ALKALI–RARE GAS PHOTODISSOCIATION LASERS: APPLICATIONS TO LASER PHYSICS AND ATOM-ATOM INTERACTIONS

BY

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DISSE RATION

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ABSTRACT

This dissertation describes several experiments in which alkali–rare gas laser systems are utilized as a simple platform with which to isolate and study atom-atom interactions and fundamental physical processes that are ill-understood or have never been investigated previously. Specifically, the minimum allowable energy separation between levels 2 and 3 in a three-level laser system has been investigated experimentally, as have two-photon absorption processes in atomic Rb and Cs.
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CHAPTER 1
INTRODUCTION

Since the field of laser physics began, the demonstration of a number of laser systems has inspired intense investigation into the fundamental properties describing their gain media. Excimer lasers are a prime example of this phenomenon. Because of the potential power and usefulness of these intense, coherent, ultraviolet sources, an interest in excited rare gas dimers and rare gas–halide mixtures exploded in the scientific community shortly after the first experimental demonstration of an excimer laser, generating experimental and theoretical studies which blurred boundaries between the disciplines of laser engineering and physical chemistry [1]. Excimer lasers have since become “workhorse” tools for materials processing [2, 3], medicine [4–6], and semiconductor fabrication [7, 8], as well as basic science research [9, 10], and the ubiquity of excimers is due in large part to the development of these lasers to a level of maturity only achievable with a comprehensive understanding of their gain media.

Just in the last decade, the demonstration of atomic alkali lasers pumped as three-level lasers has reinvigorated the study of alkali vapor and alkali–rare gas mixtures. In that vein, this dissertation describes several experiments in which laser systems of this class are utilized as a simple platform with which to isolate and study atom-atom interactions and fundamental physical processes that are ill-understood or have never been investigated previously. Because of their central importance in this dissertation, an overview of these alkali laser systems will be presented briefly in the following sections.

1.1 Three-Level Atomic Alkali Lasers

Since the 2003 demonstration by Krupke et al. of a rubidium vapor laser pumped on the $5^2P_{3/2} \leftarrow 5^2S_{1/2}$ ($D_2$) transition and lasing on the $5^2P_{1/2} \rightarrow 5^2S_{1/2}$ ($D_1$) transition of ru-
bidium [11], alkali-vapor lasers have been the subject of intense study [12–19]. The majority of alkali lasers in the literature have been pumped in a similar fashion to that first rubidium laser. These lasers, which are pumped on the $D_2$ line and lase on the $D_1$ line of the alkali atom, utilize pump wavelengths which are easily achievable with current diode laser technology [20]. Because of this compatibility, this class of lasers is referred to as diode pumped alkali lasers, or DPALs (see Figure 1.1).

$$\Delta \varepsilon$$

$$\Delta \varepsilon$$

$$\lambda_{\text{pump}} (D_2 \text{ Line})$$

$$\lambda_{\text{laser}} (D_1)$$

$$\lambda_{\text{pump}} (D_2 \text{ Line})$$

$$\lambda_{\text{laser}} (D_1)$$

Figure 1.1: Generic energy level diagram for a DPAL laser. The dashed transition, $np^2P_{3/2} \rightarrow np^2P_{1/2}$, indicates non-radiative relaxation.

While the alkalis have always been of interest to scientists because of the relative simplicity of their electronic configuration (i.e., their single valence electron), still these laser systems have had a noticeable impact on the literature concerning the fundamental chemical physics of alkali atoms, and alkali/rare-gas/hydrocarbon vapor mixtures.
1.2 Alkali–Rare Gas Lasers

In 2008, Readle et al. demonstrated an atomic cesium laser pumped by the photodissociation of Cs-Ar excimers [21]. This was the first demonstration of a new class of alkali–rare gas lasers commonly referred to in the literature as excimer-pumped atomic lasers, or XPALs. These lasers differ from DPALs in that they rely on molecular interactions between alkali–rare gas pairs to generate appreciable absorption from the $X^2\Sigma_{1/2}^+$ state to the $B^2\Sigma_{1/2}^+$ dissociative excited state of the alkali–rare gas complex. Figure 1.2 shows the absorption feature associated with $X \rightarrow B$ transitions in a Cs-Ar mixture. These transitions are manifested as an absorption satellite ($\lambda_{\text{peak}} = 836.7$ nm) to the blue side of the $D_2$ line of Cs ($\lambda_{D_2} = 852.1$ nm). All alkali–rare gas mixtures exhibit analogous satellites, but their contours and spectral-offset with respect to the $D_2$ transition depend on both the alkali and rare gas atom in the mixture. By optically pumping an alkali–rare gas system on this satellite, population is promoted from the $X^2\Sigma_{1/2}^+$ state to the $B^2\Sigma_{1/2}^+$ state of the alkali–rare gas pair. From this excited state, the pair dissociates into an excited alkali atom and a ground-state rare gas atom. The isolated excited-state alkali atom is in its $n^2P_{3/2}$ state, from which the $D_2$ transition originates. Then, the excited atom either emits on the $D_2$ line, or non-radiatively (collisionally) relaxes to the $n^2P_{1/2}$ state and then emits on the $D_1$ line. As an example of the laser cycle of a typical alkali–rare gas laser, the relevant molecular potential energy curves for the Cs-Ar laser are shown in Figure 1.3.

This method of achieving lasing on the D lines of the alkalis has several advantages over the DPAL method, one of which is that the acceptance bandwidth afforded by pumping on the blue satellite of the $D_2$ line of the alkalis can be up to 5 THz FWHM, whereas the linewidths for the alkali $D_2$ lines collisionally broadened by the presence of rare-gases and/or hydrocarbons, on which pumping occurs in the DPAL method, are typically about 10–20 GHz. The breadth of the blue satellite better matches easily achievable linewidths for high-power, CW diode laser arrays than does the collisionally broadened $D_2$ line of the alkali atom. When diode lasers are used to pump DPAL lasers, some pump light can be completely unutilized, transmitting uninhibited at the wings of the $D_2$ line absorption. In contrast, the entire emission profile from a diode laser array would be utilized in pumping
Figure 1.2: Absorption spectrum for a Cs-Ar gas mixture. The blue satellite is a product of interactions between argon and cesium, and it corresponds to \( X^2\Sigma^+ \rightarrow B^2\Sigma^+ \) transitions of the alkali–rare gas pair. This blue satellite is so named because it lies to the blue side of the \( D_2 \) line of the alkali atom.

an alkali–rare gas photodissociation laser.

Several alkali–rare gas lasers have appeared in the literature since 2008 [22–25]. While these lasers were initially proposed as an alternative to the DPAL lasing scheme as a spatial mode conversion technique for diode lasers, they stand apart from DPAL in that they rely on the interactions between the alkali and rare gas atoms of the gain medium in order to function correctly. Already, the demonstration of this class of lasers has renewed the interest of the scientific community in investigating the fundamental properties of alkali–rare gas mixtures [26–28], and the experiments and results presented in the following chapters are examples of how these systems can be utilized as sensitive platforms for studying atom-atom
Figure 1.3: Interaction potentials for the Cs-Ar XPAL system, with pump and laser transitions labeled. The arrow representing optical excitation is for illustrative purposes only, and it does not accurately represent the breadth of the range of internuclear separation over which optical transitions can occur between the $X\Sigma$ and $B\Sigma$ states.

This dissertation describes several experiments which highlight the usefulness of these alkali–rare gas laser systems in 1) studying atom-atom interactions within the gain medium of the laser utilized, and 2) experimentally investigating fundamental concepts of laser physics. Chapter 2 begins with a discussion of an experiment in which the Cs-Ar-Kr laser was used to study the minimum energy separation between states $|2\rangle$ and $|3\rangle$ in a three-level laser system, which is a fundamental question of laser physics. The results of this experiment are then followed by a section about the Na-Xe laser system which, in light of the results described earlier in the chapter, cannot be made to lase by direct atomic pumping due to the small
energy difference between the Na 3p $^2$P states compared to kT. Chapter 3 describes atomic collisions, electronic transitions in diatomic systems, and the quantum mechanics involved in these topics. Then, a computer simulation which calculates alkali–rare gas absorption spectra at the wings of the D$_2$ transition of the alkali atom is discussed, with results specific to Cs-Ar presented. The experiments presented in Chapter 4 showcase the usefulness of alkali–rare gas lasers for the fundamental study of properties of the gain media. Chapter 5 is a brief conclusion.
As mentioned in Chapter 1, the broad acceptance bandwidth for pumping alkali–rare gas lasers is one of the most advantageous features of these systems for the purposes of using diode laser arrays as the pump source. The ∼5 nm width of the blue satellite of the D\textsubscript{2} line broadened by collisions with a rare gas is much more compatible with the linewidth of high-power diodes than is the 10–20 GHz linewidth of the collisionally broadened atomic D lines. Additionally, as the following section will show, the breadth of the blue satellite is useful for studying the minimum-allowable energy difference between states in a three-level laser system.

2.1 Probing the Minimum Energy Separation between Two Levels in a Three-Level System

From the initial conception of the laser until today, an established truism of laser physics has been that a two-level system cannot lase, and systems which can be driven to lase must therefore have at least three energy levels. But what is the minimum energy separation required between two energy levels in a three-level system such that these two levels can be considered discrete, and the system can lase? This is a question that has been unasked and unanswered by the laser science community since the first demonstration of the laser until now.

As a first-pass glimpse into the character of a three-level system with thermally coupled upper states, the rate equations for such a system have been investigated. A partial energy-level diagram for a generic three-level laser system is shown in Figure 2.1 in which states 1 and 2 of the system are thermally mixed. Setting \( \gamma_{12} = \gamma_{21} e^{-\Delta \epsilon/kT} \) forces the populations
of states 1 and 2 to conform to the Boltzmann distribution. The values of $\gamma_2$ and $\gamma_1$ are simply $1/\tau_2$ and $1/\tau_1$, respectively.

\[
\dot{N}_0 = \left( \frac{I_{\text{pump}} \sigma_{20}}{E_{20}} \right) \left( N_2 - \frac{g_2}{g_0} N_0 \right) + \left( \frac{I_{10} \sigma_{10}}{E_{10}} \right) \left( N_1 - \frac{g_1}{g_0} N_0 \right) + \frac{N_1}{\tau_1} + \frac{N_2}{\tau_2},
\]

(2.1a)

\[
\dot{N}_1 = \gamma_{21} \left( \frac{g_1}{g_2} N_2 - e^{-\Delta \epsilon/kT} N_1 \right) + \left( \frac{I_{10} \sigma_{10}}{E_{10}} \right) \left( \frac{g_1}{g_0} N_0 - N_1 \right) - \frac{N_1}{\tau_1},
\]

(2.1b)

\[
\dot{N}_2 = \gamma_{21} \left( e^{-\Delta \epsilon/kT} N_1 - \frac{g_1}{g_2} N_2 \right) + \left( \frac{I_{\text{pump}} \sigma_{20}}{E_{20}} \right) \left( \frac{g_2}{g_0} N_0 - N_2 \right) - \frac{N_2}{\tau_2}
\]

(2.1c)

Spontaneous emission from state 2 has been neglected in this model because, in the case of
the alkali-noble gas laser system, population transfer into and out of state 2 is dominated
by the pumping term and the thermalization of states 1 and 2. Therefore, the last terms in
each of the above expressions for \( \dot{N}_0 \) and \( \dot{N}_2 \), \( \frac{N_2}{\tau_2} \) and \( -\frac{N_2}{\tau_2} \), respectively, have been neglected.

If the system is at threshold, then \( N_1 = \frac{g_1}{g_0} N_0 \), and the system of rate equations becomes

\[
\begin{align*}
\dot{N}_0 &= \left( \frac{I_{pump} \sigma_{20}}{E_{20}} \right) \left( N_2 - \frac{g_2}{g_0} N_0 \right) + \frac{N_1}{\tau_1}, \\
\dot{N}_1 &= \gamma_{21} \left( \frac{g_1}{g_2} N_2 - e^{-\Delta \epsilon/kT} N_1 \right) - \frac{N_1}{\tau_1}, \\
\dot{N}_2 &= \gamma_{21} \left( e^{-\Delta \epsilon/kT} N_1 - \frac{g_1}{g_2} N_2 \right) + \left( \frac{I_{pump} \sigma_{20}}{E_{20}} \right) \left( \frac{g_2}{g_0} N_0 - N_2 \right)
\end{align*}
\]

If the system is in a steady-state, then \( \dot{N}_0 = \dot{N}_1 = \dot{N}_2 = 0 \). \( \dot{N}_2 = 0 \) can be reduced to an
equation for \( I_{pump} \) in terms of \( N_1 \) and \( \Delta \epsilon/kT \):

\[
\dot{N}_2 = 0 = \gamma_{21} \left( e^{-\Delta \epsilon/kT} N_1 - \frac{g_1}{g_2} N_2 \right) + \left( \frac{I_{pump} \sigma_{20}}{E_{20}} \right) \left( \frac{g_2}{g_0} N_0 - N_2 \right)
\]

\[
\left( \frac{I_{pump} \sigma_{20}}{E_{20}} \right) \left( \frac{g_2}{g_0} N_0 - N_2 \right) = \gamma_{21} \left( e^{-\Delta \epsilon/kT} N_1 - \frac{g_1}{g_2} N_2 \right)
\]

\[
I_{pump} = \left( \frac{\gamma_{21} E_{20}}{\sigma_{20}} \right) \left( \frac{\gamma_{21} \frac{g_1}{g_2} N_2 - e^{-\Delta \epsilon/kT}}{\frac{g_2}{g_0} N_0 - N_2} \right)
\]

\( \dot{N}_1 = 0 \) yields an expression for \( N_2 \) in terms of \( N_1 \):

\[
\dot{N}_1 = 0 = \gamma_{21} \left( \frac{g_1}{g_2} N_2 - e^{-\Delta \epsilon/kT} N_1 \right) - \frac{N_1}{\tau_1}
\]

\[
\left( \frac{\gamma_{21} g_1}{g_2} \right) N_2 = \left( 1/\tau_1 + \gamma_{21} e^{-\Delta \epsilon/kT} \right) N_1
\]

\[
N_2 = \left( \frac{1/\tau_1 + \gamma_{21} e^{-\Delta \epsilon/kT}}{\gamma_{21} \frac{g_1}{g_2}} \right) N_1
\]

Combining the expression for \( I_{pump} \) and \( N_2 \) yields the following expression for \( I_{pump} \) at
threshold, or $I_{\text{min}}$:

$$I_{\text{min}} = \gamma_{21} \left( \frac{E_{20}}{\sigma_{20}} \right) \left( \frac{g_2}{g_1} \left( \frac{1/\tau_1 + \gamma_{21} e^{-\Delta \epsilon/kT}}{\gamma_{21} \frac{\sigma_1}{\sigma_2}} \right) - e^{-\Delta \epsilon/kT} \right)$$

(2.2)

Figure 2.2: Minimum pump intensity vs. $\Delta \epsilon/kT$. As $\Delta \epsilon/kT \to 0$, $I_{\text{min}} \to \infty$.

For the curve of Figure 2.2, the parameters for the rate equations have been chosen as follows:
\[ \gamma_{21} = 1 \times 10^{12} \text{s}^{-1} \]
\[ \tau_1 = 30.3 \text{ ns} \]
\[ E_{20} = (11737 + \Delta \epsilon) \text{ cm}^{-1} = 11947 \text{ cm}^{-1} \]
\[ g_1 = 4 \]
\[ g_2 = 2 \]
\[ \sigma_{20} = 2 \times 10^{-17} \text{ cm}^2 \]

The results of this simplified model indicate that as \( \Delta \epsilon/kT \) approaches 0, the threshold pump intensity approaches \( \infty \). (This is to be expected, because for \( \Delta \epsilon/kT=0 \), the system has only two distinct energy levels, and in the limit of infinite pumping, the population in the upper state can at most match that in the lower state.) However, no obvious inflection point exists on this curve to assign significance to a particular “threshold” value for \( \Delta \epsilon/kT \), beyond which the laser ceases to operate. However, experimental investigation has revealed a more definite break point for this energy separation, as will be seen in the following discussion.

2.1.1 Cs-Ar-Kr Experiments

The Cs-Ar photodissociation laser is ideal for investigating the minimum requisite energy separation between two states in a three-level laser system. As illustrated by the partial energy level diagram of the Cs-Ar laser shown in Figure 2.3, the upper two levels of this system are collisionally coupled. Therefore, the populations of these states can be assumed to be equilibrated (by collisions) and, thus, they can be expected to conform to a Boltzmann distribution \( \left( \frac{N_2}{N_1} = e^{(E_{2} - E_{1})/kT} \right) \) and can be directly varied by sweeping the temperature of the system. Additionally, population in state \( |0\rangle \) can be photoexcited to state \( |2\rangle \) by photons in a wide range of energy \(( \sim 70 \text{ cm}^{-1} \text{ FWHM})\), which directly corresponds to the range of initial kinetic energy of the molecule in state \( |2\rangle \). In other words, the energy difference between states \( |2\rangle \) and \( |1\rangle \), \( \Delta \epsilon \), can be continuously tuned by varying the photon energy used to pump the laser. Therefore, pump photon energy and gas temperature provide means by which the Cs-Ar system can be continuously tuned between three and two levels.

The experiments described in this section utilized a Cs-Ar-Kr mixture rather than using Ar as the sole perturber rare gas atom. Readle observed (Ref. [22]) that the addition of
a second perturber to an alkali–rare gas system can provide enhanced absorption on the blue satellite of the D2 line of the alkali atom, and in the case of Cs-Ar-Kr, the satellite absorption peak matches that of Cs-Ar. These observations indicate that the presence of Kr in the gas mixture serves to primarily enhance the absorption of the Cs-Ar complex, which corresponds to greater output energy for the Cs-Ar-Kr laser system than for Cs-Ar under identical pumping conditions [22]. For these experiments, utilization of a three-body mixture was necessary to provide adequate laser output to fit the measured excitation spectra to an exponential function through an order of magnitude, as described below.

The diagram of Figure 2.4 represents the experimental arrangement used for this investigation. A pulsed Nd:YAG (532 nm)-pumped dye laser/amplifier chain was utilized as a tunable pump source for the Cs-Ar-Kr laser. A dye mixture of Styrl 9 in propylene carbon-
Nd:YAG-Pumped Dye Laser/Amplifier Chain

Variable Attenuator

Oven

10 cm

Alkali-Rare Gas Cell

R > 99%

Detector

Detector

Detector

Filter

Figure 2.4: Experimental arrangement for measuring Cs-Ar-Kr excitation spectra.

The cylindrical borosilicate cell used in these experiments was 4 inches long by 1 inch in diameter. The windows of the cell were angled at 11° in a trapezoidal configuration in order to eliminate parasitic lasing between them. A thermocouple was affixed to the side of the cell with Kapton tape (stable up to 673 K), allowing the gas temperature to be deduced while the cell was inside the oven. A small copper rod mounted to the optical table on which
the experimental apparatus sat was fed through a small hole in the side of the oven and was
positioned so that it was in contact with the cell wall close to the thermocouple, creating a
preferential condensation point on the cell wall for Cs vapor. This “cold finger” prevented
Cs metal from condensing on the windows of the cell and improved the accuracy with which
Cs vapor density could be deduced from measurements of the thermocouple temperature.
The oven used was a one-temperature oven with a single heating element connected to a
\(~90\) V AC source which was controlled by a PID temperature controller. The temperature
control loop allowed for the gas mixture temperature to be determined to within \(\pm 3\) K.

Using the arrangement shown in Figure 2.4 and described above, hundreds of excitation
spectra of the Cs-Ar-Kr laser were measured at different temperatures. A small selection
of these spectra is shown in Figure 2.5, which displays the ratio of the output pulse energy
to the pump pulse energy versus the difference between pump photon energy and Cs-Ar-Kr
laser photon energy (\(\Delta \epsilon\)). The vertical axis is logarithmic in scale. The scale of the horizontal
axis corresponds to the energy difference between the two upper states in the laser system,
which demonstrates the continuous tunability of this system from 3 to 2 levels.

The particular spectra of Figure 2.5 are displayed for the purpose of demonstrating the
temperature dependence of the laser behavior under tuning of the energy defect, \(\Delta \epsilon\). It is
clear that for the spectrum measured at a gas temperature of 446 K, the laser output decay
is much more gradual than that of the spectrum measured at 458 K as \(\Delta \epsilon\) is tuned toward
0. This indicates that as the kinetic energy of the gas is increased, the energy defect must
be made larger to compensate for increased thermal mixing of states \(|1\rangle\) and \(|2\rangle\). The red
and blue spectra were measured at 451 K and 456 K, respectively. The orange spectrum
measured at 483 K shows that \(kT\) can be increased to the point that states \(|1\rangle\) and \(|2\rangle\) are
so appreciably mixed that laser action can no longer be sustained.

In order to quantify the temperature dependence of the laser output decay, around 200
excitation spectra have been fit to single exponential functions of the form \(A \cdot e^{\Delta \epsilon/\epsilon_T}\), and
an example is shown in Figure 2.6. In this figure, the peak of the excitation spectrum at
215 cm\(^{-1}\) is labeled \(\Delta \epsilon_o\). This peak value for \(\Delta \epsilon\) is constant for all the excitation spectra
measured, and will be used as a point of reference in the following discussion.

For each excitation spectrum measured, a value of \(\epsilon_T\) has been extracted, and Figure 2.7(a)
Figure 2.5: Representative excitation spectra for the Cs-Ar-Kr laser system. Displays these values as a function of kT. Figure 2.7(b) plots the data in an alternate fashion, displaying the integrated area under the excitation spectra versus kT. In both panels of this figure, a critical value of 0.7kT for the energy separation between states |1⟩ and |2⟩ corresponding to the peak of the excitation spectra, ∆εo, is explicitly visible. This value corresponds to a degeneracy-weighted Boltzmann factor of \((g_2/g_1)e^{-\Delta\epsilon_m/kT} = 0.25\). This result tells us that in the case of the Cs-Ar-Kr laser, once the energy separation between the two upper states dips below 0.7kT, the system rapidly collapses.

This critical value for the energy separation between states 2 and 3 in a three-level system does not obviously stand out as an inflection point or other explicit marker in the results of the simple rate equation model described above (see Figure 2.2). However, this value for energy separation does correspond to the point where the pump intensity required to
Figure 2.6: Excitation spectrum for the Cs-Ar-Kr laser with an exponential fit superimposed.

maintain population inversion in the model system doubles from its asymptotic value at $\Delta \epsilon >> kT$.

This result is significant for several reasons. The experiment described here is the first experiment designed to probe this fundamental principle of laser physics. A “rule-of-thumb” for the minimum separation between states in a laser system has been utilized in laser physics since it was proposed by Schawlow and Townes in 1958 that, “There is no requirement that the pumping frequency be much higher than the frequency emitted as long as the difference in frequency is much greater than $kT/h$, which can assure the possibility of negative temperatures” [29]. In other words, as long as the states in a laser system are separated by many times $kT$, that system can surely be driven to lase. The result described here explicitly shows that this lower bound for energy separation can be reasonably decreased to at least $0.7kT$. This result also explicitly demonstrates, however, that there is a practi-
Figure 2.7: Two representations of the data which clearly reveal a critical value for $\Delta \epsilon$ at $0.7 \times kT$, which corresponds to a degeneracy-weighted Boltzmann factor of 0.25. (a) Exponential constants for excitation spectra of the Cs-Ar-Kr laser versus $kT$. (b) The integrated area under the excitation spectrum versus $kT$.

cal limit to the minimum energy separation between the two upper states of a three-level laser, below which the two upper states increasingly thermally mix and the system collapses.

(The experiments described in this section were previously reported in *Applied Physics Letters* [30].)
2.2 Simultaneous Lasing on Both D Lines of Na

Visible light resonant with the principal series electronic transitions of sodium \( (3^2P_{3/2,1/2} \rightarrow 3^2S_{1/2}) \) is used both to study the chemistry of the mesosphere [31–34] and to generate laser guide stars for use in conjunction with adaptive optics for correcting telescope images from the effects of atmospheric aberrations [35, 36]. Currently, the equipment used to generate coherent radiation at these wavelengths includes ring dye lasers [37], frequency-summed pairs of Nd:YAG lasers [38–41], and coherently combined frequency-doubled Raman fiber lasers [42]. However, these apparatuses are quite complex and require constant maintenance. At the W. M. Keck Observatory in Hawaii, for example, laser system faults caused the laser guide star facilities to be unusable for 12% of the weather-permitted observation time from November 2004 to May 2006 [43]. The dye laser system used at this facility requires an estimated 35.5 man hours to calibrate and operate for each night of observation and is susceptible to dye degradation and contamination, which can hinder or halt data taking during observations [43]. To ensure that the laser emission from these systems is locked onto the sodium doublet wavelengths, absorption of the laser in a sodium vapor cell or laser-induced fluorescence from a sodium vapor cell must be continually monitored and used to control the orientation of intracavity tuning optics [44], increasing the bulk, complexity, and cost of these systems even further.

The oscillator is the most complex portion of a laser guide star system, because it encompasses all the necessary machinery for locking the laser output frequency onto the D lines of sodium. Thus, one of the most practical ways that guide star systems could be improved would be to simplify the oscillator, and a sodium-based laser system emitting on the D lines would immediately serve this purpose because the gain medium itself would frequency-lock the output to the D lines, eliminating the need for external frequency feedback loops and the moving parts comprising them. The Na-Xe laser system presented in this chapter is not the first report of lasing on the D lines of sodium, but it is to date the most practical sodium laser scheme for improving guide stars in this way.
2.2.1 Previous Sodium D-Line Lasers

Stimulated emission on the sodium doublet by way of photodissociation of NaI has been previously reported [45]. In that experiment, sodium iodide molecules were photodissociated into Na(3p $^2P$) and I(5p 5 $^2P_{3/2}$) upon absorbing a UV photon from a frequency-mixed Nd:YAG laser ($\lambda=212.8$ nm, $E_\lambda=5.8$ eV). This scheme allows a population inversion to be easily achieved between the 3p $^2P_{1/2}$ and 3s $^2S_{1/2}$ states of sodium because once excited-state sodium emits and relaxes to the ground state, free sodium and iodine atoms rapidly recombine, depleting the free sodium ground-state population. Strong stimulated emission on the sodium D$_1$ line in particular was reported via this method. This technique was later used to generate lasing in NaBr [46], where an ArF ($\lambda=193$ nm, $E_\lambda=6.4$ eV) excimer laser was used to photodissociate NaBr molecules into Na(3p $^2P$) and Br(4p 5 $^2P_{3/2}$), and output on both the D$_1$ and D$_2$ lines of sodium was detected. While this photodissociation method readily provides a population inversion in sodium, the quantum efficiency of these sodium-halide systems is between 33% and 36% (compared to ~95% for the Na-Xe photodissociation laser described later in this chapter), which amounts to ~4 eV of heat inserted into the system for every photon emitted from these lasers. This excess heat makes the sodium-halide photodissociation lasers impractical for the purposes of replacing the oscillator of a laser guide star system.

Lasing on the D lines of sodium has also been previously reported in a Na-He mixture [47] in which population inversion between the sodium 3p $^2P$ and 3s $^2S_{1/2}$ states was attributed to “optical collisions” where optical transitions coincide with collisions between Na and He atoms. In this process the pump photon simultaneously promotes the Na atom to 3p $^2P$ and imparts the remainder of its energy on the colliding atoms as kinetic energy. While this process involves an alkali–rare gas mixture, it is quite different from the excitation mechanism utilized in this work. The blue absorption satellite of Na-He peaks at $\lambda=530$ nm (1890 cm$^{-1}$ from the D$_2$ resonance) [48] while the output from the sodium-helium laser pumped by optical collisions is most intense when the pump laser is detuned just 60 cm$^{-1}$ from the D$_2$ resonance of sodium. Therefore, the process by which the excited states of sodium are populated in the collisionally pumped sodium laser cannot be attributed to
photodissociation of Na-He pairs.

As mentioned earlier, alkali lasers based on cesium, rubidium, and potassium which emit on the D\textsubscript{1} line of the alkali atom have been generated by directly pumping the D\textsubscript{2} line. While amplified spontaneous emission has been observed on the D\textsubscript{1} line of sodium in ethane, methane, and ethylene \cite{49}, lasing on the D\textsubscript{1} line of sodium by direct pumping on the D\textsubscript{2} line has not been reported. With or without the presence of hydrocarbon molecules to quickly collisionally relax the 3\textit{p} \textsuperscript{2}\textit{P} excited-state population of sodium into the lower 3 \textit{2P}\textsubscript{1/2} state, achieving lasing on the D\textsubscript{1} line by pumping on the D\textsubscript{2} line in sodium vapor is believed to be difficult. The fine structure energy splitting of the 3\textit{p} \textsuperscript{2}\textit{P} states of sodium is 17.2 cm\textsuperscript{-1} while kT=352 cm\textsuperscript{-1} for [Na]=1.7 \times 10\textsuperscript{13} cm\textsuperscript{-3} (a typical alkali number density for direct atomic pumping of alkali lasers \cite{11}). So, for the three-level system of atomic sodium with this number density, the energy difference between the two excited states would be 0.06\times kT. In light of the results of the experiment described in the previous section however, maintaining a population inversion in a three-level system becomes increasingly difficult as the difference in energy between the excited states decreases below \sim 0.7\times kT \cite{30}.

In contrast, by pumping on the absorption satellite of the D\textsubscript{2} transition of sodium in xenon, which peaks at \lambda \approx 560 nm (see Figure 2.8 \cite{48}), the energy difference between the two excited states in the laser would be 880 cm\textsuperscript{-1}, which is >2\times kT for [Na] \sim 10\textsuperscript{15} cm\textsuperscript{-3}. This energy difference makes pumping a sodium D-line laser in this way feasible, and the spectral breadth of the blue satellite is advantageous from a laser engineering standpoint, as will be discussed below.

### 2.2.2 The Na-Xe Photodissociation Laser

Lasing has been achieved in a sodium-xenon mixture of [Xe]=1.6\times 10\textsuperscript{18} cm\textsuperscript{-3} and at T=593 K and 623 K, corresponding to [Na] of 5.4 \times 10\textsuperscript{14} cm\textsuperscript{-3} and 1.4 \times 10\textsuperscript{15} cm\textsuperscript{-3}, respectively, using a frequency-doubled Nd:YAG (\lambda=532 nm)-pumped dye laser (Rhodamine 6G in methanol) as the pump source. The arrangement used for this experiment was similar to that shown in Figure 2.4. The cavity mirrors were reflective in the visible (\sim 500–650 nm), with the high-reflector and the output coupler having reflectivities of >99\% and \sim 50\%, respectively.
An output spectrum for the Na-Xe laser is shown in Figure 2.9. This spectrum was collected using a photomultiplier tube mated to a 0.67 m Czerny-Turner monochromator with a 1200 g/mm grating having a blaze wavelength of 630 nm. Each data point in this figure corresponds to 20 integrated laser pulses. A higher-resolution scan of D$_2$ laser emission was measured with the same monochromator, and is shown in the inset to Figure 2.9. The bandwidth of this scan is instrument-limited by the monochromator to $\approx$58 GHz.

Lasing was confirmed by ensuring that measurable laser emission disappeared upon blocking the high-reflector of the laser cavity, by the observation of a threshold (see Figure 2.11), and by the shortened temporal pulse of the sodium laser with respect to that of the pump laser, as shown in Figure 2.10. The data of Figure 2.11 were collected using a fiber-coupled
spectrometer with a first-order resolution of 1.4 nm full width at half maximum (FWHM) coupled to a CCD array. Each point on the plot corresponds to the integrated area from $\lambda$=584.9 nm to 592.4 nm under a single spectral curve collected with this spectrometer. The data of Figure 2.10 were measured using a photodiode.

![Spectra of the Na-Xe laser output](image)

**Figure 2.9:** Spectra of the Na-Xe laser output. The inset shows a more dense scan of the $D_2$ laser line.

The spectrum of Figure 2.9 suggests that there is appreciable thermal mixing between the $3 \, ^2P_{3/2}$ and $3 \, ^2P_{1/2}$ states, because both D lines are lasing. In this particular spectrum, the $D_1$ output intensity appears to be half that of the $D_2$, but this ratio is not constant over time. In fact, over the course of 30 minutes of continual pumping of the laser system, the $D_1$ laser emission gradually vanishes. This appears to be due to transmission losses introduced at the windows of the Na-Xe borosilicate cell caused by sodium vapor reacting with the
inner surfaces of the cell windows under the intense dye laser pumping. However, based on the degeneracy ratio of 4:2 between the $3^2P_{3/2}$ and $3^2P_{1/2}$ states of Na, one would expect increased losses at the windows of the gain cell to cause preferential lasing on the D$_1$ line to dominate, contrary to the results presented here. D$_2$ emission dominates for a couple of reasons.

When Na-Xe pairs in the $X^2\Sigma_{1/2}^+$ state are photoexcited to the $B^2\Sigma_{1/2}^+$ state, dissociation of these pairs preferentially populates the $3^2P_{3/2}$ state of Na. Also, it has been experimentally determined that the collisional cross section for Na($3^2P_{1/2}$)$\rightarrow$Na($3^2P_{3/2}$) is nearly twice that for Na($3^2P_{3/2}$)$\rightarrow$Na($3^2P_{1/2}$) [50], which indicates that collisional excitation of Na in the $3^2P_{1/2}$ state to $3^2P_{3/2}$ is preferential to collisional quenching of population in the $3^2P_{3/2}$
state to $3\,^2P_{1/2}$. These phenomena ensure a majority of the population in the P states of Na remains in the $3\,^2P_{3/2}$ state, from which D$_2$ emission originates.

$$\lambda_p = 560\,\text{nm}$$

$$[\text{Xe}] = 1.6 \times 10^{19}\,\text{cm}^{-3}$$

$$T = 593\,\text{K}$$

$$[\text{Na}] = 5.4 \times 10^{14}\,\text{cm}^{-3}$$

$$T = 623\,\text{K}$$

$$[\text{Na}] = 1.4 \times 10^{15}\,\text{cm}^{-3}$$

Figure 2.11: Relative threshold measurements for the Na-Xe laser at two different temperatures. The apparent decrease in slope at higher temperature is likely due to increased ground-state absorption resulting from a greater number density of Na atoms in the gas mixture.

The linewidth of the D$_2$ emission was determined using a Fabry-Perot interferometer with a free spectral range of 1 cm$^{-1}$, and a finesse of $\approx 25$. An interferogram of the sodium D$_2$ laser emission is shown in Figure 2.12 (a), and a line-out across the center of this interferogram is shown in 2.12 (b). According to the expression [51]

$$\Delta \nu = \frac{2R_1 \Delta R_1}{(R_2^2 - R_1^2)} \times \Delta \nu_{FSR}$$  \hspace{1cm} (2.3)$$

where $\Delta \nu$ is the linewidth in question, $R_1$ and $R_2$ are the radii of the first and second of the
bright fringes (progressing radially outward), respectively, and $\Delta \nu_{FSR}$ is the free spectral range of the interferometer, this interferogram indicates that the linewidth of the D$_2$ laser is $9.2\pm0.6$ GHz. This corresponds to a collisional broadening coefficient for the sodium D$_2$ line by xenon of 18.4 MHz/Torr (at 300 K), which is greater than, but in reasonable agreement with, the broadening coefficient reported by Demtröder [51] of 14.5 MHz/Torr.

An excitation spectrum was also measured for the Na-Xe D$_2$ laser, and is shown in Figure 2.13(a). This spectrum shows that the peak output intensity from the Na-Xe laser occurs when $\lambda_{pump} \approx 560$ nm, which is consistent with the absorption spectrum of Chung et al., shown for comparison in Figure 2.13(b) [48].

In summary, simultaneous lasing on the D$_1$ and D$_2$ lines of sodium has been achieved by pumping on the blue satellite of the sodium D lines which absorbs most strongly at 560 nm for Na-Xe. This laser system possesses several advantageous traits over previously demonstrated sodium lasers. The quantum efficiency of this laser is $\sim 95\%$, compared to $\sim 34\%$ from sodium halide lasers emitting on the D lines of sodium, which means that very little excess energy is coupled into the gain medium as heat. Also, because the blue satellite of the D$_2$ line of sodium in xenon has a bandwidth of about 4 nm FWHM, the source used to pump this laser does not need to be locked on to a precise frequency within that satellite to effectively pump the laser. If a sodium laser were to be demonstrated using the atomic energy levels of sodium as a three-level system—which is unlikely to occur for the reasons stated above—the quantum efficiency would be an incredible 99.9\%. But the pump source for this laser would then need to be locked onto the D$_2$ line to achieve lasing on the D$_1$ line, which would be counter-productive for the purpose of reducing complexity in a guide star. The pump acceptance bandwidth for the Na-Xe laser gives it a high degree of tolerance for frequency fluctuations and broad linewidths in the pump source used. Because of these reasons, and because the output frequency of this laser is automatically locked onto the D lines of sodium by the gain medium itself, the Na-Xe laser has the potential to significantly minimize the complexity of sodium guide star laser systems.

(The experiments described in this section were previously reported in *Applied Physics Letters* [25].)
Figure 2.12: Interferogram from the Na-Xe D₂ laser line. This interferogram was measured using a Fabry-Perot etalon with a free spectral range of 1 cm⁻¹. Panel (a) shows the interferogram image, which was captured using a telescope and an intensified CCD camera. Panel (b) shows a line-out across the center of this captured image. The calculated linewidth from this image is 9.2±0.6 GHz, which is consistent with the collisional broadening factor cited by Demtröder (Ref. [51]) for the broadening of the sodium D₂ line by xenon.
Figure 2.13: Comparison of (a) Na-Xe laser excitation spectrum and (b) Na-Xe blue satellite absorption spectrum (from [48]).
In order to make accurate predictions concerning the number density of absorbing pairs in an alkali–rare gas mixture, the potential curves for the important molecular states of the laser—namely the $X\Sigma_{1/2}^+$ and the $B\Sigma_{1/2}^+$ states—must be precisely determined. A computational technique has been devised for the determination of optimized potential energy curves of these states. In this chapter, this technique will be described, and results pertaining to the Cs-Ar system will be presented.

3.1 Background: Atomic Collisions, Wavefunctions, and Optical Transitions

Ground-state alkali–rare gas atom pairs are so weakly bound that, at temperatures sufficient to achieve alkali number densities of $\geq 10^{14}$ cm$^{-3}$, they can be reasonably treated as a colliding pair of free atoms. (Specifically, the van der Waals minima for alkali–rare gas pairs ranges from 0.9 cm$^{-1}$ for Cs-He, up to 107.3 cm$^{-1}$ for Cs-Xe [52], while kT is $\geq 285$ cm$^{-1}$ for [Cs]$\geq 10^{14}$ cm$^{-3}$.) In the absence of a strong optical field, and at the energies of interest for the gas mixtures used in this work, these collisions are elastic. Thus, the ground-state wavefunctions for these systems can be determined by solving the Hamiltonian for an elastic collision between ground state alkali and rare gas atoms. This Hamiltonian has the form [53]

$$
\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V(R) + \frac{\hbar^2 J(J+1)}{2\mu R^2}\right)\Psi_J(R) = E\Psi_J(R)
$$

(3.1)

where $V(R)$ is the interaction potential for the system and $J$ is the angular quantum number. The third term on the left-hand side of this equation accounts for the rotational energy of
the pair described by the wavefunction $\Psi_J(R)$. These rotational effects are brought about by the reaction of the pair to the central force between them instigated by the interaction potential, $V(R)$, and therefore the maximum number of rotational terms we consider, $J_{\text{max}}$, should be determined by the total kinetic energy of the colliding pair and the radial “extent” of the central force between them.

3.1.1 Angular Momentum in Atomic Collisions

A simple example may help elucidate the method which has been used to determine a reasonable value for the extent of the central potential and thus, $J_{\text{max}}$. In the case of an infinite sphere potential between two colliding particles, the potential energy of the system is zero (the particles do not interact) when the distance between them is greater than some threshold value, $R_{\text{ext}}$ (and $R_{\text{ext}} = d$ in Figure 3.1). When the distance between them is less than $d$, the particles collide and scatter according to the impact parameter, $b$, as shown in Figure 3.1. This parameter is defined by the expression

$$b = \frac{L}{\sqrt{2\mu\epsilon}} \quad (3.2)$$

where $L$ is the magnitude of the angular momentum, $\mu$ is the reduced mass, and $\epsilon$ is the kinetic energy for the pair. Quantum mechanically, $L$ is defined as $\sqrt{\hbar^2J(J+1)} \simeq \hbar J$. The impact parameter of a collision only has a physical meaning when it is within the range of particle separation where the particles interact according to the potential that describes the collision. In the case of the infinite sphere potential, the threshold value for the impact parameter—above which no interaction occurs, and thus, the particles do not collide—is $b_{th} = d$. Defining a threshold value for the impact parameter in this way determines a relationship between $\epsilon$ and $J_{\text{max}}$ (the maximum value of $J$ to be considered for the collision) because the effects of angular momentum need only be taken into account when the particles interact in such a way as to cause a deflection of one particle off of the other. The relationship
between $\epsilon$ and $J_{\text{max}}$ in the case of the infinite sphere potential is defined as follows:

$$J_{\text{max}} = \frac{d\sqrt{2\mu\epsilon}}{\hbar}$$

(3.3)

So, with the “extent” of the interaction potential for this collision defined, it is clear that the range of angular momenta which should be considered is dependent on the energy of the colliding pair. A relationship between the energy of the colliding pair and the maximum necessary angular momentum to be considered can be determined for an alkali–rare gas atomic collision in a similar fashion, and this will be described later in this chapter. (For a more comprehensive quantum mechanical treatment of atomic collisions, see Murrel and Bosanac [53], or Atkins and Friedman [54].)

Angular momentum in this quantum mechanical model is manifested in an additional term contributing to the interaction potential for the system. With this term included, the effective interaction potential is of the form

$$U_{\text{eff}} = U(R) + \frac{\hbar J(J + 1)}{2\mu R^2}$$

(3.4)

So, in order to simulate accurate absorption spectra, wavefunctions must be calculated for a reasonable range of energies $\epsilon$ (according to the Boltzmann distribution for the temperature of the gas mixture) and for the range of $J$ values from 0 to $J_{\text{max}}(\epsilon)$ for each value of $\epsilon$.

### 3.1.2 Calculating Collision Wavefunctions

The results described later in this chapter are based on a two-atom system modeled quantum mechanically as two one-dimensional interaction potential curves—one for each of the molecular states of importance. Because the system is weakly bound in the ground state (van der Waals well depth $\epsilon \approx 0.15kT$ for Cs-Ar at $T=473$ K), bound states inside the well have been neglected, and $E = 0$ cm$^{-1}$ for the system is set equal to the value of the ground state interaction potential at the dissociated atom limit. Calculating wavefunctions for the one-dimensional, unbound potentials of this work has been accomplished using a method devised by Cooley in 1961 [55]. The Cooley method was designed to calculate the radial
wavefunctions, $\psi(R)$, of a diatomic system characterized by the radial Schrödinger wave equation

$$\psi'' = (U(R) - E) \psi(R)$$  \hspace{1cm} (3.5)\

where $U(R)$ is the interaction potential and $E$ is the total energy for the system. By using a refined second-order central difference approximation for the second derivative of the wavefunction in conjunction with the Numerov formula, Cooley devised the following
\[
\psi_i = \frac{2\psi_{i-1}(1 - \frac{h_0^2}{12}(U_{i-1} - E)) - \psi_{i-2}(1 - \frac{h_0^2}{12}(U_{i-2} - E)) + h_0^2\psi_{i-1}(U_{i-1} - E)}{(1 - \frac{h_0^2}{12}(U_i - E))}
\]  

(3.6)

where \(h_0\) is the radial step size, \(U_i\) is the value of the potential at position \(i\), and \(E\) is the energy for the wavefunction. By defining \(\psi_0 = 0\) and \(\psi_1 = \{a\text{ small, arbitrary, non-zero number}\}\), this equation can be used to compute relative wavefunctions for any radial potential by integrating outward in \(R\). The error in the wavefunctions calculated by this method is roughly \(-\frac{h_0^6}{240} \int dR\psi^2\).

Normalization of free-particle wavefunctions can be accomplished using the energy normalization technique of Buckingham [56,57]. As a collision wavefunction is calculated outward in \(R\), its amplitude stabilizes as the pair interaction potential approaches the asymptotic limit, which is the sum of the potential energy values for the separated atoms. This wavefunction is then scaled so that its stable amplitude at large \(R\) is equal to [58]

\[
P = 10^{-4} \times \left(\frac{8c\mu}{\hbar\epsilon}\right)^{1/4} = 0.27844 \left(\frac{\mu}{\epsilon}\right)^{1/4}
\]

(3.7)

(in units of \((\text{cm}^{-1} \cdot \text{Å})^{1/2}\)) where \(c\) is the speed of light, \(\hbar\) is Planck’s constant, \(\mu\) is the reduced mass for the atomic pair, and \(\epsilon\) is the kinetic energy of the state. This normalization technique, in tandem with the Cooley method for solving the radial Schrödinger equation described above, allows for non-iterative calculation of unbound wavefunctions [58].

3.1.3 Contributions to Interatomic Potentials

A wealth of literature is available concerning the interactions within two-atom systems [52, 59–62]. Many functional forms for atomic interaction potentials have been proposed with varying degrees of complexity. In the late 1920s, S. C. Wang performed a calculation wherein he determined that there is a long-range attractive force between hydrogen atoms (each
modeled as an electron oscillator, or dipole), the potential energy of which is \[ u(R) = -C_6 R^{-6} \] (3.8)

London described this effect [64] in terms of the force between two polarizable atoms which induce dipoles in one another. Based on his description, this has been dubbed the London dispersion force.

The Pauli exclusion principle for fermions results in a repulsive force between atoms, preventing the overlap of electron clouds. This is a much shorter-range interaction than the dispersion force, as electron cloud overlap only becomes significant when the interatomic distance for an atom pair is on the order of the atomic radii. To describe this repulsive interaction, many different functional forms have been used. Slater and Kirkwood, and later Buckingham, used a decaying exponential of the form \( Ae^{-\rho R} \) to describe this repulsion [65, 66], although this is prone to give non-physical results at small \( R \) values when used in conjunction with a long-range interaction term proportional to \( -R^{-6} \), as the attractive term will always overtake the exponential repulsion at some \( R \)-value. Higher-order terms of \( 1/R \) are more commonly used to describe the repulsive force between atoms in simulations today. A simple potential function that is commonly used in simulations is a \((12, 6)\), or Lennard-Jones potential, which describes the repulsion between nuclei and the dispersion forces between atoms with terms proportional to \( R^{-12} \) and \( -R^{-6} \), respectively [67]. The main advantage of this potential for the purposes of computation is that its repulsive term is proportional to the square of its attractive term, which reduces computation time for each interaction considered in a simulation.

While interactions between atoms and molecules nearly always involve short-range repulsion and often long-range attraction, too, sometimes the character of the potential for the range of internuclear separation between these regimes (3 Å < \( R < 6 \) Å, in the case Cs-Ar) is not well described by simple, two-term potential functions. Quantum effects cannot be ignored in the Cs-Ar system, and the results of \textit{ab initio} calculations [68–70] have been utilized to determine an appropriate qualitative form for the interaction potential corresponding to the B state of Cs-Ar used in the spectral simulation described below.
3.1.4 Franck-Condon Overlap, Optical Transitions, and Absorption Spectrum Calculations

With the wavefunctions calculated according to the method described above for both the ground state and the excited state, relative transition strengths between these states can be readily calculated. Molecules undergoing electronic transitions via the absorption or emission of one or more photons obey the Franck-Condon principle, which states that because the nuclei of the molecule are so much more massive than its electrons, the internuclear separation of the molecule remains constant during optically excited electronic transitions. Quantum mechanically, this means that the most probable optical transitions in a molecule are those between states which have a high degree of wavefunction overlap spatially [54].

The optical transition probability between two states is proportional to the dipole moment, and is given by

\[
\langle \psi' | \mu(R) | \psi'' \rangle = \int_0^\infty \psi'^* \mu(R) \psi'' dR
\]

(3.9)

where \(|\psi''\rangle\) and \(|\psi'\rangle\) are the lower and upper state wavefunctions, respectively, and \(\mu(R)\) is the electric dipole moment for the transition. The electric dipole moment, given by

\[
\mu = \sum_i q_i r_i
\]

(3.10)

where \(q_i\) and \(r_i\) are the charge and position of particle \(i\), respectively, can be reasonably approximated by a constant with respect to internuclear separation, and this approximation has been made in the model described in Section 3.2. Therefore, the transition dipole moment can be approximated as follows:

\[
\langle \psi' | \mu(R) | \psi'' \rangle \approx \mu \int_0^\infty \psi'^* \psi'' dR = \mu \langle \psi' | \psi'' \rangle
\]

(3.11)

The relative intensity of an optical transition between states of energy \(\epsilon''\) and \(\epsilon'\) under the constant dipole approximation is proportional to the square of the overlap integral

\[
S(\epsilon', \epsilon'') = |\langle \psi'(\epsilon') | \psi''(\epsilon'') \rangle|^2
\]

(3.12)
which is known as the Franck-Condon factor for the transition.

After calculating the effective interaction potentials, sets of wavefunctions for both the ground and excited states, and the corresponding Franck-Condon factors for these sets of wavefunctions, a relative absorption spectrum can be calculated by the following formula [71]:

\[
k(\lambda) \approx \frac{1}{\lambda} [N_A][N_B] \sum_{J=0}^{J_{\text{max}}} \int_{\epsilon_j=0}^{\epsilon_{j_{\text{max}}}} \int_{\epsilon_{j'}=0}^{\epsilon_{j_{\text{max}}}} (2J + 1) e^{-\frac{\epsilon_{j'}}{kT}} S(\epsilon_j', \epsilon_{j''}) d\epsilon_{j''} d\epsilon_j
\]

(3.13)

This calculation weighs the Franck-Condon factors corresponding to the transition probabilities between states according to the rotational state degeneracy, \((2J+1)\), and the thermal degeneracy of the ground state as accounted for in the Boltzmann distribution, \(e^{-\frac{\epsilon}{kT}}\). This function \(k\) is then linearly proportional to the absorption spectrum for the pair of interaction potentials used.

3.2 Cs-Ar Absorption Spectrum Simulation

With the quantum mechanical foundation laid in the previous section, the application of these techniques to the simulation of the Cs-Ar \(X^2\Sigma^+_{1/2} \rightarrow B^2\Sigma^+_{1/2}\) absorption spectrum will be discussed below. This simulation has been used to iteratively refine the upper state interaction potential based on experimental absorption data.

3.2.1 The Cs-Ar \(X\Sigma\) State and Pair Energy Considerations

First, a sound \(X^2\Sigma^+_{1/2}\) state needed to be determined, and several experimental results were found in the literature toward this end. Based on the scattering experiments of Malerich et al. [72], the repulsive potential between colliding ground-state \((X\Sigma^+_{1/2})\) Cs-Ar pairs can be described by

\[
U_{X,\text{rep}}(R) = (3.23 \times 10^7 \text{ cm}^{-1} \text{ Å}^{8.6}) \times R^{-8.6}
\]

(3.14)

This repulsive potential is accurate in the range of internuclear separation of 2.9-4.7 Å, which corresponds to a potential energy range of 0.007-0.4 eV (56-3226 cm\(^{-1}\)) [72]. Nayfeh et al. experimentally determined the van der Waals well depth of the Cs-Ar interaction potential
to be $-43 \text{ cm}^{-1}$ at 10.4 au (5.5 Å) [73]. This is consistent with the experiments of Buck and Pauly [74] and with calculations of Hedges et al. [75] which predict the well depth to be $\sim 45 \text{ cm}^{-1}$. For this attractive portion, the Cs-Ar interaction potential of Cvetko et al. has been used, because it exhibits a van der Waals well depth of 43 cm$^{-1}$ at $R=5.5$ Å, and it incorporates experimentally determined multipolar interaction terms and other parameters from several different sources [52]. This potential has the form

$$U_{X,Cvetko}(R) = \begin{cases} \frac{C_6}{120} \left( \frac{b}{3} \right)^6 (ae^{-bR} - \chi e^{-(2/3)bR} - e^{-(1/3)bR}) & bR \leq 16.6 \\ \frac{C_6}{120} \left( \frac{b}{3} \right)^6 ae^{-bR} - \frac{C_6}{R^6 - Q^2R^4} & br \geq 16.6 \end{cases} \quad (3.15)$$

where $C_6$ is the London dispersion coefficient, $Q$ is defined in terms of several multipolar coefficients as

$$Q = \left( \frac{C_8 C_{10}}{C_6^2} \right)^{1/6}, \quad (3.16)$$

$b$ is related to the radial electron densities of the unperturbed atoms, and $a$ is a free parameter, adjusted by Cvetko et al. for best agreement between the radial position of the zero-crossing of their functional representation of the interaction potential and the reported potentials of other groups. $\chi$ is determined by the necessity for continuity in the interaction potential at $bR=16.6$, and is defined as

$$\chi = \frac{14.6 + 0.918(Qb)^2}{1 - (Qb/16.6)^2} \quad (3.17)$$

In order to combine these repulsive and attractive portions of the interaction potential for the Cs-Ar $X\Sigma$ state, a joining function has been employed [76]:

$$F(R) = \frac{1}{(1 + e^{a(R-R_s)})^b} \quad (b > 0) \quad (3.18)$$

In this function, $a$ and $b$ are adjustable parameters which dictate the behavior of the joining function in the transition region, and $R_s$ is approximately the value of internuclear separation at which the joining function transitions from 0 to 1. Outside of ensuring that the joined potential is consistent with the repulsive portion in the region in which the results of Malerich
et al. are accurate and that the van der Waals well is of the correct depth and in the correct location, $a$ and $b$ have been selected so that $|\frac{d^2U_x}{dr^2}|$ is minimized. The resulting joined interaction potential for the Cs-Ar $X^2\Sigma^+_1/2$ state is shown in black in Figure 3.2, along with the repulsive potential of Malerich et al. and the ground state potential of Cvetko. This ground state potential is qualitatively similar to those of the $ab\text{ initio}$ calculations found in the literature [68–70] (see Figure 3.3 for comparison), but experimental data corroborates its accuracy.

![Interaction Potential](image)

**Figure 3.2:** Interaction potential used in this model for the ground $(X^2\Sigma^+_1/2)$ state of Cs-Ar (solid black curve), along with the experimentally determined repulsive potential of Malerich et al. (dashed green curve) and the X state of Cvetko et al. (dashed red curve).

Next, to ensure accuracy in the physical model used to calculate the absorption spectrum, a comprehensive range of pair energies and rotational states to include in the calculation must be determined. With the ground state interaction potential for Cs-Ar defined, it is possible
to extract from this a reasonable threshold value for $R_{ext}$, for the purpose of determining the relationship between pair energy ($\epsilon$) and the maximum angular momentum state to consider, $J_{\text{max}}$. In order to determine $R_{ext}$, a threshold value for the magnitude of the derivative of the interaction potential between the colliding pair, $|\frac{dU}{dR}|$, must be judiciously chosen, below which the interactions between the pair are assumed to have negligible effect. $R_{ext}$ will be assumed to be the point in internuclear separation (from $R = 0$, outward) at which the derivative of the interaction potential decreases to this value. Figure 3.4 shows how $J_{\text{max}}$ vs. $\epsilon$ changes for different threshold values for $|\frac{dU}{dR}|$ for the ground state potential shown in Figure 3.2, and thus different values for $R_{ext}$. In this figure, $R_{ext} = 8.86\text{Å}, 9.78\text{Å}, 10.74\text{Å}, \text{and } 11.67\text{Å}$, corresponding to $|\frac{dU}{dR}| = 6 \text{ cm}^{-1}/\text{Å}, 4 \text{ cm}^{-1}/\text{Å}, 2 \text{ cm}^{-1}/\text{Å}, \text{and } 1 \text{ cm}^{-1}/\text{Å}$, respectively.
For this model, the exact choice of $|\frac{dU_{XX}}{dR}|$ within this range has a negligible effect on the predicted spectrum, and the threshold value for $|\frac{dU_{XX}}{dR}|$ was chosen to be $2 \text{ cm}^{-1}/\text{Å}$, which corresponds to $R_{ext} = 10.74\text{Å}$. The top panel of Figure 3.5 shows the relationship between $J_{max}$ and pair energy in the ground state.

The values for pair energy are assumed to conform to a Boltzmann distribution. The data against which the simulation results were compared in this work were measured at $T=474 \text{ K}$, and so the corresponding Boltzmann distribution (shown in the middle panel of Figure 3.5) was used to weigh the contributions to the spectrum. The bottom panel of Figure 3.5 shows the total state degeneracy distribution vs. ground state energy for the Cs-Ar system at $T=474 \text{ K}$, which represents the product of the integrated rotational state degeneracies for $J$
Figure 3.5: Rotational and thermal state distributions and the product of these distributions vs. total state energy. The shaded region in the bottom panel indicates the energy states which were considered for this simulation—about 90% of all states represented by the distribution.
values from 0 to $J_{max}$ and the Boltzmann distribution of the middle panel. Over 90% of the energy states represented by this distribution were accounted for in this simulation, and this portion of the state distribution is represented by the shaded region of the bottom panel of Figure 3.5.

3.2.2 Parametric Form of the Cs-Ar $B^2\Sigma_{1/2}^+$ State and Absorption Spectrum Simulation

Initially, it was thought that a functional form could be devised to represent the $B^2\Sigma_{1/2}^+$ state for Cs-Ar using several of the terms described in the previous section, and while the excited states for alkali–rare gas pairs are not as well-understood as the ground states, some general trends relating the ground and excited states have been found. For instance, Zhu et al. calculated van der Waals ($C_6$) coefficients for the $X\Sigma$, $A\Pi$, and $B\Sigma$ states for Na-He, K-He, and Rb-He [77]. Their results indicated that these dispersion coefficients increased by roughly a factor of three from the ground state to the $B^2\Sigma_{1/2}^+$ excited state for each pair investigated. While they did not calculate this coefficient for Cs-Ar, their results can be extrapolated to conclude that the attractive term in the excited state due to the dispersion force is of greater magnitude than that for the ground state, and assuming a factor of three increase from the ground state, $C_6$ for the $B^2\Sigma_{1/2}^+$ state of Cs-Ar would be $\sim 6 \times 10^6 \text{cm}^{-1}\text{Å}^6$.

However, a simple functional form with only a few terms does not accurately represent the interactions between cesium and argon at small internuclear separation. In fact, a few $ab\ initial$ investigations can be found in the literature in which the $B^2\Sigma_{1/2}^+$ interaction potential between cesium and argon were calculated based not only on semiclassical effects like long-range dipole-dipole forces and short-range fermionic repulsion, but also on the quantum mechanical interactions between the states of the individual atoms, including many highly excited states of the alkali atom [68–70]. Figure 3.6 shows three such curves for the Cs-Ar B state which are all qualitatively similar in that they all exhibit a shoulder at small internuclear separation. However, the amplitude and exact position of this shoulder, as well as the depths and positions of the minima on either side of it, differ between these three curves, and these differences cause the resulting absorption spectra to differ as well. Figure
3.7 shows two simulated spectra generated from the potentials of Blank et al. [70], and Dhiflaoui and Berriche [69] using the spectral simulation method of this work, superimposed on an experimental absorption spectrum. From this figure it is clear that these *ab initio* calculations do not produce potential curves that precisely predict the spectral position of the blue satellite of the D<sub>2</sub> transition for Cs in Ar, nor do their spectral contours overlap those of the experimental blue satellite. However, the differences between the undulations of the experimental spectrum and those in the calculated spectra are not extreme, and the predicted peak positions are within 20 nm of the experimental peak. These observations indicate that the consensus among *ab initio* calculations found in the literature concerning the general form of the B state for Cs-Ar is valid. Therefore, a parametrized B state of this
Figure 3.7: Simulated Cs-Ar absorption spectra generated using the $X^2\Sigma^{+}_{1/2}$ and $B^2\Sigma^{+}_{1/2}$ states of Blank et al. [70] and Dhiflaoui and Berriche [69] compared with the experimental absorption spectrum of Cs-Ar. Both \textit{ab initio} potential sets fail to predict the correct satellite position and precise contours of the experimental spectrum.

The general form has been used for this simulation/optimization routine.

It is assumed that minor changes in the common shape of these \textit{ab initio} interaction potentials could produce predicted absorption spectra that more precisely agree with the experimental spectrum for Cs-Ar. Based on this assumption, the Cs-Ar $B^2\Sigma^{+}_{1/2}$ interaction potential of Blank \textit{et al.} [70] has been separated into four regions as illustrated in Figure 3.8. In order to achieve increasingly better agreement between simulated and experimental absorption spectra, the B state potential was modified through the stretching or compressing—in R and in amplitude—of these individual regions, which were then reassembled at their end points to form a new, continuous interaction potential. Continuity was ensured in the
modified potential and its first derivative by the fact that at each of the region boundaries, the first derivative of the potential with respect to internuclear separation is zero. Therefore, no matter what stretching or compressing is performed on the amplitudes of each region of the potential, this zero-derivative is preserved, thus preserving continuity of the potential and its first derivative over its entire length.

![Figure 3.8: The B^2Σ^+_{1/2} state of Cs-Ar calculated by Blank et al. [70], separated into four regions at points along the potential where \( \frac{dU}{dr} = 0 \). These boundaries were chosen to preserve the continuity of the first derivative of the potential along its entire length upon independent manipulation of each region.](image)

Calculation of the absorption spectrum corresponding to the \( \chi \Sigma \) and \( \varnothing \Sigma \) states for Cs-Ar was performed using the method represented by Equation 3.13. Each absorption spectrum calculation was accompanied by the calculation of an entire set of wavefunctions for the \( \varnothing \Sigma \) state according to the Numerov-Cooley method described above [55]. The ground state
remained constant throughout these simulations, and wavefunctions for this state were pre-calculated. Transitions have only been considered between states where $\Delta J = 0$. While this approximation is contradictory to the transition selection rule for linear molecules that states $\Delta J = \pm 1$, the phase shift between wavefunctions differing by a single quantum of angular momentum is minor, and it can be ignored for the sake of computational simplicity. So, for each $J$ in the range $J = 0$ to $J_{\text{max}}$, the Franck-Condon factors for all the wavefunctions in the ground and excited states with energies appropriate for that value of $J$ are calculated.

A representative color map of Franck-Condon factors is shown in Figure 3.9 for $J = 0$. The horizontal and vertical axes of this plot represent the atom pair energies above the dissociation asymptote in the excited and ground states, respectively. The strong Franck-Condon factors calculated for $\epsilon' = \epsilon''$ correspond to absorption on the Cs D$_2$ line ($6^2S_{1/2} \rightarrow 6^2P_{3/2}$). The off-diagonal contributions to the color map correspond to absorption to the blue and red sides of the D$_2$ line for $\epsilon'' < \epsilon'$ and $\epsilon'' > \epsilon'$, respectively. The vertical demarcation at $\epsilon' \approx 220$ cm$^{-1}$ is a result of the barrier in the B$\Sigma$ state at $R \approx 4.5$ Å, which prevents wavefunction oscillation for $R < 4.5$ Å in states with energy less than $\sim 220$ cm$^{-1}$.

Franck-Condon factors such as those of Figure 3.9 were weighed according to both the Boltzmann factor for the ground state energy as well as the degeneracy of the rotational state, were integrated with respect to upper and lower state energy, and were then summed over all $J$ values to calculate the absorption spectrum for Cs-Ar.

### 3.2.3 Optimization of B$\Sigma$ State Potential

Optimization was achieved through the use of the simplex minimization algorithm [78]. This algorithm evaluates the function to be minimized at $N+1$ equidistant points, called a “simplex,” in the $N$-dimensional parameter space of the function. There is a complementary simplex opposite each point in a simplex, and when the point in the initial simplex which produces the maximum function output is determined, the complimentary simplex corresponding to that point is chosen as the new simplex to be evaluated. This process is repeated, and over the course of many iterations, a minimum value for the function is found. While there is no guarantee that the final minimum value determined in this manner is
Figure 3.9: A color map (in logarithmic-scale) representing the Franck-Condon factors for J=0. The left and bottom axes represent ground-state and excited-state pair energy above the dissociation asymptote, respectively. The effect of the characteristic “shelf” in the BΣ state at R≈4.5 Å is explicit in this color map; the vertical demarcation at $\epsilon' \approx 220$ cm$^{-1}$ results from the fact that excited-state pairs with total energy below this value (which corresponds to the shelf height above the dissociation asymptote) are represented by wavefunctions which do not oscillate for $R < 4.5$ Å. The abrupt change in the color map corresponds to the abrupt change in the internuclear region of oscillation for wavefunctions at this excited-state pair energy.
global, this routine provides a clever means of optimizing a function with many potentially interdependent variables [78].

The function which was optimized for this work accepted nine parameters corresponding to horizontal and vertical stretch for each region of the piecewise B state potential shown in Figure 3.8 and a parameter corresponding to a shift of the entire potential curve outward or inward with respect to internuclear separation. The function then returned a value corresponding to the error between the resulting simulation and the experimental absorption spectrum. In order to improve the agreement between the simulated and experimental blue satellite peak positions, the error function was initially defined as

\[
err(k_{\text{sim}}(\vec{s}; \lambda), k_{\text{exp}}(\lambda)) = |\lambda_{\text{sat.peak,exp}} - \lambda_{\text{sat.peak,sim}}|
\]  

(3.19)

where \(\lambda_{\text{sat.peak,exp}}\) and \(\lambda_{\text{sat.peak,sim}}\) are the blue satellite peak positions of experiment and simulation, respectively. After the optimization routine achieved a match in peak position using this error function, another error function was used to improve the agreement between the experimental and simulated spectral contours. This error function was defined as

\[
err(k_{\text{sim}}(\vec{s}; \lambda), k_{\text{exp}}(\lambda)) = \sum_i \left( \frac{k_{\text{sim}}(\lambda_i) - k_{\text{exp}}(\lambda_i)}{k_{\text{exp}}(\lambda_i)} \right)^2
\]  

(3.20)

where \(k_{\text{sim}}\) is the simulated spectrum, \(k_{\text{exp}}\) is the experimental spectrum, \(\vec{s}\) is the nine-dimensional vector comprised of the parameters used to produce \(k_{\text{sim}}\), and \(\lambda_i\) is the \(i\)th discrete component of the wavelength range over which the absorption spectra are defined. This error function not only accounts for the squared difference between the experimental and simulated spectra, but also weighs this difference by the amplitude of the experimental spectrum at every wavelength. This serves to minimize the contribution of small-percentage errors to the value returned by the function. The use of these two error functions and the routine described above produced improved spectral agreement between simulation and experiment, as described below.
3.2.4 Results and Discussion

Figure 3.10 shows the optimized spectrum produced by this work, along with simulated spectra generated using X and B potentials from the literature [69,70]. The peak wavelength of the optimized blue satellite matches that of the experimental spectrum, and its curvature to the red side of the peak is in excellent agreement, too. The biggest discrepancy between the simulated and experimental spectra is in the shape of the spectrum directly on the blue satellite peak. Still, the optimized spectrum shows marked improvement in agreement with experiment over the spectra predicted by the un-modified \textit{ab initio} potentials. The optimized X and B state potentials of this work are shown in Figure 3.11, along with the potentials from the literature. While agreement between simulated and experimental absorption spectra has been improved in the optimization of this work, this figure shows that the optimized B state potential preserves the qualitative shape of the calculated B states from the literature. Thus, the quantum mechanical interactions between the Cs and Ar atoms which give rise, in particular, to the shoulder in the B state at R \( \approx 4 \) Å have not been neglected, but have been refined so as to better reproduce the results of experiment.

The results of this optimization routine can be used to better predict the behavior of alkali–rare gas laser systems. Specifically, the blue absorption satellite of the D\textsubscript{2} line, which is the absorption feature on which alkali–rare gas laser systems are pumped, is the result of optical excitation of alkali–rare gas pairs within a narrow range of internuclear separation. Figure 3.12 is presented to explicitly illustrate this fact. The top half of this figure shows a few radial wavefunctions for the optimized X\Sigma and B\Sigma interaction potentials of this work superimposed on the potentials themselves (where J=0), versus internuclear separation (R). These wavefunctions have been arbitrarily scaled in amplitude for the purpose of clarity, and they are positioned vertically so that their oscillations center around the energy value which they represent (above the dissociation asymptote). The bottom half of this figure shows the cumulative overlap integrals for the wavefunctions of the top panel, also plotted versus internuclear separation. At each value of R, the curves presented in these plots represent the overlap between the wavefunctions indicated, integrated from 0 to R. Regions in which these overlap integrals increase monotonically with R correspond to pair separations which
Figure 3.10: The optimized absorption spectrum of Cs-Ar from this work compared with those calculated by Pascale and Vandeplanque [68], Dhiflaoui and Berriche [69], and Blank et al. [70]. The potentials resulting from the optimization routine of this work maintain qualitative agreement with those from the literature.

contribute strongly to the total overlap integral, and thus, to the absorption strength at the transition energy represented by the particular wavefunctions of the overlap.

The top cumulative overlap integral corresponds to absorption on the blue satellite peak for Cs-Ar, where the wavelength of the absorbed photon is 836.7 nm, and the difference in energy between this photon and the transition energy for the Cs D$_2$ line is 216 cm$^{-1}$. It is clear from this plot that the Cs-Ar pairs which contribute most strongly to blue satellite peak absorption are those with internuclear separations in the range of $\sim$4.3–5.5 Å. The bottom plot corresponds to absorption on the atomic Cs D$_2$ transition, and this plot indicates that pairs which are separated by as little as $\sim$5.5 Å contribute to atomic D$_2$ absorption. This
indicates that, in the context of optical absorption, the perturbations to the $6s\ ^2S_{1/2}$ and $6p\ ^2P_{3/2}$ states of Cs caused by the proximity of an argon atom are negligible for $R \sim 5.5$ Å. This observation validates the sufficiency of the approximation made in this model concerning the value of the impact parameter for collisions between Cs and Ar atoms.

The information gleaned from the cumulative overlap integral of Figure 3.12 corresponding to blue satellite absorption allows precise prediction of the fraction of Cs atoms in a particular Cs-Ar gas mixture which can contribute to Cs-Ar laser action; given a normalized nearest-neighbor distribution describing the gas mixture—and assuming $[\text{Ar}]\gg[\text{Cs}]$, thereby ensuring that the nearest atomic neighbor of any cesium atom is argon—integration

Figure 3.11: The $X^2\Sigma_{1/2}^+$ and $B^2\Sigma_{1/2}^+$ states of Cs-Ar from this work compared with those calculated by Pascale and Vandeplanque [68], Dhiflaoui and Berriche [69], and Blank et al. [70]. The potentials resulting from the optimization routine of this work maintain qualitative agreement with those from the literature.
Figure 3.12: Representative wavefunctions for the X and B states, as well as cumulative overlap integrals for these wavefunctions, which correspond to blue satellite and \( \text{D}_2 \) absorption for the middle and bottom panels, respectively.

of this distribution over the range in internuclear separation from 4.3 to 5.5 Å yields the fraction of cesium atoms in the mixture which are part of a Cs-Ar pair capable of absorption on the \( \text{D}_2 \) blue satellite and which can therefore be excited in pumping the Cs-Ar laser. Thus, optimization of the interaction potentials between alkali–rare gas pairs in the manner described in this section can assist in understanding the behavior of these lasers and in their design.
CHAPTER 4

APPLICATION OF ALKALI–RARE GAS LASERS
TO THE STUDY OF ATOM-ATOM INTERACTIONS

Alkali–rare gas laser systems are not only a novel platform for studying laser physics, but because of their reliance on atomic interactions for effective optical pumping, they also serve as sensitive tools for studying the physics within their own gain media.

4.1 The Role of Photoionization in the Performance of the Cs-Ar Laser

The behavior of the Cs-Ar laser system has been interpreted and utilized in conjunction with a numerical model created by Palla et al. [79] to investigate the two-photon ionization cross section for Cs* (6p \(^{2}\)P\(_{3/2}\)) at \(\lambda_{\text{pump}}=836.7\) nm and its effect on the behavior of this laser system.

It has been proposed that photoionization will pose a great hindrance in the scaling up to high power CW output (\(\sim\)1 kW and beyond) of an alkali-noble gas laser of the type described in this dissertation [80]. According to the calculations of Knize et al., the photoionization rate for a 10-atmosphere Cs exciplex laser would be greater than \(10^5\) per second, which would rapidly deplete the neutral Cs population in the gas, spoiling the gain of the laser unless the gain medium were circulated at a near supersonic flow rate. However, the experimental results described in this section demonstrate (with the aid of the BLAZE computer model of Palla et al. [79]) that photoionization in a Cs exciplex laser is much less detrimental than the calculations of Knize suggest.

The experiments described in this section utilized a pulsed dye laser which exhibited instantaneous intensities from \(\sim\)100 kW-cm\(^{-2}\) up to 3 MW-cm\(^{-2}\) as the pump source for the Cs-Ar laser. This order-of-magnitude output range of the dye laser was crucial for
studying the highly intensity-dependent effect of two-photon absorption. A diagram of the experimental arrangement for these investigations is shown in Figure 4.1. This apparatus was similar to that described in Chapter 1 of this document, except that the borosilicate Cs-Ar cell was housed in an oven inside of a 52 cm linear cavity as opposed to an L-shaped cavity. The cavity end mirror and output coupler had reflectivities at 852 nm of >99% and 50%, respectively, and each mirror had a 3 m radius of curvature. A dye solution of LDS-821 (Styryl 9M) in propylene carbonate was used in the pump laser for these experiments.

![Figure 4.1: Experimental arrangement.](image_url)

The pump wavelength ($\lambda_P$) was fixed at 836.7 nm for the duration of the experiments described in this section, which corresponds to the peak of the blue satellite for the Cs D$_2$ line in Cs-Ar mixtures. Pump pulse energy, Cs-Ar laser pulse energy, and unabsorbed pump energy were all recorded on a per-shot basis as the pump intensity was swept through its output range, and some of the data measured during these experiments are shown in Figure 4.2. This figure shows the expected increase in laser threshold as the temperature of the system, and thus the ground-state gaseous Cs density, increases. This increase in Cs number density requires greater pump energy to obtain a population inversion on the Cs D$_2$ line.
Figure 4.2: Output pulse energy ($\lambda_L=852.1$ nm) versus absorbed pump energy ($\lambda_P=836.7$ nm) for the Cs-Ar laser system for temperatures 433–534 K, corresponding to cesium number densities ranging from $3.5\times10^{14}$ cm$^{-3}$ to $1.4\times10^{16}$ cm$^{-3}$. The T=474 K data are shown in semilog scale in the inset.

The inset plot of the data measured at T=474 K is presented in semilog scale to exaggerate the abrupt shift in the functional form of the laser data at low output intensity. This shift at $E_L \approx 0.4$ $\mu$J is evident in most of the data sets shown in Figure 4.2, and is attributed to saturation of the $\lambda_L=852.1$ nm laser transition, because the intracavity intensity at these output energies is $\sim 50 - 100$ W cm$^{-2}$, which is on the order of the estimated saturation intensity for the Cs D$_2$ line ($I_{sat} \sim 10$ W cm$^{-2}$). As absorbed pump energy increases past $\sim 3$ mJ, the Cs-Ar laser pulse energies “roll over,” indicating that the laser is operating in a regime in which the gain medium behaves as a saturated amplifier.

The BLAZE V computer model used to interpret the results of these experiments has
been described in detail in another publication (see [79]), and was not created as part of
this dissertation. This model has been used in the past, however, to accurately describe
the experimental behavior of alkali–rare gas lasers in terms of the physical processes occurring
in the gain medium, and several modifications were implemented in this model to accurately
portray the experimental conditions of this investigation into the role of two photon ioniza-
tion in the Cs-Ar laser system. In these experiments, as the pump pulse energy increased
from $\sim 3.5 \text{ mJ}$ to over 35 mJ, the pump beam diameter and the pump pulse duration in-
creased monotonically from $\sim 5 \text{ mm}$ to 11 mm (FWHM). Additionally, the variation of the
pump pulse energy over this range was accompanied by a variation in the pulse duration
from 6 to 11 ns (FWHM). In the computer model, the diameter (FWHM) of the pump beam
was described accurately by

$$d = A + B \times \log(E_P)$$

(4.1)

where $A$ and $B$ are constants, and $E_P$ is the pump pulse energy. While the pump pulse
duration varied with energy as described above, variation over this range was found to have
a negligible effect in the computer model, and so the pulses were modeled to be 8 ns FWHM,
irrespective of pulse energy.

The initial comparison of the computer model and experimental data revealed a systematic
experimental error in recording the temperature of the Cs-Ar mixture. The oven and cell
allowed only for accurate measurement of the cell temperature for $T \leq 450 \text{ K}$, but for higher
temperatures there was a small but significant difference between the actual temperature
for the cell and the temperature measurement. The difference in these temperatures ($\delta T = T_{\text{exp}} - T_{\text{model}}$) rises from 0 K at $T_{\text{exp}} = 454 \text{ K}$ to 24 K for $T_{\text{exp}} = 534 \text{ K}$.

As mentioned above, in these experiments the extent of the range of values for the instan-
taneous pump power was beyond 3 MW. This instantaneous pump power was considerably
greater than pump powers previously utilized to pump alkali–rare gas laser systems [21–24].
Therefore, the incorporation of intensity-dependent loss mechanisms for the Cs $6p^2P_{3/2}$ state
into the BLAZE V model was deemed necessary. Single-photon absorption from this state
at the pump wavelength ($\lambda_P = 836.7 \text{ nm}$) is not a likely source of loss, as the differences in
energy between a pump photon and the $8s^2S_{1/2} \leftrightarrow 6p^2P_{3/2}$ and $6d^2D_{5/2} \leftrightarrow 6p^2P_{3/2}$ reso-
nances of Cs are \( \sim 636 \text{ cm}^{-1} \) (19 THz) and \( \sim 1050 \text{ cm}^{-1} \) (31 THz), respectively. Assuming the pressure broadening coefficients for these transitions are on the order of those for the D lines, the linewidth of these resonances broadened by \([\text{Ar}]=1.6 \times 10^{19} \text{ cm}^{-3}\) is \(< 0.5 \text{ cm}^{-1}\).

And, assuming that the lineshape of these transitions can be described by a Lorentzian, the absorption cross section \(636 \text{ cm}^{-1}\) to the blue side of the \(8s\) \(^2S_{1/2} \leftarrow 6p\) \(^2P_{3/2}\) transition peak (where the absorption of a single pump photon from the Cs(\(6p\) \(^2P_{3/2}\)) state terminates) is roughly six orders of magnitude less than that at the transition peak. Because the energy detuning between the \(6d\) \(^2D_{5/2} \leftarrow 6p\) \(^2P_{3/2}\) transition and the pump photon energy is nearly twice that for the \(8s\) \(^2S_{1/2} \leftarrow 6p\) \(^2P_{3/2}\) transition, photoionization of the \(6p\) \(^2P_{3/2}\) state via the sequential absorption of two photons has been ruled out as a dominant channel for population loss from this state. Thus, the dominant photoionization channel for this state is assumed to be non-resonant two-photon ionization from the \(6p\) \(^2P_{3/2}\) state (see Figure 4.3, which shows a diagram representing the process considered). In making this assumption, any perturbations of the \(8s\) \(^2S_{1/2}\) or \(6d\) \(^2D_{5/2}\) excited states of Cs caused by the presence of Ar have been neglected, and thus, transitions between excited Cs-Ar molecular states have been ignored. Further spectroscopic studies of the Cs-Ar interaction potentials corresponding to Cs(\(6p, 6d, 8s\)) + Ar in the separated atom limit are necessary to confirm or deny the validity of this assumption.

For the purposes of determining the effects of non-resonant two photon ionization on the behavior of the Cs-Ar laser, the nonlinear process

\[
\text{Cs}(6p\; ^2P_{3/2}) + 2h\nu \xrightarrow{\sigma^{(2)}} \text{Cs}^+\; (^1S_0) + e^- + \Delta E
\]

was included in the BLAZE V model, where \(\sigma^{(2)}\) is the two-photon ionization cross section in units of cm\(^4\) W\(^{-1}\) and \(\Delta E\) is the energy difference between the ionization potential for Cs and the termus for the absorption of two pump photons from the Cs \(6p\) \(^2P_{3/2}\) state. The model predictions for \(\sigma^{(2)} \leq 10^{-27} \text{ cm}^4\text{W}^{-1}\) are shown in Figure 4.4, superimposed on the data of Figure 4.2. Figure 4.4 shows the computer simulation results as solid lines on top of experimental data. The experimentally measured temperature is labeled, as is the computer predicted temperature—the lower temperature of the two—where appropriate. These model
predictions are essentially unchanged by variations of over a factor of two in the assumed values of cross sections and lifetimes for the model, but because this simulation involves low-lying states of the atomic alkalis, most of these parameters describing the states of interest in the model are well known.

Once the effects of two-photon ionization were incorporated into the model, an upper bound on the value of the two-photon ionization cross section was determined by sweeping the value of this cross section and comparing the resulting simulation predictions with experimental results. Figure 4.5 shows the model predictions for several different values of the two-photon ionization cross section superimposed onto the data measured at 474 K (where $[Cs]=1.9 \times 10^{15}$ cm$^{-3}$). The solid lines in this figure show the model predictions for this tem-
perature and Cs number density for different $\sigma^{(2)}$ values between $1.4 \times 10^{-27}$ cm$^4$W$^{-1}$ and $1 \times 10^{-24}$ cm$^4$W$^{-1}$. The simulation agrees well with the experiments for $\sigma^{(2)} \leq 10^{-25}$ cm$^4$W$^{-1}$. However, when the value for $\sigma^{(2)}$ is set above $3.5 \times 10^{-25}$ cm$^4$W$^{-1}$, the model predicts laser output pulse energies that clearly deviate from the experimentally measured values. These model predictions are consistent across all six data sets of Figure 4.2. Another example of the comparison of model predictions with experimental data is shown in Figure 4.6 for the data measured at 514 K ([Cs] = $7.4 \times 10^{15}$ cm$^{-3}$). In this figure, there is a clear discrepancy between model predictions and experiment for $\sigma^{(2)}$ values of $1.4 \times 10^{-25}$ cm$^4$W$^{-1}$ and above.

The results of Figures 4.5 and 4.6, along with those for the four other data sets measured, suggest that $\sigma^{(2)}$ is no larger than $8 \times 10^{-26}$ cm$^4$W$^{-1}$. For an 836.7 nm optical field intensity of 3 MW cm$^{-2}$, this value corresponds to a single photon ionization cross section of $2.4 \times$
$10^{-19}$ cm$^2$. The population loss rate for the Cs $6p^2P_{3/2}$ state due to two-photon ionization by a 3 MW cm$^{-2}$ optical field is $3 \times 10^6$ s$^{-1}$. It has previously been predicted that in operating a Cs-Ar laser system, a 500kW cm$^{-2}$ optical pump field would cause a population loss rate of $2.7 \times 10^6$ s$^{-1}$ for the Cs $6p^2P_{3/2}$ state [80]. However, the results of the investigation described in this chapter indicate that a pump field of this intensity would result in a loss rate of $8 \times 10^4$ s$^{-1}$—about 1.5 orders of magnitude less than the calculated value of Ref. [80]. There are many likely causes for the discrepancy between the results of this chapter and Ref. [80].

For example, in the prior calculation, photoionization from the $np^2P_{1/2,3/2}$ states of the alkalis was described by a single-photon process involving the absorption of radiation reso-
nant with the D$_1$ or D$_2$ lines of the alkali atom in question [80]. This is inaccurate, however, because the photoionization of any of the alkali atoms in its lowest excited states would require the absorption of at least two photons resonant with its principal series transitions. Also, the cross section describing the single photon ionization process in the calculation of Ref. [80] was assumed to be $2 \times 10^{-17} \text{ cm}^2$. Although there are few data available for comparison with the results of this chapter or with Ref. [80], Nayfeh et al. [81] estimated the single photon ionization cross section for the Cs 7$p$ states to be $3 \times 10^{-18} \text{ cm}^2$ at $\lambda = 455 \text{ nm}$, which is about one order of magnitude smaller than that used in Ref. [80].

This section has shown that based on careful comparison of the predictions of the BLAZE V model [79] and experimental results for a Cs-Ar 852.1 nm laser pumped by a pulsed laser
with intensities of up to $3 \text{ MW cm}^{-2}$, an upper bound of $8 \times 10^{-26} \text{ cm}^4\text{W}^{-1}$ for the two-photon ionization cross section of the Cs $6p \, ^2P_{3/2}$ state has been determined. Confidence in the validity of this upper bound is reinforced by the fact that the modified model of Palla et al. accurately predicts experimental data for this laser system for a range of Cs number density that spans nearly two orders of magnitude. This result indicates that, contrary to the conclusion of Ref. [80], photoionization losses from the lowest excited states of the alkalis are not likely to have a significant effect on high-power CW alkali–rare gas laser systems. This experiment has also shown that the behavior of alkali–rare gas laser systems can be used to study fundamental properties of the gain medium itself.

(The experiments described in this section were previously reported in *Applied Physics Letters* [82].)

### 4.2 Experimental Determination of the Ratio between the Two-Photon Absorption Cross Section of Rb at $\lambda \approx 760$ nm and the $X\Sigma \rightarrow B\Sigma$ Absorption Cross Section of Rb-Xe

The blue satellite for the D$_2$ line of Rb in the Rb-Xe system peaks at $\sim 760$ nm. Coincidentally, the $7s \, ^2S_{1/2}$ state of Rb is accessible from ground ($5s \, ^2S_{1/2}$) by two-photon absorption at $\lambda \sim 760$ nm. Because of the overlap between the two-photon absorption of atomic Rb and the blue satellite absorption of Rb-Xe, the Rb-Xe laser can be used as a sensitive tool for studying this two-photon process.

In photopumping the Rb-Xe laser, these two phenomena have been observed—photoexcitation of Rb-Xe pairs to populate the Rb$^*(5p \, ^2P_{3/2})$ state, and two-photon absorption of ground state Rb ($5s \, ^2S_{1/2}$) at $\lambda \approx 760$ nm, populating the Rb $7s \, ^2S_{1/2}$ state. Figure 4.7 shows an energy-level diagram depicting these processes. In this figure, Rb-Xe X$\rightarrow$B excitation is represented by a red arrow centered at $\sim 6.5 \, \AA$, but this is for illustrative purposes only; the excitation of Rb-Xe pairs can occur over a range of several angstroms in internuclear separation. In the calculation of this section, it has been assumed that any Rb-Xe pair with
internuclear separation of 1 nm or less can contribute to Rb-Xe $X \rightarrow B$ absorption.

![Energy level diagram of important states for $5s^2 S_{1/2} \rightarrow 7s^2 S_{1/2}$ absorption and pumping of the Rb-Xe laser. $X \Sigma$ and $B \Sigma$ potentials reproduced from [62].](image)

Figure 4.7: Energy level diagram of important states for $5s^2 S_{1/2} \rightarrow 7s^2 S_{1/2}$ absorption and pumping of the Rb-Xe laser. $X \Sigma$ and $B \Sigma$ potentials reproduced from [62].

The two-photon absorption process was detected by the presence of a dip in the laser excitation spectrum of the Rb-Xe laser, an example of which is shown in Figure 4.8. The amplitude of this dip in Figure 4.8 appears to be roughly 5/8 that of the laser output directly to the blue side of the dip ($\frac{E_L(\lambda_P=559.85)-E_L(\lambda_P=560.0)}{E_L(\lambda_P=559.85)} = \frac{5}{8}$). Given that ratio of the magnitude of the two processes, the relationship between the two phenomena is expressed as

$$\frac{I_P \sigma}{h \nu}[\text{RbXe}] = \left( \frac{8}{5} \right) \frac{I_P^2 \sigma^{(2)}}{h \nu}[\text{Rb}]_0$$

where $I_P$ is the pump intensity, $h \nu$ is the pump photon energy, $\sigma$ is the RbXe absorption cross section for the $X^2 \Sigma^+_{1/2} \rightarrow B^2 \Sigma^+_{1/2}$ transition at the pump photon wavelength, $[\text{RbXe}]$
Figure 4.8: Excitation spectrum for the Rb-Xe laser.

is the number density of RbXe pairs resonant with this transition, $\sigma^{(2)}$ is the two-photon absorption cross section for Rb at the pump photon wavelength, and $[\text{Rb}]_0$ is the number density of Rb atoms that are not in a RbXe pair accounted for in $[\text{RbXe}]$.

It is assumed that the Rb and Xe atoms approximately conform to a Hertz nearest-neighbor distribution [83], given by

$$P(R) = 4\pi R^2 n e^{-(4/3)\pi R^3 n} dR$$  \hspace{1cm} (4.4)$$

where $R$ is the internuclear separation between a particle and its nearest neighboring particle in the gas, $n$ is the number density of atoms in the gas (which is approximated by $[\text{Xe}]$), and $P(R)$ is the distribution of nearest neighbor distances in the gas mixture. This distribution
was originally calculated by Hertz for an ideal (non-interacting) gas, and alkali–rare gas mixtures are admittedly non-ideal. However, because the number density of xenon in these experiments is several orders of magnitude greater than that of rubidium, and because rare gases exhibit nearly ideal behavior at the pressures and temperatures employed for the experiments of this dissertation, the Hertz distribution is a reasonable approximation of the nearest neighbor distribution for these Rb-Xe gas mixtures.

Because the number density of xenon is several orders of magnitude greater than that for rubidium, the nearest neighbor for each rubidium atom is assumed to be a xenon atom. Therefore, the fraction of Rb atoms with a nearest neighbor within 1 nm is assumed to be part of an absorbing RbXe molecular pair, and [RbXe] is defined as follows:

$$[\text{RbXe}] = \left( \int_0^{1\text{nm}} P(R)dR \right) \times [\text{Rb}]$$  \hspace{1cm} (4.5)

[Rb]₀ is the remainder of [Rb] not accounted for in [RbXe], so [Rb]₀ = [Rb] − [RbXe].

In the Rb-Xe mixture of interest, T ≃ 472 K, [Rb] ∼ 10^{15} \text{ cm}^{-3}, and [Xe]=1.6 \times 10^{19} \text{ cm}^{-3}. Carrying out the integration above, [RbXe] = 6.5 \times 10^{13} \text{ cm}^{-3}, and [Rb]₀ = 9.3 \times 10^{14} \text{ cm}^{-3}. With these number densities accounted for, Equation 4.3 now reduces to

$$\frac{I_P \sigma}{h\nu}[6.5 \times 10^{13} \text{ cm}^{-3}] = \left( \frac{8}{5} \right) \frac{I_P^2 \sigma^{(2)}}{h\nu}[9.3 \times 10^{14} \text{ cm}^{-3}]$$

$$\sigma[6.5 \times 10^{13} \text{ cm}^{-3}] = \left( \frac{8}{5} \right) I_P \sigma^{(2)}[9.3 \times 10^{14} \text{ cm}^{-3}]$$  \hspace{1cm} (4.6)

For the data of Figure 4.8, the pump pulse energy, E_p ≈ 6 mJ, the pulse duration is about 8 ns, and the cross-sectional area of the pump beam is about 2.25 \times 10^{-2} \text{ cm}^{2}, so I_p = 33 \text{ MW/cm}^{2}, and the relationship between the single-photon absorption cross section for RbXe and the two-photon cross section for Rb is

$$\sigma = (7.6 \times 10^8 \text{ W/cm}^{2}) \times \sigma^{(2)}$$  \hspace{1cm} (4.7)

for I_p = 33 \text{ MW/cm}^{2}, [Rb] ∼ 10^{15} \text{ cm}^{-3}, and [Xe]=1.6 \times 10^{19} \text{ cm}^{-3}.
The above routine is just one example of the ~ 80 calculations that were performed in this way to determine the relationship between the absorption cross section of Rb-Xe and the two-photon cross section of Rb. For these measurements, [Rb], [Xe], and $I_p$ were varied in order to reveal any dependence of this procedure on these parameters, and to ensure the validity of this simple analysis. For each excitation spectrum measured, the ratio between $\sigma$ and $\sigma^{(2)}$ was calculated. These ratios were binned into a histogram which is shown in Figure 4.9, which shows a grouping of calculated ratios around $\sim 10^9$ cm$^2$/W. The mean value for the ratio is $(9.7 \pm 0.6) \times 10^8$ cm$^2$/W.

![Figure 4.9](image.png)

Figure 4.9: Histogram of $\sigma/\sigma^{(2)}$ values calculated from Rb-Xe laser excitation spectra.

Figure 4.10 shows the calculated absorption cross section for the Rb-Xe blue satellite. This curve was calculated by dividing the absorption coefficient for Rb-Xe at $T=473$ K by the fraction of [Rb] represented by the integrated area under the Hertz nearest neighbor...
distribution (where \( n = \text{[Xe]} = 1.6 \times 10^{19} \text{ cm}^{-3} \)) from 0 to 10 Å. According to this figure, the absorption cross section for Rb-Xe at the peak of the blue satellite is \( 5.4 \times 10^{-16} \text{ cm}^2 \). Using this deduced absorption cross section at the peak of the blue satellite and the cross section ratio calculated from this work, the two-photon cross section for the \( 5S \rightarrow 7S \) transition of Rb is estimated to be \( 5.6 \times 10^{-25} \text{ cm}^4 / \text{W} \). Using the procedure of Chapter 3 to refine the interaction potentials for Rb-Xe and thus more accurately define the range of internuclear separation over which Rb-Xe blue satellite absorption occurs would allow for an improved calculation of the absorption cross section for Rb-Xe by more precisely defining appropriate limits of integration for the nearest neighbor distribution. Nevertheless, to the author’s knowledge, this result is the first published attempt to measure the two-photon cross section for the \( 5S \rightarrow 7S \) transition of Rb. Furthermore, this experiment is yet another example of the use of an alkali–rare gas laser as a platform for studying atom-atom interactions and physics of the gain medium.
Figure 4.10: Absorption cross section for the Rb-Xe blue satellite versus wavelength. This was measured at 473 K ([Rb]=9.2×10^{14} cm^{-3}) with [Xe]=1.6×10^{19} cm^{-3}. The cross section was calculated by dividing the absorption coefficient by the Rb number density weighed by the Hertz nearest-neighbor distribution integrated from 0 to 10 Å, where n was assumed to be equal to [Xe].
CHAPTER 5
CONCLUSION

The experiments described in this dissertation demonstrate some of the power of alkali–rare gas laser systems for fundamental study and for practical use. Chapter 2 showed that, because the energy defect between the two upper states can be continuously tuned by changing the pump wavelength for the system, these systems are unique platforms for the study of fundamental laser physics. The behavior of the Cs-Ar laser system as it was tuned from 4 to 2 levels revealed a critical value for the energy separation of the two excited states in a three-level laser of $0.7 \times kT$, below which the laser output rapidly collapses. This signifies the fact that the two upper states are so appreciably mixed when the energy difference between them is reduced to this critical value that as the energy difference between them decreases past this value, the laser transforms into a two-level system. The behavior of the sodium-xenon laser was interpreted in light of this experiment. Because the energy difference between the 3P states of sodium is only $17 \text{ cm}^{-1}$, which was $\sim 0.05 \times kT$ for the Na-Xe gas mixture constituting the gain medium for the Na-Xe laser, these two states were so thermally mixed that the sodium laser emitted simultaneously on both the D$_1$ and D$_2$ lines of sodium ($3p \ ^2\text{P}_{1/2} \rightarrow 3s \ ^2\text{S}_{1/2}$ and $3p \ ^2\text{P}_{1/2} \rightarrow 3s \ ^2\text{S}_{1/2}$, respectively). The spectroscopic investigation of Chapter 3 produced a simulated absorption spectrum exhibiting greater agreement with experimental data than has been achieved in the past. This implies that the *ab initio* Cs-Ar interaction potential curves of Blank *et al.* [70] which were modified as a result of this work are more accurate than any of the Cs-Ar interaction potentials found in the literature which were calculated from first principles but which do not reproduce the precise spectral position of the Cs D$_2$ blue satellite peak. These modified interaction potentials can be used to make more accurate predictions of the behavior of ground-state and excited Cs-Ar pairs than have been achievable in the past. Also, further study of the gain media of these lasers can be
performed by investigating the behavior of the laser systems themselves, as the experiments of Chapter 4 demonstrate. These experiments make use of the non-linear sensitivity of the laser output to relatively small fluctuations in absorption strength of the alkali–rare gas mixture to study optical properties of the alkali species in the gain medium.

It is unclear at present whether this class of lasers will be found worthy of commercialization or of further development as a high-power directed energy weapon. But, whatever the commercial fate of alkali–rare gas photodissociation lasers, these systems provide unique experimental opportunities for studying laser physics and atom-atom interactions.
REFERENCES


