Two-color photoassociation spectroscopy of the $3\Sigma^+$ state of Cs$_2$
Abstract

We present a spectroscopic study of the $a^3\Sigma_u^+$ state of the Cs$_2$ molecule. Using two-color photoassociation, we have observed several deeply-bound vibrational levels and their hyperfine and rotational sub-structure. Near-degeneracy between a deeply-bound sub level of the $a^3\Sigma_u^+$ state and a high-lying level of the $X^1\Sigma_g^+$ state could offer a narrow-linewidth microwave transition that has enhanced sensitivity to possible changes in the quantity $\mu \equiv \frac{m_e}{m_p}$.
Acknowledgements

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Chapter 1

Introduction

Modern theories of fundamental interactions can accommodate a variation of fundamental "constants" during the evolution of the universe. Generally a "constant" can be defined as a free parameter in a theory whose value cannot be calculated from known physics [5]. Each theory thus contains a minimum set of "constants". Some "constants" have assigned units and others are dimensionless ratios. P. A. M. Dirac [6] postulated that "constants" (as parameters in theories) constituted ways of characterizing the current state of the universe. The idea of a possible variation of physical "constants" arises from the assumption that in the relationships between physical quantities, the form of the dynamics does not change but rather that the "constants" vary per some undiscovered physics. If one "constant" is observed to vary, then the likelihood grows that others also vary. Time variation of physical "constants" violates the postulate of Local Position Invariance (LPI). LPI is part of the Einstein Equivalence Principle which is the basis of the theory of General Relativity. The study of time variation of physical constants appears to be a natural starting point for the study of physics beyond the Standard Model and General Relativity [7].

The process of measuring time variation of "constants" with dimensions can be device and space-time dependent and hence is difficult to conceptualize. However the metrology of dimensionless "constants" is largely free from this complication, so most discussions of the field concentrate on such dimensionless quantities. Experimental observations of variation of fundamental "constants" can be carried out over very different time scales using e.g. astrophysical and laboratory tests. A comparison of the measurements from these methods can yield insight into new physical models. In all cases the limits from astrophysical and laboratory based observations on time variation of
“constants” are strong [5]. By coincidence in most cases the apparent strength of the limit \( \frac{\Delta n(c)}{T} \) (the fractional change in the constant divided by the observation time \( T \)) is comparable from these very different experiments.

The time variation of fundamental “constants” can cause small shifts in molecular spectra [5]. The precise measurement of some of these shifts requires many steps. These include:

1. Crude spectroscopy to roughly determine molecular energy levels.
2. Choice of a pair of levels with long lifetimes so narrow spectral lines can be observed.
3. Preparation of a sample of molecules with population preferentially in one state of the pair of levels whose energy difference will be measured.
4. A way to drive transitions between the pair of levels and to measure the resulting population transfer.

This thesis describes the crude spectroscopy of the ground state manifold of \( \text{Cs}_2 \). Our interest in the spectroscopy and production of \( \text{Cs}_2 \) molecules is driven by a desire to implement a scheme for extremely sensitive measurements of the time variation of the electron-proton mass ratio, \( \mu \equiv \frac{m_e}{m_p} \).

The organization of this thesis is as follows. The first chapter introduces the general motivations and background for our experiment. In the second chapter we present an overview of key theoretical concepts and work related to our study. In our third chapter we talk about the details of the experimental setup. In the fourth chapter, we summarize of our results and in the last chapter, we present the conclusions that we can draw from our study.

### 1.1 A test for time variation of \( \mu \equiv \frac{m_e}{m_p} \)

The electron-proton mass ratio, \( \mu \equiv \frac{m_e}{m_p} \) is a dimensionless “constant” and as such its possible time variation is suitable for study. Interestingly, some theoretical studies [8, 9] suggest that the variation in the \( \mu \) may be linked to and considerably larger than the variation in other constants such as the fine structure constant \( \alpha_{EM} \). The current limits on the time variation of \( \mu \) are summarized in Table 1.1.

All searches for the variation in \( \mu \) (and other constants) involve comparing two frequencies: the frequency of some transition \( \nu_{\text{exp}} \) that is sensitive to changes in \( \mu \), and a stable frequency reference.
Table 1.1: Current limits on the time-variation of constants of interest. † Comparison of geochemical ages of K-Ar and Rb-Sr. * Comparison of H$_2$ rovibrational spectra from Quasars to spectra at rest. ** by comparing the ratio of hyperfine structure and fine structure in Cs and Mg atomic beam standards. Note $g_p$ is the proton gyromagnetic factor.

($\nu_{ref}$). For our purposes we assume that the stable frequency reference is an optical clock transition in some atom. It is possible to express the frequency of such an optical atomic transition as,

$$E_{ref} \propto X_{ref} \cdot \frac{e^2}{a_0},$$  \hspace{1cm} (1.1)$$

where $X_{ref}$ is a dimensionless number of order unity, $R_\infty$ denotes a Rydberg, the atomic unit of energy and $E_{ref} = h\nu_{ref}$ is the energy of the reference transition. Note that $E_{ref}$ is independent of $\mu$ (to first order). In general, we require that our experimental transition energy $E_{exp} = h\nu_{exp}$ have an explicit dependence on $\mu$. In order to have sensitivity to a variation in $\mu$,

$$E_{exp} \propto X_{exp} \cdot R_\infty \cdot f(\mu),$$  \hspace{1cm} (1.2)$$

where $f(\mu)$ is some function of $\mu$ and $X_{exp}$ is a dimensionless number of order unity. A high sensitivity to $\mu$ implies a large value of absolute sensitivity ($\frac{\partial\nu_{exp}}{\partial\mu}$). As our experiment measures the variation in $\mu$ by comparing $\nu_{exp}$ and $\nu_{ref}$, we also require that the relative sensitivity ($\frac{\partial\nu_{exp}}{\partial\nu_{ref}}$), i.e. the fractional change in $\nu_{exp}$, be as large as possible.

Diatom molecular vibrational energy levels match these requirements well as we explain here. Let us examine the sensitivity of a molecular vibrational energy level to changes in the mass ratio $\mu$. For our initial discussion, we follow the simple approach discussed in Budker, Kimball and DeMille [11]. In the harmonic approximation we model a molecule as two masses on a spring. The spring constant $k$ actually depends on the shape of the electronic energy curve, but we can crudely estimate the size of $k$ from the fact that an excursion of a few $a_0$ (Bohr radii) from the equilibrium separation between atoms will cause the molecule to almost dissociate. The vibrational energy of a high lying level $\sim \frac{1}{2} k a_0^2$ is hence comparable to the dissociation energy, which is due to quantum
electrostatics and hence of order $\sim h c R_\infty$. Thus

$$k \frac{a_0^2}{2} \sim h c R_\infty,$$

(1.3)

which implies:

$$k \sim \frac{h c R_\infty}{a_0^2} \sim \frac{e^2}{a_0^3}.$$  

(1.4)

The angular frequency of molecular vibration $\omega_{vib}$ is given by,

$$\omega_{vib} = \sqrt{\frac{k}{M}} = \sqrt{\frac{k}{m_c M}} = \sqrt{\frac{k}{m_c A \mu}},$$

(1.5)

where $M \equiv A \cdot m_p$ is the reduced mass of the two atoms and $A$ is some dimensionless constant that depends on the species of atoms forming the diatomic molecule. From the above results we can estimate $\omega_{vib}$ as,

$$\omega_{vib} \sim c R_\infty \sqrt{\mu},$$

(1.6)

where we have ignored all dimensionless constants of order unity. Thus in the harmonic approximation, the energy $E_n$ of the $n^{th}$ molecular vibrational level (relative to the bottom of the molecular potential well) is given by

$$E_n = n \hbar \omega_{vib},$$

(1.7)

$$E_n \propto R_\infty \sqrt{\mu} \cdot n$$

(1.8)

From the above expressions we see that the variation in $E_n$ upon a change in $\mu$ is given by

$$dE_n = \frac{1}{2} E_n \frac{d\mu}{\mu} \propto n,$$

(1.9)

so that higher vibrational levels have greater absolute sensitivity to possible changes in $\mu$.

In theory one could take advantage of this enhanced sensitivity to $\Delta \mu$ by measuring the energy splitting between the first ($n'=0$) and the $n^{th}$ vibrational levels in the same molecular electronic potential well (see Figure 1.2(a)). However it important to note that in such a scheme, while the absolute frequency sensitivity to changes in $\mu$ is large ($\nu_{exp} \propto n$), the relative sensitivity is not enhanced: $\frac{\omega_{exp}}{\nu_{exp}}$ is independent of $n$. 

4
Technological problems currently limit the stability of frequency measurement in any range (microwave through optical) at the level $\Delta f/f$ to $10^{-15}$. More generally systematic shifts (e.g. the Doppler effect) tend to be more severe in absolute terms for higher frequencies. All taken together these factors prohibit a very sensitive measurement of the time variation of $\mu$ using transitions between the $n = 0$ and $n^{th}$ vibrational level of the same molecular electronic state.

An attractive alternative is to use two separate molecular wells, with very different depths (see Figure 1.2(b)). As discussed before, a high-lying ($n^{th}$) vibrational level with energy ($E_A$) in the potential well of larger depth is much more sensitive to possible changes in $\mu$ than a low-lying $n^{th}$ vibrational level of energy ($E_B$) in the shallower well. If the two levels $E_A$ and $E_B$ by chance are nearly degenerate, then $\nu_{\text{exp}} = E_A - E_B$ can be small while $\frac{\partial \nu_{\text{exp}}}{\partial \mu}$ remains large. Hence, study of this splitting can give both large absolute sensitivity and large relative sensitivity to changes in $\mu$.

To make this statement more concrete, we must consider the dependence of each energy level on $\mu$. The shapes of the electronic potential wells (which are determined by electronic motion) are independent of $m_p$. The energy separation between the bottoms of the two wells ($E_{A0} - E_{B0} = X_{AB}R_\infty$, where $X_{AB}$ is a dimensionless number of order unity. The experimental transition frequency is given by,

$$E_{\text{exp}} \propto (E_A + E_{A0}) - (E_B + E_{B0})$$

$$E_{\text{exp}} \propto (E_A - E_B) + (E_{A0} - E_{B0})$$

$$E_{\text{exp}} \propto (\hbar \omega_A - \hbar \omega_B) + cR_\infty$$

$$\nu_{\text{exp}} \propto cR_\infty \cdot \sqrt{\mu} \cdot (n - n') + cR_\infty$$

As seen in equation 1.10, all the terms are dependent on $R_\infty$. In the ratio of this transition frequency $\nu_{\text{exp}}$ to an atomic optical clock transition $\nu_{\text{ref}}$ (given by $X_{\text{ref}} \cdot c \cdot R_\infty$), the dependence on $R_\infty$ cancels.

The level structure of the Cs$_2$ molecule appeared promising for implementing this scheme. The ground state manifold of the Cs$_2$ molecule has two states; $a^3\Sigma_u^+$ (triplet) and $X^1\Sigma_g^+$ (singlet) which asymptotically go to the same atomic dissociation limit ($6s_{1/2} + 6s_{1/2}$). Also the $a^3\Sigma_u^+$ (triplet) state in Cs$_2$ has well-depth of some 290 cm$^{-1}$ and the $X^1\Sigma_g^+$ (singlet) state has a well-depth of $\sim 3649.884$ cm$^{-1}$ [12]. As the triplet state is much shallower than the singlet state the variation in the its vibrational energies due to changes in $\mu$ is much smaller than that of the singlet state and hence

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we neglect it in further discussion. Spectroscopic studies suggest the presence of nearly degenerate
singlet and triplet levels up to \( \sim 40 \text{ cm}^{-1} \) below dissociation [12]. The singlet and triplet states
of the \( \text{Cs}_2 \) molecule are not affected by stray electric fields and hence \( \nu_{\text{exp}} \) measurements are not
affected by noise from these sources.

In practice the harmonic approximation for the molecular potential well breaks down. For
example in a real diatomic molecule, such as \( \text{Cs}_2 \) the force between the two atoms constituting
the molecules at large internuclear distances, is inversely proportional to a power of the distance
between them, hence the atoms do not feel a significant attractive force (unlike in the case of
harmonic motion). Also the molecule is more correctly modeled as a vibrating rotor (as opposed to
a rigid rotor) once these changes are accommodated in the model used for describing the molecule,
we can use the Dunham expansion to account for the actual dependence of energy on vibrational
quantum number. For a molecule in a vibrational state \( v \) and the lowest rotational state \( J = 0 \),
the energy is given by

\[
E(v, J = 0) = \sum_{i=1}^{\infty} Y_{i0}(v + 1/2)^i
\]

The coefficients \( Y_{i0} \) in the terms of the Dunham expansion are inversely proportional to the square
root of the reduced mass \( M \) of the two nuclei in the molecule [13]:

\[
Y_{i0} = K_{i0}(M)^{-1/2},
\]

where \( K_{i0} \) is a constant which depends on the specific diatomic molecule. We now consider the
effect of an isotope shift i.e. if the molecule was made from a different isotope of the same atom,
then the energy level would shift by

\[
dE(v) = - \sum_{i=1}^{\infty} \frac{1}{2} Y_{i0}(v + 1/2)^i \frac{dM}{M},
\]

where \( dM/M \) is the fractional difference in isotopic masses. If we hold the electron mass \( m_e \)
constant, then the effect of a change in the mass ratio \( \mu \) is analogous to a change in the reduced
mass \( M \). Note that holding \( m_e \) constant is conceptually convenient since \( m_e \) enters the atomic unit
of energy through the expression \( \frac{\hbar^2}{2m_e} \sim \alpha^2 m_e \). The reduced mass \( M \) depends on the mass ratio \( \mu \) as,

\[
M \equiv A m_p \equiv \frac{A m_e}{\mu}
\]
Substituting this into Equation 1.16 with the appropriate algebra for a change of variables, the shift in the energy level due to a change in the mass ratio $\mu$ is given by

$$dE(v) = \sum_{i=1}^{\infty} Y_{i0}(v + 1/2)^i \frac{d\mu}{\mu}.$$  \hfill (1.18)

The Dunham expansion for the $X^1\Sigma_g^+$ state is known [14], so by using equation 1.16 we can extract the dependence of the singlet vibrational levels on $\mu$. This is shown in Figure 1.1. In the limit where the triplet state is assumed to have negligible dependence on the changes in $\mu$, Figure 1.1 also reflects the approximate changes in our experimental transition frequency for unit change in $\mu$.

From the Figure we can see that for levels close with binding energies $\lesssim 40$ cm$^{-1}$ below dissociation (corresponding to $v \approx 130$) in the singlet state, the sensitivity of the experiment is given by $\frac{dE}{d\mu} \sim 300$ cm$^{-1}$. We take this as our benchmark, since our collaborator E. Tiesinga has predicted a near-degeneracy between the singlet and the triplet at this binding energy. [ht]

![Figure 1.1: Variation of $dE_{X^1\Sigma_g^+}/d\mu$ vs. binding energy from the atomic asymptote. Levels near $v \equiv 130$ (B.E. $\sim 40$ cm$^{-1}$) move by about 300 cm$^{-1}$ for a unit change in $\mu$.](ht)

Next we explore the possible sensitivity of an experiment based on these levels. The $X^1\Sigma_g^+$ and
Figure 1.2: A schematic of the proposed scheme for enhanced sensitivity to $\frac{\partial \Delta E_{ab}}{\partial \mu}$. (a) A molecular potential well is schematically displayed with vibrational levels. The dependence of the $n^{th}$ vibrational energy on $\mu$ is displayed. (b) A schematic of the proposed measurement where vibrational levels from two overlapping electronic potentials are near-degenerate (as shown in the blown up portion). The experimental transition frequency $\nu_{exp}$ is much smaller than $E_n$. (c) In the case of Cs$_2$, the low-lying vibrational levels of the $a^3\Sigma^+_u$ state (with a shallower well like state B in (b)) and high-lying vibrational levels of the $X^1\Sigma^+_g$ state (with a deep well like state A in (b)) are near-degenerate.
$a^3\Sigma_u^+$ states of Cs$_2$ are long lived. In an experiment where the molecules freely fall through a region where an RF pulse driving the singlet-triplet transition is applied, we are likely to see a linewidth primarily determined by the free fall of the molecules. If we assume that the molecules fall about $d=10\,\text{cm}$ before they leave the detection volume, the time $t$ for which they are in the detection volume (assuming $g = 980\,\text{cm/s}^2$) is

$$t = \sqrt{2dg} = 0.14\,\text{s}. \quad (1.19)$$

We will see a linewidth in our RF transition (upto factors of order unity) of

$$\Delta(\nu_{exp}) \approx \frac{1}{2\pi t} \approx 1\,\text{Hz}. \quad (1.20)$$

Let us crudely estimate the possible sensitivity of a measurement based on this scheme in Cs$_2$. The current limits on $dp/\mu$ are $\sim 10^{-15}$ per year. Thus with $\frac{\partial \nu_{exp}}{\partial p} \sim 300\,\text{cm}^{-1} \sim 10^4\,\text{GHz}$, this would correspond to a shift in the line center of about $10^{-2}\,\text{Hz}$ per year. To improve this limit by a factor of 100 we require an average accuracy of about $10^{-4}\,\text{Hz}$. If for example, our transition frequency is $1\,\text{GHz}$, this would require us to maintain stability at the level of $10^{-13}$. This is well above the state-of-the-art stability $10^{-15}$ achieved by many atomic clocks [15]. If $\Delta \nu$ is the measured shift in the frequency of the experimental transition. Then for $N$ measurements of $\Delta \nu$, with a signal-to-noise $s_N$, the $\delta \nu$ is the desired precision of the experiment is given by $\delta \nu = \frac{\Delta \nu}{(s_N)^{1/2}N}$. If we have a 10% noise on each measurement, we will require $10^6$ measurements to reach our desired precision. At a repetition rate of 1 Hz, data corresponding to a single measurement of $\mu$ could be collected in a period of $\sim 20$ days. The same experiment would be repeated a year later and this would offer an estimate of the time variation of $\mu$ with an accuracy dramatically surpassing current limits.

Though the transition between a $^3\Sigma$ and a $^1\Sigma$ state seems ideal for this scheme, selection rules forbid it. However two effects break the selection rule; firstly hyperfine mixing between near-degenerate levels allows for M1 transitions and secondly fine structure mixes the $\Sigma$ states with higher $\Pi$ states and allows for E1 transitions (second-order spin-orbit mixing).

In sum, we would like to gain as much spectroscopic information about the triplet ground state of Cs$_2$ with the hope of either directly observing or predicting the position of a nearly degenerate pair of singlet and triplet levels in the ground state manifold of the Cs$_2$ molecule. This is the prime
motivation of for our spectroscopic study.

1.2 Photoassociation Spectroscopy

Precision spectroscopy of molecules is often limited by Doppler broadening and/or the large internal partition function of a molecular sample. These limitations can be overcome to a significant extent by cooling molecules [16].

Building on the success of cooling and trapping of atoms [17, 18, 19, 20], photoassociation is a robust technique to control the dynamics of atom-atom collisions. This controlled dynamics can be used to conduct spectroscopy of molecular bound states or to actually produce ultracold molecules (translational temperature $T \leq 1\text{mK}$). Photoassociation of cooled and trapped atoms through single and multi-photon transitions in particular has achieved great success in the study of ultracold dimers. Among the dimers that have been investigated with this technique are Li$_2$[21], Na$_2$[22], K$_2$[23], Rb$_2$[24], Cs$_2$ [2, 25], H$_2$ [26], He$_2$ [27], Ca$_2$[28], Yb$_2$[29], Sr$_2$[30], NaCs [31], KRb[32], and RbCs [33, 34, 35]. Photoassociation of ultracold molecules has opened the door to studies of long-range molecular states [36], and of quantum scattering properties [37]. Additionally experiments based on photoassociation techniques have been proposed to study molecular interferometry [38], highly-correlated quantum many-body states such as BCS-like superfluids [39], supersolid and checkerboard states, two-dimensional Bose metals [40], limited-dimensional gases [41], controlled ultracold chemical reactions [42, 43], scalable quantum computation [44] and tests of fundamental symmetries [45].

A Magneto Optical Trap (MOT) is typically used to produce a cold atomic sample (translational temperature $T \sim 100\mu\text{K}$). The kinetic energy of the atoms in such a sample is much smaller than the internal energy scales of the molecule (electronic, vibrational, fine-structure, hyperfine and rotational), and is comparable to the size of even smaller effects (AC/DC Stark shifts, electronic and nuclear Zeeman splitting, isotope shifts, centrifugal barriers, natural linewidth and pressure shifts or widths). This enables us to carry out detailed Doppler-free spectroscopy of molecular states.

In the photoassociation process cold molecules are formed in a short-lived excited state. These excited molecules can spontaneously decay back into free atoms, or into metastable ground state molecules. The translational temperature of the ground state molecules so formed is comparable to the colliding atoms. The transition rate from free atoms to metastable molecules depends on the
density of the atom cloud and/or the intensity and detuning of the photoassociation laser. Given the large number of atoms (~10^8 atoms) and high densities in the MOT (~10^{11} cm^{-3}), production of a large number of metastable molecules (~10^5 s^{-1}) has been demonstrated [1].

One notes however that while spontaneous emission does produce a sample of cold molecules, the excited state molecules decay to a mixture of ground states and hence spontaneous emission alone does not produce a large number of cold molecules in a single quantum state. To produce sizable numbers of translationally cold molecules in a state-selective fashion, one must start with a BEC of Cs and then use a combination of photoassociation and stimulated emission processes to coherently transfer population between the atomic and molecular states. Similar processes starting from an incoherent source of cold atoms like a MOT will be less effective at state-selective production. In our present experiment we are only exploring the spectroscopy of the states, although state-selective production of molecules is a natural extension of our work. In the following sections we discuss the basic ideas in single photon and two-photon photoassociation schemes.

### 1.2.1 Single color photoassociation

As shown in Figure 1.3, the basic photoassociation (PA) process involves a collision between two cold alkali atoms and a photon with energy \( h\nu_{PA} \). Neutral atoms in their ground state usually interact at long-ranges via a van der Waals force. This force is very weak and for the purposes of this discussion we can ignore it. The photoassociation light couples the ground-state free atoms \( A(ns) \) with an excited (short-lived) molecular state \( A2^+[\nu, J] \):

\[
A(ns) + A(ns) + h\nu_{PA} \rightarrow A2^+[\nu, J].
\] (1.21)

The potential curve associated with the excited molecular state \( A2^+ \) asymptotically dissociates into an atomic pair where at least one of the atoms is in an excited state, e.g. \( A(ns)A(np) \). The label \( \nu \) denotes the vibrational quantum number of the level and \( J \) is the rotational quantum number. This process of going from two free atoms to a molecular level in the excited state is referred to as free-bound excitation. As the temperature of the colliding atoms is small, and the photoassociation laser has a very small linewidth (~ 1 MHz), the rotational sub-structure can be resolved ensuring that only one particular \( J \) level is excited. The excited molecular state \( A2^+[\nu, J] \) formed usually has a lifetime comparable to the atomic state (~ 30 ns) and decays via spontaneous emission either to
free atoms (by emitting a photon of energy $\hbar \nu_{sp}$ or ground state molecules (by a photon of energy $\hbar \nu'_{sp}$). We summarize this process in the equations 1.22:

$$A_2^+[\nu, J] \rightarrow A(ns) + A(ns) + \hbar \nu_{sp},$$

$$A_2^+[\nu, J] \rightarrow A_2[\nu', J'] + \hbar \nu'_{sp}. \quad (1.22)$$

The free atoms formed from decay can have sufficient kinetic energy to actually leave the trap volume. This process of going from a single bound excited state molecular level to two free atoms is referred to as bound-free relaxation. The process of going from an excited molecular level to bound levels in the molecular ground state is referred to as bound-bound relaxation.

![Schematic of single-color photoassociation](image)

Figure 1.3: Schematic of single-color photoassociation. Potential curves are taken from Ref. [1]. Free atoms ($A(ns) + A(ns)$) are photoassociated into an excited rovibronic state $A_2^+[\nu, J]$ by a photon with energy $\hbar \nu_{PA}$, typically this occurs at large internuclear separation. The excited molecules $A_2^+[\nu, J]$ either emit a photon with energy $\hbar \nu_{SP}$ and decay back to hot free atoms, or emit a photon with energy $\hbar \nu'_{SP}$ and decay into ground state molecules $A_2[\nu', J']$.

In quantum mechanical terms, photoassociation can be described as follows. If $r$ is the inter-
nuclear separation between the atoms forming the molecule. The initial state of the atoms in the scattering process is $\Psi_s(r)$, a suitably symmetrized sum of products of atomic wavefunctions. The output state of this scattering process is $\Psi_e(r)$, a bound molecular level in the excited state. Molecular bound state wavefunctions are similar to the eigenfunctions of a harmonic oscillator, which for high-lying vibrational levels are peaked at the turning points of the potential well. The probability $P_{se}$ of the transition between the states is proportional to the Franck-Condon overlap integral:

$$P_{se} \propto \left( \int \Psi_s(r)\Psi_e(r)dr \right)^2. \quad (1.23)$$

As seen in Figure 1.3, the scattering atomic state wavefunction $\Psi_s(r)$ has a large overlap with the excited state wavefunction $\Psi_e(r)$ at the internuclear distance $R_P$. $R_P$ is the classical turning point of the bound molecular resonance. Photoassociation can only occur when the energy difference between the two free atoms and the metastable state is equal to the energy of the photon $h\nu_{PA}$. The photoassociation rate at such a resonance depends on $\Psi_s(R_P)$.

Other free atom states with kinetic energy $\varepsilon$ also have good overlap with $\Psi_e(r)$ in the region of $R_P$ and hence a considerable fraction of the excited state decays back to hot free atoms. For bound-bound relaxation, the transition probability between the excited state $\Psi_e(r)$ and the ground state with wavefunction $\Psi_g(r)$ is proportional to the bound-bound Franck-Condon factor:

$$P_{eg} \propto \left( \int \Psi_e(r)\Psi_g(r)dr \right)^2 \quad (1.24)$$

$R_C$ is the Condon radius, it is a classical turning point of the bound ground-state. The spontaneous decay from the excited-state to the bound ground-state occurs with the emission of a photon with energy $h\nu_{sp}$. The relaxation rate depends on the overlap between the ground state $\Psi_g(R_C)$ and the excited state $\Psi_e(R_C)$.

We have taken advantage of an unusual property of Cs$_2$ that gives very large bound-bound relaxation probabilities. In the case of Cs$_2$, a double-well occurs in the potential curve of the $0_g^-$ dissociating to the $6s_{1/2} + 6p_{3/2}$ threshold due to an avoided crossing with the $0_g^-$ dissociating to the $6s_{1/2} + 6p_{1/2}$ threshold [25]. The double-well structure allows for the build up of the wavefunction amplitude at some intermediate internuclear distance (i.e. between the long-range part of the molecular curve and the short-range repulsive wall). This allows us to have a good Franck-Condon factor for decay into $a^3\Sigma_u^+$ as shown in Figure 1.3 [2, 25]. The high Franck-Condon factor enables
us to use this state to access deeply-bound triplet ground state levels. Most excited state molecular potentials do not display such a double-well structure and hence do not decay with good probability into ground bound states. We note in passing that the double-well structure arises from an avoided crossing with another molecular curve. Both $0^+_g$ states arise due to the fact that spin-orbit interaction mixes the $3\Sigma^+_g$ and the $3\Pi_g$ states.

The value $R_P$ and $R_C$ are determined by the shapes of the excited and ground state molecular potentials. Most generally the long-range molecular potential curve $V(r)$ of the ground state is given by

$$V(r) = V_{vdw}(r) + V_{exchange}(r) + \frac{\hbar^2 l(l + 1)}{2\mu r^2}$$

In equation 1.25, $r$ is the internuclear separation. $V_{vdw}$ is the contribution of the van der Waals interaction terms, $V_{exchange}$ is the interaction energy due to the overlap of electron wavefunctions, $l$ is the relative angular momentum of the colliding atom pair and the last term represents the centrifugal potential.

As shown in Figure 1.4, at large internuclear separation ($\sim 100\ a_0$) the centrifugal term in the scattering potential dominates over other terms in Equation 1.25. Due to the low temperatures in the MOT, only low angular momentum pairs can cross the centrifugal barrier and make it to shorter separation where photoassociation to the states of interest occurs.

1.2.2 Two-color photoassociation

The transition between the excited bound state and the ground bound state described in the section above can also be stimulated with another photon ($h\nu_{probe}$). Such a stimulated transition can be used conduct spectroscopy of the ground state or to selectively populate a specific ground state. The idea was first implemented in the spectroscopic study of the scattering length of Li [21].

$$A(ns) + A(ns) + h\nu_{PA} \rightarrow A^*_2[\nu, J]$$

$$A^*_2[\nu, J] + h\nu_{probe} \rightarrow A_2[\nu', J']$$

For the purpose of spectroscopy, a standard way of implementing this two-photon transition process is to have a photoassociation laser fixed on a particular photoassociation resonance frequency. A second (probe) laser is then scanned across a bound-bound resonance, coupling the upper state of the photoassociation to a bound level of the ground state. The probe causes an Autler-Townes splitting.
Figure 1.4: The centrifugal barrier for the ground state of the Cs₂ molecule (See Eqn. 1.25). The value of $C_6$ taken is as $6836$ a.u [46], and the exchange energy is neglected as it is small compared to the barrier height. The barrier height varies with the angular momentum $l = 0, 1, 2, 3, 4$. 

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of the of the free-bound resonance. The Autler-Townes splitting causes the photoassociation to proceed at a lower rate. A schematic of the two-color photoassociation process used in our work is presented in Figure 1.5.

1.3 Study of Cs$_2$

As stated earlier our interest in the spectroscopy of the $a^3\Sigma_u^+$ state stems from a desire to measure the time variation of the electron-proton mass ratio, $\mu$. The potential curves associated with the $a^3\Sigma_u^+$ (triplet) state and the $X^1\Sigma_g^+$ (singlet) state both asymptotically dissociate to the $6s_{1/2} + 6s_{1/2}$ atomic limit. The low-lying vibrational levels of the $a^3\Sigma_u^+$ state and the high-lying vibrational levels of the $X^1\Sigma_g^+$ state can be nearly degenerate. The high-lying vibrational levels of the $X^1\Sigma_g^+$ have higher sensitivity to possible changes in $\mu$ than the low-lying vibrational levels of the $a^3\Sigma_u^+$ state. Thus a transition between a high-lying vibrational level of the $X^1\Sigma_g^+$ state and a near degenerate low-lying vibrational level of the $a^3\Sigma_u^+$ has enhanced sensitivity to possible changes in $\mu$. Mixing between the near degenerate levels of the $X^1\Sigma_g^+$ state and the $a^3\Sigma_u^+$ allows us to drive a microwave transition between them using the mixing-induced magnetic dipole amplitude. The transition will have narrow linewidth because both levels have long lifetimes. For sufficiently close levels, the transition frequency will lie in the microwave range. The shift in the center frequency of this transition gives us a measure of the variation in the electron-proton mass ratio. The objective of our study was to observe near-degenerate vibrational levels in the singlet and triplet states.

The single color photoassociation of Cs$_2$ used in this work can be summarized as,

$$\text{Cs}(6s) + \text{Cs}(6s) + h\nu_{PA} \rightarrow \text{Cs}_2^+\left[0_0^+(6s_{1/2} + 6p_{3/2}; \nu, J)\right].$$  \hfill (1.28)

Here we use the standard molecular notation $\Omega_{g/u}^{+/−}$ to describe a molecular state in Hund's Case (c). $\Omega$ is the projection of total angular momentum of the state on the internuclear axis. The letter $g/u$ denotes the symmetry of the electronic wavefunction about a plane perpendicular to the internuclear axis. The symmetry of the electronic wavefunction remains either unchanged (even/gerade“$g$”) or only changes sign (odd/ungerade/“$u$”) when reflected through this plane. For states with $\Omega = 0$, it is also necessary to indicate the symmetry of the electronic wavefunction about a plane containing the internuclear axis. This symmetry is denoted by the superscript $+/−$ indicating whether the wavefunction does/does not change sign upon reflection through a plane.
Figure 1.5: Schematic of two-color photoassociation used in our experiment. We use the photoassociation laser with energy $h\nu_{PA}$ to make excited state Cs$_2$ molecules. Some fraction of these molecules spontaneously decay into metastable high-lying vibration levels in ground state of Cs$_2$ (labeled (1)). The molecules in this high-lying vibrational levels of the ground state are ionized by the laser with energy $h\nu_{ion}$. The probe laser with energy $h\nu_{probe}$ causes an Autler-Townes splitting of the excited state peak when it comes into resonance with a bound-bound transition from the excited state to a deeply bound vibrational level (labeled (2)) in the ground state. The splitting of the free-bound transition peak disrupts the usual decay into the high-lying ground states and causes a depletion in the Cs$_2^+$ ions produced by the ionization laser.
containing the internuclear axis. The label $\nu$ denotes the vibrational quantum number of the level and $J$ is the rotational quantum number. The $6s_{1/2} + 6p_{3/2}$ denotes that this level dissociates to those particular atomic states.  As stated earlier the excited state molecules decay via spontaneous emission into either free atoms or ground state molecules.

$$\text{Cs}_2^*[0_g^- (6s_{1/2} + 6p_{3/2}); \nu, J] \rightarrow \text{Cs}(6s) + \text{Cs}(6s) + \hbar \nu,$$  \hspace{1cm} (1.29)$$

$$\text{Cs}_2^*[0_g^- (6s_{1/2} + 6p_{3/2}); \nu, J] \rightarrow \text{Cs}_2[a^3\Sigma_u^+; \nu', J'] + \hbar \nu'. \hspace{1cm} (1.30)$$

The method we use to detect photoassociation is to ionize the ground state molecules formed in the bound-bound relaxation process using multi-photon transitions, and collect the subsequent molecular ions. This processes can be summarized as

$$\text{Cs}_2[a^3\Sigma_u^+; \nu', J'] + n_1 \hbar \nu_{\text{ion}} \rightarrow \text{Cs}_2^+(\nu_1, J_1) + e^-, \hspace{1cm} (1.31)$$

here $\hbar \nu_{\text{ion}}$ is the photon energy required for multi-photon ionization. Figure 1.6(b) shows the details of the ionization scheme used in our experiment.

When used in conjunction with a specific resonance in the photoassociation process, we can conduct spectroscopy of the Cs$_2$ in the $a^3\Sigma_u^+$ state by carefully scanning $\nu_{\text{probe}}$. As explained in the section on two-color photoassociation, $\nu_{\text{probe}}$ will couple the $[0_g^- (6s_{1/2} + 6p_{3/2}); \nu, J]$ state with a bound level in the ground state and this will split the photoassociation resonance. We choose a particular rovibrational level of the $0_g^- (6s_{1/2} + 6p_{3/2})$ to photoassociate to, and then we scan $\nu_{\text{probe}}$ over a frequency range that our collaborator E. Tiesinga’s theoretical calculations indicate should be appropriate to drive bound-bound resonances. The two-color spectroscopy can be described as

$$\text{Cs}(6s) + \text{Cs}(6s) + h\nu_{PA} \rightarrow \text{Cs}_2^*[0_g^-; \nu, J]; \hspace{1cm} (1.32)$$

$$\text{Cs}_2^*[0_g^-; \nu, J] + h\nu_{\text{probe}} \rightarrow \text{Cs}_2[a^3\Sigma_u^+; \nu', J']; \hspace{1cm} (1.33)$$

Photoassociation of Cs was theoretically treated in Ref. [47]. Observations of peaks corresponding to $0_g^- [2, 25]$ and $1_u[1]$ (dissociating to the $6s_{1/2} + 6p_{3/2}$ threshold) in ion spectra pointed to the presence of favorable decay channels from these states into the $a^3\Sigma_u^+$ and the $X^1\Sigma_g^+$ ground states. This suggested that these excited states had a double-well structure. Trap-loss studies also displayed the presence of levels corresponding to $0_g^- , 0_u^+, 1_g (6s_{1/2} + 6p_{3/2})$ states [48]. The shapes
of the relevant potential curves are shown in Figure 1.6(a). The existing data on these Cs$_2^+$ states enabled the prediction of Franck Condon factors for decays to the $^3\Sigma_u^+$ and $^1\Sigma_u^+$ states [49].

Two-color spectroscopy of weakly-bound levels of Cs$_2$ was previously carried out in other labs [50]. These experiments used only photoassociation resonances in the $1_u$ ($6s_1/2 + 6p_3/2$) state and the ground states were probed from dissociation down to binding energies of a few cm$^{-1}$. Our work represents an extension of these previous determinations of ground state energy levels, to states that are much more deeply bound (with binding energy as large as $\sim 50$ cm$^{-1}$). Such spectroscopy improves the understanding of the Cs$_2$ ground state manifold in the region of most interest for experiments sensitive to a change in $\mu$. 

Figure 1.6: Potential curves of the cesium dimer, reproduced from Ref. [2]. The schemes for photoassociation and ionization used in Ref [2] were also used in our experiment. (a) potential curves relevant to photoassociation. (b) curves relevant to ionization.
Chapter 2

Theoretical overview

In this chapter we examine the theoretical considerations that guided various parts of the experiment. Our discussion initially focusses on key concepts in molecular physics, and how these relate to the states we use in our spectroscopy. We discuss a theoretical calculation of the $a^3\Sigma_u^+$ state's structure that serves as the starting point for the spectroscopic investigation. We also cover the selection rules and angular-factor calculations which influenced our choice of key experimental parameters.

2.1 General introduction to the structure of the diatomic molecule

If we consider a diatomic molecule with no internal angular momentum then we can resolve its motion into two parts, the motion of the center of mass and the motion relative to the center of mass. The center of mass motion is described in a coordinate system oriented to some arbitrary point in space (space-fixed coordinates) and the motion relative to the center of mass is most conveniently described in a reference frame attached to the internuclear axis (body-fixed coordinates). For the purpose of this discussion we use the following notation: $\hat{Y}$ is a vector and $Y = |\hat{Y}|$ is its magnitude.

We can represent the Hamiltonian of the molecule $H_{Mol}$ as

$$H_{Mol} = H_{CM}(\vec{X}) + H_0(\vec{r}_e, \vec{R}).$$

(2.1)

Here $\vec{X}$ is the position of the molecule's center of mass in a space-fixed coordinate system, $\vec{r}_e$ is the
position of the electrons, relative to the center of mass in the body-fixed coordinate system and $\vec{R}$ is the internuclear separation in the body-fixed coordinates. $H_{CM}(\vec{X})$ is the Hamiltonian describing the center of mass motion; for a molecule of reduced mass $M$ moving in free space,

$$H_{CM}(\vec{X}) = -\frac{\vec{P}_X^2}{2M}. \quad (2.2)$$

Here $\vec{P}_X$ is the canonical momentum corresponding to $\vec{X}$. $H_0$ is the Hamiltonian describing the motion relative to the center of mass and it can be written as:

$$H_0(\vec{r}_e, \vec{R}) = H_E(\vec{r}_e, \vec{R}) + H_N(\vec{R}), \quad (2.3)$$

where

$$H_E(\vec{r}_e, \vec{R}) = \sum_i \frac{\vec{p}_i^2}{2m_i} + V_E(\vec{r}_e, \vec{R}), \quad (2.4)$$

$$H_N(\vec{R}) = \sum_k \frac{\vec{p}_k^2}{2M} + V_N(\vec{R}). \quad (2.5)$$

In the equations above, $\vec{p}_i$ and $\vec{p}_k$ are the momentum operators corresponding to the electronic and nuclear motion respectively, $H_E(\vec{r}_e, \vec{R})$ is the electronic Hamiltonian, $H_N(\vec{R})$ is the nuclear Hamiltonian, $V_E(\vec{r}_e, \vec{R})$ is the electronic potential energy, $V_N(\vec{R})$ is the nuclear potential energy (repulsive), the index $i$ denotes summation over all electrons, and the index $k$ denotes summation over all nuclei. If we neglect spin-orbit and other relativistic effects, the electronic potential energy $V_E(\vec{r}_e, \vec{R})$ can be written as

$$V_E(\vec{r}_e, \vec{R}) = -\sum_{k=1,2} \sum_i \frac{Z_k e^2}{|\vec{r}_{ik}|} + \sum_{i>j} \frac{e^2}{|\vec{r}_{ij}|}. \quad (2.6)$$

Here $Z_k$ is the atomic number of nucleus $k$, $|\vec{r}_{ik}|$ is the position of the $i^{th}$ electron with respect to nucleus $k$ in the body-fixed coordinate system and $\vec{r}_{ij}$ is the relative position of two electrons $i$ and $j$ in the body-fixed coordinate system.

The nuclear repulsive potential $V_N(\vec{R})$ can be written as,

$$V_N(\vec{R}) = \frac{Z_1 Z_2 e^2}{\vec{R}}, \quad (2.7)$$
where $Z_1$ and $Z_1$ are the atomic numbers of the two nuclei in the molecule. In the Born-Oppenheimer approximation (or the adiabatic approximation) we neglect the coupling of the electronic and nuclear motions. Thus it is possible to write the molecular wavefunction $\Psi$ as:

$$\Psi = \Psi_e(\vec{r}_e)\Psi_N(\vec{R}),$$  \hspace{1cm} (2.8)

where $\Psi_e(\vec{r}_e)$ is the electronic part and $\Psi_N(\vec{R})$ is the nuclear part. $\Psi_e(\vec{r}_e)$ can be obtained by solving the electronic Schrödinger wavefunction,

$$(H_E(\vec{r}_e, \vec{R}) + V_N(R))\Psi_e(\vec{r}_e) = E_e \Psi_e(\vec{r}_e),$$  \hspace{1cm} (2.9)

For a given nuclear configuration the nuclear potential $V_N(R)$ is a constant and hence the eigenenergy of the electronic wavefunction $E_e$, is a function of the internuclear separation $R$. Together with $V_N(R)$ it defines an effective potential $U(R)$ for the nuclear motion.

$$U(R) = E_e(R) + V_N(R).$$  \hspace{1cm} (2.10)

The nuclear part of the molecular wavefunction, $\Psi_N(\vec{R})$ can then be obtained by solving the nuclear Schrödinger equation,

$$H_N \Psi_N(\vec{R}) = \left( -\frac{\hbar^2}{2} \sum_k \frac{1}{M_k} \nabla_k^2 + U(R) \right) \Psi_N(\vec{R}) = E \Psi_N(\vec{R})$$  \hspace{1cm} (2.11)

Equation 2.11 is a central-force problem and hence the radial ($R$) and angular ($\theta, \phi$) degrees of freedom are de-coupled. The radial motion of the two nuclei along the internuclear axis corresponds to vibration, and the angular motion of the two nuclei corresponds to rotation of the molecule about an axis perpendicular to the internuclear axis. We can therefore write the Hamiltonian of the nuclear motion as,

$$H_N(R) = -\frac{\hbar^2}{2M_r} \left( \frac{\partial^2}{\partial R^2} + \frac{2}{R} \frac{\partial}{\partial R} \right) + U(R) + \frac{l(l+1)}{2M_r R^2}$$  \hspace{1cm} (2.12)

where $l$ is the relative angular momentum of the two nuclei, and $M_r$ is the reduced mass of the molecule. If we neglect the interaction between vibration and rotational motion of the nuclei, we
can write the nuclear wavefunction as,

$$\Psi_N(\vec{R}) = \frac{1}{R} \Psi_\nu(R) Y_l^m(\theta, \phi),$$  \hspace{1cm} (2.13)

where $\Psi_\nu(R)$ represents the radial wavefunction of the nuclei and $Y_l^m(\theta, \phi)$ represents the angular wavefunction.

By applying the separation of variables process, we can get the eigenenergies of angular wavefunction

$$E_{\text{rot}} = l(l+1)\hbar B_e,$$  \hspace{1cm} (2.14)

where $B_e = \frac{\hbar}{8\pi^2 I_e}$,  \hspace{1cm} (2.15)

and $I_e = M_r v_e^2$.  \hspace{1cm} (2.16)

and the radial wavefunction can be obtained by the solution to the equation,

$$-\frac{\hbar^2}{2M_r} \frac{d^2}{dR^2} \Psi_\nu(R) + \left[-\frac{l(l+1)}{2M_r R^2} + E - U(R)\right] \Psi_\nu(R) = 0$$  \hspace{1cm} (2.17)

The eigenenergy of the radial wavefunction $\Psi_\nu(R)$ in the harmonic approximation is

$$E_\nu = \nu \hbar \omega_e$$  \hspace{1cm} (2.18)

In the molecular states of interest to this experiment the interaction energy $U(R)$ is approximated by a multipolar expansion

$$U(R) = D_e - \sum_n \frac{C_n}{R^n} \hspace{1cm} n = 1, 2, 3...$$  \hspace{1cm} (2.19)

where, $D_e$ is the dissociation energy of the molecule, and the $C_n$ are long-range coefficients.

The total energy of the molecular state neglecting relativistic effects is roughly given by

$$E = T_e + \nu \hbar \omega_e + l(l+1)\hbar B_e,$$  \hspace{1cm} (2.20)

where $T_e = U(R_e)$.  \hspace{1cm} (2.21)

Here $R_e$ is the equilibrium separation of the molecule. The typical energy scales in the diatomic molecule are $T_e \sim 10,000$ cm\(^{-1}\), $\hbar \omega_e \sim 100$ cm\(^{-1}\) and $B_e \sim 1$ cm\(^{-1}\). As we go towards larger inter-
nuclear separations, the vibrational structure shows a marked departure from harmonic behavior and anharmonic terms have to be considered. Figure 2.1 gives us a visual comparison of these three energy scales.

The total eigenfunction of the molecular state $\Psi$ has the following symmetries:

- **Parity:** This is the symmetry with respect to coordinate inversion. A molecular eigenfunction is said to be negative (positive) if it does (not) change sign upon inversion of coordinates. As the vibrational wavefunction $\Psi_v$ depends only on the magnitude of $R$, the overall parity of the eigenfunction is determined by $\Psi_e$ (electronic) and $Y_l^m(\theta, \phi)$ (rotational).

- **In the case of a homonuclear diatomic molecule, a molecular eigenfunction is said to be anti-symmetric “a” (symmetric “s”) if it does (not) change sign upon exchange of nuclei.**

The diatomic molecular states of interest to us are complicated by the presence of internal angular momenta. These angular momenta can be described using the following quantum numbers:

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24

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1. $\vec{L} = \vec{L}_1 + \vec{L}_2$, the total orbital angular momentum which is the sum of the individual electron orbital momenta $\vec{L}_1$ and $\vec{L}_2$;

2. $\Lambda$, the projection of $\vec{L}$ on the internuclear axis;

3. $\vec{S} = \vec{S}_1 + \vec{S}_2$, the total spin which is the sum of the individual electron spins $\vec{S}_1$ and $\vec{S}_2$;

4. $\Sigma$, the projection of $\vec{S}$ on the internuclear axis; and

5. $\vec{I} = \vec{I}_1 + \vec{I}_2$, the total nuclear spin which is the sum of the individual nuclear spins $\vec{I}_1$ and $\vec{I}_2$.

The nuclear spin has a pronounced effect on the overall symmetry of the molecule. The total wavefunction $|\Psi_{\text{mol}}\rangle$ of a diatomic molecule with nuclear spin included can be written as [3]

$$|\Psi_{\text{mol}}\rangle = \Psi \Psi_I,$$  \hspace{1cm} (2.22)

here $\Psi$ is given by Equation 2.8 and $\Psi_I$ is the nuclear spin wavefunction. In the case of Cs$_2$, the nuclei are fermions with $I_1 = I_2 = (7/2)$. Thus the overall eigenfunction $|\Psi_{\text{mol}}\rangle$ must be antisymmetric under exchange of nuclei.

Depending on the angular momentum coupling we have different ways of representing the angular momentum part of the molecular wavefunction. These are called the Hund's cases for angular momentum. There are two Hund's cases of interest to us (see also figure 2.2):

1. Hund's case (b): Where $\Lambda = 0$, and $\vec{S}$ is only weakly coupled to the internuclear axis. Here the states are labeled as $2S+1\Sigma$, where the letter $\Sigma$ represents $\Lambda = 0$. This is the case for the a$^3\Sigma^+_u$ state studied here.

2. Hund's case (c): Where the electronic spin-orbit coupling is stronger than the coupling of the electronic angular momenta to the internuclear axis. Here rather than $\vec{L}$ and $\vec{S}$, the appropriate quantum numbers for each electron are $\vec{J}_1 = \vec{L}_1 + \vec{S}_1$ and $\vec{J}_2 = \vec{L}_2 + \vec{S}_2$ where 1, 2 represent the two valence electrons in Cs$_2$. The total electronic angular momentum $\vec{J}_e = \vec{J}_1 + \vec{J}_2$ couples to the internuclear axis, with projection $\Omega$. The states are labeled simply by $\Omega$.

The electronic wavefunction $\Psi_e$ has the following additional symmetries (see Figure 2.2):

1. Symmetry with respect to a plane through the axis of the molecule. This symmetry is identified by attaching the superscript "\(^+\)" or "\(^-\)" after the state, e.g. $^3\Sigma^+$. A "\(^+\)" symmetry
state does not change sign and a "-" symmetry state does change sign upon inversion about
the plane.

2. Symmetry with respect to a plane perpendicular to the axis of the molecule. This symmetry
is identified by attaching the subscript "g" or "u" after the state. Eg \(^3\Sigma_g\). A "g" or gerade
symmetry state does not change sign and a "u" or ungerade symmetry state changes sign
upon inversion about the plane.

Thus, the electronic wavefunction in Hund’s case (b) can be labeled as \(^{2S+1}A^+\) and a Hund’s
case (c) wavefunction can be labeled as \(\Omega^+/\Omega^-\).

Based on these considerations, we can write the parity and symmetry of the overall wavefunction.
The total parity is given by

\[
P_{\text{wavefunction}} = P_{\text{electronic}} \times P_{\text{rotation}}. \tag{2.23}
\]

The parity of a rotational wavefunction \(\Psi_r\) with quantum number \(l\) is given by,

\[
P_{\text{rotation}} = (-1)^l. \tag{2.24}
\]

The parity of each electronic wavefunction \(\Psi_e\) depends on the orbital angular momentum \(\Omega\) or \(\Lambda\),
and the \(g/u\) symmetry as shown in Table 2.1.

<table>
<thead>
<tr>
<th>(\Psi_e)</th>
<th>(l) even</th>
<th>(l) odd</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Sigma_g^+)</td>
<td>(+,s)</td>
<td>(-,a)</td>
</tr>
<tr>
<td>(\Sigma_u^+)</td>
<td>(+,a)</td>
<td>(-,s)</td>
</tr>
<tr>
<td>(\Sigma_g^-)</td>
<td>(-,a)</td>
<td>(+,s)</td>
</tr>
<tr>
<td>(\Sigma_u^-)</td>
<td>(-,s)</td>
<td>(+,a)</td>
</tr>
</tbody>
</table>

Table 2.1: A table summarizing the symmetries of the electronic state and the rotational state
reproduced from Ref. [3]. The column marked “\(\Psi_e\)" is the electronic state and the columns on the
right list the symmetries of the wavefunction for even and odd \(l\) (rotational quantum number). The
table is read as follows: An electronic state labeled \(\Sigma_g^+\) with even rotational angular momentum \(l\)
has an overall "+" symmetry and is "s(symmetric)" upon exchange of nuclei. The symmetries of
Hund’s case (c) molecular states are obtained from this table by replacing \(\Lambda\) (here \(\Lambda = 0\) labeled
as \(\Sigma\)) with \(\Omega\) (here \(\Omega = 0\)). For example the Hund’s case (c) state 0\(^-\_\) with \(l\) even has an overall
symmetry of "-" and is anti-symmetric under the exchange of nuclei.

Next we consider contributions to the molecular energies due to couplings between various
angular momenta. In our states, these include spin-orbit interaction (described by \(H_{SO}\), spin-spin
Figure 2.2: Hund’s cases of interests and symmetries of the molecule. (A) Hund’s case (b); Here \( \Lambda = 0 \), and \( \vec{J} = \vec{L} + \vec{S} \) (\( \vec{J} \) is the total electron angular momentum), \( \vec{L} \perp \hat{n} \) and \( \vec{S} \) is decoupled from \( \hat{n} \) (B) Hund’s case (c), \( \vec{L} + \vec{S} = \vec{J}_e \) for each atom, \( \vec{J}_e \) has a projection \( \vec{\Omega} \) on the internuclear axis, and \( \vec{J} = \vec{\Omega} + \vec{I} \) (\( \vec{J} \) is the coupling of the total electron angular momentum and rotation angular momentum), (C) \(+/-\) symmetry, under reflection through a plane through internuclear axis, and (D) \( g/u \) symmetry about plane perpendicular to internuclear axis.

interaction (\( H_{SS} \)), and hyperfine interaction (\( H_{HFS} \)) [51, 13]:

(HSO)

\[
H_{SO} = \sum_i V^{SO}_i \vec{L}_i \cdot \vec{S}_i
\]  

(2.25)

HSS

\[
H_{SS} = \sum_{i,j} V^{SS}_{ij} \vec{S}_i \cdot \vec{S}_j
\]  

(2.26)

HFS

\[
H_{HFS} = \sum_{i,k} a I_{iz} L_{iz} + b \vec{I}_k \vec{S}_i + c I_{kz} S_{iz}
\]  

(2.27)

where the indices \( i, j \) are for the electrons, \( k \) is for the nuclei, \( \vec{S}_i \) and \( \vec{L}_i \) are the spin and the orbital angular momentum of the \( i^{th} \) electron respectively and \( S_{iz} \) is the projection of the spin on the internuclear axis. \( V^{SO}_i \) and \( V^{SS}_i \) are the \( R \)-dependent coupling coefficients. \( \vec{I}_k \) is the nuclear spin of each nucleus, \( I_{kz} \) is its \( z \)-component, and \( a, b, c \) are \( R \)-dependent constants [52, 53].

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2.2 Molecular states used in our spectroscopy

Our spectroscopy requires a closer inspection of the following states: the $0_g^-$ state dissociating to the $6s_{1/2} + 6p_{3/2}$ threshold; the $a^3Σ_g^+$ (triplet) and $X^1Σ_g^+$ (singlet) states both of which dissociate to the $6s_{1/2} + 6s_{1/2}$ threshold; and the free (scattering) state of the atoms above the $6s_{1/2} + 6s_{1/2}$ threshold. In the notation used here, the projection of the quantum numbers in kets are defined in either a space-fixed (SF) or body-fixed (BF) coordinate system.

2.2.1 The $0_g^-$ ($6s_{1/2} + 6p_{3/2}$) state

In Hund's case (c) notation, $0_g^-$ represents a state with projection of electronic angular momentum $\Omega=0$. The $0_g^-$ ($6s_{1/2} + 6p_{3/2}$) and the $0_g^-$ ($6s_{1/2} + 6p_{1/2}$) states arise due to mixing of the $3Σ_g^+$ and the $3Π_g$ short-range (Hund's case (a)) states. Due to spin-orbit interaction, the two resultant curves repel each other [2, 25]. Due to this repulsion, the $0_g^-$ ($6s_{1/2}6p_{3/2}$) state has a double-well structure.

Extensive spectroscopy of this outer well exists, yielding a precisely fitted potential curve [2, 25]. This enabled the calculation of Franck-Condon factors for decay into the ground state manifold.

The nuclear spin-statistics connection demands that the overall eigenfunction corresponding to the $0_g^-$ ($6s_{1/2} + 6p_{3/2}$) be anti-symmetric under exchange of nuclei. For the $0_g^-$ ($6s_{1/2} + 6p_{3/2}$) state, the angular momenta couple in the following fashion:

$$\bar{I} = \bar{I}_1 + \bar{I}_2 = \frac{7}{2} + \frac{7}{2} = 7, 6, ..., 0;$$
$$\bar{J}_e = \bar{J}_{1e} + \bar{J}_{2e} = \frac{1}{2} \oplus \frac{3}{2} = 2, 1;$$
$$\rightarrow \Omega = 0 \quad (2.28)$$

For the $0_g^-$ ($6s_{1/2} + 6p_{3/2}$) state since the binding energies of the levels are much smaller than the atomic electronic $e$ splitting, the total electronic orbital angular momentum $\bar{L} = \bar{L}_1 + \bar{L}_2$ is still a good quantum number,

$$\bar{L} = \bar{L}_1 + \bar{L}_2 = 1 \oplus 0 = 1 \quad (2.30)$$

The $0_g^-$ ($6s_{1/2} + 6p_{3/2}$) state can only arise from linear combinations of $3Σ_g^+$ state and a $3Π_g$ state at short-range. This implies that $S=1$ is a well-defined quantum number. We surmise that $\bar{L}$ and $\bar{S}$ add to give us a angular momentum $\bar{J}_e = \bar{L} + \bar{S} = 1 \oplus 1 = 2, 1$ that is perpendicular to the internuclear axis $\hat{n}$.
Now we can write a quantum number $\mathbf{J} = \mathbf{L} + \mathbf{S} + \mathbf{I}$ describing the total angular momentum of $[0_g^- (6s_{1/2} + 6p_{3/2}); \nu, J]$ state. Finally the total angular momentum of the $0_g^- (6s_{1/2} + 6p_{3/2})$ state is written as

$$\mathbf{F} = \mathbf{J} + \mathbf{I}$$

(2.31)

Since $\Omega = 0$, there is no hyperfine interaction in this state and $\mathbf{I}$ and $\mathbf{J}$ are completely decoupled. By reading the appropriate row in Table 2.1 we observe the correlation between allowed rotational and nuclear spin states shown in Table 2.2. Bose symmetry for a $0_g^-$ state ensures that $F = J + I$ is odd. For example, for $I=$even(odd), Table 2.2 tells us that $I$ can only odd(even) values. For a state with $\tilde{\Omega} = 0$ (where $J = L$) the sum $F = I + J$ is always odd.

<table>
<thead>
<tr>
<th>1</th>
<th>Permitted $I$</th>
<th>Total Parity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Even (+;a)</td>
<td>$I = 7, 5, 3, 1$</td>
<td>$-1^{I+1}$</td>
</tr>
<tr>
<td>Odd (+;s)</td>
<td>$I = 6, 4, 2, 0$</td>
<td>$-1^I$</td>
</tr>
</tbody>
</table>

Table 2.2: A table summarizing the parity and the permitted nuclear spin components for the $0_g^- (6s_{1/2} + 6p_{3/2})$ state.

In order to calculate the transition dipole matrix elements, it is convenient to cast the wavefunction of the $0_g^- (6s_{1/2} + 6p_{3/2})$ state into a basis set of space fixed-quantum numbers. The wavefunction $|e\rangle$ of the rovibrational state $\nu, J$ of the $0_g^-$ state can be written as

$$|e\rangle = |0_g^- \nu J M I M_I\rangle = \xi_{\nu J}(R)\sqrt{\frac{2J + 1}{4\pi}} D_{M0}^{J*}(\phi, \theta, 0)|0_g^-; R\rangle_{BF} \times |IM_I\rangle_{SF}$$

$$= \xi_{\nu J}(R)Y_{JM}(\theta \phi)|0_g^-; R\rangle_{BF}|IM_I\rangle_{SF},$$

(2.32)

Here $D_{M0}^{J*}$ is a Wigner rotation matrix, which describes the transformation of the body-fixed wavefunction into space-fixed coordinates; $|0_g^-; R\rangle_{BF}$ is the $R$-dependent electronic wavefunction of the $0_g^-$ state in the body-fixed frame; and $\xi_{\nu J}(R)$ is the radial wavefunction. This model assumes that the nuclear spin $I$ is just a spectator. The energy of the states is given by $E = B_{\nu J}(J + 1)$ and is independent of the nuclear spin. The $R$-dependent electronic wavefunction $|0_g^-; R\rangle_{BF}$ is determined by the spin-orbit mixing between the two $0_g^-$ states described using the Movre-Pichler model [54],

$$|0_g^-; R\rangle_{BF} = \sum_{\ell} a_{\ell}(R)|L_{\ell}A_{\ell}S_{\ell}\rangle_{BF}.$$  

(2.33)

Here the electronic orbital angular momentum $L = 1$ and the states $|L_{\ell}A_{\ell}S_{\ell}\rangle_{BF}$ are the Hund’s
case (a) \(^{2S+1} \Lambda_g\) electronic states. For the 0\(^{-}\) state the sum can be approximated by just two terms:

\[
|0^{-}; R\rangle_{BF} = a_\Pi(R) \left\{ \frac{|111 - 1\rangle_{BF} + |1 - 111\rangle_{BF}}{\sqrt{2}} \right\} + a_\Sigma(R)|1010\rangle_{BF},
\]

i.e. a linear combination of one \(^3\Pi_g\) state and one \(^3\Sigma^+_g\) state. The coefficients \(a_\Pi(R)\) and \(a_\Sigma(R)\) are the eigenfunctions of the matrix describing the mixing of the \(^3\Pi\) and \(^3\Sigma^+\) states [54],

\[
V_{MP} = \begin{pmatrix}
\frac{\sqrt{3} \Delta}{3} & -\frac{2 \Delta}{3} \\
\frac{\sqrt{3} \Delta}{3} & -\frac{\sqrt{3} \Delta}{3} - \frac{3 \Delta}{2}
\end{pmatrix}
\]

Here \(\Delta\) is the atomic p-state spin-orbit splitting and the zero of the energy is set at the \(s_{1/2} + p_{3/2}\) asymptote. In the long range state, \(C_3/R^3\) is much smaller than the atomic spin-orbit splitting. If we neglect the terms dependent on \(C_3\) in \(V_{MP}\), the eigenvectors of this approximate \(V_{MP}\) give us \(a_\Pi(R) = \frac{1}{\sqrt{3}}\) and \(a_\Sigma(R) = \frac{\sqrt{2}}{3}\). The product of three Wigner rotation matrices \((D_{\lambda \lambda, M_{\lambda \lambda}}^L D_{M_{\lambda \lambda}, M_{\lambda \lambda}}^S D_{M_{\lambda \lambda}, M_{\lambda \lambda}}^T)\) yields \(D_{\lambda \lambda}^T Y_{\lambda \lambda}(\theta \phi)\) to the wavefunction and thus the entire state may then be written in space-fixed coordinates as

\[
|e\rangle = \xi_{\nu J}(R) \sum_{M_{\lambda \lambda}, M_{\lambda \lambda}} \left[ c_{i, \Pi}^{J M_{\lambda \lambda}, M_{\lambda \lambda}} \sqrt{2} a_\Pi(R) + c_{i, \Sigma}^{J M_{\lambda \lambda}, M_{\lambda \lambda}} \sqrt{2} a_\Sigma(R) \right] Y_{\lambda \lambda}(\theta \phi)|1M_{\lambda \lambda}, 1M_{\lambda \lambda}\rangle_{SF},
\]

where

\[
c_{i, \Lambda}^{J M_{\lambda \lambda}, M_{\lambda \lambda}} = \sum_{l} \sqrt{\binom{2J + 1}{2l + 1}} \times (-1)^m \sum_{j} (2j + 1) \begin{pmatrix}
1 & 1 & j \\
M_{\lambda \lambda} & M_{\lambda \lambda} & -m_j
\end{pmatrix} \begin{pmatrix}
1 & 1 & j \\
\Lambda & -\Lambda & 0
\end{pmatrix}
\times \begin{pmatrix}
J & j & l \\
M & -m_j & -m
\end{pmatrix} \begin{pmatrix}
J & j & l \\
0 & 0 & 0
\end{pmatrix}.
\]

Here \(m = M - M_{\lambda \lambda} - M_{\lambda \lambda}\) and \(m_j = M_{\lambda \lambda} + M_{\lambda \lambda}\), and the quantities in the brackets are 3-j symbols.

### 2.2.2 The \(^a^3\Sigma^+_u\) state

In Hund's case (b) notation, \(^3\Sigma^+_u\) represents a state with \(\Lambda = 0\). As there is no projection of the
electronic angular momentum along the internuclear axis, the total electron spin \( \vec{S} \) is uncoupled from the internuclear axis and we have no first-order spin-orbit effects. As we are in a triplet state, with \( S = 1 \), coupling between the electron spin \( \vec{S} \) and the nuclear spin \( I \) and this leads to pronounced hyperfine structure. The coupling of the nuclear spin \( I \) is described per case by \[ \text{(2.39)} \]

with good quantum numbers given by

\[
\begin{align*}
I &= I_1 + I_2 = \frac{7}{2} + \frac{7}{2} = 7, 6, ..., 0; \\
\vec{S} &= 1; \\
\vec{f} &= I + \vec{S} = 8, 7, 6, ..., 0; \\
\vec{F} &= \vec{f} + \vec{I}
\end{align*}
\]

To first approximation, \( \vec{f} \) is decoupled from the internuclear axis. In this approximation a state with quantum numbers \( I, S, f, I, F \) has an energy due to hyperfine structure and rotation given by

\[
E(I, S, f, I, F) = B_\alpha l(l + 1) + \frac{A_{HF}}{4} \{f(f + 1) - S(S + 1) - I(I + 1)\}
\]

where \( B_\alpha \) is the rotational constant for this state and \( A_{HF} \) is the Cs atomic hyperfine splitting.

By reading the appropriate row in Table 2.1 we observe the following correlation between the parity, the rotational angular momentum \( l \), and the nuclear spin \( I \).

<table>
<thead>
<tr>
<th>( I )</th>
<th>Permitted ( I )</th>
<th>Parity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Even (+,a)</td>
<td>( f = 7, 5, 3, 1 )</td>
<td>(-1^l)</td>
</tr>
<tr>
<td>Odd (-,s)</td>
<td>( f = 6, 4, 2, 0 )</td>
<td>(-1^{l+1})</td>
</tr>
</tbody>
</table>

Table 2.3: A table summarizing the parity and the permitted nuclear spin components for the \( a^3\Sigma_u^+ \) state.

In addition to the hyperfine splitting, second-order spin-orbit effects also give substantial energy shifts in the \( a^3\Sigma_u^+ \) state. Spin-orbit coupling mixes the \( ^3\Sigma \) state with higher lying \( \Pi \) states, which leads to shifts in the \( a^3\Sigma_u^+ \) state that are second-order in \( H_{SO} \). The net energy contribution due to second-order spin-orbit interaction can be written as

\[
\Delta E_{2ndSO} = \sum_\Pi \frac{\langle 3\Sigma|H_{SO}|\Pi\rangle \langle \Pi|H_{SO}|3\Sigma \rangle}{E_\Sigma - E_\Pi},
\]

where \( H_{SO} \) is the spin-orbit Hamiltonian. We can write the operator corresponding to the second-
order spin-orbit interaction as

\[
H_{2\text{ndSO}} = \sum_{\Pi} \frac{H_{SO}^{\Pi} \langle \Pi | H_{SO}^{\Pi} \rangle}{E_{\Sigma}^{\Pi} - E_{\Pi}^{\Pi}} \Rightarrow H_{2\text{ndSO}} \propto T_{(\Sigma)}^{(2)} T_{(L)}^{(2)}.
\]

(2.45)

(2.46)

Here \(T_{(K)}^{(2)}\) is a rank two tensor that depends on angular momentum \(K\). The only conserved component of the electron orbital momentum \(\vec{L}\), is \(\vec{\Lambda}\), and by definition \(\vec{\Lambda} \parallel \hat{n}\). Thus in the body-fixed frame

\[
T_{(L)}^{(2)} \rightarrow T_{(\vec{n})}^{(2)}.
\]

(2.47)

If we transform from the body-fixed frame to the space-fixed frame, \(T_{(\vec{n})}^{(2)} \rightarrow T_{(l)}^{(2)}\), and we can rewrite Equation 2.45 as

\[
H_{2\text{ndSO}} \propto T_{(S)}^{(2)} T_{(l)}^{(2)}.
\]

(2.48)

Since the electron spin \(S\) and the nuclear spin \(I\) are coupled to form \(\vec{f}\) in our representation, we can finally write

\[
H_{2\text{ndSO}} \propto T_{(f)}^{(2)} T_{(l)}^{(2)}.
\]

(2.49)

The matrix elements of this tensor product give us the energy shifts of interest. Thus the second-order spin-orbit interaction manifests as a coupling between the \(f = I + S\) and the \(l\) (nuclear rotation) quantum numbers with strength comparable to a rotational energy. For example the diagonal elements of \(H_{2\text{ndSO}}\) are [55],

\[
E_{2\text{ndSO}} = \langle \Sigma f, l, F | H_{2\text{ndSO}} | \Sigma f, l, F \rangle
\]

(2.50)

\[
E_{2\text{ndSO}} \propto C(C + 1)
\]

(2.51)

\[
C = F(F + 1) - f(f + 1) - l(l + 1),
\]

(2.52)

Off-diagonal elements can be computed in a similar fashion (see Ref. [55]).

Again for computational purposes, it is convenient to cast the wavefunction of the bound level of the \(a^3\Sigma_u^+\) state in terms of a space-fixed basis set:

\[
|b\rangle = |\nu l(SI)f, F M_f\rangle = \phi_{\nu l}(R) \sum_{m_m} \langle l m f m_f | F M_f \rangle Y_{\nu l}(\theta \phi) Y_{m m}(S I) f m_f |SF\rangle.
\]

(2.53)
Here $\vec{F} = \vec{l} + \vec{f}$, and $\phi_{vl}(R)$ is the radial wavefunction for the state with vibrational quantum number $\nu$ and rotational quantum number $l$. As seen from Table 2.3, for even (odd) $l$, we have odd(even) values of $I$, and as $S = 1$, spin-statistics dictate that $S + I + l$ is even. In a space-fixed basis written in terms of the basis $|L, M_L, S, M_S, I, M_I\rangle$, the wavefunction for this state is given by

$$|b\rangle = \sum_{mm_f M_S M_I} (im f m_f | FM_F \rangle \langle SM_S IM_I | f m_f \rangle Y_{l m}(\theta \phi)|00 SM_S, IM_I \rangle_{SF}$$  \hspace{1cm} (2.54)$$

### 2.2.3 The $X^1\Sigma^+_g$ state

In Hund’s case (b) notation, $^1\Sigma^+_u$ represents a state with $\Lambda = 0$, and $S = 0$. The simplified model of the diatomic molecule (without any internal spins) is ideal for describing this state. The state has no first-order fine-structure (as both $L = 0$ and $S = 0$) or hyperfine structure (as $S = 0$) but there are small second-order hyperfine and spin-orbit effects similar to the second-order spin orbit effects in the $a^3\Sigma^+_u$ state. These states can be described with the quantum numbers $l, I$ alone, with energy $E(l, I) = B_0^X l(l + 1)$. Here $B_0^X$ is the rotational constant for this state.

### 2.2.4 The scattering state of the free atoms

The ground state scattering wavefunction can be described in space-fixed coordinates as

$$|\psi\rangle \equiv Y_{l m}(\theta \phi)[f_a m_a, f_b m_b]_{SF} |\psi_E(R)\rangle.$$  \hspace{1cm} (2.55)$$

Here each atom is described by $|f_a m_a\rangle_{SF}$ ($f_a = 3$ or 4, is the total atomic angular momentum, including the orbital, spin and nuclear spin components), the curly brackets indicate a suitably symmetrized sum over the two values of $f_a$ and $\epsilon = (-1)^l$. As usual $l$ is the mechanical orbital angular momentum of the atoms. $E$ is the energy of the collision, and $\psi_E(R)$ is the radial wavefunction of the scattering state. For a doubly polarized Cs sample (the case of interest to our experiment), where $|f_a m_a\rangle_{SF} = |44\rangle_{SF}$, this simplifies in our preferred basis set $|L, M_L, S, M_S, I, M_I\rangle$ to

$$|\psi\rangle = Y_{l m}(\theta \phi)[LM_L SM_S IM_I]_{SF} |\psi_E Y_{l m}(\theta \phi)|00 11, 77\rangle_{SF},$$  \hspace{1cm} (2.56)$$

where the total electron orbital angular momentum is $L = 0$, the total electron spin is $S = 1$, and the total nuclear spin is $I = 7$. Bose symmetrization for these states requires that $S + I + l$ is even.
2.3 Selection rules and angular factors

2.3.1 Selection rules

The selection rules tell us which transitions are allowed. The allowed transitions are determined by parity and symmetry of the wavefunctions involved in the transition. Transitions between these states are possible with the following selection rules [3],

\[ + \leftrightarrow - \] (2.57)
\[ a \leftrightarrow a \] (2.58)
\[ s \leftrightarrow s \] (2.59)
\[ g \leftrightarrow u \] (2.60)
\[ \Delta F = \pm 1,0 \] (2.61)
\[ \Delta M_F = \pm 1,0 \] (2.62)

The relative strengths of the various transitions, depend heavily on the constituent angular momenta of both states of the transition. In the next section we discuss how the angular factors describing the transition strengths are calculated.

2.3.2 Angular factor calculations

We have already described the states of interest in space-fixed coordinates using the \( L, M_L, S, M_S \) and \( I, M_I \) basis. We are interested in the matrix elements of dipole transitions between the spin-polarized atomic scattering state (with \( l=0 \)) and the excited \( 0^-_g \) \((6s_{1/2} + 6p_{3/2})\) state; and of those between the excited state and the ground \( a^3\Sigma_u^+ \) state. We choose \( l = 0 \) because the low temperature of our atoms ensures that only s-wave scattering occurs. For light of polarization \( \sigma \), the electronic dipole moment operator \( d_\sigma \) responsible for the transition only acts on the electronic orbital wavefunction \( |L, M_L\rangle_{SF} \). The excited state has \( L = 1 \) and the ground scattering states have \( L = 0 \), so we are interested in matrix elements of the form \( \langle L M_L | d_\sigma | L' M_L' \rangle \).

We use the space-fixed forms of the excited \( 0^-_g \) \((6s_{1/2} + 6p_{3/2})\) state \( |e\rangle \) as shown in equation 2.56 and the ground scattering state \( |g\rangle \) as shown in equation 2.54. We are considering only s-wave scattering \((l = 0, m = 0)\) of two spin-polarized atoms \((M_S = 1 \text{ and } M_I = 7)\). For \( \sigma^+ \) light
\[ \langle \varepsilon | d_\sigma | g \rangle = \int dR \xi \varphi J(R) \Psi_E(R) \left[ c^{JM,11}_{0,\Pi} \sqrt{2a_{\Pi}(R)} + c^{JM,11}_{0,\Sigma} \sqrt{2a_{\Sigma}(R)} \right] |11|d_\sigma|00 \] (2.63)

The \[ \int dR \xi \varphi J(R) \Psi_E(R) \] term in the transition dipole matrix element is the Franck-Condon factor, and we define the remainder of the expression as the angular factor \( A(l; J, M; \sigma) \). We always used \( \sigma^+ \) light on our free-bound photoassociation resonance. After substituting the values of \( a_{\Pi} \) and \( a_{\Sigma} \) obtained earlier from our approximate \( V_{MP} \),

\[ A(0, J, M, +) = \left[ c^{JM,11}_{0,1} + c^{JM,11}_{0,0} \right] . \] (2.64)

Calculating the \( c^{JM,11}_{0,\Lambda} \) terms using Mathematica we see that \( A(0, J, M, +) \) is only non-zero for \( J = 2, M = 2 \). This suggests that if we conduct photoassociation of a spin-polarized sample of Cs atoms at low temperatures (so that only s-wave \( l = 0 \) scattering occurs), molecules can only be formed in the \( J = 2 \) rotational level of the \( 0^+_g \) excited molecular state. This example highlights the non-trivial nature of the angular momentum couplings.

Using the space-fixed form of the excited \( 0^+_g \) (6s1/26p3/2) state \( |e\rangle \) (equation 2.56) and the \( a^3\Sigma^+_u \) state \( |b\rangle = |\nu'(17)FM_F\rangle \) (equation 2.54), the bound-bound dipole transition matrix element for a photon of polarization \( d_\sigma \) is given by

\[ \langle e|d_\sigma|b\rangle = \int dR \xi \varphi J(R) \phi \nu',J(R) \sum_{m,m_f} \langle lm, fm_f|FM_F \rangle \times \sum_{M_L, M_S} \langle 1M_s T | fm_f \rangle \left[ c^{JM,ML,MS}_{0,\Pi} \sqrt{2a_{\Pi}(R)} + c^{JM,ML,MS}_{0,\Sigma} \sqrt{2a_{\Sigma}(R)} \right] |1M_L|d_\sigma|00 \] (2.65)

Again the expression in Equation 2.65 was used to define an angular factor \( A(J, M; F, M_F; \sigma) \) describing the strength of these bound-bound transitions.

### 2.4 Predictions of the energy level calculations

It is possible to construct an estimate of the singlet and triplet potentials from known spectroscopic data in combination with previous \textit{ab initio} calculations. Table 2.4 provides a list of data used by our collaborator at NIST Maryland, E. Tiesinga, to produce an estimate of the potentials displayed
in Figure 2.9. The potential form used in the fit for the \(X^1\Sigma_g^+\) and \(a^3\Sigma_u^+\) states was

\[ V(R) = F(R)V_{\text{short-range}} + (1 - F(R))V_{\text{long-range}}; \]

\[ V_{\text{short-range}} = V_{KS}(R) + V_{\text{corr}}; \]

\[ V_{\text{long-range}} = \frac{C_6}{R^6} + \frac{C_8}{R^8} + V_{\text{exchange}}. \]  

(2.66) 
(2.67) 
(2.68)

Here \(V_{KS}\) is the \textit{ab initio} potential from the paper by Krauss and Stevens \([56]\) and \(V_{\text{corr}}\) is a correction potential to move the short range part of \(V_{KS}\). The dispersive part of the potential was joined to the short-range part with a smoothing function \(F(R)\), which varies from 0 to 1 over a narrow range around 18 \(a_0\). Standard methods were used to solve the coupled multi-channel Schrödinger equations to obtain the bound states in the long range part of the curve (below the \(6s_{1/2} + 6s_{1/2}\) dissociation threshold). The results are shown in Figure 2.3. Based on this, it is possible to calculate the sensitivity of the splitting to \(d\mu/\mu\) as shown in figures 2.4, 2.5 and 2.6. The estimates from this calculation predict a sensitivity of \(\frac{dE}{d\mu} \approx 350\ \text{cm}^{-1}\) for levels bound by 40 cm\(^{-1}\) from dissociation. This compares favorably with our earlier estimates. The \(R\)-dependence of the hyperfine coupling was ignored i.e. the atomic hyperfine splitting was used to predict the hyperfine structure depicted in Figure 2.7 and Figure 2.8.

The \(a^3\Sigma_u^+\) and \(0_g^-\) potentials \([2, 25]\) were used by E. Tiesinga to generate vibrational wavefunctions, and from these Franck-Condon factors for the transitions between these states were determined. The results are shown in Figure 2.10. These predictions served as the starting points for the two-color photoassociation study we undertook in this investigation. For convenience we summarize the predictions of our collaborator in Figure 2.11.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissociation Energy (D_e) ([56])</td>
<td>282.2925 cm(^{-1})</td>
<td>-</td>
</tr>
<tr>
<td>Vibrational frequency (\omega_e) ([56])</td>
<td>12.29 cm(^{-1})</td>
<td>-</td>
</tr>
<tr>
<td>Equilibrium separation (r_e) ([57])</td>
<td>11.84 (a.u.)</td>
<td>-</td>
</tr>
<tr>
<td>Long Range Coefficient (C_6)</td>
<td>6860 (a.u.)</td>
<td>.36 %</td>
</tr>
<tr>
<td>Long Range Coefficient (C_8)</td>
<td>(8.60 \times 10^5) (a.u.)</td>
<td>2 %</td>
</tr>
<tr>
<td>scattering length (a_f)</td>
<td>2440 (a.u.)</td>
<td>1 %</td>
</tr>
<tr>
<td>Exchange potential coeff. (\gamma) ([58])</td>
<td>5.542384</td>
<td>-</td>
</tr>
<tr>
<td>Exchange potential coeff. (A) ([56])</td>
<td>(1.1044643 \times 10^{-2}) a.u.</td>
<td>-</td>
</tr>
<tr>
<td>Exchange potential coeff. (28) ([58])</td>
<td>(1.069946) a.u.(^{-1})</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2.4: A table of parameters used in the fit for the Cs\(_2\) \(a^3\Sigma_u^+\) state courtesy our collaborator E. Tiesinga \([4]\).
Figure 2.3: Predictions of vibrational structure for the long range parts of the singlet and triplet potential. Only s-wave \( l = 0 \) are shown. The x-axis represents binding energy from from the \( f=3+f=3 \) atomic asymptote. The y-axis represents triplet state character of the state. The green lines denote triplet levels, the black lines denote singlet levels and the red lines are mixed levels. This figure was reproduced from correspondence with our collaborator E. Tiesinga. The color coding is arbitrary but consistently followed throughout this text.
Figure 2.4: A closeup of the predictions of energy level structure from 0-300 GHz below the f=3+ f=3 atomic asymptote. Only s-wave ($l = 0$) states are shown and the y-axis represents percentage triplet character of the state. The upper graph shows the calculated energy shift due to a change in $\mu$ of $d\mu/\mu = 10^{-5}$. Near dissociation the levels are strongly mixed, note the large numbers of red lines but these levels have low sensitivity to changes in $d\mu/\mu$. This figure was reproduced from correspondence with our collaborator E. Tiesinga.
Figure 2.5: A closeup of the predictions of energy level structure from 400-750 GHz below the \( f=3 + f=3 \) atomic asymptote. Only s-wave \( (l = 0) \) states are shown and the y-axis represents percentage triplet character of the state. The upper graph shows the energy shift due to a change \( \mu \) of \( d\mu/\mu = 10^{-5} \). At 532 GHz, singlet and triplet levels are predicted to lie close together and hence strongly mixed lines (red) are present inside a clump of triplet lines (green). These states were targeted in our spectroscopy experiment. This figure was reproduced from correspondence with our collaborator E. Tiesinga.
Figure 2.6: A closeup of the predictions of energy level structure from 1000-1500 GHz below the $f=3+f=3$ atomic asymptote. Only s-wave ($l = 0$) states have shown and the y-axis represents percentage triplet character of the state. The upper graph above shows the energy shift due to a change in $\mu$ of $d\mu/\mu = 10^{-5}$. At 1225 GHz, singlet and triplet levels are predicted to lie close together; though no mixed lines are seen, the singlet and triplet levels are predicted to be spaced by $\sim 5$ GHz and they have high sensitivity to $d\mu/\mu$. These states were also targeted in our spectroscopy experiment. This figure was reproduced from correspondence with our collaborator E. Tiesinga.
Figure 2.7: Predictions of hyperfine structure for the singlet and triplet sub-levels predicted to lie near 1225 GHz below the f=3+f=3 atomic asymptote. The y-axis is the binding energy of the states with respect to the f=3+f=3 atomic asymptote. The x-axis is the quantum number $f = I + S$. Our spectroscopy with spin polarized atoms ($I = 7$) ensured that $f = 8, 7, 6$ only. This figure was reproduced from correspondence with our collaborator E. Tiesinga.
Figure 2.8: Predictions of hyperfine structure for the singlet and triplet sub-levels predicted to lie near 532 GHz below the $f=3+f=3$ atomic asymptote. The $y$-axis is the binding energy of the states with respect to the $f=3+f=3$ atomic asymptote. The $x$-axis is the quantum number $f = I + S$. Our spectroscopy with spin polarized atoms ($I = 7$) ensured that $f = 8, 7, 6$ only. Note that unlike the previous case of the 1225 GHz levels, here the singlet lies in the middle of the triplet hyperfine cluster. This figure was reproduced from correspondence with our collaborator E. Tiesinga.
Figure 2.9: Calculated ground-state and excited-state molecular potentials of Cs$_2$ relevant to this work. The excited state curve (blue) is obtained from fits to spectroscopy [2, 25], and the ground state curves (green and red) are calculations by our collaborator E. Tiesinga. This figure was reproduced from correspondence with our collaborator E. Tiesinga.
Figure 2.10: Franck Condon factors are shown for transitions between various vibrational levels $\nu$ of the outer well of the $0^+_g$ state and the $a^3\Sigma_u^+$ state. The estimated binding energies of the vibrational levels of the $a^3\Sigma_u^+$ state are given in Figure 2.3. This figure was reproduced from correspondence with our collaborator E. Tiesinga.
Figure 2.11: This figure summarizes the predictions of our collaborator E. Tiesinga. (1) shows us the predicted energy splitting corresponding to vibration, (2) shows us the predicted energy splitting due to hyperfine interaction, (3) depicts the predicted energy splitting due to rotation and (4) shows us the effects of second order spin-orbit coupling. Note that the energy scales in (3) and (4) are the same and that the red crosses in (3) represents levels that are forbidden due to symmetry considerations, and the red crosses in (4) represent levels which cannot be accessed due to our particular experimental scheme.
Chapter 3

Experimental apparatus and techniques

3.1 An overview

In this chapter we present the details of our experimental setup. We used a vapor cell Magneto-Optical Trap (MOT) as the source of our cold Cs atoms. The trapped atoms are spin polarized and subsequently photoassociated to an excited molecular state by a homemade frequency stabilized external-cavity diode laser. The metastable molecules formed by spontaneous decay of the photoassociation resonance were ionized using a pulsed dye laser and the ions were collected in a time-of-flight spectrum using an ion detector. A frequency stabilized Ti:Sapphire ring laser was carefully tuned over various frequency ranges to observe dips in the ion signals due to the two-color photoassociation effect.

It is important to note that the investigation of the RbCs photoassociation spectrum [33, 34, 35] chronologically predates the study of the Cs$_2$ ground states in our laboratory. As a result most of the apparatus used in the Cs$_2$ was actually a progressively modified version of the earlier RbCs related spectroscopy setup. The features that were common to the RbCs setup and the Cs$_2$ setup will be discussed at length, but features unique to the RbCs study (such as the instrumentation related to measuring the trap-loss spectrum) have been left out of this thesis for the sake of brevity.

We initially attempted the two-color photoassociation spectroscopy with an unpolarized atomic sample using the scheme depicted Figure 1.5. Despite scanning our Ti:Sapphire ring laser over
various frequency ranges we could not observe any dips due to a two-color photoassociation effect. We attribute to this to the sensitivity of the two-color photoassociation effect to the angular factors for the free-bound and bound-bound transitions.

The organization of this chapter is as follows: we begin by discussing photoassociation spectroscopy and related instrumentation. Subsequently we look at Magoito-Optical Trapping, related instrumentation (the external cavity diode laser and the Ti:Sapphire laser) and optimization of MOT parameters. Here we also present the details of the scheme used to spin polarize the trapped atoms. After that we present an extended discussion on the stabilization of diode laser frequencies. Lastly we review the functioning of the pulsed lasers, the ion detector and associated electronics used to produce a time-of-flight spectrum of the molecules formed due to photoassociation.

3.2 Intensity requirements for two-color photoassociation

The process of two-color photoassociation has been theoretically treated in reference [59]. For the process described in Figure 1.5 if both photoassociation and probe lasers are on resonance, then the Autler-Townes splitting $\Delta_{AT}$ [59] is given by

$$\Delta_{AT} = 2\hbar \Omega_{eb}. \tag{3.1}$$

Here $\hbar \Omega_{eb}$ is the molecular Rabi coupling for the bound-bound step, which can be written as

$$\hbar \Omega_{eb} = (2\pi I_{\text{probe}}/c)^{1/2} \langle e \sigma | d \tau | b \rangle. \tag{3.2}$$

Here $I_{\text{probe}}$ is the intensity of the probe laser. The transition dipole matrix element $\langle e \sigma | d \tau | b \rangle$ is given roughly by the product of $\Lambda_{eb}$ the angular factor of the bound-bound transition and $\langle \nu_e | \nu_b \rangle$, the overlap integral for the bound-bound transition; and a typical atomic dipole matrix element $\langle a | d | b \rangle \sim e a_0$. The width of the single-color photoassociation resonance is $\approx 5 \text{ MHz}$. Equations 3.1 and 3.2 allow us to estimate the intensity $I_{\text{probe}}$ required to split the single-color peak by a few times its natural linewidth as described below.

For the Cs atomic resonance ($6s_{1/2} \rightarrow 6p_{3/2}$) the natural linewidth is $\approx 5 \text{ MHz}$. The intensity ($I_{\text{sat}}^{Cs}$) required to saturate this transition is $\approx 1 \text{ mW/cm}^2$. By comparison to this, the saturation
intensity of the bound-bound transition if assume an angular factor $A_{cb}^2 = 0.1$

$$I_{sat}^{cb} = \frac{I_{sat}^{C_p}}{(\langle \nu_e | \nu'_b \rangle)^2 A_{cb}^2}, \quad (3.3)$$

Our collaborator E. Tiesinga's calculations (Figure 2.10) indicate bound-bound Franck-Condon factors in the range of 0.1. This implies that the saturation intensity of the bound-bound transition ($I_{sat}^{cb}$) is $\approx 100 \text{ mW/cm}^2$. Let $I_{probe}$ be the intensity required to broaden the bound-bound transition till its splits the single color peak by $\sim 15 \text{ MHz}$ (three times the natural linewidth of the PA resonance, so that we see well resolved peaks). Then substituting $I_{probe}$ and $I_{sat}^{cb}$ into Equation 3.2 gives us

$$(2\pi I_{probe}/c)^{1/2} = \hbar \Omega_{cb} = \frac{15}{8} \cdot (2\pi I_{sat}^{cb}/c)^{1/2} \langle e | d_\sigma | b \rangle. \quad (3.4)$$

From Equation 3.4 we see that $I_{probe} \approx 10 \times I_{sat}^{cb} \approx 10\text{W/cm}^2$.

### 3.3 Lasers

We used a homemade external cavity diode laser to generate $\nu_{PA}$ and a Coherent 699 Ti:Sapphire laser to generate $\nu_{probe}$. Before we describe the details of these systems in the following sections, we present a brief description of a simple laser system. A simple laser consists of a gain medium, a cavity with small loss and an energy pump. The gain medium is an optically active substance with an energy level structure that can cycle population between absorptive and emissive states. The energy pump disturbs the thermal equilibrium between emissive and absorptive states in the gain medium and creates a population inversion. In an inverted gain medium the rate of induced emission exceeds the rate of induced absorption. Any spontaneous emission inside the active medium is amplified by the inverted population. The cavity provides a closed path for most photons emitted inside the gain medium and concentrates the emitted flux into its resonant modes. When the inversion sustained by the pumping overcomes the losses in the cavity the entire system oscillates at a frequency dictated by the gain curve of the medium and modes of the cavity. The active medium has a refractive index and this shifts the frequencies of the cavity modes but all modes of the resonant cavity where the gain exceeds the losses can support oscillation at the mode frequency. The gain curve is prone to spectral-gain saturation effects and this can cause mode competition. This latter effect tends to
influence the frequency and power in the output modes [60].

3.3.1 A homemade external cavity diode laser

An external cavity diode laser (ECDL) consists of a laser diode and an external cavity formed by the back facet of the diode and a diffraction grating.

The laser diode

Most basic laser diodes in the 750-890nm range consist of layers of Al$_x$Ga$_{1-x}$As semiconductor with various kinds of doping. Usually the diode comprises an active region of Al$_x$Ga$_{1-x}$As that is sandwiched between two cladding regions of Al$_y$Ga$_{1-y}$As. A typical structure of this kind is displayed in Figure 3.1. Injecting current into this region adds minority carriers which can radiatively recombine with the majority carriers and in the process emit frequencies dictated by the semiconductor band gap. The spontaneous emission from this kind of recombination has a wide spectral range of ~ 10 nm. Above a threshold value, the injected current pumps a population inversion in the active region. This inversion forms the basis for amplification of the recombination photons and thus the active region of the diode acts as the gain medium of the laser.

The optical size of the active region is usually determined by the variation in the index of refraction inside the region. With a careful variation of the index of refraction it is possible to confine a spatial mode of light to a small channel in this region. To achieve optical feedback manufacturers specially cleave the edges of the semiconductor, coat the back surface with a high-reflectivity coating and coat the front facet with a reduced reflectivity coating. This effectively places a Fabry-Perot cavity around the semiconductor and lasing occurs when the gain per pass (over the path enclosed by the cavity) exceeds the loss per pass [61]. The radiation from a laser diode operating above threshold is usually single axial mode as the diffusion length of the minority carriers is much larger than the wavelength of the emitted light. This ensures that no spatial hole burning occurs and the gain of the medium is spatially homogeneously saturated. The lateral dimensions of the diode however exceed the diffusion length and given the relatively few cavity modes, it is possible to have multi-mode lasing. This spatial inhomogeneity in the lateral dimension can sometimes manifest as axial multi-mode behavior due to the coupled nature of lateral and longitudinal modes [63].

As shown in Figure 3.1 the output beam diffracts off the edges of the active layer and diverges rapidly along the shorter dimension of the active region as it exits the diode. Most applications
Figure 3.1: A sketch of a AlGaAs Heterostructure diode. This sketch is a modification of the sketch presented in reference [62]. The output light diffracts from the edges of the active region (dark grey layer) and diverges rapidly along the shorter dimension of the active layer. The beam is polarized parallel to the long dimension of the active layer. It is important to note that the layers have not been depicted to scale and the height (shortest dimension) of the active layer is typically 100 times smaller than its length (longest dimension).
require the use of a multi-element aspheric lens to produce a collimated beam. The lens has to be anti-reflection coated to avoid causing optical feedback into the diode cavity. The polarization of the axial mode is usually parallel to the plane of the active layer as the TE mode dominates over TM modes. The emission peak of a laser diode usually consists of a single mode peak ~ 20 MHz wide with two relaxation sidebands spaced at ~ a few GHz. These sidebands correspond to damped oscillations in the inversion. In addition to this other modes are spaced by ~ 10 GHz. The linewidth of the single-mode peak is determined by a number of factors including output power, optical feedback and temperature [62].

**Tuning the laser diode frequency**

The frequency of the laser diode's output can be tuned by changing the temperature, the current, the ambient pressure, and by applying a magnetic field. We limit our discussion to the tuning with respect to the current and the temperature as these are the easiest to implement. Tuning involves smoothly moving the cavity modes and the gain curve with respect to each other. When a mode no longer has enough gain to lase, the laser output frequency jumps to another mode which has higher gain. The output frequency of a solitary diode is extremely sensitive to optical feedback as the cavity is small and has low finesse. Also the gain curve is relatively flat in frequency and hence any stray radiation leaking back into the cavity can easily cause a gain saturation in the entire active region. It must be noted that any attempt at modulating the frequency also produces a modulation of the amplitude; however in most cases this is very small and for the purpose of our experiment, it has been neglected.

Changing the temperature usually serves as the mechanism for coarse tuning. The cavity modes and the gain curve both depend on temperature through the refractive index and the bandgap respectively. In AlGaAs lasers the gain curve tunes more rapidly than the cavity modes and hence the frequency of the laser hops to the red with rising temperature. Usually changing the temperature changes the frequency by \( \approx -0.3 \text{ nm/K} \).

The current usually changes the frequency by two mechanisms, either by changing the injection or by Joule heating of the active region. The effect of the former is quite small and easily overwhelmed by the Joule heating for large changes in the current and for slow tuning (\( \leq 1 \text{ MHz} \)). For faster tuning or smaller current changes or tuning below threshold, the injection variation has a greater effect. Generally for large current changes above threshold and for slow tuning, we see a
change of -1 GHz/mA.

**Limitations on laser diode performance**

The laser power usually exits the semiconductor via the front facet. This facet is usually a few hundred microns across and even a small ~ 10 mW output through this results in power densities of ~ 1MW/cm². This can locally heat the semiconductor to a high temperature (1000 K) [64].

The front facet of the diode also contains a small layer of non-inverted semiconductor; this region suffers additional absorptive losses and as a result temperatures here can be close to the melting point of GaAs (~ 1400 K). The positive temperature dependence of the absorption coefficient in the non-inverted semiconductor feeds a thermal runaway phenomena and any attempt to put power in the range of 10MW/cm² through the front facet can create a melt in the GaAs that rapidly travels into the body of the diode and causes catastrophic damage [65]. Optical feedback can easily ramp the output power through the front facet and hence is one of the major causes of catastrophic optical damage (COD).

In addition to optical feedback, the diode’s active region is also prone to damage from electrostatic discharge (ESD). Discharges can cause large currents to flow through the diode and cause irreversible changes in the size and shape of the active region. Another problem that frequently manifests with diodes is that accidentally reverse biasing the diode sends a large current in the opposite direction through the active region. This usually burns the diode. In order to avoid back-biasing the diode most configurations have protection diodes (in forward and reverse biased mode) placed in parallel with the laser. A number of RC networks are also placed in series with the diode to provide transient suppression. In the Figure 3.2 we present a simple circuit we employed in our homemade laser to protect against electronic discharge and reverse biasing. The diode is usually at greatest risk to ESD when the cables connecting it to the diode current supply are accidentally disconnected; to guard against this eventuality we have placed a normally closed relay in series with diode.

**Role of the grating**

The use of an external cavity exploits the sensitivity of the laser diode to optical feedback and expands the ability to control the output frequency of the laser diode. The most inexpensive external optical feedback scheme utilizes a grating on an adjustable mount. If the diode is anti-
reflection coated on the output facet, the grating and the high reflectivity back facet of the diode form the laser cavity. As the grating is dispersive, it wavelength selects the light being fed back into the diode and thus provides tunability.

In most diodes the output facet of the chip tends to reflect a small amount of light back into the active region. This usually causes the diode to lase at a characteristic frequency with a relatively large linewidth. Any optical feedback arranged with the help of external optics has to compete against this internal feedback. The functioning of the laser then becomes a complicated interaction of the internal cavity with the external cavity and this creates severe tunability problems. To get around this, a multi-layer anti-reflection coating is deposited on to the output facet of the diode. These coatings generally reduce the reflectivity to a fraction of a percent and make the diode extremely sensitive to optical feedback from external optics.

In our lasers the grating is mounted in Littrow configuration, in which the first order refracted beam is directly coupled back into the diode. The amount of light fed back into the diode is determined by the absolute efficiency of the grating. This efficiency usually differs for different polarizations of the light.

The wavelength of the output light is now dictated by the external cavity mode and the center wavelength of the grating feedback. The cavity mode is selected by the distance between the

Figure 3.2: The laser diode protection circuit used in our homemade diode laser. D1 is a 1N4001 diode and D2 is a 1N5233 zener diode with a reverse turn on voltage that just exceeds the forward conduction voltage of the laser diode.

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grating and the diode back facet, and the center wavelength of the grating is selected by the angle of the grating. To achieve continuous tuning we must change the position and angle of the grating synchronously. This is accomplished by rotating the grating about a carefully chosen pivot point [66].

We can tune the frequency of the cavity microscopically by making small changes to the grating angle and position. The most common way of doing this involves using a piezoelectric transducer (PZT). Materials like crystalline quartz deform when a large electric field is applied to them. This property is called piezoelectric deformation. A commercially available PZT usually consists of a number of small discs of piezoelectric material sandwiched between electrical plates. This stacking of several layers of material enables the PZT to deform by several microns for a small voltage (~10V). An actuator of this kind can turn the grating by a small angle and thus change the wavelength at which the Littrow condition is met. The PZT often offers continuous tuning in the range of 1 GHz per volt applied to the actuator. In order to avoid coupling mechanical oscillators into the cavity the actuator is connected with limp (24 AWG) wires. As the PZT comprises layers of insulator between thin slices of conducting electrode, electrically it behaves like a capacitor. Common PZT capacitances are in the range of 1000 pF. Piezoelectric materials are unable to deform in phase with electrical stimuli when driven with signals above 400 Hz. This manifests as non-linearity in the PZT's frequency response and forms a major limitation of the PZT. PZTs can have a polarity and maximum voltage rating; care must be taken to ensure that PZT drivers respect these limits, as a failure to do so results in irreversible damage to the PZT crystal. Additionally care must be taken to ensure that the mechanical loading on the PZT does not exceed specified limits. Fortunately for the ECDL designs we used these considerations had already been factored in. A schematic of the PZT is provided in Figure 3.3.

The homemade external cavity diode laser (see Figure 3.5) used in our work was similar in construction to popular Littrow designs [67, 68, 69, 70] and had been built in our group for an unrelated experiment a year earlier. We replaced the diode and grating in the assembly and added some protection circuitry to render it suitable for our use. As shown in Figure 3.4, we used a SDL 5421-G1 (120 mW at 180 mA) laser diode from the JDS Uniphase corporation. We used a 15mm × 15mm × 3mm, 1800 lines/mm float glass, hi-modulation holographic grating from Richardson Gratings Lab (Part. No. 8399-FL-330H). The grating had a 500 nm blaze wavelength and had been gold plated. The grating was not ideal for our wavelength ~ 852 nm but it was available in
Figure 3.3: A schematic of the PZT used in our experiment. The total capacitance of the PZT $C_T = C_1 + C_2 + C_3$ was around 1000 pF. The large dashed arrows pointing vertically in the figure represent the direction of deformation.
Figure 3.4: The laser diode and grating used in our photoassociation laser. We used a standard Thorlabs diode mount and collimating lens.

our lab from an earlier experiment.

The homemade laser proved to be easy and inexpensive to construct. The Newport Ultima U100-P mount provided excellent mechanical stability and the LT230220P-B focussing tube assembly could be positioned at any point within the UPA-PAI adapter and hence the pivot point of the grating assembly could be modified with ease to give us continuous scans ~ 10 GHz with the Thorlabs PE4 Piezo actuator. A Thorlabs TEC 2000 temperature controller was used to stabilize the temperature of the mount. The TEC 2000 sensed the temperature with a Melcor Thermo-Electric Cooler (TEC) (Part No. CP 1.0-127-08L). The temperature was sensed with 10KΩ thermistor. However as we used an uncoated diode in our setup, the laser displayed poor tuning with temperature.
Figure 3.5: A sketch of our external cavity diode laser. The key parts are labeled.
3.3.2 The Ti:Sapphire Laser

We use a Coherent 699 ring laser system to generate our probe laser light as it is tunable over large ranges, gives high power and has a narrow linewidth. The Coherent 699 ring laser system has Ti:Sapphire gain medium that is pumped by a Coherent Verdi V-10 Diode pumped laser.

The Verdi is a solid-state diode-pumped, frequency-doubled Nd:YVO₄ laser that gives a 10 W beam at 532 nm [71]. Servo loops on the power output, the temperature of the doubling crystal, the diode temperature, the Vanadate temperature and etalon temperature provide highly stable operation. The diode bars that pump the Vanadate crystal are located inside a temperature stabilized fiber-coupled assembly inside the power supply. The entire laser operation is controlled by a dedicated CPU. The entire system is cooled by a closed loop water circulating system.

The 899-21 is ring laser with a Ti:Sapphire lasing medium. It has active and passive frequency control. The laser can be scanned using an external CPU supplied with the system. Passive frequency control is achieved with the use of intracavity filters and etalons. A birefringent filter allows a broadband operation with a bandwidth of 2 GHz and intracavity etalons offer a bandwidth of 10 MHz. Active frequency control is achieved by an electronic servo loop that locks the frequency of the laser to a very stable reference cavity. This narrows the linewidth to 500 kHz. The reference cavity can be scanned continuously over a range of ~ 30 GHz and a feed-forward circuit moves the laser frequency accordingly. Between the etalons, the birefringent filter and the cavity feed-forward, it is possible to electronically tune the laser to almost any point within the range of the high reflection coatings on the mirrors. Electronic tuning is carried out using the Autoscan program from Coherent Inc.

3.4 The Magneto Optical Trap (MOT)

The Magneto Optical Trap (MOT) technique [17] is a standard way of producing samples of translationally cold alkali atoms. The basic working of the MOT relies on atoms repeatedly absorbing near-resonant light and then emitting it isotropically. The MOT technique uses an anti-Helmholtz coil configuration to produce a space-dependent Zeeman splitting in the atoms. Orthogonal counter-propagating beams with opposing helicities tuned close to an atomic transition provide a closed pumping scheme to enable repeated absorption and emission of photons. This scheme is demonstrated in Figure 3.6. A closed pumping scheme as depicted in Figure 3.7 uses two sets of lasers,
Figure 3.6: Schematic of the MOT process. (a) A depiction of the counter-propagating beams and relative orientation of the magnetic field coils and (b) The Zeeman splitting caused by the anti-Helmholtz field as a function of one of the axis of the trap.
Figure 3.7: Choice of levels for the MOT scheme. The data regarding the frequencies is from [?].

the trapping beams near the $f = 4(6s_{1/2}) \rightarrow f' = 5(6p_{3/2})$ transition, and the repumping beams on the $f = 3(6s_{1/2}) \rightarrow f' = 4(6p_{3/2})$ transition. The repumping laser is necessary because the trap laser also drives the $f = 4(6s_{1/2}) \rightarrow f' = 4(6p_{3/2})$ transition off-resonantly. The $f' = 4(6p_{3/2})$ state can spontaneously decay to the $f = 3(6s_{1/2})$ state which does not scatter the trap light. The repumping light thus drives this population back into the $f' = 4(6p_{3/2})$, which can decay to the desired $f = 4(6s_{1/2})$ state.

It is possible to characterize the velocity spread $\Delta v$ of the atoms in a MOT in terms of a temperature $T$;

$$\frac{1}{2} k_B T = \frac{1}{2} m(\Delta v)^2. \quad (3.5)$$
The repeated scattering of MOT light exerts a dissipative force that narrows of this velocity distribution of the atoms.

The number of atoms trapped is proportional to the velocity of the fastest atom that can be captured by the MOT [20]. Once trapped, the atoms undergo collisions with atoms in the background vapor, with other atoms in the trap, and with photons scattered by other trapped atoms. These three collision processes contribute to loss mechanisms from the trap. Typically one can produce an atom cloud with \( N \sim 10^7 \) atoms, a density of \( n_p \sim 10^{10} \) atoms/cm\(^{-3}\) and a temperature \( T \lesssim 1 \) mK with this technique [17].

We desire a higher density as the single-color photoassociation rate is proportional to the density [72]. The dark Spontaneous Optical force Trap (SPOT) offers a robust way of producing higher densities and lower temperatures than a standard MOT, while still loading a large number of atoms. In a standard MOT the atoms trapped at the center continue to scatter MOT light. This scattering process serves to limit the density and temperature of the MOT. The dark SPOT technique relies on imaging a hole in the repumping beams onto the position of the MOT. In the absence of repumping light, the atoms are pumped by the trap light into the \( f = 3(6s_{1/2}) \) state which is "dark to" (does not scatter) trap light. This reduces reabsorption of MOT light. In practice however some repump light continues to leak into the dark spot. In order to offset the effect of this leakage, the hole is also filled with a "depump" beam tuned to \( f = 4(6s_{1/2}) \rightarrow f' = 4(6p_{3/2}) \) transition. This beam pumps any population at the center of the MOT in the \( f = 4(6s_{1/2}) \) state into the "dark" state. With this technique it is possible to produce an atom cloud with \( N \sim 10^8 \) atoms, a density of \( n_p \sim 10^{11} \) atoms/cm\(^{-3}\) and a temperature of \( T \approx 100 \mu \)K [19].

In our setup the density was measured in the following way. First all MOT beams (the trap, repump and depump beams) were simultaneously shut off. Then a weak "fill-in" beam (tuned to the \( f = 3(6s_{1/2}) \rightarrow f' = 4(6p_{3/2}) \) transition) was turned on for 1 ms to pump all the atoms from the \( f = 3 \) state to the \( f = 4 \) state. After this, two absorption imaging beams detuned \( \Delta \) from the \( f = 4 \rightarrow f' = 5 \) transition were simultaneously applied to the MOT. The absorption shadow of the atom cloud was imaged on two triggered cameras (EDC-2000N Electrim Corporation). All beam switching was accomplished using acoustooptic modulators (AOMs) from the Neos Corporation. The data from the cameras was collected on a Labview program running on a CPU.

We collected two images in rapid succession, the first with a MOT and the second without a MOT. These two images were compared to give us a clearer idea of the absorption profile. From
the two images we calculated the absorption depth and the width $\tilde{w}$ of the MOT respectively. The cameras were calibrated earlier; the width is obtained in pixels from the image and then multiplied by the pitch ($2.1 \times 10^{-2}$ mm/pixel) to get the width in millimeters. The image without the MOT gave us an idea of the original intensity $I_0$ of the beam. The detuning of the absorption imaging beams $\Delta$ (set with the help of a Radio Freuncy Voltage Controlled Oscillator (RF-VCO)) is also noted. With all these parameters at our disposal, $n_p$ the density of the MOT, is obtained by substituting the values of $I, I_0, \Delta$, and $\tilde{w}$: 

$$n_p = \frac{1}{\sigma_0 \tilde{w}} \left( \frac{2}{\pi} \right)^{1/2} \ln \left( \frac{I_0}{I} \right) (1 + \frac{2\Delta}{\Gamma})^2$$  \hspace{1cm} (3.6)

In the above equation, $\sigma_0$ is the resonant cross-section for the $f = 4 \rightarrow f' = 5$ transition; it is given by the expression [73]

$$\sigma_0 = \frac{3\lambda^2}{2\pi} L^{f'}_f |C^{f'}_f|^2.$$  \hspace{1cm} (3.7)

Here $L^f_f$ is the line strength, $C^f_f$ is the Clebsch-Gordan Coefficient, and the bar indicates an average over all the $f = 4, m_f$ sub-levels. We averaged over the sub-levels because our atoms are unpolarized in this measurement. We calculate $\sigma_0$ to be $1.9 \times 10^{-9}\text{cm}^2$. $\Gamma \approx 5\text{MHz}$ is the natural linewidth of the transition. The number of atoms $N$ in the MOT is given by [73]

$$N = \tilde{w}^3 n_p (\frac{\pi}{2})^{3/2}.$$  \hspace{1cm} (3.8)

The density was optimized by adjusting the alignment of the trap, repump and depump beams, and by adjusting the intensities of the repump and the depump beams. We also occasionally tweaked the detuning of the trap beam. After following such an optimization procedure we measured the density to be $n_p \approx 4 \times 10^{11}\text{cm}^{-3}$ and the number of atoms to be $N \approx 2 \times 10^8$.

The temperature of the MOT was measured during the earlier RbCs spectroscopy experiment. The temperature of the MOT depends in a complicated way on parameters like the alignment, the relative intensities and detunings of the beams and the strength of the magnetic field; thus optimizing the temperature is difficult. In our experiment we need to know the temperature of the MOT for the following reasons:

- the ground state molecules formed as a result of the spontaneous decay of the metastable state created in the single-color photoassociation have the same temperature as the atoms.
These molecules do not scatter trap light and leave the trap region at a velocity determined by their temperature. In our experiment all the manipulation to the molecular states has to be done over time scales smaller than the time it takes for a molecule to exit the trap volume,

- reducing the temperature increases the photoassociation rate [72]; and
- as described in Figure 1.4 and Equation 1.25, the height of the centrifugal barrier determines which scattering states can participate in the collision. If the temperature of an atomic sample is high, then higher scattering states ($l=1,2,3$ etc...) will be able to cross the barrier and participate in the collision. We wish to restrict our scattering states to $l=0$ ($s$-wave) as then the experimental system would closely match the simplifying assumptions used in the angular factors calculation presented in Chapter 3.

A relatively crude measurement of the temperature was sufficient for this, and thus the measurement taken at the time of the RbCs experiment was not repeated in our Cs$_2$ experiment. For completeness however, we briefly describe the measurement technique.

To measure the temperature of the MOT, we image the MOT twice using the same lasers and cameras used in our density measurement setup. The first image is taken with the MOT in steady state immediately after the trap beams are turned off. The second is taken after allowing the atom cloud to expand for a time $t$. If $\tilde{w}_0$ is the width of the atom cloud before expansion and $\tilde{w}_t$ is the width of the atom cloud after expansion, then $T$, the temperature of the MOT is given by

$$T = (\tilde{w}^2_t - \tilde{w}^2_0) - \frac{m}{4k_B t^2}. \quad (3.9)$$

From the typical values of $t$ required to allow the cloud to expand to twice its size, the temperature of the MOT was determined to be $T \approx 100 - 200 \mu$K.

It is also possible to estimate the temperature from the number of rotational peaks seen in the photoassociation spectrum. If the temperature is higher, then colliding pairs with higher rotational angular momentum $l$ can cross the centrifugal barrier and participate in the single color photoassociation process (the observed total angular momentum is $J = L + S + l$). For the $0^+_g$ $(6s_{1/2} + 6p_{3/2})$ state, where $L=1$ and $S=1$. Thus the observed strength of the various lines directly reflects the partial waves involved in the photoassociation[74]. Our results were identical to other photoassociation spectra which were taken with atoms at $T \approx 100 \mu$K. Thus the two independent temperature measurements appear to be consistent.
In the following sections we briefly discuss the details of the construction of the MOT

### 3.4.1 Vapor Cell and the Magnetic Coils

Our MOT chamber is a standard multi-Conflat flange chamber from Kimball Physics. Two custom multi-flanges from Sharon Vacuum Inc. were added to increase optical access ports. The viewports, feedthroughs and UHV compliant wires used in the present version of the setup are standard parts from Insulator Seal Inc. and the MDC Corporation. The entire chamber was assembled following standard UHV cleaning and handling techniques. The chamber is mounted on three custom-made aluminum mounts and aluminum extrusions from 80/20 Inc. are used to create a frame around the setup. The frame holds aluminum breadboards that host the optics. In Figure 3.12(a) we present a schematic of the chamber. The chamber was initially pumped down to $10^{-7}$ Torr using a turbo pump from Alcatel Corp., and then it was baked to remove water and other impurities that were attached to the chamber walls. Presently an 8 liter/second ion pump from Varian Associates provides sufficient pumping keep the pressure inside the chamber to $10^{-9}$ Torr. The pump current serves as a measure of the vapor pressure inside the chamber. The alkali vapor inside the chamber is obtained by heating or cooling two "cold-finger" setups attached to the main chamber. These cold fingers consist of a few milligrams of Cs or Rb metal inside a glass tube that is packed between peltier coolers that heat or cool the metal. This changes the vapor pressure in the cold finger and alkali vapor diffuses into the main chamber via a UHV valve.

A pair of custom built aluminum mounts house approximately 100 turns of insulated copper wire that serve as out MOT coils. The coils slip on the custom built multi-flange and are mounted with their windings in opposite directions. This creates an anti-Helmholtz configuration with zero field at the center of the MOT chamber. The coil mounts are water cooled. The desired field gradient for MOT operation can be created by running a current of 8 Amps through the coils.

### 3.4.2 Spin polarization

An unpolarized sample contains atoms with their spins oriented randomly with respect to the photoassociation laser (homemade ECDL) and the probe laser (Ti:Sapphire laser), so for an $l=0$ ($s$-wave) collision, our atoms have all possible values $|F| = |f_a + f_b| + l = 8, 7, 6, ...0$ and hence $M_F$ can take values from $8, 7, ..., -7, -8$. Even when the probe laser is tuned to a bound-bound resonance, the angular factor averaged over all possible values of $F, M_F$ is very small and the transition dipole
moment for the bound-bound step is negligible. As a result of this the photoassociation resonance does not experience a sizable Aulter-Townes splitting and the ion signal from the photoassociation resonance does not change appreciably. A polarized sample enables us to selectively pick transitions with high angular factors.

To polarize the atoms we need to apply a magnetic field that orients the atomic spins and then apply a weak polarizing laser tuned to some atomic transition that pumps us into a particular spin state. A schematic of the pumping process of interest to us is depicted in Figure 3.8.

Due to our choice of a Dark Spot configuration, the MOT produces atoms in the $f = 3$ state. For our experiment we want atoms in the $f = 4, M_f = 4$ state so that for an $l=0$ collision, the total angular momentum $F = l + f_a + f_b = 8$ and $M_F=8$. By starting from the stretched state $F = 8, M_F = 8$ we ensure that the angular factor for the single-color photoassociation step (with $\sigma^+$ polarization on the photoassociation laser) has a large angular factor, and that we end up in a single quantum state with $F = 9, M_F = 9$ (corresponding to $J = 2, M_J = 2, I = 7, M_I = 7$ as described in Equation 2.63). To achieve this, we carefully switch on the fill in beam and the depump beam in a particular order and the combination of the two acts as our spin-polarizing beam.
Due to the presence of large amounts of aluminium used in making mounts for coils, breadboards and optics around our chamber, all attempts to quickly impose a field at the center of the MOT were frustrated by large eddy currents in the aluminium mounts. This forced us to choose a complicated scheme for introducing our quantizing field $B$.

In order to spin-polarize the Cs cloud, we need a relatively small field to appear very quickly at the MOT. We achieved this by switching our MOT coils from an anti-Helmholtz to a Helmoholtz configuration. This causes the field at the center of the MOT to rise from zero to $\sim 40$ Gauss in 10 ms. We measured the field using a Hall probe. If the MOT coils are repeatedly switched between an anti-Helmholtz and Helmoholtz configuration, the slow rise and fall of the field force the net field to oscillate about some low average value. By adjusting the frequency at which we switch between two configurations, we were able to create the desired value of field at the MOT. The circuit and control sequence used to switch the field is shown in Figure 3.9.

The sequence of laser pulses used for spin-polarization is shown in Figure 3.10. First the MOT (trap, repump and depump) beams are turned off using RF switches on the input to the AOMs. At this point in time the atoms are primarily in the $f = 3$ state. At the same time the “fill-in beam” (tuned to the $f = 3 \rightarrow f' = 4$ frequency) is turned on. This pumps all the $f = 3$ dark state atoms into the $f = 4$ state. The magnetic field control signals are switched almost simultaneously with the MOT beams and $B$ field gradually builds up to a value $B \sim 4G$ along the z-axis by about 1 ms. At this time the depump beam is switched back on and, relative to the direction of the $B$ field, it has a $\sigma^+$ polarization. The combination of the depump and the fill-in beam provide the optical pumping required for the spin-polarization into the $f = 4, m_f = 4$ state.

The Photoassociation laser is turned on at 1.5 ms and stays on till $\sim 100 \mu s$ before the arrival of the ionization pulse. This cycle is clocked to the Advanced Q-Switch trigger signal from the Quanta Ray Nd:YAG laser driver and repeats at 10 Hz. The spin-polarization of the atoms is confirmed by reproducing the photoassociation spectra from polarized atoms observed earlier [1].

### 3.4.3 MOT Optics

The MOT optics scheme is fairly standard, with most of the optics and mounts from the Thorlabs Corporation. Due to the large distance between the lasers and the chamber, single-mode optical fibers were used to deliver the beams to the experiment and thus to prevent sensitivity to beam drift. The beams were expanded close to the chamber. A dark spot was created in the repump beam

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Figure 3.9: Switching the field in our experiment. (a) The circuit used to switch the direction of the current in one of the coils. We used four PN60N06 n-channel MOSFETs to switch the current direction in Coil 2. (b) The control sequence used to drive the gate input of the FETs and the resulting changes in the magnitude of $B$. In the first part of this graph we show the response of $B$ to a sudden change in the control signal. Note that due to the large eddy currents in the setup, $B$ responds slowly and gradually rises to 40 G in about 10 ms. As we switch the control signal back the $B$ field gradually falls back zero. In the later part of the graph we show the effect of rapidly switching control signal to the FETs. This causes $B$ to oscillate about a lower value. The behavior in the later part of the graph reflects the procedure actually used in our spin-polarization technique.
using the a small piece of tape on a piece of anti-reflection coated glass. Most of the wave plates used in the setup to create the orthogonally polarized counter-propagating beams were purchased from Meadowlark Optics and CVI Laser.

In addition to the usual MOT optics we have optics for three other setups around our chamber:

1. MOT imaging setup: This comprises two crossed beams of low intensity tuned to the $f = 4 \rightarrow f' = 5$ transition directed into two triggered cameras. These are used to measure the number of atoms in the MOT and the density of the MOT by imaging the shadow formed by the absorption in the atom cloud.

2. The Two-color photoassociation optics: This is a set of mirrors and beam splitters which combine our depump beam and our probe beam(Ti:Sapphire). As stated earlier, a combination of the depump beam and the fill-in beam acts as our polarizing beam. An additional set of mirrors is used to counter-propagate the photoassociation beam (from our homemade ECDL). Several waveplates are used to set the polarization of these beams relative to the polarizing magnetic field.

3. The Ionization Detection setup: This consists of high power optics used to direct the ionization beam from the pulsed dye laser onto the MOT.
Figure 3.11: The chamber with all the parts labeled (the cold fingers have been suppressed for ease of viewing).

A schematic of the optics used in our setup is depicted in Figure 3.12.

### 3.4.4 The Sacher ECDL

We used a Sacher TEC 100 tunable external cavity diode laser to generate the frequencies required for our Magneto Optical Trap (MOT). The TEC 100 uses an anti-reflection coated laser diode in conjunction with a grating in Littrow configuration to produce an output beam of ~ 40 mW at a diode current of ~ 80 mA. The output frequency can be tuned through large amounts (10 nm < Δλ < 90 nm) with the coarse frequency adjustment screw on the back of the grating mount, or tuned continuously over a range of ≈ 10 GHz by adjusting the voltage applied to a PZT in the grating mount. The laser head (depicted schematically in Figure 3.13) has additional circuitry comprising a relay and diodes to protect the laser. A thermoelectric cooler and a temperature
Figure 3.12: A schematic of the chamber and optics used in our experiment. The layout of the beams with respect to the atoms and the field is shown, (1) Photoassociation beam, (2) MOT Beams, (3) MOT imaging beams, (4) Polarizing beam (also our depump beam), (5) probe beam, (6) MOT Coils, (7) Ball of Cs Atoms, (8) ionization beam, (9) ion detector, (10) opposing electrode. The black arrow represents the direction of the polarizing field nominally downward.
Figure 3.13: A sketch of the Sacher TEC 100 tunable external cavity diode laser. The key parts are (1) anti-reflection coated laser diode in mount, (2) grating mount with piezoelectric transducer, (3) output laser beam, (4) electronics (5) wavelength adjust screw (6) diode collimation adjustment, (7) Thermoelectric Cooler for temperature control (the AD590 temperature sensor is not shown), (8) cavity adjustment screw, (9) grating, (10,11) 9-pin D-shell connectors for temperature controller and diode current driver, (12) LEMO connector for piezoelectric transducer drive voltage, (13) Bias-T connector for high frequency modulation of diode current.

sensor (AD590) provide a means to stabilize the temperature of the entire cavity and the diode. The TEC 100 unit is generally available with a current driver, a PZT driver and a temperature controller.

For the RbCs spectroscopy experiment, four TEC 100 lasers were purchased from Sacher Lasertechnik. These were used to generate the Rb trap (12816.49 cm\(^{-1}\)), Rb repump (12816.55 cm\(^{-1}\)), Cs trap (11732.18 cm\(^{-1}\)) and Cs repump (11732.49 cm\(^{-1}\)) frequencies. In our experiment we only used the Cs frequencies.

Our experience with the Sacher lasers was not positive. On the one hand, the units were easy to tune and had a reasonable amount of protection circuitry built into the laser head, so we rarely destroyed any laser diodes. On the other hand, the entire Sacher design is made from aluminum, presumably chosen due to its superior thermal characteristics. However the use of aluminium

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mounts proved problematic. Firstly, the mounts for the collimating lens, the PZT and the cavity were not spring loaded but rather simple flexure mounts. The aluminum flexures tended to deform easily, and in the case of the cavity adjustment screw the deformation was difficult to undo. Secondly the adjustment screws and the holes they threaded into were made from a harder material (possibly steel). This meant that turning the screw would deform the softer aluminium and hence the cavity was prone to slow drifts as the deformation manifested.

The choice of construction material, however, was a minor problem when compared to the electronics that Sacher provided with the lasers. The Sacher electronics was poorly engineered and susceptible to noise from ground loops and pickup. We replaced the Sacher-supplied PZT driver with indigenous electronics due to serious ground loop issues. The current and temperature control electronics appeared to be prone to low frequency drifts and behaved erratically at times. From our contact with Sacher representatives, it appeared that we had purchased what was the first generation of their electronics. From subsequent discussions with others in the field, a number of our complaints about the electronics were addressed by Sacher in its subsequent models.

As the laser head was not hermetically sealed, attempts to mechanically isolate the laser head using Sorbothane foam pads were only marginally effective. The large hole in the plastic cover for the output beam greatly increased sensitivity to acoustic pickup and low frequency environmental drifts. This behavior degraded the effectiveness of the saturated absorption spectroscopy-based frequency stabilization schemes used with these lasers. The unreliable behavior of the frequency locks on the Sacher lasers often reduced the time available for experiments to painfully short intervals of $\approx 15$ minutes.

### 3.4.5 Injecting a laser diode

In the case of the trap laser frequencies, the power output of the Sacher TEC 100 was insufficient. In order to boost the power output we “injection-locked” another laser diode to the output of the Sacher TEC 100.

Usually a laser diode emits a characteristic frequency because the front facet optically feeds back into the active region. If the front facet is coated with an anti-reflection coating that minimizes the reflection from it, the laser ceases to lase. At this point if radiation from an external source is made incident on the diode, the output frequency and mode of the laser diode is completely determined by the external source. This phenomenon is called “injection-locking” and can occur
even in uncoated diodes if the intensity of the light from the external source exceeds the intensity of the feedback from the front facet.

In our setup we used frequency-locked light from a saturated absorption setup (henceforth called the master laser) to seed a free running anti-reflection coated diode (henceforth called the slave diode) in a thermally stabilized, optically isolated mount, manufactured by the OFR Optics Corporation. The diode used in the Cs setup is from SDL and was coated by Sacher Lasertechnik. The slave diode used in the Rb setup was from Intelite Inc. and was not coated. The temperature of the OFR mount is controlled using a Peltier cooler (Melcor) and an electronic circuit from Wavelength Electronics. The stabilized current in the slave diode is supplied from a current controller also from Wavelength Electronics.

The exact optical setup used to inject the slave diode is depicted in Figure 3.14. The actual process of alignment of the beams from the master laser and the slave is quite involved. The output of the slave laser diodes was examined on a Fabry Perot optical spectrum analyzer from Coherent Inc. The output power from this slave after the optical isolator was \( \sim 80 \) mW when the current through the diode was 120 mA.

### 3.5 Stabilization of laser frequencies

External cavity diode lasers offer a robust and inexpensive way of generating narrow linewidth light in certain frequency ranges. Frequency stabilization of these lasers has been demonstrated using several schemes. In our experiment we used frequency-modulated spectroscopy of saturated absorption features in a glass vapor cell to lock the frequency of the single-mode diode lasers used in our MOT. We used a different method, based on the transmission spectrum of a Fabry-Perot interferometer, to frequency-stabilize the homemade external cavity diode laser used for the first step of the photoassociation process. Table 3.1 lists all the stabilized optical frequencies used in our experiment and any related atomic references.

An external cavity diode laser is prone to frequency noise due to:

- noise on the laser diode current,

- drift in the temperature of the setup, resulting in the drift in the temperature of the diode itself, or in the external cavity length,

- mechanical noise changing the external cavity length, and
Figure 3.14: AR Coated SDL laser from Sacher in OFR laser mount. (1) Polarized beam from frequency stabilized master laser, (2) baseplate, (3) polarizing beam splitter, (4) λ/2 waveplate, (5) optical isolator (Faraday rotator and polarizer), (6) collimating lens with micro-positioning mount (7) AR coated laser diode in mount, (8) housing for Melcor peltier cooler, and (9) output beam.

<table>
<thead>
<tr>
<th>Name</th>
<th>Atomic Reference</th>
<th>Frequency(cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cesium Trap Laser</td>
<td>(F = 4 \rightarrow F' = 5)</td>
<td>11732.183</td>
</tr>
<tr>
<td>Cesium Repump Laser</td>
<td>(F = 3 \rightarrow F' = 4)</td>
<td>11732.481</td>
</tr>
<tr>
<td>Cesium Depump Laser</td>
<td>(F = 4 \rightarrow F' = 4)</td>
<td>11732.174</td>
</tr>
<tr>
<td>MOT Imaging Laser</td>
<td>(F = 4 \rightarrow F' = 5)</td>
<td>11732.183*</td>
</tr>
<tr>
<td>Fill-in Beam</td>
<td>(F = 3 \rightarrow F' = 4)</td>
<td>11732.481**</td>
</tr>
<tr>
<td>Polarizing Beam</td>
<td>(F = 4 \rightarrow F' = 4)</td>
<td>11732.481†</td>
</tr>
<tr>
<td>Photoassociation laser</td>
<td>((F = 4,4) \rightarrow 0_y (6s_{1/2} + 6p_{3/2})(\nu, J))</td>
<td>11676 cm⁻¹ - 11730.0 cm⁻¹</td>
</tr>
</tbody>
</table>

Table 3.1: Stabilized frequencies needed for our experiment. For the atomic reference lines, \(F\) is the initial state and \(F' = 4\) is the excited state. *we need to be able to independently adjust the detuning of this laser, **same as the repump laser, †same as the depump beam.
environmental fluctuations changing the refractive index of the external cavity.

To minimize the effect of all of these noise sources we use feedback loops. To control the noise on the current, we use a stabilized current source. We use a feedback loop comprising a Thermo-Electric Cooler (TEC) and temperature sensor to control the drift in the temperature. To compensate for the noise from mechanical noise in the cavity and environmental changes, we use loops feeding back to the diode current and to the piezoelectric transducer on the grating mount.

Feedback Loops

The generalized feedback loop is shown in Figure 3.15. This loop relies on negative feedback to operate in a predictable fashion. The loop couples a portion of the output into the input with the opposite sign as the input. This process reduces the overall gain of the loop but stabilizes it against deviation. It is possible by careful choice of components to induce a specific frequency response out the loop-gain. If in the setup described in Figure 3.15, the criteria

![Figure 3.15: A generalized feedback loop, G is the closed-loop gain, A is the open-loop gain, and f is the feedback fraction. All the aforementioned quantities are functions of the frequency ω](image)

\[ G = \frac{V_o}{V_i} = \frac{A}{1 + fA} \]
Figure 3.16: A simplified schematic of the laser frequency control loop. The Laser generates a frequency $\nu_L$; due to various factors described in the text, this frequency tends to drift around on various timescales. The laser frequency is compared with a reference frequency $\nu_{Ref}$ on a spectrometer and a signal proportional to the difference $\nu_L - \nu_{Ref}$ is generated. This signal passes through the feedback circuit (labeled $F$) and is converted into an error signal $V_{err} = F(\nu_L = \nu_{Ref})$ which is applied to the control input of the laser. We desire that the error signal be reduced to zero, i.e. $\nu_L = \nu_{Ref}$.

$$fA < 1,$$  \hspace{1cm} (3.10)

$$|A| \gg 1,$$ \hspace{1cm} (3.11)

are satisfied, then

$$V_0 = V_i.$$  \hspace{1cm} (3.12)

As stated in the caption for Figure 3.15, the open-loop gain is a function of the frequency,

$$A(\omega) = A_0(\omega) e^{i\phi(\omega)}.$$  \hspace{1cm} (3.13)

We are attempting to stabilize for example, the frequency of an external cavity diode laser to an external frequency reference. A schematic of the feedback loop required for this is presented in Figure 3.16. The criteria in Equation 3.10 can thus be recast as,

$$|fA_0| < 1 \text{ when } \phi(\omega) = \pi,$$  \hspace{1cm} (3.14)

$$A_0 \gg 1.$$  \hspace{1cm} (3.15)
In all physical systems, $A(\omega)$ eventually falls as a function of $\omega$. This creates a functional relationship between $A_0(\omega)$ and phase $\phi(\omega)$. As the gain $A_0(\omega)$ rolls off, the phase shift $\phi(\omega)$ of the open-loop gradually climbs towards $\pi$. Increasing phase-shift is cause for considerable concern because a overall phase shift of $\pi$ will change the sign of the feedback and cause the loop to oscillate. In order to avoid this, we attempt to change the open-loop gain $A_0(\omega)$ so that it is far below unity by the time this $\pi$ phase-shift occurs in frequency. This idea is schematically represented in Figure 3.17. The open loop gain curve presented in Figure 3.17 represents an ideal case. Most physical systems have complicated frequency responses and phase shift of the loop shows all sorts of features. A more useful design concept under the circumstances is the phase margin. The phase margin at a frequency $\omega$ is

$$\Phi = \pi - \Phi(\omega), \quad (3.16)$$

where $\Phi(\omega)$ is the loop phase shift at that frequency. Stable operation requires the phase margin to be as large as possible when the feedback $|fA_{\theta}|$ and a small phase margin manifests as ringing in
the closed loop. In order to design stable loops, one must introduce frequency-dependent features into the loop gain. The features are commonly classified as;

1. Integral Gain: Here the gain is proportional to $\omega^{-1}$. This feature permits the loop to sum over low frequency changes before it responds to them, i.e. the response of the loop lags the change. In terms of phase margin, the integral gain provides good phase margin and high gain at low frequencies.

2. Proportional Gain: Here the gain of the loop is independent of the frequency. Proportional gain is ideal for intermediate frequencies.

3. Differential Gain: The gain of the loop rises with frequency; this makes for a faster response at higher frequencies as the loop anticipates the change and moves to correct it. Differential gain moves the phase margin in a direction opposite to the integral gain, as the loop now leads the change.

Designing a stable feedback loop consists of carefully adjusting the values of these three stages so as to maximize the gain of the loop at any given frequency. A typical Proportional, Integral, Differential (PID) gain curve is shown in Figure 3.18. In our experiment we used a variation of this basic PID loop idea.

3.5.1 Feeding back to the piezoelectric transducer

If the length of the external cavity could be changed in such a way that the change nulled any drift in the laser frequency, then it would be possible stabilize the laser output. A grating mounted on a PZT can provide such a compensation mechanism, at least at lower frequencies where the PZT still offers a linear response. In our experiments the PZT used on most of our gratings could not respond faster than 500 Hz and its conversion factor was $\sim 1$GHz/Volt. The frequency response of the PZT driver to the error signal has to be carefully tailored to ensure that the gain on the PZT rolls off well before 500 Hz as shown in Figure 3.20. In our circuit this is accomplished by changing the $R$ and $C$ values on the integrator stage depicted in Figure 3.19. When not feeding back to the PZT, the controller can be used to tune the cavity; for this purpose a coarse and fine offset voltage and a ramp can be added to the PZT in place of the error signal. The switching between the feedback signal and the ramp signal is achieved via a DPDT switch labeled "SW" in the figure.
Figure 3.18: A typical PID loop bode plot showing the open loop and the closed loop gain. We have overlaid a plot of the phase margin associated with such a loop. Commonly held design ideas mandate that the phase margin be kept below $-135^\circ$. 

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Figure 3.19: A schematic of a PZT feedback and control circuit. An error signal is given as input to the circuit and the output is written to the PZT. This was used to control the PZT on the Sacher ECDL. We also have an input to apply a ramp to the PZT. This enables us to continuously tune the frequency of the laser around an atomic resonance and see the entire absorption profile before locking to a feature of our choice. The variable setpoint control is vestigial it was added into the circuit as a means to verify that the laser was locked. If our laser was locked to the external reference, slowly moving the setpoint by a few mV would cause the error signal from lock to trace the slope of the dispersion waveform. If on the other hand the laser was not in lock, then the error signal would not follow the setpoint.
Figure 3.20: A schematic of the feedback loops used on the Sacher ECDL. \( f_1 \), the PZT feedback gain rolloff is \( \sim 10 \text{ Hz} \) and \( f_2 \), the current feedback gain rolloff is \( \sim 10 \text{ kHz} \).
3.5.2 Feeding back to the current

To control drifts in the laser output above 500 Hz, we feed back to the laser diode current. Typically the laser diode frequency responds linearly to the current up to \( \sim 300 \text{ kHz} \) [61], and this can serve as a robust way of compensating for the fast frequency fluctuations. In our setup we have deliberately rolled off the gain at much lower frequencies due to limitations imposed on us by the way our error signal is generated. Additionally, at lower frequencies where the current and PZT loops overlapped, the phase margin reduced and ringing could be observed as we tuned the setpoint around. The exact origin of unexpected reduction in the phase margin was never exactly determined but was attributed to some electronic phase shifts in the Sacher laser driver. To reduce the ringing, the gain of the current feedback loop was rolled off giving it a differential gain near DC as shown in Figure 3.20. The gain of the current feedback was altered by choosing the resistor and capacitor values on the last two op-amps in the circuit depicted in Figure 3.21.

3.5.3 Monitoring the frequency

To lock the frequency of a laser, we can reference it to an atomic resonance or to a Fabry-Perot fringe. We implemented both these schemes in our setup.

**Saturated Absorption**

Atomic resonances obtained by spectroscopy of a vapor can be used as a frequency reference; however the random thermal motion of the atoms causes Doppler shifts that broaden the resonance. For a vapor of atoms (mass \( M \)) at temperature (\( T \)) the Doppler-broadened width of a transition of frequency \( \nu_0 \) is [60]

\[
\nu_D = 2 \sqrt{2 (\ln 2)^{1/2} \frac{k_B}{c} \sqrt{T}} \sqrt{\frac{T}{M} \nu_0}
\]  

(3.17)
Figure 3.22: Sub-Doppler spectra used to lock the frequencies of our MOT lasers. (a) Cs Trap frequency, (b) Cs re-pump frequency, (c) FM or derivative spectra of the trapping transition, and (d) the same for the repump transition. The y-axis in the graph represents the voltage and is different for each graph.

At room temperature for a gas of Cs atoms, this width is \( \sim 400 \text{ MHz} \). If a number of transitions are close together then their Doppler profiles merge into each other yielding an asymmetric lineshape. The use of two counter-propagating beams, a strong pump beam and a weak probe beam, enables us to observe spectral features smaller than a Doppler width. These usually manifest as the so-called Lamb dips or Bennett holes in the absorption profile. In addition to such dips, the sub-Doppler features also include crossover peaks or dips formed midway between two Lamb dips [60]. Figure 3.22 shows the sub-Doppler spectrum for the two transitions used in the Magneto-Optical trapping of Cs.

We briefly describe the relevant features of the saturated absorption spectroscopy scheme used to lock our MOT lasers (as shown in Figure 3.23). Light from a Sacher ECDL is passed through an optical isolator, and a small fraction is passed through the vapor cell along opposite directions. The pump beam is frequency shifted with respect to the probe beam with an acousto-optic modulator (AOM). In addition to placing an RF offset on the pump frequency, the AOM also frequency modulates the pump with respect to the probe. This enables lock-in detection of the sub-Doppler features in the probe absorption spectrum. The probe is directed into the photo diode and the photocurrent is used to generate an error signal for the feedback electronics. The laser output from
Figure 3.23: A schematic of a saturated absorption spectroscopy setup used in our experiment.

this scheme is not exactly at the MOT frequencies; hence up to two additional AOMs are required to shift the locked output to the desired detuning. The noise on the stabilized MOT lasers is $\leq 1$ MHz as calculated from the residual error signal.

**Fabry-Perot Interferometer**

As shown in Figure 3.24 successive fringes in the spectrum of a Fabry Perot interferometer (FPI) are separated in frequency by the free spectral range (FSR). For a confocal FPI of length $L_{FP}$ the free spectral range is given by

$$FSR = \frac{c}{2L_{FP}}$$

(3.18)
For light of wavelength $\lambda_1$, adjacent peaks occur at

$$d_{1a} = n\frac{\lambda_1}{2},$$  \hspace{1cm} (3.19)

$$d_{1b} = (n + 1)\frac{\lambda_1}{2},$$  \hspace{1cm} (3.20)

$$d_{1b} - d_{1a} = \frac{\lambda_1}{2},$$  \hspace{1cm} (3.21)

where $d_{1a}, d_{1b}$ are the lengths of the FPI cavity corresponding to adjacent fringes. For light of wavelength $\lambda_2$ similarly we have,

$$d_{2a} = m\frac{\lambda_2}{2},$$  \hspace{1cm} (3.22)

$$d_{2b} = (m + 1)\frac{\lambda_2}{2},$$  \hspace{1cm} (3.23)

$$d_{2b} - d_{2a} = \frac{\lambda_2}{2}.$$  \hspace{1cm} (3.24)

Both cavity length changes, $d_{1b} - d_{1a}$ and $d_{2b} - d_{2a}$ correspond to an frequency interval of one free spectral range. As long as $\lambda_1$ and $\lambda_2$ are close ($\sim$ 10 nm), the distances, $d_{1b} - d_{1a}$ and $d_{2b} - d_{2a}$ corresponding to one free spectral range in frequency are the equal (to within 10nm/$\Delta F S R$). Thus if we observe the peaks corresponding to $\lambda_1$ and $\lambda_2$ spaced by a distance $d$ on the FPI, the frequency difference between them (up to an integral multiple of the FSR) is given by,

$$\frac{c}{\lambda_1} - \frac{c}{\lambda_2}) \text{mod}(FSR) = \frac{d}{d_{2b} - d_{2a}} \times FSR$$  \hspace{1cm} (3.25)

If $\lambda_1$ is locked to some atomic transition, then the spacing $d$ between it and the laser $\lambda_2$ can be used to monitor the drift in the frequency of $\lambda_2$.

This scheme was used with the transmission spectrum of a Coherent Model 216 Spectrum Analyzer to periodically lock the frequency of the Titanium:Sapphire laser used in our experiment. The Model 216 consists of an FPI of free spectral range 300 MHz with a PZT to vary the length of the cavity. The transmitted light was sent to a photodiode at the back of the spectrum analyzer and the signal from the photodiode was acquired using Labview software on an external CPU. An error signal was computed using the distance (more precisely the voltage applied to the PZT in the FPI) between the Ti:Sapphire peak and a peak corresponding to a locked Cs repump laser.

We attempted to extend this scheme to lock our homemade ECDL. However, the feedback loop
implemented in the Labview software of the external CPU proved too slow to be effective in locking the homemade ECDL and so an alternative locking scheme was devised.

For a confocal Fabry-Perot cavity with free spectral range $\delta \nu$, the fringe width $\Delta \nu$ is given by,

$$\Delta \nu = \frac{\delta \nu}{F}$$  \hspace{1cm} (3.26)

where $F$ is the finesse of the cavity. The observed finesse of the Model 216 FPI is about 200 and this gives us a fringe width of $\sim 1$ MHz. We tune the FPI cavity length to the center of a peak corresponding to one of our MOT lasers, which is locked to an atomic frequency reference. Drifts in the length of the cavity manifest as a decrease in the transmitted intensity of the light and we use the transmission signal on the photodiode to create the error signal necessary for the feedback to the PZT that tunes the cavity length. Again frequency modulation using an AO allows lock-in detection of the derivative signal.

Once the cavity length is locked to a stable reference frequency, we lock our homemade ECDL to the cavity in the following fashion. We split off a small fraction of the homemade ECDL beam and using an AOM we tune it to a cavity resonance. By looking at FPI transmission spectrum corresponding to our homemade ECDL on the photodiode, we generate an error signal to feedback
to the homemade ECDL. The manner in which we discriminate between the transmission spectrum corresponding to the stabilized reference frequency and the homemade ECDL is discussed in the next section.

3.5.4 Frequency Modulated spectroscopy

In order to improve signal to noise on the error signal generated from the frequency monitoring, we have used various forms of frequency modulation spectroscopy. The basic idea of frequency modulation spectroscopy is as follows. Consider a frequency dependent optical signal $V(\omega)$ that is peaked at some frequency $\omega_0$. For small frequency displacements $\Delta \omega$ around $\omega_1$ we can expand $V(\omega)$ as a Taylor series. To first order this series may be written as

$$V(\omega) = V(\omega_1) + \left( \frac{\partial V}{\partial \omega} \right)_{\omega_1} \Delta \omega. \quad (3.27)$$
If we sinusoidally dither the frequency of the laser probing this optical feature so that

\[ \omega = \omega_1 + a_0 \sin(\Omega t), \quad (3.28) \]

then the Taylor expansion to first order is given by,

\[ V(\omega) = V(\omega_1) + \left( \frac{\partial V}{\partial \omega} \right)_{\omega_1} a_0 \sin(\Omega t). \quad (3.29) \]

Note that the derivative term \( \left( \frac{\partial V}{\partial \omega} \right)_{\omega_1} = 0 \) at the feature's peak, i.e. when \( \omega_1 = \omega_0 \) and also has a large slope here. In order to extract the derivative term from Equation 3.29 as a function of \( \omega_1 \), we use a phase-sensitive detector. We multiply or mix \( V(\omega) \) with a pure sine wave of frequency \( \Omega \) that is phase locked to the dither signal. After mixing we can write the signal as

\[ V_{\text{out}} = V(\omega) \times \sin(\Omega t) = V(\omega_1) \times \sin(\Omega t) + \left( \frac{\partial V}{\partial \omega} \right)_{\omega_1} \frac{a_0}{2} (1 - \cos(2\Omega t)), \quad (3.30) \]

where we have trigonometrically re-expressed the \( \sin^2(\Omega t) \) term. If we now filter out the high frequency parts of \( V_{\text{out}} \) we are left with only the derivative term.

\[ V_{\text{out}}^{\text{filtered}} = \left( \frac{\partial V}{\partial \omega} \right)_{\omega_1} \frac{a_0}{2}. \quad (3.31) \]

In the context of our Sacher ECDL we use an AOM and a RF VCO to dither the saturated absorption pump frequency with respect to the probe beam. The RF output of the VCO (center frequency \( \approx 80-100 \text{ MHz} \), modulation depth \( \approx 10 \text{ MHz} \) was modulated at 100 kHz. The resulting derivative peaks are shown in Figure 3.22. The derivative spectrum of the absorption is ideal for locking our ECDL as it offers a sharp slope with a minimum-maximum separation that corresponds to the width of the absorption feature and is zero at the locking point. We measure the noise on our locks by comparing the size of the residual error signal with the total height of the derivative feature and multiplying the ratio by the width of the peak. The circuits used in this process are presented in Figure 3.26 and Figure 3.27.

In the locking scheme for the homemade ECDL, as mentioned earlier, a small fraction of the Cs repump beam was split off and passed through an AOM. The AOM introduced a dither at 130 kHz on the Cs repump beam frequency and made it possible to shift the frequency of this beam. The FPI cavity was subsequently locked to the Cs repump peak using the derivative signal from the

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Figure 3.26: A schematic of the circuit used to obtain a derivative spectrum for locking our Sacher ECDL.

Figure 3.27: A schematic of the RF VCO control circuit used to dither the frequency of our Sacher ECDL. An stage consisting of an RF Amplifier from Minicircuits Corp. and a RF switch was placed between the VCO circuit and the AOM. The dither input to the RF VCO circuit comes from the mixer board depicted in Figure 3.26.
transmission spectrum. We split off a fraction of the homemade ECDL beam and used an AOM to move it into resonance with the FPI cavity. The frequency of the homemade ECDL beam was dithered (modulation depth 2-3 MHz), by modulating the diode current at 90 kHz. The different dither frequencies on the homemade ECDL and the Cs repump beam enabled us to demodulate the signals independently using two separate SRS510 Lock-in amplifiers from Stanford Research Systems. The linewidth of the homebuilt ECDL in lock was found to be $\sim 1$ MHz.

### 3.6 Photoionization and detection of molecular ions

We use a pulsed dye laser to generate the laser frequencies needed for ionization of the Cs$_2$ molecules formed in the photoassociation process. The ionization scheme is identical to earlier work [2].

#### 3.6.1 The pulsed dye laser

The ionization pulses are generated using a Sirah Cobra, a tunable dye laser. The Sirah [75] is pumped with the s-polarized 532 nm output of a Quanta-Ray PRO-series Nd:YAG laser [76].

The Sirah consists of a dye cell with a resonator around it. The resonator cavity contains two gratings that can be used to tune the frequency. The output of the resonator beam is amplified by directing it into another part of the dye cell. An external pump circulates dye through the cell at a fixed speed. The pump energy entering the Sirah is divided between the resonator and the amplifier stages. Electronic tuning of the frequency is obtained by moving the gratings and tuning the resonator. This is done using an external CPU and servo motors. The company supplies a program to enable the tuning from a Labview environment. The frequency output of the laser depends on the choice of resonator optics and the dye used. We used LDS 722 dye to produce $\sim 15$ mJ of output power at a wavelength of 715.9 nm.

The Quanta-Ray PRO-series Nd:YAG laser consists of a neodymium-doped yttrium aluminum garnet crystal that is pumped with argon flash lamps. The crystal rod is placed at the focus of an ellipse and each lamp has its own cavity. This ensures that most of the energy emitted from the lamps is focused into the Nd:YAG rod. The excited state in the Nd:YAG crystal has a long lifetime and a large population inversion can be built up. If oscillation is prevented while the inversion builds up and then suddenly permitted, the cavity will emit a large pulse of energy. This is known as Q-switching the cavity. In our laser this results in output pulses that are $\sim 5$-7 ns wide.
and have a peak power output of 15 MW/cm². The frequency width of the laser ~ 10 GHz. In our setup, the output of the YAG rod is passed through a doubling crystal to obtain 532 nm light.

### 3.6.2 Time of flight

The ions created by the ionization pulse travel through an electric field created by the cathode on the ion detector and a diametrically opposing electrode. The approximate electric field is ~ 1000 V/cm. Assuming that the ions start at rest, the time of flight in the field as a function of mass $M$ of the ion is given by the expression,

$$t_{TOF}(M) = \sqrt{\frac{2d^2M}{eV}}$$

(3.32)

where $d$ is the distance between the electrodes and $V$ is the potential difference between them.

The data acquisition system attached to the ion detector is triggered using the argon lamps and only the data arriving on the detector a few $\mu$s after the trigger is collected using a Labview DAQ system. We observed well-resolved ion spectra, and a well separated peak corresponding to the Cs₂ molecular ion is seen. A Stanford Research Systems SRS PS-350 (5000V-25W) supply was used to power the electrode.

### 3.6.3 The Ion detector

A Burle Magnum 5901 Channeltron detector is used as our ion detector. The Channeltron is a channel electron multiplier which consists of several millimeter sized lead silicate glass tubes that are specially processed to enhance their electrical conductivity and secondary emission characteristics. An ion strikes the cathode and sprays a burst of electrons in the general direction of the multiplier tube. The doped inner wall of the tube subsequently amplifies the input event and creates a large electrical signal. The Magnum has a typical gain of $10^7$ at 2.2 kV bias voltage. The Magnum has been optimized for pulse counting and hence it displays a relatively flat pulse height distribution as a function of incident ion flux. The Magnum detectors used in our experiment initially failed due to the deposition of alkali vapor on them. In order to ensure that there was no deposition a special arrangement was made to heat the detector mount from outside the chamber and the detector was always kept powered up. This ensured that the detector remained operational in the alkali vapor environment for a long time. A Stanford Research Systems SRS PS-350 (5000V-25W) supply was
used to power the detector.

3.6.4 Ionization signal calibration

In order to observe dips in the ion signal resulting from two-color photoassociation, we had to ensure that the ion detector was operating in a linear regime. The rough size of the signal corresponding to linear operation had been determined in the earlier RbCs spectroscopy study. However we were concerned that prolonged exposure to the alkali vapor environment inside the chamber could have altered the gain of the detector; thus we repeated this calibration. We reproduced the two-color spectra observed using the $1_u (6s_{1/2} + 6p_{3/2})$ states as the single-color photoassociation resonance [50, 77, 78]. Despite the exposure it appeared that the calibration had not changed.
Chapter 4

Experimental results

Here we present the results of our spectroscopic study.

4.1 Two-color photoassociation spectra

As stated before, we photoassociate cold Cs atoms from a MOT to a rovibrational level \((\nu, J)\) in the outer well of the \(0^+_1\) \((6s_{1/2} + 6p_{3/2})\) state. We lock our photoassociation laser frequency \((\nu_{PA})\) to this free-bound resonance. We monitor the ion signal from the decay of the excited state molecules as we tune the probe laser frequency \((\nu_{Probe})\) and look for dips in the ion signal from a bound-bound resonance.

Our initial attempts to conduct the two-color photoassociation study with unpolarized atoms were unsuccessful. We concluded that this was due to the sensitivity of the two-color transition dipole matrix element to angular factors. The use of an unpolarized sample of atoms forces us to average the angular factor over all possible orientations of the spin. The average angular factor is very small, thus the two-color transition dipole matrix element is negligible and we do not see any dips in our ion signal. So we attempted the same experiment with atoms polarized in the \(F = 4, M_F = 4\) state. It must be noted that at the time we started the experiment, we did not have a very clear idea of the angular factors. It was only after the first set of peaks were obtained that our collaborator, E. Tiesinga provided us with a way to calculate the angular factors (as discussed in Chapter 2).

Initially we used the \(\nu = 17, J = 2\) level as the intermediate state. We chose this level because, as shown in Figure 2.10, our collaborator E. Tiesinga predicted a high Franck-Condon factor for
decay from the \( \nu = 17 \) state to vibrational levels in the \( \text{a}^3\Sigma_u^+ \) with a binding energy of \( \sim 1225 \) GHz below the \( f = 3 + f = 3 \) atomic asymptote. Tiesinga’s calculations also predicted (see Figures 2.7 and 2.6) that these levels would be near-degenerate with high-lying vibrational levels in \( X^1\Sigma_g^+ \) state. The rotational level \( J = 2 \) and the the \( \sigma^+ \) polarization of the PA (photoassociation) laser was selected from a crude estimate of the angular factor. Our crude assumptions suggested that a photon with \( \sigma^+ \) polarization driving the free-bound transition would increase the projection \( M_F \) of the total angular momentum \( F \) of the scattering state \( (f = 4 + f = 4, l = 0, F = f_a + f_b + l = 4 + 4 + 0 = 8, M_F = 4 + 4 = 8) \) by one unit and give us an excited state with \( F = 9, M_F = 9 \).

For the \( \text{Cs}_2 \) \( 0_g^- (\nu, J) \) state, as \( F = I + J, M_F = M_I + M \) and as the atoms are spin-polarized \( (I = 7, M_I = 7) \), the \( F = 9, M_F = 9 \) state could only arise from a rotational level \( J = 2, M = 2 \).

More sophisticated angular factors calculations based on the approach described in Chapter 2 later confirmed this notion. We used \( \sigma^+ \) light on the probe laser (as shown in figure 4.1) as we felt that a resonant \( \sigma^+ \) photon would stimulate a transition from the \( \nu = 17, J = 2, I = 7, F = 9, M_F = 9 \) excited state level to a \( \text{a}^3\Sigma_u^+ \) bound level with total angular momentum \( F = 8, M_F = 8 \).

We naïvely expected the angular factor for such a transition to be large. We observed three dips with binding energies close to predicted levels at 1100, 1225, and 1357 GHz below the \( f = 3 + f = 3 \) dissociation limit. These observed dips could have been due to bound-bound resonances with vibrational levels in another excited molecular state. We confirmed that these dips corresponded to transitions into the ground state manifold by changing the intermediate state from \( \nu = 17, J = 2 \) to \( \nu = 16, J = 2 \). We observed dips at \( \nu_{\text{probe}} \) values shifted to the red by precisely the \( \nu = 17, J = 2 - \nu = 16, J = 2 \) splitting, as expected if the original signals correspond to transitions into the \( \text{a}^3\Sigma_u^+ \) state. This process is schematically represented in Figure 4.1.

In Figures 4.2 and 4.3 we show the spectra obtained for both resonances coupling to the state located 1214.3405 GHz below the \( f = 3 + f = 3 \) dissociation limit. This level was observed using both the \( 0_g^- (\nu = 17, J = 2) \) and the \( 0_g^- (\nu = 16, J = 2) \) intermediate levels. The binding energy of this level was determined as follows. We used a scanning Fabry-Perot interferometer (Toptica FPI 100, FSR 1 GHz, finesse 200 [79]) as a source of frequency markers. The position of the probe laser peak on the FPI scan when the laser was tuned to resonance was compared to the position of the FPI peak with the laser tuned to a nearby known \( \text{Cs}_2 \) photoassociation peak (this reference peak was seen by an increase in the ion signal) at frequency \( \nu_{\text{ref}} \).

In order to remove the possibility of drift in the interferometer, the position of \( \nu_{\text{probe}} \) was
measured with respect to the peak corresponding to $\nu_{PA}$. If the Cs$_2$ photoassociation peak was more than one free spectral range away, we counted the number of FPI fringes to obtain the desired difference in frequency. The binding energies of this level as determined from two different intermediate levels, agreed to within 10 MHz. Raw ion detector signal data corresponding to all the dips observed with these intermediate levels are shown in the appendix. We also used the $0_g^{-}$ $\nu = 4, J = 2$ state as an intermediate level and observed dips corresponding to predictions of binding energy near 506 GHz and 432 GHz. Raw ion detector signal data corresponding to these dips are shown in the appendix.

Figure 4.1: A schematic of the procedure used to ensure that the dips observed with the $\nu = 17, J = 2$ intermediate level were indeed due to a stimulation to the ground state manifold.
Figure 4.2: Dip with \( B.E. = 1214.34(42) \) GHz below \( (f=3+f=3) \) atomic asymptote. This was observed using \( 0_\alpha^\pm (\nu = 17, J = 2) \) state as an intermediate level. The photoassociation frequency was 11681.328(10) cm\(^{-1}\) which corresponds to the \((4,4) \rightarrow 0_\alpha^- (\nu = 17, J = 2)\) transition. The calibration frequency was 11722.547(10) cm\(^{-1}\) which corresponds to the \((4,4) \rightarrow 0_\alpha^- (\nu = 69, J = 2)\) transition. The offset between the calibration frequency and the anchor frequency measured on the FPI was 2.991(6) GHz. The anchor frequency was found to be 11722.448(10) cm\(^{-1}\). The polarization of the probe laser was \( \sigma^+ \).
Figure 4.3: Dip with $B.E. = 1214.33(42)$ GHz below $(f=3+f=3)$ atomic asymptote. This was observed using $0^{-}_g (\nu = 16, J = 2)$ state as an intermediate level. The photoassociation frequency was $11679.989(10)$ cm$^{-1}$ which corresponds to the $((4,4) \rightarrow 0^{-}_g (\nu = 16, J = 2))$ transition. The calibration frequency was $11720.955(10)$ cm$^{-1}$ which corresponds to the $((4,4) \rightarrow 0^{-}_g (\nu = 66, J = 2))$ transition. The offset between the calibration frequency and the anchor frequency measured on the FPI was $-4.590(6)$ GHz. The anchor frequency was found to be $11721.109(10)$ cm$^{-1}$. The polarization of the probe laser was $\sigma^-$. 
Using the approach discussed in Chapter 2, we calculated the dipole matrix elements for the transition $0_g^- (\nu, I = 7, J = 2, F = 9, M_F = 9) + \sigma^- \rightarrow a^3\Sigma_u^+(\nu', f, l, F = 10, M_F = 10)$ using Equation 2.65. We obtained non-vanishing angular factors for transitions to hyperfine and rotation sub-states (with $f = 8, l = 2, 4, f = 7, l = 4$ and $f = 6, l = 4$). Our collaborator had predicted that hyperfine and rotational sub-structure (with spacings in the $\approx 7$-8 GHz for hyperfine and $\approx 0.5$ GHz for rotation) would be present inside each vibrational level of the $a^3\Sigma_u^+$ state.

In order to explore such structure, we changed the polarization of the probe laser to $\sigma^-$. The scheme used for investigating hyperfine and rotational features depicted in Figure 4.4. With $\sigma^+$ polarization on the probe laser, we initially only saw one large feature corresponding to the $f = 8, l = 0$ hyperfine manifold. With the $\sigma^-$ we observed additional dips at spacings close to the predicted spacings between the $f = 8, 7, 6$ hyperfine sub-levels. For visual reference we present a scan in the $f = 8$ manifold in 506 GHz bound resonance in Figure 4.5.

We also calculated dipole matrix elements for the transition $0_g^- (\nu, I = 7, J = 2, F = 9, M_F = 9) + \sigma^- \rightarrow a^3\Sigma_u^+(\nu', f, l, F = 8, M_F = 8)$. We obtained non-vanishing angular factors for transitions to hyperfine and rotation sub-states (with $f = 8, l = 0, 2, 4, f = 7, l = 2, 4$ and $f = 6, l = 2, 4$). We expected that these features would be spaced by the same amount as the hyperfine structure observed earlier with the $\sigma^-$ light. This prompted us to scan over the similar frequency ranges with $\sigma^+$ light on the probe laser. We observed some additional features in the $f = 7$ manifold using this configuration. The raw ion signal data corresponding to these is presented in the appendix.

The hyperfine and rotation spectra observed from various vibrational levels were very similar and in qualitative accord with our expectations, except in the 506 GHz bound level. Here, in the $f = 7$ hyperfine manifold we observed an additional dip with $\sigma^-$ polarization on the probe laser (hence corresponding to $F = 10, M_F = 10$). The additional dip is shown in figure A-22. The figure also shows a scan corresponding to the 432 GHz bound level, which is also observed from the $\nu = 4, J = 2$ intermediate state.

To recapitulate our results, we have observed features corresponding to five vibrational levels (with their $f = 8, l = 0, F = 8, M_F = 8$ dips) bound by 430.95(42) GHz, 505.07(42) GHz, 1091.86(42) GHz, 1214.34(42) GHz, 1343.94(34) GHz, and 1480.52(39) GHz below the $f = 3 + f = 3$ atomic asymptote. These correspond to predicted vibrational levels with nominal binding energies of 432 GHz, 506 GHz, 1100 GHz, 1225 GHz, and 1497 GHz. We have failed to observe any spectra with binding energies near 1000 GHz (using the $0_g^- (\nu = 16, J = 2)$ level as the intermediate state).

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Figure 4.4: Scheme used to study hyperfine and rotation features. This scheme can access levels with \( f = 6, 7, 8 \) and \( l = 0, 2, 4 \).
Figure 4.5: An example of a scan showing substructure of the 506 GHz bound level. This was observed using the $0_g^-(\nu = 4, J = 2)$ state as the intermediate state. This peak corresponds to an inferred hyperfine quantum number of $f = 8$. The photoassociation frequency was 11661.925(10) cm$^{-1}$ which corresponds to the $((4,4) \rightarrow 0_g^- (\nu = 4, J = 2))$. The relative binding energy of the dip to the anchor dip was -0.448(30) GHz, the absolute binding energy of the anchor dip was -505.07(42) GHz from $f=3+f=3$ atomic asymptote. The polarization of the probe laser was $\sigma^-$. 

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Figure 4.6: Scans of the $f = 7$ hyperfine manifold of the 506 GHz bound level with $\sigma^-$ (blue) and $\sigma^+$ (red) polarization on the probe laser. The additional peak in the 506 GHz bound level is seen in the scan with $\sigma^-$ polarization on the probe laser. For comparison we also present a similar set of scans of the $f = 7$ manifold of the 432 GHz bound level. Both levels are observed using $0^-(\nu = 4, J = 2)$ as the intermediate state. Note that the scans with $\sigma^+$ polarization on the probe laser have nearly identical structure for both the 506 GHz and the 432 GHz level.

and near 603 GHz (using the $0^-(\nu = 4, J = 2)$ level as the intermediate state). The hyperfine and rotational sub-structure of the observed vibrational levels has been explored. In the 432 GHz, 506 GHz, 1100 GHz, and 1225 GHz levels we have observed additional lines spaced by $\approx 7-8$ GHz. This spacing agrees with our collaborator E. Tiesinga’s estimate of the hyperfine splitting between the $f = 8, 7$ and 6 sublevels. In all the vibrational levels we have also observed features spaced by $\approx 500$ MHz in the $f = 8$ manifold. This spacing is comparable to predictions of rotational splitting. We have observed an unexpected dip in the $f = 7$ hyperfine manifold of the 505.07(42) GHz bound level. All the observed dips and scans undertaken are summarized in Figure 4.7, and Table 4.1 gives the absolute and relative frequency positions of the dips.

The columns in table 4.1 are labeled as follows: Label denotes the nominal binding energy of the level in the ground state manifold (as taken from our collaborator E. Tiesinga’s predictions).
<table>
<thead>
<tr>
<th>Label</th>
<th>ν_{PA} (cm⁻¹)</th>
<th>ν_{cal} (cm⁻¹)</th>
<th>Offset (GHz)</th>
<th>ν_{anc} (cm⁻¹)</th>
<th>Abs. B.E. (GHz)</th>
<th>Rel. B.E. (GHz)</th>
<th>f</th>
<th>P</th>
<th>W (MHz)</th>
<th>D (% depl)</th>
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<td>(4, 4) → ν = 102, J = 2 11729.950(8)</td>
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<td>11729.986(8)</td>
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<td>11722.448(10)</td>
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<td>-</td>
<td>30</td>
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<td>11676.913(10)</td>
<td>430.95(42)</td>
<td>-0.434(40)</td>
<td>8</td>
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<td>30</td>
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Table 4.1: A summary of our results. The column headers are explained in the chapter text.
$\nu_{PA}$ shows the quantum numbers and the frequency of the PA resonance. The notation \((4,4) \rightarrow \nu = 17, J = 2\) means an atom pair with \(f = 4 + f = 4\) is driven to the \(0^+_g(\nu = 17, J = 2)\) level. $\nu_{cal}$ shows the quantum numbers and frequency of the nearby Cs$_2$ $0^+_g$ PA resonance used to calibrate the absolute frequency of the observed dips. We define the anchor line for each vibrational level as the line corresponding to the least-bound state observed with $\sigma^+$ light. Offset is the frequency difference between the calibration line peak and the peak of the anchor line as measured on the Fabry-Perot interferometer. $\nu_{ane} = \nu_{cal} - \text{Offset}$ is the absolute frequency position of the anchor line. Abs. B.E is the binding energy of the anchor line with respect to the \(f = 3 + f = 3\) atomic asymptote. Rel. B.E. is the position of the other states in a vibrational level relative to the anchor line (here a minus sign means less bound). $f$ is the inferred hyperfine quantum number $f = I + S$. $P$ denotes the circular polarization of the probe laser light used to see a given level. $W$ is the approximate width of the ion dip resonance; $D$ is the approximate percentage depletion of the resonance.

Next we discuss uncertainties. No uncertainty has been ascribed to either $W$ or $D$ due to the difficulty in fitting a Gaussian to our observed lines. The $\nu_{PA}$ frequencies are known to within an uncertainty of 300 MHz from Ref.[25]. The study in reference [25] used an Iodine cell to measure the position of the deeply bound vibrational levels in the outer-well of the $0^+_g(6s_{1/2} + 6p_{3/2})$ state while the Cs atomic transition was used to measure the positions of high-lying vibrational levels (binding energy $\leq$ 5 cm$^{-1}$). The absolute uncertainty in the position of levels measured with the Iodine peaks was reported as 300 MHz, while the absolute uncertainty of the PA spectra relative to the Cs atomic peak was 150 MHz. As a result of this, the uncertainty in our calibration frequency $\nu_{cal}$ is 300 MHz except for the calibration frequencies used for 1497 and the 1357 levels, where the uncertainty is 150 MHz. In the case of the 1497 level, there was a problem identifying the $J=2$ peak in the calibration resonance, because the rotational structure for high lying vibrational states in the $0^+_g(6s_{1/2} + 6p_{3/2})$ outer well is not resolved. Thus for this state an additional 200 MHz uncertainty was summed in quadrature to the uncertainty from [2, 25]. The uncertainty in the FPI offset is 6 MHz. This is determined by comparing the width of the peak on the FPI scan to the FSR of the FPI. The linearity of the probe laser scan is $\approx$ 150 MHz over the entire range (30 GHz) [80]. We typically scan our probe laser over 1 GHz, this gives us an uncertainty in the probe laser frequency of 5 MHz. Some of the peaks in the $f = 7$ manifold were mapped with respect to the largest peak in this manifold (rather than directly comparing to the anchor peak). We assign the uncertainty
in $\nu_{\text{anc}}$ to be the quadrature sum of the uncertainty in $\nu_{\text{cal}}$ and the uncertainty in the FPI offset. The uncertainty in the Abs. B.E. is the quadrature sum of the uncertainties in $\nu_{\text{anc}}$ and $\nu_{PA}$. The uncertainty in the Rel. B.E. column is the uncertainty relative to the position of the anchor peak; it is not the absolute uncertainty of each peak. As discussed earlier the Rel. B.E. measurements are made by comparing the position of the probe laser when it is resonant with the $\nu_{\text{anc}}$ and when it resonant with another line in the hyperfine and rotation sub-structure. In each case, the position of the probe laser peak is measured with respect to a reference laser peak on an FPI scan. The position of the center of each line is assigned an uncertainty of $\approx 20$ MHz (approximately half the width of the dip). By summing each of these in quadrature, we find the uncertainty in the position of a resonance (irrespective of whether it is the anchor peak or some hyperfine-rotation sub-structure) is 21 MHz. Thus the uncertainty in the Rel. B.E. is the quadrature sum of the uncertainty in the positions of the reference laser peak and probe laser peak of the FPI scan. This is $\approx 30$ MHz.
Figure 4.7: All the peaks observed with various intermediate states in our experiment. The x-axis conveys no physical meaning, it merely serves to display data. The y-axis is the energy spacing between observed peaks and the position of the anchor peak in each vibrational level as predicted by our collaborator E. Tiesinga scaled to the Cs atomic hyperfine splitting (9.192 GHz). The numbers in black (432, 506, 603, etc...) are the predicted nominal binding energies of the vibrational levels. The vertical straight lines in various colors indicate the range of the probe laser scan. The colored symbols (stars, triangles, dots) represent observed dips. The legend of the graph indicates which color and symbol are used to represent the peaks and scan ranges corresponding to a particular intermediate level and probe polarization. A large black dot is used to represent vibrational levels that were predicted but not observed in our spectra.
Chapter 5

Analysis and conclusions

Our interest in the $a^3\Sigma_u^+$ state of Cs$_2$ was sparked by the possibility of using a microwave transition between closely-spaced vibrational levels of the $a^3\Sigma_u^+$ state and the $X^1\Sigma_g^+$ state as a probe for the time-variation of the electron-proton mass ratio $\mu$. Though we started this experiment with the primary aim of studying the $a^3\Sigma_u^+$ state of Cs$_2$, our greatest hope throughout the experiment was to observe an accidental degeneracy. Second-order hyperfine interaction between the $a^3\Sigma_u^+$ and $X^1\Sigma_g^+$ is expected to strongly mix the states near accidental degeneracies and this mixing can either perturb the $a^3\Sigma_u^+$ levels, or make mixed $X^1\Sigma_g^+$ levels visible. It was with that in mind, that we had deliberately restricted our spectroscopic investigation to states where the levels were expected to be closely spaced.

We now report some progress towards these goals. We have observed spectra that clearly correspond to the predicted vibrational structure of the $a^3\Sigma_u^+$. We have seen fairly regular hyperfine and rotational spectra that are in broad agreement with predictions. There appears to be an unexpected feature in the $f = 7$ manifold in the 506 GHz bound level, which we believe may correspond to a perturbed $X^1\Sigma_g^+$ vibrational level. In this chapter, we discuss how we interpret our spectra. In §5.1 of this chapter we detail the attempts made to understand the spectra. In §5.2 we present an unsuccessful attempt to assign the lines in the hyperfine and rotation spectrum using an angular factors calculation. In §5.3 we explore the possibility that the extra dip in the $f = 7$ manifold in the 506 GHz bound level is a singlet peak, and finally in §5.4 we examine our options for future investigations.
5.1 Understanding the spectra

Our spectra consist of dips in the ion signal to due disruption of the single-color photoassociation to the intermediate state. The disruption stems from an Autler-Townes splitting of the free-bound photoassociation peak. The extent to which the peak is split depends on the Rabi frequency of the bound-bound transition. Ideally each bound-bound resonance would completely split the free-bound photoassociation resonance and hence the ion signal should be entirely depleted. We have rarely observed two-color dips that complete deplete the ion signal (within the limit of our signal-to-noise). More generally, the percentage depletion varies considerably across our spectra and we have seen a large number of dips that only deplete the ion signal by a small amount. We attribute this to a combination of factors listed below.

Our probe laser was scanned with a finite step size (usually 7.5 MHz). This limits the size of the smallest features we can see in our two-color spectrum. We did not reduce our step-size as taking a large number of steps usually meant longer scans and the MOT was seldom stable over long intervals of time.

A small molecular Rabi coupling would imply a small Autler-Townes splitting. The Rabi coupling of the bound-bound transition depends on the product of the Franck-Condon factor, the angular factor for the transition and the effective intensity of the bound-bound excitation beam. The effective intensity of the bound-bound excitation beam depends on the overlap between the MOT, the photoassociation beam, and the probe laser beam. In the course of the experiment, this overlap was observed to drift. We attempted to keep this drift to a minimum by repeatedly tuning the probe laser to the position of a known dip in the spectrum and maximizing the depletion.

Low Franck-Condon factors can also reduce the molecular Rabi coupling. We have consistently observed strong “anchor lines” for all the vibrational levels. The angular factors for all the anchor lines seen with the same intermediate state are the same. Our inability to observe “anchor lines” corresponding to the 1000 GHz bound vibrational level (from our v=16, J=2 intermediate state) and the 603 GHz bound vibrational level (from our v=4, J=2 intermediate state) can be attributed solely to small Franck-Condon factors. We conclude from this that our collaborator’s Franck-Condon factor predictions are not entirely correct.

The molecular Rabi coupling can also be diminished due to poor angular factors. In the case of other peaks in the hyperfine and rotation spectrum of a particular vibrational level, the Franck-Condon factor does not vary and yet we observe a wide variation in the size of the dip over this
scale. We attribute this to a variation in the angular factors for the various hyperfine and rotation transitions.

We appear to have qualitatively verified the vibrational predictions however our measured binding energies are all smaller than those predicted by our collaborator. The difference between the observed and predicted energies grows monotonically in size as the binding energy increases.

Hyperfine and rotational spectra appear to reproduce predicted values for hyperfine splitting (\( \sim 7-8 \text{ GHz} \)). From Table 4.1 we see that the finer features in the hyperfine and rotation spectra in the \( f = 7 \) manifold were not observed for the 1100 GHz state. We attribute this to a combination of small angular factors and a poor Franck-Condon factor.

The initial set of predictions for hyperfine and rotation structure from our collaborator had excluded the off-diagonal effect of the second-order spin-orbit coupling \([81, 56]\). Once this effect was included in the predictive framework, it was found that the agreement with observed spectra improved dramatically as shown in Figures 5.1 and 5.2.

5.2 Angular factor calculation

In our observations of hyperfine and rotational structure, we used both \( \sigma^+ \) and \( \sigma^- \) polarization on the downward excitation light and observed distinct spectra with the two polarizations. To explain these results we attempted a calculation of the angular factors describing the relative transition strengths for each of our downward transition schemes (i.e. schemes using a \( \sigma^+ \) photon and a \( \sigma^- \) on the downward stimulation laser).

We calculated angular factors describing the strength of the bound-bound transitions using Mathematica. We carried out two sets of calculations: the first where the effect of the terms containing \( C_3 \) on the elements of the \( V_{MP} \) matrix in Equation 2.35 is ignored, and the second where the effect of the \( C_3 \) is included. The \( C_3 \) should have a more pronounced effect on the spectra of deeply bound levels in the outer well of the 0\(_g^-\) excited state (such as the \( v = 4, J = 2 \)). For high-lying states like the \( v = 16 \) or the \( v = 17 \), the effect should be smaller. Our results are shown in Table 5.1.

As seen from the Table 5.1, the calculation predicts that the angular factors for transitions to the \( |l,f,F,M_F\rangle = |2,8,8,8\rangle \) with \( \sigma^+ \) light are comparable to the angular factors for transitions to \( |l,f,F,M_F\rangle = |2,8,10,10\rangle \) with \( \sigma^- \). However as seen in Table 4.1 in Chapter 4, we have only observed the latter but not the former. The inability to see this predicted peak caused us to question
Selection rules $\sigma^+ \rightarrow F_{\text{tot}}^{\text{obs}} = 8,9,10$ and $\sigma^- \rightarrow F_{\text{tot}}^{\text{obs}} = 10$

Figure 5.1: An overlay of the predictions for the hyperfine and rotation features with second-order spin-orbit interaction and observed spectra. The letters $s,d,g,i$ denote rotational states with $l=0,2,4,6$ respectively. This figure has been reproduced from our correspondence with our collaborator E. Tiesinga.
Selection rules $\sigma^+ \rightarrow F_{\text{tot}} = 8,9,10$ and $\sigma^- \rightarrow F_{\text{tot}} = 10$

$(SI) f = (17)7$

Figure 5.2: A blow-up of the $I + S = 7$ part of the hyperfine and rotation spectrum and predictions for the same. This figure has been reproduced from our correspondence with our collaborator E. Tiesinga.
Table 5.1: A calculation of the angular factors describing the relative strengths of the bound-bound transitions, with and without the effect of $C_3$. $P$ is the polarization of the downward excitation light. $l$ is the rotational quantum number. $f$ is the $I + S$ value ($I = 7$ for our experiment). $F$ is $l + f$, $M_F$ is the projection of $F$. AF(1) is the square of the angular factor calculated using Equation 2.65. AF(1) is calculated neglecting $C_3$ and AF(2) is calculated including $C_3$. The value of $C_3$ is from [25].

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our angular factors. Neglecting $C_3$ causes the angular factors to change visibly, but neither case seems to fully explain our observations. For example we have seen three dips in the $f = 7$ manifold with $\sigma^+$ light for the 1225 GHz bound level, while we have only seen two dips with $\sigma^+$ in the same manifold for the 506 and 432 GHz levels. The extra dip observed in the $f - 7$ manifold of the 1225 GHz level lies tantalizingly close to the predicted position of the $|l, f, F, M_F\rangle = |2, 8, 9, 8\rangle$ level in Figure 5.2, however the angular factor calculations predict that the probability for seeing this dip should be higher in the 506 and the 432 GHz level than in the 1225 GHz level. Several similar discrepancies amplified the notion that the angular factor calculation is inadequate to describe our results.

One possible avenue for error in our angular factors calculation is that it assumes that the $0^-$ state is a mixture only of the $3\Pi$ and the $3\Sigma^+$ states associated with the $6s + 6p$ asymptote. This is an oversimplification, and including other terms might considerably alter the angular factors. Removing the problems in the angular factors is necessary for fully understanding the spectra, but remains to be accomplished.

### 5.3 The singlet state

The unexpected line in the $f = 7$ manifold of the 506 GHz state is our only candidate for a possible singlet level. Comparing it to the corresponding manifold in the 432 GHz level, which is driven from the same upper state ensures that we are free of any complications from a change in angular factor that may arise from the intermediate state. An unfortunate fact is we were not able to confirm that the unexpected dip is necessarily due to a downward stimulation. Usually we accomplish this by moving to another nearby intermediate state and looking for the dip at a frequency shifted by the splitting between the intermediate states. However in this peculiar case, the Franck-Condon factors for accomplishing this were unfavorable. The peaks due to the $0^- (\nu = 3, J = 2)$ upper state are much smaller than the peaks due to the $0^- (\nu = 4, J = 2)$ upper state causing unacceptably low signal to noise; and the $0^- (\nu = 5, J = 2)$ upper state has small Franck-Condon factors for coupling to the 506 GHz bound level in the ground state.

The calculations by our collaborator E. Tiesinga had predicted that an accidental degeneracy between the singlet and triplet levels was likely near $f = 7$ manifold of the 506 GHz level. However, the position of the vibrational levels of the singlet state are spectroscopically known only to within an uncertainty of $\sim 15$ GHz relative to dissociation [46]. This leaves considerable ambiguity in the
calculation. Tiesinga is attempting to examine the effect on the spectrum of moving the singlet potential with respect to the triplet potential. In theory the hyperfine mixing between the two states should perturb the triplet levels; however this effort may not offer a dramatic resolution to our problems, as the effect of the hyperfine mixing is less prominent for the high \( ^{\Gamma} \) states we can observe. Investigations into this were still underway at the time of writing this thesis.

### 5.4 Future directions

The data generated from the experiment should be sufficient for improving the quality of the fits to the triplet ground state potential. Used in conjunction with earlier data \([46, 78, 4]\), it should be possible to build an improved fit for both the singlet and triplet ground state potentials. This could shed some light on the position of the singlet state with respect to the triplet vibrational level at 506 GHz. It may be noted that even with levels at a depth of 506 GHz below dissociation, a transition between the singlet and triplet states is expected to shift by \( \approx 166 \, \text{cm}^{-1} \) for a unit change in \( \mu \) (refer Figure 2.5). This is still sufficient for giving a large improvement over current limits, using our proposed test of time variation of \( \mu \). A complete fit of all available data will require serious computational time and our collaborator T. Bergeman at SUNY Stony Brook is presently investigating this. The exact size of the transition matrix element between the singlet and triplet is also worthy of further investigation as it will tell us the amount of RF power needed to drive this transition. We have seen that the second-order spin-orbit interaction has a sizable effect on the spectrum. This indicates significant off-diagonal mixing of the \( a^3\Sigma_u^+ \) state with the \( ^1\Pi_u \) states. A \( ^1\Pi_u \) component gives rise to E1 transition matrix elements to the \( X^1\Sigma_g^+ \) state. Hence, it is possible that in addition to the M1 transition dipole due to hyperfine interaction, there may even be a significant E1 transition dipole between the states.

If these issues are resolved favorably, we visualize the following scheme to actually measure the singlet-triplet transition. We start with a Cs BEC, and we efficiently populate the desired triplet level using a STIRAP scheme (counter-intuitive sequence) \([82]\). The singlet-triplet transition can be driven by applying an RF pulse. The population of the triplet state can be monitored using state-selective ionization. The state-selective ionization could be accomplished with relatively minimal additional spectroscopy of the higher lying electronic states of Cs\(_2\).
Appendix: Raw Spectroscopic data

Here we present all the raw data corresponding to all the dips we have seen in our experiment.

The lines observed with the $0^+_g$ ($\nu = 17, J = 2$) state as an intermediate level while using $\sigma^+$ polarization on $\nu_{probe}$ are shown in Figures A-1, A-2, and A-3.

The lines observed with the $0^+_g$ ($\nu = 16, J = 2$) state as an intermediate level while using $\sigma^+$ polarization on $\nu_{probe}$ are shown in Figures A-4, A-5, A-6, A-7, and A-8.

The lines observed with the $0^+_g$ ($\nu = 16, J = 2$) state as an intermediate level while using $\sigma^-$ polarization on $\nu_{probe}$ are shown in Figures A-9, A-10, A-11, A-12, A-13, A-14, A-15, and A-16.

The x-axis in these graphs denotes the binding energy of the observed dips relative to the anchor dip. A negative value of relative binding energy denotes a hyperfine and rotation sub-level that is less bound than the anchor level.

The lines observed with the $0^+_g$ ($\nu = 4, J = 2$) state as an intermediate level while using $\sigma^+$ polarization on $\nu_{probe}$ are shown in Figures A-17, A-18, A-19 and A-20.

The lines observed with the $0^+_g$ ($\nu = 4, J = 2$) state as an intermediate level while using $\sigma^-$ polarization on $\nu_{probe}$ are shown in Figures A-21, A-22, A-23, A-24, A-25, and A-26. The x-axis in these graphs denotes the binding energy of the observed dips relative to the anchor dip. A negative value of relative binding energy denotes a hyperfine and rotation sub-level that is less bound than the anchor level.
Figure A-1: Dip with B.E. = 1091.86(42) GHz below (f=3+f=3) atomic asymptote. This was observed using the 0^- (ν = 17, J = 2) state as an intermediate level. The photoassociation frequency was 11681.328(10) cm\(^{-1}\), which corresponds to the ((4, 4) \rightarrow 0^- (ν = 17, J = 2)) transition. The calibration frequency was 11718.183(10) cm\(^{-1}\), which corresponds to the ((4, 4) \rightarrow 0^- (ν = 59, J = 2)) transition. The offset between the position of the calibration peak and the anchor line on the FPI was -5.363(6) GHz. The frequency of the anchor line was calculated to be 11718.362(10) cm\(^{-1}\). This dip has an inferred hyperfine quantum number of f = 8.
Figure A-2: Dip with $B.E. = 1214.34(42)$ GHz below $(f=3+f=3)$ atomic asymptote. This was observed using the $0_7^-$ ($\nu = 17, J = 2$) state as an intermediate level. The photoassociation frequency was $11681.328(10)$ cm$^{-1}$, which corresponds to the $(4, 4) \rightarrow 0_7^- (\nu = 17, J = 2)$ transition. The calibration frequency was $11722.547(10)$ cm$^{-1}$, which corresponds to the $(4, 4) \rightarrow 0_7^- (\nu = 69, J = 2)$ transition. The offset between the position of the calibration peak and the anchor line on the FPI was $2.991(6)$ GHz. The frequency of the anchor line was calculated to be $11722.448(10)$ cm$^{-1}$. This dip has an inferred hyperfine quantum number of $f = 8$. 

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Figure A-3: Dip with $B.E. = 1343.93(34)$ GHz below $(f = 3 + f = 3)$ atomic asymptote. This was observed using the $0_g^- (\nu = 17, J = 2)$ state as an intermediate level. The photoassociation frequency was 11681.328(10) cm$^{-1}$, which corresponds to the $(4, 4) \rightarrow 0_g^- (\nu = 17, J = 2)$ transition. The calibration frequency was 11726.759(5) cm$^{-1}$, which corresponds to the $(4, 4) \rightarrow 0_g^- (\nu = 83, J = 2)$ transition. The offset between the position of the calibration peak and the anchor line on the FPI was -0.345(6) GHz. The frequency of the anchor line was calculated to be 11726.770(5) cm$^{-1}$. This dip has an inferred hyperfine quantum number of $f = 8$. 

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Figure A-4: Dip with $B.E. = 1091.86(42)$ GHz below ($f=3+f=3$) atomic asymptote. This was observed using the $0_\sigma^-$ ($\nu = 16, J = 2$) state as an intermediate level. The photoassociation frequency was $11679.989(10)$ cm$^{-1}$, which corresponds to the $((4,4) \rightarrow 0_\sigma^- (\nu = 16, J = 2))$ transition. This dip was not measured using a photoassociation resonance. The dip was measured solely with the Burleigh WA1500 wavemeter. The anchor dip was observed at $11717.02(02)$ cm$^{-1}$ and the photoassociation frequency measured on the wavemeter was $11679.98(02)$ cm$^{-1}$. This dip has an inferred hyperfine quantum number of $f = 8$. 

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Figure A-5: Dip with $B.E. = 1214.33(42)$ GHz below $(f=3+f=3)$ atomic asymptote. This was observed using the $0^+_{g^-}(\nu = 16, J = 2)$ state as an intermediate level. The photoassociation frequency was $11679.989(10)$ cm$^{-1}$, which corresponds to the $(4,4) \rightarrow 0^+_{g^-}(\nu = 16, J = 2)$ transition. The calibration frequency was $11720.955(10)$ cm$^{-1}$, which corresponds to the $(4,4) \rightarrow 0^+_{g^-}(\nu = 66, J = 2)$ transition. The offset between the calibration peak and the anchor line on the FPI was $-4.590(6)$ GHz. The frequency of the anchor line was calculated to be $11721.109(10)$ cm$^{-1}$. This dip corresponds to an inferred hyperfine quantum number of $f = 8$. 

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Figure A-6: An example of a scan showing hyperfine and rotation structure corresponding to the level with $B.E.=1214.33(42)$ GHz below $(f=3+6, f=3)$ atomic asymptote. This was observed using the $0_g^- (\nu = 16, J = 2)$ state as an intermediate level. These dips correspond to an inferred hyperfine quantum number of $f = 7$. The photoassociation frequency was $11679.989(10)$ cm$^{-1}$ ($4,4 \rightarrow 0_g^\nu = 16, J = 2$), $B.E.r_{el}= 6.975(30)$ GHz, $B.E.r_{el}= 7.075(30)$ GHz, and $B.E.r_{el}= 8.185(30)$ GHz.
Figure A-7: Dip with $B.E. = 1343.94(42)$ GHz below $(f=3+f=3)$ atomic asymptote. This was observed using the $0_{g}^{-} (\nu = 16, J = 2)$ state as an intermediate level. The photoassociation frequency was $11679.989(10)$ cm$^{-1}$, which corresponds to the $[(4, 4) \rightarrow 0_{g}^{-} (\nu = 16, J = 2)]$ transition. This dip was not measured using a photoassociation resonance. The dip was measured solely with the Burleigh WA1500 wavemeter. The anchor dip was observed at $11717.02(02)$ cm$^{-1}$ and the photoassociation frequency measured on the wavemeter was $11679.98(02)$ cm$^{-1}$. This dip has an inferred hyperfine quantum number of $f = 8$. 

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Figure A-8: Dip with \( B.E. = 1480.52(42) \) GHz below \((f=3+f=3)\) atomic asymptote. This was observed using the \( 0_-(\nu = 16, J = 2) \) state as an intermediate level. The photoassociation frequency was \( 11679.989(10) \) cm\(^{-1}\), which corresponds to the \((4, 4) \rightarrow 0_-(\nu = 16, J = 2)\) transition. The calibration frequency was \( 11729.950(8) \) cm\(^{-1}\), which corresponds to the \((4, 4) \rightarrow 0_-(\nu = 102, J = 2)\) transition. The offset between the calibration peak and the anchor line on the FPI was \(-1.100(6)\) GHz. The frequency of the anchor line was calculated to be \( 11729.986(8) \) cm\(^{-1}\). This dip has an inferred hyperfine quantum number of \( f = 8\).
Figure A-9: An example of a scan showing hyperfine and rotation structure corresponding to the level with $B.E. = 1091.86(42)$ GHz below ($f=3+f=3$) atomic asymptote. This was observed using the $0^+_{\varrho} (\nu = 16, J = 2)$ as an intermediate level. This dip has an inferred hyperfine quantum number of $f = 8$. The photoassociation frequency was $11679.989(10)$ cm$^{-1}$, which corresponds to the $(4,4) \rightarrow 0^+_{\varrho} (\nu = 16, J = 2))$ transition. The relative binding energy of the dip to the anchor line was $-0.564(30)$ GHz.
Figure A-10: An example of a scan showing hyperfine and rotation structure corresponding to the level with $B.E. = 1091.86(42)$ GHz below ($f=3$+$f=3$) atomic asymptote. This was observed using the $0_g^-$ ($\nu = 16, J = 2$) state as an intermediate level. This dip has an inferred hyperfine quantum number of $f = 7$. The photoassociation frequency was $11679.989(10)$ cm$^{-1}$, which corresponds to the $((4,4) \rightarrow 0_g^- (\nu = 16, J = 2))$ transition. The relative binding energy of the dip to the anchor line was $6.911(30)$ GHz.

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Figure A.11: An example of a scan showing hyperfine and rotation structure corresponding to the level with $B.E. = 1091.86(42)$ GHz below $(f=3+f=3)$ atomic asymptote. This was observed using the $0^{-}_g (\nu = 16, J = 2)$ state as an intermediate level. This dip has an inferred hyperfine quantum number of $f = 6$. The photoassociation frequency was $11679.989(10)$ cm$^{-1}$, which corresponds to the $(4,4) \rightarrow 0^{-}_g (\nu = 16, J = 2)$ transition. The relative binding energy of this dip to the anchor line was $14.923(30)$ GHz.
Figure A-12: An example of a scan showing hyperfine and rotation structure corresponding to the level with $B.E. = 1214.33(42)$ GHz below $(f=3+f=3)$ atomic asymptote. This was observed using the $0^+_g (\nu = 16, J = 2)$ state as an intermediate level. This dip has an inferred hyperfine quantum number of $f = 8$. The photoassociation frequency was 11679.989(10) cm$^{-1}$, which corresponds to the $(4,4) \rightarrow 0^+_g (\nu = 16, J = 2)$ transition. The relative binding energy of this dip to the anchor line was -0.578(30) GHz.
Figure A-13: An example of a scan showing hyperfine and rotation structure corresponding to the level with $B.E. = 1214.33(42)$ GHz below $(f=3+f=3)$ atomic asymptote. This was observed using the $0_g^-$ ($\nu = 16, J = 2$) as an intermediate level. This dip has an inferred hyperfine quantum number of $f = 7$. The photoassociation frequency was $11679.989(10)$ cm$^{-1}$, which corresponds to the $((4,4) \rightarrow 0_g^- (\nu = 16, J = 2))$ transitions. The relative binding energy of this dip to the anchor line was $7.000(30)$ GHz.
Figure A-14: An example of a scan showing hyperfine and rotation structure corresponding to the level with $B.E.=1214.33(42)$ GHz below ($f=3+f=3$) atomic asymptote. This was observed using the $0_g^- (\nu = 16, J = 2)$ state as an intermediate level. This dip has an inferred hyperfine quantum number of $f = 6$. The photoassociation frequency was $11679.989(10)$ cm$^{-1}$, which corresponds to the $(4,4 \rightarrow 0_g^- (\nu = 16, J = 2))$ transition. The relative binding energy of this dip to the anchor line was $15.006(30)$ GHz.
Figure A-15: An example of a scan showing hyperfine and rotation structure corresponding to the level with \( B.E. = 1343.94(42) \) GHz below \((f=3+f=3)\) atomic asymptote. This was observed using the \( 0^{-}_{g} (\nu = 16, J = 2) \) state as an intermediate level. This dip has an inferred hyperfine quantum number of \( f = 8 \). The photoassociation frequency was \( 11679.989(10) \text{ cm}^{-1} \), which corresponds to the \( (4,4) \rightarrow 0^{-}_{g} (\nu = 16, J = 2) \) transition. The relative binding energy of this dip to the anchor line was -0.600(30) GHz.
Figure A-16: An example of a scan showing hyperfine and rotation structure corresponding to the level with $B.E. = 1480.52(42)$ GHz below $(f=3+f=3)$ atomic asymptote. This was observed using the $0^+_g (\nu = 16, J = 2)$ as an intermediate level. This dip has an inferred hyperfine quantum number of $f = 8$. The photoassociation frequency was $11679.989(10)$ cm$^{-1}$, which corresponds to the $((4,4) \rightarrow 0^+_g (\nu = 16, J = 2))$ transition. The relative binding energy of this dip to the anchor line was $-0.621(30)$ GHz.
Figure A-17: Dip with \( B.E. = 505.07(42) \) GHz below \((f=3+f=3)\) atomic asymptote. This was observed using the \( 0^- (\nu = 4, J = 2) \) state as an intermediate level. The photoassociation frequency was \( 11661.925(10) \) cm\(^{-1}\), which corresponds to the \((4, 4) \rightarrow 0^- (\nu = 4, J = 2)\) transition. The calibration frequency was \( 11679.240(10) \) cm\(^{-1}\) \((3, 3) \rightarrow 0^- (\nu = 15, J = 2)\) transition. The offset between the position of the calibration peak and the anchor line on the FPI was \(-4.387(6)\) GHz. The frequency of the anchor line was calculated to be \( 11679.385(10) \) cm\(^{-1}\). This dip has an inferred hyperfine quantum number of \( f = 8 \).
Figure A-18: An example of a scan showing hyperfine and rotation structure corresponding to the level with $B.E.=505.07(42)$ GHz below $(f=3+f=3)$ atomic asymptote. This was observed using the $0^-_g (\nu = 4, J = 2)$ state as an intermediate level. At least one of these dips corresponds to an inferred hyperfine quantum number of $f = 7$, the quantum numbers corresponding to the other dip are under investigation. The photoassociation frequency was 11661.925(10) cm$^{-1}$, which corresponds to the $(4,4) \rightarrow 0^-_g (\nu = 4, J = 2))$ transition. The relative binding energies of the two dips with respect to the anchor line are $7.528(30)$ GHz and $7.550(30)$ GHz.
Figure A-19: Dip with $B.E. = 430.95(42)$ GHz below $(f=3+f=3)$ atomic asymptote. This was observed using the $0_g^- (\nu = 4, J = 2)$ state as an intermediate level. The photoassociation frequency was 11661.925(10) cm$^{-1}$, which corresponds to the $(4,4) \rightarrow 0_g^- (\nu = 4, J = 2)$ transition. The calibration frequency was 11677.237(10) cm$^{-1}$, which corresponds to the $(4,4) \rightarrow 0_g^- (\nu = 14, J = 2)$ transition. The offset between the position of the calibration peak and the anchor line on the FPI was 9.722(6) GHz. The frequency of the anchor line was calculated to be 11676.913(10) cm$^{-1}$. This dip has an inferred hyperfine quantum number of $f = 8$. 

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Figure A-20: An example of a scan showing hyperfine and rotation structure corresponding to the level with $B.E. = 430.95(42)$ GHz below $(f=3+f=3)$ atomic asymptote. This was observed using the $0_7^-(\nu = 4, J = 2)$ state as an intermediate level. These dips correspond to an inferred hyperfine quantum number of $f = 7$. The photoassociation frequency was $11661.925(10)$ cm$^{-1}$, which corresponds to the $(4, 4) \rightarrow O_7^- (\nu = 4, J = 2))$ transition. The binding energy of these dips with respect to the anchor line is $7.000(30)$ GHz.
Figure A-21: An example of a scan showing hyperfine and rotation structure corresponding to the level with $B.E. = 505.07(42) \text{ GHz}$ below $(f=3+f=3)$ atomic asymptote. This was observed using the $0_g^-(\nu = 4, J = 2)$ state as an intermediate level. This dip has an inferred hyperfine quantum number of $f = 8$. The photoassociation frequency was $11661.925(10) \text{ cm}^{-1}$, which corresponds to the $(4,4) \rightarrow 0_g^-(\nu = 4, J = 2)$ transition. The binding energy of this dip with respect to the anchor line is $-0.448(5) \text{ GHz}$. 

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Figure A-22: An example of a scan showing hyperfine and rotation structure corresponding to the level with $B.E. = 505.07(42)$ GHz below (f=3+f=3) atomic asymptote. This was observed using the $0_g^-$ ($\nu = 4, J = 2$) state as an intermediate level. These dips correspond to an inferred hyperfine quantum number of $f = 7$. The photoassociation frequency was 11661.925(10) cm$^{-1}$, which corresponds to the ($(4, 4) \rightarrow 0_g^-(\nu = 4, J = 2)$) transition. The binding energy of these dips with respect to the anchor line is $7.446(30)$ GHz and $7.625(30)$ GHz.
Figure A-23: An example of a scan showing hyperfine and rotation structure corresponding to the level with \( B.E. = 505.07(42) \) GHz below \((f=3+f=3)\) atomic asymptote. This was observed using the \( 0_g^- (\nu = 4, J = 2) \) state as an intermediate level. This dip has an inferred hyperfine quantum number of \( f = 6 \). The photoassociation frequency was \( 11661.925(10) \text{ cm}^{-1} \), which corresponds to the \( \left( (4,4) \rightarrow 0_g^- (\nu = 4, J = 2) \right) \) transition. The binding energy of this dip with respect to the anchor line is \( 15.731(30) \) GHz.
Figure A.24: An example of a scan showing hyperfine and rotation structure corresponding to the level with $B.E. = 430.95(42)$ GHz below ($f=3+f=3$) atomic asymptote. This was observed using the $0_g^{-}(\nu = 4, J = 2)$ state as an intermediate level. This dip has an inferred hyperfine quantum number of $f = 8$. The photoassociation frequency was $11661.925(10)$ cm$^{-1}$, which corresponds to the $(4,4 \rightarrow 0_g^{-}(\nu = 4, J = 2))$ transition. The binding energy of this dip with respect to the anchor line is $-0.434(40)$ GHz.
Figure A-25: An example of a scan showing hyperfine and rotation structure corresponding to the level with $B.E.=430.95(42)$ GHz below ($f=3+f=3$) atomic asymptote. This was observed using the $0_g^-(\nu=4, J=2)$ state as an intermediate level. This dip has an inferred hyperfine quantum number of $f = 7$. The photoassociation frequency was $11661.925(10)$ cm$^{-1}$, which corresponds to the ($4,4 \rightarrow 0_g^-(\nu=4, J=2)$) transition. The binding energy of this dip with respect to the anchor line is $7.469(30)$ GHz.
Figure A-26: An example of a scan showing hyperfine and rotation structure corresponding to the level with $B.E. = 430.95(42)$ GHz below ($f=3+f=3$) atomic asymptote. This was observed using the $0^{-}_{\nu}$ ($\nu = 4, J = 2$) state as an intermediate level. This dip has an inferred hyperfine quantum number of $f = 6$. The photoassociation frequency was $11661.925(10)$ cm$^{-1}$, which corresponds to the $(4,4 \rightarrow 0^{-}_{\nu}(\nu = 4, J = 2))$ transition. The binding energy of this dip with respect to the anchor line is $15.549(30)$ GHz.
Bibliography


