Master’s Thesis

Toward Direct Laser Cooling of Dipolar Molecules

presented by

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September 25, 2018

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Declaration of Authorship

I hereby certify that this thesis is entirely my own work except where otherwise indicated. Passages and ideas from other sources have been clearly indicated.

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Stuttgart, September 25, 2018
Abstract

This work comprises the design and construction of an optics setup and experimental control system to directly laser cool the dipolar molecule barium monofluoride (BaF). Similar work has been done with other diatomic molecules; however, BaF has not been successfully laser cooled and as such extensive calculations were needed to determine both the energy levels of the hyperfine ground states as well as the dipole transition branching ratios from the excited to ground states. The complex level structure mandates a cooling scheme for BaF consisting of several lasers—needed to address branching into additional rovibrational energy levels—upon which an experimental optical setup was designed and a significant portion constructed. Since the experiment as a whole required a computer control system for fast and accurate timing of experimental runs, an experimental control system was built and programmed to synchronize the creation of BaF molecules with both the optical equipment and data acquisition devices. As an early test of the optics and experimental control systems, absorption spectroscopy measurements were carried out on the main cooling transition. The measurements showed a close agreement between the theoretically predicted and experimentally determined energy levels; thus, the systems constructed should allow for direct laser cooling of BaF in the near future.
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1. Introduction

1.1. A Brief History of Cold Molecular Physics

Atomic, molecular, and optical physics has been a burgeoning field since the first experiments successfully laser cooled neutral atoms using optical light forces in the 1980’s [1]. Breakthroughs such as Zeeman slowing [2], optical molasses [3] and magnetic trapping [4] led to the creation of Bose-Einstein condensates (BEC) by Cornell, Wieman [5] and Ketterle [6] in the mid 1990’s. The initial success of these experiments was followed by a wide array of further developments including atom interferometry [7], cold fermions [8], dipolar quantum gases [9,10] and optical lattices [11] which have been used to study quantum many-body systems [12], perform precision measurements [13] and build atomic clocks [14] and quantum computers [15].

Until recently almost all experiments used atoms as they allow laser cooling through the optical scattering force and closed optical cycling. Molecules were initially assumed too difficult to laser cool due to their complex level structure—which features rovibrational states not found in atoms and prevents closed optical cycling. However, a number of theoretical developments about a decade ago paved the way for the experimental realization of laser cooling of dipolar molecules. The first of these theoretical developments was a seminal paper by Di Rosa [16] which demonstrated that some molecules are viable for laser cooling due to their highly diagonal Franck-Condon factors—which alleviates vibrational branching problems. A later paper by Stuhl et al. [17]—from Jun Ye’s group at JILA—on the possibility of a magneto-optical trap (MOT) for polar molecules suggested that angular momentum selection rules in conjunction with parity selection rules could be used to suppress rotational losses in the laser cooling process.

Dave DeMille’s group at Yale first demonstrated both optical cycling [18] and laser cooling of a diatomic molecule—strontium fluoride (SrF)—along one dimension. This was shortly followed by Jun Ye’s group demonstrating a two dimensional magneto-optical trap using yttrium (II) monoxide (YO) [19]. Since then a number of groups have demonstrated three dimensional MOTs with DeMille’s group using SrF [20], and both John Doyle’s group at Harvard and Mike Tarbutt’s group at
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Imperial College using calcium monofluoride (CaF) [21,22].

1.2. Applications of Ultracold Molecules

Ultracold atoms have been used to demonstrate many interesting phenomena and ultracold molecules have the potential to either improve the work of ultracold atoms or open up entirely new fields of research.

1.2.1. Many-Body Physics

Polar molecules have large, tunable anisotropic electric dipole-dipole interactions which are two to four orders of magnitude larger than that of the largest magnetic atoms’ magnetic dipole-dipole interactions. Thus, these strongly interacting molecules potentially allow the exploration of strongly correlated many-body systems—particularly in conjunction with optical lattices. Optical lattices are formed by creating standing waves using interfering far-detuned laser beams. The optical dipole force leads to a periodic arrangement of traps, where molecules are trapped either in the intensity minima or maxima of the standing wave pattern [23]. These ‘crystals of light’ have a large range of applications in quantum simulation as they provide extremely clean systems, with perfect control over most parameters and versatile methods to probe them [11]. This makes optical lattices an excellent environment to realize and study textbook Hamiltonians from condensed matter.

1.2.2. Fundamental Physics

Molecules are surprising candidates for studying fundamental physics as the energy scales at which atomic physics is done is small compared to that of particle physics accelerators; however, due to their complex structure, molecules are excellent candidates for studying several fundamental physics problems.

Electron Electric Dipole Moment

The electron’s electric dipole moment (eEDM) is predicted by the Standard Model to have a value which is impossible to currently measure; however, extensions to the Standard Model predict a somewhat larger and measurable value for the eEDM. These Standard Model extensions can therefore be tested by experimentally establishing an upper limit on the eEDM which will in turn yield insight into time-reversal invariance, CP violation and the origin of matter-antimatter asymmetry.
Although particle colliders are generally used for measuring elementary particle properties, molecules can be used for precision measurement of the eEDM as shown by Sandars [24, 25]. When exposed to an electric field, a finite eEDM should lead to a small but potentially detectable change in the molecular energy levels. The advantage of molecules lies in the fact that a polarized molecule creates an effective electric field significantly larger than the electric fields generated in the lab [26], allowing for an extremely accurate experimental determination of the eEDM and one with a significantly higher sensitivity than similar experiments with atoms. Since the effective electric field increases with the molecule’s mass, Ed Hind’s group at Imperial works with the heavy molecule YbF and, in recent years, has determined an upper limit to the eEDM [27, 28]. The ACME collaboration has since improved the accuracy of the measurement by another order of magnitude [29].

### Nuclear Anapole Measurement

In recent years, proposals have been put forth to study atomic parity violations using ultracold molecules. Molecules with an unpaired electron spin can be used to measure the nuclear anapole moment and thus determine a portion of the nuclear-spin-dependent parity violation (NSD-PV) [30]. Ultracold molecules are particularly useful in this endeavor as they feature near-degenerate energy levels of opposite parity, due to their rotational states, which increases the sensitivity of the measurement [31]. Furthermore, this degeneracy, and thereby sensitivity, can be further enhanced via the application of magnetic fields [32].

### 1.2.3. Ultracold Chemistry

Chemical equations are highly dependent on thermal effects and as such the underlying quantum mechanical behaviour of the chemical reaction is obscured in normal temperature regimes. By using ultracold molecules, these chemical processes can be studied in the absence of most thermal effects with quantum mechanics playing an important role in collisions and effects such quantum tunneling becoming apparent [33]. Additionally, the chemical reactions can be controlled via external magnetic or electric fields [34].

### 1.3. Barium Monofluoride

The goal of our experiment is to laser cool barium monofluoride (BaF). BaF was chosen for several reasons with the first being that BaF has highly diagonal Frank-Condon factors and is thus a viable candidate for laser cooling. Although a
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<table>
<thead>
<tr>
<th>Isotope</th>
<th>130Ba</th>
<th>132Ba</th>
<th>134Ba</th>
<th>135Ba</th>
<th>136Ba</th>
<th>137Ba</th>
<th>138Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abundance (%)</td>
<td>0.106</td>
<td>0.101</td>
<td>2.417</td>
<td>6.592</td>
<td>7.854</td>
<td>11.23</td>
<td>71.70</td>
</tr>
</tbody>
</table>

Table 1.1.: Relative natural abundance of the various barium isotopes [37]. Fluorine has only one stable isotope $^{19}$F and thus the overall natural abundance of BaF is dictated by the Ba isotopes.

number of alkaline-earth monofluorides (i.e. SrF, CaF, etc.) have diagonal Frank-Condon factors, BaF additionally has a large mass which is useful when measuring fundamental properties of the molecule (such as the eEDM or the nuclear anapole moment) as a larger mass corresponds to a higher measurement sensitivity [30]. Furthermore, BaF has both a bosonic isotope $^{138}$BaF (for use towards a molecular BEC) and a fermionic isotope $^{137}$BaF—used for fundamental physics measurements—each with relatively large natural abundances (see Table 1.1). Another benefit of BaF is its predicted favorable collisional properties which could prove useful in either evaporative [35] or sympathetic cooling [36]. Lastly, the atomic transition wavelengths for the BaF cooling scheme lie between 850-900 nm allowing inexpensive diode lasers to be built for laser cooling.

1.4. Direct Laser Cooling of BaF

1.4.1. Scattering Force

The scattering force due to a laser is considered with a basic two level scheme. If the laser frequency is resonant with the molecular transition, the molecule will be excited due to the absorption of a photon. After some time, the molecule will decay back to the ground state and emit a photon via spontaneous emission. Photons in the absorption process are always incident from the same direction, whereas the decay photons are emitted in random directions (see Fig. 1.1). Therefore, a net transfer of momentum to the molecule from the laser occurs along the laser’s axis of propagation. Since the momentum imparted to the molecule by a single photon is minuscule, $p = \hbar k$; many photon scattering events are needed to slow the molecule and thus optical cycling is required in which the molecule is excited, decays and is excited again *ad infinitum*.

With atoms, closed optical cycling can often be achieved with only one to two lasers. However, the situation is substantially more complicated for molecules due to their additional rovibrational energy levels which provide significantly more decay channels. As such there are no molecules currently known for which closed optical cycling can occur; however, for a subset of molecules—including BaF—quasi-closed
1.4. Direct Laser Cooling of BaF

Figure 1.1.: The light scattering force [38]. Photons from the laser are incident from the left and are absorbed to excite the molecule. When the molecule decays, a photon is emitted in a random direction so that there is a net force $F_{\text{scatt}}$ along the laser’s axis of propagation.

cycling is possible in which enough scattering events are achieved to cool the molecule before it is lost to unaddressed rovibrational states.

1.4.2. Energy Levels in BaF

Diatom molecules have, in addition to the electronic energy levels found in atoms, vibrational and rotational states. The rotational states arise from the molecule’s asymmetry and rotational angular momentum, whereas the vibrational states are due to vibrational motion caused by interactions between the molecule’s two atoms. Since fully solving Schroedinger’s equation with electronic, vibrational and rotational considerations is not practical, the energies are generally decoupled (Born-Oppenheimer approximation) so that the total energy $E$ is given as follows [39]

$$E = E_{el} + E_{\nu} + E_{r}$$

where $E_{el}$ is the electronic energy, $E_{\nu}$ is the vibrational energy and $E_{r}$ is the rotational energy. However, in spectroscopic papers the energy and molecular spectroscopic constants are generally expressed in units of cm$^{-1}$ and as such Eq. 1.1 is rewritten as [39]

$$T = T_{e} + G + F$$

(1.2)
where $T$ is the total energy, $T_e$ is the electronic energy, $G$ is the vibrational energy and $F$ is the rotational energy.

**Electronic Energy Levels**

In atoms, the electronic state’s principal quantum number is given by $n$; however, in molecules, letters are used to denote the electronic states with $X$ representing the ground state, and the excited states represented by capital letters $A$, $B$, $C$ and so forth in ascending alphabetical order\(^1\). As stated previously, the energy for the electronic levels is given by $T_e$ and can usually be found in spectroscopic papers for the various electronic energy levels. Generally, $T_e$ is on the order of hundreds of nanometers and these transitions are addressable with lasers.

**Vibrational Energy Levels**

The vibrational motion between the molecule’s two atoms is described with a harmonic oscillator (the motion of the two molecules is treated in the reduced mass frame) with additional correction terms to better model the interatomic potential. This results in an anharmonic oscillator \([40]\)

\[
G(\nu) = \omega_e \left( \nu + \frac{1}{2} \right) - \omega_e \chi_e \left( \nu + \frac{1}{2} \right)^2 + \omega_e y_e \left( \nu + \frac{1}{2} \right)^3 \tag{1.3}
\]

where $\omega_e$ is the vibrational constant and $\omega_e \chi_e$ and $\omega_e y_e$ are constants contributing to the anharmonicity.

**Rotational Energy Levels**

The rotational energy equations are given by considering the diatomic molecule to be a non-rigid rotor as \([41]\)

\[
F_{\nu}(J) = B_{\nu} J (J + 1) - D_{\nu} J^2 (J + 1)^2 \tag{1.4}
\]

where $B_{\nu}$ is the rotational constant and $D_{\nu}$ is the centrifugal distortion term. Since the rotation is affected by molecule’s vibrational state, each term in the rotational energy expansion must include a vibrational correction so that

\[^1\text{In some cases, an excited state with lower energy has a higher alphabetic value than another excited state with a higher energy. This is generally a historic artifact in which the high energy state was discovered first and thereby assigned the lower alphabetic value. Note, that when an excited state has a multiplicity different from that of the ground state, the labels become lower case letters a, b, c; however, these states are not relevant for the system at hand.}\]
\[ B_\nu = B_e - \alpha_e \left( \nu + \frac{1}{2} \right) + \gamma_e \left( \nu + \frac{1}{2} \right)^2 \]  

(1.5)

and

\[ D_\nu = D_e - \beta_e \left( \nu + \frac{1}{2} \right)^2 \]  

(1.6)

where \( B_e, \alpha_e, \gamma_e, D_e \) and \( \beta_e \) are all molecular constants found in spectroscopic papers [42]. The spacing between the rotational levels is generally in the GHz (microwave) range.

**Level Scheme**

Of primary concern for this thesis is the ground state \( X^2\Sigma^+ \) of BaF as well as the first two excited states \( A^2\Pi_{1/2} \) and \( A^2\Pi_{3/2} \) (these states are addressed in detail in Chapter 2 with the molecular term notation discussed in Sec 2.1.2). The ground state is split into rotational manifolds denoted by \( N \) (with parity \((-1)^N\)) which are each comprised of fine structure levels given by \( J \) (see Fig. 1.2). The excited state is split into fine structure states via \( \Lambda \)-doubling (see Sec 2.3.1) and these fine structure states are further split into two opposite parity states. All the ground and excited states furthermore are split into vibrational states \( \nu \) (see Fig. 1.3).

**1.4.3. BaF Optical Cycling**

To optically cycle BaF, a transition is driven from the \( N = 1 \) rotational manifold in the ground state \( X^2\Sigma^+ \) to the positive parity \( A^2\Pi_{1/2} \) excited state. Rotational branching is suppressed via the appropriate choice of fine structure levels and thus no rotational repumping lasers are needed\(^2\). Decays into additional ground state vibrational levels \( \nu \) cause molecular losses from the main cooling transition \( \nu = 0 \to \nu' = 0 \), where \( \nu' \) is the vibrational level of the excited state. However, the use of repumping lasers stems these losses by transferring molecular population back to the zeroth vibrational state. The first repumper drives the \( \nu = 1 \to \nu' = 0 \) transition, the second repumper the \( \nu = 2 \to \nu' = 1 \) transition and finally the last repumper drives the \( \nu = 3 \to \nu' = 2 \) transition.

\(^2\)Hyperfine structure states in the \( N = 1 \) rotational manifold of the \( X^2\Sigma^+ \) state must all be addressed—which is done with frequency sidebands.
Figure 1.2.: Level scheme of the BaF for the ground state $X^2\Sigma^+$ and the first two excited states $A^2\Pi_{3/2}$ and $A^2\Pi_{1/2}$. The ground state is split into rotational states $N$ and then fine structure states $J$. The excited states $A^2\Pi_{1/2}$ and $A^2\Pi_{3/2}$ are fine structure states which are further split into two non-degenerate opposite parity states. By driving a transition (solid green lines) from the $N = 1$ ground state to the positive parity $A^2\Pi_{1/2}$ excited state the only rotational decay channels (dotted pink lines) are back to the $N = 1$ ground state due to angular momentum selection rules. Finally, the hyperfine structure is omitted here for clarity, but a detailed introduction is given in Chapter 2.
Figure 1.3: The vibrational energy level structure for the $N = 1$ rotational manifold in the $X^2\Sigma^+$ ground state and the $A^2\Pi_{1/2}$ state in BaF along with the proposed laser cooling and optical cycling setup developed by Chen et al. [43] to address the vibrational branching.
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states \( \nu' = 0 \) \( \nu' = 1 \) \( \nu' = 2 \) \( \nu' = 3 \) \( \nu' = 4 \)
\( \nu = 0 \) 0.9508 0.0483 \( 9.1 \times 10^{-4} \) \( 1.9 \times 10^{-6} \) 4.5 \times 10^{-7} \\
\( \nu = 1 \) 0.0476 0.8539 0.0956 0.0030 1.3 \times 10^{-5} \\
\( \nu = 2 \) 1.5 \times 10^{-3} 0.0925 0.7581 0.1412 0.0065 \\
\( \nu = 3 \) 2.7 \times 10^{-5} 5.1 \times 10^{-3} 0.1347 0.6643 0.1841 \\
\( \nu = 4 \) 4.6 \times 10^{-7} 1.3 \times 10^{-4} 0.0104 0.1733 0.5738

Table 1.2: Franck-Condon factors for the decay from A\( ^2 \Pi_{1/2}(\nu') \) positive parity state to the \( N = 1 \) rotational manifold in the X\( ^2 \Sigma^+(\nu) \) state [43].

### Vibrational States and Franck-Condon Factors

The decay from one vibrational state in the excited state \( \nu' \) to a vibrational state in the ground state \( \nu \) can be calculated with the help of the Franck-Condon factors \( q_{\nu'\nu} \), which are the overlap integrals of the vibrational states’ wavefunctions squared [44]

\[
q_{\nu'\nu} = |\langle \nu | \nu' \rangle|^2. \tag{1.7}
\]

The branching ratios can then found using [40]

\[
b_{\nu'\nu} = \frac{q_{\nu'\nu} \omega_{\nu'\nu}^3}{\sum_{k=0}^{\infty} q_{\nu'k} \omega_{\nu'k}^3} \tag{1.8}
\]

where \( \omega_{\nu'\nu} \) is the transition frequency between the two vibrational states. The Franck-Condon factors have been calculated for the A\( ^2 \Pi_{1/2}(\nu') \) to X\( ^2 \Sigma^+(\nu) \) transition in BaF by the Yan group [43] (see Table 1.2). Similar to other monofluorides, BaF possesses highly diagonal Franck-Condon factors and as such, only a few repumping lasers are needed to address the molecules lost from the main cooling transition.

### Supression of Rotational Branching

Although BaF has additional rotational states, angular momentum and parity selection rules are used to determine a set of transitions which allow for closed cycling among rotational states [17]. These selection rules dictate that the change in the total angular momentum \( \Delta J \) for a dipole transition must be [41]

\[
\Delta J = 0, \pm 1. \tag{1.9}
\]

Additionally, for a dipole transition the parity of the final state must be opposite the parity of the initial state.
Therefore, by driving a transition from either $J = 1/2$ or $J = 3/2$ in the $N = 1$ rotational manifold of the $X^2\Sigma^+$ state to the positive parity $A^2\Pi_{1/2}$ state (see Fig. 1.2), only decays back to the $N = 1$ rotational manifold are possible. Thus, one laser$^3$ is enough to suppress rotational branching and achieve closed cycling among rotational states. Driving other transitions in the molecule results in decays to multiple rotational state manifolds (see Appendix C) and requires significantly more lasers$^4$.

1.5. Experimental Goals

The experimental goal is to create a molecular magneto-optical trap (MOT) which will provide a starting point for any further physics including the study of fundamental physics, many-body physics or cold chemistry. There are several experimental components and systems which must be built to yield this molecular MOT:

- **Molecular Beam**-Before the molecules can be laser cooled or trapped they must first be created and initially cooled. This is a highly non-trivial task and discussed more in depth in Sec 1.5.1.

- **Laser Systems**-Molecules require a number of lasers for optical cycling and cooling. These lasers are used to slow the molecular beam, cool and trap the molecules in the MOT and lastly to image the molecules. To achieve this, the lasers must have narrow line spacing, sufficiently high power and be frequency stabilized for several hours at a time.

- **Molecular Beam Slowing**-Since the molecules comprising the molecular beam need velocities below a certain threshold to be trapped by the MOT, a method of slowing the molecular beam should be implemented. Currently, there are two general methods for slowing the beam: either using a broadband laser [45] along the molecular beam’s axis of propagation and/or chirping the

---

$^3$The rotational sublevels in the ground state are substantially split; however, the fine structure states within a rotational manifold are split by approximately 100 MHz and are thus experimentally addressable using a single laser with frequency sidebands.

$^4$The number of rotational repumping lasers is multiplied by the number of vibrational repumping lasers need to get the total number of repumping lasers.
1. Introduction

Figure 1.4.: Proposed experimental setup for cooling BaF. The BaF molecules are created by the ablation laser in the cryostat and proceed as a molecular beam through the experimental setup from right to left. Upon exiting the cryostat, the molecules will be slowed either with chirp cooling or a molecular Zeeman slower. Two optical access cubes allow interaction with the beam for either observation or manipulation (e.g., fluorescence detection, beam deflection or transverse cooling). Upon entering the MOT which has several optical access ports, the molecules will be cooled by six lasers (two counter-propagating lasers along each axis).

frequency of the laser [46]. Recent proposals have also discussed using either a molecular Zeeman slower [47] or Zeeman-Sisyphus slower [48].

- **Remixing Dark States** Since the proposed laser scheme only uses one polarization to drive transitions, molecules will be lost to dark states. Therefore, magnetic fields are used to remix the dark $m_F$ states with the $m_F$ states the lasers address. Alternatively, a Pockels cell can be used to quickly switch the polarization of the driving laser.

- **MOT** After the preceding components have been designed and constructed, the MOT itself can be built—which will involve a vacuum chamber with optical axis ports for the cooling lasers, as well as coil configurations to create magnetic fields for trapping the molecules.
1.5. Experimental Goals

1.5.1. Generation of Molecular Beam

Before the laser systems can be utilized to either cool molecules or even probe them via spectroscopy, the molecular beam must be created. Although many atomic physics experiments simply heat elements in an oven to create an atomic gas for laser cooling, BaF requires ablation and buffer gas cooling. A plume of BaF molecules is created by ablating a BaF$_2$ target with a high power laser. However, as the molecules are extremely hot and the population of molecular energy levels follows a Boltzmann-Maxwell distribution, hardly any molecules reside in the ground state (which the laser system targets). Therefore, a helium buffer gas cools the molecules and transfers population to the molecule’s ground state. Tobias Sixt spent the last year constructing and characterizing a cryostat setup for the creation of our molecular beam [49] and only a brief description of the setup is included here.

**Target**

Several methods can be used to create molecules with ablation—of which two are discussed here. The first and simplest method is to ablate a BaF$_2$ crystal directly. Although this method was initially used, the molecular yield is low and thus the second method was adopted in which the BaF$_2$ crystal is crushed into a powder, mixed with CaF$_2$ powder$^5$ and then pressed and baked to create a solid target. This method substantially increased both the number of molecules seen after ablation as well as the lifetime of the targets.

**Ablation Laser**

The laser used for ablating the target is a Continuum Minilite laser with an operation wavelength of 1064 nm. The output energy is 42.8 mJ with 5±2 nsec pulses focused onto the ablation target with a spot size of approximately 100 µm. Since the power is high, the laser is completely enclosed.

**Cryostat and Buffer Gas Cooling**

The HDL-5 cryostat dewar from Infrared Laboratories consists of a liquid nitrogen dewar directly over a liquid helium dewar. The cell containing the target is mounted underneath and in thermal contact with the helium dewar (see Fig. 1.5). Two windows on either side of the cryostat allow optical access to the target as do two corresponding windows on the cell. The ablation laser enters through these

$^5$The CaF$_2$ is added to keep the target from crumbling; for the measurements taken in this thesis a 95/5 ratio of BaF$_2$ to CaF$_2$ was used.
optical access ports and is incident on the target, which creates a plasma plume of BaF molecules. A helium buffer gas line is placed in the cell and the ablated molecules experience collisions with the cold helium atoms—modeled by hard sphere collisions—thereby cooling them to cryogenic temperatures and increasing the molecular population in the ground state. The cell is designed with an aperture such that a molecular beam exits the cell towards the rest of the experimental setup.

1.5.2. Laser Cooling System and Master’s Thesis

The main cooling laser and three repumping lasers require a substantial optics setup. This thesis addresses the overall optical design of the system, as well as the construction and characterization of the main cooling and first repumping lasers. In addition to the optics which were designed and built, an extensive experimental control system—both hardware and software—was implemented which allowed electronic control of experimental devices, as well as experimental data acquisition. Furthermore, initial spectroscopic data was taken which allowed the extensive calculations done on the molecule’s energy levels to be verified.
1.5. Experimental Goals

**Figure 1.5.** Cryostat setup for creating the molecular beam. The cryostat dewar has a liquid nitrogen (LN$_2$) dewar under which resides a liquid helium (LHe) dewar. Shielding extends from the LN$_2$ container around the LHe to reduce heating from black-body radiation. Underneath the LHe container is a metal cell which contains the BaF$_2$ target. The helium buffer gas passes through the buffer gas line, is precooled and then enters the cell to cool the molecular plume—which is created by ablating the BaF$_2$ target. This process creates a molecular beam which exits the aperture and enters the experiment.
2. Theory

In this chapter, the various angular momentum coupling schemes for the ground state $X^2\Sigma^+$ and the excited states $A^2\Pi_{1/2}$ and $A^2\Pi_{3/2}$ are described. The coupling schemes lead to the calculation of the molecule’s full energy spectrum as well as the eigenfunctions of the ground state. Using the eigenfunctions of both the ground and excited states allows the dipole transition elements to be calculated—which further informs the structure of the experimental setup.

2.1. Hund’s Cases and Molecular Notation

In Sec 1.4.2 it was shown that quasi-closed optical cycling between the ground state $X^2\Sigma^+$ and the first excited state $A^2\Pi_{1/2}$ can be used to achieve laser cooling. Although the principal quantum numbers for the electronic states were already discussed (given by letters, see Sec 1.4.2), the remaining notation used to describe the angular momentum of the states needs to be detailed as it differs substantially from the notation used for atoms. In particular, the molecular notation heavily relies on the angular momentum coupling between the molecule’s electronic angular momentum, spin and rotational angular momentum.

2.1.1. Hund’s Cases for BaF

Hund’s cases are a method to describe how the electronic angular momentum and rotational angular momentum of the molecule are coupled together. Since this coupling occurs in various ways depending on the molecular state, the different Hund’s cases describe differing coupling regimes. However, only Hund’s case (a), used for the excited state, and Hund’s case (b), used for the ground state, are described here.

Hund’s Case (a)

Fig. 2.1 shows the coupling scheme for Hund’s case (a) which is the case used for the excited state $A^2\Pi_{1/2}$. First, the electronic orbital angular momentum $L$
2. Theory

Figure 2.1.: Angular momentum coupling in Hund’s case (a) [41]. The electronic angular momentum \( L \) couples to the internuclear axis and the spin \( S \) then couples to \( L \) so that \( \Lambda \) and \( \Sigma \) can be described as the projections of \( L \) and \( S \) on the internuclear axis respectively. The spin-orbit coupling of \( L \) and \( S \) gives \( \Omega \)—along with its projection along the internuclear axis \( \Omega \)—which then couples to the rotational angular momentum of the nuclei \( R \) to give the total angular momentum \( J \).

Strongly couples to the internuclear axis via electrostatic interactions. Next, the spin \( S \) couples to the orbital angular momentum via spin-orbit coupling to form\(^1\) \( \Omega \)

\[
\Omega = L + S \tag{2.1}
\]

Next, the projection of \( \Omega \) onto the internuclear axis, which is denoted as \( \Omega \), is given as

\[
\Omega = \pm \Omega \tag{2.2}
\]

since \( \Omega \) always points along the internuclear axis. Similarly, the projection of electronic angular momentum and the projection of spin \( S \) onto the internuclear axis can be defined as \( \Lambda \) and \( \Sigma \) respectively. Using these two projections yields a second definition of \( \Omega \)

\[
\Omega = \Lambda + \Sigma \tag{2.3}
\]

\(^1\)When dealing with a simple atomic case, the orbital angular momentum and spin couple together to form the total angular momentum \( J \). This corresponds to \( \Omega \) in the Hund’s case (a) model.
Figure 2.2: Coupling in Hund’s case (b) [41] which is used for the ground state. The projection $\Lambda$ of the angular momentum $L$ onto the internuclear axis couples with the rotational angular momentum of the nuclei $R$ to form the intermediary angular momentum $N$. In the ground state $\Lambda = 0$ and thus $N = R$. Finally, $N$ couples to the spin $S$ to give the total angular momentum $J$.

Now, $\Omega$ couples to the rotational angular momentum of the diatomic molecule’s nuclei $R$ to give the total angular momentum $J$

$$J = \Omega + R \quad (2.4)$$

The basis state for Hund’s case (a) can be written with good quantum numbers as $|\eta, \Lambda, S, \Sigma, J, \Omega\rangle$ where $\eta$ represents quantum numbers not explicitly stated. $S$ and $J$ are the quantum numbers corresponding to $S$ and $J$ respectively (i.e. the $\hat{L}_z$ operators in the general angular momentum theory). The remaining good quantum numbers all correspond to projections of an angular momentum along the internuclear axis.$^2$

Hund’s Case (b)

In Hund’s case (b)—which is used for the ground state $X^2\Sigma^+$—the electronic angular momentum $L$ no longer couples to the spin $S$ (although this case can also be used for very weak coupling of $L$ and $S$). Instead, the projection of $L$ on the $\hat{L}_z$ operators in the general angular momentum theory which return the projection of the angular momentum $L$ along a quantization axis $z$. 

$^2$
internuclear axis (\(\Lambda\)) couples with the angular momentum of the nuclei rotation \(R\) (see Fig. 2.2) to form the intermediary angular momentum vector \(N\)

\[N = \Lambda + R\]  \hspace{1cm} (2.5)

Next, \(N\) and the spin \(S\) couple together to give the total angular momentum of the molecule \(J\)

\[J = N + S\]  \hspace{1cm} (2.6)

Using the above insights, the basis for Hund’s case (b) can be described with good quantum numbers \(|\eta, \Lambda, N, S, J\rangle\).

### 2.1.2. Molecular State Notation

Although the notation for molecular states may seem strange, the previous description of the Hund’s cases makes it fairly straightforward. The molecular notation is given as follows

\[2S+1|\Lambda|_{\Omega}\]  \hspace{1cm} (2.7)

where again \(\Lambda\) is the projection of the electronic angular momentum \(L\) on the internuclear axis and \(S\) is the electronic spin. In the simpler atomic notation, the orbital angular momentum states of the atom are denoted as \(S \rightarrow |L| = 0, P \rightarrow |L| = 1, D \rightarrow |L| = 2, \text{ etc.}\); however, in molecular notation the molecular electronic states are described with \(\Lambda\) instead: \(\Sigma \rightarrow |\Lambda| = 0, \Pi \rightarrow |\Lambda| = 1, \Delta \rightarrow |\Lambda| = 2\) [44] (i.e. Greek letters are used rather than Latin letters)\(^3\). \(\Omega\) is not a good quantum number for certain Hund’s cases [such as Hund’s case (b)] and is removed from the notation [44].

### 2.2. Ground State

The molecular ground state of BaF is given by \(X^2\Sigma^+\) so that \(S = 1/2\) and \(|\Lambda| = 0\). Since the quasi-closed optical cycling scheme utilizes all the hyperfine levels of the \(N = 1\) rotational manifold, it is imperative to calculate the energies of the various rotational hyperfine levels and thereby determine the correct transition laser

\(^3\)For the \(\Sigma\) state this can be somewhat confusing since the projection of the electronic spin \(S\) onto the internuclear axis is also denoted as \(\Sigma\). Even so, it is fairly easy to keep the two separated as when the variable is used as a projection of spin, it comes unadorned with superscripts and subscripts that denote a molecular state.
frequencies. As the ground state system is not analytically solvable, an effective Hamiltonian is used for calculation of the hyperfine structure. This effective Hamiltonian neglects electronic properties which are similar for all the hyperfine states.

2.2.1. Parity

Parity plays an important role in the description of the different ground state rotational manifolds \( N \). Since BaF is a \( \Sigma^+ \) molecule in the ground state, the parity, \( P \), of the ground state for a given rotational manifold is [41]

\[
P = (-1)^N. \tag{2.8}
\]

2.2.2. Effective Hamiltonian

The effective Hamiltonian for the ground state of BaF is given in Hund’s case (b) by [43]

\[
H_{\text{eff}} = H_R + H_{SR} + H_{\text{hfs}} \tag{2.9}
\]

where \( H_R \) represents the energy due to the molecule’s rotation, \( H_{SR} \) represents the spin-rotation coupling and \( H_{\text{hfs}} \) is the hyperfine splitting. Expanding Eq. 2.9 in terms of the good quantum numbers \( |\eta, \Lambda, N, S, J\rangle \) necessitates the introduction of the full basis states as well as the introduction of spherical tensors.

Full Basis States for Hamiltonian

In the expansion of the effective Hamiltonian the \( F \) and \( m_F \) quantum numbers are needed. These are fairly straightforward to calculate and depend on the nuclear spin quantum number \( I \). Therefore

\[
|J - I| < F < |J + I|, \tag{2.10}
\]

Using \( F \), both the value of the degenerate hyperfine states can be determined

\[
m_F = -F, -F + 1, ..., 0, ..., F - 1, F, \tag{2.11}
\]

as well as the number \( N_{m_F} \) of these degenerate states

\[
N_{m_F} = 2F + 1. \tag{2.12}
\]
2. Theory

Adding $F$ and $m_F$ and removing the $\eta$ quantum number—which the effective Hamiltonian doesn’t depend on—gives $|\Lambda, N, S, J, I, F, m_F\rangle$ as the full basis ket. For $N = 1$ in the ground state, $\Lambda = 0$, $S = 1/2$ and $I = 1/2$ (the last two are always constant for our molecule). Thus the basis states take the form

$$\phi = |\Lambda, N, S, J, I, F, m_F\rangle = |0, 1, \frac{1}{2}, J, \frac{1}{2}, F, m_F\rangle.$$  \hspace{1cm} (2.13)

Spherical Tensors and Angular Momentum

Spherical tensors are utilized extensively in molecular physics as they take advantage of the molecule’s symmetries. Here a brief description of spherical tensors is given by following Brown and Carrington [41] closely.

The spherical tensors, $T$, are used to represent quantum mechanical operators by placing the quantum mechanical operator as the tensor’s argument where, for example, $T(S)$ is the spherical tensor representation of the spin $S$ operator. A superscript denotes the rank of the tensor and a subscript denotes the axial component. Using the example found in [41]

$$T^{1}_{0}(S) = S_z$$ \hspace{1cm} (2.14)

$$T^{1}_{1}(S) = -\left(\frac{1}{\sqrt{2}}\right)(S_x + iS_y)$$ \hspace{1cm} (2.15)

$$T^{1}_{-1}(S) = \left(\frac{1}{\sqrt{2}}\right)(S_x - iS_y).$$ \hspace{1cm} (2.16)

Furthermore, the axial component can be denoted as either $p$ or $q$ which corresponds to a space-fixed (e.g. $T^{1}_{p=0}$) or a molecule-fixed (e.g. $T^{1}_{q=0}$) coordinate system respectively.

Expansion of the Effective Hamiltonian

Using spherical tensors, the terms in the effective Hamiltonian (Eq. 2.9) are written as [43]

$$H_{R} = B_{\nu}\hat{N}^{2} - D_{\nu}\hat{N}^{4}$$ \hspace{1cm} (2.17)

$$H_{SR} = \gamma_{\nu N}T^{1}(\hat{S}) \cdot T^{1}(\hat{N})$$ \hspace{1cm} (2.18)

$$H_{hfs} = b_{F}T^{1}(\hat{I}) \cdot T^{1}(\hat{S}) + c_{\nu}T^{1}_{q=0}(\hat{I})T^{1}_{q=0}(\hat{S}) + C_{\nu N}T^{1}(\hat{I}) \cdot T^{1}(\hat{N}).$$ \hspace{1cm} (2.19)
The spherical tensors in Eq. 2.17 through Eq. 2.19 can be further expanded in terms of the Hund’s case (b) good quantum numbers [43]. First, the molecular rotation portion of the Hamiltonian \( H_R \) can be written element-wise as [43]

\[
\langle \phi' | b_\nu \hat{N}^2 - D_\nu \hat{N}^4 | \phi \rangle = \delta_{N',N} \delta_{J',J} \delta_{F',F} \delta_{m'_F m_F} \\
\times (B_\nu N(N + 1) - D_\nu [N(N + 1)]^2)
\]  

(2.20)

after which the spin-rotation coupling \( H_{SR} \) becomes

\[
\langle \phi' | b_{\nu N} T^1(\hat{S}) \cdot T^1(\hat{N}) | \phi \rangle = \delta_{N',N} \delta_{J',J} \delta_{F',F} \delta_{m'_F m_F} \gamma_{\nu N} \\
\times (-1)^{N+J+S} \left\{ S \right\}^{\frac{1}{2}} \left\{ N \right\}^{\frac{1}{2}} \left\{ S \right\} \left\{ J \right\} \left\{ N \right\} \left\{ J \right\} \left\{ 1 \right\} .
\]  

(2.21)

The hyperfine portion of the effective Hamiltonian, \( H_{hfs} \), can be written as the addition of three separate expressions corresponding to the three terms in Eq. 2.19. These are

\[
\langle \phi' | b_F T^1(\hat{I}) \cdot T^1(\hat{S}) | \phi \rangle = \delta_{N',N} \delta_{F',F} \delta_{m'_F m_F} b_F (-1)^{J'+F+I+N+1+S} \\
\times \left\{ J' \right\}^{\frac{1}{2}} \left\{ J \right\}^{\frac{1}{2}} \left\{ S \right\}^{\frac{1}{2}} \left\{ I \right\}^{\frac{1}{2}} \left\{ I \right\} \left\{ J \right\} \left\{ F \right\} \left\{ J \right\} \left\{ N \right\} \left\{ J \right\} \left\{ 1 \right\} .
\]  

(2.22)

\[
\langle \phi' | c_{\nu N} T^1_{q=0}(\hat{I}) T^1_{q=0}(\hat{S}) | \phi \rangle = \delta_{N',N} \delta_{F',F} \delta_{m'_F m_F} \left( -\frac{\sqrt{30} c_\nu}{3} \right) (-1)^{J'+F+I+N} \\
\times \left\{ J' \right\}^{\frac{1}{2}} \left\{ J \right\}^{\frac{1}{2}} \left\{ S \right\}^{\frac{1}{2}} \left\{ I \right\}^{\frac{1}{2}} (2N + 1) \\
\times \left\{ N \right\} \left\{ 2 \right\} \left\{ N \right\} \left\{ I \right\} \left\{ J \right\} \left\{ F \right\} \left\{ J \right\} \left\{ N \right\} \left\{ J \right\} \left\{ 1 \right\} .
\]  

(2.23)

and

\[
\langle \phi' | C_{\nu N} T^1(\hat{I}) \cdot T^1(\hat{N}) | \phi \rangle = \delta_{N',N} \delta_{F',F} \delta_{m'_F m_F} C_{\nu N} (-1)^{2J'+F'+I+N'+1+S} \\
\times \left\{ J' \right\}^{\frac{1}{2}} \left\{ J \right\}^{\frac{1}{2}} \left\{ N \right\}^{\frac{1}{2}} \left\{ I \right\}^{\frac{1}{2}} \\
\times \left\{ I \right\} \left\{ J \right\} \left\{ F' \right\} \left\{ J \right\} \left\{ N \right\} \left\{ J \right\} \left\{ S \right\} \\
\times \left\{ J' \right\} \left\{ J \right\} \left\{ 1 \right\} .
\]  

(2.24)
Mathematical Symbols in the Expanded Effective Hamiltonian

The $2 \times 3$ matrix-like object in parentheses

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

(2.25)

is a Wigner 3j symbol and allows coupling of angular momentum $j$ and $m$. The $2 \times 3$ matrix-like object in curly brackets

$$\begin{cases} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{cases}$$

(2.26)

is a Wigner 6j symbol and finally the $3 \times 3$ matrix-like object in curly brackets

$$\begin{cases} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \\ j_7 & j_8 & j_9 \end{cases}$$

(2.27)

is a Wigner 9j symbol. The symbols $[x]^{\frac{1}{2}}$ and $\{x\}^{\frac{1}{2}}$ are given as follows [43]

$$[x]^{\frac{1}{2}} = \sqrt{2x + 1}$$

(2.28)

$$\{x\}^{\frac{1}{2}} = \sqrt{x(x + 1)(2x + 1)}.$$

(2.29)

BaF Constants in the Effective Hamiltonian

There are several constants in the expanded effective Hamiltonian that need to be defined [43]. The rotational constant $B_\nu$ is equal to

$$B_\nu = Y_{01} + Y_{11} \left( \nu + \frac{1}{2} \right) + Y_{21} \left( \nu + \frac{1}{2} \right)^2,$$

(2.30)

whereas the centrifugal distortion constant $D_\nu$ is written as

$$D_\nu = -Y_{02} - Y_{12} \left( \nu + \frac{1}{2} \right).$$

(2.31)

Furthermore, the spin-rotational constant is given by

---

4The sympy.physics.wigner Python package was used to calculate the Wigner 3j and Wigner 6j symbols; however, for the Wigner 9j symbol the package function didn’t return the correct result (referenced against Anthony Stone’s Wigner calculator [50]). Therefore, a custom Wigner 9j function was implemented (see Appendix A).
2.2. Ground State

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>cm$^{-1}$</th>
<th>MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_{01}$</td>
<td>0.2165296</td>
<td>6.491395×10$^3$</td>
</tr>
<tr>
<td>$Y_{02}$</td>
<td>-1.84291×10$^{-7}$</td>
<td>-5.52491×10$^{-3}$</td>
</tr>
<tr>
<td>$Y_{10}$</td>
<td>46940570</td>
<td>1.4072428×10$^7$</td>
</tr>
<tr>
<td>$Y_{11}$</td>
<td>-1.163429×10$^{-3}$</td>
<td>-3.487872×10$^1$</td>
</tr>
<tr>
<td>$Y_{12}$</td>
<td>-3.2567×10$^{-10}$</td>
<td>-9.7633×10$^{-6}$</td>
</tr>
<tr>
<td>$Y_{20}$</td>
<td>-1.835197</td>
<td>-5.501782×10$^4$</td>
</tr>
<tr>
<td>$Y_{21}$</td>
<td>4.346×10$^{-7}$</td>
<td>1.303×10$^{-2}$</td>
</tr>
<tr>
<td>$Y_{22}$</td>
<td>6.89×10$^{-12}$</td>
<td>2.07×10$^{-7}$</td>
</tr>
<tr>
<td>$Y_{30}$</td>
<td>3.1057×10$^{-3}$</td>
<td>9.3107×10$^1$</td>
</tr>
<tr>
<td>$Y_{31}$</td>
<td>1.432×10$^{-8}$</td>
<td>4.293×10$^{-4}$</td>
</tr>
<tr>
<td>$Y_{40}$</td>
<td>5.62×10$^{-6}$</td>
<td>1.68×10$^{-1}$</td>
</tr>
<tr>
<td>$Y_{41}$</td>
<td>1.27×10$^{-10}$</td>
<td>3.81×10$^{-6}$</td>
</tr>
</tbody>
</table>

**Table 2.1.**: Dunham Coefficients for $^{138}$BaF in units of cm$^{-1}$ given in [51]. The constants have been additionally converted to MHz for use in calculation.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>MHz</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_{00}$</td>
<td>80.984(19)</td>
<td>[52]</td>
</tr>
<tr>
<td>$\gamma_{10}$</td>
<td>-58.4(73)×10$^{-3}$</td>
<td>[52]</td>
</tr>
<tr>
<td>$\gamma_{01}$</td>
<td>112(17)×10$^{-6}$</td>
<td>[52]</td>
</tr>
<tr>
<td>$b_0$</td>
<td>63.509(32)</td>
<td>[53]</td>
</tr>
<tr>
<td>$c_0$</td>
<td>8.224(58)</td>
<td>[53]</td>
</tr>
</tbody>
</table>

**Table 2.2.**: The spin rotational constants $\gamma_{nm}$, as well as the hyperfine constant, $b_\nu$, and dipole-dipole constant, $c_\nu$, for the zeroth vibrational state—given in units of MHz.

\[
\gamma_{\nu N} = \gamma_{00} + \gamma_{10} \left( \nu + \frac{1}{2} \right) + \gamma_{01} N (N + 1)
\]

(2.32)

and the Fermi contact constant is denoted by

\[
b_F = b_\nu + \frac{c_\nu}{3}.
\]

(2.33)

In the above equations, the $Y_{nm}$ constants are the Dunham coefficients (see Table 2.1) and the $\gamma_{nm}$ constants are the spin-rotational constants (see Table 2.2). Additionally, $b_\nu$ and $c_\nu$ are the hyperfine constant and dipole-dipole constant for the given vibrational state $\nu$ respectively (see Table 2.2). The nuclear spin-rotational constant is $C_{\nu N}$. 
2. Theory

2.2.3. Effective Hamiltonian Eigenenergies and Eigenfunctions

It can be shown (see Appendix B) that the effective Hamiltonian is decoupled with respect to the rotational manifolds \( N \), and thus only the \( N = 1 \) rotational manifold used for optical cycling is directly addressed here. According to Eq. 2.6 for \( N = 1, \ J = 1/2 \) and \( J = 3/2 \) have (see Eq. 2.10) hyperfine quantum numbers of \( F = 0,1 \) and \( F = 1,2 \) respectively. The degenerate \( m_F \) values are then easily calculated with Eq. 2.11 giving a total of twelve states in the Hund’s case (b) basis. To calculate an element of the Hamiltonian matrix

\[
\langle J', F', m_{F'} | H_{\text{eff}} | J, F, m_F \rangle
\]  

where \( H_{\text{eff}} \) was extensively described in Sec. 2.2.2 and the ket of good quantum numbers for the ground state Hund’s case (b) basis is simplified from \( |\Lambda, N, S, J, I, F, m_F \rangle \) to \( |J, F, m_F \rangle \)—since the removed quantum numbers are constant for every state in the calculation.

Using Eq. 2.34 in conjunction with the basis set produces the Hamiltonian matrix seen in Table 2.3 with which the eigenenergies and eigenfunctions (see Table 2.4) are calculated. As expected, the eigenenergies are degenerate for the \( m_F \) values within a hyperfine state\(^5\). The eigenfunction states are generally called nominal Hund’s case (b) states, whereas the basis states used in the Hamiltonian calculation are called pure Hund’s case (b) states. The labeling scheme of the nominal states can be initially opaque and a short description is given using the rotational manifold \( N = 1 \) as an example.

Nominal vs. Pure Basis

The nominal states/eigenfunctions \( |J \rangle' \) are linear combinations of the pure Hund’s case (b) basis states \( |J \rangle \) and have the form

\[
|J \rangle' = c_1 |J = \frac{3}{2}\rangle + c_2 |J = \frac{1}{2}\rangle
\]  

where \( c_1 \) and \( c_2 \) are constants and all states are written only in terms of \( J \) (the \( F \), and \( m_F \) quantum numbers are the same for the superimposed states and the nominal state, see Table 2.4). The relative contributions of the pure states to

\(^5\)We note that the linear combinations of pure states differ by a sign from Chen’s [43] et al. calculations. However, we are confident in our calculations as they are consistent with the general eigenfunction equations given by Norrgard [44] (Eq. 2.18).
2.2. Ground State

Table 2.3.: Effective Hamiltonian matrix for the $N = 1$ rotational manifold in the $X^2\Sigma^+$ ground state. The Hamiltonian is given in the pure Hund's case (b) basis with simplified kets $|J,F,m_F\rangle$. The values are all in units of MHz and have been rounded to an integer value for display.

<table>
<thead>
<tr>
<th>States</th>
<th>Energies (MHz)</th>
<th>Nominal</th>
<th>Pure</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
<td>\frac{1}{2},2,-2\rangle$</td>
<td>13005</td>
<td>$</td>
</tr>
<tr>
<td>$</td>
<td>\frac{1}{2},2,-1\rangle$</td>
<td>0</td>
<td>$</td>
</tr>
<tr>
<td>$</td>
<td>\frac{1}{2},2,0\rangle$</td>
<td>0</td>
<td>$</td>
</tr>
<tr>
<td>$</td>
<td>\frac{1}{2},2,1\rangle$</td>
<td>0</td>
<td>$</td>
</tr>
<tr>
<td>$</td>
<td>\frac{3}{2},1,-1\rangle$</td>
<td>0</td>
<td>$</td>
</tr>
<tr>
<td>$</td>
<td>\frac{3}{2},1,0\rangle$</td>
<td>0</td>
<td>$</td>
</tr>
<tr>
<td>$</td>
<td>\frac{3}{2},1,1\rangle$</td>
<td>0</td>
<td>$</td>
</tr>
<tr>
<td>$</td>
<td>\frac{3}{2},0,0\rangle$</td>
<td>0</td>
<td>$</td>
</tr>
</tbody>
</table>

Table 2.4.: Eigenenergies and eigenfunctions for the the $X^2\Sigma^+$ ground state in the rotational manifolds $N = 0, 1, 2$. The values are calculated by solving the eigensystem for the effective Hamiltonian matrix in each rotational sublevel (such as Table 2.3 for $N = 1$). The eigenfunctions are given both in the nominal Hund’s case (b) basis $|J,F\rangle$ and the pure Hund’s case (b) basis $|J,F\rangle'$ with coefficients of $\alpha_1 = 0.9593$, $\beta_1 = 0.2824$, $\alpha_2 = 0.9858$ and $\beta_2 = 0.1679$ for the linear combinations of the pure basis.
the nominal states determine how the nominal states are labeled. For example, if $|c_1| > |c_2|$ then the nominal state is labeled $|J = 3/2\rangle'$ since the the pure state $|J = 3/2\rangle$ contributes to the nominal state more strongly. Conversely, if $|c_2| > |c_1|$, then the state is labeled $|J = 1/2\rangle'$.

**Hyperfine Energies and Experiment**

Determining the hyperfine energy levels is important for the experimental setup as the BaF cycling scheme simultaneously addresses all the hyperfine states in the $N = 1$ rotational manifold. Generally, this is done with a resonant electro-optical modulator (EOM) and thus the relative energy difference between the hyperfine levels must be calculated in order to determine the correct EOM driving frequencies (see Sec 3.2.6). This is done by either calculating the rotational energy separately and subtracting it from all the hyperfine energies, or by simply omitting the rotational energy $H_R$ portion of the effective Hamiltonian when calculating the eigenenergies.

**2.3. Excited State**

The first two excited states in BaF are the fine structure states $A^2\Pi_{1/2}$ and $A^2\Pi_{3/2}$ which can be described using the Hund’s case (a) basis (see Section 2.1.1) and are the result of Λ-doubling. However, similar to the ground state, each of these excited states is actually a nominal state (linear combination) composed of pure Hund’s case (a) states with this superimposed state defined by Ω-doubling.

**2.3.1. Λ-Doubling and Ω-Doubling**

Λ-doubling and Ω-doubling together, play an important role in the description of excited molecular states. Since $\Sigma$ and $\Lambda$ are both projections onto the internuclear axis they can have either positive or negative values for a given $S$ and $|\Lambda|$ in the molecular term symbol ($2S+1|\Lambda|$). As an example, and following [41], the states $A^2\Pi$ are chosen which give $S = 1/2$ and $|\Lambda| = 1$ as quantum numbers. This yields the following combinations

---

Footnote: This argument falls apart when sufficiently strong perturbations are applied.
2.3. Excited State

**Figure 2.3.** Energy level diagram for the \( \text{X}^2\Sigma^+ \) ground state in BaF with rotational manifolds \( N = 0 - 3 \) included. The fine structure and hyperfine structure is shown for each rotational manifold as well. Additionally, the energy values for both the rotational manifolds and hyperfine levels are given in units of MHz.

<table>
<thead>
<tr>
<th>MHz</th>
<th>MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>77686.706 N=3</td>
<td>77686.706 N=3</td>
</tr>
<tr>
<td>J=7/2 F=4</td>
<td>+137.540</td>
</tr>
<tr>
<td>J=7/2 F=3</td>
<td>+104.759</td>
</tr>
<tr>
<td>J=5/2 F=2</td>
<td>-146.446</td>
</tr>
<tr>
<td>J=5/2 F=3</td>
<td>-176.992</td>
</tr>
<tr>
<td>J=3/2 F=2</td>
<td>-136.190</td>
</tr>
<tr>
<td>J=3/2 F=1</td>
<td>-106.241</td>
</tr>
<tr>
<td>J=3/2 F=0</td>
<td>-67.1338</td>
</tr>
<tr>
<td>J=1/2 F=1</td>
<td>-94.9467</td>
</tr>
<tr>
<td>J=1/2 F=0</td>
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<tr>
<td>J=5/2 F=2</td>
<td>+97.1264</td>
</tr>
<tr>
<td>J=5/2 F=3</td>
<td>+104.759</td>
</tr>
</tbody>
</table>

**Figure 2.3.** Energy level diagram for the \( \text{X}^2\Sigma^+ \) ground state in BaF with rotational manifolds \( N = 0 - 3 \) included. The fine structure and hyperfine structure is shown for each rotational manifold as well. Additionally, the energy values for both the rotational manifolds and hyperfine levels are given in units of MHz.
\[ \Lambda = +1; \Sigma = +1/2; \Omega = +3/2 \]
\[ \Lambda = -1; \Sigma = +1/2; \Omega = -1/2 \]
\[ \Lambda = +1; \Sigma = -1/2; \Omega = +1/2 \]
\[ \Lambda = -1; \Sigma = -1/2; \Omega = -3/2 \]

Thus \(|\Omega| = 1/2\) or \(|\Omega| = 3/2\) leading to the two non-degenerate fine structure states \(A^2\Pi_{1/2}\) and \(A^2\Pi_{3/2}\) (\(\Lambda\)-doubling).\(^7\)

**\(\Omega\) Doubling**

The second and third entries in the above list lead to the \(A^2\Pi_{1/2}\) state, whereas the first and fourth entries lead to the \(A^2\Pi_{3/2}\) state. In actuality, both the \(A^2\Pi\) states are nominal states and therefore parity dependent linear superpositions of their respective two pure Hund’s case (a) states. Using the \(A^2\Pi_{1/2}\) state as an example

\[
||\Lambda = 1, S = 1/2, |\Omega| = 1/2, P = \pm\rangle = c_1 |\Lambda = -1, \Sigma = +1/2, \Omega = -1/2\rangle \\
\pm c_2 |\Lambda = +1, \Sigma = -1/2, \Omega = +1/2\rangle \quad (2.36)
\]

where \(P\) is the parity operator, \(||\Lambda = 1, S = 1/2, |\Omega| = 1/2, P = \pm\rangle\) is the ket for the nominal state \(A^2\Pi_{1/2}\) and \(|\Lambda = \pm 1, \Sigma = \mp 1/2, \Omega = \pm 1/2\rangle\) represents the pure Hund’s case (a) kets (both nominal and pure kets are devoid of \(J\) and \(S\) for display). The parity operator \(P = \pm\) dictates whether there is a symmetric or anti-symmetric superposition of the pure Hund’s case (a) states. Finally, the energies of the two different superposition states are non-degenerate (see Fig. 2.4 and Eq. ??)\(^8\).

\(^7\)\(J = \Omega + R = \Omega\), since \(R = 0\) for these states.

\(^8\)In the ground state \(|\Lambda| = 0\) and thus there is no \(\Lambda\)-doubling. Additionally, the Hund’s case (b) basis for the ground state does not include the the projection of spin \(\Sigma\) as a good quantum number.
2.4. Branching Ratios

Figure 2.4.: Energy level diagram for the $A^2\Pi_{1/2}$ and $A^2\Pi_{3/2}$ excited fine structure states with their respective parity splittings—all calculated from Eq. ???. The energy values for each fine structure level are given in units of GHz, whereas the parity states are given in MHz.

2.3.2. Energy Levels of Excited States

To calculate the fine structure and parity dependent energy splitting of the excited state, an equation from Rahmlow’s thesis [54] is used

$$E(J, \nu, \pm) = T_e + \omega_e \left( \nu + \frac{1}{2} \right) - \omega_e \chi_e \left( \nu + \frac{1}{2} \right)^2$$

$$+ (A_e - \alpha_A \nu) \Lambda \Sigma + \left[ B_e - \alpha_e \left( \nu + \frac{1}{2} \right) \right] J(J+1)$$

$$\mp (-1)^{J+\frac{1}{2}} \left( \frac{p + 2q}{2} \right) \left( J + \frac{1}{2} \right)$$

(2.37)

where all the molecular constants can be found in Table 2.5. The equation is useful in determining the transition energies for optical cycling (see Fig. 2.4).

2.4. Branching Ratios

The dipole transition branching ratios from the excited state $m_F'$ levels to the ground state $m_F$ levels are essential to modeling optical cycling with rate equations. However, the calculation is non-trivial as both the excited and ground states must be represented in the pure Hund’s case (a) basis—which requires several basis changes.
2. Theory

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>cm$^{-1}$</th>
<th>MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_e$</td>
<td>11962.174</td>
<td>$3.5861695 \times 10^8$</td>
</tr>
<tr>
<td>$\omega_e$</td>
<td>437.899</td>
<td>$1.31278 \times 10^7$</td>
</tr>
<tr>
<td>$\omega_e \chi_e$</td>
<td>1.854</td>
<td>$5.558 \times 10^4$</td>
</tr>
<tr>
<td>$A_e$</td>
<td>632.409</td>
<td>$1.89591 \times 10^7$</td>
</tr>
<tr>
<td>$\alpha_A$</td>
<td>-0.5068</td>
<td>$-1.519 \times 10^4$</td>
</tr>
<tr>
<td>$B_e$</td>
<td>0.212416</td>
<td>6368.07</td>
</tr>
<tr>
<td>$\alpha_e$</td>
<td>$1.2563 \times 10^{-3}$</td>
<td>37.6629</td>
</tr>
<tr>
<td>$p$</td>
<td>-0.257039</td>
<td>-7705.84</td>
</tr>
<tr>
<td>$q$</td>
<td>-0.0840</td>
<td>-2518</td>
</tr>
</tbody>
</table>

Table 2.5: Molecular constants used in the excited state energy calculation (see Eq. ??) for the zeroth vibrational state and given in units of cm$^{-1}$ [42]. Constants are additionally converted to MHz for use in calculation.

2.4.1. Changing Basis for Hund’s cases in BaF

Ground State

In Section 2.2.3, the nominal states or eigenfunctions for the ground state were calculated from the effective Hamiltonian and shown to be a linear combination of pure Hund’s case (b) states. A new notation$^9$ is introduced which describes the $u$th eigenfunction/nominal state $G_u$ as

$$G_u = \sum_{q=1}^{Q} c_{uq} |b_q\rangle$$  \hspace{1cm} (2.38)

where $|b_q\rangle$ represents the $q$th state in the pure Hund’s case (b) basis ($|\Lambda,N,S,J\rangle$) used to calculate the effective Hamiltonian. The coefficients $c_{uq}$ describing the linear combination are taken from the diagonalization of the effective Hamiltonian. Although the ground state $X^2\Sigma^+$ eigenfunctions can now be written in the pure Hund’s case (b) basis, for the dipole transition calculation they must be further converted to pure Hund’s case (a) basis states ($|\Lambda,S,\Sigma,J,\Omega\rangle$) which is done via the following equation [44,55,56]

$^9$This notation is useful since, as the sum runs over all states in the Hund’s case (b) basis, the calculation program can likewise simply loop through the multidimensional array which holds all the Hund’s case (b) basis states and their respective quantum numbers.
2.4. Branching Ratios

$$|\Lambda, N, S, J \rangle = \sum_{\Sigma=-S}^{S} \sum_{\Omega=-J}^{J} (-1)^{N-S+\Omega}(2N+1)^{\frac{1}{2}} \begin{pmatrix} J & S & N \\ \Sigma & \Lambda & -\Omega \end{pmatrix} |\Lambda, S, \Sigma, J, \Omega \rangle$$

(2.39)

$$= \sum_{\Sigma=-S}^{S} (2N+1)^{\frac{1}{2}} \begin{pmatrix} S & N & J \\ \Sigma & \Lambda & -\Omega \end{pmatrix} |\Lambda, S, \Sigma, J, \Omega \rangle$$

(2.40)

Now similar to Eq. 2.38, this can be rewritten as a sum over all pure Hund’s case (a) states

$$|b_q \rangle = \sum_{p=1}^{P} k_{qp} |a_p \rangle$$

(2.41)

where $|a_p \rangle$ represents the $p$th state in the Hund’s case (a) basis ($|\Lambda, S, \Sigma, J, \Omega \rangle$). The various $k_{qp}$ coefficients are taken from Eq. 2.40 as

$$k_{qp} = (2N+1)^{\frac{1}{2}} \begin{pmatrix} S & N & J \\ \Sigma & \Lambda & -\Omega \end{pmatrix}$$

(2.42)

Combining Eq. 2.38 and Eq. 2.41 allows each eigenfunction $G_u$ to be written as a linear combination of pure Hund’s case (a) basis states

$$G_u = \sum_{q=1}^{Q} \sum_{p=1}^{P} c_{uq} k_{qp} |a_p \rangle$$

(2.43)

**Excited State**

As shown in Section 2.3, the excited state $A^2 \Pi_{1/2}$ is a superposition of two pure Hund’s case (a) states. Here the full expression by which the nominal excited states are represented in the pure Hund’s case (a) basis is given

$$|\mp \rangle = \frac{1}{\sqrt{2}} (|\Lambda, S, \Sigma, J, \Omega \rangle \pm (-1)^{J-S} |\Lambda, S, -\Sigma, J, -\Omega \rangle)$$

(2.44)

where the parity operator $P$ is simply represented as ±. Now the above equation can be rewritten as

$$|\xi_\nu \rangle = \sum_{m=1}^{M} h_{\nu m} |a_m \rangle$$

(2.45)
where $|\xi_\nu\rangle$ represents the $\nu$th state in the nominal Hund’s case (a) basis, $|a_m\rangle$ represents the $m$th state in the pure Hund’s case (a) basis ($|\Lambda, S, \Sigma, J, \Omega\rangle$) and $h_{\nu m}$ represents the coefficients for the linear combination.

### 2.4.2. Electric Dipole Transition

The electric dipole transition operator $d$ is used to calculate the probability of a decay from an excited $m'_F$ state to a ground $m_F$ state. As previously stated the calculation must be done with both states represented in the pure Hund’s case (a) basis. The pure Hund’s case (a) basis ket is now expanded to include quantum numbers, $F$ and $m_F$, accounting for the degenerate hyperfine levels via Eq. 2.10 and Eq. 2.11. Thus $|\Lambda, S, \Sigma, J, \Omega\rangle$ becomes $|\Lambda, S, \Sigma, J, \Omega, I, F, m_F\rangle$.

The dipole transition between two pure Hund’s case (a) states is calculated via the procedure laid out in the appendix of [57]. First, the polarization of the transition of the dipole transition is calculated as follows

$$
P = m'_F - m_F$$  \hspace{1cm} (2.46)

Transitions only occur when $P = 0, \pm 1$. Furthermore, the dipole transition does not change the spin of the system and thus $\Sigma' = \Sigma$. After applying these two selection rules the dipole transition is calculated with

$$
\langle d \rangle = \langle \psi_e|T^I_P(\hat{d})|\psi_g\rangle = m_1m_2m_3
$$  \hspace{1cm} (2.47)

where $T^I_P(\hat{d})$ is the dipole transition operator in spherical tensor notation and $\psi_e$ and $\psi_g$ are excited and ground state nominal states/eigenfunctions respectively. This expression can be expanded by explicitly writing $m_1, m_2,$ and $m_3$ as

$$
m_1 = (-1)^{F'-m'_F} \begin{pmatrix} F' & 1 & F \\ -m'_F & P & m_F \end{pmatrix}
$$  \hspace{1cm} (2.48)

$$
m_2 = (-1)^{F+J'+I+1} [F']^\frac{1}{2} [F]^\frac{1}{2} \left\{ \begin{array}{ccc} J & F & I \\ F' & J' & 1 \end{array} \right\}
$$  \hspace{1cm} (2.49)

$$
m_3 = \sum_{Q=1}^{1} (-1)^{J'-\Omega'} [J']^\frac{1}{2} [J]^\frac{1}{2} \begin{pmatrix} J' & 1 & J \\ -\Omega' & Q & \Omega \end{pmatrix}
\times \langle \Lambda_e, S_e, \Sigma_e|T^I_Q(\hat{d})||\Lambda_g, S_g, \Sigma_g\rangle
$$  \hspace{1cm} (2.50)

where the expression on the end $\langle \Lambda_e, S_e, \Sigma_e|T^I_Q(\hat{d})||\Lambda_g, S_g, \Sigma_g\rangle$ is constant for all transitions and can thus be ignored.

\(^{10}\)Ignoring for now perturbations.
Programmatic Representation

Converting both the ground and excited state eigenfunctions to pure Hund’s case (a) states requires three basis changes. Thus, keeping track of all the states and coefficients is non-trivial and a programmatic approach to the calculation is taken with the custom notation previously introduced. Equation 2.47 is rewritten as

$$\langle d \rangle = \langle \psi_e | T^I_p (\hat{d}) | \psi_g \rangle = \langle \xi_\nu | T^I_p (\hat{d}) | G_u \rangle$$

(2.51)

where the excited and ground states are replaced by their respective eigenfunctions (given in Sec 2.2.3 and Sec 2.3.1). Replacing $G_u$ with Eq. 2.43 and $\xi_\nu$ with Eq 2.45 allows Eq. 2.51 to be rewritten

$$\langle d \rangle = \sum_{m=1}^{M} \sum_{q=1}^{Q} \sum_{p=1}^{P} h_{vm} c_{wp} k_{qp} \langle a_m | T^I_p (\hat{d}) | a_p \rangle$$

(2.52)

which allows the calculation program to merely complete a triple nested loop for each dipole element rather than manually sorting basis states. The branching ratios are calculated by squaring the dipole transition elements and have been calculated for the decay from the $A^2\Pi_{1/2}$ positive parity state to the $N = 1$ rotational manifold of the $X^2\Sigma^+$ state (see Table 2.6 and Fig. 2.5).\(^{11}\)

2.5. Zeeman Splitting

Magnetic fields play an important role in trapping molecules and as such, it is necessary to determine the effect of an external magnetic field on the energy levels of the molecule via the Zeeman shift. As of yet, only the Zeeman shift in the ground state has been calculated.

2.5.1. Ground State

In the ground state, the magnetic field is treated as a perturbation to the initial effective Hamiltonian. Therefore Eq. 2.9 becomes

$$H_{\text{eff}} = H_R + H_{\text{SR}} + H_{\text{hfs}} + H_Z$$

(2.53)

where following [43]

\(^{11}\)Additionally, the calculation was completed for the $A^2\Pi_{1/2}$ negative parity state to the $N = 0$ and $N = 2$ rotational manifolds of the $X^2\Sigma^+_{1/2}$ ground state (see Appendix C).
2. Theory

Table 2.6: Branching ratios for the $\Lambda^2\Pi_{1/2}$ positive parity state to the $X^2\Sigma^+$ $N = 1$ state. The excited nominal states are represented by the four columns and the nominal ground states are represented by the twelve rows. Note that when the $m_F$ values differ by more than one, the transition is restricted due to selection rules. Additionally, the total branching ratios for a single column add up to one. This provides an excellent test of the calculations effectiveness since, as stated previously, this is a closed transition and the total probability of decays from a single excited $m_F'$ state to all ground $m_F$ states should be equal to one.

<table>
<thead>
<tr>
<th>$J = 1/2$, $F = 0$, $m_F = 0$</th>
<th>$F = 1$, $m_F = -1$</th>
<th>$F = 1$, $m_F = 0$</th>
<th>$F = 1$, $m_F = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>0.2222</td>
<td>0.2222</td>
<td>0.2222</td>
</tr>
<tr>
<td>0.1282</td>
<td>0.2493</td>
<td>0.2493</td>
<td>0.2493</td>
</tr>
<tr>
<td>0.1282</td>
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<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.2051</td>
<td>0.0007</td>
<td>0.0007</td>
<td>0.0007</td>
</tr>
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<td>0.0007</td>
</tr>
<tr>
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<td>0.0000</td>
</tr>
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<td>0.0833</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.0000</td>
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<tr>
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<td>0.0833</td>
</tr>
<tr>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.1667</td>
</tr>
</tbody>
</table>

Figure 2.5: Hyperfine transitions as a function of the frequency. The transitions are plotted as Doppler broadened Gaussians, where the Gaussians are centered on the transition frequencies and the amplitudes are given by the transition strengths—which are calculated by summing all the rows in the branching ratio table (see Table 2.6) that correspond to each respective transition. The standard deviation of each Gaussian is given as 3 MHz to allow the hyperfine structure to be seen. The image gives a rough approximation of what potential spectroscopic data could look like for the given Doppler broadening.
2.5. Zeeman Splitting

\[ H_Z = \left( g_{SB} T_{p=0}^1(\hat{S}) + g_{LB} T_{p=0}^1(\hat{L}) - g_{IL} T_{p=0}^1(\hat{I}) \right) B_Z \]  \hspace{1cm} (2.54)

This can be further expanded as follows

\[ \langle \phi | g_{SB} B_{p=0}(\hat{S}) | \phi' \rangle = g_{SB} (-1)^{(F-m_F)} \left( \begin{array}{cc} F & F' \\ -m_F & m_F' \end{array} \right) \]
\[ \times (-1)^{F'+J+1+I}[F']^\frac{1}{2}[F]^\frac{1}{2} (-1)^{J'+N+1+S} \]
\[ \times [J']^\frac{1}{2}[J]^\frac{1}{2} \{S\}^\frac{1}{2} \left( \begin{array}{c} F \\ J' \\ F' \end{array} \right) \{J \ S \ N\} \]  \hspace{1cm} (2.55)

\[ \langle \phi | g_{LB} B_{p=0}(\hat{L}) | \phi' \rangle = g_{LB} (-1)^{(F-m_F)} \left( \begin{array}{cc} F & F' \\ -m_F & m_F' \end{array} \right) \]
\[ \times (-1)^{F'+J+1+I}[F']^\frac{1}{2}[F]^\frac{1}{2} (-1)^{J'+N+1+S}[J']^\frac{1}{2}[J]^\frac{1}{2} \]
\[ \times (-1)^{N-\Lambda}[N']^\frac{1}{2}[N]^\frac{1}{2} \left( \begin{array}{c} F \\ J' \\ F' \end{array} \right) \{J \ N \ S\} \]
\[ \times \left( \begin{array}{cc} N & 1 \\ -\Lambda & 0 \end{array} \right) \Lambda \]  \hspace{1cm} (2.56)

\[ \langle \phi | g_{IL} B_{p=0}(\hat{I}) | \phi' \rangle = g_{IL} \delta_{J,J'} (-1)^{(F-m_F)} \left( \begin{array}{cc} F & F' \\ -m_F & m_F' \end{array} \right) \]
\[ \times (-1)^{F'+J+1+I}[F']^\frac{1}{2}[F]^\frac{1}{2} \{I\}^\frac{1}{2} \left( \begin{array}{c} F \\ I \end{array} \right) \} \{J \ F' \} \]  \hspace{1cm} (2.57)

Since both Eq. 2.56 and Eq. 2.57 barely contribute to the Zeeman shift, only
Eq. 2.55 is used in the calculation. After adding the perturbation to the effective
Hamiltonian, the Hamiltonian is diagonalized and the eigenenergies determined
as in Sec. 2.2.3. By continually changing the magnitude of the magnetic field and
repeating this procedure, the effect of the magnetic field on the ground state’s
energy level spacing is ascertained (see Fig. 2.6).
Figure 2.6.: Energy of the $m_F$ states as a function of the magnetic field for the $X^2\Sigma^+$ ground state. This is done for the three lowest rotational manifolds in the ground state: (a) $N = 0$, (b) $N = 1$ and (c) $N = 2$. 
3. Optical Setup

Whereas in Chapter 1 the basic laser cooling scheme for BaF was described, in this chapter, the setup and characterization of the optics system is detailed. Although only the main cooling laser and first repumping laser were built during the thesis, it was necessary to design the overall optics setup for the entirety of the laser cooling scheme. This allowed the overlap of the cooling lasers to be planned and helped determine how compactly the optics should be built on the table.

3.1. Overview

3.1.1. Cesium Reference Laser

The Cs reference laser was constructed first and provides a frequency reference to a transfer cavity setup located on additional optical breadboard mounted below the main optical table. The cooling lasers must be stable at MHz levels for several hours at a time and although for cold atom experiments, the lasers can be stabilized using the atom itself—through spectroscopy on a cell with the atom in gas form—BaF does not naturally exist in the gas phase. Therefore, the Cs laser is locked to a cesium transition and this frequency reference is then used to stabilize the transfer cavity. Since the laser was previously constructed by a previous bachelor’s student [58], it is denoted only by a black box (see Fig. 3.1).

3.1.2. Cooling Lasers

As per the cooling scheme laid out in Sec. 1.4.3, there are four cooling lasers: the main cooling laser, 860 nm; the first repumping laser, 896 nm; the second repumping laser, 898 nm; and the third repumping laser, 900 nm (see Fig. 3.1). All the lasers used are external cavity diode lasers which are frequency stabilized using the transfer cavity setup located underneath the main optical table. The main cooling laser’s optical setup was constructed during the thesis and is extensively detailed, as is the first repumping laser. The remaining repumping lasers have identical optical setups to the first and are therefore not described.
3. Optical Setup

Figure 3.1: The detailed optical table setup for the main cooling laser (860 nm, blue lines) and three repumping lasers (896 nm, red lines; 898 nm, orange lines; 900 nm, green lines; and overlapped repumping lasers, purple lines). Although, the Cs reference laser also resides on the same optical table, its optical setup is not shown here.
3.2. Main Cooling Laser

3.2.1. Requirements

The optical setup for the main cooling laser was designed and constructed to meet several requirements:

- **Frequency Scan** - The laser frequency must be scannable in a small range near the main cooling transition to allow for basic spectroscopy, laser stabilization and to realize appropriate detunings from the transitions—which is needed to achieve laser cooling.

- **Frequency Lock** - It is imperative to lock the laser to the main cooling frequency for experimental runs.

- **Sidebands** - All four hyperfine levels in the $N = 1$ rotational manifold of the $X^2\Sigma^+$ ground state must be addressed via frequency sidebands in conjunction with a frequency offset—which adjusts the overall sideband positions relative to the hyperfine transition frequencies.

- **Sufficient Power** - Since cooling and imaging the molecules takes significant power, which the ECDLs cannot achieve, the cooling lasers require power amplification.

A bare-bones description of the optical setup is given as follows (see Fig. 3.2). The main cooling laser’s output beam is split into a frequency locking arm and an experimental arm. Whereas the locking arm uses the Pound-Drever Hall (PDH) scheme to lock the laser frequency, the experimental arm shifts the frequency via a double-pass AOM, amplifies the beam with a tapered amplifier and finally adds the frequency sidebands with a resonant EOM.

3.2.2. External Cavity Diode Laser

An external cavity diode laser (see Fig. 3.3) was used as the master laser due to its simple construction and ability to scan and lock the laser frequency. The ECDL combines a laser diode with a diffraction grating in the Littrow configuration—where the first-order diffracted beam is reflected back into the laser diode creating an external cavity and allowing the frequency to be tuned via changes in the grating’s
Figure 3.2.: Optical setup for the 860 nm main cooling laser (blue lines) with the repumping lasers (purple lines) overlaid at the dichroic mirror before the beam enters the fiber coupling port and the experiment.
angle. The zeroth-order diffracted beam, which contains most of the power, is directed away from the ECDL and provides the seed beam for the main cooling laser.

**Figure 3.3:** (a) The self-built 860 nm external cavity diode laser (ECDL) [59]. The laser diode (SAL-0850-060 from Sacher Lasertechnik GmbH) is placed in a metal housing (11) with the collimation lens (9) likewise placed in a holder (10)—which allows the beam to be both collimated and aligned. Upon exiting the collimation lens, the beam is incident upon a diffraction grating (7) where the first-order diffracted beam is reflected back into the laser diode for frequency tuning and the zeroth-order beam is output. The diffraction grating is glued to an adjustable metal swivel (for translation in the x-y plane) which itself sits on an adjustable plate (6) for vertical translation via three adjustable screws (1). The swivel plate allows for fine adjustment of the diffraction grating both manually via the adjustable screw (2) and electronically via the piezo crystal (4). Since the frequency of the output beam is sensitive to temperature drifts, a NTC element (8) monitors the temperature and a Peltier element (5)—placed between the adjustable plate (6) and the baseplate (3)—adjusts the temperature. Finally, all of the electronics (laser diode, piezo crystal, Peltier element and NTC) connect to a ThorLabs dual laser-temperature controller via BNC connectors (13) with the laser diode connected to its BNC via a special adapter (12).

**Frequency Adjustment**

The frequency of the laser is dependent on the laser diode’s current and temperature, as well as the diffraction grating’s position. The current and the temperature are set with a ThorLabs ITC102 dual current-temperature controller which measures the temperature via a NTC element and adjusts the temperature using a Peltier element and PID$^1$. The frequency is first roughly set through a combination of current control, temperature control and grating position, after which fine adjustments are made.

$^1$Generally, when adjusting the frequency, it is easier to change the current and grating position; changing the ECDL’s temperature requires several minutes to reach thermal equilibrium and hysteresis can be a problem.
made by slightly changing the grating position with a piezo crystal\textsuperscript{2}.

Setup

The ECDL was initially built by a preceding bachelor’s student \[59\] but produced a multi-mode beam (in frequency space) with low output power. Thus, the ECDL was reconfigured to produce the correct wavelength and power as well as to run single-mode in frequency space. After optimization, the ECDL produced approximately 30-33 mW of power at the main cooling transition frequency.

Beam Shaping and Optical Isolator

Since the beam exiting the ECDL was elliptical along the horizontal axis, a prism pair was used to increase the beam’s radial symmetry. Following the prism pair, a $\lambda/2$-waveplate (HWP) was placed in conjunction with an optical isolator (ISOWAVE I-80-SD-5-L optimized for 860 nm) to prevent back reflections from disrupting the ECDL’s operation. The HWP before the isolator aligned the beam’s polarization with the polarization axis of the optical isolator to maximize the power throughput. After the optical isolator, a small telescope was placed in the beam path to slightly increase the beam size and improve beam collimation.

Beam Splitting

Following the telescope, a HWP was placed in conjunction with a polarizing beam splitting cube (PBS). The reflected light from the PBS passes into the locking path, whereas the transmitted light enters the experimental arm. The HWP preceding the PBS sets the relative percentage of light passing into each path with approximately 1 mW generally sent to the locking arm.

3.2.3. Locking Arm

Light entering the locking path passes through a glass pick-off plate which sends approximately 4\% of the light into a fiber coupling port that connects via optical fiber to the wavelength meter and is used for frequency monitoring.

\textsuperscript{2}The piezo crystal is generally used to either lock the laser frequency via a PID or to scan the frequency with the ADwin experimental control program (see Chapter 4).
Locking Sidebands

Light transmitted through the glass plate passes into an EOM which creates frequency sidebands (see Appendix D) for the PDH frequency locking scheme. The EOM is centered in the focus of a telescope and preceded by an HWP which aligns the beam polarization with the EOM’s polarization axis. The telescope setup decreases the beam diameter to pass through the EOM’s relatively small aperture and then optimizes the outgoing beam’s diameter for the fiber coupling port.

Fiber Coupling

After the EOM, the beam passes through a HWP in conjunction with a λ/4-waveplate (QWP)—which together remove any circularly polarized light from the beam—followed by a PBS to filter any s-polarized light from the beam entering the fiber coupling port. The fiber is polarization maintaining and as such, the polarization of the beam must be aligned along the fiber’s polarization axes\(^3\) using the HWP, QWP and PBS (all placed in rotation mounts).

3.2.4. Double-Pass AOM

In the experimental arm, the beam enters a double-pass AOM setup, which is used to make fine frequency adjustments and rapidly turn the beam on and off if required. A radio frequency (RF) voltage applied to the AOM’s TeO\(_2\) crystal causes Bragg diffraction thereby splitting the outgoing beam into different diffraction orders (e.g. 0th, 1st). The first-order diffracted beam experiences a frequency shift proportional to the applied RF voltage’s frequency. Since the beam passes through the AOM twice in the double-pass configuration, the total frequency shift is twice the applied frequency. The AOM (Crystal Technology’s 3200-124) utilized has a 50 MHz scan range and therefore a 100 MHz frequency range in the double-pass configuration\(^4\).

Optical Arrangement

The beam passes through a HWP and PBS which transmit all the power into the AOM setup. The AOM is centered at the focus of a telescope—which decreases the beam diameter to fit through the AOM’s aperture—with apertures placed on either

---

\(^3\)If the beam polarization is not aligned with the fiber’s polarization axis then the fiber’s output intensity is temperature dependent—which is detrimental to the locking scheme.

\(^4\)Although the double-pass AOM can be used for spectroscopy, the frequency range is small in comparison with the fine structure splitting of the ground state. In the final experiment, the AOM will be used to either match the frequency to the hyperfine structure or red-detune the frequency for Doppler cooling.
side to pick off the first-order diffracted beam\textsuperscript{5}. Following the first pass through the AOM, the beam passes through a QWP and is then retroreflected by a mirror through the setup again. Upon reentering the PBS, the beam is reflected rather than transmitted since it picks up a 90° polarization shift after passing through the QWP twice. Finally, the beam passes into the tapered amplifier setup.

### 3.2.5. Tapered Amplifier

The master cooling laser requires significant power amplification to cool and image the BaF molecules—which is done via a tapered amplifier (TA). The tapered amplifier assembly was designed by another group within the institute (see Fig. 3.4) and consists of a holder for the TA chip with an adjustable mount on the input side for a focusing lens and a similar mount for a collimation lens on the output side. Since the TA chip is both sensitive to temperature and generates substantial heat, temperature stabilization is necessary. A Peltier element and NTC element are used in conjunction with a ThorLabs temperature controller (TED200C) to keep the temperature at approximately 20°C—which both stabilizes the output power and prevents the chip from being destroyed. Finally, the TA output power is dependent on the input beam’s polarization and a HWP is placed before the TA assembly to align the input beam’s polarization along the chip’s polarization axes.

**Chip Specifications**

A tapered amplifier chip from Coherent/Dilas (TA-0850-2000, wavelength range 843-867 nm) was used which provides up to 2000 mW of output power with an output beam divergence of approximately 50° along the vertical axis and 10-12° along the horizontal axis. The chip is controlled with a ThorLabs LDC240C laser controller providing up to 4 A of input current—the maximum allowable for the chip.

**Input Alignment and Current**

As the TA chip’s input aperture is approximately 3 µm in size, a 4.5 mm lens on the TA assembly’s input side was used to focus the 2 mm input beam down and onto the TA’s aperture. Furthermore, since the TA chip gives off amplified spontaneous emission (ASE) when current is applied, the TA was initially aligned

\textsuperscript{5}The first-order diffracted beam is positionally dependent on the AOM’s driving frequency; however, passing through the AOM twice and in opposite directions eliminates any overall positional shift.
3.2. Main Cooling Laser

**Figure 3.4:** The tapered amplifier (TA) assembly used for the 860 nm laser [60] with the housing lid removed for display and the TA chip placed inside the main copper assembly. The hollow copper screws, in the copper blocks, hold the focusing/collimation lenses and allow translation relative to the TA chip in three-dimensions—via both the copper blocks’ set screws and the hollow screws’ threads. On the left side of the main copper assembly is a small hole for a NTC element which is used in conjunction with the Peltier element—located between the copper assembly and the aluminum base—to regulate the temperature of the TA chip. The far BNC provides current to the Peltier element, the middle BNC connects the NTC element to the temperature controller and the nearest BNC provides current to the TA chip.
3. Optical Setup

Figure 3.5.: Tapered amplifier (TA) output power as a function of the input current (dots). The output power exhibits exponential behavior between 500-1500 mA after which the power depends linearly on the input current. The output power matches closely with the the manufacturer’s 1 W (dotted line) and 2 W (dash-dot line) power specifications.

by collimating the ASE exiting the input aperture and then overlapping the input beam along the ASE’s beam path. The remaining alignment was completed by walking the beam. The input current to the TA also significantly affects the output power and as such the output power was measured as a function of input current (see Fig. 3.5) to characterize the TA.

Output Alignment and Collimation

The TA assembly’s collimation lens was used to collimate along the output beam’s vertical axis, as it diverges much faster than the horizontal axis. Although a 7.5 mm focal length collimation lens was initially used, a region of high intensity was seen at the edges of the vertical axis along with an interference pattern (see Fig. 3.6)—both of which were assumed due to the lens clipping the beam. Therefore, the collimation lens was replaced with a 4.5 mm lens and as expected (see Fig. 3.7) the high intensity regions at the edge of the vertical axis substantially decreased with the interference pattern likewise reduced.

Beam Shaping and Optical Isolator

The beam profile after the TA was non-Gaussian and divergent along the slow axis; thus, three lenses were used to shape the beam with a biconvex lens placed approximately 10 cm after the TA assembly followed by a cylindrical lens along
3.2. Main Cooling Laser

**Figure 3.6.** Beam profile for the 7.5 mm collimation lens at several positions following the TA assembly. At 0.0 cm high intensity regions are clearly seen at the edges of the beam’s vertical axis.

**Figure 3.7.** Beam profile for the 4.5 mm collimation lens at several positions following the TA assembly. Although clipping still occurs, the profile along the vertical axis is significantly more Gaussian and devoid of the high intensity regions at the edges (see Fig. 3.6).
the horizontal axis and a cylindrical lens along the vertical axis. Together, these produced a roughly symmetric and collimated beam. Tapered amplifier chips are extremely sensitive to back-reflections and thus a HWP and optical isolator (identical specs to the isolator after the ECDL) followed the beam shaping optical components with the HWP maximizing power through the polarization-dependent isolator\(^6\). Although roughly collimated after beam shaping, the beam still slightly diverged—which was useful since the slight increase in beam radius kept the beam from exceeding the optical isolator’s power damage threshold of 50 W/cm\(^2\).

### 3.2.6. EOM Sidebands for Hyperfine Levels

Following the optical isolator, the beam passed through a HWP in conjunction with an EOM. The EOM was used to add frequency sidebands to address all the hyperfine levels in the \(N = 1\) rotational manifold of the \(X^2\Sigma^+\) ground state. The sidebands can be described as (see Appendix D)

\[
A e^{i\omega t + i\beta \sin(\Omega t)} = AJ_0(\beta)e^{i\omega t} + AJ_1(\beta) [e^{i(\omega + \Omega)t} - e^{i(\omega - \Omega)t}] + AJ_2(\beta) [e^{i(\omega + 2\Omega)t} + e^{i(\omega - 2\Omega)t}] \tag{3.1}
\]

\[
+ AJ_3(\beta) [e^{i(\omega + 3\Omega)t} - e^{i(\omega - 3\Omega)t}] \tag{3.2}
\]

where \(A\) is the amplitude and \(\omega\) is the main frequency of the laser. \(\beta\) is the amplitude of a sinusoidal wave with frequency \(\Omega\) applied to the beam via the EOM and \(J_n\) are Bessel functions.

**Tuning Sideband Amplitudes**

The Bessel functions (see Fig. 3.8a) give the relative strengths of the sidebands and can be tuned since the RF voltage amplitude \(\beta\) is the argument of the Bessel functions. For the hyperfine EOM, \(\beta\) is tuned such that main peak disappears (see Fig. 3.8b and Fig. 3.9b) and all the power resides in the sidebands.

**Tuning Sideband Frequencies**

It can be seen from Eq. D.13 that the \(n\)th sideband has a frequency \(f_n\)

\[
f_n = \Omega n + f_{AOM} \tag{3.3}
\]

\(^6\)Although it is preferable to place the optical isolator immediately after the TA, the output beam is too large to pass through the optical isolator’s aperture before beam shaping.
Figure 3.8: (a) Absolute value of the first three Bessel functions—corresponding to the laser’s center frequency band and the first two sets of sidebands—as a function of the RF voltage amplitude \( \beta \). (b) Intensity of the sidebands as a function of the frequency and \( \beta \). The RF voltage amplitude is set to \( \beta = 2.5 \) (dotted line), which places all the laser’s power in the four sidebands addressing the hyperfine energy levels.
where again $\Omega$ is the EOM’s RF driving frequency, $n$ is the sideband and $f_{AOM}$ is the frequency offset due to the AOM. The four hyperfine levels are not evenly distributed in frequency space and thus $\Omega$ and $f_{AOM}$ are optimized with Eq. 3.3 to target the hyperfine transitions (see Fig. 3.9a). After fitting, the sidebands each roughly cover their respective Doppler broadened transitions (see Fig. 3.9b).

**Experiment**

After tuning both the RF voltage amplitude and frequency, the sidebands looked roughly like those theoretically predicted (see Fig. 3.9c).

### 3.2.7. Cooling and Imaging

After the EOM, the beam has both the requisite power and frequency composition to cool the molecules. Thus, a HWP and PBS separate the beam into an imaging arm and a cooling arm for the experiment.

**Imaging Arm**

In the imaging arm, a pickoff plate reflects roughly 4% of the beam to a spectrum analyzer cavity—via a fiber coupling port and fiber optic cable—which is used to monitor the frequency sidebands. The transmitted beam passes into an optics setup which allows only p-polarized light to enter the polarization maintaining fiber (see Sec 3.2.3) after which the light passes through to the experiment.

**Cooling Arm**

The beam in the cooling arm passes through a dichroic mirror (850 nm short-pass) which overlaps the main cooling laser with the repumping lasers. The overlapped beams pass through an optical setup which again only transmits p-polarized light (see Sec 3.2.3) after which the light enters a polarization maintaining fiber and heads towards the experiment to cool the BaF molecules.

### 3.3. Repumping Lasers

The repumping lasers follow a similar design to the main cooling laser with a few slight differences. Since all three repumping beams have the same optical design, only the first—which was built during the thesis—is described (see Fig. 3.10).
Figure 3.9: (a) The calculated hyperfine energies (dots) for the $N = 1$ rotational manifold of the $X^2\Sigma^+$ ground state (see Sec 2.2.3) as a function of the sideband ordering. The energies are fit with a first-order polynomial (solid line, see Eq. 3.3) which provides both the EOM RF frequency $\Omega$ (39.33 MHz), and the AOM’s frequency offset $f_{\text{AOM}}$ (-20.65 MHz). (b) The strength of the optimized sidebands plotted as a function of the frequency (solid line) which can been seen to overlap the Doppler broadened hyperfine energies (dash-dot line, 12 MHz FWHM, amplitude scaled to match sidebands). (c) Measured intensity as a function of frequency for the main cooling laser’s frequency sidebands created by the EOM. The actual sideband frequency profile differs from the predicted sideband profile (b) only with regards to its additional sidebands.
3. Optical Setup

Figure 3.10.: Optical setup for the first repumping laser (896 nm, red lines). The second repumper (898 nm, orange lines) and third repumper (900 nm, green line) are overlapped onto the first repumper before passing into the TA assembly. Finally, the overlapped repumping lasers (purple lines) are overlapped onto the main cooling beam (blue line) before passing into the fiber coupling port and heading to the experiment.
3.3. Repumping Lasers

3.3.1. ECDL and Beam Shaping

The first repumping laser’s ECDL contained a Toptica (LD-0910-0050-AR-1) laser diode and was taken from another group at the institute and refurbished. The grating, current and temperature were all tuned to achieve the correct transition frequency with the laser running single-mode in frequency space and outputting approximately 30 mW of power. Since the output beam was slightly divergent and extremely elliptical upon exiting the ECDL, a small telescope was used to improve the beam’s collimation and a subsequent prism pair significantly increased the beam’s radial symmetry. After shaping, the beam passed through a HWP followed by an optical isolator (ISOWAVE I-80-SD-5-L optimized for 896 nm) which was used to prevent back reflections from interfering with the ECDL’s operation. The beam was then split into a locking arm and an experimental arm via a HWP in conjunction with a PBS.

3.3.2. Locking Arm

The locking arm of the repumping laser is similar to the main cooling laser except that a bias-T is used rather than an EOM\(^7\). The bias-T integrates with the ECDL’s circuitry and allows an RF voltage to modulate the laser diode’s current—thereby creating frequency sidebands.

3.3.3. Experimental Arm

Double-Pass AOM

As with the main cooling laser, the beam passes immediately into a double-pass AOM setup upon entering the experimental arm to slightly adjust the laser’s frequency. Similar to the main cooling laser, a Crystal Technology AOM (3200-124) was used.

Overlapping Repumping Lasers

After the double-pass AOM, the beam passes through a PBS which overlaps the second repumper (898 nm) onto the first repumper (896 nm). The two overlapped beams then pass through another PBS which overlaps the third repumping laser (900 nm) onto the first two. An HWP between the two cubes allows the relative percentage of the first two repumping beams passing through the second PBS to be set (the beams have opposite polarization after being overlapped at the first PBS).

\(^7\)Bias-T circuits are substantially cheaper than EOMs.
Finally, the three overlapped repumping beams pass through another HWP-PBS combination which allows a final adjustment of each repumping beam’s relative power percentage passing into the TA setup.

**Tapered Amplifier and EOM**

The beams enter a tapered amplifier assembly similar to the one described in Sec 3.2.5. However, a chip with a different wavelength regime is used (TA-090-2000-CM for the 896-900 nm range) and the collimation lens on the output side is a 3.1 mm rather than 4.5 mm focal length lens. The beam is then shaped and passes through an HWP and ISOWAVE optical isolator to prevent back reflections. Following the optical isolator, an EOM places frequency sidebands on the beam to target the hyperfine levels.

**Cooling and Imaging**

Following the EOM, the beam is split into an imaging arm and the main experimental arm with a HWP-PBS optical setup. The imaging arm is similar to that of the main cooling laser and has both a cavity monitoring port and an imaging port. In the experimental arm, the repumping beams reflect off the dichroic mirror (see Sec 3.2.7) and are overlapped with the main cooling laser\(^8\).

### 3.4. Transfer Cavity and Locking

#### 3.4.1. Overview

The main cooling lasers and repumping lasers require a stable frequency (MHz level) for several hours at a time. Unlike atomic experiments where the frequency is locked via spectroscopy on the atomic transition itself, BaF does not naturally exist in the gas phase and as such, a transfer cavity [61] is utilized instead. The cooling lasers are sent into the transfer cavity after which their reflectance signals are used for frequency stabilization via the ubiquitous Pound-Drever-Hall (PDH) scheme (see Appendix E) [62]. Since the transfer cavity’s length—and therefore the cooling laser’s frequencies—are susceptible to thermal drift, the transfer cavity must be stabilized with a Cs reference laser. The Cs reference laser passes through a glass cell containing cesium and is then frequency locked to an atomic transition in the spectroscopic signal via the PDH scheme. The stable Cs reference laser then

\(^8\)The dichroic mirror is used instead of a PBS as the beams must have the same polarization to pass through the polarization optics preceding the cooling fiber coupling port.
passes into the transfer cavity where its reflectance signal, in conjunction with the cavity’s piezo crystal, stabilizes the cavity length via the PDH scheme.

### 3.4.2. Transfer Cavity Optical Setup

Since the transfer cavity needs to accept several lasers (Cs reference and cooling lasers), an optical setup was constructed to overlap the beams entering the cavity and separate them again upon reflection (see Fig. 3.11). A previously constructed optical setup [59] was redesigned and reconstructed to allow the Cs reference laser and first repumping laser on one polarization arm to be overlapped with the main cooling laser and second repumping laser on a second polarization arm via a PBS cube. Upon reflectance, the optical setup separates the beams into their respective components for use in the PDH locking scheme.

### 3.5. Spectrum Analyzer Cavity

A scanning Fabry-Perot cavity (ThorLabs SA200-8B) with a wavelength range of 820-1275 nm, a free spectral range of 1.5 GHz and a finesse greater than 200 was used to monitor the lasers in frequency space. The cavity has two outputs: one of which provides the cavity transmission photodiode voltage, whereas the other gives a trigger voltage corresponding to the beginning of a cavity scan. During a cavity scan, the cavity’s piezo crystal voltage is ramped—which in turn causes the length of the cavity to change and transmission peaks to register on the photodiode. Although the scan should be linear, the non-uniform transmission peak spacing seen indicates non-linear behavior in the piezo crystal. Since, the peak spacing is used in the conversion from trace samples to frequency units (see Sec 3.5.2), the non-linearity must be characterized and corrected for.

### 3.5.1. Characterizing Cavity Non-Linearity

After taking a succession of transmission and trigger traces (see Fig. 3.12), an analysis program was written which determined both the transmission peak spacing as well as the position of the peaks after the trigger. The peak spacing was taken as a function of the position and demonstrated decaying exponential behavior—fit with an exponential function (see Fig. 3.12c). In subsequent calculations, the exponential fit corrected the conversion from trace samples to frequency.
3. **Optical Setup**

**Figure 3.11.** The optical setup for stabilizing the transfer cavity and frequency locking the main cooling laser and first two repumping lasers. The Cs reference and the 896 nm laser are overlapped with a 900 nm short-pass dichroic mirror, whereas the 860 nm main cooling laser and the 898 nm second repumping laser are overlapped with a 850 nm short-pass dichroic mirror. The first set of overlapped beams are s-polarized, whereas the second set of overlapped beams are p-polarized—which allows all the beams to be overlapped with the PBS cube and then pass into the transfer cavity. A portion of the overlapped beams are reflected from the cavity and split into their respective components via the PBS and dichroic mirrors. Finally, a 50/50 cube at the beginning of each laser’s optical path reflects a portion of the reflected signal onto that laser’s photodiode, which is then used for locking.
3.5.2. Calculating Frequency Changes

The spectrum analyzer cavity was used to measure frequency changes throughout experimental measurements\(^9\) (see Chapter 5) by monitoring changes in the first transmission peak’s position—relative to the trigger—and converting these changes to frequency. However, a peak sometimes emerged or disappeared at the trigger position which adversely affected the frequency measurement. Thus, the positions of both the first and second transmission peaks were recorded so that when a new peak appeared or the first peak disappeared, the second peak’s position supplemented the first peak’s positional data.

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\(^9\)Scanning the piezo crystal in the ECDL for the absorption spectroscopy measurements did not allow for a frequency transfer function to be used.
3. Optical Setup

Figure 3.12.: (a) Transmission photodiode trace from the spectrum analyzer cavity. (b) Trigger trace corresponding to the transmission trace in (a) which was used as a reference when determining the transmission peak positions. (c) The cavity transmission peak spacing (circles) as a function of the position—calculated by taking the position between the first two peaks relative to the trigger—demonstrated decaying exponential behavior which was then fitted with an exponential function (solid line) to characterize the cavity’s non-linearity.
4. ADwin Experimental Control

An ADwin system was implemented to provide powerful and versatile control over the cold molecule experiment at a 2 Hz run rate—much faster than typical cold atom experiments. In particular, this involved setting up the ADwin hardware and other electronics, as well as programming the system with well defined control sequences for experimental runs. A MySQL database was added to the experimental control computer to provide robust dataflow capabilities and extensive Python programs were written to synchronize analog data acquisition devices with both the ADwin system and the MySQL database. In this chapter, the most important features of the ADwin system are described as they are essential to understanding the absorption spectroscopy measurements discussed in Chapter 5.

4.1. ADwin-Pro II

Although ADwin makes several electronic control units, the ADwin-Pro II was chosen as it provides the versatility needed for control of the experimental setup. The Pro II is essentially an electronics rack accepting up to 19 different modules which provide data processing capability as well as both analog and digital inputs and outputs.

4.1.1. Modules

The ADwin currently has one processing module, two analog output modules and one digital output module installed. Although no input modules are currently used, they could be easily added in the future.

- **Processor**—The most important module and the heart of the ADwin system is the PRO-CPU-T12 processor module with Dual-Core ARM Cortex-A9 CPU, 1 GHz clock rate, 1 GB memory and 1 gigabit Ethernet connection speed. This module controls the other modules in the rack and allows computer control via an Ethernet port.
4. ADwin Experimental Control

Figure 4.1.: Bottom: ADwin Pro II Unit with CPU-T12 processing module, two analog output modules and one digital output module. Top: self-built 32 channel digital output rack which connects to the digital output module on the ADwin. The rack’s channels output via BNC connectors and can be controlled either manually or with the ADwin.

- **Analog Output**—The Pro II AOut-8/16 modules each have eight analog voltage outputs via BNC connectors and offer 16 bit resolution with a voltage range of ±10 volts.

- **Digital Input/Output**—A significant portion of the electronics in the experimental setup can be controlled via a digital TTL signal. As such, the ADwin DIO-32 module which offers 32 digital channels either for input\(^1\) or output is used. The module has a 37 pin DSub connector which is connected to a custom digital output rack with 32 BNC output channels (see Fig. 4.1).

4.2. Experimental Control Program

An in-house program was previously developed by other groups in the institute to provide a GUI interface for the ADwin and make programming experimental sequences more intuitive. In this section, a basic description of the program’s functionality and execution is given.

4.2.1. ADBasic

The ADwin is programmed with the ADbasic programming language (unique to the ADwin products yet modeled after BASIC). However, the experimental control

\(^1\)The module is currently only used for digital output in the experimental setup.
4.2. Experimental Control Program

Figure 4.2.: Main window of the experimental control program. Browsing “Primary Model” allows a previously saved experimental control sequence to be loaded, whereas the save button allows the current experimental control sequence to be saved. The profile menu must be utilized when first setting up the program.

program provides a shell over ADbasic which allows the user to forgo ADbasic programming and use only the GUI interface.

4.2.2. Experimental Control Windows

Upon opening the experimental control program a large number of windows pop open. Several of these windows are integral to the program, whereas others are somewhat superfluous and only needed for diagnostics. In this section, a description is given of the windows used to program experimental control sequences.

• **Main**—At the main window (see Fig. 4.2) the user can either begin programming a new experimental run called a “session” or import a previous session. Additionally, the Profile menu button can be used to open a dialog allowing the user to provide the hardware and MySQL database settings.

• **Card**—Defining a profile with the ADwin Pro-II’s analog and digital hardware cards will create a window corresponding to each card. These windows have the option to set both the analog voltages/digital TTL signals and their timing either manually or with experimental variables.

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MySQL database used to save the experimental run’s parameters.
4. ADwin Experimental Control

Figure 4.3.: The variables window of the experimental control program. The left column holds static variables, the center column holds variables that iterate throughout the run and the right column holds dynamic variables—which are defined by the equations below each variable.

- **Variables**: The variables window (see Fig. 4.3) allows the different types of experimental control variables to be set including: static variables, iterators (which increment every cycle), and dynamic variables (equations). An experimental sequence is programmed by setting voltages and voltage timing with these variables. The program saves these variables to a MySQL database every cycle.

4.2.3. Experimental Control Execution

When starting an experimental run (see program flow chart in Fig. 4.4), the experimental control program first sets the experimental variables, saves the variables to the MySQL database and then starts an inter-cycle Python script which can be used to control experimental equipment and/or acquire data. Finally, the experimental control program executes the experimental sequence defined in the card windows.

4.3. SQL Database

The experiment utilizes a MySQL database to save the experimental control program variables and experimental data for several reasons. First, almost any programming language can be used to read or write to the database\(^3\). Second, the database allows multiple calls to be made simultaneously, so that data may be taken on the experiment by one user, while another user reads previous experimental run

---

\(^3\)The experimental control program written in C# saves the experimental run variables to the SQL database, after which they are read out in a data analysis language such as Python.
4.3. SQL Database

Figure 4.4.: Left-side: Programmatic flow chart for the experimental control program. The program first sets all the experimental control variables and then saves them to the MySQL database. Next, the inter-cycle Python script is executed—which runs concurrently with the experimental control program. After executing the experimental control sequence the program’s counter increments and the loop restarts (the loop executes *ad infinitum* and must be manually stopped by the user). Right-side: Programmatic flowchart for the inter-cycle Python script. First, the script gets the most recent experimental control variables saved to the MySQL database—which is used as an intermediary since the script cannot directly communicate with the experimental control program. If it’s the first cycle of the experimental control sequence, then the script spawns data acquisition and data visualization subprocess scripts which run contemporaneously with the experimental control program. Next, the script updates hardware devices controlled via serial connection and finally acquires and saves basic data to the readout column of the *cycledata* table in the MySQL database.
data. Finally, the database allows read/write permissions to be implemented for protection of data and control of dataflow.

The MySQL database resides on the same computer as the experimental control so that broader network connectivity problems do not affect the data acquisition. The open source MariaDB database software is utilized with the HeidSQL program as an interface.

### 4.3.1. HeidSQL

HeidSQL (Fig. 4.5) allows easy access and manipulation of the MariaDB database and is particularly useful for setting user permissions and defining data tables for the storage of experimental data.

#### User Permissions

Setting read/write permissions for users is an important database tool. HeidSQL allows user profiles to be created with database access restricted based on both the user and location (i.e. IP address). Two user profiles were created for the experimental database:

- **Experimental Control User**-The first user has global permissions—both reading and writing—but can only access the database from the experimental control computer. This user requires global permissions so that the experimental control and data acquisition programs can both save experimental data and read it during experimental runs.

- **Data Analysis User**-The second user can access the database from any IP address (with the correct username and password). However, the user can
only read from the database so that during data analysis, the unsuspecting graduate student cannot accidentally overwrite experimental data\textsuperscript{4}.

Thus, through user permissions, a robust dataflow architecture ensues in which the experimental control computer saves data to the database with global permissions and all other computers are restricted to reading out the data with the the data analysis user.

**Experimental Control Table**

The experimental control program accesses a single table in the database called `cycledata`. For correct integration with the experimental control program, the `cycledata` table must contain specific data columns and data column formats. Each time the experimental control program cycles, a new data row is saved in the table. A brief description of the table’s data columns relevant to data acquisition are given below

- **globalCounter**- Gives the overall position within the SQL database which is useful for labeling data. The experimental control program increments this integer every cycle by one.

- **iterationOfScan**- Integer providing the number of cycles that have been completed within the experimental run. As will be seen in Section 4.4, this is queried by Python scripts to determine the current position within the experimental run.

- **variables**- The experimental control program encodes and stores all the user-defined variables in this LONGTEXT variable (large string) every cycle. The variables must therefore be decoded when read.

- **readout**- A LONGTEXT variable unused by the experimental control program and thus used by the Python programs to store simple data (such as the temperature in the lab). The data is encoded and decoded in the same manner as the **variables** column.

\textsuperscript{4}Even on the experimental control computer, data analysis programs always use the second user profile so that data cannot be corrupted.
4.4. Python Scripts

The experimental control program runs a Python script between every cycle. This is used to interface with more complex experimental devices and to handle all the experimental data acquisition (DAQ).

4.4.1. Inter-Cycle Python Script

Upon executing, the inter-cycle python script (see Fig. 4.4) reads the current experimental control variables from the last line of the MySQL database. The program then checks the iterationOfScan variable to determine whether it is the first cycle in the run and if so spawns subprocesses (separate Python scripts) for complex data acquisition and data visualization. Following this, the script updates hardware devices and then acquires and saves basic data to the MySQL database.

Hardware Control

Certain experimental devices require a serial or similar connection which must handled by the inter-cycle Python script since the ADwin can only send triggers and voltages\(^5\). Since the Python script reads the experimental control variables from the MySQL database, the experimental control variables are used by the Python script to set hardware devices\(^6\).

4.4.2. Data Acquisition and Visualization

The data acquisition is handled solely by Python scripts with data broadly categorized into basic and complex data types—each requiring different schemes to both save and label the data.

Basic Data

Basic data is relatively small in size and generally acquired and recorded only once per experimental cycle (such as a magnetic field measurement or temperature measurement) with the inter-cycle Python script. Since the data size is relatively small, it is stored in the MySQL database’s readout column which provides an

\(^5\)Although currently the hardware updates in the inter-cycle Python script, separate scripts could be spawned off as subprocesses and solely dedicated to hardware control should update timing become an issue (e.g. many devices need to be set).

\(^6\)Defining variables via the experimental control program rather than in the Python script creates a more robust system since the experimental control parameters can all be set in one location.
immediate relation between acquired data and its corresponding experimental control variables\textsuperscript{7}.

**Complex Data**

Complex data is defined as a larger dataset which cannot be efficiently stored in the MySQL database and is thus saved to the computer’s file storage system. Examples of this type of data include oscilloscope traces or images. The complex data’s relation to its experimental control parameters (a certain row in the MySQL database) is not implicitly known and must be therefore explicitly defined. For a data text file this is done by placing a header with the current globalCnt value. For complex data acquisition, the inter-cycle Python script starts data acquisition (DAQ) subprocesses (independent Python scripts) on the first cycle in an experimental run. This allows data to be saved simultaneously from multiple devices as each DAQ Python script acquires data from only one device. The segmentation further prevents errors in one data acquisition process/device from affecting the others. Lastly, the DAQ scripts connect to their respective devices only once and maintain the connection for the entirety of an experimental run.

**Data Visualization**

Although real-time visualization of data is not strictly necessary, it is often useful in helping diagnose experimental problems as they occur. Visualization subprocesses (separate Python scripts) are started by the inter-cycle Python script at the beginning of an experimental run and execute Python GUIs displaying the current data. Separating the data visualization scripts from the DAQ scripts prevents GUI errors from affecting data acquisition\textsuperscript{8}. The data visualization script monitors the directory where the data is stored so that any newly saved data can be displayed.

\textsuperscript{7}Basic data should always be stored in the database since storing data in separate text files involves significantly more programming and increases the potential for errors.

\textsuperscript{8}The simplest way to display data would be to include the GUI code with the DAQ script. However, the GUIs are prone to errors and the integrity of the data could be compromised.
5. Absorption Spectroscopy Measurements

As a test of the energy level calculations done in Chapter 1 as well as the optic setup described in Chapter 3, absorption spectroscopy was undertaken using the main cooling laser—which allowed the fine structure of the main cooling transition to be resolved.

5.1. Absorption Spectroscopy Theory

The intensity of light \( I(\omega, z) \) with frequency \( \omega \) passing a distance \( z \) through a cloud of molecules (see Fig. 5.1) is described with Beer’s law as

\[
I(\omega, z) = I_0 e^{-A(\omega, z)}
\]

where \( I_0 \) is the peak intensity and \( A(\omega, z) \) is the absorption given as

\[
A(\omega, z) = n\sigma(\omega)z
\]

with \( n \), the density of molecules per unit volume and \( \sigma(\omega) \) the frequency-dependent optical cross-section. Furthermore, the absorption has a frequency dependence due to Doppler broadening.

Doppler Broadening

At finite temperatures, the molecule velocities are Maxwell-Boltzmann distributed which causes the transition frequencies for the molecules to be Doppler shifted. This yields a Gaussian-like broadening of the absorption with a temperature dependent standard deviation of [38]

\[
\sigma_f = \sqrt{\frac{k_BT}{mc^2}\omega_0}
\]

where \( m \) is the mass of BaF, \( c \) is the speed of light, \( \omega_0 \) is the transition frequency, \( T \) is the temperature and \( k_B \) is the Boltzmann factor.
5. Absorption Spectroscopy Measurements

![Absorption Spectroscopy Diagram]

**Figure 5.1.**: Incident light is attenuated according to Beer’s law Eq. 5.1 after passing through an molecular cloud with thickness \( z \), density \( n \) and area \( A \) [38]. Additionally, each molecule has an optical cross-section of \( \sigma \) and thus the overall absorption due to the molecules is given by Eq. 5.2.

### Resonant Optical Cross-Section

Determining the resonant cross-section, \( \sigma(\omega_0) = \sigma_0 \), enables the number of molecules to be extracted from the absorption measurements and is given by [54]

\[
\sigma_0 = \frac{W_{eg}}{\Phi}
\]  

(5.4)

where \( W_{eg} \) is the transition rate between the excited and ground state and \( \Phi \) is the incident photon flux. The photon flux changes with wavelength, whereas the angular momentum of the excited and ground states effects the transition rate. Although the derivation is neglected, the optical cross section for the \( X^2\Sigma^+ J = 1/2 \) to \( A^2\Pi_{1/2} \) transition is given as

\[
\sigma_{0,1/2} = \frac{\lambda^3}{2(2\pi)^2} \sqrt{\frac{m}{8k_B T}} \frac{q_{00}}{\log 2} \frac{1}{\tau}
\]  

(5.5)

where \( \lambda \) is the transition wavelength, \( m \) the mass, \( k_B \) the Boltzmann factor, \( \tau \) the decay time and \( q_{00} \) the Franck-Condon factor for the \( 0 \rightarrow 0 \) decay. The transition from \( X^2\Sigma^+ J = 3/2 \) to \( A^2\Pi_{1/2} \) is

\[
\sigma_{0,3/2} = \frac{2J + 3}{2J + 1} \frac{J + 2}{2J + 1} \sigma_{0,1/2}
\]  

(5.6)

with \( J = 1/2 \) for the transition.
5.2. Experimental Setup

The creation of molecules in the cryostat was discussed previously (see Sec 1.5.1) and provides the basis for the absorption spectroscopy setup. Once the molecular plume is created with the ablation laser, a probe laser passes through the cloud to measure the frequency dependent absorption. The probe laser frequency is continually scanned and simultaneously recorded on the spectrum analyzer cavity (see Sec. 3.5).

5.2.1. Optical Setup

The probe laser enters the optical setup (see Fig. 5.2) through a fiber coupling port and is split with a HWP-PBS combo that transmits approximately 125 µW of the light (far below the saturation intensity) towards the cryostat—with the remaining power reflected onto a power meter to monitor intensity fluctuations. The beam transmitted through the PBS is then further transmitted through a dichroic mirror and into the cryostat. After passing through the cryostat and the molecular cloud therein, the probe beam is incident on the absorption photodiode.

5.3. Experimental Control and Data Acquisition

The experimental control and data acquisition setup detailed in Chapter 4 was essential for taking absorption spectroscopy measurements. The experimental control program scanned the probe laser frequency by ramping the analog voltage on the ECDL’s piezo crystal and simultaneously sending synchronized triggers to fire the ablation laser and record data. The electronics controlled by the experimental control program are described as follows:

- **Piezo Voltage**-the frequency was incremented by changing the ECDL’s diffraction grating angle via the piezo crystal. This was accomplished by incrementing the piezo crystal’s voltage in discrete steps with the ADwin’s analog voltage output module.

- **Ablation Laser Trigger**-the experimental control program sent triggers from the ADwin’s digital output module to fire the ablation laser. Although the ablation laser can run in stand-alone mode, the trigger mode allowed the experimental control program to synchronize the ablation shots with the data acquisition devices.
5. Absorption Spectroscopy Measurements

**Figure 5.2.** Optical setup for absorption spectroscopy with the 860 nm imaging/probe beam entering the setup via the fiber coupling port and then passing into a half-wave plate (HWP) and polarizing beam splitting cube (PBS). The PBS reflects light towards the power meter to be monitored for intensity fluctuations, whereas the light transmitted through the PBS passes through a subsequent dichroic mirror and into the cryostat. After passing through the molecular plume and exiting the cryostat, the beam is focused onto a ThorLabs PDA 10A-EC photodiode with a bandpass filter attached to remove any remaining 1064 nm light from the ablation laser. In addition to the probe beam, the ablation laser is aligned through the cell and onto the target with the dichroic mirror; however, the ablation laser and the probe beam are not perfectly overlapped (see Fig. 5.3). Although the ablation laser should be completely incident on the target, a dichroic mirror is set after the cryostat to dump any of the ablation laser’s remaining beam power onto a beam block.
5.3. Experimental Control and Data Acquisition

Figure 5.3.: Side view of the in-cell absorption spectroscopy setup. The ablation laser is incident on the target and creates a plume of molecules. The probe laser passes slightly above the target and through the molecular plume after which it exits the cryostat and is incident on the photodiode—thus registering the absorption due to the molecular plume.

- **Red Pitaya Triggers**: Triggers were sent to the Red Pitayas—essentially FPGA based oscilloscopes—which caused them to acquire data simultaneously with the ablation shots.

5.3.1. Data Acquisition

Data acquisition was handled with three different devices: two Red Pitayas which recorded oscilloscope traces and a CryoCon controller which monitored analog temperature sensors (see Fig. 5.4). The oscilloscope traces were large datasets (see Sec 4.4.2) saved to the file management system rather than the MySQL database.

- **Frequency Monitor**: The first Red Pitaya recorded both the spectrum analyzer cavity’s photodiode transmission trace and trigger trace—which were used to calculate the relative frequency change (see Sec 3.5.2).

- **Probe Laser Monitor**: The second Red Pitaya recorded the probe laser’s intensity on the absorption photodiode and simultaneously monitored the probe laser’s intensity fluctuations via the power meter.
5. Absorption Spectroscopy Measurements

Figure 5.4: Data acquisition in the absorption spectroscopy setup with orange wires representing raw dataflow (analog voltages) and blue wires representing digitized dataflow. Two Red Pitayas and one CryoCon controller monitored a total of six different data streams and relayed the information to the main control computer. The first Red Pitaya monitored both the transmission photodiode and the trigger signal on the spectrum analyzer cavity, whereas the second Red Pitaya monitored the absorption photodiode and power meter (see Fig. 5.2). Finally, the CryoCon unit monitored two temperature sensors in the cryostat: one on the baseplate and the other on the cell.

- Temperature Monitor - the CryoCon controller monitored two temperature sensors placed in the cryostat and saved the temperature data once per cycle to the MySQL database.

5.4. Data Analysis

5.4.1. Absorption

Although the probe laser’s intensity $I(t)$ is recorded, the absorption’s dependence on intensity can be solved for via Beer’s law Eq. 5.1 as

$$A(\omega, t) = n(t)\sigma(\omega)z(t) = -\log \left[\frac{I(t)}{I_0}\right] \quad (5.7)$$

where the maximum intensity $I_0$ is calculated by averaging the intensity before a shot is taken (since the density $n = 0$) via

$$I_0 = \frac{1}{T_s} \int_0^{T_s} I(t)dt \quad (5.8)$$

with $T_s$ representing the timing of the ablation shot. During an absorption trace measurement, the frequency is constant and the large absorption spike (see Fig. 5.5b).
5.5. Comparison with Theory

is due to the creation of the molecular plume—which significantly increases both the molecular density $n$ and the distance $z$ the laser passes through the cloud. Integrating the absorption with respect to time yields

$$A_{\text{tot}}(\omega) = \int_{T_s}^{T_f} A(t) dt = \sigma(\omega) \int_{T_s}^{T_f} n(t) z(t) dt = \sigma(\omega) c$$ (5.9)

where $T_f$ is the end of the trace and $c$ is

$$c = \int_{T_s}^{T_f} n(t) z(t) dt$$ (5.10)

Since the molecular plume size and density $[z(t) \text{ and } n(t)]$ are assumed roughly the same for every shot, $c$ is a constant throughout an experimental run and $A_{\text{tot}}(\omega)$ depends only on frequency.

5.4.2. Spectroscopic Analysis

After measuring $A_{\text{tot}}$ and the frequency throughout the experimental run, the total absorption is given as a function of the frequency (see Fig. 5.6) with two peaks—which correspond to the two fine structure levels $J = 1/2$ and $J = 3/2$ in the $N = 1$ rotational manifold of the $X^2\Sigma^+$ ground state—clearly seen. Spectroscopy scans with a larger frequency range were taken previously [49] and revealed several transitions in line with previous literature values. These scans thus allowed the transition probed here to be identified with certainty as the main cooling transition. The $J = 3/2$ peak in the absorption data is wider than the $J = 1/2$ peak since the difference between their respective hyperfine levels is 34 MHz and 27 MHz respectively (see Fig. 2.3). After fitting the spectroscopic data with two Gaussians, the frequency difference between the two peaks is given as $133.6 \pm 3.8$ MHz.

5.5. Comparison with Theory

In Chapter 2, the energies of the hyperfine levels, as well as the branching ratios from the excited state to the hyperfine levels of the $X^2\Sigma^+$ ground state, were calculated. The excitation branching ratios for the transition from the $X^2\Sigma^+$ state to the $A^2\Pi_{1/2}$ positive parity state are identical to the decay branching ratios previously calculated (see Sec 2.4 and Table 2.6) due to symmetries in the Wigner symbols. If we consider that the transition is driven with linearly polarized light (masking a portion of the possible excitations), then these branching ratios can be used to roughly model Doppler broadened spectroscopic data (see Fig. 2.5). These
5. Absorption Spectroscopy Measurements

Figure 5.5: (a) Probe laser intensity as a function of time (solid line). The trace shows a sharp intensity dip directly after the ablation shot (approximately 2.5 ms) corresponding to the molecular plume’s creation. As the molecules begin to either exit the cell or stick to the walls, the intensity increases again. In order to transform the data into an absorption signal, the intensity before the ablation shot is used to calculate the peak intensity $I_0$. (b) Absorption as a function of time (solid line). To calculate the overall absorption $A_{tot}$, the absorption signal is integrated from the truncation point (dotted line) to the end of the trace.
5.5. Comparison with Theory

**Figure 5.6.:** Absorption as a function of frequency for the main cooling transition. The absorption data (dots) shows two peaks corresponding to the fine structure states $J = 1/2$ (dashed line) and $J = 3/2$ (dash-dot line) in the $N = 1$ rotational manifold of the $X^2Σ^+$ ground state. The peaks are fitted with two Gaussians which allows the peak separation to be calculated as $133.6 \pm 3.8$ MHz. Each point is the average of eight absorption traces with the error bars denoting the standard deviation.

Calculations are now extended using Eq. 5.3 to give the temperature dependent Doppler broadening in the experimental temperature regime 0-10 K (Fig. 5.7a). The calculations show that above 2 K the hyperfine structure of the ground state cannot be resolved, in accord with the experimental data, but rather the hyperfine levels are superimposed to form one larger peak for each fine structure level (see Fig. 5.7b). In particular, for the temperature at which the experimental data was taken, 5.07 K, the superimposed fine structure peaks (see Fig. 5.7c) are fitted with two Gaussians which results in a theoretical peak separation of 131.95 MHz. This matches closely with the experimental separation of the peaks and is within error bounds.

However, the theoretical peaks show significantly different amplitudes, whereas the experimental peak amplitudes are similar. To account for this discrepancy, additional effects must be considered. Overall, the probe beam addresses twelve ground state levels. Due to the branching ratios and selection rules for the fluorescence decay, some of these states contribute to the absorption signal with more than one absorbed photon, while others are dark states for the given polarization. In addition, we expect the buffer gas collisions that thermalize the BaF molecules to also mix different ground state levels. Therefore, the following simple rate equations are used [40].
5. Absorption Spectroscopy Measurements

Figure 5.7: (a) Standard deviation of the Doppler broadening as a function of temperature (see Eq. 5.3) for the experimental temperature regime. (b) Transition strength as a function of temperature and frequency. As the temperature increases, the Doppler broadening causes the four hyperfine levels to merge into two fine structure levels with the data corresponding to (c) shown with a dotted line. Although the absorption lines are in actuality a convolution of a Doppler broadened Gaussian and a power broadened Lorentzian (yielding a Voigt profile), the Doppler broadening generally dominates and the power broadening is thus neglected. (c) The transition strength as a function of frequency for 5.07 K. As aforementioned, Doppler broadening obscures the hyperfine structure and results in two fine structure peaks. These were fitted with two Gaussians yielding an overall separation of 131.95 MHz.
5.6. Absorption Temperature Effects

\[
\frac{dn_i}{dt} = \sum_j \Gamma_{ij} n_j - \sum_j R_{ij} (n_i - n_j) - \sum_{k \neq i} M_{ik} (n_i - n_k) \quad (5.11)
\]

and

\[
\frac{dn_j}{dt} = -\sum_i \Gamma_{ij} n_j + \sum_i R_{ij} (n_i - n_j) \quad (5.12)
\]

where \( n_i \) is the population in the \( i \)th ground state, \( n_j \) is the population in the \( j \)th excited state, \( \Gamma_{ij} \) is the decay rate from the \( j \)th excited state to the \( i \)th ground state, \( R_{ij} \) is the excitation rate and \( M_{ik} \) is the mixing rate between the different ground state levels. The decay and excitation coefficients \( \Gamma_{ij} \) and \( R_{ij} \) are both based on the dipole transition branching ratios (see Sec 2.4), whereas the term \( M_{ik} \) represents an empiric mixing rate of unit probability between the different ground state levels. Our group has performed preliminary calculations using Eq. 5.11 and Eq. 5.12 which show that the contribution of the \( J = 3/2 \) peak to the absorption signal grows in strength relative to the \( J = 1/2 \) peak—in good accord with the experimental data. Additionally, the Doppler-broadened peaks effectively move apart since within the \( J = 1/2 \) fine structure state the \( F = 1 \) state grows in strength relative to the \( F = 0 \) state (see Fig. 5.8). Fitting two Gaussians to the theoretical data—which now includes the rate equations—results in a splitting of 135.55 MHz which is within the error bounds of the experimental data. Furthermore, the theoretical peak heights now closely match those seen from the experimental data.

5.6. Absorption Temperature Effects

The absorption is directly affected by population of molecules in the \( N = 1 \) rotational manifold of the \( X^2\Sigma^+ \) ground state. The relative population \( P(N) \) of molecules in each rotational manifold \( N \) is Maxwell-Boltzmann distributed (see Fig. 5.9a) and given explicitly by a modified equation from David Rahmlow’s thesis [54] (Eq. 4.22)

\[
P(N) = \frac{2(2J_N + 1)e^{-\frac{E_N}{k_B T}}}{\sum_{m=0}^{\infty} 2(2J_N + 1)e^{-\frac{E_m}{k_B T}}} \quad (5.13)
\]

where \( J_N \) represents the total angular momentum of the state, \( E_N \) is the rotational energy of the state, \( k_B \) is the Boltzmann factor and \( T \) is the rotational temperature\(^1\). This equation is used to calculate the relative population of the \( N = 1 \) rotational level.

\(^1\)\(2(2J_N + 1)\) is the multiplicity or the total number of \( m_f \) states in the given rotational level.
5. Absorption Spectroscopy Measurements

![Absorption Spectroscopy Graph](image)

**Figure 5.8.** Absorption as a function of frequency for the main cooling transition. The theoretical absorption is based on the rate equation model and fitted with two Gaussians which results in a peak separation of $135.55 \text{ MHz}$. The experimental absorption (dots) has been additionally corrected (pentagons) for target molecule depletion (see Appendix F) which results in excellent agreement between the experimental and theoretical peak splittings and peak amplitudes. Error bars are omitted from the experimental data points for clarity.

The charcoal aperture absorbs helium throughout run which provides insulation for the cell. However, once the charcoal becomes saturated, the unabsorbed helium increases the pressure in the cryostat and causes heating. This in turn heats the charcoal which causes it to release previously absorbed helium in a runaway process. Once all the helium is released from the charcoal, the turbofans remove the helium (on much slower timescales) reducing the pressure and thus the temperature in the cell. The charcoal then begins to absorb helium again restarting cycle.

5.6.1. Experimental Data

Although the temperature varied little for the data in Fig. 5.6 (maximum variation of $0.023 \text{ K}$), a subsequent run displayed significant temperature variation in which the temperature spiked from a baseline of approximately $6.5 \text{ K}$ to $9 \text{ K}$ twice\(^2\) (see Fig. 5.10a). This allowed the relation between absorption and temperature to be tested with the absorption showing a substantial decrease (see Fig. 5.10b) corresponding to these two temperature spikes. A double Gaussian was fit to the absorption data and subsequently subtracted from the data to remove the frequency dependence (see Fig. 5.10c). The theoretical calculation of the tem-

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\(^2\)The charcoal aperture absorbs helium throughout run which provides insulation for the cell. However, once the charcoal becomes saturated, the unabsorbed helium increases the pressure in the cryostat and causes heating. This in turn heats the charcoal which causes it to release previously absorbed helium in a runaway process. Once all the helium is released from the charcoal, the turbofans remove the helium (on much slower timescales) reducing the pressure and thus the temperature in the cell. The charcoal then begins to absorb helium again restarting cycle.
5.6. Absorption Temperature Effects

**Figure 5.9**: (a) Relative molecule population as a function of the $N$ rotational manifold in the $X^2\Sigma^+$ ground state for 4 K (circles), 10 K (diamonds) and 77 K (triangles). (b) Relative population for the $N = 1$ rotational manifold as a function of temperature.
per temperature dependent absorption is similar to that of the experimental data (see Fig. 5.10d). However, although the shape of the absorption loss is comparable, the maximum percentage decay from the theoretical calculation (about 30%) is less than the experimental value of 40% absorption decay. Additionally, when looking at the theoretical data in the baseline regime alone, it displays an almost Gaussian behavior which overlaps significantly with the transition Gaussian peaks. Thus, the lack of this somewhat Gaussian behavior in the experimental baseline data in (c) is most likely due to the Gaussian fit subtracted from the data accounting for both frequency and baseline temperature variations.

5.7. Molecule Number

The approximate number of molecules in the cell can be extracted from the absorption traces. Since the molecular cloud expands quickly after ablation, the absorption increases quickly as well. However, when the molecular plume reaches the furthest extents of the cell, molecules begin to either stick to the cell walls or exit through the aperture. Therefore, the point of maximum absorption $A_{\text{max}}$ is assumed to occur when the cell is completely and uniformly filled with molecules. Using Eq. 5.2 we find that

$$\frac{A_{\text{max}}(\omega)}{\sigma(\omega)z} = n. \quad (5.14)$$

Expressing the density as a ratio of the number of molecules divided by the cell volume $n = \mathcal{N}/V$ and only using the resonant frequency $\omega_0$ gives

$$\frac{A_{\text{max}}(\omega_0)}{\sigma_0z} = \frac{\mathcal{N}}{V} \quad (5.15)$$

with which we can solve for $\mathcal{N}$

$$\mathcal{N} = \frac{A_{\text{max}}(\omega_0)a}{\sigma_0} \quad (5.16)$$

where $V = az$ with $a$ the area in the cell perpendicular to the laser’s axis of propagation. However, the maximum absorption cross-section $\sigma_0$ is dependent on the fine structure state (as described in Sec 5.1). Thus, the number of molecules in each $N = 1$ fine structure state is calculated separately using Eq. 5.16 and then added together to give the total number of molecules in the $N = 1$ rotational manifold. Finally, this value can be used to calculated the total number of molecules (i.e. occupying all the rotational manifolds). The molecule number in the $N = 1$ rotational manifold is divided by its Boltzmann distributed relative population (see
Figure 5.10: (a) Temperature as a function of frequency for the experimental run in which the temperature was unstable and spiked. (b) The absorption as a function of frequency for the experimental run in (a) which shows absorption dips [data between the start clip (dashed lines) and end clip (dash-dot lines) lines] corresponding to the temperature spikes in (a). (c) The absorption data in (b)—excluding that between the start and end clips— is fit with two Gaussians (solid line) which are subsequently subtracted from the data to give the absorption devoid of frequency dependence. As expected, the absorption precipitously declines during the temperature spikes. (d) Theoretical absorption loss as a function of frequency for the temperatures in the experimental run with the relative populations of the $N = 1$ rotational manifold calculated using Eq. 5.13. The theoretical calculation shows a similar form to the experimental data in (c).
Sec 5.6), which gives the total number of molecules resulting from the ablation process—approximately $1.1 \times 10^{11}$ molecules.
6. Summary and Outlook

6.1. Summary

Significant progress was made towards laser cooling barium monofluoride molecules. In particular, extensive theoretical calculations were carried out which informed the laser cooling scheme and optical layout. The ground state’s effective Hamiltonian was solved to give the hyperfine energies and their eigenfunctions which were subsequently used in the calculation of the dipole transition branching ratios from the Λ2Π1/2 excited state to the Χ2Σ+ ground state. The optical setup for the entire cooling scheme was designed and a significant portion—the main cooling laser and the first repumping laser—constructed which involved several optical systems such as double-pass AOMs and tapered amplifiers. In addition to the optical setup, an ADwin experimental control system was implemented to control the entirety of the experiment. This consisted of integrating custom hardware with the control program and programming the system to handle the various electronics during experimental runs. Using both the optics setup and the experimental control system, absorption spectroscopy measurements were carried out on the main cooling transition of BaF which allowed the fine structure of the ground state to be resolved. Furthermore, the calculated hyperfine energies and dipole transition branching ratios were used to calculate a theoretical fine structure splitting for the ground state which was in good accord with the experimental results. All told the optics and experimental control systems developed are well positioned to laser cool BaF molecules in the near future.

6.2. Outlook

The next experimental goal is to detect optical cycling via fluorescence. This is done by intersecting the molecular beam with the cooling lasers and measuring the spontaneously emitted photons with a photodiode placed above (see Fig. 6.1). Although initial fluorescence was detected with a single cooling laser (see Fig. 6.2), the signal was low with about only about one photon emitted per molecule. However, simple rate equations calculations [63] similar to Eq. 5.11 and Eq. 5.12 have
6. Summary and Outlook

**Figure 6.1.** Experimental setup to detect fluorescence. The ablation laser creates molecules within the cell which are subsequently formed into a molecular beam by the charcoal aperture. Upon entering the cross, the molecular beam is intersected with the cooling lasers which causes fluorescence detected via the photodiode above.

**Figure 6.2.** The photodiode voltage as a function of time with fluorescence seen around 1 ms.

shown that applying sidebands to the main cooling laser and remixing dark $m_F$ states should appreciably increase the number of photons detected per molecule to approximately twenty—with a further rise in photon number expected upon the addition of the first repumping laser. Once optical cycling is detected, a deflection setup will be installed to cycle the main cooling laser and the first repumping laser through the molecular beam multiple times from the same direction. Successful deflection of the beam via the optical scattering force will be subsequently followed by transverse cooling of the molecular beam.
A. Python Wigner 9j Code

The Wigner 9j code in the Sympy Python package did not work correctly and therefore a custom Python Wigner 9j function (see Code A.1) was implemented.

Listing A.1: Python Wigner 9j code implemented in ground state Hamiltonian calculations.

```python
import numpy as np
from sympy.physics.wigner import wigner_3j, wigner_6j

def ninej(j1, j2, j3, j4, j5, j6, j7, j8, j9):
    kmin=np.amax(np.array([abs(j1-j9), abs(j4-j8), abs(j2-j6)]))
    kmax=np.amin(np.array([abs(j1+j9), abs(j4+j8), abs(j2+j6)]))
    klength=int(kmax-kmin)
    sumv=0
    for i in range(0, klength+1):
        k=kmin+i
        w1=wigner_6j(j1, j4, j7, j8, j9, k)
        w2=wigner_6j(j2, j5, j8, j4, k, j6)
        w3=wigner_6j(j3, j6, j9, k, j1, j2)
        sumv+=(-1)**(2*k)*(2*k+1)*w1*w2*w3
    return sumv
```

---
B. Decoupling of Effective Hamiltonian Rotational Levels

After examining the expanded effective Hamiltonian (Equations 2.20-2.24) it can be seen that a Kronecker Delta term $\delta_{N'N}$ exists in every term such that no coupling occurs between rotational manifolds. This allows the eigenenergies and eigenstates of the different rotational manifolds to be calculated separately as follows: consider two rotational manifolds $N = a$ and $N = b$ each with two sublevels—that is $a$ has states $a_1$ and $a_2$ whereas $b$ has states $b_1$ and $b_2$. The Hamiltonian matrix $c$ will have the following form

$$c_M = \begin{pmatrix} a_{11} & a_{12} & 0 & 0 \\ a_{21} & a_{22} & 0 & 0 \\ 0 & 0 & b_{11} & b_{12} \\ 0 & 0 & b_{21} & b_{22} \end{pmatrix} = \begin{pmatrix} a_M & 0 \\ 0 & b_M \end{pmatrix}$$ (B.1)

where $a_{nm}$ is given by

$$a_{nm} = \langle a_n | H_{eff} | a_m \rangle$$ (B.2)

and $a_M$ is

$$a_M = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}$$ (B.3)

with $b_{nm}$ and $b_M$ holding similar forms to $a_{nm}$ and $a_M$ respectively. The eigenvalues are found by taking the determinant of the Hamiltonian matrix and subsequently setting it equal to zero. However, since there are no terms between rotational manifolds $a$ and $b$ in the matrix, the determinant of the matrix is decoupled, that is

$$\text{Det}(c_M) = \text{Det}(a_M)\text{Det}(b_M) = 0$$ (B.4)

so that there are two cases

$$\text{Det}(a_M) = 0$$
$$\text{Det}(b_M) = 0$$
Thus, the overall eigenvalues of $c_M$ can be determined by taking the eigenvalues of the sub-matrices $a_M$ and $b_M$—each composed of only one rotational state—separately. Programmatically, this is very useful since calculating the eigensystems of smaller matrices significantly reduces the computational load\(^1\).

\(^1\)The Python code developed calculates the effective Hamiltonian’s eigensystem for a single rotational manifold at a time.
C. Branching Ratio Tables

The branching ratio calculation allows the relative decay strengths from the excited state to the ground state to be found. The procedure for this calculation was laid out in Sec 2.4. Here the explicit branching ratio tables are given. Note that the decay from $A^2\Pi_{1/2}$ positive parity state to the $X^2\Sigma^+ N = 1$ state is closed and thus the branching ratios from each excited $m_F$ (values along one column) add up to one as expected. However, for the decay from $A^2\Pi_{1/2}$ negative parity state, selection rules dictate decays into either the $N = 0$ or $N = 2$ rotational manifolds. Thus, the columns (branching ratios from a single excited $m_F$ level) from these two tables together add up to one.

<table>
<thead>
<tr>
<th></th>
<th>$F = 0$, $m_F = 0$</th>
<th>$F = 1$, $m_F = -1$</th>
<th>$F = 1$, $m_F = 0$</th>
<th>$F = 1$, $m_F = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J = 1/2$, $F = 0$, $m_F = 0$</td>
<td>0.0000</td>
<td>0.2222</td>
<td>0.2222</td>
<td>0.2222</td>
</tr>
<tr>
<td>$J = 1/2$, $F = 1$, $m_F = -1$</td>
<td>0.2222</td>
<td>0.2222</td>
<td>0.2222</td>
<td>0.0000</td>
</tr>
<tr>
<td>$J = 1/2$, $F = 1$, $m_F = 0$</td>
<td>0.2222</td>
<td>0.2222</td>
<td>0.0000</td>
<td>0.2222</td>
</tr>
<tr>
<td>$J = 1/2$, $F = 1$, $m_F = 1$</td>
<td>0.2222</td>
<td>0.0000</td>
<td>0.2222</td>
<td>0.2222</td>
</tr>
</tbody>
</table>

Table C.1.: Branching ratios for the $A^2\Pi_{1/2}$ negative parity state to the $X^2\Sigma^+ N = 0$ state. The excited nominal states are represented by the columns and the nominal ground states are represented by the rows. Note that when the $m_F$ values differ by more than one, the transition is restricted due to selection rules.
### C. Branching Ratio Tables

#### Table C.2:

<table>
<thead>
<tr>
<th></th>
<th>$F = 0, m_F = 0$</th>
<th>$F = 1, m_F = -1$</th>
<th>$F = 1, m_F = 0$</th>
<th>$F = 1, m_F = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J = 1/2, F = 0, m_F = 0$</td>
<td>0.0000</td>
<td>0.2222</td>
<td>0.2222</td>
<td>0.2222</td>
</tr>
<tr>
<td>$J = 1/2, F = 1, m_F = -1$</td>
<td>0.1282</td>
<td>0.2493</td>
<td>0.2493</td>
<td>0.0000</td>
</tr>
<tr>
<td>$J = 1/2, F = 1, m_F = 0$</td>
<td>0.1282</td>
<td>0.2493</td>
<td>0.0000</td>
<td>0.2493</td>
</tr>
<tr>
<td>$J = 3/2, F = 1, m_F = -1$</td>
<td>0.2051</td>
<td>0.0007</td>
<td>0.0007</td>
<td>0.0000</td>
</tr>
<tr>
<td>$J = 3/2, F = 1, m_F = 0$</td>
<td>0.2051</td>
<td>0.0007</td>
<td>0.0000</td>
<td>0.0007</td>
</tr>
<tr>
<td>$J = 3/2, F = 2, m_F = -1$</td>
<td>0.0000</td>
<td>0.1667</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>$J = 3/2, F = 2, m_F = -2$</td>
<td>0.0000</td>
<td>0.0833</td>
<td>0.0833</td>
<td>0.0000</td>
</tr>
<tr>
<td>$J = 3/2, F = 2, m_F = 0$</td>
<td>0.0000</td>
<td>0.0278</td>
<td>0.1111</td>
<td>0.0278</td>
</tr>
<tr>
<td>$J = 3/2, F = 2, m_F = 1$</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0833</td>
<td>0.0833</td>
</tr>
<tr>
<td>$J = 3/2, F = 2, m_F = 2$</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.1667</td>
</tr>
</tbody>
</table>

The excited nominal states are represented by the four columns and the nominal ground states are represented by the twelve rows. Note that when the $m_F$ values differ by more than one, the transition is restricted due to selection rules. Additionally, the total branching ratios for one column add up to one—which provides a test of the calculations effectiveness.

#### Table C.3:

<table>
<thead>
<tr>
<th></th>
<th>$F = 0, m_F = 0$</th>
<th>$F = 1, m_F = -1$</th>
<th>$F = 1, m_F = 0$</th>
<th>$F = 1, m_F = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J = 3/2, F = 1, m_F = -1$</td>
<td>0.1111</td>
<td>0.0278</td>
<td>0.0278</td>
<td>0.0000</td>
</tr>
<tr>
<td>$J = 3/2, F = 1, m_F = 0$</td>
<td>0.1111</td>
<td>0.0278</td>
<td>0.0000</td>
<td>0.0278</td>
</tr>
<tr>
<td>$J = 3/2, F = 1, m_F = 1$</td>
<td>0.1111</td>
<td>0.0000</td>
<td>0.0278</td>
<td>0.0278</td>
</tr>
<tr>
<td>$J = 3/2, F = 2, m_F = -2$</td>
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<td>0.1620</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>$J = 3/2, F = 2, m_F = -1$</td>
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<td>0.0810</td>
<td>0.0810</td>
<td>0.0000</td>
</tr>
<tr>
<td>$J = 3/2, F = 2, m_F = 0$</td>
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<td>0.0270</td>
<td>0.1080</td>
<td>0.0270</td>
</tr>
<tr>
<td>$J = 3/2, F = 2, m_F = 1$</td>
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<td>0.0000</td>
<td>0.0810</td>
<td>0.0810</td>
</tr>
<tr>
<td>$J = 3/2, F = 2, m_F = 2$</td>
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<td>0.0000</td>
<td>0.0000</td>
<td>0.1620</td>
</tr>
<tr>
<td>$J = 5/2, F = 2, m_F = -2$</td>
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<td>0.0047</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>$J = 5/2, F = 2, m_F = -1$</td>
<td>0.0000</td>
<td>0.0023</td>
<td>0.0023</td>
<td>0.0000</td>
</tr>
<tr>
<td>$J = 5/2, F = 2, m_F = 0$</td>
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<td>0.0008</td>
<td>0.0031</td>
<td>0.0008</td>
</tr>
<tr>
<td>$J = 5/2, F = 2, m_F = 1$</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0023</td>
<td>0.0023</td>
</tr>
<tr>
<td>$J = 5/2, F = 2, m_F = 2$</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0047</td>
</tr>
<tr>
<td>$J = 5/2, F = 3, m_F = -3$</td>
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<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>$J = 5/2, F = 3, m_F = -2$</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>$J = 5/2, F = 3, m_F = -1$</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>$J = 5/2, F = 3, m_F = 0$</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>$J = 5/2, F = 3, m_F = 1$</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>$J = 5/2, F = 3, m_F = 2$</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

The excited nominal states are represented by the columns and the nominal ground states are represented by the rows. Note that when the $m_F$ values differ by more than one, the transition is restricted due to selection rules. Furthermore, all transitions to $J = 5/2$ states are also restricted by selection rules.
D. EOM Frequency Sidebands

D.1. Overview

Electro-optic modulators (EOM) use a crystal such as LiNbO$_3$—in which the index of refraction along one crystal axis is dependent on the electric field [64]—to modulate either the amplitude or frequency of light passing through the crystal. In the optical setup described in Chapter 3, the EOMs generate frequency sidebands and therefore a derivation of an EOM’s phase modification properties is given.

D.2. Sideband Derivation

The beam passing through the EOM has an initial electric field which can be described as

\[ Ae^{i\omega t} \]  

where \( A \) is the beam’s amplitude, \( \omega \) is the frequency and \( t \) is time. Now, applying a radio-frequency (RF) voltage to the EOM’s crystal likewise adds a frequency component to the beam’s electric field that is

\[ Ae^{i\omega t + i\beta \sin(\Omega t)} \]  

where \( \beta \) is the amplitude of the RF wave and \( \Omega \) is its frequency. Expanding this expression yields

\[ Ae^{i\omega t + i\beta \sin(\Omega t)} = Ae^{i\omega t} e^{i\beta \sin(\Omega t)} \]  

D.2.1. Jacobi-Anger Expansion

The Jacobi-Anger expansion states that [65]

\[ e^{i\beta \cos(\theta)} = \sum_{n=-\infty}^{\infty} i^n J_n(\beta) e^{in\theta} \]  

(D.4)
D. EOM Frequency Sidebands

where \( J_n \) is the \( n \)th Bessel function. Now to substitute \( \theta = \phi - \frac{\pi}{2} \) into the Jacobi-Anger expansion, the following trigonometric identity is needed

\[
\cos \left( \phi - \frac{\pi}{2} \right) = \sin(\phi) \tag{D.5}
\]

as is

\[
e^{in(\phi - \frac{\pi}{2})} = e^{in\phi} e^{-in\frac{\pi}{2}} = (-i)^n e^{in\phi} \tag{D.6}
\]

which is produced with the help of Euler’s equation. Using these two equations, the substitution is performed to transform Eq. D.4 into

\[
e^{i\beta \sin(\phi)} = \sum_{n=-\infty}^{\infty} J_n(\beta) e^{in\phi} = J_0(\beta) + \sum_{n=1}^{\infty} J_n(\beta) e^{in\phi} + \sum_{n=1}^{\infty} (-1)^n J_n(\beta) e^{-in\phi} \tag{D.7}
\]

where the following equation has been taken advantage of [66]

\[
J_{-n}(\beta) = (-1)^n J_n(\beta) \tag{D.8}
\]

D.2.2. Frequency Sidebands

Substituting the time-dependent angle \( \phi = \Omega t \) into Eq. D.7

\[
e^{i\beta \sin(\Omega t)} = J_0(\beta) + \sum_{n=1}^{\infty} J_n(\beta) e^{in\Omega t} + \sum_{n=1}^{\infty} (-1)^n J_n(\beta) e^{-in\Omega t} \tag{D.9}
\]

gives an expression identical to the \( e^{i\beta \sin(\Omega t)} \) term on the right-hand side of Eq. D.3. Replacing this term in Eq. D.3 with Eq. D.9 yields

\[
A e^{i\omega t + i\beta \sin(\Omega t)} = A e^{i\omega t} \left( J_0(\beta) + \sum_{n=1}^{\infty} J_n(\beta) e^{in\Omega t} + \sum_{n=1}^{\infty} (-1)^n J_n(\beta) e^{-in\Omega t} \right) \tag{D.10}
\]

From the equation above it can be seen that the addition of the RF wave to the electric field yields an infinite series of frequency sidebands. However, as \( n \) increases towards infinity, the envelope containing the respective Bessel functions decays so that the power converges to a finite value.
D.3. Experimental EOMs

In terms of the optic’s setup, two different EOM setups are utilized. The first is the EOM used in the locking arm of the main cooling laser which only needs the first set of sidebands for the Pound-Drever-Hall locking scheme. By truncating Eq D.10 this is given mathematically as

\[ Ae^{i\omega t + i\beta \sin(\Omega t)} = A \left( J_0(\beta) e^{i\omega t} + J_1(\beta) \left[ e^{i(\omega + \Omega)t} - e^{i(\omega - \Omega)t} \right] \right) \]  

(D.11)

For the EOM used to generate frequency sidebands for the hyperfine levels, two sets of sidebands are needed and thus Eq D.10 is truncated to give

\[ Ae^{i\omega t + i\beta \sin(\Omega t)} = A J_0(\beta) e^{i\omega t} + AJ_1(\beta) \left[ e^{i(\omega + \Omega)t} - e^{i(\omega - \Omega)t} \right] + AJ_2(\beta) \left[ e^{i(\omega + 2\Omega)t} + e^{i(\omega - 2\Omega)t} \right] \]  

(D.12)

(D.13)
E. Laser Stabilization and the Pound-Drever-Hall Technique

The cooling lasers used in the experiment must be frequency stabilized for several hour at a time. In Sec 3.4 the transfer cavity and the cesium frequency reference laser were discussed, whereas here a short explanation is given of the Pound-Drever-Hall technique.

E.1. Asymmetric PID Input Signal

The frequency domain of the laser is generally analyzed via a Fabry-Perot cavity which transmits light when the frequency of the beam matches one of the resonant cavity modes. However, the transmission peaks are Lorentzian and symmetric—which becomes problematic when trying to stabilize the frequency with a PID control since the PID needs an asymmetric input signal [64]. To circumvent this problem the Pound-Drever-Hall method is used to stabilize the laser frequencies.

E.2. Pound-Drever-Hall Technique

The Pound-Drever-Hall technique uses the phase shifted reflection signal of the laser from the optical cavity. In the following we briefly describe the principle of the technique and the optical setup to obtain the desired asymmetric input signal for the PID.

The lasers used in the optical setup (see Fig. E.1) are external cavity diode lasers (ECDL) in which the laser’s frequency can be tuned via the piezo crystal attached to the diffraction grating. Upon exiting the ECDL, the laser passes through an electro-optic modulator (EOM) which places frequency sidebands on either side of the main laser frequency (see Appendix D). An oscillator signal from an electronics rack is amplified and provides the requisite radio frequency (RF) voltage to drive the EOM. Following the EOM, the beam passes through a polarizing beam splitting cube (PBS) followed by a \( \lambda/4 \) quarter waveplate (QWP) and then into the Fabry-Perot cavity. Upon reflection from the cavity, the sidebands and the main laser
frequency obtain different phase shifts with the QWP allowing the reflected beam to be separated from the incoming beam. Having passed through the QWP twice, the beam has a $90^\circ$ polarization shift so that it is reflected upon reentering the PBS and then incident on a photodiode. The photodiode signal is mixed with the oscillator signal used to drive the EOM (signal can be phase shifted) and then passes through a low-pass filter which removes high-frequency components from the signal. Although the reflectance signal is symmetric around the center frequency—and therefore not useful for PID locking—, the reflectance signal mixed with the oscillator signal creates the asymmetric PDH signal (see Fig. E.2), which can be easily calculated analytically [62]. This PDH signal is then passed to the PID which uses the roughly linear slope corresponding to the main carrier frequency to stabilize the laser frequency\(^1\).

**E.3. Cavity Lock and AOM**

The transmission peaks (and likewise the reflectance dips) in the Fabry-Perot cavity have a finite frequency spacing defined by the free spectral range (FSR). This finite spacing means that the frequency of a transmission peak will not necessarily overlap the frequency of an atomic transition and thus the AOM must be used. The ECDL is locked to the transmission peak closest in frequency to the atomic transition after which the AOM is used to shift the frequency in the experimental

\(^1\)To control the laser’s frequency, the PID continuously updates the piezo crystal’s voltage.
E.3. Cavity Lock and AOM

Figure E.2.: Typical transmission signal (top) and Pound-Drever-Hall (PDH) signal (bottom) used to lock the laser [67]. The transmission signal clearly shows the main laser frequency with frequency sidebands on either side. When the corresponding cavity reflection signal is mixed with the oscillation signal, the PDH signal results. Note that unlike the transmission signal, the PDH signal is not symmetric which allows the PID controller to lock the frequency to the inflection point corresponding to the principal transmission peak.

arm to exactly match the atomic transition. Therefore, the ECDL is frequency stabilized, and the laser frequency entering the experimental setup corresponds exactly to the atomic transition.
F. Target Decay

Currently, the ablation laser impinges on the BaF$_2$ target at the same position for the entirety of the experimental run. As a result, the molecules at this position are depleted as the number of shots taken increases—which in turn decreases the absorption signal over time. To account for this, a large number of shots were taken at a single position on the target to determine the decrease in absorption signal (see Fig. F.1). Since a decaying trend could be clearly seen, a decaying exponential was fit to the absorption signal and can be used to correct absorption data accordingly. A more detailed explanation of the absorption decay along with in-depth characterization of the target can be found in [49].

![Graph showing absorption signal as a function of shot number](image)

**Figure F.1.** The absorption signal as a function of the number of shots taken at the same spot. The absorption data (red dots) shows a significant decrease around 700 shots which deviates from the overall exponential decay trend of the data. At this point, the cryostat was refilled with helium and since the temperature rose, the absorption decreased (see Sec 5.6). When fitting the decaying exponential function (shown on the bottom left) to the absorption data, the data between the start clip line (dashed line) and the end clip line (dash-dot line) was excluded. The resulting fit was then plotted (solid line) and shows excellent agreement with the data.

The equation for the decaying exponential function is:

\[ y = ae^{-b(x + c)} + d \]
Bibliography


Acknowledgments

Here I would like to acknowledge all those who have made this thesis possible. In particular, I wish to thank:

- Professor Tilman Pfau both for his mentorship in the International Max Planck Research School program, as well as providing the opportunity to complete my thesis within his institute. I’ve enjoyed the deep care he shows for his students along with his excellent insight into various physics problems.

- Professor Harald Giessen for his assistance as my second adviser.

- Dr. Tim Langen for taking me on as master’s student in his cold molecule’s group and teaching me an immense amount about optics and atomic physics. Furthermore, Dr. Langen has helped guide me through the European academic system—which can differ significantly at times from the American one.

- Tobias Sixt for our pleasant conversations on angular momentum coupling and other theoretical oddities.

- Ralf Albrecht for initiating me into the way of correct optical layouts—the German way.

- Dr. Derek Schaeffer both for inspiring me to pursue a career in physics and continuing to mentor me during my master’s studies.

- Cameron and Miru for sharing this journey in German physics with me.

- My parents and siblings for their encouragement and for providing lots of laughs along the way.

- Ashley for her steadfast support throughout my studies abroad.