Luminorefrigeration of NaCs

by

Amy E. Wakim

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Professor Nicholas P. Bigelow

Department of Physics and Astronomy

Arts, Sciences and Engineering

School of Arts and Sciences

University of Rochester

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Polar molecules.
Formation and detection,
absolute ground state.

Curriculum Vitae

Amy E. Wakim was born in Norwich, CT on July 17, 1983. She attended the University of Rochester from 2001 to 2005, and graduated *magna cum laude* with a Bachelor of Science in Physics in 2005. She remained at the University of Rochester and received a Master of Arts in Physics in 2007. She pursued her doctoral research in experimental atomic, molecular, and optical physics with guidance from Professor Nick P. Bigelow. In August 2012, she will join KLA-Tencor.

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- A. Wakim, P. Zabawa, and N. P. Bigelow. “*Photoassociation studies of ultracold NaCs from the Cs $6^2P_{3/2}$ asymptote.*” PCCP 13, 18887 (2011)
- A. Grochola, P. Kowalczyk, J. Szczepkowski, W. Jastrzebski, A. Wakim, P. Zabawa, and N. P. Bigelow. “*Spin-forbidden $c^3\Sigma^+(\Omega=1) \leftarrow X^1\Sigma^+$ transi-*

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Abstract

We report on several experiments with kinetically ultracold NaCs created via photoassociation from dark-spot magneto-optical traps. The first set of spectroscopy experiments culminates in an optical pumping experiment to create a population of rovibrational ground state molecules.

We utilize a combination of pulsed depletion spectroscopy and photoassociation spectroscopy to assign photoassociation spectra of NaCs. These methods investigate the *ab initio* $\Omega=2$ potential energy curve and indicate a previously unknown avoided crossing between the $(3)\Omega=1$ and $(4)\Omega=1$ electronic states. We present rotational assignments of deeply bound singlet ground state molecules, an improved C_6 coefficient for the $(4)\Omega=1$ and assignments for all photoassociation resonances detuned from the Cs $6^2P_{3/2}$ asymptote belonging to the $(4)\Omega=1$ and $\Omega=2$. These photoassociation experiments result in the location of population in $X^1\Sigma^+(v=0)$.

The next set of experiments demonstrates optical pumping of NaCs to cool the initial vibrational distribution of electronic ground state molecules $X^1\Sigma^+(v \geq 4)$ into the vibrational ground state $X^1\Sigma^+(v=0)$. Our approach is based on the use of simple, commercially available multimode diode lasers selected to optically pump a population into $X^1\Sigma^+(v=0)$. We investigate the impact of the cooling process on the rotational state distribution of the vibrational ground state, and observe that an initial distribution, $J_{initial}=0-2$ is only moderately affected resulting in $J_{final}=0-4$. This method provides an inexpensive approach for creation of vibrational ground state ultracold polar molecules.

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List of Acronyms

BEC	Bose-Einstein condensate
BO	Born-Oppenheimer
CEM	Channel electron multiplier
Cs	Cesium
cw	Continuous wave
CWDS	Continuous wave depletion spectroscopy
FC	Franck-Condon
fs	Femtosecond
HL	Hönl-London
LB	Le Roy - Bernstein
LR	Long range
MA	Magneto-association
MOT	Magneto-Optical Trap
Na	Sodium
OP	Optical Pumping
PA	Photoassociation
PDS	Pulsed Depletion Spectroscopy
PEC	Potential Energy Curve
REMPI	Resonance Enhanced Multi-photon Ionization
RKR	Rydberg-Klein-Rees
SE	Schrödinger equation
TOF	Time of flight

Foreword

Chapters 3 and 4 of this thesis were jointly produced. The division of labor for each chapter is specified below.

The research in Chapter 3 was a collaboration with Patrick Zabawa and Professor Nick Bigelow. Together, Patrick and I planned the experiments, repaired equipment as needed, ran the experiments, and collected data. I performed the analysis and wrote up the results of this chapter for publication [1]. Also, we decided to collaborate with A. Grochola et al., and I wrote up a separate detailed account of the data to jointly produce [2]. In both of these publications, Patrick and Professor Bigelow provided assistance with the writing and editing.

The research in Chapter 4 was performed in collaboration with Patrick Zabawa, Marek Haruza, A. Stolyarov, and Professor Nick Bigelow. A. Stolyarov provided the much needed transition energies, transition dipole moments, and FC factor calculations from which we based the experiment. Patrick and I planned the laser system wavelength selections, and I built the optical pumping laser system. Patrick, Marek, and I worked together to align all the necessary laser systems to run the experiment and collect data. I performed the analyses and wrote up the results for publication [3]. Patrick, Marek and Professor Bigelow assisted with the editing of the paper. The vibrational optical pumping code was written by an REU student, Jennifer Hansen, with the supervision of Patrick. Originally, the code modeled transitions between the singlet ground state and the $B^1\Pi$. I inherited this code, rewrote sections of it to increase the programming efficiency, and incorporated the data from Stolyarov in order to model transitions

between the singlet ground state and the A-b complex.

Chapter 1

Introduction

The molecules discussed in this thesis consist of two alkali atoms, one sodium and one cesium. The created heteronuclear diatomic molecule will be referred to as NaCs. These molecules are weakly bound by dispersion forces and are known as van der Waals molecules. NaCs is not found in nature because it is weakly bound and easily broken apart, also Na and Cs are highly reactive with water and would create hydroxides before pairing. This particular polar molecule has a large permanent electric dipole moment making it an ideal candidate (as compared to other bi-alkalis) for experiments that take advantage of dipole-dipole interactions. The rest of this chapter is dedicated to providing a framework for understanding the experiment as it relates to the ultracold molecule community.

1.1 Ultracold Polar Molecules

The field of ultracold molecules is the result of successes in atomic laser cooling and trapping [4]. An atomic sample at ultracold temperatures (ultracold refers to a translational temperature of $<1\text{mK}$) is the reservoir from which ultracold molecules are formed via either photoassociation (PA) [5] or magnetoassociation (MA) [6]. MA is a process where a magnetic field is used to shift a ground state molecular energy into resonance with a colliding pair of atoms. This approach creates molecules in a narrow range of energies, and the experiment requires fine control of the magnetic fields which can be as large as 1000G

[7]. The created molecules are weakly bound, and these weakly bound states do not possess a sizable permanent electric dipole moment. PA, however, is a process where a colliding pair of ground state atoms absorbs a photon to form an excited state molecule which then decays to the ground state. An advantage of PA includes the creation of some very deeply bound molecules (to be discussed in Chapter 2.1.2) with a large permanent electric dipole moment (depending on the species), however, the majority of the population is dispersed over a range of energies. Typical PA experiments tend to have lower molecule formation rates and molecular densities because the atoms are sourced from Magneto-Optical Traps (MOTs) [8] as opposed to the higher phase space density found in a Bose-Einstein condensate (BEC) [9].

Each formation approach has limitations to overcome in order to produce a sample of deeply bound molecules in the lowest energy configuration (referred to as the rovibrational ground state, a combination of the lowest vibrational and rotational energies). There is significant current interest in acquiring a collection of rovibrational ground state molecules because it is the necessary starting point for a sample that is stable against collisions. These molecules may be used in the creation of dipolar crystals [10, 11], quantum computation schemes [12], and quantum chemistry investigations [13].

Laser cooling and trapping of atoms is a well established practice, however, direct laser cooling of molecules is not currently feasible. There is no closed cycling transition as molecules have numerous states compared to atoms, although efforts are being made [14]. So far, the approaches for accumulating heteronuclear molecules in the (ro)vibrational ground state either involve highly efficient yet technically challenging experimental techniques, or are relatively simple but inefficient. The earliest demonstration is a ‘pump-dump’ procedure in a

PA experiment with rubidium and cesium molecules, RbCs, [15] that transferred population in select vibrational levels to the vibrational ground state with an experimentally unconfirmed rotational distribution. Then, there is the efficient but technically challenging demonstration of magneto-association and coherent transfer of KRb [16] to the rovibrational ground state using a laser system referenced to a frequency comb. Also, direct photoassociation yields rovibrational ground state LiCs [17] and vibrational ground state NaCs [18] but with the majority of the sample distributed across a range of excited rovibrational states.

This work is an extension to the direct photoassociation method. We study the PA formation process to create a range of rovibrational states and construct a laser system to demonstrate the feasibility of optically pumping the molecules to the rovibrational ground state in preparation for future experiments. This simple approach proves to be an effective one.

1.2 Units

In much of molecular spectroscopic work, quantities are simply referred to as being in atomic units or au. The au of length is a reference to the Bohr radii measure, and 1 au is $\sim 0.529 \times 10^{-10}$ m. The au unit of energy is the Hartree. One Hartree is 27.2107 eV, or 219,474.63 wavenumbers, or 43.60×10^{-19} Joules. For the majority of this thesis, we will refer to energy in wavenumbers. This unit is a conversion of the photon wavelength, λ , to centimeters such that it is linear in energy, E.

$$\frac{1}{\lambda} = \frac{E}{hc}$$

Another relevant quantity is the permanent electric dipole moment, that is a function of internuclear separation. Deeply bound singlet ground state NaCs

molecules have the second largest dipole moment of the bi-alkalis of 4.6 Debye for a range of vibrational states $v=0\sim 40$, calculated by [19]. For higher excited vibrational states, the internuclear separation is greater and the dipole moment approaches zero near dissociation. For reference, 1 Debye is 3.33564×10^{-30} C·m.

1.3 Diatomic Molecule Primer

Here we will review a few concepts of diatomic physics necessary to the understanding of our experimental results. For a full derivation of $\hat{H}\Psi=E\Psi$ for diatomic molecules, see [20, p. 208]. The molecular hamiltonian cannot be solved exactly, but using the Born-Oppenheimer (BO) approximation [21] solutions may be found by separating the wavefunctions (Ψ) describing the nuclear and electronic motions. This is a reasonable approximation because the electrons move much faster than the nuclei and as a result, the electronic motion may be separated from the nuclear motion. For our purposes, the story begins with the solutions to the one dimensional Schrödinger equation (SE) for nuclear motion:

$$\frac{-\hbar^2}{2\mu} \frac{\partial^2 \Psi_{v,J}(r)}{\partial^2 r} + V_J(r) \Psi_{v,J}(r) = E_{v,J} \Psi_{v,J} \quad (1.1)$$

where μ is the reduced mass of the atoms, and $V_J(r) = \frac{\hbar^2}{2\mu} J(J+1) + V(r)$. The v and J subscripts refer to a specific vibrational and rotational state, respectively. The first term in $V_J(r)$ results in a repulsive barrier that is referred to as the centrifugal barrier because it increases with higher rotational states, J .

One may solve Eq.1.1 to locate the eigenvalues (rovibrational states) of the potential, $V_J(r)$. This potential is a description of the energy configuration/interaction of the two separate atoms as a function of internuclear separation, r , and is labeled by the angular momentum coupling between them. As r varies, so does the angular momentum coupling strengths. The angular momen-

Quantum Number	Definition
$I = I_A + I_B$	Total nuclear spin
S	Total electron spin
R	Rotation of nuclear framework
L	Total electronic orbital angular momentum
$F = R + L + S + I$	Total angular momentum
$J_a = L + S$	Total electronic angular momentum
M_L	$L, L-1, L-2 \dots -L$
$\Lambda = M_L $	Component of electronic orbital angular momentum along internuclear axis
$\Sigma = S, S-1, S-2 \dots -S$	Component of the total spin along internuclear axis (not defined for $\Lambda=0$)
$\Omega = \Lambda + \Sigma $	Total electronic angular momentum along molecular axis
J	Rotational level
v	Vibrational level

Table 1.1: Quantum numbers and definitions for a diatomic molecule of atoms A and B.

tum coupling cases are separated and described by Hund's cases [20, 22, 23] and there are potential energy curves (PECs) particular to each case. A PEC, while convenient for determining the internal states (vibrational and rotational states) and wavefunctions of the molecule, is not a precise description at all internuclear separations. Experimentally observed rovibrational levels may not match those of the corresponding PEC, and this reflects the inapplicability of the BO approximation.

1.3.1 Notation

The 'good' quantum numbers are those that allow solutions to Eq. 1.1. They are used for the classification of the electronic state and PEC. Table 1.1 defines all the relevant quantum numbers.

1.3.2 Hund's coupling cases

The set of quantum numbers that describe the system changes depending on the coupling of the angular momentum. For various angular momentum coupling strengths, the ‘good’ quantum numbers are defined by the Hund's cases. A complete discussion of the five Hund's coupling cases may be found here [20, 22, 23]. However, as we discuss below, only Hund's case (a) and (c) are relevant to the NaCs molecule.

Figure 1.1: Hund's case (a) diagram. Relevant quantum numbers include Λ and Σ . Here, N is the angular momentum of nuclear rotation at a right angle to the internuclear axis. It is completely determined by J and the projections of L and S .

Hund's case (a) is relevant because it describes the short range (short internuclear separation) interaction where L and S are strongly coupled to the internuclear axis, shown in Fig. 1.1. This means that L and S precess about the internuclear axis and the ‘good’ quantum numbers are their projections on the molecular axis, Λ and Σ . The rotational energy for this case is:

$$E_v = B_v[J(J+1) - \Omega^2] \quad (1.2)$$

where $J = \Omega, \Omega+1, \Omega+2, \dots$. Here, Ω is the total electronic angular momentum, $|\Lambda + \Sigma|$, and B_v is called the rotational constant and is related to the moment of inertia of the molecule.

For Hund's case (a), the quantum number Λ may be used to label the molecular state. For $\Lambda=0,1,2,3$ the corresponding state label is Σ , Π , Δ , and Φ . (Note that this Σ is for $\Lambda=0$ and not to be confused with the total spin). For $\Lambda > 0$, there is a degeneracy since Λ may be $\pm M_L$. This doubling involves the interaction between the nuclei and L , and for increasing J , the degeneracy is lifted and a splitting occurs of the levels. This is referred to as Λ doubling [22, p. 226].

Figure 1.2: Hund's case (c) diagram. Relevant quantum numbers include Ω .

Hund's case (c) is the appropriate description for long range molecules, particularly for heavier species for which spin-orbit coupling is significant [22, p. 224], such is the case for molecules containing Cs. Here, the interaction between L and S is stronger than with the nucleus, illustrated in Fig. 1.2. Therefore, their projections on the axis are not well defined, and the 'good' quantum number is Ω . For this case, the rotational energy is defined as in case (a).

For Hund's case (c), Ω is used as the state label. States with $\Omega > 0$ display behavior similar to Λ doubling, but in this case is referred to as Ω -type doubling [22, p. 229]. Table 1.2 dissects actual state labels and determines the separate components for each case. In Chapter 3, we will discuss the $\Omega=2$ state and in Chapter 4, we will mention the $\Omega=0$ component of the $b^3\Pi$ denoted by $b^3\Pi_0$. As a triplet state, Σ may be 1,0,-1 and when added to $\Lambda=1$, then $\Omega=0,1$ or 2.

Therefore, the $b^3\Pi$ has several Ω components each with their own PEC in Hund's case (c).

Hund's case	State Label	Meaning
(a)	$a^3\Sigma^+$	$a \rightarrow a, b, c, d, \dots$ Lowercase alphabetical ordering for triplet states beginning with lowest energy. $3 \rightarrow 2S+1=3$, triplet state $\Sigma \rightarrow \Lambda=0$ $+$ $\rightarrow$ even parity
(a)	$B^1\Pi$	$B \rightarrow X, B, C, D, \dots$ Uppercase alphabetical ordering for singlet states beginning with lowest energy. X is for the absolute ground state. $1 \rightarrow 2S+1=1$, singlet state $\Pi \rightarrow \Lambda=1$
(c)	$(2)\Omega=1$	$(2) \rightarrow 1, 2, 3, \dots$ Numbered ordering for states with same Ω value. $\Omega \rightarrow \Lambda + \Sigma =1$

Table 1.2: Dissection of electronic state labels for Hund's case (a) and (c).

1.3.3 Selection Rules

Next, we will briefly summarize the allowed transitions between molecular electronic states. The parity of a particular rovibrational level is an indication of the sign of the wavefunction upon reflection about the origin of the internuclear axis. It either remains unchanged or changes sign, (+) for even and (−) for odd respectively. In addition to keeping track of the parity of the state, Table 1.3 lists the selection rules where $\Delta J = J' - J''$ and J' (J'') is the excited (ground) rotational state.

There is additional notation for homonuclear molecules. Homonuclear molecules have identical nuclei and states may be labeled symmetric or antisymmetric describing the sign change of the total wavefunction upon exchange of the nuclei. These symmetric and antisymmetric cases are labeled with subscripts,

Selection Rules	
$\Delta J=0,+1,-1$	Labeled as Q,R,P branches, respectively. And, $J=0 \nrightarrow 0$
$\Delta J \neq 0$	For $\Omega=0 \rightarrow 0$
Parity	$+\leftrightarrow -, +\leftrightarrow +, -\leftrightarrow -$
For Hund's case (a):	$\Delta \Lambda=0,\pm 1$ $\Delta \Sigma=0$
$\Delta \Sigma=0$ holds less rigorously for increasing nuclear charge (ie spin-orbit interaction)	
For nuclei of equal charge:	$g \leftrightarrow u, g \leftrightarrow g, u \leftrightarrow u$

Table 1.3: Allowed transitions for diatomic molecules.

Figure 1.3: Even (+) and odd (-) parity labels for rotational states (J) belonging to a $1\Sigma^+$ and 1Π electronic states. Note the Λ doubling for the 1Π state where each parity is represented. A similar diagram may be found in [22, p. 238].

gerade (g) and ungerade (u) respectively, for parity notation. This thesis discusses heteronuclear molecules, but in Chapter 4 we will highlight experiments involving the homonuclear molecule, Cs_2 . Note that homonuclear molecules do not have a permanent electric dipole moment.

1.3.3.1 Franck-Condon principle

While there are no specific selection rules for vibrational state transitions between electronic states, they can be described and predicted by the Franck-Condon (FC) principle. Basically, it is a statement that during a transition the electron ‘jumps’ so quickly compared to the vibrational motion that the nuclei

appear stationary and maintain nearly the same relative position. According to the wave mechanics treatment, FC factors are the modulus squared of the integral over the product of the vibrational wavefunctions of the ground and excited states, essentially computing the overlap between the ground and excited vibrational states (v'' and v' respectively) for a particular internuclear separation. A Franck-Condon parabola or map plots the v' vs v'' for a range of states to indicate the regions of overlap.

$$\text{FC Factor} \equiv |\langle \Psi_{v'} | \Psi_{v''} \rangle|^2$$

The greater the wavefunction amplitude overlap of the two states, the more likely that transition may occur. The term ‘vertical’ transitions may also be used to describe this phenomenon, as the FC factor does not account for a change in the internuclear separation and a vertical line may be drawn on an energy diagram like that of Fig. 1.4 linking the ground and excited states. These factors are very sensitive to the curvature of the PECs.

1.3.4 More about Potential Energy Curves

Theory groups have provided *ab initio* PECs for NaCs in Hund’s case (a) [24], in Hund’s case (c) [25] with the inclusion of the spin-orbit interaction, and even for the NaCs ionic PECs [26]. These PECs serve as an excellent starting point for planning experiments and gauging the necessary wavelengths to drive transitions, however typically the calculated vibrational energies tend to be more than a few wavenumbers (if not tens or hundreds of wavenumbers) displaced from experimentally observed positions. The discrepancies are the result of the BO approximation not being an ideal description of the system. Therefore, experimentally determined PECs are preferable.

Figure 1.4: Potential energy curves for NaCs with Hund's case (a) labels.

PECs may be determined experimentally after accumulating spectroscopic data for the line positions of the majority of the rovibrational states. There are experimentally determined NaCs PECs for the lowest electronic states: $X^1\Sigma^+$ [27], $a^3\Sigma^+$ [27], $c^3\Sigma^+$ [2], and $B^1\Pi$ [28]. Fig. 1.4 illustrates the PEC landscape for NaCs for the two lowest atomic asymptotes using Hund's case (a) notation. The vibrational levels are represented by the horizontal lines within the PEC, and each vibrational state has rotational energies associated with it. Note that these experimentally determined PECs though labeled with Hund's case (a) actually transcend the coupling case to describe the interaction at all internuclear separations.

There is a non-crossing rule for PECs, and it has been shown that for a slow change of internuclear separation two electronic states of the same species cannot cross, see [22, p. 295] and references therein. For certain low-order ap-

proximations, two PECs may intersect, however, with the inclusion of higher order approximations (such as considering the spin-orbit effect in NaCs), there is a separation of the PECs termed an avoided crossing. The intersecting (non-intersecting) PECs are referred to as diabatic (adiabatic).

The absolute ground state, $X^1\Sigma^+$, has 87 vibrational levels with the deepest vibrational states spaced by $\sim 100 \text{ cm}^{-1}$ whereas the rotational splittings for each vibrational state is on the order of $\sim 0.1 \text{ cm}^{-1}$. These energy scales become significant when planning the spectroscopy experiments described in Chapter 2. Appendix A contains the positions of the rovibrational states ($v=0-86$, $J=0-5$) for the singlet ground state and ($v=0-24$, $J=1-5$) for the triplet ground state from [27]. Note, in Appendix A, the existence of a quasibound level in the triplet state at $J=3$. This quasibound state exists above the dissociation limit due to the centrifugal barrier created by $J>0$ from $V_J(r)$ in Eq. 1.1.

In addition to vibrational and rotational structure, molecules also have hyperfine structure, but the resolution of our experiment is not sufficient to measure it for most states. We note that the atomic hyperfine state is significant for accessing specific molecule formation pathways and we observe hyperfine structure in some of the PA spectroscopy, however, hyperfine structure is not observed in the optical pumping (luminorefrigeration) experiments.

1.3.5 $A^1\Sigma^+$ - $b^3\Pi$ Information

Fig. 1.4 illustrates the $A^1\Sigma^+$ and $b^3\Pi$ electronic states. A non-trivial amount of information on the $A^1\Sigma^+$ - $b^3\Pi$ states, or A-b complex, has contributed to the planning of the optical pumping experiments. A. Stolyarov, et al. provided the transition dipole moments, $|\mu_{ij}|^2$, and transition energies, ν_{ij} , for 350 vibrational levels (at $J=2$) of the A-b complex, with FC factors to the $X^1\Sigma^+$

(J=1) and $a^3\Sigma^+$ (J=1) states. These values are a result of their extrapolations from experimental results [29].

The transition dipole moment is defined as,

$$\mu_{i,v_i;j,v_j} = \langle i, v_i | \mu | j, v_j \rangle$$

$$\vec{\mu} \equiv e \sum_{k=1}^n r_k,$$

where n is the number of electrons. The μ_{ij} is used as a measure of the transition intensity related to the absolute transition probability.

Later, we refer to the lifetime, τ , of the excited state [23, p. 349]. The inverse of it may be calculated by summing the Einstein A coefficients linking the excited state i to the ground states j:

$$\tau_i^{-1} = \sum_j A_{ij}$$

The Einstein A coefficients are calculated directly from the transition dipole moments and transition energies where:

$$A_{ij} = |\mu_{ij}|^2 \nu_{ij}^3 \frac{8\pi^2}{3\hbar\epsilon_0}$$

The Einstein A coefficient describes the spontaneous emission of an excited state molecule whereas the Einstein B coefficient describes the stimulated emission/absorption. The B coefficient is proportional to the A coefficient and:

$$B_{ij} = \frac{|\mu_{ij}|^2}{6\hbar^2\epsilon_0 c}$$

1.3.6 LEVEL 8.0

Throughout this thesis, calculations are accomplished using a program called LEVEL 8.0 [30]. This fortran code, when compiled, generates an executable

file that accepts an input file. This input file specifies a list of points for a particular $V(r)$ to solve Eq. 1.1. The code and usage manual is generated by R. J. Le Roy from the University of Waterloo and is available to the public for download. LEVEL 8.0 solves Eq. 1.1 and calculates the rovibrational state positions (as well as quasibound states), wavefunctions, and rotational constants. It can also compute FC factors with an input file containing the ground and excited state PECs. All of the FC maps in this thesis are calculated in this way.

1.4 Outline of Thesis

Chapter two is a discussion of the atomic sample preparation, the molecule formation process, and all the spectroscopic tools used in the various experiments. These topics are fundamental to the understanding of this thesis work.

Chapter three delves into photoassociation and focuses on the molecule formation process over a specific frequency range. This exploration was necessary in order to understand the energies in our created sample. The results of this chapter enable us to find the ‘right’ formation pathway that has a relatively high molecule formation rate and creates a sample of molecules in a known range of states. We discuss the crossing of the diabatic PECs, $c^3\Sigma^+$ and $B^1\Pi$, and locate the detection pathway for a molecule in the lowest energy configuration.

Chapter four details the evolution of the optical pumping or luminorefrigeration process. The spectroscopic techniques from Chapter 3 are utilized in the data collection, and the created laser system produces the expected results. We prove the creation of the rovibrational ground state, and model the rotational state transitions involved in the cycling process.

Chapter five concludes this thesis. We discuss the unexpected proper-

ties of the excited state used in optical pumping and possible improvements to that experiment. Then, we provide an outlook for the lab and discuss future experiments involving luminorefrigeration, molecule trapping, polar crystals, and spectroscopy.

Chapter 2

Fundamentals of the Experiment

This chapter describes the building blocks for this thesis experiment, namely laser cooling and trapping, photoassociation, resonance enhanced multi-photon ionization, pulsed depletion spectroscopy, and cw depletion spectroscopy. We also discuss the data collection methods. The following provides brief descriptions for each technique which will be referred to in later chapters.

2.1 Molecule Formation

2.1.1 Laser Cooling and Trapping

To create a sample of ultracold molecules (< 1 mK), we begin with a sample of ultracold atoms created via laser cooling and trapping techniques [4, 8]. This section provides a brief description of a magneto-optical trap (MOT) for cesium and sodium atoms. Typical MOT atom numbers and densities are $\sim 10^8$ Cs atoms at $\sim 10^{10}$ cm $^{-3}$ and $\sim 10^7$ Na atoms at $\sim 10^9$ cm $^{-3}$ with translational temperatures of ~ 250 μ K. The word ‘temperature’ is used loosely from the thermodynamic definition and is a description of the kinetic energy of the atoms where $T \propto m v^2/k_B$.

The first MOT was demonstrated in 1987 [31] and it is a combination of optical and magnetic fields used to slow, cool, and confine the atoms. The optical component utilizes three sets of retroreflected laser beams propagating along orthogonal axes, intersecting at the origin as shown in Fig. 2.1a. These optical

Figure 2.1: (a) MOT laser beam configuration with anti-Helmholtz coils. (b) Magnetic field induces Zeeman splittings of the hyperfine structure providing a spatial dependence for resonant transitions. The laser frequency is detuned by amount δ to address the hyperfine states.

fields slow and cool via momentum transfer between the photons and atoms. The absorption of a photon is highly frequency dependent and therefore affected by the velocity at which the atom is moving. To compensate for the Doppler effect and create a resonant radiation field for moving atoms, the light is red detuned so atoms traveling opposite to the beam propagation will be blue shifted into resonance. When a photon is absorbed, its momentum, $\hbar\mathbf{k}$ is transferred to the atom and the energy is stored in the excited state. After decaying to the ground state, the atom radiates this energy away in a random direction, which over many cycles averages to zero. The net effect is that the atom is decelerated in the direction of the laser field. The absorbed red-detuned photon is at a lower energy than the emitted photon, thus removing energy from the system with each transition. As the atoms drift away from the center of the trap, they are slowed and no longer in resonance with the optical fields, therefore, magnetic fields are implemented to provide a restoring force and confinement. By Zeeman shifting

Figure 2.2: Hyperfine structure for Cs and Na D2 line with labeled trapping and repumping transition. A compendium of atomic data for sodium and cesium can be found here [32].

the hyperfine states, the atoms experience a spatial dependence for resonance of the optical fields and may be pushed back to the origin. The magnetic field is a quadrupole field which linearly increases from the origin with a gradient of ~ 15 G/cm created with anti-Helmholtz coils.

To ensure the atom is cycled on a closed transition, the hyperfine sublevels are addressed with the circular polarization, as illustrated in Fig. 2.1b. Typically the D2 atomic line is chosen ($S_{1/2} \rightarrow P_{3/2}$ transition). Circularly polarized light, denoted by σ^+ (σ^-), has selection rules of $\Delta F = +1$ ($\Delta F = -1$) to drive m_F transitions. Sodium and cesium have many hyperfine levels, so two laser frequencies (a trapper and repumper beam) create a closed cycling transition to avoid optically pumping atoms into an inaccessible ground hyperfine state, illustrated in Fig. 2.2. With the trapper and repumper at ~ 100 MHz detuning from the atomic transition, then $\sim 3 \times 10^4$ cycles bring a sodium atom from ~ 300 m/s to ~ 0.3 m/s on a time scale of half a millisecond.

Figure 2.3: Image of the stainless steel chamber held at $\sim 10^{-10}$ Torr. A, B and C distinguish the Cs oven, Zeeman slower, and a close-up of the Cs MOT in the TWIST [33], respectively.

The sodium and cesium atoms are supplied by heating the metallic solids (housed in separate ovens) to sublimate particles. The Cs (Na) oven is heated to 35°C (220°C), respectively. These particles escape the oven and flow into the science chamber with a valve to control atom flow. The velocity of the atoms puts a bound on the resonance condition and only atoms moving at or below the capture velocity may be trapped in the MOT. The cesium atoms can be directly loaded into the MOT, however, sodium is much lighter (and travels much faster) and must be slowed. The Zeeman slower [8] brings the sodium atoms from ~ 400 m/s to ~ 150 m/s by scattering resonant light on a closed transition and using varying magnetic fields to shift the energy levels of the slowed atoms into resonance [34].

There is a limit to the MOT atom density due to the diffusion of radiation of light when the cycling atom emits a photon that is then absorbed by other atoms. By implementing a dark-spot MOT [35] for each species, we minimize the heating effect and increase the atom density. This is accomplished by imaging a dark spot in the middle of the repumper beam onto the MOT region. This

effectively removes the repumper light from the trapped atoms, reducing the absorption and emission cycles. When atoms wander outside of the dark spot region, they may absorb the light and be pushed back into the dark region. The dark-spot MOTs increase the molecule production rate and allows population to be in one atomic hyperfine ground state level (this is significant for hyperfine entrance channels during photoassociation).

In the laboratory, spatially overlapped MOTs are created in a vacuum chamber held at a background pressure of $\sim 3 \times 10^{-10}$ Torr, limiting the collisions between the background gas with the sample. Fig. 2.3 illustrates the vacuum chamber, the cesium atomic source wrapped in foil, and the last four coils of the sodium Zeeman slower. The sodium beam lines for the trapper, repumper, and zeeman slower are generated by a Verdi pumped Coherent 699-29 ring dye laser with Rhodamine 6G laser dye. To lock the 699 to the atomic transition, we utilize frequency modulated (FM) spectroscopy (fully described here [34]). The cesium beam lines for the trapper and repumper are generated by two separate external cavity diode lasers in the Littrow configuration [36, 37]. Each is locked with proportional integral derivative (PID) circuitry using signals from a dichroic atomic vapor laser lock (DAVLL) setups, see [38] and references therein.

2.1.2 Photoassociation

Photoassociation refers to the formation of an excited state molecule and the scattering formalism was applied to cold atoms in 1987 [39]. Since then, there has been a large body of work detailed in several review articles [5, 40, 41]. Fig. 2.4 illustrates the basic principle: a pair of colliding atoms may absorb a photon, and if the photon is resonant with an excited molecular state, the pair may become a bound excited state molecule. By scanning the frequency of the PA photon, we

Figure 2.4: Diagram of photoassociation (PA) for atoms A and B. Atoms approach for a collision and at a particular internuclear separation the PA photon, resonant with an excited molecular state in $(AB)^*$, is absorbed. E_{at} is the energy between the atomic levels A and A^* , E_b is the binding energy of the molecular state and E_{th} is the thermal or kinetic energy of the colliding atoms (for μK atoms ~ 21 MHz). The excited state decays to a range of rovibrational states in the ground state, AB. A similar figure is found in [5].

observe various formation pathways through excited long range molecular states. Excited state lifetimes of NaCs are typically on the order of nanoseconds and then the molecules decay to a range of ground rovibrational states. A few advantages of PA spectroscopy include high resolution due to the lack of doppler broadening from slowly moving atoms, as well as access to long range states. Homonuclear molecules were first observed in MOT experiments with the MOT beams inducing PA [42] and later with a separate PA laser system [43–48]. More recently, PA has been used to create heteronuclear bi-alkali molecules [49–52].

Fig. 2.5a is the PA scan at 960 GHz detuning from the $(3^2S_{1/2} + 6^2S_{1/2}) \rightarrow (3^2S_{1/2} + 6^2P_{3/2})$ transition which will be mentioned in Chapter 3. This particular resonance is through the $c^3\Sigma^+(v=61)$ and we calculate the Franck-Condon factors using LEVEL 8.0 [30], shown in Fig. 2.5b, to illustrate the range of populated ground states via this PA resonance. Note that the most populated states are

Figure 2.5: (a) PA scan illustrating the molecule formation pathways available at 960 GHz detuning from the $(3^2S_{1/2}+6^2S_{1/2}) \rightarrow (3^2S_{1/2}+6^2P_{3/2})$ transition. Numbering indicates rotational states. (b) FC map of $c^3\Sigma^+(v=61, J=1)$ with singlet ground state ($J=0$). In the inset, a vertical line denotes $X^1\Sigma^+(v=6)$. These dimensionless values represent the relative distribution of the population based on the overlap of the excited state and ground state wavefunctions.

near dissociation at $v \sim 80$ or the deeply bound states at $v \leq 10$. (This will be of interest for the initial distribution used in Chapter 4.)

The structure observed in a PA scan corresponds to the rovibrational states coupled in the free $\rightarrow$ bound transition and depending on the excited molecular state, hyperfine structure may also be resolved. We may begin to understand these structures by considering the scattering process. As two atoms approach for a collision, only the lowest rotational states are available due to a repulsive centrifugal barrier in the ground state potential, V_{LR} .

The ground state long range potential is described by dispersion coefficients with the centrifugal barrier term. This form is appropriate for a molecule when the internuclear separation is large enough such that there is no overlap of the atomic electronic orbitals:

$$V(R) = \frac{\hbar^2}{2\mu} \frac{J(J+1)}{R^2} - \frac{C_6}{R^6} \quad (2.1)$$

Figure 2.6: van der Waals potential with centrifugal barrier from higher partial waves in the collision in units of temperature (degrees K) as a function of internuclear separation (Angstroms). The MOT temperature is plotted (horizontal dashed line) at $\sim 250 \mu\text{K}$.

In this equation, μ is the reduced mass of NaCs, J is the rotational angular momentum quantum number, and the ground state dispersion coefficient, C_6 , may be found here [27, 53, 54]. Fig. 2.6 illustrates this potential and the centrifugal barrier from the angular momentum. Each angular momentum component has a corresponding partial wave to describe the incoming scattering wave. The low energy system suppresses the higher order partial waves and therefore the formation of higher rotational states.

The rotational quantum number of the molecule is the sum of the available angular momentum. It includes the total angular momentum from each atom plus the contributing partial wave (ℓ_p): $J = j_{total} + \ell_p$. Here, $j_{total} = j_a + j_b + 1$ where $j_i = l + s$ and the angular momentum of each ground state atom is $j_a = j_b = 1/2$. The +1 accounts for the angular momentum contribution from the photon in photoassociation. A summary of the partial wave contribution to the various rotational states via angular momentum addition may be found in Table 2.1.

This angular momentum addition illustrates the available rotational states in the scattering process, however, the coupling is further restricted by parity

j_{total}	ℓ_p (parity)	ℓ_p Label	J'
2,1,0	0 (+)	s	2,1,0
2,1,0	1 (-)	p	3,2,1,0
2,1,0	2 (+)	d	4,3,2,1,0
2,1,0	3 (-)	f	5,4,3,2,1

Table 2.1: Available rotational states, J' , from various partial waves, ℓ_p . Note the parity of the partial waves are provided and the parity of the excited state is dependent upon the electronic state.

conservation. The ground state partial scattering waves have even (+) or odd (-) parity following $(-1)^l$ whereas the parity of bound molecular rotational state depends on the electronic state. For $\Omega=1$ and 2 electronic states with a corresponding Hund's case (a) state of $^1\Pi$ and $^3\Pi$ respectively, there is Λ doubling [22] for each rotational state and each parity component is present; therefore, each partial wave contributes to each J in Table 2.1. The lowest partial waves in the free $\rightarrow$ bound transition are typically found to be s, p and d waves creating rotationally cold molecules, $J \leq 4$. For higher rotational states in the PA spectra, higher partial waves must contribute. Due to the low energy in the collision, higher rotational states may only be accessed due to the presence of a shape resonance because the centrifugal barrier is much higher than the energy of the collision. A shape resonance occurs when the incoming scattering wave is resonant with a quasi-bound state. A quasi-bound state has an energy above the dissociation asymptote due to the repulsive barrier, and as a result a particle may tunnel from unbound to bound. In the following spectroscopy, we note the presence of an f-wave shape resonance responsible for the $J=5$ features. This conclusion is consistent with the quasibound state calculated for $a^3\Sigma^+(v=24, J=3)$.

In the laboratory, we use a Verdi pumped Coherent 899-29 Ti-Sapphire ring laser with $\sim 700\text{mW}$ at $\sim 852\text{ nm}$ with a linewidth of 2 MHz as the PA laser

system. To take PA scans, a LabView program scans the externally controlled Ti-Sapphire laser. However, for constant molecule production, the Ti-Sapphire laser may be externally locked using an etalon (called the Supercavity) with a reference beam from the Cs trapper laser. This transfer lock setup utilizes LabView to monitor and adjust the frequency of the Ti-Sapphire to maintain a frequency to within a few MHz, thereby reducing long term frequency drift due to thermal instabilities in the lab.

2.2 Molecule Detection

2.2.1 Resonance Enhanced Multiphoton Ionization

Resonance Enhanced Multiphoton Ionization (REMPI) spectroscopy is a powerful technique to label the populated vibrational state distribution. It is an absorption process that drives resonant transitions within the molecule to produce a molecular ion. The single-color, two-photon REMPI spectrum is difficult to analyze due to the dense, congested nature of the spectrum and the uncertainty in PECs for the intermediate states involved. To overcome these difficulties, we implement a three photon, single-color REMPI procedure that uses the heavily mixed and well known $A^1\Sigma^+-b^3\Pi$ complex [29], or A-b complex, as the first intermediate state to produce a sparser spectrum than the 2-photon REMPI. The solid arrows shown in Fig. 2.7 indicate the resonant vibrational state transitions for the NaCs system driven by ~ 7 ns pulses (0.6cm^{-1} linewidth) from a tunable pulsed dye laser. A portion of the spectrum is shown in Fig. 2.8a. The dependence on a second resonant excitation for ionization modulates the spectrum and decreases the probability that multiple vibrational states will be ionized by the same frequency. This modulation may suppress specific vibrational levels whose second transition are not resonant and therefore much less likely to

occur.

Figure 2.7: REMPI schematic. Solid maroon arrows indicate the driven resonant transitions to create molecular ions. The dotted arrow represents the depletion pulse in pulsed depletion spectroscopy. Hund's case (a) PECs are from [24]

We observe NaCs via time of flight (TOF) mass spectroscopy. The positive ions created during REMPI are manipulated using electric fields from the ~ -2.8 kV applied to the channel electron multiplier (CEM). The ions are funneled into the CEM where they are counted and binned by time of arrival using the multichannel scalar, allowing for species identification. The CEM is a KBL-408 purchased from SJUTS [55], and a new one was installed in 2010. Over time, the CEM acquires a coating of alkalis making it light sensitive which increases the background signal. To optimize the detection efficiency, occasional internal bake-outs of the chamber are necessary to clean the CEM.

(a) Styrl 9M REMPI spectrum

(b) LDS 867 REMPI spectrum

Figure 2.8: 3 photon REMPI spectra. Each peak corresponds to a populated vibrational level in the ground state.

To produce a molecular ion, the total REMPI photon energy must exceed the ionization threshold located at the minimum of the lowest ionic PEC [26]. For NaCs, the threshold is predicted to range from 26809 cm⁻¹ [56] to 28196 cm⁻¹ [57], and the depth of the well is not known experimentally. Above this threshold, the ionic states are a continuum and a range of energies will drive population to molecular ions, however if the total absorbed energy is greater than an ionic asymptote then photofragmentation,

is observable in the atomic channels of the TOF spectroscopy.

2.3 Molecular State Identification

2.3.1 Vibrational states - Pulsed Depletion Spectroscopy

Even with the sparser 3-photon REMPI spectrum, it is still difficult to precisely determine the originating vibrational state due to the sheer number of available transitions. (To illustrate the point, there are 87 singlet ground vibrational states, each of which may be driven to any of the >350 vibrational levels of the A-b complex on the first transition.) The solution to vibrational state identification is the addition of another pulsed dye-laser system for pulsed depletion spectroscopy (PDS). This approach unambiguously assigns the ground state vibrational population, identifies positions of vibrational levels in unknown excited states, and may assign the rotational population of a ground state vibrational level.

The PDS experiment involves two independently pumped, tunable pulsed dye lasers [58] where the first pulse (depletion pulse) arrives at the sample 120

μs before the second pulse (detection pulse) each having a 0.6 cm^{-1} linewidth. The depletion pulse is scanned through thousands of wavenumbers while the REMPI detection pulse monitors population in a single vibrational level. When the frequency of the first pulse couples a population to an excited vibrational level, there are dips in the detected population signal providing a fingerprint of the excited state. Fig. 2.9 displays this concept. The spectrum maps the excited state structure by driving transitions from $X^1\Sigma^+(v''=5)$. The dips in the spectra are $\sim 50\text{ GHz}$ wide and the data is taken in steps of 10 GHz .

Figure 2.9: Pulsed depletion spectrum. REMPI monitors population in $X^1\Sigma^+(v''=5)$ and dips identify transitions from $X^1\Sigma^+(v''=5)$ to excited state vibrational levels. Note that the vibrational assignments here are illustrative.

When the excited electronic state is well known, PDS efficiently labels the depleted ground vibrational state [59]. Utilizing a well known excited state, the $A^1\Sigma^+-b^3\Pi$ complex [29], we determine population in $X^1\Sigma^+(v=4-6, 8, 9, 11, 13, 15-17, 19, 21, 23-25, 31)$ created using a near dissociation photoassociation resonance detuned 32 GHz from the $\text{Cs } 6^2\text{P}_{3/2}$ asymptote. Fig. 2.10 overlays the assigned vibrational levels on the REMPI spectrum. Note the repeated assigned

states indicate multiple ionization pathways for a particular ground vibrational level.

Once the detected vibrational state has been assigned, PDS may be used to map an unknown electronic state. Theoretical calculations can not take into account all the perturbations in the system and experimental determination is the only way to know the precise position of a rovibrational state. Various alkali electronic states have been mapped using hot molecules [29, 60] or using an ultracold sample [61]. We use PDS on ultracold molecules to provide a description of the $c^3\Sigma^+$ [2].

Figure 2.10: REMPI scan from Fig.2.8b with assigned $X^1\Sigma^+$ vibrational states using PDS. Multiple ionization pathways are found for several ground vibrational levels.

For NaCs, there had not yet been an experimentally determined $c^3\Sigma^+$ PEC, therefore we used PDS to catalogue experimental term values for the positions of vibrational levels in the $c^3\Sigma^+$ and $B^1\Pi$ electronic states. Spin-orbit interaction couples the $c^3\Sigma^+$ and $B^1\Pi$ states permitting transitions from deeply bound singlet ground states to the lowest vibrational levels of the $c^3\Sigma^+$ state.

The PDS method is also sensitive to weak transitions due to the high pulse intensity. A $\sim 2300 \text{ cm}^{-1}$ wide spectrum is pieced together from various ground state vibrational level spectra to form a continuous landscape of the $c^3\Sigma^+$ and $B^1\Pi$ states. Splicing the scan between different vibrational levels removes the veil of Frank-Condon (FC) factors to illustrate the excited states uninterrupted by nodes in wavefunction overlap and minimizes the necessary dye changes to cover the well depth. As the amplitude of the line strengths are proportional to the FC factors, a comparison between peak amplitudes from a depletion scan using a single vibrational level and calculated FC factors may confirm the internuclear separation for the PECs. Our $c^3\Sigma^+$ data was incorporated into the data and analysis done by Grochola et al. to produce this PEC [2]. We use LEVEL 8.0 [30] and produce a list of values for the vibrational levels of $J=1$ for $c^3\Sigma^+$ and $B^1\Pi$ in Appendix B.

2.3.2 Rotational states - CW Depletion Spectroscopy

PDS was modeled after a cw depletion spectroscopy (CWDS) experiment [62]. The depletion lasers for PDS and CWDS are chosen to mode match the energy splittings of the states of interest. Because the energy splittings of the rotational states are about an order of magnitude smaller than the vibrational state splittings, a narrow linewidth cw laser is used for depletion when investigating rotational structure whereas a broad linewidth pulsed laser (that can scan many wavenumbers in a short period of time), was the natural choice for vibrational state exploration. In order to discern the rotational states of a given vibrational level, a narrow linewidth, $\sim \text{MHz}$, laser is scanned tens of GHz thereby resolving the rotational structure. Fig. 2.11 illustrates the concept where initial population (blue circles) in $J=1,3$ is driven to the excited state bound by the selection

Figure 2.11: CW depletion spectroscopy schematic. Population initially in $J''=1,3$ is driven to the excited state with the selection rule of $\Delta J=\pm 1$ for $\Delta\Lambda=0$ transitions. The wavelength scan range is qualitative and actual scans cover ~ 5 GHz. Also, note the differing ground and excited state rotational splittings representing the variation in rotational constants between ground and excited vibrational states.

rule of $\Delta J=\pm 1$ for $\Delta\Lambda=0$ transitions. Note that the excited state and ground state rotational structure differ and is described by the rotational constant, B_v . Rotational state transitions are not driven in a consecutive ordering in CWDS.

For the CWDS in this work, we used a distributed feedback diode laser with a ~ 2 MHz linewidth centered at ~ 850 nm, scanned using LabView. Fig. 2.12 illustrates the ground state rotational population for various formation pathways of $J'=1$ and 2 from the 960 GHz PA resonance. These depletion scans drive $X^1\Sigma^+(v=4) \rightarrow A\text{-b complex}(N=70)$ and the rotational states are assigned. Note the differing ground state distributions when photoassociating through various excited rotational levels.

Figure 2.12: a) Molecule formation through $J'=1$ of the 960 GHz PA resonance populates $J''=0-2$. b) Molecule formation through $J'=2$ of the 960 GHz PA resonance populates $J''=1,3$. Note that the multiple $J''=1$ assignments within the same scan represent the ± 1 transition. Due to the instability of the system, there is a fluctuation in the background signal. It is denoted by the grayed box, and the meaningful dips are well outside the noise.

2.4 Data Collection

All of the described experiments take place at a 10 Hz repetition rate, set by the repetition rate of the pulsed dye laser used for detection. Every 100 ms, the sample is formed, manipulated, and detected. Each data point in a REMPI, PDS, or CWDS spectrum is actually the average of many ionization or detection ‘shots.’ The detected ions are averaged over a fixed number of shots to produce the data points in each scan to increase the signal to noise ratio. Typical REMPI spectra have ~ 20 shots per data point, where as PDS or CWDS may range from $\sim 50-100$ shots per point depending on the signal strength and stability of the system.

2.5 Conclusion

In summary, these fundamental techniques are the tools used to probe the ultracold NaCs sample and to verify the results of the photoassociation and luminorefrigeration experiments.

Chapter 3

Photoassociation Experiments

Throughout this chapter, we will take a closer look at the formation process. We must understand photoassociation in order to optimize the placement of the initial distribution of molecular states before further cooling methods are applied, specifically we look for formation pathways that create ground state molecules, $X^1\Sigma^+(v=0)$. We approach this discussion by separating the PA resonances observed above and below the Cs $6^2P_{1/2}$ asymptote.

3.1 Photoassociation resonances detuned from the Cs $6^2P_{3/2}$ asymptote

There are five Hund's case (c) states converging to the Cs $6^2P_{3/2}$ asymptote: $\Omega = 0^+, 0^-, 1, 1, 2$. We sort our PA resonances among these states as discussed in previous work [63] by grouping resonances with the same number of rotational levels coupled in the free-bound transition and by considering the hyperfine profile. With this approach, eighteen of our PA resonances are assigned to the $\Omega=2$ and the remaining eighteen resonances belong to one of the $\Omega=1$ states, either the $c^3\Sigma^+$ or the $B^1\Pi$. The other electronic states were not considered in the PA assignment because the presence of hyperfine structure precludes the consideration of the $\Omega=0$ states. The $\Omega=2$ resonances include three or four features depending on the overall signal strength, later assigned as $J=2,3,4$, (5) whereas the $\Omega=1$ resonances include features assigned as $J=1,2,3,4,5$.

To further distinguish the PA resonances as belonging to either an $\Omega=1$ or the $\Omega=2$ electronic states, we examine the resulting ground-state population distribution from most resonances listed in Table 3.3 using PDS. These methods effectively assign the resonances because an $\Omega=2$ ($\Omega=1$) state populates weakly (deeply) bound triplet (singlet) ground states which are clearly separable.

Once the angular momentum quantum number is assigned, there is still ambiguity for the PA resonances as belonging to either the (3) $\Omega=1$ or (4) $\Omega=1$ states. Fig. 3.1 plots a portion of the PDS spectrum (black trace) and the progression of dips suggests the presence of only two electronic states. Dotted vertical lines overlaid on the spectrum indicate the $B^1\Pi$ vibrational levels and the solid vertical lines denote the PA resonances^a. The offset in the vertical line progressions indicate that the PA resonances are not part of the $B^1\Pi$. Therefore, we assign the PA resonances to the $\Omega=1$ component of the $c^3\Sigma^+$.

Throughout this chapter, we will follow the notation of Reference[28] and explicitly refer to the vibrational levels predicted by the experimentally determined PEC as belonging to the $B^1\Pi$. The binding energies for the $B^1\Pi$ states are calculated using LEVEL[30] and we find a root mean square deviation of 0.4 cm^{-1} between the PDS line positions and the eigenvalues for $B^1\Pi(v=0-52)$. LEVEL calculates 62 vibrational states in the $B^1\Pi$; however, the PEC was created utilizing data up to $B^1\Pi(v=52)$, therefore we compare only those corresponding states.

The $c^3\Sigma^+$ and $B^1\Pi$ states are a coupled system; therefore, we will refer to the observed vibrational levels in this experiment as being part of the $c^3\Sigma^+ - B^1\Pi$ complex, or c-B complex, with index N. The N indices are an ordering of

^{0a} Note that the PA detunings previously reported were taken from the trapping transition of the Cs MOT and should be shifted 9.192 GHz to the red when comparing to the PDS spectrum.

Figure 3.1: Depletion scan indicating vibrational levels of $c^3\Sigma^+$ and $B^1\Pi$ states in reference to the Cs $6^2P_{3/2}$ asymptote at 351726 GHz. We conclude that vibrational levels from $B^1\Pi(v'=44-52)$ PEC[28] (dashed lines) and the c-B complex PA resonances (solid lines) belong to the two different states.

the $B^1\Pi$ and $c^3\Sigma^+$ vibrational levels from highest to lowest binding energy, and we have catalogued the progression from the bottom of the deepest potential well to just below the asymptote. To get the range of N indices, we fit the assigned $c^3\Sigma^+$ data to a near dissociation expansion to extrapolate the last bound level and combine it with the total vibrational levels of the $B^1\Pi$ and find $N=1-136$. We also label the PA states in Hund's case (c) coupling which is the most accurate description for these long range states. In Hund's case (c) coupling, the long range components of the $c^3\Sigma^+$ and $B^1\Pi$ are typically assigned as the $(3)\Omega=1$ and $(4)\Omega=1$, respectively. Also, we note that when describing transitions, we label ground state vibrational levels with double-primes to distinguish them from excited state vibrational levels specified by a single prime.

Figure 3.2: Photoassociation scan where REMPI detects molecules populating $X^1\Sigma^+(v''=19)$. These nearly degenerate vibrational levels are identified as c-B complex($N=117$) and $\Omega=2(v'=100)$ with rotational states numbered, underlined numbering indicates $\Omega=2$ states. This scan illustrates the differences in the spectral features between the two electronic states.

Fig. 3.2 illustrates two vibrational levels, one from each state, that are

nearly degenerate. The typical hyperfine structure for both states are present with the underlined numbering distinguishing the $\Omega=2(v'=100$ and $J=2,3,4,5)$ (left to right) resonances from the c-B complex($N=117$ and $J=1,2,3,4,5)$ (left to right). Table 3.3 summarizes the assignments for all PA resonances from these two electronic states.

3.1.1 $\Omega=1$

The PA resonances categorized as being from the c-B complex from Table 3.3, all produce deeply bound singlet ground states with distributions similar to previous work[59], described in Chapter 2, modulated by FC factors. After analyzing the PA spectra, we are able assign the near dissociation PA resonance from reference[59] as c-B complex($N=128$) or $c^3\Sigma^+(v=70)$.

Fig. 3.2 is a PA scan that has eight closely spaced features spanning 10 GHz. We assign these forms as rotational levels from nearly overlapping vibrational states belonging to two separate electronic states. These levels are separated by only a few GHz and are nearly degenerate. As a result, they are resonantly coupled meaning that these states have similar properties even though the electronic states differ. We confirm the resonant coupling between $\Omega=2(v'=100)$ and c-B complex($N=117$) by observing that identical population is created in deeply bound singlet ground states from both resonances, uncharacteristic of the $\Omega=2$ states. Previous experiments have also observed resonant coupling between vibrational states that are nearly degenerate [64, 65]. Another pair of nearly degenerate states, separated by fewer than 10 GHz, are the c-B complex($N=113$) and $\Omega=2(v=98)$. However, we conclude that these states do not exhibit resonant coupling as we observe disparate ground state vibrational distributions produced by photoassociation through these two states.

3.1.1.1 C_6 Coefficient

The curvature of the long range PEC is essential to the description of the molecular electronic state. The PA resonances provide experimental data detailing the lowest rotational states of near dissociation vibrational levels that may be used to pin the curvature of the PEC as it approaches the dissociation limit. The LeRoy-Bernstein (LB) formula [66] provides a framework to study the long range PEC. It relates the binding energy, $E(v)$, of eigenstates for a potential curve as a function of vibrational level. It was derived using the Wentzel-Kramers-Brillouin (WKB) method [67, p. 435] with a potential curve, $V_{LR}(R)$. The van der Waals dispersion forces bind the NaCs molecule, therefore the long range form of the potential energy curve is:

$$V_{LR}(R) = D + \frac{C_n}{R^n}$$

where D is the dissociation energy. For the particular case of heteronuclear molecules in an excited state, $n=6,8,10\dots$ This expansion is valid for eigenstates located at an internuclear separation greater than R_{LR} , the shortest distance where there the electronic orbitals of the two atoms do not overlap. R_{LR} takes the form [66]:

$$R_{LR} = 2[\langle r^2 \rangle_A^{1/2} + \langle r^2 \rangle_B^{1/2}]$$

where r is the r.m.s distance to the outermost electron. This definition for R_{LR} is appropriate for two ground state atoms with symmetric electronic orbitals. A modified LeRoy radius, R_{mLR} , was proposed [68] to take into account the spatial extent of excited atomic orbitals. We calculate R_{mLR} for states converging to the $3^2S_{1/2}+6^2P_{3/2}$ asymptote to be either 11.1 Å or 16 Å depending on the projection of the atomic orbital angular momentum on the z-axis. A mathematica notebook for this calculation is presented in Appendix C.

The full form for the LB formula [66] is:

$$E(v) = D - \left[\hbar \left(\frac{2\pi}{\mu} \right)^{1/2} \left[\frac{n-2}{2n} \right] \frac{n}{C_n^{1/2}} \frac{\Gamma(1 + \frac{1}{n})}{\Gamma(\frac{1}{2} + \frac{1}{n})} (v_D - v) \right]^{\frac{2n}{n-2}}$$

and specifically for heteronuclears, it takes the form:

$$E(v) = D - \left[2\hbar \left(\frac{2\pi}{\mu} \right)^{1/2} \frac{\Gamma(\frac{7}{6})}{C_6^{1/6} \Gamma(\frac{2}{3})} (v_D - v) \right]^3 \quad (3.1)$$

In Eq. 3.1, v_D is a non-integer identifying the vibrational state at the point of dissociation, and μ is the reduced mass of the molecule. This expression uses the PA resonances to find the C_6 dispersion coefficient thereby describing the curvature of the potential at long range.

Using Eq. 3.1 and a least-squares fit of the c-B complex PA resonances, we find $C_6 = -9029 \pm 59$ au. The calibration and alignment of the Burleigh WA-1000 wavemeter induced ± 2 GHz uncertainty for each PA resonance. The estimated error of C_6 was determined by comparing coefficients calculated by shifting all data points to either extreme. We note that even with the associated uncertainty, our C_6 coefficient is between the theoretical values for the $(4)\Omega=1$ state.

Fig. 3.3 plots our LB fit (curve), the PA resonances (dots) as well as the LB fits generated using the theoretical C_6 coefficients[53, 54] provided in Table 3.1. The close agreement of our data with theoretical predictions indicate that the long range form of the PA electronic state is the $(4)\Omega=1$. Earlier in this section, we assigned the PA resonances as part of the $\Omega=1$ component of the $c^3\Sigma^+$ state and this long range assignment of $(4)\Omega=1$ is contrary to the typical labeling of the $c^3\Sigma^+$ as the $(3)\Omega=1$. However, if we compare the effective C_6 coefficient for the experimentally determined $B^1\Pi$ PEC[28], we find that it is closer to the $(3)\Omega=1$

Table 3.1: C_6 dispersion coefficients given in atomic units (Hartree $\times$ bohr radii⁶)

Source	State	C_6 coefficient	Fig. 3.3
Reference[53] <i>case (a)</i>	$1,3\Pi$	-10724	Dotted
Reference[54] <i>case (a)</i>	$1,3\Pi$	-7959.8	Dashed
Reference[53] <i>case (c)</i>	$(4)\Omega=1$	-10887	Dot-dashed
c-B complex PA resonances	$(4)\Omega=1$	-9029	Solid
Reference[53] <i>case (a)</i>	$1,3\Sigma^+$	-23060	
Reference[54] <i>case (a)</i>	$1,3\Sigma^+$	-18353	
Reference[53] <i>case (c)</i>	$(3)\Omega=1$	-19511	
PEC[28]	$B^1\Pi$	-15681 ^b

Figure 3.3: LeRoy-Bernstein fit to c-B complex photoassociation resonances (dots). We assign these resonances to $(4)\Omega=1$ due to the agreement with theoretical $(4)\Omega=1$ C_6 coefficients[53, 54] summarized in Table 3.1.

and coefficients labeled $1,3\Sigma^+$ in the literature. These findings predict a crossing between the experimentally determined diabatic $B^1\Pi$ PEC[28] and the $c^3\Sigma^+$ PEC at long range. The abrupt end of the PA resonances at ~ 1000 GHz detuning also supports this observation of an avoided crossing as photoassociation might not occur below it due to either predissociation [22, p. 413] or poor FC factors. Predissociation occurs when a rovibrational level overlaps with the dissociation continuum belonging to another electronic state. This is exactly the case for vibrational levels converging to the Cs $6^2P_{3/2}$ asymptote and interacting with

Figure 3.4: a) The experimentally determined $c^3\Sigma^+$ [2] and $B^1\Pi$ [28]. b) Portion of the PECs in Fig. 3.4a, to highlight the diabatic crossing of the potentials. Black dots represent the vibrational levels associated with the $c^3\Sigma^+$ and red dots are the c-B complex PA resonances.

the dissociation continuum for electronic states that are bound to the Cs $6^2P_{1/2}$ asymptote. In this case, a radiationless transition into this other dissociated electronic state may occur.

After investigation of the experimentally determined $c^3\Sigma^+$ [2] state and comparison with the experimentally determined $B^1\Pi$ [28], we find that there is indeed a crossing between these diabatic PECs. In Fig. 3.4a and Fig. 3.4b, we illustrate the two PECs and zoom in at long range where the crossing is apparent. Note that the PA resonances truncate about six vibrational levels before the actual crossing, indicating that the deeper vibrational levels are mixed to varying degrees with the $B^1\Pi$ and not favorable molecule formation channels.

^b An effective C_6 calculated by fitting the following coefficients to an R^{-6} dependence, $C_6 = 10724$, $C_8 = 1.95491 \times 10^6$, $C_{10} = -1.82987 \times 10^8$ from [28].

3.1.1.2 Rotational Assignments using Pulsed Depletion Spectroscopy

In this section, we investigate the ground rotational states that are populated via various PA channels shown in Fig. 3.5a, $J'=3-5$. Fig. 3.5a illustrates a photoassociation scan of the five rotational states, $J'=1-5$, coupled for c-B complex ($N=109$) detected by ionizing population in $X^1\Sigma^+$ ($v''=19$).

After photoassociation, the molecules decay to a range of ground state rovibrational levels. We compare ground state rotational distributions by utilizing PDS and exciting transitions between $X^1\Sigma^+(v''=4)$ and near dissociation vibrational levels in the $B^1\Pi$ state as seen in Fig. 3.5b. We resolve population in ground state rotational levels $X^1\Sigma^+(J=3,4,5)$ however spacings of $X^1\Sigma^+(J=0,1,2)$ are not resolved due to the linewidth of the pulsed laser.

From Fig. 3.5b, we conclude that the excited state used during PA has similar properties to a $^1\Pi$ state; however, the nature of the PA state could be inferred from the following arguments. PA is a long-range process, and the resonances can be described in the Hund's case (c) coupling as $(4)\Omega=1$. The $\Omega=1$ states exhibit omega-doubling which is similar to the lambda-doubling [22] observed in a $^1\Pi$ state. Also, due to a crossing between the $c^3\Sigma^+$ and the $B^1\Pi$ at large internuclear separation, $R\sim 9.5 \text{ \AA}$, the wavefunction of the PA state is characterized by $B^1\Pi$ at short range. Because there is greater overlap between the ground state and this excited state at short range, and FC factors describe 'vertical' transitions, the excited state wavefunction at short range determines transitions to deeply bound levels in the ground state.

To understand the data of Fig. 3.5b, we turn to the selection rules describing $^1\Pi \rightarrow ^1\Sigma^+$ transitions [22], requiring coupling between J states of opposite total parity. In a $^1\Pi$ state, each J is a nearly degenerate doublet of $+$ and $-$ total parity whereas the $X^1\Sigma^+$, not being degenerate in J , has the odd numbered

(a)

(b)

Figure 3.5: (a) Photoassociation scan of c-B complex(N=109) where REMPI detects molecules populating $X^1\Sigma^+(v''=19)$. Rotational assignments labeled. (b) Three pulsed depletion scans photoassociating through c-B complex(N=109, $J'=3,4$, or 5) in dashed, solid and dotted respectively. We indicate transitions from $X^1\Sigma^+(v''=4)$ to $B^1\Pi(v'=48, 49)$ (left to right) and indicate the calculated positions $R(J''=1-5)$ (right to left) with vertical lines. Transitions are calculated using LEVEL [30] and the $B^1\Pi$ PEC [28] and the $X^1\Sigma^+$ PEC[27]. Unlabeled pair of dips is c-B complex(N=111, $J=3,5$).

J's with $-$ parity and the rest have $+$ parity. As a result, transitions from the excited even J + states can couple to the ground state with P ($\Delta J=-1$) and R ($\Delta J=+1$) branches and excited odd J + levels couple with the Q ($\Delta J=0$) branch.

Figure 3.6: Illustration of the excited state emission process inferred by the measured ground state rotational distribution. Photoassociation through c-B complex(N=109, J=3-5) couples to the $+$ parity Λ doublets. Energy spacings are exaggerated.

In Fig. 3.5b, we show three depletion scans each using a different photoassociation resonance namely, $J'=3, 4$, and 5 from Fig. 3.5a. For clarity, we label the transitions from $X^1\Sigma(v''=4)$ to $B^1\Pi(v'=48, 49)$ by the $R(J'')$ transition even though PDS cannot resolve the separate P, Q and R branches in the excitation. The drop lines illustrate the spread from $J''=1-5$ (right to left) with the $J''=3, 5$ drop lines explicitly labeled. The c-B complex(N=109) J=3 (J=5) resonance is the dashed (dotted) curve indicating the PA formation process only populates J=3 (J=5) in the ground state. In these scans, odd J states in the PA couple to the ground state with a Q branch. The c-B complex(N=109) J=4 resonance is

the solid trace and both $J=3$ and $J=5$ are depleted, indicating that the even J couples with P and R branches. We conclude that the scattering channel couples to the $+$ parity states for c-B complex ($N=109$, $J=3, 4, 5$). These findings are summarized by Fig. 3.6.

3.1.2 $\Omega=2$

We observe eighteen PA resonances belonging to the $\Omega=2$ electronic state. The following discussion is divided between states that were previously observed and those that have only recently been catalogued. These findings are compared to the deperturbed $b^3\Pi_{\Omega=2}$ and *ab initio* $\Omega=2$.

3.1.2.1 Previously observed resonances

Of the 11 resonances which have been previously documented [69], there were three that have only recently been confirmed as belonging to the $\Omega=2$ progression after a claim was made that these PA resonances belonged to the $B^1\Pi$ electronic state [28]. To determine the origin of the three PA resonances in question, it is enough to consider the resulting population distribution as the $B^1\Pi$ and $\Omega=2$ electronic states couple to the singlet or triplet ground states, respectively. REMPI spectra from each PA resonance was compared and REMPI detection lines were determined using PDS to identify the populated states. We assign a REMPI detection line, populated by the PA resonances in question at -3216 GHz, -1911 GHz, -1009 GHz detuning, as $a^3\Sigma^+(v''=12,14,17)$ and determine binding energies summarized in Table 3.2. To calculate the binding energy of an unknown state, we shift its depletion scan to align to one that has been calibrated to the Cs $6^2P_{3/2}$ asymptote from a known vibrational level. The shift is the binding energy of the unknown state plus the energy of the D2 line. The displacement was

estimated by choosing a binding energy from a triplet ground state vibrational level, predicted by FC factor calculations in Fig. 3.7, to get a coarse overlap of the scans and then determined precisely by fitting a peak in each scan to a gaussian centered at the same position. The error in the binding energy arises from the uncertainty in the calibration of the pulsed dye laser to select atomic lines. The binding energies calculated from the PDS experimental values in Table 3.2 are in excellent agreement with those calculated by LEVEL [30] using the $a^3\Sigma^+$ PEC[27]. We conclude that these resonances are from the $\Omega=2$ progression because of the populated triplet ground states.

Table 3.2: Binding energies (given in wavenumbers) determined by pulsed depletion spectroscopy for $a^3\Sigma^+(v''=12, 14, 17)$ created using PA resonances $\Omega=2(v'=90,93,96)$ (given in GHz detuning from the Cs $6^2P_{3/2}$ asymptote), respectively. Also listed is the nearest vibrational state in the *ab initio* $\Omega=2$.

$a^3\Sigma^+$	Measured E_B	Calculated E_B [27]	PA Resonance (GHz)	<i>ab initio</i> $\Omega=2$ (GHz)
$v''=12$	41.54 ± 0.13	41.36	-3215.67	-3340.22
$v''=14$	26.4 ± 0.13	26.34	-1911.20	-1810.68
$v''=17$	10.85 ± 0.13	10.85	-1008.47	-1060.90

3.1.2.2 Recently observed resonances

After assigning resonances to the $\Omega=2$ progression, the pattern in the hyperfine profile and the number of coupled rotational states enables us to assign additional progressions to the $\Omega=2$ from PA spectra further detuned from the Cs $6^2P_{3/2}$ asymptote. The $\Omega=2$ electronic state provides many formation channels as deep as -19,407 GHz with observed structure illustrated in Fig. 3.11. From PA spectra, we obtain only the position of the rovibrational states without direct information as to their relative position. To obtain the relative vibrational state numbering, we fit the energies of the PA resonances to the LB formula:

Figure 3.7: The expected population distribution in the $a^3\Sigma^+$ for transitions from the RKR $\Omega=2(v'=90,93,96)$ (solid black trace) and the *ab initio* $\Omega=2$ (dashed black trace). Franck-Condon factors are calculated using LEVEL 8.0 [30]. Vertical lines are color-coded to represent the observed triplet state population for each PA resonance. Note the better agreement between the RKR $\Omega=2$ with the created population.

$$v \propto (D - E_{PA\text{resonance}})^{1/3} + v_D \quad (3.2)$$

Figure 3.8: Extrapolation of near dissociation states to find $v_D = 108.72$. Only the states denoted by circles were used in the fit as those were estimated to be at R_{LR} or $>11\text{\AA}$.

providing a linear fit to the near dissociation data. We extrapolate to find the y-intercept, v_D . Fig. 3.8 illustrates the fit to data (black dots) however, it still describes many states in the progression (blue squares). The deeper states deviate from the linear fit because they cannot be described as long range. The overall numbering was determined by incorporating vibrational state positions of the deperturbed $b^3\Pi_2(v=0-65)$ provided by A. Stolyarov.

3.1.2.3 Comparisons with the *ab initio* $\Omega=2$

Next, we compare these $\Omega=2$ states to those calculated using the *ab initio* $\Omega=2$ PEC[25] and LEVEL [30]. The *ab initio* state is $\sim 3000\text{ cm}^{-1}$ deeper with ~ 113 vibrational states as opposed to the ~ 108 vibrational levels determined experimentally. Overall, the *ab initio* positions do not describe the experimentally determined values, however there are a few states that have energies close to the PA resonances summarized in Table 3.2. Specifically, we focus on the states that are the closest in energy to the PA resonances, $\Omega=2$ ($v=90,93,96$) from the previous section, which are *ab initio* $\Omega=2(v=92,96,99)$, respectively. We calculate the predicted populated triplet ground states from the *ab initio* $\Omega=2$

[25] vibrational levels using LEVEL[30] and the experimentally determined $a^3\Sigma^+$ PEC[27]. Fig. 3.7 displays the select FC factors. Despite discrepancies in energy placement, the *ab initio* PEC predicts population in the triplet ground state that has been confirmed experimentally, represented in Fig. 3.7 by the vertical lines.

3.1.2.4 Comparisons with the deperturbed $b^3\Pi_{\Omega=2}$

We turn to the deperturbed A-b complex electronic states [29] which include $A^1\Sigma^+$, $b^3\Pi_{\Omega=0}$, $b^3\Pi_{\Omega=1}$, and $b^3\Pi_{\Omega=2}$ to gain insight about the PA resonances. These PECs are the result of a deperturbation analysis from experimental term values using an inverted channel-coupling approach taking into account the spin orbit interaction and the spin-rotational interaction [23, p. 191] between the $A^1\Sigma^+$ and the different components of the $b^3\Pi$. The experimental data consisted of transitions between $X^1\Sigma^+ \rightarrow$ A-b complex spanning ~ 10560 - 13667 cm^{-1} (where the zero-point energy is at the bottom of the singlet ground state which is 4954.24 cm^{-1} deep) with 98% of transitions to the $A^1\Sigma^+$ and $b^3\Pi_{\Omega=0}$ and 2% to the $b^3\Pi_{\Omega=1}$. The $b^3\Pi_{\Omega=2}$ is a by-product of the theory and there were no experimental observations made. However, the $A^1\Sigma^+$ and the $b^3\Pi_{\Omega=0}$ are accurate to within 0.05 cm^{-1} and it is reasonable to conclude that the $b^3\Pi_{\Omega=2}$ would be nearly as accurate over the experimentally observed energy range.

The deperturbed $b^3\Pi_{\Omega=2}$ PEC is created for each rotational state with the following form from [29]:

$$V_{3\Pi_2} = U_{b_0} + A_{01}^{SO} + A_{12}^{SO} + B[X - 2] \quad (3.3)$$

where $B \equiv \frac{\hbar^2}{2\mu r^2}$ and $X \equiv J(J+1)$. The U_{b_0} , A_{01}^{SO} , and A_{12}^{SO} terms are provided in their supplemental materials. With this expression, we compute a PEC for each rotational state $J=2$ -5. These PECs are then the input to LEVEL to compute

Figure 3.9: Note the agreement between the rotational constants of the $\Omega=2$ PA resonances (dots) and the deperturbed $b^3\Pi_{\Omega=2}$ (squares).

vibrational state energy positions. After calculating the vibrational positions of the deperturbed $b^3\Pi_{\Omega=2}$ using LEVEL, we find that the $J=2$ positions deviate as much as 16 cm^{-1} from the observed PA resonances with an 11.4 cm^{-1} standard deviation. However, there is reasonable agreement with the rotational constants as shown in Fig. 3.9.

3.1.2.5 Formation of RKR $\Omega=2$ PEC

To improve the deperturbed $b^3\Pi_{\Omega=2}$ near dissociation, we calculate an $\Omega=2$ PEC which shall be referred to as RKR $\Omega=2$ using RKR1 [70]. RKR1 is a computer program that uses the first-order semiclassical Rydberg-Klein-Rees (RKR) method which is an inversion procedure to solve Eq. 1.1 for the molecular potential energy curve from the vibrational level energies and rotational constants. Further description and more references may be found [70]. We fit a near dissociation expansion (fully described in [70]) to the set of vibrational level energies and to the rotational constants of deeply bound vibrational levels of the A-b complex and our PA resonances. These fit parameters are then inputs to the RKR1 program. We fit to data including the deperturbed $b^3\Pi_{\Omega=2}(v=0-65)$ covering vibrational levels beyond their experimentally observed energy range.

Figure 3.10: The deperturbed $b^3\Pi_{\Omega=2}$ (squares) follows a different curvature than the RKR $\Omega=2$ (circles) at long range. The red circles were used to fit V_{LR} (red solid curve) describing the electronic state with a standard deviation of 0.003 cm^{-1} as compared to the theoretical coefficients [53] (black solid curve) which deviate by $\sim 5 \text{ cm}^{-1}$. For comparison, we also include the *ab initio* $\Omega=2$ PEC (smaller blue dots).

However, the deperturbed $b^3\Pi_{\Omega=2}(v=73)$ differs from the deepest PA resonance (assigned as $v=73$) by $\sim 2 \text{ cm}^{-1}$, therefore the positions of the deperturbed vibrational states are likely very close to actual values and can be included in the RKR fits. We then use LEVEL to calculate the vibrational state positions of the resulting RKR $\Omega=2$ and find a 0.05 cm^{-1} standard deviation to the PA resonance positions which is clearly an improvement to the $\Omega=2$ PEC.

Next, we consider the long-range potential associated with the RKR $\Omega=2$. There are not enough near dissociation PA resonances to be used in a LeRoy-Bernstein (LB) C_6 dispersion coefficient calculation, therefore we fit the PEC to the form $V_{LR} = D - \frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}}$, using the red points shown in Fig. 3.10. These points range from $R > 11 \text{ Å}$ to the last PA resonance at $v=100$. We do not include any points generated beyond this state as they are extrapolations and

not data. From the V_{LR} fit, we extract C_k coefficients: $C_6 = 12107$ au, $C_8 = -3.2017 \times 10^6$ au, $C_{10} = -1.0454 \times 10^9$ au (au is hartree $\times$ (bohr radii)^k). For, $R > 11 \text{ \AA}$, these fitted parameters fit the data with a standard deviation of 0.003 cm^{-1} and the coefficients from theory ($C_6 = 10881$ au, $C_8 = -389800$ au) [53] shown in the black line in Fig. 3.10 deviate by $\sim 5 \text{ cm}^{-1}$ over this range.

To conclude, we have combined data sets of the PA resonances with data from [29] to produce an $\Omega=2$ state that describes experimental data very well.

3.1.2.6 Cs $6^2P_{3/2}$ summary

After investigating the PA resonances detuned from the Cs $6^2P_{3/2}$ asymptote and the populated ground states, no $X^1\Sigma^+(v=0)$ detection lines were located. Therefore, we extend the spectroscopy studies and detune the PA laser below the Cs $6^2P_{1/2}$ asymptote to find additional PA resonances.

3.2 Photoassociation resonances detuned from the Cs $6^2P_{1/2}$ asymptote

In this section, we focus on the $(4)\Omega=1$ formation channels, however we observe PA resonances from the $\Omega=2$, $(2)\Omega=0^+$, $(3)\Omega=0^+$, and $(2)\Omega=1$ states detuned from the Cs $6^2P_{1/2}$ asymptote. After the $(4)\Omega=1$ progression truncates at 960 GHz detuning from Cs $6^2P_{3/2}$ asymptote, the molecule formation pathways reappear below the Cs $6^2P_{1/2}$ as these states no longer predissociate. The five deeply bound PA resonances belonging to the $(4)\Omega=1$ progression, which for the rest of this section will be referred to as $B^1\Pi$, include $B^1\Pi(v=3,12,13,16,17)$ [18]. The following discussion will focus on results with an NaCs sample created via $B^1\Pi(v=13)$.

Figure 3.11: Recently observed $\Omega=2$ PA resonances.

3.2.1 $X^1\Sigma^+(v=0)$ found!

REMPI spectra taken while PA via $B^1\Pi(v=13)$ reveals detection channels for population in $X^1\Sigma^+(v=0,1)$ which were previously unknown. These detection lines are verified using PDS to drive transitions to the A-b complex. Fig. 3.12a,

Figure 3.12: (a) REMPI spectrum and only a few detection channels are present. The arrow indicates the detected vibrational state later confirmed to be $X^1\Sigma^+(v=0)$. (b) PDS scan illustrating the transitions made from the detected vibrational state at 813.25nm (blue arrow). Blue dotted lines indicate the known transitions from $X^1\Sigma^+(v=0)$ to the A-b complex confirming the state assignment.

illustrates the REMPI spectra and Fig. 3.12b shows the PDS scan that confirms the presence of $X^1\Sigma^+(v=0)$ population.

3.3 Conclusion

To conclude, we have assigned PA resonances detuned from the Cs $6^2P_{3/2}$ asymptote detected in a 34,000 GHz wide spectrum. Eighteen photoassociation resonances are assigned to the $\Omega=2$ and eighteen PA resonances originate from the $(4)\Omega=1$ state [71]. A combination of PA spectroscopy and pulsed depletion spectroscopy is used to assign these resonances based on the resulting population distribution, decipher the rotational distribution for a few of these states, and calculate an improved C_6 coefficient for the $(4)\Omega=1$. This work examines the *ab initio* $\Omega=2$ PEC [25] and verifies population in the predicted triplet ground states, confirms the line positioning of the experimentally determined $B^1\Pi$, and contributes experimentally determined vibrational positions of the $c^3\Sigma^+$. Most importantly, we have found a formation and detection pathway for $X^1\Sigma^+(v=0)$

which will be significant for the next set of experiments. By cataloguing the detected vibrational levels, we may select a resonance that creates a preferred population distribution to be optimized in vibrational cooling experiments [72, 73].

	Ω	v (N)	J=1	J=2	J=3	J=4	J=5	unknown
$b^3\Pi_2$	2	73		-19404	-19397	-19388	-19378	
	2	74		-18058	-18051	-18043		
	2	75		-16755	-16750	-16741		
	2	79			-12003	-11996		
	2	80		-10947	-10942	-10934	-10925	
	2	81			-9931	-9924	-9915	
	2	82		-8978	-8973	-8966		
	2	85		-6418	-6414	-6407	-6400	
	2	86		-5671	-5666	-5660	-5653	
	2	87		-4978	-4975	-4969	-4961	
	2	88		-4338	-4333	-4328		
	2	90		-3216	-3212	-3207	-3201	
	2	92		-2297	-2294	-2289	-2284	
	2	93		-1911	-1907	-1904	-1899	
	2	94		-1568	-1565	-1561	-1557	
	2	96		-1008	-1006	-1002		
	2	98		-608	-606	-603	-600	
	2	100		-330	-328	-326	-323	
$c^3\Sigma^+$	1	61 (109)	-959	-957	-955	-951	-947	
	1	62 (111)			-759	-756		
	1	63 (113)	-596	-594	-591	-589		
	1	64 (115)	-454	-452	-450	-448	-443	
	1	65 (117)	-333	-331	-329	-327	-324	
	1	66 (120)	-236	-235	-233	-231	-228	
	1	67 (122)		-159	-157	-155		
	1	68 (124)			-98	-96		
	1	69 (126)	-59	-58	-57	-56	-54	
	1	70 (128)	-32	-31	-30	-30	-28	
	1	71 (130)						-14
	1	72 (132)						-5
$B^1\Pi$	1	3 (25)		-33983	-33975	-33965	-33953	
	1	12 (43)	-22106	-22098		-22084	-22074	
	1	13 (45)	-20971	-20967	-20961	-20953	-20943	
	1	16 (51)	-17771	-17767	-17761	-17754	-17744	
	1	17 (53)	-16766	-16764	-16759	-16752	-16746	
	1	39 (95)	-2764	-2761	-2758	-2754	-2750	

Table 3.3: All observed photoassociation resonances from the $\Omega=2$ and (4) $\Omega=1$ electronic states. Center of mass line positions are given in GHz detuning from the Cs $6^2P_{3/2}$ asymptote with the corresponding assigned rotational states when possible. The vibrational states are assigned with v corresponding to the $b^3\Pi_2$, $B^1\Pi$ or $c^3\Sigma^+$ PEC and (N) indicates the vibrational state in the c-B complex.

Chapter 4

Luminorefrigeration of NaCs

This chapter describes experiments to increase population in the absolute ground state. The success of these experiments is a direct result from the previous chapter. Once we had located a detection wavelength for $X^1\Sigma^+(v=0)$, we were able to design experiments to manipulate and monitor the vibrational ground state population.

In this chapter, we utilize the simple and effective process of luminorefrigeration to vibrationally cool a sample of highly polar NaCs molecules created by photoassociation in an initial distribution of $X^1\Sigma^+(v \geq 4)$. The formation process initially populates low rotational states, $J_{initial}=0-2$, and we experimentally determine the rotational state dispersion after optical pumping to be $J_{final}=0-4$. The efficiency of optical pumping is determined by the Franck-Condon overlap of the ground and excited states in addition to the bandwidth of the optical pumping light. Our sample is illuminated by commercially available multimode diode lasers at wavelengths that are not energetic enough to drive population out of $X^1\Sigma^+(v=0)$, forming a dark state where population accumulates. We describe a series of experiments that explore the pumping dynamics and discuss the applicability of this approach to other alkali systems.

4.1 Introduction

Lumino-frigoriques is a term originally used by A. Kastler to describe optical pumping (OP) of sodium atoms between hyperfine states to accumulate population in a dark state [74]. The effects of optical pumping “cool” the sample when the final (dark) state is at a lower energy than the initial state. OP is ubiquitous in the laser cooling of atoms [4, 75], and has also been adopted to produce samples of ground state molecules: it has been demonstrated in Cs_2 by pumping vibrational levels with a femtosecond laser [72] or with low power broad band cw light [73], and in molecular ions by pumping rotational states [76, 77].

Next we will discuss the Cs_2 experiments in great detail because the NaCs experiment was modeled after them.

4.1.1 Cs_2

The Cs_2 experiment [72] utilized a frequency shaped, mode locked broadband ($\sim 54 \text{ cm}^{-1}$) femtosecond (fs) laser to pump an untrapped, initial distribution of singlet ground state molecules, $v_X=1-10$, into the lowest vibrational level in $\sim 60 \mu\text{s}$ by removing frequencies to the blue of 13030 cm^{-1} . By removing the energy that couples out of $v_X=0$, it becomes a dark state where population accumulates after a series of excitation and spontaneous emission cycles. It was estimated that roughly 70 percent of the initial population when pumped through the $\text{B}^1\Pi_u$ accumulated in $\text{X}^1\Sigma_g^+(v=0)$ and the process was deemed limited only by the bandwidth of the laser. A higher bandwidth would provide access to many more states to continue transferring the population. The greater the spectral width of the OP beam, the more transitions out of the ground state are coupled and loss channels are minimized.

After this proof of principle, the Pillet group demonstrated optical pump-

ing using a broadband laser diode [73]. The vibrational cooling experiment was whittled to a fraction of the cost of the previous laser system, making the process viable to a wider community. The diode operated near threshold producing 26.5 mW of light with a ~ 10 nm bandwidth, 17.1 mW of which was focused to $800\ \mu\text{m}$ on the Cs MOT. To produce the dark state, a grating dispersed the light and a mask eliminated frequencies that coupled out of $X^1\Sigma_g^+(v=0)$. It was shown that the mask can be tailored to selectively remove frequencies allowing population to accumulate in $X^1\Sigma_g^+(v=1)$ and in theory any target dark state.

These methods are designed to “cool” the vibrational degrees of freedom, yet it inherently induces rotational heating with each vibrational state transition. The Cs_2 formation process populates deeply bound singlet ground state vibrational levels with a rotational quantum numbers of $J_i=6-10$ [78]. Their simulation of femtosecond OP predicted a dispersion of rotational states to be $J_f=4-14$ during the vibrational cooling phase. To reach the rovibrational ground state, $X^1\Sigma_g^+(v=0 \text{ and } J=0)$, the Cs_2 group proposed the addition of second cw laser system with a narrow spectral width, $\sim\text{MHz}$, to mode match the spread in J state energies for Cs_2 . The frequency would couple $X^1\Sigma_g^+(v=0)$ to $B^1\Pi_u(v=3)$ to distill the rotational values and be shaped such that $X^1\Sigma_g^+(v=0 \text{ and } J=0)$ is the dark state. This rotational-OP beam must be applied during the vibrational cooling phase because as the vibrational levels are cooled, the rotational values disperse and *vice versa*.

Optical pumping methods involving either fs or cw lasers is a solution to simultaneously transfer a range of rovibrational levels to the rovibrational ground state and has the potential to be applied to many systems. Optical pumping with a fs laser offers bandwidth to drive population from many ground vibrational states at repetition rates that drive many cycles inducing a wide rotational spread.

However, a high rep rate can potentially interfere with long excited state lifetimes (like those observed in NaCs) inhibiting the pumping process. A cw approach, while limited in bandwidth, reduces the risk of multi photon excitation.

4.1.2 NaCs

Prospects for optically pumping NaCs with fs pulses [78] had been considered by the Cs₂ group. It was predicted that the highly mixed singlet/triplet character of the A-b complex would be too lossy due to the sheer number of available transitions between the A-b complex and the singlet and triplet ground states. All of these transitions were predicted to dilute the efficiency to the point of being ineffectual. As a result, several ¹Π electronic states were considered for the OP process in an attempt to limit accessible transitions. The FC maps are not well overlapped between the B¹Π and the deeper singlet ground states and as a result OP is not viable due to these poor transition moments. Experimentally, it would be difficult to drive these transitions due to a lack of commercially available laser diodes at ~600 nm. The next choice was a higher excited ¹Π state accessible with ~565 nm light for which there is much more wavefunction overlap with the singlet ground state. The calculations predicted successful OP, but decay to the lower lying electronic states (of which there are many to dilute the efficiency) were not considered. Despite the expressed reservations about the A-b complex, we chose these states for several reasons which will be discussed in the following.

4.2 Making the A¹Σ⁺-b³Π complex work for you

The A-b complex is illustrated in Fig.4.1. We choose it for OP because it minimizes the range of electronic states involved in the cycling transition, and

Figure 4.1: Optical pumping pathways in NaCs. Singlet ground state molecules are pumped through the $A^1\Sigma^+-b^3\Pi$ complex using broadband light that is not energetic enough to drive molecules out of $X^1\Sigma^+(v=0)$. Excited state molecules decay to the ground state and population in $X^1\Sigma^+(v=0)$ accumulates. The experimentally determined PECs are from [2, 27, 29, 79], shown with exaggerated vibrational level positions.

because it is a well studied system [29]. The shape and depth of the singlet ground state and A-b complex PECs are similar, therefore the OP light can drive a maximal number of ground state transitions with minimal spectral width. We note that the A-b complex has singlet and triplet spin components, therefore optical pumping can involve both the singlet and triplet ground states.

Figure 4.2: Select FC factors provided by A. Stolyarov for transitions from the $X^1\Sigma^+$ vibrational levels ($v=0-65$). Multiple transitions out of the singlet ground state are indicated with black circles for wavelengths of 979-991 nm, red squares for 1203-1209 nm, and green diamonds for 1252-1258 nm.

4.2.1 Wavelength Selection

Consider the effect of OP light with a broad spectral distribution to the red of 978.62 nm. This wavelength couples $X^1\Sigma^+(v=0) \rightarrow A-b$ complex ($N=1$), $N=1$ being the lowest vibrational level of the $\Omega=0$ component of the $b^3\Pi$, and consequently the lowest vibrational level in the excited state manifold. The A-b complex is a heavily mixed system of electronic states, therefore the effective vibrational levels are perturbed and numbered using index N . For this spectral distribution, the OP light would not be energetic enough to drive population from $X^1\Sigma^+(v=0)$ forming a dark state, yet it will pump population out of $X^1\Sigma^+(v \geq 1)$.

To choose the appropriate wavelengths, we refer to the transition dipole moment, $|\mu_{ij}|^2$, calculations performed by A. Stolyarov to find the most probable transitions between the singlet ground state and the A-b complex. Due to the experimentally confirmed initial distribution of $X^1\Sigma^+(v=4 \sim 30)$, we choose wavelengths centered at ~ 985 nm to achieve the most coverage of this vibrational state range. For population in higher lying vibrational states, the ideal wave-

length selection is ~ 1255 nm, however, we compromised with ~ 1206 nm in order to purchase readily available diode lasers. Fig. 4.2 illustrates the FC factors out of the singlet ground state with the various wavelength ranges.

To check the viability of this approach and to determine a suitable spectral bandwidth, we estimate the transition rates from $X^1\Sigma^+ \rightarrow \Omega=0$ components of the A-b complex to provide insight into the expected OP behavior. We assume a flat-top spectral intensity profile spanning 979-991 nm at 300 mW and 1203-1209 nm at 1.5 W focused to 1mm in diameter - parameters chosen to match readily available diode lasers.

$$\text{Transition Rate} = B_{ij}\rho(\nu_{ij})$$

where the Einstein B coefficient is $B_{ij} = |\mu_{ij}|^2/(6\hbar^2\epsilon_0 c)$ and ρ_{ij} is the energy density of the light [23, p. 350]. Note, there are 87 singlet ground state vibrational levels; however, transition dipole moments were available only for $X^1\Sigma^+(v=0-65)$ from [80]. Specifically, we calculate the transition rates for $X^1\Sigma^+(v=0-65)$ and conclude that a sufficient range of singlet ground state vibrational levels may be coupled via optical pumping by this experimentally feasible laser system. Of course, increasing the spectral width would couple even more levels thereby increasing the transfer efficiency to $X^1\Sigma^+(v=0)$.

This wavelength choice describes the final diode selection. Initially, we observed transfer with a single 980 nm diode. The OP experiments evolved and each version was necessary in order to lead us to the final result. In the following, we provide a brief description of each setup.

4.3 The Experiment

During the experiment, we first photoassociate (PA) NaCs from dark-SPOT magneto-optical traps. Initially, we choose a PA resonance that is part of

the $(4)\Omega=1$ progression [1], detuned 32 GHz from the Cs $6^2S_{1/2} \rightarrow 6^2P_{3/2}$ transition. This channel has a high formation rate, estimated to be $\sim 10^7$ molecules/s determined from spectroscopic results [59], the wavefunction overlap of the PA resonance with the singlet ground state calculated using LEVEL 8.0 [30], and by considering experimental geometry. This calculation is detailed in Appendix D. The ultracold molecules are not trapped and drift away from the formation/manipulation/detection region over a period of ~ 10 ms estimated from the measured kinetic temperature of ~ 250 μ K. To achieve vibrational cooling, the photoassociated NaCs sample is continuously exposed to OP light, driving the rovibrational distribution of molecules through the $A^1\Sigma^+$ and $b^3\Pi$ electronic states (A-b complex). We then probe the populated vibrational states of the NaCs sample using Resonance Enhanced Multi-photon Ionization (REMPI) where the neutral molecules are ionized and subsequently detected by a channel electron multiplier (CEM) using time of flight mass spectroscopy. Other spectroscopic techniques are employed to unambiguously determine the rovibrational state populations, such as pulsed depletion spectroscopy (PDS) [59] and cw depletion spectroscopy [62].

The initial population distribution created using the 32 GHz PA resonance, labeled $c^3\Sigma^+(v=70)$, has been shown to include $X^1\Sigma^+(v=4-6, 8, 9, 11, 13, 15, 17, 19, 21, 23, 25-27, 31)$, determined using PDS [59]. This range of vibrational states exhibits an electric dipole moment of ~ 4.6 Debye [19]. We expect that there is also population in higher singlet ground state vibrational levels from the Franck-Condon (FC) overlap of the potential energy curves (PECs) calculated using LEVEL 8.0 [30], shown in Fig. 2.5b, though we have not yet directly confirmed population of these states using REMPI.

4.3.1 Setup 1.0 and 1.1

For the initial OP trial, we chose a 2 W multimode diode laser centered at 986.5 nm with ~ 3 nm spectral width in-line with two bandpass filters (cutoff at 980 ± 1 nm) to create the dark state. The sample was continuously exposed to 20 mW and a comparison of the REMPI scans with and without optical pumping revealed an alteration in the vibrational distribution. Tailoring the amount of power and length of exposure affected the final population distribution identified by applying the PDS method.

Since this initial trial, we have removed the bandpass filters to increase the power to the sample by an order of magnitude and slewed the diode to 984.3 nm (spectral width still ~ 3 nm). Fig 4.3 clearly demonstrates that there is depletion of the NaCs signal in most vibrational levels (each peak in the REMPI scan corresponding to a vibrational level) and population in $X^1\Sigma^+(v=5)$ is completely coupled for an output power of at least 30 mW. This OP wavelength also accumulated population at 855.77 nm denoted by the dotted arrow. A wavelength of 984.3 nm drives population on the $X^1\Sigma^+(v=5) \rightarrow A\text{-b complex}(N=16)$ transition. The FC factor between these states is 0.05 which is relatively large compared to other transitions and indicates that high power diodes will be needed to drive the lesser transitions.

These trials demonstrate the need to obtain a more broadband source to maximize the ground states involved in optical pumping. A source that is at least 10 nm in spectral width will minimize the loss channels of unintentional dark states throughout the ground state potential. In addition to more bandwidth, a high resolution spectrum analyzer will be necessary to resolve the spectral profile of the OP light to ensure a continuous distribution over several nanometers. To obtain higher power and triple the current bandwidth, we will overlap beams

Figure 4.3: Photoionization scans comparing vibrational levels populated with (in orange) and without (in dark blue) optical pumping. Solid arrows indicate the $X^1\Sigma^+(v=5)$ REMPI lines that are completely depleted when OP is present. Dotted arrow indicates increased population due to OP.

from several diode lasers to manipulate the sample. Several 2 W multimode laser diodes were purchased from Intense Laser Co for this purpose.

4.3.2 Setup 2.0

We create the needed broadband OP light by overlapping the output of four 2 W 980 nm multi-mode diode lasers [81], each tuned to a slightly different wavelength, and a 2.5 W 1206 nm broad area diode laser [82]. To achieve overlap of the four 980 nm beams, we utilize polarization optics. Driving rovibrational transitions is a polarization-independent process, therefore we are able to create the OP spectrum with light that is polarized horizontally and vertically. Each pair of beams is overlapped using a polarized beam splitter cube, and they are then combined on a 50/50 beam splitter cube. Each arm of the 50/50 cube is

Figure 4.4: Relative intensities of the OP diodes. a) Combined spectral profile of the four 980 nm diodes. Vertical line indicates the transition wavelength to drive population out of $X^1\Sigma^+(v=0)$. b) The 1206 nm diode spectral profile.

sent to the chamber, intersecting at the sample. The 1206 nm light is sent to the sample via the PA beam path and those beams are overlapped with a longpass dichroic mirror.

As shown in Fig. 4.4a and b, the OP light has a spectral component centered at 985 nm with ~ 10 nm width and another component centered at 1206 nm with a ~ 5 nm width, respectively. These free-running diodes are temperature stabilized, however there is no active wavelength stabilization. The solid vertical line in Fig. 4.4a indicates the wavelength coupling $X^1\Sigma^+(v=0) \rightarrow A-b$ complex ($N=1$). The OP light is to the red of this transition satisfying the requirement for the formation of a dark state. These spectral profiles are not uniform, however, we attempt optical pumping with this setup because it is very inexpensive. The ideal spectral profile would not necessarily be uniform and is difficult to predict

due to the unknown initial population distribution. While we have experimentally verified the presence of deeply bound vibrational levels, we do not have much information about their relative populations or information regarding the distribution among the higher lying vibrational states.

4.4 Results

4.4.1 Vibrational State Manipulation

With the choice of OP light shown in Fig. 4.4, we observe significant transfer to $X^1\Sigma^+(v=0)$, determined by comparing REMPI spectra [18, 59] taken with and without OP using PDS for vibrational state assignments. To locate detection lines for the populated vibrational levels we utilize both a 2 and a 3 photon REMPI procedure which cover a range of 800-812 nm, 840-870 nm, and 535-545 nm. The REMPI wavelengths are calibrated to select atomic lines. Fig. 4.5a shows the detected vibrational states in the initial distribution with labels for the deepest states, $X^1\Sigma^+(v=4-6,19)$. The REMPI range here is selected because it contains one of the detection lines for the vibrational ground state. The state assignments in Fig. 4.5 are as described in [59] and known with high certainty due to the well known excited state assignments also from experimental data [29]. After vibrational OP, Fig. 4.5b shows the final distribution. Only the lowest three states, $X^1\Sigma^+(v=0-2)$, are populated while other vibrational levels are completely or mostly depopulated. From prior work [59] we know that another $X^1\Sigma^+(v=0)$ REMPI detection line exists in the 535-545 nm range and our OP results were confirmed in this range. Appendix E includes the REMPI scan. The 840-870 nm range did not include a detection line for the vibrational ground state, however, we observe quasi-dark states to be discussed in a later section.

OP experiments are conducted using combinations of the 985 nm and 1206

Figure 4.5: Three photon REMPI scans revealing populated vibrational levels in the singlet ground state. a) Initial distribution of vibrational levels with $X^1\Sigma^+(v=4-6,19)$ labeled. b) Final distribution after the sample is optically pumped. $X^1\Sigma^+(v=0-2)$ are populated. Vibrational assignments are experimentally confirmed using pulsed depletion spectroscopy [59]. The wavelength is calibrated against known atomic transitions to within 0.2 cm^{-1} .

nm spectral components to investigate how initial vibrational states are being pumped to ($v=0$). The 1206 nm spectral component alone does not significantly populate $X^1\Sigma^+(v=0)$; however, it does increase population in other deeply bound singlet ground states. The 985 nm spectral component saturates population driven into $X^1\Sigma^+(v=0)$ as a function of OP intensity, and when the two spectral components are combined, the transfer rate to $X^1\Sigma^+(v=0)$ is nearly doubled. This increase arises from the 1206 nm spectral component transferring population into vibrational states that are then accessible with the 985 nm component and driven to $X^1\Sigma^+(v=0)$. These results indirectly confirm the presence of higher lying vibrational levels in the initial distribution.

When the OP is optimized, we observe 50 NaCs ions in the $X^1\Sigma^+(v=0)$ detection channel per REMPI pulse. At this rate, however, we approach saturation of the standard CEM, meaning that the rate of ion bombardment is nearing the max output pulse rate, and actual production rates may be higher than those detected. A conservative estimate for the transfer rate into $X^1\Sigma^+(v=0)$ is $\sim 1 \times 10^5$ molecules/s from the initial rovibrational distribution created by the 32 GHz PA resonance. This is estimated by considering the detected ions per REMPI pulse, the detector efficiency, a geometric factor describing the ratio of detected molecules to those outside of the ionizer pulse region, and the 10 Hz experimental repetition rate. We also find accumulation in $X^1\Sigma^+(v=1, 2)$ with 45 ions per REMPI pulse from $v=1$. The spectral intensities of the diodes are low at the wavelengths driving transitions out of $v=1$ and 2 due to the fact that these wavelengths are close to the $v=0$ transition.

Due to the non-uniformity of the OP spectral intensity in Fig. 4.4, one might infer that there would be inaccessible ground vibrational states creating pockets of dark and quasi-dark vibrational states where population would persist

in the singlet ground state. A dark state is defined as one that does not couple to the excited state and a quasi-dark state is one that is coupled but still retains population. Quasi-dark states might be the result of a lack of intensity to drive transitions or the rate of excitation is less than the decay rate into that state. In the REMPI spectra, however, we find only a few quasi-dark states with population not completely depleted from $X^1\Sigma^+(v=1,2,8,13,15,19)$, and we see no evidence of a dark state other than $X^1\Sigma^+(v=0)$ when the two spectral components for OP are used. We observe depletion in the triplet ground state for $a^3\Sigma^+(v=12)$, verifying that here the triplet ground state is not a dark state. The formation and assignment of this vibrational state is discussed in [1]. The characteristics of the OP light are not optimized for this transfer, but it is clear that the triplet ground state can participate in the OP process.

To demonstrate the robust nature of OP, we utilize the 985 nm spectral component and enhance population in $X^1\Sigma^+(v=0)$ from a variety of initial vibrational distributions, created by utilizing different PA formation pathways. PA through $B^1\Pi(v=13)$ creates a distribution of deeply bound vibrational levels, $X^1\Sigma^+(v\sim 0-50)$ calculated using LEVEL [30], the $B^1\Pi$ PEC [28] and the $X^1\Sigma^+$ PEC [27]. We enhance the $X^1\Sigma^+(v=0)$ population, and detect 400 molecules/s. PA through a $(2)\Omega=0^+$ state at 3351 GHz detuning from the $6^2P_{1/2}$ asymptote populates $X^1\Sigma^+(v>30)$ based on an extrapolation of FC from [80]. OP of this distribution yields ~ 150 molecules/s in the $X^1\Sigma^+(v=0)$ detection channel.

4.4.2 Vibrational State Manipulation Simulation

The characteristics of the final setup have been implemented in a basic model. The simulation yields results that are similar to those found in the experiment.

We have created a monte carlo simulation in Mathematica to estimate the OP process for vibrational state transitions using the OP spectral profile from Fig. 4.4. The transition wavelengths and the Einstein A coefficients are provided by A. Stolyarov. These values in addition to the OP spectral profile are inputs to the program. Using the Einstein A coefficients and OP energy density function, the Einstein B coefficients are calculated and these rates are then multiplied by a time step to find the probability of a transition for a given time. This time step is chosen such that the probabilities are normalized to one and is $\sim 1 \mu\text{s}$. The program is a loop that runs n times tracking transitions for each molecule (n being the # of molecules). It begins with a molecule in an initial vibrational state and compares a random variable to the excited state transition probabilities and in that way selects the upward transition. From the chosen excited vibrational state, another random variable is used to decide the ground vibrational state for the decay transition, simulating spontaneous emission. For each excitation, the time step is added and the code tracks transitions up to a specified time corresponding to the OP exposure time of the sample. Spontaneous emission is $\sim 10^{-6}$ s for a few states but typically on the order of 10^{-7} - 10^{-8} s and approximated as instantaneous. Therefore, the decay time does not factor into the exposure time in the code.

This simulation can only model transitions between $X^1\Sigma^+(v=0-65)$ and $a^3\Sigma^+(v=0-24)$ to the A-b complex($N=1-350$) using calculations provided by A. Stolyarov [80]. This does not include all vibrational states in the $X^1\Sigma^+$ or the A-b complex electronic states. Some of the excited states are not included because they are not well known, such as A-b complex vibrational levels with binding energies from ~ 0 - 2000 cm^{-1} detuned from the Cs $6^2P_{3/2}$ asymptote. Or the transition probabilities are too low to be considered as is the case for accessible

transitions to the $c^3\Sigma^+$ electronic state. The relevant FC factors between $X^1\Sigma^+ \rightarrow c^3\Sigma^+$ are on the order of $\sim 10^{-12}$ - 10^{-18} and are negligible. The only other electronic state in this manifold is the $B^1\Pi$ state and it is not included because the OP wavelengths are not energetic enough to drive those transitions.

Figure 4.6: (a) Initial vibrational state distribution in green determined by FC factor calculations and the final distribution in blue calculated using the monte carlo simulation for $t=0.5$ ms. This time value is chosen as the relative population percentages in $v=0-2$ more closely resemble those from experimental results. (b) Population percentage as a function of OP exposure time (ms). Purple represents $X^1\Sigma^+(v=0)$, red for $X^1\Sigma^+(v=1)$ and green is $X^1\Sigma^+(v=2)$.

The initial ground state distribution is approximated by scaling calculated FC factors for $c^3\Sigma^+(v=70) \rightarrow X^1\Sigma^+$ to estimate the created vibrational distribution populated by the 32 GHz PA resonance. These calculations were performed using LEVEL [30], the experimental singlet ground state [27], and the experimentally determined $c^3\Sigma^+$ [2]. Fig. 4.6a illustrates the calculated initial distribution for $X^1\Sigma^+(v=0-30)$ in green and the calculated final distribution in blue for a total of 860 molecules. The code calculated the energy density function using the profile of the 980 nm spectral component with a total of 300 mW focused to 0.5mm and the profile of the 1206 nm component with a total of 1.5 W focused to 0.5mm. With these parameters, the code predicts $\sim 25\%$ of the population in $X^1\Sigma^+(v=0-65)$ will be transferred to $X^1\Sigma^+(v=0)$ after a 0.5 ms OP exposure

time. The molecules are estimated to remain in the interaction region up to 10 ms. Fig. 4.6b illustrates the trend in population for $X^1\Sigma^+(v=0,1,2)$ as a function of OP exposure time. For 10ms exposure, the model predicts 99% transfer to the ground state.

Experimentally, we observe a final population distribution similar to the findings at ~ 1 ms even though the exposure time should be on the order of 10ms. There are a few possible explanations. The calculations provided by Stolyarov did not include all the possible transitions that are experimentally accessible and the values that were used may not be a precise description of the coupling between the states. It should be noted that the initial distribution used in the simulation is from a calculation and the actual initial distribution is not known. Also, the probability of a transition is highly dependent upon the intensity of the OP light, and it is possible that the intensity of the OP light at the sample was less than specified in the OP code. The 980 nm spectral component was fashioned from several overlapped beams which due to experimental limitations were not perfectly overlapped as each beam had a different spatial profile. However, the code does illustrate that for similar OP light characteristics, population will accumulate in the absolute ground state.

4.4.3 Rotational State Manipulation

Here, we experimentally determine the initial rotational distribution by performing cw depletion spectroscopy on the sample. Fig. 4.7a presents the initial rotational distribution created by the 960 GHz PA resonance that is part of the $(4)\Omega=1$ progression; it creates the same ground state rotational distribution as the 32 GHz PA resonance. This PA line is used here because the scan has the best signal to noise ratio. By using the $X^1\Sigma^+(v=4) \rightarrow A-b$ complex ($N=70$)

Figure 4.7: Ground state rotational levels are labeled using cw depletion and transitions are known from [80]. Dashed areas indicate range of noise in the signal. a) Initial ground state rotational population distribution. Solid (dotted) line shows population created by (4) $\Omega=1$ PA resonance at 960 GHz through $J=1$ ($J=2$). Note both the R and P transitions are shown out of $J=1$ in the ground state. b) Final rotational population distribution by optically pumping the initial distribution created by the $J=1$ PA resonance at 32 GHz. $X^1\Sigma^+(v=0, J=0)$ is populated. The $J=1$ arrow is grayed indicating uncertainty of population in this state. The frequency is calibrated with a wavemeter known to within 0.3 GHz.

transition, we find that PA through $J=1$ in the excited state, populates $J=0,1,2$ in the singlet ground state as shown by the solid line in Fig. 4.7a. The assignments were made by comparing line positions to calculated values from [80]. Selecting the PA state is a crucial step when constructing the initial distribution and higher rotational states may be populated depending on the PA channel selected. The dotted line in Fig. 4.7a illustrates $J=1,3$ being populated via PA through $J=2$ in the excited state.

For each transition during OP, the rotational state selection rule is $\Delta J = \pm 1$

and we expect a spread in rotational states as OP drives population into $X^1\Sigma^+(v=0)$. Fig. 4.7b illustrates the rotational states that are populated within $X^1\Sigma^+(v=0)$ by driving transitions between $X^1\Sigma^+(v=0) \rightarrow A-b$ complex(N=77). From this depletion scan, we determine that the final rotational distribution populates $J_{final}=0-4$ and a significant fraction is in $X^1\Sigma^+(v=0, J=2)$. In order to interpret these results, we have modeled the rotational state transitions.

4.4.4 Rotational State Manipulation Simulation

Hönl-London Factors for $\Lambda=0$

$$\begin{aligned} S_{J''}^R &= \frac{(J''+1+\Lambda)(J''+1-\Lambda)}{J''+1} = J''+1 \\ S_{J''}^Q &= \frac{(2J''+1)\Lambda^2}{J''(J''+1)} = 0 \\ S_{J''}^P &= \frac{(J''+\Lambda)(J''-\Lambda)}{J''} = J'' \end{aligned}$$

Table 4.1: Hönl-London (HL) factors for $\Delta\Lambda=0$ transitions. These are appropriate to describe the transitions between $X^1\Sigma^+$ to the $\Omega=0$ component of the $b^3\Pi$ and $A^1\Sigma^+$. Note that regardless of an excitation or decay, J'' always refers to the ground state. A similar table may be found here [20, p. 335].

The data provided by A. Stolyarov did not include rotational information, and the OP code does not account for the change in rotational states as the molecules cycle between excited and ground states. Therefore, we use the $\Delta\Lambda=0$ Hönl-London (HL) factors [22, p. 208] in a monte-carlo simulation to model the rotational state dispersion. These HL factors, $S_{J''}^{\Delta J}$, may be found in Table 4.1. They describe the branching ratios for the $X^1\Sigma^+ \rightarrow (A^1\Sigma^+ \text{ and } b^3\Pi_0)$ rotational transitions.

We use an initial rotational state distribution of $J_{initial}=0-2$ and pump two thousand molecules between 1-6 cycles where one cycle is an excitation and decay transition. The final rotational state choice is weighted by the HL factors utilizing the selection rule of $\Delta J=\pm 1$ for $\Delta\Lambda=0$ transitions. This model predicts

Figure 4.8: Results of a monte-carlo simulation of an initial rotational distribution (striped) cycled between 1 and 6 transitions (black) or 3 and 8 transitions (gray) weighted by the Hönl-London factors for $\Delta\Lambda=0$ transitions. The final rotational distribution for 1-6 transitions (black) closely resembles experimental results.

a final population distribution centered at $J_{\text{final}}=2$ with population ranging from $J_{\text{final}}=0-6$ as depicted in Fig. 4.8. When modeling 3-8 cycles, we find the rotational population disperses over $\Delta J_{\text{final}}=0-10$ with a majority in $J_{\text{final}}=2,4,6$ which is contrary to the observed spectrum. Therefore, we infer the molecules do not undergo many transitions before populating $X^1\Sigma^+(v=0, J=2)$ due to the FC overlap of the ground and excited states.

4.5 Other Bialkalis

Luminorefrigeration may be generalized to any system where the lowest excited electronic states are well matched with the ground electronic state. We note that KCs, LiCs, and RbCs have PECs similar to NaCs for the ground state and A-b complex. For example, we calculate FC factors for the experimentally

Figure 4.9: a) FC map for KCs. b) FC map for NaCs between the $X^1\Sigma^+$ [27] and the deperturbed $A^1\Sigma^+$ [29].

determined singlet ground state [60] and deperturbed $A^1\Sigma^+$ and $b^3\Pi$ states [83] using LEVEL [30] for the KCs molecule shown in Fig. 4.9a. The calculated FC map indicates reasonable overlap and is similar in shape with the corresponding electronic states in the NaCs system shown in Fig. 4.9b. The KCs system has favorable transition moments [84] suggesting similar OP results may be obtained with appropriate laser diode selection for $\sim 988\text{-}1000$ nm coverage.

4.6 Conclusion

To conclude, we demonstrate a simple method to enhance production of ultracold, rovibrational singlet ground state molecules. This is the first application of vibrational optical pumping in a heteronuclear, highly polar sample, and we experimentally verify the rotational state distribution. Broadband cw light drives the initial population distribution from the singlet ground state to the $A^1\Sigma^+ \text{-} b^3\Pi$ complex in a series of absorption and spontaneous emission cycles and population accumulates in $X^1\Sigma^+(v=0)$ at an estimated rate of $\sim 1 \times 10^5$

molecules/s, populating $X^1\Sigma^+(v=0, J=0-4)$. A cw approach has low risk of multiphoton excitation and minimal rotational state dispersion and the efficiency is limited only by the bandwidth of the OP laser system.

Chapter 5

Conclusions

In the following, we highlight a few possibilities for the next set of experiments, and then conclude the thesis with a summary.

5.1 Future Directions

5.1.1 Luminorefrigeration

Steps may be taken to improve the efficiency of OP. For instance, a profile with more intensity at 988.12nm and 979.03nm will drive population on the $X^1\Sigma^+(v=1) \rightarrow A-b$ complex (N=1 and 2) transitions, respectively. N=1 is the lowest vibrational level of the $\Omega=0$ component of the $b^3\Pi$. After a closer look at the information provided by Stolyarov, we realized that the N=1 excited state mimics a relatively closed transition. N=1 has a lifetime of 2.5 μ s and decays 97.6% to $X^1\Sigma^+(v=0)$, 1.7% to $X^1\Sigma^+(v=1)$, 0.6% to $X^1\Sigma^+(v=2)$ and higher ground state vibrational levels are even less likely [80]. Pumping this single transition is an effective way to reduce population in $X^1\Sigma^+(v=1)$ and incoherently transfer to $X^1\Sigma^+(v=0)$.

Currently, the diodes are free-running and temperature tuned to select the wavelengths. The intensity profile of the bluest diode is configured to be as close as possible to 978.62nm, the wavelength coupling $v=0$ to the excited state, without affecting population in $v=0$. In order to get more intensity at 979nm, a mask would need to be inserted in the optical setup to block wavelengths at

or less than 978.62nm because transitions out of $v=0-2$ are too close together to be temperature tuned and selective. This was not part of setup 2.0 because the bluest diode is not ideal for lasing at $\sim 980\text{nm}$ and had only tens of mW after the beam shaping and combination with the other diodes. Therefore, we chose not to insert the mask and preserve the intensity.

Increasing the OP bandwidth would also improve the results. More laser diodes could be added to the setup, however, due to the number of lasers already involved, a better approach would be to replace the four separate 980nm diode lasers with two broad area lasers from Eagleyard. This simplification of the laser system and would also increase the OP bandwidth and power. The 980nm broad area laser diode has a 6nm bandwidth at 8W. Another possibility is to attempt optical pumping with a femtosecond laser similar to the original Cs_2 experiment [72]. Toptica's FemtoFiber Pro has an 80 MHz repetition rate and a bandwidth covering $\sim 980\text{-}1400\text{nm}$. A possible issue with this choice of laser is the repetition rate. The repetition rate would need to be less than 400 kHz so as to not drive multi-photon processes from the long-lived A-b complex($N=1$).

Rotational optical pumping will increase population in $v=0, J=0$. The current setup results in the majority of population in $(v=0, J=2)$. However, we should take advantage of the special properties of the excited state, $N=1$, to incoherently drive $X^1\Sigma^+(v=0, J=2) \rightarrow \text{A-b complex}(N=1, J=1)$ and rely on spontaneous emission to populate the rovibrational ground state by exploiting the $\Delta J=\pm 1$ selection rule. More rotational states may be driven in this way by using a diode laser with $\sim 40\text{ GHz}$ bandwidth to drive the even J'' state populations to $J''=0$.

Figure 5.1: Energy of the second order Stark shift for $X^1\Sigma^+(v=21)$. The energy is represented in units of temperature as a function of the electric field. The horizontal line indicates the temperature of the molecules, indicating which rotational levels may be trapped for a particular electric field strength. Field strengths of less than 100 kV/cm are feasible in the experiment.

5.1.2 Trapped Sample

Once the OP process is improved, this sample will need to be trapped. In previous experiments, the deeply bound molecules have been electrostatically trapped in the thin-wire-electrostatic-trap (TWIST) [33], however, this is for ground states with $J'' > 0$. More information about the TWIST may be found in this thesis [34, 85]. It relies on the second order Stark shift of the energy levels to create a potential minimum at the center of this trap. The energy dependence for a $^1\Sigma^+$ state is:

$$E_{Stark}^{(2)} = \frac{d^2 E^2}{B_v} \frac{J(J+1) - 3M_J^2}{2J(J+1)(2J-1)(2J+3)}$$

where d is the permanent electric dipole moment, E is the electric field, B_v is the rotational constant (which is 0.05445 cm^{-1} for $v=21$ [86]), J is the rotational state, and M_J is the projection of J along the direction of the electric field. Fig. 5.1 illustrates the dependence on the Stark energy shift as a function of E for various rotational states taking $M_J=0$. The rotational states $J'' > 0$ observe an attractive

potential. For a Stark shift greater than the energy of the population (the black horizontal line at $250 \mu\text{K}$ representing the energy of the molecular sample), the trap will be deep enough to confine the population. The rovibrational ground state, however, experiences a repulsive potential and is not trapped. Therefore, the TWIST might be used as a reservoir for the OP process before the final transfer to the rovibrational ground state.

5.1.3 Polar Crystals

For a sample of rovibrational ground state NaCs molecules, it may be possible to produce a polar crystal. A polar crystal is a collection of polar molecules where an electric field induces an effective dipole-dipole potential, $V_{eff}^{2D} \approx d^2/R^3$. Where d is the electric dipole moment (4.6 Debye for NaCs) and R is the molecule separation. For a system with high densities when the interaction strength, r_d , is above a certain threshold, r_{QM} defined in [10], and a temperature less than a melting temperature, T_m , then a crystalline phase transition has been calculated [10, 11]. These structures are currently purely a theoretical proposal, but their creation in the laboratory is deemed feasible for species such as SrO which has a dipole moment of 8.9 Debye [10].

These structures are stable due to their formation in optical lattices [87] created by the interference pattern from overlapping laser beams. The calculated phase transition was for a 2-d lattice with a triangular lattice site configuration. For laser beams that are red-detuned from the nearest molecular transition, then the light force causes the lattice sites, or microtraps, to occur at the intensity maxima. The lattice sites are separated by a distance, a . The microtrap depth is proportional to I_p/Δ . I_p is the peak intensity of the beam and Δ is the detuning of the laser from the nearest transition. For NaCs, the wavelength of the optical

lattice can be $\sim 1\mu\text{m}$ because the nearest transition for rovibrational ground state molecules is at $\sim 978.5\text{nm}$. When the molecules are tightly confined in the lattice and unlikely to tunnel between sites, then the formation of a polar crystal occurs for $T < T_m$ and $r_d \gg r_{QM}$:

$$T_m \approx 0.09 \frac{d^2}{a^3} \quad r_{QM} = \frac{d^2 m}{\hbar^2 a} = 18 \pm 4$$

derived in [10] and the references therein. For $a = 300\text{nm}$ (set by the wavelength and angle of overlap of the lattice laser beams), $r_d \sim 165$ and $T_m \sim 0.5\mu\text{K}$ for NaCs. Currently the molecules are $\sim 250\mu\text{K}$ and not in a regime to observe a polar crystal.

5.1.4 The Spectroscopy Business

There is the possibility of more REMPI spectroscopy to cover a wider wavelength range, in addition to pulsed depletion spectroscopy, to search for evidence of the higher lying vibrational states. This would provide direct feedback that the OP laser system is addressing population throughout the potential well. More REMPI and PDS spectroscopy could produce publications about unexplored excited electronic states, and locate more vibrational state detection lines in the singlet and triplet ground states. Also, additional initial distributions may be accessed via PA spectroscopy through higher atomic asymptotes.

Future experiments may include obtaining the value for the position of the ionization threshold. There are a few theoretical calculations predicting the position found in [88] and references therein. For a collection of molecules in the same originating state, a one-photon REMPI spectrum should provide the location of the ionization threshold simply by scanning across it.

Photofragmentation is a process where the absorption of a photon causes dissociation of the molecule. During REMPI, transitions may be driven above

Figure 5.2: *Ab initio* PECs with spin-orbit coupling for the NaCs molecule [86] in shades of black-blue. The lowest energy ionic PECs [26] are in purple, with the two lowest ionic asymptotes labeled.

an ionic asymptote causing the molecular ion to split into one atom and one ion. We have observed photofragmentation of NaCs, but we have yet to fully investigate the processes. Fig. 5.2 illustrates a few of the calculated ionic PECs [26]. Appendix F includes a REMPI spectrum illustrating the observed photofragmentation.

5.2 Summary

To conclude, this thesis describes the development of a tool that can be used to create a sample of rovibrational ground state molecules. The earliest steps in preparation for the luminorefrigeration experiments involved much photoassociation and REMPI spectroscopy to locate a REMPI detection line for $X^1\Sigma^+(v=0)$. Once this detection line was found, the collaboration with Stolyarov et al. allowed for the design and creation of an OP laser system. Finally, the implementation of cw depletion spectroscopy enabled verification of the rotational

distribution, and we found population in the rovibrational ground state. From this experiment, we realized the unique properties of $N=1$ in the A-b complex which can be utilized for the next set of experiments.

Fin

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Appendix A

$X^1\Sigma^+$ and $a^3\Sigma^+$ Rovibrational States

Tables for rovibrational levels of the $X^1\Sigma^+$ and $a^3\Sigma^+$ states. The zero-point energy is the dissociation limit at the ground state atomic asymptote.

Table A.1: Here are the vibrational energies with $J=0-5$ for the singlet ground state $X^1\Sigma^+$ [27] calculated using LEVEL 8.0 [30].

v	J=0	J=1	J=2	J=3	J=4	J=5
0	-4904.95	-4904.83	-4904.60	-4904.25	-4903.79	-4903.21
1	-4806.71	-4806.60	-4806.37	-4806.02	-4805.56	-4804.98
2	-4709.14	-4709.03	-4708.80	-4708.45	-4707.99	-4707.42
3	-4612.23	-4612.12	-4611.89	-4611.54	-4611.09	-4610.52
4	-4515.99	-4515.87	-4515.65	-4515.30	-4514.85	-4514.28
5	-4420.41	-4420.30	-4420.07	-4419.73	-4419.28	-4418.71
6	-4325.52	-4325.40	-4325.18	-4324.84	-4324.39	-4323.82
7	-4231.30	-4231.18	-4230.96	-4230.62	-4230.17	-4229.61
8	-4137.76	-4137.65	-4137.43	-4137.09	-4136.64	-4136.08
9	-4044.92	-4044.81	-4044.59	-4044.25	-4043.81	-4043.25
10	-3952.77	-3952.66	-3952.44	-3952.11	-3951.66	-3951.11
11	-3861.32	-3861.21	-3860.99	-3860.66	-3860.22	-3859.67
12	-3770.58	-3770.47	-3770.25	-3769.92	-3769.48	-3768.93
13	-3680.55	-3680.44	-3680.22	-3679.89	-3679.45	-3678.91
14	-3591.23	-3591.12	-3590.90	-3590.58	-3590.14	-3589.60
15	-3502.64	-3502.53	-3502.32	-3501.99	-3501.56	-3501.02
16	-3414.78	-3414.68	-3414.46	-3414.14	-3413.71	-3413.17
17	-3327.66	-3327.56	-3327.34	-3327.02	-3326.59	-3326.06
18	-3241.29	-3241.19	-3240.97	-3240.65	-3240.23	-3239.69
19	-3155.68	-3155.57	-3155.36	-3155.04	-3154.62	-3154.09
20	-3070.82	-3070.72	-3070.51	-3070.19	-3069.77	-3069.24
21	-2986.74	-2986.64	-2986.43	-2986.11	-2985.69	-2985.17
22	-2903.44	-2903.33	-2903.13	-2902.81	-2902.40	-2901.88
23	-2820.93	-2820.82	-2820.61	-2820.30	-2819.89	-2819.37
24	-2739.21	-2739.11	-2738.90	-2738.59	-2738.18	-2737.67
25	-2658.30	-2658.20	-2658.00	-2657.69	-2657.28	-2656.77

Table A.1 – $X^1\Sigma^+$ continued from previous page

v	J=0	J=1	J=2	J=3	J=4	J=5
26	-2578.22	-2578.12	-2577.91	-2577.61	-2577.20	-2576.69
27	-2498.96	-2498.86	-2498.65	-2498.35	-2497.95	-2497.44
28	-2420.54	-2420.44	-2420.24	-2419.94	-2419.54	-2419.04
29	-2342.98	-2342.88	-2342.68	-2342.38	-2341.98	-2341.48
30	-2266.28	-2266.18	-2265.98	-2265.68	-2265.29	-2264.79
31	-2190.46	-2190.36	-2190.16	-2189.87	-2189.47	-2188.98
32	-2115.53	-2115.43	-2115.24	-2114.94	-2114.55	-2114.07
33	-2041.51	-2041.41	-2041.22	-2040.93	-2040.54	-2040.06
34	-1968.41	-1968.32	-1968.13	-1967.84	-1967.45	-1966.97
35	-1896.26	-1896.16	-1895.97	-1895.69	-1895.30	-1894.83
36	-1825.05	-1824.96	-1824.77	-1824.49	-1824.11	-1823.64
37	-1754.82	-1754.73	-1754.54	-1754.26	-1753.89	-1753.42
38	-1685.58	-1685.49	-1685.30	-1685.02	-1684.65	-1684.19
39	-1617.35	-1617.25	-1617.07	-1616.79	-1616.43	-1615.97
40	-1550.14	-1550.04	-1549.86	-1549.59	-1549.22	-1548.77
41	-1483.97	-1483.88	-1483.70	-1483.43	-1483.07	-1482.62
42	-1418.87	-1418.78	-1418.60	-1418.33	-1417.98	-1417.53
43	-1354.85	-1354.77	-1354.59	-1354.32	-1353.97	-1353.53
44	-1291.94	-1291.86	-1291.68	-1291.42	-1291.07	-1290.63
45	-1230.16	-1230.08	-1229.90	-1229.64	-1229.30	-1228.86
46	-1169.53	-1169.45	-1169.28	-1169.02	-1168.68	-1168.25
47	-1110.08	-1110.00	-1109.83	-1109.57	-1109.24	-1108.81
48	-1051.83	-1051.75	-1051.58	-1051.33	-1050.99	-1050.58
49	-994.81	-994.72	-994.56	-994.31	-993.98	-993.57
50	-939.04	-938.95	-938.79	-938.55	-938.22	-937.81
51	-884.55	-884.47	-884.31	-884.07	-883.75	-883.34
52	-831.37	-831.29	-831.14	-830.90	-830.58	-830.19
53	-779.54	-779.46	-779.31	-779.07	-778.76	-778.37
54	-729.08	-729.01	-728.85	-728.62	-728.32	-727.93
55	-680.03	-679.95	-679.80	-679.58	-679.28	-678.90
56	-632.42	-632.34	-632.20	-631.97	-631.68	-631.31
57	-586.28	-586.21	-586.06	-585.85	-585.56	-585.19
58	-541.66	-541.59	-541.44	-541.23	-540.94	-540.59
59	-498.58	-498.51	-498.37	-498.16	-497.88	-497.53
60	-457.09	-457.02	-456.88	-456.68	-456.41	-456.06
61	-417.22	-417.15	-417.02	-416.82	-416.55	-416.22
62	-379.01	-378.95	-378.82	-378.62	-378.36	-378.04
63	-342.51	-342.45	-342.32	-342.13	-341.88	-341.56
64	-307.75	-307.69	-307.56	-307.38	-307.13	-306.83

Table A.1 – $X^1\Sigma^+$ continued from previous page

v	J=0	J=1	J=2	J=3	J=4	J=5
65	-274.77	-274.71	-274.59	-274.41	-274.17	-273.87
66	-243.61	-243.55	-243.43	-243.26	-243.03	-242.74
67	-214.30	-214.24	-214.13	-213.97	-213.74	-213.46
68	-186.89	-186.83	-186.73	-186.57	-186.35	-186.08
69	-161.40	-161.35	-161.25	-161.09	-160.89	-160.63
70	-137.87	-137.82	-137.72	-137.57	-137.38	-137.13
71	-116.32	-116.27	-116.18	-116.04	-115.85	-115.62
72	-96.77	-96.72	-96.63	-96.50	-96.32	-96.10
73	-79.22	-79.18	-79.10	-78.97	-78.81	-78.60
74	-63.69	-63.65	-63.57	-63.45	-63.30	-63.10
75	-50.14	-50.10	-50.03	-49.92	-49.77	-49.59
76	-38.53	-38.50	-38.43	-38.33	-38.20	-38.03
77	-28.80	-28.77	-28.70	-28.61	-28.49	-28.34
78	-20.82	-20.80	-20.74	-20.66	-20.55	-20.41
79	-14.49	-14.46	-14.41	-14.34	-14.24	-14.12
80	-9.62	-9.60	-9.55	-9.49	-9.41	-9.30
81	-6.02	-6.00	-5.96	-5.91	-5.83	-5.74
82	-3.48	-3.46	-3.43	-3.39	-3.32	-3.25
83	-1.79	-1.78	-1.76	-1.72	-1.67	-1.61
84	-0.77	-0.77	-0.75	-0.72	-0.68	-0.63
85	-0.24	-0.24	-0.23	-0.21	-0.18	-0.15
86	-0.04	-0.03	-0.03	-0.01		

Table A.2: Here are the vibrational energies with J=1-5 for the triplet ground state $a^3\Sigma^+$ [27] calculated using LEVEL 8.0 [30].

v	J=1	J=2	J=3	J=4	J=5
0	-207.446	-207.343	-207.188	-206.982	-206.725
1	-188.755	-188.655	-188.504	-188.303	-188.052
2	-170.934	-170.836	-170.689	-170.494	-170.250
3	-153.980	-153.885	-153.742	-153.552	-153.315
4	-137.896	-137.804	-137.666	-137.481	-137.250
5	-122.689	-122.599	-122.465	-122.286	-122.063
6	-108.365	-108.278	-108.148	-107.975	-107.759
7	-94.931	-94.848	-94.723	-94.556	-94.347
8	-82.396	-82.316	-82.195	-82.034	-81.833
9	-70.765	-70.688	-70.572	-70.418	-70.225

Table A.2 – $a^3\Sigma^+$ continued from previous page

v	J=1	J=2	J=3	J=4	J=5
10	-60.044	-59.970	-59.859	-59.712	-59.527
11	-50.236	-50.166	-50.061	-49.920	-49.745
12	-41.346	-41.280	-41.180	-41.047	-40.880
13	-33.377	-33.314	-33.220	-33.095	-32.938
14	-26.331	-26.272	-26.184	-26.067	-25.921
15	-20.239	-20.185	-20.104	-19.996	-19.862
16	-15.169	-15.120	-15.046	-14.948	-14.826
17	-10.840	-10.795	-10.727	-10.636	-10.522
18	-7.282	-7.242	-7.182	-7.103	-7.004
19	-4.555	-4.520	-4.468	-4.399	-4.313
20	-2.600	-2.571	-2.527	-2.469	-2.396
21	-1.287	-1.264	-1.230	-1.184	-1.126
22	-0.507	-0.490	-0.465	-0.431	-0.389
23	-0.129	-0.118	-0.102	-0.081	-0.055
24	-0.008	-0.004	0.002		

Appendix B

$B^1\Pi$ and $c^3\Sigma^+$ Vibrational Levels

During the pulsed depletion spectroscopy phase of the experiment, we compiled line positions for the $B^1\Pi$ and $c^3\Sigma^+$ vibrational levels. We used them to compare with the vibrational levels of the published $B^1\Pi$ PEC [28] and to collaborate to produce a $c^3\Sigma^+$ PEC [2]. Here is the list of values from the output of LEVEL 8.0 [30] for each PEC. Note that a few near dissociation levels are missing from each state which is a result of the LEVEL calculation requiring the PEC to extend to larger internuclear separation. The $c^3\Sigma^+$ has 74 vibrational levels and the $B^1\Pi$ has 62 vibrational levels.

A few rovibrational states with the smallest binding energy are not observed during PA. This is a result of the PA photon being too close to the atomic transition. Attempting to drive transitions to these highest states with the PA laser actually depletes the atomic sample and molecule production is significantly reduced.

Pulsed depletion spectroscopy may also be used to locate the dissociation asymptote of the excited state. This is not the most precise method as the linewidth of the laser is quite large, however, it is an excellent way to confirm the detected ground vibrational state (when the vibrational state splitting is large compared to the resolution of the laser). Fig. B.1 illustrates the dissociation limit as captured by the PDS spectrum from $X^1\Sigma^+(v=5)$.

Fig. B.2 illustrates a PDS spectrum and the absence of deeper vibrational levels in the $c^3\Sigma^+$.

Table B.1: $B^1\Pi$ vibrational level energies ($J=1$) and detunings (Δ) from the $6^2P_{3/2}$ asymptote calculated using LEVEL [30] and $B^1\Pi$ PEC [28].

Electronic State	Vibrational level	Energy (cm^{-1})	Δ (GHz)
$B^1\Pi$	0	10442.6	-38664.7
$B^1\Pi$	1	10495.8	-37069.5
$B^1\Pi$	2	10547.8	-35510.9
$B^1\Pi$	3	10598.5	-33990.0
$B^1\Pi$	4	10648.0	-32505.4

Table B.1 – contintued from previous page

Electronic State	Vibrational level	Energy (cm ⁻¹)	Δ (GHz)
B ¹ Π	5	10696.3	-31058.2
B ¹ Π	6	10743.2	-29652.9
B ¹ Π	7	10788.6	-28292.6
B ¹ Π	8	10832.5	-26976.0
B ¹ Π	9	10875.0	-25700.2
B ¹ Π	10	10916.3	-24463.1
B ¹ Π	11	10956.4	-23262.4
B ¹ Π	12	10995.2	-22096.6
B ¹ Π	13	11033.0	-20964.4
B ¹ Π	14	11069.7	-19864.5
B ¹ Π	15	11105.3	-18796.1
B ¹ Π	16	11139.9	-17758.9
B ¹ Π	17	11173.5	-16753.3
B ¹ Π	18	11206.0	-15779.4
B ¹ Π	19	11237.4	-14837.9
B ¹ Π	20	11267.7	-13928.9
B ¹ Π	21	11296.9	-13053.0
B ¹ Π	22	11325.0	-12210.7
B ¹ Π	23	11352.0	-11402.3
B ¹ Π	24	11377.8	-10627.4
B ¹ Π	25	11402.5	-9886.0
B ¹ Π	26	11426.1	-9178.6
B ¹ Π	27	11448.5	-8506.9
B ¹ Π	28	11469.7	-7873.7
B ¹ Π	29	11489.5	-7280.2
B ¹ Π	30	11508.1	-6722.0
B ¹ Π	31	11525.8	-6191.4
B ¹ Π	32	11542.7	-5683.6
B ¹ Π	33	11558.9	-5197.8
B ¹ Π	34	11574.4	-4734.6
B ¹ Π	35	11589.1	-4294.7
B ¹ Π	36	11602.9	-3880.3
B ¹ Π	37	11615.8	-3492.2
B ¹ Π	38	11627.9	-3129.8
B ¹ Π	39	11639.2	-2790.7
B ¹ Π	40	11649.8	-2472.6
B ¹ Π	41	11659.8	-2173.7
B ¹ Π	42	11669.1	-1894.9
B ¹ Π	43	11677.7	-1637.7

Table B.1 – contintued from previous page

Electronic State	Vibrational level	Energy (cm ⁻¹)	Δ (GHz)
B ¹ Π	44	11685.5	-1403.5
B ¹ Π	45	11692.6	-1191.3
B ¹ Π	46	11699.0	-997.5
B ¹ Π	47	11704.9	-820.4
B ¹ Π	48	11710.2	-662.1
B ¹ Π	49	11714.8	-525.7
B ¹ Π	50	11718.6	-409.8
B ¹ Π	51	11721.9	-311.0
B ¹ Π	52	11724.7	-228.4
B ¹ Π	53	11726.9	-161.0
B ¹ Π	54	11728.7	-107.6
B ¹ Π	55	11730.1	-67.0
B ¹ Π	56	11731.0	-37.8
B ¹ Π	57	11731.7	-18.4
B ¹ Π	58	11732.1	-7.0
B ¹ Π	59	11732.3	-1.7

Table B.2: c³ Σ^+ vibrational level energies (J=1) and detunings (Δ) from the 6²P_{3/2} asymptote calculated using LEVEL [30] and c³ Σ^+ PEC [2].

Electronic State	Vibrational level	Energy (cm ⁻¹)	Δ (GHz)
c ³ Σ^+	0	9627.5	-63099.3
c ³ Σ^+	1	9682.0	-61466.3
c ³ Σ^+	2	9734.9	-59881.1
c ³ Σ^+	3	9786.6	-58329.7
c ³ Σ^+	4	9837.7	-56799.6
c ³ Σ^+	5	9888.0	-55291.1
c ³ Σ^+	6	9937.6	-53803.6
c ³ Σ^+	7	9986.6	-52335.6
c ³ Σ^+	8	10035.0	-50885.5
c ³ Σ^+	9	10082.8	-49451.3
c ³ Σ^+	10	10130.2	-48031.3
c ³ Σ^+	11	10177.1	-46625.1
c ³ Σ^+	12	10223.6	-45230.6
c ³ Σ^+	13	10269.8	-43845.9
c ³ Σ^+	14	10315.7	-42469.5
c ³ Σ^+	15	10361.3	-41100.3

Table B.2 – contintued from previous page

Electronic State	Vibrational level	Energy (cm ⁻¹)	Δ (GHz)
c ³ Σ^+	16	10406.8	-39737.8
c ³ Σ^+	17	10452.0	-38381.9
c ³ Σ^+	18	10497.0	-37032.8
c ³ Σ^+	19	10541.8	-35691.2
c ³ Σ^+	20	10586.2	-34358.1
c ³ Σ^+	21	10630.4	-33034.8
c ³ Σ^+	22	10674.2	-31722.7
c ³ Σ^+	23	10717.5	-30422.8
c ³ Σ^+	24	10760.4	-29136.0
c ³ Σ^+	25	10802.9	-27863.3
c ³ Σ^+	26	10844.8	-26606.2
c ³ Σ^+	27	10886.2	-25366.7
c ³ Σ^+	28	10926.8	-24148.1
c ³ Σ^+	29	10966.6	-22954.7
c ³ Σ^+	30	11005.5	-21790.6
c ³ Σ^+	31	11043.2	-20659.3
c ³ Σ^+	32	11079.8	-19562.3
c ³ Σ^+	33	11115.2	-18499.3
c ³ Σ^+	34	11149.6	-17468.9
c ³ Σ^+	35	11182.9	-16471.2
c ³ Σ^+	36	11215.0	-15507.7
c ³ Σ^+	37	11246.0	-14579.0
c ³ Σ^+	38	11275.8	-13684.5
c ³ Σ^+	39	11304.6	-12822.6
c ³ Σ^+	40	11332.3	-11992.4
c ³ Σ^+	41	11358.9	-11193.7
c ³ Σ^+	42	11384.6	-10424.5
c ³ Σ^+	43	11409.4	-9681.0
c ³ Σ^+	44	11433.4	-8961.2
c ³ Σ^+	45	11456.5	-8267.4
c ³ Σ^+	46	11478.7	-7602.2
c ³ Σ^+	47	11500.0	-6964.2
c ³ Σ^+	48	11520.5	-6349.0
c ³ Σ^+	49	11540.4	-5752.5
c ³ Σ^+	50	11559.6	-5178.3
c ³ Σ^+	51	11577.7	-4635.0
c ³ Σ^+	52	11594.8	-4123.7
c ³ Σ^+	53	11610.8	-3642.8
c ³ Σ^+	54	11625.7	-3195.9

Table B.2 – contintued from previous page

Electronic State	Vibrational level	Energy (cm ⁻¹)	Δ (GHz)
$c^3\Sigma^+$	55	11639.5	-2782.9
$c^3\Sigma^+$	56	11652.2	-2402.0
$c^3\Sigma^+$	57	11663.9	-2050.3
$c^3\Sigma^+$	58	11674.7	-1727.9
$c^3\Sigma^+$	59	11684.4	-1437.2
$c^3\Sigma^+$	60	11692.9	-1180.5
$c^3\Sigma^+$	61	11700.3	-958.3
$c^3\Sigma^+$	62	11706.8	-765.0
$c^3\Sigma^+$	63	11712.4	-595.9
$c^3\Sigma^+$	64	11717.2	-451.8
$c^3\Sigma^+$	65	11721.2	-332.6
$c^3\Sigma^+$	66	11724.4	-235.7
$c^3\Sigma^+$	67	11727.0	-159.2
$c^3\Sigma^+$	68	11729.0	-100.6
$c^3\Sigma^+$	69	11730.4	-58.6
$c^3\Sigma^+$	70	11731.2	-31.8
$c^3\Sigma^+$	71	11731.9	-13.3

Figure B.1: Pulsed depletion spectroscopy spectrum illustrating transitions from $X^1\Sigma^+(v=5)$. The dips correspond to the vibrational level positions of the $c^3\Sigma^+$ and $B^1\Pi$ electronic states. The red dashed line indicates the energy required to dissociate $v=5$ NaCs molecules. Note the drop in the signal corresponding to this phenomena.

Figure B.2: Pulsed depletion spectroscopy spectrum illustrating transitions from $X^1\Sigma^+(v=9)$. The dips correspond to the deepest vibrational level positions of the $c^3\Sigma^+$ electronic state.

Appendix C

Modified LeRoy Radius

Here is the imported Mathematica code calculating R_{mLR} :

In Chem. Phys. Lett. 236, 242 (1995), the form for the distance at which long range effects are dominant: 1,2 being the two different atoms...

$$\begin{aligned} & \text{Rlrm}[n1-, l1-, m1-, Z1-, mN1-, \mu1-, n2-, l2-, m2-, Z2-, mN2-, \mu2-]:= \\ & 2\sqrt{3} \left(\left(\left(\frac{1}{3} - \frac{2}{3} \frac{3m1^2 - l1(l1+1)}{(2*11+3)*(2*11-1)} \right) * \left(\text{bohrradii} * \frac{mN1}{\mu1} \right)^2 * \frac{n1^4}{Z1^2} * \left(1 + \frac{3}{2} * \left(1 - \frac{l1(l1+1) - (1/3)}{n1^2} \right) \right) \right)^{.5} + \right. \\ & \left. \left(\left(\frac{1}{3} - \frac{2}{3} * \frac{3m2^2 - l2(l2+1)}{(2*12+3)*(2*12-1)} \right) * \left(\text{bohrradii} * \frac{mN2}{\mu2} \right)^2 * \frac{n2^4}{Z2^2} * \left(1 + \frac{3}{2} * \left(1 - \frac{l2(l2+1) - (1/3)}{n2^2} \right) \right) \right)^{.5} \right) \end{aligned}$$

Defining constants in the Rlrm equation:

(n1, n2):

n is the effective principle atomic quantum number, nstar, calculated by $n_0 - \alpha$,

(Z1,Z2):

Z is the effective nuclear charge,

(mN1,mN2):

mN is the mass of the nucleus in kg,

($\mu1, \mu2$):

μ is the "reduced" mass of the atom but it seems to be more of an effective mass.

(Z1,Z2) :

ZNa is a matrix containing relevant values for the effective nuclear charge for Na

orbitals: $\begin{pmatrix} 1s & 2p \\ 2s & 0 \end{pmatrix}$

ZCs is a matrix containing relevant values for the effective nuclear charge for Cs

orbitals: $\begin{pmatrix} 1s & 2p \\ 2s & 3p \end{pmatrix},$

(l1,l2):

l is the atomic electronic angular momentum,

(m1,m2):

m is the projection of l on the z axis,

alpha(l) is the quantum defect found in reference Bransden and Joachain, Physics of Atoms and Molecules (1983):

$$\alpha = \begin{pmatrix} - & 0 & 1 & 2 & 3 \\ \text{Li} & .4 & .004 & 0 & 0 \\ \text{Na} & 1.35 & .85 & .01 & 0 \\ K & 2.19 & 1.71 & .25 & 0 \\ \text{Rb} & 3.13 & 2.66 & 1.34 & .01 \\ \text{Cs} & 4.06 & 3.59 & 2.46 & .02 \end{pmatrix},$$

nstar is the effective principle quantum number:

$$\begin{pmatrix} - & \text{Li}(n_0=2) & \text{Na}(n_0=3) & K(n_0=4) & \text{Rb}(n_0=5) & \text{Cs}(n_0=6) \\ (n_0s)^2S_{1/2} & 1.588 & 1.626 & 1.771 & 1.805 & 1.869 \\ (n_0p)^2P_{1/2} & 1.966 & 2.116 & 2.32 & 2.28 & 2.392 \\ (n_0p)^2P_{3/2} & 1.966 & 2.117 & 2.235 & 2.293 & 2.362 \end{pmatrix}$$

$$\mathbf{ZNa} = \begin{pmatrix} 10.63 & 6.8 \\ 6.57 & 0 \end{pmatrix};$$

$$\mathbf{ZCs} = \begin{pmatrix} 53.9 & 50.82 \\ 40.51 & 36.58 \end{pmatrix};$$

$$\text{bohrradii} = .52917721092 * 10^{\wedge} - 10; (*\text{meters}*)$$

$$\text{massCsamu} = 132.90546;$$

$$\text{massCselectronskg} = 55 * 9.1093821 * 10^{\wedge} - 31;$$

$$\text{mNCs} = (78 * 1.674927351 * 10^{\wedge} - 27) + (55 * 1.672621777 * 10^{\wedge} - 27);$$

$$\text{massNaamu} = 22.98976928;$$

$$\text{massNaelectronskg} = 11 * 9.1093821 * 10^{\wedge} - 31;$$

$$\text{mNNa} = (12 * 1.674927351 * 10^{\wedge} - 27) + (11 * 1.672621777 * 10^{\wedge} - 27);$$

$$\text{nCs} = 6;$$

$$\text{nNa} = 3;$$

$$\text{lCs} = 1;$$

$$\text{mCs} = 1;$$

$$\text{lNa} = 0;$$

$$\text{mNa} = 0;$$

Reproducing a few quantities supplied in the paper for the homonuclear

Na₂, in units of Angstroms.

Rlrm[n1-, l1-, m1-, Z1-, mN1-, μ 1-, n2-, l2-, m2-, Z2-, mN2-, μ 2-]

$3S_\sigma+3S_\sigma$ 9.2

$3S_\sigma+3P_\sigma$ 13.4

$3S_\sigma+3P_\pi$ 9.7

Now calculating the values:

Rlrm[nstar[[1,2]],0,0,ZNa[[1,1]],mNNa, μ Na[1,1],nstar[[1,2]],0,0,ZNa[[1,1]],mNNa, μ Na[[1,1]]10¹⁰

Rlrm[nstar[[1,2]],0,0,ZNa[[1,1]],mNNa, μ Na[1,1],nstar[[2,2]],1,0,ZNa[[2,1]],mNNa, μ Na[[2,1]]10¹⁰

Rlrm[nstar[[1,2]],0,0,ZNa[[1,1]],mNNa, μ Na[1,1],nstar[[2,2]],1,1,ZNa[[2,1]],mNNa, μ Na[[2,1]]10¹⁰

9.17474

13.4441

9.70078

All the constants seem to be worked out, here is the Rlrm for NaCs that should be applicable to the A1Sigma+. Again, angstroms.

Rlrm[nstar[[3,5]],1,0,ZCs[[1,2]],mNCs, μ Cs[1,2],nstar[[1,2]],0,0,ZNa[[1,1]],mNNa, μ Na[[1,1]]10¹⁰

15.9324

All the constants seem to be worked out, here is the Rlrm for NaCs that should be applicable to the Omega=2. Again, angstroms.

Rlrm[nstar[[3,5]],1,1,ZCs[[1,2]],mNCs, μ Cs[[1,2]],nstar[[1,2]],0,0,ZNa[[1,1]],mNNa, μ Na[1,1]]10¹⁰

11.1374

Appendix D

Molecule Formation Rate

This rate is an estimate of the formation process via $c^3\Sigma^+(v=70)$. To determine a molecule formation rate of 10^7 molecules/s, we consider that the $X^1\Sigma^+(v=6)$ detection channel has 30 ions per REMPI pulse. From this value, we scale the population in all the singlet ground state vibrational levels using the FC factor calculation from LEVEL 8.0 [30]. With this estimated population distribution, we sum up all the ‘formed’ molecules and multiply by a few factors:

$$\frac{(\text{Total molecules}) \times (\text{Experimental Repetition Rate})}{(\text{Detector Efficiency}) \times (\text{Geometric Form Factor})}$$

these values happen to be:

$$\frac{34000 \text{ molecules} \times 10 \text{ Hz}}{0.4 \times 0.435} \approx 10^7 \text{ molecules/s}$$

The detection efficiency is determined from the CEM manufacturer, SJUTS. The geometric form factor is the ratio of the volume of the molecules to the REMPI beam assuming the molecules occupy a 2mm radius sphere, and the ionizer is rectangular with the highest intensity over a $1 \times 1 \times 3$ mm region centered on the sphere.

Appendix E

Optical Pumping Spectra

Fig. E.1 includes the REMPI spectra in the 540nm range. The OP (red) spectrum has been shifted vertically to more easily compare to the spectrum taken without OP (blue). The vertical lines labeling $v=0$ were determined via PDS.

Figure E.1: REMPI spectra with (red) and without (blue) optical pumping.

Appendix F

Photofragmentation Observations

The most relevant ionic PECs are plotted in Fig. 5.2. During REMPI, the absorption of photons may place the total absorbed energy above an ionic asymptote. When this occurs, the NaCs molecule may dissociate into an atom and an ion specified by the energy of the ionic asymptote. The probability of the absorption of additional photons increases with increasing intensity. Fig. F.1, illustrates a REMPI spectrum taken at a low and high pulse intensity. The high intensity scan (black) illustrates that more transitions are driven with a higher intensity photon. With more intensity, we observe fragmentation of NaCs to create either a Na ion or Cs ion. Fig. F.2 shows the high power REMPI spectrum and the data collected from the separate time of flight channels for atomic species. Note that Na (green) follows the NaCs spectrum and this ionic asymptote requires the absorption of a fourth photon. The Cs channel (purple) has much more structure indicating that the intensity of REMPI was fragmenting most of our molecular signal. In these figures, each trace has been offset from zero to more clearly see the peaks.

Figure F.1: These REMPI spectra illustrate the difference in saturation intensities and line strengths for the vibrational state transitions. At low power (blue) only the strongest transitions are present and with higher intensity (black) more features emerge.

Figure F.2: This REMPI spectrum is separated by channels identifying the atomic and molecular species that were detected during ionization. The high power intensity REMPI caused fragmentation of the NaCs and we observe similar features in the Na and Cs channels indicating that fragmentation has occurred for these detection lines. The boxes point out a few areas where the trend in fragmentation is especially clear.

Appendix G

Heteronuclear vs. Homonuclear REMPI Spectra

The homonuclear molecule, Cs_2 , has half as many atomic asymptotes as the heteronuclear molecule, NaCs . As a result, the REMPI spectrum is much simpler. Fig. G.1a and G.1b illustrates the comparison of a Cs_2 REMPI spectrum to that of NaCs for the same wavelength range.

(a)

(b)

Figure G.1: (a) Cs_2 REMPI spectrum. (b) NaCs REMPI spectrum.