Progress Towards a Measurement of the Electric Dipole Moment of the Electron using PbO*
Abstract

Progress Towards a Measurement of the Electric Dipole Moment of the Electron using PbO*

Sarah Rachel Bickman
2007

We have proposed and begun implementing an experiment to look for an electric dipole moment (EDM) of the electron, \( d_e \), using the metastable \( a(1)^3\Sigma^+ \) state of the PbO molecule. A non-zero measurement of \( d_e \) within the next few orders of magnitude beyond the current limit of \( |d_e| < 1.6 \times 10^{-27} \text{ e-cm} \) [1] would be clear evidence for physics beyond the standard model. We have designed and built a stable apparatus for the measurement of \( d_e \) using PbO* in a heated vapor cell. Using this apparatus, the \( \Omega \) doublet splitting in the \( a(1) J=1 \) state was measured to be 11.214(5) MHz. Without an applied electric field, the difference in \( g \)-factors between the \( \Omega \) doublet states was found to be \( \delta g = 31(9) \times 10^{-4} \). Measurements of the Stark shift were found to be consistent with previous measurements [2]. The counting rate has been optimized and agrees with models. Three different types of detectors with associated low-noise preamplifiers were built and tested. To improve the sensitivity, an alternate detection scheme using reexcitation to the \( C' \) state was explored and ultimately rejected in the form proposed here. In the first generation experiment, with the current fluorescence detection along the \( a(1) \rightarrow X \) transition, the expected sensitivity to an electron EDM is \( \delta d_e \approx 10^{-25} \text{ e cm/\sqrt{day}} \). Two proposals for second generation experiments are considered.
Acknowledgements

This work never could have been accomplished without constant support, advice, and kindness from many people. Most important, I would like to thank my advisor, David DeMille, who has been the best advisor I could have imagined. Despite the decade that we have worked together, his exceptional patience, skillful teaching, and brilliant ideas continue to amaze me. Without his guidance I would have left physics countless times, and I am exceptionally grateful for his continual encouragement. Working with him has been a privilege.

When it came time to form my thesis committee, it was obvious to me whom I wanted on it. I am grateful to these people not only for their time and advice on this committee, but also their time over the years. Steve Lamoreaux has helped us solve difficult problems, even before he came to Yale. I have learned much in discussions with Daniel McKinsey about how to design an experiment and make a better measurement. Thomas Appelquist's excellent explanations has made him an invaluable resource. Bonnie Fleming has been a mentor and opened up new kinds of physics to me.

I would also like to thank Larry Hunter who made some initial measurements on PbO, and since then has continued to provide advice on our more difficult problems. In addition, I would like to thank him for his years of patience and skill in teaching me as an undergraduate.

I have been fortunate to work with many talented, and supportive colleagues. I am grateful for our long friendships, and have learned much from all of them. David Kawall is the most persistent and careful person I have ever met. Paul Hamilton has consistently challenged me to think harder and work better. Yong Jiang can solve any computer or physics problem. This work never could have been accomplished without the help of many others: Frederik Bay, Valmiki Prasad, Yulia Gurevich, Amar Vutha, Richard Paolino, and Jordan Weil, and Hunter Smith.

There are many others who contributed to this work. Vincent Bernardo and the entire Gibbs
Machine Shop did much of the metal machining and advised on many of my designs. Sidney Cahn offered advice on electrical designs and many other issues. The entire DeMille group has cheerfully lifted shields on countless occasions and provided advice.

I am very lucky to have found a loving husband who is my equal in all respects, and who treats me as one. Daniel Farkas has become so much a part of my life that I cannot imagine being without him. I am looking forward to sharing our next adventure. It is an understatement to say that I am grateful to my parents. They have been my biggest source of encouragement and support and have shared every triumph and failure with me. They spent many years teaching me that “Education is not filling a bucket, but lighting a fire”—William Butler Yeats. I never could have dreamed of being here today without them. My brother, Jed, has made me laugh when all else has failed, and has been one of the most enthusiastic members of my fan club. My friends Benjamin Turek, Alexandra Gueydan, Stephen Maxwell, Iva Maxwell, and Dale Li have added much needed humor and have provided wise advice.
Contents

Acknowledgements iii

1 Introduction 1

1.1 Introduction ................................................................. 1
1.2 EDMs Violate Parity and Time Reversal Symmetries .......... 2
1.3 Direction of \( d_e \) .......................................................... 3
1.4 Overview of Relevant Particle Theory ............................. 4
1.5 General Method to Measure \( d_e \) ................................. 6
1.6 Enhancement Factors .................................................... 8
1.7 Enhancement Factor of PbO ......................................... 10
1.8 Relating a Measurement of the EDM of PbO to the EDM of Fundamental Particles 11
1.9 Other Current Experimental Approaches ....................... 12
1.9.1 Atoms ........................................................................ 12
1.9.2 Molecules ................................................................. 14
1.9.3 Solid State Materials .................................................. 17
1.10 Prospects for PbO as a System for Measuring \( d_e \) .......... 18

2 Experimental Methods 19

2.1 Level structure of PbO .................................................... 20
2.2 Excitation Sequence ....................................................... 23
2.2.1 Horizontally Polarized Light, and No Electric Field .......... 23
2.2.2 Horizontally Polarized Light, With an Applied Electric Field .... 25
2.2.3 Vertically Polarized Light and Microwave Excitation .......... 26
2.3 Quantum Beat Spectroscopy .......................................... 30
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3.1</td>
<td>Contrast of Quantum Beats in Molecules</td>
<td>34</td>
</tr>
<tr>
<td>2.4</td>
<td>Lifetime of the a(1) State and Density of Available Molecules</td>
<td>38</td>
</tr>
<tr>
<td>2.5</td>
<td>Noise Sources</td>
<td>40</td>
</tr>
<tr>
<td>2.5.1</td>
<td>Stray Magnetic Fields</td>
<td>40</td>
</tr>
<tr>
<td>2.5.2</td>
<td>Magnetic Johnson Noise</td>
<td>41</td>
</tr>
<tr>
<td>2.5.3</td>
<td>Ferromagnetic Materials</td>
<td>42</td>
</tr>
<tr>
<td>2.6</td>
<td>Common Systematic Effects</td>
<td>43</td>
</tr>
<tr>
<td>2.6.1</td>
<td>Leakage Currents</td>
<td>43</td>
</tr>
<tr>
<td>2.6.2</td>
<td>$v \times E$ Effects</td>
<td>44</td>
</tr>
<tr>
<td>2.6.3</td>
<td>Berry's phases</td>
<td>46</td>
</tr>
<tr>
<td>3</td>
<td>Apparatus</td>
<td>48</td>
</tr>
<tr>
<td>3.1</td>
<td>Vapor Cell</td>
<td>49</td>
</tr>
<tr>
<td>3.1.1</td>
<td>Material Selection</td>
<td>52</td>
</tr>
<tr>
<td>3.1.2</td>
<td>Gold Bonding Technique</td>
<td>53</td>
</tr>
<tr>
<td>3.1.3</td>
<td>Birefringence of Sapphire Windows</td>
<td>54</td>
</tr>
<tr>
<td>3.1.4</td>
<td>Stem</td>
<td>55</td>
</tr>
<tr>
<td>3.1.5</td>
<td>Plunger</td>
<td>55</td>
</tr>
<tr>
<td>3.1.6</td>
<td>Electric Field Homogeneity</td>
<td>56</td>
</tr>
<tr>
<td>3.1.7</td>
<td>Leakage Currents</td>
<td>57</td>
</tr>
<tr>
<td>3.1.8</td>
<td>Monitoring of Leakage Currents</td>
<td>57</td>
</tr>
<tr>
<td>3.1.9</td>
<td>Material Selection</td>
<td>57</td>
</tr>
<tr>
<td>3.2</td>
<td>Oven</td>
<td>62</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Eddy Current Suppression</td>
<td>68</td>
</tr>
<tr>
<td>3.3</td>
<td>Vacuum System</td>
<td>71</td>
</tr>
<tr>
<td>3.4</td>
<td>Magnetic Shielding</td>
<td>75</td>
</tr>
<tr>
<td>3.5</td>
<td>Laser Excitation</td>
<td>78</td>
</tr>
<tr>
<td>3.6</td>
<td>Microwave State Population</td>
<td>80</td>
</tr>
<tr>
<td>3.7</td>
<td>Detection</td>
<td>81</td>
</tr>
<tr>
<td>3.7.1</td>
<td>Filters</td>
<td>83</td>
</tr>
<tr>
<td>3.7.2</td>
<td>Absorbing Filters</td>
<td>88</td>
</tr>
</tbody>
</table>
6.1.2 Determination of C’ Energy Level Structure ......................................................... 168
6.1.3 Franck-Condon Factors ......................................................................................... 174
6.1.4 Ω-Doublet Splitting in the C’ state ....................................................................... 176
6.1.5 a(1) → C’ Excitation Cross Sections .................................................................... 178
6.1.6 Determination of Expected Contrast With No Electric Field ......................... 180
6.1.7 Determination of Expected Contrast With an Applied Electric Field ............... 182
6.1.8 Reexcitation Measurement Scheme ..................................................................... 186
6.1.9 a(1) → C Excitation Cross Sections ...................................................................... 193
6.2 Summary of C’ Measurements ............................................................................... 194
6.3 Microwave Detection ............................................................................................. 194
6.4 Cold Molecular Beams .......................................................................................... 198

7 Conclusions and Future Prospects

7.1 Data with Current Apparatus ................................................................................ 200
  7.1.1 Field Reversals .................................................................................................... 201
  7.1.2 Scrambled Data .................................................................................................. 202
7.2 Systematics to Investigate with Current Apparatus ........................................ 203
  7.2.1 Laser Polarization Aligned with Electric Field .................................................. 203
  7.2.2 Magnetic Field Alignment with the Electric field ............................................ 203
  7.2.3 Magnetic Field Gradients .................................................................................. 204
  7.2.4 Detuning of Laser Frequency ........................................................................... 205
  7.2.5 Non-Reversing Components of the Electric Field ............................................ 205
  7.2.6 Reversing Cables .............................................................................................. 205
  7.2.7 Monitoring Leakage Currents .......................................................................... 205
7.3 Improvements to Existing Apparatus ................................................................. 206
  7.4 Conclusions ........................................................................................................... 207

Appendix A: 3-j Symbols ......................................................................................... 208
Appendix B: Reduced Matrix Elements .................................................................... 210
Appendix C: Monte Carlo Simulation of Light Collection ...................................... 212
## List of Figures

1.1 Cartoon of how an EDM violates P- and T-symmetries .............................................. 3
1.2 Feynman diagram for an electron EDM ................................................................. 5
1.3 An example of a four-loop diagram contributing to $d_e$ in the Standard Model .... 5
1.4 Predicted and measured values for the size of $d_e$ .................................................. 7

2.1 The energy levels of the a(1) state of PbO with applied magnetic and electric fields and a non-zero $d_e$ ........................................................................ 22
2.2 The population sequence for the states used to measure $d_e$ ................................. 29
2.3 Simplest energy diagram for a system that could have quantum beats ............... 30
2.4 Simple classical picture of a radiating dipole giving rise to quantum beats ....... 31
2.5 Energy diagram showing the decay channels between one polarized level of the a(1) state and different rotational levels of the ground state ...................................................... 35
2.6 Simulated quantum beats with 50% contrast ......................................................... 39
2.7 Coordinate system for $v \times E$ effects .................................................................. 44
2.8 Energy level diagram for an atom or molecule that has a large tensor Stark splitting 45

3.1 Side view of the apparatus ...................................................................................... 50
3.2 Cross sectional top view of the apparatus ............................................................. 51
3.3 A picture of the mail cell body ................................................................................. 52
3.4 Cross-sectional view of an electrode with gold foil wrapped for maximum mechanical support ........................................................................................................... 54
3.5 Schematic for the leakage current monitoring system ............................................ 58
3.6 Typical measured resistivities of beryllium oxide and sapphire as a function of temperature .................................................................................................................. 59
3.31 The cell geometry constrains the angular distribution of the fluorescence  

3.32 The apparatus used to measure the transmission of the optical stack  

3.33 Schematic of the PMT gating circuit  

3.34 Basic transimpedance amplifier  

3.35 Noise model of a transimpedance amplifier  

3.36 Circuit diagram for the PIN photodiode detector  

3.37 Measured and predicted noise from the PIN photodiode detector  

3.38 Measured and predicted noise from the APD detector  

3.39 Circuit Diagram for the APD detector  

3.40 Recovery time of the PIN photodiode and APD detectors as a function of the size of the scattered light pulse  

3.41 Measured frequency response of the PIN photodiode transimpedance amplifier  

3.42 Power supplies for PIN photodiode preamplifier  

3.43 Simulated quantum beats measured with the APD detector  

3.44 Timing diagram for data acquisition  

3.45 Quantum beats fit with Levenberg-Marquardt algorithm  

4.1 The level diagram for the measurement of the difference in $g$-factors between the $|e\rangle$ and $|f\rangle$ sublevels  

4.2 The change in beat frequency as a function of RF frequency driving the population between the $|e\rangle$ and $|f\rangle$ states  

4.3 Rabi flopping between the $|e\rangle$ and $|f\rangle$ states  

4.4 The maximum change in quantum beat frequency versus the number of RF cycles applied to the electrodes  

4.5 The $\Omega$ doublet splitting as a function of the number of RF cycles  

4.6 Measurement of the Stark shift as a function of applied electric field  

4.7 Energy diagram with an applied magnetic and electric field allowing for Majorana spin flips  

4.8 Beat contrast vs electric field demonstrating Majorana spin flips  

5.1 Product of signal size and contrast as a function of laser power  

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
5.2 The measured frequency uncertainty as a function of temperature ........................................163
5.3 The measured frequency uncertainty as a function of laser power ........................................164

6.1 The energy structure and reexcitation scheme to the C' state .................................................167
6.2 Timing diagram for the relative delays between the two excitation lasers ..............................169
6.3 Transmission of the color glass filter used in the measurements of the C'→X fluorescence ..........................................................169
6.4 The energy of the measured rotational lines in the C'(v = 5) state ...........................................173
6.5 Quantum beats observed by driving the population to the C' state using a pulsed laser when the a(1) state was prepared in the |e) state ........................................................180
6.6 Low contrast is observed when the a(1) state is prepared in the EDM superposition state and observed via refluorescence through the C' state decays to the X state. 183
6.7 Possible decays from C'→X with an applied electric field .....................................................184
6.8 Energy level structure for the reexcitation scheme with microwave excitation ........................188
6.9 The population in the |a(1)J = 1), |a(1)J = 2) and C' levels with the microwave and C' reexcitation scheme and the measured quantum beats ...........................................192
6.10 Preliminary design of the 2nd generation experiment .........................................................197
6.11 Energy level diagram for ThO .................................................................................................199

C-1 Coordinates used for the Monte Carlo Simulation .................................................................213
C-2 The dimensions and geometry of the vapor cell .................................................................214
C-3 Coordinates used for the Monte Carlo Simulation including azimuthal angles ................221

xii
List of Tables

2.1 The relative amplitudes of the rotational lines in the $X(v = 1) \rightarrow a(1)(v = 5)$ transition .................................................. 38

3.1 Heating sequence for kiln to bond gold and sapphire or alumina ............ 53
3.2 Lanthanide solution concentrations .................................................... 89
3.3 Component values used in PIN photodiode and APD preamplifiers .......... 107
3.4 Signal sizes and shot noises for PMT, PIN photodiode, and APD detectors . . 111
5.1 Anticipated and actual improvements to the SNR ................................. 161
6.1 Measured and predicted frequencies for transitions between the $a(1) \rightarrow C'$ states .............................................................. 171
6.2 Additional lines unexpectedly seen in the transitions between the $a(1) \rightarrow C'$ states 172
6.3 The literature values for the spectroscopic constants of the $C'(v = 5)$ state compared to the values measured here .............................. 173
6.4 Measured and calculated Franck-Condon factors between the $C'$ and $X$ states . 176
6.5 Limits on the $\Omega$ doublet splitting in the $C'$ state .............................. 177
Chapter 1

Introduction

1.1 Introduction

Although there have been experimental searches for a non-zero permanent electric dipole moment of a fundamental particle for nearly 50 years, all experiments have measured values consistent with zero. A non-zero electric dipole moment (EDM) would violate time reversal (T) and parity (P) symmetries. A measurable non-zero EDM would be clear evidence of physics beyond the standard model (SM): the SM prediction for the EDM of the electron ($d_e$) is approximately 10 orders of magnitude smaller than current experimental limits. However, there is good reason to believe that a non-zero EDM could be measured. Several extensions to the SM such as supersymmetry (SUSY) predict much larger values for $d_e$ and other particle EDMs, many of that are within the next 1-2 orders of magnitude of the current experimental limit.

Most research is directed towards measuring an EDM of either the neutron or the electron or diamagnetic atoms, although there also have been searches for the EDM of the proton [3, 4], the muon [5], the neutrino [6], the $\Lambda^0$ hyperon [7], and the $\tau$ lepton [8]. This thesis is about the measurement of an EDM of the polar molecule PbO, which is primarily sensitive to $d_e$. For brevity, the scope of this thesis will be entirely limited to searches for $d_e$.

This chapter begins with a discussion of the theoretical motivation for searches for EDMs and basic experimental concepts. Next the systematic effects that are known to affect the experimental searches for $d_e$ are discussed in relation to PbO. Then several experimental searches for $d_e$ are summarized. These include the experiment that sets the best limit on $d_e$, as well as many of the ongoing or proposed searches for $d_e$. These experiments are grouped into the atomic...
searches, the molecular searches, and some new experiments that use a solid state material. Finally, this chapter concludes with a discussion of the merits and disadvantages of PbO in relation to these other ongoing and proposed experiments.

1.2 EDMs Violate Parity and Time Reversal Symmetries

A non-zero EDM violates both parity and time reversal symmetries. To see how, consider the similar Hamiltonians for an EDM and a magnetic dipole moment:

\[ H_{EDM} = -d \cdot \mathbf{E} = -d \sigma \cdot \mathbf{E} \]  
\[ H_{MDM} = -\mu \cdot \mathbf{B} = -\mu \sigma \cdot \mathbf{B} \]  

where \( d \) is the electric dipole moment, \( \mathbf{E} \) is the electric field, \( \sigma \) is the Pauli spin operator, \( \mu \) is the magnetic dipole, and \( \mathbf{B} \) is the magnetic field. Here, it is assumed that the EDM is along the spin axis of the particle. This assumption is discussed in section 1.3 and is reasonable. Although these two equations are very similar, they have very different characteristics under \( P \) and \( T \) transformations. If a parity transformation is applied to both of these equations, the axial vectors \( \sigma \) and \( \mathbf{B} \) remain invariant, but the polar vector \( \mathbf{E} \) changes sign. Therefore \( H_{EDM} \) changes sign under \( P \), but \( H_{MDM} \) remains invariant. Under a time reversal transformation, the time-dependent vectors \( \sigma \) and \( \mathbf{B} \) change sign, but the static vector \( \mathbf{E} \) remains invariant. Again \( H_{EDM} \) changes sign under \( T \), but \( H_{MDM} \) remains invariant.

A picture of how an EDM violates \( P \)- and \( T \)- symmetries is shown in figure 1.1 if the electron is imagined to have a finite size. Under a parity transformation, the direction of the EDM is reversed, but the direction of the spin remains the same. Therefore, parity is violated. Under a time reversal transformation the opposite happens: the spin direction is reversed, but the direction of the EDM remains the same. Thus, time reversal invariance is violated.

The CPT theorem states that under the combined transformations charge conjugation (C), parity (P), and time reversal (T) any Hamiltonian remains invariant [9]. This theorem is derived from the assumptions of Lorentz-invariance and locality, and is generally assumed to be valid. A consequence of this theorem is that the violation of any one of these symmetries is equivalent to the combined violation of the other two. For example, the T violation that would be exhibited
by the observation of a non-zero EDM is equivalent to CP violation. CP violation has been observed in K and B mesons \([10, 11]\). More recently, direct T violation has been observed in kaons \([12]\) and has been predicted to be measurable in B mesons at KEK \([13]\).

As an aside, a molecular dipole moment does not violate P-, T-, or CP-symmetries as a permanent dipole moment of a fundamental particle does. A molecular dipole moment only exists in the presence of an applied electric field—i.e. it is not permanent. When the direction of the electric field reverses, the direction of the dipole moment also reverses. In this scenario, no symmetries are broken.

### 1.3 Direction of \(d_e\)

If there is a non-zero \(d_e\), in what direction does it point? First, suppose that \(d_e\) does not point in the same direction as the spin axis of the electron \(S\) for all electrons. In this case, it would be possible to have more than one kind of electron since this projection \(\frac{S \cdot d_e}{|S||d_e|}\) would introduce a new quantum number for the electron. There is a great deal of experimental evidence that the electron does not have an additional quantum number. The Pauli exclusion principle states that electrons will fill all available quantum states in an atom or molecule in the order of ascending energy. Since the number of atomic levels are well understood, it is also well understood how many quantum numbers there are for an electron. This implies that \(d_e\) does not introduce a
new quantum number [14] and that the direction of $d_e$ is fixed with respect to $S$.

First, consider that $d_e$ points in a direction that is at a fixed angle with respect to $S$. This can be reduced to a linear combination of the following two situations: $d_e$ perpendicular to $S$ or along it.

Next, consider the component of $d_e$ perpendicular to $S$. This scenario is allowed, but it does not require T-violation. Theoretically, this possibility is not widely considered since it does not relate to T-violation, is not predicted in typical extensions to the SM, and would average to zero in the laboratory reference frame. It would, however, indicate electronic substructure. Mathematically, this can be expressed by the expectation value of $d_e$ since $\langle d_e \rangle = 0$ unless $d_e \parallel \langle J \rangle$.

Finally, consider that $d_e$ is along $S$. This experiment is sensitive to this scenario. This arrangement is also the scenario that is most theoretically motivated since it relates to T-violation and appears in SUSY and other SM extensions.

Since $d_e$ is not restricted to point in a particular direction, in this thesis, it will be written in vector notation.

1.4 Overview of Relevant Particle Theory

Conceptually, $d_e$ can arise from a one-loop Feynman diagram, as shown in figure 1.2a [15]. Note that this diagram is very similar to the $g$-2 diagram, which is shown in figure 1.2b. Various theories predict different couplings $f$ and $f'$, effective phases $\phi$, and different particles $X$. In the SM, however, figure 1.2a does not contribute to an EDM because there is no particle $X$ that couples to $e$ with a non-zero effective phase. Instead, a diagram of at least four loops is necessary to generate an EDM [16]. An example of a four loop diagram that contributes to a non-zero EDM in the SM is shown in figure 1.3

The SM predicts that $d_e \leq 10^{-40} \text{ e cm}$ [9], which is much smaller than the current experimental limit of $1.6 \times 10^{-27} \text{ e cm}$ [1]. If a non-zero $d_e$ were measured within the next few orders of magnitude of the current limit, it would be a clear indication of physics beyond the SM.

Essentially all extensions to the SM incorporate a heavier particle. These theories typically allow for diagrams similar to the one shown in figure 1.2a or generalizations thereof, containing additional loops. Given the similarity of the $d_e$ diagram and the $g$-factor diagram, scaling arguments can be made to estimate the size of $d_e$ based on $f$ and the mass ($m_X$) of particle
Figure 1.2: a) Feynman diagram for an EDM. \( f \) and \( f' \) are the effective couplings between the electron and any particle \( X \) and \( \phi \) is the effective CP violating phase. b) Feynman diagram for the electron g-2 value [15].

Figure 1.3: An example of a four-loop diagram contributing to \( d_e \) in the Standard Model. The cross denotes a mass insertion. Here, \( e_L \) is a left handed electron, \( e_R \) is a right handed electron, \( W \) is a \( W \)-boson, \( \gamma \) is a photon, \( u_i \) is an up quark and \( d_j \) is a down quark. Figure adapted from [17].
X [15]. In comparing these two diagrams, the only new energy scale arises from $m_X$, so by a dimensional argument

$$
\frac{d_e}{(g-2)\mu_B} \propto \left( \frac{m_e}{m_X} \right)^2.
$$

(1.3)

Therefore in CGS units,

$$
d_e \approx \sin \phi \left( \frac{\alpha}{\pi} \right)^2 \left( \frac{m_e}{m_X} \right)^2 \left( \frac{\alpha}{\pi} \right) \mu_B.
$$

(1.4)

Note that this estimate does not require any knowledge of the theory that is used to calculate the diagram shown in 1.2a. Many theories predict a value of $d_e$ within a similar range because certain general assumptions from this point lead to similar estimates. For example, $\frac{\alpha}{\pi} \approx 1$ because dimensionless coupling constants should all generally have the same order of magnitude. Furthermore, it is reasonable to assume that $\sin \phi \approx 1$ because the CP-violating phase in the CKM matrix $\delta \approx 1$ (using the standard notation) [18]. With these assumptions, and the mass of the heavy mediating particle, which is usually in the range of $M_X \sim 100$ GeV in order to address the "hierarchy problem", many theories predict $d_e$ very close to the current experimental limits [9, 17, 19]. Additional diagrams with extra loops will also contribute to $d_e$, but at a much lower level as the additional loops suppress the amplitude for these diagrams.

There are many theories that predict values for $d_e$, and some of these predictions are shown in figure 1.4 along with the current experimental results and the expected sensitivity of this experiment. Naive SUSY models have been almost entirely excluded by the current experimental bounds and several other theories will be seriously tested within the next two orders of magnitude.

1.5 General Method to Measure $d_e$

Most experiments use the same general method to measure $d_e$. It is difficult to use free electrons for a search for $d_e$ because they accelerate out of the experimental region once an electric field is applied. Instead, a neutral atom or molecule is used and the valence electrons are studied within this system. The internal structure (see section 1.6) of the atom or molecule enhances the size of the dipole moment within the system. The system is initially spin polarized perpendicular to an applied electric field and allowed to precess. The precession frequency will be proportional to the size of $d_e$. This precession frequency is usually measured using some form of interferometry.
Figure 1.4: Predicted and measured values for the size of $d_e$. The colored bands show the theoretical predictions; theories shown in blue are variations of SUSY. The black lines indicate the current experimental limit as well as the expected sensitivities of the first and second generations of this experiment.
Searches for $d_e$ are conducted by changing the direction of the electric field and looking for a correlated change in the precession frequency.

In the absence of an applied magnetic field, the precession frequency is very slow since precession is only caused by $H_{EDM}$. Since slow precession frequencies are difficult to detect, many experiments also add an additional constant magnetic field to increase the precession frequency. Then, a non-zero EDM would either increase or decrease this precession frequency depending on the relative directions of the magnetic and electric fields. By alternating the direction of the electric field and looking for a change in the precession frequency that occurs at the same periodicity, an EDM can be measured.

Since all of these experiments employ similar techniques, a general figure of merit can be established for the sensitivity of an experiment that is shot-noise limited. The energy shift due to $d_e \Delta E$ is measured with a resolution $\delta(\Delta E)$ is given by

$$\delta(\Delta E) = \frac{\hbar}{\tau C \sqrt{T \frac{dN}{dt}}}$$

where $\tau$ is the coherence time, $T$ is the total observation time, and $dN/dt$ is the counting rate [20]. The contrast $C$ is the ratio of the depth of the modulation of the signal due to the precession divided by the total signal size.

### 1.6 Enhancement Factors

At first, it seems that it would be impossible to detect an EDM in a neutral system such as an atom or molecule. According to Schiff's theorem [21], even in the presence of an applied electric field a neutral system arranges itself in such a way that there is no net force on any of the elements of the system. Thus, there is no net electric field on any of the electrons. The interaction Hamiltonian is $H=d_e \cdot \mathbf{E}$, but there is no electric field applied to the electrons, so the energy shift from this Hamiltonian is zero. However, if the atom or molecule is sufficiently heavy it will have valence electrons that are relativistic near the nucleus, Sandars demonstrated that a neutral atom can enhance the effect of $d_e$ [22, 23]. The enhancement factor $\eta$, then, is the ratio of the applied electric field $E_{\text{ext}}$ to the internal electric field inside the atom $E_{\text{int}}$ such
The total electric field at any point in space is

\[ \mathbf{E} = \mathbf{E}_{\text{int}} + \mathbf{E}_{\text{ext}}. \]  

The intuitive explanation for Sandars' theorem has long been misrepresented by saying it is magnetic, and a correct explanation has now been presented in [24]. Consider an electric dipole, which in the electron's rest frame is \( \mathbf{d}_e \), moving in the lab frame with a velocity \( \beta \). In the laboratory frame, the dipole moment is

\[ \mathbf{d}_e^L = \mathbf{d}_e - \frac{\gamma}{1 + \gamma} \beta \mathbf{d}_e \beta \]  

where \( \gamma = (1 - \beta^2)^{-1/2} \). This has an energy \( W_E \) in an electric field \( \mathbf{E} \) of

\[ W_E = -\mathbf{d}_e^L \cdot \mathbf{E} = -\mathbf{d}_e \cdot \left( \mathbf{E} - \frac{\gamma}{1 + \gamma} (\beta \cdot \mathbf{E}) \beta \right) \]  

where \( \beta = v/c \). This energy shift can be non-zero in an atom in the presence of an electric field even if the average value of the electric field is zero. This energy shift arises from the non-zero expectation value of the combined electric field and dipole moment at this point. This expectation value changes as a function of the velocity and hence the radius of the valence electron.

Now consider the same electric dipole this time moving inside an atom with a large external electric field applied to the atom. The first order energy shift in this atom due to the electric dipole will be

\[ \Delta E = -\mathbf{d}_e \langle \psi | \gamma^0 \Sigma : \mathbf{E} | \psi \rangle \]  

where \( \gamma^0 \) and \( \Sigma \) are the matrices \( \gamma^0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \), \( \Sigma = \begin{pmatrix} \sigma & 0 \\ 0 & \sigma \end{pmatrix} \).

The Lorentz contraction expressed by equation 1.8 in the transformation from the electron's rest frame to the atomic center of mass frame leads to a shift in the atomic energy levels due to
The Hamiltonian for this shift is

\[ H_{EDM} = -de\gamma^0 \Sigma \cdot \mathcal{E} \]

\[ = -de \Sigma \cdot \mathcal{E} - de(\gamma^0 - 1)\Sigma \cdot \mathcal{E}. \tag{1.11} \]

The first term in equation 1.11 does not contribute to the first order energy shift in equation 1.10, and the second term contributes

\[ \Delta E = \langle \psi | - de (\gamma^0 - 1) \Sigma \cdot \mathcal{E} | \psi \rangle \tag{1.12} \]

To make \( \Delta E \) large, most experiments use heavy atoms or molecules so that the valence electrons are very relativistic \((|\beta| \sim 1)\) near the nucleus. Additionally, large applied electric fields are used to further increase \( \Delta E \). In atoms, the polarization of the atom and hence \( \Delta E \) scales linearly with the applied electric field, so larger electric fields always lead to better sensitivity to \( de \).

In molecules, however, the polarization scales linearly at low electric fields, and then saturates at high electric fields. Therefore, in molecular EDM searches, there is an optimal electric field beyond which the sensitivity to \( de \) does not improve.

### 1.7 Enhancement Factor of PbO

In molecules, the terminology of an "enhancement" factor is not entirely accurate because diatomic polar molecules have a polarization that does not increase linearly with applied electric field as it does with atoms. Instead, as the electric field increases, the molecule becomes entirely polarized, which can be an advantage to choosing to work with a molecule. Many systematic effects will scale linearly with an applied electric field, while changing the applied electric field within the fully saturated regime will not change the effect of \( de \) on the molecule since the molecule is already fully polarized. In molecules, instead of using the terminology of an enhancement factor, the energy shift \( \langle W_d \rangle \) due to the applied electric field is used. This energy shift is usually calculated when the molecule is in an electric field that is sufficiently large to fully polarize the molecule. Since molecules polarize, the effect on the molecule due to the EDM will saturate and
will be a maximum when the molecule is fully polarized. Formally, \( W_d \) is defined as

\[
W_d = d_e^{-1} \langle a(1) | H_d | a(1) \rangle
\]  

where the electronic state of PbO used for in the measurement of \( d_e \) is the a(1) state and the Hamiltonian \( H_d \) is

\[
H_d = 2d_e \begin{pmatrix} 0 & 0 \\ 0 & \sigma \epsilon \end{pmatrix}
\]

and \( \sigma \) are the usual Pauli matrices.

It is particularly difficult to calculate what the internal effective electric field of PbO is because the ground state of PbO is not used for a measurement of \( d_e \). Instead the metastable excited a(1) state is used, which has two valence electrons. Two separate theoretical efforts have been made to calculate \( W_d \) for PbO. A semi-empirical calculation has concluded that \( |W_d| \geq 1.2 \times 10^{25} \text{ Hz/e cm} \) [25]. A configuration interaction calculation finds \( W_d = -6.1^{+1.8}_{-0.6} \times 10^{24} \text{ Hz/e cm} \) [26]. While these two results are not entirely in agreement, they agree within a factor of 2. This agreement is good enough for the current experimental status. If a non-zero EDM of PbO were measured, there would be greater theoretical motivation to improve these calculations.

1.8 Relating a Measurement of the EDM of PbO to the EDM of Fundamental Particles

This experiment measures the EDM of the a(1) state of PbO. Using the enhancement factor calculation results discussed above, this measurement can be directly related to a value of \( d_e \). However, other fundamental CP violating effects can also give rise to an EDM of PbO. These effects include electron-nucleon couplings [27]. PbO is sensitive to some of these couplings, and particularly sensitive to an electron-nucleon scalar-pseudoscalar coupling [28]. For the rest of this thesis, to shorten the notation a measurement of the permanent dipole moment of the a(1) state of PbO will be referred to as a measurement of \( d_e \).
1.9 Other Current Experimental Approaches

The rich history of interest in the measurement of $d_e$ means that historically there have been many experiments to measure $d_e$. For brevity, only current experiments will be discussed here as well as the experiment that has set the current best limit on $d_e$.

1.9.1 Atoms

Heavy atoms are excellent systems in which to measure $d_e$ since they can have enhancement factors of a few hundred, are easy to purchase and manipulate, and are spectroscopically well understood. Furthermore, very precise atomic calculations can be made to determine the enhancement factors within these atoms, so any non-zero measurement of an atomic EDM would be directly related to $d_e$.

Thallium

The current experimental limit on $d_e$ of $1.6 \times 10^{-27}$ e cm is from a measurement in a thallium beam [1] at the University of California at Berkeley from the group of E. Commins and co-workers. $^{205}$Tl has an enhancement factor of -585 [29]. This experiment used magnetic resonance with two oscillating RF fields separated by a region of high electric and a modest magnetic field. $^{205}$Tl has a nuclear spin $I = \frac{1}{2}$ and in the ground state has an orbital angular momentum $J = \frac{1}{2}$. The total angular momentum of this ground state is $F = I + J = 1$. An initial laser is used to optically pump the atoms out of the $m_F = \pm 1$ states leaving only $m_F = 0$.

The first RF field drives a $\pi/2$ pulse from the $m_F = 0$ state to a superposition of the $|m_F = +1\rangle$ and $|m_F = -1\rangle$ states, which precesses in the field region. After the field region, a second similar RF field creates a $\pi/2$ pulse that drives the atoms back to the $m_F = 0$ state. A laser probes the final state, which contains all of the information about a possible $d_e$ as well as systematics, and relative phase information between the RF fields.

Systematic effects are controlled by several reversals within the system. There are 8 atomic beams in the apparatus. Four Tl beams propagate both up and down on both sides of electric field plates. This means that the magnetic field is in the same direction for beams on different sides of these field plates, but the electric field is in the opposite direction. To reject systematic effects, four co-propagating sodium beams are used. Sodium was chosen because it has similar

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
magnetic properties to thallium but is too light to have a large enhancement factor and thus is insensitive to $d_e$.

In the end, this experiment was limited by both statistics and systematics. The systematics were primarily from $v \times E$ effects, which were somewhat controlled by only observing portions of the atomic beam and applying gradients in the magnetic field. These measurements, which were taken off-line, allowed for a separation of spurious signals from the EDM signal. With this correction, a limit of $|d_e| \leq 1.6 \times 10^{-27}$ e cm was set with a 90% confidence limit.

**Ongoing Atom Experiments**

There are several ongoing experiments in atoms. One type of these experiments uses cold trapped alkali atoms in optical lattices. These traps make long coherence times possible, which can help offset the relatively low density of atoms. There are two groups that are attempting to make far off resonant optical dipole traps for Cs. One is at the University of Texas in the group of D. Heinzen [15]. Another is at Pennsylvania State University in the group of D.S. Weiss [30]. Both of these groups have a similar approach, which is to create two side-by-side vertical traps which are loaded by a cold atomic beam. An advantage of this type of trap is that it can easily be loaded with two types of atomic species such as Rb and Cs, which allows for co-magnetometry since Rb and Cs have different enhancement factors. This co-magnetometry will be especially important because the optical dipole traps are susceptible to systematics caused by light shifts. Both of these groups are currently working on apparatus construction.

Another atomic approach in a Cs cell is being built at Princeton University by Romalis and co-workers [15] and builds on a similar successful result reported in 1989 at Amherst College [31]. The Amherst experiment used a stack of two glass cells coated with aluminum and zirconium to form electrodes. The Princeton experiment will use external electrodes instead of a tin oxide coating inside the cells. High voltage was applied to a center electrode between the cells and electrodes on the outside of the cells grounded, creating electric fields in opposite directions. A circularly polarized laser beam tuned to the cesium $6S_{1/2}F = 3 \rightarrow 6P_{1/2}$ transition optically pumps the atoms into the initial $x$-polarization of the $6S_{1/2}F = 4$ state. A very small magnetic field is applied along the $x$-axis to compensate for Zeeman light shifts produced by this pumping laser so that the precession in the cell is entirely a result of $H_{EDM}$. This precession is detected
with a probe laser directed along the y-direction and tuned to the $6S_{1/2}F = 4 \rightarrow 6P_{1/2}$ transition. Inside the vapor cell there are two different gasses: Cs and N$_2$. The Princeton experiment will add a third gas, $^{129}$Xe. The polarization of the Cs is transferred to the $^{129}$Xe nuclei by spin exchange collisions, causing large frequency shifts in the Cs electron spin resonance and the $^{129}$Xe nuclear magnetic resonance. This interaction is important because slow changes in components of the magnetic field transverse to the initial polarization axis are nearly cancelled by Cs electron spin and the $^{129}$Xe nuclear spin. The cancellation can reduce systematics such as leakage currents. This experiment is also in the construction phase.

A different approach is to use a cold fountain of Cs atoms to achieve long coherence times and large densities [32]. This approach is being developed by H. Gould at Lawrence Berkeley National Laboratory. While this approach has very long coherence times due to the low temperatures and a large number of atoms, several systematics will be difficult to control. $\mathbf{v} \times \mathbf{E}$ effects will be large. Additionally, it will be necessary to very precisely control the magnitude and reversibility of the magnetic and electric fields to avoid systematics associated with the translation of the fountain due to electrical forces on the atoms.

Francium has an enhancement factor that is 10 times larger than Cs, but it has no stable isotopes. A group at the Research Center of Nuclear Physics at Osaka University in Japan is in the early stages of developing an experiment with $^{223}$Fr, which has a lifetime of $\tau = 3.2$ minutes [15].

1.9.2 Molecules

Heavy polar molecules can have very large enhancement factors and are used in several current searches for $\mathbf{d}_e$. Unfortunately, there are some technical challenges involved in working with a molecule, which is why there have been no molecular searches for $\mathbf{d}_e$ before the ones discussed here. The molecules that are suitable for a measurement of $\mathbf{d}_e$ in the ground state have at least one unpaired valence electron, which makes them free radicals and thus chemically unstable. Free radicals cannot be contained in a vapor cell since they will react at nearly every collision and must be chemically produced inside the apparatus for the same reason. Furthermore, diatomic molecules have rotational, vibrational, and electronic energy levels. These extra degrees of freedom add many complexities. Spectroscopically, it is more difficult to isolate the energy levels.
of interest, although it is possible to identify all spectral lines. More importantly, these extra
degrees of freedom make it impossible to cool and trap large numbers of heavy polar molecules
with currently available techniques. The abundance of energy levels that are thermally populated
by the Boltzmann distribution means that the molecular population in the ground electronic
state is typically distributed over $10^3 - 10^4$ rovibrational states, thereby greatly reducing the
population of any particular molecular level.

\textbf{YbF}

The longest running molecular search for $d_e$ uses the ground $X^2\Sigma^+_{1/2}(v = 0, N = 0)$ state of
$^{174}\text{YbF}$ at Imperial College, London in the group of E. Hinds [33]. YbF was chosen for its large
internal electric field (13 GV/cm at an applied field of 8.3 kV/cm), and because the unpaired
spin makes it suitable for a measurement of $d_e$ in the ground state. Since YbF is a free radical,
it must be made within the experiment. Yb atoms are ablated with a pulsed laser and entrained
in a carrier gas of Ar or Xe with a small admixture of SF$_6$. Reactions between the SF$_6$ and
Yb create YbF. The entire gas containing Yb, YbF, SF$_6$, and Ar or Xe is released into the
interaction vacuum chamber via a pulsed valve through a nozzle. This procedure creates a
supersonically expanding beam that rotationally and translationally cools the beam, although
it still has a large forward velocity. In this beam, the translational and rotational temperature
is 1.4K, and 90% of the molecules are in the ground state.

In the ground state, there are 4 sublevels of $^{174}\text{YbF}$, since $F = 1, 0$ and $m_F = \pm 1, 0$.
As the molecular beam enters the experimental region, a pump laser removes all of the $F=1$
molecules so the molecules are in the $|F = 0, m_F = 0\rangle$ state. The molecules then enter an RF
coil where the molecules are excited to a coherent superposition $|\psi\rangle = \frac{1}{\sqrt{2}} |F = 1, m_F = 1\rangle + \frac{1}{\sqrt{2}} |F = 1, m_F = -1\rangle$. Then, the molecules travel through a long region of high electric field
and a modest magnetic field where the wave function develops a relative phase shift due to the
fields. This phase shift is

$$2\phi = 2(\pm d_e\mathcal{E}_{\text{int}} \mp \mu_B B) \tau/\hbar$$

where $\tau$ is the transit time of the molecule through the field region. Another RF coil drives
the molecule back to $F = 0$, but the final population is proportional to $\phi$. This population is
detected with a laser tuned to the Q(0) line of the $A^2\Pi_{1/2} - X^2\Sigma^+$ transition. Since the two RF
coils are not coherent and are not set to be a Ramsey pair, the signal is proportional to \( \cos^2 \phi \). Data are acquired by setting the magnetic field in the interaction region such that the signal has the steepest slope on either side of the central interference fringe.

Using this method, this experiment was able to achieve a preliminary result of \( d_e = (-0.2 \pm 3.2) \times 10^{-26} \text{ e cm} \). Although this result is \( \sim 30 \) times larger than the current limit on \( d_e \), the group is working on an improved limit [34]. The improved result is currently limited by variations in the electric field direction between the interaction region and RF regions. A future generation of this experiment hopes to increase the interaction time by further slowing the beam using a Zeeman slower to pre-cool the molecules before they enter the apparatus. While the Zeeman slower will increase the interaction time, it will decrease the counting rate.

**PbF**

A new experiment has been proposed and is in the early stages of development at the University of Oklahoma in the group of N. Shafer-Ray [35]. This experiment uses the ground state of PbF, which is a \( ^2\Pi_{1/2} \) state. A \( ^2\Pi_{1/2} \) state is a particularly advantageous state for an EDM experiment because there exists an electric field at which the magnetic moment of this state is zero. Since so many of the systematic effects that plague EDM experiments are magnetic in nature, with this molecule many systematic effects will also cancel or be significantly reduced.

**Molecular Ions**

A proposed experiment at JILA in the group of E. Cornell plans to use molecular ions such as \(^{180}HHF^+\) in the ground \( ^3\Delta_1 \) state [15]. These ions could be stored in an RF trap resulting in long coherence times. These long coherence times would compensate for the relatively small number of ions that could be trapped at any time. The \( ^3\Delta_1 \) state is predicted to have a small \( \Omega \)-doublet splitting, which would allow it to be polarized by a very small electric field and would have a very large internal electric field. The experiment will be conducted in a reference frame that is co-rotating with the RF trap. This experiment is unique in that it is impossible to reverse the direction of the electric field since it must point towards the trap center or the ions will no longer be trapped. The EDM signal is achieved by probing the different \( \Omega \)-doublet states that should have opposite frequency shifts due to \( d_e \). Since the electric field cannot be reversed and
the $g$-factor is expected to shift with the electric field as described in section 4.2, there may be systematic effects that cannot be diagnosed in this experiment. However, current calculations suggest that this shift in $g$-factor is sufficiently small that it will not be a limiting factor [36].

1.9.3 Solid State Materials

It has long been known that a measurement of $d_e$ can be conducted in a solid state material [37], but it has only been recently that suitable materials have been available and their application has been recognized [38]. The idea is to choose a material that has a lattice structure which satisfies two characteristics: 1) it has one atom that has a reasonably high enhancement factor such as Gd, and 2) it has a high electrical resistivity so that high electric fields can be applied to it with small leakage currents through the body of the material. This material will be cooled to low temperatures that will freeze out thermal fluctuations and allow for the detection of the spin polarization that a non-zero $d_e$ would create along the axis of the applied electric field.

Two experiments are underway using Gd$_3$Ga$_5$O$_{12}$, which has a crystalline form that rules out several magneto-electrical effects [38]. One experiment is being conducted by the group of S.K. Lamoreaux [39] and is at Yale University, and the other is at Indiana University by C.Y. Liu [15]. These experiments apply a strong electric field and use SQUID magnetometers to detect the magnetic field created by a non-zero $d_e$.

An alternate approach is being used at Amherst College by L. Hunter and co-workers [40] in Gd$_3$Fe$_5$O$_{12}$. The primary difference between this approach and the previous one is that here a magnetic field is applied to the sample and an electric field is measured rather than the reverse configuration. In this experiment, the sample is constructed of two C-shapes that are glued together with electrodes pressed in between the halves to form a toroid. One half of the toroid is doped with yttrium to change the compensation temperature at which the sample magnetizes. A magnetic field is created by wrapping coils around the toroid and inducing a field inside of the toroid. The signal is detected by measuring the voltage on the electrodes. The yttrium doping gives the signal a distinctive temperature characteristic, which is different from most systematic effects. With this apparatus, a preliminary result was to place a limit of $|d_e| < 5 \times 10^{-24}$ e cm. The experiment was limited by unexpected large voltages on the electrodes when the sample magnetization was reversed.
1.10 Prospects for PbO as a System for Measuring $d_e$

The next chapter will be devoted to a detailed description to the design of this experiment, but it is worth discussing a few of the merits and disadvantages of this experiment here where it can be easily compared to the other searches for $d_e$. Like the other molecular searches for $d_e$, this experiment takes advantage of the very large internal electric field $E_{int}$ of PbO. Furthermore, by working in a vapor cell, the counting rate is much higher in this experiment than in the YbF beam. This increased counting rate is at the expense of the coherence time, which is fundamentally limited by the lifetime of the metastable state.

Like YbF, PbO is relatively immune to $v \times E$ effects as a result of its tensor Stark splitting. Many of the geometric phase effects that were significant in the Berkeley thallium experiment such as Berry's phases should also be minimized as a result of this tensor Stark splitting. The tensor Stark splitting suppresses the rotation of the molecule due to magnetic fields perpendicular to the electric field axis as discussed in section 2.6.2.

Another systematic arising from Berry's phases can be problematic, however. If the direction of the electric field rotates slightly, then, the molecules will also rotate to align with the direction of the electric field. These rotations can lead to Berry's phases. In this experiment, the electric field is least homogeneous at the edges of the electrodes. Since the microwave excitation (see section 3.6) is non-resonant with the molecules in the non-homogeneous region of the electric field, the molecules that originate at the edges of the electrodes are less likely to be excited. This will reduce the sensitivity of this experiment to this systematic.

Although PbO can be polarized with a small external electric field of $\sim 20$ V/cm as a result of the small $\Omega$-doublet splitting in the $a(1)$ state, leakage currents remain the single largest potential systematic effect. As will be described in the next chapter, the $\Omega$-doublet structure of the $a(1)$ state allows for PbO to be used as an internal co-magnetometer to reject some of the systematic effects associated with these leakage currents.
Chapter 2

Experimental Methods

Many molecular searches for \( d_e \) use the ground state of the molecule to achieve long coherence times. A molecule that is suitable for a measurement of \( d_e \) in the ground state is a free radical, and free radicals are unstable molecules and cannot be used in a vapor cell. This experiment takes the novel approach of using the metastable \( a(1) \) excited state of PbO that is a \( 3\Sigma^+ \) state [41]. Since PbO is chemically stable it can be readily purchased and contained in a vapor cell.

The approach of using molecules in a vapor cell has some trade-offs, but ultimately is very promising. Recall that the energy resolution of the experiment is as given in equation 1.5. This experiment has a very high counting rate because vapor cells can have densities that are typically 8 orders of magnitude higher than densities achievable in molecular beams. Unfortunately, the coherence time is somewhat shorter. In molecular beams, the coherence time is set by the time that the molecule spends in the apparatus before flying out. For typical beams this is on the order of ms, whereas the natural lifetime of the \( a(1) \) state is 82(2) \( \mu s \) [42]. In the end, however, the tradeoff between higher counting rates and shorter coherence times appears reasonable since this experiment is expected to measure \( d_e \) an order of magnitude above the current experimental limit in the first generation and to improve upon this limit by several orders of magnitude in the second generation.

An additional feature of the \( a(1) \) state is that it is an \( \Omega \)-doublet state, which means that it has two closely spaced levels that are nearly identical except that they are of opposite parity. These levels will interact almost identically in magnetic fields, but have opposite responses to a non-zero \( d_e \). This feature allows PbO to act as an internal co-magnetometer cancelling many
systematic effects.

The spontaneous fluorescence from the a(1) state is collected and interference between the 
$m = 1$ and $m = -1$ leads to quantum beat spectroscopy. Changes in the quantum beat 
frequency are used to determine the energy splitting between the $m = 1$ and $m = -1$ levels, 
which is directly proportional to $d_e$.

### 2.1 Level structure of PbO

The ground state of PbO is a $^1\Sigma^+$ state ($\sigma^2\pi^4$) \[41\], which has all valence electrons paired, 
and therefore is unsuitable for use in a measurement of $d_e$. The metastable a(1) $^3\Sigma^+$ state 
($\sigma^2\pi^3\pi^*$) \[41\], however, is suitable for such a measurement. This state is a Hund’s case (c) state 
with $|\Omega| = 1$ \[43\]. In a Hund’s case (c) molecule, the interaction between $L$ and $S$ is stronger 
than the interaction with the internuclear axis. This means that the component of the electron 
orbital angular momentum along the internuclear axis, $\Lambda$, and the component of the electron 
spin along the internuclear axis, $\Sigma$, are not defined, but $\Omega$, which is defined as $\Lambda + \Sigma$, is still a 
good quantum number \[44\].

Since $|\Omega| = 1$ in the a(1) state, $\Omega$ can have two possible values: +1, -1, which leads to 
$\Omega$-doubling. As a result of the molecular rotation, Coriolis coupling lifts the degeneracy between 
these levels \[45\]. This $\Omega$-doublet structure has two significant advantages for an EDM experi­
ment. First, these closely spaced levels of opposite parity make it easy to polarize the molecule 
with relatively modest electric fields of $\sim 20$ V/cm. Since the applied electric field is much lower 
than in most EDM experiments, leakage currents are more manageable than they would be if it 
were necessary to apply the $\sim 100$ kV/cm fields needed to polarize atoms and some molecules. 
Furthermore, in vapor cells, the molecular density can be sufficiently high that high electric 
fields cause discharges through the vapor. Clearly, this is unacceptable for an EDM experiment. 
Thus, these modest electric fields of $\sim 20$ V/cm are a key component of why it is possible to 
perform this experiment in a vapor cell. The second advantage of the $\Omega$-doublet is that the 
levels form an internal co-magnetometer. The two levels have identical quantum numbers but 
opposite parity. The levels of the $\Omega$-doublet with parity $+(-1)^f$ are labelled $|e\rangle$ levels and the 
levels with parity $-(-1)^f$ are labelled $|f\rangle$ levels \[46\].

Without any applied fields, the a(1) state is shown in figure 2.1a. In this case, the $|e\rangle$ and
\( |f\rangle \) states are split by the \( \Omega \)-doublet splitting of 11.214(5) MHz and all of the \( m \) sublevels are degenerate. In the presence of an applied electric field the \( |e\rangle \) and \( |f\rangle \) sublevels mix and repel. The case of a fully polarizing external electric field is shown in figure 2.1b such that the \( |e\rangle \) and \( |f\rangle \) sublevels are entirely mixed. In this fully polarized case, \( \Omega \) is a good quantum number and \( \Omega \) is assigned as shown in figure 2.1b. In the presence of a sufficiently large electric field, the internuclear axis \( n_z \) aligns along the direction of the electric field. In the upper pair of \( \Omega \) doublet states the quantity \( n_z = m \cdot \Omega = 1 \), while in the lower pair of \( \Omega \) doublet states \( n_z = m \cdot \Omega = -1 \). Typically the electric field is chosen such that the Stark shift is \( \approx \) 60-100 MHz. The \( m=0 \) states do not mix. An additional magnetic field causes a Zeeman splitting as shown in figure 2.1c. The magnetic field is chosen such that the Zeeman splitting is \( \approx \) 100-300 kHz. If there is a non-zero \( d_e \), there will be an additional energy shift between the \( m = 1 \) and \( m = -1 \) levels as shown in figure 2.1d. This energy shift will be of opposite sign in the upper pair (\( n_z = 1 \)) of \( m = 1 \) and \( m = -1 \) levels than in the lower pair (\( n_z = -1 \)). This experiment measures the energy difference between the \( m = 1 \) and \( m = -1 \) in the upper pair (\( n_z = 1 \)) or the lower pair of states (\( n_z = -1 \)).

Our experiment uses the 5th vibrational state \((v' = 5)\) of the \( a(1) \) state since the Franck-Condon factors between \( \text{X}(v = 1) \rightarrow a(1)(v' = 5) \approx 50\% \). The Franck-Condon factor is a measure of the overlap of the vibrational wavefunctions between the two states, and hence a measure of the transition probability. The other large Franck-Condon factor between the \( \text{X} \) and \( a(1) \) state is \( \text{X}(v = 0) \rightarrow a(1)(v' = 5) \approx 50\% \). The rotational \( J = 1 \) state is used because it has the fewest \( m \) sublevels (the \( J = 0 \) state does not exist). Furthermore, since \( \Omega \)-doublet splitting comes from the Coriolis force, higher rotational states have larger \( \Omega \)-doublet splittings. Larger electric fields are required to fully polarize these higher rotational states and therefore they are slightly more difficult to use for this experiment. Most importantly, the size of the energy shift due to \( d_e \) decreases at larger \( J \). The energy shift due to \( d_e \) scales as

\[
\Delta \nu_{ EDM} = \frac{m}{J(J+1)}.
\]
Figure 2.1: The energy levels of the a(1) state of PbO. a) With no applied fields the Ω-doublet splitting is 11.214(5) MHz. b) A modest external applied electric field will fully polarize the |e⟩ and |f⟩ levels. c) An additional magnetic field will create a Zeeman splitting, which is shown with dashed lines. Note that the Zeeman splitting is not to scale. d) If there is a non-zero d_e there will be an additional energy shift shown by the dotted lines, which is also not to scale. The current experimental limit corresponds to an energy shift of 12 mHz. The sign of this energy shift is opposite in the upper and lower pair of Ω-doublet states.
2.2 Excitation Sequence

State population is critical for this experiment since the measurement is performed in an excited state. Three different state population schemes were used during the course of this thesis. Only the third scheme, population with microwaves, will allow for a population sequence where the $n_z = +1$ and $n_z = -1$ states can be populated on alternate pulses of the dye laser.

2.2.1 Horizontally Polarized Light, and No Electric Field

The first excitation scheme occurs when the laser driving the $X \rightarrow a(1)$ state is horizontally polarized and there is no applied electric field. Since there is no applied electric field, this case cannot be used for the final experiment. The $X$ state does not have $\Omega$-doubling and its rotational states have parity $(-1)^J$ (always an $|e\rangle$ state). The $a(1)$ state has both $|e\rangle$ (parity $(-1)^J$) and $|f\rangle$ (parity $-(-1)^J$) states. Since a photon has a parity of $-1$, the initial and final states must have opposite parity. Therefore for a $\Delta J = +1$ transition the selection rule is that $|e\rangle \rightarrow |e\rangle$.

A $\Delta J = +1$ transition is known as an R branch molecular transition. A $\Delta J = 0$ transition (Q branch) has the selection rule $|e\rangle \rightarrow |f\rangle$ and a $\Delta J = -1$ transition (P branch) has the selection rule $|e\rangle \rightarrow |e\rangle$. Since the $X$ state does not have an $|f\rangle$ state, there is no selection rule $|f\rangle \rightarrow |f\rangle$, although this is allowed in principle.

The Hamiltonian for excitation is

$$H \propto \epsilon \cdot r$$

where $\epsilon$ is the polarization of light and $r$ is the position operator. The spherical tensor components of $r$ are

$$r_- = \frac{1}{\sqrt{2}}(x - iy)$$  \hspace{1cm} (2.3)

$$r_0 = z$$ \hspace{1cm} (2.4)

$$r_+ = \frac{1}{\sqrt{2}}(-x - iy)$$ \hspace{1cm} (2.5)
such that

\begin{equation}
  x = \frac{1}{\sqrt{2}} (r_- - r_+) \tag{2.6}
\end{equation}

\begin{equation}
  y = \frac{i}{\sqrt{2}} (r_- + r_+) \tag{2.7}
\end{equation}

\begin{equation}
  z = r_0. \tag{2.8}
\end{equation}

We typically excite the R0 transition where the 0 denotes the J value in the lower state and \( J' = 1 \) in the excited state, since \( \Delta J = +1 \) for an R branch line. Since this is an R branch transition, the selection rules determine that \( |e \rangle \rightarrow |e \rangle \). In this case, the excited state \( |u_{h,\text{no } e} \rangle \) is

\begin{equation}
  |u_{h,\text{no } e} \rangle \propto \sum_{m=-1}^{1} |1, m, e \rangle \langle 1, m, e | H |0, 0, e \rangle \tag{2.9}
\end{equation}

where the form \( |J, m, e / f \rangle \) is used. Since \( e = \hat{z} \) polarized light is used, \( H \propto x \propto r_- - r_+ \), and

\begin{equation}
  |u_{h,\text{no } e} \rangle \propto \sum_{m=-1}^{1} |1, m, e \rangle \langle 1, m, e | (r_- - r_+) |0, 0, e \rangle. \tag{2.10}
\end{equation}

This can be simplified using the Wigner-Eckart theorem, which states that

\begin{equation}
  \langle \alpha', j', m' | T^{(k)} \rangle (\alpha, j, m) = (-1)^{j'-m'} \begin{pmatrix} j' & k & j \\ -m' & q & m \end{pmatrix} \langle \alpha', j'| |T^{(k)}| |\alpha, j \rangle \tag{2.11}
\end{equation}

where \( T^{(k)} \) is a tensor operator [47]. The 3-j symbol \( \begin{pmatrix} j' & k & j \\ -m' & q & m \end{pmatrix} \) is similar to a Clebsch-Gordan coefficient and is defined in Appendix A. In all of the calculations in this section, the reduced matrix element \( \langle \alpha', j'||T^{(k)}||\alpha, j \rangle \) will be a constant of proportionality and will not need to be calculated. In section 4.2, techniques for calculating the reduced matrix element will be discussed.

Using the Wigner-Eckart theorem and the fact that the operator \( r \) is a rank-one tensor \((k = 1)\), equation 2.10 becomes

\begin{equation}
  |u_{h,\text{no } e} \rangle \propto \sum_{m=-1}^{1} \left\{ \begin{pmatrix} 1 & 1 & 0 \\ -m & -1 & 0 \end{pmatrix} - \begin{pmatrix} 1 & 1 & 0 \\ -m & 1 & 0 \end{pmatrix} \right\} |1, m, e \rangle (-1)^{1-m}. \tag{2.12}
\end{equation}
3-j symbols of the form \[
\begin{pmatrix}
1 & 1 & 0 \\
-m & q & 0 \\
\end{pmatrix}
\]
are common in several of the following calculations. In order to satisfy the condition that \(m_1 + m_2 + m_3 = 0\), the only non-zero terms of this 3-j symbol occur when \(m = q\). When this condition is met,

\[
\begin{pmatrix}
1 & 1 & 0 \\
-m & q & 0 \\
\end{pmatrix} = \frac{(-1)^m}{\sqrt{3}}.
\]

(2.13)

Calculating the 3-j symbols yields

\[
|u_{n,\alpha\varepsilon}\rangle \propto -|1,1,\varepsilon\rangle + |1,-1,\varepsilon\rangle.
\]

(2.14)

### 2.2.2 Horizontally Polarized Light, With an Applied Electric Field

When there is an applied electric field \(E = E \hat{z}\), the \(|\varepsilon\rangle\) and \(|f\rangle\) sublevels in the a(1) state mix as shown in figure 2.1b. Again, with a horizontally polarized laser beam (\(\varepsilon = \hat{x}\)) tuned to an R branch transition, the selection rule is \(|\varepsilon\rangle \rightarrow |\varepsilon\rangle\). However, in this case there are \(|\varepsilon\rangle\) components in all four of the a(1) \(|m|=1\) sublevels. When the laser is tuned to R0, the excited state is \(|\Psi_{h,E}\rangle\) is populated. This state is

\[
|\Psi_{h,E}\rangle \propto \frac{1}{\sqrt{2}} \left| \begin{array}{c}
|1,1,\varepsilon\rangle + |1,1,f\rangle \\
|1,1,\varepsilon\rangle - |1,1,f\rangle \\
|1,1,\varepsilon\rangle + |1,1,f\rangle \\
|1,1,\varepsilon\rangle - |1,1,f\rangle
\end{array} \right| H |0,0,\varepsilon\rangle\]

(2.15)

where again \(H \propto \varepsilon \cdot r \propto x \propto r_- - r_+\). The Wigner-Eckart theorem is applied noting that \(\langle f| H |\varepsilon\rangle = 0\), and requiring that all 3-j symbols satisfy \(m_1 + m_2 + m_3 = 0\). By applying 2.13, this simplifies to

\[
|\Psi_{h,E}(t = 0)\rangle \propto \left( -|1,1,\varepsilon\rangle - |1,1,f\rangle \right) + \left( |1,-1,\varepsilon\rangle - |1,-1,f\rangle \right)
\]

(2.16)

\[
+ \left( -|1,1,\varepsilon\rangle + |1,1,f\rangle \right) + \left( |1,-1,\varepsilon\rangle + |1,-1,f\rangle \right).
\]
These states evolve over time according to the energy separation between them caused by the Zeeman and Stark shifts. At a later time the state in a perfectly homogeneous field would be

$$|\Psi_{h,e}(t)\rangle \propto -e^{i(\omega_Z+\omega_S)t}(|1,1,e) + |1,1,f)\rangle + e^{i(-\omega_Z+\omega_S)t}(|1,-1,e) - |1,-1,f)\rangle$$

$$- e^{i(\omega_Z-\omega_S)t}(|1,1,e) - |1,1,f)\rangle + e^{i(-\omega_Z-\omega_S)t}(|1,-1,e) + |1,-1,f)\rangle \quad (2.17)$$

where $\omega_Z = E_{Zeeman}/\hbar$ and $\omega_{Stark} = E_{Stark}/\hbar$. If the electric field were perfectly homogeneous, the coherence between all four sublevels would remain for all times. However, the electric field is sufficiently inhomogeneous that the coherence between the upper and lower sublevels is washed out quickly. The coherence between the $m = +1$ and $m = -1$ sublevels in the upper ($n_z = +1$) and lower ($n_z = -1$) state remains, so that there are two (relatively incoherent) pairs of coherent excited states. These coherent excited states are

$$|n_z = +1\rangle \propto -(|1,1,e) + |1,1,f)\rangle e^{i\omega_Z t} + (|1,-1,e) - |1,-1,f)\rangle e^{-i\omega_Z t} \quad (2.18)$$

$$|n_z = -1\rangle \propto -(|1,1,e) - |1,1,f)\rangle e^{i\omega_Z t} + (|1,-1,e) + |1,-1,f)\rangle e^{-i\omega_Z t}. \quad (2.19)$$

Although there is an applied electric field in this population scheme, this scheme is not suitable for a measurement of $d_e$. Our detection scheme cannot distinguish between the population in the upper and lower $\Omega$-doublet states $|n_z = +1\rangle$ and $|n_z = -1\rangle$, and therefore measures both at once. Since the energy shift due to $d_e$ has an opposite sign in these two sublevels, detecting both sublevels at once will cancel the effect of a non-zero $d_e$ if they have the same $g$-factor.

### 2.2.3 Vertically Polarized Light and Microwave Excitation

There were three primary requirements for an excitation scheme for measuring $d_e$. First, this scheme must work when there is an applied electric field. Second, the population sequence must only populate either $n_z = +1$ or $n_z = -1$, since the detection cannot discriminate between these two sublevels. Third, switching between measuring $n_z = +1$ and $n_z = -1$ as frequently as possible reduces many sources of magnetic noise. Therefore, it was necessary to choose a state population sequence that was able to switch between populating the $n_z = +1$ and $n_z = -1$ states on alternate shots of the dye laser. The dye laser operates at 100 Hz, so the state population sequence must be able to switch between populating $n_z = +1$ and $n_z = -1$ in at least 10 ms.
The population sequence starts when the dye laser transfers the population from the \( |X, v = 1\rangle \) ground state to the \( |a(1), v = 5\rangle \) state. The laser is tuned to the R0 line and is vertically polarized (in the \( \hat{z} \) direction). The excitation Hamiltonian is \( H \propto \epsilon \cdot r \propto \hat{z} \propto r_0 \), so the laser excites the state \( |u_0\rangle \), given by

\[
|u_0\rangle \propto \sum_{m=-1}^{1} |1, m, e\rangle \langle 1, m, e| r_0 |0, 0, e\rangle . \tag{2.20}
\]

Applying the Wigner-Eckart theorem will yield 3-j symbols of the form \( \begin{pmatrix} 1 & 1 & 0 \\ -m & 0 & 0 \end{pmatrix} \). Since a non-zero 3-j symbol satisfies the relation \( m_1 + m_2 + m_3 = 0 \), \( m = 0 \). This simplifies \( |u_0\rangle \) to

\[
|u_0\rangle \propto |1, 0, e\rangle . \tag{2.21}
\]

Next, \( \hat{z} \)-polarized microwaves are used to transfer the population to the \( |a(1), J = 2, m = 0\rangle \) state. Between rotational states, the parity selection rule requires \( |e\rangle \rightarrow |e\rangle \), so the \( J = 2 \) state will also be an \( |e\rangle \) state. Again, the Hamiltonian is \( H \propto r_0 \). The microwaves excite the state

\[
|u_{J=2}\rangle \propto \sum_{m=-2}^{2} |2, m\rangle \langle 2, m| r_0 |1, 0\rangle . \tag{2.22}
\]

Since a photon only carries one unit of angular momentum, it can only drive a \( \Delta J = \pm 1,0 \) transition, so only the \( m = \pm 1,0 \) terms can survive. Applying the Wigner-Eckart theorem and ignoring the 3-j symbols that are zero by the requirement that \( m_1 + m_2 + m_3 = 0 \) gives

\[
|u_{J=2}\rangle \propto |2, 0, e\rangle . \tag{2.23}
\]

Next, in the limit of high electric field such that the molecules are completely polarized, \( \hat{x} \)-polarized microwaves are used to transfer the population to a coherent superposition state (see figure 2.2). This coherent superposition state can be either \( n_z = +1 \) or \( n_z = -1 \) depending on the frequency of the microwaves. The microwave frequency can be switched quickly allowing for switching between populating \( n_z = +1 \) or \( n_z = -1 \) each time the X–a laser fires. Even though there is a small energy difference between the \( m = +1 \) and -1 states due to the Zeeman splitting, the frequency spectrum of the microwaves is chosen to be broad enough to cover this energy splitting and equally populate both \( m \) sublevels. The microwave Doppler width of \( \sim 42 \, \text{kHz}, \)
however, is narrow enough to distinguish between the $n_z = +1$ and $n_z = -1$ levels. This is unlike the laser, which cannot distinguish between these levels since the laser transition has a Doppler width of $\sim 800$ MHz.

When the $\hat{x}$ polarized microwaves are tuned to $n_z = +1$, the Hamiltonian is $H \propto r_- - r_+$ and the state populated is

$$|u_e\rangle \propto [(1,1,e) + (1,1,f)][(r_- - r_+)(2,0,e) [(1,1,e) + (1,1,f)]$$

$$+ (1,0,e)(r_- - r_+)(2,0,e) [1,0,e) + (1,1,e) - (1,1,f)][(r_- - r_+)(2,0,e) [1,1,e) - (1,1,f)] .$$

Using the Wigner-Eckart theorem with the usual assumptions that only non-zero 3-j symbols will be shown, this equation becomes

$$|u_e\rangle \propto \left(\begin{array}{ccc} 1 & 1 & 2 \\ -1 & 1 & 0 \end{array}\right) [(1,1,e) + (1,1,f)] + \left(\begin{array}{ccc} 1 & 1 & 2 \\ 1 & -1 & 0 \end{array}\right) [(1,1,e) - (1,1,f)] .$$

(2.25)

Calculating the 3-j symbols yields

$$|u_e\rangle \propto - [(1,1,e) + (1,1,f)] + [(1,1,e) - (1,1,f)] .$$

(2.26)

The combination $(1,1,e) + (1,1,f) = |n_z = +1, m = +1\rangle$. Similarly, $(1,1,e) - (1,1,f) = |n_z = +1, m = -1\rangle$, such that

$$|u_e\rangle \propto - |n_z = +1, m = +1\rangle + |n_z = +1, m = -1\rangle .$$

(2.27)

A similar calculation to $n_z = -1$ yields

$$|u_e\rangle \propto - |n_z = -1, m = +1\rangle + |n_z = -1, m = -1\rangle .$$

(2.28)

**Microwave State Preparation**

The microwave state preparation discussed in this section requires microwave pulses that are short enough in duration to coherently populate both sublevels. The duration and amplitude of these pulses is chosen such that they form a “pi pulse" [48]. A pi pulse occurs when the oscillating
Figure 2.2: The population sequence for the a(1) state starts with a z-polarized dye laser tuned to 570 nm which populates the m=0 state of the a(1) state. Then, z-polarized microwaves populate the $J=2$, $m=0$ state. On alternate pulses of the dye laser, x-polarized microwaves are tuned to be resonant with either the $n_z=+1$ or $n_z=-1$ states of the $\Omega$ doublet. $\Delta=11.214$ MHz is constant, but $\delta$ varies with the applied electric field. At an applied electric field of 52 V/cm, $\delta=37.8$ MHz. Note that the diagram is not to scale.
field $V(t) = \mathcal{E} \cos \nu t$ has an amplitude $\mathcal{E}$ such that $\mathcal{E} t \mu = \pi$. In this case $\mu = e \langle f \mid r \mid i \rangle$ is the electric dipole moment of the atom or molecule where $|f\rangle$ is the final state and $|i\rangle$ is the initial state. The pi pulse condition is chosen such that population is completely transferred from one state to the other state.

### 2.3 Quantum Beat Spectroscopy

Quantum beats can occur in systems where there are two excited states that have a small energy difference [49, 50]. These energy levels must be coherently excited and must then either decay to a common ground state or be coherently stimulated to a common state. In this system, quantum beats can be observed if a broad excitation source is used to coherently excite the two $n_z=1$ states simultaneously or alternately the two $n_z=-1$ state simultaneously. The beats are usually observed by detecting the fluorescence from these excited states to a common level in the ground state. Since these states must be coherently excited, narrow linewidth lasers are not necessary and in fact not wanted for the excitation process. Instead, short excitation pulses, which have a large frequency width, are necessary. Here, where microwaves are used for the final excitation pulse, the microwave pulses are deliberately kept short so that they have a large frequency width. During the lifetime of the excited state, the coherent excited state will evolve and interference between the states will cause maxima and minima in the intensity distribution of the fluorescence.

In the simplest classical picture, quantum beats can be pictured as a radiating dipole (see figure 2.4). A simple atomic system that can exhibit quantum beats is an atom in a $p$-state which is in a superposition of $m=\pm 1$ states. Classically, this is a dipole oriented along $\hat{x}$ or $\hat{y}$.
depending on the phase. This system will be used as an example for the rest of this section. Radiation from this p-state is preferentially emitted in the plane perpendicular to the axis of the dipole. A fixed detector will detect intensity maxima and minima as the dipole rotates such that it is aligned or anti-aligned with the detector.

![Diagram of a radiating dipole giving rise to quantum beats](image)

Figure 2.4: Simple classical picture of a radiating dipole giving rise to quantum beats. The dipole rotates in a plane perpendicular to the magnetic field and preferentially emits photons perpendicular to the dipole axis. As this dipole axis rotates, the radiation exhibits maxima and minima in the intensity reaching the fixed detectors much like a lighthouse shines a rotating beam of light.

In this experiment, once the coherent superposition of the $m=+1$ and $-1$ levels are populated, the Zeeman splitting between these two levels causes the state to evolve, giving rise to quantum beats. The energy difference of the $m = 1$ and $m = -1$ levels of the $\Omega$-doublet is detected using quantum beats. The frequency of the beats is directly proportional to the energy difference between the states.

A quantum description of quantum beat spectroscopy involves the interference between the closely spaced sublevels, which in this case are the $m$ sublevels [51]. In general, a complete quantum mechanical description of quantum beat spectroscopy consists of three steps: excitation to the sublevels of interest, evolution of the sublevels, and detection of the state of interest. In all of the examples discussed in this thesis the first step of excitation occurs by exciting from a single quantum state.

The first step of Zeeman quantum beat spectroscopy is the excitation population sequence that prepares the initial state. In the cases discussed in this thesis, the initial state can be

31
prepared in any of the three ways discussed in section 2.2 so that the initial state is given by either equation 2.14, equations 2.18 and 2.19, 2.27, or 2.28.

In the presence of an applied magnetic field, the Zeeman effect causes an energy shift of the \( m \) and \( m' \) sublevels. The energy shift is

\[
\Delta E = g_{\text{eff}} m \mu_B B = \hbar m \omega_z
\]  

(2.29)

where \( g_{\text{eff}} \) is the effective \( g \)-factor, \( \mu_B \) is the Bohr magneton, and \( B \) is the applied magnetic field. The initial state evolves so that at a later time \( t \) the molecule is in the state

\[
|\Psi(t)\rangle = e^{im_1 \omega_z t} |J, m_1 \rangle + e^{i\phi + im_2 \omega_z t} |J, m_2 \rangle.
\]  

(2.30)

At a time \( t \) this state absorbs or emits a photon with polarization \( \epsilon \). The Hamiltonian for this interaction is

\[
\hat{H} = -e \mathbf{E} \cdot \mathbf{r} \propto \epsilon \cdot \mathbf{r}
\]  

(2.31)

where \( \mathbf{E} \) is the electric field of the photon. The measured intensity associated with the decay to all final states

\[
I(t) \propto \sum_f \sum_q |\langle f | \epsilon_q \cdot \mathbf{r}_{-q} |\Psi(t)\rangle|^2
\]  

(2.32)

where \( |f\rangle \) is the final state, and \( q \) denotes all possible polarizations of the photon. The photon polarization in the final state is summed over as these represent separate final states. This is different from exciting with \( \hat{x} \) polarized light, which is the sum of the spherical tensors \( r_- - r_+ \), which form a single polarization of light. Equation 2.32 is often calculated using the Wigner-Eckart theorem.

A simple example of Zeeman quantum beats is the fictionalized decay of the excited state in equation 2.14 to a single ground state \( |J=0, m=0\rangle \) as shown in figure 2.3. To simplify notation, for the rest of this section, all ket notation will be in the form \( |J, m\rangle \). At later times, this state evolves as

\[
|\Psi(t)\rangle = \frac{1}{\sqrt{2}} \left(-e^{i\omega_z t} |1, +1\rangle + e^{-i\omega_z t} |1, -1\rangle \right).
\]  

(2.33)

A fixed detector looking in the \( \hat{y} \) direction can detect photons with either \( \hat{x} \) or \( \hat{z} \) polarization.
such that by applying equation 2.32 the measured intensity is proportional to

\[ I(t) \propto |\langle 0, 0 | \mathbf{e}_z \cdot \mathbf{r} | \Psi \rangle|^2 + |\langle 0, 0 | \mathbf{e}_z \cdot \mathbf{r} | \Psi \rangle|^2. \]

(2.34)

Applying equations 2.7, 2.8, 2.33 yields

\[
I(t) \propto \left| -\sqrt{2} e^{i\omega z t} \left[ \langle 0, 0 | r_- | 1, 1 \rangle - \langle 0, 0 | r_+ | 1, 1 \rangle \right] + \sqrt{2} e^{-i\omega z t} \left[ \langle 0, 0 | r_- | 1, -1 \rangle - \langle 0, 0 | r_+ | 1, -1 \rangle \right] \right|^2 
+ \left| e^{i\omega z t} \langle 0, 0 | r_0 | 1, 1 \rangle + e^{-i\omega z t} \langle 0, 0 | r_0 | 1, -1 \rangle \right|^2.
\]

(2.35)

The intensity can be calculated by applying the Wigner-Eckart theorem. Since the reduced matrix elements are common to all terms in the intensity distribution, they are a proportionality constant and will be ignored in this calculation. Again, all zero 3-j matrix elements will be ignored. Then, the intensity is

\[
I(t) \propto \left| -\frac{1}{\sqrt{2}} e^{i\omega z t} \begin{pmatrix} 0 & 1 & 1 \\ 0 & -1 & 1 \end{pmatrix} - \frac{1}{\sqrt{2}} e^{-i\omega z t} \begin{pmatrix} 0 & 1 & 1 \\ 0 & 1 & -1 \end{pmatrix} \right|^2.
\]

(2.36)

In this case, the 3-j symbols for the \( \hat{z} \) polarized photons are zero since \( m_1 + m_2 + m_3 \neq 0 \). Physically, it is unsurprising that these 3-j symbols are zero since in this coordinate system \( \hat{z} \) polarized photons cause \( \Delta m = 0 \) transitions. Since there are no \( |m|=1 \) ground states, a \( \Delta m = 0 \) transition cannot occur. Calculating the 3-j symbols for the \( \hat{x} \) polarized photons gives

\[
I(t) \propto \left| -\frac{1}{\sqrt{6}} e^{i\omega z t} - \frac{1}{\sqrt{6}} e^{-i\omega z t} \right|^2.
\]

(2.37)

Writing this expression in a more familiar form and dropping the proportionality constant yields

\[
I(t) \propto 1 + \cos 2\omega z t.
\]

(2.38)

Therefore decay intensity modulates at twice the Zeeman precession frequency.

There are several advantages of quantum beat spectroscopy for this experiment. First, it does not require the use of narrow linewidth lasers for excitation or detection. No detection
laser is necessary if fluorescence detection is used. If absorption detection is used, any laser that is broad enough to cover the energy difference between the excited states and drive them to a single common energy level without driving other transitions is sufficient. Second, quantum beat spectroscopy is Doppler-free. The signal that is being measured is the intensity modulation due to the interference between the excited state energy levels. The photon that is emitted from a moving molecule has a Doppler shift in the lab frame, but the quantum beat signal is due to the energy difference between the levels. Since both energy levels are almost equally Doppler shifted, the Doppler shifts nearly cancel. The Doppler shift from the slightly different energy levels is

\[ \Delta \nu_b = \frac{\Delta \nu}{c} \nu_b. \] (2.39)

For a typical molecular velocity of 300 m/s, and a typical quantum beat frequency of 300 kHz, the Doppler shift is 0.3 Hz. This is very small compared to the linewidth, which is \( \Delta \nu_b \sim \frac{1}{2\pi \tau} \sim 3 \) kHz. Therefore, for these purposes quantum beats are nearly Doppler free, and Doppler shifts need not be considered.

### 2.3.1 Contrast of Quantum Beats in Molecules

In this experiment, contrast is the extent to which the intensity is modulated. In the example in the last section, 100% contrast was achieved because the energy level structure is simple. In more complicated systems such as molecules, the maximum contrast is limited by multiple decay channels, not all of which give rise to beats (see figure 2.5).

The initial state for the level structure shown in figure 2.5, which is relevant for the EDM measurement, is given by equation 2.27. The time evolved state is

\[ |u_\xi(t)\rangle \propto -e^{i \omega x t} \left[ |1,1,\ell\rangle + |1,1,f\rangle \right] + e^{-i \omega z t} \left[ |1,-1,\ell\rangle - |1,-1,f\rangle \right]. \] (2.40)

Again, the detector is pointing in the \( \hat{y} \) direction so that \( \hat{x} \) and \( \hat{z} \) polarized photons can be detected. In this case, however, there are multiple final states \( |j,m\rangle \), so that the detected
Figure 2.5: Energy diagram showing the decay channels between one polarized level of the \( a(1) \) state and different rotational levels of the ground state. Only the decay channels where both the \( m=+1 \) and \( m=-1 \) \( a(1) \) state decay to the same \( X \) state give rise to quantum beats, and all other decay channels create background fluorescence. Here the \( a(1) \) state is shown in the presence of a strong electric field that completely polarizes the molecule. Therefore all \( |m|=1 \) states have equal components of \( |e\rangle \) and \( |f\rangle \) parities.
intensity is

\[ I(t) \propto \sum_{j,m} |\langle j, m | \hat{z} \cdot r | u(t) \rangle|^2 + |\langle j, m | \hat{z} \cdot r | u_c(t) \rangle|^2 \]  \tag{2.41}

\[ I(t) \propto \sum_{j,m} |\langle j, m | \frac{r - r_+}{\sqrt{2}} | u_c(t) \rangle|^2 + |\langle j, m | r_0 | u_c(t) \rangle|^2. \]  \tag{2.42}

Expanding out the intensity in terms of the possible values of \( j \) and \( m \) gives

\[ I(t) \propto \left| -e^{i\omega z t} \langle 0, 0, e| \frac{r - r_+}{\sqrt{2}} |1, 1, e\rangle + |1, 1, f\rangle \right|^2 \]
\[ + \left| -e^{i\omega z t} \langle 0, 0, e| r_0 |1, 1, e\rangle + |1, 1, f\rangle \right|^2 \]
\[ + \sum_{m=-1}^{1} \left\{ \left| -e^{i\omega z t} \langle 1, m, e| \frac{r - r_+}{\sqrt{2}} |1, 1, e\rangle + |1, 1, f\rangle \right|^2 + \left| -e^{i\omega z t} \langle 1, m, e| \frac{r - r_+}{\sqrt{2}} |1, -1, e\rangle - |1, -1, f\rangle \right|^2 \right\} \]
\[ + \left| -e^{i\omega z t} \langle 2, m, e| r_0 |1, 1, e\rangle + |1, 1, f\rangle \right|^2 + \left| -e^{i\omega z t} \langle 2, m, e| r_0 |1, -1, e\rangle - |1, -1, f\rangle \right|^2 \right\} \]

This expression can be simplified by applying the parity selection rules for the transition so that

\[ I(t) \propto \left| -e^{i\omega z t} \langle 0, 0, e| \frac{r - r_+}{\sqrt{2}} |1, 1, e\rangle + e^{i\omega z t} \langle 0, 0, e| \frac{r - r_+}{\sqrt{2}} |1, -1, e\rangle \right|^2 \]
\[ + \left| -e^{i\omega z t} \langle 0, 0, e| r_0 |1, 1, e\rangle + e^{i\omega z t} \langle 0, 0, e| r_0 |1, -1, e\rangle \right|^2 \]
\[ + \sum_{m=-1}^{1} \left\{ \left| -e^{i\omega z t} \langle 1, m, e| \frac{r - r_+}{\sqrt{2}} |1, 1, e\rangle + |1, 1, f\rangle \right|^2 + \left| -e^{i\omega z t} \langle 1, m, e| \frac{r - r_+}{\sqrt{2}} |1, -1, e\rangle - |1, -1, f\rangle \right|^2 \right\} \]
\[ + \sum_{m=-1}^{1} \left\{ \left| -e^{i\omega z t} \langle 2, m, e| \frac{r - r_+}{\sqrt{2}} |1, 1, e\rangle + |1, 1, f\rangle \right|^2 + \left| -e^{i\omega z t} \langle 2, m, e| \frac{r - r_+}{\sqrt{2}} |1, -1, e\rangle - |1, -1, f\rangle \right|^2 \right\} \]
\[ + \sum_{m=-1}^{1} \left\{ \left| -e^{i\omega z t} \langle 1, m, e| r_0 |1, 1, e\rangle + |1, 1, f\rangle \right|^2 + \left| -e^{i\omega z t} \langle 1, m, e| r_0 |1, -1, e\rangle - |1, -1, f\rangle \right|^2 \right\} \]

This expression can be rewritten with the Wigner-Eckart theorem. Again, the 3-j symbols

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
that do not satisfy the condition that \( m_1 + m_2 + m_3 = 0 \) will be set to zero (see Appendix A).

\[
I(t) \propto \left| \frac{-e^{i\omega z t}}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 1 \\ 0 & -1 & 1 \end{pmatrix} - \frac{e^{-i\omega z t}}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 1 \\ 0 & 1 & -1 \end{pmatrix} \right|^2 \langle 0||r||1 \rangle^2 \\
+ \left| (-1) \frac{-e^{i\omega z t}}{\sqrt{2}} \begin{pmatrix} 1 & 1 & 1 \\ 0 & -1 & 1 \end{pmatrix} + \frac{e^{-i\omega z t}}{\sqrt{2}} \begin{pmatrix} 1 & 1 & 1 \\ 0 & 1 & -1 \end{pmatrix} \right|^2 \langle 1||r||0 \rangle^2 \\
+ \left| -e^{i\omega z t} \begin{pmatrix} 1 & 1 & 1 \\ -1 & 0 & 1 \end{pmatrix} - e^{-i\omega z t} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 0 & -1 \end{pmatrix} \right|^2 \langle 1||r||1 \rangle^2 \\
+ \left| (-1) \frac{-e^{i\omega z t}}{\sqrt{2}} \begin{pmatrix} 2 & 1 & 1 \\ 0 & -1 & 1 \end{pmatrix} - \frac{e^{-i\omega z t}}{\sqrt{2}} \begin{pmatrix} 2 & 1 & 1 \\ -2 & -1 & 1 \end{pmatrix} \right|^2 \langle 2||r||0 \rangle^2 \\
+ \left| (2.43) \right|
\]

where the reduced matrix elements are not the same for all final states. Calculating the 3-j symbols reduces this expression to

\[
I(t) \propto \left\{ \frac{1}{3} + \frac{1}{3} \cos (2\omega z t) \right\} \langle 0||r||1 \rangle^2 + \left\{ \frac{1}{2} + \frac{1}{6} \cos (2\omega z t) \right\} \langle 1||r||1 \rangle^2 + \left\{ \frac{13}{30} + \frac{1}{30} \cos (2\omega z t) \right\} \langle 2||r||1 \rangle^2 \\
(2.43)
\]

Without additional information about the reduced matrix elements this expression cannot be reduced further. In this case, the reduced matrix elements can be derived from the relative intensities of the fluorescence from rotational lines when the laser driving the \( X \rightarrow a(1) \) transition is tuned to the appropriate levels (see Appendix B). For each rotational line, it is necessary to relate the measured rotational strength \( I_{rot} \) to the reduced matrix element. For a \( z \) polarized laser beam

\[
I_{rot}(J' \rightarrow J) \propto \sum_{m'=-J'}^{J'} \sum_{m=-J}^{J} \left| \langle X, J', m' | r_0 | a(1), J, m \rangle \right|^2. \quad (2.44)
\]

Applying the Wigner-Eckart theorem, this becomes

\[
I_{rot}(J' \rightarrow J) \propto \sum_{m'=-J'}^{J'} \sum_{m=-J}^{J} \left| (-1)^{J'-m'} \begin{pmatrix} J' & 1 & J \\ -m' & 0 & m \end{pmatrix} \right|^2 \langle J'||r||J \rangle^2. \quad (2.45)
\]

For R, Q, and P branches the sum over 3-j symbols for a common \( J \) is the same since for
Table 2.1: The relative amplitudes of the rotational lines in the $X(v = 1) \rightarrow a(1)(v = 5)$ transition and the calculated reduced matrix elements.

| Rotational Line | $I_{rot}$ | Reduced Matrix Element | Amplitude $\langle J||r||2 \rangle$ |
|-----------------|-----------|------------------------|----------------------------------|
| R1              | 1         | $|1||r||2 \rangle$     | 1                                |
| Q2              | 0.8       | $|2||r||2 \rangle$     | 0.8                              |
| P3              | 0.6       | $|3||r||2 \rangle$     | 0.6                              |

Therefore, $I_{rot}(J' \rightarrow J) \propto \langle J' ||r|| J \rangle^2$.

With the values calculated in table 2.1 and assuming $\langle J - 1 ||r|| J \rangle : \langle J ||r|| J \rangle : \langle J + 1 ||r|| J \rangle$ is the same for $J=1$ and $J=2$, the expected quantum beat signal from fluorescence detection is

$$I(t) \propto 1 + 0.5 \cos 2\omega t.$$  \hspace{1cm} (2.47)

Therefore the maximum expected contrast is $\sim 50\%$.

The observed contrast is significantly smaller and is $\sim 10-12\%$. Simulated quantum beats with 50% contrast are shown in figure 2.6 and the observed quantum beats are shown in figure 3.45. The discrepancy between the calculated and observed contrast is not understood at this time.

2.4 Lifetime of the a(1) State and Density of Available Molecules

As discussed above, the ground state of PbO is a $^1\Sigma^+$ state and the a(1) state is a $^3\Sigma^+$ state. If PbO were a Hund's case (a) molecule, this transition would be forbidden because $\Delta \Sigma = 0$ in electronic transitions [44]. This transition is only weakly allowed because PbO is a Hund's case (c) molecule. This weak transition leads to a relatively long lifetime for the a(1) state of $82(2)$ $\mu$s [42]. In a vapor cell, this lifetime is further shortened by state quenching and spin quenching collisions with other PbO molecules and the cell walls. The density of the PbO vapor
is controlled by the temperature of the vapor, and it is chosen such that the lifetime of the state is approximately 50 µs. At these temperatures using the most optimistic available data on the partial pressure of PbO, there are expected to be \( \sim 3 \times 10^{15} \) molecules/cm\(^3\) in the cell [52]. However, not all of these molecules are in a useful rovibrational state. Before the laser excitation, at a temperature of \( \sim 1000 \) K, only 0.03\% start in the correct \( v = 0, J = 0 \) rovibrational state to be excited by the laser. This means that the useful available density of molecules in the cell is at most \( \sim 10^{12} \) molecules/cm\(^3\). Note that this useful density of molecules is very low compared to the total density of molecules, and is one of the disadvantages of working with a thermal sample of molecules. Significant effort is being made to cool molecules for exactly this reason [53].

In order to detect as many of these molecules as possible, a vapor cell with wide optical access was built, as discussed in the next chapter. The components of the apparatus are discussed in the next chapter with attention to the features of PbO that made construction of the apparatus particularly difficult. The apparatus was designed for maximal excitation and detection efficiencies, low magnetic noise, and quick alternation between measuring \( n_z = \pm 1 \) levels of the \( \Omega \) doublet. Additionally, since PbO vaporizes at \( \sim 700^\circ \) C, the vapor cell was enclosed in an oven that was turned off during each measurement to further reduce magnetic noise.
2.5 Noise Sources

As with most EDM experiments such as the ones discussed in section 1.9, this experiment is sensitive to many possible sources of noise. Since all of these experiments operate in a similar way, they are sensitive to similar noise sources, and therefore these noise sources will be discussed generally. This discussion is applicable to many of these experiments. Most of the noise arises from the fact that the magnetic moment of the electron is so much larger than the electric dipole moment. This energy difference can be clearly seen by comparing the energies of a free electron under the Hamiltonians in equations 1.1 and 1.2 in typical laboratory fields. In a very small but typical uncontrolled laboratory magnetic field of 1 μG, the energy shift of an atom with a magnetic dipole moment of one Bohr magneton is $9 \times 10^{-27}$ erg or 1 Hz. In a very large laboratory field of 100 kV/cm, the same atom with a typical atomic enhancement factor of 500 and with the current limit of $d_e < 1.6 \times 10^{-27} e \text{ cm} \ [1]$ would have an energy shift of $1 \times 10^{-31}$ erg or 10 μHz. Clearly, magnetic fields are significant potential problem for these experiments.

2.5.1 Stray Magnetic Fields

Few EDM experiments are fundamentally limited by noise from stray magnetic fields, but most go to great lengths to shield the experiment from stray fields and cut data taken during magnetically noisy times. For this reason, several layers of magnetic shielding made of magnetically permeable alloys such as Conetic are used as passive magnetic shielding. Some experiments use co-magnetometers to reject or correct data taken during magnetically noisy periods (for example [1, 30]). This second atomic species should have a small enhancement factor, but a similar $g$-factor, to the species that is being studied. Comagnetometers, however, can be problematic as interactions between the different species can be a source of instability or additional noise [9]. This experiment uses the Ω-doublet structure of the a(1) state as a co-magnetometer as will be discussed in the next chapter. The co-magnetometer can be used to reject stray magnetic fields from noise and some of the systematic effects discussed in section 2.6. Since the co-magnetometer is internal to the structure of PbO and is not from an additional species, no additional instability and noise are introduced.
2.5.2 Magnetic Johnson Noise

Johnson noise is generated by the thermal agitation of electrons within conductors, and this charge can generate magnetic fields that can perturb some experiments [54]. Most experiments are only sensitive to the Johnson noise in the conductors that are closest to the experiment (i.e., the electrodes and perhaps the magnetic shielding).

In this experiment, the electrodes extend inside of the vapor cell and are cylindrically symmetric. One electrode extends down from the top of the vapor cell, and the other extends up from the bottom of the vapor cell. The magnetic field generated by Johnson noise is generated by two cylindrically symmetric electrodes in the x-y plane. These generate an electric field in the \( \hat{z} \) direction which is

\[
(\Delta(B_z)^2)_{\omega}(r) = \frac{2kT}{\pi} \frac{\omega}{4\pi} \left( \frac{\mu_0}{4\pi} \right)^2 \int D_z^2(r - r')d^3r'
\]

(2.48)

where \( \Delta B_z \) is the magnetic field generated in the \( \hat{z} \) direction, \( \frac{\mu_0}{4\pi} \) is the permeability of free space, \( \omega \) is the current fluctuation frequency, \( \sigma \) is the conductivity, and the integrand is

\[
D_z(r - r') = \left( \hat{z} \times \frac{r - r'}{|r - r'|^3} \right) \cdot \hat{z}.
\]

(2.49)

This integral will reach a singularity at the electrodes, so to calculate the Johnson noise in this vapor cell, the integral was calculated over the entire volume within one thickness of the electrodes. Since the electrodes have been designed to be thin, this has been considered a reasonable approximation. The experimental conditions are \( T=1000 \text{ K} \), \( \sigma = \frac{1}{7.86 \times 10^{-8}} \text{ \Omega m} \) [52], and \( \tau=50 \mu s \). The radius of the electrodes \( r=1.125'' \), and the thickness of the electrodes \( t \) is 0.007''. Despite the high temperatures of the vapor cell, it was calculated that the expected magnetic Johnson noise in the vapor cell from the electrodes is \( (\Delta B_z)^2 = 0.02nG/\sqrt{Hz})^2\tau^{-1}. \)

This can be expressed in terms of the coherence time of the experiment \( \tau \) and the bandwidth of the measurement \( \omega \) as

\[
(\Delta B_z)^2 = (\Delta B_z\omega)^2 \frac{2\pi}{\tau}.
\]

(2.50)

For each data point taken with a \( \tau = 50 \mu s \) lifetime, the magnetic Johnson noise from the electrodes will be \( \Delta B_z=2.5 \mu G \). This corresponds to a frequency width of \( \delta\nu = 2gB\mu_B = 13 \).
Hz. This is well below the shot noise limit for each data point. As discussed in section 5.2 the 
frequency resolution of each data point is $\delta \nu = 1800$ Hz.

Magnetic Johnson noise from the magnetic shielding has been calculated to be even smaller. In this calculation, it was assumed that only the magnetic Johnson noise from the inner shield contributed to the total magnetic noise as the inner shield would shield noise from all shields outside of it. The magnetic Johnson noise from the magnetic shielding was calculated to be $(0.1 \ pG)^2 \tau^{-1}$ at the center of the cell [55]. For simplicity, this calculation was not done over the cell volume.

In this experiment there is also a thick and large aluminum vacuum chamber surrounding the vapor cell. This vacuum chamber is at room temperature and is $18''$ in length, has an inner diameter of $14''$ and an outer diameter of $16''$. The conductivity of aluminum is $\sigma = 2.65 \times 10^{-8} \ \Omega \ m$ [52]. The magnetic Johnson noise from the vacuum chamber was calculated to be $(3 \ pG)^2 \tau^{-1}$ at the center of the cell. Again, since this noise is well below the shot noise limit of the experiment, this calculation was not done over the cell volume.

2.5.3 Ferromagnetic Materials

One common check for systematic effects in these experiments is to reverse the direction of the magnetic field. In the absence of an EDM, reversing the magnetic field direction reverses the direction of the spin precession of the molecules, but does not change the measured precession frequency. If the magnitude of the magnetic field changes, however, the precession frequency will change. Most experiments apply a magnetic field by driving current through coils. The direction of magnetic field is easily reversed by switching the sign of current in these coils. Since ferromagnetic materials are hysteretic, the magnetic field may not reverse perfectly when these materials are present. The presence of these ferromagnetic materials can change the magnitude and/or direction of the magnetic field when the direction of the current is reversed. For this reason, ferromagnetic materials are not used anywhere inside the magnetic shielding of these experiments.

The magnetic shielding used to shield the experiment from outside magnetic noise is ferromagnetic and is highly magnetically permeable and hysteretic. These shields are degaussed after each time the current in the coils is reversed. The degaussing process works by driving the
shields with an oscillating magnetic field that is ramped on and off. After the magnetic field is strong enough to saturate the hysteresis curve, the field is ramped off. Since the oscillating field is symmetric around zero, the field domains remain centered around zero and the shields remain demagnetized after degaussing.

2.6 Common Systematic Effects

Just as experiments to measure $d_e$ are plagued by similar sources of noise, they also have similar sources of systematic effects. Again, many of the systematic effects arise from magnetic fields. Magnetic field effects that reverse at the same frequency as the electric field reversal are particularly insidious because these effects mimic a non-zero EDM and can lead to systematic errors.

2.6.1 Leakage Currents

Electric fields are applied to the interaction region across electrodes, and despite good electrical insulation, it is possible for current to flow between the electrodes. The current path that leads to a magnetic field that best simulates a non-zero EDM is one in which the current spirals around the interaction region inducing a magnetic field parallel to the electric field. In this worst case scenario, the current will reverse every time the electric field reverses. The magnetic field induced by these leakage currents will also reverse synchronously.

To control this systematic, leakage currents are kept as small as possible in these experiments. Again, co-magnetometers can be used to reduce the significance of this effect. In this experiment, the $\Omega$-doublet energy level structure of PbO allows for the sign of the energy shift due to $d_e$ to be reversed without reversing the direction of the electric field. This energy level structure acts as an internal co-magnetometer. Nevertheless, leakage currents remain the most significant potential systematic error in this experiment because insulators are much less resistive at high temperatures. Ceramics, which are the insulating materials used in this experiment, have ionic conduction pathways that increase exponentially at increasing temperature. Since this experiment is performed at 700°C, the leakage currents in this experiment are much higher than those in experiments performed at room temperature (for example see [31]).
According to relativity, any particle moving in an electric field will also be acted upon by a magnetic field. In SI units,

$$B = \frac{1}{c^2} (v \times E).$$  \hspace{1cm} (2.51)

In experiments conducted in atomic or molecular beams, this systematic is particularly dangerous because the beam velocity clearly defines a preferential direction for the atoms or molecules. In the coordinate system shown in figure 2.7, the primary forward direction of the atomic or molecular beam is in the $y$ direction. According to equation 2.51, the velocity component that is in the $y$ direction combined with the electric field in the $z$ direction can cause a magnetic field in the $x$ direction. If the primary magnetic field is misaligned it also has a component in this direction, the $v \times E$ effect causes a magnetic field that adds to the primary magnetic field. Therefore this effect causes an additional shift in the precession frequency.

This systematic can also be problematic for experiments in vapor cells. In experiments conducted in vapor cells, such as this one, certain sections of the Boltzmann distribution known as velocity classes can be preferentially excited or detected through a variety of experimental imperfections. Then the atoms or molecules have a preferential direction just as in beam experiments. For example, if the excitation laser were slightly detuned, the laser would preferentially excite molecules in a particular velocity class as a result of the Doppler effect. If the laser were red detuned, it would be more resonant with the molecules moving towards the laser beam whereas a blue detuned laser would be more resonant with molecules moving away from the laser beam. If this preferential direction is perpendicular to the electric field, again by equation 2.51 they...
Figure 2.8: Energy level diagram for an atom or molecule that has a large tensor Stark splitting.

experience a magnetic field. In most vapor cell experiments, the laser beam is directed into a window that is perpendicular to the electric field plates, so detunings in the laser frequency would indeed create molecules that are moving in a direction perpendicular to the electric field. In a cell, however, it is easier to change the parameter that is creating a preferential direction. In this case, changing the laser frequency slightly and looking for changes in the EDM signal will give an indication of how significant $\mathbf{v} \times \mathbf{E}$ effects are.

Similar to leakage currents, $\mathbf{v} \times \mathbf{E}$ effects will exhibit the same periodicity as the reversal of the electric field direction and will be difficult to distinguish from an EDM signal. Again, co-magnetometers can be used to reduce this systematic since $\mathbf{v} \times \mathbf{E}$ creates a magnetic field.

Some experiments are inherently less sensitive to this effect as a result of choosing a system in which the tensor Stark splitting is larger than the Zeeman splitting [56]. Essentially, this means that the atom or molecule is more affected by electric fields than magnetic fields. This makes the applied electric field the natural quantization axis for the system. The atom or molecule will strongly align with the direction of the electric field rather than tipping towards the direction of the magnetic field. This strong alignment in the electric field direction is true regardless of whether the magnetic field is not parallel to the electric field as a result of misalignments or motional magnetic fields. In these systems, the tensor Stark splitting creates an energy diagram for the state such as the one shown in figure 2.8. In an applied electric field, the energy difference between the $m=0$ and $|m|=1$ states is much larger than the energy of the magnetic field from $\mathbf{v} \times \mathbf{E}$. The magnetic field can only connect states of $|\Delta m|=0,1$, since electromagnetic fields only carry one unit of angular momentum. The energy difference between the $m=0$ and $|m|=1$ states is so much larger than the energy of the magnetic field from $\mathbf{v} \times \mathbf{E}$, this effect is not sufficient to tip the atoms or molecules with a tensor Stark splitting. PbO is one of the experiments that is
less sensitive to this effect. For example, an order of magnitude estimate of \( v \times E \) effects in PbO suggests that they are quite small. For a magnetic field in the \( \hat{x} \) direction, the induced mixing due to \( v \times E \) effects is

\[
\Delta E = \frac{\langle J = 1, m = +1 | \mu g B_x | J = 1, m = 0 \rangle \langle J = 1, m = 0 | \mu g B_x | J = 1, m = -1 \rangle}{\Delta E_{\text{Stark}}} \quad (2.52)
\]

where \( g \) is the \( g \)-factor. Using the Wigner-Eckart theorem, this reduces to

\[
\Delta E = \frac{\langle \mu g B \rangle^2}{72 E_{\text{Stark}}} \quad (2.53)
\]

where \( B \sim \frac{|v||E|}{\epsilon} \) is the magnitude of the magnetic field induced by the \( v \times E \) effect. For a typical molecular velocity of 300 m/s, an electric field of \( E \sim 100 \) V/cm, and a Stark shift \( \Delta E_{\text{Stark}} = 60 \) MHz, this leads to frequency shifts of \( \Delta E / \hbar \sim 4 \times 10^{-11} \) Hz, or a false EDM signal of \( d_{e,\text{false}} \sim 10^{-35} \) e cm. Clearly, even with this order of magnitude estimate, these shifts are much too small to be a problem for this experiment.

### 2.6.3 Berry’s phases

If an external parameter is varied adiabatically, it is possible for a state to acquire a geometric phase factor known as a Berry’s phase. Since EDM experiments measure the accumulated phase due to \( H_{\text{EDM}} \), they are also very sensitive to Berry’s phases. A phase can accumulate if the quantization axis is moved by changing external fields during the interaction time. This phase accumulation can be significant if \( v \times E \) effects are significant enough to tip the quantization axis \[57\]. Since \( v \times E \) effects are negligible in PbO, Berry’s phases arising from \( v \times E \) are also expected to be negligible. However, Berry’s phases can also accumulate in regions where the electric field varies. Since the molecule will always align strongly with the direction of the electric field, as the molecule passes through different regions with different directions of the electric field the molecule tips. This tipping of the molecule allows the molecule to acquire a net phase.

Berry’s phases have been shown to be particularly troubling for experiments conducted in traps where the trapping fields affect the particle trajectories \[58, 59\]. In this experiment, this effect is not relevant since \( v \times E \) effects are negligible in PbO. Additionally, when the molecules
in the $a(1)$ state collide with the wall or other molecules to change directions the metastable state is quenched. As a result the molecules do not change directions while being observed. Furthermore, the $\Omega$-doublet structure acts as a co-magnetometer largely cancelling this effect.
Chapter 3

Apparatus

Unlike many experiments that can be largely designed with commercially available parts, nearly every component of this experiment has been designed and built specifically for this work. This is a result of the very strict requirements of this experiment, which include exquisite control over magnetic fields and the fact that PbO must be contained within a vapor cell heated to 700 °C, while maintaining wide optical access. Although most of the design requirements are discussed in the relevant sections below, three primary issues drove the design of all aspects of the experiment, and therefore are discussed here.

First, as discussed in section 2.5, this experiment is very sensitive to uncontrolled magnetic fields, so no ferromagnetic materials have been used inside of the four layers of magnetic shielding that are used in the experiment. Furthermore, special care has been taken to minimize currents flowing inside the shielded region when the experiment is taking place. For example, the vapor cell is heated by an oven powered by resistive heaters that are turned off before each measurement. Custom built non-ferrous co-axial feedthroughs were designed to reduce the magnetic fields from the electrical connections, and special non-magnetic thermocouples were designed. All dissimilar metals are electrically insulated to prevent the thermocouple effect from causing currents.

Second, the experimental resolution is limited by the excitation and detection efficiencies, so a large amount of optical access to the vapor cell is necessary. Since the angular distribution of spontaneously emitted fluorescence from the molecules is nearly isotropic, a large solid angle of detection is necessary to detect a significant fraction of the fluorescence. In addition, three types of photodetectors were investigated in an attempt to maximize the detection efficiency for
the experiment.

Third, PbO vaporizes at ~ 700°C, so it is necessary to use an oven and vapor cell that can withstand this temperature in the presence of PbO vapor. Great care has been taken in the choice of materials used in both the oven and cell. In particular, the choice of materials to be used as an electrically insulating spacer between the electrodes and guard rings is critical since this spacer determines the leakage currents in the cell.

This chapter discusses the apparatus that has been designed for and used in this experiment. The chapter starts with a discussion of the mechanical apparatus starting from the inside with the vapor cell, oven, heat shields, and vacuum chamber, and proceeding to the outside where the magnetic shielding forms the outer layer of the mechanical apparatus. The lasers and microwaves used for populating the EDM superposition state are discussed followed by a summary of the optics in the detection system and the three types of detectors that have been designed and built for use in the experiment. A cross sectional side view of all of these components is shown in figure 3.1. The magnetic shielding, magnetic field coils, vacuum chamber, heat shielding, oven, vapor cell, and lightpipes are also shown in cross section from the top in figure 3.2.

3.1 Vapor Cell

In addition to the requirements for optical access, the ability to withstand high temperatures, and electrical insulation, there were three requirements for the vapor cell. First, the vapor cell must have a cold spot where a condensed PbO reservoir can be maintained. Second, there must be some way to evacuate and re-seal the cell. Third, electrodes must create an electric field that is homogeneous to ~1% over the cell volume.

The cell is an alumina box with four 2" diameter sapphire windows bonded on the four horizontal faces (see figure 3.3). Reentrant gold electrodes and guard rings are inserted into the top and bottom of the cell. These electrodes and guard rings are supported by an alumina structure and electrically insulated using beryllium oxide and/or sapphire spacers to reduce the leakage currents in the cell. All ceramic surfaces are highly polished, so the contact surfaces between the electrodes, guard rings, spacers, and cell are formed by flat-on-flat pressure seals. Since the cell, the oven that heats the cell, and the surrounding heat shields are in vacuum, it is possible to initially evacuate the vapor cell at low temperatures through a small hole. This
Figure 3.1: Cross sectional side view of the apparatus. The parts shown here are: a) vacuum chamber b) heat shields c) oven d) cell e) aluminum tube for vacuum f) four almost cylindrical layers of magnetic shielding g) four layers of bottom end caps of magnetic shielding h) aluminum supports for the magnetic shielding i) aluminum tube for vacuum j) connection to the turbo and roughing pumps for vacuum k) plunger apparatus l) four layers of top end caps of magnetic shielding m) degaussing coils for the cylindrical magnetic shields n) quartz lightpipe extending into the vacuum chamber o) plastic lightpipe extending in air out of the magnetic shields p) optical filters q) a light cone r) PMT and associated electronics.
Figure 3.2: Cross sectional top view of the apparatus. The parts shown here are: a) the four nearly cylindrical magnetic shields b) the brass threaded rods used for the transverse magnetic field coils c) the coils used for the magnetic field in the vertical direction d) the vacuum chamber e) the heat shields f) the oven g) the vapor cell h) the X-a(1) excitation laser propagating through quartz lightpipes extending into the vacuum chamber i) fluorescence collected with quartz lightpipes j) detection optics and detector k) microwave horn and electronics.
hole is resealed with a movable alumina plunger. This process occurs at temperatures that are sufficiently low that the PbO that escapes from the cell is negligible. A reservoir of PbO remains condensed in a stem tube that extends 2 7/8" below the bottom electrode.

3.1.1 Material Selection

Although PbO is not a free radical and therefore is thermodynamically stable, PbO reacts with many standard high-temperature materials. For example, PbO is used to make glass, so when it is heated with quartz it makes lead glass. To ensure that materials for the cell would not react with PbO, we heated up a variety of materials in vacuum in the presence of PbO. Many ceramic and crystalline materials such as alumina, sapphire, beryllium oxide, and yttrium aluminium garnet (YAG) do not react with PbO at these temperatures. Boron nitride, quartz, and frit glass (a silicon based glassy eutectic), however, were not compatible. Gold does not react with PbO, but copper, tantalum, zirconium, and molybdenum are not suitable for use.
Table 3.1: Heating sequence for kiln to bond gold and sapphire or alumina.

### 3.1.2 Gold Bonding Technique

Since so few materials are available for use in a vapor cell, it was necessary to develop bonding techniques to attach cell windows and to create electrodes. Primarily, a vapor cell was necessary to contain the PbO vapor so that high densities of PbO could be maintained for long periods of time. Additionally, since PbO corrodes quartz, and the oven is partially made out of quartz, it was necessary that the cell bonds be at least moderately vacuum tight. Furthermore, it was necessary to develop a technique where cell windows could be added sequentially without destroying previously made bonds, since the cell is a box with windows on four sides. Several brazing compounds were tested, but did not survive exposure to PbO. Additionally, an attempt was made to make bonds out of layers of gold and silver heated in vacuum to the melting temperature of gold. The silver was supposed to wet the alumina surface and the gold would seal the area. This technique never wet the surface sufficiently, and the gold always formed balls at the edges of the seal. Similarly, bonds made out of melted gold were found to to form balls at the edges of the seal, and did not seal around the entire surface.

Following Bailey and Black [60] gold seals were made by applying pressure to the sealing surface and then heating in air to just below the melting temperature of gold. The pressure was applied by placing a 3"x5.5"x9.5" granite block on top of the sample. This process was done in a kiln that was programmed as shown in table 3.1. This technique can be repeated as necessary and each successive heating cycle under pressure strengthens the existing bonds. Heating cycles without pressure do not change the existing bonds. The gold forms a vacuum tight bond with polished sapphire or alumina, but not roughened quartz. Unpolished sapphire or alumina did not bond as well since the bonding technique requires good contact between the

<table>
<thead>
<tr>
<th>Step</th>
<th>Program</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ramp at 420°C per hour to 200 °C</td>
</tr>
<tr>
<td>2</td>
<td>Stay at 200 °C for 10 minutes to equalize kiln temperature</td>
</tr>
<tr>
<td>3</td>
<td>Ramp at 420°C per hour to 600 °C</td>
</tr>
<tr>
<td>4</td>
<td>Stay at 600 °C for 10 minutes to equalize kiln temperature</td>
</tr>
<tr>
<td>5</td>
<td>Ramp at 420°C per hour to 800 °C</td>
</tr>
<tr>
<td>6</td>
<td>Stay at 800 °C for 10 minutes to equalize kiln temperature</td>
</tr>
<tr>
<td>7</td>
<td>Ramp at 420°C per hour to 1026 °C</td>
</tr>
<tr>
<td>8</td>
<td>Stay at 1026 °C for 60 minutes to create bond</td>
</tr>
<tr>
<td>9</td>
<td>Ramp at 420 °C per hour to room temperature</td>
</tr>
</tbody>
</table>
materials. To create exposed metallic electrodes, a roughened quartz plate was placed on top of the electrodes or guard rings while bonding. Since roughened quartz does not bond to the gold, the gold would only bond to the alumina or sapphire on one surface and be exposed on the other surface. It was found that this technique creates stronger, more reliable bonds with sapphire than alumina, and also that it works best when both sides of the gold are bonded to a ceramic. As a result, the electrodes were bonded on the surface of sapphire plates. The gold that formed the electrode was bent around to the other side of the sapphire plate and also bonded between the sapphire plate and the supporting tube for further structural support for the foil (see figure 3.4). Without this additional bond, the foil tends to slowly come detached from the sapphire plate after several heating and cooling cycles.

3.1.3 Birefringence of Sapphire Windows

Since the only two transparent materials that we know do not react with PbO are YAG and sapphire, the cell windows must be made out of one of these two materials. YAG is an isotropic crystal and is not birefringent, but it is very expensive to buy large YAG windows. Sapphire windows, by contrast, are readily available in large diameters, and therefore are used as cell windows. The crystalline structure of sapphire is identical in two directions, but a third axis has a different index of refraction, which leads to birefringence. The sapphire windows used in the cell are “c-axis”, which means that the axis with a different index of refraction is oriented perpendicular to the plane of the window, which minimizes birefringence. The sapphire windows used in the cell are guaranteed by the manufacturer to have the c-axis perpendicular to the plane of the window to within 1°. The first set of c-axis windows ordered from this manufacturer were found to have a birefringence consistent with a c-axis ordination misaligned with the plane of
the window by as much as 20°. The windows on the current vapor cell have a birefringence that is consistent with the specification of a c-axis orientation within 1° of the plane of the window. Since the cell window is usually not aligned perpendicular to the incoming laser beam better than 1°, this orientation is sufficient. At the moment, this effect is not corrected for as it is expected that the rotation of the laser polarization due to this birefringence is negligible compared to other misalignments. However, the effects due to birefringence will be exaggerated by tilting the cell to test for systematic effects.

3.1.4 Stem

In order to control the vapor pressure in the cell and to keep the PbO from condensing on the cell windows, there must be a controlled place within the cell that is held at a cooler temperature than the rest of the cell. For this purpose, a stem tube extends 2 7/8” below the cell and was heated by a separate stem heater in the oven. Since the power in this stem heater could be controlled separately from the other heaters in the oven, the stem could always be set to a temperature that was 10-15°C lower than the cell body. A reservoir of condensed PbO was maintained in this stem. Since the cell is formed of mostly vacuum tight seals, in principle, this reservoir only needs to consist of the \( N_{\text{vapor}} = 3 \times 10^{15} \) molecules that are vaporized at the operating temperature of 700°C. However, since it is difficult to measure such a small quantity, and PbO is relatively cheap, \( \sim 0.1 \) g or \( N_{\text{PbO}} = \sim 10^{20} \) molecules are in the reservoir. Early versions of the cell were filled with PbO of natural isotopic abundance, but the current cell is filled with at least 99% \( ^{208}\text{PbO} \). The isotopic purity increases the signal size and decreases backgrounds. \( ^{208}\text{PbO} \) has a natural abundance of 52.4%, so the isotopically enriched sample increases the signal size by almost a factor of 2. Furthermore, other \( ^{206}\text{PbO} \) and \( ^{207}\text{PbO} \) rotational lines are weakly excited by the X\( \rightarrow a(1) \) laser. These additional rotational lines either do not contain quantum beats, or have quantum beats at different frequencies. Therefore, decreasing the abundance of these isotopes in the cell increases the contrast of the beats by a few percent.

3.1.5 Plunger

Since other gases quench the a(1) state of PbO, it was necessary to evacuate the cell to \( 10^{-5} - 10^{-6} \) Torr before heating the cell and vaporizing the PbO. The cell is inside a vacuum chamber,
so it is possible to evacuate the cell by opening a small hole in the top plate and top electrode. However, once the cell is evacuated, it is necessary to reseal this hole so that PbO does not escape. A polished alumina plunger is raised and lowered above this hole by means of a movable vacuum feedthrough. A right angle gear shaft allows the plunger to be raised and lowered by a connection that extends out of the shields. This plunger is manually raised and lowered \(~2\,\text{cm}\) so that the bottom of the plunger remains well heated before coming in contact with the cell. If the plunger were to be much cooler than the cell before contacting the cell, it may cause large thermal gradients that are known to crack alumina.

### 3.1.6 Electric Field Homogeneity

The electric field inside the cell must be as homogeneous as possible to reduce possible systematic effects such as Berry's phases. Furthermore, an inhomogeneous electric field can be the dominant broadening mechanism for the linewidth of the microwave transitions. The reentrant electrodes and guard rings were designed with the goal of keeping the electric field as homogeneous as possible. The resulting field was modelled to be homogeneous to the 1\% level in the region of the cell between the electrodes. For a typical Stark shift in this experiment of 60 MHz, a 1\% inhomogeneity over the cell volume only causes a width in the spectral lines of 600 kHz, which is tiny compared to the laser \(~800\,\text{MHz}\) Doppler width of the X->a(1) transition. However, the Doppler width of the microwave transition is \(~44\,\text{kHz}\), so the 600 kHz width from the electric field broadening is significant. This additional broadening limits the population efficiency using microwaves.

Paul Hamilton has measured the electric field homogeneity to be consistent with the 1\% design specifications by applying an electric field to the cell and using a microwave transition. This population sequence starts with a horizontally polarized laser (see section 2.2.2). Resonant weak microwaves (see section 3.6) in the \(\vec{z}\) polarized direction are used to drive the population to the \(|J = 2)\) state. The disappearance of beats in the \(J = 1\) state is monitored as the microwave frequency is scanned. From the width of the microwave transition, the electric field homogeneity was determined to be consistent with the design specifications.

The electric fields are created by voltages applied to the electrodes. These voltages are carefully controlled so that they can be reversed as accurately as possible. First, a master
voltage is generated by a programmable voltage standard (Electronic Development Company, Model 501J). This voltage standard is specified to have a resolution of 10 μV and a ripple plus noise of less than 5.2 μVrms [61]. The output of this voltage supply is used to generate voltages at precise multiples of the master voltage by a precision amplifier. The schematic of this precision amplifier is shown in [62]. This amplifier has been demonstrated to reverse the output voltages exactly within a standard deviation of 3 mV over 3 days and a peak deviation of 10 mV over a similar time [62].

3.1.7 Leakage Currents

Despite the Ω-doublet structure of the a(1) state, it is still necessary to keep leakage currents as small as possible, and much effort went into the selection and measurement of materials to be used as insulators in the cell. For the first generation experiment described in this thesis, the goal is to keep leakage currents below 10 μA, and further improvement will be necessary for a second-generation experiment with better sensitivity to de. This 10 μA goal is set because a current of this magnitude making a 1/4 turn around the vapor cell corresponds to a false EDM signal of 10^{-28} e cm.

3.1.8 Monitoring of Leakage Currents

Constant monitoring of the leakage currents in the cell will allow us to reject data taken when the leakage currents are too high. To this end four separate, identical circuits were built to monitor the leakage current from each of the two electrodes and each of the two guard rings. The leakage current monitoring circuit transforms the current to a voltage across a 100 kΩ resistor that is kept floating high at the electrode voltage as shown in figure 3.5.

3.1.9 Material Selection

While many materials are excellent insulators at room temperature, there were four factors that made it difficult to find an appropriate material. First, as mentioned in section 3.1.1, many materials are not compatible with PbO at 700°C. Second, the resistivity of insulators drops exponentially with increasing temperature, so many materials that are ideal at room temperature are poor insulators at higher temperatures. Third, the materials tested must be
Figure 3.5: Schematic for the leakage current monitoring system. The input voltage is read across a 100kΩ resistor in series with the cell. In order to keep the high voltage isolated from leakage paths to ground, the measurement electronics must have a floating ground. The AD204 is ideal for this measurement because it produces a floating +7.5 V and -7.5 V power supply that can be used to power another low drift, low power instrumentation amplifier. The low drift InAmp is an AD621 and was chosen to have a low input voltage noise of 0.28 μVp-p, to allow for low noise amplification of the leakage currents across the 100 kΩ resistor. The AD621 has an additional fixed gain of 10. The AD204 has a non-inverting gain of 5 and transforms the floating voltage output from the AD621 to a voltage referenced to ground. The AD204 is powered with a AD246 clock driver that transforms a +15 V signal to a 25 kHz square wave with an amplitude of +15 V. In summary, the output voltage of this circuit is referenced to ground and is the leakage current with a transimpedance amplification of $5 \times 10^6$. 

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
available in sizes large enough to be used in the cell. Fourth, many of the measured leakage currents are much larger than implied by the known volume resistivity. This implies that the leakage is across the surface of the material, not through the volume of the material, so surfaces must be kept as clean as possible. These problems with surface leakage currents have been found with all three of the best insulating materials found. With all of these requirements, the three best insulating materials that were found are high purity alumina, high purity sapphire, and beryllium oxide.

The resistivity of the materials was tested by placing them inside of an oven and a vacuum chamber with electrodes on both sides of the material. A voltage was applied across the electrodes and the current in the leads to the electrodes was monitored. In this measurement system, it is impossible to distinguish between leakage currents between the electrodes, leakage currents through the leads, and leakage currents to ground. For example, typical resistivities measured in this method are shown in figure 3.6.

Better measurements can be made using three-electrode configurations that allow for separate measurements of volume and surface leakage currents. This three-electrode configuration was used for some material tests, but cannot be used in-situ in the cell while the experiment is running. Three (or more) electrode configurations have two leads at high voltages with high...
High Voltage Electrode

Grounded Electrode

Figure 3.7: A three electrode configuration is used for more precise measurements of leakage currents. Since there is no voltage difference between the two high voltage electrodes little or no current flows between these electrodes. This configuration minimizes surface currents and allows for a measurement of the volume current.

impedance to ground. Since the voltage difference between the two electrodes at high voltages is very small, the leakage currents between these electrodes should also be small (see figure 3.7). The outer high voltage connector should shield the inner high voltage connector allowing for the separation of surface and volume currents [63]. Unfortunately, a three electrode leakage current monitoring system cannot be used in-situ, but was used for many tests off-line. These off-line tests were performed both in air and vacuum using a kiln and test chambers.

In the oven, leakage currents between the electrodes and guard rings were consistently measured at the ~5-10 µA level when 100-300 V was applied across the cell. These leakage currents were measured in a variety of different ways. Initial measurements were taken by simply applying a voltage across the cell and measuring the current drawn by the supply. This method yielded results that were difficult to interpret, as leakage to ground could not be distinguished from leakage across the cell. These measurements yielded results ranging from leakages of 1 µA to 100 µA. Paul Hamilton has taken measurements where voltage is applied to a single electrode or guard ring while the other electrodes and guard rings are grounded. The currents in all electrodes and guard rings are simultaneously monitored using the four channel electronic leakage current monitoring circuit shown in figure 3.5. With this method, it is possible to determine where currents are flowing. For example, as shown in figure 3.8 voltage is applied to the top
guard ring while all other electrodes and guard rings are grounded. The current in both guard rings and both electrodes are monitored. Since the sum of all currents in the other two electrodes and bottom guard ring is not equal to the current in the top guard ring, the additional current must be travelling directly to ground. Unfortunately, there is no way to know whether or not these leakage currents to ground are causing magnetic fields in the $z$ direction, so they must be considered as dangerous as the leakage currents through the cell. Therefore, it will be necessary to determine whether the path to ground is causing a magnetic field in the $z$ direction. This can be done using the co-magnetometer created by the $\Omega$ doublet of the a(1) state.

Leakage currents through the cell body have been observed to be roughly independent of which material (beryllium oxide or sapphire) is used for the insulating spacer between pieces of the cell. Preliminary tests suggest that the bottom electrode may have the largest leakage currents to ground. It would be unsurprising if the bottom electrode has the largest leakage currents to ground since this electrode rests on the stem. The stem is electrically connected to the quartz oven through a thermocouple in the stem (see figure 3.9). If necessary, isolating this path with an additional sapphire tube may improve the leakage currents from the bottom electrode.

In general, only high purity alumina such as 99.99% alumina has a sufficiently high resistance
Figure 3.9: The bottom electrode (a) is resting on a sapphire and alumina base that is attached to the stem tube (b). The stem tube is wedged between the quartz oven (c) and a thermocouple which is surrounded by an alumina tube (d). Since none of these pieces are made of very high purity materials, they are believed to have lower resistivities than the insulating spacers used in the cell. Thus, the bottom electrode is expected to have a larger leakage current to ground than the other electrode or guard rings. The leakage from the bottom electrode may be reduced by adding a high purity sapphire tube between the stem tube and the thermocouple.

to be used as an insulator in the oven. The only exception is the plunger, which is made of 97% alumina, but is not expected to increase the leakage currents to ground. The plunger touches the cell, but then extends out of the hot zone of the oven to a much cooler region outside of the heat shields. At lower temperatures, alumina is an excellent insulator, so this path from the top electrode to ground should be well insulated. Since care is taken to minimize the contact between the plunger and the oven, there probably are few paths for leakage currents to occur.

3.2 Oven

PbO vaporizes at 700°, so it was necessary to construct an oven to heat the cell to at least this temperature. The oven must allow for good optical access to the cell and have a low inductance so that the power to it can be turned off before every measurement. The first version of this oven is described in more detail in reference [64]. A new oven built on this general design was used in these experiments, although several modifications were made to the design and construction. The basic parts of the oven are shown in figures 3.10 and 3.11, and the oven completely built with heat shields on is shown in figure 3.12.

There are twelve separate tantalum heating elements in the oven, which are each driven separately by a single supply. The heating elements are a cylindrical stem, a cylindrical plunger,
Figure 3.10: Picture of the main body of the oven. A tantalum heat shield is attached directly to the outside of the window, plunger, stem, top, and bottom heaters. The tantalum foils are pressed between the opaque quartz plates that are grooved to support the foils. Tabs from these foils extend out from the quartz to allow for connections to the terminal blocks.
Figure 3.11: A 3-D drawing of the oven without heat shields.
Figure 3.12: A 3-D drawing of the oven with 3 layers of OP1 quartz heat shielding. A layer of tantalum heat shielding is bolted to the inner layer of quartz shielding and two layers of copper heat shielding are bolted to the outer two layers of quartz shielding.
a flat top plate, a flat bottom plate, four flat side plates, and four cylindrical windows. The tantalum foils are designed in a zig-zag configuration to minimize their inductance. The foils are cut using laser machining, and are pre-cleaned by heating in vacuum before they are used in the oven. Tantalum is a good heating element in vacuum, but after 1-2 months of use in our oven it becomes brittle due to crystallization and oxidization and breaks.

The new oven is made out of an opaque OP1 quartz body and tantalum foils that fit into grooves machined into the quartz structure. The opaque quartz was chosen because it absorbs much of the blackbody radiation and re-radiates it at a more uniform temperature (see figure 3.13). The previous oven was made of transparent quartz that was coated with a high-emissivity paint.

In retrospect, opaque quartz may have been a poor choice for an oven and heat shield material. The body of the previous oven was made out of a transparent quartz since quartz can be machined, can be safely thermally cycled and is sufficiently electrically insulating for the oven. Opaque quartz is made by deliberate inclusion of many small (20-100 μm) air bubbles embedded in the material. Unfortunately, it seems air is slowly diffusing out of the bubbles and oxidizing the tantalum foils.

Figure 3.13: Light is not well transmitted through opaque quartz, and this transmission is not a strong function of wavelength in the IR where most of the blackbody radiation is. For comparison, the opaque quartz shields are 3.2 mm thick, and most quartz parts of the oven are 2.0 mm thick. Figure courtesy of Technical Glass Products [65].
The heat shields for the new oven were also made out of OP1 since there was a concern that eddy currents in metal shields would be problematic. Furthermore, the structural rigidity of these shields compared to the thin foil shields used on the previous oven appeared attractive. Again, since OP1 absorbs much of the blackbody radiation, it was thought that the shields would absorb the radiation and reradiate it back into the oven. Apparently, this process is not nearly as efficient as reflective shields, since it is impossible to heat the oven above 400°C with OP1 shields alone with the available power levels. To solve this problem, additional layers of reflective heat shielding were added to the OP1 shields by mechanically bolting thin reflective foils to the quartz shields. The inside of the inner layer of OP1 shields was covered inside with a layer of tantalum foil, and the two outer layers with copper foil. In addition, a layer of tantalum foil is wrapped around the window heaters of the oven, the stem, the plunger, and on the outside of the top and bottom heating elements to add another layer of heat shielding. With all this additional shielding, it is now possible to heat the oven to the necessary temperatures of ~700°C.

Despite all of the added heat shielding, the new opaque quartz oven is not as efficient as the old oven was. There are two possibilities for this. First, the new oven is made out of the same heating elements as the old oven, but is spaced out further to allow for a larger cell and more connections inside the oven. Since the solid angle covered by heaters is smaller, it is likely that the efficiency of the oven is inherently smaller. Second, since the inner pieces of the new oven are made of opaque quartz, this opaque quartz absorbs the blackbody radiation directly from the tantalum foils and reradiates it at a more uniform temperature. If this process is not very efficient, the cell may not be exposed to as much direct radiation from the oven. As inner pieces of the quartz oven break, they are being replaced with parts made of transparent quartz to solve this potential problem. Currently, approximately half of the inner quartz pieces are made out of transparent quartz, but there has not yet been a noticeable change in the power necessary to heat the oven. Therefore, it is likely that the heating process is sufficiently efficient through OP1 quartz.

To avoid replacing the tantalum foils, several other materials for heating elements were tested. A 50/50 alloy of gold-palladium was found unsuitable for heating because poor material homogeneity created hot spots where the foil broke. Nickel foils seemed ideal, but after repeated heating it was found that they slowly evaporate. The magnetic properties of nickel were not
an issue since the nickel was heated well above the Curie temperature. A special alloy of iron, chromium, and aluminum made by Kanthal is being investigated for future use. Unfortunately, this Kanthal alloy outgasses during the heating process, and there is significant concern that this outgassed material contains ferromagnetic material that will stick to areas of the vacuum system that will not be heated above the Curie temperature. This ferromagnetic material could cause systematic effects.

Unlike the first oven, the new oven was designed to not use any ceramic glues or high emissivity paint in case either of these substances made the leakage currents worse in the cell. It is suspected that these glues and paints outgas and the outgassed materials can stick to the cell surfaces, contaminating them. To avoid using glue, the supporting tabs for connecting the foils to wires extending out of the oven are made out of the same quartz piece as the foil supports.

Making connections to the cell inside the oven required placing two holes midway up on the corners of the oven. Through these holes, there are nine connections to the vapor cell. Eight of these consist of four pairs of redundant connections to each electrode and guard ring that are made of gold wire and threaded with beryllium oxide beads and then passed through bent quartz tubes that are supported by a corner bracket. The corner bracket is only attached to the outer heat shield (see figure 3.14). These materials should be very good insulators since they are only at ~200-300°C, much colder than the rest of the parts of the oven. This should reduce the leakage currents to ground from the connections to the guard rings and electrodes, as well as provide strain relief for these fragile connections. The ninth connection is a single gold lead threaded with alumina beads that is connected to all four windows on the vapor cell. This allows for these windows to be grounded.

Ceramic terminal blocks are used to make connections between leads extending into the oven and leads that are connected to the vacuum feedthroughs. The thermocouples are also attached to these terminal blocks.

### 3.2.1 Eddy Current Suppression

Since the experiment is very sensitive to magnetic fields, and the oven is heated by driving current through heating elements that will create stray magnetic fields, it is necessary to turn off the ovens during the measurement time. A measurement is made every 10 ms, so the ovens
Figure 3.14: The leads to the guard rings and electrodes are beaded with BeO beads and then threaded into the oven inside quartz tubes. The quartz tubes are supported by an alumina block. Since this structure is cooler than the rest of the oven, it reduces the leakage currents to ground. It also provides strain relief for these fragile connections, since they are made out of thin gold wire.
must be turned off in ~1 ms to maintain a reasonable duty cycle. Despite the low inductance configuration of the foils, it was found that turning off a DC current in these foils induced eddy currents in the vacuum can that persisted for several hundred ms. To avoid this problem, a waveform was designed to minimize the eddy currents. This waveform is an 11 kHz sine wave that is ramped on and off for 1 ms before and after the measurement and is entirely off for the 1 ms period during which the measurement is made. The slope of the ramps on and off is determined according to the Blackman pulse shape [66]. To understand how this waveform minimizes eddy currents, consider the eddy current generated at a time $t_0$ by the current in the oven when it falls from a maximum positive amplitude to zero. The eddy current will decay exponentially. At some later time $t_r$, a second eddy current of opposite sign will be generated by a negative pulse of current in the oven. If the relative amplitudes of the positive and negative currents in the oven are adjusted so that the first and second eddy currents cancel, then the total eddy currents will be minimized. The Blackman pulse shape minimizes the eddy currents by adjusting the relative amplitude of the sine wave current in the ovens appropriately.

Since the best waveform to suppress eddy currents is a high frequency AC current, and the heater foils are designed to have a resistance of a few Ohms when hot, audio amplifiers were used to power the oven. Originally Hafler P3000 and P4000 amplifiers were used, but it was found that these amplifiers cannot continuously source their rated power of 400 W and 550 W respectively. Valmiki Prasad found that the maximum continuous safe power for the P3000 is 275 W, and for the P4000 the maximum safe power is 390 W. Ten of these Hafler amplifiers are still in use, but as they break they are being replaced by QSC RMX1450 amplifiers, which are rated to 700 W, and have been found to continuously safely produce 760 W.

With twelve different heaters requiring connections within the vacuum can and an equal number of amplifiers, it is necessary to have a constant and easily accessible monitoring system to check for problems. Two separate monitoring systems are used. The first is a box of LEDs and fuses (see figure 3.15). If there is sufficient voltage across in the heaters, these LEDs will turn on. If the current is higher than 10A which often happens when a heater is shorted to ground, the fuse will blow protecting the amplifier. (The Hafler amplifiers do not have internal fuses that blow fast enough to protect them.) A second circuit (see figure 3.16) is used to continuously monitor the voltage across the heaters as well as the current in the heaters. From
this information the resistance of the foils can be calculated, as can the power dissipated by each foil. This circuit must be a completely differential floating measurement because introducing a ground to one output of the audio amplifiers causes the amplifier to overdrive and burn out.

### 3.3 Vacuum System

The oven and cell are inside an aluminum vacuum can that has a 14" inner diameter, 16" outer diameter and is 18" high. Several copper strips with tubes for water cooling soldered on are clamped or screwed onto the vacuum can: one on the top of the can, one on the bottom, and two bands encircling the can. The water cooling keeps the chamber temperature below 40°C when the flow rate is 1 gallon/minute. Another aluminum tube is attached to the vacuum can and extends through the base of the magnetic shielding and out past the shields to where a TMP151/361 Leybold Turbopump evacuates the system (see figure 3.1). The turbopump is backed by a Leybold Trivac 4/8 B rotary vane vacuum pump. With this system, the pressure in the vacuum as measured with an ion gauge remains between $10^{-6} - 10^{-5}$ Torr.

Several unusual techniques have been employed in the design of parts for this vacuum system to eliminate ferromagnetic materials and reduce any potential currents flowing through the can due to the thermoelectric effect. The entire vacuum can and most components are made of aluminum. The copper cooling bands and plates are electrically insulated from the aluminum chamber by a layer of Sil-Pad and thermally conductive grease. Sil-Pad is a flexible plastic material that is sold in sheets and is thermally conductive, but electrically insulating. The thermal grease is intended to fill in gaps between the Sil-Pad and the copper or aluminum, but it is not known whether this grease increases the thermal conductivity. The electrical insulation prevents any voltage difference developing between the aluminum and copper due to the thermoelectric effect. If these voltages were to build up, it is possible that current loops
Figure 3.16: Circuit used to monitor the current through and voltage across one heater foil. There are twelve copies of this circuit. This circuit uses two AD629 INAmps to measure the differential floating voltage across a resistor. The current sent through the heater foils is measured by the AD629 reading the floating voltage across a 0.1 Ω resistor. This resistor is effectively a low impedance sense resistor for measuring the current. The output of the AD629 is a voltage that is equivalent to this current multiplied by 0.1. Similarly, the voltage across the heater foils is also measured by reading the floating voltage across a resistor with an AD629. In this case, a voltage divider chain is created with two 510 Ω resistors with a 10 Ω resistor in between. This chain forms a high impedance voltage divider for measuring the voltage across the heater foil. The voltage read across the 10 Ω resistor is 1/100 of the voltage that is across the heater foil.
Figure 3.17: The non-magnetic co-axial feedthroughs used on the vacuum system are shown here. O-ring seals are made between plastic spacers that separate the inner and outer brass pins. Three co-axial pairs are mounted onto an alumina flange, which can be attached to the vacuum chamber.

could be induced in the chamber creating uncontrolled magnetic fields.

To further reduce the magnetic fields inside the chamber, custom brass co-axial feedthroughs on alumina flanges were designed and built for use with all electrical signals passing through the vacuum chamber. Although it is possible to buy commercial co-axial feedthroughs, some of the components are ferromagnetic. The co-axial feedthroughs built here consists of two brass pins that are separated by plastic spacers and o-ring seals. The o-ring seals are fixed in place by threads on the inner brass pin that compress the plastic spacers and maintain an o-ring seal between the brass and the plastic (see figure 3.17). Each co-axial feedthrough is clamped onto a polished alumina flange with another o-ring. This flange has been designed to be the same size as a standard QF40 vacuum flange for easy adaptability to existing vacuum components. These alumina flanges are bolted onto the vacuum chamber with brass screws and aluminum supporting rings. Occasionally this force cracks an alumina flange, so o-rings are placed between the alumina flange and aluminum supporting ring to relieve the stress on the alumina flange. All connections to these feedthroughs are made with coaxial cables that have been specially purchased and tested to contain no ferromagnetic materials.

There are only a few standard types of thermocouples that do not contain ferromagnetic materials or are mounted on a ferromagnetic feedthrough. One is a S-type thermocouple that contains one platinum wire; unfortunately platinum becomes brittle when it is exposed to quartz at high temperatures in vacuum. The other standard non-magnetic thermocouples are type
Figure 3.18: The voltage across the Au-Au/Pd thermocouples as a function of temperature.

C, made of tungsten and rhenium, which are very brittle. Since the thermocouples are not rigidly mounted to the oven, any brittle thermocouples are likely to break. Therefore, custom thermocouples were made out of one gold wire and one 60/40 gold-palladium alloy wire. The voltage across these thermocouples as a function of temperature is shown in figure 3.18.

The final unusual aspect of the vacuum chamber is the way that light is coupled into and out of the chamber. Polished quartz rods that are 2" in diameter and range in length from 12" to 18" are inserted into the chamber in all 4 optical directions. These rods are placed 0.5 to 1 cm away from the cell and are used to conduct light into and out of the chamber. Through total internal reflection, two lightpipes transmit all of the fluorescence light entering them at angles below 45°. The laser is shone through the chamber and cell via the other two lightpipes. The microwaves are directed into one of these lightpipes anti-parallel to the laser direction. In addition to the light and microwave transmission properties, these lightpipes have two additional advantages. First, the lightpipes extend into the hot zone of the oven. Since something in the oven outgasses a black substance that tends to coat all cold materials in the chamber, the extension of the optical access into the hot zone is critical. (The source of the black substance is unknown, but it is suspected that it arises from the tantalum foils used as resistive heaters in the oven.) Second, quartz absorbs some of the blackbody radiation from the oven and reradiates some power, so the lightpipes decrease the amount of power necessary to heat the oven.
3.4 Magnetic Shielding

As mentioned above, the vacuum chamber rests inside 4 layers of Co-netic magnetic shielding that is 0.030" thick and was annealed in a hydrogen furnace at 1050-1100°C. The shields are each a half-square with rounded corners, which makes them approximately half-cylindrical. When two matching half-cylinders are joined, the shields range in size from 24" in diameter and 73" high to 48" in diameter and 92" high. End caps are placed on the top and bottom of each shield. There is a 4" diameter hole in the center of both end caps. The aluminum vacuum system extends through the hole in the bottom end cap and the hole in the top end cap is used to feed electrical and water connections into the shields. Additionally, there are several holes around the circumference of the shields. Some are from a previous experiment and are not used, but 4 holes along the midplane of the cylinders are used for access to the lightpipes. The two lightpipes used for the laser beam do not extend beyond the shields. Around each hole there is an additional cylinder of magnetic shielding that surrounds the hole and extends outward. Since the base of this cylinder has a flat piece of magnetic shielding that is used to bolt it to the main shields, these cylinders are called “top hats”. Since external magnetic fields drop off exponentially inside of a cylinder, the fields that can enter through these shields are quite small when the length of the cylinder is twice the diameter. Almost all of the top hats used on these shields meet this condition. The ones that do not meet this condition have a shorter length because they would otherwise hit the next layer of shielding.

The four layer top and bottom end caps are permanently fixed in place by an aluminum support structure (shown in figure 3.1). This support structure was designed to permanently suspend the top end cap in a way that would not interfere with the addition or removal of the half-cylinder magnetic shields that form the sides of the magnetic shielding. This support structure also raises the bottom end cap off the floor so that vacuum components and wires can be routed beneath the shields. When the side shielding is not in place, the support structure is also used as the starting point to mount a wooden platform and staircase around the chamber that allows for easier access to the chamber. When in place, the half-cylinders are bolted together so that they form a tight seal around the edges of the top and bottom end caps. The magnetic shielding is most effective when there is good contact between the surfaces of the metal. All bolts used on the shields are brass to eliminate ferromagnetic materials. Since the larger two
half-cylinder shields are quite large and heavy, a rolling cart with a hydraulic lift is used along with a ball-bearing platform to slide these shields into place.

The magnetic shielding is degaussed using coils that are wrapped around them. The end caps have coils wrapped around the top hats that extend outside the holes in the center of the caps. The cylindrical pieces have two pairs of coils wrapped radially around the outside of each cylinder as shown in figure 3.19. In order to degauss the shields, these coils must be able to create a sufficiently strong field to completely polarize all of the magnetic domains within the shields along a particular direction. Ideally, the coils would be wrapped lengthwise around the shields and create a magnetic field that rotates radially around the axis of the shields. Unfortunately, this geometry was found to both be difficult to construct, and not much more efficient due to eddy currents induced in the supporting aluminum structure of the shields. With the geometry shown in figure 3.19, the field created by the coils wrapped radially around the shields is largely vertical. Once the shields are saturated, this field extends around the shields and creates a dipole field pattern. The shields are degaussed by driving current through the coils sequentially. The shields are first degaussed starting from the outer shields and proceeding to the inner shield, then starting from the inner shield and proceeding to the outermost shield. This sequence of degaussing first demagnetizes the outermost shields in the best configuration for shielding to the environment, but will induce a small magnetization on the inner shields. Degaussing from the inner shields to the outermost shields removes this additional magnetization. A 220 V, 20 A, 60 Hz motor controlled variac is used to slowly ramp up and down the current in the degaussing coils.

Once these shields are degaussed, their shielding factor can be approximated by assuming that they are cylindrical. This approximation is reasonable since the corners of the shields are rounded. If the shields were cylindrical, the transverse shielding factor for each layer would be

\[ S_T = \frac{B_t}{B_0} = \frac{\mu t}{2R} \]  

(3.1)

where \( B_0 \) is the homogeneous magnetic field before introducing the shield and \( B_t \) is the field inside the shield, \( \mu \) is the permeability, \( t \) is the thickness, and \( R \) is the radius [9]. For example, the inner shield in this experiment has permeability of 30,000 [67], a thickness of 0.030" , and a radius of 12" leading to \( S_T \approx 38 \). With all four layers of shielding, this experiment has a
Figure 3.19: The cylindrical section of a magnetic shield is shown along with the two radially wrapped pairs of coils that are used to degauss them. The magnetic field created by these degaussing coils eventually saturates the shields in the vertical direction and causes field lines as shown here that radiate around the shields.

calculated $S_T \approx 4 \times 10^5$. In the axial direction, the shielding is not as good. The axial shielding factor of a finite cylinder is

$$S_A \approx \frac{2\mu t R^{1/2}}{L^{3/2}}$$

(3.2)

where $L$ is the length of the cylinder [9]. Using this equation, the axial shielding of all four layers of shielding is $S_A \approx 10^4$. In practice, both $S_T$ and $S_A$ are probably lower than these calculated values for two reasons. First, there are a large number of holes in the shields. These holes are covered by “top hats” of mu metal that should reduce the magnetic fields that enter through the holes, but are not completely effective. Secondly, the shields have been bent and banged upon for years, which decreases the permeability.

The magnetic shielding has the additional benefit of homogenizing the magnetic field that is applied with coils inside the shields in the vertical direction. This magnetic field permeates the inner magnetic shield, and slightly magnetizes it along the direction of the applied magnetic field. This additional magnetization in the vertical direction effectively homogenizes the field at the center of the coils and shields.

A small $\sim 200$ mG field is created in the $z$ direction by field coils wrapped in a configuration similar to a Helmholtz configuration, but with different dimensions to account for the homogenizing effects of the magnetic shielding. These coils rest outside the vacuum chamber, but inside
the magnetic shielding and create a field in the $z$-direction. These coils have a mean radius of 10.694" and are separated by a mean distance of 10.47". Each coil consists of 300 turns of 28 AWG wire. These coils are driven by a current supply from Electronic Development Company (Model 522), which can supply up to 100 mA with a resolution of 1 ppm and a noise less than 600 μV from 0.1 Hz to 100 kHz [68]. Currently, these coils are driven with a single power supply and are in series so that there is the same current in both of the coils. Additional anti-Helmholtz coils in the $z$ direction will occasionally be used to create magnetic field gradients to check for systematic effects.

There are 4 pairs of auxiliary coils that create magnetic fields in the $x$ and $y$ directions. Two of these coils are configured in a Helmholtz configuration, and two are configured in an anti-Helmholtz configuration. The Helmholtz coils will be used to tip the magnetic field to adjust the relative alignment of the magnetic and electric field axes. At times, this relative alignment may be exaggerated to test for systematic effects associated with this alignment as it will be difficult to tell when it is well aligned. The anti-Helmholtz coils will be used to apply magnetic field gradients, which are also used as diagnostics for systematics. All 4 pairs are made out of threaded rods that are mounted vertically around the chamber at a diameter of 19.356" and connected together with magnet wire. These coils are driven with Hewlett Packard power supplies (6181C and 6177C).

### 3.5 Laser Excitation

The first step of the experiment is to populate the metastable $a(1) \ ^3\Sigma^+$ state of PbO via laser excitation. Since the transition from the $X\rightarrow a(1)$ state is only weakly allowed, it is difficult to drive this transition. High power lasers are necessary, and pulsed lasers are the only reasonable solution. The transition is at ~570.2 nm, which is a wavelength that is easily accessible with a dye laser. The generation of this laser beam starts with the pump laser, which is a Q-switched Spectra Physics Lab 190-100 532 nm wavelength doubled Nd:YAG laser with a repetition rate of 100 Hz. The Nd:YAG laser is rated to produce 7-10 ns, 100 mJ pulses, but when the flash-lamps are new can have powers as high as 130 mJ/pulse. The Nd:YAG laser is powered by two pairs of flash lamps that each fire on alternate cycles of 50 Hz. These flash lamps are continuously cooled by deionized water that is cycled through the housing for the lamps. A temperature
stabilized non-linear crystal is used to double the \(~325\) mJ output of this cavity at \(1064\) nm to yield \(~120\) mJ of \(532\) nm light. The measured powers match the specifications for most of the lifetime of the flash lamps, but begins to decrease as the flash lamps age [69].

All timing for the experiment is referred to a TTL pulse from the Nd:YAG electronics that is synchronized to the Q-switch. This pulse is used to trigger a Berkeley Nucleonics Corporation Model 500 pulse generator, which provides timing delays for all other components in the experiment.

The frequency doubled Nd:YAG beam is directed into a Lambda Physik SCANmate 2E laser that uses Rhodamine 6G dye. At three different points, a partially reflecting mirror directs a portion of the Nd:YAG beam into the dye laser. The first Nd:YAG beam pumps the dye in the oscillator cuvette. A lasing cavity is formed around this cuvette using a grating and an end mirror. Amplified spontaneous emission (ASE) from the dye is mostly blocked with a series of apertures. An etalon inside the cavity limits the bandwidth of the laser to \(~1\) GHz. The second Nd:YAG beam pumps a pre-amplifier, which is in the same dye-cuvette as the oscillator, but passes through the cuvette at a different point. The third Nd:YAG beam pumps the amplifier cuvette; after this stage of amplification the power is typically 20 mJ/pulse. The beam that is output from this laser is vertically polarized.

Immediately after the dye laser there is a telescope that expands the beam to approximately \(1"\) diameter. A piece of glass is used to pick off a part of this beam to be sent to an external etalon and a Coherent WaveMaster wavemeter. The external etalon is used as a diagnostic for determining whether the dye laser is running single mode, and whether it has a high ratio of lasing power to ASE. The primary beam is sent through a \(\lambda/2\) wave-plate and a Glan-Laser beam splitting cube to ensure high-purity linear polarization. The orientation of the beam splitting cube determines the orientation of the polarization of the laser beam. The orientation of this cube is set manually, so it is probably cannot be aligned so that the polarization of the laser is parallel to the electric field direction to better than \(1^\circ\). After the Glan-Laser polarizer, the beam is expanded to a \(2"\) diameter using another telescope.

It has been hypothesized that the ASE from the dye laser is a significant source of backgrounds in the experiment for two reasons. First, it causes additional scattered light that is unnecessary since it is non-resonant with the molecular transition. Second, some of the ASE
can be resonant with other rotational lines in PbO that causes a fluorescent background with the same time characteristics as our signal. This background reduces the contrast of the quantum beats. To try to solve these problems, a 2" diameter interference filter from Omega Optical was placed at the end of the second beam expanding telescope. This filter had a center wavelength of 571.5 nm ± 1 nm and a full width half maximum (FWHM) of 5 ± 1 nm. Unfortunately, this filter is apparently too broad to block the ASE as the contrast was not significantly increased with this filter in place. Currently, this filter is not used.

3.6 Microwave State Population

It was necessary to develop a state population scheme that could reliably populate only states with $n_z = +1$ or $n_z = -1$, since these states have opposite energy shifts in the presence of a non-zero EDM. Furthermore, many sources of magnetic noise can be reduced if the state population scheme can quickly switch between populating these states as described in section 2.2. More details on the development of this population scheme will be presented in [62]. There are two possibilities for a two-step microwave excitation process that can be used to populate these states.

Microwave generation starts with a two channel arbitrary waveform generator that is used to output frequency-swept waveforms each consisting of two pulses at ~32 MHz. When EDM data is being taken, a pseudo-randomly driven switch will select which of these two pulses is directed into the frequency multiplication chain as each of these waveforms corresponds to the excitation of one $\Omega$ doublet. The ~32 MHz signal is multiplied up by 32 times to ~1 GHz, filtered, and mixed with 13.1 GHz microwaves from a phase locked dielectric resonator oscillator. A waveguide filter removes the low sideband leaving a signal at 14.1 GHz, which is doubled to the nominal splitting between the $J = 1$ and $J = 2$ states of 28.2 GHz. This signal is currently amplified to 1/2 W, but this amplifier is being replaced with a 4 W amplifier to improve the efficiency of the state population sequence. A high power switch is used to direct the microwaves into either an $\hat{x}$- or $\hat{z}$-polarized mode of an orthomode transducer that is connected to a conical horn. The horn is placed behind a teflon tube which connects to a 2" diameter quartz rod that extends into the vacuum chamber and ends 1 cm away from the vapor cell. The rod acts as a guide for the microwaves.
Both microwave excitation schemes start by using a vertically polarized laser tuned to R0 to excite to \(|a(1), J = 1, m = 0, e\rangle\). The first population sequence is shown in both figures 2.2 and 3.20a. Here, a \(\hat{z}\)-polarized microwave pulse is used to transfer the population from the \(|a, v = 5, J = 1, m = 0, e\rangle\) state to the \(|a, v = 5, J = 2, m = 0, e\rangle\) state. As described in section 2.2.3, the microwave pulses are short and the frequencies are swept. The \(\hat{z}\) pulse is \(\sim 100\) ns long and has a frequency sweep range of 20 MHz. A second \(\hat{x}\)-polarized pulse transfers the population to the EDM superposition state as written in either equation 2.27 or 2.28. This pulse is approximately 1 \(\mu\)s with a frequency sweep range of 6 MHz. By changing the center frequency of this pulse either \(n_x = +1\) or \(n_x = -1\) can be populated. The length and depth of frequency modulation for both pulses have not been completely optimized at this time.

The second population sequence is shown in figure 3.20b. This sequence first uses a \(\hat{x}\)-polarized microwave pulse to populate the \(m = \pm 1\) levels of the \(J = 2\) state. Then, a \(\hat{z}\)-polarized microwave pulse creates the EDM superposition state in the \(J = 1\) level. Again, by changing the center frequency of the second pulse, either \(n_x = +1\) or \(n_x = -1\) can be populated.

The microwave population sequence could be simplified if the laser were tuned to excite along the R1 transition to excite \(|a(1), J = 2\rangle\). Unfortunately, this transition results in significant extra background fluorescence since R1 is in the bandhead of the X–\(a(1)\) transition. There are several populated states such as the the \(J = 2 m = \pm 1\) states that reduce the contrast. Several other rotational lines are also within the linewidth of the laser, and fluorescence from these lines significantly reduces the contrast.

With this population sequence, quantum beats have been observed with 3% contrast corresponding to 25% transfer of the population. It is expected that the higher power 4 W amplifier will improve this efficiency.

### 3.7 Detection

For the first generation experiment described here, fluorescence detection is used. The spontaneous decays between the \(a(v' = 5)\) and \(X(v'' = 0)\) states are detected. Significant work has been done to optimize the filtering and detection of this signal. To optimize the filters and detector used, a Monte Carlo simulation was made to trace photons emitted in the cell and calculate the probability of these photons being detected after travelling through all of the optical com-
Figure 3.20: a) In this pulse sequence, first \( z \)-polarized microwaves are used to populate the \( |J = 2, m = 0\rangle \) state. Then, a second \( x \)-polarized microwave pulse is used to create the EDM superposition state. Changing the frequency of the \( x \)-polarized microwaves determines whether \( n_z = +1 \) or \( n_z = -1 \) is populated. b) In this pulse sequence, \( x \)-polarized microwaves are used to coherently populate \( \frac{1}{\sqrt{2}} (|J = 2, m = +1\rangle + |J = 2, m = -1\rangle) \). Then, \( z \)-polarized microwaves are used to coherently transfer this population to the \( \frac{1}{\sqrt{2}} (|J = 1, m = +1\rangle + |J = 1, m = -1\rangle) \). The frequency of the \( z \)-polarized microwaves determines whether \( n_z = +1 \) or \( n_z = -1 \) is populated.
Figure 3.21: The spectrum of an ideal blackbody at 700°C is shown in its entirety and a detail in the region near the interference filters used for this experiment.

ponents. The simulation takes into account the non-isotropic distribution of photons emitted from the a(1) state, the effects of the Winston Cones (described below), and the transmission of all filters at all angles. The results of this simulation have been checked against measurements of the transmission of each optical component individually and all combinations of the optical components together.

3.7.1 Filters

Two significant sources of background can be minimized using appropriate optical filters. The first background source is from the blackbody radiation of the oven. An ideal blackbody at 700°C would have a spectrum that is peaked at ∼2.8 μm, but there is still a significant amount of radiation at lower wavelengths, including the detection wavelength of 548 nm (see figure 3.21). To block as much of this blackbody radiation as possible, two types of filters are used: IR blocking color glass and narrow band interference filters. A piece of 2mm thick KG1 Schott color glass is placed against the exit of the lightpipe and is used to block the majority of the IR radiation. A sapphire window which is surrounded by water cooling is placed on the other side of this color glass filter to cool the filter, which heats up significantly from absorbing the IR radiation. Sapphire is a good heat conductor so this window effectively cools the color glass
filter.

On the other side of this sapphire window there are two bandpass interference (IF) filters. For normal incidence, one cuts on at 544±2 nm and cuts off at 560±2 nm. The cut on and cut off wavelengths are where the filters achieve 50% of the peak transmission. This filters is made using Omega’s 3RD Millennium Technology Alpha Gamma technique, which has higher transmission and a steeper cut-off than standard interference filters. The second IF filter is a standard IF filter with a 10 nm bandpass centered around 550 nm. Several standard interference filters with different central wavelengths and bandwidths have also been tested. Unlike color glass filters that have a transmission that is largely insensitive to incident angles, the transmission of interference filters has a strong dependence on the incident angle. Interference filters are made with a series of coatings of two or more different materials of different indices of refraction. Since these coatings are only a multiple of a few 1/2 wavelengths thick, only light that is close to the correct wavelength is transmitted and all other wavelengths are attenuated. (Unfortunately, light at harmonics of the primary frequency can also be transmitted and must be blocked with color glass filters, which are often built into the IF filter.) Light entering the filter at an angle has a longer path length, so the wavelengths of light that match the 1/2 wavelength condition for transmission are farther to the blue of the wavelengths that are transmitted at normal incidence. The central wavelength $\lambda$ of the filter as a function of incident angle $\theta$ is given empirically by

$$\lambda(\theta) = \lambda_0\left[1 - \left(\frac{n_0}{n^*}\right)^2 \sin^2 \theta\right]^{\frac{1}{2}}$$

where $n_0$ is the index of refraction of the surrounding material, $n^*$ is an effective index of refraction of the filter, and $\lambda_0$ is the central wavelength at $\theta=0$ [70]. At angles above 30°, the peak transmission of the filter at the central wavelength also starts to decrease.

In the absence of backgrounds, to maximize transmission at the fluorescence wavelength $\lambda_f$, an ideal IF filter would have a broad bandwidth and a central wavelength that is shifted to the red of $\lambda_f$. This design will allow as much of the signal to pass through the filter as possible. In the Monte Carlo simulation (described in section 3.7.4), the distribution of photons exiting the lightpipe into air as a function of angle is broad, as is shown in figure 3.28. To transmit all of these photons, a broad interference filter (~40 nm bandpass) is necessary. Unfortunately, the interference filter cannot be made too broad due to the scattered light from the laser at ~570
nm and the increased blackbody radiation to the red of $\lambda_f$.

The blackbody radiation transmitted through the IF filters was measured by placing the IF filters at the end of the lightpipes. After a chopping wheel that was synchronized to the current waveform in the ovens, a 0.5" diameter optical fiber bundle collected the light transmitted through the IF filters and transmitted it to the monochromator. Since the fiber bundle has a wide acceptance angle it will not limit the angular distribution of light collected, which has passed through the interference filter. The fiber bundle scrambles the angular distribution of light so that the output of the fiber has the same angular distribution regardless of the input angular distribution. The monochromator was set to have a slit width of 750 $\mu$m, which is equivalent to a spectral resolution of 2.4 nm. The light transmitted through the monochromator was monitored with a Hamamatsu R329EGP PMT with a nominal gain of $3 \times 10^6$ (see figure 3.22). With this apparatus, the blackbody spectrum was measured as shown in figure 3.23. For comparison, the blackbody spectrum is also shown for a configuration where the system was sensitive only to light incident at small angles, in figure 3.24. The data at small angles was collected by removing the fiber bundle and directly placing the monochromator behind the IF filter. It was expected that when two Omega filters are used instead of two standard interference filters, the blackbody and signal transmission would both increase by approximately a factor of 13. In practice, it has been observed that the blackbody transmission has increased by a factor of 5, and the signal has only increased by a factor of 3. The results of this measurement indicate that the increased transmission of blackbody through the Omega filter is entirely a result of its higher peak transmission and larger bandwidth as compared to a standard interference filter. It is not understood why the blackbody has not increased as much as was expected. Furthermore, it is especially unclear why the transmission of the signal has not increased as much as the transmission of the blackbody. These discrepancies are currently under investigation. One possibility is that some of the mounting for the optics may be reducing the angular distribution of the fluorescence.

The second significant background source in this experiment is scattered light from the pulsed dye laser. None of the optical surfaces inside the vacuum chamber can be anti-reflection (AR) coated. Standard AR coatings are not rated to work at 700°C, and we have not tested them for use in this experiment. As a result, there is a significant amount of laser light scattered off
Figure 3.22: The apparatus used to measure the blackbody spectrum through the interference filters.

Figure 3.23: The measured blackbody spectrum transmitted through the interference filters. The transmitted light is at a broad range of angles from normal incidence up to angles of $\sim 45^\circ$. The relative intensities within this plot are on the same scale and the apparatus was designed so that the intensities on this plot can be directly compared. The relative intensities here are on a different scale from the relative intensities in the next plot.
these windows. Without any filtering, each time the dye laser fires, $10^{10}$ photons from the laser would hit the PMT, but only an expected $N_{act,PMT} = 5 \times 10^5$ photoelectrons of fluorescence from the a(1) state are detected from each laser pulse. This scattered light pulse is significantly attenuated by the IF filters, but is still significant. This scattered light saturates the detector for a time depending on the detector, the filters, and the front-end electronics. To minimize this scattered light, the IF filter must have a bandpass that is narrow enough to block as much of this scattered light as possible. Each of the two IF filters used here at normal incidence has an optical density (OD) of 5.9 at 570 nm, for a total OD of 11.8. This OD should entirely block the scattered light. Probably, any light that is transmitted through the first IF filter is transmitted as a result of imperfections in this filter. The transmitted light is not blocked by the second filter, which has similar imperfections. Additionally, the excitation and detection transitions are chosen so that the excitation wavelength is to the red of the detection wavelength, and so can be better blocked by the interference filter at all incident angles. Unfortunately, this choice necessitates exciting the $X(v = 1)\rightarrow a(v' = 5)$ transition at 570.2 nm and detecting along $a(v' = 5)\rightarrow X(v = 0)$ at 548.5 nm. As a result of the Boltzmann distribution, there only is $1/3$ as much population in the $X(v = 1)$ state as the $X(v = 0)$ state.

Figure 3.24: The measured blackbody spectrum transmitted through the interference filters both at all angles and when limited to small angles. The relative intensities within this plot cannot be compared. The relative intensities here are on a different scale from the relative intensities in the previous plot.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
3.7.2 Absorbing Filters

While the central wavelength of an interference filter shifts as a function of the angle of the incident light, absorbing filters have the same spectral profile for all incident angles. Color glass filters are available in longpass and bandpass varieties, but are not made as shortpass filters. Since this experiment would most benefit from a filter that would cut out the scattered light from the laser and the blackbody radiation, which are both primarily to the red of the fluorescence, a shortpass absorbing filter would be ideal. Another problem with the commercially available color glass filters is that they tend to have very broad slopes for the transmission as a function of wavelength. Together, these characteristics make it impossible to find a color glass filter that can be used with the existing interference filters to further block the blackbody radiation without attenuating the signal.

Since commercially available absorbing filters do not exist, alternate materials were explored for suitability as absorbing filters. Rare earth lanthanide ions are known to have narrow spectral lines when dissolved in liquid solutions. These atoms have a valence shell of 4f electrons, which are environmentally shielded by the 6s electrons, which are at a larger radius. Solutions containing Sm$^{3+}$, Nd$^{3+}$, Ho$^{3+}$, and Er$^{3+}$ were individually placed in a glass cell that was 2" in diameter and 24" long. These solutions were chosen because prior data suggested that they would have spectral lines that would absorb at wavelengths in the bandpass of the Omega Optical interference filters that range from 544 nm to 560 nm [71, 72]. The concentrations of these solutions are listed in table 3.2. A xenon lamp was directed through the sample and into a 1/4 m Digikrom monochromator, which had a slit width corresponding to a spectral resolution of 2.4 nm. The output of the monochromator was sent through an order sorting color glass filter and detected with a large area PIN photodiode. The transmission of these solutions was calibrated compared to the transmission of this apparatus when the cell was filled with deionized water.

The transmission of these solutions is shown in figures 3.25 and 3.26. Unfortunately, none of these solutions will work as an absorber for this experiment. The only ion that does not have significant residual absorption at the detection wavelength of 548 nm from a spectral line is Sm$^{3+}$. All of the solutions of Sm$^{3+}$ showed significant decreased transmission at all wavelengths for unknown reasons. At first, it was hypothesized that this decreased transmission was a result of the acid concentration in the solution. However, the transmission of a solution of 37%
Table 3.2: Concentrations and compounds dissolved to form the lanthanide solutions tested as absorbing filters to be used with the interference filters.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Compound Dissolved</th>
<th>Solvent</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm$^{3+}$</td>
<td>Sm(NO$_3$)$_3$ 6H$_2$O</td>
<td>H$_2$O</td>
<td>125 g/1250 mL</td>
</tr>
<tr>
<td>Sm$^{3+}$ conc.</td>
<td>125 g Sm(NO$_3$)$_3$6H$_2$O+100 g Sm$_2$O$_3$</td>
<td>H$_2$O+HCl</td>
<td>53 g Sm$^{3+}$/1390 mL</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>NdCl$_3$ XH$_2$O</td>
<td>H$_2$O</td>
<td>50g/1200 mL</td>
</tr>
<tr>
<td>Ho$^{3+}$</td>
<td>Ho$_2$O$_3$</td>
<td>HCl</td>
<td>3.1 g/1200 mL</td>
</tr>
<tr>
<td>Ho$^{3+}$ conc.</td>
<td>Ho$_2$O$_3$</td>
<td>HCl</td>
<td>9.4 g/1200 mL</td>
</tr>
<tr>
<td>Er$^{3+}$</td>
<td>ErCl$_3$ XH$_2$O</td>
<td>H$_2$O</td>
<td>4.1 g/950 mL</td>
</tr>
</tbody>
</table>

Figure 3.25: The measured absorption of the lanthanide solutions that absorb to the red of the detection wavelength at 548 nm are shown as a function of wavelength. Nd$^{3+}$ is not a good choice of absorber for this experiment since it will attenuate the signal as the spectral line still absorbs at 548 nm. Sm$^{3+}$ was found to have decreased transmission at higher concentrations for unknown reasons, and therefore is also not a good absorber to be used as a filter as it will attenuate the signal.

hydrochloric acid and water was high, proving this hypothesis false. Since significant attenuation of the signals is unacceptable, none of these solutions will be used as an absorbing filter.

An alternative to an absorbing filter would be to use a Christiansen filter [73, 74]. These filters are made out of small glass beads immersed in a liquid with a matching refractive index at the desired transmitted wavelength. If the liquid is designed to have a high dispersion, other wavelengths will not be transmitted through this filter. Hunter Smith is currently working on developing a filter that will be narrow enough for this experiment.
Figure 3.26: The measured absorption of the lanthanide solutions that absorb to the blue of the detection wavelength at 548 nm are shown as a function of wavelength. Both Ho$^{3+}$ and Er$^{3+}$ are not suitable for an absorbing filter since the spectral lines are still absorbing at the detection wavelength of 548 nm.

### 3.7.3 Winston Cones

The lightpipes have a 2" diameter, but many optical components do not come with 2" clear apertures, so it is necessary to compress the fluorescence light so it passes through smaller optical components. Since the fluorescence enters the lightpipe from a range of locations and a range of angles, a lens will not focus the light efficiently. Instead, the most efficient way to concentrate the light is to use a non-imaging optical concentrator known as a Winston Cone [75]. Since there is no dissipation in an ideal Winston cone, it conserves the phase space area $a^2 \theta^2$, where $a$ is the radius of the aperture and $\theta$ is the semiangle of the beams accepted. The equation of revolution for this concentrator can be expressed in terms of the acceptance angle $\theta_{\text{max}}$, the length of the concentrator $L$, and the radius of the output aperture $a'$. These parameters are related by two equations, which also determine the radius of the input aperture $a$. The equations that determine the shape of the Winston Cone are

$$L = (a + a') \cot \theta_{\text{max}}, \quad (3.4)$$

and

$$a = \frac{a'}{\sin \theta_{\text{max}}}. \quad (3.5)$$
The equation for the surface of revolution of the concentrator is

\[
(r \cos \theta_{\text{max}} + z \sin \theta_{\text{max}})^2 + 2a'(1 + \sin \theta_{\text{max}})^2 r - 2a' \cos \theta_{\text{max}}(2 + \sin \theta_{\text{max}}) - a'^2(1 + \sin \theta_{\text{max}})(3 + \sin \theta_{\text{max}}) = 0.
\]

(3.6)

The coordinates for this equation are shown in figure 3.27.

Two different shapes of Winston Cones were made out of Lexan, which is a transparent plastic. The first Winston Cone (labelled Winston Cone I) was made to concentrate light from the 2" diameter lightpipes into the 45 mm of clear aperture for a standard 2" diameter interference filter. This Winston Cone has \(a=1"\), \(a'=0.9"\). The total length of this cone is 2" since there is an additional straight section to make machining easier. The curved section of the cone has \(L=0.92"\). Winston Cone II is designed to concentrate the light from the interference filter diameter to a 1" diameter to be used with the photodiode described below. Winston Cone II has \(a=0.9"\) and \(a'=0.5"\) with a curved length \(L=2.84"\). Again, this cone also has a straight section so that the total length is 4". To conserve phase space, these cones increase the angular spread of the light at the output, as shown in figure 3.28.

The angular distribution of light leaving Winston Cone II depends on whether the light is exiting to air or to another optical element. The index of refraction of the optical elements is significantly higher than the index of refraction of air, so the angular distribution of light inside these optics is smaller than the angular distribution in air. Optical elements are coupled together with an index matching grease, so the angular distribution between elements does not
Figure 3.28: Distribution of angle of light exiting the lightpipe and both Winston Cones. The lightpipe does not change the angular distribution of the light since all of the light enters the lightpipe at less than the critical angle and thus none is lost. The lightpipe is totally internally reflecting and does not change the area of the light distribution or the angular distribution. The Winston Cones, however, do lose some of the light and change the angular range and area of the light, so it does matter whether the light distribution is at the entrance or the exit of the cones. This distribution depends on whether it is observed exiting into air or exiting into a material with a high index of refraction such as plastic. Note that no interference filter was used in this simulation, but that this angular information is necessary to model how the interference filters will work.
change significantly. Both Winston Cones increase the angular distribution of light, and with the increase severe for Winston Cone II. As shown in figure 3.28, the angular distribution of Winston Cone II when exiting into Lexan is already very broad and extends over all possible forward directions. When exiting into air, this distribution cannot become broader, so more photons are internally reflected backwards in the cone and cannot be detected. Therefore, Winston Cone II is always coupled to the next optical element (the photodiode) with optical coupling grease to prevent backwards reflections.

### 3.7.4 Monte Carlo Model of Detection

As mentioned above, a detailed Monte Carlo model was made to model the position and angular distribution of light through all of the optical elements. Light rays originating in the vapor cell between the electrodes with the angular distribution expected from photons emitted from the a(1) state of PbO are traced through all of the optical elements.

The simulation begins by choosing an arbitrary point between the electrodes for the origin of the light ray. The quantum beat fluorescence does not have an isotropic angular distribution. To find the correct distribution, consider the initial state in equation 2.27. The time evolved state is

\[
|uE(t)\rangle \propto -e^{i\omega t} \left[ |1, 1, e\rangle + |1, 1, f\rangle \right] + e^{-i\omega t} \left[ |1, -1, e\rangle - |1, -1, f\rangle \right] \quad (3.7)
\]

This state will decay to the ground state with a photon emitted in a direction \( \hat{k} \) described by

\[
\hat{k} = \hat{x}\sin \theta \cos \varphi + \hat{y}\sin \theta \sin \varphi + \hat{z}\cos \theta. \quad (3.8)
\]

The possible polarizations for this photon are orthogonal to \( \hat{k} \), and can be written as

\[
\begin{align*}
\hat{e}_1 &= \hat{x}\cos \theta \cos \varphi + \hat{y}\cos \theta \sin \varphi - \hat{z}\cos \theta, \\
\hat{e}_2 &= -\hat{x}\sin \varphi + \hat{y}\cos \varphi.
\end{align*} \quad (3.9)
\]

The distribution of fluorescence can be calculated using the formalism described in section 2.3. As described in section 2.3.1, the excited state can decay to multiple ground states. To simplify this derivation, however, only a single ground state, the \( |J = 0, m = 0, e\rangle \) state will be considered. Decays to all other ground states yield similar distributions. In this decay, the parity selection
rule is \( |e \rangle \rightarrow |e \rangle \), so the measured intensity emitted per unit solid angle is

\[
\frac{dI(t)}{d\Omega} \propto |\langle X, 0, 0, e | \hat{e}_1 |u_2(t)\rangle|^2 + |\langle X, 0, 0, e | \hat{e}_2 |u_2(t)\rangle|^2. \tag{3.11}
\]

Using equations 3.7, 3.9, and 3.10, the intensity per solid angle can be rewritten as

\[
\frac{dI(t)}{d\Omega} \propto -\langle 0, 0, e | [e^x \cos \theta \cos \varphi + e^y \cos \theta \sin \varphi - e^z \cos \varphi] | 1, 1, e \rangle e^{i\omega z t} \\
+ \langle 0, 0, e | [e^x \cos \theta \cos \varphi + e^y \cos \theta \sin \varphi - e^z \cos \varphi] | 1, -1, e \rangle e^{-i\omega z t}^2 \\
+ -\langle 0, 0, e | [-e^x \sin \varphi + e^y \cos \varphi] | 1, 1, e \rangle e^{i\omega z t} + (0, 0, e | [-e^x \sin \varphi + e^y \cos \varphi] | 1, -1, e \rangle e^{-i\omega z t}^2. \tag{3.12}
\]

The Hamiltonians for the light polarizations are:

\[
H \propto e_x \cdot r = x \propto \frac{1}{\sqrt{2}} (r_+ - r_-), \quad H \propto e_y \cdot r = y \propto \frac{1}{\sqrt{2}} (r_+ + r_-), \quad H \propto e_z \cdot r = z \propto r_0.
\]

By using these Hamiltonians, the intensity can be calculated and simplified by applying the Wigner Eckart theorem. In this calculation, terms with \( m_1 + m_2 + m_3 \neq 0 \) are eliminated and equation 2.13 is applied. Therefore, the intensity is

\[
\frac{dI(t)}{d\Omega} \propto |[\cos \theta \cos \varphi - i \cos \theta \sin \varphi] e^{i\omega z t} + [-\cos \theta \cos \varphi + i \cos \theta \sin \varphi] e^{-i\omega z t}|^2 \\
+ |[\sin \varphi - i \cos \varphi] e^{i\omega z t} + [\sin \varphi + i \cos \varphi] e^{-i\omega z t}|^2. \tag{3.13}
\]

Simplifying this expression yields

\[
\frac{dI(t)}{d\Omega} \propto 4 \cos^2 \theta \cos^2 (\omega t + \varphi) + \sin^2 (\omega t + \varphi) d\Omega. \tag{3.14}
\]

The term \( \sin^2 (\varphi + \omega z t) \) is the usual term containing the quantum beats and has no spatially dependent component, unlike what the current simulation predicts. The term \( 4 \cos^2 \theta \cos^2 (\omega t + \varphi) \) will have a combined angle and polarization such that it does not contribute significantly to the observed beats.

The basic principle of the simulation is that an initial starting condition for a ray of light is chosen. This ray of light is then traced through the system. One of three things will happen to this ray: it will miss the initial light pipe that collects the ray, it will be lost in the detection optics, or it will hit the detector. (All details of the simulation can be found in Appendix C).

This simulation traces the ray through the apparatus until it is lost and counts the ratio of rays...
that hit the detector to the ones that do not hit the detector.

The initial starting conditions are chosen such that the ray must originate between the electrodes in the vapor cell. This ensures that the ray is from a molecule that is in a uniform electric field. The initial angle of the ray is chosen according to a randomized distribution that satisfies equation 3.14. Since angular coordinates are used for the initial conditions and $d\Omega = \sin \theta d\theta d\varphi$, the initial angular distribution is chosen such that it has a $\sin^3 \theta$ dependance. This factor is incorrectly chosen. It was chosen such that there was a factor of $\sin \theta$ to account for the distribution of fluorescence as described in equation 3.14. There was an additional factor of $\sin^2 \theta$ to account for a spatial component of the quantum beat distribution, which does not appear in equation 3.14. The simulation should be redone with the correct angular distribution. The initial angular dependence has no weighting in $\varphi$.

The ray is then traced through the cell until it hits the face of the lightpipe. If it hits the electrodes, or does not exit through the cell windows, it is lost. Furthermore, it must hit the face of the lightpipe, or else it is lost. The distance between the cell and the lightpipe has been a difficult parameter to determine. At various times in the simulation and the experiment this distance $d_{cell,lp}$ has been made very small ($d_{cell,lp} \approx 0.1\"$) or much larger ($d_{cell,lp} \approx 0.5\"$). In the simulation, the angular acceptance and the fraction of photons collected depends significantly on $d_{cell,lp}$. Varying $d_{cell,lp}$ over this range can change the simulated collected light by as much as 20%.

In the simulation, the rays are traced through the optics stack (see Appendix C for details). It is assumed that the optical coupling gel eliminates reflections between optical elements in the stack. (This assumption is not perfect as these optical elements do have slightly different indices of refraction.) Any ray that hits an unpolished edge of an optic such as the edge of the IR blocking glass, the edge of the IF filter, or the edge of the sapphire cooling window is considered lost.

Modelling the Winston Cones is done with the same ray-tracing techniques. Again, the condition for total internal reflection for $\psi$ must be met for a ray to propagate. In the Winston Cones, it is possible for rays to reflect several times before exiting. It is assumed that a photon that reflects within the Winston Cones for more than five reflections is lost. The simulation is found to be completely insensitive to the number of reflections $N_{ref}$ as long as $N_{ref} > 5$ and
nearly insensitive for \( N_{\text{ref}} \geq 3 \).

To model the transmission through the IF filter, several steps are necessary. First, data is taken for the transmission of this filter as a function of wavelength at normal incidence. This data is fit to an 8th order polynomial function to turn it into an analytic function \( T(\lambda) \) that can be used to determine the transmission at any wavelength. This angle will determine the effective wavelength \( \lambda(\phi) \) of this ray as it passes through the IF filters. This effective wavelength is determined by

\[
\lambda(\phi) = \lambda_0 \left[ 1 - \left( \frac{n_{\text{glass}}}{n^*} \right)^2 \sin^2 \phi \right]^{\frac{1}{2}}
\]

(3.15)

where \( \lambda_0 \) is the initial wavelength of the ray, \( n_{\text{glass}} \) is the index of refraction of glass, and \( n^* \) is the effective index of refraction of the filter. Note that this equation has the same form as equation 3.3. Then \( T(\lambda(\phi)) \) is computed for this ray at some angle. Unfortunately, equation 3.15 breaks down at large angles and the transmission of the filter smaller than predicted. To take into account this effect, if \( \psi \) is found to be larger than 30°, the total transmission \( T_{\text{total}} \) is set to decrease by 1.5% for each additional degree above 30°. The total transmission is

\[
T_{\text{total}} = \begin{cases} 
T(\lambda(\phi)) & : \phi < 30 \\
T(\lambda(\phi)) - 0.015 \times (\phi - 30) & : \phi \geq 30
\end{cases}
\]

(3.16)

Rays are traced throughout the system under the principle that the optics are closely joined together. Therefore, the point where the ray leaves one optic is assumed to be the point where the ray enters the next optic. The results of a typical simulation run are shown in figure 3.29.

Although the PbO \( \text{a}(1)(v=5) \) state fluoresces primarily at 548 nm and 570 nm (and more weakly at longer wavelengths), a better idea of the transmission of the optical elements can be obtained by using the simulation to find the total transmission of the optical stack as a function of wavelength. Furthermore, the transmission as a function of wavelength is necessary for calculating the transmission of the blackbody radiation through the optical stack. With the same IF filter shown in figure 3.29 centered at 572 nm and with a 40 nm bandpass, the modelled transmission as a function of wavelength is shown in figure 3.30. This 40 nm bandpass filter was chosen so that decays from \( \text{a}(1)(v = 5) \rightarrow X(v = 1) \) at 570 nm and \( \text{a}(1)(v = 5) \rightarrow X(v = 0) \) at 548 nm could be simultaneously monitored. Ultimately, this choice of filter was not feasible as the filter allowed for the transmission of too much scattered light from the laser. However,
Figure 3.29: The transmission through a series of optics as a function of angle of the photons is modelled with the Monte Carlo simulation. The IF filter used here was a 40 nm bandpass filter centered at 572 nm and the distribution is shown as a function of the a) 548 nm detection wavelength corresponding to the $a(v=5)\rightarrow X(v'=0)$ transition and the b) 570 nm detection wavelength corresponding to the $a(v=5)\rightarrow X(v'=1)$. All angles are shown for light in Lexan.
Figure 3.30: The transmission of the optical stack with two Winston Cones and an IF filter that is centered at 572 nm and has a 40 nm bandpass is modelled as a function of wavelength.

the Winston Cones and optical stack were designed to work with this filter.

Several tests were performed on the optics to ensure that the Monte Carlo simulation reflects realistic conditions. The first test is a geometric confirmation that the angular spread of molecules in the simulation reflects the geometry of the light rays exiting the vapor cell. In the Monte Carlo simulation, the most probable angle for light to enter the lightpipe is at 22°. For a molecule in the center of the cell, the geometrical constraints that the light enter the lightpipe without hitting an electrode or guard ring constrains the maximum angle to 23° (see figure 3.31).

Next, the assumption that the Winston Cones could maintain five reflections without significant attenuation was tested. This assumption was tested by shining a laser into a Winston Cone and comparing the input and output power as a function of the number of reflections. For at least three reflections, no attenuation of power was found. It was difficult to align the laser in such a way that the light would clearly reflect more than three times. However, the data suggests that light can survive inside the Winston Cone for at least five reflections. As light travels through the Winston Cone it acquires a very large angular distribution. Unless the Winston Cone is coupled to the detector with an index matching gel or grease, much of the light is lost. The angular distribution can extend up to 90°.

Several different methods were employed to make sure that the measurements of the transmission through the optical elements matched the simulation. First, LEDs at a few different wavelengths were scanned across the input face of all of the optical elements at a variety of
angles. This method was difficult to compare to the simulation. The LEDs had a spectral width that spanned several nm and thus were not easy to compare to the monochromatic light from PbO. Furthermore, the angular distribution of light emitted from the LEDs ranges over 10-20° and is not easy to collimate.

Another testing method used a nitrogen pumped dye laser that was coupled into a multi-mode optical fiber as shown in figure 3.32. The collimated output of the fiber was mounted on a 2-dimensional translational stage and a rotating base. This method eliminated the problems with the broad spectral and angular distributions from the LEDs. With this method, the average transmission of the optical stack was consistent with simulations at a variety of incident angles. It was not possible to make point-by-point comparisons with the simulation, however, since the transmission of the Winston Cones at the edges is very sensitive to the input angle and position of the light.

Finally, an integrated method of comparison was used. In this method, the nitrogen pumped dye laser was again coupled into a multi-mode fiber and the collimated output was shone through a diverging lens and an optical diffuser and then into the stack of optics. Since this light is expected to have a broad angular distribution similar to the distribution of the fluorescence, this measurement is close to an exact simulation of the expected signal. Both light sources should have a large angular distribution that is peaked in the forward direction. In the case

Figure 3.31: A molecule at the center of the cell emits fluorescence that can only be detected at a maximum angle of 23° as a result of the geometrical constraints of the electrodes and guard rings and the distance to the lightpipe. Here, a cross sectional side view of the cell is shown with the relevant dimensions for calculating these cutoff angles.
Figure 3.32: A top view of the apparatus used to measure the transmission of the optical stack including both Winston Cones and the interference filter that is centered at 572 nm and has a 40 nm bandpass.
of the fluorescence this peaking is a result of the dipole radiation pattern. In the case of the simulation, the direction of the light source behind the diffuser will define a preferential forward direction for the light. The transmission of this light was again consistent with the simulations. In this case the detector was placed at a fixed point and the light collected was compared when the Winston Cones were present and when there was no additional light guide. The presence of the Winston Cones increased the light collection by 5.7 times, exactly matching the models.

For all simulations and tests, optical coupling grease (LS-1246-10) was used between the elements in the stack of optics. This grease reduced the reflections off of the surfaces of optics by minimizing the change in the index of refraction. The grease has an index of refraction of 1.46, so it does not make a perfect match between all optical components, which range from sapphire having an index of refraction of 1.77 [76] to Lexan which has an index of refraction of 1.59 [77]. However, the grease does significantly reduce the reflections at the interfaces compared to the reflections with air at the boundaries. However, this grease is difficult to use and can only be removed with isopropanol or acetone. Acetone cannot be used on Lexan since it dissolves plastics and isopropanol mixed with the grease leaves an optically opaque residue. This residue can be removed with methanol, but it is difficult to fully clean an optic after exposure to the grease. In an attempt to avoid these problems, a curing Nye SmartGel OCK-451 was also tested. This curing gel was difficult to mix and expensive and did not reduce the reflections more than the coupling grease, so it is not used.

3.7.5 Detectors

Three different types of detectors have been built and tested. All three types have advantages and drawbacks. PMTs are useful for detecting small signals since their dynode structure allows for noise-free gain. At the possible detection wavelengths of 548 nm and 570 nm, however, they only have a maximum quantum efficiency (q.e.) of ~ 15%. PIN photodiodes, by contrast, have no gain stage and require low-noise pre-amplification electronics, but have a q.e. of ~ 85% at these wavelengths. A detector that has some advantages of both PMTs and PIN photodiodes is an avalanche photodiode (APD), which has a moderate gain and again has a q.e. of ~ 85%. Unlike PMTs, however, the gain stage of an APD adds noise. Another critical characteristic of these detectors for this experiment is the size in which they can be purchased. PMTs can easily
be purchased in large sizes such as 6" diameters, while the largest PIN photodiodes that can be easily purchased are the 28 mm x 28 mm ones described here. The largest available APDs are even smaller, and the biggest one that was feasible for use in this experiment was only 16 mm in diameter.

All of the detectors built for this experiment must satisfy the same three requirements. First, the intrinsic noise in the amplifier must be less than the anticipated shot noise, so that the amplifier noise will not significantly contribute to the overall noise on the detected signal. Originally, the signal sizes were anticipated to be much larger than they are now expected to be, so it was expected that it would be possible to build a sufficiently low noise amplifier for a PIN photodiode. With the current signal sizes, PIN photodiodes do not meet this requirement, which is why other detectors were designed and built. The second requirement is that since the detector is exposed to a large pulse of scattered light from the excitation laser, the preamplifier must be able to recover quickly from such a pulse. Most of the data in this thesis was taken with an Electron Tubes 9850B PMT, and this tube with the associated electronics recovers from the scattered light in ≈10 μs. It has been a goal to make all detectors recover in at least this time. (Since the lifetime of the a(1) state in the cell is only ≈50 μs, this recovery time cannot be much longer.) Originally, it was hoped that the PIN photodiode and APD detector could recover from the scattered light quickly enough to allow the IF filter bandwidth to be broadened and even transmit the laser wavelength. Broadening the IF filters would have greatly increased the signal sizes. Unfortunately, these detectors (i.e. the sensor plus the associated preamplifier) could not be made to recover quickly enough, and the filter bandwidth needed to remain narrow in order to decrease the scattered light and allow for faster recovery times. The third requirement was that the bandwidth of the detector must be at least \( \geq 900 \) kHz to allow for unattenuated detection of quantum beats at \( \sim 300 \) kHz. This was satisfied by all three detectors.

3.7.6 PMTs

PMTs have the advantage of having a very large noise-free gain stage, and thus are preferable for measuring small signals. PMTs work through the photo-electric effect. A sensitive photocathode is exposed to incoming light and electrons are emitted from the photocathode and collected and amplified on a series of biased dynodes. The high voltage bias on these dynodes accelerates...
electrons to the next dynode. Each time an electron hits a dynode more electrons are released from the dynode, amplifying the signal.

This technology has several limitations. First, as mentioned above the photoelectric effect is much more efficient for higher energy (blue) photons and therefore the quantum efficiency of these PMTs at 548 nm is only 5-15%. Second, the large scattered light from the laser would saturate the PMT if the high bias voltage were not gated off during the laser pulse. Even with gating, scattered light transients are a significant source of backgrounds. Finally, photocathodes are known to degrade over time and with use, although this effect has not been observed here [78].

Primarily, two different PMTs were used during the duration of this thesis. An Electron Tubes 9850B was used for most of the data presented here. This tube has a specified 9% q.e. at 550 nm, but discussions with the manufacturer suggested that the actual q.e. for this tube could range from 4% to 9% [79]. The gain × q.e. of this tube at 550 nm has been measured to be 604 and 425 at different times during the duration of this thesis with a bias voltage of -925 V. Assuming a 9% q.e., the measurement of gain × q.e. yields a gain of 6720 or 4720. This measurement was made by directing an LED through a 1/4 m Digikrom monochromator and detecting the output with the PMT and a large area PIN photodiode. Since the q.e. of the PIN photodiode is large and known, it can be used to calibrate the measured output of the PMT. A gating circuit used to reduce the gain on the PMT during the scattered light pulse is a standard circuit, shown in [64]. With this gating circuit, the tube and electronics recover from the scattered light in ~10-12 μs.

To improve the counting rate for the detection of the a(1)→X fluorescence, the Electron Tubes PMT was replaced with two Hamamatsu R329EGP prismatic window PMTs. These specific PMTs are measured by the manufacturer to have a q.e. of 14.7% and 15.2% at λ = 548 nm. This q.e. is much higher than for the Electron Tubes PMTs both because these tubes were specifically selected for their high q.e., and because they have a prismatic faceplate. The prismatic faceplate increases the average number of times a photon hits the photocathode thereby effectively increasing the q.e. The other advantage of these PMTs over the Electron Tubes PMT is that they are linearly focused with a focusing electrode. Focusing electrodes are useful for gating applications since they concentrate the electrons from the photocathode before the first dynode. Reversing the voltage drop between the focusing electrode and the photocathode
provides a particularly strong potential barrier for the electrons to cross, improving the gating efficiency. This dynode structure makes gating more efficient than the Electron Tubes PMT, which is linearly focused, but does not have a focusing electrode. The gating circuit used with the Hamamatsu PMTs is almost entirely reproduced from [80], and is shown in figure 3.33 with one key modification. This modification is to directly connect the photocathode to the power supply board. The circuit in [80] connects the photocathode to the power supply board with a 100 kΩ resistor. Removing this resistor reduces the time it takes for the PMT to return to the full gain after the gating pulse occurs.

In addition to the gating circuit, another small circuit was added to the PMT electronics for reading out the signal. The anode current is transformed to a voltage with a 1.5 kΩ resistor to ground. A cable driver is used to amplify this voltage by a factor of two and lower the output impedance of the circuit.

Two nearly identical PMT gating and readout circuits were built following the schematic shown in figure 3.33. There are small variations of a few volts in the exact voltage applied to each dynode of the PMTs when the different circuits are used to bias the PMTs. This variation is a result of variations in the diodes used in the power board shown in figure 3.33. The gain of one PMT with its gating circuit has been measured to be 5244. The gain of the other PMT with its gating circuit has been measured to be 7682. This difference is attributed to manufacturing differences in the dynodes that have lead to different gain versus voltage profiles for these PMTs.

With the new gating circuit, the Hamamatsu PMTs are much better than the Electron Tubes PMTs at recovering from scattered light. With the same ~150 pC of photoelectrons produced by the scattered light, the Hamamatsu PMT recovers in 4.7 μs including the majority of the electronic transients from the gating pulse. This scattered light charge was measured with a photodiode with a known quantum efficiency. By contrast, the Electron Tubes PMT recovers in ~10-12 μs, with large residuals from the electronic transients persisting for the next ~20 μs.

There is a large electronic transient caused by gating the Hamamatsu PMT. This transient appears to be caused by voltages induced on the anode by the large voltage changes on the focusing electrode and the first dynode. While shielding the anode from the focusing electrode and first dynode has reduced this transient, it has not eliminated it. Despite this electronic transient, the gain of the Hamamatsu PMT has been measured to recover within 1 μs of the
Figure 3.33: Schematic of the PMT gating circuit, which is almost entirely reproduced from [80]. All capacitances are in $\mu$F and all resistors are in $\Omega$. PC is the photocathode output, DY1 is the first dynode, PS is the P-channel source voltage, PB is the P-channel gate bias, FE is the focusing electrode, FG is floating ground, NB is the N-channel gate bias voltage, and HV is the PMT high voltage input.
gating pulse being turned off as long as the gating pulse remains less than 5 \(\mu s\) in duration.

When detecting with PMTs, care was taken to keep the scattered light from the laser at a minimum. Two excitation and detection schemes were used. The first scheme was used for most of the time, and involved exciting on the \(X(v = 1) \rightarrow a(v' = 5)\) at transition at 570 nm and detecting on the \(a(v' = 5) \rightarrow X(v'' = 0)\) at 548 nm. This detection scheme allowed for efficient blocking with interference filters, as the laser was to the red of the detection wavelength. The second excitation and detection scheme was the reverse: here we excited on the \(X(v = 0) \rightarrow a(v' = 5)\) transition at 548 nm, which increases the signal size by a factor of 3 from the increase in the population from the Boltzmann distribution. Then, detection occurred on the \(a(v' = 5) \rightarrow X(v'' = 1)\) transition at 570 nm. Since this detection wavelength is to the red of the laser, interference filters are inefficient, and so two pieces of absorbing Schott OG550 color glass filters were used in addition to an interference filter to help block the laser light.

### 3.7.7 Transimpedance Amplifiers

All three of the detectors used here (PMTs, PIN photodiodes, and APDs) operate by converting photons to electrons. The created electrons form a current, which is more conveniently measured as a voltage. As a result of their large gain stage, PMTs create a large current that is easily converted to a voltage by measuring it across a small resistor. Since this resistor can be small, typical RC time constants are also small enough to allow for fast measurement. With PIN photodiodes and APDs, the currents are much lower and in order to measure them, much larger resistors are needed. In this case, the RC time constants are typically large and can limit the measurement speed. To avoid this problem, transimpedance amplifiers are used. A basic transimpedance amplifier is shown in figure 3.34. In this amplifier, the only path for the current from the detector is through the feedback resistor \(R_f\). The voltage at the output of the amplifier is \(V_{out} = R_f i_{sig}\) where \(i_{sig}\) is the signal current from the detector. The relevant RC time constant of the detector and amplifier is \(R_f C_f\). The advantage of the transimpedance amplifier is that the gain \(R_f\) of this amplifier can be large while the detector remains fast, if \(C_f\) is small.
Figure 3.34: A basic transimpedance amplifier with a feedback resistor $R_f$ and a feedback capacitor $C_f$.

<table>
<thead>
<tr>
<th>Component</th>
<th>Name</th>
<th>PIN photodiode detector</th>
<th>APD detector</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_f$</td>
<td>feedback resistor</td>
<td>600 kΩ</td>
<td>2 kΩ</td>
</tr>
<tr>
<td>$C_f$</td>
<td>feedback capacitor</td>
<td>0.26 pF</td>
<td>62 pF</td>
</tr>
<tr>
<td>$C_a$</td>
<td>amplifier capacitance</td>
<td>120 pF</td>
<td>20 pF</td>
</tr>
<tr>
<td>$\varepsilon_v$</td>
<td>amplifier voltage noise</td>
<td>0.5 nV/√Hz</td>
<td>1.7 nV/√Hz</td>
</tr>
<tr>
<td>$i_n$</td>
<td>amplifier current noise</td>
<td>0.1 pA/√Hz</td>
<td>2.0 pA/√Hz</td>
</tr>
<tr>
<td>$i_{dark}$</td>
<td>dark current shot noise</td>
<td>80 fA/√Hz</td>
<td>0.3 pA/√Hz</td>
</tr>
<tr>
<td>$C_j$</td>
<td>sensor capacitance</td>
<td>200 pF</td>
<td>130 pF</td>
</tr>
<tr>
<td>$R_s$</td>
<td>sensor series resistance</td>
<td>~1 Ω</td>
<td>~1 Ω</td>
</tr>
</tbody>
</table>

Table 3.3: Component values and the manufacturer specifications for the relevant parameters for the parts used in PIN photodiode and APD preamplifiers. The value for $i_n$ for the PIN photodiode is a typical current noise for a FET from [82]. The values for $R_s$ are approximate and guessed based on typical values for these components [28].

3.7.8 Noise in Transimpedance Amplifiers

Both the PIN photodiode and the APD required a low noise transimpedance amplifier as front-end electronics for the detectors. Since the PIN photodiode does not have any internal gain and the APD only has a modest gain, the noise characteristics of the transimpedance amplifier are critical when trying to achieve shot-noise limited detection.

The noise of a transimpedance amplifier can be modelled as shown in figure 3.35 [81]. All noise components are ultimately referenced to their amplitude at the output of the transimpedance amplifier. A real photodiode can be modelled as an ideal photodiode in parallel with a capacitor $C_j$ and a shunt resistor $R_j$, plus a resistance $R_s$ in series with the other components. In addition, the circuit model includes the feedback capacitance $C_f$ and resistance $R_f$ and the amplifier input capacitance $C_a$. To better understand which noise components are relevant, the component values and manufacturer specifications for the relevant parameters used in the PIN photodiode preamplifier and APD preamplifier are shown in table 3.3. These values will be used in calculating the noise contributions below.
Figure 3.35: Noise model of a transimpedance amplifier. Here, a real photodiode is modelled as an ideal photodiode in parallel with a junction capacitance $C_j$, a shunt resistance $R_j$ and a series resistor $R_s$. This photodiode is biased by a voltage source that has a voltage noise $e_V$. $R_j$ has a Johnson noise $e_{J,j}$ and $R_s$ has a Johnson noise $e_{J,s}$. $i_{dark}$ is the shot noise on the dark current from the photodiode. The amplifier has some input capacitance $C_a$ and has an input voltage noise $e_n$ and an input current noise $i_n$. The feedback resistor $R_f$ has a Johnson noise $e_{J,f}$. There is a feedback capacitor $C_f$. 

$Z_f = R_f(1 + jωR_f C_f)$

$Z_j = R_j(1 + jωR_j C_j)$

$C_i = C_a + C_j$
The idea was to choose components so that the shot noise on the signal at the output of the detector would be larger than the electronic noise of the detector. For a signal current $I_{\text{sig}} = \frac{Ne}{\tau} \exp(-t/\tau)$, the current noise spectral density due to the shot noise on the signal, at the input of the amplifier is

$$i_{\text{sn}} = \sqrt{2eI_{\text{sig}}} \sqrt{FG}.$$  

(3.17)

Here $G$ is the intrinsic gain of the detector; $G=1$ for a PIN photodiode, while $G=200$ for the APD used. Also, here $F$ is the “additional noise factor”, which arises from the Fano factor [83]. For the PIN photodiode without gain $F=1$, while for an APD $F \geq 2$ as a result of the nature of the gain process [84]. In the case of the APD (630-70-73-500) used here, this additional noise was measured as indistinguishable from $F=2$.

To calculate what voltage the signal current $I_{\text{sig}}$ and the shot noise on this signal current $i_{\text{sn}}$ will cause at the output of the amplifier, it will be helpful to simplify the model of the transimpedance amplifier. To simplify this model, the resistances and capacitances will be written in terms of their complex impedances wherever possible. The complex impedances are shown in figure 3.35 and defined as

$$Z_f = \frac{R_f}{1 + i\omega R_f C_f}$$

and

$$Z_j = \frac{R_j}{1 + i\omega R_j C_i}$$

(3.18)

(3.19)

where $C_i = C_j + C_o$. At the output of the amplifier the signal current $I_{\text{sig}}$ causes a voltage drop across $R_s$ of and $Z_j$. In order to keep the negative input to the op-amp at a virtual ground, the op-amp must supply a current that cancels $I_{\text{sig}}$. Therefore,

$$\frac{V_{\text{out}}}{Z_f} = I_{\text{sig}}.$$  

(3.20)

Simplifying this equation yields,

$$V_{\text{out}} = Z_f I_{\text{sig}}.$$  

(3.21)

The shot noise on the signal will be amplified similarly as it is also a current produced at the same point in the system. At the output of the amplifier the noise due to the shot noise on the
signal is
\[ \delta V_{sn} = Z_f \sqrt{2eI_{sig}} \sqrt{FG}. \] (3.22)

Originally, it was anticipated that with the PIN photodiode detector, it would be possible to detect \( N_{exp, PD} = 5 \times 10^8 \) photoelectrons arriving in an approximately exponentially decaying signal after the dye laser pulse with a time constant of \( \tau = 50 \) \( \mu \)s. Currently, with better understanding of the laser excitation efficiency, it is now known that \( N_{act, PD} = 3 \times 10^6 \) photoelectrons will be detected after each laser excitation pulse. \( N_{exp, PD} = 5 \times 10^8 \) photoelectrons yields a shot noise \( \delta V_{sn, exp} = 430 \) nV/\( \sqrt{\text{Hz}} \) with \( R_f = 600 \) k\( \Omega \) as used in the PIN photodiode while \( N_{act, PD} = 3 \times 10^6 \) photoelectrons yields \( \delta V_{sn, act} = 30 \) nV/\( \sqrt{\text{Hz}} \). In the APD circuit, as a result of the smaller area, the anticipated signal sizes are smaller. Assuming \( N_{act, APD} = 7 \times 10^5 \) photoelectrons, yields \( \delta V_{sn, act} = 20 \) nV/\( \sqrt{\text{Hz}} \) with \( R_f = 2 \) k\( \Omega \) as used for the APD circuit. The relevant frequency range for this detector is between 100-500 kHz, which is the frequency range in which quantum beats are detected. A summary of these signal sizes and corresponding shot noises is shown in table 3.4.

All of the resistances in the model in figure 3.35 have intrinsic Johnson noise. The voltage noise spectral density \( e_J \) across a resistance \( R \) \[82\] is given by
\[ e_J = \sqrt{4k_BTR}. \] (3.23)

This noise is generated by a resistor that is in parallel with a capacitor. \( e_{JJ} \) creates a current \( I_{e,Jf} = \frac{e_{JJ}}{R_f} \) through \( R_f \). To keep \( V_L = 0 \), this current must be cancelled by an equal current from the op-amp. This current has a voltage drop across \( Z_f \) to cause
\[ \delta V_{JJ} = I_{e,Jf}Z_f = \frac{e_{JJ}}{1 + \omega C_f R_f}. \] (3.24)

The Johnson noise from \( R_f \) is often one of the largest noise sources, but it is also adjustable as compared to the signal size. Neglecting bandwidth considerations, the signal at the output scales as \( R_f \), while \( \delta V_{JJ} \) scales as \( \sqrt{R_f} \). Therefore, a large value of \( R_f \) will minimize the effect of this noise source relative to the signal. When a short RC time constant is not necessary, making \( R_f \) as large as possible minimizes this noise contribution. In the case of the PIN photodiode, however, \( R_f C_f \) limited the 3dB point to \(~900\) kHz, which was the largest acceptable time.
Table 3.4: The signal size, shot noise, and total amplifier noise for the PMT, PIN photodiode, and the APD detectors. All noise figures are quoted at their respective maximum values within the frequency range 100-500 kHz.

<table>
<thead>
<tr>
<th>Name</th>
<th>PMT</th>
<th>PIN Photodiode</th>
<th>APD</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{\text{exp}}$</td>
<td>anticipated count rate</td>
<td>$5 \times 10^8$</td>
<td>$3 \times 10^6$</td>
<td>$7 \times 10^5$</td>
</tr>
<tr>
<td>$N_{\text{act}}$</td>
<td>actual count rate</td>
<td>$5 \times 10^5$</td>
<td>$3 \times 10^6$</td>
<td>$7 \times 10^5$</td>
</tr>
<tr>
<td>$I_{\text{sig,exp}}$</td>
<td>anticipated signal current</td>
<td>$2 \times 10^{-6}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$I_{\text{sig,act}}$</td>
<td>actual signal current</td>
<td>$2 \times 10^{-9}$</td>
<td>$1 \times 10^{-8}$</td>
<td>$2 \times 10^{-9}$</td>
</tr>
<tr>
<td>$V_{\text{sig,exp}}$</td>
<td>anticipated signal size</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V_{\text{sig,act}}$</td>
<td>actual signal size</td>
<td>$2 \times 10^{-2}$</td>
<td>$6 \times 10^{-3}$</td>
<td>$8 \times 10^{-4}$</td>
</tr>
<tr>
<td>$i_{\text{sn,exp}}$</td>
<td>anticipated shot noise current</td>
<td>$8 \times 10^{-13}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$i_{\text{sn,act}}$</td>
<td>actual shot noise current</td>
<td>$2 \times 10^{-14}$</td>
<td>$6 \times 10^{-14}$</td>
<td>$4 \times 10^{-14}$</td>
</tr>
<tr>
<td>$\delta V_{\text{sn,exp}}$</td>
<td>anticipated shot noise voltage</td>
<td>430</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\delta V_{\text{sn,act}}$</td>
<td>actual shot noise voltage</td>
<td>200</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>$\delta V_{\text{det}}$</td>
<td>amplifier noise at 300 kHz</td>
<td>9</td>
<td>220</td>
<td>8</td>
</tr>
</tbody>
</table>
constant for a detector to measure unattenuated quantum beats at ~300 kHz. $C_f$ had already been minimized to the lowest possible value to allow for the largest value of $R_f$ while maintaining this RC time constant. For both preamplifiers, $\delta V_{Jf}$ was one of the largest noise sources at low frequencies close to 100 kHz. For the PIN photodiode preamplifier, it was $\sim 100$ nV$\sqrt{\text{Hz}}$, and for the APD preamplifier it was $\sim 6$ nV$\sqrt{\text{Hz}}$. For the APD, this noise source could have been further reduced (relative to the signal) with a larger resistor.

A second significant Johnson noise source is from the series resistance of the detector $R_s$. The voltage noise $e_{Js}$ is created directly at the negative input to the op-amp, so the op-amp creates a current to cancel the voltage at this negative input. The current from the op-amp must flow through $Z_f$, $R_s$ and $Z_j$. The three resistances form a voltage divider, and this voltage divider chain is similar to that formed by a non-inverting op-amp. The output voltage is

$$\delta V_{Js} = \left(1 + \frac{Z_f}{R_s + Z_j}\right) e_{Js}. \quad (3.25)$$

In most cases, $R_s$ is on the order of a few Ohms, and $Z_j$ is very large both because $R_j$ is on the order of a few GOhms and $C_j$ is usually on the order of a few hundred pF. The relevant frequency range for this detector is 100-500 kHz, where quantum beats will be detected. Filters can be used to remove noise at all other frequencies. In the frequency range for the detector, $Z_j \gg R_s$ since $R_j$ is large, and the frequency is not sufficiently high for $C_j$ to dominate and be in the high frequency limit where $Z_j \to 0$. Therefore, in equation 3.25, $R_s$ can be ignored and

$$\delta V_{Js} \approx \left(1 + \frac{Z_f}{Z_j}\right) e_{Js}. \quad (3.26)$$

Equation 3.26 is used to model the noise spectrum from the transimpedance amplifiers, but conceptually, it can be better understood in the high frequency limit. In this high frequency limit, $\omega R_f C_f \gg 1$, and $\omega R_j C_s \gg 1$ and equation 3.26 can be further reduced to

$$\delta V_{Js} \approx \frac{C_i}{C_f} e_{Js}. \quad (3.27)$$

where it has been assumed that $\frac{C_i}{C_j} \gg 1$. Now, it is apparent why this noise source can become so significant. $C_i = C_a + C_j$ can be large: the sensor capacitance $C_j$ is fixed by the choice of
detector and if FETs are used, the amplifier capacitance $C_a$ is often increased to be nearly as large as $C_j$. In the case of the PIN photodiode $C_i \approx 320$ pF. On the other hand, $C_f$ is kept to be small to decrease the RC time constant of the amplifier. Together, the gain on $e_{j_s}$ can be large, making it a significant noise source. It is not known exactly what the value of $R_s$ is for either the PIN photodiode or the APD. In both cases it is estimated to be $\sim 1 \Omega$, as this value is typical for these devices, and matches the measured noise spectra [28]. For the PIN photodiode this noise is $\delta V_{j_s} \sim 10-50$ nV/$\sqrt{\text{Hz}}$ at 500 kHz and is one of the dominant noise components at high frequencies. For the APD, this noise source is insignificant since the ratio of $C_i/C_f$ is smaller, and $\delta V_{j_s}$ is on the order of 0.1 nV/$\sqrt{\text{Hz}}$ at 500 kHz in this case.

The final source of Johnson noise is the resistance $R_j$ across the sensor. Similar to the calculation of $e_{j_s}$ above, the op-amp will create a current to cancel the voltage created by $e_{j_j}$ at the negative input of the op-amp. Again, this current must travel through $Z_f$, $R_s$, and $Z_j$. As in the calculation of $e_{j_f}$ the $e_{j_j}$ creates a current through $R_j$, but the op-amp creates a current through $Z_j$. As before, a voltage divider model can be used for these resistors. In this case, the gain is similar to that formed by an inverting op-amp, and the voltage at the output is

$$\delta V_{j_j} = \frac{Z_f}{R_s + R_j} e_{j_j}. \quad (3.28)$$

Again, $R_s \ll R_j$, so this reduces to

$$\delta V_{j_j} \approx \frac{Z_f}{R_j} e_{j_j}. \quad (3.29)$$

At low frequencies where $R_f \gg \frac{1}{\omega C_f}$, this expression reduces to

$$\delta V_{j_j} \approx \frac{R_f}{R_j} e_{j_j} \quad (3.30)$$

Usually, $R_f$ is on the order of kOhms at most, since higher resistances make reasonable bandwidths impossible to achieve. The sensor resistance $R_j$ is usually on the order of a few GOhms. Together, these resistances limit the gain of $e_{j_j}$ so that it is not a significant noise source. In the case of the PIN photodiode, $R_{j_j}$ was measured with a voltage divider circuit powered by the $V_{bias} = -90$ V bias voltage and formed by $R_j$ and a resistor to ground $R_g = 520$ kΩ. The voltage measured across $R_g$ was $V_g = 10$ mV, implying that since $V_g = V_{bias} \frac{R_g}{R_{j_j}}$, $R_{j_j} \approx 5$ GΩ.

In the PIN photodiode circuit, at low frequencies, $V_{j_j} \sim 0.1$ nV/$\sqrt{\text{Hz}}$. In the APD, $R_j$ is
similarly large, although it was not successfully measured nor was it specified by the manufacturer. Calculations for all large values of $R_j$ for the APD circuit suggest that this noise source is not significant for the APD circuit. Compared to the other noise sources in both circuits, the Johnson noise from $R_j$ is negligible.

In addition to Johnson noise, the two other significant noise sources are the voltage noise $e_n$ and the current noise $i_n$ of the amplifier. These are intrinsic to the amplifier, but are not fundamental noise sources; better amplifiers have lower values of $e_n$ and $i_n$. The lowest voltage noises can be found on amplifiers that use an external JFET as an input stage, as discussed below. The voltage noise $e_n$ is created at the same point in the amplifier as $e_{je}$ and is amplified similarly. At the output of the amplifier, the input voltage noise of the amplifier $e_n$ contributes

$$\delta V_{en} = \left(1 + \frac{Z_f}{R_s + Z_j}\right) e_n.$$  \hspace{1cm} (3.31)

Since $R_s \ll Z_j$ at the relevant frequencies, this equation can be simplified to

$$\delta V_{en} = \left(1 + \frac{Z_f}{Z_j}\right) e_n.$$  \hspace{1cm} (3.32)

This form of the equation is used to model the noise, but for conceptual purposes can be further simplified for frequencies higher than the relevant range of 100-500 kHz. At very high frequencies such that $\omega R_f C_f \gg 1$ and $\omega R_f C_i \gg 1$, this simplifies to

$$\delta V_{en} \approx \frac{C_i}{C_f} e_n.$$  \hspace{1cm} (3.33)

Again, it is assumed that $\frac{C_i}{C_f} \gg 1$. With small signal sizes, $\delta V_{en}$ can be the most significant noise source in a transimpedance amplifier. For the PIN photodiode preamplifier, at high frequencies such that $\omega R_f C_f \gg 1$, the voltage noise is $\delta V_{en} = 260 \text{ nV}/\sqrt{\text{Hz}}$ despite the significant effort to keep this noise small by using low noise FETs as the front end of the preamplifier. For the APD preamplifier, $\delta V_{en}$ is insignificant, because the ratio of $C_i/C_f$ is much smaller. Although this amplifier has the same frequency response considerations as the PIN photodiode amplifier, the APD amplifier requires less gain so $R_f$ can be smaller and $C_f$ can be larger. Therefore, the ratio of $C_i/C_f$ is smaller and the noise from $e_n$ is not amplified as much. In the APD preamplifier,
\( \delta V_{in} \sim 1 \text{nV/\sqrt{Hz}}. \)

The input current noise \( i_n \) is amplified by the transimpedance gain of the amplifier. Therefore, this current noise has a similar gain as the signal current and the shot noise current. At the output of the amplifier,

\[
\delta V_{in} = Zf i_n. \tag{3.34}
\]

Usually the input current noise on the amplifier can be reduced to acceptable levels by using JFET inputs. Standard operational amplifiers can have larger values of \( i_n \) that can make this term significant. With the JFET inputs on the PIN photodiode preamplifier, the output noise due to \( i_n=0.1 \text{pA}/\sqrt{\text{Hz}} \) is \( \delta V_{in} \sim 60 \text{nV}/\sqrt{\text{Hz}}. \) Since a standard operational amplifier was used for the APD preamplifier, current noise was more significant. For the APD detector, the output noise due to \( i_n=2.0 \text{pA}/\sqrt{\text{Hz}} \) was the second most significant noise component at \( \delta V_{in} \sim 4 \text{nV}/\sqrt{\text{Hz}}. \)

Another insignificant source of current noise is the shot noise on the dark current in the sensor. Since the dark current is small compared to the anticipated signal sizes, the shot noise on this dark current is also very small compared to the shot noise on the anticipated signals. Again, this current is attenuated by the RC time constant of the amplifier so that at the output of the amplifier it gives a voltage noise

\[
\delta V_{dark} = Z f i_{dark}. \tag{3.35}
\]

The dark currents used in these calculations were taken from the manufacturers specifications. For the PIN photodiode, \( i_{dark}=80 \text{fA}/\sqrt{\text{Hz}} \), so \( \delta V_{dark} \) is tiny at \( 90 \text{pV}/\sqrt{\text{Hz}} \) [85]. Similarly, for the APD \( i_{dark}=0.3 \text{pA}/\sqrt{\text{Hz}} \), so \( \delta V_{dark} \) is completely negligible at \( 0.6 \text{pV}/\sqrt{\text{Hz}} \) [86].

For the PIN photodiode transimpedance amplifier, it was necessary to keep the total electronic noise as low as possible, with the goal that it be lower than the anticipated level of shot noise. For \( N_{exp,PD} = 5 \times 10^8 \), the PIN photodiode preamplifier barely met this goal, while for \( N_{act,PD} = 3 \times 10^6 \) the goal is not met. The APD detector did barely meet this goal for \( N_{act,APD} = 7 \times 10^5 \), and could be further improved to detect even smaller signals with shot noise limited sensitivity.
3.7.9 PIN Photodiode

From a noise perspective, there were two critical choices of components for the PIN photodiode preamplifier. First, the FETs used in the front end of the preamplifier shown in figure 3.36 were chosen for their low voltage noise. Second, $R_f=600 \, \text{k}\Omega$ was chosen so that its Johnson noise was smaller than the anticipated noise from shot noise on a signal of $N_{\text{exp,PD}}=5 \times 10^8$ photoelectrons/laser pulse for the first 100 $\mu$s of the approximately exponential decay. In order to keep the 3 dB bandwidth of the amplifier $f_{3\text{dB}} \geq 1 \, \text{MHz}$ for unattenuated detection of quantum beats at $\sim 300 \, \text{kHz}$, it is then necessary to keep $C_f \leq 0.26 \, \text{pF}$. The Hamamatsu S3584-08 photodiode used to detect the signals has a capacitance $C_j \approx 200 \, \text{pF}$ when reverse biased with -90 V, and has resistances of $R_j \sim 5 \, \Omega$ and $R_s \sim 5 \Omega$. As discussed in section 3.7.8, with these values the significant noise sources are $e_{js}$, $e_{JF}$, and $e_n$. All contribute $\delta V_{\text{out}} \sim 10^{-7} \, \text{V}/\sqrt{\text{Hz}}$. As described in section 3.7.8, $e_{js}$ and $e_n$ are largest at high frequencies, so they contribute $\delta V_{\text{out}} \sim 10^{-7} \, \text{V}/\sqrt{\text{Hz}}$ at $\sim 200 \, \text{kHz}$ and increase at higher frequencies. $e_{JF}$ is largest at low frequencies, and is $\delta V_{\text{out}} \sim 10^{-7} \, \text{V}/\sqrt{\text{Hz}}$ below $\sim 100 \, \text{kHz}$ and decreases at higher frequencies. The largest noise source is in the high frequency limit of $\omega R_f C_j \gg 1$ where, $\delta V_{\text{en}} \approx e_n C_f^2 \approx 800 e_n \approx 400 \, \text{nV}$. $e_{js}$ and $i_n$ contribute very little to the noise (see figure 3.37).

It is impossible to buy an op-amp with low enough $e_n$ for these purposes, so it was necessary to design a custom amplifier. The first stage of this amplifier was a low noise JFET input stage, which had very low $e_n$ [87]. The voltage noise of the JFETs can be further reduced by putting $m$ JFETs in parallel resulting in a combined noise of $e_n=\sqrt{e_{\text{JFET}}/m}$. The input stage used two IF9030 JFETs in parallel, each of which had $e_n=0.5 \, \text{nV}/\sqrt{\text{Hz}}$ [88]. This JFET input stage did not have a sufficiently high voltage gain to achieve the desired transimpedance gain of $V_{\text{f_{in}}} = 6 \times 10^5 \, \Omega$, so this stage is followed by an op-amp. The gain of the JFET amplifier is sufficiently large that the input noise of the op-amp is negligible.

In principle, as many JFETs as necessary can be used in parallel to reduce the voltage noise to an acceptable level. In practice, however, there are two limitations. The ultra-low noise JFETs used here have a significant gate-source capacitance $C_{\text{JFET}}=60 \, \text{pF}$. Since the noise at the output of the amplifier at high frequencies scales as $e_n C_f \propto \frac{1}{\sqrt{m}}(C_j + mC_{\text{JFET}})$, the number of parallel JFETs has an optimum value $m \approx C_j/C_{\text{JFET}}$ [82]. Also, since $e_{js}$ is of the same order as $e_n$ and these contribute in the same manner, there is little improvement to the noise.
Figure 3.36: Circuit diagram for the PIN photodiode detector. D1 is the large-area Hamamatsu S3584-08 photodiode. D2 are BAS70-04 Schottky diodes chosen for their small capacitance and low forward voltage. D3 are small signal HSMP-3822-BLK diodes, which allow for more current conductance than the Schottky diodes. D4 are also HSMP-3822-BLK diodes, chosen for their low capacitance. When the preamplifier is saturated, these diodes provide a low resistance path in the feedback loop. Since the JFETs Q1 and Q2 drift with temperature, P1 and P2 are used to finely adjust the voltages at the inputs of U1 so that the two inputs are at the same DC voltage. Q1 is chosen for its low voltage noise, and is an IF9030 from InterFET. Q2 is used in a cascode configuration to increase the speed of the JFETs and is a 2N4856A from InterFET. U1 is an AD797, which was chosen for its high speed, low noise, and fast overdrive recovery. U2 is an AD829, which is a cable driver chosen for its fast overdrive recovery.
once $e_n \lesssim e_{J,F}$.

Requirements for the second stage of amplification (the op-amp) were also strict. In order to meet the high frequency transimpedance gain of the entire preamplifier, it is necessary to have a closed loop voltage gain of $G_{v,cl} \approx \frac{G}{G_f} \sim 1000$. The JFET stage of the amplifier only has a gain of $G_1 \sim 60$, determined by $G = g_m R_d$ where the JFET transconductance is $g_m = 0.02 \, \text{S}$ and the drain resistance is $R_d = 3 \, \text{k}\Omega$. The gain of this stage is reduced at high frequencies by the Miller effect [82]. A cascode configuration with two 2N4856A JFETs significantly reduced this effect [89]. Despite the cascode, the second stage of the amplifier must have a very high gain and large bandwidth to have enough open loop gain to sufficiently drive the closed loop gain of the transimpedance amplifier. To meet these requirements an Analog Devices AD797 was chosen, which has a gain bandwidth product (GBW) of 110 MHz and $e_{n2} = 0.9 \, \text{nV/}/\sqrt{\text{Hz}}$. In addition to the high GBW of the AD797, this op-amp was chosen for its fast recovery from overdrive. This fast recovery was necessary to allow the op-amp to recover from the large scattered light pulse from the dye laser. The output cable driver was chosen to be an AD829, which also recovers quickly from overdrive.

With these components, the noise on the PIN photodiode and accompanying transimpedance amplifier was measured to be less than 400 nV/√Hz for frequencies below 500 kHz as shown in figure 3.37. With the expected signal size of $N_{act,PD} = 3 \times 10^6$ photoelectrons arriving after each laser shot, the expected shot noise on the signal was $\sim 30 \, \text{nV/}/\sqrt{\text{Hz}}$, so the electronic noise would be significantly larger than the shot noise for most realistic beat frequencies. There is a trade-off in the choice of detector. The PIN photodiode detector would allow for the largest counting rates of all of the detectors considered as a result of its large area and high q.e. However, since it was impossible to build a sufficiently low noise amplifier to allow for shot noise limited detection, it was ultimately decided that these detectors were unsuitable for use in the experiment.

3.7.10 APDs

Since it was impossible to achieve shot noise limited detection with the PIN photodiodes, an APD detector was built for use in the apparatus. The noise design of the transimpedance amplifier for the APD is much less stringent since the APD has an internal nominal gain $G \approx 200$. Furthermore, since the gain of the APD adds noise, the contribution from shot noise at the
output of the APD will be $\sqrt{2G}$ larger than the shot noise from the PIN photodiode. Both of these factors make it possible to choose $R_f$ to be much smaller, and in this case it was chosen to be $R_f = 2$ k\Omega. Thus, at the output of the amplifier, $\delta V_{sn} = 20$ nV/$\sqrt{\text{Hz}}$ with a signal size of $N_{act,APD} = 7 \times 10^5$ photoelectrons/laser pulse. With $C_J = 140$ pF, it is now possible to estimate the noise terms. $R_j$ and $R_s$ give insignificant noise contributions. Similarly, $e_n$ is no longer the limiting noise source in the amplifier, so no front-end JFETs were used in the design of this transimpedance amplifier. Instead the transimpedance amplifier is made from a single op-amp, the AD797, which has again been chosen for its high GBW and fast overdrive recovery time. The AD797 has $e_n = 0.9$ nV/$\sqrt{\text{Hz}}$ and $i_n = 2.0$ pA/$\sqrt{\text{Hz}}$. At the output of the transimpedance amplifier, $\delta V_{ff} \approx 5.8$ nV/$\sqrt{\text{Hz}}$. The voltage noise is almost insignificant since $\delta V_{e_n} \approx 1.3$ nV/$\sqrt{\text{Hz}}$. The current noise is the largest expected noise contribution at $\delta V_{i_n} \approx 3.7$ nV/$\sqrt{\text{Hz}}$ while the predicted shot noise is $\delta V_{sn} = 20$ nV/$\sqrt{\text{Hz}}$. The various noise contributions along with the measured noise are shown in figure 3.38.

In addition to the noise sources already discussed, there are two other noise sources with the APD detector, which were negligible with the PIN photodiode detector. The first is the shot noise in the dark current of the APD $\delta V_{dark}$. This is negligible compared to the shot noise on the expected signal. The second source arises from the noise on the bias voltage for the APD. The photodiode bias voltage was supplied by batteries, but the necessary high bias voltage for
the APD makes this difficult. A high voltage power supply was used and filtered to provide acceptable noise characteristics for the APD detector.

With these noise requirements, the final design of the transimpedance amplifier for the APD is shown in figure 3.39. This detector was able to easily meet the requirement that the total noise be less than the anticipated shot noise on the signal. Ultimately, this detector was not used because of its small area. This APD has a 16 mm diameter active area, but comes in a 1" diameter case. To achieve the same SNR with the APD and the PMT, the APD must detect at least twice as many photoelectrons since the gain stage adds some noise. Given the geometrical constraints, it is impossible to design a Winston Cone that meets this criterion. Tiling multiple APDs and using several smaller Winston Cones was also discussed, but this option also did not meet the criterion of increasing the number of counted photoelectrons sufficiently to justify its use.

3.7.11 Recovery Time

In addition to the noise requirements, the detectors must also be able to recover from the scattered light from the dye laser that is injected in a ~5 ns duration. The amplifier saturates...
Figure 3.39: Circuit Diagram for the APD detector. D1 is the APD, and is the 630-70-73-500 from Advanced Photonix, chosen for its large area. D2 is a BAS70-04 Schottky diode, chosen for its low forward voltage and low capacitance. D3 is a HSMP-3822-BLK diode chosen for low capacitance. U1 is an AD797, chosen for low-noise, high speed and fast overdrive recovery. U2 is an AD829, a high speed cable driver with fast overdrive recovery.
from this scattered light, and then recovers with some small ringing. The "recovery time" is defined as the time that the amplifier takes to ring down to $1/e$ of the voltage of the signal at its peak. The recovery time of the amplifier depends on the size of the scattered light pulse.

Originally, the PIN photodiode amplifier was intended to be used with a broad IF filter that would allow for the detection of decays along two vibrational channels: $a(v = 5) \rightarrow X(v' = 0)$ and $a(v = 5) \rightarrow X(v' = 1)$. The Franck Condon factors for these decay channels are approximately equal, so detecting both channels at once would double the detected signal. Since the excitation occurred along the one of these transitions ($X(v'' = 0) \rightarrow a(v''' = 5)$) at 550 nm, a significant amount of scattered light was transmitted through this filter. At one time, the lightpipes were chipped; this increased the scattered light. Under these conditions, the scattered light signal was measured to be equivalent to 220 nC of photoelectrons. At later times, with unchipped lightpipes the scattered light with this filter was measured to be equivalent to 1.6 nC of photoelectrons. The PIN photodiode detector and the APD detector both saturated for at least 50 $\mu$s after being exposed to 220 nC of scattered light.

To reduce the scattered light, two color glass Schott OG570 filters were added to the filter stack. Each piece of this color glass transmitted 70% of the 570 nm light from the $a(v = 5) \rightarrow X(v' = 1)$ decays, but blocked both the excitation and fluorescence light at 548 nm from $a(v = 5) \rightarrow X(v' = 0)$. The color glass was not an ideal filter, for several reasons. First, color glass works as a filter by absorbing light. These filters often reemit red-shifted photons that are in the bandpass of interest. For this reason the color glass filters were placed before the IF filters in an attempt to reduce the detected reflorescence. Second, these filters blocked roughly 50% of the expected signal by blocking one of the vibrational decays. Third, the filters only have 70% transmission at the wavelength of the other vibrational decay further attenuating the measured signal. Despite these problems, the Schott glass did reduce the scattered light to a more manageable 1.5 nC. At this lower level of scattered light both the PIN photodiode and APD can recover quickly enough to be used. The recovery time as a function of injected charge from scattered light is shown in figure 3.40 for both detectors.

As shown in figure 3.36, three modifications were made to the design of the PIN photodiode transimpedance amplifier to improve the recovery time. First, clamping diodes were placed between the output of the photodiode or APD and ground to shunt large input photocurrents to
Figure 3.40: Graph of the recovery time of the detectors versus the size of the scattered light pulse. The recovery time is the time it takes the detector to reach $1/e$ of the signal level.

ground. Two kinds of small signal and Schottky diodes were used and both kinds were chosen for their low capacitance so as not to significantly contribute to $C_t$. The Schottky diodes are HSMP-3822-BLK diodes (which allow for a high current); and BAS70-04 diodes (which have a low forward voltage drop). These diodes were placed in opposite directions to damp additional electronic ringing due to the scattered light pulse. This modification was also used in the APD transimpedance amplifier. Second, diodes were placed in the feedback loop to allow for a low resistance path when the amplifier was saturated. These HSMP-3822-BLK diodes were again chosen for their low capacitance. Three were put in series to further reduce their capacitance. These diodes were not necessary in the APD amplifier because $R_f$ is much smaller. Finally, the cascode in the JFET stage improved the recovery time by increasing the bandwidth of this stage of the amplifier.

Two other methods were tried to reduce the recovery time of the PIN photodiode amplifier, but these methods were not successful and were not incorporated into the final design. The first was to add a power booster in the feedback loop to source more current through the diodes in the feedback loop. This method was abandoned because the additional component required making the feedback traces longer; this in turn increased the stray capacitance and therefore decreased the bandwidth. The second method was to inject charge of the opposite sign into the transimpedance amplifier at the junction between the PIN photodiode and the input of the transimpedance amplifier. This was done using another PIN photodiode arranged in the
opposite orientation, with a laser diode shone into it to supply the charge. Unfortunately, the improvement from this charge cancellation was negligible and therefore was removed.

**Frequency Response**

In order to achieve the desired bandwidth of ~1 MHz with a feedback resistor of 600 kΩ in the PIN photodiode transimpedance amplifier, it is necessary to keep the feedback capacitance $C_f < 0.26$ pF. Since the diodes used to decrease the scattered light recovery time have a combined capacitance of 0.2 pF, it is necessary to keep all other possible capacitances extremely low. For this reason, three 200 kΩ resistors were used in series to create the feedback resistor. Additionally, the circuit board was designed to keep the traces relating to the components in the feedback loop as short as possible by placing feedback components on the opposite side of the circuit board from the amplifying components. Ground planes were placed on all available surfaces on the circuit board and two inner layers of the circuit board were also grounded. The 3dB bandwidth of the circuit was measured as $\approx 900$ kHz, implying $C_f \approx 0.3$ pF (see figure 3.41). The smaller $R_f$ in the APD amplifier makes it much less sensitive to frequency limitations and this amplifier could be made to have a bandwidth of at least 10 MHz if necessary. Our present APD detector has a bandwidth of 1 MHz.
Final Transimpedance Design

The final design of these detectors incorporated all of the elements discussed above. The final design for the PIN photodiode detector is shown in figure 3.36 and the final design for the APD detector is shown in figure 3.39. Wherever possible, surface mount components were used as they are smaller, and can be used on both sides of a circuit board further reducing the lead lengths. All cabling connected to the circuit boards was made of coaxial cable to reduce pick-up of extra noise.

Both preamplifiers were powered with supplies that were designed to be low noise and still supply sufficient current for the circuits. These power supplies are shown in figure 3.42. Here, a PowerOne linear DC supply is used to supply +18 and -18 V to 7815 and 7915 voltage regulators. These voltage regulators power low noise OP77 op-amps, which provide +12 V and -12 V outputs that are referenced to stable LM399H voltage references. BUF634 power boosters are used to increase the current output of these amplifiers. The power supply for the bias voltage was filtered to remove high frequency noise components and was used to bias the PIN photodiode.

To test the APD, a simulated signal was created using an LED driven by an arbitrary waveform generator and a pulsed dye laser pumped by a nitrogen laser. The waveform generator was programmed to modulate the LED at 500 kHz with an exponentially decaying amplitude. The amplitude of this signal was equivalent to \( N_{test,APD} = 2 \times 10^8 \) photoelectrons/laser pulse. (Currently, it is estimated that the actual signal sizes with the APD will be \( N_{act,APD} = 7 \times 10^5 \) photoelectrons/laser pulse, which is significantly smaller than was tested in this setup.) The scattered light in the test was 1.5 nC, which is equivalent to a scattered light from detecting at the excitation wavelength. With this setup, the APD detected a simulated signal as shown in figure 3.43. This test demonstrates that the APD can detect quantum beats at the desired frequency with no attenuation after ~10 \( \mu \)s.

As mentioned above, it was decided that neither the PIN photodiode detector nor the APD detector was suitable for use in the experiment at this time. The signal sizes are too small for the electronic noise in the PIN photodiode amplifier to be smaller than shot noise. Winston Cones cannot be designed to make APDs feasible since they come in small sizes. Larger area APDs were investigated, but were found to intrinsically have a very long recovery time from the scattered light.
Figure 3.42: Power supplies for preamplifier. The ±18V power supplies powering these components are powered by a PowerOne AC/DC converter. This circuit can supply 200 mA continuously, and up to 500 mA for short times. The noise on these power supplies is less than 2 nV/√Hz for all frequencies between 10 Hz and 1 MHz. U1 are 7815 and 7915 voltage regulators. U2 is a LM399H voltage reference, which was chosen for its stability. U3 are low-noise OP77 op-amps, and U4 is a BUF634 power-boosting amplifier. The two -45 V power supplies are batteries.
Figure 3.43: Simulated quantum beats at 500 kHz measured with the APD detector and scattered light equivalent to 1.5 nC of injected charge. The same signal is shown with no scattered light to demonstrate that the detector recovers from the scattered light and all transients in less than 10 µs.

### 3.7.12 Final Choice of Detectors

Ultimately, the sensitivity of the experiment to $\Delta \Phi$ is limited by the signal-to-noise ratio (SNR). All three types of detectors could be used in the experiment, but the one with the best SNR will yield the best sensitivity to $\Delta \Phi$. Given the current understanding of the laser excitation efficiency, it is now estimated, and has been confirmed by measurement that for each laser pulse $N_{act,PD}=3 \times 10^6$ fluorescence photons are available to hit the detector. During the same time interval of $\tau=50 \mu$s, approximately 5 times as many blackbody photons are incident on the detector. The SNR will be calculated for all three detectors in the case where both signal and blackbody photons are considered.

With 2" diameter PMTs, all of the photons hit the photocathode. The 15% q.e. means that there are $N_{act,PMT} = 5 \times 10^5$ photoelectrons/laser pulse from the signal. There are 5 times as many blackbody photons, so in total there are $N_{PMT,total} = 3 \times 10^6$ photoelectrons/laser pulse. The peak current is

$$I_{\text{sig,peak}} = \frac{N_{PMT,total}e}{\tau}$$

and the shot noise on this current is

$$i_{\text{sn,peak}} = \sqrt{2ieI_{\text{sig,peak}}}.$$
In this case, $I_{\text{sig,peak}} = 9 \times 10^{-9}$ A, and $i_{\text{sn,peak}} = 5 \times 10^{-14}$ A. Since PMTs have essentially noise free gain, only shot noise is relevant for the SNR. Since the bandwidth for detection will be the same for all three detectors, bandwidth will not be considered in the calculation of SNR. The SNR for the peak signal is $\frac{I_{\text{sig,peak}}}{i_{\text{sn,peak}}} = 2 \times 10^5$.

APDs have a higher q.e. of $\eta_{qe} = 85\%$ than PMTs, but have smaller area. The Monte Carlo simulation was used to simulate how many photoelectrons could be collected with this smaller area and with optimal Winston Cones. The collection efficiency with the APDs is $\eta_{col} = 25\%$. In total, the APDs are predicted to collect $N_{\text{act,APD}} = N_{\text{tot}} \eta_{qe} \eta_{col} = 7 \times 10^5$ signal photoelectrons/laser pulse could be detected. Additionally, there are 5 times as many blackbody photons, so the total number of expected photoelectrons is $N_{\text{APD,total}} = 4 \times 10^6$ photoelectrons/laser pulse. Therefore, $I_{\text{sig,peak}} = \frac{N_{\text{APD,total}}}{F} = 10^{-8}$ A. In calculating $i_{\text{sn,peak}}$, the amplification noise of $F=2$ must be considered so $i_{\text{sn,peak}} = 9 \times 10^{-14}$ A. The SNR for the peak signal is $\frac{I_{\text{sig,peak}}}{i_{\text{sn,peak}}} = 1 \times 10^5$. Tiling multiple APDs does not improve the SNR. It was found that given the geometry of these large area APDs, even with the use of fiber optics or Winston Cones it is impossible to tile them efficiently such that significantly more light is collected.

With photodiodes it is possible to collect almost all of the available $N_{\text{act,PD}} = 3 \times 10^6$ photoelectrons/laser pulse, but the detector noise also contributes to the SNR. Again, the blackbody size is 5 times the signal size, so the total number of photoelectrons is $N_{\text{PD,total}} = 2 \times 10^7$ photoelectrons/laser pulse. To be able to compare the detector noise and the shot noise on the signal, both the signal and the shot noise on the signal must be calculated at the output of the detector. To simplify the calculations, all SNR will be calculated at the peak of the signal. The current due to the photoelectrons is $I_{\text{sig}} = \frac{N_{\text{e}}}{e}$. For a 50 $\mu$s lifetime, $I_{\text{sig}} = 5 \times 10^{-8}$ A. With a feedback resistor $R_f=600$ k$\Omega$, $V_{\text{sig}} = R_f I_{\text{sig}} = 0.03$ V. Using equation 3.22, the shot noise on this signal is $\delta V_{\text{sn}} = 8 \times 10^{-8} V/\sqrt{\text{Hz}}$. At a realistic beat frequency of $\nu_b = 300$ kHz, the detector noise is $\delta V_{\text{det}} = 220$ nV/\sqrt{\text{Hz}}. Putting all of these elements together yields a SNR of

$$SNR = \frac{V_{\text{sig}}}{\sqrt{\delta V_{\text{sn}}^2 + \delta V_{\text{det}}^2}}.$$  

(3.38)

Then, the peak SNR is also $1 \times 10^5$/laser pulse.

PMTs have the largest SNR even though their q.e. limits the number of photoelectrons...
that are detected. The added noise in the gain stage of the APD and the added noise from the preamplifier in the PIN photodiode decrease their SNR despite the higher counting rates. For this reason, PMTs are used to detect the quantum beats.

3.8 Data Acquisition and Analysis

Throughout this thesis, much care has been taken to acquire and analyze data quickly and accurately. When the experiment is running, the laser fires every 10 ms, and fluorescence data is recorded for the 200 μs following the laser pulse. The data are recorded in 16 bit format, which exceeds the data acquisition card’s resolution. 1000 data points are recorded after each pulse to yield a digitization rate of 5 MHz. Therefore, every 10 ms 2000 bytes of data are recorded, which is equivalent to 17 GB of data/24 hour day. While this data sample size is small compared to those acquired by high energy physics groups, it is much larger than what most table top experiments typically acquire. With standard and readily available computers it is now possible to store this much data, so most of our efforts have gone into developing software to analyze data quickly.

3.9 Data Acquisition Hardware

Data are acquired using LabView with two National Instruments data acquisition (DAQ) cards. One of these cards (NI PCI 6023E) has a 5 MHz bandwidth on two of the input channels, which is sufficiently fast for measuring the quantum beats without any attenuation. The other channels on this DAQ card and the slower card (NI PCI 6111) are used to monitor the thermocouples and the leakage currents. These cards are connected to BNC-2110 boxes for easy compatibility with BNC connectors.

A third National Instruments card is used for controlling instruments so that they can be synchronized with the DAQ process. This card is an 68 channel digital I/O card (SCB-68 with NI PCI 6534) used to send binary information to the the programmable voltage standard for the electric field. Other pins are occasionally used to control other instruments as needed.
3.10 Measurement Sequence

There are several types of data discussed in this thesis. All of these are taken with different configurations of lasers and applied fields, but all have the same basic measurement sequence. The Nd:YAG laser produces a TTL trigger pulse that is timed to coincide with its Q-switch that is coincident with the leading edge of the light pulse from the laser. This TTL pulse is used as the primary clock for the DAQ sequence. The clock pulse is sent to a Berkeley Nucleonics Model 500 Pulse generator that generates additional TTL pulses with variable delays and widths to be used for other instruments. Since the Nd:YAG TTL pulse occurs every 10 ms, delayed pulses from the pulse generator can be used as pre-triggers for any instrument requiring a trigger before the next Nd:YAG TTL pulse. As shown in figure 3.44a, these pulses are used to trigger the oven drive pulses, which are generated by a waveform programmed into an arbitrary waveform generator (Agilent 33120A). As shown in figure 3.44b, the DAQ card is triggered simultaneously with the clock pulse. The PMT is gated off for 1-5 μs before and after the clock. When microwaves are used to populate the a(1) state, the microwave population pulses occur in the 1-5 μs after the clock. All data is acquired in the 200 μs after the clock.

3.11 Data Analysis

Data analysis is not inherently complicated, but was made more complex because we wanted to fit the data as quickly as it was acquired. This on-line fitting allows for quick identification of potential problems with the experiment.

3.11.1 Fitting Function

We fit quantum beat data to a function of the form

\[ I(t) = \alpha S(t) \left[ 1 + ce^{-t/T_b} \cos(2\pi \nu t + \phi) \right] + d + P(t) + \beta L(t). \]  

(3.39)

Here \( P(t) \) is an electronic transient from switching off the PMT gain, and \( L(t) \) is the residual signal from the scattered light [90]. Both of these signals are recorded off-line. \( S(t) \) is a decaying function, approximately exponential with a decay time equal to the lifetime of the a(1) state in the vapor cell. This function also takes into account the geometric factors of the cell, and
Figure 3.44: The timing for the experiment is initiated by a clock pulse coincident with the Q-switch of the Nd:YAG laser. a) The envelope of the current in the heaters. b) The timing for the PMT gate, the microwave excitation, and the DAQ card trigger are all referenced to the laser clock. All triggering operates with TTL pulses, and the edge times of these pulses is not critical for the timing sequence. Pre-triggers are generated by taking the previous clock pulse and introducing a delay with the pulse generator.
therefore is not an exact exponential. These geometric factors account for the fact that molecules are excited by regions of the cell that can be accessed by the laser beam. The molecules travel during the state lifetime, so the ones that decay towards the end of the signal have a different spatial distribution than the ones at the beginning of the signal. $d$ is the dc offset from blackbody radiation and other backgrounds. $S(t)$, $P(t)$, and $L(t)$ can be determined by taking “scrambled” data without quantum beats. The additional parameters include the finite beat contrast $c$, the beat decay lifetime $T_b$, the scaling factor $a$ for amplitude differences between $S(t)$ and $I(t)$, the beat frequency $\nu_b$, and the beat phase $\phi$.

Typically data is taken first by observing quantum beats, then by observing “scrambled” data. Scrambled data are obtained in three different ways. First, when the magnetic shields are not present, a large inhomogeneous magnetic field can be applied to the cell to scramble the polarization of the molecules in the cell. The second case occurs when quantum beats are prepared with a horizontal laser beam (see sections 2.2.1 and 2.2.2). Then, to create “scrambled” data, the laser polarization is changed to be vertical such that only the $|J = 1, m = 0\rangle$ state is populated. Since only a single state is populated with this vertical beam, no beats are observed creating “scrambled” data. The third case occurs when the initial state of the quantum beats is prepared with the microwaves (see section 2.2.3), but the microwave transition is not driven. Then, the molecules remain in the $|J = 1, m = 0\rangle$ state and no quantum beats are observed. In any of these cases, both the quantum beat data and the scrambled data are saved, and before analysis the first $\sim 10 - 12 \mu$s of data is removed because the scattered light from the laser has saturated the PMT. In the analysis program that was used for the data in this thesis, the DC value was determined by fitting the scrambled data to an exponential function with a DC offset. This DC offset was used for $d$ for both $S(t)$ and $I(t)$. In a new data analysis program that will be used to fit EDM data, the average of the end of both $S(t)$ and $I(t)$ are taken and subtracted off before fitting. This analysis program is still under development, and the final determination for how these DC offsets will be assigned is under discussion.

In order to fit the data, initial estimates of the parameters are derived from each data set. The frequency $\nu_b$ is estimated by performing a fast fourier transform. The contrast $c$ is estimated by finding a local maximum and local minimum in the data, finding the difference, and then dividing this difference by the maximum amplitude of the chopped data set. The initial phase,
Figure 3.45: The quantum beats shown here were acquired in 0.14 s of data acquisition and averaged before fitting to 0.09 s of scrambled data. The fitting function is described in equation 3.39.

state lifetime, and beat lifetime are not guessed for each data set. These parameters do not vary between data sets significantly, so they are manually entered into the program after the first data set has been analyzed. The data are fit with a standard Levenberg-Marquardt algorithm from Numerical Recipes in C++ [91]. The results of this fitting routine are shown in figure 3.45.

3.11.2 Optimization of Computation

In order to optimize the speed of this computation, the fitting program was run while being timed on a line-by-line basis. Using this software, several small tricks were employed to speed up the fitting. First, the Levenberg-Marquardt algorithm requires calling derivatives of the fitting functions. These derivatives contain many of the same mathematical terms, so to avoid recalculating these terms they were calculated once and stored and recalled by the program. Secondly, it was found that compiling the fitting program on two different C++ compilers yielded different fitting times. Clearly, the choice of compiler is critical. The Microsoft Visual C++ compiler release version is used. Third, using initial parameters for the fitting function close to the correct values significantly reduced the computation time. These values were determined for each data set as described in section 3.11.1.
Chapter 4

Measurements of PbO Structure

Before the experimental scheme that was discussed in chapter 2 could be implemented, a number of preliminary measurements on PbO needed to be made. These measurements made it possible to determine the fields necessary to prepare the a(1) state for a measurement, and to determine the degree to which the Ω doublet structure can be used to reject magnetic noise.

A previous thesis [64] was devoted to the preliminary spectroscopy and the first measurements of the g-factor difference of the two Ω doublet levels of the a(1) state. Here, a more precise determination of the g-factor difference between these two levels is presented. The uncertainty on the difference in g-factors will ultimately determine the level at which this experiment can reject systematics and magnetic noise as described in sections 2.2, 4.2.

Using the same data as for the measurement of the g-factor difference, a measurement of the Ω doublet splitting was made. This splitting is used in the determination of the microwave frequencies used to populate the two pairs of $n_z = +1$ and $n_z = -1$ levels used to search for $d_e$.

Next, using similar techniques to the ones used to measure the g-factor difference, the Stark shift of the a(1) state was measured. This quantity is necessary to determine the applied electric fields necessary to fully polarize the a(1) state such that the internal electric field of the molecule is maximized. Combined with the g-factor data, this measurement completes the characterization of the a(1) state sufficiently to allow for a measurement of $d_e$. 

134
4.1 Measurement of $g$-factor Difference and the $\Omega$-doublet Splitting

The $\Omega$ doublet only works as a co-magnetometer to the extent that the $g$-factors of the states $n_z = +1$ and $n_z = -1$ are known. The Landé-$g$ factors $g_e$ and $g_f$ respectively of the $|e\rangle$ and $|f\rangle$ levels are not exactly the same, so it is necessary to measure this difference to calculate the $g$-factors of the states $n_z = +1$ and $n_z = -1$.

Previously, the difference in $g$-factors $\delta g = g_e - g_f$ was measured by tuning the $X \rightarrow a$ laser alternately to the R0 or Q1 lines, which by parity selection rules only allows for the excitation of the $|e\rangle$ and $|f\rangle$ states respectively [64]. It takes several minutes to change the laser frequency between R0 and Q1. During this time delay, the magnetic field was changing since magnetic shielding was not used. The changing magnetic field was the dominant source of error in the previous measurement of $\delta g$.

In this thesis, the laser was always tuned to R0 so that the laser populated the $|e\rangle$ state. Then, on alternate blocks of 60 laser shots (0.6 s), an RF electric field was applied to the electrodes in the cell just after the laser pulse to drive the molecules to the $|f\rangle$ state (see figure 4.1). The resulting quantum beats were fit (see section 3.11). By varying the frequency of the RF pulse, the fraction of the population that is transferred from the $|e\rangle$ to the $|f\rangle$ states changes. The beat frequency in the $|e\rangle$ and $|f\rangle$ states is different as a result of the different Landé-$g$ factors in the two states. Hence, the observed beat frequency shifts as a function of the RF frequency.

The beat frequency $\nu_b$ is extracted from the usual quantum beat signal. In this case, however, the oscillating term consists of beats from both the $|e\rangle$ and $|f\rangle$ states. The measured oscillating
term in the data $S_{osc}$ is

$$S_{osc} = A_e(1 + \cos 2g_e \mu_B B t) + A_f(1 + \cos 2g_f \mu_B B t)$$  \hspace{1cm} (4.1)

where $A_e$ and $A_f$ are the respective populations of molecules in the $|e\rangle$ and $|f\rangle$ states, $\mu_B$ is the Bohr magneton, and $B$ is the magnetic field. Since $g_e$ and $g_f$ are close to the same value, they cannot be easily distinguished, and the measured beat frequency is the weighted sum of the populations. The RF pulse has some amplitude and duration that can be characterized by the Rabi frequency $\Omega_R$ where

$$\Omega_R = \frac{|\langle X|\tau|a(1)\rangle|\epsilon_{RF}}{\hbar}. \hspace{1cm} (4.2)$$

If the RF pulse is perfectly adjusted so that $\Omega_R t = \pi$ the population is completely transferred between $X\rightarrow a(1)$ and a "pi pulse" is achieved. When a perfect pi pulse is achieved, $A_e = 0$ and $A_f = 1$. In this limit, the difference in $g$-factors between the $|e\rangle$ and $|f\rangle$ states can be seen. If $A_e = 0$ and $A_f = 1$,

$$\nu_{b,f} = \frac{1}{2\pi} 2g_f \mu_B B. \hspace{1cm} (4.3)$$

Alternately, if no RF field is used, then $A_e = 1$ and $A_f = 0$, so

$$\nu_{b,e} = \frac{1}{2\pi} 2g_e \mu_B B. \hspace{1cm} (4.4)$$

Therefore, if perfect population transfer were possible,

$$\delta g = g_e - g_f = 2\pi \frac{\nu_{b,e} - \nu_{b,f}}{2\mu_B B}. \hspace{1cm} (4.5)$$

Since the exact condition for full population transfer is not known, the RF frequency and amplitudes are varied and a combined function is used to measure the beat frequency difference $\Delta \nu_b$ between having the RF field on and RF field off. This beat frequency difference is

$$\Delta \nu_b = \nu_b(\Omega_R) - \nu_b(\Omega_R = 0). \hspace{1cm} (4.6)$$
Figure 4.2: The change in quantum beat frequency $\Delta \nu_b$ versus the frequency of the RF pulse $\omega$. The maximum change in beat frequency occurs when the RF pulse is matched to the $\Omega$-doublet splitting. This maximum change in beat frequency is related to the difference in $g$-factors between the $|e\rangle$ and $|f\rangle$ states. This data was taken with a pulse length of $t \sim 5 \mu s$ and an electric field amplitude $A = 0.12 \text{ V/cm}$.

The fitting function for $\Delta \nu_b$ is

$$\Delta \nu_b = \frac{\nu_b}{\Omega_R^2 + (\omega - \Delta_\Omega)^2} \sin^2 \left( \pi t \sqrt{\frac{\Omega_R^2}{(\omega - \Delta_\Omega)^2}} \right)$$

(4.7)

where $\nu_b$, $\Omega_R$, and $\Delta_\Omega$ are fit parameters. The time duration of the RF electric field pulse is $t$. From this fit, two separate measurements can be made: the $\Omega$ doublet splitting $\Delta_\Omega$ from the variation versus RF frequency $\omega$, and the difference in $g$-factors from the height $\nu_b$. In principle, the Rabi frequency $\Omega_R$ is also measured, but in practice it is not well constrained by this data.

Using this method, as shown in figure 4.2, the transition between the $|e\rangle$ and $|f\rangle$ states was driven with different pulse durations corresponding to 7, 14, 21, 28, 35, 56, and 112 cycles of the RF transition, with the amplitude of the pulse correspondingly adjusted to theoretically maintain the pi pulse condition (see section 2.2.3). In principle, as long as the pi pulse condition is maintained, the maximum beat frequency shift $\nu_b$ and the $\Omega$ doublet splitting $\Delta_\Omega$ should be insensitive to the number of RF cycles. However, as the number of RF cycles increases, the
pulse time increases. The frequency width of the pulse $\gamma$ is related to the time of the pulse $t$ as

$$\gamma = \frac{1}{2\pi t}.$$  \hspace{1cm} (4.8)

Therefore, the frequency resolution increases for larger $t$; this allows for a more precise measurement of $\Delta_{\Omega}$, and should yield the same result for $\delta \nu_b$. In this case, it was found that all of the fits to the data yield results that are consistent within 2 standard deviations. As a consistency check, by tuning the laser to the Q1 transition, the $|f\rangle$ state was populated and a transition was driven between the $|f\rangle \rightarrow |e\rangle$ states with 56 RF cycles. This data also yielded consistent results within 2 standard deviations. From the maximum change in beat frequencies, the $g$-factor difference of was reported to be $\delta g = g_e - g_f = -31(9) \times 10^{-4}$ in [90]. This result is in good agreement with the results of $\delta g = 25(13) \times 10^{-4}$ obtained from the previous method [90].

The uncertainty in this measurement primarily reflects the uncertainty on the efficiency of the pi pulse transfer. The measured beat frequency reflects the population in both the $|e\rangle$ and $|f\rangle$ sublevels, with less than pure populations washing out the difference in $g$-factors between the two states. The precession frequency is measured to be $\nu_b = A_e \nu_e + A_f \nu_f$, so when the population is in both $|e\rangle$ and $|f\rangle$ the precession frequency is between $\nu_e$ and $\nu_f$. The measured $\delta g$ in equation 4.5 depends on $\nu_e - \nu_f$.

A measure of how well the population was transferred between the $|e\rangle$ and $|f\rangle$ states is whether Rabi flopping can be observed. Rabi flopping occurs when the population is coherently transferred back and forth between two levels as the strength of the driving pulse is increased. The driving pulse can be increased either by increasing the duration of the pulse (ie, the number of RF cycles at a fixed applied voltage) or increasing the voltage at a fixed number of RF cycles. Unfortunately, no data was taken by changing the number of RF cycles at a fixed voltage. There was, however, data taken at a fixed number of RF cycles and varying the applied voltage. In this case, two separate experimental limitations prevented Rabi flopping from being observed. The first limitation was that the RF source could not provide enough power to observe full Rabi flopping. Therefore, the power was just enough to supply $\Omega_r t \sim \pi$ and was not able to achieve $\Omega_r t = 2\pi$. The second limitation is that the pi pulse transfer efficiency is not perfect and so the population difference gets washed out. In this limitation, some of the population is efficiently transferred by a pi pulse where $\Omega_{r,1} t = \pi$, but due to field inhomogeneities in other parts of the...
Figure 4.3: The efficiency of the pi pulse transfer can be quantified by how well the population Rabi flops. Here the population is characterized by the change in beat frequency when the RF field is used to populate the state versus when it is not. Some population transfer along $|e\rangle \rightarrow |f\rangle \rightarrow |e\rangle$ is observed, but not enough to fully quantify the efficiency of the pi pulse transfer. The RF amplitude is quoted in the volts applied to the electrodes as it is not well known how this relates to the actual RF electric field. The electrode spacing is 5 cm, so if the field were homogeneous, the RF amplitude would be in the quoted volts/5 cm.

As the power is increased, the population that originally achieved a pi pulse now begins to transfer the population from the $|f\rangle$ state back to the $|e\rangle$ state since $\Omega_{r,1} t > \pi$. With this increased power, the parts of the cell that are subject to a smaller RF field now begin to achieve a pi pulse so that $\Omega_{r,2} t = \pi$. Since these two populations are not in phase, they wash out the observed Rabi flopping. The attempts to observe Rabi flopping are shown in figure 4.3. The data shown in this figure are not a strong measure of the pi pulse efficiency due to these limitations.

Some measure of how well the pi pulse was achieved can be determined by the apparent lifetime of the quantum beats. If there is significant population in both the $|e\rangle$ and $|f\rangle$ states, then the lifetime of the beats will be shortened due to the interference of the population in both of the states. For example, consider the extreme case where the RF pulse can only transfer 50% of the population from the $|e\rangle$ state to the $|f\rangle$ state. In this case equation 4.1 reduces to

$$S_{osc} = (1 + \cos 2 g_e \mu_B B t) + (1 + \cos 2 g_f \mu_B B t).$$

(4.9)
The interference $\frac{\Delta S_{\text{osc}}}{S_{\text{osc}}}$ between the terms at the beat lifetime $\tau_b$ is

$$\frac{\Delta S_{\text{osc}}}{S_{\text{osc}}} = \frac{\delta g}{g} \nu_b \tau_b. \quad (4.10)$$

This is equivalent to a $\sim9\%$ decrease in the lifetime for a 50\% population transfer, or $\tau_b = 100 \mu s$ a decrease of 10 $\mu s$. In fact, on resonance, no decrease in quantum beat lifetime was found, within the uncertainty of 5 $\mu s$. If the pi pulse were 70\% efficient, the remaining population in the $|e\rangle$ state would reduce the lifetime by 5 $\mu s$, so it is determined that the pi pulse is at least 70\% efficient. This sets the 30\% uncertainty on the measurement of $\delta g$.

An additional uncertainty on the measurement of $\delta g$ is assigned based on a discrepancy in the data. For the data set taken with 56 RF cycles shown in figure 4.2, the data for the RF frequency $\omega \sim \Delta \Omega$ gives a significantly larger value for $\Delta \nu_b$ than was deduced from the fit to equation 4.7. For this data set, the actual data points for $\omega \sim \Delta \Omega$, $\Delta \nu_b$ is measured to be $\sim17\%$ larger than it is determined from the fit to equation 4.7. Clearly, the fitting function is not fully describing the data. To conservatively account for this discrepancy, in [90] the uncertainties we assigned to be 30\%, so that $\delta g = -31(9) \times 10^{-4}$. This assumption may be acceptable, as shown in figure 4.4 where the the maximum change in beat frequency $\delta \nu_b$ is shown as a function of the number of RF cycles applied to the electrodes. These two parameters should not be related, so this data should be uncorrelated. Since this uncertainty is conservative, the overall uncertainty on $\delta g$ remains 30\%.

The $\Omega$-doublet splitting was measured to be 11.214$\pm$0.005 MHz. The uncertainty in this measurement is a combination of statistical and systematic shifts. A known systematic is due to ac Stark shifts. An oscillating electromagnetic field $A \sin \omega t$ can be rewritten as $\frac{iA}{2}(e^{-i\omega t} - e^{i\omega t})$. The non-resonant exponential component $\frac{iA}{2}e^{-i\omega t}$ is typically ignored; however, this component leads to a small frequency shift known as the Bloch-Siegert shift [92]. The Bloch-Siegert shift $\omega_{BS}$ is

$$\omega_{BS} = \frac{A^2 \mu_{e-f}}{\omega_0} \quad (4.11)$$

where $\omega_0$ is the resonant frequency of the transition and $\mu_{e-f}$ is the electric dipole matrix element. The largest amplitude RF pulses were used when these pulses had the shortest duration at 7 cycles. The amplitude of these pulses was $A \sim 0.96$ V/cm, the and the resonant frequency
Figure 4.4: When the RF frequency is resonant, the maximum change in quantum beat frequency $\delta \nu_b$ is observed. The fitted values of $\delta \nu_b$ maximum beat frequencies are graphed as a function of the number of RF cycles. These parameters should be uncorrelated. The 30% uncertainties assigned to this measurement in [90] are shown for comparison in blue and the central value is shown with the dashed line.

is $\omega_0 = 11.214$ MHz. The dipole moment for the a(1) state is $\mu_{a(1)} = 1.64 \text{ MHz/(V/cm)}$ [2], and the transition dipole moment between the $|e\rangle$ and $|f\rangle$ states is $\mu_{e-f} = \frac{\mu_{a(1)} m_J}{J(J+1)} = \frac{\mu_{a(1)}}{2} = 0.82 \text{ MHz/(V/cm)}$. Therefore, the Bloch-Siegert shift contributed a maximum offset of $\omega_{BS} = 6 \times 10^{-2}$ MHz. Given this offset, it was expected that the data taken with the fewest RF cycles would correspond to the smallest measurements of $\Delta \Omega$. In fact, a slight trend towards the opposite behavior was observed as shown in figure 4.5. For the 7 RF cycle data, the largest $\Omega$ doublet splittings were observed. Since this discrepancy could not be explained by the Bloch-Siegert shift, and was not explored by further measurements, a conservative uncertainty of 0.005 MHz was assigned to the measurement of $\Delta \Omega$.

4.2 $g$-factors with Applied Electric Fields

Until now, it has been assumed that the $n_z = +1$ and $n_z = -1$ $\Omega$-doublet states have the same nearly Zeeman splitting as $\delta g$ is small (see section 4.1). In the presence of an applied electric field, however, this splitting increases significantly. The $|m| = 1$ components of the $J = 1$ and $J = 2$ rotational states mix [93]. These states are separated by $\sim 28.2$ GHz, so the mixing is weak, but is significant enough to change the measured frequencies of the upper and lower pair
of EDM states by several kHz. To understand how this occurs, it is easiest to assume that the electric field is sufficiently large to entirely polarize both the $J = 1$ and the $J = 2$ states so that the wavefunction of the molecule has definite $n_z$ and $\Omega$. Then, before mixing with other rotational levels, the states are

$$|\psi\rangle = \frac{1}{\sqrt{2}} \{ |J, m, \Omega = 1\rangle + (-1)^p |J, m, \Omega = -1\rangle \} \quad (4.12)$$

where $p$ denotes the parity of the state. Levels with different $J$ mix, so in this case state $J$ will mix with state $J = J + 1$. To first order in perturbation theory the mixed state will be

$$|\psi'\rangle = |J, m, \Omega\rangle + \frac{(J + 1, m, \Omega) D_z |J, m, \Omega\rangle}{2B_{rot}(J + 1)} \mathcal{E} |J + 1, m, \Omega\rangle \quad (4.13)$$

where $D_z$ is the dipole moment in the molecule-fixed frame, $B_{rot}$ is the rotational constant, and $\mathcal{E}$ is the applied electric field. Note that only states of the same $m$ and the same $\Omega$ mix. Applying the Wigner-Eckart theorem to equation 4.13 yields

$$|\psi'\rangle = |J, m, \Omega\rangle + \frac{(J + 1, m, \Omega D_z |J, \Omega\rangle}{2B_{rot}(J + 1)} \mathcal{E} \sqrt{J + 1 - m \sqrt{J + 1 + m}} \sqrt{J + 1 \sqrt{2J + 1 \sqrt{2J + 3}}} |J + 1, m, \Omega\rangle \quad (4.14)$$
where the reduced matrix element is expressed in the laboratory frame. In order to calculate
the reduced matrix element, it must be transformed to the molecule-fixed frame. There is an
identity that relates the rotating molecular frame to the laboratory frame, which is formally
expressed in [94], but is more useful in the form [95]

\[
\langle \Omega', J'| T^{(k)} | \Omega, J \rangle = \sum_{q'} (-1)^{J'-\Omega'} \sqrt{(2J'+1)(2J+1)} \left( \begin{array}{ccc}
J' & k & J \\
-\Omega' & q' & \Omega 
\end{array} \right) \langle \Omega'| T_{q'}^{(k)} | \Omega \rangle . \tag{4.15}
\]

Here \( T_{q'}^{(k)} \) is a tensor operator, \( \langle \Omega', J'| T^{(k)} | \Omega, J \rangle \) is in the laboratory frame, and \( \langle \Omega'| T_{q'}^{(k)} | \Omega \rangle \) is in
the molecule frame. In this equation, the sum over \( q' \) indicates a sum over 3-j symbols where \( q' \)
is all possible values of the projection of the spherical tensor \( T_{q'}^{(k)} \). Applying this transformation
formula to equation 4.14 yields

\[
|\psi'\rangle = |J, m, \Omega\rangle + \frac{\epsilon}{2B_{\text{rot}}} \sqrt{(J+1)^2 - m^2} \sum_{q'=m}^{1} (-1)^{J+1-q'} \left( \begin{array}{ccc}
J & 1 & J \\
-\Omega & q' & \Omega 
\end{array} \right) \langle \Omega'| D_{q'}^{(k)} | \Omega \rangle |J+1, m, \Omega\rangle . \tag{4.16}
\]

No generality is lost for the a(1) state of PbO if the 3-j symbol is calculated for \( \Omega = 1 \) as the same
result is obtained when \( \Omega = -1 \). When calculating this expression, only the \( q = 0 \) component
survives, and the matrix \( \langle \Omega| D_{0}^{(k)} | \Omega\rangle = 1 \) since the dipole moment and \( \Omega \) are both aligned along
the internuclear axis. Therefore,

\[
|\psi'\rangle = |J, m, \Omega\rangle + \frac{\epsilon}{2B_{\text{rot}}} \sqrt{J+2J+1 - m^2} \left( \begin{array}{ccc}
J & 1 & J \\
-\Omega & 0 & \Omega 
\end{array} \right) |J+1, m, \Omega\rangle . \tag{4.17}
\]

To first order in perturbation theory, the Zeeman energy of the states is also perturbed
according to

\[
E_{\text{mixed}} = \langle \psi'| G_{||} \Omega n_{z} | \psi' \rangle \tag{4.18}
\]

where \( G_{||} \) is the parallel component of the \( g \)-factor along the internuclear axis, \( B \) is the applied
magnetic field, and \( n_{z} \) is the internuclear axis, which is now strongly aligned with the large
externally applied electric field. Keeping only terms that are first order in $E/B_{rot}$, this becomes

$$
E_{\text{mixed}} = \langle J, m, \Omega | B G \parallel \Omega_{nz} | J, m, \Omega \rangle 
+ \frac{\sqrt{J+1} \sqrt{J+1/2} - m^2}{2B_{rot}(J+1)\sqrt{J+1/2} + \frac{\Omega}{J+1/2}} \partial E \langle J + 1, m, \Omega | B G \parallel \Omega_{nz} | J, m, \Omega \rangle.
$$

(4.19)

The first matrix element can be expanded with the Wigner-Eckart theorem as

$$
\langle J, m, \Omega | B G \parallel \Omega_{nz} | J, m, \Omega \rangle = \sum_{q=-1}^{1} (-1)^{J-m} \begin{pmatrix} J & 1 & J \\ -m & q & m \end{pmatrix} \langle J, \Omega || B G \parallel \Omega_{nz} || J, \Omega \rangle.
$$

(4.20)

Only the $q = 0$ component remains, so this matrix element reduces to

$$
\langle J, m, \Omega | B G \parallel \Omega_{nz} | J, m, \Omega \rangle = \frac{m}{\sqrt{J+1/2} + \frac{\Omega}{J+1/2}} \langle J, \Omega || B G \parallel \Omega_{nq} || J, \Omega \rangle.
$$

(4.21)

Applying equation 4.15 yields

$$
\langle J, m, \Omega | B G \parallel \Omega_{nz} | J, m, \Omega \rangle = \frac{m\sqrt{2J+1}}{\sqrt{J+1/2} + \frac{\Omega}{J+1/2}} \sum_{q=-1}^{1} (-1)^{J-q} \begin{pmatrix} J & 1 & J \\ -\Omega & q' & \Omega \end{pmatrix} \langle \Omega || B G \parallel \Omega_{nq'} || \Omega \rangle.
$$

(4.22)

Again, only the $q = 0$ component is non-zero so

$$
\langle J, m, \Omega | B G \parallel \Omega_{nz} | J, m, \Omega \rangle = \frac{m\Omega}{J(J+1)} \langle \Omega || B G \parallel \Omega_{n0} || \Omega \rangle.
$$

(4.23)

Calculating the matrix element gives

$$
\langle J, m, \Omega | B G \parallel \Omega_{nz} | J, m, \Omega \rangle = \frac{m\Omega^2 B G \parallel}{J(J+1)}.
$$

(4.24)

The second matrix element is calculated using the same technique. First, applying the Wigner-Eckart theorem to this matrix element yields

$$
\langle J + 1, m, \Omega | B G \parallel \Omega_{nz} | J, m, \Omega \rangle = (-1)^{J+1-m} \sum_{q=-1}^{1} \begin{pmatrix} J + 1 & 1 & J \\ -m & q & m \end{pmatrix} \langle J + 1, \Omega || B G \parallel \Omega_{nz} || J, \Omega \rangle.
$$

(4.25)
Again, only the \( q = 0 \) component survives so that
\[
\langle J + 1, m, \Omega | B G_\| \Omega n_z | J, m, \Omega \rangle = \frac{\sqrt{(J + 1)^2 - m^2}}{\sqrt{J + 1} \sqrt{2J + 1} + \sqrt{2J + 3}} \langle J + 1, \Omega | B G_\| | J, \Omega \rangle. \tag{4.26}
\]

Applying equation 4.15 gives
\[
\langle J + 1, m, \Omega | B G_\| \Omega n_z | J, m, \Omega \rangle = \frac{\sqrt{(J + 1)^2 - m^2}}{\sqrt{J + 1}} \sum_{q' = -1}^{1} (-1)^{J + 1 - \Omega} \begin{pmatrix} J + 1 & 1 & J \\ -\Omega & q' & \Omega \end{pmatrix} \langle \Omega | B G_\| | \Omega_n q' | \Omega \rangle. \tag{4.27}
\]
and this expression can be reduced by calculating the 3-j symbol. Again, this expression is the same for \( \Omega = +1 \) and \( \Omega = -1 \) and only the \( q = 0 \) components survive so that this expression reduces to
\[
\langle J + 1, m, \Omega | B G_\| \Omega n_z | J, m, \Omega \rangle = \frac{\sqrt{J + 2} \sqrt{(J + 1)^2 - m^2}}{(J + 1) \sqrt{2J + 3} \sqrt{2J + 1}} \langle \Omega | B G_\| | \Omega_n q' | \Omega \rangle. \tag{4.28}
\]
Calculating the matrix element yields
\[
\langle J + 1, m, \Omega | B G_\| \Omega n_z | J, m, \Omega \rangle = \frac{B G_\| \Omega \sqrt{J + 2} \sqrt{(J + 1)^2 - m^2}}{(J + 1) \sqrt{2J + 3} \sqrt{2J + 1}}. \tag{4.29}
\]

Putting these matrix elements together, \( E_{\text{mixed}} \) is
\[
E_{\text{mixed}} = \frac{\Omega^2 B G_\|}{J(J + 1)} \left\{ 1 + \frac{dE J^2(J + 2)(J + 1)^2 - m^2}{Br \Omega(J + 1)(2J + 1)(2J + 3)} \right\}. \tag{4.30}
\]
and the effective \( g \)-factor \( g_{\text{eff}} \) is
\[
g_{\text{eff}} = \left( 1 + \frac{dE J^2(J + 2)(J + 1)^2 - m^2}{Br \Omega(J + 1)(2J + 1)(2J + 3)} \right) \frac{G_\|}{J(J + 1)}. \tag{4.31}
\]

For a \( J = 1 \) state, the Stark induced change in \( g \)-factor depends on the product of \( m \) and \( \Omega \). Since \( m \Omega = +1 \) for \( n_z = +1 \) and \( m \Omega = -1 \) for \( n_z = -1 \), this effect leads to a difference in measured \( g \)-factor between the \( n_z = +1 \) and \( n_z = -1 \) states.

This effective \( g \)-factor can be observed by applying an electric field which is on the order of the size necessary to polarize the molecule, and then using a horizontally polarized excitation laser to simultaneously populate all four \( m \) sublevels of the \( a(1) \) \( J = 1 \) state. In the Fourier
transform of the resulting quantum beats (see section 2.3), two peaks are seen. Currently this
effect is under study by Paul Hamilton.

4.3 DC Stark Shifts

A static electric field applied to the a(1) state mixes the \(|e\rangle\) and \(|f\rangle\) sublevels with the same
value of \(m_J\). The diagonal matrix element of the electric dipole operator \(\hat{\mu}\) is

\[
\mu_{J,m_J} = \langle e, J, m_J | \hat{\mu} | f, J, m_J \rangle. \tag{4.32}
\]

This can be written in terms of states of definite parity by writing it in terms of \(\Omega = \pm 1\) since

\[
|e\rangle = \frac{1}{\sqrt{2}}(|\Omega = +1\rangle + |\Omega = -1\rangle) \quad \text{and} \quad |f\rangle = \frac{1}{\sqrt{2}}(|\Omega = +1\rangle - |\Omega = -1\rangle). \tag{4.33}
\]

Applying the Wigner-Eckart theorem yields

\[
\mu_{J,m_J} = \frac{1}{2} \left\{ \langle \Omega = +1, J, m_J | \hat{\mu} | \Omega = +1, J \rangle + \langle \Omega = -1, J, m_J | \hat{\mu} | \Omega = -1, J \rangle \right\}
\]

Equation 4.15 can be used to to rewrite this equation. Since \(\hat{\mu}\) is a vector operator, it cannot
connect states of \(\Delta \Omega = 2\), and only terms where \(\Omega = \Omega'\) survive. Keeping only the non zero
terms, this expression reduces to

\[
\mu_{J,m_J} = \frac{1}{2} \sum_q \sum_{q'} (-1)^{J-m_J} \begin{pmatrix} J & 1 & J \\ -m_J & q & m_J \end{pmatrix} \left\{ (-1)^J \begin{pmatrix} J & 1 & J \\ -1 & q' & 1 \end{pmatrix} \langle \Omega = +1 | \hat{\mu} | \Omega = +1 \rangle - \langle \Omega = -1 | \hat{\mu} | \Omega = -1 \rangle \right\} (2J + 1). \tag{4.35}
\]
The matrix element \( \langle \Omega = +1 | \hat{\mu} | \Omega = +1 \rangle = +\hat{\mu} \) since the electric dipole operator is aligned along the internuclear axis, as is \( \Omega \). Calculating the 3-j symbols yields

\[
\mu_{Jm_J} = \frac{m_J \mu_a}{J(J+1)}.
\] (4.36)

The electric field causes a Stark shift with two states of mixed parity separated in energy by

\[
\Delta E = \sqrt{\Delta \Omega^2 + (\mu_{Jm_J} E)^2}
\] (4.37)

where \( \Delta \Omega \) is the \( \Omega \)-doublet splitting [90]. The molecule-fixed dipole moment in the \( a(1) \) state is \( \mu_a = 1.64(3) \) MHz/(V/cm) [2].

The DC Stark shift of the \( a(1) \) state was measured using a method very similar to the measurement of the \( \Omega \)-doublet splitting. The laser was tuned to the R0 transition so that the \( |e, m = \pm 1 \rangle \) states were populated with no applied electric field. Then, the electric field was adiabatically ramped up over 2.5 \( \mu s \); next, an RF \( \pi \) pulse was applied to transfer the population to the \( |f, m = \pm 1 \rangle \) states. The electric field was then adiabatically ramped down over 2.5 \( \mu s \). Finally, the beat frequency was determined. When the RF frequency was far from resonance, the population was not transferred to the \( |f \rangle \) state, and so the beat frequency was characterized by \( g_e \). If the RF frequency was close to resonance, the beat frequency was characterized by \( g_f \). By scanning the RF frequency and measuring the beat frequency, the RF resonance condition can be determined exactly as was determined for the measurement of the \( \Omega \)-doublet splitting.

This method was limited by two factors. First, at the time that this measurement was taken, the vapor cell was not the final version shown in chapter 3. Instead, the vapor cell was a smaller cube with a side length of 2.5". The electrodes formed by gold foils placed on the top and bottom of the cell created inhomogeneous electric fields. This measurement was very sensitive to the position of the excitation \( X \rightarrow a(1) \) laser, which excited molecules in different regions of the cell and therefore sampled different electric fields. Also, at slightly higher electric fields, the Stark shift was large enough to match the Zeeman shift. This brought the \( m_J = -1 \) and \( m_J = 0 \) levels into degeneracy (see figure 4.7). Majorana spin flips depopulated the \( m_J = -1 \) levels decreasing the beat contrast. At higher electric fields, the beat lifetime contrast again increased although not to the level obtained at with no applied electric field, as shown in figure 4.7.
Figure 4.6: Measurement of the Stark shift as a function of applied electric field.

Figure 4.7: At small applied electric fields (~3 V/cm) the $m = -1$ level is degenerate with the $m = 0$ level. This degeneracy allows for Majorana spin flip transitions to occur between these levels and depletes the population in the $m = -1$ level.

4.8. In this cell, the electrode spacing was much larger than the electrodes, causing significant inhomogeneities in all directions causing the field direction to tip. These tipped fields scrambled the beats and reduced the contrast. In the more homogeneous electric fields created in cells used at later times, the beat contrast routinely reaches the same ~10 – 12% at high electric fields that is observed with no applied electric field.

The Stark shifts measured in figure 4.6 are consistent with the expectations based on $\mu_a=1.64(3)$ MHz/(V/cm) [2]. Furthermore, large electric fields of 50 V/cm have been applied to the cell with no evidence of breakdown. At these large electric fields, the $|e\rangle$ and $|f\rangle$ levels should be sufficiently polarized to achieve a polarization of $P = \langle J_e \cdot \vec{n} \rangle \approx 1$, which corresponds to essentially a complete mixing of the $\Omega$-doublet states, forming eigenstates of definite $\Omega$. 

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
4.4 Summary of Measurements of a(1) State

Along with the preliminary measurements necessary for the microwave transitions [62], the measurements presented here constitute all of the preliminary measurements of PbO that are necessary for the design and construction of an experiment to measure $d_e$. These measurements allow for an understanding of the different precession frequencies for the $n_z = \pm 1$ levels of the $\Omega$ doublet, which allows for cancellation of magnetic field noise. A precise measurement of the $\Omega$ doublet splitting and knowledge of the Stark shifts are necessary for the determination of the microwave frequencies that are used.
Chapter 5

Measurements of Signal Magnitudes

The measurements of the $g$-factor difference, the $\Omega$ doublet splitting, and the Stark shift were all made using a preliminary version of the apparatus that was intended for use to measure $d_e$. Originally, it was anticipated that a number of straightforward improvements to the apparatus would increase the signal size detected with this apparatus. In the process of investigating various detectors and optics, it became clear that the signal sizes could not be made as large as originally anticipated. The measured efficiency of the laser excitation to the a(1) state is not as great as calculated. The smaller signal size makes PIN photodiodes infeasible as detectors, further reducing the signal size since the PMTs that are used have a lower quantum efficiency (q.e.) and must be better protected from scattered light from the pulsed laser.

Currently, a relatively straightforward detection scheme is being used for the measurement of $d_e$. This detection scheme involves detecting spontaneous fluorescence from three rotational branches: $|a(1), v' = 5, J = 1\rangle \rightarrow |X, v = 0, J = 0, 1, 2\rangle$ with PMTs. Interference filters are used to reject some of the blackbody radiation from the ovens, and only one straight sided cone is used to compress the area of the collected fluorescence.

5.1 Calculated Signal Sizes

The anticipated signal size can be calculated by separately calculating the number of available molecules in the correct state $N_a$ and detection efficiency $\eta_d$. $N_a$ depends on the number of molecules $N_X$ in the $X(v = 1, J = 0)$ state which the laser excites and on the efficiency with which they are excited $\eta_e$. $N_X$ depends on the temperature of PbO, which determines the
density of PbO and the number of molecules that start in the correct ro-vibrational state. \( N_a \) depends both on the temperature and on the laser power and bandwidth.

In the experiment as currently configured, the molecules will be excited along the \(|X, v = 1, J = 0\rangle \rightarrow |a(1), v' = 5, J' = 1\rangle\) transition. The fraction that start in the \( v = 1 \) state is

\[
\frac{N_{X,v=1}}{N_{X,\text{tot}}} = \frac{e^{-E(v=1)/kT}}{\sum_{v'=0}^{\infty} e^{-E(v)/kT}}
\]

where \( E(v) = \omega_e(v + \frac{1}{2}) \). For the X state of PbO \( \omega_e = 720.8 \text{ cm}^{-1} \) \([96]\). At a typical operating temperature of 710°C, \( N_v \approx 0.23 \). Similarly, the fraction that start in the correct rotational state is

\[
\frac{N_{X,J=0}}{N_{X,\text{tot}}} = \frac{e^{-BJ(J+1)/kT}}{\sum_{J=0}^{\infty} (2J+1) e^{-BJ(J+1)/kT}}
\]

where \( B \) is the rotational constant. In the \( X(v = 1) \) state \( B = 304411 \text{ cm}^{-1} \) \([96]\), so \( \frac{N_{X,J=0}}{N_{X,\text{tot}}} = 4.5 \times 10^{-4} \). Therefore the fraction of molecules starting in the correct rovibrational state is only \( \frac{N_{X,v=1,J=0}}{N_{X,\text{tot}}} = 1.0 \times 10^{-4} \).

To know how many molecules are in the cell, it is necessary to know the vapor pressure since \( N_X \propto P(\text{PbO}) \) where \( P(\text{PbO}) \) is the pressure of PbO. However, there is a wide discrepancy in the reported vapor pressures for PbO. For most of this thesis work, the vapor pressure listed in the CRC \([52]\) was used. Recently, however, a number of measurements, in our experiment have indicated that this vapor pressure is significantly too high. There are four independent measurements of \( P(\text{PbO}) \) in our vapor cell. The first, and most compelling, is a preliminary measurement of the absorption of microwaves in the X state between the \( J = 0 \) and \( J = 1 \) rotational states. The absorption measured here depends on the difference in populations of these levels by the Boltzman distribution and \( P(\text{PbO}) \). This measurement indicates a partial pressure of PbO that is a factor of \(~30\) times lower than the pressure extrapolated from the CRC. At this time, this measurement has not been repeated and is only a preliminary result.

The second measurement is a measurement of the microwave absorption of the \( a(1) \) state. In this measurement, the excitation efficiency \( \eta_a \) of the laser populating the \( a(1) \) state is unknown and is coupled into the measured population of PbO. Assuming that this laser is as efficient as calculated, the measurement of the microwave absorption in the \( a(1) \) state agrees with a \( P(\text{PbO}) \) that is \(~30\) times lower than reported in the CRC. Given that the laser efficiency is
not well known, the assumptions that relate this measurement to \( P(\text{PbO}) \) are not necessarily correct. Third, a measurement of the spectra of the \( B(1) \) state was performed by measuring the absorption of a diode laser beam [97]. Since this measurement did not use the same excitation laser and did not use any of the same detection optics, it should be an independent measurement of \( P(\text{PbO}) \). Again, a calculation of the expected signal sizes in this measurement using the partial pressure listed in the CRC yielded a result that was ~35 times higher than the measured signal. This is again consistent with \( \frac{\rho}{\rho_{\text{CRC}}} \approx \frac{1}{35} \) where \( \rho \) is the density of PbO and \( \rho_{\text{CRC}} \) is the reported density of PbO in the CRC. There are significant uncertainties in the calculation that relates this measurement to the partial pressure of PbO, again making this only a rough indication of \( P(\text{PbO}) \). Fourth, the fluorescence detection described in the rest of this section agrees with this conclusion about a lower vapor pressure. As with the previous measurements, several assumptions are used in this calculation and many of these assumptions may not be well founded. In summary, there is some indication that we have measured that the partial pressure of PbO in our vapor cell is lower than expected, but currently it cannot be confirmed.

Subsequent literature searches have yielded measurements of the vapor pressure of PbO ranging from ~2-100 times lower than the vapor pressure in the CRC [98, 99, 100, 101]. All of these papers report that some \( \text{Pb}_2 \text{O}_2 \) and \( \text{Pb}_4 \text{O}_4 \) is created when PbO is vaporized. These papers differ on the relative partial pressure of \( \text{Pb}_2 \text{O}_2 \) and \( \text{Pb}_4 \text{O}_4 \) as compared to PbO, but these pressures may be significant. Unfortunately, we have no way of measuring the partial pressure of \( \text{Pb}_2 \text{O}_2 \) or \( \text{Pb}_4 \text{O}_4 \) in our vapor cell. If, however, it is assumed that \( P(\text{PbO}) \) is much larger than these other species and that the partial pressure is much smaller than reported in the CRC, the measured collisional cross sections in the cell become larger than typical molecular cross sections. We have measured the collisional cross sections of PbO based on the CRC partial pressure of PbO assuming that there are no other species present [90]. This collisional cross section is consistent with cross sections from most other molecules. If the partial pressure of PbO is much lower, than the measured collisional cross section would be much higher making it inconsistent with most other molecules. Therefore, the presence of other species in the cell may help to reduce the collisional cross section, so that it is more consistent with the cross sections measured for other molecules. Unfortunately, given that there is no way of confirming the presence of these other species, this hypothesis cannot be confirmed.
Given the discrepancy in the literature and the lack of definite knowledge about processes in our system that would influence the partial pressure of PbO, it is impossible to calculate a precisely known density of PbO in our system. For this calculation, the partial pressure of PbO listed in the CRC will be used with the understanding that this pressure overestimates \( N_X \) by a significant factor. The reason for this choice is that many measurements in this laboratory have been made under this assumption and it will be useful to compare the measurements to this calculation made with this overestimated partial pressure.

At a typical operating temperature of \( T = 710^\circ C \), the CRC-reported vapor pressure of PbO is \( P = 9.6 \times 10^{-3} \) Torr [52]. The volume of the cell is \( V \approx 100 \) cm\(^3\), so according to the ideal gas law \( PV = N_{X,tot} k_B T \), there are in total \( N_{X,tot} \approx 9 \times 10^{15} \) molecules in the cell. Since \( \frac{N_{X^{1/2},J=0}}{N_{X,tot}} = 1.0 \times 10^{-4}, N_{X,\nu=1,J=0} \approx 9 \times 10^{11} \) molecules.

To determine \( \eta_e \), we use the fact that the cross section for excitation is

\[
\sigma_{exc} = \frac{1}{2\pi} \lambda^2 \frac{2J' + 1}{2J + 1} \frac{\gamma_{partial}}{\gamma_{Doppler}}
\]

where \( \lambda \) is the wavelength of the transition, \( \gamma_{partial} \) is the decay rate of \( a(1) \) into a specific rovibrational level of \( X \), and \( \gamma_{Doppler} \) is the Doppler width [102]. Collisional broadening is insignificant compared to Doppler broadening and will be ignored. The branching fraction is

\[
B \approx \frac{|a(1),\nu'=5,J'=1)\rightarrow X,\nu'=5,J'=0)}{|a(1),\nu=5,J=1)\rightarrow all} \approx 0.2, \text{ so } \gamma_{partial} \approx \frac{B}{2\pi \tau_a} \approx 600 \text{ Hz where } \tau_a \text{ is the lifetime of the } a(1) \text{ state.}
\]

The Doppler width [55] is

\[
\gamma_{Doppler} = \frac{\omega_0}{2\pi c} \sqrt{\frac{2k_B T}{M}}
\]

where \( \omega_0 \) is the angular frequency of the transition, \( k_B \) is the Boltzmann constant, \( T \) is the temperature, and \( M \) is the mass. In order to convert this Doppler width to the full width-half maximum (FWHM) of the absorption profile, \( \gamma_{Doppler} \) needs to be multiplied by an additional factor of \( 2\sqrt{\ln 2} \). Therefore, the FWHM Doppler width for a transition at \( \lambda = 570 \) nm and \( T = 710^\circ C \) is \( \gamma_{Doppler} = 2\pi \times 800 \) MHz. This implies that \( \sigma_{exc} \approx 2 \times 10^{-16} \) cm\(^2\). The dye laser that drives the X–a(1) transition typically has a power of 1 W and is expanded to a diameter of 3.8 cm. This power is equivalent to \( \Phi = 1.2 \times 10^{15} \) photons/cm\(^2\) per laser pulse. The excitation

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
efficiency is

$$\eta_e = \sigma_{exc} \Phi$$

and therefore the calculated excitation efficiency is $$\eta_e \approx 0.2$$. The total number of excited molecules $$N_a$$ is

$$N_a = \eta_e N_{X,v=1,j=0} \approx 0.2 \times 9 \times 10^{11} \approx 2 \times 10^{11}$$ molecules per pulse of the dye laser.

The detection efficiency is more difficult to calculate, but has been explicitly verified as discussed in chapter 3. Monte-Carlo simulations have been used to determine that $$\eta_M = 4\%$$ of the fluorescence in the cell enters each lightpipe. The lightpipes are calculated to be 100% internally reflecting. Their transmission has been measured to be consistent with a 4\% reflection at each glass-to-air interface indicating that there is no absorption in the lightpipe. Since these reflections off the surface of the lightpipe are accounted for separately, the lightpipe is considered 100\% transmitting. Once the light enters the lightpipe, the angular distribution is compressed as a result of the higher index of refraction. Then, all of the light entering them is at angles less than the critical angle of $$\sin^{-1} \frac{n_0}{n_{eff}} = 43^\circ$$ where $$n_0 = 1$$ is the index of refraction of air and $$n_{eff} = 1.46$$ is the index of refraction of quartz [52]. These angles are referenced to the normal to the flat input face of the lightpipe. The fluorescence then passes through an IR blocking colored glass filter, which is $$\eta_{IR} = 90\%$$ transmitting, a sapphire cooling window, and an interference (IF) filter. Several IF filter configurations have been tested during this thesis. As a benchmark, the smallest signal sizes have been observed using no coupling grease between the filters so that there are reflections between all optical interfaces. With 13 air to glass or glass to air interfaces, the reflections reduce the transmission so that $$\eta_{ref} = 58\%$$. The IF filters used with the smallest signal sizes are two standard IF filters with a maximum transmission of 50\% and a 10 nm bandpass centered at 550 nm. Taking into account the angular distribution of photons incident upon these filters (see section 3.7.4), the total transmission of the two IF filters is $$\eta_{IF} = 7\%$$. The 9850 Electron Tubes PMT that was used for many of the quantum beat measurements in this thesis was specified to have a q.e. of $$\eta_{qe} = 9\%$$. We assume this value here although there can be large variations between tubes in the actual q.e. [103]. An additional factor of 2 is lost in the detection since only the decays to the $$|X, v = 0\rangle$$ state are observed; the Franck-Condon factor (see section 6.1.3) from the $$|a(1), v' = 5\rangle$$ state to the $$|X, v = 0\rangle$$ state is $$\sim 0.5$$. Therefore, the efficiency due to the branching ratio is

154
The total detection efficiency is \( \eta_d = \eta_R \eta_r \eta_{ref} \eta_{IF} \eta_{qe} \eta_{BR} \sim 7 \times 10^{-5} \). Therefore, the expected count rate is \( N_{calc,PMT} = \eta_d N_a = 1 \times 10^7 \) photoelectrons/laser pulse. Based on our recently updated knowledge of the vapor pressure, we expect that the density of PbO has been overestimated in this calculation by a factor of \( C = 30 \), so that the updated expected count rate is \( N_{exp} = \frac{N_{calc}}{C} = 4 \times 10^5 \) per pulse. Actual count rates with this configuration were to be \( N_{meas,PMT} = 5 \times 10^4 \) photoelectrons/laser pulse. The data were taken when a natural abundance of PbO was used, further decreasing the expected signal by a factor of 2 to \( N_{exp, nat} \sim 2 \times 10^5 \) per pulse. Therefore, the measured count rates are a factor of 4 smaller than expected. Given that several factors in this calculation have significant uncertainties, this is not surprising. Thus, the measured count rates were almost consistent with the correction that the density is lower than is reported in the CRC by a factor of \( C \approx 30 \) [52]. The numbers reported in this section are lower \( N_{act,PMT} \) used throughout the rest of this thesis as a result of several improvements made to the apparatus. These improvements include using one Omega IF filter and the higher q.e. Hamamatsu PMT.

The discrepancy between the calculated and measured signal sizes is currently believed to be entirely a result of the difference in densities of PbO. If so, the excitation efficiency \( \eta_e \) calculated here is apparently correct. Microwave absorption measurements of the depletion of the population in the \( X(v = 1, J = 0) \) state confirm that \( \eta_e \) is consistent with the calculation here. Since the Monte Carlo model of the detection system also has been tested in some detail (see section 3.7.4), it seems likely that the detection efficiency calculated here is correct.

Some of the data taken in this thesis has used excitation along the \( |X, v = 0, J = 0 \rangle \rightarrow |a(1), v' = 5, J = 1 \rangle \) transition and detection along the \( |a(1), v' = 5, J = 1 \rangle \rightarrow |X, v = 1, J = 0 \rangle \) transition. In principle, this excitation scheme should yield larger counting rates since there are three times more molecules in the \( |X, v = 0, J = 0 \rangle \) state than the \( |X, v = 1, J = 0 \rangle \) state. Unfortunately, in order to reduce the scattered light to a level that is sufficiently low for the PMT to recover, it was necessary to add two pieces of OG-570 colored glass to the detection optics when exciting along this transition. This reduced the scattered light significantly, but also reduced the signals so that they were comparable to signals observed when exciting the \( |X, v = 1, J = 0 \rangle \rightarrow |a(1), v' = 5, J = 1 \rangle \) transition and detecting along the \( |a(1), v' = 5, J = 1 \rangle \rightarrow |X, v = 0, J = 0 \rangle \) transition.
5.2 Attempted Improvements to SNR

This section discusses all improvements that were tried during the course of this thesis. As a benchmark, all improvements will be scaled to the observed $N_0 = 5 \times 10^4$ photoelectrons/laser pulse [90] when none of the following improvements had been made.

The first attempted improvement was to increase the laser power. Before it was discovered that the partial pressure of PbO in the cell may be overestimated, it was thought that the calculations of the excitation efficiency indicated that the transition was far from saturation. Therefore, it was thought that increasing the laser power would increase the signal size linearly. When the benchmark data was taken, the dye laser routinely produced 1 W, which was far from the rated 3 W. As a result of better alignment, it was possible to increase the laser power to 3 W. Additionally, by retroreflecting the laser beam through the vapor cell, the effective power was expected to increase by an additional factor of ~1.5. (The optics in the vacuum chamber are not anti-reflection coated, decreasing the available laser power upon retroreflection.) It was found, however, that while the signal size increases with laser power the contrast of the quantum beats decreases. Since many background signals also increase in size with increasing laser power, it is not a good figure of merit to simply look at the signal size. Instead a better figure of merit is the SNR

$$\frac{\text{Signal}}{\text{Noise}} = \frac{cN}{\sqrt{N + b}}$$

(5.6)

where $c$ is the contrast, $N$ is the signal size, and $b$ is the background. In figure 5.1 the product $cN$ is shown as a function of laser power.

Now that it is hypothesized that the partial pressure of PbO is significantly lower than originally expected, it is likely that the laser excites a reasonable fraction of the molecules in the cell (on the order of 20-30%). Therefore, increasing the laser power will not necessarily increase the signal sizes linearly. It is difficult to use a laser to drive transitions with more than 50\% efficiency as the laser stimulates both excitation and deexcitation processes. In this regime, it is possible that the laser is causing power broadening, which is an indication that the transition is saturated. When power broadening occurs, the signal size increases as the square root of the laser power with an electric field $E$ [104]. In this regime, even though the transition amplitude
Figure 5.1: a) The product of signal size and contrast does not increase with increasing laser power. As indicated in equation 5.6, this is proportional to the SNR for the experiment. b) The contrast and signal size as a function of power.
is saturated, the transition linewidth $\gamma_S$ grows as

$$\gamma_S = \gamma \sqrt{1 + S}$$  \hspace{1cm} (5.7)

where $\gamma$ is the unBroadened linewidth. $S$ is the saturation parameter defined as

$$S = \left( \frac{e^{- (X/\gamma)^{1/2} \tilde{\epsilon}}}{\hbar \gamma} \right)^2.$$ \hspace{1cm} (5.8)

Since the experiment is probably in this regime, instead of using the maximum laser power, the optimal laser power to yield the highest SNR will be used.

The second attempted improvement was also straightforward. Much of the early data was taken with a natural isotopic abundance of PbO. By switching to $^{208}$PbO the signal sizes are increased by a factor of 2, as the natural isotopic abundance is 52.4%. This factor of 2 increase in signal size was observed. It was expected that the isotopically pure PbO would also increase the contrast. In addition to the lasing wavelength, the dye laser emits a broad background from amplified spontaneous emission (ASE). Some of the ASE is resonant with other rotational lines, which have the same exponentially decaying time signature as the signal thereby reducing the contrast. By reducing the number of molecules that can be excited by the ASE, it was expected that the contrast would improve by a factor of 2.5. This expected factor of 2.5 was determined by estimating that we should have approximately 50% contrast as calculated in section 2.3.1.

Then, it was assumed that the observed 10% contrast was a result of two factors. First, the R6 transition is close to the R0 transition, and it was expected that R6 contributes 25% of the background fluorescence that reduces the contrast. The rest of the background fluorescence was attributed to rotational lines that were excited by the broad ASE background from the laser. It was thought that by increasing the number of molecules that are resonant with the laser, the signal would increase by a factor of two, while the backgrounds would remain the same. Apparently, this assumption is wrong, since switching to $^{208}$PbO actually improved the contrast by only a factor of 1.3.

The third improvement was to replace the narrow (10 nm bandpass) standard IF filters with broader IF filters. Two different types of broad IF filters were tested. The first was a standard IF filter centered at 572 nm with a 40 nm bandpass. This filter was designed to allowed for the
detection of decays to both the $X(v = 0)$ and $X(v = 1)$ state. Since the Franck-Condon factors from the $a(1)(v = 5)$ state to both of these states are approximately equal, detecting both decays would have increased the signal sizes by an additional factor of 2. This filter could not be used since the laser is at one of the decay wavelengths. Scattered light from the laser saturated all detectors. The second broad IF filter was a combination of two Omega 3rd Millennium filters. These filters have a bandpass of 544 nm-560 nm, and each have 90% peak transmission (see section 3.7.1). These filters were expected to increase the signal sizes by a factor of 9 as a result of their higher transmission and larger bandpass. They were observed to increase the signal by a factor of 3.3. The difference between the predicted and measured signal increase is currently not understood and is under study. Currently, the best filter configuration is to use one narrow 10 nm bandpass IF filter with one Omega filter. The high transmission of the Omega filter increases the signal size, yet it still blocks scattered light from the laser. The narrow filter is more efficient at blocking blackbody radiation and further blocks the scattered light from the laser.

Blackbody radiation was also expected to increase with broader IF filters, but was observed to increase much more than expected. Blackbody radiation was expected to increase similarly to the signal size, but was found to increase much more. This expectation was based on scaling the transmission of blackbody through a similar Omega filter. The test filter was smaller than the filters used for the final detection, so the transmission through the test filters needed to be scaled to the appropriate area of transmission. With the test filter, the rest of the area was masked off to block all light transmission. The observed increase in blackbody radiation in switching to the Omega filters was 5 times, whereas the signal only increased 3.3 times. Again, this effect is under study. It is currently hypothesized that the angular distribution of photons in the detection system is different than has been simulated in the Monte Carlo simulation described in section 3.7.4. The difference may be a result of the way that the lightpipe is mounted inside of the vacuum chamber.

Blackbody radiation is a significant source of noise, and many ideas have been explored to reduce it. Currently none have been implemented as a result of the extreme difficulty and expense. Absorbing filters, as discussed in section 3.7.2 have been tested, but do not seem feasible. Another idea to reduce the blackbody while preserving the signal size has been to build
a reverse Winston Cone, which would expand the fluorescence to a large area, but decrease the angular spread. Then, a narrow bandpass IF filter could efficiently block the blackbody radiation while transmitting the signal. Unfortunately, IF filters cannot be made in large sizes and still maintain the uniform central wavelength and narrow bandpass necessary to decrease the blackbody while maintaining the signal size. It would be possible, but expensive, to create an array of smaller tiled IF filters with the necessary central wavelength and narrow bandpass.

Coupled to the choice of interference filter and detector was the choice of the excitation wavelength for the laser. The Boltzmann distribution of population in the ground state is such that there is a factor of 3 more population in the \( X(v = 0) \) state than the \( X(v = 1) \) state, so it would seem natural to excite to the \( a(1)(v = 5) \) state from the \( X(v = 0) \) state. The detector, however, must be able to recover from the additional scattered light that is transmitted through the IF filter. IF filters cannot block wavelengths to the red as efficiently. At various times in this thesis, excitation has occurred from the \( X(v = 0) \) state resulting in the expected gain of \(~3\) in signal size. This gain was observed with the use of color glass filters, which decreased the gain by a factor of 3, for no net gain in signal. Overall, this factor of 3 improvement from the Boltzmann factor cannot be used in the actual experiment since the scattered light has saturated all detectors.

Finally, the last expected gain in signal size was from the implementation of photodiodes as detectors. Photodiodes have a quantum efficiency that is \(~9\) times larger at 550 nm than Electron Tubes 9850 PMTs and therefore increase the signal size. Unfortunately, as discussed in section 3.7.12 the signal size is not sufficiently high to use photodiodes. Since these much higher q.e. devices cannot be used, modestly higher q.e. PMTs were used. The new R329EGP Hamamatsu PMTs have a q.e. of \( \eta_{eq} = 15\% \), which is a factor of 1.6 higher than the \( \eta_{eq} = 9\% \) than the specification on the 9850 Electron Tubes PMTs.

In summary, the expected and actual improvements to the SNR are listed in table 5.1.

In the current experimental configuration, the laser excitation occurs along the \( |X, v = 1, J = 0\rangle \to |a(1), v' = 5, J = 1\rangle \) transition. Then, there is microwave excitation to the superposition state used to measure \( \delta_e \), which further reduces the number of molecules in the correct state as compared to direct excitation with a horizontally polarized laser. The detection is currently performed using a lightpipe, an IR blocking glass, a sapphire window, and two IF filter.
Table 5.1: Anticipated and actual improvements to the signal and backgrounds. The broad interference filter was never successfully used with a detector since it did not block any scattered light from the laser. This scattered light saturated all detectors and did not allow for a measurement of the signals or backgrounds. Since the actual q.e. of the old PMT (Electron Tubes 9850) is not known and can only be measured in conjunction with the gain, the improvement due to the higher q.e. of the PIN photodiodes and new PMTs (Hamamatsu R329EGP) is not known.

<table>
<thead>
<tr>
<th>Improvement</th>
<th>Currently Used?</th>
<th>Anticipated Signal Increase</th>
<th>Anticipated Contrast Increase</th>
<th>Anticipated Background Increase</th>
<th>Actual Signal Increase</th>
<th>Actual Contrast Increase</th>
<th>Actual Background Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increase Laser Power</td>
<td>N</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>0.6</td>
<td>1</td>
</tr>
<tr>
<td>Retroreflect Laser</td>
<td>N</td>
<td>1.5</td>
<td>1</td>
<td>1</td>
<td>1.5</td>
<td>0.4</td>
<td>1</td>
</tr>
<tr>
<td>2 detectors</td>
<td>N</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Pure $^{208}$PbO</td>
<td>Y</td>
<td>2</td>
<td>2.5</td>
<td>1</td>
<td>2</td>
<td>1.3</td>
<td>1</td>
</tr>
<tr>
<td>Broad IF filter</td>
<td>N</td>
<td>20</td>
<td>1</td>
<td>20</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>Omega IF filter</td>
<td>N</td>
<td>9</td>
<td>1</td>
<td>9</td>
<td>3.3</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>excite from $X(v = 0)$</td>
<td>N</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Photodiode q.e.</td>
<td>N</td>
<td>9</td>
<td>1</td>
<td>9</td>
<td>?</td>
<td>1</td>
<td>?</td>
</tr>
<tr>
<td>R329EGP PMT q.e.</td>
<td>Y</td>
<td>1.6</td>
<td>1</td>
<td>1.6</td>
<td>?</td>
<td>1</td>
<td>?</td>
</tr>
</tbody>
</table>
One IF filter is a standard 50% transmitting 10 nm bandpass IF filter centered at 550 nm, and this filter blocks out much of the blackbody radiation. The second filter is an Omega filter with high transmission (~90%) and cut on wavelengths of 544 nm and 560 nm. The light is collected with Hamamatsu R329EGP PMTs with 15% q.e. so that the total signal size is $N_{\text{meas}} = 2 \times 10^5$ photoelectrons/laser shot. The total blackbody size is $2 \times 10^{10}$ photoelectrons/second, or $1 \times 10^6$ photoelectrons over the 50 μs lifetime of the state in the cell. These count rates were observed when there was a problem with the optical coupling grease that was not coupling the optics correctly. Once discovered, this problem was easy to fix. Unfortunately, at this time the signal and background count rates have not been measured again. It is expected that they will increase now that this problem has been fixed. Given the improvements that have been made, the signal was expected to increase by a factor of 6.4, and was observed to increase by a factor of 4.8. The background was expected to increase by a factor of 3.2 and was observed to increase by a factor of 20. This increase in background is attributed to changes made in the oven that increased the blackbody radiation. When the sum of signal and background is shot noise limited, but the noise from the background is dominant, the frequency resolution of the experiment per laser pulse [64] is

$$\delta \nu = \frac{4}{2 \pi c \tau \sqrt{N}} \sqrt{\frac{B}{S_0}}$$  (5.9)

where $N$ is the total number of detected photons, $B$ is the background size, and $S_0$ is the signal size at $t = 0$. With the microwave excitation, the expected contrast is 3%. For these signal and blackbody sizes, then, the predicted frequency resolution per laser shot per detector is $\delta \nu = 1800$ Hz. Therefore the predicted frequency resolution is 130 Hz/√Hz for two detectors. With this frequency resolution it will take 20.5 days just to reach the current limit for $d_e$ assuming 100% measurement duty cycle and two detectors. Possible improvements to the SNR will be discussed in chapter 7. Realistically, assuming that data is collected for 10 days with a 30% duty cycle with 2 detectors, the ultimate sensitivity of this experiment to $d_e$ is $5 \times 10^{-26}$ e-cm. This is 30 times worse than the current limit.
5.3 Optimal Conditions

In order to get the best SNR, the frequency uncertainty was measured as a function of temperature and laser power. For both parameters there are competing factors that determine the optimal conditions. When the temperature is increased the density of PbO increases, which will increase the SNR as a function of temperature. A fit to the data listed in the CRC [52] has the pressure of PbO as a function of temperature $T$ as

$$P = e^{21.875}e^{-20604/T}$$

where $P$ is in Torr and $T$ is in Kelvin. However, there are two factors that decrease the SNR as a function of $T$. First, blackbody radiation also increases as a function of $T$. Second, the lifetime of the state and the quantum beats is decreased as the density of PbO and other species increases, due to the increased frequency of collisions. Therefore, it is unsurprising that there is an optimal temperature. The measured frequency uncertainty is shown as function of temperature in figure 5.2. These measurements were taken without the microwave excitation, without an electric field and by using a horizontally polarized laser. This increases the contrast of the beats and therefore increases the frequency resolution.

The measured frequency uncertainty is also a function of the laser power. The signal sizes
increase with increasing laser power, but the contrast decreases with increasing laser power as a result of possible power broadening. As a result of this phenomenon, the measured frequency uncertainty as a function of laser power does not continue to decrease at increasing laser power as expected (see figure 5.3). Again, these measurements were taken without an electric field and without microwave excitation. The laser was horizontally polarized.

Even at the optimal conditions, the measured frequency uncertainties shown in figures 5.2 and 5.3 are a factor of 2 larger than predicted by equation 5.9. Currently, this is believed to be a problem with the data analysis program. The data analysis program has been demonstrated to fit simulated data with uncertainties that are \(~2\) times larger than the noise added to this simulated data. Correcting this problem in the analysis program is currently a high priority.

### 5.4 Conclusions on Signal Sizes

In summary, there are several interrelated problems that contribute to limiting the signal size that can be measured in this experiment. Since the partial pressure of PbO is probably significantly smaller than was originally anticipated, the signals are not large enough to allow for shot noise limited use of photodiodes. Blackbody radiation is a significant source of backgrounds, and therefore IF filters with wider bandpass regions cannot be used. This wider bandpass region
would increase the measured signal size. Nevertheless, several improvements have been made. Isotopically pure PbO has increased the signal sizes by a factor of 2. PMTs with higher q.e. have increased the signal sizes. Finally, adding a second detection channel will double the signal size.
Chapter 6

Development Towards Future Generations

The current configuration of the experiment does not have a sufficiently high SNR to detect \( d_e \) at the desired level. Therefore, the improvement of the first generation experiment and the design of a second generation experiment has been a high priority.

During this thesis, a reexcitation fluorescence detection scheme was explored. First, preliminary spectroscopic measurements for this detection scheme were conducted. Then, the detection scheme was tested first in the absence of an applied electric field, then with an applied electric field. Ultimately, the detection scheme failed with an applied electric field, so this scheme was not implemented.

Two proposals are being discussed for a second generation experiment. The first uses microwave absorption in a resonant microwave cavity to detect absorption along a rotational transition. The second uses a cold molecular beam of ThO, which has a long lived \( 3\Delta \) state. Both of these proposals would dramatically improve the SNR over the first generation and thereby improve the sensitivity to \( d_e \).

6.1 Laser Reexcitation to the \( C' \) state

6.1.1 Introduction

After it was found that the scattered light from the 548 nm X→a excitation laser saturated photodiodes, avalanche photodiodes, and photomultiplier tubes, new detection schemes were
C' v=5, J=1

a (l) to C' laser
1114 nm

C' to X fluorescence
367 to 475 nm

a(1) v=5, J=1

X v=0, J=0

Figure 6.1: Energy level structure for the C' detection scheme and the measurement of the rotational structure. First the a(1) state is populated using the methods described in section 2.2. Then, a laser at ~1114 nm drives the a(1) → C' transition, which spontaneously decays to the X state. The fluorescence from the C' → X transition is measured. This method is also used to measure the rotational structure of the C' state. Here the case of the excitation of the C'(v = 5, J = 1) state is shown, but a variety of rotational states were excited by varying the frequencies of both the X to a(1) laser and the a(1) to C' laser. Fluorescence from spontaneous decays from the C'(v = 5) state to the X(v = 0, 1, 2, 3, 4, 5) states is collected.

explored. One of these detection schemes was a laser reexcitation to the C' electronic state. In this scheme, the a(1) state is populated as discussed in chapter 2. Then, instead of detecting the quantum beats via spontaneous fluorescence, an infrared laser at 1114 nm drives the spin-sensitive transition to the C'(v = 5) state. Spontaneous fluorescence from the C' → X state is detected and collected with a PMT as shown in figure 6.1. There are three main advantages to this detection scheme. First, nearly 100% contrast is expected since the a(1) state is driven to a single level. Second, the detection wavelength is far from both excitation wavelengths, allowing for efficient blocking of scattered laser light. Third, the detection wavelength is far to the blue reducing the blackbody radiation in the bandpass of the filters.

There are two complications to this measurement scheme. First, the C'(v = 6) state has a lifetime of 3.4(2) µs [42] and the C'(v = 5) state has been observed to have a similar lifetime. This lifetime acts as a low-pass filter on the quantum beats. With slower quantum beats, however, this is not a significant problem with this measurement scheme. A more serious complication is the Ω-doublet structure of the C' state, which allows for phase cancellation of the quantum beats. Ultimately as discussed below this phase cancellation makes it impractical to measure
quantum beats using the $C'$ state.

### 6.1.2 Determination of $C'$ Energy Level Structure

Prior to this work, the rotational spectroscopy of the $C'$ state had been measured in the $v = 6$ band [42], but there was no current data available for the $v = 5$ state that was sufficiently accurate. The first necessary measurement was to determine the energy level structure of the $C'(v = 5)$ state to find the $J=1$ energy level. The previous best known spectroscopic constants for the $C'$ state [105] are listed in table 6.3 along with the constants that were measured here.

First, the $X(v = 0) \rightarrow a(v' = 5)$ state was populated using a Nd:YAG pumped pulsed dye laser tuned to 548.2 nm. This laser was tuned to a variety of rotational lines. In order to drive the $a(v' = 5) \rightarrow C'(v'' = 5)$ transition, a high-intensity laser at 1114 nm was needed. This wavelength is not accessible with standard dye lasers, so a Raman converter was used. The output of a Nd:YAG pumped Sirah dye-laser using Pyrromethene 597 dye (Cobra, Sirah Laser- und Plasmatechnik GmbH) at 578 nm was directed through a $H_2$ Raman cell (Light Age, LAI 101 PAL-RC). This cell is essentially a 0.5 m long stainless steel tube that circulates hydrogen gas at a pressure of 400 psi. Two windows on the ends of the cell are slightly curved to focus incoming collimated light in the center of the cell and recollimate at the output. The Raman cell coherently produces frequency sidebands offset from the input frequency by the vibrational splitting of the $H_2$ ground state, which is 4155.25 cm$^{-1}$. The second sideband produced the 1114 nm light that was necessary for the reexcitation. Unfortunately, this dye laser and Raman cell were in another laboratory, so the 1114 nm light was directed into a 55 m long, high power multi-mode fiber (Thorlabs TEQS Hard Polymer Clad Fiber FT600EMT). A lens was used to recollimate the light exiting the laser. At times, both lasers were polarized using beam splitting cubes. The frequencies of both lasers was measured using a Coherent Wavemaster wavemeter. This wavemeter has an accuracy of 0.005 nm (0.04 cm$^{-1}$) and a resolution of 0.001 nm (0.008 cm$^{-1}$) [106]. The uncertainty on the measurement of the frequency of the $X \rightarrow C'$ laser was determined by the linewidth of the Sirah laser, which is 5 GHz at 570 nm, or 0.09 cm$^{-1}$ at 8970 cm$^{-1}$.

The timing and triggering between the two Nd:YAG lasers that pumped the two dye lasers was set up to allow for a relative delay between the pulses (see the timing diagram shown in figure
Q-switch pulse from YAG laser pumping the 548.2 nm dye laser at 100 Hz

Delayed pulse from BNC 500 pulse generator at a variable delay time at 100 Hz

Output of divides-by-10 trigger at 10 Hz which triggers the YAG laser pumping the Sirah dye laser at 10 Hz

Figure 6.2: Timing diagram for the relative delays between the two excitation lasers.

Figure 6.3: Transmission of the color glass used as a filter for the detection of the $C'(v = 5)$ to $X$ decays. The black lines indicate the wavelengths of the $C'(v = 5) \rightarrow X(v)$ decays.

6.2). The Q-switch sync of the Nd:YAG laser that pumped the 548.2 nm dye laser formed the clock for the experiment at 100 Hz. This Q-switch sync signal triggered a Berkeley Nucleonics Corporation 500 pulse generator, which allowed for a variable and programmable delay. This delayed pulse was sent to a divides-by-10 switch, whose 10 Hz output triggered the Nd:YAG laser that pumped the 578 nm laser. The variable delay between the two lasers allowed for the transition between the $a(1)$ and $C'$ state to occur at variable times.

The $C'(v = 5)$ state decays to a broad range of the vibrational states of the $X$ state. Since these decays are far in wavelength from the excitation lasers, broad filters can be used in front of the detection PMT so that many of these vibrational decays can be observed. The $|C', v'' = 5\rangle \rightarrow |X, v''' = 0 - 9\rangle$ decays occur between 376nm and 457nm. A piece of color glass (Oriel 59820) was used as the filter, whose transmission is shown in figure 6.3. The transmission of this filter allows for the detection of the decays to the $X \: v = 0$ to $v = 9$ states. The fluorescence is integrated.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
starting 1.5 $\mu$s after the $a(1) \rightarrow C'$ laser fires and continues for 8 $\mu$s. Since a colored glass filter was used, refluorescence from the filter caused a significant scattered light pulse directly after the laser pulse. The integration starting 1.5 $\mu$s after this laser pulse removed the effects of this scattered light pulse.

Using this setup, the $X \rightarrow a(1)$ laser was tuned to several lines in the R and Q branches as shown in table 6.1. The $a(1) \rightarrow C'$ laser was scanned to look for the P, Q, and R branch lines. The Q branch in the $a(1) \rightarrow C'$ transition was difficult to observe and was only seen in a few cases. The intensity of the Q branch decreases rapidly with increasing $J$, since the Hönl-London factor for a $\Delta \Omega = 0$ transition is

$$
\Omega^2_J = \frac{(2J'' + 1)\Omega'^2}{J''(J'' + 1)} = \frac{(2J' + 1)\Omega'^2}{J'(J' + 1)},
$$

where the single primed letters refer to the upper state and the double primed letters refer to the lower state [44].

In addition to the large lines listed in table 6.1, a number of smaller and originally unexpected lines were observed. These lines were found to be caused by the fact that the $X \rightarrow a(1)$ laser was broader than expected. These lines were all determined to originate from $X \rightarrow a(1)$ transitions that were not intended to be excited. They are listed and assigned in table 6.2. These additional lines can be quite intense. For example, when exciting on the transition $X \rightarrow a(1)$ along the R0 line and $a(1) \rightarrow C'$ along the Q1 and R1 lines, the unexpected lines excited are from the $X \rightarrow a(1)$ R6 line, which then is excited along the $a(1) \rightarrow C'$ R7 and P7 lines. The primary lines are roughly two times larger than the unexpected lines. In some ways, it is unsurprising that the unexpected lines have such a high intensity. In the $X \rightarrow a(1)$ transition, the R6 line (unexpected) is $\sim$4 times more intense than the R0 line (primary), and in the $a(1) \rightarrow C'$ transition the R7 and P7 lines (unexpected) are expected to be $\sim$5 times larger than the Q1 and R1 lines (primary).

Combining the data from tables 6.1 and 6.2 allows for the determination of a new value for the spectroscopic constants of the $C'(v = 5)$ state. A fit to this data yields $G(v = 5) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + ... = 2625.1(1)$ cm$^{-1}$ and $B(v = 5) = .2395(3)$ cm$^{-1}$. The data and the fit are shown in figure 6.4. A comparison of these results and the previous spectroscopic constants for the $C'$ state are shown in table 6.3.
Table 6.1: Measured and predicted frequencies for transitions between the a(1)→C' states. The predicted frequencies are calculated from constants for the X and a(1) states from [96] and constants for the C' state from [105]. The uncertainty on all measured frequencies is 0.09 cm⁻¹. Two of the rotational lines in the a(1)→C' transition (R10, and R11) were measured to be at lower than expected frequencies. The reason for this shift is unknown.

<table>
<thead>
<tr>
<th>X→a(1) line</th>
<th>X→a(1) freq. (cm⁻¹)</th>
<th>a(1)→C' predicted freq. (cm⁻¹)</th>
<th>a(1)→C' measured freq. (cm⁻¹)</th>
<th>a(1)→C' line</th>
</tr>
</thead>
<tbody>
<tr>
<td>R0</td>
<td>18240.34</td>
<td>8973.32</td>
<td>8973.48</td>
<td>Q1</td>
</tr>
<tr>
<td>R0</td>
<td>18240.34</td>
<td>8974.31</td>
<td>8974.47</td>
<td>R1</td>
</tr>
<tr>
<td>R6</td>
<td>18240.18</td>
<td>8970.53</td>
<td>8970.36</td>
<td>P7</td>
</tr>
<tr>
<td>R6</td>
<td>18240.18</td>
<td>8977.97</td>
<td>8977.51</td>
<td>R7</td>
</tr>
<tr>
<td>R9</td>
<td>18238.18</td>
<td>8969.73</td>
<td>8969.05</td>
<td>P10</td>
</tr>
<tr>
<td>R9</td>
<td>18238.18</td>
<td>8974.69</td>
<td>8975.94</td>
<td>Q10</td>
</tr>
<tr>
<td>R9</td>
<td>18238.18</td>
<td>8980.15</td>
<td>8979.16</td>
<td>R10</td>
</tr>
<tr>
<td>R10</td>
<td>18237.25</td>
<td>8969.51</td>
<td>8970.80</td>
<td>P11</td>
</tr>
<tr>
<td>R10</td>
<td>18237.25</td>
<td>8980.92</td>
<td>8976.95</td>
<td>R11</td>
</tr>
<tr>
<td>R11</td>
<td>18236.14</td>
<td>8969.32</td>
<td>8968.33</td>
<td>P12</td>
</tr>
<tr>
<td>R11</td>
<td>18236.14</td>
<td>8981.72</td>
<td>8980.23</td>
<td>R12</td>
</tr>
<tr>
<td>R12</td>
<td>18234.90</td>
<td>8969.16</td>
<td>8967.93</td>
<td>P13</td>
</tr>
<tr>
<td>R12</td>
<td>18234.90</td>
<td>8982.55</td>
<td>8980.77</td>
<td>R13</td>
</tr>
<tr>
<td>Q1</td>
<td>18239.73</td>
<td>8973.32</td>
<td>8973.51</td>
<td>Q1</td>
</tr>
<tr>
<td>Q1</td>
<td>18239.73</td>
<td>8974.31</td>
<td>8974.46</td>
<td>R1</td>
</tr>
<tr>
<td>Q7</td>
<td>18235.90</td>
<td>8970.53</td>
<td>8970.33</td>
<td>P7</td>
</tr>
<tr>
<td>Q7</td>
<td>18235.90</td>
<td>8977.97</td>
<td>8977.49</td>
<td>R7</td>
</tr>
</tbody>
</table>
Table 6.2: The X→a(1) laser was broader than expected and some additional rotational lines in a(1) were accidentally excited. These accidentally excited a(1) states were also excited to C' and observed. The transition frequencies to the C' states shown in this table are from these additionally excited rotational lines. Again, the predicted frequencies are calculated using constants for the X and a(1) states from [96] and the constants for the C' states from [105]. All frequencies are in cm\(^{-1}\) and the uncertainty on all measured frequencies is 0.09 cm\(^{-1}\).
Figure 6.4: The energy of the measured rotational levels in the $C'(v = 5)$ state along with a fit to these levels to determine the spectroscopic constants of the vibrational level. The fitting function is $E = T_e + G + B J (J + 1)$ where $T_e = 24947$ cm$^{-1}$ [105].

<table>
<thead>
<tr>
<th>Constant</th>
<th>Literature Value</th>
<th>Measured Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_e$</td>
<td>24947</td>
<td></td>
</tr>
<tr>
<td>$\omega_r$</td>
<td>494</td>
<td></td>
</tr>
<tr>
<td>$\omega_r \omega_e$</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>$G(v = 5)$</td>
<td>2626.25</td>
<td>2625.1(1)</td>
</tr>
<tr>
<td>$B_e$</td>
<td>0.248</td>
<td>0.2395(3)</td>
</tr>
<tr>
<td>$D_e$</td>
<td>0.25$\times 10^{-6}$</td>
<td>0.2395(3)</td>
</tr>
<tr>
<td>$F(v = 5)$</td>
<td>0.248</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.3: The literature values for the spectroscopic constants of the $C'(v = 5)$ state compared to the values measured here. The literature values are from [105] and all units are cm$^{-1}$. 

173
6.1.3 Franck-Condon Factors

In order to determine the best filter for the detection scheme for the \( C' \rightarrow X \) decays, it was necessary to measure the Franck-Condon factors between these states. The transition probability between vibrational levels in two different electronic states is determined by the Franck-Condon factor between these two states. The Franck-Condon factor is a measure of the overlap of the vibrational wavefunctions of the two states. The idea behind Franck-Condon factors is that when an electron makes the transition between electronic states, the transition happens in a time that is small compared to the characteristic vibration time of the nuclei. Therefore, during the transition, the nuclei remain fixed at the same relative distance. Thus, the overlap of the vibrational wavefunctions in the two states enters the transition probability.

To the extent that the interatomic potential is known and the Born-Oppenheimer approximation holds sufficiently that the wavefunction of the state can be separated into independent electronic, vibrational, and rotational wavefunctions, Franck-Condon factors can be calculated \[44, 45\]. The Franck-Condon factor is

\[
FC = \left| \int \Psi^*_v(R)\Psi'_v(R)dR \right|^2
\]

(6.2)

where \( v \) denotes the vibrational state, and \( R \) is the radius. The vibrational potential can be approximated by a harmonic oscillator potential. To simplify the equations, define \( x = R - R_e \) where \( R_e \) is the equilibrium radius. These equilibrium radii can be calculated from the rotational constants \( B \) such that

\[
R_e = \frac{h}{\pi\sqrt{8} B c m_\mu}
\]

(6.3)

where \( m_\mu \) is the reduced mass. The rotational constants for \( X \) are taken from \[96\] and the rotational constant for \( C'(v = 5) \) is the one calculated in section 6.1.2.

In a simple harmonic oscillator approximation the wavefunction is

\[
\Psi_v = N_v e^{-\frac{1}{2}ax^2}H_v(\sqrt{a}x)
\]

(6.4)

where \( N_v \) is a normalization factor, \( a = 4\pi^2m_\mu\nu_{osc}/h \) and \( H_v \) are Hermite polynomials. This calculation was done in CGS units. The vibrational frequency \( \nu_{osc} \) is the classical vibrational
frequency and can be found using

\[ G(v) = \frac{\nu_{0ac}}{c}(v + \frac{1}{2}). \] (6.5)

Here \( G(v) \) is defined as the usual the spectroscopic constant as

\[ G(v) = \omega_e(v + \frac{1}{2}) - \omega_e \xi_e(v + \frac{1}{2})^2. \] (6.6)

Using this formalism, the Franck-Condon factors were calculated for the \( C'(v = 5) \rightarrow X(v=\text{all}) \) transitions. The results of this calculation are shown in table 6.4.

Measuring the Franck Condon factors is a much more accurate way of determining them. The decay rates from the corresponding vibrational levels were measured allowing for the calculation of the Franck-Condon factors. These decay rates were measured by piping the fluorescence from the cell through a fiber bundle and into a monochromator. A blue-sensitive photomultiplier tube (Burle 8850) with photon-counting electronics was used to measure the output of the monochromator. This PMT was used because it has a larger q.e. at blue wavelengths. The same colored glass filter as was used before (Oriel 59820) was placed between the phototube and monochromator to block scattered light from the lasers. The signal was normalized to account for the filter transmission. The monochromator was tuned to the expected wavelengths of the decay and the number of detected photons was counted.

The measured decay rates \( \Gamma_v \) are closely related to the Franck Condon factors by

\[ \text{F.C.} \propto \frac{\Gamma_v}{\omega^3} \] (6.7)

where \( \omega \) is the frequency of the \( C' \rightarrow X \) decays. The total measured Franck-Condon factors are normalized so that they add to 1.

The measured Franck-Condon factors are shown in table 6.4 along with the calculated Franck-Condon factors. The calculated Franck-Condon factors do not match well with the measured factors. It is believed that these calculated Franck-Condon factors are so inaccurate because the potential of the \( C'(v = 5) \) state is not very well known and is significantly anharmonic. The approximation of using a simple harmonic oscillator potential for these wavefunctions is probably
Table 6.4: Measured and calculated Franck-Condon factors. The discrepancy is attributed to the anharmonicity of the wavefunctions, which is not taken into account in this calculation. The Franck-Condon factors may be large to higher vibrational states, but could not be measured to these states because the color glass filter did not transmit at these wavelengths.

6.1.4 Ω-Doublet Splitting in the C' state

As an Ω = 1 state, the C' state has an Ω-doublet structure. The Ω-doublet splitting of this state was not directly observed, but limits on its size can be placed by the spectroscopy done here. To first order the Ω-doublet splitting $\Delta \nu_{|e\rangle-|f\rangle}$ increases with rotational number $J$ as

$$\Delta \nu_{|e\rangle-|f\rangle} = (B_v^e - B_v^f)J(J + 1) = qJ(J + 1)$$

where $q = B_v^e - B_v^f$ is the Ω doublet splitting parameter [44]. With the experimental setup available, it was not possible to directly drive a transition between the $|e\rangle$ and $|f\rangle$ states of the C' state. However, the $|e\rangle$ and $|f\rangle$ states of the C' state were individually populated by driving different R and Q branches in the X→a(1) transition. In the X→a(1) transition parity selection rules determine that R branch transitions are $|e\rangle \rightarrow |e\rangle$ (see section 2.2.1) and that Q branch transitions are $|e\rangle \rightarrow |f\rangle$. Therefore, the X→a(1) transition on an R branch transition populates
The $|e\rangle$ and $|f\rangle$ states of the $C'$ state were separately populated via different levels of the $a(1)$ state. From the measured frequencies of the $a(1)\rightarrow C'$ transitions, the $\Omega$-doublet splitting parameter in the $C'$ state $q < 2 \times 10^{-3} \text{ cm}^{-1}$. In this table, all energies are in cm$^{-1}$.

Table 6.5. The $|e\rangle$ and $|f\rangle$ states of the $C'$ state were separately populated via different levels of the $a(1)$ state. From the measured frequencies of the $a(1)\rightarrow C'$ transitions, the $\Omega$-doublet splitting parameter in the $C'$ state $q < 2 \times 10^{-3} \text{ cm}^{-1}$. In this table, all energies are in cm$^{-1}$.

<table>
<thead>
<tr>
<th>$X\rightarrow a(1)$</th>
<th>$a(1)$ state</th>
<th>$a(1)\rightarrow C'$ freq.</th>
<th>$a(1)\rightarrow C'$</th>
<th>$C'$ state</th>
<th>$B^a_{C} - B^b_{C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R0</td>
<td>$a(1), J = 1, e)$</td>
<td>8973.48(9)</td>
<td>Q1</td>
<td>$C', J = 1, f)$</td>
<td>$(2\pm6) \times 10^{-2}$</td>
</tr>
<tr>
<td>Q1</td>
<td>$a(1), J = 1, f)$</td>
<td>8973.51(9)</td>
<td>Q1</td>
<td>$C', J = 1, e)$</td>
<td></td>
</tr>
<tr>
<td>R0</td>
<td>$a(1), J = 1, e)$</td>
<td>8974.47(9)</td>
<td>R1</td>
<td>$C', J = 2, e)$</td>
<td>$(2\pm20) \times 10^{-3}$</td>
</tr>
<tr>
<td>Q1</td>
<td>$a(1), J = 1, f)$</td>
<td>8974.46(9)</td>
<td>R1</td>
<td>$C', J = 2, f)$</td>
<td>$(7\pm20) \times 10^{-4}$</td>
</tr>
<tr>
<td>R5</td>
<td>$a(1), J = 7, e)$</td>
<td>8970.36(9)</td>
<td>P7</td>
<td>$C', J = 7, e)$</td>
<td></td>
</tr>
<tr>
<td>Q7</td>
<td>$a(1), J = 7, f)$</td>
<td>8970.33(9)</td>
<td>P7</td>
<td>$C', J = 7, f)$</td>
<td>$(4\pm20) \times 10^{-4}$</td>
</tr>
<tr>
<td>R6</td>
<td>$a(1), J = 7, e)$</td>
<td>8977.51(9)</td>
<td>R7</td>
<td>$C', J = 8, e)$</td>
<td></td>
</tr>
<tr>
<td>Q7</td>
<td>$a(1), J = 7, f)$</td>
<td>8977.49(9)</td>
<td>R7</td>
<td>$C', J = 8, f)$</td>
<td></td>
</tr>
</tbody>
</table>

The $\Omega$ doublet splitting in the $C'$ state was measured by first tuning the $X\rightarrow a(1)$ laser to an R branch and a Q branch transition that had the same value of $J$ in the $a(1)$ state. For example, two such lines are R0 and Q1. R0 excited $|a(1), J = 1, e)$ and Q1 excited $|a(1), J = 1, f)$. Then, the $a(1)\rightarrow C'$ laser was kept at the same transition. The frequency where this transition has a maximum amplitude was measured.

The $\Omega$ doubling in the $a(1)$ state is sufficiently small that it cannot be resolved by the laser and can be ignored. The $a(1)\rightarrow C'$ laser will drive transitions between $|a(1), e) \rightarrow |C', f)$ and $|a(1), f) \rightarrow |C', e)$. If the $\Omega$ doubling in the $C'$ state is sufficiently large, there will be a measurable frequency difference between the $|a(1), e) \rightarrow |C', e)$ transition and the $|a(1), f) \rightarrow |C', f)$ transition. For example, the $a(1)\rightarrow C'$ laser was kept tuned to the R1 line so that when the $X\rightarrow a(1)$ laser was tuned to R0 the transition was $|a(1), J = 1, e) \rightarrow |C', J = 2, e)$. When the $X\rightarrow a(1)$ laser was tuned to Q1 the transition was $|a(1), J = 1, f) \rightarrow |C', J = 2, f)$. The frequencies for all corresponding R and Q branch transitions are shown in table 6.5. From these data, $q < 2 \times 10^{-3} \text{ cm}^{-1}$ in the $C'$ state. For comparison, in the $a(1)$ state $q = 1.869 \times 10^{-4} \text{ cm}^{-1}$ and in the B state $q = 1.168 \times 10^{-4} \text{ cm}^{-1}$.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
6.1.5 \(a(1) \rightarrow C'\) Excitation Cross Sections

From the intensities of the collected fluorescence, the resonant absorption cross section of the \(C'\) state as excited from the \(a(1)\) state can be determined. The apparent measured absorption cross section \(\sigma_{\text{abs,app}}\) is given by

\[
\sigma_{\text{abs,app}} = \frac{W_{\text{eg}}}{\Phi},
\]

where \(W_{\text{eg}}\) is the excitation rate of molecules due to stimulated absorption and \(\Phi\) is the flux of photons [55]. Under our conditions, the linewidth of the laser \(\gamma_{\text{laser}}\) is larger than the Doppler width \(\gamma_D\) [104] and so some of the laser photons are off resonant and cannot be absorbed.

The absorption cross section \(\sigma_{\text{abs,D}}\) that would be experienced by a narrowband laser (with \(\gamma_{\text{laser}} \ll \gamma_D\)) is

\[
\sigma_{\text{abs,D}} = \sigma_{\gamma,D} \frac{\gamma_{\text{laser}}}{\gamma_D}.
\]

Under our conditions, \(\gamma_D = 425 \text{ MHz}\) and \(\gamma_{\text{laser}} = 5 \text{ GHz}\). Finally, for molecules at rest (i.e. in the absence of Doppler broadening) probed by a narrowband resonant laser, the resonant absorption cross section \(\sigma_{\text{abs}}\) is

\[
\sigma_{\text{abs}} = \sigma_{\text{abs,D}} \frac{\gamma_D}{\gamma_{\text{natural}}},
\]

where \(\gamma_{\text{natural}} = \frac{1}{2\pi\tau}\) is the natural width in linear frequency units and \(\tau = 3.4 \mu\text{s}\) is the lifetime [55]. This experimentally determined value of \(\sigma_{\text{abs}}\) can be compared to the theoretical value

\[
\sigma_{\text{abs}}^{(t)} = \frac{\lambda}{2\pi} \frac{2J' + 1}{2J + 1} \frac{\gamma_p}{\gamma_{\text{tot}}},
\]

Here, \(\gamma_p\) is the partial width due to the spontaneous decay rate and \(\gamma_{\text{tot}}\) is the total width of the transition. The factor \(J'\) is the angular momentum of the final state and \(J\) is the angular momentum of the initial state.

The determination of \(\sigma_{\text{abs}}\) from our \(a(1) \rightarrow C'\) excitation data depends on a number of imprecisely determined factors such as the PMT q.e., and the calculation will have significant uncertainties dominated by such factors. We calculate \(\sigma_{\text{abs}}\) based on data from a single rotational line, the Q1 transition of \(a(1) \rightarrow C'\).

In order to make an estimate of \(\sigma_{\text{abs}}\), it is necessary to know how many molecules were in the \(a(1)\) state that could have been driven to the \(C'\) state. To calibrate the population in the
a(1) state, the fluorescence along the $|a(1), v' = 5, J = 1\rangle \rightarrow |X, v = 1, J = 0\rangle$ transition was observed. This monitored fluorescence was well understood as it occurred with the same optics that were studied in section 3.7. This calibration fluorescence indicated that $N_a \sim 6 \times 10^8$ molecules were in the a(1) state in the cell.

The optics for the $C' \rightarrow X$ fluorescence detection were less well understood as they had not been previously modelled and tested. These optics, however, are quite similar to those used in the detection of $a(1) \rightarrow X$ fluorescence, so many of the factors remain the same. The same lightpipe, IR blocking filter glass, and sapphire window, are used. The only difference is that instead of a narrow band IF filter, a colored glass filter was used. The transmission of this colored glass filter was measured (see figure 6.3) and when multiplied by the measured Franck-Condon factors gives an average filter transmission of $T = 38.4\%$ of the photons from the $C' \rightarrow a(1)$ decays. Since no optical coupling grease was used in the detection optics, reflections off of the optical surfaces need to be taken into account, reducing the detection efficiency. Overall, the detection efficiency is estimated to be $\eta_d = 2.4 \times 10^{-3}$, assuming an average PMT q.e. of $\eta_q = 20\%$ at these wavelengths of 360 nm-475 nm [103].

The $C' \rightarrow X$ fluorescence was measured to be $N_{C'\rightarrow X} = 8.0 \times 10^3$ photoelectrons/laser pulse. Accounting for $\eta_d$, it is estimated that there are $N_{C'} = \frac{N_{C'\rightarrow X}}{\eta_d} \sim 3 \times 10^6$ molecules/laser pulse in the $C'$ state in the cell. For the $t = 7$ ns laser pulses, the excitation rate from the a(1) state to the $C'$ state is $W_{eg} = \frac{N_{C'}}{N_a} \sim 7 \times 10^5$ molecules/second.

The excitation laser driving the $|a(1), v' = 5, J = 1\rangle \rightarrow |C', v'' = 5, J = 1\rangle$ transition had an energy of $E_{a(1)\rightarrow C'} \sim 0.7$ mJ/pulse, and linewidth $\gamma_{laser}=5$ GHz. The laser was expanded to radius $r = 1.9$ cm so that it illuminated an area $A = \pi r^2=11$ cm$^2$. The laser had a pulse duration of $t=7$ ns. The flux was

$$\Phi = \frac{E_{a(1)\rightarrow C'}}{h \nu_{laser} A t} \quad (6.13)$$

where $\nu_{laser} = \frac{c}{\lambda}$ and $\lambda = 1114$ nm. Therefore, $\Phi = 5 \times 10^{22}$ photons/(cm$^2$ s).

With all of these components calculated, it is now possible to calculate the cross section. Given several uncertainties in this measurement process, these cross sections are accurate within a factor of 1-3 times this reported value. Using equation 6.9, $\sigma_{abs,app} = 1.4 \times 10^{-17}$ cm$^2$. From equation 6.10, $\sigma_{abs,D} = 1.6 \times 10^{-16}$ cm$^2$, and from equation 6.11 $\sigma_{abs} = 1.5 \times 10^{-12}$ cm$^2$. For comparison, in [42] the $X \rightarrow a(1)$ cross section was reported to be $\sigma_{abs,D} \sim 3 \times 10^{-17}$ cm$^2$, although
Figure 6.5: Quantum beats observed by driving the population to the $C'$ state using a pulsed laser. The time between the $X\rightarrow a(1)$ and $a(1)\rightarrow C'$ laser pulses was changed to observe these beats. The beats were observed in this case because only the $|a(1), e\rangle$ state is populated so the phase cancellation between the $|e\rangle$ and $|f\rangle$ states does not occur.

It is now believed that this cross section may be off by a factor of 4 due to a calculational error. Again for comparison, the theoretical value for the $a(1)\rightarrow C'$ cross section including Doppler broadening is $\sigma_{abs}^{(t)} \sim 5 \times 10^{-15}$ cm$^2$.

6.1.6 Determination of Expected Contrast With No Electric Field

Once the frequency for the $|a(1), J=1\rangle \rightarrow |C', J=1\rangle$ transition was determined, it was possible to measure the $a(1)$ state evolution by probing it via excitation to the $C'$ state. The $X\rightarrow a(1)$ laser was horizontally polarized and the initial $a(1)$ state was prepared as described in section 2.2.1. By varying the delay time between the two lasers and integrating the fluorescence from the $C' \rightarrow X$ state, the expected beats can be observed as shown in figure 6.5.

To better understand the quantum beats in figure 6.5, the formalism developed in section 2.3 will be used. To simplify the notation, all states will be written in the form $|\text{state}, J, m, e/f\rangle$. The time evolved state is given by equation 2.14. To write it in the notation used in this section, this initial state is

$$|\psi_{\text{init}}(t)\rangle \propto -e^{i\omega z t} |a(1), 1, 1, e\rangle + e^{-i\omega z t} |a(1), 1, -1, e\rangle. \quad (6.14)$$
The $a(1) \rightarrow C'$ laser is tuned to the Q1 transition so the selection rule $|e\rangle \rightarrow |f\rangle$ applies. This laser has $\hat{z}$ polarization so the Hamiltonian is $H \propto x \propto \frac{1}{\sqrt{2}}(r_- - r_+)$. This laser transfers the population to the $C'$ state $\phi(t)$ that is

$$|\phi(t)\rangle \propto \sum_{m=-1}^{1} \left[ -e^{i\omega z t} \langle C', 1, m, f | \frac{1}{\sqrt{2}}(r_- - r_+) | a(1), 1, 1, e \rangle | C', 1, m, f \rangle + e^{-i\omega z t} \langle C', 1, m, f | \frac{1}{\sqrt{2}}(r_- - r_+) | a(1), 1, -1, e \rangle | C', 1, m, f \rangle \right] .$$

(6.15)

This expression can be simplified by applying the Wigner Eckart theorem, and simplifying the 3-j symbols by discarding all terms with $m_1 + m_2 + m_3 \neq 0$ and applying equation 2.13 to reduce the rest of the terms. Therefore,

$$|\phi(t)\rangle \propto (e^{i\omega z t} - e^{-i\omega z t}) |C', 1, 0, f \rangle .$$

(6.16)

Similar to the process described in section 2.3.1, this state will decay to several ground state levels. Since the molecule is in a $J = 1$ state, it can decay to $J = 0, 1, 2$ states just as shown in figure 2.5. As always, the parity selection rules must be considered. Decays to $J = 0$ and $J = 2$ are $|\Delta J| = 1$ transitions, so the selection rule is $|e\rangle \rightarrow |e\rangle$ and $|f\rangle \rightarrow |f\rangle$. Since the $C'$ state is an $|f\rangle$ state and the $X$ state only contains $|e\rangle$ states, these transitions cannot occur. The decay to $J=1$ can occur since here $\Delta J = 0$, so the selection rule is $|f\rangle \rightarrow |e\rangle$. As before, the detector points in the $\hat{z}$ direction, so decays with $\hat{y}$ or $\hat{z}$ polarization can be detected. The Hamiltonians for these polarizations are $H \propto y \propto \frac{1}{\sqrt{2}}(r_- + r_+)$ and $H \propto z \propto r_0$. The measured intensity is

$$I(t) \propto \left| \frac{i}{\sqrt{2}} \langle X, 1, 1, e | r_+ | C', 1, 0, f \rangle (-e^{i\omega z t} + e^{-i\omega z t}) \right|^2 + \left| \frac{i}{\sqrt{2}} \langle X, 1, -1, e | r_- | C', 1, 0, f \rangle (-e^{i\omega z t} + e^{-i\omega z t}) \right|^2 .$$

(6.17)

Again, applying the Wigner Eckart theorem, neglecting terms that are zero, and using equation 2.13, the intensity simplifies to

$$I(t) \propto 1 - \cos 2\omega z t .$$

(6.18)

These quantum beats have a different phase than the beats from fluorescence from the $a(1) \rightarrow X$ decays in equation 2.43. Equation 6.18 predicts 100% contrast for quantum beats with no
applied electric field, which is consistent with the measurements in figure 6.5.

### 6.1.7 Determination of Expected Contrast With an Applied Electric Field

The $C'$ state is a $^3\Sigma^-$ state with $\Omega = 1$ and so it has a similar $\Omega$-doublet structure to the $a(1)$ state. The $a(1) \rightarrow C'$ excitation laser is broad enough to cover both $\Omega$-doublets, so it will drive all allowed transitions between the $a(1)$ state and the $C'$ state.

The measurement described in section 6.1.6 was repeated with an applied electric field. Here the $a(1)$ state was prepared in a superposition of the $m = \pm 1$ states of the $n_z = +1$ state of the $\Omega$ doublet level as described in section 2.2. This measurement represents the quantum beats that can be observed once the $a(1)$ state is prepared so that $d_e$ can be measured. As shown in figure 6.6, quantum beats with low contrast were observed when the $a(1)$ state was prepared in this way. The microwave amplifiers used while taking this data were much lower power than the amplifiers that will be used for the experiment, so the signal sizes were not as large as in section 6.1.6. Although the signal sizes were significantly smaller than in section 6.1.6, the noise remained the same. This resulted in data with a lower SNR than in the direct population of the $m = \pm 1$ states with the $\hat{x}$-polarized laser. To reduce the noise, all data was taken in a configuration where first data was taken with microwaves were used to populate the $n_z = +1$ state and measuring the integrated fluorescence, then the backgrounds were subtracted by repeating the data point without microwave excitation. Without the microwave excitation, no fluorescence should have been observed allowing for total background subtraction. The SNR ratio for this data was, however, sufficiently large that if this analysis were incorrect and quantum beats with large contrast could have been observed, they would have easily been resolved. Any quantum beats with a contrast larger than 10% could have been resolved.

Again, using the formalism developed in section 2.3, the data in figure 6.6 can be understood. The initial state is given by equation 2.28. At later times the $a(1)$ state is

$$|n_z = +1(t)\rangle \propto \frac{e^{i\omega t}}{\sqrt{2}} \{|a(1), 1, 1, e\rangle + |a(1), 1, 1, f\rangle\} + \frac{e^{-i\omega t}}{\sqrt{2}} \{|a(1), 1, -1, e\rangle - |a(1), 1, -1, f\rangle\} \tag{6.19}$$

Just as in the case with no applied electric field, the $a(1) \rightarrow C'$ laser is tuned to the Q1 transition so the selection rule $|e\rangle \rightarrow |f\rangle$ applies. This laser has $\hat{z}$ polarization so the Hamiltonian is
Figure 6.6: The a(1) state was prepared in the correct superposition state to take EDM data. Then, the a(1) → C' laser was used to drive the population to the common \(|C', v' = 5, J = 1, m = 0⟩\) level. Quantum beats are observed with low contrast as predicted by the quantum beat description described in this section. There should be little or no DC offset in this plot as the backgrounds are subtracted in the configuration where the data is taken. The data was taken first by populating the \(n_z = +1\) state with microwaves and measuring the integrated fluorescence. The backgrounds were subtracted by taking the same data without driving the microwave transition. In this background measurement configuration no fluorescence should have been observed allowing for a total subtraction of the backgrounds.
Figure 6.7: Possible decay channels from the $C'$ state to the X state with an applied electric field. The decays from the $|e\rangle$ state are shown in red, and the decays from the $|f\rangle$ state are shown in blue.

\[
H \propto x \propto \frac{1}{\sqrt{2}} (r_- - r_+). \text{ This laser transfers the population to the } C' \text{ state } |\phi(t)\rangle \text{ that is}
\]

\[
|\phi(t)\rangle \propto \sum_{m=-1}^{1} \frac{e^{i\omega z t}}{2} \left\{ \langle C', 1, m, f | (r_- - r_+) |a(1), 1, 1, e\rangle |C', 1, m, f\rangle \\
+ \langle C', 1, m, e | (r_- - r_+) |a(1), 1, 1, f\rangle |C', 1, m, e\rangle \right\} \\
+ \frac{e^{-i\omega z t}}{2} \left\{ \langle C', 1, m, f | (r_- - r_+) |a(1), 1, -1, e\rangle |C', 1, m, f\rangle \\
- \langle C', 1, m, e | (r_- - r_+) |a(1), 1, -1, f\rangle |C', 1, m, e\rangle \right\}
\]

(6.20)

To simplify this expression, the Wigner Eckart theorem is used. All terms with $m_1 + m_2 + m_3 \neq 0$ vanish and equation 2.13 is used to calculate the remaining terms. Therefore, $|\phi(t)\rangle$ reduces to

\[
|\phi(t)\rangle \propto \left( -e^{i\omega z t} - e^{-i\omega z t} \right) |C', 1, 0, e\rangle - \left( e^{i\omega z t} + e^{-i\omega z t} \right) |C', 1, 0, f\rangle
\]

(6.21)

The $C'$ state decays to the ground state X. As before, the detector points in the $\hat{z}$ direction, so $\hat{y}$ and $\hat{z}$ polarized photons can be detected. The Hamiltonians for these polarizations of
photons are $H \propto y \propto \frac{i}{\sqrt{2}} (r_- + r_+)$ and $H \propto z \propto r_0$, respectively. The significant difference between this calculation and the calculation without an applied electric field is that the $C'$ state now contains population in both $|e\rangle$ and $|f\rangle$ parity states. Now, the parity selection rules allow the decays of the $C', J = 1$ level to all three of the ground state rotational levels ($J = 0, 1, 2$). The possible decay channels are shown in figure 6.7. The measured intensity is

$$I(t) \propto \left| \left( -e^{i\omega Z t} - e^{-i\omega Z t} \right) \langle X, 0, 0, e | r_0 | C', 1, 0, e \rangle \right|^2$$

$$+ \left( \frac{i}{\sqrt{2}} \left( -e^{i\omega Z t} + e^{-i\omega Z t} \right) \langle X, 1, 1, e | r_+ | C', 1, 0, f \rangle \right|^2$$

$$+ \left( \frac{i}{\sqrt{2}} \left( -e^{i\omega Z t} + e^{-i\omega Z t} \right) \langle X, 1, -1, e | r_- | C', 1, 0, f \rangle \right|^2$$

$$+ \left( \frac{i}{\sqrt{2}} \left( -e^{i\omega Z t} - e^{-i\omega Z t} \right) \langle X, 2, 1, e | r_+ | C', 1, 0, e \rangle \right|^2$$

$$+ \left( \frac{i}{\sqrt{2}} \left( -e^{i\omega Z t} - e^{-i\omega Z t} \right) \langle X, 2, 1, e | r_- | C', 1, 0, e \rangle \right|^2$$

$$+ \left( -e^{i\omega Z t} - e^{-i\omega Z t} \right) \langle X, 2, 0, e | r_0 | C', 1, 0, e \rangle \right|^2 \right) \right) \right) (6.22)$$

Again, this can be simplified with the Wigner Eckart theorem, and reduced by requiring that all 3-j symbols satisfy $m_1 + m_2 + m_3 = 0$ and calculating the 3-j symbols to yield

$$I(t) \propto \frac{1}{3} \cos^2 \omega Z t \left| \langle X, 0 | r | C', 1 \rangle \right|^2 + \frac{1}{6} \sin^2 \omega Z t \left| \langle X, 1 | r | C', 1 \rangle \right|^2$$

$$+ \frac{7}{30} \cos^2 \omega Z t \left| \langle X, 2 | r | C', 1 \rangle \right|^2 \right). \right) \right) (6.23)$$

To further reduce this expression, more information is needed about the reduced matrix elements.

A relationship between the reduced matrix elements in equation 6.23 can be derived from the decay rates from the $|C', 1, 0, e\rangle$ and $|C', 1, 0, f\rangle$ states to the X state. The decay rate [55] is

$$\gamma = \sum_{J'} \frac{4\omega_0^3}{3\hbar^3} \left| \langle X, J'||r|C', J \rangle \right|^2 \right) \right) (6.24)$$

where $\omega_o$ is the frequency of the decays at 376-457 nm. For the molecules in the $|C', 1, 0, e\rangle$ state the decay rate is

$$\gamma_{ee} = \frac{4\omega_0^3}{27\hbar^3} \left| \langle X, 0 | r | C', 1 \rangle \right|^2 + \left| \langle X, 2 | r | C', 1 \rangle \right|^2 \right). \right) \right) (6.25)$$

185
For the molecules in the \(|C', 1, 0, f\) state, the decay rate is

\[ \gamma(f) = \frac{4\omega_0^3}{27\hbar^3} \left| \langle X, 1 | r | C', 1 \rangle \right|^2. \]  

(6.26)

The decay rate from \(|C', 1, 0, e\) is the same as the decay rate from \(|C', 1, 0, f\), so the reduced matrix elements can be related such that

\[ \left| \langle X, 0 | r | C', 1 \rangle \right|^2 + \left| \langle X, 2 | r | C', 1 \rangle \right|^2 = \left| \langle X, 1 | r | C', 1 \rangle \right|^2. \]  

(6.27)

The usefulness of this relationship will become more apparent after rewriting equation 6.23 as

\[ I(t) \propto \cos^2 \omega z t \left[ \frac{\left| \langle X, 0 | r | C', 1 \rangle \right|^2}{\left| \langle X, 1 | r | C', 1 \rangle \right|^2} + \frac{7}{10} \cos^2 \omega z t \frac{\left| \langle X, 2 | r | C', 1 \rangle \right|^2}{\left| \langle X, 1 | r | C', 1 \rangle \right|^2} + \frac{1}{2} \sin^2 \omega z t. \]  

(6.28)

Now, in the extreme case where all of the decays from \(|C', 1, 0, e\) \(\rightarrow\) \(|X, J = 0\), \(|X, 0 | r | C', 1\rangle = \langle X, 1 | r | C', 1\) and \(|X, 2 | r | C', 1\rangle = 0. Then,

\[ I(t) \propto \frac{3}{4} + \frac{1}{4} \cos 2\omega z t \]  

(6.29)

and the expected contrast is \(\sim 33\%\). In the opposite extreme case where all of the decays from \(|C', 1, 0, e\) \(\rightarrow\) \(|X, J = 2\), \(|X, 2 | r | C', 1\rangle = \langle X, 1 | r | C', 1\) and \(|X, 0 | r | C', 1\rangle = 0. Then,

\[ I(t) \propto \frac{1}{5} + \frac{1}{30} \cos 2\omega z t \]  

(6.30)

and the expected contrast is \(\sim 16\%\). Therefore, the expected contrast is in the range 16-33\%. For comparison, the expected contrast for the \(a(1)\rightarrow X\) decays is \(\sim 50\%\), (but is observed to be \(\sim 12\%\)). The fit to the data in figure 6.6 indicates a 4(3)% contrast.

### 6.1.8 Reexcitation Measurement Scheme

Originally, it was thought that a reexcitation scheme could work by directly using a laser to slowly excite the \(a(1)\rightarrow C'\) transition. Fluorescence could be continuously observed in the \(C' \rightarrow X\) decays. As shown above, this scheme will not contain high-contrast quantum beat information. Once it was understood that this scheme would not produce high-contrast beats, an alternate
scheme using both microwave excitation and fluorescence excitation was discussed.

In this scheme (shown in figure 6.8) the EDM superposition state would be populated as is described in section 2.2. Then, there would be two short, but intense \( \hat{x} \)-polarized microwave pulses separated by \( \sim 100 \, \mu s \) tuned to the |a(1), \( J = 1 \rangle \rightarrow |a(1), \( J = 2 \rangle \) transition. A CW laser tuned to the a(1)\( \rightarrow C' \) transition would slowly transfer the population from the |a(1), \( J = 2 \rangle \) state to the |C', \( J = 3 \rangle \) state. Detection would occur by monitoring fluorescence from spontaneous decays from the C' state to the X state. In this scheme, the phase of the quantum beats must be approximately known before starting. The first microwave pulse \( R_{12,a} \) would be timed to occur at a maximum amplitude of the sine wave component of the quantum beats. This pulse is a "normalization" pulse that is used to determine the amplitude of the population in the a(1) state. This microwave pulse is at the resonant frequency of the \( J = 1 \) to \( J = 2 \) transition at \( \omega_0 \), has a duration \( \delta t_1 \) and has a rate of population transfer \( R_1 \) when on:

\[
R_{12,a} = \begin{cases} 
0 & : t < t_1 \\
R_1 & : t_1 < t < t_1 + \delta t_1 \\
0 & : t > t_1 + \delta t_1.
\end{cases}
\]

(6.31)

Here \( t_1 \) is the time of the first microwave pulse and \( \delta t_1 \) is the duration of this pulse. Then, assuming that the initial state is prepared in the a(1) state at \( t = 0 \), the coupled differential equations for the population in the |a(1), \( J = 1 \rangle \) state \( N_{a,1} \), the population in the |a(1), \( J = 2 \rangle \) state \( N_{a,2} \) and the population in the C' state \( N_{C'} \) are

\[
\frac{\partial N_{a,1}}{\partial t} = -\frac{N_{a,1}}{\tau_a} - N_{a,1} R_{12,a} (1 - \cos \omega_Z t) + N_{a,2} R_{12,a} (1 - \cos \omega_Z t) \quad (6.32)
\]

\[
\frac{\partial N_{a,2}}{\partial t} = -\frac{N_{a,2}}{\tau_a} - N_{a,2} R_{12,a} (1 - \cos \omega_Z t) + N_{a,1} R_{12,a} (1 - \cos \omega_Z t) \quad (6.33)
\]

\[
- N_{a,2} R_{aC'} + N_{C'} R_{aC'} \]

\[
\frac{\partial N_{C'}}{\partial t} = -\frac{N_{C'}}{\tau_{C'}} + N_{a,2} R_{aC'} - N_{C'} R_{aC'}. \quad (6.34)
\]

Here, \( \tau_a = 50 \, \mu s \) is the lifetime of the a(1) state in the cell. Similarly, \( \tau_{C'} = 3.4 \, \mu s \) is the lifetime of the C' state [42].

A laser-induced population transfer occurs between the |a(1), \( J = 2 \rangle \) state and the C' state. The rate of this population transfer \( R_{aC'} \) will depend on the power of this laser. In section 187

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Figure 6.8: In this reexcitation measurement scheme, the state population sequence for the $|a(1), J = 1\rangle$ state is shown in green. First, the $|a(1), J = 1, m = 0\rangle$ state is populated with the laser. Next, microwaves are used to transfer the population to the $|a(1), J = 2, m = 0\rangle$ state, and then to a coherent superposition of the states used to measure an EDM as described in section 3.6. Once the $J = 1$ states are populated, two short pulses of microwaves are used to transfer some of the population to the $|a(1), J = 2, m = 0\rangle$ state (shown in black). This population transfer preserves the phase information in the a(1) state. Reexcitation then occurs to the $C'$ state with a CW laser (shown in red) and fluorescence is observed in the decays from the $C' \rightarrow X$ state (shown in blue).
6.1.5, it was found that the absorption cross section $\sigma_{abs,D}$ is small, so it is difficult to drive the $a(1)\rightarrow C'$ transition with high population transfer. Therefore, much laser power is needed. The highest power CW laser that is commercially available at the necessary wavelength of 1114 nm is $\sim 10$ W. It will take on the order of $100 \mu$s to transfer all of the population in the $a(1)$ state to the $C'$ state with 10 W of laser power. It was found that $\eta_e = 5\%$ of the molecules were transferred along the $a(1)\rightarrow C'$ transition by the pulsed dye laser with a power $P = 0.7 \text{ mJ/7 ns}$ pulse. Since the linewidth of this laser is $\gamma_{\text{laser,pulse}} = 5 \text{ GHz}$, a laser with a $\gamma_{\text{laser,CW}} = 500 \text{ MHz}$ linewidth would require a power of $P_{\text{req}} = \frac{P}{\eta_e} \tau_{a(1)} \gamma_{\text{laser,CW}} = 20 \text{ W CW}$ to completely transfer the population during the $\tau_{a(1)} = 50 \mu$s lifetime. Realistically, a 5 W laser is assumed, corresponding to a transfer rate $R_{aC'} = [200 \mu s]^{-1}$ lifetime.

The initial starting conditions for solving these coupled differential equations are $N_{a,1}(t = 0) = 1$, $N_{a,2}(t = 0) = 0$, and $N_{C'}(t = 0) = 0$. After numerically solving these equations, the normalization signal $I_{\text{norm}}$ is defined as the integrated fluorescence from the $C' \rightarrow X$ decays between the time of the pulse $t_1$ and the time of the second pulse $t_2$

$$I_{\text{norm}} = \frac{1}{\tau_{C'}} \int_{t_1}^{t_2} N_{C'} dt.$$  \hspace{1cm} (6.35)

A similar method is used to determine what the observed signal would be after the second microwave pulse. This pulse would be timed to occur when the slope of the sine wave component of the quantum beats is at a maximum. In the small region around this point of maximum slope, the quantum beat signal can be approximated by a line where

$$S(t) = a + bt$$  \hspace{1cm} (6.36)

where $a$ is the intercept and $b$ is the slope. In this small region $\omega_s \propto \phi \propto b$ where $\phi$ is the phase of the beats. If there is a change in the phase $S(t)$, then $t \rightarrow t + \delta t$. Therefore,

$$S(t + \delta t) = a + bt + b\delta t.$$  \hspace{1cm} (6.37)

The second microwave pulse $R_{12,\beta}$ at a fixed time will measure a corresponding change in $S(t) \propto b\delta t$. Therefore, at the point of maximum slope, there is a maximum sensitivity to a
change in the phase of the quantum beat signal. To further enhance the sensitivity, this pulse will be delayed from the first pulse by a long time \( t_2 \sim \tau_{a(1)} - 2\tau_{a(1)} \) so that the phase in the \( a(1) \) state will have had a long time to accumulate. When the slope of the sine wave is maximized, phase of the sine wave cause large changes in the amplitude of the quantum beat signal around this point. The second microwave pulse \( R_{12,\beta} \) occurs at time \( t_2 \), has a rate of transfer \( R_2 \) and has a duration \( \delta t_2 \). This pulse is

\[
R_{12,\beta} = \begin{cases} 
0 & : t < t_2 \\
R_2 & : t_2 < t < t_2 + \delta t_2 \\
0 & : t > t_2 + \delta t_2.
\end{cases}
\] (6.38)

The coupled differential equations are

\[
\frac{\partial N_{a(1),1}}{\partial t} = -\frac{N_{a(1),1}}{\tau_{a(1)}} - N_{a(1),1}R_{12,\beta}(1 - \cos \omega z t) + N_{a(1),2}R_{12,\beta}(1 - \cos \omega z t) \tag{6.39}
\]

\[
\frac{\partial N_{a(1),2}}{\partial t} = -\frac{N_{a(1),2}}{\tau_{a(1)}} - N_{a(1),2}R_{12,\beta}(1 - \cos \omega z t) + N_{a(1),1}R_{12,\beta}(1 - \cos \omega z t) - N_{a(1),2}R_{aC'} + N_{C'}R_{aC'} \tag{6.40}
\]

\[
\frac{\partial N_{C'}}{\partial t} = -\frac{N_{C'}}{\tau_{C'}} + N_{a(1),2}R_{aC'} - N_{C'}R_{aC'}. \tag{6.41}
\]

The initial conditions to solve this equation are the populations in all three states from the first microwave pulse at time \( t_2 \). The signal pulse \( I_{\text{sig}} \) is

\[
I_{\text{sig}} = \frac{1}{\tau_{C'}} \int_{t_2}^{\infty} N_{C'}dt. \tag{6.42}
\]

It is necessary to subtract out the fluorescence during the integration time from \( t_2 \to \infty \) that was caused by the normalization pulse. This additional fluorescence is \( I_{\text{bkd}} \) and is

\[
I_{\text{bkd}} = \frac{1}{\tau_{C'}} \int_{t_2}^{\infty} N_{C'}dt \tag{6.43}
\]

where \( N_{C'} \) has been solved under the conditions that only \( R_{12} \) occurs.

Using this method, the simulated populations in the \( |a(1), J = 1\rangle, |a(1), J = 2\rangle \), and \( C' \) states is shown in figure 6.9a. If the timing of \( R_{12,\beta} \) is changed slightly, the measured ratio of the fluorescence \( \frac{I_{\text{sig}} - I_{\text{bkd}}}{I_{\text{norm}}} \) reflects the quantum beats observed. These quantum beats are shown...
in figure 6.9b. The relative timing between these two plots shows that the timing of the two microwave pulses are arranged so that the first pulse is at a maximum of the oscillation, and the second pulse is at the point of maximum slope of the quantum beats.

While this measurement scheme was calculated to be feasible, it seemed technically challenging and not competitive with the direct measurement of a(1)→X fluorescence. The estimates of the SNR using this measurement scheme were not significantly better than measuring a(1)→X fluorescence directly. Since \( \sigma_{abs} \) is small, and the Doppler width is large, it is difficult to drive the a(1)→C' transition, and much laser power is needed. The highest power CW laser that is commercially available at the necessary wavelength of 1114 nm is \( \sim \)10 W. Given the low absorption cross section for transitions between the a(1) and C' states, and the Doppler width of the transition, it will take on the order of 100 \( \mu s \) to transfer all of the population in the a(1) state to the C' state. The backgrounds are significantly lower in this measurement scheme as a result of the blue detection wavelength, which decreases the detected blackbody radiation. Furthermore, the different excitation wavelengths of 550 nm, and 1114 nm and detection wavelengths of \( \sim \)375-425 nm allows for efficient use of filters to block scattered light. An additional advantage is that the detection wavelength is such that PMTs have a higher q.e. than at the current detection wavelength of 550 nm. Unfortunately, several factors decrease the signal size reducing the overall SNR. First, a fundamental limitation of this measurement scheme is that the probe microwave pulse must occur when the quantum beats have a phase corresponding to a maximum slope of the oscillation. This occurs at the half of the maximum amplitude, which decreases the signal size by a factor of two. Second, the largest feasible CW laser that could be purchased was 10 W. Even with this power, the a(1)→C' transition would take \( \sim \)100 \( \mu s \) to be fully driven; meanwhile the the a(1) state is also decaying to the X state, further decreasing the reexcitation measured signal. With all of these factors, and realistic expectations for microwave excitation efficiency\((\sim \)25%) with the a(1)→C' excitation efficiency \((\sim \)50%), the estimated signal sizes were \( I_{sig} \sim 3 \times 10^3 \) photoelectrons/laser shot with a similar size of blackbody. The blackbody radiation was estimated by the measurements made with the filters used for this measurement. The current due to this count rate is \( I_{sig} = \frac{N_e}{\tau_{a(1)}} \), where the lifetime \( \tau_{a(1)} \sim \)50 \( \mu s \).

The SNR is

\[
SNR = \frac{I_{sig}}{\sqrt{I_{sig}^2 + I_{an,bb}^2}}
\]

(6.44)
Figure 6.9: a) The population in the $a(1) J = 1$ state is considered to be 1 at $t = 0$, and shown along with the populations of the $a(1) J = 2$ and $C'$ states in the microwave and $C'$ reexcitation detection scheme. b) As $t_2$ is varied, the measured signal maps out quantum beats. Note that the timing for the pulses in a) are chosen so that the normalization pulse occurs at the maximum amplitude of one of these quantum beats and the signal pulse occurs at the maximum slope of a quantum beat.
where $i_{sn}$ is the shot noise on the signal. The shot noise is defined in equation 3.37 where $F=1$.

Similarly, $i_{sn,bb}$ is the shot noise on the blackbody radiation. For this signal size, the estimated SNR is SNR=40 per laser shot. This SNR should be compared to the a(1)→X fluorescence where the signal sizes are estimated to be as large as $N_{act,PMT} = 5 \times 10^5$ photoelectrons/laser shot with a background that is 5 times larger. The estimated SNR in this case is SNR=300 per laser shot. Since the estimated SNR is larger for monitoring the a(1)→X fluorescence, the simpler detection scheme will be used.

During the discussion of this detection scheme, it was realized that multiple pulse detection schemes cannot be used to probe long lived states. Say that a multiple pulse detection scheme is used to detect the phase $\phi_1$ in state $|a\rangle$ by driving a transition between states $|a\rangle$ and $|b\rangle$. The measured intensity $I(t)$ will modulate as a result of the phase evolution in state $|a\rangle$. If there are multiple pulses between states $|a\rangle$ and $|b\rangle$ during the lifetime of state $|b\rangle$, some of the remaining population in $|b\rangle$ can be transferred back to state $|a\rangle$ with a new phase $\phi_2$. As additional measurement pulses occur, more population is added to the $|a\rangle$ state with phase $\phi_1$. These additional phases complicate the measured $I(t)$ and can possibly lead to systematic effects.

6.1.9 a(1)→C Excitation Cross Sections

The problem of reexcitation to the C' state arises from the fact that the C' state is an $\Omega = 1$ state with $\Omega$ doubling small compared to $\gamma_D$. If there were another similar state with $\Omega = 0$, it would be possible to observe the spin orientation of the a(1) state by driving transitions to this $\Omega = 0$ state. Since the $\Omega = 0$ state would only have one parity in each rotational level, the interference between the opposite parity levels would not cancel the quantum beats. Several $\Omega = 0$ electronic states has been observed via direct excitation from the X state [105]. One such state is the C state and it is an $3\Sigma^-$ state like the C' state. The only difference is that the C' state has $\Omega = 1$ while the C state has $\Omega = 0$. If the C state couples to the a(1) state, it would be a much better state to use for a reexcitation measurement scheme. Unfortunately, previous attempts to observe a transition between the a(1) and C states failed [42].

In order to maximize the chance to observe the transition between the a(1)→C state, every attempt was made to maximize the number of molecules in the a(1) state. The X→a(1) laser was
tuned to R15 so that there were $N_a = 9 \times 10^8$ molecules in the $a(1)$ state per laser shot. From the constants listed in [105], it was calculated that the $|a(1), v' = 5, J = 16 \rangle \rightarrow |C, v'' = 6, J = 15, 16, 17 \rangle$ transition occurs at $\sim 8872$ cm$^{-1}$. The $a(1) \rightarrow C$ excitation laser was scanned over a broad range from $8838.95$ cm$^{-1}$ to $8897.55$ cm$^{-1}$, but the transition was not observed. The noise floor of this measurement was equivalent to $N_C = 8 \times 10^4$ molecules in the $C$ state. Therefore, the excitation rate $W_{eg}$ was $W_{eg} < \frac{N_C}{N_a} = 1 \times 10^4$. The $a(1) \rightarrow C$ excitation laser had the same energy $E_{a(1) \rightarrow C} = 0.66$ mJ/pulse as the $a(1) \rightarrow C'$ excitation laser. Using equation 6.13, the laser flux was $\Phi = 5 \times 10^{22}$ photons/(cm$^2$ s). The lifetime of the $C$ state is $\tau_C = 2.96$ $\mu$s, so the natural width $\gamma_{natural} = \frac{1}{2\pi\tau_C} = 5.38 \times 10^4$ Hz. Since the wavelength is nearly the same as before, the Doppler width is still $\gamma_D = 425$ MHz. Using the definitions in equations 6.9, 6.10, and 6.11, $\sigma_{abs,app} < 3 \times 10^{-19}$ cm$^2$, $\sigma_{abs,D} < 4 \times 10^{-18}$ cm$^2$, and $\sigma_{abs} < 3 \times 10^{-14}$ cm$^2$.

Since this transition could not be observed using a high intensity pulsed laser, it is doubtful that it could be observed using a CW laser. Therefore, the $C$ state is not currently a candidate for a reexcitation detection scheme from the $a(1)$ state.

### 6.2 Summary of $C'$ Measurements

Although the reexcitation scheme to the $C'$ or $C$ states will not be used, much has been learned during the measurements of these states. Primarily, useful reexcitation can only occur to states that either do not have $\Omega$ doubling or where the $\Omega$ doubling is greater than the Doppler width of the transition.

### 6.3 Microwave Detection

A second generation experiment based on absorption detection is being considered. Absorption detection has two significant advantages over fluorescence detection. First, it is possible to detect all of the photons that interact with the molecules since the absorbed probe beam is directed through the molecular sample and detected on the other side of the cell. This is a much more efficient process than needing to cover a large solid angle of the cell with detectors. Second, the contrast of the beats could be greatly improved if the absorption of the beam were to a specific energy level that only had transitions with quantum beats. If all absorptive transitions had
beats, the contrast could be increased to 100% and the sensitivity of the experiment could be greatly improved.

Unfortunately, there are several technical difficulties in designing a method of absorptive detection, and so this technique was not used for any of the data presented or proposed in this thesis. Despite an extensive search, there is no known electronic state of PbO that couples to the a(1) state strongly enough to provide significant absorption on a probe. The C' state is the only known state that couples to the a(1) state. For any realistic absorption measurement using this state, it will be necessary that the laser linewidth \( \gamma_{\text{laser}} \) approximately match the Doppler linewidth \( \gamma_D = 425 \text{ MHz} \). In section 6.1.5 it was measured that \( \sigma_{\text{abs,D}} = 1.5 \times 10^{-15} \text{ cm}^2 \). The fractional absorption \( \Delta I \) will be

\[
\frac{\Delta I}{I} = n_a \sigma_{D,\gamma} L
\]

where \( n_a \) is the density of molecules in the a(1) state and \( L \) is the length of the cell. A reasonable cell length is \( L = 1 \text{ m} \). The density of PbO is unknown as discussed in section 5.1, but the highest estimate for the density in the a(1) state is \( n_a = 2 \times 10^9 \text{ molecules/cm}^3 \). Therefore, the expected absorption is \( \Delta I = 3 \times 10^{-4} \). This is a small, but not impossible, absorption to monitor.

It would, however, be much easier to use a microwave beam as an absorptive probe. From the microwave population techniques discussed in section 3.6, it is known that it is possible to drive a transition between the rotational \( J = 1 \) and \( J = 2 \) lines in the a(1) state at 28.2 GHz. Currently, a possible design for a second generation experiment is being discussed using this transition.

There are some technical considerations that need to be taken into account in the design of this new apparatus. First, the counting rate will be increased by having a long cell so that the microwave beam can interact with the most molecules. Second, the microwave beam should be sufficiently weak so that it does not drive a significant proportion of the population to the \( |a(1), J = 2\rangle \) state. Third, the microwaves must have a horizontal polarization so that they couple to the common \( |a(1), J = 2, m = 0\rangle \) state. To preserve the horizontal polarization and to have the most uniform detection, it is best to have a Gaussian beam with a \( TEM_{00} \) mode.

This measurement scheme has several additional advantages. Instead of the difficult fluorescence detectors, a microwave bridge detector can be used. A microwave bridge essentially is an interferometer that allows for the cancellation of amplitude noise. A preliminary design for this
One significant consideration for the design for the measurement scheme for this apparatus is the presence of ac Stark shifts [55]. Transitions are generally driven by sinusoidally oscillating fields, as would be the case here (see section 4.1). A constant microwave beam used for an absorption measurement would cause an ac Stark shift, and the significance of this shift must be taken into account when designing an absorption measurement scheme. If ac Stark shifts are sufficiently problematic, two intense pulses of microwaves can be used to measure the population of the $|a(1), J = 1\rangle$ levels at two discrete times. This measurement scheme would be similar to the one discussed in section 6.1.8 where the first pulse calibrates the amplitude of the beats and the second pulse measures the phase of the beats.

The preliminary design for the oven and vapor cell consists of many elements that are significantly different from the current apparatus. The microwave absorption measurement would require a long (~50 cm) cylindrical cell with 12 rods going down the length of the cell that will be used to create the electric field. These rods will be entirely supported by the sapphire windows on the end of this cylindrical cell, so leakage currents should be isolated to the regions at the ends of the cell and will not lead to such a large systematic effect. Although the construction of this cell will rely on gold-to-sapphire and gold-to-alumina bonding techniques similar to the ones discussed in section 3.1.2, this cell will be significantly more complex. The cylindrical bonds necessary are more difficult, and there are many more parts to simultaneously bond. The heaters for this cell would be more stable than the ones used for the current generation experiment since they could be made to run the length of the cell. These heaters could be co-axial ceramic and tantalum or tungsten wires and could be made to be mechanically stable, unlike the current tantalum foils.

This design is still being investigated, and many questions remain. Is it possible for a microwave beam to propagate down the cell length without exciting higher TEM modes in the cell? How will the rods for the electric field be supported and attached to the cell windows? The thickness of these cell windows should be carefully considered so that they do not reflect the microwaves. What is the optimal detection scheme here? Currently, the most troubling of these questions is how the vapor cell will be constructed. It is not clear how to create a vacuum tight seal between the electric field rods and the cell windows. Additionally, the technology exists to
Figure 6.10 Preliminary design of the 2nd generation experiment.

- High-temperature ceramic tube wall
- ~15 cm diam., 30 cm long cylinder
- Laser
- Mirror
- Rod electrodes for transverse E-field
- "Bridge" optical insulating mirror
- Horn lens
- Magic tee
- Magic cavity mirror
- Detector
make a plunger work with this cell, but careful thought will be required to incorporate this plunger into the final design.

Initially, it appears that there will be solutions to all of the unresolved questions and that this design will be much more stable than the current apparatus. Amar Vutha is currently testing solutions for attaching the electrodes to the cell windows with vacuum tight seals and coating sapphire rods with gold leaf for electrical conductivity.

6.4 Cold Molecular Beams

An alternate scheme has been proposed for a second generation experiment to search for $d_e$, and is currently under investigation by Amar Vutha. This scheme employs some of the techniques that are being developed to make cold molecular beams by ablating molecules into a cell filled with a buffer gas of helium at 4 K [108, 109]. While these techniques have been known for a long time, they have recently been rediscovered and are now being further explored. The buffer gas cools the molecules to 4 K, and the molecules leave the cell through slits placed in the side of the cell. Since these molecules are much colder than the $\sim 1000$ K molecules used in this generation of the experiment, the Boltzmann distribution over rovibrational levels is much narrower.

These cooled molecules cannot be easily worked with in a vapor cell. In order to cool them, they must be mixed with a high density of helium atoms that would depolarize the spin of the state. It is not currently possible to trap a high density of these molecules separately from the helium. Thus, it is necessary to consider working in a beam of molecules from this buffer gas cell. This should not significantly reduce the counting rate as initial data has suggested that it is possible to make beams with as much as 50% of the ablated molecules exiting the cell. Surprisingly, the angular distribution of these beams is much narrower than have been previously observed in beams [110]. Both of these effects will increase the counting rate compared to previous atomic and molecular beam experiments.

The molecule chosen for this beam should have a metastable excited state that has a lifetime that is at least as long as the time that the molecules will spend in the beam. Again, $\Omega$-doublets will be useful for rejecting systematics, so a triplet state would be best. From the existing data, it seems that $^{232}$ThO has all of the necessary properties. It has a nuclear spin $I_{\text{Th}}=0$, and has a low lying $^3\Delta$ metastable state $H$. This state will have $\Omega$-doubling. Naive scaling arguments
suggest that the lifetime of this state should be long, and that the internal electric field of this state will be 2-3 times larger than HfF\(^+\), which has been calculated to be \(|W_d|=6 \times 10^{24} \text{ Hz/(e cm)}\) [111]. Using calculational methods described in [112] it should be possible to calculate the internal electric field of ThO. Finally, the energy structure of ThO suggests that it will be possible to detect the population of the \(H\) state by reexciting to either the \(C\) or \(E\) states and detecting the fluorescence to the ground state \(X\). The energy diagram for ThO is shown in figure 6.11. The wavelengths for these transitions are easily accessible with diode lasers and can be detected with PMTs. Since the excitation and detection wavelengths are so different, scattered light from the laser can easily be blocked with interference filters.

Currently, there are two open questions as to the feasibility of \(^{232}\text{ThO}\) and the ultimate sensitivity to \(d_e\). First, what is the lifetime of the \(^3\Delta\) metastable state? While it is estimated that this lifetime is long, it has never been measured. Second, what is the ablation yield of ThO? ThO will be made by ablating ThO\(_2\), which is a refractory material with a melting temperature of 3300\(^\circ\text{C}\) [52]. It is not known whether this high melting temperature will decrease the ablation yield compared to that seen from other materials.
Chapter 7

Conclusions and Future Prospects

Using the apparatus and measurements described in this thesis, the experiment will soon begin to take data. With the current detection method of observing $a(1) \rightarrow X$ fluorescence, only $N_{\text{meas}} = 2 \times 10^5$ photoelectrons/laser pulse are detected. The blackbody radiation is approximately 5 times larger than the signal, significantly limiting the SNR. Therefore, data taken with the current system will not allow for a competitive measurement of $d_e$. Nevertheless, taking preliminary data with this low SNR will provide a useful demonstration that the experimental technique works as planned. This chapter discusses how this data will be taken including what tests will be performed to check for possible systematic effects. Finally, there will be a discussion of some possible improvements to the SNR.

7.1 Data with Current Apparatus

It is expected that data will be taken with the current apparatus starting in the next few months. The first data set will be taken under optimal conditions where all parameters are set to the best known values. Assuming that there are no obvious problems with this data set, then, additional data sets will be taken with the experimental parameters slightly varied. Varying these parameters will help determine whether there are systematic effects that are skewing the measurement. If none of these parameters are found to cause systematic effects, additional data will be taken under optimal conditions to further improve the statistical sensitivity to $d_e$. 

200

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
7.1.1 Field Reversals

The data to measure \( d_e \) will be taken in blocks of alternating \( \Omega \)-doublet levels, electric field directions, and magnetic field directions. The alternation between \( \Omega \)-doublet levels will occur as frequently as possible. The current plan is to probe \( n_z = +1 \) and \( n_z = -1 \) on alternating laser shots in a randomized order. As discussed in section 2.2, the \( n_z = +1 \) and \( n_z = -1 \) levels operate as a co-magnetometer when measured in succession. Measuring these levels as frequently as possible reduces the sensitivity to magnetic noise.

The electric field will be reversed more slowly, since it will take a while for transient currents associated with this reversal to decay. There is an inherent RC time constant associated with this switching that is equivalent to the resistance of the cell and the capacitance of the leads to the cell. After switching the voltage on the electrodes and guard rings, there will be a period of time when the electric field may not have reached its full value. As a result, it is necessary to wait on the order of 10 RC time constants after switching the field before taking data. The duty cycle of the experiment is the ratio of the time spent taking data compared to the time spent preparing the experiment. In order to keep the duty cycle of the experiment reasonably high, the electric field will not be reversed more often than 100 RC time constants. From settling times in measurements of leakage currents, the expected RC time constant is on the order of 100 ms to 1 s, so the electric field would be reversed every 10 s to 100 s. Since the main signature for a non-zero \( d_e \) is a change in frequency when the direction of the electric field is reversed, it is beneficial to change the electric field this frequently and not wait for much longer time scales when it may be difficult to directly compare beat frequencies.

The magnetic field direction will also be switched with a period on the order of 1 hour. Switching the magnetic field direction will require degaussing the magnetic shields, which takes several minutes. Applying the same principle of keeping the duty cycle of the experiment high, it is undesirable to spend too much time switching the field rather than taking data. Again, reversing the magnetic field is a useful diagnostic for rejecting systematics, so it is useful to switch the field during a typical data set.

Between the necessary delays in switching the electric and magnetic fields, the duty cycle for the experiment is expected to be at most 80%, and will probably be closer to 70%. The additional delays will come from time spent readjusting the laser frequency and power, both of
which drift over several hours. Additional time may be spent ensuring that the heaters are all still operating correctly.

### 7.1.2 Scrambled Data

As discussed in section 3.11.1, quantum beat data are fit to a function determined from data taken without quantum beats. Before the magnetic shields were installed, data without quantum beats were taken by applying a large inhomogeneous scrambling magnetic field. It will be impossible to take “scrambled” data in this way during the measurement of $d_e$, as such a field would magnetize the magnetic shields. The magnetic shields could be degaussed, but as discussed above, degaussing takes several minutes. To keep the duty cycle of the experiment high, it would be best to find another way of obtaining data without quantum beats. An alternate method is to measure fluorescence by simply not driving the microwave transitions. Since the laser populates the $|X, J = 1, m = 0\rangle$ state, without any additional microwave excitation, there are no quantum beats. This method has two disadvantages. First, taking data without beats in this configuration will further reduce the duty cycle of the experiment as it will take up time that could have otherwise been used to probe the states that are sensitive to $d_e$. Second, the $m = 0$ state has a slightly different fluorescence pattern than the superposition state $\frac{1}{\sqrt{2}}(|m = +1\rangle + |m = -1\rangle)$. The $m = 0$ state has a fluorescence distribution slightly peaked in the $\hat{z}$ direction, while the superposition state has a close to $\sin^2 \theta$ distribution as a result of the dipole radiation from this state. While this difference in fluorescence distributions does not make a large difference in the measured signals, it will make a small difference, possibly skewing the data analysis.

Paul Hamilton has proposed that “scrambled” data can be better extracted from the quantum beat data by using a method similar to the data analysis methods used for the muon $g-2$ experiment [113]. This method starts by averaging quantum beat data acquired after several shots of the dye laser to create a well known quantum beat data sample. Since the frequency and phase of the quantum beats is fairly well known, this data set can be shifted in time by a $\pi$ phase shift and then added to itself. The resulting sum will have no residual quantum beats in all higher harmonics in even orders. To remove the residual beats in all higher odd orders, the data set is added with a $2\pi$ phase shift. The final summed data set can then be used as a “scrambled” data set to which quantum beat data can be fit. Since this method relies on data
that is continuously taken, it will not reduce the duty cycle of the experiment and it represents
the actual fluorescence distribution of the molecules.

7.2 Systematics to Investigate with Current Apparatus

As discussed in sections 2.5 and 2.2, the a(1) state of PbO is expected to be relatively immune to
many common systematic effects in EDM experiments. However, to ensure that these predictions
are correct and that the experimental design works as specified, many experimental parameters
will be changed to see if these parameters can induce a false EDM signal at a measurable level.

7.2.1 Laser Polarization Aligned with Electric Field

The direction of the electric field defines the $\hat{z}$ axis of this experiment since the molecules will
align along the direction of the electric field. The laser is nominally vertically polarized when it
emerges from the dye laser, but as discussed in section 3.5, it passes through a half wave plate
and a Glan-Laser polarizer to ensure vertical polarization. Both the half wave plate and the
polarizer are mounted on rotation stages to allow for these optics to be rotated, which will tip
the polarization of the laser. It will be very difficult to align the laser polarization so that it is
parallel to the electric field to better than 1°. Any misalignments will cause a small component
of the laser polarization to be perpendicular to the electric field direction (i.e. polarized in
the $\hat{x}$ direction). $\hat{x}$-polarized light will excite all four $|m| = 1$ sublevels simultaneously causing
quantum beats with a phase that is set by the time when the laser fires. Since this phase will
be different from the phase of the beats that are created by the population that is prepared by
the microwave state preparation, this extra population from the laser misalignment will slightly
decrease the contrast of the observed beats. To verify that this explanation is correct and that
there are no additional systematics from the laser misalignment, additional data will be taken
after exaggerating this effect by badly misaligning the laser polarization by $\sim 5°$.

7.2.2 Magnetic Field Alignment with the Electric Field

Just as it is difficult to align the laser polarization with the electric field, it is similarly difficult
to align the direction of the magnetic field with the electric field. The magnetic field direction is
fixed by the placement of the nearly Helmholtz coils that are used to create the field inside the
shield in the \( \hat{z} \) direction. The direction of the magnetic shield can be tilted by driving current through the \( \hat{x} \) and \( \hat{y} \) coils described in section 3.4.

A misalignment of the magnetic field allows for small components of the magnetic field to be perpendicular to the electric field i.e., in the \( \hat{x} \) or \( \hat{y} \) direction. To first order, a misaligned magnetic field does not change the measured quantum beats at all as a result of the tensor Stark splitting of the a(1) state (see section 2.6.2). To higher orders, the components of the magnetic field in the \( \hat{x} \) and \( \hat{y} \) directions will not be able to change the energy level structure of the a(1) state of PbO significantly compared to the Stark shift, and should not be able to cause a systematic effect. The a(1) state has a large tensor Stark splitting. A magnetic field in either the \( \hat{x} \) or \( \hat{y} \) direction is equivalent to a spin raising or lowering operator. The Zeeman shift is normally much smaller than the Stark shift, and misalignments from the magnetic field will cause spin raising and lowering operators with even smaller energies further suppressing this effect. To ensure that the magnetic field misalignment does not cause any additional systematic effects that could cause a false measurement of \( d_e \), some data will be taken with this effect exaggerated, using the \( \hat{x} \) and \( \hat{y} \) coils around the vacuum chamber. To get an idea of how large these shifts need to be to matter, a very large field misalignment would be on the order of \( \delta B_{xy} = 100 \) \( \mu \)G corresponding to \( \theta_B \approx \frac{\delta B_{xy}}{B_0} \approx 10^{-3} \) rad. Just as for \( \mathbf{v} \times \mathbf{E} \) effects, a field misalignment will shift the energy levels by

\[
\Delta E \sim \frac{(\mu_B \theta_B \delta B_{xy})^2}{E_{\text{Stark}}}. \tag{7.1}
\]

For a typical Stark shift \( E_{\text{Stark}} \approx 60 \) MHz, the energy shift is \( \Delta E = 0.1 \) mHz. This is equivalent to a false EDM of \( d_{e,\text{false}} = 2 \times 10^{-29} \) e cm, and is well below the expected resolution of this experiment.

### 7.2.3 Magnetic Field Gradients

Magnetic field gradients are known to decrease the beat contrast and the beat lifetime. Molecules in one region of the cell precess with a frequency determined by the magnetic field in that region of the cell, while molecules in another region of the cell precess with a frequency determined by the different magnetic field in this region. Since the detection system is non-imaging and therefore cannot resolve the position from which the detected photon originates, the net effect of an inhomogeneous magnetic field is to wash out the phase of the beats and decrease the contrast.
of the beats. This effect is particularly pronounced as the molecules precess since there is more time for the molecules to de-phase shortening the lifetime of the beats.

Again, to check for systematic effects, magnetic field gradients will be deliberately applied at times while data is being taken. Magnetic field gradients can be applied in the \( \hat{z} \) and \( \hat{y} \) direction with the coils described in section 3.4. While it is not expected that these gradients will cause systematic effects, it is a possible that a coupling between these gradients and inhomogeneities in the electric field could lead to an incorrect measurement of \( d_e \).

7.2.4 Detuning of Laser Frequency

As discussed in section 2.6.3, this experiment is potentially sensitive to Berry's phases if the laser is detuned in such a way that molecules travelling in a particular direction are preferentially excited. To ensure that this effect is not a problem for this experiment, data will be taken with the laser deliberately detuned both to the red and the blue of the optimal laser frequency.

7.2.5 Non-Reversing Components of the Electric Field

If the electric field does not reverse perfectly, a significant systematic effect can occur. The \( g \)-factors for \( n_z = +1 \) and \( n_z = -1 \) change as a function of electric field (see section 4.2). To check for this possible systematic, a non-reversing component of the electric field will occasionally be deliberately applied to the cell.

7.2.6 Reversing Cables

Like most EDM experiments, this experiment will ultimately measure \( d_e \) by subtracting the measured beat frequency with the electric field pointing along \( \hat{z} \) from the measured beat frequency with the electric field pointing along \( -\hat{z} \). If there are small magnetic fields associated with the voltage reversal, this can simulate an EDM. By reversing which leads are attached to the top/bottom electrodes and guard rings, it can be determined whether any possible magnetic fields from these cables are causing an inaccurate measurement of \( d_e \).

7.2.7 Monitoring Leakage Currents

Leakage currents are expected to scale somewhat with the applied electric field. In the cell, it seems that Ohms law does not apply exactly, as the insulators are ceramics with ionic conduction
paths. However, it does seem to be true that at larger applied voltages, there are somewhat larger leakage currents. A useful diagnostic for the effect of leakage currents will be to measure $d_e$ as a function of the applied electric field $E$. Since the molecule will fully polarize at high electric fields, $d_e$ should remain constant as a function of $E$ at high fields. The $g$-factors are expected to scale linearly with the applied electric fields, so the change in $g$-factor with electric field $\Delta g(E) \propto E$. If the leakage currents also scale linearly with $E$, then the quantum beat frequency $\nu_b \propto E^2$. If however, the leakage currents do not contribute to $\nu_b$, then the measured beat frequency will be $\nu_b \propto E$. By varying $E$ and seeing how $\nu_b$ changes, the effect of leakage currents can be determined.

7.3 Improvements to Existing Apparatus

Currently, the sensitivity to $d_e$ is not as high as is ultimately desired for the first generation. A few straightforward modifications to the existing apparatus are being considered.

First, the existing excitation and detection scheme has been designed to minimize the scattered light that enters the PMTs. Since the IF filters block wavelengths to the red of the central wavelength, the excitation wavelength is chosen to be to the red of the detection wavelength. This excitation process is three times less efficient than the optimal scheme. Currently, excitation occurs at 570 nm ($X(v = 1) \rightarrow a(1)(v = 5)$) and detection occurs at 548 nm ($a(1)(v = 5) \rightarrow X(v = 0)$). Exciting at the detection wavelength of 548 nm would increase the signal by a factor of 3 since the population in this vibrational state is 3 times larger due to the Boltzmann distribution. A better gating circuit on the PMT would allow the PMT to recover more quickly from larger scattered light pulses. Currently, $\sim 10^{10}$ photons are scattered into the PMT at the wavelength of the laser. In Hagen et. al. [114], a gating circuit is reported with attenuations of $5 \times 10^6$. Taking into account the PMT q.e., with such a gating circuit only 300 photoelectrons would be detected, and it seems likely that the PMT would recover from such a small scattered light pulse. Therefore, building such a gating circuit is a high priority for future improvements. One significant issue needs to be considered in building this gating circuit. The gating circuit in [114] depends on gating the photocathode, which works for the PMTs used in that paper. The PMTs used in this experiment have a bialkali photocathode, which has a higher resistance than all other photocathodes. This will limit the possible switching time for voltages

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
across this photocathode. It needs to be investigated whether this gating circuit will work as efficiently when the focusing electrode and first dynode are gated instead of the photocathode.

Second, blackbody radiation could possibly be reduced. One option to reduce the blackbody radiation is to use gold coated heat shields. Gold is a very efficient reflector of blackbody radiation as it reflects infrared radiation well. Unfortunately, gold does not bond to quartz, so gold cannot be plated on the existing quartz shields without a magnetic binder. However, gold does bond to sapphire, so new heat shields could be made of sapphire. Then, gold leaf foil could be bonded on to these shields. Similarly, another alternative would be to make the outer surface of the oven out of sapphire and bond gold foil on to these surfaces.

7.4 Conclusions

To summarize, an apparatus to measure $d_e$ has been designed and constructed. Furthermore, this apparatus has been stabilized so that data can be continuously collected for long times. With this apparatus, several key measurements have been made to ensure the feasibility of this experiment. The $\Omega$-doublet splitting of the $a(1)$ state has been measured, as has the $g$-factor difference between the $|e\rangle$ and $|f\rangle$ sublevels in the absence of an applied electric field. Future measurements of the $g$-factor will be necessary with an applied electric field. The DC Stark shifts have been confirmed. The counting rate for the experiment has been determined and significant effort has been made to understand and maximize this rate while minimizing the backgrounds. Unfortunately, it seems that ultimately the counting rate may be limited by the lower partial pressure of PbO in the cell than was originally anticipated. To maximize the counting rate, three different detectors were designed and built, and several different combinations of optics for collecting the fluorescence were modelled and tested. An alternate detection scheme using reexcitation to the $C'$ energy level was explored, but ultimately rejected as a result of the complexities due to the $\Omega$-doublet structure in the $C'$ state. Finally, preparations are underway for a measurement of $d_e$ using the current fluorescence detection. This measurement is expected to be sensitive to $d_e$ at the level of $10^{-25}$ e cm/$\sqrt{\text{day}}$. Initial estimates of either second generation experiment is expected to improve the current experimental limit by at least 2-3 orders of magnitude.
Appendix A: 3-j Symbols

3-j symbols are used throughout this thesis to relate angular momenta. The 3-j symbol [47] is similar to a Clebsch-Gordan coefficient and is defined as

\[
\begin{aligned}
\begin{pmatrix}
  j_1 & j_2 & j_3 \\
  m_1 & m_2 & m_3
\end{pmatrix} &= \delta_{m_1+m_2+m_3,0}(-1)^{j_1-j_2-j_3} \times \\
&\left(\frac{(j_1+j_2-j_3)!(j_1-j_2+j_3)!(j_2-j_1+j_3)!(j_1-m_1)!(j_1+m_1)!(j_2-m_2)!(j_2+m_2)!(j_3-m_3)!(j_3+m_3)!}{(j_1+j_2+j_3+1)!}\right)^{\frac{1}{2}} \\
&\sum_k k!(j_1+j_2-j_3-k)!(j_1-m_1-k)!(j_2+m_2-k)!(j_3-j_2+m_1+k)!(j_3-j_1-m_2+k)!
\end{aligned}
\]

This function is only non-zero when all \( j_i \) and \( m_i \) are integral or half-integral and when \( j_i \geq m_i \geq 0 \) for each value of \( i \). Furthermore, \( j_1 + j_2 + j_3, m_1 + m_2 + m_3, \text{ and } j_1 - j_2 - m_3 \) must be integral so that the 3-j symbol is real. Finally, the values of \( j_i \) must satisfy the three inequalities

\[
\begin{aligned}
  j_1 + j_2 &\geq j_3 \\
  j_2 + j_3 &\geq j_1 \\
  j_3 + j_1 &\geq j_2
\end{aligned}
\]

Throughout this thesis, similar 3-j symbols are used. The symbols most frequently used are
calculated below using Mathematica [115]. These symbols are:

\[
\begin{pmatrix}
J & 1 & J + 1 \\
-m & 0 & m
\end{pmatrix} = \frac{(-1)^{J-m} \sqrt{J+1-m\sqrt{J+1+m}}}{\sqrt{J+1\sqrt{2J+1}}} \quad (A-5)
\]

\[
\begin{pmatrix}
J & 1 & J \\
-m & 0 & m
\end{pmatrix} = \frac{(-1)^{m-J} m}{\sqrt{J\sqrt{J+1\sqrt{2J+1}}}} \quad (A-6)
\]

\[
\begin{pmatrix}
J & 1 & J - 1 \\
-m & 0 & m
\end{pmatrix} = \frac{(-1)^{m-J} \sqrt{J-m\sqrt{J+m}}}{\sqrt{J\sqrt{2J-1}}} \quad (A-7)
\]

\[
\begin{pmatrix}
J & 1 & J + 1 \\
-m & \pm 1 & m
\end{pmatrix} = 0 \quad (A-8)
\]

\[
\begin{pmatrix}
J & 1 & J \\
-m & \pm 1 & m
\end{pmatrix} = 0 \quad (A-9)
\]

\[
\begin{pmatrix}
J & 1 & J - 1 \\
-m & \pm 1 & m
\end{pmatrix} = 0. \quad (A-10)
\]
Appendix B: Reduced Matrix Elements

It is well known that the relative intensities of the P, Q, and R rotational branches change as a function of $J$, the rotational quantum number. If PbO were a Hund's case (a) molecule, it would be possible to calculate the relative intensities of rotational transitions between electronic states using Hönl-London factors [44]. Hönl-London factors are formulas that account for the number of different magnetic sublevels in both electronic states and the coupling between the electronic states.

The Hönl-London factors do not apply to PbO since this molecule exhibits behavior between a Hund's case (a) molecule and a Hund's case (c) molecule. Therefore, the reduced matrix elements $\langle J' || r || J \rangle$ cannot be directly calculated. However, measurements of the relative intensities of the rotational branches P, Q, and R can provide information on the reduced matrix elements $\langle J' || r || J \rangle$. An $X \rightarrow a(1)$ transition with a $\hat{z}$-polarized laser has a Hamiltonian $H \propto \varepsilon \cdot r \propto \hat{z} \propto r_0$ and an intensity

$$I(t) \propto \sum_{m} \sum_{m'} |\langle J', m' | r_0 | J, m \rangle|^2.$$  

Here, $m'$ denotes the magnetic sublevels in the $a(1)$ state and $m$ the magnetic sublevels in the $X$ state. Using the Wigner-Eckart theorem this reduces to

$$I(t) \propto \sum_{m} \sum_{m'} \left| \left( \begin{array}{cc} J' & 1 \\ -m' & 0 \end{array} \right) \right|^2 |\langle J' || r || J \rangle|^2.$$  

If the relative intensities of the transitions are known, the relative strengths of the reduced matrix elements $\langle J' || r || J \rangle$ can be estimated.
In section 2.3.1, the reduced matrix elements \( \langle J' = 0 | r | J = 1 \rangle \), \( \langle J' = 1 | r | J = 1 \rangle \), and \( \langle J' = 2 | r | J = 1 \rangle \) are needed to calculate the expected contrast of the quantum beat signal. To determine these reduced matrix elements, knowledge of the relative intensities of the R0, Q1, and P2 lines are necessary. Unfortunately, in both the spectra of \( X(u = 0) \rightarrow a(1)(v = 5) \) and \( X(u = 1) \rightarrow a(1)(v = 5) \), some of these spectral lines are at the same frequency as other, stronger rotational lines. Hence, it is difficult to extract the desired information. If the ratio of the matrix elements does not change rapidly with \( J \), the ratio of the reduced matrix elements from higher values of \( J \) such as \( J = 2 \) to \( J' + 1 \), \( J \), and \( J' - 1 \) to find the approximate ratio for the reduced matrix elements from \( J = 1 \). The next series of rotational lines that can be compared is R1, Q2, and P3. The relative strengths of these lines is shown in table 2.1. In principle, this assumption could be improved by measuring the behavior of the ratio of matrix elements as a function of \( J' \). This test would require a spectrum with several well isolated rotational lines for series \( J \rightarrow J' + 1, J', J' - 1 \). Unfortunately, a spectrum with additional such series is not currently available, so this comparison has not been made.
Appendix C: Monte Carlo

Simulation of Light Collection

The Monte Carlo takes into account many details of this experiment that are quite specific to the apparatus developed here. The primary aspects of this simulation are discussed in section 3.7.4, but more details will be given here. The simulation is programmed in C++. This main program is called “raytrace.cpp” and is saved on several computers in the laboratory. This program uses several routines from Numerical Recipes in C++ [91]. All random numbers are generated by the routine “ran2.” Roots of polynomial equations are solved using “laguer.” “zroots” finds complex coefficients of the roots a polynomial of nth order.

The simulation starts by finding initial points \((x, y, z)\) for the origin of the ray. These coordinates are defined in figure C-1 with the origin at the center of the cell. The initial point of the ray should lie between the electrodes. The geometry of the cell is shown in figure C-2. First two random numbers \(R_x\) and \(R_y\) are generated between 0 and 1. Then,

\[
x = \left( R_x - \frac{1}{2} \right) L
\]

\[
y = \left( R_y - \frac{1}{2} \right) L
\]

are set where \(L=3.5\)" is the length of the cell. Then, the program calculates \(r = \sqrt{x^2 + y^2}\). If \(r > r_{elec}\), the program chooses another set of random numbers for \(R_x\) and \(R_y\). Similarly, a random number \(R_z\) is chosen between 0 and 1 to determine \(z\):

\[
z = \left( R_z - \frac{1}{2} \right) h_{elec}
\]
Figure C-1: Coordinates used for the Monte Carlo simulation. A sample light ray is shown in red. The detector and light collection optics are in the \( \hat{y} \) direction.

where \( h_{\text{elec}} = 1.5'' \) is the distance between the electrodes.

The initial angles of the ray \((\theta, \varphi)\) are also defined in figure C-1. \( \theta \) has a \( \sin^3 \theta \) distribution. This distribution was incorrectly used to account for the \( \sin \theta \) factor from the spherical coordinates used and the (incorrect) \( \sin^2 \theta \) factor from the distribution of fluorescence from PbO (see section 3.7.4). This factor of \( \sin^2 \theta \) is not quite correct, and should be replaced with an isotropic distribution. The subroutine "sindist" accounts for this distribution by defining a function \( F(\theta) \) as

\[
F(\theta) = \sin^3 \theta. \tag{C-4}
\]

Then, a random number \( R_\theta \) is chosen between 0 and 1, and \( \theta = R_\theta \pi \). A second random number \( R \) is chosen between 0 and 1. If \( R > F \), a new value of \( R_\theta \) and \( R \) are chosen and the process is repeated until \( F(\theta) < R \) [91]. The process to choose \( \varphi \) is simple. A random number \( R_\varphi \) is chosen and \( \varphi = 2\pi R_\varphi \).

Now that the initial conditions have been chosen, they are passed to the subroutine "thetafinder," which traces the light through the cell. This subroutine starts by converting \( \theta \) and \( \varphi \) into rec-
Figure C-2: The dimensions and geometry of the vapor cell. The length of the cell is $L=3.5''$; the height of the cell is $h=2.5''$. Reentrant electrodes form a uniform electric field with electrodes that are separated by a distance $h_{elec}=1.5''$ and have a radius of $r_{elec}=1.125''$. The guard rings further homogenize the electric field and have a radius of $r_{gr}=1.375''$. Cell windows with a radius of $r_{win}=1.0''$ allow for optical access.
The path of the ray is traced to see if it hits the electrodes or guard rings and if it exits the cell window. The ray position at the windows \((x_{\text{win}}, y_{\text{win}}, z_{\text{win}})\) is found by

\[
x_{\text{win}} = x + d_x q \tag{C-8}
\]
\[
y_{\text{win}} = y + d_y q \tag{C-9}
\]
\[
z_{\text{win}} = z + d_z q. \tag{C-10}
\]

where \(q \equiv \frac{1}{d_y} \left( \frac{y}{2} - y \right)\). At the cell windows where \(y_{\text{new}} = \frac{y}{2}\), the condition that \(z_{\text{new}} < \frac{h_{\text{element}}}{2}\) is imposed to account for occlusion of the windows by the electrodes. A better simulation would impose this condition at the position of the guard rings. The condition that \(|z_{\text{win}}| < \frac{h_{\text{element}}}{2}\) is conservative and slightly reduces the angular distribution.

If \(x_{\text{win}}^2 + z_{\text{win}}^2 > r_{\text{win}}^2\), then the ray does not exit the window, and is considered lost. This procedure is repeated to see whether the ray hits the end of the lightpipe. The lightpipe has a radius \(r_{\text{lp}} = 1''\), and can be of any length \(L_{\text{lp}}\). The angle between the input ray and the normal to the lightpipe is \(\phi\) and is given by

\[
\phi = \tan^{-1} \left( \frac{\sqrt{\sin^2 \theta \cos^2 \varphi + \cos^2 \theta}}{\sin \theta \sin \varphi} \right). \tag{C-11}
\]

where \(\theta\) and \(\varphi\) are as shown in figure C-1. Once inside the lightpipe, the angular distribution is compressed due to the higher index of refraction, and the angle \(\phi_1\) of the refractive ray relative to the normal is given by

\[
\phi_1 = \sin^{-1} \left( \frac{n_0}{n_1} \sin \phi \right). \tag{C-12}
\]

As the ray travels through the sapphire cell window and enters the lightpipe, some of the rays are discarded to account for the reflections off of these surfaces. These rays are considered...
to be equally distributed between s- and p- polarizations and hence have a transmission $T$ [116] of

$$T(\phi) = \frac{n_1 \cos \phi_1}{n_0 \cos \phi} \left( \frac{2n_0 \cos \phi}{n_0 \cos \phi + n_1 \cos \phi_1} + \frac{2n_0 \cos \phi}{n_0 \cos \phi + n_1 \cos \phi_1} \right)^2. \quad \text{(C-13)}$$

Here, $n_0 = 1$ is the index of refraction of vacuum, and $n_1$ is the index of refraction of the sapphire or quartz. For each of these faces, a random number $R_{\text{ref},j}$ is generated where $j = 1, 2, 3$ to account for each of the faces. $R_{\text{ref},j}$ is between 0 and 1, and if it is larger than the transmission probability $T(\phi)$, then the ray is considered lost.

If the ray successfully enters the lightpipe, the subroutine "lptrace" is called. Again, since the angular distribution is compressed due to Snell's law, the new direction of the ray must be found. Snell's law is usually written in the form

$$n_a \sin \alpha_a = n_b \sin \alpha_b \quad \text{(C-14)}$$

where $n_a$ ($n_b$) is the index of refraction in medium $a$ ($b$) and the light ray has an angle with respect to the normal of $\alpha_a$ ($\alpha_b$). This equation assumes the coplanarity of the rays and the normal is understood. The full vector form of Snell's law [75] is

$$n_a r_a \times n = n_b r_b \times n \quad \text{(C-15)}$$

where $n$ is the normal to the surface, $r_a$ is the direction of the ray in medium $a$, and $r_b$ is the direction of the ray in medium $b$. Multiplying both sides vectorially by $n$ yields

$$n_a r_a = n_b r_b + (n_a r_a \cdot n - n_b r_b \cdot n)n. \quad \text{(C-16)}$$

This equation can be applied to our case where $n_a = n_1$, $n_b = 1$. Since the normal vector is parallel to $\hat{y}$, equation C-16 can be written in terms of the vector components

$$d_{x,1} = \frac{1}{n_1} d_x \quad \text{(C-17)}$$
$$d_{y,1} = \frac{1}{n_1} d_y + \cos \phi_1 - \frac{1}{n_1} \cos \phi \quad \text{(C-18)}$$
$$d_{z,1} = \frac{1}{n_1} d_z \quad \text{(C-19)}$$
where $\phi$ is defined in equation C-11 and $\phi_1$ is defined in equation C-12. With these components $d_1$ is the new direction of the ray within the cone. This vector is not normalized; a normalized unit vector with the direction of $d_1$ is defined as $\hat{d}_1$. Then, the ray is traced as it bounces down the edge of the lightpipe, which has a radius $r_{lp}$. The position $(x_{hit}, y_{hit}, z_{hit})$ where the ray hits the lightpipe can be derived from solving four coupled equations. These equations are solved for $y_{hit}$. These equations are

\[
x_{hit} = x_{lp} + L_{lp}d_{x,1} \\
y_{hit} = y_{lp} + L_{lp}d_{y,1} \\
z_{hit} = z_{lp} + L_{lp}d_{z,1} \\
r_{lp}^2 = x_{hit}^2 + z_{hit}^2
\]  

where $(x_{lp}, y_{lp}, z_{lp})$ are the position coordinates of the origin of the ray (either from the entrance of the lightpipe or from the previous wall hit) and $L_{lp}$ is the length of the lightpipe. Solving equations C-20-C-23 yields

\[
y_{hit} = \frac{1}{d^2} \left( d^2y_{lp} - d_{y,1}(d_{z,1}x_{lp} + d_{z,1}z_{lp}) \right) \\
\pm \sqrt{d_{y,1}^2d_{z,1}^2 \left( r_{lp}^2 - x_{lp}^2 \right) + 2d_{z,1}d_{y,1}x_{lp}r_{lp} + d_{y,1}^2 \left( r_{lp}^2 - z_{lp}^2 \right)}
\]

where $d = \sqrt{d_{x,1}^2 + d_{z,1}^2}$. It is possible for $y_{hit}$ to yield values that are not physical as there are two solutions to this equation, so a check is done to ensure that $y_{hit} > y_{lp}$. (The - sign in this equation should never be called, but a test of the program’s validity is whether or not this sign is used.) If $y_{hit} > L_{lp}$, the ray exits the lightpipe without reflecting. Then, the $x$ and $y$ points where the ray exits are calculated using equations C-20 and C-22. If $y_{hit} < L_{lp}$, it is checked to see that the condition for total internal reflection is met. To do this, the normal to the lightpipe surface at the hit point is found. The normal is defined by the unit vector $\hat{n}_{lp}$ with components.
The angle at which the ray hits the light pipe is

\[ \phi_{\text{hit}} = \cos^{-1} \left\{ \hat{n} \cdot \hat{d}_1 \right\}. \] (C-28)

If \( \phi_{\text{hit}} < \sin^{-1} \frac{1}{n_1}, \) then the ray is lost. (In fact, no rays are lost due to this condition, as this requirement is met for any ray that can enter the front face of the lightpipe.) After hitting the lightpipe, the new normalized direction for the ray \((d_{x,lp}, d_{y,lp}, d_{z,lp})\) is

\[ \hat{d}_{lp} = \hat{d}_1 - 2 \hat{d}_1 \cdot \hat{n}. \] (C-29)

As long as the ray is inside the lightpipe (ie \(y_{\text{hit}} < L_{lp}\)) the routine "lptrace" is called to continue to trace the ray down the lightpipe.

After the ray exits the lightpipe, it enters the IR blocking color glass, which is modelled with the subroutine "irblocking." This routine ensures that any ray that hits the edge of the glass is lost, as the edge is not polished. The input position and direction of the rays is taken from the output position and direction of the rays from the previous optic. All of the angles in this routine are considered to be in glass. The rays are traced to the output position \(\hat{d}_{ir}\) using equations similar to the ones in equations C-20-C-22. If \(x_{ir}^2 + z_{ir}^2 > r_{\text{glass}}^2\), where \(r_{\text{glass}}\) is the radius of the glass, the ray is considered lost. This condition is equivalent to the ray hitting the edge of the optic during transmission. If the ray is not lost, the output position and angle are used as inputs for the next optical element. Next, the ray travels through the sapphire cooling window using subroutine "sapphire." This routine is identical to "irblocking" except that it uses a different radius for the radius of the optical element. Again, if the ray hits the edge of this optic, it is considered lost.

When Winston Cones are used, they are placed in the optical stack after the sapphire
window. Two nearly identical subroutines are used for the Winston Cones: “coneltrace” and “cone2trace.” The only difference between these routines are dimensions of the Winston cones. Conceptually, the Winston Cones are modelled in the same way the lightpipes are modelled. A light ray is traced as a straight line with a parametric equation

\[ \begin{align*}
x &= x_p + d_{x,c} t \\
y &= y_p + d_{y,c} t \\
z &= z_p + d_{z,c} t
\end{align*} \] (C-30)

where \((x_p, y_p, z_p)\) is the origin of the ray (the last reflection or the point where the light enters the cone.) The direction of the light ray is defined as the unit vector \(\mathbf{d}_c = (d_{x,c}, d_{y,c}, d_{z,c})\) and is the direction of the light ray from the previous optic or from the previous reflection. This direction is calculated for the angle inside the plastic.

The surface of revolution for the Winston Cone [75] is defined by

\[ r_c^2 = 4f(y_c + f) \] (C-33)

where \(f\) is the focal length of the parabolic cone, defined by \(f = a'(1 + \sin \Theta_{\text{max}})\). \(\Theta_{\text{max}}\) is the maximum input angle for this cone, defined as

\[ \frac{a}{a'} = \frac{1}{\sin \Theta_{\text{max}}}. \] (C-34)

Here \(a'\) is the radius of the output (smaller) face of the cone and \(a\) is the radius of the (larger) input face. For Winston Cone I, \(a' = 0.9''\) and \(a = 1''\); for Winston Cone II, \(a' = 0.5''\) and \(a = 0.9''\). These radii determine the length of the Winston Cones \(L_{WC}\) since

\[ L_{WC} = (a + a') \cot \Theta_{\text{max}}. \] (C-35)

For the cone, the coordinates are shown in figure C-3, and the surface of revolution is

\[ r_c^2 = 4f(z_c + f). \] (C-36)

219
The intersection of equations C-30-C-32 with the surface of revolution defined by equation C-36 is where the ray reflects off the surface of the Winston Cone. The solution for the \( y \)-coordinate where this occurs is very complicated, and so quantities necessary to evaluate the solution are defined and combined in the final result. These quantities are

\[
A \equiv d_{x,c}^2 \cos^2 \Theta_{\max} + d_{y,c}^2 \frac{a'^2}{a^2} + d_c^2 \cos^2 \Theta_{\max} \tag{C-37}
\]

\[
B \equiv -2a'd_{y,c} \cos \Theta_{\max} \frac{a'}{a} + 4d_{y,c}f \cos \Theta_{\max} + 2d_{x,c}x_p \cos^2 \Theta_{\max} + 2d_{x,c}x_p \cos^2 \Theta_{\max} + 2d_{x,c}x_p \frac{a'^2}{a^2} - 2d_{x,c}LWC \frac{a'^2}{a^2} \tag{C-38}
\]

\[
C \equiv -4f^2 - 2Ly_p \frac{a'^2}{a^2} + y_p^2 \frac{a'^2}{a^2} + 4d' \frac{a'}{a} + L^2 \frac{a'^2}{a^2} + z_p^2 \cos^2 \Theta_{\max} + 2a' \cos \Theta_{\max} \frac{a'}{a} - 2a' \cos \Theta_{\max} \frac{a'}{a} - 4fL \cos \Theta_{\max} + x_p^2 \cos^2 \Theta_{\max} + 4fy_p \cos \Theta_{\max} + a'^2 \cos^2 \Theta_{\max} \tag{C-39}
\]

\[
D \equiv -2d_{y,c} \cos \Theta_{\max} \frac{a'}{a} \tag{C-40}
\]

\[
F \equiv 2a' \cos^2 \Theta_{\max} + 2L \cos \Theta_{\max} \frac{a'}{a} - 2d_{y,c} \cos \Theta_{\max} \frac{a'}{a} + 4f \frac{a'}{a} \tag{C-41}
\]

These quantities are used in the polynomial equation \( Gt^4 + Ht^3 + Jt^2 + Kt + M = 0 \). Here

\[
G = -A^2 + D^2d_{x,c}^2 + D^2d_{x,c}^2 \tag{C-42}
\]

\[
H = -2AB + 2Dd_{x,c}^2F + 2Dd_{x,c}^2F + 2D^2d_{x,c}x_p + 2D^2d_{x,c}z_p \tag{C-43}
\]

\[
J = -B^2 - 2AC + d_{x,c}^2F^2 + d_{x,c}^2F^2 + 4Dd_{x,c}Fx_p + D^2x_p^2 + 4Dd_{x,c}Fz_p \tag{C-44}
\]

\[
K = -2BC + 2d_{x,c}F^2d_{x,c} + 2DFx_p^2 + 2d_{x,c}F^2z_p + 2DFz_p^2 \tag{C-45}
\]

\[
M = -C^2 + F^2x_p^2 + F^2z_p^2 \tag{C-46}
\]

The roots of this polynomial equation are solved using “zroots” and then sorted to find the single solution that physically makes sense, namely one that indicates real, positive value of \( t \) that will also indicate a \( y_{\text{hit}} \) position that is greater than the previous \( y \)-position. Once the value of \( t \) is known, the position \( y_{\text{hit}} \) can be calculated using equation C-32. If the value of \( y_{\text{hit}} \) is not inside the cone, then the position where it exits the cone output face is calculated by tracing the path of the ray using equations similar to C-20-C-22. If it does hit the edge of the cone, then

\[220\]
Figure C-3: Coordinates used for the Monte Carlo simulation including the azimuthal angle $\Phi$ which is defined in reference to the parabola axis. Here, $r'_c$ is an arbitrary point along the surface of revolution and $f$ is the focus of the parabola. In polar coordinates, the parabola axis is defined as $\tan \rho = \tan \Theta_{\text{max}}$ [75].

The $x_{\text{hit}}$ and $z_{\text{hit}}$ positions where the ray reflects off of the cone are calculated with equations C-30 and C-32.

To find the angle at which the ray is reflected, the normal to the surface at the hit position must be found. Following the procedure outlined in [75], the normal is most easily found by defining an angle $\Upsilon$ as shown in figure C-3. Unfortunately, this reference defines the Winston cone as starting from the small radii and proceeding to the large radii. In this simulation the opposite occurs, so this coordinate system needs to be reversed. To relate the two coordinate systems, a new coordinate $y'$ is defined as $y' = L - (y_p + d_{y,c} y_{\text{hit}})$. Then, the angle is

$$\Upsilon = \cos^{-1}\left\{ \frac{y'^3 + 4f y'^2 \cos \Theta_{\text{max}} + 4f^2 y' \cos^2 \Theta_{\text{max}} - 4f \frac{a'}{a} \sqrt{f(y' + 2f \cos \Theta_{\text{max}})^2(f + y' \cos \Theta_{\text{max}})}}{4f^2 y' + y'^3 + (8f^3 + 6f y'^2) \cos \Theta_{\text{max}} + 8f^2 y' \cos^2 \Theta_{\text{max}}} \right\}. \tag{C-47}$$

$\Upsilon$ essentially defines the distance along the length of the cone. A second angle is necessary to specify the azimuthal coordinate. This angle $\Phi$ is defined as referenced to the $x$-axis:

$$\Phi = \begin{cases} \tan^{-1}\left\{ \frac{2x_{\text{hit}}}{z_{\text{hit}}} \right\} & : \ x_{\text{hit}} < 0 \\ \tan^{-1}\left\{ \frac{2x_{\text{hit}}}{z_{\text{hit}}} \right\} + \pi & : \ x_{\text{hit}} \geq 0. \end{cases} \tag{C-48}$$

221
Now, two vectors $a$ and $b$ are defined to help determine the normal. The components of these vectors are defined in [75]:

$$a_x = 2f \frac{\cos(\Theta_{\text{max}} - \Upsilon) \cos \Phi}{1 - \cos \Upsilon} + 2f \frac{\cos \Phi \sin(\Theta_{\text{max}} - \Upsilon) \sin \Upsilon}{(1 - \cos \Upsilon)^2} \tag{C-49}$$

$$a_y = 2f \frac{\sin \Theta_{\text{max}} - \Upsilon}{1 - \cos \Upsilon} - 2f \frac{\cos(\Theta_{\text{max}} - \Upsilon) \sin \Upsilon}{(1 - \cos \Upsilon)^2} \tag{C-50}$$

$$a_z = 2f \frac{\cos(\Theta_{\text{max}} - \Upsilon) \sin \Phi}{1 - \cos \Upsilon} + 2f \frac{\sin(\Theta_{\text{max}} - \Upsilon) \sin \Upsilon \sin \Phi}{(1 - \cos \Upsilon)^2} \tag{C-51}$$

and

$$b_x = a' \sin \Phi + 2f \frac{\sin(\Theta_{\text{max}} - \Upsilon) \sin \Phi}{1 - \cos \Upsilon} \tag{C-52}$$

$$b_y = 0 \tag{C-53}$$

$$b_z = -a' \frac{\cos \Phi - 2f \cos \Phi \sin(\Theta_{\text{max}} - \Upsilon)}{1 - \cos \Upsilon} \tag{C-54}$$

The normal to the cone can be written in rectangular components taking care to note that when the direction of the Winston cone was reversed, a left handed coordinate system was created so all dot and cross products are defined slightly differently. This choice of a left handed coordinate system is not ideal, but is a result of a previous simulation, which was incorporated into this one. The normal to the cone $n_{\text{cone}}$ is finally written as

$$n_{z, \text{cone}} = \frac{-a_x b_x + a_z b_y}{\sqrt{|a|^2 |b|^2 - |a \cdot b|^2}} \tag{C-55}$$

$$n_{y, \text{cone}} = \frac{a_x b_y - a_z b_z}{\sqrt{|a|^2 |b|^2 - |a \cdot b|^2}} \tag{C-56}$$

$$n_{x, \text{cone}} = \frac{a_y b_z - a_z b_y}{\sqrt{|a|^2 |b|^2 - |a \cdot b|^2}} \tag{C-57}$$

If this were a right handed coordinate system, this equation could be written as

$$\hat{n} = \frac{\hat{a} \times \hat{b}}{\sqrt{|a|^2 |b|^2 - |a \cdot b|^2}} \tag{C-58}$$

The angle of incidence must meet the criteria for total internal reflection, or else the ray is considered lost. This criteria is

$$\cos^{-1} \{d_e \cdot n_{\text{cone}}\} \tag{C-59}$$
Finally, the new direction of the ray $\mathbf{d}_{\text{new, cone}}$, which is also a unit vector, is defined as
\[
\mathbf{d}_{\text{new, cone}} = \mathbf{d}_c - 2(\hat{n}_\text{cone} \cdot \mathbf{d}_c)\hat{n}_\text{cone}
\]  
(C-60)

The transmission interference of the filter with a nominal center wavelength of $\lambda_0$ is modelled with the program “ifilter.” This program always uses the angle of the ray inside glass. The initial position of this ray $(x_{IF}, y_{IF}, z_{IF})$ is set equal to the point where the ray exits the previous optic, and the initial direction of the ray $\mathbf{d}_{IF}$ is set equal to the direction where the ray exits the previous optic. First, the ray is traced through the filter to see if it hits the edge of the filter. If it does, it is considered lost as the edges of this filter are not polished. Then, to find the transmission of the ray through the filter, the angle of the ray relative to the normal to the filter, $\phi_{IF}$, is found using
\[
\phi_{IF} = \tan^{-1}\left\{ \frac{\sqrt{d_{x,IF}^2 + d_{z,IF}^2}}{d_{y,IF}} \right\}
\]  
(C-61)

Then, the equivalent center wavelength of the IF filter $\lambda_c$ is calculated as
\[
\lambda_c = \lambda_0\left[1 - \left(\frac{n_1}{n^*}\right)^2 \sin^2\phi_{IF}\right]^{\frac{1}{2}}
\]  
(C-62)

where $n^*=2.05$ is the effective index of refraction of the filter and $n_1$ is set to be between $n_1 = 1.5-1.8$, depending on whether the surrounding elements are plastic, glass, or sapphire. At normal incidence the transmission of the filter has been measured as a function of $\lambda'$, and this data is fit to an 8th order polynomial function $T(\lambda')$. The transmission probability of a ray with a wavelength $\lambda$ and at an angle $\phi_{IF}$, which gives the filter a central wavelength $\lambda_c$ is calculated as
\[
T(\lambda) = \begin{cases} 
T(\lambda_c(\phi_{IF})) & : \phi_{IF} < 30^\circ \\
T(\lambda_c(\phi_{IF})) - 0.015(\phi_{IF} - 30) & : \phi_{IF} \geq 30^\circ
\end{cases}
\]  
(C-63)

Then, a random number $R_{IF}$ between 0 and 1 is generated. If $R_{IF} > T(\lambda, \phi_{IF})$, the ray is lost.

As discussed throughout this appendix a few improvements should be made to this code. These improvements are:

1. The angular distribution of fluorescence is currently modelled as a $\sin^3 \theta$ distribution.
A factor of \( \sin \theta \) comes from the spherical coordinates in the simulation. A factor of \( \sin^2 \theta \) is incorrectly attributed to the derivation in section 3.7.4. This factor of \( \sin^2 \theta \) should be replaced with an isotropic distribution.

2. The current simulation models incorrectly models how the light is occluded by the electrodes. The current simulation assumes that if the vertical position of the ray \( z \) at the window is larger than the electrode spacing, then the ray is lost. A better simulation would model whether or not the ray actually hits the electrodes.

3. It would be better if the Winston cone were defined in such a way that a left handed coordinate system was not needed.


[28] D. DeMille. Private communication.


[34] E. Hinds. Private communication.


228

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.


[61] Model 501J ±100mV to ±10V Programmable DC Voltage Calibrator by Electronic Development Company a division of Krohn-Hite Corporation.


[71] W.T. Carnall, P.R. Fields, and K. Rajnak. Electronic energy levels in the trivalent lanthanide aquo ions. I Pr³⁺, Nd³⁺, Pm³⁺, Sm³⁺, Dy³⁺, Ho³⁺, Er³⁺, and Tm³⁺. The Journal of Chemical Physics, 49,10:4424-4442, 1968.

[72] W.T. Carnall, P.R. Fields, and K. Rajnak. Spectral intensities of the trivalent lanthanides and actinides in solution II. Pm³⁺, Sm³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Dy³⁺, and Ho³⁺. The Journal of Chemical Physics, 49, 10:4412-4423, 1968.


[85] *Si Photodiodes and Charge Sensitive Amplifiers for Scintillation Counting and High Energy Physics by Hamamatsu*.


[93] M.G. Kozlov. The following derivation is from a private communication.


233


