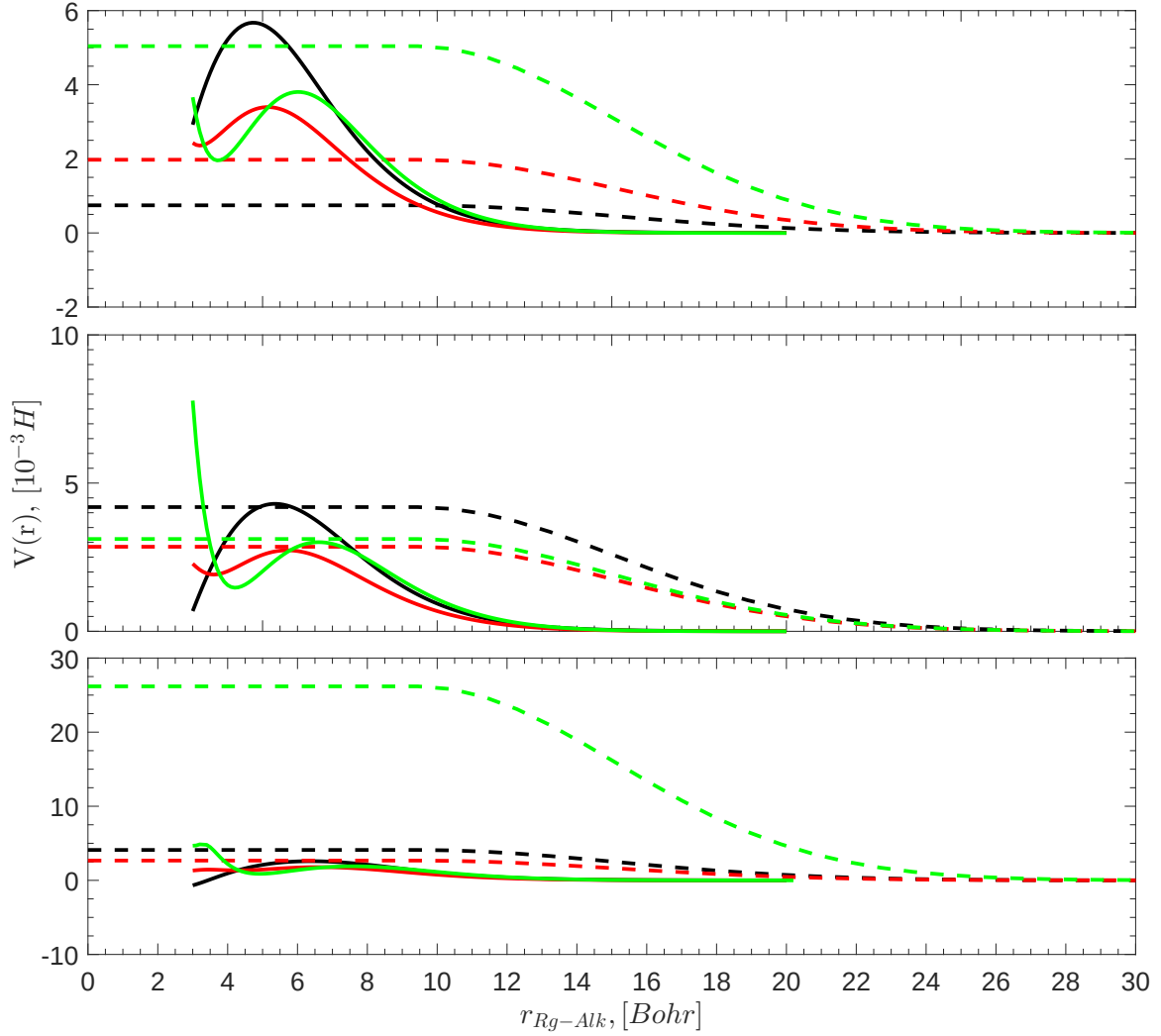


Figure 51. The theoretical (—) and predicted (---) potentials for collisions of K (top), Rb (middle), Cs (bottom) in collisions with He (black), Ne (red), and Ar (green) [24]. The predicted potentials are shallower and wider than the ab initio potentials.

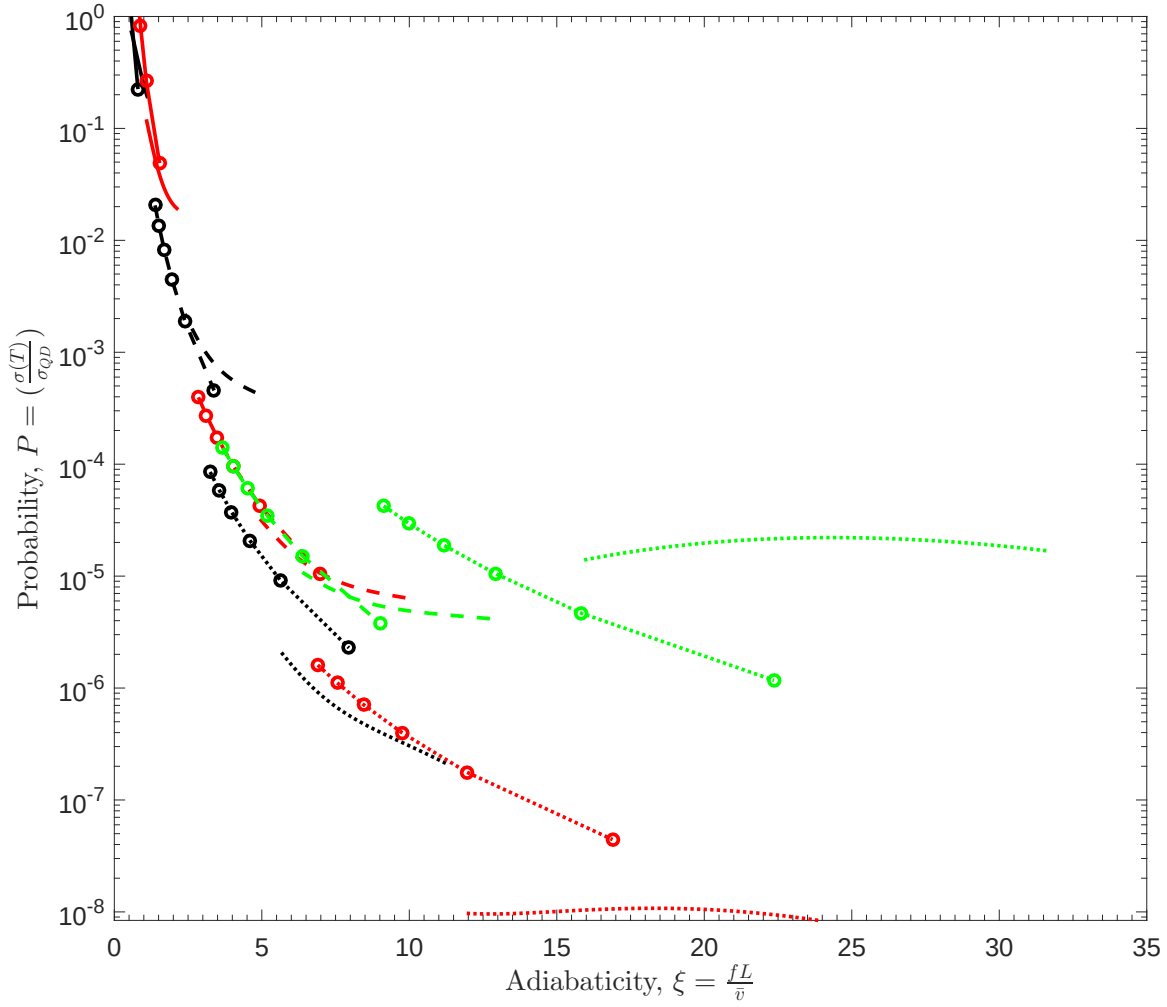


Figure 52. The prediction of Eq. (109) is shown as a line with circle markers corresponding to a temperature range of 100 to 1000 K. The lines without markers correspond to full quantum mechanical calculations of the cross-sections conducted by Lewis et al [107]. The different line types correspond to K (—), Rb (---) and Cs (···) and with colors corresponding to He (black), Ne (red) and Ar (green).

temperature dependence predominantly at higher temperatures. The low temperature behavior is underestimated in the full quantum mechanical development. The Cs-He prediction is closest in temperature dependence but underestimates the overall probabilities by an order of magnitude. The Cs-Ne and Cs-Ar probabilities are also off by approximately an order of magnitude. It is also worth noting that the Cs-Ar prediction is substantially higher than the Cs-Ne prediction, which is consistent with our anomalously high V_0 . These higher fidelity theoretical calculations are very sensitive to the ab initio potential energy surfaces, with accuracy less than 10 cm^{-1} required for collision induced shifts [120, 24]. The advantage of the current semi-classical calculation with approximate potential energy surfaces is the development of a broadly applicable scaling law with only a few empirical parameters.

As an example of the predicted temperature dependent rates, we turn to evaluating the $5^2P_{3/2} \rightarrow 5^2P_{1/2}$ mixing cross-section for the Rb-He DPAL system. Fig. 53 compares the most comprehensive experimental observations for the temperature dependence [62] with the current prediction. Gallagher's very early work [62] remains the best reported temperature dependent values. His fit to the observations employed a two-term temperature dependence:

$$Q(T) = \sum_{i=1}^2 K_i \Gamma(n_i + 2) \left(\frac{2kT}{\mu v_0^2} \right)_i^n \quad (111)$$

where $K_1 = 3.4 \times 10^{-20} \text{ cm}^2$, $K_2 = 490 \times 10^{-20} \text{ cm}^2$, $n_1 = 3$, $n_2 = 0.5$ and $v_0 = 10^5 \text{ cm/sec}$. At $T = 400 \text{ K}$, the mixing rate is $k = 1.92 \times 10^{-12} \text{ cm}^3/\text{atom-s}$, increasing to $2.99 \times 10^{-12} \text{ cm}^3/\text{atom-s}$ at 500 K . At 20 atmospheres of He at 400 K , the mixing time is 1.42 ns , or 18.5 cycles per radiative lifetime (26 ns). The current prediction for the rate coefficient, using the recommended values $L = 0.5 \text{ nm}$, $w = 0.3 \text{ nm}$, and

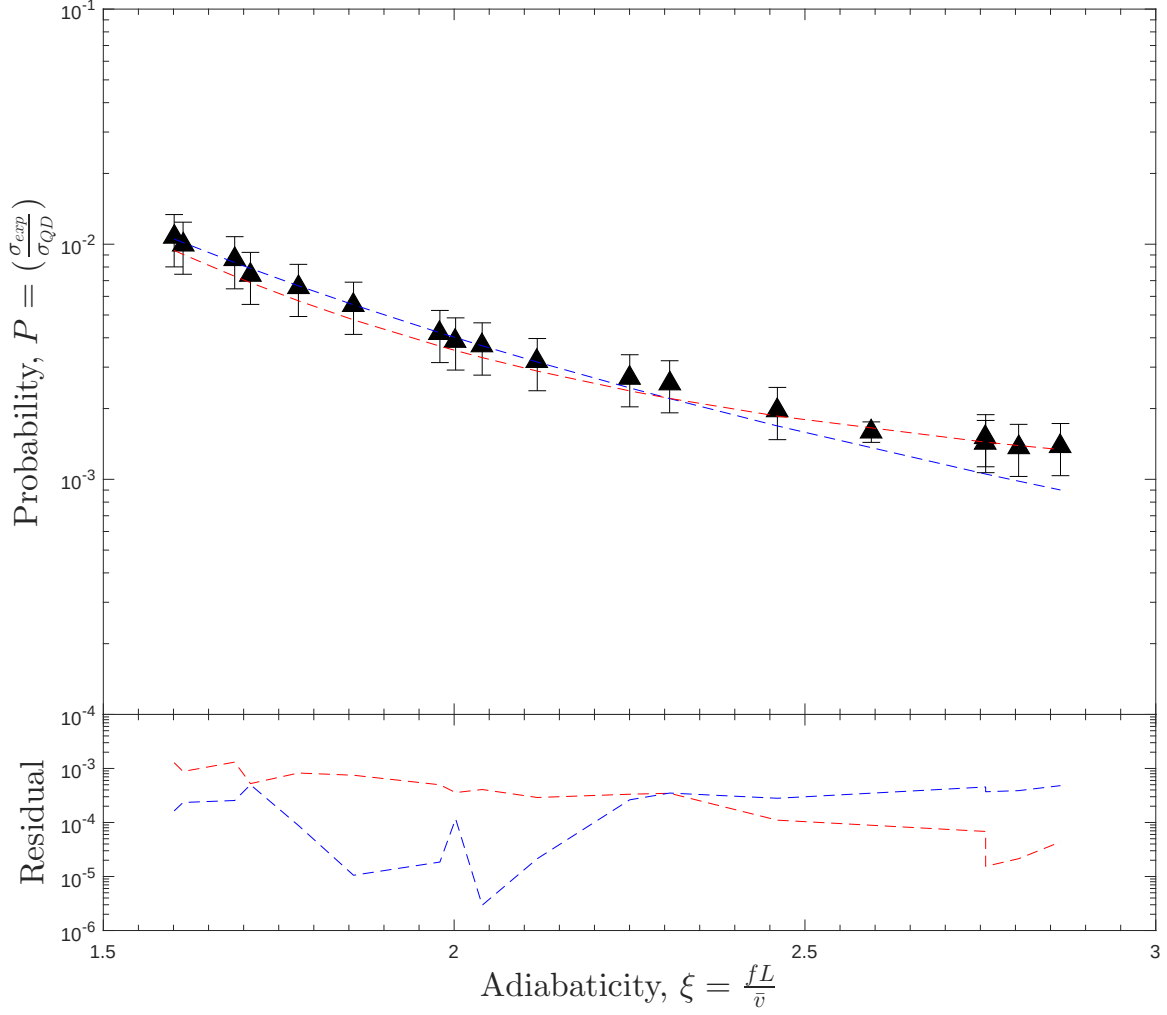


Figure 53. Equations (111) and (112) are compared to the Rb-He probabilities. Gallagher's empirical model, Eq. (111), is represented by the dashed red curve and the current model, Eq. (112), is represented by the dashed blue line. Both models agree to within 30%.

$V_0 = 4.19 \times 10^{-3}$ H is:

$$k(T) = 5.58 \times 10^{-16} \sqrt{T} \left(\frac{51089}{T} e^{-32524/T} + \left(1 - \frac{226}{\sqrt{T}} e^{-16262/T} \operatorname{Erfi}\left(\frac{127.523}{\sqrt{T}}\right) \right)^2 \right) \quad (112)$$

where T is the temperature in Kelvin. This yields the second curve in Fig. 53. The two rates agree to within 30% across the temperature range 279 to 893 K with our prediction yielding more accurate results for temperatures above 400 K. We prefer the current result, as the full alkali-rare gas database is unified with Eq. (109). It is worth noting that at elevated pressures, three-body collisions enhance the rate, Rb-He $k_{3b} = 1.19 \times 10^{-32}$ cm⁶/atom²-s [169].

7.5 Conclusion

The experimental spin-orbit mixing cross-sections have been collected from the literature and reviewed in terms of the adiabaticity and rare-gas interaction. The data show a consistent trend for He, and most of the Ne, probabilities with a positive enhancement from that trend as a function of polarizability. Using an approximate “square-Gaussian” effective potential and a straight-line trajectory in a time-dependent perturbation theory development, an analytic expression for the probability of energy transfer in alkali-rare gas collisions has been derived. The expression is dependent on the magnitude of the effective potential, V_0 , the flat top distance, L , and the onset width of the Gaussian w . A fixed L and w of 5Å and 3Å, respectively, are suitable for matching the complete alkali database. The temperature dependence for any alkali-rare gas cross-section can be extracted from the provided expression if V_0 is used to set the magnitude of the curve. There is good agreement between the analytic model and the full quantum mechanical development at high temperatures

for K and Rb but the data and analytic model show a steeper trend with decreasing temperature than the full numerical approach predicts.

Further testing of this model is required, especially in the non-adiabatic cases of Li, Na and K as well as the extremely adiabatic cases of Cs-Ar, Kr, Xe where temperature dependent rate coefficients have not yet been measured. The formulation may also apply to the mixing of the Halogens for the $^2P_{1/2} \rightarrow ^2P_{3/2}$ transition. However, additional temperature dependent rate measurements will be required. The halogens would be a particularly interesting case as the spin-orbit splittings range from 400 cm^{-1} in fluorine to 7600 cm^{-1} in iodine which corresponds to adiabaticities of 4.3 (F-He) to 360 (I-Xe) at 300 K, a much wider range than in the alkali-rare gas collision of $\xi = 0.0024$ to 26.3;

VIII. Conclusions

This work has involved detailed spectroscopy of the excited states of the rare gases as they pertain to the development of the diode-pumped rare gas system. Towards this end the development of a high-pressure, large-volume discharge was a significant effort in this work. Several discharges were designed and tested to include longitudinal and transverse, radio-frequency capacitively-coupled dielectric-barrier discharges and some minor testing of a micro-cathode sustained discharge array. Most diagnostics were conducted using the longitudinal and transverse designs for ease of operation.

Using phase-sensitive techniques to measure the line shapes, signal-to-noise ratios on the order of 100 were achieved with single-frequency and multi-frequency modulation schemes. This signal-to-noise ratio is a significant improvement over the optical emission methods used to first measure the broadening and shift rates in the late 1970s and early 1980s and facilitates a more careful study of the line shapes. This work contributed the pressure broadening and shift rates for three transitions in collisions with Ar and He with errors below 10% for the 801.699 nm and 795.036 nm transitions which terminate on a metastable lower level and errors below 26% for the 800.836 nm transition which terminates on a resonance level. The shift rates were measured with errors below 25% and 45% for the metastable and resonance cases, respectively. Gas temperature in the plasma was measured using the Doppler width of the Voigt profile which provides a line-of-sight average fit and was found to be approximately 440 ± 20 K. Previous errors varied from 10% to as high as 100% of the published values at a wide variety of temperatures. The broadening and shift rate of the 842.696 nm resonance transition was also measured with errors of 3.1% and 10.5% at a temperature of 320 ± 20 K. The measured rates are summarized in Tab. 8. Significant residuals were observed in the low pressure line shapes which correspond to non-Voigt behavior which is associated with velocity-changing collisions

Table 8. The pressure broadening and shift rates measured in this work are summarized below. Negative shift values correspond to red-shifts.

λ	T (K)		2.5%	5%	10%	25%	pure Ar
801.699 nm ($1s_5 \rightarrow 2p_8$)	440 $\pm$ 20	$2\gamma/P$ β/P	17.55 $\pm$ 1.11 1.55 $\pm$ 0.26	15.54 $\pm$ 0.6 2.05 $\pm$ 0.35	14.18 $\pm$ 0.65 1.81 $\pm$ 0.30	14.19 $\pm$ 0.61 1.67 $\pm$ 0.3	– –
800.836 nm ($1s_4 \rightarrow 2p_6$)	440 $\pm$ 20	$2\gamma/P$ β/P	16.85 $\pm$ 4.42 1.99 $\pm$ 0.71	16.66 $\pm$ 1.16 2.18 $\pm$ 0.43	17.85 $\pm$ 0.78 0.72 $\pm$ 0.32	– –	– –
795.036 nm ($1s_3 \rightarrow 2p_4$)	440 $\pm$ 20	$2\gamma/P$ β/P	18.91 $\pm$ 1.61 5.38 $\pm$ 0.41	20.32 $\pm$ 1.45 4.04 $\pm$ 0.65	16.59 $\pm$ 1.22 2.94 $\pm$ 0.48	17.54 $\pm$ 0.95 4.61 $\pm$ 0.72	– –
842.696 nm ($1s_4 \rightarrow 2p_8$)	320 $\pm$ 20	$2\gamma/P$ β/P	– –	– –	– –	– –	38.5 $\pm$ 1.2 –1.9 $\pm$ 0.2

and correlations between those collisions and phase-changing collisions.

From these line shapes the behavior of the metastable and resonance densities was also analyzed. The densities were found to be maximal at the lowest pressures and to decrease rapidly with increasing pressure due to a longitudinal contraction of the plasma that results in a shorter path length and a decrease in the production rate of the states. The $1s_5$ metastable level consistently had higher densities generally an order of magnitude larger than the $1s_4$ and $1s_3$ levels. At low-pressures flow velocity and RF power were shown to moderately increase the excited state production but the mechanism that relates the flow velocity to the plasma is not well understood.

This work also examined the behavior of the $1s_5$ state under high intensity fields using sub-Doppler methods which lead to a rich analysis of the sub-Doppler spectra in optically thick media. Laser absorption spectroscopy, a Doppler-limited technique, inter-modulated fluorescence spectroscopy and sub-Doppler saturation spectroscopy, both Doppler-free techniques, were used in order to study the medium. The Doppler-free techniques require the use of two counter-propagating beams, one pump at high intensity and a probe at low intensity. The observed sub-Doppler line shape was modified from the expected form due to opacity in the medium. The inter-modulated fluorescence spectroscopy allowed us to observe the signal as a function of propagation distance and it was found that the probe was significantly attenuated due to absorption in nearly all plasma conditions. This was validated at low-power using the laser absorption spectroscopy technique. The observed structure was then associated with the opacity and was dependent on the RF power, which increases both metastable production and path length, and laser intensity, which reduces the opacity to the probe by saturating the medium. At laser intensities of 15 kW/cm^2 , unusual behavior was observed and is likely a result of coupling between the plasma and the laser beam causing local gradients in the electron density due to modifications of the

local reduced electromagnetic field.

A significant goal of this project was to demonstrate the viability of a rare gas laser system and a five-level model was developed in order to analyze the kinetics and optical physics of the system. The model was parametrized by the electron temperature and density. The absolute magnitude of the populations were found to be dependent predominantly on the electron temperature with their relative values dependent strongly on the electron density and weakly on gas temperature. The model was bench-marked against recent continuous-wave laser demonstrations conducted by PSI. It was then applied to data collected in a discharge that failed to achieve lasing and it was found that there was insufficient metastable density, due to a low electron temperature. An optimal lasing condition was considered and it was found that for a metastable density of $2.5 \times 10^{13} \text{ cm}^{-3}$ and a pump intensity of 10 kW/cm^2 the volume necessary to achieve a 100 kW system is just 36 cm^3 .

In addition to the spectroscopy of the rare gas atoms, an analysis of the alkali-rare-gas spin-orbit mixing cross sections was conducted. The experimental cross sections were converted to probabilities using a quantum-defect-derived cross section and were found to trend strongly with adiabaticity, the suddenness of a collision. The adiabaticity is a function of the interaction length, relative velocity and the spin-orbit splitting with smaller splittings corresponding to less adiabatic, or more-sudden collisions. Deviations from the adiabatic cross-section were observed and correlated with the C_6 dispersion coefficient. Beyond a simple organization of the database, this work developed a temperature-dependent rate using a time-dependent perturbation theory approach to the alkali-rare gas interaction. This theoretical rate was able to match the full experimental database with the use of a single fit parameter. The only other temperature-dependent model was provided by *Gallagher* who provided an phenomenological model requiring four fit parameters and knowledge of the rates.

The rate provided in this work requires only a single measurement to set the absolute scale of the rate and is predictive of the temperature dependence. In a working diode-pumped alkali laser the large pump laser intensities create temperature gradients that can influence laser operation and beam quality making a detailed knowledge of the temperature-dependence of the spin-orbit mixing rates extremely important, particularly to the modeling efforts that try to account for the fluid dynamics as well as the kinetics of the gain medium. The proposed temperature dependence for the Rb-He interaction is given as

$$k(T) = 5.58 \times 10^{-16} \sqrt{T} \left(\frac{51089}{T} e^{-32524/T} + \left(1 - \frac{226}{\sqrt{T}} e^{-16262/T} \operatorname{Erfi}\left(\frac{127.523}{\sqrt{T}}\right) \right)^2 \right) \quad (113)$$

where T is the temperature in Kelvin. This rate is suggested as an improvement over the previous temperature dependent expression and should be used in future calculations of the Rb-He DPAL.

8.1 Future Work

There is still a significant volume of work for the development of the diode-pumped rare gas laser both in regards to the detailed spectroscopy as well as the development of a high-pressure, large-volume discharge. In regards to the detailed spectroscopy, the pressure broadening and shift rates, their temperature dependencies and the details of the low-pressure line shapes are all integral parts to understanding the behavior of the gain medium. These details also serve to inform the *ab initio* potentials that have not yet been calculated in detail for the Ar-He interaction and have only been calculated for a small subset of potential energy surfaces in the Ar-Ar interaction. As there are a significant number of potential surfaces due to the four s states and

ten p states in Ar, a significant effort must be lead for both spectral measurements, kinetic studies and accurate calculations, all necessary to fully characterize the gain medium.

The development of a large-volume, atmospheric-pressure discharge is perhaps the most integral part of the proposed work. Current laser demonstrations have been conducted in high-rep rate pulsed discharges with small volumes (less than 0.5 cm^3) or in cw microwave micro-discharges with miniscule volumes (less than $1 \times 10^{-4} \text{ cm}^3$). Based on the model analysis a volume of 36 cm^3 for a reasonable pump intensity of 10 kW/cm^2 over a 2 cm length at atmospheric pressure is required for a high-energy laser system. It has been made clear that simple discharge configurations where the geometry and driving frequency govern the plasma dynamics are insufficient for the rare gas laser. The solution is in a plasma-reactor type discharge where the efficiency of a microdischarge is leveraged to act as an electron source for a large-volume, atmospheric pressure discharge. The proposed electron source is in the form a microhollow cathode discharge array (MHCDA) run at radio-frequencies, shown in App. D in Fig. 85. The electric field inside these $100 \text{ }\mu\text{m}$ holes is on the order of 100 Td which produces high-energy electrons. This MHCDA is then placed above a third electrode that is positively biased, on the order of 100 V, to extract electrons into the larger volume. A schematic of this discharge as well as several driving circuits can be found in App. D, Fig. 86. The gap between the two plates can be varied from 0.2 to 1 cm and the area is scalable in a simple fashion. This design produces plasmas at volumes on the order of 1 cm^3 easily, with scalability to the order of 10 cm^3 a relatively straightforward endeavor.

Once this discharge has been developed there are a myriad of laser demonstrations that can be conducted as well as scaling analyses similar to what has been conducted for the DPAL over the last 15 years. There has been a fixation with using

the metastable lower level as a ground-state for a DPAL-like three-level laser. This requires significant narrowing of current diode technology which, while already having been achieved, is of great expense for a one-off system. Using the resonance levels, which have high populations due to being radiation trapped, in a pure-Ar discharge may facilitate a less aggressively narrowed diode source. These resonance levels have broadening rates on the order of 40 MHz/Torr for the $1s_4$ level and as high as 100 MHz/Torr for the $1s_2$ level. A complete analysis of all potential lasing cycles and their efficiencies should be one of the first tests conducted once an appropriate discharge has been developed.

In addition to identifying viable laser cycles, the scaling behavior of the plasma must also be studied using high peak intensity pulsed laser systems. Pulsed sources allow us to scale pump intensities to the MW/cm² level facilitating a detailed study of both the scalability of an given laser cycle as well as the coupling between a high intensity laser field and the plasma. This scaling behavior is dependent on the spin-orbit mixing rates between both p states and s states. In order to fully characterize the behavior of the medium, the temperature dependence of these mixing rates is of particular interest and, in the context of Ch. VII, their trends with adiabaticity. An initial analysis indicates that the rates of the Kr and Ar atoms in self-collisions and collisions with He do not show the observed trend as a function of adiabaticity. Indeed, the rates appear to be independent of energy splitting which may point to the diabaticity of the potential energy surfaces, or the significant coupling between the large number of surfaces, as the main driver of the mixing rate, as opposed to the strength of a single avoided crossing.

The rare gas laser system is a viable DPAL alternative that currently only suffers from having an insufficient source of excited state atoms. While complex effects like the coupling between a pump laser and the plasma may serve to limit the peak

efficiency or output intensity of the rare gas laser system, the wavelength diversity available for both strategic and tactical applications cannot be ignored. This may result in niche applications for the rare gas system but the high-gain and low electrical power requirements serve to ensure the viability of the system. All in all, the rare gas laser is a potentially high-reward system given sufficient investment, both financial and in manpower, with the potential to satisfy a significant number of needs from alternative wavelength lasers with efficient atmospheric transmission to a high-energy laser candidate.

Appendix A. Ar-He Five-Level Model Rate Table

The rates for the mechanisms summarized in Fig. 6 are given in the tables below. Tab. 9 provides the Einstein A coefficients for the optical transitions. The term in parenthesis for the $1s_4$ state is the radiatively trapped rate used in the model

Tab. 10 provides the electron-impact excitation rates for production from the ground state to all five levels considered in the model as well as intra-multiplet (p-p), and inter-multiplet (s-p) spin-orbit mixing rates.

Tab. 11 gives the intra-multiplet (s-s and p-p) spin-orbit mixing rates and their corresponding Arrhenius law form used in the model as well as the super-elastic collision rate which acts as the main quenching mechanisms for the Ar-He interaction.

Tab. 12 provides rates for intra-multiplet (s-s and p-p) and inter-multiplet (s-p) spin-orbit mixing rates as well as the super-elastic collision rate, or quenching rate, for the Ar-Ar interaction.

Table 9. The Einstein A coefficients are provided for the states considered in the model. The rate in parenthesis is the radiatively trapped rate used in the model.

Mechanism	Einstein A coefficient, γ (10^7 s^{-1})	Reference
$Ar(1s_4) \rightarrow Ar(1S_0) + He$	11.8 (1.18)	[98]
$Ar(2p_8) \rightarrow Ar(1s_4)$	0.928	[98]
$Ar(2p_8) \rightarrow Ar(1s_5)$	2.15	[98]
$Ar(2p_9) \rightarrow Ar(1s_5)$	3.3	[98]
$Ar(2p_{10}) \rightarrow Ar(1s_4)$	0.543	[98]
$Ar(2p_{10}) \rightarrow Ar(1s_5)$	1.89	[98]

Table 10. The mechanisms and rates are given for the electron impact excitation and spin-orbit mixing of Ar s and p states.

Mechanism	Rate Coefficient, γ (10^{-9} cm ³ /s)	Reference
$\text{Ar}(1S_0) + e^- \rightarrow \text{Ar}(1s_5) + e^-$	$2.7 \text{ Exp} \left(\frac{-11.9}{T_e} \right)$	[209]
$\text{Ar}(1S_0) + e^- \rightarrow \text{Ar}(1s_4) + e^-$	$3.5 \text{ Exp} \left(\frac{-12.3}{T_e} \right)$	[209]
$\text{Ar}(1S_0) + e^- \rightarrow \text{Ar}(2p_{10}) + e^-$	$2 \text{ Exp} \left(\frac{-13.0}{T_e} \right)$	[209]
$\text{Ar}(1S_0) + e^- \rightarrow \text{Ar}(2p_9) + e^-$	$1.9 \text{ Exp} \left(\frac{-13.5}{T_e} \right)$	[209]
$\text{Ar}(1S_0) + e^- \rightarrow \text{Ar}(2p_8) + e^-$	$2.2 \text{ Exp} \left(\frac{-13.6}{T_e} \right)$	[209]
$\text{Ar}(1s_5) + e^- \rightarrow \text{Ar}(2p_{10}) + e^-$	$2.2 \text{ Exp} \left(\frac{-13.6}{T_e} \right)$	[209]
$\text{Ar}(1s_4) + e^- \rightarrow \text{Ar}(2p_{10}) + e^-$	$190 \text{ Exp} \left(\frac{-1.69}{T_e} \right)$	[209]
$\text{Ar}(1s_5) + e^- \rightarrow \text{Ar}(2p_9) + e^-$	$150 \text{ Exp} \left(\frac{-2}{T_e} \right)$	[209]
$\text{Ar}(1s_4) + e^- \rightarrow \text{Ar}(2p_9) + e^-$	$86 \text{ Exp} \left(\frac{-1.85}{T_e} \right)$	[209]
$\text{Ar}(1s_5) + e^- \rightarrow \text{Ar}(2p_8) + e^-$	$86 \text{ Exp} \left(\frac{-1.73}{T_e} \right)$	[209]
$\text{Ar}(1s_4) + e^- \rightarrow \text{Ar}(2p_8) + e^-$	$100 \text{ Exp} \left(\frac{-2}{T_e} \right)$	[209]
$\text{Ar}(2p_8) + e^- \rightarrow \text{Ar}(2p_9) + e^-$	$400T_e^{0.6}$	[209]
$\text{Ar}(2p_8) + e^- \rightarrow \text{Ar}(2p_{10}) + e^-$	$400T_e^{0.6}$	[209]
$\text{Ar}(2p_9) + e^- \rightarrow \text{Ar}(2p_{10}) + e^-$	$400T_e^{0.6}$	[209]
$\text{Ar}(1s_5) + e^- \rightarrow \text{Ar}(2p_4) + e^-$	$100T_e^{0.6}$	[209]

Table 11. The mechanisms and rate coefficients for the Ar-He interaction are given. The rate coefficients in brackets correspond to the Arrhenius law modification made to several of the rates.

Mechanism	Rate Coefficient, γ (10^{-11} cm ³ /s)	Reference
$\text{Ar}(1s_4) + \text{He} \rightarrow \text{Ar}(1s_5) + \text{He}$	$0.01 [30 \text{ Exp} \left(-\frac{2401.91}{T} \right)]$	[75]
$\text{Ar}(2p_8) + \text{He} \rightarrow \text{Ar}(2p_9) + \text{He}$	$4.5 [30 \text{ Exp} \left(-\frac{569}{T} \right)]$	[75]
$\text{Ar}(2p_8) + \text{He} \rightarrow \text{Ar}(2p_{10}) + \text{He}$	$0.4 [30 \text{ Exp} \left(-\frac{1295.25}{T} \right)]$	[75]
$\text{Ar}(2p_9) + \text{He} \rightarrow \text{Ar}(2p_{10}) + \text{He}$	$1.6 [30 \text{ Exp} \left(-\frac{879.36}{T} \right)]$	[75]
$\text{Ar}(2p_8) + \text{He} \rightarrow \text{Ar}(1S_0) + \text{He}$	$0.1 \left(\frac{T}{300} \right)^{0.5}$	[75]
$\text{Ar}(2p_9) + \text{He} \rightarrow \text{Ar}(1S_0) + \text{He}$	$0.2 \left(\frac{T}{300} \right)^{0.5}$	[75]
$\text{Ar}(2p_{10}) + \text{He} \rightarrow \text{Ar}(1S_0) + \text{He}$	$0.0041 \left(\frac{T}{300} \right)^{0.5}$	[75]

Table 12. The mechanisms and rate coefficients are provided for the Ar-Ar interaction.

Mechanism	Rate Coefficient, γ (10^{-11} cm ³ /s)	Reference
$Ar(2p_{10}) + Ar \rightarrow Ar(1s_5) + Ar$	$1.5 \left(\frac{T}{300}\right)^{0.5}$	[209]
$Ar(2p_{10}) + Ar \rightarrow Ar(1s_4) + Ar$	$1.5 \left(\frac{T}{300}\right)^{0.5}$	[209]
$Ar(2p_9) + Ar \rightarrow Ar(1s_5) + Ar$	$3 \left(\frac{T}{300}\right)^{0.5}$	[209]
$Ar(2p_9) + Ar \rightarrow Ar(1s_4) + Ar$	$3 \left(\frac{T}{300}\right)^{0.5}$	[209]
$Ar(2p_8) + Ar \rightarrow Ar(1s_5) + Ar$	$4 \left(\frac{T}{300}\right)^{0.5}$	[209]
$Ar(2p_8) + Ar \rightarrow Ar(1s_4) + Ar$	$4 \left(\frac{T}{300}\right)^{0.5}$	[209]
$Ar(2p_8) + Ar \rightarrow Ar(2p_9) + Ar$	$1.1 \left(\frac{T}{300}\right)^{0.5}$	[75]
$Ar(2p_8) + Ar \rightarrow Ar(2p_{10}) + Ar$	$1.1 \left(\frac{T}{300}\right)^{0.5}$	[75]
$Ar(2p_9) + Ar \rightarrow Ar(2p_{10}) + Ar$	$2.6 \left(\frac{T}{300}\right)^{0.5}$	[75]
$Ar(2p_8) + Ar \rightarrow Ar(1S_0) + Ar$	$1.5 \left(\frac{T}{300}\right)^{0.5}$	[75]
$Ar(2p_9) + Ar \rightarrow Ar(1S_0) + Ar$	$2.5 \left(\frac{T}{300}\right)^{0.5}$	[75]
$Ar(2p_{10}) + Ar \rightarrow Ar(1S_0) + Ar$	$0.59 \left(\frac{T}{300}\right)^{0.5}$	[75]

Appendix B. Pressure Broadening and Shift Data

The figures of data not presented in Ch. IV are provided in this appendix.

B.1 Lineshapes

This section consists of the line shapes presented in a side-by-side format comparing two mixtures for the 795.036 nm and 801.699 nm transitions and in single figures for the 800.836 nm transition. Residuals are presented below each line shape corresponding to a Voigt fit of the measured data.

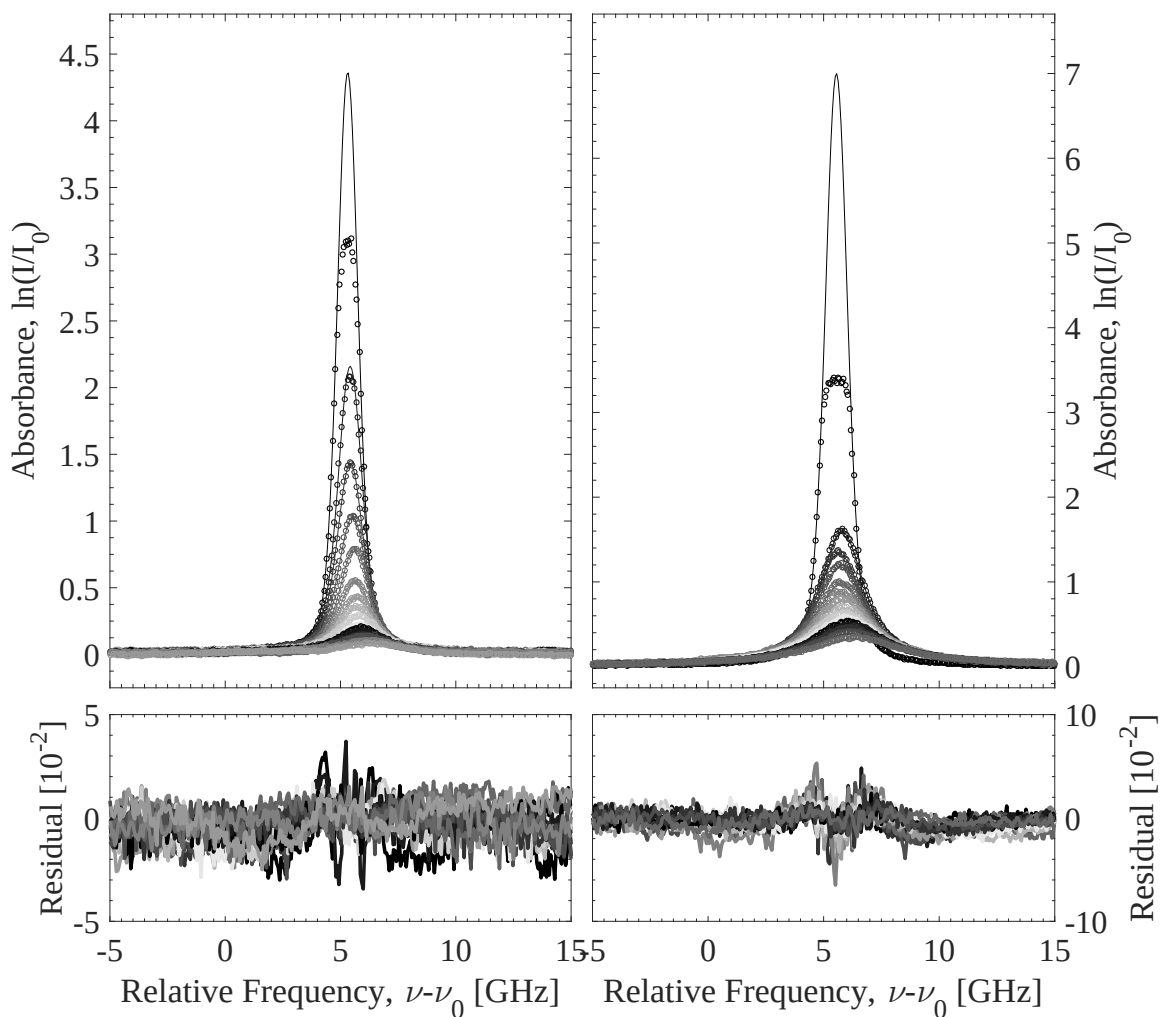


Figure 54. Absorption spectra of 795.036 nm transition line shape in 2.5% (left) and 5% (right) Ar-He mixtures. The pressure increases from 10 to 170 Torr where the 10 Torr case has the highest absorbance and narrowest linewidth.

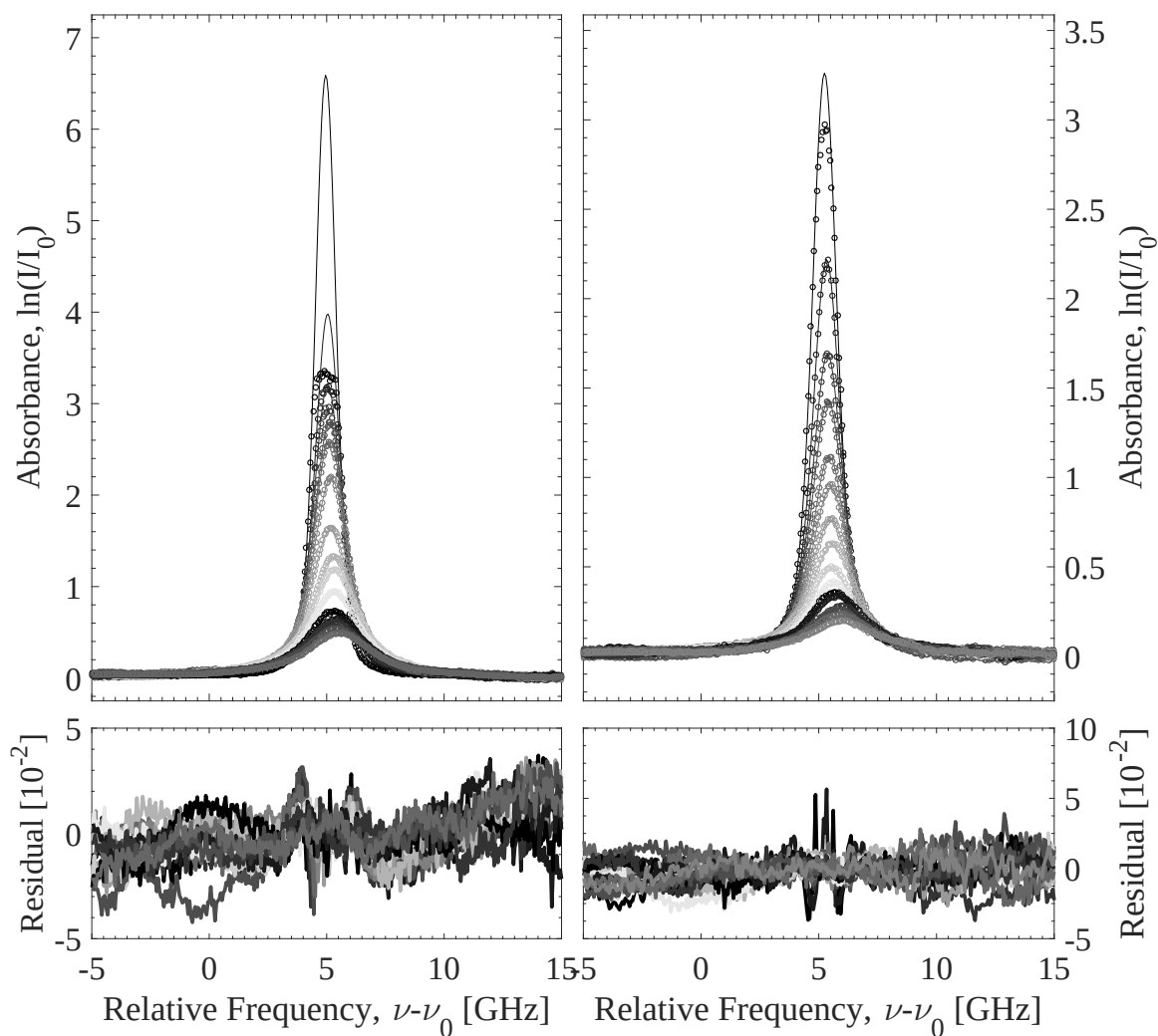


Figure 55. Absorption spectra of 795.036 nm transition line shape in 10% (left) and 25% (right) Ar-He mixtures. The pressure increases from 10 to 170 Torr where the 10 Torr case has the highest absorbance and narrowest linewidth.

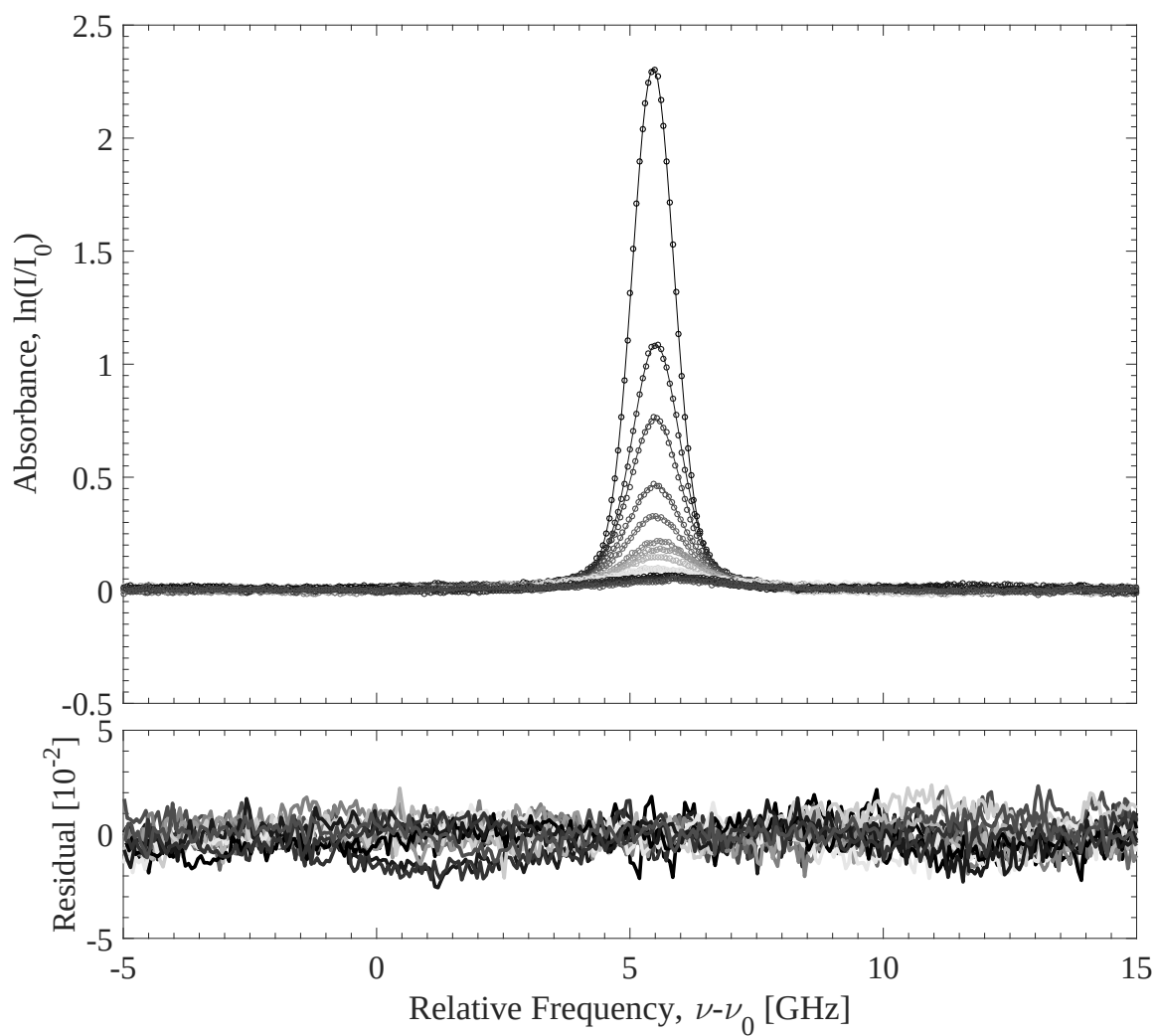


Figure 56. Absorption spectra of 800.836 nm transition line shape in a 2.5% Ar-He mixture. The pressure increases from 10 to 150 Torr where the 10 Torr case has the highest absorbance and narrowest linewidth.

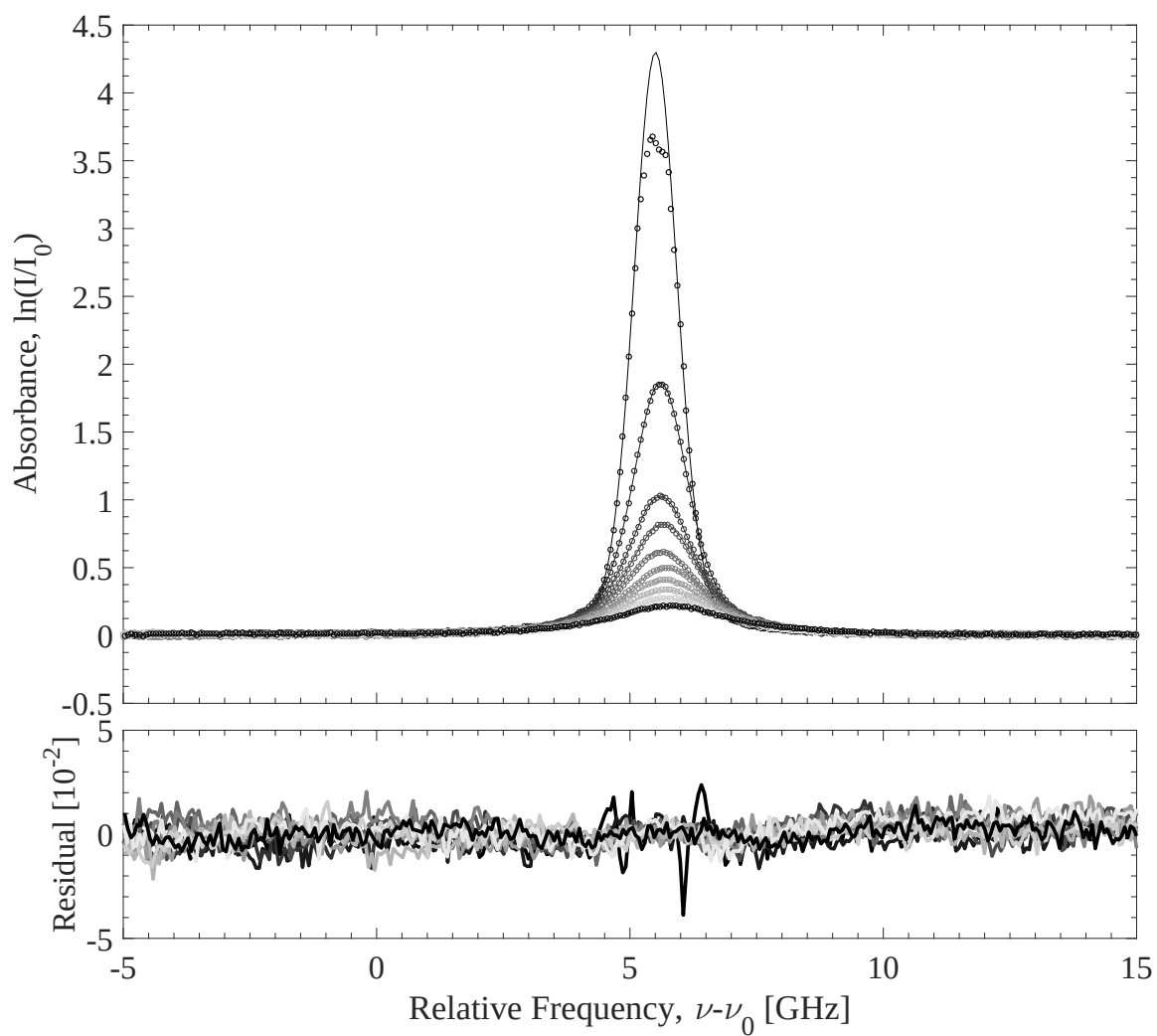


Figure 57. Absorption spectra of 800.836 nm transition line shape in a 5% Ar-He mixture. The pressure increases from 10 to 150 Torr where the 10 Torr case has the highest absorbance and narrowest linewidth.

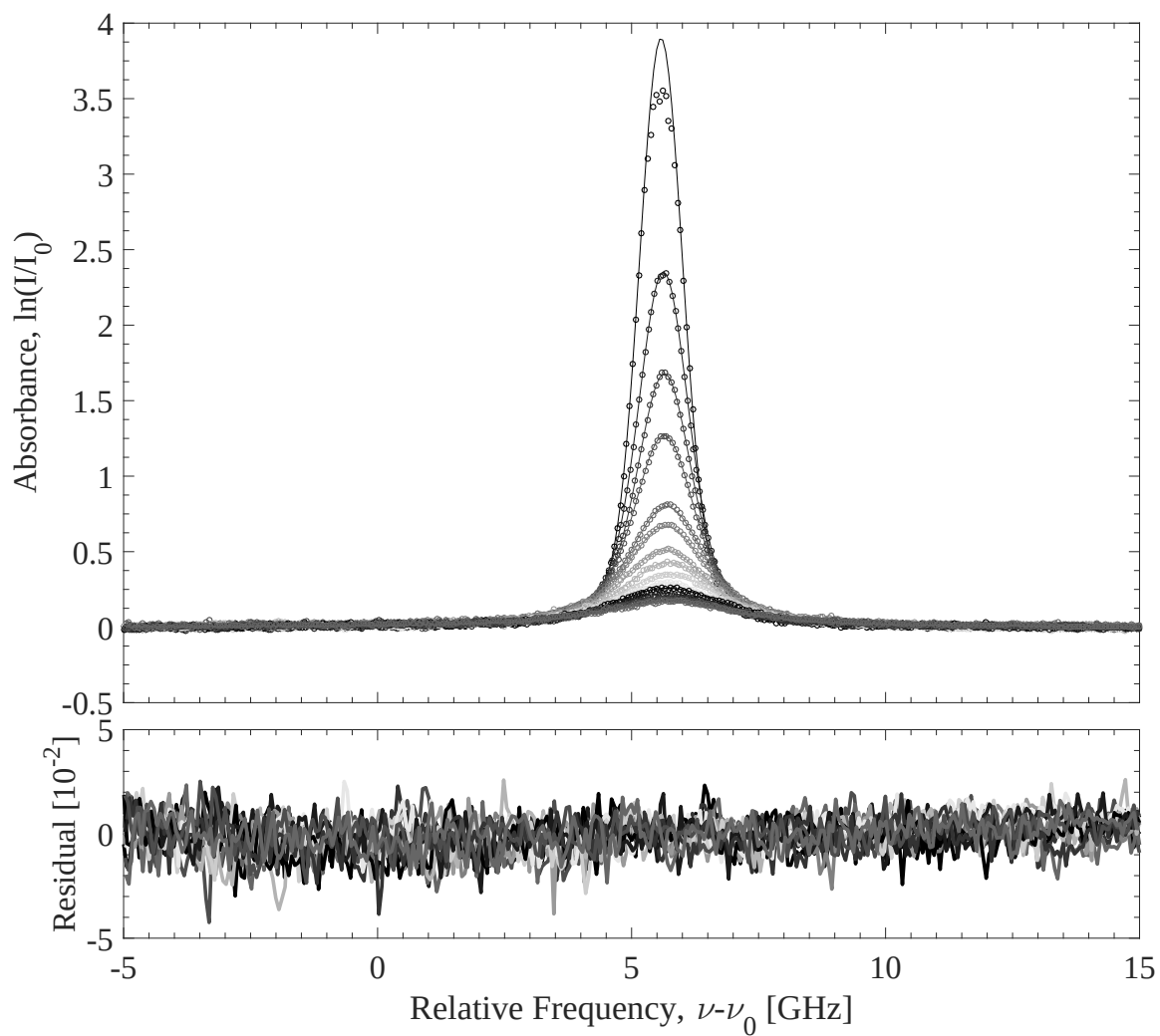


Figure 58. Absorption spectra of 800.836 nm transition line shape in a 10% Ar-He mixture. The pressure increases from 10 to 160 Torr where the 10 Torr case has the highest absorbance and narrowest linewidth.

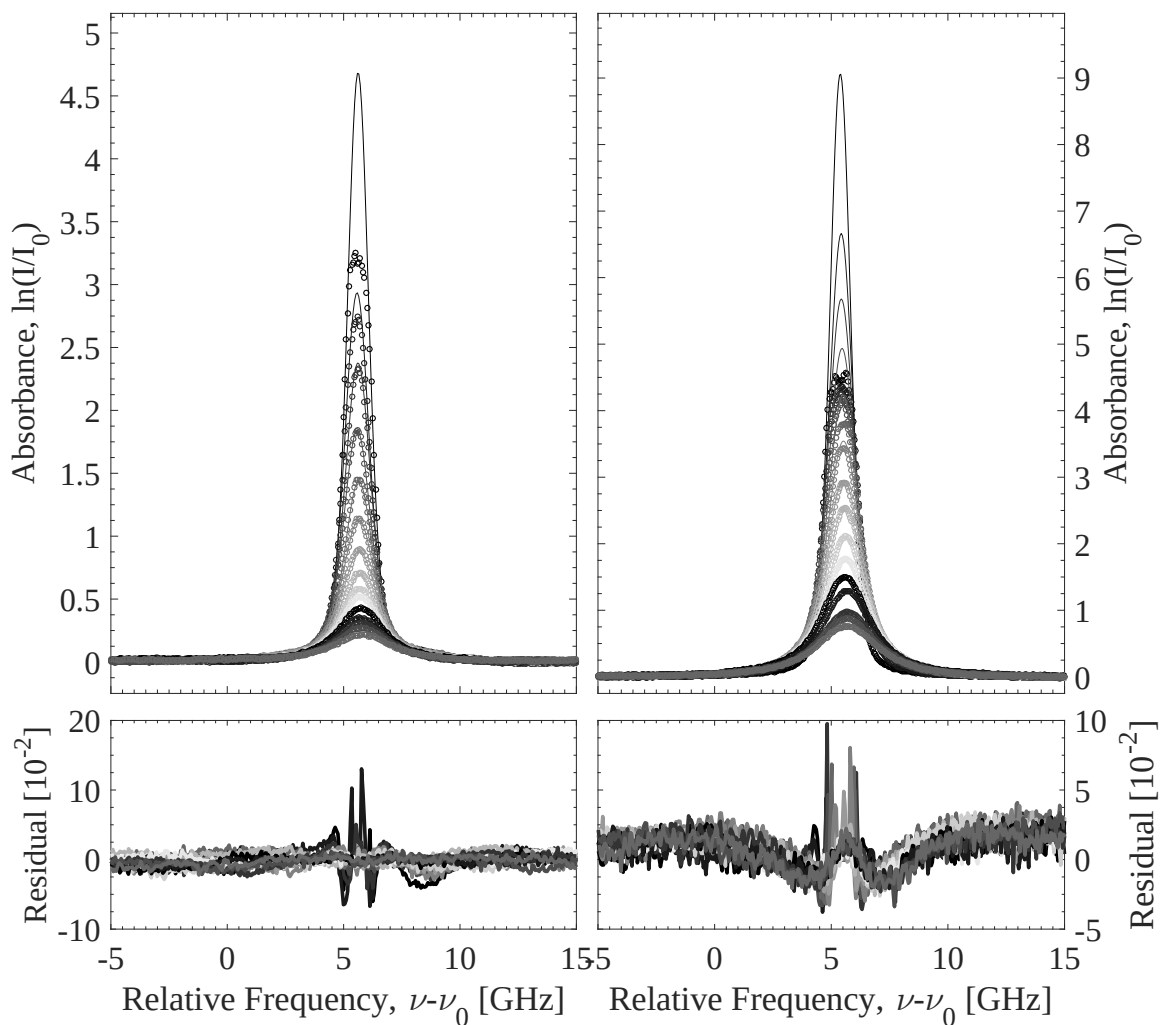


Figure 59. Absorption spectra of 801.699 nm transition line shape in 2.5% (left) and 5% (right) Ar-He mixtures. The pressure increases from 10 to 160 Torr where the 10 Torr case has the highest absorbance and narrowest linewidth.

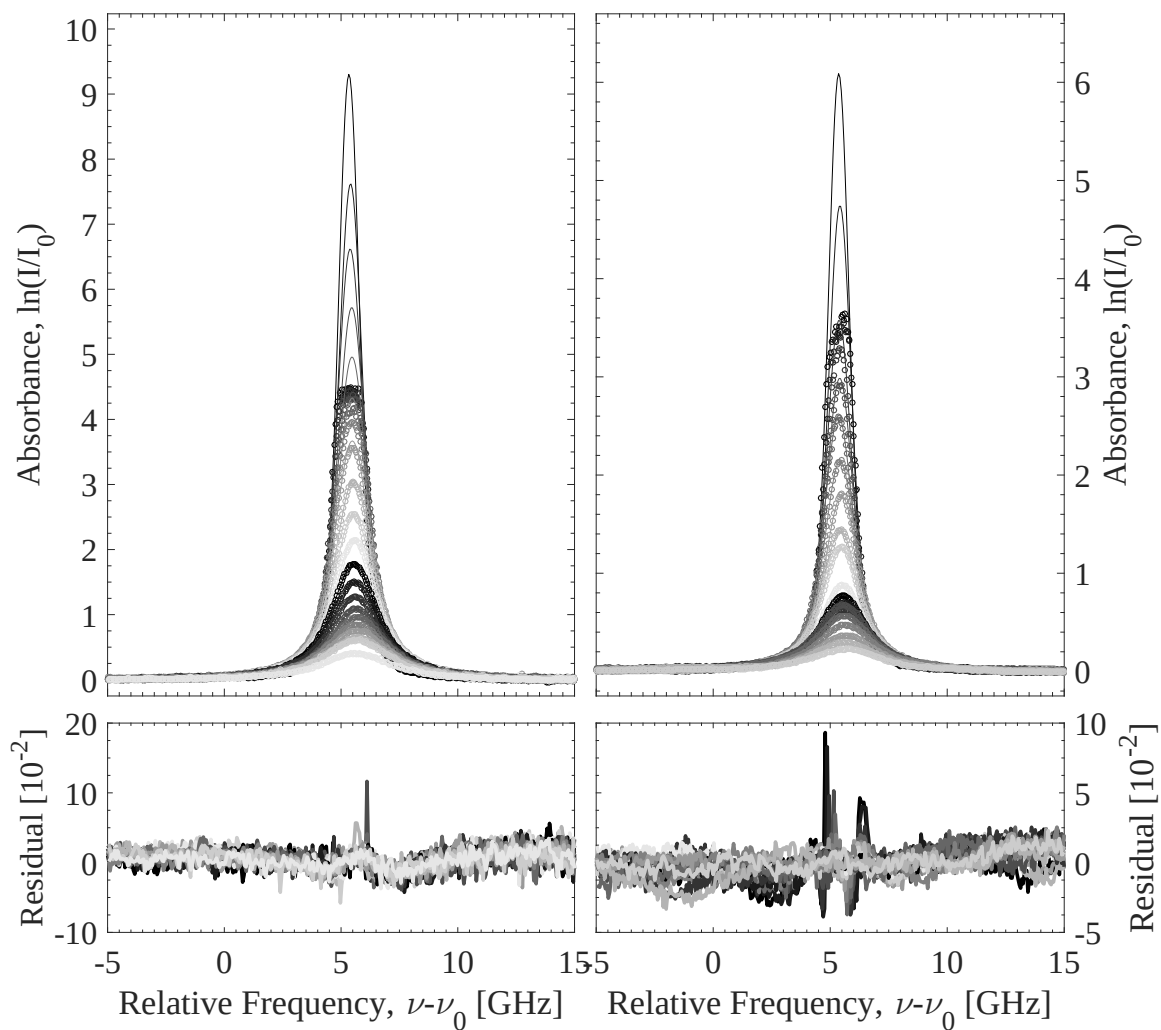


Figure 60. Absorption spectra of 801.699 nm transition line shape in 10% (left) and 25% (right) Ar-He mixtures. The pressure increases from 10 to 170 Torr where the 10 Torr case has the highest absorbance and narrowest linewidth.

B.2 Number Density, Lorentzian Width, Lorentzian Shift, and Doppler Width

In this section four-box plots are presented each corresponding to a single transition and mixture for the full measured pressure range. The displayed parameters are the number density (top, left), Doppler width (bottom, left), Lorentzian Width (top, right) and Lorentzian Shift (bottom, right). These values have been extracted from the Voigt fits presented in the previous section.

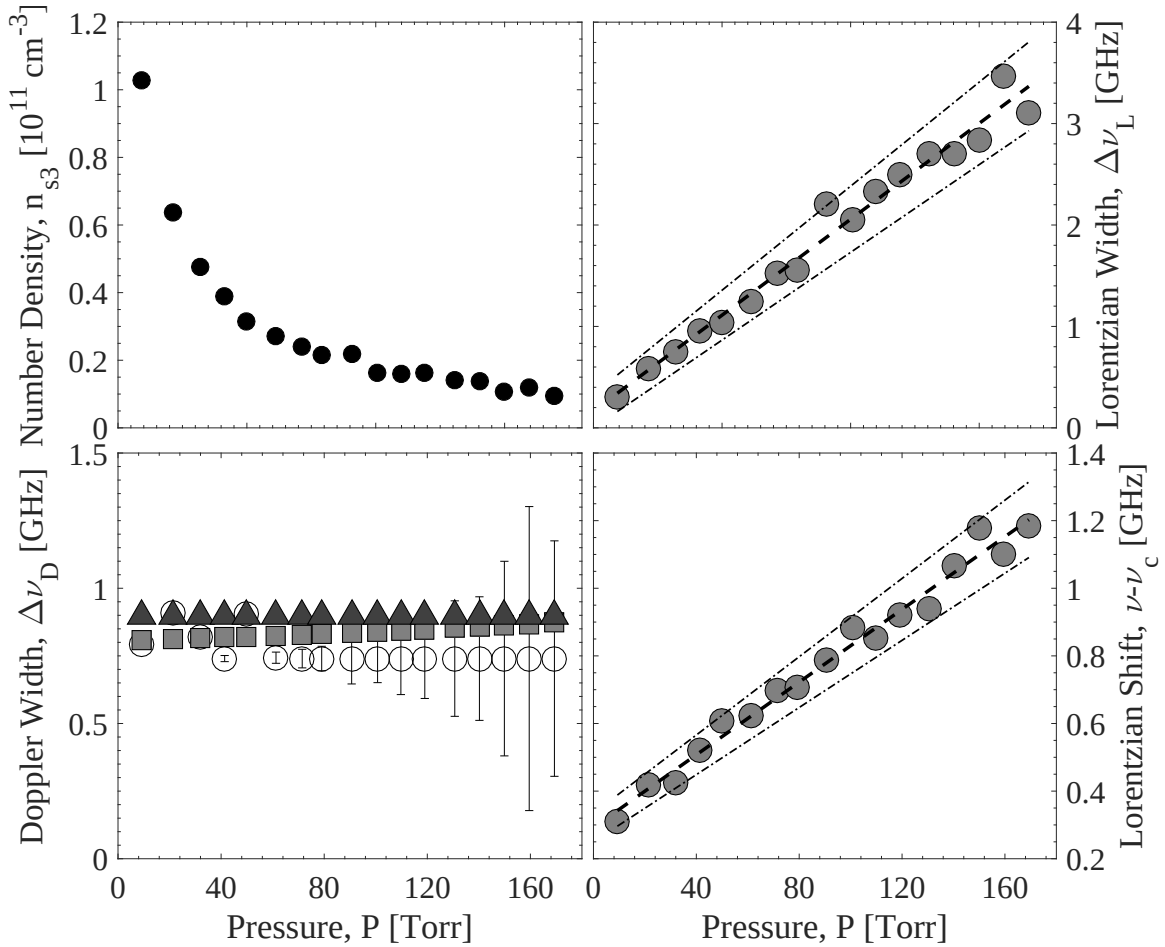


Figure 61. Number Density (top,left), Doppler width (bottom,left), Lorentzian width (top,right) and Lorentzian shift (bottom,right) for the 795.036 nm transition in a 2.5% Ar-He mixture. The Doppler width plot contains the floating ($\circ$), fixed ($\blacktriangle$), and exponential ($\blacksquare$) trends.

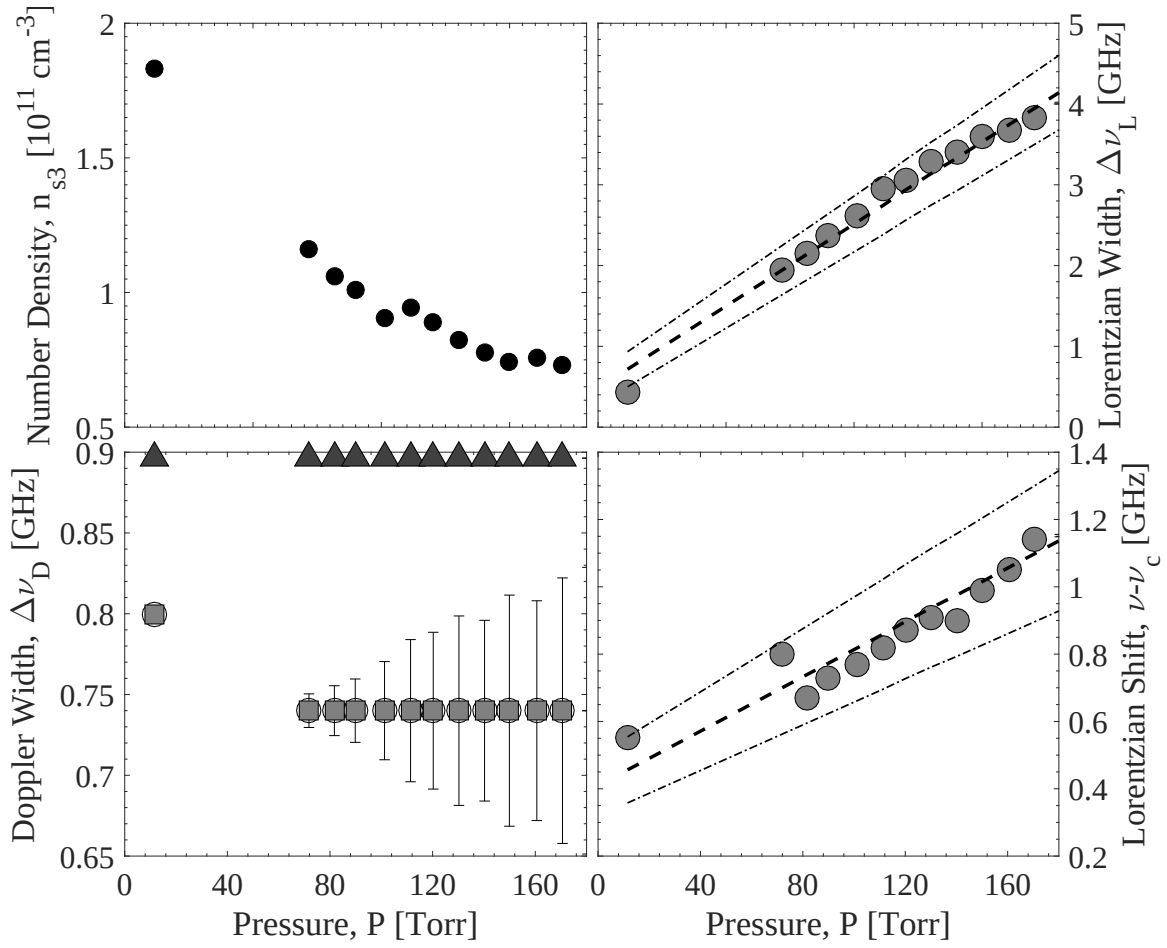


Figure 62. Number Density (top,left), Doppler width (bottom,left), Lorentzian width (top,right) and Lorentzian shift (bottom,right) for the 795.036 nm transition in a 5% Ar-He mixture. The Doppler width plot contains the floating (○), fixed (▲), and exponential (■) trends.

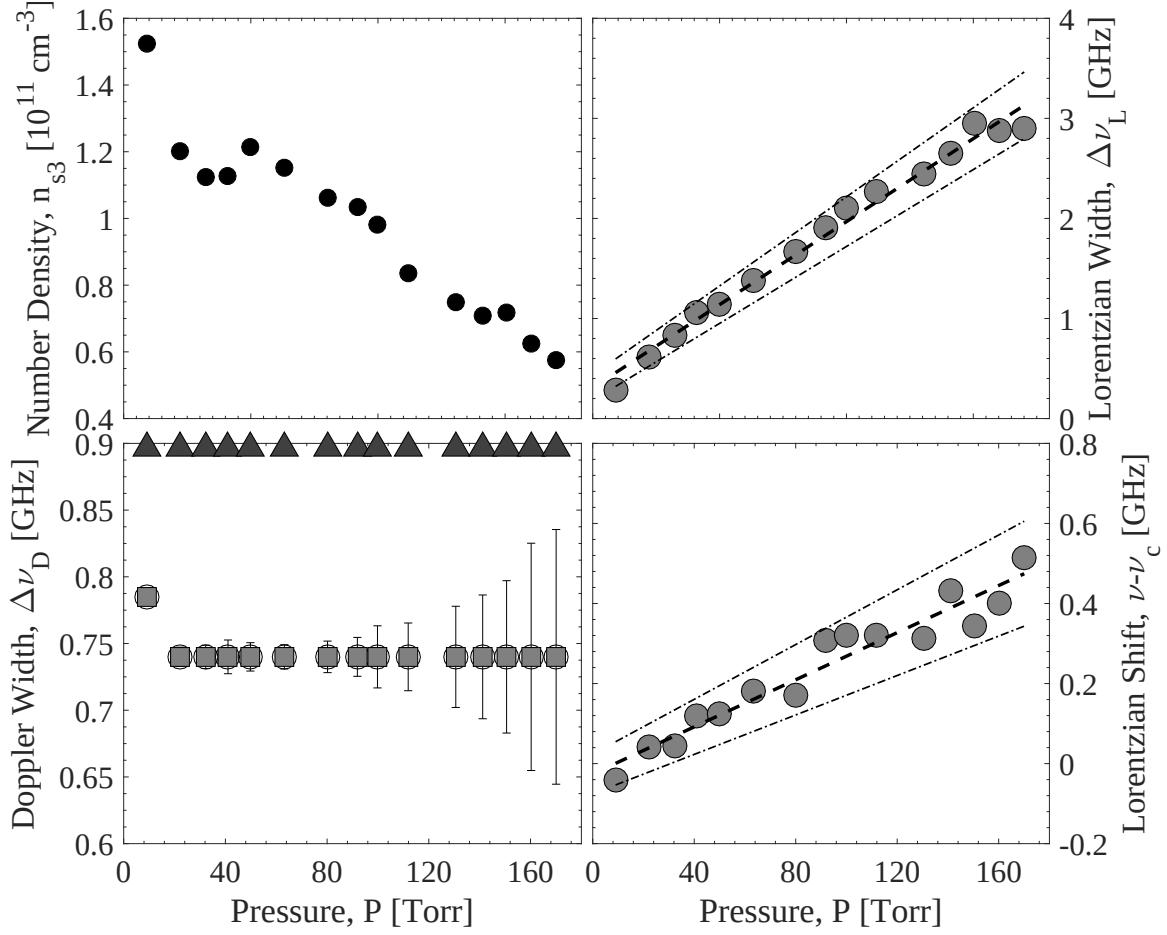


Figure 63. Number Density (top,left), Doppler width (bottom,left), Lorentzian width (top,right) and Lorentzian shift (bottom,right) for the 795.036 nm transition in a 10% Ar-He mixture. The Doppler width plot contains the floating ($\circ$), fixed ($\blacktriangle$), and exponential ($\blacksquare$) trends.

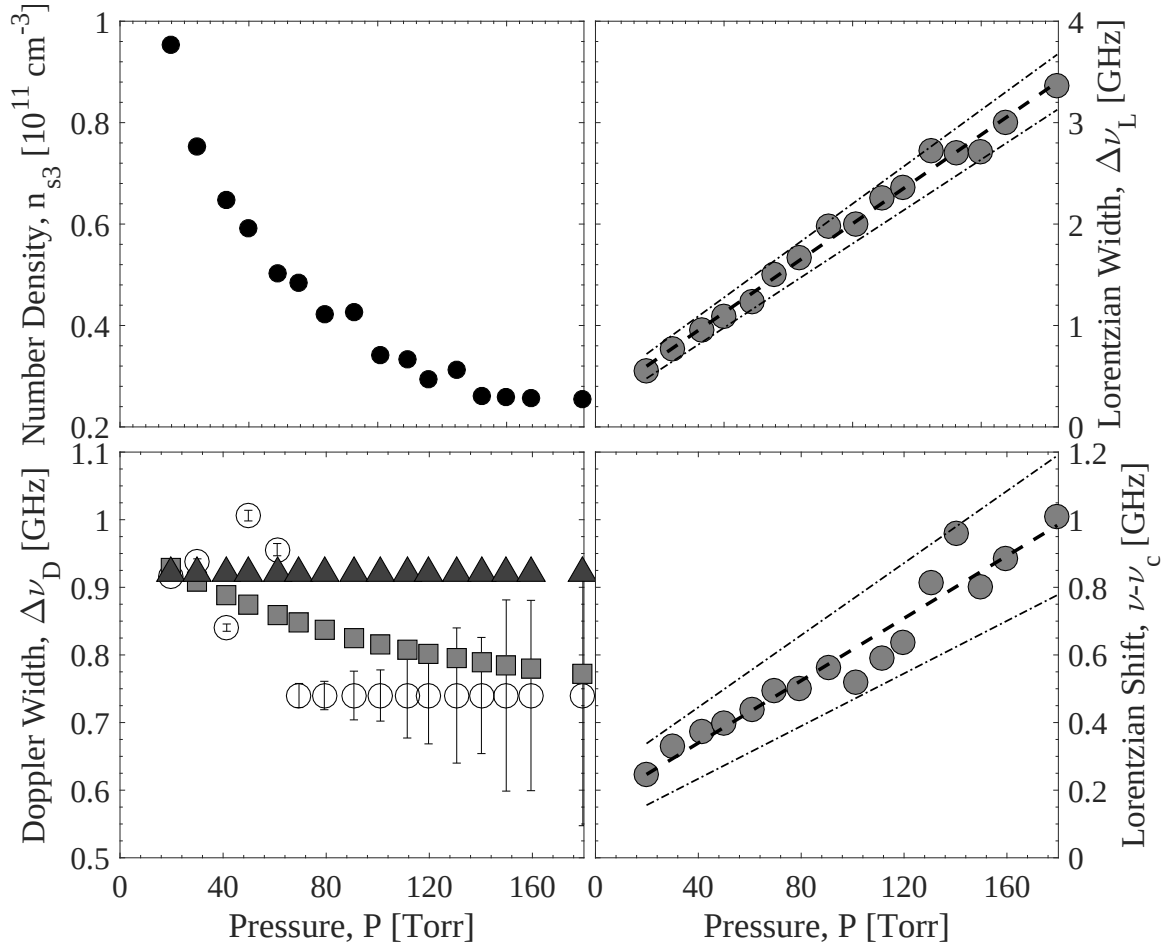


Figure 64. Number Density (top,left), Doppler width (bottom,left), Lorentzian width (top,right) and Lorentzian shift (bottom,right) for the 795.036 nm transition in a 25% Ar-He mixture. The Doppler width plot contains the floating ($\circ$), fixed ($\blacktriangle$), and exponential ($\blacksquare$) trends.

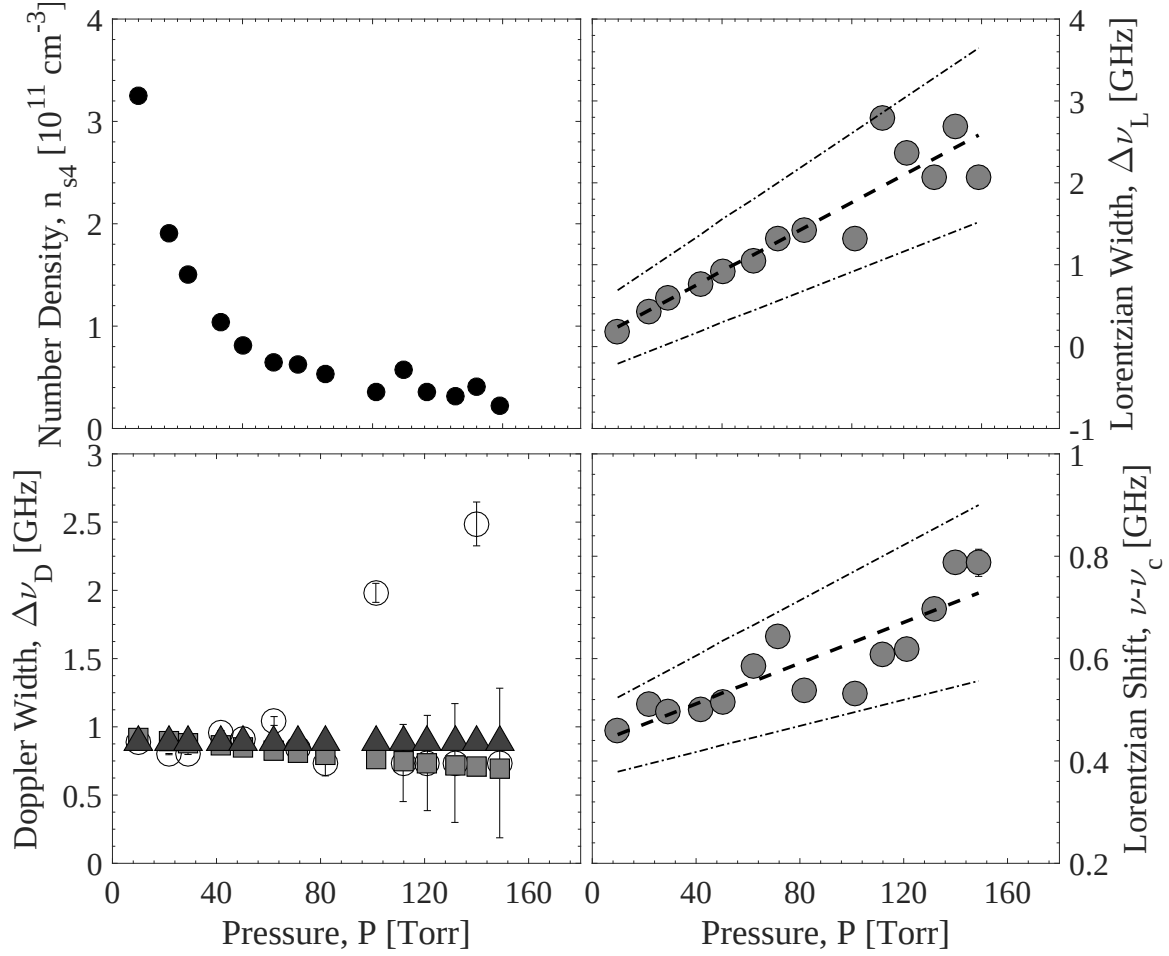


Figure 65. Number Density (top,left), Doppler width (bottom,left), Lorentzian width (top,right) and Lorentzian shift (bottom,right) for the 800.836 nm transition in a 2.5% Ar-He mixture. The Doppler width plot contains the floating (○), fixed (▲), and exponential (■) trends.

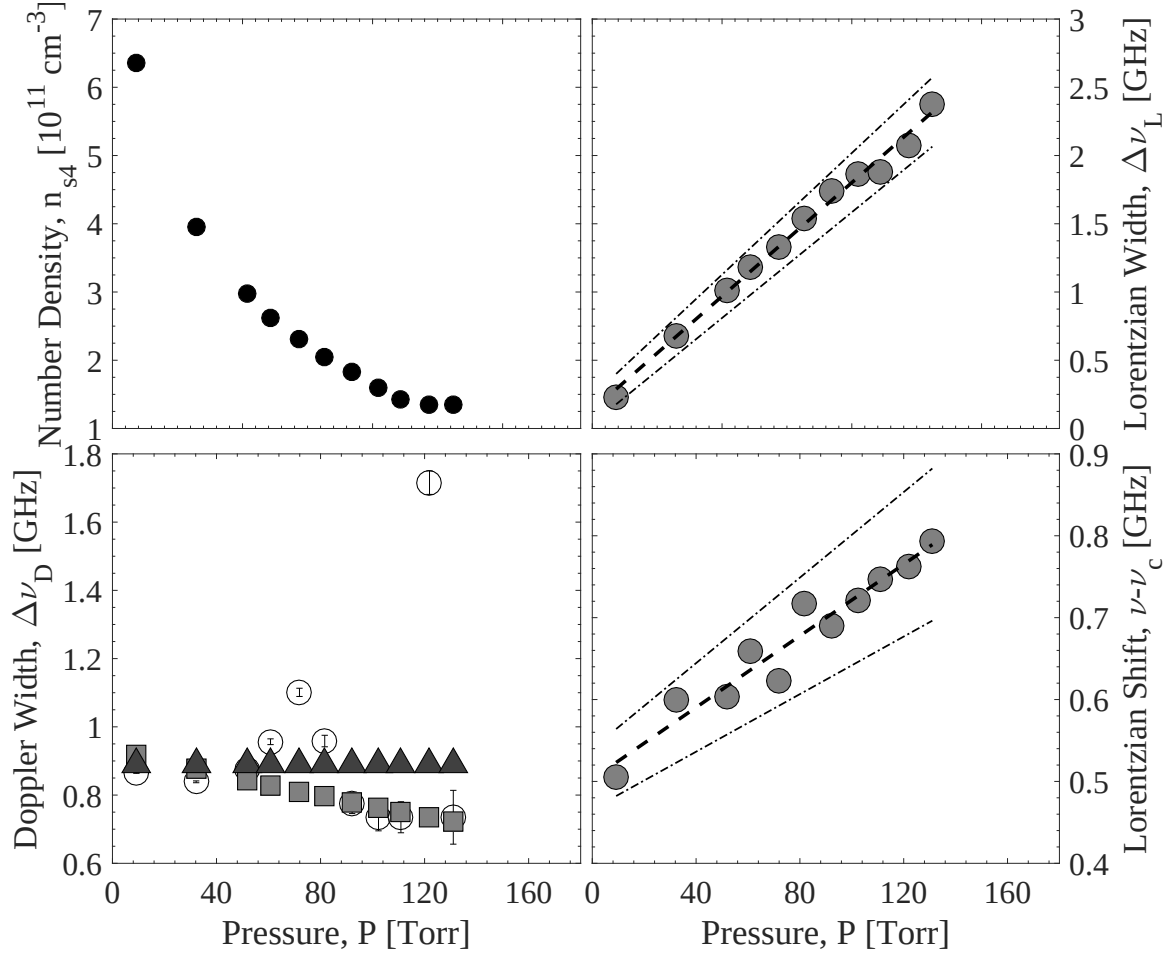


Figure 66. Number Density (top,left), Doppler width (bottom,left), Lorentzian width (top,right) and Lorentzian shift (bottom,right) for the 800.836 nm transition in a 5% Ar-He mixture. The Doppler width plot contains the floating (○), fixed (▲), and exponential (■) trends.

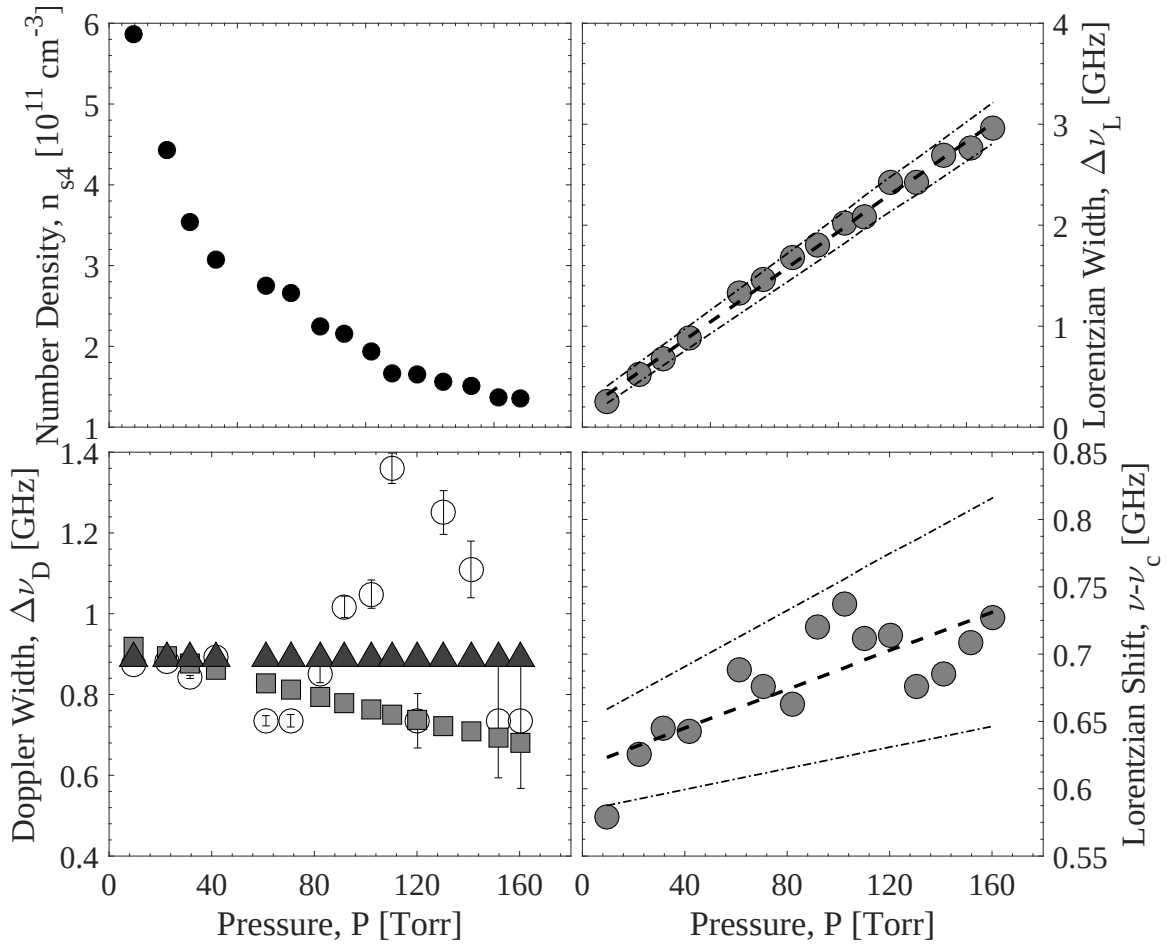


Figure 67. Number Density (top,left), Doppler width (bottom,left), Lorentzian width (top,right) and Lorentzian shift (bottom,right) for the 800.836 nm transition in a 10% Ar-He mixture. The Doppler width plot contains the floating ($\circ$), fixed ($\blacktriangle$), and exponential ($\blacksquare$) trends.

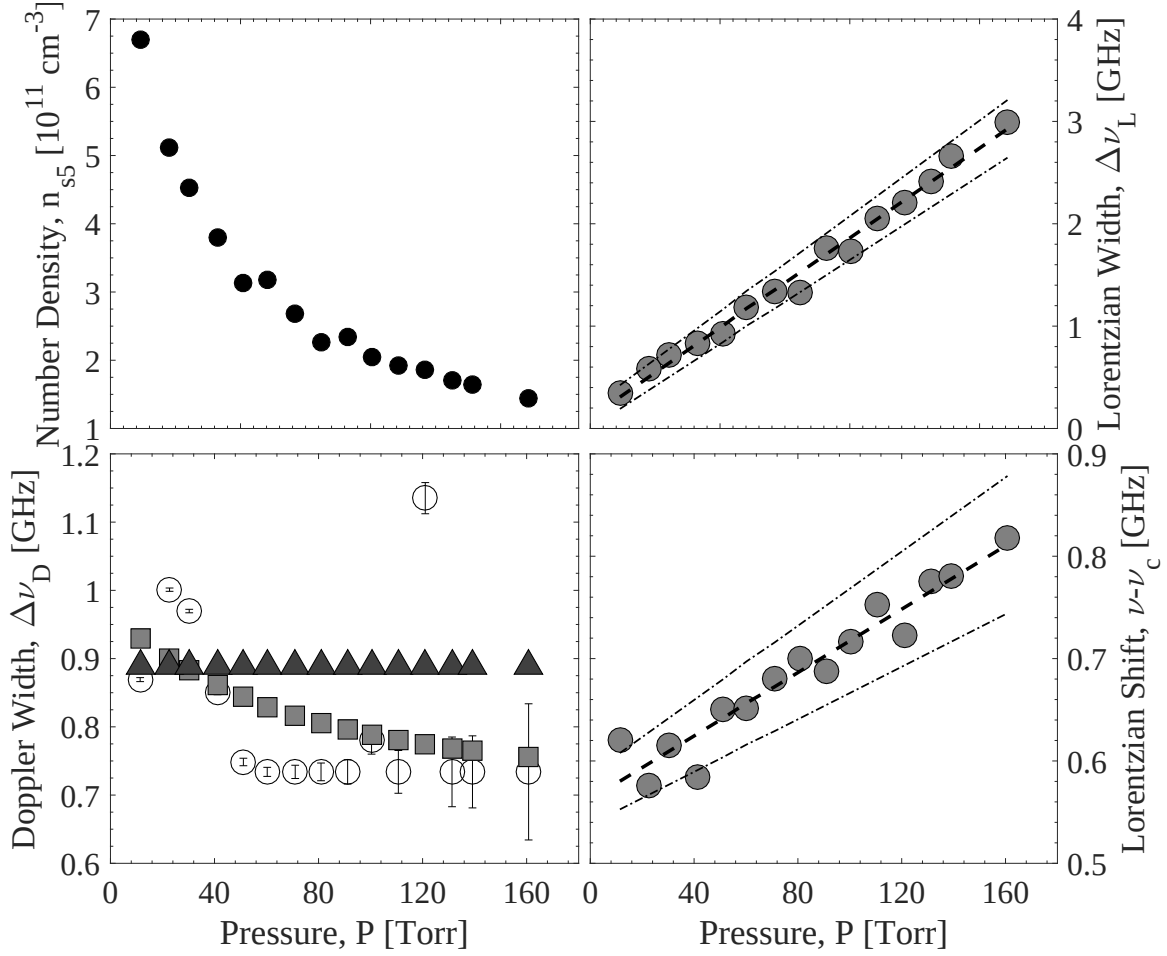


Figure 68. Number Density (top,left), Doppler width (bottom,left), Lorentzian width (top,right) and Lorentzian shift (bottom,right) for the 801.699 nm transition in a 2.5% Ar-He mixture. The Doppler width plot contains the floating ($\circ$), fixed ($\blacktriangle$), and exponential ($\blacksquare$) trends.

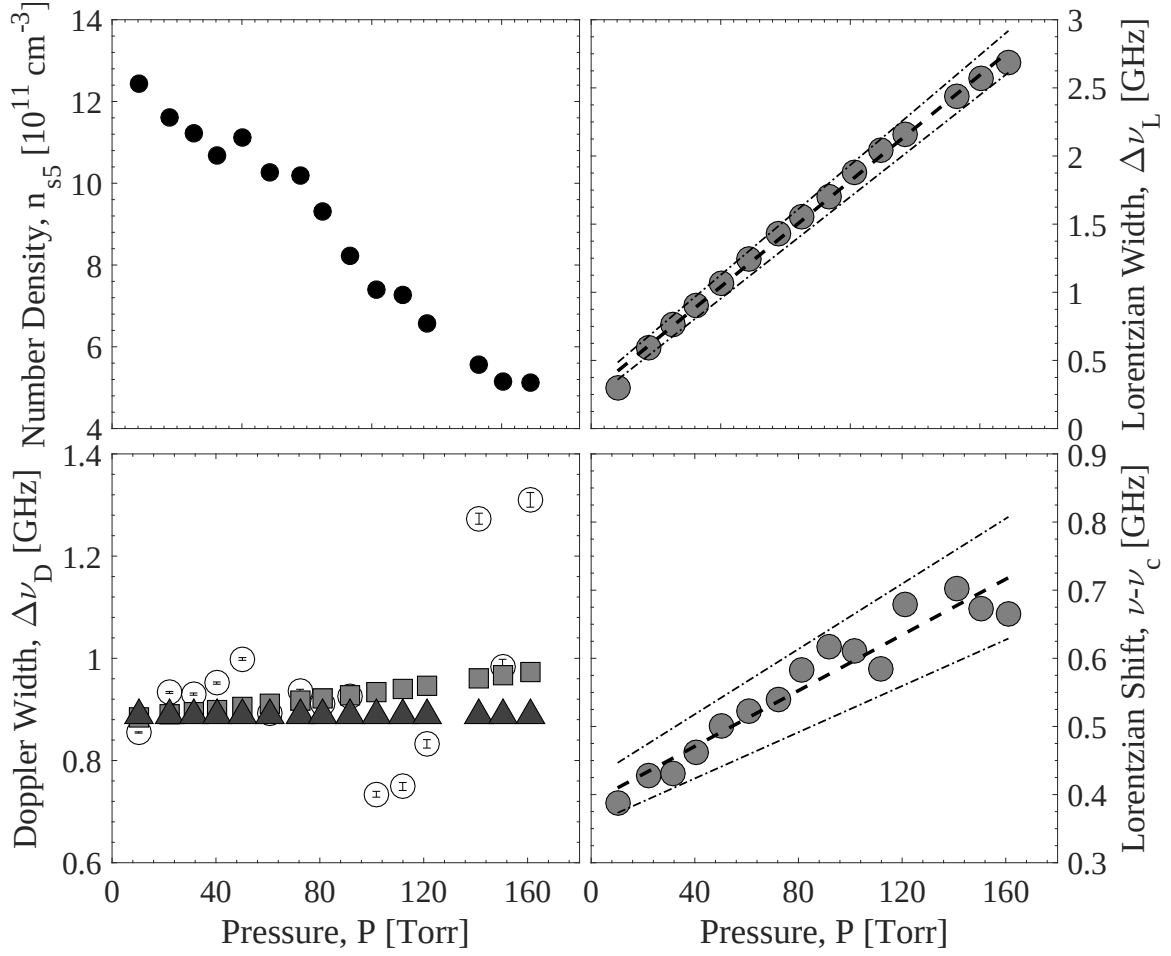


Figure 69. Number Density (top,left), Doppler width (bottom,left), Lorentzian width (top,right) and Lorentzian shift (bottom,right) for the 801.699 nm transition in a 5% Ar-He mixture. The Doppler width plot contains the floating ($\circ$), fixed ($\blacktriangle$), and exponential ($\blacksquare$) trends.

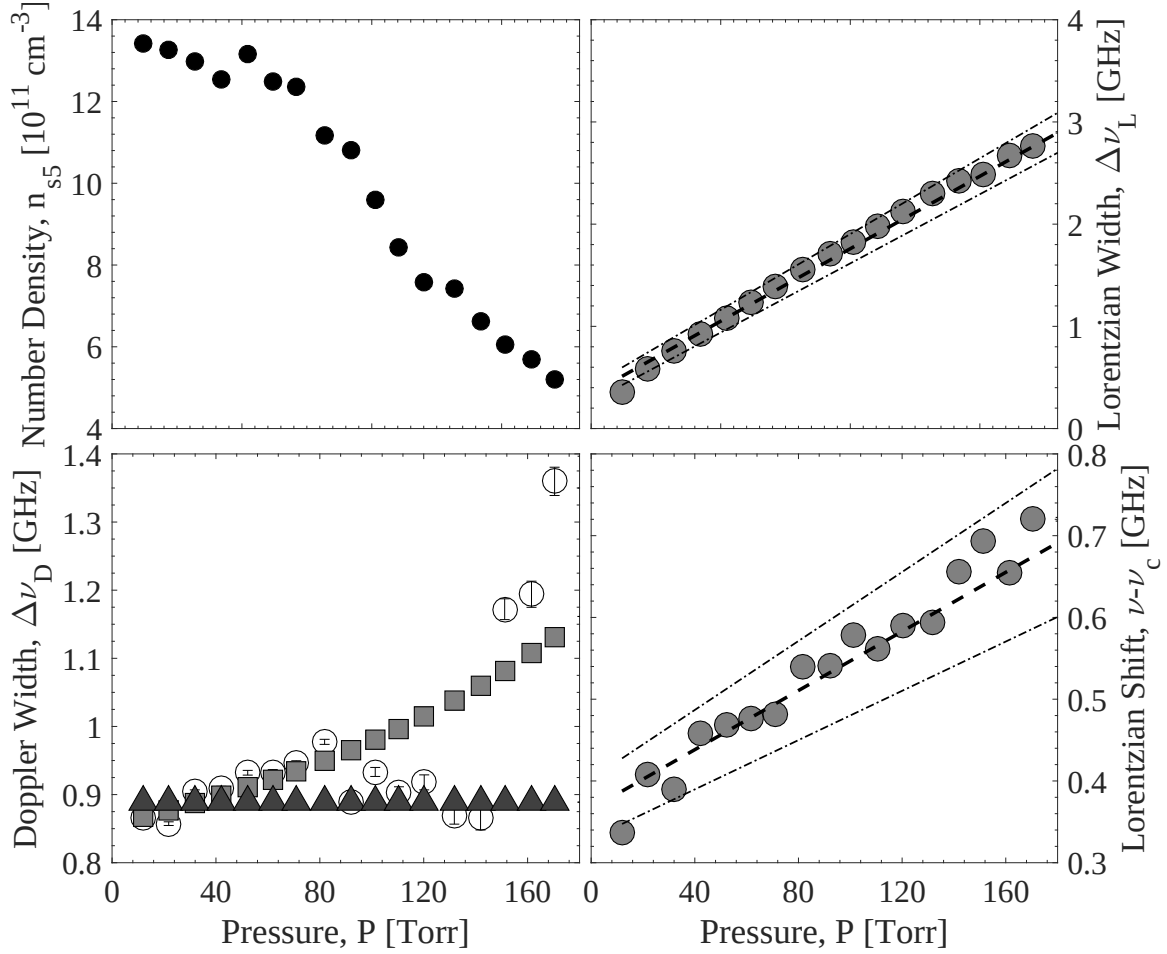


Figure 70. Number Density (top,left), Doppler width (bottom,left), Lorentzian width (top,right) and Lorentzian shift (bottom,right) for the 801.699 nm transition in a 10% Ar-He mixture. The Doppler width plot contains the floating ($\circ$), fixed ($\blacktriangle$), and exponential ($\blacksquare$) trends.

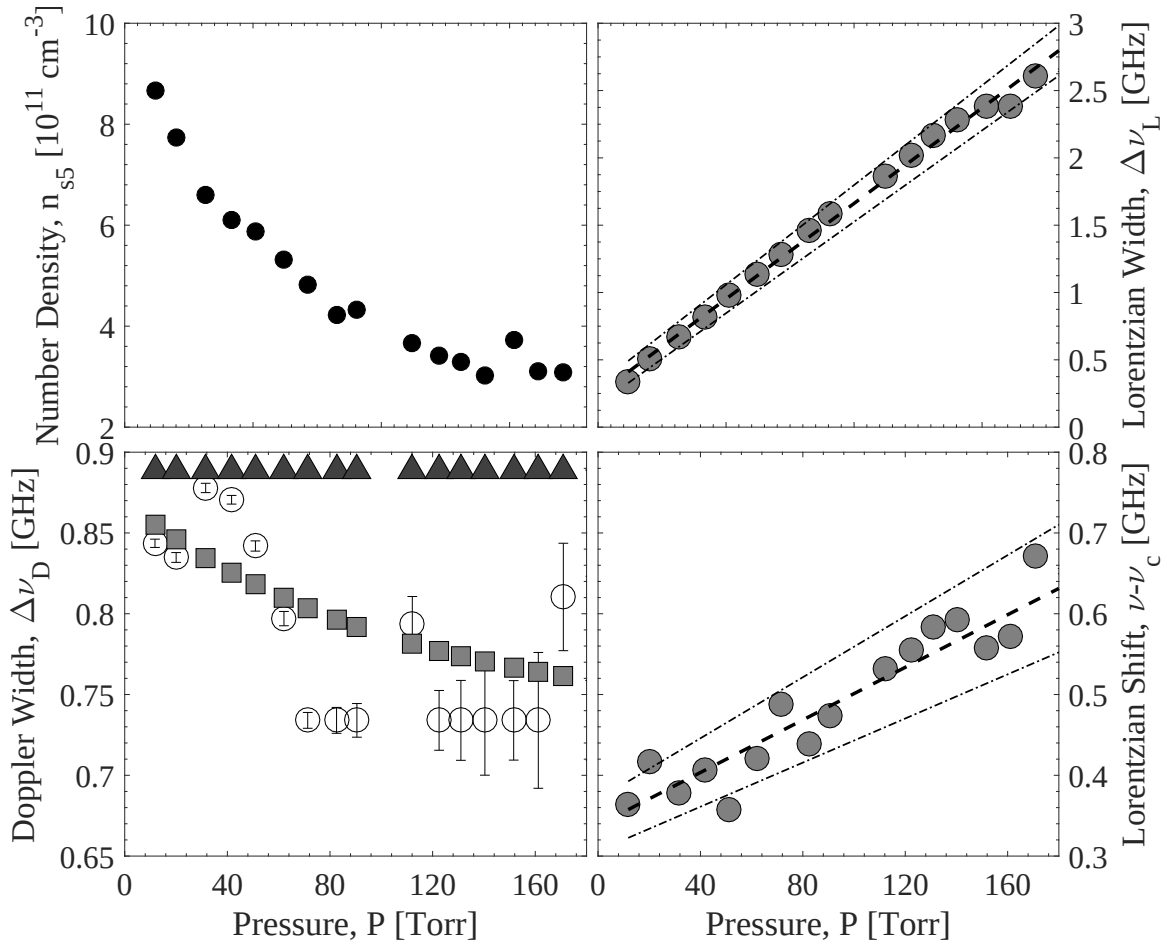


Figure 71. Number Density (top,left), Doppler width (bottom,left), Lorentzian width (top,right) and Lorentzian shift (bottom,right) for the 801.699 nm transition in a 25% Ar-He mixture. The Doppler width plot contains the floating ($\circ$), fixed ($\blacktriangle$), and exponential ($\blacksquare$) trends.

Appendix C. Saturation Spectroscopy Data

This appendix provides the data not presented in Ch. VI.

C.1 Laser Absorption Spectroscopy Data

This section presents the laser absorption spectroscopy measurements ($\circ$) with the corresponding Voigt fits ($-$) and the residuals for those fits. The line shapes are given side-by-side to compare pressures.

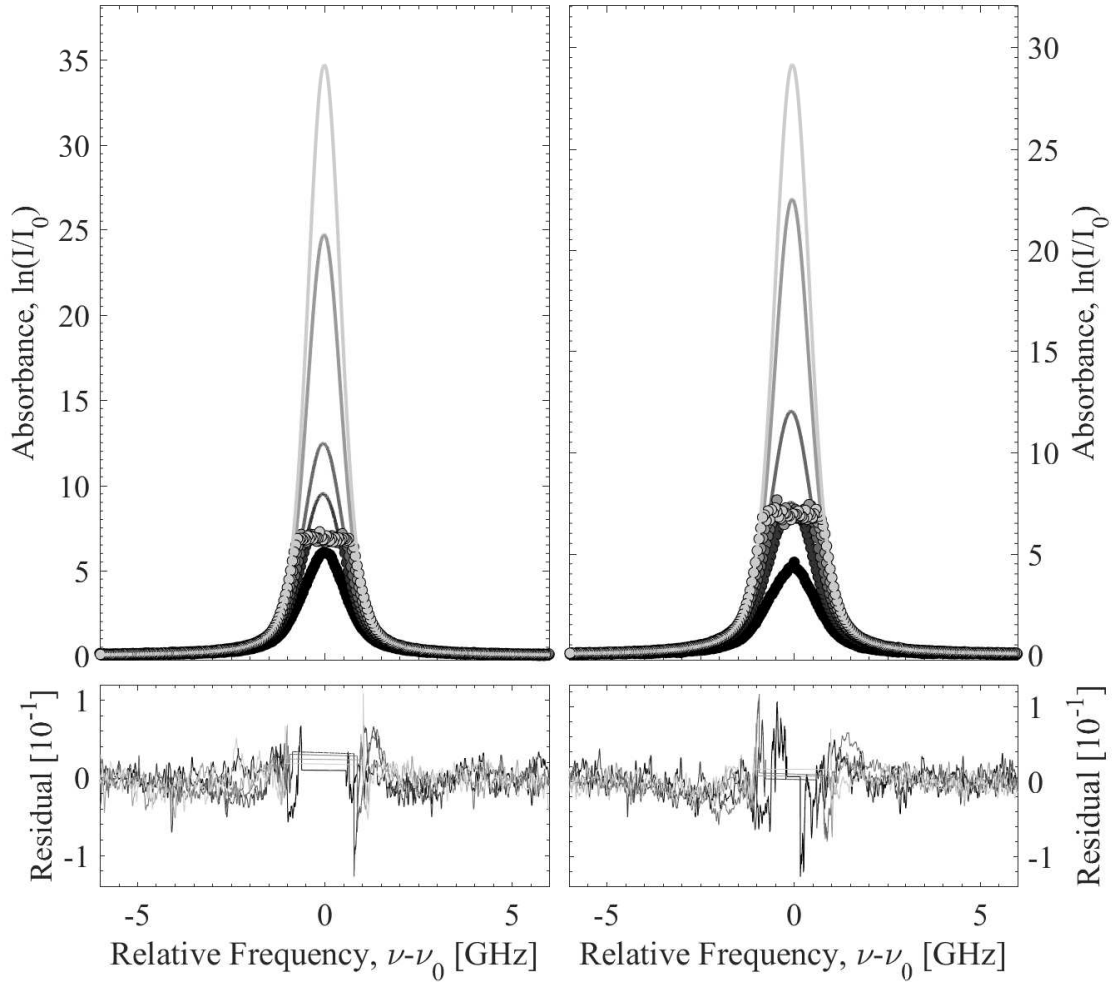


Figure 72. The absorbance is shown for the 811 nm transition in pure Ar at 5 (left) and 10 (right) Torr at 1 W ($\bullet$), 5 W ($\circ$), 10 W ($\circ$), 25 W ($\circ$), and 40 W ($\circ$)

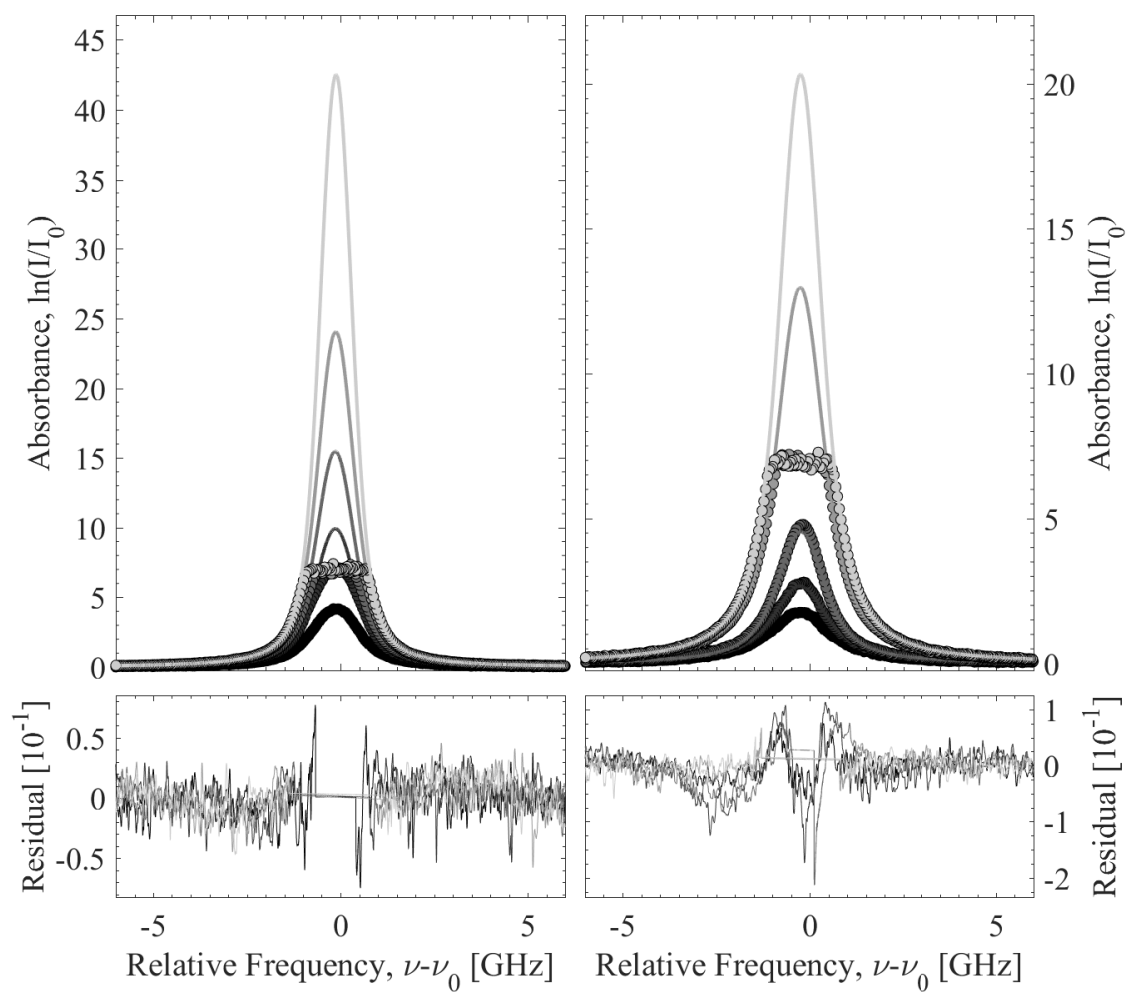


Figure 73. The absorbance is shown for the 811 nm transition in pure Ar at 25 (left) and 50 (right) Torr at 1 W (●), 5 W (○), 10 W (●), 25 W (○), and 40 W (○)

C.2 Intermodulated Fluorescence Spectroscopy Data

In this section the intermodulated fluorescence spectroscopy data is presented. The figures are split into three sections corresponding to the zones depicted in Fig. 36 where zone 1 (top), zone 2 (middle), and zone 3 (bottom) are the downstream positions of 2.5 cm, 12.5 cm and 17.5 cm relative to the upstream (left) entrance of the pump. The images are given for various RF powers with the darker lines corresponding to higher RF powers.

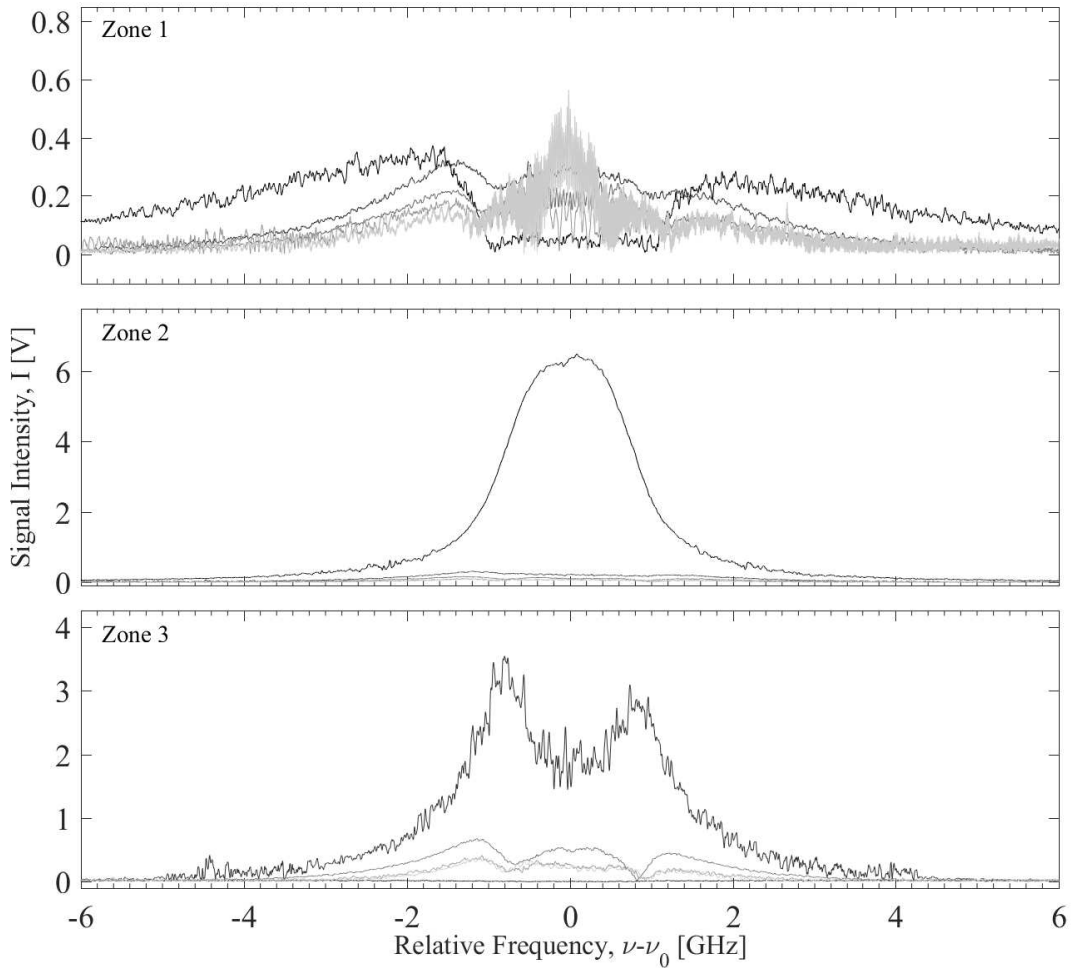


Figure 74. The intermodulated-fluorescence spectra is shown for the 811 nm transition in pure Ar at 5 Torr and RF powers of 1 W (—), 5 W (—), 10 W (—), 25 W (—), and 40 W (—). The zones correspond to downstream positions of 2.5 cm (1), 12.5 cm (2), 17.5 cm (3).

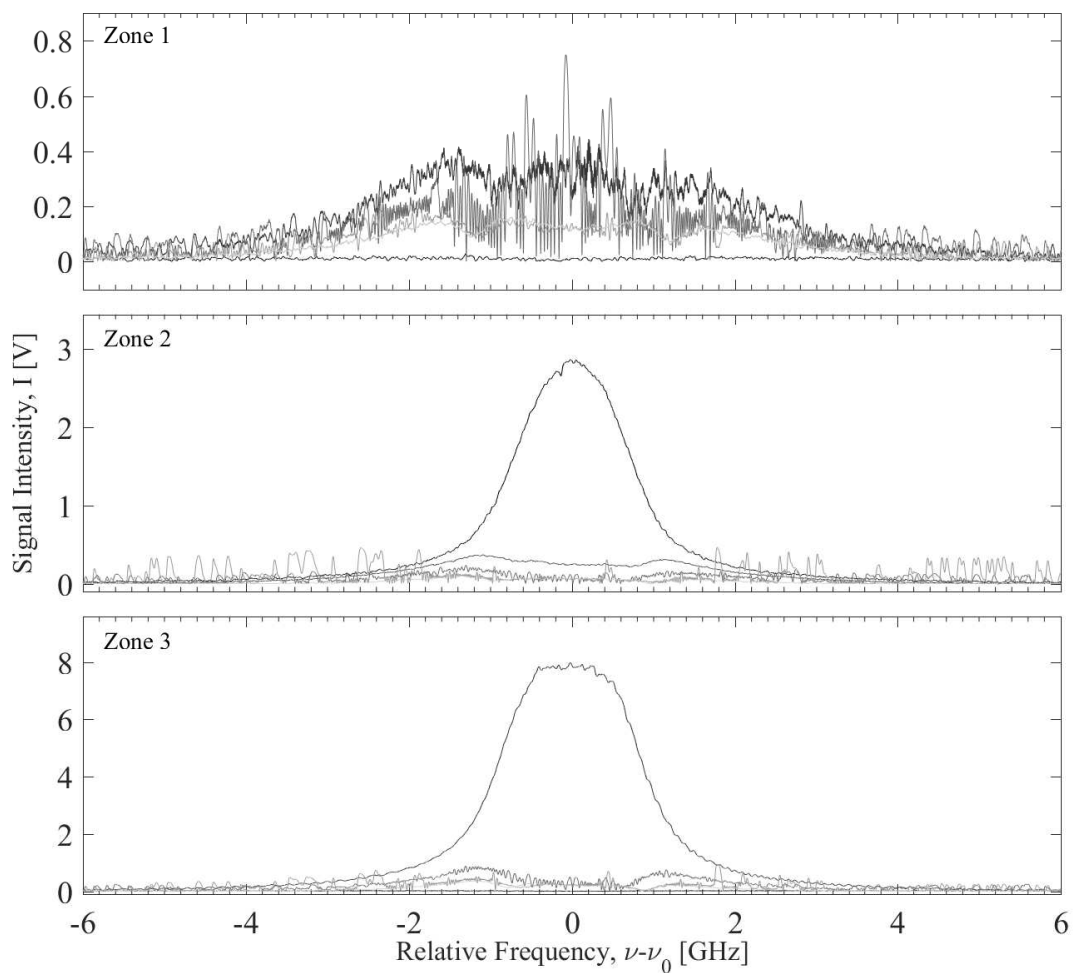


Figure 75. The intermodulated-fluorescence spectra is shown for the 811 nm transition in pure Ar at 10 Torr and RF powers of 1 W (—), 5 W (—), 10 W (—), 25 W (—), and 40 W (—). The zones correspond to downstream positions of 2.5 cm (1), 12.5 cm (2), 17.5 cm (3).

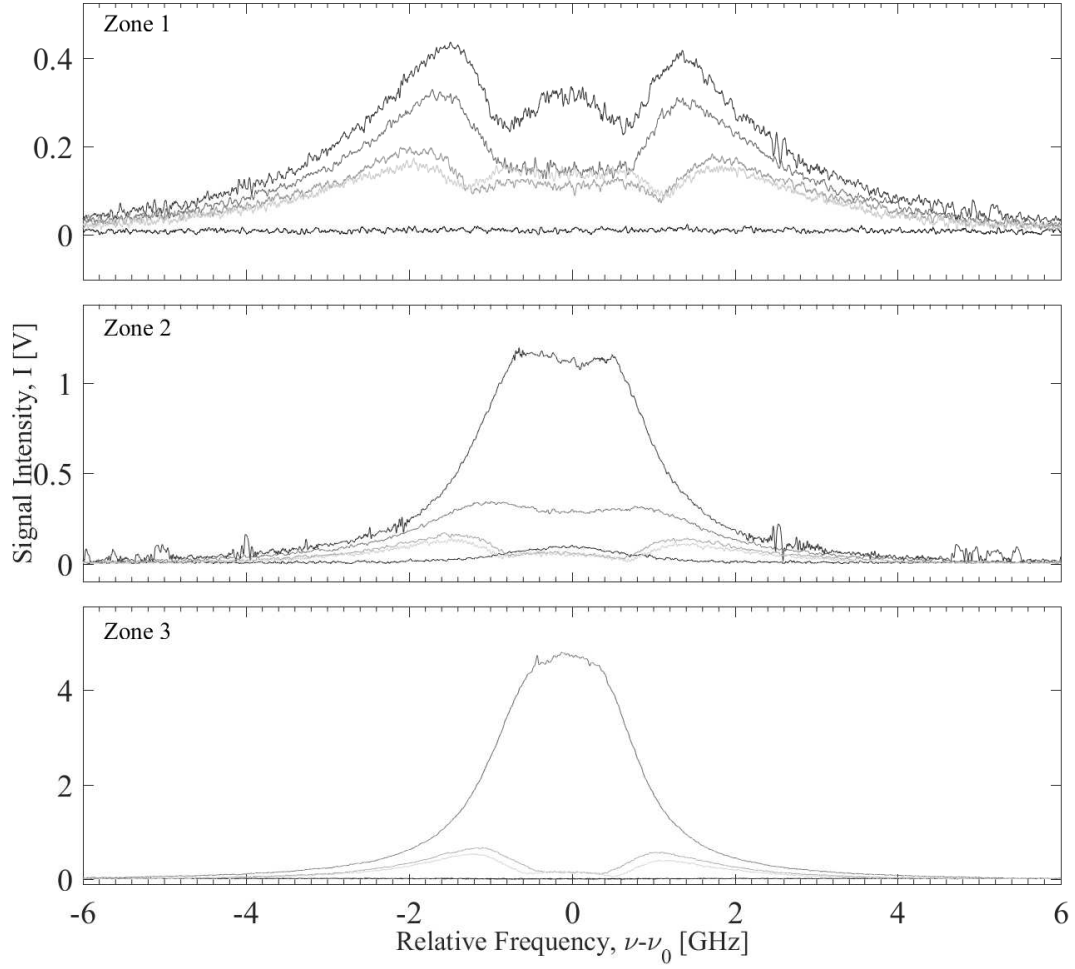


Figure 76. The intermodulated-fluorescence spectra is shown for the 811 nm transition in pure Ar at 25 Torr and RF powers of 1 W (—), 5 W (—), 10 W (—), 25 W (—), and 40 W (—). The zones correspond to downstream positions of 2.5 cm (1), 12.5 cm (2), 17.5 cm (3).

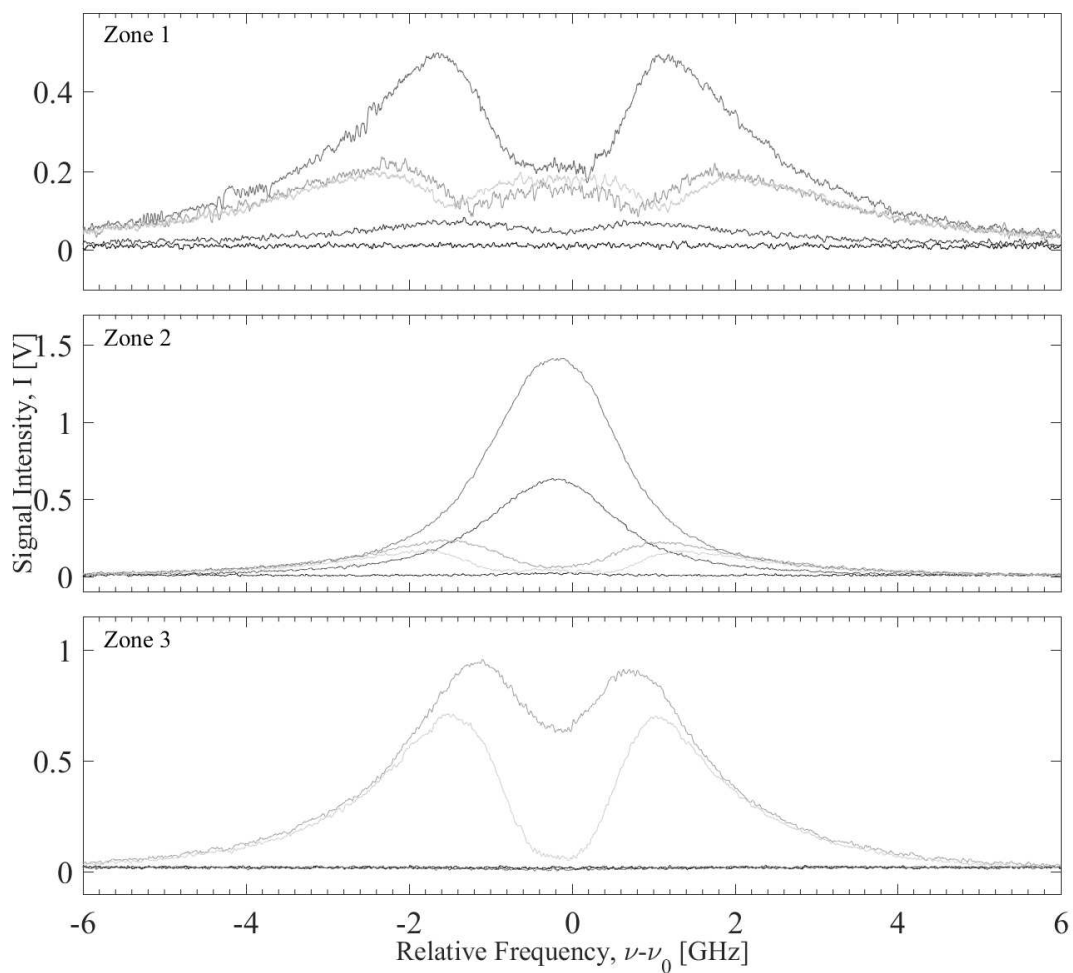


Figure 77. The intermodulated-fluorescence spectra is shown for the 811 nm transition in pure Ar at 50 Torr and RF powers of 1 W (—), 5 W (—), 10 W (—), 25 W (—), and 40 W (—). The zones correspond to downstream positions of 2.5 cm (1), 12.5 cm (2), 17.5 cm (3).

C.3 Saturation Spectroscopy Data

The sub-Doppler saturation spectroscopy and highly-saturated absorption spectroscopy are presented in this section. The figures are composed of data from two different pressures, displayed side-by-side, with the saturated absorbance (top), residual of a single or dual Voigt fit (middle), and the sub-Doppler lineshape (bottom) composing the three figures. The lighter gray lines correspond to higher RF powers. After Fig. 82, the format changes. Fig. 83 presents the influence of an increasing probe intensity on the line shapes at 5 Torr and Fig. 84 presents the influence of the varying pump laser intensity on the line shapes at both 5 and 50 Torr.

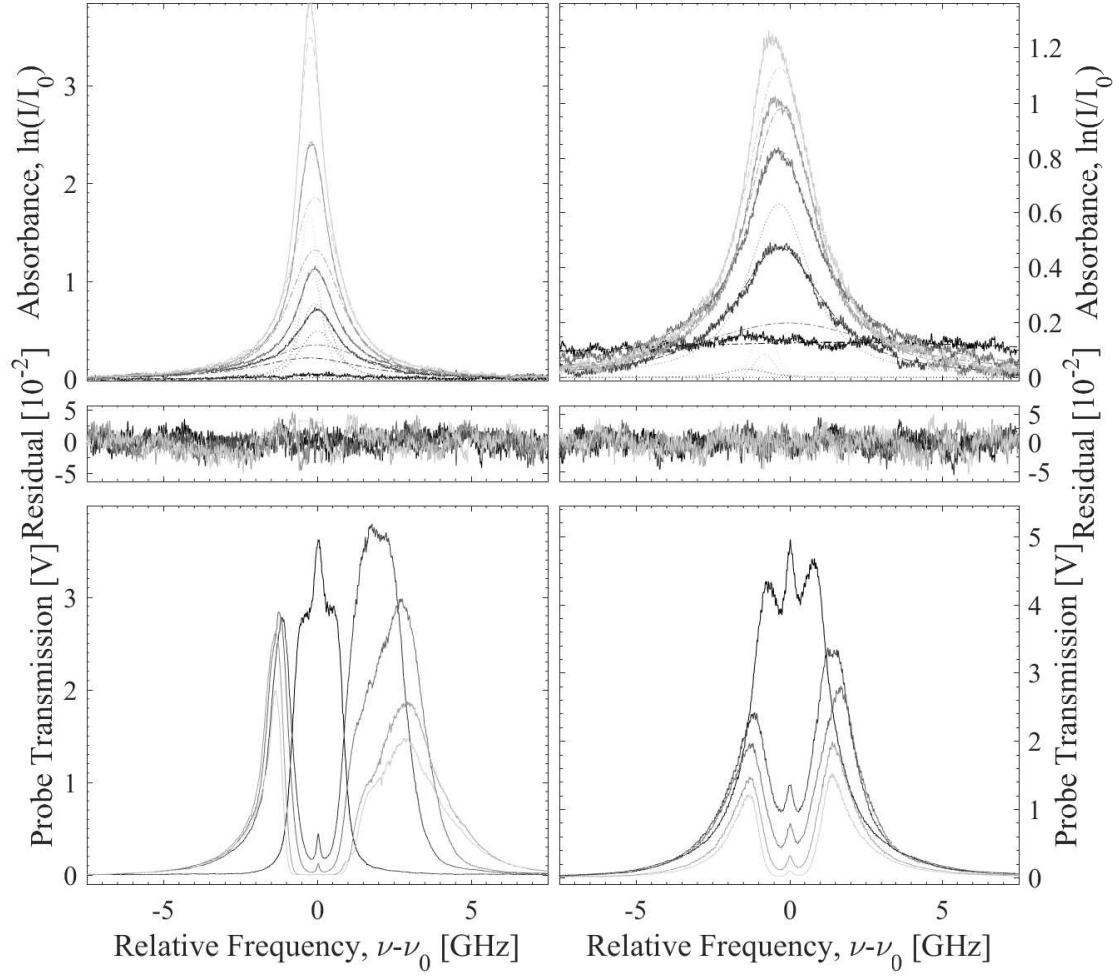


Figure 78. The saturated absorbance (top) and sub-Doppler spectra (bottom) is shown for the 811 nm transition in pure Ar at 1.3 (left) and 3.6 (right) Torr at RF powers of 1 W (—), 5 W (—), 10 W (—), 25 W (—), and 40 W (—). The pump intensity is 18 W/cm^2

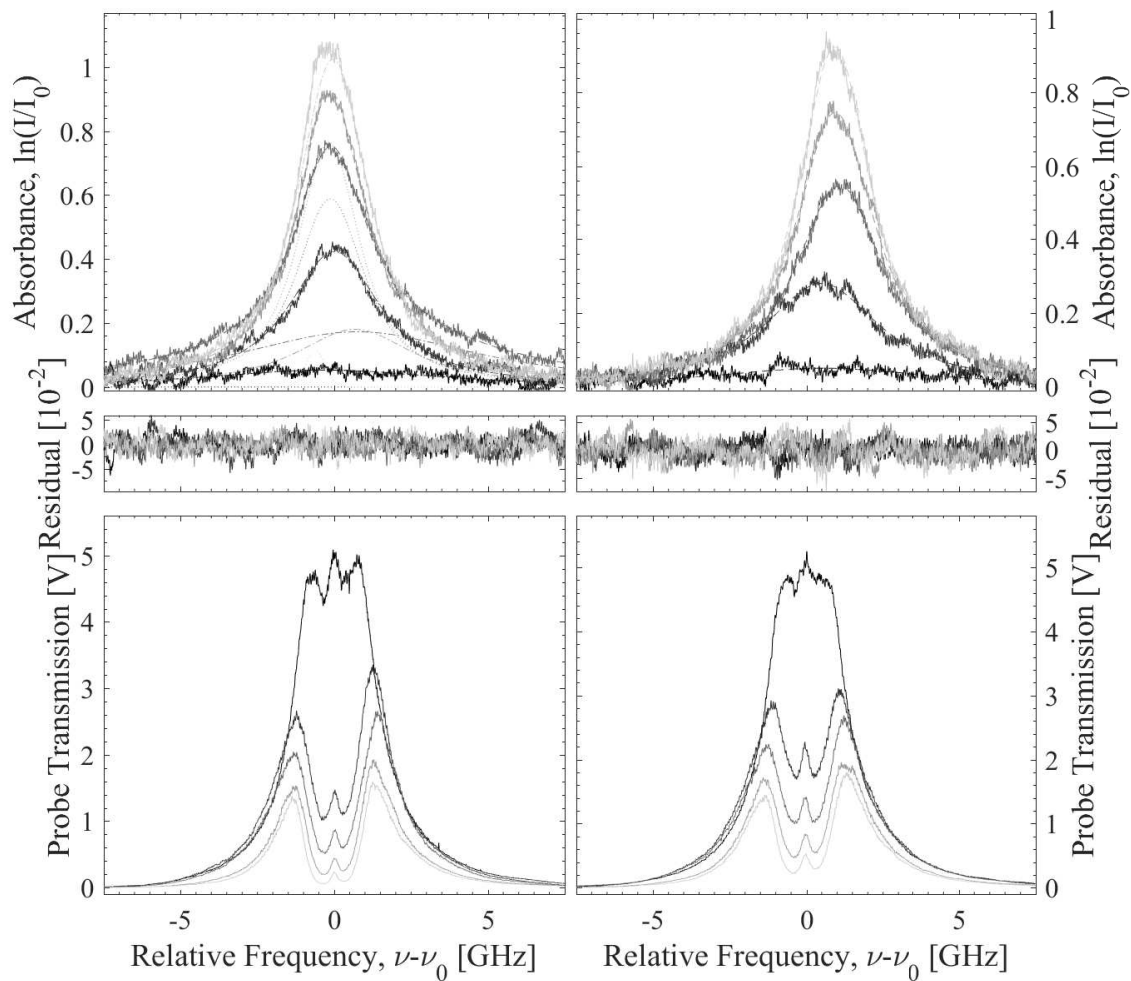


Figure 79. The saturated absorbance (top) and sub-Doppler spectra (bottom) is shown for the 811 nm transition in pure Ar at 5 (left) and 10 (right) Torr at RF powers of 1 W (—), 5 W (---), 10 W (—), 25 W (---), and 40 W (—). The pump intensity is 18 W/cm^2

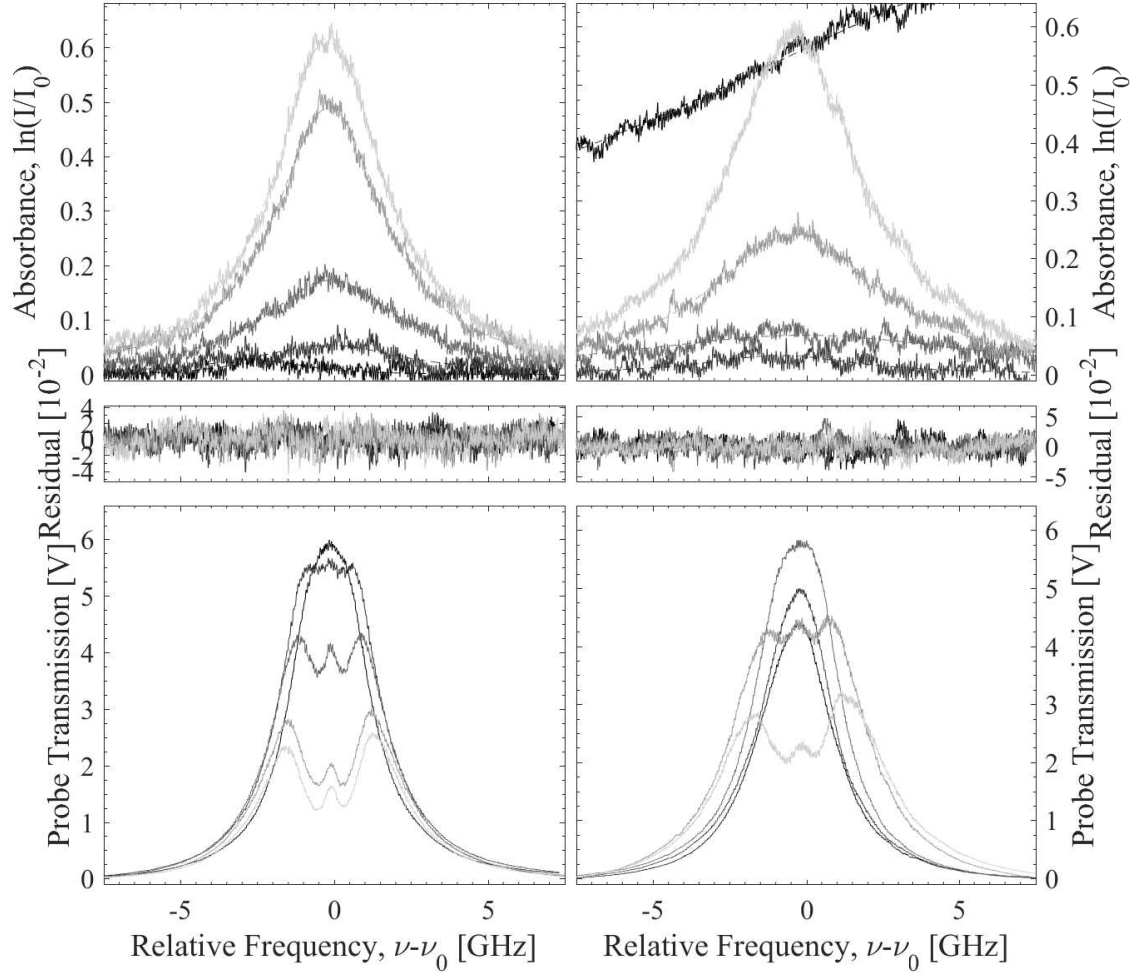


Figure 80. The saturated absorbance (top) and sub-Doppler spectra (bottom) is shown for the 811 nm transition in pure Ar at 25 (left) and 50 (right) Torr at RF powers of 1 W (—), 5 W (—), 10 W (—), 25 W (—), and 40 W (—). The pump intensity is 18 W/cm^2

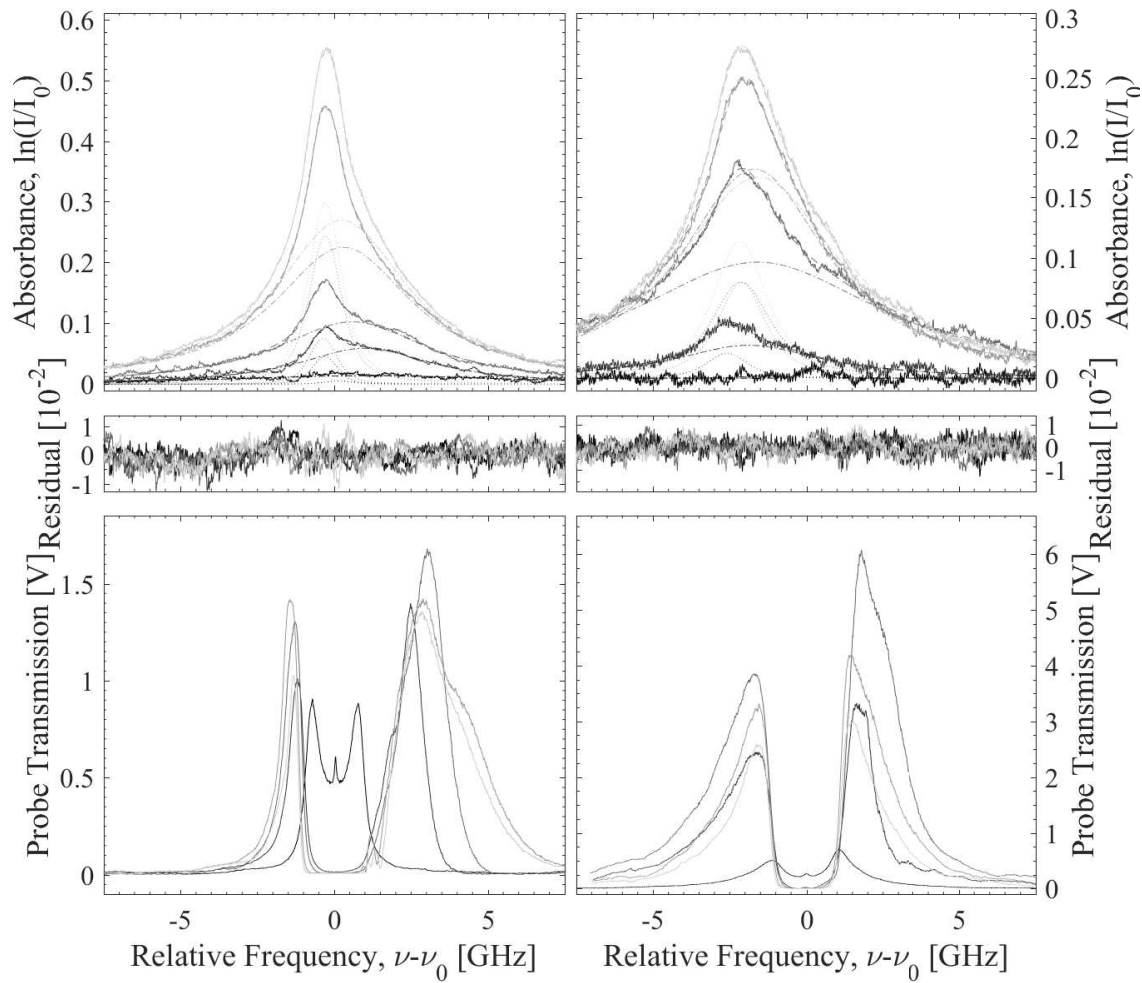


Figure 81. The saturated absorbance (top) and sub-Doppler spectra (bottom) is shown for the 811 nm transition in pure Ar at 1.3 (left) and 3.6 (right) Torr at RF powers of 1 W (—), 5 W (—), 10 W (—), 25 W (—), and 40 W (—). An optic has been placed on in the pump beam path to bring the intensity up to 15 kW/cm².

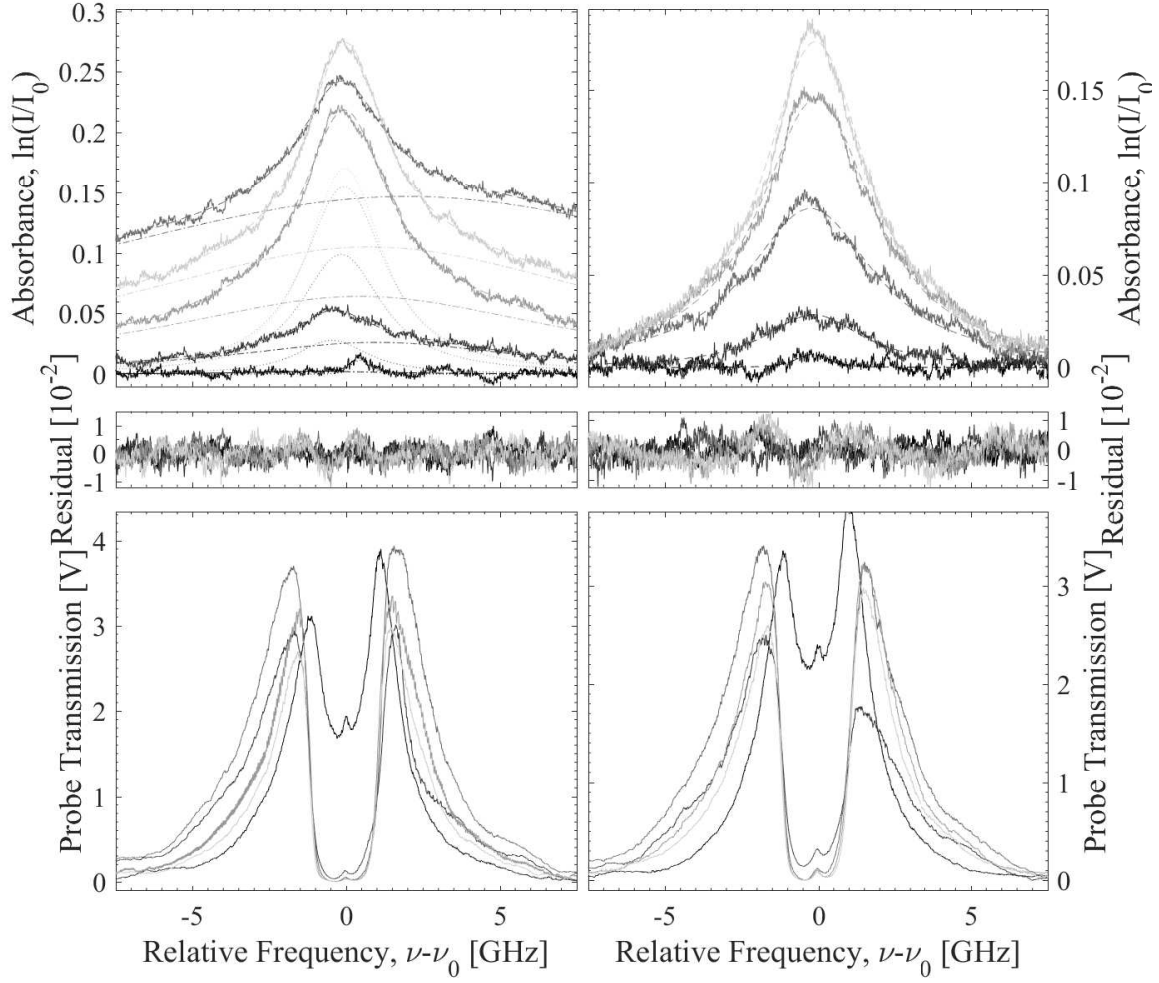


Figure 82. The saturated absorbance (top) and sub-Doppler spectra (bottom) is shown for the 811 nm transition in pure Ar at 5 (left) and 10 (right) Torr at RF powers of 1 W (—), 5 W (—), 10 W (—), 25 W (—), and 40 W (—). An optic has been placed on in the pump beam path to bring the intensity up to 15 kW/cm².

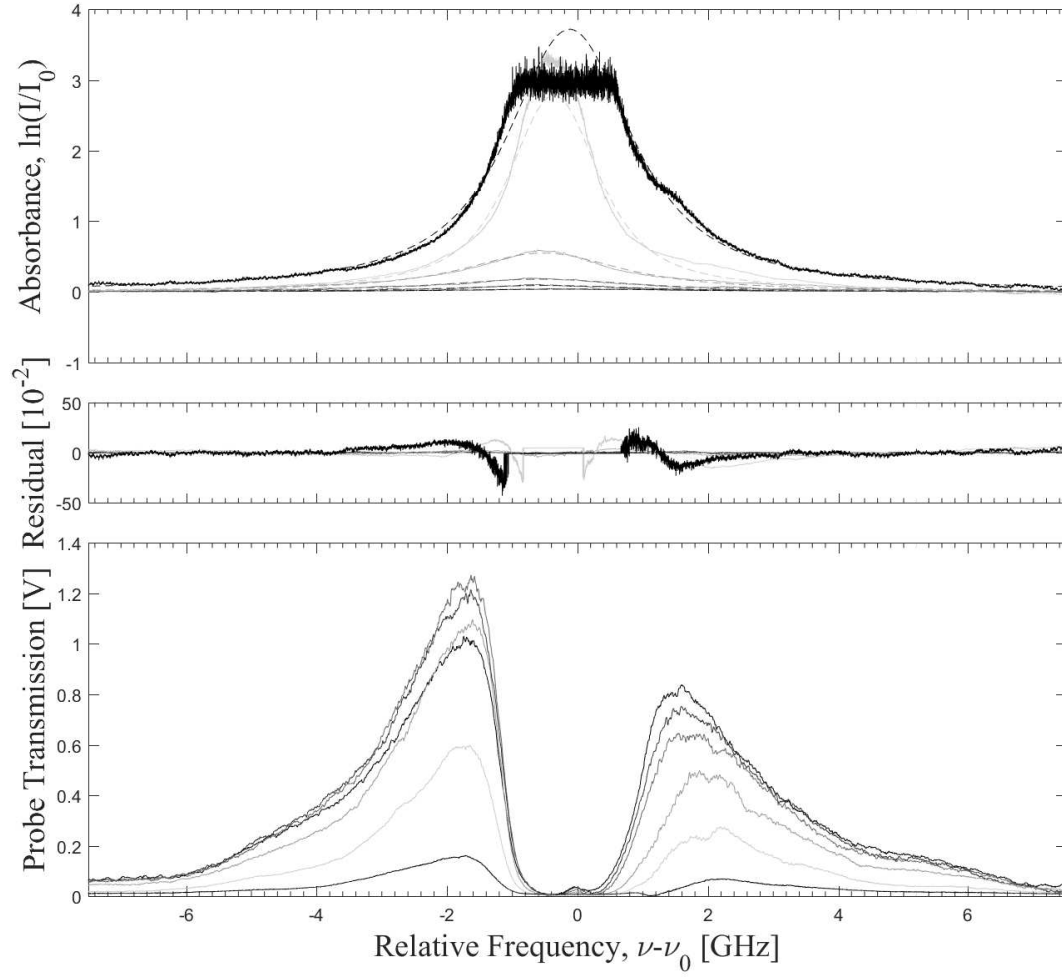


Figure 83. The saturated absorbance (top) and sub-Doppler spectra (bottom) is shown for the 811 nm transition in pure Ar at 5 Torr. The probe intensity is varied from 0.1 (—) to 1.8 W/cm² (---).

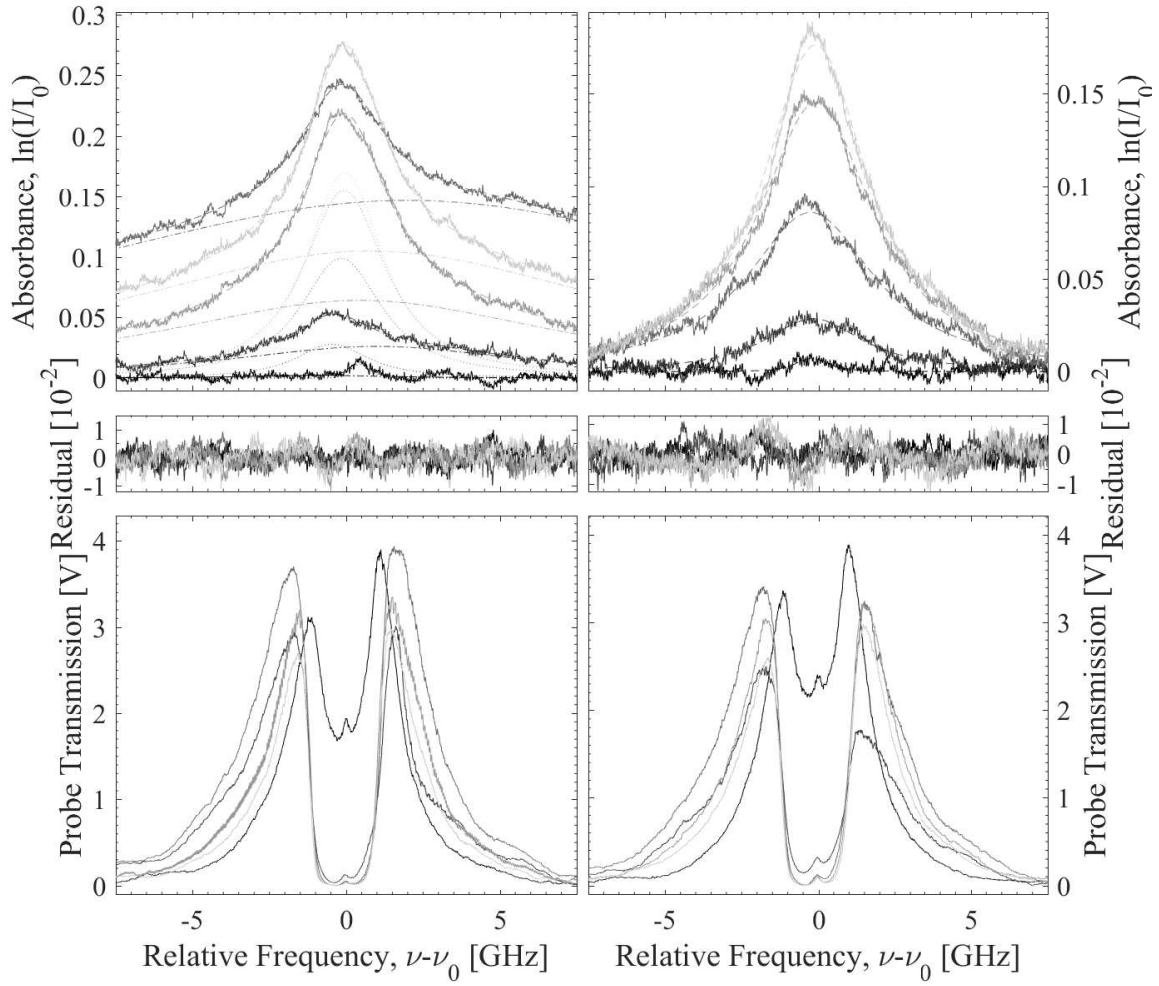


Figure 84. The saturated absorbance (top) and sub-Doppler spectra (bottom) is shown for the 811 nm transition in pure Ar at 5 (left) and 50 (right) Torr. The pump intensity is varied from 1.8 (—) to 17.7 W/cm^2 (---).

Appendix D. Microcathode Structured Array Schematic

The schematics for the microhollow cathode discharge array and the microcathode structure array are shown in Fig. 85 and Fig. 86, respectively. The microhollow cathode array is composed of a three-layer substrate consisting of a copper foil (35.5 μm thick), a fiber-glass reinforced epoxy (256 μm thick) and a second copper foil. The holes Fig. 85 are 15 mil (381 μm) in diameter and compose a 12 x 44 array, totaling 528 holes. Diameters from 50 μm to 700 μm are being considered in the design.

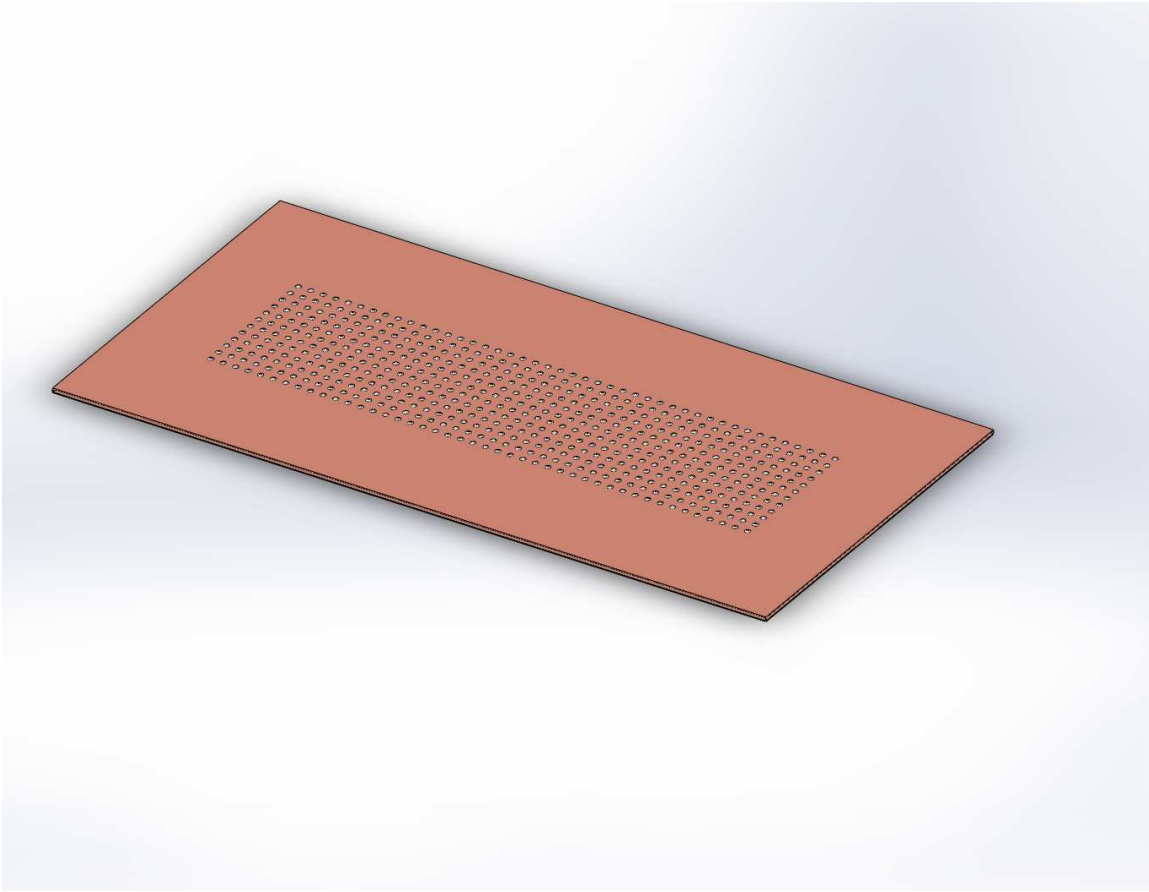


Figure 85. The microhollow cathode discharge array is shown. The three-layer substrate has 15 mil (381 μm) holes drilled into an array of 12 x 44, totaling holes 528.

The microcathode structured array is composed of a microhollow cathode array spaced by a third electrode, here a simple copper plate. There are several different

wiring schemes shown in Fig. 86 where circuit (b) will be the primary testing design. The spacing between the MHODA and the third electrode can be varied from 2 to 15 mm.

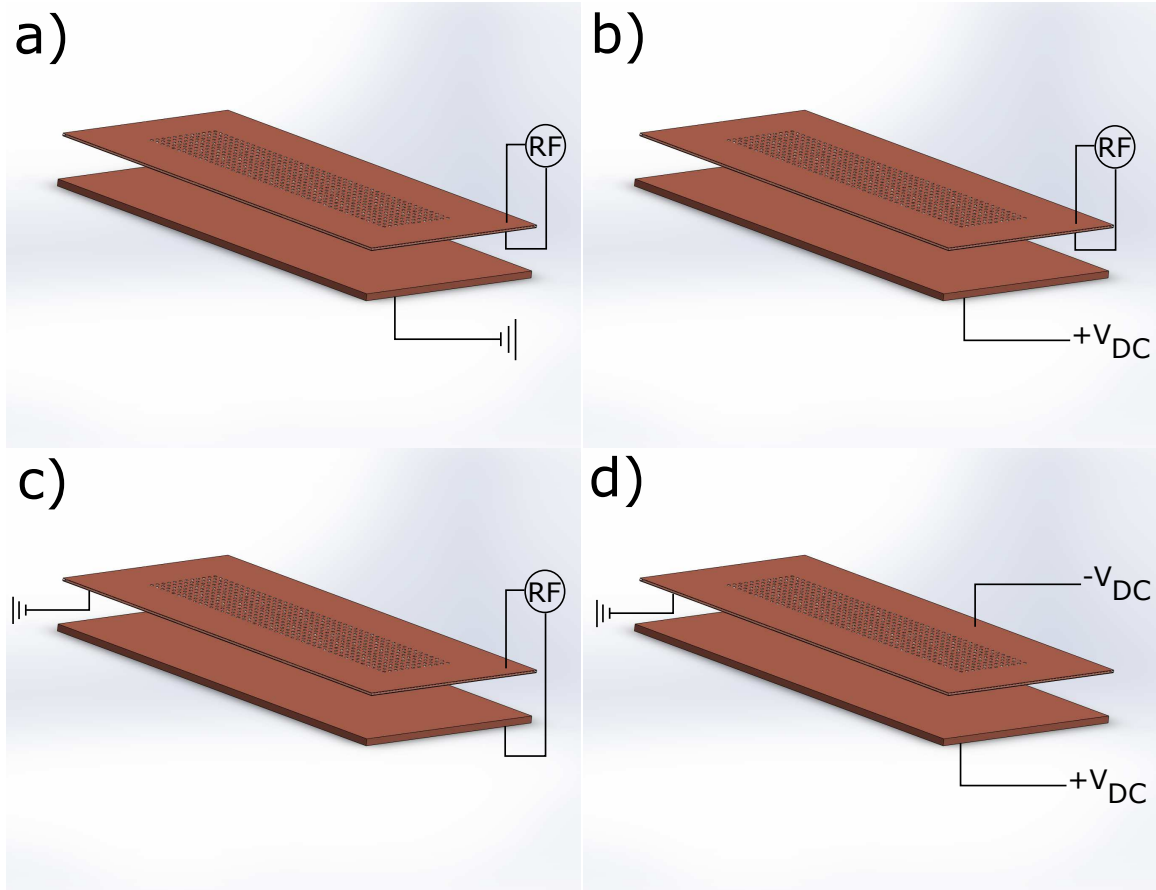


Figure 86. Several different circuit schemes are shown for operation of the microcathode structured array. The schemes are single RF (a), hybrid RF/DC (b), large-gap RF (c), and pure DC (d).

Bibliography

1. Milton Abramowitz and Irene A. Stegun, editors. *Handbook of Mathematical Functions With Formulas, Graphs, and Mathematical Tables*. National Bureau of Standards, 10 edition, 1972.
2. D. P. Aeschliman, R. A. Hill, and D. L. Evans. Collisional broadening and shift of neutral argon spectral line. *Phys. Rev. A*, 14(4):1421, 1976.
3. A.M. Akulshin, V.A. Sautenkov, V.L. Velichansky, A.S. Zibrov, and M.V. Zverkov. Power broadening of saturation absorption resonance on the d2 line of rubidium. *Opt. Commun.*, 77(4):295 – 298, 1990.
4. A. W. Ali and H. R. Griem. Theory of resonance broadening of spectral lines by atom-atom impacts. *Phys. Rev.*, 140(4A):A1044–A1049, 1965.
5. Nicole Allard and John Kielkopf. The effect of neutral non-resonant collisions on atomic spectral lines. *Rev. Mod. Phys.*, 54:1103–1182, 1982.
6. C. G. Aminoff, J. Javanainen, and M. Kaivola. Collision effects in velocity-selective optical pumping of sodium. *Phys. Rev. A*, 28:722–737, 1983.
7. P. W. Anderson. Pressure broadening in the microwave and infrared regions. *Phys. Rev.*, 76(5):647–661, 1949.
8. SN Bagaev and VP Chebotaev. Frequency stability and reproducibility of the 3.39 μm he- ne laser stabilized on the methane line. *Appl. Phys.*, 7(1):71–76, 1975.
9. Ladislav Bárdos and Hana Baránková. Cold atmospheric plasma: Sources, processes, and applications. *Thin Solid Films*, 518(23):6705–6713, 2010.
10. B. D. Barmashenko, S. Rosenwaks, and M. C. Heaven. Static diode pumped alkali lasers: Model calculations of the effects of heating, ionization, high electronic excitation and chemical reactions. *Opt. Commun.*, 292:123–125, 2013.
11. Harry Bateman, W Magnus, Fritz Oberhettinger, and Francesco Giacomo Tricomi. *Higher transcendental functions*, volume 1. McGraw-Hill New York, 1953.
12. T. J. Beahn, W. J. Condell, and H. I. Mandelberg. Excitation-transfer collisions between rubidium and helium atoms. *Phys. Rev.*, 141:83–87, 1966.
13. K. H. Becker, H. Kersten, J. Hopwood, and J. L. Lopez. Microplasmas: scientific challenges & technological opportunities. *Eur. Phys. J. D*, 60(3):437–439, 2010.
14. KH Becker, KH Schoenbach, and JG Eden. Microplasmas and applications. *J. Phys. D: Appl. Phys.*, 39(3):R55, 2006.

15. R.W. Berends, W. Kedzierski, and L. Krause. 52p12-52p32 fine-structure mixing in potassium atoms induced by collisions with noble gases. *J. Quant. Spectrosc. Radiat. Transfer*, 37(2):157–164, 1987.
16. P. R. Berman, J. E. M. Haverkort, and J. P. Woerdman. Collision kernels and transport coefficients. *Phys. Rev. A*, 34:4647–4656, 1986.
17. P. R. Berman, T. W. Mossberg, and S. R. Hartmann. Collision kernels and laser spectroscopy. *Phys. Rev. A*, 25:2550–2571, 1982.
18. Paul R. Berman. Study of collisions by laser spectroscopy. In D.R. Bates and Benjamin Bederson, editors, *Advances in Atomic and Molecular Physics*, volume 13, pages 57 – 112. Academic Press, 1978.
19. G.K. Bhowmick, B.N. Jagatap, S.A. Ahmad, and V.B. Kartha. Line shapes of saturated absorption spectra in hollow cathode discharges. *Spectrochimica Acta Part A: Molecular Spectroscopy*, 48(11):1539 – 1546, 1992.
20. A Bielski, S Brym, J Szudy, R S Trawinski, and J Wolnikowski. Pressure effects on 2p53p-2p55d and 2p53p-2p56d transition in neon. *J. Phys. B: At. Mol. Opt. Phys.*, 24:4909, 1991.
21. A Bielski, J Pospieszny, J Szudy, R S Trawinski, and J Wolnikowski. Low pressure broadening and shift of 3p54s-3p5np ($n = 4, 5, 6$) argon spectral lines perturbed by he, ne, ar. *J. Phys. B: At. Mol. Opt. Phys.*, 23:2003, 1990.
22. B. Bieniak, K. Fronc, S. Gateva-Kostova, M. Głódź, V. Grushevsky, J. Klavins, K. Kowalski, A. Rucińska, and J. Szonert. Excitation transfer between the rubidium 5^2d fine-structure levels in collisions with ground-state rubidium atoms: Experiment and theory. *Phys. Rev. A*, 62:022720, 2000.
23. L Blank and David E. Weeks. Impact broadening, shifting, and asymmetry of the D_1 and D_2 lines of alkali-metal atoms colliding with noble-gas atoms. *Phys. Rev. A*, 90:022510, 2014.
24. L Blank, David E. Weeks, and Gary S. Kedziora. $M + ng$ potential energy curves including spin-orbit coupling for $m = k, rb, cs$ and $ng = he, ne, ar$. *J. Chem. Phys.*, 136(12):124315, 2012.
25. Nicolaas Bloembergen, CKN Patel, P Avizonis, RG Clem, A Hertzberg, TH Johnson, T Marshall, RB Miller, WE Morrow, EE Salpeter, et al. Report to the american physical society of the study group on science and technology of directed energy weapons. *Rev. Mod. Phys.*, 59(3):S1–S201, 1987.
26. A V Bogachev, Sergey G Garanin, A M Dudov, V A Eroshenko, S M Kilikov, G T Mikaelian, V A Panarin, V O Pautov, A V Rus, and Stanislav A Sukharev. Diode-pumped caesium vapour laser with closed-cycle laser-active medium circulation. *Quantum Electron.*, 42(2):95, 2012.

27. C Brechignac, R Vetter, and P R Berman. Influence of collisions on saturated-absorption profiles of the 557 nm line of kr i. *J. Phys. B: At. Mol. Phys.*, 10(17):3443, 1977.
28. C. Brechignac, R. Vetter, and P. R. Berman. Study of velocity-changing collisions in excited kr using saturation spectroscopy. *Phys. Rev. A*, 17:1609–1613, 1978.
29. P Cahuzac, E Marie, O Robaux, R Vetter, and P R Berman. The effect of velocity-changing collisions upon saturated-absorption profiles: the laser line of xenon at $\lambda = 3.51 \mu\text{m}$. *J. Phys. B: At. Mol. Phys.*, 11(4):645, 1978.
30. P. H. Cahuzac, O. Robaux, and R. Vetter. Pressure broadening studies of the $3.51 \mu\text{m}$ line of xenon by saturated amplification techniques. *J. Phys. B: Atom. Mol. Phys.*, 9(18):3165, 1976.
31. Th Callegari, X Aubert, A Rousseau, JP Boeuf, and LC Pitchford. Microhollow cathode sustained discharges: comparative studies in micro-and equivalent macro-cell geometries. *Eur. Phys. J. D*, 60(3):581–587, 2010.
32. Joseph A Cardoza. A simple model for fine structure transitions in alkali-metal noble-gas collisions. Master’s thesis, Air Force Intitute of Technology, 2015.
33. P. Cerez, A. Brillet, C. N. Man-Pichot, and R. Felder. He-ne lasers stabilized by saturated absorption in iodine at 612 nm. *IEEE Trans. Instrum. Meas.*, 29(4):352–354, 1980.
34. G. D. Chapman and L. Krause. Sensitized fluorescence in vapors of alkali metals: Viii. energy transfer between the 4 2p levels in potassium induced by inelastic collisions. *Can. J. Phys.*, 44(4):753–768, 1966.
35. Hui Chen, Hebin Li, Yuri V. Rostovtsev, Mikhail A. Gubin, Vladimir A. Sautenkov, and Marlan O. Scully. Near-infrared saturation spectroscopy of cesium molecules using a diode laser. *J. Opt. Soc. Am. B*, 23(4):723–726, 2006.
36. G. H. Copley. A comparison of foreign gas broadening and shift of neon and argon emission lines. *J. Quant. Spectrosc. Radiat. Transfer*, 16:377–384, 1976.
37. G. H. Copley and D. M. Camm. Pressure broadening and shift of argon emission lines. *J. Quant. Spectrosc. Radiat. Transfer*, 14:899–907, 1974.
38. Tiffany L. Correll, Vlasta Horvatic, Nicol Omenetto, James D. Winefordner, and Cedomil Vadla. Experimental evaluation of the cross-sections for the $\text{cs}(6d) \rightarrow \text{cs}(7p_j)$ and $\text{cs}(6d5/2) \rightarrow \text{cs}(6d3/2)$ collisional transfer processes induced by he and ar. *Spectrochim. Acta, Part B*, 61(6):623 – 633, 2006.
39. R. D. Cowan and G. H. Dieke. Self-absorption of spectrum lines. *Rev. Mod. Phys.*, 20(2):418–455, 1948.

40. C. J. Cuneo, Jeffery J. Maki, and D. H. McIntyre. Optically stabilized diode laser using high-contrast saturated absorption. *Appl. Phys. Lett.*, 64(20):2625–2627, 1994.
41. M. Czajkowski, D. A. McGillis, and L. Krause. Sensitized fluorescence in vapors of alkali metals: V. energy transfer in collisions between cesium and inert gas atoms. *Can. J. Phys.*, 44(1):91–103, 1966.
42. E. I. Dashevskaya, E. E. Nikitin, and A. I. Reznikov. Theory of collisionally induced intramultiplet mixing in excited alkali atoms. *J. Chem. Phys.*, 53(3):1175–1180, 1970.
43. E.I. Dashevskaya and E.E. Nikitin. Inelastic transitions between the fine-structure components of alkali-metal atoms in the case of adiabatic collisions. ii. calculations of cross sections. *Opt. Spectrosc.*, 22:473–476, 1967.
44. F. de Tomasi, M. Allegrini, E. Arimondo, G. S. Agarwal, and P. Ananthalakshmi. Collision-enhanced resonance of laser-diode-excited cs in a buffer gas. *Phys. Rev. A*, 48:3820–3829, 1993.
45. F. de Tomasi, M. Allegrini, E. Arimondo, L. Windholz, and G. Pichler. Line-shape changes in an optically thick na vapour with a buffer gas. *Opt. Commun.*, 112(5):289 – 295, 1994.
46. John B. Delos. Theory of electronic transitions in slow atomic collisions. *Rev. Mod. Phys.*, 53:287–357, 1981.
47. Wolfgang Demtröder. *Laser Spectroscopy, Volume 1*. Springer, fourth edition, 2008.
48. Wolfgang Demtröder. *Laser Spectroscopy, Volume 2*. Springer, fourth edition, 2008.
49. A V Demyanov, I V Kochetov, and P A Mikheyev. Kinetic study of a cw optically pumped laser with metastable rare gas atoms produced in an electric discharge. *J. Phys. D: Appl. Phys.*, 46(37):375202, 2013.
50. J. Dhiflaoui and H. Berriche. One-electron pseudopotential investigation of csar van der waals system including the spin-orbit interaction. *J. Phys. Chem. A*, 114(26):7139–7145, 2010.
51. O. Di Lorenzo-Filho, P. C. de Oliveira, and J. R. Rios Leite. Saturation spectroscopy of infrared molecular transition in an optically thick cell. *Opt. Lett.*, 16(22):1768–1770, 1991.
52. O. Di Lorenzo-Filho and J. R. Rios Leite. Line shapes of saturated absorption spectroscopy in optically thick media. *Phys. Rev. A*, 58:1139–1145, 1998.

53. P. Dupla and F. Spiegelmann. A pseudopotential hole-particle treatment of neutral rare gas excimer systems. i. formalism. *J. Chem. Phys.*, 105(4):1492–1499, 1996.
54. P. Dupla and F. Spiegelmann. A pseudopotential hole-particle treatment of neutral rare gas excimer systems. ii. the rydberg states of the ar*2 dimer. *J. Chem. Phys.*, 105(4):1500–1515, 1996.
55. Julianne Elward-Berry and Michael J. Berry. Lithium [$\text{li}^*(2^2p_{1/2,3/2})$] fine structure transitions induced by collisions with noble gas atoms. *J. Chem. Phys.*, 72(8):4500–4509, 1980.
56. Ben Eshel, Joseph A. Cardoza, David E. Weeks, and Glen P. Perram. Role of adiabaticity in controlling alkali-metal fine-structure mixing induced by rare gases. *Phys. Rev. A*, 95:042708, 2017.
57. Ben Eshel, Christopher A Rice, and Glen P Perram. Pressure broadening and shift rates for ar (s–p) transitions observed in an ar–he discharge. *J. Quant. Spectrosc. Radiat. Transfer*, 179:40–50, 2016.
58. Ben Eshel, David E. Weeks, and Glen P. Perram. The role of adiabaticity in alkali atom-fine structure mixing. *Proc. SPIE*, 8962:896207–896207–9, 2014.
59. M. B. Faist and R. B. Bernstein. Computational study of elastic and electronically inelastic scattering of br by ground state i atoms: Role of potential curve crossing. *J. Chem. Phys.*, 64(7):2971–2984, 1976.
60. H.M. Foley. The pressure broadening of spectral lines. *Phys. Rev.*, 69:616–628, 1946.
61. Louis Galatry. Simultaneous effect of doppler and foreign gas broadening on spectral lines. *Phys. Rev.*, 122:1218–1223, 1961.
62. Alan Gallagher. Rubidium and cesium excitation transfer in nearly adiabatic collisions with inert gases. *Phys. Rev.*, 172(1):88–96, 1968.
63. Jun Gao, Yongle He, Pengfei Sun, Zhifan Zhang, Xinbing Wang, and Duluo Zuo. Simulations for transversely diode-pumped metastable rare gas lasers. *J. Opt. Soc. Am. B*, 34(4):814–823, 2017.
64. Jun Gao, PengFei Sun, XinBing Wang, and DuLuo Zuo. Modeling of a dual-wavelength pumped metastable argon laser. *Laser Phys. Lett.*, 14(3):035001, 2017.
65. M. A. Gearba, J. F. Sell, B. M. Patterson, R. Lloyd, J. Plyler, and R. J. Knize. Temperature dependence of rb 5p fine-structure transfer induced by 4he collisions. *Opt. Lett.*, 37(10):1637–1639, 2012.

66. Hans R. Griem. *Spectral line broadening by plasmas*. Academic Press, 1974.
67. Hans R. Griem. *Principles of Plasma Spectroscopy*. Cambridge University Press, 1997.
68. E. M. Guild and G. A. Pitz. Private Communication, January 2015.
69. M.R. Guy, E.M. Guild, J.W. Young, I.O. Sheets, and G.A. Pitz. Pressure induced hyperfine shift and broadening rates of the and transitions of rubidium with he, ar, , and. *J. Quant. Spectrosc. Radiat. Transfer*, 169:14 – 22, 2016.
70. G. D. Hager and G. P. Perram. A three-level analytic model for alkali metal vapour lasers part i: Narrow band optical pumping. *Appl. Phys. B*, 101:45, 2010.
71. Gordon D. Hager, Gordon E. Lott, Aaron J. Archibald, L. Blank, David E. Weeks, and Glen P. Perram. High pressure line shapes for cs d1 and d2 lines and empirically informed interaction potentials. *J. Quant. Spectrosc. Radiat. Transfer*, 147:261–273, 2014.
72. Gordon D. Hager and Glen P. Perram. A three-level analytic model for alkali metal vapour lasers part ii: broadband optical pumping. *Appl. Phys. B*, 112(4):507, 2013.
73. Jiande Han, Leonid Glebov, George Venus, and Michael C. Heaven. Demonstration of a diode pumped metastable ar laser. *Opt. Lett.*, 38(24):5458–5461, 2013.
74. Jiande Han and Michael C. Heaven. Gain and lasing of optically pumped metastable rare gas atoms. *Opt. Lett.*, 37(11):2157, 2012.
75. Jiande Han and Michael C. Heaven. Kinetics of optically pumped ar metastables. *Opt. Lett.*, 39(22):6541–6544, 2014.
76. Jiande Han and Michael C. Heaven. Kinetics of optically pumped kr metastables. *Opt. Lett.*, 40(7):1310–1313, 2015.
77. Jiande Han, Michael C. Heaven, Daniel Emmons, Glen P. Perram, David W. Weeks, and William F. Bailey. Pulsed discharge production of ar* metastables. *Proc. SPIE*, 9729:97290D–2, 2016.
78. H. J. M. Hanley. The viscosity and thermal conductivity coefficients of dilute argon, krypton, and xenon. *J. Phys. Chem. Ref. Data*, 2(3):619–642, 1973.
79. Serge Haroche and Francis Hartmann. Theory of saturated-absorption line shapes. *Phys. Rev. A*, 6:1280–1300, 1972.
80. J. E. M. Haverkort, J. P. Woerdman, and P. R. Berman. Experimental determination of na noble-gas velocity-changing and fine-structure-changing collision kernels. *Phys. Rev. A*, 36:5251–5264, 1987.

81. M. C. Heaven. Pulsed discharge diode pumped ar* laser. Presented at the Directed Energy Professional Society 19th Annual Symposium, 02 2017.
82. William Russell Hindmarsh and Judith M Farr. Collision broadening of spectral lines by neutral atoms. *Prog. Quantum Electron.*, 2:143–214, 1973.
83. H.P. Hooymayers and C.Th.J. Alkemade. Relationship between cross section for doublet mixing and massey parameter for alkali-noble gas atom collisions. *Chem. Phys. Lett.*, 4(5):277 – 279, 1969.
84. M Hugon, F Gounand, P R Fournier, and J Berlande. Collisional processes of rubidium in the s and d rydberg states with helium. *J. Phys. B: At. Mol. Phys.*, 13(8):1585, 1980.
85. Edward J. Hurd, Jeremy C. Holtgrave, and Glen P. Perram. Intensity scaling of an optically pumped potassium laser. *Opt. Commun.*, 357:63–66, 2015.
86. Gerald C. Manke II and Gordon D. Hager. A review of recent experiments and calculations relevant to the kinetics of the hf laser. *J. Phys. Chem. Ref. Data*, 30(3):713–733, 2001.
87. I Jackowska and M Lukaszewski. Cross sections for j mixing in 8d and 9d states of caesium in collisions with noble-gas atoms. *J. Phys. B: At., Mol. Opt. Phys.*, 23(12):2097, 1990.
88. Herrick L. Johnston and Edward R. Grilly. Viscosities of carbon monoxide, helium, neon, and argon between 80 and 300k. coefficients of viscosity. *J. Phys. Chem.*, 46(8):948–963, 1942.
89. J. A. Jordan and P. A. Franken. Collision-induced mixing in the first excited states of sodium and potassium. *Phys. Rev.*, 142:20–25, 1966.
90. Humayun Md. Kabir and M. C. Heaven. Collisional relaxation of the kr(4p55p) states in he, ne and krypton. *J. Phys. Chem. A*, 115:9724–9730, 2012.
91. Hidetoshi Katori and Fujio Shimizu. Lifetime measurement of the $1s_5$ metastable state of argon and krypton with a magneto-optical trap. *Phys. Rev. Lett.*, 70:3545–3548, 1993.
92. Jung B. Kim, H. A. Kim, H. S. Moon, and H. S. Lee. High-contrast saturated absorption spectrometer with a grating reflector as an optical frequency locker. *Appl. Opt.*, 36(12):2459–2461, 1997.
93. Kelly A. Kluttz, Todd D. Averett, and Brian A. Wolin. Pressure broadening and frequency shift of the D_1 and D_2 lines of rb and k in the presence of ^3he and n_2 . *Phys. Rev. A*, 87:032516, 2013.

94. N. Konjevic. Plasma broadening and shifting of non-hydrogenic spectral lines: present status and applications. *Phys. Rep.*, 316:339, 1999.
95. N. Konjevic, M. S. Dimitrijevi, and W. L. Wiese. Experimental stark widths and shifts for spectral lines of neutral atoms (a critical review of selected data for the period 1976 to 1982). *J. Phys. Chem. Ref. Data*, 13(3):649, 1984.
96. N. Konjevic, A. Lesage, J. R. Fuhr, and W. L. Wiese. Experimental stark widths and shifts for spectral lines of neutral and ionized atoms (a critical review of selected data for the period 1989 through 2000). *J. Phys. Chem. Ref. Data*, 31(3):819, 2002.
97. N. Konjevic and W. L. Wiese. Experimental stark widths and shifts for non-hydrogenic spectral lines of ionized atoms. *J. Phys. Chem. Ref. Data*, 5(2):259, 1976.
98. A. Kramida, Yu. Ralchenko, J. Reader, and NIST ASD Team. NIST Atomic Spectra Database (ver. 5.2), [Online]. Available: <http://physics.nist.gov/asd> [2015, June 25]. National Institute of Standards and Technology, Gaithersburg, MD., 2014.
99. L. Krause. Collisional excitation transfer between the $^2p_{1/2}$ and $^2p_{3/2}$ levels in alkali atoms. *Appl. Opt.*, 5(9):1375–1382, 1966.
100. William Krupke, Raymond J. Beach, V. Keith Kanz, and Stephen A. Payne. Resonance transition 795-nm rubidium laser. *Opt. Lett.*, 28(23):2336, 2003.
101. LD Landau. On the theory of transfer of energy at collisions ii. *Phys. Z. Sowjetunion*, 2(46):7, 1932.
102. MP Langevin. Une formule fondamentale de théorie cinétique. *Annales de Chimie et de Physique*, 5:245–288, 1905.
103. C. S. Lee, D. M. Camm, and G. H. Copley. Van der waals broadening of argon absorption lines. *J. Quant. Spectrosc. Radiat. Transfer*, 15:211–216, 1975.
104. R. J. Leiweke and B. N. Ganguly. Diode laser spectroscopic measurements of gas temperature in a pulsed dielectric barrier discharge using collisional broadening and shift of 1s3-2p2 and 1s5-2p7 argon transitions. *J. Appl. Phys.*, 113:143302, 2013.
105. A. Lesage. Experimental stark widths and shifts for spectral lines of neutral and ionized atoms a critical review of selected data for the period 2001-2007. *New Astronomy Reviews*, 52:471535, 2009.
106. Charleton D. Lewis, David E. Weeks, and Glen P. Perram. Diode pumped alkali laser kinetics: comparison of theory and experiment. *Proc. SPIE*, 8381:83810A, 2012.

107. Charlton D Lewis, II. *Non-Adiabatic Atomic Transitions: Computational Cross Section Calculations of Alkali Metal-Noble Gas Collisions*. PhD thesis, Air Force Institute of Technology, 2011.
108. M Lukaszewski and I Jackowska. Fine-structure mixing in the 9d state of caesium induced in collisions with noble-gas atoms. *J. Phys. B: At., Mol. Opt. Phys.*, 21(21):L659, 1988.
109. M Lukaszewski and I Jackowska. J mixing in nd ($n=10-14$) states of caesium induced in collisions with noble-gas atoms. *J. Phys. B: At., Mol. Opt. Phys.*, 24(8):2047, 1991.
110. G Lj Majstorovic, N V Ivanovic, N M Sisovic, S Djurovic, and N Konjevic. Ari and nei spectral line shapes for an abnormal glow discharge diagnostics. *Plasma Sources Sci. Technol.*, 22(4):045015, 2013.
111. T. R. Mallory, W. Kedzierski, J. B. Atkinson, and L. Krause. 9^2d fine-structure mixing in rubidium by collisions with ground-state rb and noble-gas atoms. *Phys. Rev. A*, 38:5917–5920, 1988.
112. Jay Marmo, Hagop Injeyan, Hiroshi Komine, Stuart McNaught, Jason Machan, and Jeff Sollee. Joint high power solid state laser program advancements at northrop grumman. *Proc. SPIE*, 7195:719507–719507–6, 2009.
113. F Masnou-Seeuws. Fine-structure transitions in sodium-rare-gas collisions. *J. Phys. B: At. Mol. Phys.*, 3(11):1437, 1970.
114. F Masnou-Seeuws and R McCarroll. Use of hund’s coupling scheme in the theory of fine structure transitions in atom-atom collisions: application to $na(3p)-he$ collisions. *J. Phys. B: At. Mol. Phys.*, 7(16):2230, 1974.
115. B. H. McGuyer, R. Marsland, B. A. Olsen, and W. Happer. Cusp kernels for velocity-changing collisions. *Phys. Rev. Lett.*, 108:183202, 2012.
116. J M Mestdagh, J Berlande, J Cuvellier, P de Pujo, and A Binet. Fine-structure transitions in $k(^4p)$ induced by rare gases and diatomic molecules. *J. Phys. B: At. Mol. Phys.*, 15(3):439, 1982.
117. Pavel A Mikheyev, Alexander K Chernyshov, Nikolay I Ufimtsev, Ekaterina A Vorontsova, and Valeriy N Azyazov. Pressure broadening of ar and kr $(n+1)s\ [3/2]\ 2\rightarrow(n+1)p\ [5/2]\ 3$ transition in the parent gases and in he. *J. Quant. Spectrosc. Radiat. Transfer*, 164:1–7, 2015.
118. Pavel A Mikheyev, Jiande Han, Amanda Clark, Carl Sanderson, and Michael C Heaven. Production of ar metastables in a dielectric barrier discharge. In *XXI International Symposium on High Power Laser Systems and Applications*, pages 102540X–102540X. International Society for Optics and Photonics, 2017.

119. W. S. Miller, C. V. Sulham, J. C. Holtgrave, and G. P. Perram. Limitations of an optically pumped rubidium laser imposed by atom recycle rate. *Appl. Phys. B*, 103(4):819, 2011.
120. Woody S. Miller, Christopher A. Rice, Gordon D. Hager, Mathew D. Rotandaro, Hamid Berriche, and Glen P. Perram. High pressure line shapes of the rb d_1 and d_2 lines for ^4he and ^3he collisions. *J. Quant. Spectrosc. Radiat. Transfer*, 184:118–134, 2016.
121. J. Mitroy and J.-Y. Zhang. Long-range dispersion interactions. ii. alkali-metal and rare-gas atoms. *Phys. Rev. A*, 76:032706, 2007.
122. Geol Moon and Heung-Ryoul Noh. Analytic calculation of linear susceptibility in velocity-dependent pump-probe spectroscopy. *Phys. Rev. A*, 78:032506, 2008.
123. Geol Moon and Heung-Ryoul Noh. A comparison of the dependence of saturated absorption signals on pump beam diameter and intensity. *J. Opt. Soc. Am. B*, 25(12):2101–2106, 2008.
124. R Andrew Motes and Richard W Berdine. *Introduction to high-power fiber lasers*. Directed Energy Professional Society, 2009.
125. P. S. Moussounda and P. Ranson. Pressure broadening of argon lines emitted by a high pressure microwave discharge (surfatron). *J. Phys. B: At. Mol. Phys.*, 20:949, 1987.
126. E Munoz-Serrano, G Hagelaar, Th Callegari, JP Boeuf, and LC Pitchford. Properties of plasmas generated in microdischarges. *Plasma Phys. Controlled Fusion*, 48(12B):B391, 2006.
127. P Munster and J Marek. Determination of cross sections of excitation transfer between the fine-structure components of $\text{cs}(7^2p)$, $\text{rb}(6^2p)$ and $\text{rb}(7^2p)$ induced by collisions with rare-gas atoms. *J. Phys. B: At. Mol. Phys.*, 14(6):1009, 1981.
128. E. E. Nikitin. Nonadiabatic transitions between fine-structure components of alkali atoms upon collision with inert-gas atoms. *J. Chem. Phys.*, 43(2):744–750, 1965.
129. E. E. Nikitin. Inelastic transitions between the fine structure components of alkali metal atoms in case of adiabatic collisions. i. general theory. *Opt. Spectrosc.*, 22:379, 1967.
130. E.E. Nikitin. *Advances in Chemical Physics, Volume 28: The Excited State in Chemical Physics*, chapter V, pages 317–378. John Wiley & Sons, Inc., 1975.
131. Michal Nikodem and Gerard Wysocki. Measuring optically thick molecular samples using chirped laser dispersion spectroscopy. *Opt. Lett.*, 38(19):3834–3837, 2013.

132. H R Noh and H S Moon. Analytical solutions of the susceptibility for doppler-broadened three-level atomic systems. *J. Phys. B: At., Mol. Opt. Phys.*, 45(24):245002, 2012.
133. Heung-Ryoul Noh. Susceptibility for doppler-broadened two-level atoms in pump-probe spectroscopy: analytical solutions revisited. *J. Opt. Soc. Am. B*, 33(3):308–312, 2016.
134. M. J. O’Callaghan and A. Gallagher. Sodium doppler-free collisional line shapes. *Phys. Rev. A*, 39:6190–6205, 1989.
135. I. E. Olivares, A. E. Duarte, T. Lokajczyk, A. Dinklage, and F. J. Duarte. Doppler-free spectroscopy and collisional studies with tunable diode lasers of lithium isotopes in a heat-pipe oven. *J. Opt. Soc. Am. B*, 15(7):1932–1939, 1998.
136. Ronald E. Olson. Fine structure transition cross sections for several alkali + rare gas systems. *Chem. Phys. Lett.*, 33(2):250 – 253, 1975.
137. P. G. Pappas, M. M. Burns, D. D. Hinshelwood, M. S. Feld, and D. E. Murnick. Saturation spectroscopy with laser optical pumping in atomic barium. *Phys. Rev. A*, 21:1955–1968, 1980.
138. Hae Il Park, Tae Il Lee, Ki Wan Park, Hong Koo Baik, Se-Jong Lee, and Kie Moon Song. Formation of large-volume, high-pressure plasmas in micro-hollow cathode discharges. *Appl Phys Lett*, 82(19):3191–3193, 2003.
139. Sung-Jin Park, Jack Chen, Clark J Wagner, Nels P Ostrom, Chang Liu, and J Gary Eden. Microdischarge arrays: a new family of photonic devices (revised*). *IEEE J Sel Topics in Quantum Electron*, 8(2):387–394, 2002.
140. J. Pascale and R. E. Olson. Total cross sections for $\text{Na}(3^2p_{1/2} \rightarrow 3^2p_{3/2}) + \text{rare gas collisions}$. *J. Chem. Phys.*, 64(9):3538–3543, 1976.
141. J. Pascale and P. M. Stone. Semiclassical calculations of cross sections for fine-structure transitions in $\text{Rb}(62p)$ and $\text{Cs}(82p)$ colliding with rare gas atoms. *J. Chem. Phys.*, 65(12):5122–5132, 1976.
142. Glen P. Perram, Salvatore J. Cusumano, Steven T. Fiorino, and Robert L. Hengehold. *An Introduction to laser weapon systems*. Directed Energy Professional Society, 2010.
143. Ioannis D. Petsalakis, Giannoula Theodorakopoulos, Heinz-Peter Liebermann, and Robert J. Buekner. Potential energy curves and dipole transition moments for electronic states of ArHe and HeHe . *J. Chem. Phys.*, 115:6365, 2001.
144. M Pimbert. Transfert d’excitation électronique, par collision atomique, entre niveaux levs d’un atome de CsI . *J. Phys. France*, 33(4):331–343, 1972.

145. L. G. Piper, J. E. Velazco, and D. W. Setser. Quenching cross sections for electronic energy transfer reactions between metastable argon atoms and noble gases and small molecules. *J. Chem. Phys.*, 59(6):3323–3340, 1973.
146. Bruce Pitre, A. G. A. Rae, and L. Krause. Sensitized fluorescence in vapors of alkali metals: Vi. energy transfer in collisions between rubidium and inert gas atoms. *Can. J. Phys.*, 44(4):731–740, 1966.
147. John Pitre and L. Krause. Sensitized fluorescence in vapors of alkali metals: Ix. energy transfer in collisions between sodium and inert gas atoms. *Can. J. Phys.*, 45(8):2671–2681, 1967.
148. Greg A. Pitz, Charles D. Fox, and Glen P. Perram. Pressure broadening and shift of the cesium d_2 transition by the noble gases and n_2 , h_2 , hd , d_2 , ch_4 , c_2h_6 , cf_4 , and ^3he with comparison to the d_1 transition. *Phys. Rev. A*, 82(4):042502, 2010.
149. Greg A. Pitz, Charles D. Fox, and Glen P. Perram. Transfer between the cesium $6^2p_{1/2}$ and $6^2p_{3/2}$ levels induced by collisions with h_2 , hd , d_2 , ch_4 , c_2h_6 , cf_4 and c_2f_6 . *Phys. Rev. A*, 84(3):032708, 2011.
150. Greg A. Pitz, Donald M. Stalnaker, Eric M. Guild, Benjamin Q. Olier, Paul J. Moran, Steven W. Townsend, and David A. Hostutler. Advancements in flowing diode pumped alkali lasers. *Proc. SPIE*, 9729:972902, 2016.
151. Greg A. Pitz, Douglas E. Wertepny, and Glen P. Perram. Pressure broadening and shift of the cesium d_1 transition by the noble gases and n_2 , h_2 , hd , d_2 , ch_4 , c_2h_6 , cf_4 , and ^3he . *Phys. Rev. A*, 80(6):062718, 2009.
152. Richard K. Preston, Chris Sloane, and William H. Miller. Semiclassical theory of collisionally induced fine-structure transitions in fluorine atoms. *J. Chem. Phys.*, 60(12):4961–4969, 1974.
153. S. G. Rautian and I. I. Sobel'man. The effect of collisions on the doppler broadening of spectral lines. *Soviet Physics USPEKHI*, 9(5):701, 1967.
154. W. T. Rawlins, K. L. Galbally-Kinney, S. J. Davis, A. R. Hoskinson, and J. A. Hopwood. Laser excitation dynamics of argon metastables generated in atmospheric pressure flows by microwave frequency microplasma arrays. *Proc. of SPIE*, 8962:896203, 2014.
155. W. T. Rawlins, K. L. Galbally-Kinney, S. J. Davis, A. R. Hoskinson, J. A. Hopwood, and M. C. Heaven. Optically pumped microplasma rare gas laser. *Opt. Express*, 23(4):4804–4813, 2015.
156. R H G Reid. Differential cross sections for excited alkali-inert gas collisions. *J. Phys. B: At. Mol. Phys.*, 8(18):L493, 1975.

157. R. H. G. Reid and A. Dalgarno. Fine-structure transitions and shape resonances. *Phys. Rev. Lett.*, 22:1029–1030, 1969.
158. R H G Reid and R F Rankin. The eigenphase formulation of fine-structure transition cross sections. *J. Phys. B: At. Mol. Phys.*, 11(1):55, 1978.
159. M. V. Romalis, E. Miron, and G. D. Cates. Pressure broadening of rb d_1 and d_2 lines by ^3he , ^4he , n_2 , and xe: Line cores and near wings. *Phys. Rev. A*, 56(6):4569–4578, 1997.
160. Matthew D. Rotondaro and Glen P. Perram. Collisional broadening and shift of the rubidium d_1 and d_2 lines ($5^2s_{1/2} \rightarrow 5^2p_{1/2}, 5^2p_{3/2}$) by rare gases, h_2 , d_2 , n_2 , ch_4 , and cf_4 . *J. Quant. Spectrosc. Radiat. Transfer*, 57(4):497–507, 1997.
161. Matthew D. Rotondaro and Glen P. Perram. Role of rotational-energy defect in collisional transfer between the $5^2P_{1/2,3/2}$ levels in rubidium. *Phys. Rev. A*, 57:4045–4048, 1998.
162. Hiroyuki Sasada and O Kubota. Frequency of lamb-dip-stabilized $1.52\ \mu\text{m}$ he-ne lasers. *Appl. Phys. B*, 55(2):186–188, 1992.
163. A. Sasso, G. M. Tino, M. Inguscio, N. Beverini, and M. Francesconi. Investigation of collisional lineshapes of neon transitions in noble gases' mixtures. *IL NUOVO CIMENTO*, 10(8):941–957, 1988.
164. Nivard Scheel and Virginia Griffing. Interaction energy of an alkali metal with a rare gas. *J. Chem. Phys.*, 36(6):1453–1458, 1962.
165. C. Schmidt-Inglesias, R. Corbaln, and L. Roso. Revealing of hidden resonances through high-contrast absorption spectroscopy. *Opt. Commun.*, 98(1):72 – 76, 1993.
166. C. Schmidt-Inglesias, L. Roso, and R. Corbalan. Saturation spectroscopy in optically thick three-level gas media. *Opt. Lett.*, 15(1):63–65, 1990.
167. C. Schmidt-Inglesias, L. Roso, and R. Corbaln. On the resolving power of high-contrast saturated absorption spectroscopy. *Opt. Commun.*, 90(4):251 – 254, 1992.
168. Karl H. Schoenbach and Kurt Becker. 20 years of microplasma research: a status report. *Eur. Phys. J. D*, 70(2):29, 2016.
169. J F Sell, M A Gearba, B M Patterson, D Byrne, G Jemo, T C Lilly, R Meeter, and R J Knize. Collisional excitation transfer between rb(5p) states in 50 - 3000 torr of ^4he . *J. Phys. B: At., Mol. Opt. Phys.*, 45(5):055202, 2012.
170. C. Y. She and J. R. Yu. Doppler-free saturation fluorescence spectroscopy of na atoms for atmospheric application. *Appl. Opt.*, 34(6):1063–1075, 1995.

171. Jong W. Shon and Mark J. Kushner. Excitation mechanisms and gain modeling of the high-pressure atomic ar laser in he/ar mixtures. *J. Appl. Phys.*, 75(4):1883–1890, 1994.
172. I. Siara, E. S. Hrycyshyn, and L. Krause. Sensitized fluorescence in vapors of alkali atoms. xiii. $6^2p_{1/2}$ - $6^2p_{3/2}$ excitation transfer in rubidium, induced in collisions with noble gas atoms. *Can. J. Phys.*, 50(16):1826–1832, 1972.
173. I. N. Siara, H. S. Kwong, and L. Krause. Sensitized fluorescence in vapors of alkali atoms xiv. temperature dependence of cross sections for $7^2p_{1/2}$ - $7^2p_{3/2}$ mixing in cesium, induced in collisions with noble gas atoms. *Can. J. Phys.*, 52(11):945–949, 1974.
174. P. W. Smith and R. Hänsch. Cross-relaxation effects in the saturation of the 6328-Å neon-laser line. *Phys. Rev. Lett.*, 26:740–743, 1971.
175. D. N. Stacey and J. M. Vaughan. Pressure broadening and oscillator strengths in argon. *Phys. Letters*, 11(2):105–106, 1964.
176. Robert H Stark and Karl H Schoenbach. Direct current high-pressure glow discharges. *J. Appl. Phys.*, 85(4):2075–2080, 1999.
177. Clifford V. Sulham, Glen. P. Perram, Michael P. Wilkinson, and David A. Hostutler. A pulsed, optically-pumped rubidium laser at high pump intensity. *Opt. Commun.*, 283(21):4328–4332, 2010.
178. J. Supronowicz, J. B. Atkinson, and L. Krause. Fine-structure mixing in 7^2d and 8^2d rb atoms, induced in collisions with ground-state atoms and molecules. *Phys. Rev. A*, 30:112–118, 1984.
179. J. Supronowicz, J. B. Atkinson, and L. Krause. 6^2d fine-structure mixing in rubidium induced in collisions with ground-state rb and noble-gas atoms and with n_2 molecules. *Phys. Rev. A*, 31:2691–2694, 1985.
180. S. Svanberg, G.-Y. Yan, T. P. Duffey, W.-M. Du, T. W. Hänsch, and A. L. Schawlow. Saturation spectroscopy for optically thick atomic samples. *J. Opt. Soc. Am. B*, 4(4):462–469, 1987.
181. K. Tachibana, H. Harima, and Y. Urano. Measurement of collisional broadening and the shift of argon spectral lines using a tunable diode laser. *J. Phys. B: At. Mol. Phys.*, 15:3169, 1982.
182. Claire Tendero, Christelle Tixier, Pascal Tristant, Jean Desmaison, and Philippe Leprince. Atmospheric pressure plasmas: A review. *Spectrochim. Acta, Part B*, 61(1):2 – 30, 2006.

183. J Tenenbaum, E Miron, S Lavi, J Liran, M Strauss, J Oreg, and G Erez. Velocity changing collisions in saturation absorption of u. *J. Phys. B: At. Mol. Phys.*, 16(24):4543, 1983.
184. William J. Thompson. Numerous neat algorithms for the voigt profile function. *Computers in Physics*, 7(6):627, 1993.
185. Douglas E. Thornton, Grady T. Phillips, and Glen P. Perram. Velocity changing collisions in the laser saturation spectra of ^{87}Rb $\{D2\}$ $f'' = 2$. *Opt. Commun.*, 284(12):2890 – 2894, 2011.
186. H. Tran and J.-M. Hartmann. An isolated line-shape model based on the keilson and storer function for velocity changes. i. theoretical approaches. *J. Chem. Phys.*, 130(9):094301, 2009.
187. H. Tran, J.-M. Hartmann, F. Chaussard, and M. Gupta. An isolated line-shape model based on the keilsonstorer function for velocity changes. ii. molecular dynamics simulations and the q(1) lines for pure h₂. *J. Chem. Phys.*, 131(15):154303, 2009.
188. H. Tran, N. H. Ngo, J.-M. Hartmann, R. R. Gamache, D. Mondelain, S. Kassi, A. Campargue, L. Gianfrani, A. Castrillo, E. Fasci, and F. Rohart. Velocity effects on the shape of pure h₂o isolated lines: Complementary tests of the partially correlated speed-dependent keilson-storer model. *J. Chem. Phys.*, 138(3):034302, 2013.
189. Cedomil Vadla, Vlasta Horvatic, and Kay Niemax. Radiative transport and collisional transfer of excitation energy in cs vapors mixed with ar or he. *Spectrochim. Acta, Part B*, 58(7):1235 – 1277, 2003.
190. O. Vallee, P. Ranson, and J. Chapelle. Measurement of broadening of argon lines and oscillator strengths of resonance lines. *J. Quant. Spectrosc. Radiat. Transfer*, 18:327–336, 1977.
191. Philip L. Varghese and Ronald K. Hanson. Collisional narrow effects on spectral line shapes measured at high resolution. *Appl. Opt.*, 23:2376–2385, 1984.
192. J. E. Velazco, J. H. Kolts, and D. W. Setser. Quenching rate constants for metastable argon, krypton, and xenon atoms by fluorine containing molecules and branching ratios for xef* and krf* formation. *J. Chem. Phys.*, 65(9):3468–3480, 1976.
193. Joseph T. Verdeyen. *Laser Electronics*. Prentice Hall, third edition, 1995.
194. AJ Wallard. Frequency stabilization of the helium-neon laser by saturated absorption in iodine vapour. *J. Phys. E: Sci. Instrum.*, 5(9):926, 1972.

195. J. Wawrzynski and J. Wolnikowski. Broadening and shift of the 3p54p-3pp54d argon spectral lines in pure argon, ar-ne and ar-he mixtures. *Phys. Scr.*, 33:113, 1986.
196. P. Wcislo, F. Thibault, H. Cybulski, and R. Ciurylo. Strong competition between velocity-changing and phase- or state-changing collisions in h₂ spectra perturbed by ar. *Phys. Rev. A*, 91:052505, 2015.
197. P. Wcislo, H. Tran, S. Kassi, A. Campargue, F. Thibault, and R. Ciurylo. Velocity-changing collisions in pure h₂ and h₂-ar mixture. *J. Chem. Phys.*, 141(7):074301, 2014.
198. N. P. Wells, T. U. Driskell, and J. C. Camparo. Fine-structure mixing in rb-xe elastic collisions and isoclinic point asymmetry. *Phys. Rev. A*, 92:022505, 2015.
199. J. Wolnikowski, J. B. Atkinson, J. Supronowicz, and L. Krause. $7^2d_{\frac{3}{2}} - 7^2d_{\frac{5}{2}}$ excitation transfer in rubidium induced in collisions with ground-state rb and noble-gas atoms. *Phys. Rev. A*, 25:2622–2628, 1982.
200. J. Wolnikowski, J. Wawrzynski, A. Bielski, and J. Szudy. Pressure effects on some argon spectral lines belonging to the 3p54p-3p5nd (n = 5 - 7) transitions. *Phys. Scr.*, 35:153, 1987.
201. Sheldon S.Q. Wu, Thomas F. Soules, Ralph H. Page, Scott C. Mitchell, V. Keith Kanz, and Raymond J. Beach. Resonance transition 795-nm rubidium laser using ³he buffer gas. *Opt. Commun.*, 281(5):1222 – 1225, 2008.
202. Dong-Hai Yang and Yi-Qiu Wang. Study on the saturation absorption of cesium. *Opt. Commun.*, 74(1):54 – 58, 1989.
203. Zining Yang, Guangqi Yu, Hongyan Wang, Qisheng Lu, and Xiaojun Xu. Modeling of diode pumped metastable rare gas lasers. *Opt. Express*, 23(11):13823–13832, 2015.
204. James Yardley. *Introduction to molecular energy transfer*. Academic Press, 1980.
205. Nathan D. Zamoski, Gordon D. Hager, Wolfgang Rudolph, and David A. Hostutler. Experimental and numerical modeling studies of a pulsed rubidium optically pumped alkali metal vapor laser. *J. Opt. Soc. Am. B*, 28(5):1088, 2011.
206. Clarence Zener. Low velocity inelastic collisions. *Phys. Rev.*, 38:277–281, 1931.
207. J.-Y. Zhang and J. Mitroy. Long-range dispersion interactions. i. formalism for two heteronuclear atoms. *Phys. Rev. A*, 76:022705, 2007.
208. B. V. Zhdanov, T. Ehrenreich, and R. J. Knize. Highly efficient optically pumped cesium vapor laser. *Opt. Commun.*, 260(2):696–698, 2006.

- 209. Xi-Ming Zhu and Yi-Kang Pu. A simple collisional-radiative model for low-temperature argon discharges with pressure ranging from 1 pa to atmospheric pressure: kinetics of paschen 1s and 2p levels. *J. Phys. D: Appl. Phys.*, 43(1):015204, 2010.
- 210. B. G. Zollars, H. A. Schuessler, J. W. Parker, and R. H. Hill. Inelastic collisions between selectively excited rubidium 6^2d -state atoms and noble-gas atoms: Fine-structure-state mixing. *Phys. Rev. A*, 28:1329–1337, 1983.
- 211. J. Zweiback, G. Hager, and W. F. Krupke. High efficiency hydrocarbon-free resonance transition potassium laser. *Opt. Commun.*, 282(9):1871–1873, 2009.

REPORT DOCUMENTATION PAGE				<i>Form Approved</i> <i>OMB No. 0704-0188</i>							
The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.											
1. REPORT DATE (DD-MM-YYYY) 15-06-2017		2. REPORT TYPE Dissertation		3. DATES COVERED (From - To) June 2013 - June 2017							
4. TITLE AND SUBTITLE Linear and Nonlinear Spectroscopy of Optically-Thick Argon and Argon-Helium Plasmas in Radio-Frequency Dielectric-Barrier Discharges				5a. CONTRACT NUMBER							
				5b. GRANT NUMBER							
				5c. PROGRAM ELEMENT NUMBER							
6. AUTHOR(S) Eshel, Ben				5d. PROJECT NUMBER							
				5e. TASK NUMBER							
				5f. WORK UNIT NUMBER							
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Institute of Technology Graduate School of Engineering and Management (AFIT/EN) 2950 Hobson Way Wright-Patterson AFB OH 45433-7765				8. PERFORMING ORGANIZATION REPORT NUMBER AFIT-ENP-DS-17-J-011							
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Harro Ackerman High-Energy Laser Joint Technology Office 801 University Blvd Se, Ste 209 Albuquerque, NM 87106 505-248-8208, Harro.Ackerman@jto.hpc.mil				10. SPONSOR/MONITOR'S ACRONYM(S)							
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)							
12. DISTRIBUTION/AVAILABILITY STATEMENT Distribution Statement A. Approved for Public Release; Distribution Unlimited											
13. SUPPLEMENTARY NOTES This work is declared a work of the U.S. Government and is not subject to copyright protection in the United States.											
14. ABSTRACT An argon-helium plasma formed in a radio-frequency dielectric-barrier discharge has been studied for application to a diode-pumped rare gas laser using both linear and non-linear spectroscopic techniques. The pressure broadening and shift rates have been measured for four Ar s to p transitions in both pure Ar and Ar-He gas mixtures with improved precision over previously measured values. These broadening and shift rates are crucial to efficiently coupling the diode radiation into the gain medium. The Ar plasma was also studied under high-intensity laser fields to examine the saturation behavior and a numerical line shape was developed to qualitatively describe the observed trends. Additionally, the spin-orbit mixing rates of the alkali-metal—rare-gas interaction was organized using adiabaticity with deviations correlated to the polarizability of the interacting pair. A time-dependent perturbation theory model was developed in order to predict the temperature dependence of these rates and was shown to be in good agreement with the full database of measured cross-sections.											
15. SUBJECT TERMS Rare gas laser, laser absorption spectroscopy, saturation spectroscopy, plasma kinetic laser model, pressure broadening and shift rates											
16. SECURITY CLASSIFICATION OF: <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%; padding: 2px;">a. REPORT</td> <td style="width: 33%; padding: 2px;">b. ABSTRACT</td> <td style="width: 33%; padding: 2px;">c. THIS PAGE</td> </tr> <tr> <td style="text-align: center; padding: 2px;">U</td> <td style="text-align: center; padding: 2px;">U</td> <td style="text-align: center; padding: 2px;">U</td> </tr> </table>			a. REPORT	b. ABSTRACT	c. THIS PAGE	U	U	U	17. LIMITATION OF ABSTRACT UU		18. NUMBER OF PAGES 233
a. REPORT	b. ABSTRACT	c. THIS PAGE									
U	U	U									
			19a. NAME OF RESPONSIBLE PERSON Dr. Glen P. Perram, AFIT/ENP								
			19b. TELEPHONE NUMBER (Include area code) (937) 255-3636 x4504 glen.perram@afit.edu								

Reset