

Imperial College London
Department of Physics

Towards sympathetic cooling of molecules using ultracold atoms

Caleb John Hope Rich

Submitted in part fulfilment of the requirements for
the degree of Doctor of Philosophy in Physics, June 2022

Abstract

Ultracold molecules can be used for a wide range of applications, including quantum chemistry, tests of fundamental physics, and quantum simulation. These goals hinge on the ability to produce a gas of polar molecules at high phase-space density. Sympathetic cooling offers a promising route to bring laser-cooled molecules into this regime.

In this thesis, we make progress towards sympathetic cooling of CaF molecules with ultracold Rb atoms. Both species are loaded into a magnetic trap and we study collisions between them. Rotationally-excited molecules are found to collide inelastically with the atoms with a rate coefficient close to the universal limit. In the rotational ground state, no inelastic collisions are observed but an upper bound is placed on the inter-species inelastic loss rate coefficient. An attempt was made to observe thermalization between the two species is observed, which places an upper limit on the elastic cross section.

Transverse cooling of the molecular beam used for loading the MOT is implemented, increasing the number of molecules captured by a factor of 3.5. Benefiting from this, both species are loaded into a 1D optical lattice - demonstrating the first mixture of atoms and laser-cooled molecules in an optical trap. We observe rapid loss of molecules when cotrapped with the atoms, even for molecules in the rotational ground state. This is attributed to elastic collisions with the atoms, which have a temperature close to the trap depth for molecules. To circumvent this, it is necessary to cool the atoms further in a deep optical trap. Cooling of Rb atoms in a lattice and an optical dipole trap (ODT) is demonstrated using a Λ -enhanced gray molasses and we succeed in cooling the atoms down to 18 μ K in an ODT of depth 1 mK. At this temperature, sympathetic cooling of the molecules in the ODT should be observable.

Acknowledgements

First of all, thank you to my supervisors Mike and Ben for their guidance and support. Any coherence in what follows can be credited to Mike - your insight and optimism ensure that I leave any meeting with you both enlightened and enlivened. Thank you to Ben for sharing a portion of your immense lab knowledge.

Thanks to the rest of the CaF team: Sarunas and Arijit, thanks for teaching me everything about the experiment. Without your help, through good times and bad, this work would have been impossible and a lot less enjoyable. Thanks also to Jonas – your support and can-do attitude helped see me through the final part of the lab work. Thank you to all of the many lab predecessors who built parts of the experiment: Bharath, Noah, Hannah and many others. Finally, good luck to the new generation of CaF: Qinshu, Yixin, and Kai. I couldn't be leaving the experiment in better hands.

I would also like to thank all the people involved with CCM – you have made it a really great place to work. In particular, thanks to Jon and Dave whose technical support we could not do without, and to Sanja, who keeps the group running smoothly and looks after us all.

To CQD cohort 10, it has been a pleasure getting to know all of you and I wish you all good luck for the future. Many thanks to Miranda for organizing everything and keeping us all on track.

I am very grateful to have many great friends who have supported me and made my life better. Thank you to the Snake Pit: Adam, Carlotta, Hannah, Jamie, Jake, and Josh; to my eternal lab partner, Toby; to Alex, David, Ewan, Felix, and the rest of the Fellowship; and to Bertie, Stefan and many other Merton mates. Thanks to Jacob, I couldn't imagine a better housemate to endure Covid lockdowns with than you - thanks for the puzzles, the craft beers, and the animal facts. Hannah and Allan, thanks for putting up with me in my last months of writing.

Last but not least, thank you to my family. Mum and Dad, thank you for encouraging and supporting me in everything I do and for putting up with the curiosity and fiddling that made me the scientist I am today. Thanks to my sisters, Rosie and Jessie, for always having my back. Finally, thank you to Molly, who brightens my life in countless ways.

To my grandparents: Colin, Ruth, Joyce, and Eric

Declaration

I declare that the work presented in this thesis is my own and that any material from other sources is appropriately referenced. The copyright of this thesis rests with the author. Unless otherwise indicated, its contents are licensed under a Creative Commons Attribution-Non Commercial 4.0 International Licence (CC BY-NC). Under this licence, you may copy and redistribute the material in any medium or format. You may also create and distribute modified versions of the work. This is on the condition that: you credit the author and do not use it, or any derivative works, for a commercial purpose. When reusing or sharing this work, ensure you make the licence terms clear to others by naming the licence and linking to the licence text. Where a work has been adapted, you should indicate that the work has been changed and describe those changes. Please seek permission from the copyright holder for uses of this work that are not included in this licence or permitted under UK Copyright Law.

Parts of the work described in this thesis have been published in the following articles:

- S. Jurgilas, A. Chakraborty, C. J. H. Rich, B. E. Sauer, M. D. Frye, J. M. Hutson, and M. R. Tarbutt, “Collisions in a dual-species magneto-optical trap of molecules and atoms”, *New J. Phys.* 23, 075004 (2021)
- S. Jurgilas, A. Chakraborty, C. J. H. Rich, L. Caldwell, H. J. Williams, N. J. Fitch, B. E. Sauer, M. D. Frye, J. M. Hutson, and M. R. Tarbutt, “Collisions between Ultracold Molecules and Atoms in a Magnetic Trap”, *Phys. Rev. Lett.* 126, 153401 (2021)

Contents

List of Figures	21
1 Introduction	23
1.1 Why ultracold molecules?	23
1.1.1 Quantum chemistry	23
1.1.2 Many-body physics and quantum simulation	24
1.1.3 Quantum information processing	25
1.1.4 Tests of fundamental physics	26
1.2 Producing cold and ultracold molecules	27
1.2.1 Indirect methods	27
1.2.2 Direct methods	28
1.3 This thesis	32
1.4 Contributions of the author and others	32
2 Background theory	34
2.1 Atomic and molecular structure	34

2.1.1	Structure of ^{87}Rb	35
2.1.2	Diatomic molecules	37
2.1.3	Structure of CaF	41
2.2	The two-level atom interacting with light	44
2.2.1	The optical Bloch equations	46
2.2.2	Scattering force	47
2.3	Doppler cooling	49
2.3.1	Optical molasses	49
2.3.2	The Doppler limit	50
2.4	Magneto-optical trapping	51
2.4.1	Adapting the MOT for molecules	53
2.4.2	Scattering in multi-level systems	56
2.5	Sub-Doppler cooling	57
2.5.1	AC Stark shifts and polarization gradients	58
2.5.2	Sisyphus cooling	59
2.5.3	Gray molasses cooling	63
2.6	Ultracold collisions	65
2.6.1	Elastic scattering of distinguishable particles	65
2.6.2	Elastic scattering of indistinguishable particles	69
2.6.3	Inelastic and reactive collisions	71

3	Experimental setup	72
3.1	Introduction	72
3.2	Molecular source	73
3.3	Lasers	75
3.3.1	CaF	75
3.3.2	Rb	80
3.3.3	Frequency stabilization	82
3.4	Rb 2D MOT	84
3.5	Main chamber	85
3.5.1	MOT coils	85
3.5.2	Optical setup	87
3.5.3	Imaging	87
3.5.4	Microwaves	93
3.5.5	Shim coils	93
3.6	Loading a dual-species MOT	94
4	Collisions between Rb and CaF in a magnetic trap	96
4.1	Loading the magnetic trap	97
4.1.1	CaF	97
4.1.2	Rb	101
4.1.3	Magnetic trapping and imaging	102
4.2	Collision measurements	102

4.2.1	Loss rate coefficient measurement	103
4.2.2	Loss rates in different molecular states	107
4.2.3	Looking for thermalization	109
5	Transverse cooling of CaF	113
5.1	1D cooling	114
5.1.1	Setup	114
5.1.2	Results	116
5.1.3	Simulations	118
5.2	2D cooling	122
5.2.1	Setup	122
5.2.2	Results	124
5.2.3	Simulations	128
5.3	Outlook and conclusion	130
6	CaF and Rb in a 1D optical lattice	132
6.1	Introduction	132
6.2	Theory	132
6.3	Loading the atoms	134
6.3.1	Dark SPOT	134
6.4	Loading the molecules	138
6.4.1	Compressed MOT	138

6.4.2	Sub-Doppler cooling	139
6.5	Lattice characterization	140
6.5.1	Trap frequencies	140
6.5.2	Temperature measurements	144
6.5.3	Lifetime	145
6.6	Collisions in the optical lattice	145
6.6.1	Collisions in $N = 1$	145
6.6.2	State preparation	147
6.6.3	Collisions in $N = 0$	147
7	Λ-enhanced grey molasses of Rb in optical traps	150
7.1	Introduction	150
7.2	Cooling in free space	150
7.3	Cooling in the optical lattice	154
7.3.1	Heating	157
7.4	Cooling in the optical dipole trap	158
7.4.1	Cooling protocols	162
7.5	Density effects	165
7.6	Outlook	166
8	Conclusion	170
A	AC Stark effect in the $5^2P_{3/2}$ manifold of Rb	173

List of Figures

2.1	Energy level structure of the D1 and D2 lines of ^{87}Rb	37
2.2	Schematics of the coupling schemes in Hund's case (a) and (b)	40
2.3	Energy level diagram of the $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Pi$ states in CaF	42
2.4	Schematic of the MOT mechanism in 1D	52
2.5	Methods of disrupting the dark state in the dual-frequency MOT and the RF MOT	55
2.6	Sisyphus cooling	60
2.7	Gray molasses cooling and heating	64
3.1	Overview of the experiment	73
3.2	Schematic of buffer gas cell	74
3.3	CaF transitions driven in the experiment	75
3.4	Hyperfine structure of the $X^2\Sigma^+(N = 1, v = 0)$ state of CaF and frequency sidebands of CaF lasers	78
3.5	Schematic of CaF optical setup	79
3.6	Scheme of laser frequencies for Rb	81
3.7	Schematic of Rb optical setup	81

3.8	Schematic of electronic setup for offset locking	83
3.9	Schematic of the the 2D MOT of Rb	84
3.10	MOT coils	86
3.11	Optical setup around the main chamber	88
3.12	Optical setup for absorption imaging	91
3.13	Calibration of the shim coils	94
3.14	Loading of the CaF MOT	95
4.1	Microwave spectroscopy of CaF	99
4.2	Single-species loss of CaF and Rb in the magnetic trap	103
4.3	Loss rate measurement in the state $ 1, 2, 2\rangle$	104
4.4	Spatial distributions of CaF and Rb after the magnetic trap	106
4.5	Loss rate of CaF molecules in the state $ 1, 2, 2\rangle$ due to Rb versus effective density of Rb	107
4.6	Loss of CaF molecules prepared in the state $ 1, 1^+, 1\rangle$	108
4.7	Loss of CaF molecules prepared in different states	108
4.8	Temperature measurement of CaF molecules by ballistic expansion after the magnetic trap	110
4.9	Thermalization measurement of CaF in the magnetic trap	111
5.1	Schematic of transverse cooling setup	115
5.2	Time of flight measurements at CCD1 and CCD2	116
5.3	Transverse cooling of the beam in 1D	117

5.4	Energy levels and frequency structure of the $B^2\Sigma^+(N=0) \leftarrow X^2\Sigma^+(N=1)$ transition	118
5.5	Simulation results of transverse cooling in 1D	121
5.6	Schematic of the extension of the transverse cooling setup to 2D	123
5.7	Frequency calibration and transverse cooling of the beam in 2D	125
5.8	Enhancement in MOT number versus transverse cooling parameters	127
5.9	Simulation results of transverse cooling in 2D	128
5.10	Improvements to the transverse cooling setup	131
6.1	Setup for the dark SPOT	135
6.2	Dark SPOT	136
6.3	Lattice trapping light optical setup	137
6.4	Loading of Rb atoms into the optical lattice	138
6.5	Compressed MOT of CaF	138
6.6	Schematic of laser frequencies and hyperfine energy levels for three-frequency and single-frequency molasses of CaF	139
6.7	Loading of CaF molecules into the optical lattice	140
6.8	Parametric heating setup	141
6.9	Loss of atoms due to parametric heating	142
6.10	Variation of radial trap frequency with axial distance along lattice	143
6.11	Temperature measurement of Rb and CaF in the lattice	144
6.12	Temperature as a function of lattice trap laser power	144

6.13	Single-species loss of Rb and CaF in the optical lattice	145
6.14	Loss of molecules in the $N = 1$ manifold from the lattice	146
6.15	Driving the microwave transition $ 1, 0, 0\rangle \leftrightarrow 0, 1, 0\rangle$ in the optical lattice	148
6.16	Loss of molecules in state $ 0, 1, 0\rangle$ from the lattice with and without Rb	149
7.1	Schematic of relevant energy levels in ^{87}Rb and the laser frequencies used for Λ -enhanced gray molasses (ΛGM)	151
7.2	Temperature of atoms as a function of hold time in the ΛGM	152
7.3	Temperature of atoms after being held in the ΛGM as a function of various parameters	153
7.4	Cooling and loss in the ΛGM applied in the optical lattice	154
7.5	Temperature of atoms in an optical lattice after the ΛGM as a function of cooling light detuning and intensity	156
7.6	Shift in the detuning Δ_S of the transitions $ F = 1, m_F\rangle, F = 2, m_F\rangle \rightarrow \tilde{F}', m'_F\rangle$ due to the AC Stark effect	156
7.7	Heating in the lattice	158
7.8	Temperature of atoms in the optical dipole trap (ODT) after ΛGM as a function of cooling light detuning	159
7.9	Temperature of atoms as a function of hold time in the ΛGM applied in the ODT	160
7.10	Effective kinetic temperature of atoms after ΛGM applied in the ODT as a function of ODT hold duration after cooling	162
7.11	Schematic of the protocol for strobed and pulse cooling	163
7.12	Temperature of atoms after strobed cooling as a function of the strobing parameters	164

7.13	Temperature of atoms after pulsed cooling as a function of the pulse parameters	164
7.14	Effect of atom density on Λ GM cooling into the ODT	167
7.15	Axial trap potential of the ODT and trap depth as a function of power for a horizontal or tilted ODT beam	168
8.1	Scalar AC polarizability of Rb and CaF as a function of wavelength	172
A.1	AC Stark shifts of the hyperfine states in the $5^2P_{3/2}$ manifold of Rb	175

Chapter 1

Introduction

1.1 Why ultracold molecules?

The unprecedented level of control offered by ultracold atoms has led to a wide range of applications, from precision measurements [1] to quantum simulation [2] and information processing [3]. By extending the techniques used for cooling atoms, in recent years it has become possible to cool molecules down to ultracold temperatures. Due to their rich internal structure and large permanent electric dipole moments, ultracold molecules can extend and supplement the applications offered by ultracold atoms in many areas [4].

1.1.1 Quantum chemistry

At the temperatures accessible by conventional chemistry experiments, reaction dynamics necessarily involve averages over many degrees of freedom, such as the rotational, vibrational and hyperfine states of the reactant molecules. In contrast, ultracold molecules can provide a highly controllable system where the initial states of the reactants can be precisely selected, opening up whole avenues of research into the role that these initial quantum states play in the outcome of potential chemical reactions [5].

From a classical perspective, working at ultracold temperatures would seem to pose a problem.

As the temperature decreases, the speed of the reactants also falls leading to vanishing rates of collision [6]. However, this is not the full picture. At ultracold temperatures, the de Broglie wavelength becomes comparable to the scale of the interaction potential and the system has to be treated quantum mechanically. In this case, the rate of inelastic collisions for distinguishable particles¹ instead becomes independent of the collision energy at very low temperatures, as shown by Wigner [7].

Detailed calculations have shown that in addition to being finite, rates of chemical reactions can be large at ultracold temperatures, even in the presence of a potential barrier [8], due in part to quantum tunnelling. Reaction rates are also drastically impacted by other quantum effects such as resonances with quasi-bound states [9] and geometric phases [10], which are very sensitive to the form of the interaction potential. By studying these behaviours in the ultracold regime, new light may be shed on the fundamental processes behind chemical reactions which can help shape our understanding of chemistry. In addition, the profound impact of the interaction potential on the chemical properties of ultracold molecules opens up another possibility. External fields can be used to influence chemical reactions by altering the potential, allowing unprecedented control of chemical reactions [11].

1.1.2 Many-body physics and quantum simulation

Since the first Bose-Einstein condensation of atoms almost three decades ago [12, 13], there have been many interesting developments in the field of quantum gases. Bose-Einstein condensates and degenerate Fermi gases of many different atomic species have been produced [14–17] and rich non-linear phenomena such as superfluidity [18], quantized vortices [19], and solitons [20] have been observed. In most cases, the interactions between atoms in these quantum gases are dominated by the short-range and isotropic contact interaction. However, the development of quantum gases of highly magnetic atoms (such as Cr [21], Dy [22], and Er [23]) with magnetic dipole moments of several μ_B has led to a whole new range of behaviours such as roton excita-

¹For indistinguishable particles, quantum statistics plays a role and the behaviour depends on whether the particles are bosons or fermions.

tions [24] and the formation of quantum droplets [25] and supersolids [26], due to the relatively large magnetic dipole-dipole interactions between these atoms.

Polar molecules, on the other hand, have permanent electric dipole moments on the order of ea_0 , which lead dipole-dipole interactions that are stronger by a factor of

$$\frac{\mu_0 \mu_B^2}{(ea_0/\epsilon_0)} \sim 10^4 \quad (1.1)$$

in comparison to those found in magnetic atoms [27]. Furthermore, by manipulating the internal states of the molecules with external fields, the strength and even the shape of the interaction potential between the molecules can be tailored [28]. This strength and flexibility allows vast new regimes to be explored with quantum gases of molecules, thus testing our fundamental understanding of many-body physics.

Quantum gases have also been used to study models applicable to condensed matter physics. This was initiated by the observation by Jaksch et al. [29] that atoms in optical lattices can be used to probe the Bose-Hubbard model, which is important across condensed matter physics, including in the field of superconductivity. The experimental realization of this, as well as the quantum phase transition from Mott insulator to superfluid which is a feature of the model, paved the way for quantum simulation of condensed matter systems with ultracold atoms [30]. Due to their long-range dipole-dipole interactions and rich internal structure, ultracold molecules trapped in optical lattices [31] or arrays of optical tweezers [32] offer to extend the range of models that can be simulated. This includes many models relevant to quantum magnetism such as the XXZ model [33, 34].

1.1.3 Quantum information processing

Ultracold molecules have also been put forward as a promising platform for quantum information processing. A seminal proposal by DeMille [35] envisages a quantum computer made up of ultracold molecules trapped in a 1D array, with the qubits encoded in the orientation of the molecules relative to applied electric field. The strong dipole-dipole interactions present in

molecules can then be leveraged to perform fast two-qubit gate operations. By applying an additional linear field gradient across the array, the varying Stark shifts of the molecules permit site-selective one-qubit gates to be executed with microwaves. Readout of the final state is then done with state-selective ionisation of the molecules.

There are many advantages to the proposed scheme, a large number of which have been demonstrated experimentally. Long coherence times have been measured in ultracold molecules - around 100 ms in rotational states [36] and over 5.4 s in nuclear spin states that have been proposed as qubit storage states [37]. Two-qubit gates have been implemented with molecules trapped in optical tweezers, with gate times on the order of tens of milliseconds [38, 39] and tens of thousands of molecules have been trapped in optical lattices showing the potential scalability of this method of quantum computing [40].

Many interesting theoretical proposals have been developed following DeMille's lead that strengthen the appeal of ultracold molecules for quantum information processing. These include using more than two levels in molecules to encode information in the form of qudits thus increasing scalability [41], the use of rotational states to implement quantum error correcting codes [42], and the addition of Rydberg atoms to mediate faster quantum gates between molecules [43, 44].

1.1.4 Tests of fundamental physics

While the Standard Model of particle physics has had great success in predicting and describing countless physical processes, it is far from its goal of being a so-called 'theory of everything'. Various phenomena such as dark matter, dark energy and matter-antimatter asymmetry still remain unexplained, which prompts the search for new physics beyond the Standard Model. Many proposed extensions to the Standard Model have effects that can be measured with high precision spectroscopy of molecules [45, 46]. Thus, these experiments can be used to either probe physics beyond the Standard Model or put constraints on the proposed extensions.

For example, extensions to the Standard Model that seek to explain matter-antimatter asymmetry generally do so by introducing additional sources of CP-violation [47]. This leads to much

larger predicted values of the electron electric dipole moment (eEDM), which would cause a potentially measurable shift in transition frequencies of atoms or molecules in an applied electric field [48]. This effect is magnified in polar molecules, as their larger polarizability leads to much larger effective fields experienced by the electrons [49]. As a result, the most precise measurements to date of the eEDM have been performed with molecules [50, 51].

Molecules have also been used to measure the possible variation of fundamental constants such as the electron-proton mass ratio μ and the fine-structure constant α , which is a feature of some theories proposed to explain dark energy [52, 53]. The different sensitivities to μ and α offered by transitions in molecules compared to those in atoms, as well as the varied effect of different systematic uncertainties, mean that measurements with molecules allow more stringent bounds to be placed on these variations than with atoms alone [54].

The tests of fundamental physics laid out above would benefit greatly from the use of ultracold molecules [55]. Lower temperatures lead to increased coherence times and, if trapped, ultracold molecules can be interrogated for much longer compared to experiments on molecular beams. This will increase the precision of these measurements, boosting their sensitivity to new physics beyond the Standard Model.

1.2 Producing cold and ultracold molecules

There are two routes towards producing cold and ultracold molecules: indirect methods, where ultracold atoms are bound together to produce molecules, and direct methods, which proceed by cooling of pre-formed molecules. In the following section, a brief introduction to both approaches is given.

1.2.1 Indirect methods

Ultracold molecules produced by indirect methods have been the centrepiece of many pioneering experiments. Starting with a sample of ultracold atoms, molecules are formed by either photo-

or magneto-association [56, 57]. The resulting molecules are in highly-excited vibrational states and thus very weakly bound but can be transferred by stimulated Raman adiabatic passage (STIRAP) to lower lying states [58] and even to the absolute ground state [59].

The range of molecules that can be produced by indirect methods is naturally limited to those containing atoms that can be laser cooled. The first molecules produced in this way were homonuclear molecules of alkali atoms [60, 61]. By expanding to mixtures of alkali atoms, the first ultracold polar molecules were formed [62, 63] and, since then, molecules involving closed-shell atoms have come into reach, first as homonuclear molecules [64] and then as heteronuclear molecules with alkali atoms [65, 66].

In recent years, association of degenerate mixtures of atoms has allowed the production of the first quantum gas of polar molecules [67]. However, further collisional cooling of polar molecules has faced the issue of rapid losses by inelastic collisions [68–71], even in non-reactive molecules [69–71]. This has led to the application of various schemes for shielding molecules from inelastic collisions by using strong electric fields in quasi-2D geometries [11] or by resonant shielding with DC electric fields [72] or microwaves [73]. Recently, these techniques have allowed direct evaporative cooling of molecules to below quantum degeneracy [74, 75]. In parallel to this, sympathetic cooling of polar molecules with ultracold atoms has been demonstrated [76], offering a potential alternative pathway to quantum degeneracy.

1.2.2 Direct methods

Direct methods of producing ultracold molecules have their origins in cold molecular beams. These were produced either by supersonic expansion [77] or later with cryogenic buffer gas sources [78]. Various techniques to decelerate these molecular beams have also been developed using electric and magnetic fields, allowing many molecular species to be trapped [79]. More recently, by extending the laser cooling techniques first applied to atoms, molecular beams have been decelerated using radiation pressure and the molecules captured in magneto-optical traps - a great starting point for many further experiments [80].

Supersonic expansion

For close to 50 years, supersonic expansion has been used to create cold beams which have formed the basis of countless experiments with molecules [77]. To produce a cold beam by supersonic expansion, an inert gas (such as He or Ne) at high pressure is allowed to expand rapidly into a vacuum through a small nozzle. Collisions during the expansion cause the thermal motion of the atoms to be transferred to forward velocity, producing a fast beam with a small spread of velocities. A species of interest can be seeded into the beam and will be cooled by the same mechanism.

Cryogenic buffer gas cooling

Early successes in trapping cold molecules were achieved using buffer gas cooling. This works by injecting or producing a molecule of interest inside a cryogenically-cooled cell in the presence of an inert cold buffer gas. Thermalization with the buffer gas via elastic collisions then cools the molecules down to low temperatures whilst removing energy from the rotational and vibrational degrees of freedom [81].

Using this technique, Weinstein et al. [82] succeeded in trapping CaH molecules in a magnetic trap at a temperature of 400 mK. Since then, several other molecular species have been trapped at temperatures below 1 K [83]. These traps can contain up to 2×10^8 molecules at peak densities approaching $1 \times 10^8 \text{ cm}^{-3}$ in some cases. Trap lifetimes were initially less than a second but have since risen, with a lifetime of over 20 s observed in an experiment with NH molecules [84].

Cryogenic buffer gas cooling can also be used to create cold beams of molecules. If the buffer gas cell has a small aperture, then some of the molecules will escape. Depending on the dimensions of the cell and the density of buffer gas within it, the flow of molecules out of the cell can be enhanced by hydrodynamic entrainment [85]. The mean speeds of beams from cryogenic buffer gas sources are generally much lower than those created by supersonic expansion [78]. Moreover, for many molecules, the flux of buffer gas beams is much larger than in supersonic beams. These properties make buffer gas beams highly favourable for many applications including for laser

slowing and cooling.

Deceleration of molecular beams

The forward speed of molecular beams limits the amount of interrogation time achievable in an experimental apparatus. Furthermore, for all but the slowest buffer gas beams², directly loading molecules into traps from molecular beams is not possible. To allow molecules to be trapped or to simply extend the interrogation time possible in an experiment, various techniques have been developed to decelerate molecular beams.

This goal was first achieved in 1999 with the development of the Stark decelerator for molecules [87]. In an applied electric field, polar molecules will experience a shift in energy depending on their internal state due to the Stark effect. This shift is positive for some states (known as low-field-seeking states) and negative for others (known as high-field-seeking states). If the electric field is inhomogeneous, as a molecule in a low-field-seeking state moves to a region of higher field, its kinetic energy will be transferred to potential energy. By switching the field off at this point, the potential energy will be removed. This process can be repeated many times, slowing the molecule further with each iteration. A Stark decelerator employs this method to slow molecules by applying electric fields that are synchronously switched at the correct rate so that the molecules will be constantly decelerated.

Molecular beams slowed using Stark decelerators have been used to load traps, starting with ammonia molecules confined in an electrostatic trap [88] and expanding to a large variety of other traps and storage rings [79]. Modifications of this method have allowed molecules in high-field-seeking states to be decelerated [89]. Zeeman deceleration, an analogous method using magnetic fields instead of electric fields, has been used to slow a molecular beam of non-polar paramagnetic molecules [90] and load them into a magnetic trap [91]. Many other methods have also been used to decelerate cold molecular beams, such as optical Stark deceleration [92] and rotating electrostatic guides [93].

²Direct magnetic trap loading of CaF from a beam of mean speed $\sim 30 \text{ m s}^{-1}$ with optical pumping has been reported [86].

Further cooling of these trapped molecules has been demonstrated by direct evaporative cooling [94] and by opto-electric Sisyphus cooling [95]. Sympathetic cooling with co-trapped atoms has been suggested as an alternative approach and good progress has been made towards this with the confinement of both atoms and molecules in the same magnetic trap [96].

Laser cooling

Spurred on by the resounding successes of laser cooling as applied to atoms, many wondered whether these techniques might be applied to molecules. Here, the complex energy level structure that underlies many of the potential applications of ultracold molecules becomes a double-edged sword. In order to successfully apply laser cooling to molecules, the almost inevitable branching to various rotational and vibrational states during excitation must be tamed without requiring a prohibitive number of laser frequencies.

One leap forward was made by Di Rosa [97], who noted that, for certain classes of molecules, there are transitions where, once excited, the molecule is highly likely to return to its original vibrational state when it decays. A cooling scheme was proposed based on this that would allow an estimated 10^4 photons to be scattered without significant loss of molecules from the cooling cycle. Further developments followed with a proposal for a magneto-optical trap of TiO molecules [98] which utilised selection rules to eliminate rotational branching, thus reducing the number of lasers needed for repumping.

Experimentally, the first successes came when Shuman et al. demonstrated deflection [99] and transverse cooling [100] of a beam of SrF molecules. Soon after, the technique was extended to repump more vibrational levels, allowing enough photons to be cycled to slow the beam [101]. Another molecular species was brought into the fold when cooling of a beam of YO was demonstrated, along with the first magneto-optical compression of a molecular beam [102]. This paved the way for the first 3D magneto-optical trap (MOT) of molecules, achieved with SrF in 2014 [103]. CaF was the next molecular species to be loaded into a MOT, which was achieved by our group in 2017 [104] and by researchers at Harvard in the same year [105]. Since then the set of molecules that have been trapped in 3D MOTs has widened to YO molecules

[106] and even a polyatomic molecule, SrOH [107]. Further cooling of molecules after the MOT has brought laser-cooled molecules to temperatures below the Doppler limit for the first time [104], allowing the loading of magnetic traps [108, 109], optical dipole traps [110, 111] and arrays of optical tweezer traps [32].

1.3 This thesis

In this work, our progress towards sympathetic cooling of laser-cooled CaF molecules with Rb atoms is detailed. For this purpose, we study collisions between CaF and Rb, both in a magnetic trap and in a 1D optical lattice. The thesis is structured as follows. In chapter 2, the background theory relating to atomic and molecular structure and laser cooling is developed which will serve as a foundation of the rest of the thesis. Chapter 3 describes the setup that was used to carry out the experiments detailed in this thesis. In chapter 4, our investigation of collisions between Rb and CaF in a magnetic trap is presented, including the effect of different molecular states on the rate of inelastic collisions. A first attempt is made to observe sympathetic cooling of the molecules with the atoms. The subject of chapter 5 is transverse cooling of the CaF molecular beam with the aim of increasing the number of molecules we are able to trap. Both CaF and Rb are loaded into a 1D optical lattice in chapter 6. The lattice is characterized and collisions between the two species are observed. Chapter 7 presents our implementation of Λ -enhanced gray molasses cooling of Rb, both in a 1D optical lattice and a focussed beam dipole trap. This can be used to bring the temperature of the Rb atoms to very low temperatures and may allow sympathetic cooling of CaF to be observed.

1.4 Contributions of the author and others

The complexity of the CaF-Rb experiment often demands that work be done as a team. Therefore, it is important to indicate where others have contributed to the results presented in this thesis. The experimental setup as described in chapter 3 was already assembled before I joined

the experiment but an overview is included here to give context for the rest of the thesis.

The experimental results presented in chapter 4 were obtained by Sarunas Jurgilas, Arijit Chakraborty and me. In chapter 5, the various setups for transverse cooling were designed and constructed by me; the experimental data was taken by Sarunas, Arijit and me; and the simulations were done by me. In chapter 6, the dark SPOT for Rb was implemented by me; the setup for optical trapping was built by Sarunas and me; and all experimental results were obtained by Sarunas and me. In chapter 7, the setup was assembled by me; the experimental data in free space and in the optical lattice were taken by Sarunas and me; and all further data was taken by me.

Chapter 2

Background theory

This chapter details the essential theory that underpins the experimental results presented in the later chapters of this thesis. The first section is a description of the structure of the atom (^{87}Rb) and the molecule ($^{40}\text{Ca}^{19}\text{F}$, hereafter CaF) that are central to this work. Then, we set out the dynamics of a two-level atom interacting with monochromatic light and the scattering force that results. Armed with this, we examine Doppler cooling in optical molasses and the magneto-optical trap. We then extend the theory to multi-level atoms to understand various sub-Doppler cooling mechanisms that will be used throughout this thesis. Finally, a summary of the theory of ultracold collisions is given.

2.1 Atomic and molecular structure

To apply laser cooling to an atom or molecule, it is necessary to find a ‘closed’ transition, where many photons may be scattered before the atom or molecule is transferred to a state that is not addressed by any laser. In this section, I will present the energy level structures of ^{87}Rb and CaF, as well as the transitions used to cool both species down to ultracold temperatures.

2.1.1 Structure of ^{87}Rb

As with other alkali atoms, the ground state electron configuration of ^{87}Rb ($[\text{Xe}] 5s$) consists of a single unpaired valence electron in the outer shell. To a first approximation, the inner electrons simply shield the valence electron from the charge of the nucleus, so we have a hydrogen-like system with a single electron around a nucleus with charge $+e$.

The lowest lying electronic states above the ground state are those where the single valence electron has been excited to a higher orbital. The energy of these states is largely determined by the orbital of the excited electron, labelled by nl where n is the principal quantum number and l is the azimuthal quantum number. For Rb, the lowest lying orbital above the $5s$ is the $5p$, as shown in figure 2.1.

The spin-orbit interaction cause the splitting of these energy levels into what is known as the fine structure. To a good approximation, the electronic states are eigenstates of the operators $\hat{\mathbf{L}}^2$, $\hat{\mathbf{S}}^2$, and $\hat{\mathbf{J}}^2$, where $\hat{\mathbf{L}}$ is the orbital angular momentum, $\hat{\mathbf{S}}$ is the electron spin angular momentum, and $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$ is the total electronic angular momentum. The eigenvalues of $\hat{\mathbf{L}}^2$, $\hat{\mathbf{S}}^2$, and $\hat{\mathbf{J}}^2$ are $\hbar^2 L(L+1)$, $\hbar^2 S(S+1)$, and $\hbar^2 J(J+1)$ respectively and we label each electronic level by the orbital of the outer electron and its term symbol, conventionally written as¹:

$$n^{2S+1}L_J, \quad (2.1)$$

where the value of L is indicated by a letter from the sequence $\{S, P, D, F, G, \dots\}$ corresponding to values of $L = \{0, 1, 2, 3, 4, 5, \dots\}$.

If relativistic effects were neglected, each configuration would be degenerate with respect to S with degeneracy $(2S+1)$, known as the spin multiplicity. However, the spin-orbit interaction couples L and J and lifts this degeneracy, splitting each term into levels labelled by J , where J takes values from $|L-S|$ to $L+S$.

In ^{87}Rb , we have a single electron sitting outside closed shells and so $S = 1/2$ and L is simply

¹Since the inner electrons form closed shells, L is just the orbital angular momentum quantum number l of the outer electron and we drop l from the configuration, as it is redundant.

determined by the orbital of the single electron. The 5s ground state term is thus $^2S_{1/2}$ and each term with $L > 0$ splits into two levels with $J = L \pm 1/2$. For the 5p, this leads to terms $^2P_{1/2}$ and $^2P_{3/2}$, with the former being lower in energy.

Finally, we consider the hyperfine structure which arises from the interaction between the spin of the nucleus and the electrons. This couples $\hat{\mathbf{I}}$ and $\hat{\mathbf{J}}$ to form the total angular momentum $\hat{\mathbf{F}} = \hat{\mathbf{I}} + \hat{\mathbf{J}}$ and splits each of the terms into hyperfine levels labelled by F where F ranges from $|I - J|$ to $I + J$.² In ^{87}Rb , the nucleus has spin $I = 3/2$, so the ground state ($5^2S_{1/2}$) splits into two hyperfine components with $F = 1, 2$, as does the $5^2P_{1/2}$. The $5^2P_{3/2}$, however, has four components with $F = 0, 1, 2, 3$.

Each hyperfine state is $(2F + 1)$ -fold degenerate but will split in an external magnetic field into magnetic sublevels due to the Zeeman effect. Each sublevel can be labelled by its value of m_F , where m_F is the eigenvalue of the $\hat{F}_z$ operator, corresponding to the component $\mathbf{F}$ along the magnetic field direction, z .

Transitions

The transitions from $5^2S_{1/2}$ to $5^2P_{1/2}$ and $5^2P_{3/2}$ are known as the D_1 and D_2 line, respectively. The transitions can be driven by light with a wavelength of around 795 nm on the D_1 line and around 780 nm on the D_2 line [112].

The electric dipole transitions between the hyperfine levels of each state follow the selection rules $\Delta F = 0, \pm 1$ and $\Delta m_F = 0, \pm 1$. From these we can see that the transition $5^2S_{1/2} (F = 2) \rightarrow 5^2P_{3/2} (F = 3)$ is closed and therefore amenable to laser cooling with a single laser. In reality, when driving this transition, there is a non-negligible chance of exciting the atom to $5^2P_{3/2} (F = 2)$ which can decay to the $F = 1$ level in the ground state. As a result, it is necessary to repump atoms from the $F = 1$ level using a secondary laser.

² I and F are defined such that the eigenvalues of $\hat{\mathbf{I}}^2$ and $\hat{\mathbf{F}}^2$ are $\hbar^2 I(I + 1)$ and $\hbar^2 F(F + 1)$ respectively.

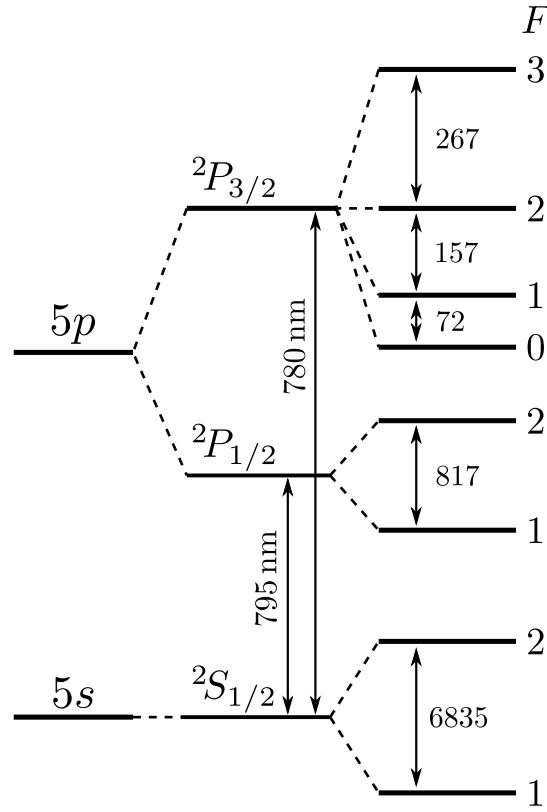


Figure 2.1: Energy level structure of the D1 and D2 lines of ^{87}Rb , showing the fine and hyperfine structure. The energy spacings of the hyperfine levels are given in units of $h \times \text{MHz}$.

2.1.2 Diatomic molecules

Molecules have a richer and more complex energy level structure in comparison to atoms. In addition to the electronic state, the vibrational and rotational state of the molecule also contribute to the energy. By making the Born-Oppenheimer approximation, we can separate out the contribution of the electronic, vibrational and rotational states and write the total energy as

$$E = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}}. \quad (2.2)$$

The terms are in order of their relative magnitude; in diatomic molecules, we typically have $E_{\text{elec}} \sim 10^2 E_{\text{vib}} \sim 10^4 E_{\text{rot}}$.

Electronic structure and molecular term symbols

Unlike in atoms, the potential seen by the electrons in molecules lacks spherical symmetry. This means that the operator $\hat{\mathbf{L}}^2$ does not commute with the Hamiltonian and L is no longer a good

quantum number. In diatomic molecules, the spherical symmetry is replaced by cylindrical symmetry around the inter-nuclear axis. To take advantage of this symmetry, we define a body-fixed coordinate system with the axis z' fixed to the inter-nuclear axis. The projection of the orbital angular momentum along this axis, $\hat{L}_{z'}$, commutes with the Hamiltonian and we can identify Λ as a good quantum number where $\hbar\Lambda$ is the eigenvalue of $\hat{L}_{z'}$.

In analogy with atoms, each electronic state of a molecule can be ascribed a term symbol which is written in the form

$$[\text{Letter}]^{(2S+1)}|\Lambda|^{+/-}. \quad (2.3)$$

The first part denotes the electronic state with a unique letter from the sequence $\{X, A, B, C, \dots\}$ where X labels the ground state, A the first excited state, B the second excited state and so on. The value of $|\Lambda|$ is denoted by a symbol from the sequence $\{\Sigma, \Pi, \Delta, \Phi, \dots\}$ corresponding to $\{0, 1, 2, 3, \dots\}$, respectively. Finally, the superscript $+/-$ is used to label states with $\Lambda = 0$ according to their reflection symmetry through any plane containing the nuclear axis.

Vibrational structure

After the electronic motion, the next biggest contribution to the energy is from the vibrational energy of the nuclei. The nuclei move in an effective potential, $V(r)$, that depends on their separation, r , due to the electrostatic interaction between the two nuclei and the energy of the electronic state. Since the molecule is bound, there exists an equilibrium separation, r_0 , at which the potential is minimized. Expanding around this minimum to second order, we obtain the well-known Schrödinger equation for the harmonic oscillator with energy eigenvalues given by

$$E_\nu = \hbar\omega_\nu \left(\nu + \frac{1}{2} \right), \quad (2.4)$$

where $\omega_\nu = \sqrt{k/\mu}$, $k = V''(r_0)$, and μ is the reduced mass of the nuclei. This is a reasonable approximation for lower vibrational states where the wavefunction is localized close to r_0 , however for higher vibrational states the anharmonicity of the potential is more apparent. One

function that has been used to model this effect with some success is the Morse potential

$$V(r) = D \left(1 - e^{-a(r-r_0)}\right)^2. \quad (2.5)$$

Solving the Schrödinger equation with this potential leads to energy eigenvalues given by

$$E_\nu = \hbar\omega_v \left(\nu + \frac{1}{2}\right) - \hbar\omega_v x_e \left(\nu + \frac{1}{2}\right)^2 \quad (2.6)$$

where

$$\omega_v = \frac{2Da^2}{\mu}, \quad x_e = \frac{a\hbar}{2\sqrt{2\mu D}}. \quad (2.7)$$

Rotational structure

As well as vibrating, the nuclei in the molecule can also rotate. The rotational Hamiltonian can be written as

$$H = \frac{\hat{\mathbf{R}}^2}{2\mu r^2} \quad (2.8)$$

where $\hat{\mathbf{R}}$ is the rotational angular momentum of the nuclei. To a first approximation, we can replace the separation r with its equilibrium value r_0 and the Hamiltonian becomes that of a rigid rotor

$$H = B\hat{\mathbf{R}}^2 \quad (2.9)$$

with $B = 1/2\mu r_0^2$. This forms a rotational ladder of levels with energies given by

$$E_R = BR(R+1). \quad (2.10)$$

This is a reasonable approximation for lower rotational levels however as the rotational energy increases so does the centrifugal force between the two nuclei. This causes the equilibrium separation r_0 to increase with increasing R . A better approximation to the rotational energy can then be found from the expansion

$$E_R = B_\nu R(R+1) - D_\nu R^2(R+1)^2 + \dots \quad (2.11)$$

where the added terms are known as the centrifugal distortion corrections and the subscripts ν indicate that the factors depend on the vibrational state as

$$B_\nu = B_e - \alpha_e \left(\nu + \frac{1}{2} \right) + \dots, \quad (2.12)$$

$$D_\nu = D_e + \beta_e \left(\nu + \frac{1}{2} \right) - \dots. \quad (2.13)$$

Hund's cases

As with the atomic case, it is useful to identify the angular momenta present, the relative strengths of the couplings between them, and the good quantum numbers that result. The possible coupling schemes are known as Hund's cases (a)-(e). The structure of CaF, and indeed of most diatomic molecules, is well described by Hund's cases (a) and (b).

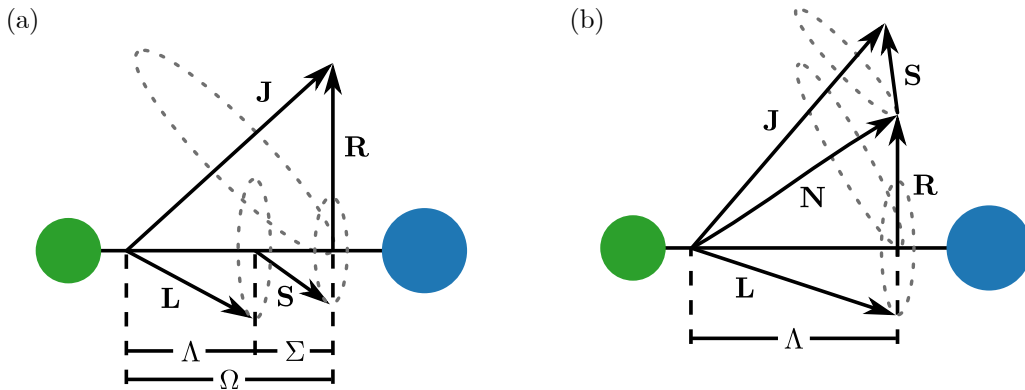


Figure 2.2: Schematics of the coupling schemes in Hund's case (a) and (b), described in the main text

In Hund's case (a), $\mathbf{L}$ is strongly coupled to the inter-nuclear axis by electrostatic forces. The total electronic spin $\mathbf{S}$ is then coupled to $\mathbf{L}$ by the spin-orbit interaction and so is also coupled to the inter-nuclear axis. The electronic motion is weakly coupled to the angular momentum from the molecular rotation $\mathbf{R}$ and so we form the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S} + \mathbf{R}$. In this case, the basis states are $|\Lambda\rangle |S, \Sigma\rangle |J, \Omega\rangle$ which have good quantum numbers defined by

$$\hat{L}_z |\Lambda\rangle = \hbar \Lambda |\Lambda\rangle, \quad (2.14a)$$

$$\hat{\mathbf{S}}^2 |S, \Sigma\rangle = \hbar^2 S(S+1) |S, \Sigma\rangle, \quad (2.14b)$$

$$\hat{S}_z |S, \Sigma\rangle = \hbar \Sigma |S, \Sigma\rangle, \quad (2.14c)$$

$$\hat{\mathbf{J}}^2 |J, \Omega\rangle = \hbar^2 J(J+1) |J, \Omega\rangle, \quad (2.14d)$$

$$\hat{J}_z |J, \Omega\rangle = \hbar \Omega |J, \Omega\rangle. \quad (2.14e)$$

For diatomic molecules, we have the relationship $\Omega = \Lambda + \Sigma$ as $\mathbf{R}$ must be perpendicular to the inter-nuclear axis.

In Hund's case (b), the spin-orbit interaction is weak compared to the rotational energy of the molecule. Thus, although $\mathbf{L}$ is still strongly coupled to the inter-nuclear axis, $\mathbf{S}$ is not and Σ is no longer a good quantum number. Instead, $\mathbf{L}$ first couples to the molecular rotation $\mathbf{R}$ to form $\mathbf{N} = \mathbf{L} + \mathbf{R}$, and then $\mathbf{S}$ couples with $\mathbf{N}$ to form the total angular momentum $\mathbf{J}$. The basis states in this case are $|\Lambda\rangle |N, S, J\rangle$ with good quantum numbers defined by

$$\hat{L}_z |\Lambda\rangle = \hbar \Lambda |\Lambda\rangle, \quad (2.15a)$$

$$\hat{\mathbf{N}}^2 |N, S, J\rangle = \hbar^2 N(N+1) |N, S, J\rangle, \quad (2.15b)$$

$$\hat{\mathbf{S}}^2 |N, S, J\rangle = \hbar^2 S(S+1) |N, S, J\rangle, \quad (2.15c)$$

$$\hat{\mathbf{J}}^2 |N, S, J\rangle = \hbar^2 J(J+1) |N, S, J\rangle. \quad (2.15d)$$

In states with $\Lambda = 0$, there is no spin-orbit interaction and therefore this case is most appropriate.

2.1.3 Structure of CaF

The electronic states of CaF relevant for this work are the ground state $X^2\Sigma^+$, the state $A^2\Pi$ and the state $B^2\Sigma^+$, as shown in figure 2.3.

The state $X^2\Sigma^+$ has $\Lambda = 0$ and so is well-described by Hund's case (b). Since there is no orbital angular momentum $\mathbf{L}$, the total angular momentum is just the sum of the spin and the nuclear angular momenta, so $\mathbf{N} = \mathbf{R}$ and $\mathbf{J} = \mathbf{S} + \mathbf{R}$. Each rotational level with $N > 0$ is split into two components that have $J = N \pm 1/2$, due to the spin-rotation interaction.

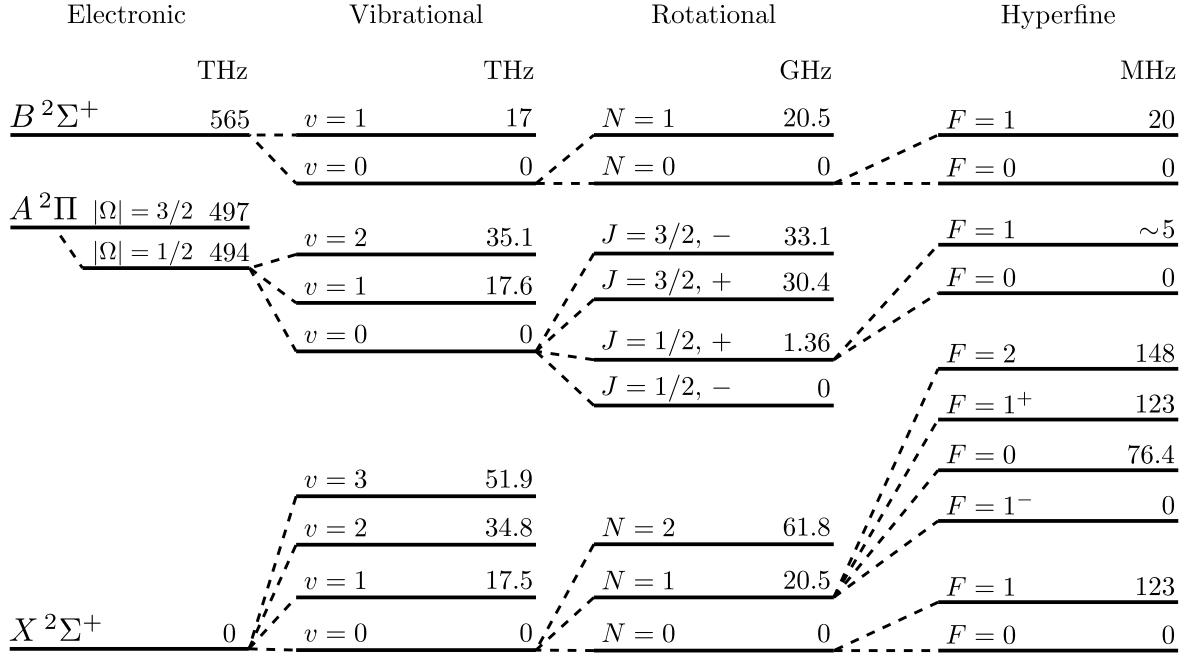


Figure 2.3: Energy level diagram of the $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Pi$ states in CaF, showing the electronic, vibrational, rotational and hyperfine structure of relevant states. At each stage, the sub-levels most relevant to the work in this thesis are selected. The energy of each state is given relative to the lowest energy state in each manifold and expressed in frequency units. The symbols (+/-) show the parity of the rotational levels in the $A^2\Pi_{1/2}$ ($v=0$) state.

The hyperfine interactions further mix these states to produce hyperfine states labelled by F , where $\mathbf{F} = \mathbf{I} + \mathbf{J}$. The calcium nucleus has no total spin and the fluorine nucleus has a spin of $I = 1/2$, giving CaF a total nuclear spin of $I = 1/2$. Both the spin-rotation and hyperfine interactions are of similar strength, and so the energy levels produced by the combination of the two are generally said to form the hyperfine structure. The hyperfine states in the $N = 1$ manifold, which are the ones utilized for laser cooling, are labelled by $F = 1^-, 0, 1^+, 2$, in order of increasing energy. The superscripts $+/-$ are used to distinguish the two levels with $F = 1$, where the $+$ ($-$) denotes the state with higher (lower) energy. The ground rotational state, $N = 0$, is split into two hyperfine states with $F = 0$ and $F = 1$. The parity of each state is determined by the value of N : states with even N have positive parity ($p = +$) and states with odd N have negative parity ($p = -$).

The state $A^2\Pi$ is the first excited electronic state. In this state, the orbital angular momentum is non-zero and the spin-orbit interaction is strong, which makes Hund's case (a) most appropriate. The spin-orbit interaction splits the states into those with $|\Omega| = 1/2$ and those with

$|\Omega| = 3/2$, labelled as $A^2\Pi_{1/2}$ and $A^2\Pi_{3/2}$, respectively. However, both the rotational part and the spin-orbit part of the molecular Hamiltonian cause coupling of these states to the nearby $B^2\Sigma^+$ state [113]. This lifts the degeneracy of states with $\Omega = \pm 1/2$ and $\Omega = \pm 3/2$, splitting them into pairs of states with opposite parity. This effect is known as Λ -doubling. For the rotational level $J = 1/2$, that is most relevant for this work, the state with $p = +$ lies 1.36 GHz above the $p = -$ state [113]. For laser cooling of CaF, we excite the molecule to the positive parity state, which is further split into two hyperfine components with $F = 0$ and $F = 1$. These two states are not well resolved as they are only separated by approximately 5 MHz [114]. The $A^2\Pi$ state decays to the $X^2\Sigma^+$ at a rate $\Gamma = 2\pi \times 8.3$ MHz [114].

The next highest electronically excited state $B^2\Sigma^+$ has a similar structure to the ground state $X^2\Sigma^+$ and so is also best described by Hund's case (b). The states relevant to this work are located in the $N = 0$ manifold, which contains two hyperfine states with $F = 0$ and $F = 1$, separated by 20 MHz [115]. The $B^2\Sigma^+$ state has a decay rate of $\Gamma = 2\pi \times 6.3$ MHz [116] and decays almost entirely to $X^2\Sigma^+$ with the branching ratio to the A state being less than 1×10^{-6} [117].

Transitions

For electric dipole transitions that change the electronic state, the relevant selection rules are

$$\Delta J = 0, \pm 1 \text{ but } J = 0 \nleftrightarrow J' = 0, \quad (\text{SR1})$$

$$p = \pm \leftrightarrow p' = \mp, \quad (\text{SR2})$$

$$\Delta m_F = 0, \pm 1 \text{ but } m_F = 0 \nleftrightarrow m'_F = 0 \text{ if } \Delta F = 0, \quad (\text{SR3})$$

$$\Delta F = 0, \pm 1 \text{ but } F = 0 \nleftrightarrow F' = 0. \quad (\text{SR4})$$

If we consider the decay of state $A^2\Pi_{1/2} (J = 1/2, p = +)$ to states in $X^2\Sigma^+$ and recall that for each value of N there are two spin-rotation components with $J = N \pm 1/2$, rule SR1 restricts the value of $N = 0, 1, 2$. Taking into account the parity rule (SR2) further reduces this to $N = 1$, since this is the only one with negative parity. Therefore, the transition

$A^2\Pi_{1/2}(J = 1/2, p = +) \leftarrow X^2\Sigma^+(N = 1)$ is rotationally closed. The same two selection rules ensure that the transition $B^2\Sigma^+(N = 0) \leftarrow X^2\Sigma^+(N = 1)$ is also rotationally closed.

Since the effective nuclear potential is different for different electronic states, there are no selection rules governing the vibrational quantum numbers in electronic transitions. The branching ratio for transitions from vibrational state ν in the excited state A/B to vibrational state ν' in the ground state X is instead largely determined by the Franck-Condon factors

$$P_{\nu,\nu'}^{A/B} = \left| \int f_{A/B,\nu'}(r) f_{X,\nu}(r) dr \right|^2. \quad (2.17)$$

where $f_{i,\nu}(r)$ is the nuclear vibrational wavefunction within the electronic level $i = X, A, B$, labelled by ν . In order to sufficiently close the transition, it is necessary to use a molecule that has transitions for which the matrix of Franck-Condon factors is highly diagonal so that leakage to other vibrational levels is small. For CaF, the $A \leftarrow X$ and $B \leftarrow X$ transitions are largely associated with excitations of the unpaired electron, which is largely localized around the Ca nucleus. Therefore, the effective nuclear potential is almost identical and the nuclear vibrational wavefunctions are very similar. As a result, the Franck-Condon factors for the $A(\nu' = 0) \leftarrow X(\nu = 0)$ and $B(\nu' = 0) \leftarrow X(\nu = 0)$ transitions given by [118, 119]

$$P_{0,0}^A = 0.964, \quad P_{0,0}^B = 0.999 \quad (2.18)$$

are very close to unity. This means that many photons can be scattered without losing molecules from the cooling cycle and adding vibrational repump lasers can further close the transition, allowing even more photon scattering events.

2.2 The two-level atom interacting with light

To understand the atom-light interaction, we start by considering an atom with a ground level $|g\rangle$ and an excited level $|e\rangle$, separated in energy by $\hbar\omega_0$, interacting with an electric field given

by $\mathbf{E}(t) = \mathcal{E}\hat{\mathbf{e}}\cos(\omega t)$. The Hamiltonian for this system is

$$H = \hbar\omega_0 |e\rangle\langle e| - \mathbf{d} \cdot \mathbf{E}(t), \quad (2.19)$$

where $\mathbf{d}$ is the dipole operator, which has matrix elements

$$\langle g|\mathbf{d}|g\rangle = \langle e|\mathbf{d}|e\rangle = 0, \quad (2.20)$$

$$\langle g|\mathbf{d}|e\rangle = \langle e|\mathbf{d}|g\rangle = \mathbf{d}_{ge}. \quad (2.21)$$

By moving to the rotating frame defined by:

$$|g\rangle \rightarrow |g\rangle, \quad |e\rangle \rightarrow e^{-i\omega t} |e\rangle \quad (2.22)$$

and making the rotating wave approximation, we obtain the transformed Hamiltonian

$$\tilde{H} = -\hbar\Delta |e\rangle\langle e| + \frac{\hbar\Omega}{2}(|g\rangle\langle e| + |e\rangle\langle g|), \quad (2.23)$$

where we have defined the detuning $\Delta = \omega - \omega_0$ and the Rabi frequency $\Omega = -\mathcal{E}(\mathbf{d}_{ge} \cdot \hat{\mathbf{e}})/\hbar$.

If we write the state as

$$|\psi\rangle = c_g(t) |g\rangle + c_e(t) |e\rangle, \quad (2.24)$$

and substitute it into the Schrödinger equation

$$\frac{d}{dt} |\psi\rangle = \frac{1}{i\hbar} \tilde{H} |\psi\rangle, \quad (2.25)$$

we get the coupled differential equations

$$\dot{c}_g(t) = -\frac{i\Omega}{2} c_e(t), \quad (2.26a)$$

$$\dot{c}_e(t) = -\frac{i\Omega}{2} c_g(t) + i\Delta c_e(t). \quad (2.26b)$$

If the atom is initially in the ground state ($c_g(0) = 1, c_e(0) = 0$), then these equations have the

solution

$$c_g(t) = e^{i\Delta t/2} \left[\cos\left(\frac{\bar{\Omega}t}{2}\right) - i\frac{\Delta}{\bar{\Omega}} \sin\left(\frac{\bar{\Omega}t}{2}\right) \right], \quad (2.27a)$$

$$c_e(t) = -ie^{i\Delta t/2} \frac{\Omega}{\bar{\Omega}} \sin\left(\frac{\bar{\Omega}t}{2}\right), \quad (2.27b)$$

where $\bar{\Omega}$ is the modified Rabi frequency given by

$$\bar{\Omega} = \sqrt{\Omega^2 + \Delta^2}. \quad (2.28)$$

The probability of finding the system in the excited state at time t is then

$$P_e(t) = |c_e(t)|^2 = \left(\frac{\Omega}{\bar{\Omega}}\right)^2 \sin^2\left(\frac{\bar{\Omega}t}{2}\right). \quad (2.29)$$

2.2.1 The optical Bloch equations

The time evolution of the density operator $\tilde{\rho}$ is given by

$$\frac{d\tilde{\rho}}{dt} = \frac{1}{i\hbar} [\tilde{H}, \tilde{\rho}] + \left(\frac{d\tilde{\rho}}{dt}\right)_{\text{sp}} \quad (2.30)$$

where the last term describes the effect of spontaneous decay on the system. From this, we obtain the optical Bloch equations given by

$$\frac{d\tilde{\rho}_{ee}}{dt} = \frac{i\Omega}{2}(\tilde{\rho}_{eg} - \tilde{\rho}_{ge}) - \Gamma\tilde{\rho}_{ee}, \quad (2.31)$$

$$\frac{d\tilde{\rho}_{gg}}{dt} = -\frac{i\Omega}{2}(\tilde{\rho}_{eg} - \tilde{\rho}_{ge}) + \Gamma\tilde{\rho}_{ee}, \quad (2.32)$$

$$\frac{d\tilde{\rho}_{ge}}{dt} = -(\Gamma/2 + i\Delta)\tilde{\rho}_{ge} - \frac{i\Omega}{2}(\tilde{\rho}_{ee} - \tilde{\rho}_{gg}), \quad (2.33)$$

$$\frac{d\tilde{\rho}_{eg}}{dt} = -(\Gamma/2 - i\Delta)\tilde{\rho}_{eg} + \frac{i\Omega}{2}(\tilde{\rho}_{ee} - \tilde{\rho}_{gg}), \quad (2.34)$$

where we have defined the spontaneous decay rate $\Gamma = \frac{\omega_0^3}{3\pi\epsilon_0\hbar c^3} |\langle g|\mathbf{d}|e\rangle|^2$. The dissipation due to the spontaneous decay terms means the density matrix will reach a steady state, which we

find by setting $d\rho/dt = 0$, leading to

$$\rho_{ee}^{(ss)} = \frac{\Omega^2}{\Gamma^2 + 2\Omega^2 + 4\Delta^2}, \quad (2.35a)$$

$$\rho_{eg}^{(ss)} = \frac{-i\Omega(\Gamma + 2i\Delta)}{\Gamma^2 + 2\Omega^2 + 4\Delta^2}, \quad (2.35b)$$

$$\rho_{gg}^{(ss)} = 1 - \rho_{ee}^{(ss)}, \quad (2.35c)$$

$$\rho_{ge}^{(ss)} = (\rho_{eg}^{(ss)})^*. \quad (2.35d)$$

We can define dimensionless units

$$s = 2\Omega^2/\Gamma^2, \quad \delta = \Delta/\Gamma \quad (2.36)$$

and write equations 2.35a and 2.35b as

$$\rho_{ee}^{(ss)} = \frac{s}{2(1 + s + 4\delta^2)}, \quad (2.37)$$

$$\rho_{eg}^{(ss)} = \frac{-\sqrt{2s}(1 + 2i\delta)}{2(1 + s + 4\delta^2)}. \quad (2.38)$$

Since the Rabi frequency Ω is proportional to the electric field, the saturation parameter is proportional to the intensity of the radiation and therefore we can write

$$s = I/I_{\text{sat}}, \quad (2.39)$$

where I_{sat} is the saturation intensity given by

$$I_{\text{sat}} = \frac{c\epsilon_0\Gamma^2\hbar^2}{4|\langle g|\mathbf{d} \cdot \hat{\mathbf{e}}|e\rangle|^2}. \quad (2.40)$$

2.2.2 Scattering force

We now consider a two-level system interacting with a plane wave. The electric field is given by $\mathbf{E}(\mathbf{r}, t) = \mathcal{E}\hat{\mathbf{e}}\cos(\mathbf{k} \cdot \mathbf{r} - \omega t)$. Following the same procedure as before we can write the

transformed Hamiltonian as

$$\tilde{H} = -\hbar\Delta |e\rangle\langle e| + \frac{\hbar\Omega}{2}(e^{i\mathbf{k}\cdot\mathbf{r}} |g\rangle\langle e| + e^{-i\mathbf{k}\cdot\mathbf{r}} |e\rangle\langle g|). \quad (2.41)$$

We now introduce the operator for the force on the atom:

$$\hat{\mathbf{F}} = -\nabla\tilde{H} = \frac{i\hbar\mathbf{k}\Omega}{2}(e^{i\mathbf{k}\cdot\mathbf{r}} |g\rangle\langle e| - e^{-i\mathbf{k}\cdot\mathbf{r}} |e\rangle\langle g|). \quad (2.42)$$

By taking the expectation value, we get

$$\mathbf{F} = \langle\hat{\mathbf{F}}\rangle = \frac{i\hbar\mathbf{k}\Omega}{2}(e^{i\mathbf{k}\cdot\mathbf{r}}\tilde{\rho}_{eg} - e^{-i\mathbf{k}\cdot\mathbf{r}}\tilde{\rho}_{ge}). \quad (2.43)$$

If we consider a stationary atom at the origin, we see that the Hamiltonian is identical to that in equation 2.23. As a result, we can use our results from the previous section to evaluate the force on the atom in the steady state:

$$\mathbf{F} = \frac{i\hbar\mathbf{k}\Omega}{2}(\tilde{\rho}_{eg}^{(ss)} - \tilde{\rho}_{ge}^{(ss)}) = \frac{\hbar\Omega^2\Gamma\mathbf{k}}{\Gamma^2 + 2\Omega^2 + 4\Delta^2}. \quad (2.44)$$

This can be written as

$$\mathbf{F} = \frac{s\Gamma\hbar\mathbf{k}}{2(1+s+4\delta^2)} = \tilde{\rho}_{ee}^{(ss)}\Gamma\hbar\mathbf{k}. \quad (2.45)$$

This last expression has a intuitive explanation. By absorbing a photon from the beam and emitting a photon by spontaneous decay, the atom gets a net momentum kick of $\hbar\mathbf{k}$.³ The rate of this scattering is given by:

$$R_{sc} = \tilde{\rho}_{ee}^{(ss)}\Gamma = \frac{\Gamma}{2} \frac{s}{1+s+4\delta^2}. \quad (2.46)$$

The force is the rate of change of momentum which is $R_{sc}\hbar\mathbf{k}$, giving us the same expression as in equation 2.45.

³The spontaneous decay does not contribute as the probability of emission $P(\hat{\mathbf{k}})$ along a particular direction given by the unit vector $\hat{\mathbf{k}}$ has inversion symmetry $P(-\hat{\mathbf{k}}) = P(\hat{\mathbf{k}})$. Thus, the net momentum change is $\int P(\hat{\mathbf{k}})\hat{\mathbf{k}}d\Omega = 0$.

2.3 Doppler cooling

2.3.1 Optical molasses

Consider an atom moving in 1D between two counter-propagating plane waves with equal intensity. In the low-intensity regime and ignoring interference between the two beams, the force on the atom can be written as the sum of the force from each beam:

$$F \approx F_+ + F_- = \frac{s\Gamma\hbar k}{2[1 + s + 4(\delta - kv/\Gamma)^2]} - \frac{s\Gamma\hbar k}{2[1 + s + 4(\delta + kv/\Gamma)^2]}. \quad (2.47)$$

where the terms involving kv have been added to the detuning to account for the Doppler shift due to the motion of the atom at a velocity v . To find the force at low velocities, we can expand equation 2.47 to first order in v to get

$$F \approx \frac{8\hbar k^2 \delta s}{(1 + s + 4\delta^2)^2} v. \quad (2.48)$$

If we choose $\delta < 0$, then we can see that the force acts in the opposing direction to the velocity and will tend to damp the velocity of the atom towards zero. We can write the force as

$$F \approx -\alpha v, \quad (2.49)$$

with the damping constant α given by

$$\alpha = \frac{8\hbar k^2 |\delta| s}{(1 + s + 4\delta^2)^2}. \quad (2.50)$$

This arrangement with counter-propagating beams red-detuned from a transition is known as an optical molasses. This is easily extended to three dimensions with one set of counter-propagating beams along each dimension. In this case, the force can be generalized to

$$\mathbf{F} = -\alpha \mathbf{v}. \quad (2.51)$$

2.3.2 The Doppler limit

Following [120], the minimum temperature achievable by Doppler cooling alone can be determined by considering the change in the mean energy of the atoms due to the cooling force:

$$\left(\frac{dE}{dt}\right)_{\text{cool}} = \langle \mathbf{F} \cdot \mathbf{v} \rangle = -\alpha \langle v^2 \rangle. \quad (2.52)$$

As well as this, scattering of photons by the atom causes random momentum kicks which lead to heating. At zero velocity, the probability of scattering a photon from each beam is the same and so this can be thought of as a random walk in momentum space. Each scattering event consists of an absorption from a random direction and a subsequent emission again in a random direction, therefore this causes the mean square momentum to increase according to:

$$\left(\frac{d\langle p^2 \rangle}{dt}\right)_{\text{heat}} = 2R_{\text{sc}}(\hbar k)^2. \quad (2.53)$$

The increase in energy due to these fluctuations is given by

$$\left(\frac{dE}{dt}\right)_{\text{heat}} = \frac{1}{2m} \left(\frac{d\langle p^2 \rangle}{dt}\right)_{\text{heat}} = \frac{R_{\text{sc}}(\hbar k)^2}{m}. \quad (2.54)$$

At equilibrium, the rate of cooling and the rate of heating should be balanced and so we can set the sum of equations 2.52 and 2.54 to be equal to zero, which gives the following relation:

$$\langle v^2 \rangle = \frac{R_{\text{sc}}(\hbar k)^2}{\alpha m} = \frac{\hbar \Gamma}{2m} \frac{1 + s + 4\delta^2}{8|\delta|}. \quad (2.55)$$

This can be converted to temperature using $T = m\langle v^2 \rangle/k_{\text{B}}$:

$$T_D = \frac{\hbar \Gamma}{2k_{\text{B}}} \frac{1 + s + 4\delta^2}{8|\delta|}. \quad (2.56)$$

So, the temperature of atoms subjected to Doppler cooling is minimized for light with low intensity ($s \rightarrow 0$), detuned by $\Delta = -\Gamma/2$, which gives a minimum temperature of

$$T_{\text{D,min}} = \frac{\hbar \Gamma}{2k_{\text{B}}}. \quad (2.57)$$

Soon after the first demonstration of optical molasses, it was noted that atoms were being cooled to much lower temperatures than $T_{D,\min}$ [121]. This quickly led to the proposal of new so-called sub-Doppler cooling mechanisms and the development of the theory underlying them [122, 123], which will be outlined in section 2.5.

2.4 Magneto-optical trapping

An optical molasses provides a cooling force to the atom but no confining force. In order to add a confining force, the idea of a magneto-optical trap (MOT) was developed [124]. This introduces a spatially-varying magnetic field to the optical molasses. By adjusting the polarization of the light, the atom can be made to preferentially absorb photons from the beam that will force it back to the centre of the trap.

To demonstrate the principle of a MOT in more detail, consider an atom with a ground level with no angular momentum $F = 0$ and an excited level with $F' = 1$, as shown in figure 2.4. The excited level is three-fold degenerate at zero magnetic field. When a magnetic field $\mathcal{B} = \mathcal{B}_z \hat{\mathbf{z}}$ is applied, the excited level splits into its Zeeman sublevels labelled by $m_F = -1, 0, 1$ with energy shifts given by

$$\Delta E = g_F m_F \mu_B \mathcal{B}_z, \quad (2.58)$$

where g_F is the Landé g factor for the $F = 1$ level and we have taken the quantization axis to be fixed in the direction of $\hat{\mathbf{z}}$, regardless of the direction magnetic field. In the MOT, an inhomogeneous magnetic field, $\mathcal{B}(\mathbf{r})$, is applied to the atom so that shift of the Zeeman sublevels varies with position. As before, for simplicity we will take the 1D case as an example and then generalize to 3D. If we take the field to have a zero at the origin, then in the vicinity we can expand the field to first order as

$$\mathcal{B}(z) \approx bz. \quad (2.59)$$

In a similar fashion to the optical molasses, we again have counter-propagating beams that are red-detuned of the transition at zero field but now we choose the beams to be circularly polarized. Taking $b > 0$ as shown in figure 2.4, both beams are right-hand circularly polarized,

so that the beam travelling along the positive z direction drives σ^+ transitions ($\Delta m_F = +1$) and the beam travelling in the negative z direction drives σ^- transitions ($\Delta m_F = -1$).⁴

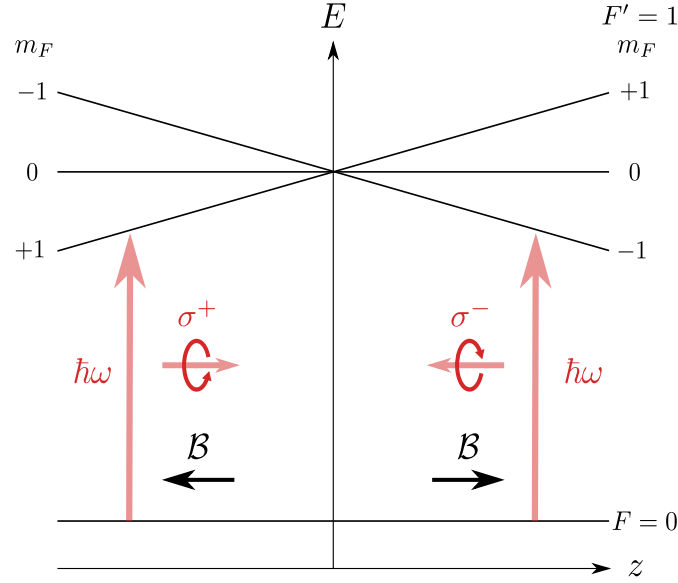


Figure 2.4: Schematic of the MOT mechanism in 1D. The magnetic field $\mathcal{B}$ depends linearly on the position z . The black lines show the energy E of the Zeeman levels of the ground and excited state as a function of z . The counter-propagating light beams, labelled σ^+ and σ^- , have circular polarizations with the correct handedness to drive the transition with $\Delta m_F = +1$ and $\Delta m_F = -1$ respectively. The light in both beams has frequency ω which is red-detuned from the resonance at zero magnetic field.

For an atom at rest at the origin, the net force from the two beams cancel, as they are equally detuned from the transition. If the atom is displaced in the positive z direction, then the $m_F = -1$ state is shifted downwards bringing the transition to this state closer to resonance with the red-detuned light. Only the beam propagating towards $-z$ can drive this transition. Conversely, if the atom is displaced in the negative z direction, the transition to $m_F = +1$ comes closer to resonance and this transition is driven by the beam propagating towards $+z$. As a result, the atom will scatter more photons from the beam propagating in the opposite direction to its displacement, which we will label the restoring beam, and will experience a net force back towards the origin.

The force on the atom in the low intensity regime can be modelled by adding a position

⁴Again, this is with the quantization fixed along $\hat{\mathbf{z}}$. Alternatively, one can take the quantization axis to be along the direction of the local magnetic field. In this case, the Zeeman energy shift is $\Delta E = g_F m_F \mu_B |\mathcal{B}_z|$ and so for negative z in figure 2.4 the Zeeman sublevels would instead be labelled $m_F = +1, 0, -1$ in decreasing energy and the positive z beam would drive σ^- transitions and the negative z beam would drive σ^+ .

dependent term to the detuning of each beam in equation 2.47 due to the Zeeman shift:

$$F \approx \frac{s\Gamma\hbar k}{2[1 + s + 4(\delta - kv/\Gamma - g_F\mu_B bz/\hbar\Gamma)^2]} - \frac{s\Gamma\hbar k}{2[1 + s + 4(\delta + kv/\Gamma + g_F\mu_B bz/\hbar\Gamma)^2]}. \quad (2.60)$$

As above, we can expand this to first order in v and z to find

$$F = -\alpha v - \beta z, \quad (2.61)$$

where

$$\beta = \frac{g_F\mu_B b}{\hbar\Gamma}\alpha. \quad (2.62)$$

The MOT can be straightforwardly extended to 3D by adding two more sets of opposing circularly polarized beams. The magnetic field gradient is often produced using a pair of coils in the anti-Helmholtz configuration, which generates a quadrupole magnetic field. Near the centre of the pair of coils the field can be expanded as:

$$\mathcal{B} = \frac{b}{2} \begin{pmatrix} -x \\ -y \\ 2z \end{pmatrix}. \quad (2.63)$$

Note that the field is cylindrically symmetric around the z axis and the gradient at the centre is twice as large along the z direction as it is in the x and y direction since the field must satisfy $\nabla \cdot \mathcal{B} = 0$.

2.4.1 Adapting the MOT for molecules

The MOT as described in the previous section works well for many atomic species, however, when attempting to apply this to CaF, we run into two problems. Firstly, the excited state ($A^2\Pi_{1/2}$) of the main laser cooling transition in CaF has a very small Zeeman splitting, due to the contributions of the spin and orbital angular momentum to the magnetic moment being almost equal and opposed [125]. If we consider the effect of having no Zeeman splitting in the

excited state on the MOT described in the previous section, we can see that the MOT force disappears in this case. This is because it is precisely the Zeeman splitting that means that photons are preferentially absorbed from the confining beam and not the anti-confining beam. Furthermore, it can be shown more generally that for transitions with any value of F and F' where the Zeeman splitting is small in the excited state, the trapping force will be greatly reduced [126].

In the previous section, we also assumed that the angular momentum for the upper state is larger than that of the ground state ($F' = F + 1$). As a result of this, if the atom is excited by the restoring beam, it will necessarily decay to a state where it can again be excited. This means that many photons can be scattered and the confining force can be very large. MOTs that operate on transitions with $F' = F + 1$ are known as type-I MOTs and make up the vast majority of atomic MOTs including the Rb MOT described in this work.

For CaF, the angular momentum selection rules that are leveraged to rotationally close the transition mean that we will in general be exciting transitions with $F' \leq F$. MOTs that operate on these types of transitions, known as type-II MOTs, have been used to trap atoms [127] but were found to have much weaker confining forces. When the restoring beam excites the molecule on these transitions, it will eventually be pumped into a dark state and will no longer be able to scatter photons from the beam. The molecule will then have to be repumped by the anti-restoring beam or the orthogonal beams and the restoring force will be greatly reduced.

In order to circumvent both these problems, two techniques have been used. The first, known as the dual frequency MOT, adds a second laser frequency blue-detuned of the transition with opposite polarization. An example of the dual-frequency MOT mechanism is shown in figure 2.5a, for a transition with $F = 1$ and $F' = 1$ and no Zeeman splitting in the excited state. If the molecule is in the sublevel $m_F = +1$ then it will scatter photons from the red-detuned restoring beam until it is transferred to the $m_F = -1$ sublevel. In this state the blue-detuned beam will be able to excite the molecule and scatter more photons. Any molecules in the state $m_F = 0$ will be quickly transferred to $m_F = \pm 1$. The presence of the blue-detuned light with

opposite polarization thus destabilizes any dark states. Care must be taken however as the blue-detuned component can also lead to Doppler heating. This can be mitigated by having the red-detuned beam closer to resonance than the blue-detuned beam, in which case Doppler cooling dominates over Doppler heating.

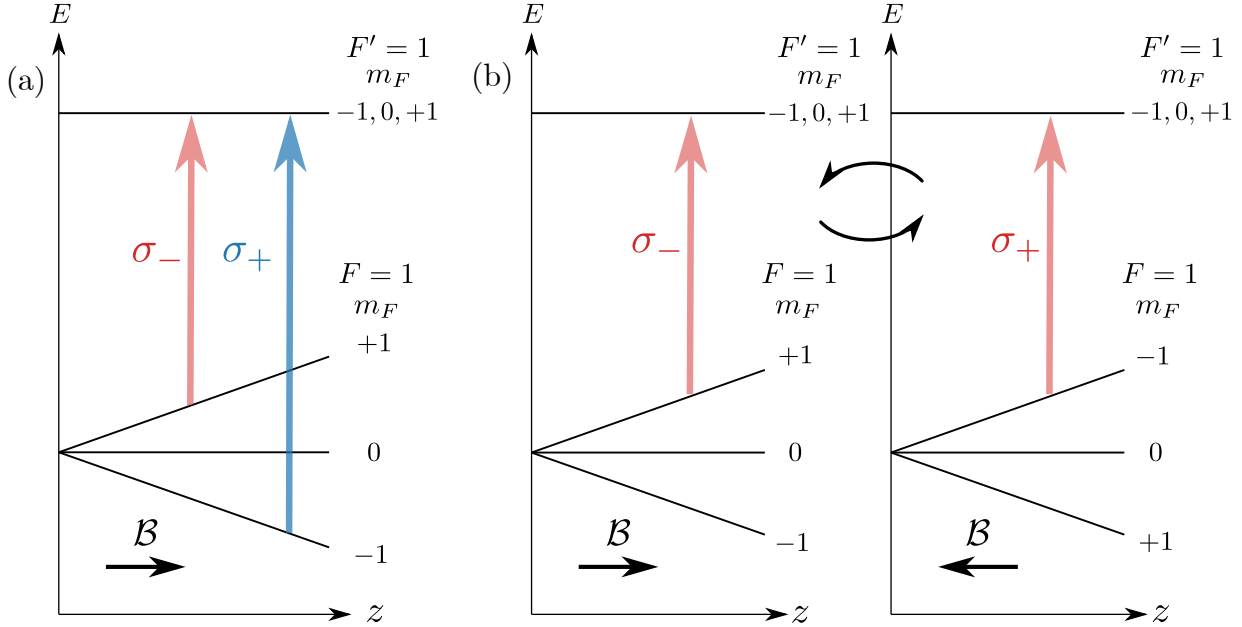


Figure 2.5: Methods of disrupting the dark state in (a) the dual-frequency MOT and (b) the RF MOT on an $F = 1 \rightarrow F' = 1$ transition. In (a), a second blue detuned beam of opposite polarization is added to repump the dark state $m_F = -1$. In (b), the magnetic field $\mathcal{B}$ and the polarization are synchronously reversed at high frequencies, flipping between the two cases shown.

The first molecular MOT in 3D used the dual frequency approach to trap SrF molecules [103]. Following on from this, MOTs of CaF [104, 105, 128] and YO [129] were produced based on the dual-frequency effect. In this work, the dual-frequency MOT is used for confining and cooling CaF molecules.

The second technique is known as the RF MOT. In this case, both the polarization of the beams and the direction of the magnetic field gradient are switched, as shown in figure 2.5b. This must be done fast enough that the molecule does not follow the change in the magnetic field adiabatically but instead remains in the same m_F state (relative to the quantization axis fixed along $\hat{\mathbf{z}}$) when the field reverses.⁵ If a molecule is pumped to the dark state of one polarization,

⁵If the quantization axis is taken to be along the magnetic field, then the molecule must diabatically transfer from m_F to $-m_F$ as the field reverses.

when the polarization is switched it will be able to be excited once more. The magnetic field must be switched simultaneously so that the confining beam is again closer to resonance to provide a net force back to the centre.

The principle of the RF MOT was first demonstrated on a beam of YO molecules, allowing them to be compressed in 2D by magneto-optical forces [102]. It has since been applied in 3D to trap molecules of SrF [130], CaF [105], YO [106], and, more recently, CaOH molecules [107].

2.4.2 Scattering in multi-level systems

In CaF, the ground state has relatively closely spaced hyperfine levels that will all be populated during the cooling cycle. By solving the rate equations for a multi-level system, an expression for an estimate of the scattering rate can be derived [55, 130]. This has the form

$$R_{\text{sc}} = \Gamma \frac{n_g}{(n_g + n_e) + 2 \sum_{j=1}^{n_g} (1 + \Delta_j^2/\Gamma^2) I_{\text{sat},j}/I_j} \quad (2.64)$$

where n_g (n_e) is the number of ground (excited) states, I_j is the intensity of the laser driving the transition from the j th ground state, Δ_j is its detuning from resonance and $I_{\text{sat},j} = \pi \hbar c \Gamma / (3 \lambda_j^3)$ is the saturation intensity of the transition in an equivalent two-level system with wavelength λ_j .

In the CaF MOT detailed in this thesis, the laser driving each transition has the same intensity ($I_j = I/n_g$), each laser is equally detuned from resonance with the transition it is driving ($\Delta_j = \Delta$) and all the lasers are of a similar wavelength so that $I_{\text{sat},j} = I_{\text{sat}}$. In this case, the scattering rate can be rewritten in the same form as the scattering rate of a two-level system

$$R_{\text{sc}} = \frac{\Gamma_{\text{eff}}}{2} \frac{s_{\text{eff}}}{1 + s_{\text{eff}} + 4\delta^2} \quad (2.65)$$

where

$$\Gamma_{\text{eff}} = \frac{2n_e}{n_g + n_e} \Gamma, \quad s_{\text{eff}} = \frac{I}{I_{\text{sat,eff}}} = \frac{2(n_g + n_e)}{n_g^2} \frac{I}{I_{\text{sat}}}. \quad (2.66)$$

For the $A^2\Pi_{1/2}(J = 1/2, p = +) \leftarrow X^2\Sigma^+(N = 1)$ transition, the ground state has $n_g = 24$ sublevels and the excited state has $n_e = 4$ sublevels. This means that the maximum scattering rate is reduced by a factor of $2/7$ and the intensity needed to saturate the transition is increased by a factor of $72/7$, compared to an equivalent two-level system.

2.5 Sub-Doppler cooling

As mentioned in section 2.3.2, atoms in optical molasses routinely reach temperatures well below the Doppler limit. To explain this, two distinct sub-Doppler cooling mechanisms were proposed: Sisyphus cooling and orientation-based cooling [122, 123]. Both schemes share very similar properties. Firstly, they rely on the atom having multiple levels in the ground state. This introduces two new effects, namely optical pumping and differential AC stark shifts, which are essential for both cooling schemes. Secondly, the polarization gradients that result from the interference of cooling beams of different polarization play a vital role. For this reason, both schemes are also referred to more generally as polarization gradient cooling. Both cooling mechanisms are present in the MOT and red-detuned molasses of Rb that is described in this work. In the following section, we will restrict our scope to Sisyphus cooling, as this captures all of the important aspects of polarization gradient cooling.

Polarization gradient cooling was originally applied on transitions of the form $F \rightarrow F' = F + 1$. However, a new method of sub-Doppler cooling was later developed [131, 132] which utilized transitions with $F' \leq F$. For these transitions, there is always at least one dark state formed from a superposition of Zeeman sublevels in the ground state that is decoupled from the field for a fixed polarization, as encountered in the previous section. Under certain conditions, the presence of dark and bright states can be leveraged to provide a sub-Doppler cooling force. Since both dark and bright states are involved, this is known as gray molasses cooling and is used in this work for cooling both CaF molecules and Rb atoms.

2.5.1 AC Stark shifts and polarization gradients

The effect of the AC stark shift on a two level system can be found by diagonalizing the two-level Hamiltonian in equation 2.23. In the presence of the field, the energy eigenstates are found to be

$$|+\rangle = \sin(\theta) |g\rangle + \cos(\theta) |e\rangle, \quad (2.67a)$$

$$|-\rangle = \cos(\theta) |g\rangle - \sin(\theta) |e\rangle, \quad (2.67b)$$

where θ is defined as

$$\tan(2\theta) = -\frac{\Omega}{\Delta} \quad (2.68)$$

for $0 \leq \theta < \pi/2$. These states have well-defined energies given by

$$E_{\pm} = -\frac{\hbar\Delta}{2} \pm \frac{\hbar\sqrt{\Omega^2 + \Delta^2}}{2} = -\frac{\hbar\Delta}{2} \pm \frac{\hbar\bar{\Omega}}{2} \quad (2.69)$$

In the limit where $\Omega/\Delta \ll 1$ we can expand $\bar{\Omega}$ as

$$\bar{\Omega} \approx \Delta \left(1 + \frac{\Omega^2}{2\Delta^2} \right) \quad (2.70)$$

so the energies of the two states become

$$E_- = \frac{\hbar\Omega^2}{4\Delta}, \quad E_+ = -\hbar\Delta - \frac{\hbar\Omega^2}{4\Delta}. \quad (2.71)$$

In the limit of zero field, $|-\rangle$ adiabatically connects to the ground state and $|+\rangle$ connects to the excited states and so we can consider the effect of the field is to introduce equal but opposite AC stark shifts to the ground and excited states given by

$$\Delta E_g = \frac{\hbar\Omega^2}{4\Delta}, \quad \Delta E_e = -\frac{\hbar\Omega^2}{4\Delta}. \quad (2.72)$$

The AC Stark shift is proportional to the intensity of the light but also depends on its polarization via the Rabi frequency. If the intensity or polarization of the light varies in space,

then there can be a spatial dependence of the AC Stark shift and a force can be exerted on the atom, known as the dipole force. It is this force that is exploited in Sisyphus and gray molasses cooling.

This result can be extended to atoms with multiple Zeeman sublevels in the ground state. In this case, each sublevel will still be shifted in energy by an amount proportional to the intensity of the light. However, for a given polarization, the sublevels will not couple equally well to the light, resulting in different AC stark shifts. These differential AC stark shifts are essential for both Sisyphus and gray molasses cooling.

2.5.2 Sisyphus cooling

The origin of the damping force in Sisyphus cooling can best be understood by taking the example of an atom with a ground state with angular momentum $F = 1/2$ and an excited state with angular momentum $F' = 3/2$. The atom moves in one dimension along the direction of two counter-propagating beams that are linearly polarized at right angles to each other (known as $\text{lin}\perp\text{lin}$). The interference between the two beams causes the polarization to vary in space periodically, from one handedness of circular polarization to the other and back again over a period of $\lambda/2$ where λ is the wavelength of the light.

If the atom is in the region where the polarization drives only σ_+ transitions, it is clear from figure 2.6a, that it will be pumped to the $m_F = +1/2$ level in the ground state. Because it has a larger Clebsch-Gordon coefficient, this state couples more strongly to this polarization than $m_F = -1/2$, and so the AC stark shift will be larger for $m_F = +1/2$ than for $m_F = -1/2$. Thus, the atom will be pumped into the state with the larger AC stark shift and the same is true for light driving σ_- transitions. For red-detuned light ($\Delta < 0$), the AC stark shift is negative and this means that the atom is always preferentially pumped to the state with lower energy.

Now consider an atom moving slowly through the changing polarization gradient, as illustrated in figure 2.6b. The atom starts in the $m_F = +1/2$ level in the ground state, having been optically

pumped there. As the atom moves, the changing polarization means it will be travelling up a potential hill and so its kinetic energy will be transferred to potential energy by the dipole force. At the top of the potential hill the polarization will change to σ_- . At this point the atom will be optically pumped to the state $m_F = -1/2$ and so be transferred again to the bottom of the potential hill and the process continues. The potential energy is dissipated due to the difference in energy between the absorbed and emitted photon. In this way, the atom will gradually lose kinetic energy and be cooled.

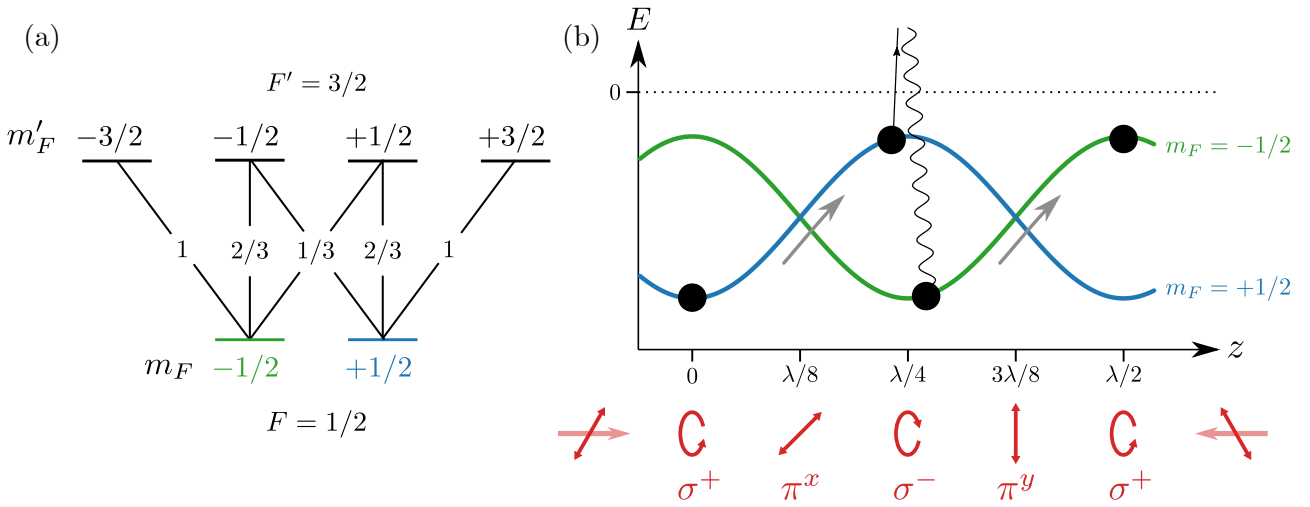


Figure 2.6: Sisyphus cooling: (a) Zeeman structure of an atom with a ground state with angular momentum $F = 1/2$ and an excited state with angular momentum $F' = 3/2$. The relative strength of each transition is given. (b) The two solid lines show how the energy of the $m_F = -1/2$ (green) and $m_F = +1/2$ (blue) states varies due to the AC Stark shift in a standing wave formed by two red-detuned beams with orthogonal linear polarizations at $\pm 45^\circ$ to the x axis. The red arrows show how the resultant polarization varies along the standing wave. The black circles show an example trajectory of an atom, which illustrates the Sisyphus cooling mechanism explained in the main text.

This simple model demonstrates the origin of the mechanism, but, in reality, the optical pumping does not happen instantaneously at the top of the potential hill as described. Instead, it happens gradually with a rate that is proportional to the scattering rate

$$\Gamma_p \propto R_{sc}. \quad (2.73)$$

The rate of optical pumping can be compared to the rate at which the polarization of the light

changes as the atom moves through the light field given by

$$\Gamma_1 \propto kv. \quad (2.74)$$

Sisyphus cooling works best when these two rates are roughly equal, thus we can define a critical velocity for Sisyphus cooling given by

$$v_c \approx R_{\text{sc}}/k. \quad (2.75)$$

For high velocities ($v \gg v_c$), the polarization changes too rapidly and there is not enough time for the atom to be sufficiently optically pumped to the lower state before the polarization changes and the cooling becomes inefficient. For low velocities ($v \ll v_c$), the polarization changes slowly and the optical pumping happens while the atom is climbing the hill instead of at the top of it so the cooling force is reduced.

At low velocities, we can assume the damping force is linear so $F = -\alpha v$. We can derive an order of magnitude estimate of the damping coefficient of Sisyphus cooling, based on simple arguments. As before the cooling power of a linear damping force is given by

$$\frac{dE}{dt} \sim -\alpha v^2. \quad (2.76)$$

From our simple model, when the atom is optically pumped it loses an amount of energy proportional to the Stark shift ΔE_g and this happens at a rate proportional to R_{sc} . Thus, the cooling power can be written as

$$\frac{dE}{dt} \sim -R_{\text{sc}} \Delta E_g. \quad (2.77)$$

The cooling is most effective when $v \approx v_c$ and so combining this with equations 2.75 to 2.77, we can estimate

$$\alpha \sim \frac{k^2 \Delta E_g}{R_{\text{sc}}} \quad (2.78)$$

In the limit of large detuning ($\delta \gg 1$) and small intensity ($s \ll 1$), this can be simplified further

since

$$\Delta E_g \sim \hbar \Gamma \frac{s}{|\delta|}, \quad (2.79a)$$

$$R_{sc} \sim \Gamma \frac{s}{\delta^2}, \quad (2.79b)$$

and so

$$\alpha \sim \hbar k^2 |\delta|. \quad (2.80)$$

A more in-depth analysis [122] shows that this is indeed the form of the damping coefficient at low velocities. This raises two important points. Firstly, if we compare this expression to the damping coefficient for Doppler cooling under optimum conditions

$$\alpha = \hbar k^2 s, \quad (2.81)$$

it is clear that the damping due to the Sisyphus cooling can be substantial compared to that of the Doppler force at large detunings and low intensities. However, it should be noted that the critical velocity scales according to

$$v \sim \frac{\Gamma s}{k \delta^2} \quad (2.82)$$

and so, in this regime, the range of velocities over which the Sisyphus force is effective becomes very small.

Secondly, the damping coefficient is independent of intensity and proportional to the detuning but the heating rate from scattering is proportional to intensity and inversely proportional to the detuning in this regime. Thus, by reducing the intensity and increasing the detuning, it seems this mechanism would allow cooling to arbitrarily low temperatures.

There is a natural limit to the cooling, however. Our treatment relies on the ability to treat the motion of the atom classically. For a small enough velocity, the atom becomes sufficiently delocalized that it becomes necessary to quantize the motion. This is important when the de Broglie wavelength of the atom $\lambda' = \frac{h}{mv}$ approaches the wavelength of the light λ , which is true

for velocities on the order of the recoil velocity

$$v_r \sim \frac{\hbar k}{m}. \quad (2.83)$$

This corresponds to a temperature given by

$$T_r = \frac{\hbar^2 k^2}{2mk_B}, \quad (2.84)$$

known as the recoil temperature.

2.5.3 Gray molasses cooling

To illustrate the mechanism of gray molasses cooling, we consider an atom moving through a light field with varying intensity and polarization. The light addresses a transition with $F' \leq F$ so there will be at least one dark state and one bright state but we consider only one of each for simplicity. The bright state will experience an AC Stark shift in the light field that depends on the position of the atom. As shown in figure 2.7a, for blue-detuned light ($\delta > 0$), the bright state ($|b\rangle$) sits at higher energy than the dark state ($|d\rangle$), which is completely decoupled from the field and so has no AC stark shift. The bright state will have its maximum energy where intensity is highest, which is also where the rate of optical pumping to the dark state is maximized. Thus, an atom that has climbed to the top of a potential hill is more likely to be optically pumped to the dark state. The kinetic energy of the atom that was transferred to potential energy by climbing the hill is then lost during the transfer to the dark state and so the atom is cooled.

Once in the dark state, however, the atom needs to be transferred back into the bright state for the cooling to continue. Since the polarization of the light field varies in space, the make-up of the dark state varies as well. An atom that is moving very slowly through the field will adiabatically follow the dark state but, for finite velocities, there is a chance that the atom will

make a non-adiabatic transition to the bright state with probability [133]:

$$P_{d \rightarrow b} \approx \left| \frac{\hbar v \langle d | \frac{d}{dz} | b \rangle}{E_b - E_d} \right|^2. \quad (2.85)$$

where E_b and E_d are the energies of the bright and dark state respectively. Thus, the transition back to the bright state is most likely wherever the energy difference between the dark and bright states is smallest, which occurs at the regions of lowest intensity. For $\delta > 0$, this corresponds to the bottom of a potential valley in the bright state. So, after the transition the atom can then ride up another potential hill and the cooling process continues.

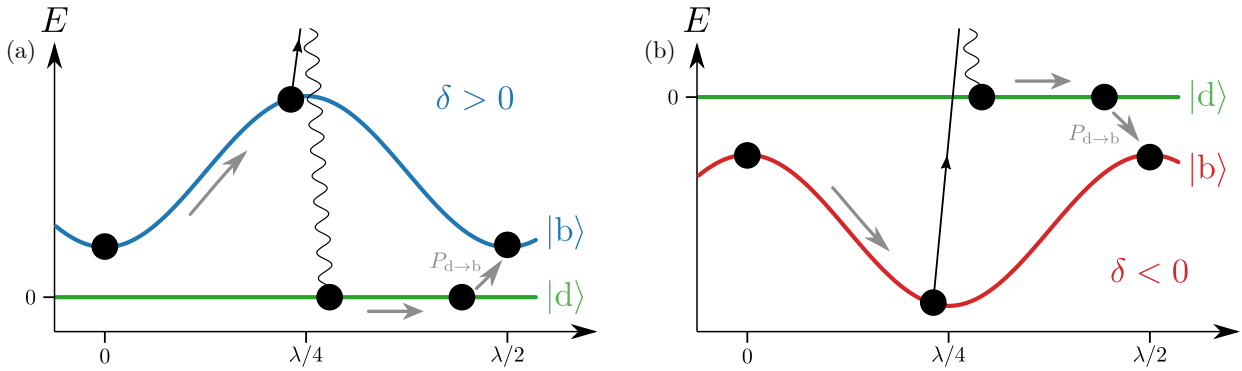


Figure 2.7: (a) Gray molasses cooling: the solid line shows the AC Stark shift of the bright state (blue) and the dark state (green) in a blue-detuned light field with varying polarization and intensity. The atom rides up the potential hill in the bright state, losing kinetic energy before being optically pumped to the dark state. The atom is non-adiabatically transferred back to the bright state with a probability $P_{d \rightarrow b}$ that is largest when the two states are closest in energy. (b) Heating due to a similar mechanism at red detuning. The atom rides down a potential hill before being optically pumped preferentially at the bottom of a potential valley. The non-adiabatic transitions occur from the dark state to the bright state near the top of a potential hill and so the atoms will be heated.

If the light is red-detuned from resonance ($\delta < 0$), the bright state sits below the dark state. In this arrangement, shown in figure 2.7b, the atom will ride down a potential hill before being optically pumped preferentially at the bottom of a potential valley. The non-adiabatic transitions occur from the dark state to the bright state near the top of a potential hill and so the atoms will be heated.

It is clear, then, that gray molasses cooling has the opposite detuning dependence than Doppler cooling and there will always be competition between these two forces. For red-detuned light, Doppler cooling dominates at high velocities but is outweighed by sub-Doppler heating at low

velocities [134]. This is exactly the situation in molecular MOTs and leads to temperatures that are generally higher than those of conventional atomic MOTs [135].

2.6 Ultracold collisions

In this section, the theory of scattering at low temperatures will be briefly summarised.

2.6.1 Elastic scattering of distinguishable particles

We consider two distinguishable particles with no internal structure located at $\mathbf{r}_1$ and $\mathbf{r}_2$ that interact via a potential $V(\mathbf{r})$ that only depends on their displacement $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$. By ignoring the centre-of-mass motion and working in the centre-of-mass frame, the wavefunction of the two particles is given by the solution to the Schrödinger equation

$$\hat{H}\psi(\mathbf{r}) = \left[\frac{\hat{\mathbf{p}}^2}{2\mu} + V(\mathbf{r}) \right] \psi(\mathbf{r}) = E\psi(\mathbf{r}). \quad (2.86)$$

where $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass of the two particles with masses m_1 and m_2 and $\hat{\mathbf{p}}$ is the momentum operator corresponding to $\mathbf{r}$. The kinetic energy operator can be expanded as

$$\frac{\hat{\mathbf{p}}^2}{2\mu} = \frac{\hat{p}_r^2}{2\mu} + \frac{\hat{\mathbf{L}}^2}{2\mu r^2}, \quad (2.87)$$

where $\hat{p}_r$ is the radial momentum operator and $\hat{\mathbf{L}}$ is the angular momentum operator.

If we assume the potential between the two atoms is isotropic ($V(\mathbf{r}) = V(r)$), then the Hamiltonian $\hat{H}$ commutes with both $\hat{\mathbf{L}}^2$ and $\hat{L}_z$. The eigenstates of $\hat{H}$ can therefore be written as

$$\psi_{LM}(r, \theta, \phi) = \frac{R_L(r)}{r} Y_{LM}(\theta, \phi). \quad (2.88)$$

Here, $Y_{LM}(\theta, \phi)$ are the spherical harmonics which are eigenstates of $\hat{\mathbf{L}}^2$ and $\hat{L}_z$

$$\hat{\mathbf{L}}^2 Y_{LM}(\theta, \phi) = \hbar^2 L(L+1) Y_{LM}(\theta, \phi), \quad \hat{L}_z Y_{LM}(\theta, \phi) = \hbar M Y_{LM}(\theta, \phi), \quad (2.89)$$

and $R_L(r)$ are solutions to the equation

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + V_{\text{eff}}(r) \right] R_L(r) = ER_L(r). \quad (2.90)$$

Thus, we have reduced the problem to a 1D Schrödinger equation with an effective potential given by

$$V_{\text{eff}}(r) = V(r) + \frac{\hbar^2 L(L+1)}{2\mu r^2}. \quad (2.91)$$

For $L > 0$, we see that there is a term added to the potential, which causes a so-called centrifugal barrier that increases with higher values of L .

As the separation between the particles increases towards infinity, the interaction potential must decrease towards zero. Therefore, if the particles approach each other with well-defined momentum $\hbar k$, the radial wavefunctions must be the sum of plane waves, which we write as

$$R_L(r) \rightarrow e^{2i\delta_L(k)} e^{ikr} + (-1)^{L+1} e^{-ikr} \quad \text{as } r \rightarrow \infty, \quad (2.92)$$

where $\delta_L(k)$ is the scattering phase shift. The wavefunction can be decomposed into a sum over the eigenstates of $\hat{H}$ as

$$\psi_k(r, \theta, \phi) = \sum_{LM} c_{LM} \frac{R_L(r)}{r} Y_{LM}(\theta, \phi). \quad (2.93)$$

In the limit of $r \rightarrow \infty$, we can also write the wavefunction as a sum of incident and scattered waves. Taking the momentum to be along the z axis, this has the form

$$\psi_k(r, \theta, \phi) = e^{ikr \cos \theta} + f(k, \theta, \phi) \frac{e^{ikr}}{r}. \quad (2.94)$$

The elastic scattering cross-section is then given by

$$\sigma_{\text{el}}(k) = \int |f(k, \theta, \phi)|^2 d\Omega, \quad (2.95)$$

where $d\Omega$ is the element of solid angle in the direction defined by θ and ϕ .

By applying a partial wave expansion, the elastic scattering cross-section can be broken down

into a sum

$$\sigma_{\text{el}}(k) = \sum_L \sigma_L(k), \quad (2.96)$$

where terms in the sum can be shown to be related to the scattering phase shifts by the expression

$$\sigma_L(k) = \frac{4\pi}{k^2} (2L + 1) \sin^2 \delta_L(k). \quad (2.97)$$

The s-wave regime

If the energy of the colliding particles is very low, then the centrifugal barrier will prevent particles with $L > 0$ from reaching the region where they will be significantly affected by the potential. In this case, only the part of the wavefunction with $L = 0$ will contribute to the scattering and the sum will reduce to a single term

$$\sigma_{\text{el}}(k) = \frac{4\pi}{k^2} \sin^2 \delta_0(k). \quad (2.98)$$

By solving the Schrödinger equation for $k \rightarrow 0$, it can be shown [136] that at very low energies this becomes independent of k and can be written as

$$\sigma_{\text{el}}(k \rightarrow 0) = 4\pi a^2, \quad (2.99)$$

and so the elastic scattering cross section is determined wholly by the the scattering length a defined by

$$\lim_{k \rightarrow 0} k \cot \delta_0(k) = -\frac{1}{a}. \quad (2.100)$$

This is known as the s-wave regime.

For Rb atoms colliding with CaF molecules, the long range part of the potential can be approximated by a van der Waals type interaction

$$V(r) \approx -\frac{C_6}{r^6}. \quad (2.101)$$

By finding the maximum of $V_{\text{eff}}(r)$, it can be shown that the height of the centrifugal barrier in this case is given by

$$E_L^b = \frac{2}{C_6^{1/2}} \left(\frac{\hbar^2 L(L+1)}{6\mu} \right)^{3/2}. \quad (2.102)$$

Using the estimated value of $C_6 = 3084 E_h a_0^6$ for the interaction between an Rb atom and CaF molecule found in [137], the height of the potential barrier for $L = 1$ can be found to be $E_1^b/k_B \approx 134 \mu\text{K}$. At temperatures below this, the scattering cross section is dominated by s-wave scattering.

Gribakin and Flambaum [138] show that the scattering length for this potential can be well approximated by

$$a = \bar{a} \left[1 - \tan \left(\Phi - \frac{\pi}{8} \right) \right]. \quad (2.103)$$

Here, $\bar{a}$ is the mean scattering length given by

$$\bar{a} = \left(\frac{2\mu C_6}{\hbar^2} \right)^{1/4} \times 0.477988... \quad (2.104)$$

and Φ is a phase found from the WKB integral

$$\Phi = \int_{r_0}^{\infty} \sqrt{\frac{2\mu V(r)}{\hbar^2}} dr, \quad (2.105)$$

where r_0 is the position of the classical inner turning point in the potential $V(r)$. For the CaF-Rb system, the mean scattering length is $35.7 \text{ \AA}$ [137].

From equation 2.103, it is clear for values of Φ given by

$$\Phi = \frac{5\pi}{8} + n\pi, \quad n = 1, 2, 3..., \quad (2.106)$$

the scattering length diverges. This corresponds to the appearance of a new bound state at the threshold of the potential well, leading to a scattering resonance. Furthermore, the scattering length as a function of Φ is periodic with a period of π and varies between negative and positive infinity between these divergences. As a result, the scattering length can be seen to depend sensitively on the energy of the last bound state. This is very hard to predict from ab initio

models and thus experimental data is needed to steer theoretical calculations of scattering properties.

2.6.2 Elastic scattering of indistinguishable particles

For elastic collisions involving indistinguishable particles, the scattering properties depend on whether the particles are bosons or fermions. The Pauli exclusion principle demands that the two-particle wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ be symmetric under exchange of the two particles for identical bosons and anti-symmetric for identical fermions. Thus, we must have

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \pm \Psi(\mathbf{r}_2, \mathbf{r}_1), \quad (2.107)$$

where the upper sign corresponds to bosons and the lower sign to fermions.

In the centre-of-mass frame, exchange of the two particles is equivalent to the transformation

$$\mathbf{r} \rightarrow -\mathbf{r}. \quad (2.108)$$

Therefore we must demand that

$$\psi(\mathbf{r}) = \pm \psi(-\mathbf{r}). \quad (2.109)$$

In spherical coordinates, this becomes

$$\psi(r, \theta, \phi) = \pm \psi(r, \pi - \theta, \phi + \pi). \quad (2.110)$$

It follows from the definition of the spherical harmonics [139] that

$$Y_{LM}(\pi - \theta, \phi + \pi) = (-1)^L Y_{LM}(\theta, \phi). \quad (2.111)$$

Thus, in equation 2.93 for identical bosons only terms with even L contribute to sum, whereas for identical fermions only the terms with odd L contribute.

Applying the same symmetry considerations, the asymptotic wavefunction defined in equation 2.94 must be rewritten as

$$\psi_k(r, \theta, \phi) = \frac{1}{\sqrt{2}} (e^{ikr \cos \theta} \pm e^{-ikr \cos \theta}) + \frac{1}{\sqrt{2}} [f(k, \theta, \phi) \pm f(k, \pi - \theta, \phi + \pi)] \frac{e^{ikr}}{r}, \quad (2.112)$$

and so the elastic scattering cross-section becomes

$$\sigma_{\text{el}}(k) = \frac{1}{2} \int |f(k, \theta, \phi) + f(k, \pi - \theta, \phi + \pi)|^2 d\Omega. \quad (2.113)$$

After applying the partial wave expansion, the elastic scattering cross-section can then be written as

$$\sigma_{\text{el}}(k) = \sum_{\text{even } L} \sigma_L(k) \quad (2.114)$$

for identical bosons and

$$\sigma_{\text{el}}(k) = \sum_{\text{odd } L} \sigma_L(k) \quad (2.115)$$

for identical fermions, where

$$\sigma_L(k) = \frac{8\pi}{k^2} (2L + 1) \sin^2 \delta_L(k). \quad (2.116)$$

Thus, in the s-wave regime the elastic cross-section for collisions between identical fermions will vanish at low temperatures, as the first partial wave to contribute is the p-wave. However, for identical bosons, such as ^{87}Rb atoms prepared in the same state, the elastic cross-section is given by

$$\sigma_{\text{el}}(k) = \frac{8\pi}{k^2} \sin^2 \delta_0(k), \quad (2.117)$$

which, in the limit, $k \rightarrow 0$ tends to

$$\sigma_{\text{el}}(k \rightarrow 0) = 8\pi a^2. \quad (2.118)$$

2.6.3 Inelastic and reactive collisions

In addition to elastic collisions, atoms and molecules can undergo inelastic and reactive collisions. In inelastic collisions, the internal states of the colliding particles can change, releasing or absorbing energy. This can cause loss from a trap if the energy liberated during the collision is large enough or if the particle is transferred to a state that is not confined by the trap. For atoms or molecules prepared in their absolute ground state, inelastic collisions are greatly suppressed at ultracold temperatures due to the conservation of energy.

Reactive collisions are those that change the chemical make up of the colliding particles. For instance, in a collision between a CaF molecule and a Rb atom, the reactions $\text{CaF} + \text{Rb} \rightarrow \text{Ca} + \text{RbF}$ or $\text{CaF} + \text{Rb} \rightarrow \text{CaRb} + \text{F}$ can take place. Both these reactions are endothermic, requiring 0.53 eV [140] and 5.32 eV [141] of additional energy, respectively. At ultracold temperatures, this is far above the total kinetic energy of the two collision partners and so reactive collisions between CaF and Rb are not energetically allowed.

For collisions between CaF molecules, the situation is quite different as the reaction $\text{CaF} + \text{CaF} \rightarrow \text{CaF}_2 + \text{Ca}$ is barrierless and exothermic releasing 0.53 eV of energy [142]. Thus, reactive collisions can lead to loss even when the molecules are prepared in the ground state.

As we reach higher densities in our experiment, it may become necessary to avoid the loss due to these reactive collisions. For this purpose, techniques for shielding the CaF molecules reactive and inelastic collisions have been investigated using microwaves [143] and DC electric fields [144]. Microwave shielding was successfully used by Anderegg et al. to reduce the loss rate of CaF molecules in merged optical tweezers by a factor of 6 [73].

At very high densities, losses via three-body collisions start to become non-negligible. In our experiment, the densities of CaF molecules currently obtained are relatively low and so three-body loss does not need to be considered. For Rb atoms prepared in the ground state, the three-body loss rate coefficient for thermal clouds has been measured to be $L_3 = (4.3 \pm 1.8) \times 10^{-29} \text{ cm}^6 \text{ s}^{-1}$ [145]. This means that, except for the densest clouds of Rb trapped in the dipole and optical lattice in chapters 6 and 7, three-body loss of Rb atoms can be neglected.

Chapter 3

Experimental setup

3.1 Introduction

In this chapter, the apparatus used for all the experiments detailed in later chapters will be presented. An overview of the experiment is shown in figure 3.1. A cold molecular beam of CaF is produced from a cryogenic buffer gas source in the source chamber. The beam initially travels towards the main chamber with a mean forward velocity of around 140 m s^{-1} but is subsequently decelerated by radiation pressure from a counter-propagating laser beam that addresses the $B \leftarrow X$ transition. This slows some of the molecules to velocities low enough to be captured in a MOT in the main chamber.

Attached to the main chamber is a small glass cell, in which a 2D MOT of Rb atoms is formed. A push beam is then used to load the atoms from the 2D MOT into the main chamber, where they are captured in a 3D MOT. Both the atoms and molecules can be loaded into a translatable magnetic trap, which allows them to be transferred to the tweezer chamber. The tweezer chamber was not used for any experiments in this thesis, but work is underway to capture molecules and atoms in optical tweezers in this chamber in future.

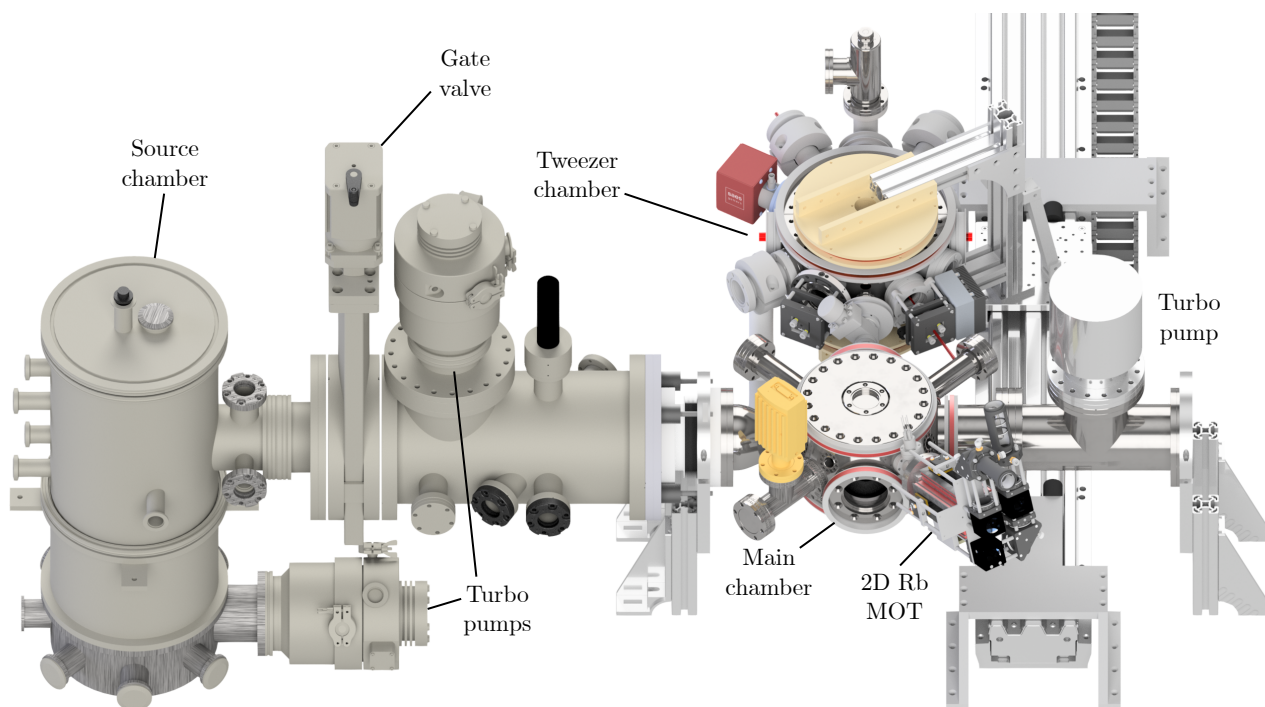


Figure 3.1: Overview of the experiment

3.2 Molecular source

The cryogenic buffer gas source is presented in detail in [146] and so is only briefly summarised here. CaF molecules are produced inside a copper cell, shown in figure 3.2. The cell sits atop a cold head, which is cooled to 4 K by a two-stage cryocooler. A rod of calcium is mounted inside the cell and two inlets allow cold helium and room temperature SF_6 to flow into the cell. The flow rates of the helium and SF_6 are controlled by two flow controllers and are usually maintained at 0.3 sccm and 0.05 sccm, respectively. The capillary through which the SF_6 flows is insulated from the rest of the cell by a small Vespel spacer to prevent the SF_6 from freezing within the capillary.¹

The process of forming a cold molecular beam is started by ablating the calcium rod with a laser pulse from a Nd:YAG laser. This releases calcium atoms into the cell, which react with the SF_6 gas to produce molecules of CaF . The molecules then thermalize with the cold helium and exit the cell through a 3 mm aperture. The calcium rod can be rotated using a vacuum feedthrough, which allows new areas of the rod to be exposed to the laser ablation.

¹The melting point of SF_6 is around 222 K at 1 atmosphere.

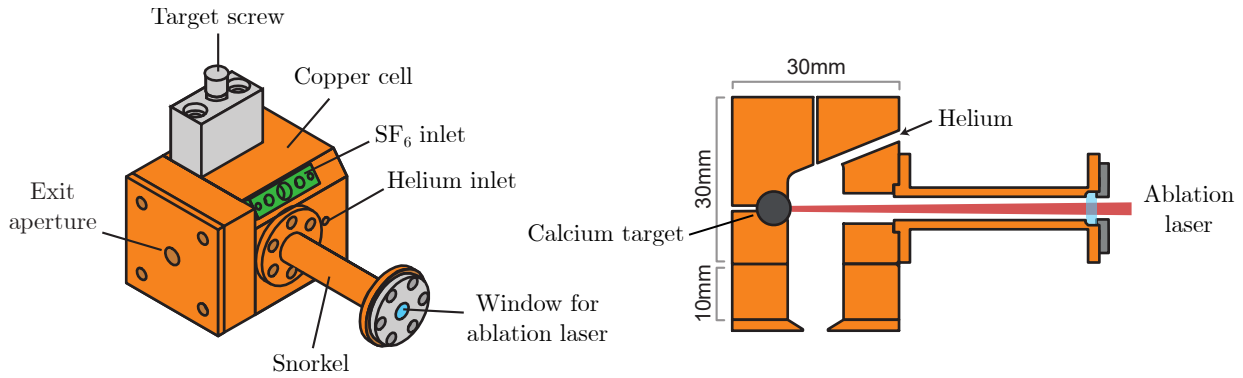


Figure 3.2: Schematic of buffer gas cell (left) and horizontal cross section (right). Adapted from [146].

The cell is almost entirely surrounded by a copper cylinder that is also bolted to the cryostat. The entire inside surface of the cylinder is coated with coconut charcoal, which acts as an efficient cryopump of helium when cooled to temperatures below 8 K [147]. This reduces the background pressure of helium in the source chamber. During normal experimental operation, the pressure in the source chamber rises to about 2×10^{-7} mbar.

The copper cylinder is enclosed by an aluminium radiation shield connected to the 40 K stage of the cryocooler, which reduces the radiative heat load onto the 4 K cold head. In both the copper cylinder and the radiation shield, there is a circular cut-out that is aligned with the cell aperture, allowing the molecules to pass through. The molecules exit the source chamber into the slowing chamber through an in-vacuum shutter (Uniblitz LS6S2Z0-EC-105), at a distance of 35 cm from the cell exit aperture. After the pulse of CaF molecules passes through, the shutter is closed to stop helium flowing into the rest of the vacuum system.

Over the course of a day, the performance of the source gradually declines. The source signal can be restored to its original level by heating the source to room temperature before cooling it down again. This is done by turning off the cryocooler and switching on a heater mounted on the cold head. When the source temperature increases by a few Kelvin, the pressure rises sharply to around 0.1 mbar due to the release of helium adsorbed by the charcoal. To ensure consistent performance, the temperature of the source must be increased further to around room temperature. This might be due to the accumulation of frozen SF₆ in the cell, which impedes thermalization of the helium with the cell wall.

3.3 Lasers

The experiment requires many lasers, each of which must be stabilized to an external frequency reference. For the slowing and cooling of CaF, light with five different wavelengths is required. On top of this, frequency sidebands must be added to address the hyperfine structure of the molecule. As discussed in section 2.1.1, only two lasers are needed for laser cooling of Rb and light for other purposes, such as optical pumping, is then derived from these two lasers.

3.3.1 CaF

The relevant transitions for slowing and cooling CaF are shown in figure 3.3. The main lasers used are $\mathcal{L}_{00}^S$ for slowing and $\mathcal{L}_{00}^C$ for cooling in the MOT. The other lasers are for repumping the leaks to other vibrational levels in the ground state. For the slowing, only one vibrational repumper ($\mathcal{L}_{10}^S$) is required, but for the MOT three repumpers are needed ($\mathcal{L}_{10}^C$, $\mathcal{L}_{21}$, and $\mathcal{L}_{32}$). The two $v = 1$ vibrational repumpers ($\mathcal{L}_{10}^C$ and $\mathcal{L}_{10}^S$) are both derived from the same laser.

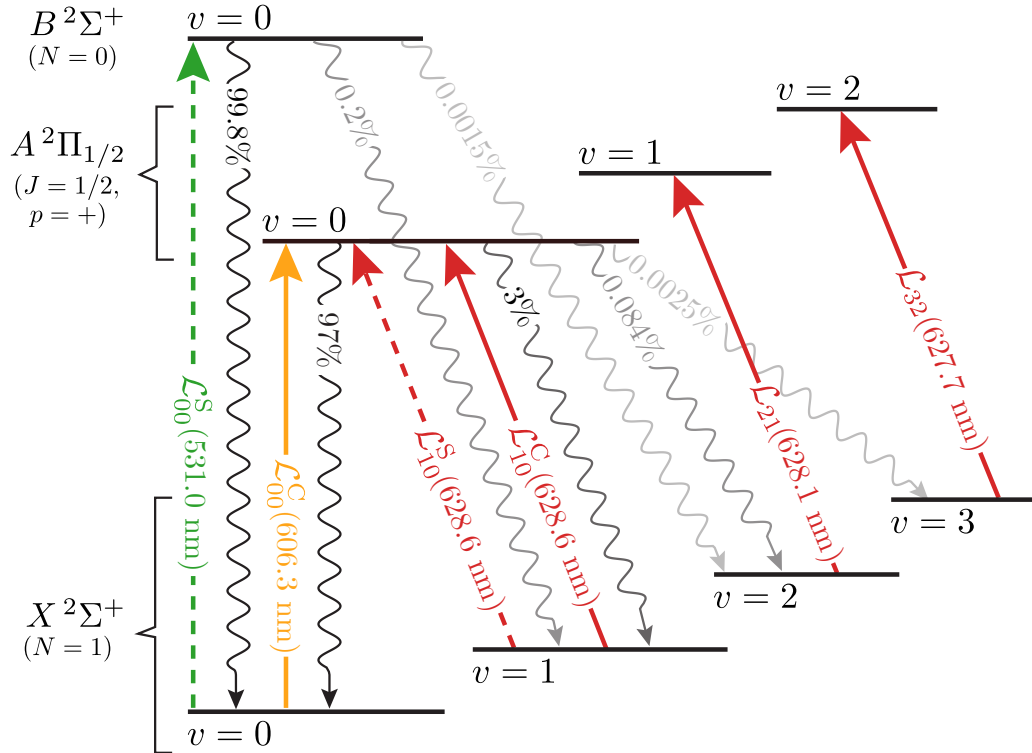


Figure 3.3: Simplified structure of CaF with laser transitions relevant for slowing (dashed lines) and the MOT (solid lines) highlighted. The wavy lines show the branching ratio of each excited states into the different vibrational levels. Adapted from [128].

The main cooling light ($\mathcal{L}_{00}^C$) and the light for the $v = 1$ repumpers ($\mathcal{L}_{10}^C$ and $\mathcal{L}_{10}^S$) are generated from two very similar laser systems. In both, infrared light (at 1212 nm and 1257 nm, respectively) is generated by an external-cavity diode laser² (ECDL). This is amplified in a Raman fibre amplifier (MPB VRFA-P), before being frequency doubled by second-harmonic generation in a non-linear crystal. The frequency of both laser systems can be finely tuned by adjusting the length of the external cavity of the ECDL with a piezoelectric actuator.

The main slowing light, $\mathcal{L}_{00}^S$, is also derived from frequency-doubling of infrared light. In this case, a Quantel Eyrsa Yb fibre laser seeded with a distributed feedback (DFB) laser³ is used to provide light at 1062 nm for doubling. The DFB laser is tunable by a piezoelectric actuator which allows fast frequency modulation by applying tensional strain on the DFB laser cavity [148].

The laser systems that provide the $\mathcal{L}_{21}$ and $\mathcal{L}_{32}$ light are leader-follower setups. The leader in each case is a distributed Bragg reflector (DBR) laser diode from the Ferdinand Braun Institute. On their own, each of these DBR lasers produce a maximum 20 mW of power at the correct wavelength, however this is insufficient for our needs once all the losses from the rest of the optical setup are taken into account. To increase the output power, light from each of the DBR lasers is used to seed a higher power laser diode.

For the DBR diodes to operate at the correct wavelengths, their temperatures must be carefully controlled. Each diode is placed inside a hermetically-sealed box, which is water cooled to $(15 \pm 1)^\circ\text{C}$ and held at rough vacuum. The mount of each DBR diode is further cooled with a Peltier element to its operating temperature of around 12°C and regulated at this temperature by a Wavelength Electronics MPT-2500 temperature controller using feedback from a thermocouple mounted close to the diode. Finer temperature stabilization is achieved by using an internal temperature control system within the diode which is driven by a Thorlabs TED200C temperature controller, allowing stabilization within a range of $\pm 0.002^\circ\text{C}$. The frequency of the DBR lasers can be coarsely controlled by adjusting the diode temperature. For finer control, the diode current can be varied, which is used for locking.

²Toptica DL Pro

³Koheras from NKT Photonics

The high power diodes used in the follower setups are Ushio HL63263DG for $\mathcal{L}_{32}$ and HL63163DG for $\mathcal{L}_{21}$, which operate at 638 nm and 633 nm, respectively, at room temperature. To tune the operating wavelengths to those needed for the experiment, the diodes must be cooled to -5°C for $\mathcal{L}_{32}$ and -20°C for $\mathcal{L}_{21}$. Similarly to the DBRs, the diodes are each placed in a hermetically-sealed and water-cooled box. A stack of two Peltier elements are used to cool the diodes further, the bottom one maintained at constant current and the top one regulated using feedback from a thermocouple close to the diode.

The output beam of each DBR diode is shaped with an anamorphic prism pair and coupled to a polarization-maintaining (PM) fibre before being delivered to the follower for injection locking. Optical isolators are placed at the output of the leader and the follower to eliminate unwanted feedback that would otherwise make them unstable. Light from the leader is injected into the follower via the rejection port of the follower's output isolator and the output of the follower is monitored on a Fabry-Perot cavity to detect whether the injection lock is functioning correctly.

For all of the lasers, sidebands must be added to address all of the hyperfine components in the ground state of CaF. The sidebands added to each laser are shown in figure 3.4 and the optical setup needed to generate these sidebands using a number of acousto-optic modulators (AOMs) and electro-optic modulators (EOMs) is shown in figure 3.5. Pick-offs along the beam paths allow a small fraction of the light of each laser to be split off so that the sideband structure can be monitored with an optical cavity.

The main slowing light ($\mathcal{L}_{00}^S$) has sidebands added with a 24 MHz EOM. It then passes through a single-pass AOM which is used for switching the light off after slowing so as not to disturb the MOT. The laser is chirped to account for the changing Doppler shift of the molecules as they slow (described in more detail in section 3.6). The slowing repump light ($\mathcal{L}_{10}^S$) is not chirped but instead broadened in frequency over the entire range of Doppler shifts by passing through a chain of three EOMs driven at 72 MHz, 24 MHz, and 8 MHz. This spreads the power of the laser over a range of frequencies with a width of a few hundred MHz. The double-pass AOM acts as a switch, so that the full laser power can be diverted to $\mathcal{L}_{10}^S$ for slowing before being redirected to $\mathcal{L}_{10}^C$ for the MOT stage. The main slowing light ($\mathcal{L}_{00}^S$) and the slowing repump

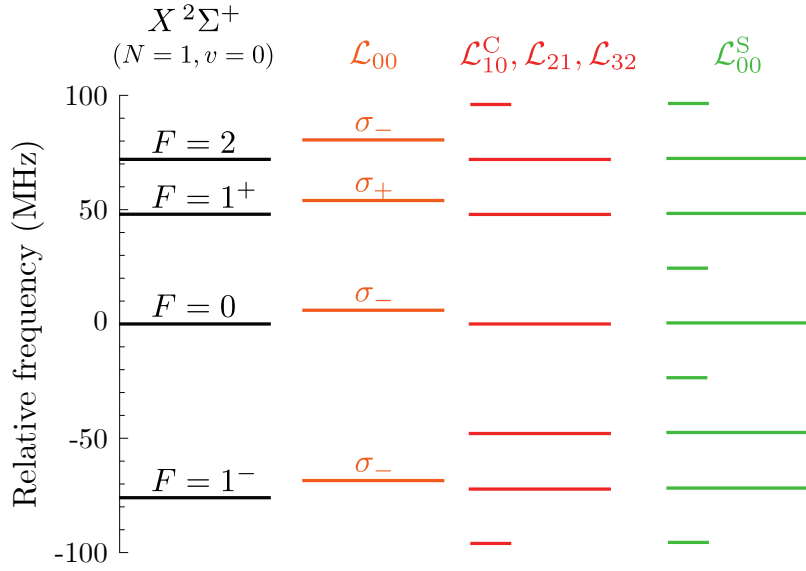


Figure 3.4: Hyperfine structure of the $X^2\Sigma^+(N = 1, v = 0)$ state of CaF and stick spectra showing the frequency sidebands added to the lasers to address the hyperfine levels. The slowing repump $\mathcal{L}_{10}^S$ is not shown but is frequency-broadened over the entire range. Adapted from [128]

($\mathcal{L}_{10}^S$) are each coupled into PM fibre and delivered to the experiment.

For the main cooling light $\mathcal{L}_{00}^C$, it is necessary to have sidebands of orthogonal polarization to generate the correct arrangement for the dual-frequency MOT scheme, described in section 2.4.1. First, the beam is directed through a double-pass AOM operating at 110 MHz, which is used for fast switching and for fine control of the detuning and intensity. The output is split into two orthogonal polarization components with an intensity ratio of approximately 3:1. The stronger beam is sent through a EOM driven at 72 MHz to produce first order sidebands of roughly the same intensity as the carrier. This arm will address the $F = 1^-, 0, 2$ hyperfine levels in the ground state. The remaining $F = 1^+$ level is addressed by the weaker beam, which is shifted in frequency by a single-pass AOM operating at 48 MHz. Each arm is then coupled into a PM fibre.

For the MOT vibrational repumps ($\mathcal{L}_{10}^C$, $\mathcal{L}_{21}$, and $\mathcal{L}_{32}$), the sidebands are generated by modulating the light with a single EOM placed in each beam. The EOMs are driven at 24 MHz with enough power so that second order and higher sidebands are present but the first order is extinguished. The $v = 1$ repump, $\mathcal{L}_{10}^C$, is coupled into its own optical fibre. The other two repumps, $\mathcal{L}_{21}$ and $\mathcal{L}_{32}$, are combined on a 90:10 beamsplitter before being coupled into a PM optical fibre. Although 90% of the $\mathcal{L}_{32}$ light is lost in this arrangement, only a very small

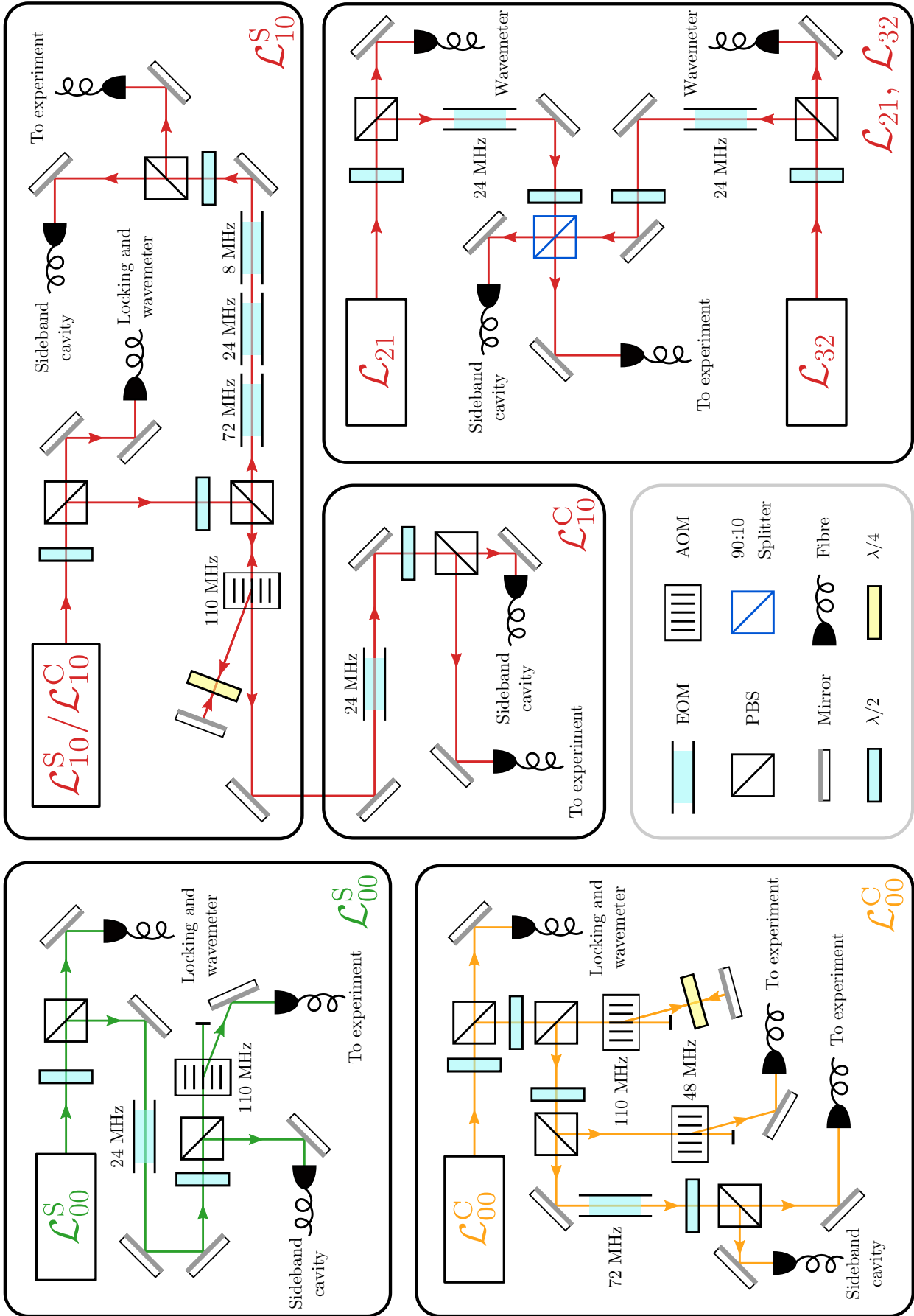


Figure 3.5: Schematic of optical setup for preparing the light for slowing and cooling CaF.

amount of power is needed at the experiment to effectively repump the $v = 3$ level. The light that exits through the other port is used for checking the status of the injection locking. All the light needed for the MOT ($\mathcal{L}_{00}^C$, $\mathcal{L}_{10}^C$, $\mathcal{L}_{21}$, and $\mathcal{L}_{32}$) is combined in a Schäfter & Kirchhoff fibre cluster which uses an arrangement of dichroic waveplates and polarizing beamsplitters to mix all the components into a single PM fibre which is sent to the experiment.

A small part of the output of each laser is picked off and used to lock the laser with a transfer cavity lock system which is described in section 3.3.3.

3.3.2 Rb

The laser frequencies needed for cooling, manipulating and imaging the Rb atoms are shown in figure 3.6. These are produced from a pair of tapered amplifier (TA) systems from Toptica. One TA provides the 2D and 3D MOT cooling light ($\mathcal{L}_{\text{Rb}}^{2\text{D},\text{C}}$ and $\mathcal{L}_{\text{Rb}}^C$) and all the other light that addresses the $F = 2$ hyperfine level: the optical pumping light ($\mathcal{L}_{\text{Rb}}^{\text{OP}}$), the 2D MOT push beam ($\mathcal{L}_{\text{Rb}}^P$) and the absorption imaging light ($\mathcal{L}_{\text{Rb}}^{\text{AI}}$). The other TA provides the 2D and 3D MOT repump light ($\mathcal{L}_{\text{Rb}}^{2\text{D},\text{R}}$ and $\mathcal{L}_{\text{Rb}}^R$), which addresses the $F = 1$ hyperfine level. We label these the cooling and repump lasers, respectively. Each TA has an auxiliary output where a small part of the beam is picked off for diagnostics and locking. The main output of the cooling laser is split into two unequal components: the stronger one being used for $\mathcal{L}_{\text{Rb}}^C$, $\mathcal{L}_{\text{Rb}}^P$ and $\mathcal{L}_{\text{Rb}}^{\text{AI}}$ and the weaker one for $\mathcal{L}_{\text{Rb}}^{2\text{D},\text{C}}$ and $\mathcal{L}_{\text{Rb}}^{\text{OP}}$. The two cooling beams and the repump beam are coupled separately into three high power optical fibres to be taken to the experiment.

Figure 3.7 show the optical setup at the experiment table. Light is picked off from the stronger cooling beam (labelled Cooling 1) for the absorption imaging probe beam and the 2D MOT push beam and a small amount of power from weaker beam (labelled Cooling 2) is split off for optical pumping. AOMs are used to switch the beams and allow fine control of the frequency of each component. The repump light is divided on the table and mixed with the 2D MOT and 3D MOT light. The 3D MOT and repump light is further divided into two and coupled into a pair of 1-3 fibre splitters from Evanescence Optics (labelled 3D MOT A and B in figure 3.7), which deliver the light to the chamber for a six-beam MOT.

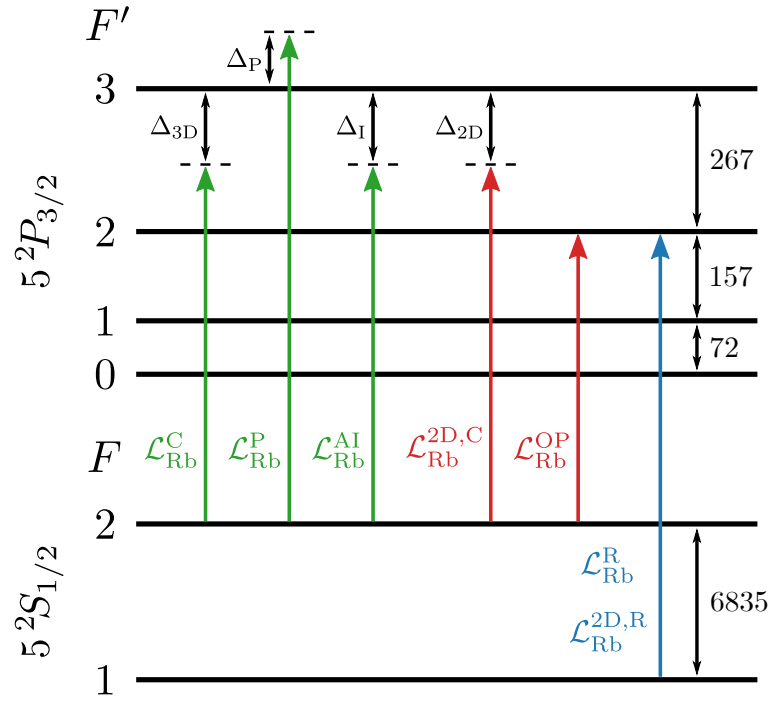


Figure 3.6: Scheme of laser frequencies for Rb. The purpose of each laser frequency from left to right is: 3D MOT cooling light ($\mathcal{L}_{\text{Rb}}^{\text{C}}$), push beam ($\mathcal{L}_{\text{Rb}}^{\text{P}}$), absorption imaging light ($\mathcal{L}_{\text{Rb}}^{\text{AI}}$), 2D MOT cooling light ($\mathcal{L}_{\text{Rb}}^{2\text{D,C}}$), optical pumping ($\mathcal{L}_{\text{Rb}}^{\text{OP}}$), 3D MOT repump ($\mathcal{L}_{\text{Rb}}^{\text{R}}$), and 2D MOT repump ($\mathcal{L}_{\text{Rb}}^{2\text{D,R}}$). The numbers to the right are the spacings between the energy levels given in units of $h \times \text{MHz}$.

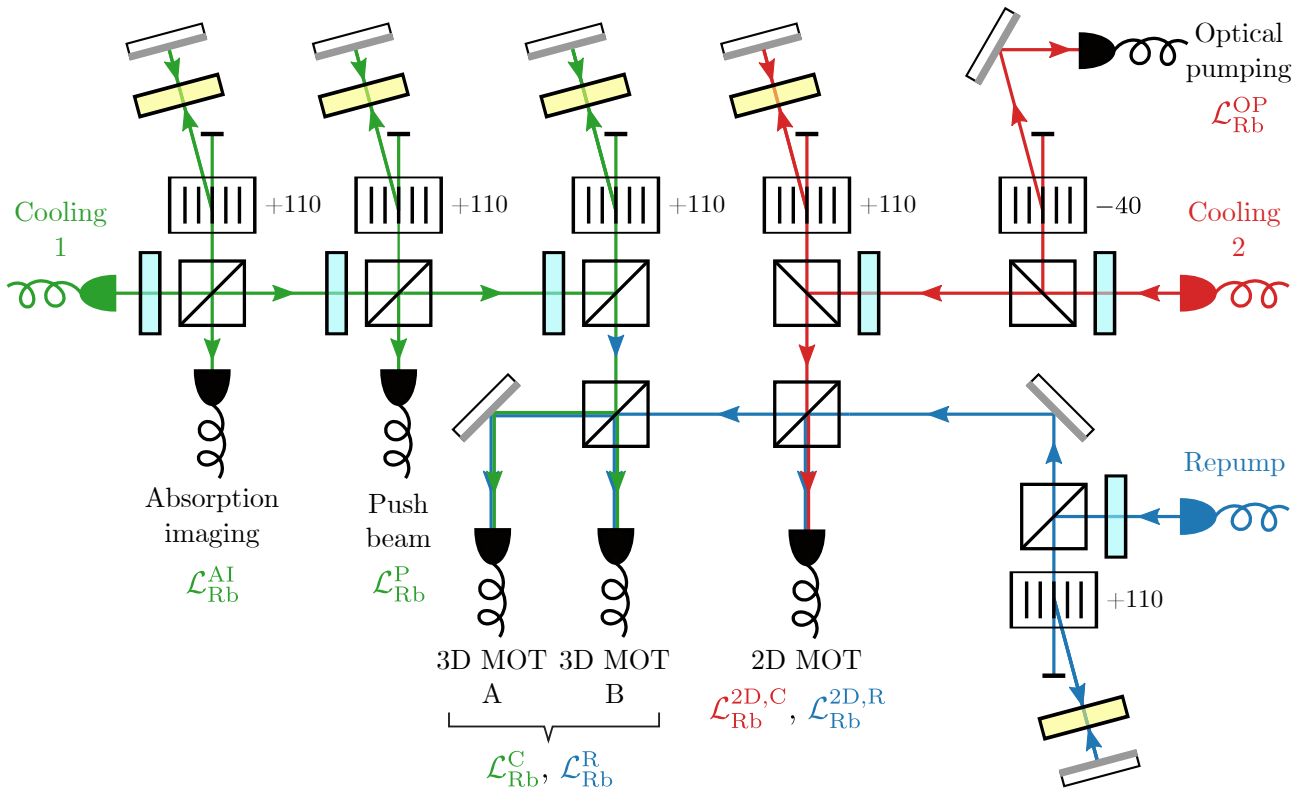


Figure 3.7: Schematic of optical setup for cooling, imaging and optically pumping Rb atoms. The number next to each AOM gives its central frequency.

We find that the number of Rb atoms loaded into the 3D MOT is optimized for $\Delta_{2D} = -15$ MHz, $\Delta_{3D} = -25$ MHz and $\Delta_P = 16$ MHz and these are the values used for loading the MOT in all further experiments.

3.3.3 Frequency stabilization

Reference laser

The reference laser is a 780 nm ECDL locked to the $F = 2 \rightarrow F = 2, 3$ crossover resonance of the D_2 line in ^{87}Rb using a sub-Doppler dichroic atomic vapor laser lock (DAVLL) setup described in detail in [149]. When locked, the reference laser has a linewidth of around 200 kHz with long-term drifts on the order of 1 MHz per day. All of the other lasers are locked to this reference laser, either by offset locking in the case of the Rb lasers or by transfer cavity locking for the CaF lasers.

Offset locking

Electronic offset locks are used to lock both the cooling and repump lasers for Rb. For each offset lock, the light from the reference laser and the laser to be locked are coupled into the same optical fibre so that their spatial modes are well-matched. The output of the fibre is incident on a fast photodiode and the interference between the two beams leads to a low-frequency optical beat note, which is detected by the photodiode. The beat note is amplified and mixed down with the output of a Voltage Controlled Oscillator (VCO), which generates frequency components at the sum and difference of the beat note frequency and the VCO frequency.⁴

The frequency of the mixed down beat note must be converted to a DC signal to be fed back to the laser. To do this, a side-of-filter technique is used, as illustrated in figure 3.8. The signal is split by a power splitter into two arms. One output is attenuated with a fixed 6 dB attenuator and the other arm is attenuated by a fixed 3 dB attenuator and passes through a low-pass filter

⁴A filter may be added to remove one of these signals but, if they are well separated, this is not necessary.

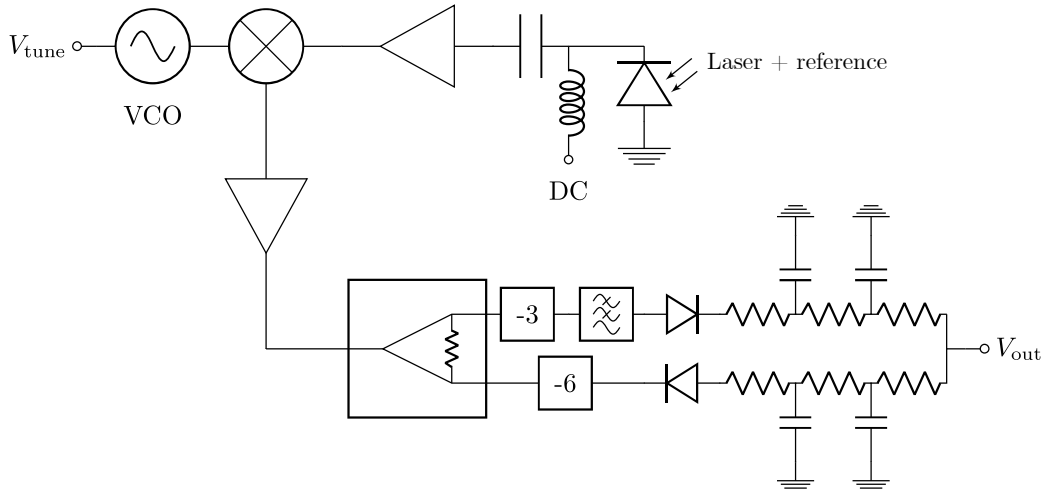


Figure 3.8: Schematic of electronic setup used for offset locking, described in detail in the main text. Adapted from [149].

(the reference filter). In each arm, a diode followed by a second-order low-pass filter converts the RF signal to a voltage that is proportional to its amplitude. The components are identical for each arm but the direction of the diode is swapped, giving the voltages opposite polarities. The voltages are then added on a resistive divider.

When the frequency of one of the components of the mixed down beat note is at the 3 dB point of the reference filter, then the attenuation of each arm is equal and the voltages sum to zero. At higher or lower frequencies, the attenuation of each arm will be unbalanced leading to a non-zero voltage, with its sign depending on the direction of the deviation from the 3 dB point. Thus, this setup creates a feedback signal (V_{out}) with a zero crossing which can be used to lock the laser. This is fed to a PI controller which stabilizes the laser based on the feedback. The lock point of the laser can be controlled by varying the tuning voltage of the VCO (V_{tune}).

Transfer cavity lock

The CaF lasers are stabilized using a transfer cavity lock (TCL) system. A small amount of light from each of the lasers is coupled into one of two scanning Fabry-Pérot cavities along with light from the reference laser. The cavity is scanned and the transmission spectra of all the lasers are recorded with photodiodes and sent to the computer. The spectra are fitted with Lorentzians to determine the cavity voltage at which the transmission is maximized. The

position of the transmission peak of the reference laser is used to lock the length of the cavity by feeding back to the offset of the scan ramp. The other lasers can then be locked based on the positions of their transmission peaks, relative to the reference peak.

3.4 Rb 2D MOT

The 2D MOT is formed in a glass cell attached to the main chamber by a 4-way cross, as shown in figure 3.9. Rb atoms are loaded from thermal vapour maintained by dispensers located in the other arms of the cross. The dispensers are operated by applying a current, typically in the range of 3 A–4.5 A. A differential pumping tube sits between the 2D MOT cell and the main chamber, which prevents the Rb vapour from affecting the background pressure in the main chamber. Once cooled in the 2D MOT, the atoms are loaded through the differential pumping tube into the main chamber by a push beam that propagates along the axis of the trap.

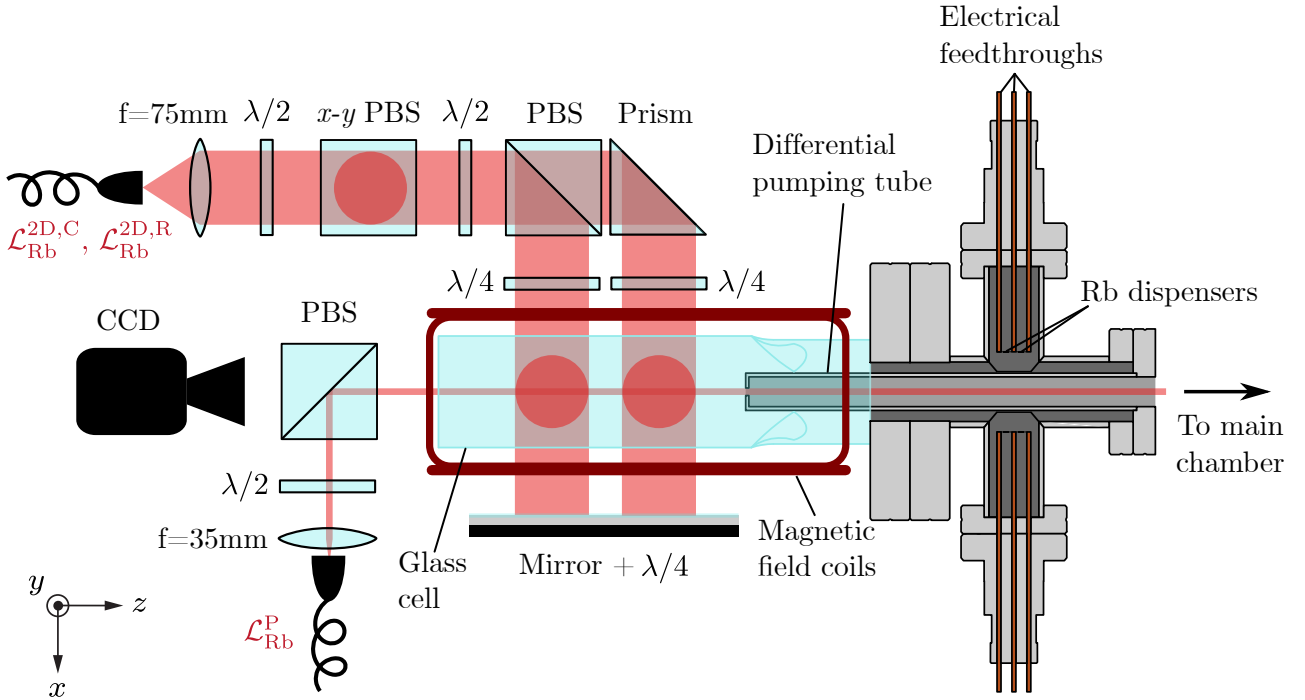


Figure 3.9: Schematic of the the 2D MOT: Rb atoms from the dispensers are trapped in a 2D MOT in the glass cell. The 2D MOT light ($\mathcal{L}_{\text{Rb}}^{2\text{D},\text{C}}$ and $\mathcal{L}_{\text{Rb}}^{2\text{D},\text{R}}$) is split between the x and y MOT beams on the $x - y$ PBS. The optics for producing the MOT light in the x direction is shown. A similar setup produces the beams in the y direction. The CCD is used for monitoring the fluorescence of the 2D MOT as a diagnostic.

The 2D MOT light is collimated to form a beam with a $1/e^2$ radius of 7 mm, before being split

into two beams, one for each dimension. The beams are split again to increase the volume of the cooling region so more atoms can be captured. Quarter-wave plates are used to set the correct polarization for the MOT. After propagating through the glass cell, the beams are retroreflected by a mirror which is coated with a layer that acts as a quarter-wave plate, producing the correct polarization for the counter-propagating beams.

3.5 Main chamber

3.5.1 MOT coils

The quadrupole magnetic field necessary for the MOT is generated by a pair of coils inside the main chamber, shown in figure 3.10. The design and operation of these coils is detailed in [150] and summarised here. Each coil is made up of two laser-cut copper spirals. A layer of aluminium nitride (AlN) is sandwiched between the two spirals and the whole assembly is secured by two alumina (Al_2O_3) clamps on the top and bottom. Electrical connection between the two spirals is made with a small screw that traverses the AlN layer. The coils are supplied with current through vacuum-compatible insulated copper wires that are connected to electrical feedthroughs and slots in the alumina layers allow the gaps between the coils to be pumped out efficiently. The AlN layers are bolted to a copper spacer, which fixes both coils in place.

The coils are driven by a home-built⁵ power supply that allows the direction of current in each of the coils to be controlled. In anti-Helmholtz configuration, the coils produce an axial field gradient of 30 G cm^{-1} when operated at 10 A, which is sufficient for our needs. Although the supply can provide up to 35 A to the coils, we find that even after increasing the current to 15 A, the pressure in the chamber increases by an order of magnitude within 20 s of operation. This is likely due to heating and out-gassing of the black paint applied to the coils to reduce scattered light. The current in the coils can be switched rapidly with a $1/e$ rise/fall time of 500 μs .

⁵Designed and built by Noah Fitch.

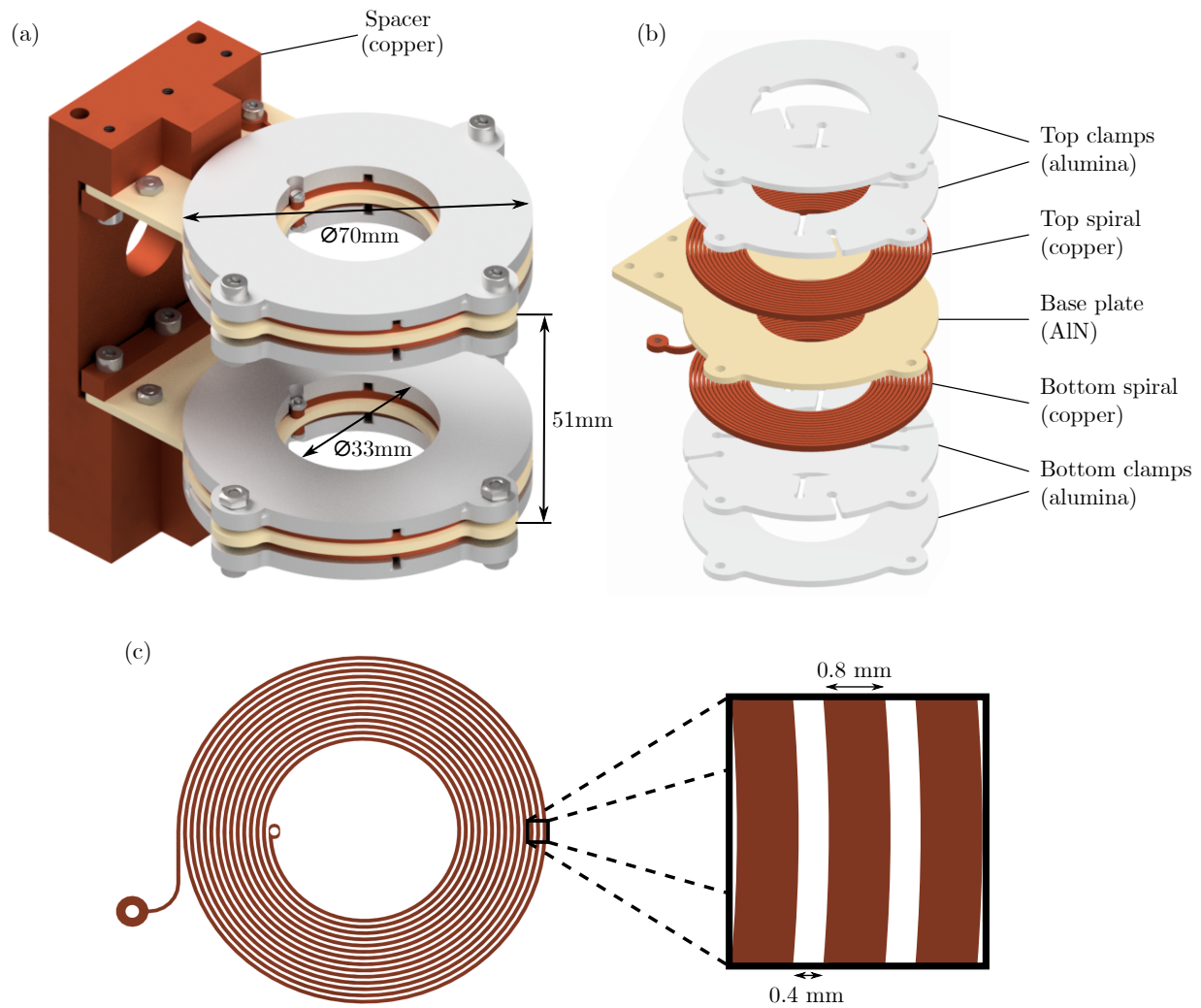


Figure 3.10: MOT coils: (a) Full assembly of the coils including copper spacer. (b) Exploded view showing the individual layers making up each coil. The top and bottom spirals are connected in series. (c) Close-up of coils showing dimensions of the laser cut spiral.

3.5.2 Optical setup

The optical setup around the main chamber is shown in figure 3.11. Once combined in the fibre cluster and brought over to the experiment, the light for the CaF MOT is roughly collimated with a Schäfter and Kirchhoff beam expander to a $1/e^2$ beam radius of 8.1 mm. The MOT beams contain up to 120 mW of $\mathcal{L}_{00}^C$ power. To maximize the intensity, the CaF MOT is formed by a single beam which is folded through the chamber three times before being retroreflected. The beam is adjusted to be slightly convergent to mitigate any intensity imbalance caused by imperfect transmission through the many optical elements in the beam path.

For the Rb MOT, the light comes from six separate beams. Each beam is expanded to a $1/e^2$ radius of 10 mm and contains up to 10 mW of cooling laser power and 2 mW of repump power. These beams are combined with the CaF MOT beams on dichroic mirrors, as shown in figure 3.11. Dichroic quarter-wave plates are used to ensure the polarization of the light is correct for the CaF and Rb MOT beams.

The CaF slowing light ($\mathcal{L}_{00}^S$) and slowing repump ($\mathcal{L}_{10}^S$) are combined on a PBS and mixed with the Rb optical pumping beam ($\mathcal{L}_{Rb}^{OP}$) on a dichroic mirror before entering the chamber. The Rb absorption imaging light enters through a CF16 viewport angled at 21° to the horizontal plane.

3.5.3 Imaging

Fluorescence

The CaF MOT is imaged using fluorescence imaging. A lens of diameter 50.8 mm and focal length 60 mm is placed in the vacuum chamber so that the light collected from the MOT is focused to infinity. Outside of the vacuum chamber, the light passes through a bandpass filter with a centre frequency of around 606 nm to filter out scattered light of other wavelengths. Finally, an aspheric lens with focal length 28.6 mm is used to focus the light down onto a CCD camera (ORCA-R2). The magnification of the imaging system can be determined by

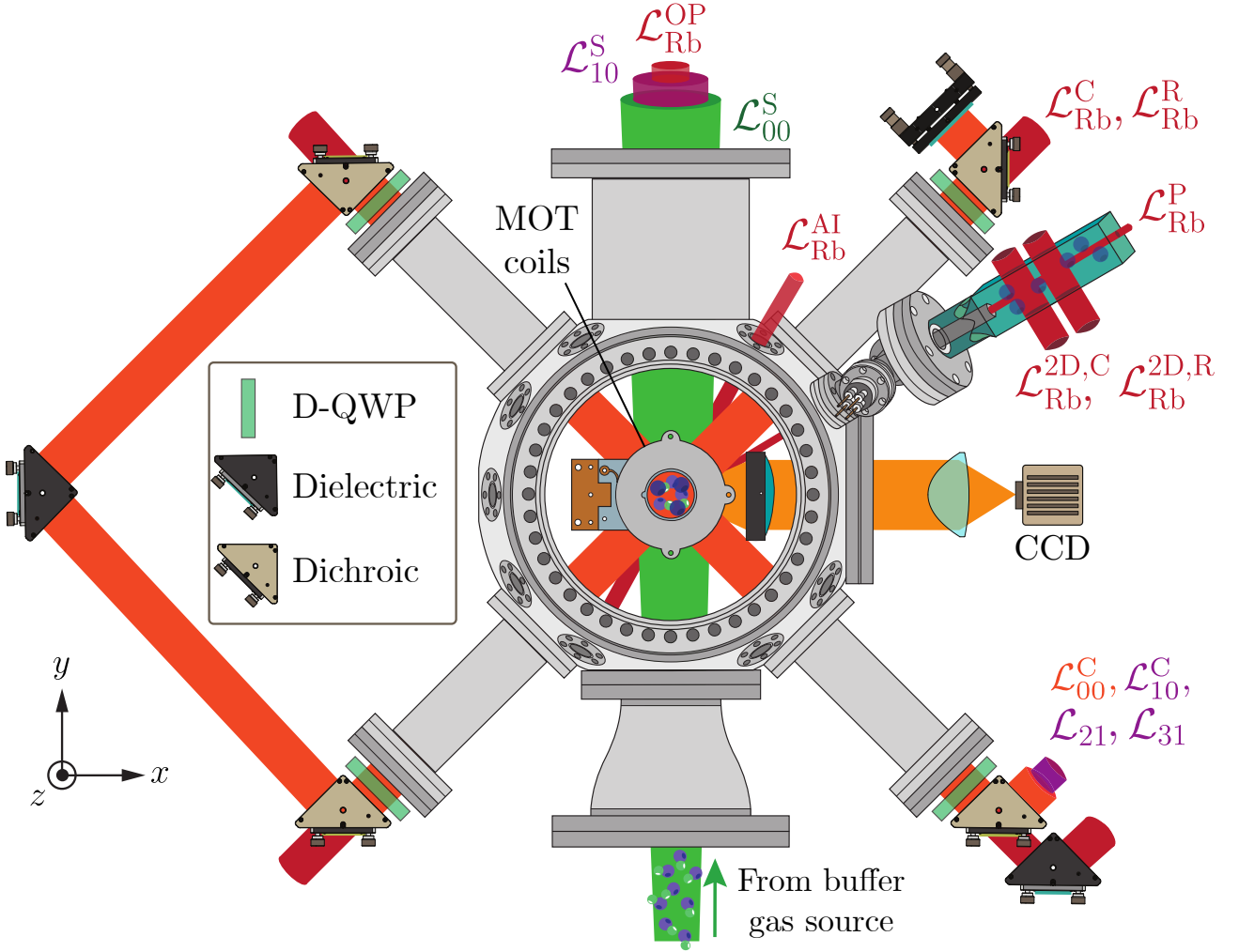


Figure 3.11: Optical setup around the main chamber: the CaF MOT light is wrapped around the chamber and combined with the Rb MOT beams on dichroic mirrors. The polarization of the MOT beams for both species are controlled with dichroic quarter-wave plates (D-QWP) positioned in front of each viewport. Adapted from [151].

letting the cloud drop and comparing the apparent acceleration of the cloud under gravity with the accepted value. This leads to a measured magnification of 0.47(1), consistent with the calculated value of 0.48.

The camera electronics converts the number of incident photons N_{ph} to a number of counts, N_{c} . This can be used to recover the number of photons by using the expression

$$N_{\text{ph}} = \frac{C}{G\eta_{\text{Q}}} \frac{(N_{\text{c}} - N_{\text{off}})}{N_{\text{sat}}} \quad (3.1)$$

where C is the full well capacity, G is the amplifier gain, η_{Q} is the quantum efficiency, N_{off} is the camera offset and N_{sat} is the number of counts at saturation. N_{sat} is related to the bit depth b by $N_{\text{sat}} = 2^b - 1$ and the values of the other constants can be found in [152].

Some of the photons detected by the camera come from background scatter in the chamber. To address this, two measures are taken. Firstly, the inside of the vacuum chamber is blackened using ultra-high vacuum compatible black paint to reduce scattering. Secondly, we take regular images of the background under identical conditions but without any molecules present. By subtracting these background images from the MOT images, we effectively isolate the fluorescence emitted by the molecules. If the scattering rate of the molecules is known, the number of photons in the background-subtracted image can be used to determine the number of molecules present. When the camera is exposed for a time t_{exp} , the total number of photons scattered will be $R_{\text{sc}}t_{\text{exp}}$. However, only a small fraction of these scattered photons reach the camera. To account for this, we introduce the collection efficiency, η_{c} , which accounts for the geometric efficiency (the fraction of the total solid angle where the scattered photons can reach the detector) and the transmission of the optical elements between the molecules and the camera. The number of molecules is then

$$N = \frac{(N_{\text{ph}} - N_{\text{ph}}^0)}{R_{\text{sc}}t_{\text{exp}}\eta_{\text{c}}} \quad (3.2)$$

where N_{ph}^0 is the number of photons recorded in the background image.

The scattering rate in the MOT can be measured by turning off $\mathcal{L}_{21}$ and observing the rate of decay of fluorescence as the molecules are optically pumped into the $v = 2$ vibrational state.

The scattering rate found using this method is $R_{\text{sc}} = 2.08(13) \text{ s}^{-1}$ [128]. For our system, the collection efficiency has a value of $\eta_c = 2.3(1) \%$, which is found by measuring the transmission and calculating the geometric efficiency by ray tracing⁶ [153]. The uncertainty in this value comes from the measurements of the transmission of all of the optical elements in the imaging system. The systematic errors due to these two factors leads to an uncertainty on all measurements of the number of molecules of $\pm 7.6\%$.

Absorption

The Rb atoms can be imaged using the same fluorescence imaging system by replacing the bandpass filter with a suitable neutral density (ND) filter to avoid saturating the camera. However, to get a reliable measure of atom number for the denser Rb clouds, it is necessary to use absorption imaging. As shown in figure 3.12, the absorption probe light is brought to the experiment in a PM fibre and the output is collimated to form a beam with waist radius 5 mm. The light is then circularly polarized before entering the chamber. During absorption imaging, the shim coils (described in section 3.5.5) zero the background magnetic field and apply a 400 mG field in the direction of propagation of the absorption light, ensuring accurate circular handedness relative to this axis. As the light propagates through the atom cloud, it is absorbed and the density profile is imprinted as a shadow in the beam. The 4-f system shown in figure 3.12 is then used to image the absorption of the atoms onto a CCD.

For a weak⁷ probe beam propagating along the z direction through the atom cloud, the intensity will vary as

$$\frac{\partial I(x, y, z)}{\partial z} = -n(x, y, z)\sigma I(x, y, z) \quad (3.3)$$

where $n(x, y, z)$ is the number density of the atoms and σ is the absorption cross-section of an

⁶The geometric efficiency could also be measured by introducing an aperture into the imaging system between the two lenses. As the size of the aperture is increased, the signal from the molecules should initially increase before saturating. The aperture diameter at which the signal saturates can then be related to the geometric efficiency by simple ray optics.

⁷More precisely, for a beam with $I \ll I_s$.

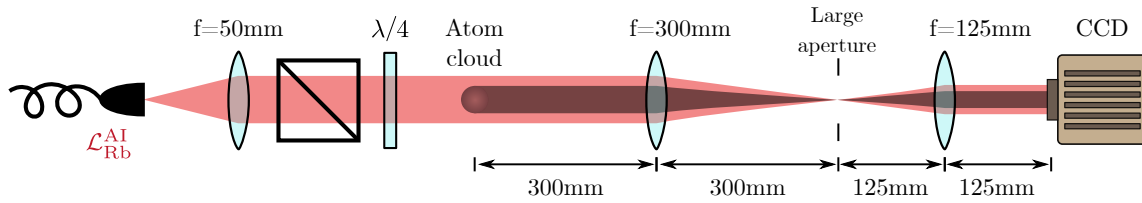


Figure 3.12: Optical setup for absorption imaging: the absorption imaging light is collimated and circularly polarized with a quarter-wave plate, before being sent into the chamber. The absorption profile of the atom cloud is then imaged onto a CCD using a 4f-system. A large 1 cm diameter aperture was placed in the Fourier plane to block out excess background scatter. This aperture is optional and, since it reduces the spatial resolution of the imaging system, should be removed when imaging smaller clouds.

atom. After traversing the atom cloud, the intensity profile of the beam will be

$$I(x, y) = I(x, y, 0) \exp \left(-\sigma \int_0^\infty n(x, y, z) dz \right) = I(x, y, 0) e^{-\text{OD}(x, y)} \quad (3.4)$$

where in the last step we have defined the optical density

$$\text{OD}(x, y) = \sigma \int_0^\infty n(x, y, z) dz. \quad (3.5)$$

This is often written as

$$\text{OD}(x, y) = \sigma n_{\text{cl}}(x, y) \quad (3.6)$$

where $n_{\text{cl}}(x, y)$ is the column density. The total number of atoms in the cloud is then

$$N_{\text{at}} = \int_{-\infty}^\infty \int_{-\infty}^\infty n_{\text{cl}}(x, y) dx dy = \frac{1}{\sigma} \int_{-\infty}^\infty \int_{-\infty}^\infty \text{OD}(x, y) dx dy. \quad (3.7)$$

The absorption cross-section is in general a function of the detuning and polarization of the light and the relative population of the Zeeman sublevels of the atoms. However, if a small magnetic field is applied along the beam and the probe beam is circularly polarized to drive only σ^+ transitions, the atoms will be optically pumped into the stretched state $|F = 2, m_F = +2\rangle$. The atoms in this state will only be excited on the cycling transition $|F = 2, m_F = +2\rangle \rightarrow |F' = 3, m'_F = +3\rangle$. Thus, we have an effective two-level system and the absorption cross-section

becomes

$$\sigma = \frac{\sigma_0}{1 + 4\Delta^2/\Gamma^2} \quad (3.8)$$

where $\sigma_0 = 3\lambda^2/2\pi$ is the resonant absorption cross-section of a two-level system coupled by a transition with wavelength λ .

The optical density is measured by taking three images: one with the atoms present and the probe beam on, labelled $I_{\text{at}}(x, y)$; one with no atoms present and the probe beam on, labelled $I_{\text{p}}(x, y)$; and one with no probe beam and no atoms, labelled $I_0(x, y)$. The OD is calculated by

$$\text{OD}(x, y) = -\ln \left[\frac{I_{\text{at}}(x, y) - I_0(x, y)}{I_{\text{p}}(x, y) - I_0(x, y)} \right]. \quad (3.9)$$

The probe beam used for the imaging has an intensity of $0.02I_{\text{sat}}$ and is switched on for $100\ \mu\text{s}$ for each image. During the imaging, the repump beam is also switched on so that any atoms in the $F = 1$ hyperfine level are also imaged. The systematic uncertainties of our absorption imaging setup are treated in detail in [150].

Size and temperature

In addition to the number of atoms or molecules captured, the density distribution of the cloud can also be measured by imaging. Since the images obtained are 2D, the entire 3D density distribution cannot be reconstructed. However, by making certain assumptions, we can deduce the 3D distribution. For instance, in the MOT we assume that the cloud has a cylindrically-symmetric Gaussian distribution given by⁸

$$n(x, y, z) = \frac{1}{(2\pi)^{3/2}\sigma_r^2\sigma_a} \exp\left(-\frac{x^2 + y^2}{2\sigma_r^2} - \frac{z^2}{2\sigma_a^2}\right). \quad (3.10)$$

Under this assumption, the unknown widths σ_r and σ_a can be determined from the images.

We measure the temperature of the clouds by ballistic expansion. If the cloud is at thermal equilibrium and is released from the trap, then the size of the cloud should increase from its

⁸At thermal equilibrium in a cylindrically-symmetric harmonic trap, this assumption is also valid.

initial size σ_0 as

$$\sigma(t) = \sqrt{\sigma_0^2 + \frac{k_B T}{m} t^2} \quad (3.11)$$

Therefore, by taking a series of images at different times after the release and measuring the size of the cloud, the temperature T of the atoms or molecules can be inferred by fitting to equation 3.11.

3.5.4 Microwaves

Microwaves with frequency of around 20 GHz are used for coherent control of the rotational states of the CaF molecules. The microwaves are generated by a Gigatronics 7100 synthesizer and then frequency-doubled and controlled with a fast switch. A microwave horn transfers the microwaves into the experiment through one of the viewports.

3.5.5 Shim coils

Around the outside of the main chamber, shim coils in Helmholtz configuration for each of the three dimensions are used to provide bias fields at the centre of the chamber. To calibrate the shim coils, we drive a magnetically-sensitive transition between the rotational states of the CaF molecule using microwaves. The full experimental sequence is given in section 4.1.1. The transition $|N = 1, F = 0, M_F = 0\rangle \leftrightarrow |N = 0, F = 1, M_F = +1\rangle$ is driven which has a frequency shift due to the magnetic field $\mathcal{B}$ of $\mu_B |\mathcal{B}| / h$. The magnetic field along each dimension is proportional to the current in each shim coil so we can write

$$|\mathcal{B}| = \sqrt{(\mathcal{B}_x^0 + \beta_x I_x)^2 + (\mathcal{B}_y^0 + \beta_y I_y)^2 + (\mathcal{B}_z^0 + \beta_z I_z)^2} \quad (3.12)$$

where $\mathcal{B}_i^0$ is the component of the background field without the shim coils, β_i is a constant of proportionality and I_i is the current running through the shim coil that generates field in the direction of $i \in \{x, y, z\}$.

In figure 3.13, the calculated magnetic field $|\mathcal{B}|$ is shown as a function of the current in each

of the shim coils. After each scan, the current is set to the value that minimizes $|\mathcal{B}|$, which corresponds to zeroing the field in that direction. By fitting equation 3.12 in each case, we find the calibrations $\beta_x = 766(1) \text{ mG A}^{-1}$, $\beta_y = 599(1) \text{ mG A}^{-1}$, and $\beta_z = 2202(22) \text{ mG A}^{-1}$. These calibrations can be used to calculate the currents needed in each coil to produce a field in an arbitrary direction.

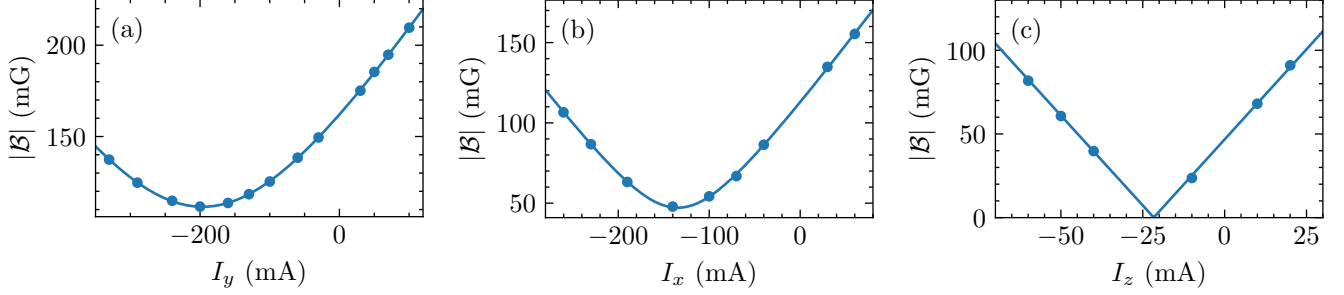


Figure 3.13: Calibration of the shim coils: for each point a magnetically-sensitive transition in CaF is driven and the magnitude of the magnetic field is deduced from the measured frequency shift. By varying the current flowing through the shim coils that generate a field in the (a) y, (b) x and (c) z directions and fitting to equation 3.12, all of the unknown variables can be deduced. After each iteration, the current is chosen which minimizes the magnitude of the magnetic field to zero the field in each direction.

3.6 Loading a dual-species MOT

In this section, the experimental sequence used to load a dual-species MOT of Rb and CaF will be summarized. This forms the starting point for the results presented in this thesis. We have also studied collisions between the two species in the MOT [151] but those results are not presented here.

The MOT of Rb is loaded first. Atoms are accumulated in the 2D MOT and transferred to the main chamber by the push beam. This loads atoms into the 3D MOT at a rate of $2 \times 10^9 \text{ atoms s}^{-1}$. The loading continues until the 2D MOT beams ($\mathcal{L}_{\text{Rb}}^{2\text{D,C}}$ and $\mathcal{L}_{\text{Rb}}^{2\text{D,R}}$) are turned off. In this way, the initial number of atoms in the MOT can be varied by controlling the load time.

Immediately after this, the loading process of the the CaF MOT begins. The ablation laser fires and a pulse of CaF molecules is created in the source chamber. The slowing ($\mathcal{L}_{00}^S$) and slowing repump ($\mathcal{L}_{10}^S$) beams are turned on 2.4 ms after the ablation pulse to decelerate the molecules. For the first 1 ms, $\mathcal{L}_{00}^S$ is held at a constant frequency, resonant with molecules travelling at 140 m s^{-1} . It is then chirped linearly⁹ by 240 MHz over 11.6 ms to follow the changing Doppler shift of the molecules. The slowing light is turned off 15 ms after the ablation pulse and CaF molecules begin to be captured in the MOT. Within 40 ms of the ablation pulse, the MOT is fully loaded, as shown in figure 3.14.

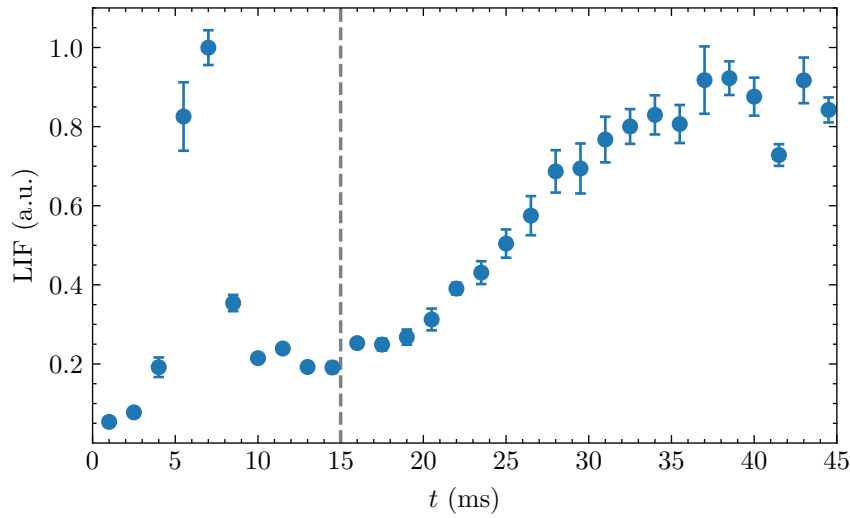


Figure 3.14: Loading of the CaF MOT: The points show the amount of fluorescence detected in the MOT region as a function of time after the ablation. The dashed line indicates when the slowing light turns off. Any fluorescence detected before this time comes from unsloved molecules, which cannot be captured by the MOT. After this, the loading begins and the fluorescence increases until the MOT is fully loaded.

⁹From chapter 6 onwards, an exponential frequency ramp was used. More detail on this can be found in [150].

Chapter 4

Collisions between Rb and CaF in a magnetic trap

Sympathetic cooling of molecules with ultracold atoms provides a promising route to molecular samples with very low temperatures and high phase space densities. This was recently demonstrated in the work of Son et al. [76]. In the experiment, NaLi molecules were trapped with Na atoms in a 1D optical lattice. The Na atoms were then evaporatively cooled and, by thermalization with the atoms, the molecules were sympathetically cooled down to a temperature of 220 nK with their phase space density increasing by a factor of 20. Although the molecules were not prepared in the ground electronic state, the low rate of loss compared to the rate of thermalization was sufficient to allow highly efficient sympathetic cooling.

Many other molecular species [69–71] have been plagued with high loss rates in optical traps. This occurs even when the molecules are non-reactive and are prepared in the absolute ground state so that there appear to be no inelastic loss channels. This puzzling observation has been attributed to the formation of long-lived complexes which lead to loss, either by excitation of the complex by trap light [154, 155] or by another process that has not been fully explained theoretically [156]. By performing experiments in a magnetic trap where no light is present, it is likely that this loss process will be eliminated. On the other hand, molecules cannot be trapped magnetically in their absolute ground state and so there is always an open loss channel

through the process of spin relaxation. However, theoretical work [157, 158] suggests that loss through this mechanism should be slow.

This chapter gives a summary of experiments carried out in the magnetic trap to investigate collisions between ultracold CaF molecules and Rb atoms. This includes measurements of the inelastic loss rate coefficient, analysis of the dependence of the loss on the quantum state of the molecules and an attempt to measure thermalization between the two species.

4.1 Loading the magnetic trap

The starting point for the following experiments is the dual-species MOT of CaF and Rb, loaded with the protocol described in section 3.6. In the following section, I will detail the steps taken to load the atoms and molecules into the magnetic trap, where collisions between the two species will be investigated.

4.1.1 CaF

To reduce the temperature of the molecules in the MOT, we lower the intensity of the CaF MOT cooling laser, $\mathcal{L}_{00}^S$, over 4 ms to 20% of its original value. The intensity remains at this value for 10 ms, during which we acquire an image of the molecule cloud. From the image, the initial molecule number in the MOT, $N_{\text{CaF}}^{\text{MOT}}$, is calculated.

Sub-Doppler cooling

After cooling in the MOT, the molecules are transferred into a blue-detuned optical molasses. The laser $\mathcal{L}_{00}^C$ is turned off and its frequency is shifted 20 MHz to the blue by changing the drive signal of the double-pass 110 MHz AOM. After a wait time of 1 ms, during which the frequency of the drive signal settles, $\mathcal{L}_{00}^C$ is turned back on at full intensity. The quadrupole field necessary for the MOT is also switched off. The molecules cool to 100 μK in the molasses and are held for 10 ms while any residual fields from eddy currents die away.

Optical pumping

To optically pump the molecules, we reduce the intensity of $\mathcal{L}_{00}^C$ to 1% of its initial value and increase the RF power delivered to the 72 MHz EOM modulating $\mathcal{L}_{00}^C$ such that the power in the carrier is reduced to zero, as in [108]. Since the carrier is meant to address the state $|N, F, M_F\rangle = |1, 0, 0\rangle$, in its absence the molecules will accumulate in this state. Using this scheme, up to 60% of the molecules can be pumped to the target state, with the efficiency limited by off-resonant excitation due to the remaining sidebands.

Microwave transfer

To transfer the molecules in the state $|1, 0, 0\rangle$ to a magnetically trappable state, the rotational transitions shown in figure 4.1a are driven using microwave π pulses. In the $N = 0$ and $N = 1$ manifolds, there are four magnetically trappable states - for our study of collisions, we focus on three of these: $|0, 1, 1\rangle$, $|1, 2, 2\rangle$, and $|1, 1^+, 1\rangle$. This allows us to investigate the effect of the rotational state of the molecules ($N = 0$ or $N = 1$) on the collisional properties, as well as the influence of being in a spin-stretched state ($|0, 1, 1\rangle$ and $|1, 2, 2\rangle$) or non-spin-stretched state ($|1, 1^+, 1\rangle$).

To prepare the molecules in each of these three states, we start by driving a π pulse on a downwards transition either to $|0, 1, 1\rangle$ or $|0, 1, 0\rangle$ (indicated by the blue and red arrows in figure 4.1a, respectively). Then, by applying a ‘blow away’ pulse, a pure sample of molecules in a single state can be produced. The slowing light, $\mathcal{L}_{00}^S$, is turned on for 3 ms at resonance with the molecules in $N = 1$, pushing them out of the MOT region whilst leaving behind the molecules that have been transferred to $N = 0$.

After the blow away pulse, if the molecules were prepared in $|0, 1, 1\rangle$, they can be left in this state or transferred to the state $|1, 2, 2\rangle$ with a π pulse (green arrow in figure 4.1a). If the molecules were prepared in the state $|0, 1, 0\rangle$, they are then transferred to $|1, 1^+, 1\rangle$ (purple arrow in figure 4.1a).

In order to find the correct frequency to drive all these transitions, we perform microwave

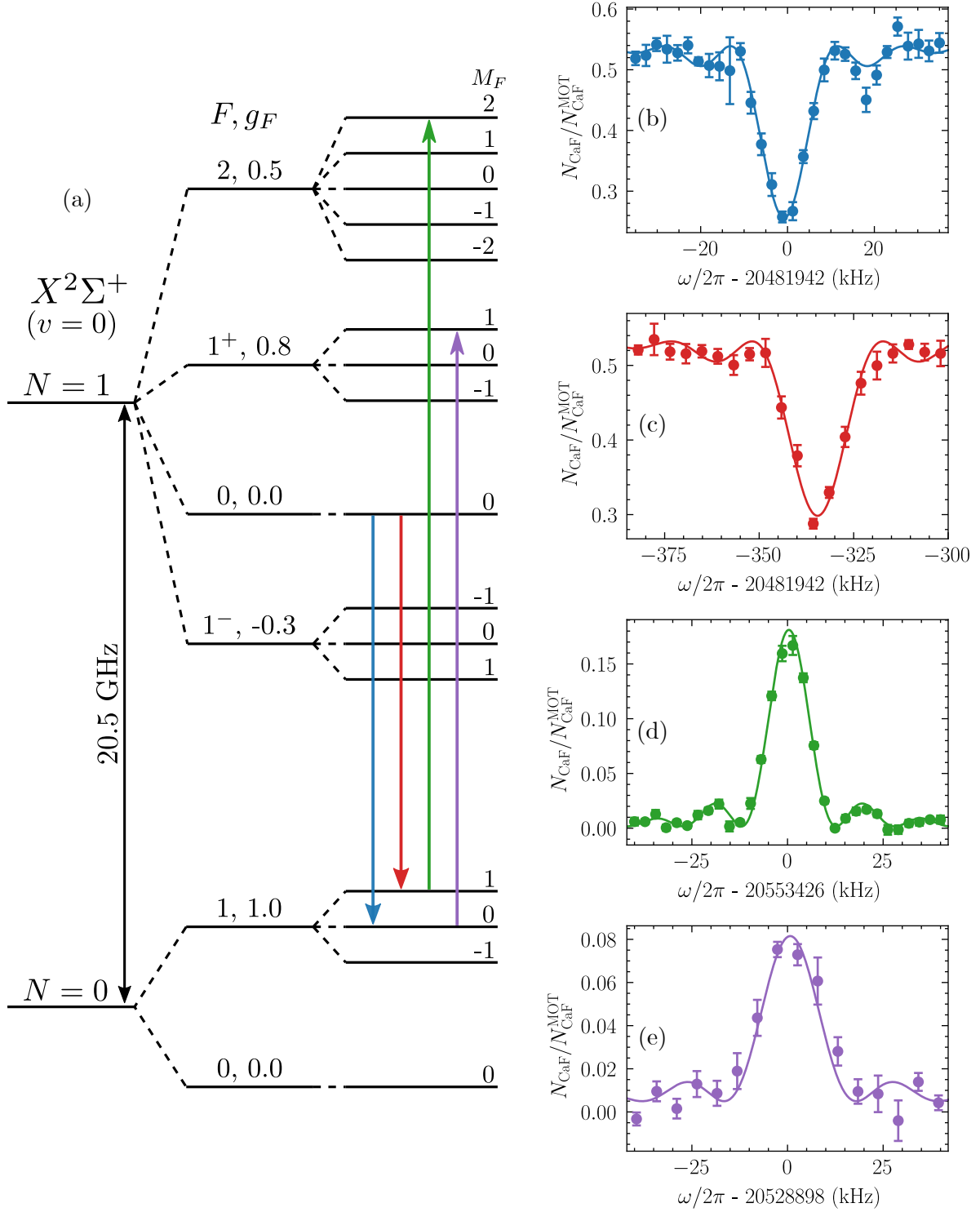


Figure 4.1: Microwave spectroscopy of CaF: (a) hyperfine and Zeeman structure of the $N = 0$ and $N = 1$ rotational levels in the $X^2\Sigma^+$ state of CaF. The coloured arrows show the microwave transitions driven to prepare the molecules in the desired state. (b-e) fraction of molecules recaptured into the MOT after a π pulse addressing the colour-coded transition as a function of microwave frequency. For (b & c), the molecules are optically pumped into $|1, 0, 0\rangle$ prior to the microwave pulse. For (d & e), this is followed by a resonant π pulse on the red or blue transition, respectively and a blow away pulse to prepare a pure sample of molecules in the addressed $N = 0$ state before the measurement. Each point is the average of at least 7 iterations and the error bars are the standard errors.

spectroscopy on the molecules after the blue molasses. We apply a known magnetic field of 240 mG to separate the transitions with $\Delta M_F = 0, \pm 1$. Due to multiple reflections of the microwaves within the chamber, the polarization is not well-defined and all of these transitions can be driven.

First, we drive the transition $|1, 0, 0\rangle \leftrightarrow |0, 1, 0\rangle$, which is not sensitive to the magnetic field. The microwaves are turned on for a duration of $t_\pi = 70 \mu\text{s}$, which drives a π pulse between the two states at resonance. After this, the molecules are recaptured into the MOT by turning on the MOT field and switching on the red-detuned cooling light. Since this light only addresses molecules in the $N = 1$ manifold, any molecules that have been transferred to $N = 0$ will not return to the MOT. The number of molecules recaptured, N_{CaF} , is measured by fluorescence imaging. To reduce the effect of shot-to-shot fluctuations in the number of molecules loaded into the MOT, we normalize this to the initial number of molecules in the MOT, $N_{\text{CaF}}^{\text{MOT}}$. This also eliminates the uncertainty due to the systematic error introduced by imperfect knowledge of the collection efficiency and scattering rate.

Figure 4.1b shows the fraction of molecules recaptured as a function of the microwave frequency, ω . The data are fitted with a modified version of the Rabi lineshape (equation 2.29) given by

$$\frac{N_{\text{CaF}}}{N_{\text{CaF}}^{\text{MOT}}} = r_0 + \frac{r_0 \eta}{1 + (\omega - \omega_0)^2 / \Omega^2} \sin^2 \left(\frac{\pi}{2} \sqrt{1 + \frac{(\omega - \omega_0)^2}{\Omega^2}} \right) \quad (4.1)$$

where r_0 is the fraction of molecules remaining when no microwaves are applied, η is the overall efficiency of the optical pumping and the microwave transfer, and ω_0 is the resonant frequency of the transition. The Rabi frequency, Ω , is fixed to be π/t_π and all the other variables are kept as free parameters in the fit. We find an overall efficiency of $\eta = 52(1)\%$, which is likely dominated by the efficiency of the optical pumping.

Figure 4.1c shows the result of the same experiment but now driving the magnetically-sensitive transition $|1, 0, 0\rangle \leftrightarrow |0, 1, 1\rangle$. More microwave power is used which broadens the transition, making it less sensitive to small changes in the magnetic field. This leads to a reduced π pulse time of $t_\pi = 50 \mu\text{s}$. The fit gives an efficiency of $\eta = 44(1)\%$, slightly lower than for the

insensitive transition. This may be due to a small residual magnetic field gradient over the cloud of molecules, which would reduce the coherence time.

Next, we drive the transitions back to $N = 1$ after the blow away pulse. With the molecules prepared in the state $|0, 1, 1\rangle$, figure 4.1d shows the fraction of molecules recaptured into the MOT after a π pulse on $|0, 1, 1\rangle \leftrightarrow |1, 2, 2\rangle$ as a function of the microwave frequency with $t_\pi = 70 \mu\text{s}$. On resonance, 17.9(3) % of the molecules in the initial MOT are transferred to the state $|1, 2, 2\rangle$. Comparing this to the fraction of molecules that are transferred in the first pulse, we can see that the second microwave transition has an efficiency of 76(2) %.

Finally, with the molecules prepared in the state $|0, 1, 0\rangle$, we drive the transition $|0, 1, 0\rangle \leftrightarrow |1, 1^+, 1\rangle$ after the blow away. The fraction of molecules recaptured into the MOT is shown in figure 4.1e as a function of the microwave frequency for a π pulse of length $t_\pi = 50 \mu\text{s}$. This transition is magnetically sensitive and so has a smaller efficiency.

4.1.2 Rb

The Rb atoms are loaded into the magnetic trap in a two step process. First the atoms are held in a red-detuned optical molasses. Over a period of 10 ms, the detuning of $\mathcal{L}_{\text{Rb}}^{\text{C}}$ is ramped to -48 MHz and the intensity is decreased by a factor of 10. At the end of the ramp, the temperature of the atoms is $40 \mu\text{K}$.

To prepare the atoms in a magnetically trappable state, we use the laser $\mathcal{L}_{\text{Rb}}^{\text{OP}}$, which is resonant with the transition $F = 2 \rightarrow F' = 2$, to optically pump the atoms. A 230 mG field is applied along the direction of propagation of the beam to define the quantization axis. By using a combination of a half-wave plate and quarter-wave plate, the polarization of the beam is fixed so that only σ^+ transitions can be driven. The repump light, $\mathcal{L}_{\text{Rb}}^{\text{R}}$, is kept on to repump any atoms that decay into the $F = 1$ level in the ground state. After scattering a few photons, the atoms should be transferred to the stretched state $|F = 2, m_F = 2\rangle$.

4.1.3 Magnetic trapping and imaging

Once the atoms and molecules are prepared in the desired state, the MOT coils are turned back on, with all light turned off, to create a magnetic quadrupole trap with an axial field gradient of 30 G cm^{-1} . The atoms and molecules remain in the trap for a variable time, t , after which the field is turned off. The final step is to measure the number of molecules that remain. This is done by recapturing the molecules in a MOT. For experiments with molecules in $N = 1$, we simply turn the MOT back on. For experiments done with molecules in $N = 0$, we first transfer them back to $N = 1$ using a microwave π pulse, and then turn the MOT back on. Fluorescence imaging is then used to determine the number of molecules remaining, $N_{\text{CaF}}(t)$. We also record the number of atoms remaining, $N_{\text{Rb}}(t)$, by absorption imaging. In the following measurements, we load up to around 1.5×10^9 atoms and 1×10^3 molecules into the magnetic trap.

4.2 Collision measurements

To reduce the shot-to-shot fluctuation in the number of molecules trapped in the MOT, we normalize our measurements of molecule number after the magnetic trap by calculating the ratio

$$r_{\text{CaF}}(t) = \frac{N_{\text{CaF}}(t)}{N_{\text{CaF}}^{\text{MOT}}}. \quad (4.2)$$

Since the density of atoms in the trap is six orders of magnitude larger than that of the molecules, we can neglect the loss of molecules due to inelastic molecule-molecule collisions. Under this approximation, we can write the evolution of the ratio $r_{\text{CaF}}(t)$ as

$$\dot{r}_{\text{CaF}}(t) = \left(-\Gamma_{\text{CaF}}^0 - \Gamma_{\text{CaF-Rb}} e^{-\Gamma_{\text{Rb}} t} \right) r_{\text{CaF}}(t) \quad (4.3)$$

where the first term in the brackets accounts for the single-body loss of molecules from the trap in the absence of atoms and the second term comes from the loss of molecules due to inelastic collisions with the atoms. The exponential factor in the second term models the loss of atoms

over time in the magnetic trap. This is motivated by our observation that the number of atoms in the trap fits well to an exponential decay, suggesting that the loss of atoms is dominated by single-body loss due to collisions with background gas.

We also find that in the absence of atoms the number of molecules decays exponentially, due to both collisions with background gas and vibrational excitation by blackbody radiation. The single-body decay rates of both species, Γ_{Rb} and Γ_{CaF}^0 , vary negligibly between experiments. These rates are calculated by fitting exponential decays, as shown in figure 4.2, and are found to be $\Gamma_{\text{Rb}} = 0.313(5) \text{ s}^{-1}$ and $\Gamma_{\text{CaF}}^0 = 0.35(1) \text{ s}^{-1}$.

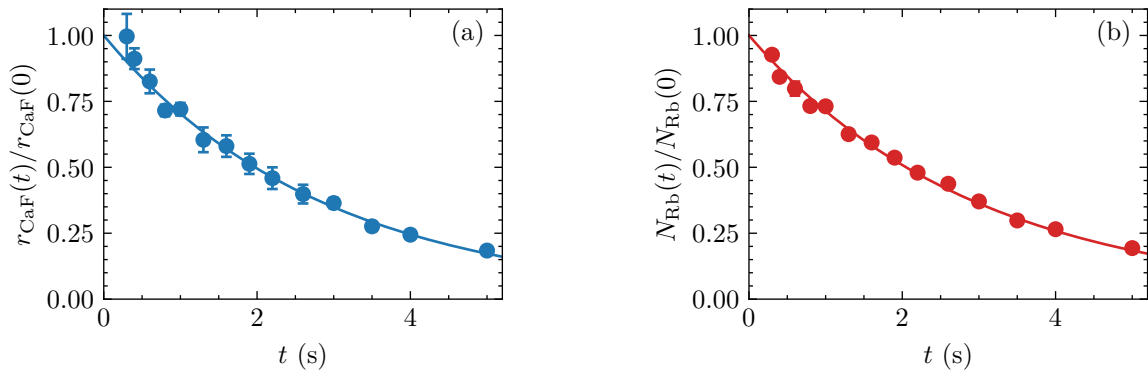


Figure 4.2: Loss of (a) CaF and (b) Rb in the magnetic trap in the absence of the other species. Lines are fits to single exponential decays.

The solution of equation 4.3 is given by

$$r_{\text{CaF}}(t) = r_{\text{CaF}}(0) \exp\left(-\Gamma_{\text{CaF}}^0 t - \frac{\Gamma_{\text{Rb-CaF}}}{\Gamma_{\text{Rb}}} (1 - e^{-\Gamma_{\text{Rb}} t})\right). \quad (4.4)$$

By fitting dual-species data to this model, we can extract the loss rate of CaF due to Rb, $\Gamma_{\text{Rb-CaF}}$, with this and $r_{\text{CaF}}(0)$ as free parameters. An example for the state $|1, 2, 2\rangle$ is shown in figure 4.3, where we determine the loss rate to be $\Gamma_{\text{Rb-CaF}} = 0.368(44) \text{ s}^{-1}$.

4.2.1 Loss rate coefficient measurement

The collision-induced loss rate of CaF, $\Gamma_{\text{Rb-CaF}}$, can be written as

$$\Gamma_{\text{Rb-CaF}} = k_2 N_{\text{Rb}}(t=0) \int f_{\text{Rb}}(\mathbf{r}) f_{\text{CaF}}(\mathbf{r}) d^3r = k_2 n_{\text{Rb}}^{\text{eff}}, \quad (4.5)$$

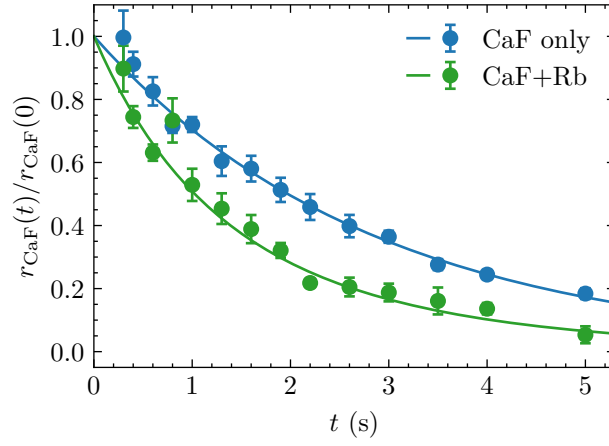


Figure 4.3: Fraction of CaF molecules left after hold time t in the magnetic trap in the presence of Rb (green) or alone (blue). Each point is the mean and standard deviation of six measurements. The solid lines are a fit to a single exponential decay for CaF only and a fit to equation 4.4 for CaF in the presence of Rb. The molecules are in state $|1, 2, 2\rangle$ while the atoms are in state $|2, 2\rangle$.

where the factor k_2 is the inelastic loss rate coefficient and $f_s(\mathbf{r})$ is the density distribution of species s normalized such that

$$\int f_s(\mathbf{r}) d^3r = 1. \quad (4.6)$$

In equation 4.5, we have defined the quantity

$$n_{\text{Rb}}^{\text{eff}} = N_{\text{Rb}}(t=0) \int f_{\text{Rb}}(\mathbf{r}) f_{\text{CaF}}(\mathbf{r}) d^3r, \quad (4.7)$$

which is a measure of the effective density of Rb, taking into account the overlap of the two clouds. Some care must be taken to calculate this overlap integral. In thermal equilibrium in a trap with potential $U(\mathbf{r})$, the distribution of each species will be distributed according to the Boltzmann distribution

$$f(\mathbf{r}) \propto \exp\left(-\frac{U(\mathbf{r})}{k_B T}\right). \quad (4.8)$$

In the magnetic quadrupole trap, the potential experienced by an atom or molecule with magnetic moment μ , including gravity, is given by

$$U(x, y, z) = \mu b \sqrt{\frac{x^2 + y^2}{4}} + z^2 + mgz, \quad (4.9)$$

where b is the axial field gradient and g is the acceleration due to gravity which acts in the $-z$ direction. With this potential, the spatial distribution is given by

$$f(x, y, z) \propto \exp\left(-\frac{\mu b}{k_B T} \sqrt{\frac{x^2 + y^2}{4} + z^2} - \frac{mg}{k_B T} z\right). \quad (4.10)$$

We can then define

$$\ell = \frac{k_B T}{\mu b}, \quad \gamma = \frac{mg}{\mu b}, \quad (4.11)$$

and normalize the distribution to find

$$f(x, y, z) = \frac{(\gamma^2 - 1)^2}{32\pi\ell^3} \exp\left(-\sqrt{\frac{x^2 + y^2}{4\ell^2} + \frac{z^2}{\ell^2}} - \gamma\frac{z}{\ell}\right). \quad (4.12)$$

Integrating this along x and y , we get the profile along z

$$g(z) = \frac{(\gamma^2 - 1)^2}{4\ell} \left(1 + \frac{|z|}{\ell}\right) \exp\left(\frac{-|z| - \gamma z}{\ell}\right). \quad (4.13)$$

We find experimentally that the axial profiles of the atoms and molecules after the magnetic trap fit reasonably well to this model, in spite of the fact that the molecules are unlikely to have thermalized in the trap. The equivalent profile for the radial direction has no known analytical form, however we find that the radial profiles fit well to Gaussian distributions given by

$$h(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{x^2}{2\sigma^2}\right). \quad (4.14)$$

We therefore approximate the distribution of each species as

$$f_s(x, y, z) = h_s(x)h_s(y)g_s(z). \quad (4.15)$$

Figure 4.4 shows the images of the CaF and Rb clouds after 300 ms in the magnetic trap, along with the profiles along x and z and fits to $h_s(x)$ and $g_s(z)$ respectively. This allows us to

compute the overlap integral analytically:

$$\int f_{\text{Rb}}(\mathbf{r}) f_{\text{CaF}}(\mathbf{r}) d^3r = \frac{A_{\text{Rb}}^2 A_{\text{CaF}}^2 \bar{\ell} \left[C^2 (4\bar{\ell}^2 - 3\ell_{\text{Rb}}\ell_{\text{CaF}}) - 4\bar{\ell}^2 (4\bar{\ell}^2 + \ell_{\text{Rb}}\ell_{\text{CaF}}) \right]}{4\pi(\sigma_{\text{Rb}}^2 + \sigma_{\text{CaF}}^2)(2\bar{\ell} + C)^3 (B_{\text{Rb}}\ell_{\text{CaF}} + B_{\text{CaF}}\ell_{\text{Rb}})^3} \quad (4.16)$$

where

$$A_s = \gamma_s^2 - 1, \quad B_s = \gamma_s - 1, \quad C = \gamma_{\text{Rb}}\ell_{\text{CaF}} + \gamma_{\text{CaF}}\ell_{\text{Rb}}, \quad \bar{\ell} = \frac{\ell_{\text{Rb}} + \ell_{\text{CaF}}}{2}. \quad (4.17)$$

In the following measurement, the value of the overlap integral varies in the range 3.1 cm^{-3} to 4.2 cm^{-3} .

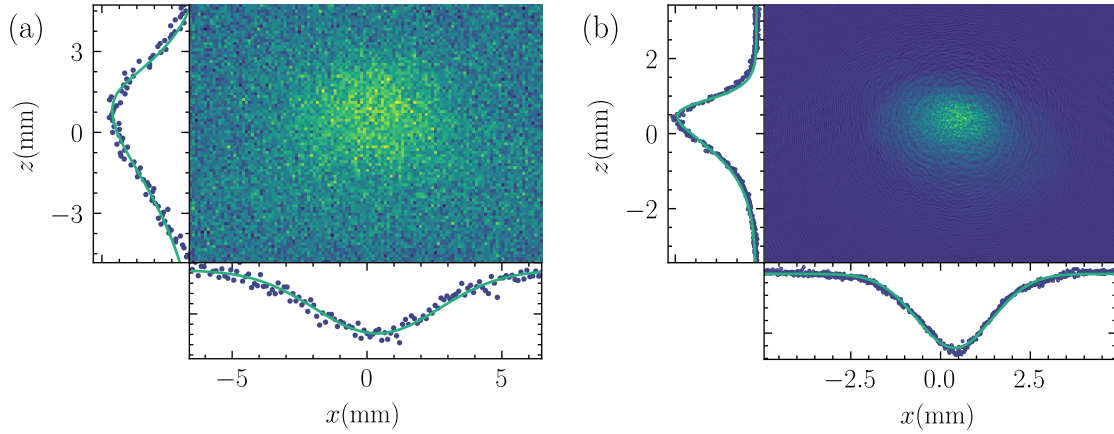


Figure 4.4: Fluorescence images of (a) CaF and (b) Rb after 300 ms in the magnetic trap. Plots are profiles in x and z directions. Solid lines are fits to $h_s(x)$ and $g_s(z)$ from the main text.

To determine the inelastic loss rate coefficient k_2 we perform loss rate measurements for different loading durations of the Rb MOT. This varies both the number of Rb atoms loaded into the trap (N_{Rb}) and the size of the cloud in the magnetic trap, leading to different values of the effective density ($n_{\text{Rb}}^{\text{eff}}$). For each measurement, we measure N_{Rb} and fit the axial and radial distributions of the atom and molecule clouds with the functional forms given in equations 4.13 and 4.14. Using the values of the fit parameters ($\gamma_s, \ell_s, \sigma_s$ with $s \in \{\text{Rb}, \text{CaF}\}$), we calculate the overlap integral using equation 4.16 which allows us to determine the $n_{\text{Rb}}^{\text{eff}}$ using equation 4.7. The result of plotting the loss rate $\Gamma_{\text{Rb-CaF}}$ for different values of $n_{\text{Rb}}^{\text{eff}}$ is shown in figure 4.5 for molecules in the state $|1, 2, 2\rangle$. By fitting a straight line to the data we find the loss rate

coefficient to be $k_2 = (6.6 \pm 1.5) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. The uncertainty in this value is found using a bootstrapping procedure detailed in [159].

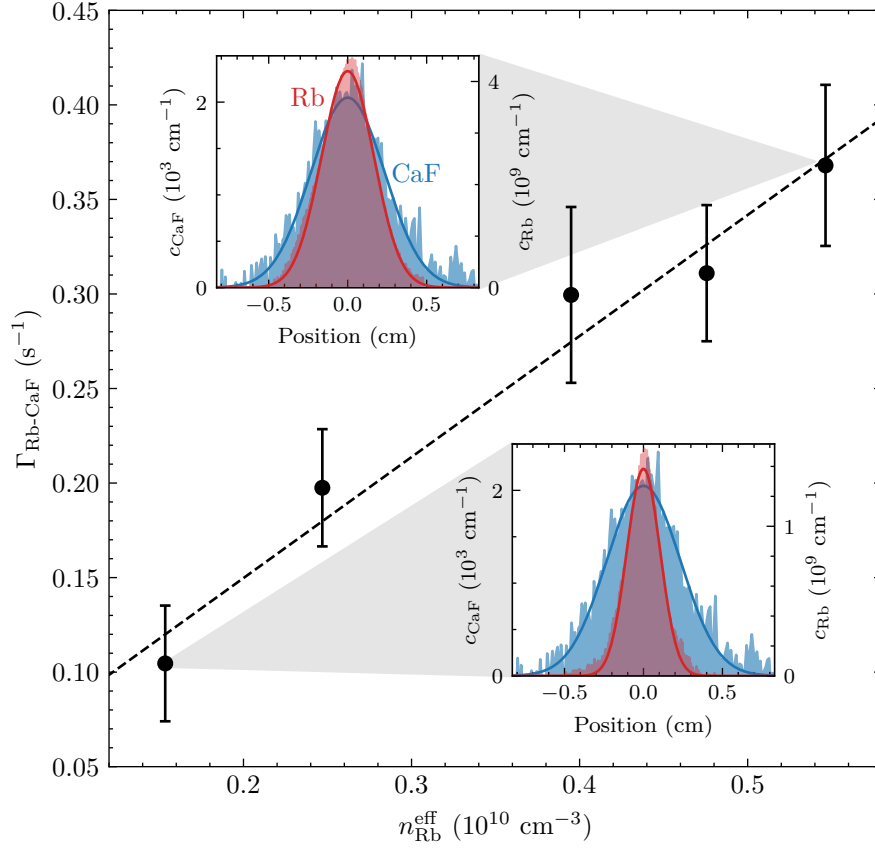


Figure 4.5: Loss rate, $\Gamma_{\text{Rb-CaF}}$, of CaF molecules in the state $|1, 2, 2\rangle$ due to Rb versus effective density of Rb, $n_{\text{Rb}}^{\text{eff}}$. The dashed line is a linear fit. Insets show radial distributions of CaF and Rb clouds, $c_s = \int f_s(x, y, z) dy dz$, for the points indicated.

4.2.2 Loss rates in different molecular states

In our measurement of the loss rate above, both the atoms and the molecules were prepared in spin-stretched states. Previous studies have found inelastic collisions between molecules and atoms can be greatly suppressed in this arrangement [76, 160]. To test whether this is the case here, we initialize the molecules in the state $|1, 1^+, 1\rangle$ which is not spin-stretched and measured the loss rate as before. From the data presented in figure 4.6, we find that the loss rate coefficient for this state is $k_2 = (5.7 \pm 1.8) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, close to the value found for $|1, 2, 2\rangle$, which suggests that the inelastic loss does not depend strongly on the hyperfine state in the $N = 1$ manifold.

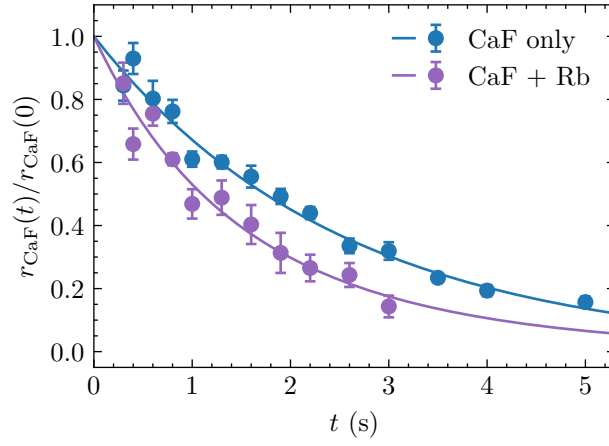


Figure 4.6: Loss of CaF molecules prepared in the state $|1, 1^+, 1\rangle$ with and without Rb present.

A clear difference in behaviour is seen when the molecules are prepared in the state $|0, 1, 1\rangle$, as shown in figure 4.7. The loss rate coefficient in this state is found to be consistent with zero and has an upper limit of $k_2 < 5.8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, with 95% confidence. This is at least an order of magnitude lower than for the states in the $N = 1$ rotational manifold.

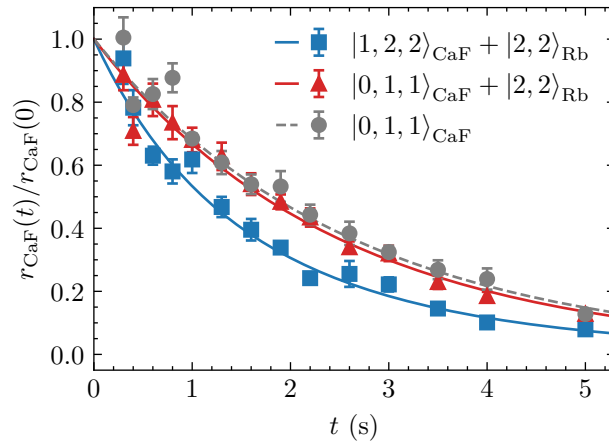


Figure 4.7: Loss of CaF molecules prepared in different states. Red and blue solid lines are fits to equation 4.4 in the main text and the gray dashed line is a fit to a single exponential.

The far larger inelastic collision rates in the $N = 1$ manifold compared to the $N = 0$ manifold suggest that collisions which change the rotational state of the molecule are the dominant collisional loss mechanism. For states in the $N = 1$ manifold, these collisions are energetically allowed and release $\sim 1 \text{ K}$ of energy, which is far greater than the trap depth of 1.5 mK . In addition, at the end of the collision the molecule will end up in the $N = 0$ manifold, which will not be detected by our imaging procedure. For both these reasons, molecules involved in rotation-changing collisions will be lost. Conversely, in the $N = 0$ manifold rotation-changing

collisions are energetically forbidden and so the only open loss channel from the state $|0, 1, 1\rangle$ is spin relaxation. Thus, our results show that loss by spin relaxation is at least an order of magnitude slower than by rotation-changing collisions.

4.2.3 Looking for thermalization

The relatively small inelastic loss rate in the state $|0, 1, 1\rangle$ is promising for the prospect of sympathetic cooling. However, to further investigate the potential of this approach, we need to measure the rate of thermalization due to elastic collisions. Since the atoms and molecules are loaded into the trap with temperatures T_{Rb} and T_{CaF} respectively, we can expect the difference in the temperatures of the two species $\Delta T = T_{\text{CaF}} - T_{\text{Rb}}$ to change according to [76, 161]:

$$\frac{d(\Delta T)}{dt} = -\Gamma_{\text{th}}\Delta T, \quad (4.18)$$

where Γ_{th} is the rate of thermalization. This can be related to the rate of elastic collisions between the two species Γ_{el} by

$$\Gamma_{\text{th}} = \frac{\eta}{3}\Gamma_{\text{el}}. \quad (4.19)$$

The quantity η is a dimensionless constant that parameterizes the average amount of energy transferred by each collision and is defined to be

$$\eta = \frac{4m_{\text{Rb}}m_{\text{CaF}}}{(m_{\text{Rb}} + m_{\text{CaF}})^2}, \quad (4.20)$$

such that $3/\eta \approx 3.1$ is the number of collisions per particle needed for thermalization. The elastic collision rate can be further broken down into

$$\Gamma_{\text{el}} = n_{\text{Rb}}^{\text{eff}}\sigma_{\text{el}}\bar{v}_{\text{rel}}, \quad (4.21)$$

where $n_{\text{Rb}}^{\text{eff}}$ is the effective density of Rb defined as before, σ_{el} is the elastic collision cross-section and $\bar{v}_{\text{rel}}$ is the mean relative velocity. Assuming the distribution of velocities of each species is

close to a Boltzmann distribution, v_{rel} is given by

$$\bar{v}_{\text{rel}} = \sqrt{\frac{8k_{\text{B}}}{\pi} \left(\frac{T_{\text{Rb}}}{m_{\text{Rb}}} + \frac{T_{\text{CaF}}}{m_{\text{CaF}}} \right)}. \quad (4.22)$$

The experimental procedure is the same as outlined before for the inelastic collision measurements¹ except now we measure the temperature of the atoms and molecules when they are released from the trap by ballistic expansion. An example measurement for CaF is shown in figure 4.8 after a hold time of 0.6 s in the magnetic trap. From the linear fits to the radial and axial sizes, we find temperatures of 216(41) μK and 172(13) μK , respectively.

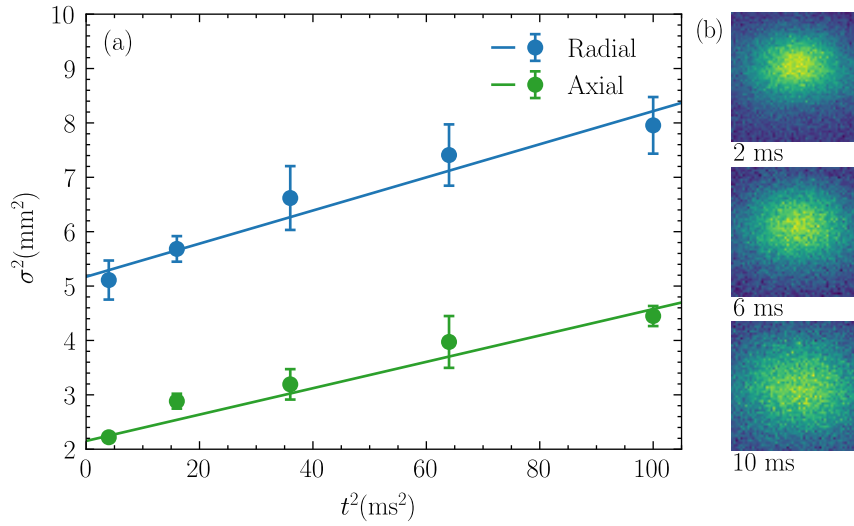


Figure 4.8: Temperature measurement of CaF molecules by ballistic expansion after the magnetic trap: (a) points and error bars are from 4 repeat measurements; solid lines are linear fits. (b) shows images of the cloud after different expansion times, integrated over the 4 experimental runs.

Figure 4.9 shows an attempt to observe thermalization between the two species. For CaF molecules alone in the trap, the heating rate is consistent with zero, as found in a similar setup in our group [108]. When trapped in the presence of colder Rb atoms, the temperature of the molecules remains constant within the uncertainties.

Although no thermalization is observed, it is instructive to calculate the maximum value of the

¹A new optical pumping scheme was implemented prior to this measurement which resulted in more efficient loading of the magnetic trap. Further detail can be found in [150].

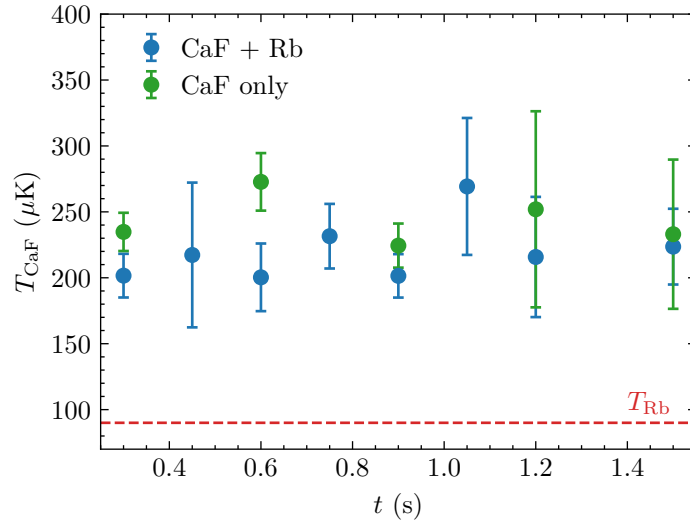


Figure 4.9: Temperature of CaF molecules alone (blue) and co-trapped with Rb atoms (green) in the magnetic trap as a function of hold time. The points and error bars are mean and standard error from 4 experimental runs. The dotted red line shows the temperature of the Rb atoms which remains constant throughout.

elastic cross-section (σ_{el}) that would be consistent with this data, assuming that there is no heating in the trap. Since the change in temperature difference is small, we can assume that the mean relative velocity $\bar{v}_{\text{rel}}$ remains roughly constant. As before, the effective density of Rb changes due to the loss of atoms from the trap and we again model this as an exponential decay, giving

$$\frac{d(\Delta T)}{dt} = -\Gamma_{\text{th}}^0 \exp(-\Gamma_{\text{Rb}} t) \Delta T \quad (4.23)$$

where Γ_{th}^0 is the initial rate of thermalization. Solving for the temperature of the molecules, we obtain

$$T_{\text{CaF}}(t) = (T_{\text{CaF}}^0 - T_{\text{Rb}}) \exp \left[-\frac{\Gamma_{\text{th}}^0}{\Gamma_{\text{Rb}}} (e^{-\Gamma_{\text{Rb}} t} - 1) \right] + T_{\text{Rb}}. \quad (4.24)$$

With Γ_{Rb} and T_{Rb} fixed to their separately determined values of $0.313(5) \text{ s}^{-1}$ and $90 \mu\text{K}$, respectively, the largest value of Γ_{th}^0 consistent with the data in figure 4.9 is $\Gamma_{\text{th}}^0 = 0.05 \text{ s}^{-1}$. This would correspond to a elastic cross-section of approximately $1 \times 10^{-12} \text{ cm}^2$.

For comparison, the elastic cross-section used in [137] for modelling sympathetic cooling of CaF with Rb atoms is roughly $\sigma_{\text{el}} \approx 3.6 \times 10^{-12} \text{ cm}^2$. We can also compare our estimate to the value found for collisions of NaLi with Na given by $\sigma_{\text{el}} \approx 2.4(5) \times 10^{-11} \text{ cm}^2$ [76]. This, coupled with the low inelastic rate coefficient of $k_2 = (4.0 \pm 1.3) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, was sufficient for very

effective sympathetic cooling.

However, since no thermalization was observed in our experiment, it is impossible to determine anything about the elastic collisions between the two species with confidence. As a result, further work is needed in order to be able to study inter-species elastic collisions. In order to do this, there are two main way that our experiments could be improved.

Firstly, the number of molecules trapped could be increased. This would allow us to make measurements at longer hold times with acceptable accuracy due to a better signal-to-noise ratio. One technique to increase the number of trapped molecules is transverse cooling of the molecular beam which will be explored in chapter 5.

Secondly, the effective density of Rb, $n_{\text{Rb}}^{\text{eff}}$, can be increased, which will speed up the rate of collisions, both elastic and inelastic. Due to the relative sizes and differential gravitational sag of the two clouds in the magnetic trap, $n_{\text{Rb}}^{\text{eff}}$ is largely limited by the overlap between the two species. This would be improved in a trap with greater confinement, such as an optical dipole trap, which is implemented in chapter 6.

Chapter 5

Transverse cooling of CaF

The beam of CaF molecules that exits the cryogenic buffer gas source diverges as it travels towards the main chamber. This divergence reduces the total flux of molecules that reach the capture region of the MOT. By reducing the spread of transverse velocities, transverse cooling produces a collimated beam of molecules, which increases the fraction of molecules that can be captured.

Transverse cooling was originally applied to atoms to increase the radiant intensity or ‘brightness’ of atomic beams [162, 163]. Later it was extended to molecules, with the first demonstration of laser cooling of molecules being transverse cooling of a beam of SrF [100]. Since then transverse cooling has been adapted to a wide range of molecules including YbF in 1D [164] and 2D [165] and polyatomic molecules such as SrOH [166] and YbOH [167].

In this chapter, we present the results of applying transverse cooling to the beam of CaF molecules that is used to load the MOT. Transverse cooling of the molecules is first demonstrated in 1D, however no increase in molecules captured into the MOT is observed in this case. The transverse cooling setup is then extended to cool the molecules in 2D, and the number of molecules captured in the MOT is increased by a factor of 3.5. The cooling process is simulated by solving the optical Bloch equations to gain an understanding of the underlying mechanisms.

5.1 1D cooling

5.1.1 Setup

The light used for transverse cooling is derived from a 5 W laser from *Azurlight Systems* operating at 531 nm, close to the $B \leftarrow X$ transition in CaF. An electro-optic modulator (EOM) is used to add sidebands to the light to address the hyperfine components of the ground state. The EOM is driven at 72 MHz with enough RF power to produce 1st order sidebands with the same intensity as the carrier and a scanning Fabry-Perot cavity is used to monitor the modulation. The light is then coupled into a polarization-maintaining single mode fibre to bring it over to the experiment.

At the experiment, the light from the fibre is collimated to produce a beam with a $1/e^2$ diameter of 3.7 mm. The beam passes through two cylindrical lenses (with focal lengths of $f_1 = 30$ mm and $f_2 = 300$ mm) in a telescope configuration to expand the beam in one dimension. After this, the beam is elliptical with $1/e^2$ axes of 37 mm and 3.7 mm. The beam is then directed into the molecular beam through a circular viewpoint located 170 mm away from the aperture of the buffer gas source and retro-reflected with a mirror. The major axis of the intensity profile is aligned along the direction of the beam, as shown in figure 5.1, so that the time spent by the molecules in the cooling region is maximized.

The slowing beam is turned off for these experiments to allow us to see the effect of transverse cooling on the beam without any additional effects due to slowing. However, the slowing repump laser ($\mathcal{L}_{10}^S$) is kept on to repump any molecules that may be transferred to the $v = 1$ level during transverse cooling.

To detect the molecules, two CCD cameras are placed along the beam. The first (CCD1) is positioned at the transverse cooling region and collects the fluorescence of the molecules due to the transverse cooling light. This is used to perform spectroscopy to deduce the frequency of the cooling light relative to the transition. The second CCD (CCD2) images the fluorescence of the molecules in the MOT beams, allowing us to measure both the number of molecules

reaching the MOT region and the transverse profile of the beam.

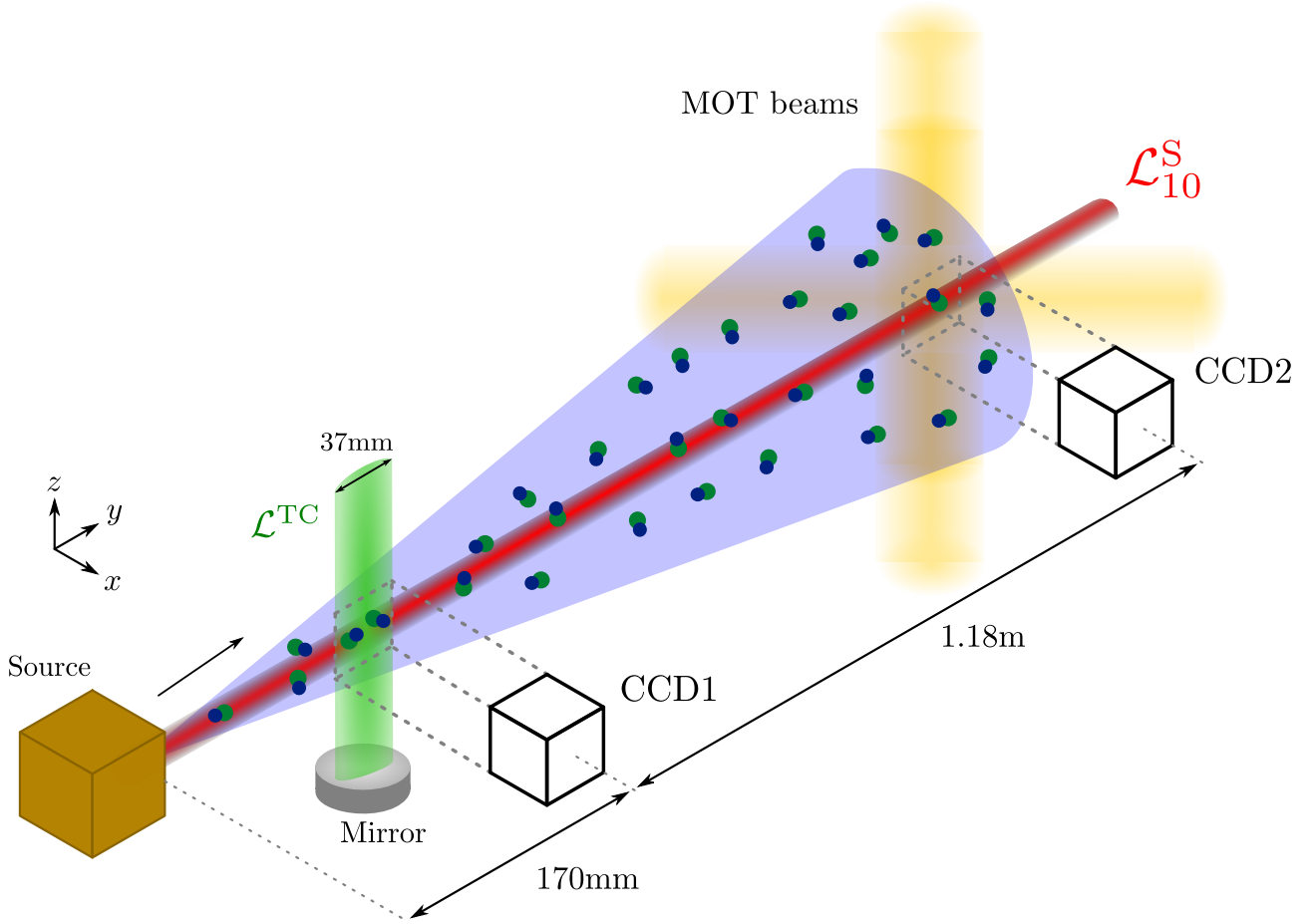


Figure 5.1: Schematic of transverse cooling setup: The CaF molecules exit the source as a diverging beam and travel a short distance to the transverse cooling region. They interact with the transverse cooling light and the fluorescence is collected by CCD1. The molecules then proceed to the main chamber where they are imaged in the MOT beams by CCD2. The slowing repump, $\mathcal{L}_{10}^S$, remains on during the transverse cooling stage to repump any molecules that decay to $v = 1$.

All of the laser frequencies used to repump the vibrational levels detailed in chapter 3 are present in the MOT beams and the beams are apertured down to a diameter of a few millimeters. The frequency of the MOT beams are tuned so that the vertical MOT beam is resonant with the molecules. The high longitudinal velocity of the molecular beam of around 140 m s^{-1} ensures that the other MOT beams, which propagate at 45° to the molecular beam, are Doppler shifted out of resonance by approximately $\pm 163 \text{ MHz}$.

Figure 5.2 shows the fluorescence detected from CCD1 and CCD2 as a function of time after the YAG pulse. In the results that follow, CCD1 is triggered at $t = 1 \text{ ms}$ with an exposure time of 1 ms and CCD2 is exposed at $t = 5 \text{ ms}$ for 5 ms . The green dashed line in figure 5.2a shows

the time at which the slowing light would usually turn on. This means the vast majority of the molecules would have passed through the transverse cooling region by the time the slowing turns on and there should be no effect of the slowing beam on the molecules while they are in the cooling region.

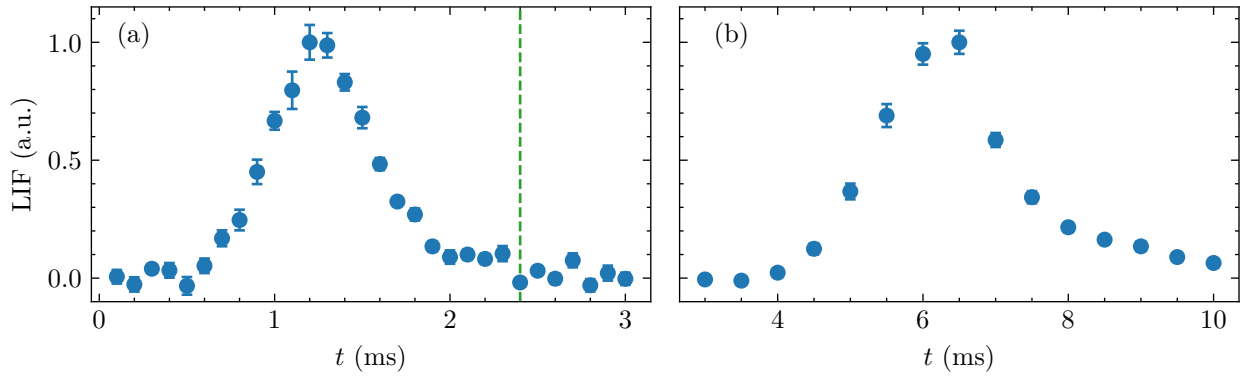


Figure 5.2: Integrated fluorescence at (a) CCD1 and (b) CCD2 at time t after the YAG pulse. Each point and error bar is the mean and standard error of 10 iterations. The green dashed line shows when the slowing light would ordinarily be turned on for loading the MOT.

5.1.2 Results

Figure 5.3a shows the profile of the fluorescence of the molecular beam in the MOT beams with the transverse cooling laser off, as imaged by CCD2. The width of the transverse distribution without cooling is very broad and fills up the entire field of view vertically. When the transverse cooling laser is on, we see the distribution change as the frequency is tuned. At certain frequencies, we see a depletion of molecules at the centre of the beam and increased flux on either side of the central region, as shown in figure 5.3b, and at others we see a concentration of molecules in the centre of the beam, as seen in figure 5.3c.

In order to quantify this effect, we calculate the fraction of the total fluorescence (N_c/N_{tot}) contained in an area of $4.13 \text{ mm} \times 9.66 \text{ mm}$ at the centre of the image, indicated by the white dashed lines in figures 5.3b and 5.3c. This is shown in figure 5.3d, along with the total fluorescence detected at the cooling region, measured with CCD1. The detuning, Δ , was chosen relative to the frequency of maximum fluorescence in the cooling region. Around the peaks in fluorescence at $\Delta = 0 \text{ MHz}$ and $\Delta = -75 \text{ MHz}$, we see that the fraction of molecules in the

central region is depleted when the light is red-detuned relative to the peak and increases when the light is blue-detuned.

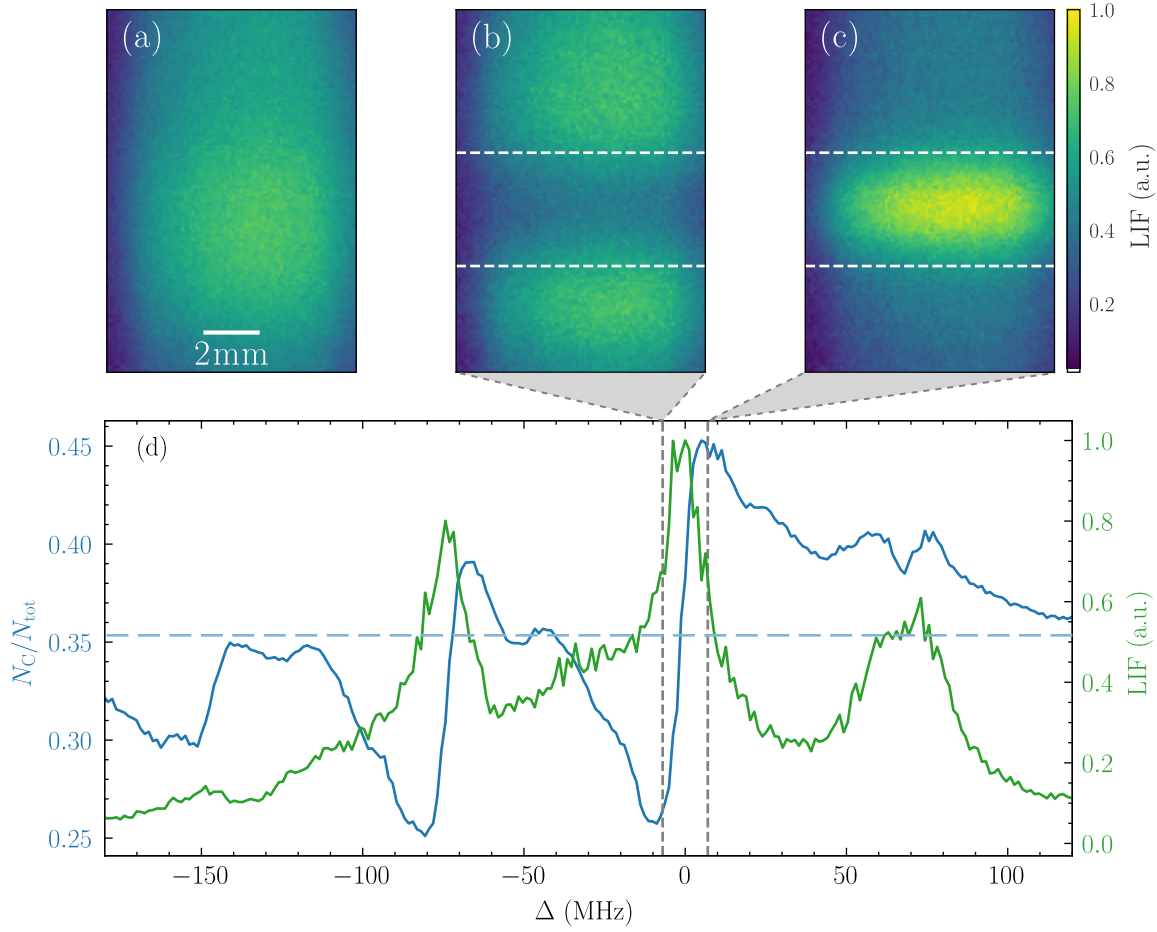


Figure 5.3: Transverse cooling of the beam in 1D: (a) Image of the beam at CCD2 with no cooling light applied. (b,c) Images of the beam at CCD2 with transverse cooling light at $\Delta = -7$ MHz and 7 MHz, respectively. (d, blue) Integrated fluorescence in the region indicated by the white dashed lines in (b-c) normalized by the total fluorescence at CCD2 as a function of detuning. The blue dashed line shows the value of this ratio when no cooling is applied. (d, green) Total fluorescence at the transverse cooling region, as measured by CCD1, as a function of detuning.

As shown in figure 5.4, the hyperfine structure of both the X and B states leads to a number of transitions displaced from each other by frequencies on the order of a few natural linewidths ($\Gamma = 2\pi \times 6.4$ MHz). This makes it difficult to disentangle the mechanisms involved with the cooling, as, at different detunings, a single frequency component may be red-detuned of one transition but similarly blue-detuned of another. Nevertheless, we see from the figure that when Δ is just a few MHz, the frequency components of the light are blue-detuned from their nearest transition for $\Delta > 0$ and red-detuned for $\Delta < 0$. Thus, figure 5.3 suggests that we

see enhancement in the central region for blue-detuned light and a depletion for red-detuned light. In order to better understand the effects of our cooling scheme, it is necessary to perform simulations to model the effects of the light on the cooling.

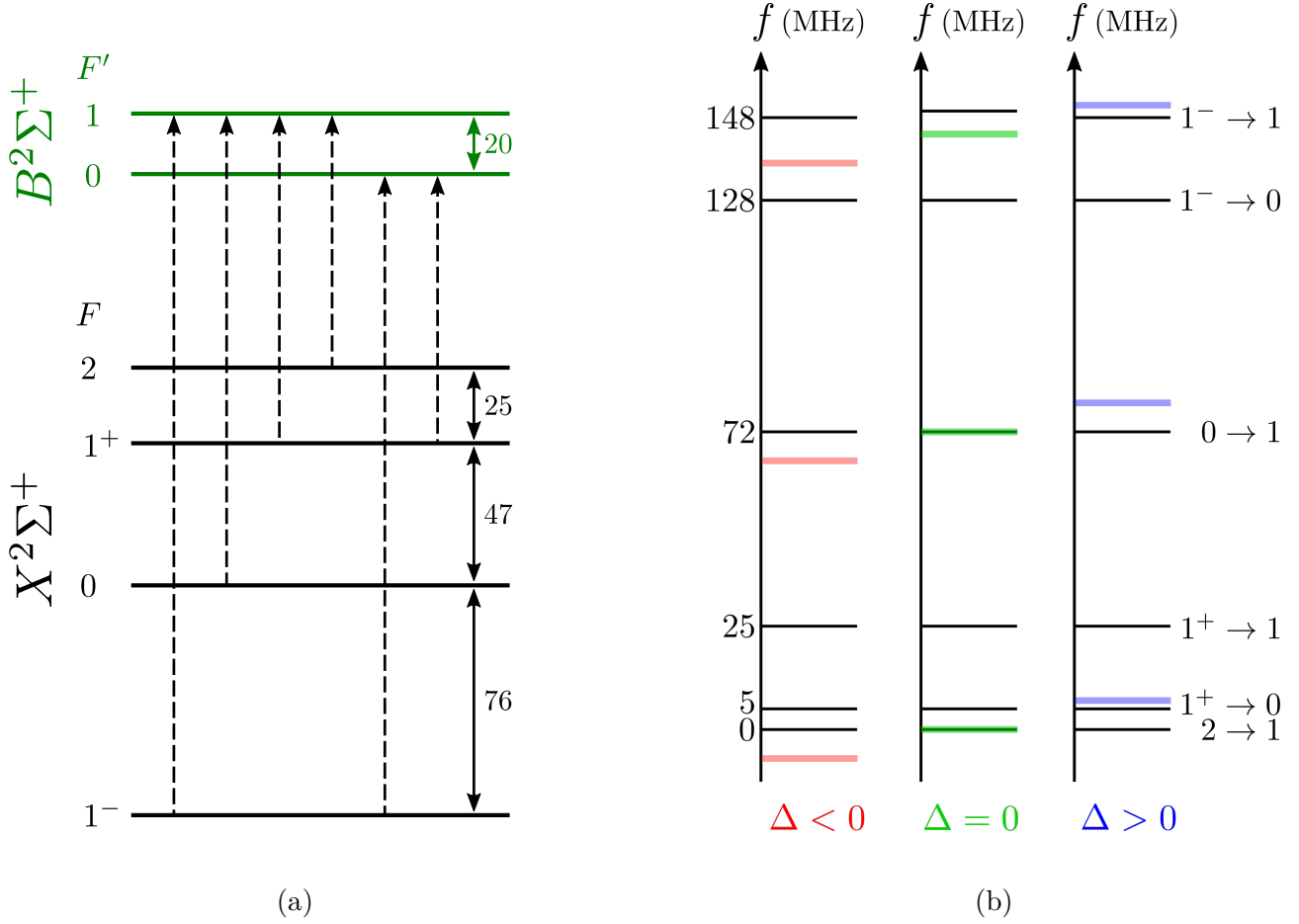


Figure 5.4: Energy levels and frequency structure of the cooling transition (a) Hyperfine structure of the X and B states labelled by the total angular momentum F . The allowed transitions are indicated with the arrows and the energy spacing between the levels is given in units of $h \times \text{MHz}$ (b) Frequencies of the six allowed transitions and the frequency components of the transverse cooling light at detunings of $\Delta = -7 \text{ MHz}$ (red), 0 MHz (green) and 7 MHz (blue).

5.1.3 Simulations

To simulate the effect of the transverse cooling, we solve the optical Bloch equations (OBEs) for a molecule being dragged through the appropriate laser field at a constant velocity, $\mathbf{v}$, as described in [135], following the treatment of Gordon and Ashkin [168] and Ungar et al. [123]. The Hamiltonian of the system (ignoring the centre of mass motion which will be treated

classically) is given by

$$H = H_{\text{mol}} + H_{\text{f}} + H_{\text{int}}, \quad (5.1)$$

where

$$H_{\text{mol}} = \sum_i \hbar \omega_i |i\rangle\langle i|, \quad (5.2)$$

$$H_{\text{f}} = \frac{1}{2} \int \left(\epsilon_0 \mathbf{E}^2 + \frac{\mathbf{B}}{\mu_0} \right) d^3r, \quad (5.3)$$

and

$$H_{\text{int}} = -\mathbf{d} \cdot \mathbf{E} - \boldsymbol{\mu} \cdot \mathbf{B}. \quad (5.4)$$

Here $|i\rangle$ are the internal states of the molecule each with energy $\hbar \omega_i$, $\mathbf{E}$ and $\mathbf{B}$ are the electric and magnetic field operators and $\mathbf{d}$ and $\boldsymbol{\mu}$ are the electric and magnetic dipole moment operators. The magnetic field is taken to be constant and we expand the electric field as

$$\mathbf{E}(\mathbf{r}, t) = \sum_{\mathbf{k}} \left(\mathbf{E}_{\mathbf{k}}(\mathbf{r}) e^{-i\omega_{\mathbf{k}}t} + \mathbf{E}_{\mathbf{k}}^\dagger(\mathbf{r}) e^{i\omega_{\mathbf{k}}t} \right). \quad (5.5)$$

It is convenient to work in the Heisenberg picture and define the molecular operators

$$\sigma_{ij} = e^{-i(\omega_i - \omega_j)t} |i\rangle\langle j|. \quad (5.6)$$

The operators $\mathbf{d}$ and $\boldsymbol{\mu}$ can be written in terms of the molecular operators as

$$\mathbf{d} = \sum_{i,j} \langle i|\mathbf{d}|j\rangle \sigma_{ij} e^{i(\omega_i - \omega_j)t} \quad (5.7)$$

and

$$\boldsymbol{\mu} = \sum_{i,j} \langle i|\boldsymbol{\mu}|j\rangle \sigma_{ij} e^{i(\omega_i - \omega_j)t}. \quad (5.8)$$

The OBEs can be found from the Heisenberg equation of motion

$$\frac{d\sigma_{ij}}{dt} = \frac{i}{\hbar} [H, \sigma_{ij}], \quad (5.9)$$

where the decay terms are introduced via the radiation reaction approximation by adding a reaction field to the electric field operator given by

$$\mathbf{E}_{\text{RR}} = \frac{1}{6\pi\epsilon_0 c^3} \frac{d^3 \mathbf{d}}{dt^3} \approx \frac{ik^3}{6\pi\epsilon_0} \mathbf{d}. \quad (5.10)$$

In the final step, we have replaced the wave vectors for the individual laser fields by a single wave vector, k .

The OBEs derived in this way can be found in [135] in full. We then round the transition frequencies (ω_i) and the laser frequencies ($\omega_{\mathbf{k}}$) to multiples of ω_{min} and the components of the velocity to multiples of ω_{min}/k , where $\omega_{\text{min}} = 10^{-2}\Gamma$. This ensures the equations are periodic with period $\mathcal{T}$, given by $\mathcal{T} = 2\pi/\omega_{\text{min}}$. As a result, it can be proven that the solutions to these equations will reach a periodic quasi-steady state with the same period $\mathcal{T}$, after any transients relating to the initial conditions die away [169].

We solve the rounded OBEs, starting with the molecule in the maximally mixed state over the ground sub-levels. After propagating our solution for a long time ($t = 2000\Gamma^{-1}$), the system should reach the periodic quasi-steady state. The operator corresponding to the force can be shown to be given by

$$\hat{\mathbf{F}} = -\nabla H = \nabla [\mathbf{d} \cdot \mathbf{E}(\mathbf{r}, t)]. \quad (5.11)$$

To find the average force experienced by the molecule, we take the expectation value of this operator on the state and average this over one period. By doing this over a further period and checking the agreement of the two results, we can confirm whether the system has evolved into the periodic steady state.

We do this for a random selection of initial positions and laser phases and average the values obtained to find a mean value for the force. Repeating this for a selection of velocities, we can find the form of the velocity-dependent forces that lead to heating and cooling.

For the 1D cooling setup, we only need to consider the component of the velocity parallel to the cooling beams. Due to the symmetry of the situation, the force is always parallel to the velocity. The acceleration due to this force as a function of speed is shown in figure 5.5 for light

detuned by $\Delta = -7$ MHz and 7 MHz.

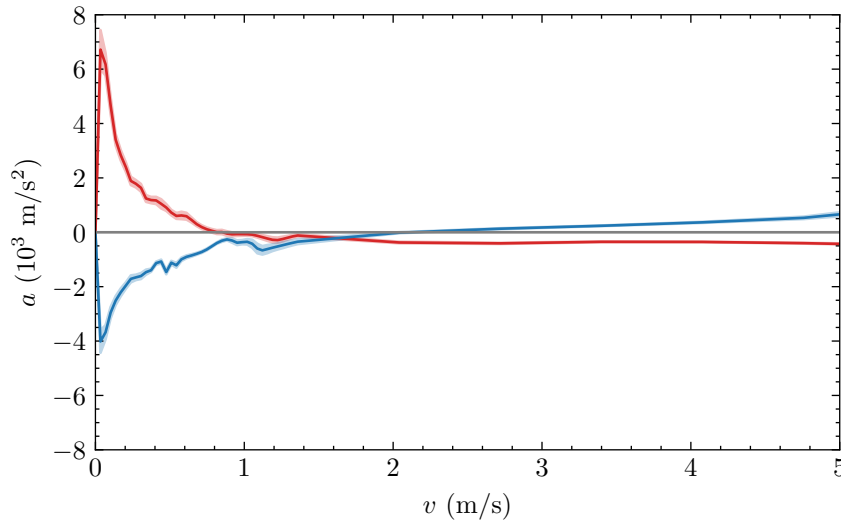


Figure 5.5: Simulation results of transverse cooling in 1D: The average acceleration is calculated at different speeds for molecules in the transverse cooling light with intensity $I = 129I_{\text{sat}}$ and detunings of $\Delta = -7$ MHz (red) and $\Delta = 7$ MHz (blue). EOM frequency sidebands spaced by 72 MHz are included up to second order. The magnetic field is 200 mG at 45° to the linear polarization of the light. Each point is the average of 20 iterations and the shaded bands are the 67% confidence interval.

The behaviour for the two different cases can be explained by the presence of Doppler and sub-Doppler forces which act in opposition to each other. For red-detuned light, we expect the Doppler force to act in the opposite direction to the velocity and to be dominant at higher velocities. The sub-Doppler force, on the other hand, acts in the direction of the velocity and is only appreciable at lower velocities. For blue detunings, the situation is similar but with the directions reversed¹.

In both cases, we can define a critical speed, v_c , at which the sub-Doppler and Doppler forces are balanced and the acceleration is zero. For $\Delta = -7$ MHz, molecules below this speed are accelerated until they reach v_c or they leave the cooling region. Molecules above this speed are decelerated towards the critical speed. This leads to a bimodal transverse velocity distribution in the direction of cooling with molecules bunched near $\pm v_c$. As the beam propagates onward from the cooling region this causes the two-lobed beam profile with a depletion of molecules in the central region and an enhancement in density on either side of the central region that is

¹For an equal and opposite detuning, one might expect to get symmetric acceleration curves with the same magnitude but opposite direction, as in [134]. This is the case for isolated transitions but the closely spaced hyperfine structure and the sidebands of the laser mean that this symmetry is broken.

seen in figure 5.3b.

For $\Delta = 7$ MHz, molecules with speeds below the critical speed are decelerated towards rest, whereas those above are accelerated to higher speeds. As a result, the transverse velocity distribution of the beam will become more peaked around zero, which explains the increased density of molecules in the central region of the profile, seen in 5.3a.

5.2 2D cooling

Although we saw the effects of transverse cooling in the main chamber, we were not successful in increasing the number of molecules that were captured in the MOT with 1D transverse cooling. This may be due to the relatively low critical velocity of the cooling which only allows a small range of transverse velocities to be cooled. We decided to move on to 2D cooling, which in [165] has been shown to have a much larger critical velocity and to produce a much brighter beam of YbF molecules than in the 1D case.

5.2.1 Setup

To extend the transverse cooling into 2D, we wrapped the transverse cooling beam around the chamber, as shown in figure 5.6. The beam passes through the chamber horizontally and then again vertically before being retroreflected. Care was taken to align horizontal and vertical beams so that their intersection was along the line from the source aperture to the centre of the main chamber.

A number of modifications were made in addition to wrapping the beam around the chamber. Firstly, the transverse cooling beam was made larger along its smaller axis to a waist diameter of 5.3 mm and the larger axis was shrunk to 31.8 mm. The light was brought over to the experiment through a fibre with a higher input power damage threshold to reduce intensity fluctuations at higher power. Finally, a pair of coils were added to produce a controllable magnetic field along the direction of the molecular beam.

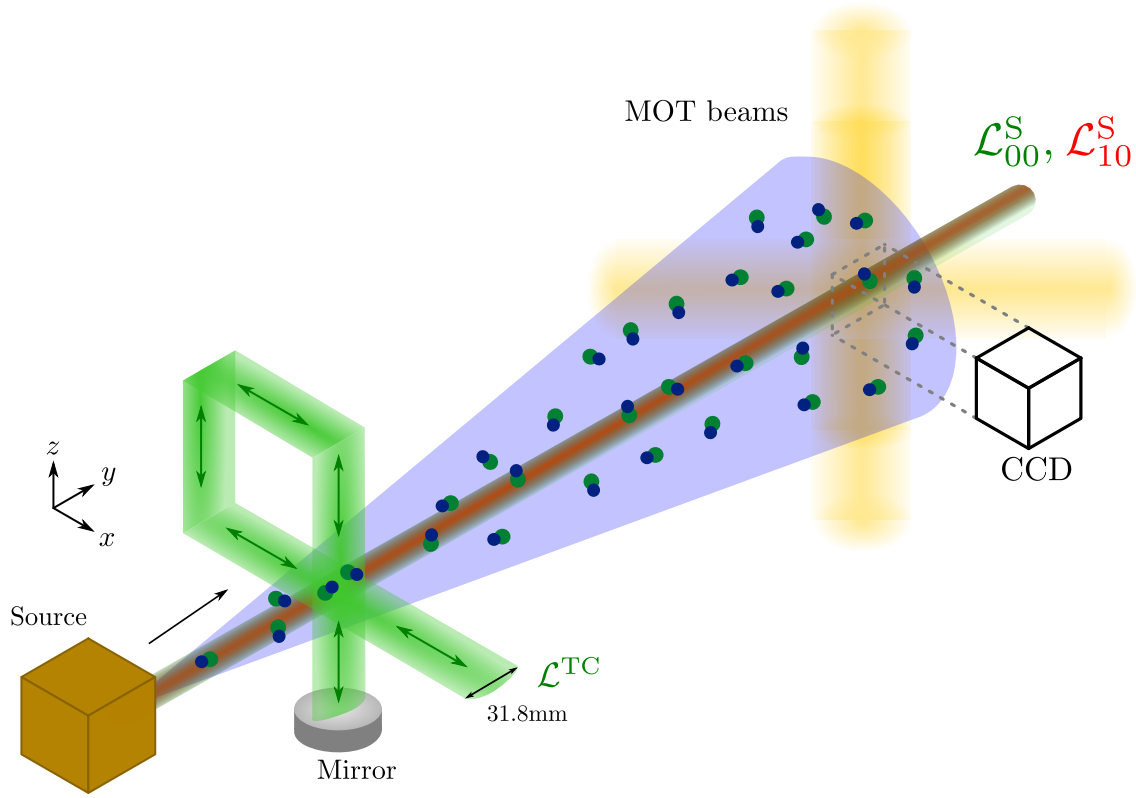


Figure 5.6: Schematic of the extension of the transverse cooling setup to 2D: Molecules are transversely cooled in two dimensions before being slowed and loaded into the MOT. The MOT fluorescence is then measured with a CCD.

We also took the further step of calibrating the detuning of the laser by diverting some light before the EOM into a fibre going to the main chamber. This single-frequency beam was collimated and directed into the MOT. As the frequency is scanned and the laser comes into resonance with one of the transitions, molecules will scatter photons from the beam and be pushed out of the MOT. By identifying the detunings where this happens, we can deduce the relative detunings that correspond to transitions between different hyperfine levels. The results for beam intensities of 80 mW/cm^2 and 8.2 mW/cm^2 are shown in figure 5.7a.

The absorption features of the molecules in the MOT measured in this way may be broadened and shifted by the Zeeman effect due to the quadrupole magnetic field and by AC stark shift from the trapping light. Assuming the MOT forms at the magnetic field zero, the range of fields experienced will be $\Delta\mathcal{B} \approx b\sigma$, where b is the field gradient at the centre and σ is the size of the MOT. Typically, we have $\sigma = 1 \text{ mm}$ and $b = 30 \text{ G cm}^{-1}$ so $\Delta\mathcal{B} \approx 3 \text{ G}$. If the Zeeman substates of each F level were evenly populated, this would lead to a broadening of the transitions by

around $\mu_B \Delta \mathcal{B} / h \approx 4$ MHz but no overall shift. However, the MOT light likely results in an uneven population of the Zeeman substates, causing a small shift, but this should be no larger than the broadening. We estimate the AC stark shifts due to the MOT light to be on the order of a linewidth. In hindsight, it would be better to perform such a calibration in free space before recapturing in the MOT. This would mean any shifts and broadening due to the magnetic field and MOT light would be avoided.

5.2.2 Results

After the calibration, we scanned the frequency of the transverse cooling light and measured the ratio of the number of molecules captured in the MOT with transverse cooling applied ($N_{\text{MOT}}^{\text{TC}}$) to the number captured in the absence of transverse cooling (N_{MOT}^0). With the EOM modulating the light at 72 MHz to produce three equal sidebands, an increase in MOT number by a factor of two was measured. This increase was found to be optimized at an EOM frequency of 63.5 MHz. The full scan at this frequency is shown in figure 5.7b.

We see an enhancement in the MOT number at several different values of the laser detuning with peak values separated by around 60 MHz. At $\Delta = 7$ MHz (indicated as (i) in the diagram), where we saw an increase in the central region in the 1D case, there is in fact a decrease in the MOT number by at least a factor of two. On the other hand, at $-30 \text{ MHz} < \Delta < -10 \text{ MHz}$ and $-100 \text{ MHz} < \Delta < -70 \text{ MHz}$ where we saw a lack of molecules in the central region, we see an increase in the MOT number. This is maximized locally at (ii) with $\Delta = -17$ MHz, where the MOT number is more than doubled by transverse cooling.

The global maximum enhancement, however, occurs at a much lower detuning - around $\Delta = -73$ MHz, signified by (iii) in the diagram. In this case it is important to note that the 2nd order sidebands of the light are not negligible, and, as shown in figure 5.7c, one of these sidebands is close to the two transitions from $F = 1^-$ preventing the molecule from being pumped out of the cooling cycle into this state.

The fact that we see an enhancement in MOT number in the ranges of detuning where we saw

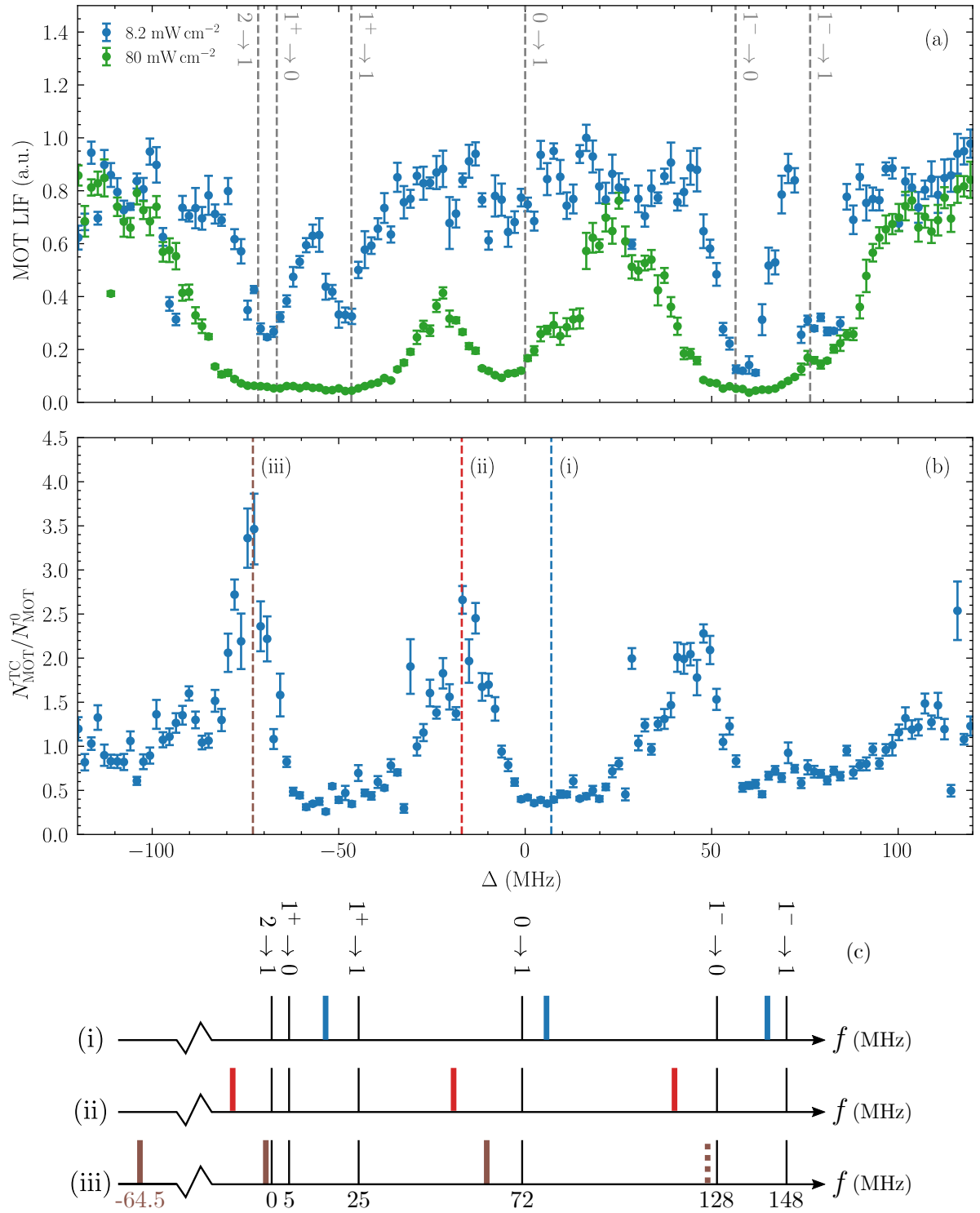


Figure 5.7: (a) Number of molecules trapped in the MOT in the presence of light of a single frequency from the transverse cooling laser at two different intensities. Approximate estimates of the detunings of the transitions between different hyperfine levels are shown by the grey dashed lines and labelled above in the form $F \rightarrow F'$. (b) Effect of 2D transverse cooling on MOT number. The ratio of the MOT number with transverse cooling ($N_{\text{MOT}}^{\text{TC}}$) to the MOT number without transverse cooling (N_{MOT}^0) is shown as a function of laser frequency. Each data point is the average of 6 experimental runs and the error is derived from the standard deviation of these measurements. (c) The frequency of the fundamental and 1st order sidebands for the detunings (i-iii) indicated in (b) are shown relative to the transition frequencies. The dashed line in (iii) represents the 2nd order sideband.

a depletion of the central region in the 1D setup suggests that Doppler cooling is responsible for the enhancement. This is counter-intuitive as one would expect that, by reducing the divergence of the molecular beam as much as possible, sub-Doppler cooling should lead to an increase in MOT number. The depletion in MOT number we see when applying sub-Doppler cooling could be explained if the critical velocity, v_c , is lower than the maximum transverse velocity of the molecules that make it to the MOT region. In this case, the Doppler heating that dominates above the critical velocity will accelerate some of these molecules to higher transverse velocities and they will no longer enter the MOT region. Conversely, when the light is red-detuned, although molecules with low transverse velocity will be accelerated towards the critical velocity by sub-Doppler heating, they will still reach the MOT region. Molecules at higher velocities, which would not normally be trapped by the MOT, will be decelerated towards the critical velocity, allowing some of them to make it to the MOT region.

In the previous experiments, the cooling light was linearly polarized at an angle of $\phi = 45^\circ$ relative to the applied magnetic field which is directed along the molecular beam and has a magnitude of 0.8 G. Figure 5.8a shows how the enhancement of the MOT number depends on the angle ϕ between the magnetic field and the linear polarization of the cooling light, when the magnitude of the magnetic field is 0.4 G. We see that the enhancement is reduced at $\phi = 0$. In this arrangement, the cooling light can only drive π transitions, taking the quantization axis to be along the magnetic field. The molecules will then be pumped to either of the dark states $|F = 2, m_F = \pm 2\rangle$, which reduces the scattering rate and inhibits the cooling.

When the angle ϕ is non-zero, two effects disturb any potential dark states. Firstly, since the horizontal and vertical beams have different linear polarization (although both have the same angle to the magnetic field), this leads to spatially-varying polarization throughout the cooling region. Molecules moving through the cooling region can be non-adiabatically transferred between the dark and bright states. Secondly, the dark states for non-zero ϕ are generally superpositions of different Zeeman sub-levels. In this case, the magnetic field will cause dark states to evolve into bright states.

Figure 5.8b shows the effect of the magnetic field with $\phi = 45^\circ$. We can see the enhancement

due to transverse cooling increases with increasing magnetic field, as expected due to remixing of dark states, up to a maximum around 1.2 G. Above this value, the enhancement decreases with increasing magnetic field. As shown in [170], if a magnetic field is used to destabilize dark states, the maximal scattering rate is found when the rate of evolution from a dark to a bright state $\delta_{d \rightarrow b} \approx \mu_B B / \hbar$ is roughly equal to the Rabi frequency Ω . When $\delta_{d \rightarrow b} > \Omega$, the Zeeman broadening leads to a decrease in the scattering rate. This is likely the origin of the decrease in enhancement at larger magnetic fields.

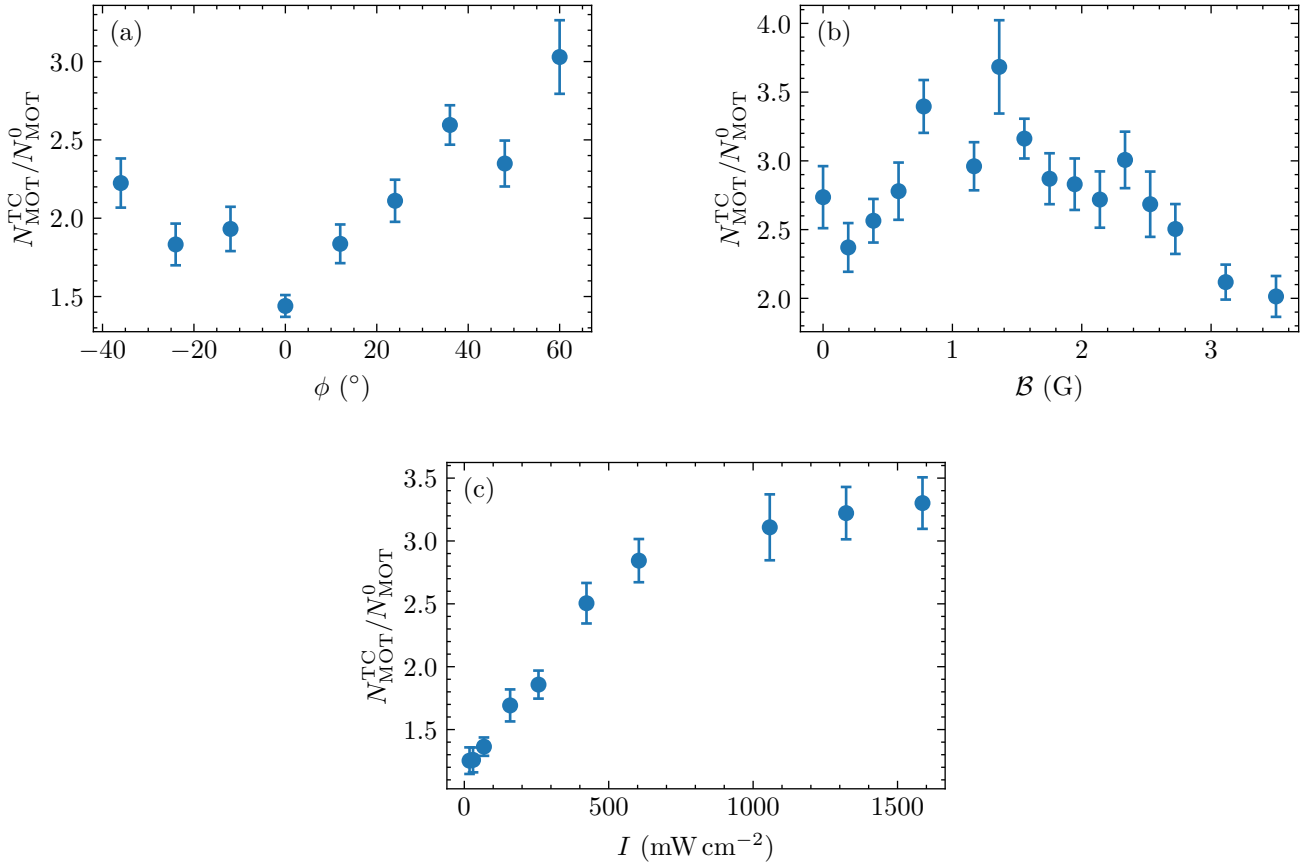


Figure 5.8: Enhancement in MOT number versus transverse cooling parameters: (a) $N_{\text{MOT}}^{\text{TC}}/N_{\text{MOT}}^0$ versus ϕ with $B = 0.4$ G and $I = 1590$ mW cm^{-2} , (b) $N_{\text{MOT}}^{\text{TC}}/N_{\text{MOT}}^0$ versus B with $\phi = 45^\circ$ and $I = 1590$ mW cm^{-2} , and (c) $N_{\text{MOT}}^{\text{TC}}/N_{\text{MOT}}^0$ versus I with $\phi = 45^\circ$ and $B = 1.56$ G. Points and error bars are mean and standard error from 15 experimental runs.

Figure 5.8c shows the enhancement of molecule number in the MOT as a function of intensity of the transverse cooling beam. The effect of the cooling increases with intensity initially but starts to saturate at around 600 mW cm^{-2} . This points to Doppler cooling as the source of the enhancement, since the capture velocity of Doppler cooling depends on the rate of photon

scattering, which saturates at high intensities. For sub-Doppler cooling, the capture velocity increases with increasing intensity so the enhancement should increase without saturating as more and more molecules are cooled.

5.2.3 Simulations

In order to adapt the previous simulations to the 2D case, for each iteration we choose a direction of motion by uniformly sampling the angle of the velocity relative to a fixed axis. We then average over this as we do with the other parameters such as laser phase and initial position.

In figure 5.9, we can see the results for the detunings (i) $\Delta = 7$ MHz and (ii) $\Delta = -17$ MHz and (iii) $\Delta = -73$ MHz. The acceleration curves have roughly the same shape as in the 1D case, again reflecting the opposing Doppler and sub-Doppler forces. For the case of $\Delta = 7$ MHz the critical speed is higher than in the 1D case with a value of v_c of about 2.75 m s^{-1} . This is the same as the critical speed for $\Delta = -17$ MHz. However, for $\Delta = -73$ MHz the critical speed is lower at approximately 2 m s^{-1} .

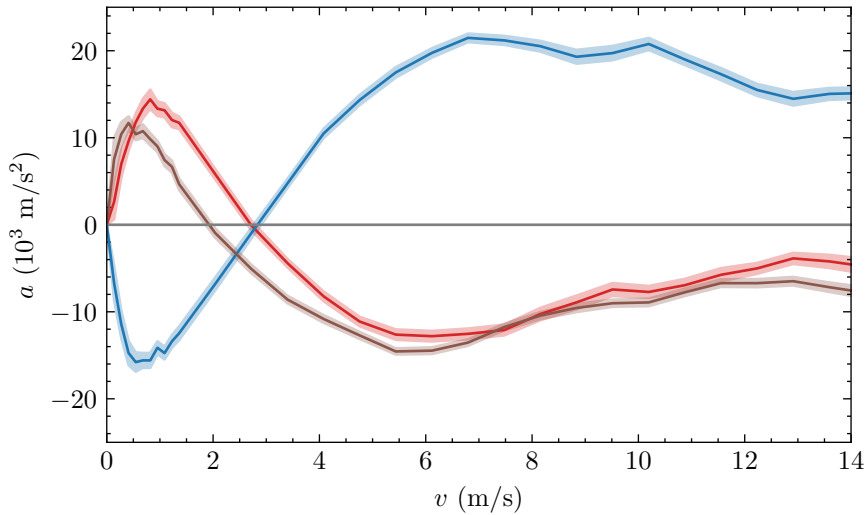


Figure 5.9: Simulation results of transverse cooling in 2D: The average acceleration is calculated at different speeds for molecules in the transverse cooling light with intensity $I = 129I_{\text{sat}}$ and detunings of $\Delta = 7$ MHz (blue), $\Delta = -17$ MHz (red) and $\Delta = -73$ MHz (brown). EOM frequency sidebands spaced by 63.5 MHz are included up to second order. The magnetic field is 1 G at 45° to the linear polarization of the light. Each point is the average of 100 iterations and the shaded bands are the 67% confidence interval.

To try to understand how the cooling leads to an increase in MOT number, it is important to know the range of transverse velocities for which a molecule will be captured in the MOT. From the data in chapter 3, we can see that loading of molecules into the MOT begins at around 20 ms after the YAG pulse. The exact capture volume of the MOT is unknown but we can estimate it by assuming that a molecule is captured if it enters the region where the MOT beams intersect within their $1/e^2$ radius. For the MOT beams, the $1/e^2$ radius is 8.2 mm and since they propagate at an angle of 45° to the molecular beam, the area of the projection of this region along the direction of the molecular beam can be approximated by a circle of radius $\sqrt{2} \times 8.2 \text{ mm} \approx 11.6 \text{ mm}$. Thus, any molecules with transverse speeds above $v_{\text{cap}} \approx 0.58 \text{ m s}^{-1}$ should not be captured in the MOT.

This seems to be at odds with the results of the simulations, since for the detunings where we see an enhancement in the MOT number ($\Delta = -17 \text{ MHz}$ and $\Delta = -73 \text{ MHz}$), the force curves suggest that the molecules below v_{cap} will all be accelerated towards higher velocities. This should lead to a decrease in MOT number instead of an enhancement. Along the same lines, light at $\Delta = 7 \text{ MHz}$ should increase the number of molecules that make it to the capture region of the MOT, but this is not seen in the experiment.

The reasons for this discrepancy are not known for certain. It is possible that the simulations do not accurately capture the dynamics and the actual critical velocity is in fact lower than the transverse capture velocity of the MOT. Also, the effects of slowing on the transverse velocity distribution of the beam have not been considered. These include transverse heating due to scattering of photons from the slowing light and additional transverse cooling due to the slight convergence of the slowing beam.

We can obtain an estimate of the impact of transverse heating due to the scattering of photons during the slowing. If we assume that, on average, each time a photon is scattered the longitudinal velocity decreases by the recoil velocity $v_r = \hbar k/m \approx 1.27 \text{ cm s}^{-1}$, then it takes approximately $N = 10^5$ scattering events for a molecule to be decelerated from the mean speed of 140 m s^{-1} to the capture velocity of the MOT given by 11 m s^{-1} [128]. Each time a photon is scattered, it gives the molecule a momentum kick of $\hbar k$ in a random direction. This is

a random walk in velocity space and leads to a root mean squared spread of the transverse velocity given by

$$\sqrt{\langle \Delta v_{\perp}^2 \rangle} = \sqrt{\frac{2N}{3}} v_r \approx 3.3 \text{ m s}^{-1}. \quad (5.12)$$

Thus, the effect of the transverse heating cannot be ignored. Further modelling of the influence of the slowing, as well as a more detailed treatment of MOT loading might explain why we see an improvement in the MOT number with Doppler cooling.

5.3 Outlook and conclusion

To increase the length of the cooling region, we modified the source chamber by adding a new transverse cooling chamber², shown in figure 5.10a. This has windows with dimensions $125 \times 34 \text{ mm}$, increasing the available length of optical access by a factor of 3. In addition, coils were added for controlling the magnetic field in all dimensions.

With this new chamber in place, we tried several different optical setups to try to improve the enhancement of the MOT number. This could be done by raising the capture velocity of the sub-Doppler cooling so that it starts to increase the number of molecules captured instead of decrease or by increasing the interaction time with the Doppler cooling light so that molecules with higher transverse velocity can be brought down to the critical velocity.

To increase the capture velocity of sub-Doppler cooling, we implemented a multi-pass setup, similar to that in [164], where smaller beams are used but these are retroreflected many times through the cooling region. This increases the intensity of the cooling light, which should increase the capture velocity of the sub-Doppler cooling. However, in this setup we again found that the enhancement was maximized at the detunings where Doppler cooling is present.

Finally, we increased the cooling length of the region in a setup similar to the one described in section 5.2.1, except that the beam is wrapped around again to form another identical cooling region next to the first, as shown in figure 5.10b. Although this increased the cooling length

²Designed by Jonas Rodewald

by a factor of two, no increase in the enhancement due to Doppler cooling was found. Thus, there appears to be another unknown factor limiting the effectiveness of transverse cooling.

The Doppler cooling force could potentially be increased with a different choice of sidebands. The optimal frequency structure of the light is likely to have the same frequency spacing as the transitions. Applying this light with a red-detuning should give the largest Doppler cooling force but these sidebands are difficult to generate.

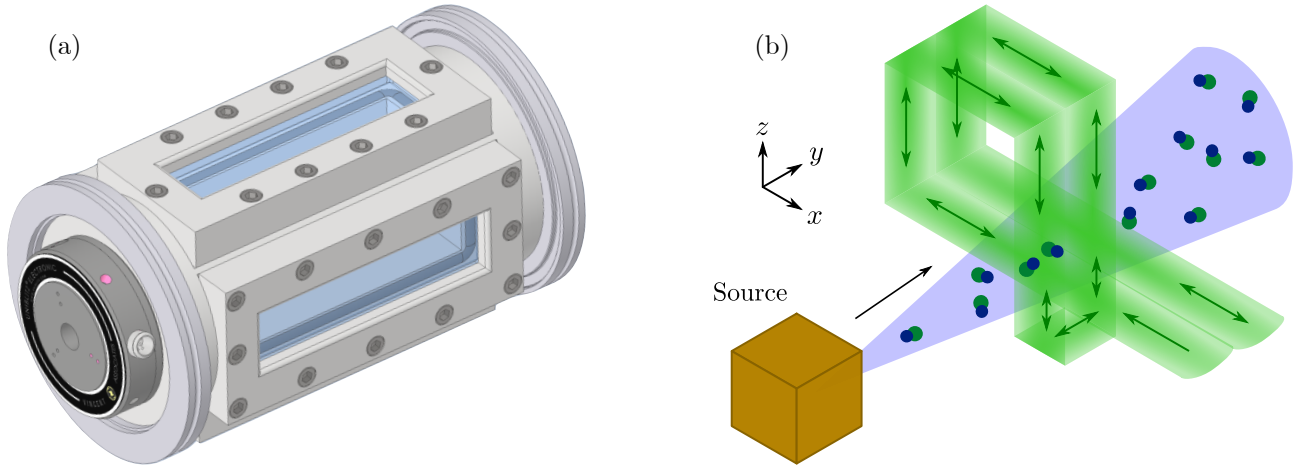


Figure 5.10: (a) New transverse cooling chamber with larger optical access. (b) Modified beam path to increase cooling length. This is the arrangement currently used on the experiment.

Chapter 6

CaF and Rb in a 1D optical lattice

6.1 Introduction

To further investigate elastic collisions between CaF molecules and Rb atoms, it is necessary to increase the effective density of the atoms. One way of doing this is by loading both species into an optical trap, which can have a much smaller trapping region than a typical magnetic trap. This is especially true in optical lattices where the sub-wavelength scale of the trapping potential leads to very strong confinement.

This chapter focuses on our experiments with CaF and Rb in a 1D optical lattice. The experimental procedure for loading both species is discussed. This is followed by characterization of the trap and the observation of collisions between the two species inside the lattice.

6.2 Theory

Optical traps work by exploiting the AC Stark shift of atoms and molecules. As shown in chapter 2, for a two-level atom this is given by

$$\Delta E_g = -\frac{\hbar\Omega^2}{4\Delta} = -\frac{3\pi c^2\Gamma}{2\omega_0^3} \frac{I}{\Delta}. \quad (6.1)$$

where the last expression follows from the definition of Ω and Γ . For light that is far-enough detuned, the rotating wave approximation is no longer valid and a term must be added to the shift giving

$$\Delta E_g = -\frac{3\pi c^2 \Gamma}{2\omega_0^3} \left(\frac{1}{\omega - \omega_0} + \frac{1}{\omega + \omega_0} \right) I. \quad (6.2)$$

This is often written in the form

$$\Delta E_g = -\frac{\alpha(\omega)}{2\epsilon_0 c} I, \quad (6.3)$$

where $\alpha(\omega)$ is known as the AC polarizability of the trapped species. For a multilevel atom, the contributions to the AC stark shift due to all of the allowed transitions must be included. Nevertheless, equation 6.3 still holds but with a more complicated dependence on ω .

If $\alpha(\omega)$ is positive, as it is for light red-detuned from any nearby transitions, the atom or molecule will be attracted to regions of higher intensity. In this case, an optical trap can be created by focusing a Gaussian beam. Although this provides tight confinement of the atoms or molecules in the direction transverse to the beam, the trapping forces are a lot weaker along the longitudinal direction. One way to remedy this is by implementing an optical lattice by retro-reflecting the beam. This creates a standing wave, where the intensity is spatially modulated with a period of $\lambda/2$. As a result, the atoms or molecules are very tightly confined in the longitudinal direction, near the antinodes of the standing wave.

The shape of the potential can be calculated by considering the electric field of the incident and reflected beams (ignoring the wavefront curvature and Gouy phase) which are given by

$$\mathbf{E}_i = \mathbf{E}_{i,0} \frac{w_0}{w(z)} \exp\left(\frac{-r^2}{w(z)^2}\right) \exp(-ikz), \quad (6.4)$$

$$\mathbf{E}_r = \mathbf{E}_{r,0} \frac{w_0}{w(z)} \exp\left(\frac{-r^2}{w(z)^2}\right) \exp(ikz), \quad (6.5)$$

with

$$w(z) = w_0 \sqrt{1 + \left(\frac{z}{z_R}\right)^2}, \quad z_R = \frac{\pi w_0^2}{\lambda}, \quad (6.6)$$

for an incident beam with waist radius w_0 and wavelength λ propagating along z . The intensity

distribution of the lattice is given by

$$I(r, z) = \frac{\epsilon_0 c}{2} |\mathbf{E}_i + \mathbf{E}_r|^2 = \frac{\epsilon_0 c}{2} \left(\frac{w_0}{w(z)} \right)^2 \exp \left(\frac{-2r^2}{w(z)^2} \right) |\mathbf{E}_{i,0} \exp(-ikz) + \mathbf{E}_{r,0} \exp(ikz)|^2. \quad (6.7)$$

For a perfectly reflected beam, $\mathbf{E}_{r,0} = \mathbf{E}_{i,0}$ and so we can write the intensity distribution as

$$I(r, z) = 2\epsilon_0 c \left(\frac{w_0}{w(z)} \right)^2 \exp \left(\frac{-2r^2}{w(z)^2} \right) |\mathbf{E}_{i,0}|^2 \cos^2(kz). \quad (6.8)$$

The total power of the incident beam is given by

$$P = \frac{\pi w_0^2 \epsilon_0 c}{4} |\mathbf{E}_{i,0}|^2 \quad (6.9)$$

so we can write

$$I(r, z) = \frac{8P}{\pi w_0^2} \left(\frac{w_0}{w(z)} \right)^2 \exp \left(\frac{-2r^2}{w(z)^2} \right) \cos^2(kz). \quad (6.10)$$

The trap potential is then given by

$$U(r, z) = -U_0 \left(\frac{w_0}{w(z)} \right)^2 \exp \left(\frac{-2r^2}{w(z)^2} \right) \cos^2(kz), \quad (6.11)$$

where we have defined the trap depth U_0 as

$$U_0 = \frac{4\alpha P}{\epsilon_0 c \pi w_0^2}. \quad (6.12)$$

6.3 Loading the atoms

6.3.1 Dark SPOT

To load the highest density of Rb atoms into the optical lattice, we used a dark spontaneous-force optical trap (dark SPOT). First developed by Ketterle et al. [171], this trap is similar to the MOT but has a central region where there is no repump light. In this region, atoms are pumped to the $F = 1$ ground state which is effectively dark to the trap light thus reducing the

rescattering and attenuation of the trap light that limits the density of standard MOTs.

In addition to increasing the density prior to loading the lattice, Kuppens et al. [172] find that a dark SPOT also reduces losses due to hyperfine-changing collisions during the loading of the lattice, as the atoms mostly populate the lower hyperfine state. This allows more atoms to be loaded into the lattice.

To transfer the atoms into the dark SPOT, we first load the Rb MOT as before. After loading, we turn the usual repump beams off and turn on two ‘hollow’ repump beams. These beams have a ring-shaped intensity distribution with a dark central region, in order to produce an area in the centre of the MOT where there is no repump light present. The setup for producing these ‘hollow’ beams and introducing them into the main chamber is shown in figure 6.1.

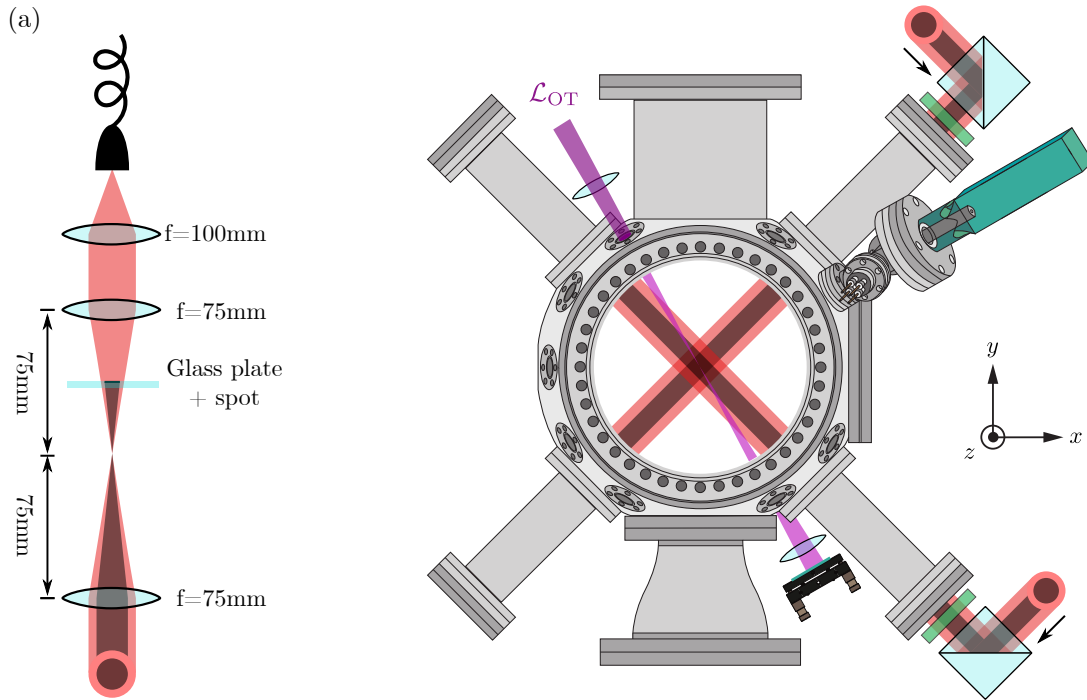


Figure 6.1: Setup for the dark SPOT: (a) the arrangement for producing both the ‘hollow’ repump beams (b) the two ‘hollow’ beams are mixed with the MOT cooling light on the two PBSs shown. At the intersection of the two beams, a small dark region is formed where there is no repump light. The optical lattice trapping light $\mathcal{L}_{OT}$ is also shown. Not to scale.

The two dark SPOT repump beams are collimated before passing through a 1:1 telescope. A glass plate with a small opaque dot in the centre is positioned near the focal point between the two lenses. This creates a dark spot in the centre of the beam, which is imaged into the cloud.

By moving the glass plate, the size and position of the dark region can be controlled.

Absorption images of the cloud can be used to examine the effects of the dark SPOT. By turning the repump light off when imaging on the $|F = 2, m_F = 2\rangle \leftrightarrow |F = 3, m_F = 3\rangle$ transition, the number of atoms in the $F = 2$ ground state, N_2 , can be measured. The total number of atoms, N_T can also be obtained as usual. We can then deduce the number of atoms in the $F = 1$ state by using the relation $N_1 = N_T - N_2$. Figure 6.2a shows the fraction of atoms in each state at time t after transfer to the dark SPOT. The fraction of atoms in the $F = 1$ state increases until a new equilibrium is reached after around 5 ms. During this time, we also see the cloud decrease in size by almost a factor of 3 in the radial direction and a factor of 2 in the axial direction, as shown in figure 6.2b. As a result, the density of the cloud increases by a factor of 15 from $4 \times 10^{10} \text{ cm}^{-3}$ to $6 \times 10^{11} \text{ cm}^{-3}$.

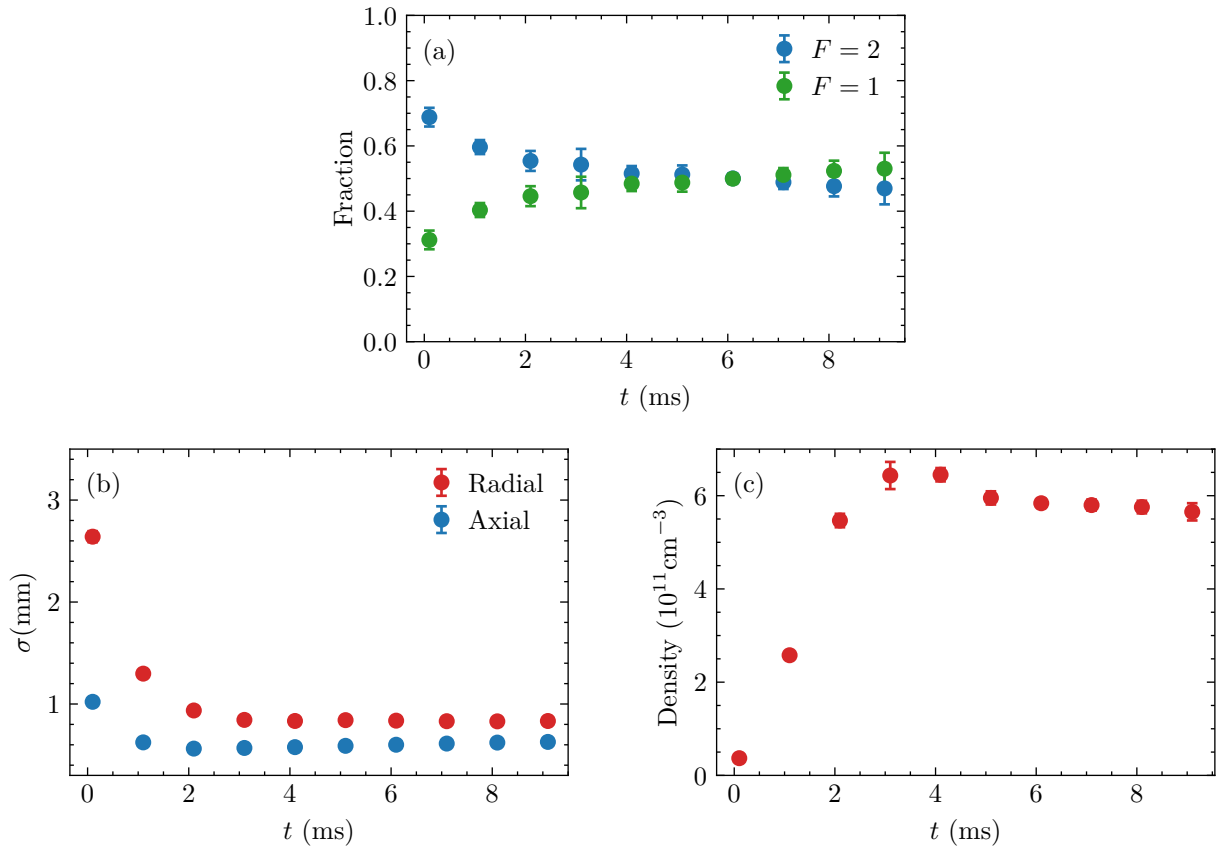


Figure 6.2: Dark SPOT: (a) fraction of atoms in ground state levels $F = 1$ and $F = 2$ (b) size of the atom cloud and (c) cloud density as a function of the time t after the switch to the dark SPOT. Each point is the average of 5 experimental runs and the error bars are the standard deviation of the results.

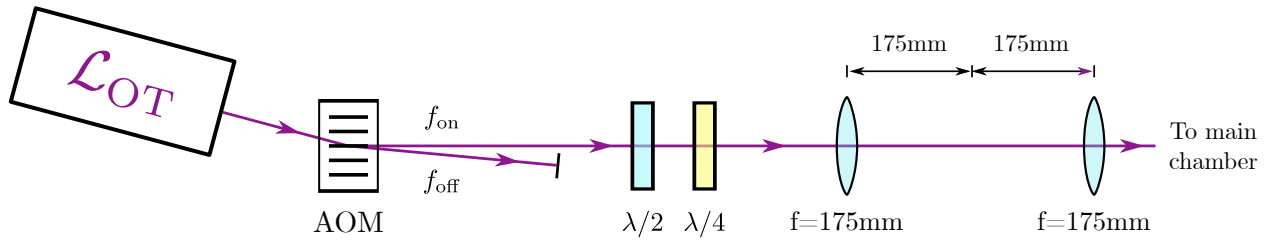


Figure 6.3: Lattice trapping light optical setup for switching, controlling the polarization and collimating the beam.

The trapping light for the lattice, $\mathcal{L}_{OT}$, is derived from a fibre laser from Azurlight systems, which can produce 45 W of light at 1064 nm. As shown in figure 6.3, the beam passes through a high-power AOM that is used as a switch. To avoid thermal drifts, the RF power to the AOM remains constant but the frequency of the signal is used to control the direction of the light. By switching between two frequencies, f_{on} and f_{off} , the beam can be directed to the experiment or onto a beam block, respectively. The polarization of the beam can be controlled with a combination of a half-wave plate and a quarter-wave plate. Finally, the beam passes through a 1:1 telescope and the distance between the two lenses is adjusted to collimate the beam before it is delivered to the main chamber.

At the main chamber, the light is focused by a lens with focal length 175 mm, which can be seen in figure 6.1b above. This is placed so that the focus is at the centre of the main chamber. When the beam exits the chamber, an identical lens collimates the beam which is then retroreflected to produce the lattice.

To load atoms from the dark SPOT into an optical lattice, we turn on the lattice trapping light, $\mathcal{L}_{OT}$, at the same time as switching to the dark SPOT. The number of atoms loaded as a function of the overlap time between the dark SPOT and the optical lattice is shown in figure 6.4, measured by absorption imaging of the cloud after release from the trap. After about 40 ms, the trap is fully loaded. To get an accurate measurement of how many atoms are loaded, it is necessary to wait at least 50 ms after the dark SPOT turns off so that the atoms that are not loaded have time to fall out of the imaging region.

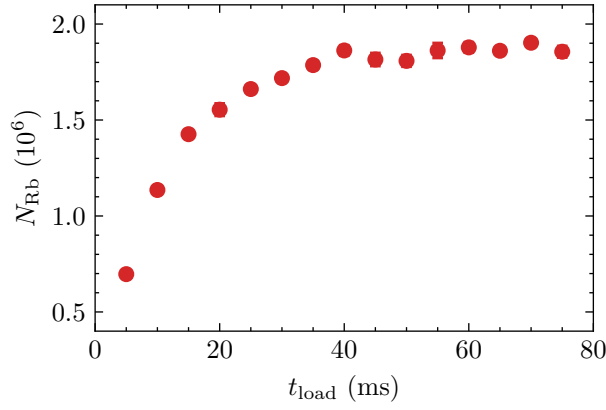


Figure 6.4: Loading of Rb atoms into the optical lattice: The number of Rb atoms remaining after being held in the trap for 70 ms is measured as a function of the overlap time t_{load} between the dark SPOT and the optical lattice. The points and error bars are the mean and standard error of 6 iterations. Where not visible, error bars are smaller than the points.

6.4 Loading the molecules

6.4.1 Compressed MOT

As with the atoms, it is beneficial to increase the density of the molecule cloud prior to transfer to the optical lattice. For this, we add a compressed MOT (CMOT) stage, where the magnetic field gradient is ramped up linearly over 10 ms. The size of the MOT as a function of the final field gradient is shown in figure 6.5. For field gradients up to 75 G cm^{-1} , the size of the MOT decreases in both the axial and radial dimensions, leading to an increase in density by a factor of 2.4.

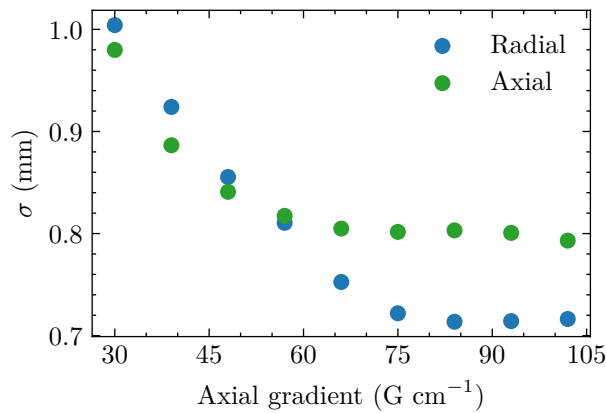


Figure 6.5: Compressed MOT of CaF: Size of the molecule cloud as a function of the final axial field gradient.

6.4.2 Sub-Doppler cooling

After the CMOT, we transfer the molecules to a blue-detuned molasses, similar to that described in section 4.1.1. However, during our investigations, it was found that lower temperatures could be reached by removing the sideband addressing the $F = 1^+$ level in the ground state, as illustrated in figure 6.6a. This has also been demonstrated by Anderegg [173]. By turning off the single-pass AOM, this sideband can be extinguished and the molecules reach a temperature of 75 μK .

After this step, we move to a single-frequency molasses, as described in [174]. The laser $\mathcal{L}_{00}^C$ is again switched off and the modulation due to the EOM is turned off by switching the RF drive. The laser frequency is increased by around 200 MHz so that the remaining single laser frequency is blue-detuned by $\delta f_{\text{SFM}} \approx 146$ MHz from the $F = 1^-$ transition, as depicted in figure 6.6b. The laser is switched on again and the molecules cool in the single frequency molasses down to around 10 μK .

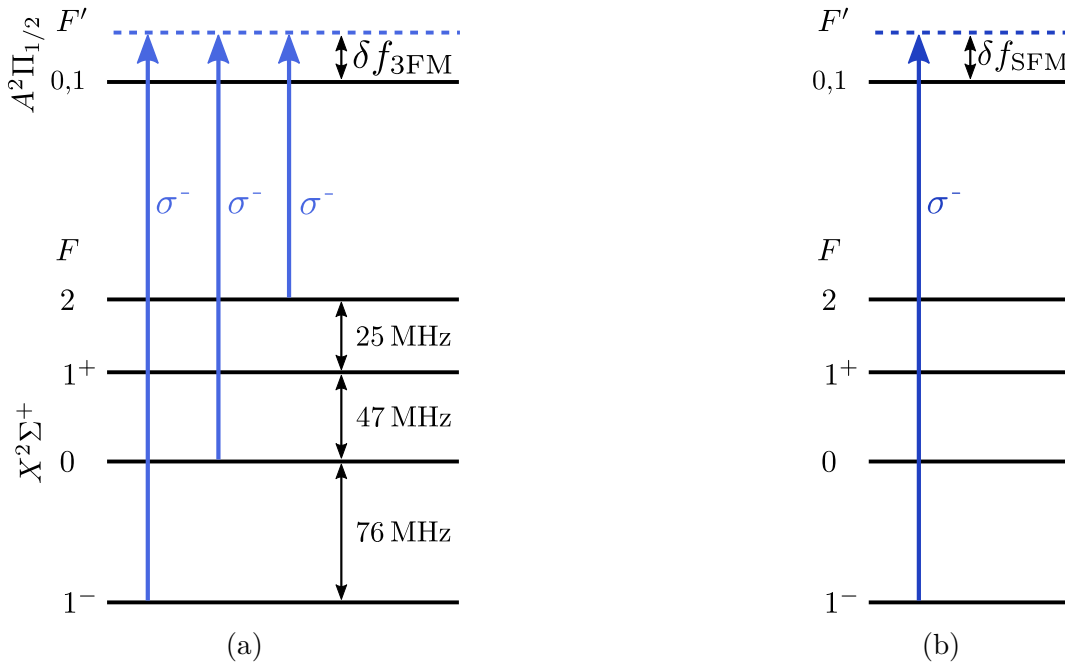


Figure 6.6: Schematic of laser frequencies and hyperfine energy levels for (a) three-frequency molasses and (b) single-frequency molasses.

The lattice is switched on at the start of the single-frequency molasses and molecules begin to load into trap. To examine the loading, we vary the duration of the single-frequency molasses,

before holding the molecules in the lattice for 150 ms with no cooling light present. The number of trapped molecules is then measured by returning the molecules to the MOT and imaging the fluorescence. As shown in figure 6.7, the number of molecules in the trap increases rapidly at first, but it takes around 150 ms to reach the maximum number loaded, after which there are approximately 200 CaF molecules in the trap. The two timescales suggest two different loading mechanisms - molecules that happen to overlap with the lattice when it is first turned on are loaded immediately, while other molecules in the molasses diffuse into the lattice on a much slower timescale.

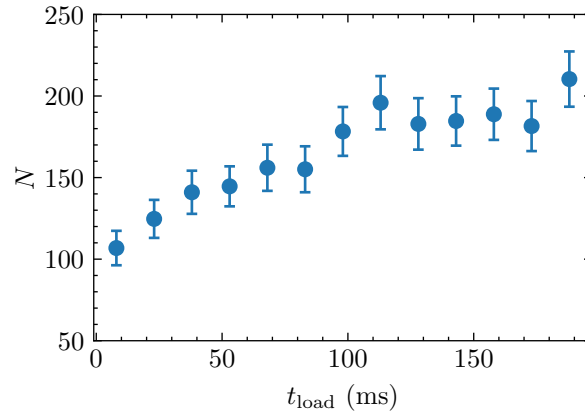


Figure 6.7: Loading of CaF molecules into the optical lattice: The overlap time t_{load} between the single-frequency molasses and the optical lattice is varied and the number of molecules is measured after 150 ms in the trap. The points are the mean of 16 iterations and the error bars represent the combined uncertainty of the standard error and the systematic error in the number measurement.

6.5 Lattice characterization

6.5.1 Trap frequencies

We can expand the lattice potential given in equation 6.11 around the origin to second order as

$$U(r, z) \approx -U_0 \left[1 - \left(\frac{2}{w_0^2} \right) r^2 - \left(\frac{1}{z_R^2} + k^2 \right) z^2 \right]. \quad (6.13)$$

Since we have $w_0 \gg \lambda$, this means that $k \gg 1/z_R$ and so we can approximate this as

$$U(r, z) \approx -U_0 \left[1 - \left(\frac{2}{w_0^2} \right) r^2 - k^2 z^2 \right]. \quad (6.14)$$

Thus, the trap is approximately harmonic near the origin with trap frequencies given by

$$\nu_r = \frac{1}{2\pi} \sqrt{\frac{4U_0}{mw_0^2}}, \quad (6.15)$$

$$\nu_z = \frac{1}{2\pi} \sqrt{\frac{2U_0 k^2}{m}}. \quad (6.16)$$

As a result, we can determine the parameters that characterize the potential by measuring the trap frequencies. To do this we modulate the trap depth by a small amount, so that the potential now varies periodically in time as

$$U(r, z, t) = (1 + \epsilon \cos 2\pi\nu t)U(r, z) \quad (6.17)$$

with $\epsilon \ll 1$. When the modulation frequency, ν , is set to double the trap frequency, parametric heating occurs which causes loss of atoms from the trap [175].

In the experiment, the trap depth is controlled by varying the intensity of the optical lattice. To add a small intensity modulation to the optical lattice beam, the RF drive to the switching AOM was split into two parts. One part of the signal was modulated by a variable frequency generated by a direct digital synthesizer (DDS). This was then combined with the other unmodulated part of the signal to produce a small amplitude modulation, as shown in figure 6.8.

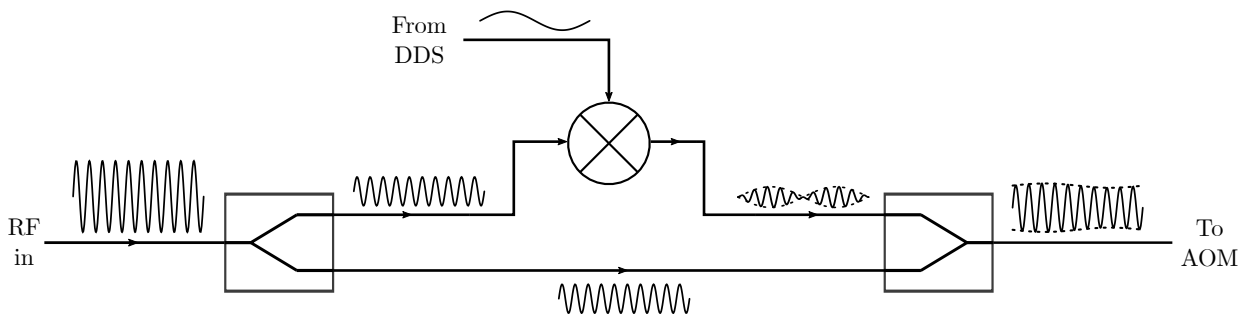


Figure 6.8: Parametric heating setup: A small intensity modulation of variable frequency is added to the RF signal to the AOM by mixing part of it with a sinusoidal waveform generated by a DDS.

The number of atoms left in the optical lattice after 200 ms of amplitude modulation with varying frequency is shown in figure 6.9. We see two broad resonances: one at $\nu \approx 10$ kHz and one at $\nu \approx 1.7$ MHz, corresponding to radial and axial parametric heating, respectively.

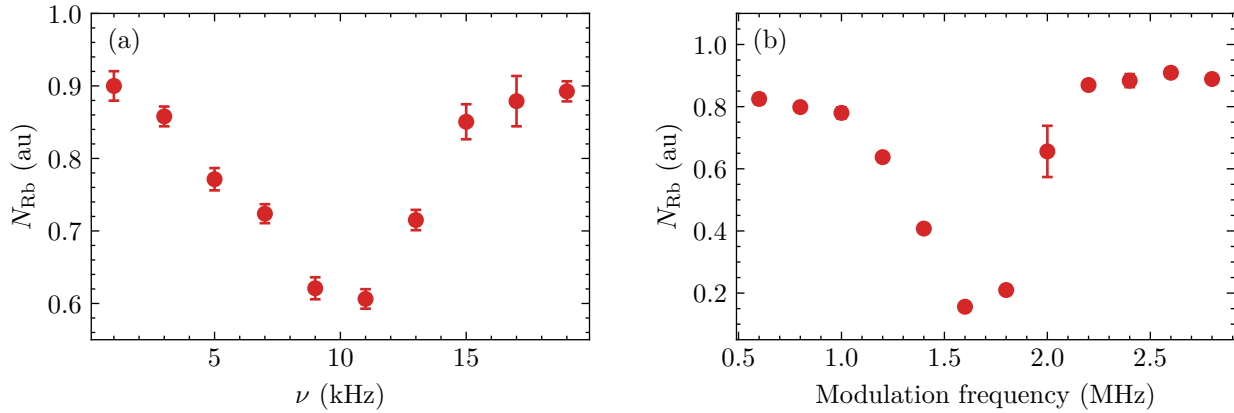


Figure 6.9: Loss of atoms due to parametric heating: The trap depth is modulated for 200 ms at variable modulation frequency, ν . We see loss features corresponding to the (a) radial and (b) axial parametric resonances. Each point is the mean of 3 measurements and the error bar is the standard deviation.

If we take slices along the axial direction of the trap and fit inverted Gaussian distributions to the resonances, we can see a variation in the central frequency of the radial resonance for each section as shown in figure 6.10. This is due to the variation in waist size along the beam. By expanding the potential around the centre of a lattice site located at z_j , we find that near the bottom of the lattice site

$$U(r, z_j) \approx -\frac{U_0}{1 + (z_j/z_R)^2} \left(1 - \frac{2r^2}{w(z_j)^2} \right) \quad (6.18)$$

which leads to a reduced radial trap frequency of

$$\nu_r(z_j) = \frac{\nu_r(0)}{1 + (z_j/z_R)^2}. \quad (6.19)$$

We cannot resolve each lattice site individually so we fit the central resonance frequency for each slice to the average radial trap frequency over that slice. From the fit we can deduce the Rayleigh range of the trapping beam to be $z_R = 4.1(1)$ mm and the radial trap frequency at the focus to be, $\nu_r(0) = 5.60(1)$ kHz.

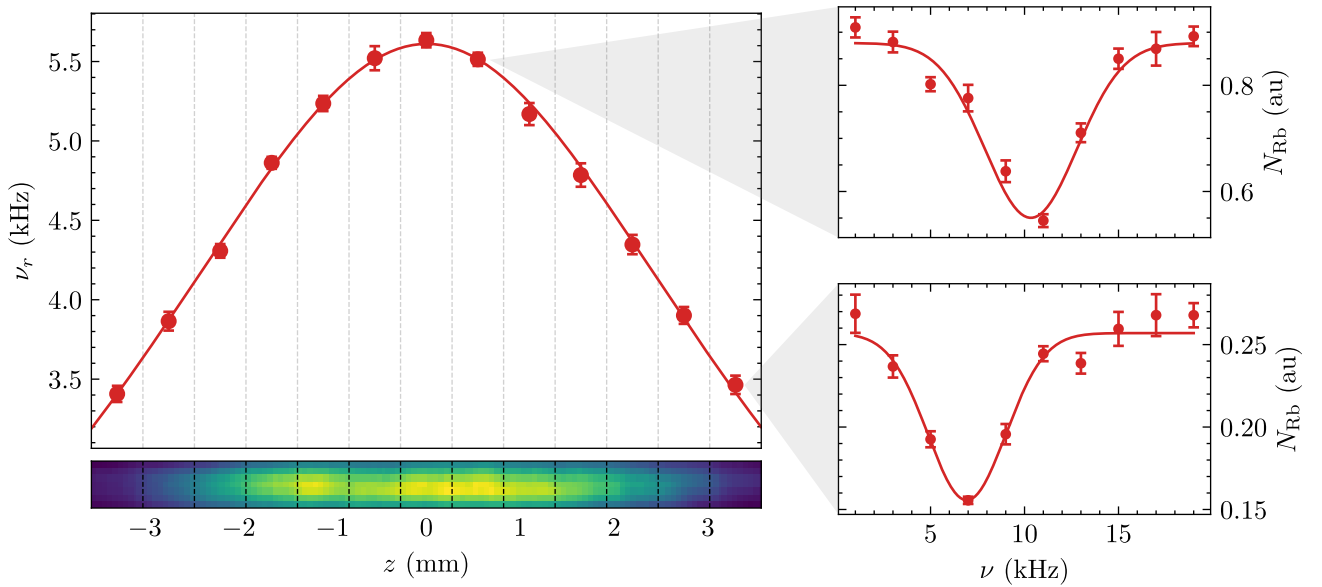


Figure 6.10: Variation of radial trap frequency with axial distance along lattice: Each point is the result of fitting an inverted Gaussian profile to the parametric heating curve of each slice, as shown in the subplots on the right, and extracting the central frequency of the Gaussian. Error bars represent the error on the central frequency from the fit. The solid line is a fit to equation 6.19. Below is an image of the atoms in the lattice, showing the slices used for each point.

We also expect a variation in the axial trap frequency along the axial direction. However, since the heating in this case causes the atoms to move along the lattice in the axial direction rather than escape radially, this means that atoms at any point along the beam may be lost by elastic collisions with the parametrically heated atoms. As a result, we see similarly broadened parametric heating resonances at any slice along the trap. So, we roughly estimate the maximal trap frequency from the data to be $\nu_z(0) \approx 0.9$ MHz.

The lattice beam has a measured power of $P = 18$ W and using equations 6.15 and 6.16 we can estimate the beam waist to be $w_0 = 38.5$ μm . This is consistent with measurements performed on a test setup using a lens identical to the one focusing the beam into the chamber. This waist size is compatible with the Rayleigh range measured above with the inclusion of an M^2 factor of 1.07.

6.5.2 Temperature measurements

The temperature of the atoms and molecules can be measured by ballistic expansion. The trapping laser $\mathcal{L}_{\text{OT}}$ is turned off and the atoms or molecules are allowed to expand, as shown in figure 6.11. We find a linear relationship between the trap laser power and the temperature of the atoms and molecules, which can be seen in figure 6.12. For Rb, loading into a trap that is deeper by 1 mK increases the temperature of the trapped atoms by $78(3) \mu\text{K}$. For CaF, a similar increase in trap depth for loading would lead to a temperature increase of $32(7) \mu\text{K}$.

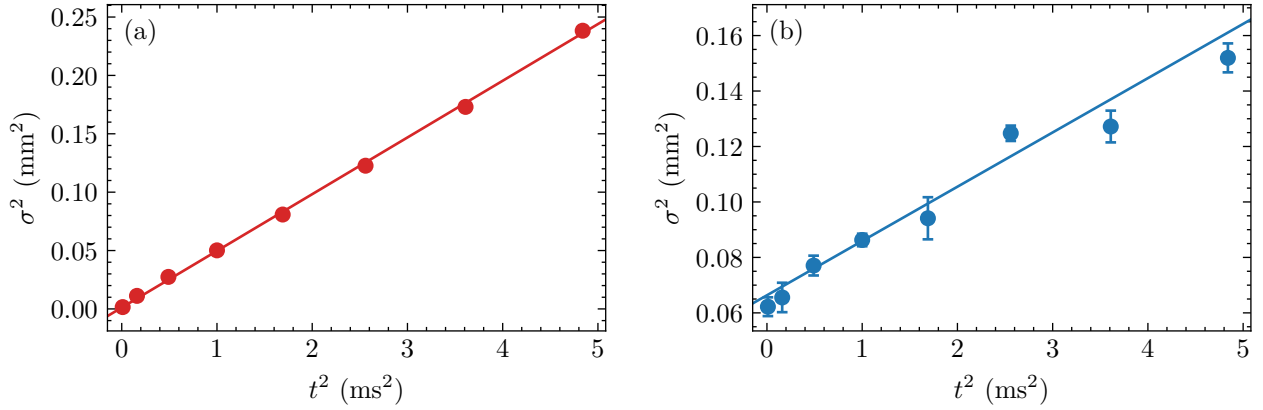


Figure 6.11: Temperature measurement of (a) Rb and (b) CaF in the lattice by ballistic expansion at a trap laser power of 24.5 W

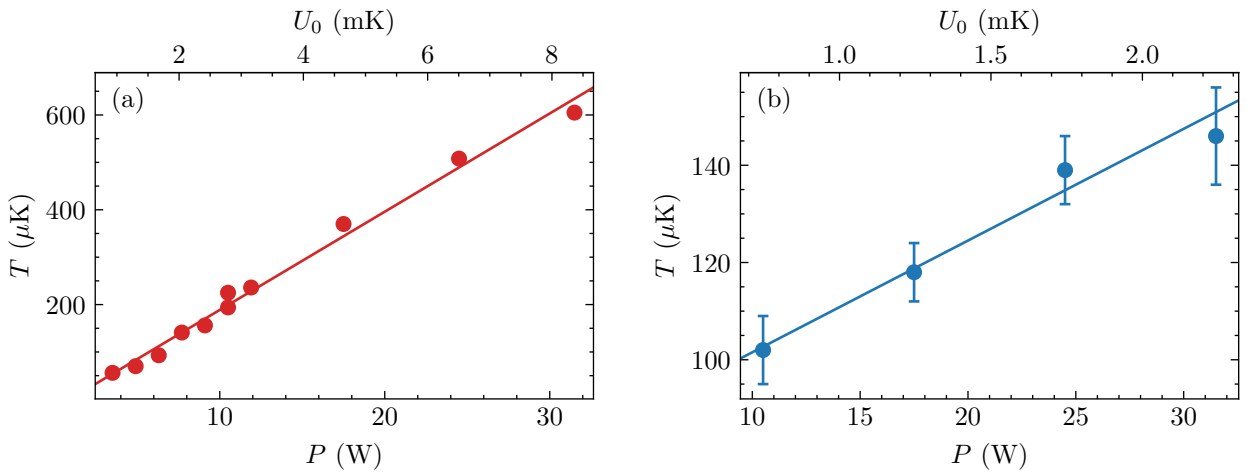


Figure 6.12: Temperature of (a) Rb and (b) CaF as a function of trap laser power, P . Calculated trap depth is also shown on the top axis.

6.5.3 Lifetime

We also measured a lifetime of both species in the optical lattice at 36 W, as shown in figure 6.13. As in chapter 4, to reduce the effect of shot-to-shot number variations, we normalize the number of molecules and atoms to the number of each species in the MOT. We define

$$r_{\text{Rb}}(t) = N_{\text{Rb}}(t)/N_{\text{Rb}}^{\text{MOT}}, \quad r_{\text{CaF}}(t) = N_{\text{CaF}}(t)/N_{\text{CaF}}^{\text{MOT}} \quad (6.20)$$

where $N_s(t)$ is the number of species s after time t in the lattice and N_s^{MOT} is the number in the initial MOT. Exponential fits to the data yield a lifetime of the Rb atoms in the lattice of 1.12(2) s. This is similar for the CaF molecules where the lifetime is measured to be 1.07(6) s.

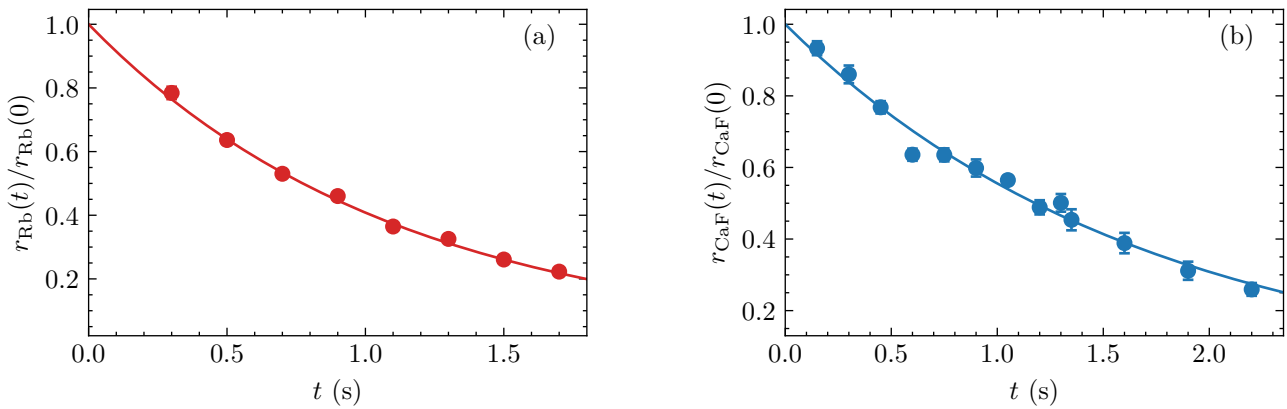


Figure 6.13: Loss of (a) Rb and (b) CaF in the optical lattice: Solid lines are fits to an exponential decay. Points and error bars are mean and standard error of 6 experimental runs for Rb and 9 experimental runs for CaF.

6.6 Collisions in the optical lattice

6.6.1 Collisions in $N = 1$

Since the Rb MOT takes up to 1 s to fully load, it would be beneficial to load the atoms into the lattice first so that molecules are not lost unnecessarily from the trap. However, the molecules that are loaded into the lattice are in states in the $N = 1$ manifold and, bearing in mind the

results from chapter 4, we expect a large inelastic loss rate of the molecules in this state when Rb atoms are present in the trap. To test this hypothesis, we attempt to load the molecules in these states into the lattice with the atoms. First, the Rb MOT is loaded as described above and the atoms are transferred to the optical lattice. Directly afterwards, the CaF MOT is loaded and then we attempt to transfer the molecules into the lattice, as before.

In figure 6.14, we see the result of this attempt to load both species. Figure 6.14a shows the distribution of Rb atoms in the optical lattice. Figure 6.14b shows the distribution of CaF molecules loaded into the lattice in the absence of Rb. Finally, figure 6.14c shows the distribution of CaF molecules after being loaded into the lattice in the presence of Rb atoms and held for 50 ms while the remaining molecules fall out of the imaging region under gravity. No molecules are present in the region where the cloud overlaps with the distribution of the Rb atoms, due to inelastic collisions between the atoms and molecules. In these experiments, the molecules are being lost about 100 times faster than in the magnetic trapping experiments, implying that the effective density is about 100 times larger. This makes us optimistic that the atoms and molecules will thermalize if we can eliminate the loss. To do this, it is necessary to load the molecules first before loading the atoms into the trap. The molecules must then be prepared in a state in the $N = 0$ manifold, where the inelastic collision rate is much lower, before the atoms are loaded. Figure 6.14c also demonstrates that the atoms and molecules are confined to the microscopic traps formed by the standing wave. If they were free to move through the lattice, we would expect molecules to be lost throughout the distribution, but we see that they are only lost in the region where there are atoms.

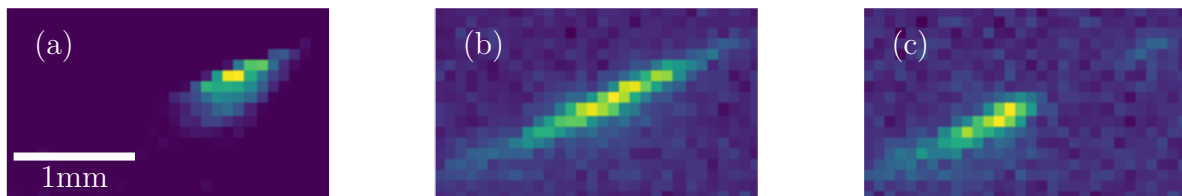


Figure 6.14: Loss of molecules in the $N = 1$ manifold from the lattice: The distribution in the lattice of (a) Rb alone, (b) CaF alone and (c) CaF in the presence of Rb. In all three images, the atoms and/or molecules are held in the lattice for 50 ms prior to imaging.

6.6.2 State preparation

After loading the CaF molecules into the lattice, we prepare the molecules by optically pumping to the state $|N = 1, F = 0, M_F = 0\rangle$ using the scheme detailed in section 4.1.1. However due to the AC Stark shift of the molecules in the optical lattice, the frequency of the optical pumping light must be shifted from the optimal frequency in free space.

After optically pumping the molecules, we can transfer the molecules in $|1, 0, 0\rangle$ to the state $|0, 1, 0\rangle$. Figure 6.15a shows a Rabi flop on the $|1, 0, 0\rangle \leftrightarrow |0, 1, 0\rangle$ transition driven with resonant microwaves. The ratio of the number of molecules recaptured into the MOT with the microwaves applied, N_{CaF} , to the number recaptured in the absence of microwaves, N_{CaF}^0 , is measured as a function of the duration of the microwave pulse. The time needed to drive a π pulse is found to be $t_\pi \approx 50 \mu\text{s}$.

Figure 6.15b shows the fraction of molecules remaining in the $N = 1$ manifold after a π pulse as a function of microwave frequency. The central frequency is shifted from the free-space value, $\omega_0/2\pi = 20\,481\,942 \text{ GHz}$, by $-5.4(4) \text{ kHz}$, due to the differential AC Stark shift between the two levels. By fitting the modified Rabi lineshape given in equation 2.29 for a π pulse with a duration of $50 \mu\text{s}$, we find an overall efficiency of $25(1)\%$ for preparing the molecules in the state $|0, 1, 0\rangle$.

After transferring to $|0, 1, 0\rangle$, the molecules remaining in the $N = 1$ manifold are removed with a resonant blow-away pulse, as described in section 4.1.1. At the end of the sequence, the molecules are then transferred back to the state $|1, 0, 0\rangle$ with a π pulse on the $|1, 0, 0\rangle \leftrightarrow |0, 1, 0\rangle$ transition for detection. Figure 6.15c shows Rabi flops on this transition after the blow-away.

6.6.3 Collisions in $N = 0$

Once the molecules are prepared in the state $|0, 1, 0\rangle$, the atoms are loaded into the lattice. Figure 6.16 shows the loss of molecules prepared in this state from the trap after being held for time t with the atoms. We see rapid loss from the trap and measure a lifetime of $37(4) \text{ ms}$.

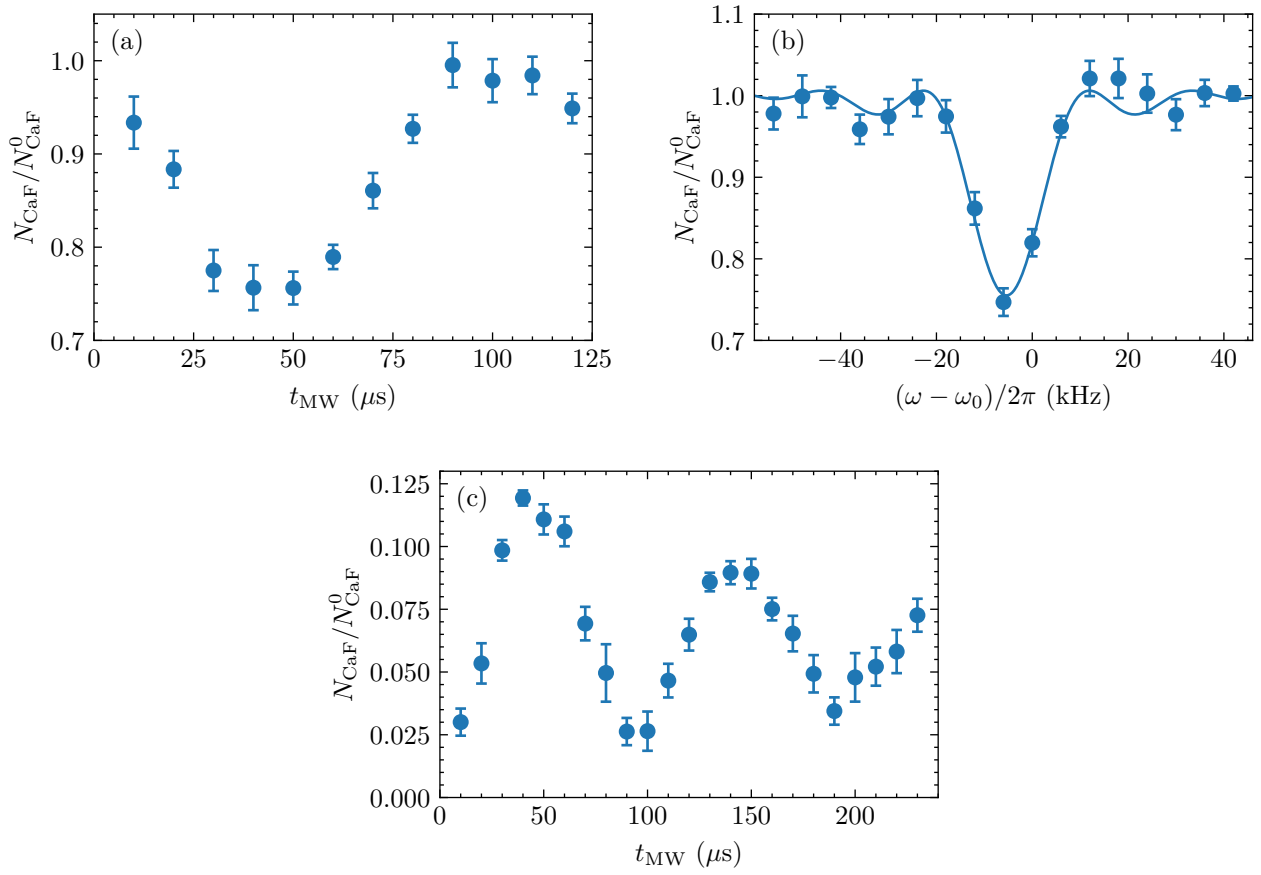


Figure 6.15: Driving the microwave transition $|1,0,0\rangle \leftrightarrow |0,1,0\rangle$ in the optical lattice: (a) Rabi flops between the two states after optical pumping. (b) number of molecules remaining in the $N = 1$ manifold after a $50\,\mu\text{s}$ pulse as a function of microwave frequency. (c) Rabi flops between the two states after the blow-away. In (b), the solid line is from a fit to the modified Rabi lineshape given in equation 2.29 for a π pulse with a duration of $50\,\mu\text{s}$

This might be explained by inelastic collisions between the atoms and the molecules. However, the molecules are in the rotational ground state, so the only possible inelastic channels are hyperfine-changing collisions and light-assisted collisions. Given the upper bound to the hyperfine-changing rate coefficient found in the magnetic trap, this is not a likely cause. Collisions assisted by the lattice light also seem unlikely because the frequency of the light is very far below any electronic resonances. Instead, we consider another possible cause. Since the atoms are hotter than the molecules at a given trap depth and the trap depth for the molecules is smaller by a factor of 3.7 than the trap depth for the atoms, we must also consider possible loss due to elastic collisions. The data here were taken at a laser power of $10.5\,\text{W}$, which corresponds to a temperature of $199\,\mu\text{K}$ for the atoms and about $100\,\mu\text{K}$ for the molecules. This is a considerable fraction of the trap depth for the molecules of $750\,\mu\text{K}$ and so elastic collisions with

Rb atoms could transfer enough energy to allow molecules to escape the trap. To eliminate this as a potential mechanism of loss and to see sympathetic cooling, it is necessary to cool the atoms well below the temperature of the molecules. That is the subject of the next chapter.

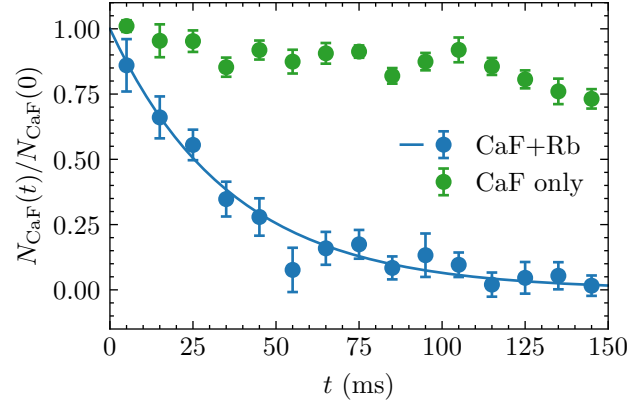


Figure 6.16: Loss of molecules in state $|0, 1, 0\rangle$ from the lattice with and without Rb: The solid line is a fit to a single exponential decay. Points and error bars are mean and standard error of 10 iterations.

Chapter 7

Λ -enhanced grey molasses of Rb in optical traps

7.1 Introduction

We have previously used red-detuned molasses to cool Rb down to temperatures of around $40\,\mu\text{K}$. We find that this method becomes ineffective in the presence of deep optical traps and the atoms are very rapidly lost from the trap when the molasses is applied. To avoid this loss and reach lower temperatures, we decided to implement a Λ -enhanced grey molasses (ΛGM). This technique has been used to cool ^{87}Rb atoms down to temperatures of around $4\,\mu\text{K}$ in free space [176] and to load them into an optical dipole trap [177], suggesting that it may not be affected by the higher density clouds and AC stark shifts that could interfere with the cooling.

7.2 Cooling in free space

To implement a ΛGM , we need to generate the light to coherently address the $F = 1$ and $F = 2$ hyperfine states. We do this by modulating the light from the cooling laser, $\mathcal{L}_{\text{Rb}}^{\text{C}}$, with an EOM (*Qubig PM-Rb 6.8*). The EOM is driven at a frequency $f_{\text{EOM}} = E_{\text{HFS}}/h + \delta$, where

$E_{\text{HFS}}/h = 6.834\,682\text{ GHz}$ is the hyperfine splitting in the ground state of ^{87}Rb .

To verify that our ΛGM setup works effectively, we first investigated the cooling in free space. For the following experiments, we first load the Rb MOT, then transfer the atoms to a red-detuned optical molasses as described in section 4.1.1, where they are held for 10 ms. After this, both the cooling and repump lasers ($\mathcal{L}_{\text{Rb}}^{\text{C}}$ and $\mathcal{L}_{\text{Rb}}^{\text{R}}$) are switched off and $\mathcal{L}_{\text{Rb}}^{\text{C}}$ is detuned to the red over 3 ms by sending a voltage ramp to its offset lock. The frequency is set so that it is blue-detuned by Δ from the $F = 2 \rightarrow F = 2$ transition, as shown in figure 7.1. $\mathcal{L}_{\text{Rb}}^{\text{C}}$ is turned back on and the EOM is switched on to provide the coherent repump light that addresses the $F = 1$ hyperfine state. The intensity of the light addressing $F = 1$ is set to 10 % of the intensity of the light addressing $F = 2$. This is done by adjusting the RF power delivered to the EOM whilst monitoring the sidebands with a Fabry-Perot cavity.

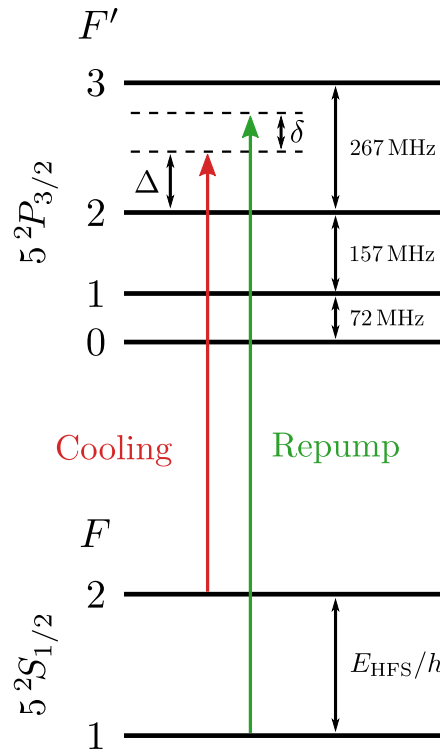


Figure 7.1: Schematic of relevant energy levels in ^{87}Rb and the laser frequencies used for ΛGM .

The temperature of the atoms after the ΛGM is measured by ballistic expansion. Figure 7.2 shows the temperature of the atoms, T , as a function of ΛGM duration, $t_{\Lambda\text{GM}}$. Fitting an exponential decay to these data gives a $1/e$ time of $236(7)\,\mu\text{s}$. We then set $t_{\Lambda\text{GM}} = 5\text{ ms}$ and vary the other experimental parameters. Figure 7.3a shows the temperature of the atoms as

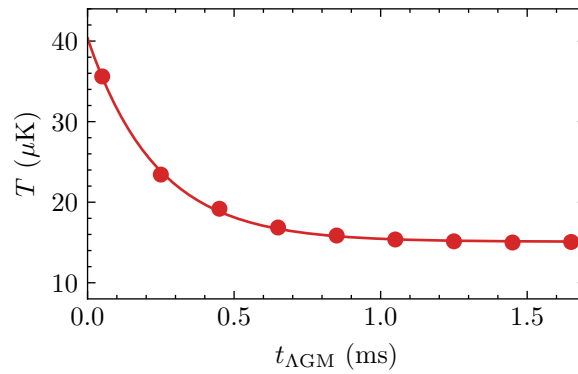


Figure 7.2: Temperature of atoms as a function of hold time in the Λ GM: Points are average of 4 experimental runs and error bars are smaller than the points. Solid line is fit to exponential decay.

a function of the detuning Δ . The temperature initially decreases with increasing Δ , as the light is detuned further to the blue of the $F = 1, 2 \rightarrow F' = 2$ transitions. However, as the frequency of the cooling light approaches the $F = 2 \rightarrow F' = 3$ resonance, the temperature increases rapidly. This is due to excitation on the transition $F = 2 \rightarrow F' = 3$ destroying the Raman coherence between the states in the $F = 1$ and $F = 2$ manifolds.

In figure 7.3b, the dependence of the temperature on the two-photon detuning, δ , is shown. Around the Raman resonance condition at $\delta = 0$, the temperature is sensitive to very small changes in the two-photon detuning. Similar to [176], we find the temperature of the atoms to be minimized just below the Raman resonance, at $\delta = -0.2$ MHz.

Figure 7.3c shows the dependence of the final temperature of the atoms on the intensity of the cooling light expressed as I/I_{sat} where $I_{\text{sat}} = 1.669 \text{ mW/cm}^2$ is the saturation intensity of ^{87}Rb . We see that for intensities such that $10I_{\text{sat}} \lesssim I < 20I_{\text{sat}}$, lower intensity leads to lower temperature. The initial decrease is likely due to lower scattering of the cooling light which would cause heating. However, decreasing the intensity of the cooling light also decreases the capture velocity of the molasses. If this is too low, then there will be a large fraction of the atoms with velocities lower than the capture velocity. In this case, the Λ GM would cause heating of these atoms. This might explain the increase in temperature for intensities below $10I_{\text{sat}}$.

For optimal cooling in the Λ GM, the magnetic field in all directions must be zeroed. Figure 7.3d

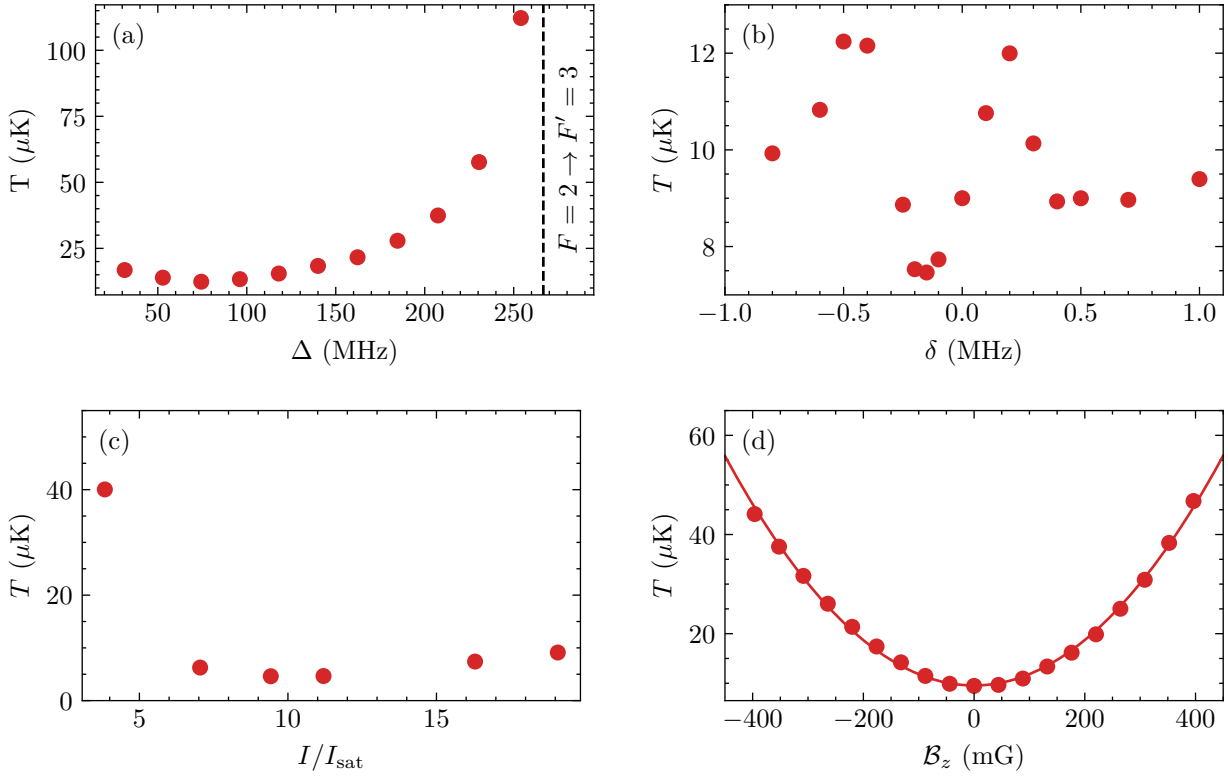


Figure 7.3: Temperature of atoms after being held in the Λ GM for 5 ms as a function of various parameters: (a) T vs Δ , with $\delta = -0.2$ MHz and $I = 19.2I_{\text{sat}}$, (b) T vs δ , with $\Delta = 65.2$ MHz and $I = 19.2I_{\text{sat}}$, (c) T vs I , with $\Delta = 65.2$ MHz and $\delta = -0.2$ MHz, and (d) T vs $\mathcal{B}_z$, with the magnetic fields in the x and y direction already zeroed. The other parameters are $\delta = -0.2$ MHz, $\Delta = 65.2$ MHz and $I = 19.2I_{\text{sat}}$. Solid line is fit to $T = T_0 + \alpha\mathcal{B}_z^2$, with T_0 and α as free parameters. Points are average of 4 experimental runs and error bars are smaller than the points.

shows the temperature as a function of the magnetic field along z , $\mathcal{B}_z$, with the field in the other two axes already set to zero. The effect of the magnetic field on the molasses can be elucidated by a simple model. The gray molasses relies on optical pumping from bright states into dark states at regions of high intensity, followed by non-adiabatic transfer back to a bright state at a region of low intensity. If a magnetic field is present, it will cause Larmor precession of the state of the atom with period $t_B = h/\mu\mathcal{B}$ where μ is the magnetic moment of the atom. This will disrupt the cooling process if the period of the precession is comparable to the time taken for an atom to move from an intensity minimum to an intensity maximum (given by $\lambda/4v$ where λ is the wavelength and v is the speed of the atom). Therefore, we can expect that the cooling will not work effectively at speeds below $v = \lambda\mu\mathcal{B}/4h$. If we take this as the mean speed of our atoms, this corresponds to a temperature of $T = \frac{\pi m}{8k}(\lambda\mu\mathcal{B}/4h)^2$. Assuming that

$\mu \approx \mu_B$, we have the relationship $T = \alpha \mathcal{B}^2$ with $\alpha \approx 300 \mu\text{K}/\text{G}^2$. The solid line in figure 7.3d is a fit to the model $T = T_0 + \alpha \mathcal{B}_z^2$, from which we find $\alpha = 229(3) \mu\text{K}/\text{G}^2$, remarkably close to our model given its simplicity.

7.3 Cooling in the optical lattice

After optimizing the Λ GM in free space, the cooling was then applied to atoms trapped in the 1D optical lattice. The Rb atoms are loaded into the lattice as detailed in chapter 6. After the end of the dark SPOT, the cooling laser is chirped and the EOM is switched on as in the previous section. The Λ GM is applied for a time, $t_{\Lambda\text{GM}}$, before the cooling light is turned off. The atoms are then held in the lattice for an additional 100 ms before being released for imaging.

Figure 7.4a shows the final temperature of the atoms as a function of the duration of the Λ GM. An exponential decay is fitted to the data giving a $1/e$ time of 4.6(8) ms. As well as having a much slower timescale than in free space, the Λ GM in the lattice also causes loss, as shown in figure 7.4b, which was not observed in free space. The $1/e$ time from the fitted exponential decay is 5.3(3) ms.

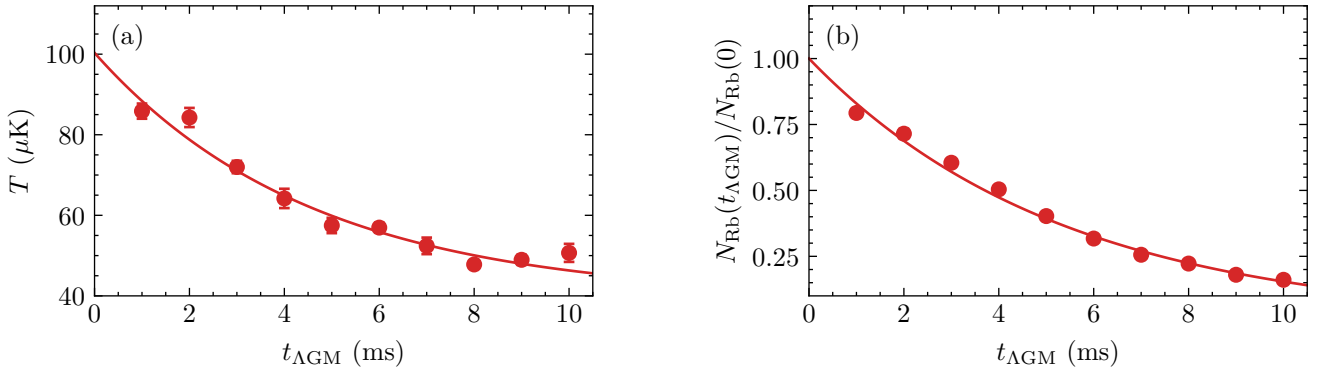


Figure 7.4: Cooling and loss in the Λ GM applied in the optical lattice: (a) temperature of the atoms and (b) fraction of atoms remaining after Λ GM of duration $t_{\Lambda\text{GM}}$. Parameters for the cooling are $\Delta = 35$ MHz, $\delta = -0.2$ MHz and $I = 19.2I_{\text{sat}}$. The lattice beam has power $P = 7.78$ W. Points and error bars are mean and standard error of 4 iterations.

To optimize the cooling in the lattice while still retaining a large fraction of the trapped atoms,

we limit the Λ GM duration to $t_{\Lambda\text{GM}} = 2$ ms. The atoms are held for 100 ms in the lattice before imaging. In figure 7.5a, we see the temperature of the atoms as a function of the detuning Δ . The cooling is most effective over a small range of detunings from $\Delta = 80$ MHz to 120 MHz with an optimum temperature at $\Delta = 92$ MHz of $155(1)$ μK , much higher than the lowest temperature attained in free space.

To explain the different behaviour observed when applying the Λ GM in the lattice, the impact of the AC Stark effect on the transition frequencies must be taken into account. In the ground state manifold ($5^2S_{1/2}$), there is no tensor part of the AC polarizability and, since the lattice trapping light is linearly polarized, the vector part of the AC polarizability is also zero. Only the scalar part remains, which causes all of the hyperfine states to shift in energy by

$$\Delta E(5^2S_{1/2}) = -\frac{\alpha_0(\omega)I_T}{2c\epsilon_0} \quad (7.1)$$

where $\alpha_0(\omega)$ is the AC scalar polarizability and I_T is the intensity of the lattice trapping light.

In the excited state manifold ($5^2P_{3/2}$), both the scalar and tensor parts of the AC polarizability contribute, leading to a more complicated response. A full treatment of the AC Stark effect in this state is given in appendix A. The tensor part of the AC Stark Hamiltonian causes mixing of the hyperfine states with different values of F' but with the same value of m'_F . As a result, m'_F is still a good quantum number but F' is not. We label each of the eigenstates according to the state they adiabatically connect to in the limit of zero intensity, so that $|\tilde{F}' = F', m'_F\rangle$ is the state that connects to $|F', m'_F\rangle$. Within each group of states with the same $\tilde{F}'$, the pairs of states with the same value of $|m'_F|$ are degenerate. Figure 7.6 shows the detuning Δ_S of the frequencies of all transitions $|F = 2, m_F\rangle \rightarrow |\tilde{F}', m'_F\rangle$ as a function of the trapping light intensity, relative to the transition $|F = 2, m_F\rangle \rightarrow |F' = 2, m'_F\rangle$ at zero intensity. Since all levels in the ground state are shifted equally, this is also the shift in detuning for the transitions $|F = 1, m_F\rangle \rightarrow |\tilde{F}', m'_F\rangle$, relative to $|F = 1, m_F\rangle \rightarrow |F' = 2, m'_F\rangle$ at zero intensity.

The range of detunings accessible in the experiment is roughly between the $|F = 2, m_F\rangle \rightarrow |F' = 2, m'_F\rangle$ and $|F = 2, m_F\rangle \rightarrow |F' = 3, m'_F\rangle$ resonances marked by the horizontal dashed lines

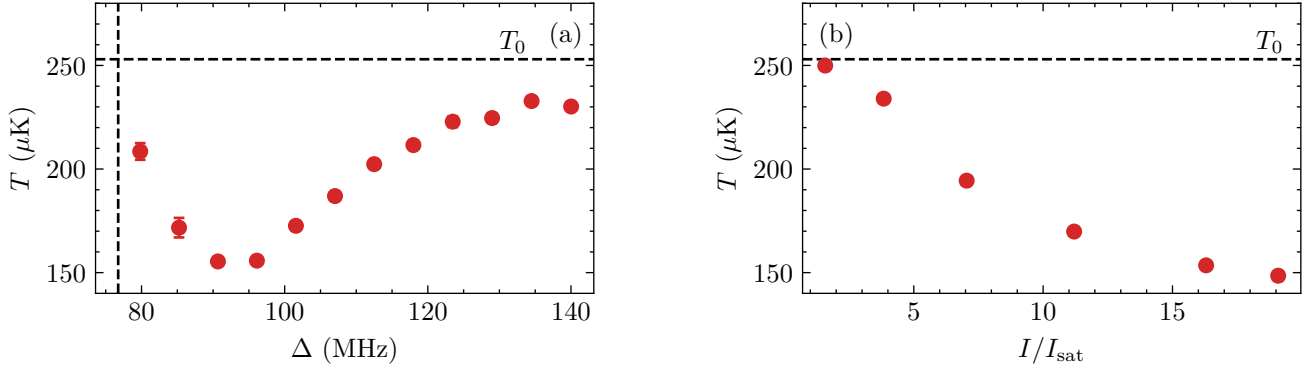


Figure 7.5: Temperature of atoms in an optical lattice after the Λ GM as a function of (a) the detuning Δ with $I = 19.2I_{\text{sat}}$, and (b) the intensity I of the cooling light with $\Delta = 92$ MHz. In both cases, $\delta = -0.2$ MHz and the lattice beam has power $P = 15.6$ W. The horizontal dashed lines labelled T_0 show the temperature without cooling applied. Points and error bars are mean and standard error of 4 points.

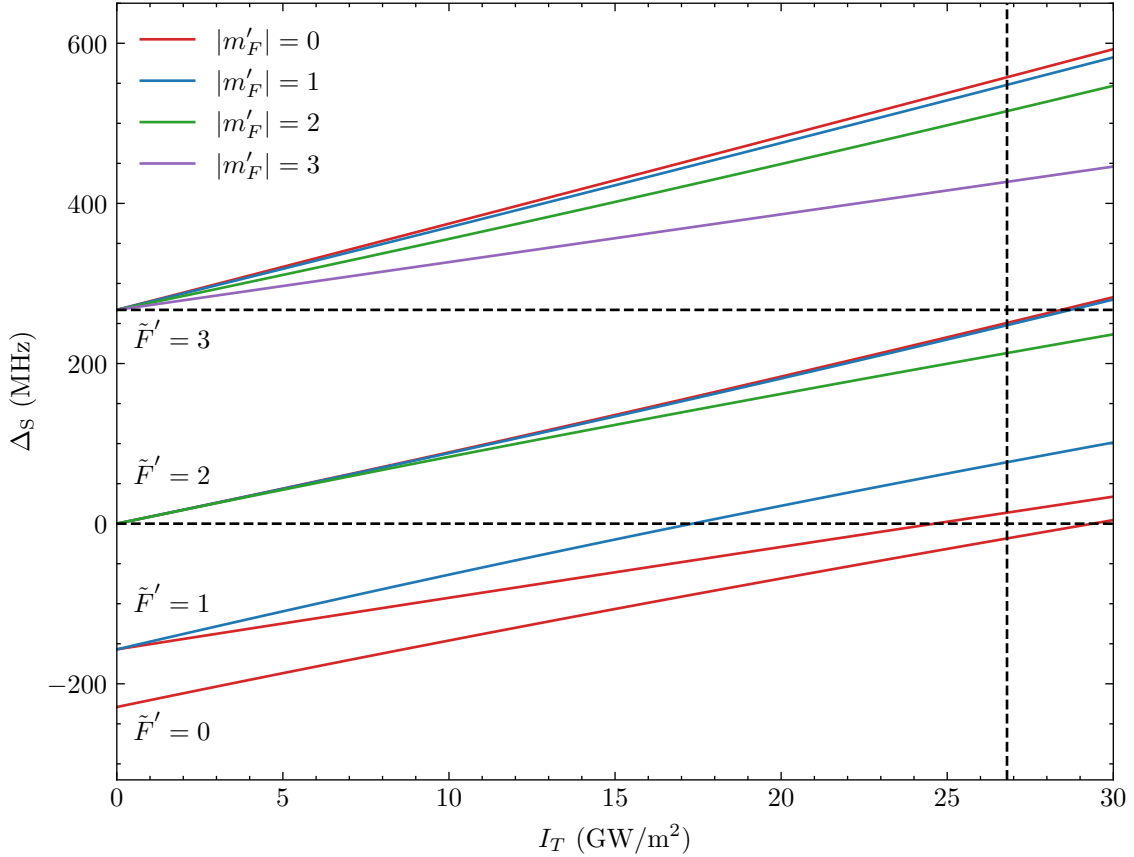


Figure 7.6: Shift in the detuning Δ_S of the transitions $|F=1, m_F\rangle, |F=2, m_F\rangle \rightarrow |\tilde{F}', m'_F\rangle$ due to the AC Stark effect, given relative to the $|F=1, m_F\rangle, |F=2, m_F\rangle \rightarrow |\tilde{F}'=2, m'_F\rangle$ transition at zero intensity. The horizontal dashed lines give the approximate range of detunings of the cooling light accessible in the experiment. The vertical dashed line is the peak intensity in the lattice with $P = 15.6$ W.

in figure 7.6. The vertical dashed line indicates the peak intensity of the lattice trapping light experienced by the atoms for $P = 15.6$ W. Here, we can see that the Stark shifts of the transition frequencies mean that cooling light is red-detuned from the $|F = 1, m_F\rangle, |F = 2, m_F\rangle \rightarrow |\tilde{F}' = 2, m'_F\rangle$ transitions for $\Delta < 250$ MHz, which is likely to lead to heating. The range of detunings where the the cooling was found to be most effective ($\Delta = 80$ MHz to 120 MHz) corresponds to being blue-detuned by up to 40 MHz from the transition $|F = 1, m_F\rangle, |F = 2, m_F\rangle \rightarrow |\tilde{F}' = 1, m'_F = \pm 1\rangle$, which is marked with a vertical dashed line in figure 7.5a. This suggests that effective cooling is limited to this small range of detunings because this is where the gray molasses cooling due to being blue-detuned of the transitions $|F = 1, m_F\rangle, |F = 2, m_F\rangle \rightarrow |\tilde{F}' = 1, m'_F\rangle$ is dominant over the heating due to being red-detuned from $|F = 1, m_F\rangle, |F = 2, m_F\rangle \rightarrow |\tilde{F}' = 2, m'_F\rangle$. The cooling may also work between $|F = 1, m_F\rangle, |F = 2, m_F\rangle \rightarrow |\tilde{F}' = 2, m'_F\rangle$ and $|F = 1, m_F\rangle, |F = 2, m_F\rangle \rightarrow |\tilde{F}' = 3, m'_F\rangle$ but the range of detunings needed for this was not accessible in the experiment.

The effect of the intensity of the cooling light on the temperature of the atoms is again different to that found in free space. As shown in figure 7.5b, the temperature of the atoms after the molasses decreases with increasing intensity. This could be due to the increasing capture velocity with intensity. Since the atoms start at a higher temperature compared with the free space molasses, a higher capture velocity is required to effectively cool the atoms and as a result higher intensities are needed compared to free space. No change in the optimum value of the detuning δ was found compared to its free space optimum, $\delta = -0.2$ MHz.

7.3.1 Heating

Although we can successfully reduce the temperature of the atoms in the lattice with the application of AGM, we find that the temperature of the trapped atoms increases slowly over time after the initial cooling period. Figure 7.7 shows the temperature after a hold time of t_{hold} in the lattice for atoms cooled for 20 ms compared with atoms that have no cooling applied. We speculate that the gradual increase in temperature is due to parametric heating of the atoms

caused by phase fluctuations of the lattice laser which shake the lattice sites. The laser used to seed the 1064 nm amplifier has a large broad peak in its phase noise density between 1 MHz to 2 MHz and the parametric resonance corresponding to the axial lattice frequency sits in this range. We were not able to investigate this hypothesis quantitatively. Instead, we decided to study cooling in the optical dipole trap where phase noise does not lead to position variation of the trapping potential as it does in the lattice, allowing us to avoid this source of parametric heating.

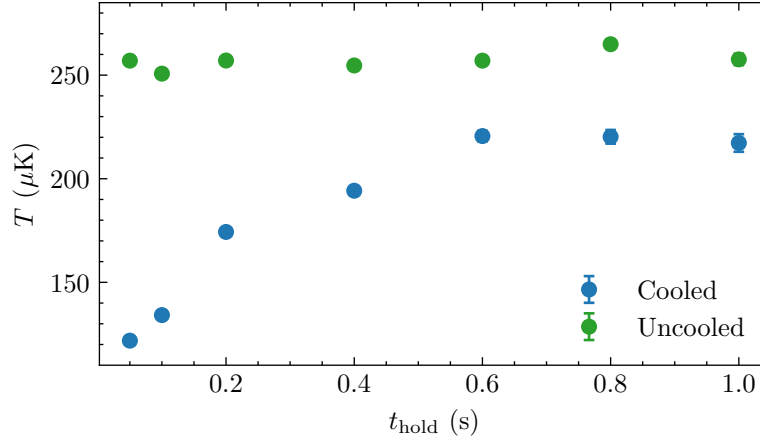


Figure 7.7: Heating in the lattice: blue points show temperature after Λ GM followed by a hold time in the lattice of t_{hold} , green points show the temperature after being held in the lattice for t_{hold} with no cooling applied. Points and error bars are mean and standard error of 4 experimental runs.

7.4 Cooling in the optical dipole trap

The ODT is formed using the same setup as the optical lattice but with a beam block replacing the retroreflecting mirror. For the following experiments, the power of the ODT beam was set to $P = 15.6$ W, unless stated otherwise. The atoms are loaded into the ODT with the same procedure used for loading the lattice.

For a beam with power P and waist size w_0 , the trap frequencies of the ODT are given by

$$\omega_r = \frac{1}{w_0^2} \sqrt{\frac{4\alpha P}{m\epsilon_0 c\pi}}, \quad \omega_z = \frac{1}{w_0 z_R} \sqrt{\frac{2\alpha P}{m\epsilon_0 c\pi}} \quad (7.2)$$

where $z_R = \pi w_0^2/\lambda$. With $P = 15.6$ W and $w_0 = 38.5$ μm , the trap frequencies are $\omega_r = 2\pi \times 2.6$ kHz and $\omega_z = 2\pi \times 16$ Hz.

We apply the Λ GM for 4 ms in the ODT and then hold the atoms in the ODT for an additional 14 ms. The final temperature of the atoms as a function of detuning Δ is shown in figure 7.8. The peak intensity of the trap light experienced by the atoms is $I_T = 6.7$ GW/m² and at this intensity at the cooling light will be resonant with the $|F = 1, m_F\rangle, |F = 2, m_F\rangle \rightarrow |\tilde{F}' = 2, m'_F\rangle$ at $\Delta = 59$ MHz for $m'_F = 0$, at $\Delta = 58.5$ MHz for $m'_F = \pm 1$, and at $\Delta = 56.5$ MHz for $m'_F = \pm 2$. As expected, we can see that the temperature of the atoms is higher when the light is close to resonance with or red-detuned from these transitions, which are marked by the dashed vertical lines in figure 7.8. The cooling is optimized for $\Delta = 72$ MHz, yielding a temperature of 40 μK . For $\Delta > 72$ MHz, the cooling becomes less efficient as the detuning increases. This is similar to the dependence on frequency we find in free-space, although the cooling works effectively over a smaller range and the optimal detuning is much closer to resonance with $|F = 1, m_F\rangle, |F = 2, m_F\rangle \rightarrow |\tilde{F}' = 2, m'_F\rangle$ than the optimal detuning in free-space relative to $|F = 1, m_F\rangle, |F = 2, m_F\rangle \rightarrow |F' = 2, m'_F\rangle$.

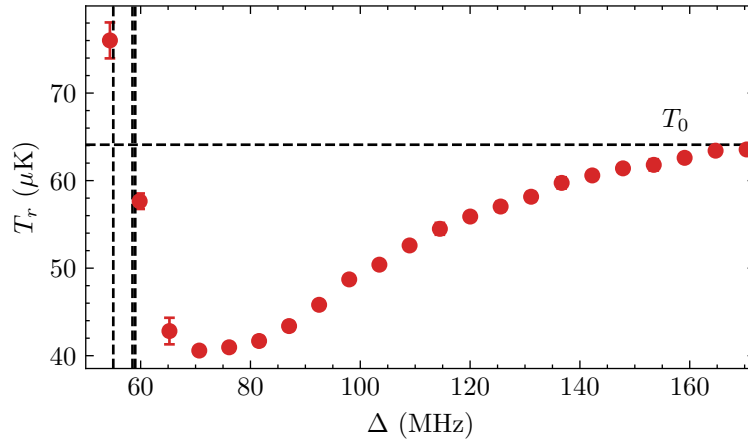


Figure 7.8: Temperature of atoms in the ODT after Λ GM of duration 4 ms and then held for 14 ms. T_0 shows the temperature of the atoms with no cooling applied. Parameters for Λ GM are $\delta = -0.2$ MHz and $I = 19.2I_{\text{sat}}$. Points and error bars are mean and standard error of 4 experimental runs.

Figure 7.9 shows the axial and radial temperature of the atoms in the ODT as a function of the duration of the cooling $t_{\Lambda\text{GM}}$, measured directly after the Λ GM. The solid lines are fits to exponential decays which give $1/e$ time constants of 390(10) μs for the axial temperature and

1.2(1) ms for the radial temperature. From these data, we can see that the timescale for cooling is about 3 times longer in the radial direction compared to the axial direction where the cooling rate is slightly slower than for Λ GM in free space.

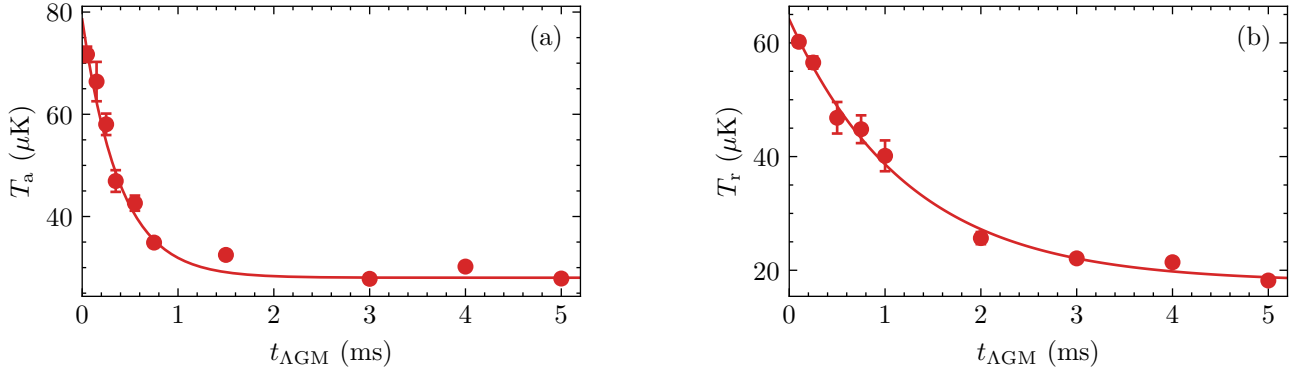


Figure 7.9: Temperature in the (a) axial and (b) radial direction directly after Λ GM applied for a duration of $t_{\Lambda\text{GM}}$. Parameters for Λ GM are $\Delta = 49$ MHz, $\delta = -0.2$ MHz, and $I = 19.2I_{\text{sat}}$. Points and error bars are mean and standard error of 4 iterations.

To understand the difference in timescales for cooling, it is instructive to consider the damped harmonic motion of the atoms in the trap. For each direction, the equation of motion is given by

$$\ddot{x} + \gamma\dot{x} + \omega_0^2 x = 0, \quad (7.3)$$

where x is the displacement, γ is the damping coefficient, and ω_0 is the frequency of the oscillator in the absence of damping. The solution to this equation for the underdamped case ($\omega_0 > \gamma/2$) is well-known:

$$x(t) = Ae^{-\gamma t/2} \cos(\omega t + \phi) \quad (7.4)$$

where $\omega = \sqrt{\omega_0^2 - (\gamma/2)^2}$ and A and ϕ are constants determined by the initial conditions. To get the velocity, we differentiate this:

$$v = \dot{x}(t) = -\frac{1}{2}Ae^{-\gamma t/2} [\gamma \cos(\omega t + \phi) + 2\omega \sin(\omega t + \phi)]. \quad (7.5)$$

The kinetic energy of the oscillator is given by:

$$E_k = \frac{1}{2}m\dot{x}^2 = \frac{1}{8}mA^2e^{-\gamma t} [\gamma \cos(\omega t + \phi) + 2\omega \sin(\omega t + \phi)]^2. \quad (7.6)$$

Ignoring the periodic variation with period ω , we can see that the damping causes the kinetic energy to decrease with a timescale given by $\tau = 1/\gamma$. The potential energy, given by

$$E_p = \frac{1}{2}m\omega^2 x^2 = \frac{1}{2}m\omega^2 A^2 e^{-\gamma t} \cos^2(\omega t + \phi), \quad (7.7)$$

also decays on the same timescale.

The situation is very different for the overdamped oscillator, however. In this case, the solution to equation 7.3 is

$$x(t) = Ae^{-\gamma_+ t/2} + Be^{-\gamma_- t/2}, \quad (7.8)$$

where A and B are determined by the initial conditions and $\gamma_{\pm} = \gamma \pm \sqrt{\gamma^2 - 4\omega_0^2}$. We can see that the motion decays on two different timescales. In the limit of heavy damping ($\gamma \gg \omega_0$), we find

$$\gamma_+ \approx 2\gamma, \quad \gamma_- \approx 2\omega_0^2/\gamma \ll \gamma_+, \quad (7.9)$$

and so one timescale is much faster than the other. The fast timescale leads to a decay of the energy with a timescale given by $\tau = 1/2\gamma$ - twice as fast as in the underdamped case.

Assuming the radial motion is underdamped, from the exponential fit in figure 7.9b, we find that the damping coefficient is $\gamma = 800(50) \text{ s}^{-1}$. Comparing this to the axial trap frequency, it is clear that the axial motion is strongly overdamped ($\omega_z \ll \gamma/2$). Therefore, we expect the cooling to take twice as long in the radial direction compared to the axial direction. This explains some of the discrepancy between the cooling timescales in the two directions.

A large fraction of the kinetic energy in the axial direction is removed by the cooling, however the potential energy of the atoms has hardly changed. When the cooling stops, the atoms will start to move towards the centre of the trap converting the potential energy back into kinetic energy. Since the atoms are not in thermal equilibrium during this process, we cannot assign a temperature to the cloud. However, from the time-of-flight measurement we can deduce the spread of velocities σ_{v_i} in each direction and from this we define an effective kinetic temperature

(EKT), given by

$$\Theta_i = \frac{m\sigma_{v_i}^2}{k}, \quad i \in \{a, r\}. \quad (7.10)$$

Once the cloud reaches thermal equilibrium, this quantity will give the true temperature.

In figure 7.10, we see the EKT of the atoms held in the ODT for a variable time t_{hold} after the Λ GM has been applied for 4 ms. Over a quarter period of the axial motion (≈ 15 ms), the EKT of the atoms increases, eventually settling at around $70 \mu\text{K}$ as the cloud thermalizes. Further oscillations in the EKT due to the harmonic motion are damped away either by collisions or anharmonicity of the trapping potential. The radial EKT of the cloud also increases but at a slower rate, reaching a steady state at $50 \mu\text{K}$. This is likely due to thermalization between the axial and radial directions either by collisions or by mixing of the two directions due to the inseparability of the potential.

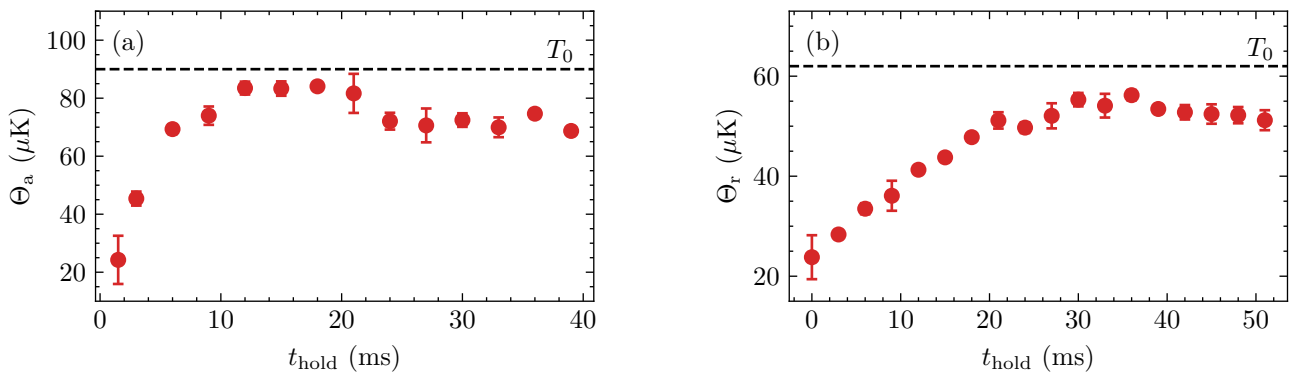


Figure 7.10: Effective kinetic temperature in the (a) axial and (b) radial direction after 4 ms of Λ GM cooling followed by a variable hold time of t_{hold} in the ODT. The dashed line labelled T_0 shows the (true) temperature of the atoms with no cooling applied. Parameters for Λ GM are $\Delta = 69$ MHz, $\delta = -0.2$ MHz, and $I = 19.2I_{\text{sat}}$. Points and error bars are mean and standard error of 4 iterations.

7.4.1 Cooling protocols

In order to reduce the temperature even further, it is necessary to intersperse pulses of Λ GM with intervals of free evolution in the ODT. We investigated two different approaches to this. The first, which we will refer to as strobed cooling, involves quickly switching between short pulses of cooling and periods of free evolution. The aim of this method is to effectively reduce

the average damping due to the Λ GM so that the axial motion becomes underdamped and the axial potential energy can be removed. Figure 7.11 shows a schematic of the pulsing sequence, where we have shown the cooling time per pulse t_c , the free evolution time per pulse t_f , and the number of pulses N_p . The damping will be reduced by a factor of $D = t_c/(t_c + t_f)$, where D is the duty cycle. Taking $\gamma \approx 800 \text{ s}^{-1}$ and $\omega_z \approx 2\pi \times 16 \text{ Hz}$, the axial motion should be underdamped for $D \lesssim 25\%$.

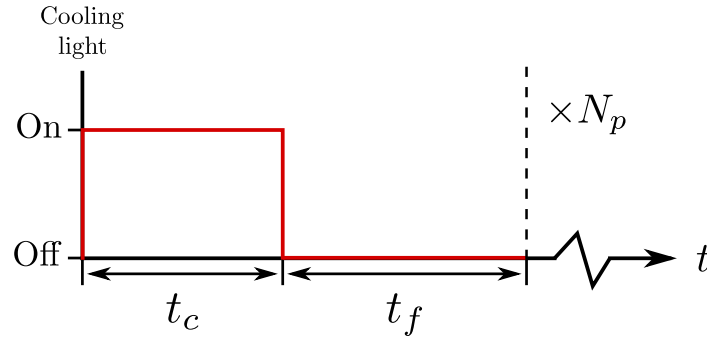


Figure 7.11: Schematic of the protocol for strobed and pulse cooling, with the cooling time per pulse t_c , the free evolution time per pulse t_f , and the number of pulses N_p labelled.

Figure 7.12 shows the resulting radial temperature of the cloud after applying the strobed cooling and holding the atoms in the ODT for a further 50 ms to allow them to equilibrate. As shown in figure 7.12a, the temperature decreases as more pulses are added to the sequence, tending towards a minimum temperature of around 30 μK .

The importance of the periods of free evolution can be seen in figure 7.12b. The duration of free evolution after each pulse of cooling, t_f , is varied. We see a clear increase in temperature as the duty cycle approaches $D = 25\%$, which is consistent with the prediction based on the model of the overdamped axial motion.

In figure 7.12c, the cooling time per pulse t_c is varied. As expected, decreasing t_c leads to higher temperatures. Therefore, it is not possible to reduce the overall cooling time by reducing both t_c and t_f proportionately thus keeping the duty cycle D the same for a fixed number of pulses.

The second approach is to intersperse longer periods of Λ GM with periods of free evolution comparable to the settling time of the axial temperature. We will refer to this as pulsed cooling. Figure 7.13 shows the radial temperature after equilibration after pulsed cooling. As the cooling

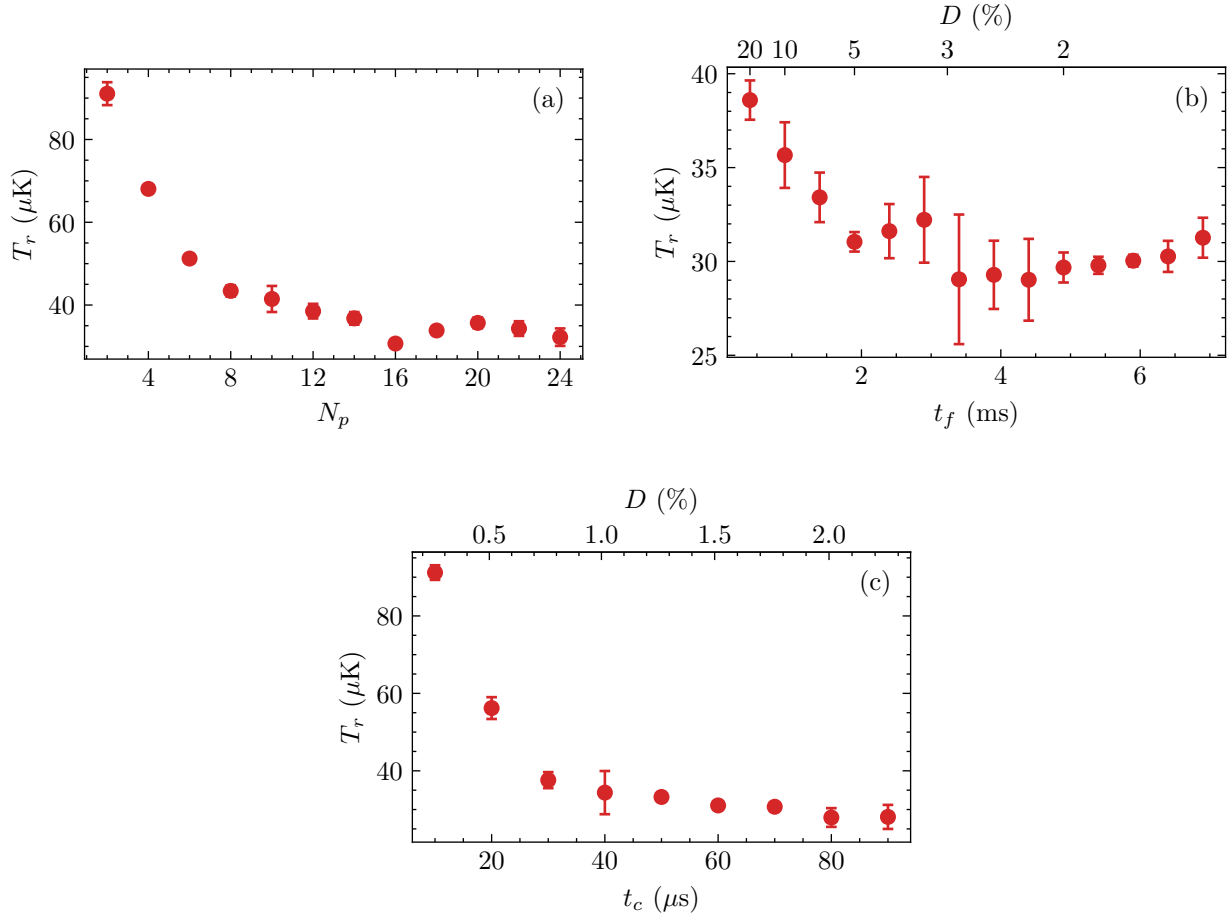


Figure 7.12: Strobed cooling: radial temperature as a function of pulse parameters. (a) varying N_p whilst holding $t_c = 0.1$ ms and $t_f = 1.9$ ms, (b) varying t_f whilst holding $t_c = 0.1$ ms and $N_p = 24$, and (c) varying t_c while holding $t_f = 3.9$ ms and $N_p = 24$. Atoms are held for 50 ms in the ODT after cooling. Points and error bars are mean and standard error of 4 experimental runs.

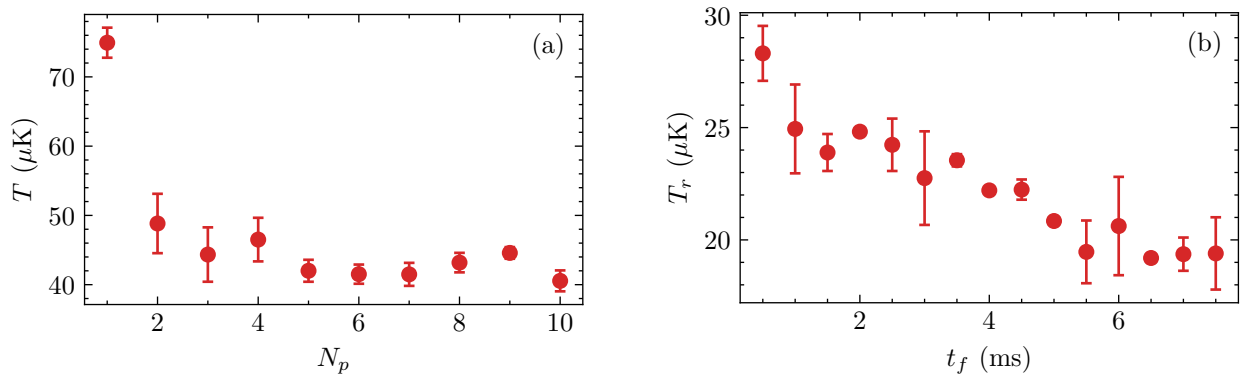


Figure 7.13: Pulsed cooling: radial temperature as a function of pulse parameters. (a) varying N_p whilst holding $t_c = 0.5$ ms and $t_f = 9.5$ ms and (b) varying t_f whilst holding $t_c = 0.5$ ms and $N_p = 24$. Atoms are held for 50 ms in the ODT after cooling. Points and error bars are mean and standard error of 4 experimental runs.

time per pulse, t_c , is larger than for the strobed cooling, the decrease in temperature per pulse is initially larger as shown in figure 7.13a. By extending the number of pulses N_p , we can reach lower temperatures. Figure 7.13b shows the temperature after 24 pulses for various values of t_f . The temperature decreases as t_f increases as for the strobed cooling. A minimum temperature of 18 μ K was reached by applying 24 pulses with $t_c = 0.5$ ms and $t_f = 7.5$ ms.

7.5 Density effects

We find that the effectiveness of the cooling in the ODT depends on the number density of atoms in the trap. To investigate this, the number of atoms loaded into the ODT was varied. The atoms were held in the trap for 500 ms before the cooling was applied. After 4 ms in the AGM, the atoms were held in the trap for 14 ms to equilibrate, before being released. In addition to measuring the radial temperature by ballistic expansion, the number of atoms was measured with absorption imaging after 2 ms of free expansion, to reduce diffraction effects due to the small size of the cloud in the ODT.

To estimate the number density before cooling, we assume the trap is harmonic with radial trap frequency ω_r and axial trap frequency ω_z . At thermal equilibrium, the density distribution of the atoms in the trap is given by

$$n(x, y, z) = n_0 \exp \left(-\frac{x^2 + y^2}{2\sigma_r^2} - \frac{z^2}{2\sigma_z^2} \right), \quad (7.11)$$

where

$$\sigma_i = \sqrt{\frac{k_B T}{m\omega_i^2}}, \quad i \in \{r, z\}. \quad (7.12)$$

The integral of this over all space should give the total number of atoms N so we have

$$N = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} n(x, y, z) dx dy dz = n_0 \sigma_r^2 \sigma_z (2\pi)^{3/2}, \quad (7.13)$$

and thus the peak density is given by

$$n_0 = \frac{N}{(2\pi)^{3/2} \sigma_r^2 \sigma_z}. \quad (7.14)$$

In figures 7.14a and 7.14b, we see the temperature of the atoms with and without the cooling applied for different peak number densities. Although there is some positive correlation between the peak number density and temperature of the atoms in the ODT without the cooling applied, as shown in figure 7.14a, the temperature after cooling depends more strongly on the peak number density, which can be seen in figure 7.14b.

The effect of the density is made clearer when the cooling is applied in a deeper ODT. Figures 7.14c and 7.14d show a similar measurement but with the ODT beam power increased to 35.0 W. At this trap depth, there is no clear trend in the temperature with increasing number density without cooling applied, as shown in figure 7.14c. When the cooling is applied, we see that the atoms are cooled to a higher temperature compared to the shallower trap and that there is a stronger dependence on density.

This effect could be due to heating by rescattering of photons. At higher densities, photons emitted by the atoms are more likely to be reabsorbed by another atom in the trap causing heating. Although the dark states set up by the Λ GM are supposed to reduce the scattering rate, these dark states may be disturbed by the trapping light from the ODT which causes differential AC stark shifts for the different Zeeman levels.

7.6 Outlook

We have demonstrated that we can cool atoms in the ODT down to temperatures of 18 μ K at a trap depth of 1 mK by applying pulsed cooling in the Λ GM. For the CaF molecules, this would correspond to a trap depth of around 44 μ K.

The low trap depth for molecules is due to the effect of gravity. Since the beam is oriented at 21° to the horizontal, there is a component of gravity along the axis of the beam where the

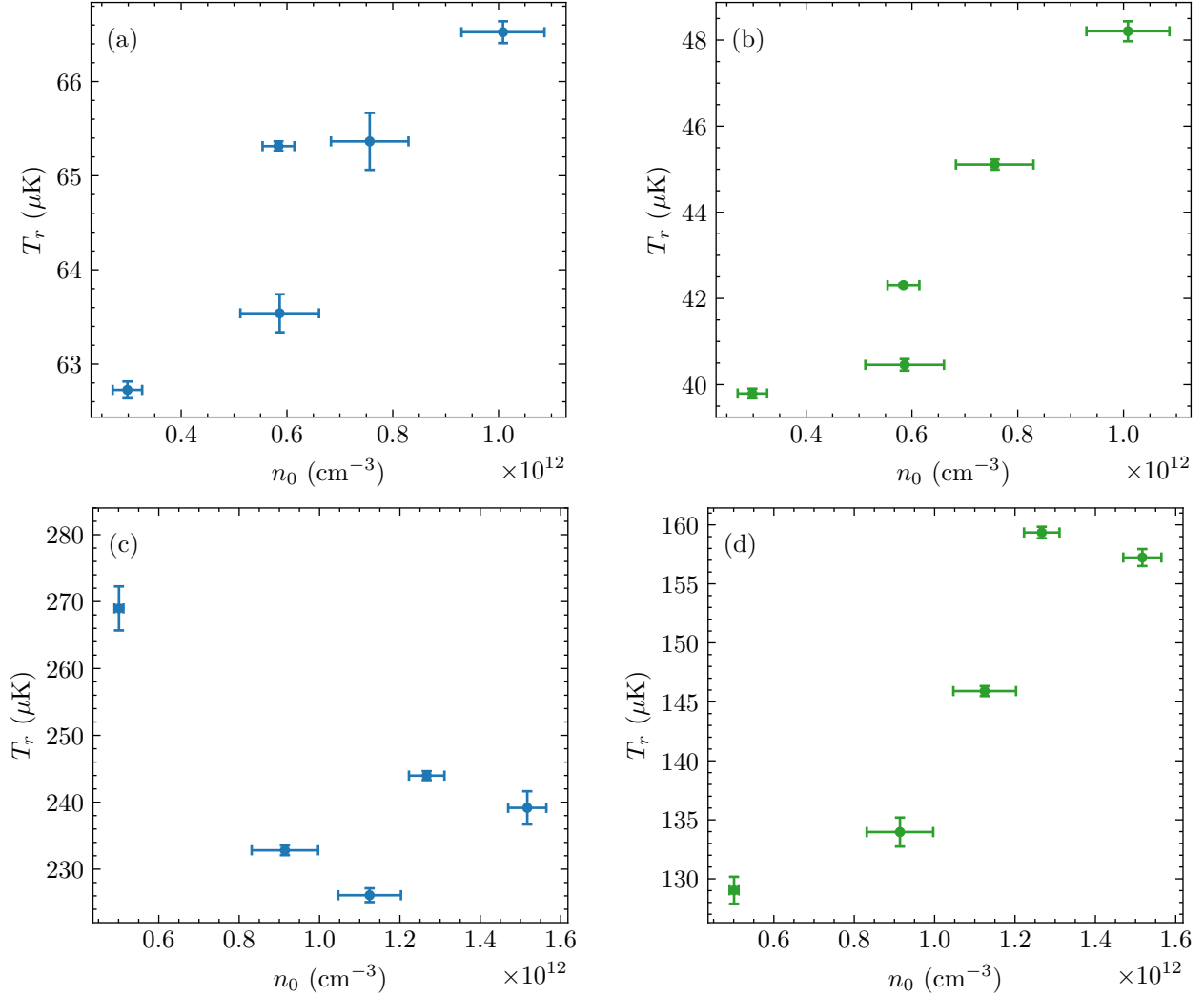


Figure 7.14: Effect of density on cooling: (a) radial temperature of atoms in ODT after being held for 518 ms with no cooling applied. (b) radial temperature of atoms in ODT after being held for 500 ms, followed by Λ GM for 4 ms and then held for 14 ms. (c,d) the same experiment with the ODT power increased to $P = 35$ W and the detuning Δ increased to 145 MHz to account for the increased AC stark shift. Error bars are from average and standard error of 5 experimental runs. Uncertainty in density is dominated by the uncertainty in estimating the number by absorption imaging.

confinement is weaker. This causes the trap to ‘tilt’ as shown in figure 7.15a. By having the beam along the horizontal direction, gravity acts along the radial direction which has much stronger confinement, so the ‘tilt’ is less significant. As shown in figure 7.15b, this increases the trap depth for the molecules by around a factor of 6 for a beam with power 15.6 W.

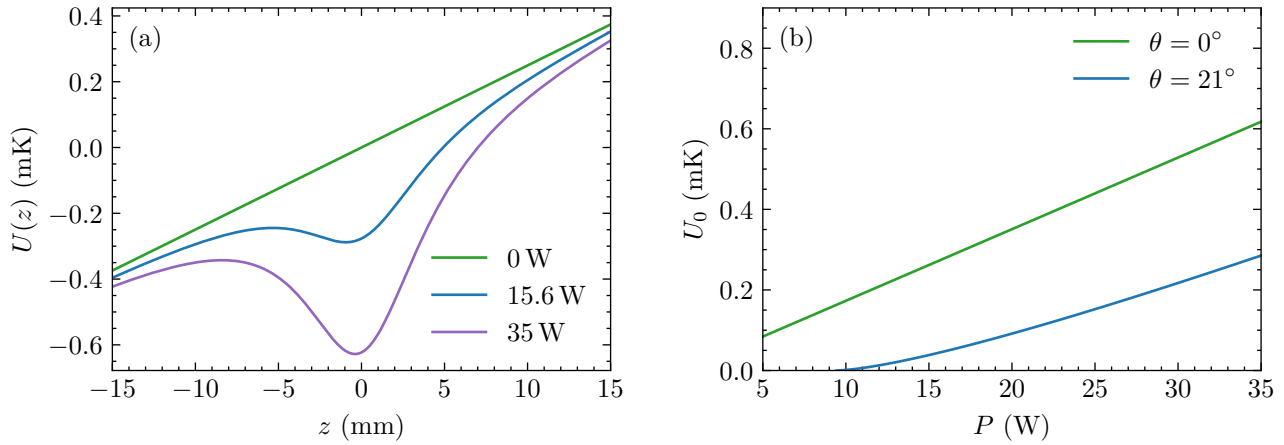


Figure 7.15: (a) profile of the trap potential for CaF molecules along the axis of the beam, including the effect of gravity. The profile is shown for ODT beam powers as function of the axial distance along the beam z with the focus at $z = 0$. (b) trap depth for CaF molecules as a function of the ODT beam power for the current setup ($\theta = 21^\circ$) and for a horizontal beam ($\theta = 0^\circ$).

We are able to load CaF molecules into the ODT with the trap laser power at 35 W, which corresponds to approximately the same trap depth as a horizontal ODT operated at 15.6 W, and we measure their temperature to be approximately $75 \mu\text{K}$. As we saw in the previous section, however, the ΛGM is less effective at this ODT beam power, and we cannot reduce the temperature of the atoms below that of the molecules. Work is currently underway to move the the ODT beam into the horizontal plane so the trap depth can be increased without increasing the trap laser power. By splitting the ODT laser into two and intersecting the two beams, we can produce a crossed ODT. This solves the issue of weak confinement along the axial direction and would make the pulsed cooling schemes unnecessary, hopefully allowing quicker cooling.

Finally, we are working to implement ΛGM on the D_1 line of ^{87}Rb at 795 nm. This has been shown to work more effectively for alkali atoms where the hyperfine levels of the excited state of the D_2 transition are not well separated [178]. Although this is not the case for ^{87}Rb , ΛGM on the D_1 line has been successfully used for loading ^{87}Rb into optical tweezers [179] and, since

there is no tensor AC Stark shift in the excited state for the D_1 transition, this should make the application of the cooling simpler and hopefully more robust.

Chapter 8

Conclusion

In this work, we have made progress towards sympathetic cooling of CaF molecules with ultracold Rb atoms. First, we studied inelastic collisions between the molecules and atoms in the magnetic trap. In the first rotationally excited state, we measured an inelastic loss rate coefficient of $k_2 = (6.6 \pm 1.5) \times 10^{-11} \text{ cm}^3/\text{s}$, close to the universal limit. By transferring the molecules to the rotational ground state, the inelastic collisions are greatly suppressed by at least an order of magnitude. An attempt was made to observe thermalization between the two species but this was limited by the effective density of Rb atoms and the number of molecules trapped.

To boost the number of molecules captured, transverse cooling of the beam of CaF was implemented. By studying the effect of the cooling in 1D and 2D, we were able to infer which cooling mechanism was responsible - namely, Doppler cooling. After optimization, the number of molecules captured in the MOT was increased by a factor of 3.5.

The improvement in molecule number brought about by transverse cooling helped us to load CaF molecules into a 1D optical lattice along with the Rb atoms, where the effective density of Rb atoms is orders of magnitude higher than in the magnetic trap. We characterized the trap with the atoms and showed that we could coherently control the trapped molecules with microwaves. When the molecules were prepared in the state $|N = 1, F = 0, M_F = 0\rangle$, we found that the molecules were rapidly lost when the atoms were loaded. This is consistent with the

large inelastic loss rate measured in the magnetic trap for states in the $N = 1$ manifold. In the state $|N = 0, F = 1, M_F = 0\rangle$, the lifetime of CaF molecules in the trap was longer but still well below the lifetime of molecules alone in the trap. We attribute this loss to elastic collisions with the atoms, which have a temperature similar to the trap depth of the molecules.

Finally, we applied Λ -enhanced gray molasses cooling to Rb atoms, first in a 1D optical lattice and then an optical dipole trap. By employing pulses of cooling followed by free evolution, the temperature of the atoms was reduced to 18 μ K in an ODT with a trap depth of 1 mK. We expect this to be far below the temperature of molecules confined in a horizontal trap with the same trap beam power, which should allow sympathetic cooling to be observed.

For further cooling, it will likely be beneficial to evaporatively cool the atoms. To do this, it may be necessary to overcome the issue of the trap being deeper for the atoms than for the molecules. Figure 8.1 shows the polarizability of CaF and Rb as a function of wavelength. In the range shown, except for near the Rb resonances at 780 nm and 795 nm, there is no single trap wavelength that will result in a deeper trap for Rb than for CaF. Instead, this problem could be remedied by adding a second optical trapping laser to the experiment with a wavelength that is red-detuned for the molecules but blue-detuned for the atoms. This would increase the trap depth for the molecules but would be anti-trapping for the atoms thus leading to a reduced trap depth [180]. For this purpose, the wavelength of this laser should be chosen to be somewhere in the centre of the grey region shown in figure 8.1, far removed both from the CaF $A \leftarrow X$ transition at 606 nm and the D_2 line of ^{87}Rb at 780 nm so that any heating due to scattering of trap light is minimized.

Another potentially simpler way to selectively reduce the trap depth is to prepare the atoms in a state that is sensitive to a magnetic field (e.g. $|F = 1, m_F = +1\rangle$) and the molecules in an insensitive state (e.g. $|N = 0, F = 1, M_F = 0\rangle$). By applying a magnetic field gradient, the trap could be ‘tilted’ for the atoms without affecting the trapping potential for the molecules. This has been successfully done to accelerate the evaporative cooling of Cs atoms [183].

Once the molecules are sympathetically cooled by the atoms and the phase space density of the molecules increases towards degeneracy, it will be necessary to shield the CaF molecules

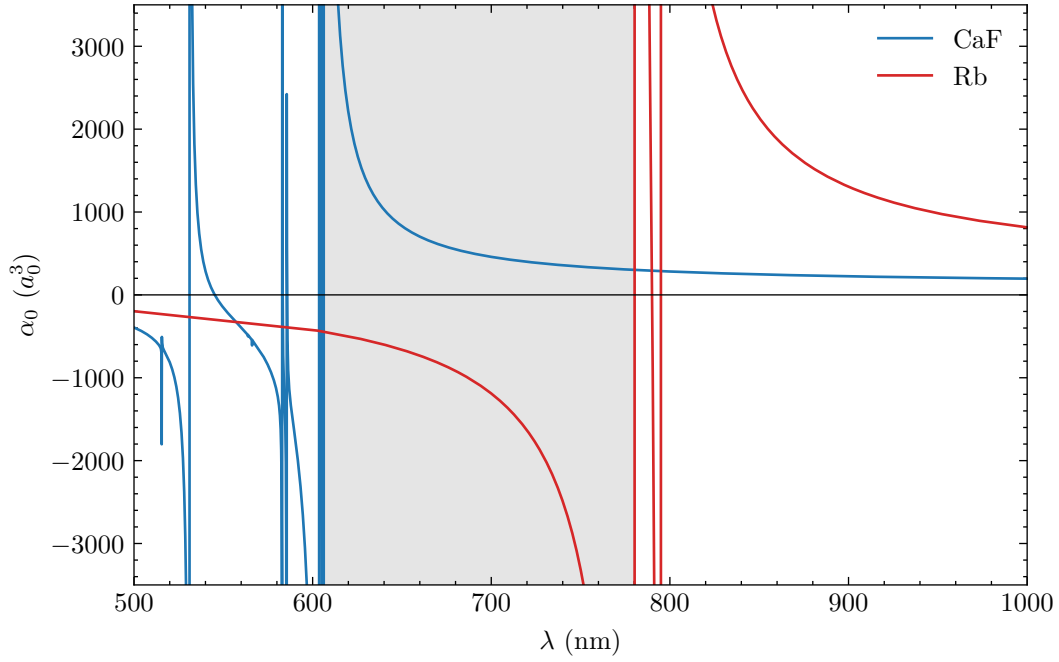


Figure 8.1: Scalar AC polarizability (α_0) of Rb and CaF given in atomic units as a function of wavelength (λ). The data for Rb comes from [181] and the data for CaF comes from [182]. The grey shaded band shows the range of wavelengths most suitable for an additional second trapping/anti-trapping laser as mentioned in the main text.

from reactive bimolecular collisions. Work is underway on a new CaF experiment in our group which aims demonstrate shielding using resonant DC electric fields, as proposed in [144].

The mixture of atoms and molecules in the ODT could also be used to investigate interspecies Feshbach resonances which are predicted to exist at magnetic fields below 1000 G [184] and may be employed to control collisions between the two species. These resonances could also be harnessed to form polyatomic molecules, which are an excellent platform for quantum simulation [185, 186], quantum computing [42, 187], and tests of fundamental physics [188, 189]. All of these applications benefit from presence of closely-spaced states of opposite parity that allow polyatomic molecules to be fully polarized with relatively small electric fields.

Finally, CaF molecules confined alone in the 1D optical lattice can be used as a molecular clock for probing the fundamental variation of physical constants [54, 190]. As such, our experiment will serve as a node in a network of atomic and molecular clocks searching for physics beyond the standard model.

Appendix A

AC Stark effect in the $5^2P_{3/2}$ manifold of Rb

We write the total Hamiltonian as

$$H = H_0 + H_S \quad (\text{A.1})$$

where H_0 is the field-free Hamiltonian of the atom and H_S the Hamiltonian describing the AC Stark effect. For the intensities we are using, the AC Stark shift is much less than the fine structure spacing so we only need to consider the effect within the subspace of the hyperfine structure of each state. The field-free Hamiltonian is given in the coupled $|F, m_F\rangle$ basis by

$$H_0 = \sum_{F, m_F} E_F |F, m_F\rangle\langle F, m_F|. \quad (\text{A.2})$$

For linearly polarized light, H_S is given in the decoupled $|I, m_I, J, m_J\rangle$ basis by [191]

$$H_S = -\frac{I}{2c\epsilon_0} \sum_{m_I, m_J} \left[\alpha_0(\omega) + \alpha_2(\omega) \frac{3m_J^2 - J(J+1)}{J(2J-1)} \right] |I, m_I, J, m_J\rangle\langle I, m_I, J, m_J|. \quad (\text{A.3})$$

where I is the intensity of the light and $\alpha_0(\omega)$ and $\alpha_2(\omega)$ are the scalar and tensor AC polarizabilities, respectively. We choose to work in the coupled basis and the matrix elements of H_S can be written in this basis as

$$\langle F, m_F | H_S | F', m'_F \rangle = -\frac{I}{2c\epsilon_0} \sum_{m_I, m_J} \left[\alpha_0(\omega) + \alpha_2(\omega) \frac{3m_J^2 - J(J+1)}{J(2J-1)} \right] \times \\ \langle F, m_F | I, m_I, J, m_J \rangle \times \langle I, m_I, J, m_J | F', m'_F \rangle. \quad (\text{A.4})$$

The last two factors in the expression are Clebsch-Gordan coefficients, which are only non-zero if

$$m_F = m_I + m_J = m'_F. \quad (\text{A.5})$$

Therefore, H_S is diagonal in m_F and so m_F remains a good quantum number. In addition, H_S is invariant under the transformation

$$m_I \rightarrow -m_I, \quad m_J \rightarrow -m_J, \quad (\text{A.6})$$

so degenerate states at zero intensity with the same value of $|m_F|$ will experience the same Stark shift and remain degenerate. The tensor polarizability term in the Hamiltonian mixes states with the different values of F and so this is no longer a good quantum number.

The eigenstates and energy shifts can be found by diagonalizing the full Hamiltonian. We label the eigenstates as $|\tilde{F}, m_F\rangle$ where $\tilde{F}$ is the value of F of the hyperfine state that the eigenstate adiabatically connects to in the limit of zero intensity. For states in the $5^2P_{3/2}$ manifold in Rb, the scalar and tensor polarizabilities are given by $\alpha_0 = -1149(29)$ and $\alpha_2 = 563(24)$ in atomic units, respectively [191]. The resulting energy shifts due to the AC stark effect are shown as a function of the intensity in figure A.1.

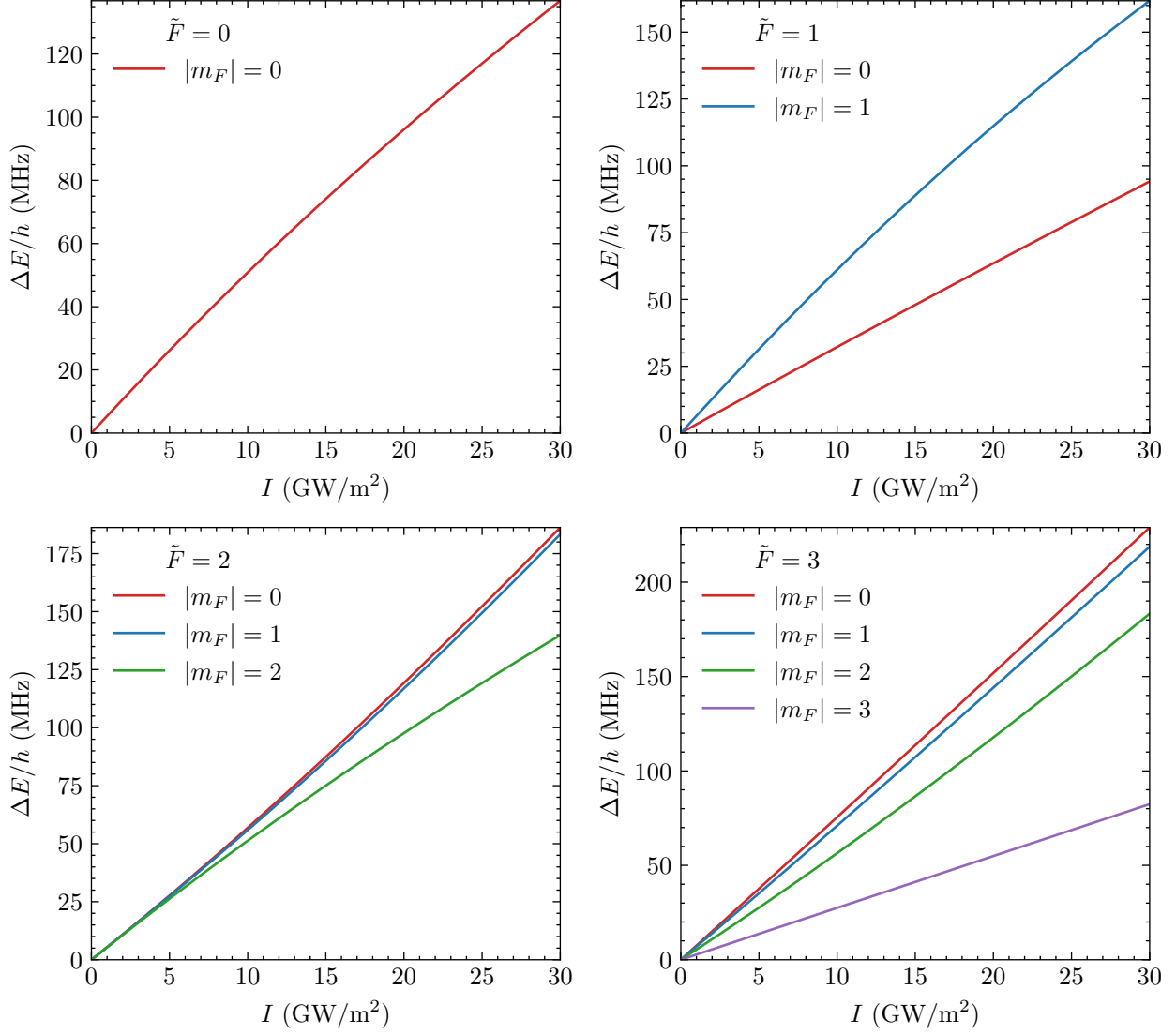


Figure A.1: AC Stark shifts of the hyperfine states in the $5^2P_{3/2}$ manifold of Rb as a function of intensity. The states are divided into panels according to their value of $\tilde{F}$ and for each panel the energy shift of the levels are given relative to the hyperfine state with $F = \tilde{F}$ at zero intensity.

Bibliography

- [1] A. D. Ludlow, M. M. Boyd, J. Ye, E. Peik and P. O. Schmidt, “Optical atomic clocks”, *Rev. Mod. Phys.* **87**, 637 (2015).
- [2] I. Bloch, J. Dalibard and S. Nascimbène, “Quantum simulations with ultracold quantum gases”, *Nature Phys* **8**, 267 (2012).
- [3] W. S. Bakr, J. I. Gillen, A. Peng, S. Fölling and M. Greiner, “A quantum gas microscope for detecting single atoms in a Hubbard-regime optical lattice”, *Nature* **462**, 74 (2009).
- [4] L. D. Carr, D. DeMille, R. V. Krems and J. Ye, “Cold and ultracold molecules: science, technology and applications”, *New J. Phys.* **11**, 055049 (2009).
- [5] M. T. Bell and T. P. Softley, “Ultracold molecules and ultracold chemistry”, *Molecular Physics* **107**, 99 (2009).
- [6] J. Pérez Ríos, *An Introduction to Cold and Ultracold Chemistry: Atoms, Molecules, Ions and Rydbergs* (Springer International Publishing, Cham, Switzerland, 2020).
- [7] E. P. Wigner, “On the Behavior of Cross Sections Near Thresholds”, *Phys. Rev.* **73**, 1002 (1948).
- [8] N. Balakrishnan and A. Dalgarno, “Chemistry at ultracold temperatures”, *Chemical Physics Letters* **341**, 652 (2001).
- [9] N. Balakrishnan, “On the role of van der Waals interaction in chemical reactions at low temperatures”, *The Journal of Chemical Physics* **121**, 5563 (2004).
- [10] B. K. Kendrick, J. Hazra and N. Balakrishnan, “The geometric phase controls ultracold chemistry”, *Nat. Commun.* **6**, 7918 (2015).

- [11] M. H. G. de Miranda, A. Chotia, B. Neyenhuis, D. Wang, G. Quémener, S. Ospelkaus, J. L. Bohn, J. Ye and D. S. Jin, “Controlling the quantum stereodynamics of ultracold bimolecular reactions”, *Nat. Phys.* **7**, 502 (2011).
- [12] M. H. Anderson, J. R. Ensher, M. R. Matthews, C. E. Wieman and E. A. Cornell, “Observation of Bose-einstein condensation in a Dilute Atomic Vapor”, *Science* **269**, 198 (1995).
- [13] K. B. Davis, M.-O. Mewes, M. R. Andrews, N. J. Van Druten, D. S. Durfee, D. M. Kurn and W. Ketterle, “Bose-Einstein Condensation in a Gas of Sodium Atoms”, *Phys. Rev. Lett.* **75**, 3969 (1995).
- [14] C. C. Bradley, C. A. Sackett, J. J. Tollett and R. G. Hulet, “Evidence of Bose-Einstein Condensation in an Atomic Gas with Attractive Interactions”, *Phys. Rev. Lett.* **75**, 1687 (1995).
- [15] D. G. Fried, T. C. Killian, L. Willmann, D. Landhuis, S. C. Moss, D. Kleppner and T. J. Greytak, “Bose-Einstein Condensation of Atomic Hydrogen”, *Phys. Rev. Lett.* **81**, 3811 (1998).
- [16] B. DeMarco and D. S. Jin, “Onset of Fermi Degeneracy in a Trapped Atomic Gas”, *Science* **285**, 1703 (1999).
- [17] F. Pereira Dos Santos, J. Léonard, J. Wang, C. J. Barrelet, F. Perales, E. Rasel, C. S. Unnikrishnan, M. Leduc and C. Cohen-Tannoudji, “Bose-Einstein Condensation of Meta-stable Helium”, *Phys. Rev. Lett.* **86**, 3459 (2001).
- [18] C. Raman, M. Köhl, R. Onofrio, D. S. Durfee, C. E. Kuklewicz, Z. Hadzibabic and W. Ketterle, “Evidence for a Critical Velocity in a Bose-Einstein Condensed Gas”, *Phys. Rev. Lett.* **83**, 2502 (1999).
- [19] M. W. Zwierlein, J. R. Abo-Shaeer, A. Schirotzek, C. H. Schunck and W. Ketterle, “Vortices and superfluidity in a strongly interacting Fermi gas”, *Nature* **435**, 1047 (2005).
- [20] J. Denschlag, J. E. Simsarian, D. L. Feder, C. W. Clark, L. A. Collins, J. Cubizolles, L. Deng, E. W. Hagley, K. Helmerson, W. P. Reinhardt, S. L. Rolston, B. I. Schneider

- and W. D. Phillips, “Generating Solitons by Phase Engineering of a Bose-Einstein Condensate”, *Science* **287**, 97 (2000).
- [21] A. Griesmaier, J. Werner, S. Hensler, J. Stuhler and T. Pfau, “Bose-Einstein Condensation of Chromium”, *Phys. Rev. Lett.* **94**, 160401 (2005).
- [22] M. Lu, N. Q. Burdick, S. H. Youn and B. L. Lev, “Strongly Dipolar Bose-Einstein Condensate of Dysprosium”, *Phys. Rev. Lett.* **107**, 190401 (2011).
- [23] K. Aikawa, A. Frisch, M. Mark, S. Baier, A. Rietzler, R. Grimm and F. Ferlaino, “Bose-Einstein Condensation of Erbium”, *Phys. Rev. Lett.* **108**, 210401 (2012).
- [24] L. Chomaz, R. M. W. Van Bijnen, D. Petter, G. Faraoni, S. Baier, J. H. Becher, M. J. Mark, F. Wächtler, L. Santos and F. Ferlaino, “Observation of roton mode population in a dipolar quantum gas”, *Nature Phys* **14**, 442 (2018).
- [25] H. Kadau, M. Schmitt, M. Wenzel, C. Wink, T. Maier, I. Ferrier-Barbut and T. Pfau, “Observing the Rosensweig instability of a quantum ferrofluid”, *Nature* **530**, 194 (2016).
- [26] L. Tanzi, E. Lucioni, F. Famà, J. Catani, A. Fioretti, C. Gabbanini, R. N. Bisset, L. Santos and G. Modugno, “Observation of a Dipolar Quantum Gas with Metastable Supersolid Properties”, *Phys. Rev. Lett.* **122**, 130405 (2019).
- [27] T. Lahaye, C. Menotti, L. Santos, M. Lewenstein and T. Pfau, “The physics of dipolar bosonic quantum gases”, *Rep. Prog. Phys.* **72**, 126401 (2009).
- [28] M. A. Baranov, M. Dalmonte, G. Pupillo and P. Zoller, “Condensed Matter Theory of Dipolar Quantum Gases”, *Chem. Rev.* **112**, 5012 (2012).
- [29] D. Jaksch, C. Bruder, J. I. Cirac, C. W. Gardiner and P. Zoller, “Cold Bosonic Atoms in Optical Lattices”, *Phys. Rev. Lett.* **81**, 3108 (1998).
- [30] M. Greiner, O. Mandel, T. Esslinger, T. W. Hänsch and I. Bloch, “Quantum phase transition from a superfluid to a Mott insulator in a gas of ultracold atoms”, *Nature* **415**, 39 (2002).

- [31] A. Chotia, B. Neyenhuis, S. A. Moses, B. Yan, J. P. Covey, M. Foss-Feig, A. M. Rey, D. S. Jin and J. Ye, “Long-Lived Dipolar Molecules and Feshbach Molecules in a 3D Optical Lattice”, *Phys. Rev. Lett.* **108**, 080405 (2012).
- [32] L. Anderegg, L. W. Cheuk, Y. Bao, S. Burchesky, W. Ketterle, K.-K. Ni and J. M. Doyle, “An optical tweezer array of ultracold molecules”, *Science* **365**, 1156 (2019).
- [33] M. Lewenstein, A. Sanpera and V. Ahufinger, *Ultracold atoms in optical lattices: simulating quantum many-body systems*, 1st ed (Oxford University Press, Oxford, U.K, 2012).
- [34] J. A. Blackmore, L. Caldwell, P. D. Gregory, E. M. Bridge, R. Sawant, J. Aldegunde, J. Mur-Petit, D. Jaksch, J. M. Hutson, B. E. Sauer, M. R. Tarbutt and S. L. Cornish, “Ultracold molecules for quantum simulation: rotational coherences in CaF and RbCs”, *Quantum Science and Technology* **4**, 14010 (2018).
- [35] D. DeMille, “Quantum Computation with Trapped Polar Molecules”, *Phys. Rev. Lett.* **88**, 067901 (2002).
- [36] S. Burchesky, L. Anderegg, Y. Bao, S. S. Yu, E. Chae, W. Ketterle, K.-K. Ni and J. M. Doyle, “Rotational Coherence Times of Polar Molecules in Optical Tweezers”, *Phys. Rev. Lett.* **127**, 123202 (2021).
- [37] P. D. Gregory, J. A. Blackmore, S. L. Bromley, J. M. Hutson and S. L. Cornish, “Robust storage qubits in ultracold polar molecules”, *Nat. Phys.* **17**, 1149 (2021).
- [38] Y. Bao, S. S. Yu, L. Anderegg, E. Chae, W. Ketterle, K.-K. Ni and J. M. Doyle, “Dipolar spin-exchange and entanglement between molecules in an optical tweezer array”, *arXiv:2211.09780*.
- [39] C. M. Holland, Y. Lu and L. W. Cheuk, “On-Demand Entanglement of Molecules in a Reconfigurable Optical Tweezer Array”, *arXiv:2210.06309*.
- [40] J. G. Danzl, M. J. Mark, E. Haller, M. Gustavsson, R. Hart, J. Aldegunde, J. M. Hutson and H.-C. Nägerl, “An ultracold high-density sample of rovibronic ground-state molecules in an optical lattice”, *Nature Phys* **6**, 265 (2010).

- [41] R. Sawant, J. A. Blackmore, P. D. Gregory, J. Mur-Petit, D. Jaksch, J. Aldegunde, J. M. Hutson, M. R. Tarbutt and S. L. Cornish, “Ultracold polar molecules as qudits”, *New J. Phys.* **22**, 013027 (2020).
- [42] V. V. Albert, J. P. Covey and J. Preskill, “Robust encoding of a qubit in a molecule”, *Phys. Rev. X* **10**, 031050 (2020).
- [43] C. Zhang and M. Tarbutt, “Quantum computation in a hybrid array of molecules and rydberg atoms”, *PRX Quantum* **3**, 030340 (2022).
- [44] K. Wang, C. P. Williams, L. R. Picard, N. Y. Yao and K.-K. Ni, “Enriching the Quantum Toolbox of Ultracold Molecules with Rydberg Atoms”, *PRX Quantum* **3**, 030339 (2022).
- [45] M. Safronova, D. Budker, D. DeMille, D. F. J. Kimball, A. Derevianko and C. W. Clark, “Search for new physics with atoms and molecules”, *Rev. Mod. Phys.* **90**, 025008 (2018).
- [46] D. Mitra, K. H. Leung and T. Zelevinsky, “Quantum control of molecules for fundamental physics”, *Phys. Rev. A* **105**, 040101 (2022).
- [47] S. Barr, “A review of CP violation in atoms”, *Int. J. Mod. Phys. A* **08**, 209 (1993).
- [48] T. Chupp, P. Fierlinger, M. Ramsey-Musolf and J. Singh, “Electric dipole moments of atoms, molecules, nuclei, and particles”, *Rev. Mod. Phys.* **91**, 015001 (2019).
- [49] E. A. Hinds, “Testing time reversal symmetry using molecules”, *Phys. Scr.* **T70**, 34 (1997).
- [50] V. Andreev, D. G. Ang, D. DeMille, J. M. Doyle, G. Gabrielse, J. Haefner, N. R. Hutzler, Z. Lasner, C. Meisenhelder, B. R. O’Leary, C. D. Panda, A. D. West, E. P. West, X. Wu and ACME Collaboration, “Improved limit on the electric dipole moment of the electron”, *Nature* **562**, 355 (2018).
- [51] T. S. Roussy, L. Caldwell, T. Wright, W. B. Cairncross, Y. Shagam, K. B. Ng, N. Schlossberger, S. Y. Park, A. Wang, J. Ye and E. A. Cornell, “A new bound on the electron’s electric dipole moment”, [arXiv:2212.11841](https://arxiv.org/abs/2212.11841).

- [52] S. Truppe, R. J. Hendricks, S. K. Tokunaga, H. J. Lewandowski, M. G. Kozlov, C. Henkel, E. A. Hinds and M. R. Tarbutt, “A search for varying fundamental constants using hertz-level frequency measurements of cold CH molecules”, *Nat. Commun.* **4**, 2600 (2013).
- [53] J. Kobayashi, A. Ogino and S. Inouye, “Measurement of the variation of electron-to-proton mass ratio using ultracold molecules produced from laser-cooled atoms”, *Nat. Commun.* **10**, 3771 (2019).
- [54] G. Barontini, L. Blackburn, V. Boyer, F. Butuc-Mayer, X. Calmet, J. R. Crespo López-Urrutia, E. A. Curtis, B. Darquié, J. Dunningham, N. J. Fitch, E. M. Forgan, K. Georgiou, P. Gill, R. M. Godun, J. Goldwin, V. Guarrera, A. C. Harwood, I. R. Hill, R. J. Hendricks, M. Jeong, M. Y. H. Johnson, M. Keller, L. P. Kozhiparambil Sajith, F. Kuipers, H. S. Margolis, C. Mayo, P. Newman, A. O. Parsons, L. Prokhorov, B. I. Robertson, J. Rodewald, M. S. Safronova, B. E. Sauer, M. Schioppo, N. Sherrill, Y. V. Stadnik, K. Szymaniec, M. R. Tarbutt, R. C. Thompson, A. Tofful, J. Tunesi, A. Vecchio, Y. Wang and S. Worm, “Measuring the stability of fundamental constants with a network of clocks”, *EPJ Quantum Technol.* **9**, 1 (2022).
- [55] M. R. Tarbutt, B. E. Sauer, J. J. Hudson and E. A. Hinds, “Design for a fountain of YbF molecules to measure the electron’s electric dipole moment”, *New J. Phys.* **15**, 053034 (2013).
- [56] K. M. Jones, E. Tiesinga, P. D. Lett and P. S. Julienne, “Ultracold photoassociation spectroscopy: Long-range molecules and atomic scattering”, *Rev. Mod. Phys.* **78**, 483 (2006).
- [57] T. Koehler, K. Goral and P. S. Julienne, “Production of cold molecules via magnetically tunable Feshbach resonances”, *Rev. Mod. Phys.* **78**, 1311 (2006).
- [58] K. Winkler, F. Lang, G. Thalhammer, P. V. D. Straten, R. Grimm and J. H. Denschlag, “Coherent Optical Transfer of Feshbach Molecules to a Lower Vibrational State”, *Phys. Rev. Lett.* **98**, 043201 (2007).

- [59] K.-K. Ni, S. Ospelkaus, M. H. G. de Miranda, A. Pe'er, B. Neyenhuis, J. J. Zirbel, S. Kotochigova, P. S. Julienne, D. S. Jin and J. Ye, "A High Phase-Space-Density Gas of Polar Molecules", *Science* **322**, 231 (2008).
- [60] P. D. Lett, K. Helmerson, W. D. Phillips, L. P. Ratliff, S. L. Rolston and M. E. Wagshul, "Spectroscopy of Na_2 by photoassociation of laser-cooled Na", *Phys. Rev. Lett.* **71**, 2200 (1993).
- [61] J. D. Miller, R. A. Cline and D. J. Heinzen, "Photoassociation spectrum of ultracold Rb atoms", *Phys. Rev. Lett.* **71**, 2204 (1993).
- [62] A. J. Kerman, J. M. Sage, S. Sainis, D. DeMille and T. Bergeman, "Production of Ultracold, Polar RbCs^* molecules via photoassociation", *Phys. Rev. Lett.* **92**, 033004 (2004).
- [63] M. W. Mancini, G. D. Telles, A. R. L. Caires, V. S. Bagnato and L. G. Marcassa, "Observation of Ultracold Ground-State Heteronuclear Molecules", *Phys. Rev. Lett.* **92**, 133203 (2004).
- [64] S. Stellmer, B. Pasquiou, R. Grimm and F. Schreck, "Creation of ultracold Sr_2 molecules in the electronic ground state", *Phys. Rev. Lett.* **109**, 115302 (2012).
- [65] V. Barbé, A. Ciamei, B. Pasquiou, L. Reichsöllner, F. Schreck, P. S. Żuchowski and J. M. Hutson, "Observation of Feshbach resonances between alkali and closed-shell atoms", *Nat. Phys.* **14**, 881 (2018).
- [66] A. Guttridge, M. D. Frye, B. C. Yang, J. M. Hutson and S. L. Cornish, "Two-photon photoassociation spectroscopy of CsYb : ground-state interaction potential and interspecies scattering lengths", *Phys. Rev. A* **98**, 022707 (2018).
- [67] L. De Marco, G. Valtolina, K. Matsuda, W. G. Tobias, J. P. Covey and J. Ye, "A degenerate Fermi gas of polar molecules", *Science* **363**, 853 (2019).
- [68] S. Ospelkaus, K.-K. Ni, D. Wang, M. H. G. de Miranda, B. Neyenhuis, G. Quémener, P. S. Julienne, J. L. Bohn, D. S. Jin and J. Ye, "Quantum-State Controlled Chemical Reactions of Ultracold KRb molecules", *Science* **327**, 853 (2010).

- [69] T. Takekoshi, L. Reichsöllner, A. Schindewolf, J. M. Hutson, C. R. Le Sueur, O. Dulieu, F. Ferlaino, R. Grimm and H.-C. Nägerl, “Ultracold Dense Samples of Dipolar RbCs molecules in the rovibrational and hyperfine ground state”, *Phys. Rev. Lett.* **113**, 205301 (2014).
- [70] J. W. Park, S. A. Will and M. W. Zwierlein, “Ultracold Dipolar Gas of Fermionic ^{23}Na ^{40}K Molecules in Their Absolute Ground State”, *Phys. Rev. Lett.* **114**, 205302 (2015).
- [71] M. Guo, X. Ye, J. He, M. L. González-Martínez, R. Vexiau, G. Quémener and D. Wang, “Dipolar Collisions of Ultracold Ground-State Bosonic Molecules”, *Phys. Rev. X* **8**, 041044 (2018).
- [72] K. Matsuda, L. De Marco, J.-R. Li, W. G. Tobias, G. Valtolina, G. Quémener and J. Ye, “Resonant collisional shielding of reactive molecules using electric fields”, *Science* **370**, 1324 (2020).
- [73] L. Anderegg, S. Burchesky, Y. Bao, S. S. Yu, T. Karman, E. Chae, K.-K. Ni, W. Ketterle and J. M. Doyle, “Observation of microwave shielding of ultracold molecules”, *Science* **373**, 779 (2021).
- [74] G. Valtolina, K. Matsuda, W. G. Tobias, J.-R. Li, L. De Marco and J. Ye, “Dipolar evaporation of reactive molecules to below the Fermi temperature”, *Nature* **588**, 239 (2020).
- [75] A. Schindewolf, R. Bause, X.-Y. Chen, M. Duda, T. Karman, I. Bloch and X.-Y. Luo, “Evaporation of microwave-shielded polar molecules to quantum degeneracy”, *Nature* **607**, 677 (2022).
- [76] H. Son, J. J. Park, W. Ketterle and A. O. Jamison, “Collisional cooling of ultracold molecules”, *Nature* **580**, 197 (2020).
- [77] R. Campargue, *Atomic and molecular beams: the state of the art 2000* (Springer, Berlin, 2001).
- [78] N. R. Hutzler, H.-I. Lu and J. M. Doyle, “The Buffer Gas Beam: An Intense, Cold, and Slow Source for Atoms and Molecules”, *Chem. Rev.* **112**, 4803 (2012).

- [79] S. Y. T. Van De Meerakker, H. L. Bethlem, N. Vanhaecke and G. Meijer, “Manipulation and Control of Molecular Beams”, *Chem. Rev.* **112**, 4828 (2012).
- [80] M. R. Tarbutt, “Laser cooling of molecules”, *Contemporary Physics* **59**, 356 (2018).
- [81] J. M. Doyle, B. Friedrich, J. Kim and D. Patterson, “Buffer-gas loading of atoms and molecules into a magnetic trap”, *Phys. Rev. A* **52**, R2515 (1995).
- [82] J. D. Weinstein, R. deCarvalho, T. Guillet, B. Friedrich and J. M. Doyle, “Magnetic trapping of calcium monohydride molecules at millikelvin temperatures”, *Nature* **395**, 148 (1998).
- [83] R. V. Krems, W. C. Stwalley and B. Friedrich, eds., *Cold molecules: theory, experiment, applications* (CRC Press, Boca Raton, 2009).
- [84] E. Tsikata, W. C. Campbell, M. T. Hummon, H.-I. Lu and J. M. Doyle, “Magnetic trapping of NH molecules with 20 s lifetimes”, *New J. Phys.* **12**, 065028 (2010).
- [85] S. E. Maxwell, N. Brahms, R. deCarvalho, D. R. Glenn, J. S. Helton, S. V. Nguyen, D. Patterson, J. Petricka, D. DeMille and J. M. Doyle, “High-Flux Beam Source for Cold, Slow Atoms or Molecules”, *Phys. Rev. Lett.* **95**, 173201 (2005).
- [86] H.-I. Lu, I. Kozyryev, B. Hemmerling, J. Piskorski and J. M. Doyle, “Magnetic Trapping of Molecules via Optical Loading and Magnetic Slowing”, *Phys. Rev. Lett.* **112**, 113006 (2014).
- [87] H. L. Bethlem, G. Berden and G. Meijer, “Decelerating Neutral Dipolar Molecules”, *Phys. Rev. Lett.* **83**, 1558 (1999).
- [88] H. L. Bethlem, G. Berden, F. M. H. Crompvoets, R. T. Jongma, A. J. A. van Roij and G. Meijer, “Electrostatic trapping of ammonia molecules”, *Nature* **406**, 491 (2000).
- [89] H. L. Bethlem, A. J. A. Van Roij, R. T. Jongma and G. Meijer, “Alternate Gradient Focusing and Deceleration of a Molecular Beam”, *Phys. Rev. Lett.* **88**, 133003 (2002).
- [90] E. Narevicius, A. Libson, C. G. Parthey, I. Chavez, J. Narevicius, U. Even and M. G. Raizen, “Stopping Supersonic Beams with a Series of Pulsed Electromagnetic Coils: An Atomic Coilgun”, *Phys. Rev. Lett.* **100**, 093003 (2008).

- [91] Y. Segev, M. Pitzer, M. Karpov, N. Akerman, J. Narevicius and E. Narevicius, “Collisions between cold molecules in a superconducting magnetic trap”, *Nature* **572**, 189 (2019).
- [92] R. Fulton, A. I. Bishop and P. F. Barker, “Optical Stark Decelerator for Molecules”, *Phys. Rev. Lett.* **93**, 243004 (2004).
- [93] X. Wu, T. Gantner, M. Koller, M. Zeppenfeld, S. Chervenkov and G. Rempe, “A cryofuge for cold-collision experiments with slow polar molecules”, *Science* **358**, 645 (2017).
- [94] B. K. Stuhl, M. T. Hummon, M. Yeo, G. Quéméner, J. L. Bohn and J. Ye, “Evaporative cooling of the dipolar radical OH”, *Nature* **492**, 396 (2012).
- [95] A. Prehn, M. Ibrügger, R. Glöckner, G. Rempe and M. Zeppenfeld, “Optoelectrical Cooling of Polar Molecules to Submillikelvin Temperatures”, *Phys. Rev. Lett.* **116**, 063005 (2016).
- [96] N. Akerman, M. Karpov, Y. Segev, N. Bibelnik, J. Narevicius and E. Narevicius, “Trapping of Molecular Oxygen together with Lithium Atoms”, *Phys. Rev. Lett.* **119**, 073204 (2017).
- [97] M. D. Rosa, “Laser-cooling molecules: Concept, candidates, and supporting hyperfine-resolved measurements of rotational lines in the A-X(0,0) band of CaH”, *Eur. Phys. J. D* **31**, 395 (2004).
- [98] B. K. Stuhl, B. C. Sawyer, D. Wang and J. Ye, “Magneto-optical Trap for Polar Molecules”, *Phys. Rev. Lett.* **101**, 243002 (2008).
- [99] E. S. Shuman, J. F. Barry, D. R. Glenn and D. DeMille, “Radiative Force from Optical Cycling on a Diatomic Molecule”, *Phys. Rev. Lett.* **103**, 223001 (2009).
- [100] E. S. Shuman, J. F. Barry and D. DeMille, “Laser cooling of a diatomic molecule”, *Nature* **467**, 820 (2010).
- [101] J. F. Barry, E. S. Shuman, E. B. Norrgard and D. DeMille, “Laser Radiation Pressure Slowing of a Molecular Beam”, *Phys. Rev. Lett.* **108**, 103002 (2012).
- [102] M. T. Hummon, M. Yeo, B. K. Stuhl, A. L. Collopy, Y. Xia and J. Ye, “2D Magneto-Optical Trapping of Diatomic Molecules”, *Phys. Rev. Lett.* **110**, 143001 (2013).

- [103] J. F. Barry, D. J. McCarron, E. B. Norrgard, M. H. Steinecker and D. DeMille, “Magneto-optical trapping of a diatomic molecule”, *Nature* **512**, 286 (2014).
- [104] S. Truppe, H. J. Williams, M. Hambach, L. Caldwell, N. J. Fitch, E. A. Hinds, B. E. Sauer and M. R. Tarbutt, “Molecules cooled below the Doppler limit”, *Nat. Phys.* **13**, 1173 (2017).
- [105] L. Anderegg, B. L. Augenbraun, E. Chae, B. Hemmerling, N. R. Hutzler, A. Ravi, A. Collopy, J. Ye, W. Ketterle and J. M. Doyle, “Radio Frequency Magneto-Optical Trapping of CaF with high density”, *Phys. Rev. Lett.* **119**, 103201 (2017).
- [106] A. L. Collopy, S. Ding, Y. Wu, I. A. Finneran, L. Anderegg, B. L. Augenbraun, J. M. Doyle and J. Ye, “3D Magneto-Optical Trap of Yttrium Monoxide”, *Phys. Rev. Lett.* **121**, 213201 (2018).
- [107] N. B. Vilas, C. Hallas, L. Anderegg, P. Robichaud, A. Winnicki, D. Mitra and J. M. Doyle, “Magneto-optical trapping and sub-Doppler cooling of a polyatomic molecule”, *Nature* **606**, 70 (2022).
- [108] H. J. Williams, L. Caldwell, N. J. Fitch, S. Truppe, J. Rodewald, E. A. Hinds, B. E. Sauer and M. R. Tarbutt, “Magnetic Trapping and Coherent Control of Laser-Cooled Molecules”, *Phys. Rev. Lett.* **120**, 163201 (2018).
- [109] D. J. McCarron, M. H. Steinecker, Y. Zhu and D. DeMille, “Magnetic Trapping of an Ultracold Gas of Polar Molecules”, *Phys. Rev. Lett.* **121**, 013202 (2018).
- [110] L. Anderegg, B. L. Augenbraun, Y. Bao, S. Burchesky, L. W. Cheuk, W. Ketterle and J. M. Doyle, “Laser cooling of optically trapped molecules”, *Nat. Phys.* **14**, 890 (2018).
- [111] T. K. Langin, V. Jorapur, Y. Zhu, Q. Wang and D. DeMille, “Polarization Enhanced Deep Optical Dipole Trapping of Λ -cooled Polar Molecules”, *Phys. Rev. Lett.* **127**, 163201 (2021).
- [112] D. A. Steck, *Rubidium 87 D Line Data*, 21st Nov. 2019.
- [113] R. W. Field, D. O. Harris and T. Tanaka, “Continuous wave dye laser excitation spectroscopy $\text{CaF } A^2\Pi_r - X^1\Sigma^+$ ”, *Journal of Molecular Spectroscopy* **57**, 107 (1975).

- [114] T. E. Wall, J. F. Kanem, J. J. Hudson, B. E. Sauer, D. Cho, M. G. Boshier, E. A. Hinds and M. R. Tarbutt, “Lifetime of the $A(v' = 0)$ state and Franck-Condon factor of the $A-X(0-0)$ transition of CaF measured by the saturation of laser-induced fluorescence”, *Phys. Rev. A* **78**, 062509 (2008).
- [115] M. R. Tarbutt and T. C. Steimle, “Modeling magneto-optical trapping of CaF molecules”, *Phys. Rev. A* **92**, 053401 (2015).
- [116] P. J. Dagdigian, H. W. Cruse and R. N. Zare, “Radiative lifetimes of the alkaline earth monohalides”, *The Journal of Chemical Physics* **60**, 2330 (1974).
- [117] S. Truppe, H. J. Williams, N. J. Fitch, M. Hambach, T. E. Wall, E. A. Hinds, B. E. Sauer and M. R. Tarbutt, “An intense, cold, velocity-controlled molecular beam by frequency-chirped laser slowing”, *New J. Phys.* **19**, 022001 (2017).
- [118] M. Dulick, P. F. Bernath and R. W. Field, “Rotational and vibrational analysis of the CaF $B^2\Sigma^+ - X^2\Sigma^+$ system”, *Can. J. Phys.* **58**, 703 (1980).
- [119] M. Pelegrini, C. S. Vivacqua, O. Roberto-Neto, F. R. Ornellas and F. B. C. Machado, “Radiative transition probabilities and lifetimes for the band systems $A^2\Pi - X^2\Sigma^+$ of the isovalent molecules BeF, MgF and CaF”, *Braz. J. Phys.* **35**, 950 (2005).
- [120] P. D. Lett, W. D. Phillips, S. L. Rolston, C. E. Tanner, R. N. Watts and C. I. Westbrook, “Optical molasses”, *J. Opt. Soc. Am. B* **6**, 2084 (1989).
- [121] P. D. Lett, R. N. Watts, C. I. Westbrook, W. D. Phillips, P. L. Gould and H. J. Metcalf, “Observation of Atoms Laser Cooled below the Doppler Limit”, *Phys. Rev. Lett.* **61**, 169 (1988).
- [122] J. Dalibard and C. Cohen-Tannoudji, “Laser cooling below the Doppler limit by polarization gradients: simple theoretical models”, *J. Opt. Soc. Am. B* **6**, 2023 (1989).
- [123] P. J. Ungar, D. S. Weiss, E. Riis and S. Chu, “Optical molasses and multilevel atoms: theory”, *J. Opt. Soc. Am. B* **6**, 2058 (1989).
- [124] E. L. Raab, M. Prentiss, A. Cable, S. Chu and D. E. Pritchard, “Trapping of Neutral Sodium Atoms with Radiation Pressure”, *Phys. Rev. Lett.* **59**, 2631 (1987).

- [125] J. Devlin, M. Tarbutt, D. Kokkin and T. Steimle, “Measurements of the Zeeman effect in the $A^2\Pi$ and $B^2\Sigma^+$ states of calcium fluoride”, *Journal of Molecular Spectroscopy* **317**, 1 (2015).
- [126] M. R. Tarbutt, “Magneto-optical trapping forces for atoms and molecules with complex level structures”, *New J. Phys.* **17**, 015007 (2015).
- [127] M. Prentiss, E. L. Raab, D. E. Pritchard, A. Cable, J. E. Bjorkholm and S. Chu, “Atomic-density-dependent losses in an optical trap”, *Opt. Lett.* **13**, 452 (1988).
- [128] H. J. Williams, S. Truppe, M. Hambach, L. Caldwell, N. J. Fitch, E. A. Hinds, B. E. Sauer and M. R. Tarbutt, “Characteristics of a magneto-optical trap of molecules”, *New J. Phys.* **19**, 113035 (2017).
- [129] S. Ding, Y. Wu, I. A. Finneran, J. J. Bureau and J. Ye, “Sub-Doppler Cooling and Compressed Trapping of YO molecules at μK Temperatures”, *Phys. Rev. X* **10**, 021049 (2020).
- [130] E. B. Norrgard, D. J. McCarron, M. H. Steinecker, M. R. Tarbutt and D. DeMille, “Submillikelvin Dipolar Molecules in a Radio-Frequency Magneto-Optical Trap”, *Phys. Rev. Lett.* **116**, 063004 (2016).
- [131] M. S. Shahriar, P. R. Hemmer, M. G. Prentiss, P. Marte, J. Mervis, D. P. Katz, N. P. Bigelow and T. Cai, “Continuous polarization-gradient precooling-assisted velocity-selective coherent population trapping”, *Phys. Rev. A* **48**, R4035 (1993).
- [132] M. Weidemüller, T. Esslinger, M. A. Ol’shanii, A. Hemmerich and T. W. Hänsch, “A Novel Scheme for Efficient Cooling below the Photon Recoil Limit”, *Europhys. Lett.* **27**, 109 (1994).
- [133] A. Messiah, *Quantum mechanics* (Dover Publications, Garden City, NY, 2020).
- [134] J. A. Devlin and M. R. Tarbutt, “Three-dimensional Doppler, polarization-gradient, and magneto-optical forces for atoms and molecules with dark states”, *New J. Phys.* **18**, 123017 (2016).

- [135] J. A. Devlin and M. R. Tarbutt, “Laser cooling and magneto-optical trapping of molecules analyzed using optical Bloch equations and the Fokker-Planck-Kramers equation”, *Phys. Rev. A* **98**, 063415 (2018).
- [136] L. D. Landau and E. M. Lifshitz, *Quantum mechanics: non-relativistic theory*, 3d ed. (Pergamon Press, Oxford, UK, 1977).
- [137] J. Lim, M. D. Frye, J. M. Hutson and M. R. Tarbutt, “Modeling sympathetic cooling of molecules by ultracold atoms”, *Phys. Rev. A* **92**, 053419 (2015).
- [138] G. F. Gribakin and V. V. Flambaum, “Calculation of the scattering length in atomic collisions using the semiclassical approximation”, *Phys. Rev. A* **48**, 546 (1993).
- [139] A. Edmonds, *Angular momentum in quantum mechanics* (Princeton University Press, Princeton, NJ, 1957).
- [140] S. R. Langhoff, C. W. Bauschlicher and H. Partridge, “Theoretical dissociation energies for the alkali and alkaline-earth monofluorides and monochlorides”, *The Journal of Chemical Physics* **84**, 1687 (1986).
- [141] G. Gopakumar, M. Abe, M. Hada and M. Kajita, “Dipole polarizability of alkali-metal (Na, K, Rb)–alkaline-earth-metal (Ca, Sr) polar molecules: Prospects for alignment”, *The Journal of Chemical Physics* **140**, 224303 (2014).
- [142] D. Sardar, A. Christianen, H. Li and J. L. Bohn, “Four-body singlet potential-energy surface for reactions of calcium monofluoride”, *Phys. Rev. A* **107**, 032822 (2023).
- [143] T. Karman and J. M. Hutson, “Microwave shielding of ultracold polar molecules”, *Phys. Rev. Lett.* **121**, 163401 (2018).
- [144] B. Mukherjee, M. D. Frye, C. R. Le Sueur, M. R. Tarbutt and J. M. Hutson, “Shielding collisions of ultracold CaF molecules with static electric fields”, *Phys. Rev. Research* **5**, 033097 (2023).
- [145] E. A. Burt, R. W. Ghrist, C. J. Myatt, M. J. Holland, E. A. Cornell and C. E. Wieman, “Coherence, correlations, and collisions: what one learns about bose-einstein condensates from their decay”, *Phys. Rev. Lett.* **79**, 337 (1997).

- [146] S. Truppe, M. Hambach, S. M. Skoff, N. E. Bulleid, J. S. Bumby, R. J. Hendricks, E. A. Hinds, B. E. Sauer and M. R. Tarbutt, “A buffer gas beam source for short, intense and slow molecular pulses”, *Journal of Modern Optics* **65**, 648 (2018).
- [147] D. W. Sedgley, A. G. Tobin, T. H. Batzer and W. R. Call, “Cryopumping for fusion reactors”, in, *Nuclear Engineering and Design. Fusion* **4**, 149 (1987).
- [148] *NKT photonics app notes*, (2020) <https://www.nktphotonics.com/wp-content/uploads/2022/01/wavelength-tuning-of-koheras-fiber-lasers-updated.pdf> (visited on 18/09/2023).
- [149] K. N. Jarvis, “The Blue-Detuned Magneto-Optical Trap”, PhD thesis (Imperial College London, 2018).
- [150] S. Jurgilas, “Collisions Between Laser-Cooled Atoms and Molecules”, PhD thesis (Imperial College London, 2021).
- [151] S. Jurgilas, A. Chakraborty, C. J. H. Rich, B. E. Sauer, M. D. Frye, J. M. Hutson and M. R. Tarbutt, “Collisions in a dual-species magneto-optical trap of molecules and atoms”, *New J. Phys.* **23**, 075004 (2021).
- [152] *ORCA-R2 technical note*, (2015) https://www.unige.ch/bioimaging/photonic/application/files/2614/7748/5988/SCAS0055E_C10600-10B_tec.pdf (visited on 15/05/2023).
- [153] M. Hambach, “Development of a magneto-optical trap for CaF molecules”, PhD thesis (Imperial College London, 2017).
- [154] P. D. Gregory, J. A. Blackmore, S. L. Bromley and S. L. Cornish, “Loss of Ultracold $^{87}\text{Rb}^{133}\text{Cs}$ Molecules via Optical Excitation of Long-Lived Two-Body Collision Complexes”, *Phys. Rev. Lett.* **124**, 163402 (2020).
- [155] Y. Liu, M.-G. Hu, M. A. Nichols, D. D. Grimes, T. Karman, H. Guo and K.-K. Ni, “Photo-excitation of long-lived transient intermediates in ultracold reactions”, *Nat. Phys.* **16**, 1132 (2020).

- [156] R. Bause, A. Schindewolf, R. Tao, M. Duda, X.-Y. Chen, G. Quémener, T. Karman, A. Christianen, I. Bloch and X.-Y. Luo, “Collisions of ultracold molecules in bright and dark optical dipole traps”, *Phys. Rev. Research* **3**, 033013 (2021).
- [157] R. V. Krems, A. Dalgarno, N. Balakrishnan and G. C. Groenenboom, “Spin-flipping transitions in $^2\Sigma$ molecules induced by collisions with structureless atoms”, *Phys. Rev. A* **67**, 060703 (2003).
- [158] M. Morita, M. B. Kosicki, P. S. Żuchowski and T. V. Tscherbul, “Atom-molecule collisions, spin relaxation, and sympathetic cooling in an ultracold spin-polarized $\text{Rb}(^2S) - \text{SrF}(^2\Sigma^+)$ mixture”, *Phys. Rev. A* **98**, 042702 (2018).
- [159] S. Jurgilas, A. Chakraborty, C. J. H. Rich, L. Caldwell, H. J. Williams, N. J. Fitch, B. E. Sauer, M. D. Frye, J. M. Hutson and M. R. Tarbutt, “Collisions between Ultracold Molecules and Atoms in a Magnetic Trap”, *Phys. Rev. Lett.* **126**, 153401 (2021).
- [160] M. T. Hummon, T. V. Tscherbul, J. Kłos, H.-I. Lu, E. Tsikata, W. C. Campbell, A. Dalgarno and J. M. Doyle, “Cold $\text{N} + \text{NH}$ Collisions in a Magnetic Trap”, *Phys. Rev. Lett.* **106**, 053201 (2011).
- [161] A. Mosk, S. Kraft, M. Mudrich, K. Singer, W. Wohlleben, R. Grimm and M. Weidemüller, “Mixture of ultracold lithium and cesium atoms in an optical dipole trap”, *Appl. Phys. B* **73**, 791 (2001).
- [162] A. Witte, T. Kisters, F. Riehle and J. Helmcke, “Laser cooling and deflection of a calcium atomic beam”, *J. Opt. Soc. Am. B* **9**, 1030 (1992).
- [163] M. A. Joffe, W. Ketterle, A. Martin and D. E. Pritchard, “Transverse cooling and deflection of an atomic beam inside a Zeeman slower”, *J. Opt. Soc. Am. B* **10**, 2257 (1993).
- [164] J. Lim, J. R. Almond, M. A. Trigatzis, J. A. Devlin, N. J. Fitch, B. E. Sauer, M. R. Tarbutt and E. A. Hinds, “Laser Cooled YbF molecules for measuring the electron’s electric dipole moment”, *Phys. Rev. Lett.* **120**, 123201 (2018).
- [165] X. Alauze, J. Lim, M. A. Trigatzis, S. Swarbrick, F. J. Collings, N. J. Fitch, B. E. Sauer and M. R. Tarbutt, “An ultracold molecular beam for testing fundamental physics”, *Quantum Sci. Technol.* **6**, 044005 (2021).

- [166] I. Kozyryev, L. Baum, K. Matsuda, B. L. Augenbraun, L. Anderegg, A. P. Sedlack and J. M. Doyle, “Sisyphus Laser Cooling of a Polyatomic Molecule”, *Phys. Rev. Lett.* **118**, 173201 (2017).
- [167] B. L. Augenbraun, Z. D. Lasner, A. Frenett, H. Sawaoka, C. Miller, T. C. Steimle and J. M. Doyle, “Laser-cooled polyatomic molecules for improved electron electric dipole moment searches”, *New J. Phys.* **22**, 022003 (2020).
- [168] J. P. Gordon and A. Ashkin, “Motion of atoms in a radiation trap”, *Phys. Rev. A* **21**, 1606 (1980).
- [169] V. I. Yudin, A. V. Taichenachev and M. Y. Basalaev, “Dynamic steady state of periodically driven quantum systems”, *Phys. Rev. A* **93**, 013820 (2016).
- [170] D. J. Berkeland and M. G. Boshier, “Destabilization of dark states and optical spectroscopy in Zeeman-degenerate atomic systems”, *Phys. Rev. A* **65**, 033413 (2002).
- [171] W. Ketterle, K. B. Davis, M. A. Joffe, A. Martin and D. E. Pritchard, “High densities of cold atoms in a *dark* spontaneous-force optical trap”, *Phys. Rev. Lett.* **70**, 2253 (1993).
- [172] S. J. M. Kuppens, K. L. Corwin, K. W. Miller, T. E. Chupp and C. E. Wieman, “Loading an optical dipole trap”, *Phys. Rev. A* **62**, 013406 (2000).
- [173] L. Anderegg, “Ultracold molecules in optical arrays: from laser cooling to molecular collisions”, PhD thesis (Harvard University, 2019).
- [174] L. Caldwell, J. A. Devlin, H. J. Williams, N. J. Fitch, E. A. Hinds, B. E. Sauer and M. R. Tarbutt, “Deep laser cooling and efficient magnetic compression of molecules”, *Phys. Rev. Lett.* **123**, 033202 (2019).
- [175] L. D. Landau and E. M. Lifshitz, *Mechanics*, 3d ed (Pergamon Press, Oxford, UK, 1976).
- [176] S. Rosi, A. Burchianti, S. Conclave, D. S. Naik, G. Roati, C. Fort and F. Minardi, “ Λ -enhanced grey molasses on the D2 transition of Rubidium-87 atoms”, *Sci. Rep.* **8**, 1301 (2018).

- [177] D. S. Naik, H. Eneriz-Imaz, M. Carey, T. Freearge, F. Minardi, B. Battelier, P. Bouyer and A. Bertoldi, “Loading and cooling in an optical trap via hyperfine dark states”, *Phys. Rev. Res.* **2**, 013212 (2020).
- [178] F. Sievers, N. Kretschmar, D. R. Fernandes, D. Suchet, M. Rabinovic, S. Wu, C. V. Parker, L. Khaykovich, C. Salomon and F. Chevy, “Simultaneous sub-Doppler laser cooling of fermionic ^6Li and ^{40}K on the D_1 line: theory and experiment”, *Phys. Rev. A* **91**, 023426 (2015).
- [179] M. O. Brown, T. Thiele, C. Kiehl, T.-W. Hsu and C. A. Regal, “Gray-Molasses Optical-Tweezer Loading: Controlling Collisions for Scaling Atom-Array Assembly”, *Phys. Rev. X* **9**, 011057 (2019).
- [180] R. Onofrio and C. Presilla, “Reaching Fermi Degeneracy in Two-Species Optical Dipole Traps”, *Phys. Rev. Lett.* **89**, 100401 (2002).
- [181] P. Barakhshan, A. Marrs, A. Bhosale, B. Arora, R. Eigenmann and M. S. Safronova, *Portal for High-Precision Atomic Data and Computation (version 2.0)*. University of Delaware, Newark, DE, USA, <https://www.udel.edu/atom> (visited on 18/09/2023).
- [182] M. Tarbutt, personal communication.
- [183] C.-L. Hung, X. Zhang, N. Gemelke and C. Chin, “Accelerating evaporative cooling of atoms into Bose-Einstein condensation in optical traps”, *Phys. Rev. A* **78**, 011604 (2008).
- [184] R. C. Bird, M. R. Tarbutt and J. M. Hutson, “Tunable Feshbach resonances in collisions of ultracold molecules in $^2\Sigma$ states with alkali-metal atoms”, arXiv:2302.14687.
- [185] M. L. Wall, K. Maeda and L. D. Carr, “Simulating quantum magnets with symmetric top molecules”, *Annalen der Physik* **525**, 845 (2013).
- [186] M. L. Wall, K. Maeda and L. D. Carr, “Realizing unconventional quantum magnetism with symmetric top molecules”, *New J. Phys.* **17**, 025001 (2015).
- [187] P. Yu, L. W. Cheuk, I. Kozyryev and J. M. Doyle, “A scalable quantum computing platform using symmetric-top molecules”, *New J. Phys.* **21**, 093049 (2019).

- [188] I. Kozyryev and N. R. Hutzler, “Precision measurement of time-reversal symmetry violation with laser-cooled polyatomic molecules”, *Phys. Rev. Lett.* **119**, 133002 (2017).
- [189] I. Kozyryev, Z. Lasner and J. M. Doyle, “Enhanced sensitivity to ultralight bosonic dark matter in the spectra of the linear radical SrOH”, *Phys. Rev. A* **103**, 043313 (2021).
- [190] M. Kajita, “Precise Measurement of Transition Frequencies of Optically Trapped $^{40}\text{Ca}^{19}\text{F}$ Molecules”, *J. Phys. Soc. Jpn.* **87**, 104301 (2018).
- [191] Y.-J. Chen, L. F. Gonçalves and G. Raithel, “Measurement of Rb $5P_{3/2}$ scalar and tensor polarizabilities in a 1064-nm light field”, *Phys. Rev. A* **92**, 060501 (2015).