Producing, trapping and controlling ultracold CaF molecules

by

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Abstract

From studies of fundamental physics to quantum technologies the production of ultracold molecules will have a huge impact across a range of applications. For many years laser cooling, which became an invaluable tool in cold atomic physics, was deemed to be too impractical for application to molecules. Nevertheless, laser cooling has now been demonstrated for a few molecular species.

Using a frequency-chirped laser slowing technique, the velocity distribution of a pulse of CaF molecules is compressed and slowed from 180 m/s to about 10 m/s. These slow molecules are then captured in a magneto-optical trap. I present measurements that show how the number of molecules, the photon scattering rate, the oscillation frequency, damping constant, temperature, cloud size and lifetime depend on the key parameters of the magneto-optical trap, especially the intensity and detuning of the main cooling laser. The trap contains up to $2 \times 10^4$ molecules, the maximum photon scattering rate is $2.5 \times 10^6$ s$^{-1}$ per molecule, the maximum oscillation frequency is 100 Hz, the maximum damping constant is 500 s$^{-1}$, and the minimum rms radius of the trapped cloud is 1.5 mm. A minimum temperature of 730 $\mu$K is obtained by ramping down the laser intensity to lower values. To reach lower temperatures, the cloud is loaded into a blue-detuned optical molasses, which cools the molecules to 55 $\mu$K, well below the Doppler-limiting temperature. I characterise the cooling process and suggest the sub-Doppler mechanisms responsible. These ultracold molecules are the optically pumped into a single quantum state, and coherently transferred between selected hyperfine components of the ground and first-excited rotational states. Finally, the ultracold, state-selected molecules are loaded into a magnetic trap that has a lifetime of about 1 s.
Declaration

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Chapter 1

Introduction

The field of ultracold atomic physics began in the 1970’s following on from the invention of narrow, tuneable lasers. With this improved spectroscopy, absorption lines were now limited by the Doppler width of the atomic source rather than the laser linewidth. Laser cooling was soon proposed by Hansch and Schawlow in 1975 [1]. The first demonstration of longitudinal laser cooling was demonstrated by Andreev et al. in 1981 [2]. The group demonstrated cooling of a sodium beam from an initial temperature of 573 K to an effective, relative-motion temperature of 1.5 K. This experiment, and others, were limited by the changing Doppler shift of the atoms as they decelerate. As this happens the atoms shift out of resonance with the slowing beam and so the amount of deceleration possible is limited. Two methods were proposed to overcome this. The addition of a spatially varying magnetic field which uses the Zeeman effect to shift the slowing atoms back into resonance was demonstrated by Philips and Metcalf in 1982 [3]. They achieved around 15,000 absorptions which decelerated the atoms to about 40% of the initial velocity. The second technique is to rapidly scan the frequency of the slowing laser, to keep it resonant with the decelerating atoms. This technique, referred to as chirped slowing, was first demonstrated in 1984 [4]. This experiment achieved similar results to the Zeeman method and the two techniques went on to be equally successful at slowing atoms to rest, or even reversing their direction [4, 5]. At this point thoughts turned to trapping. It was determined that using three pairs of counter-propagating beams an optical trap could be implemented to hold atoms. This led to the demonstrations of the first optical molasses in 1985 [6] and, with the addition of a quadrupole magnetic field, the first magneto-optical trap (MOT) in 1987 [7]. After this the small field of ultracold atomic physics exploded. Since then dozens of species of atomic MOTs have been made in hundreds of labs across the world and the MOT became the starting point for most ultracold atomic physics experiments.

Laser cooling was not the only technique being investigated. Magnetic trapping of
neutral particles was first demonstrated in 1985 \cite{8} before the first MOT. Once in a magnetic trap the atoms are distributed according to their temperature and it was discovered that by lowering the trapping potential it was possible to remove the hottest atoms and that elastic collisions between the atoms would lead to rethermalisation of the cloud at a lower temperature. This technique was named evaporative cooling and was demonstrated in 1986 \cite{9} where atomic hydrogen was cooled to 30 µK with densities of $10^{14}$ cm$^{-3}$, close to the requirement for a Bose-Einstein condensate, BEC. However, further progress was limited by inelastic collisions which caused trap loss and heating. Evaporative cooling was then applied to laser cooled alkali atoms and this quickly led to the realisation of a BEC of rubidium atoms with a temperature of 170 nK and a number density of $2.5 \times 10^{12}$ cm$^{-3}$ \cite{10}.

Ultracold atoms led to major developments across a vast range of fields. Research into atom optics has enabled the motion of atoms to be controlled by external fields in much the same way as traditional optics control the motion of light. Examples include mirrors \cite{11} and lenses \cite{12} created by magnetic fields. Other components include beam-splitters \cite{13} and diffraction gratings \cite{14}. The development of these components led to atom interferometers \cite{15, 16} which allowed for many new measurements to be made \cite{17}. Experiments have been developed to measure gravitational acceleration \cite{13}, the Sagnac effect \cite{18} and the index of refraction of dilute gases \cite{19}.

Ultracold atoms can be loaded into optical lattices and with the development of quantum gas microscopes \cite{20} it became possible to simulate quantum systems. Investigations have been made into strongly interacting bosons \cite{21} as well as magnetic phenomena \cite{22} and thermalisation of quantum systems \cite{23}. Ultracold atoms also allowed for huge advancements in precision metrology. The most precise clock to date is an optical lattice clock of strontium atoms at $< 60$ nK. This clock has a precision of $5 \times 10^{-19}$ \cite{24}.

Ultracold molecules could offer even more than atoms, but they are difficult to create and laser cooling was believed to be far too impractical to implement. However, a possible subset of molecules, suitable for laser cooling, was identified in 2004 \cite{25} and a feasible technique was proposed in 2008 \cite{26}. The experimental field of laser cooling molecules is less than ten years old. Despite this there are now a handful of molecules which have been trapped and cooled to cold ($< 1$ K) and ultracold ($< 1$ mK) temperatures. This thesis will describe the experiments on laser cooling and trapping of calcium fluoride (CaF) molecules.
1.1 Why cold molecules?

Molecules have rotational and vibrational degrees of freedom, which are absent for atoms. They also interact much more strongly with applied electric fields, with microwave fields and with each other. These properties make them more suitable than atoms for many potential new applications and areas of study. Here I will present an overview of a few applications, with a particular focus on those which could be realised with CaF.

1.1.1 Cold collisions and chemistry

There are two distinct research branches involving collisions between ultracold atoms and molecules. The first is to investigate and understand collisions and chemical reactions. At room temperature collisions between molecules are dominated by thermal motion and are very difficult to control. At cold and ultracold temperatures the collisions could be manipulated by external fields. The mechanisms behind any reactions will be dominated by different effects, such as tunneling. Investigating chemical reactions with high levels of control over the molecules will give insight into the effects of molecular alignment and symmetry in collisions [27]. They will also increase our understanding of quantum systems.

The second branch is to use collisions for sympathetic cooling. Trapped atoms can undergo elastic collisions which, combined with evaporative cooling, allows the temperature of the cloud to be lowered dramatically. The numbers and densities required for this are far higher than have been achieved with laser-cooled molecules so far. However a combined trap of atoms and molecules might be able to overcome this. If the elastic collision cross sections dominate over the inelastic then sympathetic cooling of the molecules by the atoms could be possible. A handful of experimental [28] and theoretical [29] investigations have observed, or predicted, high inelastic scattering rates which would prevent sympathetic cooling. Some sympathetic coolants investigated theoretically, such as hydrogen, have favourable ratios of elastic to inelastic collision cross sections, but are difficult to produce experimentally [30]. A recent paper [31] studied sympathetic cooling of CaF molecules using ultracold rubidium or lithium and suggests that cooling with Rb can be efficient provided the molecules are in the ground rotational state. The paper suggests that sub-microkelvin molecules can be produced by sympathetic cooling using evaporatively cooled Rb atoms.

1.1.2 Quantum Simulation

Polar molecules offer advantages for quantum simulation and quantum computation systems. They have large permanent electric dipole moments which means that they can be
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easily controlled using electric fields and entangled via dipole-dipole interactions. By coupling together rotational states with microwave fields, and making use of the spin-rotation coupling within each molecule and the dipole-dipole interaction between molecules, it is possible to make a very versatile quantum simulator. An optical lattice with a single polar molecule per site would enable the study of strongly-interacting quantum systems and the realisation of lattice spin models [32, 33].

1.1.3 Precision Spectroscopy

The Standard Model of particle physics successfully describes all known elementary particles and three of the four fundamental forces. However, it has a number of shortcomings which suggest that it cannot be a complete theory. For example, it predicts an almost equal amount of matter and antimatter in the universe, which there is not. It also fails to incorporate gravity. A number of extensions to the Standard Model have been developed. Many of those which aim at unifying gravity with the other forces also predict variation, in time and space, of fundamental constants. Theories which aim to understand the observed matter-antimatter asymmetry tend to predict values for the electron’s electric dipole moment (eEDM) that are many orders of magnitude larger than in the Standard Model. There is already a great deal of research being conducted into observing these effects. The fine structure constant $\alpha$ has been probed rigorously with ultracold atoms and extremely tight bounds have been set on its variation. Measurements of the proton-to-electron mass ratio $\mu$, however, are far behind. This is because atoms are not very sensitive to $\mu$, but the vibrational levels in molecules are. Hence, vibrational spectroscopy of molecules can offer improved measurements. So far the best direct measurement was made with a fast beam of SF$_6$ molecules [34]. Using a slow, cold beam of molecules would offer an increase in measurement time by several orders of magnitude and hence the same increase in sensitivity. Molecules are also more sensitive to the eEDM than atoms and the three most precise measurements have all used molecules. The first molecular measurement was done using YbF molecules in 2011 [35]. This was then improved upon using a cryogenic buffer gas beam of thorium oxide [36]. Most recently, a new measurement using trapped HfF$^+$ ions reached a similar sensitivity to the ThO measurement [37]. All of these measurements probe the region where popular extensions of the Standard Model predict a non-zero eEDM, but so far all the results have been consistent with zero. The next generation of eEDM experiments will benefit from cold, slow molecules as there will be an increased interaction time [38].
1.2 Making Cold Molecules

Laser cooling is a relatively new method for producing cold (\(\lesssim 1\) K), and ultracold (\(\lesssim 1\) mK), molecules. There are many other methods, which are usually grouped into indirect and direct methods. The indirect methods form molecules by associating ultracold atoms, while direct methods involve cooling molecules directly. Here I will present a brief overview of some of the techniques. More detailed discussions can be found for indirect methods in \([39]\) and direct methods in \([40]\) and references therein.

1.2.1 Indirect Methods

The ability to cool atoms to microkelvin temperatures and below has been possible for over twenty years. This can therefore be a strong starting point for creating molecules of similar temperatures. The two most common techniques are photoassociation and magnetoassociation through a Feshbach resonance. Whilst they are both able to produce ground state molecules at very low temperatures they are limited to molecules composed of atoms which are themselves amenable to laser cooling.

**Photoassociation** When two atoms \((A \text{ and } B)\) collide in the presence of laser light they can be excited by the laser into an electronically excited molecular bound state \((A^* + B)\). This is illustrated in figure 1.1(a). Here, \(E_{th}\) is the incident thermal collision
energy of the atom pair, \( E_{\text{at}} \) is the energy required to excite one atom, here atom \( A \), and \( E_b \) is the binding energy of the molecular vibrational level. The upwards arrow labelled PA indicates the laser which is resonant with the transition frequency between the two atoms in the electronic ground state and the molecule in the excited state. This state is unstable and hence will quickly decay to the electronic ground state or back to two free atoms. The likelihood that two atoms will form a molecule is described by the photoassociation rate. This rate depends on the density of the atoms, the Franck-Condon overlap between the continuum of the two atoms and the bound state, and the detuning of the laser. In order to make this process efficient the initial distribution of velocities should be small making the spread in frequencies needed to drive the photoassociation process small, ideally comparable to the natural linewidth of the transition. This is achieved by using ultracold atoms, below \( 1 \) mK. There is a large body of work demonstrating the photoassociation of homonuclear as well as heteronuclear species \[41\]. However the technique has been limited by low molecule yield and also a lack of quantum state control. The Franck-Condon overlap between free atoms and a bound molecular state is only significant for very high-lying vibrational states, so photoassociation always produces electronically excited molecules in highly excited vibrational levels. When these molecules decay to the electronic ground-state, they again tend to populate high-lying vibrational levels. Thus, it is particularly difficult to produce molecules in the absolute ground state this way. If the collision happens in the presence of a second laser with frequency \( \nu_2 \) then the excited state can be coupled to a low-lying vibrational level. Recent work by the Zelevinsky group however has demonstrated complete control over the molecular and continuum quantum state \[43\]. They photoassociate atoms trapped in an optical lattice to form molecules at \( \sim 5 \) \( \mu \)K in a single quantum state which are also trapped in the lattice. However the process is still inefficient producing only small numbers of molecules.

**Magnetoassociation** Here an external magnetic field is used to alter the potential energy of two colliding atoms \[42\]. Figure 1.1(b) illustrates the method. Two atoms collide in a particular configuration of hyperfine and Zeeman states. This is known as the entrance channel, and the corresponding potential is shown by the blue curve in figure. Also shown is the potential curve for a different configuration of hyperfine and Zeeman states, known as a closed channel. One of the molecular states of this closed channel has the energy \( E_{\text{cl}}(B) \) which can be tuned with a magnetic field \( B \). A Feshbach resonance occurs when the energy of a bound state in one hyperfine configuration is close to the energy of a scattering state consisting of two free atoms in a different hyperfine configuration. By tuning the magnetic field a Feshbach resonance can cause the colliding atoms to combine into a bound molecular state. Molecules can be created in this way from thermal clouds or BECs of atoms. Both homonuclear and heteronuclear diatomic
molecules can be created using this technique. The temperatures achievable are very low, down to 350 nK \[44\]. The technique produces molecules in highly excited vibrational states but it can be followed by STIRAP to transfer the population to a low-lying state \[45\]. This technique has similar limitations to photoassociation. It can only produce molecules whose constituents are amenable to laser cooling. It is a complex method requiring ultracold samples of two species.

1.2.2 Direct Methods

The requirement of associating laser cooled atoms is very restrictive. Therefore many direct methods of cooling molecules were developed. I will describe them here before discussing laser cooling of molecules.

**Stark and Zeeman Deceleration** Stark deceleration of molecules was first demonstrated in 1999 for CO. These molecules were decelerated from 225 m/s to 98 m/s \[47\]. A Stark decelerator relies on time varying high and low electric field regions. Figure 1.2(a) shows the field generated by electrodes in a Stark decelerator and the energy shift observed by a molecule. Pairs of electrodes alternate between being grounded and being oppositely charged creating electric field hills, with peaks between the charged electrodes and zero field between the grounded ones. Molecules can either be weak field seeking (wfs), meaning that their energy increases with electric field strength, or strong field seeking (sfs), meaning their energy decreases. Let’s consider a molecule in a wfs state. This molecule will gain internal energy as it travels into a high field area and hence its kinetic energy will decrease. Just as the molecule is approaching the peak field the electrodes are switched: those which were grounded are now charged and vice versa. This means that the molecule, with its reduced velocity, now faces another electric field hill.
By switching the electrodes at a rate comparable to the local velocity of the molecules they can be decelerated. The field is largest close to the electrodes and so the decelerator focuses the wfs molecules and they follow oscillatory trajectories through the decelerator. However, once the molecules are slowed below $\sim 100$ m/s they become over-focused and can crash into the electrodes [48]. The decelerator can only slow molecules with a small initial velocity distribution. It is a good technique to produce a beam for high resolution spectroscopy but it is an inefficient way of producing molecules which are slow enough to be captured in a magneto-optical trap. Several species have been slowed by Stark deceleration, including ND$_3$ [49], OH [50], LiH [51] and CaF [52].

A Zeeman decelerator uses magnetic fields created by coils instead of electric fields, but the principle is the same and it is subject to similar problems. The first demonstration of Zeeman deceleration of molecules was in 2008. Researchers slowed pulsed O$_2$ from 389 to 83 m/s [53]. Since then Zeeman deceleration has also been demonstrated for CH$_3$ [54] and He$_2$ [55].

**Travelling Wave Decelerator** An extension of a Stark decelerator, referred to as a travelling wave decelerator, can be used to slow molecules to rest and avoids many of the problems present in traditional Stark decelerators, namely over-focusing and small phase-space acceptance. The trap is made from many ring electrodes each controlled by a voltage creating an electric field trap. By sinusoidally modulating the voltages in time the trap will move along the decelerator. This 3D trap is loaded moving at the velocity of the molecules. The frequency is then lowered and the trap starts moving slower, as do the molecules. The first demonstration of this was shown for CO [56], where researchers decelerated the molecules from 288 to 144 m/s. The technique has since been shown to bring NH$_3$ molecules to rest [57] and has been used to load the first molecular fountain [58]. A beam of SrF molecules has also been decelerated using a 4 m long traveling-wave Stark decelerator, removing 85% of the initial kinetic energy [59]. The travelling wave decelerator is a versatile deceleration method which is applicable to many molecules which could not be laser cooled.

**Bichromatic Slowing** A dual frequency retro-reflected laser beam can be used to change the momentum of, and hence cool, molecules. Here the momentum of a photon is transferred to the molecule during both absorption and stimulated emission. This is referred to as the bichromatic force. The setup requires two counter-propagating beams consisting of two frequencies spaced $\pm \delta$ around a transition frequency, as illustrated in figure 1.3. Consider each beam as a train of beat notes, where the power is set such
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Figure 1.3: Simple $\pi$-pulse model of the optical bichromatic force on an atom. Two-color beams impinge from each direction, offset by frequencies $\pm \delta$ from resonance at $\omega_a$. For large molecular velocities $v$, Doppler offsets of $\pm k v$ must also be added as shown. The frequency pairs at $\pm \delta$ give rise to a series of rf beat notes, each with an area of approximately $\pi$. Alternating cycles of excitation from the right and stimulated emission from the left produces a large decelerating force directed to the left. The direction is controlled by the relative phase of the beat notes from each direction. Reproduced with permissions from [60].

that each beat is a $\pi$ pulse. A pulse in one direction will excite the molecule and remove $\hbar k$ of momentum, then the second pulse, from the other direction, will cause stimulated emission and will remove another $\hbar k$. Since the molecules undergo stimulated emission the upper state lifetime doesn’t impose a limit on the scattering rate. The power can be increased significantly and so the slowing can happen over a very short time period. Cooling can also occur during this process as spontaneous emission still happens. The bichromatic force has been used to slow a beam of metastable helium atoms [60] and to deflect a molecular beam of SrOH [61].

Optoelectrical Sisyphus Cooling  Cooling of molecules to sub millikelvin temperatures has been demonstrated for gaseous formaldehyde inside an electric trap [62]. The trap produces a boxlike potential with strongly increasing electric-field gradients at the edges. Cooling requires control over the rotational state of the molecules, as shown in figure [1.4]. Consider a molecule initially in a state with a strong Stark interaction, such as $M = \pm 3$. When the molecule reaches the edge of the trap it climbs the field gradient and loses kinetic energy. Near its turning point, it comes into resonance with radio-frequency radiation which transfers it to a state with a weaker Stark interaction, such as $M = \pm 1$. The molecule then moves back down a smaller gradient, so some of the kinetic energy has been permanently removed. In order to repeat this, the molecules are optically pumped back to the state with the strong Stark interaction while they are in the flat-bottom region of the trap. This pumping is achieved via a combination of IR and microwave radiation, and involves an irreversible spontaneous emission event, so that it is a one-way process.
Centrifuge Decelerator  The centrifuge decelerator [63] is constructed of a static circular guide surrounding two rotating electrodes which spiral inwards, forming the centrifuge, illustrated in figure 1.5(a). The molecules enter through a gap in the guide and begin traveling around the ring. The spiral is rotating at a given angular velocity Ω. Molecules with sufficient velocity to catch up with the opening of the spiral will enter the centrifuge. As they travel towards the center of the spiral they must climb a potential hill caused by the centrifuge. The energy they lose is $E = -\frac{1}{2}M(\Omega r)^2$, where $M$ is the mass of the molecules and $r$ is the distance to the axis of rotation of the centrifuge. The exit of the centrifuge is angled perpendicular to its plane. By changing the angular velocity of the centrifuge the final velocity distribution of the molecules can be controlled. The origin of the decelerating force appears different in the two frames of reference, see figure 1.5(b). In the rotating frame the quadrupole electric field serves as a guide and the centrifugal potential decelerates the molecules. In the laboratory frame the electric field causes the deceleration as the electric field vector is not normal to the longitudinal velocity of the molecules in this frame. This technique can be used to slow molecules from a continuous source and therefore produce a slow, continuous beam which can be trapped. The technique is experimentally complicated, however it is versatile and applicable to all polar molecules.

1.3 Laser Cooling

Doppler cooling uses the principle of momentum conservation: a photon is absorbed by a molecule, transferring its momentum to the molecule. By counter-propagating a
laser beam with a molecular beam each photon absorption will reduce the velocity of the molecule. After a certain time a second photon is spontaneously emitted. This happens in a random direction and so the emission has no overall effect on the mean forward velocity of the molecule. The velocity change per photon ($\delta v$) depends on the mass of the atom/molecule ($M$) which is being decelerated and the wavelength ($\lambda$) of the slowing light. It is calculated by $\delta v = \frac{h}{\lambda M}$. A typical slowing experiment will require $\sim 10^4$ photon scattering events in order to bring molecules to rest. Therefore a closed cycling transition is required. However, molecules have vibrational and rotational degrees of freedom as well as the electronic energy levels present in atoms. This means that in most cases after just a few photon scattering events a molecule will end up in a different state and will no longer scatter photons preventing slowing and cooling.

However, a careful choice of molecule and transition can make laser cooling a viable option. Criteria for choosing a molecule which is suitable for laser cooling were presented in 2004 by DiRosa [25]. They are:

1. A short excited state lifetime and hence a high scattering rate allowing for rapid laser cooling.
(2) No intervening electronic states to which the upper state could decay.
(3) A highly diagonal Franck-Condon matrix.

In order to fulfill requirement (1) it is necessary to drive electronic transitions because vibrational and rotational states have long lifetimes. To have a closed cycling transition it is therefore important to follow requirement (2), although the presence of intervening electronic levels is not a problem provided the coupling between the two states is sufficiently small. The third requirement addresses the issue of the vibrational structure of molecules. The probability of decay to any given vibrational level is governed by the overlap between the wavefunctions of the excited and ground states. Molecules with a highly diagonal Franck-Condon matrix have a high probability of retaining their vibrational quantum number \( v \) when decaying to the electronic ground state. Cooling on the \( v = 0 \rightarrow v' = 0 \) transition for such molecules would require only a small number of higher vibrational levels to be addressed in order to sufficiently close the cycling transition.

With the number of vibrational repump lasers limited it was then necessary to consider the rotational structure. Decay between rotational levels are constrained by the total angular momentum selection rule \( \Delta N = 0, \pm 1 \), therefore requiring up to three lasers per vibrational level. However in 2008 Stuhl et al. suggested that driving a transition from a ground state with rotational quantum number \( N = 1 \) to an excited state with \( N = 0 \), would prevent two of the three decay channels. The molecule would have to decay back to its initial rotational level. This removes the need for rotational repump lasers. However, it does lead to one more complication. The higher rotational number in the ground state leads to the existence of extra sublevels which cannot all be coupled to the excited state. This can be overcome by destabilisation of the dark states, as described later in the thesis.

Following this it became possible to consider laser cooling as a source of cold molecules. In 2009 the DeMille group demonstrated deflection of a molecular beam of strontium fluoride [64] followed by transverse laser cooling in 2010 [65]. The same group went on to demonstrate longitudinal laser cooling in 2012 [66]. The Ye group then showed transverse laser cooling, and magneto-optical compression of YO in 2013 [67]. Longitudinal laser slowing and cooling was again demonstrated at Imperial College London for calcium fluoride in 2014 [68]. The Doyle group also work with CaF and they achieved slowing to below 15 m/s in 2016 [69], shortly followed by publication of our slowing results [70] which will be discussed in detail in chapter 3. There are new experiments working on laser cooling of barium hydride [71], barium fluoride [72] and ytterbium fluoride [73].
There has also recently been interest in extending laser cooling from diatomic to polyatomic molecules. A selection of suitable polyatomic molecules have been identified in [74]. In general, exchanging the fluorine-like atom in a diatomic molecule with a pseudohalogen such as CN or a functional group like OH or CH$_3$ will produce a polyatomic molecule which is amenable to laser cooling. One-dimensional laser cooling of SrOH has been demonstrated, where the transverse temperature of the molecules was reduced to 750 $\mu$K [75].

In order to slow molecules to rest it is necessary to account for the changing Doppler shift of the molecules as they decelerate. So far this has been achieved by either broadening or scanning the laser frequency. For atoms, the most common laser slowing method is the Zeeman slower, where a tapered magnetic field is used so that the Zeeman shift of the cycling transition exactly compensates the Doppler shift at all points along the slower. However, as previously mentioned, the requirements for laser cooling of molecules leads to many magnetic sublevels in the ground state, all of which need to be coupled to the excited state. These magnetic sublevels each experience a different shift. Thus, a traditional Zeeman slower would not work. A modification has been proposed which applies a large static magnetic field along with a traditional tapered field. This puts the molecules into the strong field region of the Zeeman effect [76]. At this point the electron spin decouples from other sources of angular momentum and the molecules can either be in $m_S = +1/2$ or $m_S = -1/2$. On a laser cooling transition the ground state splitting is large but the excited state splitting can be very small. This creates a 3-level system in which slowing can occur by pumping on one state in the usual way and having a broad linewidth beam repump the other. This technique is predicted to be applicable to a range of molecules and decelerate them down to speeds around the capture velocity of a MOT. It has the added advantage that it can be used continuously and so could be used to decelerate sequential pulses of molecules into a trap.
Figure 1.6: Energy levels as a function of increasing magnetic field for $F_l = 0$ and $F_u = 1$. The dashed red line represents the restoring beam, red-detuned from the transition resonance, which has $\sigma^+$ polarisation and so can drive transitions from $M = 0$ to $M = -1$.

1.4 Trapping

Once atoms/molecules are slow the next step is to trap them. In this section I will briefly describe various trapping techniques employed for atoms and molecules.

1.4.1 Magneto-optical Trap

A magneto-optical trap (MOT) both confines and cools, and it is the workhorse of ultra-cold atomic physics. It consists of three pairs of red-detuned counter-propagating laser beams and a magnetic quadrupole field. The field splits up degenerate Zeeman levels. Figure 1.6 illustrates the formation of a traditional, type-I MOT with $F_u = 1$ and $F_l = 0$. The laser beam that pushes displaced atoms/molecules back towards the centre of the trap, where the magnetic field is zero, is referred to as the confining beam, while the opposite beam is called the anti-confining beam. In the traditional MOT, the confining beam has $\sigma^-$ polarisation, meaning that, in absorption, it drives a $\Delta M = -1$ transition. By correctly choosing the light polarisation and the field direction the atoms will experience a frictional and confining force. In figure 1.6 the strongest transition is to the $M = -1$ Zeeman state, since this transition is closest to resonance with the red-detuned light. This transition can only be driven by the confining beam, leading to trapping.

For molecules a type-II MOT, with $F_u = F_l + 1$, must be used. This leads to the presence of dark states, which complicates the creation of a MOT. Nevertheless, four molecule MOTs have now been demonstrated. The first was a MOT of SrF molecules produced in Yale by the DeMille group [77, 78]. Next came two MOTs of CaF, the one I describe in this thesis and also in [79, 80], followed by one in the Doyle group at Harvard.
At JILA, the Ye group have made a MOT of YO molecules, though this work has not yet been published.

1.4.2 Conservative Traps

In a MOT the molecules continuously scatter photons. For many applications it is necessary to transfer them into a conservative trap. These traps have long lifetimes and, unlike a MOT, the internal state of a molecule is preserved, which is needed for any application that involves quantum control. Also, for other cooling methods, e.g. sympathetic cooling, evaporative cooling, sideband cooling, etc. it’s necessary to use a conservative trap.

Magnetic Traps  The interaction between an external magnetic field and the magnetic moment of an atom/ molecule presents the possibility of a magnetic trap. The simplest magnetic trap was proposed by Wolfgang Paul in 1953. It consists of a pair of coils set up in anti-Helmholtz configuration to produce a quadrupole magnetic field. There is a field minimum at the geometric centre of the coils where the trap will form, with the coldest molecules at the bottom of the trap. Magnetic trapping of molecules was demonstrated before laser cooling in 1998. A trap of calcium hydride molecules was made with around $1 \times 10^8$ molecules at $400 \pm 50$ mK with a lifetime of $\sim 2$ seconds [82]. Following this, a selection of molecular species have been loaded in magnetic traps including OH [83], NH [84] and CaF [85]. However, these traps are at high temperature $\sim 30$ mK. Ultracold CaF molecules have recently been loaded into a magnetic trap, as described in chapter 6 and reference [86]. Ultracold SrF has been transferred into a magnetic trap by the DeMille group as described in [87].

Dipole Traps  A trap can be made using a single, strongly focused laser beam. The trapping relies on the light shift (or ac Stark shift) of the ground state, which is proportional to intensity and is negative when the light is red-detuned from all relevant transitions. There is an intensity gradient across the beam leading to a position dependent light shift. This leads to a pulling force towards the centre, the dipole force. The size of this force depends on the light intensity, the transverse position of an atom and the beam waist. There is also a longitudinal force confining the atoms in this direction. Here the force depends on the focusing of the beam and crucially the detuning which can be chosen such that the dipole force outweighs the scattering force. An optical dipole trap of CaF molecules has recently been demonstrated by the Doyle group [88].

Electric Traps  Polar molecules can also be trapped in electric traps. An electrostatic trap again uses the Stark shift. An electrostatic trap for neutral particles was proposed
in 1980 \[89\]. By using electrodes it is possible to create an electric quadrupole field with a zero at the centre. It is energetically favourable for molecules to be at the field minimum, hence they can be trapped. The first demonstration for molecules was using ammonia \[49\]. Since then other species have been held in electrostatic traps including NaCs \[90\] and \(\text{H}_2\) in Rydberg states \[91\]. Electrostatic traps provide good localization however the field gradients cause large Stark broadening which make such traps unsuitable for precision spectroscopy or collisions experiments. A box-like trap has been developed and used to store \(\text{CH}_3\text{F}\) \[92\]. Across the majority of the trap the electric field is uniform but at the edges there are very steep gradients. This trap has been developed with \(1/e\) lifetimes of \(\sim 12\) s. It is in this trap that molecules have been cooled using the optoelectrical Sisyphus cooling described earlier.

### 1.5 This Thesis

In this thesis I will describe the CaF laser cooling experiment, from the production of the molecular pulse to coherent control over the quantum state of the molecules. This experiment would not have been possible without the support of a team. However, all experimental data presented in this thesis was taken and analysed by me. I also built the optics set-up for the experiment. Where comparisons to models have been included I have acknowledged who built the model. The chapters are arranged in the following way. Chapter 2 provides an introduction to molecular structure, notation and the field-matter interactions which will be important for the rest of the thesis. Chapter 3 will briefly discuss the buffer gas source and then present the data for optimising laser slowing, resulting in the first ever demonstration of using chirped laser slowing to decelerate molecules to within the capture velocity of a MOT. Chapter 4 is an in depth investigation into the set-up and properties of the world’s first CaF MOT, only the second molecular MOT ever made. Chapter 5 presents the sub-Doppler cooling data achieved in the blue-detuned molasses. This results in the first ever demonstration of cooling molecules to below the Doppler limit. Chapter 6 shows the preliminary quantum control and magnetic trapping data. This resulted in the first ever pure sample of laser-cooled molecules in a selectable, single quantum state, held in a magnetic traps. Chapter 7 is an outlook for the future of the experiment and includes a list of possible modifications which should increase the phase-space density of the molecular sample, which is the current limiting factor for many future applications.
Chapter 2

Molecular structure, notation and interactions

In this thesis I will describe the application of laser cooling techniques to calcium fluoride molecules. This will require a detailed understanding of the energy structure of CaF and the interaction of molecules with external fields. Laser cooling has traditionally only been applied to atoms because even diatomic molecules have a significantly more complex energy-level structure. In a molecule the presence of multiple nuclei causes a breaking in the spherical symmetry of the atom. This leads to additional degrees of freedom the main components of which are due to the atoms oscillating relative to each other or rotating around one another. This chapter will briefly cover the structure and notation for diatomic molecules and CaF in particular. I will also describe the field-molecule interactions relevant to the experiments.

### 2.1 Molecular Structure and Notation

The time-independent Schrodinger equation for a multi-electron, multi-nucleus molecule can be solved approximately by applying the Born-Oppenheimer approximation \[93\]. The Born-Oppenheimer approximation allows the wavefunction of a diatomic molecule to be separated into three parts: electronic, vibrational and rotational. Figure 2.1 illustrates the energy level structure of a typical diatomic molecule. The electronic levels are typically separated by hundreds of THz, vibrational levels (v) by tens of THz and rotational levels (R) by tens of GHz. These splittings mean we can address electronic transitions with optical photons, vibronic transitions can be accessed with far-IR photons and rotational transitions with microwaves.
2.1.1 Electronic Structure

The electronic levels in molecules are labelled \( X, A, B, \ldots \) indicating that the molecule is in its ground, first, second, etc. electronic state. These states are characterised by a term symbol describing the spin, orbital and total angular momenta. Let’s first consider the electronic orbital and spin angular momenta, \( \hat{L} \) and \( \hat{S} \). For atoms these both commute with the Hamiltonian making \( L \) and \( S \) good quantum numbers. However, in molecules the spherical symmetry of the internal electric field is broken. Therefore we must consider their projections onto the internuclear axis, defined as the \( z \) axis. The projections are labelled \( \Lambda \) and \( \Sigma \) for \( \hat{L}_z \) and \( \hat{S}_z \) respectively. The sign of \( \Lambda \) corresponds to the direction of the orbital angular momentum being either clockwise (positive) or anti-clockwise (negative) about \( z \). A reflection operator acting on an eigenfunction with eigenvalue \( \hbar \Lambda \) will convert it to the same eigenfunction with eigenvalue \( -\hbar \Lambda \). Both of these eigenfunctions have the same energy, to first order, and so are degenerate for \( \Lambda \neq 0 \). The states are hence labelled according to \(|\Lambda|\), the notation is

\[
\begin{array}{c|c|c|c|c|}
\Lambda \text{ value} & 0 & 1 & 2 & 3 \\
\hline
\text{Symbol} & \Sigma & \Pi & \Delta & \Phi \\
\end{array}
\]
For Λ = 0 the degeneracy is not present. Under reflection Σ states are either unchanged, and hence are labelled Σ⁺ or change sign, and hence labelled Σ⁻. For Λ ≠ 0 this degeneracy is broken by the mixing of different electronic states leading to two nearby levels of opposite parity which is known as λ-doubling. To complete the term symbol we must also consider the total angular momentum (\( \mathbf{J} \)). Again we use the projection onto the internuclear axis, Ω where Ω = |Λ + Σ|. We now have all the components in the term symbol for molecules, which is given by \( ^{2S+1}ΛΩ \). The ground state for CaF has Λ = 0 and \( S = 1/2 \), it is also unchanged under reflection and so the term symbol is \( X^2Σ^+ \).

### 2.1.2 Vibrational structure

The two nuclei vibrate around the equilibrium internuclear distance, leading to discrete vibrational levels labelled by the quantum number \( v \). The energy eigenstates can be accurately calculated using the following power series [94]

\[
E_v = \omega_v(v + \frac{1}{2}) - \omega_v x_v(v + \frac{1}{2})^2 + \omega_v y_v (v + \frac{1}{2})^3 + ... \tag{2.1}
\]

Here, \( \omega_v \) is the vibrational constant and \( x_v, y_v, ... \) are anharmonic constants of decreasing size. For low \( v \) the first term is a good approximation because the system behaves like a harmonic oscillator with \( \omega_v = \hbar \sqrt{k_{\text{nuc}}/m_r} \), where \( k_{\text{nuc}} \) is the spring constant and \( m_r \) is the reduced mass of the atoms. The additional terms account for anharmonicity and cause the spacing between vibrational levels to decrease with increasing \( v \).

### 2.1.3 Rotational structure

The two nuclei rotate about their centre of inertia, leading to rotational levels labelled by the quantum number \( R \). The energy eigenstates can be accurately calculated for all values of \( R \) using the following power series [94]

\[
E_{\text{rot}} = B_v R(R + 1) - D_v R^2(R + 1)^2 + ... \tag{2.2}
\]

The first term represents the energy levels of a quantum rigid rotor where \( B_v \) is a rotational constant that is a function of the vibrational level. The second term represents centrifugal distortion and \( D_v \) is a stretching constant, again a function of the vibrational level. The vibrational and rotational degrees of freedom are connected, hence why the constants depend slightly on the vibrational level. This is because the moment of inertia changes with vibrational excitation, and this then changes the rotational constant.

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2.1.4 Angular Momentum Coupling and Hund’s cases

The various sources of angular momentum can couple together in different ways. As a result the good quantum numbers are molecular state dependent and can be described by five idealised situations, called Hund’s cases (a)-(e) which characterise these couplings. The most appropriate case is chosen by considering:

1. the energy difference between neighbouring electronic states, $E_{el}$
2. the spin-orbit splitting, $E_{s.o.}$
3. the rotational energy splitting, $E_r$.

The two cases we will consider in the experiment are (a) and (b). Their conditions are summarised in table 2.1 and their couplings are illustrated in figure 2.2.

<table>
<thead>
<tr>
<th>Hund’s case</th>
<th>Electronic</th>
<th>Spin-Orbit</th>
<th>Rotational</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>strong</td>
<td>intermediate</td>
<td>weak</td>
</tr>
<tr>
<td>(b)</td>
<td>strong</td>
<td>weak</td>
<td>intermediate</td>
</tr>
</tbody>
</table>

Table 2.1: Table summarising the coupling strength conditions for Hund’s cases (a) and (b).

**Hund’s case (a)**  Here $\hat{L}$ is strongly coupled to the internuclear axis and $\hat{S}$ is coupled to $\hat{L}$. So $\Lambda$, $\Sigma$ and $\Omega$ are well-defined. The interaction between $\hat{R}$ and the electronic motion is very weak. The good quantum numbers are $\Lambda, S, \Sigma, J$ and $\Omega$.

**Hund’s case (b)**  $\hat{L}$ is again strongly coupled to the internuclear axis, making $\Lambda$ well-defined. However, the spin-orbit coupling is weak. Thus, $\hat{L}$ first couples to $\hat{R}$ to form $\hat{N} = \hat{L} + \hat{R}$ which in turn couples to $\hat{S}$ to make $\hat{J} = \hat{N} + \hat{S}$. Therefore the good quantum numbers are $\Lambda, N, S$ and $J$. States with $\Lambda = \Sigma$ have no spin-orbit coupling and so are described by Hund’s case (b).
2.1.5 Hyperfine Structure

Molecules which have a nuclear spin experience further splitting of states. The nuclear spin, $I$, leads to a nuclear magnetic moment which interacts with the magnetic field produced by the electrons. When $I > 1/2$, there can also be higher-order moments such as an electric quadrupole moment which interacts with the electric field gradient at the nucleus. These interactions split $J$ levels into hyperfine levels $F$, defined as $\hat{F} = \hat{J} + \hat{I}$. Each quantum state $F$ is composed of $2F + 1$ projection sublevels labelled $m_F$.

2.2 Electric Dipole Transitions

In the experiment we will drive electric dipole transitions. These must obey a few rules outlined in the following table.

<table>
<thead>
<tr>
<th>Parity</th>
<th>$\Delta P = \pm 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vibration</td>
<td>no selection rules</td>
</tr>
<tr>
<td>Rotation</td>
<td>$\Delta J = 0, \pm 1, J = 0 \leftrightarrow J' = 0$ $\Delta m_J = 0, \pm 1$</td>
</tr>
</tbody>
</table>

Table 2.2: Selection rules governing electric dipole transitions.

These rules are important as we will need to drive a closed transition in the experiment. Rotational changes are governed by selection rules and so it is possible to rotationally close the transition by driving $J' = 0 \leftarrow J = 1$. Notice that there are no selection rules governing the vibrational levels. Here we must consider the branching ratios between the states. A particular vibrational branching ratio is the ratio of the Einstein A coefficient between the excited state vibrational level $v'$ and the ground state vibrational level of interest $v$ divided by the sum of the A coefficients for decays to all vibrational levels in the ground state. The Einstein A coefficient is defined in the following way:

$$A_{v',v} = \frac{\omega_{v',v}^3}{3\hbar c^3\epsilon_0} |\langle e,v,R|\hat{\mu}|e',v',R'\rangle|^2,$$  \hspace{1cm} (2.3)

where $\omega_{v',v}$ is the transition frequency between the two levels, and $\hat{\mu}$ is the dipole moment operator. By applying a Taylor expansion around the equilibrium internuclear separation ($r_0$) we get

$$A_{v',v} = \frac{\omega_{v',v}^3}{3\hbar c^3\epsilon_0} \left( |\langle e,v,R|\mu(r_0)|e',v',R'\rangle|^2 + (r - r_0) \frac{d}{dr} |\langle v|\mu(r_0)|v'\rangle|^2 \right) + \ldots$$ \hspace{1cm} (2.4)
Here, the first part is simply the electric dipole moment of the molecule multiplied by the Franck-Condon factor (FCF), defined as the square of the overlap integral of the two vibrational wavefunctions. For large probability overlap the FCF is a good approximation of the branching ratio. However for small values the second part of the expansion also needs to be considered as the two parts become comparable in size. Theoretical predictions usually calculate only the FCF, whereas experiments depend on the branching ratios. Calculations can give a sense of the branching ratios but they generally need to be verified or measured experimentally, especially when they’re small.
2.3 State details for CaF

Calcium fluoride is a good molecule for laser cooling for several reasons. Its electronic and rovibrational structure have been extensively studied \[95, 96, 97, 98\]. CaF has a highly diagonal Franck-Condon matrix meaning that it is unlikely to change vibrational state during an electronic transition. It is a relatively light molecule with two known transitions suitable for laser cooling and deceleration, one at 531 nm and the other at 606 nm. For the first, the single-photon recoil velocity is 1.3 cm/s, while for the second it is 1.1 cm/s. Figure 2.3 shows the substructure of the relevant levels in CaF. The three states we address are \(X^2\Sigma^+, A^2\Pi_{1/2}\) and \(B^2\Sigma^+\). These each have hyperfine structure due to the \(I = 1/2\) nuclear spin of the fluorine atom. The details of each state are given below.

**X^2\Sigma^+** This is the lowest energy state and it is best described by Hund’s case (b). In the experiment we address the \(N = 1\) state. This is split into four components due to spin-orbit and hyperfine interactions. \(N = 1\) couples to \(S = 1/2\) to give two levels with \(J = 1/2\) and \(J = 3/2\) split by the spin-rotation interaction which has the form \(\hat{N} \cdot \hat{S}\). Each of these is then further divided into two by the hyperfine interaction with the nuclear spin \(I = 1/2\). Thus there are four levels: \((J = 3/2, F = 2)\), \((J = 3/2, F = 1)\), \((J = 1/2, F = 0)\) and \((J = 1/2, F = 1)\), shown in figure 2.3. The hyperfine interaction mixes states with the same \(F\) but different \(J\) meaning \(J\) is not really a good quantum number for the two levels with \(F = 1\). To distinguish these two \(F = 1\) states we use a +/- superscript to indicate...
the higher/lower energy level, not to be confused with the state parity, which for both states is negative.

\[ B^2\Sigma^+ \] This state is also best described by Hund’s case (b). In this state we address the \( N = 0 \) level. Therefore there is no spin-orbit splitting, and \( J = \frac{1}{2} \). The hyperfine interaction leads to two levels \( F = 0, 1 \). These are separated by \( 20 \pm 5 \text{ MHz} \) [99]. Both states have positive parity.

\[ A^2\Pi_{1/2} \] This state is best described by Hund’s case (a). \( S = \frac{1}{2} \) couples to \( L = 1 \) to give two states with \( \Omega = \frac{1}{2} \) and \( \frac{3}{2} \). \( \Omega \) then couples with the rotational quantum number \( R \), which leads to a ladder of states with \( J = 1/2, 3/2, 5/2, \text{etc.} \) Every \( J \) state is actually a pair of states with opposite parity which are split by the \( \Lambda \)-doubling interaction. Each of which is further split into two by the hyperfine interaction. In the experiment, we address the positive parity component of the lowest rotational state within \( \Omega = 1/2 \), which has \( J = \frac{1}{2} \). This is split into two hyperfine levels with \( F = 0 \) and \( F = 1 \). These two states are very close in frequency and have not been resolved. In [99], it is argued that this interval must be smaller than 10 MHz and a value of 4.8 MHz is suggested, based on the known hyperfine interval of the negative parity component of this state [98].

### 2.3.1 Transitions Addressed

We address transitions between \( X^2\Sigma^+(N = 1) \) and either \( A^2\Pi_{1/2}(J = 1/2, p = +) \) or \( B^2\Sigma^+(N = 0) \). Figure 2.4 shows the wavelengths and branching ratios of these various transitions. The slowing transitions are illustrated by dashed lines and the solid lines represent the MOT transitions. Both of these excited states have high probability of decaying back to the initial ground state, making them good for laser cooling. For decays into \( X(v = 0) \) and \( X(v = 1) \) the branching ratios quoted are calculated [100, 101]. The other branching ratios were measured either during the slowing experiment [70] or in the MOT [79]. The slowing light drives the \( B(v' = 0) \leftarrow X(v = 0) \) transition which has a higher branching ratio than the MOT transition \( A(v' = 0) \leftarrow X(v = 0) \). The slowing transition requires only one vibrational repump to be sufficiently closed. The MOT requires two more vibrational levels to be addressed in order to attain a good lifetime. Despite the favourable branching ratios the \( B \leftarrow X \) transition is not suitable for a MOT because the splitting of the hyperfine levels is comparable to the linewidth [99]. In order to rotationally close the transitions we drive molecules from the \( N = 1 \) level of the ground state to \( N = 0 \) (or \( J = 1/2 \)) in the excited state. This leads to dark Zeeman sublevels in the ground state which, if not addressed, would prevent laser cooling. This problem is discussed in section 3.4.5 for the slowing experiment and section 4.1 for the MOT. It is also necessary to address molecules in all four ground state hyperfine levels. The
separation of these is such that a combination of electro- and acousto-optical modulators can be used to add the required frequency components to each laser in order to address each hyperfine level. For future work, e.g. studying collisions, it will be preferable to have the molecules in the ground rotational state. This can be done by using microwave pulses to transfer molecules between rotational levels. The dotted line in figure 2.4 indicates this microwave transition at 20.5 GHz. This will be investigated in chapter 6.
Figure 2.5: Zeeman splitting for the four hyperfine levels in $X^2\Sigma^+(N = 1)$ with respect to $X^2\Sigma^+(N = 0, F = 0)$. The levels which increase in energy as the field increases are labelled weak field seeking (wfs) and the levels whose energy decreases are strong field seeking (sfs).

### 2.4 Field-molecule interactions

Throughout the experiment external fields are used to control the molecules. These can take the form of radiation pressure, as with the slowing, but also the shifting of states and transfer of population between different states.

#### 2.4.1 Zeeman Effect

A particle with a magnetic moment will experience an energy shift in the presence of an external magnetic field. If a state is shifted to higher energy with magnetic field then it is known as weak field seeking (wfs) and if it is shifted to lower energy then it is known as strong field seeking (sfs). We will consider the effect for a molecule in the ground electronic state. The effective Zeeman Hamiltonian is

\[ \hat{H}_Z = g_S \mu_B \hat{S} \cdot \hat{B}, \]  

(2.5)

where $g_S$ is the electron g-factor which is approximately 2. This Hamiltonian doesn’t include the anisotropic correction or the rotational or nuclear Zeeman interactions. These are typically three orders of magnitude smaller than the electronic term and so can be neglected. The full Hamiltonian can be found in [102] and the eigenvalues are shown in figure 2.5.
Molecular structure, notation and interactions

Table 2.3: Table showing \( g_F \) for the four hyperfine components in \( X^2\Sigma^+(v = 0, N = 1) \) as calculated by the approximate and full Zeeman Hamiltonians.

<table>
<thead>
<tr>
<th>( F )</th>
<th>( g_F ) approx.</th>
<th>( g_F ) full</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>1⁺</td>
<td>0.833</td>
<td>0.795</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1⁻</td>
<td>-0.333</td>
<td>-0.295</td>
</tr>
</tbody>
</table>

The eigenvalues can easily be found in low and high fields by using perturbation theory. Let’s consider an external magnetic field aligned along the \( z \)-axis. The energy is given by the expectation value of the Hamiltonian which is

\[
\langle \hat{H}_Z \rangle = g_S \mu_B B \langle \hat{S}_Z \rangle. \tag{2.6}
\]

Let us first consider the effect in low field, when the Zeeman shift is much smaller than the hyperfine splitting. We must consider the coupled basis \( |N, S, J, I, F, m_F\rangle \). Therefore to calculate \( \langle \hat{S}_Z \rangle \) we must apply the projection theory to account for the angular momentum couplings. Hence the Zeeman shift is calculated by:

\[
\langle \hat{H}_Z \rangle = g_s \mu_B B \langle \hat{S}_Z \rangle = g_s \mu_B B \frac{\langle \hat{S} \cdot \hat{J} \rangle}{J(J + 1)} \langle \hat{J}_Z \rangle = g_s \mu_B B \frac{\langle \hat{S} \cdot \hat{J} \rangle}{J(J + 1)} \frac{\langle \hat{J} \cdot \hat{F} \rangle}{F(F + 1)} \langle \hat{F}_Z \rangle = g_F \mu_B B m_F. \tag{2.7}
\]

where

\[
g_F = g_s \frac{1}{2} \frac{S(S + 1) + J(J + 1) - N(N + 1)}{J(J + 1)} \frac{1}{2} \frac{F(F + 1) + J(J + 1) - I(I + 1)}{F(F + 1)}. \tag{2.8}
\]

From this we can calculate the values for \( g_F \). Table 2.3 shows these values for the \( X^2\Sigma^+(v = 0, N = 1) \) state along with the actual values calculated using the full Zeeman Hamiltonian. Equation 2.5 leads to the correct values for the \( F = 2 \) and \( F = 0 \) states. The disparity for the \( F = 1⁺ \) and \( F = 1⁻ \) states is because these states are not states with pure \( J \), but are instead mixtures of \( J = 1/2 \) and \( J = 3/2 \). Equation 2.5 shows that in small fields the energy change is linear with field and states with \( m_F = 0 \) experience no first order Zeeman shift.

In large fields the Zeeman shift will be greater than the hyperfine effect so the calculation can be done the uncoupled basis \( |N, m_N\rangle |S, m_S\rangle |I, m_I\rangle \). This allows us to easily
calculate the Zeeman shift:

\[ \langle \hat{H}_Z \rangle = g_S \mu_B B m_S. \] (2.9)

In large fields the energy change is again linear with magnetic field, for all states. The \( m_S = 1/2 \) states are all weak-field seekers, while the \( m_S = -1/2 \) states are all strong-field seekers. Intermediate fields cause mixing between states of the same \( m_F \) but different \( F \) leading to non-linear shifts for all states apart from those with unique values of \( m_F \). In \( X^2\Sigma^+(N = 1) \) these are the \( F = 2, m_F = \pm 2 \) levels.

The Zeeman effect is required in a MOT, where the shifting of different states enables the preferential scattering of photons from the confining beam.

### 2.4.2 ac Stark effect

A particle with an electric dipole moment, \( \mu \) will experience a splitting of its energy levels in the presence of an external electric field with amplitude \( E_0 \). The Hamiltonian for interaction with linearly polarised light is

\[ \hat{H}_S = \hat{\mu}_z E_0 \hat{z} \] (2.10)

where the light is polarised along \( \hat{z} \). We can analyse this using perturbation theory where the energy change \( \Delta E_i \) of state \( i \) due to light at frequency \( \omega \) is calculated by

\[ \Delta E_i = \langle i | \hat{H}_S | i \rangle + \sum_j \frac{|\langle i | \hat{H}_S | j \rangle|^2}{E_j - E_i - \hbar \omega}. \] (2.11)

The first part gives zero for all levels because \( \hat{\mu}_z \) has odd parity. The second part involves summing the interaction over every level. The electric dipole transition selection rules limit the number of states which can be included. Also, if the frequency of the light is nearly resonant with one specific transition then the interaction between these two levels will dominate. For a transition from the ground state, \( g \), to excited state, \( e \), the effect becomes

\[ \Delta E = \frac{|\langle g | \hat{H}_S | e \rangle|^2}{E_e - E_g - \hbar \omega} \]
\[ = \frac{|\langle g | \hat{\mu}_z | e \rangle|^2 E_0^2}{\hbar (\omega_0 - \omega)} \]
\[ = \frac{\hbar \Omega^2}{\Delta}. \] (2.12)
Therefore, the energy shift depends on the Rabi frequency \( \Omega = \frac{|\langle g|\hat{\mu}_z|e\rangle|E_0}{\hbar} \) and the detuning of the light from resonance \( \Delta = \omega_0 - \omega \).

The ac Stark effect enables sub-Doppler cooling of molecules in a molasses, as will be shown in section 5.1.

### 2.4.3 Scattering rate

Photons will scatter from atoms/molecules at a rate depending on the intensity of the light \( (I_0) \), the detuning from a transition \( (\Delta) \), the spontaneous decay rate \( (\Gamma) \) and the saturation intensity of the transition \( (I_s = \frac{\pi h c \Gamma}{3 \lambda^3}) \). A simple rate model \[38\] can be used to predict the scattering rate of the molecules for a multilevel system. This approximation assumes that all ground states \( (n_g) \) are coupled to all excited states \( (n_e) \) with equal strength and it comes from solving the Optical Bloch equations. From \[80\] we know that the scattering rate can be calculated by

\[
R_{sc} = \frac{\Gamma_{\text{eff}}}{2} \frac{s_{\text{eff}}}{1 + s_{\text{eff}} + 4\Delta^2/\Gamma^2},
\]

where

\[
\Gamma_{\text{eff}} = \frac{2n_e}{n_g + n_e} \Gamma,
\]

and

\[
s_{\text{eff}} = \frac{I_0}{I_{s,\text{eff}}} = \frac{2(n_g + n_e)}{n_g^2} \frac{I_0}{I_s}.
\]

The scattering rate determines the efficiency of laser slowing, described in section 3.4.5 as well as determining the temperature, capture velocity, oscillation frequency and damping constant of the MOT, described in section 4.4.

### 2.4.4 Coherent population transfer

The Rabi model \[103\] describes the population transfer between two states coupled by an oscillating external field with amplitude \( E_0 \) and driving frequency \( \omega \), which is close to the transition frequency \( \omega_0 \). This leads to an interaction Hamiltonian given by

\[
\hat{H}_{\text{int}}(t) = -\hat{\mu}_z \cdot \hat{E}_0 \cos \omega t.
\]

The wavefunction at any time for a two level system can be written as

\[
\Psi(r, t) = c_1(t)|1\rangle + c_2(t)|2\rangle e^{-i\omega_0 t}.
\]
Molecular structure, notation and interactions

Solving the time-independent Schrödinger equation for a two level system leads to two coupled equations describing the changing amplitudes of the two states

\[ i\hbar \frac{dc_1(t)}{dt} = c_2 \hbar \Omega^* \left( \frac{e^{i(\omega-\omega_0)t} + e^{-i(\omega+\omega_0)t}}{2} \right) \]

\[ i\hbar \frac{dc_2(t)}{dt} = c_1 \hbar \Omega \left( \frac{e^{i(\omega+\omega_0)t} + e^{-i(\omega-\omega_0)t}}{2} \right). \]

Here \( \Omega \) is the Rabi frequency, as previously defined. We now take the Rotating Wave Approximation which assumes that terms including \( \omega + \omega_0 \) oscillate at twice the frequency of the field and therefore their time dependence averages out over the longer timescales of the evolution of the coefficients \( c_1 \) and \( c_2 \). This is a good approximation for when the field is oscillating close to resonance. The coupled equations are now simplified and can be differentiated to form two uncoupled equations

\[ \frac{d^2 c_1}{dt^2} - i\Delta \frac{dc_1}{dt} + \frac{\Omega^2}{4} c_1 = 0 \]  \hspace{1cm} (2.20)

and

\[ \frac{d^2 c_2}{dt^2} + i\Delta \frac{dc_2}{dt} + \frac{\Omega^2}{4} c_2 = 0 \]  \hspace{1cm} (2.21)

where \( \Delta = \omega - \omega_0 \) is the detuning from resonance. Now let’s consider the case where the molecule begins in state \( |1\rangle \). This means that \( c_1(0) = 1 \) and \( c_2(0) = 0 \) and equations (2.20) and (2.21) can be solved to give an expression for the probability of the molecule being in the excited state \( P_2 = |c_2(t)|^2 \)

\[ |c_2(t)|^2 = \frac{\Omega^2}{\Omega'^2} \sin^2 \left( \frac{\Omega't}{2} \right) \]  \hspace{1cm} (2.22)

where \( \Omega' = \sqrt{\Omega^2 + \Delta^2} \) is the detuned Rabi frequency. Figure 2.6 shows \( P_2(t) \) for a resonant external field with \( \Omega = 1 \). It is clear that the probability of populating the excited state is maximised when \( t = \pi/\Omega \). This is referred to as a \( \pi \)-pulse. The population is transferred into an equal linear superposition of the ground and excited states when \( t = \pi/2\Omega \), known as a \( \pi/2 \)-pulse.

State transfer by this method is important in Ramsey spectroscopy which is a fundamental technique used across AMO physics applications. In this thesis we will need to use \( \pi \)-pulses to achieve quantum control over the molecules by transferring the population between different \( m_F \) states, described in section 6.3.2.
Figure 2.6: Rabi curve for a two level system in a resonant external oscillating field, with $\Omega = 1$ showing the probability of a molecule being in state $|2\rangle$ versus pulse time $t$. 
Chapter 3

Laser Slowing

This chapter will cover the laser slowing experiment. These results are also presented in [70].

3.1 Introduction

We choose to slow on the $B^2\Sigma^+(v = 0, N = 0) \leftarrow X^2\Sigma^+(v = 0, N = 1)$ transition. This has a branching ratio of $99.8\%$. So by addressing only the $v = 0$ and $v = 1$ state we can sufficiently close the transition and scatter over 30,000 photons before half of the molecules are lost. To repump the population that leaks to $v = 1$, we drive the $A^2\Pi_{1/2}(v = 0, J = 1/2, p = +) \leftarrow X^2\Sigma^+(v = 1, N = 1)$ transition. This addresses a different excited state to the main slowing transition meaning that the scattering rate is almost double compared to previous work [68].

3.1.1 Slowing and Cooling

It is important to note that the slowing light must be red-detuned from the transition frequency. This is to account for the Doppler shift observed by the molecules. Molecules travelling at velocity ($v$) will observe a frequency shift ($\Delta \nu$) of the laser light at frequency ($\nu_0$) according to

$$\Delta \nu = \frac{v}{c} \nu_0. \quad (3.1)$$

Therefore we can choose the detuning such that the light is resonant with a particular velocity class. The velocity dependence of the Doppler shift means that the molecules are also cooled as they decelerate. Molecules which start on resonance with the cooling light scatter photons at a high rate, but this rate decreases as they are decelerated away from resonance. Molecules which start with a higher velocity will have their scattering rate increase as they decelerate towards resonance and then decrease, so these molecules will
Figure 3.1: Results from a Fokker-Planck type model showing laser slowing and cooling. The initial distribution, shown in blue, has a mean velocity of 125 m/s and a standard deviation of 30 m/s. The red curve shows the velocity profile after 1 ms of interaction with light which is resonant with molecules travelling at 150 m/s. The blue dots show a recorded initial velocity distribution.

decelerate the most. Molecules starting with a lower velocity will scatter at a slow rate and only decelerate slightly. This therefore leads to a bunching in the velocity spread and the beam cools. The way the velocity distribution changes over time can be modeled using the equation

$$\frac{\partial}{\partial t} q(v, t) = -\frac{\partial}{\partial v} (F(v)q(v, t))$$

(3.2)

which is a type of Fokker-Planck equation [104] where we have neglected diffusion. $q(v, t)$ is the time evolved velocity distribution and the scattering force is $F(v) = R_{sc}(v)h/\lambda$ and $R_{sc}(v)$ is the scattering rate, defined in equation [2.13]. Figure 3.1 shows an example, where I solve equation [3.2] for an initial Gaussian velocity distribution with mean velocity of 125 cm/s and a standard deviation of 30 m/s. The initial distribution is shown in blue and the blue dots show a recorded velocity distribution. The scattering force is detuned to interact with molecules travelling at 150 m/s. The red curve shows the velocity profile after 1 ms of scattering events. The red curve shows that molecules which were travelling at velocities between 130 m/s and 180 m/s have been decelerated. After the light pulse they have velocities between 110 m/s and 130 m/s. This shows clearly both slowing and cooling. This is an idealised system with no molecule loss from the cooling cycle. Each molecule is assumed to scatter at a rate only dependent on its velocity. For a more realistic simulation one would need to consider the transverse velocity of the molecules, their spatial distribution, the gaussian intensity profile of the light and the presence of dark states.
3.2 Experimental Set-up

Figure 3.2: Schematic showing the experimental set up used in the laser slowing experiments described in this chapter. Not to scale.

Figure 3.2 shows the experimental set-up used for the laser slowing experiments.

3.2.1 Molecular Source

To create the CaF molecules we use a pulsed, cryogenic buffer gas source running at a repetition rate of 2 Hz. This technique is relatively well established for the production of intense, slow molecular beams [105, 106, 107]. The CaF source was developed whilst I worked on the lasers and optics set-up. Here, I will give a brief overview of the set-up. For a more detailed discussion see [108]. The CaF molecules are produced inside a copper cell which is cooled by a cryocooler to 4 K. A calcium target is ablated by a pulsed Nd:Yag laser in the presence of SF\textsubscript{6} gas. Room temperature SF\textsubscript{6} is continually flowing into the cell at a flow rate of 0.01 sccm. Helium is also injected into the cell at 0.3 sccm. It enters through a copper tube which is thermally connected to the cryocooler, cooling the gas to 4 K. The CaF molecules thermalise via elastic collisions with the helium, reaching around 10 K. The molecules exit the cell at z = 0 through a 3.5 mm diameter aperture. A copper cylinder surrounding the cell is thermally anchored to the cryocooler and the inside surface is coated with charcoal. When charcoal is cooled to below 8 K it acts as a pump for helium which reduces the amount of helium gas in the vacuum chamber. The chamber is pumped with a turbo pump and reaches a room temperature pressure of 10^{-7} mbar. The source produces $5 \times 10^{10}$ molecules/steradian/pulse in the desired N=1 state, travelling with an average velocity of around 150 m/s. The pulse has a very narrow temporal distribution when leaving the source. Figure 3.3 (a) shows the molecular signal recorded 2.5 cm downstream of the source. We see that the molecules have all left the...
Figure 3.3: Typical time of flight profiles recorded at (a) 2.5 cm and (b) 53 cm downstream of the source cell.

cell about 100 µs after the ablation pulse. At this point the pulse has a temporal width of 280 µs, and this short initial duration leads to a strong correlation between speed and arrival time relation further downstream. Figure 3.3(b) shows the molecular pulse 53 cm downstream. The peak arrival time of 3.14 ms indicates an average forward speed of 170 m/s.

The source requires little maintenance. We find that a single ablation spot can produce a reliable flux of molecules for around $10^4$ shots. After this the signal size starts to decay and so we rotate the target rod, exposing a new spot for ablation. At the end of every day we empty the charcoal cryopumps of helium by heating them. This is necessary because once the cryopumps have become saturated with helium the pressure in the chamber increases, causing the molecular signal to decrease. At temperatures above 20 K the helium is released from the charcoal and can be pumped away by the turbo pumps. After two days of running the experiment we find that the signal will decay suddenly and can’t be revived either by turning the target or emptying the cryopumps. The only way to get back to optimal signal is to heat up the source to at least 300 K. This process takes around 6 hours. We have 50 W power resistors attached to the cryocooler which we use to heat the source. Once a sufficiently high temperature is reached we then turn off the heaters and turn on the cryocooler bringing the temperature back down to 4 K. This whole process takes around 12 hours and so we do this every night as it ensures we never lose signal. Other than this nightly cycling of the source, no regular maintenance is required.

The molecules leave the source chamber and are collimated by an 8 mm aperture at $z = 35$ cm and enter the slowing chamber. The slowing chamber is at a pressure of $6 \times 10^{-8}$ mbar, and is connected to the source chamber via bellows. This vibrationally isolates the slowing chamber from the cryocooler. Along the length of the slowing chamber
there is a pair of magnetic field coils arranged in Helmholtz configuration, which can be used to produce a static field throughout the chamber. The magnetic field destabilizes dark states in the $N = 1$ ground states, ensuring that all states can be driven to the $N = 0$ excited state.

### 3.2.2 Lasers

In the laser slowing experiment a total of five lasers are used. The first is the ablation laser. This is a pulsed Nd:Yag laser which emits 5 ns long pulses of 5 mJ at 1064 nm, running at a repetition rate of 2 Hz. There are then three lasers addressing molecular transitions: one for slowing, one as a repump and a third for detection. The main slowing laser, $\mathcal{L}_{00}$, addresses the $B^2\Sigma^+(v = 0, N = 0) \leftrightarrow X^2\Sigma^+(v = 0, N = 1)$ transition at $\lambda_{\text{slow}} = 531$ nm. This laser is an amplified frequency-doubled 1062 nm fibre laser (Quantel Eylsa). The repump, ($\mathcal{L}_{10}$), transition is $A^2\Pi_{1/2}(v = 0, J = 1/2, p = +) \leftrightarrow X^2\Sigma^+(v = 1, N = 1)$ at $\lambda_{\text{repump}} = 628$ nm, and the detection laser drives the $A^2\Pi_{1/2}(v = 0, J = 1/2, p = +) \leftrightarrow X^2\Sigma^+(v = 0, N = 1)$ transition at 606 nm. These are both fibre-amplified frequency-doubled laser systems. The seed lasers are Toptica DL pro lasers which emit at 1256 nm and 1212 nm for the repump and detection beams respectively. The seed beam is fibre coupled into an amplifier where it gets amplified to 8 W (from 70 mW). The amplified light then passes through a doubling crystal where the frequency is doubled. These systems are made by MPB. The repump laser is capable of producing 1.8 W of light at 628 nm and the detection laser can emit 1 W of 606 nm. The slowing and repump beams are combined using a polarizing beam cube and are coupled into a polarization maintaining fibre, the output of which is expanded, to a FWHM of 3.5 mm, before entering the slowing chamber. The ground state hyperfine structure must be addressed by each laser. To do this, frequency sidebands are added to each laser by electro-optical modulators (EOMs).
Laser Slowing

Figure 3.5: (a) Fluorescence spectrum obtained by scanning the 606 nm probe with only a single frequency showing the four hyperfine levels. (b) Fluorescence spectrum obtained by scanning the 606 nm probe laser over 385 MHz using TCL. The enhanced central peak shows the frequency shift at which each sideband addresses a hyperfine level i.e. light is resonant with the molecules in all four hyperfine states.

Figure 3.4(a) shows the optics set-up used to create the sidebands and combine the beams for the slowing experiment. The specifics of the sideband structure for the slowing and repump beams depends on the experiment and will be described later. For the probe laser the sidebands are made by first splitting the light in the ratio 3 : 1 on a polarizing beam cube. The first part passes through an EOM resonant at 74.5 MHz, driven to produce the zeroth and first orders, addressing $F = 2$, 0 and 1$. The other part of the light passes through an acousto-optical modulator (AOM) at 48 MHz and we pick off the negative first order, addressing $F = 1^+$. Figure 3.4(b) shows the spectrum for the probe light, the dashed lines indicate the position of the hyperfine levels.

A very high level of control is required over the frequencies of the lasers. To achieve this a fifth laser is used which serves as a stable frequency reference for all the other lasers. This is a Toptica DL100 at 780nm which is locked, using polarisation spectroscopy, to the $F = 2 - F = 3$ component of the D2 transition in $^{87}$Rb. This lock is stable to better than 1 MHz on short time scales. Light from each laser is coupled into a scanning Fabry-Perot cavity (Thorlabs SA200-5B with a 1.5 GHz free spectral range) and detected using photodiodes. The signals from each photodiode are sent to a homemade program called transfer cavity lock (TCL), which is described in [109]. The cavity is stabilized to the reference laser and the frequencies of the other lasers are then stabilized to the cavity, by sending a voltage to the laser. The frequency of a laser can be accurately scanned this way too, by changing the applied voltage. The frequency stability of the lasers is then better than 2 MHz.

To find the frequency of a transition the relevant laser is used as an orthogonal probe and scanned using TCL. Figure 3.5(a) shows the hyperfine spectrum recorded with the 606 nm probe beam, with no frequency sidebands. Here we can see the four hyperfine
levels clearly. We want to address all four hyperfine levels and so we next add the frequency sidebands and scan again. Figure 3.5(b) shows this spectrum. The large central peak is the lock point as it corresponds to the frequency where all hyperfine levels are addressed simultaneously. This central peak gives ten times the signal of the highest peak in part (a). The smaller peaks on either side correspond to frequencies where some, but not all of the hyperfine components are addressed. Once locked the slowing and repump lasers need then to be red detuned to compensate for the Doppler shift.

### 3.3 Data acquisition and analysis

The molecules can be detected at three positions; \( z = 2.5 \text{ cm} \), \( z = 53 \text{ cm} \) and \( z = 130 \text{ cm} \), shown in figure 3.2. In general the data presented in this section was recorded at the furthest detector and normalised by the height of the signal recorded at the first detector. This was necessary due to large shot-to-shot fluctuations in the source flux. Photomultiplier tubes (PMTs) are used to collect the laser induced fluorescence (LIF) signal from the molecules as they pass through a probe beam. Figure 3.6(a) shows the optics used to image the molecules onto the PMT. Inside the chamber there is a spherical mirror facing the PMT positioned one radius of curvature (50 mm) beneath the probe beam. The fluorescence from the molecules is imaged onto the PMT using a pair of lenses. The first is placed one focal length \((f_L)\) above the molecular beam and collimates the fluorescence. The second is placed one focal length from the PMT cathode, focusing the light. A mask in front of the photocathode, 16 mm along x and 8 mm along z shown in figure 3.6(b), helps to reduce background scatter. An interference filter blocks scattered light from the slowing and repump laser beams. The probe beam has a power of 5 mW and a \(1/e^2\) diameter of 6 mm. At the furthest detection point there are two detection ports, one perpendicular to the molecular beam path and a second at 60 degrees allowing time of flight and velocity measurements to be made (see 3.3.1). The data presented in this chapter were recorded using alternating “cooled” and “control” shots, with the slowing light on and off, respectively. By doing this we can control for decay in source signal over time.

#### 3.3.1 Velocity Analysis

The velocity distribution of the molecules can be measured by utilizing the velocity dependence of the Doppler shift. The probe beam is angled at 60° to the molecular beam and its frequency is scanned. The measured resonant frequency of a molecule can therefore be used to determine its velocity.
Laser Slowing

Figure 3.6: (a) Schematic showing the optics set-up for imaging molecules onto a PMT. A spherical mirror collects light scattered away from the PMT. Two lenses are used to collimate and then focus the light onto the PMT. An interference filter is used to block light from $\mathcal{L}_H$ and $\mathcal{L}_\infty$, and a mask is used to block scattered background light. (b) shows the dimensions of the mask.

Figure 3.7 shows our analysis method, where the control data is shown in grey and the cooled data in blue. The angled probe beam is scanned, in steps of 2.5 MHz, over 250 MHz. This frequency range covers the Doppler shift for molecules traveling between 230 m/s and stationary. For each frequency we record, and average, five time of flight (tof) profiles, both with and without $\mathcal{L}_{00}$. When averaged over all frequencies we get a tof much like the ones we record with the orthogonal probe, see figure 3.7(a). By selecting a narrow time window (0.5 ms) in the tof we obtain the frequency spectrum associated with molecules arriving at this time. Figure 3.7(b) shows the frequency spectrum measured for molecules arriving within the time window shown by the dashed red lines in figure 3.7(a). We fit the sum of three gaussians to the frequency spectrum and extract from the fit the frequency of the largest peak. This corresponds to the mean velocity of molecules arriving within our chosen time window. The other peaks are due to the frequency sidebands. The conversion from frequency to velocity ($v$) is:

$$v = \frac{\Delta \nu c}{\nu_0} \cos(60^\circ)$$  \hspace{1cm} (3.3)

where $\Delta \nu$ is the difference in frequency between the orthogonal resonance and the peak in the $60^\circ$ spectrum, $\nu_0$ is the orthogonal resonant frequency and $c$ is the speed of light. We then assign this velocity to the arrival time. We find that the width of the peak in the spectrum for a time window of 0.5 ms is about the same as the width obtained with the orthogonal probe, showing that there is little spread in the velocities for these molecules. By repeating this step across the entire time of flight we can produce a graph, like the one in figure 3.7(c) showing arrival time versus velocity. We then fit an interpolative function.
Figure 3.7: Method for obtaining velocity profiles: measure the time of flight and associated frequency spectrum by scanning the frequency of the probe laser at the 60° port. Split the time of flight into narrow bands (a - indicated by dashed red lines) and fit gaussian functions to the associated frequency spectra (b), fit an interpolative function to correlate the arrival time to velocity (c) and then convert the time of flight plot into a velocity profile (d). In the plots the control data is shown in grey and the slowed data in blue. Reproduced from [70].

to correlate arrival time with velocity, which enables us to convert the tof into a velocity profile, see figure 3.7(d).
3.4 Results

3.4.1 Initial Experiments

In the early experiments the detunings of the slowing and repump beams were set to be resonant with molecules traveling at 180 m/s ($v_{\text{start}}$). Both beams have sidebands added to address the hyperfine structure of the ground state, shown in figure 3.9(a). The slowing light is switched on at $t_{\text{start}}$, 1 ms after the ablation pulse so that all molecules have left the cryogenic cell before they start interacting with the light. The slowing light is turned off at $t_{\text{end}} = 7$ ms, which is before the slow molecules reach the detector. This gives the slowed molecules time to separate from the unslowed ones before they are detected. This is advantageous for the slowing experiment as it is obvious from the time-of-flight profiles if the slowing is working. The repump light is applied continuously for both the control and cooled shots. The beams are collimated with a full width at half max of 3.5 mm and the intensities are 390 mW/cm² and 360 mW/cm² for the slowing and repump beams respectively.

Figure 3.8 shows (a) time of flight and (b) velocity distribution plots for this experiment where the control and cooled data are in red and blue respectively. From this plot we can see that molecules with a high initial velocity, arriving before about 6.5 ms, do not interact with the slowing light. The control and cooled signals match until this time, then there is a sudden dip in the cooled signal. The minimum corresponds to molecules traveling at around 180 m/s which are resonant with the slowing light. The slow peak in the velocity distribution shows that the molecules have been decelerated by 90 m/s. Once a molecule has decelerated by 90 m/s its resonant frequency will have changed by 170 MHz. According to equation [2.13] its scattering rate will now be less than 1% of the full scattering rate. Therefore keeping the slowing light on longer is not an efficient way of further decelerating the molecules. Instead the changing Doppler shift needs to be
accounted for. We explore two methods to do this. Firstly broadening the laser frequency as used in previous work \[66,110,69\] and secondly by chirping the frequency.

### 3.4.2 Frequency Broadening Results

Here I will describe the results achieved by frequency broadened slowing. Both the slowing and repump lasers are broadened using three consecutive EOMs resonant at 72 MHz, 24 MHz and 8 MHz, with 90% of the power lying within 250 MHz. Figure 3.9 shows the frequency spectrum used recorded using a scanning Fabry-Perot cavity. This frequency spread corresponds to a spread in velocity of 130 m/s. The overall detuning can be set arbitrarily to interact with different velocity ranges. The spectrum of light shown in figure 3.9(b) has quite sharp drops in intensity at around ±100 MHz. The velocity corresponding to the low-frequency edge in the spectrum is referred to as the cut-off velocity. The scattering rate falls off sharply for molecules with lower velocities than this. Figure 3.10 shows time of flight and corresponding velocity profiles for three different detunings. The frequency spectrum used is shown in shaded green. Figure 3.10(b) shows that smaller detunings lead to slower final velocities.

The velocity profiles show a narrowing in distribution indicating cooling of the molecular pulse. However, the distribution in arrival times is very broad, especially for the slowest set. With the frequency broadened technique all molecules scatter photons at the same rate irrespective of their velocity, until they reach the cut-off velocity. Molecules which have a low initial velocity decelerate to the cut-off velocity early on in the interaction time whilst faster molecules take longer to decelerate. The long, and variable free flight time leads to the temporally wide pulse observed in figure 3.10(a) even though the velocity distribution is narrowed, figure 3.10(b). The final velocity of the molecules is
Figure 3.10: Panel (a) shows the time of flight data recorded for three different detunings of the slowing light and (b) shows the respective, measured, velocity profiles. Control profiles are shown in grey and the dashed black curves are simulation results. Shaded area in (b) show the spectrum of light used in each case. Coloured bands around the solid lines in (b) indicate 68% confidence limits. Reproduced from \[70\].

much slower than the cut-off velocity. This is the same effect as seen in figure \[3.8\] where the molecules continue to scatter photons even though they are Doppler shifted away from resonance.

Figure \[3.10\] (b) shows that we can slow molecules to 50 m/s using this technique. However the number of molecules decreases the more they are decelerated. The reason for this will be discussed in section \[3.4.4\]. We found that changing the detuning to even lower values did not enable us to detect molecules below 50 m/s.

### 3.4.3 Frequency Chirping Results

The second way to address the changing Doppler shift of the molecules is to apply a linear chirp to the slowing and repump lasers. They will then stay resonant with the decelerating molecules. The two lasers are chirped with rates $\alpha$ and $\alpha \lambda_{\text{slow}} / \lambda_{\text{repump}}$ for the slowing and repump respectively. The chirp is implemented by sending a voltage, in a triangle wave, to the laser controllers. Two variable attenuators are used to set the two chirp rates from the same voltage function. The lasers are chirped so that at the end of the cooling period they are resonant with molecules traveling at speed $v_{\text{end}} = v_{\text{start}} - \alpha \lambda_{\text{slow}} (t_{\text{end}} - t_{\text{start}})$. 
Changing the rate $\alpha$ can be done by changing either the interaction period or the amplitude of the triangle wave. Setting the optimum chirp rate depends on the scattering rate of the molecules. If the laser chirps too slowly then the molecules will decelerate out of resonance with the laser and spend some time in free flight before the laser frequency catches up again. If the laser chirps too quickly then the molecules won’t keep up and they will fall out of resonance behind the laser chirp and will stop being decelerated.

Figure 3.11 shows the (a) time-of-flight profiles and (b) velocity profiles recorded for various $\alpha$ over the same interaction time of 6 ms. Here the initial detuning is kept the same ($v_{\text{start}} = 180$ m/s), while the final detuning is varied. It can be seen from both the time-of-flight and velocity profiles that the larger the chirp the bigger the deceleration. Figure 3.11(a) shows that the distribution in arrival time doesn’t broaden out as much as for the frequency-broadened technique. This is because the chirp causes time-dependent slowing. Molecules with a low initial velocity do not become resonant with the light until the faster molecules have decelerated to the same speed. Even at 50 m/s there is still an obvious peak in the time of flight, which was not there in the frequency broadened experiment. The number of molecules in the slow peak, however, decreases as the final speed decreases in much the same way as the frequency-broadened experiment.

We have demonstrated slowing of molecules from 180 m/s to 50 m/s using this frequency chirped technique. However, increasing the chirp amplitude further did not produce a slower signal. Further optimisation was needed to reach lower velocities, and this is described in section 3.4.5.

### 3.4.4 Missing Molecules

From sections 3.4.2 and 3.4.3 it is evident that fewer molecules are detected the more they are decelerated. In this section I will describe the tests we did to search for these molecules.

**Leaks to other vibrational or rotational levels** We first checked that molecules weren’t being pumped into a state which is not addressed by the lasers. Possible decay channels are shown in figure 3.12(a). The first place to check for a leak was to the second excited vibrational level of the ground electronic state. A variety of chirp amplitudes were applied to the cooling light and the molecules were detected on the $A^2\Pi_{1/2}(v = 2, J = 1/2, p = +) \leftarrow X^2\Sigma^+(v = 2, N = 1)$ transition at 494.757 THz. Figure 3.12 (b) shows an example where a chirp amplitude of 130 MHz was applied. It was found that approximately 4% of the initial distribution is pumped into $v = 2$. For this
Figure 3.11: Plots showing laser slowing for various chirp rates, $\alpha$, $t_{\text{start}} = 1$ ms, $t_{\text{end}} = 7$ ms, $v_{\text{start}} = 178$ m/s. (a) shows the time of flight profiles and (b) shows the measured velocity profiles both with cooling on (solid coloured) and off (solid grey). The dashed black curves are simulation results. The vertical dashed lines in (b) indicate $v_{\text{start}}$ (red) and $v_{\text{end}}$ (coloured). The coloured bans around the solid lines in (b) indicate 64% confidence intervals. Plot reproduced from [70].
Figure 3.12: (a) Level structure showing possible decays out of slowing cycle. Solid arrows indicate slowing and repump lasers, dashed lines show possible decays. Black - electric dipole transitions, purple - magnetic dipole or electric quadrupole transitions, orange - decay via A state. (b) Time of flight plots for a 130MHz chirp. Black curves show the control TOF, no cooling, and the red curves show the cooled TOF. The dashed curves show the population detected in $v=0$ and the solid curves show the population in $v=2$. 4% of the molecules which start in $v=0$ end up in $v=2$ in this example.

Another possible source of loss is decay to a different rotational level; specifically N=0, 2 or 3. Decay into states N=0 or N=2 could occur via three routes. If a molecule decays via the A state it would have to change parity twice and so end up in a rotational state of the wrong parity. Alternatively the molecules can reach $N = 0$ or $N = 2$ through a magnetic dipole or electric quadrupole transitions, where the parity doesn’t change. Decay could also happen to the N=3 rotational state, where there is a weakly allowed decay route to the $F=2$ hyperfine level caused by hyperfine mixing of rotational states. Small leaks were found into the N=0 and N=2 states of 0.5% and 1.5% respectively. There was no observable population increase in the N=3 state. From these measurements we conclude that population loss to dark states is too small to account for the loss observed in the experiment.

**Divergence and Transverse Heating**  Slower molecules have higher divergence, which could account for the observed loss of molecules. The natural divergence of the beam is due to the initial transverse velocity, which is not reduced as the molecules are slowed.
Figure 3.13: The transverse and longitudinal position of a molecule starting at the origin when scattering photons at 2 MHz. The dashed red line shows the position with no cooling light on, the green line shows the effect of the natural divergence for a transverse velocity of 1 m/s with slowing and the orange line shows the combined effect of the natural divergence and transverse heating caused by photon scattering events.

On the contrary, there is some transverse heating due to the emission of a photon, which happens in a random direction during the slowing, leading to a random walk. Simple calculations show the severity of these two effects. Figure 3.13 shows the transverse versus longitudinal distance for molecules with an initial forward velocity of 170 m/s and an initial transverse velocity of 1 m/s. The dashed line shows the natural divergence of the beam with no slowing. The solid lines show the effect of slowing from 170 to 14 m/s including natural divergence alone and with transverse heating, shown in green and orange respectively. In this figure $z, x = 0$ m is the position of a molecule when the cooling light is turned on. This plot shows that the transverse width of the beam is around four times larger after slowing than in the free flight case. This large divergence would decrease the number of molecules detected by the probe beam. From further simulations, carried out by Noah Fitch and Mike Tarbutt, we concluded that this was the cause of the loss of molecules.
3.4.5 Optimising for Slow Molecules

Now that we have demonstrated that laser cooling works to decelerate CaF molecules the next step is to optimise the process to decelerate as many molecules as much as possible. We need to decelerate them to within the capture velocity of a molecular MOT, predicted to be around 10 m/s.

**Laser Intensity**  The scattering rate, and thus the efficiency of laser slowing, is dependent on the laser intensity. The number of photons scattered will increase with the intensity of the slowing laser until a saturation point is reached. Until this point, the excitation rate of molecules is directly proportional to the laser intensity. If the excitation rate is much bigger than the spontaneous decay rate $\Gamma$ then a further increase in laser intensity will not result in an increase of scattered photons. For a two level system driven by an intensity much greater than saturation the molecules will be in a steady state with half the population in the ground state and half in the excited state. For the CaF experiment there are 12 possible ground states (including magnetic sublevels) and 4 excited states; above saturation each of these levels will be equally populated.

The effect of the intensity was tested by running cooling experiments for both frequency chirping and broadening techniques. For the chirping a rate of 22 MHz/ms was used and for the broadening the detuning was set to interact with molecules at 178 m/s. In the chirped case the saturation intensity was found to be 350 mW/cm$^2$ and for the frequency broadened it was 750 mW/cm$^2$. It isn’t surprising that the frequency broadened technique requires higher intensity to saturate the slowing as the total power is spread over many more sidebands than in the chirped case.

**Remixing Dark States**  There are dark states amongst the ground state sublevels of the cooling transition. If nothing is done to address these dark states then the molecules will very quickly decay to them and leave the cooling cycle.

Two methods were investigated to solve this; firstly an applied static magnetic field. This works by causing the states to precess around the axis of the magnetic field and hence remix the dark states. It is expected that a precession frequency on the order of the scattering rate will optimise the remixing. For this experiment that is a few MHz, which requires a field of few Gauss. It is important that the direction of the magnetic field is not parallel to the polarisation of the light, but beyond that it is found to be very insensitive to the angle. If the size of the magnetic field is too small then the states will remix slowly reducing the scattering rate, if it is too large the magnetic sublevels would
be Zeeman shifted out of resonance with the slowing light.

We investigate the effect of the size of the magnetic field for both slowing techniques. In order to measure the effect we record the peak arrival time of the molecules as a function of the magnetic field. The later the molecules arrive the more they’ve been slowed. With no magnetic field present the molecules aren’t slowed at all because they are pumped into a dark state too quickly. For increasing magnetic field the molecules arrive later indicating that the remixing is happening more efficiently and so the scattering rate is increased. The amount of slowing levels off around 5 G.

The second method is to modulate the polarisation of the light between linear and circular. This is done by passing the linearly polarised slowing light through an EOM angled at 45 degrees to the polarisation of the light. This technique will be optimised when the modulation frequency is comparable to the scattering rate. We found that switching the polarization at 5 MHz with no magnetic field applied produced the same results as a 5 G field. For all data presented in this chapter a static field of 5 G is applied along the length of the slowing chamber. We chose to use this method because it is simpler to implement.

Converging slowing beam In order to counter the molecular beam divergence described in section 3.4.4 we focus the slowing beam to introduce a small transverse component to the photon momentum. The convergence was limited by laser power and window size. The beam FWHM at $z = 1$ m was 7 mm and at $z = 0$ it was 1.77 mm. Figure 3.14 (a) shows the change in slowing using the frequency broadened technique with two different initial detunings (352 and 308 MHz) for a collimated (green) and converging (red) beam. For both detunings the signal is larger for the converging beam but the molecules are decelerated less. We believe that this is due to the decreasing beam intensity along the interaction region which causes the scattering rate to decrease as molecules travel and therefore reduces the overall efficiency of the slowing. Figure 3.14 (b) compares the effects of converging and collimated beams for the chirped slowing method. For all chirp rates the converging beam increases the signal, but again tends to give slightly faster molecules in the slowed pulse. As before, this is probably due to the reduced intensity towards the end of the slowing region. However the velocity difference for the chirped case is small and the signal increase is large, therefore we expect that now by increasing the chirp amplitude we will be able to achieve lower velocities.
Figure 3.14: Time of arrival plots for slowing using a converging beam (red) and a collimated beam (green). Control ToFs are shown in grey to show the reader the consistency of the source between these two scans. (a) shows the effect when using the frequency-broadened slowing method and (b) shows the frequency chirped results.
3.4.6 Reaching the capture velocity

The narrow velocity distribution and the signal enhancement gained with the converging beam for chirped slowing, lead us to further pursue this method. By changing the chirp rate and interaction time we optimised the slowing and decelerated the molecules to below 20 m/s.

In order to achieve this a chirp of 37 MHz/ms is applied with an initial detuning of 310 MHz, corresponding to $v_{\text{start}} = 178$ m/s. It was found that to maximise the number of slow molecules it is beneficial to have a short period of time when the slowing light is on before starting the chirp, at $t_{\text{chirp}}$. This allows molecules which start off faster than $v_{\text{start}}$ to be decelerated. By chirping immediately these fast molecules get left behind, but by waiting 500 $\mu$s we bunch the initial velocity distribution increasing the total number of molecules which are slowed. We also found it important to turn on the slowing light as late as possible so as to minimise the amount of time molecules spend travelling at low velocities before being detected. This reduces the apparent loss due to the increased divergence of the slowest molecules, which was found to be crucial for observing, and then maximising for, very slow molecules. We avoided doing this previously because the absence of a free-flight time makes the time-of-flight profiles more difficult to interpret.

Figure 3.15 shows the (a) time of flight profile and (b) velocity distribution for a chirp of 37 MHz/ms applied from $t_{\text{chirp}} = 4$ ms until $t_{\text{end}} = 12$ ms with the light turning on at $t_{\text{start}} = 3.5$ ms. The plots show control (grey) and cooled (blue) profiles. Part (b) clearly shows a peak of molecules arriving with a velocity centered at 15 m/s. The dashed line shows results from a numerical simulation and the shaded area indicates the 68% confidence limits on the velocity measurements. The slow peak contains 5% of the initial distribution. Knowing the number of molecules produced by the source per shot we calculate that about $1 \times 10^5$ molecules are detected per pulse within a velocity interval of $15 \pm 5$ m/s.

3.5 Conclusion

The data in this chapter demonstrates slowing of a beam of CaF molecules using either frequency-chirping or frequency-broadening. The two methods were found to be comparable when decelerating down to 50 m/s. In order to reach velocities close to the capture velocity of the MOT the chirped method was superior. By studying losses to unaddressed states we conclude that around $3 \times 10^4$ photons can be scattered before half of the molecules are lost from the cooling cycle. This corresponds to slowing of 390 m/s, far greater than required for our molecular beam. The greatest source of molecule loss is due
Figure 3.15: (a) Time of flight profile and (b) velocity distribution showing molecules decelerated to 15 m/s for $t_{\text{start}} = 3.5$ ms, $t_{\text{chirp}} = 4$ ms, $t_{\text{end}} = 12$ ms, $\alpha = 37$ MHz/ms, $v_{\text{start}} = 178$ m/s and a converging laser beam with 100 mW in $L_{10}^0$ and 110 mW in $L_{10}^1$. The dashed line shows results from a numerical simulation, the blue line shows the measured velocity distribution, control and cooled data are shown in grey and blue. The coloured band in (b) indicates the 68% confidence limits. Reproduced from [70]

to increased divergence for slow molecules. Hence, it is best to minimise the free-flight distance after slowing. The molecules should reach their final velocity as late as possible, i.e. when they reach the detector or the MOT volume. The number of slow molecules is also increased when the slowing light converged towards the molecular source. Using this technique we produce a pulse of molecules with a very narrow velocity distribution, which we can precisely control with the parameters of the chirp. Thus, our method appears very well suited for loading a MOT.
Chapter 4

Magneto-Optical Trap

This chapter will cover the details of the magneto-optical trap. Sections 4.3 and 4.4 are based closely on [80].

4.1 Introduction

A magneto-optical trap (MOT) uses velocity- and position-dependent forces to confine molecules within the trap. This requires a magnetic quadrupole field and six beams addressing a closed optical transition. The magnetic field, $B$, separates out the Zeeman sublevels according to equation 2.5. The trap will form at the magnetic field zero. The MOT requires a closed transition and so just like for the slowing we drive from $N = 1$ to $N = 0$ leading to dark ground states. This leads to zero trapping force in 1D and only a weak confinement in 3D, as explained in Ref. [99]. Figure 4.1 (a) illustrates this problem for a transition from $F = 1$ to $F = 0$. The dashed line represents the restoring beam that pushes a molecule towards the centre of the trap. A molecule in the $X(F = 1, m_F = 1)$ state can be driven by the $\sigma^-$ light into $A(F = 0)$, pushing the molecule towards the centre of the trap. It then has an equal probability of decaying into $X(F = 1, m_F = 1)$, $X(F = 1, m_F = 0)$ and $X(F = 1, m_F = -1)$. Only for the first case would the molecule be pumped again by the restoring beam. If a molecule decays to $m_F = -1$ it can only be pumped by light with $\sigma^+$ handedness, which means it will be pushed by the anti-restoring beam. If a molecule decays to $m_F = 0$ it won’t be able to be pumped at all and is dark to both the restoring and the anti-restoring beams. This latter problem is overcome in 3D since the orthogonal beams can drive population out of the $m_F = 0$ state. This leads to very weak confinement. Two methods have been demonstrated which lead to strong confinement, an rf-MOT and a dual-frequency MOT. In the former both the direction of the magnetic gradient and the handedness of the light are switched at a rate that is approximately equal to the scattering rate. This method is used by the DeMille [111, 112] and Doyle [81] groups. The dual-frequency scheme was proposed in reference
Figure 4.1: 1D schematics showing pumping for (a) normal configuration and (b) the dual-frequency configuration. The coloured circles represent molecules which can be pumped, by the beam of matching colour (detuning), the black circle shows the dark state.

[99]. Figure 4.1 (b) shows a 1D schematic illustrating this method. Here one hyperfine level is addressed by two frequency components of opposite handedness. One component is red detuned from resonance, as in a normal MOT while the second is blue detuned. A molecule starting in the \( X(F = 1, m_F = 1) \) state will be pumped by the red-detuned, \( \sigma^- \) beam, pushing it towards the centre of the trap. A molecule in the \( X(F = 1, m_F = -1) \) state will be pumped by the blue-detuned, \( \sigma^+ \) beam, again pushing it towards the centre of the trap. This leads to a strong confining force. This is the technique we choose to use.

In CaF the separation between the \( F = 2 \) and upper \( F = 1 \) hyperfine levels is only 24 MHz. Hence, the laser component which is red detuned of the upper \( F = 1 \) level will also act as the blue-detuned component for the \( F = 2 \) level. This ensures a strong trapping for molecules in the \( F = 2 \) level. When they are in the other hyperfine levels they are only weakly confined but they spend enough time in the \( F = 2 \) level to be adequately trapped. The MOT transition is \( A^2\Pi_{1/2}(v = 0, J = 1/2) \leftarrow X^2\Sigma^+(v = 0, N = 1) \).

From figure 2.4 we know that the branching ratio for this transition is not as good as for the slowing transition. However the hyperfine splitting in the \( B^2\Sigma^+ \) state is neither large nor small compared to the linewidth, which could be problematic. The hyperfine components of the \( A^2\Pi_{1/2}(v = 0, J = 1/2) \) are unresolved and so we chose this state. In order to achieve a MOT lifetime of 100 ms we need three vibrational repumps addressing \( X(v = 1, 2 \text{ and } 3) \).
As well as trapping, the MOT also cools the molecules. If we assume only Doppler cooling there is a minimum theoretical temperature referred to as the Doppler temperature. When an excited molecule spontaneously emits a photon it does so in a random direction, and so the momentum kicks average to zero. However the mean squared velocity is not zero and so heat is supplied to the molecule. The Doppler temperature occurs when the heating and cooling rates are equal. This is determined by the spontaneous decay rate ($\Gamma$) of the cooling transition. It will also depend on the scattering rate, and hence intensity and detuning, however there is a minimum which is given by

$$T_D = \frac{\hbar \Gamma}{2 k_B}.$$  

For CaF this temperature is 198 $\mu$K.

### 4.2 Experimental Setup

Here I will present the setup for the MOT, shown in figure 4.2. The source and slowing chambers are much the same as described in the previous chapter. The only difference is that the slowing chamber has been shortened. The distance from the target to the MOT position is 120 cm. The MOT chamber, illustrated in figure 4.2(a) is attached to the slowing chamber by bellows, vibrationally isolating the MOT chamber from the compressor of the cryocooler. There is a differential pumping tube between the two chambers. It is 200 mm long with a 20 mm diameter. The pressure in the MOT chamber is $2 \times 10^{-9}$ mbar, when the experiment is running. Figure 4.2(b) shows how the coils are mounted inside the chamber. The MOT coils are made up of two pairs of copper spirals set up in anti-Helmholtz configuration. Each spiral has eight turns, and these are sandwiched around and between AlN plates. The AlN plates are thermally connected to
### 4.2.1 Optics and lasers

**MOT light** There are four transitions addressed in the MOT by lasers denoted \( \mathcal{L}_{ij} \) where \( ij \in \{00, 10, 21, 32\} \). They drive the transitions \( A^2 \Pi_{1/2}(v = j, J = 1/2, p = +) \leftarrow X^2 \Sigma^+ (v = i, N = 1) \), shown in figure 2.4. The main laser, \( \mathcal{L}_{00} \), is at 606 nm. The other three are vibrational repumps at 628 nm. Each beam has to address the four hyperfine levels in the ground state. Figure 4.3 (b) shows the sideband structure used in the MOT and for the slowing. Figure 4.3 (a) shows the optics setups for all lasers involved in the experiment. Each laser has an extra beam pick off (not shown) at the start of the beam path sending a small amount of light to the wavemeter and to the transfer cavity for a copper block which acts as both a heatsink to the chamber and also, once blackened, provides a dark backdrop for imaging. The blackening will be described in the data acquisition discussion.
Magneto-Optical Trap

locking. Figure 4.3(a) panel (3) shows the beam path for the $L_{00}$ light. The beam passes through a half waveplate rotating the polarisation so that it will be transmitted by the polarising beam spitter (PBS). We use a double pass AOM at 110 MHz to control the intensity ($I_{00}$) and frequency (detuning $\Delta_{00}$) of the light. This laser is the same as the probe laser in the slowing experiment and the frequency sidebands are added in the same way. For $L_{00}$ the sidebands addressing $F=2,0,1^-\ldots$ have opposite polarisation to the one addressing $F=1^+$. To achieve this the light is split into two parts on a PBS and then each part is modulated to address the hyperfine structure. This correctly prepares the light for the dual frequency MOT.

Figure 4.3(a) panels(2 and 4) show the paths of the three vibrational repumps. They have sidebands added by a 24 MHz EOM addressing the hyperfine structure with a couple of extra frequencies present. The powers in the repumps are 100, 10 and 0.5 mW for $L_{10}$, $L_{21}$ and $L_{32}$ respectively. The $L_{10}$ light is derived from the same laser as $L_{s10}$. The other two repumps are home-built leader-follower systems described in section 4.2.2

The frequency of each laser is given in table 4.1. We find these by using each laser as a transverse probe, in the same way as for the slowing experiment. All lasers, other than $L_{00}$ are locked to resonance. For $L_{00}$ there is a critical frequency at which a MOT is formed on half of all shots. We refer to this frequency as zero detuning, $\Delta_{00} = 0$. If the frequency is higher than this then no MOT is formed and if the frequency is lower than this then a stable MOT is formed. We set the frequency to be $\Delta_{00} = -0.75\Gamma$. This frequency produces the largest MOT signal.

All MOT beams are combined in a multiport fibre coupled beam combiner$^1$. This maintains the polarisations of each beam and combines them into a single fibre. The output is collimated with a $1/e^2$ radius of 8.1 mm. Figure 4.2(a) shows the horizontal path of the beam which is folded and then retro-reflected to produce the six MOT beams. The beam passes through a quarter waveplate before entering the chamber changing the polarisation to be circular. On exiting the chamber there is another quarter waveplate rotating the polarisation to linear$^7$. We do this for each pass through the chamber because mirrors don’t maintain circular polarisation well. The handedness of the vertical beams is opposite to that of the horizontal beams.

Slowing Light  We use chirped frequency slowing to load the MOT. $L_{s00}$ has sidebands added to address the hyperfine structure as shown in figure 4.3(b). For the repump laser

$^1$Schafter Kirchoff.
Table 4.1: Lasers used in the experiment, the transitions they drive, and their frequencies and powers.

<table>
<thead>
<tr>
<th>Laser</th>
<th>Transition</th>
<th>Role</th>
<th>Frequency (GHz)</th>
<th>Power (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mathcal{L}_{10}$</td>
<td>$B(0) \leftarrow X(0)$</td>
<td>Slowing</td>
<td>564581.3</td>
<td>120</td>
</tr>
<tr>
<td>$\mathcal{L}_{10}$</td>
<td>$A(0) \leftarrow X(1)$</td>
<td>Slowing repump</td>
<td>476958.0</td>
<td>130</td>
</tr>
<tr>
<td>$\mathcal{L}_{00}$</td>
<td>$A(0) \leftarrow X(0)$</td>
<td>MOT</td>
<td>494431.3</td>
<td>80</td>
</tr>
<tr>
<td>$\mathcal{L}_{10}$</td>
<td>$A(0) \leftarrow X(1)$</td>
<td>MOT $v = 1$ repump$^d$</td>
<td>476958.0</td>
<td>100</td>
</tr>
<tr>
<td>$\mathcal{L}_{21}$</td>
<td>$A(1) \leftarrow X(2)$</td>
<td>MOT $v = 2$ repump</td>
<td>477298.7</td>
<td>10</td>
</tr>
<tr>
<td>$\mathcal{L}_{32}$</td>
<td>$A(2) \leftarrow X(3)$</td>
<td>MOT $v = 3$ repump</td>
<td>477627.6</td>
<td>0.5</td>
</tr>
</tbody>
</table>

$^aX(i) : X^2\Sigma^+(v = i, N = 1); \ A(i) : A^2\Pi_1(v = i, J = \frac{1}{2}, p = +); \ B(i) : B^2\Sigma^+(v = i, N = 0)$.

$^b$Accurate to 600 MHz, from wavemeter accuracy.

$^c$Full power in a single beam.

$^d$This light is derived from the same laser as $\mathcal{L}_{10}$.

The two slowing beams are combined in a fibre. The output is linearly polarised at 45° to the static magnetic field of 5 G. The light enters the chamber with a $1/e^2$ radius of 9 mm at the MOT converging to 1.5 mm at the source. The initial detuning of $\mathcal{L}_{00}$ is $-270$ MHz and so is resonant with molecules traveling at 145 m/s. The light is turned on at $t_{\text{start}} = 2.4$ ms and the chirp begins at $t_{\text{chirp}} = 3.5$ ms at $\alpha = 24.5$ MHz/ms.

4.2.2 Leader-follower set-up

The majority of the lasers used in the experiment are commercial. However, for the $\mathcal{L}_{21}$ and $\mathcal{L}_{32}$ we only need relatively small amounts of power, 10mW and 0.5mW respectively. We use distributed Bragg reflector (DBR) diodes, built by the Ferdinand Braun Institute, to provide a locking signal for higher powered diodes in a leader-follower set-up. This is when a low power, frequency locked laser (leader) is used as a seed to provide optical feedback to a higher powered diode (follower) which will hence emit at the same frequency as the leader. The DBR diodes are designed to run at the required wavelengths when temperature stabilised to around 12 °C. These diodes can emit a maximum power of 20 mW. This is insufficient for the experiment as the light has to have pick offs for
Figure 4.4: Schematic showing the optical set-up for the leader-follower system used to create the $L_{21}$ and $L_{32}$ light. The leader light is shown by a solid red line and the follower light is shown by a dashed red line.

The wavemeter and the locking cavity as well as passing through a variety of optics and fibres. The leader-follower set-up is shown in figure 4.4. Each DBR diode has an internal temperature control system. As well as this the diodes are mounted within hermetically sealed boxes which are water cooled to $15 \pm 1 \, ^\circ C$. The diode mount is then further cooled to approximately running temperature by a peltier, the temperature is regulated using thermocouple and a Wavelength Electronics TEC. The diode temperature system is connected up to a Thorlabs TED200C temperature controller and so is stable to within 0.002 $^\circ C$. The output of the diode first passes through an anamorphic prism pair which squashes the horizontal axis of the beam spot to make it more circular. The light is then focused through an optical isolator, providing isolation of around 35 dB. It was found that two isolators considerably improved the stability of the diodes by blocking any light from the follower diode. After the isolator the beam passes through a half-waveplate (hwp) and then a polarising beam cube which splits the light into two parts. The first of which is coupled into a fibre to provide the light for the follower. The second is further split into two parts, one of which goes to the wavemeter and the other is for the transfer cavity lock.

We use different diodes for the two followers; HL63163DG which outputs 170 mW of 637 nm light for $L_{21}$ and HL63133DG which outputs 100 mW of 633 nm light for $L_{32}$. The specification wavelength of these diodes is much higher than the transition wavelengths of 628.1 nm and 627.7 nm. We are able to use these diodes at lower wavelengths by cooling them. The rule of thumb for these diodes is the wavelength decreases by 1 nm
per 5 °C. Therefore, the two diodes need to be cooled to −25 °C and −5 °C. To set the temperature we first turn the diodes on with an output power of around 20 mW. We then lower the temperature whilst recording the frequency. Once the frequency is close we then turn up the current so that the output power is around 100 mW for $L_{21}$ and 40 mW for $L_{32}$. These are the powers we want to run at. The frequency will have decreased as the power was turned up and so the temperature will have to be adjusted again, and then the current will need to be tweaked. We do this because the output power increases as the temperature is lowered and we don’t want to blow up the diode. The diodes are housed within hermetically sealed boxes which are water cooled to 15 °C, the same as the DBR diodes. The diode mount consists of two stages, the first stage has two peltiers, connected in series, held between the housing floor and the base of an aluminium block. The peltiers are run in constant current mode and lower the temperature of the block to close to the required running temperature. We place a sheet of graphite on both sides of each peltier in order to maximise thermal contact. On top of this block we have a specially designed diode mount. It has an inset underneath for a peltier as well as a threaded hole which allows a screw and a washer to hold a thermocouple in place. The diode itself is mounted in an adjustable collimation tube\(^2\) and is connected to power via a protection circuit\(^3\). The collimation of the beam was found to be crucial for successful frequency locking. In order to set the collimation we use a camera to image the beam a few cm after the collimator and again on the other side of the room around 4 m away. If the beam is not well collimated then the diode has a tendency to run multimode. The entire laser housing is kept under vacuum at around 1 mBar, because the diodes have to be cooled below the condensation point of water.

After exiting the housing the beam first passes through an isolator which has accessible rejection ports. This is necessary as the beam from the leader enters the follower diode via this port. We overlap the rejected follower beam with the leader beam and couple it into the exit of the leader fibre in order to ensure maximal overlapping of the beams. The half waveplate placed after the rejection port allows us to vary the amount of leader power which enters the follower diode. In general we find that 1mW is a good amount of power, too little power and the diode won’t follow and too much power leads to extra modes appearing in the follower frequency and can cause the diode to break. In order to achieve optimal following we find that the quality of the free-running mode of the follower diode is very important. These diodes have wavelength regions over which they can run single mode and be scanned by changing the current applied. There are also regions where they run multimode, at which point they will not follow the input.

\(^2\)Thorlabs LTN330-A.
\(^3\)Thorlabs SR9A.
frequency. Each diode has different regions in which it can run single mode. You are
lucky if this overlaps with the desired wavelength. If it does not then the diode should
be set to the closest frequency possible whilst still having a mode-hop free scan range of
a few mA.

The beam which is transmitted through the isolator first passes through a glass plate
pick-off. This beam is coupled into the wavemeter which allows us to first set the running
conditions for the follower and then to monitor the following. The main beam must then
pass through a Glan-Taylor polariser which has an extinction ratio of 100,000 : 1. After
this the beam passes through an EOM, resonant at 24 MHz, to add the sidebands shown
in figure 4.3. We find that the high level of control over the polarisation is necessary
for the EOM to work well. Any light of incorrect polarisation is not modulated by the
EOM. Therefore, if the linearity of the laser drifts over time then the sideband structure
will also change and this will affect the experiment. Following on from the EOM the
light is then split into two. The lower power beam is coupled into a fibre and then into a
cavity so the following and the sideband structure can be monitored. The higher power
beam is coupled into a fibre, the output of which is combined on a 90:10 beamsplitter
with the other follower beam and then both beams are coupled into the fibre cluster for
the experiment. Only a very small amount (0.5 mW) of $L_{32}$ is required so this beam is
combined in the 10% arm of the splitter.

4.2.3 Data Acquisition

To image the MOT we use either a PMT or a CCD camera and record the fluorescence
scattered by the MOT from the main MOT beam at 606 nm. Inside the chamber there
is a 2 inch diameter, 60 mm focal length lens positioned one back focal length from the
MOT (50 mm). This lens collects the fluorescence and collimates it. Outside the chamber
there is a second lens, 100 mm away from the first. This is a 40 mm diameter, 28.6 mm
focal length lens. This lens focuses the light onto the PMT/camera chip and gives a mag-
nification of 0.5. Before the second lens there is a bandpass filter which transmits light at
606 nm whilst blocking background scatter from the 628 nm lasers. There is a lot of light
in the chamber from the MOT beams and so in order to minimise background scatter
everything is blackened. The MOT coils, AlN support plates, and an octagonal enclosure
are all painted black. We wrap the copper heat sink in black foil providing a dark
background for the imaging. From numerical ray tracing, transmission measurements
and the specified quantum efficiency of the camera, we calculate a detection efficiency of

4Hamamatsu Orca R2.
5Alion MH2200.
6Acktar spectral black.
1.5(2)%. We measure a background of $8.5 \times 10^4$ photons s$^{-1}$mm$^{-2}$ when the MOT beams are at full power (85 mW per pass). We can compare this to the fluorescence collected from a single molecule which is $3.6 \times 10^4$ photons s$^{-1}$. We are easily able to image each individual MOT, however we typically sum together 50 images giving a standard deviation in the number of molecules detected of 3%. The shot-to-shot number fluctuations measured is 20%. We believe that this is due to instability in the frequency of $L_{00}$ and source fluctuations. Figure 4.5(a) shows a typical image summed over 50 shots with (b) radial and axial intensity profiles, data shown by red dots, with gaussian fits, shown in blue. This image contains $10^4$ molecules and has a radial gaussian width of 1.2 mm and an axial gaussian width of 0.8 mm.

### 4.3 Loading the MOT

#### 4.3.1 Slowing Parameters

In section 3.4.5 we optimised the slowing parameters for slow molecules. However at this point we didn’t know the properties of the MOT-to-be. Once we could make a MOT we were then able to optimise the slowing for MOT loading. As previously we found that a static magnetic field of 5 G was sufficient to remix the dark sublevels. We also use the same dimensions for the converging slowing beam. As mentioned previously we chose to broaden out the frequency spectrum of the slowing repump light and only chirp $L_{00}$. 
From the slowing chapter we know that there are many parameters affecting the velocity and number of slow molecules. We optimised for three of these. In all cases the slowing light was turned on at $t_{\text{start}} = 2.5$ ms, the chirp started at $t_{\text{chirp}} = 3.4$ ms and the chirp rate was $\alpha = 24.5$ MHz/ms. We measured the velocity in the MOT chamber and found that this chirp rate produced the highest number of molecules with speeds below 15 m/s at this position. We set the overall detuning ($\Delta_{10}^s$) and width ($\delta\nu_{10}^s$) of the $\mathcal{L}_{10}^s$ light by again maximising the observed signal. We find these values to be $\Delta_{10}^s = -220$ MHz and $\delta\nu_{10}^s = 360$ MHz, with 90% of the power lying within this bandwidth. We investigated the effect of $t_{\text{end}}$, which is the time the slowing light was turned off at, and the power in the slowing beam.

Figure 4.6(a) shows the relative number of molecules loaded as we vary $t_{\text{end}}$. The red points show measured data and the blue points are generated by a simple MOT loading model. This model is an extension of the simulations used to model the slowing in [70]. The metrics used are that molecules which arrive at the MOT within a 1 cm diameter disk, with forward speeds below 10 m/s, and arrival times greater than $t_{\text{end}}$ will be trapped. We call this number $N_{\text{trappable}}(t)$. Without modeling any of the details of the capture process itself, we can estimate the number of trapped molecules to be 

$$\left[ \int_{t_{\text{end}}}^{t} N_{\text{trappable}}(t') \, dt' \right] e^{-\frac{(t-t_{\text{end}})}{\tau}}$$

where $\tau = 95$ ms is the measured lifetime.

By keeping the initial detuning $\delta f_{\text{initial}} = -270$ MHz, $\alpha$ and $t_{\text{chirp}}$ fixed and varying $t_{\text{end}}$ we are changing the total frequency change $\delta f_{\text{slowing}} = \alpha(t_{\text{end}} - t_{\text{chirp}})$ and the final resonant velocity $v_{\text{end}} = -\left( \delta f_{\text{initial}} + \delta f_{\text{slowing}} \right) \lambda_{00}$. Increasing $t_{\text{end}}$ reduces the final velocity of the slowest molecules. The number of trapped molecules initially increases with $t_{\text{end}}$. However, if $t_{\text{end}}$ is too large many of the molecules reach zero velocity before they arrive at the MOT and so the trapped number falls again. The number in the MOT is largest when $t_{\text{end}} = 14.2$ ms, corresponding to $\delta f_{\text{slowing}} = 265$ MHz. The coloured band indicates the fluctuations in the 50-image averages (the shot-to-shot fluctuations are 7 times larger). These fluctuations are large for $t_{\text{end}} = 14.2$ ms, so we prefer to use $t_{\text{end}} = 15$ ms [$\delta f_{\text{slowing}} = 285$ MHz] where the fluctuations are far smaller while the average number is only a little less. This is the value of $t_{\text{end}}$ we use for all subsequent data. The simulations show the same overall trends as in the experiment, but predict a large peak when $t_{\text{end}} = 13.25$ ms which we do not see in the experiment. To understand this peak, it is helpful to study the velocity distributions found from the simulations. Figure 4.6(b) shows the simulated velocity distributions for three values of $t_{\text{end}}$. When $t_{\text{end}} = 12$ ms, the velocity distribution has a narrow peak at 24 m/s, which are molecules that have faithfully followed the chirp, followed by a broad, faster distribution consisting of molecules which have fallen behind the chirp. For this value of $t_{\text{end}}$, there are hardly any molecules
4.3.2 Trapping molecules

Using the slowing settings described above we can load a MOT. Figure 4.8 (a) shows the fluorescence of molecules in the MOT region as a function of time, recorded by a PMT. The dotted vertical line shows \( t_{\text{end}} = 15 \) ms. The orange curve shows the arrival time distribution when there is no slowing applied. The blue curve shows the distribution when the slowing is applied but no molecules are captured because only one MOT beam is used and the magnetic field is off. At early times, up until 7.3 ms, the slowed and unslowed curves are similar because the fastest molecules (> 165 m/s) do not interact with the slowing light. Then there is a dip in the slowed signal, followed by a broad bump at later times, corresponding to molecules that have been slowed. The dashed
Figure 4.7: (a) Fluorescence from the MOT region detected on a PMT, as a function of time. Orange: free flight (experiment); Blue: slowed (experiment); Dashed purple: slowed (simulation); Red: trapped molecules (experiment). The slowing chirp ends at $t_{end} = 15$ ms (vertical dotted line), giving $\alpha(t_{end} - t_{chirp}) = 285$ MHz. The powers of $L_{s00}$ and $L_{s10}$ are 120 mW and 130 mW respectively. The orange and blue curves are recorded with a single beam of the MOT light and no magnetic field, whereas the red curve is recorded with all six beams and the magnetic field on. The red curve has been scaled down by a factor of 3 for the reasons described in the text. (b) Comparison of experiment and simulation for MOT loading. Red: experimental data from (a). Black: simulation results showing the arrival-time distribution of molecules that arrive later than 15 ms, pass through a 1 cm diameter disk in the plane of the MOT, and have velocity below 10 m/s. Dashed purple: integration of the black signal multiplied by an exponential decay with a time constant of 95 ms, and scaled to best match the experimental data. Reproduced from [80].

Figure 4.8: (a) Fluorescence from the MOT region detected on a PMT, as a function of time. Orange: free flight (experiment); Blue: slowed (experiment); Dashed purple: slowed (simulation); Red: trapped molecules (experiment). The slowing chirp ends at $t_{end} = 15$ ms (vertical dotted line), giving $\alpha(t_{end} - t_{chirp}) = 285$ MHz. The powers of $L_{s00}$ and $L_{s10}$ are 120 mW and 130 mW respectively. The orange and blue curves are recorded with a single beam of the MOT light and no magnetic field, whereas the red curve is recorded with all six beams and the magnetic field on. The red curve has been scaled down by a factor of 3 for the reasons described in the text. (b) Comparison of experiment and simulation for MOT loading. Red: experimental data from (a). Black: simulation results showing the arrival-time distribution of molecules that arrive later than 15 ms, pass through a 1 cm diameter disk in the plane of the MOT, and have velocity below 10 m/s. Dashed purple: integration of the black signal multiplied by an exponential decay with a time constant of 95 ms, and scaled to best match the experimental data. Reproduced from [80].
purple curve is from a slowing simulation. The red curve shows the distribution when
the MOT magnetic field is on and all six beams are present. From figure 4.10 we know
that the increased intensity due to the six beams increases the fluorescence by a factor
of 2. Furthermore, the source flux changes between datasets, the PMT efficiency may be
altered by the MOT magnetic field, and there may be dark states that are robust for one
beam but not for six. To account for these changes we scale the red curve down by a
factor of 3 so that red and blue signals match at early times, where the signal is due only
to fast molecules which are hardly affected by the MOT. The red curve starts to deviate
significantly from the blue curve at $t \approx 10$ ms. Molecules with speeds around 50 m/s start
arriving around this time, and although these molecules are too fast to be trapped they
are slow enough for the MOT to have a large effect on their speed so that they remain in
the MOT region for longer than otherwise. For this reason, the signal increases, though
still follows the same shape as the slowed profile. Molecules do not start accumulating
in the trap until the slowing light is turned off because this light pushes molecules out of
the trapping region. At $t = t_{\text{end}}$ there is a rise in signal as molecules become trapped in
the MOT, followed by a decline as they are gradually lost to dark states.

Figure 4.8(b) compares experiment and simulation results for MOT loading. The red
curve is the same experimental data as shown in (a). The black curve shows the simulated
arrival-time distribution of trappable molecules that arrive at the MOT region and the
dashed purple curve shows the integral of these molecules. The height has been scaled
to give a good match with the experiment. We see that almost all molecules load during
a 20 ms time window following $t_{\text{end}}$. The shape of the simulated MOT loading curve
matches well with the measured one during this time window. This analysis gives a clear
picture of which molecules in the beam are captured by the MOT, which is especially
important in designing strategies to increase the number of molecules loaded.

4.4 Properties of the MOT

In this section we show how the properties of the MOT vary with the key parameters
of the setup, mainly the total peak intensity in the MOT ($I_{00}$) due to all six beams of
$L_{00}$, the detuning ($\Delta_{00}$) of $L_{00}$, and the axial magnetic field gradient ($dB/dz$). When
not being varied these are set to be $I_{00} = 400$ mW/cm², $\Delta_{00} = 0.75$ Γ and $dB/dz = 30.6$ G/cm. These standard parameters are also used for fluorescence imaging, unless
otherwise stated. Simulations of the MOT behaviour have been included because they
make a useful comparison to the experimental data. They were done by Michael Tarbutt
and are based on multi-level rate equations [99, 113].
4.4.1 Scattering Rate

In order to calculate the number of molecules in an image we need to know the scattering rate. This was measured by recording the fluorescence of the MOT using a PMT, and turning off $L_{21}$ at time $t' = 55$ ms. We observe the decay into $v = 2$ and measure the $1/e$ decay constant, $\tau_2$. Figure 4.9 shows an example of a scattering rate measurement where the time constant is $\tau_2 = 572(7)$ $\mu$s giving a scattering rate of $2.08(13) \times 10^6$ s$^{-1}$.

The scattering rate is $R_{sc} = 1/(b_2 \tau_2)$, where $b_2$ is the branching ratio for the excited state to decay to $v = 2$. In order to determine $b_2$ we compare the fluorescence in the MOT of the $A(v = 0) \rightarrow X(v = 0)$ decay at 606 nm and to the $A(v = 0) \rightarrow X(v = 2)$ decay at $\lambda_{20} = 652$ nm. To isolate these two frequencies we use bandpass filters placed in between the two imaging lenses, where the light is collimated. We switch back and forth between these two filters, and record images both with and without molecules. By subtracting these two images we remove any background laser scatter. Each filter has a transmission of greater than 93%, and importantly the filter which transmits at $\lambda_{20}$ has a transmission of less than $10^{-6}$ at 606 nm, which is small enough to neglect. We use these measurements plus the specified transmissions for the lenses and window as well as the quantum efficiency of the camera to calculate $b_2$ according to:

$$b_2 = \frac{b_0 I_2}{I_0} \frac{T_{\lambda_{00}}^{\text{lens1}} T_{\lambda_{00}}^{\text{lens2}} T_{\lambda_{00}}^{\text{window}} T_{\lambda_{00}}^{\text{filter0}} T_{\lambda_{20}}^{\text{camera}}}{T_{\lambda_{20}}^{\text{lens1}} T_{\lambda_{20}}^{\text{lens2}} T_{\lambda_{20}}^{\text{window}} T_{\lambda_{20}}^{\text{filter2}} T_{\lambda_{20}}^{\text{camera}}}.$$  \hspace{1cm} (4.2)

Here $I_2/I_0$ is the measured fluorescence ratio, $b_0 = 0.987^{+0.013}_{-0.019}$ is the branching ratio to $v = 0$ \cite{98}, $T_{\text{lens1(2)}}^{\lambda}$ is the transmission of lens 1(2), $T_{\text{window}}^{\lambda}$ is the transmission of the vacuum viewport, $T_{\text{filter0(2)}}^{\lambda}$ is the transmission of the filter that isolates the fluorescence
to \( v = 0(2) \), and \( \epsilon_{\text{camera}}^\lambda \) is the quantum efficiency of the camera, all at wavelength \( \lambda \). All transmissions and quantum efficiencies are taken from data supplied by the manufacturers. The result is \( b_2 = 8.4(5) \times 10^{-4} \). This is 40\% smaller than the theoretical value of \( 1.2 \times 10^{-3} \) given in [100].

From equation [2.13] we know that the scattering rate depends on both the intensity and detuning of the MOT light and so we investigate this. Using the method described above, we measure the scattering rate for many different values of intensity and detuning and then compare to the model given by equation [2.13]. Figures [4.10]a and (c) show the measured and simulated scattering rate versus \( I_{00} \), along with fits to equation [2.13] and the associated fit parameters. Both the experimental and simulated results fit well to this model. The values of \( I_{s,\text{eff}} \) are in agreement with each other and are close to that predicted by equation [2.15]. The simulation gives \( \Gamma_{\text{eff}} \) close to the value of 0.29\( \Gamma \), predicted by equation [2.14] but the experimental value is a factor of 2 smaller than simulated. This difference could be caused by optical pumping into coherent states that, for short periods, are dark to the MOT light, an effect which cannot be captured by the rate model. There are no stable dark states for molecules that move quickly enough through the non-uniform magnetic field and light polarization, but there may be states that are decoupled from the light for long enough to limit the scattering rate. Figure [4.10]b and (d) show the measured and simulated scattering rate versus \( \Delta_{00} \), along with fits to equation [2.13]. The fit to the measurements is unconvincing, though the fit parameters are consistent with those found in (a), showing that equation [2.13] is sufficient to represent the dependence of the scattering rate on both intensity and detuning. The simulated data fits well to the model but with parameters somewhat different to those found in (c).
Figure 4.10: Scattering rate versus intensity and detuning of $L_{00}$: (a,b) measured, (c,d) modeled. Solid lines are fits to equation (2.13), and the fit parameters are given in each case.

4.4.2 Number of molecules

We first investigate how to maximize the number of molecules in the MOT. The filled points in figure 4.11(a) show how this number depends on the power of $L_{00}^s$. For powers below 20 mW we observe no molecules in the MOT. Above this threshold the number increases roughly linearly until it saturates at a power near 120 mW. The open points are the results of simulations done for various $L_{00}^s$ powers. The simulations predict the same trends as we observe, with two notable exceptions. First, they predict that the trapped number will fall above a certain power, because at high power the molecules reach low speed too early. We do not see this effect in the experiment. Second, the simulations exhibit high sensitivity to the exact power (the sharp structures are not noise). The experimental data does not have the resolution to see this. We have also investigated how the number of molecules depends on the power of $L_{10}$. The nominal power is 130 mW, and we see no difference if we halve or double this value.

Figure 4.11(b) shows the relative number of molecules as a function of $I_{00}$. The number increases with intensity until 200 mW/cm², above which it remains constant within 10%. We note that we still load 10% of this maximum number when $I_{00}$ is only 2% of $I_{00}^s$. Figure 4.11(c) shows the relative number of molecules versus $\Delta_{00}$. This shows a parabolic dependence with a maximum at $\Delta_{00} = -0.75\Gamma = -2\pi \times 6.2$ MHz. No MOT is formed when the light is blue-detuned or when it is red-detuned by more than 1.8$\Gamma$. Figure 4.11(d) shows the relative number of molecules versus magnetic field gradient.
Figure 4.11: Relative number of molecules trapped as a function of (a) power of slowing laser $\mathcal{L}_{00}$, (b) $I_{00}$ (c) $\Delta_{00}$ and (d) $dB/dz$. The uncertainty in the number due to shot-to-shot fluctuations is 3%. The MOT is imaged at 60 ms with an exposure time of 30 ms and averaged over 50 shots. In (a), the filled points are measurements while the open points are from slowing simulations.

$dB/dz$. We observe a MOT once $dB/dz > 10$ G/cm, and obtain the most molecules when $dB/dz = 30$ G/cm. As the field gradient is increased beyond this, there is a slow decline in the number of trapped molecules, suggesting that the trap capture volume starts to decrease at these higher gradients.

4.4.3 Oscillation frequency and damping constant

We consider the motion of the molecules in the direction of the slowing laser, since it is straightforward to give the molecules a push in this direction, and because the camera views this axis. Consider a molecule with displacement $x$ and velocity $v$ along this axis, interacting with the six MOT beams. At low intensity, $s_{\text{eff}} \ll 1$, the total scattering rate is the sum of the scattering rates from each beam individually, so it is easy to identify the force exerted by a single beam. This is not the case at higher intensities. Nevertheless, the force due to one of the MOT beams in the horizontal plane may be written as

$$F_{\pm}(x, v) = \mp \frac{h k}{\sqrt{2}} \frac{\Gamma_{\text{eff}}}{2} \frac{s_{\text{eff}}/6}{1 + s_{\text{eff}} + 4(\Delta \pm \frac{\Delta v}{\sqrt{2}} \pm g_{\text{eff}} \mu_{B} A x / h)^2 / \Gamma^2}$$

(4.3)

where $k = 2\pi/\lambda$ is the wavevector, $\Delta$ is the laser detuning, $g_{\text{eff}}$ is an effective magnetic g-factor for the transition, $A$ is the magnetic field gradient in the horizontal plane, $s_{\text{eff}}$
Figure 4.12: (a) Fluorescence images of the MOT at various times after a radial push. Each image is a 0.5 ms exposure averaged over 30 shots. (b) Radial displacement versus time after the push, showing the damped harmonic motion of the MOT. Here, $\Delta_{00} = -0.75\Gamma$ and $I_{00} = 200 \text{ mW/cm}^2$. Points: experimental data. Line: fit to equation (4.8).

is the saturation parameter for all six beams, and the factors of $\sqrt{2}$ account for the $45^\circ$ angle between the MOT beams and the $x$-axis. Here, in the numerator we have used the intensity of the single beam applying the force, while in the denominator we have used the intensity of all six beams to account for the saturation of the scattering rate by the full intensity. This approximation is known to work well for the modest saturation parameters used in this work [114]. The parameter $g_{\text{eff}}$ accounts for there being multiple transitions each with a different $g$-factor. It is a free parameter that characterises the strength of the trapping force. The total force in the $x$-direction is

$$F = 2(F_+ + F_-) = m x'' , \quad (4.4)$$

where $m$ is the mass and the factor of 2 accounts for there being two pairs of horizontal MOT beams. Using a Taylor expansion about $x = x' = 0$, we obtain

$$x'' = -\omega^2 x - \beta x', \quad (4.5)$$

where $\omega$, the trap oscillation angular frequency, is given by

$$\omega^2 = -\frac{4\sqrt{2} \Gamma_{\text{eff}} k(\Delta/\Gamma) g_{\text{eff}} \mu_B A s_{\text{eff}}}{3m \Gamma (1 + s_{\text{eff}} + 4\Delta^2/\Gamma^2)^2}, \quad (4.6)$$

and $\beta$, the damping constant, is

$$\beta = -\frac{4 \Gamma_{\text{eff}}}{3m \Gamma} \frac{\hbar k^2(\Delta/\Gamma) s_{\text{eff}}}{(1 + s_{\text{eff}} + 4\Delta^2/\Gamma^2)^2}. \quad (4.7)$$

To measure the radial trap oscillation frequency, $f = \omega/(2\pi)$, and the damping constant, $\beta$, we pulse on $\mathcal{L}_{00}^a$ for 0.5 ms to push the cloud in the radial direction. We then image the cloud after various delay times using an exposure time of 0.5 ms, which is short
Figure 4.13: Oscillation frequency versus intensity and detuning of $\mathcal{L}_{00}$: (a,b) measured, (c,d) modelled. Solid lines are fits to $\omega/(2\pi)$ given by equation (4.6), and the fit parameters are given in each case. Typical fluctuations in repeat measurements are 5%.

compared to the oscillation period. Figure 4.12(a) is a sequence of such images showing the damped oscillation of the cloud. We integrate each image over the axial coordinate to give radial distributions, and then fit a Gaussian model to each distribution to obtain the central position of the cloud at each time. Figure 4.12(b) shows the mean radial displacement versus time. A suitable solution of equation (4.5) for the displacement from the equilibrium position $x_0$ is

$$x - x_0 = ae^{-\beta t/2} \cos(\sqrt{(\omega^2 - \beta^2/4)}t - \phi),$$

(4.8)

where $a$ is the amplitude of oscillation and $\phi$ is a phase. All the oscillation data presented here fit well to this model. Figure 4.12(b) shows an example of this fit for the case where $\Delta_{00} = -0.75\Gamma$ and $I_{00} = 200$ mW/cm$^2$. For these parameters, we find $f = 93(5)$ Hz and $\beta = 363(40)$ s$^{-1}$. Here, the uncertainties are the standard deviations of repeated measurements.

Figures 4.13(a,c) show the measured and simulated oscillation frequency as a function of $I_{00}$. The measured frequency increases with $I_{00}$ until it reaches a maximum at 400 mW/cm$^2$. The measured and simulated frequencies are in excellent agreement, differing by less than 20% across the whole range of intensities. We fit these data to the frequency given by equation (4.6). In this equation, all the parameters are known apart from $g_{\text{eff}}$, $\Gamma_{\text{eff}}$ and $I_{s,\text{eff}}$. The first two appear only as a product, so the free parameters
of the fit are $g_{\text{eff}} \Gamma_{\text{eff}}$, which is a measure of the strength of confinement, and $I_{s,\text{eff}}$ which sets the intensity required to reach the strongest confinement. The measurements and simulations fit well to this simple model, with the best fit parameters given in the figure. They show that the saturation intensity appropriate to the oscillation frequency is considerably higher than that found for the scattering rate – it takes more power to trap the molecules than might be expected from the scattering rate data. It is peculiar that the experimental and simulated oscillation frequencies are in such good agreement even though the scattering rates differ by a factor of 2. Figures 4.13(b,d) show the measured and simulated oscillation frequency as a function of $\Delta_{00}$, along with fits to equation (4.6). Both experiments and simulations suggest that the maximum $f$ occurs very close to resonance, requiring a large $I_{s,\text{eff}}$ in equation (4.6) for a good fit. As with the scattering rate data, the best fit parameters obtained from the intensity dependence and detuning dependence are consistent with one another. It is interesting that, over the range of $\Delta$ explored here, the oscillation frequency shows a weak and simple dependence on $\Delta$ despite the small interval ($3\Gamma$) between the upper two hyperfine states.

Figures 4.14(a,c) show the measured and simulated damping constant as a function of $I_{00}$. We see that the measured values of $\beta$ are far smaller than the simulated ones across the whole intensity range. At low intensities, $I_{00} < 25 \text{ mW/cm}^2$, the measured $\beta$ is 2–3 times smaller than simulated, while at high intensities the discrepancy is a factor of 5–10.
In the experiment, $\beta$ has a maximum near 100 mW/cm$^2$, while in the simulations the maximum is beyond 750 mW/cm$^2$. Damping constants much smaller than the simulated ones are also found in both the dc and rf MOTs of SrF \[78,111\]. We tentatively attribute this to the effect of the polarization gradient force. This force has the opposite sign to the Doppler cooling force, and dominates at low velocities, especially when the intensity is high \[115\]. This could result in a reduced damping constant, with a higher reduction factor at higher intensities. Despite the discrepancy between experiment and simulation, both datasets follow equation (4.7), as can be seen by the fits in figures 4.13(a,c). The much weaker damping in the experiment is reflected by a much smaller $\Gamma_{\text{eff}}$, and the shift of the maximum to lower intensity in the experiment is reflected by a smaller $I_{s_{\text{eff}}}$. Figures 4.14(b,d) show the measured and simulated damping constant as a function of $\Delta_{00}$. We see that $\beta$ gradually decreases as $|\Delta_{00}|$ approaches zero, which is the opposite behaviour to $f$. Thus, the choice of detuning is a trade-off between maximizing $f$ and $\beta$. Unlike the dependence on $I_{00}$, the experimental dependence on $\Delta_{00}$ does not seem to follow equation (4.7). The simulation results do roughly follow this equation however.

### 4.4.4 Temperature

To measure the temperature of the MOT we record fluorescence images after various free expansion times. We first load the MOT with the maximum number of molecules by using the intensity $I_{00}$ and detuning $\Delta_{00}$. At $t = 50$ ms we either ramp the intensity to a new value over a period of 20 ms or we jump the detuning to a new value. At $t = 75$ ms we turn off the magnetic field and $L_{00}$ so that the cloud is free to expand. After a free expansion time $\Delta t$, $L_{00}$ is turned back on with the standard parameters $I_{00}$ and $\Delta_{00}$, and the fluorescence is imaged for 1 ms. Figure 4.15(a) shows the expansion of the cloud in a sequence of images for several $\Delta t$. Each image is the sum of 20 repeats of the measurement. For each image, we sum over the axial (radial) coordinate to obtain...
the radial (axial) distribution. To each distribution we fit the Gaussian model $n(x) = Ae^{-(x-x_0)^2/(2\sigma^2)}$. Figures 4.15b,c show $\sigma^2$ versus $(\Delta t)^2$ for the axial and radial directions. For free expansion, the rms width $\sigma$ follows $\sigma^2 = \sigma_0^2 + k_B T (\Delta t)^2/m$, where $\sigma_0$ is the initial rms width and $T$ is the temperature. Molecules in the wings of the cloud scatter at a slightly lower rate than those at the centre due to the change of laser intensity across the cloud. This slightly reduces the apparent size of the cloud, and since the effect is stronger for larger clouds the relation between $\sigma^2$ and $(\Delta t)^2$ becomes slightly non-linear. We account for this by fitting the data to $\sigma^2 = \sigma_0^2 + k_B T (\Delta t)^2/m + a (\Delta t)^4$. For high temperatures, $T \sim 12$ mK, inclusion of the $(\Delta t)^4$ term in the fit typically gives a temperature about 10% higher than otherwise. This effect reduces for colder clouds. Figures 4.15b,c show examples of the fit where the axial and radial temperatures are found to be $T_z = 2.1$ mK and $T_\rho = 1.9$ mK. The temperatures for the two directions are always close, so we take the geometric mean $T = T_\rho^{2/3} T_z^{1/3}$.

There are other potential systematic errors in these temperature measurements. Firstly we consider whether the finite exposure time of 1 ms introduces any temperature change. The image is taken with no magnetic field and so there is no trapping force. However there is still a velocity dependent force, which may either cool or heat the molecules depending on their velocity [115]. To quantify this effect we took temperature measurements using various exposure times. We found that a 1 ms exposure time leads to an overestimate in temperature by $0.3 \pm 0.5$ mK for a temperature of 12 mK. Again this effect reduces for lower temperatures. Another consideration is the magnification of the imaging system. This may not be uniform across the field of view. As the cloud expands, and drops under gravity, its shape could be distorted. We measured the magnification across the entire field of view relevant to our data and found that the uniformity is better than 3%. To do this we placed a screen with a grid pattern at the position of the MOT and measured the imaged grid spacing. The slight non-uniformity has a negligible effect on the temperature. Finally we consider the effect of a non-uniform magnetic field across the cloud. A gradient would accelerate the molecules, and since the magnetic moment depends on the hyperfine component and Zeeman sub-level, the acceleration would be different for different molecules. We calculate that this effect contributes to a velocity spread of less than 0.5 cm s$^{-1}$ after 10 ms of expansion. This is negligible for all temperatures.

The expected temperature can be expressed in terms of the damping constant $\beta$ and a velocity-independent momentum diffusion coefficient $D$, following a standard treatment [116] extended to three dimensions. For a force that is linear with momentum, $\vec{F} = -\beta \vec{p}$, the cooling power is $P_{\text{cool}} = \beta p^2/m = 2\beta E$, where $E$ is the kinetic energy. The heating power is $P_{\text{heat}} = \frac{d}{dt} \frac{\langle p^2 \rangle}{2m} = D/m$. Here, we have used the definition $2D = \frac{d}{dt} \langle \langle p^2 \rangle - \langle p \rangle^2 \rangle$, and the fact that $\langle p \rangle = 0$. Equating the heating and cooling powers we find an equilibrium energy $E = \frac{1}{2} k_B T = \frac{D}{2m\beta}$. If the light field has no intensity gradients, so that there is no
heating due to fluctuations of the dipole force, the momentum diffusion is due only to the two randomly-directed recoils per absorption-spontaneous emission cycle:

\[ 2D = 2(h\kappa)^2 R_{sc}. \]  

This gives us the temperature

\[ T = \frac{1}{3} \frac{(h\kappa)^2 R_{sc}}{k_B m}. \]  

Using equations (2.13) and (4.7) for \( R_{sc} \) and \( \beta \) we obtain an expression for the Doppler temperature:

\[ T_D = -\frac{h\Gamma^2}{8k_B\Delta}(1 + s_{\text{eff}} + 4\Delta^2/\Gamma^2). \]  

This is identical to the Doppler temperature for a two-level atom. We note that the expression for \( D \) is modified slightly at intermediate intensities, and that fluctuations of the dipole force can alter \( D \) considerably when there are intensity gradients [116]. Nevertheless, equation (4.11) has been verified for a three-dimensional MOT in conditions where sub-Doppler processes are ineffective [117].

Figure 4.16(a) shows the temperature versus \( I_{00} \) together with the Doppler temperature given by equation (4.11). At full intensity \( (I_{00}) \), the temperature is 13 mK, which is 17 times higher than expected from equation (4.11). The temperature decreases as the intensity decreases, reaching a minimum at 9 mW/cm\(^2\) where it is 960 \( \mu \)K, 4 times the Doppler temperature. These observations are similar to those reported by others [111, 81]. When the intensity is reduced below 9 mW/cm\(^2\), the temperature increases again. According to equation (4.10), the temperature is related in a simple way to the scattering rate and the damping constant. Since we have measured \( T \), \( R_{sc} \) and \( \beta \) across a wide
range of intensities, we can test whether this relation is accurate for our MOT. Using linear interpolations over the measured values of $R_{sc}$ [figure 4.10(a)] and $\beta$ [figure 4.14(a)] at various intensities, and equation (4.10), we obtain the expected temperature shown by the dashed line in figure 4.16(a). This shows exactly the same intensity dependence as we measure. The temperature found from equation (4.10) is higher than the Doppler temperature because the damping constant is smaller than predicted. The measured temperature is higher again, by a factor of 2 for intensities below 10 mW/cm$^2$ and by a factor of 3 at higher intensities. This shows that the diffusion constant is higher than that given by equation (4.9). This might be due to dipole force fluctuations which are not included in equation (4.9). We note that excess heating at high intensity is also seen in atomic MOTs [118, 119] and various explanations have been given such as the effect of coherences between excited state sub-levels [120] and transverse intensity fluctuations of the MOT beams [121].

Figure 4.16(b) shows how the temperature depends on $\Delta_{00}$ at both high intensity (400 mW/cm$^2$) and low intensity (4 mW/cm$^2$). At high intensity the temperature is highest at $\Delta_{00} = -0.75 \Gamma$ and decreases at both larger and smaller detunings. At low intensity the temperature decreases as $|\Delta_{00}|$ decreases, until $\Delta_{00} = -0.5 \Gamma$ where it reaches a minimum of 730 $\mu$K, 3.5 times the Doppler temperature.

### 4.4.5 Cloud size

The filled points in figure 4.17(a) show the rms radial size of the cloud, $\sigma_0$, as a function of $I_{00}$. We can interpret these data with the help of the equipartition theorem which relates $\sigma_0$ to $\omega$ and $T$:

$$\sigma_0 = \sqrt{\frac{k_B T}{m \omega^2}}. \quad (4.12)$$

As $I_{00}$ is reduced from 500 to 50 mW/cm$^2$ the cloud size decreases. This is because $T$ falls by a factor of 7 over this intensity range, see figure 4.16 whereas $\omega$ only falls by 50%, see figure 4.13. As $I_{00}$ decreases further the cloud size increases because $\omega$ falls while $T$ stops falling and then starts increasing. The open points in figure 4.17(a) are the predictions of equation (4.12) for those values of $I_{00}$ where we have measured both $\omega$ and $T$. These predictions agree well with the measurements between 5 and 500 mW/cm$^2$. At lower intensity, the measured size is smaller than predicted by equation (4.12). We do not know the reason. Figure 4.17(b) shows the size of the cloud versus $\Delta_{00}$. The cloud is smallest when $\Delta_{00} = -0.75 \Gamma$ and grows rapidly as $|\Delta_{00}|$ increases, reflecting the decrease in $\omega$. Figure 4.17(c) shows that the size of the cloud decreases as the magnetic field gradient increases up to the maximum value used in this work, $dB/dz = A = 41$ G/cm. From equations (4.6) and (4.12) we expect the relation $\sigma_0 = \zeta (dB/dz)^{-1/2}$. This model
Figure 4.17: (a) Radial size of MOT versus intensity, $I_{00}$, showing measurements (filled, red points) and the prediction of equation (4.12) (open blue points). The size is expressed as the rms radius in the radial direction. (b) Radial size of MOT versus detuning, $\Delta_{00}$. (c) Radial size of MOT versus axial magnetic field gradient. Points: measurements. Line: fit to $\sigma_0 = \zeta(dB/dz)^{-1/2}$. In (a) the values of $\sigma_0$ are obtained from the same ballistic expansion data that give the temperatures in figure 4.16(a). In (b) and (c) the size is obtained by imaging the MOT directly for various values of $\Delta_{00}$ and $dB/dz$. 

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fits quite well to the data, as shown in figure 4.17(c), and gives a best fit parameter of $\zeta = 9.7(1)$ mm(G/cm)$^{1/2}$.

## 4.4.6 Loss rate

For times $t > 50$ ms, the fluorescence decays exponentially as molecules are lost from the MOT. Figure 4.18 shows the loss rate versus the scattering rate, which we control via the intensity $I_{00}$. The relation between $R_{sc}$ and $I_{00}$ is obtained from the fit shown in figure 4.10(a). The loss rate increases approximately linearly with $R_{sc}$ as we would expect if the loss is due to a leak out of the cooling cycle. The linear fit shown in figure 4.18 gives a branching ratio for this leak of $6.3(5) \times 10^{-6}$. The loss could be to a higher-lying vibrational state, or it could be due to magnetic dipole or electric quadrupole transitions that connect the excited state to rotational states $N = 0$ and $N = 2$. We note that the linear fit to the loss rate data gives a statistically significant negative intercept of $-3.8(1.2)$ s$^{-1}$, which is not physical. This hints at a more complicated dependence on the scattering rate.

When the temperature of the cloud becomes comparable to the trap depth, the high energy molecules will spill out of the trap and increase the loss rate. This loss mechanism was considered in the context of the first molecular MOT [77], where the rate for the process was approximated as

$$R_{\text{loss}} = \frac{2}{\pi} \omega_{\rho} e^{-m \omega_{\rho}^2 r_{\text{trap}}^2 / (2 k_B T)}.$$  \hspace{1cm} (4.13)

This result assumes that the oscillation is lightly damped and that the force is linear in the displacement out to the trap radius, $r_{\text{trap}}$. These are poor approximations, figure 4.12(b) shows oscillations are damped, and the MOT force is only linear near the centre of the trap [88]. But nevertheless we can expect the order of magnitude of the loss rate to be given by this equation. Our simulations of the MOT show that the restoring force has a turning point at a radial distance of about 8 mm. Choosing this value for $r_{\text{trap}}$, and
Figure 4.19: (a) Initial velocities and displacements used in measurements to determine the capture velocity. (b) Percentage of molecules recaptured into the MOT for each of the initial points in (a), indicated here by their velocities. Filled points: measurements. Open points: fit to the model described in the text.

using our measured values of $\omega_p$ and $T$, equation (4.13) give $R_{\text{loss}} = 1 \text{ s}^{-1}$ at the highest intensity where the scattering rate is $2.6 \times 10^6 \text{ s}^{-1}$. This contribution to the loss rate falls very rapidly as the intensity is reduced because $T$ falls faster than $\omega_p$. For example, lowering the scattering rate by 15% reduces $R_{\text{loss}}$ by a factor of 200. Thus, this loss mechanism could only be significant at the very highest intensity explored. Interestingly, the data point at the highest scattering rate in figure 4.18 does indeed lie significantly above the linear fit to the data.

4.4.7 Capture Velocity

It is difficult to measure the capture velocity of the MOT directly. Instead, we measure the escape velocity by pushing the MOT and measuring the fraction of molecules that are lost as a function of their speed. We then infer the capture velocity from these results, with the help of a simple model. To apply an impulsive push, we turn off $L_{00}$ and pulse on the slowing light, $L^{s}_{00}$, for a short time $t_{\text{push}}$. The molecules are at the zero of the MOT magnetic field where states dark to the polarization of $L^{s}_{00}$ are not destabilized effectively, so we found it necessary to modulate the polarization of $L^{s}_{00}$ to reach a sufficient scattering rate. We also reduced the size of the slowing beam to 3 mm $1/e^2$ radius, in order to increase the applied force. For various push parameters, we first determine the initial displacement and velocity of the cloud, $x_i = x(t_{\text{push}})$ and $v_i = v(t_{\text{push}})$, by imaging the cloud at various times after $t_{\text{push}}$ with the MOT magnetic field turned off. Figure 4.19(a) shows the set of $\{x_i, v_i\}$ pairs used. Then, for each push, we turn the MOT back on at $t = t_{\text{push}}$ and measure the fraction of molecules recaptured by imaging the MOT at $t = t_{\text{push}} + 20 \text{ ms}$. Figure 4.19(b) shows this fraction versus $v_i$, where the $v_i$ should be understood as $\{x_i, v_i\}$ pairs.
Were the initial displacements negligible, it would be simple to determine the capture velocity from these measurements. Since they are not, we use a model to interpret the results. This was done by Luke Caldwell. In this model, the force in the direction \( (x) \) of the slowing light is given by equation (4.4). To account for the intensity distribution of the MOT beams we make the replacement \( s_{\text{eff}} \to s_{\text{eff}}(\frac{x}{\sqrt{2}}) \) in equation (4.3), where \( s_{\text{eff}}(r) = I_{00}(r)/I_{s,\text{eff}}, \) and \( I_{00}(r) \) has a Gaussian intensity distribution with a \( 1/e^2 \) radius of 8.1 mm, truncated at a radius of \( r_{\text{trunc}} = 15 \) mm. Using this force, we solve the equation of motion for a distribution of initial coordinates in phase-space and for a time long enough that the distribution of final coordinates separates into two components, one with \( x \) close to zero and the other with \( x \gg r_{\text{trunc}} \). This gives a contour in phase space, \( v_{\text{sep}}(x) \), which separates molecules that will be recaptured from those that escape. We then calculate the fraction of molecules from the initial phase-space distribution that lie inside this contour. We use a Gaussian spatial distribution centred at \( x_i \) with rms radius equal to the measured one, \( \sigma_0 = 2.0 \) mm, and a Gaussian velocity distribution centred at \( v_i \) and characterized by the measured temperature of 12 mK. This gives the simulated recapture fraction for each \( \{x_i, v_i\} \) pair used for the measurement. In applying this procedure, it is not clear what values of \( \Gamma_{\text{eff}}, I_{s,\text{eff}} \) and \( g_{\text{eff}} \) to use, so we keep them as free parameters. We compare the simulated results to the measured ones for a wide range of these free parameters and choose the parameter set that gives the smallest value of \( \chi^2 \). The open circles in figure 4.19(b) show the results that fit best. They are found for \( \Gamma_{\text{eff}} = 0.15\Gamma, I_{s,\text{eff}} = 50 \) mW/cm\(^2\), and \( g_{\text{eff}} = 0.25 \), all reasonable values. This comparison between model and measurements gives us a best estimate for \( v_{\text{sep}}(x) \). The capture velocity, \( v_c \), is the largest velocity a molecule that starts at the edge of the MOT can have if it is to be captured, \( v_c = v_{\text{sep}}(-r_{\text{trunc}}) \). The result is \( v_c = 11.2 \pm 1.2 \) m/s. The MOT simulations described in [99] predicted a capture velocity of 20 m/s, but this used larger beams, higher power and a slightly different polarization configuration. Repeating these simulations for the exact parameters used in the experiment we find a capture velocity of 14 m/s, close to our measured value.

### 4.5 Conclusions

During the course of our study, we have settled on a set of standard parameters for making a good MOT, which we summarize here. We turn the slowing light on at \( t_{\text{on}} = 2.4 \) ms and apply a frequency chirp to \( L_{00}^a \) at a rate of 24.8 MHz/ms between \( t_{\text{chirp}} = 3.5 \) ms and \( t_{\text{end}} = 15 \) ms. The slowing repump laser, \( L_{10}^a \), is detuned by \(-220 \) MHz and frequency broadened using a set of sidebands spaced by 8 MHz such that 90% of the power falls within a 360 MHz band. The MOT coils and the MOT light are on during the slowing period. The main MOT light, \( L_{00} \), has a detuning of \(-6 \) MHz, while all MOT repump
lasers are on resonance. The total intensity at the MOT due to all six beams of $L_{00}$ is 500 mW/cm$^2$, and the MOT beams have a $1/e^2$ radius of 8.1 mm. The axial magnetic field gradient is 30 G/cm.

Despite the complexity of the level structure and the need to avoid optical pumping into dark states, the CaF MOT behaves much like a normal atomic MOT in many respects. The intensity dependence of the scattering rate, trap frequency and damping constant all conform to the analytical results based on an effective two-level model, and do so over a very wide range of intensities, although somewhat different values for the free parameters of these equations are needed in each case. The trap frequency is in excellent quantitative agreement with that predicted from rate equation simulations, whereas the scattering rate is a factor 2 smaller than expected and the damping constant is typically a factor of 5–10 smaller. We tentatively attribute the reduction of the damping constant to polarization gradient forces [115], though that remains to be verified. For our parameters, we measure a capture velocity of $11.2 \pm 1.2$ m/s, consistent with our simulation. The temperature of the MOT is considerably higher than the Doppler temperature, especially at high intensity. It is also a factor of 2-3 higher than predicted by equation (4.10) when we use our measured values of the scattering rate and damping constant. This shows that the elevated temperature is a consequence of two factors, a reduced damping constant and some excess heating above that given by the diffusion constant in equation (4.9). The reasons for the reduced damping and the enhanced diffusion would make an interesting topic for future study. We find that the usual relation (equation (4.12)) between MOT size, temperature and trap frequency holds for our MOT, except at very low intensity where there seems to be a discrepancy. As expected, the size of the cloud scales inversely with the square root of the magnetic field gradient. Molecules are lost from the MOT with a typical rate of about $10^{-1}$ s$^{-1}$, and this loss rate scales linearly with scattering rate. The data is consistent with a leak out of the cooling cycle with a branching ratio of about $6 \times 10^{-6}$. The lifetime, $\sim 100$ ms, is short by the standards of atomic MOTs, but is adequate for most purposes. The next stage is to cool the molecules below the Doppler limit and load them into a conservative trap with a long lifetime $\sim 1$ s.
Chapter 5

Blue Detuned Molasses

From the previous chapter we know that the temperature of the molecules in the MOT is limited to around 900 $\mu$K, four times the Doppler limit. In order to cool the molecules further we use sub-Doppler cooling forces present in molasses [122], specifically the grey molasses method, which has previously been used to cool atoms [123]. The experimental results described in this chapter are also presented in [79].

5.1 Introduction

Detailed calculations for the sub-Doppler cooling of atoms and molecules with dark states can be found in [115]. The sub-Doppler cooling relies on a Sisyphus mechanism where optical pumping between sub-levels leads to a strong friction force at low velocities. This requires light fields with non-uniform polarization and/or intensity. The light for the molasses is the same as for the MOT, $\mathcal{L}_{00}$, but it is blue detuned from the transition frequency. Figure 5.1 illustrates the cooling method for molecules moving in 1D. The upper part of the figure shows the local polarization. The lower part shows the ac Stark shift of the ground levels with the thick purple arrows indicating the internal state of a molecule. The ground state has dark Zeeman sublevels which cannot couple to the local polarization, and bright states which can. Consider driving a transition from $F = 1$ to $F = 0$. In a region with $\sigma^+$ light only molecules in the $m_F = -1$ state will be coupled by the light, the other states will be dark. A molecule in a bright state observes a potential hill caused by the ac Stark shift. From equation 2.12 we know that this energy shift is proportional to the square of the Rabi frequency and inversely proportional to the detuning. In our experiment the detuning is the same for all sub levels, however the Rabi frequency is different as it depends on the electric dipole transition moment which is different for each sub-level. The cooling sequence is numbered in figure 5.1. (1) A molecule in a bright state will lose kinetic energy as it moves through the light field. (2)
Figure 5.1: Schematic showing the Sisyphus mechanism used to reach sub-Doppler temperatures. The upper part shows the local polarisation and the lower parts show the AC Stark shifts of the ground states. A molecule in a bright state will observe a potential hill (1). The cooling mechanism relies on optical pumping near the intensity maxima (2) and non-adiabatic transitions from a dark to bright state near the intensity minima (3).

The molecule is optically pumped into a dark state. The probability of pumping is proportional to the square of the Rabi frequency. Therefore a molecule is more likely to be pumped when it is experiencing a large ac Stark shift, near the top of the potential hill. This can occur when the light intensity is highest, for systems with intensity gradients but even in a situation with constant intensity the changing dipole transition strength caused by the polarisation gradient will lead to preferential pumping for molecules at the top of the potential hill. The molecule, now in a dark state, continues to move through the changing polarization allowing it to (3) non-adiabatically switch back to a bright state. This happens preferentially at the minima of the potential hill, where the energies of the bright and dark states are similar. Following this a molecule will repeatedly lose energy and hence cool.

In the experiment the molecules see counter-propagating $\sigma^+\sigma^-$ beams in 3D. This system is complicated to describe but has been simulated using the Optical Bloch Equations in [115]. A molecule moving through these 3D fields will experience gradients in both polarisation and intensity. This leads to spatially varying ac Stark shifts, optical pumping probabilities and non-adiabatic transition probabilities, all of which are required for the sub-Doppler cooling mechanism to work. The results from [115] predict strong friction forces leading to cooling far below the Doppler limit.
5.2 Experimental Details

The sub-Doppler cooling experiment uses the same experimental set-up as described for the MOT, with the addition of three pairs of shim coils, in Helmholtz configuration, arranged around the MOT chamber. This allows for control over the local magnetic field at the position of the MOT.

In order to load molecules efficiently into the molasses we first load the MOT using the optimal parameters. The MOT is then imaged at \( t = 40 \text{ms} \). This gives an initial number of molecules loaded for each experiment which is used to normalise against number fluctuations. At \( t = 50 \text{ms} \), \( I_{00} \) is ramped down by a factor of 100 to \( I_{00} = 4.6 \text{ mW cm}^{-2} \) over 20 ms. This reduces the temperature to below 1 mK. At \( t = 72 \text{ms} \), the shim coils are turned on to variable values. At \( t = 75 \text{ms} \), the MOT coils are turned off. At \( t = 76 \text{ms} \), we jump \( \Delta_{00} \) to +3\( \Gamma \) and \( I_{00} \) to a higher (variable) value. This is done by changing both the frequency and amplitude of the rf signal to the AOM that controls \( I_{00} \) and \( \Delta_{00} \) see figure 4.3(a), panel (3). The molecules are held in the molasses for 5 ms before being released. The temperature is measured via ballistic expansion, as with the MOT. To image the molecules after the molasses \( L_{00} \) is returned to full intensity and the frequency is jumped back to the MOT frequency. To measure the temperature we use an exposure time of 1 ms and record the cloud size after 3, 6, 9, 12 and 15 ms.

5.3 Results

The aim of the blue-detuned molasses experiment was to minimise the temperature of the molecules. To do this we investigated the effect of both the light and magnetic field. The temperature was found to have little dependence on detuning between \( \Delta_{00} = +2\Gamma \) and \( \Delta_{00} = +4\Gamma \). We chose to set the molasses detuning to be +3\( \Gamma \). We observe no loss in the number of molecules when loading the molasses.

5.3.1 Magnetic Field

The cooling process is disrupted by the presence of a magnetic field. If the Larmor precession time between bright and dark states is comparable to the time taken for a molecule to move between the intensity minima and maxima then the cooling becomes inefficient. The mean velocity would be limited to around \( v \approx \mu \lambda B/(4h) \), where \( \mu \) is the magnetic moment. This is equivalent to a temperature of \( T \approx (\pi m/8k_B)(\mu \lambda B/4h)^2 \). Therefore the temperature is expected to depend quadratically on the magnetic field \( T = aB^2 \) with
Figure 5.2: Temperature versus magnetic field in the y-direction recorded with $I_{00} = 460 \text{ mW cm}^{-2}$. Red points show recorded data. Blue line shows quadratic fit with curvature of $5740 \pm 30 \mu \text{K/mT}^2$. The dashed line shows the minimum Doppler temperature.

$a = 12,500 \mu \text{K mT}^{-2}$ and hence we need to minimise the local magnetic field.

There are two significant sources of magnetic field which we removed first. A magnetic field is applied throughout the slowing region of the experiment in order to avoid optical pumping into dark states during the slowing process. The coils that generate this field also produce a significant magnetic field at the MOT. We therefore modified the experiment so that these coils are turned off once the MOT has loaded. Before loading the molasses we turn off the MOT coils. This leads to eddy currents and residual magnetic fields in the chamber which take some time to dissipate. To account for this we wait for 1 ms after turning off the coils before loading the molasses.

With these initial adjustments made we next minimise the temperature of the molecules by changing the current in each pair of shim coils individually. Figure 5.2 shows the temperature of molecules for different magnetic fields in the y direction. The data is recorded at $I_{00} = 460 \text{ mW cm}^{-2}$. The dashed line shows the minimum Doppler temperature. The data show a quadratic dependence on magnetic field, as predicted. The red line shows a quadratic fit to the data, $T = aB^2$, where $a = 5,740 \pm 30 \mu \text{K mT}^{-2}$. This is consistent with the simple model described earlier given its approximate nature. In the x and z directions we obtain similar relations but they are minimised at 0.0 mT and so no current is required. This is because the background field in the lab is predominantly in the vertical (y) direction caused by the Earth’s magnetic field.
5.3.2 Intensity

Figure 5.3(a) shows the temperature of molecules at different intensities of $L_{00}$. These data are all recorded with the three shim coils set to minimise the temperature. The temperature of the molecules decreases with decreasing intensity from 500 mW cm$^{-2}$ until it reaches a minimum of 46 $\mu$K at around 100 mW cm$^{-2}$. For intensities lower than this the cooling becomes less efficient and the molecules don’t cool as much. This behaviour matches that observed for atoms in a grey molasses [123]. Figure 5.3(b) shows a temperature measurement using the ballistic expansion method giving a temperature of 62±2 $\mu$K. The upper part of the figure shows the recorded images. The final image was taken after 13 ms expansion time and the cloud has only expanded slightly but it is starting to drop due to gravity. The red points show the data and the blue line shows a linear fit from which we extract the temperature.

5.3.3 Cooling Period

Figure 5.4 shows the temperature of the molecules after various hold times in the molasses. The data show molecules cooling towards a base value of around 100 $\mu$K. These data were recorded at 460 mW cm$^{-2}$. The dashed line shows the minimum Doppler temperature and the red dots show the data. The cooling happens quickly and after 0.5 ms the molecules are already below the Doppler limit. The blue line shows an exponential decay with a 1/e time constant of 361 ± 2 $\mu$s. The efficiency of the cooling is less at lower intensities and so we always hold the molecules in the molasses for 5 ms, to allow the minimum temperature to be reached.
5.4 Increasing phase-space density

We will now consider the phase-space density of the cloud as many future applications require this to be high. Phase-space density $\rho$ is directly proportional to number density $N$ and inversely proportional to $T^3$. Therefore as well as decreasing the temperature, high phase-space densities can also be achieved by increasing the number density. Whilst in the molasses the molecules are not trapped, however their expansion is very slow compared to the time required for them to cool to their base temperature. Therefore, the molasses reduces the temperature of the cloud whilst maintaining its density. This leads to a large increase in the phase space density of the sample. The peak number density reached is $n = (0.8 \pm 0.2) \times 10^5 \text{ cm}^{-3}$ corresponding to a phase space density of $\rho = (2.4 \pm 0.6) \times 10^{-12}$. This is 1,500 times higher than in the initial MOT. It can be increased further by compressing the MOT prior to loading the molasses. Increased density of the MOT will lead to increased density in the molasses.

During the course of investigating the molasses, we found that changing the spacing of the $F = 2, F = 0$ and $F = 1^-$ frequency sidebands reduces the FWHM of the MOT. The frequency driving the EOM which produces these sidebands is now driven at 70.5 MHz, instead of the 74.5 MHz which was used for all data previously discussed. This increases the number density by a factor of 4 due to an increased MOT spring constant. The loading of the MOT is unaffected by this new sideband structure and the number of molecules captured remains the same.
5.4.1 Compressed MOT

For a given number of molecules $N$, the number density of a MOT depends on the thermal motion of each molecule in the trapping potential. If we consider the trapping potential to be a simple harmonic well then the cloud will adopt a Gaussian density distribution with a rms radius $\langle \sigma_i \rangle$ given by the equipartition theorem

$$k_B T_i = \kappa_i \langle \sigma_i \rangle^2,$$

(5.1)

where $\kappa_i = m \omega_i^2$ is the spring constant of the trap and $i = x, y, z$. As the temperature is in equilibrium then $T_x = T_y = T_z = T$ and the spring constants behave as $2\kappa_x = 2\kappa_y = \kappa_z = \kappa$ where $z$ is the vertical direction. Therefore the peak number density can be approximated as

$$n \sim N \left( \frac{\kappa}{k_B T} \right)^{3/2}.$$  

(5.2)

$\kappa$ is directly proportional to the magnetic field gradient and so by increasing the field gradient $n$ will increase. We increase the magnetic field gradient linearly between $t = 40$ and $50$ ms and hold it at the higher gradient ($B'$) for $5$ ms. Figure 5.5 shows the number density $n$ as a function of $B'$ in the compressed MOT (cMOT). Increasing $B'$ to $113$ G cm$^{-1}$ increases $n$ to $3.4 \times 10^6$ cm$^{-3}$, a factor of $5.3$ greater than in the initial MOT. If the number of molecules and the temperature are conserved in the compression then we expect $n \propto (B')^{3/2}$, from equation 5.2 resulting in a factor of $7.3$ increase in density. We find that the number of molecules is conserved but that $T$ increases. This explains the smaller observed factor. For all subsequent data we use $B' = 69$ G cm$^{-1}$. We choose not to ramp to a higher field gradient because the coils start getting very hot and out-gassing which increases the pressure in the chamber.

Once we have compressed the MOT we then decrease the laser intensity to lower the temperature of the molecules. Figure 4.16(a) shows that the temperature of the cloud is minimised at $I_{00} = 9$ mW cm$^{-2}$. Figure 4.17(a) shows that the FWHM of the cloud in minimised at $50$ mW cm$^{-2}$. We want to achieve the highest $n$ and so we now lower the intensity of the MOT light to $50$ mW cm$^{-2}$ between $t = 55$ and $t = 59$ ms. It is then held until $t = 63$ ms at which point $L_{00}$, and the MOT coils are turned off. At this intensity the temperature of the cloud is around $2$ mK. Next we load the molecules into the blue detuned molasses. We now load at full intensity $I_{00} = 400$ mW cm$^{-2}$ with the detuning still at $+3\Gamma$. The increased final temperature of the MOT makes loading directly into a low intensity molasses inefficient. The molasses is loaded at $I_{00}$ for $0.5$ ms. The intensity is then lowered in steps of $t = 0.5$ ms to $50, 30$ and $20\%$ of $I_{00}$. This procedure decreases the temperature to around $55$ $\mu$K without any loss in molecules. We have now increased
the phase space density by a further factor of 3 by compressing the MOT.

5.5 Conclusion

Here we have demonstrated that we can lower the temperature of molecules to $\sim 50 \, \mu K$ by loading them into a blue-detuned molasses. We are also able to increase the phase space density to $\rho \approx 7.5 \times 10^{-12}$ by first compressing the MOT and then loading into a blue-detuned molasses and lowering the intensity. The blue-detuned molasses has no trapping force and so now we need to load the molecules into a trap whilst conserving the current size and temperature. This was the first ever demonstration of cooling of molecules to below the Doppler limit.
Chapter 6

Coherent Quantum Control and Magnetic Trapping

Following the molasses we want to transfer the molecules into a conservative trap with a long lifetime. We chose to use a magnetic trap. This is easy to implement in the experiment as we can use the same coils to make the magnetic trap as used for the MOT. We also want a pure sample of molecules in a single, selectable, quantum state. In this chapter I will present both magnetic trapping and coherent quantum state control. The data presented is preliminary but has since been optimised and can be found in [80], where a pure sample of molecules in a single selectable quantum state was trapped for the first time. In this chapter we will only consider the $X^2\Sigma^+(v = 0)$ level and the relevant quantum state will be labelled as $|N, F, m_F\rangle$.

6.1 Experimental Recap

The experimental procedure at this point is as follows. At $t = 0$ the pulse of CaF molecules is created. At $t_{\text{start}} = 2.4$ ms the slowing light is turned on and then chirped at a rate of $\alpha = 24$ MHz/ms between $t_{\text{chirp}} = 3.5$ ms and $t_{\text{end}} = 15$ ms. The molecules are loaded into the MOT at an intensity $I_{00}^0 = 400$ mW/cm$^2$, a detuning $\Delta_{00}^0 = -0.75$ $\Gamma$ and a magnetic gradient $dB/dz = 30$ G/cm. At $t = 40$ ms we take an image, providing a reference for the number of molecules loaded for each shot. Between $t = 40$ ms and $t = 50$ ms the field gradient is linearly ramped up to 69 G/cm leading to the compressed MOT. The intensity of the MOT light is then ramped down to $0.1I_{00}^0$ between $t = 55$ ms and $t = 59$ ms. $L_{00}$ and MOT coils are turned off at $t = 63$ ms. At $t = 64$ ms the light is turned back on at $I_{00}^0$ and $\Delta_{00}^0 = 3$ $\Gamma$. The molecules are now in the blue-detuned molasses. After 0.5 ms $I_{00}$ is stepped down to 0.5, 0.3 and $0.2I_{00}^0$ in 0.5 ms steps. The resulting cloud contains around $1 \times 10^4$ molecules at a temperature of 55 $\mu$K.

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6.2 Magnetic Trapping

A magnetic trap works for molecules in weak field seeking states. For CaF this means that half of the ground state Zeeman sub-levels cannot be trapped. For those molecules in a wfs state, the strength of the trap depends on the magnetic moment which is different for different $m_F$ levels leading to a variation in trap depth observed by the molecules. In the experiment the trapping field is produced by the MOT coils. Any light leaking into the magnetic trap will reduce the lifetime by pumping molecules into strong field seeking states and so we installed mechanical shutters in the $L_{00}$ and $L_{s0}$ beams. This is necessary because the AOMs which normally control the light do not provide complete extinction. To measure the number of molecules trapped $L_{00}$ is turned back on and an image is recorded.

6.2.1 Preliminary Results

In order to investigate the magnetic trap we load molecules directly from the molasses. The molasses light is turned off at $t_{\text{mag}} = 67$ ms and the coils are turned on. Figure 6.1 shows the number of molecules retained in the trap for different field gradients. The image is recorded after a trap hold time of 200 ms and the number is normalised to the initial number of molecules loaded into the MOT. The number of molecules in the magnetic trap increases with field gradient, this is due to two factors. Firstly, the gradient required to hold a molecule up against gravity differs for each state. The required gradient is 10, 13, 21, 35 G/cm for the $|2, 2\rangle$, $|1^+, 1\rangle$, $|2, 1\rangle$ and $|1^-, -1\rangle$ states respectively. Therefore higher fields can support more of these states. Secondly, some states only become magnetically
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\[ \tau = 548 \pm 45 \text{ ms} \]

Figure 6.2: (a) Example decay curve for a He flow rate of 0.6 sccm. The data are shown in blue and the exponential fit is in red. (b) 1/e lifetime of magnetic trap versus He flow rate.

trappable with high fields, this can be understood from figure 2.5. At low field the \( m_F = 0 \) levels are agnostic to the field, however as the field increases they become strong or weak field seeking and molecules in \( |1, 1, 0\rangle \) and \( |1, 2, 0\rangle \) can be trapped. We found that when the coils are kept on for hundreds of milliseconds at high current they get hot and outgas. For this reason we do not try higher fields, and the rest of the data in this chapter was recorded at a field gradient of 30 G/cm. This gradient causes no observable increase in pressure in the chamber, even after 1 s of running the coils.

As well as the number of molecules, we also want to investigate the lifetime of the trap. Having eliminated all light we now want to look at the effect of the helium flow rate. To measure this we image the trap at various times after \( t_{\text{mag}} \). Figure 6.2(a) shows an example lifetime curve, where an exponential decay, shown in red, has been fitted to the data, shown in blue. This plot shows the lifetime measurement recorded at a helium flow rate of 0.6 sccm and gives a 1/e trap lifetime of \( 548 \pm 45 \) ms. Figure 6.2(b) shows the lifetime of the magnetic trap for various helium flow rates in the source chamber. It shows that the lifetime increases with decreasing flow rate. This indicates that the limiting factor to the lifetime is collisions with the background helium gas. This could be removed by adding a mechanical shutter inside the machine to disrupt the flow of the gas. The lifetime of the trap exceeds 1 s when using a flow rate of 0.15 sccm. However, with this low flow rate we lose out on the number of molecules created in each pulse, hence the large error in the lifetime fit shown by the error bar in figure 6.2(b). We chose to continue running the source with 0.3 sccm of helium. This still gives us a long lifetime \( > 800 \) ms.
Figure 6.3: Illustration showing the quantum control sequence. The blue circles represent molecule population, size not to scale. The sequence is (1) optical pumping by $L_{00}$ of molecules into $|1, 0, 0\rangle$. (2) Microwave $\pi$-pulse transferring population into $|0, 1, 1\rangle$. (3) Clean up beam, $L_{00}^\delta$ pushes all molecules left in $N = 1$ out of trap region. (4) Microwave $\pi$-pulse transferring the population into $|1, 2, 2\rangle$. The pink shaded regions show the periods when magnetic trapping can occur.

### 6.3 State Control

Having demonstrated a magnetic trap for molecules, we now want to transfer the population into a single quantum state. At the end of the molasses step the molecules are distributed across the 24 states of $X(v = 0, N = 1)$ and $X(v = 1, N = 1)$. We first optically pump the molecules into $|1, 0, 0\rangle$ and then use microwaves to coherently transfer the molecules between $N = 1$ and $N = 0$. Figure 6.3 illustrates the control scheme we use.

#### 6.3.1 Optical Pumping

The first stage is to pump as many molecules as possible into a single state, represented by step (1) in figure 6.3. To do this we turn off the frequency sideband addressing $|1, 0, 0\rangle$ in the $L_{00}$ beam causing population to accumulate in this state. This is achieved by turning up the amplitude of the EOM such that the carrier frequency is eliminated, to within the noise level of detection. We put a limit on the size of the amplitude remaining at $< 1\%$. After the molasses step we pulse on $L_{00}$, with the new sidebands, and the molecules are pumped into $|1, 0, 0\rangle$. This is a strong field seeking state and so the molecules cannot be trapped in a magnetic trap. We use this fact to measure the efficiency of the pumping. After the pumping step we load a magnetic trap and hold it for 50 ms. We then turn on $L_{00}$, with its normal sideband configuration, and record the number of molecules. By waiting for 50 ms before imaging we ensure that all molecules in non-trappable states have left the region. By repeating this with and without the pumping we can get an idea of what proportion of the molecules are being transferred. To achieve optimal pumping the detuning is set to be resonant with the transition and the intensity is lowered to $0.01 I_{00}^0$. 

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The light is pulsed on for 100 $\mu$s and approximately 60% of the population is transferred into $|1,0,0\rangle$. We believe that this is limited by the residual power in the carrier and off resonant scattering from the other frequency components. However, with most of the molecules in a single state we can next try to coherently transfer them into $N = 0$.

### 6.3.2 Microwave Transfer

Transitions between rotational levels can be addressed using microwaves. We send a microwave pulse into the chamber after the optical pumping. The microwave pulse is created by a two-channel microwave synthesizer and a frequency doubler which are connected via a switch and then coupled through a horn to free space. The microwaves enter the MOT chamber through the back of the final slowing mirror. Inside the chamber the microwave polarisation is poorly defined meaning we can drive transitions with $\Delta M_F = -1,0,+1$. We want to transfer the molecules into a single quantum state and therefore we must separate out the $m_F$ states in frequency. To do this we apply a constant, uniform field of $\sim 60 \text{ mG}$ which separates the $|0,1,0\rangle$ and $|0,1,1\rangle$ states by around 100 kHz. We find that this field can be applied throughout the experiment and without disrupting any of the previous steps. To measure the efficiency, and hence optimise the transfer, the microwaves are pulsed on for a duration $t_\mu$ and then the MOT is remade and the number of molecules is recorded. Molecules which have been transferred into $N = 0$ cannot be captured in the MOT and so we will observe pumping as a loss in molecules.

### 6.3.3 Preliminary Results

Here I will demonstrate the transfer of molecules into three different quantum states. We start by pumping the molecules into $N=0$, $F=1$ which has a predicted transition frequency of $\omega_{01} = 20481.9605 \text{ MHz}$. First we looked for the transition to $|0,1,0\rangle$ because it is insensitive to magnetic field and so stray background fields shouldn’t affect the transition frequency. Figure 6.4(a) shows the microwave spectroscopy recorded with a power of $-6$ dBm for a pulse duration of $\tau_\mu = 130 \mu$s. Here the frequency is recorded as the difference between the frequency applied ($\omega$) and $\omega_{01}$. The minimum value is not zero, as one might expect. This is due to the residual molecules which weren’t optically pumped in the previous step. The red line in figure 6.4(a) shows the fit to the data using the model $y_0 + Af(\Omega, \omega - \omega_0, \tau_\mu)$, where $y_0$ is the fraction recaptured for no microwave pulse, $A$ is an amplitude and $f$ is the Rabi lineshape for a two level system given by

---

\[^1\text{Windfreak SynthHD}\]

\[^2\text{Pasternack PE8603}\]
Figure 6.4: (a) Microwave spectroscopy showing pumping into $|0, 1, 0\rangle$. The red line shows fits to the Rabi lineshape for a $\pi$-pulse of 130 $\mu$s, with background, amplitude and central frequency as free parameters. (b) Rabi oscillations between $|1, 0, 0\rangle$ and $|0, 1, 0\rangle$ showing $\pi$-pulse conditions are $-6$ dBm and 130 $\mu$s.

Equation 2.22, $\tau_{\mu 1}$ is fixed and we leave $y_0, A$ and $\omega_0$ as free parameters. The fit gives $y_0 = 0.58$, consistent with the MOT lifetime and $A = -0.28$. The microwave transfer efficiency can therefore be calculated as $\epsilon_{mw} = A/(0.6y_0)$, where 0.6 is the optical pumping efficiency. We therefore have a microwave transfer efficiency of 81%. Figure 6.4(b) shows the number of molecules recaptured in the MOT after a resonant microwave pulse at $-6$ dBm for various pulse lengths. The highest number of molecules will be transferred when driving a $\pi$-pulse, see figure 2.6. Hence, we can determine that a pulse length of 130 $\mu$s will give a $\pi$-pulse. It is possible to model the Rabi oscillations as well, however further investigation into the behaviour of the microwave pulses was required. This is discussed in [86].

Next we look at transferring the molecules into $|0, 1, 1\rangle$, illustrated by step (2) in figure 6.3. This state is magnetically trappable and so is preferable to $|0, 1, 0\rangle$ for future applications. This transition is magnetically sensitive and so is susceptible to field gradients and fluctuations. Figure 6.5(a) shows microwave spectroscopy recorded with a power of 13 dBm and a pulse duration of 70 $\mu$s. The spectrum is wider and not as deep as that in figure 6.4(a). We believe that this is because of field inhomogeneities across the cloud. The fit to the data is also much worse. It gives $y_0 = 0.5$, which is lower than expected from the MOT lifetime, and $A = -0.06$ giving a microwave transfer efficiency of only 20%. Figure 6.5(b) shows a Rabi curve recorded at 13 dBm, indicating a $\pi$-pulse condition of 70 $\mu$s. The Rabi curve dampens quickly, which might also be due to magnetic field fluctuations. For future work we improve the magnetic field control within the set-up, however for these early experiments we have sufficient signal to demonstrate that the coherent transfer methods are working.
To make a pure sample we push the molecules remaining in $N = 1$ out of the trap region by turning on the slowing light for 1 ms, illustrated by step (3) in figure 6.3. All molecules are now in a single, magnetically trappable, quantum state. However, in order to detect the molecules we first have to pump them back into $N = 1$. We use a second microwave pulse to drive the molecules into $|1, 2, 2\rangle$, step (4) in figure 6.3. The frequency for this transition is predicted to be $\omega_{12} = 20553.4252$ MHz. Molecules in both $|0, 1, 1\rangle$ and $|1, 2, 2\rangle$ states have very similar magnetic g-factors and so the transition between them should be almost magnetically insensitive. Figure 6.6(a) shows the transfer into $|1, 2, 2\rangle$ as we scan across the transition with a power of 5 dBm and a duration of 70 $\mu$s. The molecules were first pumped in $|0, 1, 1\rangle$ and then held in a magnetic trap for 40 ms, step (a) in figure 6.3. The magnetic field was then turned off and the second microwave pulse was applied before imaging. Here the base line is zero showing that the push beam removed all molecules which were left behind after the first microwave pulse. The quality of this pulse is low and a Rabi lineshape cannot be fitted. However, after all of these steps, the number of molecules remaining is 9% of the number initially loaded into the MOT. The losses include the loss due to the lifetime of the MOT and magnetic trap, the inefficiency of the optical pumping step and the inefficiencies of the two microwave transfer steps. Figure 6.6(b) shows the Rabi curve. The signal to noise is low due to low molecule number, however it is clear that the $\pi$-pulse conditions are 5 dBm and $t_\mu = 70$ $\mu$s. This transition is magnetically insensitive and so it can be driven both in free space and in a magnetic trap. We tested both of these situations and achieved similar transfer efficiencies. The molecules can be held in a magnetic trap in either state. The shaded pink regions in figure 6.3 show the magnetic trap options.
6.4 Conclusion

Here we have demonstrated, for the first time, the loading of molecules into a magnetic trap in a single, selectable, quantum state. Since these early results the process has been improved and we can now create an ultracold, pure sample of $\sim \mathbf{8},000$ molecules in a magnetic trap with a lifetime approaching $2 \text{s}$. Coherent control of the quantum state of molecules is required for many applications including quantum simulation and investigation into controlled chemical reactions.
Chapter 7

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7.1 Increasing Molecule Number

One of the major current limitations to ultracold molecule experiments is the slowing stage. Buffer gas sources can reliably produce a high flux, typically $10^{11}$ molecules/steradian/pulse of a large variety of molecular species. However, the number which can be captured is currently stuck at around 6 orders of magnitudes below this, indicating the inefficiency of the slowing step. Here I will present a few proposed methods to overcome this problem.

Transverse Cooling  From figure 3.13 we know that a combination of initial transverse temperature and heating from photon scattering events leads to a large loss in the number of molecules which reach the capture volume of the MOT. A region of transverse cooling before the laser slowing starts could reduce the first problem drastically. Sub-Doppler 1D cooling has recently been demonstrated for YbF. They cooled a buffer gas beam of molecules to $< 100 \, \mu$K in the transverse direction [73]. The experiment uses two beams which enter the cooling region from opposite sides of the chamber and are reflected back and forth between two parallel mirrors 38 times over a distance of 200 mm. This leads to a highly collimated molecular pulse. A simulation for CaF suggests that with a 300 mm transverse cooling region the number of molecules which could be captured by the MOT would increase by almost an order of magnitude. This prediction still includes transverse heating from the slowing. The addition of a second transverse cooling region close to the MOT could potentially increase the trappable flux even more.

Zeeman-Sisyphus  A novel technique proposed in the CCM uses static magnetic field gradients and optical pumping to slow molecules [125]. This method is illustrated in figure 7.1. Potential hills are created by alternating high magnetic field segments with zero
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field. However unlike in traditional Zeeman decelerators here the magnets are permanent. A molecule in a wfs state will lose energy as it enters the region of high field. As it approaches the top of the hill it will be optically pumped into a sfs state by a laser which is detuned from resonance to match the Zeeman shift experienced by a molecule at a given magnetic field. Now the molecule is in the sfs state and will observe a potential hill as it travels towards an area of low field. At a certain field it will be optically pumped by a second laser frequency back into the wfs state and so the cycle continues. The molecules are always seeing a force which opposes their motion. This design has the advantage that all molecules will be included in the slowing. Those which start in the wrong state will join in one stage later. The efficiency of transfer between the two states at a chosen field has been tested and found to be almost 100% reliable [126]. Given that the excited state decays to $m_S = -1/2$ and $m_S = +1/2$ with equal probabilities, an average of only two photon scattering events will be required to transfer molecules to the other state. The technique is predicted to be very efficient at slowing and cooling molecules to around 80 m/s. Below this the magnets will start over-guiding the molecules and they will be lost. So for applications requiring slow, intense, collimated molecular beams the Zeeman-Sisyphus decelerator is a strong, and versatile, candidate. It requires far fewer photon scattering events than direct laser slowing making it amenable to molecules which would be difficult to laser cool. It would also be applicable to a continuous source to create a slow, intense flow of molecules which would be useful for precision measurements or collision experiments. We intend to install the decelerator into the CaF experiment and use it to slow molecules to around 50 m/s before applying a short region of laser cooling to load the MOT. This is predicted to increase the number of molecules captured by around an order of magnitude.

Other methods for increasing phase-space density We have a few other ideas to increase the phase-space density. These are mostly methods to increase the number of molecules. We could pump molecules from $N = 0$ and $N = 2$ into $N = 1$ near the source, therefore increasing the number which could be slowed. Shortening the slowing length would reduce the transverse spatial distribution in molecules after the slowing. This could be possible by increasing the chirp rate or using an optimised chirp that is not linear in time. Another option is to use neon as the buffer gas in the source. The group has had recent success at building a neon buffer gas source for YbF and the pulse was found to have much higher flux, with a similar velocity distribution. It was also found that the flux increased with increasing repetition rate. This would offer the possibility of loading multiple shots. We could also increase the density of the cloud by compressing more in either the MOT or the magnetic trap. We also stand to gain density by using
Figure 7.1: (a) Illustration of the Zeeman-Sisyphus technique. A molecule in the ground state (black dot) travels through two consecutive regions of high magnetic field. The molecule is periodically pumped by one of the two lasers between the weak-field and strong-field seeking state such that it is always being decelerated. Reproduced with permissions from [125] (b) A photograph of the fully constructed slower ready to be installed in the experiment.

a blue-detuned MOT. A recent paper has demonstrated a type-II blue-detuned MOT of Rb [127], which achieves a phase-space density a million times higher than a red-detuned type-II MOT, like the one we use.

7.2 Future Experiments

The experimental set-up is being modified to enable two new experiments to be conducted. The source and slowing sections of the experiment will remain the same but the MOT chamber will be modified. The beams and coils for the CaF MOT will be the same but the chamber will have extra ports to enable overlap with rubidium and transport of the molecules into a second chamber for a tweezer trap experiment.

Overlapping with rubidium There is a lot of interest in the study of atom-molecule collisions, a brand new field of research. If we could study collisions between Rb and CaF this could improve the understanding of molecule-molecule collisions which are preventing the formation of BECs of bialkali molecules. The structure of CaF is far simpler than molecules such as RbCs [128] and so a combination of experiment and theory could provide valuable insight into these effects. In our experiment the new chamber will have
a rubidium cell attached to it inside which we will make a 2D Rb MOT. This will then be pushed into the main chamber where the atoms can be captured in a tetrahedral MOT. The CaF molecules will simultaneously be captured in the normal MOT and then cooled to sub-Doppler temperatures. The first investigation will be into the overlapped MOTs; we currently do not know if the two traps could coexist. The next step is to transfer the molecules into a single level of the rotational ground state and load both species into a magnetic trap. We then will investigate elastic, inelastic and reactive collisions. If we find the elastic scattering rate to be favourable then this could provide a route to lower temperatures via sympathetic cooling.

**Optical tweezers** We also want to load molecules into an array of optical tweezer traps. In order to do this we need to move the molecules into a different, specially designed chamber. This chamber will be attached onto one side of the MOT chamber. The experimental procedure will be to put the molecules into a magnetic trap. We will use a pair of external coils to make an overlapped magnetic trap which can then be moved along a track. This will carry the trapped molecules into the tweezer chamber. Once there the molecules will be transferred into another magnetic trap created by internal coils. The chamber will allow both a MOT and molasses to be formed. Inside this chamber there will be a lens to focus the light to create the tweezer trap. We will begin by investigating loading and optimise the parameters to achieve a quick loading time. The next stage of the experiment will be to create an array of these traps which will allow us to investigate dipole-dipole interactions and will lead to quantum simulation.

### 7.3 Conclusion

Over the duration of my PhD I have developed and applied a frequency-chirped laser slowing technique to decelerate a pulse of CaF molecules from 180 m/s to within the capture velocity of a MOT, the first ever demonstration of this for molecules. Next, I loaded the molecules into a magneto-optical trap, only the second of its kind in the world. I then studied the loading and trapping properties of the MOT. Following on from this I demonstrated sub-Doppler cooling of the molecules using a blue-detuned molasses. This was the first time molecules had been cooled to below the Doppler limit. Finally I demonstrated, for the first time, coherent quantum control over the molecules, allowing me to load them into a magnetic trap, in a single, selectable quantum state. This work has led to the publication of 4 papers [70, 80, 79, 86]. The only other current method for producing molecules at such low temperature is to associate ultracold atoms. This technique is limited to using atoms which are themselves amenable to laser cooling. Direct laser cooling opens up a whole new class of molecules with different properties and
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applications. It will provide the basis for many future applications requiring ultracold molecules.
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