Photoassociation and Feshbach Resonance Studies in Ultra-Cold Gases of ⁶Li and Rb Atoms

by

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Abstract

This thesis presents an experimental apparatus capable of producing and studying ultracold mixtures of ⁶Li and Rb, and progress towards the creation of ultra-cold ground state ⁶Li₂ and LiRb molecules. Ultra-cold experiments with molecules have applications in many quantum computation and simulation experiments. We discuss elements of the apparatus which are important to these experiments, including electric field plates in air capable of producing fields up to 18 kV/cm, and a laser system for photoassociation spectroscopy based on two Ti:Sapphire lasers phase locked to the same optical frequency comb. With respect to ⁶Li and ⁸⁵Rb mixtures, we report on the observation of six Feshbach resonances, which represent an important step towards molecule production and future experiments in this heteronuclear mixture. In addition, we demonstrate the production of a BEC of ⁶Li₂ Feshbach molecules, a degenerate Fermi gas of ⁶Li and the formation of BCS pairs.

In the ⁶Li system, we report on the high resolution spectroscopy of the v' = 20 - 26vibrational levels of the $c(1^{3}\Sigma_{g}^{+})$ potential and the v' = 29 - 35 vibrational levels of the $A(1^{1}\Sigma_{u}^{+})$ potential. In the $A(1^{1}\Sigma_{u}^{+})$ potential, we find that the v' = 31 and v' = 35 levels have the largest transition strength and are therefore good candidates to use as intermediate states in molecule formation. We demonstrate atom-molecule dark states in the BEC-BCS crossover regime and additionally use dark-state spectroscopy to make extremely high resolution measurements of the least bound N'' = 0 ro-vibrational levels in the $X(1^{1}\Sigma_{g}^{+})$ and $a(1^{3}\Sigma_{u}^{+})$ potential. In addition, we present spectroscopy of all ten N'' = 0 and N'' = 2 rovibrational levels in the $a(1^{3}\Sigma_{u}^{+})$ potential and furnish a preliminary interpretation of the observed energy structure.

Finally, we report on the observation of anomalous Autler-Townes and dark-state spectrum. Using an extension to the standard three level model, we show that these anomalous profiles are due to degeneracies that exist in the bound molecular states, and to the choice of polarization of the coupling fields. These results have a direct impact on molecule formation, and provide a clear guide to future experiments.

Preface

All the work presented in this thesis was conducted on an apparatus in the Quantum Degenerate Gas laboratory at the University of British Columbia, Point Grey campus. I was heavily involved in the design and construction of the apparatus with the exception of the home-built Rb and Li master lasers discussed in Section 2.1. I was also heavily involved in the data taking and analysis of all of the results presented in this thesis.

The ratchet lock technique presented in Section 2.3 has been published in W. Gunton et al., Optics Letters **40** pp. 4372-4375 (2015) [78]. Figure 2.16 was made by Kirk Madison, Fig. 2.17 was made by me, and both appear in [78]. I was responsible for the rebuild of the frequency comb discussed in the section, with assistance from Julien Witz and Art Mills.

The design of the Zeeman Slower presented in Section 3.1 and the vacuum system discussed in Section 2.2 was led by William Bowden as a Master's thesis project [99]. The construction of this iteration of the apparatus was built in collaboration with William Bowden, Steven Novakov, Kahan Dare and Mariusz Semczuk. The results presented in Section 3.1 have been accepted for publication in Review of Scientific Instruments [125], and I am the second author on the paper. Figures 3.5, 3.6, and 3.7 appear in the manuscript and were made by me.

Chapter 4 is heavily based on a manuscript that has been published in W. Gunton et al., Review of Scientific Instruments 87(3) (2016) [142]. The construction of the electric fields plates and associated high-voltage electronics was carried out with the help of Gene Polovy, and the majority of the data was taken in collaboration with Mariusz Semczuk. Figures 4.8, 4.9, 4.10, 4.12, 4.13, and 4.14 appear in the manuscript and were made by me.

In Chapter 5, Fig. 5.3 was made by C. Chin et al., and appears in [10]. Figure 5.4 was made by S. Simonucci et al., and appears in [147]. The results of Section 5.1.3 have been published in W. Gunton et al., Phys. Rev. A. 88, 062510 (2013) [165]. The data in this section was taken in collaboration with Mariusz Semczuk. Figures 5.6 and 5.7 were made by me, Mariusz Semczuk, and Kirk Madison and appear in [165].

The results of Section 6.1.1 have been published in M. Semczuk et al., Phys. Rev. A 87, 052505 (2013) [84] on which I am the second author. Figure 6.2 was made by Nikesh S. Dattani and appears in [84]. The results of Section 6.1.2 have been published in W. Gunton et al., Phys. Rev. A 88, 062510 (2013) [85]. The theoretical analysis of the molecular potentials presented in these two papers was done by Nikesh S. Dattani and is not included in this thesis.

The analysis of the electromagnetically induced transparency (EIT) spectra (including that of the dark state spectroscopy data) presented in Chapter 6 was done by me using a simulation that I originally wrote and was modified and updated (and cleaned up) by Ted van der Weerden. The analysis of the eigenstates of the N'' = 2 level in Section 6.3.2 was done by me, using code that was written by Fernando Luna. The high resolution dark state spectroscopy and the atom-molecule dark state data presented in Sections 6.1.3 and 6.3.1 has been published in M. Semczuk et al., Phys. Rev. Lett. **113**, 055302 (2014) [159]. The data in this section was taken in collaboration with Mariusz Semczuk. Figure 6.5 was made by me and appears in [159]. Figure 6.11 was made by Mariusz Semczuk and appears in [98].

Chapter 7 presents results that have been published in B. Deh et al., Phys Rev. A 82, 020701(R) (2010) [52], on which I am the second author. The data in this section was taken in collaboration with Ben Deh, Bruce Klappauf, and Mariusz Semczuk. The theoretical analysis was done by Zuan Li. Figures 7.1 and 7.2 were made by Ben Deh and the latter appears in [52]. Figure 7.3 was made by Zuan Li.

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List of Abbreviations

ABM asymptotic bound state model AOM acousto-optic modulator BCS Bardeen-Cooper-Schrieffer **BEC** Bose-Einstein condensate **CDT** crossed optical dipole trap ECDL extended cavity diode laser EDFA erbium-doped fiber amplifier **EIT** electromagnetically induced transparency FC Franck-Condon **FR** Feshbach resonance HNLF highly non-linear fiber ITO indium tin oxide **MOT** magneto-optical trap mBEC molecular Bose-Einstein condensate **NEG** non-evaporable getter **ODT** optical dipole trap **OFC** femtosecond optical frequency comb **PA** photoassociation **PZT** piezoelectric transducer **RGA** residual gas analyzer STIRAP stimulated raman adiabatic passage **TA** tapered amplifier **WDM** wavelength division multiplexer

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Chapter 1

Introduction

The field of Atomic, Molecular, and Optical (AMO) Physics encompasses the study of interactions between matter and matter and/or matter and light which occur on a small scale, where quantum effects play a role in the interactions. Rapid developments and new methods for cooling and controlling atomic and molecular systems brought with them the ability to study gases in an extremely "clean" (high precision) setting. These developments were highlighted by the formation of the first Bose-Einstein Condensate (BEC) in 1995 with systems of ⁸⁷Rb [1], Na [2] and ⁷Li [3]. Several years later degeneracy was reached in Fermionic systems using ⁴⁰K [4] and ⁶Li [5]. These degenerate Fermi gases differ from their bosonic counterparts in that the Pauli exclusion principle forbids identical particles from occupying the same quantum state. This unique property plays a key role in many physical effects, from electrical conductivity in metals to the stability of white dwarf and neutron stars, and motivates the interest in, and study of, fermionic systems.

The ability to reach these quantum regimes, where the quantum nature of the particles and the underlying Bose or Fermi statistics play a role, requires that the thermal de Broglie wavelength

$$\lambda_{\rm db} = \sqrt{\frac{2\pi\hbar^2}{mk_BT}}\,,\tag{1.1}$$

is on the same order as the interparticle spacing, given by $n^{-1/3}$ where n is the density. This transition is often characterized by the phase space density of the gas, where $PSD = n\lambda_{db}^3$, where the transition from a classical gas to a quantum gas occurs when the PSD is of order one. Given the scaling of the thermal de Broglie wavelength with temperature (see Eq. 1.1), reaching this quantum regime requires both relatively high density and low temperatures¹. While many experimental techniques can produce cold atoms and molecules, laser cooling

¹In this context, high density truly is a relative term. In ultra-cold experiments, "high density" means a density on the order of 10^{13} /cm³. If this density is compared to that of air (on the order of 10^{19} /cm³), the relativity of the term "high" is evident!

is unique in its ability to achieve phase space densities on the order of, or larger than, one. For example, buffer gas cooling and stark deceleration can reach typical temperature of tens to hundreds of mK while achieving densities on the order of 10^6 /cm³ to 10^8 /cm³, which corresponds to phase space densities on the order of 10^{-15} to 10^{-13} [6, 7, 8]. In contrast, laser cooling can reach temperatures on the order of tens to hundreds of nK with densities on the order of 10^{13} /cm³, corresponding to phase space densities greater than one.

In ultra-cold experiments, control is achieved over both the internal structure (i.e., the quantum state of the atom) and the external degrees of freedom (i.e., the translational motion). In addition, because they are almost stationary in the lab frame, the atoms can be trapped and investigated for long times. Somewhat unique to these systems is that the trapped sample can be considered a "dillute" gas, in the sense that the distance between particles (on the order of 100 nm) is much larger than the characteristic size of the particle (typically on the order of one $a_0 \approx 0.05$ nm). Because of this, collisions between particles are dominated by binary encounters and thus two-body interactions. Moreover, in the limit of low energy, the interactions can be characterized by a single parameter (the *s*-wave scattering length) which describes the effective range of the interactions². In the absense of any resonance effects, this background scattering length is on the order of 10-100 a_0 , or a few nm. The extended range of the interactions (relative to the size of the atoms) is due to a dipole-induced dipole interaction, which results in a Van der Waals potential that scales like $-C_6/r^6$ at long range [9].

Ultra-cold gases can be controlled by tuning the strength of the interactions (i.e., modifying the *s*-wave scattering length) with external fields (for example, with Feshbach resonances (FRs) in the case of magnetic fields [10]) or by changing the dimensionality of the system through the use of optical lattices[11]. This control allows the ultra-cold atomic systems to enter a regime were many-body physics such as Bardeen-Cooper-Schrieffer (BCS) pairing and superfluidity can be studied [12, 13].

More recently, experiments have started to extend the control achieved in atomic gases to molecules, in both homonuclear systems (for example, Cs₂ [14, 15], Rb₂ [16, 17] and Sr₂ [18]) and heteronuclear systems (for example, ${}^{40}K^{87}Rb$ [19, 20], ${}^{87}Rb^{133}Cs$ [21, 22],

²In ultra-cold gases, *p*-wave (and higher) collisions are strongly suppressed if the collision energy is less than the potential barrier associated with the rotational energy required by angular momentum conservation. The *p*-wave barrier height for bi-alkali collisions is typically on the order of a few mK, which leads to *s*-wave collisions dominated at the typical collision energies on the order of a few μ K or less.

⁷Li¹³³Cs [23], and ²³Na⁴⁰K [24]). Broadly speaking, research into ultra-cold molecules is significant because they have much richer and more interesting interactions compared to atoms, which arise from their magnetic and electric dipole (and higher order) moments. In addition, molecules possess a richer internal structure that makes them even more useful than atoms as tools to, for example, study many-body quantum dynamics [25, 26, 27], realize quantum simulators [28, 29], and test fundamental laws of nature [30, 31, 32].

The interest in dipole-dipole interactions lies in their longer range character, as the interaction energy scales like $1/r^3$. This is in contrast to the $1/r^6$ scaling of the Van der Waals interaction between ground state atoms, which are short range in comparison to the interparticle spacing that can be realized in ultra-cold systems (in light of this, the interaction between atoms is typically described by the "contact interaction"). Moreover, the dipole-dipole interaction is anisotropic, and the interaction can be attractive or repulsive depending on the relative orientation of the electric dipoles during a collision. These long-range dipole-dipole interactions are required for many theoretical proposals for quantum computation [28, 29], or proposals to study phenomena in other realms of physics. For example, it is possible to simulate more complicated many-body Hamiltonians important to condensed matter physics [25, 26, 27].

While the dipole-dipole interaction can be either magnetic or electric in nature, the strength of the achievable interaction energies varies considerably. For example, the ratio of interaction energies between two electric (μ_{el}) and two magnetic (μ_{mg}) dipoles scales like

$$\frac{E_{\rm dd,el}}{E_{\rm dd,mg}} \propto c^2 \left(\frac{\mu_{\rm el}}{\mu_{\rm mg}}\right)^2,\tag{1.2}$$

where c is the speed of light. Some of largest magnetic moments in ultra-cold systems have been realized using Dysprosium [33, 34] where $\mu_{mg} \approx 10\mu_B$ (and μ_B is the Bohr magneton), or Chromium [35, 36] where $\mu_{mg} \approx 6\mu_B$. On the other hand, typical bi-alkali polar molecules have electric moments on the order of 1 D [37, 38]. Comparing these two cases using Eq. 1.2, it can be seen that the strength of the electric dipole interaction is more than two orders of magnitude stronger than the magnetic dipole-dipole interaction at a similar distance.

Although polar molecules are said to have a permanent electric dipole moment, this permanent moment exists only in the molecule frame. In the laboratory frame (and in the absence of an external electric field) there is no fixed orientation of the molecular axis, and the average electric dipole moment is zero. Therefore, an external electric field is required to polarize the molecule along the field direction. The advantage of polarizing an ensemble of polar molecules over, for example, atoms, lies in the magnitude of the required electric field. As the effect of a dc electric field is to couple rotational states with different parity [39, 40], the required field strength to polarize an ensemble can be estimated by comparing the size of coupling term due to the electric field to the energy difference between adjacent rotational states. In this case, the coupling term is [39]

$$H = \vec{d} \cdot \vec{E} = e\epsilon z \,, \tag{1.3}$$

where $\vec{d} = e\vec{z}$ is the electric dipole moment, $\vec{E} = \epsilon \hat{z}$ is the dc electic field (applied along the *z*-axis), *e* is the electron charge, and ϵ is the magnitude of the electric field. In this case, the Bohr radius is used as an estimate of *z*. In the case of atoms, the coupled rotational states are states of different electronic orbital angular momentum, where the splitting is on the order of hundred of THz, and the required electric fields are on the order of 100 MV/cm. However, in heteronuclear molecules, the electric field can couple states of different nuclear orbital angular momentum where the splitting can be on the order of tens of GHz. This leads to required electric field strengths on the order of a few to tens of kV/cm, which is in the range of electric fields that are experimentally realizable.

Aside from the control over both the external and internal degrees of freedom provided by ultra-cold systems, the need for ultra-cold systems to study much of the physics associated with long-range dipole-dipole interactions can be seen by considering the typical energy and time scales associated with these interactions. For example, the interaction energy associated with electric dipole of 1 D separated by 266 nm (this length scale is chosen as it is the lattice spacing associated with a 532 nm optical lattice) is $E \approx \hbar \times 10$ kHz $\approx k_B \times 500$ nK. Ultra-cold experiments based on laser cooling therefore represent an ideal system, as this range of temperatures is currently experimentally achievable³.

Ultra-cold molecules are also a useful tool in the study of ultra-cold chemistry [41]. With polar molecules at ultra-cold temperatures, the outcome of a reaction can depend on the orientation and movement of the molecule in three dimensions. For example, it has been shown that it is possible to suppress chemical reactions using the repulsive nature of the "side-by-side" long range dipole-dipole interaction [42]. For molecules with a non-zero

³For example, see ground state KRb molecules which have been formed with a peak density of 10^{12} /cm³ and at a temperature of 350 nK [19, 20].

spin, it has also been predicted that the elastic and inelastic collision rates can be modified by an external magnetic field [43, 44]. The density of these molecule-molecule resonances is expected to be substantially higher than for atoms due to the more complex internal structure of molecules, related to the large number of rovibrational states.

The creation to ultra-cold molecules can generally follow two paths. The first (and perhaps most obvious) method is to directly laser cool molecules [45]. However, due to their complex internal structure, it is often hard to find a closed transition on which to laser cool. Although it has been demonstrated that laser cooling is possible for SrF [46, 47], these molecules are far from the ultra-cold regime, and it is still not a widely used technique for the creation of ultra-cold molecules. The second approach is to form ultra-cold molecules from ultra-atoms using a coherent population transfer via stimulated raman adiabatic passage (STIRAP) [48]. Here, ultra-cold atoms are associated into loosly bound Feshbach molecules, either through three body recombination or by adiabatically sweeping across a FR [10]. Then, the loosely bound Feshbach molecules are coherently transferred (i.e., transferred without heating) into a deeply bound molecular state using two coherent lasers. In this case, the binding energy of the molecule is carried away by the laser fields. This method has proved enormously successful for both the formation of homonuclear and heteronuclear molecules⁴.

1.1 Motivation

The long term goal of our experiment is the creation and study of LiRb molecules. These molecules are of particular interest because they are expected to have a large electric dipole moment in the ground singlet potential (4.2 D [37]) and a moderately large moment in the lowest lying triplet potential (0.37 D [38]). This is the largest permanent electric dipole moment of all the bi-alkali molecules, save for LiCs [37]. Moreover, the size of the electric dipole moment in the triplet state is on the order of the size of the dipole moment of the ground singlet state of KRb, while the triplet LiRb molecule still has a non zero spin. Polar molecules with a non zero spin degree of freedom are crucial, for example, in proposals to study lattice-spin models [26].

In addition to LiRb molecules, we also have a strong interest in studying heteronuclear

 $^{^4\}mathrm{In}$ fact, all of the homonuclear and heteronuclear molecules referenced in this section have been created using STIRAP.

 ${}^{6}\text{Li}_{2}$ molecules. Fermionic atomic systems such as ${}^{6}\text{Li}$ are unique in the respect that loosely bound Feshbach molecules can be produced with a higher efficiency than in bosonic gases (as the Pauli exclusion principle reduces collisional relaxation of these Feshbach molecules to deeply lying state). In addition, ${}^{6}\text{Li}_{2}$ is chemically stable with respect to collisions with other Feshbach pairs. These properties make it relatively simple to achieve a molecular Bose-Einstein condensate (BEC) of ${}^{6}\text{Li}_{2}$ Feshbach molecules and, by extension, possible to achieve a BEC of ground state molecule using STIRAP. In addition, the ${}^{6}\text{Li}_{2}$ system is a good candidate to, for example, study the stability of alkali-metal dimers in the lowest lying triplet state with respect to spin relaxation to the ground singlet state or with respect to trimer formation [38], and to search for magnetically tunable molecular scattering resonances [43, 44].

Experimentally, the recipe for forming ultra-cold molecules is similar for both homonuclear and heteronuclear dimers. The first step is the formation of loosely bound Feshbach molecules, which requires the knowledge of the location of the Feshbach resonances for the particular mixture. These Feshbach molecules are then coherently transferred to a ground bound molecular state using a two-photon Raman transition. This process uses an intermediate state which, in this case, is an excited electronic state of the molecule. Therefore, spectroscopic knowledge of the energy levels in the accessible excited and ground molecular states are essential and must be determined (if not already known) using one-color and twocolor photoassociation spectroscopy. In addition, the two photon process must be coherent, and therefore the two lasers must be phase coherent.

However, the technical challenges of forming LiRb or ${}^{6}\text{Li}_{2}$ molecules vary considerably. Specifically, Feshbach molecules of LiRb are inherently unstable [49], and the ground state molecules themselves are unstable with respect to chemical reactions that form alkali-metal dimers and trimers [38]. Therefore, the creation of (long lived) LiRb molecules requires that the molecules be separated in a three-dimensional optical lattice. For this reason, we choose to first focus on working towards ${}^{6}\text{Li}_{2}$ molecules and experiments with mixtures of (as opposed to molecules) of ${}^{6}\text{Li}$ and Rb.

As it turns out, there are many interesting opportunities that arise working towards the formation of ground state molecules. In the context of this thesis, the dual species work involves experiments with mixtures of 6 Li and Rb (rather than a direct focus on molecule formation), and we have observed FRs in the LiRb mixtures that are some of the broadest

known in heteronuclear mixtures [50, 51, 52]. These resonances are also an effective tool that can be used to efficiently sympathetically cool ⁸⁵Rb using ⁶Li. Additionally, the LiRb system has a large mass imbalance between the bosonic (Rb) and fermionic (Li) species. One implication of this mass imbalance is that it may be more feasible to experimentally observe the appearance of Efimov states, which manifest themselves as a series of minima or maxima in the three body loss coefficient that are equally spaced on a ln *a* scale [53, 54]. In addition, there are many proposals to study novel quantum phases, pairing phenomena and quantum impurity problems using Bose-Fermi mixtures with tunable interactions [55, 56, 57].

With respect to the formation of ⁶Li₂ molecules, FRs in ⁶Li have been well studied, and there exists a broad Feshbach resonance near 832 G which is ideal for the creation of loosely bound Feshbach molecules [58, 59, 60]. These Feshbach molecules are an ideal starting point for the formation of ground state molecules. Therefore, the next step is to determine the location of the bound excited state molecular levels that can be used as a suitable intermediate state. To this end, we performed spectroscopy on the excited triplet $c(1^{3}\Sigma_{g}^{+})$ and excited singlet $A(1^{1}\Sigma_{u}^{+})$ potentials and the lowest lying triplet $a(1^{3}\Sigma_{u}^{+})$ and ground singlet $X(1^{1}\Sigma_{g}^{+})$ potential to which the excited states can (respectively) couple. The focus of the ⁶Li work in this thesis is on the spectroscopy of these potentials, and the creation and understanding of the atom-molecule dark states. These dark states arise in the presence of fields which couple the excited state to both the initial state (either a two-atom scattering state or a loosely bound Feshbach molecule) and to a bound molecular state. Of note is that the $a(1^{3}\Sigma_{u}^{+})$ potential is very shallow, supporting only ten bound vibrational levels⁵. Spectroscopy of all ten vibrational levels of this potential offers a fully characterized molecule potential in the ${}^{6}\text{Li}_{2}$ system, which is interesting to the *ab initio* community as few-electron atoms represent a tractable system with which experimental measurements and theory can be rigorously compared⁶.

Atom-molecule dark states are based on the principle of EIT [61] and are a vital first step to coherent population transfer via STIRAP [48]. They are also an incredibly useful tool in the high resolution spectroscopy and lifetime measurements of bound states in the ground singlet $X(1^{1}\Sigma_{g}^{+})$ and lowest lying triplet $a(1^{3}\Sigma_{u}^{+})$ potentials [62, 63]. In addition,

 $^{{}^{5}}$ The binding energy of the ground vibrational level is on the order of 9 THz, and therefore all 10 vibrational levels are accessible with our Ti:Sapphire based laser system.

⁶Note, however, that even knowledge of the energies of every bound state in the potential (a discrete set) does not allow one to uniquely determine the (continuous) potential energy curve.

dark-states and photoassociation near the broad Feshbach resonance at 832 G can be used as a probe of the many-body state of paired ⁶Li atoms that exist in the BEC-BCS crossover regime [64, 65].

There is also wide interest in the ability to control the scattering length on a fast time scale and with a high degree of spatial resolution in order to study, for example, nonequilibrium dynamics in a strongly interacting Fermi gas [66]. However, these proposals require control of interactions on a timescale $\tau_F \approx \hbar/E_F \approx 10 \ \mu s$ for $E_F \approx k_B \times 1 \ \mu K$ [67]. An obvious tool that can achieve both high spatial resolution and fast temporal control is optical fields. Optical fields have been used to control the *s*-wave scattering length near a magnetic Feshbach resonance [68, 69] and to induce optical Feshbach resonances [67, 70, 71, 72]. However, many of the practical applications of these methods are limited by light induced inelastic losses. The use of a dark state can allow for control of the scattering length while suppressing the spontaneous scattering through quantum interference [67, 70], and has been recently demonstrated using ⁶Li [73].

1.2 Outline of Thesis

The goal of this thesis is, first and foremost, to present (and provide context for) the results of our experiment and describe the methods used in obtaining these results. However, a secondary goal was to write a document that I would have found helpful to read in the early stages of my graduate career. That is, a document that outlines what we do, why we do it, and most importantly how we do it. While some information may appear to be obvious or "known", many are ideas, thoughts or explanations that I would have found helpful (and often still do find helpful) to have in a single place.

Chapter 2 describes the important "hardware" required for the production of ultracold ⁶Li and Rb. This chapter briefly introduces the atomic structure of ⁶Li and Rb, and discusses the impact of the atomic structure on the requirements for the laser cooling light. Section 2.1 details how we generate the laser cooling light for the ⁶Li and Rb magnetooptical trap (MOT), as well as the light used in the Zeeman slower, for optical pumping, and for absorption imaging. In late 2014 (and into 2015), we made substantial changes to our apparatus to include a Zeeman slower in order to make the system more robust for dual species experiments. Section 2.2 introduces and discusses the design and construction of our vacuum system, the effusive sources and the magnetic coils used to create external magnetic fields.

One of the key requirement for experiments with dark-states and STIRAP is that the two fields are phase coherent during the time in which the light is exposed to the atoms [74]. When the binding energy of the ground state is small (on the order of 100s of MHz) it is possible to use an acousto-optic modulator (AOM) to shift the frequency of a single laser to create the desired frequency difference between the two beams [75]. However, when the target ground state is deeply bound (or even moderately bound), two separate lasers must be used. To achieve phase coherence between the two lasers. In our experiment, the lasers are individually phase locked to a femtosecond frequency comb [76]. The comb which we use was originally built by the lab of David Jones at The University of British Columbia [77], but was rebuilt and modified to improve the self-referencing branch, and to add a measurement branch used to stabilize the Ti:Sapphire lasers⁷. Section 2.3 describes the details of the this frequency comb. In addition, this section discusses the two Ti:Sapphire lasers, their lock to the frequency while the other is scanned when both lasers are locked to the frequency comb [78].

Chapter 3 explains the preparation and detection of cold atoms (that is, the sequence of events that occur in a single experimental cycle). This chapter begins where nearly all coldatom experiments begin - with a MOT. As part of the upgrade to our apparatus, we now use a Zeeman slower as the atom source for the MOT. Section 3.1 outlines the operating principles of Zeeman slowers, and discusses the features that are unique or important to our implementation. This section also includes a characterization of the MOT and Zeeman slower⁸. Section 3.2 describes the two optical dipole traps (ODTs) that are used in our setup, and discusses strategies for the transfer of ⁶Li and Rb from the MOT to the ODT, and the subsequent evaporation. One of the advantages of ultra-cold systems, and specifically trapping in an ODT, is the ability to prepare an atomic ensemble in a particular hyperfine or Zeeman state. This allows for experimental control over the scattering state which is useful in, for example, our Feshbach resonance experiments. Section 3.3 describes the procedure for optically pumping ⁸⁵Rb, and for the state selection of ⁶Li in large magnetic fields.

⁷In this rebuild, the oscillator itself remained the same.

⁸While the details of laser cooling are not discussed, this information is readily available in textbooks, for example [79].

Finally, Section 3.4 describes our imaging techniques - namely, fluorescence and absorption imaging. This section also discusses imaging 6 Li at high magnetic fields, as well as Zeeman state selective imaging of 85 Rb.

Before our experiment began to focus on ${}^{6}Li_{2}$ molecules, we were motivated to study the effects of electric fields on atomic collisional resonances [80, 81], guided by a proposal regarding the effects of electric fields on FRs in ultra-cold LiRb mixtures [82]. These effects required electric fields in excess of 20 kV/cm, and we set out to build transparent electrodes that could be added to our system outside of the vacuum. As the electric fields of interest are greater than the dielectric breakdown of air, we had to find a way to physically prevent the flow of charge through air. The solution was to imbed an indium tin oxide (ITO) coated dielectric substrate inside of stack of two more transparent substrates, where the outer layers have a much higher dielectric strength than air. Chapter 4 is focused on a discussion of the design, and the implementation of these field plates in our setup. Specifically, Section 4.1 details the design of the electric plates and the associated high voltage components, and Section 4.2 discusses the testing and characterization of the plates using spectroscopic measurements of the dc Stark effect in ⁸⁵Rb. While we were able to produce fields of up to approximately 18 kV/cm, we were severely limited by a large loss of atoms that occurred when we applied large voltages to the plates. In addition, we observed a decay of the electric field strength over time (when the plates were held at a high voltage), as well as a residual field that remained after the plates were grounded. Section 4.3 describes these effects, with we attribute to free charges (primarily electrons) produced by field emission of grounded metal parts within the vacuum chamber. Due to these limitations, we were unsuccessful in observing the proposed effects on LiRb FRs. However, these electric field plates will play an important role in experiments with polar molecules, where electric fields on the order of 10 kV/cm are required to achieve partial lab frame alignment of the electric dipole moment of the molecules [83].

Chapter 5 shifts the focus of this thesis to the ⁶Li and ⁶Li₂ system. This chapter serves as an overview of the theory and background necessary for the discussion of the results presented in Chapter 6. Section 5.1 introduces the two-atom scattering state which serves as the initial state for many of our photoassociation and dark state experiments, as well as the bound states that exist in the ⁶Li₂ molecule. This section also discusses *s*-wave Feshbach resonances in the mixtures of the $|1\rangle$ and $|2\rangle$ states, and the experimental realization of a molecular BEC and BCS-like pairs in our setup. Section 5.2 outlines the different types of spectroscopy experiments that we perform, and discusses dark-states and STIRAP. This section also introduces and discusses the usefulness and limitations of the standard three level model for dark-states that is used in the analysis of much of our results. Additionally, this section discusses a mechanism that we believe suppresses the effects of laser decoherence on the atom-molecule dark state in a regime where the initial state is only weakly coupled to the excited state.

At long last, Chapter 6 presents the new and novel observations that have resulted from our work with ⁶Li and ⁶Li₂ molecules. The single color spectroscopy of the $c(1^{3}\Sigma_{a}^{+})$ and $A(1^{1}\Sigma_{u}^{+})$ potential are discussed in Section 6.1.1 and 6.1.2 respectively. Our measurements of the $c(1^{3}\Sigma_{q}^{+})$ potential are the first to observe and quantify the spin-spin and spin-rotation coupling constants. In the $A(1^{1}\Sigma_{u}^{+})$ potential, we also check the viability of performing STIRAP by measuring the coupling strength of the $|a\rangle \rightarrow |e\rangle$ transition as a function of vibrational level, and as a function of magnetic fields above and below the broad Feshbach resonance near 832 G (i.e., in the BEC-BCS crossover regime). In both the $c(1^{3}\Sigma_{q}^{+})$ and $A(1^{1}\Sigma_{u}^{+})$ potential, we observe ro-vibrational levels that have not yet been observed in cold-atom experiments, and have resulted in significant improvements to the theoretical potentials for these states⁹. Section 6.1.3 presents dark state spectroscopy of the two least bound levels (v'' = 37 and v'' = 38) of the $X(1^1\Sigma_q^+)$ potential. In particular, the v'' = 37level is measured at magnetic fields above and below the Feshbach resonance. As the v'' = 38 vibrational level is not bound at these magnetic fields, the v'' = 37 vibrational level is necessary for dark-state studies of the BEC-BCS crossover regime and for dark-state control of FRs [67, 70, 73]

With the relevant levels in the ${}^{6}\text{Li}_{2}$ system, it turns out that is not possible to experimentally realize a system that contains only three levels (i.e., the standard system used to describe STIRAP and dark-states). Section 6.2 discusses how the presence of these degenerate levels leads to unexpected profiles to appear in the Autler-Townes and dark-state spectrum. Specifically, we observe an anomalous third feature that appears in the Autler-Townes spectrum (which is typically associated with only two features), which we attribute to an interference between possible excitation pathways. However, this interference is distinct from that which leads to dark-states as it does not require phase coherence between the

⁹The theory work based off our experimental data was performed by Nike S. Dattani, and is not discussed in this thesis. Details of this work, and of the updated model potentials can be found in [84, 85].

probe and control fields. In addition, we observe a poor dark-state revival when particular states are used in the $a(1^{3}\Sigma_{u}^{+})$ and $c(1^{3}\Sigma_{g}^{+})$ potentials. We attribute this to a decoherence mechanism which results from additional couplings of the dark state to decaying excited states that provide a mechanism for loss. We show that both of these effects are dependent on the polarization of the pump and control field. In the context of STIRAP, an understanding of these decoherence mechanism is vital, as the maximum transfer efficiency is directly related to the fidelity of the dark state.

Section 6.3 presents a measurement of the N'' = 0 and N'' = 2 rotational levels of all 10 vibrational levels in the lowest lying triplet $a(1^{3}\Sigma_{u}^{+})$ potential using two-color photoassociation spectroscopy. For the least bound v'' = 9 vibrational level, we use dark-state spectroscopy to measure the binding energy of all three hyperfine levels in the N'' = 0 rotational level. The absolute uncertainty of these measurements represents an improvement by a factor of over 40 compared to previous measurements [86, 87]. We find that the measured energy difference between hyperfine manifolds deviates from the standard treatment of hyperfine structure in high lying vibrational levels [88, 89]. The dark-state spectroscopy of the F'' = 1 hyperfine manifold displays an experimental demonstration of the decoherence mechanism discussed in Section 6.2. The measurements of the binding energy, and understanding of the dark-state behavior is crucial in the work towards STIRAP and the creation of ground triplet state molecules. In the N'' = 2 ro-vibrational levels, we observe a set of three features, separated by hundreds of MHz that, for the deeply bound vibrational levels, correspond to the three J'' states. For the high lying vibrational levels, the size of the hyperfine coupling and spin-spin coupling are of similar magnitude, and the eigenstates of the system appear to be a linear superposition of all three J'' states.

Chapter 7 shifts the focus back to our work on mixtures of ⁶Li and Rb. Specifically, Section 7.1 discusses our strategies for the production of ultra-cold Bose-Fermi mixtures, and Section 7.2 reports the position, width and open channel atomic states associated with six FRs in the LiRb mixture for magnetic fields between 300 and 1000 G. Knowledge of the location of these Feshbach resonances will guide future work with these mixtures, and are required to form loosely bound Feshbach molecules that are a vital first step towards molecule production.

Finally, Chapter 8 summarizes the results of this thesis and outlines the future directions of the experiment. The results of this thesis provide a clear path towards the production of ${}^{6}\text{Li}_{2}$ molecules in the near term. In addition, the upgrades and development of the appratus motivate working in earnest with LiRb mixtures.

On the Topic of Notation

In order to be consistent throughout, this thesis uses lowercase letters to represent quantum numbers in atoms and uppercase letters to represent quantum numbers in molecules. In addition, quantum numbers with a single prime (i.e., f' or F') represent quantum numbers of an excited state of an atom or molecule. Likewise, quantum numbers with a double prime (i.e., F'') represent quantum numbers of a molecule in either the ground singlet or lowest lying triplet potential. Unless otherwise noted, quantum numbers without a prime refer to ground state atoms or molecules that are associated with the two-atom scattering state or Feshbach molecules (i.e., the initial state used in photoassociation experiments).

Chapter 2

Experimental Setup

2.1 Laser Cooling Light

The focus of our experiment is laser cooling and trapping of two alkali metals: ⁶Li and Rb^{10} . As an introduction to these atoms, this section briefly discusses the contributions to the atomic structure. The obvious starting point of this discussion is the electronic configuration. For ⁶Li, which consists of 3 electrons and 3 protons, the ground state electron configuration is (including the empty first excited electronic orbital)

$$1s^2 2s^1 2p^0$$
, (2.1)

where the number represents the principal quantum number n, the letter represents the electron orbital angular momentum l, and the superscript represents the number of electrons in each orbital. The empty p orbital represents the first excited state, and is shown in reference to the following discussion. For Rb, which consists of 37 electrons and 37 protons the ground state electon configuration is

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 04s^2 5p^6 5s^1 5p^0. (2.2)$$

For both ⁶Li and Rb (and all the alkali metals), the ground state electron configuration has a single valence electron in an *s* orbital. The first available excited state of the electron is a *p* orbital, as indicated by the first empty electronic orbital in Eqs. 2.1 and 2.2.

Coupling between the spin of the electron s and the orbital angular momentum of the electron l gives rise to fine structure, where the additional term in the Hamiltonian has the form $\vec{l} \cdot \vec{s}$. In this case, it is useful to work in the basis where the total electronic angular momentum $\vec{j} = \vec{l} + \vec{s}$ is a good quantum number, and can take on values ranging from l + s

¹⁰An excellent resource for more detailed information on these atomic species has been written by Dan Steck for ⁸⁵Rb [90] and ⁸⁷Rb [91], and by Michael Gehm for ⁶Li [92].

down to |l - s| in integer steps. Each fine structure state is labeled by the term symbol

$$^{2s+1}l_j$$
. (2.3)

For the alkalis, the ground electronic state has s = 1/2 and l = 0, which leads to a single fine structure state labeled by j = 1/2. The first electronically excited state is a p orbital, where l = 1. Therefore, j can take on two values, either j = 1/2 or j = 3/2. The ${}^{2}S_{1/2} \rightarrow {}^{2}P_{1/2}$ transition is referred to as the D_{1} transition, while the ${}^{2}S_{1/2} \rightarrow {}^{2}P_{3/2}$ transition is referred to as the D_{2} transition. In ⁶Li , these two transition frequencies are seperated by approximately 10 GHz [92], while in Rb the splitting is on the order of 7 THz [90, 91].

Additionally, coupling between the spin of the nucleus i and the total angular momentum j leads to hyperfine structure, where this additional perturbation has the form $\vec{j} \cdot \vec{i}$. Similiar to the fine structure case, it is useful to work in the basis where the total angular momentum including nuclear spin $\vec{f} = \vec{j} + \vec{i}$ is a good quantum number, and f can take on values ranging from j + i down to |j - i| in integer steps.

More specifically, the hyperfine structure is due to an interaction of the magnetic field from the proton (which constitutes a magnetic dipole in the case of a non-zero nuclear spin) with the electron spin. Given the proton dipole $\vec{\mu}$, the associated magnetic field is

$$\vec{B} = \frac{\mu_0}{4\pi r^3} \left[3(\vec{\mu} \cdot \hat{r})\hat{r} - \vec{\mu} \right] + \frac{2\mu_0}{3} \vec{\mu} \delta^3(\vec{r}) \,. \tag{2.4}$$

The first term leads to an energy correction that is proportional to the expectation value of $1/r^3$ and vanishes for any wave function that is spatially symmetric (i.e., a state with l = 0). The second term leads to the Fermi-contact interaction and is non-zero only if the electron wavefunction is non-zero at the position of the nucleus (for example, the l = 0state). When considering the hyperfine splitting of the ground (l = 0, a s orbital) and first excited (l = 1, a p orbital) states, the hyperfine interaction in the ground state is much larger than in the first excited state.

The details of the hyperfine structure of ⁶Li and Rb directly impact the requirements on the laser cooling light. These details, along with the generation of the laser cooling light, are discussed in the following two sections. Of note is that the majority of our laser cooling light is generated on a single "master table" and fiber coupled to all of the experiments in the lab for amplification. This details in this thesis focuses on the amplification and frequency shifting schemes for both species. Full details on our home built masters lasers, and the saturated absorption spectroscopy which we use to reference and stabilize the lasers can be found the Masters thesis of Keith Ladoucer [93], Janelle van Dongen [94] and Swati Singh [95].

2.1.1 Lithium Light

A ⁶Li atom has a nuclear spin i = 1. Therefore, in the ${}^{2}S_{1/2}$ fine structure manifold, this gives rise to two hyperfine levels, namely f = 1/2 and f = 3/2. These two hyperfine manifolds are split by $3/2 \cdot a_{2S} \approx 228$ MHz, where a_{2S} is the magnetic dipole hyperfine constant which determines the strength of the hyperfine interaction (see Table 2.1). Likewise, in the first electronically excited state, the ${}^{2}P_{1/2}$ fine structure manifold also has two possible hyperfine manifolds, corresponding to f = 1/2 and f = 3/2. The ${}^{2}P_{3/2}$ fine structure manifold has three possible hyperfine manifolds, corresponding to f = 1/2, 3/2, 5/2. The magnitude of the splitting of the hyperfine levels in the excited state is also determined by the magnetic dipole hyperfine constant and, in the case of the ${}^{2}P_{3/2}$ manifold, the electric quadrupole hyperfine constant. The value of these constants is summarized in Table 2.1.

Property	Symbol	Value (MHz)
$2^2 S_{1/2}$ magnetic dipole constant	a_{2S}	152.1368407
$2^2 P_{1/2}$ magnetic dipole constant	$a_{2P_{1/2}}$	17.386
$2^2 P_{3/2}$ magnetic dipole constant	$a_{2P_{3/2}}$	-1.115
$2^2 P_{3/2}$ electric quadrupole constant	$b_{2P_{3/2}}$	-0.10

Table 2.1: Magnetic dipole and electric quadrupole hyperfine constants of the ground state and first excited state of ⁶Li. Note that only the $2^2 P_{3/2}$ fine structure manifold has a non zero electric quadrupole hyperfine constant. Values from [92, 96, 97].

Our MOT operates on the D_2 transition, with the "pump" light near the $f = 3/2 \rightarrow f' = 5/2$ transition frequency and the "repump" light near the $f = 1/2 \rightarrow f' = 3/2$ transition frequency. However, the splitting of the hyperfine levels in the ${}^2P_{3/2}$ is on the order of a few MHz, which is less than the natural linewidth of the transition. In this case, the pump light excites all three hyperfine manifolds with similar rates. Since the f' = 3/2 and f' = 1/2 excited manifolds can decay to the lower f = 1/2 ground hyperfine manifold, the population in the upper f = 3/2 ground hyperfine manifold is rapidly depleted. Therefore,

the repump light must have a similar scattering rate (i.e., intensity) as the pump light, and consequently also contributes to cooling and exerts a radiation pressure force on the MOT which is comparable to the pump light.

As the splitting of the ground hyperfine levels is approximately 228 MHz, both the pump and repump light can be derived from the same master laser. In our case, our master laser is Toptica DL Pro, which we lock 50 MHz blue of the MOT pump transition. The locking error signal is generated with saturated absorption spectroscopy using a frequency modulation scheme [93, 94, 95]. Details of specific beam paths and layouts can be found in the PhD thesis of Mariusz Semczuk [98]. After optical isolators, the output power of the laser is about 15 mW, which is split three ways between the error signal generation, the offset lock for the high field imaging master and amplification for the experiment. The latter two pathways are discussed below.

MOT and Zeeman Slower

The portion of the master light destined for the experiment is used to seed a "slave" amplifier, which is based off of a Mitsubishi ML 101J27 laser diode. These diodes are specified to emit at a wavelength of 660 nm at 25° C with a driving current of 120 mA. However, around 72°C the free running wavelength is between 670 and 671 nm (near the required wavelength for 6Li). Although running the laser diode at higher temperatures significantly reduces the output power, we have found that we can achieve reasonable output powers (on the order of 60 mW) by increasing the current to a range between 350 and 450 mA. While this current is well above the damage threshold at room temperature, it does not appear to damage the diodes at the high temperatures at which we operate. The output of this slave is split into two arms using a 50/50 fiber splitter from Evanescent Optics, where each output of the fiber splitter has a power of 15 mW.

Light from one of the output ports is used to generate the light for the Zeeman slower. The light is used to seed a home-built tapered amplifier (TA) based off of an Eagleyard EYP-TPA-0670-00500-2003-CMT02-0000 chip. The output of the TA is fiber coupled into a 50 m long single-mode, polarization-maintaining fiber and sent to the experiment table. On this table, the light is frequency shifted to match the desired detuning for the slowing beam using an AOM in a double pass configuration. We operate this AOM with an RF driving frequency of 63 MHz, and use the negative first order diffraction such that the slowing beam is 76 MHz red of the pump transition. The output mode of the TA is quite poor and, as such, we typically only couple approximately 110 mW out of 350 mW through the long fiber. After the double pass AOM we have approximately 30-35 mW available for the slowing beam¹¹.

Light from the second output port is used to generate the MOT pump and repump beams. The slave light is used to seed a second slave, and the output of this slave is coupled into a short fiber. The output of the fiber is used to seed two TAs from Sacher Lasertechnik (TPA-0670-0500). We fiber couple seeding light so that the source of seed beam can be changed without impacting the alignment of the seed beam for both TAs. When new, these TAs output about 450 mW. However, we have found that the power degrades rather quickly over time and we typically achieve 300 to 350 mW output power. We have also found that the output spectrum of the TAs varies with the seeding power, as shown in Fig. 2.1. Typically, we use 18-20 mW to seed both amplifiers.

To generate the MOT pump light, the seed beam is up shifted by 108 MHz using a single pass AOM, and the output of the TA is downshifted by a double pass AOM to give a frequency that is centered 45 MHz red of the pump transition. To generate the MOT repump light, we only up shift the output of a second TA with a double pass AOM to give a frequency that is centered 40 MHz red of the repump transition. Both beams are coupled in separate 50 m long single-mode, polarization-maintaining fibers and sent to the experiment table where they are combined and then split three ways for each of the orthogonal axes of the MOT. When the TAs were new, we were able to achieve about 100 mW of power in each beam on the experiment table. After multiple years of operation, we typically have about 40 mW of each beam. However, we recently replaced the chip in the pump TA and currently achieve 115 mW of pump and 35 mW of repump power¹². Although we have a mechanical shutter on the experimental table, we use the two double pass AOMs for precise timing of the MOT beams. A summary of this layout is shown in Fig. 2.2.

In late 2015, we made a modification to our system in order to increase the power available for the slowing beam, and to ensure that we had adequate power to seed both of the commercial TAs with 20 mW. The output of the first slave is still split with a 50/50

¹¹Note that the double pass efficiency is low because we are using an 80 MHz AOM, and operating at the edge of the region where high efficiency is possible.

¹²Although more power is nice, we found that the additional power in the pump beam does not increase the loading rate of steady state number in our MOT. This is discussed in Section 3.1.



Figure 2.1: Spectrum of light from the Sacher TAs when the seed power is 20 mW (solid black line) and 12 mW (dashed red line). We have found that the MOT and ODT perform better when the TAs are seeded with 20 mW, which may be due to the improvement in the output spectrum at high seed powers.

fiber splitter, and one output continues to seed the home-built TA. However, the output of this TA is now used to seed both of the commercial TAs. The second output of the fiber splitter is sent directly to our experiment table, and through the double pass AOM used to set the frequency of the slowing beam. The light after the double pass seeds a slave and the output of this slave is used for the slowing beam. The slave is seeded with approximately 2 mW of power, and we are able to achieve approximately 60 mW of power in the slowing beam. These changes are summarized in Fig. 2.3.

Imaging

For our standard absorption imaging at zero magnetic field, we image on the MOT pump transition. For this light, we pick off a portion of the MOT pump beam and couple it into one of two import ports of a 50/50 fiber splitter. When an image is taken, we use the double pass AOM that controls the frequency of the light to set it on resonance with the $f = 3/2 \rightarrow f' = 5/2$ transition. Similarly, the repump light used in imaging is picked off from



Figure 2.2: Layout of amplifier setup for the generation of ⁶Li light. The Toptica master seeds a slave laser, and the output of this slave is used to seed a home-build TA and a second slave. The output of the home-built TA is used for the Zeeman slower light, and the second slave is used to seed two commercial TAs which amplify the MOT pump and repump light. See text for details. The light is generated on our "master table" and is sent to the experiment table through 50 m long single-mode, polarization-maintaining fibers.



Figure 2.3: Updated layout of the ⁶Li amplifier setup to reflect changes made as of late 2015. These changes were made to increase the power of the slowing beam and to ensure that there was adequate power to seed both commercial TAs. In this new layout, the home-built TA is now used to seed the commercial TAs. Additionally, light from the first slave is sent directly to our experiment table. Here, it is frequency shifted before used to seed a second slave which generates the amplified slowing beam light.

the MOT repump beam and coupled into a second fiber. The output of this fiber is sent counter-propagating to the imaging beam (see Section 3.4 for details).

We also take absorption images of ⁶Li atoms in the presence of a large magnetic field (on the order of 500-800 G), where the imaging transition is on the order of 1 GHz red of the pump transition at 0 G¹³. To generate this light, we use a separate home-built extended cavity diode laser (ECDL) based on the Roithner RLT6720MG diode laser [98]. This laser is offset locked to the Toptica master, where the offset frequency is set with a VCO (the ADF4350 chip from Analog Devices). The output of this master laser is amplified by another slave laser and the slave output is frequency shifted with a double pass AOM. This AOM serves two purposes. First, it allows fast timing control of the light and power adjustment. Secondly, the AOM allows the frequency of the laser to be shifted by upwards of 80 MHz, which enables us to reach the required transition frequency to image two separate spin states in ⁶Li without the need to change of the offset lock frequency.

Given that the Toptica master (to which the high field imaging master is locked) is 50 MHz blue of the pump transition, the offset beat between the two lasers is given by

$$f_{\text{beat}} = |\delta - 2f_{\text{aom}} - 50|,$$
 (2.5)

where δ is the detuning of the high field imaging master after the double pass AOM, measured relative to the pump transition frequency. The driving frequency of the AOM is f_{aom} , and all frequencies are measured in MHz.

The light after the double pass AOM is coupled into a 50 m long single-mode, polarizationmaintaining fiber which sends the light to the experiment table. On this table, the fiber is butt-coupled to the second input port of the 50/50 fiber splitter used for the absorption imaging light. One of the outputs of this fiber splitter is used to send light down the imaging axis. The use of the fiber splitter allows us to switch between imaging at high field and zero field without any physical modifications to the apparatus. Details of the offset lock circuit can be found in the PhD thesis of Mariusz Semczuk [98].

 $^{^{13}}$ The details of the high field imaging setup are discussed in detail in Sec. 3.4. The specific transition are shown in Fig. 3.19 and the associated transition frequencies are given in Eq. 3.43.

2.1.2 Rubidium Light

In our experiment, we can work with both ⁸⁵Rb or ⁸⁷Rb. The two isotopes differ in the nuclear spin, where the i = 5/2 for ⁸⁵Rb and i = 3/2 for ⁸⁷Rb, and this leads to a differing hyperfine structure.

In ⁸⁵Rb, the ²S_{1/2} manifold is split into two hyperfine manifolds corresponding to f = 2, 3 where the splitting between these manifolds is ≈ 3 GHz. In the excited state, the ²P_{1/2} manifold is also split into two hyperfine levels where f = 2, 3. The ²P_{3/2} manifold has four possible hyperfine manifolds corresponding to f = 1, 2, 3, 4. Details of the hyperfine structure and energy splitting for ⁸⁵Rb can be found in [90].

In ⁸⁷Rb, the ²S_{1/2} manifold is also split into two hyperfine manifolds corresponding to f = 1, 2. In this case, the splitting between these manifolds is ≈ 6 GHz. In the excited state, the ²P_{1/2} manifold is also split into two hyperfine levels where f = 1, 2 and the ²P_{3/2} manifold has four possible hyperfine manifolds corresponding to f = 0, 1, 2, 3. Details of the hyperfine structure and energy splitting for ⁸⁵Rb can be found in [91].

For both the ⁸⁵Rb and ⁸⁷Rb MOT, we operate on the D_2 transition, where the "pump" light for ⁸⁵Rb (⁸⁷Rb) is near the $f = 3 \rightarrow f' = 4$ ($f = 2 \rightarrow f' = 3$) transition frequency and the "repump" light is near the $f = 2 \rightarrow f' = 3$ ($f = 1 \rightarrow f' = 2$) transition frequency. Unlike ⁶Li, the energy difference between adjacent hyperfine manifolds in the excited state is much larger than the natural linewidth of the transition. Therefore, the "pump" transition is (nearly) closed. However, off resonance transitions to the f' = 3 (f' = 2) manifold can decay to the f = 2 (f = 1) ground hyperfine manifold. Since the rate of these off resonant excitations is suppressed due to the large detuning (on the order of hundreds of MHz), only a weak repump beam is necessary to repump atoms back into the cooling transition.

Because the spitting of the ground state hyperfine manifolds is on the order of GHz, it is not practical to use a single laser for both the pump and repump light. Therefore, we have four separate masters lasers (two for each of the pump and repump for both Rb isotopes). We use an identical locking scheme for both ⁸⁵Rb or ⁸⁷Rb and as such, the following discussion is applicable to both isotopes.

MOT and Zeeman Slower

Each of the masters lasers is a home-built ECDL based off of the GH0781JA2C chip from Sharp, and is locked to the atomic transition using saturated absorption spectroscopy com-
bined with a frequency modulation scheme [93, 94, 95]. The output from each master laser is used to injection lock a slave laser, which is based on the Intelite MLD790100S5P chip. The output of each slave laser is fiber coupled into a distribution box, which uses fiber splitters from Evanescent Optics to provide four output ports for each master laser. This distribution scheme allows multiple experiments in our lab to work with either ⁸⁵Rb and ⁸⁷Rb at the same time, and easily switch between the two species by simply changing the port to which a fiber is connected¹⁴. The master lasers for both the pump and repump light are locked 180 MHz red of resonant transition frequency.

For our experiment, the pump light from the distribution box is used to seed a second slave, and the output of that slave is coupled into a 50 m long single-mode, polarizationmaintaining fiber which sends the light to the experiment table. On the experiment table, this light is used to inject a fiber coupled TA from Sacher Lasertechnik (TEC-400-0780-2500). We use approximately 14 mW of power to seed the TA and the output power is typically 1 W when the TA is run at 2800 mA¹⁵. The output of the TA is split using a polarizing beam cube between a path for light for the MOT pump beam and the slowing beam. In each path, a double pass AOM is used to up shift the frequency such that it has the desired detuning from the pump transition. This layout is summarized in Fig. 2.4.

The repump light from the distribution box is immediately fiber coupled to the experiment table using a 50 m long single-mode, polarization-maintaining fiber. On the experiment table the output of this fiber is used to seed an additional slave. The output of this slave is up shifted in frequency with a double pass AOM such that it is on the repump transition resonance. After the double pass AOM, the light is split on a polarizing beam cube for distribution to the MOT and Zeeman slower axes. For each of the two axes, the repump light is then combined (using another beam cube) with the pump light destined for the MOT or Zeeman slower. Note that the repump light that is sent down the Zeeman slower axis also acts as a repump for the MOT as the Zeeman slower passes directly through the MOT¹⁶. After the double pass AOM we typically have 30 mW of repump power available. This layout is also summarized in Fig. 2.4.

¹⁴That said, all of the experiments discussed in this thesis use ⁸⁵Rb.

¹⁵We normally run the TA at lower currents the power requirements (about 100 mW between the slowing light and the MOT light) after frequency shifting for the experiment are much lower than the maximum output of the TA.

¹⁶In fact, we found no decrease in loading rate or steady state number is all of the repump light is sent down the Zeeman slower axis. This is discussed in greater detail in Section 3.1.



Figure 2.4: Layout of the amplifier setup for Rb light generation. We use a separate laser for the pump and repump light, which is amplified and sent to a fiber based distribution box. For our experiment, the pump light is amplified using a second slave, and is sent to the experiment table where it is amplified again by a commercial TA. The output of this TA is split into two paths, one for the Zeeman slower slowing beam and one for the MOT pump beam. Each path is frequency up shifted by a double pass AOM. The repump light is sent to our experiment table, where it is used to seed a slave laser. The output of the slave is frequency shifted by a double pass AOM and then split to send light to both the MOT and Zeeman slower. The pump and repump light destined for the MOT and Zeeman slower are combined on a final beam cube. For clarity in this schematic, after the final amplification step the repump is shown as a dashed line while the pump is shown as a solid line. The combined pump and repump beams are as a thick solid line.

Imaging and Optical Pumping

For the Rb absorption imaging light, we pick off a portion of the MOT pump beam after it has been frequency shifted by the double pass AOM and couple the light into the same fiber as the ⁶Li absorption imaging light. This fiber is one of two input ports for a 50/50 fiber splitter that is designed for 670 nm light. At 780 nm, over 90% of the power goes into one of the two output ports from the splitter¹⁷. For hyperfine pumping of the atoms to upper hyperfine manifold before the image is taken, we simply use the MOT repump light directed along the MOT axis.

The light that we use for optical pumping is also picked off from the MOT pump and repump beams and coupled into a single fiber¹⁸. At the input of the fiber, use we

¹⁷Therefore, obviously, we choose to use this output port for the imaging beam.

¹⁸The MOT pump and repump beams are used as the optical depump and optical pumping beams respectively. The details of our optical pumping scheme are discussed in detail in Section 3.3

use a half-wave plate and a Glan-Thompson polarizer to ensure that both beams have the same polarization. The output of this fiber is sent down the same axis used for the photoassociation laser light, and is collinear with one of the arms of the ODT (see Fig. 3.9).

2.2 Vacuum System and Apparatus

Our experimental apparatus is constructed of two sections: a "science" section which contains the MOT region and the ODT, and a "source" section which contains the effusive sources for both ⁶Li and Rb. The two sections are separated by a differential pumping tube, which helps maintain a pressure differential between the sections. On overview of the appartus can be seen in Fig. 2.5, which shows the Soldiworks drawing of the experiment. This section presents an overview of the construction of the apparatus, the effusive sources, and details of some of the hardware used in the experiment. Additional information can be found in the Master's thesis of William Bowden [99].

Source Side

On the source side, the two effusive ovens are attached to two ports of a standard 2.75-inch four-way cross. In addition, the top port of the cross is used to attach an ion pump (Varian VacIon Plus 20 Starcell), a non-evaporable getter (NEG) (SAES CapaciTorr D 400-2) and a bakeable all metal valve via another four way cross. The all metal valve is used to connect the source side to our pumping station during the bake-out. A gate valve (VAT Vacuum Valves Series 010) separates this source chamber from a standard 6-way 2.75-inch cross.

The 6-way cross is used to add a mechanical shutter which can block the atomic beam when the apparatus is not in use, and a copper feed through which we use as a cold finger to reduce the background pressure of Rb. On the two unused horizontal ports perpendicular to Zeeman slower axis we attach viewports such that we can see the atomic shutter and have optical access to the atomic beam before it enters the slowing region. The layout of this 6-way cross section is shown in Fig. 2.6. Optical access to this section also helps in the alignment of the slowing beam, which can be reflected off of the mechanical shutter. Additionally, we have used this optical access to send in repump light for both ⁶Li and Rb in an attempt to hyperfine pump the atoms into the slowing transitions before they enter





Figure 2.5: Solidworks drawing of the experiment apparatus. The apparatus is split into two sections by a gate valve. On the left hand side is the "science" section, which includes Zeeman slower and the optically polished quartz cell containing the MOT. On the right hand side is the "source" section, which contains the effusive ovens for ⁶Li and Rb (see Fig. 2.7). These two sections are separated by a differential pumping tube (see Fig. 2.6), which helps maintain a pressure differential between the sections. Not shown are the compensation coils located around the quartz cell (see Fig. 2.10).



Figure 2.6: Cross-sectional view of the 6-way cross which contains the atomic beam shutter, cold finger and differential pumping tube. This cross is separated from the effusive sources (to the right, not shown) by a gate valve. The differential pumping tube is constructed from a stainless steel rod which is bolted to the zero-length CF reducer.

the slower¹⁹. The 6-way cross is attached to the Zeeman slower via a 2.75-inch to 1.33inch CF reducer. Bolted to this reducer is a differential pumping tube constructed from a 12 cm stainless steel rod with a diameter of 6 mm (see Fig. 2.6). The conductance of the differential pumping tube and other components in the system are given in Table 2.2.

The Zeeman slower itself is constructed from a 17 mm stainless steel tube, onto which we wound eight segmented coil sections. Each coil section is separated by a large metal

 $^{^{19}}$ Unfortunately, this did not show any improvement in the loading rate. Details of the effect of repump light on the loading rate of 6 Li and Rb is discussed in Section 3.1.

Part	Length (cm)	Diameter (cm)	C (L/s)
Differential Pumping Tube	12	0.6	0.85
Zeeman Slower	30	1.8	9
2.75-inch Cross	15	3.6	143
Quartz Cell	35	3	42

2.2. Vacuum System and Apparatus

Table 2.2: Calculated hydrogen conductances for various vacuum components in our experiment.

plate which helps to cool the coils. The diameter of the Zeeman slower tube is chosen such that the coil windings are as close to the slowing axis as possible in order to decrease the current requirements. In addition, the small diameter increases the differential pumping between the source and science sections, and is also compatible with 1.33-inch CF parts. We found that the metal cooling plates were sufficient to cool the Zeeman slower even in continuous operation at highest currents required for ⁶Li. Each coil segment consisted of 20 axial windings and 25 radial windings with 16 AWG Kapton coated wire. The current in each coil segment can be controlled "on-line" through a computer controlled current driver [99].

Effusive Sources

Our effusive sources were designed with one key requirement in mind: maximize the center line intensity of the atomic beam (i.e., maximize the flux of atoms that are emitted directly down the Zeeman slower axis) while at the same time limiting the off-axis intensity in order to preserve the lifetime of the sources²⁰. One possible way to achieve this requirement is to use a recirculating source, where thermal gradients wick back and recollect atoms which are emitted off-axis [100]. We choose an alternative technique, where microtubes are press fit into the opening in the effusive source²¹. These microtubes effectively collect the majority of atoms exiting the source off-axis without compromising the intensity of the center line beam.

In a dual species Zeeman slower, the design is complicated by the fact that both effusive

 $^{^{20}}$ We intentionally isolated the sources from the rest of the vacuum system with a gate valve such that it is possible to replace the sources while minimizing the effect on the rest of the vacuum system. However, this replacement is a non trivial task and should be avoided if possible. Hence, the emphasis on maximizing the source lifetime.

²¹Other designs that use microtubes require a retaining bar or plug [101]. However, found that press fitting the tubes held them sufficiently secure.

sources must emit down the same axis. Additionally, the temperature requirement of the two sources are often very different and care must be taken to prevent backflow between reservoirs $[102]^{22}$. In our design, we use two effusive ovens which are thermally and physically isolated, while the output of each sources is vertically offset from one another other, as shown in Fig. 2.7. This design is based on that by Wille et al. [103, 104], except that our sources are made from standard commercially available vacuum parts.

The ⁶Li oven consists of a 1.33-inch nipple which we lined with nickel mesh to ensure that ⁶Li does not leak out of the oven²³. It was also crucial to use nickel gaskets in any part of the source that may come in contact with melted ⁶Li, as copper gaskets are very quickly corroded by ⁶Li. A cleaned chunk of enriched 95% ⁶Li is placed inside the nipple, and the oven is heated with a band heater on the front and back flange of the nipple. More information on our cleaning technique is given in the following section on the bake-out.

The Rb effusive oven consists of a Rb ampoule from ESPI Metals that is held in a flexible belows. After the bake-out, the belows is used to break the ampoule. Care must be taken to ensure that the ampoule is not broken before the bake-out, as doing so will result in a near total loss of Rb during the bake-out. Similar to the ⁶Li source, we heat the Rb source with two band heaters on the belows and the flange located near the exit of the source.

Science Side

On the science side of the experiment, the MOT region is centered on an optically polished quartz cell from Helma, which is not AR coated. The dimensions of the cell are $30 \times 30 \times 100$ mm with a wall thickness of 5 mm. The cell is connected at both ends to 2.75-inch CF flanges where, on one end, this connection is made through a stainless steel bellows.

The fixed end of the cell is connected to the output of the Zeeman slower through a conical 2.75-inch to 1.33-inch reducer. We had hoped to use a zero-length reducer in order to minimize the distance between the end of the Zeeman slower and the MOT region. However, because the zero length reducer uses a threaded hole to attach to the 1.33-inch side, we did not have enough clearance between the final metal fin and the 1.33-inch flange to fit the required screw. However, we were able to minimize the impact of the additional length by using the MOT coils as the final slower segment (see Section 3.1 for more details).

 $^{^{22}}$ For example, in our case, the Rb source is held near 100°C and the 6 Li source is held around 400°C

 $^{^{23}}$ In tests without the nickel mesh, we found that the 6 Li was wicked out of the oven within a few hours.



Figure 2.7: Solidworks drawing of the ⁶Li and Rb effusive source. The ⁶Li source is attached to the right port of the 4-way cross, and consists of a nipple lined with nickel mesh. The microtubes are inserted into a small hole drilled in the CF blank sandwiched between the two nipple flanges. The Rb source is attached to the bottom port of the 4-way cross. A glass Rb ampoule is placed inside the flexible bellows and is broken after the bake-out. The microtubes are press fit into a small hole milled from the oven "cap" that extends into the cross. The inset shows a view of the oven outputs looking down the Zeeman slower axis, and demonstrates that the output of each source is vertically offset from one another.

The bellows end of the cell is connected to a 2.75-inch four-way cross. We use a viewport on the opposite port of the cross for the Zeeman slower beam. On the top port, we attached a second four way cross to which an ion pump and a NEG are mounted. Attached to the bottom port of the cross is an all-metal-valve which is used to connect our pumping station during the bake-out. The conductance of the cell and the 4-way cross are given in Table 2.2.

Oven Loading and Bake-out

As ⁶Li is highly reactive with both organic and inorganic reactants (including nitrogen and hydrogen), the ⁶Li that we purchase comes packed in oil in order to protect it from reaction with air. To load ⁶Li into the effusive source, we first clean the ⁶Li chunk with petroleum ether to remove any residual oil, and then use a clean razor blade to remove an exterior layer from all sides of the chunk. This is performed in a pure argon (or helium) environment to minimize the exposure of the ⁶Li chunk to air²⁴. After cleaning, the ⁶Li is placed in the oven nipple and immediately attached to a separate chamber on our pump out station. At this point, we heat the ⁶Li oven to 500°C for about six hours to remove any remaining containments. The oven is then backfilled with argon and transferred to the main apparatus. We estimate that we load about 3 g of ⁶Li , which is expected to yield a lifetime of four years of continuous operation at 450°C.

The maximum temperature of our bake-out is limited to just under 200°C by the rotary feed through for the atom beam shutter. We attached our pump-out station (which contains a turbo pump, a backing scroll pump and a residual gas analyzer (RGA)) to the all-metal valves on both the science and source side. We use two connections to the apparatus so that we are not pumping one of the sections through the differential pumping tube. We performed an initial bake-out for about 5 days during which we heat the NEGs to increase the partial pressure of H₂ in the system. This is done in order to increase the pumping of H₂ from the system, and to regenerate the NEGs. This first stage takes about a week, and is performed without the ⁶Li effusive source attached such that the ⁶Li is not contaminated by the high hydrogen background pressure. At this point, the Rb ampoule has not broken and therefore the Rb is unaffected.

After this initial stage, we backfill the system with argon and attach the loaded ⁶Li effusive source. This second bake-out stage also took place at a temperature just under 200°C and lasted about two weeks. After this bake-out, we initially had issues with the pressure in our source chamber. In our attempts to diagnose the issue, we had the pumping station (and therefore the turbo pump and RGA) attached only to the science side of the experiment. However, over the course of about a month, we found that the pressure issues went away. We attribute this to additional pumping by the turbo pump, ion pump and NEG during

²⁴We originally used a glove box, but we found that it was easier to work in a large clear plastic bag that is filled with a positive pressure of either argon of helium.

this time²⁵. We are now able to obtain MOT lifetimes on the order of 100 s^{26} and lifetimes in the low power ODT on the order to tens of seconds, which is more than sufficient for our experiment.

MOT and Compensation Coils

We generate the quadrupole magnetic field for the MOT and the homogenous magnetic field used during the experiments with a set a water cooled coils run in an anti-Helmholtz or Helmholtz configuration, respectively. We use a 100 V / 50 A power supply from Sorensen (SGI 100/50), and the resistance of our coils is designed to match the limits of the power supply in order to maximize the magnetic fields that we can generate. As the coils are run in series, this limits the resistance of each coil to be slightly less than 1 Ω^{27} . Physical constraints in the experiment limited the inner radius of the coils to 4 cm, the outer radius to 8 cm and the coil separation to 4.5 cm. Through a simulation of the magnetic field, we found that best resistance match used 14 AWG wire with 21 radial windings and 10 axial windings, gaving a coil resistance of 0.88 Ω . A summary of the achievable magnetic field and field gradient is given in Table 2.3.

Coil	Homogenous Field (G/A)	Axial Gradient $(G/(A \cdot cm))$
MOT	25.8	6.15
X-Compensation	2.67	_
Y-Compensation	1.45	_
Z-Compensation	13.9	3.6

Table 2.3: Magnetic field produced by the MOT and compensation coils. The x and y comp are only used to apply a homogenous offset field. The x and y axes are defined to lie in the horizontal plane, with the y-axis collinear with the slowing beam axis, see Fig. 2.10.

To provide cooling for the coils, the coils are immersed in water by winding them inside a watertight housing. The coil housing is constructed from Delrin, and consists of a lid, base and a retaining ring. The retaining ring is necessary to prevent the inside walls of

 $^{^{25}\}mathrm{And}$ just a little bit of luck...

²⁶This lifetime is the decay rate of a very small MOT with the atom shutter closed. In a small MOT, losses that are density dependent (for example, light assisted collisions) are small, and the dominant source of loss is through collisions with background gases. Nevertheless, light assisted losses do still contribute to the loss rate, and therefore this measured decay time provides an upper lime on the loss rate due to background collisions.

²⁷While the resistance at room temperature can be 1 Ω , running the coils at a large current can increase the temperature of the wire, which in turn increases the resistance.

the housing from bulging at high water pressures. A water tight seal is achieved through the use of two o-rings between the lid and the outer wall and the base and the inner wall. The inside surface of the lid and base of the coil housing is milled to have dams in order to force the water to flow through all parts of the coil, as shown in Fig. 2.8. In addition, we placed a spacer between every two radial windings to ensure that each winding was in direct contact with water. A cross sectional view of the coil design is shown in Fig. 2.9. We tested that the coil housing was able to handle a pressure of 80 PSI, which corresponded to a flow rate of 8.6 L/min. At this flow rate, the temperature of the coils rose to 41° C when run at 50 A. Full details of the coil design and testing can be found the Master's thesis of William Bowden [99].

The apparatus also has a set of three orthogonal compensation coils, which we use to apply a small (i10 G) offset homogenous magnetic field. This field allows us to move the zero of the MOT quadrupole field to help balance the radiation pressure from the Zeeman slower beam, and to move the positive of the MOT to overlap it with the focus of the ODT during the transfer from the MOT to the ODT. These coils are also used to cancel for any residual magnetic field at the location of the atoms. The compensation coils along the horizontal x and y axes are constructed by winding Kapton wire on a rectangular plastic housing²⁸. The vertical compensation coils are concentric with the MOT coils, and located just above (below) the top (bottom) MOT coil. They have an inner diameter of 9.5 cm and an outer diameter of 13 cm and there are approximatly 15 radial windings and 5 axial windings. The z-compensation coils are also used to provide a magnetic field gradient to counter any inhomogeneities in bias field applied during experiments, or to compensate for gravity at low ODT depths²⁹. The location of the compensation coils is shown in Fig. 2.10. A summary of the achievable magnetic field and field gradient (as a function of current) is given in Table 2.3.

2.3 Photoassociation Laser System

The light that we use for photoassociation must meet two key requirements: first, the light needs to be widely tunable and second, our uncertainty on the frequency determination

²⁸In a previous iteration, we used a metal housing. However, we found that the metal would knick the Kapton wire and cause the coils to short.

²⁹Without this gradient field, both field inhomogeneities and gravity lead a tipping of the trapping potential and a loss of atoms from the ODT. This is discussed in more detail in Section 3.2.



Figure 2.8: View of the coil housing without the lid. The inside surface of the base (and lid, not shown) of the coil housing is milled to have dams in order to force the water to flow through all parts of the coil. The water flows into the 'V' shaped regions, and then is forced up through the coils. The lid has a similar 'V' shape pattern, but offset such that the water is forced down through the coils and into the next 'V' shaped section on the base.



Figure 2.9: Cross sectional view of the MOT coil design. The coil housing in constructed from Delrin, and consists of a lid, base and a retaining ring. A water tight seal is achieved through the use of two o-ring between the lid and the outer wall and the base and the inner wall. A spacer is placed between very two radial windings to ensure that each winding was in direct contact with water.



Figure 2.10: Location of the compensation coils relative to the MOT coils and the location of the MOT. The x-compensation coil produces a field that runs perpendicular to the cell axis in the horizontal plane, while the y-compensation coil produces a field that runs parallel to the cell axis. The z-compensation coil is the black object mounted concentric to the MOT coils, and produces a field that in the vertical direction. Not shown is the second z-compensation coil which is mounted in a similar fashion below the bottom MOT coil.

needs to be at a level that is below the natural linewidth of the photoassociation transitions (on the order of 10 MHz). For experiments that require coherence (for example, dark state spectroscopy or STIRAP, discussed in section 5.2.2) we require that the lasers have a narrow relative linewidth such that they are phase coherent during the illumination time of the atomic ensemble³⁰. We meet these requirements by employing two cw Ti:Sapphire lasers which are phase locked and referenced to the same femtosecond optical frequency comb.

 $^{^{30}}$ In the context of our experiments, "narrow" means a relative linewidth of less than 100 kHz. However, a relative linewidth that is lower than this relaxes other requirements, and can make such experiments less technically challenging. This is discussed in greater detail in Section 5.2.2.

2.3.1 Femtosecond Optical Frequency Comb

The femtosecond optical frequency comb (OFC) that we use was originally built by the lab of David Jones at UBC [77] several years before we started our photoassociation experiments in earnest. Later, we rebuilt and modified some parts of the comb and added a second measurement branch which is used to stabilize the Ti:Sapphire lasers. However the oscillator itself remained the same. A detailed description of OFCs and ultrafast physics can be found in [105, 106].

Unlike cw lasers, which are forced to lase on only one longitudinal cavity mode, pulsed lasers lase on many cavity modes at the same time, and rely on interference between cavity modes to create a pulsed output. This interference requires a fixed phase relationship between cavity modes, and is achieved through mode locking. In our setup, the oscillator is based on an erbium-doped fiber laser (similar to [107, 108, 109]) where mode locking is achieved through nonlinear polarization rotation [110]. This technique relies on nonlinear intensity-dependent rotation of the polarization in the optical fiber, combined with polarization optics within the oscillator, to create an artificial saturable absorber. This saturable absorber has an intensity dependent loss which is low for high intensities and high for low intensities such that the maximum gain occurs for short pulses. Mode locking is achieved empirically by tuning two sets of wave plates (a half-wave plate and a quarter-wave plate) placed on either side of an optical isolator³¹, situated in the small free space section of the oscillator (see Fig. 2.11). Our oscillator produces sub 100 fs pulses at a repetition rate of $f_{\rm rep} = c/L = 125$ MHz, where L is the total roundtrip length of the cavity.

In the time domain, the output pulse (of any pulsed laser) can be split into a carrier and envelope component (see Fig. 2.12), where the envelope frequency is $2\pi f_{\rm rep}$, the carrier frequency is ω_c . There also exists a phase offset between the peak of the envelope and the peak of the nearest carrier wave, which is called the carrier envelope offset phase $\psi_{\rm ceo}$. This offset phase evolves as a function of time due to differences in the group velocity v_g and phase velocities v_p in the fiber, owing to its dispersive nature³². This results in a change of

³¹An optical isolator is used instead of a polarizer to ensure that light only travels in one direction and there is no standing wave in the cavity.

³²The group velocity and the phase velocity determine the velocity of the envelope and carrier wave respectively. They are related by $v_g = v_p(1 - k/n^{dn}/dk)$. The two velocities are equal only in the case of zero dispersion, where $\frac{dn}{dk} = 0$.



Figure 2.11: Schematic of the frequency comb and associated locking electronics. Shown are fiber segments (maroon), free space segments (red) and electronic connections (blue). Mode locking of the oscillator is achieved using nonlinear polarization rotation, and the mode locking position is tuned using a pair of half and quarter wave plates on either side of an optical isolator. These components are located in the short free space section of the cavity. The repetition rate of the oscillator is controlled by a fiber collimator mounted on a PZT, while a fiber AOM external to the oscillator is used for fast control of f_{ceo} . We also use slow feedback on the oscillator pump diode to ensure that the correction does not exceed the AOM tuning range, where the diffraction efficiency of the AOM is small. The negative first order of the AOM is split into the measurement branch (MB) and the self-referencing branch (SR), where the comb light is amplified and broadened (see text for details). In both branches, we use a fiber polarization controller (PC) to optimize the broadening in the highly nonlinear fiber (HNLF). The Erbium doped fiber amplifiers (EDFA) are pumped with 980 nm pump diode, and coupled into the erbium doped fiber using a wavelength division multiplexer (WDM). In the measurement branch, a f - 2f interferometer based on a PPLN crystal is used to measure and stabilize the carrier envelope offset phase. For the lock of $f_{\rm rep}$ and $f_{\rm cep}$ the RF signal from the photodiodes is sent through a bandpass filter (BPF), and the error signal is generated using a phase frequency discrimator (PFD) or a mixer.

 $\psi_{\rm ceo}$ from pulse to pulse of [105]

$$\Delta\psi_{\rm ceo} = \left(\frac{1}{v_g} - \frac{1}{v_p}\right) L\omega_c \,. \tag{2.6}$$

In the frequency domain, the output of the oscillator produces a comb of frequency elements which are spaced by $f_{\rm rep}$ and centered on ω_c over a frequency range given by the inverse of the pulse width in the time domain, as shown in Fig. 2.12. The frequency elements, if extrapolated to zero frequency, are offset from zero by the carrier envelope offset frequency



Figure 2.12: Output of the frequency comb in the time domain (top panel) and frequency domain (bottom panel). In the time domain the carrier envelope offset phase ψ evolves at a constant rate due to the difference in group and phase velocity in the dispersive elements of the oscillator. From pulse to pulse, the phase difference between the peak of the envelope (dashed line) and the nearest peak of the carrier (solid line) changes by an amount given by $\Delta \psi$. The output pulses have a width of τ , and the period of the pulses is related the inverse of $f_{\rm rep}$. In the frequency domain, the output of the oscillator is a comb like structure, where the comb elements (solid lines) are separated by $f_{\rm rep}$ with a bandwidth related to the inverse of the pulse width τ . If the comb elements are extrapolated back to near zero frequency (dashed lines), the offset of the first comb element from zero frequency is the carrier envelope offset frequency $f_{\rm ceo}$. Therefore, the frequency of the $n^{\rm th}$ comb element is $f_n = nf_{\rm rep} + f_{\rm ceo}$.

$$f_{\rm ceo} = \left(\frac{1}{2\pi}\right) \frac{\Delta\psi_{\rm ceo}}{T} = \left(\frac{\Delta\psi_{\rm ceo}}{2\pi}\right) f_{\rm rep} \,. \tag{2.7}$$

Therefore, the frequency of n^{th} comb elements is given by

$$f_n = nf_{\rm rep} + f_{\rm ceo} \,. \tag{2.8}$$

In order for the OFC to be used to reference and stabilize our Ti:Sapphire lasers, both $f_{\rm ceo}$ and $f_{\rm rep}$ must be known and actively stabilized. Both $f_{\rm rep}$ and $f_{\rm ceo}$ can be stabilized via feedback to the power of the pump laser [111, 112]. Alternatively, $f_{\rm rep}$ can be stabilized by adjusting the round trip cavity length either by using. This can be achieved by using a fiber stretcher [108] or, if the oscillator has a free space section, mounting one of the fiber collimators on a PZT [107]. However, these methods suffer from the disadvantage that the feedback for f_{rep} and f_{ceo} are coupled. We tried to reduce the coupling by using an single pass fiber AOM (Brimrose AMM-100-8-70-1550-3FP) placed external to the oscillator to provide fast corrections for f_{ceo} . Stabilization of f_{rep} was achieved by adjusting the oscillator length with a fiber collimator mounted on a PZT. However, we found that long term drifts in f_{ceo} required corrections larger than the bandwidth of the AOM (on the order of a few MHz). This required adding a slow feedback onto the pump current, where the correction signal is generated by integrating the output of the first servo loop. In addition, due to imperfections in the mounting of the fiber collimator on the PZT, the alignment of the oscillator is slightly changed when the cavity length is varied, which influences f_{ceo} . While we were unable to completely decouple the stabilization of $f_{\rm rep}$ and $f_{\rm ceo}$, this setup has proven to be quite stable and the comb will typically stay locked over the course of a day.

Light is coupled out of the oscillator using a 90/10 fiber splitter. This out coupled light is split again by a second 90/10 splitter such that we have two output ports from the oscillator. We use the low power output to stabilize $f_{\rm rep}$, and the high power output is sent through the fiber AOM and then split with a 50/50 fiber splitter. The two outputs of this splitter are used for the self-referencing branch (to determine and stabilize $f_{\rm ceo}$) and the measurement branch (to reference and stabilize the Ti:Sapphire lasers). Note that the effect of the AOM is to shift every comb element by the same frequency. Both the referencing and measurement branch occur after the AOM, therefore this frequency shift can be absorbed into $f_{\rm ceo}$. In our case, we use the negative first order from the AOM, which is driven with approximately 300 mW of RF at 100 MHz, generated by a homebuilt tunable VCO.

Rep Rate Lock

We stabilize $f_{\rm rep}$ by sending the oscillator light from the low power output to a photodiode which produces RF signals at integer multiples of $f_{\rm rep}$. The photodiode output is sent through a band pass filter centered at $3f_{\rm rep} = 375$ MHz and then mixed with the output of stable RF source³³ which determines the set point of $f_{\rm rep}$. The RF source itself is referenced to a GPS disciplined quartz oscillator (Menlo Systems GPS 6-12). The mixed error signal is sent to a servo loop which produces the correction signal sent to the PZT inside the oscillator. This lock is summarized in Fig. 2.11. While the stability of $f_{\rm rep}$ is determined by the stability of the RF source, the stability of a comb tooth in the optical frequency is on the order of 10⁶ larger, due to the multiplicative *n*-factor in Eq. 2.8. However, this multiplicative factor can be reduced by a factor of *m* by locking to the *m*th harmonic of the rep rate. It is for this reason that we choose to lock the third harmonic³⁴.

Referencing Branch

Stabilizing the carrier envelope offset phase, and thus f_{ceo} (see Eq. 2.7), is slightly more involved than stabilizing f_{rep} . One possible approach is to use another stable optical reference to stabilize the comb element nearest to the optical frequency of the stable source. However, the major difficulty is that this method itself requires a very stable optical reference. Instead, stabilization of f_{ceo} is typically achieved via self-referencing in an f - 2finterferometer [113, 114]. In this method, the comb light is broadened to cover an octave (i.e., a factor of two in frequency), and a heterodyne measurement between the direct and frequency doubled light on the blue end of the octave is used to extract f_{ceo} .

In our case, the octave spans from 1 μ m to 2 μ m as the comb light is centered at 1550 nm. Considering the octave-spanning light from the comb, let the frequency of the n^{th} comb element at 2 μ m be $f_n = nf_{\text{rep}} + f_{\text{ceo}}$. The corresponding comb element at 1 μ m will be given by the $2n^{\text{th}}$ element - that is, $f_{2n} = 2nf_{\text{rep}} + f_{\text{ceo}}$. By frequency doubling the direct comb light at 2 μ m, one can create a copy of the comb at 1 μ m, where the frequency of the comb elements are given by $2f_n = 2nf_{\text{rep}} + 2f_{\text{ceo}}$. The difference between the direct

 $^{^{33}}$ For all the data in this paper, we used an RF synthesizer from HP (model number 8663A). However, it recently stopped working and has been replaced with another HP synthesizer (model number 8660B) while we attempt to repair it.

 $^{^{34}}$ In addition to reducing the multiplicative factor, locking to a higher harmonic also reduces the 1/f noise present in the signal. Ideally, one would lock to the highest harmonic possible. Our choice of the third harmonic was limited by the availability of band pass filters in the lab at the time the comb was constructed.

and doubled comb light at 1 μ m is then

$$2f_n - f_{2n} = (2nf_{\rm rep} + 2f_{\rm ceo}) - (2nf_{\rm rep} + f_{\rm ceo}) = f_{\rm ceo}, \qquad (2.9)$$

which gives the carrier envelope offset frequency. With f_{ceo} determined, it can then be stabilized to a stable external RF source.

To generate the octave spanning comb light (often called a supercontinuum), we use an erbium-doped fiber amplifier (EDFA) to amplify the light, which is then broadened in a highly non-linear fiber (HNLF)³⁵. After the 50/50 splitter after the AOM at the output of the comb we typically have a few mW of average power, which is amplified to approximately 100 mW when measured after the HNLF. A single mode (SM) "pre-chirp" fiber is spliced before the EDFA, where the length of the fiber is set to make the output spectrum from the amplifier as broad as possible (typically on the order of 50-100 nm). This pre-chirp fibers compensates for the pulse chirp out of the oscillator, and compresses the pulse before it enters the EDFA. This high peak power in the EDFA causes a broadening of the pulse spectrum due to (in addition to standard chromatic dispersion effects) self-phase modulation³⁶. Therefore, the broadest spectrum out of the EDFA is achieved when the pre-chirp fiber is set such that the pulse into the EDFA has minimum pulse width. The EDFA is pumped with light at 980 nm, which is coupled into the erbium doped fiber using a wavelength division multiplexer (WDM).

To generate the supercontinuum, the amplified light from the EDFA is broadened in the HNLF. Because the broadening in the HNLF is strongly dependent on the intensity of the light into the fiber, another segment of SM fiber is spliced between the EDFA and the HNLF in order to further compress and maximize the intensity of the pulse into the HNLF. This method works because the single mode fiber (SMF-28) has anomalous dispersion at 1550 nm, while the EDFA has normal dispersion. We also use a fiber polarization controller, placed before the pre-chirp fiber, to optimize and tune the supercontinuum generated by the HNLF. While ideal SM fibers have cylindrical symmetry, typically the fibers exhibit some birefringence (for example, due to bending of the fiber). The result is that the orthog-

³⁵For a review of supercontinuum generation and the associated non-linear effects, see [115]

³⁶Self-phase modulation is the phenomenon where a pulse travelling through a medium interacts with the medium and imposes a phase modulation on itself (hence the name), which results from an intensity dependent refractive index. The amount of broadening is dependent on the magnitude of time derivative of the phase change and the peak intensity, and therefore is the amount of broadening is larger for short pulses.

onal polarizations in the fiber exhibit a different group delay. The polarization controller helps compensate for the polarization mode dispersion and is simply tuned empirically to maximize the spectral broadening out of the HNLF. This layout is summarized in Fig. 2.11. The length of the initial pre-chirp fiber and second compression fiber are on the order of 1 m.

Frequency doubling the comb light is done using a periodically poled lithium niobate crystal (PPLN) from Covesion (model number SHG7-0.5-10). The crystal is 0.5 mm thick and 10 mm in length. It contains poling periods of 29.5 μ m to 32.5 μ m in 0.5 μ m steps, which allows frequency doubling of light in the range of about 2000 nm to 2250 nm. Coarse phase matching is achieved by cycling through the poling periods by translating the crystal perpendicular to the input beam. Fine tuning of the phase matching is achieved via temperature control. For this, we used a general purpose temperature controller (ThorLabs TC200) which gives a temperature stability of 0.1°C. The direct and doubled light is sent through a narrow interference filter in order to remove frequencies that do not contribute to the heterodyne signal, and then through a focusing lens (mounted with xy translation) and onto an avalanche photodiode for detection. We did not find that we had to make any special effort in order to ensure a spatial overlap between the direct and doubled light, aside from making small adjustments to the position of the focusing lens on occasion.

In our modifications to the existing comb, we added the AOM and the 50/50 fiber splitter, and spliced the existing self-referencing branch onto one of the splitter outputs. Although this branch already contained the pre-chirp and compression fiber, it was not optimized for the current pulse shape out of the oscillator, nor for the change in power as a result of adding the AOM and 50/50 splitter. We choose to optimize the broadened output from the HNLF by making modifications to only the pre-chirp fiber. To do this, we spliced an additional long length (a few meters) of SM fiber into the existing fiber path, and slowly reduced the length of the fiber by cutting out segments a few cms in length and re-splicing. The final length of this fiber was set such that we achieved the highest amount of power in both the direct and doubled comb light near 1 μ m. Unfortunately, our optical spectrum analyzer was only sensitive up to 1750 nm, so it was not possible to directly measure the power on both the red and blue end of the supercontinuum at the same time. Instead, we used a sensitive spectrometer to monitor the direct and doubled light at 1 μ m. We differentiated between the direct and doubled light by inserting and removing



Figure 2.13: Comb spectrum our of the oscillator (red dashed line) and after supercontinuum generation in the HNLF (black solid line). The supercontinuum extends up to 2 μ m, but our optical spectrum analyzer is not sensitive to wavelengths above about 1700 nm. We generate our self referencing signal using direct and doubled comb light at 1017 nm.

the PPLN crystal used for frequency doubling. Empirically, we found that we achieved the largest heterodyne signal using an interference filter centered at 1017 nm. Figure 2.13 shows the spectrum of the output of the comb at the output of the oscillator and after the supercontinuum generation in the HNLF.

In reality, the heterodyne measurement between the direct and doubled comb light doesn't just produce one beat note, as suggested by Eq. 2.9. Instead, we observe a forest of beat notes owing to interference between comb elements separated by n other elements, where n is an integer. If one considers the lowest frequency beatnote $(f_{\text{beat}} < f_{\text{rep}}/2))$, its frequency is

$$f_{\text{beat}} = \begin{cases} f_{\text{ceo}} & \text{if } f_{\text{ceo}} < f_{\text{rep}}/2 \\ f_{\text{rep}} - f_{\text{ceo}} & \text{if } f_{\text{ceo}} > f_{\text{rep}}/2 . \end{cases}$$
(2.10)

Likewise, the third beat frequency (which is the one we lock and readout) is

$$f_{\text{beat}} = \begin{cases} f_{\text{rep}} + f_{\text{ceo}} & \text{if } f_{\text{ceo}} < f_{\text{rep}}/2 \\ 2f_{\text{rep}} - f_{\text{ceo}} & \text{if } f_{\text{ceo}} > f_{\text{rep}}/2 . \end{cases}$$
(2.11)

The ambiguity in the beat note can be solved by increasing the carrier-envelope offset frequency and noting the change in the beat note frequency. In our setup, the AOM provides an ideal means by which to do this: the AOM diffracts into the minus first order, so increasing the VCO frequency acts to increase the RF frequency driving the AOM but decrease f_{ceo} . Therefore, if the AOM driving voltage is increased and the third offset beat moves right (left) then $f_{ceo} > f_{rep}/2$ ($f_{ceo} < f_{rep}/2$). With this ambiguity solved, the unique value of f_{ceo} is

$$f_{\rm ceo} = \begin{cases} f_{\rm beat} + f_{\rm rep} & \text{if } f_{\rm ceo} < f_{\rm rep}/2\\ 2f_{\rm rep} - f_{\rm beat} & \text{if } f_{\rm ceo} > f_{\rm rep}/2. \end{cases}$$
(2.12)

We choose to stabilize the carrier-envelope offset frequency to 172.1 MHz, such that the beat note is far from the rep rate signal (which occur at integer multiples of 125 MHz), and all other harmonics of the beat frequency. The output of the avalanche photodiode is sent through a band pass filter centered at this frequency, with a 3 dB bandwidth of 20 MHz. This output is compared with a reference RF frequency provided by an Agilent (model number 8648A) synthesizer³⁷ using a phase frequency discriminator (PFD). A correction signal is generated by a loop servo which feeds back onto the VCO modifying the RF driving frequency sent to the fiber AOM. We also use this correction signal as an error signal for a slow integrator, the output of which feeds back onto the pump current of the oscillator. This ensures that there is no dc correction sent to the AOM, in order that the driving frequency of the AOM remains within a window (about 1 MHz centered on 100 MHz) where the diffraction efficiency is high. The locking electronics are summarized in Fig. 2.11.

Measurement Branch

The other output from the 50/50 fiber splitter is used for the measurement branch. In this branch, we use an identical fiber setup to that used in the referencing branch (described

 $^{^{37}}$ Note that we use the same synthesizer to reference both Ti:Sapphire lasers, see Section 2.3.2 for more details.

above). We generate a broadened comb spectrum such that it can be frequency doubled to match the scanning range of our Ti:Sapphire lasers. Since our Ti:Sapphire lasers have a tuning range of about 760 nm to 820 nm, we only want to slightly broaden the comb spectrum to span from approximately 1520 nm to 1640 nm. To start, we tried to adjust the length of the pre-chirp fiber to achieve the broadest spectrum out of the EDFA, without using any HNLF afterwards. However, we were only able to achieve reasonable doubled power (i.e., power in the scanning range of the Ti:Sapphire lasers) in the range 770 nm to 800 nm, corresponding to 1540 nm to 1600 nm in the comb spectrum³⁸. We made some attempts to compress the pulse width with additional SM fiber before the HNLF. However, since we didn't need to achieve a large broadening, carefully minimizing the pulse width wasn't crucial to achieving the required spectrum³⁹.

The output of the measurement branch is split into two independent locking arms for each Ti:Sapphire with a polarizing beam cube. The comb light in each arm is frequency doubled by a PPLN crystal with an input wavelength range of 1530 to 1620 nm (Covesion MSHG1550-0.5-20) or 1600 to 1720 nm (Covesion MSHG1650-0.5-20) depending on the desired frequency of the Ti:Sapphire laser. The crystals have a length of 20 mm. Note that the doubling efficiency in the PPLN crystal scales with the square of the intensity and linearly with length. As such, to achieve a large intensity it is crucial to focus the beam into the crystal. However, focusing to too small of a waist results in a large divergence such that the beam is only intense for a small portion of the crystal length. Maximum doubling efficiency can be achieved when the Rayleigh length of the focused beam is on the order of half of the crystal length. With this setup, we have been able to achieve greater than 0.5 mW of doubled power across the wavelength range of the Ti:Sapphire lasers. The details of the Ti:Sapphires and of their lock to the comb are discussed in the next section.

2.3.2 Ti:Sapphire Lasers

All of our photoassociation measurements use light from two cw Ti:Sapphires ring lasers (899-21) made by Coherent⁴⁰. These lasers are an ideal light source of photoassociation

³⁸So close!

³⁹To quote from my lab book: "Got a little frustrated, just spliced the HNLF into the setup to see what would happen" followed some time later by "Spectrum actually looks pretty good!".

⁴⁰In truth, one of the lasers was originally an 899-01, which comes without a tweeter mirror for active stabilization of the output frequency. However, we purchased a tweeter mirror and effectively upgraded this laser to an 899-21.

experiments because the output is a high power, well polarized, single longitudinal mode that is widely tunable over a wide range of wavelength. The tunability of the laser is important so that it is possible to access multiple vibrational levels in a molecular potential, and also because the exact location of the molecular levels is not always well known and can require searches spanning a few hundred MHz to a GHz.

The wide tunability of the laser comes from the gain medium⁴¹ which is pumped with a narrow linewidth 532 nm laser (Coherent V18) and emits in a wavelength range of about 670 nm to 1100 nm. The largest limitation on the effective output wavelength range is the mirror set in the cavity. Coherent supplies three typical mirror sets which allow a broadband tuning range of 700-825 nm ("short"), 790-930 nm ("medium") and 925-1000 nm ("long"). The optics in our lasers are a mix of the short and medium sets, and provide a broadband tuning range of about 760 nm to 820 nm.

Because the ring cavity can support many longitudinal modes at the same time, the laser contains elements that suppress the gain at all but one longitudinal mode⁴². To have the laser lase on a single longitudinal mode requires that the transmission of all the frequency selective elements be maximum (or close to maximum) at the same frequency, as demonstrated in Fig. 2.14. These elements include a birefringent filter, and a thin and thick etalon.

The birefringent filter is a birefringent plate with thickness l where the index of refraction of the ordinary and extraordinary input polarization components is (in general) different⁴³. In this case, the filter is a uniaxial crystal, where the index of refraction is different along one axis of the crystal, referred to as the optics axis. The ordinary polarization refers to light polarized perpendicular to the plane that contains the propagation vector \vec{k} and the optic axis and extraordinary polarization refers to light polarized in the plane containing \vec{k} and the optics axis. Due to the difference in the index of refraction between the ordinary and extraordinary axis Δn , the filter effectively acts like a phase retarder which rotates the polarization of the input light. This polarization rotation is dependent on the wavelength of the light and, in particular, certain wavelengths (where $l\Delta n/\lambda = m$, where m is an integer)

⁴¹The gain medium is a samphire (Al_2O_3) crystal doped with Titanium ions (Ti^{3+}) .

 $^{^{42}}$ An excellent resource on the details of these elements, and the experimental realization of single mode lasers, see [116].

⁴³The type of birefringent filter in the Ti:Sapphires is a "Lyot filter", made from a stack of three birefringent plates. This has the effect of producing a more narrow transmission peak than just a single plate. However, general operation principle is the same as in the case of single plate.

will experience no polarization rotation.

The birefringent filter is inserted in the cavity at Brewster's angle, such that the transmission through the output facet of the filter is polarization dependent. In this way, particular wavelengths of light will experience the least loss, and the Ti:Sapphire will preferentially lase at these particular frequencies. Wavelength tuning is accomplished by rotating the filter about an axis perpendicular to its surface, such that the index of the refraction of the extraordinary polarization component is changed. In turn, this influences Δn and thus, the wavelengths for which the transmission loss is minimum. In the Ti:Sapphires, the transmission function of the filter is periodic, with a spacing of approximately 225 GHz.

Housed within the intercavity assembly (ICA) are the thick and thin etalon. The thin etalon is made from a glass plate where the angle of the plate with respect to the cavity beam (and thus, the effective thickness of the glass) is controlled with a galvo. Tuning the thin etalon angle allows the preferred lasing mode (i.e., frequency of the laser) to be changed in 10 GHz steps. The thick etalon is constructed from two prisms mounted on a PZT which can be used to adjust their separation. Tuning the thick etalon plate separation enables one to select the specific cavity mode on which the laser lases, where the spacing of the cavity modes in the Ti:Sapphire lasers is 180 MHz. The transmission of the frequency selective elements is summarized in Fig. 2.14.

Each of the etalons acts like a small optical cavity which has a transmission maximum at frequencies which satisfy [116]

$$\nu_n = \frac{nc}{2nt\cos\theta}\,,\tag{2.13}$$

which depends on the thickness t of the element (or the separation of the elements in the case of the thick etalon), the angle θ between the normal to the surface and the cavity beam and the index of refraction n of the element. It is from the transmission function of the etalon elements that the naming of the etalons becomes clear: increasing the thickness (or separation) of the elements means a closer spacing of the frequency transmission maxima. Therefore, the "thin" etalon has a small thickness, which results in a larger spacing between thin etalon modes, while the "thick" etalon has a large thickness and results in a smaller spacing between thick etalon modes.

The output mode of the laser (i.e., the laser frequency) can be selected using (in order) the birefringent filter, thin etalon, and thick etalon to move the laser frequency within



Figure 2.14: Transmission of the frequency selective elements in the Ti:Sapphire lasers. Shown (not to scale) in order of the separation of the transmission maximum are the mirror set (black line), birefringent filter (blue line), thin etalon (red line) and thick etalon (green line). The black dashed line represents the net gain of all elements combined, and illustrates that a single longitudinal mode (thick vertical lines) can be selected out of all the possible longitudinal modes (other short thin vertical lines) by proper alignment of all frequency selective elements.

180 MHz of the desired value. Final adjustments can be made by changing the cavity length (and sometimes making small corrections to the thick etalon if the laser hops to a different cavity mode). This final frequency tuning is accomplished by translating one of the cavity mirrors mounted on a PZT (called the "tweeter mirror"). Most 899-21 lasers also have an additional glass slab mounted on a galvo inside the cavity which can be used to make larger adjustments to the cavity length. We noticed an unexpected decrease in power when we operated the laser with this element in place, so we removed it from both lasers⁴⁴. While this element is important to scan over a tuning range greater than the throw of the PZT will allow, almost all of our scans required a range of less than 1 GHz (or could easily be split up in multiple scans each with a range on the order of 1 GHz or less), which can be done using only the PZT.

Both Ti:Sapphire lasers are coupled to the experiment through an optical fiber. In order to reduce the effect of polarization drifts in the fiber, we use a Glan-Thompson polarizer

 $^{^{44}\}mathrm{If}$ only all problems were this easy to solve...

before the fiber to ensure both lasers have the same linear polarization, and are launched onto one the two orthogonal fiber axes ⁴⁵. Using the same fiber also assures that the two fields have the same spatial mode at the experiment. The beams are overlapped with the ODT beams using a dichroic beam splitter (see Fig. 3.9) and are focused to a waist of approximately 50 μ m, which is slightly larger than the waist of the ODT beams. This ensures that all the atoms held in the cross are illuminated by the PA light.

Frequency Stabilization

The 899-21 has a control box which can be used to stabilize the laser frequency using an external reference cavity (which is also available from Coherent). However, we chose to use our own locking circuitry, in part so that we had greater control over the lock and because one of our lasers was an upgraded 899-01 laser, which did not have its own control box ⁴⁶. The PZTs that control the thick etalon and tweeter mirror are driven by a home built high voltage PZT driver, which outputs up to 400 V. The galvo on which the thin etalon is mounted is driven by a commercial dc power supply, and we limit the output current to a maximum of ± 0.5 A (the galvo is bidirectional and can be driven with current running in either direction).

The error signal used to stabilize and reference the Ti:Sapphire laser frequency to the FFC is generated through a heterodyne beat between the frequency doubled light from the measurements arm of the comb (see Section 2.3.1) and the cw laser. This heterodyne beat is compared to the output of a stable RF synthesizer using a phase/frequency discriminator (PFD) based on the AD9901 chip, and we feedback a correction signal onto the tweeter mirror PZT. The correction signal is derived from a commercial laser servo from Vescent Photonics (D2-125) and amplified by our home built high voltage PZT drivers, as shown in Fig. 2.15.

Due to the comb like frequency structure of the OFC, the optical heterodyne of the cw laser with the comb will produce a series of RF beat notes at $f_{\text{beat}} = \pm f_{\text{beat}}^{(0)} + m f_{\text{rep}}$, where m = 0, 1, 2 and $f_{\text{beat}}^{(0)}$ is the frequency difference between the laser frequency and the nearest comb element. In addition to the heterodyne beats, the photodetector output will

⁴⁵We use polarization-maintaining fibers, where the fibers are made to have a strong birefringence. Therefore, linear polarization will only be maintained during propagation through the fiber if the light is launched into the fiber along one of the two orthogonal fiber axes.

 $^{^{46}}$ We also starting experiencing some issues with the Coherent lock box which we could not easily debug, and it became easier to work with our own locking system.



Figure 2.15: Layout of the beam paths and locking electronics for stabilizing and referencing the Ti:Sapphire lasers to the FFC. A heterodyne measurement is made between light from the Ti:Sapphire and the frequency comb, which is frequency doubled in a PPLN crystal. The heterodyne beat is referenced to a stable RF source, and a correction signal is fed back onto a PZT mounted cavity mirror. In order to scan the laser without changing the repetition rate of the comb, we employ ratchet lock scheme (see text), where the Ti:Sapphire light is frequency shifted by a double pass AOM (the ratchet AOM) before comparison with the comb. The fast lock AOM and the feed forward AOM allow us to implement a second fast lock on Ti:Sapphire light, where fast corrections are made to the pre-stabilized light from the Ti:Sapphire. We also actively stabilize the thick etalon in the Ti:Sapphire cavity in order to increase the long term stability and the mode hope free scanning range of the laser (see text for details). A small portion of the light out of the laser is sent to a commercial wavemeter (WM) to aid with frequency determination. Free space beam paths are represented in red, while fiber segments are magenta and electronic connections are blue.

also contain RF frequencies at integer multiples of $f_{\rm rep}$. In order to minimize noise in the locking signal, it is advantageous to choose $f_{\rm beat}$ such that it is well separated from the harmonics of $f_{\rm rep}$ and all other beatnote signals. The ideal spacing is achieved by setting $f_{\rm beat}^{(0)} = f_{\rm rep}/4^{47}$. In our case, we use the third beatnote in the series at 281.25 MHz. The output of the photodetector is immediately sent through a band pass filter centered at the same frequency, with a 3 dB bandwidth of 34 MHz (KR Electronics 3032). This effectively filters out all other RF signals, and the remaining RF signal is amplified before it is send

 $^{^{47}}$ This choice of f_{beat} is also critical in our ratchet lock scheme, which is discussed in the next section.

to the PFD.

It is also crucial to apply feedback to the thick etalon in order that the laser remains locked and mode hop free for long times, or to be able to scan the laser frequency more than a few tens of MHz. Temperature fluctuations, or a change in the laser frequency (i.e., when the laser frequency is scanned) can cause the transmission maximum of the thick etalon mode to drift away from being centered on the desired laser frequency (see Fig. 2.14). To ensure that the thick etalon mode follows the frequency changes of the laser, we built a separate lock closely based on the design used by the commercial Coherent control box. We apply a 2 kHz dither signal to the thick etalon control, and monitor the output power of the laser on a photodiode. This signal is sent to a lock in amplifier which demodulates the signal. The output from the lock in amplifier is related to the slope of the thick etalon transmission function. We feedback on the thick etalon driving voltage with a correction signal obtained by integrating the output of the lock-in amplifier. This locking scheme is summarized in Fig. 2.15.

With the locking scheme described above, we are able to achieve a relative linewidth of $\Delta \nu = 160$ kHz between the two lasers. This relative linewidth is measured using a heterodyne beatnote between the two lasers where the frequency difference of the Ti:Sapphires is set to be less than 24 GHz, such that is observable on a fast photodiode.

We have recently implemented a "fast" lock (similar to the design presented in [117]), where we use an external single pass AOM to make short time scale corrections on the output of the laser. The error signal for this lock is derived in a similar fashion to that of our PZT lock, but the "fast" AOM is placed in the beam path after the heterodyne beat for the PZT lock (see Fig 2.15). In this way, the "fast" lock is responsible for narrowing the linewidth of a pre-stabilized laser. This is advantageous because the achievable frequency excursion of the single pass AOM (on the order of 1 MHz) limits the size of the corrections that can be made with this lock. Another approach is to integrate the output of the AOM lock and feedback on the PZT in order that the PZT handles the dc (or close to dc) correction signal. However, our preliminary testing indicated that this serial method much less successful and less stable than employing two separate locks. The details of this additional lock will be discussed in the PhD thesis of Gene Polovy. With this additional lock, our preliminary results show that we can achieve a relative linewidth on the order of tens of Hz.

Frequency Determination

The frequency of the laser can be determined with an accuracy of 60 MHz using a commercial wavemeter (Bristol 621A-NIR). However, our photoassociation experiments require that we are able to determine the frequency of the laser with an uncertainty that is less (ideally much less) than the natural linewidth of the transitions (on the order of 10 MHz). For these requirements, the OFC is an ideal metrology tool [118].

Using the FFC as a reference, the frequency of the laser is given by,

$$f_{\rm CW} = f_{\rm n,780} \pm f_{\rm het}$$

$$= m f_{\rm rep} + 2 f_{\rm ceo} \pm f_{\rm het} ,$$
(2.14)

where f_{het} is the frequency of the heterodyne beat between the laser and the comb light and m is an integer which represents the comb line multiple to which the laser is locked (see Eq. 2.8). The \pm sign refers to whether the laser is locked to a comb line that is higher (minus sign) or lower (plus sign) in the frequency of the laser. It is possible to determine the correct sign by monitoring the beat frequency and slightly increasing or decreasing f_{rep} . If the beat signal increases (decreases) when f_{rep} is increased (decreased), then the comb line is located at a higher (lower) frequency than the Ti:Sapphire light.

The value of the integer m can be determined from the wavemeter frequency readout of $f_{\rm CW}^{48}$ and the known information about $f_{\rm rep}$, $f_{\rm ceo}$ and the heterodyne beat frequency via

$$m = \left[\frac{f_{\rm CW} \mp f_{\rm het} - 2 \cdot f_{\rm ceo}}{f_{\rm rep}}\right].$$
(2.15)

Again, the \pm symbol refers to whether the frequency of the comb line is higher (plus sign) or lower (minus sign) than the frequency of the cw light. Note that the sign here is opposite to that in Eq. 2.14.

In order to determine the uncertainty on the frequency determination using the comb, we measured the $5S_{1/2} \rightarrow 5P_{3/2}$ atomic transition frequencies of ⁸⁵Rb using a vapor cell. In a method similar to that described in [77], we compared the known values of these transitions with the frequency determined using the method described above. To reduce systematic effects due to residual magnetic fields, we enclosed the vapor cell and associated optics in

⁴⁸With the requirement that the uncertainty of the frequency readout from the wavemeter be less than half of the repetition rate of the comb.

a μ -metal tube. From these measurements, we determined that the absolute frequency of the readout was ± 600 kHz.

Frequency Scanning and Ratchet Lock

The most straightforward way to change the frequency of a laser referenced to an OFC is to change the value of $f_{\rm rep}$, which modifies the frequency of the $m^{\rm th}$ comb element to which the laser is referenced. This allows for a scanning range of many GHz, typically limited by the mod hop free tuning range of the laser or the extent to which $f_{\rm rep}$ can be varied in the OFC. In our experiment, we can use an external control of the RF synthesizer to which $f_{\rm rep}$ is referenced to change the reference frequency. At the optical frequencies at which we typically operate, $n \approx 3 \times 10^6$ and, since we lock $f_{\rm rep}$ using its third harmonic, a change to the reference frequency of 1 Hz corresponds to a change of approximately 1 MHz in the optical frequency of the Ti:Sapphire. However, this method does not allow for the independent referencing and tuning of two (or more) lasers as all of their frequencies will be affected by the change of $f_{\rm rep}$. In our case, many of our photoassociation experiments that involve both Ti:Sapphires rely on keeping one laser at a fixed frequency while the other is scanned (for more details on these experiments, see Section 5.2).

There are many examples of more universal schemes that overcome this issue. For example, instead of scanning $f_{\rm rep}$ it is possible to scan $f_{\rm het}$. However, this approach is complicated by the degeneracy of the beatnote when the laser frequency approaches a midpoint between comb teeth, and when the laser frequency approach one of the comb teeth. It is possible to jump over these "dead zones", but more complicated techniques are required (see, for example [119, 120, 121]). An alternative approach is to use an EOM to shift $f_{\rm ceo}$ by changing the optical phase of the light during the time between subsequent comb pulses, which has been demonstrated in [122, 123].

The approach that we employ uses an AOM the shift the frequency of the laser before it is compared to the OFC. The distinct advantage here is that the frequency of the laser can be changed without changing f_{beat} , and thus RF electronics only need to work well over a narrow frequency band. However, the scanning range of an AOM is typically limited to, at most, a few hundred MHz. This limitation is overcome through a ratchet scheme which climbs the lock point up or down a ladder of comb teeth, as shown in Fig. 2.16. In general,



Figure 2.16: Illustration of the ratchet scanning method. In (a) the laser frequency $f_{\rm L}$ (vertical thick green line) is shifted down in frequency by $2f_{\rm aom}$ before comparison with the comb element at f_n (vertical thin black line). In (b) the AOM tuning bandwidth spans $f_{\rm rep}$ and near the high end of the range the scan is stopped and $f_{\rm aom}$ is returned to it initial value and the laser re-establishes the lock to the line f_{n+1} . In (c) the AOM tuning bandwidth is only $f_{\rm rep}/2$ and both the AOM frequency and the polarity of the error signal must be changed in order for the lock to be re-established. In this case, the lock alternates between being referenced to a comb tooth that is high in frequency, and one that is lower in frequency than the Ti:Sapphire. In our case, we employ the method in (c) as the scanning range of our double pass AOM is only $f_{\rm rep}/2$. See text for details. Figure and caption (modified) from [78].

with this scheme, the locked lasers frequency is

$$f_{\rm L} = n f_{\rm rep} + f_{\rm ceo} \pm f_{\rm het} + 2 f_{\rm aom} \,, \qquad (2.16)$$

where we set up the AOM in a double pass configuration such that the laser frequency is shifted down before the heterodyne comparison (i.e., we use the negative first order). As such, a change in f_{aom} results in a change of f_L because the lock electronics adjust f_L in order to keep f_{beat} constant. In our setup, we lock using the third beat note in the series such that $f_{beat} = 2f_{rep} + f_{rep}/4$, and the comb tooth to which we lock is higher in frequency than the laser frequency. We use negative servo polarity such that if the laser frequency increases, the beat frequency will decrease and the servo responds by decreasing the laser frequency. At this starting point, $f_{aom} = 75$ MHz and the laser frequency is

$$f_{\rm L} = f_{n+2} + 2f_{\rm aom} - f_{\rm beat}$$

= $(n+2)f_{\rm rep} + f_{\rm ceo} + 2f_{\rm aom} - f_{\rm beat}$ (2.17)
= $nf_{\rm rep} + f_{\rm ceo} + 2f_{\rm aom} - f_{\rm rep}/4$,

where f_n is the frequency of the comb tooth nearest to the laser frequency and, correspondingly, f_{n+2} is the frequency of the comb tooth to which we lock. At this point, we can scan the laser frequency by changing the driving frequency of the AOM until we have reached $\Delta f_{aom} = f_{rep}/2 = 62.5$ MHz which corresponds to $f_{aom} = 106.5$ MHz. At this point, we switch the polarity of the error signal⁴⁹ and, at the same time, the AOM driving frequency is returned to $f_{aom} = 75$ MHz. Now, the frequency of the laser light is

$$f_{\rm L} = f_{n-2} + 2f_{\rm aom} + f_{\rm beat}$$

= $(n-2)f_{\rm rep} + f_{\rm ceo} + 2f_{\rm aom} + f_{\rm beat}$ (2.18)
= $nf_{\rm rep} + f_{\rm ceo} + 2f_{\rm aom} + f_{\rm rep}/4$,

where the laser is now locked the a comb tooth that is at a lower frequency than the laser frequency. Although the servo polarity is still negative, because the error signal has been inverted, if the laser frequency increases and thus the beat frequency increases, the servo will still respond by decreasing the laser frequency. The ratchet can be continued in a similar fashion such that when the error signal polarity is inverted again (such that it returns to the initial setting), the laser will now be locked to the f_{n+3} comb tooth, and the laser frequency will be higher than the starting value by f_{rep} .

By repeating this process, $f_{\rm L}$ can be moved an arbitrary amount while maintaining the lock to the comb. This scheme also allows a second laser to also be referenced to the comb and held at a constant frequency. The key to this method is exploiting the finite response time of the PID controller. This allows us to change the comb element to which the laser is locked without disengaging the phase-locked loop and without affecting $f_{\rm L}$, due to the fact that $f_{\rm aom}$ is also changed at the same time.

An illustration of this technique is shown in Fig. 2.17. Here, we show the measured heterodyne beat note between the fixed frequency laser and the laser tuned using this ratchet method, both phase locked to the OFC comb, as a function of the driving frequency of the double pass AOM. Although the frequency difference for this measurement was 10 GHz in order that the heterodyne beat was visible on a fast photodiode, we have also used this method to bridge a 58 GHz gap (our spectroscopy of the $X(1^{1}\Sigma_{q}^{+})$ state) and

⁴⁹We switch the polarity of the error signal by inverting the output of the PFD. We do this instead of inverting the correction signal so that in the event there is any integrated correction signal the driving voltage of the tweeter mirror PZT does not undergo a discrete jump in position.



Figure 2.17: Measured heterodyne beat note (black dots) between the fixed frequency laser and the variable-frequency laser, both phase locked to the OFC. The beat note is shown as a function of the driving frequency of the double-ass AOM. The solid (dashed) lines represent the expected heterodyne beat note frequency with a negative (positive) servo polarity. The horizontal dashed-dot lines represent the jump of the AOM driving frequency, where the difference in the doubled-passed AOM shift is $f_{\rm rep}/2$ and the resulting $f_{\rm beat}$ is unchanged except for the comb element responsible for the beat not changes. See text for details. Figure and caption (modified) from [78].

an 8 THz gap (our spectroscopy of the $a(1^{3}\Sigma_{u}^{+})$ state). In our setup, discrete jumps are limited to be at most $2\Delta f_{aom} = 20$ MHz by the bandwidth of the band pass filters. For these jumps, we find the lock is re-established within 6 ms. For continuous sweeps which include the discontinuous lock point jump we can achieve rates up to 200 MHz/s and for small continuous sweeps using only the double pass AOM (i.e., without the need to switch the polarity of the error signal) we can achieve sweep rates of > 3 GHz/s.

The major limitation of this method is that the phase coherence between the two lasers is not maintained during the frequency scan at the point when the hand-over between modes of the comb is performed. In theory, this hand over can be done is a fully phase coherent way by executing the frequency change in a time that is short compared to the $1/f_{\rm rep}$ and timed with the bright interval of the pulse train from the OFC, for which all the comb modes have the same optical phase. However, if this phase coherence is required, it is likely that the EOM based methods [123] would be preferable because the update and settling time of an EOM is typically much shorter than that of an AOM. However, for all of our work, we only require phase coherence when the lasers are kept at a fixed frequency difference and therefore this ratchet scheme is applicable and was much more easily implemented.

Chapter 3

Preparation and Detection of Cold Atoms

A day in the life of a cold atom experiment may appear to be rather repetitive. As most of the common techniques to extract information from the system are destructive, almost any measurement (whether the goal be optimization, calibration, or scientific in nature) requires many repeated runs. In each repeated run, an identical (or nearly identical, given shot to shot fluctuations that can exist in the system) sample is created, and the effect of a particular setting of one parameter is observed. For each subsequent run, the value of the parameter is changed such that its effect on the ensemble over a given range can be observed.

In our experiment, each individual run follows the same basic recipe: hot atoms leave an effusive oven and are slowed into a cold atomic beam in the Zeeman slower. This cold atom beam acts as the atom source for the MOT, which is the standard starting point for almost all ultra-cold atom experiments. After the MOT is loaded, the atoms are transferred to the ODT. In the ODT we perform an additional forced evaporation step in order to further cool the atoms. At this point, we can also prepare the atoms in particular spin states, depending on the requirements of the experiments. After the conclusion of this preparation stage, we perform the planned experiment on the atoms. For example, in a search for Feshbach resonances we may apply a homogenous magnetic field. Or, in the case of photoassociation or dark state measurements, we illuminate the atoms with the photoassociation light. After this "science" step, we take an image of the atoms, which gives us a method of quantifying the number of atoms that remain and, in some cases, the spatial profile of the ensemble. This entire procedure produces a single data point at a single parameter, and is repeated as many times as necessary to map out the behavior with respect to some changing parameter. In general, the entire procedure takes between 5 and 10 s to produce a single data point.
This section covers the details of these steps for both ⁶Li and Rb. Section 3.1 discusses the Zeeman slower, which is used as the cold atom source for our MOT. Section 3.2 introduces ODTs, and provides the details surrounding the transfer of ⁶Li and Rb into the ODT, and the subsequent evaporation. Section 3.3 provides the details of our optical pumping scheme for Rb, and discusses how we prepare our ⁶Li ensemble in a particular spin state (or states). Finally, Sec. 3.4 describes how we image the atoms through absorption or fluorescence imaging, and the techniques we use to perform state selective imaging with either species.

3.1 MOT and Zeeman Slower

At its inception, our ultra-cold ⁶Li and Rb machine was built to be extremely simple and compact. The atomic source for the ⁶Li MOT was an effusive oven placed 10 cm from the center of the MOT, and the MOT captured the low velocity tail of the atomic velocity distribution from the oven. The Rb MOT was loaded from an atomic vapor provided by commercial ⁸⁵Rb vapor dispensers. The details of this setup can be found in [93, 98, 124]. Although this apparatus proved extremely successful and robust for single species operations, the background ⁸⁵Rb pressure required to load a sufficiently large ⁸⁵Rb MOT was high enough that it severely limited the size of the ⁶Li MOT. A more in depth discussion of this issue can be found in Chapter 7, which details our experiments with the ⁶Li +⁸⁵Rb mixture.

In an effort to improve the pressure in the science chamber (i.e., our glass vacuum cell) for dual species experiments, we rebuilt our apparatus to include a Zeeman slower that provided a cold atomic beam of ⁶Li or Rb to act as the atom source for our MOT. This section briefly outlines the operating principle of Zeeman slowers, and discusses the specifics that are unique or important to our implementation. Full details on the construction of the Zeeman slower and the effusive sources can be found in the Master thesis of William Bowden [99] and in [125].

Zeeman Slower Theory

A Zeeman slower relies on the photon scattering force to decelerate atoms along a longitudinal axis to create a cold (i.e., slow) atomic beam with a high flux. The photon scattering force

$$F_{\rm sc} = \frac{\hbar\omega\Gamma}{2c} \cdot \frac{s}{1+s+\left(\frac{2\delta}{\Gamma}\right)^2},\tag{3.1}$$

is a function of the frequency of the slowing light (which depends on the atomic species being slowed), the saturation parameter $s = I/I_{\text{sat}}$, and the detuning of the slowing beam from the atomic resonance

$$\delta = \delta_{\rm L} + \frac{\omega v}{c} - \frac{\mu B}{\hbar} \,. \tag{3.2}$$

This detuning has contributions from three different sources. The first term in Eq. 3.2 accounts for the detuning of the slowing beam from the atomic resonance. The second term accounts for the Doppler shift of the slowing light due to the velocity of the atoms. In this case, it is assumed that v is positive, and the Doppler shift blue-shifts the slowing light because the atom's velocity is opposite to the propagation direction of the slowing beam. Finally, the third term represents the shift in the atomic transition frequency due to the Zeeman shift in a field of strength B, where μ is the relative magnetic moment between the ground and excited state used as the slowing transition. If μ is positive (negative), the transition energy increases (decreases) with increasing field, which results in a red shift (blue shift) of the slowing light.

In order for an atom to be effectively slowed over the entire length of the slower, the net detuning of the slowing beam must be close to zero along the length of the slower. If the detuning of the slowing beam is fixed (i.e., $\delta_{\rm L}$ is constant), then the magnetic field profile must change in order to compensate for reduced blue shift from the Doppler effect as the atoms slow.

The required field profile can be found by considering that the velocity of an atom with an initial velocity v_i , which undergoes a constant deceleration a, at a distance z along the slower (where z = 0 is defined to be the start of the slower) is

$$v_f = \sqrt{v_i^2 - 2az} \,. \tag{3.3}$$

If this velocity is used in Eq. 3.2, along with the assumption that the net detuning of the slowing beam is zero, the required magnetic field profile is found to be

$$B(z) = \frac{\hbar\omega v_i}{c\mu} \sqrt{1 - \frac{2az}{v_i^2}} - \frac{\hbar\delta_{\rm L}}{\mu}.$$
(3.4)

From the term under the square root in Eq. 3.4, it can be seen that the length of the slower is limited to $z_0 \leq v_i^2/(2a)$. Physically, this is the length where the atoms final velocity is zero, and the magnetic field compensates only for the detuning the slowing light. In a real slower, if this length is reached before the atoms are captured in a MOT, the slowing light will accelerate the atoms in the opposite direction (i.e., the atoms will turn around).

The deceleration of the atoms is limited by the finite scattering rate (Eq. 3.1) and takes on a maximum value of a_{max} in the limit where $s \gg 1$ and $\delta = 0$. The acceleration that the atoms undergo is typically some fraction of a_{max} , such that $a = \eta a_{\text{max}}$ and $0 < \eta < 1$. This acceleration is often chosen to ensure that the field gradient satisfies the adiabatic slowing condition [99]

$$\left|\frac{dB(z)}{dz}\right| \ll \frac{\hbar\omega a_{\max}}{c\mu v(z)},\tag{3.5}$$

throughout the entire length of the slower⁵⁰.

This poses a problem for simultaneously slowing two (or more) species in a fixed length slower. That is, although the scattering force may be similar for different species, the maximum acceleration may not be (because the acceleration is inversely proportional to the mass of the atom). This means the required field gradient may vary substantially for the different species. In fact, it can be shown that for efficient simultaneous slowing of two species, the ratio [99]

$$\frac{\eta_1}{\eta_2} = \frac{m_1 \mu_1 \omega_2 \Gamma_2}{m_2 \mu_2 \omega_1 \Gamma_1} \tag{3.6}$$

must be on the order of one. For ⁶Li and ⁸⁵Rb , this ratio is equal to 0.04, owing largely to the large mass difference between the two species. This limitation has been overcome by the group of Stamper-Kurn [126] using a three stage design which creates a different effective length of the slower for ⁶Li and Rb. However, even if efficient slowing of both ⁶Li and Rb can be achieved, the optimal parameter space for the ⁶Li and Rb MOTs do not overlap, and running a dual species ⁶Li +Rb MOT can diminish the MOT size for both species. For these reasons, we use a sequential loading technique, which requires the Zeeman slower to only slow a single species at a time⁵¹.

⁵⁰Note that this statement isn't entirely true. In his thesis, William Bowden writes: "The maximum gradient is inversely proportional to velocity, which makes the adiabatic condition more stringent for faster moving atoms. Therefore, the strategy of uniformly stretching the field by changing η is not ideal, rather it is better to vary η depending on velocity at that particular location in the slower" [99].

⁵¹More details about the full sequential loading technique, including the transfer to the ODT can be found in Chapter 7.

It is important to note that a Zeeman slower generally only provides slowing along the axis of the slowing beam. When the transverse velocity spread of the atomic beam becomes significant compared to the longitudinal velocity of the beam, beam blooming can occur. If blooming begins to occur far from the MOT region, the atomic beam can diverge enough that a large fraction of the atoms in the beam do not reach the MOT, which limits the capturable flux. Therefore, it is important to minimize the distance between the end of the slower and the MOT⁵².

Details of Our Design

Our design is similar to that of the group of Hackermüller [128], where the magnetic field for the Zeeman slower is generated with a segmented coil design. The current in each of the separate segments of coil is computer controlled, which allows us to easily optimize the required current in each coil and to switch between the optimal coil gradient for each species. Additionally, we partially mitigate the problem of beam blooming by disengaging the atoms from the Zeeman slower with a large field gradient created by the final coil segment, which we refer to as the "disengagement coil". This forces the atoms to exit the Zeeman slower moving at a velocity where blooming is not a major issue. The final slowing occurs in the magnetic field produced by the MOT coils, such that the atoms are captured in the MOT before the effects of blooming have a significant impact on the flux. The approximate magnetic field produced by the Zeeman slower coils and the MOT coils used when slowing ⁶Li and ⁸⁵Rb are shown in Fig 3.1.

As the magnetic field decreases along the length of the slower, we require that the relative magnetic moment of the slowing transition be positive such that the Zeeman shift of the slowing transition decreases as the atoms propagate through the slower. This energy shift matches the decreasing blue shift due to the Doppler shift of the atoms as they are slowed. The consequence of this choice is twofold: first, we must cool on a σ^+ transition, such that the excited state energy decreases faster than the ground state energy in the decreasing magnetic field. Second, since both the Zeeman shift of the slowing transition and the Doppler shift are small at the end of the slower, the detuning of the slowing beam must also be small, and is typically on the same order of magnitude as the detunings of the

 $^{^{52}}$ Alternatively, it has also been shown that an additional beam can be used to provide transverse cooling inside the slower [127]. However, this is not used in our design.



Figure 3.1: The magnetic field profile produced by the Zeeman slower coils and the MOT coils used for slowing ⁶Li (top panel) and ⁸⁵Rb (bottom panel). The distance is measured relative to the position of the MOT. The region between the two vertical dashed lines indicates the area between the end of the Zeeman slower and the region where the final slowing stage occurs. This final slowing stage uses the magnetic field produced by the MOT magnetic field coils.

MOT beams⁵³.

In our slower, we slow on the D₂ transition between stretched states in the ground and excited hyperfine manifolds. At zero magnetic field, these states connect to the $|f = 3, m_f = 3\rangle$ and $|f' = 4, m'_f = 4\rangle$ states for ⁸⁵Rb and $|f = 3/2, m_f = 3/2\rangle$ and $|m'_f = 5/2, m'_f = 5/2\rangle$ states for ⁶Li. In ⁶Li, the magnetic field in the majority of the slower is large enough that the atoms are in the hyperfine Pachen-Back regime, and the slowing transition is correctly labeled by the projection of the nuclear spin m_i and the total orbital angular momentum m_j on the magnetic field axis. In this regime, the states used for slowing are the $|m_j = 1/2, m_i = 1\rangle$ and $|m'_j = 3/2, m'_i = 1\rangle$ states. The energies of the relevant states and the slowing transition are shown in Fig. 3.2 for ⁶Li and Fig. 3.3 for ⁸⁵Rb.

We performed a full optimization of the loading rate for both ⁶Li and ⁸⁵Rb. We started by setting the slowing beam detuning and magnetic field gradients based on a "virtual

⁵³The choice of the actual value of the detuning depends on a combination of the slower length, the capture velocity of the MOT, and the highest initial atom velocity that you want to slow. This is discussed in more detail in the Master's thesis of William Bowden [99].



Figure 3.2: ⁶Li hyperfine structure in an external magnetic field. Shown with thick red lines are the states that we use as the slowing transition in our Zeeman slower. At zero magnetic field, these states correlate to the $|f = 3/2, m_f = 3/2\rangle$ and $|m'_f = 5/2, m'_f = 5/2\rangle$ states. At high field (greater than 100 G) they correlate to the $|m_j = 1/2, m_i = 1\rangle$ and $|m'_j = 3/2, m'_i = 1\rangle$ states. Note the magnetic field range for the ground and excited state is chosen such that the energy splitting between states that differ in m_i is visible. The given energy is relative to the hyperfine center of gravity.

slower" simulation [99]. We then scanned the current of each coil about the calculated value to find the current through each coil that gave the maximum loading rate. We repeated this procedure for different choices of η and MOT parameters until we found an overall maximum in the loading rate. Because many of the parameters are strongly coupled, the optimal settings we found may only correspond to a local maximum. However, the loading rates were comparable to that reported in prior work on multi-species Zeeman slowers operating at similar oven temperatures and are more than sufficient to meet our requirements. The final loading parameters for the ⁶Li and ⁸⁵Rb MOTs are given in Tab. 3.1, and the currents that we used in each coil segment are given in Tab. 3.2.

Once we had determined the optimal settings, we measured the loading rate of both



Figure 3.3: ⁸⁵Rb hyperfine structure in an external magnetic field. Shown with thick red lines are the states that we use as the slowing transition on our Zeeman slower. At zero magnetic field, these states correlate to the $|f = 3, m_f = 3\rangle$ and $|f' = 4, m'_f = 4\rangle$ states. Not shown is the f = 2 manifold in the ${}^2S_{1/2}$ level, which is approximately 3 GHz lower in energy than the f = 3 manifold at zero field. The given energy is relative to the hyperfine center of gravity.

species as a function of the slowing beam power. The result of this measurement is shown in Fig. 3.4. Although on the surface it may seem that increasing the slowing beam power would be beneficial, there are two important considerations.

First, in the case of a σ^+ slower, the slowing beam is not far detuned from the atomic resonance, and therefore imparts a non-trivial radiation pressure force on the MOT. At large beam intensities, this force can push the MOT outside of the region where the MOT beams overlap. In our setup, we attempt to compensate for this by focusing the slowing beam through the slower, so that the beam intensity at the MOT is much less than the beam intensity inside the slower. Additionally, we use the compensation coils to move the zero of the quadrupole field in order to compensate for the radiation pressure force, and

	Rb	Li
Slowing Beam Pump Detuning (MHz)	-85	-76
Slowing Beam Pump Power (mW)	15	60
Slowing Beam Repump Detuning (MHz)	0	—
Slowing Beam Repump Power (mW)	12	—
MOT Pump Beam Detuning (MHz)	-15	-45
MOT Pump Beam Power (mW)	40	30
MOT Repump Beam Detuning (MHz)	0	-40
MOT Repump Beam Power (mW)	10	40
MOT Axial Gradient (G/cm)	15.4	67.4

Table 3.1: Optimal loading parameters for the ⁶Li and ⁸⁵Rb MOT. The pump detuning for ⁸⁵Rb is with respect to the $f = 3 \rightarrow f' = 4$ D2 transition while for ⁶Li it is with respect to the $f = 3/2 \rightarrow f' = 5/2$ transition at zero magnetic field. The repump detuning for ⁸⁵Rb is with respect to the $f = 2 \rightarrow f' = 3$ D2 transition while for ⁶Li it is with respect to the $f = 1/2 \rightarrow f' = 5/2$ transition at zero magnetic field. The MOT beams have a radius of 9 mm, and the power is split between three retroreflected arms of the MOT.

shift the MOT so that it is well centered on the three orthogonal MOT beams. However, as Fig. 3.4 shows, the loading rate of the Rb MOT is severely diminished at large slowing powers. We believe this is, in part, due to this effect.

Second, too large of an intensity can actually result in a decrease in the loading rate if the atoms are stopped (or turned around) prior to reaching the MOT. We believe this effect is also partially responsible for the rollover in the loading rate of ⁸⁵Rb shown in Fig. 3.4. We believe that we see this rollover for ⁸⁵Rb and not for ⁶Li because ⁸⁵Rb exits the slower at a lower velocity and encounters a smaller magnetic field. This means that at high slowing beam intensities, the slowing transitions can be power broadened such that an atom which should be moving slowly enough to disengage from the slowing field will actually continue to be slowed, and eventually stopped or turned around.

Empirically, we also found that the ⁸⁵Rb loading rate was greatly improved when we added a repump beam that was collinear with the slowing beam. The loading rate as a function of the repump power along the slowing beam axis is shown in Fig. 3.5. We also tried to send the repump light down an axis transverse to the slowing beam near the output of the effusive source. With this configuration, we did not notice any improvement to the loading rate. This suggests that the increase in the loading rate was due to the repump beam pumping atoms back into the slowing transition within the slower, and not simply optically pumping the atoms into the slowing transition before they entered the slowing

Coil Num.	$I_{\rm Li}$ (A)	$I_{\rm Rb}$ (A)
1	6.7	0.81
2	4.2	0.61
3	3.8	0.50
4	3.2	0.43
5	3.0	0.36
6	2.3	0.28
7	2.0	0.29
8	3.2	0.00

3.1. MOT and Zeeman Slower

Table 3.2: The current used in each coil segment for the ⁶Li and ⁸⁵Rb Zeeman slower. Coil one is the coil that is closest to the oven (i.e., at the start of the slower). The eighth coil is the "disengagement coil" (see text). The field profile produced by these currents is shown in Fig. 3.1.



Figure 3.4: The effect of slowing beam power on the MOT loading rate for ⁶Li (red squares) and ⁸⁵Rb (black dots). We attribute the rollover of the Rb loading rate at high slowing beam powers to a combination of two effects: first, the atoms being stopped or turned around prior to reaching the MOT and second, the radiation pressure of the slowing beam pushing the MOT outside of an optimal region.

field.

We suspect this is the case because the polarization of our slowing light is not perfect, and the slowing beam likely also drives π and σ^- transitions. Therefore, off resonance transitions likely occur from the stretched ground state to the $|f' = 4, m'_f = 3\rangle$ or $|f' = 4, m'_f = 2\rangle$



Figure 3.5: The effect of adding hyperfine repumping light to the slowing beam on the loading rate of the ⁸⁵Rb MOT. These data were taken using the parameters listed in Table 3.1, and the rate is normalized to the peak loading rate. Figure from [125].

states or to the $|f' = 3, m'_f = 3\rangle$ or $|f' = 3, m'_f = 2\rangle$ states. Although the transition rate to the $|f' = 3\rangle$ states is suppressed due to the large detuning (on the order of hundreds of MHz), decay to the $|f = 2\rangle$ manifold is possible. In this case, repump light is required to repump the atoms back into the $|f = 3\rangle$ ground state manifold.

However, in the ⁶Li slower, we did not see any improvement in the loading rate with the inclusion of a repump beam. We believe that this is the case for two reasons. First, at the large magnetic fields in the ⁶Li slower, the system is well within the Paschen-Back regime. In this regime, the projection of the nuclear spin must be conserved during an electric dipole transition. Therefore, transitions to any of the other excited states with $m'_j = 3/2$ are disallowed because each other state differs in the projection of the nuclear spin. Second, even if the polarization of the light is not perfectly circularly polarized, the only other possible transition that the slowing light can excite is to the $|m'_j = 1/2, m'_i = 1\rangle$ state. However, this transition is detuned from the slowing beam by over a GHz for the majority of the slower, which greatly suppresses the transition rate to this state. In addition, while the detuning of this transition is much smaller in the final slowing stage which takes place in the magnetic field provided by the MOT, repump light is already present due to the MOT beams.

Characterization of MOT and Zeeman Slower

To characterize the Zeeman slower, MOT, and the pressure in the science chamber, we measured the loading rate, MOT lifetime, and steady state atom number for both species as a function of the temperature of the effusive source⁵⁴. In addition, we measured the lifetime of ⁶Li atoms in our low power IPG ODT (see Section 3.2 for more information). In order to estimate the quality of the vacuum, it is better to rely on the ODT lifetime, as it provides a more true measure of the loss rate due to collisions with background gases. In the MOT, the lifetime is also impacted by light assisted collisions and these effects become more pronounced for large MOTs where the density is high. We used the ⁶Li ODT for both the ⁸⁵Rb and ⁶Li measurement in order that that the measured lifetimes were directly comparable.

Figure 3.6 shows these measurements for the ⁶Li MOT as a function of the temperature of the ⁶Li effusive oven. In this case, the ⁸⁵Rb MOT was "off" (i.e., held at room temperature). For low source temperatures, the MOT lifetime is much larger than the ODT lifetime due to fact that the MOT trap depth is more than three orders of magnitude larger than the ODT depth [129]. As the oven temperature is increased, the MOT lifetime decreases due to increasing MOT density, and the ODT lifetime begins to decrease due to increased collisions with background gases emitted by the oven. We choose a standard operational temperature of about 400 °C in order strike a balance between a reasonable loading rate and the ODT lifetime⁵⁵.

Figure 3.7 shows these measurement for the 85 Rb MOT as a function of the temperature of the 85 Rb effusive source. In this case, the 6 Li effusive source was held at 400 °C. In the Rb MOT, high densities are achieved at low oven temperatures, and we find that MOT lifetime is always less than the ODT lifetime. We typically operate the 85 Rb effusive source at a temperature of about 80-100 °C, again chosen to balance the 85 Rb loading rate and the ODT lifetime.

The Zeeman slower and the MOT represent the first step in an ultra-cold atom exper-

⁵⁴Note that the MOT lifetime presented here is the characteristic loading time of the MOT, found from a fit of the atom number as a function of loading to $N(t) = N_0(1 - \exp(-t/\tau))$, and not the decay time of the MOT.

 $^{^{55}}$ The limit on the lifetime of the ODT is that the lifetime needs to be longer than the timescale for our forced evaporation ramps, which are on the order of 2-4 s.



Figure 3.6: The effect of the ⁶Li source temperature on the ⁶Li loading rate (black dots), steady state atom number (blue triangles), MOT lifetime (red diamonds), and the Li ODT lifetime (green squares). For this measurement, the Rb source was "off" (i.e., held at room temperature). Figure from [125].



Figure 3.7: The effect of the ⁸⁵Rb source temperature on the ⁸⁵Rb loading rate (black dots), steady state atom number (blue triangles), MOT lifetime (red diamonds), and the Li ODT lifetime (green squares). For this measurement, the ⁶Li source was held at 400 °C. Figure from [125].

iment. Typically, the MOT temperature is on the order of a few hundred μ K, which is approximately 3 orders of magnitude higher than the temperatures required for degeneracy, and at which we perform the majority of experiments. In order to further cool the atoms, we transfer the atoms from the MOT to an ODT. The details of these traps and their implementation in our apparatus are discussed in the following section.

3.2 Optical Dipole Traps

Optical-dipole traps (ODT) are an ideal tool for ultracold experiments, as they have the ability to trap any polarizable particle, atom, or molecule. Straightforward experimental control of the trapping potential is provided via the intensity of the laser, which easily allows for forced evaporative cooling. Additionally, because the trapping potential relies on off-resonant light, atomic samples trapped in an ODT can be prepared in a particular spin configuration and external electric and/or magnetic fields can be easily applied. An excellent review of dipole traps can be found in [130], while the Quantum Optics notes by D. Steck [131] provide a detailed discussion of the complex polarizability, dipole force and photon scattering rate.

The dipole potential in an ODT results from the interaction of the induced dipole moment (induced by the trapping field) interacting with the trapping field to produce a dipole potential given by

$$U_{\rm dip} = \frac{-\vec{d} \cdot \vec{E}}{2} , \qquad (3.7)$$

where the factor of 1/2 comes from the fact that the dipole is induced. The induced dipole moment is defined as

$$\vec{d}^{(+)} = -e\vec{x}^{(+)} = \alpha(\omega)\vec{E}^{(+)}$$
(3.8)

where $\alpha(\omega)$ is the frequency dependent polarizability⁵⁶, and gives a measure of how easily the incident light induces a dipole moment.

In addition to the dipole force (which is responsible for the trapping potential) the interaction of the trapping light and the atoms results in a radiation pressure force. This force is due to photon scattering, which can lead to a heating of atoms held within the trap and can result in trap loss. The dipole potential and the photon scattering rate are related

⁵⁶In general, this polarizability is complex.

to the real and complex part of the polarizability, respectively

$$U_{\rm dip} = -\frac{1}{2\epsilon_0 c} \operatorname{Re}[\alpha(\omega)] I(\vec{r})$$
(3.9)

$$\Gamma_{\rm sc} = \frac{1}{\hbar\epsilon_0 c} \operatorname{Im}[\alpha(\omega)]I(\vec{r})$$
(3.10)

where the intensity is related to the electric field amplitude in the usual way

$$I(\vec{r}) = 2\epsilon_0 c |\vec{E}^{(+)}|^2.$$
(3.11)

Note that the force resulting from the dipole potential is proportional to the gradient of the intensity, and acts to trap atoms in a potential well.

During each photon scattering event in the dipole trap, the atom will gain, at most, $4E_{\text{recoil}} = 4(\hbar^2 \omega^2)/(2mc^2)$ of energy⁵⁷. Therefore, one can define the heating rate due to photon scattering as

$$\dot{E}_{\text{heat}} = \Gamma_{\text{sc}} \times 4E_{\text{recoil}} = \Gamma_{\text{sc}} \frac{\hbar^2 \omega^2}{mc^2} \,. \tag{3.12}$$

In most cases, the dipole potential and scattering rate can be well approximated using a two level model, where the energy levels are separated by $\Delta E = \hbar \omega_0$, and the detuning of the dipole trap light (with frequency ω) from the atomic resonance is $\Delta = \omega - \omega_0$. In the case of large detuning, where Δ is much larger than the natural linewidth of the two level transition γ , the dipole potential from Eq. 3.9 and photon scattering rate from Eq. 3.10 can be expressed as

$$U_{\rm dip} = -\frac{3\pi c^2 \gamma}{2\omega_0^3} \left(\frac{1}{\omega_0 - \omega} + \frac{1}{\omega_0 + \omega}\right) I(\vec{r}) \tag{3.13}$$

$$\Gamma_{\rm sc} = \frac{3\pi c^2 \gamma^2}{2\hbar\omega_0^3} \left(\frac{\omega}{\omega_0}\right)^3 \left(\frac{1}{\omega_0 - \omega} + \frac{1}{\omega_0 + \omega}\right)^2 I(\vec{r}) = \left(\frac{\omega}{\omega_0}\right)^3 \left(\frac{\gamma}{\omega_0 - \omega} + \frac{\gamma}{\omega_0 + \omega}\right) \frac{U_{\rm dip}}{\hbar}.$$
(3.14)

In the general case, where the dipole trap light couples more than two levels (for example, couplings to bound molecular levels in the excited states or higher lying excited atomic

⁵⁷The actual gain in energy will depend on the direction of the emitted photon. However, to estimate the heating rate, we will assume that the atom gains the maximum kinetic energy possible.

states), then Eqs. 3.13 and 3.14 must be summed over all applicable levels.

The scaling of the dipole potential and the photon scattering rate with intensity and detuning become more apparent in the limiting case where the rotating wave approximation can be applied. This approximation holds when the frequency of the dipole trap light is far enough from resonance such that $|\Delta| \ll \gamma$, but is close enough to ω_0 such that

$$\frac{\omega}{\omega_0} \approx 1 \quad \text{and} \quad \omega_0 - \omega \ll \omega_0 + \omega \,.$$
 (3.15)

In this regime, the expression for the dipole potential and the scattering rate becomes

$$U_{\rm dip} = \frac{3\pi c^2 \gamma}{2\omega_0^3} \cdot \frac{I(\vec{r})}{\Delta}$$
(3.16)

$$\Gamma_{\rm sc} = \frac{3\pi c^2 \gamma^2}{2\hbar\omega_0^3} \cdot \frac{I(\vec{r})}{\Delta^2} = \left(\frac{\gamma}{\Delta}\right) \left(\frac{U_{\rm dip}}{\hbar}\right) \,, \tag{3.17}$$

and it can be seen that the dipole potential scales like I/Δ , while the scattering rate (which is responsible for heating within the trap) scales like I/Δ^2 . Therefore, in order to create the largest trapping potential while maintaining a long lifetime (i.e., a small scattering rate), one should operate with large detunings and high intensity. In most cases, this can be achieved using infrared fiber lasers where the wavelength in the range of 1100 nm, or with CO₂ lasers where the wavelength is 10.6 μ m.

It should be noted that the rotating wave approximation made in Eqs. 3.16 and 3.17 are not well justified in our case, given that the wavelengths of the ODTs used in this apparatus are 1090 nm and 1064 nm, while the transitions wavelengths of ⁶Li and Rb are 671 nm and 780 nm, respectively. Specifically, Eq. 3.16 underestimates the trap depth by approximately 20%, while Eq. 3.17 overestimates the scattering rate by about a factor of two. Therefore, the full form given in Eqs. 3.13 and 3.14 in the absence of the rotating wave approximation must be used for any quantitative estimations of trap depth and scattering rate.

Optical dipole traps are formed (typically, and in our case) by focusing a Gaussian beam with a total power P to a minimum beam radius (i.e., beam waist) of w_0 . The intensity of this focused beam, as a function of the radial and axial coordinate, is

$$I(r,z) = \frac{2P}{\pi w^2(z)} \exp\left(-\frac{2r^2}{w^2(z)}\right) , \qquad (3.18)$$

where the beam radius as a function of longitudinal position is

$$w(z) = w_0 \sqrt{1 + \left(\frac{z}{z_0}\right)^2}$$
(3.19)

and z_0 is the Rayleigh range, given by

$$z_0 = \frac{w_0^2 \pi}{\lambda} \,. \tag{3.20}$$

With this, the trap depth U_0 is defined as the dipole potential (see Eq. 3.13) where r = z = 0 and the intensity of the dipole trap light is $I = 2P/\pi w_0^2$. Likewise, the photon scattering rate can be defined in a similar fashion using Eq. 3.14.

When the atomic ensemble is at a temperature $k_BT \ll U_0$, it can be assumed that the atoms are concentrated near the focus of the beam, and the ODT potential can be approximated as harmonic. Taking $\frac{z}{z_0} \ll 1$ and $\frac{r}{w} \ll 1$, the trapping potential becomes

$$U(r,z) \approx U_0 \left[1 - 2\frac{2r}{w_0} - \frac{z}{z_0} \right] = -U_0 + \frac{1}{2}m\omega_r^2 r^2 + \frac{1}{2}mz^2\omega_z^2, \qquad (3.21)$$

where the right hand side is in the form of a standard harmonic potential. Comparing the left hand and right hand side of Eq. 3.21 gives the trapping frequencies for the radial and axial directions to be

$$\omega_r = \sqrt{\frac{4U_0}{mw_0^2}} \quad \text{and} \quad \omega_a = \sqrt{\frac{2U_0}{mz_0^2}}.$$
(3.22)

One downside to a standard optical dipole trap produced from a single focused Gaussian beam is that the trapping potential is much weaker along the longitudinal axis compared to the radial axis. A small beam waist (on the order of tens of μ m) is required to produce sufficiently deep traps to capture atoms from a MOT. However, despite the tight focusing, the Rayleigh length is still long, and results in a much lower axial trapping frequency relative to the radial trapping frequency. Given that the collision rate scales with the trapping frequency⁵⁸, weak confinement along the axial direction can negatively impact thermalization times and evaporation efficiency in addition to decreasing the critical temperature required

⁵⁸This can be seen by noting that the collision rate is given by $\gamma = n\sigma\bar{v}$, where *n* is the density, σ is the collisional cross section and \bar{v} is the average thermal velocity. For a Gaussian density distribution, the peak density (and therefore the peak collision rate) $n_0 \propto N/(\sigma_x \sigma_y \sigma_z)$ where $\sigma_i = \sqrt{\frac{k_{\rm B}T}{m\omega_i^2}}$ and ω_i is the trapping frequency along the i = x, y, z axis. Therefore, $\gamma \propto \omega_x \omega_y \omega_z$, given the collisional cross section and average thermal velocity are constant.

for BEC formation (see Section 5.1.3 for more detail).

To increase the axial confinement, one can employ a crossed optical dipole trap (CDT) where two focused beams cross at some small angle α (see inset to Fig. 3.8). The second focused beam is often the first beam recycled after its first pass through the trapping region, which has the advantage that it increases the total available power and creates a trap that is tightly confining in all three dimensions. Given that the radial symmetry of the trap is broken, one must now define trapping frequencies ω_x , ω_y , and ω_z along three orthogonal trap axes. These trap frequencies, normalized to the frequency when the crossing angle is zero, are shown in Fig. 3.8. From this, it is clear that even a small crossing angle provides a large increase in confinement. Note that the trapping frequency ω_z does not change as a function of angle, as this axis is perpendicular to the propagation direction of the beam. At a crossing angle of approximately 20°, we expect a factor of 30 improvement of confinement (see Fig. 3.8).



Figure 3.8: CDT trap frequencies as a function of the crossing angle. If the crossing angle is zero, ω_y corresponds to the axial trap frequency and $\omega_{x,z}$ corresponds to the radial trap frequency (see Eq. 3.22), as shown in the inset. As the crossing angle is increased, ω_x and ω_y are modified as these axes lie in the same plane as the two crossing beams, while ω_z remains at the same value. When the beams are collinear, the normalized $\omega_y = 0.006$. In our setup, we use a crossing angle of roughly 20° which corresponds to a normalized $\omega_y = 0.177$ and an increase in confinement of a factor of 30.

The trapping frequencies can be measured through parametric excitation [132], in which a modulating force (provided by varying the power of the trapping laser at a set frequency) acts on the potential. When the modulation frequency is equal to twice the trapping frequency (or any sub harmonic), the trapped atoms are efficiently heated. This manifests itself as an observable decrease in the atom number as atoms are heated enough to escape the trap. Therefore, by varying the modulation frequency one can map out the trapping frequencies of the trap. This type of measurement also allows for an experimental determination of the beam waist using Eq. 3.13 and 3.22, given the power in the dipole trap beam is well known. Knowledge of the trap frequencies is also crucial to determine the critical temperature for BEC formation or the creation of BCS pairs.

An added level of complexity when working with two (or more) species in the same ODT results from the scaling of trap parameters with the frequency of the atomic transition and the detuning of the dipole trap beam from the atomic transition. In the case of ⁶Li and Rb with a dipole trap wavelength of 1090 nm, the ratio of trap depths between the two species is $U_{\rm Rb}/U_{\rm Rb} \approx 2.5$, due to the fact that the trapping laser is further detuned from the atomic resonance for ⁶Li (671 nm) than Rb (780 nm). Moreover, because the photon scattering rate scales like the detuning squared, $\Gamma_{\rm Rb}/\Gamma_{\rm Li} \approx 5.8^{59}$. However, because Rb is much more massive than Li, the ratio of the heating rates (see Eq. 3.12) is only $\dot{E}_{\rm Rb}/\dot{E}_{\rm Li} \approx 0.4$.

Experimental Trap Setup

In our experiment, we employ two CDTs that lie in a plane horizontal to the optical table. The beam paths of both lasers are shown in Fig. 3.9. The arms cross at an angle of approximately 20°, and each laser propagates collinear with the other (i.e., they are spatially overlapped). The first (high power) trap is formed from a 100 W multi-longitudinal mode laser (SPI Lasers, SP-100C-0013) with a center wavelength of 1090 nm and a linewidth exceeding 1 nm. Each arm is focused to a waist of approximately 45 μ m. The second (low power) trap is formed from a 20 W single longitudinal mode laser (IPG Photonics, YLR-20-1064-LP-SF) with a center wavelength of 1064 nm and a linewidth of less than 10 kHz. Each arm of this laser is focused to a waist of approximately 35 μ m. In the following discussion, the high power laser will be referred to as the "SPI" laser, and the low power laser will be

 $^{^{59}{\}rm The}$ actual ratio depends on the wavelength of the laser, and if one is using the rotating wave approximation.

referred to as the "IPG" laser. Table 3.3 gives the calculated trap depth, scattering rate, heating rate, and estimated trapping frequencies for ⁶Li and Rb in the high power SPI and low power IPG trap.

While Rb atoms in the MOT are easily capture is easily trapped in a low power trap, the higher temperature of the ⁶Li MOT, combined with a lower ODT depth at a fixed laser power (compared to Rb), means that efficient transfer of ⁶Li from the MOT to the ODT requires a deep trap, which we generate using high power. Therefore, we initially transfer ⁶Li from the MOT to the high power SPI trap, and later transfer into the low power IPG trap after an evaporative cooling stage. We choose to work in the low power trap because it is well polarized, has a narrow linewidth, and the trap depth can be precisely tuned even at very low powers via an AOM.

	SPI: 1090 nm (45 μ m)		IPG: 1064 nm (35 μ m)	
	$^{6}\mathrm{Li}$	Rb	⁶ Li	Rb
$U \ (\mu K/W)$	18.5	44.4	31.5	77.4
$\Gamma (s^{-1}/W)$	0.0038	0.0220	0.0072	0.0434
$\dot{E} \ (\mu {\rm K} {\rm ~s}^{-1} / {\rm W})$	0.4016	0.164	0.7964	0.3417
$\omega_{x,y,z} \; (\mathrm{Hz}/\sqrt{W})$	(1110, 200, 1120)	(450, 80, 460)	(1860, 330, 1890)	(770, 135, 780)

Table 3.3: Properties of the high power (SPI) and low power (IPG) dipole traps. The trap depth (U), scattering rate (Γ) and heating rate (\dot{E}) are calculated using Eqs. 3.13, 3.14 and 3.12 respectively. The trap frequencies ($\omega_{x,y,z}$) are calculated using the curvature of the potential at the trap center. These values assume a crossing of 20° and a waist of 45 μ m for the SPI and 35 μ m for the IPG. The power is the total power used in the trap. That is, the sum of the power in both arms, or equivalently, twice the power delivered by the laser to the optics.

The SPI has a built-in power and modulation control, where the output of the laser can be enabled with a digital TTL signal and the output power of the laser can be set via a scaled input analog voltage. When the SPI laser is initially turned on, the output power can experience relaxation oscillations of up to 20 times the set point power. In order to suppress these oscillations, the turning on the laser to some set power is accomplished by first turning on the laser to 2 W (regardless of the final power), waiting approximately $300 \ \mu$ s, and then increasing the analog input voltage to the final value corresponding to the set power [133]. In all, the laser reaches the set point power in approximately $400 \ \mu$ s after the turn-on command is issued. To turn off the laser the TTL input is set to low and the



Figure 3.9: Schematic of the beam paths for the high power (SPI) and low power (IPG) dipole traps and photoassociation (PA) laser. Also shown is the axis used for absorption imaging (IMG, shown with a dotted line). The optics on the top level are built on a raised breadboard (large solid rectangles) for increased stability. On the bottom level, the SPI optics are mounted on the optical table. The IPG optics are mounted upside down to the bottom of breadboard (large dashed rectangle) with the exception of the two lenses and the shutter, which are mounted on the optical table, but at the same beam height as the other IPG optics. The focal length of each lens (in mm) is indicated by the number near each lens. The three periscope pairs are labeled by a,b, and c. The dashed beam path between periscope (c) is raised above the height of the experiment.

laser power is extinguished after a short delay of 15 μ s.

The IPG laser power is controlled with a high efficiency AOM from Gooch and Housego (part number: 97-01672-11) operated in a single pass configuration. With this AOM, we achieve a maximum efficiency of about 90%. We drive the AOM with an RF frequency of 110 MHz and a maximum RF power of 2.5 W. As the output of the IPG has a well defined linear polarization, we orient the output fiber of the IPG such that the field is linearly polarized in the vertical direction at the AOM, which is important to achieve the highest diffraction efficiency. Although the zero order from the AOM is sent into a beam dump, we also have a water cooled mechanical shutter (based off of a solenoid) which we use to shutter

the IPG beam when the trap is not in use. We use a right angle $periscope^{60}$ to match the beam height to that of the SPI trap. This periscope rotates the polarization of the IPG to lie in the horizontal plane⁶¹. The IPG trap is then overlapped with the SPI beam on a dichroic beam splitter (Semrock LPD01-1064RS-25) designed to transmit 1090 nm and reflect 1064 nm, and afterwards follows the same beam path as the SPI laser. This ensures a good spatial overlap between the two dipole traps and improves the transfer efficiency of ⁶Li from the SPI to the IPG. The details of the transfer from the MOT to the ODT and between the two dipole traps are discussed below.

Mitigating Thermal Lensing

In a previous iteration of this apparatus, in which we used a Pyrex cell, we noticed significant thermal lensing and beam distortion. and permanent damage spots on the cell when the SPI laser was operated at powers greater than 20 W. Initial testing on a quartz slab showed no lensing effect, which motivated switching to a quartz cell in the current iteration of the setup. In order quantify the lensing effect between the two cells, we measured the beam radius after a single pass through each cell. The horizontal and vertical radii as a function of the laser power are shown in Fig. 3.10, which indicates that the lensing effects are significantly reduced with the quartz cell. However, a more precise measurement can be made by tracking the location of atoms as a function of time while held in the trap. Even with the quartz cell, we found that the focus of the beams still move by approximately 1.3 mm with a time constant of 1.4 s when the laser power is set to 100 W. Therefore, we make an effort to operate the SPI laser at high powers for only short times in order to minimize this effect.

Transfer of ⁶Li to the ODT

To transfer ⁶Li from the MOT to the ODT, we use a two stage process where we compress and cool the MOT. We start this process by turning off the Zeeman slower light and increasing the coil gradient from 67 to 92 G/cm (11 A to 15 A), while at the same time shifting the frequency of the pump and repump to 11 MHz below resonance and decreasing

 $^{^{60}}$ That is, a periscope in which the direction of the output beam differs by only 90° to the output.

⁶¹Historically, the IPG laser was sent to the cell at Brewster's angle in order to minimize the reflections from the cell. This required that the polarization of the beam lie in the horizontal plane. At the small angle of incidence that we use currently, the difference in the reflection coefficient between vertically and horizontally polarized light is minimal.



Figure 3.10: Effect of thermal lensing on the ODT beam shape. Shown is the SPI beam radius through a Pyrex cell (red squares) and Quartz cell (blue diamonds) as a function of power along the horizontal (top) and vertical (bottom) axes. Also shown is the beam radius with no cell (black circles). This indicates a strong lensing effect with the Pyrex cell which modifies the beam radius. This effect does not exist with the Quartz cell.

the power in each beam to approximately 20 mW. During this initial stage, the SPI laser is turned on and we apply a small compensation field to adjust the position of the MOT to overlap with the crossing of the dipole trap beams. These parameters are held for 10 ms. In the second stage, we decrease the detuning of the pump and repump to 3 MHz below resonance and further reduce the power in each beam to approximately 5 mW. We also make another slight adjustment to the compensation field to ensure the MOT center remains overlapped with the crossing of the dipole trap beams. After another 2.5 ms, we turn off the magnetic field (both the quadrupole and compensation field) and we optically pump to the lower hyperfine state (f = 1/2) by turning off the repump light 400 μ s before the pump light. The produces an incoherent mixture of roughly equal populations of atom in the $m_f = 1/2$ ($|1\rangle$) and $m_f = -1/2$ ($|2\rangle$) states. Without this optical pumping stage, we observe extremely rapid trap losses (on the order of a few ms) due to hyperfine relaxation. We find the optimal compensation field empirically, by varying the size and direction of the field along three axes (which moves the MOT position along the three axes) and optimizing the number of atoms transferred into the trap.

The number of atoms that we transfer to the SPI at 100 W trap saturates at about 1.5×10^6 atoms, and becomes independent of the size of the MOT when the MOT number exceeds 30×10^6 atoms. We believe this saturation is due to density dependent losses⁶² that occur during the transfer of atoms from the MOT to ODT, which are more severe in the ODT because the largest achievable ODT depth is orders of magnitude (typically in the mK range) lower than the MOT (typically in the K range). For this reason, we typically load a small MOT in a short time in order to reduce the cycle time of the experiment, and transfer about 1.3×10^6 atoms to the cross SPI trap at 100 W.

Although we have made an effort to optimize the transfer parameters to produce the most efficient transfer, many of the parameters are coupled (for example, the power and detuning of the pump and repump beams) and the number of free parameters is large enough that doing a full N dimension search is not possible. However, in general, we found that the transfer efficiency is much more sensitive to the settings during the short second stage of the transfer. In particular, the transfer was found to be most sensitive to the detunings of the pump and repump and the compensation coil settings.

A final consideration during the transfer from the MOT to the ODT arises due to the nature of the Zeeman slower beam, which is only a few tens of MHz further detuned from the atomic transition than the MOT beams. Since the Zeeman slower beam imparts a large radiation pressure force on the MOT, it is possible that when the slowing beam is shuttered the MOT moves to an unstable position. Therefore, it is important to visually ensure that the MOT is stable in both the standard loading location, and the location where the transfer occurs.

Evaporation of ⁶Li in the ODT

Directly after the transfer of atoms to the SPI trap, the trap depth is approximately 3.7 mK and the ensemble temperature is on the order of 500 μ K. In order to produce an ultra-cold ensemble, we perform free and forced evaporative cooling in order to decrease the temper-

⁶²These losses include spin exchange collisions, hyperfine changing collisions, and light-assisted losses that include photoassociation and fine-structure changing collisions. A discussion of cold collision processes can be found in a review by Julienne et. al. [134].

ature by about three orders of magnitude. An excellent description of forced evaporative cooling can be found in the thesis of K. O'Hara [135], in which it is shown that forced evaporative cooling in an ODT follows a general scaling law

$$\frac{N_f}{N_i} = \left(\frac{U_f}{U_i}\right)^{\frac{1}{2}\left(\frac{3}{\eta-3}\right)},\tag{3.23}$$

where N is the atom number in the dipole trap and $\eta = U/k_B T$ is the ratio of the ODT depth to the ensemble temperature. For ⁶Li, efficient cooling occurs when $\eta \approx 10$. This scaling law can be used as a benchmark for the efficiency of our forced evaporative cooling ramps.

As efficient evaporation requires fast thermalization, we therefore perform our forced evaporation ramps in the presence of a homogenous magnetic field in order to increase the collisional cross section between the atoms⁶³. Although it is possible to achieve very large scattering lengths near the broad *s*-wave Feshbach resonance at 832 G (see Section 5.1.2), we perform our evaporation at 300 G, and see no change in the evaporation efficiency at higher fields. We believe this may be the case because, in the unitary limit where $k^2a^2 \gg 1$, the scattering cross section is independent of the magnetic field (on which the scattering length depends), but is limited by the de Broglie wavelength. That is,

$$\lim_{k^2 a^2 \gg 1} \frac{4\pi a^2}{1 + k^2 a^2} = \frac{4\pi}{k^2} = \frac{\lambda_{\rm dB}^2}{\pi} = \frac{2\hbar^2}{mk_B T} \,. \tag{3.24}$$

For high temperatures, the unitary limit clamps the collisional cross section to that which is achievable near 300 G. At lower temperatures, the gain in cross section by evaporating at fields close to the Feshbach resonance only impacts the evaporation efficiency if the ramp rate is too fast compared to the thermalization rate. It is also possible that in our setup there are additional losses that turn on at high fields due to, for example, three-body losses or losses induced by magnetic field noise. We do, however, see a minimum in the evaporation efficiency near the zero crossing of the scattering length near 530 G and when the magnetic field is less than 150 G.

In spite of our optimization attempts, we found that the evaporation in the SPI laser at

⁶³It is possible to compensate for low thermalization times by performing a slower evaporation ramp. However, the timescale of the evaporation is limited by the finite lifetime of the trap. This finite lifetime is imposed by the photon scattering rate and the background collisional losses.

high power was always less efficient than evaporation in the IPG⁶⁴. Due to the inefficient evaporation and to minimize the time that the laser was on at high power, we perform a fast evaporation from 100 W to 50 W of power in 100 ms. This typically results in a loss of about 25% of the trapped atoms (from 1.3×10^6 atoms to approximately 1×10^6 atoms), corresponding to $\eta = 7$. At this point, we begin the transfer of atoms to the IPG trap by turning on the IPG trap to its set power (typically 15 W) in 10 ms, and then turning off the SPI in 500 ms in a linear fashion. We found that the transferred number was very insensitive to the parameters of the transfer, including the IPG turn on time, the power of the SPI when the transfer begins, and the time over which the SPI turns off. Our transfer process typically results in about 250×10^3 atoms in the IPG trap at a temperature of approximately 55 μ K. A timing diagram of this evaporation can be seen in Fig. 3.11.

After the transfer to the IPG trap, we perform a series of linear ramps of different durations to reach the desired final temperature (see Fig. 3.11). Each linear ramp was optimized by choosing a final power and modifying the duration of the ramp in order to maximize the remaining number. At low trap depths, we find that a large loss of atoms occurs due to a "tipping" of the potential due to the residual magnetic field gradient and the force of gravity. To compensate for this, we turn on an additional "gradient" coil. For this, we use the compensation coils which is concentric with the upper Feshbach coil.

If the goal of the experiment is to produce ultra cold Feshbach molecules, we switch the magnetic field to a set value near the Feshbach resonance at a trap depth which corresponds to a temperature greater than the binding energy of the Feshbach molecules. In this way, when the final evaporation is performed, the atoms will form Feshbach molecules via three body recombination as the ensemble energy becomes lower than the molecular binding energy (see Section 5.1.3. With this method, we are able to achieve efficient evaporation ramps where $\eta \approx 10$. For example, evaporation to degeneracy is shown in Fig. 5.6 and discussed in detail in Section 5.1.3. Figure 3.11 also shows typical atom number and temperatures (measured via a time of flight measurement) at different points on the evaporation ramp. Note that the atom number listed in Fig. 3.11 is the number measured using our high field imaging setup. This technique only measures the population of one of the two spin states, and undercounts this state by approximately a factor of two due to polarization considerations (see Sec 3.4 for a detailed discussion). Therefore, the total atom number in the trap

 $^{^{64}}$ One possible reason for this may be intensity noise the laser, as we do not perform any intensity stabilization at this time.



Figure 3.11: Timing diagram of the transfer from the SPI trap (dashed line) to the IPG trap (solid line), and the following evaporation to degeneracy in the IPG. The vertical dashed dot line represents the point in the evaporation when we switch the magnetic field from 300 G to 754 G such that the following evaporation cools the atoms in the Feshbach molecule state. At the end of the evaporation ramp, the magnetic field can be changed to the value at which we want to perform our experiment. The typical temperature and atom number at a few characteristic locations along the evaporation are given. Note that the atom number listed is the number measured using our high field imaging setup. This technique only measures the population of one of the two spin states, and undercounts this state by approximately a factor of two due to polarization considerations (see Sec 3.4 for a detailed discussion). The atom number listed in the figure is the inferred total atom number, based off of the high field imaging measurements.

is approximately four times larger than the number calculated from the high field imaging measurement. The atom number given in Fig. 3.11 is the inferred atom number based off of these measurements.

For our spectroscopy work at 0 G, we turn off the homogenous field at the end of the evaporation ramp. To compensate for the residual magnetic field that persists due to the earth's magnetic field and any other magnetic sources near the cell we apply a compensation field using the compensation coils. It is not possible to use the gradient coil to help oppose the tipping of the trapping potential and, at the same time, minimize the residual field. This leads to a large loss of atoms at very low trap depths where the "tipping" is significant.

However, we were still able to achieve an atom number of a few 10^4 at a temperature of 800 nK, while ensuring that the residual magnetic field was less than 20 mG⁶⁵. In many cases, we stop the evaporation ramp at higher trap depths in order to increase the atom number. This has little effect on the spectroscopy results as the Doppler broadening is only approximately 200 kHz at temperatures as high as 10 μK . This broadening is still much smaller than the natural linewidth of the transitions, and is a few times smaller than the typical width of our observed dark state features.

Transfer of Rb to the ODT

The transfer of Rb to the ODT proceeds in a much simpler (although similar) way than the ⁶Li transfer. The transfer takes place in one stage, where we slightly increase the magnetic field gradient from 15 to 25 G/cm (2.5 to 4 A) while simultaneously applying small homogenous compensation field to move the center to the MOT to the location of the dipole trap. We typically leave the detuning of the pump ($\approx 3\Gamma$) and repump (on resonance) beams at the values used for the MOT loading, but we decrease the power in an attempt to reduce light assisted losses during the transfer. We hold these parameters for 50 ms, and then turn off the magnetic field. In order to optically pump the Rb atoms into the lower hyperfine state, we turn off the repump light 400 μ s before the pump light. Because we can achieve a colder final temperature of the Rb MOT than the ⁶Li MOT and the ODT depth for Rb is more than twice as deep as for 6 Li, we can typically transfer a large number of atoms without much optimization. For example, when we work with small MOTs, where density dependent losses in the transfer process are small, we transfer approximately 350×10^3 atoms into a 15 W ODT from a MOT of 720×10^3 atoms, which gives a transfer efficiency of nearly 50%. Much of our work with ⁸⁵Rb was in the context of mixtures with ⁶Li, and a more detailed discussion on loading both ⁸⁵Rb and ⁶Li into the ODT can be found in Chapter 7.

We typically transfer the Rb MOT directly into the low power IPG trap (rather than into the high power SPI trap) for three reasons. First, we can easily achieve the required trap depths (and atom number) in the IPG trap without the complications of having to transfer the atoms from the SPI to the IPG for further evaporation. Second, we found

⁶⁵More details on this measurement, and the procedure to minimize the residual field can be found in the PhD thesis of Mariusz Semczuk [98].

that loading Rb into a deep trap resulted in a higher starting temperature relative to the trap depth, which resulted in a lower evaporation efficiency. In fact, we found that we could achieve larger atom numbers at the same final temperature by loading directly into a weaker trap than through evaporation from a deeper trap. Finally (and perhaps most importantly) we found that the SPI laser drove hyperfine changing transitions between the two ground hyperfine states.

To investigate these transitions, we measured the number of the atoms in the f = 3state of ⁸⁵Rb using absorption imaging without the standard step of optically pumping the trapped atoms into this state (see Section 3.4 for a discussion of the imaging procedure). This way, any atoms that populate the f = 3 state when the image is taken are driven to this state by the SPI⁶⁶. The population in this state as a function of the hold time in the SPI is shown in Fig. 3.12. The transition follows an exponential curve, with a time constant of 120 ms when the power of the SPI is set to 20 W. After long times in the SPI, the population of atoms in the f = 3 state tends to approximately 35% of the total atom number. We found that we could effectively stop this population transfer by continuously "depumping" the ensemble, using light tuned near the $f = 3 \rightarrow f' = 3$ resonance (see Fig. 3.12). With this depumping light, we also see an increase in the overall lifetime in the SPI (from 1.3 s to 2.9 s), and no observable change in the overall atom number. We believe that the SPI laser has longitudinal modes which have a frequency separation close to the energy difference between the ground hyperfine levels in 85 Rb (≈ 3 GHz), which drives two-photon Raman transitions between the levels. Note that we do not see a similar effect in 6 Li, where the separation of the ground hyperfine levels is only ≈ 228 MHz.

3.3 Optical Pumping and State Selection

After the transfer of atoms from the MOT to the ODT, we perform a short hyperfine pumping procedure (discussed in Section 3.2) to ensure that the atoms are in their ground hyperfine state (f = 1/2 in the case of ⁶Li and f = 2 in the case of ⁸⁵Rb). After this pumping stage, the atoms typically populate all possible Zeeman states with roughly equal population. However, one of the major advantages of trapping in an ODT is that the lack of near-resonant light and external dc fields allows for the ability to prepare an atomic ensemble

 $^{^{66}\}mathrm{We}$ have confirmed that in the IPG trap we see no atoms in an absorption image without the optically pumping step.



Figure 3.12: Evidence of two-photon (stimulated) hyperfine changing transitions for ⁸⁵Rb driven by the SPI ODT. The atom number in the f = 3 ground state is shown as a function of the hold time in the SPI trap with (red squares) and without (black circles) a "depump" beam tuned near the $f = 3 \rightarrow f' = 3$ atomic resonance. As atoms are initially pumped into the f = 2 ground state during the loading of the ODT, we believe that the appearance of atoms in the f = 3 state is due to two-photon Raman transitions between the f = 2 and f = 3 hyperfine levels, which are driven by the SPI laser. The time constant of the fit to the f = 3 population as a function of time (black line) is 120 ms. We can suppress these transitions using a "depump" beam. Note that this beam does not cause any change in the overall atom number (i.e., it does not cause any additional light assisted loss in the ODT).

in a particular Zeeman state. This is advantageous because it allows experimental control over the atomic scattering states. For example, this is useful in our Feshbach resonance experiments because the resonances occur for particular pairings of the ⁶Li and Rb Zeeman states (see Chapter 7 and in particular Table 7.1). The ability to prepare an atomic ensemble in just one particular state (or explicitly not in a particular state) gives control over which Feshbach resonances are possible. Additionally, preparing a system in the stretched states Zeeman states, where $|m_f| = f$, ensures that the ensemble will be stable with respect to two-body spin relaxation due to conservation of the total angular momentum projection during such a collision.

This section describes our optical pumping scheme for ⁶Li and ⁸⁵Rb. While the data

presented is for ⁸⁵Rb, the method discussed is easily applied to ⁸⁷Rb, accounting for the different atomic transition frequencies. It should be noted that for ⁶Li, because the ground hyperfine state has only two levels, we typically do not optically pump as much as "optically reduce", where we selectively remove the population of one of the two projection states.

Optical Pumping of ⁸⁵Rb

In the presence of a small external magnetic field⁶⁷, each of the hyperfine levels is split into 2f + 1 degenerate levels, where the energy of each m_f projection state relative to the energy of the state in the absence of the magnetic field is

$$E_{\rm Z} = g_f \mu_B B m_f \tag{3.25}$$

where

$$g_f = g_j \frac{f(f+1) + j(j+1) - i(i+1)}{2f(f+1)}, \qquad (3.26)$$

and

$$g_j = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}.$$
(3.27)

In Eq. 3.25, μ_B is the Bohr magneton, which is approximately equal to the electron's intrinsic spin magnetic moment. It's useful to note that a magnetic moment of μ_B corresponds to an frequency shift of approximately 1.4 MHz/G. For Rb, the g-factor for the f = 2 (f = 3) manifold is $g_f = -1/3$ ($g_f = 1/3$), which corresponds to an energy shift of $-0.47 \cdot m_f$ MHz/G ($0.47 \cdot m_f$ MHz/G) [90]. When we optically pump ⁸⁵Rb, we apply a small dc magnetic field in order to set the quantization axis, and to break the degeneracy in the hyperfine manifolds. Typically this field is on the order of 1 G, such that the maximum energy shift of any of the stretched states is only a few MHz, and is less than the natural linewidth of the atomic transition.

For ⁸⁵Rb, we optically pump using light driving the D₂ transition between the f = 2hyperfine level in the ${}^{2}S_{1/2}$ manifold and one of the hyperfine levels in the ${}^{2}P_{3/2}$ manifold. The possible hyperfine levels in the ${}^{2}P_{3/2}$ to which the light can couple is limited to f' =1,2,3 by electric dipole selection rules. If the pumping light is polarized such that it drives σ^{+} (σ^{-}) transitions, each photon absorption will increase (decrease) m_{f} by one unit. On

⁶⁷For Rb, the magnetic field can be considered small when it is less than a few hundred Gauss. When we optically pump Rb, we typically use fields on the order of 1 G, which is safely within the low field regime.

the other hand, each photon emission will, on average, not change m_f . The net result of multiple scattering events is that the atomic population will tend to populate one of the stretched states, either $m_f = 2$ or $m_f = -2$. For the following discussion, we will assume that we are optically pumping to the $m_f = 2$ state using σ^+ polarized light.

Ideally, the final stretched state to which we optically pump into would be a dark state (i.e., a state for which photon scattering is disallowed due to electric dipole selection rules). This can be achieved through the correct choice of the excited hyperfine state to which the optical pumping light couples. For σ^+ polarized light, the f' = 2 manifold is sufficient, because some π polarized light would be required to drive a transition out of the $|f = 2, m_f = 2\rangle$ state. The ideal case, however, is to use the f' = 1 manifold, where the stretched state is also dark with respect to π transitions. However, note that if the f' = 1 hyperfine manifold is used, the optical pumping light must include some π light such that the $|f = 2, m_f = 1\rangle$ state is not also dark. Another significant advantage of using the f' = 1 manifold is that decay to the f = 3 ground hyperfine level is disallowed and this, aside from off-resonant transitions to the f' = 2 hyperfine manifold, ensures the optical pumping transition is closed.

In our experiment, we use the $f = 2 \rightarrow f' = 2$ transition, in part because the light that we use for optical pumping is picked off from the same light that we use for the MOT repump beam. This light is set up to have a frequency that is resonant on the $f = 2 \rightarrow f' = 3$ transition after up shifting by 180 MHz in a double pass AOM, but the bandwidth of the AOM is not large enough to allow us to bridge the 93 MHz gap required to reach the f' = 1state. As a consequence of using the $f = 2 \rightarrow f' = 2$ transition, decay to the f = 3state is possible which causes the atoms to eventually populate the upper (f = 3) ground hyperfine state. This requires the use of a "depump" beam⁶⁸, for which we use light picked off from the MOT pump beam, resonant on the $f = 3 \rightarrow f' = 4$ transition in the absence of any ac Stark shifts. We are unable to tune the depump beam to the $f = 3 \rightarrow f' = 3$ transition for similar reasons as the optical pump beam: the "depump" is set to be near the MOT pump transition ($f = 3 \rightarrow f' = 4$) using a double pass AOM, which does not have the bandwidth to bridge the 120 MHz gap to the f' = 3 state. Therefore, we rely on off-resonance transitions to the f' = 3 state for depumping, from which decay to the f = 2state is permissible. We couple both the optical pumping light and the "depump" light into

⁶⁸Named as such because this beam does the opposite of the repump beam in the MOT. That is, the "depump" light depumps atoms from the f = 3 to the f = 2 ground hyperfine level.

the same optical fiber. Out of the fiber, the light propagates along the same path as the photoassociation light (see Section 2.3), and is focused to a waist of approximately 50 μ m. We use a half-wave plate and a quarter-wave plate at the output of the fiber to ensure the light is circularly polarized.

When we perform optical pumping in the ODT, we have to compensate for the ac Stark shift of the trap unless we momentarily turn off the ODT. With Rb, it is possible to turn the trapping light off and on fast enough such that the majority of the atoms are recaptured and therefore there is minimal loss of atoms. For Rb, we find that an off period of up to 20 μ s results in no loss of the Rb atoms from the ODT. Due to timing limitations, the shortest modulation period we could achieve was about 3 μ s. However, even for this shortest modulation time we experience a large loss of ⁶Li atoms from the trap. This is likely because ⁶Li is much lighter than Rb, and therefore the atomic cloud expands much faster during the time in which the ODT is off⁶⁹. For our experiments with ⁶Li and Rb mixtures, the loss of ⁶Li is an issue because we load Rb into an ODT that already contains ⁶Li (see Chapter 7). Therefore, we perform all of our optical pumping in the presence of the ODT and compensate for the associated ac Stark shift by frequency shifting our light.

In order to determine the correct frequency for the light, we used the optical pumping light to pump atoms from the f = 2 to the f = 3 ground hyperfine state via the accessible hyperfine states in the ${}^{2}P_{3/2}$ manifold. We then took an absorption image of the atoms that populated the f = 3 state, and measured this population as a function of the optical pumping beam detuning. The result of this measurement for two trap powers, and the case where the laser was modulated off and on (such that there should be no ac Stark shift) is shown Fig. 3.13. Here, we can see the $f = 2 \rightarrow f' = 3$ and the $f = 2 \rightarrow f' = 2$ transitions, split by approximately 61 MHz, roughly consistent with the expected splitting of 63.4 MHz [90]. The effect of the ac Stark shift due to the ODT is to blueshift the transition, requiring a correspondingly larger frequency of the optical pumping beam. In the case where the laser is modulated off and on, it appears that there is still some shift of the transition. This may be a result of an offset in the locking frequency of our master lasers, or an indication that the ODT light is not completely extinguished during the entire

⁶⁹Of course, the rate at which the atomic ensemble expands is dependent on the temperature of the ensemble. For Rb, these test were done at a temperature of approximately 50 μ K. For Li, these tests were run at a temperature of 10 μ K. It is possible that this modulation technique would be more effective after a further forced evaporation. However, overcoming the ac Stark shift of the ODT was not a problem, so we did not investigate this issue further.

time the optical pumping light is on.

Critical to the efficiency of the optical pumping scheme is that the magnetic field is aligned along the propagation axis of the optical pumping beam. This ensures that the circularly polarized light drives σ transitions. Figure 3.14 shows the population in the stretched states as a function of the magnetic field angle, where the field is defined to lie in the horizontal plane. We also optimize the pumping efficiency by empirically tuning the power in the optical pumping and depumping beam. Although these powers are strongly coupled to the time in which the optical pumping light is on, we found that a time of 10 ms and powers on the order of 50-100 μ W gives us the highest efficiency. More power or longer times resulted in a loss of atoms from the trap, presumably due to heating.

To measure the efficiency of our optical pumping scheme, we used the state selective imaging technique described in Section 3.4. This technique relies on RF transitions to selectively transfer atoms from the f = 2 to f = 3 hyperfine level before an absorption image is taken. From the 11 possible RF transitions, we can determine the population in the each of the five m_f projection states in the f = 2 manifold (see Fig. 3.20 and the accompanying discussion in Section 3.4). Without optical pumping, we find that ⁸⁵Rb atoms are roughly equally distributed between the five f = 2 projection states, as expected. After optical pumping, we find that approximately 60% of the population is in the target stretched state, while almost no population remains in the opposite stretched state. The total atom number in both cases (with and without optical pumping) is the same. Figure 3.15 shows the raw population measurement using the state selective imaging technique, as well as the calculated population in each of the projection states. We believe one reason that we are not able to achieve higher efficiencies is the fact that the stretched state is not a dark state, and we are unable to fully eliminate the polarization components that can drive π transitions from the pumping light. Nevertheless, if a pure state population is required, it is possible to selectively clean out the remaining population in the unwanted states by applying an RF field to transfer atoms in a particular projection state in the f = 2 manifold to the f = 3manifold, while at the same time applying a strong depump beam. The strong depump beam acts to heat the atoms such that they leave the ODT.



Figure 3.13: ⁸⁵Rb atom number in the f = 3 ground hyperfine manifold, measured with an absorption image immediately after using the optical pumping beam to pump atoms from the f = 2 to the f = 3 manifold. The resonant frequencies shift as a function of the trap power due to the ac Stark shift in the ODT. The detuning is relative to the $f = 2 \rightarrow f' = 3$ atomic transition. Therefore, the single large peak in the top panel and the right peak in the bottom two panels represents the $f = 2 \rightarrow f' = 3$ transition. Likewise, the left peak in the bottom two panels represents the $f = 2 \rightarrow f' = 3$ transition. The measured splitting between these transitions is 61.6 MHz and 61.2 MHz when the trap power is 7 W and 15 W respectively, which is roughly consistent with the expected difference of 63.4 MHz [90]. In the case where the laser is modulated off and on, the peak atom number appears at a detuning of -6.7 MHz, which suggests that that there is still some shift of the transition. This may be the result of an offset in the locking frequency of our master lasers, or an indication that the ODT light is not completely extinguished during the entire time the optical pumping light is on.



Figure 3.14: Percentage of ⁸⁵Rb atom population in one of the $|f = 2, m_f = 2\rangle$ and $|f = 2, m_f = -2\rangle$ stretched states after optical pumping as a function of the magnetic field angle. Efficient optical pumping to the $|2, 2\rangle$ ($|2, -2\rangle$) state occurs when the optical pumping light drives σ^+ (σ^-) transitions. The polarization of the optical pumping beam is set to be circularly polarized using a half-wave plate and a quarter-wave plate. Therefore, this light will drive σ transitions when the magnetic field is directed along the propagation axis of the light (either co- and counter-propagating). This is consistent with the measured difference in magnetic field angle (183°) between the maximum populations in the two stretched states. The angle is measured in the horizontal plane relative to an axis that is collinear with the long axis of the vacuum cell.

State Selection of ⁶Li

As previously noted, we have not done any true optical pumping of ⁶Li, aside from hyperfine pumping to the f = 1/2 hyperfine level at the conclusion of the transfer from the MOT to the ODT. This results in an incoherent mixture of roughly equal population in the two projection states. At magnetic fields greater than approximately 100 G, the Zeeman energy dominates over the hyperfine energy and a three state manifold exists that consists of the $|1\rangle$, $|2\rangle$, and $|3\rangle$ states (see Fig. 5.1 and the more detailed discussion of the ⁶Li system in Section 5.1). The energy splitting between these three states is approximately 80 MHz. The $|1\rangle$ and $|2\rangle$ states asymptotically connects to the $|f = 1/2, m_f = \pm 1/2\rangle$ hyperfine states and are roughly equally populated after the ODT transfer is complete. The $|3\rangle$ state asymptot-



Figure 3.15: ⁸⁵Rb state population with (right side) and without (left side) optical pumping. Without optical pumping, we have a roughly equal population in each Zeeman state. With pumping, we find that approximately 60% of the population is in the target stretched state, while almost no population remains in the other stretched state. The total atom number in both cases is the same. The top two panels show the result of the state selective imaging technique discussed in Section 3.4. In this technique, an RF pulse is used to transfer atoms from a particular projection state in the f = 2 manifold to the f = 3 hyperfine level. Then, an absorption image is used to measure the population in the f = 2 manifold can be extracted (see Section 3.4). The result of this calculation is shown in the bottom panel. For this measurement, we used a magnetic field of approximately 1 G which corresponds to an energy difference of 470 kHz between adjacent projection states (see Eq. 3.25).
ically connects to the $|f = 3/2, m_f = -3/2\rangle$ hyperfine state, which is initially unpopulated after the transfer to the ODT.

State selection in ⁶Li is achieved using a "spin cleanup" technique, where we use light to blow out the atomic population from any of the $|1\rangle$, $|2\rangle$, and $|3\rangle$ states. For this, we use the same light that is used for high field imaging of ⁶Li (see Section 3.4 for details). This effectively removes all of the population from the target state, with no effect on the population in either of the other two states.

Using RF pulses, population can be transferred between the $|1\rangle$ and $|2\rangle$ states or the $|2\rangle$ and $|3\rangle$ states. Additionally, it is also possible to create a coherent ensemble between two of these spin states. The energy difference between the $|1\rangle$ and $|2\rangle$ states and the $|2\rangle$ and $|3\rangle$ states as a function of magnetic field is shown in Fig. 3.16. These RF transitions are quite narrow, on the order of a few kHz. However, it is relatively easy to find the correct transition frequency by sweeping the RF frequency (rather than irradiating the atoms with a single frequency pulse) and looking for atom loss out of the state which is initially populated⁷⁰. This allows one to quickly cover hundreds of kHz in only a few experimental cycles. Once loss has been observed from one sweep window, the precise transition frequency RF pulses. Details of the RF antenna can be found in [98].

3.4 Imaging Techniques

With as many moving parts as there often are in ultra cold experiments, extracting quantifiable information from such a system is surprisingly simple. There are only two standard observables in ultra cold atom experiments from which almost every other quantity of interest can be determined: atom number and temperature⁷¹. These quantities are typically determined by taking a picture of the atoms, where the two most common imaging techniques are fluorescence imaging and absorption imaging.

⁷⁰The maximum range of the sweep window that will result in observable loss is dependent on the total available RF power. Typically, we have found that a sweep range of ± 10 kHz strikes a good compromise between loss and the ability to cover a large range in a short time given our (not so great) antenna and 2 W RF amplifier.

⁷¹Most other quantities require knowledge of the atom number or temperature as a function of some other parameter. For example, the location of a photoassociation resonance or a Feshbach resonance can be determined by monitoring the atom number as a function of the frequency of the photoassociation light or magnetic field, respectively.



Figure 3.16: RF frequencies of the $|1\rangle \rightarrow |2\rangle$ (bottom panel) and the $|2\rangle \rightarrow |3\rangle$ (top panel) transition in ⁶Li as a function of magnetic field. The RF transition frequencies at select magnetic fields are given in MHz. More information on the $|1\rangle$, $|2\rangle$, and $|3\rangle$ states be found in Section 5.1 and specifically Fig. 5.1, which shows the magnetic field dependence of the six ⁶Li Zeeman levels.

Fluorescence imaging captures photons scattered by the atomic ensemble, and provides a highly sensitive measurement of the atom number. In our case, we perform fluorescence imaging by recapturing atoms in the MOT and therefore this technique is unable to provide information about the spatial distribution of the atoms, which is necessary for simple methods of temperature determination⁷². On the other hand, absorption imaging provides an *in situ* measurement of the optical density of the cloud, from which it is possible to extract both atom number and temperature. With absorption imaging, it is also possible to make state selective atom number measurements, or to image the atoms in the presence of an external magnetic or electric field. This section briefly discusses each imaging sys-

 $^{^{72}}$ That is not to say that fluorescence imaging in general cannot provide information about the spatial distribution. For example, in quantum gas microscope experiments use fluorescence imaging, but the atoms are held fixed in an optical lattice [136].

tem, and the implementation of each in our apparatus. For all of the imaging discussed in this section, we use a Pixelink camera (model number PL-B771G) that images along the horizontal plane (see Fig. 3.9).

3.4.1 Fluorescence Imaging

Fluorescence imaging allows a determination of the atom number by counting the number of photons scattered by the atoms on a camera or photodiode. Given known quantities of the system, a calibration factor can be used to convert the total pixel count (PC) in the image to a true atom number. This calibration factor, which has units of atoms/PC, is given by

$$C_{\rm atoms} = \frac{1}{L \cdot \eta \cdot K \cdot P_{\rm atom}}, \qquad (3.28)$$

where L is the loss of light due to transmission through the cell, K is the camera calibration which provides a conversion from power to pixel counts, P_{atom} is the total power scattered by a single atom, and

$$\eta = \frac{A_{\text{camera}}}{A_{\text{total}}} = \frac{\pi r_{\text{lens}}^2}{4\pi l^2} = 2.1 \times 10^{-3}$$
(3.29)

is the solid angle captured by the camera. In our case, $r_{\text{lens}} = 22/2$ mm is the effective radius of the imaging lens⁷³, which is placed l = 120 mm from the cell.

We determine the camera calibration constant K by shining a laser beam of a known power into the imaging system and measuring the total pixel count in the resulting image of the beam. We include the dependence on the image exposure time in the calculation through the camera calibration constant. That is, we use a different camera calibration constant for each exposure time. The camera calibration constant for both ⁶Li and Rb for representative exposure times is given in Table 3.4. We typically use exposure times on the order of a few to tens of ms. The fact that the exposure time appears to be non-linear in time may indicate that there is an offset between the set exposure time and the true exposure time. This is not an issue for our atom number calibration because we determine the calibration factor based off of the set exposure time.

The total power scattered by a single atom is given by the photon energy times the

 $^{^{73}}$ The lens is a standard one inch diameter lens, but the effective area is reduced due to a threaded ring used to mount the lens.

3.4. Imaging Techniques

Exposure Time (ms)	$K_{\rm Rb} \ ({\rm PC/nW})$	$K_{\rm Li} ({\rm PC/nW})$
1	7.4×10^3	8.3×10^3
2.5	$16.8 imes 10^3$	15.4×10^3
5	$26.8 imes 10^3$	$27.3 imes 10^3$
10	—	$51.2 imes 10^3$

Table 3.4: Pixelink camera calibration factors for ⁶Li and Rb. The calibration factors were determined by shining a laser beam of known power into the imaging system and measuring the total counts in the resulting image of the beam. The units of the calibration factor are pixel counts (PC) per nW. Although we did not measure a calibration constant for Rb with an exposure time of 10 ms, it (and any other time) can be extrapolated (or interpolated) from the measured values. The fact that the exposure time appears to be non-linear in time may indicate that there is an offset between the set exposure time and the true exposure time. This is not an issue for our atom number calibration because we determine the calibration factor based off of the set exposure time.

photon scattering rate

$$P_{\text{atoms}} = \frac{hc}{\lambda} \Gamma_{\text{sc}} = \frac{hc}{\lambda} \frac{\Gamma}{2} \cdot \frac{s}{1+s+(\frac{2\delta}{\Gamma})^2}, \qquad (3.30)$$

where Γ is the natural linewidth, $s = I/I_{sat}$ is the saturation parameter, and δ is the detuning of the light from the atomic resonance. The sensitivity (and thus the calibration) of the measurement at a fixed exposure time can be adjusted by changing the total power and detuning the light. For measurements with ⁶Li, we set the power and detunings of the MOT pump and repump beams to be equal. The power that is used in the calculation is the power of one of the pump or repump beams, as the atoms will only scatter photons from either the pump or repump beams at a single time. In the case of Rb, we consider only the power to the MOT pump beam.

To determine the intensity of the light illuminating the atoms in the MOT, we measure the power using a power meter that has an aperture diameter of .95 cm and assume that the intensity is constant over that area. Given that the MOT beams are approximately one inch in diameter, and the atoms are located near the center of each beam, we believe this approximation is reasonable. We account for the loss of light due to the quartz vacuum cell by measuring the power before and after the cell, and calculate the loss coefficient for each interface. We find that the transmission per interface is approximately 93% along the two horizontal axes, and approximately 95% along the vertical axis.

We primarily use MOT recapture fluorescence imaging as a means to measure the atom

number in the MOT, as it is technically challenging to take an absorption image of a MOT (see the next section on absorption imaging for details). To take an image of a ⁶Li MOT, we tend to decrease the detuning to a few natural linewidths and decrease the power in order to compress the size of the MOT, such that it fits on the camera chip. For Rb, we often keep the detunings similar to that of the MOT and simply adjust the power or the exposure time to ensure the image is not saturated. After this image, we turn the MOT light off and on to ensure that no atoms are held in the MOT and take a second background image. This background image is subtracted from the atom image, and we sum over the subtracted image to determine the total pixel count and, using the calibration constant in Eq. 3.28, the atom number. An example of these images for a ⁶Li MOT is shown in Fig. 3.17.



Figure 3.17: Example of a fluorescence image of a ⁶Li MOT. The background image (center) is subtracted from the atom image (left) to account for any scattered light that enters the imaging system during the exposure. The background image uses the same parameters as the atom image, except that we ensure there are no atoms by turning the MOT beams off and on before the image is taken. The atom number is found by summing the pixel count in subtracted image (right), and using the correct calibration factor from Eq. 3.28. Note that in this example, the gain of the atom and background image was increased after the image was taken in order to illustrate the background light that is common to both images. In the true image, the saturation of the atom cloud is not present.

To take a fluorescence image of the atoms trapped in the ODT, we recapture the trapped atoms in a MOT by turning off the ODT laser while simultaneously turning on the MOT beams and the quadrupole field. For this step, the MOT beams and quadrupole field are set to the settings that we use for the fluorescence image (discussed above) rather than the settings that we use in the standard operation of the MOT. Immediately after, we take an image of the recaptured atoms followed by a background image. In this case, it is possible that a small number of atoms may load into the MOT during the image exposure time. However, the same number of atoms will load into the MOT during the background image exposure time, such that the subtracted image will only show those atoms that were originally trapped in the ODT. We can also close the atom shutter such that there is no cold atom beam source, which can greatly minimize this issue.

3.4.2 Absorption Imaging

Absorption imaging detects the presence of atoms by measuring the decrease in light intensity in a near (or on) resonance beam that passes through the atomic cloud. The decrease in intensity is described by the Beer-Lambert law

$$\frac{dI}{dz} = -n(z)\sigma(z)I(z), \qquad (3.31)$$

where z is the propagation axis of the imaging beam. The decrease in intensity is related to the atomic density n, absorption cross section σ , and the intensity of the light I. In general, the density, cross section and intensity can vary as a function of z. The intensity of the imaging beam at a particular position z can be found by integrating Eq. 3.31, which gives

$$I(z) = I_0 \exp\left(-\int_{-\infty}^z n(z')\sigma(z')dz'\right).$$
(3.32)

By definition, the scattering rate is the absorption cross section times the incoming photon flux per unit time (i.e., $I/\hbar\omega$). Therefore, the absorption cross section can be written as

$$\sigma = \frac{\Gamma\hbar\omega}{2I} \cdot \frac{s}{1+s+(\frac{2\delta}{\Gamma})^2} = \frac{\sigma_0}{1+s+(\frac{2\delta}{\Gamma})^2},$$
(3.33)

where

$$\sigma_0 \equiv \frac{\hbar\omega\Gamma}{2I_{\rm sat}} = \frac{3\lambda^2}{2\pi} \,. \tag{3.34}$$

If one sets the absorption imaging beam to be on resonance (i.e., $\delta = 0$) and the intensity low enough such that $s \ll 1$, then the absorption cross section can taken to be σ_0 (and is independent of z). In addition, we ensure that the diameter of the absorption beam is much larger than the size of the cloud, such that we can assume that the beam intensity is constant over the size of the cloud. In this limiting case, the intensity of the absorption beam at the detector⁷⁴ (from Eq. 3.32) simplifies to

$$I_d = I_0 \exp\left(-\sigma_0 \tilde{n}\right) \to \ln\left(\frac{I_d}{I_0}\right) = -\sigma_0 \tilde{n}, \qquad (3.35)$$

where \tilde{n} is the atomic column density. The quantity $\ln(I_d/I_0)$ is the column optical density of the cloud, and is a function of the two axes transverse to the propagation direction.

Experimentally, the column optical density can be measured by taking an image with atoms (where the camera will observe a decrease in intensity at locations where the beam passes through the cloud), and a background image without atoms. In order to account for any dark counts or stray light in the system, we subtract from both images a "dark" image taken in the absence of the imaging light, but with all other parameters the same as the atom and background image. The measured column optical density is then

$$\sigma_0 \tilde{n} = -\ln\left(\frac{I_{\text{atoms}} - I_{\text{dark}}}{I_{\text{bkg}} - I_{\text{dark}}}\right) \,. \tag{3.36}$$

The column optical density is calculated for each camera pixel. Therefore, the atom number per pixel can be found by multiplying the column density by the effective area of the camera pixel, and taking into account the magnification of the imaging system. The atom number per pixel is then

$$N_{\rm pixel} = -\ln\left(\frac{I_{\rm atoms} - I_{\rm dark}}{I_{\rm bkg} - I_{\rm dark}}\right) \cdot \frac{A_{\rm pixel}}{M^2 \sigma_0}, \qquad (3.37)$$

where M is the magnification of the imaging system. In our current setup with the Pixelink camera, $A = 4.95^2 \ \mu m^2$, and we use a one-to-one imaging setup where $M = 1^{75}$. To find the total atom number, we sum the atom number per pixel over a small region of interest that contains the atomic cloud, and subtract from it the summed atom number in an identically sized adjacent region. We also normalize the light level in the atom image to that of the background image to avoid over or undercounting due to intensity fluctuations. Figure 3.18 gives an example of the atom, background, and false colour image showing the calculated atom number per pixel.

It is crucial that during the exposure time of the image only the light from the absorption

⁷⁴Assuming that the detector is placed somewhere after the beam passes through the atomic cloud, which seems pretty reasonable.

 $^{^{75}\}mathrm{We}$ also verified the pixel size by fitting the displacement of the cloud as it falls due to gravitational acceleration.



Figure 3.18: Example of an absorption image of a ⁶Li ODT. In the atom image (left), the atoms scatter light from the imaging beam, which decreases the intensity of the beam at the location of atoms. The background image (center) is taken with the same parameters, but without any atoms present. The column optical density can be found by dividing the atom image by the background image (right). The atom number per pixel can be calculated from the optical column density using Eq. 3.37, and the total atom number is found by summing over a small region that contains the atom cloud.

imaging beam is incident on the atoms. However, for both ⁶Li and Rb the imaging beam is picked off from the MOT beam after the double pass AOM used to set the frequency (see Sec. 2.1). Therefore, the MOT beams must be blocked with a physical shutter to ensure that no light is incident on the atoms through the MOT axis during imaging. In the case of the dipole trap, this is easily achieved by closing a mechanical shutter after the trap has been loaded, and well before an absorption image is taken. However, an absorption image of the MOT requires the ability to block the MOT in a time scale that is faster than the expansion time of the cloud⁷⁶. In our current system, the fastest shuttering times we have been able to achieve are on the order of a few hundred μ s, limited by the swing speed of the mechanical shutter arm and the beam size. The maximum suitable expansion times for the MOT are less than 100 μ s, a limit which is placed by the high temperature and (relatively) low density of the atoms in the MOT. For this reason, we predominantly use absorption imaging for the dipole traps, and recapture fluorescence imaging for the MOT. In general, we do not need to carefully measure the temperature or spatial distribution of the MOT,

 $^{^{76}}$ In addition, the beam should be shuttered symmetrically so that the radiation pressure from the MOT beams does not push the MOT to an unstable region. This can either be achieved with an AOM or with a shutter that is placed at the focus of a beam.

so this is not an issue in our experiment.

Another important consideration is that the absorption beam stay on resonance for the duration of the image. In general, the atoms will be accelerated along the propagation direction of the imaging beam, which will act to red shift the frequency of the light. This issue is more pronounced with ⁶Li than with Rb, owing to the large mass difference between the species. To counteract this effect, the exposure time of the image is kept short, such that the acceleration of the atoms is small and the absorption beam is not noticeably detuned. Although the general method for absorption imaging of ⁶Li and Rb (discussed above) is similar, there are a few crucial differences.

In Rb, we image on the $f = 3 \rightarrow f' = 4$ (the MOT pump) transition. However, because we hyperfine pump to the f = 2 state after loading the ODT, we must repump the atoms into the imaging state prior to taking the image. To do this, we turn on the MOT repump light, which is tuned on resonance to the $f = 2 \rightarrow f' = 3$ transition, for approximately 50 μ s before the image is taken. After the pumping stage, the MOT repump light is turned off and we take an absorption image of the ensemble. For Rb, we use an exposure time of 80 μ s.

In ⁶Li, we also image on the MOT pump transition, which drives the $f = 1/2 \rightarrow {}^2P_{3/2}$ transition. However, as the hyperfine splitting in the ${}^2P_{3/2}$ manifold is less than the natural linewidth of the transition, the pump beam excites transitions to all three (f = 1/2, 3/2, 5/2)hyperfine manifolds in the ${}^2P_{3/2}$, some of which can decay back to the f = 1/2 ground hyperfine manifold. Therefore, a repump beam tuned on the $f = 1/2 \rightarrow {}^2P_{3/2}$ transition is necessary. This beam is aligned such that it is roughly counter-propagating to the absorption imaging beam to help counter the acceleration of the atoms due scattering from the absorption imaging beam (see Fig. 3.9). For ⁶Li, we use an exposure time of 60 μ s.

It is also possible to image 6 Li at large magnetic fields, where a closed imaging transition does exist, and repump light is not necessary. This is discussed in more detail in the high field imaging section at the end of this chapter.

Temperature Measurement

Absorption imaging can also be used to measure the temperature of the atoms along a particular axis by monitoring the spatial width of the atomic cloud as a function of free expansion time⁷⁷. An *in situ* (that is, in the presence of the ODT, or immediately after the ODT has been turn off such that the atoms have had no time to expand) absorption image can be fit to a Gaussian profile which represents the initial position distribution of the atoms

$$P_i(x) = \frac{1}{\sqrt{2\pi\sigma_0}} \exp\left(\frac{-x^2}{2\sigma_0^2}\right).$$
(3.38)

The velocity distribution of the atoms is given by the Maxwell-Boltzmann distribution

$$f(v_x) = \left(\frac{m}{2\pi k_B T_x}\right) \exp\left(\frac{-mv_x^2}{2k_B T_x}\right), \qquad (3.39)$$

where T_x is the temperature of the atomic ensemble along the axis of interest (in this case, whatever the x-axis represents, which in our case is either the horizontal or vertical axis) and m is the mass of a single atom (or molecule, in the case of a temperature measurement of, for example, Feshbach molecules). The position distribution after some expansion time is given by

$$P_f(x,t) = \int_{-\infty}^{\infty} P_i(x) f(v_x) dx$$
$$= \int_{-\infty}^{\infty} P_i(x) f\left(\frac{x_f - x}{t}\right) dx$$
$$= \frac{1}{\sqrt{2\pi}\sigma_f(t)} \exp\left(\frac{-x^2}{2\sigma_f^2(t)}\right), \qquad (3.40)$$

where

$$\sigma_f(t) = \sqrt{\sigma_0^2 + \frac{k_B T_x t^2}{m}}.$$
(3.41)

Here, the integral is noted to be a convolution of the initial position distribution and the velocity distribution. As such, the width of the resulting Gaussian is simply the widths of the initial position distribution and velocity distribution added in quadrature. The temperature can be found by fitting the measured spatial width of the cloud as a function of the expansion time, using the temperature as a free parameter. As the absorption image is a 2D representation of the cloud, we find a temperature along the horizontal and vertical

⁷⁷This method is often called a "time of flight" temperature measurement because it is based on measuring how far an atom moves in a given time period. From this information, one can extract the velocity distribution of the atomic ensemble and temperature of the atom.

axes of the cloud, which are defined with respect to the camera axis.

It is important to note that this method, as described above, is only valid under three assumptions: the velocity distribution is well described by a Maxwell-Boltzmann distribution, the position distribution is well described by a Gaussian, and the atoms or molecules are non-interacting during the free expansion. For ⁶Li, we can ensure the third assumption by performing this measurement at the *s*-wave scattering length zero crossing near 528 G [137]. However, we have not seen a significant deviation in temperature for measurements (at typical densities between 5×10^{11} cm⁻³ and 10^{12} cm⁻³) performed at the zero crossing compared to the magnetic fields (near 750 G) that we use for ⁶Li high field imaging.

⁶Li High Field Imaging

At large magnetic fields⁷⁸ the eigenstates of the ⁶Li system are well described by the quantum numbers m_j and m_i , which represent the projection of the orbital and electron spin angular momentum on the magnetic field axis respectively, as shown in Fig. 3.19. The eigenstates form natural triplets, where the three states in each manifold have the same projection of orbital angular momentum m_j , and differ only in the projection of the nuclear spin m_i . The three lowest hyperfine levels that we trap in our ODT (the $|1\rangle$, $|2\rangle$, and $|3\rangle$ states) are separated by approximately 80 MHz. Since this separation is much greater than the natural linewidth of the transition to the ${}^2P_{3/2}$ state, this allows for state selective imaging of these states at high magnetic fields. At zero field these three states correspond to the $|f = 1/2, m_f = 1/2\rangle, |f = 1/2, m_f = -1/2\rangle$ and $|f = 3/2, m_f = -3/2\rangle$ states respectively, while at large field they correspond to the $|m_i = -1/2, m_i = 0, \pm 1\rangle$ states.

In the hyperfine Paschen-Back regime, the selection rules for an electric dipole transition are simply that

$$\Delta m_j = 0, \pm 1 \quad \text{and} \quad \Delta m_i = 0, \qquad (3.42)$$

which ensures that there is only a single allowable transition to the ${}^{2}P_{3/2}$ state. Namely, a transition to the $m'_{j} = -3/2$ manifold if we use σ^{-} polarized light. Due to the small hyperfine constant in the ${}^{2}P_{3/2}$ manifold, the three m_{i} projection states are only separated by

⁷⁸Here, large refers to a field larger than approximately 100 G, for which the ⁶Li system is within the hyperfine Paschen-Back regime, where the hyperfine interaction is disrupted and s and i are decoupled and individually coupled to the axis of the external magnetic field. More details specific to the ⁶Li system can be found in Chapter 5.



Figure 3.19: Magnetic field dependence of the Zeeman levels in the ${}^2S_{1/2}$ manifold (bottom panel) and ${}^2P_{3/2}$ manifold (top panel). In the ${}^2S_{1/2}$ manifold, the three states which make up the $m_j = {}^{1/2}$ manifold at high field are shown with dashed lines, while the $m_j = {}^{-1/2}$ manifold is shown with a solid line. In the ${}^2P_{3/2}$ state each of m_j manifolds contains three levels which differ in the projection of the nuclear spin. The splitting between these states is approximately 1.7 MHz. The thick arrows indicate the three transitions used to image the $|1\rangle$, $|2\rangle$ and $|3\rangle$ states. The detuning of these transitions from the zero field transition energy are given in Eq 3.43.

approximately 1.7 MHz (much less than the natural linewidth of the transition). However, due to the selection rule that $\Delta m_i = 0$ (i.e., the photon cannot couple to the spin degree of freedom), each of the $|1\rangle$, $|2\rangle$, and $|3\rangle$ states has only *one* state to which it can couple in the $m'_j = -3/2$ manifold. This state is the state with an identical nuclear spin projection. Therefore, at high field the imaging transition for each of the three states is closed, and no repump light is required. The thick black arrows in Fig. 3.19 indicate these closed imaging transitions for the $|1\rangle$, $|2\rangle$ and $|3\rangle$ states. The detuning of these three transitions (in MHz) relative to the zero field $f = 1/2 \rightarrow {}^2P_{3/2}$ (i.e., the MOT pump) transition frequency f_0 as function of magnetic field are

$$f_{|1\rangle} - f_0 = -1.4 \cdot B + 158$$

$$f_{|2\rangle} - f_0 = -1.4 \cdot B + 82$$

$$f_{|3\rangle} - f_0 = -1.4 \cdot B ,$$

(3.43)

where the subscript indicates the state being imaged and B is the magnetic field measured in Gauss.

Note that these imaging transitions require the imaging field be circularly polarized such that it drives a σ^- transition. However, we currently image along an axis which is perpendicular to the vertical bias magnetic field. At best, the polarization of the imaging field can be made up of equal parts LCP and RCP light if the field is linearly polarized perpendicular to the magnetic field axis. This means that only half of the light has the correct polarization, and results in an undercounting of the atom number in a particular state by roughly a factor of two.

To understand this undercounting, consider the atom number calculated per pixel using Eq. 3.37. The intensity of the imaging light for each pixel is directly related to the number of photons incident on each pixel. For an imaging beam where all the photons can be scattered by the atoms (i.e., all the photons have the correct polarization and the correct frequency) then

$$N_{\rm pixel} \propto \ln\left(\frac{n_{\rm atoms}}{n_{\rm back}}\right) ,$$
 (3.44)

where n_{atoms} and n_{back} are the number of photons incident in each pixel in the atom and background image respectively. If additional light is added to the imaging beam which does not interact with the atoms (i.e., has the wrong polarization or the wrong frequency) then the number of photons incident on each pixel is increased by an amount n_{addn} and the calculated number becomes

$$N'_{\rm pixel} \propto \ln\left(\frac{n_{\rm atoms} + n_{\rm addn}}{n_{\rm back} + n_{\rm addn}}\right)$$
 (3.45)

As $n_{\text{atoms}} \leq n_{\text{back}}$, the ln term in Eq. 3.45 will always be smaller than in Eq. 3.44 (independent of n_{addn}) and therefore the atom number will be undercounted. However, the magnitude of this underestimation depends on $n_{\text{atoms}}/n_{\text{back}}$ and n_{addn} . In the specific case of high field imaging, half the light is of the correct polarization, and half is of the wrong polarization. Therefore, $n_{\text{back}} = n_{\text{addn}}$ and Eq. 3.45 simplifies to

$$N'_{\rm pixel} \propto \ln \left[0.5 \left(1 + \frac{n_{\rm atoms}}{n_{\rm back}} \right) \right]$$
 (3.46)

In the limiting case where $n_{\rm atoms}/n_{\rm back} \approx 1$ (i.e., the limit of low optical density, where very few photons are scattered out of the beam) then $N/N' \approx 2$, and we therefore undercount by a factor of 2. When $n_{\rm atoms}/n_{\rm back} < 1$ then N/N' > 2 and the atom number is undercounted by more than a factor of 2. Empirically, we find that that the atom number determined from high-field imaging is approximately 4.5 times smaller than in the standard absorption imaging case at 0 G. Given that a factor of two can be accounted for by the fact that we are only imaging half of the atoms (either the $|1\rangle$ or $|2\rangle$ state), this suggests that the undercounting due to the incorrect polarization component in the imaging light is approximately a factor of 2.25^{79} .

This high field imaging technique can also be used to image Feshbach molecules formed near the broad Feshbach resonance at 832 G. This is because the Feshbach molecules are so weakly bound that the energy needed to break the bond shifts the absorption transition frequency by an amount that is less than the natural linewidth of the transitions [138]. In fact, this high field imaging technique is crucial to image Feshbach molecules. If the magnetic field is ramped to 0 G for imaging, the Feshbach molecules follow the bound molecular state responsible for the Feshbach resonance and become deeply bound, and therefore "invisible" to the absorption imaging beam.

Rb State Selective Imaging

In our standard absorption imaging, we use the MOT repump beam to pump atoms from the f = 2 to the f = 3 hyperfine manifold before the image is taken. However, it is also possible to use an RF field to transfer atoms between these two hyperfine manifolds. Unlike ⁶Li, magnetic fields greater than 1000 G are required in order to be in the hyperfine Paschen-Back regime. Therefore, for the fields of interest in our experiment (and specifically those used in this state selective imaging procedure), the Zeeman effect breaks the 2f + 1degeneracy of each of the hyperfine levels, and results in a linear energy shift proportional to m_f , where the energy shift between adjacent m_f levels in the f = 2 and f = 3 hyperfine

⁷⁹In general, the undercounting of the atom number is not just limited to incorrect polarization. Any off-resonant frequency components in the imaging beam will have a similar effect.



Figure 3.20: Possible RF transitions between the f = 2 and f = 3 states in ⁸⁵Rb. The thin dashed lines show the energy of the two hyperfine manifolds in the absence of a magnetic field, while the thick solid lines show the energy of each state in a small magnetic field. The energy splitting between adjacent m_f states is .47 MHz/G. The possible RF transitions are labeled with dashed arrows (representing π transitions) and solid arrows (representing σ transitions). These RF transitions are used instead of the MOT repump beam to pump atoms out of the f = 2 manifold and into the f = 3 manifold when we perform state selective imaging.

levels is approximately .47 MHz/G^{80} .

In the presence of a small magnetic field, the energy splitting between adjacent hyperfine m_f states is much larger than the linewidth of the RF transitions (which we observe to be on the order of a few kHz⁸¹), such that there are 11 distinct transitions frequencies that will couple specific projection states in the f = 2 manifold to the f = 3 manifold, as shown in Fig. 3.20. Therefore, using one of these RF transitions instead of a repump beam allows for a measurement of the number of atoms in one (or two) projection states in the f = 2 manifold.

One way to measure the population in each of the five m_f states is to drive only the

 $^{^{80}}$ This is described in detail in Sec 3.3 in the context of optical pumping.

⁸¹Note that the natural linewidth of these transitions is exceedingly small, as the lifetime of the ground hyperfine states is nearly infinite. Therefore, the observed linewidth is set by the magnetic field fluctuations in our setup.

 π transitions (the dashed lines in Fig. 3.20) where $\Delta m_f = 0$ due to selection rules. A complementary method is to determine the population from the remaining six transitions where $\Delta m_f = \pm 1$. If the measured atom number from a specific RF transition is N_i , where i = a, b, c, d, e, f labels the RF transitions as in Fig. 3.20, then the population in each projection state is

$$N_{-2} = N_a$$

$$N_{-1} = N_b - N_a$$

$$N_0 = [(N_c - N_b + N_a) + (N_d - N_e + N_f)]/2$$

$$N_1 = N_e - N_f$$

$$N_2 = N_f,$$
(3.47)

where the subscript on the left hand side represents the m_f projection state in the f = 2 manifold.

An example of such a measurement is given in Fig. 3.15, where this technique is used to measure the efficiency of our optical pumping technique. While the actual atom number calculated using the π transitions and the σ transitions may not agree (if, for example, the polarization of the RF field is such that it does not drive π and σ transitions with equal probability), the relative population of each state (i.e., the percentage of the total population in each state) should agree. Figure 3.15 also shows the relative atom number calculated with this technique.

Chapter 4

Electric Field Plates

In many AMO experiments that work with (or plan on working with) polar molecules, it is essential to be able to apply dc electric fields greater than 5 kV/cm. The interest in polar molecules arises from the existence of a permanent electric dipole moment, which lead to interactions that are long range and spatially anisotropic. Electric dipole moments in the lab frame are induced by an external electric field⁸² because, in the absence of electric fields, there is no fixed orientation of the molecular axis and the average electric dipole moment in the lab frame is zero.

The largest effect of a dc electric field with strength \mathcal{E} is a mixing of closely adjacent rotational states where $\Delta N = \pm 1$ [40]. For small fields, this mixing leads to an induced electric dipole which is parallel to the electric field and has a magnitude

$$\langle D \rangle \propto \frac{D\mathcal{E}}{B},$$
 (4.1)

where D is the magnitude of the permanent electric dipole moment and B is the rotational constant of the molecule. For large fields, where the field strength is larger than some critical value $(\mathcal{E}_c \equiv B/D)^{83}$, the result in Eq. 4.1 is not valid, and $\langle D \rangle$ approaches its maximum value D. For example, for KRb in the singlet rovibrational ground state level $\mathcal{E} \approx 4 \text{ kV/cm}$, and a calculation done by K. Ni [83] shows that at $\mathcal{E} = 100\mathcal{E}_c = 400 \text{ kV/cm}$ the induced electric dipole moment is about 92% of the permanent electric dipole moment. However, all hope is not lost: A field of 10 kV/cm can achieve partial lab frame alignment, and about 50% of the maximum electric dipole moment [83]. For the LiRb system, we expect to require approximately the same magnitude of electric field in order to realize a substantial (relative to the maximum value) induced electric dipole moment. In the rovibrational singlet ground state of LiRb (the $X^1\Sigma^+$ state) the rotational constant is about 6.5 GHz

 $^{^{82}}$ In the frame of the molecule, there always exists a permanent electric dipole moment owing to the preference of the elections to be nearer to one molecule than the other.

⁸³If B is in GHz and D in Debye, then $\mathcal{E}_c = (B/D) \cdot 1.986$ in kV/cm.

[139] while the permanent electric dipole moment is expected to be 4.2 Debye [140], which gives $\mathcal{E}_c \approx 3 \text{ kV/cm}$.

In addition to future work with polar molecules, the primary motivation for the creation of these electric field plates was a proposed experiment which involved measurements of the effect of electric fields on atomic and molecular collision resonances [80, 81, 82]. The proposal suggests that an electric field can shift the position of existing magnetic Feshbach resonances or induce a Feshbach resonance for a particular partial wave collision that previously only existed for a different partial wave (i.e., an *s*-wave induced resonance that appears at the same location as an intrinsic *p*-wave resonance). The shift and width of the induced resonance is a function of the applied electric field, and the size of the permanent electric dipole moment. In particular, studying the effect of electric fields on heteronuclear Feshbach resonances in ⁶Li +Rb mixtures requires electric fields in excess of 20 kV/cm. Specifically, an electric field of 20 kV/cm will produce a shift of approximately 15% of the experimental width of the *s*-wave Feshbach resonance at 394 G or 938 G (see Chapter 7) between ⁶Li and ⁸⁵Rb. Even higher fields are needed for less polar mixtures like KRb [19], RbCs [21, 22], or NaK [24].

Introduction and Design Challenges

Many AMO experiments involving the application of electric fields share the same requirements - namely, electrodes that do not limit optical access and that have extremely low residual magnetism. Thin transparent conducting films (TCFs), such as ITO, applied to a transparent dielectric substrate satisfy these requirements. The ability to place the electrodes outside of a vacuum chamber allows for the addition of electric field capability after the design or construction of the apparatus. In addition, placing the electrodes in air simplifies the vacuum design, and can increase the flexibility of an experiment (most obviously because they can be added and removed when necessary).

The primary limitation to creating large electric fields is dielectric breakdown. This phenomenon occurs when free electrons are accelerated to sufficiently high energies by an electric field such that they impact ionize atoms or molecules in the surrounding medium or in the electrode itself. This leads to an avalanche production of many more electrons and ions (by electron impact ablation) generating an electric arc that rapidly reduces the field. This process, known as Townsend discharge, limits the maximum electric field that can be generated when the flow of charge through the medium exceeds the current supplied by the high voltage source. Breakdown also leads to material damage of the electrodes and other surfaces due to ablation and X-ray generation through bremsstrahlung which can also damage materials and sensitive electronics. One obvious challenge to creating large electric fields with a TCF is that electric discharge and the ion ablation that accompanies it can easily destroy a thin film (see Fig. 4.1c). Thus, suppressing discharge of any kind is of key importance.

Even when complete dielectric breakdown does not happen (and an electric arc is not present), discharge can still occur and is often evident from a corona discharge occurring near sharp edges (see Fig. 4.1). The large curvature associated with an edge of a conductor causes a large potential gradient (i.e. a large local electric field) which can lead to field electron emission followed by a local dielectric breakdown. Field emission and corona formation can be suppressed by designing electrodes without sharp edges (i.e. by using large-diameter, round-shaped conductors) and by polishing the surface to remove microscopic surface roughness. However, without physically stopping an ion avalanche resulting from Townsend discharge, the maximum achievable field is still limited by the dielectric breakdown of the medium.

Previous Work

Transparent electrodes capable of creating moderately high fields (on the order of 5 kV/cm) for experiments with ultra-cold molecules have been realized with ITO coated glass (#CH-50IN-S209 from Delta Technologies) by the group of Ye and Jin [19, 27, 141]. The ITO glass was left exposed and the dielectric breakdown and discharge from the plates was limited by covering all nearby conductors with many layers (4-5) of Kapton tape. With this system they claim to be able to apply up to ± 5 kV on each plate without breakdown, generating a 9 kV/cm field with a plate separation of 1.36 cm. They observed that for applied voltages of ± 3 kV on each plate (corresponding to 5.2 kV/cm field) a residual electric field would remain after the plates were discharged [83]. They conjectured that their pyrex glass cell (made from Borofloat by Starna Cells) developed a residual electric polarization.

Other groups working with polar molecules have produced moderate electric fields of up to 2 kV/cm using either ITO slides [24] or using four parallel rods placed at the corners of the vacuum cell [21]. In both cases, the maximum achievable field (on the order of a few kV/cm) is smaller than the fields needed to achieve large lab frame alignment of polar molecules (> 10 kV/cm) or for experiments involving electric fields and Feshbach resonances (> 20 kV/cm). More importantly, the maximum achievable field in all three cases is limited by the maximum voltage that can be applied to the plates (or rods) without causing damage (via dielectric breakdown or corona formation) to nearby experimental components or the plates or rods themselves.



Figure 4.1: Left: Illustration of the effects of Townsend discharge and ion avalanche. In (a) an electric arc is established due to the breakdown of air across a 2 cm gap between a grounded metal rod and the tip of an exposed wire near 45 kV. In (b) the output current of the high voltage supply is limited and the electric arc is not sustained. Nevertheless, the faint blue glow of a corona discharge near the tip of the wire is visible indicating field electron emission. In (c), an ITO coated slide is shown, and the deleterious effects of discharge are apparent. At (1) the ITO coating appears darker and was damaged by corona discharge at the corners where the local electric field is highest. At (2), the glass cracked and broke due to electrical arcing. Conductive epoxy (3) was used to glue and electrically connect the conductor to the ITO coating and was insulated using RTV silicone adhesive. Right: Effect of discharge through glass insulator near connection of high voltage cable to a prototype electric field plate. In this case, the thickness of the glass (2 mm) was not enough to prevent electrical breakdown to a ground point placed against the glass.

4.1 Design of Electric Plates and HV Components

In our design for the electric field plates, we also used a TCF of ITO. However, since we wanted to achieve electric fields larger than the dielectric breakdown of air (roughly 20 kV/cm), we had to find a way to physically prevent the flow of charge through air. To do this, we embedded the ITO coated dielectric substrate inside of a stack of two more transparent substrates (making a glass sandwich⁸⁴) where the outer layers have a much higher dielectric strength than air.

The largest field that can be achieved with two parallel plates with a potential difference V between them while separated by a distance d is $\mathcal{E}_{\text{max}} = V/d^{85}$. This holds in the limit where the side length of the plates is much greater than the separation of the plates. However, in our setup the plates will need to be separated by about 4 cm (given the dimensions of the vacuum cell and the thickness of the glass used to shield the ITO), which is on the order of a reasonable side length for the plates. In order to estimate the reduction in field strength due to the finite size of the plates we calculated the expected electric field at a location centered between the plates, corresponding to field that the trapped atoms would experience. Figure 4.2 shows the expected field as a function of side length for a square plate and for a rectangular plate where the length of one side is fixed at 7.5 cm. This fixed side length was chosen as it was largest standard commercially available length of ITO. We decided to design the final version of the plates to have a conductive surface with a dimension of 7.5 cm \times 10 cm, as this size maximized the electric field strength ($\approx 85\%$ of the theoretical maximum strength) and homogeneity inside the cell given the limitations imposed by other elements in the apparatus. We also built a "trial" set of plates (before committing to the larger design) which had a conductive surface that measured just under $3 \text{ cm} \times 3 \text{ cm}$. With this size plate, the maximum achievable field was limited to about 60% of the theoretical maximum value.

To build the plates, an ITO coated glass slide from SPI Supplies (5 cm \times 7.5 cm \times 0.7 mm) was laid onto a borosilicate glass flat (5 mm thick) with the coating side down and partially overlapping two strips of aluminum foil, which extend the conductive layer area to a 7.5 cm \times 10 cm area. We used aluminum foil to extend the conductive surface

⁸⁴While electrifying delicious, we did not get FDA approval for its public consumption.

⁸⁵The maximum field also depends on the dielectric constant of the material(s) between the plates. For this discussion, assume k = 1. The effect that the dielectric constant of the plate themselves and the vacuum cell have on the largest achievable field is discussed in greater deal in Section 4.2



Figure 4.2: Expected electric field strength normalized to the largest achievable field as a function of plate size. Black (solid) line is a square plate with the given dimensions and the blue (dashed) line is a rectangular plate with one fixed side length of 7.5 cm. The horizontal black (blue) dot-dashed lines and corresponding circle (diamond) show the expected field strength for the prototype (final) plate design.

because optical access was not required far away from the cell and plate center. The ITO slide was glued to the aluminum foil using a silver conductive epoxy. Next, we applied 5-minute epoxy made by Devcon to the area just outside of the ITO slab up to the edge of the bottom glass plate and another glass plate was pressed to the top to complete the stack. At least a 1 cm border filled with epoxy existed between the conductor and the edge of the glass sandwich, which ensured that a dielectric breakdown would not occur through the epoxy. A long flat conductor embedded in the sandwich connects the foil strip to the center conductor of a high voltage coaxial cable (polyethylene RG-8U). Fig. 4.3 shows a picture and schematic of the entire assembly. We found that the connection to the plate was a weak spot for breakdown. To make this connection more stable and well insulated, the end of the high voltage coaxial cable was stripped of its ground shield and inserted into a 10 cm long cylindrical tube made of either Teflon or acrylic⁸⁶ with a wall thickness of 5 mm that extended down to the lower glass plate. We used 5-minute epoxy to affix the tube to the

⁸⁶Both Teflon and acrylic were found to be suitable although it was important to roughen the Teflon surface before gluing to improve the bond.

glass, and to fill the inside of the tube to act as electrical insulation for the exposed wire. To further secure the assembly, rubber mastic tape (.065 thickness from 3M/Scotch) was wrapped around the tube and the areas where the tube and glass assembly contacted (not shown in Fig. 4.3).



Figure 4.3: (a) Picture and (b) schematic (not to scale) of the electric field plate assembly. A high voltage coaxial cable (polyethylene RG-8U) with a 20 cm length stripped of its ground shield (1) is inserted into a 10 cm cylindrical tube of either Teflon or, here, acrylic (2) that extends down to the lower glass plate, and the center conductor connects to a flat metal conductor (3) that extends to aluminum foil strips (4) that contact the ITO coated glass slab (5). Insulating epoxy (6) glues the heterostructure together, maintains the positions of all elements, and fills the gap between the external glass plates (7).

We also built a high voltage switching network (similar to an H bridge) to control the polarity of the voltages applied to the plates. The network is constructed using four single pole double throw Gigavac high voltage relays (G71C771) and two Glassman 60 kV supplies (EH60R01.5), as shown in Fig. 4.4. Four 1 M Ω Ohmite ceramic resistors (OY105KE) were placed in series between the high voltage supplies and the electric field plates in order to limit the current spikes that occur during charge and discharging. In addition, each of the four possibles pathways from the voltage supplies to either of the electric field plates is connected to ground through a 75 kV, 16 W, 1 G Ω Ohmite high voltage resistor (MOX96021007FTE). These resistors ensured that all non-operational arms of the network are grounded and allow a path for a (potential) rapid discharge of the charges stored on the electric field plates. The effect of these resistors on the charging and discharging time of the plates are discussed more in Section 4.2.

In addition to the electric plates, care had to be taken to insulate all electrical connections, including those to or between resistors or those between lengths of cable. This was achieved by embedding all connections inside of an extruded 1 inch diameter acrylic rod or block. To make the connections, a through hole was drilled along the axis of the rod through which the two cables were inserted. A perpendicular access hole was drilled, and used to solder the connection. Care was taken to ensure that solder connections had no sharp edges, and Super Corona Dope (from MG Chemicals) was applied to the connection to help insulate and resist corona formation. Finally, all the holes were filled with 5-minute epoxy or melted resin wax⁸⁷. An example of a high voltage connection is given in Fig. 4.5. Due to the lack of availability of commercial high voltage connectors, almost all of the high voltage connections used in this apparatus were permanent and hand-made.

4.2 Testing and Characterization

To test the plates for weak spots where dielectric breakdown might occur, we placed a ground cable at various locations around the plate, and slowly energized the plates up to a maximum of 60 kV (limited by the high voltage supplies). Using the design presented above, we observed that no arcing would occur when a grounded conductor was placed touching any part of the assembly with the plate energized to either ± 60 kV. Given the minimum distance from the inner conductor surfaces to the outside of the assembly was 5 mm, this corresponded to a maximum electric field strength sustained across the outer

 $^{^{87}}$ We found that filling volumes through narrow channels was more easily done with wax than the viscous epoxy. However, all the connections were made using 5-minute epoxy. Melted resin wax was only used to insulate the 1 G Ω resistors in the high voltage switching network.



Figure 4.4: Bottom: Schematic for the high voltage switching network for the field plates. The $R_1 = 4 \text{ M}\Omega$ resistor in series with the electric field plates helps limit the instantaneous current spikes during the charging and discharging of the plates, while the $R_2 = 1 \text{ G}\Omega$ resistor in each connection arm ensures that all non-operational arms are well grounded, and allows for a fast discharge of the plates when the supply is disconnected. The high voltage relays are controlled via an optically isolated digital switch. Top Left: Assembly for the first two HV switches (labeled B) directly after the power supplies. The four black squares (labeled R_2) are acrylic blocks that contain the connections to the 1 G Ω resistors, which extend vertically downwards and are attached to a ground plane. Top Right: Housing for the second set of high voltage relays (labeled A), along with the 4 G Ω current limiting resistor (labeled R_1) are enclosed inside a grounded metal box. The resistors are embedded inside an acrylic block, which is filled in with 5-minute epoxy. A second identical housing holds the second high voltage relay and current limiting resistor used for the other electric field plate.



Figure 4.5: Example of a high voltage connection between two polyethylene RG-8U high voltage cables. The stripped cable is inserted into a through hole drilled along the axis of an acyclic rod. The conductor is soldered through a perpendicular access hole. This hole is then filled in with 5-minute epoxy to insulate the connection.

glass substrate of 120 kV/cm.

During testing of the switching network, we noted that charging and discharging the plates occasionally had detrimental effects on electronic equipment in close proximity to the switching network. We attributed this to transient spikes and/or radiation produced during the charging period. To avoid these effects on our experimental electronics, the switching network was placed 10 m from the experimental setup in an adjacent room, and the high voltage relays were controlled via optically isolated digital switches in order to isolate them from our experimental control systems. Near the experiment (that is, in the same room as the experiment), we ran as much of the high voltage cable as possible through grounded metal pipes.

Figure 4.6 shows how we incorporated two of these field plates into our system. Although we experienced a loss of power due to reflections from the transparent substrates (which were not AR coated) and the ITO substrate (for which the transmission around 670 nm and 780 nm is about 80%), we did not experience any significant decrease in the MOT performance. When the electric field plates were operated in the laser cooling setup, we placed a grounded cable next to the connection between the high voltage cable and the plate to ensure that, in the event of a failure of this component, the arc would not be to the optical table or to other equipment in the apparatus.

Note that the measurements taken with the electric field plates were done in the previous



Figure 4.6: The placement of the field plates on our quartz vacuum cell. A grounded support rod holding the atomic beam shields is near to the top plate and is, unfortunately, a source of electrons by field electron emission when the top plate is positively biased.

iteration of the setup, without the Zeeman slower. While Rb atoms were introduced into the vacuum with an atomic dispenser placed 30 cm from the trapping region, ⁶Li atoms were supplied to the trapping region by an atomic beam formed directly from an effusive oven. In order to prevent the buildup of ⁶Li emitted by the oven within the main section of the chamber, a series of beam shields were used. These shields were mounted on a metal support rod that ran along the top of the cell, as pictured in Fig. 4.6. More detail on this setup can be found in the PhD thesis of M. Semchzuk [98].

4.2.1 Timing of Charging and Discharging

In this high voltage assembly, we used two 60 kV / 1.5 mA power supplies from Glassman High Voltage (model number EH60R01.5) with one set to negative polarity, and the other to positive polarity. These power supplies have a total internal HV assembly capacitance of 900 pF (not including the output cable), a 1.5 k Ω series limiting resistor⁸⁸ and a 1.5 G Ω bleed resistor⁸⁹. The power supply has a specified rise time constant of 60 ms and, with a 75% resistive load, the fall time constant will be the same as the rise time constant. However, with no external load resistance the fall time constant is on the order of seconds (roughly $\tau = RC = 1.35$ s in the absence of any load).

Additionally, the rise time of 60 ms only holds if the total capacitance (including both

⁸⁸This resistor is internal to the power supply, and is placed in series with the load in order to limit the output current of the power supply. We added an additional 4 M Ω resistor in order to further limit the maximum current during charging and discharging.

⁸⁹This is the resistance that the power supply (and any associated load) will discharge through.

the load and internal capacitance) is low enough that the maximum current the supply can deliver will charge the net effective capacitance faster than the time constant. This time scale is given by

$$t = \frac{CV}{I_{\text{max}}} \,. \tag{4.2}$$

For our supplies, the quoted rise time holds if the total capacitance is less than 1.25 nF, which limits the load capacitance to about 350 pF. The components which make up the load capacitance are the electric fields plates, the high voltage cable, and any parasitic capacitances (for example, from the high voltage connections). The capacitance of the high voltage cable is about 30 pf/ft, which is much larger than the capacitance of the electric field plates (on the order of 1-5 pF from geometric considerations). However, because we placed the power supplies and the switching electronics far away from the experiment, this required a long length of high voltage cable. We measured the total capacitance of the system by limiting the output current of the power supply and measuring the time for the system to reach the set voltage⁹⁰. With a current limit of 75 μ A, the system took 720 ms to reach 20 kV which gives a total capacitance of 2.7 nF. This corresponds to approximately 60 ft or 18 m of high voltage cable, ignoring parasitic capacitance. We estimated there is 50 ft of high voltage cable between the power supply and the plates, so this is a reasonable measured capacitance. However, this means that the time to charge the plates (to 60 kV) is limited to a minimum of a few hundred ms. Note that we have also neglected the rise time for the load capacitor and load resistance, since this is on the order of 7 ms, given the load resistance is 4 M Ω and the load capacitance is 1.8 nF.

A slightly faster approach to charging the plates is to first charge up the power supply with the high voltage switch open (see Fig. 4.4), and then close the switch. This way, when the switch is closed the instantaneous charging current is provided by the energy stored in the capacitance of the HV supply. This will cause an instantaneous voltage drop that depends on the ratio of the two capacitances. After the voltage drop, the power supply will then recharge the voltage at the time scales discussed above. Given our estimation of the total cable capacitance, this drop will be on the order of 60%. This large drop is due to the large capacitance from the high voltage cable that is place after the switch. This drop could be made much smaller either by placing the switch closer to the experiment (and moving

⁹⁰Note that we did not monitor the voltage of the plates directly. Any measurement of the voltage was done via an analog output on the high voltage power supply itself. When the electric plates were connected to the power supply, we assume the plates are at the same potential as the supply.

the cable to the power supply side of the switch) or by stripping the cable of the grounded shielding to reduce to eliminate the cable capacitance.

If the plates (and all the HV cable) are discharged through the power supply, the time constant for discharge is about 4 s. An alternative is to flip the high voltage switch to disconnect the plate and power supply, and connect each separately to ground. Now, the plate will discharge through the 1 G Ω resistor in the switching network. Due to the large cable capacitance in our setup, the time constant for this discharge is still about 2.7 s. This discharge can be made faster (and, theoretically, much faster than the limit of 1.3 s if the plates discharge through the power supply, which is limited by the internal capacitance and bleed resistor) in a similar way to improving the charge time: by decreasing the load capacitance on the plate side of the switch.

In reality, we were not too concerned with the discharge time of the plates as we can image the atoms in the presence of an electric field by detuning frequency of the imaging beam (see Section 4.2.2). Therefore, we could turn off the field and wait for a complete discharge after a run was completed. In addition, we found that using a turn on time faster than a few hundred ms (typically when the field was switched in instantaneously using the high voltage relays) caused a larger atom loss than a slow turn on. We believe this effect is likely due to a rapid acceleration of electrons inside the vacuum chamber, which collide with atoms in the ODT resulting in loss⁹¹. Given this, we typically turn the field on in about 250 ms which was easily achievable even with the additional load capacitance of the system.

4.2.2 Electric Field Measurement

In our setup, the minimum field plate conductor separation is limited to 4 cm by the vacuum cell (3 cm) and the outer glass plate on the electrode assembly (5 mm). However, because of the high dielectric constant of the glass on the electrode assembly and the quartz cell, the field is larger than simply the voltage difference ΔV divided by the physical distance d. In addition to the modification of the field strength due to the dielectrics, the field strength is also affected by the finite size of the plates. In the case of a single dielectric⁹² the strength

⁹¹Details on the loss that we observe from both the MOT and ODT as a function of the plate voltage can be found in Section 4.3.3.

 $^{^{92}}$ Or, in the case where the dielectric constant is the same for both the glass on the electrode assembly and the cell.

of the electric field at the location of the atoms (in vacuum) is

$$|E| = K \cdot \frac{\Delta V}{d} \cdot \frac{d}{d - t(1 - 1/\kappa)} = K \cdot \frac{\Delta V}{d} \cdot \eta, \qquad (4.3)$$

where K is a dimensionless factor to account for finite size of the plates (see Fig. 4.2, t is the total thickness of the dielectric layers, d is the physical separation between the conducting layers and κ is the dielectric constant of the dielectric between the plates. When there are two dielectric layers with thickness t_1 and t_2 and dielectric constant κ_1 and κ_2 the strength of the electric field is

$$|\mathcal{E}| = K \cdot \frac{\Delta V}{d} \cdot \frac{\kappa_1 \kappa_2 d}{\kappa_1 \kappa_2 d + t_1 (\kappa_2 - \kappa_1 \kappa_2) + t_2 (\kappa_1 - \kappa_1 \kappa_2)} = K \cdot \frac{\Delta V}{d} \cdot \eta , \qquad (4.4)$$

which simplifies to Eq. (4.3) when $\kappa_2 = 1$, equivalently $t_2 = 0$ or $\kappa_1 = \kappa_2$.

In our setup, the quartz cell ($\kappa \approx 4.5$) walls have a total thickness of 1 cm, and the borosilicate glass plates ($\kappa \approx 4.6$) the dimensionless quantity η is approximately 1.6, and K = .87 for the large plates. Thus, by applying ± 60 kV to each plate, we expected to obtain a field of approximately 42 kV/cm.

In order to measure the electric fields produced by the plates, we performed *in situ* spectroscopy on a sample of laser cooled ⁸⁵Rb atoms inside the vacuum cell with the plates energized, and measured the dc Stark shift of the ⁸⁵Rb pump transition. In the limit of weak coupling (where the Stark shift of each hyperfine level is small compared to the hyperfine splitting) the dc Stark shift is [90]

$$\Delta E_{|j,i,f,m_f\rangle} = -\frac{1}{2}\alpha_0 \mathcal{E}^2 - \frac{1}{2}\alpha_2 \mathcal{E}^2 [3m_f^2 - f(f+1)]k, \qquad (4.5)$$

where

$$k = \frac{[3x(x-1) - 4f(f+1)j(j+1)]}{(2f+3)(2f+2)f(2f-1)j(2j-1)},$$
(4.6)

and

$$x = f(f+1) + j(j+1) - i(i+2), \qquad (4.7)$$

and α_0 and α_2 are the scalar and tensor polarizability respectively. Since the ground state hyperfine splitting in ⁸⁵Rb is 3 GHz, the limit on the weak field limit comes from the hyperfine splitting of the excited state. The pump transition couples to the f = 4 state of the $5^2 S_{3/2}$ manifold, so Eq. 4.5 is valid when ΔE is less than about 100 MHz, which corresponds to fields of less than approximately 30 kV/cm⁹³.

The tensor polarizability is only non zero for the excited $5^2S_{3/2}$ state, so the effect of an electric field is to shift the ground f = 3 hyperfine level down by a fixed amount and to break the m_f degeneracy in the excited state. In the presence of an electric field, the energy difference between the ground and excited states is changed by

$$\Delta E = \frac{1}{2} \left(\alpha_0^{(P)} - \alpha_0^{(S)} \right) \mathcal{E}^2 - \frac{1}{2} \alpha_2^{(P)} \mathcal{E}^2 \left[3m_f^2 - f(f+1) \right] k \,, \tag{4.8}$$

where the quantum numbers refer now to the excited state.

From Eq. 4.8, it can be seen that the "pump" transition is broadened and shifted to lower frequencies (see Fig. 4.7). The relevant polarizabilities in this case are $\alpha_0^{(P)} - \alpha_0^{(S)} = h \cdot 0.01340 \text{ Hz}/(\text{V/cm})^2$ and $\alpha_2^{(P)} = h \cdot -0.0406 \text{ Hz}/(\text{V/cm})^2$ [90]. An example of the expected dc Stark shift as a function of applied voltage for the small prototype plate is shown in Fig. 4.8. In order to determine the value of the electric field strength given a measured dc Stark shift, we assumed that the state population is evenly distributed among the m_f states, and we use the weighted mean Stark shift of the pump transition. Any associated uncertainty on the determination of the field strength is due to the unknown state populations. As a reference, if the spin population were all in the $|m_f| = 3$ states, we would underestimate the field by about 20% and if the population were all in the $m_f = 0$ we would overestimate the field by about 10%.

We performed two types of spectroscopic measurements, an example of which are shown in Fig. 4.9 for a potential difference across the plates of $\Delta V = 40$ kV. In each case, we used the shift in the resonance frequency of the pump light from the "on resonance" case, defined the be the detuning in the absence of a Stark shift (i.e., with the plates off)⁹⁴. In the first case, we measured the ⁸⁵Rb MOT fluorescence as a function of the detuning of ν_{pump} from resonance with ν_{repump} set on resonance. In the presence of an electric field, the largest detuning from the resonant case for which the MOT will operate shifts to lower frequencies, as shown in Fig. 4.9. However, an accurate determination of the electric field from the

 $^{^{93}}$ Although we had hoped to measure fields larger than this, technical issues prevented us from measuring fields larger than 18 kV/cm. At the very least, this made the analysis of the Stark spectroscopy more straightforward.

⁹⁴In some cases, this was not always at a detuning of zero which is likely due to a small offset in the location of the lock.



Figure 4.7: The dc Stark shift of the ground (f = 3) and excited state (f' = 4) levels is illustrated. The scalar polarizability is larger in the excited state and it therefore shifts down more than the ground state. The tensor polarizability (zero for the ground state) shifts the excited state levels up by an amount proportional to m_f^2 . Thus the pump transition moves to lower frequencies and also broadens somewhat indicated by the "min" and "max" transition energy differences.

overall shift is confounded by the broadening of the operating point of the MOT and due the unknown residual Zeeman shift resulting from light pressure imbalances which push the MOT center into a region where the magnetic field is non-zero.

In the second case, we performed a magnetic-field-free measurement of the absorption of the atoms. For this, we imaged the shadow cast by the 85 Rb atomic cloud in a laser beam tuned to the "pump" transition with the MOT light and magnetic field extinguished. The absorption profile was integrated, and the total integrated signal is plotted as a function of the imaging light detuning. In the presence of an electric field, the maximum signal is seen to shift to lower frequencies (see Fig. 4.9). In addition, the transition is expected to broaden due to the broken degeneracy of the excited hyperfine manifold (see Fig. 4.7). However, the standard deviation of the spread in transition frequencies at 14 kC/cm is only 2 MHz (see the grey shaded region in Fig. 4.8 and therefore, the transition is only expected to broaden by approximately 10%. This is consistent with the observed widths in Fig. 4.9 - that is, a width of 4.2 MHz in the absence of an electric field and a width of 4.5 MHz at 14 kV/cm.



Figure 4.8: Expected dc Stark shift as a function of applied voltage. The solid line represents the mean shift assuming that the state population is evenly distributed among the m_F states. This is calculated by computing finding the weighted average of the five distinct transition frequencies (see Fig. 4.7). The grey shaded region is the standard deviation of this weighted average, and represents the expected broadening of the transition. The dashed lines are the maximum minimum shift assuming the atomic population is entirely in the $m_f = 0$ and $|m_f| = 3$ state respectively. The electric field at a given voltage is determined using Eq. 4.4 where K = .58 and $\eta = 1.6$. The black dots are the measured dc Stark shift at the given plate voltage. These measurements were taken using the smaller prototype plates. The error on the measured dc Stark shift is smaller than the size of the dots. Figure from [142].

One disadvantage of this method is that it requires multiple experimental cycles in order to determine the field strength (here, each integrated signal for a fixed detuning is a separate experimental run). This is in contrast to the first method, where the frequency of the pump beam can be swept from large to small detuning, while the MOT fluorescence is captured on a photodiode (or a camera with a very fast exposure time). For the majority of the data presented in the following sections, we were concerned with how the magnitude of the measured electric field varied with time. Therefore, the first method (i.e., quickly sweeping the MOT pump field) was used to measure the strength of the electric field.

When we first installed the prototype (small) plates into the system for testing we measured the dc Stark shift as a function of the applied potential difference. The result is



Figure 4.9: The influence of the dc Stark effect on the operation of the 85 Rb MOT (a and b) and on the integrated absorption of a laser beam by the cold 85 Rb atomic cloud in the absence of a magnetic field versus detuning (c and d). In (a) and (b), the MOT fluorescence is plotted versus the pump detuning. With no electric field present, the MOT operates for detunings as small as -2 MHz, whereas this transition point shifts down by more than 11 MHz with a field of 14 kV/cm applied by the plates. The dashed line indicates the fluorescence level consistent with no atoms trapped. In (c) and (d) the integrated absorption of a imaging beam (with the MOT light extinguished) is plotted as a function of the detuning of the imaging light from resonance. A repumping beam was simultaneously applied during the absorption measurement. The frequency at which the absorption is maximum shifts down by 13.9 MHz corresponding to the expected shift from the applied electric field of 14 kV/cm. The solid line is a fit to the data where the mean value for the fits are -0.6 MHz in (c) and -14.5 MHz in (d). Figure from [142].

shown in Fig. 4.8. Overlaid is the theoretical value of the mean, maximum and minimum expected dc Stark shifts given the expected electric strength at each potential difference using Eq. 4.4 where K = .58 and $\eta = 1.6$. In this case, it is interesting to note that the electric field (and thus, the dc Stark shift) scaled as expected with the applied potential difference. This indicates that there is no shielding mechanism that turned on at large field strengths. This observation is extremely different then what we observed when we installed the larger field plates. The next section discusses these observations.

4.3 Field Shielding and Trap Loss

When we tried to apply large voltages, corresponding to fields in excess of 15 kV/cm, we noticed a large loss of atoms from the MOT and ODT. This loss was the primary reason why we could not verify fields larger than 18 kV/cm using *in situ* dc Stark measurements. In addition, we observed the decay of the electric field strength over time while the plates were held at a high voltage, as well as a residual field that remained after the plates were grounded. We believe the bulk of these effects were due to field emission of electrons within the vacuum from the support rod on the beam shield. Our observations suggest that it is critical to ensure that the vacuum chamber near the field region is free of any charge sources.

4.3.1 Electric Field Shielding

Initially, we studied the reduction of the electric field due to shielding as a function of the time the plates were connected to the high voltage supplies. We first grounded one plate and applied either a positive or negative bias voltage of 40 kV to the other plate. The behavior shown in Fig. 4.10 suggests that the applied voltage is shielded by the movement of free charges and the number of these charges, and thus the extent of the shielding, is influenced by the polarity of the bias voltage as well as the choice of which plate is energized and which is grounded. Based on the data, we believe that the free charges responsible for this shielding behavior are primarily electrons produced by field emission of grounded metal parts within the chamber. For sufficiently high voltages, we believe that these free electrons can be accelerated to energies high enough to produce, upon collision with the cell walls, secondary positive ions that can also migrate and lead to shielding.



Figure 4.10: The measured electric field strength at the center of the cell versus the time the plates are kept energized. In all four cases, one plate is biased at either ± 40 kV, while the other plate is grounded. The low initial value and rapid reduction in the voltage occurs when the top plate is biased with ± 40 kV (red squares). We note that the top plate is close to the metal support of the beam shield, and this behavior suggests that field emission of electrons is responsible for the rapid build-up of shielding charges. In the other cases, where the field emission rate of electrons should be lower, we observe a slower and less complete shielding of field at the center of the cell. Figure from [142].

Fig. 4.10 shows the electric field strength measured some time after the plates were connected to the high voltage supply. Each data point is an average of four measurements. In order to minimize the effects of accumulated charges from previous measurements, the plates were run with the opposite polarity between each measurement, and we waited approximately 20 minutes before starting a data run for the next time in the series.

When the upper plate is positively biased, the shielding is the most rapid and dramatic. This large and rapid shielding is in contrast to the moderate and slower shielding in all other configurations even when the lower plate is positively biased (with the upper plate grounded). We believe that this asymmetry is due to the atomic beam shield (see Fig. 4.6) which has a metal support rod that runs along the top of the cell. This support rod is made from stainless steel and is grounded by virtue of its contact with a CF flange that also supports the lithium oven. Moreover, this rod was within a few cm from the conductive
layer inside the top electrode. A large positive voltage applied near the grounded support rod is expected to lead to a much larger electron field emission than an equally large negative voltage.

We also observed shielding in the other configurations including those with a negative bias. Any electrons on the surface or shallowly embedded inside the quartz cell wall will be accelerated away towards the grounded support rod or towards the opposite grounded plate when a negative bias is applied to a plate. These electrons will acquire a considerable kinetic energy and could produce secondary positive ions when they impact the opposite cell wall or grounded support rod. These positive ions will be accelerated back towards the negative plate and will also create secondary electrons when they impact the cell wall. We believe that this process is what leads to more electric field shielding for longer "on times". Based on the shielding behavior, the rates of secondary ion and electron production appear to be similar for the other three configurations. In summary, the shielding behavior appears to be distinct in the case when the upper plate is positively biased and field emission of electrons from the grounded support rod is most probable.

The electric field plates were also operated with a positive bias on one plate and a negative bias on the other. Figure 4.11 shows the field strength as a function of time when the total potential difference is 40 kV and 60 kV for either field polarities. Even when the total potential difference is the same as in Figure 4.10 where only one plate is biased, the field decay as a function of time is much weaker. Only when the total potential difference is increased to 60 kV (such that each plate is now biased with ± 30 kV) does the shielding become significant. This behavior continues to suggest that the shielding behavior is most dependent on the bias of the top plate (strongest when large and positive) and more weakly dependent on the total potential difference between the two plates.

To simulate using the plates as part of an experiment that requires multiple repeated runs, we measured the field strength as a function of the run number with total potential difference of 40 kV. In this case, the expected electric field at the center of the cell was 14.0 kV/cm. During each experimental cycle, the plates were energized for 500 ms, and the time between each run was approximately 20 s. The top panel of Fig. 4.12 shows the measured field strength after each run. It is evident that some of the shielding charges that are produced while the plates are on linger in the cell region during the time the plates are grounded leading to more and more free charges available for shielding and lower measured



Figure 4.11: The measured electric field strength at the center of the cell versus the time the plates are kept energized, in the case that one plate is positively biased and the other negatively biased. The top (bottom) panel is the case where the total potential difference between the plates is 60 kV (40 kV), such that each plate is biased at ± 20 kV (± 30 kV). The solid lines indicate the expected electric field for each case, and the dashed (black) and dot-dashed (red) lines indicate the measured residual field when the plates where turned off for an upwards (downwards) field.

fields for subsequent runs. The configuration with the upper plate positively biased (red squares) leads to a much larger number of shielding charges such that after the first run, with the plates on for just 500 ms, the field is already shielded to a value below 10 kV/cm. This is consistent with our observations in the case of a single positively biased top plate, shown in Fig. 4.10. By the 20th run, the measured field in this configuration was only 7.5 kV/cm - approximately half the expected field. When the upper plate is negatively biased and the lower plate positively biased (black circles), we observe, for the first few runs, a field magnitude very close to the expected field for the potential difference between the plates. However, with each subsequent run, the measured field is less as a result of the



Figure 4.12: The effects of shielding on the electric field strength over sequential experimental runs. The field is either kept in the same polarity for each run (top panel) or the polarity is switched between each run (bottom panel). In each run, the plates were energized for 500 ms before the field strength was measured. There is approximately 20 s between each run. The shielding observed in the top panel can be partially mitigated by alternating the polarity of the field between sequential runs. Figure from [142].

lingering of the shielding charges during the off time of the plates.

It is neither helpful to have an electric field that changes in strength during the course of an experiment, nor to have a field that is weaker than theoretical achievable value due to a large amount of shielding. We attempted to fix both problems by flipping the field direction between each experimental run. As shown in the bottom panel of Fig. 4.12, we found that after a few polarity changes, the field strength reached a steady state value of 12 kV/cm. This is larger than the maximally shielded value, though not as large as the expected field of approximately 14 kV/cm.

4.3.2 Residual Fields

Not only did free charges within the chamber act to shield the electric field during the time in which the plates were energized, they also resulted in a residual electric field that persisted within the vacuum cell after the electrodes were grounded.

As in the case of field shielding, the residual field was greatest when a large positive bias was applied to the top plate. For example, 250 ms after a 40 kV positive bias voltage was applied to the top plate (while keeping the bottom plate grounded), the measured electric field strength in the center of the cell was 9 kV/cm, and 250 ms later after the top plate was grounded, a 5 kV/cm residual electric field was observed in the center of the cell. Although we did not verify this, we assume that the residual electric field was oriented antiparallel to the expected field direction and was equal to the difference between the expected field magnitude and the measured field magnitude for each configuration. Figure 4.11 shows the residual field after the plates had been energized for 10 s in the case where a total potential difference of 40 kV or 60 kV was applied, using both a positive and negative bias. Notice that the residual field is larger for the case where the positively biased plate is at the top of the cell.

These observations suggest that the shielding charges that are created and accumulate while the plates are energized actually become embedded in the quartz cell walls such that they do not immediately leave when the plates are grounded. Nevertheless, we observed that it was possible to remove the residual field by running the electric field plates in the opposite polarity. This was the primary motivation for the construction of the high voltage switching network and appears to be critical when free charges (or, more importantly, a source of free charges) exist near the electric field region.

4.3.3 Trap Loss

In addition to the shielding effects, we also observed a loss of 85 Rb atoms held in the MOT when large voltages were applied to the plates. This observed atom loss was the primary technical limitation preventing us from measuring fields with a strength greater than 18 kV/cm. In addition, we also observed a loss of ⁶Li atoms held in the MOT and ODT. Since our interest was in applying large electric fields to ultra-cold atoms held in an ODT, we studied the loss of ⁶Li from the ODT.

As Fig. 4.13 shows, we found that the ⁶Li atom loss was larger, and became observable

at a smaller plate voltages, when using a positive bias voltage versus a negative bias voltage. Moreover, the loss due to the positive bias was larger when the upper plate was charged and the lower plate was grounded. This asymmetry is consistent with our field shielding observations where the accumulation of shielding charges is largest when the upper plate was positively biased. In the case of a negatively biased plate (with the other plate grounded), there is almost no difference in the atom loss associated with the two configurations. Along with the observations of field shielding, this suggests that collisions with accelerated electrons and secondary ions within the chamber are responsible for the atom loss from the ODT.



Figure 4.13: Loss of ⁶Li atoms from the ODT as a function of the negative (top panel) and positive (bottom panel) plate voltage with the second plate grounded. The atom loss is much stronger when a positive bias is used (especially when the top plate is positively biased) due to strong field emission of electrons of the support arm of the beam shield. The weaker loss when a negative bias is used is attributed to the acceleration of free electrons that already exist within the vacuum or that are partially embedded and subsequently ejected from the quartz cell during the on time of the plate bias. Figure from [142].

Although we did not see observable loss from the ⁶Li MOT when only one plate was charged even up to 40 kV (corresponding to an expected electric field of 15 kV/cm), we did observe ⁶Li atom loss from the MOT when both plates where charged (one with a negative bias, and the other with a positive bias) such that the total potential difference between the plates was larger than 50 kV. The loss in this configuration for both the MOT and the ODT is shown in Fig. 4.14. It is interesting to note that loss from the ODT for either field polarity is approximately the same in the case where only the bottom plate is positively biased while the top plate is held at ground (see Fig. 4.13) for the same plate voltage, even though the total potential difference is twice as large. Potentially, this suggests a modification of the field lines in the cell (because the beam shield is always held at ground) such that less of the field emitted electrons predominantly travel through a region of space that is not occupied by the ODT.

It is interesting to note that the loss from the ODT for the same potential bias of a single plate is approximately the same in the case where only the bottom plate is positively biased (see Fig. 4.13), even though the total potential difference is much greater. In addition, the loss is weaker in the case where the plates have an opposite bias when the top plate is positively biased. Potentially, this suggests a modification of the field lines in the cell (because the beam shield is always held at ground) such that less of the field emitted electrons do not travel through the ODT. In general, these loss observations indicate that the loss rate (similar to that for elastic collisions with neutral atoms [129]) is smaller from a deeper trap (for the same electric field plate potential difference), and suggests that not all collisions ionize atoms (which would result in trap loss regardless of the trap depth).

4.3.4 Tests with Small Prototype Plates

In our prototyping stage, some initial tests were conducted with smaller electric field plates. In particular, the conductive layer was constructed out of a much smaller ITO slide, measuring just under 3 cm \times 3 cm. Using these smaller plates, even at similar applied voltages and observed fields up to 15 kV/cm, we did not observe field shielding or the trap loss effects described above. This is clear in Fig. 4.8 where the measured electric field scales as expected with the applied voltage. In this case, we concluded that no shielding effects turn on as the voltage is increased. As both plates were centered on the quartz cell, we attribute this difference in behavior to the larger distance between the plates and the beam shield



Figure 4.14: Loss of ⁶Li atoms from the ODT (top panel) and MOT (bottom panel) as a function of the absolute value of the plate bias. In this case, one plate has a positive bias, and the other has a negative bias. Figure from [142].

support rod. We believe that this observation re-enforces the hypothesis that field emission of electrons from the top of the beam shield is largely responsible for the fast shielding of the electric field and the atoms loss. Therefore, in order to achieve large electric field strengths, commensurate with the potential difference applied across the plates, it is crucial to ensure that the region inside of the vacuum chamber near to the plates is free of any charge source (for example, grounded metal parts).

Chapter 5

Overview of ⁶Li₂ **System and Photoassociation**

The homonuclear Li_2 system provides a relatively easy (as compared to LiRb) system in which to build our knowledge base and techniques for making ultra-cold molecules. At the same time, ⁶Li pairs play a role in many-body physics of the BEC-BCS crossover regime, and can be used to improve our understanding of coherent processes with respect to atom-molecule dark states. The broad Feshbach resonance in ⁶Li allows for very efficient evaporation in ODTs from which we can access many different regimes of interest in ultracold physics, such as weakly or strongly interacting degenerate Fermi gases, to molecular BECs and BCS pairs.

5.1 Introduction to ⁶Li and ⁶Li₂ System

In the absence of a magnetic field, the $2^2 S_{1/2}$ ground state of ⁶Li has two hyperfine levels (f = 1/2 and f = 3/2) separated by approximately 228 MHz. In the presence of a magnetic field, the spin dependent part of the single atom Hamiltonian is

$$H_{\rm int} = a_{\rm hf} \left(\vec{s} \cdot \vec{i} \right) + \vec{B} \cdot \frac{2\mu_e \vec{s} - \mu_N \vec{i}}{\hbar}, \qquad (5.1)$$

where the first term represents the atomic hyperfine interaction whose strength is governed by the atomic hyperfine constant $a_{\rm hf}$. In the case of the $2^2 S_{1/2}$ ground state of ⁶Li, $a_{\rm hf} = a_{2\rm S} \approx 152.2$ MHz (see Section 2.1.1 and Table 2.1). The second term represents the Zeeman interaction, which can be treated as a perturbation to the system when it is much smaller than the hyperfine interaction. This occurs for $B \ll a_{2\rm S}/\mu_e \approx 10$ G, the so called "low field limit"⁹⁵.

⁹⁵For ⁶Li and most of the alkali atoms, $\mu_e \gg \mu_N$.

The six Zeeman sublevels from the two ground hyperfine states in ⁶Li (two from the $f = \frac{1}{2}$ manifold and four from the $f = \frac{3}{2}$ manifold) are often labeled as states $|1\rangle$ to $|6\rangle$ in order of increasing energy, as shown in Fig. 5.1. At low fields the Zeeman states can be written in the hyperfine basis, where the states are labeled by $|f, m_f\rangle$. However, at large magnetic fields when the Zeeman splitting is comparable to (or larger than) the hyperfine splitting, the hyperfine coupling is broken by the external magnetic field, and f is no longer a good quantum number. In this case, the atoms are treated as being in a pure product state basis labeled by $|i, m_i\rangle |s, m_s\rangle$. In general (that is, at any magnetic field) the eigenstates of Eq. 5.1 can be written as a linear superposition of the $|i, m_i\rangle |s, m_s\rangle$ states in the form [143]

$$c_{-\frac{1}{2}} \left| m_s = -\frac{1}{2}, m_i = m_f + \frac{1}{2} \right\rangle + c_{\frac{1}{2}} \left| m_s = \frac{1}{2}, m_i = m_f - \frac{1}{2} \right\rangle,$$
(5.2)

where s = 1/2 and, for ⁶Li, i = 1. Each of the six eigenstates can be written in the form of Eq. 5.2 where m_f takes on the six allowed values from the projection of f = 1/2 and f = 3/2 onto the magnetic field axis [143]. This implies that, in general, only the total spin projection m_f is a good quantum number. Table 5.1 summarizes the quantum numbers associated with each of the six states in the low field and high field regimes.

State Label	High Field $ m_i, m_s\rangle$	Low Field $ f, m_f\rangle$
$ 1\rangle$	1,-1/2 angle	$ 1/2,1/2\rangle$
$ 2\rangle$	0,-1/2 angle	$\left 1/2,-1/2 ight angle$
$ 3\rangle$	-1,-1/2 angle	$ 3/2, -3/2\rangle$
$ 4\rangle$	$ -1, 1/2\rangle$	$ ^{3/2}, -^{1/2}\rangle$
$ 5\rangle$	0,1/2 angle	$ 3/2, 1/2\rangle$
$ 6\rangle$	$ 1,1\!/2 angle$	$ 3/2,3/2\rangle$

Table 5.1: State labels for the six Zeeman sublevels in the ground ${}^{2}S_{1/2}$ manifold of ⁶Li. Note that i = 1, s = 1/2, and for the ground state l = 0. The high field limit is valid for $B \gg 10$ G.

In our experiment, the three states of most interest are the states which, at high magnetic field, make up the $m_s = -1/2$ manifold. The states $|1\rangle$ and $|2\rangle$, which correspond to the two degenerate spin projections of the f = 1/2 hyperfine level at 0 G, are the states initially trapped in the ODT. The third state, $|3\rangle$ is often used in RF spectroscopy at high magnetic



Figure 5.1: The six Zeeman states corresponding to the two ground hyperfine states in ⁶Li. At large magnetic fields, f is no longer a good quantum, and the states are labeled by $|i, m_i\rangle |s, m_s\rangle$, see Table 5.1. As shown, the six Zeeman sublevels are often labeled as states $|1\rangle$ to $|6\rangle$ in order of increasing energy. In our experiment, ⁶Li atoms are prepared in the two lowest hyperfine states $|1\rangle$ and $|2\rangle$.

fields, or experiments involving three-component Fermi gases [144]. The general form of these three states, following from Eq. 5.2 are [143]

$$|1\rangle = \sin\theta_{+} \left|\frac{1}{2}; 0\right\rangle - \cos\theta_{+} \left|-\frac{1}{2}; 1\right\rangle$$
(5.3)

$$|2\rangle = \sin\theta_{-} \left|\frac{1}{2}; -1\right\rangle - \cos\theta_{-} \left|-\frac{1}{2}; 0\right\rangle$$
(5.4)

$$|3\rangle = \left|-\frac{1}{2}; -1\right\rangle \,, \tag{5.5}$$

where

$$\sin \theta_{\pm} = \frac{1}{\sqrt{1 + (Q^{\pm} + R^{\pm})/2}} \tag{5.6}$$

$$Q^{\pm} = \frac{(\mu_N + 2\mu_e)B}{a_{\rm hf}} \pm \frac{1}{2}$$
(5.7)

$$R^{\pm} = \sqrt{(Q^{\pm})^2 + 2} \,. \tag{5.8}$$

When B = 0 G, it can be seen that $\sin \theta_+ = \cos \theta_- = \sqrt{1/3}$ and $\cos \theta_+ = \sin \theta_- = \sqrt{2/3}$, while at high magnetic fields (satisfying $B \gg a_{2S}/\mu_e$) $\sin \theta_{\pm} = 0$ and $\cos \theta_{\pm} = 1$. Note that, using the appropriate Clebsh-Gordan coefficients, the eigenstates in Eq. 5.3–5.5 can be written in the $|f, m_f\rangle$ basis, which are good quantum numbers at small magnetic fields.

5.1.1 Two-Atom Scattering State

Most relevant to much of the discussion in this chapter is not the uncoupled free atom states, but rather the two-atom scattering state. At low magnetic fields (typically $B \approx 0$ G where we work with a weakly interacting Fermi gas) this scattering state acts as the initial state in our photoassociation (PA) experiments. At large magnetic fields, this two-atom scattering state is coupled to a bound state in the $X(1^1\Sigma_g^+)$ potential, resulting in a broad FR near B = 832 G. At these high fields, the dressed molecule state (which is a superposition of the v'' = 38 bound state in the $X(1^1\Sigma_g^+)$ potential and the two-atom scattering state) is the initial state for photoassociation. The details for the Feshbach resonance and scattering state at high fields is discussed in greater detail in Section 5.1.2.

In the ODT, we trap atoms in an incoherent mixture of the $|1\rangle$ and $|2\rangle$ states. At low magnetic fields, this is the only stable hyperfine mixture because it cannot decay through inelastic two-body collisions due to the conservation of m_f . At high magnetic fields, it is possible to create stable mixtures of the $|1\rangle$, $|2\rangle$ and $|3\rangle$ states. However, our photoassociation experiments to date have focused solely on $|1\rangle$ and $|2\rangle$ state mixtures. Therefore, the two-atom scattering that we will consider is a mixture of these two hyperfine states. Because the atoms are fermions, the two-atom scattering state must be antisymmetric, and therefore the incoming channel for two-atom scattering must be

$$|12\rangle = \frac{1}{\sqrt{2}} \left[|1\rangle_1 |2\rangle_2 - |2\rangle_1 |1\rangle_2 \right], \qquad (5.9)$$

where the subscripts label the first and second atom.

The scattering state in Eq. 5.9 is more illuminating when written in the $|S, m_S; I, m_I\rangle$ basis using Eqs. 5.3–5.5 (and the applicable Clebsh-Gordan coefficients). Here, $\vec{S} = \vec{s_1} + \vec{s_2}$ and $\vec{I} = \vec{i_1} + \vec{i_2}$ are the total electronic and nuclear spin respectively. Note that the total electronic spin can take on two possible values (S = 0, 1) which represent a collisional state that has singlet (S = 0) and triplet (S = 1) character. Written in this basis, the scattering state is [143]

$$|12\rangle_{B} = \sin\theta_{+}\sin\theta_{-}|1,1;1,-1\rangle + \sin\theta_{+}\cos\theta_{-}\left(\sqrt{\frac{1}{3}}|0,0;0,0\rangle - \sqrt{\frac{2}{3}}|0,0;2,0\rangle\right) \quad (5.10)$$

$$+\cos\theta_{+}\sin\theta_{-}\left(\sqrt{\frac{1}{3}}|0,0;0,0\rangle + \sqrt{\frac{1}{6}}|0,0;2,0\rangle - \sqrt{\frac{1}{2}}|1,0;1,0\rangle\right)$$
(5.11)

$$+\cos\theta_{+}\cos\theta_{-}|1,-1;1,1\rangle$$
 (5.12)

At B = 0 (where $\sin \theta_+ = \cos \theta_- = \sqrt{1/3}$ and $\cos \theta_+ = \sin \theta_- = \sqrt{2/3}$), the two-atom scattering state reduces (quite nicely) to

$$|12\rangle_{B=0} = \sqrt{\frac{2}{9}} \left(|1,1;1,-1\rangle + |1,-1;1,1\rangle - |1,0;1,0\rangle\right) + \sqrt{\frac{1}{3}} \left|0,0;0,0\rangle , \qquad (5.13)$$

which has both triplet (first term) and singlet (second term) character.

Foreshadowing the labeling of the ⁶Li₂ molecular states (see Section 5.1.4), it is useful to once again rewrite the scattering state in Eq. 5.13, this time in the molecular basis $|NSIJF\rangle$ where N is the nuclear orbital angular momentum, $\vec{J} = \vec{N} + \vec{S}$ is the total angular momentum apart from the nuclear spin (recall that L = 0 for the ground state of ⁶Li), and $\vec{F} = \vec{J} + \vec{I}$. At the temperatures where photoassociation is performed in our system (typically < 2 μ K), p-wave (and higher-order) collisions are greatly suppressed. Therefore, the initial two-atom scattering state has N = 0, which corresponds to an s-wave collision. Although s-wave collisions are disallowed in a spin polarized fermionic system due to the Pauli-exclusion principle, they are permissible using the $|12\rangle$ hyperfine mixture. In this molecular basis, the scattering state at 0 G is

$$|12\rangle_{B=0} = \sqrt{\frac{2}{3}} |0, 1, 1, 1, 0\rangle + \sqrt{\frac{1}{3}} |0, 0, 0, 0, 0\rangle , \qquad (5.14)$$

which follows directly from Eq. 5.13 and the appropriate Clebsh-Gordan coefficients. The value of F in both admixture states is constrained to be F = 0 due to symmetry considerations. That is, states with a total spin $(\vec{G} = \vec{f_1} + \vec{f_2})$ of $G = f_1 + f_2, f_1 + f_2 - 2, ...$ are symmetric while states with $G = f_1 + f_2 - 1, f_1 + f_2 - 3, ...$ are antisymmetric [89]. In order that the scattering state be antisymmetric, the total spin G must be antisymmetric because in an s-wave collision (for which N = 0) the spatial part of the wavefunction is, by definition, symmetric. For atoms in the $|1\rangle$ and $|2\rangle$ state, $f_1 = f_2 = 1/2$ and this therefore restricts the total spin to G = 0 (the other possibility from angular momentum addition, G = 1, is symmetric). For this scattering state, since N = L = 0, the total spin G is the same as F. The details of the symmetry considerations for the molecular states are discussed in greater detail in Section 5.1.4.

At high magnetic fields (satisfying $B \gg a_{2S}/\mu_e$) where $\sin \theta_{\pm} = 0$ and $\cos \theta_{\pm} = 1$, the two-atom scattering state in Eq. 5.10 written in the $|S, M_S; I, M_I\rangle$ basis is

$$|12\rangle_B = |1, -1; 1, 1\rangle . \tag{5.15}$$

The pure triplet character of this two-atom scattering state can be understood because the uncoupled free atom states ($|1\rangle$ and $|2\rangle$) have the same spin projection ($m_{s_1} = m_{s_2} = -1/2$), and only vary in the nuclear spin projection. Therefore, the total spin of this spin polarized ensemble must be S = 1. In the molecular basis $|N, S, I, J, F\rangle$, the scattering state at large magnetic fields is

$$|12\rangle_B = \sqrt{\frac{1}{6}} |0, 1, 1, 1, 2\rangle - \sqrt{\frac{1}{2}} |0, 1, 1, 1, 1\rangle + \sqrt{\frac{1}{3}} |0, 1, 1, 1, 0\rangle , \qquad (5.16)$$

where $m_F = 0$ for all three states because $m_S + m_I = 0$. However, this scattering state is not the actual eigenstate at high magnetic field because of coupling to other states. In ⁶Li, two *s*-wave Feshbach resonances occur for the $|1\rangle$ and $|2\rangle$ state mixtures due to a coupling of the scattering state with two bound states in the $X(1^1\Sigma_g^+)$ potential. The coupling of the scattering state with the bound molecular state modifies the initial state used in photoassociation. It's important to note that the entrance channel state is not a single state, but rather a continuum of states that differ in the relative momentum of the colliding atomic pair. The origins and implications of these Feshbach resonances are discussed in the following section. Although the two-atom scattering state exists in the continuum of the $2^2S_{1/2} + 2^2S_{1/2}$ interatomic potential, the energy of the initial state differs from the asymptotic energy of the potential (from which the binding energy of the bound states are defined). In the absence of magnetic field, the energy of the f = 1/2 hyperfine level is lower than the asymptotic energy by (see Eq. 5.1)

$$\Delta E = a_{\rm hf}(\vec{s} \cdot \vec{i}) = \frac{a_{2\rm S}}{2} [f(f+1) - i(i+1) - s(s+1)] = -a_{2\rm S}.$$
(5.17)

Given this, the initial unbound two-atom scattering state is $-2a_{2S}$ below the hyperfine center of gravity of the $2^2S_{1/2} + 2^2S_{1/2}$ threshold. The energy of the hyperfine center of gravity corresponds to the same energy as the $2^2S_{1/2} + 2^2S_{1/2}$ asymptotic energy. In the presence of a magnetic field, the scattering state energy is further modified by the Zeeman shift of the $|1\rangle$ and $|2\rangle$ levels. This energy shift has been calculated, and is shown (as a function of magnetic field) in Fig. 5.2. Note that this energy shift means that the binding energy of the molecular state cannot be inferred directly from the photoassociation laser frequency. In the case of the excited states, the binding energy is computed by adding $2a_{2S}$ to the D₁ transition energy [145] and subtracting the measured photon energy for the PA loss feature. For the ground states, the binding energy is computed by adding $2a_{2S}$ to the difference in photon energy between the two PA lasers at the frequencies which correspond to the two-photon resonance.

5.1.2 s-wave Feshbach Resonances in the $|12\rangle$ Hyperfine Mixture

This section introduces the basic physics of FRs and some of the more important and relevant properties of the resonances and the associated Feshbach molecules. Following this, the details of the *s*-wave FRs in the $|12\rangle$ hyperfine mixture and the resulting modifications to the initial photoassociation state $|a\rangle$ are discussed. More detailed information regarding Feshbach resonances can be found in two excellent reviews by Chin et al. [10] and Julienne et al. [146]. In addition, there are many useful references which discuss the specifics of Feshbach resonances in the Li system [67, 70, 143, 147, 148, 149, 150].

Feshbach resonances in ⁶Li have been very well studied experimentally, starting with the measurement of the scattering length zero crossing near 528 G in 2002 [137]. This was closely followed by a demonstration of magnetic field control of elastic scattering [151]



Figure 5.2: Magnetic Field dependence (solid lines) of the $|1\rangle$ and $|2\rangle$ states. The dashed line is a sum of the energies of the $|1\rangle$ and $|2\rangle$ states, and represents the energy difference between the initial unbound two-atom scattering state and the hyperfine center of gravity of the $2S_{1/2} + 2S_{1/2}$ threshold. The energy of the hyperfine center of gravity corresponds to the same energy as the $2S_{1/2} + 2S_{1/2}$ asymptotic energy. This energy must be accounted for in the determination of the binding energies of the bound molecular states.

and a measurement of the interaction energy [152] near the s-wave Feshbach resonance at 832 G. Shortly after, three groups reported the conversion of a atomic Fermi gas to a stable molecular Bose gas [58, 59, 60]. Finally, RF spectroscopy on weakly bound molecules was used to precisely determine the Feshbach molecule binding energy in 2005 [153] and to precisely characterize the Feshbach resonance in 2013 [154]. For mixtures of the $|1\rangle$ and $|2\rangle$ states, there also exists three p-wave resonances between 150 and 220 G and a narrow s-wave resonance near 543 G, which are discussed in [155].

Feshbach resonances can be understood by considering a scattering event with two channels⁹⁶: the open (or entrance channel) of the two colliding atoms, and a closed channel which represents a molecular potential that can support bound states at energies near the

 $^{^{96}}$ The internal states of a particle in the initial (before) and final (after) scattering states are known as a channel. Since atoms have internal structure, the initial and final scattering channels can, in theory, be different.



Figure 5.3: Two channel model of a Feshbach resonance. $V_{bg}(R)$ represent the potential of the two colliding particles, with collisional energy E. $V_c(R)$ represents an molecular state potential which supports a low energy bound state at an energy E_c , near the collisional energy. If the two channels have different magnetic moments, the energy difference E- E_c can be tuned with a magnetic field. In the case of the *s*-wave resonance in ⁶Li, the entrance channel near the resonance is a two-atom scattering state of nearly pure triplet character, and the closed channel the ground singlet potential. At zero magnetic field, the entrance and closed channel asymptotes are degenerate. However, in the presence of an external magnetic field, the entrance channel shifts down in energy relative to the closed channel. Figure from [10].

collision energy (see Fig. 5.3). In the presence of an external magnetic field, the energy of the two atom system is modified. The size of the energy shift is governed by the Zeeman Hamiltonian, where the energy shift is proportional to the magnetic field strength and the magnetic dipole moment. If the two channels have different magnetic moments, then the energies of the two states will move relative to each other. In this way, an external magnetic field can be used to vary the energy difference between the collision energy and the energy of the weakly bound closed channel state. When the energy difference between the two states is small, coupling between the states can lead to strong mixing between the channels and new eigenstates with energies different from the uncoupled channel energies.

Physically, when the energy of the weakly bound state approaches the collisional energy

from below (above), the coupling pushes the energy of the new dressed colliding state upwards (downwards), which acts like an effective repulsive (attractive) interaction, and modifies the scattering length to be more positive (negative). A FR occurs when the magnetic field is tuned such that the weakly bound state is degenerate with the energy of the uncoupled entrance channel state. Near the FR, the scattering length (as a function of magnetic field) can be modeled as

$$a(B) = a_{\rm bg} \left(1 - \frac{\Delta}{B - B_0} \right), \tag{5.18}$$

where $a_{\rm bg}$ is the scattering length associated with the entrance channel far from the Feshbach resonance, Δ is the resonance width and is defined with respect to the zero crossing of the scattering length, which occurs at a magnetic field Δ away from the location of the FR B_0 .

Properties of Feshbach Resonances

In the discussion of Feshbach resonances and scattering physics, a useful set of quantities are the van der Waals length and energy [10]

$$R_{\rm vdW} = \frac{1}{2} \left(\frac{2\mu C_6}{\hbar^2}\right)^{1/4}$$
 and $E_{\rm vdW} = \frac{\hbar^2}{2\mu} \frac{1}{R_{\rm vdW}^2}$, (5.19)

which are related to the C_6 coefficient that characterizes the long range part of the interatomic potential. A closely related alternative length and energy scale is the mean scattering length and energy (introduced in [156]), where

$$\overline{a} = [4\pi/\Gamma(1/4)^2] R_{\rm vdW} = 0.955978 \dots R_{\rm vdW}$$
(5.20)

$$\overline{E} = \frac{\hbar^2}{2\mu\overline{a}^2} = 1.09422\dots E_{\rm vdW}, \qquad (5.21)$$

and $\Gamma(x)$ is the gamma function. Additionally, a dimensionless background scattering length can be defined by $r_{\rm bg} = a_{\rm bg}/\bar{a}$. Physically, $R_{\rm vdW}$ approximates the outer turning point for low *l* molecules, beyond which the wavefunction decays exponentially, and therefore characterizes extent of the vibrational motion (i.e., the "size" of the molecule). The exception is that of a universal "halo" molecules, which are discussed below. For ⁶Li: $C_6 = 1393.39$ a.u., $R_{\rm vdW} = 31.26a_0$ and $E_{\rm vdW} = 29.47$ mK or 614 MHz.

Near a FR, the coupling between the closed and entrance channel mixes the entrance

channel into the closed channel, forming a "dressed" state. In the limit that $a \gg \overline{a}$ and $|E_b| \ll E_{\rm vdW}$ (where $|E_b|$ is the binding energy of the weakly bound state responsible for the resonance), the physics takes on universal behavior. Here, the details of the interaction (for example, the C_6 coefficient that defines the long range part of the potential) are irrelevant. In this regime, the interaction is characterized solely by the scattering length a, and the binding energy of the (universal) dressed molecule state is simply

$$E_b = \frac{\hbar^2}{\mu a^2} \propto (B - B_0)^2 \,, \tag{5.22}$$

where μ is the reduced mass of the two atom system. Note that in this regime, the binding energy scales like the square of the magnetic field, rather than the linear scaling that exists far from resonance. These molecules form a quantum "halo" state, where the molecular wavefunction extends to distances well past $R_{\rm vdW}$.

Due to the mixing of the entrance channel into the closed channel, the dressed molecule eigenstate is a mixture of the closed and entrance channel

$$|\Psi_b\rangle = \sqrt{Z} |c\rangle + \sqrt{1-Z} |e\rangle , \qquad (5.23)$$

where Z defines the closed channel fraction.

A two-channel square well model (for details, see [10, 157, 158]) can be used to model the physics of FRs, and specifically the near-threshold bound and scattering states. This model is particularly useful because it is analytically solvable. With this, near the Feshbach resonance, where $B \to B_0$ and $a \to +\infty$, the closed channel fraction is [10]

$$Z = \frac{2}{s_{\rm res} r_{\rm bg}} \left| \frac{B - B_0}{\Delta} \right| \,, \tag{5.24}$$

where

$$s_{\rm res} = \frac{a_{\rm bg}}{\overline{a}} \frac{\delta \mu \Delta}{\overline{E}} \tag{5.25}$$

and $\delta \mu = \mu_e - \mu_c$ is the difference in the magnetic moment between the colliding atoms in the open channel and the magnetic moment of the weakly bound state in the closed channel.

The resonance strength $s_{\rm res}$ provides a convenient way to classify FRs into two different types: "narrow" resonances (where $s_{\rm res} \ll 1$) which are closed channel dominated, and "broad" resonances (where $s_{\rm res} \gg 1$) which are entrance channel dominated. It is important to note that the bound state is universal (that is, the binding energy is solely a function of the s-wave scattering length) only for $Z \ll 1$, when the closed channel fraction is small. From Eq. 5.24 it can be seen that $Z \ll 1$ when $|B - B_0| \ll s_{\rm res} r_{\rm bg}|\Delta|$. This implies that for entrance channel dominated resonances, the bound state is universal over a large fraction of the resonance width. Correspondingly, the bound state is universal over a small fraction of the resonance width for closed channel dominated resonances. Regarding the nomenclature "broad" and "narrow": although "broad" resonances often have a large resonance width and "narrow" resonances often have a small resonance width, this is not always the case⁹⁷. Therefore, the classification of resonances is best done using the resonance strength, rather than just the resonance width. Table IV in [10] provides a summary of the properties for select Feshbach resonances in both homonuclear and heteronuclear system. The properties Feshbach resonances in the $|12\rangle$ hyperfine mixture are also given in Table 5.2.

_	channel	B_0 (G)	l	Δ (G)	$a_{\rm bg}/a_0$	$\delta \mu / \mu_B$	$s_{\rm res}$	$r_{\rm bg}$
	$ 12\rangle$	834.1	s	-300	-1405	2.0	59	-47
	$ 12\rangle$	543.25.1	s	0.1	60	2.0	0.001	2.0
	$ 11\rangle$	159.14	p	—	—	2.0	_	_
	$ 12\rangle$	185.09	p	_	_	2.0	_	_
	$ 22\rangle$	214.94	p	_	_	2.0	_	_

Table 5.2: Properties of s and p-wave Feshbach resonances in ⁶Li for a hyperfine mixture of the $|1\rangle$ and $|2\rangle$ states. For p-wave resonances, several properties are not defined (indicated by a –). Numbers from [10].

Origin of the *s*-wave Resonances in ⁶Li

The origin of the s-wave Feshbach resonance in ⁶Li lies in a coupling between the least bound v'' = 38 level of the $X(1^{1}\Sigma_{g}^{+})$ potential, and the two-atom scattering state which, at high magnetic fields, has almost purely triplet character (see Eq. 5.14 and surrounding text). The least bound state in the $X(1^{1}\Sigma_{g}^{+})$ potential has a total nuclear spin of I = 0 or 2, a binding energy of approximately 1.38 GHz, and a vanishing magnetic moment near zero field (because S = 0). Thus, with increasing magnetic field, the energy of the entrance channel state relative to the closed channel varies with a slope of $dE/dB = -2\mu_{B}$ solely

 $^{^{97}}$ For example, the ⁷Li 737 G resonance where $s_{\rm res} = 0.8$, but $\Delta = -192.3~G~[10].$

due to the Zeeman shift of the energy of the two-atom scattering state⁹⁸.

Following the description of the Feshbach resonances given by Simonucci et al. [147], in the absence of any coupling between the closed and entrance channels the energy of the bound states crosses the threshold of the entrance channel at about 550 G (see Fig. 5.4). However, the hyperfine interaction (which is not diagonal in the $|S, m_S; I, m_I\rangle$ basis) induces a coupling between states with $\Delta I = \Delta S = 1$. In this case, these two states are the closed channel singlet states and the entrance channel scattering state. However, it is possible to write a linear combination of the two v'' = 38 singlet bound levels

$$|\Phi_{\rm U}\rangle = \frac{1}{3} \left(|0,0;0,0\rangle + 2\sqrt{2} |0,0;2,0\rangle \right) \,, \tag{5.26}$$

that completely decouples from the triplet state. The narrow s-wave resonance at 543 G is due a coupling of this state through a second order process to the entrance channel [67]. This state maintains its singlet character as it crosses the entrance channel threshold.

By virtue of orthogonality, the other linear combination is

$$|\Phi_{\rm C}\rangle = \frac{1}{3} \left(2\sqrt{2} |0,0;0,0\rangle - |0,0;2,0\rangle \right)$$
(5.27)

which couples to the triplet entrance channel and undergoes an avoided crossing. This coupling strongly modifies the character of this weakly bound state beyond the avoided crossing, and the state takes on nearly full triplet character. Above approximately 650 G, this state is a weakly bound halo molecule state (defined by Eq. 5.23) where $Z \ll 1$. The energy of this state moves almost parallel to the entrance channel, crossing the entrance channel threshold at the location of the broad *s*-wave resonance at 832 G (see inset in Fig. 5.4). Note that the triplet potential (due to the large background scattering length) is known to have a virtual state very near the threshold energy⁹⁹. It is to this virtual state energy that the Feshbach molecule state asymptotically tends to above the FR at 832 G (see Fig. 5.4).

⁹⁸Note that $\mu_B = 9.274 \times 10^{-24} \text{ J/T} = 1.3996 \text{ MHz/G}.$

⁹⁹Marcelis et al [150] give an excellent description of a virtual state: "The energy associated with [a] virtual state is negative, but there is no proper physical bound state associated with this energy. A virtual state can be regarded as a nearly bound state that behaves much like a real bound state in the inner region of the interaction potential. Only in the asymptotic region $(r \to \infty)$ does the virtual state discover it does not quite fit to the size of the interaction potential, and the virtual state exponentially explodes". One has to feel some empathy for the poor state that, as far as I know, never did anything to deserve its fate.



Figure 5.4: Origin of s-wave Feshbach resonance in ⁶Li. In the absence of coupling, the closed channel v'' = 38 level of the $X(1^{1}\Sigma_{g}^{+})$ state (dashed blue line) crosses the threshold energy of the entrance channel two-atom scattering state (black dotted line) near 550 G. When coupling between the two channels is turned on via the hyperfine interaction, one linear combination of the singlet states decouples from the entrance channel (i.e., still follows the blue dashed line), and is responsible for the narrow s-wave resonance at 543 G. The other orthogonal superposition state couples to the triplet entrance channel and undergoes an avoided crossing (solid red line). The inset shows that the energy of the Feshbach molecule state (solid red line) tends towards the energy of the triplet virtual state (long dashed green line), crossing the entrance channel threshold energy (black dotted line) near 832 G, resulting in the broad Feshbach resonance at this magnetic field. Figure from [147].

In the context of photoassociation near the broad Feshbach resonance (at magnetic fields above 650 G), there are two possible initial states to consider. The first is the two-atom scattering states, which is an entrance channel state with momentum k that has nearly pure triplet character (see Eq. 5.14). The second is the weakly bound dressed Feshbach molecule state which, written in the $|S, M_S; I, M_I\rangle$ basis, is

$$\begin{aligned} |\Psi_b\rangle &= \sqrt{Z} |c\rangle + \sqrt{1-Z} |e\rangle \\ &= \sqrt{Z} |\Phi_{\rm C}\rangle + \sqrt{1-Z} |e\rangle \\ &= \frac{\sqrt{Z}}{3} \left(2\sqrt{2} |0,0;0,0\rangle - |0,0;2,0\rangle \right) + \sqrt{1-Z} |1,-1;1,1\rangle . \end{aligned}$$

$$(5.28)$$

In the molecular basis $|NSIJF\rangle$, the Feshbach molecule state can be written as

$$|\Psi_b\rangle = \frac{\sqrt{Z}}{3} \left(2\sqrt{2} |00000\rangle - |00200\rangle \right) + \sqrt{1-Z} \left(\sqrt{\frac{1}{6}} |01112\rangle - \sqrt{\frac{1}{2}} |01111\rangle + \sqrt{\frac{1}{3}} |01110\rangle \right)$$
(5.29)

where the entrance channel state in this basis is from Eq. 5.16. The closed channel fraction Z is much less than one for fields above 650 G. This fraction has been measured by Partridge et al [64] and our group [98, 159], with both results closely matching theoretical predictions done by Romans and Stoof [160]. The measured and theoretical value for Z are shown in Fig. 5.5.

There is a weak hyperfine coupling (and therefore a weak mixing) between the continuum states and the dressed bound state. Therefore, it is possible to photoassociate to both the $A(1^{1}\Sigma_{u}^{+})$ and $c(1^{3}\Sigma_{g}^{+})$ potential from either the scattering state or from the Feshbach molecule state. Experimentally, we can determine whether the initial state is the loosely bound Feshbach molecule, or a thermal ensemble (i.e., the two-atom scattering state) by the varying the final temperature of the ensemble, and the magnetic field at which we evaporate. The creation of Feshbach molecules (and the following evaporation to degeneracy), and the creation of BCS pairs (on the high magnetic field side of the FR) are discussed in the next section.

5.1.3 Degenerate Gases

The broad s-wave Feshbach resonance acts as an excellent tool to control the s-wave scattering length from large and positive on the low magnetic field size to large and negative on the high magnetic side. In the fermionic ⁶Li system, a > 0 allows for the creation of weakly bound Feshbach molecules which have bosonic character, and the ability to create



Figure 5.5: Closed channel fraction (Z) of Feshbach molecule state. Red squares are data from Partridge et al. [64], and black circles are data from our experiment [98, 159]. The dashdotted line shows theoretical predictions done by Romans and Stoof, digitized from [160]. The grey region corresponds to the strongly interacting regime where $k_{\rm F}|a| > 1$, which occurs near the Feshbach resonance at 832 G. This magnetic field is indicated by the vertical dashed line.

an molecular Bose-Einstein condensate (mBEC). When a < 0 on the high magnetic field side, cooling below the critical temperature allows for the formation of BCS-like pairs. In both cases, the system is in the strongly interacting regime. It is also possible to create a weakly interacting degenerate Fermi gas where a is small (or zero). This is often done at a zero crossing of the *s*-wave scattering length at B = 527.5 G. However, degeneracy can also be achieved at (or near) 0 G, which is useful because it allows for the elimination of magnetic fields (and the associated systematic shifts on the photoassociation resonances). In our experiment, we have the ability to create any of the above systems. They are briefly discussed below, and more detail can be found in PhD thesis of M. Semczuk [98].

Near the Feshbach resonance, the binding energy of the Feshbach molecule is a function of the *s*-wave scattering length,

$$E_{\rm b} = \frac{\hbar^2}{2ma^2} , \qquad (5.30)$$

and is typically on the order of a few tens of kHz at the fields of interest. For example, at 770 G (where the scattering length is assumed to be 200 nm), the binding energy is

approximately 40 kHz or 2 μ K [138].

A convenient method of forming Feshbach molecules in ⁶Li is atom-molecule thermalization, which relies on three-body recombination. This method was employed by S. Jochim et al in 2003 to create a pure gas of optically trapped molecules [59] and soon after an mBEC of ⁶Li₂ molecules in the group of Grimm [161] and Ketterle [138]. In this method, three free atoms collide to form a bound Feshbach molecule, and the remaining free atom carries away the binding energy in the form of kinetic energy. A simple description of this process assumes that the three body recombination rate scales like the square of the total scattering cross section for a two body collision. In this case

$$\gamma_{3B} \propto \sigma_s^2 = \left(\frac{4\pi a^2}{1+k^2 a^2}\right)^2 ,$$
 (5.31)

where k is the wave number, given by

$$k = \frac{\sqrt{2mE}}{\hbar} \ . \tag{5.32}$$

It can be seen that in the low temperature limit $(k^2a^2 < 1)$ that $\gamma_{3B} \propto a^4$, while for higher equilibrium ensemble temperatures $(k^2a^2 > 1)$, $\gamma_{3B} \propto 1/k^4 \propto 1/T^2$. As might be expected, this simple model states that Feshbach molecule formation is enhanced close to the Feshbach resonance, and at lower temperatures¹⁰⁰. In fact, the statement can be made more explicit by requiring $k^2a^2 < 1$ for efficient molecule formation which, using Eq. 5.30, can be written as

$$\frac{k_B T}{E_b} < 1 \qquad \text{for efficient Feshbach molecule formation} . \tag{5.33}$$

The result follows from a balance between the three-body recombination process that forms molecules, and two-body dissociation processes that break the molecules. A more formal description of this atom-molecule conversion process is presented by Cheng Chin and Rudolf Grimm [164] which shows that for a non degenerate gas, the equilibrium between

¹⁰⁰It should be noted that the theoretical work of D.S. Petrov [162] and J.P. D'Incao and B.D. Esry [163] showed the relevant three body loss coefficient for a two component Fermi gas scaled like a^6 in the low temperature limit, rather than the a^4 scaling suggested by Eq. 5.31. Nevertheless, the conclusion that molecule formation is enhanced close to the Feshbach resonance and at low temperatures holds.

the phase space density of molecules ϕ_{mol} and atoms ϕ_{at} follows the relation

$$\phi_{\rm mol} = \phi_{\rm at}^2 \exp\left(\frac{-E_b}{k_B T}\right). \tag{5.34}$$

The Boltzmann factor is determined by the ratio of the binding energy of the Feshbach molecule E_b (which is negative on the low field side of the FR, as the Feshbach molecule is bound), and the thermal energy of the ensemble given by k_BT . This factor can greatly enhance the formation of molecules even for low atomic phase space densities, and is consistent with the statement in Eq. 5.33. However, this factor appears to suggest that molecule formation would be greatly enhanced at large E_b and should be largest in the limit that $E_b \to \infty$ (i.e., very far from the Feshbach resonance), where all atoms should accumulate in the molecule state. However, this argument neglects the effects of the energy released during the molecule formation process. This energy (equal to the binding energy of the molecule) heats the sample and reduces the atomic phase space density, which in turns reduces the molecular phase space density and thus the number of molecules that form.

This motivates striking a balance between using a magnetic field which corresponds to a small E_b and the achievable final ensemble temperature and atom/molecule number. Therefore, our recipe for Feshbach molecule formation is to cool a thermal ensemble of ⁶Li in an ODT at 754 G such that the condition in Eq. 5.33 can be satisfied given our final equilibrium temperature, which is on the order of 300 nK at the lowest temperatures we can achieve.

Molecular Bose-Einstein-Condensates

Since the Li_2 Feshbach molecule is bosonic, a mBEC is formed if the molecule density in the trap exceeds the critical density,

$$n_c = \frac{2.612}{\lambda_c^3} , \qquad (5.35)$$

where

$$\lambda_c^3 = \sqrt{\frac{2\pi\hbar^2}{mk_B T_c}} \ . \tag{5.36}$$

 T_c is the critical temperature,

$$k_B T_c = 0.94 \cdot \hbar \bar{\omega} N^{1/3} , \qquad (5.37)$$

which is related to the trapping potential through the mean trap frequency, $\bar{\omega} = [\omega_x \omega_y \omega_z]^{1/3}$ and the total molecule number N. Figure 5.6 shows an example of the trap temperature relative to the critical temperature during a standard evaporation ramp used to achieve a mBEC in our system, as well as the formation of an mBEC in our system, highlighted by the appearance of a bi-modal distribution, where the spatial width (in the absence of interactions) of the condensed fraction is determined by the trap geometry (i.e., the ground state wavefunction of the harmonic potential formed by the ODT).



Figure 5.6: Left: Atom number and temperature as a function of the optical dipole trap power during a standard evaporation ramp to form a mBEC, which happens when the ensemble temperature falls below the critical temperature (given by Eq. 5.37). The efficiency of the evaporation is characterized by a scaling law which depends on by $\eta = U_0/k_B T$ (the ratio of the trap depth to the ensemble temperature), see section 3.2. Right: Formation of an mBEC in our system, highlighted by the appearance of a bi-modal distribution. From top to bottom, the temperature of the cloud is T = 710 nK ($T/T_c \approx 1.2$), T = 230 nK ($T/T_c \approx 0.9$), T = 110 nK ($T/T_c \approx 0.8$), T = 65 nK ($T/T_c \approx 0.6$). Figure from [165].

Degenerate Fermi Gases and BCS Pairs

On the high magnetic field side of the FR, the Feshbach molecule state is unbound and therefore the system remains fermionic, forming a degenerate Fermi gas if the equilibrium temperature falls below the Fermi energy, which is given by

$$E_F = \hbar \bar{\omega} (6N)^{1/3} . \tag{5.38}$$

Unlike a bosonic system, no phase transition occurs unless an attractive interaction is present. It just happens that the high magnetic field side of the Feshbach resonance has a negative scattering length, corresponding to an attractive interaction. In this case, BCS-like pairs will form when the equilibrium temperature is below the critical temperature for pair formation,

$$T^* = 0.61T_F \exp\left(\frac{-\pi}{2k_F|a|}\right), \qquad (5.39)$$

where the Fermi wave number is related to the Fermi energy in the usual way (see Eq. 5.32). In the strongly interacting regime, where $|k_Fa| \gg 1$, the critical temperature for pair formation is simply related to the Fermi temperature. Following a similar evaporation as in the mBEC case (see Fig. 5.6), except at a different magnetic field (typically 840 G), we can form BCS pairs, which show the characteristic pairing gap in RF spectroscopy shown in Fig. 5.7).

At 0 G, the singlet s-wave scattering length is $a_S \approx 46a_0$ and the triplet s-wave scattering length is $a_T \approx -2160a_0$ [86, 135, 166], where $a_0 = 0.529$ Å is the Bohr radius. In this regime, $k_F|a| \ll 1$ (termed the "weakly-interacting" regime) and, although the critical temperature for BCS-like pair formation is extremely low (see Eq. 5.39), it is possible to cool to temperatures much lower than the Fermi temperature and achieve a degenerate Fermi gas. More information on the details of BCS pairing, the BEC-BCS crossover regime, and the relationship to superconductivity can be found the review by Chen et al. [167].

5.1.4 ⁶Li₂ Bound Molecular States

This section serves as an introduction to the state labeling and properties of the bound molecule states of a homonuclear molecule, as well as the selection rules which govern the photoassociation processes. The angular momentum coupling schemes vary from molecule to molecule, depending on the strength (and type) of the involved perturbations. For linear



Figure 5.7: Emergence of BCS Pairing signal in RF spectroscopy. Atoms in the $|2\rangle$ state are flipped to the $|3\rangle$ state by the application of an RF field at 81.34 MHz (which corresponds to a field of 839.2 G). Free $|2\rangle$ atoms undergo the transition at a zero offset, whereas an additional energy corresponding to the pairing gap must be added to flip those bound to a $|1\rangle$ state atom as a BCS pair. Figure from [165].

molecules these different cases are summarized by Hund's coupling cases, characterized by the choice of basis corresponding to the "good" (well-defined) quantum numbers. A more detailed discussion of the Hund's coupling cases can be found in many texts on molecular systems (for example, [168, 169, 170]). For diatomic molecules the most common are Hund's case (a) and (b), the latter being most applicable in the case of ⁶Li₂, and are discussed below.

Hund's Case (a)

In Hund's case (a), the total orbital angular momentum of the electrons in the unfilled orbital electrons $\vec{L} = \vec{l_1} + \vec{l_2}$, and the total spin $\vec{S} = \vec{s_1} + \vec{s_2}$ are strongly coupled to the internuclear axis¹⁰¹. In this case, the projection of \vec{L} (denoted by m_L) and \vec{S} (denoted by m_S) on the internuclear axis are well defined. To classify the electronic states of the molecule, these projections are typically labeled using the quantum numbers

$$\Lambda = |m_L|, \quad \Lambda = 0, 1, 2, \cdots, L \tag{5.40}$$

$$\Sigma = m_S, \quad \Sigma = S, S - 1, \cdots, -S.$$
(5.41)

The electronic state is classified by the absolute value of m_L because the energy of a particular m_L projection state does not depend on the direction of \vec{L} with respect to the electric field direction (that is, the internuclear axis). This is in contrast to the projection of m_S , where the energy of a particular m_S projection does depend on the orientation of \vec{S} with respect to the axial magnetic field (which results from the orbital motion of the electrons).

The total angular momentum (apart from nuclear spin) is

$$\vec{J} = \vec{N} + \Omega \hat{z} \,, \tag{5.42}$$

where \vec{N} is the rotational angular momentum of the nuclei perpendicular to the molecular axis and $\Omega = \Lambda + \Sigma$ is the projection of the total electronic angular momentum onto the internuclear axis. Therefore, in Hund's case (a), the set of good quantum numbers is $(n, J, S, \Lambda, \Sigma, \Omega)$ where *n* represents all other quantum numbers of the electronic and vibrational state.

Hund's Case (b)

In Hund's case (b), the total orbital angular momentum of all electrons \vec{L} is still strongly coupled to the internuclear axis, but the total spin \vec{S} is not. Formally, this is the case when the coupling of \vec{L} with the molecular axis is stronger than the coupling of \vec{L} with \vec{S} . This holds when $\Lambda = 0$ (i.e., the projection of the orbital angular momentum of the electrons along the internuclear axis is zero) and there is therefore no axial magnetic field to couple

¹⁰¹By "coupled strongly", one means that the individual coupling of \vec{L} and \vec{S} to the internuclear axis is larger than the direct coupling between \vec{L} and \vec{S} .

the total spin to the axis, or for molecules with small spin-orbit coupling (when $\Lambda \neq 0$). In this case, Σ and Ω are no longer good quantum numbers. Instead, Λ (the projection of \vec{L} on the internuclear axis) and the rotational angular momentum of the nuclei \vec{N} combine to form the angular momentum $\vec{K} = \vec{N} + \Lambda \hat{z}$, which couples to \vec{S} to form the total angular momentum (apart from nuclear spin)

$$\vec{J} = \vec{S} + \vec{K}$$
 where $\vec{K} = \vec{N} + \Lambda \hat{z}$. (5.43)

Therefore, in Hund's case (b), the set of good quantum numbers is (n, K, J, Λ) where n represents all other quantum numbers of the electronic and vibrational state.

Spin-Spin / Spin-Rotation and Hyperfine Structure

In the preceding discussion of the two Hund's cases, the assumption has been made that magnetic interactions involving the electron spin \vec{S} are perturbatively small. In addition, the fact that the atomic nuclei have a non-zero spin has been ignored. However, the magnetic interactions of the electron spin and the non-zero nuclear spin play a role in the energy structure of the molecules.

In particular, for ${}^{3}\Sigma$ states, where S = 1 and $\Lambda = 0$, a magnetic interaction arises between the spin magnetic dipole moments of the two unpaired electrons (the "spin-spin coupling"). The form of the spin-spin interaction is [170, 171, 172]

$$H_{\rm SS} = \frac{\mu_0}{4\pi} \left[\frac{\vec{u_1} \cdot \vec{u_2}}{r^3} - \frac{3(\vec{u_1} \cdot \vec{r})(\vec{u_2} \cdot \vec{r})}{r^5} \right]$$

$$= \frac{g_e^2 \mu_B^2 \mu_0}{4\pi} \left[\frac{\vec{s_1} \cdot \vec{s_2}}{r^3} - \frac{3(\vec{s_1} \cdot \vec{r})(\vec{s_2} \cdot \vec{r})}{r^5} \right]$$
(5.44)

where $\vec{s_1}$ and $\vec{s_2}$ are the spins of the individual electrons, g_e is the g-factor of a free electron, and r is the interelectronic distance¹⁰². As an order of magnitude estimate for the energy scale of the spin-spin interaction, using the typical internuclear Li-Li distances of 2-10 Å in Eq. 5.44 with $s_1 = s_2 = \hbar/2$ gives 50-500 MHz. However, it is clear from Eq. 5.44 that the strength of the interaction varies strongly with the size of the molecule, and is much stronger for more deeply bound vibrational levels. The spin-spin coupling can also be represented by a Hamiltonian with the form $\hat{H}_{SS} = 2\lambda_{\nu}[\hat{S}_z^2 - \hat{S}^2]/3$, where λ_{ν} is the spin-spin

 $^{^{102}}$ In truth, since the electron is not simply a point charge, r represents an average intelectronic distance.

coupling constant and represents the strength of the interaction [171, 172]. The subscript ν simply indicates that the value depends on the vibrational level. The value of this constant as function of internuclear distance has been calculated by B. Minaev [171], and takes on values between -650 MHz and -50 MHz for internuclear distances corresponding to 2 Å and 10 Å respectively.

A second magnetic interaction energy is due to a coupling between the total electron spin \vec{S} and the rotational motion of the nuclei \vec{N} . The interaction is of the form $\hat{H}_{\rm SR} = \gamma_{\nu} \vec{N} \cdot S$, where γ_{ν} represents the strength of the spin-rotation coupling [170, 171, 172]. In general, the strength of the interactions that involve only the electron spin are larger than interactions that involve the nucleus due to difference in the electron and proton mass. In the case of ${}^{6}{\rm Li}_{2}$, the spin-rotation interaction is approximately an order of magnitude smaller than the spin-spin coupling, with γ_{ν} on the order of -15 MHz (see [84] and the spectroscopy presented in Section 6.1.1).

These interactions break any degeneracy that exists in the states labeled by $\vec{J} = \vec{N} + \vec{S}$. Therefore, each sublevel with a given $N(\geq S)$ consists of 2S + 1 sublevels, and the number of sublevels is equal to the spin multiplicity. However, for N < S, the number of sublevels is equal to the rotational multiplicity (2N + 1). Since the electron spin of ⁶Li is s = 1/2, the total spin of ⁶Li₂ is either S = 0 or S = 1. For the singlet molecular potentials, there is no spin-spin or spin-rotation coupling. For the triplet molecular potentials, in the case where the spin-spin and spin-rotation couplings are small relative to the rotational constant $(B_{\nu} >> |\lambda_{\nu}|, |\gamma_{\nu}|)^{103}$ the rotational energy is given by [168, 169, 173]

$$E_{J=N+1} = B_{\nu}N(N+1) - \frac{2N+2}{2N+3}\lambda_{\nu} + \gamma_{\nu}(N+1)$$

$$E_{J=N} = B_{\nu}N(N+1)$$

$$E_{J=N-1} = B_{\nu}N(N+1) - \frac{2N}{2N-1}\lambda_{\nu} + \gamma_{\nu}N.$$

(5.45)

As the spin-spin coupling is much stronger than spin-rotation coupling $(|\lambda_{\nu}| \gg |\gamma_{\nu}|)$, the energy ordering results from the λ_{ν} terms. For the three states in Eq. 5.45, the ordering (in energy from low to high) is (J = N), (J = N + 1), (J = N - 1) because λ_{ν} is negative [84]. For the $a(1^{3}\Sigma_{u}^{+})$ potential, it is expected that the spin-spin coupling term is also negative and of similar magnitude [171], therefore it is likely that the ordering of the levels is the

¹⁰³This condition is easily satisfied since $B_{\nu} > 1$ GHz for even the highest lying vibrational levels.

same as in the $c(1^{3}\Sigma_{q}^{+})$ potential.

In addition to rotational perturbations, the fact that the nuclear spin of atomic ⁶Li (i = 1) is not zero gives rise to hyperfine structure, due to interactions between the nuclear and electronic magnetic moments. In this case, the total angular momentum (which now includes nuclear spin) is defined as

$$\vec{F} = \vec{J} + \vec{I}. \tag{5.46}$$

Term Symbols and Symmetry

Molecular potential energy curves are labeled by the molecular term symbol

$$^{2S+1}\Lambda^{+/-}_{\Omega,(g/u)},$$
 (5.47)

where $\vec{S} = \vec{s_1} + \vec{s_2}$ is the total electronic spin quantum number. The quantum number Ω is dropped for molecules which are characterized by Hund's case (b), because Ω is not well defined. Similar to the atomic spectroscopic notation, the value of the quantum number Λ is given a corresponding Greek letter. Potentials with $\Lambda = 0$ are called Σ states¹⁰⁴ and states with $\Lambda = 1, 2, 3$ are called Π , Δ , and Φ states respectively. In addition, electronic potential terms are often preceded by a letter. The ground singlet state is labeled X, and the next state which is accessible through an optically allowed transition from the ground singlet state is labeled A, then B, etc. States which are not accessible from the ground state (i.e., states in a triplet potential) are given the lower-case labels a, b, c etc. With this notation, the lowest lying triplet potential is labeled a, and the next triplet potential is labeled b, etc.

The superscript +/- represents the parity of the electronic wavefunction upon reflection about any plane that contains the internuclear axis. The subscript g/u represents the symmetry of the molecular wavefunction under an inversion of all nuclear coordinates about the center of the molecule. Wavefunctions (or potentials) labeled with g (gerade) have even parity and those labeled with u (ungerade) have odd parity. As a consequence of the g/usymmetry, the sign of the electronic wavefunction either stays the same (g) or changes (u) when reflected about the molecule center [168]. The implication of the +/- and g/u

¹⁰⁴Not to be confused with the quantum number Σ which represents the projection of the electronic spin along the internuclear axis in Hund's case (a).

symmetry properties is that particular rotational states (specified by the quantum number N) are only associated with particular values of total nuclear spin (specified by the quantum number I)¹⁰⁵.

It is possible to classify the rotational levels of the molecule by the behavior of the total eigenfunction with respect to a reflection at the origin (i.e., $\vec{r} \rightarrow -\vec{r}$). The rotational level is considered positive (negative) if the sign of the eigenfunction is unchanged (changed) under the reflection. The total eigenfunction can be written as product of a electronic, vibrational and rotational contributions [168]

$$\Phi = \Phi_e \frac{1}{r} \Phi_v \Phi_r \,. \tag{5.48}$$

The vibrational term is always unchanged under a reflection about the origin as it depends only on the magnitude of the internuclear distance. The change in sign of the electronic term is determined by the +/- parity introduced above [168]. The parity of the rotational term is determined by the quantum number N where even N corresponds to no change in the sign of the rotational term and odd N corresponds to a change in sign¹⁰⁶. Therefore, the positive or negative classification of the rotational level is determined by whether N is even or odd, and the +/- parity of the electronic term. Specifically, for Σ^+ states even (odd) N correspond to a positive (negative) rotational level, and for Σ^- states even (odd) N correspond to a negative (positive) rotational level.

When the two nuclei are identical (as is the case with ⁶Li₂), one must also consider the symmetry with respect to an exchange of the nuclei. This exchange can be broken up into two steps: first, a reflection of all particles about the origin, followed by a reflection of only the electrons about the origin. The sign change of the eigenfunction for the reflection of all particles about the origin is determined by the positive or negative classification of the rotational level (discussed above), while the sign change for the reflection of only the electrons is determined by the g/u symmetry. Therefore, for Σ_g states (negative) positive rotational levels are (anti)symmetric, and for Σ_u states (positive) negative are (anti)symmetric. This symmetry property determines the symmetry of the nuclear spin part of each eigenstate and, correspondingly, the allowed values of I (the total nuclear spin). In the case that $i_1 = i_2$, I

¹⁰⁵An excellent textbook resource for the details of the symmetry properties of diatomic molecules and selection rules "Spectra of Diatomic Molecules" by G. Herzberg [168].

¹⁰⁶Technically, it is determined by the quantum number $\vec{K} = \vec{N} + \Lambda \hat{z}$. However, this thesis considers Σ states only, where $\Lambda = 0$ and therefore $\vec{K} = \vec{N}$.

is symmetric for $I = i_1 + i_2, i_1 + i_2 - 2, \ldots$ and antisymmetric for $I = i_1 + i_2 - 1, i_1 + i_2 - 3, \ldots$

Together, these symmetry considerations restrict which rotational states are associated with particular values of the total nuclear spin. In the case of the ⁶Li₂, there are three possible values of the total nuclear spin (I = 0, 1, 2) since the nuclear spin of each atom is i = 1. Additionally, for the photoassociation work in this thesis, we only consider Σ^+ states (see Fig. 5.8). Therefore, for states with "g" inversion symmetry, the even (odd) values of N have a nuclear spin of I = 0, 2 (I = 1) and for states with "u" inversion symmetry, the even (odd) values of N correspond to I = 1 (I = 0, 2). A summary of the rotational levels and corresponding allowed quantum numbers can be found in Table 5.3.

In this thesis, and in the bulk of our photoassociation work, we label states (both bound molecular states and the two-atom scattering state) using the basis consisting of the quantum numbers (n, N, S, I, J, F) where *n* contains information relating to the electronic potential and the vibrational level. The allowed pairings of *N* and *I* are determined through symmetry considerations, and the values of *J* and *F* can be found via angular momentum addition. While the full Hamiltonian of the system (including spin-orbit, spin-rotation, spin-spin and hyperfine interactions) is not diagonal in this basis, this set of quantum numbers are approximately good (because the associated coupling are weak) and they form a convenient basis in which to properly label the observed photoassociation resonances and frame the discussion around the allowed transitions¹⁰⁷.

In the absence of spin-spin or spin-rotation coupling, it is also possible to define the total spin $\vec{G} = \vec{S} + \vec{I}$. The total spin can also be defined with respect to the total spin angular momentum of the initial unbound molecular state, using the vector sum of the f quantum numbers for the individual atoms: $\vec{G} = \vec{f_1} + \vec{f_2}$. Similar to the symmetry of the total nuclear spin, states $G = f_1 + f_2$, $f_1 + f_2 - 2$,... are associated with spin states that are symmetric under the exchange of the nuclear coordinates, while stats with $G = f_1 + f_2 - 1$, $f_1 + f_2 - 3$,... are antisymmetric. In our system, ⁶Li is prepared in the lower hyperfine state f = 1/2 and therefore G = 0, 1 in the initial collisions. Given this, all even partial wave collisions (where N = 0, 2, 4, ...) have a total spin G = 1. A summary the total spin associated with each

¹⁰⁷Note that in the $a(1^{3}\Sigma_{u}^{+})$ potential, the spin-spin and hyperfine interactions are of equal size, and the quantum numbers J and F are manifestly not good quantum numbers. In this case, the eigenstates can be expressed as a linear superposition of the $|NSIJF\rangle$ basis states. This is discussed in more detail in Section 6.3.2.

	Electronic	Nuclear	Allowed	Total				
State	spin	spin	rotational states	spin				
Initial colliding states								
			$N = 0, 2, 4, \dots$	G = 0				
_			$N = 1, 3, 5, \dots$	G = 1				
Excited states								
$c(1^3\Sigma_a^+)$	S = 1	I = 0	$N = 0, 2, 4, \dots$	G = 1				
5		I = 1	$N = 1, 3, 5, \dots$	G=0,1,2				
		I=2	$N = 0, 2, 4, \dots$	G=1,2,3				
$A(1^1\Sigma_u^+)$	S = 0	I = 0	$N = 1, 3, 5, \dots$	G = 0				
		I = 1	$N = 0, 2, 4, \dots$	G = 1				
		I=2	$N = 1, 3, 5, \dots$	G=2				
Ground states								
$a(1^3\Sigma_u^+)$	S = 1	I = 0	$N = 1, 3, 5, \dots$	G = 1				
		I = 1	$N = 0, 2, 4, \dots$	G=0,1,2				
		I=2	$N = 1, 3, 5, \dots$	G=1,2,3				
$X(1^1\Sigma_q^+)$	S = 0	I = 0	$N = 0, 2, 4, \dots$	G = 0				
3		I = 1	$N = 1, 3, 5, \dots$	G = 1				
		I=2	$N = 0, 2, 4, \dots$	G=2				

Table 5.3: Allowed rotational levels and corresponding nuclear spin configurations for ${}^{6}\text{Li}_{2}$. Note that G is only a good quantum number in the limit where the spin-spin and spinrotation couplings are small. The initial colliding state has both S = 1 and S = 0 character (see Section 5.1.1).

potential can be found in Table 5.3.

Accessible Levels and Selection Rules

Since the two-atom scattering state at 0 G contains both singlet and triplet characters (see Eq. 5.13), it is possible to access both singlet and triplet excited electronic potentials. The seven lowest energy potentials of ⁶Li₂ are shown in Fig. 5.8, along with a gray band that represents that wavelength range of our photoassociation lasers (which operate in a range from 760 nm to 820 nm). In all, there are five electronic molecular potentials for which bound vibrational levels fall within this energy band, and they are summarized in Table 5.4. In this thesis, we focus on the $c(1^{3}\Sigma_{g}^{+})$ and $A(1^{1}\Sigma_{u}^{+})$ excited potentials and the $a(1^{3}\Sigma_{u}^{+})$ and $a(1^{3}\Sigma_{u}^{+})$ ground potentials. For electric dipole radiation, the selection rule is that $\Delta F = 0, \pm 1$ and $\Delta m_{F} = 0, \pm 1$ with that restriction that $F = 0 \nleftrightarrow F = 0$ and $\Delta m_{F} \neq 0$



Figure 5.8: The first seven potentials of Li₂. The grey band represents the energy range accessible by our current Ti:Sapphire lasers, which includes five potentials: c,b,A,B,C. Of particular interest is the c and A potentials (bold lines), due to their usefulness as intermediate states for molecule formation. The potentials in this figure are based on the numerical calculations published in [174].

when $\Delta F = 0^{108}$. In addition, the parity of the electronic wavefunction must change, which restricts allowed transitions to those that satisfy $g \to u$ or vice versa. This results from conservation between the total angular momentum of the initial state plus photon system

¹⁰⁸The particular value of Δm_F which is allowed in an electric dipole transition is determined by the polarization of the light.
and the final state, and the fact that for electric dipole transitions the photon carries one unit of angular momentum. In Hund's case (b), the spin is only very weakly coupled to the other angular momentum such that both S and I are considered well defined and do not change during the transition (because the photon does not couple directly to the spin degree of freedom) so $\Delta S = \Delta I = 0$. With this, $\Delta J = 0, \pm 1$ which implies $\Delta K = 0, \pm 1$. In this thesis, we will be concerned with transitions between Σ states¹⁰⁹ where $\Delta K = 0$ is

Potential	$A(1^1\Sigma_u^+)$	$c(1^3\Sigma_g^+)$	$B(1^1\Pi_u)$	$C(2^1\Sigma_g^+)$	$b(1^3\Pi_u)$
ν	29-35	20-26	0-4	0-4	32-38

Table 5.4: List of excited molecular potentials in ⁶Li that are accessible with our photoassociation lasers (with a wavelength range from 760 nm to 820 nm). The excited $A(1^{1}\Sigma_{u}^{+})$ and $c(1^{3}\Sigma_{g}^{+})$ potentials, ground singlet $X(1^{1}\Sigma_{g}^{+})$ potential, and lowest lying triplet $a(1^{3}\Sigma_{u}^{+})$ potential are used in this thesis.

forbidden¹¹⁰. Therefore, we are concerned only with transitions that have $\Delta N = \pm 1$ and $\Delta S = \Delta I = 0$. These selection rules mean that certain states in the excited (and ground) molecular potentials are not accessible due to the nature of the two atom scattering state in Eq. 5.13. Specifically, the singlet part of the two atom scattering state has a total nuclear spin of I = 0 and the triplet part has a total nuclear spin of I = 1, which must be conserved during any electric dipole transition. A summary of the accessible levels in the initial state, excited state, and ground state is shown in Fig. 5.9. A summary of the selection rules are given in Table 5.5.

It is important to note that these selection rule assume that J is a good quantum number, which implies that the hyperfine interaction is small compared to the spin-spin and spin-rotation terms. This is valid in the excited potentials of ⁶Li₂, where the hyperfine constant is small. However, in the ground state this is not necessarily the case. An example of this is the N'' = 2 manifold of the $a(1^{3}\Sigma_{u}^{+})$ state, discussed in Section 6.3. In this case, the selection rules can used only if the eigenstates of the potential are expressed in the $|NSIJF\rangle$ basis, where the eigenstates will, in general, be linear superposition of the bare $|NSIJF\rangle$ states.

¹⁰⁹Where Σ here refers to the projection of the total angular momentum of all electrons on the internuclear axis. That is, $\Lambda = |m_L| = 0$.

¹¹⁰This forbidden transition is a consequence of the positive and negative symmetry property of the each rotational level. The transition dipole matrix element between states with the same symmetry of the rotation level is zero [168], and therefore for Σ states, where the symmetry of like K = N rotational levels is the same, transitions where $\Delta K = \Delta N = 0$ are disallowed.

Quantum Number	Selection Rule	Exceptions
parity	$g \leftrightarrow u$	
N	$\Delta N = \pm 1$	_
S	$\Delta S = 0$	_
Ι	$\Delta I = 0$	_
J	$\Delta J=0,\pm 1$	$J=0 \nleftrightarrow J=0$
F	$\Delta F=0,\pm 1$	—
m_F	$\Delta m_F = 0, \pm 1$	$m_F = 0 \nleftrightarrow m_F = 0$ if $\Delta F = 0$

Table 5.5: Electric dipole selection rules in ${}^{6}\text{Li}_{2}$ for $\Sigma \to \Sigma$ transitions. Note that these selection rules do not necessarily prevent transitions from occurring between energy eigenstates for which J or other quantum numbers are not good (i.e. don't commute with H). The selection rule for m_{F} depends on the polarization of the light and the type of transition $(\pi, \sigma^{+} \text{ or } \sigma^{-})$ driven by the light.



Figure 5.9: Summary of the accessible levels used in photoassociation. The initial state is a two atom scattering state, which has both singlet ($|00000\rangle$) and triplet ($|01110\rangle$) character. Note that the N'' = 2 rotational level in the $a(1^{3}\Sigma_{u}^{+})$ and $X(1^{1}\Sigma_{g}^{+})$ state is also accessible, but not shown. More details on the accessible levels of the N'' = 2 rotational level of $a(1^{3}\Sigma_{u}^{+})$ state can be found in Section 6.3 and specifically Fig. 6.21.

5.2 Photoassociation

One of the key requirements for the formation of ultra-cold ground state molecules is the knowledge of the location of the intermediate (excited state) molecular levels and final (ground state) molecular levels that will be used in the transfer process. Additionally, the transition frequencies must be known at a precision that is at or below the natural linewidth of the transition (typically on the order of 10 MHz). Photoassociation is a widely used spectroscopy method in which a colliding atom pair absorbs a photon to form an excited molecule (for an excellent review, see [175]), which can easily meet these requirements.

Photoassociation spectroscopy has previously been performed using the ⁶Li system in a MOT, where the ensemble temperatures is on the order of a mK [89, 176]. Due to the temperature of the ensemble, the observed spectral width of the photoassociation features is limited by Doppler broadening to tens of MHz. In our system, photoassociation spectroscopy is performed in an ODT where forced evaporative cooling allows us to achieve temperatures of less than 1 μ K, where the Doppler broadening is on the order of 100 kHz, and is much smaller than the natural linewidth.

Experimentally, when photoassociation is used to explore the energy levels of excited molecular states (called here "single-color" photoassociation), a single laser is scanned near the predicted transition energy of the colliding pair and the excited molecule state. When the photon energy, $h\nu_{\rm PA}$, matches the energy difference between the two states, excitedstate molecules form. This process leads to an observed atom loss from the ODT because the excited molecule either decays to a molecule in the ground state [177] (which cannot be seen by absorption imaging) or disassociates into two free atoms each with enough kinetic energy to leave the trap.

For reference in the following discussion, the state and naming convention of the radiation fields and transitions are outlined in Fig. 5.10. In general, we use two different lasers to couple an excited state $|e\rangle$ to both a bound ground molecular state $|g\rangle$ and to an initial state $|a\rangle$, where both $|a\rangle$ and $|g\rangle$ have the same parity, which is opposite to that of $|e\rangle$. The initial state $|a\rangle$ is either the two-atom scattering state at low field (typically $B \approx 0$ G) or the Feshbach molecule state at fields near the broad *s*-wave Feshbach resonance at 832 G. The probe field (with a photon energy $\hbar\omega_1$) couples states $|a\rangle \rightarrow |e\rangle$ with a strength given by the Rabi frequency Ω_1 and a detuning δ . The control field (with a photon energy ω_2) couples states $|g\rangle \rightarrow |e\rangle$ with a strength given by the Rabi frequency Ω_2 and a detuning Δ . The two photon detuning (that is, the difference in the energy difference between the two photon energies and the energy difference between the states $|a\rangle$ and $|g\rangle$) is given by $\Delta - \delta$.



Figure 5.10: The three level system used in photoassociation spectroscopy, atom-molecule dark state formation and STIRAP. The initial state $|a\rangle$ represents either a colliding atom or Feshbach molecule pair, while the states $|e\rangle$ and $|g\rangle$ represent excited and ground bound molecular states, respectively. The parity of states $|e\rangle$ and $|g\rangle$ are the same, and a direct coupling between the two states is disallowed by selection rules. The probe field (ω_1) couples states $|a\rangle \rightarrow |e\rangle$ with a strength given by the Rabi frequency Ω_1 and a detuning $\Delta + \delta$. The control field (ω_2) couples states $|g\rangle \rightarrow |e\rangle$ with a strength given by the Rabi frequency Ω_2 and a detuning Δ . The two-photon detuning is given by δ . State $|a\rangle$ is assumed to be long lived on the timescale of the relevant experiments, while the molecular states decay with rates given by $\gamma_e = 10$ MHz and γ_g , which is not known.

5.2.1 Spectroscopy Overview

The focus of single color spectroscopy (that is, photoassociation spectroscopy performed using only the probe field, coupling states $|a\rangle \rightarrow |e\rangle$) is to identify intermediate excited state levels that can be used in two-color spectroscopy of the ground singlet $X(1^{1}\Sigma_{g}^{+})$ and lowest lying triplet $a(1^{3}\Sigma_{u}^{+})$ potentials, and in the formation of ground state molecules in either of these states. This requires finding states that strike the best compromise between a good Frank-Condon overlap with the initial state (either a Feshbach molecule or an unbound colliding pair) and the final state in either the $X(1^{1}\Sigma_{g}^{+})$ or $a(1^{3}\Sigma_{u}^{+})$ potential. Conveniently, the intermediate states that meet this requirement are easily accessible by our Ti:Sapphire lasers. There are, in fact, five different molecular potentials that are accessible given the scanning range of our Ti:Sapphire lasers (see Fig. 5.8). However, the focus of our single color work is on the $A(1^{1}\Sigma_{u}^{+})$ (v' = 29 - 35) and $c(1^{3}\Sigma_{g}^{+})$ potentials (v' = 20 - 26). A summary of these results is provided in Section 6.1

At the temperatures at which photoassociation is performed, p-wave (and higher-order) collisions are greatly suppressed and the initial unbound molecular state has N = 0, corresponding to an s-wave collision¹¹¹. For dipole transitions between Σ states (which are under consideration here) the selection rule for dipole transitions (discussed in Section 5.1.4) state that $\Delta N = \pm 1$, so the only accessible rotational level in the $A(1^{1}\Sigma_{u}^{+})$ or $c(1^{3}\Sigma_{g}^{+})$ potential has N' = 1. Note that it is possible to increase the cross section for p-wave collisions by performing photoassociation in close proximity to a p-wave Feshbach resonance between the $|1\rangle$ and $|2\rangle$ states at 185.1 G [84]. We have demonstrated this enhancement for photoassociation to the $c(1^{3}\Sigma_{g}^{+})$ potential, and this work is discussed in greater detail in [84, 98]. The photoassociation laser is locked and referenced to an optical frequency comb (see Section 2.3.1), which provides an absolute uncertainty on the position of the resonance features of ± 600 kHz. Aside from possible systematic uncertainties arising from, for example, ac Stark shifts and Zeeman shifts of the molecular levels, the uncertainty on the frequency determination of the photoassociation laser is the dominant source of uncertainty.

Photoassocation spectroscopy can be extended to a three level system in order to measure the location (that is, binding energy) of bound states in the ground singlet $X(1^1\Sigma_g^+)$ or lowest lying triplet $a(1^3\Sigma_u^+)$ potential. To do this, a strong control field $(\Omega_2 \gg \gamma_e)$ is used

¹¹¹For a spin polarized fermionic system, s-wave collisions are generally disallowed due to the Pauli-exclusion principle. However, we use a spin-mixture in the lowest ground hyperfine level (f = 1/2) for which s-wave collisions are permissible.

to dress the $|g\rangle \rightarrow |e\rangle$ transition. In the rotating frame, this dressed interaction is described by the Hamiltonian

$$H = \hbar \begin{bmatrix} 0 & \Omega_2/2\\ \Omega_2/2 & \Delta \end{bmatrix}$$
(5.49)

where Ω_2 represents the coupling strength, and Δ is the detuning of the control field from the $|g\rangle \rightarrow |e\rangle$ transition. The dressed eigenstates¹¹² of the system are

$$|+\rangle = \sin \psi |g\rangle + \cos \psi |e\rangle ,$$

$$|-\rangle = \cos \psi |g\rangle - \sin \psi |e\rangle ,$$
(5.50)

where

$$\tan 2\psi = \frac{-\Omega_2}{\Delta} , \qquad (5.51)$$

and the associated eigenenergies of these two states are

$$E_{\pm} = \frac{\Delta \pm \sqrt{\Delta^2 + \Omega_2^2}}{2} \ . \tag{5.52}$$

It can be seen that if the control field is tuned close the transition frequency between states $|e\rangle$ and $|g\rangle$, the coupling of the two states produces a shift in energy of the excited molecule state¹¹³.

Experimentally, we use a weak probe field (such that $\Omega_1 \ll \gamma_e$) that is held a frequency which matches the energy splitting between the initial state $|a\rangle$ and some intermediate state $|e\rangle$. In the absence of the control field, atom loss will be observed due to photoassociation of the two-atom scattering state to an excited molecular state. However, if the control field is applied at the same time (and at the correct frequency), a reduction in atom loss will be observed because the energy of a photon in the probe beam will no longer match the energy splitting between $|a\rangle$ and the dressed excited state (see Fig. 5.11). Since the intermediate state has a rotational quantum number of N' = 1, the accessible rotational levels in the $X(1^1\Sigma_g^+)$ and $a(1^3\Sigma_u^+)$ potentials are $N'' = 0, 2^{114}$. The binding energy of the ground state is determined from the frequency difference between the probe and control

¹¹²Typically the "dressed states" are combined with the related photon numbers from the radiation fields. They are not explicitly included here for simplicity.

¹¹³This shift could be thought of an ac-Stark shift of the excited state energy due to the coupling with the ground state.

¹¹⁴With the exception that for the $X(1^{1}\Sigma_{g}^{+})$ potential, where the N'' = 2 rotational level of the least bound v'' = 38 vibrational level is not bound.



Figure 5.11: Top: Result of single-color PA to the v' = 31 level of the $A(1^1\Sigma_u^+)$ potential. Bottom: Result of two-color PA, where ω_1 is held fixed at the resonance frequency from the single-color scan (top image) and ω_2 is scanned near the $|g\rangle \rightarrow |e\rangle$ transition, where the ground molecular state is the least bound v'' = 38, N'' = 0 level of the $X(1^1\Sigma_g^+)$ potential. When the photon energy of the control field matches the $|g\rangle \rightarrow |e\rangle$ transition frequency, a suppression of the loss induced by the probe field is seen.

fields. Once these levels have been located using this technique, this information can be used to perform extremely high resolution using an atom-molecule dark state, discussed in Section 5.2.2.

Autler-Townes Splitting

An Autler-Townes doublet [178] is a natural extension of the system described in section 5.2.1 and the Hamiltonian in Eq. 5.49, which provides a simple method to measure the coupling strength of the control field, Ω_2 . In this case, the control field is held fixed on the

 $|g\rangle \rightarrow |e\rangle$ resonance and the probe field is scanned around the known $|a\rangle \rightarrow |e\rangle$ transition frequency. When $\Delta = 0$, the eigenstates in Eq. 5.50 become

$$|+\rangle = \frac{1}{\sqrt{2}} (|g\rangle + |e\rangle) ,$$

$$|-\rangle = \frac{1}{\sqrt{2}} (|g\rangle - |e\rangle) ,$$

(5.53)

which are split in energy by (from Eq. 5.52) $\Delta E = \hbar \Omega_2$.

Both dressed eigenstates in Eq. 5.53 can be coupled to $|a\rangle$ by the probe beam since $\langle \pm | \hat{d} | a \rangle \neq 0$ due the component fraction of state $|e\rangle$ in both states. This coupling produces trap loss via the same mechanism as standard single-color photoassociation. Therefore, as the frequency of the probe field is scanned, two resonance features are seen, which are split in energy by $\hbar\Omega_2$.

5.2.2 Dark States and Stimulated Raman Adiabatic Passage

Stimulated Raman Adiabatic Passage (STIRAP) provides a method of transferring molecular populations between specific states of the same parity (which are otherwise forbidden with electric dipole transitions) with high efficiency. This technique has been demonstrated in both homonuclear systems (Cs₂ [14, 15], Rb₂ [16, 17], Sr₂ [18]) and heteronuclear systems (40 K⁸⁷Rb [19, 20], 87 Rb¹³³Cs [21, 22], 7 Li¹³³Cs [23], 23 Na⁴⁰K [24]). This makes STIRAP an excellent tool for the production of ultra-cold ⁶Li₂ molecules in either the ground spin-singlet $X(1^{1}\Sigma_{g}^{+})$ or lowest spin-triplet $a(1^{3}\Sigma_{u}^{+})$ potential, starting from an ensemble of ⁶Li₂ Feshbach molecules (which have both singlet and triplet character near the broad Feshbach resonance near 832 G).

STIRAP relies on the creation of a coherent state

$$|\psi\rangle = c_1 |a\rangle + c_2 |g\rangle , \qquad (5.54)$$

which is an admixture of the initial Feshbach molecule state $|a\rangle$ and the final ground molecular state $|g\rangle$, and contains no component of the lossy intermediate state $|e\rangle^{115}$. The prob-

¹¹⁵That is, $|e\rangle$ can decay to states which are outside the three level system, and are not connected to either of the other two states by the light fields.

ability of excitation of the coherent state in Eq. 5.54 to the excited state $|e\rangle$ depends on

$$A = \langle e | \vec{d} \cdot \vec{\epsilon} | \psi \rangle = c_1 \langle e | d | a \rangle \epsilon_1 + c_2 \langle e | d | g \rangle \epsilon_2$$

= $\Omega_1 c_1 + \Omega_2 c_2$, (5.55)

where Ω_1 and Ω_2 are the Rabi frequency of the probe field (ϵ_1 , which couples $|a\rangle \rightarrow |e\rangle$) and control field (ϵ_2 , which couples $|g\rangle \rightarrow |e\rangle$) respectively (see Fig 5.10). The state is considered "dark" if the amplitude for photon absorption from the probe and control fields is zero. Setting A = 0 in Eq. 5.55 leads to the condition

$$c_2 = -\frac{\Omega_1}{\Omega_2} c_1 \,. \tag{5.56}$$

However, the matrix element in Eq. 5.55 is only valid at one specific time. Extending Eq. 5.55 to be a function of time gives

$$A(t) = c_1 e^{\left(\frac{-iE_a t}{\hbar}\right)} \Omega_1 e^{\left(-i\omega_1 t\right)} + c_2 e^{\left(\frac{-iE_g t}{\hbar}\right)} \Omega_2 e^{\left(-i\omega_2 t\right)}, \qquad (5.57)$$

where E_a and E_g are the energy of the $|a\rangle$ and $|g\rangle$ states and ω_1 and ω_2 are the frequencies of the probe and control laser. In order that A(t) in Eq. 5.57 be zero for all time, it can be seen that the exponents in both terms must be equal, and therefore the laser frequencies must satisfy the two-photon resonance condition

$$\omega_2 - \omega_1 = \frac{E_a - E_g}{\hbar} \,. \tag{5.58}$$

A coherent state, which has the form of Eq 5.54 and satisfies the condition in Eq. 5.56, can be created by dressing the system with the probe and control laser fields. In this case, the Hamiltonian that describes the dressed three level system can be written, using the rotating wave approximation¹¹⁶, as [48]

$$H(t) = \hbar \begin{bmatrix} -i\gamma_a/2 & \Omega_1(t)/2 & 0\\ \Omega_1(t)/2 & -i\gamma_b/2 + (\delta) & \Omega_2(t)/2\\ 0 & \Omega_2(t)/2 & -i\gamma_g/2 + (\delta - \Delta) \end{bmatrix},$$
(5.59)

¹¹⁶For details on the rotating wave approximation for three (and higher) level systems, see Chapter 13 and 14 of "The Theory of Coherent Atomic Excitation" by B. Shore [179].

where $i\gamma_{a,e,g}$ are included as phenomenological terms which represent the decay rate from each of the three states. As shown in Fig. 5.10, δ and Δ represent the detuning on the probe and control lasers, respectively. In the case that the single-photon and two-photon resonance conditions are satisfied (that is, $\delta = \Delta = 0$), the three eigenstates (neglecting the phenomenological decay terms) of the Hamiltonian in Eq. 5.59 are

$$|a^{+}\rangle = \frac{1}{\sqrt{2}} \left(\sin \theta \, |a\rangle + |e\rangle + \cos \theta \, |g\rangle \right) \,, \tag{5.60}$$

$$|a^{0}\rangle = \cos\theta \,|a\rangle - \sin\theta \,|g\rangle , \qquad (5.61)$$

$$|a^{-}\rangle = \frac{1}{\sqrt{2}} \left(\sin \theta \, |a\rangle - |e\rangle + \cos \theta \, |g\rangle \right) \,, \tag{5.62}$$

where the mixing angle is defined as

$$\tan \theta = \frac{\Omega_1}{\Omega_2}, \qquad (5.63)$$

and the associated eigenenergies are

$$E^{\pm} = \pm \frac{\hbar}{2} \sqrt{\Omega_1^2 + \Omega_2^2} , \qquad (5.64)$$

$$E^0 = 0$$
 . (5.65)

The "dark state" $|a^0\rangle$ satisfies the condition in Eq. 5.56. Since the dark state has no contribution from (and no probability of excitation to) the lossy bare state $|e\rangle$, it provides a direct (and lossless) connection between the initial state and the final ground molecule state. Moreover, the relative contribution of $|a\rangle$ and $|g\rangle$ to the dark state can be experimentally controlled via the ratio of the two Rabi frequencies, which is directly related to the amplitude of the fields.

To perform STIRAP, the two laser fields are turned on in the so called "counter intuitive" pulse sequence. In this sequence, the control field pulse begins before the probe field pulse, such that the initial dark state is entirely composed of the initial state $|a\rangle$. After a set delay time, the probe field pulse begins, and the dark state is now composed of an admixture of the initial state $|a\rangle$ and the ground molecule state $|g\rangle$ due to the non zero intensity of both fields (see Eq. 5.61 and 5.63). At the end of the pulse sequence only the probe field is on, and the dark state is entirely composed of the ground molecule state $|g\rangle$. This pulse



Figure 5.12: Bottom: The "counter intuitive" pulse sequence used in STIRAP, where the black (solid) curve represents the Rabi frequency of the control field, which is turned on (and off) before the probe field, represented by the red (dashed) curve. Top: The population in $|a\rangle$ state (blue dashed line) and the $|g\rangle$ state (black solid line) as a function of time during the pulse sequence. This process transfers the initial population in the $|a\rangle$ state to the ground molecule state.

sequence and the population dynamics during the pulse sequence are shown in Fig. 5.12.

The high efficiency of STIRAP relies on the dark state adiabatically following the ratio of the two Rabi frequencies, such that at t = 0, $|a^0\rangle = |a\rangle$ and a later time t = T, $|a^0\rangle = |g\rangle$. Non-adiabatic coupling to the lossy excited state can be considered small if [48]

$$|\langle a^{\pm} | \dot{a}^{0} \rangle| \ll \left| \frac{E^{\pm} - E^{0}}{\hbar} \right| . \tag{5.66}$$

Using Eqs. 5.60, 5.61, and 5.63, this leads to a local adiabaticity condition [48],

$$\left|\frac{\dot{\Omega}_1 \Omega_2 - \Omega_1 \dot{\Omega}_2}{\Omega_1^2 + \Omega_2^2}\right| \ll |E^{\pm} - E^0|$$
(5.67)

which must be satisfied at all times.

In the case of smooth pulse shapes, a global adiabaticity condition can be found by

taking the time average of the left-hand side of Eq. 5.67. This results in the condition

$$\Delta \tau \sqrt{\Omega_1^2 + \Omega_2^2} > 10 \,, \tag{5.68}$$

where $\Delta \tau$ is the time in which both fields are on, and the value of 10 is suggested by Bergmann et al. as "obtained from experience and numerical simulation studies" [48].

For Gaussian pulse shape, Gaubatz et al. [180] have shown that non-adiabatic losses are minimized for a pulse delay equal to the pulse width, such that the time in which both fields are on equals the pulse width (that is, $\Delta \tau = \tau$). Additionally, it can be seen from Eq. 5.67 that non-adiabatic losses are minimized when the probe and control Rabi frequencies are equal (that is, $\Omega_1 = \Omega_2 \equiv \Omega$). Thus, the global adiabaticity condition in Eq. 5.68 reduces to

$$\Omega > \frac{10}{\tau\sqrt{2}} . \tag{5.69}$$

Because STIRAP is a coherent process, the relative phase of the two coupling fields must be predictable (i.e., vary at a constant rate) throughout the transfer. This condition is also apparent in Eq. 5.58, which states that the two-photon detuning must be zero for all times. In truth, the effect of dephasing depends both on the dephasing rate and the transition time over which the $|g\rangle$ state population varies from initially unpopulated to populated. Ivanov et al. [74] have shown that, in the adiabatic limit, the loss of transfer efficiency depends exponentially on the dephasing rate (to which the dephasing of the coupling fields contributes) and the transition time. Thus, an important timescale for the STIRAP process is given by the coherence time of the two lasers.

In our apparatus, the coupling fields are derived from two Ti:Sapphire lasers locked to a optical frequency comb. Using only the "slow" lock, we have a measured heterodyne beatnote width of approximately 100 kHz. This limits the coherence time (and therefore the pulse width of the probe and control fields) to approximately 10 μ s. Thus, from Eq. 5.69, we require $\Omega > 700$ kHz. However, with the new "fast" lock, we can achieve linewidths of less than 1 kHz, such that we only require $\Omega > 7$ kHz if the pulse width is 1 ms. While this time scale is likely longer than a reasonable choice for the pulse time (due to, for example, the potential short finite lifetime of the ground molecule state we may choose to populate), the narrow linewidths greatly reduce the constraints on the required Rabi frequencies.

Dark State Spectroscopy

The existence of an atom-molecule (or molecule-molecule dark state, in the case that the initial state is a Feshbach molecule pair) provides a robust method of measuring the binding energy of bound levels, as previously demonstrated in Rb_2 [75] and in metastable He [62].

Spectroscopy done using a dark state has several advantages over the two-color photoassociation spectroscopy described in section 5.2.1. First, the two-photon resonance linewidth (i.e., the width of the dark state feature) is related the control coupling strength and can be more than an order of magnitude smaller than what is achievable using two-color photoassociation spectroscopy. Second, the location of the resonance only depends on the energy difference between the two lasers, which makes the measurement insensitive to the singlecolor detuning. Additionally, any systematic errors or shifts in the frequency readout of the lasers subtract out. Although the absolute uncertainty on the frequency measurement made using the frequency comb is ± 600 kHz, the absolute uncertainty on the frequency difference between the two Ti:Sapphires locked the comb is only 1 kHz (see section 2.3.1 for more details).

The eigenstates of the dressed three level system can be written in a more illuminating form as the dark state (from Eq. 5.61)

$$|\text{Dark}\rangle = |a^0\rangle = \frac{\Omega_2 |a\rangle - \Omega_1 |g\rangle}{\sqrt{\Omega_1^2 + \Omega_2^2}} ,$$
 (5.70)

and a bright state, which is a superposition of the two remaining eigenstates (Eqs. 5.60 and 5.62)

$$|\text{Bright}\rangle = \frac{1}{2}(|a^+\rangle + |a^-\rangle) = \frac{\Omega_1 |a\rangle + \Omega_2 |g\rangle}{\sqrt{\Omega_1^2 + \Omega_2^2}}$$
(5.71)

For this type of experiment, the probe and control field are turned on at the same time, such that the initial ensemble in state $|a\rangle$ is projected onto the bright and dark states, as given in Eqs. 5.70 and 5.71. The fields remain on for some time, T, during which the population which has been projected into the bright state leaves the trap. After this time, the fields are turned off at the same time¹¹⁷. When the fields are turned off, the population that was in the dark state is projected back onto the initial state $|a\rangle$. Therefore, the expected revival height (that is, the suppression of loss due to the existence of the dark state) is given

¹¹⁷Experimentally, to protect from any effects of timing jitters, the control field is turned on a few μ s before, and turned off a few μ s after, the probe field.



Figure 5.13: Atom-molecule dark state at 0 G formed using the v'' = 38, N'' = 0 of $X(1^1\Sigma_g^+)$ potential, and the v' = 31, N' = 1 level of the $A(1^1\Sigma_u^+)$ potential as the intermediate state. The black line represents a fit to our data using the three level model described in this section (see text for details).

by

$$|\langle \mathbf{a} | \operatorname{Dark} \rangle|^2 \times |\langle \operatorname{Dark} | \mathbf{a} \rangle|^2 = \frac{\Omega_2^4}{(\Omega_1^2 + \Omega_2^2)^2} .$$
 (5.72)

It can be seen that, in order to achieve a good signal for dark state spectroscopy, there are two conditions on the strength of Ω_2 : first, we require $\Omega_2 \ll \gamma_e$, such that we do not create an Autler-Townes doublet and have a narrow dark state feature. Second, we require that $\Omega_2 \gg \Omega_1$ such that a large suppression of loss is observed. An example of this sharp suppression of single-color photoassociation loss, seen around the two-photon resonance due to the existence of the dark state, is shown in Fig. 5.13.

As the dark state is a coherent state, it requires that the two lasers are phase coherent during the time in which the light illuminates the atoms¹¹⁸. If the relative phase of the two lasers evolves with time in a non constant way, then the probability of excitation from the

 $^{^{118}}$ Note that this statement is simply a restatement of the two-photon resonance condition from Eq. 5.58.

dark state to the excited $|e\rangle$ state from Eq. 5.57 is related to

$$A(t) = c_1 e^{\left(\frac{-iE_a t}{\hbar}\right)} \Omega_1 e^{\left(-i\omega_1 t + i\phi(t)\right)} + c_2 e^{\left(\frac{-iE_g t}{\hbar}\right)} \Omega_2 e^{\left(-i\omega_2 t\right)}, \qquad (5.73)$$

where $\phi(t)$ is the (time dependent) relative phase of the two fields. If the conditions in Eq. 5.56 and 5.58 are satisfied then

$$A(t) = c_1 \Omega_1 e^{\left(-i\left(\frac{E_a}{\hbar} + \omega_1\right)t\right)} \left[e^{i\phi(t)} + 1\right] .$$
(5.74)

In the case that $\phi(t)$ takes on a constant value for all time, it can be incorporated into Ω_1 , and A(t) = 0. This is simply a statement that initial phase difference between the two fields can be set arbitrarily, as long as the phase evolution as a function of time proceeds in a well defined and constant way. However, If $\phi(t)$ is not constant for all time, and the time scale of the phase evolution is non-adiabatic, then $A(t) \neq 0$ and the dark state is not dark for all times. Physically, this decoherence manifests itself as loss from the now "grey state", which experimentally is observed as a decrease in the dark state revival height as a function of time.

This impact of the laser decoherence can be seen by considering a simple model that accounts for the projection loss resulting from a non-adiabatic relative phase jump ϕ between the two lasers. In this case, immediately before phase jump the dark state is

$$|\text{Dark}_{-}\rangle = \frac{\Omega_2 |a\rangle - \Omega_1 |g\rangle}{\sqrt{\Omega_1^2 + \Omega_2^2}},$$
(5.75)

which will project onto the new eigenstates of the dressed system, given by Eqs. 5.70 and 5.71 and incorporating the new phase of associated with Ω_1 relative to Ω_2 . Specifically, the bright state immediately after the phase jump (from Eq. 5.71 with the inclusion of the relative phase jump) is

$$|\text{Bright}_{+}\rangle = \frac{\Omega_1 |a\rangle + \Omega_2 e^{i\phi} |g\rangle}{\sqrt{\Omega_1^2 + \Omega_2^2}} \,. \tag{5.76}$$

Therefore, the projection of the original dark state onto the new bright eigenstate is

$$|\langle \text{Dark}_{-}| \operatorname{Bright}_{+} \rangle|^{2} = \frac{2\Omega_{1}^{2}\Omega_{2}^{2}(1 - \cos \phi)}{(\Omega_{1}^{2} + \Omega_{2}^{2})^{2}},$$
 (5.77)

and this fraction of the population is effectively lost from the system due to the finite lifetime

of the $|e\rangle$ state.

To determine the effect of this projection loss over the total time T in which the light is on, we assume that the lasers undergo a relative phase jump of, on average, $\phi = \pi/2$ on a timescale τ given by the inverse of the relative linewidth of the photoassociation lasers. The fraction of atoms that remain (i.e., the height of the dark state relative to the height in the case of perfectly phase coherent lasers) will be

$$\frac{N}{N_0} = \left(1 - \frac{2\Omega_1^2 \Omega_2^2}{(\Omega_1^2 + \Omega_2^2)^2}\right)^{T/\tau}.$$
(5.78)

When $\Omega_1 = \Omega_2$, the fraction of atoms in the dark state is simply $(1/2)^{T/\tau}$, and the dark state is decimated on a timescale on the order of τ . For the experiments discussed in this thesis, the two photon linewidth is approximately 160 kHz, which corresponds to $\tau = 6.2 \ \mu$ s.

However, many of our experiments are done in a regime where the coupling strength of the $|a\rangle \rightarrow |g\rangle$ transition is very weak, such that $\Omega_1 < 1$ kHz and therefore $\Omega_2/\Omega_1 \gg 1$. In this case, the fraction of atoms that remain scales like

$$\frac{N}{N_0} \approx \left(1 - \frac{2\Omega_1^2}{\Omega_2^2}\right)^{T/\tau} \,. \tag{5.79}$$

If $\Omega_2/\Omega_1 = 1000$, then even after 1 s the fraction of atoms remaining is over 70%. In practice, the ratio of Ω_2/Ω_1 in our experiments is likely larger than 1000, and this large ratio of acts to suppress the loss or decoherence of the dark state due to the dephasing of the photoassociation lasers. We have seen this effect in much of our dark state spectroscopy at 0 G, where we observe near complete revivals of dark states for hold times of 2 s. The details of these measurements are discussed in more detail in Section 6.1 and Section 6.3 in the context of dark state spectroscopy of the $X(1^1\Sigma_g^+)$ and $a(1^3\Sigma_u^+)$ state respectively.

Fitting Using the Three Level Model

The three level model described by the Hamiltonian in Eq. 5.59 can also be used to numerically simulate the expected Autler-Townes or dark state spectra and to fit the spectra we observe. This fit can be used to extract the precise location of the two photon resonance (because the detuning of the control field Δ is a free parameter) and, in some cases, determine the probe and control Rabi frequencies (because Ω_1 and Ω_2 can also be free parameters in the fit). However, this model has limitations that must be kept in mind when interpreting the results of the fit. Specifically, this model does not correctly simulate the loss dynamics when the initial state is not a bound pair. That is, it does not take into account the effect of two-body collisions on the loss rate. Nevertheless, this model proves to extremely useful in the interpretation and understanding of the general behavior of the dark state and Autler-Townes spectrum, and in determining the precise binding energy of states probed using dark state spectroscopy¹¹⁹. The details and limitations of this model are discussed in the following section. For simplicity, we will consider a system with only three levels. However, the following discussion can be extended to a system with N levels [179], as is done in the analysis presented in Section 6.2 with respect to the effect of degenerate levels on the EIT spectra and in 6.3 regarding the spectroscopy of the $a(1^3\Sigma_u^+)$ potential.

The time evolution of the population in the states $|a\rangle$, $|g\rangle$, and $|e\rangle$ is described by the time dependent Schrödinger equation

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H |\psi(t)\rangle , \qquad (5.80)$$

where

$$|\psi(t)\rangle = \begin{bmatrix} a(t)\\ e(t)\\ g(t) \end{bmatrix}$$
(5.81)

is the state vector that contains the (time dependent) probability amplitudes a(t), e(t) and g(t) for the states $|a\rangle$, $|e\rangle$, and $|g\rangle$ respectively. Using the Hamiltonian in Eq. 5.59, the Schrödinger equation can be used to produce a set of differential equations

$$\begin{split} i\dot{a} &= \frac{1}{2}[-i\gamma_{a}a - \Omega_{1}e] \\ i\dot{e} &= \frac{1}{2}[(-i\gamma_{e} + 2\delta)e - \Omega_{1}a + \Omega_{2}g] \\ i\dot{g} &= \frac{1}{2}[(-i\gamma_{g} + 2(\delta + \Delta))g + \Omega_{2}e] \end{split}$$
(5.82)

that can be numerically solved. Depending on the situation, Ω_1 , Ω_2 , δ and Δ can be made time dependent or set to a constant value. Experimentally, we measure the population of the $|a\rangle$ state and are therefore interested in the expected population fraction that remains

¹¹⁹Note that this three level model could be modified or enriched to model the effects of two-body collisions. However, we are not interested in extracting the true two-body loss rates, and we therefore choose to simply use the model "as-is".

in the $|a\rangle$ state after some time (i.e., the probability of the system being in state $|a\rangle$), which is given by $|a(t)|^2$. Note that $|a(t)|^2 + |e(t)|^2 + |g(t)|^2 \neq 1$ because the inclusion of the nonhermitian term in the Hamiltonian that takes into account decay from each of the three states out of system.

In the case that $\Omega_2 = 0$ (i.e., just a simple two level system), and in the limit that $\Omega_1 \ll \gamma_e$, the $|a\rangle$ state population follows a simple exponential decay with a loss rate Γ^{120} . This population evolution is manifestly a single body loss process, where $\dot{N} = -\Gamma N$. When $\Omega_2 \neq 0$ and the two-photon resonance condition is not satisfied, the $|a\rangle$ state population still follows a simple exponential decay. However, the loss rate Γ is modified (to be smaller) if the two-photon detuning is small. This decrease in loss rate is due to a partial quantum interference of excitation pathways. When $\delta = \Delta = 0$ (i.e., the two photon resonance condition is satisfied) a dark state is created and no population loss is observed due to a full quantum interference of the excitation pathways¹²¹.

This exponential loss is a valid description of the dynamics when the initial state is a single state (for example, a Feshbach molecule). However, in many of our experiments, collisions between particles play an important role, and the dynamics of the loss are governed by two-body losses. In this case, the local loss rate is

$$\dot{n}(\vec{r},t) = -\frac{1}{2} \langle K_2(\vec{r}) \rangle [n(\vec{r},t)]^2 , \qquad (5.83)$$

where $\langle K_2(\vec{r}) \rangle$ is the two-body loss rate constant averaged over the relative momentum [73], and $n(\vec{r},t)$ is the position and time dependent total density. The two-body loss rate constant depends on the inelastic scattering cross section, and is implicitly of function of the probe and control field detunings and powers. The factor of 1/2 comes from the fact that we have an equal population in the $|1\rangle$ and $|2\rangle$ states (i.e., $n_1(\vec{r}) = n_2(\vec{r}) = n(\vec{r})/2$). Under the assumption that the spatial atomic distribution is constant as the total number decreases, and that the Rabi frequencies of the probe and control fields are not spatially dependent (this is true if the size of the beams is large compared to the spatial extent of the clouds)

¹²⁰If $\gamma_e = 0$ then time evolution of the $|a\rangle$ and $|g\rangle$ states show Rabi flopping. In the case where Ω_1 is not much smaller than γ_e , the time evolution is more complicated, showing evidence of both Rabi flopping and exponential decay. However, as $\gamma_e \approx 2\pi \cdot 10$ MHz and typically $\Omega_1 \leq 2\pi \cdot 1$ MHz, the limiting case of $\Omega_1 \ll \gamma_e$ is valid for the work presented in this thesis.

¹²¹There is, however, some loss associated with the turn on and turn off the laser fields if it is not done adiabatically. This "projection" loss of the initial $|a\rangle$ state onto the dark state (when the fields are turned on), and then the dark state back onto the $|a\rangle$ state (when the fields are turned off) is given in Eq. 5.72.

the atom loss rate is [73]

$$\dot{N} = -\frac{\bar{n}}{2N} \langle K_2 \rangle N^2 = -\Gamma_2 N^2 \,.$$
 (5.84)

Moreover, for a Gaussian atomic spatial distribution, \bar{n}/N is constant and Γ_2 is only a function of K_2 (and thus depends on the probe and control Rabi frequencies). The solution to Eq. 5.84 is

$$N(t) = \frac{N_0}{1 + N_0 \Gamma_2 t}, \qquad (5.85)$$

which is different from the exponential time evolution that results from the numerical integration of the three level model. In the low loss limit ($\Gamma t \ll 1$), the atom loss rate from the three level model is

$$\lim_{\Gamma t \ll 1} N_0 e^{-\Gamma t} = \frac{N_0}{1 + \Gamma t} \,, \tag{5.86}$$

which connects to the two-body atom loss (Eq. 5.85) where $\Gamma = N_0 \Gamma_2$. Physically, this limit represents the situation when the change in density is small (i.e., small loss).

In general, a consequence of the different behavior of the atom number as a function of time is that the three level model will overestimate the atom loss rate for low densities. This manifests itself as an overestimation of atom loss when Γt is large (i.e., when the three level model predicts a large decrease in atom number). A simple illustration of this is given in Fig. 5.14, where the loss rate Γ from the three level model is used in Eq. 5.85 to predict the spectrum when two-body loss dynamics are considered. However, aside from the overestimation of loss for particular probe detunings (where Γ is large), it can be seen that the general shape of the spectrum remains unchanged. Most importantly, the location of the two photon resonance (where the maximum dark state revival occurs) is the same. In addition, we note that it is possible to reproduce the spectrum predicted by two-body loss using the three level model by allowing γ_e to vary in the fit (see Fig. 5.14). This is possible because in the limit that $\Omega_1 \ll \gamma_e$, the excited state decay rate γ_e predominantly determines the width of the single color resonance, and Ω_1 (in conjunction with the probe and control detunings) determines the magnitude of the overall loss¹²².

Although the three level model does not accurately model the underlying dynamics of the loss process when two-body collisions are involved, it is a very simple model that can match our dark state spectrum, and precisely determine the location of the two-photon resonance.

¹²²Physically, this is the case because the atoms can only be lost as quickly as they are "put" in the excited state, which is determined by Ω_1 .



Figure 5.14: Model dark state spectrum predicted from one-body and two-body loss. The black dashed line shows the normalized population in the $|a\rangle$ state as a function of the probe beam detuning determined using the three level model. The loss rate Γ for a particular probe detuning is found from the normalized atom number, and used in Eq. 5.85 to predict the normalized $|a\rangle$ state population when two-body loss dynamics are considered (red solid line). Although the general shape of the spectrum remains unchanged, the three level model overestimates loss. For these spectrum we used $\Omega_1 = 2\pi \cdot 0.5$ MHz, $\Omega_2 = 2\pi \cdot 5$ MHz and $\gamma_e = 2\pi \cdot 10$ MHz. It is possible for the three level model to reproduce the spectrum predicted by the two-body loss model if both Ω_1 and γ_e are changed. For $\Omega_1 = 2\pi \cdot 0.46$ MHz, $\Omega_2 = 2\pi \cdot 5$ MHz and $\gamma_e = 2\pi \cdot 11.5$ MHz, the three level model spectrum (black dots) is the same as that from the two-body loss model. In all cases, $\Delta = 0$.

In addition, the three level model is easily extended to N levels in order to simulate the effect of degeneracies in the $|e\rangle$ and $|g\rangle$ states, where we are primarily concerned with the general shape of the EIT spectrum. In summary, we therefore use this three level model, while keeping in mind a few important points:

• In the case of dark-states and Autler-Townes spectra with an initial state that does not rely on collisions (i.e., Feshbach molecules), the three level model is valid and can be used to find, in addition to the location of the two photon resonance, the values of Ω_1 and Ω_2 (for example, see Sections 6.1.2 and 6.1.3).

- When the initial state involves collisions, we use this model only to extract the precise location of the two-photon resonance. Although the "fit" matches our observed spectrum, it is not a true "fit" with respect to the underlying two-body loss dynamics. In addition, for much of our dark state spectra at 0 G the "on-time" of the fields is on the order of seconds. In these cases, it is not computationally viable to numerical integrate the differential equations in Eq. 5.82. We therefore use a short integration time in order to fit our data to determine the two-photon resonance location, but this renders the other fit values meaningless.
- The three level (and higher order) model does accurately represent the general behavior of the Autler-Townes and dark state spectrum. Therefore, the results of the N level model used to explain and investigate the impact of degeneracy on the EIT spectrum are valid. That is, dark-states (or "grey"-states) arise from a quantum interference of excitation pathways and the existence of these interference pathways does not depend on the chosen model.

Chapter 6

${}^{6}\mathbf{Li}_{2}$ Spectroscopy

This chapter presents the new novel observations that have results from our spectroscopy work with ⁶Li and ⁶Li₂ molecules. Although there are five excited state potentials which have vibrational levels that are accessible with our photoassociation lasers (these levels are listed in Table 5.4), we focused our efforts on probing the $c(1^{3}\Sigma_{g}^{+})$ and $A(1^{1}\Sigma_{u}^{+})$ potentials. These potentials are the focus of our work because they represent the intermediate states that are needed to access the ground singlet $X(1^{1}\Sigma_{g}^{+})$ potential and the lowest lying triplet $a(1^{3}\Sigma_{u}^{+})$ potential. This is important both in the context of spectroscopy of the ground state potentials, and the creation of ground state molecules via STIRAP.

The result of the spectroscopy of the excited $c(1^{3}\Sigma_{g}^{+})$ and $A(1^{1}\Sigma_{u}^{+})$ potentials, and the ground $X(1^{1}\Sigma_{g}^{+})$ potential (along with information specific to each measurement) is presented in Section 6.1. A detailed analysis of the lowest lying triplet potential, where we measure the N'' = 0 and N'' = 2 rotational levels for all ten bound vibrational levels is given in Section 6.3. For the least bound v'' = 9 vibrational level, we use dark state spectroscopy to measure the binding energy of all three hyperfine levels in the N'' = 0 rotational level.

In addition, Section 6.2 discusses the implications of degenerate levels on our observed Autler-Townes and dark-state spectrum. In particular, we observe an anomalous third feature in the Autler-Townes spectrum, and a poor dark state revival for the F'' = 1ground state hyperfine manifold. We discuss these effects in the singlet system, where the $A(1^{1}\Sigma_{u}^{+})$ and $X(1^{1}\Sigma_{g}^{+})$ potentials are used as the $|e\rangle$ and $|g\rangle$ states respectively, as well as in the triplet system where the $c(1^{3}\Sigma_{g}^{+})$ and $a(1^{3}\Sigma_{u}^{+})$ potentials are used.

6.1 Summary of Spectroscopy

For all the spectroscopy measurements, we load 6 Li into our ODT and perform a series of evaporation ramps to reach our desired final ensemble temperature. This procedure is described in Section 3.2. Typically, we reach a final ensemble temperature of 800 nK (corresponding to $T/T_{\rm F} = 0.8$) composed of a few 10⁴ atoms in an equal incoherent mixture of the $|1\rangle$ and $|2\rangle$ states. At this point, any bias magnetic field is turned off, and all that remains is a small residual field due to the earth's magnetic field and/or any other magnetic field sources near the setup. It is possible to measure the strength of this field using RF transitions in ⁶Li, and compensate for the field using the three orthogonal compensation coils placed near the cell. We make an effort to perform spectroscopy in a very shallow trap (at the expense of atom number) in order to reduce the effects of thermal broadening and the inhomogeneous ac Stark shift produced by the ODT potential.

After the atom sample has been prepared, PA light from our Ti:Sapphire laser (or lasers, in the case of spectroscopy of ground potentials) illuminates the atomic cloud for some fixed exposure time. In the case of spectroscopy of the excited state, the PA light is a single beam that propagates collinearly with one of the arms of the CDT and is focused to a waist of 50 μ m. The exposure time is chosen such that we see appreciable loss of atoms when the PA laser is tuned near resonance. Typically, a long time scale (on the order of seconds) is required because of the small Franck-Condon (FC) factor between the two-atom scattering state and the excited states at (or near) 0 G. Note this FC factor can be greatly enhanced by performing spectroscopy near the *s*-wave Feshbach resonance at 832 G, such that the exposure time can be reduced to tens of μ s.

6.1.1 Spectroscopy of the $c(1^{3}\Sigma_{q}^{+})$ Potential

Initially, we performed spectroscopy at 834 G in order to enhance the collision rate between the $|1\rangle$ and $|2\rangle$ states. One of the effects of the enhanced collision rate is a broadening of the feature to approximately 1 GHz, well above the natural linewidth of about 10 MHz. This allowed us to quickly scan over many GHz using a large step size to find the approximate location of each vibrational level. We then traced the location of each feature back to 0 G. At this point, we observed that each vibrational level had associated with it three features, each of which corresponds to a particular J' manifold (see Fig. 6.1). The broken degeneracy of the N' = 1 level is due to spin-spin and spin-rotation coupling, which is discussed in Section 5.1.4. Finally, we performed a high resolution scan of each of the three J' features for each of the seven accessible vibration levels (v' = 20 - 26). The location of each of the experimentally measured resonance features are given in Table 6.1.

The uncertainty on the location of each resonance feature has a variety of sources: first,



Figure 6.1: Normalized ⁶Li atom number as a function of the photoassociation laser energy after a 2 s hold time. The three resonances correspond to a transition from the two-atom scattering state where N = 0 to the v' = 21 vibrational level in the $c(1^{3}\Sigma_{g}^{+})$ excited state where N' = 1 and J' = 1, 2, 0 (from left to right). For this measurement, the ensemble temperature was 15 μ K.

the absolute uncertainty of our determination of the laser frequency is limited to ± 600 kHz due to limitations on our ability to verify the absolute uncertainty on the frequency readout via the frequency comb. Second, the measured location of the resonance position may be shifted from the true location because of an ac Stark shifts due to the CDT or PA beams. Third, systematic shifts can occur due to Zeeman shifts in the case that the residual magnetic field is not exactly zero. In order to determine the relative impact of each uncertainty source, we measured the shift rate of the resonance position due to each possible source of systematic uncertainty¹²³.

Due to the large number of observed photoassociation features we choose to use the J' = 1 feature of the v' = 26 vibrational level, and assumed that the shift rate of the other features would be similar in magnitude to this state. However, for systematic effects due to the non-zero magnetic field, we checked the shift rate for all three J' levels of the

 $^{^{123}}$ Except for the uncertainty in the determination of the laser frequency, which is a fixed quantity.

6.1. Summary of Spectroscopy

	J' = 1	J' = 2	J' = 0
v'	(GHz)	(GHz)	(GHz)
20	366861.3537	366861.6031	366862.0645
21	371574.6820	371574.9245	371575.3754
22	376121.6465	376121.8818	376122.3234
23	380501.7789	380502.0079	380502.4363
24	384714.6916	384714.9134	384715.3313
25	388760.1018	388760.3254	388760.7322
26	392637.9166	392638.1235	392638.5195

Table 6.1: Location of measured PA resonances (i.e., the frequency of the PA laser at the photoassociation resonance) for seven vibrational levels in the $c(1^{3}\Sigma_{g}^{+})$ potential. The three resonances associated with each vibrational level correspond to a transition from the twoatom scattering state where N = 0 to the v' = 21 vibrational level in the $c(1^{3}\Sigma_{g}^{+})$ excited state where N' = 1 and J' = 0, 1, 2. The absolute uncertainty on each measurement is ± 600 kHz.

v' = 26 vibrational level. In the case of the J' = 1 and J' = 2 levels, we observed a splitting of the resonance feature as the magnetic field was increased. In these cases, we tracked the movement of the center of gravity of the feature. The shift rate for each source is summarized in Table 6.2, along with the expected shift of the resonance location at the laser intensities ($I_{\rm PA} = 635 \text{ W/cm}^2$ and $I_{\rm ODT} = 7.5 \text{ kW/cm}^2$) and residual magnetic field ($\approx 400 \text{ mG}$) that were used in the experiment. As all of the systematic shifts are small compared to the absolute uncertainty of the frequency comb, we concluded that the absolute uncertainty in each of the measurements is $\pm 600 \text{ kHz}$.

		shift rate (kHz per)			systematic shift (kHz)		
v'	J'	ODT	PA	B Field	ODT	PA	B Field
26	0	_	_	$+75\pm30$	_	_	$+30\pm12$
26	1	-19 ± 1.2	$+471\pm433$	-91 ± 18	-142 ± 9	$+300\pm274$	-36 ± 7
26	2	_	—	$+46 \pm 28$	_	—	$+18\pm11$

Table 6.2: Shift rate and systematic shift for PA resonances in the $c(1^{3}\Sigma_{g}^{+})$ potential. The units of shift rate are kHz/(kW/cm²) for the ODT and PA and kHz/G for the magnetic field. The systematic shift is listed given the laser intensities ($I_{PA} = 635 \text{ W/cm}^{2}$ and $I_{ODT} = 7.5 \text{ kW/cm}^{2}$) and residual magnetic field ($\approx 400 \text{ mG}$) that were used in the experiment.

From the spacing of the J' levels and the expected spacing given by Eq. 5.45, we extracted the spin-spin and spin-rotation constants (λ_{ν} and γ_{ν} , respectively) for each vibra-

tional level. The value of these constants for each vibrational level are given in Table 6.3. In addition, Fig. 6.2 shows a comparison between the measured value of λ_{ν} with the predicted values from an *ab initio* calculation done by B. Minaev [171]. Note that the uncertainty on the *ab initio* values is on the order of a few tens of MHz due to the estimated error on the original calculations, errors associated with our digitization of the data, and the fact that the calculations was likely done for ⁷Li rather than ⁶Li. Given this, we observe a reasonable agreement with the predicted values of λ_{ν} , which adds credence to our model used to label the three observed features.

v'	λ_{ν} (MHz)	γ_{ν} (MHz)
20	-348.2	-14.5
21	-339.4	-14.5
22	-331.1	-14.7
23	-321.7	-14.2
24	-312.2	-14.4
25	-303.6	-14.0
26	-294.3	-14.3

Table 6.3: Values for the spin-spin λ_{ν} and the spin-rotation γ_{ν} interaction constant for the $c(1^{3}\Sigma_{g}^{+})$ potential, determined from the peak spacings reported in Table 6.1 and Eq. 5.45. The uncertainty on each value is ± 400 kHz and results from the uncertainty in the PA resonance positions.

We also observed *p*-wave photoassociation features (where the initial colliding state has N = 1), which allows us to probe the N' = 2 rotational level in the $c(1^{3}\Sigma_{g}^{+})$ potential. This was achieved by stopping the evaporation at a higher temperature, and applying a magnetic field of 185 G (close to the *p*-wave Feshbach resonance at 185.1 G [155]) in order to enhance *p*-wave collisions. More information on these measurements can be found the PhD thesis of M. Semczuk [98].

Previous measurements performed on the $c(1^{3}\Sigma_{g}^{+})$ potential have probed the deeply lying v' = 1 - 7 levels of both ⁶Li and ⁷Li using Fourier transform infrared spectroscopy (FTIR) [181, 182], and the high lying vibrational levels v' = 62 - 90 in ⁷Li and v' = 56 - 84in ⁶Li by photoassociation of atoms in a MOT [176]. Therefore, our measurements bridge a gap in the $c(1^{3}\Sigma_{g}^{+})$ potential where no measurements of these vibrational levels previously existed. In addition, these measurements are the first to observe and quantify the spin-spin and spin-rotation coupling constants.



Figure 6.2: Comparison of the experimentally determined (red circles) and *ab initio* computed (black squares) spin-spin interaction constant λ_{ν} as a function of the vibrational quantum number for the $c(1^{3}\Sigma_{g}^{+})$ potential. Note that the uncertainty on the *ab initio* values is on the order of a few tens of MHz due to the estimated error on the original calculations, errors associated with our digitization of the data, as the fact that the calculations was likely done ⁷Li rather than ⁶Li. The dashed lines are a guide to the eye only. Figure from [84].

6.1.2 Spectroscopy of the $A(1^{1}\Sigma_{u}^{+})$ Potential

The $A(1^{1}\Sigma_{u}^{+})$ potential is much more extensively studied than the $c(1^{3}\Sigma_{g}^{+})$ state. All 87 vibrational levels from v' = 0 to the disassociation limit (v' = 88) where measured by C. Linton et al. using FTIR spectroscopy [183], albeit with an absolute uncertainty that is up to 500 times larger than what is presented here. Photoassociation spectroscopy has also been performed in a MOT for the vibrational levels v' = 62 - 88 [89, 176]. The focus of our work is on the vibrational levels v' = 29 - 35, where we probe the N' = 1 levels (which are particularly relevant for future experiments in the ultra-cold regime and for the creation of ground state molecules using STIRAP) which were not studied in the FTIR experiments.

Measuring (and finding) the seven vibrational levels proceeded in a very similar manner to that described above for the $c(1^{3}\Sigma_{g}^{+})$ potential. In this case, however, we ensured the residual magnetic field was < 20 mG by applying a compensation field using the three orthogonal compensation coils. For these measurements, the CDT intensity was 9.6 kW/cm²

and the PA laser intensity was 65 W/cm^2 . We also fully characterized the systematic shifts of the resonance location that occur because of an ac Stark shift due to the CDT and the PA laser for each vibrational level. The photoassociation resonance location and the shift rate due to the ODT and PA lasers are given in Table 6.4^{124} . In addition, the location of each PA resonance under field-free conditions can be inferred from the shifts rates, and is also listed in Table 6.4.

<i>v</i> ′	Measured (GHz)	Field-Free (GHz)	ODT shift rate $kHz/(kW/cm^2)$	PA shift rate $kHz/(kW/cm^2)$
29	363113.1067	363113.1058	199(6)	-745(661)
30	368015.0436	368015.0492	-546(11)	-2120(738)
31	372780.6714	372780.6709	44(4)	-73(228)
32	377406.2393	377406.2401	-79(6)	803(707)
33	381887.7859	381887.7848	100(5)	80(253)
34	386221.1190	386221.1181	73(5)	272(265)
35	390401.8749	390401.8750	-9(10)	-826(437)

Table 6.4: Experimentally measured PA resonances in the $A(1^{1}\Sigma_{u}^{+})$ potential. These resonances correspond to a transition from an initial unbound molecule state with N = 0, I = 0 to the v^{th} vibrational level with N' = 1, I' = 0. For these measurements, the CDT intensity was 9.6 kW cm⁻² and the PA laser intensity was 65 W cm⁻². The absolute uncertainty in each of the measurements is ± 600 kHz. For the shift rates, the number in brackets is an estimation of the 1σ uncertainty on the last digit(s).

We found that the 1σ statistical uncertainty on the fit to each resonance location and to the extrapolated field-free resonance location was typically on the order of 250 kHz, which is small compared to the absolute uncertainty of the frequency comb (± 600 kHz). Therefore, similar to the $c(1^{3}\Sigma_{g}^{+})$ state, we concluded that the absolute uncertainty in each of the measurements is ± 600 kHz. Note that since the magnetic field was kept below 20 mG, and the singlet state should have no (or negligible) coupling to the magnetic field (because S' = I' = 0), we assume that there are no systematic shifts due to the small residual magnetic field.

In order to check the viability of performing STIRAP in the ⁶Li system using the singlet potentials, we also performed single color spectroscopy at magnetic fields near the Feshbach resonance and at temperatures where we formed Feshbach molecules or (on the high

 $^{^{124}}$ Again, we assumed that the shifts produced by the CDT and PA laser are independent, and the shift is linear with the laser intensity.

magnetic field side of the resonance) BCS pairs (see Section 5.1.3). The quantity of interest here is the magnitude of the Rabi frequency Ω_1 of the transition which couples $|a\rangle \rightarrow |e\rangle$. In order to extract Ω_1 from our single color measurements, we used the three level model described by the Hamiltonian in Eq. 5.59 and numerically integrated the three differential equations found using the time dependent Schrödinger equation (see Eq. 5.82). We used this numerical simulation to fit the spectra of our single color photoassociation, using Ω_1 as a free parameter. In this case, three level model is valid because the initial state is a bound state (i.e., there is no reliance on collisions). In addition, this method is only practical when the hold time (i.e., the time in which the atoms are illuminated by the PA light) is on the order to tens of microseconds or less, because the integration time becomes unwieldy for longer hold times. Therefore, this measurement can only be performed when Ω_1 is on the order of $2\pi \times 100$ kHz or larger which, thankfully, was case for these measurements. In the fit, we fix $\gamma_e = 2\pi \cdot 10$ MHz as it is correlated to Ω_1 .

We first measured the Rabi frequency as a function of the power of the photoassociation laser for six of the accessible vibrational levels in the $A(1^{1}\Sigma_{u}^{+})$ potential at 754 G. As the Rabi frequency scales like the magnitude of the field, that is $\Omega = K\sqrt{P}$, we used a linear fit to the measured Rabi frequencies as a function of \sqrt{P} for each level to extract K^{125} . Physically, K is a measure of the strength of the coupling between $|a\rangle$ and the particular $|e\rangle$ vibrational level. The value of K for each vibrational level is shown in Fig. 6.3, which indicates that the v' = 31 and v' = 35 levels have the largest FC factor with the initial state. Note that we can reasonably expect to have about 100 mW available for photoassociation. At 754 G, this corresponds to $\Omega_1 \approx 2\pi \times 930$ kHz for the v' = 31 and v' = 35 levels. Note that although the Rabi frequency is not constant over the entire sample because of the finite width of the PA laser, this method of fitting of loss feature effectively spatially averages the Rabi frequency. However, the maximum variation of the Rabi frequency is only on the order of 20%, given the focus size of the PA beams ($\approx 50 \ \mu m$), the spatial width of the sample ($\approx 25 \ \mu m$) and that $\Omega \propto \sqrt{I}$.

Given that the initial state $|a\rangle$ near the Feshbach resonance is a superposition of the open channel (which has triplet character) and closed channel (which has singlet character), where the fraction of the superposition state which has closed channel character varies

¹²⁵We choose perform this fit as a function of power because it is a more natural unit to use with respect to our experiment. In our setup, the PA beams have a $1/e^2$ intensity radius of 50 μ m, and therefore 1 mW corresponds to an intensity of 13 W/cm².



Figure 6.3: Ω_1 as a function of vibrational level in the $A(1^1\Sigma_u^+)$ potential at 754 G. This indicates that the v' = 31 and v' = 35 levels have the largest FC factor with the initial state. Note that we can reasonable expect to have about 100 mW available for PA, which at 754 G this corresponds to $\Omega_1 \approx 2\pi \times 930$ kHz. For conversion to intensity, the $1/e^2$ intensity radius of the photoassociation laser is approximately 50 μ m, and 100 mW corresponds to an intensity of 1300 W/cm².

with magnetic field (see Section 5.1.2), we have the ability to tune Ω_1 using the magnetic field. We measured Ω_1 as a function of magnetic field for v' = 31, by first evaporating to approximately 300 nK, where $T/T_F = 0.4$ at 759 G, and then moving the magnetic field to the value of interest to perform single color photoassociation. At each field, the power of the photoassociation laser was kept fixed at 100 mW and the hold time was set to 5 μ s. If necessary, the hold time was lengthened to ensure that we achieved greater than 50% atom loss (this was only required at fields greater than 820 G when the Rabi frequency is smaller than $2\pi \times 200$ kHz). Finally, the magnetic field was returned to 759 G for imaging the remaining atoms in the ODT.

Figure 6.4 shows the dependence of Ω_1 on magnetic field, as well as the measured atom number if the photoassociation light was not turned on. Our data indicates that Rabi frequencies of greater than 1 MHz are possible, while still maintaining a reasonable molecule number. The decrease in molecule number at lower fields may be due to a decrease in the three body loss suppression that occurs near the Feshbach resonance, or due to a unknown technical detail in the apparatus. Previously, it has been reported that the Feshbach pair becomes short lived at fields below 600 G [64]. Note that the singlet nature of the Feshbach molecule pair (and thus, the Rabi frequency) varies smoothly as a function of magnetic field, even across the Feshbach resonance at 832 G [64, 159, 160].



Figure 6.4: Measured Rabi frequency Ω_1 (black dots) for the field coupling the Feshbach molecule state $|a\rangle$ to the excited molecule state $|e\rangle$. Also shown is the atom number (red squares) measured in the absence of the photoassociation light for each magnetic field. Note that the singlet nature of the Feshbach molecule pair (and thus, the Rabi frequency) varies smoothly as a function of magnetic field, even across the Feshbach resonance at 832 G.

6.1.3 Spectroscopy of the $X(1^{1}\Sigma_{g}^{+})$ Potential

The singlet potential offers a fairly simple system in which to study dark states and initial attempts towards the creation of ultra-cold molecules using STIRAP. This is because both the initial state $|a\rangle$ and the ground molecule state $|e\rangle$ are non-degenerate, because S = I = N = 0 (see Section 6.2 for more details). In addition, there is negligible coupling of the states to magnetic fields, so the binding energy of the excited and ground bound molecular states do not change as a function of the magnetic field strength. This makes it fairly straightforward (experimentally) to switch between experiments with no field, or

experiments near the s-wave Feshbach resonance at 832 G.

At zero field, the least bound level that we can access is the N'' = 0 rotational state of the v' = 38 vibrational level because the N'' = 2 rotational is not bound. At fields above the narrow s-wave FR at 543.3 G, this level (which is now a "dressed" Feshbach molecule state) is only very loosely bound and, and eventually disappears as a bound state when it crosses threshold near 832 G. Therefore, for experiments at large magnetic field, the v'' = 37vibrational level becomes the "effective" least bound state that is used in the formation of dark states and potential first attempts at STIRAP. For these reasons, we focused on these two vibrational levels in our initial spectroscopy of the $X(1^1\Sigma_q^+)$ potential.

We first found the approximate locations of each level using two-color spectroscopy, as described in Section 5.2. Armed with this information, we performed high resolution dark state spectroscopy of the levels of interest. We performed these measurements with approximately 50×10^3 atoms at a temperature of 600 nK, corresponding to $T/T_{\rm F} \approx 0.6$ and ensured the residual magnetic field was below 20 mG. We choose to use the v' = 31 level in the $A(1^1\Sigma_u^+)$ state as the intermediate state $|e\rangle$ because it had the smallest shift rates due the ac Stark shift from the ODT and PA beam. However, this choice of intermediate state is, in some respects, arbitrary.

We set the control field frequency to match the frequency found from two-color spectroscopy, and scanned the pump field about the location of the $|a\rangle \rightarrow |e\rangle$ transitions found from single color spectroscopy. Due to the control field, we see a dark state when the frequency difference of the lasers matches the frequency difference of the states $|a\rangle$ and $|g\rangle$. We fit the spectra using the three level model (described in Section 5.2.2) to extract the precise location of the two photon resonance. This frequency difference for the two least bound vibrational levels at 0 G, and for select magnetic fields around the Feshbach resonance at 832 G for the v'' = 37 level are given in Table 6.5. In addition, Table 6.5 gives the binding energy of the two least bound levels at 0 G, which is found by by adding $2a_{2s}$ to the difference in photon resonance (see Section 5.1.1). Note that although the frequency difference which satisfies the two photon resonance condition for the v'' = 37 level appears to be dependent on the magnetic field, this change in energy can be solely accounted for by the energy change of the two-atom scattering state (see Fig. 5.2).

Because these measurements measure a difference in frequency, any systematic errors

		B	$\nu_2 - \nu_1$	Binding Energy
<i>v''</i>	N'' = F''	(G)	(GHz)	(GHz)
38	0	0	1.321671(21)	1.625945(21)
37	0	0	58.260(1)	58.564(1)
37	0	754	56.364(1)	—
37	0	804	56.225(1)	—
37	0	838.8	56.127(1)	_

6.1. Summary of Spectroscopy

Table 6.5: Experimentally measured energy difference between the initial state $|a\rangle$ and the v'' = 37 and v'' = 38 vibrational levels in the $X(1^{1}\Sigma_{g}^{+})$ potential. The number in brackets is an estimation of the 1σ uncertainty on the last digit(s). For the v'' = 38 level, we performed a full study of the systematic error. This was not done for the v'' = 37 level, and we estimate the error on each measurement is at most 1 MHz. Note that although the frequency difference which satisfies the two photon resonance condition for the v'' = 37 level appears to be dependent on the magnetic field, this change in energy can be solely account for by the energy change of the two-atom scattering state (see Fig. 5.2).

due to the measurement uncertainty of the PA laser frequencies (in our case ± 600 kHz) subtract out. Therefore, the absolute uncertainty of these measurements is limited only by the other systematic effects in the system (namely, ac Stark shifts from the ODT and PA lasers). For the v'' = 38 level, we performed a full study of the systematic error, which reduced the absolute uncertainty to ± 21 kHz. We did not carefully measure the systematic shift for the v'' = 37 level, however we made an effort reduce these effect by using a shallow ODT and small PA powers ($I_1 = 100 - 500$ W cm⁻² and $I_1 = 20 - 200$ W cm⁻²). We estimate that the error on the location of the two photon resonance is at most ± 1 MHz.

For the dark state measurements performed at magnetic fields near the s-wave Feshbach resonance at 832 G, the initial $|a\rangle$ state can be either a thermal ensemble of atoms, Feshbach molecules (for fields below the resonance) or BCS-like pairs (for fields above the resonance). This initial state $|a\rangle$ is determined experimentally by the temperature of the ensemble and the choice of magnetic field. That is, for fields below 832 G we are able to form Feshbach molecules via three body recombination when the temperature of the ensemble is below the binding energy of the Feshbach molecules. For fields above 832 G, we can form BCSlike pairs if the temperature of the ensemble is below the critical temperature for pair formation¹²⁶.

¹²⁶The details of the formation of Feshbach molecules and BCS pairs is discussed in more detail in Section 5.1.3.

In particular, when a degenerate Fermi gas is prepared above the FRs such that there are BCS-like pairs present, the dark state is a coherent superposition of these pairs and the bound molecules in the $|g\rangle$ state. We confirmed that the dark state is created without disrupting the many-body pairing physics by performing RF spectroscopy in the presence of the optical coupling fields. We observed an RF spectrum similar to that in Fig. 5.7, which is consistent with the presence of pairing.

Motivated by the prospect of studying dark-states in the BEC-BCS crossover regime and the use of the dark states for STIRAP, we took dark state spectrum as a function of magnetic field above and below the Feshbach resonance. We found that the revival height of the dark state appears to show an abrupt decrease in height for magnetic fields below 829 G, as shown in Fig. 6.5. For these measurements, we set $\Omega_1 \approx 2\pi \times 200$ kHz and $\Omega_2 \approx 2\pi \times 2$ MHz, and used an exposure time of 40 μ s.

In addition, we verified that Ω_1 is continuous in this regime, and from these measurements extracted the closed channel fraction Z of the initial state¹²⁷. As a function of magnetic field

$$\Omega_{1}(B) = \langle a | \vec{d} \cdot E | e \rangle = \langle \Phi_{b} | \vec{d} \cdot E | e \rangle$$

$$= \sqrt{Z} \langle \Phi_{C} | \vec{d} \cdot E | e \rangle$$

$$= \sqrt{\frac{8Z}{9}} \langle 00000_{v''=38} | \vec{d} \cdot \vec{E} | 10011_{v'=31} \rangle$$

$$= \sqrt{\frac{8Z}{9}} \Omega_{0},$$
(6.1)

where $|\Phi_{\rm C}\rangle$ is the closed channel fraction of the weakly bound Feshbach molecule state $|\Phi_b\rangle$ (see Eq. 5.28 and 5.29). The states in the last line of Eq. 6.1 are expressed in the $|NSIJF\rangle$ basis, where the subscript serves as a reminder of the electronic potential and vibrational level to which each state is associated. We determine Ω_0 from an Autler-Townes measurements using the v'' = 38 and v' = 31 vibrational levels at 0 G, where Ω_0 plays the role of the bound-to-bound coupling field Ω_2 . The calculated value of Z can be found from

$$Z = \left(\frac{9}{8}\right) \left(\frac{\Omega_1}{\Omega_0}\right)^2,\tag{6.2}$$

¹²⁷This was done, in part, as a "sanity check" to ensure that a parameter which is known to vary continuously [64, 160] across the Feshbach resonance did so in our system.



Figure 6.5: Top Panel: The revival height of the dark state as a function of magnetic field on both sides of the Feshbach resonance (indicated by the vertical dashed line). In this measurement, the initial state $|a\rangle$ are either Feshbach molecules or BCS-like pairs. The excited state $|e\rangle$ is the v' = 31 vibrational level in the $A(1^{1}\Sigma_{u}^{+})$ potential and the ground bound state $|g\rangle$ is the v'' = 37 vibrational level of the $X(1^{1}\Sigma_{g}^{+})$ potential. For magnetic fields above 829 G, we observe near complete revival on the two-photon resonance (see insets). Bottom Panel: Measured closed channel fraction Z of the dressed molecule state (black circles). Also shown (red squares) is a similar measurement by Patridge et al. [64] and theoretical predictions done by Romans and Stoof, digitized from [160]. The grey region corresponds to the strongly interacting regime where $k_{\rm F}|a| > 1$. Figure from [159].

and is shown in the lower panel of Fig. 6.5. We note that our observations are consistent with those reported by Patridge et al. [64].

We made a brief attempt at transferring the loosely bound Feshbach molecules to the v'' = 37 ground molecular state via STIRAP at a magnetic field of 754 G. This magnetic field was chosen to achieve a balance between having a large Ω_1 and a reasonable molecule number (see Fig. 6.4). After the initial STIRAP pulse, we left the probe field for approximately 20 μ s such that any remaining Feshbach molecules would be lost from the trap, and then

performed a reverse STIRAP step. However, we saw no evidence of transfer to or from the bound molecule state. We believe this is likely, in part, due to the low efficacy of the dark state at this magnetic field.

The poor revival height of the dark state suggest that there is a decoherence mechanism present in the system. Decoherence of the dark state can be caused by, for example, a finite lifetime of the $|a\rangle$ or $|g\rangle$ states or by collisions. However, it is unlikely that either collisions or finite state lifetimes is responsible for the observed effect. The lifetime of the $|a\rangle$ or $|g\rangle$ state or the collision rate would need to be on the order of 100 kHz or larger in order to explain the observed revival height reduction, which is not a reasonable estimate for this system. Secondly, and more importantly, there is no clear reason why the state lifetime or the collision rate would vary abruptly across the magnetic field corresponding the the FR. In particular, the collision rate scales proportional to the scattering cross section, which is unitary limited in the region where we observe the abrupt change (i.e., $k^2a^2 \gg 1$, see Eq. 3.24). Therefore, the collision rate should depend only on the ensemble temperature (not the scattering length), which is the same for each measurement taken at each magnetic field.

The obvious change between the two regimes is the existence of the two-body bound state (i.e., the Feshbach molecule state) on the low magnetic field side of the resonance (where the scattering length is positive) which exists in addition to the two-atom scattering state (see Chapter 5). If the probe and control lasers are tuned to match the two photon resonance condition for one of the two states (either the scattering state or the Feshbach molecule state) then the two-photon resonance condition cannot be met for the other state. In general, this would result in a "grey-state", where the interference that leads to the dark-state is not complete, and atom loss from this "grey-state" could be observed. However, the binding energy of the Feshbach molecule state for fields at or above 750 G is less than 20 kHz. This energy difference is much smaller than the observed width of the dark-state, and additionally is smaller than the two-photon linewidth of the lasers (≈ 100 kHz) used for these experiments¹²⁸.

¹²⁸For these measurements, the PA beams were recycled along the same optical path as the ODT laser. This recycling causes a rotation of the polarization of the probe and control fields. We have seen evidence that this can affect the dark state revival height (Section 6.2 for details). While the polarization of the probe and control field is the same above and below the magnetic field where we observe the abrupt change in revival height changes, the polarization of the probe and control fields may play a role in the observed spectrum. This is currently under investigation.
While we cannot currently explain the abrupt change of the revival height, we have observed similar anomalous EIT spectrum for other dark state and/or Autler-Townes measurements in our experiments that may guide future investigation of this effect. We believe that these anomalous spectra are the result of degeneracies that exist in the energy structure of the ⁶Li system, as well as the choice of the polarization of the control and probe field, and are discussed in the following section.

6.2 Degenerate Levels

With the relevant energy levels in the ${}^{6}\text{Li}_{2}$ system, it is not possible to experimentally realize the ideal three level model. Even at large magnetic fields, a degeneracy persists in the accessible levels of both the $A(1^{1}\Sigma_{u}^{+})$ and $c(1^{3}\Sigma_{g}^{+})$ potentials. In the case of the $A(1^{1}\Sigma_{u}^{+})$ level, there is no coupling to the magnetic field since S = I = 0. Although the $c(1^{3}\Sigma_{g}^{+})$ triplet does strongly couple to the magnetic field (S = I = 1), ⁶Li has a very small atomic hyperfine constant in the $2^{2}P_{3/2}$ state, which results in a threefold degeneracy due to the projection of the nuclear spin.

6.2.1 Singlet States: Five Level Model

The simplest achievable level system is a five level system, for which the $|e\rangle$ level is the triply degenerate $|00100\rangle$ state in the $A(1^{1}\Sigma_{u}^{+})$ potential and the $|g\rangle$ level is the non-degenerate $|00000\rangle$ state in the $X(1^{1}\Sigma_{g}^{+})$ potential. When there is no (or a very small) magnetic field, the $|a\rangle$ state is the singlet like $|00000\rangle$ admixture of the two-atom scattering state between two ⁶Li atoms in the F = 1/2 ground state.

One can start to examine the effect of degenerate levels by following the traditional description of Autler-Townes splitting (see Section 5.2.1). The dressed Hamiltonian of the system (including the strong control field, the $|g\rangle$ state, and the triply degenerate $|e\rangle$ state) is a simple extension of the Hamiltonian in Eq. 5.49, giving

$$H = \frac{\hbar}{2} \begin{bmatrix} 0 & \Omega_2^{\sigma^-} & \Omega_2^{\pi} & \Omega_2^{\sigma^+} \\ \Omega_2^{\sigma^-} & 2\Delta & 0 & 0 \\ \Omega_2^{\pi} & 0 & 2\Delta & 0 \\ \Omega_2^{\sigma^+} & 0 & 0 & 2\Delta \end{bmatrix}$$
(6.3)



Figure 6.6: States and couplings in the five level model, where the excited state $|e\rangle$ is triply degenerate and the ground state $|g\rangle$ and initial state $|a\rangle$ are non-degenerate. $\Omega_2^{\sigma^-}$, Ω_2^{π} and $\Omega_2^{\sigma^+}$ are the Rabi frequencies which couple the state $|g\rangle$ to the states $|e_{-1}\rangle$, $|e_0\rangle$, and $|e_1\rangle$ where $\Delta m_{\rm F} = -1, 0, +1$ respectively. The probe field coupling (Ω_1) couples the $|a\rangle$ state to the $|e\rangle$ state in the same way, but is not explicitly shown.

when the basis $|\psi\rangle = (a, e_{-1}, e_0, e_1)$ is used. In this Hamiltonian, $\Omega_2^{\sigma^-}$, Ω_2^{π} and $\Omega_2^{\sigma^+}$ are the Rabi frequencies which couple the state $|g\rangle$ to the states $|e_{-1}\rangle$, $|e_0\rangle$, and $|e_1\rangle$ where $\Delta m_{\rm F} = -1, 0, +1$ respectively (see Fig. 6.6). The detuning of the control field from the $|g\rangle \rightarrow |e\rangle$ transition frequency is given by Δ .

In general, the Rabi frequency for a transition between state $|i\rangle$ and state $|j\rangle$ is

$$\Omega_{ij} = \frac{\vec{d_{ij}} \cdot \vec{E}}{\hbar} \,, \tag{6.4}$$

where \vec{E} is the electric field amplitude (including the polarization of the field) and

$$\vec{d_{ij}} = \langle i | \, \hat{d} \, | j \rangle \tag{6.5}$$

is the transition electric dipole matrix element for the $|i\rangle \rightarrow |j\rangle$ transition, which can be broken into a spatial part and a spin part.

The type and strength of the transitions that the photoassociation light drives can be

controlled by via the polarization of the light. Both the probe and control fields propagate collinear to each other, and perpendicular to a small vertical magnetic field which defines the quantization axis (see Fig. 6.7). The two PA fields are linearly polarized at some angle with respect to the vertical axis, and this angle can be independently controlled for both the probe and control field. When the field is polarized along the vertical axis the light drives π transitions, and when it polarized along the horizontal axis the light drives σ^+ and σ^- transitions. For the following discussion we define θ to be the angle that the probe field polarization makes with the vertical axis and ϕ the relative angle between the probe and control field polarization, as shown in Fig. 6.7. With this, the Rabi frequency for each of the three possible transitions can be written as function of the polarization angles θ and ϕ as

$$\hbar \cdot \Omega_2^{\sigma^-} = \frac{d_{\sigma^-} E_2 \sin\left(\theta + \phi\right)}{\sqrt{2}} \tag{6.6}$$

$$\hbar \cdot \Omega_2^{\pi} = d_{\pi} E_2 \cos\left(\theta + \phi\right) \tag{6.7}$$

$$\hbar \cdot \Omega_2^{\sigma^+} = \frac{d_{\sigma^+} E_2 \sin\left(\theta + \phi\right)}{\sqrt{2}}, \qquad (6.8)$$

where E_2 is the total control electric field magnitude. In general, the transition dipole matrix element is different for each transition. However, in the case of the $A(1^1\Sigma_u^+)$ state, the spin part of each matrix element is equal, and we assume that the spatial part is also equal because the coupling is to three degenerate states.

The eigenstates (not normalized) of the Hamiltonian in Eq. 6.3 in the case where $\Delta = 0$ are

$$|\pm\rangle = \pm \sqrt{\Omega_2^{\sigma^{-2}} + \Omega_2^{\pi^2} + \Omega_2^{\sigma^{+2}}} |g\rangle + \Omega_2^{\sigma^{-}} |e_{-1}\rangle + \Omega_2^{\pi} |e_0\rangle + \Omega_2^{\sigma^{+}} |e_1\rangle$$
(6.9)

$$0_1 \rangle = -\frac{\Omega_2^{\pi}}{\Omega_2^{\sigma_-}} |e_{-1}\rangle + |e_0\rangle \tag{6.10}$$

$$|0_2\rangle = -\frac{\Omega_2^{\sigma+}}{\Omega_2^{\sigma-}} |e_{-1}\rangle + |e_1\rangle .$$
 (6.11)

The eigenenergies of the $|\pm\rangle$ states are

$$E_{\pm} = \hbar \sqrt{\Omega_2^{\sigma-2} + \Omega_2^{\pi^2} + \Omega_2^{\sigma+2}}$$
(6.12)

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Figure 6.7: Polarization angles of probe and control fields. We define θ to be the angle that the probe field polarization makes with the vertical axis and ϕ the relative angle between the probe and control field polarization. Each field can be decomposed into a horizontal and vertical component, driving transition where $\Delta m_F = \pm 1$ (σ^+ and σ^-) and $\Delta m_F = 0$ (π) respectively. Both field propagate collinear to each other along \vec{k} , which is perpendicular to the axis of the bias magnetic field (along the vertical z-axis) as shown.

relative to the field free energy of the $|e\rangle$ state, while the $0_{1,2}$ are not shifted (i.e., the two states have an eigenenergy of E = 0).

These four dressed eigenstates are probed by a weak probe beam which couples the initial state $|a\rangle$ to the degenerate excited state $|e\rangle$. Similar to the control field, the relative strength of the coupling from the $|a\rangle$ state to each of the degenerate excited states can be controlled through the polarization of the field. The Rabi frequency for each of the three possible transitions can be written as a function of θ (the angle that the probe field polarizations makes with the vertical axis) as

$$\hbar \cdot \Omega_1^{\sigma^-} = \frac{d_{\sigma^-} E_1 \sin\left(\theta\right)}{\sqrt{2}} \tag{6.13}$$

$$\hbar \cdot \Omega_1^{\pi} = d_{\pi} E_1 \cos\left(\theta\right) \tag{6.14}$$

$$\hbar \cdot \Omega_1^{\sigma^+} = \frac{d_{\sigma^+} E_1 \sin\left(\theta\right)}{\sqrt{2}}, \qquad (6.15)$$

where E_1 is the total probe field amplitude.

Noting the definition of the Rabi frequency in Eq. 6.4, the probability of excitation on the $|a\rangle \rightarrow |\pm\rangle$ transition is related to

$$\langle a | \hat{d} \cdot \vec{E} | \pm \rangle = \Omega_1^{\sigma-} \cdot \Omega_2^{\sigma-} + \Omega_1^{\pi} \cdot \Omega_2^{\pi} + \Omega_1^{\sigma+} \cdot \Omega_2^{\sigma+} \propto \sin(\theta + \phi) \sin(\theta) + \cos(\theta + \phi) \cos(\theta)$$

$$\propto \cos(\phi) .$$
(6.16)

Likewise, the probability of excitation on the $|a\rangle \rightarrow |0_{1,2}\rangle$ transition (using the $|0_1\rangle$ state as an example) is related to

$$\langle a | \hat{d} \cdot \vec{E} | 0_1 \rangle = \Omega_1^{\sigma-} \cdot \Omega_2^{\pi} + \Omega_1^{\sigma-} \cdot \Omega_2^{\pi} + \propto -\cos\left(\theta + \phi\right) \sin\left(\theta\right) + \sin\left(\theta + \phi\right) \cos\left(\theta\right)$$

$$\propto \sin\left(\phi\right).$$

$$(6.17)$$

Remarkably, the observed spectra depends only the relative polarization angle between the probe and control fields. In particular:

- In the case of collinear polarization ($\phi = 0^{\circ}$), a standard Autler-Townes doublet is always observed. In this case, the system is essentially reduced to an effective simple three level system.
- In the case of orthogonal polarization (φ = 90°), the only loss feature appears at the location that would expected in the absence of the control field¹²⁹. This can be understood by considering that the superposition states which are coupled by the probe field are formally orthogonal to the superposition states that are coupled by the control field. Therefore, the probe field probes the |e⟩ manifold as if the control field did not exist.
- In all other cases, three loss features are observed. This is most pronounced when $\phi = 45^{\circ}$, where the loss probability from the $|\pm\rangle$ and $|0_{1,2}\rangle$ states are equal.

It is worth noting that the observed spectra is not merely a summation of the spectra one would expect by treating each of the degenerate excited states as a separate three level

¹²⁹Colloquially, we refer to this as a "single-color feature" since the behavior looks the same as that produced in single color photoassociation using only the probe laser.

system, and summing the result of each individual system. Rather, the observed spectrum depends on interference between excitation pathways. However, this result does not require any phase coherence between the probe and control fields, since the phase evolution of the two fields is common to every term that appears in either Eq. 6.13 or 6.16. In addition, the splitting of the doublet from the field free energy (i.e, the eigenenergies of the state given by Eq. 6.9 relative to the eigenenergies of the state given by Eq. 6.10 and 6.11) is independent of the polarization direction of both the probe or control field.

A more general approach to the effect of degenerate levels is to dress the entire system with both the probe and control fields. In the case of this five level system, the full dressed Hamiltonian is

$$H(t) = \hbar/2 \begin{bmatrix} -i\gamma_a & \Omega_1^{\sigma^-} & \Omega_1^{\pi} & \Omega_1^{\sigma^+} & 0\\ \Omega_1^{\sigma^-} & 2\delta - i\gamma_e & 0 & 0 & \Omega_2^{\sigma^-}\\ \Omega_1^{\pi} & 0 & 2\delta - i\gamma_e & 0 & \Omega_2^{\pi}\\ \Omega_1^{\sigma^+} & 0 & 0 & 2\delta - i\gamma_e & \Omega_2^{\sigma^+}\\ 0 & \Omega_2^{\sigma^-} & \Omega_2^{\pi} & \Omega_2^{\sigma^+} & 2(\delta - \Delta) - i\gamma_g \end{bmatrix},$$
(6.18)

where δ is the detuning of the probe field from the $|a\rangle \rightarrow |e\rangle$ transition and Δ is, as before, the detuning of the control field from the $|g\rangle \rightarrow |e\rangle$ transition. The phenomenological terms $i\gamma_{a,e,g}$ are added to the Hamiltonian to represent the decay (or loss) rate from the $|a\rangle, |e\rangle$ and $|g\rangle$ state respectively to outside of the system. Here, we set γ_a and γ_g to be zero. In general, γ_a and γ_g can be non zero due to off-resonance radiative loss from the control and probe field respectively, or if the states themselves have a decay mechanism.

The dynamics (and final state population) of the system can found by numerically integrating the five differential equations found using the time dependent Schrödinger equation. Figure 6.8 summarizes the results of this simulation for three relevant relative (and interesting) polarization angles: $\phi = 0^{\circ}$ (top panel), $\phi = 45^{\circ}$ (middle panel) and $\phi = 90^{\circ}$ (bottom panel).

An interesting result of this simulation is that in the case of $\phi \neq 0^{\circ}$ no dark state occurs at the two-photon resonance. Formally, this is because all of the eigenstates of the system for $\delta = \Delta = 0$ have a non zero transition probability to the lossy $|e\rangle$ states or, alternatively, because each of the eigenstates has some component fraction of the lossy $|e\rangle$ state. This result can be understood by considering that the dark state (in a three level



Figure 6.8: Numerical simulation of five level Hamiltonian as a function of the relative angle of the probe and control polarization. Top: Collinear polarization ($\phi = 0^{\circ}$), where a standard Autler-Townes doublet is always observed. Middle: Three loss features are observed when the polarization of the probe and control beam are not collinear or orthogonal. This is most pronounced when $\phi = 45^{\circ}$ (pictured). Bottom: Orthogonal polarization ($\phi = 90^{\circ}$), the only loss feature appears at the location that would expected in the absence of the control field.

system) is due to an interference between the two transition pathways to the $|e\rangle$ state. When $\phi \neq 0^{\circ}$, this interference is weakened (i.e., is no longer completely destructive) due to additional non-symmetric couplings between the $|a\rangle$ and $|g\rangle$ state and the $|e\rangle$ state by the probe and control fields. Figure 6.9 shows the expected revival height of the dark state as a function of the relative polarization angle ϕ . This result is important for any attempts to create ground state molecules via STIRAP, as the maximum achievable transfer efficiency is directly related to the fidelity of the dark state. In fact, these results suggest that in the



Figure 6.9: Calculated dark state revival height in a five level system, as a function of the relative polarization angle between the probe and control beam. For this simulation, $\Omega_2/\Omega_1 = 10$ and $\Omega_2/\gamma_e = 0.7$. When $\phi \neq 0^\circ$, this interference is weakened (i.e., is no longer completely destructive) due to additional non-symmetric couplings between the $|a\rangle$ and $|g\rangle$ state and the $|e\rangle$ state by the probe and control fields. The top panels shows the expected atom number as a function of the two photon detuning for three characteristic angles (indicated on the plot by the black dots).

case of a system with degenerate levels, it is crucial to ensure that the polarizations of both fields are collinear.

Experimental Demonstration

Currently, both the probe and control fields are coupled through the same polarization maintaining fiber to the experiment table, where they are spatially overlapped with the second pass of the ODTs. This configuration makes it possible to easily create colinear and orthogonal polarizations by coupling the probe and control fields along the same or orthogonal axes of the fiber, respectivly. At the output of the fiber on the experiment table, a HWP is used to set θ (the angle the probe field polarization makes with the vertical) without changing ϕ since the waveplate will act on both the probe and control fields in the same manner. Our observations, shown in the top panel of Fig. 6.10, show good agreement with the expected behavior for the case of colinear polarization ($\phi = 0^{\circ}$) and orthogonal polarization ($\phi = 90^{\circ}$). The observed behavior was consistent for $\theta = 0^{\circ}, 45^{\circ}$, and 90°. This data used the v' = 31 level of the $A(1^{1}\Sigma_{u}^{+})$ potential as the $|e\rangle$ state and the v'' = 38 level of the $X(1^{1}\Sigma_{a}^{+})$ potential as the $|g\rangle$ state.

In order create polarizations that are neither colinear nor orthogonal, one of the probe or control beams must be coupled into the polarization fiber off of the fiber axis. In this type of configuration, the polarization state of the light is not necessarily preserved within the fiber. Therefore, the relative polarization of the fields at the output of the fiber is not necessarily the same as at the input. Moreover, it is possible that the relative polarization can drift in time, often on a timescale of a few seconds to a minute which is similar to that of an experimental run¹³⁰. As such, it is hard to determine an exact (and constant) value of ϕ , but nevertheless it is possible to create a configuration where $\phi \neq 0^{\circ}$ or $\phi \neq 90^{\circ}$. In this configuration, the bottom panel of Fig. 6.10 shows the appearance of three loss features, consistent with the expected behavior. In order to carefully control the relative polarization angle of the two fields, we would need to couple into two independent fibers and rotate the polarization of each field using a HWP after the fibers. The fields would then be combined using a non-polarizing beam splitter. However, for the purposes of creating a "clean" system where the polarizations are collinear it is sufficient to couple both field into a single fiber, ensuring that the beams are launched into the fiber along the fiber axis.

In a previous iteration of the experiment, the probe and control fields were initially sent along the first pass of the ODT and recycled around for a second pass (along with the ODT beam), as shown in Fig. 6.11^{131} . This was intended to increase the total power available for photoassociation. However, as the recycling optics where not always oriented such that the beams reflected at an angle of 90°, the polarization of the probe and control fields on

¹³⁰If the polarization of the light into a polarization maintaining fiber is not well aligned with one of the fiber axes, the fiber acts as a high order waveplate. This makes the output polarization sensitive to very small changes in temperature or mechanical stress on the fiber, and results in an output polarization that can be time dependent. This effect is easily observed by placing a polarizing optic at the output of the fiber, and monitoring the transmitted power.

¹³¹More information about this previous setup can be found in the PhD thesis of Mariusz Semczuk [98].



Figure 6.10: Experimentally observed Autler-Townes splitting in a five-level system. Top Panel: Collinear polarization (red squares, dashed red line) produce the standard Autler-Townes doublet while orthogonal polarizations (black circles, solid black line) produces only a loss feature at the location loss is expected in the absence of the control field. Bottom Panel: Spectra observed when $\phi \neq 0^{\circ}$ and $\phi \neq 90^{\circ}$ (that is, the polarization directions of the probe and control field are not parallel or perpendicular). The black line is only a guide for the eye, which demonstrates the appearance of three loss features (and no dark state). Due to technical difficulties (see text) it is hard to determine the actual value of ϕ .

the second pass were rotated with respect to the first pass. It was in this setup that we originally observed the appearance of three features shown in Fig. 6.12. Even when the probe and control fields were collinear to each other, we were unable to achieve just an Autler-Townes doublet. We believe this occurred because, although the polarization of the probe and control field on each pass was collinear, there existed photons that had a relative polarization angle $\phi \neq 0$ (for example, a probe photon from the first pass, and a control photon from the second pass). We noticed a difference in depth of the middle loss feature



Figure 6.11: The arrangement of the ODT and PA beams used in a previous iteration of the experiment. The IPG and SPI ODTs were overlapped using a dichroic mirror (BS2) and the PA light was combined with the IPG using a second dichroic mirror (BS1). Both the ODT and PA beams were recycled around for a second pass above the cell (indicated by the dashed lined). The recycling optics were not oriented such the incident and reflected beam made a right angle, and as such caused a rotation of the polarization of the reflected beams. Figure from [98].

(the anomalous "single-color" feature which was dependent on the orientation of the field (i.e., whether the field was polarized along the vertical or horizontal axis). We suspect this is due to a difference in the amount of polarization rotation caused by the recycling optics when the field polarization incident to the recycling optics is horizontal or vertical. It is also worth noting that recycling the beams also created a lattice for both the probe and control field which were offset from each other by an unknown amount. This offset in the lattice between the probe and control fields is due a difference phase accumulation during propagation along the recycling beam path due to the different frequencies of each beam.

Due the difficulties associated with recycling the photoassociation beams, we converted to only using a single pass (as described above, corresponding to the data shown in Fig, 6.10). Although there is a loss in total available power, we estimate that the largest achievable



Figure 6.12: Observation of three loss features when the photoassociation beams were recycled. The three loss features persisted even when the polarization of the probe and control fields was collinear. This occurred because, although the polarization of the probe and control field on each pass was collinear, there existed coupling photons that had a relative polarization angle $\phi \neq 0$ (i.e., a probe photon from the first pass, and a control photon from the second pass) Top: both beams are polarized along the vertical. Bottom: both beams are polarized along the horizontal. We suspect the difference in the depth of the middle feature is due to a difference in the amount of polarization rotation caused by the recycling optics.

Rabi frequency will only decrease by $\approx 25\%$ from the recycled case. This is due to the fact that $\Omega \propto \sqrt{I}$, and the lost power from multiple transmissions through the cell and the mirrors along the recycling beam path.

6.2.2 Effect in Triplet States

The effect of degenerate levels is also apparent in the triplet system. Here, the system consists of the first excited triplet $c(1^{3}\Sigma_{g}^{+})$ potential and the lowest lying triplet $a(1^{3}\Sigma_{u}^{+})$ potential. In this case, the energy level structure of the $|e\rangle$ and $|g\rangle$ state is more complex because the total electron spin is not zero (i.e., S = 1). In particular, this spin leads to multiple J' manifolds in the $|e\rangle$ state - that is, J' = 0, 1, 2 because N' = 1 and J' = N' + S'. In addition, the relevant states in the triplet potential also have a non-zero nuclear spin (I = 1), and therefore each J' manifold has associated hyperfine structure. In the $|e\rangle$ state, all the hyperfine manifolds in a particular J' manifold are nearly degenerate due to the small hyperfine constant associated with the asymptotic atomic state of the potential.

Moreover, unlike the ground singlet $X(1^1\Sigma_g^+)$ potential, where the N'' = 0 rotational level consists of a single non-degenerate state, the $a(1^3\Sigma_u^+)$ potential has three distinct hyperfine manifolds (F'' = 0, 1, 2) associated with the J'' = 1 manifold. The energy difference between the adjacent hyperfine manifolds will be related to the atomic hyperfine splitting of the ground state, and are on the order of 100 MHz. The energy structure for the triplet system, consisting of states from the $a(1^3\Sigma_u^+)$ and $c(1^3\Sigma_g^+)$ potentials is summarized in Fig. 6.13.

The observed spectrum for a two-color photoassocation or dark state experiment is complicated by two main factors. First, the possible levels that the probe and control laser can couple to can be limited by the selection rule that $m_F = 0 \iff m_F = 0$ if $\Delta F = 0^{132}$. In addition, the existence of near degenerate hyperfine manifolds in the $|e\rangle$ state introduces a mechanism for decoherence, because it is possible (in some cases) for the control laser to couple certain $|g\rangle$ states to $|e\rangle$ states for which the probe laser cannot couple to the $|a\rangle$ state. Specifically, the $|a\rangle$ state has F = 0, and it therefore cannot couple to the F' = 0, F' = 2 or F' = 3 manifolds in the $|e\rangle$ state.

To investigate these effects, the five level model introduced in Section 6.2 is extended to an N level model, where N is the total number of states to be considered in the system. As was done previously, the coupling strength for each possible transition is determined by Eqs. 6.4 and 6.5, which take into account the polarization of the light, the field strength

¹³²This selection rule did not play a role in the spectrum of the singlet system because both the $|a\rangle$ and $|g\rangle$ states had a different F quantum number than the only $|e\rangle$ state.

 $F = 0 \quad F = 1 \qquad F = 2 \qquad F = 3$ $J' = 0 \qquad --- J' = 2 \qquad ---- J' = 2 \qquad ----- \qquad |e\rangle = |111J'F'\rangle$ $c(1^{3}\Sigma_{g}^{+})$ $J = 1 \qquad ---- \qquad |g\rangle = |0111F''\rangle$ $a(1^{3}\Sigma_{u}^{+})$

Figure 6.13: Summary of energy structure in the relevant states of the $a(1^{3}\Sigma_{u}^{+})$ and $c(1^{3}\Sigma_{g}^{+})$ ⁶Li₂ potentials, corresponding the triplet system. The states are labeled in the $|NSIJF\rangle$ basis. In the excited state N' = 1 and in ground state N'' = 0. The F label represents the hyperfine state in either the $|e\rangle$ state or the $|g\rangle$ state. Note that the splitting between J' levels in the excited state and F'' levels in the ground state is on the order of 100 MHz. The $|a\rangle$ state is the part of the two atom scattering state which has triplet character (see Eq. 5.13). Due to the selection rules that $\Delta F = 0, \pm 1$ and $m_{F} = 0 \nleftrightarrow m_{F} = 0$ if $\Delta F = 0$, the $|a\rangle$ state can only couple the F' = 1 manifold in the excited state.

(both of which are parameters which can be tuned experimentally), and the transition dipole matrix element for each possible transition. While we have done simulations which include all 37 levels, we found that the splitting between J' levels in the excited state, and F'' levels in the N'' = 0 ground state are sufficiently large that it is possible to consider a system which includes only a single J' manifold in the $|e\rangle$ state, and a single F'' manifold in the $|q\rangle$ state¹³³.

To illustrate the result on the observed spectrum, the following discussion will consider the situation where the probe lasers is tuned near the J' = 1 manifold in the excited state. Within this J' state, there are three degenerate hyperfine levels, which correspond to F' = 0, 1, 2 as shown in Fig. 6.13. The control laser is tuned to be on resonance with one of the F'' = 0, 1, 2 hyperfine manifolds in the ground state to the J' = 1 manifold in the

¹³³Here, sufficiently large implies large relative to the natural linewidth of the transitions, and to the linewidth of the laser light such that the coupling strength is sufficiently small that it can be neglected in the model. When we compare the output of the 37 level model to a model which just includes a single J' and F'' manifold, we see no noticeable difference.

excited state. This situation is also relevant for the high resolution dark state spectroscopy of the v'' = 9, N'' = 0 ro-vibrational level discussed in Section 6.3.1.

Coupling to F'' = 0

The case where the $|g\rangle$ state is the F'' = 0 manifold is the simplest of the three cases to consider. Both the $|g\rangle$ and $|a\rangle$ state cannot couple to the F' = 0 or F' = 2 state in the $|e\rangle$ state manifold due to the selection rules that $\Delta F = 0, \pm 1$ and $m_F = 0 \Leftrightarrow m_F = 0$ if $\Delta F = 0$. As such, the only excited manifold to which the $|e\rangle$ and $|g\rangle$ states can couple to is the F' = 1 manifold. Therefore, the observed spectrum is the same as that predicted by the five-level model discussed in the previous section (in the context of the singlet state). In this case, a high fidelity dark state (or, in the Autler-Townes regime, a standard Autler-Townes doublet) can be achieved when the polarization of the probe and control fields are collinear.

Coupling to F'' = 1

The situation becomes more interesting when the $|g\rangle$ state is chosen to be the F'' = 1manifold. In this case, coupling of the $|F'' = 1, m''_F = 0\rangle$ state to the $|F' = 1, m'_F = 0\rangle$ state is disallowed due to selection rules. If the probe and control fields are polarized such that they both drive π transitions, the control field is effectively eliminated from the system as it cannot couple any of the levels in the $|g\rangle$ state to the only $|e\rangle$ state (the $|F' = 1, m'_F = 0\rangle$ state) which is coupled to the $|a\rangle$ state. The relevant states and couplings are shown in Fig. 6.14 with dashed lines. The result is that the observed spectrum is independent of the control field power or detuning¹³⁴. In this case, no dark state can exist as there are no interference pathways and the observed spectra will look like a single color photoassociation feature.

If the probe and control field polarizations are set such that they both drive σ^+ and σ^- transitions, it is now possible for the probe and control fields to couple to the same excited state, as shown by the solid lines in Fig. 6.14. Typically, this would result in high fidelity dark state. However, in this case the control field can also couple all of the m'_F

 $^{^{134}}$ An additional consequence of the lack of coupling between relevant levels in the ground and excited state is that it is also impossible to see a suppression of loss in a two color photoassociation measurement, or an Autler-Townes doublet.



Figure 6.14: The relevant states when the ground state is the F'' = 1 manifold and the excited state is the J' = 1 manifold in the $a(1^{3}\Sigma_{u}^{+})$ and $c(1^{3}\Sigma_{g}^{+})$ potential respectively. The possible couplings due to the probe and control fields are shown for π transitions (dashed lines) and σ transitions (solid lines). Note that $|F' = 1, m'_{F} = 0\rangle \rightarrow |F'' = 1, m''_{F} = 0\rangle$ transition is disallowed due to selection rules. The coupling of the $|g\rangle$ state to the F' = 2 excited state provides a decoherence mechanism for the dark state. Not shown is the F' = 0 state, which is not coupled to the relevant states by either the probe or control.

projection states in the $|g\rangle$ manifold to the F' = 2 hyperfine manifold in the $|e\rangle$ state¹³⁵. Effectively, this couples the dark state to a decaying excited state, and acts as a decoherence mechanism for the dark state. This decoherence creates a "grey-state", and decreases the dark state revival height. The theoretical spectrum is shown in Fig. 6.15 for a typical case where $\Omega_2/\Omega_1 = 10$.

As there are no selection rules that disallow couplings from the $|g\rangle$ manifold to the F' = 2 manifold in the excited state, there is no choice of polarizations for the probe and control beam that will produce a dark state with a large revival height. This is a consequence of either the lack of an interference pathway necessary for a dark state to exist in the first place, or the added decoherence caused by the coupling of the dark state to other decaying excited states. We have observed this effect in our high resolution measurement

¹³⁵The control field, which in this case drives transitions where $\Delta m_F = \pm 1$, can also couple the $|F'' = 1, m''_F = \pm 1\rangle$ states to the $|F' = 0, m'_F = 0\rangle$ excited state. However, as the probe field can only couple the $|a\rangle$ state to the $|F' = 1, m'_F = \pm 1\rangle$ excited states, this coupling does not play a role in the decoherence.



Figure 6.15: Expected atom number as a function of the probe detuning when the $|g\rangle$ state is the F'' = 1 state. The probe and control fields are set to drive σ transitions and $\Omega_2/\Omega_1 = 10$. As a reference, the dashed line shows the spectrum in the absence of coupling to the F' = 2 manifold. The dark state revival height is reduced due to decoherence caused by coupling the dark state to a decaying excited state (in this case, the F' = 2 manifold). The relevant states involved in the process are shown in Fig. 6.14. We have observed this effect in our high resolution measurement of the binding energy of the $|N'' = 0, F'' = 1\rangle$ hyperfine level in the v'' = 9 level of the $a(1^3\Sigma_u^+)$ potential, discussed in Section 6.3. The observed suppressed dark state (i.e., a "grey-state") is shown in Fig. 6.17.

of the binding energy of the $|N'' = 0, F'' = 1\rangle$ hyperfine level in the v'' = 9 level of the $a(1^{3}\Sigma_{u}^{+})$ potential, discussed in Section 6.3. The suppressed dark state (i.e., a "grey-state") is shown in Fig. 6.17.

Coupling to F'' = 2

If the $|g\rangle$ state is chosen to be the F'' = 2 manifold, it is possible to eliminate the decoherence with a suitable choice for the probe and control polarizations. If the probe and control polarization is chosen such that the fields drive π transitions, the applicable excited state is the $|F' = 1, m'_F = 0\rangle$ state. The control field will couple this excited state to the $|F'' = 2, m''_F = 0\rangle$ ground state. The two other possible couplings to the excited state due to

the control field are to the $|F' = 0, m'_F = 0\rangle$ and $|F' = 2, m'_F = 0\rangle$ states. However, both of these transitions are disallowed by selection rules. Therefore, the system effectively reduces to the simple three level system.

When the polarization of the control is set such that the fields can also drive σ transitions, it is possible for the control field to couple the F'' = 2 ground state manifold to the F' = 2 excited state manifold. The coupling acts as a decoherence channel for the dark state, and results in a similar "grey-states" as discussed previously for the F'' = 1 ground state manifold, and shown in Fig. 6.15.

It is important to reiterate that there are substantial differences between the dark state spectra for each of the three ground state hyperfine manifolds. For the F'' = 0 and F'' = 2hyperfine manifolds it is always possible to choose the polarization of the probe and control fields to achieve a "good" dark state that is well described by the simple five (or three) level model. However, for the F'' = 1 hyperfine manifold, there is no choice of polarization that give a large dark state revival height. This suppression of the dark state for the F'' = 1manifold holds even if the J' = 0 or J' = 2 excited state manifold is used.

Control and Impact of Coupling Decoherence

The decoherence effect can be approximated by a more simple four level model in which the $|a\rangle$, $|e\rangle$ and $|g\rangle$ states remain, and we introduce a fourth $|e'\rangle$ state. This $|e'\rangle$ state is taken to be degenerate with the $|e\rangle$ state¹³⁶, and it is assumed that the $|e'\rangle$ state can only couple to the $|g\rangle$ state.

In the absence of coupling to the $|e'\rangle$ state, the dark state state (which is an eigenfunction of the dressed three level Hamiltonian given in Eq. 5.59) is an admixture of the $|a\rangle$ and $|g\rangle$ states (see Eq. 5.70). The decoherence rate of the dark state $|a^0\rangle$ will be related to the matrix element

$$\langle e' | \vec{d} \cdot \vec{E} | a^0 \rangle = \frac{\Omega_1}{\sqrt{\Omega_1^2 + \Omega_2^2}} \langle e' | \vec{d} \cdot \vec{E} | g \rangle = \frac{\Omega_1}{\sqrt{\Omega_1^2 + \Omega_2^2}} \cdot \Omega_3 , \qquad (6.19)$$

where Ω_3 is the Rabi frequency for the $|g\rangle \rightarrow |e'\rangle$ transition. It can be seen that the decoherence rate depends both on the coupling strength to the $|e'\rangle$ state, and to the size of the $|g\rangle$ state admixture of the dark state. This admixture component in turn depends on

¹³⁶In general, it is not necessary that this additional $|e'\rangle$ be degenerate with the $|e\rangle$ state. However, in this specific case we want the control field to also be on resonance with the additional $|e'\rangle$ state.

the relative sizes of the probe and control Rabi frequency, given by Ω_1 and Ω_2 respectively. In order to observe a large dark state revival, it is required that $\Omega_2 \gg \Omega_1^{137}$, such that Eq. 6.19 simplifies to

$$\langle e' | \vec{d} \cdot \vec{E} | a^0 \rangle \approx \frac{\Omega_1}{\Omega_2} \cdot \Omega_3 \,.$$
 (6.20)

This suggest that the effect of this decoherence mechanism can be suppressed increasing the ratio Ω_2/Ω_1 , such that the dark state is predominantly made up of the $|a\rangle$ state. The reason for this suppression is similar to the suppression of dark state loss from laser decoherence discussed in Section 5.2.2. However, when the coupling between the $|q\rangle$ state and the $|e'\rangle$ state is a result of the control field, the coupling strength of the $|g\rangle \rightarrow |e\rangle$ transition and the $|g\rangle \rightarrow |e'\rangle$ transition will be similar (i.e., $\Omega_2 \approx \Omega_3$)¹³⁸. In this case, the suppression due to the increase in Ω_2 is offset by the correspondingly large increase in Ω_3 and the decoherence rate tends to a constant value (which is set by the magnitude of Ω_1). Therefore, the dark state revival height is related to the magnitude of Ω_1 and the "on-time" of the lasers. For a fixed Ω_1 and "on-time", the dark state revival height becomes constant as a function of Ω_2/Ω_1 . The constant value to which the dark state revival height tends is determined by the overall atom loss in the absence of the control field. This can be understood by considering that the atom loss due to excitation on the $|a\rangle \rightarrow |g\rangle$ is set by the same two parameters (Ω_1 and the "on-time" of the light) that determine the atom loss due to decoherence from the dark state. This can be seen in Figure 6.16, which shows the expected dark state revival height as a function of Ω_2/Ω_1 for a fractional atom loss of 0.2 and 0.6 in the absence of the control field. That is, the loss that would be seen in the case of a single-color photoassociation experiment.

While Eq. 6.19 also suggests that the decoherence rate can be suppressed by decreasing Ω_1 (which has the same effect on the dark state $|g\rangle$ component as increasing Ω_2), in order for the dark state to be visible there must be observable loss of atoms from the $|a\rangle$ state in the absence of the control field. Decreasing Ω_1 increases the exposure time required for such an experiment, and negates the decrease in the decoherence rate. Moreover, in the context of STIRAP, the highest transfer efficiency is typically achieved when $\Omega_1 = \Omega_2$. Therefore, for experiments with STIRAP, it is important to avoid systems where this decoherence

¹³⁷The control Rabi frequency must also satisfy $\Omega_2 \ll \gamma_e$. These requirements are discussed in Section 5.2.2.

¹³⁸The two Rabi frequencies are not exactly equal due to differences in the transition electric dipole matrix element. However, accounting for the possible variations due to this term, Ω_2 and Ω_3 are still approximately equal.



Figure 6.16: Effect of additional couplings to the $|g\rangle$ state on the dark state revival height, using the simplified four-level model. The solid line represents the dark state revival height when there are no additional couplings from the $|g\rangle$ state (i.e., the standard three-level model). The revival height in the presence of decoherence, when $\Omega_3 = \Omega_2$, is shown in the case where the fractional atom loss is 0.2 (dashed line) and 0.6 (dashed-dot line) in the absence of the control field. In both cases, the suppression of decoherence due to the increase in Ω_2 is offset by the correspondingly large increase in Ω_3 . For this simulation $\gamma_e = 2\pi \cdot 10$ MHz and $\Omega_1 = 2\pi \cdot 0.5$ MHz. The fractional atom loss in the absence of the control field is determined by the "on-time" of the light, which is set to 3 μ s and 10 μ s for a fraction loss of 0.2 and 0.6 respectively.

mechanism is present.

6.3 Characterization of $a(1^{3}\Sigma_{u}^{+})$ Potential

In addition to the spectroscopy of the $c(1^{3}\Sigma_{g}^{+})$ and $A(1^{1}\Sigma_{u}^{+})$ potentials, and the two least bound vibrational levels of the $X(1^{1}\Sigma_{g}^{+})$ potential, we measured the binding energy of the N'' = 0 and N'' = 2 rotational levels of all 10 vibrational levels in the lowest lying triplet $a(1^{3}\Sigma_{u}^{+})$ potential. This particular potential is unique in that it is the simplest $a(1^{3}\Sigma_{u}^{+})$ potential in a neutral diatomic molecule that can support bound states¹³⁹. Therefore, detailed and high resolution data on the bound levels in this potential may be useful for building and testing molecular potentials calculated from first principles.

Knowledge of this potential is also of interest in our experiment for a variety of reasons. As the potential is only approximately 10 THz deep, the most deeply bound vibrational level is easily accessible with our Ti:Sapphire lasers¹⁴⁰, and is an obvious starting point for the creating of ground state molecules via STIRAP. Moreover, since the triplet state has a non-zero spin, these molecules would have a magnetic moment and should exhibit magnetically tunable scattering resonances, akin to Feshbach resonances in atomic systems.

An additional open question regarding triplet molecules is whether they are meta-stable with respect to spin relaxation to the ground singlet state. ⁶Li₂ molecules may be a good candidate to answer this question because they can be produced with a higher efficiency than most other cold molecules as they are chemically stable with respect to collisions with other ⁶Li₂ molecules and ⁶Li atoms. However, while the molecules may be stable with respect to dimer formation, it has been shown theoretically by Tomza et al. [38] that alkalidimers in the $a(1^{3}\Sigma_{u}^{+})$ state may be chemically reactive with respect to trimer formation. Both possibilities (spin relaxation and trimer formation) motivate a measurement of the lifetime of ⁶Li₂ triplet molecules. Such a measurement requires knowledge of the location of the bound states in the $a(1^{3}\Sigma_{u}^{+})$ potential, and the ability to create, at the very least, a dark state comprised of such molecules.

The $a(1^{3}\Sigma_{u}^{+})$ potential has been previously studied using FTIR spectroscopy [182]. In this work, Linton et al. report on the eight lowest lying vibrational levels (v'' = 0 to v'' = 7) and observe rotational levels up the disassociation limit for each of the vibrational levels. More precise measurements using two color photoassociation in a MOT have been performed on the least bound v'' = 9 vibrational level by Abraham et al. [86] and Scholder et al. [87].

In our measurements, we have used dark state spectroscopy to measure the binding energy of the v'' = 9, N'' = 0 ro-vibrational level. These measurements represent an improvement in absolute uncertainty over the previous measurement in a cold-atom system by a factor of over 40. In addition, we resolve the hyperfine structure of this level and find

¹³⁹The $a(1^{3}\Sigma_{u}^{+})$ potential in the only neutral diatomic molecules that is more simple (H₂) cannot support bound states [184].

¹⁴⁰For comparison, accessing the v'' = 0 level of the $X(1^1\Sigma_g^+)$ state would require a UV laser.

that the energy difference of adjacent hyperfine states deviates from the standard treatment of the hyperfine structure outlined by Moerdjik and Varhaar [88, 89]. This measurement is discussed in detail in Section 6.3.1. In addition, Section 6.3.2 details the binding energy measurements and observed structure of the remaining nine (v'' = 0 - 8) N'' = 0 rovibrational levels and all ten (v'' = 0 - 9) N'' = 2 ro-vibrational levels.

For all of the measurements, we used the J' = 1 manifold of the v' = 20 vibrational level in the $c(1^{3}\Sigma_{g}^{+})$ potential as the $|e\rangle$ state. Given that both two color and dark state spectroscopy experiments measure the binding energy of the target $|g\rangle$ state via the energy difference between the probe and control fields, there is nothing unique about our choice of the $|e\rangle$ state.

6.3.1 High Resolution Spectroscopy of |v'' = 9, N'' = 0 Manifold

We performed the high resolution dark state spectroscopy of the v'' = 9, N'' = 0 rovibrational manifold of the $a(1^{3}\Sigma_{u}^{+})$ potential using a similar method to the dark state spectroscopy of the $X(1^{1}\Sigma_{g}^{+})$ potential discussed in Section 6.1. As shown in Fig. 6.13, we expect the N'' = 0 rotational level to have three hyperfine states (F'' = 0, 1, 2) arising from the three possible projections of the total nuclear spin I = 1 with respect to \vec{S} , and that the splitting of these levels is on the same order as the atomic hyperfine splitting (i.e., ≈ 100 MHz). To start, we first found the approximate location of each hyperfine state using two-color spectroscopy, similar to that presented in Section 6.3.2 for the remaining ro-vibrational levels in this potential.

To observe a dark state, we set the control field to match the $|g\rangle \rightarrow |e\rangle$ transition, and scanned the probe field about the location of the $|a\rangle \rightarrow |e\rangle$ transition. For each of the hyperfine states, we observed the dark state spectra shown in Fig. 6.17. We performed these measurements with an atomic ensemble with approximately 50×10^3 atoms at a temperature of 800 nK, corresponding to $T/T_{\rm F} \approx 0.8$. To minimize the systematic shifts due to the Zeeman effect, we ensured that the magnitude of the residual magnetic field was less than 20 mG. The wavefunction overlap of the $|a\rangle \rightarrow |e\rangle$ transition is small, and therefore the probe Rabi frequency Ω_1 was less than $2\pi \times 1$ kHz. In order to induce single color loss of 40-80% in 1 s, we used probe intensities in the range 100-500 W/cm². In order to observe a strong dark state revival height (in the absence of any decoherence effects) and to avoid inducing a large Autler-Townes splitting of the excited state, we set the control Rabi frequency such that $\Omega_2/\Omega_1 \gg 1$ and $\Omega_2 \ll \gamma_e$. We found intensities in the range 20-200 W/cm² were sufficient, which corresponds to $2\pi \times 250$ kHz $< \Omega_2 < 2\pi \times 1$ MHz.

Although the 1 s exposure time is much larger than the coherence time of the lasers, we were still able to observe high fidelity dark-states for the F'' = 0 and F'' = 2 hyperfine levels (top and bottom panels of Fig. 6.17)¹⁴¹. We attribute this to a suppression of the dark state decoherence due to the large ratio of Ω_2 to Ω_1 (this mechanism is discussed in detail in Sec. 5.2.2). However, we were not able to find experimental parameters that would improve the revival height of dark state corresponding to the F'' = 1 hyperfine state (middle panel of Fig. 6.17). We believe that this poor revival height is due to decoherence caused by a coupling of the dark state to additional decaying excited states by the control field (see Fig. 6.15 and the corresponding discussion in Section 6.2.2).

For each of the dark states, we used the three level model (described in Section 5.2.2) to fit the observed spectrum in order to extract the precise location of the two photon resonance. This method of fitting is advantageous because it directly accounts for any small detuning of the control field. This small detuning is evident for all the dark-states in Fig. 6.17, as the peak of the dark state revival is slightly offset from the center of underlying single color photoassociation feature.

In order to determine the field-free binding energy of each of the hyperfine levels, we measured the shift-rate of the dark state due to the ac Stark shifts induced by the probe and control lasers and the ODT. This was done by measuring the dark state spectra for several ODT, probe, and control laser powers and extracting the two-photon resonance position for each parameter set. The shift-rate due to the ODT and PA lasers are given in Tab. 6.7. The energy difference between the control and probe laser frequencies which corresponds to the field free two-photon resonance and the corresponding binding energy of each of the three hyperfine states are given in Tab. 6.6. Note that the binding energy is found by adding $2a_{2S}$ to the measured laser frequency difference, as the energy of the two-atom scattering state lies below the $2^2S_{1/2} + 2^2S_{1/2}$ asymptote by $2a_{2S}$. Because the binding energy is determined from a difference in frequency of the two PA lasers subtract out. Therefore, the given uncertainty is only limited by the statistical uncertainty on the fit of the two-photon resonance, and of the extrapolation to the field-free case. The absolute uncertainty on the

¹⁴¹For these measurements, the two photon linewidth of our Ti:Sapphire lasers was ≈ 100 kHz, which corresponds to a coherence time of $\approx 10 \ \mu s$.



Figure 6.17: Dark state spectrum for the F'' = 2 (top), F'' = 1 (middle) and F'' = 0 (bottom) levels in the v'' = 9, N'' = 0 ro-vibrational level of the $a(1^3\Sigma_u^+)$ potential. The solid line is a fit to the spectrum using the three level model outline in Section 5.2.2. For these measurements, we used the J' = 1 manifold of the v' = 20 vibrational level in the $c(1^3\Sigma_g^+)$ potential as the $|e\rangle$ state. We were not able to find experimental parameters that would improve the revival height of dark state corresponding to the F'' = 1 hyperfine state. We believe that this poor revival height is due to decoherence caused by a coupling of the dark state to additional decaying excited states by the control field. For the F'' = 0 and F'' = 2 hyperfine manifolds it is always possible to choose the polarization of the probe and control fields to achieve a good dark state which is well described by the simple five (or three) level model. For details, see Fig. 6.15 and the discussion in Section 6.2.2.

<i>v</i> ″	N''	F''	$\begin{array}{c} \nu_2 - \nu_1 \\ (\text{GHz}) \end{array}$	Binding Energy (GHz)
9	0	2	24.010649(46)	24.314923(46)
9	0	1	24.163035(105)	24.467309(105)
9	0	0	24.238372(54)	24.542646(54)
9	0	\cos	—	24.391021(43)

frequency difference of the two Ti:Sapphire lasers is less than 1 kHz, determined using a heterodyne beat between the two lasers. (see Section 2.3).

Table 6.6: Experimentally measured energy difference between the initial state $|a\rangle$ and the three hyperfine manifolds of the v'' = 9, N'' = 0 ro-vibrational manifold in the $a(1^{3}\Sigma_{u}^{+})$ potential. Also given is the calculated binding energy of the hyperfine center of gravity (cog) based on a weighted average of the binding energy of the three hyperfine manifolds. The binding energy is calculated by adding $2a_{2S}$ to the measured frequency difference because the energy of the two-atom scattering state lies below the $2^{2}S_{1/2} + 2^{2}S_{1/2}$ asymptote by $2a_{2S}$. The number in brackets is an estimation of the 1σ uncertainty on the last digit(s).

<i>v</i> ″	N''	F''	ODT shift rate (kHz/W)	Probe shift rate (kHz/mW)	Control shift rate (kHz/mW)
9	0	2	104 ± 31	3.2 ± 2.5	30.1 ± 6.3
9	0	1	-84 ± 72	-4.6 ± 4.0	20.8 ± 7.3
9	0	0	115 ± 43	-5.2 ± 2.9	7.1 ± 11.4

Table 6.7: Measured shift rate of the three hyperfine manifolds of the v'' = 9, N'' = 0ro-vibrational manifold in the $a(1^{3}\Sigma_{u}^{+})$ potential. The shift of the dark state feature is due to an ac Stark shift induced by the two photoassociation lasers and the ODT laser. From these shift rates, we extract the field-free binding energy of the three hyperfine levels given in Tab. 6.6. The $1/e^{2}$ intensity radii of the ODT and PA lasers are approximately 35 μ m and 50 μ m respectively.

In the long-range approximation, where electron overlap is ignored, the molecular hyperfine constant can be directly related to the atomic hyperfine constant a_{2S} [89], and the Hamiltonian which describes the hyperfine interaction can be written as [88, 89]

$$H_{\rm HF} = a_{2s} \left(\vec{s_1} \cdot \vec{i_1} + \vec{s_2} \cdot \vec{i_2} \right) = \frac{a_{2s}}{2} \left(\vec{S} \cdot \vec{I} + (\vec{s_1} - \vec{s_2}) \cdot (\vec{i_1} - \vec{i_2}) \right) , \qquad (6.21)$$

where $\vec{S} = \vec{s_1} + \vec{s_2}$ and $\vec{I} = \vec{i_1} + \vec{i_2}$ are the total electron and nuclear spin of the two-

atom system, respectively. The second term in Eq. 6.21 mixes the singlet and triplet states and is typically neglected when the energy difference between the nearest singlet and triplet levels is large compared to the hyperfine interaction¹⁴². Neglecting this term, the associated energies of the hyperfine levels (relative to the hyperfine center of gravity) are

$$E_F = \frac{a_{2s}}{4} \left[F(F+1) - S(S+1) - I(I+1) \right].$$
(6.22)

In this case, F is defined by $\vec{F} = \vec{I} + \vec{S}$. For the rotational level of interest here, N = 0and therefore, in the molecular basis used in this thesis, $\vec{J} = \vec{N} + \vec{S} = \vec{S}$ and $\vec{F} = \vec{J} + \vec{I}$ is simply $\vec{F} = \vec{S} + \vec{I}$. The expected energy difference between adjacent hyperfine states based on Eq. 6.22, and the measured energy difference from our dark state measurement is given in Tab. 6.8. It is interesting to note that the measured hyperfine splitting differs from the theoretical splitting by 2σ to 7σ , and cannot be accounted for by simply modifying a_{2S} .

States	$\Delta E_{\rm exp}$ (MHz)	ΔE_{theory} (MHz)	δ/σ
$F'' = 2 \leftrightarrow F'' = 1$	152.386(114)	152.137	2.2
$F'' = 1 \leftrightarrow F'' = 0$	75.337(118)	76.068	-6.2
$F'' = 2 \leftrightarrow F'' = 0$	227.723(63)	228.205	-7.5

Table 6.8: Predicted and measured energy differences between hyperfine levels in the v'' = 9, N'' = 0 ro-vibrational level of the $a(1^{3}\Sigma_{u}^{+})$ potential. The theoretical energy difference is calculated from Eq. 6.22. The last column shows the difference between the experiment and theory energy difference ($\delta = \Delta E_{exp} - \Delta E_{theory}$) normalized to the uncertainty on the experimental energy difference. The discrepancy between the predicted and measured value cannot be accounted for by simply modifying a_{2s} .

6.3.2 Low Resolution Spectrscopy of N'' = 0 and N'' = 2 Levels

In addition to the high resolution dark state spectroscopy of the v'' = 9, N'' = 0 rovibrational level of the $a(1^{3}\Sigma_{u}^{+})$ potential, we used two color photoassociation to measure the binding energy of the N'' = 0 and N'' = 2 rotational levels of the remaining vibrational levels in this potential. We performed these measurements with the same experimental parameters as the high resolution spectroscopy experiments. That is, the atom number is

¹⁴²In this case, the strength of the hyperfine interaction is given by $a_{2s} \approx 152$ MHz, and the nearest N = 0 singlet states are the v'' = 37 and v'' = 38 levels, which have a binding energy of ≈ 1.3 GHz and 56 GHz respectively. This corresponds to a separation from the v'' = 9, N'' = 0 ro-vibrational level of ≈ 23 GHz and 32 GHz.

 $N \approx 50 \times 10^3$ at a temperature of $T \approx 800$ nK corresponding to $T/T_{\rm F} \approx 0.8$. In this case, we keep the frequency of the probe laser fixed on the $|a\rangle \rightarrow |e\rangle$ transition, such that it induces approximately 50% loss in 1 s and we scan the control laser in the region near to the expected $|g\rangle \rightarrow |e\rangle$ transition frequency. When the control laser frequency matches a particular $|g\rangle \rightarrow |e\rangle$ resonance, we observe a suppression of single color loss (see Section 5.2.1 for more details).

N'' = 0 Levels

As with the high resolution spectroscopy of the v'' = 9, N'' = 0 ro-vibrational level, we expect to see three hyperfine manifolds associated with each of the remaining nine N'' = 0ro-vibrational levels. Table 6.9 gives the measured frequency difference between the control and probe lasers which corresponds to each of these hyperfine manifolds. The hyperfine manifolds are ordered, from smallest to largest binding energy, as F'' = 2, 1, 0 (see Eq. 6.22). When all three levels were not observed, the hyperfine manifold label for the observed features were assigned based off of the energy difference between the observed levels. This was the case for the v'' = 5 and v'' = 0 vibrational levels, where we did not observe the F'' = 2 hyperfine manifold. For these measurements we used 5 mW of probe and 5 mW of control power (corresponding to an intensity of approximately 70 W/cm²) with the exception of the v'' = 0 vibrational level where we used 30 mW (420 W/cm²).

Table 6.9 also reports the binding energy of the hyperfine center of gravity and the "strength" of each transition. The center of gravity binding energy is calculated from a weighted average of the binding energy of the three hyperfine levels. In the case where all three levels were not visible, the cog binding energy is approximated from the energy separation of the observed levels, based off of Eq. 6.22. In order that the center of gravity binding energy reported in Table 6.9 is given with respect to the $2^2S_{1/2} + 2^2S_{1/2}$ asymptote, $2a_{2S}$ is added to the laser frequency difference to account for the energy difference of the two-atom scattering state relative to the $2^2S_{1/2} + 2^2S_{1/2}$ asymptote. An estimate of the Frank-Condon factor (i.e., the overlap of the wavefunction of the ground and excited state) is is found from the width of the F'' = 0 hyperfine feature, which was observed for all ten ro-vibrational levels. This width of the feature for each vibrational level is normalized to the largest width from the v'' = 2 level. For the v'' = 0 vibrational level, which required additional power (30 mW instead of 5 mW), the normalized strength is adjusted by a factor

]	hyperfine manifold	ł		
	F'' = 2	F'' = 1	F'' = 0	\cos	$\operatorname{strength}$
v''	(GHz)	(GHz)	(GHz)	(GHz)	(arb. units)
9	24.010649(46)	24.163035(105)	24.238372(54)	24.391021(43)	0.022
8	163.90	164.09	164.17	164.30	0.076
7	491.63	491.77	491.86	492.01	0.155
6	1037.14	1037.29	1037.37	1037.52	0.230
5	—	1806.91	1806.99	[1807.13]	0.076
4	2798.88	2799.02	2799.15	2799.26	0.185
3	4010.90	4011.02	4011.09	4011.26	0.656
2	5441.96	5442.09	5442.22	5442.34	1.000
1	7094.35	7094.49	7094.58	7094.419	0.144
0	_	8974.55	8974.63	[8974.79]	0.008

Table 6.9: Location of the hyperfine manifolds in all ten N'' = 0 ro-vibrational levels in the $a(1^{3}\Sigma_{u}^{+})$ potential. The hyperfine manifolds are (in order of increasing binding energy) labelled as F = 2, 1, 0 (see Eq. 6.22). When all three manifolds were not observed, the hyperfine labels are assigned based off of the energy difference between the observed features. Also given is the binding energy of hyperfine center of gravity (cog), which is calculated from a weighted average of the binding energy of the three hyperfine manifolds. In the case where all three features were not visible, the center of gravity binding energy is approximated from the energy separation of the observed levels (these cases are denoted with square brackets). In order that the center of gravity binding energy reported in Table 6.9 is given with respect to the $2^2S_{1/2} + 2^2S_{1/2}$ asymptote, $2a_{2S}$ is added to the laser frequency difference to account for the energy difference of the two-atom scattering state relative to the $2^2S_{1/2} + 2^2S_{1/2}$ asymptote. The column labeled "strength" gives an estimate of the Frank-Condon factor, which is based on the width of the F'' = 0 hyperfine manifold and is normalized to the largest value from the v'' = 2 level. The estimated uncertainty on these measurements are ± 10 MHz, with the exception of the v'' = 9 vibrational level, where the error on the last digit(s) is indicated by the number in brackets. The peak locations and center of gravity binding energy for the v'' = 9 ro-vibrational level are from the dark state spectroscopy measurements discussed in Section 6.3.1. For the two-color spectroscopy measurements, we used 5 mW of probe and 5 mW of control light, with the exception of the v'' = 0 vibrational level where 30 mW of control power was used.



Figure 6.18: Two-color spectroscopy of v'' = 8, N'' = 0 ro-vibrational level. The three features correspond the three hyperfine manifolds in this state and are labeled, in order of increasing binding energy (i.e., left to right) as F = 2, 1, 0.

of $\sqrt{5/30} \approx 0.4$ due to the scaling of the Rabi frequency with the field amplitude (see Eq. 6.4).

We used a constant control power for each measurement (with the exception of the most deeply bound vibrational level) so that we could easily compare the relative strength of each of the transitions. For the v'' = 1, 5, 7, 8, and 9 vibrational levels, we were able to resolve all three hyperfine manifolds. In these cases, the peak locations in Table 6.9 are found by fitting each hyperfine feature to a Gaussian function. Figure. 6.18 shows an example of the two color spectrum for the v'' = 8 vibrational level. For some transitions, the wave function overlap between the $|e\rangle$ and $|g\rangle$ states was large enough that the hyperfine features were sufficiently broadened such that they overlapped. An example of a small amount of broadening, for which the hyperfine levels are still resolvable, is in spectrum of the v'' = 7vibrational level shown in Fig. 6.19. An example of broadening for which the two right features are nearly overlapped is shown in Fig. 6.20 in the case of the spectrum from the v'' = 2 vibrational level. In these cases, the location of each hyperfine manifold given in Table 6.9 is estimated off of the three peak locations rather than a fit to a Gaussian function.



Figure 6.19: Two-color spectroscopy of v'' = 7, N'' = 0 ro-vibrational level. The three features correspond the three hyperfine manifolds in this state and are labeled, in order of increasing binding energy (i.e., left to right) as F = 2, 1, 0. In this case, the two right most features are beginning to overlap due to the increasing strength of the $|g\rangle \rightarrow |e\rangle$ transition.

Given that we did not perform a detailed study of any systematic effects on the peak locations or other sources of uncertainty, we estimate the absolute uncertainty of these measurements to be ± 10 MHz. This estimation is likely rather conservative, and is based on the possible detuning of the probe beam on the $|a\rangle \rightarrow |g\rangle$ transition, the resolution (i.e., step size) of our measurement (5 MHz), and the statistical uncertainty of the fits and/or peak determination.

N'' = 2 Levels

In the $|NSIJF\rangle$ molecular basis, each N'' = 2 ro-vibrational level of the $a(1^{3}\Sigma_{u}^{+})$ potential is expected to have three J'' manifolds (because S'' = 1), where each J'' manifold is associated with three hyperfine manifolds (because I'' = 1), for a total of nine possible states. Specifically, the three J'' states are J'' = 1, 2, 3, and the hyperfine manifolds associated with each of the three J'' manifolds are F'' = 0, 1, 2, F'' = 1, 2, 3 and F'' = 2, 3, 4 respectively.

However, the states in the $|NSIJF\rangle$ basis are only eigenstates of the system when the hyperfine interaction is small compared to the spin-spin and spin-rotation interaction. For



Figure 6.20: Two-color spectroscopy of v'' = 2, N'' = 0 ro-vibrational level. While three features are still visible, the strength of the $|g\rangle \rightarrow |e\rangle$ transition broadens each peak enough that the two right most features (corresponding to the F'' = 1 and F'' = 0 hyperfine manifolds) are almost overlapped. In this case, the location of each hyperfine manifold given in Table 6.9 is estimated off the three peak locations rather than a fit to a Gaussian function.

this potential, the strength of the hyperfine interaction is on the order of $a_{2S} \approx 150$ MHz, while the magnitude of the spin-spin constant λ_{ν} is expected to be similar to that of the $c(1^{3}\Sigma_{g}^{+})$ potential, which is also on the order of a hundred to hundreds of MHz $[171]^{143}$. Therefore, the eigenstates of the system are not simply the $|NSIJF\rangle$ basis states, but rather linear superpositions of the $|NSIJF\rangle$ basis states. Consequently, each eigenstate can take on the character of multiple J'' states. Nevertheless, the total number of eigenstates states (nine) remains unchanged.

The observed two color spectrum is also influenced by the choice of the $|e\rangle$ state used for the measurement. In the excited triplet $c(1^{3}\Sigma_{g}^{+})$ potential, there exists three J' states, corresponding to J' = 0, 1, 2. If the eigenstates of the $a(1^{3}\Sigma_{u}^{+})$ potential were simply the $|NSIJF\rangle$ states (i.e., there was no mixing of basis states) then one would expect only

¹⁴³Specifically, see Fig. 2 of [171] which gives the spin-spin parameter for the $a(1^{3}\Sigma_{u}^{+})$ and $c(1^{3}\Sigma_{g}^{+})$ potential as a function of the interatomic distance. The spin-spin parameter is smallest for the high lying vibrational levels (on the order of 50 to 100 MHz), and increases in magnitude for the more deeply bound vibrational levels (up to approximately 400 MHz for the most deeply bound levels).

particular J'' states to be visible for certain choices of the J' excited state, owing to the selection rule that $\Delta J = 0, \pm 1$. For example, if the $|e\rangle$ state is taken to be the J' = 0 manifold, then only the J'' = 1 manifold in the ground state would be observable. Likewise, if the J' = 1 manifold is used as the $|e\rangle$ state, then only the J'' = 1 and J'' = 2 manifolds could be observed. However, mixing of the basis states invalidates this simple picture, and suggests that more features may be visible than expected if the J' = 0 or J' = 1 manifolds is used as the $|e\rangle$ state.

The two color spectrum for the v'' = 9, N'' = 2 ro-vibrational level when each of the three possible J' manifolds is used as the $|e\rangle$ is shown in Fig. 6.21. Of note is the three sets of peaks, and that the appearance of each of the three sets of peaks is independent of the choice of the $|e\rangle$ state. This suggests that each set of peaks is not associated with only a single J'' manifold. For this particular measurement, we used the largest control power possible. However, technical reasons limited the maximum power that was available when we used different J' excited states¹⁴⁴. For the J' = 0, 1, 2 level, we used 55 mW, 60 mW and 200 mW respectively.

While a detailed analysis of the energy structure of this potential is left as future work, we made an attempt to gain a qualitative understanding of the energy structure¹⁴⁵. For this, we diagonalized a Hamiltonian which included a rotational term and a spin-spin and spinrotation interaction term (as discussed in Section 5.1.4). The strength of these terms are parameterized by the constants B_v , λ_{ν} , and γ_{ν} respectively. In addition, the Hamiltonian includes the magnetic hyperfine interaction in the form [185]

$$H_{\rm HF} = a\Lambda(\vec{I}\cdot\hat{r}) + b(\vec{I}\cdot\vec{S}) + c(\vec{I}\cdot\hat{r})(\vec{S}\cdot\hat{r}), \qquad (6.23)$$

where \hat{r} is the unit coordinate vector along the molecular axis. However, for Σ states, $\Lambda = 0$ and the first term in Eq. 6.23 can be neglected. Therefore, the hyperfine interaction is parameterized by the constants b and c. For this particular discussion, we have also neglected the electric quadrupole interaction. For each of the nine eigenstates of the N'' = 2

¹⁴⁴The strength of the three different $|a\rangle \rightarrow |e\rangle$ transitions is different, and therefore we require a different amount of probe power to induce the same fraction of single color loss for some transitions. In order to ensure that the probe and control fields have the same polarization, we are forced to use a polarizing beam cube (or a Glan-Thompson polarizer) which means that an increase in the probe power will result in a decrease in control power.

¹⁴⁵The code that was used in this analysis was written by Fernando Luna, a student in the group of Roman Krems at the University of British Columbia.



Figure 6.21: Two-color spectrum for the v'' = 9, N'' = 2 ro-vibrational levels, using the J' = 0 (top), J' = 1 (middle) and J' = 0 (bottom) manifold in the v'' = 20 vibrational level of the $c(1^{3}\Sigma_{g}^{+})$ potential as the $|e\rangle$ state. We believe that we can see all three sets of peaks from all three J' manifolds because the eigenstates in the $a(1^{3}\Sigma_{u}^{+})$ potential are a linear superposition of the $|NSIJF\rangle$ basis states. For example, see the top panel of Fig. 6.22 when $\nu = -50$ MHz, which is the relevant size of the spin-spin coupling for this vibrational level. Note that the control powers are different for each of the three different $|e\rangle$ states. For the J' = 0, 1, 2 level, we used 55 mW, 60 mW and 200 mW respectively.

rotational level, we found the projection of the eigenstate onto the J'' = 1, 2, 3 basis states. The result of this diagonalization and projection for three different choices of λ_{ν} is shown in Fig 6.22. Here, we set the hyperfine constants to be b = 71 MHz and c = 10 MHz, such that the diagonalization reproduced the observed hyperfine energy splitting of the N'' = 0rotational manifold. In addition, we set $\gamma_{\nu} = -14$ MHz, based on the assumption that the spin-rotation coupling is of similar magnitude and size to that of the $c(1^{3}\Sigma_{g}^{+})$ potential. In Fig. 6.22, the J'' component fraction is given for all nine states, where the states are ordered (left to right) from least to most bound, such that the order is the same as the experimental data shown in Fig. 6.21 and Fig. 6.23.

For the loosely bound v'' = 9 vibrational level, the value of the spin-spin constant is expected to be small and negative [171] and therefore the case in the top panel of Fig. 6.23 where $\lambda_{\nu} = -50$ MHz is most applicable. Here, the three left most states are strongly associated with the J'' = 1 level (with some J'' = 2 component), while the remaining six are, in general, mixtures of the J'' = 2 and J'' = 3 levels. However, some of these eigenstates contain some component of the J'' = 1 state, and are thus able to couple to the J' = 0excited state, as is shown in Fig. 6.21. In addition, only when the J' = 2 excited manifold is used can the control laser couple to J'' = 3 component fraction of the eigenstates (for example, the state labeled 5, 8 or 9 in Fig 6.22). This increase in coupling appears to be consistent with the spectrum shown in Fig. 6.21¹⁴⁶.

In the case of the more deeply bound vibrational levels, the magnitude of the spinspin coupling parameter is expected to increase (see [171] and the spectroscopy data of the $c(1^{3}\Sigma_{g}^{+})$ potential presented in Section 6.1). As shown in Fig. 6.22, this results in a decrease of the mixing between J'' basis states, as the spin-spin constant becomes larger than the size of the hyperfine interaction. In this limit, the energy structure can be thought of as made up of three sets of the J'' levels, where the ordering from least to most deeply bound is given by Eq. 5.45. In this case, the ordering is J'' = 1, J'' = 3, J'' = 2 as shown the bottom panel of Fig. 6.22. Therefore, for a low lying vibrational state probed using, for example, the J' = 1 excited state manifold as the $|e\rangle$ state, one would expect to see a suppression of

¹⁴⁶The additional control power used for the J' = 2 data will also cause a broadening of the features. However, as the power was increased by approximately a factor of four over that of the J' = 1 or J' = 2 data, this would result in an increase of Ω_2 by approximately a factor of two. This alone cannot account for the increase in width. It is also possible that the wavefunction overlap is larger for this particular transition. However, both of theses mechanisms should result in a symmetric broadening of the spectrum and not the additional structure will appear (most obviously in the right most set of peaks).



Figure 6.22: $|J''\rangle$ components of the N'' = 2 eigenstates in the $a(1^{3}\Sigma_{u}^{+})$ potential for three different choices of λ_{ss} (see text for the values of the other parameters). Shown is the projection of each of the nine eigenstates of the N'' = 2 rotational level onto the J'' = 1, 2, 3basis states. The states are arranged in order (left to right) from least to most bound. This ordering is the same as the experimental data shown in Fig. 6.21 and Fig. 6.23. For the high lying vibrational levels, the spin-spin coupling is expected to be on the order to -50 MHz, and the top panel is the relevant picture. Here, the eigenstates are a linear superposition of the J'' = 1, 2, 3 states. When the spin-spin coupling constant is larger than the hyperfine interaction, as is thought to be the case for the deeply bound vibrational levels, the J''mixing is reduced, and the eigenstates tend to the $|NSIJF\rangle$ basis states.

the middle set of peaks. This set of peaks corresponds to the J'' = 3 manifold, and coupling to the J' = 1 manifold is disallowed by selection rules. This suppression is observed in the two-color spectrum of the v'' = 1, N'' = 2 ro-vibrational level shown in Fig. 6.23. Here, we believe the left most set of peaks is associated with the J'' = 1 manifold, and the right most set of peaks is associated with the J'' = 2 manifold.



Figure 6.23: Two-color spectroscopy of v'' = 1, N'' = 2 ro-vibrational level. For this data, the excited state $|e\rangle$ is the J' = 1 manifold of the v' = 20 vibrational level in the $c(1^{3}\Sigma_{g}^{+})$ potential. For this more deeply bound level, we believe the spin-spin coupling is larger than the hyperfine coupling, and the eigenstates are approximately given by the $|NSIJF\rangle$ basis states. In this case, the right most peak corresponds to J'' = 2 manifold, and the left most set of peaks corresponds to the J'' = 1 manifold. The middle peak, which would correspond to the J'' = 3 manifold (seen in Fig. 6.21) is suppressed because the control field cannot couple states with $\Delta J = 2$.

The splitting of the eigenenergies of the diagonalized Hamiltonian is consistent with the observed energy difference between the left and right peaks for the deeply bound levels. For example, in the case of the v'' = 1 vibrational level, we observe a splitting of ≈ 540 MHz. An estimate of the spin-spin coupling parameter for this level is ≈ 300 MHz¹⁴⁷, and the predicted energy difference between the two observed J'' manifolds using this value (with the other parameters at the same values as above) is approximately 530 MHz. For the loosely

¹⁴⁷This value is taken from Fig. 2 of [171], where $r \approx 4 \text{\AA}$ is assumed from Table 1 of the same reference
bound vibrational levels, the total energy excursion of the N'' = 2 rotational level (i.e., the energy difference between the highest and lowest bound levels) generally agrees with the diagonalized Hamiltonian, but all of the energy splittings between individual features do not. This may be a result of an incomplete spectra as even when using the J' = 2 excited state we do not observe all nine possible states, or this may indicate that additional terms in the Hamiltonian are necessary to fully describe the system. While this is not a full or complete analysis of the energy structure, we believe it serves as a qualitative picture on which to build and it may aid with the complete interpretation of the observed spectra.

We observed the same general structure for each of the ten vibrational levels in the $a(1^{3}\Sigma_{u}^{+})$ potential, where three sets of features are separated by approximately a hundred to hundreds of MHz, with the exception of the v'' = 7 and v'' = 6 vibrational level where only a big feature was observed. For the low lying vibrational levels, the three sets of features correspond to the three J'' manifolds. We associated this single feature for v'' = 0 with the "3rd Peak" (J'' = 2), as the J'' = 2 manifold appears to have the largest transition strength in the low lying vibration levels. The frequency difference between the control and probe laser corresponding to the location of each of these features is given in Table 6.10. In addition, Table 6.10 gives the rotational constant for each vibrational level, found from the measured energy difference between the N'' = 0 and N'' = 2 manifolds.

<i>v</i> ″	1 st Peak (GHz)	2 nd Peak (GHz)	$3^{ m rd}$ Peak (GHz)	B_v (GHz)
9	16.00	16.16	16.24	1.28
8	148.29	148.47	148.57	2.54
7	469.15	469.36	_	3.69
6	1008.69	1008.91	—	4.69
5	1772.99	1773.23	1773.37	5.55
4	2760.28	2760.53	2760.69	6.36
3	3967.76	3968.04	3968.19	7.11
2	5394.49	5394.78	5394.96	7.83
1	7042.57	7042.82	7043.11	8.55
0	_	_	8918.93	9.21

Table 6.10: Locations of v'' = 0 to v'' = 9, N'' = 2 ro-vibrational levels in the $a(1^{3}\Sigma_{u}^{+})$ potential. The values given correspond to the frequency difference between the control and probe laser. While we cannot assign quantum numbers to each state, we report the position of the three sets of features observed for each vibrational level (see, for example, Fig. 6.21 and Fig. 6.23). Here, the three features refer to the three sets of peaks are separated by approximately a hundred to hundreds of MHz. For the low lying vibrational levels, the three sets of peaks correspond to the three J'' manifolds. When only two features were observed, we assign the peak number based off of the energy difference between the two features. In the case of the v'' = 0 vibrational level, we associated the single feature with the "3rd Peak", as it appears to be the strongest in the low lying vibration levels. The rotational constant of each vibrational level is found from the measured energy difference between the N'' = 0 and N'' = 2 manifolds. For this data set, we used 5 mW of probe and 5 mW of control light, with the exception of the v'' = 0 vibrational level where 40 mW of control power was used.

Chapter 7

Heteronuclear Mixtures: ${}^{6}Li + {}^{85}Rb$

The long term goal of our lab has always been to work with the heteronuclear ${}^{6}\text{Li}$ + Rb system, to produce ultra-cold LiRb molecules. While we have the capability to laser cool both ⁸⁵Rb and ⁸⁷Rb, all the work discussed in this section is with ⁸⁵Rb, and is labeled as such. The LiRb system introduces new technical challenges, but at the same time also offers the possibility of new and interesting physics owing to the strong and anisotropic interactions associated with polar molecules. In particular, the LiRb system is expected to have one of the largest electric dipole moments in the ground singlet potential (4.2 D [37]) and in the lowest lying triplet potential (0.37 D [38]). In fact, the permanent electric dipole moment of LiRb in the largest of all the bi-alkali molecules, save for LiCs [37]. This is significant because the dipole moment in the triplet potential is on the order of the size of the dipole moment of the ground singlet state of KRb (0.6 D [37]), one of the most studied ultra-cold (below 1 μ K) polar molecules, while the triplet ⁶Li₂ molecule still has a non zero spin. However, unlike in ⁶Li₂, Feshbach molecules of LiRb are inherently unstable, and are therefore susceptible to fast losses due to inelastic collisions [49]. In addition, the ground-state molecules themselves are unstable with respect to chemical reactions that form alkali-metal dimers and trimers [38].

The ability to create a system with both a permanent (and large) electric dipole moment and a spin degree of freedom is crucial in proposals to study lattice-spin models and quantum computation [26]. Additionally, there are many proposals to study novel quantum phases, pairing phenomena and quantum impurity problems in Bose-Fermi mixtures with tunable interactions (for example, [55, 56, 57]).

One of the most interesting advantages of the LiRb mixture is the large mass imbalance between the bosonic and fermionic species. One clear example is that of the Efimov effect the emergence of a geometric series of three-body bound states appearing at specific values of the two-body scattering length (which can controlled by a FR), which occurs when the s-wave scattering length is much larger than the characteristic size of the interatomic potential r_0^{148} [53, 54]. One manifestation of Efimov states is the appearance of a series of minima or maxima in the three-body loss coefficient that are equally spaced on a ln |a|scale. That is, if the first resonance appears at some scattering length $a_-^{(0)}$, then the N^{th} resonance will occur at the scattering length $a_-^N = a_-^{(0)} \exp(\pi N/s_0)$, where the universal scaling factor only depends on the quantum statistics of the constituent atoms, their mass ratio, and the number of resonant interactions. To experimentally verify the equal spacing, the scattering length must be varied by an amount equal to $(\exp(\pi/s_0))^4$ such that three features are visible. For equal mass systems, the scaling factor is 22.7 [186], and therefore a must be able to be varied by 22.7⁴, which is (to be kind) experimentally reduced when the system is comprised of a heavy boson and a light fermion. In the case of LiRb, the scaling factor falls just short of the LiCs, with a scaling factor of 4.877 [186], for which the geometric scaling of Efimov states has been observed by the groups of Weidemüller [187] and Chin [188].

The large mass imbalance also leads to competing requirements for laser cooling, as each species has their own narrow set of parameters in which they can be effectively trapped and cooled. For example, the optimal magnetic field gradient for the ⁶Li (or ⁸⁵Rb) MOT leads to sub-optimal¹⁴⁹ performance for the other species. Additionally, the depth of the ODTs vary by over a factor of two (see section 3.2), which creates an added challenge for the simultaneous trapping of both ⁶Li and ⁸⁵Rb.

The focus of this section is on the experimental demonstration of broad FRs in ⁶Li - ⁸⁵Rb mixtures. The knowledge of the location of these FRs provides an important experimental "knob" which can be used to control the scattering length, and is a vital first step towards the production of ultra-cold ground-state molecules or a search for Efimov physics. Additionally, FRs can be used to enhance evaporative cooling of atomic gases and, in our experiment specifically, the resonances can be used to efficiently sympathetically cool ⁸⁵Rb using ⁶Li.

¹⁴⁸Although r_0 is not known precisely, an order of magnitude estimate is $r_0 = 15 a_0$. [186].

¹⁴⁹It's best to tread lightly when speaking poorly of the performance of one of the atomic species. There are a lot of them, and tend to stick together.



Figure 7.1: Schematic of setup used for LiRb Feshbach resonance search. The Li atomic source is an effusive oven placed 10 cm away from the MOT region, and 85 Rb was captured from a atomic vapor provided by commercial Rb vapor dispensers placed on the same feed through as the Li oven. The dipole trap was created from two beams which crossed at an angle of approximately 14°.

7.1 Production of Ultra-Cold Bose-Fermi Mixtures

The majority of the work with the LiRb system presented in this thesis was done in a previous iteration of the setup which is described in detail in [93, 98, 124]. In this setup, no Zeeman slower was used. Instead, the ⁶Li MOT source was a small atomic oven placed close to the trapping region, and ⁸⁵Rb was captured from a atomic vapor provided by commercial ⁸⁵Rb vapor dispensers (Alvatec AS-3-Rb-50-V). The ODT was created from two beams which crossed at an angle of approximately 14°, creating a CDT. A schematic of this setup is shown in Fig. 7.1. With setup, there are several difficulties that arise from the atom sources, and the differing requirements for laser cooling and trapping ⁶Li and ⁸⁵Rb. The largest (and insurmountable) drawback of using a vapor loaded MOT for ⁸⁵Rb is that the loss rate due to collisions with the background ⁸⁵Rb atoms limits the largest achievable

size of the ⁶Li MOT. In fact, both the loading rate (and thus, the steady state atom number) of the ⁸⁵Rb MOT and the loss rate from the ⁶Li MOT are proportional to the ⁸⁵Rb vapor pressure in the cell. This means that a large ⁸⁵Rb MOT comes at the expense of a small ⁶Li MOT (and vica versa). To quantify this, the ⁶Li MOT number can be written in terms of the ⁸⁵Rb MOT number as [124]

$$N_{\rm Li}^{\infty}(N_{\rm Rb}^{\infty}) = \frac{N_{\rm Li}^{\infty}(0)}{1 + N_{\rm Rb}^{\infty}/\epsilon},\tag{7.1}$$

where $N_{\text{Li}}^{\infty}(0)$ is the ⁶Li MOT number when the background ⁸⁵Rb vapor pressure is zero, and ϵ is a constant that determines the size of the ⁸⁵Rb MOT which decreases the ⁶Li MOT number by a factor of two. In this setup, $\epsilon \approx 4 \times 10^6$ atoms. That is, the reduction in the ⁶Li MOT number occurs even in the absence of loading a ⁸⁵Rb MOT, and was one of the primary motivations for switching to a cold atom beam from the Zeeman slower as the atomic source for both ⁶Li and Rb. This reduction is simply due to the background vapor of Rb, and not due to light assisted heteronuclear losses.

If the ⁶Li and ⁸⁵Rb MOTs are run simultaneously (and are spatially overlapped) additional losses are present due to the heteronuclear loss terms and light assisted collisional loses [124]. Moreover, the ⁶Li and ⁸⁵Rb MOT are optimized at incompatible magnetic field gradients: the ⁶Li MOT experiences a dramatic increase in performance at gradients above 30 G/cm, while the ⁸⁵Rb number is greatly reduced at gradients above 28 G/cm. An additional constraint is introduced by the optical dipole traps in our system. In order to transfer a large fraction of our ⁶Li MOT into the ODT, we require a deep trap which we create using the 100 W SPI laser (see Section 3.2). However, we found that this laser drives hyperfine changing collision in ⁸⁵Rb , and at high powers (>15 W) produces hot samples of ⁸⁵Rb that reduce the evaporation efficiency and final atom number. Given this, ideally the ⁸⁵Rb MOT would be transferred into the dipole trap formed by our narrow frequency 20 W IPG laser. However, it was (and still is not) possible to trap ⁶Li directly in this laser. In general, the ideal starting points in the ODT for ⁶Li and ⁸⁵Rb are not compatible.

To overcome these challenges, instead of running a traditional dual-species MOT, where both species are cooled together in a dual-MOT and are transferred simultaneously to an ODT, we employee a sequential system. Here, we initially load a ⁶Li MOT and transfer the atoms to a deep ODT using our high power trapping laser. Then, while holding ⁶Li in the ODT, we quickly form a ⁸⁵Rb MOT which is transferred the same ODT after it had been ramped down to a lower power or, ideally, after the ⁶Li atoms are transferred into the low power ODT.

The transfer of ⁶Li takes place in the same method as described in Section 3.2. We perform an initial evaporation at a magnetic field that enhances the thermalization between ⁶Li atoms, typically around 300 G or 800 G. At the ODT depth at which we would like to load ⁸⁵Rb atoms, we turn off the homogenous magnetic field, and turn on a magnetic quadrupole field (all while holding Li in the in the ODT). We load ⁸⁵Rb MOT, and the atoms are transferred to the ODT by shifting the zero of quadrupole field to overlap the atomic cloud with the ODT. We made some effort to offset the ODT from the MOT location to reduce the loss of ⁶Li atoms held in the ODT while the ⁸⁵Rb MOT is loading¹⁵⁰. However, we found that we experience a loss of about a factor of two in the number of ⁶Li from the ODT during the loading of the ⁸⁵Rb MOT and subsequent transfer to the ODT. The load time of the ⁸⁵Rb MOT is chosen to strike a balance between the number of ⁶Li atoms remaining in the ODT, we can again perform a forced evaporation ramp to further cool the trapped atoms of both species.

7.2 LiRb Feshbach Resonances

As we were preparing to perform the experimental search for FRs, our "good" low power ODT laser broke, and we were forced to proceed with the experiment using the "bad" high power ODT laser which drives hyperfine changing collisions in ⁸⁵Rb. In addition, this data was taken using a Pyrex cell (before we switched to a quartz cell) which was easily damaged by, and caused a lensing of, the high power trapping beam. This limited us to a maximum power of 20 W per beam.

Nevertheless, we proceed in a similar manner as described in Section 7.1. Specifically, we loaded a ⁶Li MOT of a few 10⁶ atoms directly from the effusive oven, and transferred 10⁵ atoms into the CDT. The two beams were focused to a waist of 42 μ m and 49 μ m crossing at an angle of 14°. The CDT was then ramped down to 15 W (7.5 W per beam) in 500 ms while applying a homogenous magnetic field of 840 G. At the end of this forced evaporation

¹⁵⁰It turns out that not much effort is necessary to ensure the ODT and the MOT are not centered at the same location.

stage, there were approximately 5×10^4 atoms remaining. While holding ⁶Li in the CDT, we loaded a MOT of 10^5 ⁸⁵Rb atoms in 300 ms and transfered them to the CDT. Losses of both species ensued during this transfer and after the ⁸⁵Rb MOT light is extinguished the CDT contained approximately 10^4 of both ⁶Li and ⁸⁵Rb atoms. At this point, the temperatures were 150 μ K for ⁸⁵Rb and 70 μ K for ⁶Li. For these measurements, the ⁶Li atoms were prepared in a roughly incoherent equal mixture of the two spin projections of the f = 1/2 hyperfine manifold, and the ⁸⁵Rb atoms were prepared in a roughly equal incoherent mixture of the five spin projections of the f = 2 ground hyperfine manifold, for a total of 10 possible open channel spin states.

To detect FRs, we perform a second evaporative ramp in the CDT from 15 to 11 W in 500 ms while applying a homogenous magnetic field of a variable value. During this ramp, we observe a loss of ⁶Li due to cross-species thermalization and two body spin relaxation (for unstable spin mixtures). We did not notice any discernible loss of ⁸⁵Rb which we believe is because the ⁶Li atoms are much less deeply confined and less massive than ⁸⁵Rb. We detect the occurrence of a FR by observing magnetic fields at which additional losses of ⁶Li occur due to the modification of the interspecies scattering length, such that the ⁶Li atoms undergo heating and leave the trap due to a rapid thermalization with ⁸⁵Rb. We focused on magnetic fields in the range of 300 G to 550 G, and 910 G to 1000 G because within these ranges, none of the predicted FRs¹⁵¹ in the ten spin states were overlapping. We also observed a number of resonances in a range between 0 G and 300 G. However, the large number of overlapping resonances and the inefficient pumping the ⁶Li and ⁸⁵Rb made a detailed analysis difficult. The results of our scans are shown in Figure 7.2.

In order to verify that the features we observed are due to FRs between ⁶Li and ⁸⁵Rb, we performed an identical run except that no ⁸⁵Rb atoms were transferred from the MOT to the CDT. The ⁶Li atom number shown in Fig. 7.2 is normalized to this case. We believe that the minimum ⁶Li atom number for each resonance loss feature is a finite fraction of the initial atom number because the ⁶Li population is evenly distributed between the two magnetic sublevels of the f = 1/2 hyperfine state, and the loss of both spin states would require thermalization collisions in ⁶Li to exceed the collision rate between ⁶Li and ⁸⁵Rb atoms.

Each resonance feature in Figure 7.2 corresponds to a FR associated with a different

¹⁵¹These predictions were guided by previous theoretical analysis of FRs in ⁶Li -⁸⁷Rb mixtures done by our group [189].



Figure 7.2: Normalized ⁶Li atom number after an evaporation ramp with ⁸⁵Rb present as a function of magnetic field. All 10 spin states in the lowest hyperfine manifold were populated. The dots are individual experimental runs and the solid lines are fits of the resonance loss features to a sum of Gaussian functions. Rapid cross species thermalization and, for unstable spin mixtures, two-body spin relaxation leads to lithium atom loss. No ${}^{6}\text{Li}{-}^{85}\text{Rb}$ FRs were apparent between 600 and 900 G, and from 50 to 250 G there was a broad loss feature due to multiple, overlapping FRs. Figure from [52].

open channel spin state, which can be labeled using the uncoupled atomic states. In order to identify the atomic state pair responsible for each resonance, we attempted to optically pump the ⁸⁵Rb atoms towards the $|f = 2, m_f = 2\rangle$ or $|f = 2, m_f = -2\rangle$ hyperfine states. However, because the CDT laser drove two-photon stimulated Raman transitions between the f = 2 and f = 3 ground hyperfine manifolds of ⁸⁵Rb (see Section 3.3), we had to apply a weak beam of light tuned near the $f = 3 \rightarrow f' = 2$ transition to keep the ⁸⁵Rb population in the f = 2 hyperfine state. Unfortunately, this impacted our ability to efficiently optically pump ⁸⁵Rb , and caused our spin state preparation degraded over time. That said, we were able to vary the hyperfine population of ⁸⁵Rb enough to notice a change in amplitude of the ⁶Li atom loss of certain resonances dependent on which stretched state we optically pumped towards. The position, width, and open channel atomic states associated with each of the

atomic states		B_{exp}	Δ_{\exp}	$B_{\rm thy}$	$\Delta_{\rm thy}$	$\Delta B_{\rm est}$
$ f,m_f\rangle_{^{6}\mathrm{Li}}$	$ f,m_f angle_{ m 85Rb}$	(G)	(G)	(G)	(G)	(G)
$ 1/2,1/2\rangle$	$ 2,-2\rangle$	315.4(5.8)	65.2(5.8)	312.1	>100	60.8
$ 1/2, -1/2\rangle$	$ 2,-2\rangle$	466.4(3.6)	47(3.5)	466.7	>100	47.0
$ 1/2, 1/2\rangle$	$ 2,1\rangle$	393.9(0.8)	3.92(0.29)	393.0	33.5	5.1
$ 1/2, -1/2\rangle$	$ 2,1\rangle$	401.9(0.8)	4.24(0.32)	402.5	27.5	3.2
$ 1/2, 1/2\rangle$	$ 2,-1\rangle$	950.5(9.1)	6.32(0.47)	937.77	76.3	7.1
$ 1/2, -1/2\rangle$	$ 2,-1\rangle$	975(10)	7.28(0.55)	961.3	77.5	7.2

7.2. LiRb Feshbach Resonances

Table 7.1: Experimentally measured s-wave FRs for ${}^{6}\text{Li}{-}^{85}\text{Rb}$. The experimentally determined width Δ_{exp} is the full width at half maximum of the trap loss feature. The uncertainty in the resonance positions (B_0) are indicated in brackets, and are a quadrature sum of the uncertainty in the fit to the experimental data and the uncertainty in the magnetic field. Also included are the theoretically predicted positions and resonance width (defined by Eq. 5.18). Finally, ΔB_{est} is a qualitative estimation of the width found by defining an effective width as the range of magnetic field for which the s-wave scattering cross section is above a threshold value. See text for more detail.

six resonances is given in Table 7.1.

Comparison to Theory

The details of the theoretical work and analysis of these FRs is described in more detail in [52, 189] and is briefly described here for completeness.

To compute the s-wave elastic collision cross section as a function of magnetic field, a full coupled-channels scattering calculation was used, where the collision energy used in the calculations corresponds to an ensemble temperature of 100 μ K. The potentials are based on *ab initio* calculations for the LiRb dimers [37, 190], and adjusted to reproduce the known experimentally measured resonances in the LiRb system.

Because the coupled channel calculation can be intensive and time consuming, we employed the asymptotic bound state model (ABM) [189, 191] for a preliminary fit. This model is used to compute the energies of the least bound singlet and triplet states in the $X^{1}\Sigma$ and $a^{3}\Sigma$ potentials respectively as a function of magnetic field. We then search for a crossing of these energies with the energy of the open channel (colliding atom) state. The only free parameters in this model are the energy of the least bound singlet and triplet state at zero magnetic field. These two parameters are adjusted until the correct open and closed (least bound states) channels cross at a magnetic field found experimentally to correspond to the location of a FR. Though this cannot predict the exact location the FR, in the limit where the coupling between the open and closed channel is small it provides a good estimate of the resonance locations.

Once the energies of the least bound states are found, the full singlet and triplet potentials are tuned to reproduce these energies by changing the short range repulsive barrier¹⁵² Small final refinements are made to the updated potentials to reproduce the location of the experimental observed resonances. As a sanity check, the modified potential can also reproduce the FRs found in previous studies of the LiRb mixtures for ⁶Li +⁸⁷Rb [50] and ⁷Li+⁸⁷Rb [51]. The theoretically calculated *s*-wave elastic cross section as a function of magnetic for the six open channel spin states for which a FR was observed is given in Fig. 7.3.

The theoretical width of the FR (defined by ΔB in Eq. 5.18) is not always relevant to the expected width of the loss features that we observed. This is because the experimental width of the resonance, which is related to atom loss, is a dynamical process and requires a simulation of the ensemble dynamics including the two and three body elastic and inelastic collisional cross sections to be properly determined. However, in an attempt to compare the measured width to some theoretical width, we defined a theoretical width for each resonance to be the magnetic field region where the *s*-wave elastic cross section is greater than some value. This value was varied until a reasonable agreement with the measured width was achieved. We found this cross section to be $\sigma_{\rm el} > 3.6 \times 10^5 a_0$. The width of the magnetic field ranges for which $\sigma_{\rm el}$ exceeds this value for each of the six measured resonances is given in Table 7.1, as well as the theoretical width defined by Eq. 5.18.

 $^{^{152}}$ Only the short range behavior is modified because the long range behavior of the potentials is well known [190].



Figure 7.3: Theoretically predicted s-wave elastic cross section for ⁶Li and ⁸⁵Rb mixtures as a function of magnetic field for 6 of the 10 spin states in the lowest hyperfine manifold, corresponding to the spin states for which a Feshbach resonance was observed. The black solid (red dashed) lines are for the cross section with ⁶Li in the $|f = 1/2m_f = -1/2\rangle$ ($|f = 1/2, m_f = 1/2\rangle$) state, while the three panels correspond to ⁸⁵Rb in the (a) $|f = 2, m_f = +1\rangle$, (b) $|f = 2, m_f = -1\rangle$, and (c) $|f = 2, m_f = -2\rangle$ states.

Chapter 8

Conclusion

The field of AMO physics has been, and continues to be, a rapidly evolving field. The development of techniques for laser cooling and control of atomic and molecular systems was highlighted by the formation of degenerate gases - first using bosons, leading to the creation of a BEC, and followed several years later using fermions and the observation of a degenerate Fermi gas. More recently, the control achieved in atomic gases has been extended to both homonuclear and heteronuclear molecules. More recent advances in AMO physics have allowed experiments the potential to move beyond a direct study of atoms and molecules and into a regime where the atoms and molecules themselves are used as a tool to study phenomena important in other realms of physics, including the properties of strongly interacting many-body quantum systems with anisotropic interactions. Much of this work relies on an ever increasing control and understanding of atomic and molecular interactions, both between other atoms or molecules and with light.

This thesis presents work that represents substantial experimental progress towards the creation of LiRb and ${}^{6}\text{Li}_{2}$ molecules, as well as a study of interactions in ultra-cold gases of ${}^{6}\text{Li}$, and in mixtures of ${}^{6}\text{Li}$ and Rb. We have demonstrated the capability to produce a mBEC of weakly bound ${}^{6}\text{Li}_{2}$ Feshbach molecules and a degenerate Fermi gas of ${}^{6}\text{Li}$. We can create this degenerate Fermi gas in both in the weakly interacting regime at 0 G, and in the strongly interacting regime (just above the broad *s*-wave Feshbach resonance at 832 G) where it is possible to observe BCS pairing. To make our apparatus more robust for experiments with ${}^{6}\text{Li}$ and Rb mixtures, we separated the atomic sources from the "science" section of the experiment (via a differential pumping tube), and now use a Zeeman slower as the atom source for our dual species MOT. This was motivated by the fact that the background Rb vapor pressure required to load a Rb MOT (in the absence of a Zeeman slower or other cold atom source) is high enough that it severely limits the size of the ${}^{6}\text{Li}$ MOT.

Motivated by the idea of studying the effects of electric fields on atomic collisional

resonances, and future experiments with LiRb mixtures and polar molecules, we built and designed electric field plates that could be added to our setup outside of the vacuum. The plates show no indication of arcing for fields of up to 120 kV/cm, and we directly verified the production of fields of up to 18 kV/cm. This field is large enough to achieve partial lab frame alignment of LiRb molecules, and over 50% of the maximum electric dipole moment. However, we found that the production of even larger electric fields was primarily limited by a large loss of atoms from the MOT or ODT when we applied large voltages to the plates, as well as a residual field that persisted after the plates were grounded. This thesis has discussed these observations, which suggest that the bulk of the effects are due to field emission of electrons from within the vacuum chapter.

For the work with atom-molecule dark states and future work with STIRAP, we have built a photoassociation laser system which is based on two tunable cw Ti:Sapphire lasers. These two lasers are referenced and phase locked to a femtosecond frequency comb. With this setup, we easily achieve a relative two-photon linewidth of approximately 100 kHz, and have recently implemented an extremely promising "fast" lock where we observe a two-photon linewidth on the order of a few tens of Hz.

⁶Li: Results and Future Directions

This thesis has reported on the spectroscopy of the $c(1^{3}\Sigma_{g}^{+})$ and $A(1^{1}\Sigma_{u}^{+})$ potentials, which are (and will be) used as the intermediate excited state in the creation of atom-molecule dark states and STIRAP. With the singlet potential, we have investigated the viability of performing STIRAP by forming Feshbach molecules and measuring the coupling strength of the $|a\rangle \rightarrow |e\rangle$ transition for each accessible vibrational at magnetic fields near the broad *s*-wave FR. We found that the v' = 31 and v' = 35 vibrational levels show the most promise, and we are able to achieve Rabi frequencies of approximately $\Omega_{1} = 2\pi \times 1$ MHz at 754 G.

We have also reported on the high resolution dark-state spectroscopy of the N'' = 0, v'' = 38 and v'' = 37 ro-vibrational levels of the ground singlet $X(1^1\Sigma_g^+)$ potential. At magnetic fields near the broad s-wave FR at 832 G, the v'' = 38 level is no longer bound, and therefore knowledge of the v'' = 37 vibrational level are necessary for dark-state studies of the BEC-BCS crossover regime and for dark state control of FRs.

To round off the spectroscopy results, we present a measurement of the binding energy of the N'' = 0 and N'' = 2 rotational levels of all 10 vibrational levels in the lowest lying triplet $a(1^{3}\Sigma_{u}^{+})$ potential. With the exception of the least bound v'' = 9 vibrational level, none of 10 vibrational levels have been previously measured in an ultra-cold system. For the N'' = 0 rotational levels, we observe three hyperfine manifolds corresponding to F'' = 0, 1, 2. For the v'' = 9 vibrational level, we used dark-state spectroscopy to improve the absolute uncertainty of hyperfine center of gravity by over a factor of 40. Moreover, we report on a discrepancy between the measured hyperfine splitting and the standard treatment of the hyperfine interaction of high lying vibrational levels. In the analysis of the N'' = 2 rotational levels, we present a simple picture based on the diagonalization of a Hamiltonian that includes a rotational term, hyperfine interactions, and spin-spin and spin-rotation couplings. While a detailed analysis of the energy structure has been left for future work, we believe our analysis provides a qualitative picture which can explain, and may aid in the complete interpretation of, the observed spectra.

Experiments with atom-molecule dark states and STIRAP rely on coherence, and therefore an understanding of any decoherence effects is of the utmost importance. One such decoherence mechanism exists in ⁶Li due to potential degeneracies of the $|e\rangle$ and $|g\rangle$ levels. We observe that these degeneracies lead to unexpected EIT spectra. Specifically, we observed an anomalous third feature that appears in the Autler-Townes spectrum and a poor dark state revival height when particular states in the $a(1^{3}\Sigma_{u}^{+})$ and $c(1^{3}\Sigma_{g}^{+})$ potentials are used. An understanding of the cause of these mechanisms is vital, as the maximum transfer efficiency in STIRAP is directly related to the fidelity of the dark state. We have investigates these effects using an extension of the standard three level model, and find that both effects are dependent on the polarization of the probe and control field and, in some cases, on the choice of the $|e\rangle$ and $|g\rangle$ states.

While our initial attempts at transferring Feshbach molecules to a more deeply bound state using STIRAP were unsuccessful, we believe that an incomplete understanding of the decoherence mechanism present in the system was likely partially to blame. With our improved understanding of the energy structure and which levels are most suitable for STIRAP, there is now a clear route to the production of both singlet and triplet ground state molecules. In addition, improvements that have been made to the apparatus - namely, the ability to have a well defined polarization of the PA light and an upgrade to the "fast" Ti:Sapphire lock that enable us to achieve a much smaller two-photon linewidth of the PA lasers - provide a reason for optimism regarding the realization of a successful STIRAP experiment. Formation of triplet molecules in particular would allow our group to study, for example, the stability of alkali-metal dimers in the lowest lying triplet state with respect to spin relaxation to the ground singlet state or with respect to trimmer formation [38]. In addition, the non-zero spin of these molecules suggests that they should display tunable molecular scattering resonances [43, 44].

In addition to experiments directly related to the creation of ${}^{6}\text{Li}_{2}$ molecules, the technical capabilities of our experiment enable us to study other interesting physics. The ability to form atom-molecule dark states in the BEC-BCS crossover regime can be used a probe of the many-body state of paired ${}^{6}\text{Li}$ atoms that exist this regime [64, 65]. These atom-molecule dark-states have recently been shown to be an excellent tool for the optical control the *s*-wave scattering length [73], and can enable studies of the dynamics of a unitary quantum gas [66]. Moving away from dark states, the addition of a 1D optical lattice to our experiment would enable us to study collisions in quasi-2D geometries. For example, there are predictions that both elastic and inelastic collisions would be greatly suppressed in quasi-2D [192].

⁶Li+Rb: Results and Future Directions

This thesis has described the preparation of ultra-cold mixtures of Li and Rb, specifically focusing on a sequential loading approach, where we initially transfer ⁶Li atoms from a MOT to the ODT. Then, while holding ⁶Li in the ODT we quickly form a ⁸⁵Rb MOT, which is transferred to the same ODT after it has been ramped down in power. This procedure is motivated by the incompatibility of the optimal settings for the ⁶Li and Rb MOTs and the factor of two difference in the depth of the ODTs for the two species.

We have reported on the observation of six FRs between 300 and 1000 G, which are some of the broadest known in heteronuclear mixtures and can be an effective tool to sympathetically cool Rb with ⁶Li. These Feshbach resonances also represent an important first step towards a search for Efimov resonances, which require the ability to tune the scattering length over a large range.

The formation of LiRb molecules will require that the Feshbach molecules be formed and stored in a 3D optical lattice, which may represent a longer term project for this experiment. However, with respect to near term experiments with ⁶Li and Rb mixtures, there are some clear directions which represent "low-hanging fruit". The most obvious is a full study of FRs between ⁶Li and Rb, specifically focusing on fields between 0 and 300 G and over 1000 G. In our previous experiments with FRs we were limited to a maximum field of 1000 G by the total resistance of the coils. However, the new coils that we installed in our experiment are capable of reaching up at 1500 G. A second clear experimental direction is single color and two color photoassociation of LiRb. Given our experimental abilities, this type of experiment should be relatively easy to perform. In addition, the search for the excited state levels can be based on and guided by recent work in ⁷Li⁸⁵Rb in a heat pipe [139, 193] and in a dual-species MOT [194, 195]. An obvious extension to the two-color spectroscopy of LiRb is a measurement of the triplet and singlet state dipole moments of LiRb molecules. For this experiment, we would measure the dc Stark shift of the two-color photoassociation resonances as a function of an applied dc electric field.

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Appendix A

List of Publications

- B. Deh, W. Gunton, B. G. Klappauf, Z. Li, M. Semczuk, J. Van Dongen and K. W. Madison, "Giant Feshbach resonances in ⁶Li-⁸⁵Rb mixtures.", Phys. Rev. A, 82, 020701(R), August (2010) [52].
- M. Haw, N. Evetts, W. Gunton, J. Van Dongen, J. L. Booth, K. W. Madison, "Magneto-optical trap loading rate dependence on trap depth and vapor density.", J. Opt. Soc. Am. B, 29(3), pp.475-483, March (2013).
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- W. Gunton, M. Semczuk and K. W. Madison, "Realization of BEC-BCS-crossover physics in a compact oven-loaded magneto-optic-trap apparatus.", Phys. Rev. A, 88, 023624, August (2013) [165].
- 5. W. Gunton, M. Semczuk, N. S. Dattani and K. W. Madison, "High resolution photoassociation spectroscopy of the ${}^{6}\text{Li}_{2} A(1^{1}\Sigma_{u}^{+})$ state.", Phys. Rev. A, 88, 062510, December (2013) [85].
- M. Semczuk, W. Gunton, W. Bowden and K. W. Madison, "Anomalous Behavior of Dark States in Quantum Gases of ⁶Li.", Phys. Rev. Lett., **113**, 055302, July (2014) [159].
- W. Gunton, M. Semczuk and K. W. Madison, "Method for independent and continuous tuning of N lasers phase-locked to the same frequency comb.", Opt. Lett., 40(18), pp.4372-4375, September (2015) [78].
- W. Gunton, G. Polovy, M. Semczuk, K. W. Madison, "Transparent Electrodes for High E-Field Production Using A Buried ITO Layer.", Rev. Sci. Instrum., 87(3), March (2016) [142].
- W. Bowden, W. Gunton, M. Semczuk, K. Dare and K. W. Madison, "Dual Species Effusive Source and Zeeman Slower for Cold Atom Experiments.", Accepted by Rev. Sci. Instrum., April (2016) [125].