Optical Synthesis and Ultracold Reactions of Triplet $^6$Li Molecules

by

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**Optical Synthesis and Ultracold Reactions of Triplet $^6$Li Molecules**

submitted by Gene Polovy in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics.

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Abstract

In this thesis, we present the creation, via stimulated Raman adiabatic passage, and preliminary lifetime measurements of deeply bound triplet molecules of $^6\text{Li}_2$ in several rovibrational levels of the $a(^3\Sigma^+_u)$ molecular potential, including the lowest lying state in this potential. In addition to being the first experimental demonstration of the formation of these dimers, these results will serve as the basis for our ongoing efforts to reliably determine the rate constants responsible for the finite lifetimes of these ultracold molecules and may shed light on some of the mysteries surrounding the quantum state dependence of chemical reactions in the ultracold regime. Moreover, all of the tools - including a robust laser cooling system for $^6\text{Li}$, an ultra-low phase noise Raman laser system and various software recipes for the automation of data collection and analysis - and experimental techniques developed in this study can also be used for the creation of heteronuclear LiRb molecules. Unlike our $^6\text{Li}_2$ homonuclear molecules which only have a magnetic dipole moment, the LiRb polar molecules are predicted to also have a large electric dipole in the lowest lying triplet state. These characteristics combined with a three dimensional optical lattice would give us precise control over several degrees of freedom and enable us to perform quantum simulations of exotic condensed matter systems.

We also present the design and performance of a coherent source of Lyman-$\alpha$ radiation that was used by the ALPHA collaboration at CERN for laser cooling anti-hydrogen for the purpose of experimentally verifying the predictions of the standard model.
Lay Summary

In this thesis, we present the creation, using a specialized sequence of laser pulses, and preliminary lifetime measurements of Lithium-6 molecules that are 1,000,000 times colder than outer space, in several quantum configurations. In addition to being the first experimental demonstration of the formation of these molecules, these results will serve as the basis for our ongoing efforts to reliably determine metrics that quantify the longevity of these molecules and may shed light on some of the mysteries surrounding chemical reactions in the ultra-cold regime. Moreover, all of the instrumentation, software and experimental techniques developed in this study can also be used for the creation of ultracold Lithium-Rubidium molecules, which have several quantum properties that could be used for performing quantum simulations of exotic condensed matter systems.

We also present the design and performance of a laser system that was used by the ALPHA collaboration at CERN for experimentally verifying the predictions of the fundamental theories in particle physics that could help us to better understand the origin of the universe.
Preface

The majority of the research and development presented in this dissertation relates to the sequence of steps we took to create and determine the loss rate constants of deeply bound $^6$Li dimers in the triplet state. This work was carried out at the Quantum Degenerate Gases laboratory at the University of British Columbia, Point Grey Campus. The Lyman-$\alpha$ generation project was conducted in the laboratory of Professor Takamasa Momose at the same university.

Optical Synthesis and Ultracold Reactions of Triplet $^6$Li Molecules

The most impactful technical contributions I made to the creation of deeply bound $^6$Li dimers are listed below in chronological order:

1. In collaboration with Kahan Dare, I diagnosed and solved a technical problem that was causing our injection locked diode lasers to lose lock frequently and operate at half of their manufacturer specified optical power.

2. With Kirk W. Madison’s guidance, I completely re-designed and re-built the laser system used for laser cooling and imaging $^6$Li.

3. With Kirk W. Madison’s guidance and Julian Schmidt’s and Kahan Dare’s assistance, I designed and implemented of an ultra-low phase-noise Raman laser cooling system for the creation of deeply bound $^6$Li dimers.

4. I wrote an image processing program that uses principal component analysis (PCA) to significantly improve the signal-to-noise ratio (SNR) we can achieve at low atom numbers with absorption imaging.
5. I wrote a substantial amount of software in Python to analyze data, program various hardware devices and automate experimental sequences.

The most significant scientific contributions I made to the creation of deeply bound $^6$Li dimers are listed below in chronological order:

1. I implemented a time-efficient means of analyzing single-color, two-color, Autler-Townes and dark state spectroscopy data and collected a substantial portion of the data presented in chapter 6 of this thesis.

2. I identified and solved the problem that was preventing us from realizing stimulated Raman adiabatic passage (STIRAP) to deeply bound molecular states in the $a(^3\Sigma_u^+)$ molecular potential of $^6$Li and was the first person to ever observe evidence of STIRAP to one of these deeply bound states.\footnote{After making several tweaks to the experimental sequence (see chapter 7 for details) to get unambiguous and accurate measurements of the decay rate constants for the deeply bound $^6$Li molecules mentioned above and those for the remaining four vibrational levels, we plan to publish this work in a peer review journal.}

**VUV Coherent Source for Laser Cooling of Antihydrogen and Other Projects**

In addition to creating ultracold $^6$Li dimers (discussed above), I was involved in the following projects:

1. I played a crucial role in building a narrowband solid state VUV coherent source for laser cooling of antihydrogen, analyzed all of the data shown in [104] and wrote the manuscript for this paper.

2. I worked on a collaboration experiment whose intended purpose was to create RbH molecules from a cold beam of atomic Hydrogen and $^{85}$Rb atoms in magneto-optical trap (MOT) by photo-association. My contribution was building and maintaining every aspects of the MOT together with Thomas Prescott and later modifying the atomic beam portion of the apparatus in an effort to increase the flux.
3. To assist the pressure atom sensor (PAT) team at the QDG lab, I wrote a single channel scattering code capable of handling very large partial waves.

4. I worked with Will Gunton to design optically transparent electrodes capable of producing electric fields as high as 120 kV/cm in air without arcing. These results are published in [63].
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List of Abbreviations

AOM acousto-optic modulator
BCS Bardeen-Cooper-Schrieffer
BEC Bose-Einstein condensate
CODT crossed optical dipole trap
DDS direct digital synthesizer
DP double-pass
ECDL extended cavity diode laser
EDFA erbium-doped fiber amplifier
EIT electromagnetically induced transparency
FC Franck-Condon
FFC femto-second frequency comb
FR Feshbach resonance
HNLF highly non-linear fiber
LO local oscillator
MB Maxwell-Boltzmann
mBEC molecular Bose-Einstein condensate
MOT magneto-optical trap
ODT optical dipole trap
PA photo-association
PBS polarizing beam splitter
PM polarization maintaining
PZT piezo-electric transducer
List of Abbreviations

**REMPI** resonantly enhanced multi-photon ionization

**SA** saturated absorption

**SP** single-pass

**STIRAP** stimulated Raman adiabatic passage

**TA** tapered amplifier

**TF** Thomas-Fermi
Acknowledgements

First, I would like to thank Kirk W. Madison for the wealth of knowledge and skills he has directly or indirectly bestowed upon me throughout my graduate career. Aside from the basic theory I learned in my undergraduate physics classes and the (limited) experience I had with software development, I had virtually no practical skills when I started working at the Quantum Degenerate Gases (QDG) Lab. Kirk’s tutelage and several engineering classes allowed me to improve as a software developer and become a capable optical engineer, systems engineer and physicist - fully equipped for a career in either academia or industry. In addition to helping me develop technical expertise, Kirk facilitated my development as a leader and project manager by giving me the opportunity to train 13 students with a wide range of technical backgrounds and supervise the projects they undertook. Because of my keen interest in the business aspects of the lab, I have also had the chance to play a key advisory role in discussions concerning equipment purchases, hiring, project planning, strategy and risk management.

Second, I would like to acknowledge Mariusz Semczuk who started his PhD at the QDG lab just as I was finishing my undergraduate degree. Not only did he become a good friend, but he also introduced me to Kirk, encouraged me to join the lab and was one of the first people to train me in the early days of my graduate career. I am thankful for this and for the memories we shared outside of work, particularly those involving his prized leather jacket.

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Finally, I would like to thank my parents, Sergiy Polovy and Larysa Shymko, for the love, support and guidance they have given me throughout my life.
Chapter 1

Introduction

Recent technological breakthroughs in laser cooling have led to the birth and rapid expansion of ultracold atomic and molecular physics. When the thermal or de Broglie wavelength, \( \lambda_{dB} = \sqrt{2\pi \hbar^2 / mk_B T} \), of particles at ultracold temperatures \( T < 0.001 \text{ K} \) exceeds the inter-particle spacing, quantum mechanical effects can easily be observed \[91\]. Studies of the interactions between ultracold atoms have even led to the creation of completely new states of matter: Bose-Einstein condensation of atoms and molecules \[4, 19, 37, 57, 175\] and Bardeen-Cooper-Schrieffer (BCS) like pairs \[13, 21, 26, 64, 138\], which closely resemble their condensed matter counterparts. The natural next level of complexity was the (laser induced) creation - from atoms cooled by relatively well established techniques - and study of ultracold molecules\[2\]. Stimulated Raman Adiabatic Passage or STIRAP is a technique first conceived by Bergmann et al. \[12\] that relies on the creation and evolution of a coherent dark state. It has been the workhorse of high efficiency conversion of atoms to molecules in the ultracold community. Several groups have used this process to successfully create deeply bound homonuclear and heteronuclear Alkali molecules \[35, 36, 66, 87, 110, 114, 122, 148, 152, 165\].

In this dissertation, we focus primarily on the coherent population transfer via STIRAP of loosely bound ultracold Feshbach molecules of fermionic \(^6\text{Li}\) (created by evaporative cooling in an optical tweezer by methods similar to those described in \[80, 81, 116, 117, 119\]) to deeply bound molecular states in the in the \(a^{3\Sigma_u^+}\) molecular potential and study the chemical properties of these states. In doing so, we aspire to gain insights into the quantum state dependence of chemical reactions in the ultracold regime for these alkali dimers. As a bonus, to create these dimers, we also had to build most of the hardware and develop the

\[2\]Direct cooling of molecules is also an active research area. For more information about Zeeman and Stark decelerators, direct laser cooling of molecules see, for example, \[143, 156\].
human capital required for producing polar molecules of $^6\text{Li}^{85}\text{Rb}^{3}$ in bound states of the $a(3\Sigma_u^+)$ molecular potential - a longer term goal that is outside the scope of this dissertation.

Unlike our $^6\text{Li}_2$ triplet molecules which have a magnetic dipole moment due to their non-zero spin, but no permanent electric dipole moment, triplet $^6\text{Li}^{85}\text{Rb}$ molecules would have both a 0.37 Debye [155] electric dipole moment (which is comparable to that of $\text{KRb}$ molecules in their absolute ground state [114, 115]) and a magnetic dipole moment. Placing these (chemically unstable) polar molecules in a 3-dimensional optical lattice would enable us to study lattice-spin models and simulate exotic condensed matter phenomena by creating systems with equivalent Hamiltonians while maintaining a level of control over the system that is unavailable in more conventional condensed matter experiments [106].

In the chapters that follow, we place emphasis on the following topics: the design and construction of a robust laser cooling system for $^6\text{Li}$ atoms and a low phase-noise Raman laser system for quantum state manipulation, the search for and characterization of the desired quantum states for coherent population transfer using single-color and two-color molecular spectroscopy, our implementation and optimization of STIRAP for population transfer to deeply bound states in the $a(3\Sigma_u^+)$ molecular potential and measurements of the lifetimes of these molecules. Although the last topic is an ongoing project, the preliminary measurements demonstrated here will prove to be instrumental for the determination of decay rates and for understanding the underlying quantum chemical reaction mechanisms.

In addition to using laser cooling techniques for the creation of ultra-cold $^6\text{Li}$ dimers, we also discuss the application of the same technology to even more fundamental problems in realm of particle physics. We focus on the design and construction of a narrowband solid state vacuum ultra-violet (VUV) coherent source for laser cooling magnetically trapped antihydrogen at CERN [3, 104]. As we show in chapter 8, this pulsed VUV source was constructed from an injection seeded Ti:Sapphire based unstable resonator and two non-linear stages - second harmonic generation in a BBO crystal followed by third harmonic generation in a mixture of Krypton and Argon gas. After we built this laser at UBC, it was transported to CERN and used by the ALPHA collaboration to cool antihydrogen and establish new

---

3 Although we do not discuss the laser cooling and trapping $^{85}\text{Rb}$ and $^{87}\text{Rb}$ in this thesis because this topic is irrelevant to its central theme, our laser cooling apparatus is fully equipped for working with these species as well as $^6\text{Li}$. 
Chapter 1. Introduction

frontiers in the search for violations of charge conjugation, parity transformation, and time reversal (CPT) symmetries as part of an ongoing validation effort for the standard model [3].
Chapter 2

Laser Cooling Apparatus

In this chapter, our objective is to acquaint the reader with the operation of the laser cooling apparatus and several measurement techniques. We place strong emphasis on the details that have not been published elsewhere and those that are most relevant to the second half of this dissertation.

To provide a roadmap for the reader before diving into the details, we show a simplified timing sequence for collecting a single data point in typical experiment in Figure 2.1. (Every measurement is destructive, so we are forced to repeat this sequence for every data point.) First, we load atoms into a magneto-optical trap (MOT) in about 5 seconds. Second, we change several experimental parameters to compress the MOT and cool the atoms to about 500 $\mu$K. This step takes about 5 ms. Third, we transfer the atoms to another kind of trap called an optical dipole trap (ODT), which confines the atoms via a conservative force created by a focused high power laser beam, which is detuned by about 400 nm from the nearest atomic resonance. Fourth, we use a technique called evaporative cooling to further cool the atoms. The length of this step ranges from about 10 ms to several seconds and we can reach ensemble temperatures below 100 nK. Fifth, we execute the “science” step, where we manipulate the atoms in some way. For example, this could be photo-association spectroscopy or the creation of deeply bound molecules via stimulated Raman adiabatic passage (STIRAP). Finally, we use resonant light to take an absorption image of the atom cloud for the purpose of extracting the atom number or the spatial distribution of the cloud\(^4\). Depending on the experiment, the length of the entire sequence varies from about 10 s to 30 s. The steps described in the sequence above are programmed into python.

\(^4\)We also have the ability to take fluorescence images of the atomic cloud. Although this technique was used for optimizing the atom number in the MOT on numerous occasions, it was not used to collect any of the data presented in this dissertation, so we make no further mention of it. For more information, see we refer the reader to [17, 63, 139, 157].
2.1 Fine and Hyperfine Structure of $^6\text{Li}$

Figure 2.1: The timing sequence executed to collect a single data point. It takes about 5 s to load the MOT, 5 ms to compress and cool it and transfer the atoms to the ODT, 0-10 seconds (depending on the desired final temperature) to further cool the atoms using evaporative cooling in the ODT, 0-30 seconds to manipulate the atoms, and 1-10 seconds to image and grab data from several measurement devices.

2.1 Fine and Hyperfine Structure of $^6\text{Li}$

Lithium-6 is an alkali metal with the following electron configuration: $1s^22s^12p^0$. Thus, it has two electrons in its first $s$ orbital, where the principal quantum number $n = 1$, and one electron in its second $s$ orbital where $n = 2$. Like Hydrogen, it has a single valence electron and is therefore termed a *hydrogenic*. Due to coupling between the orbital $l$ and

---

5This is a reference to the University of Texas in Austin, where it was developed.
spin $s$ degrees of freedom, which gives rise to an $l \cdot s$ term in the Hamiltonian, we get the fine structure splitting of 10.056 GHz for the first electronically excited state. Because of this coupling, $l$ and $s$ are no longer good quantum numbers, so we define the total angular momentum as $j = l + s$ and label the fine structure states using term symbols:

$$2s+1_l^j$$

where $s = 1/2$ (for all of the alkalis), $l$ is the orbital angular momentum and $j$ varies from $|l + s|$ to $|l - s|$ in integer steps. For example, the ground state has $l = 0$ (s-orbital) and $j = s = 1/2$, so its term symbol is $2S_{1/2}$. The first excited state splits into the $2P_{1/2}$ and $2P_{3/2}$ states because $l = 1$ (p-orbital) and $j = 1/2$ or $3/2$. These states and the fine structure splitting are shown in Figure 2.2. The associated spectroscopic lines are called the D$_1$ and D$_2$ lines. Similar to the $l \cdot s$ coupling, the total angular momentum $j$ couples to the nuclear spin $i$, which gives rise to a $j \cdot i$ term in the Hamiltonian and results in the hyperfine splitting of the $j$-levels. Again, we define a new quantum number $f = j + i$. Analogously to $j$, $f$ can range from $|j + i|$ to $|j - i|$ in integer steps. The hyperfine splittings between the $f$-levels are also shown in Figure 2.2. For a discussion of the physical origin of this term, see, for example, [53, 60, 131]. In addition, the hyperfine constants and other properties of $^6$Li can be found in [6, 55, 159].

2.2 Laser Cooling and Magneto-Optical Traps

2.2.1 Simple Description of Laser Cooling

In Figure 2.3, we show an alkali atom (e.g. $^6$Li) in its ground state with some velocity $v$. Suppose we launch a photon of frequency $\nu$ at the atom. In the atom’s frame of reference, this photon’s frequency will be Doppler shifted either to the red (lower frequency) or to the blue (higher frequency) depending on the direction of travel of the atom. If the shifted frequency $\nu'$ of the photon is near resonant with the transition from the atom’s ground state to its first excited state, the atom has some probability of absorbing it. After absorbing a photon, the atom gets a momentum kick in the direction of propagation of the incident
2.2. Laser Cooling and Magneto-Optical Traps

Figure 2.2: Fine and hyperfine structure of $^6$Li. The level splittings were retrieved from [55]. For the remainder of this dissertation, the D$_2$ transitions will be most relevant. The D$_1$ transitions will be mentioned later in this chapter in the context of sub-Doppler cooling of $^6$Li - an upgrade that is still in progress.

The atom then re-emits a photon in a random direction by spontaneous emission. While any individual re-emission event leads to a net change in the momentum, the momentum change due to spontaneous emission is zero on average because the re-
emission direction is random. If we now add a second counter-propagating beam, the atom will be subjected to a net radiation pressure force that opposes motion along one axis and is proportional to $v$. For a more detailed description of laser cooling and its limitations, see [29, 102, 124].

![Figure 2.3: Cartoon picture of laser cooling. An incident photon from a laser beam is absorbed by an atom in its ground state and re-emitted in a random direction by spontaneous emission. The net change in the momentum of the atom is in the direction of the incident photon.](image)

### 2.2.2 Vacuum System and Zeeman Slower

In addition to the hardware we need to implement laser cooling and trapping of $^6\text{Li}$ in a MOT, we also need an ultra-high vacuum and source of $^6\text{Li}$ atoms. The former is shown in Figure 2.4. The vacuum is maintained by means of two ion pumps and one non-evaporative getter (NEG) pump and is on the order of $1 \times 10^{-10}$ Torr on the left hand side of the chamber (the “science” side). By heating a solid chunk of Lithium, we generate a hot flux of gaseous Lithium atoms that pass through a differential pumping stage made up of microtubes. These tubes collimate the atomic beam for the purpose of preventing the majority of (untrappable) Lithium atoms from reaching the “science” side (left hand side) of the chamber and unnecessarily contaminating the vacuum. If we simply allowed this atomic beam to propagate into the region with the glass cell where we trap the atoms, we would
only be able to trap a very small portion of the atoms emitted, those moving very slowly at the tail end of the Maxwell-Boltzmann (MB) distribution. For this reason, we need to begin cooling the atoms with a counter-propagating slowing beam before they enter the trapping region. While it is straight-forward to slow a single velocity class with a single frequency laser source in the manner we described above, targeting many velocity classes simultaneously requires additional hardware. We do this by means of a Zeeman slower - a concept first devised by William Phillips et al. [102, 125]. The idea is to generate a magnetic field, which varies along the axis of propagation of the atomic beam, that shifts the energy levels of the atoms (via the Zeeman effect) in a way that makes a single frequency laser source near resonant with a broad distribution of velocities throughout their journey through the chamber. At the entrance to the Zeeman slower, the magnetic field is such that the atoms at the highest velocity class are resonant and are slowed enough that they join atoms in another velocity class just below the first. These atoms then enter the next spatial region where the field is slightly lower and all the atoms in this slightly lower velocity class are slowed. This process continues in space and time as the atoms propagate down the slower until all of the atoms from the initial high velocity class down to some low velocity class are swept down together to a velocity just below the lowest velocity class addressed, chosen to be below the capture velocity of the MOT.

We have only provided a cursory overview of this system because the design and characterization of the vacuum chamber and Zeeman slower are well documented in [16, 17]. Since Zeeman slowers are the backbone of the majority of laser cooling experiments, the theory and implementation of a wide variety of Zeeman slower designs are covered extensively in the literature (e.g. [63, 102, 124, 125]).

### 2.2.3 Magneto-Optical Trap

The elements we have described so far do not constitute a trap. Rather, they are a means of slowing the atoms in one direction and do not spatially localize them. To create a MOT, we apply very similar concepts to those described above, but in a slightly different way. Two new ingredients are needed: cooling from all directions and a means of applying a stronger force in the direction of the trap center when the atoms move away from this
2.2. Laser Cooling and Magneto-Optical Traps

Figure 2.4: The design of the vacuum chamber showing the two ion pumps, NEG pump, Zeeman slower coils, MOT coils, the Lithium oven, glass cell and the slowing beam. The red circle in the middle of the glass cell is meant to indicate the location where the $^6\text{Li}$ MOT is formed. This figure was retrieved from [63].

location. The former requirement is fulfilled through the use of three pairs red detuned laser beams that intersect at the geometric center for the trap. These six beams and the atom cloud are shown in Figure 2.5. To satisfy the second requirement, we add spatially varying magnetic field that is zero at the center of the trap and increases away from the center. (Experimentally, this field profile is obtained by running current through the MOT coils in the anti-Helmholtz configuration.) If an atom moves away from the trap center, where the magnetic field is zero, its energy levels shift in a state dependent way due to the Zeeman effect such that the laser beam opposing its displacement from the trap center (with a particular circular polarization) is closer to a transition resonance in the atom than the oppositely propagating beam (with the same circular polarization but traveling in the opposite direction). As a result, the radiation pressure due to photon scattering from this beam is larger than the opposing beam, and the atoms is pushed back to the center of the trap. For a deeper discussion of the theoretical framework behind the operation of MOTs, we refer the reader to [30, 53, 101].

So far, we have been implicitly making two assumptions: that the laser intensity is well below the saturation intensity (so that stimulated processes can be ignored) and that the transition is closed. The former is easily achieved by making the MOT beams large and
setting the laser powers appropriately. However, the second assumption is false when a single frequency laser source is employed. For a $^6$Li MOT operating on the D$_2$ line, a closed transition does not exist because an excited state atom can decay to either the $f = 1/2$ state or the $f = 3/2$ state (see Figure 2.2) at low magnetic fields. To get around this problem, we need to use two laser frequencies, which are often referred to as the pump and re-pump, separated by the hyperfine splitting of the ground state (228.2 MHz). The re-pump field re-excites atoms that fall into the $f = 3/2$ state, which would otherwise remain dark with respect to the pump light, ensuring the continuation of the absorption and re-emission cycle we need for efficient laser cooling. Due to the rapid depletion rate of the ground $f = 3/2$ state in $^6$Li, which is a consequence of the very small splitting between the $f$-levels of the $^2P_{3/2}$ state, the re-pump intensity must be comparable to the pump intensity.

2.3 Lithium Laser System

While the addition of a Zeeman slower significantly improved the MOT loading rate and the vacuum relative to what we had prior to the upgrade described in [17], the stability of the system degraded and the need for maintenance on a daily basis rose dramatically. This happened both due to elevated complexity of the system and because of aging equipment. Hence, we designed and built a new system with emphasis placed on long-term stability and modularity. These characteristics were achieved by limiting the lengths of free space regions and de-coupling them through extensive use of fiber interconnects. In the subsections that follow, we describe the design and performance of the system in 2.3.1 and briefly mention a sub-Doppler cooling mechanism that relies on the D$_1$ transition and what we hope to gain by implementing it.

2.3.1 $^6$Li Laser System Design

It is natural to divide the laser system into three parts based on their respective roles and physical locations:

1. Laser sources and initial amplification stage.

\footnotesize \textsuperscript{6}Due to budgetary constraints, we were unable to immediately replace our rapidly deteriorating tapered amplifiers and were forced to compensate for their poor performance with daily maintenance efforts.
Figure 2.5: A sketch of the three pairs of counter-propagating MOT beams and the atomic cloud. In our setup, three of the six beams are retro-reflected versions of their counterparts.

2. Frequency shifting and second amplification stage.

3. Widely tunable optical circuit for imaging $^6\text{Li}$ at high magnetic fields

We discuss each of them in detail below.

**Laser Sources and Initial Amplification Stages**

The setup implemented on our *master* table is shown in Figure 2.6. It consists of two TOPTICA DL Pro external cavity diode lasers (ECDLs) and the associated frequency
stabilization schemes, two injection locked slave lasers (SLs) and two frequency shifting stages.

The D₂ master is locked +50 MHz above the D₂ pump transition \((f = 3/2 \rightarrow f' = 5/2)\). The error signal is generated by demodulating - via lock-in detection - a sinusoidally dithered saturated absorption (SA) spectroscopy signal. A details of the optical layout, locking electronics and the construction of the Lithium heat-pipe used for the Doppler free spectroscopy can be found in [86, 139, 146, 157].

Since the D₁ transition is only \(\approx 10 \text{ GHz} \) away from the D₂ transition (see Figure 2.2), we generate and detect with the inexpensive HFD6180-421 package - which includes a GaAs PIN photodiode and a transimpedance amplifier (TIA) - a heterodyne beat note between the D₁ and D₂ master lasers. With a direct digital synthesizer (DDS), locked to the Menlo Systems GPS-8 10 MHz reference, followed by a chain of non-linear conversion stages and amplifiers serving as a local oscillator (LO), this beat note is then mixed down to \(\approx 400 \text{ MHz} \) and directed to a home-built phase-frequency-discriminator (PFD), which outputs a signal proportional to the phase error. With this as the error signal, we phase lock the D₁ master to the D₂ master by feeding back on the laser diode current and the PZT attached to the grating in the D₁ ECDL via the TOPTICA Digilock 110, an FPGA based loop filter. We discuss the concept of phase locking in greater detail in chapter 3 in the context of our spectroscopy system. The linewidths of the beat-note is approximately 500 kHz, so the linewidth of each laser must be below this value. We do not seek to better quantify the performance of each laser because the upper bound of 500 kHz would be more than adequate performance for this application.

The remainder of the light from the D₂ master is used for injection locking slave lasers S₁ and S₃. (The latter is used to generate light for imaging at high magnetic fields and will be discussed in greater detail in the paragraphs below.) Similarly, the D₁ master injects slave laser S₂. The outputs of S₁ and S₂ pass through acousto-optic modulars (AOMs) that each shift the frequency of the incident light by +108 MHz and can be switched on and off independently. The former is required for generating the correct laser frequencies for the D₂ magneto-optic-trap (MOT) and the latter is required for quickly (in a few microseconds) switching between the D₁ and D₂ light for the output of this stage and therefore also the
2.3. Lithium Laser System

subsequent stage. The outputs of the AOMs are then combined on a polarizing beam splitter (PBS). Next, we pass an equal proportion of the two beams through an optical isolator (resulting in a loss of 50% per beam) and couple the combined light into a polarization maintaining (PM) fiber which goes to the amplifier system, where, in addition to amplification, we shift the frequencies again with AOMs to generate the pump and re-pump light for the MOT and for absorption imaging at low magnetic fields.

Figure 2.6: Master table layout. The abbreviations $\lambda/2$, PBS, $S_i$, SP, PD and OI refer to a half-wave plate, polarizing beam splitter, injection locked slave laser $i$, single pass AOM, photo-detector and optical isolator, respectively. While we do not show this explicitly in the figure, this system has one OI placed after every master laser and injection locked slave laser to prevent unwanted reflections from disturbing or damaging the laser diodes. The OI directly before the fiber to TA$_0$ serves two purposes: to combine the D$_1$ and D$_2$ light and to provide an additional 30 dB of protection for $S_1$ and $S_2$ against the back propagating light from TA$_0$.

Frequency Shifting and Second Amplification Stage

Shown in Figure 2.7 (a), this stage receives seeding light ($\approx$ 27 mW) for a home-built tapered amplifier (based on the Eagleyard EYP-TPA-0670-00500-2003-CMT02-0000 chip),
2.3. Lithium Laser System

TA₀, from the appropriately labelled output of the previous stage. Next, the fiber-coupled output of TA₀ is divided into the pump and re-pump paths and used to seed two TOP-TICA BoosTAs. (The astute reader may have noticed that the single-pass AOM shifts the frequency of the re-pump path back to +50 MHz and initiatively conclude that the two single-pass AOMs in the previous stage are superfluous. While this would be true if our objective was only to generate D₂ light, these additional AOMs are necessary for the purpose of quickly switching between D₁ and D₂ light for the sub-Doppler cooling procedure we aim to implement.) Finally, the double-pass (DP) AOMs [98] (IntraAction ATD-1001A1 and ATD-801A1) allow us to achieve detunings anywhere from -70 MHz to 0 MHz with respect for the pump and re-pump D₂ transitions. For the D₁ light (which will be tuned blue of the pump and re-pump resonances), we have the same frequency scanning range and have the freedom to choose the optimal laser frequency for seeding TA₀. (The latter is achieved simply by changing the frequency of the RF reference used for the PFD.) When we initially built this part of the system, TA₁ and TA₂ were outputting 250 mW and 220 mW respectively, and the power out of the fibers labelled ”MOT Pump” and ”MOT Re-Pump” were 135 mW and 90 mW.[7]

Widely Tunable Optical Circuit for Imaging ⁶Li at High Magnetic Fields

The energy eigenvalues of ⁶Li for the hyperfine manifolds of the ²S₁/₂ and ²P₃/₂ levels are shown as a function of the magnetic field in Figure 2.8. These eigenvalues were calculated using the mathematica script included in [56]. For all of the photo-association experiments discussed in this dissertation, we operate at high fields where the good quantum numbers are mj and mi. Specifically, we populate the two lowest energy levels: |1⟩ = |1, −1/₂⟩ and |2⟩ = |0, −1/₂⟩. To image states |1⟩ and |2⟩ using absorption imaging (more on this below), we must produce laser frequencies that couple them to the |1, −3/₂⟩ and |0, −3/₂⟩ levels (Δmi = 0), respectively, in the ²P₃/₂ manifold. (In Figure 2.8 the splittings between the three mj = −3/₂ levels are not visible because are very small.) Unlike imaging close to 0 G,

[7] Since then, the power has dropped signaling the imminent failure of the chips and the need for replacements. Due to the moderate power requirements of our D₂ MOT, this has yet to have an impact on the number of atoms we can load into the optical dipole trap and therefore inconsequential for all of the measurements discussed in this thesis. However, much higher intensities are required for D₁ cooling, so the chips will need to be replaced before we can add this capability to our experimental sequence.
2.3. Lithium Laser System

![Diagram of lithium laser system]

Figure 2.7: Amplification of cooling light (a) and generation of high-field imaging light (b). The abbreviations $\lambda/2$, PBS, S$_i$, TA$_j$, SP, DP and OI refer to a half-wave plate, polarizing beam splitter, injection locked slave laser $i$, tapered amplifier $j$, single pass AOM, double pass AOM and optical isolator, respectively. While we do not show this explicitly in the figure, this system has one OI placed after every injection locked slave laser and tapered amplifier to prevent unwanted reflections from disturbing or damaging the laser diodes and TA chips, respectively.

A re-pump beam is not required at high magnetic fields because these transitions are closed [63]. To implement this system, we simply inject another SL, S$_3$, with light directly out of the D$_2$ master (+50 MHz), and shift its frequency three times with AOMs. The layout is shown in Figure 2.7 (b). The advantages of this design are listed below:

1. An additional ECDL (or similar laser) and the associated locking electronics are not required.

2. We can easily switch which state we would like to image every time we run the experimental sequence.
3. The wide scanning range of two cascaded DPs (IntraAction IntraAction ATD-2001A1) allows us to image the atoms over a $\approx 300$ G range of magnetic fields or, equivalently, from -750 MHz to -1150 MHz with respect to the zero-field pump transition frequency. (The AOMs used for this setup are deflectors from IntraAction with a center frequency of 200 MHz.)

4. A mechanical shutter is not required because we drive both DPs with the same RF source and have well under a nanowatt of leakage light when the RF is switched off. The only disadvantage is being unable (without adding another AOM) to extend the tuning range further. So far, there has not been a reason for doing so. Finally, a small fraction of the unshifted light from $S_3$ is coupled into the fiber that injects the last SL, $S_4$, used to generate light for the Zeeman slower. The frequency of the light out of $S_4$ is shifted by -126 MHz via a DP. The remainder of optical layout required for producing a $^6$Li MOT is quite standard and has remained unchanged. We invite the reader to explore the details presented in [16, 17, 63].

2.3.2 Gray Molasses Cooling

Many Alkali metals can be cooled to sub-Doppler temperatures via the Sisyphus effect [24, 32, 125, 132] before they are transferred into an ODT and cooled further via evaporative cooling. This makes it much easier to produce degenerate quantum gases of these species while retaining a large number of atoms. Due to the unresolved hyperfine structure of the $^2P_{3/2}$ manifold, we cannot take advantage of this cooling mechanism for $^6$Li. However, several groups have implemented a gray molasses cooling stage that relies on the $D_1$ transition and leads to similar results [22, 50, 51, 59, 133, 144]. By virtue of gray molasses cooling, these groups were able to load more than ten million atoms into their ODTs while we sometimes struggle to load two million atoms. It is for this reason that we purchased a second ECDL and implemented the frequency switching scheme described above. After replacing our dying TA chips, we hope to also take advantage of the five-fold increase in the signal to noise ratio (SNR) we would gain by seamlessly adding gray molasses cooling to our toolbox.
2.4 Optical Dipole Trap

In our discussion of laser cooling and MOTs, we were concerned with the dissipative force associated with atoms scattering near resonant photons. Since this is the dominant effect in the regime where the field intensity is low and the detuning is small, we ignored a second conservative force that is dominant in the opposite extreme - where the field intensity is high and the detuning is very large. In this section, we will do the opposite by ignoring the dissipative force and concentrating on the conservative force. Specifically, we will demonstrate that high intensity far detuned lasers can be used used to create optical dipole traps or optical tweezers that enable us trap atoms and cool them to sub-µK temperatures.

Figure 2.8: Energy eigenstates of the $^2S_{1/2}$ (a) and $^2P_{3/2}$ (b) levels in $^6$Li as a function of magnetic field. For imaging at high magnetic fields, we rely on transitions from the lowest two $^2S_{1/2}$ levels with $m_j = -1/2$ to the $m_j = -3/2$ levels with the same $m_i$ values in the $^2P_{3/2}$ manifold. At high fields, these transitions are closed and no re-pumping laser is required.
2.4. Optical Dipole Trap

2.4.1 Basic Theory

The interaction Hamiltonian for a two-level system interacting with an electric field is given by

\[ \hat{H}_I = -\mu \cdot E(r) \]  

(2.2)

where \( \mu \) is the dipole moment operator and \( E(r) \) is the electric field. For a very large negative (or red) detuning, \( \Delta \), from the resonance frequency, \( \omega_0 \), it can be shown that the ground state \( |g\rangle \) shifts down while the excited state \( |e\rangle \) shifts up in energy [61, 63, 157].

These intensity dependent energy shifts or ac Stark shifts are given by

\[ \Delta E_e = \frac{3\pi c^2}{2\omega_0^3} \left( \frac{\Gamma}{\Delta} \right) I \]  

(2.3)

\[ \Delta E_g = -\frac{3\pi c^2}{2\omega_0^3} \left( \frac{\Gamma}{\Delta} \right) I \]  

(2.4)

where \( \Gamma \) is the natural linewidth of the transition [61]:

\[ \Gamma = \frac{\omega_0^3}{3\pi\epsilon_0\hbar c^3} |\langle e|\mu|g\rangle|^2 \]  

(2.5)

For a Gaussian beam incident on the atoms, the resulting ground state potential is given by

\[ U_{\text{dip}}(r) = \frac{3\pi c^2}{2\omega_0^3} \left( \frac{\Gamma}{\Delta} \right) I(r) \]  

(2.6)

where

\[ I(r) = I(r, z) = \frac{2P}{\pi W^2(z)} \exp \left( -\frac{2r^2}{W^2(z)} \right) \]  

(2.7)

In equation (2.7) \( P \) is the optical power and \( W(z) \) is the beam waist given by

\[ W(z) = W_0 \sqrt{1 + \left( \frac{z}{z_0} \right)^2} \]  

(2.8)

where \( W_0 \) is the minimum beam waist and \( z_0 = W_0^2 \pi/\lambda \) is the Rayleigh length [147].

The gradient of this potential, \( F_{\text{dip}} = -\nabla U_{\text{dip}}(r) \), is a dipole force that pushes atoms to the
2.4. Optical Dipole Trap

region of highest intensity thereby creating an optical dipole trap. Since this trap is almost harmonic near its center and the atoms coalesce in the region where \( z \ll z_0 \) and \( r \ll W_0 \), we gain several experimentally relevant insights by Taylor expanding Equation 2.6 around \((r, z) = (0, 0)\) and equating the resulting expression to that of an ideal harmonic trapping potential:

\[
U(r, z) \approx U_0 \left( 1 - \frac{2r^2}{W_0^2} - \frac{z^2}{2z_0^2} \right) = U_0 + \frac{1}{2} m \omega_r^2 r^2 + \frac{1}{2} m \omega_z^2 z^2
\]  

(2.9)

where the trap depth \( U_0 \) is the trapping potential at \((r, z) = (0, 0)\) and \( \omega_r \) and \( \omega_z \) are the trapping frequencies along the radial and axial directions, respectively. By equating powers of \( r \) and \( z \), we get the following expressions for \( \omega_r \) and \( \omega_z \):

\[
\omega_r = \frac{2}{W_0} \sqrt{\frac{|U_0|}{m}}
\]  

(2.10)

\[
\omega_z = \frac{1}{z_0} \sqrt{\frac{|U_0|}{m}}
\]  

(2.11)

Finally, it is important to briefly mention that the dissipative force we have ignored so far in this section is responsible for heating in the trap. In the limit where \( \Delta \gg \Gamma \), the photon scattering rate is given by

\[
\Gamma_{sc} = \frac{1}{\hbar} \left( \frac{\Gamma}{\Delta} \right) U_{dip}
\]  

(2.12)

Above, we assumed that scattering losses are negligible for very large detunings because \( \Gamma_{sc} \propto 1/\Delta^2 \) while \( U_{dip} \propto 1/\Delta \). To quantitatively confirm the validity of this assumption in the context of our \(^6\text{Li} \) ODT, we can compute the scattering rate as a function of trapping power using the \(^6\text{Li} \) D-line data from [55] and the results of our beam waist measurements (see appendix A). For the \(^6\text{Li} \) D lines, \( \Gamma/2\pi = 5.9 \) MHz and \( \omega_0/2\pi = 446.8 \) THz. The detunings and beam waists for our SP-100C-0013 SPI fiber laser (100 W, 1090 nm center frequency, 2 nm optical bandwidth and randomly polarized) and YLR-20- 1064-LP-SF IPG fiber laser (15 W, 1064 nm, single frequency and linearly polarized) are shown in the table below:
2.4. Optical Dipole Trap

Plugging these values into Eq. 2.12 yields \( \Gamma_{sc}^{\text{SPI}} = (0.085 \text{ s}^{-1} \text{W}^{-1})P \) and \( \Gamma_{sc}^{\text{IPG}} = (0.041 \text{ s}^{-1} \text{W}^{-1})P \), where \( P \) is the trapping power in watts. These calculations show that the scattering rate is small on the time scale of a typical experiment (several seconds), even at a trapping power of 100 W. However, since each scattering event heats the atoms by one photon recoil energy and we need to bring the atomic cloud to a much lower temperature in most experiments, we typically do the “science” step at low trapping powers.

2.4.2 Experimental Realization

A careful inspection of equations 2.10 and 2.11 reveals that \( \omega_r \gg \omega_z \) because \( z_0 \gg W_0 \). This implies a much weaker confinement in the axial direction than the radial direction. To achieve strong confinement in all directions, we use a crossed optical dipole trap (CODT) with a crossing angle of \( \alpha \) of 20 degrees. (For details concerning how this angle was chosen, see [63, 139].) A simplified schematic of this layout is shown in Figure 2.9 and applies to both of our two trapping lasers\(^8\), which are overlapped spatially via a dichroic mirror (not shown) and propagate collinearly through this network of mirrors and lenses. Each trapping laser is focused onto the compressed and cooled MOT (the vacuum chamber is omitted for simplicity) with a 250 mm lens, re-collimated with another 250 mm lens and then focused a second time on the MOT to increase the trap depth and to produce tighter confinement in the axial direction. We control the intensity incident on the atoms via an analog input and a calibrated external AOM (Gooch and Housego 97-01672-11) for the 100 W SPI laser. For the second 15 W IPG laser, we rely exclusively on a second calibrated external AOM (same model). As we show in appendix B, this arrangement results in \( \omega_y \approx \omega_x \) and \( \omega_z \approx 0.15 \omega_x \). Relative to a single arm trap, the increase in confinement is about 20 times for the z-direction and the drop in confinement for in the x-direction is < 2% [63] relative to

<table>
<thead>
<tr>
<th>Trapping Laser</th>
<th>( W_0 ) (( \mu \text{m} ))</th>
<th>( \Delta/2\pi ) (THz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPI</td>
<td>40</td>
<td>-171.76</td>
</tr>
<tr>
<td>IPG</td>
<td>58</td>
<td>-165.04</td>
</tr>
</tbody>
</table>

\(^8\)For trapping \(^6\)Li, our 100 W SPI laser would be sufficient. The IPG laser is only required for trapping Rb because trapping in the SPI results in loss of Rb due to multi-photon processes. We mention it here because the ability to trap using a laser with a different wavelength is advantageous for the verification of lifetimes of deeply \(^6\)Li\(^2\) molecules.
2.4. Optical Dipole Trap

what it would be for $\alpha = 0$ degrees. Finally, we also show a photo-association (PA) beam that originates from our spectroscopy system and is overlapped by means of a dichroic with the second arm of the CODT. We will explore the origin of this beam in chapter 3 and its purpose in the second half of this dissertation.

![Simplified schematic of our crossed optical dipole trap.](image)

**Figure 2.9:** Simplified schematic of our crossed optical dipole trap. The first arm is focused onto the MOT with a 250 mm focal length lens. The second (re-cycled) arm is first re-collimated with another 250 mm focal length lens and focused a second time on the MOT. The angle between the two arms is $20^\circ$. Also, we show how the photo-association (PA) beam is combined with the second arm of the CODT on a dichroic mirror and focused via the same lens onto the atoms captured in the CODT.

2.4.3 Evaporative Cooling

After transferring approximately 2 million $^6$Li atoms from the MOT to the SPI CODT ($U_0/k_B \approx 3$ mK at our maximum trapping power of 100 W), we initiate a process called evaporative cooling. Through this process, we can cool the atoms from a temperature of $\approx 500 \, \mu$K to temperatures as low as $\approx 100$ nK. In principle, this entails simply lowering the trap depth such that the hot atoms escape the trap and the cold atoms remain in the trap. In practice, doing this while minimizing atom loss is quite challenging and has been the subject of many experimental and theoretical studies including [1, 38, 39, 83, 92, 118]. For the purpose of achieving efficient evaporative cooling of $^6$Li in our setup, we have found the doctoral thesis of Kenneth O’Hara [117] the most comprehensive reference. In particular,
O’Hara shows that the evaporation follows a scaling law given by

\[
\frac{N_f}{N_i} = \left( \frac{U_f}{U_i} \right)^{\frac{1}{2} \left( \frac{1}{\eta - 3} \right)}
\]

(2.13)

where \(N_f/N_i\) and \(U_f/U_i\) are the ratios of the atom number and trap depth, respectively, at the end of the evaporation and the beginning of the evaporation and \(\eta := U/k_B T \approx 10\). From an experimental perspective, achieving efficient evaporative cooling requires two ingredients: a high thermalization rate and the freedom to adjust the speed and shape of evaporation ramps. To achieve the former, we need to significantly increase the collision rate by adjusting the effective collisional size or scattering cross-section \(\sigma\) of the atoms. We do this by means of the broad Feshbach resonance in \(^6\text{Li}\) at 832 G \([15, 27, 116, 136]\) - a quantum mechanical lever that allows us to tune the interactions between the atoms by changing the value of the homogenous magnetic field produced by our Helmholtz coils. To avoid diverting the focus of this section, we postpone discussing this complex and rich phenomenon until chapter \([4]\) and illustrate the main point via the cartoon representation shown in Figure 2.10. We fulfill the second requirement by calibrating the AOMs we use for the CODTs and using our control system to create piecewise intensity ramps (linear and exponential) into the DDSs driving the AOMs via the python front end. Each ramp has a starting and stopping power and a parameter (slope or time constant) that specifies the speed of the evaporation. The values of these evaporation parameters and evaporation fields were optimized empirically in a sequential fashion. Despite our best efforts, we were unable to achieve the optimal efficiency (\(\eta \approx 10\)) for the high power portion of the evaporation (possibly due to the heating that results from scattering and intensity noise at the highest powers). The evaporation efficiency improves significantly after most of the atoms coalesce in the cross (as opposed to the wings of the trap) at trapping powers below 12 W. This part of the evaporation is shown in Figure 2.11 for both the SPI trap and the IPG trap.
2.4. Optical Dipole Trap

Figure 2.10: Cartoon representation of the change in the collision cross section of the atoms in the ensemble due to the Feshbach resonance near 832 G. If we think of each atom as a billiard ball with some radius $r$ at $B = 0$ G, then changing the magnetic field to 755 G (close to the Feshbach resonance near 832 G) is equivalent to increasing the radius of the balls to $r' \gg r$. As a result, the collision rate significantly increases.
2.4. Optical Dipole Trap

Figure 2.11: The Normalized atom number is plotted with respect to the normalized trap depth for a forced evaporation in the SPI (a) and IPG (b). According to the fits to the O’Hara scaling law, $\eta = 10.07 \pm 0.13$ for evaporation in the SPI and $\eta = 10.00 \pm 0.11$ for evaporation in the IPG. In both cases, the maximum trapping power was 12 W and the magnetic field was held at 755 G for this portion of the evaporation ramp. The dashed red line seen in both plots is the “ideal” ($\eta = 10$) evaporation ramp.
2.5 RF Spin Mixing

For the efficient production of Feshbach molecules - without which we would be unable to perform most of the photo-association experiments discussed later in this thesis - we need a 50:50 mixture of $|1\rangle$ and $|2\rangle$ state atoms (see chapter 4 for details about state naming conventions) at the end of the forced evaporation. To correct for any population imbalance, we used decoherence to our advantage. For an atom fixed in space and in the presence of a uniform magnetic field $B$, RF photons with frequency $f_{RF} = (E_{|2\rangle}(B) - E_{|1\rangle}(B))/h$ would couple the $|1\rangle$ and $|2\rangle$ states and induce coherent Rabi flopping between them. Since we want to produce an incoherent mixture of the $|1\rangle$ and $|2\rangle$ states with equal population, this coherent Rabi flopping is not adequate. However, both of these assumptions are false: the atoms do move around the trap and the magnetic field has a small gradient. Hence, the energy difference and the precession speed are spatially varying. This means that an ensemble of atoms that were initially in phase and thus constituting a pure state will eventually be completely out of phase and we end up with an incoherent 50:50 mixture of $|1\rangle$ and $|2\rangle$ state atoms.

Experimentally, we do this by driving a home-built antenna at $\approx 80$ MHz (several loops of copper wire) with a 30 W RF power amplifier. Because the source and load impedances were not matched, only a small fraction of the power incident on the antenna is radiated. This sequence is turned on during our forced evaporation at 755 G, which takes place over several seconds - more than enough time for the atoms to circulate around the trap and de-phase.

2.6 Absorption Imaging

When laser light resonant with an atomic transition passes through a cloud of ultra-cold atoms, some of it is absorbed by the atoms and the remainder can be captured on a CCD camera. Thus, we can determine the atom number and the shape of the atom cloud from

---

9 This amplifier has protection circuitry built it that prevents reflections from damaging it.
the reduction in the pixel count. The Beer-Lambert law tells us that

\[
\frac{\partial I(x, y, z)}{\partial z} = -\sigma_{\text{abs}} n(x, y, z) I(x, y, z)
\]  

(2.14)

where \( I(x, y, z) \) is the intensity, \( n(x, y, z) \) is the density of the atoms and \( \sigma_{\text{abs}} \) is the absorption cross section. For intensities much lower than the saturation intensity \( I_{\text{sat}} \) and on resonance, \( \sigma_{\text{abs}} \) is given by [147]:

\[
\sigma_{\text{abs}} = \frac{3\lambda^2}{2\pi}
\]  

(2.15)

Solving equation [2.14] leads to the following expression for the column density:

\[
\tilde{n}(x, y) = \int_0^d n(x, y, z')dz' = \frac{1}{\sigma_{\text{abs}}} \log \left( \frac{I_0(x, y)}{I(x, y)} \right)
\]  

(2.16)

where \( I_0(x, y) \) is the intensity incident on the CCD in the absence of atoms. Then, the atom number that corresponds to pixel \( ij \) is \( N_{ij} = \tilde{n}_{\text{ave}}(x_i, y_j)A_{\text{pixel}} \), where \( \tilde{n}_{\text{ave}}(x_i, y_j) \) is the mean value of \( \tilde{n}(x, y) \) on a square of area \( A_{\text{pixel}} \). Finally, the total atom number is \( N = \Sigma N_{ij} \). (If the magnification of the imaging system differs from unity, \( A_{\text{pixel}} = A_{\text{pixel}}/M^2 \) should be substituted for \( A_{\text{pixel}} \). In our system, \( M = 1 \).)

The most trivial implementation of absorption imaging entails getting \( I(x, y) \) and \( I_0(x, y) \) by capturing an image with and without atoms, respectively. The latter is often referred to as the background image. While this simple approach had been sufficient for the experiments described in [63, 139], the signal to noise ratio (SNR) we got when the atom number dropped below 30,000 was inadequate for our STIRAP experiments. The problem was the imperfect correlation between the interference fringes that show up in atom images and background images. This is because the images are taken at slightly different times and the interference fringes are moving in time. (For example, a fringe may appear at one location in the atom image and at a different location in the background image.) However, by constructing an orthonormal basis from an array of background images, it is possible to create a better background for the region where atom cloud is located for a given atom image. (In practice, we found that an array of 30 background images is sufficient.) Using this basis, it is possible to calculate the coefficients needed to expand the portion of the atom image
without atoms as a linear combination of basis images. With these coefficients, we construct the background image for the atom image that includes the region obscured by the atoms. The combination of this method (see [48] for the mathematical formulation) and using a small circular region of interest (ROI) in the image processor led to a significant reduction in the apparent fluctuations in our atom number, enabling us to collect reliable data with just a few thousands of Feshbach molecules. For example, the standard deviation of a set of 40 identical experimental sequences, where the mean atom number is approximately 10,000, is a factor of 3 lower when the circular ROI and fringe removal algorithm are used.

So far, we have been making the assumption that a quantization axis is not defined i.e. that we are imaging at $B = 0$ G. However, when we image atoms or Feshbach molecules - which are essentially atoms as far as imaging is concerned since their binding energy is negligible and they fall apart into atoms after the first scattering event - at high fields, only 50% of the imaging beam has the correct polarization and the two states we image (which extrapolate to $|1/2, 1/2\rangle$ and $|1/2, -1/2\rangle$ in the $|f, m_f\rangle$ basis) are no longer degenerate. It was shown empirically that this results in under-counting the total atom number by a factor of 4.5 [63].
Chapter 3

Raman Laser System 10

Inducing stimulated Raman transitions in physical systems requires mutual phase coherence between two optical sources. Certain applications are particularly demanding with regard to the degree of phase coherence required including quantum state control and quantum gate operations with trapped ions [164], quantum control of molecular states [35, 36, 87, 114, 165], electromagnetically induced transparency (EIT) [70, 97], and atom interferometry [89, 111]. In some cases, the two optical fields for the Raman transition can be derived from the same laser source using frequency shifting elements, and thus the detrimental effect of laser phase noise is minimized. When the frequency difference of the two fields exceeds the range of frequency shifting actuators, an optical phase-locked-loop (PLL) can be used to phase-lock two independent optical sources. Optical PLLs require a measurement of the optical phase (typically by heterodyne) and feedback to a frequency or phase correction actuator either placed inside [89, 111] or outside the laser cavity [163, 172]. Unlike the intra-cavity options, the addition of external actuation does not require redesigning an existing laser cavity and results in modest optical power penalties (10-20%).

In this chapter, we explore the level of phase noise reduction that can be achieved using a simple modification to an existing laser locking setup. This modification involves sampling the optical field of a laser already locked to a frequency reference and using an external acousto-optic modulator (AOM) to further reduce the phase noise of the optical field by fast electronic feedback to the VCO controlling the AOM. In addition to being straightforward to add to an existing system, this secondary locking system is simple to configure and inherently stable since it is independent of the primary lock of the laser to the reference. Moreover, we show that the VCO output can be used to simultaneously

10A substantial portion of the text and figures presented here originate from a manuscript titled “Phase noise reduction of mutually tunable lasers with an external acousto-optic modulator” that we are in the process of submitting to a peer reviewed journal. They have been re-printed here with permission.
drive a second AOM allowing fast intensity control of the phase locked optical field. This method is also compatible with previously demonstrated schemes for realizing continuous tuning of a laser locked to a frequency comb [65, 107]. Using two independently tunable lasers equipped with this locking system, we demonstrate quantum state manipulation of ultra-cold $^6$Li dimers using Stimulated Raman Adiabatic Passage (STIRAP) in Chapter 7.

### 3.1 Introduction to Optical Phase Locked Loops

An optical phase-locked loop (OPLL) is a method for transferring the coherence of a stable optical reference laser to another laser. In an OPLL, the reference laser (a femto-second frequency comb in our case) is used to down-convert the optical frequency of the laser we wish to lock down to the RF domain via optical heterodyning. This is done by spatially overlapping the two lasers (which must have the same polarization) on an AC coupled photodetector that outputs an RF signal at the difference frequency between the two sources - a beat-note. (The photo-detector acts as the optical analog of an RF mixer.) For readers familiar with traditional phase-locked loops (PLLs), it may be helpful to think of this signal as the analog of a voltage controlled oscillator (VCO).

A simplified block diagram of a PLL (optical or RF) in the phase-domain representation is shown in Figure 3.1 where PD is a phase detector (or phase frequency detector), $C(s)$ is the transfer function (in the Laplace domain) of the loop filter and $G(s)$ is the transfer function of the system we wish to control - the plant. The purpose of this negative feedback loop is to make the phase difference $\Delta \phi = \phi_{out} - \phi_{ref}$ constant and, consequently, $d\phi_{out}/dt = d\phi_{ref}/dt$ or $f_{out} = f_{ref}$. In an OPLL, $\phi_{out}$ is the phase of the RF beat-note between the reference laser and the laser we aim to lock and $\phi_{ref}$ is the phase of an RF source, typically a synthesizer with very low phase noise. If the beat note is locked, then the optical frequency of the laser we are controlling is offset locked to the reference laser. Thus, the absolute phase stability of the laser we are controlling is determined by the phase-noise suppression provided by the OPLL and the phase stability of the reference laser. When an appropriate function with optimized corner frequencies and gains is chosen for $C(s)$, the PLL corrects for the low frequency phase-jitter and can be thought of as a high-pass filter applied to the
3.1. Introduction to Optical Phase Locked Loops

Phase noise of the laser. This is illustrated in Figure 3.2.

![Simplified block diagram of an OPLL in the phase-domain representation](image)

Figure 3.1: Simplified block diagram of an OPLL in the phase-domain representation, where PD is a phase detector (or phase frequency detector), $C(s)$ is the transfer function (in the Laplace domain) of the loop filter and $G(s)$ is the transfer function of the system we wish to control - the plant.

![Cartoon illustration of the phase noise of free running VCO or beat-note and a phase-locked VCO or beat note](image)

Figure 3.2: A cartoon illustration of the phase noise of free running VCO or beat-note and a phase-locked VCO or beat note. A well designed and tuned PLL heavily suppresses the low frequency components of the single-side band phase noise spectrum.

For a typical PLL, the transfer function of the plant is simply an ideal integrator, $G_{VCO}(s) = K_{VCO}/s$ and feedback is provided via the VCO’s control voltage. However, for the OPLLs we use to lock our Ti:Sapphires, we have two actuators and two feedback loops that can be tuned independently for reasons that will become clear in section 3.3.
the low bandwidth and high dynamic range PZT-based lock, we use a type II PLL with a home-built phase frequency detector. For the high bandwidth and low-dynamic AOM-based PLL, we use a type I PLL with a simple passive mixer in saturation as the phase detector. (Since the PZT-based loop keeps the frequency locked, a type II PLL is not required in the latter case. For a discussion of the limitations of a type I PLL and advantages of a type II PLL, see, for example, [129].) For the PZT-based loop, the transfer function of the plant is a simple low pass response:

\[ G_{\text{PZT}}(s) = \frac{K_{\text{PZT}}}{s + \omega_{\text{PZT}}} \]  

(3.1)

where \(\omega_{\text{PZT}} \approx 2\pi \cdot 10\text{ kHz}\) is the corner frequency determined by the capacitance of the PZT and the output impedance of its high voltage driver and \(K_{\text{PZT}}\) is a constant. For this loop, we use an empirically tuned PI\(^2\) controller as \(C(s)\). For the AOM-based loop, the transfer function is approximately given by

\[ G_{\text{AOM}} = \frac{K_{\text{AOM}}e^{-s\tau}}{s + \omega_{\text{AOM}}} \]  

(3.2)

where \(\tau \approx 80\text{ ns}\) is the loop delay and the \(\omega_{\text{AOM}} \approx 2\pi \cdot 1.5\text{ MHz}\) and \(K_{\text{AOM}}\) is a constant. The physical origins of \(\tau\) and \(\omega_{\text{AOM}}\) are time it takes for the acoustic wave in the AOM to reach the laser beam and the time it takes to propagate across the beam. For this loop, we used an ultra-low noise and high slew rate analog loop filter from Vescent Photonics (model D2-125). Of the four available options\(^{11}\), we achieved the highest loop bandwidth with the PID configuration. (Contrary to our intuition and the result of a MATLAB simulation, setting a large derivative gain was crucial for maximizing the closed loop bandwidth. Perhaps, this resulted in pole-zero cancellation and allowed us to set a higher overall gain before the onset of oscillation.) A more appropriate loop filter transfer function may exist for this plant, but this would require a custom design. To avoid this complexity, we chose to settle for what may be sub-optimal performance.

In this section, we provided a cursory overview of PLLs and alluded to several concepts in control theory. For a more thorough discussion of these topics, we refer the reader to [7, 43, 129].

\(^{11}\)PI, PI\(^2\), PID and PI\(^2\)D
3.2 Femto-Second Frequency Comb

While the primary focus of this chapter is to discuss the development and performance of our Raman laser system, we must take a short detour to briefly introduce the reader to our femto-second frequency comb (FFC) - the optical reference. We aim to provide only a high-level overview of the key features of this laser and highlight the performance limitations that are relevant to our Raman laser system. For an in-depth discussion complete with the optical and electronic schematics for this laser, we refer the reader to the PhD thesis of William Gunton [63]. We begin by describing the properties of an ideal FFC in the next subsection and discuss the specifics our Erbium doped fiber FFC in the subsections that follow.

3.2.1 Ideal Optical Frequency Comb

A cartoon representation of the spectrum of an ideal FFC is shown in 3.3. Unlike a continuous wave (CW) laser, this laser simultaneously oscillates on many frequencies separated by integer multiples of the repetition rate, \( f_{\text{rep}} = c/2L \), where \( c \) is the speed of light in the laser cavity (which is primarily made of silica for the case of our fiber laser) and \( L \) is the length of the cavity. The center frequencies of the elements or teeth of this idealized Dirac comb are given by \( \nu_n = f_{\text{ceo}} + nf_{\text{rep}} \), where \( n \) is an integer and \( f_{\text{ceo}} \) is the carrier offset frequency. For an ideal FFC, \( f_{\text{ceo}} \) and \( f_{\text{rep}} \) are simply constants that determine the center frequencies of an infinite series of delta functions. (As we will discuss in the next section, both of these quantities must be stabilized via OPLLs for our FFC.) Since the inverse Fourier transform of a Dirac comb in frequency with periodicity \( f_{\text{rep}} \) is another Dirac comb in time with periodicity \( T = 1/f_{\text{rep}} \), this laser must be pulsed.
3.2. Femto-Second Frequency Comb

3.2.2 Erbium Doped Fiber FFC

In a real laser, the finite frequency bandwidth of the gain medium sets a lower bound on the pulse duration. For our Er-doped fiber oscillator, this pulse duration is approximately 77 fs [107]. Hence, there exist a $\nu_{n_{\text{min}}}$ and a $\nu_{n_{\text{max}}}$ and the comb teeth do not extend all the way down to $f_{\text{ceo}}$ (or up to infinity) in frequency.

Achieving pulsed operation or mode-locking in practice requires inserting a passive or active element into the laser cavity that leads to high cavity losses for low intensities (CW output) and low cavity losses at high intensities (pulsed output). As a result, this element changes the laser dynamics such that the cavity modes are compelled to maintain a fixed phase relationship and interfere constructive only when $t = t_0 + mT$, where $t_0$ is a constant and $m$ is an integer. For our FFC oscillator, we use an artificial saturable absorber for passive mode-locking. This method relies on the non-linear (intensity dependent) polarization...
rotation that takes place in the single mode (SM) fibers as well as several wave-plates and a Faraday isolator in the free space region of the cavity (see [65]). For additional information about Er-doped fiber oscillators and this method of mode locking, we invite the reader to review Appendix C and [2, 77, 153, 154, 160].

To create a FFC from a mode locked laser, $f_{\text{rep}}$ and $f_{\text{ceo}}$ must be stabilized via active feedback. (The exception to this are difference frequency FFCs, which have no offset [173] and therefore only require stabilization for $f_{\text{rep}}$.) To stabilize the former, we sample the field directly out of the oscillator and send it to a home-built low noise photo-detector (Hamamatsu S5973 photo-diode followed by two monolithic low noise amplifiers). In the frequency domain, we observe $f_{\text{rep}}$ and its harmonics. To derive the error signal, we use the 8663A RF synthesizer (which receives an ultra-stable 10 MHz reference input from the Menlo Systems GPS-8 frequency reference) as the local oscillator (LO) to mix the harmonic at $3f_{\text{rep}} \approx 376$ MHz down to DC. With this intermediate frequency (IF) signal acting as the error input for the loop filter (Vescent Photonics D2-125 Laser Servo), we lock the cavity length by feeding back on a PZT in the free space portion of the cavity. Locking the $f_{\text{ceo}}$ is a more involved process. The first step is octave broadening the output of the oscillator (after amplifying it with an Er-doped fiber amplifier or EDFA) in a highly non-linear fiber (HNLF) such that the spectrum extends from 1 $\mu$m to 2 $\mu$m. The heterodyne beat note between the doubled (from 2 $\mu$m to 1 $\mu$m) and the fundamental comb at 1 $\mu$m is thus $2nf_{\text{rep}} + 2f_{\text{ceo}} - (2nf_{\text{rep}} + f_{\text{ceo}}) = f_{\text{ceo}}$.\footnote{In reality, we see copies of $f_{\text{ceo}}$ beat notes at $nf_{\text{rep}} \pm f_{\text{ceo}}$. We can extract $f_{\text{ceo}}$ by reading any of them using a frequency counter.} We convert this beat note into a phase error using a home built phase-frequency detector and provide feedback via the current pumping the 980 nm pump diode for the oscillator. (This laser diode is pumped by a home-built current driver with an analog modulation input.) In the next subsection, we conclude this overview by discussing the performance of the PLLs used for the stabilizing $f_{\text{rep}}$ and $f_{\text{ceo}}$ and their relevance to STIRAP. For a more complete introduction to FFCs, we invite the reader to consult [8, 112, 135, 150, 169].
3.2.3 Performance Metrics Relevant to STIRAP

As we mentioned above and will discuss in greater detail in the chapters that follow, STIRAP is very sensitive to the relative phase coherence between the two optical sources used for the population transfer, but relatively insensitive to their individual phase coherence. When an FFC is used as an optical reference for a Raman laser system, the relative phase coherence between the Raman lasers can be no better than the relative phase coherence between the comb teeth the Raman lasers are locked to. Noise in the \( f_{ceo} \) lock does not effect the relative phase coherence because it is common to every laser locked to the FFC. Thus, our \( \approx 100 \) kHz linewidth is perfectly adequate for the \( f_{ceo} \) lock. Since we lock \( f_{rep} \) using its third harmonic, we expect the phase noise between comb teeth \( m \) and \( n \) to scale monotonically as a function of the frequency separation \( |\Delta \nu| = |\nu_m - \nu_n| = |m - n|f_{rep} \). We attempt to indirectly estimate the frequency scaling of the phase noise in section 3.4, but observe no clear increase in phase noise from 0.3 GHz to 12.2 GHz. It is difficult to predict based on this data what the increase in phase noise is at, for example, \( \approx 9 \) THz (the frequency separation required for accessing the \( v'' = 0 \) levels in the \( a(3\Sigma_u^+) \) potential). To measure it, we would need an even more stable optical reference. However, we can predict how quickly it would need to scale in order to have a significant effect on the Raman laser system via a back-of-the-envelope calculation. In Figure 3.4, we show the phase noise of the comb at 376 MHz. At a 10 kHz offset (noise at lower frequencies is irrelevant for STIRAP unless the transfer time is very long), the phase noise is approximately -132 dBc/Hz. In Figure 3.7, the phase noise at the same frequency offset is -88 dBc/Hz. Thus, the phase noise would need to increase at a rate of 4.9 dBc/Hz per THz. Regardless of the accuracy of this estimate, we do not see a drop in STIRAP efficiency when we switch from the least bound vibrational level to the lowest vibrational level. Thus, it is clear that the performance of the comb is currently not a bottleneck for us. (This may change for deeply bound levels in the lowest lying single potential.) More demanding applications may require a more stable FFC. To significantly improve the performance of our comb, we would need to lock it to an optical (rather than RF) reference and potentially introduce an intra-cavity EOM actuator to increase the closed loop bandwidth of the PLL used for the \( f_{rep} \) lock (see [11, 72, 74, 75, 113, 151]). The alternative is purchasing a commercial solution from Menlo
3.2. Femto-Second Frequency Comb

Systems or TOPTICA Photonics.

Figure 3.4: Phase noise spectrum of the third harmonic (376 MHz) of the FFC’s repetition-rate.
3.3 System Design

A schematic for the system with an additional external AOM-based phase-locked-loop (PLL) is shown in Figure 3.5 where (a) shows the entire system consisting of the laser to be stabilized, optical reference, locking branch and experiment branch. Subfigures (b) and (c) show the phase/frequency correction actuator and the associated locking electronics, respectively.

In our experiment, the frequency of a Ti:sapphire laser (TS1) is pre-stabilized by electronic feedback to a piezoelectric transducer controlling the cavity length. The PZT lock uses light sampled directly out of the laser and is thus independent and decoupled from the AOM-based lock that follows. A phase-frequency-discriminator (PFD) is used instead of a mixer to extend the capture range of the PZT lock. Pre-stabilization eliminates DC frequency errors and minimizes the dynamic range requirements of the AOM-based lock. The decoupling of the two locks allows them to be independently optimized for performance and stability and avoids complications associated with designing customized loop filters for coupled feedback loops.

The phase noise of the pre-stabilized light is further reduced using feedback to an AOM actuator as shown in figure 3.5(b). To achieve a high closed loop bandwidth, we focus the input beam ($1/e^2$ intensity diameter of 1.5 mm) with a 300 mm lens and minimize the...
acoustic wave propagation delay by translating the AOM such that the beam is incident on the crystal as close as possible to the source. This results in a propagation delay of 135 ns and a 10-90% rise time of 80 ns. We maximize the actuator dynamic range and minimize residual amplitude variation from fiber coupling the deflected beam by placing a collimating lens as close to the AOM as possible. Here, 200 mm was chosen because of the need to block the un-diffracted beam. The AOM deflected beam is re-collimated and is, to first order, parallel to the lens optic axis independent of the deflection angle (i.e. AOM frequency). As a result, the power through the fiber is almost constant over a driving frequency range of several MHz and drops to 80% at ±6 MHz away from our center frequency of 63 MHz. As shown in (b), the shifted beam is combined with a second laser (entering the L2-in port), passed through a Glan-Thompson (GT) polarizer, and coupled into an SM/PM fiber to ensure mode overlap. The heterodyne beat is detected on a photodiode in block (c). In the AOM locking branch, we measure the heterodyne beat of TS1 entering the L1-in port with the Fiber-based Frequency Comb (FFC) entering the L2-in port. In block (b) of the experiment branch we combine TS1 with light from a second TS laser (TS2) or the FFC (not shown) to diagnose the phase noise of the light generated for the STIRAP experiment.

In (c), a mixer generates an error signal by combining a reference RF signal and the filtered and amplified heterodyne beat-note between the frequency doubled (via a PPLN crystal) FFC and TS1. The output of the VCO (Mini-Circuits ROS-70-119+), whose control input is driven by a Vescent Photonics D2-125 loop filter, is used to issue a correction signal for the optical field. The VCO output is split and amplified by two power amplifiers (PA). The amplified signals (RF1 and RF2) are sent to the locking branch AOM and to the experiment branch AOM generating a copy of the corrected light field. The amplitude of the RF sent to the experiment arm AOM can be independently controlled via a voltage controlled attenuator (VCA) without perturbing the lock. We achieve pulse shaping in an open loop configuration using an SRS DS345 arbitrary waveform generator. For applications that require further reduction of the amplitude noise, a stabilization control loop can be added.

To perform STIRAP, a second Ti:sapphire (TS2) laser is used. The arrangement is almost identical, but includes a double pass AOM immediately after the laser block which
permits scanning the laser frequency without changing the FFC’s repetition rate (see \[65\] for details). For the diagnostics measurement in figure 3.7, TS2 is combined with TS1 in block (b) of the experiment section.

### 3.4 Performance

Out-of-loop measurements of the power spectrum and single-sideband (SSB) phase noise of the heterodyne beat-note between a locked Ti:Sapphire laser and the FFC are shown in Figure 3.6 under different locking conditions. We achieve a sub-Hz -3 dB linewidth (not resolved with our RF spectrum analyser) and a level of noise suppression for the experiment branch (AOM\(_E\)) similar to the locking branch (AOM\(_L\)) above 3 kHz. For example, at a 10 kHz offset, the SSB phase noise is \(-92\) dBc/Hz and \(-88\) dBc/Hz for the locking branch and experiment branch, respectively. The larger phase noise of the AOM\(_E\) measurement below 3 kHz results from vibrations of optical elements that are not common to both the AOM\(_E\) and AOM\(_L\) paths. Similar low frequency noise is evident in the heterodyne beat measurement between TS1 and TS2 (see Figure 3.7) using fields from the experiment branches. While this has a negligible effect on the STIRAP efficiency demonstrated here, other applications including atom interferometry are more sensitive to noise at these frequencies [89, 111]. Rearranging the optical components, using higher quality optomechanical mounts and adding acoustic dampeners would reduce this phase noise generated after the lock.
3.4. Performance

Figure 3.6: Power spectrum and SSB phase noise of an out-of-loop heterodyne measurement between TS1 and the FFC. For the power spectrum measurements, the resolution bandwidth is 300 Hz for the wide span and 1 Hz for the narrow span. The results are shown for two locking conditions: with only the lock of the TS1 cavity length engaged (PZT) and with both the cavity length and the external AOM-based lock engaged (AOM). The subscripts 'L' and 'E' correspond to two different out-of-loop measurements: one is a measurement of the heterodyne generated by a copy of the fields incident on the locking photodiode (L) and the other is a measurement of the heterodyne between the FCC and a copy of the corrected TS1 field generated by a second AOM.
3.4. Performance

Figure 3.7: Power spectrum and SSB phase noise of the heterodyne beat between the experiment arms of TS1 and TS2 for three frequency differences, $|\Delta f| = |f_2 - f_1| \approx |N - M| \cdot f_{\text{rep}}$, where TS1 (TS2) is locked to the $N^{th}$ ($M^{th}$) comb element and $f_{\text{rep}} = 125.6$ MHz is the FFC repetition rate. The exact separation depends on the frequency of the double pass AOM we use for scanning one of the lasers. The resolution bandwidth is 300 Hz for the wide span and 1 Hz for the narrow span. Jitter in the FFC pulse repetition rate, which defines the comb element spacing, is expected to produce frequency/phase fluctuations in the heterodyne between the two Ti:Sapphire lasers that increases with $|N - M|$ and thus $|\Delta f|$. However, we do not resolve an increase in the phase noise for frequency separations from 0.3 GHz to 12.2 GHz. The elevated noise floor of the black trace and the slight asymmetry of the blue trace result from the frequency dependence of the detector noise floor and a slow polarization drift in our fiber combiners, respectively.
3.5 Summary

In this chapter, we demonstrated phase noise reduction using an external AOM for mutually tunable Ti:Sapphire lasers phase-locked to an FFC. We added feedforward arms (with similar performance) whose amplitudes can be arbitrarily shaped without disturbing the phase lock. As we will discuss in chapter 7, we then used this system to perform quantum state control in $^6\text{Li}_2$ dimers using STIRAP. While we were unable to achieve phase noise-reduction down to the shot noise level because of the inherent acoustic delay of the AOM actuators used and because of the limited configuration options of our loop filters, we believe that increasing the closed loop bandwidth of the OPLL is possible. This could be achieved with AOMs that do not require angle tuning and consequently have a significantly shorter acoustic delay [162, 168] or with custom loop filters whose transfer functions are optimized for this plant.
Chapter 4

Feshbach Resonances and the $^6$Li$_2$ System

In this chapter, we aim to establish a naming convention for the single atom, two atom and molecular states (where possible), discuss Feshbach resonances and the criterion for creating Feshbach molecules (which are essential for STIRAP), and state the selection rules for dipole transitions for $^6$Li dimers at high magnetic fields. We begin with an overview of the hyperfine and Zeeman splitting in $^6$Li atoms.

4.1 $^6$Li Hyperfine Structure and Zeeman Splitting

In chapter 2, we introduced the hyperfine and Zeeman splitting in $^6$Li for the purpose of determining the optical frequencies required for laser cooling these atoms. Here, we elaborate on the origins of these effects and set the stage for magnetically induced Feshbach resonances.

Since the atoms in the ODT rapidly decay to the electronic ground state after the MOT light is extinguished, $l = 0$. In the absence of external fields, we only need to consider the hyperfine splitting, which takes place due to interactions between the total angular momentum of the electron $j = l + s = s$ (because $l = 0$) and the angular momentum of the nucleus $i$. The hyperfine hamiltonian $H_{hf}$ is given by

$$\hat{H}_{hf} = a_{hf} \mathbf{j} \cdot \mathbf{i} = a_{hf} \mathbf{s} \cdot \mathbf{i}$$

(4.1)

where $a_{hf}$ is the hyperfine constant. Due to this coupling, $j$ is no longer a good quantum number, so we let $f = j + i = s + i$ be the total angular momentum. Then, $f^2 = f \cdot f =$
4.1. $^{6}\text{Li}$ Hyperfine Structure and Zeeman Splitting

$s^2 + i^2 + 2s \cdot i$ and we can express $\hat{H}_{\text{hf}}$ as

$$\hat{H}_{\text{hf}} = \frac{a_{\text{hf}}}{2} (f^2 - i^2 - s^2)$$

(4.2)

If we now apply this to an eigenstate of $f^2$, $|f, m_f\rangle$, we get

$$\hat{H}_{\text{hf}} |f, m_f\rangle = \frac{a_{\text{hf}}}{2} \left[ f(f+1) - i(i+1) - s(s+1) \right] |f, m_f\rangle = E_{\text{hf}} |f, m_f\rangle$$

(4.3)

For $^{6}\text{Li}$, $i = 1$, $s = 1/2$, $f = 3/2$, $1/2$ for the $^{2}\text{S}_{1/2}$ levels. Hence, $E_{\text{hf}} = a_{\text{hf}}/2$, $-a_{\text{hf}}$, and the hyperfine splitting is $3a_{\text{hf}}/2 = (3/2)152.1 \text{ MHz} = 228.2 \text{ MHz}$ - the value shown in Figure 2.2. (We could repeat this calculation with $l = 1$ to calculate the hyperfine splittings for the excited state.)

Introducing a uniform magnetic field pointed in the $z$ direction gives rise to Zeeman splitting, which breaks the degeneracy between the $m_f$ levels. The Hamiltonian responsible for this interaction is given by

$$\hat{H}_{Z} = B \cdot \left( \frac{2\mu_e s - \mu_i i}{\hbar} \right) = B_z \left( \frac{2\mu_e s_z - \mu_i i_z}{\hbar} \right)$$

(4.4)

where $\mu_e$ and $\mu_i$ ($\mu_i \ll \mu_e$ for $^{6}\text{Li}$) are the electronic and nuclear magnetic moments of the atom, respectively, and $B$ is the applied magnetic field. Since $|i, m_i\rangle$ is an eigenstate of $i_z$ and $|s, m_s\rangle$ is an eigenstate of $s_z$, this Hamiltonian is diagonal in the $|i, m_i\rangle|s, m_s\rangle$ basis, not in the $|f, m_f\rangle$ basis. Hence, for small magnetic fields ($< 10 \text{ G}$ for $^{6}\text{Li}$), we treat the Zeeman splitting as the perturbation and label states in the coupled $|f, m_f\rangle$ basis. For large magnetic fields, the Zeeman effect dominates, so we label the states in the uncoupled $|i, m_i\rangle|s, m_s\rangle$ basis. (For a general form that is valid for magnetic fields in the intermediate range, see [49].) In table 4.1, we provide the shorthand notation for the states at low and high magnetic fields. They are written in ascending order in energy. At the end of the sequence for loading the dipole trap, we have a mixture of the $|1\rangle$ and $|2\rangle$ states. Because $m_F = m_{f_1} + m_{f_2}$ is a conserved quantity (for spherically symmetric interactions), these states cannot decay via inelastic collisions making this a stable mixture at low fields. At high fields, the states $|1\rangle$, $|2\rangle$ and $|3\rangle$ are stable [120]. For the remainder of this dissertation,
4.2 Brief Introduction to Scattering Theory and Feshbach Resonances

Many-body collisions are rare in a dilute ultracold gas because the atomic density is low and the mean inter-particle distance is much greater than the size of the collision complex (or equivalently the scattering length). Hence, it is sufficient to consider only two-body collisions. In the center of mass coordinate frame, we split the space dependent part of the Hamiltonian into two parts: a center of mass part and a relative motion part. The former is irrelevant in scattering calculations because it drops out [91]. The problem then reduces to considering a virtual particle moving in a centrally symmetric potential $V(r)$ about a fixed collision center. The Hamiltonian for this system (in atomic units) is given by

$$\hat{H} = \hat{H}_{\text{rel}} + \hat{H}_{\text{hf}} + \hat{H}_Z$$

(4.5)

where $\mu = m_1 m_2 / (m_1 + m_2) = m^2 / (2m) = m / 2$ is the reduced mass and $\hat{H}_{\text{rel}}$ is the relative motion Hamiltonian given by [91]

$$\hat{H}_{\text{rel}} = -\frac{1}{2\mu r} \frac{\partial^2}{\partial r^2} r + \frac{i(\theta, \phi)^2}{2\mu r^2} + \hat{V}$$

(4.6)

Table 4.1: Complete basis for the ground state in the coupled and uncoupled representation for the atomic states of $^6$Li. In general, the atomic states are superpositions of these basis vectors. At very small (large) fields, the $|f, m_f\rangle$ ($|i, m_i\rangle|s, m_s\rangle$) states are approximately equal to the eigenstates of the Hamiltonian.

we will be concerned with just the $|1\rangle$ and $|2\rangle$ states at high fields.

### 4.2 Brief Introduction to Scattering Theory and Feshbach Resonances

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(4.6)
4.2. Brief Introduction to Scattering Theory and Feshbach Resonances

In this equation
\[ \hat{l}^2(\theta, \phi) = -\left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \]  
(4.7)
is the rotational angular momentum operator and $\hat{V}$ is the potential energy operator which couples the orbital and electronic spin degrees of freedom. It asymptotically approaches zero for large $r$.

4.2.1 Single Channel Scattering

If we ignore $\hat{H}_{hf}$ and $\hat{H}_Z$ (for now), the problem reduces to a single collision channel and the solution to the Schrödinger equation for $r \to \infty$ is a superposition of an incoming plane wave and an outgoing spherical wave and is given by

\[ \psi(r, \theta, \phi) = A \left( e^{ikz} + f(k, \theta, \phi) e^{ikr} \frac{\cos \theta}{r} \right) \]  
(4.8)

where $f(k, \theta, \phi)$ is the scattering amplitude and $k = \sqrt{2\mu E}/\hbar$ is the wavenumber [91]. Since we only consider cases where the scattered wave is symmetric with respect to the $z$-axis, the scattering amplitude is actually independent of $\phi$ and we can expand the scattered wave function as a sum of Legendre polynomials $P_l$ such that

\[ \psi(r, \theta) = \sum_{l=0}^{\infty} F_l(k, r) P_l(\cos \theta) \]  
(4.9)

where $F_l(k, r)$ is the radial part of the wave function [91]. Each term in the sum is a partial wave with orbital momentum quantum number $l$. (Here, we are only concerned with $s$-wave scattering, where $l = 0$.) The scattering amplitude can be determined by matching solutions to the Schrödinger equation in several spatial regions. We do not show that here and instead invite the reader to see the complete derivation in either [91] or [124].

The differential cross section is related to the scattering amplitude by

\[ \frac{d\sigma}{d\Omega} = |f(k, \theta, \phi)|^2 \]  
(4.10)

where $d\Omega$ is a small solid angle through which particles scatter. The experimentally relevant
4.2. Brief Introduction to Scattering Theory and Feshbach Resonances

quantity for us is the integral cross section, which is given by

\[
\sigma(k) = \int d\Omega |f(\theta)|^2
\]  

(4.11)

where we integrate over all solid angles. This quantity can be thought of as the collisional size of the particles. Thus, if we can increase \(\sigma(k)\) (the size of the “billiard balls”), we also increase the collision rate. To do this, we need to have multiple collision channels whose interaction potentials can be tuned by means of a lever we can control experimentally. This powerful tool is called a Feshbach resonance and the lever is the magnetic field.

4.2.2 Multi-Channel Scattering and Feshbach Resonances

When we include the hyperfine and Zeeman interactions (equation 4.5), we get one collision channel for each state, so two atoms can either enter and exit via the same channel (elastic collision) or via different channels (inelastic collision). The second option results in trap loss. By virtue of the Zeeman effect, it is possible to change the asymptotic energy of the potential energy surface associated with each collision channel. In particular, when two channels have different magnetic moments, it is possible to tune the continuum of the open channel such that it is degenerate with a bound state (typically the least bound state) of a closed channel, as shown in Figure 4.1. The resulting coupling between a bound molecular state and a free atom state gives rise to a Feshbach resonance (FR). Near a Feshbach resonance and at ultra-cold temperatures, the cross section is given by

\[
\sigma = 4\pi a^2
\]  

(4.12)

where \(a\) is the real (or elastic) part of the scattering length which can be determined from coupled channels calculations (multi-channel scattering theory) provided the singlet and triplet potentials used are known accurately in the vicinity of their least bound states [27]. The real part of the \(s\)-wave (\(l = 0\)) scattering length \(a\) is given by

\[
a(B) = a_{bg} \left(1 - \frac{\Delta B}{B - B_0}\right)
\]  

(4.13)
4.2. Brief Introduction to Scattering Theory and Feshbach Resonances

where $a_{bg}$ is the background scattering length (far from the resonances positions), $\Delta_B$ is the width of the resonance (see [27, 124] for precise definition) and $B_0$ is the position of the resonance, where the elastic scattering length grows to infinity. Since the cross section $\sigma \propto a^2$ according to equation 4.12 we would expect it to diverge, at a Feshbach resonance. In reality, it does not. We can see this if we include a second order correction [27]:

$$\sigma(k) = 4\pi \frac{a^2}{1 + a^2k^2}$$  \hspace{1cm} (4.14)

When the scattering length diverges, this expression simplifies to

$$\sigma(k) = \frac{4\pi}{k^2} = \frac{\lambda_{dB}^2}{\pi}$$  \hspace{1cm} (4.15)

where $\lambda_{dB}$ is the de Broglie wavelength, which depends on the wave vector or, equivalently, the temperature. Thus, the cross section levels off and would only diverge if we managed to reach absolute zero.

\[\text{Energy}\]

\[\text{Least Bound State}\]

\[\text{Closed Channel}\]

\[\text{Continuum}\]

\[\text{Open Channel}\]

Figure 4.1: A sketch of the effective potentials for an open channel and a closed channel. When the energy of the least bound state of the closed channel is close to degenerate with the threshold energy, a Feshbach Resonances occurs.
4.3. The Scattering State and Feshbach Molecule Formation

Feshbach resonances in $^6$Li and other species have been studied extensively \[9, 14, 27, 49, 58, 71, 79, 82, 84, 96, 119, 137, 145, 167, 174\]. For enhancing the efficiency of forced evaporative cooling and Feshbach molecule creation, we rely on the extremely broad ($\delta_b = -300$ G) s-wave resonance at 832 G. On the low side of this resonance, the scattering length $a$ is positive because there is a weakly bound molecular state just below the continuum, and it is possible to form these molecules by 3-body recombination and to make a molecular Bose-Einstein Condensate of them at sufficiently low temperatures. We note that the effective interaction on this side of the resonance is repulsive since the scattering length is positive \[34, 78, 149\]. For magnetic fields below the resonance at 832 G, where the scattering length $a$ is negative, it possible to create Bardeen-Cooper-Schrieffer (BCS) like pairs \[15, 161, 171\]. Both of these regimes have been explored with our apparatus \[64\]. However, our goal in this study is to determine the decay rate constants for deeply bound $^6$Li$_2$ triplet molecules. For reasons that will become clear in chapter 7, we operate on the BEC side of the resonance, but actively avoid creating a mBEC. Instead, we aim to produce a thermal gas of Feshbach molecules without forming a mBEC. In the next section, we discuss these loosely bound molecules and return to the idea of (not) forming a mBEC in chapter 7.

4.3 The Scattering State and Feshbach Molecule Formation

As we mentioned above and in chapter 2, we have a 50:50 mixture of the $|1\rangle$ and $|2\rangle$ state at the end of the forced evaporative cooling stage (at 755 G). Since $^6$Li is a fermion, the two atom wave function $|12\rangle$ must be anti-symmetrized:

$$|\psi\rangle_{12} = \frac{1}{\sqrt{2}} (|1\rangle_1|2\rangle_2 - |2\rangle_1|1\rangle_2)$$  \hspace{1cm} (4.16)

where the subscripts refer to atoms 1 and 2. In the absence of p-wave collisions, which are suppressed for temperatures below 2 $\mu$K, the scattering state in the molecular basis $|N, S, I, J, F\rangle$ is given by \[63, 140, 141\]

$$|\psi\rangle_{12} = \sqrt{\frac{1}{6}}|0, 1, 1, 1, 2\rangle - \sqrt{\frac{1}{2}}|0, 1, 1, 1, 1\rangle \sqrt{\frac{1}{3}}|0, 1, 1, 0\rangle$$  \hspace{1cm} (4.17)
4.3. The Scattering State and Feshbach Molecule Formation

These quantum numbers originate from the rotational angular momentum of the nuclei, $N$, the total electronic spin $S = s_1 + s_1$, the total nuclear spin $I$, the total angular momentum except for the nuclear part, $J = N + S$ (when $L = 0$), and the total angular momentum, $F = N + S + I$. As our discussion in the previous section suggested, the coupling between the open channel and closed channel near a FR resonance results in a dressed state, which is a superposition of a dimer ($v'' = 38$, singlet potential) and the incoming state [49]. The former is a singlet state ($S = 0$) and the latter is a triplet state ($S = 1$). This means that it is possible to photo-associate these molecules into excited singlet and triplet states. In the $|N, S, I, J, F\rangle$ basis, this state is given by

$$|\psi_B\rangle = \frac{\sqrt{Z}}{3} \left( 2\sqrt{2}|0, 0, 0, 0, 0\rangle - |0, 0, 2, 0, 0\rangle \right) + \sqrt{1-Z} \left( \sqrt{\frac{1}{6}}|0, 1, 1, 2\rangle - \sqrt{\frac{1}{2}}|0, 1, 1, 1\rangle \sqrt{\frac{1}{3}}|0, 1, 1, 0\rangle \right)$$

(4.18)

where $Z$ is the closed channel fraction measured in [123, 139, 140] and predicted in [130]. Over the range of magnetic fields over which we typically do photo-association (700-755 G), $Z$ is on the order of $10^{-3}$, so this state is open channel dominated and therefore almost entirely a triplet state. It is for this reason that we obtain much higher Rabi frequencies when we photo-associate these Feshbach molecules to excited triplet states.

These loosely bound molecules are created by a three-body recombination process that takes place during atom-molecule thermalization [28, 63, 78, 121]. When three atoms collide, two of them form a Feshbach molecule and the third flies way with the binding energy converted to kinetic energy. Paintner et al. show using statistical arguments that the Feshbach molecule fraction $N_{FM}/N_{total}$ is given by the following transcendental equation [121]:

$$\frac{(1 - N_{FM}/N_{total})^2}{N_{FM}/N_{total}} = 6 \left( \frac{T}{T_F} \right)^3 \exp \left( \frac{E_b}{k_B T} \right)$$

(4.19)

where $T_F = \hbar \omega \sqrt{6N_{total}}$ is the Fermi temperature and $E_b = -\hbar^2/2ma^2$ is the binding energy of the Feshbach molecule[13]. If the Feshbach molecule fraction $N_{FM}/N_{total} \ll 1$, then

---

13This expression is only valid near a Feshbach resonance.
4.4 Excited State and Deeply Bound State Labelling and Selection Rules

the expression in equation (4.19) simplifies to

\[
\frac{N_{FM}}{N_{total}} = \frac{1}{6} \left( \frac{T_F}{T} \right)^3 \exp \left( -\frac{E_b}{k_B T} \right) = \frac{1}{6} \left( \frac{T_F}{T} \right)^3 \exp \left( \frac{\hbar^2}{2mk_B Ta^2} \right)
\]

(4.20)

Clearly, in this limit, we can increase the Feshbach molecule fraction by decreasing the scattering length, ceteris paribus. Thus, a large Feshbach molecule fraction can still be obtained at a relatively high temperature by setting the magnetic field further away from resonance so as to decrease the scattering length - a point we will return to in the context of STIRAP in chapter 7. Although we only showed this in limit where the Feshbach molecule fraction is small, this statement holds for larger Feshbach fractions.

4.4 Excited State and Deeply Bound State Labelling and Selection Rules

Angular momentum coupling schemes for molecules are highly complex and different for every molecule. Even for a molecule as simple as $^6$Li$_2$, fully characterizing molecular states and the associated transition probabilities requires extensive numerical studies that are beyond the scope of this dissertation. However, we can gain insight from the theoretical and experimental results discussed in [63, 139, 141], which are valid for $^6$Li$_2$ molecules in singlet states (whose magnetic dipole moment is zero) for any magnetic field and for $^6$Li$_2$ molecules in triplet states at $B = 0$ G. In addition, Hund’s coupling cases (a)-(e) [20, 41, 68] are a starting point for angular momentum couplings of diatomic molecules. They state which terms in the molecular Hamiltonian dominate over others and, consequently, which quantum numbers are approximately “good”. Hund’s coupling case (b) is the best match for the states of $^6$Li$_2$ we work with because the total electronic angular momentum $\mathbf{L} = \ell_1 + \ell_2 = 0$, so its projection $m_L = 0$ and the coupling of $\mathbf{L}$ to the total spin $\mathbf{S} = s_1 + s_2$ is weak. As a result, the total angular momentum (aside from the nuclear spin) $\mathbf{J} = \mathbf{S} + \mathbf{N} + \Lambda \hat{z} = \mathbf{S} + \mathbf{N}$, where $\mathbf{N}$ is the angular momentum associated with the nuclear motion and $\Lambda = |m_L| = 0$ [63]. If we now add the nuclear spin, we get the total angular momentum $\mathbf{F} = \mathbf{J} + \mathbf{I} = \mathbf{S} + \mathbf{N} + \mathbf{I}$. Since the value of $s$ for each atom is 1/2, the total spin $S = 1$ or 0. It is tempting to assume

\footnote{Again, this is only valid near a Feshbach resonance.}
that a similar argument would hold for the total nuclear spin $I$. However, the value of $I$

for a molecular state of $^6\text{Li}_2$ depends on the parity of the electronic wave function upon

reflection about a plane containing the internuclear axis, the symmetry of the molecular

wave function with respect to an inversion of all of nuclear coordinates, and the value of $N$.

For all of the triplet states considered in this dissertation, $I = 1$ \textsuperscript{[63]}. The two symmetry

considerations are typically included in the term symbol for a molecular potential. Similar
to the term symbols for atoms, molecular term symbols are specified as follows:

\[
2S+1\Lambda^+/_- g/u
\]

For all of the potentials we will be considering, $\Lambda = 0$. This is denoted by $\Sigma$ in the term

symbol. The $+/-$ in the superscript refers to parity of the electronic wavefunction with

respect to reflections through a plane containing the internuclear axis and $u/g$ refers to

coordinate reversal symmetry with respect the center of the molecule, $r \rightarrow -r$. (The

letters stand for gerade and ungerade, which mean even and odd in German, respectively.)

Since a term symbol is not always unique, a letter often precedes it. For example, the

lowest lying and second excited triplet potentials in $^6\text{Li}_2$ are denoted $a(1^3\Sigma_u^+)$ and $c(1^3\Sigma_g^+)$.

(Capital letters are used for the singlet potentials.) These are the only two potentials we

will be concerned with.

The selection rules for molecular transitions in $^6\text{Li}_2$ when spin-spin coupling and spin-

rotation coupling are negligible are \textsuperscript{[63]}

\[
g \leftrightarrow u, \ \Delta N = \pm 1, \ \Delta S = 0, \ \Delta I = 0, \ \Delta J = 0, \pm 1, \ \Delta F = 0, \pm 1, \ \Delta m_F = 0, \pm 1. \quad (4.21)
\]

The first rule states that the parity of the wave function with respect to the center of the

molecules must change in an electric dipole transition. The second rule states that the

orbital angular momentum of the nuclei must change by one unit when a photon (which

carries one unit of angular momentum) is absorbed. The third rule states that neither $S$

nor $I$ can change because the photon does not couple to the spin degrees of freedom. The

remaining rules are consequences of the first three. There are two exceptions: $\Delta J \neq 0$ if

$J = 0 \rightarrow J' = 0$ and $\Delta m_F \neq 0$ if $\Delta F = 0$. 
In the presence of a large magnetic field, \( J \) and \( F \) are no longer good quantum numbers, but the remaining selection rules are still approximately valid (because a photon does not couple to the spin degrees of freedom):

\[
g \leftrightarrow u, \quad \Delta N = \pm 1, \quad \Delta S = 0, \quad \Delta I = 0, \quad \Delta m_F = 0, \pm 1. \tag{4.22}
\]

For the triplet part of the Feshbach molecular state in equation 4.18, \( N = 0 \), so \( m_N = 0 \).

Also, we have already stated that \( m_L = 0 \), \( m_S = m_{s_1} + m_{s_2} = -1/2 - 1/2 = -1 \), \( m_I = m_i_1 + m_i_2 = 0 + 1 = 1 \) and \( m_F = m_N + m_L + m_S + m_I = 0 \). We can excite the Feshbach molecules to any vibrational level \( v' \) in the \( c(1^3\Sigma_g^+) \) potential that is accessible by our lasers. (For STIRAP, we chose \( v' = 20 \) vibrational level because this choice results in a larger Rabi frequency than what we achieve with higher vibrational levels. We are unable to tune our lasers to the wavelengths required for vibrational levels below \( v' = 20 \).) Regardless of the vibrational level, \( N' = 1 \), so \( m'_{N} = 0, \pm 1 \). Because photons do not interact with the spin degrees of freedom, \( m_S \) and \( m_I \) remain unchanged, so \( m'_F = m'_{N} = 0, \pm 1 \). As we show in chapter 6, we can choose which of these levels we couple to by changing the polarization of the photo-association light. With \( \pi \) polarized light, we target only the (lowest lying) \( m'_F = m'_N = 0 \) state, which will serve as the intermediate state \( |e\rangle \) for STIRAP. Similarly, we can target any vibrational level in the \( a(1^3\Sigma_g^+) \) potential. This time, we can target \( N'' = 0 \) and \( N'' = 2 \) states. The laser frequencies required to reach these rotational levels and the associated binding energies (at \( B = 0 \) G) are listed in [63]. For the \( N'' = 0 \) states, \( m_{N''} = 0 \), so only one level is accessible regardless of which of the three excited state levels we choose. (For the \( N'' = 2 \), we presume it is possible to access several states, but only dealt with the \( m_{N''} = 0 \) level in this study.) We believe that the \( v'' = 0 \) level with \( S = 1, I = 1, m_S = -1, m_I = -1, m_N = 0 \) is the lowest lying level in the \( a(1^3\Sigma_g^+) \) and discuss the creation of molecules in this state (and others) and their lifetime in chapter 7.

\[\text{\footnotesize{Actually, we can couple weakly to other } m_S \text{ levels due to the spin-spin and spin-rotation interactions, which we have neglected here. With Feshbach molecules created from a different spin mixture, we believe it is possible to couple strongly to these states, but have not demonstrated this experimentally. For additional information about these interactions, see [20, 99, 108].}}\]
Chapter 5

Three Level Model: for Modeling Autler-Townes and Dark State Spectroscopy

In this chapter, we discuss the three level model, which is a good approximation for the photoassociation process we study using real molecular systems described in the next two chapters. Using this abstraction, we explain the origin of the Autler-Townes splitting, how stimulated Raman adiabatic passage (STIRAP) works and derive the Hamiltonian for a three level system driven by two fields is given by

$$\hat{H}(t) = \hat{H}_0 + \hat{H}_I^p + \hat{H}_I^s$$  \hspace{1cm} (5.1)

where $\hat{H}_0$ is the Hamiltonian for the bare states $|g\rangle$, $|a\rangle$ and $|e\rangle$ shown in Figure 5.1. $\hat{H}_I^p$ is the interaction Hamiltonian associated with the probe field (which couples $|a\rangle$ and $|e\rangle$) and $\hat{H}_I^s$ is the interaction Hamiltonian associated with the Stokes field (which couples $|g\rangle$ and $|e\rangle$). These three Hamiltonians are defined as follows:

$$\hat{H}_0 = \hbar((\omega_{ge} - \omega_{ae})|a\rangle\langle a| + \omega_{ge}|e\rangle\langle e|)$$ \hspace{1cm} (5.2)

$$\hat{H}_I^p(t) = -(\hat{p} \cdot \hat{E}_0^p) \cos(\omega_p t) = \hbar \Omega_p \cos(\omega_p t)(|a\rangle\langle e| + |e\rangle\langle a|)$$ \hspace{1cm} (5.3)

$$\hat{H}_I^s(t) = -(\hat{p} \cdot \hat{E}_0^s) \cos(\omega_s t) = \hbar \Omega_s \cos(\omega_s t)(|g\rangle\langle e| + |e\rangle\langle g|)$$ \hspace{1cm} (5.4)
where $\omega_{ge}$ and $\omega_{ae}$ are the resonance frequencies for the bare states, $\hat{\mu}$ is the dipole moment operation, $\hat{\epsilon}^p$ and $\hat{\epsilon}^s$ are the polarization vectors for the fields, $E_0^p$ and $E_0^s$ are the field amplitudes, $\omega_p$ and $\omega_s$ are the driving frequencies and $\Omega_p = -\langle a| (\hat{\mu} \cdot \hat{\epsilon}^p)|e\rangle E_0^p / \hbar$ and $\Omega_s = -\langle g| (\hat{\mu} \cdot \hat{\epsilon}^s)|e\rangle E_0^s / \hbar$ are the probe and Stokes Rabi frequencies. After we drop the counter-rotating terms, the full Hamiltonian (in matrix form) becomes

$$\hat{H}(t) = \frac{\hbar}{2} \begin{pmatrix} 0 & 0 & \Omega_s e^{-i\omega_st} \\ 0 & 2(\omega_{ge} - \omega_{ae}) & \Omega_p e^{-i\omega_pt} \\ \Omega_s e^{i\omega_st} & \Omega_p e^{i\omega_pt} & 2\omega_{ge} \end{pmatrix}$$  \tag{5.5}$$

where rows (columns) 1, 2 and 3 correspond to $|g\rangle$, $|a\rangle$ and $|e\rangle$, respectively. \footnote{For an alternative derivation of the Hamiltonian in the dressed state picture, see, for example, \cite{12, 63}.}

5.1 **Autler-Townes Splitting and STIRAP**

To explain the Autler-Townes doublet and dark states, it is helpful to get rid of the time dependence by working in the dressed state picture and sufficient (for our purposes) to impose the restriction that $\Delta_p = \Delta_s = 0$. This is because we will always be in this regime for STIRAP and the level shifts due to the probe field will be negligible in our Autler-Townes scans because we will use a weak probe Rabi frequency. With these simplifications, the dressed picture Hamiltonian is given by \cite{31, 52}

$$\hat{H}_D = \frac{\hbar}{2} \begin{pmatrix} 0 & 0 & \Omega_s \\ 0 & 0 & \Omega_p \\ \Omega_s & \Omega_p & 0 \end{pmatrix}$$ \tag{5.6}$$

The eigenvalues of this Hamiltonian are simply $E^0 = 0$ and $E^\pm = \pm \hbar \sqrt{\Omega_p^2 + \Omega_s^2 / 2}$ and its eigenvectors are \cite{12, 40, 52, 63}

$$|a^0\rangle = \cos \theta |a\rangle - \sin \theta |g\rangle, \quad |a^\pm\rangle = \frac{1}{\sqrt{2}} (\sin \theta |a\rangle \pm |e\rangle \pm \cos \theta |g\rangle)$$ \tag{5.7}$$

\footnote{For an alternative derivation of the Hamiltonian in the dressed state picture, see, for example, \cite{12, 63}.}
where \( \tan \theta = \frac{\Omega_p}{\Omega_s} \). Of these three eigenstates, only \( a^0 \) has no component in the \( |e\rangle \) state. This coherent superposition is known as a dark state because it has zero probability of excitation to the \( |e\rangle \) state. This is the reason STIRAP is such an effective method for population transfer. Before we explore this notion further, we will first discuss the Autler-Townes doublet and its value as a preparatory step for STIRAP.
5.1. Autler-Townes Splitting and STIRAP

The probe field which couples the initial (Feshbach molecule) state $|a\rangle$ to an excited state $|e\rangle$. It is characterized by its frequency $\omega_p$, Rabi frequency $\Omega_p$ and detuning $\Delta_p$ with respect to $\omega_{ae}$. Similarly, the Stokes field, which couples the final state $|g\rangle$ to the excited state $|e\rangle$, is characterized by analogous variables: $\omega_s$, $\Omega_s$ and $\Delta_s$. Of the three states, $|e\rangle$ has by far the shortest lifetime or, equivalently, the highest loss rate $\Gamma_{\text{loss}}$, which is on the order of 10 MHz. Hence, we can regard any Feshbach molecules transferred to the $|e\rangle$ state as lost because they are either ejected from the trap or fall stochastically into various bound states. Either way, they become invisible to our imaging light.

Figure 5.1: Three level system dressed by a probe field and Stokes field. The probe field which couples the initial (Feshbach molecule) state $|a\rangle$ to an excited state $|e\rangle$. It is characterized by its frequency $\omega_p$, Rabi frequency $\Omega_p$ and detuning $\Delta_p$ with respect to $\omega_{ae}$. Similarly, the Stokes field, which couples the final state $|g\rangle$ to the excited state $|e\rangle$, is characterized by analogous variables: $\omega_s$, $\Omega_s$ and $\Delta_s$. Of the three states, $|e\rangle$ has by far the shortest lifetime or, equivalently, the highest loss rate $\Gamma_{\text{loss}}$, which is on the order of 10 MHz. Hence, we can regard any Feshbach molecules transferred to the $|e\rangle$ state as lost because they are either ejected from the trap or fall stochastically into various bound states. Either way, they become invisible to our imaging light.
5.1. Autler-Townes Splitting and STIRAP

5.1.1 Autler-Townes Splitting

As we saw above, the two states with non-zero probabilities of excitation to the \(|e\rangle\) state have energy eigenvalues \(E^\pm = \pm \hbar \sqrt{\Omega_p^2 + \Omega_s^2}/2\). In the limit where \(\Omega_s \gg \Omega_p\) (the weak probe regime), we can neglect \(\Omega_p\). Then, the energy splitting between these states is simply \(\hbar \Omega_s\). Hence, as we scan the frequency of the probe laser, we observe two loss features separated by \(\Omega_s/2\pi\) in laser frequency - the Autler-Townes doublet. For our purposes, the significance of this is a simple way to measure \(\Omega_s\) at some Stokes laser power and be then able to calculate the laser power required for any desired \(\Omega_s\). (There is no third loss feature because \(|a^0\rangle\) cannot be excited.)

5.1.2 STIRAP

Stimulated Raman adiabatic passage is a clever sequence used for high efficiency population transfer. It exploits the fact that the projection of the dark state \(|a^0\rangle\) onto the \(|a\rangle\) and \(|g\rangle\) states can be controlled by adjusting the probe and Stokes Rabi frequencies (laser powers). Before describing the laser pulse sequence and the resulting evolution of the dark state, it is helpful to look at the two extremes. When \(|\Omega_s| > 0\) and \(|\Omega_p| = 0\), \(|a^0\rangle = |a\rangle\). Conversely, when \(|\Omega_p| > 0\) and \(|\Omega_s| = 0\), \(|a^0\rangle = |g\rangle\). Since the sample of Feshbach molecules we prepare is the \(|a\rangle\) state, the projection of this state onto the dark state \(\langle a|a^0(t = t_0)\rangle = 1\) if only the Stokes laser is turned on initially. As shown in Figure 5.2, we initially make \(\Omega_s\) large and then slowly increase \(\Omega_p\) while slowly decreasing \(\Omega_s\). In doing so, we allow the dark state to evolve adiabatically from the \(|a\rangle\) state to a coherent superposition of the \(|a\rangle\) and \(|g\rangle\) states without populating the lossy \(|e\rangle\) state (in the absence of decoherence mechanisms). Eventually, \(|\Omega_s|\) goes to zero and \(|\Omega_p|\) reaches its maximum, so the dark state becomes \(|g\rangle\), completing the population transfer. In Figure 5.2, we also show the reverse process that we must perform for detection purposes. While it is possible to detect deeply bound molecules directly via resonantly enhanced multi-photon ionization (REMPI), our apparatus is not equipped for REMPI, which requires a pulsed laser and electrodes inside the vacuum. So, we instead re-create Feshbach molecules via reverse STIRAP after we finish interrogating the deeply bound molecules. For a review of REMPI, we refer the reader to [90].

In the idealized picture we painted above, we left out a number of crucial experimental
5.1. Autler-Townes Splitting and STIRAP

details, which we will now discuss. Specifically, we mentioned that we must allow the
dark state to evolve slowly from \( |a\rangle \) to \( |g\rangle \) to achieve efficient population without explicitly
defining what this means and we neglected to address the issue of laser phase jumps and
other decoherence mechanisms. We can simultaneously address these issues by means of a
simple adiabaticity condition derived in [12, 54, 85]:

\[
\Omega_{\text{eff}} \Delta \tau = \sqrt{\Omega_p^2 + \Omega_s^2} \Delta \tau > 10 \tag{5.8}
\]

where \( \Delta \tau \) is the time during which the probe and Stokes pulses overlap and the numerical
value 10 was determined via numerical simulations and empirically. This formula has the
following three key implications on the experimental realizations of STIRAP:

1. Over the course of the STIRAP sequence, the effective Rabi frequency \( \Omega_{\text{eff}} \) should
remain constant. Since \( \Omega_p \) and \( \Omega_s \) are zero at the beginning and end of the (forward)
STIRAP sequence, respectively, their maxima must be equal to \( \Omega_{\text{eff}} \). As we will
see in the next chapter, the Franck-Condon overlap between the \( |a\rangle \) and \( |e\rangle \) states is
significantly lower than that of any accessible \( |e\rangle \) and \( |g\rangle \) combination. Hence, the
maximum \( \Omega_{\text{eff}} \) we can achieve is approximately equal to the maximum probe Rabi
frequency we can achieve with available laser powers\(^{17}\).

2. The minimum required duration of the sequence is determined by the Rabi frequencies
we can achieve. In previous studies [35, 36, 66, 87, 110, 114, 122, 148, 152, 165], the
highest achieved probe Rabi frequency \( \Omega_p \) has been on the order of \( 2\pi \cdot 10 \text{ MHz} \)
and the lowest was on the order of \( 2\pi \cdot 10 \text{ kHz} \). The optimal pulse durations and
delays that correspond to these Rabi frequencies have typically varied between several
microseconds to several milliseconds. We operate with \( \Omega_p \approx 2\pi 4 \text{ MHz} \) and obtained
the highest transfer efficiency for \( \Delta \tau \approx 10 \text{ \mu s} \).

3. It is implicitly implied that Raman lasers must remain phase-coherent with each other

\(^{17}\)Technically, it is slightly lower than this because we couple the pump and probe beams into the same
fiber with the same polarization. Hence, we must take away some power from the probe field to get the
required Stokes power. However, in practice, this amount is only 10% for the bound-to-bound transitions
with the lowest FC overlap and even less for the rest. Since the \( \Omega_p \propto P_p \), a 10% reduction in power results
in just a 5% reduction in \( \Omega_p \).
throughout the sequence. Relative phase jumps prevent the dark state from evolving adiabatically, cause projections onto the other two eigenstates and ultimately lower the efficiency of the process.

The three points above and the fact that we restricted ourselves to $\Delta_p = \Delta_s$ in this section suggest that we need four pieces of information to implement STIRAP for every three level system we will consider: $\Omega_p$ as a function of the probe laser power, $\Omega_s$ as a function of the Stokes laser power, $\omega_{ae}$ and $\omega_{ge}$\(^\text{18}\). This requires high resolution spectroscopy (the subject of the next chapter) and a robust fitting model for analyzing the data. We derive this model in the next section.

\(^{18}\)It is possible to perform STIRAP with $\Delta_p \neq 0$ and $\Delta_s \neq 0$ as long as the relative detuning $\delta = \Delta_p - \Delta_s \approx 0$. For example, this has been demonstrated by K. K. Ni et al.\(^\text{115}\). However, knowledge of $\omega_{ae}$ and $\omega_{ge}$ is still required for setting $\delta \approx 0$. To maximize the coupling strength, we consistently operate with $\delta \approx \Delta_p \approx \Delta_s \approx 0$. 
5.2 Derivation of an Analytical Fitting Function for Two-Color Photo-Association Data

Our goal in this section is to derive an expression for fitting experimental data of photo-association induced trap loss. Since a molecule that absorbs a photon is lost from the trap, we can solve this problem deriving an expression for the absorption coefficient, which is related to the imaginary part of the first order susceptibility $\chi^{(1)}(-\omega_p, \omega_p)$ (subsection 5.2.1). Then, we will use this to calculate the absorption coefficient and obtain an analytical expression for the number of Feshbach molecules remaining in the trap as a function of the...
5.2. Derivation of an Analytical Fitting Function for Two-Color Photo-Association Data

probe and Stokes detunings and Rabi frequencies and the exposure time \(5.2.2\). This expression will be valid as long as the probe Rabi frequency \(\Omega_p\) is sufficiently weak.

### 5.2.1 Derivation of \(\chi^{(1)}(-\omega_p, \omega_p)\) in the Weak Probe Regime

The expectation value of the polarization density in the atomic cloud for our dressed three-level system is given by the following expressions \([52, 127]\):

\[
P(t) = \varrho \left( \mu_{ae} \rho_{ae} e^{-i\omega_{ae}t} + \mu_{ge} \rho_{ge} e^{-i\omega_{ge}t} + \text{c.c.} \right)
\]

\[
= \frac{1}{2} \epsilon_0 \left( E_p \chi^{(1)}(-\omega_p, \omega_p) e^{-i\omega_{ae}t} + E_s \chi^{(1)}(-\omega_s, \omega_s) e^{-i\omega_{ge}t} + \text{c.c.} \right)
\]

where \(\varrho\) is the particle density, \(\mu_{ae}\) and \(\mu_{ge}\) are dipole matrix elements, and \(\rho_{ea}\) and \(\rho_{eg}\) are elements of the density matrix. Hence,

\[
\chi^{(1)}(-\omega_p, \omega_p) = \frac{2 \varrho \mu_{ae}}{\epsilon_0 E_p^2} \tilde{\rho}_{ea} = -\frac{2 \varrho \mu_{ae}^2}{\epsilon_0 \hbar \Omega_p^2} \tilde{\rho}_{ea}
\]

where \(\tilde{\rho}_{ea} = \rho_{ea} \exp(i\omega_{p}t)\). To obtain an expression for \(\tilde{\rho}_{ea}\), we need to solve the Liouville equation \([31, 127]\):

\[
\dot{\rho} = \frac{i}{\hbar} [\hat{\rho}, \hat{H}] - \gamma \hat{\rho} \leftrightarrow \dot{\rho}_{ij} = \frac{i}{\hbar} [\hat{\rho}, \hat{H}]_{ij} - (\gamma \hat{\rho})_{ij}
\]

where \(\dot{\rho} = \Sigma \hat{P}_{i} |\psi_i\rangle \langle \psi_i|\) is the density operator and \(\gamma\) represents phenomenological decay rates. The coupled differential equations for the off-diagonal elements or coherences of the density matrix are given below:

\[
\dot{\rho}_{ga} = - (\gamma_{ga} - i \delta) \tilde{\rho}_{ga} + i \frac{\Omega_p}{2} \tilde{\rho}_{ge} - i \frac{\Omega_a}{2} \tilde{\rho}_{ea}
\]

\[
\dot{\rho}_{ea} = - (\gamma_{ea} - i \Delta_p) \tilde{\rho}_{ea} + i \frac{\Omega_p}{2} (\rho_{ee} - \rho_{aa}) - i \frac{\Omega_a}{2} \tilde{\rho}_{ga}
\]

\[
\dot{\rho}_{eg} = - (\gamma_{eg} - i \Delta_s) \tilde{\rho}_{eg} + i \frac{\Omega_s}{2} (\rho_{ee} - \rho_{gg}) - i \frac{\Omega_p}{2} \tilde{\rho}_{ag}
\]
5.2. Derivation of an Analytical Fitting Function for Two-Color Photo-Association Data

where $\Delta_s = \omega_{ge} - \omega_s$ is the Stokes, $\Delta_p = \omega_{ae} - \omega_p$ is the probe detuning, $\delta = \Delta_p - \Delta_s$ is the two-photon detuning and we introduced the following substitutions the fast exponential terms: $\rho_{ga} = \tilde{\rho}_{ga} \exp(-i(\omega_p - \omega_s)t)$, $\rho_{ea} = \tilde{\rho}_{ea} \exp(-i\omega_p t)$, $\rho_{eg} = \tilde{\rho}_{eg} \exp(-i\omega_s t)$. Since the $|a\rangle$ state is the only long lived state and the dark state is predominantly the $|a\rangle$ state when $\Omega_s \gg \Omega_p$, the populations must be $\rho_{aa} \approx 1$, $\rho_{ee} \approx \rho_{gg} \approx 0$. Plugging these approximations into 5.13, 5.14, 5.15 yields

$$0 = -(\gamma_{ga} - i\delta) \tilde{\rho}_{ga} + \frac{i\Omega_p}{2} \tilde{\rho}_{ge} - \frac{i\Omega_s}{2} \tilde{\rho}_{ea} \tag{5.16}$$

$$0 = -(\gamma_{ea} - i\Delta_p) \tilde{\rho}_{ea} - \frac{i\Omega_p}{2} - \frac{i\Omega_s}{2} \tilde{\rho}_{ga} \tag{5.17}$$

$$0 = -(\gamma_{eg} + i\Delta_s) \tilde{\rho}_{ge} + \frac{i\Omega_p}{2} \tilde{\rho}_{ga} \tag{5.18}$$

$$\tilde{\rho}_{ea} = -\frac{2i\Omega_p (\gamma_{eg} (\gamma_{ga} - i\delta) + i\gamma_{ga} \Delta_s + \delta \Delta_s + \frac{\Omega_s^2}{4})}{4(\gamma_{ga} - i\delta)(\gamma_{ea} - i\Delta_p)(\gamma_{eg} + i\Delta_s) + (\gamma_{ea} - i\Delta_p)\Omega_p^2 + (\gamma_{eg} + i\Delta_s)\Omega_s^2} \tag{5.19}$$

In the weak probe regime, we can neglect the terms with $\Omega_p^n$ where $n > 1$ in the numerator and denominator. In this approximation, the expression becomes

$$\tilde{\rho}_{ea} = -\frac{2i\Omega_p (\gamma_{ga} - i\delta)}{4(\gamma_{ga} - i\delta)(\gamma_{ea} - i\Delta_p) + \Omega_s^2} \tag{5.20}$$

Finally, plugging this result into equation 5.11 and taking the imaginary part yields\(^\text{19}\)

$$\text{Im}\left\{\chi^{(1)}(-\omega_p, \omega_p)\right\} = \frac{2\mu_{ae}^2}{\varepsilon_0 \hbar} \left( \frac{8\delta^2 \gamma_{ea} + 2\gamma_{ga}(\Omega_s^2 + 4\gamma_{ga}\gamma_{ea})}{|4(\gamma_{ga} + i\delta)(\gamma_{ea} + i\Delta_p) + \Omega_s^2|^2} \right) \tag{5.21}$$

5.2.2 Relation to Number of Trapped Feshbach Molecules

The (probe) absorption coefficient is defined as follows [147]:

$$a(-\omega_p, \omega_p) = 2k_0 \text{Im} \{n(-\omega_p, \omega_p)\} \approx k_0 \chi^{(1)}(-\omega_p, \omega_p) \tag{5.22}$$

\(^{19}\)Note that it is common to include a factor of $1/2$ in front of $\gamma$. To make equation 5.20 conform to this convention, we would simply need to make the following substitutions: $\gamma_{ij} \rightarrow \Gamma_{ij}/2$. 

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where \( n(-\omega_p, \omega_p) \) is the complex refractive index given by

\[
n(-\omega_p, \omega_p) = \sqrt{1 + \chi^{(1)}(-\omega_p, \omega_p)} \approx 1 + \frac{\chi^{(1)}(-\omega_p, \omega_p)}{2}
\] (5.23)

The Beer-Lambert law states that

\[
\frac{\partial I}{\partial z} = \frac{\partial}{\partial t} \left( \frac{\partial N_{\text{photon}}}{\partial V} \right) h\nu = -a(-\omega_p, \omega_p)I
\] (5.24)

Since a Feshbach molecule (FM) that absorbs a photon is either ejected from the trap or rendered invisible to our imaging light, \( dN_{\text{photon}} = dN_{\text{FM}}. \) Next, we substitute \( \Omega_p = -\mu_{ae}E_0^p/\hbar \) and \( I = \epsilon_0 c(E_0^p)^2/2 \) into [5.24] and integrate over volume to get

\[
\frac{dN_{\text{FM}}}{dt} = -\Omega_p^2 \xi N_{\text{FM}}
\] (5.25)

where \( \xi \) is the expression in the parentheses in equation [5.21]. The solution to this ODE is simply

\[
N_{\text{FM}}(t) = N_{\text{FM}}(0) \exp \left( -\Omega_p^2 t \left\{ \frac{8\delta^2 \gamma_{ea} + 2\gamma_{ga}(\Omega_s^2 + 4\gamma_{ga}\gamma_{ea})}{4(\gamma_{ga} + i\delta)(\gamma_{ea} + i\Delta_p) + \Omega_s^2} \right\} \right)
\] (5.26)

This equation will prove to be an indispensable tool for fitting Autler-Townes and dark state scans in chapter 6, where we analyze a collection of spectroscopic measurements to extract the parameters we need as a prelude to STIRAP to \(|g\rangle\) states in the \( a(1^3\Sigma_u^+) \) potential.
Chapter 6

Molecular Spectroscopy at High Magnetic Fields

To create deeply bound molecules in the $a(1^3\Sigma_u^+)$ potential via STIRAP from loosely bound Feshbach molecules, we first needed to use high resolution spectroscopy to find the desired states and determine the probe Rabi frequency $\Omega_p$ and Stokes Rabi frequency $\Omega_s$ as functions of their respective laser powers. The states we are able to access with our Ti:Sapphire lasers are shown in Figure 6.1. In the next chapter, we will use this information to set $\Omega_p \approx \Omega_s$ for the purpose of preserving adiabaticity during STIRAP. To do this, we followed this sequence of steps (not necessarily in this order):

1. Find a suitable $|e\rangle$ (intermediate state) using single color spectroscopy. The requirements are a sufficiently large Frack-Condon (FC) overlap with both $|a\rangle$ (the Feshbach molecule state) and $|g\rangle$ (the final state) and accessibility with available laser sources (a Ti:Sapphire ring laser in our case).

2. Determine the natural linewidth of this state and use a lifetime measurement to get an expression for $\Omega_p$ as a function of laser power using equation 6.1.

3. Find a deeply bound state in the $a(1^3\Sigma_u^+)$ using two color spectroscopy.

4. Use equation 5.26 to deduce the magnitude of $\Omega_s$ as a function of laser power by splitting the excited state into an Autler-Townes doublet and scanning the probe laser near the single color resonance.
5. Verify that the two-photon detuning $\delta = 0$ when both the probe detuning $\Delta_p \approx 0$ and the Stokes detuning $\Delta_s \approx 0$ by doing the same scan in the dark-state regime, where a narrow revival is observed when the two-photon resonance condition is satisfied.
6.1 Single Color Spectroscopy

Since the procedure is the same for the other states we targeted, we summarize the results for these states in a condensed format at the end of this chapter.

6.1 Single Color Spectroscopy

In this section, we discuss items 1 and 2 of the list provided in the introduction: finding and characterizing an excited state to determine if it meets the requirements of STIRAP.

6.1.1 Finding Excited States

As a starting point for finding a suitable excited state, we used two sets of data:

1. The locations of seven vibrational levels in the $1^3\Sigma_g^+$ potential at $B = 0$ Gauss published in [141]. We choose this triplet potential for the following reasons: we knew the approximately locations of the states, our goal was to form molecules in the lower triplet state and our Feshbach molecular state is predominantly a triplet state. Hence, we can obtain much higher probe Rabi frequencies by coupling to excited triplet states than singlet states.

2. An unpublished calculation of FC factors by Xuan Li, which predicts that the $v' = 20$ level has a larger FC factor than any other level we can access with our laser system. (We later confirmed empirically that the maximum Rabi frequency we can achieve is lower for the $v' = 21$ level than the $v' = 20$ level and assumed that the trend would continue for higher vibrational levels.)

By running the broad probe laser frequency scan - in the vicinity of the state locations at $B = 0$ Gauss for $v' = 20$ vibration level - shown in Figure 6.2, we found three manifolds of states at $B = 755$ Gauss. Additional details about this scan are provided in the caption.
6.1. Single Color Spectroscopy

Figure 6.2: Spectroscopy of the \( v' = 20 \) manifold of the \( c(1^3\Sigma_g^+) \) at 755 G. Using the location of this vibrational level at 0 G \[141\] as a starting point, we scanned the frequency of the probe laser over a 12 GHz span. The polarization was aligned approximately diagonally with respect to the quantization axis defined by the magnetic field direction to ensure that we had a mixture of \( \pi, \sigma_+ \) and \( \sigma_- \) light (for the purpose of accessing the maximum possible number of levels) and set the laser power to 170 mW (the maximum we can achieve). Because \( m_S = -1 \) for the initial state, we observe strong coupling to the three \( m_S' = -1 \) levels - the large dip near the middle of the plot (not resolved in this figure due to power broadening) - in this vibrational manifold. The coupling to the higher energy states is weak but not zero because although \( \Delta m_S = 0 \), the total spin projection is not perfectly well defined for these states due to spin-spin and spin-rotation coupling. The three levels we observe in each \( m_S' \) manifold differ in \( m_N' \) and \( m_F' \). For the three (unresolved) states in the broad feature, \( m_I' = 1, m_S' = -1 \), so \( m_F' = m_I' + m_S' + m_N' = m_N' = \{0, +1, -1\} \). The \( m_F' = m_N' = 0 \) state is the lowest lying state, as we show in Figure 6.3.

The coupling to the states in the two higher frequency manifolds is weak, but not zero because although \( \Delta m_S = 0 \), the total spin projection is not perfectly well defined for these states due to spin-spin and spin-rotation coupling. Because we observed strong coupling to the lower energy manifold, we decided to closely examine it. As shown in Figure 6.3, the broad feature actually consists of three states. By rotating the laser polarization to be parallel to the vertically aligned magnetic field to produce exclusively \( \pi \) light, we were able
6.1. Single Color Spectroscopy

to completely "turn off" the two transitions near 230 MHz and obtained a strongly coupled and isolated intermediate state for STIRAP. Next, we discuss several measurements from which we can calculate the Rabi frequency as a function of laser power.

Figure 6.3: Spectroscopy of the $v' = 20, m_S = -1$ levels in the $c(1^3\Sigma_g^+)$ at 755 G. For these levels, $m'_I = 1, m'_S = -1$, so $m'_F = m'_I + m'_S + m'_N = m'_N = \{0, +1, -1\}$ in order of increasing energy. By rotating the laser polarization such that it is parallel to the quantization axis set by the magnetic field, we can turn off the transition to the two higher energy states and obtain an isolated excited state for STIRAP.

6.1.2 Measuring the Rabi Frequency

In the absence of a Stokes field, our model simplifies to that of a two-level system with a characteristic decay rate $\Gamma(\Delta)$:

$$N(t) = N(0) \exp\left(-\frac{|\Omega_p|^2}{\Gamma} t\right) \quad (6.1)$$

In the weak-excitation limit, the Fourier transform of this equation is simply a Lorentzian
6.1. Single Color Spectroscopy

[147]. Hence,

\[ N(\Delta) = \frac{A}{\Delta^2 + \Gamma^2/2} \quad (6.2) \]

where \( A \) is a constant. The measurement of the natural linewidth of the \( |v,N,m_s,m_F\rangle = |20,1,-1,0\rangle \) state is shown in Figure 6.4. Knowing \( \Gamma \), we can obtain \( \Omega_p \) at this power by setting \( \Delta = 0 \), scanning the exposure time and fitting the data to the exponential in 6.1. This is shown in Figure 6.5. Since \( \Omega_p \propto \sqrt{P_p} \), we can now calculate \( \Omega_p \) for any probe power. That is, \( \Omega_p/2\pi = 34.7 \text{ kHz} \sqrt{P_p/(8 \times 10^{-3} \text{ mW})} \). With our maximum probe power of 130 mW, \( \Omega_p/2\pi = 4.4 \text{ MHz} \) - similar to the value used by Ni et al in [114]. As we show in the next chapter, this state is adequate for implementing STIRAP. Next, we find and characterize a set of \( |g\rangle \) states.

[Figure 6.4: Fine scan of the single color feature fit to Lorentzian lineshape at \( B = 755 \text{ Gauss} \). (We later confirmed that the magnetic moment of this state is approximately equal to that of the initial state by repeating this scan at both 700 Gauss and 839 Gauss. In both cases, the \( \nu_p^0 \) was unchanged.) To prevent power broadening, the laser power was set to 4 \( \mu \text{W} \). The exposure time was 1 ms. From the fit, we obtain, \( \nu_p^0 = 366861.2520 \text{ GHz}, \Gamma/2\pi = 6.7 \text{ MHz} \).]
6.2 Two-Color Spectroscopy

In this section, we discuss the remaining three steps in the sequence: finding a deeply bound state in the $a(1^3\Sigma_u^+)\,$ potential at high magnetic fields, using an Autler-Townes spectrum to determine the Rabi frequency of the Stokes laser as a function of power and, finally, confirming that the two-photon resonance condition ($\delta = 0\,$) is satisfied when both $\Delta_p \approx 0\,$ and $\Delta_s \approx 0\,$.

6.2.1 Finding Deeply Bound States

With the probe laser frequency set such that $\Delta_p = 0\,$ with respect to the excited state discussed above (we will refer to it generically as the $|e\rangle\,$ state for brevity here), we induce rapid atom loss; however, when we scan the frequency of the Stokes laser across the two-color resonance (where $\delta = \Delta_p = \Delta_s = 0\,$) we couple the $|e\rangle\,$ and $|g\rangle\,$ states. This AC stark

Figure 6.5: Number of atoms in the $|1\rangle\,$ state as a function of exposure time with $\Delta = 0\,$, $P_p = 8.0 \, \mu W$ at $B = 755\,$ Gauss. At this laser power, $\Omega_p/2\pi = 34.7\,$ kHz.
6.2. Two-Color Spectroscopy

shift shifts or splits the $|e\rangle$ state such that the probe laser is no longer resonant with it resulting in suppression of loss.

To narrow down the search, we use the locations of the hyperfine manifolds at $B = 0$ Gauss, which are tabulated in [63]. If we assume that the states at high fields are located at most a few GHz away, we can quickly find the new states by scanning the frequency of the Stokes laser, $\nu_s$. (We make this assumption because the magnetic moment of these states should be on the order of double the magnetic moment of a $^6\text{Li}$ atom or $2 \times 1.4 \text{ MHz/G}$. With this magnetic moment, the shift at 755 G would be 2.1 GHz.) A broad scan of $\nu_s$ is shown in Figure 6.6. A fine scan of the more deeply bound broad feature is shown in Figure 6.7.

![Figure 6.6: Two-color spectroscopy of the $v'' = 0$ manifold of the $a(1^3\Sigma_u^+)$ potential at 755 G (broad scan). The probe power is set to 50 $\mu$W (just high enough to achieve full loss in the absence of the Stokes laser) with an exposure time of 1000 $\mu$s. A high Stokes laser power of 60 mW is used to broaden the two-color resonances. The polarization of both laser fields is rotated to 45 degrees with respect to the quantization axis set by the magnetic field to ensure that we do not miss any two-color resonances we have the ability to access. (We later confirmed by repeating a portion of this scan that the small feature seen in this plot was an experimental artifact, not a second two-color resonance.)](image-url)
6.2. Two-Color Spectroscopy

Figure 6.7: Two-color spectroscopy of the \( \nu'' = 0 \) manifold of the \( a(1^3\Sigma_u^+) \) potential at 755 G (fine scan). Here, \( P_p = 500 \mu \text{W}, P_s = 12 \text{ mW}, \) the exposure time is 100 \( \mu \text{s} \) and the polarization of both laser fields is rotated to 45 degrees with respect to the quantization axis set by the magnetic field. We only observe a single two-color resonance corresponding to the state with \( m_I'' = 0 \) since our initial Feshbach molecular state is \( m_I = 0 \) and the photon absorption does not couple to the nuclear spin. The other two nearby states have a different nuclear spin projection \( m_I = \pm 1 \). From the Gaussian fit, we obtain \( \nu_0^S = 375836.0223 \text{ GHz} \).

6.2.2 Dark State Spectroscopy

Having found \( \nu_0^p \) and \( \nu_0^S \) using single color and two-color spectroscopy, it is useful to confirm that these frequencies are accurate by setting the Stokes laser to resonance and scanning the probe laser to produce a signature dark state spectrum. (This technique is also useful for accurately measuring the binding energies of bound states as demonstrated in \([109, 166]\).) When \( \Delta_p = \Delta_s = \delta = 0 \), we expect to see almost complete suppression of loss or electromagnetically induced transparency (EIT) provided that \( \Omega_s \gg \Omega_p \). (If \( \Omega_s \) is too large, however, we will instead observe an Autler-Townes doublet. Empirically, we found that \( \Omega_s/\Omega_p \approx 10 \) produced the desired spectrum. Before determining the laser power dependence of \( \Omega_s \), finding the correct power ratio must be done empirically.) A dark state
scan for the excited and bound levels discussed above is shown in Figure 6.8. We fit the data to equation 5.26\textsuperscript{20} to extract $\Delta_s/2\pi = 0.11$ MHz. This shows that the aggregate error of our single color and two color measurements was about 0.1 MHz. As we will show in the next chapter, the width of our STIRAP features is 0.2-0.3 MHz, so being accurate to even $\pm 1$ MHz and scanning over a 2 MHz span would be sufficient.

![Figure 6.8: Dark state spectrum at 755 G with $P_p = 8$ mW, $P_s = 15$ mW, an exposure time of 10 $\mu$s and a trapping power of 140mW. The excited state $|e\rangle = |v, N, m_s, m_F\rangle = |20, 1, -1, 0\rangle$ and the deeply bound state $|g\rangle$ is the lowest lying $v = 0$, $N = 0$ level we can access via this excited state in the $a(1^3\Sigma_u^+)$ potential. From the fit, we extract $\Delta_S/2\pi = 0.11$ MHz.](image)

6.2.3 Autler-Townes Spectroscopy

The final pre-requisite for STIRAP is finding $\Omega_s$ as a function of laser power. We need this information to set $\Omega_s \approx \Omega_p$ - a requirement for efficient STIRAP. Having confirmed

\textsuperscript{20}Technically, equation 5.26 is not completely valid because the probe power used for this scan is not sufficiently weak. While some of the calculated fit parameters may be inaccurate because of this, the parameter we are interested in here $\Delta_s$ depends only on the symmetry of the spectrum with respect to $\nu_p - \nu_p^0 = 0$. Hence, the equation is still adequate for this purpose.

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that the measured $\nu_p^0$ and $\nu_s^0$ are sufficiently accurate for our purposes via the dark state scan above, we can repeat this scan with a lower probe power to see an the Autler-Townes doublet. As we showed in the previous chapter, when the Stokes laser is on resonance, the excited state splits symmetrically and the Stokes Rabi frequency $\Omega_s$ is equal to this energy gap (in angular frequency units). An Autler-Townes scan - for the same $|e\rangle$ and $|g\rangle$ states as the dark state scan in Figure 6.8 - is shown in Figure 6.9. From the fit to equation 5.26 we extract $\Omega_s/2\pi = 22.51 \text{ MHz}$ when $P_s = 10 \text{ mW}$. Since $|\Omega_s(P_s)| \propto \sqrt{P_s}$, $\Omega_s(P_s)/2\pi = 22.51 \text{ MHz}\sqrt{P_s/(10 \text{ mW})}$.

![Figure 6.9: Autler-Townes spectrum at 755 G with $P_p = 450 \mu\text{W}, P_s = 10 \text{ mW},$ an exposure time of 20 $\mu$s and a trapping power of 140mW. The excited state $|e\rangle = |v, N, m_s, m_F\rangle = |20, 1, -1, 0\rangle$ and the deeply bound state $|g\rangle$ is the lowest lying $v = 0, N = 0$ level we can access via this excited state in the $a(1^3\Sigma_u^+)$ potential. From the fit, we extract $\Omega_s/2\pi = 22.51 \text{ MHz}$.](image-url)
6.3 Tabulated Transition Frequencies and Coupling Strengths of All Considered Levels

Above, we established a straightforward procedure for finding excited and deeply bound states and for characterizing the associated transition strengths. We followed the same sequence of steps for a number of other levels and summarize the results that are relevant for STIRAP in tables 6.1 and 6.2. Since the measured $\Omega_p$ and $\Omega_s$ values are dependent on optical alignment and the accuracy of the laser power measurement, the values shown below should be considered approximate. The error could be as high as a factor of 2. This level of accuracy is sufficient for implementing STIRAP because it is possible to see a signal provided that the Stokes laser power is in the correct order of magnitude. (The probe power is always maximized.) As long as we can obtain a weak signal as a starting point, it is trivial to scan the amplitude of a laser over one order of magnitude to improve the transfer efficiency. In the tables, the Rabi frequencies we provide were extrapolated to a laser power of 1 W for consistency. The data in appendix A in conjunction with these values can be used to calculate the expected Rabi frequencies for an arbitrary intensity. Having made these prerequisite measurements, we now proceed to discussing our implementation of STIRAP and the lifetimes of deeply bound $^6$Li$_2$ triplet molecules.

<table>
<thead>
<tr>
<th>$\nu'$</th>
<th>$N'$</th>
<th>$B$ (G)</th>
<th>$\nu_p$ (GHz)</th>
<th>$\Omega_p(P_p = 1 \text{ W})/2\pi$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1</td>
<td>700, 755, 839</td>
<td>366861.2522</td>
<td>12.3</td>
</tr>
<tr>
<td>21</td>
<td>1</td>
<td>755</td>
<td>371574.5777</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Table 6.1: Probe laser frequencies and Rabi frequencies for two excited states.
### 6.3. Tabulated Transition Frequencies and Coupling Strengths of All Considered Levels

<table>
<thead>
<tr>
<th>$\nu'$</th>
<th>$N'$</th>
<th>$\nu''$</th>
<th>$N''$</th>
<th>$B$ (G)</th>
<th>$\nu_s$ (GHz)</th>
<th>$\Omega_s(P_s = 1\text{ W})/2\pi$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>755</td>
<td>375836.0223</td>
<td>135.9</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>700</td>
<td>375780.2835</td>
<td>135.9</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>700</td>
<td>372303.578</td>
<td>4226.1</td>
</tr>
<tr>
<td>21</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>700</td>
<td>372303.578</td>
<td>3415.3</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>5</td>
<td>0</td>
<td>700</td>
<td>368668.3772</td>
<td>342.1</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>6</td>
<td>0</td>
<td>700</td>
<td>367898.7643</td>
<td>1316.1</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>7</td>
<td>0</td>
<td>700</td>
<td>367353.2512</td>
<td>779.4</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>8</td>
<td>0</td>
<td>700</td>
<td>367025.5601</td>
<td>803.6</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>9</td>
<td>0</td>
<td>755</td>
<td>366885.6354</td>
<td>425.6</td>
</tr>
</tbody>
</table>

Table 6.2: Stokes laser frequencies and Rabi frequencies for five deeply bound states.
Chapter 7

Creation and Lifetimes of Deeply Bound $^6\text{Li}_2$ Molecules

In this chapter, we demonstrate coherent population transfer from a loosely bound Feshbach molecular state of $^6\text{Li}$ (recall that the $|\text{FM}\rangle$ is an s-wave molecule, $N'' = 0$, with both spin singlet and triplet character) to more deeply bound states in the triplet $a(3\Sigma^+_u)$ potential. As the intermediate state $|e\rangle$, we use the lowest lying $v' = 20, N' = 1$ level in the triplet $1\Sigma_g^+$ potential [131]. We also discuss the measured lifetimes of deeply bound state to gain insight into the mechanisms behind the chemical reactions that induce trap loss.

In the previous chapter, we tabulated the laser frequencies and Rabi frequencies (as a function of laser power) for several optical transition of interest for STIRAP to the deeply bound levels in the $a(1\Sigma^+_u)$ potential. To implement STIRAP, we simply needed to switch from the square pulses we used for two-color spectroscopy to appropriately timed adiabatic pulses (see chapter 5 for details) whose amplitudes correspond to (approximately) equal Rabi frequencies. Since we have no means of detecting deeply bound molecules directly, we use the reverse pulse sequence to convert the deeply bound molecules back into Feshbach molecules (see Figure 5.2). In addition, we use fields resonant with the atomic transitions, which originate from the same optical source as the light we use for absorption imaging at high magnetic fields, to expel any $|1\rangle$ or $|2\rangle$ state atoms (paired or not) that remain after the forward STIRAP sequence.
7.1 Experimental Implementation and Optimization of STIRAP

To create deeply bound molecules and later re-create Feshbach molecules, we executed a specific sequence of steps for every deeply bound $|g\rangle$ state. First, we used the data from the previous chapter to calculate the laser powers for which $\Omega_{s}^{\text{max}} = \Omega_{p}^{\text{max}}$. We set the maxima of the Gaussian pulses (programmed via the Stanford Research DS345 arbitrary waveform generators) to these values through a combination of manual half-wave-plates rotations and programmed pulse amplitude settings. Second, we choose and set a pulse width that satisfies the adiabaticity condition for STIRAP (equation 5.8). Influenced by the similarities between our system and that of Ni et al in [114], we made our initial attempts with their optimal pulse width and delay - 20 µs. We later found that the optimal values for both the pulse width and delay for our system is 10 µs. Third, it is crucial to ensure that the Feshbach molecules we image at the end of a forward and reverse STIRAP sequence (see Figure 5.2) had been deeply bound molecules prior to the reverse STIRAP sequence. The alternatives are free atoms and Feshbach molecules that were neither associated into deeply molecules nor lost from the trap as a result of excitation to the $|e\rangle$ state. This could happen due to imperfect beam pointing for Feshbach molecules and would be guaranteed to happen for free atoms that photo-associate on a 100-1000 ms time scale. The solution is to use light that is far off-resonant for the deeply bound molecules and resonant for the free atoms and the Feshbach molecules (for both the $|1\rangle$ state and the $|2\rangle$ state) to induce loss after the forward STIRAP sequence. Conveniently, our imaging light for high magnetic fields meets these requirements and two 5 µs pulses (one for each state) are sufficient for accomplishing our objective. Fourth, the STIRAP resonance is very narrow and prone to shifting slightly for a variety of experimental reasons (e.g. alignment), so we normally set the frequency of the Stokes laser to the resonance frequency for the $|e\rangle$ state to $|g\rangle$ state transition and scan the probe laser in fine steps (e.g. 50 kHz) over a several MHz span around the measured $|a\rangle$ to $|e\rangle$ resonance frequency. An example of a STIRAP lineshape (average of 10 runs) is shown in Figure 7.1 for a $v'' = 9 \ N = 0$ level. Fifth, we set the probe laser frequency to the optimal value, where the two-photon resonance condition is satisfied, and scan the
amplitude of the Stokes laser to optimize the STIRAP efficiency. (Empirically, we found that the STIRAP efficiency is not very sensitive to this parameter as long as it is above a threshold and not exceedingly high.) This step allows us to correct for slight experimental drifts and measurement uncertainties (with regards to Rabi frequencies) in chapter 6. This concludes our sequence for achieving and optimizing STIRAP.

Figure 7.1: Feshbach molecule number after a forward and reverse STIRAP sequence to the lowest lying $v'' = 9$ level as a function of the probe laser’s frequency. To transfer the population from the Feshbach molecule state, $|a\rangle$, to the deeply bound state, $|g\rangle$, we first trigger the Stokes pulse such that the dark state, $|DS\rangle = |a\rangle$ initially. Then, as we slowly turn on the probe laser and simultaneously lower the Stokes laser’s power, the dark state adiabatically evolves into the final (deeply bound) state, $|g\rangle$, when the two-photon detuning $\delta$ is close to zero. At this point, we turn on a field that is resonant with the atomic transition for the $|1\rangle$ state for 5 $\mu$s and then a second field that is resonant with the atomic transition for the $|2\rangle$ state for 5 $\mu$s to expel any residual atoms or Feshbach molecules from the trap. Finally, we repeat this sequence in reverse to re-create and detect the initial Feshbach molecule state.

After going through the procedure described above, we achieve a round trip STIRAP efficiencies of $\approx 50\%$ or (presumably) $\approx 70\%$ each way. We are still investigating why it is
not higher. The possibilities include the following:

1. The efficiency is actually higher than the apparent efficiency because molecules that form in other deeply bound states (as a result of spontaneous emission from the $|e\rangle$ state) collide with the Feshbach molecules after reverse STIRAP inducing loss. (The undesired molecules that may be forming would also collide with deeply bound molecules. However, by triggering the reverse sequence shortly after the forward sequence ends, we can minimize the interaction time and the resulting losses.) The impact of this effect would be diminished if we minimized the time these molecules have to collide with Feshbach molecules by imaging the Feshbach molecules immediately after reverse STIRAP. Currently, there is a $\approx 100$ ms delay between these events - more than enough time for collisions to take place. If we make the assumptions that all of our losses are caused by this effect and that any collision between a Feshbach molecule and a deeply bound molecule results in loss, then it is easy to show that our one way STIRAP efficiency could be as high as 85%.

2. There could be residual laser phase noise that leads to decoherence and results in populating the short lived $|e\rangle$ state. As we saw in chapter 3, we were unable to bring the phase noise of our photo-association laser down to the shot noise level for large frequency offsets. Mitigating this problem would require faster AOM actuators or extensive changes to the laser system (either purchasing lasers with no phase noise outside the bandwidth of our AOM-based OPLL or constructing an OPLL based on faster actuators).

3. Projective losses of the dark state can occur due to the small discontinuous steps at the beginning and end of the Gaussian pulses shown in Figure 7.2. Based on the size of the intensity jumps (6-7% of the amplitude), we estimate that the projective losses are approximately 20%. We have recently replaced our Gaussian pulses with Blackman pulses that should eliminate this problem.

4. Intensity noise in the photo-association fields. In the derivation of equation 5.8, it is assumed that the pulses are smooth. If high frequency intensity noise modulates the smooth pulse envelope, the pulses may not be adiabatic. The best way to mitigate
7.1. Experimental Implementation and Optimization of STIRAP

Figure 7.2: Gaussian pulses used for STIRAP. Because these pulses are truncated, we suffer from projection losses at four instances during the sequence. We estimate that our round trip efficiency drops by about 20% in total as a result of these losses. By using Blackman pulses, we can eliminate the discontinuities while preserving adiabaticity during the rest of the sequence. For a deeply bound molecule lifetime measurement, we typically use RF switches to quickly turn off the RF applied to both the shutter AOM and the pulse shaping AOM to prevent leakage of photo-association light. Leakage from the Stokes laser would result in single-color photo-association of deeply bound molecules to the excited state and could significantly impact the apparent lifetime. Leakage from the probe laser should not effect the deeply bound molecules, but we shutter it completely as well as a precaution. For every measurement, we also trigger two ≈ 5 µs long pulses (not shown) resonant with the |1⟩ and |2⟩ states, respectively, but invisible to the deeply bound molecules. These pulses eject any residual atoms or Feshbach molecules immediately after forward STIRAP sequence. In the absence of the STIRAP pulses, zero Feshbach molecules show up in the absorption image thus confirming deeply bound molecule formation.

this would be to produce the pulses via negative feedback rather than the open loop method we have been using. We believe this is unlikely to be the dominant problem because the pulses appear smooth on an oscilloscope trace.

5. Noise and inhomogeneity in the magnetic field. Differences in the magnetic moments of the states involved in STIRAP give rise to a two-photon resonance condition that
depends on both time and space. Luckily, we observed that the shift in the two photon resonance is \(< 1\) MHz when we change the field from \(700\) G to \(755\) G. If we assume that it is \(1\) MHz (an upper bound), then the shift is about \(20\) kHz/G. Since the STIRAP lineshape is about \(200\) kHz wide, the temporal noise or field inhomogeneity would need have to be quite large to produce a noticeable effect because it would take a \(\approx 5\) G shift to “break” the two-photon resonance. Since we assumed a generous upper bound for the differential magnetic moment, this number is probably much higher than \(5\) G for our sample. It is therefore unlikely that this has a significant impact on our STIRAP efficiency. We mention this factor for completion because it is a serious concern for STIRAP that involves states with radically different magnetic moments. For example, it is discussed in the context of RbCs in \([30]\).

6. Since our CODT is created by Gaussian beams, the AC Stark shift on the Feshbach molecules in the wings of the trap is different than that of the atoms near the center. This is also true for the deeply bound molecules we create. As a result, the two-photon resonance condition is not satisfied for the atoms in the wings and the STIRAP efficiency may be reduced. (This would also imply losses due to the creation of additional molecules in other deeply bound states.) Briefly turning off the CODT during STIRAP and reverse STIRAP would reveal the severity of this problem and may noticeably improve our round-trip STIRAP efficiency.

7.2 Derivation of the Molecule Lifetime Model

To extract physically meaningful information from the deeply bound molecule lifetime measurements presented in the next section, we first need to derive a model to which we can fit the data. We begin with the time derivative of the cloud density distribution, which is given, up to third order, by \([61]\)

\[
\dot{n}(r, t) = -\alpha n(r, t) - \beta n^2(r, t) - \gamma n^3(r, t)
\]  

(7.1)
7.2. Derivation of the Molecule Lifetime Model

where \( n(r,t) \) is the density distribution of the cloud at time \( t \) and \( \alpha \geq 0, \beta \geq 0 \) and \( \gamma \geq 0 \) are the rate constants for one-, two- and three-body losses, respectively. Experimentally, it would be challenging for us to accurately capture the spatial distribution of the deeply bound molecules, especially for very dilute samples. It would be advantageous to mold this equation into a form that would enable us to use the total atom number as the primary observable. Hence, we integrate equation (7.1) over all space to get

\[
\dot{N}(t) = -\alpha N(t) - \beta \int_{-\infty}^{\infty} n^2(r,t) d^3r - \gamma \int_{-\infty}^{\infty} n^3(r,t) d^3r
\]

(7.2)

To obtain \( \alpha, \beta \) and \( \gamma \) from this form of the equation, we would still need the density distribution (unless \( \beta = \gamma = 0 \)). We can simplify this equation if we assume that the deeply bound molecules move around the trap volume (and redistribute) much faster than their half-life such that \( n(r,t) \) is simply a 3-dimensional Gaussian distribution with a time varying amplitude (for a thermal cloud) or

\[
n(r,t) = n_0(t) \exp \left( -\frac{x^2}{2\sigma_x^2} \right) \exp \left( -\frac{y^2}{2\sigma_y^2} \right) \exp \left( -\frac{z^2}{2\sigma_z^2} \right)
\]

(7.3)

where \( \sigma_i = \omega_i^{-1} \sqrt{k_B T/m_{\text{Li}_2}} \) \(^{21}\) With this ansatz, we can easily evaluate the integrals in equation (7.2) to get

\[
\int_{-\infty}^{\infty} n(r,t) d^3r = 2\sqrt{2\pi^{3/2}} \sigma_x \sigma_y \sigma_z n_0(t) = N(t)
\]

(7.4)

\[
\int_{-\infty}^{\infty} n^2(r,t) d^3r = \pi^{3/2} \sigma_x \sigma_y \sigma_z n_0^2(t) = \frac{1}{8\pi^{3/2} \sigma_x \sigma_y \sigma_z} N^2(t)
\]

(7.5)

\[
\int_{-\infty}^{\infty} n^3(r,t) d^3r = \frac{2}{3} \sqrt{\frac{2}{3}} \pi^{3/2} \sigma_x \sigma_y \sigma_z n_0^3(t) = \frac{1}{24\sqrt{3} \pi^{3/2} \sigma_x^2 \sigma_y^2 \sigma_z^2} N^3(t)
\]

(7.6)

\(^{21}\)Of course, this simplifying assumption is the most accurate for short hold times because the distribution shape at time \( t \) is only partially determined by that of the initial Feshbach molecule cloud (the initial condition to the differential equation). Since the molecule-molecule interactions are different for the \( |g \rangle \) state, the distribution could evolve in time away from the initial distribution. A more sophisticated analysis would involve capturing the shape of the distribution for every experimentally measured hold time.
7.2. Derivation of the Molecule Lifetime Model

Plugging these expressions into equation (7.2) yields

$$\dot{N}(t) = -\alpha N(t) - \frac{\beta}{8\pi^{3/2}\sigma_x\sigma_y\sigma_z} N^2(t) - \frac{\gamma}{24\sqrt{3}\pi^{3}\sigma_x^2\sigma_y^2\sigma_z^2} N^3(t)$$

(7.7)

$$= -\alpha' N(t) - \beta' N^2(t) - \gamma' N^3(t)$$

(7.8)

While it is possible to solve this differential equation analytically, the solution for an initial molecule number $N_0 = N(0)$ is a transcendental equation. Rather than solve the root finding problem, we chose to solve the ODE numerically using the module “ode” in scipy.

So far, we have assumed that the atomic cloud follows Maxwell-Boltzmann statistics. However, this solution would be invalid if the molecules (which are composite Bosons) form a molecular Bose-Einstein condensate (mBEC). In terms of the chemical potential $\mu$, trapping potential $U(r)$ and coupling constant from the Gross-Pitaevskii equation $g$ [62, 126], the density distribution of a BEC is given by [80]

$$n(r) = \frac{\mu - U(r)}{g} \Theta(\mu - U(r))$$

(7.9)

where

$$\mu = \frac{\hbar\bar{\omega}}{2} \left( \frac{15aN}{a_{ho}} \right)^{2/5}$$

(7.10)

$$U(r) = \frac{1}{2}m\bar{\omega}^2r^2$$

(7.11)

$$g = \frac{4\pi\hbar^2a}{m}$$

(7.12)

and $\Theta(x)$ is the Heaviside function. In equations 7.10, 7.11 and 7.12, $U(r)$ is assumed to be a harmonic potential with a mean trap frequency $\bar{\omega} = (\omega_x\omega_y\omega_z)^{1/3}$, $a$ is the scattering length and $a_{ho} = \sqrt{\hbar/m\bar{\omega}}$. If we again assume that $n(r, t) = n_0(t)n(r)$, we get the following result:

$$\dot{N}(t) = -\alpha N(t) - \beta \frac{15^{2/5}(aN(t))^{7/5}}{14\pi a^2 \left( \frac{\hbar}{m\bar{\omega}} \right)^{6/5}} - \gamma \frac{5^{4/5}(aN(t))^{9/5}}{56\sqrt{3}\pi^2a^3 \left( \frac{\hbar}{m\bar{\omega}} \right)^{12/5}}$$

(7.13)

Given that $\sigma_i \propto \omega_i^{-1}$ in equation 7.7, the two body loss term in this equation is propor-
7.3. Deeply Bound Molecule Lifetime Measurements

The functional similarity between these terms, if we have a mixture of a BEC and a thermal cloud, it would be very difficult to determine whether we are observing two body or three body losses and even more difficult to reliably extract the values of $\beta$ and $\gamma$ from the data. Because $\beta' \propto \bar{\omega}^6$ and $\gamma' \propto \bar{\omega}^{12}$ for a thermal sample (and the difference is less obvious for a mBEC), it is advantageous to work with a thermal sample and avoid forming a mBEC. The condensed fraction is given by [80]

$$\frac{N_{\text{BEC}}}{N_{\text{total}}} = 1 - \left(\frac{T}{T_c}\right)^3$$  \hspace{1cm} (7.14)

where $T_c$ is the critical temperature:

$$T_c \approx 4.5 \left(\frac{\bar{\omega}/2\pi}{100 \text{ Hz}}\right) N^{1/3} \text{nK}$$  \hspace{1cm} (7.15)

Hence, to have a purely thermal sample, we must operate above $T_c$. Although we intended to operate in the regime where $T > T_c$, our quest for increasing the Feshbach molecule fraction by evaporating to lower trap depths may have inadvertently led us to the mBEC regime. For this reason, we extract decay rates for both cases (thermal and mBEC) in the analysis that follows. While neither method will yield accurate values of the rate constants when the mBEC fraction is neither 0 nor 1 (unless the dominant loss mechanism is one-body loss), we can still gain valuable insight from this analysis and use the results to guide future measurements.

7.3 Deeply Bound Molecule Lifetime Measurements

As we saw in chapter 4, the $N'' = 0$ deeply bound states we can access (when $|a\rangle = |FM\rangle$ is the Feshbach molecule state specified by equation 4.18) via STIRAP have $m_I'' = 1$, $m_S'' = -1$, $m_N'' = 0$, and $m_F'' = 0$. No other state should be strongly coupled to our intermediate state $|e\rangle$. This is also true for the only $N'' = 2$ level we accessed because we are using $\pi$ polarized fields ($m_N' = m_N''$). Since every state can be specified by this common set of
7.3. Deeply Bound Molecule Lifetime Measurements

quantum numbers and \(v''\) and \(N''\), we will omit, for brevity, the common part of the state labels for the remainder of this section.

Our goal is to gain insight into the physics behind the decay of the molecules. While we will be unable to definitively identify the reaction mechanism responsible for the loss of the deeply bound molecules we create without theoretical support, it is possible to eliminate some candidates by determining experimentally whether the loss rate is dominated by a one-, two- or three-body mechanism. For most of the ultracold alkali molecules that have been probed experimentally to date, the dominant loss mechanism has been two-body losses \([128]\). If this is also the case for \(^6\text{Li}_2\), then the reaction mechanisms for the ground triplet state are

\[
\text{Li}_2(a^3\Sigma^+) + \text{Li}_2(a^3\Sigma^+) \rightarrow \text{Li}_3 + \text{Li} \quad (7.16)
\]

\[
\text{Li}_2(a^3\Sigma^+) + \text{Li}_2(a^3\Sigma^+) \rightarrow \text{Li}_2(X^1\Sigma^+) + \text{Li}_2(T) \quad (7.17)
\]

where \(T\) could be \(X^1\Sigma^+\) or \(a^3\Sigma^+\) \([155]\). For higher vibrational levels, rovibrational relaxation is another possibility.

We now attempt to deduce whether one-, two- or three-body losses dominate by taking advantage of the trap frequency dependence of the coefficients in equations \(7.7\) and \(7.13\). One way to do this is to compare the loss rate in a single arm ODT to that in a CODT \(^{23}\). The axial trap frequency for a single arm ODT is approximately 20 times lower than the lowest trap frequency component for a CODT with our crossing angle \([63]\) if the total trapping power is unchanged. As a result, we expect a factor of \(\sqrt{2} \times \sqrt{20} \approx 4\) reduction in the effective trap frequency \(\bar{\omega}\), where the \(\sqrt{2}\) comes from drop in the trapping power. (The optical power in the second trapping arm remained unchanged.) Figure \(7.3\) shows a lifetime measurement for the \(v'' = 0, N'' = 0\) state in a single arm ODT and a CODT. Details are provided in the caption. Since the loss rate changed significantly, the dominant loss mechanism is clearly not a one-body process. For a thermal cloud, the decay could not be due to a three-body process because the difference between the two data sets would be even more dramatic, according to equation \(7.7\). For a mBEC, we cannot reach this conclusion \(^{23}\). Since the photo-association beam is overlapped with the second arm, we had to misalign the CODT such that the first arm was not overlapped with the MOT and the pointing of the second arm was unchanged.
Figure 7.3: Lifetime measurements for the lowest hyperfine state of the $v'' = 0$, $N'' = 0$ ro-vibrational level in a single arm ODT and a CODT (SPI laser). For each measurement, we used two models for fitting the data: the solutions to equations 7.7 (solid lines) and 7.13 (dotted lines) with $\alpha = \gamma = 0$. Since we did not measure the trap frequency for the single arm trap, we assumed that $\omega_r \approx \omega_x = \omega_y$ and that the axial frequency is a factor of $20 \pm 5$ lower in the single arm trap, for a fixed trapping power. (These assumptions are justified in [63].) The $\beta$ coefficients determined from these least squares fits and several additional parameters are shown in table 7.1 and agree within the bounds of the uncertainties in both cases. The agreement is significantly better when we make the assumption that the sample is a mBEC (Thomas-Fermi distribution).

simply by inspection. Since $\gamma$ is a constant, we should be able to extract the same value from both data sets or, equivalently, we expect $\gamma_{\text{SA}}/\gamma_{\text{cross}} = 1$, where the subscripts SA and cross refer to a single arm ODT and a CODT, respectively. Since we used the same magnetic field for both measurements, $\gamma_{\text{SA}}/\gamma_{\text{cross}} = (\gamma'_{\text{SA}}/\gamma'_{\text{cross}}) (\bar{\omega}_{\text{cross}}/\bar{\omega}_{\text{SA}})^{12/5} = 3.8 \pm 1.8 > 1$, where $\gamma'_{\text{SA}}$ and $\gamma'_{\text{cross}}$ were determined by fitting the data to a pure three-body decay law for a mBEC. Thus, the dominant loss mechanism is a two-body process and we can assume that one- and three-body losses are negligible ($\alpha = \gamma = 0$ in equations 7.7 and 7.13). This simplification allows us to extract the two-body loss rate $\beta$ by fitting the solutions to these differential
7.3. Deeply Bound Molecule Lifetime Measurements

equations to the $v^{\prime\prime} = 0$, $N^{\prime\prime} = 0$ data in Figure 7.3, the $v^{\prime\prime} = 0, 5, 9$, $N^{\prime\prime} = 0$ data in Figure 7.4 and several additional data sets for other rovibrational levels. To differentiate between the two-body loss rate predicted assuming a pure Maxwell-Boltzmann (MB) distribution or a pure Thomas-Fermi (TF), we will refer to them as $\beta_{\text{MB}}$ and $\beta_{\text{TF}}$, respectively. These coefficients and other relevant parameters for all of the states we populated are shown in table 7.1. First, it is clear that $\beta_{\text{MB}}$ is approximately an order of magnitude larger than $\beta_{\text{TF}}$ for every state. Moreover, if we assume that every close range collision leads to chemically induced loss, then the temperature independent loss rate for s-wave collisions is approximately

$$\beta_{\text{th}} = 2\pi \left( \frac{2\hbar C_6}{\mu^3} \right)^{1/4} = 3.7 \times 10^{-10} \text{ cm}^3/\text{s} \quad (7.18)$$

where $C_6^{\text{Li}_2} \approx 4 \times C_6^{\text{Li}} = 4 \times 1389 = 5556$ a.u. [44, 170] and $\mu$ is the reduced mass of $^6\text{Li}_2$ [73, 128]. This estimate of the upper bound for the loss rate is also an order of magnitude smaller than the values of $\beta_{\text{TF}}$ we calculated and makes their credibility highly questionable. With the exception of the entry in the third row (which is inconsistent with rows one and two), the values of $\beta_{\text{TF}}$ are approximately equal within the bounds of the uncertainties suggesting that we may be in the regime where every collision leads to loss. It is important to emphasize that the $v^{\prime\prime} = 0$, $N^{\prime\prime} = 0$ state - which is different from all the other states because it is the lowest energy (triplet) state and cannot decay by rovibrational relaxation mechanisms - is not exempt from this trend. However, we cannot definitively conclude that the cloud was a mBEC. According to our calculations, our cloud could not have been fully condensed for any of these measurements. (The large uncertainty in the condensed fraction is due to the large uncertainty in our temperature and trapping power measurements. Using a time-of-flight measurement to determine the temperature and measuring the trap frequencies at the trapping power used for the measurement would alleviate this problem.) making these preliminary results inconclusive. For this reason, we propose a sequence of steps for unambiguously determining the rate constants in chapter 9.
7.3. Deeply Bound Molecule Lifetime Measurements

Figure 7.4: Lifetime measurements of the lowest hyperfine states of three ro-vibrational levels in the $a(\Sigma^+_u)$ potential. All three levels have $N'' = 0$ and vary in $v''$, which takes on the values 0, 5 and 9. For these measurements, we used a CODT created by the IPG laser. Again, we used two models for fitting the data: the solutions to equations 7.7 (solid lines) and 7.13 (dotted lines) with $\alpha = \gamma = 0$. The $\beta$ coefficients determined from these least squares fits and several additional parameters are shown in table 7.1.
7.3. Deeply Bound Molecule Lifetime Measurements

Table 7.1: Two body loss rate coefficients and related quantities for several \( v'' \) and \( N'' \) states under two assumptions: the cloud is either a pure thermal MB distribution or a pure Bose-condensed sample with a Thomas-Fermi distribution. We denote the loss rates \( \beta_{MB} \) and \( \beta_{TF} \), where the subscripts refer to Maxwell-Boltzmann and Thomas-Fermi, respectively. At 700 G and 755 G, the scattering lengths are \((3.15 \pm 0.10)a_0 \times 10^3\) and \((1.49 \pm 0.10)a_0 \times 10^3\), respectively [117, 119]. These values were used for computing \( \beta_{TF} \). The column title “Conf.” refers to the configuration of the optical dipole trap. The first letter refers to the trapping laser and could be S for SPI and I for IPG. The second letter denotes whether the trap was a CODT (C) or a single arm trap (O). The trap frequencies and temperatures were calculated based on the data in appendix B and the forced evaporation scaling law (equation 2.13). Using these quantities and upper and lower bounds for the Feshbach molecule number, we calculate a range for the condensed fraction. Finally, we use equations 7.7 and 7.13 we determined \( \beta_{MB} \) and \( \beta_{TF} \).

<table>
<thead>
<tr>
<th>( v'' )</th>
<th>( N'' )</th>
<th>( B ) (G)</th>
<th>Conf.</th>
<th>( T ) (nK)</th>
<th>( \phi ) (krad/s)</th>
<th>CF (%)</th>
<th>( \beta_{MB} ) (cm(^3)/s)</th>
<th>( \beta_{TF} ) (cm(^3)/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>755</td>
<td>(S,O)</td>
<td>126 ± 32</td>
<td>0.46 ± 0.06</td>
<td>0-36</td>
<td>((8.0 \pm 5.0) \times 10^{-9})</td>
<td>((4.4 \pm 1.0) \times 10^{-10})</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>755</td>
<td>(S,C)</td>
<td>270 ± 70</td>
<td>1.83 ± 0.21</td>
<td>0-94</td>
<td>((2.9 \pm 1.5) \times 10^{-9})</td>
<td>((5.4 \pm 0.8) \times 10^{-10})</td>
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<tr>
<td>0</td>
<td>0</td>
<td>700</td>
<td>(I,C)</td>
<td>337 ± 80</td>
<td>1.21 ± 0.14</td>
<td>0-37</td>
<td>((2.2 \pm 1.1) \times 10^{-9})</td>
<td>((1.0 \pm 0.2) \times 10^{-9})</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>700</td>
<td>(I,C)</td>
<td>337 ± 80</td>
<td>1.21 ± 0.14</td>
<td>0-37</td>
<td>((1.0 \pm 0.5) \times 10^{-8})</td>
<td>((4.9 \pm 1.0) \times 10^{-10})</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>700</td>
<td>(I,C)</td>
<td>271 ± 65</td>
<td>1.09 ± 0.12</td>
<td>0-66</td>
<td>((7.0 \pm 4.0) \times 10^{-9})</td>
<td>((3.2 \pm 0.7) \times 10^{-10})</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>700</td>
<td>(I,C)</td>
<td>271 ± 65</td>
<td>1.09 ± 0.12</td>
<td>0-66</td>
<td>((5.6 \pm 2.8) \times 10^{-9})</td>
<td>((3.6 \pm 0.5) \times 10^{-10})</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>700</td>
<td>(I,C)</td>
<td>271 ± 65</td>
<td>1.09 ± 0.12</td>
<td>0-66</td>
<td>((4.1 \pm 2.4) \times 10^{-9})</td>
<td>((2.7 \pm 0.7) \times 10^{-10})</td>
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<tr>
<td>8</td>
<td>0</td>
<td>700</td>
<td>(I,C)</td>
<td>271 ± 65</td>
<td>1.09 ± 0.12</td>
<td>0-66</td>
<td>((4.0 \pm 2.0) \times 10^{-9})</td>
<td>((3.1 \pm 0.5) \times 10^{-10})</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>755</td>
<td>(I,C)</td>
<td>271 ± 65</td>
<td>1.09 ± 0.12</td>
<td>0-66</td>
<td>((2.8 \pm 1.4) \times 10^{-9})</td>
<td>((3.2 \pm 0.5) \times 10^{-10})</td>
</tr>
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</table>
Chapter 8

Narrow-Band Solid State VUV Source for Laser Cooling of Antihydrogen

We describe the design and performance of a solid-state pulsed source of narrowband (< 100 MHz) Lyman-α radiation designed for the purpose of laser cooling magnetically trapped antihydrogen. Our source utilizes an injection seeded Ti:Sapphire amplifier cavity to generate intense radiation at 729.4 nm, which is then sent through a frequency doubling stage and a frequency tripling stage to generate 121.56 nm light. Although the pulse energy was limited to 12 nJ with a repetition rate of 10 Hz when [105] was written, we expected to obtain greater than 0.1 µJ per pulse after replacing damaged optical components in the amplifier cavity and improving the efficiency of the frequency tripling stage.

8.1 Introduction

As the simplest and best understood atom in the periodic table, Hydrogen appeared to be the natural choice for early laser cooling experiments. Despite this, the first and only study of the optical cooling of Hydrogen was published in 1993 [142], many years after several alkalis were successfully cooled and trapped. The reason for this is the inherent difficulty of producing coherent radiation at the laser cooling transition for Hydrogen - 121.56 nm or Lyman-α. Numerous broadband pulsed Lyman-α sources were developed in the late 1970s and early 1980s [10, 33, 69, 88, 93, 94, 95, 100, 158]. These were suitable for many spectroscopic applications, but not for laser cooling, which requires, for efficient cooling, the
bandwidth of the source to be less than or equal to the natural linewidth ($\Gamma \approx 100 \text{ MHz}$) of the transition [142]. The development of the first narrow-band ($\Delta \nu \approx 40 \text{ MHz}$) Lyman-\(\alpha\) source in 1987 [23] made it possible to laser cool Hydrogen, trapped in a magnetic trap and pre-cooled cryogenically, to less than 3 mK [142]. Nevertheless, low repetition rate pulsed sources cannot be used for conventional laser cooling experiments, which rely on magneto-optical traps (MOTs) for efficient cooling and trapping of large atomic populations, and interest in coherent Lyman-\(\alpha\) sources subsided until a new application emerged - laser cooling of trapped antihydrogen. In particular, the ALPHA collaboration successfully trapped antihydrogen in a magnetic trap at a translational temperature of 500 mK [5, 42] and, more recently, used the trapped antimatter to test for charge, parity and time (CPT) symmetry violations. Using two-photon spectroscopy, they found that the 1S-2S transition frequency of antihydrogen is the same as that of Hydrogen at a relative precision of $2 \times 10^{-10}$ [3]. In other words, they saw no evidence of CPT violations. To reach the level of accuracy required for these measurements, the trapped antihydrogen must first be cooled to a translation temperature of 20 mK and, for this, a high power ($\sim 0.05 \text{ \mu W}$) Lyman-\(\alpha\) source with a 100 MHz linewidth is required, according to simulations [42]. Two continuous wave (CW) Lyman-\(\alpha\) sources, which rely on a four-wave mixing scheme in gaseous Mercury, have been realized [47, 134], but they are not yet capable of delivering sufficient power (and one of them relies on dye lasers). Here, we present an alternative approach - a narrow band ($< 100 \text{ MHz}$) pulsed solid-state Lyman-\(\alpha\) source. Our motivation was to create a solid-state source to avoid the maintenance and additional safety issues associated with a dye-laser-based source. Simulations have shown that a narrow-band pulsed source that produces 0.05 \(\mu\)J per shot at a repetition rate of 10 Hz is capable of cooling a trapped antihydrogen atom down to 20 mK [42]. While the maximum Lyman-\(\alpha\) output we have demonstrated here - by frequency tripling a 7.2 mJ pulse of 364.7 nm light - is only 12 nJ, we are confident that more than 0.1 \(\mu\)J is possible with this system as we have observed more than 19 mJ per pulse of 364.7 nm radiation\footnote{The authors of [3] glance over most technical details and we have been unable to find the power used for the experiment elsewhere in the literature.}. However, due to optical damage in the 729.4 nm amplifier crystal, we were unable to maintain an output power greater than 7.2 mJ per pulse at 364.7 nm. If the required average power is achieved, this Lyman-\(\alpha\)
source should be capable of laser cooling trapped anti-hydrogen, from 500 mK to 20 mK.

8.2 Apparatus

The laser system shown in Fig. 8.1 consists of a pulsed Ti:Sapphire amplifier seeded by a narrow linewidth ($< 1 \text{ MHz}$) semi-conductor laser (Toptica Photonics TA Pro) operating at 729.4 nm, an anti-reflection coated type I BBO crystal for second harmonic generation (SHG) at 729.4 nm (Castech Inc.) and a third harmonic generation (THG) and detection chamber.

8.2.1 Ti:Sapphire Amplifier and SHG

To obtain the intensities required for efficient SHG and THG while maintaining a narrow linewidth, we used an injection seeded pulsed Ti:Sapphire amplifier based on [46]. This amplifier is an unstable resonator that consists of two brewster cut Ti:Sapphire crystals (10 mm in diameter, 36.8 mm in path length, GT Advanced Technologies), a convex graded reflectivity mirror ($f = -5 \text{ m}$, INO) coated for 729.4 nm, a high reflector (HR) and two isosceles brewster prisms for coarse wavelength selection. As demonstrated previously in [46], in order to approach the Fourier Limit, each crystal is pumped by a pulsed frequency doubled Nd:YAG laser (532 nm, 10 Hz repetition rate) from both sides and injection seeded with a CW diode laser ($\Delta \nu < 1 \text{ MHz}$) operating at 729.4 nm. The output of the amplifier is then sent into a coated type I BBO crystal (dimensions: $7 \text{ mm} \times 7 \text{ mm} \times 8 \text{ mm}$), to produce 364.7 nm radiation. After the second harmonic (364.7 nm) is spatially separated from the fundamental beam (729.4 nm) by means of two Pellin Broca prisms, it is sent to the THG chamber, where we produce and detect Lyman-\(\alpha\) radiation.

8.2.2 Lyman-\(\alpha\) Generation and Detection

To generate Lyman-\(\alpha\) radiation, we used non-resonant THG in a mixture of Krypton and Argon - an approach that has been demonstrated a number of times in the literature [10, 23, 33, 69, 88, 93, 95, 158]. A resonant four-wave-mixing (FWM) scheme was also successfully demonstrated with a broadband dye-laser source by Michan et al. [103]. However, THG
8.2. Apparatus

Figure 8.1: Laser arrangement and non-linear optical stages. The Ti:Sapphire amplifier cavity is seeded by a narrow linewidth semi-conductor laser (Toptica Photonics TA Pro) via a uncoated CaF$_2$ beam splitter (BS) with a reflectivity of $\sim 0.5\%$. The two Ti:Sapphire crystals are pumped from both sides by a pulsed Nd:YAG laser (Quanta-Ray Pro). The pump power is distributed evenly between the four arms. The amplified light exits the cavity via the output coupler (OC). It is then sent through a coated BBO crystal. The second harmonic is separated from the fundamental beam (not shown), with two Pellin Broca prisms and routed to the THG chamber. The beam is then focused by an MgF$_2$ lens $L_1$ ($f = 100$ mm) onto a mixture of Krypton and Argon gas. Finally, Lyman-$\alpha$ radiation is produced by non-resonant THG, recollimated by an MgF$_2$ lens $L_2$ ($f = 200$ mm) and detected by a solar-blind photo-multiplier tube (PMT). Two Lyman-$\alpha$ filters are placed between $L_2$ and the PMT to prevent 364.7 nm light from reaching the PMT (not shown).
8.3. Results

(which requires only one beam) was chosen here because of its technical simplicity and the availability of high energy pump sources. In Fig. 8.1 we show that radiation from the SHG stage is sent into the THG chamber, which consists of an MgF$_2$ focusing lens $L_1$ ($f = 100$ mm), an input port for the Krypton-Argon mixture, an MgF$_2$ recollimating lens $L_2$ ($f = 200$ mm), two Lyman-α filters and a solar-blind photo-multiplier tube (PMT). In our implementation, the first lens $L_1$ focuses the slowly diverging 364.7nm beam (with a vertical diameter of 6mm and a horizontal diameter of 3mm, based on a burn card measurement) onto the gas mixture to reach the intensities required for efficient THG. The generated Lyman-α is then recollimated with lens $L_2$, sent through two Lyman-α filters (to prevent the 364.7nm beam from passing) and detected by the PMT. Using the response function, gain curve and quantum efficiency of the PMT (Hamamatsu R972) we extract from the raw signal the temporal profile of the Lyman-α beam and its pulse energy. To confirm the production of Lyman-α, we verified that the PMT signal vanished in the absence of Krypton.

8.3 Results

In this section, we describe the results we obtained at the SHG and THG stages. A detailed description and characterization of the injection seeded Ti:Sapphire amplifier can be found in [46] and [45].

8.3.1 Second Harmonic Generation (SHG) Stage

Pulse Energy

In Fig. 8.2 the average pulse energy of the SHG beam (364.7nm) $E_{\text{SHG}}$ is plotted as a function of pump pulse energy $E_p$. This data was taken with the cavity unlocked and in an environment with an abundance of acoustic noise (generated by turbo-pumps from a nearby apparatus). As a result, large fluctuations in the pulse energy were observed. We fit this data to the following model:

$$E_{\text{SHG}} = \alpha \cdot (E_p - E_{\text{TH}})^2 \cdot \Theta (E_p - E_{\text{TH}})$$  \hspace{1cm} (8.1)
8.3. Results

Figure 8.2: SHG pulse energy at 365 nm as a function of the pulse energy of the 532 nm pump for the 729.4 nm seeded amplifier.

Figure 8.3: SHG pulse energy with $E_P = 310$ mJ as a function of time with the amplifier cavity locked. The observed power fluctuations are correlated with fluctuations in the Nd:YAG pump laser. The mean pulse energy is 16.0 mJ and the standard deviation is 1.4 mJ.

where $\alpha = (5.7 \pm 2.8) \times 10^{-4}$ mJ$^{-1}$ is a proportionality constant, $E_{TH} = 150 \pm 27$ mJ is the pump power at the 729.4 nm lasing threshold and $\Theta$ is the Heaviside step function. Further optimizations of the amplifier cavity enabled us to reach the SHG pulse energies shown in Fig. 8.3 with $E_P = 310$ mJ, where the mean pulse energy is 16.0 mJ and the standard deviation is 1.4 mJ. However, due to the environmental conditions of the facility at CERN and imperfections in one of the Ti:Sapphire crystals, we were forced to lower the pump power to avoid further damaging the crystal. For this reason, all of the data presented in 8.3.1 and in section 8.3.2 were taken at lower pump powers. After replacing the crystal and alleviating problems due to the environment, we expect to consistently achieve the powers shown in 8.3.
8.3. Results

Figure 8.4: (a) SHG temporal pulse shape with the cavity not in resonance with the seed laser. (b) Spectrum of the pulse in (a). (c) SHG temporal pulse shape with the cavity near resonance with the seed laser. (d) Spectrum of the pulse in (c).

**Pulse Shape**

In Fig. 8.4 (a) and (b), respectively, we show the intensity as a function of time for a 364.7 nm pulse and the spectrum of this pulse when the amplifier cavity is not in resonance with the seed frequency. The spectrum consists of a dominant peak (which corresponds to the envelope of the temporal profile) and two side lobes, which account for the modulation seen in the temporal profile. The full width at half maximum (FWHM) of the temporal profile $\Delta t_{\text{FWHM}}$ and the FWHM of the spectrum $\Delta \nu_{\text{FWHM}}$ are $31.6 \pm 1.7$ ns and $26.1 \pm 1.2$ MHz, respectively. Similarly, the temporal profile and spectrum of a pulse generated when the amplifier was tuned to be near resonance with the seed laser are shown in Fig. 8.4 (c) and (d). As expected, the side-bands (which correspond to other cavity modes) are suppressed. For this pulse, $\Delta \nu_{\text{FWHM}} = 32.8 \pm 1.0$ MHz and $\Delta t_{\text{FWHM}} = 24.7 \pm 0.5$ ns. In the next section, we find that operating the Ti:Sapphire amplifier cavity off-resonance with respect to the input seed frequency results in higher pulse energies and more efficient THG than operating near resonance.
8.3. Results

8.3.2 THG Stage

The Lyman-α intensity is proportional to $\chi^2 N^2 I_{\text{SHG}}^3 F$, where $\chi$ is the third order susceptibility, $N$ is the number density of the Krypton, $I_{\text{SHG}}$ is the intensity of the 364.7 nm beam and $F$ is the phase matching factor. In the limit of a tight focus, the phase-matching factor is maximized when $b \cdot \Delta k = b \cdot (k_{121.56 \text{ nm}} - 3 \cdot k_{364.7 \text{ nm}}) = -2$, where $b$ is the confocal parameter of the beam (assuming a TEM$_{00}$ mode) \[69\]. However, because the Lyman-α intensity is also proportional to $N^2$, adjusting the Krypton density to satisfy the phase matching condition alone is insufficient to optimizing the Lyman-α intensity and the problem becomes a three parameter optimization for the focal length of the focusing lens $L_1$ and the pressures of Krypton and Argon in the mixing chamber. Based on previous results from preliminary dye-laser experiments and some empirical optimization, we chose an $f = 100$ mm MgF$_2$ lens for $L_1$ and set the Krypton pressure to 84 mTorr and the Argon pressure to 200 mTorr.

With the amplifier cavity locked via a simple side-lock near resonance, we observed the temporal profiles shown in Fig. 8.5 (a) and (c) for the 364.7 nm and 121.6 nm pulses, respectively. The corresponding spectra are shown in Fig. 8.5 (b) and (d). The temporal and spectral widths of the 364.7 nm pulse are given by $\Delta t_{\text{FWHM}} = 20.9 \pm 3.0$ ns and $\Delta \nu_{\text{FWHM}} = 44.3 \pm 2.1$ MHz, respectively. As shown in Fig. 8.5, this 5.0 mJ pulse produces a Lyman-α pulse with a temporal width of $\Delta t_{\text{FWHM}} = 11.5 \pm 0.5$ ns and a spectral width of 76.8 ± 2.9 MHz. The energy of the Lyman-α pulse is approximately 2 nJ. Remarkably, locking the cavity not near resonance with the seed laser resulted in higher THG efficiency. In Fig. 8.6, we again show the temporal and spectral profiles of the 364.7 nm and 121.46 nm pulses (same naming scheme as Fig. 8.5). Here, the side bands in the spectrum of 364.7 nm pulse are more pronounced with respect to the central peak, but the overall pulse energy is also larger - 7.2 mJ. Because of the shorter pulse duration and higher peak intensity in the 364.7 nm pulse, we observe a slightly broader spectral profile - $\Delta \nu = 83.2 \pm 0.8$MHz - and a higher pulse energy - 12 nJ - for the 121.46 nm pulse. Its temporal width $\Delta t_{\text{FWHM}}$ is 11.2 ± 0.3ns.
8.3. Results

Figure 8.5: Temporal and spectral profiles of the 364.7 nm and 121.46 nm pulses with the amplifier cavity locked close to resonance with the seed laser. (a) Temporal profile of the 364.7 nm pulse. (b) Spectral profile of the 364.7 nm pulse. (c) Temporal profile of the 121.46 nm pulse. (d) Spectral profile of the 121.46 nm pulse.

Figure 8.6: Temporal and spectral profiles of the 364.7 nm and 121.46 nm pulses with the amplifier cavity locked far from resonance with the seed laser. (a) Temporal profile of the 364.7 nm pulse. (b) Spectral profile of the 364.7 nm pulse. (c) Temporal profile of the 121.46 nm pulse. (d) Spectral profile of the 121.46 nm pulse.
8.4 Summary

We made significant progress toward developing a narrow-band solid state Lyman-α source capable of laser cooling magnetically trapped anti-hydrogen to 20mK. Further optimization of both the pulsed amplifier stage and the THG were required to achieve this at the time of writing the manuscript for [105]. To reach a pulse energy of 0.05μJ (the value used in the simulation [42]), we needed to achieve stable operation at pulse energies close to those shown in Fig. 8.3 and determine the focal length of the focusing lens and the Krypton and Argon pressures that optimizes the THG conversion efficiency. We note that if the conversion efficiency remained constant, simply increasing the SHG pulse energy to 16 mJ should have resulted in approximately 132 nJ of Lyman-α.
Chapter 9

Conclusion and Outlook

This study documents the first successful attempt to create, using STIRAP, deeply bound triplet molecules of $^6\text{Li}_2$ - in the lowest hyperfine states of several rovibrational levels of the $a(^3\Sigma_u^+)$ potential - and examine their chemical properties. On our path toward this goal, we designed and built a robust laser system for cooling $^6\text{Li}$, which will allow us to implement an enhanced laser cooling mechanism that relies on the D$_1$ transition, and a Ti:Sapphire-based Raman laser system with the best (to our knowledge) phase noise suppression of any solid state laser system with only an AOM for fast actuation. We also added various automation routines that will continue to accelerate the rate of data collection and experimental parameter optimization for years to come, wrote a program to process absorption images with high fidelity that will be used for virtually every future experiment conducted with this apparatus, and created a library of scripts for processing photo-association and molecular lifetime data. These ingredients will prove useful not only for future studies involving $^6\text{Li}$, but also greatly simplify the path toward creating polar $^6\text{Li}^{85}\text{Rb}$ molecules - a long term goal for the QDG lab and a means of exploring exotic phenomena in many body physics. Finally, we built a solid-state VUV laser system that allowed researchers in the ALPHA collaboration to use laser cooling in a novel way to cool magnetically trapped antihydrogen and make significant advances in their quest for violations of the charge, parity, and time reversal symmetries. They did this by confirming that the 1S-2S transition frequency of antihydrogen is equal to that of Hydrogen at a relative precision of $2 \times 10^{-10}$ [3].

While we made significant progress in our study of the chemical reactions that take place between the deeply bound $^6\text{Li}_2$ molecules we create, a few crucial unresolved issues remain. To unequivocally determine the two-body loss rate constant for each molecular state, we need to know whether the sample is a thermal gas or a mBEC and the trap frequencies
of the deeply bound molecules. For the reasons discussed in chapter 7, it is advantageous to work with a pure thermal gas, so we should operate above the critical temperature while maintaining a sufficiently large number of Feshbach molecules. Experimentally, this entails terminating our evaporative cooling ramp at a higher trap depth and changing the magnetic field to a value at which the three-body recombination rate is relatively high (e.g. 700 G) such that we get efficient Feshbach molecule formation without crossing the critical temperature\textsuperscript{26}. Doing this and validating our temperature estimates via time-of-flight expansion measurements would ensure that the sample is thermal. Next, we need to investigate how the trap frequencies change after we form deeply bound molecules. So far, we have been implicitly assuming that the trap frequencies remain the same after the population transfer. However, it would be quite coincidental if that were the case because the sum of the AC stark shifts associated with all of the excited states of $^6\text{Li}_2$ would have to add up to the same value as AC stark shift for $^6\text{Li}$ atoms. The optimal solution would be to match the trap frequencies of the deeply bound molecules to those of the Feshbach molecules by measuring the former directly or by other means. Once these two conditions are met for each deeply bound state, we will be able to reliably determine the two-body loss rate for every vibrational level in the $a(^3\Sigma_u^+)$ potential and may observe never-before-seen exotic quantum chemical processes.

\textsuperscript{26}After the field is changed, it is necessary to wait several tens of milliseconds for the Feshbach molecules to form.
Bibliography


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Bibliography


Appendix A

Beam Profile Measurements

To calculate the intensities of our dipole trapping lasers and photo-association lasers, we need the powers and beam parameters. Here, we extract the latter for each beam. The beam waist of an ideal Gaussian beam is given by equation A.1.

$$W(z) = W_0 \sqrt{1 + \left(\frac{z}{z_0}\right)^2}$$ \hspace{1cm} (A.1)

where the $z_0 = \pi W_0^2 / \lambda$ is the Rayleigh length. In practice, aberrations increase the minimum beam waist to approximately $4W_0/3$ \[147\]. Hence, equation A.1 becomes

$$W(z) = W'_0 \sqrt{1 + \left(\frac{z}{z_0}\right)^2} \approx \frac{4}{3} W_0 \sqrt{1 + \left(\frac{z}{z_0}\right)^2}$$ \hspace{1cm} (A.2)

In the sections that follow, we will use this model to extract the beam parameters from least squares fits of beam profile measurements for the SPI CODT beams, IPG CODT beams and photo-association beam.

A.1 SPI Beam Profiles

The beam waist of the SPI laser (1090 nm) along the $x$ and $y$ directions is shown as a function of distance along the optical axis in Figure A.1 for both trapping arms. The beam parameters extracted from the fit are included in the caption.
A.2 IPG Beam Profiles

The beam waist of the IPG laser (1064 nm) along the $x$ and $y$ directions is shown as a function of distance along the optical axis in Figure A.2 for both trapping arms. The beam parameters extracted from the fit are included in the caption.

Figure A.1: Beam profile measurements for the first (a) and second (b) arms of the SPI CODT. For the first arm, $W'_{0x} = 41.45 \pm 0.58 \mu m$, $W'_{0y} = 36.88 \pm 0.91 \mu m$, $z_{0x} = 3.32 \pm 0.03 \text{ mm}$, $z_{0y} = 2.75 \pm 0.04 \text{ mm}$ and the distance between the $x$ and $y$ foci is $\Delta_{\text{foci}} = 0.6 \pm 2.9 \text{ mm}$. For the second arm, $W'_{0x} = 40.52 \pm 0.58 \mu m$, $W'_{0y} = 37.91 \pm 0.72 \mu m$, $z_{0x} = 3.35 \pm 0.04 \text{ mm}$, $z_{0y} = 3.13 \pm 0.06 \text{ mm}$ and the distance between the $x$ and $y$ foci is $\Delta_{\text{foci}} = 1.1 \pm 7.4 \text{ mm}$.

Figure A.2: Beam profile measurements for the first (a) and second (b) arms of the IPG CODT. For the first arm, $W'_{0x} = 53.10 \pm 0.31 \mu m$, $W'_{0y} = 58.99 \pm 0.13 \mu m$, $z_{0x} = 4.59 \pm 0.02 \text{ mm}$, $z_{0y} = 5.12 \pm 0.01 \text{ mm}$ and the distance between the $x$ and $y$ foci is $\Delta_{\text{foci}} = 4.6 \pm 4.1 \text{ mm}$. For the second arm, $W'_{0x} = 47.85 \pm 0.92 \mu m$, $W'_{0y} = 55.65 \pm 0.07 \mu m$, $z_{0x} = 4.44 \pm 0.08 \text{ mm}$, $z_{0y} = 5.88 \pm 0.01 \text{ mm}$ and the distance between the $x$ and $y$ foci is $\Delta_{\text{foci}} = 4.2 \pm 5.5 \text{ mm}$. 

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A.3 Photo-Association Beam Profile

The beam waist of the photo-association beam along the $x$ and $y$ directions is shown as a function of distance along the optical axis in Figure A.2. The beam parameters extracted from the fit are included in the caption.

![Graph showing beam profile measurements for the photo-association beam at 798 nm.](image)

Figure A.3: Beam profile measurements for the photo-association beam at 798 nm. $W_{0x}' = 36.82 \pm 1.01 \mu m$, $W_{0y}' = 39.08 \pm 0.51 \mu m$, $z_{0x} = 4.20 \pm 0.12 \text{ mm}$, $z_{0y} = 4.94 \pm 0.09 \text{ mm}$ and the distance between the $x$ and $y$ foci is $\Delta_{\text{foci}} = -1.4 \pm 13.4 \text{ mm}$. 
Appendix B

Trap Frequency Measurements

One of the most unambiguous methods of measuring the trapping frequencies of an ODT is perturbing the trap by changing the pointing of the trapping laser (by stepping the frequency of an AOM or by other means) for some length of time and then returning it to its normal position. As a result of this step displacement, the center of the atom cloud begins to oscillate at the trap frequencies around the equilibrium position. Since the trapping frequencies are proportional to $\sqrt{I}$, where $I$ is the intensity of the trapping laser incident on the atoms, making a measurement at a single trapping power is sufficient. (As a precaution, we validated these measurements by also measuring the trap frequencies at four times the laser power and confirmed that the trap frequencies doubled, as expected.)

We were able to use this technique for the CODT formed by the SPI laser, but not for the CODT formed by the IPG laser because of the orientation of a periscope used for this aligning this trap. Changing the AOM frequency results in the trap splitting into two arms rather than simply a shift in the cross. Hence, we made the measurement for the IPG trap in a single arm and used this in conjunction with insights from the SPI data to calculate the trap frequencies for the IPG CODT. To extract the oscillation frequencies from the waveforms we obtained, we use the following fitting function:

\begin{equation}
    x_0(t) = mt + b + A \sin(2\pi ft + \phi) \exp\left(-\frac{t}{\tau}\right) \tag{B.1}
\end{equation}

Next, we checked for consistency between equations 2.6 and 2.10. The former relies on the accuracy of the power measurement while the latter relies on the accuracy of the trap frequency measurement. The accuracy of both methods is strongly dependent on the validity

\footnote{Parametric excitation induced by amplitude modulation [25] of the trapping laser is another way of measuring the trapping frequencies. It is more difficult to interpret and validate because an array of harmonics and subharmonics of the trapping frequency are observed.}
B.1 SPI CODT

and interpretation (when there is strong astigmatism) of the beam waist measurements in Appendix [A] (The functional dependency on $W_0$ is not the same.) It is important to note an implicit assumption we are making: while equation 2.10 was originally derived for a single arm trap (which has cylindrical symmetry), we are assuming that $\omega_x \approx \omega_y \approx \omega_z$ for our small crossing angle in a CODT based on the simulation results presented in [63]. The data and analysis are shown in the sections that follow.

B.1 SPI CODT

According to the fit in Figure [B.1], $\omega_x/2\pi = 552.2 \pm 5.9$ Hz and $\omega_z/2\pi = 81.6 \pm 1.9$ Hz when the trapping power is $70 \pm 5$ mW and $60 \pm 4$ mW in the first and second arms, respectively. The simulation described in [63] shows that $\omega_y \approx \omega_x$. It is important to note that this trap is, in part, created by a small gradient in the magnetic field.

![Figure B.1: Trap frequency measurements for the x direction (a) and z direction (b) with 70 ± 5 mW and 60 ± 4 mW of laser power in the first and second arms, respectively (SPI laser). Based on the fit of the data in (a), $\omega_x/2\pi = 552.2 \pm 5.9$ Hz. For this measurement, the trap was displaced for 100 ms by changing the AOM frequency by 1 MHz, the cloud expansion time was 2 ms and the magnetic field was set to 755 G. Based on the fit of the data in (b), $\omega_z/2\pi = 81.6 \pm 1.9$ Hz. Here, the trap was displaced for 500 ms by changing the AOM frequency by 0.5 MHz, the cloud expansion time was 2.5 ms and the magnetic field was set to 755 G.](image)

The astigmatism in the SPI beam is very mild and $W_0 \approx 38 \mu$m. Using equations 2.6 and 2.10 we get $U_0/k_B = 2.73$ $\mu$K or $U_0/k_B P = 21$ $\mu$K/W and $U_0/k_B = 3.14$ $\mu$K or $U_0/k_B P = 24.2$ $\mu$K/W, respectively. The discrepancy may be due to the additional trapping
potential generated by the slight magnetic field gradient, which is not accounted when we use equation [2.6]. If so, the depth of this additional trap is approximately 0.4 μK.

### B.2 IPG ODT

According to the fit of the data in Figure [B.2] $\omega_{y}/2\pi = \omega_{x}/2\pi = \omega_{r}/2\pi = 1400.3 \pm 8.4$ Hz at $5 \pm 0$ W. According to the above data for the SPI trap, we should expect $\omega_{z} \approx 207$ Hz for an IPG cross trap. At this large trapping frequency, the effect of the field gradient is negligible.

![Figure B.2: Trap frequency measurement for the y direction with 5 ± 0.5 W of laser power in the first arm (IPG laser). Based on the fit of the data, $\omega_{y}/2\pi = 1400.3 \pm 8.4$ Hz. For this measurement, the trap was displaced for 0.25 ms by changing the AOM frequency by 0.5 MHz, the cloud expansion time was 0.3 ms and the magnetic field was set to 755 G.](image)

Since the IPG beam is astigmatic, we have to guess what the effective $W_0$ is based on the data and fits in Appendix [A]. With a choice of $W_0 \approx 58 \mu$m, equations [2.6] and [2.10] agree that the trap depth $U_0/k_B = 47 \mu$K. This implies that the $U_0/k_B P = 4.7 \mu$K/W.
Appendix C

Passive Mode-Locking via Non-Linear Polarization Rotation

C.1 Non-Linear Polarization Density in an Isotropic Medium

If we neglect its small birefringence, we can treat an optical fiber (that is not polarization maintaining) as an isotropic and centrosymmetric medium. Since there is no second order response in a centrosymmetric medium, the dominant non-linear term is the third order polarization density $P^{(3)}$. To determine the nature and strength of this effect, we need to first explore the symmetry properties of the third order susceptibility tensor $\chi^{(3)}_{ijkl} = \chi^{(3)}_{ijkl}(\omega_4 = \omega_1 + \omega_2 + \omega_3)$. We begin by determining which tensor elements are non-zero. This can be done without knowing the precise quantum mechanical nature of the interaction and instead we rely on the classical anharmonic oscillator model - a modified Lorentz oscillator model. (We caution the reader that this is just an outline of the complete derivation presented in [18].) In this case, the restoring force is given by

$$F^r = -m\omega_0^2 r + mb(r \cdot r)r$$  \hspace{1cm} (C.1)

where $r$ is the displacement, $m$ is the mass of an electron, $\omega_0$ is the natural frequency of oscillation in the absence of non-linear effects and $b$ is a parameter that characterizes the strength of the non-linear effects. The first term in equation (C.1) corresponds to a harmonic potential and the second represents the non-linear correction to this potential. (If we set $b = 0$, this would reduce to the Lorentz oscillator model.) The equation of motion is
then

\[ \ddot{r} + 2\gamma \dot{r} + \omega_0^2 r - mb(r \cdot r) = -e\tilde{E}(t) = -e \left( E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + E_3 e^{-i\omega_3 t} + \text{c.c.} \right) \] (C.2)

where \( \gamma \) is the damping constant, \( e \) is the charge of an electron and \( \tilde{E}(t) \) is the driving electric field. To determine the third order response of this system this, we expand \( r(t) \) in a power series in \( \lambda \) as follows:

\[ r(t) = \lambda r^{(1)}(t) + \lambda^2 r^{(2)}(t) + \lambda^3 r^{(3)}(t) \] (C.3)

After inserting this form into equation (C.2), it is relatively straight-forward to show that the \( r^{(2)} = 0 \) and derive an expression for \( r^{(3)} \) at an oscillation frequency \( \omega_q \). Each component of the third order polarization density at this frequency is then given by

\[ P^{(3)}_i(\omega_q) = -Ne \left( \sum_{jk} \sum_{mnp} \chi^{(3)}_{ijkl}(\omega_1 = \omega_1 + \omega_2 + \omega_3)E_j(\omega_m)E_k(\omega_n)E_l(\omega_p) \right) \] (C.4)

where \( N \) is the number density of dipoles. Finally, the third order susceptibility is given by

\[ \chi^{(3)}_{ijkl}(\omega_1 = \omega_1 + \omega_2 + \omega_3) = \frac{Ne^4 (\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})}{3\varepsilon_0 m^3 D(\omega_q)D(\omega_m)D(\omega_n)D(\omega_p)} \] (C.5)

where \( D(\omega_\xi) = \omega_\xi^2 - \omega_0^2 - 2i\omega_\xi\gamma \). Since we are interested in the propagation of light though a non-linear medium as opposed to harmonic generation, we can immediately simplify the result in equation (C.5) as follows:

\[ \chi^{(3)}_{ijkl}(\omega = \omega + \omega - \omega) = \frac{Ne^4 (\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})}{3\varepsilon_0 m^3 D(\omega)D(-\omega)} \] (C.6)

Clearly, \( \delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} = 0 \) if the value of one of \( i, j, k \) or \( l \) only appears once in the subscript of \( \chi^{(3)}_{ijkl} \). This leaves us with 21 non-zero elements. For \( i = j = k = l, \delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} = 3. \) For every other non-zero element, \( \delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} = 1. \)
C.1. Non-Linear Polarization Density in an Isotropic Medium

Explicitly, this implies the following:

\[
\chi_{1111} = \chi_{2222} = \chi_{3333} \quad \text{(C.7)}
\]
\[
\chi_{1122} = \chi_{1133} = \chi_{2211} = \chi_{2233} = \chi_{3311} = \chi_{3322} \quad \text{(C.8)}
\]
\[
\chi_{1212} = \chi_{1313} = \chi_{2323} = \chi_{2121} = \chi_{3131} = \chi_{3232} \quad \text{(C.9)}
\]
\[
\chi_{1221} = \chi_{1331} = \chi_{2112} = \chi_{2332} = \chi_{3113} = \chi_{3223} \quad \text{(C.10)}
\]

It is important to note that, by using the model presented above, we have restricted ourselves to (highly) non-resonant electronic non-linearities - the case we are considering for an Erbium-doped fiber at 1550nm. However, equations (7)-(10) are valid for all centrosymmetric isotropic media. For our choice of frequencies, the following relations are also generally valid [18]:

\[
\chi_{1111} = \chi_{1122} + \chi_{1212} + \chi_{1221} \quad \text{(C.11)}
\]
\[
\chi_{1122} = \chi_{1212} \quad \text{(C.12)}
\]

and equation (C.4) simplifies to

\[
P_i^{(3)}(\omega) = 3\epsilon_0 \sum_{jkl} \chi_{ijkl}^{(3)}(\omega = \omega+\omega-\omega)E_j(\omega)E_k(\omega)E_l(\omega) = 6\epsilon_0\chi_{1122} (E \cdot E^*) E_i + 3\epsilon_0\chi_{1221} (E \cdot E^*) E_i \quad \text{(C.13)}
\]

For the case of highly non-resonant electronic non-linearities, we can simplify this equation even further since it is clear from equation (C.7) that

\[
\chi_{1111} = 3\chi_{1122} = 3\chi_{1212} = 3\chi_{1221} \quad \text{(C.14)}
\]

However, we will use the more general form shown in equation (C.13) in the derivations that follow and simply remember that, in our case, \(\chi_{1122} = \chi_{1221}\). In vector form, the non-linear (NL) polarization density is given by

\[
P_{NL} = \epsilon_0 A (E \cdot E^*) E + \frac{1}{2}\epsilon_0 B (E \cdot E) E^* \quad \text{(C.15)}
\]
C.2. Non-Linear Polarization Rotation in an Isotropic Medium

where \( A = 6\chi_{1122} \) and \( B = 6\chi_{1221} \). (In our case, \( A = B \).) Equipped with equation (C.15), we can now show that an isotropic Kerr medium (such as a silica fiber) rotates an incident elliptical polarization state and that the angle of rotation depends on the intensity of the incoming light.

C.2 Non-Linear Polarization Rotation in an Isotropic Medium

For the purpose of this derivation, it is convenient to express the complex amplitudes of the driving electric field and the non-linear polarization density in the circular polarization basis rather than the usual Cartesian basis:

\[
\tilde{E}(z,t) = E(z)e^{-i\omega t} + \text{c.c.} = (E_+ \hat{\sigma}_+ + E_- \hat{\sigma}_-) e^{-i\omega t} + \text{c.c.} \quad (C.16)
\]

\[
\tilde{P}_{NL}(z,t) = P_{NL}(z)e^{-i\omega t} + \text{c.c.} = (P_+ \hat{\sigma}_+ + P_- \hat{\sigma}_-) e^{-i\omega t} + \text{c.c.} \quad (C.17)
\]

where

\[
\hat{\sigma}_\pm = \frac{\hat{x} \pm i\hat{y}}{\sqrt{2}} \quad (C.18)
\]

In the discussion that follows, we will need the identities that are proven below:

\[
\hat{\sigma}_\pm^* = \hat{\sigma}_\mp = \frac{\hat{x} \mp i\hat{y}}{\sqrt{2}} = \hat{\sigma}_\pm^* \quad (C.19a)
\]

\[
\hat{\sigma}_\pm \cdot \hat{\sigma}_\pm = \frac{1}{2} \begin{pmatrix} 1 \\ \pm i \end{pmatrix} \cdot \begin{pmatrix} 1 \\ \pm i \end{pmatrix} = 0 \quad (C.19b)
\]

\[
\hat{\sigma}_\pm \cdot \hat{\sigma}_\mp = \frac{1}{2} \begin{pmatrix} 1 \\ \pm i \end{pmatrix} \cdot \begin{pmatrix} 1 \\ \mp i \end{pmatrix} = 1 \quad (C.19c)
\]

Our goal is to solve the non-linear wave equation to obtain a simple input-output (IO) relationship between the incoming field and the outgoing field (assuming no reflections). This
will enable us to add this element (Kerr medium) to our existing arsenal of (linear) polarization manipulation tools. We begin by massaging equation (C.15) into a more convenient form. Using the above identities, it is trivial to show that

\[ \mathbf{E} \cdot \mathbf{E}^* = (E_+ \hat{\sigma}_+ + E_- \hat{\sigma}_-)(E_+^* \hat{\sigma}_+^* + E_-^* \hat{\sigma}_-^*) = (E_+ \hat{\sigma}_+ + E_- \hat{\sigma}_-)(E_+^* \hat{\sigma}_-^* + E_-^* \hat{\sigma}_+^*) = |E_+|^2 + |E_-|^2 \]

(C.20a)

Substituting these results into equation (C.15) yields

\[ P_\pm = \epsilon_0 \left( A |E_+|^2 + |E_-|^2 \right) E_\pm + B (E_+ E_-) E_+^* \]
\[ = \epsilon_0 \left( A \left( |E_+|^2 + |E_-|^2 \right) + B |E_\mp|^2 \right) E_\pm \]
\[ = \epsilon_0 \left( A \left( |E_+|^2 + |E_-|^2 \right) + A |E_\mp|^2 - A |E_\mp|^2 + B |E_\mp|^2 \right) E_\pm \]
\[ = \epsilon_0 \left( A |E_\pm|^2 + (A + B) |E_\mp|^2 \right) E_\pm \]

For an electric field, whose \( z \) dependence appears only in its phase, propagating in the +z direction, the term in the parentheses is independent of \( z \). Making this assumption makes physical sense if we ignore losses (and gain) within the Kerr medium. (If there are no losses or reflections, the input and output power should be equal.) We will henceforth refer to this quantity as \( \chi_{\pm}^{NL} \).

\[ \chi_{\pm}^{NL} = A |E_\pm|^2 + (A + B) |E_\mp|^2 \]  

(C.21)

We can now express the components of \( \mathbf{P}_{NL} \) (in the circular polarization basis) as follows:

\[ P_\pm = \epsilon_0 \chi_{\pm}^{NL} E_\pm \]  

(C.22)

The non-linear wave equation for an isotropic medium is given by

\[ \nabla^2 \tilde{\mathbf{E}}(r, t) = \frac{\epsilon^{(1)}}{c^2} \frac{\partial^2 \tilde{\mathbf{E}}(r, t)}{\partial t^2} + \frac{1}{\epsilon_0 c^2} \frac{\partial^2 \tilde{\mathbf{P}}_{NL}(r, t)}{\partial t^2} \]  

(C.23)
where \( \epsilon^{(1)} = \left( n^{(1)} \right)^2 \) and \( n^{(1)} \) is the linear refractive index of the material. In our simplified picture, the electric field has no \( x \) and \( y \) dependence, so we can simplify equation (C.23):

\[
\frac{\partial^2 E_\pm}{\partial z^2} = -\frac{\epsilon^{(1)} \omega^2}{c^2} E_\pm - \frac{\omega^2}{\epsilon_0 c^2} P_\pm = -\frac{\omega^2}{c^2} \left( \epsilon^{(1)} + \chi_{\pm}^{NL} \right) E_\pm
\]  
(C.24)

If we assume that the wave just before the fiber is \( E_\pm(z = 0) = A_\pm \) (implying that there is no reflected wave), the solution is simply

\[
E_\pm = A_\pm e^{ik_{\pm}z}
\]  
(C.25)

where

\[
k_{\pm} = \frac{\omega}{c} \sqrt{\epsilon^{(1)} + \chi_{\pm}^{NL}} = \frac{n^{(1)} \omega}{c} \sqrt{1 + \frac{1}{\epsilon^{(1)}} \chi_{\pm}^{NL}} \approx \frac{n^{(1)} \omega}{c} \left( 1 + \frac{1}{2\epsilon^{(1)}} \chi_{\pm}^{NL} \right)
\]  
(C.26)

We assumed above that \( \chi_{\pm}^{NL}/\epsilon^{(1)} \ll 1 \) because \( \chi^{(3)} = 2.5^{-22} \text{ m}^2/\text{V}^2 \) for silica [18]. As we will show below, it is instructive to express \( k_{\pm} \) in terms of a common and differential part. Hence, we define two new quantities \( \bar{k} \) and \( \Delta k \) and let \( k_{\pm} = \bar{k} \pm \Delta k \), where

\[
\bar{k} = \frac{k_+ + k_-}{2} = \frac{n^{(1)} \omega}{c} \left( 1 + \frac{1}{4\epsilon^{(1)}} \left( \chi_+^{NL} + \chi_-^{NL} \right) \right) = \frac{n^{(1)} \omega}{c} \left( 1 + \frac{1}{4\epsilon^{(1)}} \left( 2A + B \right) \left( |E_+|^2 + |E_-|^2 \right) \right)
\]  
(C.27)

\[
\Delta k = \frac{\omega}{2cn^{(1)}} \left( \chi_+^{NL} - \chi_-^{NL} \right) = \frac{\omega B}{4cn^{(1)}} \left( |E_-|^2 - |E_+|^2 \right)
\]  
(C.28)
Thus, the electric field at the output of the Kerr medium $E(z = d)$ can be expressed in terms of the input field $E(z = 0)$ as follows:

$$
E(z = d) = E_+(z = d)\hat{\sigma}_+ + E_-(z = d)\hat{\sigma}_-
$$

$$
= A_+e^{ik_d}\hat{\sigma}_+ + A_-e^{-ik_d}\hat{\sigma}_-
$$

$$
= e^{i\Delta k_d} \left( A_+e^{i\Delta k_d}\hat{\sigma}_+ + A_-e^{-i\Delta k_d}\hat{\sigma}_- \right)
$$

$$
= e^{i\Delta k_d} \left( E_+(z = 0)e^{i\Delta k_d}\hat{\sigma}_+ + E_+(z = 0) - e^{-i\Delta k_d}\hat{\sigma}_- \right)
$$

$$
= e^{i\Delta k_d} \begin{bmatrix} e^{i\Delta k_d} & 0 \\ 0 & e^{-i\Delta k_d} \end{bmatrix} E(z = 0)
$$

The exponential $e^{i\Delta k_d}$ is just an overall phase term. The interesting physics is contained in the diagonal matrix whose physical meaning will become clear shortly. For now, it is important to emphasize that $\Delta k$ is a function of the intensity of the electric field. We can write the above results in the following short-hand notation:

$$
E(z = d) = M_{CB}^{\text{KERR}}E(z = 0) \tag{C.29}
$$

### C.3 Simple Ring Cavity Implementation

In this section, we will show that the simple structure shown in Figure C.1 can be used to construct an artificial saturable absorber. This structure represents a single round trip in a ring cavity. It consists of a polarizer, quarter wave-plate (QWP), the Kerr medium (optical fiber) and a half wave-plate (HWP). It is the simplest (and by no means the best) structure capable of achieving additive pulse mode-locking (APM) that relies on non-linear polarization rotation in an isotropic optical fiber. In section 4.2, we develop the Jones matrix formalism required to analyze the structure shown in Figure C.1. We then use this machinery developed in section 4.2 to demonstrate in section 4.3 that this structure can operate as an artificial saturable absorber.
C.3. Simple Ring Cavity Implementation

C.3.1 Jones Matrix Formalism

To arrive at the result we seek, it is convenient to work with the Jones matrix formalism, so we devote this section to defining the matrices we will need for the remainder of the derivation. We will be expressing the polarization state of the light in the linear \((E_x, E_y)\) and circular \((E_+, E_-)\) bases. To convert between them, we will use the basis transformation \(U\) and its inverse \(U^{-1}\):

\begin{equation}
U = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & i \\ i & 1 \end{bmatrix}, \quad U^{-1} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix}
\end{equation}

Using \(U\) and \(U^{-1}\), we can use the relations below to convert Jones vectors from the linear basis to the circular basis and vice versa.

\begin{equation}
\begin{bmatrix} E_+ \\ E_- \end{bmatrix} = U \begin{bmatrix} E_x \\ E_y \end{bmatrix}, \quad \begin{bmatrix} E_x \\ E_y \end{bmatrix} = U^{-1} \begin{bmatrix} E_+ \\ E_- \end{bmatrix}
\end{equation}

Figure C.1: Simple polarization additive-pulse mode locking structure.
Similarly, we can transform Jones matrices in the linear basis to Jones matrices in the circular basis and vice versa as follows

\[
M_{CB} = UM_{LB}U^{-1}, \quad M_{LB} = U^{-1}M_{CB}U
\]  
(C.32)

To mathematically describe the rotation of the wave-plates with respect to the x-axis, we will also need the rotation matrix

\[
R(\theta) = \begin{bmatrix}
\cos(\theta) & \sin(\theta) \\
-\sin(\theta) & \cos(\theta)
\end{bmatrix}
\]  
(C.33)

If we rotate an element represented by a Jones matrix \( M \) by an angle \( \theta \), we obtain (in the linear basis) another matrix \( M(\theta) \). This is just another linear transformation given by

\[
M(\theta) = R(-\theta)MR(\theta)
\]  
(C.34)

In the linear basis, the Jones matrices for a half-wave-plate (HWP), quarter-wave-plate (QWP) and an x-polarizer are defined as follows

\[
M^{(LB)}_{\text{HWP}} = \begin{bmatrix}
1 & 0 \\
0 & -1
\end{bmatrix}, \quad M^{(LB)}_{\text{QWP}} = \begin{bmatrix}
1 & 0 \\
0 & i
\end{bmatrix}, \quad M^{(LB)}_{\text{POL}} = \begin{bmatrix}
1 & 0 \\
0 & 0
\end{bmatrix}
\]  
(C.35)

If we rotate the fast and slow axes of these elements by an angle \( \theta \), we obtain

\[
M^{(LB)}_{\text{HWP}}(\theta) = \begin{bmatrix}
\cos(2\theta) & \sin(2\theta) \\
\sin(2\theta) & -\cos(2\theta)
\end{bmatrix}, \quad M^{(LB)}_{\text{QWP}}(\theta) = \frac{1-i}{2} \begin{bmatrix}
i + \cos(2\theta) & \sin(2\theta) \\
\sin(2\theta) & i - \cos(2\theta)
\end{bmatrix}
\]  
(C.36)

Next, using equation (C.32), we find the circular basis representations of these matrices

\[
M^{(CB)}_{\text{HWP}}(\theta) = \begin{bmatrix}
0 & -ie^{i2\theta} \\
ie^{-i2\theta} & 0
\end{bmatrix}, \quad M^{(CB)}_{\text{QWP}}(\theta) = \frac{1+i}{2} \begin{bmatrix}
1 & -e^{i2\theta} \\
e^{-i2\theta} & 1
\end{bmatrix}, \quad M^{(CB)}_{\text{POL}} = \frac{1}{2} \begin{bmatrix}
1 & -i \\
i & 1
\end{bmatrix}
\]  
(C.37)
The last element we will need in the derivation below is the Jones matrix for the Kerr medium (fiber) itself. In the previous section, we derived this matrix in the circular basis

\[
M_{KERR}^{CB} = e^{ikd} \begin{bmatrix}
e^{i\Delta kd} & 0 \\
0 & e^{-i\Delta kd}
\end{bmatrix}
\] (C.38)

In the linear basis, this matrix is given by

\[
M_{KERR}^{LB} = e^{ikd} \begin{bmatrix}
\cos(\Delta kd) & -\sin(\Delta kd) \\
\sin(\Delta kd) & \cos(\Delta kd)
\end{bmatrix}
\] (C.39)

When written in this representation, it is clear that this matrix is just another rotation matrix, but with a twist. Since the angle of rotation depends on \(\Delta k\), it is intensity dependent. It also depends on the input polarization state of the light. For example, if the input polarization state is linear, the angle of rotation will be zero regardless of the intensity. This can be seen by examining equation (C.28), which shows that, for an even mixture of \(E_+\) and \(E_-\), \(\Delta k = 0\). This equation also suggests that it is advantageous to make the input state purely right-hand-circularly polarized or purely left-hand-circularly polarized because this would maximize the angle of rotation. However, this is also not very useful (for the scheme we are considering) because one cannot distinguish with a linear polarizer between different purely circular states. Hence, we will need to make the input field elliptically polarized. The output polarization will then be the same polarization ellipse (its shape will remain unchanged) rotated by an intensity dependent angle.

### C.3.2 Constructing an Artificial Saturable Absorber

At last, we have all of the ingredients necessary to construct a simple artificial saturable absorber. We now return to Figure [C.1](#) and begin by qualitatively predicting the outcome we will derive below analytically. As shown in Figure [C.1](#) we always start the trip around the cavity with x-polarized light directly out of the polarizer. The QWP oriented at some angle \(\theta_1\) transforms this polarization state \(E_0\) into an elliptically polarized state \(E_1\). This state enters the fiber (Kerr medium) and gets rotated by an intensity dependent angle \(\Delta kd\). This polarization state \(E_3\) exits the fiber with a new orientation, but with its shape and
handedness unchanged. Finally, the HWP oriented at some angle \( \theta_2 \) with respect to the x-axis rotates the polarization ellipse by an intensity independent angle and it returns to the x-polarizer. The projection parallel to the x-axis passes and the remainder of the light gets rejected. Since the angle by which the Kerr medium rotates the polarization ellipse is intensity dependent, we have the liberty of choosing angles \( \theta_1 \) and \( \theta_2 \) such that the losses are low for high intensities and high for low intensities. In doing so, we have added an intensity dependent lossy element into the cavity. In other words, we have created an artificial saturable absorber.

To make the above qualitative discussion more concrete, we now proceed to derive the output intensity after a single round trip assuming, for simplicity, that every element is loss-less and ignoring the amplification produced by the Erbium doped fiber. Let the polarization state directly out of the polarizer be

\[
E^{\text{CB}}_0 = U \begin{pmatrix} A_0 \\ 0 \end{pmatrix} = \frac{A_0}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix} \tag{C.40}
\]

After the QWP, the state is given by

\[
E^{\text{CB}}_1 = M^{(\text{CB})}_Q(\theta_1) E_0 = \frac{A_0}{\sqrt{2}} \begin{pmatrix} e^{i\theta_1} (\cos(\theta_1) + \sin(\theta_1)) \\ ie^{-i\theta_1} (\cos(\theta_1) - \sin(\theta_1)) \end{pmatrix} \tag{C.41}
\]

To compute the angle \( \Delta kd \), we need to first determine \( |E_+|^2 \) and \( |E_-|^2 \) for the light entering the fiber from \( E^{\text{CB}}_1 \). The result is

\[
|E_\pm|^2 = \frac{A_0^2}{2} (1 \pm \sin(2\theta_1)) \tag{C.42}
\]

After the fiber, the polarization state is given by

\[
E^{\text{CB}}_2 = M^{\text{CB}}_K E_1 = \frac{A_0}{\sqrt{2}} e^{i\kappa} \begin{pmatrix} e^{i(\theta_1 + \Delta kd)} (\cos(\theta_1) + \sin(\theta_1)) \\ ie^{-i(\theta_1 + \Delta kd)} (\cos(\theta_1) - \sin(\theta_1)) \end{pmatrix} \tag{C.43}
\]

where

\[
\kappa = \frac{n^{(1)} \omega}{c} \left( 1 + \frac{3A}{4e^{(1)}} A_0^2 \right), \quad \Delta k = -\frac{\omega A}{4en^{(1)}} \sin(2\theta_1) A_0^2 \tag{C.44}
\]
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The state after the HWP in the linear basis (LB) is

$$E_{3}^{LB} = U^{-1} M_{HWP}^{(CB)}(\theta_2) E_{2}^{CB} = \frac{A_0}{2} e^{i \frac{\pi}{2}} \begin{pmatrix} e^{-i \alpha} (\cos(\theta_1) + \sin(\theta_1)) + e^{i \alpha} (\cos(\theta_1) - \sin(\theta_1)) \\ -ie^{-i \alpha} (\cos(\theta_1) + \sin(\theta_1)) + ie^{i \alpha} (\cos(\theta_1) - \sin(\theta_1)) \end{pmatrix}$$

(C.45)

where $\alpha = \theta_1 + \Delta kd - 2 \theta_2$. Finally, the x-polarizer selects the x-component of $E_{3}^{LB}$ and we end up with the following state after a complete round trip

$$E_{4}^{LB} = M_{POL}^{(LB)} E_{3}^{LB} = \hat{x} \frac{A_0}{2} e^{i \frac{\pi}{2}} \left( e^{-i \alpha} (\cos(\theta_1) + \sin(\theta_1)) + e^{i \alpha} (\cos(\theta_1) - \sin(\theta_1)) \right)$$

(C.46)

Using equation (C.46), we can easily compute the ratio of the output intensity and input intensity

$$\frac{I_{out}}{I_{in}} = \frac{1}{2} \left( 1 + \cos(2\theta_1) \cos(2\alpha) \right)$$

(C.47)

$$= \frac{1}{2} \left( 1 + \cos(2\theta_1) \cos(2(\theta_1 + \Delta kd - 2 \theta_2)) \right)$$

(C.48)

$$= \frac{1}{2} \left( 1 + \cos(2\theta_1) \cos \left( 2(\theta_1 - 2 \theta_2) - \frac{\omega A}{2cn(1)} \sin(2\theta_1) dA_0^2 \right) \right)$$

(C.49)

This result may not appear to be particularly illuminating, but we can make several worthwhile observations. First, it is clear that $I_{out}/I_{in} \leq 1$, as expected. For the equality to hold, we would need to send into the Kerr medium a linear polarization. However, as we pointed out previously, this would not be useful because the result would not be an artificial saturable absorber. Second, for a fixed fiber length, the intensity depends on three variables: $\theta_1$, $\theta_2$ and the intensity we would like to optimize for, which is represented in the above expression by $|A_0|^2$. Finding the optimal configuration for constructing a mode-locked laser is not trivial (it is not just a matter of finding the maxima of the above expression) and requires a more sophisticated treatment that is beyond the scope of this report. We briefly discuss this in the section below.
C.4 Concluding Remarks

We have shown that an isotropic Kerr medium (such as an optical fiber) rotates the polarization state of an incoming elliptically polarized beam by an intensity dependent angle. By placing this element, a QWP, HWP and a polarizer into an optical cavity, we can construct an intensity dependent loss element - an artificial saturable absorber. To determine the optimal wave-plate angles, we would need to consider the dynamics of the laser, dispersion, self amplitude modulation (SAM), self phase modulation (SPM), the gain profile of the Erbium doped fiber, other lossy elements in the cavity and a number of other factors. To account for dispersion, we would require solve the non-linear wave equation in the slow varying envelope (SVE) approximation and take into account that the linear refractive index is wavelength dependent. It would also require several other metrics that can be obtained from the Master Equation for mode-locking [67, 154]. In practice, this optimization is often done empirically with the help of an optical spectrum analyzer. Also, we have only discussed the simplest implementation of this type of passive mode locking. By including additional elements (e.g. wave-plates and Faraday rotators), it is possible to achieve mode locked operation with lower round trip losses. For a more involved treatment of this problem, we invite the reader to consult [67, 154].