### Prospects for laser cooling and trapping aluminum monochloride

Jamie C. Shaw, PhD

University of Connecticut, 2022

Laser cooling of atoms has ushered in a platform for studying light matter interactions with unprecedented control. Over the last 20 years, the techniques in laser cooling have become refined enough to enable specific diatomic and polyatomic molecules be directly laser cooled into the ultracold regime. The presence of permanent electric dipole moments and rich internal molecular structure offers molecules access to a range of novel applications outside the scope of atomic systems. These include stringent tests of fundamental physics, such as probes for dark matter and searches for an electron EDM, as well as realizations of strongly interacting quantum many-body systems and quantum computing/simulations. However, effectively implementing many of these applications rests upon achieving higher molecule trap densities than in current systems. In this dissertation, we introduce a diatomic species new to the field of direct laser cooling which is a strong candidate for overcoming these limitations. Following constructing and characterizing a cryogenic buffer gas source to produce these molecules, we use a system of custom built high power UV lasers operating near  $\sim 260$  nm to provide measures of optical cycling rates and loss channels in this molecule.

## Prospects for laser cooling and trapping aluminum monochloride

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#### Doctor of Philosophy Dissertation

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# Chapter 1

# Introduction

#### 1.1 Historical perspective

#### 1.1.1 Ultracold atoms

Laser cooling of atoms has ushered in a platform for studying light-matter interactions with exceptional control. Early seminal work through the 1970s and 80s led to the understanding that if an atom can be made to preferentially absorb and re-emit photons repeatedly, the resulting radiative force can be leveraged to both slow and corral atoms into a spatially confined trap where their collective behavior will begin to follow quantum statistics [1, 2]. A reduction to motional degrees of freedom in these systems was initially envisioned as a way to reduce Doppler broadening for both improved atomic spectroscopy as well as atomic time keeping (clocks) [3]. However, the ensuing developments in laser-based cooling techniques have not only led to the experimental realization of both the Bose-Einstein condensate (BEC) [4] and degenerate Fermi gas [5], but have also introduced an entirely new subfield to atomic, molecular, and optical physics, in which ultracold systems with quantum state control are being used worldwide to rigorously test fundamental physical theories.

#### 1.1.2 Ultracold molecules

Gaining similar control over molecules serves as a natural extension to these ultracold systems and promises similarly significant advances to both science and technology [6, 7]. On one hand, control over individual quantum states offers a platform for explicitly studying fundamental questions in quantum chemistry. On the other, the presence of permanent electric dipole moments (inherent to heteronuclear molecules) leads to a number of unique applications ranging from sensitive tests of physics beyond the standard model [6, 8], to strongly interacting many-body systems [9, 10] and quantum information processing [11–13]. Unfortunately, bringing molecules into the ultracold regime is made increasingly difficult both by the addition of rotational and vibrational degrees of freedom as well as collisional loss due to head-to-tail dipolar attraction [14].

Early on, a number of groups envisioned ways to form molecules in the ultracold regime by the in-direct means of associating previously laser-cooled atoms via either photo-association [15, 16] or magneto-association [17]. These methods have been highly successful for certain alkali atoms and have led to the demonstration of degenerate Fermi gases of both <sup>40</sup>K<sup>87</sup>Rb (KRb) and <sup>23</sup>Na<sup>40</sup>K (NaK) molecules [18, 19]. In both groups, evaporative cooling of these dipolar molecules has been achieved by applying either DC electric fields [20, 21] or microwaves [19] to suppress inelastic collisions. Although extremely successful, the in-direct methods of molecule production used in these experiments limit access to the variety molecular species that may be used. A growing number of applications requiring specific molecular properties has motivated extending direct laser cooling methods to encompass molecules. Over the last 10 years, combined efforts have developed effective laser cooling protocols to this end. To date, a number of diatomic, as well as now polyatomic, molecules have been laser slowed and radiatively trapped using a modified version of the standard atomic magneto-optical-trap (MOT) [22– 26]. While this has been a tremendous achievement, the densities in these molecular MOTs are currently at least four orders of magnitude lower than in their atomic counter-parts [24]. This has not stopped groups from implementing subsequent sub-Doppler cooling methods and transferring into either conservative optical [27–29] or magnetic [30, 31] traps where long rotational coherence times as well molecule-molecule collisions can be studied. However, the densities in current molecular MOTs place a practical limitation on the use of laser-cooled molecules for a variety of applications aimed to study strongly interacting quantum systems.

#### 1.2 Direct laser cooling of molecules

The success of laser-based cooling methods hinges on the ability of a particle to repeatedly scatter photons from a laser source, or optically cycle, transferring many units of photon momentum in the process. The most developed method of optical cycling relies on spontaneous decay to return an excited particle to its electronic ground state. For this cycle to continue, each spontaneous decay must be limited to populating the initial quantum state of the system. A molecule at room temperature with an optical transition and mass > 20 amu, requires scattering >  $10^4$  photons to bring to rest. For specific atoms, selection rules

enable cycling transitions closed to this level and are typically only limited by off-resonant excitation to nearby states with undesirable decay paths.

While similarly closed electronic and rotational transitions can often be found in molecules, vibrational decay does not follow simple angular momentum selection rules. Minimizing vibrational branching from the optical cycle relies instead on selecting molecules which have a high degree of overlap in the vibrational wave-functions of both electronic states. This is characterized by a highly diagonal Franck-Condon Factor (FCF) matrix [32] and is found in a growing subset of diatomic and polyatomic molecules.

#### **1.2.1** Current limitations

So far, the molecules that have been laser cooled (SrF, CaF, YO, CaOH, CaH, YbF, and SrOH) all have diagonal FCFs. These molecules optically cycle between electronic states which each have one unpaired valence electron, much like alkali atoms. However, unlike in atomic systems, these molecules require driving transitions to excited states with lower angular momentum to prevent rotational branching [33, 34]. This leads to stationary dark Zeeman sublevels which must be continuously remixed for optical cycling to continue. In this situation, the large number of additional ground-state sublevels contributes towards a ~ 10 times reduced maximum photon scattering rate, and therefore optical force, relative to in atoms. The reduced densities of current molecular MOTs can largely be attributed to long slowing distances, which reduce the solid angle and available flux in the molecular beam, coupled with comparatively smaller MOT capture velocities. In these systems, the trapping efficiencies from the molecular source are  $\leq 10^{-4}$ . Thus, as a route to increased MOT densities, we may either increase the molecule number during production or the magnitude of the optical forces themselves associated with slowing and trapping.

#### 1.2.2 Aluminum monochloride

Molecules with closed electron shells have several properties that appear advantageous for laser cooling, in general, as well as producing molecular MOTs with increased densities. Unlike in the free radicals that have previously been laser cooled, a paired electronic shell serves to suppress two-body losses and may offer higher peak molecule densities during the initial production prior to laser cooling. With regards to optical forces, rotational closure can be achieved in these molecules by optically cycling between states of equal angular momenta [35]. These types of transitions will produce a dark state for any type of polarization, however, this can be avoided by modulating laser polarization [36]. Provided that these dark states are remixed, the reduced number of ground states mitigates the penalty to optical forces present in current molecular systems.

Among closed shell molecules, aluminum monochloride (AlCl) has been identified as being a particularly strong candidate [32] for laser cooling as it is predicted to have highly diagonal FCFs [37–40] as well as both a short excited state lifetime of ~ 5 ns and high energy transition at  $\lambda \sim 262$  nm. The latter two properties suggest that the optical cycling transition of AlCl should offer a high scattering rate that may be leveraged to achieve shortened slowing distances (large solid angle and molecular flux) and high MOT capture velocities. With the predicted FCFs, producing a molecular MOT of AlCl should be possible with three lasers: one for optical cycling and two more for repumping vibrational loss. A trapped sample of AlCl offers access to a number of fruitful applications. A permanent electric dipole moment of 1.3 Debye [41] provides an ideal platform for studying strongly interacting quantum many-body systems and their dipolar collective dynamics [42]. Like an alkaline earth atom, between the states of the strong optical cycling transition also lies a narrow-line transition which provides a unique opportunity to probe both dipolar interactions with exceptional sensitivity as well as variations in fundamental constants between measurements using AlCl molecules on earth and those detected in red-shifted galaxies [43, 44].

Molecules with similar structures to AlCl are also currently being investigated by other groups, such as aluminum monofluoride (AlF) [45–48] and thalium monofluoride (TlF) [49, 50]. In these molecules, a combined lack of spin-rotation structure due to a closed electron shell and relatively weak hyperfine interaction leads to a peculiar situation where the span of the ground state hyperfine structure falls within the natural transition linewidth, leaving it unresolved. While recent experiments indicate that this unresolved ground state can lead to reduced scattering rates and optical forces [46, 50], the impact of such effects on different molecular species is not well understood. As a result, characterizing optical cycling properties of AlCl is important for understanding of this largely unexplored physical situation.

#### 1.3 Dissertation organization

The work of this dissertation is the culmination of many of the projects I undertook throughout my time as a graduate student at UConn. This spans both SrF and AlCl molecules, various laser systems, vacuum systems, electronics, and moving lab spaces partway through (among others). The organization of the remainder of this thesis is as follows: In Chapter 2, we outline the requirements on molecule production for direct laser cooling experiments and discuss the system used for producing both SrF and AlCl molecules. In Chapter 3, we introduce a novel four-level optical cycling scheme which enables background free fluorescence imaging of molecules. In Chapter 4, details relevant to laser cooling AlCl are discussed. In Chapter 5, we introduce the laser technology developed in order to probe and manipulate AlCl molecules. In Chapter 6, properties of a buffer gas cooled molecular beam of AlCl are examined. Chapter 7 provides high resolution fluorescence spectroscopy of the  $A^1\Pi$  state hyperfine structure in AlCl. In Chapter 8, we demonstrate optical cycling AlCl through radiative deflection of a molecular beam and extract experimental values for two branching ratios. This is followed by simulations of characteristics of AlCl molecules in a 3D MOT given in Chapter 9. In Chapter 10, we summarize the work of this dissertation and provide an outlook for future work with AlCl.

## Chapter 2

# Experimental setup and molecular source

In this chapter, a brief introduction to molecular beam production will be given highlighting this process as a key component to the overall setup of molecular laser cooling experiments. First, the problem facing direct laser cooling will be presented, namely that we are after a somewhat goldilocks condition in production in order to optimize laser cooling and trapping efficiency. We then consider the temperature dependence of vibrational and rotational degrees of freedom and how these many be leveraged using a cyrogenically cooled system to achieve our production goals. I will then present our version of this system, showing the initial characterizations we performed using SrF molecules to benchmark the performance prior to studying our new diatomic species, AlCl.

#### 2.1 Molecular beam sources

#### 2.1.1 Vibrational and rotational distributions

Moving from an individual atom to the simplest of diatomic molecules opens the door to many new challenges when laser cooling. In addition to resulting in a larger and more complex energy level structure, the energies associated with vibrational and rotational modes tend to be low enough to be thermally excited, leaving a large distribution of occupied energy levels for the respective ro-vibrational degrees of freedom. In view of laser cooling a molecular gas, this amounts to a dramatic reduction in the number of molecules of the ensemble which may be addressed by a limited number of lasers. Exactly what effect this will have on a chosen molecule will depend specifically on the energy level spacings of the system.

An initial sense of scale for this effect can be found by estimating the temperature for which energy approximates the level spacing for a given degree of freedom. This is known as the characteristic temperature and is defined by the following,

$$\Theta = h\epsilon/k,\tag{2.1}$$

where h and k are the Planck and Boltzmann constants, respectively. Here,  $\epsilon$  represents the zeroth order spectroscopic constant corresponding to the degree of freedom in question (for electronic, vibrational and rotational modes, we have  $T_{\rm e}$ ,  $\omega_{\rm e}$ ,  $B_{\rm e}$ ). For reference, in Table 2.1, we provide a list of characteristic temperatures calculated for a few of the simplest molecules as well as many diatomic molecules that are the subject of current laser cooling experiments. From this list, we first note that electronic transitions have been neglected, as they tend to lie in the optical spectrum with energy spacings equivalent to > 10,000 K, making them

Species	vibration	rotation
$\overline{\mathrm{H}_{2}}$	6340 K	88 K
CH	$4117~{\rm K}$	$21 \mathrm{K}$
$N_2$	$3397~\mathrm{K}$	$2.9~\mathrm{K}$
$O_2$	$2276~{\rm K}$	$2.1~\mathrm{K}$
CaH	$1870 {\rm K}$	$6.2~\mathrm{K}$
YO	$1240~{\rm K}$	$0.56~{ m K}$
AlF	$1156 { m K}$	0.80 K
MgF	$1025~{\rm K}$	0.75 K
CaF	$837~\mathrm{K}$	$0.49~{ m K}$
$\mathrm{SrF}$	$724~\mathrm{K}$	$0.36~{ m K}$
AlCl	$693~\mathrm{K}$	$0.35~\mathrm{K}$
BaF	$675 \mathrm{~K}$	0.31 K

TABLE 2.1: Characteristic temperatures for various diatomic molecules in their ground electronic state. Spectroscopic constants obtained from NIST webbook [51].

sufficiently immune to thermal excitation. On the other hand, both vibrational and rotational energy scales are sensitive to temperatures that are accessible in the lab. While excitation of vibrational levels require relatively high temperatures, these are easily achieved via the typical molecule production methods (laser ablation) which will be discussed further in this section. By contrast, even for the lightest of molecules, rotational splittings are considerably lower than the energies associated with room temperatures, which leads to a large distribution of populated rotational states for all diatomic molecules under ordinary conditions.

For a given molecule, a direct calculation for these distributions provides their explicit temperature dependence. This can be done using the normalized occupation probability using given by

$$P_i(\beta) = \frac{g_i e^{-\beta\epsilon_i}}{\sum_{i=0}^{\infty} g_i e^{-\beta\epsilon_i}},$$
(2.2)

where  $g_i$  is the degeneracy of states,  $\epsilon_i$  is the energy, and as usual,  $\beta = 1/(kT)$ , with k and T as Boltzmann's constant and temperature, respectively. We then take the energy spacings for both rotation and vibration to zeroth order,  $\epsilon_{\rm vib} = h\omega_e(\nu+1/2)$  and  $\epsilon_{\rm rot} = B_e h J (J+1)$ , to find the following distributions,

$$P_{\rm vib} = \frac{e^{-\beta h\omega_e(v+1/2)}}{\sum_{v=0}^{\infty} e^{-\beta h\omega_e(v+1/2)}} = 2 \sinh\left(\beta h\omega_e/2\right) e^{-\beta h\omega_e(v+1/2)},$$
(2.3)

$$P_{\rm rot} = \frac{(2J+1)e^{-\beta B_e h J(J+1)}}{\sum_{J=0}^{\infty} (2J+1)e^{-\beta B_e h J(J+1)}}.$$
(2.4)

Using spectroscopic constants for SrF, we plot these distributions in Fig. 2.1, with insets showing the dependence of the lowest 4 vibrational or rotational state populations on temperature. A molecular gas with low internal temperature serves to compress the ro-vibrational distribution to only populating a small number of states, thereby maximizing state populations. Therefore, in laser cooling experiments, it is vital for the molecular species to be introduced into the experiment in a way which will ensure the necessary low internal temperature. To this end, we rely on a technique known as cryogenic buffer gas cooling to generate bright beams of internally cold molecules.

#### 2.1.2 The Cryogenic Buffer Gas Beam Source

Cryogenic buffer gas beam sources (CBGBs) use a flow of a cold, inert gas, usually helium or neon (known as the buffer gas), to bring the molecular species of interest into thermal equilibrium through inelastic collisions, leading to a collapse of the occupied rovibrational state distribution [52–55]. This buffer gas is supplied to a cryogenically cooled cell in which molecules are introduced either via a capillary fill



FIGURE 2.1: Vibrational (left) and rotational (right) energy distributions for SrF molecules at various temperatures. Population versus temperature for the lowest energy states of each distribution is provided as an inset to each figure.

line or by laser ablation of a solid precursor. In either case, the species of interest becomes entrained within the buffer gas flow and exits the cell through a small hole to form a beam. The velocities of molecules within these molecular beams similarly follow a distribution with mean values typically in the range of ~ 50 and 200 m/s. Through advances in slowing techniques using radiation pressure [56, 57], this mean velocity can be reduced sufficiently to within the ~ 10 m/s capture velocity of typical molecular magneto-optical traps (MOTs) [22].

In our group, we constructed a CBGB source that closely follows one used in the Yale group for producing and laser cooling SrF molecules [53]. However, in our system we use a two-stage pulse-tube refrigerator (Cryomech PT420) which is paired with a closed liquid helium reservoir [58] between the refrigerator's second-stage and the cooled copper cell (Fig. 2.2), known as a "damping pot". When liquified at its base temperature, this reservoir contains  $\sim 7$  g (1.7 moles) of helium which offers a large thermal mass (with heat capacity  $\sim 16$  J/K) to both dampen temperature oscillations from the refrigerator and allow the source to readily absorb



FIGURE 2.2: Images from the behind of our group's cyrogenic buffer gas source with the rear radiation shields removed to show in a): (1) the source walls (300 K), (2) 30 K, and (3)  $\sim 2.6$  K radiation shields. In (4) the helium fill line is shown wound several times around a copper rod to ensure helium is in equilibrium with the 2.6 K stage. In b) we show (5) the refrigerator secondstage, (6) liquid helium reservoir, and the (7) cell. A sapphire window on the back of the cell enables a probe laser to measure along the molecular beam axis.

thermal loads from the ablation laser with limited heating. This provides for a more constant source temperature during operation, which is desirable to ensure reproducible molecular beam properties including flux, forward velocity, and rotational state distribution. We note that an equivalent thermal mass using copper alone at 2.6 K is impractical and would require cooling  $\sim 400$  kg of material. However, rare-earth alloy plates have been successfully used to dampen thermal oscillations in a similar manner [59], which may be a practical and fast change to existing CBGBs which desire a similar effect provided by a damping pot used here.

Associated with beneficial properties of the large thermal mass are longer source

cool-down and warm-up times. To counter these increased timescales, our design limits the additional thermal mass to 6 kg of machined aluminum and copper parts while largely replicating the source geometry of Ref. [53]. Our design cools from 295 K to 2.5 K in ~ 2 hours and can warm-up to 280 K in ~ 4 hours, allowing rapid prototyping. This temperature profile is given in Fig. 2.3a). When needed, we reduce warm up times by applying ~ 0.5 W of 808 nm laser light to the cell to increase the liquid helium evaporation rate. We have also found that flowing helium while warming (with all turbo pumps off and only our diaphragm pump on) helps to provide thermal links in the source, resulting in even faster warm up times. However, in doing this one has to be careful of condensation forming on the windows of the source. We remedy this by applying a high-power lamp to the source exterior for aiding in evaporation.



FIGURE 2.3: Thermal properties of our cryogenic buffer gas source. a) Typical source cool-down and warm-up curves measured over several hours for the refrigerator first-stage (dashed blue line), second-stage (dotted red line) and cell (solid black line). b) Short-term temperature stability for the same three regions as a). Temperature oscillations at the 1.4 Hz period of the pulse-tube refrigerator are visible at all three regions.

At base temperature, the cell and refrigerator second-stage are stable to  $\pm 5$  mK and  $\pm 60$  mK, respectively. This can be seen in Fig. 2.3b). For reference, without the helium reservoir the second-stage temperature stability is typically  $\pm 200$  mK

as the refrigerator pulses [60]. These larger oscillations have been reported to correlate with a  $\sim 25$  % peak to peak variation in molecular beam flux [53] forcing several experiments to synchronize their repetition rates to the period of the pulse-tube refrigerator to recover reproducible pulses of molecules [49, 56].

#### 2.2 Laser stabilization

The large number of frequencies associated with molecular transitions limits the number of laser stabilization methods that can be practically implemented. The typical saturated absorption methods used for many atomic laser cooling experiments is restrictive for several reasons. For instance, it is rare to find atomic or molecular gases that have transitions lying near enough to the required frequency of the molecular transition being studied. Even if a transition at the needed frequency can be found, it is unlikely that one will similarly find the additional transitions to reference the other lasers needed for a cooling experiment. Given this situation, the desired laser must be referenced to a separate laser which has itself been stabilized to an atom or molecule.

In our experiment, we do this using a scanning Fabry-Pérot cavity whose timeaveraged length is referenced to the  $5s_2 \rightarrow 3p_4$  neon transition at 632.8 nm from a Helium-Neon laser (HeNe). This is a well-established technique that is used several groups but generally follows that described in Ref. [61]. Here, we provide a brief description.

In this method, the HeNe reference laser is aligned to a Fabry-Pérot cavity whose length is repeatedly scanned using a piezo-electric transducer (PZT). The amplitude of this scan is set to be sufficient to detect two cavity fringes in transmission. Changes to the average value of the cavity length manifest as changes in the separation of these fringe positions. Following each cavity scan, a LabVIEW program (described in Ref. [62]) calculates the HeNe fringe separation and provides feedback to the cavity PZT offset voltage in order to maintain a fixed fringe spacing. This amounts to transferring the frequency stability of the HeNe to the length of the Fabry-Pérot cavity. The optical spectrum of the scanning Fabry-Pérot provides a calibration for the relative frequency of other lasers aligned to the cavity. A lock condition for laser stabilization is determined by calculating the peak positions of these lasers and comparing them against those of the HeNe.

#### 2.2.1 The polarization stabilized HeNe reference

To reduce experimental costs, in this work we use a Uniphase 1007 HeNe laser tube purchased from "Laser Sam", which is polarization stabilized following the procedure given in Ref. [63]. The HeNe tube length is chosen such that it supports two neighboring longitudinal modes with orthogonal polarizations. Changes to the HeNe tube length lead to a shift in the position of neighboring modes within the HeNe gain curve. This results in a corresponding imbalance in the power of each emitted polarization and allows changes in the HeNe tube length, and thus laser frequency, to be detected by detecting polarization rotation. A polarizing beamsplitter is used to direct each polarization component onto a current subtracting photodetector with high transimpedance gain. The resulting signal is used as a measure of error relative to the case of equal balance in polarization components. To apply feedback, this signal is amplified by a loop filter composed of a proportional gain stage followed by a double integral gain stage (PII) and fed through a linearized MOSFET<sup>1</sup> to control the current through a thin film heater that is wrapped around the HeNe tube. This system is placed in an enclosure to help maintain a fixed pressure environment. In agreement with Ref. [64], we measure a closed loop feedback bandwidth of roughly  $f_{-3dB} \approx 200$  Hz. Beat note measurements between identical systems indicate a short term stability on the order of ~ 1 kHz and a week long stability below 1 MHz.

#### 2.2.2 Athermal transfer cavity

While the average length of the Fabry-Pérot transfer cavity is referenced to the HeNe laser, the PZT used to tune it's length has a limited range. Changes to the optical path length arise from both thermal expansion of the cavity and changes in the refractive index of air due to pressure and temperature. Minimizing the effect of the first mechanism can be accomplished by affixing the cavity mirrors on a low expansion coefficient spacer, e.g. zerodur, ultralow expansion glass (ULE), etc. These materials however, are fairly expensive. Alternatively, one can choose materials for the cavity components such that their combined thermal expansion cancels. Of these options the latter can be made considerably cheaper and for systems that are length controlled, such as here, they provide sufficient athermal characteristics for a generic PZT to supply the required tuning range.

For the work presented in this thesis, we use the same cavity design discussed in Ref. [62]. In this design, two identical spherical mirrors are spaced by a distance equal to their radius of curvature (ROC). This leads to a resonator in which the number of longitudinal modes reduces to two degenerate groups of modes, one

<sup>&</sup>lt;sup>1</sup>The inherent nonlinearity associate with transistors can be removed by placing the transistor within the feedback loop of an operational amplifier (op-amp). We use this technique here to convert voltage to current in a linear fashion.

consisting of all odd modes and the other of all even [65]. These modes alternate every half free spectral range (FSR) which results in an effective FSR given by

$$FSR = \frac{c}{4L},\tag{2.5}$$

rather than the typical FSR = c/2L for a linear cavity. Here, c and L are the speed of light and the cavity length, respectively. This type of Fabry-Pérot is known as a confocal cavity and is useful in the sense that, by virtue of its mode degeneracy, it is largely insensitive to laser alignment and allows simultaneous mode-matching of different wavelengths. Not only does this reduce the need to correct for daily drifts in mirror alignment but it enables several lasers to be coupled into the same cavity without unnecessary difficulty. In the design used in our group, as used in Ref. [62], the two opposing mirrors are mounted in stainless steal end-caps that are separated by a quartz spacer and machined to lengths such that their combined thermal expansion coefficient nominally cancels. Fine threads allow for adjusting the cavity length such that the confocal condition can be found.

Given the athermal characteristic of these cavities, physical length changes due to temperature are largely suppressed. However, to overcome pressure changes we place each cavity in a conflat vacuum housing with windows on either side. With external changes to pressure isolated, changes to index of refraction, and therefore optical path length, stem only from pressure changes due to changing temperatures. While we could vacuum out these cavities, it is found to be unnecessary. One can see this by considering the temperature and pressure dependence of the refractive index of air [66] and how this couples to the cavity length. For a laser in the visible, such as our HeNe, this sensitivity is on the order of  $\Delta f / \Delta T \approx 200$  kHz/°C. For reasonable laboratory conditions this leads to temperature drifts below the linewidth of the cavities themselves.

The original design of these cavities places the scanning PZT between the stainless steel surface and the curved side of the mirror. To gain a restoring force when the PZT length contracts, an o-ring is sandwiched between the flat mirror side and a retaining ring. This design makes changing mirrors and making general modifications easy. However, using this method, we have found it difficult to both realize nearly the full free stroke length of the PZT as well as achieve linear cavity scans. As a result, in the cavities used for locking and performing spectroscopy we have moved to epoxying the PZT to both the stainless steal and curved mirror surfaces. This provides improved linearity during a cavity scan and considerably larger tuning length (75 – 95% of the free stroke length for a Noliac NAC2123 PZT).

#### 2.3 Absorption spectroscopy

#### 2.3.1 Determining molecule numbers

To determine the properties of our molecular beam we use both absorption and fluorescence spectroscopy methods. The benefit of absorption is that it provides a measure of molecular column density and its temporal distribution through a fraction loss in detected laser power. It is often useful to convert this fractional absorption into a detected number of molecules. The Beer-Lambert law relates the absorbed fraction to the column density intersected by the laser beam,  $\eta(t)$ , and is defined by,

$$\frac{I_t}{I_0} = e^{-\eta(t)\sigma(\nu)L},\tag{2.6}$$

where L is the interaction length through the gas, and  $I_0$  and  $I_t$  are the incident and transmitted laser intensities. Here,  $\sigma(\nu)$  represents the absorption cross section, and in the absence of any broadening mechanisms it is given for a  $J \to J'$  transition by

$$\sigma_0 = \frac{\lambda^2}{2\pi} \frac{2J' + 1}{2J + 1} \frac{A_{j,i}}{\Gamma},$$
(2.7)

where  $A_{i,j}$  is the Einstein A coefficient for the resonant transition and  $\Gamma$  is the total spontaneous decay rate from the excited state. We note that when the excited state has only one decay path, or one that dominates decay, we have  $A_{i,j} = \Gamma$ . In the presence of Doppler-broadening, this absorption cross section must be modified. This is done using,

$$\sigma_D = \frac{\sqrt{\pi}}{2} \frac{\Gamma}{\Gamma_D} \sigma_0, \qquad (2.8)$$

where we have  $\Gamma$  and  $\Gamma_D$  as the natural and Doppler-broadened linewidths, respectively [67]. For measurements outside of the cell, we can estimate the total number of molecules intersecting the laser by integrating the flux over time,

$$N = v_{\rm f} A_{\rm beam} \int \eta(t) dt = \frac{v_{\rm f} A_{\rm beam}}{\sigma_{\rm D} L} \int \ln\left(I_0/I_t\right) dt.$$
(2.9)

Here,  $v_f$  is the forward velocity of the molecular beam and  $A_{\text{beam}}$  is the crosssectional area of the laser beam at the measured distance of the cell, which is determined by either geometric constraints or previous measurements of beam divergence. A useful figure of merit is the number of molecules per unit solid angle per pulse, known as the beam brightness. This can be found via dividing Nby the half angle,  $2\pi$ . One should note that this treatment does not account for other broadening mechanisms such as power broadening, collisional broadening, or transit time broadening. However, unlike Doppler broadening, which is typically out of user control, each of these other mechanisms can be limited with appropriate consideration. For instance, both power broadening and transit-time broadening are effects that the user can control<sup>2</sup>; sufficiently low laser intensities will eliminate the wings of the lorentzian laser profile from causing off-resonant absorption, while selecting an appropriate beam size will rid the effect that time-energy uncertainty has on frequency resolution (e.g. a beam going 100 m/s should be probed with a laser beam of  $d_{1/e^2} \gg 0.1$  mm).

For measurements within the cell, we must further consider collisional broadening which is constrained by the helium flow rates necessary (for a given cell geometry) for molecules to reach a thermal equilibrium with the helium atoms. This depends on several factors but is often not a significant problem for these systems. To see this, we must take a few more steps in our calculation; this will be shown later in Chapter 6.

#### 2.4 Initial source characterization with SrF

Beams of cold and slow molecules from cryogenic buffer gas sources have played a central role in recent improved precision measurements [68, 69], high-resolution spectroscopy [45, 49], and the direct laser cooling and trapping of molecules at ultracold temperatures [70, 71].

 $<sup>^{2}</sup>$ This can often be a limitation for fluorescence measurements as low detection efficiency at times requires higher laser powers to scatter more photons. However, one can often trade off intensity for interaction time to achieve the same effect.



FIGURE 2.4: Diagram representing the cryogenic buffer gas source constructed for this work as described in the text. A pressed precursor (in this case  $SrF_2$ , and later Al:KCl) is epoxied to a copper enclosure (cell) and cryogenically cooled to ~ 2.6 K. Liberated molecules from a pulsed ablation laser are sympathetically cooled by a steady flow of <sup>4</sup>He gas into the cell and emit to form a beam through an exit aperture. A charcoal plate with a 6 mm hole is placed a distance 34 mm from the cell exit to limit the helium gas load down stream. The cell is held within a black body radiation shield lined with activated charcoal and held at ~ 2.6 K. A second radiation shield encloses this and is held at ~ 25 K. The entire system is placed in an aluminum enclosure that is activate pumped by a turbo. Molecules are probed via absorption outside of the cell as indicated.

We initially characterized this source using SrF molecules that allowed us to benchmark our system performance against that of the SrF molecule experiment in the DeMille group. Following the procedures described in Ref. [62], we use a pressed powder of  $SrF_2$  that is loaded into the buffer gas cell and ablated via a pulsed, doubled Nd:YAG laser. This laser is focused onto the target by a 200 mm focal length lens. While this laser is capable of pulse energies beyond 100 mJ/pulse, for experiments with SrF, we operated this laser using lower pulse energies (15 mJ/pulse) in order to replicate the conditions used in the DeMille group. Pulse-to-pulse fluctuations with this laser were measured to be  $\sim 1\%$ , largely independent of laser repetition rate, which can be tuned from 1-55 Hz. As shown in the Fig. 2.4, cold helium buffer gas enters the cell through a fill line at the rear and exits through a conical face. This has a 40° half-angle and a 3 mm diameter aperture. For initial tests with SrF, our typical helium buffer gas flow rate was 15 standard cubic centimeters per minute (sccm), equivalent to an in-cell steady-state helium density of  $10^{16}~{\rm cm^{-3}}$  and a Reynolds number of  $\approx 60$  (calculable via methods described in Ref. [55]). At this flow rate the vacuum inside the cryogenic source chamber is  $10^{-7}$  Torr, maintained by  $\sim 700 \text{ cm}^2$  of cold charcoal cryopump. Throughout this work a cold charcoal covered plate, containing a 6 mm diameter hole, is positioned 34 mm in front of the cell exit aperture to reduce the helium gas load downstream. Previous studies have shown that the location of this plate can strongly affect the molecular beam brightness [53, 54].

Properties of the molecular beam are optically probed here using the  $X^2\Sigma(v = 0, N = 1)$  to  $A^2\Pi_{1/2}(v' = 0, J' = 1/2)$  transition at 663 nm. As shown in Fig. 2.5, the resolved hyperfine components of the X state are addressed by laser phase modulation. We use a home-built electro-optical modulator (EOM) tuned via a tank circuit (following details provided in Ref. [72]) to be resonant at ~ 42 MHz. We use this laser for both absorption measurements ~ 20 mm downstream of the cell exit aperture (see Fig. 2.4) as well as fluorescence detection ~ 940 mm downstream.


FIGURE 2.5: Energy structure of SrF molecules relevant for measurements made in this chapter. A probe laser is tuned to address  $X^2 \Sigma_{1/2}(v'' = 0, N'' = 1 \rightarrow A^2 \Pi(v' = 0, J' = 1/2)$  transition. For a given vibrational level, v, and rotational level N, the ground state is split by the spin-rotational interaction and further by hyperfine interactions. To address this resolved hyperfine structure an electrooptical modulator is used to generate sidebands at  $\sim 42$  MHz onto the probe laser. In the excited state, no such spin-rotation interaction is present leaving the F = 0 and F = 1 levels of the J' = 1/2 state unresolved. The inset shows the modulated laser spectrum superimposed on the hyperfine structure.

An example profile of absorption outside the cell is provided in Fig. 2.6. To extract the number of molecules exiting the cell in the  $X^2\Sigma(v=0, N=1)$  state we use Eqn. 2.9 and integrate the temporal absorption profile. At ablation repetition rates of 1-2 Hz, where other helium buffer gas sources typically operate [53, 73, 74], our source produces similar pulses as were seen in SrF in [53], producing  $\approx 10^{11}$ molecules per steradian per pulse, with each pulse extending over a duration of  $\sim 20$  ms.



FIGURE 2.6: A typical temporal absorption profile of a molecular plume of SrF probed ~ 2 cm downstream from the cell exit aperture. This measurement was taken with a new ablation target corresponds to at molecular density of  $n_{\rm SrF} \simeq 10^8 {\rm ~cm^{-3}}$  and a brightness of ~  $10^{11} {\rm ~molecules/sr/pulse}$ .

### 2.4.1 Forward and transverse velocities

Upon exiting the cell, collisions boost the molecular beam forward velocity. We measure this forward velocity using the Doppler shift between probe beams aligned transverse and counter-progating to the molecular beam. Laser-induced-fluorescence (LIF) is collected and imaged onto an electron-multiplying CCD (EMCCD) (Andor iXon+ 885). Each fluorescence image is the integrated temporal profile of each molecular pulse which is then spatially integrated to obtain total detected fluorescence counts. Using this method, we measure a forward velocity of  $\approx 140$  m/s, with a FWHM of  $\approx 50$  m/s, approaching the forward velocity of the helium buffer gas ( $\approx 170$  m/s) [55]. We also measure the transverse velocity spread of the beam using Doppler broadening but do so through absorption measurements outside of

the cell. From this, we estimate a FWHM spread of  $\sim 80$  m/s, corresponding to a FWHM angular spread of 30°.

#### 2.4.2 Rotational temperature

We further extract the rotational temperature of the beam by determining the relative populations in the  $X^2\Sigma(v=0, N=0-4)$  levels. This is done by driving transitions from  $X^2\Sigma_{1/2}(v''=0, N''=0-4)$  to  $A^2\Pi_{1/2}(v'=0, J'=1/2-9/2)$  and scaling the integrated fluorescence counts according to the calculated rotational branching ratios (the explicit formulas which determine these for a  $X^2\Sigma_{1/2} \leftarrow A^1\Pi$  transition can be found in Ref. [75]). Following this procedure we find an internal rotational temperature of  $T_{\rm rot} = 1.0(2)$  K. Here molecules cool rotationally to below the cell temperature due to isentropic cooling near the cell aperture [76]. This corresponds to a rotational population of  $\approx 50$  % in the  $X^2\Sigma(v=0, N=1)$  state. These parameters are in agreement with measurements performed on a source with similar geometry by the Yale group using SrF [53].

Through these measurements we were able to validate the baseline performance of our constructed system. We used the remaining time between this milestone and an upcoming departmental move to evaluate system performance under conditions of higher repetition rates.

# 2.5 High repetition rate production of SrF molecules

Current molecular MOTs provide both confining and damping forces that are comparable to those of atomic MOTs. However, these molecular systems capture significantly fewer molecules and have correspondingly lower densities. This can largely be attributed to the low trappable flux due to the diverging nature of these molecule beams, as well as the limited molecule numbers associated with individual molecular pulses. And while interactions between laser-cooled molecules have been recently observed [29], many proposed future applications will require larger trapped samples at higher density than are currently realized. More efficient slowing techniques are presently being pursued by multiple groups [77–81], and the production of brighter, slower molecular beams remains an active and complementary area of research [82–86].

The addition of a liquid helium damping pot offers an increased power handling capability for our source. This minimizes temperature variations that stem from the energy deposited during laser ablation. The resulting reduced sensitivity offers a route to increased time-averaged molecule yield by increasing molecule production rates. Typical molecular MOT lifetimes are relatively short ( $\sim 100-500$  ms), restricting experiments that run at 1-2 Hz ablation frequencies to a single pulse of molecules per MOT loading. A straightforward way to increase MOT molecule numbers is therefore to increase the number of molecular pulses that arrive in the MOT region within the MOT lifetime. This corresponds to simply increasing the repetition frequency of the ablation ablation.

To verify that increased ablation frequencies result in increased molecule production, we repeat the same absorption method previously described, with a transverse absorption probe beam located ~ 2 cm downstream from the cell. However, we intensity stabilize the probe beam using an acousto-optic modulator (AOM) to limit power fluctuations over the necessary timescales for our measurements<sup>3</sup>. Our implementation for the servo loop is similar to that described in Ref. [87],

<sup>&</sup>lt;sup>3</sup>Initial tests were first performed using the auto-balanced photodetector described in Appendix D. However, this method was difficult to implement without AC coupling of the signal and was therefore not ultimately used.

except that we replace the frequency mixer with a voltage variable attenuator (VVA). The following measurements used a DC-coupled signal to ensure variations between subsequent pulses would be clear. To do this, we split the intensity stabilized probe beam into signal and reference paths of equal power and direct them onto separate detectors. These detectors were placed  $\sim 3$  m from the ablation laser to minimize optical pickup. The DC component of each beam is removed via summation with a stable reference voltage. The resulting signal and reference voltages are then subtracted from each other. Using the above method provided probe signals with  $\leq 0.1\%$  amplitude fluctuations.



FIGURE 2.7: Absorption and cell temperature traces measured over 1.5 seconds of source operation for ablation rates of (a) 10 Hz, (b) 20 Hz and (c) 55 Hz. During these measurements the source temperature (d) increased by 40 mK (dash blue line), 80 mK (dotted red line) and 200 mK (solid black line) respectively. The time needed to cool back to 2.64 K was 1 s, 30 s and 70 s for 10, 20 and 55 Hz operation respectively.

In Fig. 2.7, absorption traces show the temporal behavior of our molecular beam for ablation frequencies of 10, 20, and 55 Hz in Fig. 2.7a), b), and c), respectively. We

note that variations to the number of detected molecules can range by  $\approx \pm 50\%$ depending the spot ablated on the target. However, for a single ablation spot, Fig. 2.7 indicates that ablation at 10 and 20 Hz provides for consistent production corresponding to  $10^{12}$  and  $2\times10^{12}$  time-averaged molecules/sr/sec, respectively (Figs. 2.7a and 2.7b). However, at  $f_{\rm rep} = 55$  Hz, we consistently observe a  $\sim$ 10 % decrease in brightness ( $\propto$  the time-integrated absorption signal) over the first 2-5 pulses. While Fig. 2.7d shows negligible change over the corresponding timescale, slow thermal diffusion through the cell limits the time constants for the temperature sensor. In-cell absorption measurements show this initial decrease in brightness is correlated with decreasing in-cell molecular density in N = 1 and we observe extraction efficiency from the cell remains fixed to within  $\sim 50$  %. We find this decrease in yield is temporary; a 100 ms pause in ablation pulses is sufficient to recover the original yield from the next pulse using the same ablation spot. These findings are consistent with rapid initial heating that is not detected by our sensors. Over longer timescales, we see the cell temperature eventually increases by 40, 80 and 200 mK over 1.5 seconds of operation at 10, 20 and 55 Hz respectively (Fig. 2.7d). Independent of this effect, following the initial decay in brightness observed when ablating at 55 Hz, we measure a time-averaged yield of  $5 \times 10^{12}$  molecules/sr/sec (Fig. 2.7c).

In studying high-repetition rate ablation, we found a critical dependence on the helium buffer gas flow rate through the cell, specifically at the highest rate of 55 Hz. We show this effect in Fig. 2.8. At flow rates of 2 and 5 sccm, the initial yield per ablation pulse is reduced by factors of 10 and 5, respectively, relative to 15 sccm. We attribute the decrease in yield here to insufficient buffer gas density for complete thermalization. Although this could be confirmed by rotational temperature measurements at 55 Hz ablation, this was not studied. At 2 sccm, limited molecule numbers are detected in the beam after 250 ms of operation while a flow of 5 sccm is sufficient to consistently produce pulses of molecules and realize  $10^{12}$  molecules/sr/sec. Note that the sporadic spikes in Fig. 2.8a, visible at flows of 2 and 5 sccm, are ~ 100  $\mu$ s pulses of  $10^8 - 10^9$  molecules/sr and are not optical pickup due to the ablation laser. At flows of 10 sccm we begin to continuously detect molecules exiting the cell with a brightness of  $3 \times 10^{12}$  molecules/sr/sec, increasing to  $7 \times 10^{12}$  molecules/sr/sec at 20 sccm. At



FIGURE 2.8: Absorption versus helium buffer gas flow at a 55 Hz ablation repetition rate. (a) From top to bottom, the helium flow rates were 2, 5, 10, 15 and 20 sccm and the data are discussed in the text. These measurements were recorded in a random order using the same ablation spot on the target and highlight the temporary nature of the decrease in brightness measured over the first 2-5 pulses. (b) Time-averaged flux versus helium buffer gas flow rate for those flows that consistently produced pulses of molecules.

15 sccm and 55 Hz, the beam begins to become continuous, as successive molecular pulses do not return to the baseline level. This corresponds to beam brightness varying between successive pulses by  $\sim 80 \% 20$  mm downstream from the cell. We project that for this repetition rate the spread in forward velocity will reduce amplitude variation to  $\sim 60 \%$  by a distance 1.5 m downstream.

In general, we find that the source performance is robust for 55 Hz operation when using helium buffer gas flow rates  $\geq 10$  sccm and a lower flow rate of  $\geq 5$  sccm is sufficient to sustain continuous operation at repetition rates of 10 and 20 Hz. Other groups using helium-based cryogenic sources typically use lower buffer gas flow rates, between 1-5 sccm [24, 25, 53, 74], and several have reported erratic source behavior for ablation repetition rates > 5 Hz [53, 74]. It is possible that these observations are due to insufficient helium flow. However, it is likely that specifics of cell geometry are critical for cell extraction under high repetition rates, just as they are for beam characteristics such as temporal width and forward velocity. One modification to our cell geometry was made in efforts to test this; the conical cell exit was replaced with a flat 0.5 mm thick copper plate containing a 3 mm diameter aperture. Under this condition molecular beams with similar brightness were observed, leading us to conclude that our conical exit aperture is not related to this high repetition performance, although it appears to have been a factor for extraction efficiency when using a capillary-fed cryogenic source with a similar cell geometry [83]. In addition, for our system, raising the cell temperature by 2.0(3) K was not seen to negatively affect high repetition rate performance after accounting for the  $\approx 30\%$  corresponding change to rotational population due to temperature. Having said this, the measured 30% change in population highlights the importance of limiting heating during source operation to ensure reproducible beam properties. Using this source design we have constructed a second buffer gas source which has been confirmed to produce similar high repetition rate beams using SrF molecules as a test species.

As a demonstration of the stable and continuous nature of these molecular beams we produce uninterrupted pulses of SrF molecules at 55 Hz over a 60 second duration using a buffer gas flow rate of 15 sccm (Fig. 2.9). This duration was chosen to avoid depleting an already heavily used target (compare absorption signal between the new target in Fig 2.6. During this time, the ablation spot was moved every  $\sim 10$  s to restore the decaying ablation yield, leading to an extracted mean brightness of  $\sim 3 \times 10^{12}$  molecules/sr/sec along with a cell temperature increase of 0.6 K. The main limit on continuous operation during these measurements was the variable nature of the ablated target and the challenge of continuously locating bright spots. We speculate that considerably longer operation times would be within reach when using a new target. Free-radical production methods that ablate metals in the presence of a reactant gas (e.g.  $SF_6$ ) have also been shown to produce brighter, more reproducible beams [74] and could potentially work well with this source design at high ablation repetition rates for longer durations. With 15 mJ/pulse from the ablation laser, and operating at 55 Hz,  $\sim$  800 mW of incident power is deposited onto the cell. We find that at this level of power dissipation the cell achieves a steady-state temperature of 3.5 K after  $\sim 5$  minutes of continuous operation. Once this steady-state is reached, we find no evidence for liquid helium evaporation within the damping pot reservoir, indicated by both a maintained steady-state as well no measured change in pressure from the gas tank supplying helium to the damping pot. By measuring the steady-state temperature versus incident power we determine a temperature increase at thermal equilibrium of  $\approx 1 \text{ mK/mW}$  of input power. Assuming a durable target is used, the absolute limit on operation time would be set by saturation of the cryopump defined by



FIGURE 2.9: A continuous beam of SrF molecules produced over 60 s showing (a) absorption and (b) the cell temperature. The mean brightness measured during this minute was  $\sim 3 \times 10^{12}$  molecules/sr/sec and afterwards the cell required  $\sim 2$  minutes to cool back down to 2.6 K.

the amount of activated charcoal in the system. In our design, a continuous flow of 15 sccm of helium was maintained for 10 hours before saturation occurred (indicated by a rapid change in source pressure). The amount of helium required to saturate a charcoal cryopump scales with charcoal surface area. Therefore the duration of continuous operation can readily increased by increasing the charcoal in the source.

# Chapter 3

# Background free detection with optical cycling enhancement

In this chapter, we propose and demonstrate a fluorescence imaging technique using SrF molecules. The work discussed in this chapter was performed in part as a means to verify our imaging system following the construction of our high vacuum beam line. This also served as an intermediate project as we prepared to disassemble our lab space to relocate to a newly constructed building. Here, we provide a motivation for this technique followed by a description of the technique itself. After discussing the experimental setup, we demonstrate the technique and provide an analytic rate equation model that shows reasonable agreement with our measurements. We demonstrate the versatility of this technique by applying it to extract the forward velocity of our SrF molecular from a Doppler-shifted spectrum and discuss other relevant molecules for which this method is applicable. Finally, we show a derivation of the associated rate equation model that is used in the main section of this chapter.

# 3.1 Motivation

High-fidelity detection of ultracold molecules is central to almost all of their proposed applications and is a growing area of research [88–90]. Popular sensitive detection methods for molecules, such as resonance-enhanced multi photon ionization (REMPI) and fluorescence detection using photomultiplier tubes, lack the spatial-information necessary to extract often essential properties such as position, density, lattice filling fraction or optical tweezer occupancy. To date, the densities of directly cooled samples of molecules are several orders of magnitude too low for absorption imaging to be viable [31], and this technique has been limited to dense samples of molecules assembled from pairs of laser-cooled atoms [91].

Imaging fluorescence onto a charge-coupled device (CCD) camera is a powerful method for detecting molecules with spatial-information and is a natural choice for laser-coolable species with optical cycling transitions. Unfortunately, the multilevel optical cycling schemes used in molecules demand high laser intensities for both laser cooling and trapping [22]. Since both absorbed and emitted photons occur at the same wavelength, imaging fluorescence in these systems is often hampered by the residual scattered laser light from within an experiment, resulting in a large background signal dominated by shot noise. While subtracting off this background via background subtraction helps for visual purposes, it neither improves available dynamic range or the inherent noise imprinted on an image. Overcoming this limitation is commonly achieved by blackening the internal reflective surfaces of vacuum chambers and placing other scattering elements, such as windows, a sufficient distance from where molecules are imaged. While successful, this method restricts optical access [92] and will likely pose a barrier to many future ultracold molecule applications which require such access and necessarily introduce nearby scattering surfaces (e.g. chip-based microtrap arrays [93–95] or superconducting circuits [96]). As a result, there is a need in the direct laser cooling molecule community for improved imaging techniques. In what follows, we demonstrate one such technique that can be implemented in a straightforward way in existing laser cooling molecule experiments.

# 3.2 Resonance Raman optical cycling (RROC)

In this approach, the techniques of resonance Raman scattering and optical cycling are combined to enable molecules possessing diagonal FCFs to spontaneously emit multiple photons at frequencies shifted away from the driving laser fields. As such, we name this technique resonance Raman optical cycling (RROC). Much like techniques used to image fluorophores, such as those relying on Stokes-shifted fluorescence and vibrationl relaxation to offer continuous photon scattering, this technique provides a straightforward approach to separating fluorescence and laser light using only optical components. In this way, the detected scattered background light is suppressed by a factor of ~  $10^6$ , providing a route to high sensitivity fluorescence detection using single molecules in high background light environments.

### 3.2.1 Characteristics

The general technique of RROC requires two independent lasers applied to molecules with near-diagonal Franck-Condon factors (FCFs). As shown in Fig. 3.2a), a Stokes laser excites population from the electronic ground state with vibrational quantum number v = 0 to an electronic excited state with v' = 1. Molecules then



FIGURE 3.1: (a) Relevant energy levels for RROC in SrF addressed by the  $\mathscr{L}_{01}$  and  $\mathscr{L}_{10}$  lasers. Diagonal vibrational branching ratios (VBRs) ensure that > 95 % of LIF from both excited states is at 663 nm. (b) RROC population versus number of spontaneously emitted photons per molecule. SrF molecules have a 0.98 average probability of remaining in the RROC system following spontaneous emission. Inset, photograph of the illuminated imaging region with no measures to reduce scattered laser light.

spontaneously decay with near unit probability into v = 1 within the electronic ground state and spontaneously emit photons shifted *down* in energy by  $\approx \omega_e$ compared to the Stokes laser (where  $\omega_e$  is the ground state vibrational constant). This is followed by excitation by an anti-Stokes laser from v = 1 in the electronic ground state into v'=0 within the electronic excited state. Molecules then return with high probability back into the original v = 0 electronic ground state via spontaneous emission which is shifted up in energy by  $\approx \omega_e$  relative to the anti-Stokes laser.

Alternating excitation of molecules by the Stokes and anti-Stokes lasers can continue in this system until a dark vibrational ground state with v > 1 is populated, provided that rotationally closed transitions are used and dark sublevels are continuously remixed, such as with external magnetic fields [97] or otherwise [36].For current laser cooled molecules, such as SrF, this can correspond to as much as ~ 50 cycles around the four-level system and  $\sim 100$  spontaneously emitted photons per molecule (Fig. 3.1b). Using a bandpass filter, these photons can be readily isolated from those of the Stokes and anti-Stokes excitation lasers.



FIGURE 3.2: Schematic of the experimental setup showing the cryogenic source, imaging region and camera setup with 1. condenser lens, 2. commercial 50 mm  $f \setminus 0.95$  lens, 3. 10 mm iris, 4. 1 : 1 telescope and 5. bandpass filter.

Using an interference filter, we image laser-induced fluorescence (LIF) onto an electron multiplying CCD (EMCCD) (Andor iXon+ 885), using RROC,  $\approx 1$  m downstream from the source. Up to three transverse passes of a laser beam (2 mm  $1/e^2$  diameter) below the camera excite molecules with light from a Stokes laser ( $\mathcal{L}_{01}$ ) at 642 nm and an anti-Stokes laser ( $\mathcal{L}_{10}$ ) at 686 nm (Fig. 3.2). Here,  $\mathcal{L}_{vv'}$  denotes a laser tuned to the  $X^2\Sigma^+ | v, N^P = 1^- \rangle \rightarrow A^2\Pi_{1/2} | v', J'^{P'} = 1/2^+ \rangle$  transition, where N is the angular momentum excluding spin,  $\vec{J} = \vec{N} \pm \vec{S}$  (where S = 1/2 is the electron spin), P is the parity, and prime indicates the excited state. Radio-frequency (R.F.) sidebands are added to each laser to address the resolved ground state spin-rotation and hyperfine structure, and dark ground state sublevels are remixed using a 2 G magnetic field applied at 45° to the linear polarizations of the  $\mathcal{L}_{01}$  and  $\mathcal{L}_{10}$  lasers. Following excitation, diagonal FCFs in SrF ensure that

almost all LIF is at 663 nm. Aside from an optical filter, no additional measures are taken to reduce scattered laser light (see Fig. 3.2).

The imaging optics include a 15 nm FWHM bandpass filter centered at 662 nm to transmit LIF to the camera while blocking scattered laser light. A 1:1 telescope ensures that rays make an angle-of-incidence with the filter  $\leq 15^{\circ}$  for efficient transmission of LIF and effective blocking of Stokes laser light  $\mathcal{L}_{01}$ ; a 10 mm iris, placed before the telescope reduces spherical aberrations and has negligible impact on the field of view. As a final precaution, the inside walls of the imaging assembly are lined with black felt to reduce residual internal reflections. We measure the imaging system to suppress scattered laser light at 642 and 686 nm, relative to LIF at 663 nm, by factors of 10<sup>5</sup> and 10<sup>7</sup> for  $\mathcal{L}_{01}$  and  $\mathcal{L}_{10}$ , respectively. Given the variety of imaging conditions presented in the literature, we use normalized units to compare the scattered light background signal in our system against other experiments, and typically detect 40 photons/sec/mm<sup>2</sup>/mW. To the best of our knowledge, this is 2× below the lowest value previously reported in a molecular laser cooling experiment, which used a blackened vacuum chamber [98].

In Fig. 3.3, we show the effect of using RROC. In these images, background subtraction is used to remove the bias offset built into the camera. Initially, as shown in Fig. 3.3a), molecules are initially probed and imaged using a 34 mW of  $\mathcal{L}_{01}$ alone as a means to calibrate for the number of photons cycled using RROC. Here, the detected LIF decreases as the molecules propagate downstream during a  $\approx 50 \ \mu$ s interaction with the  $\mathcal{L}_{01}$  laser. These molecules are optically pumped into the dark  $X^2\Sigma | v = 1, N = 1 \rangle$  state, scattering an average emission of 1 photon per molecule. The addition of 30 mW of  $\mathcal{L}_{10}$  enables molecules to optically cycle via RROC, leading to an increase in detected LIF by a factor of  $\epsilon \approx 13$  compared to the  $\mathcal{L}_{01}$  alone case (Fig. 3.3b). This increase indicates that, on average,



FIGURE 3.3: Single-shot background subtracted fluorescence images recorded for (a)  $\mathcal{L}_{01}$  alone, (b)  $\mathcal{L}_{01}$  and  $\mathcal{L}_{10}$ , and (c)  $\mathcal{L}_{00}$ . In each case, on average, molecules spontaneously emit 1, 13 and  $\approx 60$  photons, respectively, as they travel from left to right during a 30 ms exposure. (d) Integrated horizontal LIF profiles highlight the 13× LIF increase  $\epsilon$  between (a) and (b) and show evidence of molecules being pumped into dark states for case (a) and (c). For clarity, the LIF images and profiles for (a) and (c) have been multiplied by factors 3 and 6, respectively.

each molecule has scattered 13 photons, completing ~ 6 loops around the RROC four level system, and there is no decrease in detected LIF as molecules move downstream. Here, the mean RROC photon scattering rate is approximated using  $R_{\rm sc} = 13/50 \ \mu {\rm s} \approx 3 \times 10^5 \ {\rm s}^{-1}$ , roughly an order of magnitude less than typical photon scattering rates for molecules [99]. In this case, 95 % of detected photons are due to LIF. By applying  $\mathcal{L}_{10}$  alone we probe for molecules originally in the  $X^2\Sigma | v = 1, N = 1 \rangle$  state and detect no LIF in this configuration. This shows that the increased LIF detected when adding  $\mathcal{L}_{10}$  to  $\mathcal{L}_{01}$  is due to RROC and not to exciting previously dark molecules originally in  $X^2\Sigma | v = 1, N = 1 \rangle$ . The largest RROC LIF increase measured during this work was  $\epsilon \approx 20$ .

To compare the typical optical cycling approach [100] against RROC, molecules are excited with 7 mW of light from a  $\mathcal{L}_{00}$  laser at 663 nm. In SrF, this system has nearly the same level of vibrational closure as when RROC is used (Fig. 3.1b). In this case, both scattered laser light and LIF are now at the same wavelength and are transmitted through our imaging system. As is seen in Fig. 3.3c), detected LIF decreases as molecules travel downstream as they are optically pumped into  $X^2\Sigma | v = 1, N = 1 \rangle$ , after each molecule spontaneously emits  $\approx 60$  photons. In this case the imaging sensitivity is reduced due to an increased scattered light background resulting in only 1 % of detected photons being due to LIF despite a  $60/13\sim4.6$  fold increase in the average number of photons emitted per molecule vs RROC. A  $150\times$  decrease in EMCCD gain was also necessary to avoid saturation. We note that all three LIF images in Fig.3.3 are single exposures with a 30 ms duration to match the pulse duration below the camera.

We use multilevel rate equations [101, 102] to model RROC, using  $\mathscr{L}_{01}$  and  $\mathscr{L}_{10}$ lasers and compare this against the typical optical cycling approach, using  $\mathscr{L}_{00}$ and  $\mathscr{L}_{10}$  lasers to form a  $\Lambda$ -system. A detailed account of this calculation can be found in Appendix G. In this model, we assume equal intensities for the two lasers used in both systems. The maximum photon scattering rate in a multilevel system is  $R_{\rm sc}^{\rm max} = \Gamma N_e/(N_g + N_e)$ , where  $\Gamma$  is the natural linewidth and  $N_g$  and  $N_e$  are the number of ground and excited state sublevels, respectively [100]. For RROC, the



FIGURE 3.4: Calculated scattering rate versus laser intensity for the typical optical cycling approach  $(\cdots)$  and RROC (—) alongside measured RROC scattering rates. Below saturation, for fixed laser intensities the calculated RROC scattering rate in SrF is  $\approx 27 \times$  smaller than that for the standard approach, in reasonable agreement with our measurements.

maximum photon scattering rate is roughly twice that attainable in the  $\Lambda$ -system due to the increased number of excited state sublevels available; however, we note that a  $\Lambda$ -system can be avoided by repumping through a different electronic state [103].

In practice, an increased scattering rate for RROC is challenging to realize, due to high laser intensity demands, since the photon excitation rate  $R_{\rm ex} \propto q_{v'v}I$ [101], where  $q_{v'v}$  is the transition FCF and I is the laser intensity, and effective RROC excites weak transitions with FCFs ~ 0.01. For fixed laser intensities below saturation, the decrease in scattering rate when moving from the  $\Lambda$ -system to RROC can be approximated by  $(q_{00} + q_{01})/(q_{01} + q_{10})$ , which is a factor of  $\approx 27$  for SrF. We use the measured LIF increase,  $\epsilon$ , over a fixed 50  $\mu$ s interaction time to measure the RROC scattering rate as a function of laser intensity, while keeping the  $\mathcal{L}_{01}$  and  $\mathcal{L}_{10}$  intensities equal, and find reasonable agreement with the rate equation model [Fig. 3]. Our model also accurately predicts scattering rates reported by others using a  $\Lambda$ -system with SrF to within a factor ~ 2 [22, 99].

#### 3.2.2 Demonstration

To demonstrate the versatility of RROC, we use a variant of this technique to measure the forward velocity distribution in our molecular beam. Here, we remove the R.F. sidebands from the  $\mathcal{L}_{01}$  laser and choose to excite two non-rotationally closed transitions,  $X^2\Sigma^+ | v = 0, 1, N^P = 0^+ \rangle \rightarrow A^2\Pi_{1/2} | v' = 1, 0, J'^{P'} = 1/2^- \rangle$ , with  $\mathcal{L}_{01}$ and  $\mathcal{L}_{10}$ , since the ground state hyperfine structure consists of only two levels spanning ~ 100 MHz, which simplifies interpretation of the Doppler-shifted LIF profile.

Initially we perform spectroscopy below the camera with negligible Doppler shift using a single transverse laser beam which, at first, contains only  $\mathcal{L}_{01}$  (Fig. 3.5a **I**). This is followed by the same frequency scan of  $\mathcal{L}_{01}$  but with  $\mathcal{L}_{10}$  present and fixed on resonance to enable RROC [Fig. 3.5a ]. The LIF increase measured between these two cases,  $\epsilon$ , reveals the average number of RROC photons scattered below the camera when addressing a specific hyperfine ground state; we measure 2.6 and 2.0 photons for the F = 1 and F = 0 ground states, respectively. The ratio of these values is dictated primarily by rotational branching into dark states and is close to the expected value of ~ 1.4.



FIGURE 3.5: (a) Transverse ( $\blacksquare$   $\square$ ) and counterpropagating (•) LIF spectra and images, as described in the text, reveal the molecular beam forward velocity profile. LIF images for the transverse and counterpropagating cases are the average of 6 and 24 experimental cycles, respectively. Lorentzian fits are applied to the transverse data (— —) and the longitudinal line (- - -) to guide the eye. (b) Wavelength separation ( $\Delta\lambda$ ) between emitted LIF and  $\mathcal{L}_{01}$  versus  $\omega_e/T_e$ for a selection of molecules studied today. RROC should be straightforward to implement for molecules with  $\omega_e/T_e \gtrsim 0.03$  and  $\Delta\lambda \gtrsim 20$  nm.

The single-frequency  $\mathcal{L}_{01}$  laser is then applied counterpropagating to the molecular

beam, while keeping the  $\mathcal{L}_{10}$  laser transverse and below the camera, but now with three passes. Here,  $\mathcal{L}_{01}$  rapidly shelves 2/3 of the molecules Doppler-shifted onto resonance into  $X^2\Sigma | v = 1, N = 0 \rangle$  upstream of the detection region, before  $\mathcal{L}_{10}$ acts to readout this shelved population for detection. The remaining 1/3 of resonant molecules are lost into the dark  $X^2\Sigma | v = 1, N = 2 \rangle$  state due to rotational branching and, on average, SrF molecules scatter 2.3 photons before 1/e of the original population remains. Detected LIF as a function of the  $\mathcal{L}_{01}$  frequency gives the forward velocity distribution in our molecular beam [Fig. 3.5a •]. Using the F = 1 level as a reference, we determine a mean forward velocity of  $\approx 140$  m/s and a FWHM of  $\approx 70$  m/s. This approach is similar to that in Refs. [56, 104], which uses a ladder type two-photon transition to produce one UV photon per molecule. However, RROC can produce multiple photons per molecule and requires only one excited electronic state, which may be advantageous for polyatomic or short-lived radioactive molecules with little spectroscopic data available [105, 106].

#### 3.2.3 Suitability to other molecules

RROC is applicable to a large subset of molecules with diagonal FCFs. Implementing this technique can be straightforward when  $\mathcal{L}_{01}$  and  $\mathcal{L}_{10}$  for a given molecule differ in wavelength from the emitted LIF by  $\Delta \lambda \gtrsim 20$  nm and are readily separated using an off-the-shelf bandpass filter. This occurs when  $\omega_e/T_e \gtrsim 0.03$ , where  $T_e$  is the minimum electronic energy, and includes species actively studied today such as BaF [107, 108], CaH [109], CaOH [110], CaOCH<sub>3</sub> [111], CaF [112, 113], CH [114], OH [115], RaF [106], SrF [116], ThO [117], YbF [118], YbOH [105] and YO [119] (Fig. 3.5b). We note that for polyatomic species, the relevant vibrational constant  $\omega_e$  refers to the symmetric stretching mode [110]. RROC may also be possible for molecules with  $\omega_e/T_e < 0.03$ , such as AlCl [40, 120], AlF [46] and MgF [121] where  $\Delta \lambda \approx 3$ , 4 and 9 nm, respectively, provided that custom bandpass filters are available. An alternative approach when  $\omega_e/T_e < 0.03$  could be the excitation of transitions with  $\Delta v = 2$  using  $\mathcal{L}_{02}$  and  $\mathcal{L}_{20}$  lasers. However, these transitions have even smaller FCFs and would demand a corresponding increase in the RROC laser intensities to maintain the same excitation rates.

Through realizing RROC in SrF, we have detected up to an average of  $\approx 20$  scattered photons per molecule in our molecular beam, limited by the 50  $\mu$ s interaction time, while suppressing background laser light signals by  $\sim 10^6.$  Integrating RROC into existing laser cooling experiments for detecting trapped molecules would offer increased LIF signals compared to this work through significantly longer interaction times, and would simply require replacing the  $\mathscr{L}_{00}$  laser for a  $\mathscr{L}_{01}$  laser. The inclusion of a  $\mathcal{L}_{21}$  repump laser would allow RROC to produce more photons per molecule before the dark  $X^2\Sigma | v = 3, N = 1 \rangle$  state is populated (~ 2000 photons for SrF) but would also decrease the photon scattering rate by introducing more ground state sublevels into the system. Including a  $\mathcal{L}_{32}$  repump laser would allow even more photons to be scattered (>  $10^4$  photons for SrF), with sufficient interaction time, and give no further decrease in the photon scattering rate. RROC realizes a platform for sensitive fluorescence detection of single molecules in high background light environments, similar to  $\Lambda$ -enhanced gray molasses cooling ( $\Lambda$ cooling) used to image molecules in a blackened vacuum chamber where scattered laser light and LIF are at the same wavelength [29, 89]. We speculate that  $\Lambda$ cooling could also be possible using RROC to cool and image trapped molecules with negligible detected scattered laser light, albeit at a reduced photon scattering rate.

An important consideration for RROC is the high laser intensities required to drive the weak optical transitions employed. In SrF we measure a maximum photon scattering rate that is ~ 10× smaller than typical values using laser intensities that are ~ 10 - 20× greater than the intensities commonly used in molecular MOTs beams [22, 99]. For trapped samples, higher RROC laser intensities (and photon scattering rates) could be realized using small imaging laser beams or large mode enhancement cavities [122] that specifically address the  $\leq 5 \text{ mm}^3$  volume typically occupied by the molecules.

In summary, we have proposed and demonstrated a technique that combines Raman scattering and optical cycling for molecules with diagonal FCFs. This resonance Raman optical cycling (RROC) can manipulate molecules to behave like efficient fluorophores with discrete absorption and emission profiles that are readily separated for sensitive fluorescence detection in high background light environments. The production of Stokes-shifted fluorescence from fluorophores has been crucial within the life-sciences over the last century, leading to advances such as super-resolution spectroscopy [123] and in vivo fluorescence imaging [124]. RROC extends this approach to cold and ultracold molecules for robust high-fidelity readout in any setting for the advancement of molecular quantum science.

# Chapter 4

# Aluminum monochloride

So far, the work presented here has focused on manipulating and detecting SrF molecules. In this chapter, the focus will shift to a new molecular species, aluminum monochloride (AlCl). For comparison, key features associated with molecules like SrF will be highlighted and a discussion of general considerations that make certain molecules good candidates for laser cooling will be provided. Following this, relevant properties of AlCl will be covered, which will provide a basis for the remaining work in this thesis.

# 4.1 Identifying candidate molecules

Like all molecules directly laser cooled to date, SrF possesses an unpaired valence electron and optically cycles between  $X^2 \Sigma_{1/2}$  and  $A^1 \Pi_{1/2}$  states which is analogous to the  ${}^2P_{1/2} \leftrightarrow {}^2S_{1/2} D_1$  lines in alkali atoms. This transition has a doublet electronic structure, and these molecules are known free radicals. In general, these molecules are composed of one alkaline earth or alkaline earth-like atom around which the unpaired valence electron is localized. During excitation, the electron is promoted with negligible change to the molecular bond length (described by rotational constants) and "stiffness" (described by vibrational constants). This has made these molecules a logical choice for laser cooling as this property leads to highly diagonal Franck-Condon factors (FCFs).

While the existing low trapped molecule numbers of molecular MOTs is in part due to the available number of molecules produced from the buffer gas source (see Chapter 2), the cycling properties of current systems also play a role in the captured solid angle and therefore captured number. As a result of the electronic structure in molecules with a  ${}^{2}\Sigma_{1/2}$  ground state, obtaining rotational closure requires driving a transition to an excited state with lower angular momentum. As a consequence, this both leads to magnetic dark states which must be remixed via external magnetic fields (see, for example Ref. [62]), and an overall reduction to the maximum available scattering rate due to the increased number of ground states relative to excited states [100]. In general, this is given by,

$$R_{\rm sc,max} = \frac{n_e}{n_e + n_g} \Gamma, \tag{4.1}$$

where  $n_e$  and  $n_g$  are the number of excited and ground states in the optically cycling transition and  $\Gamma$  is the natural transition linewidth.

To improve trapping efficiency from a molecular beam there are several properties a molecule should possess in addition to diagonal FCFs. In general, these properties should lead to an increased acceleration, and in turn, to a reduced slowing distance (z). The corresponding increase in beam solid angle ( $\Omega \propto 1/z^2$ ) from this reduction provides a larger molecular flux into the MOT trapping region. To find these

properties, we consider the dependence of acceleration on the following parameters,

$$a \propto \frac{h}{m \lambda \tau}.$$
 (4.2)

Here, m,  $\lambda$ , h, and  $\tau$  are the mass, transition wavelength, Planck's constant, and excited state lifetime of the molecule, respectively. What the above relation indicates can be intuitively understood by the fact that a low mass and short transition wavelength inherently provides a large photon recoil velocity. With a short lived excited state, the molecule can then experience many units of this photon momentum transfer per unit time, leading to a high scattering rate and large net force. As a result, we also gain a reduced number of scattered photons necessary to slow and trap which should ease the requirements on FCFs.

### 4.2 Singlet molecules

Similarities like those between alkali atoms and the molecules presently being laser cooled can also be found between a different class of molecules and alkaline-earth atoms. In this class, each electron is paired with another forming a closed electron shell. Analogous to an alkaline-earth atom, with  ${}^{1}S_{0}$  and  ${}^{1}P_{1}$  electronic states, this leads to both a  ${}^{1}\Sigma_{0}$  ground state and  ${}^{1}\Pi_{1}$  excited state, which may be used for optical cycling.

A closed electron shell provides a number of properties that are generally attractive for laser cooling. By virtue of this pairing, driving the cycling transition tends to require more photon energy than for molecules with an open shell (unpaired spin). The implication of this can be seen through the Einstein coefficient for spontaneous emission which is the inverse of excited state lifetime [101],

$$\frac{1}{\tau} = A_{eg} = \frac{g_g}{g_e} \frac{4\alpha \omega_{eg}^3}{3c^3} |\langle g | \boldsymbol{r} | e \rangle|^2.$$
(4.3)

Here,  $g_g$  and  $g_e$  describe the degeneracy of the two states. The  $\omega_{eg}^3$  factor in Eqn. 4.3 makes the rate of spontaneous emission characteristically fast for high energy transitions, leading to short lifetimes for these  ${}^1\Pi$  states. This provides the potential for correspondingly high scattering rates and, for a given mass, larger recoil velocities. Together, this should provide larger optical forces. In addition to these favorable dynamics, the closed electron shell also provides both a reduction to the complexity of energy structure (discussed further in the next section) and an inherent immunity to two-body chemical reactions, which will become important at sufficiently high densities.

While these molecules appear as strong candidates for direct laser cooling, it is important to mention that they are not new to ultracold physics. Thus far, ultracold molecules assembled from previously cooled atoms have exactly this structure. Nevertheless, these experiments could still benefit from increased trapped molecule numbers, which, in addition to extending molecule diversity, makes direct laser cooling of molecules with this structure valuable.

### 4.3 Aluminum monochloride

For our work, we have selected the molecule aluminum monochloride (AlCl) which possesses a  $A^1\Pi \leftrightarrow X^1\Sigma^+$  cycling transition and was originally proposed for laser cooling back in 2004 by Di Rosa [32] due to its predicted large  $A_{00}$  (thus high expected scattering rate) [125, 126] and diagonal FCFs [126] – a common trend among aluminum monohalide molecules. More recently, ab-initio studies have further supported this, leading to an estimated  $A^1\Pi$  state lifetime of  $\tau = 5.4(5)$  nm [37–39, 126] and a FCF estimate in the v'' = 0 band of  $q_{00} = 0.9991(2)$  [37–40] and further indicating that this molecule is a strong candidate for laser cooling.

It should be noted that there were other aluminum monohalide molecules proposed and even more monohalides, in general, since then, i.e., AlH, AlF, BH, TlF. Each of these molecules has a similarly attractive singlet transition, two of which are currently under investigation (AlF [45, 46] and TlF [49]). For AlCl, this transition lies near 262 nm which is close enough to a frequency quadrupled Nd:YAG that optics are well-developed and commercially available, making AlCl uniquely situated in terms of laser technology. While this is far enough into the UV to be both beneficial for laser cooling while also challenging, this wavelength greatly reduces difficulty associated with finding adequate optical components.

AlCl occurs in two different isotopes, <sup>27</sup>Al<sup>35</sup>Cl and <sup>27</sup>Al<sup>37</sup>Cl, with relative natural abundances determined by that of chlorine atoms: this is about 4 to 1. Aside from small shifts in spectroscopic constants, the behavior of these two isotopes will be very similar, so in this work we concentrate on <sup>27</sup>Al<sup>35</sup>Cl due to its higher abundance. The aluminum and chlorine atoms have nuclear spins of 5/2 and 3/2, respectively, which leads to a rich hyperfine structure. This offers a large parameter space for exploring long-range dipole-dipole interactions arising from a relatively large predicted permanent electric dipole moment in the  $X^1\Sigma^+$  state of 1.3 Debye [41]. For optical transitions, the short excited state lifetime of the  $A^1\Pi$  state, discussed above, corresponds to a large natural linewidth of  $\Gamma/(2\pi) \simeq$ 30(3) MHz due to time-energy uncertainty; whereas the ground hyperfine structure spans only ~ 11 MHz. This leaves the entire ground state hyperfine structure spectroscopically unresolved, enabling a single frequency laser to address the entire manifold, independent of its linewidth. We note that this situation is not entirely new, but has seen somewhat limited theoretical attention and only recently has it been studied experimentally [46, 50].

Over 100 years ago, Jevons and co-workers observed the strong emission band occurring at ~ 261 nm in AlCl [127]. In this work, silicon tetrachloride (SiCl<sub>4</sub>) was introduced to a nitrogen-filled discharge tube to investigate how this modifies the resulting spectra. Although only identified in later work [128], this group recognized that formation of AlCl from liberated chlorine atoms binding with the aluminum electrodes [128] gave rise to a tight "line-like" band near 261 nm. A higher resolution study followed this work and led to the first tentative assignment of the ro-vibrational structure but noted that line positions were likely obscured by transitions in Al atoms [129]. Since this early work, a number of studies have compiled lists of higher precision rotational and vibrational spectroscopic constants [130, 131]. Most recently, our collaborators at UC Riverside have provided the highest resolved optical spectra of the  $X^1\Sigma^+ \leftrightarrow A^1\Pi$  transition and produced refined rotational constants for the  $A^1\Pi$  state [40]. For the  $X^1\Sigma^+$  state, microwave spectroscopy can and has been utilized to generate sufficiently high precision measurements of the hyperfine structure [132, 133]. By comparison, similar resolution data has yet to be measured for the electronically excited  $A^{1}\Pi$  state. As a result, further investigation into the excited hyperfine structure will be presented in Chapter 7.

### 4.4 Structure overview

The difference in the electronegativity between the aluminum and chlorine atom (1.55) lead to a polar covalent molecular bond that is stronger than the bond of any molecule currently being laser cooled. This makes the idea of optically

cycling in such a molecule interesting since it is not initially clear the electronic and vibrational degrees of freedom are decoupled in the same was as described in  $X^2\Sigma_{1/2}$  molecules. By closer inspection, one finds that the high electronegativity of the chlorine atom has the effect of largely confining its 7 valence electrons and attracting aluminum's 3 towards it. While this bond is technically polar covalent, it has a lot of ionic character just as the other metal halides listed previously [41, 130]. Due to the particular similarities between AlCl and AlF, it is interesting to compare the structure of their cycling transitions.

AlCl and AlF differ in their electro-negativities which leads to slightly different molecular orbitals. In AlCl (AlF), the  $X^1\Sigma^+$  ground state occupies a  $9\sigma$  ( $7\sigma^2$ ) orbital, which has mostly Al 3s character. Excitation promotes the shared Al valence electron to the  $4\pi$  ( $3\pi$ ) orbital, which is mostly of Al 3p character, forming either a  ${}^{1}\Pi$  or  ${}^{3}\Pi$  state. In the former case, the excited electron retains its pairing from the ground state electron, allowing for a similarly closed electron shell even though the excited electron now has angular momentum. For both molecules, the  $A^{1}\Pi \leftrightarrow X^{1}\Sigma^{+}$  cycling transition is believed to be similar to the  $3p \leftrightarrow 3s$  transition of atomic aluminum [130]; laser excitation largely promotes the Al atom without affecting the halide. As pointed out by Ref. [46] for AlF, this occurs without significant modification of either rotational or vibrational constants and allows for a high probability of decay to the initial vibrational state. Similarities among these molecules suggest a similar situation for AlCl, which is reflected in both theoretical predictions and spectroscopic constants.

### 4.5 Electronic loss

Spontaneous decay from the  ${}^{1}\Pi$  state in AlCl molecules can occur along two different paths, as shown in Fig. 4.2. In the first, the excited electron can decay from the  $A^{1}\Pi$  state while retaining its spin orientation, forming the lowest orbital defined by the  $X^1\Sigma^+$  state. In the second, by flipping spin, the molecule will form the open shell  $a^3\Pi$  state. Although the latter path is spin-forbidden, the presence of the spin-orbit interaction in the  $a^3\Pi$  state makes S and L not good quantum numbers, strictly speaking, and leads to slight coupling (or mixing) of different values of S and L. Since there is nonzero angular momentum in the  $A^{1}\Pi$  state, this leads to a small leakage path from the optical cycle, at a rate determined by the ratio of spontaneous emission rates of the two transitions. As an estimate for this loss channel, we can look to the Einstein A coefficients associated with each decay path. These have been calculated for AlCl via ab-initio methods by Wan et al. [37]. This work predicts that the leading Einstein A coefficients for the two paths in AlCl are  $A_{00}(A^1\Pi \to X^1\Sigma^+) = 199,791,000 \ s^{-1}$  and  $A_{00}(A^1\Pi \to a^3\Pi_{0^+}) = 114 \ s^{-1},$ making decays to the triplet state an expected factor of  $\sim 1.7 \times 10^{-6}$  times less frequent than the main cycling transition, therefore indicating that this should be a relatively small loss channel. These predictions are consistent with the empirical findings for the similar loss mechanism in AlF molecules [45].

# 4.6 Effective Hamiltonian

To further understand how optical cycling might occur in AlCl we break down the remaining structure arising from various internal interactions. In terms of the description given above, these interactions act as small perturbations to the overall molecular orbitals of the  ${}^{1}\Sigma$  and  ${}^{1}\Pi$  states but can nevertheless be considerably large relative to the linewidth of continuous-wave lasers used for laser cooling. A reasonable attempt at isolating the contributing effects, so as to understand where the levels lie, relies heavily on the separation of degrees of freedom provided by the Born-Oppenheimer approximation. As with SrF, the approximation allows us to write down an effective Hamiltonian to capture the effects of angular momentum coupling among molecular rotation and the independent spins of both electrons and nuclei. The remaining work of this chapter was done in collaboration with John Daniel at University of California Riverside. Our goal in this effort was to develop an effective Hamiltonian to describe AlCl to the accuracy sufficient for modeling system dynamics. I will provide core elements of this work but refer the reader to Ref. [134] for a more thorough discussion.

In the absence of external fields, a general effective Hamiltonian that encompasses all aspects relevant to AlCl is given in Eqn. 7.183 of Ref. [135]. This can broadly be written as four components, given by,

$$H = H_{\rm e} + H_{\rm vib} + H_{\rm rot} + H_{\rm fs} + H_{\rm hfs} \tag{4.4}$$

where  $H_{\rm e}$  and  $H_{\rm vib}$  describe electron and vibration energies,  $H_{\rm rot}$  describes the rotational structure of the molecule, and  $H_{\rm fs}$ , and  $H_{\rm hfs}$  are composed of terms describing the fine structure and hyperfine structure. For each electronic state, a different set of specific terms is required due to differences in the interactions leading to their splittings. For the  $X^1\Sigma^+$  and  $A^1\Pi$  states in AlCl the leading



FIGURE 4.1: Vector diagram for Hund's case (a) coupling.

contributions are described by

$$H_{X^{1}\Sigma^{+}} = H_{e} + H_{vib} + H_{rot} + H_{Q_{0}}$$
(4.5)

$$H_{A^{1}\Pi} = H_{e} + H_{vib} + H_{rot} + H_{\Lambda d} + (H_{LI} + H_{Q_{2}}).$$
(4.6)

Here,  $H_{\Lambda d}$  describes the fine structure component of  $\Lambda$ -doubling while  $H_{LI}$  and  $H_Q$ describe the magnetic hyperfine interaction of the nuclear spin with the electronic orbital angular momentum and the electric hyperfine interaction of the nuclear quadrupole moments with the electric-field gradients at each nucleus. Note that  $H_Q$  has two different orientations in a  ${}^1\Pi$  state, corresponding to both along the internuclear axis  $(H_{Q_0})$  and perpendicular to it  $(H_{Q_2})$ .

We choose to describe both states by a Hund's case (a) coupling scheme [135], as depicted in Fig. 4.1. This follows the choice for other molecules with the same

electronic configuration [45, 136] but is also the most common coupling scheme. Here, the orbital angular momentum is assumed to be strongly coupled to the internuclear axis by the electrostatic field produced by the two nuclear charges [137]. As a result, the electronic spin angular momentum S couples to L through spin-orbit coupling, making neither L nor S good quantum numbers. Instead, we use the projections of L and S onto the internuclear axis and denote them  $\Lambda$ and  $\Sigma$ , respectively. The sum of these projections is further denoted by  $\Omega$ . The resulting total projection  $\Omega$  is coupled with the end-over-end molecular rotation R to form total angular momentum vector  $J = \Omega + R$ . Considering the states of interest in AlCl,  $J = \Lambda + R$  for the  $A^1\Pi$  state and J = R for the  $X^1\Sigma^+$  state.

In addition to the coupling given by Hund's case (a) we handle the angular momentum of the individual nuclear spins by first coupling J to the Al nuclear spin  $I_{Al}$  to form the intermediate angular momentum quantum number  $F_1$ . This is then coupled in turn to the Cl nuclear spin  $I_{Al}$  to give the full angular momentum F with magnetic projection  $m_F$ . This provides us with basis states given by  $|\eta, \Lambda, J, F_1, F, m_F\rangle$ , where  $\eta$  encompasses those elements not listed such as electronic energy and vibration. The ordering of the splitting caused by these couplings is illustrated in Figure 4.2, with a decreasing energy scale from left to right. In the following subsections, each Hamiltonian term past  $H_e$  will be discussed for the  $X^1\Sigma^+$  and  $A^1\Pi$  states separately. For each Hamiltonian term presented, the form useful for evaluating matrix elements is given in Appendix F, along with various relationships that were found to be useful for evaluating these terms.



FIGURE 4.2: AlCl energy structure relevant to optical cycling. Energy level spacing is increasingly magnified moving from left to right for visualization. The levels associated with the optical cycling transition are indicated by shaded grey regions.

# 4.7 Vibrational structure

Each electronic state is split into vibrational levels spaced according to the power series expansion given by Ref. [135],

$$G(v) = \omega_e(v+1/2) - \omega_e \chi_e(v+1/2)^2 + \omega_e y_e(v+1/2)^3 + \dots,$$
(4.7)

where  $\omega_e$  is the vibrational constant, and both  $\omega_e \chi_e$  and  $\omega_e y_e$  are higher order terms used to approximate the anharmonic contributions to the vibrational potential energy curve. Each electronic energy level has its own set of  $\omega_e$ ,  $\omega_e \chi_e$ ,  $\omega_e y_e$ constants. For scale, the spacings between lowest vibrational energy levels are  $\Delta \nu \simeq 14.3$  THz and  $\Delta \nu \simeq 13.2$  THz for the  $X^1 \Sigma$  and  $A^1 \Sigma$  states, respectively, but one should note that these spacing decrease for increasing vibrational quanta.
Spontaneous decay from the  $A^1\Pi$  state into an excited vibrational level of the  $X^1\Sigma^+$  state provides another mechanism of loss from the optical cycle. In contrast with states of angular momentum, vibration itself does not follow simple selection rules for an electronic decay<sup>1</sup>. This is because anharmonicity of the molecular potential makes high order decay paths possible. Moreover, our interest is not only in the allowed decay paths but also in their line strengths. Therefore, to understand this loss channel the overlap in vibrational wavefunctions, known as FCFs, is directly calculated by,

$$q_{v',v''} = |\langle \psi_{v'} | \psi_{v''} \rangle|^2.$$
(4.8)

While one can often find values for FCFs in the literature, predicted from ab-initio methods or spectroscopic data, or even produce them by oneself using various programs [139, 140], describing the distribution of vibrational decay that is observed experimentally requires translating these into vibrational branching ratios, or VBRs. This is done by weighting the FCFs by  $\nu^3$  and normalizing them to all possible decay paths<sup>2</sup> according to,

$$VBR_{v',v''} = \frac{\nu^3 q_{v',v''}}{\sum_i^\infty \nu_i^3 q_{v',v''}},\tag{4.9}$$

where  $\nu$  is the transition frequency. This conversion provides a value for the VBR that is closer to one than the FCFs shows. The discrepancy between VBR and FCF becomes more dramatic as the relative energy scaling of electronic states to vibrational states decreases (as  $T_e/\omega_e$  decreases), meaning that the extent to which

<sup>&</sup>lt;sup>1</sup>Chapter 7.1 of Ref. [138] provides a discussion of selection rules stemming from vibrational decay of harmonic and slightly anharmonic vibrational potentials

<sup>&</sup>lt;sup>2</sup>There is another equivalent definition to this which uses the Einstein  $A_{00}$  coefficient;  $VBR_{v',v''} = A_{v',v''} / \sum_{i}^{\infty} A_{v',v''}$ .

the FCF will underestimate the true branching is larger for molecules with longer transition wavelengths and smaller reduced masses, e.g. molecules like CH, CaH, and BaH. In the case of AlCl, however, the FCF provides a close approximation to the VBR. In Chapter 8, we will get an experimental estimate for the relevant VBRs for laser cooling AlCl.

## 4.8 Rotational structure

Each vibrational level of the ground and excited electronic state is composed of a substructure, described in Hund's case (a) by the total angular momentum, J = R + L. This simplifies to R in the  $X^{1}\Sigma^{+}$  state, describing end-over-end rotation of the molecule, which may take on a minimum value of J = R = 0. As seen in Figure 4.2, this picture fails in the  $A^{1}\Pi$  state as L = 1 and we must use the total J which leads to a larger minimum value of J = 1.

Another power series expansion is used to describe energies associated with each rotational level within a given vibrational level. This given by (Ref. [135]),

$$F_v(J) = B_v J(J+1) - D_v J^2 (J+1)^2 + H_v J^3 (J+1)^3 + \dots,$$
(4.10)

where  $B_v$  is the rotational constant describing the molecule in equilibrium and both  $D_v$  and  $H_v$  are higher order terms that used to account for the changes of rotational energy due to vibration. These constants are unique to a given electronic and vibrational level.

## 4.9 Dunham expansion

The energy contribution for the new vibrational and rotational degrees of freedom are given as the combined energies described above, namely,

$$T(v, J) = G(v) + F_v(J).$$
 (4.11)

However it is convenient to recast this as a double power series known as the Dunham expansion,

$$T(v,J) = \sum_{k,l} Y_{kl} (v+1/2)^k [J(J+1) - \Lambda^2]^l, \qquad (4.12)$$

where for most molecules (not light ones) the coefficients,  $Y_{kl}$ , are well-approximated by the rotational and vibrational spectroscopic constants [135],

$$Y_{00} = T_e, \ Y_{10} \approx \omega_e, \ Y_{20} \approx \omega_e \chi_e, \ Y_{01} \approx B_e, \ Y_{02} \approx D_e, \ Y_{11} \approx \alpha_e.$$
(4.13)

In this work, we use the Dunham coefficients provided by Ref. [131] for the electronic ground state and those found by the Hemmerling group [40] for the excited state. For AlCl, the coefficients are very similar for both X and A states, leading to a difference of only  $\simeq 100$  MHz between transition energies between electronic states with common J. This result is consistent with the argument that the cycling Al atom is largely decoupled from rotational and vibrational degrees of freedom. As can be seen in the spectra of Chapter 7, this results in the main J = 1 cycling transition spectrally overlapping with other higher J levels.

### 4.9.1 Parity

Mathematically, parity describes how an object transforms under inversion of its spatial coordinates. In quantum mechanics, we can the use the parity operator  $\Pi$  to perform this transformation on wavefunctions to determine their parity,

$$\Pi |\psi(r)\rangle = |\psi(-r)\rangle = \pm |\psi(r)\rangle.$$
(4.14)

This is simply another way to state whether a wavefunction is even or odd. Because there is no wavefunction overlap between even and odd functions there is a requirement on the parity of a wavefunction in order for a matrix element to be nonzero. The dipole operator d is an operator of position which is a rank 1 tensor, making it have odd parity. As a result, under a dipole transition the only nonzero matrix elements are those for which the connected states are described by opposite parity, providing another selection rule for transitions. In molecules, this is of particular significance because it places a further constraint on spontaneous emission in addition to those provided by angular momentum selection rules alone [75, 135].

As shown in Figure 4.2, rotational states alternate parity in the ground state, whereas in the excited state, each rotational line has both parities which changes ordering between states. This is due to the  $\Lambda$ -doubling discussed in the following section. To make this easier, an alternative naming convention is often used. In this convention, levels with parity  $(-1)^J$  and  $(-1)^{J+1}$  are labeled e and frespectively. This leads to the useful result that for our  ${}^{1}\Sigma^{+}$  ground state all rotational levels are labeled by e and in the excited  ${}^{1}\Pi$  the e, f ordering remains fixed.

## 4.9.2 Fine-structure: Λ-doubling

In the Hund's case (a) coupling scheme, L is not well defined as it is not a good quantum number. Instead, the projection of L onto the internuclear axis,  $\Lambda$ , is used. For  $\Lambda > 0$  this leads to an orbital degeneracy, as the projection of Lcan take on  $\Lambda = \pm 1$ , forming two states of opposite parity. This situation can be viewed classically as electrons orbiting clockwise and counter-clockwise about the internuclear axis. Rotation of the molecule lifts the degeneracy of the two orbital directions in the presence of a  $\Sigma$  state. Eigenfunctions are formed by symmetric and antisymmetric linear combinations of the two original degenerate states (Eqn. 6.234 of Ref. [135]). Thus in the  $A^1\Pi$  state each rotational level is then further split by this electronic interaction with rotation, known as  $\Lambda$ -doubling. One should note that a similar situation comes about due to nonzero spin from the  $\Sigma$  projection, making the term  $\Omega$ -doubling perhaps more generally appropriate given that  $\Omega = \Lambda + \Sigma$ . Nonetheless, this interaction for a <sup>1</sup> $\Pi$  state can be described in Hund's case (a) coupling with the Hamiltonian element (for the general form, see Eqn. 7.137 of Ref. [135]),

$$H_{\Lambda d} = -\frac{q_0}{2} (\Lambda_+^2 J_-^2 + \Lambda_-^2 J_+^2) = -q_0 \sum_{q=\pm 1} e^{-2iq\phi} T_{2q}^2(\boldsymbol{J}, \boldsymbol{J})$$
(4.15)

where both the standard and tensor operator forms have been given. On the left, we see the raising and lowering operators connect states with  $\Delta \Lambda = \pm 2$ , connecting  $\Lambda = \pm 1$  states in the  $A^1\Pi$  state. This is reflected by the rank 2 tensor used to describe the interaction. The two levels of the  $\Lambda$  doublet are symmetrically split by an amount (Sec. 11.3 of Ref. [135]),

$$\Delta E_{\Lambda d} = \frac{q_0}{2} (-1)^J J (J+1). \tag{4.16}$$

As pointed out by Hofsäss *et al.* in Ref. [46], another loss mechanism from the  $A^1\Pi$ state is possible via mixing between opposite parity  $\Lambda$ -doublet states. The closely spaced  $\Lambda = \pm 1$  levels of a given rotational state become mixed in the presence of an external electric field, which can result in a change of parity in the excited state, breaking of the parity selection rule and forming a loss channel by allowing the  $A^1\Pi$  state to decay to a dark rotational level. The sensitivity to external fields, and therefore loss, depends on the spacing between  $\Lambda = \pm 1$  states. However, for AlF this effect can be mitigated by controlling external fields to the level of ~ 1 V/cm. While we may expect similar sensitivities for AlCl based on similarities between these molecules, there are no reported values for  $q_o$  in the literature. Although the measurements provided in Chapter 7 can in principle be used to extract this value, as of writing, this has not been done. As a result, for the remainder of this work, the effects of  $\Lambda$ -doubling are neglected from the effective Hamiltonian.

### 4.9.3 Rotational branching

Calculating rotational branching requires finding the matrix elements of the electric dipole operator. This is in general represented by  $\mathbf{d} = -\boldsymbol{\mu}_{e} \cdot \mathbf{E} = -q \ \mathbf{r} \cdot \mathbf{E}(\mathbf{t})$ , which in spherical tensor notation is written as  $T_{p}^{1}(\mathbf{d})$ . This operator is a rank 1 tensor which means it has the effect of connecting states of neighboring J but can also connect states of the same J provided parity is allowed to change (by changing electronic or vibrational states). We can see the allowed rotational coupling by calculating the transition line strengths. This requires calculating of the transition dipole matrix elements and enables determining the rotational branching ratios (RBRs). For this calculation, I make use of references [141–143]. In general, the transition line strength is defined by,

$$S_{J',J''} = \sum_{m',m''} |\langle \psi_{m'} | T_p^1(\boldsymbol{d}) | \psi_{m''} \rangle|^2, \qquad (4.17)$$

where  $\psi_{m'}$  and  $\psi_{m''}$  are the upper and lower magnetic wavefunctions of the transition, respectively. In the current context, these wavefunctions are given by our basis states  $|\eta, \Lambda, J, F_1, F, m_F\rangle$ . This can be separated into its electronic, vibrational, and rotational factors under the Born-Oppenheimer approximation,

$$S_{J',J''} = q_{v',v''} |R_e|^2 \mathcal{G}_{J',J''}, \qquad (4.18)$$

where,  $R_e$ ,  $q_{\nu',\nu''}$ , and  $\mathscr{G}_{J',J''}$  are the electronic transition moment (in atomic units), FCF, and the Hönl-London factor, respectively; the last of which provides the intensity distribution for rotational lines within a vibrational level.  $\mathscr{G}_{J',J''}$  provides all needed information for this calculation and requires only evaluating the irreducible tensor component  $|\langle \Lambda', J' | | T_p^1(\mathbf{d}) | | \Lambda'', J'' \rangle |^2$ . However, for those learning to use spherical tensor operators we provide a more direct calculation using the complete basis vector  $|\eta, \Lambda, J, I_{Al}, F_1, I_{Cl}, F, m_F \rangle$  and neglect elements of the evaluation where relevant to do so. We will run through this evaluation making use of Wigner 3-J symbols, but note that this can equivalently be done with Clebsch-Gordon coefficients [75, 135].

The first step to evaluating  $\mathcal{G}_{J',J''}$  is applying the Wigner-Eckart theorem (Eqn. F.1) to give,

$$\langle \eta', \Lambda', J', I_{\rm Al}, F'_{1}, I_{\rm Cl}, F', m'_{F} | T^{1}_{p}(\boldsymbol{d}) | \eta'', \Lambda'', J'', I_{\rm Al}, F''_{1}, I_{\rm Cl}, F'', m''_{F} \rangle =$$

$$(-1)^{J'-m'_{F}} \begin{pmatrix} J' & 1 & J'' \\ -m'_{F} & p & m''_{F} \end{pmatrix} \langle \eta', \Lambda', J', I_{\rm Al}, F'_{1}, I_{\rm Cl}, F' | |T^{1}_{q}(\boldsymbol{d})| | \eta'', \Lambda'', J'', I_{\rm Al}, F''_{1}, I_{\rm Cl}, F'' \rangle$$

$$(4.19)$$

All information needed for branching ratios and selection rules up to rotation is contained in the reduced matrix element, specifically in quantum numbers up to J, so we ignore the leading phase factor and 3 - J symbol as well as  $F_1$  and F. This simplifies the reduced matrix element to  $\langle \eta', \Lambda', J' | |T_q^1(\mathbf{d})| |\eta'', \Lambda'', J'' \rangle$ . Next, since the electric dipole moment of the molecule is defined with respect to the internuclear axis, we must rotate  $T_p^1(\mathbf{d})$  from laboratory-fixed coordinates (indicated by subscript p) to the molecule-fixed frame (indicated by subscript q). This is done by a Wigner rotation (Eqn. F.12). Upon squaring, we have,

$$|\langle \eta', \Lambda', J'|| \sum_{q} D^{1}_{.q}(\omega)^{*} T^{1}_{q}(\boldsymbol{d}) ||\eta'', \Lambda'', J''\rangle|^{2} = \sum_{q} (2J'+1)(2J''+1) \begin{pmatrix} J' & 1 & J'' \\ -\Lambda' & q & \Lambda'' \end{pmatrix}^{2} |\langle \eta'| T^{1}_{q}(\boldsymbol{d}) |\eta''\rangle|^{2},$$
(4.20)

where  $q = 0, \pm 1$  for a rank 1 tensor. The final reduced matrix element describes both the  $R_e^2$  and  $q_{v',v''}$  terms of  $S_{J',J''}$  as  $\eta$  contains elements associated with electronic and vibrational energy. Therefore, we find that the Hönl-London factor takes to the following form,

$$\mathscr{S}_{J',J''} = \sum_{q} (2J'+1)(2J''+1) \begin{pmatrix} J' & 1 & J'' \\ -\Lambda' & q & \Lambda'' \end{pmatrix}^2.$$
(4.21)

The electric dipole selection rules can be directly read out from the 3-J symbol of Eqn. 4.21. The top line is zero unless it satisfies the triangle conditions, telling us the rotational selection rule  $\Delta J = 0, \pm 1$ . Similarly, the bottom provides the same one for  $\Lambda$  since  $q \in [-1, 0, +1]$ , i.e.,  $\Delta \Lambda = 0, \pm 1$ . As we would expect, this tells us that the  $X^1\Sigma^+$  state, with  $\Lambda = 0$ , can be coupled to either  $\Lambda = \pm 1$  states in  $A^1\Pi$ . However, the required change in parity further restricts the  $\Delta J = 0, \pm 1$  rule and fixes any state to coupling with a maximum of two others.

There are three types of rotational transitions allowed under the parity and dipole selection rules. These are often denoted as P, Q, and R which describe the  $\Delta J = J' - J'' = -1, 0, +1$  lines, respectively. By the e/f parity convention, a ground  ${}^{1}\Sigma^{+}$ state has *e*-parity for all rotational levels, leading to  $e \leftrightarrow e$  transitions described by P and R, and the  $f \leftrightarrow e$  transition by Q. Figure 4.2 shows that P and R lines are not rotationally closed; excitation with  $\Delta J = -1$  or +1 makes decay paths along both  $\Delta J = \pm 1$  available. Conversely, parity and dipole selection rules provide rotational closure for all values of J for Q-type transitions ( $\Delta J = 0$ ). We note that this analysis holds for all molecules possessing the  ${}^{1}\Sigma^{+} \leftrightarrow {}^{1}\Pi$  transition. However, states with higher multiplicities obey a different set of selection rules, e.g.  ${}^{2}\Sigma^{+/-} \leftrightarrow {}^{2}\Pi$  transitions are rotationally closed via the lowest P-line ( $J'' \leftarrow$ J'). Nevertheless, the same procedure used here can be used to arrive at the corresponding results for these other transitions. Figure 4.3 shows the allowed transitions for our system in a convenient representation known as a Herzberg diagram<sup>3</sup>.

<sup>&</sup>lt;sup>3</sup>The Herzberg diagram becomes particularly useful when dealing with states of higher multiplicity. A good example of this is a transition to a  $a^3\Pi$  state, where selection rules are more complicated and the larger number of states lead to difficulties in schematically representing the connected pathways.



FIGURE 4.3: Herzberg diagram for  $A^1\Pi \leftrightarrow X^1\Sigma^+$  electronic transition. Dashed grey, solid black, and solid grey lines indicate P, Q, and R transitions, respectively.

Because R and P lines are rotationally open, they are useful probes for information such as rotational state population as the maximum number of photons absorbed or emitted is directly determined by rotational branching. This makes their branching ratios of interest. Evaluation of Eqn. 4.21 is accomplished by noting that J' = J'' - 1 and J' = J'' + 1 for P and R transitions, respectively, and referring to the 3-J symbol analytic forms provided in Eqn. F.2. This results in the following Hönl-London factors for  $\Delta \Lambda = \pm 1$  for  ${}^{1}\Pi \leftrightarrow {}^{1}\Sigma^{+}$  transitions,

$$\begin{split} \Delta J & \qquad \mathcal{S}_{J',J''} \\ P(J'') : \mathcal{S}_{J''-1,J''}, & \qquad \frac{(J'' - \Lambda'')(J'' - \Lambda'' - 1)}{2J''} & = \frac{J''}{2} - \frac{1}{2}, \ J'' \ge 2 \\ Q(J'') : \mathcal{S}_{J'',J''}, & \qquad \frac{(J'' - \Lambda'')(J'' + \Lambda'' + 1)(2J'' + 1)}{2J''(J'' + 1)} = J'' + \frac{1}{2}, \ J'' \ge 1 \\ R(J'') : \mathcal{S}_{J''+1,J''}, & \qquad \frac{(J'' + \Lambda'' + 1)(J'' + \Lambda'' + 2)}{2J'' + 2} & \qquad = \frac{J''}{2} + 1, \ J'' \ge 0, \end{split}$$

where the right hand side has been evaluated for  $\Lambda'' = 0$ . To find the rotational branching ratios (RBRs) we normalize each Hönl-London factor relative to all allowed decay paths leading to

$$RBR^{P}(J'') = \frac{\mathscr{S}_{P}(J'')}{\mathscr{S}_{P}(J'') + \mathscr{S}_{R}(J''-2)} = \frac{J''-1}{2J''-1}, \quad J'' \ge 2$$
(4.22)

$$RBR^{Q}(J'') = \frac{\mathscr{G}_{Q}(J'')}{\mathscr{G}_{Q}(J'')} = 1, \qquad \qquad J'' \ge 1 \qquad (4.23)$$

$$RBR^{R}(J'') = \frac{\mathscr{S}_{R}(J'')}{\mathscr{S}_{R}(J'') + \mathscr{S}_{P}(J''+2)} = \frac{J''+2}{2J''}, \quad J'' \ge 0,$$
(4.24)

which can be checked for consistency against [46, 75]. We note that there are differences in the literature regarding the presence of a scaling coefficient on the equations for  $\mathscr{G}_{J',J''}$ . This factor cancels in the branching ratios and is unimportant for this result. This inconsistency has been highlighted and addressed recently in Ref. [143]. For reference, the lowest rotational states relevant to this work have been provided in Table 4.1.

J''	$RBR^P(J'')$	$RBR^R(J'')$
0	0	2/3
1	0	3/5
2	1/3	4/7
3	2/5	5/9
4	3/7	6/11
5	4/9	7/13

TABLE 4.1: Rotational branching ratios for the lowest P and R lines in a singlet transition.

It is relevant at this point to discuss the assumptions made in this calculation. Here, we have made two rather clear assumptions; that the Born-Oppenheimer approximation is valid and the dipole transitions are the only mechanism for decay. The first one is a safe assumption while the second requires further consideration. Higher order transitions in the multipole expansion are typically several orders of magnitude weaker than electric dipole transitions, however, there is yet another means by which decay is possible that has been missed by neglecting hyperfine contributions. For this, we must first discuss the hyperfine structure.

# 4.10 Hyperfine structure

Both the aluminum and chlorine nuclei in AlCl are sensitive to interactions with electronic and rotational degrees of freedom, leading to further splitting from the total angular momentum level, J, and the  $\Lambda$ -doublets discussed in the previous section. For both X and A states, the span of the hyperfine structure due to these interactions reduces as total angular momentum J increases. While the dominant mechanisms for this splitting differs between the two states, the interaction from the Al nucleus is always largest. For this reason, we choose to couple  $I_{\rm Al}$  to J to form the intermediate quantum number  $F_1$ , and couple this to  $I_{\rm Cl}$  to give the final quantum number F.

### 4.10.1 X state hyperfine structure

In the  $X^1\Sigma^+$  state, the interactions between the electric-field gradient at each nucleus and their corresponding quadrupole moments have been found previously to be the dominant source of splitting [132]. As given by Eqn. 8 of Ref. [144] or Eqn. 7.192 of Ref. [135], this interaction can be expressed as,

$$H_{Q_{||}} = \sum_{\alpha} \frac{(eq_0 Q)_{\alpha}}{4(2I_{\alpha} - 1)} (3I_z^2 - \mathbf{I}^2)_{\alpha} = \sum_{\alpha} \frac{\sqrt{6}(eQq_0)_{\alpha}}{4I_{\alpha}(I_{\alpha} - 1)} T_{q=0}^2(\mathbf{I}_{\alpha}, \mathbf{I}_{\alpha}), \qquad (4.25)$$

with the sum running over both nuclear contributions. The q = 0 subscript in the tensor representation indicates the z component for the operator, corresponding

to evaluating the diagonal matrix elements for the rank 2 tensor which physically represents evaluating the effect of the electric field gradient parallel to the internuclear axis. For this state, there are 12 hyperfine levels in J = 1, 16 in J = 2, 24 in J = 3 and so forth. The 4 levels of the rotational ground state are degenerate and cannot be driven on a Q-line to the A state as there is no J' = 0 level. However, all other levels are available.



FIGURE 4.4: Energy level diagram for  $X^1\Sigma^+$  J'' = 0 and J'' = 1 states.

In Fig. 4.4, both the J = 0 and J = 1 levels of the  $X^1\Sigma^+$  are shown with their relevant energies. The hyperfine levels of J = 0 are degenerate under the terms used in this work. By comparison, the J = 1 level has the largest splitting of  $\Delta E \simeq 11$ MHz for all other J, yet is still well within the natural linewidth of the  $\Pi^1 \leftrightarrow^1 \Sigma$  transition ( $\Gamma/(2\pi) \approx 30$  MHz). This leaves all of the rotational levels in the  $X^1\Sigma^+$  state spectroscopically unresolved due to time-energy uncertainty, enabling the complex hyperfine structure of each level to be addressed with a single laser frequency. This situation is fortuitous from this standpoint but also leads to interesting consequences that have historically been considered for simpler 3-levels systems [145–149]. This has only recently been observed in molecules like AlCl, e.g., TIF and AlF. In general, the presence of unresolved structure in the ground state leads to effects which are similar in nature to electromagneticallyinduced-transparency (EIT). In a 3-level system tuned to resonance this manifests itself as a  $\pi$  phase shift between the coherences of the two laser-driven transitions, which, in turn, leads to a cancellation of excited state probability or equivalently, the formation of a *coherent* dark state. In our situation, this provides a mechanism for slowing down the optical cycling rate of our  $A^1\Pi \leftrightarrow^1 \Sigma$  transition. In molecules, the sheer number of unresolved states makes this picture much more complicated to understand, but based on experiments with AlF [46] and TIF [50], we know that this effect varies between molecules. How this will affect AlCl is therefore of interest. We will revisit this topic briefly in Chapter 8.

### 4.10.2 A state hyperfine structure

For the  $A^1\Pi$  state, no spectroscopic studies have been previously performed with the resolution required to extract the necessary hyperfine constants. Fits from spectroscopic data presented in Chapter 7 suggest that the leading terms associated with the  $A^1\Pi$  state hyperfine structure are likely similar to those used for AlF. Under this description the splitting is dominated by a coupling between nuclear spins and electron orbital angular momentum. This is referred to as the nuclear spin-electron orbit interaction and can be expressed by,

$$H_{\rm LI} = \sum_{\alpha} a_{\alpha} I_{\alpha,z} L_z = a_{\alpha} \sum_{\alpha} T^1_{q=0}(\boldsymbol{I}_{\alpha}) \cdot T^1_{q=0}(\boldsymbol{L}), \qquad (4.26)$$

where, like in Eqn. 4.25, the matrix elements are to be evaluated in the moleculefixed frame and along the internuclear axis (q = 0). In addition to  $H_{\text{LI}}$ , we also include terms associated with the electric quadrupole interaction, as done for the X state. We note that in the  $A^1\Pi$  state there is also a possible contribution from the component perpendicular to the molecular axis, denoted with the constant  $q_2$ , which we include here. Since the parallel components are similarly given by Eqn. 4.25, we only provide the perpendicular component for the Al nucleus here,

$$H_{Q_{\perp}} = -\frac{eq_2Q}{8I_{\rm Al}(I_{\rm Al}-1)}(I_+^2 - I_-^2) = \sum_{q=\pm 1} q_2 T_{2q}^2(\boldsymbol{I}_{\rm Al}, \boldsymbol{I}_{\rm Al}), \qquad (4.27)$$

For these Hamiltonian terms, the constants  $a_{Al}$ ,  $a_{Cl}$ ,  $q_{0,Al}$ ,  $q_{0,Cl}$ , and  $q_{2,Al}$  have been determined through fitting to the spectra of R(0) presented in Chapter 7. In Fig. 4.5, we show the determined energy splittings.



FIGURE 4.5: Energy level diagram for J' = 1 for the  $A^1\Pi$  state.

### 4.10.3 Hyperfine mixing

Throughout this section we have discussed the energy structure of both the  $X^1\Sigma^+$ and  $A^1\Pi$  states assuming a Hund's case (a) basis with  $F_1 = J + I_{Al}$  and  $F = F_1 + I_{Cl}$ coupling. This provided a set of quantum numbers that were used to draw the energy level diagrams presented in Figs. 4.4 and 4.5. If we inspect the matrix elements of both Hamiltonians we find that there is a small coupling between  $F_1$  levels, indicating that  $F_1$  is not a good quantum number for the system, i.e., our present coupling scheme does not provide pure basis states. To see this, we represent each Hamiltonian matrix pictorially Fig. 4.6, with red and blue indicating positive and negative values, respectively. Here, the axes are arranged by ascending quantum number according to  $|F_1, F, m_F\rangle$  (not energy). This enables visualizing the mixing by isolating  $F_1$  regions of the matrix. In general, this mixing arises due to the quadrupole interaction with the Cl nuclear spin for the X state the nuclear spin-electron orbit interaction of the Cl nucleus for the A state.



FIGURE 4.6: Hamiltonian matrices for the  $X^1\Sigma^+ |v'' = 0, J'' = 1$  and  $A^1\Pi |v' = 0, J' = 1$  states. We denote these as  $H_X$  and  $H_A$ , respectively. The  $F_1 = J + I_{A1}$  and  $F = F_1 + I_{C1}$  angular momentum coupling leads to mixing between  $F_1$  levels of common F for both electronic states. State ordering is given in ascending quantum number, running from  $-m_F$  to  $m_F$ . Solid lines mark the boundaries between different  $F_1$  numbers and blue (red) represents negative (positive) values.

To learn the degree of this mixing, we can diagonalize each Hamiltonian independently using the standard similarity transformation

$$\widetilde{H} = U^{\dagger} \cdot H \cdot U. \tag{4.28}$$

Here,  $\tilde{H}$  represents the diagonalized Hamiltonian and U represents the eigenvector matrix composed of the eigenvectors associated with  $\tilde{H}$  as its columns. This matrix brings H into its diagonal form. Applying this transformation to each Hamiltonian and sorting the eigenvectors according to ascending quantum number leads to the U matrices shown in Fig. 4.7.



FIGURE 4.7: Eigenvector matrices corresponding to the diagonalized  $X^1\Sigma^+$  $|v''=0, J''=1\rangle$  and  $A^1\Pi |v'=0, J'=1\rangle$  Hamiltonian matrices. Each eigenvector is composed of a linear combination of  $F_1$  states of common F and  $m_F$ . State ordering is given in ascending quantum number, running from  $-m_F$  to  $m_F$ . Solid lines mark the boundaries between different  $F_1$  numbers and blue (red) represents negative (positive) values.

Columns of Fig. 4.7 provide the relative weighting of each original basis state in the linear combination. The degree of mixing is more easily represented by normalizing each basis vector and placing them on a common axis, as shown in Fig. 4.8. In this figure, the state ordering is represented in the upper bar chart and is given by ascending quantum number as before. Below these are the relative compositions of the original  $|F_1, F, m_F\rangle$  basis vectors used to create the new eigenvectors for both X and A states. This provides a useful lookup table for the composition of states depicted in the energy level diagrams of Figs. 4.4 and 4.5.



FIGURE 4.8: Relative mixing of original basis states in the eigenbasis for both X and A states.

### 4.10.4 Rotational mixing

It is also possible for rotational levels given by J quantum numbers to be of mixed character, just as is the case with hyperfine  $F_1$  numbers. This would lead to a leakage channel out of the optical cycle that breaks the rotational closure that was assumed under dipole transitions in Eqn. 4.23. This mechanism of loss was calculated for AlF molecules [45]. In this work, it was found that the magnetic interaction of Al nuclear spin in the  $A^1\Pi$  state leads to states of angular momentum F mixing between states of total angular momentum J. However, the degree of this mixing was calculated to result in a small loss channel of order  $10^{-6}$ . For AlCl, to consider this loss channel requires calculating the full transition dipole matrix, including hyperfine quantum numbers  $F_1$ , F, and  $m_F$ . Evaluating Eqn. 4.19 with all corresponding quantum numbers leads to matrix elements given by

$$\langle \eta', \Lambda, J, I_{\mathrm{Al}}, F_{1}, I_{\mathrm{Cl}}, F, m_{F} | T_{p}^{1}(\boldsymbol{d}) | \eta', \Lambda', J', I_{\mathrm{Al}}, F_{1}', I_{\mathrm{Cl}}, F', m_{F}' \rangle = (-1)^{2J+I_{\mathrm{Al}}+F_{1}+F_{1}'+I_{\mathrm{Cl}}+F+F'+1-m_{F}-\Lambda} \sqrt{(2J+1)(2J'+1)(2F_{1}+1)(2F_{1}'+1)(2F+1)(2F'+1)} \begin{pmatrix} F & 1 & F' \\ -m_{F} & 0 & m_{F}' \end{pmatrix} \begin{cases} F_{1}' & F' & I_{\mathrm{Cl}} \\ F & F_{1} & 1 \end{cases} \begin{cases} J' & F_{1}' & I_{\mathrm{Al}} \\ F_{1} & J & 1 \end{cases}$$
(4.29)   
 
$$\left[ \begin{pmatrix} J & 1 & J' \\ -\Lambda & +1 & \Lambda' \end{pmatrix} + \begin{pmatrix} J & 1 & J' \\ -\Lambda & -1 & \Lambda' \end{pmatrix} \right] | \langle \eta | T_{q}^{1}(\boldsymbol{d}) | \eta' \rangle |.$$

Note that for notational convenience we have switched the use of prime and unprimed quantum numbers to now describing ground (unprimed) and excited (primed) states. To see the effects of rotational mixing, we calculate the Hamiltonian matrix in the  $A^1\Pi$  state for more than one rotational level, J. In doing this, we observe a small mixing due magnetic interactions with the Al nuclear spin between neighboring J for excited states with common angular momentum F. This agrees with the described mixing seen in AlF. However, we find the Cl nucleus contributes additional mixing, but at level 10 times smaller than that from the Al interaction. As a result of analysis done for AlF, we expect this loss channel in AlCl to be similarly suppressed.

# 4.11 Zeeman splitting

When placed in a magnetic field, the degenerate  $m_F$  magnetic sublevels of the  $X^1\Sigma^+$  and  $A^1\Pi$  states will see a symmetric energy splitting. For each state, the

effective Hamiltonian is appended with an effective Zeeman interaction term,  $H_Z$ , that describes this magnetic field dependence.

For the  $X^1\Sigma^+$  state, the lack of orbital angular momentum leads to a largest expected splitting arising from the nuclear spin interactions with the external magnetic field. This interaction can be described by the terms,

$$H_{Z,\mathrm{IB}} = \sum_{\alpha} -g_{\alpha}\mu_{\alpha}I_{\alpha,z}B_{\mathrm{z}} = \sum_{\alpha} -g_{\alpha}\mu_{\alpha}T_{q=0}^{1}(\boldsymbol{I}_{\alpha,\mathrm{z}}) \cdot T_{q=0}^{1}(\boldsymbol{B}), \qquad (4.30)$$

where  $g_{\alpha}$ ,  $\mu_{\alpha}$ , and  $I_{\alpha}$  correspond to the g-factor, magnetic moment, and spin of both the Al and Cl nuclei, respectively [135].

In the  $A^1\Pi$  state, the orbiting electron is easily perturbed by an external field and is expected to be the leading interaction. This is given by,

$$H_{Z,LB} = g_L \mu_B L_z B_z = g_L \mu_B T_{q=0}^1(\boldsymbol{L}) \cdot T_{q=0}^1(\boldsymbol{B}), \qquad (4.31)$$

where  $g_L$  and  $\mu_B$  are the orbital g-factor and Bohr magneton.

The charge-to-mass ratio of the electron compared with the proton leads to the Bohr magneton being some ~ 2000 times larger than the nuclear magneton. Because of this, the nuclear magnetic dipole moment is by comparison small and leads to a similarly small interaction with external magnetic fields. The difference in the interaction strength can be seen in Fig. 4.9, which shows the J = 1 levels of both X and A states for increasing magnetic field.

In the  $X^1\Sigma^+$  state, the strength of the nuclear interaction with an external magnetic field is comparable to the strength of the hyperfine interactions themselves. From Eqn. 4.30, we predict fields required for Zeeman splittings to exceed that of



Magnetic field (G)

FIGURE 4.9: Zeeman splitting for  $X^1\Sigma^+$  and  $A^1\Pi$  states in AlCl. Note the  $\sim 50 \times$  magnification of the  $X^1\Sigma^+$  relative to that of the  $A^1\Pi$  state.

the natural transition linewidth to be of order 1000 G (0.1 T). By comparison, the expected sensitivity of the  $A^1\Pi$  state, calculated from Eqn. 4.31, is considerably larger. This is in contrast with the  $X^2\Sigma^+$  molecules that have been laser cooled, as these molecules have dominant magnetic sensitivities in their electronic ground state. The ability to trap AlCl molecules in a 3D MOT will depend on the details associated with Zeeman shifts in its excited state. While we have not yet performed a study to compare with the prediction of Fig. 4.9, this will likely be the subject of future work.

# Chapter 5

# Ultraviolet laser systems

# 5.1 Introduction

Direct production of coherent and intense deep-ultraviolet (DUV) radiation has been historically challenging except at specific wavelengths where rare-gas excimer lasers can be made. Nevertheless, the applications for these light sources are widespread, spanning both industry and academic needs [150–152]. A good example for this is the technique of photolithography, which nearly everyone today relies on for producing the integrated electronics that allow our smart phones and computers work. Since the minimum size of these electronic components scales with the laser wavelength used in this process, the continuation of Moore's law depends critically on the development of shorter and shorter wavelength light sources. Unfortunately, excimer lasers are not available at the wavelengths required for laser cooling AlCl. A common alternative to excimer laser sources stems from various processes of frequency conversion through crystals with noninear optical properties. For our situation, we require operation at  $\lambda \simeq 262$  nm, which at first glance seems tantalizingly close to the fourth harmonic of the well-known Nd:YAG laser occurring at 266 nm. However, in the infrared, this is more than a 14 nm difference. Unfortunately, even our repumping transitions which are just shy of 266 nm are some 4 nm from the 1064 nm fundamental wavelength of the Nd:YAG emission line, leading our group to need a custom laser source. In this chapter, I will discuss our approach to generating light at the cycling transition and repumping wavelengths of AlCl. I will provide motivation for our system requirement and then I will discuss the design and performance of the main cycling laser. Finally, I'll give a brief description of the next two lasers used for repumping vibrational decay paths.

# 5.2 Laser requirements

Options for commercial systems exist for the laser cooling transition wavelengths of AlCl; both Toptica and MSquared offer competing fourth harmonic systems. However, the expected laser power that will be required to optimize optical forces in AlCl is outside of what these companies can currently offer. We can provide a sense of scale for power requirements by the following analysis.

As previously discussed in Chapter 4, AlCl has a very complicated hyperfine structure in both ground and excited state manifolds of the main cycling transition with 144 participating magnetic sublevels. A rough estimate for the powers necessary to maximize optical forces requires first an estimate for the saturation intensity of the transition. Incorporating the effects of this multilevel system can be done following Ref. [153], however, a simpler two-level picture can provide a lower bound. For the  $X^1\Sigma^+ \leftrightarrow A^1\Pi$  transition, the natural linewidth of  $\Gamma/2\pi = 29$  MHz and

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transition wavelength at  $\lambda = 261.7$  nm leads to a large saturation intensity,

$$I_{\rm sat} = \frac{\pi h c \Gamma}{3\lambda^3} = 232 \text{ mW/cm}^2.$$
 (5.1)

For scale, the two-level saturation intensity for <sup>87</sup>Rb is only  $I_{\rm sat} \sim 2.5 \,\mathrm{mW/cm^2}$ . In comparison with other molecules being laser cooled today, the estimated saturation of Eqn. 5.1 is at least fives times higher. However, relative to AlCl, AlF has an even larger two-level saturation intensity of  $I_{\rm sat} = 0.93 \,\mathrm{W/cm^2}$  due to both a shorter transition wavelength at 227 nm and broader natural linewidth of  $\Gamma/2\pi = 84 \,\mathrm{MHz}$ . This is one drawback of molecules with ultraviolet transitions – they are require high intensities to saturate.

If we now consider trapping molecules in a 3D MOT, achieving a high capture velocity is critical to trapping a large number of molecules from our initial molecular beam velocity distribution. Maximizing the capture velocity relies on maximizing both the interaction time and forces experienced by a molecule in the MOT beams. Increasing the MOT beam diameter increases the duration of the applied force, but also decreases the beam intensity and therefore the force. With these two variables in opposition, we generally benefit from high laser powers to increase both parameters as much as possible. While this will be explored in more detail with full simulations of trapping and capture velocity in Chapter 9, here we provide a simple model to give a feel for this nonlinear dependence.

From classical kinematics we find the distance required to slow a molecule from an initial velocity under constant acceleration,

$$d_{\rm int} = \frac{v_i^2}{2a}.\tag{5.2}$$

Rearranging for  $v_i$ , we can interpret this velocity as the capture velocity, i.e., the maximum velocity that can slowed to a stop over a distance  $d_{\text{int}}$ . With the molecule acceleration,  $a = v_r R_{sc}$ , we have,

$$v_c = \sqrt{2d_{\rm int}v_r R_{sc}},\tag{5.3}$$

Considering again a two-level system, the laser light opposing the molecule's motion leads to a scattering rate  $R_{sc}$  given by,

$$R_{sc} = \frac{\Gamma}{2} \frac{s}{1 + s + 4(\Delta \mp \vec{k} \cdot \vec{v} \pm \mu_B g_{\text{eff}} B z/\hbar)^2 / \Gamma^2}.$$
(5.4)

If we assume the magnetic field gradient can be tuned such that the Zeeman shift compensates for the changing Doppler shift at all points during the molecule's deceleration (i.e., always on resonance), we may write,

$$R_{sc} = \frac{\Gamma}{2} \frac{s}{1+s}.$$
(5.5)

where s is the saturation parameter. Note that this assumption provides an overestimate to actual situation. Writing intensity in terms of laser power and the interaction region diameter provided by the beam,

$$s = \frac{I}{I_{\text{sat}}} = \frac{P}{\pi (d_{\text{int}}/2)^2 I_{\text{sat}}}.$$
 (5.6)

With the appropriate substitutions, we find an equation relating the capture velocity to beam diameter and power,

$$v_c = 2\sqrt{\frac{d_{\rm int}v_r\Gamma}{2 + I_{\rm sat}\pi d_{\rm int}^2/P}}$$
(5.7)

Here, we assume an interaction distance defined by the laser beam radius and a MOT which has been rotated by  $45^{\circ}$  in the x - y plane relative to the molecular beam. Using the relevant values for AlCl, in Fig. 5.1, we plot the capture velocity versus both laser beam diameter and power.



FIGURE 5.1: Capture velocity plotted versus both power and beam diameter using Eqn. 5.7.

From this model we capture the expected behavior: increased beam size and power lead to ever-increasing capture velocities. We also find the practical result that for a given laser power, generally set by experimental limitations, there exists an optimum beam diameter. We note that we expect a gross over-estimate of the capture velocity using this method, but nonetheless find it provides reasonable insight into the two dimensional parameter space. This situation will be studied in more detail in Chapter 9.

# 5.3 A path to ultraviolet light

In our group, we explored several ideas for generating the required UV light for laser cooling. As previously mentioned, direct sources emitting at our required wavelengths don't currently exist and so nonlinear frequency conversion from a longer fundamental wavelength was required.

Achieving coherent light at ~ 260 nm can, in principle, come from several different implementations of sum frequency generation, where two or more photons with frequencies  $\omega_1, \omega_2, ..., \omega_n$  combine to form a new photon at the sum of their frequencies,  $\sum_i \omega_i$  (Nonlinear Optics by Boyd is an excellent reference for details on both these processes and others not discussed here [154]). The conversion efficiency through this process decreases for each photon added to the sum, i.e., a two photon process is 2× more efficient than a three photon process. This, along with the fact that laser technology becomes more mature as you move toward near-infrared (NIR) and infrared (IR) spectra, led us to choose second harmonic generation (SHG) as our method for frequency conversion. In this case, two incident photons of frequency  $\omega_f$  are converted to a higher energy photon of frequency  $\omega_{\text{SHG}} = 2\omega_f$ . Using two cascaded stages of SHG allows for producing the fourth harmonic at ~ 260 nm.

## 5.4 Main cycling laser

Our system, shown in Fig. 5.2, starts with a homebuilt external cavity diode laser (ECDL) which uses a broadly tunable laser diode (Innolume: GC-1030-160-TO-200-B). For this, we use the design discussed by John Barry in Ref. [62], and tune the laser to emit infrared (IR) light at  $\lambda \simeq 1047$  nm. We split this light into two paths, one for referencing the laser frequency to our transfer lock (described in Chapter 2) and the other, 1-5 mW, is used to seed an IPG fiber amplifier (YAR-10-1050-LP-SF), which produces ~10.75 W with a clean Gaussian mode (M<sup>2</sup> ~1.05).

The amplified output is coupled into two cascaded resonant cavities that each perform second harmonic generation (SHG) to produce laser light at 523 nm followed by 261.7 nm. Both cavities use a traveling wave bowtie configuration enclosed in monolithic aluminum housings, manufactured by Agile Optic GmbH, and are mounted on a breadboard vibrationally damped by Sorbothane from the optical table. While similar to a previous design [155], we modify housing geometries to match critical parameters such as the crystal lengths and mirror radii of curvature (ROC), provided in Ref. [156].



FIGURE 5.2: Schematic of 261.7 nm laser system used for drive the  $v_{00}$  cycling transition in AlCl. Keys to figure: ECDL, external cavity diode laser; ISO, optical isolator; FC, fiber coupler; PM, polarization maintaining fiber; FA, fiber amplifier;  $\lambda/2$ , half-wave plate,  $\lambda/4$ , quarter-wave plate; PBS, polarized beamsplitter; MM, mode-matching optics; CL, collimating lenses; BD, Brewster dichroic; PZT, piezo-electric-transducer.

### 5.4.1 First doubling stage (LBO)

Following amplification, the IR output is coupled into the first resonant cavity. This cavity houses a  $4 \times 4 \times 25 \text{ mm}^3$  Lithium Borate (LBO) crystal (Castech) that is cut at Brewster's angle and temperature tuned to achieve Type I (o+o+e) non-critical phase matching. LBO is well suited for high power conversion of IR light to visible wavelengths. An extreme example of this is given in Ref. [157] where 130 W is generated at 532 nm. Similar to in this example and as can be seen in Fig. 5.2, our system uses a closed bowtie cavity formed by two plano (M1 and M2) and two curved mirrors (M3 and M4). At 1047 nm, M1 is a 3%transmissive input coupler (IC), while mirrors M2-M4 are high reflectors (HR) (>99.9 %). Mirrors M3 and M4 have a 150 mm ROC, producing an estimated waist of 48  $\mu$ m and 67  $\mu$ m (the latter expanded by the Brewster incidence) at the crystal center. The waist is  $\sim 2 \times$  larger than the optimum value given by the Boyd-Kleinman focusing parameter  $\xi$  [158]. This is done in order to reduce thermal effects in the crystal. The generated second harmonic (SH) light at 523 nm is coupled out of the cavity via M4 (T>95 % at 523 nm). Between mirrors M1 and M2 is a secondary waist that is used to ease mode-matching the fundamental beam to cavity mode. A further discussion for our mode-matching procedure can be found in Appendix A. Prior to entering the cavity a half-wave plate is used to optimally set polarization angle with respect to the tangential ordinary axis of the crystal. To maintain a precise crystal temperature, the LBO crystal is placed within a temperature-controlled metal housing with a graphite foil interface and is further enclosed by a PTFE cover to insulate it from air within the cavity housing. This element is set by an external temperature controller to  $\sim 168^{\circ}$ C. When optimized, at 10.75 W input power, we realize a  $\sim 95$  % coupling into the cavity, measured by reflected contrast, and a circulating power of  $\sim 220$  W, inferred from IR light leaked through M3. While not shown in Fig. 5.2, the Brewster cut of the crystal leads to  $\ll 1 \%$  and  $\sim 18\%$  reflections of the fundamental and SH light, respectively, off the first and second interfaces, which are used to monitor both circulating power and SH conversion. This first reflection can also be used to infer circulating power provided the nonzero reflectivity from Brewster's angle has been well calibrated. Additionally, if one is without the mirror or crystal reflectivities, as is often the case in a commercially purchased system, one can still extract the intracavity circulating power via  $P_{\rm circ} = P_{\rm in} \eta F / \pi$ , where  $\eta$  and F are the cavity contrast and finesse, respectively.

## 5.4.2 Second doubling stage (CLBO)

### 5.4.2.1 Crystal selection

Efficient frequency conversion from the high power visible light of first cavity into the ultraviolet places several requirements on the crystal of the second cavity. While the LBO crystal used in the first cavity is transmissive over a range extending well into the DUV, this crystal is unable to produce SH light below  $\sim 275$  nm due to inadequate phase matching and a resulting low effective nonlinear coefficient for fundamental light below  $\sim 550$  nm [159]. At these levels of power, Barium Borate (BBO) and Cesium Lithium Borate (CLBO) are generally considered the best options for SHG to wavelengths this far in the UV. At the fundamental wavelength for the second cavity, 523 nm, CLBO has a smaller nonlinear coefficient than BBO. This can be calculated following the relations given in Appendix C. The result is shown in Fig. 5.3.



FIGURE 5.3: Comparison of nonlinear doubling coefficients  $(d_{\text{eff}})$  for CLBO vs. BBO crystals as a function of fundemental laser wavelength.

However, the doubling efficiency also depends on walk-off angle which causes the fundamental beam to diverge along one direction in the crystal. An associated reduction to crystal intensity then leads to reduced doubling. For BBO, this walk-off is 2.5 times larger than CLBO, as seen by Fig. 5.4. Ultimately, a calculation of the single pass conversion efficiency, as described by Ref. [158], shows that these two combined effects gives rise to a higher doubling efficiency in CLBO at our wavelength than would be possible using BBO.



FIGURE 5.4: The associated walk-off angle in both CLBO and BBO crystals vs. fundamental wavelength for Type I critical phase matching.

While a calculation of doubling efficiency gives an initial indication of crystal performance, high laser intensities found in an enhancement can lead to limits on doubling efficiency due to crystal degradation. For BBO, this degradation stems from both high linear and nonlinear absorption coefficients [160, 161]. This leads to self-heating of the crystal along with a corresponding variation in phase matching along the beam's path, known as thermal dephasing, the extent to which depends on the temperature bandwidth of the crystal. This effect is made worse by formation of absorption sites from UV light and sets a practical limit on safe operating crystal intensities, and therefore attainable DUV output powers, to levels far below those which cause permanent laser induced damage. This effect is less dramatic in CLBO due to a  $\sim 10 \times$  lower linear and nonlinear absorption and a  $\sim 2 \times$  higher temperature bandwidth (i.e., phase matching  $\sim 2 \times$  less sensitive to temperature) [162–164]. However, UV-induced degradation has been shown to occur due to a separate mechanism of photorefraction [165, 166]. Nevertheless, the

UV-induced degradation in CLBO should become significant for average intensities which are  $\sim 5 \times$  higher than BBO, at  $\sim 10 \text{ kW/cm}^2$  – still more than 20× lower than CLBO's absorption-based permanent laser induced damage threshold (LIDT) [163, 167]. As result of the above considerations, CLBO was chosen over BBO for use in the second cavity to convert visible light to the desired DUV 261.7 nm wavelength.

#### 5.4.2.2 Cavity parameters

For the second cavity, we use a  $4 \times 4 \times 10 \text{ mm}^3$  CLBO crystal (Castech). The refractive indices of this crystal in the visible spectrum are insufficient to achieve the same noncritical phase matching used in the first cavity. Instead, the crystal is cut for Type I (o+o+e) critical phase matching via angle tuning. As with the first cavity, both entrance and exit crystal facets are Brewster cut rather than AR coated as these coatings are not well-developed for high UV intensities. This leads to a 18% loss of doubling light via the exit facet of the crystal. Since CLBO is strongly hygroscopic, a similar housing to the first cavity is used to maintain a  $\sim 150^{\circ}$ C crystal temperature to prevent water diffusion into the crystal lattice. This is crucial to increasing the threshold for UV-induced degradation and has similarly been shown to increase the LIDT 3-fold, see Ref. [168]. At these elevated temperatures, conversion efficiencies are known to improve due to an alleviation of distortions to the refractive index caused by both crystal processing and thermally induced shock associated with laser absorption [169, 170]. We additionally make the cavity housing a positive pressure environment by flowing in a continuous 10 sccm flow of dry air in order to maintain a clean environment for the expected high circulating powers as well as to further protect CLBO from water diffusion [167].

Following Refs. [156] and [171], two mirrors with a 200 mm ROC form a waist in the crystal center of 47  $\mu$ m and 76  $\mu$ m (the latter again expanded by the Brewster incidence). In this cavity, the crystal waist is now  $\sim 3 \times$  larger than the theoretical optimum so as to reduce thermal stress and the resulting distortion in the crystal. For the fundamental light, M5 is a 2.5 % transmissive input coupler (IC), while mirrors M6-8 are high reflectors with >99.95 % reflectivity. The light exiting the first cavity has a slight ellipiticity due to the brewster angle of the crystal. Despite this, we find that two spherical lenses (f = 125 mm and f = -75 mm)are sufficient to provide high in-coupling to the second cavity. Using reflected from M5 we measure measure  $\sim 90$  % contrast. Under these conditions we measure a corresponding circulating fundamental power of  $\sim 140$  W. The second harmonic light is picked out of the cavity using a Brewster-angled dichroic (BD) mirror set such that the second surface is at Brewster's angle for the fundamental light. The first is coated to be a high reflector for 261.7 nm and highly transmissive for 523 nm. The small fraction of fundamental light coupled out of the cavity along with the SH light was separated for the following measurements using a second Brewster-angled dichroic. Doing this, the 261.7 nm light was measured to be  $>\!99$  % pure. We note that this optic has since been replaced with a commercial harmonic beam splitter from Thorlabs and we find this is sufficient for efficient separation of fundamental and SH beams. Finally, as with the first cavity, circulating power and SHG are

### 5.4.3 Electronics

In the process of constructing the first two-stage quadrupling system for our experiment various choices in electronics were made to improve the ease of operation for people in the lab. Here we broadly discuss these improvements.

monitored using the reflecting facets of the CLBO crystal.
#### 5.4.3.1 Cavity length stabilization: choosing the correct error signal

In order for these cavities to resonate and support the high circulating laser powers required to achieve efficient doubling, the cavity length must be controlled on the level of several nanometers. This is perhaps surprising given the macroscopic size of these cavities. To see this, we can compare the fundamental resonating wavelength with the frequency spacing between subsequent longitudinal modes for the first cavity (free spectral range,  $FSR = c/L \simeq 238$  MHz). From this, we can infer a length sensitivity of  $\Delta L/\Delta \nu \simeq 4.4$  nm/MHz. With the added requirement that cavity length must track frequency changes in the pump laser, necessary for spectroscopy, each length must be actively stabilized.

To provide this stabilization, we require an optical means of determining the relationship between the laser frequency and the cavity length, which can both inform the distance and direction that the cavity is detuned from resonance – so it can be corrected. To do this, there are number of well understood techniques which rely on extracting the bipolar phase relationship stemming from dispersion across a resonance feature. Among them, we explored three of these techniques; independently implementing a Pound-Drever-Hall (PDH) lock [172], a Hansch-Couillaud (HC) lock [173], and a transmission-based dither lock<sup>1</sup> on our cavities. We note that given the broad transition linewidth in AlCl the cavity locks required here are far more relaxed than those needed for laser frequency stabilization, and therefore error signal sensitivity is not a deciding factor. A key difference between these locking techniques, instead, can be understood from Fig. 5.5.

<sup>&</sup>lt;sup>1</sup>A transmission dither lock can be realized in the limit where modulation sidebands of a PDH setup fall within the cavity linewidth and the beating optical field is detected from fundamental light exiting the cavity.



FIGURE 5.5: Lineshapes associated with Pound-Drever-Hall (PDH) Hänsch-Couillaud (HC) based cavity error signal generation. Red dots indicate stability lock points and show that the HC error signal provides stable lock points only on resonance.

While the PDH method is known to have a large capture range – the error provides the correct sign for feedback extending beyond the discriminator slope and out to the sidebands – this is only a benefit from the perspective that in a frequency stabilized laser, the cavity serves as your frequency reference. As a result, if your *laser* changes longitudinal modes in the cavity, it changes its operating frequency and must be relocked to the previous mode. By contrast, in the case of an enhancement cavity, such as here, the laser frequency is generally referenced elsewhere (see Chapter 2), and the cavity length need only be an integer multiple of the fundamental wavelength. If we consider the stable lock points in either case, indicated in Fig. 5.5 by red dots, we can see that the PDH error generates a stable lock point both at resonance and symmetrically between resonances. Whereas this has the result of "locking" without cavity build-up, for the HC lock (and any other lock which takes the form of the dispersion of a lorentzian lineshape), stable lock points only occur on resonance and a "lock" condition necessarily leads fundamental light circulating in the cavity and thus SHG. For this reason, these types of locks are particularly well suited for enhancement cavities as they are robust; if the cavity comes unlocked while the feedback loop is engaged, feedback will drive the cavity to the next neighboring longitudinal mode and regain SHG.

In our lab, we lock each doubling cavity using an HC locking scheme. This is a polarization sensitive locking technique that uses ellipticity generated from the combined reflected and leaked cavity light to determine proximity to resonance. Light reflected from the in-coupling mirror (M1 of Fig 5.2) experiences a  $\pi$  phase shift with the same polarization. However, cavity dispersion leads to light coupled into the cavity accruing a different phase shift on either side of resonance. The presence of an intracavity polarizing element (here the Brewster cut crystal) results in reflected light and leaked circulating light superposing to generate a frequency dependent polarization ellipticity. This polarization will be linear at resonance and symmetrically between resonances. Using  $\lambda/4$  and  $\lambda/2$  waveplates and a polarizing beamsplitter (PBS) then enables generating an error signal by taking the difference between polarization components.

Our choice to use an HC lock over others with a similar lineshape stems from the inherent offsets associated with this lock. Generally speaking, these offsets are seen as a negative attribute. However, in this case, these offsets guarantee that if the cavity unlocks the error will be appreciably nonzero between resonances and feedback action will reliably lead to a quick recovery. It is important to note that because our polarizing element is in the plane of the cavity, unlike described in Ref. [173], we use an additional  $\lambda/2$  waveplate (see Fig. 5.2) in order to rotate linearly polarized light by ~ 45° (actually a little more than this to compensate

for the polarizing effect of our beam sampler). This ensures that, at resonance, the reflected light is split into its horizontal and vertical components equally, providing a zero error, as required.

#### 5.4.3.2 Current sources

Our use of an ECDL for this laser system serves as a cheaper alternative to various other options. Having machined parts on hand simplified construction to selecting a diode, diffraction grating, and collimating lens. However, because the laser frequency depends on the diode injection current, these laser sources are inherently sensitive to current noise and can have a broad  $(\geq MHz)$  linewidth if care is not taken. The  $X \to A$  transition in AlCl is large enough (~ 30 MHz) that a narrow frequency laser is not required. On the other hand, maintaining a tight cavity lock requires that the length of the doubling cavity reliably follow the fluctuations of the laser frequency. For a laser source with significant frequency noise this can be a challenge as piezo-electric-transducers (PZT) tend to have relatively slow frequency response. Moreover, our cavities have linewidths of  $\Delta \nu \simeq 1$  MHz, which in the absence of high feedback bandwidth, requires a laser source with linewidths sufficiently below this. Lacking sufficient feedback bandwidth or a sufficiently narrow laser linewidth translates to fast amplitude noise on the SH light of each cavity and tends to reduce the cavity doubling efficiency. This is something we were interested in avoiding.

In each laser system, a commercially available low noise current source (Koheron DRV110) is used. For reference, comparisons between current noise measured in this current source and others previously used were made and are shown in Fig. 5.6. By measuring the frequency change in our transfer cavity while tuning the laser current we can extract a sensitivity of  $\Delta \nu / \Delta A \approx 165 \text{ kHz}/\mu\text{A}$ , which

allows us to find expected contributions to frequency noise by integrating over the 100 kHz window. For this laser diode, the Thorlabs and Toptica controllers (black and blue) provide ~ 650 kHz and ~ 350kHz of integrated frequency noise, respectively, while the low noise Koheron current source is an order of magnitude quieter, contributing only ~ 30 kHz<sup>2</sup>, likely removing the current source as a dominate source of linewidth broadening. The difference between these current sources translated direct to the cavity locking and we saw a dramatic reduction in locking error when the low current source was implemented.



FIGURE 5.6: Comparison of noise in current sources evaluated for the UV laser system.

<sup>&</sup>lt;sup>2</sup>The broadband noise associated with this measurement is limited by the FFT noise floor (Stanford Research Systems SR785). However, the dominant noise contribution stems from 1/f noise occurring at lower frequencies, making the perceived excess noise insignificant. Comparing with the Koheron datasheet, we would expect over the same frequency range an integrated noise of  $\sim 22$  kHz.

For spectroscopy, it is also useful to be able to tune these lasers continuously over a large range without mode hopping. One often accomplishes this in a diode laser by appropriately adjusting current as the PZT of the diffraction grating is tuned such that the associated modes track one another. This can be done by hand, but is convenient to do instead via electronics. Oftentimes, commercial current source provides such a feature, however, the Koheron source does not. For this reason, in order to tune over a wide range with these diodes, we designed a homebuilt feedforward circuit based on the Libbrecht-Hall design [174]. The current sensitivity for these diodes is quite low, requiring a 60 mA change to tune over a fairly normal range of 10 GHz. This requires the standard feedforward circuit in Ref. [174] to have an addition op-amp buffer which is capable of sourcing and sinking large currents from the laser diode (see Appendix D for schematics). With this, these diodes can be tuned  $\sim 28$  GHz in the IR, corresponding to  $\gtrsim 110$  GHz of mode-hop-free tuning in the UV. This enables tuning over all populated rotational levels in the molecular beam!

#### 5.4.3.3 Sum/Difference detectors

The HC locking method is a polarization sensitive technique which requires a difference photodetector. A common design for these detectors is to directly connect the anode and cathode of two oppositely biased photodiodes together, subtracting the two currents from one another. For equal laser powers on each diode, and provided that both beams contain perfectly correlated noise, this strategy can yield a detection sensitivity which is only  $\sim \sqrt{2} \times$  higher than the shot noise limit (the shot noise currents from each diode add in quadrature). As shown in Fig. 5.7, we designed our own detector using this topology and a transimpedance amplifier to convert the difference current to an amplified voltage. In this design, we both subtract the photocurrents from photodiodes A and B and amplify them (U1A) as well as sample each current via their own current mirror (Q3 and Q4) and add them back together (U1B). This allows a single detector to provide both the required error signal for locking (A-B) and a measure of the total reflected power (A+B) which is key for optimizing alignment and diagnosing problems. For the full schematic, see Appendix D.



FIGURE 5.7: Simplified circuit schematic for the sum/difference photodetectors used to lock the doubling cavities. Connecting the anode and cathode of two biased photodiodes (D1 and D2) provides current subtraction. The resulting current difference is converted to a voltage through U1A and used as the error signal. The currents flowing from the biased sides of each diode are independently copied by current mirrors (constructed using Q3 and Q4) and subsquently summed by U1B to provide a measure of the total detected signal incident on both D1 and D2.

#### 5.4.3.4 Control loops

Before the error signal generated by the sum/difference detector can be fed back to the PZT its frequency spectrum must be modified via an intermediate gain stage, often referred to as a servo, or loop filter ("Control loop" in Fig. 5.2). The objective here is to invert the error signal and apply it to the PZT, supplying as much gain as possible while ensuring it tapers to 0 dB at a frequency lower than where the phase shift becomes  $\pi$ . If this is not met, the intended negative feedback changes to positive feedback and results in oscillation. A very good resource for a detailed analysis of feedback loops can found in Ref. [175].

In our system, the PZTs used for feedback (PC4QM) exhibit resonances at rather low frequencies ( $\sim 3 - 6$  kHz) limiting the gain which can be applied while still maintaining a stable lock condition. Inherent with the choice of our seed is the 1/f noise spectrum associated with semiconductor lasers. This places a burden on our feedback loop [176, 177] and is further burdened by the resonance structure of our PZT, as resonances generate large phase shifts due to the quickly changing gain (an indirect consequence of the Kramers-Kronig relation [178]). For this work, attention was paid to the PZT resonances. Modification to both the resonance stucture as well as feedback loops were required to achieve tight cavity locks.

To evaluate the PZT resonances, two complementary approaches were used. In the first, a high pass filter was formed by a resistor combined with the PZT load. This offered a measure of circuit reactance which correlates well with PZT resonances. In the second approach, we measured the PZT displacement explicitly by using the attached mirror and additional optics to form a Michelson-Morley interferometer. In both cases, the PZT transfer function was measured using a SR785 FFT.

Figure 5.8 shows both the PZT magnitude and phase response measured using the interferometer setup. Here, a low frequency mode of  $\sim 3$  kHz is suppressed by wrapping the PZT/mirror/mass combination in indium foil prior to installing it in its corresponding mount. While this reduces the low frequency resonance, it has a negligible effect on the resonances beyond 40 kHz. While we intended on integrating a mechanical improvement into the system along the lines of [179], time constraints didn't allow for this.



FIGURE 5.8: Example PZT resonance structure of Agile Optic doubling cavity measured via a Michelson-Morley interferometer. Black and red indicate before and after wrapping the PZT/mirror/mass combination in indium foil prior to installing it in the Agile Optic mount.

The control loops used for these cavities are composed of a proportional, integral, and phase lead  $(PI\phi)$  stage. This is combined with a twin-tee notch to filter the strong > 40 kHz resonances and a low pass filter at ~ 70 kHz. Together, this provides a closed loop bandwidth near 30 kHz, sufficient for providing a tight lock between the cavity length and the in-coupling laser. Fig. 5.9a) gives a comparison between a loose lock (minimal proportional gain and a low (~ 1 Hz) integral corner) and a tight lock (optimized proportional gain and a ~ 1 KHz integral corner) for one of the IR-VIS doubling cavities. In Fig. 5.9b), the length of the same cavity is scanned and the reflected light is measured using the A+B output of the sum/difference detector. Here we show scanning the length under three conditions: i) the feedback loop turned off, ii) proportional gain only, iii) and both proportional and integral gain. Here, an asymmetry in the cavity absorption dip can be seen, indicating a difference between heating and cooling in the crystal as the cavity is brought into and out of resonance, similar to that seen in other systems [180, 181]. The increased width of this dip when proportional gain is applied corresponds to feedback driving the cavity length toward resonance and fighting the applied voltage to make the cavity scan. The cavity length is then locked to the in-coupling laser by the addition of integral gain, with the low reflected signal indicating maximum in-coupling of the fundamental light.



FIGURE 5.9: Locking performance of IR-VIS doubling cavity. a) In loop error signal power spectral density (PSD) showing large error suppression when the feedback loop it optimized. b) Reflected cavity signal when scanning with i.)PI off (no feedback), ii.) P on (proportional gain only), and iii.) PI on (both proportional and integral gain).

#### 5.4.3.5 Cavity auto-locking and relocking

With an error signal which only has stable lock points on resonance, the feedback loop automatically drives the cavity length to the next neighboring mode when an unlocking event occurs. However, this feature is limited to the tuning range of the PZT and will fail to relock when the PZT reaches either of its extremes. Fortunately, a lock is easily recovered by disengaging the feedback loop momentarily so the integrating capacitor can discharge and the output voltage can reset to its original value. Re-engaging the loop forces the cavity to lock again at the nearest mode.

This simple relock method can be integrated into the feedback electronics using a window comparator which sends a TTL signal to toggle the feedback loop open and closed when a preset voltage threshold is reached. The corresponding circuit used is given in Fig. 5.10. A mock test of this circuitry is shown in Fig. 5.11, in which the servo was run open loop allowing integration to the rails. The resetting of the integrator is seen when the thresholds set by RV1 and RV2 in Fig. 5.10 are reached.



FIGURE 5.10: Circuit diagram of the window comparator circuit used for autorelocking SHG cavities.



FIGURE 5.11: Time series of the window comparator function with the servo loop run open loop. This shows the resetting of the integrator when the voltage thresholds are met.

Furthermore, we take advantage of the A+B output of our sum/difference detectors to provide an indicator that the fiber amplifier has been turned on. With this, we apply a master override (U9A) to the relocking comparator switch (U8A) which serves to force the feedback loop to auto-relock only when the laser is turned on. This absolves anyone operating the laser from needing to play with the control electronics other than to optimize gains for different powers. Similarly, this is found to be very useful in optimizing cavity alignment while locked, which provides the highest sensitivities to adjustments. It is important to note that this method requires a polarizing element prior to the cavity to eliminate polarization drifts from the fiber amplifier output, otherwise maintaining lock requires constantly chasing polarization with a half wave plate. As can be seen in Fig. 5.2, in our system this is accomplished using high power polarizing beam splitter.

#### 5.4.4 Performance

An example of input-output powers of the first doubling cavity are shown in Fig. 5.12a) shortly after turn on, following the warm effect discussed below, and then again following 2 hours of steady state behavior. The power curves taken at these two times are nearly identical and overlapped in Fig. 5.12a), showing no indication of degradation. With 10.75 W of IR power, the cavity produces 6.6 W of SH light ( $\gtrsim 60\%$  conversion efficiency) as measured after the cavity output. Accounting for Fresnel reflection of the SH and that off the output coupler (M4), we infer a high,  $\sim 74\%$ , total conversion efficiency from the LBO crystal. We find that performance of this cavity is although we find the cavity has a slow increase ( $\sim 5$ minutes) to full power from turn-on. This warm-up appears to be independent of cavity alignment and is repeated following a momentary turn-off of the system, suggesting a thermal effect within the LBO crystal. This effect is not seen in Fig. 5.12a) as each data point was taken after this warm-up had occurred. This warmup in power coincides with the cavity optical path length monotonically increasing until a steady state is reached. This seen by an increase in required PZT voltage to compensate for the increasing effective optical path length of the cavity. From this we conclude that the warm-up effect is evidence of slight thermal effects in the crystal.

In Fig. 5.12b), an example input-output power curve of the second cavity is shown. Similar to the first cavity, the second cavity shows a monotonic change in power during warm up, as well as a monotonic increase in cavity length. However, in contrast to the first cavity, the produced 261.7 nm light tends to decay by  $\sim 20\%$ as steady state is approached during the first  $\sim 15$  min. The initial SH powers and those in steady state are shown in Fig. 5.12b). We attribute this drop in power, in part, to a thermal dephasing, or self-heating, of the crystal caused by



FIGURE 5.12: SHG output power and conversion efficiency for the first (a) and second (b) doubling cavities. Initial power and conversion efficiency are indicated by filled circles and triangles, respectively. Open circles and triangles show these measurements repeated following two hours of continuous operation. Each set of data is overlaid by a theoretical curve (grey line) calculated using measured values from both cavities and following the methods described in Ref. [182]. Grey arrows indicate the corresponding axis for each curve.

an absorption-induced temperature gradient formed along the laser propagation direction. This effect is also observed via an increase in transmission peak width when linearly decreasing, versus increasing, the cavity length, similar to that discussed previous in our LBO crystals. This effect has been observed elsewhere with lower powers when using BBO [180, 181]. We note that this behavior similar to that seen in LBO, but more dramatic. To isolate this effect from permanent crystal damage we turn off the pump laser and allow the crystal to cool for ~10 minutes. Without realignment, this amount of time is typically sufficient to recover  $\geq 90\%$ of the initial power, soon after which a reduction of only ~10% is observed when operating. The remaining power is consistently recovered following longer periods without operation (hour to day timescales), suggesting a semi-permanent distortion to the crystal's refractive index which occurs during prolonged high power operation. This recovery to a process is consistent with a the process of reannealing which is known to occur in CLBO when held at temperatures  $\gtrsim 120^{\circ}$ C [170]. With this, we have observed performance from this system recover even beyond its initial power, following one week without operating, while holding both crystals at their optimal temperatures ( $T_{\rm LBO} = 168^{\circ}$ C,  $T_{\rm CLBO} = 150^{\circ}$ C) and no system modifications. With the IR pump at a maximum power, and the first cavity producing ~7 W at 523 nm, powers as high as ~2.75 W in the DUV have been seen with a steady state power of ~2 W. When accounting for intracavity losses, this corresponds to a doubling efficiency from the second cavity as high as ~ 50%, settling to ~ 30% in steady state.



FIGURE 5.13: Example of power stability observed over an operating day. We note that fluctuations due to lab noise tend to degrade this stability. Red, green and purple show measured output powers of 1047 nm, 523 nm and 261.7 nm light, respectively.

Following ~10 minutes of operation, necessary to reach steady state, this system produces a constant output power without any further reduction over long timescales. Fig. 5.13 shows continuous steady performance over a long day of operation from an initial turn-on. Over the range of cavity length available from the PZT, a change in cavity alignment, and resulting change in SH power, can be observed from each cavity as the PZT tracks length changes during an operating day. This is due to minor cavity misalignment as the cavity length changes; one can see this by measuring the output power corresponding to successive cavity modes. We minimize this effect by limiting the allowed length tuning of each cavity ity to  $\sim \lambda/2$  (V<sub>PZT</sub> ~15 V) using the window comparators. The fluctuations seen here over longer timescales are periodic and correlate with lab temperature cycles.

This could be mitigated by using a different temperature controller on the first cavity with a more stable set-point.

Day to day operation of this system has been robust. However, months following the above data, the resistive heater in the CLBO cavity burned up due to a electrical shorting mishap. As result of this incident, the CLBO crystal and other optics were removed, the cavity was cleaned, and a new heater installed. While this laser is still capable of watt-level powers, we no longer see powers above 2 W. Instead, with proper alignment, this system produces  $\sim 1.5$  W.



FIGURE 5.14: Power curves of the first VIS-UV cavity followed heater burn out. These measurements were taken both in single pass operation as well as a closed cavity in order to evaluate potential crystal damage. A continuation of quadratic behavior up to the highest intensities suggests no damage to the CLBO crystal.

In investigating the cavity performance, we compared the doubling coefficient,  $\gamma$ , extracted from a single pass, with that obtained when the cavity is closed. This

is shown in Fig. 5.14. We note that a variation in doubling coefficient stems likely from slight errors in calibrating the leaked cavity light used to infer the high circulating powers in the cavity. Nevertheless, we see no evidence of SHG rolling off at high circulating power, suggesting that there is no damage present to the CLBO crystal. For comparison, we also calculate this doubling coefficient (following Refs. [158, 182]) for our crystal parameters and beam focus. This calculation assumes a spherically symmetric beam, yet our beam in the crystal is elliptic. For simplicity, we perform this calculation for each dimension independently  $6 \times 10^{-5} \leq \gamma_{\rm CLBO}$  – in fair agreement with our measurements.

# 5.5 Repump lasers

It is expected that repumping losses to v = 1 and v = 2 back into the main cycling transition will require two more UV laser systems in order to drive molecules along the  $v_{10}$  and  $v_{21}$  transitions (Fig. 5.15). These transitions occur ~ 4 nm to the red of the  $v_{00}$ , near  $\lambda \simeq 265$  nm. Different requirements on power led us to follow two separate paths for these repump lasers.

As seen in Fig. 5.15, repumping the v = 1 population through the  $A^{1}\Pi | v' = 0 \rangle$ state will form a  $\Lambda$ -system. As discussed in Chapter 3, saturation of the  $\Lambda$ system requires the repump laser be a factor of  $(q_{00} + q_{01})/(q_{01} + q_{10})$  higher than the  $v_{00}$  cycling laser – as a reminder,  $q_{v'v''}$  is the Franck-Condon factor between levels v' and v''. This is simply not attainable with current laser technology. Given this, we sought to generate similar powers as the  $v_{00}$  laser system previously described. We therefore use the same cavity designs, while replacing the 10.75 W fiber amplifier with one capable of producing 15 W, to provide future overhead and generally reduce the burden of the amplifier under standard operation.



FIGURE 5.15: Optical cycling scheme in AlCl with two repumping lasers.

The performance of this laser is similar to the current performance of the first laser; at the same input powers and tuned to the  $v_{00}$  transition, this system has generated steady state powers as high as 1.4 W. Tuning to the  $v_{10}$  transition instead, tends to result in a slightly lower power of ~ 1.2 W. While the LBO cavity performs well, as indicated by the power curve below, the doubling from the CLBO cavity appears to be the bottleneck. While a systematic characterization of this stage has not been performed, reflected contrast as well as mode purity of the fundamental visible light suggests that the system may benefit from improved mode-matching. Nevertheless, these powers are sufficient for our present purposes and we find this system to be reliable in the same ways described previously.

To avoid all three lasers from addressing the same excited state, population in v'' = 2 will be repumped through the  $A^{1}\Pi | v' = 1 \rangle$  state which will decay will nearly unit fidelity into  $X^{1}\Sigma^{+} | v'' = 1 \rangle$  where the  $v_{10}$  laser can repump it back to the cycling transition. For the  $v_{21}$  laser system, we expect less power to be required given that there is no  $\Lambda$ -system present. And while, relative to the  $v_{00}$  transition, this transition line strength will be weaker by a factor of  $q_{12}/q_{00}$ , we

expect the frequency with which this transition is populated to be reduced by the same factor, requiring less intensity than the first two transitions. As a result, and as shown in Fig. 5.16, this system is composed of two SHG stages which differ from those used for the  $v_{00}$  and  $v_{10}$  lasers.



FIGURE 5.16: Schematic of 265.2 nm laser system. Keys to figure: ECDL, external cavity diode laser; ISO, optical isolator; FC, fiber coupler; PM, polarization maintaining fiber; FA, fiber amplifier;  $\lambda/2$ , half-wave plate,  $\lambda/4$ , quarter-wave plate; PBS, polarized beamsplitter; MM, mode-matching optics; CL, collimating lenses; BD, Brewster dichroic; PZT, piezo-electric-transducer.

The same diode laser and ECDL design that was presented for the main cycling laser is also used here. Following amplification to ~ 10 W, light is converted from the IR to visible by a single pass through a 10 mm MgO-doped periodically poled lithium-niobate (PPLN) crystal (Covension P/N: MSHG1064-0.5-10), which uses non-critical phase-matching. This type of crystal is also known to suffer from photorefractive damage, however, this is not as easily reversible as with CLBO. The MgO doping is used to minimize this process and enable higher input powers and subsequent conversion efficiency. This is optimized by choosing the fundamental beam waist in the crystal such that the optimimum Boyd-Kleinman focusing parameter of  $\xi = 2.84$  is achieved. To do this, the high power fiber output is focused to a waist of  $\simeq 25 \ \mu m$  at the crystal center using a  $f = 35 \ mm$  lens. Using this setup, we can produce 1.5 W at ~ 530 nm with a ~ 15% conversion efficiency. The residual IR light after the first doubling stage is separated from the SHG light by a dichroic mirror, after which the IR light is directed onto a beam dump (as shown in Fig. 5.16. For ease of mode-matching, this diverging visible beam is collimited, rotated by a  $\lambda/2$  waveplate, and allowed to propagate to the appropriate location of a mode-matching lens pair. To generate UV light at  $\lambda \simeq 261.7$  nm, we use an off-the-shelf cavity design from Agile Optics. For this cavity, the four mirrors (two plano and two with a 50 mm ROC) form two waists; a symmetric in-coupling waist of 148  $\mu m$  and an asymmetric waist in the crystal of 21  $\mu m$ and 31  $\mu$ m, achieving near the optimum Boyd-Kleinman focusing parameter. At the considerably lower expected circulating powers of this cavity, we opted to use a smaller crystal waist so as to improve doubling efficiency. Similar to the previous cavities, we make use of 10 mm CLBO crystal which is again maintained between  $130 - 150^{\circ}$ C. While mirrors M6-M8 are high reflectors, mirror M5 is a 1.5% transmissive IC. From the UV cavity in this laser system, we have seen as high at 500 mW at 265 nm but more often generate steady state powers around 300 mW, sufficient for expected repumping requirements and spectroscopy.

# Chapter 6

# AlCl experimental setup, production, and beam characteristics

In this chapter, we introduce the general experimental setup that will be used for the remainder of the work in this thesis. This includes a simplified version of the vacuum system, our method for producing AlCl, and characteristics of the molecular beam which are relevant to spectroscopy, optical cycling, and probing branching ratios.

# 6.1 Experimental setup

Small modifications to the existing vacuum system were necessary for studying AlCl. Below, Fig. 6.1a) shows the relevant vacuum regions of the molecular beam line. Molecules are produced via laser ablation in the cell by the same Nd:YAG laser discussed in Chapter 2. Ablated molecules are probed via absorption in the source at two different locations, in-cell and  $\sim 2$  cm downstream from the cell exit aperture, and by LIF at a distance of  $\sim 94$  cm by an EMCCD camera. For cycling and deflection measurements, a translatable aperture is placed further downstream at  $\sim 39$  cm to allow for collimation and alignment of the molecular beam. The aperture size is adjustable, although this requires opening the vacuum system. Two sets of windows transverse to the beam allow optical access and are typically used for pumping and repumping molecules prior to fluorescence detection.



FIGURE 6.1: Schematic diagram of the experimental setup used for studying AlCl. a) Relevant vacuum system hardware used to produce and study AlCl molecules. Molecules produced via ablation in the cell can be probed via absorption prior to exiting or  $\sim 2$  cm downstream. A translatable collimating aperture allows for the beam to be both collimated and aligned with respect to the camera. This is followed by pumping and repumping regions prior to fluorescence detection via an EMCCD camera. b) A two lens or four lens imaging system is used to provide either  $\sim 1:1$  and  $\sim 1:4$  de-magnification, respectively.

By virtue of the short transition wavelength, and in comparison with SrF, the frequency separation between  $v_{01}$  and  $v_{10}$  transitions (~ 4 nm) is too small to make RROC viable. For this reason, alongside the challenge in producing an additional UV light source, we probe molecules at the same frequency as they fluoresce. A

few measures are taken to reduce stray laser light from affecting sensitivity in fluorescence detection. Firstly, we attach windows to the ends of long vacuum nipples  $(\sim 30 \text{ cm})$ , placing the scattering surface far from the camera. Secondly, each piece of vacuum hardware is coated with a highly absorptive material to minimize reflections. The vacuum nipples as well as the surface directly opposing the camera are both coated in soot applied by an acetylene flame. The 6-way vacuum junction at which these are fixed is rather coated with a highly absorptive black paint (Alion part number MH2200). Both of these blackening methods provide low outgassing and allow vacuum pressure below  $\sim 10^{-8}$  Torr to be realized in our system. We use two different lens systems for achieving different magnifications in imaging. These are assembled from off the shelf parts using lens tubes. The first is composed of two lenses of focal lengths  $f_1 = 75$  mm and  $f_2 = 60$  mm, providing a slight de-magnification. For the second system, we achieve a larger 1:4 de-magnification by adding two additional lenses of  $f_3 = 250$  mm and  $f_4 = 60$  mm which allows the two systems to be easily interchanged. These, along with the windows in the beam line, are UV-coated fused silica optics purchased from Thorlabs.

# 6.2 AlCl production

In many of the previous studies, AlCl was produced using electrical discharge in vacuum tubes, running current through aluminum wire electrodes in the presence of AlCl<sub>3</sub> [127, 128, 130, 183]. In other experiments, reactions between Al vapor and gases containing Cl atoms have been used [184–186] following the general equilibrium reaction,

$$AlX_3 + 2Al \Longrightarrow 3AlX,$$
 (6.1)

for which X=Cl here. For our purposes, this method could provide a route to high AlCl yields and further improvements in trap densities. However, this reaction takes place only at high temperatures and because AlCl is thermodynamically unstable this would require the reaction be made to occur near the cryogenic region of the source, demanding a number of involved modifications to our existing cryogenic buffer gas source. Though this may be a fruitful path to take in the future, for expediency, we chose to continue using the technique of laser ablation in initial studies of AlCl. The benefit of ablation-based production is that the technique is widely effective across a large number of precursors. This allows various different compounds to be studied without modifications to the cyrogenic system itself, underpinning the reason why this technique has been so widely adopted in the field [53, 73, 74, 104, 107–109, 118, 187]). For this work, moving from SrF to AlCl merely required identifying a method for producing a target to ablate.

#### 6.2.1 Ablation targets

Early on, as our main cycling laser came online, we pressed several different ablation targets for testing. This coincided with the other AlCl laser cooling group at UC Riverside having recently spent time studying different target compositions in their own system. We were fortunate to learn from their findings which allowed us to make quick decisions regarding the "best" target composition; for us this meant balancing AlCl yield with ease-of-production and safety.

Originally, we intended on ablating a pressed target of pure  $AlCl_3$  powder. This, however, came with safety concerns as  $AlCl_3$  is not only hygroscopic, but it reacts with  $H_2$  to form HCl gas. We quickly learned after pressing this powder that this was not something we wanted to work with as the humidity in Connecticut during the time this was being made led to the target being challenging to handle. Instead, we decided to make several composite targets from Al powder and two different chloride sources, KCl and MgCl<sub>2</sub>, per recommendations from the Hemmerling group.

In our initial tests, three different target compositions were used<sup>1</sup>: Al+KCl, Al+3KCl, and A+2MgCl<sub>2</sub> (with respective molar ratios for Al:Cl of 1:1, 1:3, and 1:4). These molar ratios were chosen for comparison to Hemmerling group results which later were published in Ref. [188]. These targets were produced following the procedure used for SrF and described in Ref. [62] – barring sintering. This procedure is as follows: the desired molar ratio of the two components are combined, ground to fine powder using a mortar and pestle, and loaded into a pellet die (13 mm ID Carver Catalog #3619) which is actively pumped on by a diaphragm pump. This is placed in a hydraulic press, and pressed at 9 tons (limited by the pellet die rating) for ~ 10 min. The density of the target, relative to its theoretical maximum, is then measured and used to determine the targets which get installed in the source. Those that are not installed are stored for later use<sup>2</sup>.



FIGURE 6.2: In cell absorption of ablation plume expanding into vacuum. Absorption probed on the  $X^1\Sigma^+ |v''=0, J''=0\rangle \rightarrow A^1\Pi |v'=0, J'=1\rangle$  line using different AlCl precursors. Traces here are an average of 4 ablations shots and inset shows the different sample targets before ablation. The different shades of grey are due to the different molar ratios of Al and Cl compounds; with Al:KCl (top), Al:3KCl (bottom), and Al:2MgCl<sub>2</sub> (right). Measurement parameters: ablation energy = 17 mJ,  $P_{\rm probe} = 130 \ \mu W$ , and He flow rate of 10 sccm.

#### 6.2.2 In cell absorption

We performed in-cell absorption spectroscopy in order to compare the yield between the three different target compositions. Because our interest is in the population of the first rotationally excited state of  $X^1\Sigma^+$ , we excite along the rotationally open R(1) transition of the  $A^1\Pi$ ,  $v' = 0 \leftarrow X^1\Sigma^+$ , v'' = 0 band. The chosen Al:KCl targets had measured relative densities of ~87% and ~91% for the 1:1 and 1:3 molar ratios, respectively (the Al:2MgCl<sub>2</sub> target was not measured as it had become brittle due to water absorption overnight). These were epoxied to

<sup>&</sup>lt;sup>1</sup>We use 97.5% aluminum powder  $3.0 - 4.5 \ \mu m$  (Thermo Fisher Scientific) which mixed with either 99% potassium chloride crystals (KCl, Thermo Fisher Scientific) or 98% magnesium dichloride (MgCl<sub>2</sub>, Thermo Fisher Scientific).

<sup>&</sup>lt;sup>2</sup>These targets are stored in atmosphere in a clean plastic bag. Placing the targets in a pumped out chamber leads to a reduction in density, so we neglect doing this.

the target holder in our cell as shown by the inset of Fig. 6.2. A sample of typical absorption traces from these targets is given in Figure 6.2, showing for the Al:KCl compositions a higher yield for a molar ratio of 1:1 than 1:3. This is consistent with the findings of Ref. [188], who showed maximum AlCl yields from Al:KCl are to be expected with equal parts Al and Cl. For the Al:2MgCl<sub>2</sub> targets, yields similar to the Al:KCl 1:1 molar ratio target is in contrast with the California group's results, however we suspect this is related to reduced target densities due to water absorption. From these results, we have adopted the Al:KCl 1:1 molar ratio as our standard target composition.

#### 6.2.3 Buffer gas cell dynamics

Following ablation, a vanishingly small number of molecules occupy the J = 1 $X^{1}\Sigma^{+}$  state probed in Fig. 6.2. These hot molecules collide both elastically and inelastically with the cold buffer gas and over several microseconds begin to populate the low lying rotational and vibrational states leading to a sharp rise in absorption. During this time the molecules diffuse toward the cell walls. Once thermalized, the vapor pressure of the molecules are expected to be low enough that molecules that diffuse into the cell walls before exiting the cell become frozen and thus attached the cell surface. On the other hand, for sufficient buffer gas flow rates, molecules will be entrained in the buffer gas and pumped out of the cell due to the differential pressure [55]. The timescales associated with these two competing processes, diffusion and pumping, determine the fraction of molecules which are extracted from the cell to form a beam. There is a large and growing body of work which discusses this as well as other relevant aspects for optimizing this value [52, 53, 74, 83, 189–193]. The discussion here pulls from many of these sources. For our purposes, we can use the in-cell absorption profiles measured above to determine how these timescales compare for our cell design.

#### 6.2.3.1 Diffusion and cell pump out times

The time for molecules to be pumped out of the cell can be described using the cell volume and conductance of the exit aperture,  $\tau_{\rm p} = V/C$  [54, 108]. At steady state, the conductance of the helium atoms in which molecules are entrained can be defined by  $C = \bar{v}_{\rm He} A_{\rm aperture}/4$ , with  $\bar{v}_{\rm He} = \sqrt{8kT/\pi m_{\rm He}}$  describing the 3D mean thermal velocity of helium atoms in the cell. These combine to give the relevant definition for the cell pump out time,

$$\tau_{\rm p} = \frac{4V_{\rm cell}}{\bar{v}_{\rm He}A_{\rm aperture}}.$$
(6.2)

In our experiment, we use a similar cell design as given in Ref. [53] in which a 25.4 mm copper block is drilled out via two perpendicular cylindrical holes of 22.9 mm diameter. We use an additional conical front face as described in Ref. [83] which has a half angle of 40° and is drilled out to have a 3 mm diameter, i.e.,  $A_{\text{aperture}} = 7 \text{ mm}^2$ . Together, this leads to a total approximate inner volume of  $V_{\text{cell}} \approx 15 \text{ cm}^3$ . The temperature of the helium atoms is generally assumed to be that of the cell temperature. In practice, however one tends to find that the in-cell rotational temperature measures slightly higher than the cell itself, even following sufficient timescales for thermalization [53]. This suggests that the actual helium temperature is elevated by the thermalization process and that one should instead use the rotational temperature as indicative of that for the buffer gas (see rotational measurements below). Using these values and Eqn. 6.2 we estimate a pump out time of  $\tau_{\rm p} \approx 15(2)$  ms and provide the associated uncertainty in order to account for the possible temperature range of the helium atoms.

To determine the timescale for diffusion, we consider the decay rate seen in the absorption temporal profile. The associated time constant is the parallel addition of both diffusion and pump out times, i.e.,  $1/\tau = 1/\tau_d + 1/\tau_p$ , from which  $\tau_d$  may be determined. In Fig. 6.3 we show the decay from the 1:1 molar ratio Al:KCl target discussed previously. From this we extract a decay time of  $\tau = 4.6(1)$  ms, giving a corresponding diffusion time of  $\tau_d \simeq 6.7(1)$  ms.



FIGURE 6.3: Decay constant extracted from in-cell absorption when ablating our standard Al:KCl composite target. In this measurement, a helium flow rate of 15 sccm was used.

One can also predict the diffusion time constant via,

$$\tau_{\rm d} = \frac{16}{9\pi} \frac{A_{\rm cell} \ n_{\rm He} \ \sigma_{\rm AlCl, He}}{\bar{v}_{\rm He}},\tag{6.3}$$

yet this requires knowledge of the collision-cross section between AlCl molecules and the helium atoms,  $\sigma_{\text{AlCl,He}}$ , at their equilibrium temperature. In this case, since we do not have this information, we find it through this equation, relying on the measured value for  $\tau_{\text{d}}$ . Here,  $n_{\text{He}}$  is the helium buffer gas density, which can be calculated through,

$$n_{\rm He} = \frac{4f_{\rm He}}{A_{\rm aperture}\bar{v}_{\rm He}},\tag{6.4}$$

where  $f_{\text{He}}$  is the helium flow rate, which in this case, was 15 sccm (1 sccm  $\approx 4.5 \times 10^{17} \text{ atoms/s}$ ). In solving Eqn. 6.3, we estimate an AlCl-<sup>4</sup>He collisional cross-section of  $\sigma_{\text{AlCl,He}} = 1.3 \times 10^{-15} \text{ cm}^2$ .

#### 6.2.3.2 Collisional broadening

An estimate for the collisional cross-section now allows us to revisit the notion of spectral broadening stemming from AlCl-Helium collisions as discussed earlier in Chapter 2. Under the assumption that an excited molecule decays back to the ground state following a collision, we can use an estimate for the collision rate (or time between collisions,  $\tau_c$ ) to provide a corresponding contribution to transition linewdith, and therefore determine the effect this may have on the validity of  $\sigma_D$ in Eqn. 2.8.

The time between molecule-atom collisions is related to the molecule average mean free path,  $\lambda_{AlCl}$ , and the helium thermal velocity,  $\bar{v}_{He}$ , through  $\tau_c = \lambda_{AlCl}/\bar{v}_{He}$ . Since the density of buffer atoms is much greater than that of the ablated molecules, the mean free path can be described, to good approximation, by Ref. [53],

$$\lambda_{\rm AlCl} = \frac{1}{n_{\rm He}\sigma_{\rm AlCl, He}\sqrt{1+m_{\rm He}/m_{\rm AlCl}}}.$$
(6.5)

where  $m_{\text{He}}$  and  $m_{\text{AlCl}}$  are the masses of helium and AlCl, respectively. Therefore, the average time between molecule-atom collisions is given by,

$$\tau_c = \left(\bar{v}_{\rm He} n_{\rm He} \sigma_{\rm AlCl, He} \sqrt{1 + \frac{m_{\rm He}}{m_{\rm AlCl}}}\right)^{-1}.$$
(6.6)

Given the helium flow rate for this measurement (15 sccm), this corresponds to  $\tau_c \simeq 2 \ \mu$ s, or an equivalent linewidth contribution of  $\Gamma_c \simeq 5 \times 10^5 \ s^{-1}$ . To put this in context, we compare this with the expected Doppler broadening. Assuming molecules move in the cell with velocities determined by their equilibrium temperature, the Doppler broadening is given by  $\Gamma_D = \bar{v}_{AlCl}/\lambda$ , where  $\bar{v}_{AlCl}$  is the mean 3D velocity of AlCl and  $\lambda$  is the transition wavelength for  $X \leftrightarrow A$  (261.7 nm). This corresponds to a Doppler broadening  $\Gamma_D \simeq 1 \times 10^8 \ s^{-1}$ , more than  $100 \times 100 \ s^{-1}$ . We therefore can conclude that for AlCl collisional broadening in the cell has a negligible effect on the Doppler-broadened absorption cross section,  $\sigma_D$ . We note, however, this is not the case for all molecules, such as CH, which has a significant broadening due to buffer gas collisions.

#### 6.2.3.3 Cell extraction

The extraction behavior of the cell can also be characterized using the ratio  $\gamma_{\text{cell}} = \tau_{\text{d}}/\tau_{\text{p}}$ . Based on our cell geometry and absorption measurements, we find that  $\gamma_{\text{cell}} \simeq 0.44$ , generally indicating that diffusion to the cell walls occurs more rapidly than molecules are extracted from the cell and that we may find higher extraction efficiencies by reducing the cell volume. In Fig. 6.4, we show both in-cell and beam

measurements ( $d \sim 2$  cm from the cell aperture). While integrating counts between these measurements suggests a ~ 10% extraction, the profiles were extracted via probes of the Q-branch and are therefore complicated by the presence of optical cycling. Nonetheless, it is clear that a large fraction of the molecules produced fail to exit the cell and future work may improve molecular yield by exploring different cell geometries. To this end, we refer the interested reader to Refs. [52, 53, 74, 83, 189–193].



FIGURE 6.4: In-cell (red) and out-of-cell (black) absorption profiles taken on the Q-branch. Both in cell and out-of-cell probe beams used similar intensities, with the probe beam located a distance  $d \sim 2$  cm from the cell aperture. In this measurement, the buffer gas flow rate was 15 sccm.

#### 6.2.4 Target consistency

Using the Al:KlC target (1:1 molar ratio), we find relatively uniform production as the ablation laser alignment is tuned. Though a systematic study of target lifetime and variations was not performed, by comparison with the previously used SrF targets, the Al:KCl targets show similar if not better consistency over longer periods of time. For this reason, we typically do not to make frequent adjustments to the ablation location. However, these targets produce significant residual "dust" within the cell as they are used. This leads to a coating on the cell walls and the transmission window for the ablation laser. Unlike SrF, this coating doesn't appear to be removed by the ablation [53], at least not in a significant way. This has the effect of reducing the energy deposited onto the target as the system ages following a target installation. Over much longer timescales (weeks of steady operation) the reduction in molecule yield can in part be attributed to this reduced window transmission, though this can often be recovered by increased ablation energy. It is also expected that this accumulation of "dust" has an impact on beam properties. For this reason, in the following measurements of rotational distribution and beam forward velocity we measured beam properties for both new and used targets. In Fig. 6.5 are pictures of these targets, both before and after heavy use, with additional images of the ablation dust seen coating all inside surfaces of the cell.

# 6.3 Beam properties

#### 6.3.1 Rotational temperature

Provided our molecules reach a thermal equilibrium with the helium buffer gas, we expect a low-temperature rotational distribution in the molecular beam. To check this, we probe for relative population in different rotational levels by driving R(J'') transitions along the  $X^1\Sigma^+$ , v = 0 band. In the cell, these measurements are



FIGURE 6.5: Comparison of new and used Al:KCl ablation targets: on the left,a) shows a typical new target before installation. On the right are images of both a heavily used target b) and inside surfaces of cell, snorkel c), conical face d), and ablation window e) coated in ablation dust.

taken by absorption just as in the previous section. However, for molecules in the beam, we instead use fluorescence detection to improve sensitivity. In both cases, transitions must be probed with sufficient intensity to saturate in order to provide a reliable measure of the rotational state population. Here, LIF measured on each transition has been scaled using calculated branching ratios to account for the varying linestrength. With this weighting, we fit a Boltzmann distribution to the data, as given in Eqn. 2.4, in order to extract an internal rotational temperature.

Figure 6.6 shows both in-cell and out-of-cell rotational distributions for two different targets, one which was newly installed (Figure 6.6a) and the other used regularly for about two months prior to the measurement (Figure 6.6). This was done to check how we should expect the experimental conditions to evolve as the target becomes used and the cell dusty. Both in-cell and out-of-cell measurements for the new target indicate slightly lower temperatures than for a target used continuously for many weeks (an estimated >  $2.5 \times 10^5$  ablation shots). However, this change is not significant, corresponding to a ~ 5% change to the J = 1 population



FIGURE 6.6: Rotational distributions for two different targets. a) a new target,b) one used regularly for a few months. In both a) and b), the lower temperature distribution corresponds to the molecules measured in the beam. A helium flow rate of 10 sccm was used for both measurements.

in the beam. We also notice that in both of these cases, we measure an in-cell temperature that is higher than the temperature of the cell ( $T_{cell} \sim 2.7$  K). As previously mentioned, this is not unusual and has been suggested to stem from an initial heating of the buffer gas from target ablation [53]. Based on the pump and diffusions times for our cell geometry, we expect that the molecules are fully thermalized. These molecules are nonetheless cooled below the cell temperature as they form a beam, indicating some isentropic expansion into the lower pressure region outside the cell. In both situations, the rotational temperatures are consistent with our observations using SrF, showing the expected source behavior using the new AlCl species.

#### 6.3.2 Forward velocity

A measure of beam forward velocity is crucial for many reasons. Regarding laser cooling, this provides a direct link to the number of photon recoil events necessary to slow and stop each molecule. For the purposes of evaluating optical forces, this measure is further required to determine the duration of time each molecule spends in the laser field, and is therefore necessary to accurately extract forces from a measurement.

The large natural linewidth of the cycling transition makes any Doppler-sensitive technique limited to a best case resolution of  $\delta v = 8$  m/s. In reality, the achievable resolution is made considerably worse by any partially resolved hyperfine structure in the  $A^1\Pi$  state. For this reason, we use an alternative method to determine the forward velocity which probes the temporal pulse evolution between measured profiles taken at different distances from the cell. These profiles are used to perform a deconvolution to extract the velocity distribution that maps one time profile to the other, as is has been discussed elsewhere [57, 73]. Here, the new limit on resolution comes from the time binning of your detection, which can easily provide  $\sim$  m/s resolution. In our case, we make measurements at two locations, the first using absorption at a distance  $d_1 \sim 1$  cm outside the cell, and the second using fluorescence collected by a camera at distance of  $d_2 \sim 94$  cm. To take a temporal profile with the camera, we set a short exposure time of 0.5 - 1 ms and step the camera delay, relative to ablation, in small increments. If we have reproducible pulses, this is equivalent to measuring the full profile in one measurement. To the extent that this isn't the case, we average several composite profiles together, but note that subsequent profiles are typically very similar to each other and an average is often not necessary. The deconvolution is then performed to provide the corresponding velocity distribution. Example profiles of both absorption outside the cell and fluorsence downstream are given in Fig. 6.7a).

In Fig. 6.7b) and c) we show two velocity profiles determined using the deconvolution procedure discussed above. Each profile was taken alongside the rotational


FIGURE 6.7: Forward velocity distributions measured using targets with different levels of use. b) a new target and c) one used regularly for a few months.In a) we show the temporal profiles corresponding to the deconvolved profile of a). Each measurement operated with a helium flow rate of 10 sccm.

temperature measurements of Fig. 6.6, providing an example of the forward velocity distributions for both a new and heavily used ablation target. For a freshly installed target, the mean forward velocity is just below 100 m/s, however, after significant use and without cleaning of the buffer gas cell, the mean forward velocity is increased substantially. Here, the velocity is increased by a factor of  $\sim 2$ . From these distributions it is evident that use of the ablation target plays a large role in the forward velocity distribution of molecules produced from our source, unlike the rotational temperature. While we do not know the exact mechanism for this variation, we believe this is in part related to the in-cell dust shown in Fig. 6.5. This has been suggested elsewhere to lead to a reduced re-thermalization of helium atoms with the cell walls, however, one would expect this to be similarly observed in the rotational temperature. Nevertheless, the change of forward velocity with target use highlights the importance of repeating this measurement when using the molecular beam to extract information which depends critically on velocity. Ultimately, these measurements indicate that this source produces relatively slow beams of AlCl molecules.

# Chapter 7

# Hyperfine-resolved $A^1\Pi$ spectroscopy

Prior studies of the  $A^1\Pi$  state were unable to resolve the hyperfine structure (HFS). The span of this structure determines what fraction of the  $X^1\Pi^+$  state can be addressed by a single frequency laser and will therefore play a critical role in the ability for AlCl to optically cycle and provide a damping force. Similarly, the complexity of this level structure carries with it a complex Zeeman splitting which must be understood in order to engineer a confining force via an external magnetic field in a MOT. At the base of this understanding is a proper assignment of the hyperfine states. In Chapter 4, we presented an effective Hamiltonian used to describe this structure. In this chapter, we present spectra used for determining the constants which are tied to those terms.

# 7.1 Experimental setup

For these measurements, we collect fluorescence via an EMCCD camera using the near 1:1 imaging system shown in Fig. 6.1, which is integrated across the entire pixel array to give a total number of counts. In this way, the EMCCD is used as a PMT, albeit with lower sensitivity. The magnification of this system is  $\sim 0.8$ , providing a transverse region of  $\sim 9$  mm that is collected on to the camera's 8 mm CCD array. A collimating aperture was not installed prior to these measurements and therefore the transverse velocities are assumed to be set by the imaging region. In this case, we expect transverse velocities of  $\sim 1$  m/s at full-width-half-maximum, giving a corresponding Doppler width of  $\sim 4$  MHz. However, spherical aberrations in the lens system lead to distortion which may change this value. Ultimately, we learn this value fitting the spectra with Voigt functions.

The measurements of this chapter are limited in their accuracy by two factors. The transfer cavity used to reference the seed ECDL laser has inherent nonlinearity throughout a scan. A calibration was not taken at the time of this measurement, however from previous calibrations we expect a systematic frequency shift of ~ 5 MHz over the cavity FSR. This places a ~ 20 MHz error bar on the data in the UV. A further uncertainty in frequency arises from hand-off from the wavemeter to transfer cavity. The wavemeter was calibrated with ~ 1 GHz accuracy relative to the D2 line of <sup>87</sup>Rb but a cavity was not used during this calibration. Therefore we assume the absolute frequency has a systematic offset of  $\pm$ FSR of the cavity. The cavity FSR is  $\Delta \nu = 750$  MHz.

### 7.2 Rotational spectra

The first beam measurements using fluorescence were focused on determining the beam's rotational temperature. At the same time, we scanned the rotational structure of AlCl to ensure we understood the transitions being driven. This allowed for a cross check against the previously known rotational lines for the  ${}^{27}Al^{35}Cl$  isotopologue. These measurements are shown in Fig. 7.1, with a) showing the corresponding transitions for the spectra in b). We overlay these data with the predicted line centers for each rotational transition using spectroscopic constants from Refs. [131, 188] and the Dunham expansion provided in Eqn. 4.12, and find good agreement. We note that for each rotational line there is a second higher frequency line for the  ${}^{27}Al^{37}Cl$  isotopologue which is also produced during ablation from the Al:KCl targets. While we identified these lines to confirm their frequencies, we did not study this carefully and therefore neglect the less abundant isotopologue from the rotational spectra given in Fig. 7.1, and note that for the remainder of this thesis any reference to AlCl is to the  ${}^{27}Al^{35}Cl$  isotopologue.

Both P and R lines probe the e levels of the J' states. Although for optically cycling we are interested in the structure of the opposite parity f levels addressed by Q lines, R and P are useful transitions for tying down the constants of the effective Hamiltonian. Based on the size of the  $\Lambda$ -doubling constant in molecules like AlCl, the e levels should be very similar in structure to those of f (see AlF in Ref. [46]). As can be seen in the spectra, these transitions are also well isolated from one another, in contrast with the Q-branch, which is tightly spaced due to similar rotational constants for the X and A states. Unlike the Q-branch, these transitions can only scatter a small number of photons which serves to ease interpretation of line strengths when extracting spectroscopic constants. Any attempt to resolve



FIGURE 7.1: Rotational spectra of  $X^1\Sigma^+ \to A^1\Pi$  of <sup>27</sup>Al<sup>35</sup>Cl isotope: a) rotational energy levels corresponding to the rotational spectra shown in b).

the hyperfine structure in the  $A^1\Pi$  state is therefore improved by probing either P or R lines. Below, we do this by probing R lines because these lines, on average, scatter more photons per molecule due to larger branching ratios into the initial ground state.

# 7.3 Hyperfine spectra

The unresolved hyperfine structure within the  $X^1\Sigma^+$  state leads to a large simplification of the spectra observed when probing a P, Q, or R branch. As a direct result, any structure that is present can be directly attributed to hyperfine structure stemming from the  $A^1\Pi$  state.

#### 7.3.1 R-branch

The lowest four R-line spectra seen in Fig. 7.1b) are shown with higher resolution in Fig. 7.2. We worked with the Hemmerling group at UC Riverside to determine the  $A^1\Pi$  state hyperfine constants from this data. We describe each energy level given by the effective Hamiltonian by a Voigt function and fit the combined profile. For the sake of computational time, we limited this fit to just the R(0) spectra. The determined line centers are indicated by vertical lines. To limit power broadening in these measurements we probe with a low intensity beam of ~ 130  $\mu$ W/cm<sup>2</sup>  $(I \approx 10^{-3}I_{sat})$ . Although our interest lies in the structure of J' = 1, given by R(0), we show the first four levels to indicate how the structure changes for increasing J'. We note that the decreasing rotational population for higher rotational ground states translates to a reduction in signal-to-noise ratio as higher R-lines are probed.

In contrast with the unresolved hyperfine structure in the  $X^1\Sigma^+$  state, the excited  $A^1\Pi$ , J' = 1 state has partially resolved hyperfine structure. This spans  $\sim 500$  MHz (or  $\approx 16\Gamma/(2\pi)$ ) and decreases to  $\sim 200$  MHz (or  $\approx 6\Gamma/(2\pi)$ ) by J' = 4. In each rotational level, the dominant contribution to splitting arises from the aluminum nuclear spin interaction with rotation and can be separately labeled by an  $F_1$  quantum number. Within each resolved feature lies a number of F sublevels, as indicated in Fig. 7.2.

The partially resolved structure in the J' = 1 *e* state is expected to similarly be present in the *f* level accessed by Q(1). While at low intensities, such as those used to probe this transition, this partially resolved structure will limit the number of



FIGURE 7.2: Hyperfine-resolved frequency scans of the R-branch in AlCl. Experimental data is represented by open circles and is overlaid by simulated spectra as solid lines. Predicted line centers are given by solid vertical lines. Subplots a) through d) show the reduced span of the  $A^1\Pi |J'\rangle$  hyperfine structure for increasing J'.

ground states addressed by the cycling laser, but power broadening should serve to improve the situation. As shown in Fig. 7.3, the J' = 1 state becomes largely unresolved when higher, but still modest, laser intensity is used. Here, we increases the laser intensity during the frequency scan to ~ 10 mW/cm<sup>2</sup> ( $I \simeq 4 \times 10^{-2} I_{sat}$ ).

#### 7.3.2 Q-branch

The identified partially resolved structure found by probing the R(0) is masked when we moved to probing on the congested Q-branch. Fig. 7.5 shows the measured structure. To aid in interpretation we provide a simulated Q-branch along



FIGURE 7.3: Frequency scan of the R(0) transition at two laser intensities, showing the effect of power broadening on spectral resolution.

with predicted line centers for a molecular beam with rotational temperature of  $T_{\rm rot} = 2$  K. While a discrepancy can be seen between spectra and simulation, the sources of which will be discussed, we note that main feature of the Q-branch is composed of 3 rotational levels, namely, J = 1 - 3. A large focus of this work has simply been to identify the makeup of this structure, as determining properties of cycling and loss require knowing which rotational levels are being addressed.

The discrepancy between theory and experiment may arise from a few sources. In this simulation we have not included the effect of  $\Lambda$ -doubling, having calculated this structure instead by positioning each hyperfine manifold of the opposite parity state according to the energies predicted by the Dunham expansion. This was



FIGURE 7.4: Measured spectra for the Q-branch in AlCl when driven along the  $X^{1}\Sigma |v'' = 0\rangle \leftrightarrow A^{1}\Pi |v' = 0\rangle$  transition (open circles). Overlaid with this data is the simulated spectra using the opposite-parity R-lines and the predicted rotational spacing. Below the spectra, predicted line centers are provided by vertical lines.

done for simplicity to convince ourselves of the rotational overlap. In doing this, the line positions of Q(1) are predicted to be have higher frequencies than we measure. It is reasonable to expect that the exact energies of each f level hyperfine component differ from the e levels by this amount. It is also possible that the current rotational constants lack the resolution needed to accurately predict the line positions. We finally note that the uncertainty associated with the spectra itself leads to a potential discrepancy between both P and R lines and the Qbranch. At the time of writing, this has not been systematically considered, but remains a subject of on-going work in the group.

As with the power broadening seen in J' = 1 from Fig. 7.3, similar broadening occurs for the Q-branch and leads to the J' = 1 hyperfine structure becoming largely unresolved. This is shown in Fig. 7.5, where repeated Q-branch scans are taken at different laser intensities. The large observed increase in fluorescence provides



FIGURE 7.5: Spectroscopic scans of the  $X^1\Sigma |v''=0\rangle \leftrightarrow A^1\Pi |v'=0\rangle$  transition at varying levels of intensity, indicating signs of optical cycling.

initial evidence for optical cycling on the Q-branch. While, in principle, scattered photon numbers can be extracted from this by calibrating this fluorescence with respect to an R or P-line [46], this is complicated by the presence of the competing and overlapped rotational levels in AlCl. As a result, this method was not utilized. For each scan we provide the corresponding intensity relative to the two-level saturation intensity of  $I_{\rm sat} = 232 \text{ mW/cm}^2$ . We find saturation occurring between  $\sim 60 - 90 I_{\rm sat}$ , but note that this is similarly skewed by the presence of multiple cycling transitions in this frequency interval (Q(1), Q(2), Q(3), etc.). In the next chapter, we will rely on radiative deflection measurements for a more sensitive probe.

# Chapter 8

# Optical cycling and branching ratios

In this chapter, we deal with initial demonstrations of optical cycling in AlCl as well as both probing and repumping molecules from v'' = 1 and v'' = 2 vibration levels. After introducing the necessary theory for the loss during an optical cycle, the experimental setup for radiative deflection measurements will be presented. Given the layered rotational structure of the Q-branch, measurements in this chapter give an average over the different effects associated with each participating rotational level. From measurements, we extract scattered photon numbers, scattering rates, and determine the saturation intensity of the cycling transition, along with values for the first three vibrational branching ratios. Finally, we find that the average of multiple J-levels sets a lower bound on these measurements.

# 8.1 Enumerating scattered photons

Evaluating optical cycling in a system requires carefully determining the number of photons that are scattered for each molecule during the measurement. Whether one uses optical pumping, increased fluorescence [46] or radiative deflection [46, 100], the scattering of each molecule follows the same physical process. There have been a few other discussions in the literature regarding the relations provided here [32, 46, 194–196]. The current purpose is to provide a self-contained reference for these relationships, as they will be referenced in the sections that follow.

During the spontaneous decay in an optical cycle, the branching ratios determine the probability that the molecule will return to the initial quantum state where the next photon can be absorbed. For each scattered photon n, the probability of remaining in the cycle decreases according to a Bernoulli process [32], which after scattering n = N photons may be written,

$$p(n=N) = \prod_{i=1}^{n=N} r_i = r^N.$$
(8.1)

On the other hand, a molecule that decays out of the cycle prior to scattering N photons will do so during its last spontaneous emission with probability (1 - r), which leads to a change in the last term of the multiplicative sum,

$$p(n < N) = \prod_{i=1}^{n < N} r_i = (1 - r) \prod_{i=1}^{n-1} r_i = (1 - r)r^{n-1}.$$
(8.2)

Here, r represents the branching ratio from the excited state. The maximum number of photons that can be scattered by a system is defined by the interaction time and scattering rate, and is written  $N_{\text{max}} = R_{\text{sc}}t_{\text{int}}$ . With the probability vanishing beyond  $N_{\text{max}}$  we can write the full piece-wise discrete probability distribution for the system [46],

$$p(n < N_{\max}) = (1 - r)r^{n-1}$$
(8.3)

$$p(n = N_{\max}) = r^{N_{\max}} \tag{8.4}$$

$$p(n > N_{\max}) = 0, \tag{8.5}$$

which allows us to describe the probability to either remain or be lost from the optical cycle following scattering  $n \leq N_{\text{max}}$  photons. It is useful to alternatively interpret these equations as describing the fractional probabilities associated with an ensemble. In this way, we can use the probability distribution to compute various relevant quantities for an experiment, such as the mean and standard deviation of scattered photons, as well as the total number for a given  $N_{\text{max}}$  and the limiting number dictated by r. To find the mean, we take number expectation value,

$$\langle n_{\rm ph} \rangle = \sum_{n=1}^{\infty} np(n)$$
  
=  $\sum_{n=1}^{N_{\rm max}} n(1-r)r^{n-1} + N_{\rm max}r^{N_{\rm max}}$   
=  $\frac{1-r^{N_{\rm max}}}{1-r}.$  (8.6)

In the limit that  $N_{\rm max} \to \infty$  Eqn. 8.6 reduces to the familiar asymptotic form of the geometric series,

$$\lim_{N_{\rm max}\to\infty} \langle n_{\rm ph} \rangle = N_{\infty} = \frac{1}{1-r}$$
(8.7)

This describes the limiting scattered photon number for a given branching ratio when scattering rates and/or interactions are not a bottleneck. This is frequently the case for transitions with significant branching ratios such as the rotationally open P and R lines. For the ensemble, the population remaining after scattering  $N_{\rm max}$  photons is now given by,

$$P(N_{\max}) = r^{N_{\max}}.$$
(8.8)

Whether one measures  $\langle n_{\rm ph} \rangle$  or directly  $N_{\rm max}$  depends on the experiment. If all molecules having scattered photons are present in a measurement then the extracted signal will represent the integrated effect from the entire ensemble, therefore providing a measure of  $\langle n_{\rm ph} \rangle$ . Detecting scattered photons by either deflection with a repumping laser or an increase in fluorescence are two examples of cases where the average photon number is measured, requiring Eqn. 8.6 to extract the maximum number of scattered photons per molecule. This would be relevant in order to learn about the maximum scattering rate, for example. Alternatively, if a repump laser is absent during a deflection measurement, the molecules that are detected will be those that remained bright during the upstream laser interaction, having scattered  $N_{\rm max}$  photons. Thus enabling use of Eqn. 8.8.

# 8.2 Radiative deflection

During an optical cycle, photons are emitted in random directions upon spontaneous decay<sup>1</sup>, leading to the average contribution to changes in both velocity and

<sup>&</sup>lt;sup>1</sup>Strictly speaking, the direction of a spontaneously emitted photon is not purely random but depends on the amount of angular momentum gained or lost during the decay. The radiation pattern of a decaying electron follows that of an oscillating dipole for  $\pi$  transitions and a rotating

direction of the molecule to being only from the absorbed photons. At the optical cycling transition wavelength of  $\lambda_{00} = 261.7$  nm, each absorbed photon carries a large momentum, giving AlCl relatively large recoil velocity,

$$v_r = \frac{\hbar k}{m_{\text{AlCl}}} \simeq 2.44 \text{ cm/s.}$$
(8.9)

Compared to the forward velocity of our molecular beam the recoil velocity is relatively small, requiring some 4000 photons be scattered to slow a beam of  $\bar{v}_{||} \approx 100$  m/s. However, transverse to the beam, velocities are considerably lower and can be further restricted using a collimating aperture. Provided the molecules are able to optically cycle, a measurement using separated pump-probe beams can provide deflection of the molecular beam by an amount which is easily detected. Using the forward velocity,  $v_{||}$ , and the propagation distance between pump and probe regions, D, the shift of the molecular beam center, d, may be converted to scattered photons through,

$$N = \frac{d}{D} \left( \frac{v_{||}}{v_r} \right), \tag{8.10}$$

where, again, N may represent either  $\langle n_{\rm ph} \rangle$  or  $N_{\rm max}$  depending on whether or not a repump laser is used.

dipole for  $\sigma^{\pm}$  transitions, leading to a spontaneous emission pattern governed by the number imbalance in the two types of transitions available for the system [67].

# 8.3 Experimental setup

For the experiments in this chapter we use the setup described in Fig. 6.1. All measurements here are made with fluorescence detection via a probe laser oriented transverse to the molecular beam and under an EMCCD camera. We use a 1:4 de-magnification imaging system in order to observe the transverse extent of our molecular beam. Upstream from the probe region we have two additional regions which can be used to pump and repump molecules and as discussed below, a translating aperture is used to collimate the molecular beam.

While not shown in Fig. 6.1, to compensate for ablation noise every neighboring data point is interleaved with a normalization case. Any given experiment is set up to automatically alternate between two cases while data is collected. This timing is synced with the central clock of the experiment derived from a LabVIEW controlled FPGA. Using this time base, data is automatically sorted and normalized in real time through a written LabVIEW vi, providing a quick method for determining effects in the system. How this is accomplished exactly depends on the particular measurement, but is typically performed using an optical shutter. For pump-probe measurements, this shutter chops neighboring data points between probe and pump-probe situations.

#### 8.3.1 Beam collimation

In addition to restricting the transverse velocity spread of the molecular beam, a collimating aperture also reduces molecular flux and therefore lowers the signal to noise of a measurement. One must strike a balance in aperture placement to minimize transverse velocity while providing enough propagation distance to resolve deflection. In practice, the placement of the aperture is often limited by the available vacuum hardware, but both the aperture size and shape are free parameters.

Depending on the size of exit aperture of the source, the system is not well described by a point source emitter. In Fig. 8.1, we depict the general geometry, though exaggerated, for a non-point source beam and the most extreme path that can be taken by a molecule.



FIGURE 8.1: Diagram for relevant geometry in molecular beam collimation.

We can relate these parameters through similar triangles to find,

$$x = \frac{(r+R)d}{L} - R \tag{8.11}$$

$$r = \frac{(x+R)L}{d} - R, \tag{8.12}$$

as well as determine the transverse velocity by  $v_{\perp} = v_{||}(r/L)$ . For our experiment,  $R = 3 \text{ mm}, L \simeq 370 \text{ mm}, \text{ and } d \simeq 940 \text{ mm}.$  For simplicity we use a Thorlabs adjustable iris which is attached to a vacuum-compatible translation stage, giving a 25 mm range of adjustment. To ease vertical alignment with the molecular beam as well as to keep signal high, we set this aperture to r = 2.8 mm. This setup can be seen in Fig. 8.2.



FIGURE 8.2: Picture of our translating molecular beam collimating aperture.

With this aperture radius the molecular beam is collimated to 1.7 m/s and spans  $2x \simeq 20$  mm in the probe region (both at FWHM). This leads to a Doppler broadening of 6 MHz, well within the natural linewidth, making effects of velocity selective pumping negligible.

#### 8.3.2 Camera calibration

We accommodate the transverse extent of the molecule beam using the previously mentioned 1:4 imaging system. This level of de-magnification in our system leads to barrel distortion in the image which is not ideal for a position sensitive measurements. We calibrate for this by imaging a ruled piece of paper and apply a polynomial fit to extract parameters needed for correcting the transverse profile. In Fig. 8.3a), we show both a distorted image and one that has been corrected along one axis. We test this by comparing translation of the collimating aperture and the peak position of detected fluorescence (Fig. 8.3b). The nonuniform intensity profile seen in these images stems from nonuniformity in the light source used



FIGURE 8.3: Camera calibration. a) A polynomial fit is used to correct for barrel distortion in our imaging system along the transverse dimension. Lines are spaced by 6.25 mm. b) We evaluate linearity of the corrected image by measuring fluorescence of the molecular beam vs. translation of the collimating aperture. Data and a linear fit are given by blue circles, and solid line, respectively.

to illuminate the lined paper. The change in intensity across the image was determined through separate measurements to be minimal and contribute a negligible error to the interpretation of data discussed in the following sections.

#### 8.3.3 Laser power calibration

The anti-reflection (AR) coatings we use to allow laser light to pass through the vacuum system of the experiment tend to damage with exposure when exposed to the wavelengths (and powers) of our UV lasers<sup>2</sup>. The timescales for this damage depend on the power and duration of exposure, but initial signs of damage are visible on the windows within minutes of use – even in the probing region where intensities are far below the estimated damage threshold of the coating ( $\approx 10 \text{ W/cm}$ ). Changes in window transmission after long-term use tends to be in the range of 5 – 10%. In general, before running an experiment we first measure the transmission in a single pass to determine the amount of loss through two windows. The measured value is then be used to calculate an estimated total power incident on the molecules after N passes through the system. As it is often the case that several passes are needed to achieve sufficient powers (or interaction times) for an experiment, we provide the following closed form relation that converts the power incident on the first window to that within the vacuum system following the  $n^{\text{th}}$  pass,

$$P_{\rm mol} = \sum_{n=1}^{n=N_{\rm pass}} T_{\rm w} (T_{\rm w}^{n-1})^2 P_{\rm in}.$$
(8.13)

Here, n and  $N_{\text{pass}}$  are the current and total number of passes through the vacuum system and  $T_{\text{w}}$  is the transmission of a single window. We note that Eqn: 8.13 does not consider the reflections off of the window surfaces and therefore provides an slight under-estimate to the actual power incident on the molecules.

<sup>&</sup>lt;sup>2</sup>Here we use Thorlabs AR coated windows with part number WG42012-UV. At  $\sim$  261 nm these windows have a CW damage threshold of  $\approx$  10 W/cm.

#### 8.3.4 Three laser system

Throughout the remainder of this chapter, references will be made to the lasers used and vibrational decay paths probed in various measurements. In Fig. 8.4, we provide the relevant electronic and vibrational energy level diagram as well as the lasers that correspond to the different situations described.



FIGURE 8.4: Relevant electronic and vibrational energy level diagram for optical cycling and vibrational branching measurements performed in this chapter.

# 8.4 Optical pumping

Before looking for deflection in our molecular beam we first checked our ability to optically pump molecules out of the main cycling transition. The dense structure of the Q-branch means that doing this requires optically cycling on a several rotational levels simultaneously. In particular, the first three J levels, J = 1 - 3, have 72, 120, and 168 respective magnetic sublevels!

A pump beam of  $d_{1/e^2} = 7.5$  mm is applied in the pumping region and tuned to address the highest peak of the Q-branch (see Fig. 7.5). This is passed transverse to the molecular beam and then retro-reflected back onto itself in order minimize radiative deflection from pushing molecules out of the camera view. With the probe laser under the camera we measure depletion of the beam by taking the ratio of pump-on to pump-off. Both pump and probe beams use linear polarization set to be in the plane of the optical table. In Fig. 8.5, we show the population remaining versus pump power (converted to intensity) for the pump beam tuned to address the Q-branch peak. It is clear from this measurement that a significant number of molecules are being optically pumped into a dark state.



FIGURE 8.5: Loss of total population as a function of laser intensity in a pump then probe experiment with both lasers tuned to address the peak of the v = 0Q-branch. The inset shows how the distribution of loss among rotational levels.

To understand how this pumping is distributed versus rotational level, we replace the probe laser, previously tuned to address  $v_{00}$ , with the laser designed for addressing  $v_{10}$  and tune its frequency to address the R-lines of the v'' = 0 ground state. We take similar curves as done with the Q-branch, varying the pump beam intensity, but now probing how the fractional population changes for each rotational level separately. The inset of Fig. 8.5 shows the remaining J-level population following a high intensity upstream pump beam ( $\sim 2.75 \text{ W/cm}^2$ ) that is tuned to the peak of the Q-branch, as before. From this distribution of depletion there are several items to note. First, we observe no loss from J'' = 0, as expected given that the Q-branch starts with J'' = 1. Now, for the remaining rotational levels, the inset of Fig. 8.5 shows significant depletion in the first three spectrally overlapped rotational levels but also in J'' = 4 and J'' = 5. Power broadening enables addressing molecules far beyond the extent of the natural linewidth which hints toward the ability to optically cycle on as many as 5 rotational levels at once. After accounting for the rotational temperature, the loss shown in Fig. 8.5 corresponds to depleting some 405 magnetic sublevels using a single laser frequency.

The missing Q(0) transition (due to a lack of J' = 0 level) in the Q-branch makes the fractional population of J'' = 0 an indicator for parity mixing in the  $A^1\Pi$ state. Under such mixing,  $\Delta J = \pm 1$  transitions provide a route to leaking into both J'' = 0 and J'' = 2. While population in J'' = 2 may continue to cycle on Q(2), population in J'' = 0 cannot and we therefore expect to find increased population here under such a leak. As seen in the inset, the population of J'' = 0remains unchanged within the measurement uncertainty given by statistical error.

# 8.5 Optical cycling

With the optical pumping measurements showing large amounts of depletion, the next considerations are both how quickly photons are being scattered and what the branching ratios are for the system. To measure optical cycling we use radiative deflection of our molecular beam. Measurements are performed without a repumping laser so that the deflected distance of the molecular beam center leads to a measure of the maximum number of photons scattered,  $N_{\rm max}$ , during the upstream laser interaction. For each measurement, we also record the loss in population by the ratio of fluorescence collected between a reference case (no pump beam present) and the deflected one. This provides the information necessary to use Eqn. 8.8 for determining the branching ratio back into the main cycling ground state. The latter result will be presented in succeeding sections.

We use a pump beam with  $1/e^2$  diameters of  $d_x = 1.6$  mm and  $d_y = 6$  mm which is single passed in the pumping region. The vertical extent of this pump beam is slightly larger than the collimating aperture ( $d_{aperture} = 5.6$  mm) to ensure all molecules are addressed by the pumping laser. The probe beam is tuned to address the same frequency of the Q-branch driven upstream. This is done for all remaining measurements that require spatial resolution, as probing instead on the R-lines did not provide the SNR needed to produce a reliable image. This leads to the unfortunate consequence that all subsequent deflection measurements give the average of optically cycling on multiple J-lines. The impact of this turns out to not be so severe but will nevertheless be discussed further at the end of this chapter.



FIGURE 8.6: Example EMCCD images for a typical radiative deflection measurement. The top images shows the reference case in which no upstream pumping laser is present. The bottom image shows a change in both position and fluorescence as the pumping laser drives molecules to optically cycle upstream. In both images, molecules propagate upwards and the horizontal width of the fluorescence image indicates transverse extent of the molecular beam. The pump propagates upstream from left to right and the probe laser is retro-reflected. The vertical extent of the fluorescence profile indicates the diameter of the laser beam.

Example images the molecular beam with and without the upstream pumping are shown on equal color scales in Fig. 8.6. For each image we apply distortion correction and fit a Gaussian profile to the integrated horizontal cross section. In Fig. 8.7, the shift in center position is plotted versus laser intensity. Along with a measured mean forward velocity of  $\bar{v}_{\parallel} \approx 120$  m/s, we use Eqn. 8.10 to convert deflection to a number of scattered photons (shown as the right axis). The deflected data is fit using D = aI/(1+I) from which we can obtain a saturation intensity. With the measured mean forward velocity of the beam and laser beam diameter  $(d_x = 1.6 \text{ mm})$ , we use  $t_{\text{int}} \simeq 13 \ \mu\text{s}$  and  $N_{\text{max}} = R_{\text{sc}}t_{\text{int}}$  to determine the maximum measured scattering rate.



FIGURE 8.7: Radiative deflection measurement versus laser intensity. In this measurement,  $\bar{v}_{||} = 120$  m/s,  $d_x = 0.8$  mm, D = 55 cm, corresponding to  $\sim 8.7$  photons/mm of deflection.

From Fig. 8.7, we find a measured saturation intensity for driving the Q-branch of  $I_{\text{sat}} = 640(10) \text{ mW/cm}^2$ , and corresponding maximum scattering rate of  $R_{\text{sc}} = 3.7(1) \times 10^6 \text{ s}^{-1}$ , or  $\Gamma/54$ . This scattering rate is lower than would be expected from the simple models discussed so far in this thesis and suggests the presence of dark states similar to those observed in TIF and AlF molecules [46, 50].

#### 8.5.1 Dark states

Optical transitions that have greater or equal ground state angular momentum than their corresponding excited state have the tendency to drive the system into a dark state, i.e., a state that is no longer coupled to the driving field. These dark states can either be angular momentum eigenstates of the Hamiltonian or coherent superpositions of angular momentum eigenstates. The former case leads stationary dark states that introduce additional leakage paths from the optical cycle. On the other hand, dark states formed by coherent superpositions of eigenstates can either be stationary, due to quantum interference effects, or nonstationary, precessing between bright and dark states at a rate that determines the maximum optical cycling rate [197, 198]. In the present case, the optical cycling transitions in AlCl correspond to ground and excited electronic states with equal angular momenta J. We therefore expect dark states to be affecting optical cycling.

Dark states can be identified by looking for states that have a vanishing probability amplitude when interacting with an external laser field of a given polarization. This procedure has been described in Ref. [36] as well as Ref. [199]. Finding the dark states amounts to finding the set of eigenvectors  $\vec{a}_{F,m}$  that solves the matrix equation

$$\vec{A} \cdot \vec{a}_{F'',m''} = 0, \tag{8.14}$$

where  $\vec{A}$  is given by

$$A_{(F',m')(F'',m'')} = \sum_{i,q} e^{-i\Delta_{i,F'',F'}t} (-1)^{q+F'-m'} \begin{pmatrix} F' & 1 & F'' \\ -m' & q & m'' \end{pmatrix} \langle \gamma', F'| |\mathbf{d}| |\gamma'', F'' \rangle E^{i}_{-q}.$$
(8.15)

Here,  $A_{(F',m')(F'',m'')}$  is a sum over each laser frequency component, *i*, and dipole transition *q*.  $\Delta_{i,F'',F'} = \omega_i - (\omega_{F'} - \omega_{F''})$  represents the detuning of each optical frequency  $\omega_i$  relative to transition resonance, with  $E_{-q}^i$  indicating the associated electric field. As usual, **d** is dipole matrix operator and both  $\gamma'$  and  $\gamma''$  represent other quantum numbers needed to specify the states [199].

The number of dark states found for the Q(1) cycling transition in AlCl depends on the number of partially resolved  $A^1\Pi$  levels that are being addressed. If we assume that power broadening is sufficient to enable addressing the entire  $A^1\Pi$ state, for linear polarization that drives  $\pi$  transitions, we find 24 coherent dark states and no dark angular momentum eigenstates. This should indicate that the dark states in J'' = 1 will evolve in time back into bright states. The effect that these states have on optical cycling will depend on their specific evolution rate, which is likely to differ among each dark state. For this reason, future work may consider separate methods to evaluate the corresponding time-dependence of these states.

A similar evaluation for dark states has been performed with AlF molecules [46]. In these molecules it was found that dark states are composed of linear superpositions of states with different values of  $F_1$  and that the smallest energy splitting between  $F_1$  levels determines the limit on optical cycling rates, namely,  $R_{sc} \simeq 17.5 \times 10^6 \ s^{-1}$ . Given that the splitting in  $F_1$  levels are the same for both AlF and AlCl molecules it is curious that AlCl molecules appear to optically cycle some ~ 3 times slower. By contrast with AlF, the dark states in AlCl are composed of a combination of superpositions between states with different  $F_1$ , F, and  $m_F$  quantum numbers. This difference between dark state compositions likely plays a role in the differences in scattering rates measured in these two systems.

It is possible to limit population from accumulating in dark states and speed up their associated time evolution by introducing additional time dependence to the system [36]. In current molecular laser cooling experiments, magnetic sensitivity in the ground state enables use of external magnetic fields to lift degeneracy among magnetic sublevels  $m_F$  of a given hyperfine level F. The resulting shifts in energy cause population to precess between  $\Delta m_F = \pm 1$  sublevels at a rate determined by the energy splitting, thus "remixing" the ground state and overcoming the inherent dark states. In  $X^1\Sigma^+$  molecules, this method cannot be used to due negligible magnetic sensitivity in the ground state. Instead, time-dependence can be gained through modulating laser polarization. This effect has been explored fairly extensively with TlF molecules [200] and has been simulated to also be effective with AlF molecules [46]. In TlF, recent work has shown that polarization modulation with lasers applied along orthogonal directions and transverse to the molecular beam can lead to large enhancements in optical cycling [201]. Although this geometry would be challenging to implement for laser slowing, transverse beams are built into the geometry necessary for a 3D magneto-optical trap (MOT). This would imply that the known "Radio Frequency MOT" technique (demonstrated with current molecular MOTs [24, 99]) may enable increased optical forces in MOTs with  $X^1\Sigma^+$  ground states.

## 8.6 Repump spectroscopy

Another confirmation for optical cycling is measuring an increased population in higher v'' levels. To observe this we collect fluorescence from molecule excitation out of these states. After initially finding the  $v_{10}$  repump transition we performed spectroscopy of populated rotational levels within the  $X^1\Sigma^+$ , v'' = 1 state using the  $v_{10}$  laser at 265 nm.

In this measurement we introduce the  $v_{10}$  repumping laser in the repumping region (see Fig. 6.1) and expand the beam to ~ 5 mm diameter. This beam passed through the experiment three times and reflected, making a N > 6 passes with an input power of  $\simeq 500$  mW. The probe laser is again made small such that it addresses a smaller solid angle of molecules than both the pump and repump lasers. Both the pump and probe regions use the same laser which is once again tuned to address the peak of the Q-branch, while the repump laser is tuned to address different rotational lines. We determine the recovered fraction using two ratios. In the first, the fluorescence is measured with and without the pump beam, indicating the fraction lost from the v'' = 0 level. The second measurement is a repeat of the first but with the repump laser introduced into the repumping region (see Fig. 6.1). Using these two ratios, the recovered fraction, R, is given by,

$$R = \frac{D - RD}{1 - D},\tag{8.16}$$

where D and RD are the population lost and returned using the first and second described measurements.



FIGURE 8.8: Rotational spectra of population optically pumped into v'' = 1. Population is repumped along  $X^1\Sigma^+ |v'' = 1\rangle \rightarrow A^1\Pi |v' = 0\rangle$  and probed using LIF measured while cycling on  $X^1\Sigma^+ |v'' = 0\rangle \leftrightarrow A^1\Pi |v' = 0\rangle$ . Calculated rotational branching ratios have been used to scale the R-branch to yield accurate values for the state populations. The horizontal line indicates the total population detected via the R-branch. After accounting for a measured 95% saturation of the  $X^1\Sigma^+ |v'' = 1\rangle \rightarrow A^1\Pi |v' = 0\rangle$  transition, measured LIF from the Q-branch coincides with the R-branch total, indicating near unity repumping. A fit to the scaled R-branch LIF provides a lower rotational temperature in v'' = 1 than measured in v'' = 0 (T = 1.3(2) K vs. T = 1.9(2) K), in agreement with the decreased optical pumping of high J levels observed in Fig.8.5.

With the total fraction of lost molecules stemming from a number of different rotational lines (Fig. 8.5) we should expect a similar distribution in the rotational levels populating v'' = 1 if this loss is due to optical cycling. This situation

is seen in Fig. 8.8, which shows a spectroscopic scan over both the Q and Rbranches driven along  $X^1\Sigma^+ |v'' = 1\rangle \rightarrow A^1\Pi |v' = 0\rangle$ , with each R-line scaled by its corresponding rotational branching ratio given in Table 4.1. In the case of efficient repumping, the summed total population of the R-branch will equal that detected on Q. Here, the horizontal line indicates this summed total, with the shaded region indicating statistical measurement uncertainty. We may further identify the repumping efficiency by determining the level of saturation achieved in the transition. By tuning the repump laser power and fitting to a saturation curve, we estimate that the repumping laser returns ~ 95% of the population within v'' = 1. Accounting for this missing 5% places the recovered fraction from the Q-branch in agreement with the summed population from the rotational levels, indicating efficient repumping of the measured population in v''=1.

As discussed for Fig. 8.5, our nominal rotational closure from the Q-branch may be violated by a change of parity in the excited the  $A^1\Pi$  state. For each J' level, this would lead to a leak into the neighboring J'' levels in proportions given by the branching ratios. Our measurement of the v'' = 1 rotational populations provides a second means to inspect the size of this leakage path. In particular, the lack of a Q(0) transition restricts the J = 0 population from optically cycling. This is reflected in Fig. 8.8 as we expect no population in the J'' = 0 level<sup>3</sup>. For the levels that are populated, we extract a rotational temperature of T $\approx 1.3(2)$  K in v'' = 1. This is colder than the temperature measured in v = 0 which was measured at the same time (T= 1.9(2) K in Fig. 6.6b). This a direct reflection of scattering rates on the Q-branch decreasing for increasing rotational levels (Fig. 8.5).

<sup>&</sup>lt;sup>3</sup>The population in the v = 1 is small enough that it is routinely not detectable in fluorescence.

# 8.7 Vibrational branching

Without repumping the population lost during radiative deflection (Fig. 8.9), the imaged molecules are those which have scattered a maximum number of photons, limited by their scattering rate and laser interaction time ( $N_{\text{max}} = R_{\text{sc}}t_{\text{int}}$ ). In this case the branching back into the v'' = 0 state (VBR<sub>00</sub>) is determined by Eqn. 8.8. By repumping population in v'' = 1 along  $X^1\Sigma^+ |v'' = 1\rangle \rightarrow A^1\Pi |v' = 0\rangle$ , VBR<sub>01</sub> is found through VBR<sub>01</sub> =  $R(1 - \text{VBR}_{00})$ , where R is given by Eqn. 8.16.



FIGURE 8.9: Remaining population in v'' = 0 versus scattered photon number in three different situations: i) the main cycling laser alone (black), allowing loss to  $v'' \ge 1$  vibrational levels ii) population v'' = 1 repumped following optical cycling laser (red), iii) populations in v'' = 1 and v'' = 2 repumped following optical cycling (blue). Circles denote measured populations for a give number of scattered photons and solid curves are fits to the data according to the function  $P(N) = r^N$ .

Since our lasers cannot tune far enough to address the  $v_{20}$  transition directly, determining the v'' = 2 population and therefore VBR<sub>02</sub> requires using two repumping stages. In the repumping region (see Fig. 6.1), population is first transferred via the  $v_{21}$  repump laser along  $X^1\Sigma^+ |v''=2\rangle \rightarrow A^1\Pi |v'=1\rangle$ . The  $v_{10}$  laser then returns v'' = 1 molecules to v'' = 0 where they are read out in the probe region via optically cycling on the Q-branch peak. For this measurement, the  $v_{00}$  pump laser is retro-reflected in order to provide a high degree of optical pumping to maximize scattered photon number and therefore sensitivity. As with determining  $VBR_{01}$  we use the value for  $VBR_{00}$  to calibrate for scattered photon number for given amount of loss in order to determine VBR<sub>02</sub>. We find the fraction returned from v'' = 2 to be highly variable using this method. This is likely due to power instabilities in the  $v_{21}$  repump laser during these measurements, but also may stem from to the two-step process required to bring the molecules back into v'' = 0. Unlike with the  $v_{10}$  repumping laser, measuring the repumped fraction from v'' = 2 versus laser intensity did not show saturation. The level of saturation achieved was challenging quantify due to the variable nature of the measurement.

In Fig. 8.9, we plot the remaining fractional population in v'' = 0 versus scattered photon number without repumping vibrational level (black), after repumping population v'' = 1, and following repumping populations in both v'' = 1 and v'' = 2. Assuming that all loss stems from decay into higher vibrational levels in the  $X^1\Sigma^+$ state, we use  $P(N) = VBR^N$  (Eqn. 8.8) as a fitting function to extract vibrational branching ratios for the three situations. This approach not only assumes that vibrational decay is the only loss mechanism but it also assumes all vibrational population has been efficiently returned to the main cycling transition. Although we have demonstrated efficient repumping of the population v'' = 1 (Fig. 8.8), this was not rigorously determined for repumping the v'' = 2 level. As a result, and due to the possible presence of additional loss mechanisms that have yet to be quantified (i.e., photo-ionization, dissociation, and magnetic dark states), the values extracted using Eqn. 8.8 should be considered as bounds on the actual vibrational branching ratios. Fits to the data provided in Fig. 8.9 give  $VBR_{00} \ge 0.9916(4)$ ,  $VBR_{01} \le 6.1(4) \times 10^{-3}$  and  $VBR_{02} \le 1.8(7) \times 10^{-3}$  and a leak from the three laser system of  $VBR_{03+} \le 5(9) \times 10^{-4}$ .

### 8.8 Considerations for multilevel optical cycling

In the current chapter, radiative deflection measurements were probed using a laser tuned to drive  $\Delta J = 0$  transitions along the measured peak of the Q-branch. In Chapter 7, Q-branch spectroscopy indicated that the similar values of X and A state rotational constants lead to the lowest three rotational levels (J = 1 - 3) having nearly identical transition frequencies (see Fig. 7.5). Moreover, measurements of both loss from the cycling transition and population transferred into v'' = 1 further suggest that power broadening, in addition to the spectral overlap of J = 1-3, results in optical cycling on the first 5 rotational levels simultaneously – all with a single laser frequency. Our measurements of both effects over all 5 rotational levels. Ideally, we would like to understand the error this provides to our determined values. An estimate for this error can be found by simulating the deflection of all 5 levels.

We simulate the effect of optically cycling simultaneously on the first 5 rotational levels using a Gaussian distribution to represent each population imaged onto the camera. Each distribution is weighted according to the relative state rotational population from an assumed T = 1.9 K molecular beam. To capture the effects of
both loss and deflection, this is further weighted by  $VBR^N$  and the distribution center shifted in accordance with experimental parameters and the recoil velocity. When combined, we have the following weighted distribution,

$$\rho(N,J) = P_{\rm rot}(J)P(N)e^{-\left(\frac{y+d(N)}{\sigma}\right)^2},\tag{8.17}$$

where  $P_{\rm rot}(J)$ , P(N), and d(N) are given by Eqns. 2.4, 8.8, and 8.10, respectively. Note that the position y accounts for the pump laser propagating in the  $-\hat{y}$  direction. We estimate a relative number of scattered photons for each level using data from the inset of Fig. 8.5. We plot the individual distributions for each J using Eqn. 8.17 as well as the sum of all distributions Fig. 8.10. The latter is normalized to the J = 1 population for clarity.



FIGURE 8.10: Simulated comparison between transverse molecule beam position for individual rotational levels versus the measured sum. This accounts for the rotational temperature distribution and shows that measured LIF, when probing on the Q-branch, underestimates scattered photon number of the J = 1 state.

The largest contribution to the perceived deflection and loss stems from the the first two rotational levels. This is due to the rotational temperature. Nevertheless, the combined profile shows a smaller transverse shift than the sum, corresponding to a perceived lower number scattered photons. Accounting for this, we infer ~ 60 photons are photons scattered from molecules in J = 1, as opposed to the measured 50 photons and thus providing an increased scattering rate for J = 1 of  $R_{sc} \simeq 4.5 \times 10^6 \ s^{-1} \ (\sim \Gamma/45)$ . While not indicated by this figure, the loss is similarly underestimated by the sum. Together, we find that the rotational average used to determine  $VBR_{00}$  results in an underestimate of the value by an amount  $\sim 3.25 \times 10^{-4}$ . This leads to the new estimate  $VBR_{00} \ge 0.9919(4)$ , and a loss from the cycle bound by  $VBR_{03+} \le 1.75(8) \times 10^{-4}$ .

### Chapter 9

## Simulations

In this chapter we consider prospects for trapping AlCl molecules in a 3D MOT. We use the effective Hamiltonian discussed in Chapter 4 and the open source PyLCP python program developed by NIST [202] to produce the equations of motion necessary for describing optical forces and molecule trajectories. In general, capturing the effects of coherences in these simulations requires evaluating the optical Bloch equations [203–205]. However, in AlCl this is very computationally demanding. The matrix used to describe the J = 1 optical cycling transition has dimensions  $144^2 \times 144^2$  and under the current construction of the PyLCP python code takes ~ 2 hours to populate using UConn's high performance computing cluster. Solving the resulting system of equations is somewhat faster, but still poses a practical limitation to running these sorts of simulations with AlCl – at least with the current methods. As a result, the following simulations use rate equations produced by PyLCP. In Chapter 5, we used a simple model to see the relationship between capture velocity and laser power. Here, we use rate equations to provide an improved prediction of this relationship.

#### 9.1 Simulated hyperfine branching

Before performing simulations, we check that our Hamiltonian is correctly interpreted by PyLCP by comparing both calculated and simulated hyperfine branching ratios  $BR_{ij}$  between ground state *i* and excited state *j*. In general, these are calculated with the transition dipole matrix elements of Eqn. 4.29 and using

$$BR_{ij} = \sum_{q} \frac{|d_{ijq}|^2}{\sum_{i} |d_{ijq}|^2}.$$
(9.1)

The sum over q represents the sum over all dipole-allowed transitions. We choose to represent the transition dipole matrix, and therefore the branching ratios, in the basis for which both X and A states are diagonal so that the branching ratios correspond to the energy level diagrams of Figs. 4.4 and 4.5. In doing this, we note again that the state labeling of these energy level diagrams are given as the linear combinations of  $F_1$  quantum numbers shown in Fig. 4.8. We transform the transition dipole matrix using the following change of basis (equivalence transformation),

$$\widetilde{d}_{ijq} = U_{X}^{\dagger} \cdot d_{ijq} \cdot U_{A}, \qquad (9.2)$$

with  $U_X$  and  $U_A$  describing the eigenvector matrices for the X and A states, respectfully. To find the  $BR_{ij}$  from excited state j in a simulation we set the initial population in the excited state and allow it to evolve in the absence of a laser field. Iterating this process over every excited sublevel results in populating the full  $BR_{ij}$  matrix. We note that defining a quantization axis in PyLCP requires an applied magnetic field. Without this, the state ordering appears to change. On the other hand, in the presence of an external magnetic field, PyLCP rediagonalizes the Hamiltonian, once again leaving the state ordering scrambled. In order to correctly identify the states then requires returning the new basis to the original basis following a simulation. The specifics of how this was performed can be found in Appendix B.



FIGURE 9.1: Comparison of the  $X^1\Sigma^+ |v'' = 0, J'' = 1 \rangle \leftrightarrow A^1\Pi |v' = 0, J' = 1 \rangle$ transition hyperfine branching ratios calculated with the transition dipole matrix (left) versus simulated with PyLCP (right). Agreement between both cases provides initial indications that both the Hamiltonian matrices and transition dipole matrix have been correctly coded into PyLCP and that the rate equations reproduce the anticipated results. A  $B_z = 1 \times 10^{-9}$  G magnetic field is used in this simulation to define the quantization axis along the z-axis. We note that by definition  $BR_{ij}$  is normalized to 1. The color scale here ranges between 0 and 0.5.

In Fig. 9.1, we show the comparison between both the calculated branching ratios and those produced via simulations using PyLCP. Agreement with the calculated result confirms that we have correctly implemented the Hamiltonian terms and transition dipole matrix, and further understand how to run the rate equations and determine state population.

#### 9.2 Molecule trajectories in a 3D MOT

PyLCP offers several useful classes for both magnetic fields and laser beam geometries. Moreover, various additional objects enable finding equilibrium forces and time evolution of state populations (the latter being used in Fig. 9.1). In our simulation we use a quadrupole field with a symmetry axis in the x - y plane. As typical, 3 pairs of retro-reflected beams are set orthogonal to one another, but are rotated by 45° about the z-axis relative to the molecular beam. This is done to increase interaction time by a factor of  $\sqrt{2}$ . Furthermore, each beam is treated as having a transverse Gaussian intensity profile. The trapping lasers drive transitions along  $X^1\Sigma^+ |v'' = 0, J'' = 1 \rangle \leftrightarrow A^1\Pi |v' = 0, J' = 1 \rangle$  and we assume no loss out of this cycle to higher vibrational levels.



FIGURE 9.2: Simulated trajectories for AlCl molecules in a 3D MOT configuration using a magnetic field gradient of  $\partial B/\partial z = -75$  G/cm. MOT beams are rotated by 45° about the z-axis and are each 25.4 mm in diameter  $(1/e^2)$  and P = 0.5 W in power. Lasers are detuning from the highest frequency J'' = 1peak by  $\Delta = -\Gamma/2$ . The x-axis here corresponds to the axis in the x - y plane that is 45° between  $\hat{x}$  and  $\hat{y}$ .

For a given set of laser and magnetic field conditions, we simulate molecule trajectories using classical kinematics, updating the molecule's position, velocity and acceleration at even time intervals ( $t_{\text{step}} \sim 1 \,\mu \text{s}$ ). In Fig. 9.2, we show the phase space diagram of optical force versus molecule position and velocity, along with several initial trajectories. Here, the magnetic field gradient is set to  $\partial B/\partial z = -75 \text{ G/cm}$ with left hand circular polarization for beams in the x - y plane. All lasers are detuned from the highest frequency J' = 1 peak by  $\Delta = -\Gamma/2$  and are chosen to have a beam diameter of  $d_{1/e^2} = 25.4 \text{ mm}$  and P = 0.5 W per laser beam. Under these conditions, we find a capture velocity of  $v_c \simeq 20 \text{ m/s}$ . However, laser beam diameter, power, detuning, and magnetic field gradient make for a large parameter space and make finding a maximum for this capture velocity not easy. In the next section we explore this parameter space to find optimized capture velocities.

#### 9.3 3D MOT capture velocity

In Chapter 5, a two-level model was used to show that MOT capture velocity scales non-trivially with laser power and beam diameter. In this model we were able to neglect detuning and magnetic field gradient as we made the assumption that a resonance condition can be satisfied at all points during the molecule's deceleration. In practice, short of chirping either the frequency of the MOT beams or the gradient of the magnetic field the best we can do is find a set of fixed parameters that optimizes capture velocity. Here, we revisit the situation of Chapter 5 using the current rate equation model.

Simulated capture velocity versus laser power is given in Fig. 9.3 for various beam diameters. In these simulations, we simulate molecule trajectories for increasing initial velocity until molecules are no longer captured by the MOT – we define this

as the capture velocity. This process is repeated each time a parameter is changed. Since the  $A^1\Pi$  state is not very sensitive to magnetic fields below a couple hundred Gauss (see Fig. 4.9), tuning of the magnetic field gradient does not dramatically change capture velocity. This can be seen by scanning laser detuning for various field gradients. As a result, the simulations of Fig. 9.3 use a fixed gradient of  $\partial B/\partial z = -75$  G/cm. Each data point corresponds to an optimum detuning found by sweeping laser frequency at different powers and then interpolating the resulting curves to find capture velocity versus power. This is repeated for each beam diameter shown.



FIGURE 9.3: Simulated capture velocity for a 3D MOT of AlCl rotated  $45^{\circ}$  about the z-axis. For each power, laser frequency detuning is optimized for a magnetic field gradient of  $\partial B/\partial z = -75$  G/cm.

The simulated results of Fig. 9.3 follow the trend found in the two-level model presented in Chapter 5 (Fig. 5.1). While capture velocities found using the rate equations are lower, this is expected as a result of not only the inability to maintain

perfect resonance at all times, but also the presence of a partially resolved  $A^{1}\Pi$ state. It is also important to remember that these simulations do not account for coherent dark states in the system. Though for sufficiently low scattering rates, the dark state evolution will be fast enough to not pose a major bottleneck to optical forces. Therefore, at low laser intensities we expect the rate equations to provide a reasonable estimate. This point is reflected in the simulation of optical cycling performed for AIF molecules [46]. To this end, one may consider the trade off between larger beam size at lower intensity and increased interaction time. In this situation, we may maximize capture velocity while minimizing the effect of dark state coherences. Lastly, as discussed in Sec. 8.5.1, the use of polarization modulation is a promising approach for overcoming dark states and regaining the otherwise expected large optical forces [36, 201]. It is therefore suspected that realizing the predicted capture velocities in the higher intensity regime may be enabled by applying the known Radio-Frequency MOT technique to AlCl [24, 99]. One should note that realizing AlCl's full potential by this method would be more technically demanding than in current systems, as it would require switching a  $3\times$ higher magnetic field gradient at frequencies greater than 10 MHz. This would require care to maintain a sufficiently low differential voltage between MOT coils so as to limit parity mixing in the  $A^1\Pi$  state. While challenging, this remains a possible path forward.

### Chapter 10

## Outlook and perspective

In this chapter we tie together the results that have been presented throughout this thesis and return to the central intent of this work; designing an experiment that might realize increased MOT densities from directly laser cooled molecules.

#### 10.1 Summary

In this work, I have presented many of my contributions to the beginnings of an experiment that will serve as the foundation for future studies of many-body ultracold molecular systems. I have introduced a molecular species new to direct laser cooling (AlCl) that has properties which suggest it is a strong candidate for overcoming limited molecular MOT densities in current experiments.

Evaluating AlCl for this purpose required constructing a cyrogenic buffer gas source for producing a bright molecular beam with cold internal temperature. This system was then characterized using a familiar molecular species (SrF) in order to benchmark its performance against results of other experiments. With confirmed operation, increasing the pulse rate for molecule production to as high as 55 Hz led to demonstrating near continuous beams of ablated molecules, amounting to a  $\sim 100 \times$  increase in time averaged molecular flux. Using SrF to further characterize the molecular beam line allowed for realizing a four-level optical cycling scheme which simultaneously drives Stokes and anti-Stoke Raman transitions. This gave way to a sensitive and background-free molecular imaging technique when both fluorescence and laser light are efficiently separated by a band-pass filter. We believe the imaging technique provides a viable path to detecting molecular MOTs in glass cells.

Following initial characterizations of our system with SrF molecules, the experiment was modified as necessary (windows, ablation targets, etc.) to begin studies with AlCl. Fundamentally, this required two new laser systems for cycling and repumping which are capable of generating watt-level powers at 261.7 nm and 265.0 nm as well as a third at 265.2 nm with power in the range of  $\sim$  500 mW. Given the demanding requirements, three custom systems were developed with a novel analog control system that enables auto-locking and re-locking of cascaded second harmonic resonant cavities. This system design was shown to generate a record-level CW power for laser light below 266 nm. After producing and characterizing a molecular beam of AlCl, the 261.7 nm laser system permitted the hyperfine structure of the  $A^1\Pi$  state in  ${}^{27}\text{Al}{}^{35}\text{Cl}$  to be resolved for the first time. Thus, high resolution spectra of both Q and R branches were recorded and used to develop an effective Hamiltonian, constructed in a combined effort with the Hemmerling group at UC Riverside, in order to determine the line centers of the 24 hyperfine levels in the  $X^1\Sigma^+ |v''=0, J''=1\rangle \leftrightarrow A^1\Pi |v'=0, J'=1\rangle$  cycling transitions of AlCl.

Identifying the J = 1 optical cycling transition in AlCl facilitated use of our

high power laser systems to evaluate optical forces. In these measurements, the extracted molecular properties corresponded to an average of the properties of several rotational levels as the optical cycling Q-branch is composed of overlapping states of different J. Nevertheless, initial measurements of optical pumping suggests a single laser frequency can optically pump > 400 magnetic sub-levels out of the cycling transition. By radiative deflection, we measure a maximum scattering rate of  $R_{sc} = 3.7 \times 10^6 \ s^{-1}$ , or  $\Gamma/54$ , corresponding to an acceleration of  $a = 9.25(3) \times 10^4 \ m/s^2$ . Measurements of vibrational branching ratios allowed placing a lower bound on decay from the  $A^{1}\Pi | v' = 0 \rangle$  state into v'' = 0 and upper bounds on those decaying into both v'' = 1 and v'' = 2. Accounting for the several cycling rotational levels, we infer vibrational branching ratios of VBR<sub>00</sub>  $\geq 0.9919(4)$ , VBR<sub>01</sub>  $\leq 6.1(4) \times 10^{-3}$ , and VBR<sub>02</sub>  $\leq 1.8(7) \times 10^{-3}$  and an increased scattering rate for molecules in J = 1 of  $R_{sc} \simeq 4.5 \times 10^6 \ s^{-1} \ (\sim \Gamma/45)$ , or  $a = 1.13(3) \times 10^5 \ m/s^2$ .

The work of this dissertation concludes with simulations of AlCl molecules in a 3D MOT. Using rate equations produced by PyLCP [202], various MOT parameters are tuned to optimize capture velocity. Experimentally realizable laser intensities offer estimated capture velocities as high as 30 m/s. Although coherent dark states are suspected to limit the accuracy of these simulations in the high intensity regime, simulations with large diameter beams and low corresponding intensity still appear to offer larger capture velocities than in current systems.

#### 10.2 Outlook

The work that has been conducted in this dissertation demonstrates that sizable optical forces can be applied to AlCl molecules, even in the presence of coherent dark states. Our measurements of branching ratios suggest that, with two repumping lasers, a sufficient number of photons may be scattered to enable directly slowing molecules from a buffer gas source. The measured large span of the excited state hyperfine structure in J' = 1 offers a route to continuously addressing the changing Doppler shift of molecules during this slowing, thus removing the need for frequency chirping or phase modulating the slowing laser. Given these results, slowing a beam of AlCl to rest appears promising and may be achievable over distances below 5 cm.

To better understand the prospect for trapping AlCl in a 3D MOT it will be important to characterize the  $A^1\Pi$  state sensitivity to magnetic fields. In viewing our simulations, generating both damping and confining forces look possible. However, neglecting coherences will likely lead actual results to diverge from simulations. This motivates further work exploring methods for overcoming the computational challenges associated with performing simulations using the optical Bloch equations. In any case, there are several interesting approaches for overcoming these dark states, such as laser frequency or polarization modulation.

Recent work with TlF molecules [201] offer an exciting prospect for using the standard RF MOT technique to overcome dark states and maximize capture velocities in a 3D MOT. Pairs of orthogonal polarization modulated laser beams appear to be key for polarization modulation to be effective in molecules TlF. As a result, this technique may not be very effective for forward slowing. The presence of a partially resolved excited state, however, also leads one to consider using an AOM to generate laser frequencies to individually address each  $F_1$  peak. Combining these techniques, one can envision a multi-frequency forward slowing path and a polarization switching MOT – provided the technical challenges of field switching at high frequencies can be overcome. Assuming a high MOT capture velocity of ~ 20 m/s and current conditions for optical forces in slowing, we estimate molecules may be trapped some ~ 3 cm from the cell aperture. While this is likely not a practical situation given the size of the source, this generally indicates a large increase in captured molecular flux relative to current systems.

Ultimately, AlCl is an exciting molecule for laser cooling and offers a different approach than has traditionally been taken in molecular cooling experiments. As with many things, time will tell how this molecule behaves, but for the moment, we remain optimistic.

#### 10.3 Perspective

My time working at UConn with Professor McCarron has been one to remember. Together we arrived at UConn and inherited the lab space of William Stwalley along with a large number of experimental apparatuses. We not only disassembled this large lab but built one of our own that was used for two years before it was taken apart and moved to a new building. Below are a number of pictures of the old and new lab spaces.



FIGURE 10.1: Picture of old lab space prior to moving buildings. Here, we have the experimental setup used to study SrF molecules.



FIGURE 10.2: Nearly empty optical table prior to moving to a new lab space. On the table is our molecular beam line.



FIGURE 10.3: Picture of the new empty lab space prior to moving in our equipment.



FIGURE 10.4: Picture of the new lab space after moving in and continuing to build the AlCl experiment.



FIGURE 10.5: Picture of the UV laser table with fiber amplifiers, doubling cavities, and related electronics. The seed lasers can be seen to the right.

## Appendix A

## Cavity mode matching

#### A.0.1 Complex beam parameter

An electromagnetic wave in free space is described by the paraxial wave (or Hemholtz) equation (see page 626 of Ref. [206]),

$$(\nabla^2 + k^2)E(x, y, z) = 0,$$
 (A.1)

where E(x, y, z) is the wave electric field amplitude and k its corresponding wavevector. There are various ways to solve this equations, many of which are well-covered in *Lasers* by Siegman [206] (Chapter 16). In general, solutions take the form,

$$E(x, y, z) = u(x, y, z)e^{-ikz},$$
(A.2)

where for cartesian coordinates u(x, y, z) is given by an Hermite-gaussian modes, whereas for cylindrical coordinates its given by Laguerre-gaussian modes. In either case, it is convenient to write this solution for a gaussian beam with spot size  $\omega_0$ and wavefront curvature  $R_0 = \infty$  as [206]

$$u(x, y, z) = \sqrt{\frac{2}{\pi}} \frac{q_0}{\omega_0 q(z)} e^{-ik(z + \frac{x^2 + y^2}{2q(z)})}.$$
(A.3)

The term q(z) contains the relevant information about the beam's wavefront curvature and waist and is known as the complex beam parameter,

$$\frac{1}{q(z)} = \frac{1}{R(z)} - i\frac{\lambda}{\pi n\omega(z)^2},\tag{A.4}$$

where again w(z) and R(z) are the beam waist and radius of curvature of the wavefront, respectively. (We will see in a moment how we define  $q_0$ ). This definition enables the standard ray transfer matrix analysis to be extended for accommodation of Gaussian beams. For a given ray transfer matrix, an incoming Gaussian beam will be transformed according to,

$$q_f(z) = \left(\frac{Aq_i(z) + B}{Cq_i(z) + D}\right),\tag{A.5}$$

where A through D are the elements of a ray transfer matrix. We may then unpack either the wavefront curvature or beam radius along the propagation direction by taking the real or imaginary part of Eqn. A.5 and rearranging.

Using this method, several useful relationships can be found for q(z) and therefore  $\omega(z)$  and R(z). As an example, if we know q(z) at a particular value of z, e.g.,  $q(z) = q_o$  at  $z = z_o$ , the value of q(z) at any subsequent point during free space propagation is determined by applying the ABCD elements of  $M_{fs}(z)$  to Eqn. A.5. Doing so results in

$$q(z) = q_o + (z - z_o).$$
 (A.6)

However, in viewing Eqn. A.4, we can see that by defining  $z_o = 0$  to be at the beam waist (where  $R(0) \to \infty$ ), when inverted, Eqn. A.4 reduces to  $q(0) = q_{\text{ focus}} = i\pi n\omega_o^2/\lambda = iz_R$ , describing a focal plane for the system. Applying this to Eqn. A.5 leads to

$$q(z) = z + iz_R,\tag{A.7}$$

allowing for a simple description of how a Gaussian beam diverges during propagation in a continuous medium of index n. Together, using equations A.4 and A.7, along with a little algebra, we recover the well known equations for a Gaussian beam freely propagating along z,

$$\omega(z) = \omega_o \sqrt{1 + \left(\frac{z}{z_R}\right)^2},\tag{A.8}$$

$$R(z) = z \left[ 1 + \left(\frac{z_R}{z}\right)^2 \right].$$
(A.9)

#### A.0.2 Mode-matching

In general, knowing the beam waist and its location is sufficient for determining the beam properties at all points along z. In the context of optical cavities, optimal coupling of the laser field to modes supported by the cavity requires matching the laser beam's wavefront curvature to that of the cavity. This is equivalent to having the laser beam focus to the same minimum waist, at the same location, as is dictated by the cavity geometry. Therefore, to optimize mode-matching to a cavity one needs the location and waist supported by the cavity and that of the incoupling laser beam (i.e., four parameters). Using Eqns. A.4 & A.5 then provides a path for choosing a suitable ray transfer matrix and corresponding lenses for matching wave-front curvatures.

While a single lens can in principle provide a suitable beam waist and location, practical considerations such as availability of optics and table space often limit this approach. Using a pair of lenses is often adequate and is what has been used in this work. Below, we provide the general calculation and a useful graphical method for finding the lens pair needed for cavity mode-matching.

For a two lens system we have a total of five matrices (and five variables); two for the focusing caused by the lenses and three to describe propagation through free-space before, after, and between them. Combining these gives the total ray transfer matrix for the system. As usual, multiplication of matrices is done from right to left.

$$M_{\text{total}} = M_{\text{fs}}(d_3) \cdot M_{\text{lens}}(f_2) \cdot M_{\text{fs}}(d_2) \cdot M_{\text{lens}}(f_1) \cdot M_{\text{fs}}(d_1).$$
(A.10)

Here, we use the thin lens approximation in our calculations. This holds so long as the lens radius is small relative to the image and object distances; for sufficiently compact mode-matching setups, calculations using thick lenses may be required. With eqs. (A.4) & (A.5) we may find the final beam waist,  $\omega_f$ , for an arbitrary  $M_{\text{total}}$ , as a function of ABCD elements,

$$\omega_f = \sqrt{\frac{\lambda}{\pi z_{R,i}} \frac{z_{R,i}^2 A^2 + B^2}{AD - BC}},\tag{A.11}$$

where  $z_{R,i} = \pi \omega_i^2 / \lambda$  with  $\omega_i$  being the initial waist of the laser occurring at z = 0, and thus  $q_i(z) = i z_{R,i}$ . For our case, we use the ABCD matrix elements of eq. (A.10) to find the resulting waist produced by the four dimensional parameter space spanned by  $d_1$ ,  $f_1$ ,  $d_2$ , and  $f_2$ . For each combination of parameters and associated waist, there is exactly one corresponding value for  $d_3$ . To find this distance, we take the imaginary part of  $q_f(z)$ , eq. (A.5), and minimize it with respect to  $d_3$ , as the location of the minimum value of  $\text{Im}(q_f(z))$  corresponds to the location of the waist,  $\omega_f$ .

In practice, while one seeks to achieve a waist matching that of the cavity mode, there are several combinations of parameters which produce this waist, all with different  $d_3$  distances. For the required waist, each  $d_3$  is related to the size of the beam at lens two and it's corresponding focal length. Given the physical constraints of one's optical layout, juggling this with the needed value of  $\omega_f$  is challenging, all while being constrained by commercially available optics. It is therefore useful to simplify interpretation using a graphical method for optimization. Below, in Fig. A.1, we provide one such method, where curves for both  $\omega_f$  and  $d_3$  are overlaid for a given set of  $\omega_i$ ,  $d_1$ ,  $f_1$ , and  $f_2$  values while varying the lens separation distance,  $d_2$ .



FIGURE A.1: Convenient method for determining the required values needed in a two lens system for mode matching. Here, as an example, we have used the values  $\omega_i = 0.9 \text{ mm}$ ,  $d_1 = 25.4 \text{ mm}$ ,  $f_1 = 125 \text{ mm}$ , and  $f_2 = -75 \text{ mm}$ .

Below, in Fig. A.2 we show the calculated beam propagation for parameters determined for mode matching from the infrared optical fiber output to in-coupling waist of the first high power doubling cavity. As with our setup, this calculation using two spherical lenses ( $f_1 = 125$  mm and  $f_2 = -75$  mm) and relies on both the paraxial and thin lens approximation.



FIGURE A.2: Calculated beam propagation for mode matching from the infrared fiber amplifier output to the in-coupling waist of the IR to VIS cavity. Here,  $\omega_i = 0.9 \text{ mm}, d_1 = 25.4 \text{ mm}, d_2 = 57.5 \text{ mm} f_1 = 125 \text{ mm}, \text{ and } f_2 = -75 \text{ mm}.$ 

Here, the beam can be seen as nearly collimated as it emits from the optical fiber at d = 0. The beam is then focused by the first positive focal length lens at d = 25.4 mm. Well before reaching its waist, the convergence rate of the beam is reduced using a negative focal length lens at d = 82.9 mm so that the desired beam waist occurs at the required location (d = 43.9 cm). We show the beam further propagating through the cavity, reflecting off a planar mirror and then off a curved mirror (d = 93.7 cm) prior to the crystal. We note that we have neglected the Brewster-angled interface into the crystal in this calculation. While not shown, measurements of the beam radius at various locations were used to confirm the calculation.

#### A.0.3 Ray tracing matrices

Below we provide the ray tracing matrices used in the above calculation.

Free space: 
$$M_{\rm fs}(d) = \begin{pmatrix} 1 & d/n_o \\ 0 & 1 \end{pmatrix}$$
 (A.12)

Thin lens: 
$$M_{\text{lens}}(f) = \begin{pmatrix} 1 & 0 \\ -1/f & 1 \end{pmatrix}$$
 (A.13)

Curved mirror vertical: 
$$M_{mv}(R,\theta) = \begin{pmatrix} 1 & 0 \\ -2\cos(\theta)/R & 1 \end{pmatrix}$$
 (A.14)

Curved mirror horizontal: 
$$M_{mh}(R,\theta) = \begin{pmatrix} 1 & 0 \\ -2/(R\cos(\theta)) & 1 \end{pmatrix}$$
 (A.15)

(A.16)

d describes the free space propagation of the beam, f gives the lens focal lens, and R and  $\theta$  are used to describe the radius of curvature and angle of incidence on a curved mirror.

## Appendix B

## Recovering state ordering in PyLCP

For any nonzero magnetic field, PyLCP diagonalizes the Hamiltonian and separately rotates the transition dipole matrix  $d_{ijq}$  into a basis in which the quantization axis is defined along  $\hat{z}$ . This is performed using the equivalence transformation,

$$\widetilde{d}_{ijq} = U_{\mathrm{X,B}}^T \cdot d_{ijq} \cdot U_{\mathrm{A,B}},\tag{B.1}$$

where  $U_{X,B}$  and  $U_{A,B}$  are used here to denote the eigenfunction matrices used for bringing  $H_X$  and  $H_A$  into their respective diagonal forms. This oftentimes leads to a different state ordering than the input basis. For large systems, such AlCl, this can be challenging in situations where one would like to read out individual state populations of, say, the ground state, following a simulation. Returning to the original basis, where the ordering is known, requires producing a matrix that can be transformed via  $U_{X,B}$  and  $U_{A,B}$ . In general, we can do this by reading out the ground state populations as one dimension of the matrix and repeating the simulation for populations beginning in each excited state to produce the other. This procedure was used in simulating the hyperfine branching ratios in Fig. 9.1.

When running individual simulations, producing the entire matrix can be time consuming and makes the above method unattractive. If our simulations are allowed to reach a steady state, however, the resulting state population will be independent of initial conditions. This allows the necessary matrix to be constructed simply by repeating the population vector from the a single simulation. Moreover, running the simulation with equal populations for all excited states generally removes the need for a steady state to be reached. In either case, we can then use the resulting ground state population vector  $\tilde{P}$  to form a new matrix – the new dimension created, again, by repeating this vector for each excited state position in the matrix. With this matrix formed, we can then transform back to the original basis to regain state ordering using

$$P = U_{\rm A} \cdot \widetilde{P} \cdot U_{\rm X}^T. \tag{B.2}$$

In PyLCP, one finds  $U_{X,B}$  and  $U_{A,B}$  through the calls rateeq.hamiltonian.U[0] and rateeq.hamiltonian.U[1], respectively.

# Appendix C

## Crystal parameter calculations

The relationship between material refractive index and wavelength is described using Sellmeier equations of the form,

$$n_i(\lambda) = \sqrt{A_i + \frac{B_i}{\lambda^2 - C_i} - D_i \lambda^2},$$
 (C.1)

where A, B, C, and D are empirically determined coefficients specific to each crystal axis for a given material. Changes in crystal temperature can effect refractive indices differently and require modification of Eqn. C.1. This can be approximated using,

$$n_i(\lambda, T) = n_i(\lambda) + \frac{dn_i(\lambda)}{dT}(T - T_o), \qquad (C.2)$$

with  $dn_i/dT$  corresponding to the temperature sensitivity of index  $n_i$  and  $T_o$  is the temperature at which the Sellmeier coefficients are defined. For the information

presented in Figs. 5.3 and 5.4, the Sellmeier coefficients used for BBO and CLBO come from Refs. [207] and [208], respectively.

A birefrigent crystal has refractive indices which depend on both polarization angle and the axis of propagation. These indices are typically denoted as ordinary and extraordinary,  $n_o$  and  $n_e$ , respectively. This type of crystal is needed for harmonic generation in order to maintain the relative phase between fundamental and harmonic waves. In the case of a uniaxial crystal, such as the ones used here (actually negative uniaxial), there is a symmetry axis in which the crystal exhibits no birefrigence. This is referred to as the optic axis. Light that is polarized perpendicular to this axis experiences index  $n_o$  for any propagation direction k, i.e., it has no angular dependence. By comparison, light polarized parallel to this axis experiences an angle-dependent extraordinary index  $n_e(\theta)$ . Under Type I phase matching, two fundamental photons at  $\omega$  combine to generate one higher energy photon at  $2\omega$  which has polarization orthogonal to the fundamental beam. This relationship allows one to use the crystal angle, leveraging the angular dependence of  $n_e$ , to tune the relative phase between the fundamental and SH waves such that  $n_e(2\omega,\theta) = n_o(\omega)$ . This is the technique of Type 1 critical phase matching, in which, for a negative biaxial crystal  $(n_e < n_o)$  fundamental photons are polarized along the ordinary axis and SH photons along the extraordinary (often denoted o + o + e) [154]. The optimum angle is given by [209],

$$\theta = \arcsin\left(\sqrt{\left(\frac{n_{e2}}{n_{o1}}\right)^2 \frac{n_{02}^2 - n_{o1}^2}{n_{o2}^2 - n_{e2}^2}}\right),\tag{C.3}$$

where  $n_{o1}$ ,  $n_{o2}$ ,  $n_{e1}$ , and  $n_{e2}$  describe the ordinary and extraordinary indices for the fundamental (1) and second harmonic (2), and are calculated using Eqn. C.1. The effective doubling coefficient  $d_{eff}$  of a nonlinear crystal varies depending on the orientation of the propagating laser relative to the optic axis. Moreover, for angles other than  $\theta = 0^{\circ}$  or  $\theta = 90^{\circ}$  the extraordinary beam (the second harmonic) experiences a separation between the Poynting vector and its propagation direction which leads to a reduction in the achievable doubling efficiency as overlap between the fundamental and SH beams reduces with propagation distance. This effect is known as walk-off and is calculated according to [209],

$$\rho = \arctan\left(\left(\frac{1}{n_{e2}^2} - \frac{1}{n_{o2}^2}\right)\frac{\sin(2\theta)}{2n_{o1}^2}\right).$$
 (C.4)

For some crystals (e.g. LBO), phase matching can be achieved through temperature tuning, i.e, non-critical phase matching, allowing for  $\theta = 0^{\circ}$  or  $\theta = 90^{\circ}$ . However, this is not possible for crystals like BBO or CLBO as they do not possess sufficient temperature dependence in their refractive indices and thus require using the method of critical phase matching.

We express the nonlinear optical coefficients for CLBO, BBO, and LBO crystals using the relations provided in Ref. [210], namely,

$$d_{\rm eff}(\rm CLBO) = d_{36} \sin\theta \ (\phi = 45^\circ), \tag{C.5}$$

$$d_{\rm eff}(BBO) = d_{11}\cos\theta + d_{31}\sin\theta \ (\phi = 0^{\circ}), \tag{C.6}$$

$$d_{\rm eff}(\rm LBO) = d_{32}\cos\phi \ (\theta = 90^\circ). \tag{C.7}$$

Here,  $d_{36}(\text{CLBO}) = 0.96 \text{ pm/V}$ ,  $d_{11}(\text{BBO}) = 1.78 \text{ pm/V}$ ,  $d_{31}(\text{BBO}) = 0.17 \text{ pm/V}$ , and  $d_{32}(\text{LBO}) = 1.18 \text{ pm/V}$ . For generating  $\lambda = 261.7 \text{ nm}$  light from a  $\lambda = 523 \text{ nm}$ fundamental beam we calculate various properties provided in Table F.1.

Property	CLBO	BBO
Phase matching angle $(\theta)$	$64^{\circ}$	49°
Walk-off angle $(\rho)$	$1.79^{\circ}$	$4.79^{\circ}$
Effective nonlinear doubling coefficient $(d_{eff})$	0.86	1.31
Temperature bandwidth	$8.3^{\circ}\mathrm{C}\cdot\mathrm{cm}$	$4.5^{\circ}\mathrm{C}~\mathrm{cm}$
Spectral bandwidth	$0.13 \text{ nm} \cdot \text{cm}$	$0.07 \text{ nm} \cdot \text{cm}$

TABLE C.1: Properties for CLBO and BBO crystals calculated using the information provided in this appendix. The stated temperature and spectral bandwidths come from Ref. [211].

# Appendix D

# **Electronic schematics**

In this appendix I provide a few electronic schematics that I designed and used throughout this work. All but the high current feedforward circuit design were printed to PCBs. It in worth noting that in circuits requiring low noise performance I tend to use capacitance multipliers following the regulated voltage. These are great tools for generating low corner frequency filters in situations where current drawn would otherwise cause an undesirable voltage drop. These circuits are covered nicely in Ref. [212].



FIGURE D.1: Sum/difference Hänsch lock detector. This circuit provides both A + B and A - B outputs with signals A and B detected on photodiodes D1 and D2.



FIGURE D.2: Hobbs autobalanced photodetector. For more information on this circuit see the following References [212–214]



FIGURE D.3: Window comparator circuit used for autolocking/relocking doubling cavities. This circuit is designed to be used



FIGURE D.4: Electronic schematic for the high current feedforward circuits used on each ECDL seed laser in the UV system. This design is a natural extension to the one initially provided in Ref [174] that allows larger currents be used for feedforward.
# Appendix E

# Optimizing Hänsch-Couillaud error signals in a doubling cavity

Here, I provide a general description of how we optimize the error signal from a Hansch-Couillaud style lock on a doubling cavity. Provided the reflected light is properly incident on the photodiodes of the difference detector, one has three variables to tune: 1)  $\lambda/2$  waveplate, 2)  $\lambda/4$  waveplate, and 3) the input offset of the servo. As shown in Chapter 5, Fig. 5.2, the system in question corresponds to a p-polarized incident beam, which upon reflection is sampled by a ~ 1% pick off and directed through the two waveplates and a PBS onto the differencing photodiodes. In such a system, the following approach is typically adequate to achieving a proper lock on the peak of resonance.

1. Set the  $\lambda/2$  waveplate so that the fast axis is at  $\theta \approx 22.5^{\circ}$  relative to vertical as this will rotate the p-polarized light by  $\approx 45^{\circ}$  relative to the plane of the table, allowing linear polarization to split equally through the PBS.

- 2. Disconnect the error signal from the servo input and zero the input offset by viewing the error monitor on an oscilloscope.
- 3. Scan the cavity and adjust the  $\lambda/4$  waveplate until a symmetric error signal is seen. This will often occur at a near zero offset.
- 4. Regardless of this offset, adjust the servo input offset such that the offresonance condition coincides with  $\sim 0$  V.
- 5. Lock the cavity and make minor input offset adjustments until the light reflected (or SHG output) is minimized, corresponding to locking at the resonance center.

Following this, the cavity should lock easily and recover from unlocking events very quickly.

# Appendix F

# Effective Hamiltonian calculations

We opt for using the tensor respresentation of the Hamiltonian terms when evaluating matrix elements as this facilitates performing a large number of calculations without the need to rederive each matrix element. The complex coupling between different angular momenta are conveniently stored in 3-j and 6-j symbols. Conversion between the standard operator form and spherical tensor form can look at first glance opaque, however, in practice, use of reference tables from various sources reduces the challenges of evaluation to simple pattern matching. But, one must still be careful for typos in these sources! Below, I provide the relations used to evaluate the Hamiltonian elements for both electronic states of AlCl.

### F.1 Tensor operator cheat sheet:

#### F.1.1 Wigner-Eckart theorem

$$\langle \eta, j, m | T_q^k(\mathbf{A}) | \eta', j', m' \rangle = (-1)^{j-m} \begin{pmatrix} j & k & j \\ -m & q & m \end{pmatrix} \langle \eta' | | T^k(\mathbf{A}) | | \eta, j \rangle, \quad (F.1)$$

where k indicates the tensor rank and q is the transition type which runs from -k to k. This can be found on pg. 163 of Ref. [135].

#### F.1.2 Selected analytic forms

Analytic forms used to evaluate the 3 - J symbols governing rotational branching ratios. These are found in Appendix C of Ref. [135].

$$\begin{pmatrix} j+1 & 1 & j \\ -m \mp 1 & \pm 1 & m \end{pmatrix} = (-1)^{j-m+1} \sqrt{\frac{(j \pm m+1)(j \pm m+2)}{(2j+1)(2j+2)(2j+3)}}$$
$$\begin{pmatrix} j & 1 & j \\ -m \mp 1 & \pm 1 & m \end{pmatrix} = \pm (-1)^{j-m} \sqrt{\frac{(j \mp m)(j \pm m+1)}{2j(j+1)(2j+1)}}$$
$$\begin{pmatrix} j-1 & 1 & j \\ -m \mp 1 & \pm 1 & m \end{pmatrix} = (-1)^{j-m} \sqrt{\frac{(j \mp m)(j \mp m-1)}{2j(2j-1)(2j+1)}}$$
(F.2)

#### F.1.3 Irreducible tensors

Tensor of rank 1:

$$\langle \eta, j | | T^1(\mathbf{A}) | | \eta', j' \rangle = \sqrt{j(j+1)(2j+1)}.$$
 (F.3)

Tensor of rank 2:

$$\langle \eta, j | | T^2(\mathbf{A}) | | \eta', j' \rangle = \delta_{j,j'} \frac{1}{6\sqrt{2}} \sqrt{(2j-1)2j(2j+1)(2j+2)(2j+3)}.$$
 (F.4)

Both relations above are found on pg. 163 of Ref. [135].

#### F.1.4 Quadrupole interaction:

$$\langle I | | T^{2}(\mathbf{Q}) | | I \rangle = \begin{pmatrix} Q \\ \overline{2} \end{pmatrix} \begin{pmatrix} I & 2 & I \\ -I & 0 & I \end{pmatrix}^{-1}$$
(F.5)

Axial component of the electric quadrupole interaction  $(eq_0Q)$  (Eqn. 8.27 of Ref. [135]). This describes the electric field gradient (negative actually) along the internuclear axis (q = 0),

$$\langle \eta', \Lambda' | T_0^2(\nabla \mathbf{E}) | \eta, \Lambda \rangle = -(q_o/2).$$
 (F.6)

States with a  ${}^{1}\Pi$  configuration also have a component of this interaction lying perpendicular to the internuclear axis ( $eq_2Q$ ). (Eqn. 7.303 of Ref. [135]).

$$\langle \eta', \Lambda = \pm 1 | T_{q=\pm 2}^2(\nabla \mathbf{E}) | \eta, \Lambda = \mp 1 \rangle = -\frac{q_2}{2\sqrt{6}}$$
(F.7)

#### F.1.5 Scalar products

It is often the case, such as with the  $H_{L \cdot I_{\alpha}}$  terms, that we must deal with scalar tensor products. To handle this, we use Eqn. 5.71 of Ref. [75].

$$\langle \eta, j_{1}, j_{2}, j, m | |T_{q_{1}}^{k_{1}}(\boldsymbol{A}_{1})T_{q_{2}}^{k_{2}}(\boldsymbol{A}_{2})| |\eta', j_{1}', j_{2}', j', m' \rangle =$$

$$\delta_{j,j'}\delta_{m,m'}(-1)^{j_{1}'+j_{2}+j} \left\{ \begin{array}{c} j_{1}' & j_{2}' & j \\ j_{2} & j_{1} & k \end{array} \right\} \langle \eta, j_{1}| |T^{k_{1}}(\boldsymbol{A}_{1})| |\eta', j_{1}'\rangle \langle \eta, j_{2}| |T^{k_{2}}(\boldsymbol{A}_{2})| |\eta', j_{2}'\rangle$$

$$(F.8)$$

#### F.1.6 Composite systems

We also often find when evaluating reduced matrix elements that we have an operator that only acts on a subset of the quantum numbers used to describe the wavefunctions. In this case we can use the following equations (Eqns. 5.72 and 5.73 of Ref. [75]), Note primes have been changed relative to Zare reference to maintain convention held by Ref. [135].

$$\langle \eta, j_1, j_2, j | |T^k(\mathbf{A}_1)| | \eta', j_1', j_2', j' \rangle =$$
  
$$\delta_{j_2, j_2'}(-1)^{j_1 + j_2 + j' + k} \sqrt{(2j' + 1)(2j + 1)} \begin{pmatrix} j_1' & j' & j_2 \\ j & j_1 & k \end{pmatrix}$$
(F.9)

or

$$\langle \eta, j_1, j_2, j | |T^k(\mathbf{A}_2)| | \eta', j'_1, j'_2, j' \rangle =$$
  
$$\delta_{j_1, j'_1}(-1)^{j_1 + j'_2 + j + k} \sqrt{(2j' + 1)(2j + 1)} \begin{pmatrix} j'_2 & j' & j_1 \\ j & j_2 & k \end{pmatrix}$$
(F.10)

#### F.1.7 Wigner rotations

A spherical tensor operator  $T_p^k(\mathbf{A})$  in laboratory-fixed coordinates can be represented in molecule-fixed coordinates using the Wigner D-matrix to rotate it onto the intermolecular axis. This is given by Eqn. 5.143 of Ref. [135] as,

$$T_p^k(\boldsymbol{A}) = \sum_q \mathcal{D}_{pq}^k(\omega)^* T_q^k(\boldsymbol{A})$$
(F.11)

Evaluation of this rotated operator is accomplishment by the Wigner-Eckart theorem,

$$\langle \eta, \Omega, j | |\Sigma_q D^k_{.q}(\omega)^* T^k(\boldsymbol{A})| |\eta', \Omega', j'\rangle =$$

$$\Sigma_q(-1)^{j-\Omega} \sqrt{(2j+1)(2j'+1)} \begin{pmatrix} j & k & j' \\ -\Omega & q & \Omega' \end{pmatrix} \langle \eta | |T^k(\boldsymbol{A})| |\eta'\rangle,$$
(F.12)

where the dot replace p is used to indicate this element has been reduced in the laboratory-fixed coordinate system as far as possible.

### **F.2** $X^1\Sigma^+$ Hamiltonian

We describe the ground electronic state using the following Hamiltonian terms,

$$H_{X^{1}\Sigma^{+}} = H_{e} + H_{\text{vib}} + H_{\text{rot}} + H_{Q_{0,\text{Al}}} + H_{Q_{0,\text{Cl}}}.$$
 (F.13)

Terms beyond  $H_{\rm rot}$  are given below.

$$\mathbf{F.2.1} \quad H_{\mathbf{Q}_{0,\mathrm{Al}}}$$

$$H_{Q,A1} = \frac{(eq_0Q)_{A1}}{4} (-1)^{J+J'+I_{A1}+F_1-\Lambda} \sqrt{(2J+1)(2J'+1)} \begin{cases} J' & I_{A1} & F_1 \\ I_{A1} & J & 2 \end{cases} \begin{pmatrix} I_{A1} & 2 & I_{A1} \\ -I_{A1} & 0 & I_{A1} \end{pmatrix}^{-1} \begin{pmatrix} J & 2 & J' \\ -\Lambda & 0 & \Lambda' \end{pmatrix}$$
(F.14)

### **F.2.2** $H_{Q_{0,Cl}}$

$$H_{Q,Cl} = \frac{(eq_0Q)_{Cl}}{4} (-1)^{2J+I_{Al}+2F'_1+I_{Cl}+F+2-\Lambda} \sqrt{(2F_1+1)(2F'_1+1)(2J+1)(2J'+1)} \\ \begin{cases} F'_1 & I_{Cl} & F \\ I_{Cl} & F_1 & 2 \end{cases} \begin{pmatrix} I_{Cl} & 2 & I_{Cl} \\ -I_{Cl} & 0 & I_{Cl} \end{pmatrix}^{-1} \begin{cases} J' & F'_1 & I_{Al} \\ F_1 & J & 2 \end{cases} \begin{pmatrix} J & 2 & J' \\ -\Lambda & 0 & \Lambda' \end{pmatrix}$$
(F.15)

### F.3 $A^{1}\Pi$ Hamiltonian

The excited electronic  $A^1\Pi$  state is describe by,

$$H_{A^{1}\Pi} = H_{e} + H_{\text{vib}} + H_{\text{rot}} + H_{\Lambda} + H_{L \cdot I_{\text{Al}}} + H_{L \cdot I_{\text{Al}}} + H_{Q_{0,\text{Al}}} + H_{Q_{0,\text{Cl}}} + H_{Q_{2},\text{Al}}, \quad (F.16)$$

where, again, terms beyond  $H_{\rm rot}$  are provided below.

### **F.3.1** $H_{\text{L}\cdot\text{I}_{\text{Al}}}$

$$H_{\text{L-I}_{\text{Al}}} = a_{Al}\Lambda(-1)^{J+J'+I_{\text{Al}}+F_{1}-\Lambda}\sqrt{(2J+1)(2J'+1)I_{\text{Al}}(I_{\text{Al}}+1)(2I_{\text{Al}}+1)} \begin{cases} J' & I_{\text{Al}} & F_{1} \\ I_{\text{Al}} & J & 1 \end{cases} \begin{pmatrix} J & 2 & J' \\ -\Lambda & 0 & \Lambda' \end{pmatrix}$$
(F.17)

Note that the  $\Lambda$  term comes from the eigenvalue of  $\mathbf{L}_z$ , i.e.  $\langle \eta, \Lambda | |T_{q=0}^1(\mathbf{L})| |\eta', \Lambda' \rangle = \Lambda$ .

### **F.3.2** $H_{\text{L}\cdot\text{I}_{\text{Cl}}}$

$$H_{L \cdot I_{\rm Cl}} = a_{Cl} \Lambda (-1)^{2J + I_{\rm Al} + 2F'_1 + I_{\rm Cl} + F + 1 - \Lambda}$$

$$\sqrt{(2J+1)(2J'+1)(2F_1+1)(2F_1'+1)I_{\rm Cl}(I_{\rm Cl}+1)(2I_{\rm Cl}+1)}$$

$$\begin{cases} F'_1 & I_{\rm Cl} & F \\ I_{\rm Cl} & F_1 & 1 \end{cases} \begin{cases} J' & F'_1 & I_{\rm Al} \\ F_1 & J & 1 \end{cases} \begin{pmatrix} J & 2 & J' \\ -\Lambda & 0 & \Lambda' \end{pmatrix}$$
(F.18)

F.3.3  $H_{Q_0,Al}$ 

$$H_{Q_{0},Al} = \frac{(eq_{0}Q)_{Al}}{4} (-1)^{J+J'+I_{Al}+F_{1}-\Lambda} \sqrt{(2J+1)(2J'+1)}$$

$$\begin{cases} J' & I_{Al} & F_{1} \\ I_{Al} & J & 2 \end{cases} \begin{pmatrix} I_{Al} & 2 & I_{Al} \\ -I_{Al} & 0 & I_{Al} \end{pmatrix}^{-1} \begin{pmatrix} J & 2 & J' \\ -\Lambda & 0 & \Lambda' \end{pmatrix}$$
(F.19)

### F.3.4 $H_{Q_0,Cl}$

$$H_{Q_{0},Cl} = \frac{(eq_{0}Q)_{Cl}}{4} (-1)^{2J+I_{Al}+2F_{1}'+I_{Cl}+F+2-\Lambda} \sqrt{(2F_{1}+1)(2F_{1}'+1)(2J+1)(2J'+1)} \\ \begin{cases} F_{1}' & I_{Cl} & F \\ I_{Cl} & F_{1} & 2 \end{cases} \begin{pmatrix} I_{Cl} & 2 & I_{Cl} \\ -I_{Cl} & 0 & I_{Cl} \end{pmatrix}^{-1} \begin{cases} J' & F_{1}' & I_{Al} \\ F_{1} & J & 2 \end{cases} \begin{pmatrix} J & 2 & J' \\ -\Lambda & 0 & \Lambda' \end{pmatrix}$$
(F.20)

### F.3.5 $H_{Q_2,Al}$

$$H_{Q_{2},Al} = \frac{(eq_{2}Q)_{Al}}{4\sqrt{6}}(-1)^{J+J'+I_{Al}+F_{1}-\Lambda}\sqrt{(2J+1)(2J'+1)}$$

$$\begin{cases} J' & I_{Al} & F_{1} \\ I_{Al} & J & 2 \end{cases} \begin{pmatrix} I_{Al} & 2 & I_{Al} \\ -I_{Al} & 0 & I_{Al} \end{pmatrix}^{-1} \left[ \begin{pmatrix} J & 2 & J' \\ -\Lambda & +2 & \Lambda' \end{pmatrix} + \begin{pmatrix} J & 2 & J' \\ -\Lambda & -2 & \Lambda' \end{pmatrix} \right]$$
(F.21)

### F.4 Transition dipole matrix: $d_q$

We calculate the transition dipole matrix elements in the Hund's case (a) coupling scheme with  $F_1 = J + I_{Al}$  and  $F = F_1 + I_{Cl}$  as follows.

$$d_{q} = (-1)^{2J+I_{A1}+F_{1}+F_{1}'+I_{C1}+F+F'+2-m_{F}-\Lambda} \sqrt{(2J+1)(2J'+1)(2F_{1}+1)(2F_{1}'+1)(2F+1)(2F'+1)} \begin{pmatrix} F & 1 & F' \\ -m_{F} & 0 & m'_{F} \end{pmatrix} \begin{cases} F_{1}' & F' & I_{C1} \\ F & F_{1} & 1 \end{cases} \begin{cases} J' & F_{1}' & I_{A1} \\ F_{1} & J & 1 \end{cases}$$
(F.22)   
 
$$\left[ \begin{pmatrix} J & 1 & J' \\ -\Lambda & +1 & \Lambda' \end{pmatrix} + \begin{pmatrix} J & 1 & J' \\ -\Lambda & -1 & \Lambda' \end{pmatrix} \right] |\langle \eta | T_{q}^{1}(d) | \eta' \rangle |$$

Hyperfine (MHz)	$X^{1}\Sigma^{+}$ [133]	$A^{1}\Pi$ [134]
$a_{ m Al}$	_	153.1(8)
$a_{ m Cl}$	_	32(2)
$(eQq_0)_{ m Al}$	-30.4081(27)	_
$(eQq_0)_{ m Cl}$	-8.8290(35)	_
$(eQq_2)_{\rm Al}$	_	96(14)

TABLE F.1: Summary of AlCl hyperfine constants used in the effective Hamiltonian. Constants for the  $A^1\Pi$  state were determined in this work.

# Appendix G

## Analytic rate equation model

Here we derive the analytic rate equation models used to compare scattering rates between the  $\Lambda$  and RROC schemes in Chapter 3.

Following the prescription provided by Ref. [102], we describe a system composed of  $N_g$  grounds states and  $N_e$  excited states by relating the ground and excited state occupation numbers,  $n_j$  and  $n_{e_i}$ , by the following system of rate equations,

$$\frac{\partial n_j}{\partial t} = \sum_i^{N_e} \left( A_{ij} n_{e_i} + R_{ij} (n_{e_i} - n_j) \right), \tag{G.1}$$

where  $A_{ij}$  and  $R_{ij}$  are the partial spontaneous emission and excitation rates between the  $i^{th}$  excited and  $j^{th}$  ground states, respectively. Evaluating the system of equations in steady state  $\left(\frac{\partial n_j}{\partial t} = 0\right)$  allows us to express the system in the following analytic form,

$$n_e = \frac{N_e}{(N_g + N_e) + \sum_{k=1}^{N_g} A_k / R_k}.$$
 (G.2)

In the denominator, the term  $A_k/R_k$  gives the ratio of emission and excitation rate and is summed over all ground levels. We note that we neglect vibrational decay beyond v'' = 1. This allows us to break the sum into separate terms to describe v'' = 0 and v'' = 1,

$$n_e = \frac{N_e}{(N_g + N_e) + \sum_{k=1}^{N_{g_1}} A_k / R_k + \sum_{i=1}^{N_{g_2}} A_i / R_i}.$$
 (G.3)

For SrF, both vibrational states have 12 ground levels, so we use the same upper limit in both sums,

$$n_e = \frac{N_e}{(N_g + N_e) + \sum_{k=1}^{N_g/2} A_k / R_k + \sum_{i=1}^{N_g/2} A_i / R_i}.$$
 (G.4)

For a given vibrational state the excitation-decay ratios of all ground levels are treated as equivalent. Under this assumption, each vibrational ground state can be viewed as composed of  $N_g/2$  decoupled two-level systems which are each addressed with equal laser intensity. In doing this, we may write  $A_k/R_k \approx A_1/R_1$  and  $A_i/R_i \approx A_2/R_2$ . Carrying out both sums then results in the multiplication of A/R with  $N_g/2$ , and allows us to write,

$$n_e = \frac{N_e}{(N_g + N_e) + \frac{N_g}{2}(A_1/R_1 + A_2/R_2)}.$$
 (G.5)

The decay rate into each ground level is dictated by vibrational branching ratios from the excited state,  $A = VBR_{v',v''}\Gamma$ , where  $\Gamma$  is inverse of the excited state lifetime. Meanwhile, the rate of excitation is related to the coupling strength of the transition,  $\Omega_{\text{vib}}^2 = q_{v',v''} \Omega_{\text{elec}}^2$ , where  $q_{v',v''}$  is the Franck-Condon factor (FCF) which describes the wavefunction overlap between ground and excited states and  $\Omega_{\text{elec}}$  is the atomic Rabi frequency. The excitation rate may then be expressed as

$$R = \frac{\Omega_{\rm vib}^2}{\Gamma} = \frac{q_{v',v''} \ \Omega_{\rm elec}^2}{\Gamma},\tag{G.6}$$

and together with the ratio A/R, becomes,

$$\frac{A}{R} = \frac{VBR_{v',v''}}{q_{v',v''}} \frac{\Gamma^2}{\Omega_{\text{elec}}^2}.$$
(G.7)

In an actual system that uses polarized light, selection rules lead to an imbalance between levels that may be driven by excitations and those which are populated via spontaneous decay. To provide a more accurate description we use the average of the decay channels from all excited states, expressed as  $\bar{s}_b$ , to weigh the spontaneous decay parameter, A, according to this imbalance. We therefore write  $A' = \bar{s}_b A$ , and refer to this average value as spontaneous emission bias. For experimentally relevant parameters, we express A/R to laser intensities through the relation  $\Gamma^2/\Omega^2 = 2I_{\text{sat}}/I$  [?]. Now, including spontaneous emission bias, we may rewrite Eq. G.7 as,

$$\frac{A'}{R} = 2\bar{s_b} \frac{VBR_{v',v''}}{q_{v',v''}} \frac{I_{\text{sat},v}}{I_v},$$
(G.8)

where I is the laser intensity used to drive each transition in a given vibrational state and can be re-expressed in terms of the total laser intensity  $I_v$  absorbed by the vibrational state as  $I = I_v/(N_g/2)$ . For each vibrational state, we define  $I_{\text{sat}}$ according to the common two-level saturation intensity [153], which we write as  $I_{\text{sat},v}$  for clarity,

$$I_{sat,v} = \frac{\pi h c \Gamma}{\lambda_v^3}.$$
 (G.9)

We note that in the limit of fast magnetic remixing in  ${}^{2}\Sigma$  molecules, which is often the case in these systems and is presently the case here, the value of  $I_{\rm sat}$  is independent of polarization. This is the reason we neglect the value of 3 in the denominator commonly found in Eq. G.9. Since the wavelengths required to drive transitions between the lowest two vibrational states do not differ significantly in SrF we approximate them as equal (assume  $\lambda = 663$  nm) and remove subscript von both  $I_{\rm sat}$ . While this is a reasonable approximation for our system it may not be for all molecules, e.g., light molecules (CH, BH etc.). Furthermore, to match our measurement conditions we assume equal intensities for all lasers and write  $I_1 = I_2 = I_v$ .

With the above terms we arrive at a general form obtained from Eq. G.5. Combining the excited state lifetime, or total spontaneous emission rate, with the excited occupation number describes the rate of scattering,  $R_{sc} = \Gamma n_e$ , for the system. As a result, generalized scattering rate may be written in the following closed form,

$$R_{sc} = \Gamma \frac{N_e}{(N_g + N_e) + \bar{s}_b \frac{N_g^2}{2} \left(\frac{VBR_1 \ \nu', \nu^{"}}{q_1 \ \nu', \nu^{"}} + \frac{VBR_2 \ \nu', \nu^{"}}{q_2 \ \nu', \nu^{"}}\right) \frac{I_{sat}}{I}}.$$
 (G.10)

For both the  $\Lambda$  and ROCC systems, we therefore have,

$$R_{sc,\Lambda} = \Gamma \frac{N_{e,\Lambda}}{(N_g + N_{e,\Lambda}) + \bar{s_b} \frac{N_g^2}{2} (\frac{VBR_{00}}{a_{00}} + \frac{VBR_{01}}{a_{01}}) \frac{I_{sat}}{I}}$$
(G.11)

$$R_{sc,BT} = \Gamma \frac{N_{e,\text{RROC}}}{(N_g + N_{e,\text{RROC}}) + \bar{s_b} \frac{N_g^2}{2} \left(\frac{VBR_{00} + VBR_{10}}{q_{10}} + \frac{VBR_{11} + VBR_{01}}{q_{01}}\right) \frac{I_{sat}}{I}}.$$
 (G.12)

While the exact analytic solution for the ROCC system would be considerably more complicated, the approximations made here provide an intuitive picture that is found to agree with the exact steady state numerical calculation to within one part in  $10^4$ . We note that as with the approximation for the  $\Lambda$  system, we treat the terms describing each vibrational ground state as the ratio of the total vibrational decay into the state divided by the FCF.

The analytic rate equations provided in Eqs. G.11 and G.12 are the theoretical models used in Fig. 3.4 of Chapter 3. They show reasonable agreement with measured data for the RROC system, despite neglecting both competition between two-level systems that share the same excited state as well as system coherences.

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