Measuring and Optimizing Fluorescence in Thallium Fluoride

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Abstract

The CeNTREX experiment, which seeks to more precisely measure the nuclear EDM of thallium with an eye towards measuring T symmetry violation, requires the ability to reliably detect the spin precession angle of almost every thallium molecule that moves through the apparatus. To that end, this thesis studies optical cycling of thallium fluoride’s $X^1\Sigma^+(\nu = 0) \to B^3\Pi_1(\nu = 0)$ transition by measuring the fluorescence that results from laser excitation of a molecular beam. Our immediate goal is to measure between 10-100 optical cycles, which should allow near unit-efficiency internal state detection. By building a new, interlaced multipass, calibrating our optical system, and further investigating the effects of microwaves on the transitions, we’ve observed an increase from approximately 30 cycles per molecule to approximately 43 cycles per molecule on the $Q(J = 1)F' = 1/2F' = 1$ transition.
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Chapter 1

Introduction

Research is formalized curiosity.

Zora Neale Hurston, 1942

This thesis focuses on achieving near-unit efficiency in detecting the thallium fluoride molecules making the $X^1\Sigma^+(\nu = 0) \rightarrow B^3\Pi_1(\nu = 0)$ transition. Achieving this efficiency is critical to the ongoing CeNTREX (Cold Molecule Nuclear Time Reversal Experiment), which seeks to more precisely measure the nuclear electric dipole moment (EDM) of thallium fluoride. In particular, the goal of CENTReX experiment is to measure the permanent nuclear EDM of thallium fluoride.
1.1 Permanent EDMs

1.1.1 What’s an Electric Dipole Moment?

To begin, we’ll look at the question of what an electric dipole moment (EDM) is. The electric potential of an arbitrary charge distribution can be described in a multipole expansion as:

\[
V(r) = \frac{1}{4\pi \varepsilon_0} \sum_{n=0}^{\infty} \frac{1}{r^{n+1}} \int (r')^n P_n \cos \alpha \rho(r') d\tau'
\]  

(1.1)

where \( n \) gives us the degree of the expansion – these degrees drop off, clearly, as \( r^{-(n+1)} \). In particular, we’re interested in the dipole term of the expansion, which goes like \( V(r) \sim \frac{1}{r^2} \), and describes the potential due to the distribution’s dipole moment. The simplest – and thus easiest to grasp – physical dipole is made up of two equal and opposite charges \( \pm q \) placed at a distance \( d \) from one another.

More generally, EDMs exist where linear charge differentials do: consider a positively charged piece of wool with more positive charge on one side. The wool has a dipole moment pointing from the more negative end to the more positive end. An abstract representation of this dipole is shown in figure 1.1. Permanent EDMs are simply permanent arrangements of these sorts of dipole moments.
1.1 Permanent EDMs

1.1.1 Why are dipoles interesting?

There are three fundamental symmetries in physics: parity (P), time reversal (T), and charge conjugation (C). These symmetries, respectively, deal with the questions of whether particles behave in a different way if their spatial configuration is reversed (P), if the direction of time is made to run backwards instead of forwards (T), or if matter and antimatter particles are interchanged (C). More rigorously, Parity sends \((t, \vec{x}) \rightarrow (t, -\vec{x})\), Time sends \((t, \vec{x}) \rightarrow (-t, \vec{x})\), and Charge Conjugation exchanges the particles in a system for their respective antiparticles. Until the middle of the 20th century, these symmetries were widely expected to hold separately, because the vast majority of fundamental physical processes do keep these as good symmetries. Most physical systems, when, for example, charge conjugation is applied, operate exhibit a behavior that can still be explained by the same fundamental laws.
Thus it came as some surprise when P violation was observed in 1957 by C.S. Wu and her collaborators, and an even further surprise when CP violation was observed in K-meson decay [13]. The 1950s also saw the development of the CPT theorem, which explicitly connects all three types of symmetries, and shows that joint CPT symmetry is a good symmetry in almost every physical system. Fortunately for physicists, the CPT theorem is in complete accordance with observational evidence: no violation of CPT has ever been found in experiment. The theorem implies that violations of one kind of symmetry also imply other symmetry violations – as an example, the P violations observed by C.S. Wu imply CT violations to preserve overall symmetries.

One of the most obvious asymmetries in the universe is the baryon asymmetry (henceforth called the BAU) – namely that the universe contains much more matter than antimatter. This asymmetry is particularly surprising since almost all known methods of producing matter produce equivalent amounts of antimatter; in particular, all pure energy to matter conversions (a category that the Big Bang presumably falls into) have this property. The best answers to this mystery involve significant C and CP symmetry breaking (not surprising, as C symmetry involves exchanging particle and antiparticle pairs) – and the latter of these demands T symmetry violation. Moreover, the extent of the violations necessary

\footnote{More precisely, any Lorentz-invariant local quantum field theory with a Hermitian Hamiltonian must have CPT symmetry.}

\footnote{To be more specific, ordinary P violations, as observed by Wu, preserve T but violate C.}
1.1 Permanent EDMs

to produce the matter dominated universe that we observe suggest far more T violating phenomena than we have thus far been able to observe.

This is one of the motivations behind the CeNTREX experiments’ search for a nuclear EDM: a particle with both spin and a permanent EDM would violate both T and P symmetries, which could help account for the BAU.

To see why permanent EDMs paired with a spin violate T symmetry, imagine a spinning bowling ball, with the direction of rotation and the three holes pointing up. In this analogy, the direction of the rotation represents the spin vector, and the direction of the holes represents the EDM vector. If we imagine recording this motion and then playing in reverse (i.e. sending \((t \rightarrow -t)\)), we would see the direction of rotation change, but the three holes would remain pointing up. In a similar way, T symmetry reverses a particle’s spin, but not its EDM.

To see why permanent EDMs paired with a spin violate P symmetry, consider a particle and its reflection in a mirror, as shown in figure 1.3. Suppose that the vector’s representing the particle’s spin and EDM are parallel. In the mirror, the positive and negative charges that create the dipole moment will switch place, leading to a ‘reversed’ EDM. Thus, permanent EDMs (when paired with a spin) violate P symmetry \(^1\). A summary of these two effects is shown below in figure

\(^1\)This analogy only works with a mirror whose normal is parallel to the dipole moment, and breaks down if we consider a mirror whose normal is perpendicular to the dipole moment, which would flip S. Nonetheless, the analogy serves as a useful visualization.
1.1 Permanent EDMs

![Diagram of time reversal and parity reversal](image)

Figure 1.2: Imagine a particle with parallel spin and EDM vectors. Time reversal changes the spin, but not the EDM, while Parity reversal changes the direction of the EDM vector, but not that of the spin.

1.3. Clearly, these two arguments only hold for particles with spin and EDM aligned in the same direction. Fortunately, we can show that they always will be: imagine, for a moment, a particle with spin that had an EDM along a different axis. This particle would require an additional quantum number to fully express the direction of this EDM, which would allow for 4 different states per particle (two for spin, two for the EDM). This, due to the Pauli exclusion principle, would lead to a very different periodic table.

We’ve seen that EDMs are important for investigating questions like the BAU, but there are also other theoretical reasons to be interested in finding permanent EDMs. Researchers often look for electron, neutron, and proton EDMs. The
1.1 Permanent EDMs

Figure 1.3: An illustration of how a particle with both spin and a dipole moment (in the same direction) violates parity symmetry. Clearly, parity flips the particle’s EDM, but not its spin, which creates a fundamentally different particle/a fundamentally different physical system.

standard model, our best and most-validated theory for elementary particles, predicts that all three of these are far too small to be detected by current experiments. However, extensions to the standard model, such as supersymmetry, predict permanent EDMs of magnitudes on the cusp of experimental sensitivity. Moreover, physicists know that the standard model is incomplete (it fails to answer questions such as the hierarchy problem, the BAU, or how gravity fits into our picture of fundamental forces). The search for a permanent EDM, then, would help to validate or disprove fundamental theories of physics.
1.1 Permanent EDMs

1.1.2 Strength of the EDM

Previous EDM experiments, including the current limit on nuclear EDM sensitivity, were set using atomic sources. The CeNTREX experiment, by contrast, seeks to surpass this limit using diatomic thallium fluoride (TlF). This has two main advantages: a large molecule and a monstrous internal electric field. This is particularly promising in light of the fact that the ACME experiment has set the (current) best limit on the electronic EDM [1].

1.1.2.1 TlF’s Size

In his paper “Measurability of nuclear electric dipole moments” Leonard Schiff noted [14],

"It is shown that for a quantum system of point, charged, electric dipoles in an external electrostatic potential of arbitrary form, there is complete shielding."

This result, known as Schiff’s Theorem, illustrates that a neutral atom of non-relativistic point particles in electrostatic equilibrium will not exhibit EDM effects, even if its constituent particles themselves have EDMs (to second order in the dipole moments). Thus, atomic EDMs are restricted to situations in which the constituent particles are relativistic (breaking the non-relativistic assumption), have finite size (breaking the point particle assumption), or are in dis-
equilibrium (breaking the last assumption). Of particular interest to us is the second case – that of finite size. This induced EDM arises from the electrostatic force balancing the strong force, which holds the nucleus together, and results in an asymmetric charge distribution throughout the atom. The magnitude of this correction (and thus the induced atomic EDM) – known as the Schiff Moment – scales as $Z^2 A^{2/3}$, where $Z$ is the atomic number and $A$ is the atomic mass. The Schiff Moment, as one will recall, is exactly what the CeNTREX experiment sets out to measure. Because the Schiff Moment scales with both the atomic number and the atomic mass, thallium makes for a good candidate source [7].

1.1.2.2 TlF’s Electric Field

More importantly, diatomic molecules, despite being noticeably harder to work with than atoms, can have extremely strong internal electric fields. In particular, thallium fluoride’s electric field (at the thallium nucleus) is approximately $\varepsilon = 10^9$ V/cm. This field is nearly four orders of magnitude stronger than the largest laboratory-produced fields. This is relevant because the energy of a dipole in an electric field is:

$$U = -\vec{d} \cdot \varepsilon$$

Clearly, if this energy can be measured, we can obtain a value for the nuclear EDM. Moreover, because the energy scales with the relevant electric field, TlF’s
strong internal field should allow for more precise measurements. There are also good reasons to think that this is a productive avenue of research. The ongoing ACME (Advance Cold Molecule Electron) experiment set the most precise bounds on the electron’s EDM by using diatomic thorium oxide (ThO), so the approach of using molecules has proven its worth. If TIF can be optically cycled enough to allow for near-unit detection efficiency, the first-generation experiment should be about 30 times more sensitive to the Schiff Moment than the aforementioned bound obtained from $^{199}Hg$ [1]. Moreover, achieving this level of optical cycling will open the door to further improvements (e.g. optical cooling and trapping) that could increase experimental sensitivity by further orders of magnitude.

### 1.2 State Detection, Optical Forces, and You

With the motivation for optically cycling thallium fluoride in mind, we can finally start describing the central goal of this thesis in detail: getting TIF to optically cycle 100 times per molecule.

#### 1.2.1 What is cycling?

We say that a molecule completes a cycle on a transition “$A \rightarrow B$” if it starts in ground state $A$, is excited to state $B$, and then transitions back to the ground
state. If a molecule repeatedly executes this cycle, the molecule is said to be cycling on the transition. Importantly, if B decays to any non-A state, the cycling comes to an end, a condition that makes cycling transitions quite rare. Fortunately, TlF has 2 transitions that theory predicts should cycle well.

1.2.2 How much cycling?

Maximum sensitivity on the first-generation CeNTREX experiment requires near-unit detection efficiency of the TlF’s internal state. The experiment requires that we be able to detect every TlF on average. Fortunately, cycling allows this because the emitted photons can be used to read out the internal state of the emitting molecule. Every time a molecule completes a cycle, it will release a photon in a random direction – and thus if a molecule cycles $x$ times, $x$ photons will be released, any one of which could be used to read out the internal state of the molecule. Unfortunately, these photon emissions can only successfully be detected by something like a photodetector, and the geometry of the experiment is such that the detectors can’t fully surround the TlF molecules while they’re cycling. Ultimately, with some variation for photodetector efficiency and solid angle covered by photodetectors, the CeNTREX experiment will require between 10 and 100 photons for near-unit detection efficiency [11].
1.2 State Detection, Optical Forces, and You

1.2.3 How much does cycling help?

The CeNTREX experiment’s sensitivity scales as $P\tau \sqrt{\dot{N}}$, where $P$ is the electric polarization, $\tau$ is the spin coherence time, and $\dot{N}$ is the detection rate. This is proportional to the detection efficiency, which we would like to approach one. Though high-quality photodectors and careful placement of them could allow for near-unit detection efficiency with as few as 10 photons per molecule, it is both desirable and theoretically possible to increase that number to 100 photons even without repumping the TlF sample (a topic that will be covered in Chapter 2).
Chapter 2

Theory and Background

Summary

This thesis focuses on the $X^1\Sigma^+ (\nu = 0) \rightarrow B^3\Pi_1 (\nu = 0)$ transition in diatomic thallium fluoride, and in order to describe the relevant physics we first describe the molecular nomenclature that the above description arises from, a brief introduction to Thallium Fluoride, and an introduction to cycling.

2.1 Thallium Fluoride

2.1.1 How to Talk About Molecules

To begin, we’ll need to understand what each symbol in the above transition means. In the literature, the label for a molecular state always begins with its
2.1 Thallium Fluoride

electronic state, with the ground state always labeled as $X$. Excited states with the same multiplicity (spin degeneracy) as the ground state are labeled with capital letters ($A, B, C, ...$), while those with a different multiplicity are labeled with lower-case letters ($a, b, c, ...$)[2]. In principle, the energy of these states follows their respective alphabetical order[2]. Thus, our transition, which goes from $X$ to $B$ is between the ground state and the second excited state. The next part of the label looks like $^{2S+1}A_{||\Omega||}$, where $S$ is the total electronic spin angular momentum, $\Lambda$ is the projection of the electronic orbital angular momentum (in units of $\hbar$ on the internuclear axis, and $|\Omega|$ is the absolute value of the projection of the total electronic angular momentum onto the same axis. $S$ and $\Omega$ take on integer (or half-integer) values, but values of $\Lambda$ are represented with capital Greek letters. A $\Lambda$ of 0 is equivalent to $\Sigma$, a $\Lambda$ of 1 is equivalent to $\Pi$, etc.

To reground this discussion, this means that in the case of our ground state ($X^1\Sigma^+(\nu = 0)$), we have $S = 0$ and $\Lambda = 0$. The + superscript has to do with the state’s parity, which will be covered below. Moreover, the lack of a subscript following the $\Sigma$ implies that $\Omega = 0$. To help differentiate between the ground and second excited states in this thesis, the quantum numbers of the latter state will be primed. The excited state ($B^3\Pi_1(\nu = 0)$) tells us that $S' = 1$, $\Lambda' = 1$, and $|\Omega'| = 1$.

\[1\text{Unfortunately, this convention is broken in the case of the } X^1\Sigma^+(\nu = 0) \rightarrow B^3\Pi_1(\nu = 0)\text{ transition above, in which the B has a different spin degeneracy than the ground state [17].}

\[2\text{Though it doesn’t come up in this thesis, this is not always the case. This convention is usually flouted because the out-of-order state was found after the others were labeled.}\]
Finally, the $\nu = n$ parts of the label describe the value of the vibrational quantum number, $\nu$. Fortunately, both of the states we’re interested in have a $\nu$ of 0, which will help simplify matters. To a rough approximation, the energies of the rotational and vibrational levels are given by the first and second terms (respectively) of the following equation:

$$E_{\nu J} = (\nu + \frac{1}{2}) \hbar \omega + \frac{\hbar^2 J(J + 1)}{2\mu r_e^2}$$  \hspace{1cm} (2.1)

Notably, the $J$ above denotes the rotational state, which will be elaborated upon shortly. Moreover, $\frac{\hbar^2}{2\mu r_e^2}$ is usually much smaller than $\hbar \omega$, which means that the vibrational energy splittings are much larger than the rotational splittings. Unfortunately, to fully understand the rotational states in TlF we’ll need to delve deeper into the associated quantum mechanics.

2.1.2 Angular Momentum and Rotational States

Angular momentum in atoms is fortuitously straightforward: the total spin quantum number $S$ and the total orbital angular momentum $L$ couple together to make $J$, the total angular momentum (excluding nuclear spin)[4]. Unfortunately, diatomic molecules like TlF are more difficult for two reasons. Firstly, diatomic molecules possess an internuclear axis. Additionally, diatomic molecules have an additional quantum number, $R$, associated with the rotational angular momen-
2.1 Thallium Fluoride

tum of the two nuclei precessing around one another. The precise ways in which these angular momenta and axes couple together vary between molecules, and so approximations must be used. TlF is best described by the basis set Hund’s case (c).

In Hund’s case (c), the total spin ($S$) and the total orbital angular momentum ($L$) couple more strongly to one another than they do to the internuclear axis. This is most common in heavier diatomic molecules, a category TlF certainly belongs to. The two couple to form $J_\alpha$, which has a projection $\Omega$ along the internuclear axis. $J_\alpha$ then couples to the rotational angular momentum ($R$), which makes up the total angular momentum less the nuclear spin (in the notation above, $J$), as seen in figure 2.1. $J$ is very important, as it specifies the molecule’s rotational state. The final two relevant spins are the nuclear spins of Thallium and Fluoride: $I_1 = 1/2$ and $I_2 = 1/2$ respectively [3]. $J$ first couples to $I_1$ to form $F_1$, then couples to $I_2$ to form the total angular momentum $F$.

The two nuclear spins also introduce hyperfine structure to the rotational states. When $I_1$ is spin up the energy of the rotational state $J$ slightly increases (and the opposite occurs when it is spin down). $I_2$ further splits the energy levels\(^1\). The result of these changes is shown in figure 2.2.

\(^1\)Notably, the energy changes scale with atomic number $Z$ and so this splitting is smaller[17]
2.1 Thallium Fluoride

Figure 2.1: A vector diagram of the angular momenta at play in Hund’s third case. Figure reproduced from [17]

Figure 2.2: An illustration of the energy splittings introduced by the two nuclear spins $I_1$ and $I_2$. On the left, we see the $J=1$ state in the absence of hyperfine structure. On the right, we see the same state with hyperfine structure.
2.1.3 Parity

We say that a state has even parity if its wavefunction obeys the transformation
\[ \Psi(-\vec{r}) = \Psi(\vec{r}), \]
whereas if \[ \Psi(-\vec{r}) = -\Psi(\vec{r}) \] we say the state has odd parity.

Fortunately, the parity of our ground state is very simple. The + in \[ X^1\Sigma^+(\nu = 0) \]
indicates that the state has even parity before \( J \) is taken into consideration. The
total wavefunction, then, will have the parity of \( J \) (as an even function multiplied
by an even function is even, and an even function multiplied by an odd
function is odd). The parity of the ground state is then \((-1)^J\). We record this
parity-dependence on \( J \) with a plus or minus superscript (e.g. \( 1^+ \) or \( 0^- \)).

Unfortunately, the excited state isn’t so simple – due to an effect called \( \Omega \)-
doubling. The excited state has \( |\Omega| = 1 \), and the eigenstates of \( \Omega \) are \[ e^{\pm\Omega\Phi}, \]
where \( \Phi \) is the polar angle with respect to the internuclear axis. These eigen-
states are the even and odd combinations of the parity eigenstates \( \sin(\Omega\Phi) \) and
\( \cos(\Omega\Phi) \). Unfortunately, absent any external fields, the parity quantum number,
\( P \), is a good quantum number, while \( \Omega \) is not. This means that every molecule
in the \( B^3\Pi_1(\nu = 0) \) state is guaranteed to have a component of the wavefunction
that either has definite even parity or definite odd parity. Each rotational level
\( J = 0, 1, 2, \ldots \) will thus contain states with both even and odd parity. To
make matters more complicated, due to perturbative coupling between electronic
states, the states of opposite parity aren’t degenerate. These opposite parity
2.1 Thallium Fluoride

Figure 2.3: An illustration of the detailed structure of the $J = 0$ rotational ground state of TlF.

states are instead split by tens of MHz in the $J' = 1$ level [6].

### 2.1.4 A More Complete Picture

This thesis is primarily concerned with the specific rotational states $J = 0$, $J = 1$, and $J' = 1$. Of all of these, $J = 0$ is the simplest. The hyperfine structure of $J = 0$ comes from the two nuclear spins ($I_1$ and $I_2$). The two combine as two half-spin angular momenta usually do: they form a triplet and singlet state [4]. If we adopt the notation $|F, m_F\rangle = m_{I_1} m_{I_2}$, the triplet state is made up of $|1, 1\rangle = \uparrow\uparrow$, $|1, 0\rangle = \frac{1}{\sqrt{2}} (\uparrow\downarrow + \downarrow\uparrow)$ and $|1, -1\rangle = \downarrow\downarrow$ and the singlet state is made up of $|0, 1\rangle = \frac{1}{\sqrt{2}} (\uparrow\downarrow - \downarrow\uparrow)$. The triplet state has a higher energy (by 13.30(72) kHz) due to the magnetic dipole-dipole interactions between the two nuclei [17].

The $J = 1$ and $J' = 1$ states are similar to each other (though they’re both more complicated that the $J = 0$ detailed above). The $J' = 1$ state has two key differences from the $J = 1$: firstly, the former state has much larger hyperfine splittings than the latter. This is because the excited state has a non-zero pro-

\footnote{\textsuperscript{1}$J = 2$ and $3$ are also relevant, but behave similarly to the $J = 1$ case.}

\footnote{\textsuperscript{2}$J' = 1$ is actually the lowest rotational level in the $B^3\Pi_1 (\nu = 0)$ state.}
2.1 Thallium Fluoride

Figure 2.4: An illustration of the detailed structure of the $J' = 1$ rotational state of TlF, not drawn to scale.

projection along the internuclear axis ($|\Omega| = 1$), which can strongly couple to $I_1$ and $I_2$. In fact, the $I_1$ splitting is 13 GHz, larger than most hyperfine splittings. By contrast, the $J = 1$ state has no projection along the internuclear axis, and thus can couple only weakly to the nuclear spins.

Secondly, the $J' = 1$ state has both even and odd parities, which gives it twice as many hyperfine states. As stated above, these states are not degenerate: for $F_1 = 3/2$ even parity states have slightly higher energies, whereas for $F_1 = 1/2$ odd parity states have slightly higher energies (though we haven’t been able to measure them precisely).

The lifetime of the excited state also informs the natural line widths of the transitions of interest. The transitions we’re interested in go to the $B^3\Pi_1(\nu = 0)$ state which has a measured lifetime of 99(9) ns [10]. This lifetime measures how long it takes for the number of molecules in the excited to state to decrease to $\frac{1}{e}$ of its
original value. This, in turn, can be related to the full-width at half-max of the natural line width via the energy-time uncertainty relation [4]:

$$\Delta E \Delta t = \hbar$$  \hspace{1cm} (2.2)

We can substitute $\tau$ in for $\Delta t$ and $h\nu$ for $\Delta E$, and obtain:

$$h\Delta \nu \tau = \frac{\hbar}{2\pi}$$  \hspace{1cm} (2.3)

$$\Delta \nu = \frac{1}{2\pi \tau}$$  \hspace{1cm} (2.4)

Plugging in 99 ns for $\tau$, $\Delta \nu = 1.61 \ (15)$ MHz. If we recall the estimates above, this is small in comparison to the hyperfine splittings of J$'=1$, but large in comparison to the hyperfine splittings of J = 1. This means that the hyperfine sublevels of J = 1 are unresolved [10]. If we want to transition molecules between J = 1 and J$'=1$ with a laser, we’ll address a linear combination of the four hyperfine J = 1 states and one J$'=1$ hyperfine state – something that will resurface in the cycling section.
2.1 Thallium Fluoride

Figure 2.5: An illustration of the P, Q, and R transitions from a ground state with rotational number J.

2.1.5 Molecular Transition Notation

Molecular transitions are usually labeled according to how they change J [17]. For an electric dipole transition, a selection rule requires that \( J' - J = -1, 0, +1 \). These transitions are respectively called P, Q, and R – and are depicted in figure 2.5. The letter is then followed by the value of J in parenthesis (e.g. a label like Q(1) denotes a transition between a J = 1 ground state and a J' = 1 excited state).

Importantly, because the hyperfine sublevels in the ground state are unresolved (while the excited state levels are resolved), a label like Q(1) actually denotes a transition between all hyperfine states in the J = 1 ground state to a single hyperfine level of J' = 1. To specify a particular Q(1) transition, we append the hyperfine level to the label. For example, this thesis often discusses the Q(1) \( F_1' = 1/2 \ F' = 0 \) and Q(1) \( F_1' = 1/2 \ F' = 1 \) transitions.
2.2 Cycling

When we excite a given transition with our laser, TlF molecules in some (linear combination of several) particular rovibrational state(s) in the ground level move to a particular excited state. After a short time spent in the excited state, the molecules then release a photon in a random direction and transition back to the ground state. If we’re able to repeatedly cause molecules to go through this cycle, we are optically cycling them.

Typical detection efficiency (including quantum efficiency) for laser-induced fluorescence range from $1 - 10\%$ [11]. This implies that require the TlF molecules to cycle between 10-100 times to detect them with near-unit efficiency. In order to assure ourselves of this, let’s imagine a detector setup similar to the one we’ve set up in our own lab, with a camera above a fluorescence source.

2.2.1 Toy Example

In the immediate future, we’d like to cycle thallium fluoride enough to detect it with near unit-efficiency. In order to approximate how much cycling this requires, we can approximate the fluorescence source as a point source and the lens as being part of a sphere, as illustrated in figure 2.6. Because there’s no directional preference in terms of photon emission, we can estimate what percentage of photons reach the camera by calculating the fraction of the sphere’s surface area is
2.2 Cycling

Figure 2.6: A diagram of the approximation used to calculate our cycling requirements.

captured by the lens. Here we refer to $a$ as being the base radius and $h$ as being the height of the cap.

\[
\text{Photon Percentage} = \frac{SA_{\text{lens}}}{SA_{\text{Sphere}}} = \frac{\pi(a^2 + h^2)}{4\pi R^2} \tag{2.5}
\]

In our apparatus, $a$ is approximately 1 inch (the radius of the lens), and $h$ is approximately .25 inches, whereas $R$ is approximately 5 inches. This leads us to a photon capture percentage of approximately 2%. However, we also have to account for the quantum efficiency of the photomultiplier tube used for detection, which is usually in the vicinity of 33% for 271 nm light [5]. This estimate would require approximately 150 cycles in order to detect, on average, one photon from each molecule. However, if we added a second detector (which wouldn’t be un-
2.2 Cycling

reasonable), we would only require 75 cycles for near-unit detection efficiency, and adding more would decrease the required amount of cycling similarly. Alternately, we could increase the size of the lens (the \(a\) in the equation above) to lower the required photon count. All of these are examples of practically achievable configurations to obtain near-unit detection efficiency.

2.2.1 Problems

In order to obtain this amount of cycling, we need to understand how likely it is that, given a molecule has been excited to a particular transition, it will return to the original, re-excitable ground state. Two things can prevent this from happening. Firstly, we could have molecules transition to a different ro-vibrational ground state. Secondly, even if the molecules do return to the original ground state, they could enter a polarization or hyperfine state that is inaccessible to our laser (which we'll henceforth refer to as dark states).

2.2.2 Rotational and Vibrational Branching

Let’s start with vibrational branching in TIF. We can estimate vibrational branching ratios via Morse potentials or via Rydberg-Klein-Rees potentials, but fortunately a previous thesis has already gone ahead and done this. Neha Spenta Wadia precisely measured the ratios between the excited \(B(\nu = 0)\) state and the various vibrational levels of the X state, labeled \(b_{0\nu}\). The upshot of this is that
2.2 Cycling

Table 2.1: Predicted and measured values of vibrational branching ratios. Reproduced from [11].

<table>
<thead>
<tr>
<th>$\nu$ = 0 (271.7 nm)</th>
<th>Morse</th>
<th>RKR</th>
<th>Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu = 0$</td>
<td>.9892(3)</td>
<td>.989(2)</td>
<td>.989(2)</td>
</tr>
<tr>
<td>$\nu = 1$</td>
<td>.003(2)</td>
<td>.0005(3)</td>
<td>15(4) * 10^{-5}</td>
</tr>
<tr>
<td>$\nu = 2$</td>
<td>.0104(2)</td>
<td>.010(2)</td>
<td>.011(2)</td>
</tr>
<tr>
<td>$\nu = 3$</td>
<td>0.00000(1)</td>
<td>&lt;0.0003</td>
<td>3(2) * 10^{-5}</td>
</tr>
<tr>
<td>$\nu = 4$</td>
<td>0.00013(1)</td>
<td>&lt;0.0002</td>
<td>13(3) * 10^{-5}</td>
</tr>
<tr>
<td>$\nu = 5$</td>
<td>0.00000(1)</td>
<td>&lt;0.0003</td>
<td>1(1) * 10^{-5}</td>
</tr>
<tr>
<td>$\nu = 6$</td>
<td>-</td>
<td>&lt;0.0002</td>
<td>1(2) * 10^{-5}</td>
</tr>
</tbody>
</table>

molecules excited to $B^3\Pi_1(\nu = 0)$ on either the R(0) or Q(1) transition have an approximately 99% chance of returning to the ground vibrational state they came from. The favorable ratio between $X^1\Sigma^+ (\nu = 0)$ and $B^3\Pi_1(\nu = 0)$ is a big factor in why we’ve chosen to cycle on this transition.

With the vibrational branching well in hand, we can turn to the rotational branching. In the case of rotational branching, we need to pay more particular attention to individual states, but we do have a few helpful selection rules. The photons emitted by TlF molecules transitioning to a ground state can only contain one unit of angular momentum, so we can require that $\Delta J = 0, \pm 1$ and $\Delta m = 0, \pm 1$.

Additionally, the laser couples states via the electric dipole operator, and can thus only drive transitions between states of opposite parity [17]. This is, incidentally, why we use the Q transitions: the parity selection rules don’t allow them to decay to the $\Delta J = \pm 1$ levels.

These selection rules let us know which states are accessible, but don’t give us
information about the relative probabilities of molecules decaying to any given state. Fortunately, we can calculate the relative probabilities with the following equation [6]:

\[
|\langle J, m, \Omega | \vec{D} \cdot \vec{E} | J', m', \Omega' \rangle|^2 \propto \frac{1}{(2J + 1)(2J' + 1)} \left( \begin{array}{ccc} J & 1 & J' \\ -\Omega & \Omega - \Omega' & \Omega' \end{array} \right)^2 \left( \begin{array}{ccc} J & 1 & J' \\ -m & m - m' & m' \end{array} \right)^2.
\] (2.6)

If we calculate all of the relative probabilities, we can divide each relative probability by the sum of the relative probabilities of every allowed transition to obtain the rotational branching ratios of whichever state we’re interested in.

### 2.2.3 Dark States

We’ll shortly see that dark states exist due to both the polarization states that the laser can’t access and hyperfine dark states that arise due to TlF’s hyperfine structure. As both are quite complicated, we’ll first give an example of a transition with polarization dark states (ignoring hyperfine structure), and then do the same for a hyperfine example.
### 2.2 Cycling

#### Table 2.2: Probabilities of Available Decay Paths for $J' = 1^+ \ m' = 0$

| $|J^P, m\rangle$       | $|1^-, 1\rangle$ | $|1^-, 0\rangle$ | $|1^-, 1\rangle$ |
|----------------------|------------------|------------------|------------------|
| Relative Probability | 1/4              | 0                | 1/4              |
| Normalized Probability| 1/2              | 0                | 1/2              |

#### 2.2.3.1 Polarization Dark States

Transitions on the Q(1) are limited by the existence of polarization dark states. The Q(1) transition is between the $J' = 1^+$ and $J = 1^-$ states, which is depicted in figure 2.7. Without loss of generality, let’s assume a laser that emits right-handed circularly polarized light. In order to illustrate the dark state, let’s also assume no rovibrational branching. Because of our laser’s polarization, we’ll only couple states where $\Delta m = m' - m = 1$. This implies that molecules in the $J = 1^- \ m = 1$ state will never be excited (since there’s no state with a larger angular momentum). This is sufficient to show the existence of polarization dark states, but we can also quickly illustrate their effects. If we take into account all
2.2 Cycling

Table 2.3: Probabilities of Available Decay Paths for $J' = 1^+ m' = 1$

| $|J^P, m\rangle$ | $|1^-, 0\rangle$ | $|1^-, 1\rangle$ |
|-----------------|-----------------|-----------------|
| Relative Probability | 1/4             | 1/4             |
| Normalized Probability | 1/2             | 1/2             |

selection rules and then find relative decay probabilities as specified above, we find the results of tables 2.2 and 2.3 [17]. Molecules cycling on this transition have an equal probability of landing in our $J = 1^- m = 1$ dark state and the one accessible bright state (as the $m = 0$ state is ruled out). This means that our total expected number of photons is the geometric sum:

$$\sum_{n=0}^{\infty} \left(\frac{1}{2}\right)^n = 2$$

(2.7)

Fortunately, this issue is comparatively easy to solve. Left-handed circularly polarized light works in exactly the opposite way (it has the rule that $\Delta m = m' - m = -1$), and so the $J = 1^- m = 1$ is bright to it. Of course, this also means that the $J = 1^- m = -1$ state is dark to left-hand circularly polarized light, but we can solve both problems at once by continuously switching between the two polarizations. Assuming a sufficiently fast switch, any molecules stuck in a state that’s dark to one kind of polarized light will be excited by the other.
2.2 Cycling

2.2.3.2 Hyperfine Dark States

Unfortunately, the picture gets even more complicated. As previously discussed, the natural linewidth $\Delta \nu = 1.61 (15)$ MHz is large in comparison to the hyperfine splittings of $J = 1$ ground states (which are hundreds of kHz). As a result, the laser doesn’t drive a transition between one ground state and one excited state: it drives a transition between a linear combination of ground states and one excited state. We call the orthogonal linear combinations of ground states that aren’t excitable by the laser hyperfine dark states.

As in the previous section, it will be helpful to go through a concrete, comparatively simple example of hyperfine dark states first.

2.2.4 Hyperfine Dark State Example

Let’s consider the $Q(1)$ $F'_{1} = 1/2$ $F' = 0$ transition driven by right-handed circularly polarized light, depicted in figure 2.8.

Notably, now that we’re dealing with the hyperfine structure, we’re no longer dealing with $J$ (the angular momentum less the nuclear spins), we’re concerned with $F$ (the total angular momentum). This is because the hyperfine structure arises from interactions with the nuclear spins. Since the excited state has $F' = 0$ it has only one magnetic level $m_F = 0$. Because we’re using right-handed circularly polarized light, the only excitable states in the $J = 1$ level are those
2.2 Cycling

Figure 2.8: A diagram of the transition used to illustrate hyperfine dark states. The transition excites a linear combination of the states highlighted by the blue oval. The orthogonal linear combination is dark.

with \( m_F = -1 \). Moreover, another selection rule ensures that the only states able to be excited to either the \( F' = 0 \) (or 2) state(s) are those with \( F = 1 \). This implies that only the two states highlighted in figure 2.8 can make this transition.

As alluded to earlier, we can’t excite a single ground state, and instead, working in the \( |F_1, F, m\rangle \) basis, excite a linear combination of \( |1/2, 1, -1\rangle \) and \( |3/2, 1, -1\rangle \).

We can also find exactly what these linear combinations are. Our bright (B) and dark (D) state are respectively defined as

\[
|D\rangle = c_1|1/2, 1, -1\rangle + c_2|3/2, 1, -1\rangle
\]
\[ |B\rangle = c_3 |1/2, 1, -1\rangle + c_4 |3/2, 1, -1\rangle \quad (2.9) \]

In order to find the dark state we can find the constants \(c_1\) and \(c_2\) such that the relative probability of that state being excited is 0. This may sound similar to equation 2.6, and we can indeed use a modified version of that equation (changed to remove transitions between states of nuclear spin projections \(m_1\) and \(m_2\)) in order to calculate where the transition amplitude is equal to zero.

\[ \begin{array}{c}
|\langle J, m_J, \Omega | \vec{D} \cdot \vec{E} | J', m'_J, \Omega' \rangle|^2 \propto \\
\delta_{m'_1} \delta_{m'_2} (2J + 1)(2J' + 1) \left( \begin{array}{ccc}
J & 1 & J' \\
-\Omega & \Omega - \Omega' & \Omega'
\end{array} \right) ^2 \left( \begin{array}{ccc}
J & 1 & J' \\
-m_J & m_J - m'_J & m'_J
\end{array} \right)^2
\end{array} \quad (2.10) \]

Unfortunately, this equation works off of \(J\), and as previously mentioned, hyperfine states are concerned with \(F\). This means that we’ll have to project the \(|1/2, 1, -1\rangle\) and \(|3/2, 1, -1\rangle\) states into the \(|J, m_J, I_1, m_{I_1}, I_2, m_{I_2}\rangle\) basis, which we can do with Clebsh-Gordon coefficients [4].

Fortunately, a previous thesis student has already done this, and we find that in
the \( |J, m_J, I_1, m_{I_1}, I_2, m_{I_2}\rangle \) basis [17]:

\[
|\frac{1}{2}, 1, -1\rangle = \frac{1}{\sqrt{3}} |1, 0\rangle \left| \frac{1}{2}, -\frac{1}{2}\right\rangle \left| \frac{1}{2}, -\frac{1}{2}\right\rangle - \sqrt{\frac{2}{3}} |1, -1\rangle \left| \frac{1}{2}, \frac{1}{2}\right\rangle \left| \frac{1}{2}, -\frac{1}{2}\right\rangle \tag{2.11}
\]

\[
|\frac{3}{2}, 1, -1\rangle = \frac{1}{\sqrt{6}} |1, 0\rangle \left| \frac{1}{2}, -\frac{1}{2}\right\rangle \left| \frac{1}{2}, -\frac{1}{2}\right\rangle + \frac{1}{2\sqrt{3}} |1, -1\rangle \left| \frac{1}{2}, \frac{1}{2}\right\rangle \left| \frac{1}{2}, -\frac{1}{2}\right\rangle - \frac{\sqrt{3}}{2} |1, -1\rangle \left| \frac{1}{2}, -\frac{1}{2}\right\rangle \left| \frac{1}{2}, \frac{1}{2}\right\rangle \tag{2.12}
\]

Moreover, we can also find the projection of the excited state, \( F_1' = 1/2 \) \( F' = 0, m_{F'} = 0 \) – which we’ll call E:

\[
E = -\frac{1}{\sqrt{6}} |1, 0\rangle \left| \frac{1}{2}, \frac{1}{2}\right\rangle \left| \frac{1}{2}, -\frac{1}{2}\right\rangle - \frac{1}{\sqrt{6}} |1, 0\rangle \left| \frac{1}{2}, -\frac{1}{2}\right\rangle \left| \frac{1}{2}, \frac{1}{2}\right\rangle \\
+ \frac{1}{\sqrt{3}} |1, -1\rangle \left| \frac{1}{2}, \frac{1}{2}\right\rangle \left| \frac{1}{2}, \frac{1}{2}\right\rangle + \frac{1}{\sqrt{3}} |1, -1\rangle \left| \frac{1}{2}, -\frac{1}{2}\right\rangle \left| \frac{1}{2}, -\frac{1}{2}\right\rangle \tag{2.13}
\]

With all of our states in the correct basis, we can directly proceed to plugging them into equation 2.10. This yields \( c_3 = \frac{-1}{\sqrt{3}} \) and \( c_4 = \sqrt{\frac{2}{3}} \) for the dark state. We can then use the Gram-Schmidt orthogonalization process to make the bright state orthogonal to it, yielding

\[
|D\rangle = \frac{-1}{\sqrt{3}} |1/2, 1, -1\rangle + \sqrt{\frac{2}{3}} |3/2, 1, -1\rangle \tag{2.14}
\]
Table 2.4: Probabilities of Available Decay Paths for $F'_1 = 1/2$ $F' = 0, m_{F'} = 0$

| $|F_1, m_F\rangle$ ($F = 1$) | $|3/2, -1\rangle$ | $|3/2, 0\rangle$ | $|3/2, 1\rangle$ | $|1/2, -1\rangle$ | $|1/2, 0\rangle$ | $|1/2, 1\rangle$ |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Relative Probability | 1/18            | 1/18            | 1/18            | 1/9             | 1/9             | 1/9             |
| Normalized Probability | 1/9             | 1/9             | 1/9             | 2/9             | 2/9             | 2/9             |

\[
|B\rangle = \sqrt{\frac{2}{3}}|1/2, 1, -1\rangle + \frac{1}{\sqrt{3}}|3/2, 1, -1\rangle \tag{2.15}
\]

With all this in hand, we can repeat the same procedure we did in the polarization dark state sub-section in order to obtain the probabilities of our decay paths from the $F'_1 = 1/2$ $F' = 0, m_{F'} = 0$ state. These results are compiled in table 2.4.

Unfortunately, our picture isn’t quite as simple as it was in the previous sub-section: molecules in dark states no longer stay there permanently. Instead, molecules in dark states (i.e. projected onto D) will eventually evolve into bright states. Consider a molecule that, at time $t_0$ is in the hyperfine dark state $|D\rangle$.

Thus far we’ve only considered the spatial wavefunction, but the full wavefunction of this molecule will be the product of its spatial and temporal wavefunctions: $\Psi(x, t) = \psi(x)\phi(t)$. As usual, the temporal component will be of the form $e^{-iEt/\hbar}$ [4]. The full wavefunction of this molecule, then, is [17]:

\[
\Psi(x, t) = -\frac{1}{\sqrt{3}}|A\rangle e^{-i(0)t/\hbar} + \sqrt{\frac{2}{3}}|B\rangle e^{-i(2\pi*176.0kHz)t} \\
= -\frac{1}{\sqrt{3}}|A\rangle + \sqrt{\frac{2}{3}}|B\rangle e^{-i(2\pi*176.0kHz)t} \tag{2.16}
\]
Table 2.5: Rotational Branching Ratios of the Hyperfine Levels of $J' = 1^+$. Adapted from [11]

| $J'^{'}$, $F'^{'}$ | $|J,P\rangle$ | $|1,1/2,0\rangle$ | $|1,3/2,1\rangle$ | $|1,3/2,2\rangle$ |
|------------------|----------------|----------------|----------------|----------------|
| $J^{P} = 1^-$    | 1              | 0.9998         | 0.860          | 0.855          |
| $J^{P} = 3^-$    | 0              | 0.0002         | 0.140          | 0.145          |

As $t$ increases, the phase factor attached to the latter term will evolve over time, taking on values between -1 and 1. When it is equal to 1/2, the dark state will have evolved into a $|B\rangle$, and will once again be excited by our laser.

2.2.5 Prescriptions and Implications

Now we can begin to consider all factors in conjunction with one another. When hyperfine structure is considered, we can have some rotational branching on our Q(1) transitions because our angular momentum selection no longer perfectly holds. Certain hyperfine levels of the $J' = 1$ state can decay to the $J = 3^-$ ground state [11].

As shown in table 2.5, the only Q(1) transitions that have the chance of cycling 100 photons are the two $F'_1 = 1/2$ states. Understanding the polarization dark states is also important. Consider the Q(1) $F'_1 = 1, F'^{'} = 1$ transition being excited by right-handed circularly polarized light, as in figure 2.9. We require our usual selection rule (that $m'_F - m_F = 1$). Looking specifically at those molecules transitioning to the $m'_F = 0$ state, we see that there are three accessible ground states. This, by the process outlined above, gives us one bright state (formed by
2.2 Cycling

Figure 2.9: A diagram of the Q(1) $F'_1 = 1/2F'' = 1$ transition driven by right handed-circularly polarized light.

a linear combination of these states) and two orthogonal dark states. This, alone, would also leave us with polarization dark states for all states with $m_f = 1, 2$. However, if we modulate the polarization, we end up with a picture much more akin to figure 2.10. In this new figure, if we optimistically assume that all dark states evolve into bright states in a relatively small amount of time, we’re limited only by our rovibrational branching factors.

If this is our only limitation, then it should possible to cycle 100 times (which would be more than sufficient for near-unit detection efficiency).

Though some further theory is detailed in Appendix B, in principle, this is everything we need to go forward. The rest of this thesis is dedicated to the experimental and engineering challenges associated with cycling TlF, along with the
2.2 Cycling

Figure 2.10: A diagram of the approximation used to calculate our cycling requirements.

difficulty associated with trying to understand exactly why we aren’t cycling 100 photons. What follows is a description of the apparatus used during the course of this experiment.
Chapter 3

Apparatus

The Experimental Apparatus

Among other things, this apparatus produces a cryogenic buffer gas of helium that cools thallium fluoride, which can then be optically cycled on the $X^1\Sigma^+(\nu = 0) \rightarrow B^3\Pi_1(\nu = 0)$ transition, and have its fluorescence detected. To that end, we’ll first discuss how to produce said buffer gas, and then move to the question of detection – namely what the relevant pieces of equipment are and how they’re used. Following that, we’ll dive into a few additional pieces of equipment, such as the multipass, in greater detail, as they form an integral part of this thesis work. Finally, we’ll discuss some additional pieces of equipment that arrived towards the end of this thesis.
Figure 3.1: A picture of the main apparatus, with a focus on the interaction region.

Figure 3.2: A schematic of the apparatus [17]. The blue lines in this schematic represent windows.
3.1 Producing the Helium Buffer Gas

3.1.1 What are CBGB’s

The TlF beam is produced via a cryogenic buffer gas beam (CBGB) source. These sources are, in principle, fairly simple. A cold cell is held at some low temperature $T_0$ while gaseous buffer atoms (in our case, helium atoms), at the same temperature, are continuously flowed through the cell. The target molecules (in our case, the TlF molecules) are injected into the cold cell by blasting/ablating a solid source of thallium fluoride with an Ultra GRM Nd:YAG laser from Big Sky Laser Technologies. This laser produces 50 mJ, 10 ns pulses. The TlF molecules produced this way enter the cold cell at a relatively high temperature ($T_{TlF}(t = 0) \gg T_0$). Fortunately, these molecules undergo many collisions with the buffer gas molecules, and their rotational and translational degrees of freedom are cooled to near $T_0$. Notably, this also requires extremely low pressures outside the cell in figure 3.2: a significant number of collisions with other types of gaseous molecules would disrupt the formation of a molecular beam. To be more specific, the pressure in CBGB must be less than approximately $10^{-5}$ torr [2].

3.1.2 Our Source

We require that our source be capable of cooling the cell (and the buffer gas) to extremely low temperatures – typically 3 degrees K. This is accomplished via a
3.1 Producing the Helium Buffer Gas

Cryomech PT415 two-stage pulse tube cryocooler. This cryocooler is thermally attached to a chamber that can be cooled down to approximately $T_0 = 2.6K$. This chamber, in turn, is surrounded by a set of heat shields that keep the cell at low temperatures even as the experiment is conducted at room temperature. In particular, the cell is contained in a radiation shield, which is also held at about $4K$. The radiation shield, in turn, is held within another radiation chamber (held at $40K$), which in turn is surrounded by a $300K$ vacuum chamber.

As noted above, the CBGB must also be kept at low pressure. This is accomplished by a set of two Pfeiffer turbos: the HiPace 700 (685 Liters/second) and the HiPace 80 (67 Liters/second), which are arranged in series such that the smaller turbo reduces the pressure differential across the larger one. Moreover, this effort requires a method of monitoring the pressure. This is accomplished in two stages. Two Pirani gauges work at relatively high pressures (between 1 atm and $10^{-4}$ torr), and one IGM402YFD Hornet ionization vacuum gauge from InstruTech which is much more sensitive, and can monitor pressures as low as $10^{-9}$ torr. The former is very useful for checking the pressure when the experiment is not running or the vacuum is being either pumped down or broken. By contrast, the latter is useful for monitoring the pressure during the experiment.

Once the chamber is at the appropriate pressure and temperature, we can begin flowing the buffer gas through, as depicted in part a of figure 3.3. Our apparatus in particular uses helium gas, which is about as chemically inert as we can
3.1 Producing the Helium Buffer Gas

Figure 3.3: A schematic of the CBGB.

manage. We are free to pick the flow rate, and must balance two competing concerns: higher flow rates increase the extraction efficiency of target molecules into the beam (which is desirable), but also increase their forward velocity (which is not). High flow rates also compromise the low pressures we require for ballistic trajectories after the molecules leave the cooling chamber. We’ve found a flow rate of about 5 standard cubic centimeters per minute to be most appropriate.

As mentioned above, the next step is to introduce TlF molecules into the chamber by ablating a solid TlF target with a Nd: YAG laser. These molecules,
which are initially hot and gaseous, are rapidly cooled by contact with the helium. Most of these molecules end up on the cell wall [2]. However, some of them get entrained in the helium buffer gas and exit the chamber through the exit aperture. This exit aperture is a 0.25 inch hole. These exiting molecules are characterized by a significant velocity in the \( x \) direction and broad distribution of velocities in the \( y \) and \( z \) directions. Left alone, this would make a rather poor beam, and so the molecules are collimated by another slit (with the same dimensions as the aforementioned exit slit) further along in the \( x \) direction.

One last detail of maintenance bears mentioning. If the apparatus as currently described were repeatedly run, helium that does not leave the CBGB source as part of the molecular beam would accumulate within the temperature shields due its their high vapor pressure. Left alone, this buildup would eventually make the experiment impossible – the TIF molecules would no longer follow ballistic trajectories. To deal with this complication, we have epoxied coconut charcoal to the cell wall, which can absorb the excess helium.

### 3.2 The Interaction Region

The interaction region contains the beating heart of the experiment, and is depicted in the figures below. The interaction region contains the space in which the aforementioned molecules interact with our UV laser to produce the desired
3.2 The Interaction Region

fluorescence (which is, of course, what we’re ultimately measuring). We’ll examine the different parts of the region from left to right (as shown in figure 3.2), or, equivalently, chronologically from the molecules’ perspective. The collimating slit, labeled in figure 3.2, blocks all TlF and He atoms with large components of their velocity in the y or z directions. Thus, the slit produces a fairly well-collimated beam moving at approximately 150 m/s in the +x direction. Additionally, this beam also contains primarily very cold atoms, as specified above. The helium atoms, because they’re chemically inert and have no transitions at the frequency of our UV lasers, can be ignored. The TlF’s temperature means that the TlF molecules primarily populate the low level rotational and vibrational states, so there are many molecules available for the $X^1\Sigma^+(\nu = 0)(J = 1) \rightarrow B^3\Pi_1(\nu = 0)(J' = 1)$ transition that we’re interested in. The TlF beam then enters the center of the interaction region, where it begins to interact with the multi-pass.

3.2.1 The Multipass

First, let’s explain exactly what we mean by a multipass. In order to extend the path length of our laser (and thus the region in which molecules can interact with it), we fold the beam length in on itself as it passes through the interaction region. As seen in figure 3.4, we reflect the beam repeatedly off of two quartz
prisms in order to get the multipass effect. We often operate such that we have 9 passes (that is, the beam passes through the chamber 9 times). 9 passes strikes a good balance between two competing effects: more passes increases the region in which the molecule sees the highest intensities, but also causes clipping on the sides of the prisms.\footnote{In order to increase the number of passes one has to move the input beam (depicted on the far-left side of figure 3.4) closer and closer to the edge of the prism. This inevitably causes clipping.}

It’s desirable for the molecules to pass through a section of light that is simultaneously long, bright, uniform, and orthogonal to the molecular beam. We want...
more passes such the molecules can repeatedly interact with the beam as they move through the interaction region, brightness for the sake of interacting with every available molecule in our sample, and uniformity for the dual purpose of optimizing our Rabi frequency (see Appendix B for more details) and improving experimental precision. However, our laser is a narrow beam of light. One way of compensating for the laser’s lack of width is to reflect it back into the chamber. Another way of compensating is by increasing the width of the beam, which we accomplish Edmunds Optics beam expander. We use this to expand the beam by a factor of approximately 2.35. Unfortunately, this relatively simple multi-pass has a two main problems. Firstly, it isn’t particularly uniform across the whole chamber: there are spots of distinctly more and less intensity, which visibly shows up in the data, as shown in figure 3.5. This occurs because as the laser light moves through the multi-pass (and repeatedly reflects off the prisms), the laser both loses power and becomes increasingly diffuse. This causes the sharp differential between the signals of the first and second left-most peaks in figure 3.4. This, in turn, makes it impossible to optimize for a Rabi frequency. Secondly, this multipass’ intensity not only decreases over the course of the multipass, it also has several directly dark spots (also visible in figure 3.4). This occurs because the beam width isn’t wide enough to intersect itself on successive multi-passes. To solve these problems, we’ve constructed the multipass depicted in figure 3.6. We’ve added an additional two prisms, each directly above or below the previous
3.2 The Interaction Region

Figure 3.5: A picture of the TlF fluorescence under the old multi-pass, with clear effects from the lack of uniformity.

prisms. As illustrated, the ‘flat’ (i.e. perfectly horizontal) multipass is identical to the one used in the simple multipass above. We’ve added a ‘tilted’ multipass that comes down at an angle and intersects the flat multipass in the center of the chamber – which is where both of them intersect with the molecular beam. This architecture allows us to add a second multi-pass, layered on top of the one we already have. Moreover, we’ve been able to slightly offset this multi-pass, such that the molecular beam is always interacting with some part of the UV light. This does a great deal to alleviate the lack of uniformity within the chamber – and the effects of this can be seen in figure 3.7. In contrast to our old data, the new data’s fluorescence decay is much more uniform. We can also be quite certain that the multi-pass is filling in the gaps: we see in figure 3.8 that any of the individual multi-passes (either the flat or the tilted variant) retains the
3.2 The Interaction Region

Figure 3.6: A view of the interaction region, with a focus on the multi-pass, from the side.

Figure 3.7: A picture of the fluorescence in the overlapped multipass.
Figure 3.8: We see here the fluorescence caused by each multi-pass. With respect to the diagram in figure 3.5, the blue curve represents the fluorescence of the flat (purely horizontal) pass, and the orange curve represents that of the tilted pass.

old problems. Additionally, at the end of the multipass, we reflect the beams back onto themselves, introducing retro-reflections that increase the total power present in the interaction region. This helps to homogenize the intensity of the passes: the strongest retro-reflections overlap the weakest passes, and vice versa. Fortunately, the beams are sufficiently weak and diffuse that they don’t cause any optical feedback when they propagate backwards in this manner.
3.2 The Interaction Region

3.2.2 Cycling Estimate

With the apparatus design in mind, we can also make an estimate of how many cycles we can expect the TlF molecules to complete while traveling through the multipass. The multipass is spread over about an 1.5 inches in the x axis, and fills most of this space with light. The molecular beam travels at approximately 150 m/s, and we can use these two pieces of information to estimate that the molecules will interact with laser light for approximately 100 µs. As noted in the previous chapter, the $X^1\Sigma^+(\nu = 0) \rightarrow B^3\Pi_1(\nu = 0)$ transition has a lifetime of approximately 100 ns. If we suppose that it will take 10 lifetimes for a molecule to cycle through available ground states, which would be consistent with previous cycling experiments, we get a limit of approximately 169 optical cycles from our interaction length. Within this approximation, there would be adequate time to complete our (hoped for) average of 100 cycles per molecule.

3.2.3 Detecting Fluorescence

The pieces of the apparatus explored thus far allow us to drive $X^1\Sigma^+(\nu = 0) \rightarrow B^3\Pi_1(\nu = 0)$ transitions in the interaction region – but we also must detect the resulting fluorescence. We do this by focusing a solid angle of the fluorescence, as shown in figure 3.9. We first collimate this light using a concave lens, then pass it through a 50 mm UV transmitting glass broad band filter that blocks...
Figure 3.9: A schematic of our detection apparatus, which works by capturing fluorescence from the interaction region, passing it through an UV transmitting filter, and focusing it into a camera.

ambient and background light. We then re-focus this light with a concave lens into a Pimax 2 (7489-0025) UV sensitive camera. The camera takes two pictures for every beam of TIF molecules that pass through the interaction region. The first picture is taken over the entire time the molecules are in the region, and the second is take after they’ve left. By subtracting the latter from the former, we can remove background light.
3.3 Additional pieces of equipment

3.3.1 The UV Lasers

Perhaps the most important pieces of equipment we have are our two lasers. Our first laser, and our only available one for the majority of this thesis, is a continuous-wave ytterbium fiber laser with a kilohertz line width (CYFL-KILO) from Keopsys, as shown in figure 3.10 [17]. This fiber laser has low noise and a narrow linewidth seed (< 70 kHz), and produces light at 1086.8 nm. It can be tuned over approximately 716 GHz.

This laser produces two beams at the same infrared frequency. The first laser, the main beam is sent into a TA-FHG Pro, which quadruples the frequency of the laser to 271.1 nm. This process is notably inefficient, turning 300 mW of IR light to about 20 mW of UV light. The other beam – a weak monitor beam – is
3.3 Additional pieces of equipment

Figure 3.11: A schematic of both the fiber laser and the frequency quadrupler for the first laser.

split into two by a beam splitter. One beam is directed into a wavemeter, which reads out the frequency (to within a few hundred MHz). The second beam is sent into a Fabry-Perot cavity, which is locked to a stable helium-neon laser from Laboratory for Science (model number 210). The fiber laser is then locked to the cavity, which allows precise control over the frequency, and minimizes drift. Our second laser is similar. It’s an external cavity diode laser from Toptica, and can ultimately produce UV laser light between 271 and 278 nm at 80 mW of power when the frequency is quadrupled. As above, there is a weak monitor beam that is split into two and sent into both a wavemeter and a Fabry-Perot cavity, as detailed above. We’ve overlapped their beams such that they follow the
3.3 Additional pieces of equipment

Figure 3.12: A schematic of the FHG (Fourth Harmonic Generator) and master laser for the second laser.

Figure 3.13: A picture of both lasers, with the first on the left, and the second, more powerful system, on the right.
3.3 Additional pieces of equipment

Figure 3.14: A picture of the acousto-optical modulator.

same path through the following components. Before sending the beam into the interaction region, we can send it through an acousto-optic modulator (henceforth AOM)\(^1\). We pass the beam through a phase EOM, which modulates the phase of the beam, which is then passed through the aforementioned Edmunds Optics beam expander, which we use to expand the beam by a factor of approximately 2.35\(^2\). This expansion serves two purposes. Firstly, it’s useful for optimizing our Rabi frequency because it helps us achieve an average intensity that is closer to optimal. Secondly, the beam’s expansion helps to illuminate a larger portion of the molecular beam’s path with UV laser light, ensuring that more molecules can make the \(X^1\Sigma^+ (\nu = 0) \rightarrow B^3\Pi_1 (\nu = 0)\) transition, thus increasing our fluorescence.

\(^1\)If we opt not to use the AOM, it can be bypassed with flip mirrors. This helps save power.

\(^2\)Strictly speaking, the beam expander is set to (6.2, J.6), which yields an expansion factor of 2.35.
3.3 Additional pieces of equipment

Finally, we pass the UV beam through an electro-optic modulator (henceforth EOM) from Conoptics, part number (350-80-DUV), shown in figure 3.15. The EOM modulates the beam’s polarization (between two orthogonal polarization) at 1 MHz. The beam makes a single pass through the EOM before proceeding into the interaction region.

3.3.2 Microwaves

3.3.2.1 Microwave Motivation

In order to further increase both the rate of optical cycling and the population available for cycling, we introduce microwaves into the interaction region using the two horns shown in figures 3.16 and 3.17.

The microwaves are generally set to 13334.6 GHz, the frequency necessary to
3.3 Additional pieces of equipment

Figure 3.16: A picture of the larger, and more commonly used, microwave horn. The input for the vertical microwaves faces the camera, and is labeled 'V'. The input for horizontal microwaves is on the side of the horn.
mix the $J = 0$ and $J = 1$ ground states. The principal idea behind the increased cycling rate is that when we are driving a Q(1) or R(0) transition, the microwaves can move molecules stuck in a hyperfine or polarization dark state to a bright state [17]. To help facilitate this, we rapidly modulate the polarization of the microwaves between two orthogonal polarizations using a switch.

The microwaves also increase fluorescence through population transfer: molecules that would otherwise never be excited by a particular transition get mixed into bright states and then start cycling themselves. The extent to which this population transfer increases fluorescence is directly equal to the total number of molecules excited by the UV laser when microwaves are on divided by the total...
3.3 Additional pieces of equipment

Table 3.1: Population Transfer on Q(1) and R(0) Transitions Driven by Two Polarizations [17]

| Transition $|F',F'\rangle$ | Excitable $J = 0$ States | Excitable $J = 1$ States | $M$ |
|-----------------|-----------------|-----------------|-----------------|
| R(0) $|1/2,0\rangle$ | 2 | 0 | 7.03 |
| R(0) $|1/2,1\rangle$ | 4 | 0 | 3.51 |
| R(0) $|3/2,1\rangle$ | 4 | 0 | 3.51 |
| R(0) $|3/2,2\rangle$ | 3 | 0 | 4.68 |
| Q(1) $|1/2,0\rangle$ | 0 | 4 | 4.19 |
| Q(1) $|1/2,1\rangle$ | 0 | 12 | 1.40 |
| Q(1) $|3/2,1\rangle$ | 0 | 12 | 1.40 |

number excited without microwaves ($\frac{N_{total}}{N_{no-microwaves}}$).

For all Q(1) and R(0) transitions, the total number of molecules mixed into bright states is equal to the total number of molecules in the J=0 and J=1 ground states. Though we probably can’t find the exact number of molecules in each, we can easily estimate the relative populations using the Boltzmann factors $e^{-E(s)/kT}$ and the state degeneracies. A summary of these results is shown in table 3.1, which shows the microwave population transfer factor as a function of state and transition.

3.3.2.2 Microwave Apparatus

We can now move directly into the equipment we use in order to produce the microwaves. The 13.3 GHz signal is produced by a SynthHD synthesizer from WindFreak Tech, which then outputs two signals. The synthesizer outputs a -6.5 dBm signal, which is raised to 38 dBm by a preamp and a power amplifier.
3.3 Additional pieces of equipment

Figure 3.18: A picture of the equipment we use to generate microwaves, with individual parts labelled.

This signal is then split by a switch, which operates at 1 MHz, 90 degrees out of phase with the laser polarization modulator. These signals are then sent into the orthogonal polarization inputs of a dual polarization horn antenna, which switches the microwaves between two orthogonal polarizations. As seen in figure 3.15, the larger horn is set to shine microwaves into the interaction region at an angle 45 degrees to the x and y axes. This results in microwaves that are polarized along the z axis and along the axis in the xy-plane perpendicular to the direction of microwave propagation [17].

The smaller horn receives a 6 dBm signal from the synthesizer, which is then passed into a pre-amp, which raises the power to 24.3 dBm. The horn then outputs microwaves of this power into the interaction region.
Chapter 4

Methods and Results

4.1 Standard Candles and Photon Counting

4.1.1 Motivation

Though we’d like to measure the amount of cycling the Q(1) $F_1 = 1/2$ $F' = 1$ transition does, it’s difficult to do this directly. Instead, we take data on the amount of fluorescence produced by the molecules on a pair of transitions, and then, from their relative intensities, compute the amount of cycling using one of the transitions as a standard candle.
4.1 Standard Candles and Photon Counting

4.1.2 Methods

As covered in the Theory section, the Q(1) $F'_1 = 1/2$ $F'' = 1$ (henceforth known as Joe) transition is one of the only transitions that has the capacity to cycle many times and has a large peak height. Borrowing astronomy’s vocabulary, we compare its fluorescence to the fluorescence of another transition with a known number of cycles. By comparing these, we hope to find the number of cycles that Joe completes: it seems straightforward that if our known transition does 5 cycles per molecule, and that Joe is five times as bright, Joe does 25 cycles. In effect, we try the following:

$$\frac{F_{Joe}}{C_{Joe}} = \frac{F_{SC}}{C_{SC}} \rightarrow C_{Joe} = \frac{F_{Joe}}{F_{SC}}C_{SC}$$  \hspace{1cm} (4.1)

Where $F$ is the measured fluorescence, $C$ is the amount of cycling per molecule, and SC stands for Standard Candle. Though it appears straightforward, there are some hidden assumptions in that calculation that we need to unpack. Fluorescence is proportional to more than just the number of cycles per molecule (e.g. fluorescence is dependent upon the number of molecules excited).

Ultimately, we expect the fluorescence ($F$) to depend on the laser power ($P$), the number of cycles per molecule ($C$), the population enhancement due to microwaves ($M$), and the degeneracy of the bright states that are excited by the
4.1 Standard Candles and Photon Counting

transition \( D \). Thus,

\[
F \propto PCMD
\]  

This proportionality also gives us some hints as to good standard candles. The \( Q(1) \) \( F'_1 = 3/2 F' = 1 \) transition (henceforth known as Cephy, short for the Cepheid Variables that astronomers use for standard candles) has the same values of \( M \) and \( D \) that Joe does, allowing us to instantly ignore those factors.

The fluorescence should only be dependent on the laser power in the case that the transition isn’t saturated. If the transition is saturated (and more laser power doesn’t increase the fluorescence or peak height), then we should safely be able to ignore this part of the proportionality. Fortunately, we have data that suggests exactly that. For Joe, we see that the power dependence levels off, and that at our maximum power we’re nearly at the peak of fluorescence. This is illustrated best in figure 4.1. For Cephy, we can more directly claim that the laser power doesn’t impact the fluorescence because we already cycle all the molecules that we possibly can. Firstly, our experimental data suggests this: figure 4.3, a typical plot of Cephy, illustrates that Cephy only fluoresces for the first part of the multipass, implying that all molecules fall into permanent dark states. This also lines up with our theoretical predictions. Molecules in the \( Q(1) \) \( F'_1 = 3/2 F' = 1 \) state transition to the rotational dark state \( J = 3 \) approximately 14.0% of the time [17]. This is more than sufficient to to cycle out nearly every molecule in the
Figure 4.1: A plot of laser power against total fluorescence for the Joe transition. The relevant power is that going into the flat multipass. Notably, our fluorescence is plateauing.

sample. Lastly, we have \( C \), the number of times the transition cycles. Though the fluorescence is clearly proportional to \( C \), we do have to assume the number of times our standard candle Cephy transitions. We do this by assuming the branching ratio of Cephy (the aforementioned 14.0% chance to land in the dark \( J = 3 \) state) dominates. This implies that Cephy cycles 7.14 times per molecule. All of this, then, gives us our method for determining the number of times Joe cycles – we take the ratio of Joe’s fluorescence to Cephy’s fluorescence and then multiply by 7.14 to get the number of photons per molecule cycled by Joe. \(^1\)

\(^1\)Unfortunately, this isn’t quite the whole story. The ablation efficiency of the TlF target we use falls off in an unpredictable manner, with frustratingly high noise. We counteract this by taking two pictures of each transition, and bookending the pictures of Joe with 2 sets of pictures of Cephy (which we then average).
4.1 Standard Candles and Photon Counting

Figure 4.2: Left: The raw image coming from a picture of Cephy. Molecules enter from the left side of the screen, and move right. Both the x and y axes are in units of pixels, and the color of each point represents the value that the cell of the CCD outputted. Right: the column-wise sum of the raw image. Importantly, we see that only the first few passes of Cephy fluoresce. The red line is an exponential fit to the data. This suggests that the molecules are in permanent dark states by the end of the multipass. The image on the left contains a visible line down the middle, which is noise from the visible light in the room.

4.1.3 Results

A full analysis of figure 4.3 can be seen in table 4.1. We alternated between pictures of Cephy and Joe, taking three of the former and two of the latter. We took the total fluorescence from each of these, and used those to compute the: average fluorescence for each transition, along with the maximum and minimum of each transition. From there, we calculated the average number of photons (from the average fluorescence of both Joe and Cephy), along with the smallest and largest number of photons. We took the difference between these and the average to be the lower and upper bounds of our instrumental error, respectively. Our average suggests 43 (-3/+5) photons per molecule. Happily, this is an increase
4.2 Calibration of the Optical System

4.2.1 Motivation

Unfortunately, our optical system and the Pimax 2 (7489-0025) UV sensitive camera we use doesn’t have a uniform detection efficiency. This poses a particular
Table 4.1: A table tabulating our corrected fluorescence for the different transitions along with the associated errors.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Microwave A</th>
<th>Microwave B</th>
<th>Phase</th>
<th>Polarization</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cephy</td>
<td>ON</td>
<td>OFF</td>
<td>ON</td>
<td>ON</td>
<td>8561419</td>
</tr>
<tr>
<td>Joe</td>
<td>ON</td>
<td>OFF</td>
<td>ON</td>
<td>ON</td>
<td>47987347</td>
</tr>
<tr>
<td>Cephy</td>
<td>ON</td>
<td>OFF</td>
<td>ON</td>
<td>ON</td>
<td>8175348</td>
</tr>
<tr>
<td>Joe</td>
<td>ON</td>
<td>OFF</td>
<td>ON</td>
<td>ON</td>
<td>49504036</td>
</tr>
<tr>
<td>Cephy</td>
<td>ON</td>
<td>OFF</td>
<td>ON</td>
<td>ON</td>
<td>7138987</td>
</tr>
</tbody>
</table>

Cephy's fluorescence is almost exclusively in the first quarter of the image (by which we mean the left-most quarter of the image). By contrast, Joe's fluorescence persists throughout the interaction region. If the camera were much more sensitive to light on its' right side, our standard candle measurement of $\frac{F_{\text{Joe}}}{F_{\text{Cephy}}}$ 7.14 would overestimate the number of photons per molecule that Joe cycles. Similarly, the divergence of the molecular beam might cause a spacial dependence that would decrease the intensity of Joe more than Cephy.

4.2.2 Methods

The easiest way to adjust for the optical system's variable efficiency was to build up a model of the efficiency as a function of the x coordinate (horizontal distance...
4.2 Calibration of the Optical System

Figure 4.4: A picture of the physical rail and mirror combination that allowed us to calibrate the camera.

in the image), and then to directly account for it in our fluorescence calculations\(^1\).

To that end, we decided to take pictures of the fluorescence from a single laser beam that intersected the molecular beam at different points across the chamber. These pictures should have had the same fluorescence values (since the beam is functionally the same at different points in the chamber absent laser interactions), and so we can compare these values in order to find the optical system’s efficiency as a function of x.

We began by installing a mirror on a rail that allowed us to precisely control where the single laser beam entered the interaction region and where it intersected the molecular beam, pictured in figure 4.4.

\(^1\)Notably, we built up a model based only on distance across the camera (the x coordinate) because we apply the correction to the summed data along the y axis.
4.2 Calibration of the Optical System

Figure 4.5: Single pass images of Q(1) $F'_1 = 1/2$ $F'' = 1$ upper splitting, which was chosen because of its large signal, at different horizontal positions to be used for calibration. This was accomplished by altering where the laser entered the interaction region. The left to right, top to bottom order denotes the (semi-randomized) order of that data.

In the chamber, pictured in figure 4.5.

We took multiple pictures at each point to deal with the complicating factor of decreasing ablation efficiency. By repeatedly photographing the fluorescence at various points, we were able to average the results and obtain fairly precise values to be used for calibration.

In order to increase our confidence in these values, we fit the decay due the decrease in the ablation efficiency for a particular position of the mirror on the rail to an exponential.
4.2 Calibration of the Optical System

Figure 4.6: Left: The unfitted fluorescences, where number denotes the semi-randomized order in which the pictures were taken. Right: The same fluorescence values, adjusted for the decay of the ablation spot.

Figure 4.7: The result of our camera calibration. This mask, once applied, adjusts for the variable efficiency of our optical system. Notably, the mask is lower at the edges: this means that the optical system has a particularly low detection efficiency there. More specifically, because the mask was normalized to have its peak at 1, the camera only has 65% efficiency at its edges.

We then fit adjusted the fluorescence values to this exponential fit, the results of which are shown in figure 4.7. These values were then used to form the mask shown in figure 4.8.

4.2.3 Results

The mask has its most dramatic effects at the edges of our images because of the particularly low detection efficiency there. This can be directly observed in
4.2 Calibration of the Optical System

Figure 4.8: Bottom Left: The uncalibrated raw image of Cephy. Bottom right: The calibrated raw image of Cephy. Top Left: Both the integrated calibrated and uncalibrated signals, integrated over the y-axis. Top right: Both the integrated calibrated and uncalibrated signals, integrated over the x-axis.

This calibration has tended to decrease our estimate of relative photon counts by a few photons. Cephy is disproportionately bright in the parts of the image where the correction is largest, and so (relative to Joe) also has its fluorescence disproportionately increased. Joe’s signal, by contrast, is distributed throughout the interaction region. Nonetheless, this calibration has given us more confidence in our results and decreased our error. This correction has already been applied to acquire the 43 photons per molecule estimate quoted in the previous section.
4.3 Exotic Multipass Configurations

4.3.1 Motivation

Though it’s already been discussed in the theory and apparatus sections, we’ll take a moment here to briefly review what our current multipass configuration is. Over the course of the semester we moved from a traditional multipass configuration to the setup shown in figure 4.10. We effectively added another ‘tilted’ beam in addition to the ‘flat’ beam that was already present in the earlier multipass. These are analogous to the red and orange lines, respectively, shown in figure 4.10. This new multi-pass setup has both increased our interaction region and helped us homogenize the intensity in the interaction region (which, in turn,
4.3 Exotic Multipass Configurations

Figure 4.10: A view of the interaction region, with a focus on the multi-pass, from the side.

should let us do things like optimize the Rabi frequency). Both of these effects should have increased our photon count, and we have some evidence that they did exactly that.

4.3.2 Methods

In order to test out the efficacy of our new multi-pass, we performed standard candle measurements as described above in three ways in succession: firstly with only the flat passes (which is analogous to our old multipass); secondly with only the tilted passes (again analogous to the old multipass); and finally with both of them together. This allowed us to isolate the effects of adding the new multipass, and help support the conclusion that the effect was caused by an increase in the size of the interaction region. The plots of these results are shown in figures 4.11
4.3 Exotic Multipass Configurations

Figure 4.11: Plots of the fluorescence found by the camera using only the flat multipass. We performed a standard candle measurement (measuring Cephy, then Joe, then Cephy again), and found that using only the flat multipass corresponded to an average of 32 photons per molecule.

through 4.13. All of these figures have three columns. The first column, as in previous sections, shows the raw fluorescence values recorded by the camera, and both axes are in units of cells in the camera’s CCD. The second column records the column-wise sums of the first image. The third column records the settings under which each picture was taken, where each setting is recorded as [Setting]: [Value] .

To make an exhaustive list of the setting meanings: "Microwave A” is a boolean variable that records the on/off state of the big microwave horn; ”Microwave A Frequency” records the value of the large microwave’s frequency; ”Microwave A Power” records the power (in dBm’s) of the signal the synthesizer outputs; ”Microwave B”, ”Microwave B Frequency”, and Microwave B Power” record exactly the same things for the smaller microwave horn; ”Phase” records whether the phase EOM was on or off; ”Transition” records the transition being cycled; ”Polarization” records the polarization of the UV laser light (e.g. off, circular, etc); ”Pic number” records the label of each picture, which we use to organize them; ”Total” records the sum of the fluorescence in every CCD cell; ”maxAve” records the average values of the 30 points nearest to the column-wise sum’s peak; ”minAve” records the average of the last 30 points; ”percentRemain” is the minAve divided by the maxAve (percentRemain thus actually records the fraction remaining); ”Flat Pass” records the number of flat passes; ”Tilt Pass” records the number of passes in the tilted multipass.
4.3 Exotic Multipass Configurations

Figure 4.12: Plots of the fluorescence found by the camera using only the tilt multipass. We performed a standard candle measurement (measuring Cephy, then Joe, then Cephy again), and found that using only the tilt multipass corresponded to an average of 29 photons per molecule.

Figure 4.13: Plots of the fluorescence found by the camera using both multipasses. We performed a standard candle measurement (measuring Cephy, then Joe, then Cephy again), and found that using the full tilt+flat multipass corresponded to an average of 43 photons per molecule.
4.3 Exotic Multipass Configurations

4.3.3 Results

We note that, though the fluorescence (and photon count) both increased when we doubled the path length, the percentage of molecules available to cycle at the end of the multipass in the overlapped multipass raises further questions.

First, let’s model the drop-off of the fluorescence as an exponential of the form $e^{-kx}$. The area under an exponential of this form for length $a$ is $(\frac{1}{k})(1 - e^{-ka})$.

Let’s further model the interleaved multipass as having double the path length of the flat or tilt multipass. The ratio of the fluorescence from the interlaced multipass to the flat (or tilt) multipass, which amounts to approximately $\frac{43}{30}$, is, in this model, $(\frac{1}{k})(1 - e^{2ka})$. This implies that $ka$ is approximately .84. This would suggest that 43% of the molecules should remain available to cycle in the flat or tilt multipass, and 18% should remain for the interleaved multipass. This matches up quite well with the data from the flat (which left 43% and 39% of molecules remaining to cycle) and the interleaved (which left 19%) multipasses, but doesn’t match the tilt multipass (which only left 23%).

Additionally, this data may point to an additional loss mechanism. If we’re cycling 43 photons per molecule with 18 passes and leaving 19% of the molecules the branching ratio isn’t 1%, it’s nearly 4% ($(0.962)^{43} = 0.19$).

Ultimately, the new multipass has clearly increased our photon count per molecule while not substantially increasing the size of the apparatus. This makes it a
4.3 Exotic Multipass Configurations

useful innovation, which may well be included in the final CeNTREX apparatus. Moreover, it has given us some clues about why it increased our photon count. The increase was most likely associated either with improved intensity uniformity or with an increase in the path length. Moreover, though we can’t rule out the former, the theoretical match between an exponential decay illustrated above and our experimental results suggest that the latter explanation may be more likely.
Chapter 5

Conclusions and Future Work

5.1 Conclusion

Detecting each molecule with near unit efficiency is a necessary prerequisite to the CeNTREX experiment. To that end, we implemented a multipass with twice the effective interaction length, calibrated the optical system we use to decrease error, included a higher-power laser and investigated its effects on the multipass, and further investigated the effects of microwaves on fluorescence (which is detailed in Appendix A). In sum, these efforts have amounted to an increase in photons per molecule from approximately 30 to approximately 43: more than enough to detect every molecule (on average) with a well-designed optical system. Moreover, we’ve also decreased the error in this experiment, and identified at least part of what was limiting us before (the size of the interaction region and the power spread throughout it). The main limitation we’ve found on our cycling seems to be the slow cycling rate: previous work has shown it to be smaller than naive expectations, and even more evidence has compounded that suggests the same
[17]. Though the slow cycling rate shouldn’t pose a problem for unit detection efficiency, it is problematic for future efforts to apply optical forces to Thallium Fluoride.

5.2 Future Directions

5.2.1 Near Term

In the immediate future, we’d like to use both of our lasers on the TlF molecular beam at the same time. This opens up several possibilities for us. Firstly, and most immediately, it gives an increase in power. Secondly, it would allow us to drive two transitions at the same time.

This might allow us to further investigate dark states by driving the Q(1) \( F'_1 = 1/2 \) \( F'_1 = 0 \) state as we drive Joe: the two should have distinct dark states, which would be a major step in understanding exactly how those dark states affect our photon cycling rates. Even beyond that, we could use one of the lasers as a repump for the 1% vibrational branching to \( \nu = 2 \) from Joe. We could then use the way this affects our fluorescence to get more information about the cycling rate. To give a concrete example, we know that the repump laser should decrease our branching fraction by about 1% by closing off a vibrational dark state. If, as suggested in the previous section, we are really losing 4% of our molecules every cycle, then a repump laser, which will change this to 3%, would cause us to have approximately 27% of molecules cycling by the end of the path length.
5.2 Future Directions

(assuming we still cycle 43 photons – (0.97)^43 = 0.27). By contrast, if we were losing 2% of our molecules every cycle, then the repump laser would cause us to have approximately 42% of the molecules cycling at the end of the path length ((.98)^43 = .42). We also expect to see a fairly dramatic increase in overall number of photons cycled.

Still in the near term, we’d like to understand exactly how the microwaves are changing the cycling rate, as discussed in Appendix A.

5.2.2 Long Term

Farther in the future, we’d like to exert optical forces on Thallium Fluoride. This step would involve changing our setup to one in which, rather than having multipasses that interact with the molecular beam from either the +y direction or the -y direction, all light comes from one side of the multipass. With 100 cycles per molecule, the molecular beam could be noticeably deflected in the direction away from the light.

We’d also like to try transverse cooling TlF. By changing the apparatus such the the UV laser points into the molecular beam on two sides (e.g. both the positive and negative y directions of the interaction region), and tuning each laser’s frequency such that each preferentially addresses the molecules moving in the negative and positive y directions, respectively. Unfortunately, this would require both a reconstruction of our apparatus and quite a bit of cycling, and so
remains a goal for the future, at least for the moment.

Our final goal for this experiment would be to completely Doppler cool the molecules, which would further increase the sensitivity of a future generation CeNTREX experiment by allowing a magneto-optical trap to be built. This goal would require approximately 23000 cycles, which would itself require repump lasers for the $\nu = 2, 3, 4$ states. Nonetheless, this would grant the CeNTREX collaboration additional orders of magnitude in precision.
Appendix A

More on Microwaves

We have some evidence to believe that the microwaves are doing more than we expected – that is to say, they’re doing more than just transferring population. Instead, they seem to change the characteristic shape of the fluorescence vs. position plots we’ve shown thus far. This suggests that the microwaves may be changing the rate of the decaying exponential, or even decreasing the time that molecules spend in dark states.

We know that 13346.6 MHz is the resonant frequency for the microwave transition (as seen in figure A.1), and scanned around that frequency in order to get some idea of what off-resonance microwaves do. The results of this experiment are seen in figure A.2.

It’s clear that the 1st and 5th pictures, which were taken with microwaves off, and the 7th picture (which was taken with microwaves tuned far off resonance) have a different characteristic decay than most seen thus far in this thesis (or even in this picture) in their column-wise sum (second photo). Rather than following
Figure A.1: A plot of the fluorescence against the microwave frequency. This clearly illustrates that 13346.6 MHz is the resonant frequency for the microwave transition.

Figure A.2: Pictures of Joe were taken with the microwaves at the following frequencies (in MHz, in order of appearance): OFF, 13318.6, 13302.6, 13366.6, 13250, 13334.6, 13334.6, OFF. 13334.6 is the resonance of the microwave transition.
an exponential decay, they seem to partially follow an exponential decay, and then enter into a new steady state.

We don’t know exactly what causes this, but one explanation is that the microwaves really are destabilizing at least one dark state. The plot would enter a new ‘steady state’ because the remaining molecules in the dark states evolve into the bright states only very slowly. Unfortunately, this doesn’t explain why the microwaves don’t improve our standard candle measurement (as an increase in cycling ought to). One possibility is that the microwaves spoil the selection rule by admixing an opposite parity state into the ground state and hence open a new decay channel that counteracts the benefit to cycling to within our experimental sensitivity.
Appendix B

Rabi Frequencies

B.1 Velocity Classes and Doppler Detuning

As will be covered in the apparatus section, our Thallium Fluoride source creates a molecular beam with a broad distribution of velocities (despite our attempts to limit this). Moreover, since we’re exciting the molecules, we also have a Doppler broadening of the spectral lines caused by the cumulative effect of the Doppler effect over the entire distribution of velocities [15].

In order to prove this to ourselves, let’s go through the standard derivation. For non-relativistic cases, the Doppler shift will be:

\[ v = \left( \frac{f}{f_0} - 1 \right) c \]  

(B.1)

where \( f \) is the observed frequency, \( f_0 \) is the rest frequency, \( v \) is the velocity of the emitting particle, and \( c \) is the speed of light. In the case of a distribution of particles (in which \( P_v(v)dv \) is the fraction of particles with velocity between \( v \) and \( v + dv \) in the relevant direction), our distribution over frequencies becomes:
\[ P_f(f) df = \frac{c}{f_0} P_v(v) df \]  \hspace{1cm} (B.2)

This will clearly broaden the frequencies we see, but to give a concrete example, we note that in the case of a Maxwell-Boltzmann velocity distribution our expression becomes:

\[ P_f(f) df = \sqrt{\frac{mc^2}{2\pi kT f_0^2}} e^{-\frac{mc^2}{2kT f_0^2} \left( f - f_0 \right)^2} \]  \hspace{1cm} (B.3)

Which we recognize as a Gaussian profile. This Doppler broadening causes each velocity class of molecule to appear have a different resonant frequency, and in sum spreads that resonant frequency (for our transition) out.

Now that we understand how our spectral lines spread out, we can move into understanding Rabi frequencies and why they limit us.

**B.2 Rabi Frequency and a Toy Model**

We’ve previously noted that our number of transitions (and consequently our photon count) is limited by the speed at which the dark states evolve into bright states. In order to try and account for this, we can make a toy model of a simpler system that hopefully captures some of the essential physics and points us in the direction of a solution.
B.2 Rabi Frequency and a Toy Model

B.2.1 What’s a Rabi Frequency?

A Rabi frequency is simply the, ”frequency of oscillation for a given atomic transition in a given light field” [12]. This is obviously and immediately relevant to our question of cycling (which we’d like to maximize, and may be limited by our cycling rates) and the question of our laser power (which affects the light field in the above definition).

The Rabi Frequency \( \chi_{i,j} \) between two levels \( i \) and \( j \) is:

\[
\chi_{i,j} = \frac{\vec{d}_{i,j} \cdot \vec{E}_0}{\hbar}
\]

(B.4)

In the above, \( \vec{d}_{i,j} \) is the transition dipole moment and \( \vec{E}_0 \) is the vector electric field amplitude (including polarization). The most important take-away here is that we can control the Rabi frequency by controlling our laser power, which directly changes \( \vec{E}_0 \). Because the Rabi frequency can effect the rate at which we move out of dark states, there may be some optimum laser power.

B.2.2 The Model

Fortunately, Jakob Kastelic, a graduate student at Yale university, has computed some results that suggest that this optimum power does in fact exist.

If the earlier parts of this section have been an assurance of anything, they should suggest this: Thallium Fluoride is complicated. Due to this inherent complexity, we use a simpler model that hopefully captures the relevant physics. Let’s imagine
B.2 Rabi Frequency and a Toy Model

Figure B.1: A schematic of the Rabi Frequency toy model. We have two unresolved ground states (of which, similar to TIF’s real structure, we can only excite superpositions) and one excited state. In the figure, we represent the ground state hyperfine splitting with $\Delta$, the laser frequency with $\omega$, the resonant frequency with $\omega_0$, the laser detuning with $\delta$, the Rabi frequency with $\Omega$, and the excited state decay rate with $\Gamma$. Reproduced from [9].

a system with two unresolved ground states (which will give us a dark state) and one excited state, as pictured in figure 2.11. Importantly, this model doesn’t have any rovibrational branching, and so we can analyze the ‘steady state’ population in any particular state (taken to mean the fraction of molecules on average in a state after a sufficiently long waiting time). If we represent the model in a density matrix and numerically solve the Liouville equation with particular parameters, we obtain the plot in figure 2.12: Moreover, we can directly obtain a link between Rabi-frequency and the excited state population, as shown in figure 2.13. All of this suggests that there is some relevant optimal laser power for the molecules. This, in turn, will help provide some theoretical backing to our results on novel multi-pass configurations.
B.2 Rabi Frequency and a Toy Model

Figure B.2: The plotted solution to the Louisville equation for the presented toy model. Each line represents the number of molecules in each state at a given time, with the excited state represented as $\rho_{ee}$. Reproduced from [9].
B.2 Rabi Frequency and a Toy Model

Figure B.3: A plot of the theoretical relationship between Rabi Frequency and the steady-state population in the excited state. Because Rabi frequency is directly related to the amplitude of incoming light, this also suggests an optimal laser power. The plot also illustrates that every different velocity class has a different detuning (and consequently a different optimal laser power). Reproduced from [9].
References


REFERENCES


