

IMPERIAL COLLEGE LONDON
DEPARTMENT OF PHYSICS

Developing an experiment to make
Bose-Einstein condensates of CaF
molecules

Jing Wu

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the degree of Doctor of Philosophy

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Statement of Originality

I declare that this thesis is my own work. Any work of others mentioned in this thesis has been properly acknowledged and referenced, and the bibliography is attached at the end of the thesis.

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Abstract

Ultracold dipolar molecular quantum gases have great potential in the study of many-body quantum systems because of their long-range dipole-dipole interactions, and they are of special importance in precise measurement of fundamental physics such as the electron's electric dipole moment and searches for varying fundamental constants. They are also important for research in quantum chemistry, and may be an interesting future platform for quantum computation.

This thesis presents the development of an apparatus to make Bose-Einstein condensates of CaF molecules. A two-stage cryogenic buffer gas source is used to produce CaF beams with a mean velocity of 150 - 200 m/s, and an intensity of 3.2×10^{10} /sr/pulse. The molecules are slowed down to the capture velocity of a magneto-optical trap (MOT) with a direct laser slowing method. A few thousand molecules are captured in the MOT, where they cool to about 1 mK. The last part of the thesis describes the next steps in the experiment: Sub-Doppler cooling, optical dipole trap and evaporative cooling to BEC in the presence of collisional shielding.

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Chapter 1

Introduction

1.1 Ultracold atoms

The idea of applying radiation pressure of light to cool a low-density gas was proposed in 1975 by T.W.Hansch and A.L.Schawlow [1]. With intense, coherent laser light covering the lower-frequency half of the Doppler-broadened spectrum, atoms feel a damping force that is approximately linear in velocity, which cools them to low temperature. This minimum temperature is called the Doppler limit. Combining radiation pressure with a magnetic field, the first magnetic-optical trap of neutral sodium atoms was created in 1987. It trapped atoms with a density of $2 \times 10^{11} \text{ cm}^{-3}$ and a temperature of $600 \text{ } \mu\text{k}$, and the trap lasted for 2 min [2]. In 1988, an optical molasses of sodium was produced in NIST, the temperature of which was $40 \text{ } \mu\text{k}$, lower than the Doppler limit by a factor of 6 [3], triggering the research of sub-Doppler cooling. In the next year, two theoretical models of polarization gradient laser cooling were raised by J. Dalibard and C. Cohen-Tannoudji, which explained the former observation [4]. The development of methods to cool and trap atoms with laser light was awarded the Nobel Prize in Physics in 1997.

When atoms are confined in a conservative trap, such as a quadrupole magnetic trap or an optical trap, evaporative cooling can be applied. It works by lowering the depth of the trap to let hot molecules escape. The remaining molecules establish a new equilibrium which corresponds to a lower average temperature. In 1986, a quadrupole magnetic trap of spin-polarized hydrogen atoms was created. By lowering the trap threshold energy, the atoms were cooled to a temperature of $30 \text{ } \mu\text{k}$, and a density of $1 \times 10^{14} \text{ cm}^{-3}$ [5].

For Bosons, there is a critical temperature corresponding to a phase transition between gases and the Bose-Einstein condensate (BEC). In a BEC, a large fraction

of Bosons occupy the lowest quantum state, and microscopic quantum mechanical phenomena become macroscopic. The first atomic BEC was produced in 1995 with rubidium-87 atoms, which was as cold as 170 nK. The number density of condensation was $2.5 \times 10^{12} \text{ cm}^{-3}$, and the lifetime exceeded 15 s [6]. Later in the same year, a BEC of sodium was created [7]. These achievements of Bose-Einstein condensation in dilute gases shared the Nobel Prize in Physics in 2001.

1.1.1 Applications of ultracold atoms

Quantum simulation

The progress of producing ultracold atomic gases has boosted many application areas. One of the most important is quantum simulation. In condensed matter physics, quantum systems are described by their Hamiltonians, featuring the interaction with external fields and between particles. Some quantum phases require high purity and extreme conditions, which makes them hard to explore. Ultracold atoms, on the other hand, can act as an analogue. They can be manipulated with high accuracy with optical, electrical and magnetic field, and impurity is never an obstacle. This approach has broadened research in many-body quantum physics. In 2002, a quantum phase transition between superfluid and Mott insulator was realised in a BEC of rubidium-87 [8]. In 2010, pure Mott phase was created in an optical lattice [9]. These studies provide some insights to the understanding of high-temperature superconductors [10]. In a Mott insulator of optical lattice, it is possible to flip any particular spin with a laser beam and microwave field, and resolve it well below the lattice spacing [11]. Non-local order in a one-dimensional Mott insulator was studied with an atom array [12]. The behaviour of quantum systems far from equilibrium is also simulated with certain optical lattices [13].

Precise measurement and fundamental physics

The hyperfine frequency of Caesium has been used as a standard of frequency and time for more than half a century [14]. The stability of atomic clocks is supported by the statistical average over a large number of atoms, but limited by the random thermal movement of the gas. As the techniques for producing ultracold atoms matured, the accuracy of atomic clocks also improved. In 2002, a calcium gas cooled to 10 μK , prepared in a MOT followed by quench cooling, was implemented as an atom interferometer, and yielded relative uncertainty below 1×10^{-15} [15]. In 2005, the optical lattice clock was invented. Strontium atoms of 2 μK were trapped in a

one-dimensional optical lattice with a depth of 20 μK . The absolute uncertainty was 2 Hz, one order of magnitude lower than atomic clocks before [16]. In the following decade, the accuracy and uncertainty of optical lattice clock has reached 10^{-18} level with a promising future to go further [17] [18].

Atomic interferometry has also been used to test fundamental physics. The Standard Model is able to explain many experimental observations, but not the observation of dark matter and dark energy. To derive theories that fix the gap, it is helpful to improve the experimental accuracy of fundamental physics constants. Atomic fountain interferometers are particularly suitable for the measurement of the fine-structure constant. In 2020, an ultracold rubidium gas determined a value of $1/\alpha \approx 37.035999206(11)$, with an unprecedented relative accuracy of 81 parts-per-trillion [19].

Quantum information

Ultracold atoms turn into quantum bits (qubits) when it comes to quantum computation, where the information is encoded as the quantum states of the atoms. The interaction between atoms, either van der Waals interaction, or dipole-dipole interaction, can be designed as quantum logic by controlling the external field. In 2021, a two-qubit gate was implemented between atoms in optical tweezer traps, with a gate time of 20 μs and a fidelity exceeding 0.998 [20]. To enhance the entanglement between qubits, a two-dimensional array of rubidium atoms was created, and the atoms were excited to Rydberg states. Rydberg excitation greatly increases the strength of entanglement with dipole-dipole interaction [21]. In the same year, a 6-qubit system of Greenberger-Horne-Zeilinger state was created and used as a platform to test quantum algorithms. Coding in the ground state, the coherence time went beyond 600 μs , more than 500 times longer than the previous work [22]. The methods to create entangled arrays with high fidelity have also been developed. In 2023, entanglement was scaled up from Bell state pairs to one-dimensional atom chain, and then towards two-dimensional plaquettes [23].

1.2 Ultracold molecules

1.2.1 Advantages over atoms

At large interatomic distances R between atoms is the van der Waals interaction which scales as $1/R^6$ and with the van der Waals coefficient C_6 . This interaction

is weak for ground-state atoms, which only interact appreciably at short range, e.g. in a lattice, only for atoms on the same site. Magnetic atoms, on the other hand, interact through a magnetic dipole moment. However, magnetic dipole interaction is much weaker than electric dipole interaction in general, and the breakthrough of their application in quantum simulation came relatively late [24].

Molecules are vastly more polarizable than atoms, so it is quite easy to introduce strong electric dipole-dipole interactions, scaling as $1/R^3$. It brings a relatively strong long-range interaction into the system. The interaction strength can be largely tuned by external electric fields. The rotational and vibrational structure of molecules give a rich degree of freedom that can be applied in quantum information and precise measurement. The coupling to microwave, electric field and magnetic field facilitate the manipulation of the Hamiltonian, which broadened the types of quantum systems to simulate.

1.2.2 Magnetoassociation and photoassociation

Researchers have studied ultracold molecular dipole systems for decades. After the achievement of quantum degenerate gases of alkali species, it became practical to produce ultracold molecules by combining two cooled atom species. This is called ‘indirect cooling’.

The most common method of this type is magnetoassociation [25] [26] [27] [28]. Two atomic gases are mixed in the same trap. By sweeping a magnetic field across a Feshbach resonance, heteronuclear molecules are formed in a weakly-bound state where the average separation of the nuclei remains large. The state is called a Feshbach state, which serves as an intermediate state. Feshbach molecules are pumped into a tightly-bound excited state, then transferred to a tightly-bound ground state by simulated emission. This technique is called stimulated Raman adiabatic passage (STIRAP). To achieve high transition rate, the wavefunction of intermediate states must have good overlap with both excited states and ground states.

In 2008, a research group in JILA created ultracold potassium rubidium gas with peak density of 10^{12} cm^{-3} and temperature of 350 nK [25]. They started with the mixture of potassium-40 and rubidium-87, both trapped in an optical dipole trap (ODT) and close to quantum degenerate. With magnetoassociation and STIRAP, KRb molecules are produced in triplet and singlet ground state. The latter possess a permanent electric dipole moment of 0.566 Debye. The first Fermi degenerate gas

of polar molecules was produced in the same group in 2019, with 2.5×10^4 KRb molecules at 50 nK [26]. It has become a frequently used procedure for preparing ultracold molecules, with abundant applications [29] [30] [31]. In 2024, the first BEC of dipolar molecules was produced by associating ultracold sodium and caesium atoms [32]. The condensate has around 200 molecules, with a temperature of 6 nK, a lifetime of 1.8 s, and a peak density of $2.0 \times 10^{12} \text{ cm}^{-3}$.

Another commonly used method is photoassociation [33] [34] [35] [36], the exploration of which started earlier than magnetoassociation. In a dual-species ultracold atomic trap, colliding atoms are excited into weakly-bound molecules in electronic excited levels with near resonant laser, then decay into ground state rovibrational levels.

In 2004, an experiment successfully assembled RbCs* in a MOT. The formation rate was around $1.5 \times 10^8 \text{ s}^{-1}$, and the dipole moment was around 1.3 Debye. Molecules spontaneously decayed to high vibrational levels of the ground state at a rate of $5 \times 10^5 \text{ s}^{-1}$ per level [33]. The distribution of population among a wide range of vibrational, rotational and hyperfine levels has always been a problem of photoassociation. In 2015, the production of vibrational ground state molecules was improved by choosing an excited state which decayed to vibrational ground state in two stages. Up to 33% of excited molecules were transferred into the absolute ground state [35]. As the optical tweezer technique developed, an experiment to photoassociate two atoms into a single weakly bound molecule produced NaCs with 69% efficiency [36].

1.2.3 Stark and Zeeman deceleration

The electric or magnetic dipole moment of polar molecules interact with an applied electric or magnetic field, and the energy shift can be used to slow their motion. An approximately sinusoidal potential can be generated using specially designed electrodes or magnets. Those with static electric fields are called Stark decelerator, and with magnetic fields are called Zeeman decelerator. As molecules fly ‘up the hill’, kinetic energy is converted to potential energy. The field is turned off at the highest position, and turned back on again once the molecules reach the position corresponding to the bottom of the hill.

The first experiment was published in 1999, where neutral CO molecules were decelerated from 225 m/s to 98 m/s by a 35 cm long Stark decelerator. $\pm 10 \text{ kV}$

was applied to the electrodes, and a field of 125 kV/cm was produced, resulting in an acceleration of -10^5 m s^{-2} [37]. A proposal of combining optical pumping and gradient cooling was published in 2016. Instead of switching external fields, molecules were optically pumped between a low-field-seeking and a high-field-seeking states [38]. This method was later applied to molecules such as CaOH [39].

1.2.4 Laser cooling and magneto-optical trapping

Magnetoassociation and photoassociation can only produce molecules from atoms that can be laser cooled. To produce ultracold molecules of other kinds, different cooling techniques are explored, and laser cooling is one among them. It targets molecules with simple ground state hyperfine levels, and large overlap of vibrational branch wavefunctions between ground state and excited state. The combination of some halogens and alkaline earth metals, such as SrF and CaF, are ideal candidates.

The starting point for experiments on laser cooling of molecules is the cryogenic buffer gas source [40]. It produces an intense slow beam which is suitable for cooling and decelerating. In 2010, a group at Yale made a breakthrough by cooling SrF close to the Doppler limit. Two repump lasers were applied to complete the optical cycle, and a magnetic field was used to drive dark Zeeman states into bright ones. The team found that Doppler cooling dominated when the light was red-detuned, and Sisyphus cooling dominated when the light was blue-detuned, and the lowest temperature has reached 10 mK [41]. The first 3D molecular MOT was produced in 2014 by the same group. A third repump laser was added relative to the previous work, to produce a very-nearly closed optical cycle. Figure 1.1(a) shows images of this very first molecular MOT. Using a time-of-flight (TOF) method illustrated in Figure 1.1(b), the temperature was determined to be around 2.5 mK, the number density to be 600 cm^{-3} . There were 300 molecules trapped for 56 ms [42].

Molecules were first cooled below the Doppler limit in 2017 in a lab at Imperial College London. Using a cryogenic buffer source [43] and frequency-chirp slowing [44], about 1.3×10^4 CaF molecules were trapped in a dual-frequency MOT with a peak density of $1.6 \times 10^5 \text{ cm}^{-3}$. The temperature was roughly 11 mK and the lifetime was 100 ms. By lowering the laser intensity, the MOT was further cooled. After that, the magnetic field was turned off, and the laser was detuned from the red side of the molecular transitions to the blue side. A 3-dimensional blue-detuned optical molasses was created. TOF measurement suggested the lowest temperature was

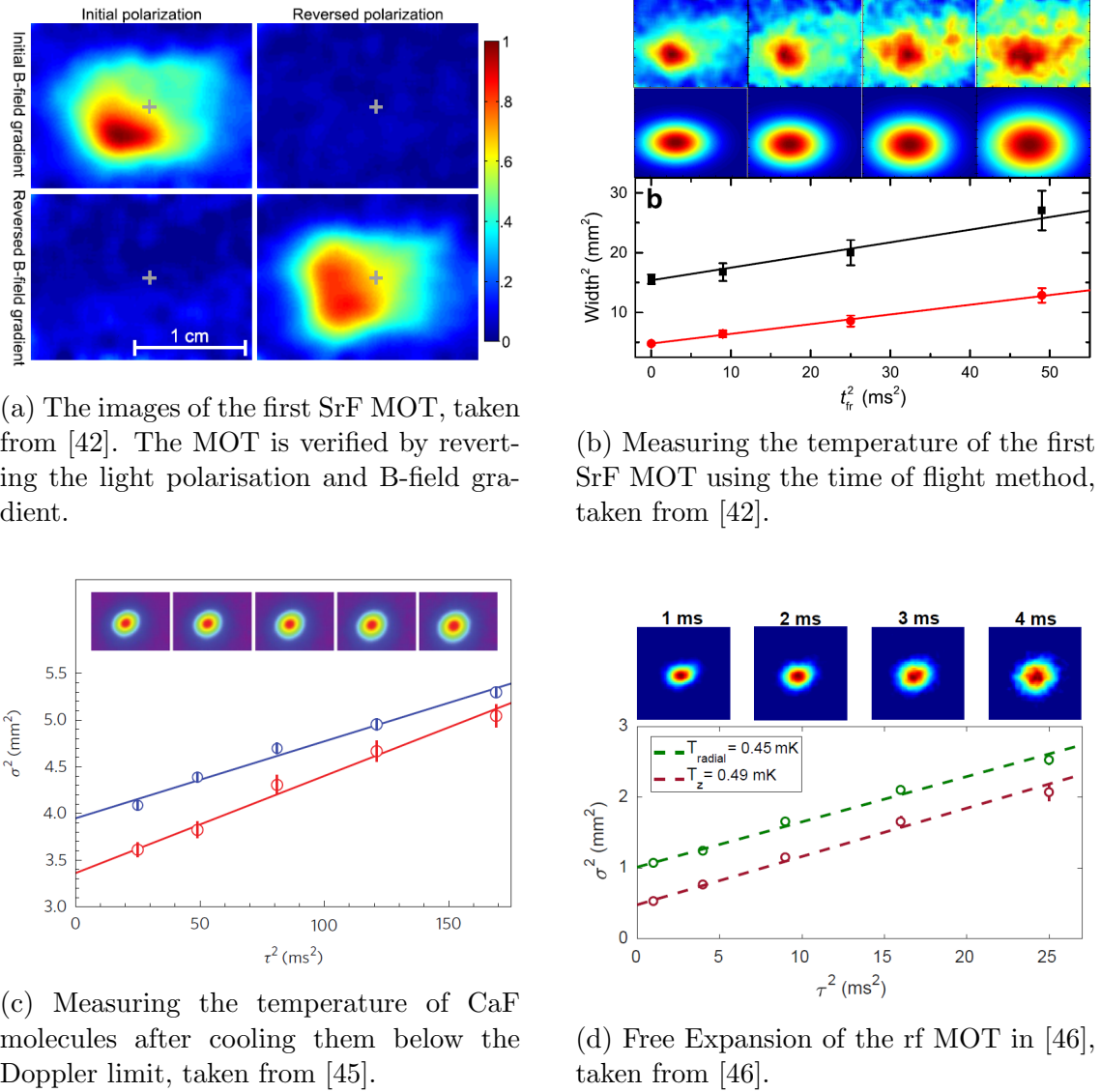


Figure 1.1: The images of MOTs mentioned in this subsection.

55 μK , the number density $0.8 \times 10^5 \text{ cm}^{-3}$ and the phase-space density 2.4×10^{-12} [45].

In 2017, an improvement in the characteristics of 3D MOT was achieved. The team compared a rf MOT with a dual-frequency MOT of CaF, where a pair of counter-propagating blue-detuned light is added to address the Zeeman dark state. Both traps had similar properties, but the rf MOT was slightly better with 1.1×10^5 molecules at 340 μK with the density of $7 \times 10^6 \text{ cm}^{-3}$, and an 85 ms lifetime [46].

There have been MOTs of other polar molecules as well. In 2013, 1D and 2D MOTs of YO were created [47]. In 2018, the first non-fluoride MOT was produced, with 1.5×10^4 YO molecules with the temperature of 7 mK. This is also the first MOT

with an intermediate state between cycling states, which is a common difficulty for molecules [48]. In 2023, the first blue-detuned MOT was created with YO molecules, aiming at applying sub-Doppler cooling force in a MOT. Its peak number density was $2.5 \times 10^8 \text{ cm}^{-3}$, two orders-of-magnitude higher than all the other molecule MOTs. The temperature was $38 \text{ } \mu\text{K}$ [49].

1.2.5 Conservative traps of ultracold molecules

In order to manipulate the rotational and vibrational states, improve the number density and cool much below the Doppler limit, molecular gases are transferred into conservative traps. There are typically two kinds of traps, magnetic quadrupole trap (MQT) and non-resonant optical dipole trap (ODT). When the ODT is focussed down to a spot size of order $1 \text{ } \mu\text{m}$, it is called an optical tweezer trap. Optical tweezers can be arranged into arrays, where Hamiltonians with long-range interaction and entanglement can be studied.

In 2018, Imperial College London successfully applied an MQT to compress CaF gas number density to $2 \times 10^6 \text{ cm}^{-3}$. The procedure is shown in Figure 1.2. After the MOT was made, it was compressed by ramping up the quadrupole field and lowering the laser intensity. Then it was trapped in a blue-molasses, and pumped into a single hyperfine component of the $N = 1$ state. After that, it was transferred to the $N = 0$ state by a π -pulse, and purified by a push light. These molecules were then held in a pure magnetic trap. A pure rotational ground state sample was created, with 5×10^3 molecules in total. Its temperature was $70 \text{ } \mu\text{K}$, with the number density $1.2 \times 10^5 \text{ cm}^{-3}$ and lifetime 2 s [50]. Similar progress was done with SrF in the same year. After trapping molecules into a rf MOT, the molecular gas was cooled to $50 \text{ } \mu\text{K}$ with blue-detuned lasers. In an MQT, molecules in the highest sublevel of the first excited rotational level were selected by microwave transition, and compressed by magnetic field. The single-state molecular gas has 600–800 molecules at a peak density of $3 \times 10^4 \text{ cm}^{-3}$ and a lifetime around 1 s [51].

Molecules were first trapped in an optical dipole trap by the Harvard group in 2018, where the number density reached $8 \times 10^7 \text{ cm}^{-3}$. A CaF MOT was produced after chirp slowing, and sub-Doppler cooled to $40 \text{ } \mu\text{K}$ by blue-detuned laser. Then an ODT turned on, which trapped the molecules with a 1068 nm laser. Measurement suggested a collection of 150 molecules of $60 \text{ } \mu\text{K}$. The lifetime of the ODT was 750 ms , and collisions with residual gas dominated the loss [52]. In 2021, with ‘ Λ -cooling’, where grey molasses and velocity-selective coherent population trapping

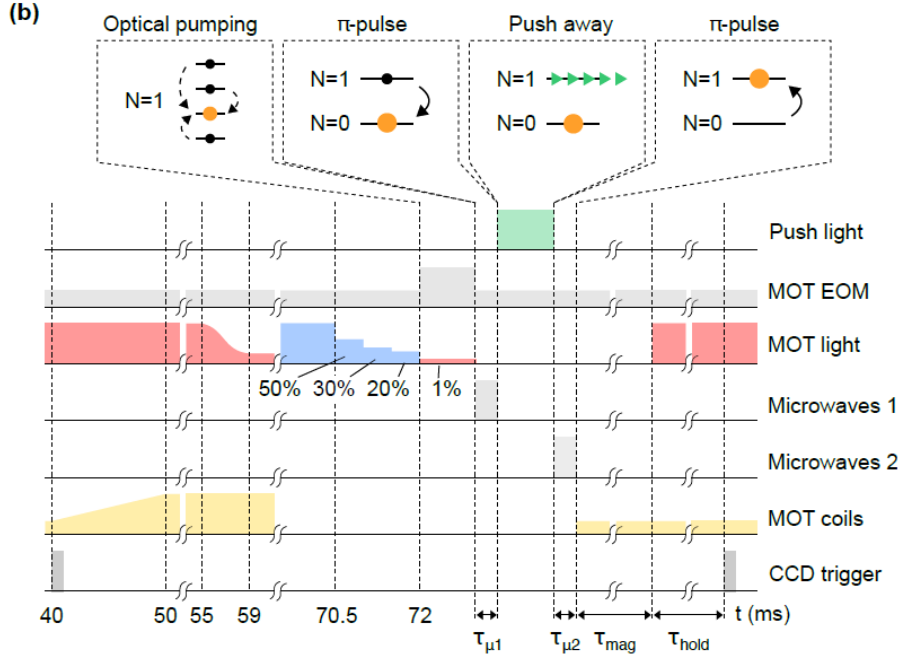


Figure 1.2: The time sequence of a compressed and purified MOT in [50]. The figure is taken from [50].

were combined, the number density has increased to $2 \times 10^9 \text{ cm}^{-3}$, achieved with SrF, and the temperature was lowered to $12 \text{ } \mu\text{K}$ [53].

The first optical tweezer array of ultracold molecules was created in 2019. It started with a MOT of 10^4 CaF molecules with 10^5 cm^{-3} number density. They were transferred into a 1064 nm ODT, with a Gaussian beam waist of $45 \text{ } \mu\text{m}$. Λ -cooling compressed the samples to a density of $3 \times 10^7 \text{ cm}^{-3}$ at $20 \text{ } \mu\text{K}$. The tweezers are produced by an acousto-optical deflector (AOD) with 780 nm lasers. Imaging with an electron multiplying camera, an array of 5 molecules was detected. Measurement suggested a loading probability of 34%, the Gaussian beam waist being $2.3 \text{ } \mu\text{m}$, and the temperature of $80 \text{ } \mu\text{K}$ [54]. The motional states of molecules are quantised in conservative potentials such as optical traps. In 2023, CaF in an optical tweezer was cooled close to its motional ground state by Raman sideband cooling, which will enhance the entanglement between molecules and increase the lifetime [55].

1.2.6 Extending to polyatomic molecules

Other than diatomic molecules, those cooling techniques have been extended to polyatomic molecules. In 2016, the scattering force due to optical cycling was detected in SrOH. The laser was applied transversely right after a buffer gas source. With one repump laser, about 100 photons were scattered per molecule, and the

molecular beam was deflected by 0.2° [56]. Half a year after that, Sisyphus cooling was successfully applied using this apparatus. With standing wave established transversely and a magnetic field to remix dark magnetic states, the temperature was reduced to about $700\ \mu\text{K}$ [57].

In 2020, 1D MOT of CaOH was created. To close the optical transition loop, 5 repump lasers are applied, including 3 electronic states, and a scattering rate of around 10^4 photons per molecule was established. The temperature in the trapped direction was reduced to $1.4\ \text{mK}$ [58]. Based on that, the first 3D MOT of triatomic molecules was produced in 2022. Six repumping lasers are involved, which increased the cycle closure to 12000 photons per molecule. The MOT had 2.0×10^4 molecules at a peak density of $3.0 \times 10^6\ \text{cm}^{-3}$. The temperature was reduced to $110\ \mu\text{K}$ after grey molasses cooling [59]. In 2023, the same research group successfully loaded CaOH molecules into an ODT, which has a number density of $3 \times 10^9\ \text{cm}^{-3}$ and a temperature of $57\ \mu\text{K}$ [60]. Later, an optical tweezer array of six elements was produced out of it [61]. Similar laser cooling scheme has also been realised in symmetric top molecules. In 2020, an ultracold CaOCH_3 beam was cooled to $1.8\ \text{mK}$ in the transverse direction [62].

1.3 Applications of ultracold molecules

1.3.1 Quantum simulation

Polar molecules are especially suitable for quantum simulation of strongly-interacting many-body quantum systems because of their electric dipole moments and relatively long lifetime. Other than that, the coupling of rotational states by microwaves provide easy manipulation of the interaction of the many-body quantum models. Finally, the wide choices of molecules extend the types of Hamiltonians that can be simulated. Those features are of great importance to the development of quantum many-body physics.

Famous spins models with topological features can be realised in this way. In 2011, a superfluidity and quantum magnetism system in an 1-dimensional fermionic KRb lattice was designed, where all the parameters of its Hamiltonian could be controlled individually [63]. In 2013, a strongly correlated topological quantum system in a 2-dimensional fermionic KRb lattice was proposed to study fractional Chern insulators [64]. In the same year, the first 3-dimensional lattice spin model of polar molecules was created with the same species of molecules. The spin interaction

was simulated by rotational states exchange under the control of microwave [65]. In 2014, quantum dynamics observation of long-range half-spin model was done on polar molecules trapped in a partially-filled optical lattice, with rotational states being quasi-spins. It provided an experimental picture far from mean-field theory, and acted as a benchmark for different theoretical models [66]. In 2021, a method of realising a 3-dimensional topological phase, Hopf insulator, was proposed, which made use of the light-field-sensitive resonance between different rotational states [67]. In this proposal, some special extensions of the Hopf insulator can be realised and detected with similar configurations. Experiments on the platform of ultracold polar molecules have helped to explore condensed matter physics, which also feedback to the development of theories in topological quantum phases and strongly-correlated quantum many-body systems.

1.3.2 Fundamental physics

Ultracold molecular gas is a fruitful area in the advance of fundamental physics, especially in test of models beyond the Standard Model (SM). The SM successfully combines three fundamental interactions though not gravity. However, it fails to explain the imbalance between matter and anti-matter, thus indicates the violation of combined charge and parity (CP) symmetry, which says the laws of physics are maintained in a system where the particles are replaced by their anti-counterparts with their spatial coordinates inverted. To resolve this problem, new models with particles that violate CP symmetry have been hypothesized. One of their predictions lies in the expected value of the electron electric dipole moment (eEDM). While the SM predicts a value at the magnitude of 10^{-38} ecm, most other models' are between 10^{-27} and 10^{-30} ecm [68]. An eEDM interacts with an electric field, which results in a coupling energy depending on the alignment. By measuring the energy difference between aligned and anti-aligned configurations, the value of the eEDM can be determined. Compared to an externally generated electric field, polar molecules have intramolecular electric fields, which can be around 10^5 stronger, thus greatly increasing the interaction energy to be measured.

The first experimental result with heavy molecules was published in 2002 by a team in Imperial College London. The system was produced by a quantum interferometer. An effusive beam of YbF was produced in an oven, and the molecules optically pumped into the absolute ground state. A pair of parallel electrodes generated a field around 3.3 kV/cm along the flying path. The experiment compared the spin precession frequency with the electric field parallel and then antiparallel

to a small applied magnetic field. From this difference, the experiment obtained a result of $(-0.2 \pm 3.2) \times 10^{-26} e \text{ cm}$ [69]. In 2012, the same team pushed the limit to $|d_e| < 10.5 \times 10^{-28} e \text{ cm}$ [70]. In 2013, even before the first 3-dimensional MOT was invented, ultracold molecular molasses was initially proposed as the reservoir of molecular fountains, a new tool for eEDM measurement [71].

The ACME Collaboration has used ThO molecules to measure eEDM. In 2014, they published a result of $|d_e| < 8.7 \times 10^{-29} e \text{ cm}$ with 90% confidence [72]. In 2018, this limit was pushed to $|d_e| < 1.1 \times 10^{-29} e \text{ cm}$ [31]. In 2023, the upper limit of eEDM was updated by an experiment with molecular ions in JILA, which made use of the 23 GV cm^{-1} intramolecular electric field in HfF^+ . This experiment set a new upper bound of $|d_e| < 4.1 \times 10^{-30} e \text{ cm}$ (90 % confidence), which remains consistent with the value predicted by the SM [73]. In 2020, a scheme to improve the uncertainty of eEDM measurement by one to two orders of magnitude was proposed. It combines magnetic lensing, transverse cooling and chirp slowing, to produce a MOT of YbF, which can then be loaded into an optical lattice. The experiment is now in progress in Imperial College London [74].

The variation of fundamental physical constants, such as the electron-to-proton mass ratio $\mu = m_e/m_p$, or fine-structure constant α , are also predicted by new theoretical models, therefore it is important to test them with experimental measurement. In 2006, a microwave spectroscopy measurement on Stark-decelerated OH molecules yielded precise frequencies. By comparing to the spectra of OH megamasers in astrophysics, the sensitivity of the fine structure constant variation, $\Delta\alpha/\alpha$, is constrained to 1 ppm over the last 10^{10} years [75]. In 2008, proposals to improve sensitivity by measuring the transition between a pair of close-to-degenerate vibrational levels which belong to different electronic states were published [76] [77]. Following this idea, an experiment with ultracold KRb yielded the most precise result with molecules, $\frac{1}{\mu} d\mu/dt = (0.30 \pm 1.0) \times 10^{-14} \text{ year}^{-1}$ [78]. The similar methodology has been extended to triatomic molecular gas, which was estimated to achieve 10^{-17} fractional uncertainty in $\delta\mu/\mu$ within one day's integration [79].

1.3.3 Quantum chemistry

Understanding and controlling molecular collisions in the ultracold regime is connected to several research frontiers. It is a test and guide of quantum chemistry models on short-range interaction, and can be used to suppress loss rate in molecular traps, which will pave the way to evaporative cooling. Other than that, the

collision between ultracold molecules and close-to-degenerate atomic gases is core to sympathetic cooling, which brings the molecules to a lower temperature region.

In 2008, the collisions between RbCs and Rb, Cs were observed in an optical trap, and successfully explained with theory [80]. In 2010, collisions of degenerate quantum gas of fermions were measured. It revealed the loss rate was highly sensitive to an external electric field, and the dependence of loss rate on the induced electric dipole moment was studied [81]. Further experiment established a good control of chemical reaction channels with an electric field, which can be used to suppress collisions and drastically improve lifetime of the system [82].

In 2020, a study of two-body interaction measured the loss rate of ground state CaF. The molecules were prepared in a MOT, loaded into an ODT, and then into tweezers. The tweezers were non-destructively imaged for their occupation numbers. After that, a pair of tweezers, either both occupied or half-occupied, are brought together in 1 ms and merged. After a series of interaction intervals, they were separated and imaged again. The one-particle lifetime was measured to be about 375 ms, and the two-particle lifetime around 16 ms. The large difference suggested two-body loss due to chemical reaction and/or the formation of complexes which were destroyed by the high intensity of the tweezer light. The two-body loss rate was measured to be $7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, which was close to the predicted universal loss rate [83]. Further study showed a suppression of loss rate to $10^{-13} \text{ cm}^3 \text{ s}^{-1}$ when an electric field of 21.7 to 24.5 kV/cm was applied [84].

In 2021, laser-cooled atoms and molecules were firstly mixed in a magnetic trap. A group in Imperial College London studied the inelastic collision rate between ultracold Rb and CaF, and the loss rate was consistent with the calculated universal loss rate. Measurement showed that rotational excitation introduced extra loss by interacting with atoms and relaxing to rotational ground states, while hyperfine and magnetic states had no influence. These conclusions are promising for sympathetic cooling [85].

1.3.4 Quantum information

A publication as early as 2002 proposed a quantum computer design with trapped dipolar molecules. In this proposal, dipolar molecules produced by photoassociation were trapped in a 1-dimension array, and their electric dipole moments were used as qubits, which were coupled by dipole-dipole interaction. A pair of electrodes provided electric field gradient to shift the resonant frequency for each qubit differently.

States of qubits could be manipulated with microwave or optical stimulated Raman process. According to calculation, a quantum computer above 10^4 qubits could be built with it [86]. As the rotational, vibrational and hyperfine levels of dipolar molecules were explored, and the technique of manipulating single molecules in a tweezer array was developed, a proposal of encoding sub-levels within a rotational manifold as qudits was published in 2020. Comparing with qubits, it takes fewer number of molecules for qudits to form the same Hilbert space. Two types of molecules, CaF and RbCs, were analysed in detail, with transitions deliberately chosen to avoid stimulating other transitions with close frequency [87].

There have been several trials to achieve quantum gates with highly variable range of interaction, long lifetime and strong coherence. In 2021, a proposal suggested trapping two molecules with different internal states in highly overlapped tweezer pairs, so the dipole-dipole interaction can be hundred times enhanced [88]. Other than that, a coherence time of 93 ms was measured in a pair of CaF qubits, much improved than previous experiments [89]. In 2023, a publication demonstrated the generation of two-qubit entanglement in CaF tweezers by long-range dipole-dipole interaction state. Measurement suggested a lower temperature could improve the coherence, and the fidelity of the Bell state was limited by excitation in the tweezers [90].

As mentioned above, quantum gates of molecules are dependent on motional states in optical traps, which requires motional state cooling to achieve high fidelity. Another popular platform for quantum computing, Rydberg atoms, have no trapping potential during excitation, which results in heating of the system. To overcome these disadvantages, a hybrid system was designed in 2022 [91]. In the scheme, quantum information was encoded in molecular pairs, but the dipole-dipole interaction was between Rydberg atoms and molecules. This design removed the dependence on the external states of molecules, as well as on the thermal movement of Rydberg atoms. The proposal shows that a two-qubit gate could be driven in $1\ \mu\text{s}$, with a fidelity up to 99.9%. As direct cooling techniques are applied on polyatomic molecules, the possibilities of using symmetric-top molecules as qubits have been discussed [92].

1.4 Aims of this thesis

The design of the apparatus for this experiment is based on an established ultracold CaF experiment introduced in [93], which aims at sub-Doppler cooling and magnetic

trapping. As an improved version of it, my experiment aims at further goals such as optical trapping and evaporative cooling, which requires a lower temperature and a higher molecular intensity. The ultimate target of my experiment, as the thesis title suggests, is to make a BEC of CaF.

The design of the main body is done by Noah Fitch at the very beginning, and the whole apparatus is built from scratch by me and my colleagues, Arijit Chakraborty and Guoqiang Tang. The apparatus can be divided into three parts: the molecular source, the beamline and the science chamber. The schematic diagram is shown in Figure 4.2. The molecular source, introduced in Chapter 3, is aimed at producing a bright and stable molecular beam by laser ablation. The beamline, with a detection chamber attached to its end, is the passage where hot molecules fly and get slowed by direct laser cooling, which is introduced in Chapter 4. The science chamber is the place for trapping, sub-Doppler cooling and condensation, where the gaseous molecules are confined, cooled below microkelvin, and finally condensate. The current achievement, a magnetic-optical trap, is introduced in Chapter 5, and the future schemes are introduced in Chapter 6.

The experiment is carried out with a joint effort. I assembled the molecular source, including the ablation laser, the gas system, the temperature controller, the data acquisition system and the probing laser, and characterised and optimised the molecular source with the help of Guoqiang. Arijit joined at the stage of laser slowing, contributing on coding, optical design and assembly, while the analysis and optimisation of the slowed molecules is done by me. After that, we worked together to build a MOT: I focused on constructing home-made seed-amplifier laser systems, while Guoqiang and Arijit managed the commercial lasers, and built the image system. Other than these, I designed a pair of electrodes for evaporative cooling.

Chapter 2

Molecular structure

To understand the procedure of making ultracold molecules, a basic knowledge of the energy levels of molecular structure is needed. This chapter gives a brief introduction to the electronic, rotational and vibrational structure of diatomic molecules. This chapter also describes the notational convention, and details of CaF energy structure, particularly the three electronic levels involved in this experiment and the sublevels within them. The second part of this chapter introduces the mechanism of laser cooling for CaF molecules.

2.1 Energy structure of diatomic molecules

Based on the fact that the mass of an electron is much smaller than the mass of a nucleus, the Born-Oppenheimer approximation is applied to analyse the energy structure of molecules. The motion of electrons and nuclei in a diatomic molecule are decoupled, the former contributing to electronic states, and the latter forming rotational and vibrational states.

To approach the model from a simple beginning, we consider the two atoms of a diatomic molecule as two hard spherical balls connected by a spring, which is the chemical bond. The oscillation of the two masses coupled by the spring results in vibrational states, and the rotation of the system around the centre of mass results in rotational states. The Coulomb interaction between electrons and nuclei results in electronic states. Labelling the electronic states by n , vibrational states by v , rotational states by R , the wavefunction can be written as [94]

$$\psi_{n,v,R,m_R}(\vec{R}_N; \{\vec{r}_i\}) = \frac{1}{R_N} \phi_n(\vec{R}_N; \{\vec{r}_i\}) f_v(R_N) Y_{R,m_R}(\Theta, \Phi), \quad (2.1)$$

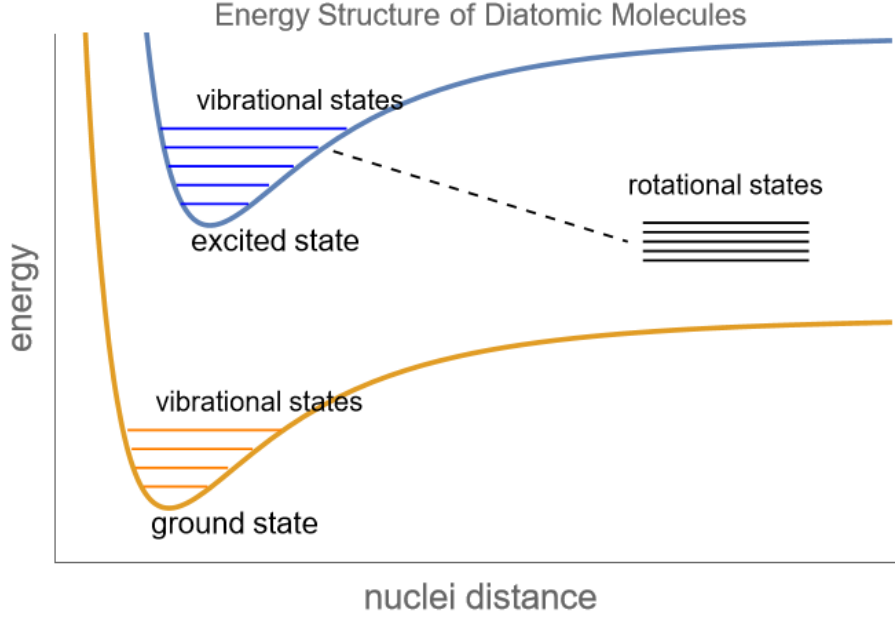


Figure 2.1: A scheme of energy structure of diatomic molecules. The orange and blue curves refer to electronic states, and the parallels inside each one are the vibrational states. If we look close into each vibrational state, there are rotational states, shown by the black lines.

where $\phi_n(\vec{R}_N; \{\vec{r}_i\})$ is the wavefunction describing movement of electrons. $\vec{R}_N$ is the relative position of two nuclei, which decomposes to (R_N, Θ, Φ) in spherical polar components. Because of the approximation explained above, it is a parameter instead of a variable in ϕ_n . The position of the electron i is referred as $\vec{r}_i$. $\frac{1}{R_N} f_v(R_N)$ is the vibrational wavefunction, and it is only determined by the relative distance of two nuclei. $Y_{R,m_R}(\Theta, \Phi)$ is the rotational wavefunction, which is just the spherical harmonic functions.

The energy difference between electronic states is on the magnitude of 100 THz, so most transitions can be addressed with lasers. Vibrational and rotational transitions are of magnitude 10 THz and 10 GHz respectively, which falls into the region of far-IR lasers and microwaves. The scheme of energy structure of a diatomic molecule is shown in Figure 2.1.

2.1.1 Electronic structure

The electron states are labelled as $X, A, B, \dots$, referring to the ground state, first excited state, second excited state and so on. The total orbital angular momentum of electrons is noted as $\vec{L}$, and the total spin angular momentum of electrons is noted as $\vec{S}$. Unlike the case of an atom, a diatomic molecule is not spherically

symmetric. Thus, neither $\vec{L}$ nor $\vec{S}$ commutes with the total Hamiltonian of the molecule. However, the system has an axial symmetry about its internuclear axis z . So the projection of $\vec{L}$ and $\vec{S}$ on this internal z -axis, represented as $\hat{L}_z$ and $\hat{S}_z$, are good quantum operators to characterise the system:

$$\hat{L}_z |\Lambda\rangle = \hbar\Lambda |\Lambda\rangle, \quad (2.2)$$

$$\hat{S}_z |\Sigma\rangle = \hbar\Sigma |\Sigma\rangle. \quad (2.3)$$

Here Λ and Σ are quantum numbers of $\hat{L}_z$ and $\hat{S}_z$ respectively. In Equation (2.2), one eigenfunction gives a pair of eigenenergy, $+\hbar\Lambda$ and $-\hbar\Lambda$, in the case of $\Lambda \neq 0$. This pair of states correspond to a pair of orbital angular momentum in opposite directions, with reference to the internuclear orientation. The degeneracy is removed when Λ couples to other angular momentum. It is called Λ -doubling, indicating they become a close pair of states with opposite parity.

Because of the degeneracy, the orbits are labelled according to $|\Lambda|$. The labels are similar to those of atomic electron orbits:

angular momentum	0	1	2	3
atom (l)	s	p	d	f
molecule (Λ)	Σ	Π	Δ	Φ

Notice that the Σ in the table above is not the quantum number of $\vec{S}_z$. In Σ state, the orbital angular momentum is zero, so there is no Λ -doubling. The parity of the electron wavefunction is noted with Σ^+ and Σ^- . Under reflection through a plane containing the internuclear axis, if the sign is unchanged/changed, it is labelled as $\Sigma^{+/-}$.

In atomic systems, the coupling between orbital angular momentum and spin angular momentum gives the total angular momentum $\vec{J}$. However, in molecular systems, the total angular momentum has three components: $\vec{J} = \vec{L} + \vec{S} + \vec{R}$, where $\vec{R}$ is the rotational angular momentum. The projection of $\vec{J}$ onto the internuclear axis has the quantum number Ω .

Based on the symbols introduced above, the electronic states of diatomic molecules are written as

$$(X, A, B\dots)^{2S+1}\Lambda_{\Omega}^{\pm}. \quad (2.4)$$

2.1.2 Vibrational structure

The nuclei of diatomic molecules vibrate around their equilibrium distance R_0 . The quantum number of vibrational states is noted by v . The vibrational energy can be approximated as

$$E_v = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 - \quad (2.5)$$

The first order represents harmonic oscillation around R_0 , where ω_e is the vibrational constant with $\omega_e = \sqrt{k/m_r}$. k is the spring constant, and m_r is the reduced mass of nuclei. $x_e, y_e, \dots$ are anharmonic constants. For the first lowest vibrational levels like the ones involved in this experiment, the harmonic oscillator is a good approximation.

2.1.3 Rotational structure

The nuclei of diatomic molecules rotate around their centre of inertia. The quantum number of rotational states is noted by R . The rotational energy can be approximated as

$$E_r = B_v R(R+1) - D_v R^2(R+1)^2 + \quad (2.6)$$

The first order represents rotation with fixed internuclear distance, where B_v is the vibrational constant. D_v is the stretching constant. Because internuclear distance varies according to vibrational states, B_v and D_v have some dependence on vibrational quantum number v .

2.1.4 Hyperfine structure

For molecules with non-zero nuclear spin, the coupling between nuclear spin $\vec{I}$ and total angular momentum $\vec{J}$ splits the energy structure further into hyperfine levels, with total angular momentum $\vec{F} = \vec{J} + \vec{I}$. Energy differences between hyperfine levels are typically in the range 1 MHz-1 GHz. In an external magnetic field, each hyperfine structure is split into $2F+1$ Zeeman sublevels.

2.1.5 Hund's cases

For the set of angular momenta mentioned above, their relative coupling strength differs in different molecules, thus the choice of bases and perturbation varies. By

Hund's case	Electronic	Spin-orbit	Rotational
a	strong	intermediate	weak
b	strong	weak	intermediate
c	intermediate	strong	weak
d	intermediate	weak	strong
e	weak	intermediate/strong	strong/intermediate

Table 2.1: Five Hund's cases and the relative coupling strength of electronic, spin-orbit and rotational states.

comparing the strength of electronic, spin-orbit and rotational interaction, diatomic molecules can be divided into five cases as shown in Table 2.1. Those cases are idealised, assuming the three interactions are largely distinguishable in strength.

Most diatomic molecules fall into Hund's case a and b. They are visualised in Figure 2.2. The Hamiltonian of spin-orbit coupling and rotational states can be written as

$$H_{total} = H_{so} + H_{rot} = A\vec{L} \cdot \vec{S} + B\vec{R}^2. \quad (2.7)$$

Hund's case a is shown in Figure 2.2(a), and is the best choice of basis when $A \gg B$. $\vec{L}$ is strongly coupled to the internuclear axis through the electrostatic interactions, and $\vec{S}$ also becomes strongly coupled to the internuclear axis via the spin-orbit interactions, so Λ , Σ and Ω are all good quantum numbers. $\vec{L}$ and $\vec{S}$ then couples with rotational states, composing the total angular momentum $\vec{J} = \vec{L} + \vec{S} + \vec{R}$. In this case, molecular states can be described with n , v , Λ , Σ , Ω , J and m_J , where m_J is the projection of $\vec{J}$ onto the lab frame z axis.

Hund's case b is shown in Figure 2.2(b), and is an appropriate basis when $A \ll B$. In this case, $\vec{L}$ couples much stronger with rotational angular momentum $\vec{R}$, giving energy levels labelled by $\vec{N} = \vec{L} + \vec{R}$. It then couples with the electron spin $\vec{S}$, forming the total angular momentum $\vec{J}$. In this case, good quantum numbers are n , v , N , J , Λ , S and m_J . For Σ states where orbital angular momentum is zero, spin-orbit interactions that split rotational levels are substituted by spin-rotation coupling, where $H_{sr} = \gamma\vec{S} \cdot \vec{R}$.

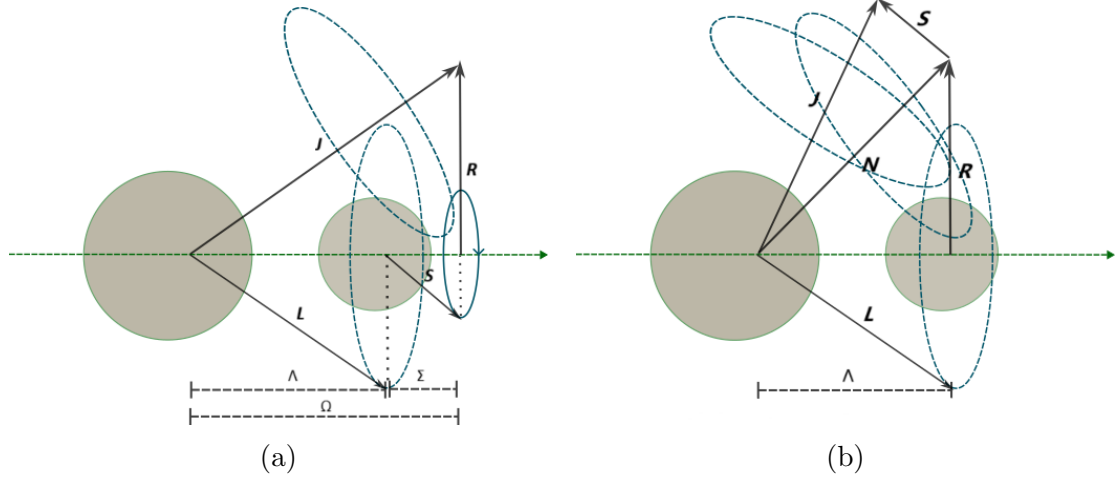


Figure 2.2: Couplings between electronic orbit momentum L , electronic spin momentum S and rotational momentum R in Hund's cases a (left) and b (right).

2.2 Energy structure of CaF

The first three electronic levels of CaF, $X^2\Sigma^+$, $A^2\Pi_{1/2}$ and $B^2\Sigma^+$ are involved in our laser cooling scheme, and two electronic transitions, namely $X - A$ and $X - B$ transitions are considered. The two atoms are bonded by ^{40}Ca giving one of its outer shell electrons to ^{19}F to form a closed shell. This leaves only one unpaired electron that is localised around Ca, similar to the case of alkali atoms. Because the valence electron is hardly involved in the chemical bond, the vibrational states hardly change when the electron is excited. Thus, when an electronic transition is addressed, the vibrational state has a large probability to be unchanged. In the three states analysed below, we take $v = 0$ as default. Different levels of energy structure are shown in Figure 2.3.

2.2.1 $X^2\Sigma^+$ state

The electronic ground state of CaF is labelled as $X^2\Sigma^+$. X indicates it is the lowest electronic state. The orbit angular momentum projected onto the internuclear axis is 0, so there is no Λ -doubling. The electronic wavefunction does not change under reflection with respect to a plane containing the internuclear axis. So the orbit-spin coupling gives way to the spin-rotation coupling, which falls into Hund's case b. The parity of rotational states alternates, starting with even $N = 0$ state. $N = 1$ of the ground state is chosen in the transition, so that molecules can be transferred to $J = 1/2$ of the excited state, which can only decay back to the $N = 1$ state. Thus, the optical loop is closed to this extent. This is based on the selection rules, and will

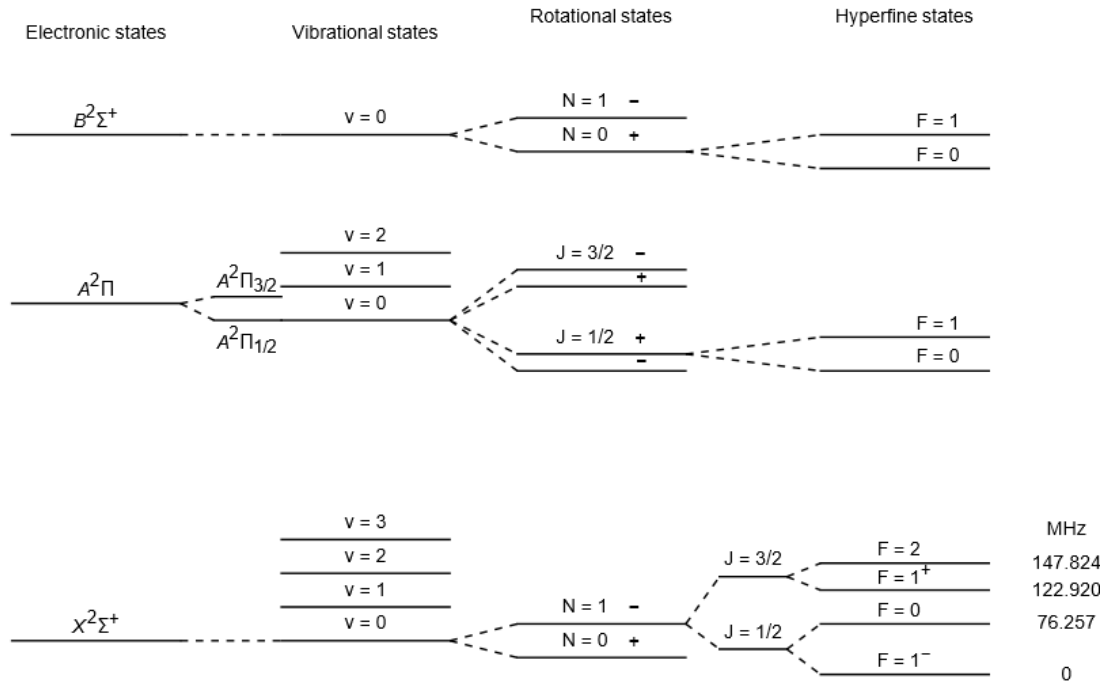


Figure 2.3: A scheme of all levels of energy structure of CaF molecules involved in this experiment. Parities are noted with $\pm$. The $A^2\Pi$ state is split by orbit-spin coupling into two levels with $\Omega = 3/2, 1/2$. Each of the J states coming from $A^2\Pi_{1/2}$ state is split by Λ -doubling. The positive parity state with $J = 1/2$ is addressed in the experiment. The hyperfine energy gaps are noted in MHz next to the levels relative to the $F = 1^-$ state, and the frequencies are calculated in [94].

be discussed with details in the next subsection. The spin angular momentum is $S = 1/2$, so the total angular momentum $\vec{J} = \vec{S} + \vec{N}$ has two possible values: $J = \frac{1}{2}$ and $J = \frac{3}{2}$. Each of them are further coupled with nuclear spin $I = \frac{1}{2}$, making the total angular momentum of the molecule: $\vec{F} = \vec{J} + \vec{I}$. In this case, there are four hyperfine states: $F = 2, 1$ for $J = \frac{3}{2}$ state, $F = 1, 0$ for $J = \frac{1}{2}$ state. The former $F = 1$ is labelled as 1^+ and the later 1^- according to their energy. The energy splitting between $F = 1^-, 0, 1^+, 2$ are shown in Figure 2.3.

2.2.2 $A^2\Pi_{1/2}$ state

The first electronic excited state of CaF is labelled as $A^2\Pi_{1/2}$. A indicates the second electronic state. The projected orbit angular momentum has $|\Lambda| = 1$, so it is labelled as Π . Angular momenta couple according to Hund's case a. The projected spin angular momentum $|\Sigma| = \frac{1}{2}$, so there are two possible values of $|\Omega|$: $\frac{1}{2}$ and $\frac{3}{2}$. When it couples with rotational states, the total angular momentum has $\vec{J} = \vec{L} + \vec{S} + \vec{R}$, and results in $J = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$. Because of Λ -doubling, each of the J states split into a pair of close levels with opposite parities. In this experiment, we focus on $J = \frac{1}{2}$ with even parity. Hyperfine structure with $I = \frac{1}{2}$ gives $F = 0, 1$. The splitting between them is at the same level of the natural width of the $X - A$ transition, so it is considered unresolved in practice.

2.2.3 $B^2\Sigma^+$ state

The second electronic excited state of CaF is labelled as $B^2\Sigma^+$. B indicates the third electronic state. Similar to $X^2\Sigma^+$ state, it falls into Hund's case b. The angular momenta are: $\Lambda = 0, S = \frac{1}{2}$. As explained in $X^2\Sigma^+$ state, $N' = 0$ is chosen to be the upper level in optical cycling, whose parity is opposite to $N = 1$ of the ground state. The total angular momentum $\vec{J} = \vec{L} + \vec{S} + \vec{R}$ has only one possible quantum number, $\frac{1}{2}$. Coupling with nuclear spin $I = \frac{1}{2}$, there are two hyperfine levels, $F = 0, 1$. The splitting between them is about 20 MHz.

2.3 Electric dipole transition

2.3.1 Selection rules

For atoms and molecules, the probability to absorb or emit a photon is calculated by Einstein coefficients. Among them, spontaneous emission is described by Einstein

A coefficients, and absorption and stimulated emission are described by Einstein B coefficients. In cases where the wavelength of light is much larger than the size of molecules, the electromagnetic wave is considered as a constant field over the size of the atom. This is called electric dipole approximation. With this assumption, Einstein coefficients are [95]

$$A_{if} = \frac{\omega_{if}^3}{3\pi\epsilon_0\hbar c^3} |\langle \psi_f | \vec{d} | \psi_i \rangle|^2, \quad (2.8)$$

$$B_{if} = \frac{\pi}{3\epsilon_0\hbar^2} |\langle \psi_f | \vec{d} | \psi_i \rangle|^2. \quad (2.9)$$

Here, i and f are labels for initial and final states, and ω_{if} is the transition frequency between them. Because $\vec{d}$ is proportional to the position vector, it is of odd parity. Only when the two wavefunctions are of opposite parity, the integral is non-zero, and the transition is allowed to happen. This is called parity selection rule, noted as $\Delta P = \pm 1$.

To calculate the integral, $\vec{d} = \sum_p d_p \hat{e}_p^*$ is written in the molecular coordinate system with spherical tensor coordinates as (μ_{-1}, μ_0, μ_1) [94]. The components are

$$d_p = \sum_{q=-1}^1 D_{p,q}^{(1)}(\Theta, \Phi) \mu_q. \quad (2.10)$$

Here, $D_{p,q}^{(1)}$ are the elements of the rotation matrix that rotate from the laboratory frame to the molecular frame. Thus, the transition dipole moment can be separated into two parts:

$$d_{if} = \sum_p \hat{e}_p^* \sum_q I_{rot} I_{vib}. \quad (2.11)$$

Here, I_{rot} stands for rotational integral, and I_{vib} stands for electronic and vibrational integral:

$$\begin{aligned} I_{rot} &= \iint_{\Omega} Y_{R',m_R'}^{f*}(\Theta, \Phi) D_{p,q}^{(1)*} Y_{R,m_R}^i(\Theta, \Phi) d\Omega \\ &= \langle R', m_R' | D_{p,q}^{(1)*} | R, m_R \rangle, \end{aligned} \quad (2.12)$$

$$\begin{aligned} I_{vib} &= \iiint_{\vec{R}_N, \vec{r}_i} \phi_{n'}^{f*}(\vec{R}_N; \{\vec{r}_i\}) f_v^{f*}(R_N) \mu_q \phi_n^i(\vec{R}_N; \{\vec{r}_i\}) f_v^i(R_N) dR_N d\vec{r}_i \\ &= \langle n', v' | \mu_q | n, v \rangle. \end{aligned} \quad (2.13)$$

According to Equation (2.12), the selection rules for rotational angular momen-

tum R is $\Delta R = 0, \pm 1$ (excluding $R' = 0 \leftarrow R = 0$), $\Delta m_J = 0, \pm 1$.

To extract information on vibrational transitions, we integrate over all electronic positions, and replace the coordinate R_N with its equilibrium value R_0 in $\phi_n(\vec{R}_N; \{\vec{r}_i\})$. The transition dipole moment can be approximately calculated as

$$\mu_q^{n,n'}(R_0) = \iiint_{\vec{r}_i} \phi_{n'}^{f*}(\vec{R}_0; \{\vec{r}_i\}) \mu_q \phi_n^i(\vec{R}_0; \{\vec{r}_i\}) d\vec{r}_i = \langle n' | \mu_q | n \rangle, \quad (2.14)$$

$$d_{if} = \sum_p \hat{e}_p^* \sum_q \mu_q^{n,n'}(R_0) I_{rot} \int_{R_N} f_{v'}^{f*}(R_N) f_v^i(R_N) dR_N. \quad (2.15)$$

Thus, Einstein coefficients are proportional to the square of the overlap of two vibrational states:

$$A_{if}, B_{if} \propto \left| \int_{R_N} f_{v'}^{f*}(R_N) f_v^i(R_N) dR_N \right|^2. \quad (2.16)$$

Under the harmonic oscillator approximation suggested in Section 2.1.2, transitions between vibrational states within the same electronic state obey the selection rule: $\Delta v = \pm 1$. However, the nuclear distance R_0 varies for different electronic states, resulting in a none-zero integral beyond the selection rule. Generally, the square of the integral is defined as the Frank-Condon Factor (FCF). Considering the spontaneous decay from vibrational level v' in an excited state to vibrational levels in the ground state, the branching ratio of decaying to a certain vibrational level v becomes

$$P_{v'v} = \frac{A_{v'v}}{\sum_{v''} A_{vv''}} = \frac{|\langle v | v' \rangle|^2 \omega_{n'v',nv}^3}{\sum_{v''} |\langle v' | v'' \rangle|^2 \omega_{n'v',nv''}^3}. \quad (2.17)$$

Here, $|\langle v | v' \rangle|^2$ is the FCF between v' and v states, and $\omega_{n'v',nv}$ is the frequency of the transition. The closer $P_{v'v}$ is to unity, the higher probability molecules decay to their original vibrational state, and the less leakage an optical cycling has.

2.3.2 Transitions in CaF

There are two electronic transitions involved in our experiment, $A^2\Pi_{1/2} \leftarrow X^2\Sigma^+$ and $B^2\Sigma^+ \leftarrow X^2\Sigma^+$. The selection rule of total angular momentum usually allows a non-zero J' state to decay to three different J states, which makes a closed absorption-emission loop impossible. This problem is solved with special choices of rotational states.

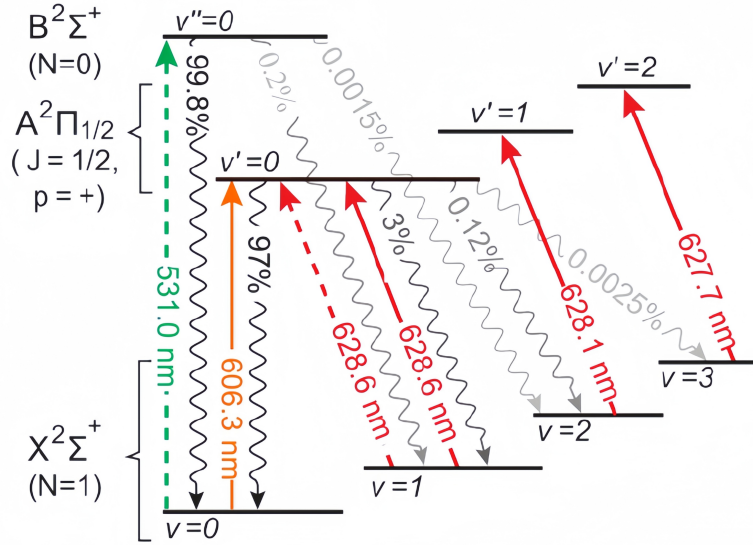


Figure 2.4: The transitions involved in this experiment. The solid lines are MOT transitions. There is a main laser (606.3 nm) and three repump lasers (628.6 nm, 628.1 nm, 627.7 nm). The dashed lines are slowing lasers. There is one main laser (531.0 nm) and a repump laser (628.6 nm). The wavy lines are branching ratios between these states. This figure is from [93].

In AX transition, the molecules are driven from $N = 1$ of the ground state. The parity of this state is odd. It is driven to the even branch of $J = \frac{1}{2}$ state of $A^2\Pi_{1/2}$. According to parity selection rule, it could decay to $N = 1$ ($J = \frac{1}{2}, \frac{3}{2}$), 3 ($J = \frac{5}{2}, \frac{7}{2}$), 5 ($J = \frac{9}{2}, \frac{11}{2}$)..., etc, but with rotational selection rules, only $N = 1$ is allowed. Thus, the cycle is closed.

In BX transition, the molecules are driven from the same ground state to the $N' = 0$ state of $B^2\Sigma^+$, which is of even parity. This state has one total angular momentum quantum number, $J' = \frac{1}{2}$. According to parity and rotational selection rules, it only decays to $N = 1$ ($J = \frac{1}{2}, \frac{3}{2}$), and the cycle is closed.

In the discussion above, we neglected the transition in vibrational states. However, because the branching ratio of $v'(v'') = 0 \rightarrow v = 0$ is not unity, some excited molecules decay to $v = 1, 2, 3$..., etc, thus moving out of the cooling cycle. To slow a molecule from a cryogenic buffer source to almost still, about 1.5×10^4 photons need to be scattered (details are described in the next subsection). To maintain 90% of the molecules in the cycle, a leakage rate of 10^{-5} is required. Thus, several repump lasers are implemented to cycle the molecules in higher vibrational states. The main and repump lasers used in our experiment are shown in Figure 2.4.

The parameters of optical cycling based on AX and BX transitions are listed in

Transition	ν (THz)	λ (nm)	Γ (MHz)	N_{repump}	$ \mu_E $ (Debye)	$b_{0,0}$
$A^2\Pi_{1/2} \leftarrow X^2\Sigma^+$	494.4323	606.3	8.3	3	3.1	97%
$B^2\Sigma^+ \leftarrow X^2\Sigma^+$	564.5823	531.0	6.3	2	3.1	99.8%

Table 2.2: The parameters for establishing AX and BX optical cycling. The frequency ν , wavelength λ and natural linewidth Γ (in MHz) are for $v' = 0 \leftarrow v = 0$ transitions. N_{repump} is the number of repump laser needed to close optical cycle for a MOT. $|\mu_E|$ is the electric dipole moment, and $b_{0,0}$ is the branching ratio for the transition between $v = 0$ and $v' = 0$.

Table 2.2. In our experiment, the main slowing transition is $(B^2\Sigma^+, v'' = 0, N'' = 0) \leftarrow (X^2\Sigma^+, v = 0, N = 1)$, abbreviated as BX . The laser for it is noted as L_{00}^S . The repump transition for slowing is $(A^2\Pi_{1/2}, v' = 0, J' = 1/2, P = +) \leftarrow (X^2\Sigma^+, v = 1, N = 1)$, the laser abbreviated as L_{10}^S . The main transition for the MOT is $(A^2\Pi_{1/2}, v' = 0, J' = 1/2, P = +) \leftarrow (X^2\Sigma^+, v = 0, N = 1)$, abbreviated as v_{00} . According to the calculation in [94], the MOT requires three repump transitions: $v' = 1 \leftarrow v = 0$ (v_{10}), $v' = 2 \leftarrow v = 1$ (v_{21}) and $v' = 3 \leftarrow v = 2$ (v_{32}). We use ‘ v ’ for MOT transitions because they are distinguished by their initial and final vibrational states. In the following text, MOT lasers are referred by their corresponding transitions, for there is hardly any confusion whether the context is about the laser or the transition it address.

The ground state, $N = 1$, $J = \frac{1}{2}, \frac{3}{2}$ are split into four hyperfine levels, and all of them are addressed with electro-optic modulators (EOM) and acousto-optic modulators (AOM).

Chapter 3

Cryogenic buffer gas source

This chapter focuses on the starting point of my experiment: a cryogenic buffer gas source. A good molecular source is expected to produce stable and bright CaF beams, and the velocity distribution is preferred to be a Gaussian function centred at 180 m/s. Here, I successfully established a two-stage cryogenic buffer gas source, from the gas system to the ablation laser, from the cell alignment to the temperature control panel. I also build the detection system and then characterised the output, identified the factors that influence the stability and signal strength. Finally, a stable molecular output is quantified.

The first section of this chapter discusses laser ablation sources, a numerical overview of buffer gas collisions and the characteristics of a molecular beam. The second section introduces my experiment setup, including the design of the source and the calculation of heat load on it, the design of the detection chamber and the measurement of the background noise, the detection optical system and the calculation of molecular flux intensity. The next section analyses the results, including the beam profile, the source stability, the impact of different parameters on the source behaviour, and the molecular flux intensity.

3.1 Theory

3.1.1 Laser ablation

The laser ablation source was first applied by R. E. Smalley at Rice University in 1981 [96], aiming to create a gaseous cluster of metal atoms for chemistry research. Over 40 years of development, it has become the most commonly used method to produce metal atoms and metal compounds in the gas phase, covering the production

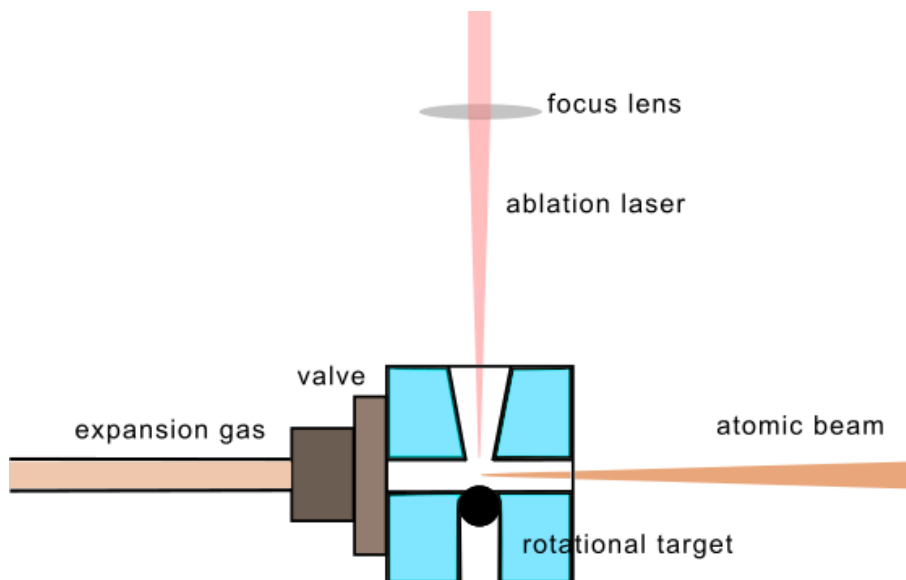


Figure 3.1: An overview of the original design of laser ablation atom source. The ablation laser, the rod and the channel of gas flow are perpendicular to each other.

of pure metal atom clusters, atomic metal neutral and ion complexes, doubly charged cation complexes and anion metal clusters [97].

The original design is shown in Figure 3.1. A metal target is made into a rod which is rotatable from the outside. Nd:YAG laser is focused by a lens, firing onto the sample surface perpendicularly. Expansion gas (helium, argon, etc.) is regulated by a valve. It runs in pulses, flies through the reaction region and blows a cluster of metal atoms out of the exit aperture. The size of the cell is several centimetres.

Compared to this original apparatus, there are several important differences in our experiment: there is another pipe connected to the cell to bring a reactant gas, SF_6 , into the reaction area; the target is fixed instead of rotatable, with motorised mirrors to control the ablation spot; the gas flow runs continuously, resulting in buffer gas cooling instead of supersonic expansion, etc. The details of these features are written in the next section.

The characteristics of the output beam are determined by a variety of parameters: the energy and focusing of the ablation laser, the frequency of ablation pulses, the alignment of the optics, the thickness of the target, the flow rate of the buffer gas and reactant gas, etc.

Stages of ablation

Conditions of the ablated material are divided into the four stages summarized in Table 3.1, mainly depending on laser intensity [98]. For low intensity and brittle metal, the surface of the original material is smashed and spread out by the laser. This is known as the spallation stage.

The next stage is threshold evaporation, where most of the YAG power is absorbed by the solid-vapour phase transition of the target. At this stage, the target begins to produce metal vapour, so that the source begins to produce wanted molecules. It is verified in our experiment that only when the ablation energy reaches a certain value will there be a distinct molecular signal. We believe this is the critical point of phase transition.

As the ablation intensity increases, vapour continuously accumulates in and around the hole drilled by the laser. It is well mixed into a stable flow of cryogenic buffer gas, colliding and cooling, forming a beam of product. This is called stationary evaporation and it is the preferred stage.

When the intensity is even higher, the reaction goes into a stage called stationary evaporation and melt ejection. As its name suggests, the target gets rather hot, and the pressure of metal vapour is high enough to eject a mixture of vapour, plasma and melted material out of the hole. The ejection has a huge influence on the beam profile, which is observed in our experiment. For the purpose of cooling and trapping molecules, this stage is wasteful because it produces high velocity molecules that are outside the slowing range [98].

Velocity modes

When a target has been used for several days, the velocity distribution changes from a Gaussian distribution to two separated Gaussian distributions. The typical signal is a combination of a sharp, fast peak and a broad, slower peak, as shown in Figure 3.2, and sometimes there are more than two peaks. They are different velocity modes. However, for newly polished targets, the signals are mostly single mode.

A possible explanation for the multi-mode velocity groups is the oscillation of the ions in the plasma [98]. When plasma is ejected from the surface of a target, it contains not only metal atoms, but also clusters, electrons and ions. Because electrons are lightest, they travel in front of the ions. The spatial displacement of

Stage	Ablation energy	Featured product	Ejection
Spallation (brittle metal)	Low	Solid original material	Yes
Threshold evaporation	Medium low	Vapour material	No
Stationary evaporation	Medium high	Vapour material and plasma	No
Stationary evaporation and melt ejection	High	Vapour material and plasma	Yes

Table 3.1: Summary of different stages of ablation and their products. Not all metals have the spallation stage. The buffer gas source often runs in stationary evaporation or stationary evaporation and melt ejection mode.

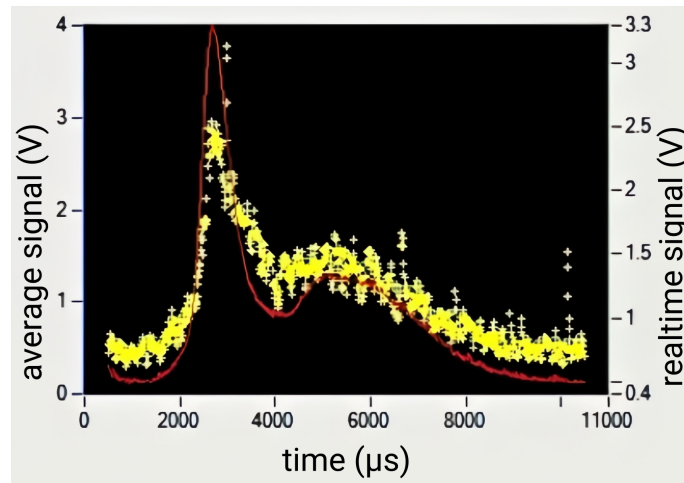


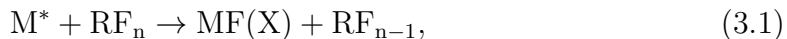
Figure 3.2: A TOF signal with two peaks. One is fast and sharp, and the other is slow and broad. The yellow points are the data of ongoing measurement, and the red curve is the average of TOF signals.

charge creates an electric field, pulling electrons back. When the charge separation is large enough, it results in damped oscillation for positive particles, so their movement differs from the movement of neutral products. The difference is passed to the neutral products by collision.

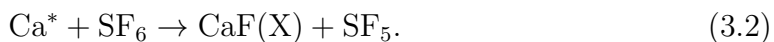
When the ablation laser hits an unsmooth area on the target surface, such as the holes in Figure 3.3, heat dissipates anisotropically. The hottest area enters the stationary evaporation and melt ejection stage, producing fast peaks. Also, the molecules are not thermalised with buffer gas uniformly, due to the geometrical limitation. The same situation happens when a target twice thicker than usual is tested: the local temperature at the reaction point is too high due to heat accumulation, so signals with fast peaks are produced even on a smooth surface.

3.1.2 Reaction

The reactions between alkaline earth metals and fluorides have been studied since the last century [99]. The most generally acknowledged reaction channel to produce monofluorides in the ground state is



where M^* stands for metals in excited states, and R stands for non-metallic elements such as nitrogen and sulphur. X stands for ground electronic state. In our experiment, the reaction is



There are other reactions, possibly sulfides, that form a white or light-yellow coating on the surface of the target, as shown in Figure 3.3. The coating lowers the reaction efficiency and reduces the beam signal, so the target needs polishing regularly. Another kind of coating with darker colour is seen on the inner surface of the window for ablation laser, which may be condensed vapour of metal.

3.1.3 Cryogenic buffer gas source

The buffer gas cooling technique was first developed in 1984 to study molecular collisions at low temperature, where thermal motion is suppressed [100]. An overview of a typical cryogenic buffer gas source is shown in Figure 3.1. The cell is connected



Figure 3.3: A photo of a used target. There are several holes drilled by YAG laser, and a layer of coating can be seen clearly.

to a cold head and shielded from room temperature radiation, so its temperature is reduced to several kelvin. Cold buffer gas flows continuously through the cell. The buffer gas is considered in equilibrium, which means the number density of buffer atoms is a constant during the experiment, between 10^{14} and 10^{17} cm^{-3} . So the main features of the molecular beam are characterised by the buffer gas flow. The most used buffer gases are ^{20}Ne and ^4He , and the latter is chosen as our buffer gas because of its lower boiling point. Laser ablation produces a hot gas at thousands of kelvin. It is mixed into the buffer gas, thermalizes with it through elastic collisions, and a bright intense beam of product is formed. In some designs there are extensions, apertures or skimmers to regulate beams as well.

Among research groups in the area of cooling and trapping dipolar molecules, a group in Harvard University first developed the buffer gas cooling apparatus, and produced molecular beams of different species [101] [40] [102]. A group in Yale University applied a cryogenic buffer gas source to produce SrF in the rovibrational ground state in 2011. The target was made of SrF_2 powder. The output beam had 140 m/s mean translational velocity, and the molecular intensity was 1.2×10^{11} molecules/sr/pulse [103].

In 2018, a group in Imperial College set up a buffer gas source with a rotating target of calcium. This source produced CaF at 150 m/s with 5×10^{10} molecules/sr/pulse [104]. Because of the implementation of a pure metal target instead of compound powder, problems associated with ablation dust are largely reduced. The source described in this chapter is based on that design.

The Reynolds number and gas flow regions

The Reynolds number is a description of the impact of a fluid or gas flow, defined as the ratio of inertial to viscous force:

$$Re = \frac{F_{inertial}}{F_{viscous}} = \frac{\rho v^2 d^2}{\mu v d} = \frac{\rho v d}{\mu}. \quad (3.3)$$

Here, viscous force is a restoring force in a material that resists deformation between its layers, and μ is the viscosity. ρ is the density of the fluid, and v is its velocity. d is a typical size of the system in length, and here we take the diameter of the output aperture.

The Reynolds number is related to the Mach number (Ma) and the Knudsen number (Kn) by:

$$Re \approx \frac{2Ma}{Kn}. \quad (3.4)$$

The Mach number is defined as the ratio of flow velocity over speed of sound, c . We take the mean thermal velocity as the velocity near the exit aperture. For monatomic buffer gas such as helium and nitrogen, with specific heat ratio $\gamma = 5/3$, the Mach number at the exit aperture is:

$$Ma = \frac{v}{c} = \sqrt{\frac{8k_B T}{\pi m}} \left(\sqrt{\frac{\gamma k_B T}{m}} \right)^{-1} \approx 1. \quad (3.5)$$

The Knudsen number is a measurement of the number of collisions. It compares the mean free path λ and the characteristic length d of the volume:

$$Kn \equiv \frac{\lambda}{d}. \quad (3.6)$$

Combining the equations above, the Reynolds number is

$$Re \approx \frac{2}{Kn} = \frac{2d}{\lambda}. \quad (3.7)$$

According to the Reynolds number, there are three types of flow.

$Re \lesssim 1$: The mean free path is larger than twice the system length, which means there are few collisions between buffer gas atoms before they go out of the aperture. Therefore, the output is just a sample of gas inside the cell, following the Maxwell Boltzmann distribution weighted by v , because the faster molecules are more likely to leave the cell in a given interval of time. Thus its velocity profile is similar to

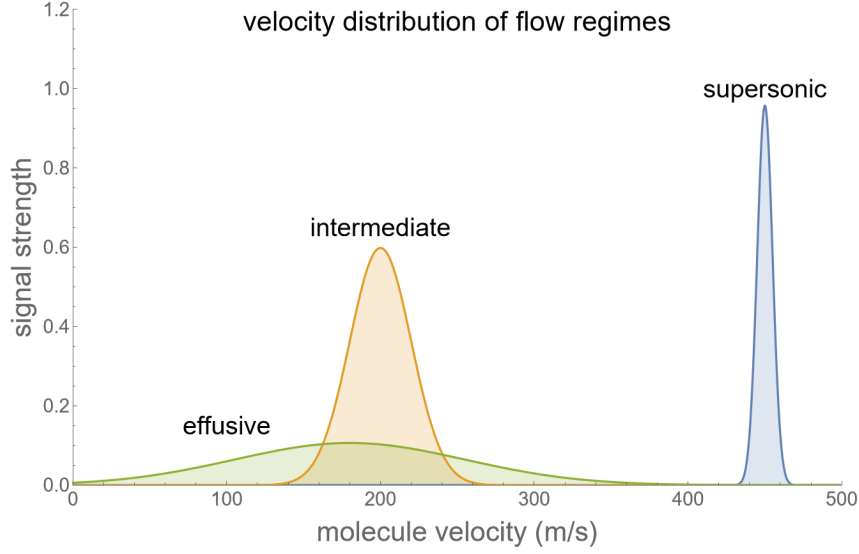


Figure 3.4: An overview of the velocity distribution of three types of flow regimes. Effusive beams are slow but broad; supersonic beams are narrow but fast; intermediate beams are a combination of both advantages.

that of a Maxwell-Boltzmann distribution. This is called the effusive regime. Oven sources mostly operate in this regime.

$Re \gtrsim 100$: The mean free path is much smaller than the system length, so there are many collisions between buffer gas atoms, and with the molecules of interest. The molecules are completely thermalised and are flushed out of the cell by the buffer gas. The output is a bright beam with narrow velocity distribution. This is called the supersonic regime. Typical expansion gas flow operates in pulses with higher flow rate than the buffer gas source, and the cell is about or slightly cooler than room temperature.

$1 \lesssim Re \lesssim 100$: The molecules collide a few tens of times in the vicinity of the exit aperture and are partially thermalised, forming an intermediate velocity distribution. This region is the one used for most buffer gas sources.

The features of the three flow regimes are shown in Figure 3.4. Effusive flows don't have enough collisions to cool molecules, and not many of the molecules are in their low rovibrational states. Supersonic beams, on the other hand, have low internal states, but are too fast to be slowed to the capture velocity of a MOT. Intermediate flows are preferred in our experiment.

Collisional cooling

According to Equation (3.7), the Reynolds number of buffer gas sources depends on the mean free path and the size of the exit aperture. The mean free path is

$$\lambda = \frac{1}{\sqrt{2}n_b\sigma_{bb}}. \quad (3.8)$$

Here, n_b is the number density of buffer gas, and σ_{bb} is the collisional cross-section in a hard sphere model, related to the van der Waals radius r_b :

$$\sigma_{bb} = 4\pi r_b^2. \quad (3.9)$$

For helium, $r_b = 140$ pm [105].

When a source is in equilibrium, the buffer gas flow into the cell, F_{in} , equals the flow rate out of the cell, F_{out} , which is estimated as

$$F_{out} = \frac{1}{4}n_b v_b A_{aperture}. \quad (3.10)$$

Here, $A_{aperture}$ is the area of the exit aperture. We have a round aperture with diameter $d = 4.5$ mm. v_b is the mean thermal velocity in the cell:

$$v_b = \sqrt{\frac{8k_B T}{\pi m_b}}, \quad (3.11)$$

where the gas temperature T is approximately the cell temperature. In our experiment, it is around 4 K when the ablation laser is on, giving $v_b \approx 150$ m/s.

With all the statements above, the Reynolds number can be written as

$$Re \approx 32\sqrt{2} \frac{F_{in}\sigma_{bb}}{\pi v_b d_{aperture}}. \quad (3.12)$$

In our experiment, gas flows are measured in a unit of volume flow rate called standard cubic centimetre per minute (sccm). The flow rate of our buffer gas, helium-4, varies between 0.5 and 2 sccm. With its mass density at room temperature (0.16 kg/m³) and the mass of helium atom (6.65×10^{-27} kg), we know that F_{in} varies between 2.0×10^{17} and 8.0×10^{17} atoms/s.

With all the calculations above, the Reynolds number of our 4K helium buffer gas source is

$$1.05 \lesssim Re \lesssim 4.21. \quad (3.13)$$

It shows that our source falls into the intermediate regime, but also very close to the effusive regime. The range of the number density and mean free path of our source can also be calculated:

$$3.35 \times 10^{20} \text{ m}^{-3} \lesssim n_b \lesssim 1.34 \times 10^{21} \text{ m}^{-3}, \quad (3.14)$$

$$2.14 \text{ mm} \lesssim \lambda \lesssim 8.56 \text{ mm}. \quad (3.15)$$

The mean free path is about the same size as the exit aperture, which agrees with the conclusion from Equation (3.13): The buffer gas beam lies at the edge of the intermediate regime, very close to the effusive one.

However, the collision between buffer gas atoms and the produced molecules, which mostly happens near the exit aperture, is what really shapes the beam profile. The mean free path of the product is defined as:

$$\lambda_p = \frac{1}{n_b \sigma_{bp} \sqrt{1 + m_p/m_b}}. \quad (3.16)$$

σ_{bp} is the cross-section between buffer gas and product. Here it is approximated by the cross-section between buffer gas atoms, which has been calculated by Equation (3.9). m_p is the molecular mass of the product, and m_b is the mass of the buffer gas. So the mean free path of CaF molecule is:

$$0.76 \text{ mm} \lesssim \lambda_p \lesssim 3.05 \text{ mm}. \quad (3.17)$$

Elastic collision between the product and the buffer gas atoms is the main mechanism for the output beam to thermalise. Using a hard sphere model of the collision process, according to [98], the kinetic energy of a CaF molecule is

$$E(n) = (E_0 - E_b) \exp(-\epsilon n) + E_b. \quad (3.18)$$

Here, n is the number of collisions, E_0 is the initial energy of the molecules, and E_b is the kinetic energy of the buffer gas. ϵ is defined by the mass ratio:

$$\epsilon = \frac{2m_p m_b}{(m_p + m_b)^2}. \quad (3.19)$$

Applying the relation between kinetic energy and temperature for gases in 3-

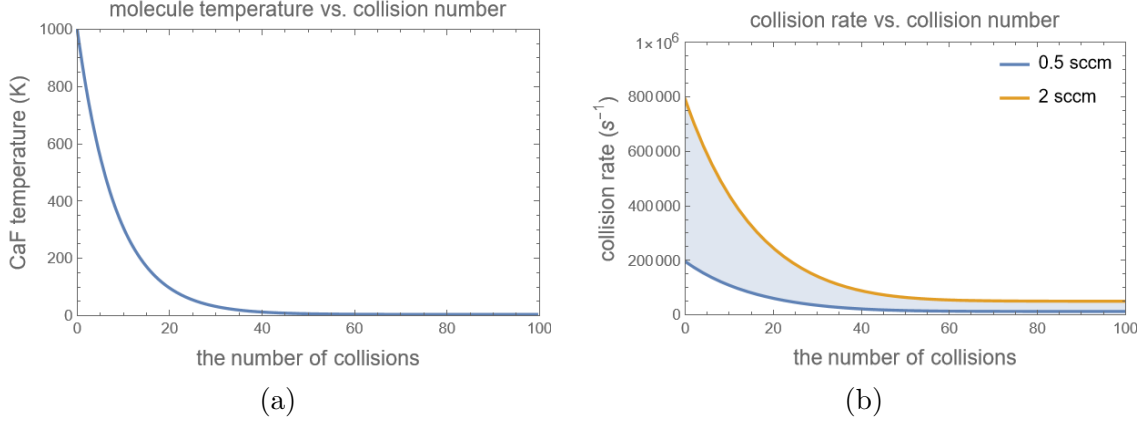


Figure 3.5: Temperature and collision rate against collision number. (a) Temperature of molecules drops exponentially against collisions with the buffer gas. (a) Collision rate decays as temperature decreases. The shaded area is all the possible value of collision rate with the buffer gas flow rate in our experiment.

dimensional space: $E = \frac{3}{2}k_B T$, the temperature after n collisions is

$$T(n) = (T_0 - T_b) \exp(-\epsilon n) + T_b. \quad (3.20)$$

The melting point of calcium is 1115 K. In our experiment, we assume the initial temperature of the molecule $T_0 = 1000$ K, and the buffer gas is as cold as the cell, so $T_b = 4.0$ K. The collision cooling curve is shown in Figure 3.5(a). It shows the temperature of the molecules drops dramatically within the first 20 collisions with the buffer gas. The length between the helium inlet and the aperture is 34 mm. According to Equation (3.17), there are tens of collisions happening in the cell before a molecule comes out, and the temperature is reduced below 100 K.

Assuming the velocity distribution of molecules is close to the Maxwell-Boltzmann distribution, the collision rate is

$$R(T) = \frac{v_p}{\lambda_p} = \sqrt{\frac{8k_B T}{\pi m_p}} \frac{1}{\lambda_p} = \beta \sqrt{T} \quad (3.21)$$

Here, the factor $\beta = \sqrt{\frac{8k_B}{\pi m_p}} \frac{1}{\lambda_p}$. According to Equation (3.17), its range is $6.2 \times 10^3 \lesssim \beta \lesssim 2.5 \times 10^4 \text{ s}^{-1} \text{ K}^{-1/2}$. The relation between collision rate and collision number is

$$R(n) = \beta \sqrt{T(n)} = \beta \sqrt{(T_0 - T_b) \exp(-\epsilon n) + T_b}, \quad (3.22)$$

which is shown in Figure 3.5(b).

Velocity distribution

We determine the velocity distribution of the molecular pulses by measuring time-of-flight (TOF) profiles, using laser-induced fluorescence as the detection method. This measures the intensity of photon scattering at a fixed place along the beam line against time. Assuming the molecules are in thermal equilibrium, they follow a shifted Maxwell-Boltzmann distribution.

The original Maxwell-Boltzmann description is

$$F(E)dE = A \exp\left(-\frac{E}{k_B T}\right) dE, \quad (3.23)$$

where E is the energy of molecules, and A is a normalization factor. For those molecules that reach the detector, their transverse velocity is negligible compared to the longitudinal velocity, because the radius of our probe beam is about 2.5 mm, but its distance from the cell is 830 mm. So molecules in this region approximately follow the 1-dimension distribution:

$$f(v)dv = \frac{1}{\beta\sqrt{\pi}} \exp\left(-\frac{v^2}{\beta^2}\right) dv, \quad (3.24)$$

$$\beta = \sqrt{\frac{2k_B T}{m}}. \quad (3.25)$$

Suppose the centre velocity is v_0 , so the shifted Maxwell-Boltzmann distribution is

$$f(v)dv = \frac{1}{\beta\sqrt{\pi}} \exp\left(-\left(\frac{v-v_0}{\beta}\right)^2\right) dv. \quad (3.26)$$

The molecular flux $\psi(v)$ is proportional to both $f(v)$ and v :

$$\psi(v)dv = \frac{Bv}{\beta\sqrt{\pi}} \exp\left(-\left(\frac{v-v_0}{\beta}\right)^2\right) dv. \quad (3.27)$$

To rewrite the distribution in terms of the arrival time t , we use the relation $t = \frac{l}{v}$, where l is the distance from the cell to the detection area:

$$\psi(t)dt = \frac{Bl/t}{\beta\sqrt{\pi}} \exp\left(-\left(\frac{v-v_0}{\beta}\right)^2\right) d\left(\frac{l}{t}\right) \quad (3.28)$$

$$= \frac{B}{\beta\sqrt{\pi}} \left(-\frac{l^2}{t^3}\right) \exp\left(-\frac{l^2}{\beta^2} \left(\frac{1}{t} - \frac{1}{t_0}\right)^2\right) dt. \quad (3.29)$$

To simplify the distribution, we assume that t is close to t_0 . So it becomes a Gaussian distribution:

$$\psi(t)dt = A \exp\left(-\frac{1}{2} \frac{(t-t_0)^2}{\sigma^2}\right) dt. \quad (3.30)$$

The normalization factor and the standard deviation is

$$A = \frac{B}{\beta\sqrt{\pi}} \left(-\frac{l^2}{t_0^3}\right), \quad (3.31)$$

$$\sigma = \frac{1}{\sqrt{2}} \frac{\beta t_0^2}{l}. \quad (3.32)$$

3.1.4 Rabi oscillation

When there are molecules flying into the region of the probe laser, which has a 1/e diameter of 4.5 mm, ground state molecules ($X, N = 1, v = 0$) are driven to the first excited state ($A, J' = 1/2, p+, v' = 0$). For a 2-level system driven by a single frequency laser, the interaction Hamiltonian is

$$H_{int} = e \cos(\omega t) \vec{E}_0 \cdot \vec{r}. \quad (3.33)$$

Here, ω is the laser frequency, $\vec{E}_0$ is the spatial electric field of the light, and $e\vec{r}$ is the dipole moment. The wavefunction of the system, $\Psi(\vec{r}, t)$, is described by a Schrödinger equation:

$$i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t} = (\hat{H}_0 + \hat{H}_{int}) \Psi(\vec{r}, t). \quad (3.34)$$

Here, $\Psi(\vec{r}, t)$ can be written as

$$\Psi(\vec{r}, t) = c_g(t) |g\rangle + c_e(t) |e\rangle e^{-i\omega_0 t}, \quad (3.35)$$

where $|g\rangle$ and $|e\rangle$ stands for the ground state and the excited state, and ω_0 is the eigen frequency of the transition between them. Coefficients $c_g(t)$ and $c_e(t)$ are related by:

$$i \frac{dc_g(t)}{dt} = c_e(t) \Omega^* \cos(\omega t) e^{-i\omega_0 t}, \quad (3.36)$$

$$i \frac{dc_e(t)}{dt} = c_g(t) \Omega \cos(\omega t) e^{i\omega_0 t}. \quad (3.37)$$

Here, Ω is Rabi frequency. It has the unit of angular frequency, and is defined as

$$\Omega = \frac{\vec{E}_0}{\hbar} \langle \phi_g | e \vec{r} | \phi_e \rangle = \frac{\mu_{gs} E_0}{\hbar}. \quad (3.38)$$

Using $\cos(\omega t) = (e^{i\omega t} + e^{-i\omega t})/2$, Equation (3.36) and Equation (3.37) can be rewritten as:

$$i \frac{dc_g(t)}{dt} = c_e(t) \Omega^* (e^{i(\omega-\omega_0)t} + e^{-i(\omega+\omega_0)t}) / 2, \quad (3.39)$$

$$i \frac{dc_e(t)}{dt} = c_g(t) \Omega (e^{i(\omega+\omega_0)t} + e^{-i(\omega-\omega_0)t}) / 2. \quad (3.40)$$

When the laser frequency ω is close to the resonant frequency ω_0 , the fast rotating term $e^{i(\omega+\omega_0)t}$ are averaged out. This is the Rotating Wave Approximation (RWA). If the detuning is $\Delta = \omega - \omega_0$, equations are further simplified:

$$i \frac{dc_g(t)}{dt} = c_e(t) \Omega^* (e^{i\Delta t}) / 2, \quad (3.41)$$

$$i \frac{dc_e(t)}{dt} = c_g(t) \Omega (e^{-i\Delta t}) / 2. \quad (3.42)$$

If all the molecules are in ground state at $t = 0$, the population in excited state at time t is

$$P_e(t) = |c_e(t)|^2 = \frac{|\Omega|^2}{|\Omega|^2 + |\Delta|^2} \sin^2 \left(\frac{\sqrt{\Omega^2 + \Delta^2}}{2} t \right). \quad (3.43)$$

For our probe laser we assume $\Delta = 0$. μ_{gs} is the matrix element of dipole moment between X ($N = 1, V = 0$) and A ($J' = 1/2, P+, v' = 0$), which is 3.1 Debye, namely $0.645 \text{ e}\text{\AA}$ [106]. E_0 is the amplitude of the electric field, which can be calculated with the beam size $r_{1/e}$ and power P :

$$\frac{P}{\pi r_{1/e}^2} = 2\epsilon_0 c |E_0|^2. \quad (3.44)$$

The typical experiment condition gives $r_{1/e} = 2.25 \text{ mm}$, $P = 1.5 \text{ mW}$. ϵ_0 is the vacuum permittivity, and c is the speed of light in vacuum. With Equation (3.38) and Equation (3.44) we have $\Omega = 2\pi \times 2.1 \text{ MHz}$.

When the molecules are excited by the probe laser, they rapidly decay to other rotational and vibrational states, so the number of photons scattered by each molecule is small. According to [107], the average number of photons scattered by each molecule is about 1.5.

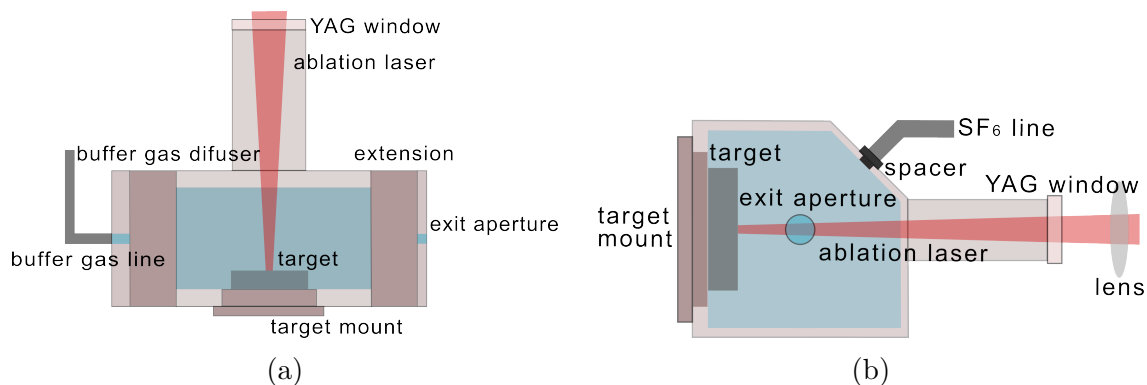


Figure 3.6: An overview of the cell in our experiment. (a) A top view of the cell with buffer gas diffuser and extension. The edge of the chamfer is drawn as a straight line across the cell, and the SF₆ inlet is not shown. (b) A side view of the cell from the exit side, without buffer gas diffuser and extension. The SF₆ line attaches to the cell on the chamfer with a spacer.

3.2 Experiment setup

3.2.1 Source configuration

The cell in this experiment is adapted from the one in Figure 3.1. The top view and side view are shown in Figure 3.6. To make it simple, the screws and threads that connect different parts, as well as other mechanic details, are neglected. The ablation laser is shown in red. It is focused by a lens and comes through a coated window connected to a copper tube, hitting perpendicularly on a Ca target. The target is mounted on a flat cylindrical holder, fixed onto the cell by four screws. The volume of buffer gas is shown in blue. Helium flows into the cell from an aperture on the left side in Figure 3.6(a), passing through a diffuser and getting mixed with the product. SF₆ flows from an aperture on the chamfer of the cell cube, 45° toward the target. Its position is demonstrated in Figure 3.6(b). There is a plastic spacer between the SF₆ gas line and the cell to prevent heat conduction, otherwise the reactant gas will be frozen inside the pipe.

The whole design of the cryogenic buffer gas source is shown in Figure 3.7. The whole chamber is pumped by a turbomolecular pump (Turbovac 450i) backed with a scroll pump. The vacuum pressure is 6.4×10^{-9} mbar when the system is cooled to experiment temperature. It rises to about 6.0×10^{-8} mbar when helium flows at 0.3 sccm, and rises to 1.5×10^{-7} when helium flows at 1 sccm. The helium that flows into the system is primarily absorbed in a sorption pump that is made from coconut charcoal glued to copper sheets and cooled to 4 K by the cryocooler. The helium gas is trapped inside the charcoal when the temperature is low enough. After

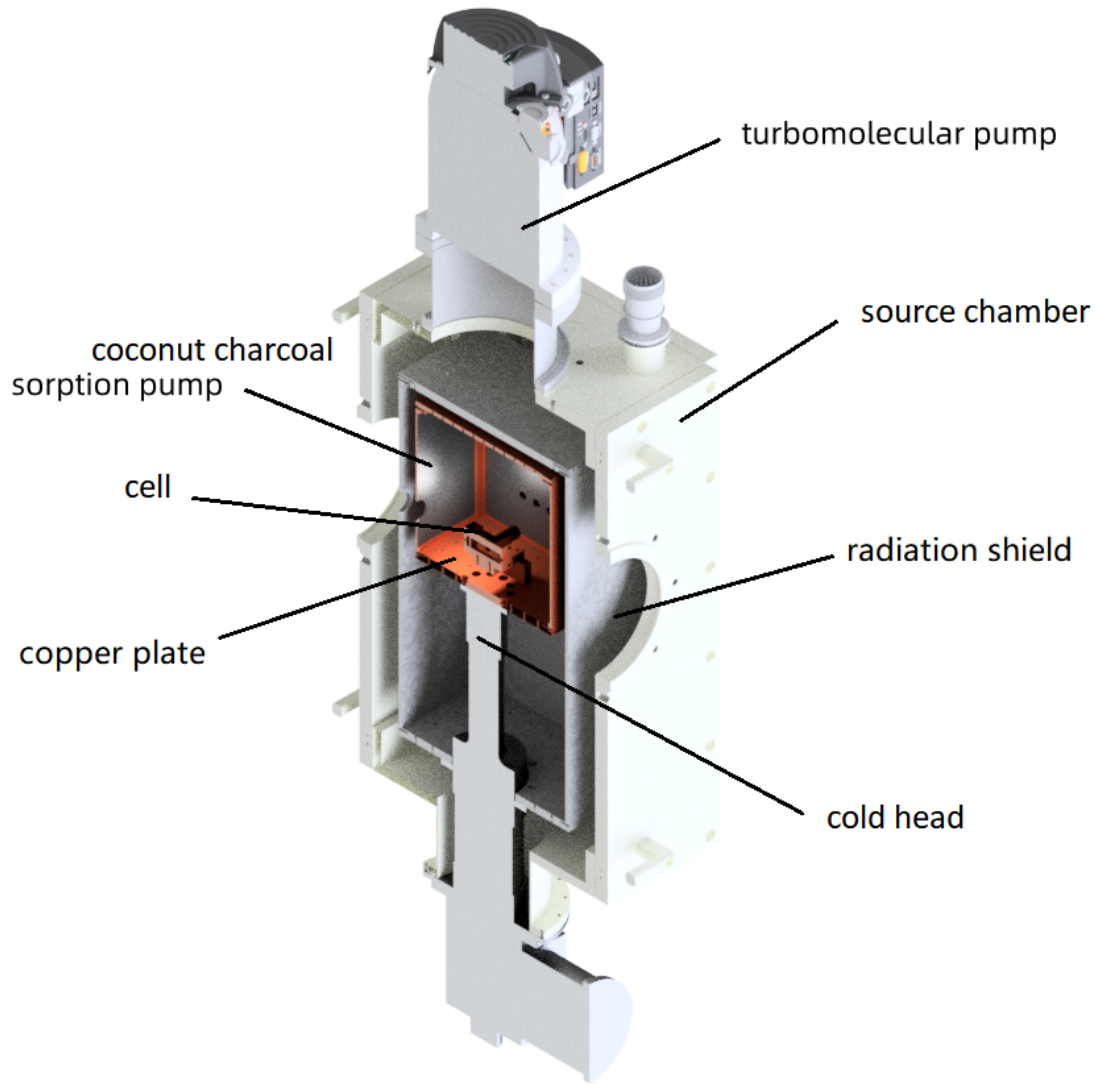


Figure 3.7: The sectional view of the source. A cold head is connected to a copper plate from below, and on the plate is a cell made of copper. There are three layers outside the cell: a charcoal sorption pump, an aluminium shield and chamber walls. There are five holes for the ablation laser to pass through the copper and aluminium shields. There are also holes for the adaption of a rotating target from the top, which requires moving the pump to one side of the wall. The sorption pump is coated with coconut charcoal to absorb buffer gas.

several months of operation, the vacuum rises to 2.5×10^{-8} mbar when no gas flow is on. This is because the charcoal sorption pump is not fresh, and both the cell and charcoal are contaminated.

Our ablation laser is 1064 nm Minilite II Nd:YAG laser produced by Amplitude. There is an anti-reflection coated lens ($f = 400$ mm) about 600 mm away from the target to focus the ablation laser. When the focused laser hits the target, a bright flash with white and purple colour can be seen from the beam line direction. The molecular source is attached to a cold head (RDE-418D4) which is connected to a two-stage cryocooler (F-50) from Sumitomo. According to the specification of the cold head, it provides cooling powers of 2.0 W and 50 W for the second and first stages respectively, when they are at 4.2 K and 50 K. In practice, the two stages are stabilised at 3.3 K and 28 K. The cell is mounted on the second stage, and when the ablation laser is not on, the temperature is around 3.3 K.

To monitor and control the temperature on different stages, a temperature controller (Lake Shore 336) with two power supplies for heaters is used. There are five DT-670 silicon diodes which are fixed to the cell, the first stage, the second stage, the outlet and the middle of the SF_6 line. To keep gases from freezing, there is a thermal insulator between the end of the pipe and the inlet of the cell. A 22.5 Ω heater attached to the SF_6 line close to the entrance of the cell is also turned on during the experiment. It is powered by the temperature controller. The power of it varies from 0.72 W to 0.97 W, most of the time at 0.88 W. So the temperature of SF_6 close to its exit can be varied from 185 K to 235 K. In this case, the cell is kept around 4.4 K, the 4K stage around 3.8 K, and the 40 K not affected.

To speed up the heat-up process, two heaters of 200 Ω are attached to two temperature stages. The two heater channels have maximum output of 50 W and 100 W, but are made for 25 and 50 Ω resistors. Thus, the actual power is much lower, and it takes overnight to warm up the whole chamber to room temperature.

3.2.2 Heat load and radiation shield

The coldest part of the system, the copper plate and the cell, are protected against heat radiation from the environment by an aluminium shielding box shown in Figure 3.7. Thus, radiation on the cell comes from two parts when the experiment is not running: the aluminium box and the leakage from room temperature through the holes in the radiation shield.

The power emitted by the aluminium shield is

$$P = \epsilon \sigma A T^4, \quad (3.45)$$

where ϵ is the Stefan-Boltzmann constant, $5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$. σ is the emissivity of the material. For aluminium it is 0.4. A is the total area of the shield, 0.56 m^2 . The temperature is around 30 K. So the total heat load $P_{al} = 0.01 \text{ W}$.

The other heat load comes from the holes in the copper and aluminium boxes, which are designed for the ablation laser and gas pipes. They enable the heat flux directly between the cell and the walls of the vacuum chamber. The radiation from room temperature is about 400 W m^{-2} , and the total area is 15 cm^2 , so the radiation $P_{room} = 0.6 \text{ W}$. This is the main part of heat load.

When the experiment is on, flowing gases carry extra heat into the cell. The heat advection, Φ_q depends on the gas density ρ , its heat capacity at constant pressure c_p , its velocity v and the temperature difference ΔT :

$$\Phi_q = \rho c_p v \Delta T. \quad (3.46)$$

For SF_6 flowing through 1/8 inch pipe at 200 K, flow rate of 0.005 sccm results in heat load of 0.12 mW. For helium in the same pipe, assuming it reaches the same temperature as the cell, 1.0 sccm flow rate gives a heat load around 4.5 mW. Both of them are negligible.

The ablation laser also carries a heat load. When it runs at 20 mJ, 2 Hz, it gives a heat load $P_{yag} = 0.04 \text{ W}$. This brings a rise of about 0.5 K to the cell temperature. When it runs at 5 Hz, the temperature rises by 0.7 K, and for 10 Hz the number is 1 K.

3.2.3 Detection

A laser induced fluorescence (LIF) method is used to detect CaF molecules. A probe laser beam resonant to the transition $(X, N = 1, v = 0) \rightarrow (A, J' = 1/2, p = +, v' = 0)$ shines perpendicularly to the molecular beam. Scattered photons are collected by a photomultiplier tube (PMT) (model: R 5070A). Detection is done in two chambers, the detection chamber and the MOT chamber, which are 83 cm and 120 cm away from the cell aperture respectively.

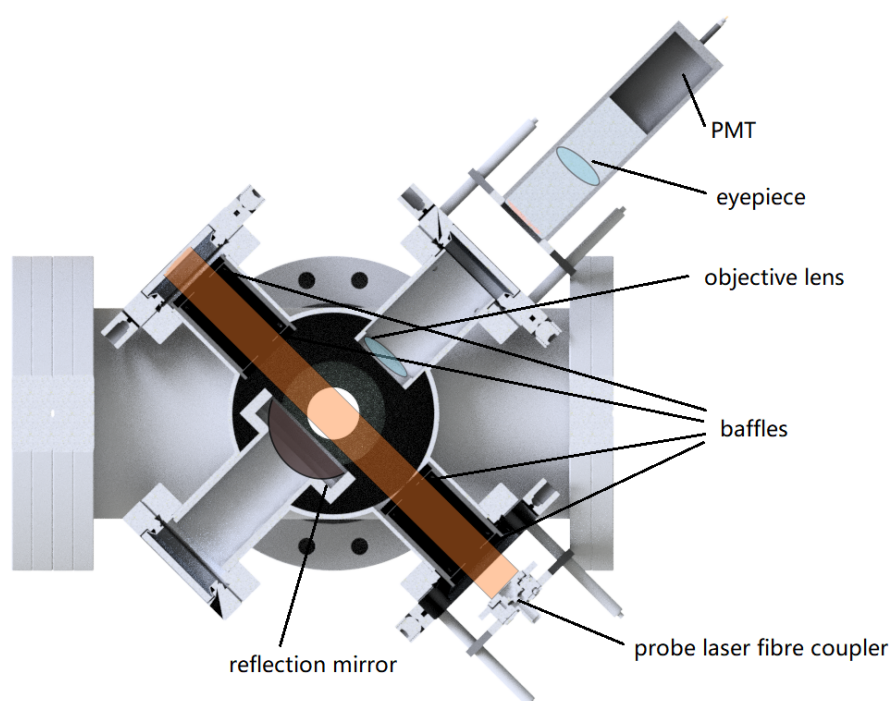


Figure 3.8: The half-section diagram of the detection chamber, with the molecular beam line perpendicular to the cut plane. The detection line is arranged in the order: PMT-eyepiece-objective lens-scattering area-concave mirror.

Detection chamber

The half-section diagram of detection chamber is shown in Figure 3.8. There are eight view ports, only four shown on the graph. The axis of the PMT, the probe laser and the beam line cross each other right in the centre. In order to enhance the signal, a concave mirror is put at the other side against the PMT to reflect the photons scattered to its side. The centre of the concave mirror coincides with the scattering centre, which improves the signal by a factor of 2. There is also a pair of lenses to collect the signal. The objective lens focus is 30 mm and the eyepiece's is 60 mm. The distance between the cell centre and the detection region is 830 mm.

PMT calibration

A PMT transfers optical signal to electric signal by photoelectric effect. Emitted electrons are amplified by dynodes to form a continuous current linear to the photon number. This current is further amplified by an amplifier to output a voltage. The model used on this chamber is R 5070A, working with a home-made amplifier. Data in this chapter is taken with an amplifying factor of 10^{-7} A/V, and the calibrated relationship between the number of photons per time unit F (MHz) and the output voltage v (V) is

$$F = 3.73v - 0.17. \quad (3.47)$$

There is another PMT in the science chamber to take data of slowed molecules. This will be introduced in the next chapter. It works with an amplifying factor of 10^{-6} A/V, and the calibration is

$$F = 0.227v + 0.086. \quad (3.48)$$

In order to reduce background noise caused by the scattering of probe light, the inside of the chamber is painted all black, including the lens mounts. At each end of the two view ports for the detection laser, there is a piece of glass arranged at the Brewster angle, which is not shown in the diagram. The Brewster angle is an incident angle between two materials, at which reflection is eliminated if the incident light is parallelly polarised to the plane of incidence. This angle is around 56.3° from air to glass. There is a half-wave plate between the fibre and the window to adjust the polarisation, so the reflection from the inner side of glass is minimised, and the transmission rate is maximised. In addition, there are four baffles (also painted black) with 10 mm holes placed inside the tubes and designed to cut out light that is scattered at the windows. When the power of the probe laser is 2 mW, the

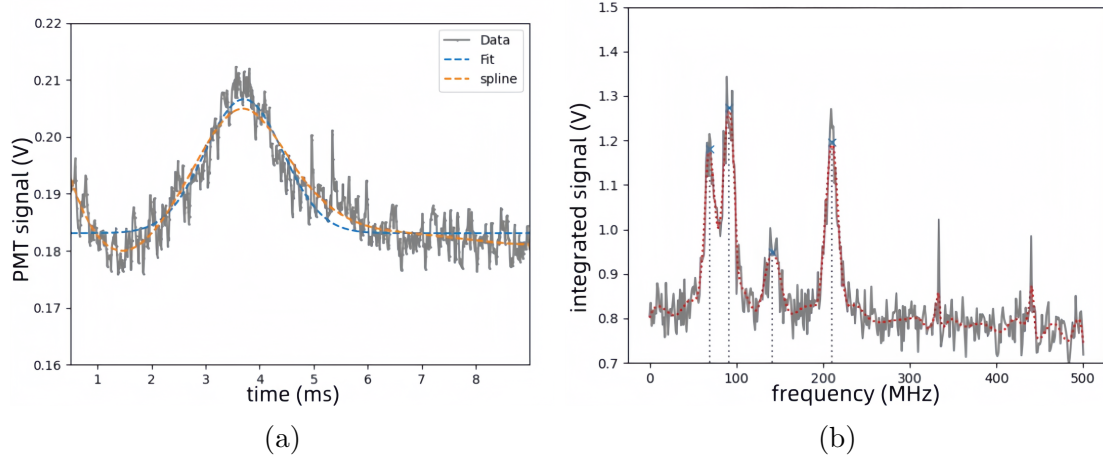


Figure 3.9: TOF signal and hyperfine spectrum detected in this experiment. (a) A TOF signal detected with probe laser at 0.6 mW, with a PMT amplifying factor 10^{-6} A/V. The recording time is slightly after $t = 0$. (b) A spectrum with four distinguishable hyperfine levels. From left to right they are: $F = 2, 1^+, 0, 1^-$.

background laser scatter registered by the PMT is about 1.2 MHz. Other sources of light, e.g. the room lights, make a negligible contribution to the background.

3.3 Results

3.3.1 Beam profile and hyperfine levels

Figure 3.9(a) is a TOF signal of the transition between $(X^2\Sigma^+, v = 0, N = 1)$ and $(A^2\Pi_{1/2}, v' = 0, J' = 1/2, p = +, F' = 1, 2)$, and Figure 3.9(b) is the spectrum obtained when the probe laser is scanned by 500 MHz. To avoid power broadening, the power of the detection laser is 0.6 mW, and all four hyperfine levels are distinguishable. We often use a power of 1.5 - 3 mW, and then the peaks not so clearly resolved. For all TOF signals in this experiment, the YAG laser flash time is defined as $t = 0$.

The peak velocity of the beam can be determined from the peak of the time-of-flight profile. It is 223.9 m/s. The frequency intervals between each of the hyperfine levels are 23.8 MHz, 50.0 MHz and 67.5 MHz. This matches the theoretical values in Figure 2.3. Because the splitting of hyperfine levels in the excited state are comparable to the natural linewidth of the transition, $F' = 1$ and $F' = 0$ are not resolvable.

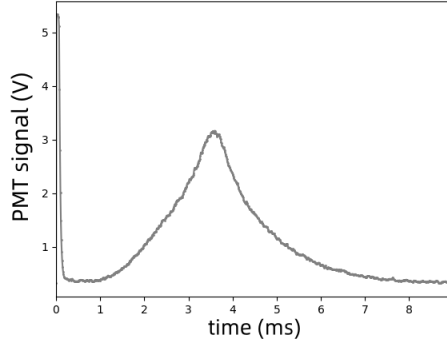


Figure 3.10: A typical signal measured with the system above, with helium 1.3 sccm, SF_6 0.08 sccm, YAG intensity 7.8 J/cm^2 and repetition rate 1 Hz. The sharp peak just after $t = 0$ is the flash of the YAG laser.

3.3.2 Calculation of the molecule flux

Figure 3.10 is an example of a time-of-flight profile measured at the detector, 830 mm from the source. The mean velocity of molecules is 233 m/s.

The geometry of the detection optical system is illustrated in Figure 3.11, according to which we can calculate how many molecules per pulse per solid angle we have in the beam. Molecules fly out from an aperture of $d = 4.5 \text{ mm}$ diameter on the cell. The divergence angle, according to [108], is about $\theta = 15^\circ$. The distance from the source to the probe area is $L = 830 \text{ mm}$. So at the centre of the detection chamber, the diameter of the beam is

$$D = 2L \tan \theta + d = 449 \text{ mm}. \quad (3.49)$$

The probe laser has an effective diameter $d_{\text{eff}} = 4 \text{ mm}$, so the number density can be considered as a constant throughout the detection volume.

The focus of the objective lens and the eyepiece are 30 mm and 60 mm respectively. The diameter of the objective lens is $D = 25.4 \text{ mm}$. The area of the PMT is 20 mm x 20 mm, and the light collection system has a magnification of 2. So, molecules are detected if they fall within an area of 4 mm high and 10 mm long, the latter noticed as l' .

The detector is 830 mm away from the source, so the solid angle covered by the detection laser is

$$\eta_d = \frac{d_{\text{eff}} \times l'}{L^2} = 0.000058 \text{ sr}. \quad (3.50)$$

Assuming photon scattering is spherically symmetric for the resonant molecules,

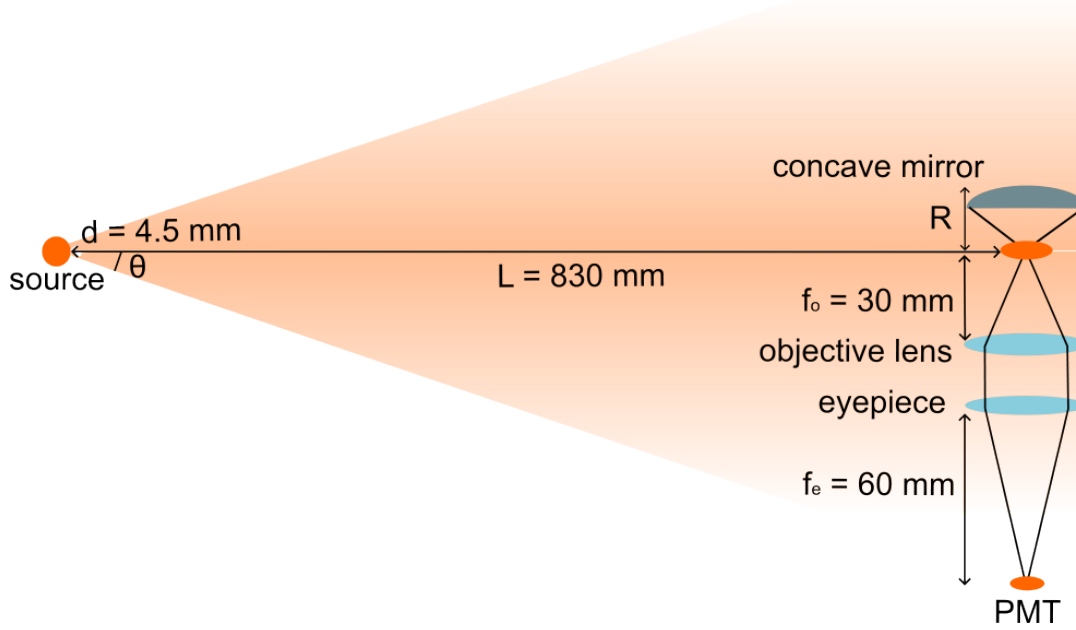


Figure 3.11: A schematic of the imaging system of the PMT in the detection chamber. The orange area is the transversely-expanded molecular beam.

with the mirror contributing a factor 2, the proportion of photons collected by the PMT is

$$\eta_c = \frac{2 \times (D/2)^2 \times \pi}{f_o^2 \times 4\pi} = 0.0896. \quad (3.51)$$

The PMT has a quantum efficiency, $\eta_q = 10\%$ according to its specification. The average number of photons scattered by each excited molecule is $s = 1.5$. In a typical beam pulse, we measure about $N_{\text{ph}} = 2.5 \times 10^4$ photons, so the molecule number intensity is

$$f_{\text{tot}} = \frac{N_{\text{ph}}}{\eta_d \eta_c \eta_q s} = 3.2 \times 10^{10} / \text{sr/pulse}. \quad (3.52)$$

If molecules slower than 190 m/s are suitable for laser cooling, the number intensity is $1.3 \times 10^{10} / \text{sr/pulse}$.

3.3.3 Parameters

Ablation laser

As is described above, there are four stages of ablation as the YAG energy changes. The energy of each YAG pulse is related to the delay between triggering the flash-lamp and triggering the Q-switch of the laser, which we call the flash-to-Q time.

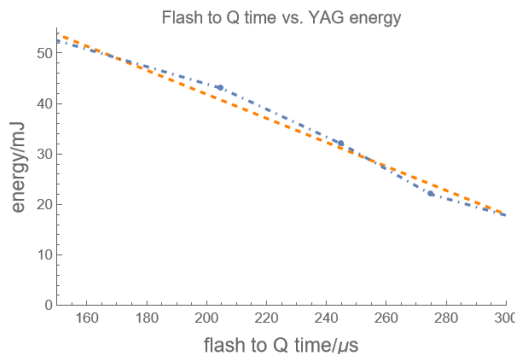


Figure 3.12: The linear relation between pulse energy and flash to Q time.

For our ablation laser (Minilite II), the pulse energy is maximized when the flash-to-Q time is $147 \mu\text{s}$. The pulse energy decreases linearly as the flash-to-Q time increases from $147 \mu\text{s}$ (Figure 3.12). Over the range shown in the plot, the relation between pulse energy E (mJ) and flash-to-Q time t (μs) is

$$E = -0.238t + 89.5. \quad (3.53)$$

The ablation laser is focused by a lens, and the diameter on the target is about 0.5 mm. The ablation laser intensity has a lot of influence on the molecular signal.

Figure 3.13(a) shows time-of-flight profiles taken at 4 different ablation energies. The flux from the source changes over time, typically decaying over time as a single spot on the target is ablated. To account for this change, time-of-flight profiles were recorded with the ablation energy decreasing from 53 mJ to 17 mJ, and then increasing back to 53 mJ. Thus, for each energy (apart from the lowest one), there are two TOF signals. The data shows that as the ablation energy increases, the molecule flux increases too, but the beam also becomes faster. It also shows the energy threshold to produce molecules is between 275 and $305 \mu\text{s}$, which corresponds to 6.8 and 8.8 J/cm^2 . Above this region the reaction is in threshold evaporation stage. Figure 3.13(b) shows the relation between the integrated signal strength and the intensity of the ablation laser. The reaction saturates after about 14 J/cm^2 .

Other than this, the position and angle of the focus lens is also significant. In this experiment, the lens has a focal length of 400 mm, and the signal is maximized when the lens is placed 600 mm from the target. At this position, three angles between the optical path and the normal line of a lens are tested: $\theta = 0^\circ$, 30° , and 60° . It turns out that 0° alignment results in the slowest signal, which is most suitable for laser slowing. Other angles result in faster peaks, sometimes more than one velocity modes, and this should be avoided.

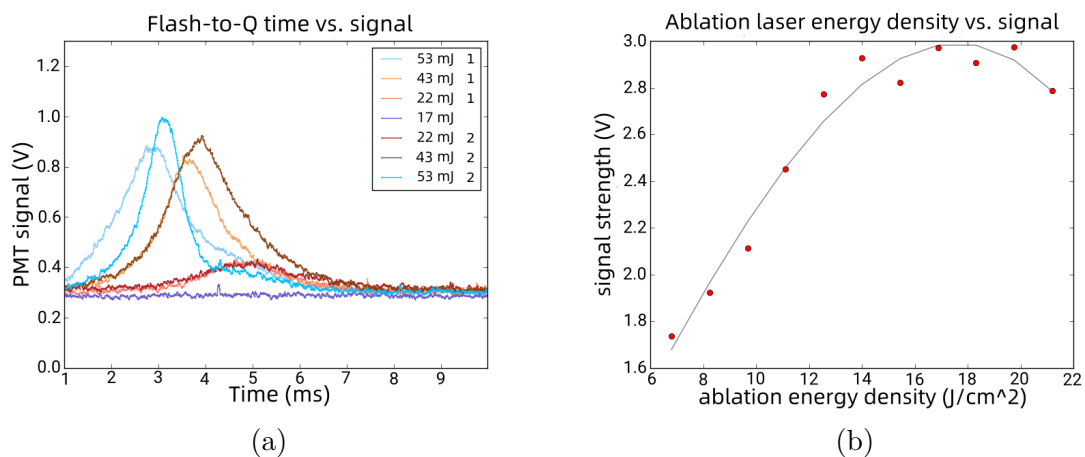


Figure 3.13: The time of flight signal and integrated signal with various ablation laser intensity. (a) Signals taken with different ablation power. The repeated measurements are marked with number 1 or 2 in time sequence, and are plotted in similar colours. There is a sudden rise between 6.8 and 8.8 J/cm², which is the threshold of ablation. Generally, the molecule number and mean velocity rise as the ablation power rises. (b) Increasing the ablation power makes the integrated signal increase, and it saturates above 14 J/cm².

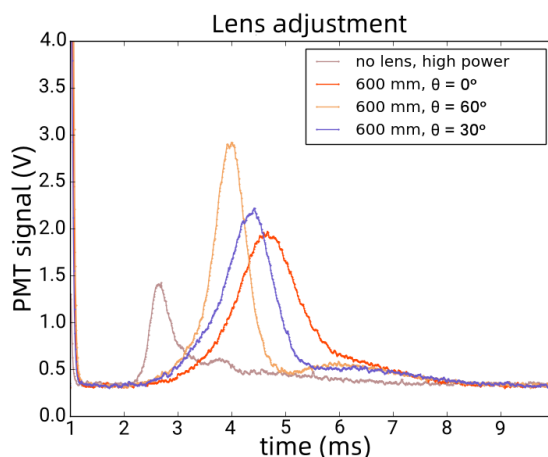


Figure 3.14: Signals measured with different lens positions. They are measured with helium flow rate 1.3 sccm, SF₆ flow rate 0.08 sccm and frequency 1 Hz.

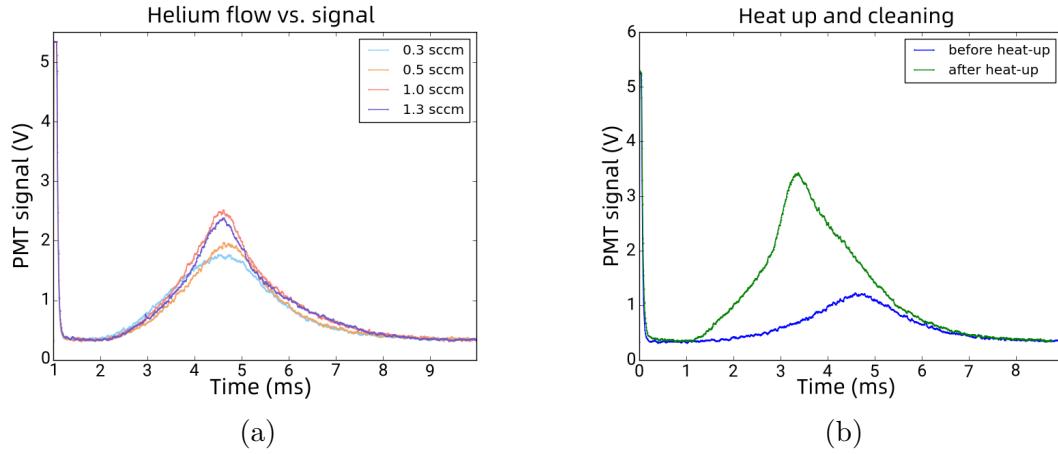


Figure 3.15: Dependence of signal on helium flow. (a) Signals produced with different helium flow rate. The signal is taken with YAG intensity 7.8 mJ/cm^2 , SF_6 flow 0.06 sccm and YAG frequency 1 Hz . (b) Signals produced before and after heat-up to room temperature. The signal is taken with YAG intensity 7.8 mJ/cm^2 , SF_6 flow 0.06 sccm , SF_6 flow 1.3 sccm and YAG frequency 1 Hz .

Helium flow

As is explained in the section above, the flow rate of buffer gas controls the number density in the cell, so it controls the collision rate and the velocity profile of the molecular beam. When the buffer gas flow is not saturated, the molecular signal gets higher as the flow rate increases. In our experiment, saturation happens after 2.0 sccm . The flow rate between 2.0 and 6.0 sccm is tested, and it turns out that changes within this area has no significant impact on the signal. According to the theory, molecular beams collide and signal vanishes when the buffer gas is over-saturated. However, our experiment has not explored this part. Figure 3.15(a) shows the influence of buffer gas flow rate on the molecular beam: the signal increased as helium goes from 0.3 sccm to 1.3 sccm , but not significantly.

After thousands of shots, the molecular signal becomes weak and slow. This might be because of helium and other gaseous products accumulating inside the first stage, and charcoal shield saturates. To test this hypothesis, the system is warmed up towards room temperature, and helium flows at 0.3 sccm overnight. As shown in Figure 3.15(b), the signal next morning improves a lot. After that, the cycle of overnight heat-up and cool-down has become a routine.

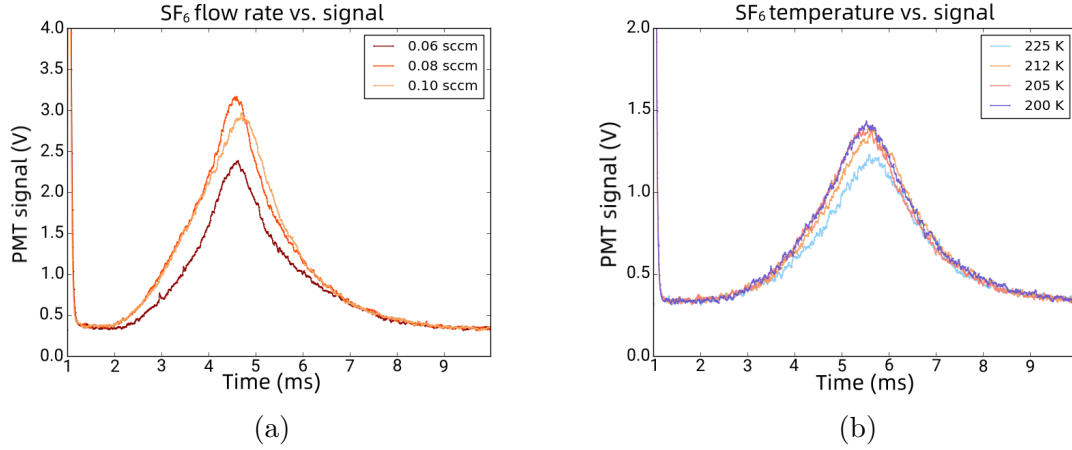


Figure 3.16: Signal dependence on SF₆, taken with helium flow rate 1.3 sccm and the frequency 1 Hz. (a) Signals taken with different SF₆ flow rate. (b) Signals taken with different SF₆ temperature from 200 K to 225 K.

SF₆ flow

The influence of SF₆ is also tested. It is noticed at the early time of the experiment, after the SF₆ inlet valve had been closed, there were distinguishable molecular signals lasting for about 2000 shots. This indicates there was always residual SF₆ in the cell during the experiment. The boiling point of SF₆ is 222.3 K at atmospheric pressure. According to Clausius–Clapeyron relation:

$$\frac{dP}{dT} = \frac{PL}{T^2 R}, \quad (3.54)$$

where R is the gas constant, $R = 8.31 \text{ J/mol/K}$, and L is the latent constant of SF₆, $L = 34.40 \text{ kJ/kg}$, the boiling point for SF₆ under 10^{-8} mbar is 139.9 K. It is very likely to have SF₆ frozen on the target. After a heater was added at the end of the SF₆ line, the signal is improved.

The influence of SF₆ flow on the signal is shown in Figure 3.16(a). It is taken with helium flow rate 1.3 sccm. The frequency is 1 Hz. Above 0.1 sccm, the flow rate of SF₆ does not have much influence on the signal strength. The gas temperature is also varied, and it turns out this does not affect the signal, as long as it is gaseous (Figure 3.16(b)). It is taken with helium flow rate 1.3 sccm and the frequency is 1 Hz.

Stability

There are three types of signal decay when the source is continuously operating, on the scale of shots, hours and days.

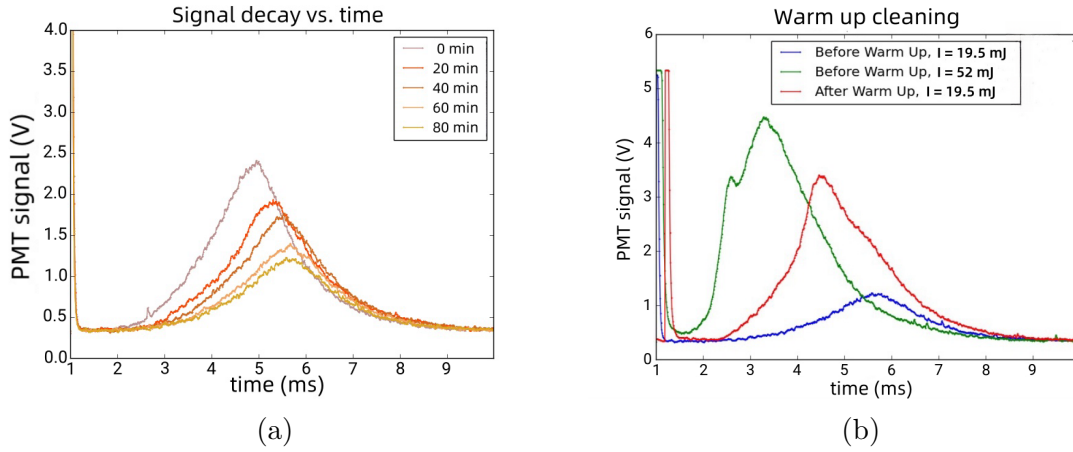


Figure 3.17: Decay of the molecular signal on the scale of hours and days. (a) Signals measured in one day with the same parameters. The gap between each measurement is 20 minutes. (b) Signals at the end of a day with ordinary and high ablation intensity, and at the next day after warm-up with ordinary intensity.

The first half hour gives the brightest beam of a day, and it is also relatively fast. After that, the system settles down, and the beams become a little bit weaker and slower. This is the stage where most of the data is taken. After thousands of shots, the signal becomes multi-peak, which means the ablation laser has drilled a hole on the reaction surface. The signal can be recovered by slightly adjusting the incident angle of the YAG laser. It is similar to rotating the target in a source that has a rotatable target. Because of this, a pair of motorised mirrors are applied to move the ablation spot periodically. However, the distance of each step varies a lot, so that the movement of the spot cannot be controlled precisely, and this plan is abandoned.

However, after hours of operation, the signal decays to 20% of its original strength, as the blue curve in Figure 3.17(b). This results in almost no signal after chirp slowing. Increasing the ablation power might bring back a fast, bright but multi-mode signal which last for a short time (green curve). The main reason of this is the gas residuals in the cell, as explained in Section 3.3.3. So the source must be cycled overnight, and in the morning the signal is bright again (red curve).

Finally, the best signal of a day decays as days go by. The signal gradually becomes weak, and any change in the laser alignment might result in several velocity groups. This is because the surface of the target has been ruined by the ablation laser, as is demonstrated in Figure 3.3. The holes and coating can only be removed by polishing, so the source chamber needs opening, and the cell needs refreshing for every two weeks.

3.3.4 Velocity distribution

The velocity distribution of a beam can be extracted from TOF profiles by cutting each signal into time spans of 0.5 ms, plotting the mean velocity of each slice against the integrated signal strength. An ideal velocity profile following the shifted Maxwell-Boltzman distribution is given by Equation (3.27). However, in practice, a velocity profile can be composed of two or more velocity groups.

Figure 3.18 shows three types of velocity profiles together with fits to Equation (3.27). Figure 3.18(a) is a preferred velocity distribution in our experiment. According to the fitting, its mean velocity $\bar{v} = 177.6$ m/s. It does not follow Equation (3.27) exactly, as there is a little wing on the faster side. Figure 3.18(b) is also an acceptable signal for our experiment. It looks like there is only one velocity peak, but fitting shows there are two modes. The two modes are shown in dashed orange lines, and they add up to be the red dashed line. Their central velocities are: $\bar{v}_1 = 177.2$ m/s, $\bar{v}_2 = 200.9$ m/s. The first peak falls into the region of laser slowing, and the second can be ignored.

However, molecular beams with profiles like Figure 3.18(c) are not welcome. The velocities of the two peaks in Figure 3.18(c) are: $\bar{v}_1 = 233.7$ m/s, $\bar{v}_2 = 322.0$ m/s.

Figure 3.19(a) shows how the velocity distribution changes with the ablation energy. When the intensity of the ablation laser goes down, although the total molecular flux decreases, there are more slow molecules, which is what is wanted in our experiment. However, the mean velocity of molecules remains above 100 m/s until the whole signal vanishes. The decay of signal within thousands of shots is shown in Figure 3.19(b). The mean velocity moves to lower values and the total signal decreases at the same time. The overall effect is that the number of molecules below 150 m/s decreases over time, which is undesirable for our experiment. It is also noticeable that the fast edge decays much faster.

3.4 Conclusion

In this chapter, we outlined the physics behind a cryogenic buffer gas source. The chapter discusses formation of molecules and the characteristics of molecular beams. After that, the structure of our apparatus, from the source to the detection chamber, is demonstrated.

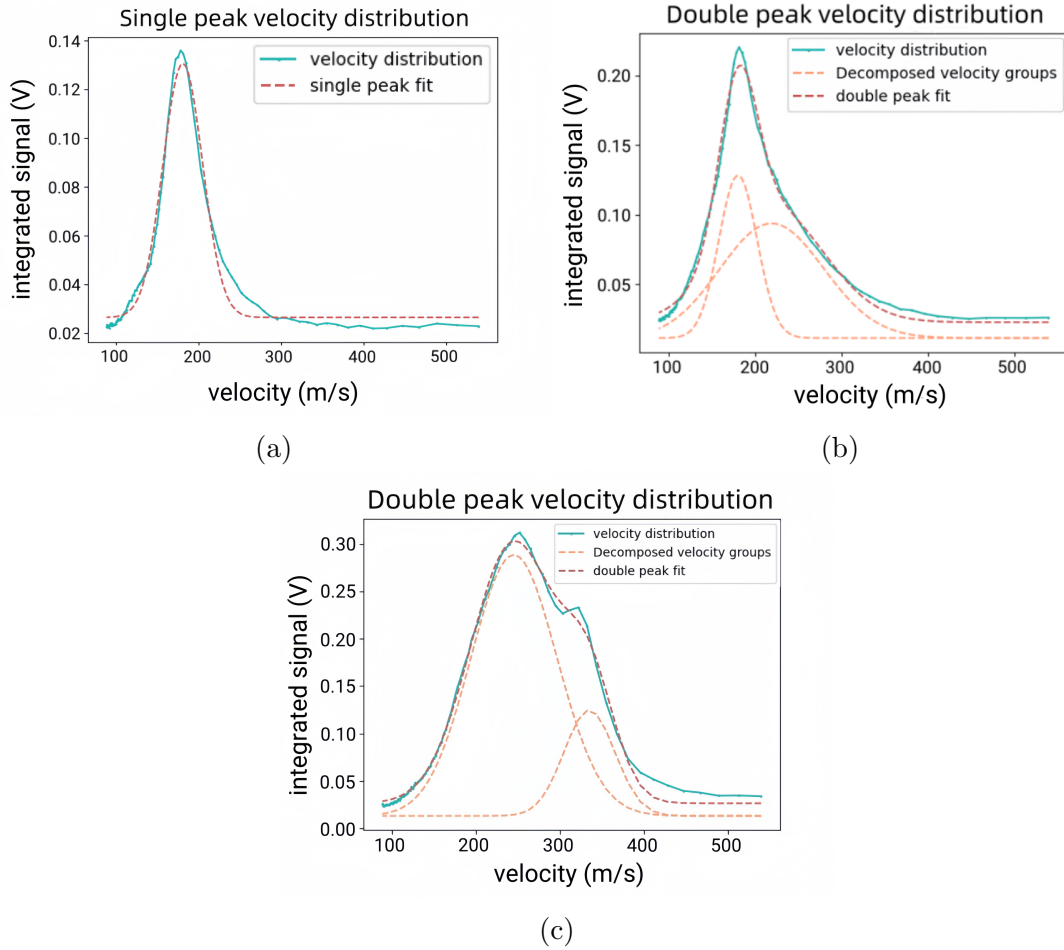


Figure 3.18: Examples of molecular beams with one or two velocity modes. Green lines are velocity profiles, dashed red lines are fits, and dashed orange lines are fits of each velocity mode. (a) A molecular beam of single velocity mode. (b) A molecular beam of single-peak velocity distribution, but composed of two velocity groups. (c) A molecular beam of double-peak velocity distribution, and composed of two velocity groups.

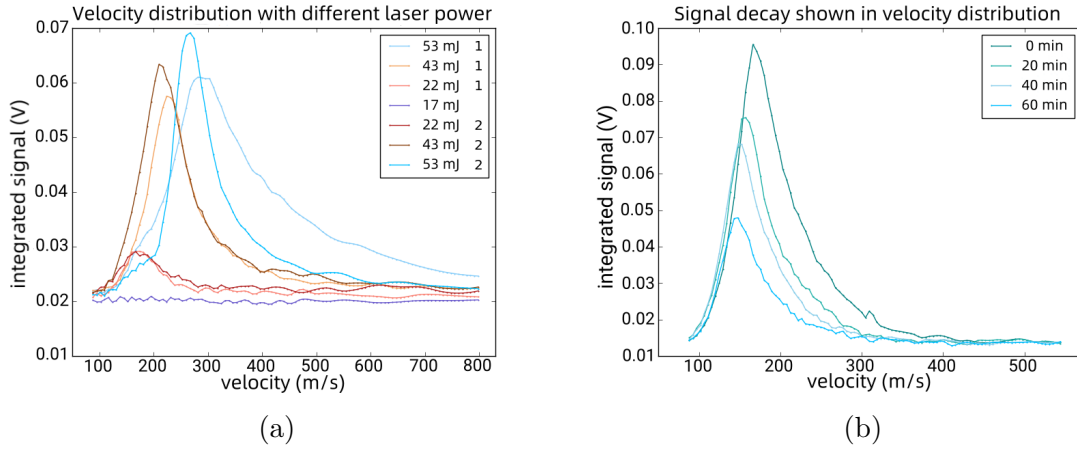


Figure 3.19: Different velocity distributions with changing ablation power or number of shots. (a) Velocity profiles with different flash to Q time. The order of measurement follows the order of plot legend. (b) Velocity profiles measured in one day with the same parameters. The gap between each is 20 minutes.

We characterise the source in terms of different parameters. The source is very sensitive to the incidence angle and energy intensity of the ablation laser. Within a reasonable range, the gas flows do not have obvious impact. The dependence on helium flow saturates above 2.0 sccm, and the signal is relatively constant for SF_6 flows between 0.05 to 0.10 sccm. However, SF_6 can be frozen at the target and harm the long term stability of the source, so a heater on its pipe is implemented and tested.

When all parameters stay unchanged, the molecular signal suffers from three kinds of decay. The one caused by holes on the target can be recovered by changing the reaction position, the one caused by residual gases is removable by thermal cycling, and the one caused by total surface damage can be seen on the target directly and recovered by polishing the target. In the last section, velocity distributions are analysed. Signals are decomposed into one or two velocity groups that follow the Maxwell-Boltzmann distribution.

Chapter 4

Laser slowing

Laser slowing is also called radiation-pressure slowing, because it makes use of the ‘collision’ between a molecule and a photon. In a simple picture, continuous collisions from the direction of motion can decelerate a particle. In this experiment, I applied two powerful lasers to ‘collide’ with the molecules, and changed the laser frequency to maximise the ‘collision rate’. This method is called chirp slowing. It is a subtle and detailed exploration to find the best parameter set to chirp this source, and I finally decelerated the molecules from 170 m/s to less than 20 m/s, qualified for a MOT.

In this chapter, the first part is to talk about the scattering force and chirp slowing: how to make these collisions happen continuously, how to calculate the acceleration it produces, and how to optimise the deceleration trajectory. After this, the experimental set-up for laser slowing is introduced, including the commercial lasers, the optics, and the chirp scheme. The last part is dedicated to the establishment and analysis of the chirp slowed molecules. The most suitable chirp parameters are found, and the capability to be trapped in a MOT is verified by detecting the velocity distribution with an angled probe.

4.1 Theory

4.1.1 Scattering force

Molecules coming out from a cryogenic buffer gas source flow at hundreds of metres per second, which is too fast to be captured in a MOT. As is introduced in Section 1.2.4, a laser beam counter-propagating to the molecular beam is applied to slow it down. Ground-state molecules absorb photons with a momentum of the

opposite direction and spontaneously decay back to the ground state. This process results in loss of velocity, and the force is called the scattering force.

To calculate the scattering force, we start from Equation (3.41) and Equation (3.42). Define new coefficients $c'_g = c_g$, $c'_e = c_e e^{i\Delta t}$, and Equation (3.41) and Equation (3.42) can be written as

$$i \frac{dc'_g(t)}{dt} = c'_e(t) \frac{\Omega^*}{2}, \quad (4.1)$$

$$i \frac{dc'_e(t)}{dt} = c'_g(t) \frac{\Omega}{2} - c'_e(t) \Delta. \quad (4.2)$$

The Hamiltonian is

$$\hat{H} = \frac{1}{2} \begin{pmatrix} 0 & \Omega^* \\ \Omega & -2\Delta \end{pmatrix}, \quad (4.3)$$

and Equation (3.34) is equivalent to a Liouville's equation:

$$\frac{d\rho}{dt} = \frac{i}{\hbar} [\hat{\rho}, \hat{H}] \quad (4.4)$$

where $\hat{\rho}$ is the density matrix of a two level system:

$$\hat{\rho} = |\Psi\rangle \langle \Psi| = \begin{pmatrix} c_g c_g^* & c_g c_e^* \\ c_e c_g^* & c_e c_e^* \end{pmatrix} = \begin{pmatrix} \rho_{gg} & \rho_{ge} \\ \rho_{eg} & \rho_{ee} \end{pmatrix}. \quad (4.5)$$

However, Rabi oscillation only describes absorption and stimulated emission, and under this condition a two level system oscillates forever. In real experiments, these systems have finite lifetime due to spontaneous decay, which is irreversible to the system.

Here we have $d\rho_{ee}/dt + d\rho_{gg}/dt = 0$ because there are only two possible states. If the decay rate of the excited state is Γ , the system is described as

$$\frac{d\rho}{dt} = \frac{i}{\hbar} [\hat{\rho}, \hat{H}] - \begin{pmatrix} -\Gamma\rho_{ee} & \Gamma\rho_{ge}/2 \\ \Gamma\rho_{eg}/2 & \Gamma\rho_{ee} \end{pmatrix}. \quad (4.6)$$

The steady-state solution for the excited state is

$$\rho_{ee} = \frac{1}{2} \frac{s}{1 + s + 4\Delta^2/\Gamma^2}. \quad (4.7)$$

Here s is a parameter related to saturation: $s = I/I_{sat}$. I_{sat} is the saturation intensity, which roughly describes the intensity of a spontaneously emitted photon:

The energy is hc/λ , the lifetime is $1/\Gamma$, and it is distributed over an area of λ^2 :

$$I_{sat} = \frac{2\pi^2\hbar\Gamma c}{3\lambda^3}. \quad (4.8)$$

Equation (4.7) sets the upper limit of the population in the excited state. When the laser intensity is saturated, $s \gg 1$ and $\rho_{ee} \approx \frac{1}{2}$.

The scattering rate is

$$R(I, \Delta) = \Gamma \rho_{ee} = \frac{\Gamma}{2} \frac{s}{1 + s + 4\Delta^2/\Gamma^2}. \quad (4.9)$$

According to [94], for a multilevel system with n_g ground states and n_e excited states, the scattering rate is

$$R(\{I_j\}, \{\Delta_j\}) = \Gamma \frac{n_e}{(n_g + n_e) + 2 \sum_{j=1}^{n_g} (1 + 4\Delta_j^2/\Gamma^2) I_{sat,j}/I_j}. \quad (4.10)$$

Here, I_j is the intensity of the laser driving transition j , and Δ_j is the laser detuning towards this transition. Because the energy gaps between the hyperfine levels of A and B states are neglected, j is summed from 1 to n_g .

In an ideal case in our experiment, all frequency components have the same detuning Δ and the same intensity, which adds up to I . The transition frequencies are close enough that they have the same saturation intensity, noted as $I_{sat,0}$. The equation is simplified to be:

$$R(I, \Delta) = \Gamma \frac{\frac{n_g+n_e}{2n_g^2} \frac{I}{I_{sat,0}} \frac{n_e}{n_g+n_e}}{\frac{n_g+n_e}{2n_g^2} \frac{I}{I_{sat,0}} + 1 + 4\Delta^2/\Gamma^2}. \quad (4.11)$$

It can be written similar to Equation (4.9):

$$R(I, \Delta) = \frac{\Gamma_{\text{eff}}}{2} \frac{s_{\text{eff}}}{1 + s_{\text{eff}} + 4\Delta^2/\Gamma^2}. \quad (4.12)$$

With new parameters

$$\Gamma_{\text{eff}} = \frac{2n_e}{n_g + n_e} \Gamma, \quad (4.13)$$

$$s_{\text{eff}} = \frac{n_g + n_e}{2n_g^2} \frac{I}{I_{sat,0}}, \quad (4.14)$$

the scattering force of a laser beam with wavenumber $\vec{k}$ is

$$\vec{F}_{sc}(I, \Delta) = \hbar \vec{k} R(I, \Delta) = \hbar \vec{k} \frac{\Gamma_{\text{eff}}}{2} \frac{s_{\text{eff}}}{1 + s_{\text{eff}} + 4\Delta^2/\Gamma^2}. \quad (4.15)$$

A molecule with mass m feels an acceleration of

$$\vec{a}(I, \Delta) = \frac{\vec{F}_{sc}(I, \Delta)}{m} = \frac{\hbar \vec{k}}{m} \frac{\Gamma_{\text{eff}}}{2} \frac{s_{\text{eff}}}{1 + s_{\text{eff}} + 4\Delta^2/\Gamma^2}. \quad (4.16)$$

4.1.2 Chirp slowing

The frequency of the slowing laser must be red-detuned to bring it into resonance with the moving molecules. The relation between the molecule velocity v and the detuning frequency $\Delta\nu$ is calculated by the Doppler shift:

$$\frac{v}{c} = \frac{\Delta\nu}{\nu_0}. \quad (4.17)$$

Here, c is the speed of light, and ν_0 is the resonant frequency for a molecule at rest.

To make full use of the laser intensity, the detuning frequency $\Delta\nu$ must change according to the velocity of the molecules. This is called chirp slowing. To reduce the velocity from v to zero at constant acceleration a , the required chirp rate is

$$\Gamma_{\text{chirp}} = \frac{\Delta\nu}{t_{\text{chirp}}} = \frac{\nu_0 v}{ct_{\text{chirp}}} = \frac{\nu_0 a}{c}. \quad (4.18)$$

In our experiment, the transition $B^2\Sigma^+ (N' = 0, v' = 0) \leftarrow X^2\Sigma^+ (N = 1, v = 0)$ is chosen for laser slowing, and the transition $(A^2\Pi_{1/2}, J' = 1/2, p = +, V' = 0) \leftarrow (X^2\Sigma^+, N = 1, v = 1)$ is chosen as the repump. As shown in Table 2.2, the BX transition has a higher frequency than the AX one, so it results in a larger momentum kick per photon. It also has a higher branching ratio, and only requires one repump laser to close the optical cycle. As shown in Figure 2.3, there are 12 Zeeman sublevels in the ground state, and 4 in the second excited state. So we have $n_g = 12$, and $n_e = 4$. The linewidth $\Gamma = 6.3$ MHz, and the resonant frequency $\nu_0 = 564.58$ THz.

According to Equation (4.14) and Equation (4.16), the largest acceleration is achieved when the total intensity I is much higher than the total saturation intensity

$n_g I_{sat,0}$, and the detuning $\Delta = 0$. This gives:

$$\frac{s_{\text{eff}}}{1 + s_{\text{eff}} + 4\Delta^2/\Gamma^2} \rightarrow 1, \quad (4.19)$$

$$\vec{a}_{max} = \frac{\hbar \vec{k}}{m} \frac{\Gamma_{\text{eff}}}{2}. \quad (4.20)$$

Thus, the maximum acceleration is $a_{max} = 2.00 \times 10^4 \text{ m/s}^2$, and the corresponding chirp rate is $\Gamma_{\text{chirp,max}} = 37.6 \text{ MHz/ms}$.

For a typical slowing beam of 300 mW, focused down to a radius of 0.5 cm, $I = 350 \text{ mW/cm}^2$. According to Equation (4.8), each of the BX transition has $I_{sat,BX} = 5.5 \text{ mW/cm}^2$, giving $s_{\text{eff}} = 3.5$. Thus, the corresponding acceleration is $a_{tp} = 1.53 \times 10^4 \text{ m/s}^2$, and the chirp rate is $\Gamma_{\text{chirp,tp}} = 28.7 \text{ MHz/ms}$. For a special case where $I = n_g I_{sat,0}$, which is the lowest acceptable intensity, we have $a_{min} = 8.0 \times 10^3 \text{ m/s}^2$, and $\Gamma_{\text{chirp,min}} = 15.0 \text{ MHz/ms}$.

However, in real experiments, there are several factors that are neglected in this simple model. First, the velocity distribution and laser spectrum are both broadened. Second, the sidebands generated by the EOM do not match the hyperfine structures in Figure 2.3 perfectly, and the laser beam profile is distorted by the EOM crystal when hundreds of mW of laser power is used. Third, there may not be perfect overlap between the molecular beam and the counter-propagating laser light. Thus, the actual best chirp rate varies around the calculated value, and is decided experimentally.

The timing sequence used for laser slowing is as follows. The slowing laser is turned on and held at a fixed frequency for a time t_{hold} . This cools the longitudinal motion, reducing the velocity spread of the molecular beam. Then the laser frequency is chirped linearly at a rate Γ_{chirp} for a time t_{chirp} .

Consider a simplified case where molecules stay in resonance with the slowing laser throughout the chirp process, which makes the acceleration a constant determined only by Γ_{chirp} , there are three situations: For a large chirp rate, molecules stop before they reach the MOT chamber; for an intermediate chirp rate, molecules arrive at the MOT chamber and get captured; for a small chirp rate, molecules are too fast to be captured in the MOT. For the last two situations, the arrival velocity is

$$v_{\text{end}} = \sqrt{v_0^2 - 2 \frac{c \Gamma_{\text{chirp}}}{\nu_0} (L_0 - v_0 t_{\text{hold}})}. \quad (4.21)$$

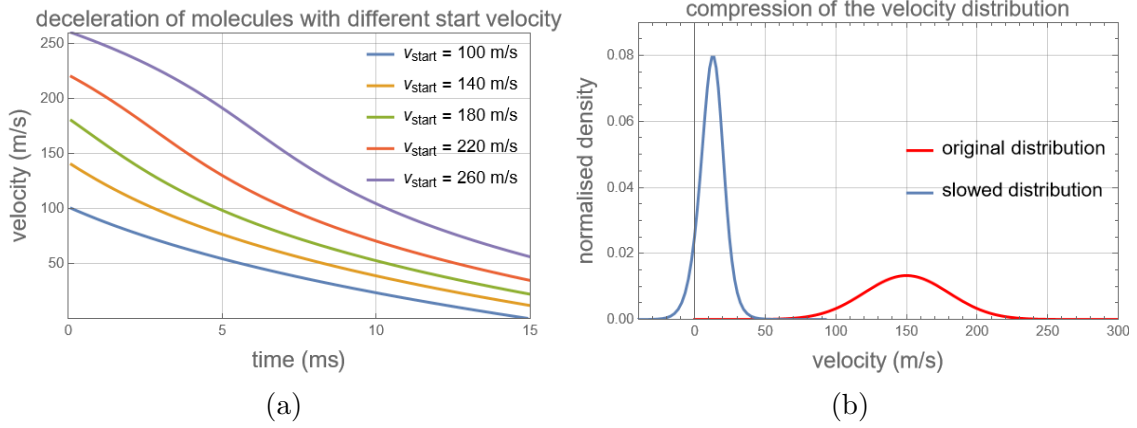


Figure 4.1: The deceleration of molecules with different velocities. The chirp parameters are written in the main text. (a) The deceleration of molecules with a start velocity of 100, 140, 180, 220, 260 m/s. (b) The compression of molecules with a Gaussian distribution.

This is a rough method to estimate the arrival velocity and alter t_{hold} when the chirp rate is close to $\Gamma_{\text{chirp,m}}$.

However, as suggested in Equation (4.17), each chirp start frequency is only resonant with one velocity group. Molecules faster than this feel a smaller deceleration, thus they can never catch up with the resonant ones, and they are not slowed within the capture velocity when they arrive at the MOT centre. The slower molecules feel a smaller deceleration at the beginning, so they ‘wait’ until the resonant group is slowed to their frequency. To sum up, the velocity distribution is compressed by chirp slowing, and the resonant group grows during the chirp process.

Figure 4.1 illustrates a chirp slowing process, in which all the leaks and losses are ignored. The chirp start frequency is -325 MHz detuned from resonance, which corresponds to molecules of speed 173 m/s. The chirp rate is 20 MHz/ms. The BX laser is 350 mW, and focused to a radius of 1.5 mm. The deceleration of molecules with a start velocity from 100 m/s to 260 m/s is shown in Figure 4.1(a). After 15 ms deceleration, the 100 m/s molecules are slowed to rest, and the 260 m/s molecules are flying at 56 m/s. The change of the velocity distribution is shown in Figure 4.1(b). The red curve is the original Gaussian distribution which centres at 150 m/s, with a standard deviation of 30 m/s. The blue curve is the final distribution after 15 ms. The distribution is largely compressed, and now is a Gaussian distribution centred at 13 m/s, with a standard deviation of 8 m/s.

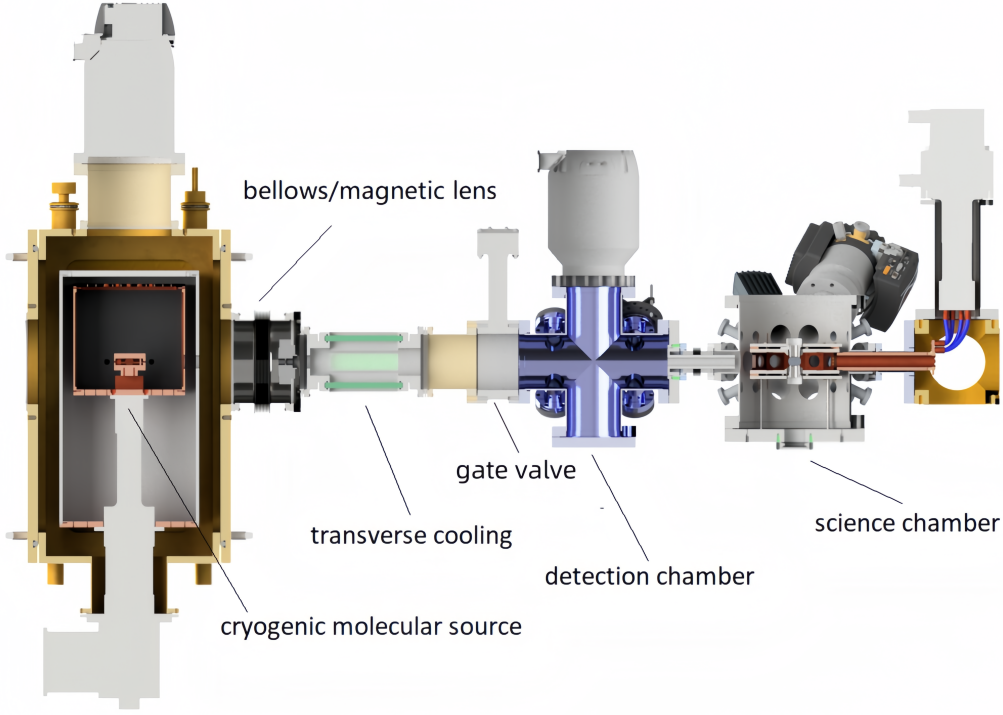


Figure 4.2: The design of the apparatus for laser slowing and MOT. The transverse cooling chamber has not been installed yet.

4.2 Experimental set-up

4.2.1 Beam line

The apparatus for laser slowing and MOT is shown in Figure 4.2. The source is connected to the downstream chamber through bellows to decouple the vibrations from the cryocooler. There is a gate valve to isolate the source from the rest of the vacuum system. The details of the detection chamber were given in Section 3.2.3, and the science chamber (MOT chamber) will be introduced in Section 5.3.1.

Figure 4.3 is a picture of the beam line in the lab. There is a pair of coils separated by 46 cm and arranged in the Helmholtz geometry to produce an approximately uniform magnetic field along the beam line. Each coil has 20 turns and is a rectangle of dimension 30 cm $\times$ 75 cm. They are supplied with a constant power supply running at 10 A, and the magnetic field in the centre is about 4 Gauss.

The field induces Larmor precession, so the bright and dark states inside the $N = 1$ ground state are mixed, and the scattering rate is increased. To optimise this effect, the precession frequency should be comparable to the scattering rate, which according to Section 4.1.1, is several MHz. The angular frequency of precession is

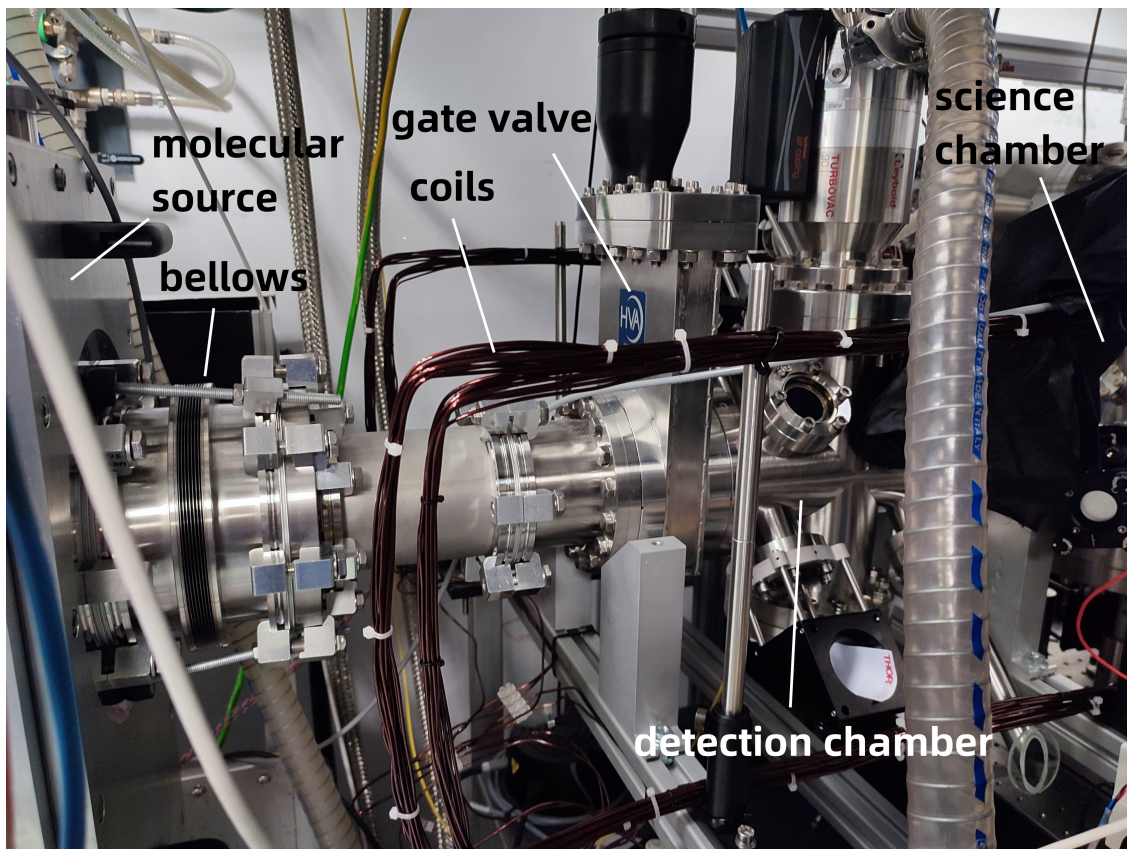


Figure 4.3: A photo of the beam line (bellows, gate valve and coils) in the lab.

given by

$$\omega = -\gamma B = \frac{-eg}{2m_e} B. \quad (4.22)$$

Here, γ is the ratio of the magnetic moment to the angular momentum. It is called the gyromagnetic ratio, equal to $\frac{eg}{2m_e}$, where m_e is the mass of the electron, and g is the g-factor relating the magnetic moment and angular momentum of a system. The precession frequency with $B = 4$ Gauss is 11×10^6 rad/s, which is comparable to the scattering rate. For a ground state molecule in $|F = 2, m_F = 2\rangle$ Zeeman level, the field introduces an energy shift of 5.6 MHz, which is the largest among all Zeeman levels, while small enough to be neglected. Further increase results in excessive Zeeman shift, driving molecules out of resonance. On the other hand, if the precession is too slow, the molecules will be stuck in dark states and the scattering rate will fall.

4.2.2 Lasers and optics

The structure of the slowing and detection optics is shown in Figure 4.4, which is a simplified top-view illustration. The collection optics for PMT 1 has been shown in Figure 3.11, so it is neglected here. The main slowing laser (L_{00}^S) and the slowing repump laser (L_{10}^S) are delivered through polarization-maintaining fibres (PMF). To achieve the highest efficiency, each of the lasers passes through a half-wave-plate (HWP) before being combined by a polarising beam splitter (PBS). The polarisation of the mixed beam is altered by another HWP after the PBS. To achieve the highest scattering rate, the polarisation of the slowing beam is set to be linear, 45° to the magnetic field. After that, the beam passes through an aperture to limit its size and reduce background scatter from the laser. To increase the intensity of the mixed beam, it is focused down by a focusing lens from a diameter of 14 mm to about 5 mm at the cell exit.

The detection chamber and PMT 1 were introduced in the last chapter. In this chapter, molecules are detected in the science chamber, 120 cm away from the cell. In Figure 4.4, probe laser 2 propagates from back to front, crossing the molecular beam perpendicularly. Probe laser 3 crosses the molecular beam with a 30° angle, so it is used to detect molecules with different velocities via their Doppler shifts. Signals are collected by a pair of lenses of 2-inch diameter. The focus length of the objective lens and the eyepiece are 50 mm and 60 mm respectively, and the calibration of PMT 2 is written in Equation (3.48).

The slowing laser is a fibre amplified and frequency doubled laser system from

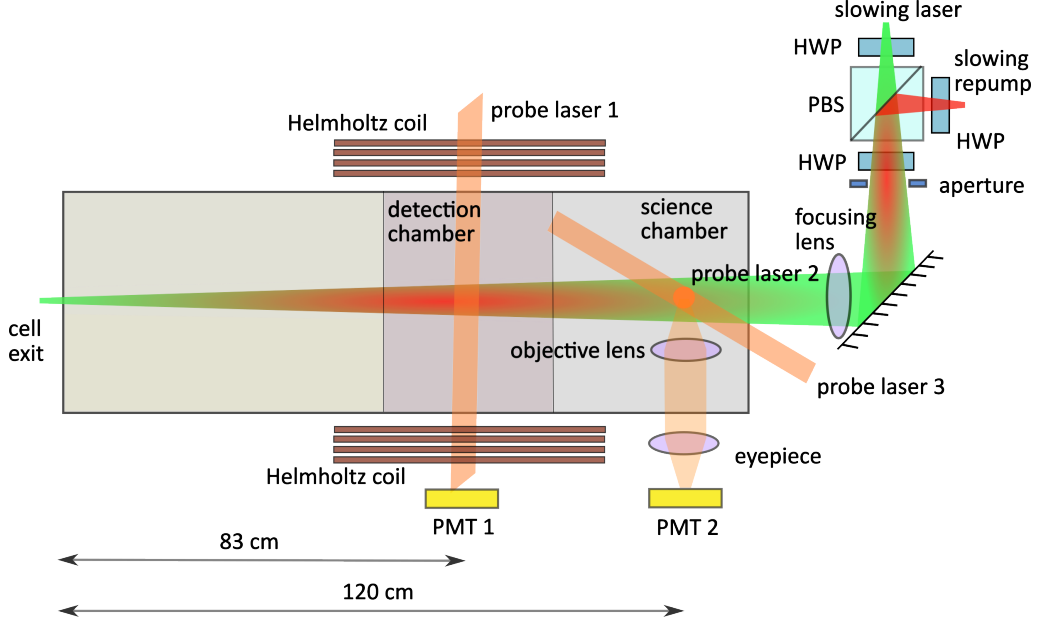


Figure 4.4: A schematic of the optics for chirp slowing. It is a view from the top. The chambers, ports for lasers and collection optics for PMT 1 are not shown.

Azurlight, composed of a seed and an amplifier. The seed is a computer-controlled infrared diode laser. The temperature, current and piezo voltage are the main factors that affect the frequency and stability of a diode laser. A similar system will be described in detail in Section 5.3.3. The seed laser is fibre-coupled into the amplifier, and passed through a doubling crystal to get the needed frequency. Its maximum output is 5 W.

The slowing repump laser, which is also used as a MOT repump laser, is generated with two infrared high power seed-amplifier systems, with the method of sum frequency generation (SFG). The seeds are 1053 and 1559 nm DFB fibre lasers from Precilasers, and the amplifiers are 10 W Yb-doped & Er-doped fibre amplifiers from the same company. The two amplified beams are passed through a frequency-summing crystal to produce the needed wavelength.

The probe laser, which is also used as the main MOT laser, is also a fibre amplified and frequency doubled laser system. The seed is a Toptica DL pro functioning at 1212 nm, and the amplifier is a Raman fibre laser made by MPB. The seed, amplifier and frequency doubler are shown in Figure 4.5(a). The controllers of the seed-amplifier system are shown in Figure 4.5(b).

The optics layout of the slowing and MOT lasers is shown in Figure 4.6. There are neutral density filters (NDF) right after the outputs. They reduce the power by 10^6 , making the system safe for optical alignment. The probe laser is switched

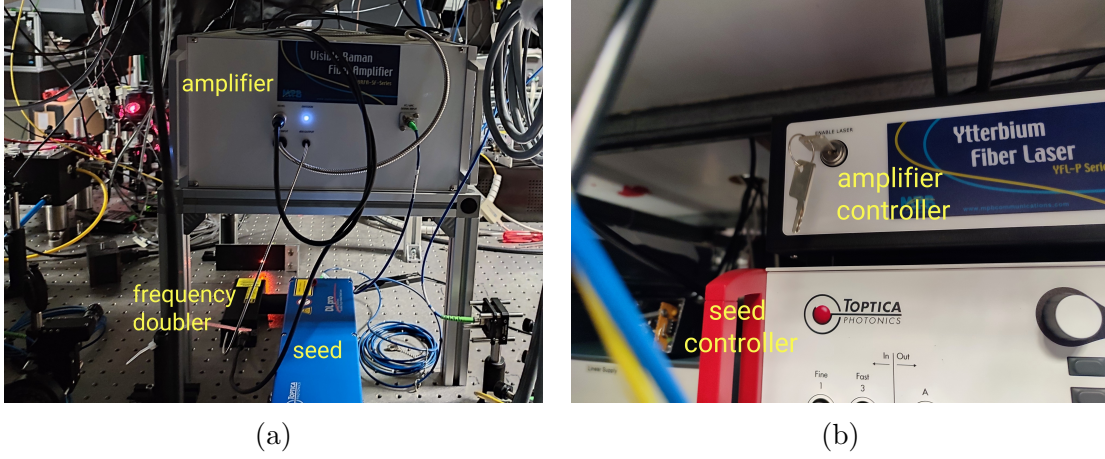


Figure 4.5: The laser system for 606 nm laser. (a) The amplifier and the seed. (b) Control panels of the amplifier and the seed.

on and off by a 110 MHz double-pass AOM. To apply the required sidebands, the light is split into 2 branches with 3:1 power ratio. The more powerful branch passes through a 73.5 MHz EOM to produce the frequency components that drive the $F = 1^-$, 0, 2 hyperfine levels, and the other passes through a 48 MHz AOM to address the $F = 1^+$ hyperfine level. The two branches are combined by a PBS again, and split into two parts. Only a small proportion ends as the PMT probe laser, and the rest is mixed with MOT repump lasers, which will be introduced in the next chapter. The main slowing laser and the slowing repump laser are both turned on and off using a single-pass AOM. The AOM for the slowing laser operates at 90 MHz, and we use its +1 order light. The AOM for the slowing repump is 110 MHz, with -1 order for slowing repump, 0 order for MOT repump.

The sidebands of the slowing laser and the slowing repump laser are both created with a 24 MHz EOM. All the sidebands are monitored by sending all light into a Fabry-Pérot cavity (FPC), which may be seen in Figure 4.7. The frequencies and amplitudes of all sidebands are checked every morning. It is worth to mention that the EOM crystal can be thermally damaged by too much power at green wavelengths, so the beam profile of the slowing laser is distorted when its power increases to more than 2 W. After weeks of experiment, the EOM can be badly damaged and the crystal has to be changed.

The frequencies of all lasers are monitored and stabilized using a wavemeter and a control programme. It reads frequencies from the wavemeter, and sends feedback signals to the lasers to stabilize their frequencies. The control element is usually a piezo-electric transducer that controls the length of the laser cavity. With proper parameters, the standard deviation of the lock can be constrained within 1 MHz.

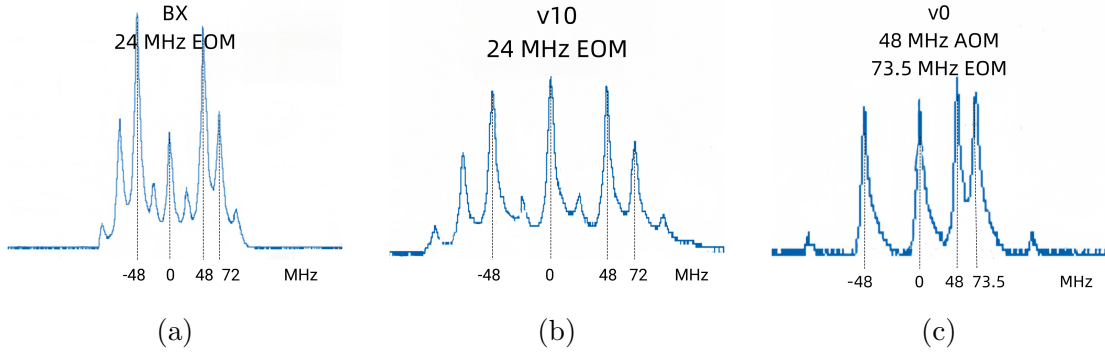


Figure 4.7: Sidebands detected with an FP cavity. (a) The frequency structure of the BX slowing laser, generated with a 24 MHz EOM. (b) The frequency structure of the slowing repump, generated with a 24 MHz EOM. (c) The frequency structure of the probe laser, generated with a 73.5 MHz EOM and a 48 MHz AOM.

When the lasers are being chirped, wavemeter lock is disabled and a ramp voltage is generated from the experiment control programme, known as MOTMaster.

Chirp scheme

The timing of the YAG trigger, laser chirps, the AOM switch and the wavemeter lock block is shown in Figure 4.8. The slowing laser is locked at the chirp-start frequency. When the hold time ends, it ramps up to resonance, as the applied voltage goes down. When the chirp ends, it stays at resonance for 2 ms and then ramps back to the locking frequency during 1 ms. This is to avoid breaking the laser with too fast chirps. Because the wavemeter reads the 0th order, and the slowing beam takes the +1 order, the lock frequency should be 90 MHz lower than the actual chirp-start frequency.

The repump laser (known as ν_{10}) is more complicated. Because it works as a slowing repump and a MOT repump in different orders, there is a 110 MHz gap between the chirp-end frequency and the MOT repump frequency in the wavemeter reading. During the time t_{hold} , it ramps from the resonant frequency to the chirp start frequency, then the chirp slowing starts. The chirp ends at 110 MHz higher than resonance, which for the -1 order branch is just at resonance. It goes back to resonance so that the 0th order works as a MOT repump. Our calibration shows that the frequency-to-voltage ratio of the slowing laser is -1361 MHz/V, and the ratio of the slowing repump laser is 335 MHz/V. According to Equation (4.17), the ratio of chirp ranges between slowing laser and slowing repump is $\nu_{BX}/\nu_{\nu_{10}}$.

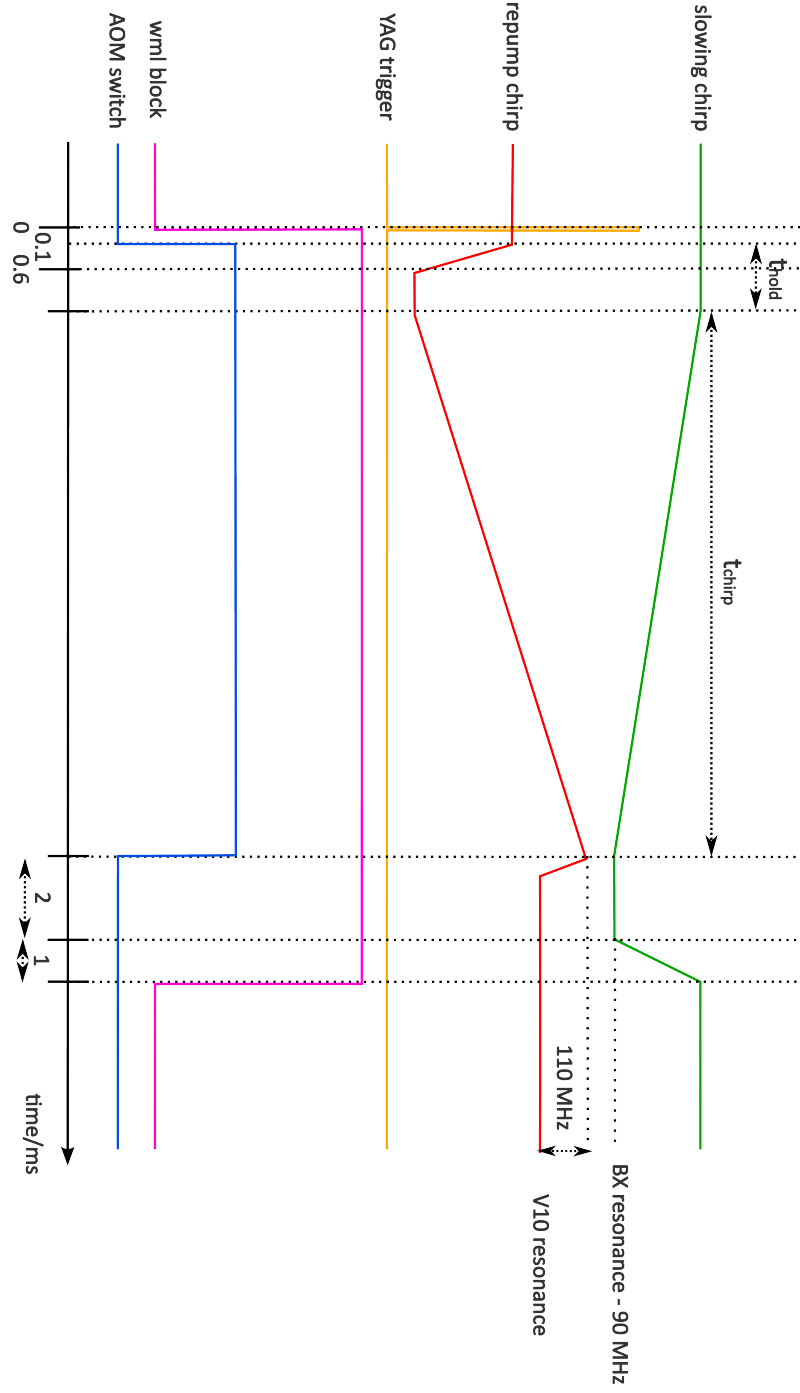


Figure 4.8: The timing sequence used for laser slowing.

DDS channel	function	frequency/MHz
0	v_{00} sideband $F = 1^+$	48
1	606 nm laser switch	110
2	v_{00} sideband $F = 2, 0, 1^-$	73.5
3	v_{21} sideband	24

(a) The channels and functions of AD9958 board 1.

DDS channel	function	frequency/MHz
0	slowing laser sideband	24
1	628 laser switch (with TTL switch)	110
2	slowing laser switch (with TTL switch)	90
3	v_{10} sideband	24

(b) The channels and functions of AD9958 board 2.

Table 4.1: The function and frequency of all DDS channels.

Direct digital synthesis

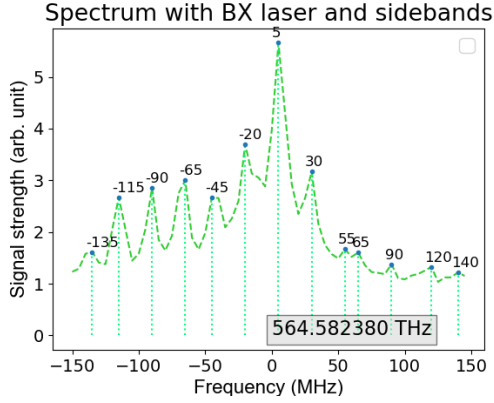
All the AOMs and EOMs are controlled by two multichannel frequency synthesizers (AD9958/59). They share a 30 MHz clock with a factor of 10 multiplication. Each of the boards has two synchronous direct digital synthesis (DDS) cores and four voltage outputs, and each of the outputs is followed by an amplifier to amplify sine wave signals. There are 8 channels in total, and there are two TTL switches for the slowing and slowing repump lasers. The details are listed in Table 4.1.

4.3 Results

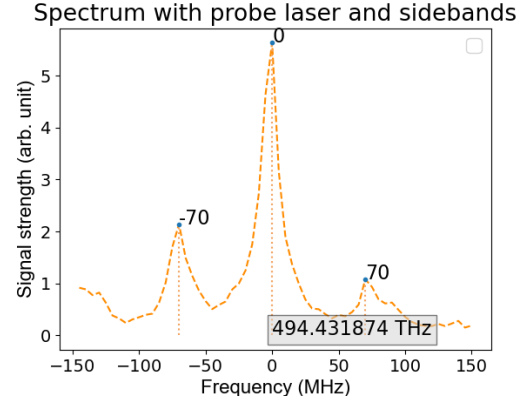
4.3.1 Spectra

To find the resonant frequency and see the effect of sidebands, we scan the frequency of each laser, collect TOF signals, and integrate over the TOF at each frequency to obtain the spectra. The results are shown in Figure 4.9. Points in the scan are spaced by 5 MHz.

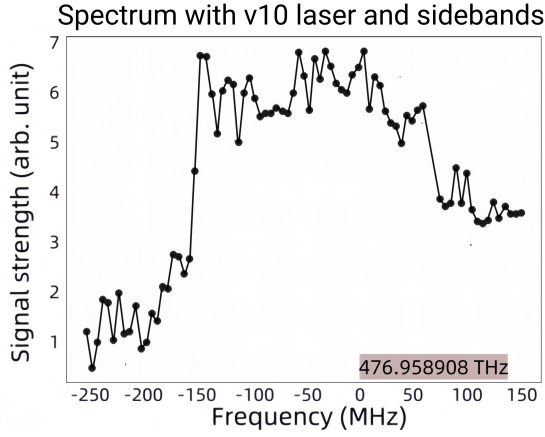
Figure 4.9(a) is the spectrum detected when the slowing laser is used as a probe laser. The laser has sidebands applied using an EOM driven at 24 MHz. The tallest peak in the spectrum corresponds to the frequency where all four hyperfine components are simultaneously resonant with frequency components present in the



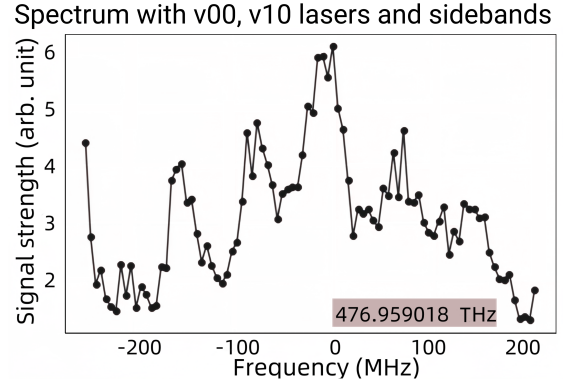
(a) The spectrum detected by BX laser with 24 MHz EOM.



(b) The spectrum detected by ν_{00} laser with four sidebands.



(c) The spectrum detected by ν_{10} laser and 24 MHz EOM (without ν_{00} laser).



(d) The spectrum detected by ν_{10} laser and 24 MHz EOM (with ν_{00} laser).

Figure 4.9: Spectra detected using various probe lasers. The offset frequency is labelled at the bottom of each plot.

laser. There is a series of peaks around the tallest peaks, with an average spacing of 25 MHz. These are frequencies where some, but not all, hyperfine components are resonant with frequencies present in the light. Figure 4.9(b) is the spectrum recorded when the probe laser is the ν_{00} laser and its four sidebands. The gap between the central and ± 1 order peak is 70 MHz, which matches the gap between hyperfine levels $F = 2, 0, 1^-$. Once again, the tallest peak in the spectrum arises when all hyperfine components of the molecule are simultaneously resonant with the laser. Figure 4.9(c) is the spectrum obtained when the probe is the ν_{10} repump laser only. Because of its low branching ratio, the resonant peaks are not distinguishable. When we have ν_{00} on resonance all the time and scan ν_{10} , the sidebands become clear, as is shown in Figure 4.9(d).

transition	resonant frequency/THz	wavemeter frequency/THz
BX	564.582475	564.582385
v_{00}	494.432094	494.431874
v_{10}	476.958908	476.959018

Table 4.2: The resonant frequency and the locking frequency used in wavemeter, whose differences are due to the laser switches in Table 4.1.

This spectroscopy determines the frequencies needed for laser slowing, as listed in Table 4.2.

4.3.2 Laser slowing

To establish the chirp slowing step by step, we start by applying a fixed frequency BX laser to the molecular beam. With good alignment, adequate laser power and proper frequency, the peak of the beam is ‘eaten up’, as is shown in Figure 4.10(a). This is done with 300 mW slowing laser power. Most of the ground state molecules are pumped into higher lying vibrational states of X , due to repeated excitation to the B state. These molecules are no longer detected which explains why there is a hole in the distribution. The position of this hole is a good way to confirm that the laser is properly Doppler-shifted into resonance. Once the frequency that drives most molecules out is found, it is taken as the chirp start frequency.

Then we bring the slowing repump in. If the frequency of v_{10} laser targets the same velocity class as the BX laser, the peak is ‘recovered’, and is shifted to later times, as is demonstrated in Figure 4.10(b). This indicates the molecules that decay to $v = 1$ state are repumped back into the laser cooling cycle and have been significantly decelerated. Assuming the peak moves from 7 ms to 8 ms, then there are around 1700 photons scattered per molecule before they go out of resonance. Due to the leakage to higher vibrational branches, and the transverse expansion, the recovered signal is slightly weaker than the original signal. For these data, the powers of the BX and v_{10} lasers were 250 mW and 190 mW respectively. We vary the frequency of the v_{10} laser across a range of ± 50 MHz, and find that the result is not sensitive to the repump frequency. This is because there is only a small amount of molecules leaking into the $v = 1$ state, so the repump transition is easily saturated.

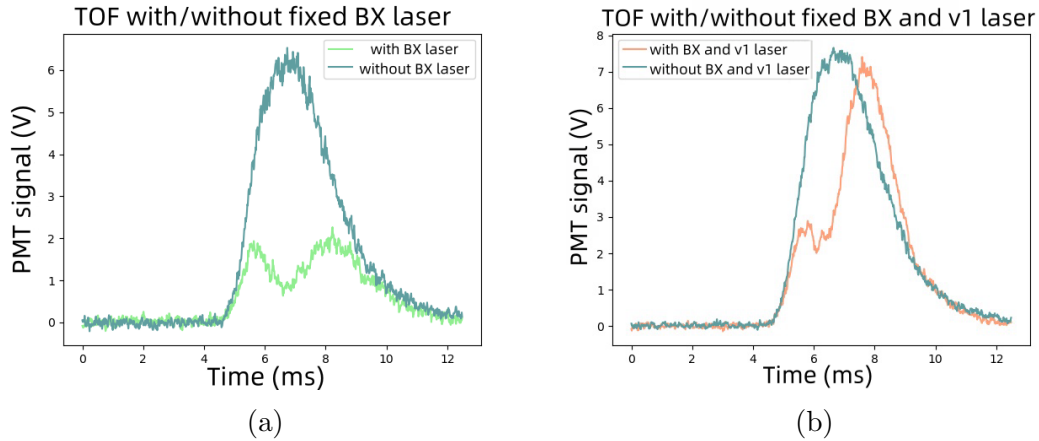


Figure 4.10: (a) TOF signals with and without the slowing laser. (b) TOF signal (orange) with slowing and repump lasers, compared to the unsloved signal (green).

4.3.3 Study of chirp parameters

To find the best parameters for chirp slowing, we vary the chirp rate, hold time and chirp range independently, aiming to maximise the signal after 15 ms in the TOF, because this indicates a ‘long tail’ which contains molecules that can be captured by a MOT. For results taken in this subsection, the BX chirp start frequency is fixed at -320 MHz detuned from the resonance, which corresponds to molecules of 197 m/s. The power of the slowing laser is 370 mW, and the slowing repump is 310 mW. The signal is averaged together with two TOF profiles.

Because the chirp rate is crucial to the chirp effect, we begin with a coarse scan of this parameter. In Figure 4.11, we keep the chirp range at 280 MHz, and vary the chirp time to be 8, 10 and 12 ms, so that the chirp rate is 35.0, 28.0 and 23.3 MHz/ms respectively. Each chirp rate is run with an unsloved comparison, and the variation of the unsloved signals are shown as the shaded blue area. The hold times for them are all 1 ms.

As written in Section 4.1.2, the chirp of the main slowing laser starts at a frequency corresponding to the peak velocity, so the molecules faster than that are ‘left out’, and the ones slower than that are ‘compressed’. In the TOF signal, it is clear that the molecules are divided into two velocity groups. As the chirp rate increases, the slower group is more and more flattened, and the ‘tail’ extends further. Within the shown chirp rates, 35.0 MHz/ms gives the longest ‘tail’, which is close to the predicted value in Figure 4.11.

If the chirp rate exceeds 35.0 MHz/ms, there is no distinct slower group, and we think the slower molecules are almost completely lost. The main mechanism of

this loss is transverse divergence, where the longitude velocity is reduced, but the transverse velocity is a constant. Consider a molecule with the transverse velocity of 1 m/s. After flying for 20 ms, it diverges from the beam line by 20 mm. The probe laser has a radius less than 10 mm, so the molecule is already out of the detection region. The best chirp rate we find does not correspond to the one calculated in Section 4.1.2, and it seems that the scattering rate is higher than expected. The reason is to be explored in the future.

Next, we fix the chirp range at 280 MHz, with 8 ms chirp time, and change the hold time, which is noted as t_{hold} in Figure 4.8. The result is shown in Figure 4.12. As the plot suggests, $t_{\text{hold}} = 2$ ms is not as good as 1 ms in producing a ‘long tail’. For a molecule flying at 150 m/s, comparing 2 ms hold time to 1 ms, it has 15 cm less to be slowed, which results in a higher velocity at the end.

Finally, we fix the chirp rate at 35.0 MHz/ms, the hold time at 1 ms, and increase the chirp range from 280 to 310 MHz by 10 MHz, which corresponds to a chirp end velocity of 27, 21, 15 and 9 m/s. The result is shown in Figure 4.13: as the chirp range increases, the peak of high velocity molecules decreases, and the lower group is more and more flattened. When the chirp range is increased further, the lower peak becomes negligible. We think in that case there are slower molecules, but they are not distinguishable from the background. Only when we make a MOT can they be seen by the camera.

4.3.4 Velocity profile with angled probe

The aim of chirp slowing is to produce molecules within the capture velocity of the MOT, which is about 20 m/s. To ensure this, we need to see the velocity distribution of the slowed molecular beam directly. In Figure 4.4, probe laser 3 is used for this. The angle between it and the beam line is 30° , so the frequency shift is converted to the velocity by

$$\frac{v \cos(\pi/6)}{c} = \frac{\Delta\nu}{\nu_0}. \quad (4.23)$$

This measurement is done with 380 mW slowing laser, and 270 mW slowing repump. We scan the frequency of the probe laser across 400 MHz, which corresponds to a velocity range from 280 m/s to 0. It is done with a step of 5 MHz, and we average together 10 scans. At each point in the frequency scan, we obtain a TOF profile. The Doppler shift is a measure of the velocity, so at each point in the spectrum the TOF is a measure of the arrival times of molecules with a certain velocity.

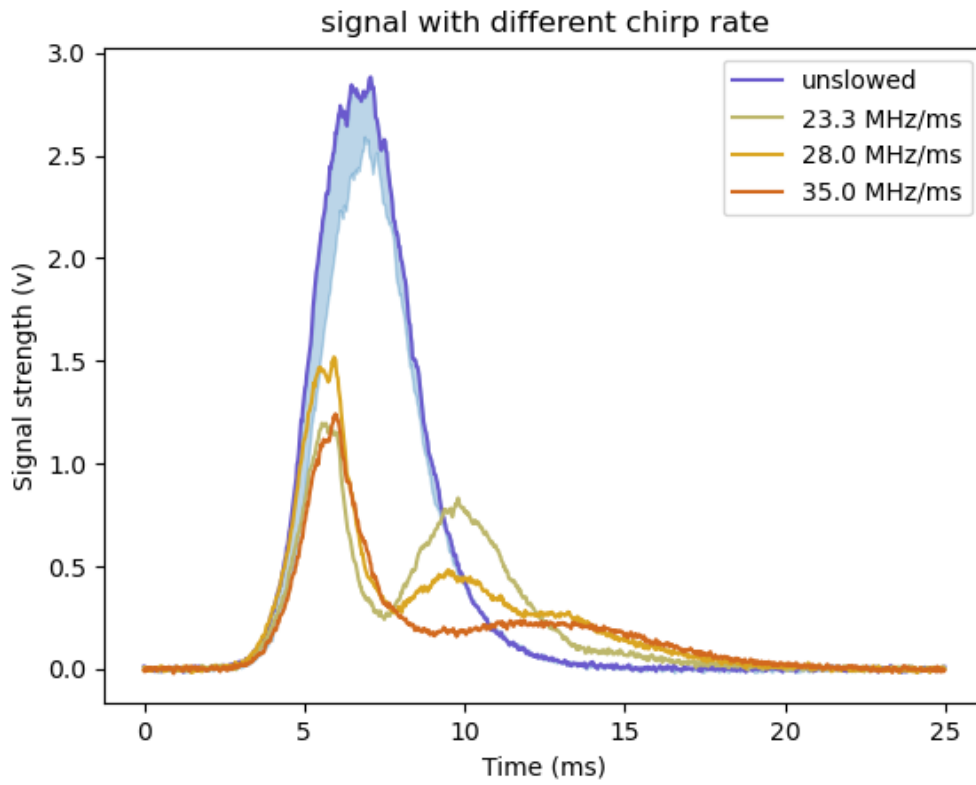


Figure 4.11: The chirp slowing signal with different chirp rate. The total chirp range is 280 MHz, and the hold time is 1 ms. The shaded area is the variation of the unslowed signal.

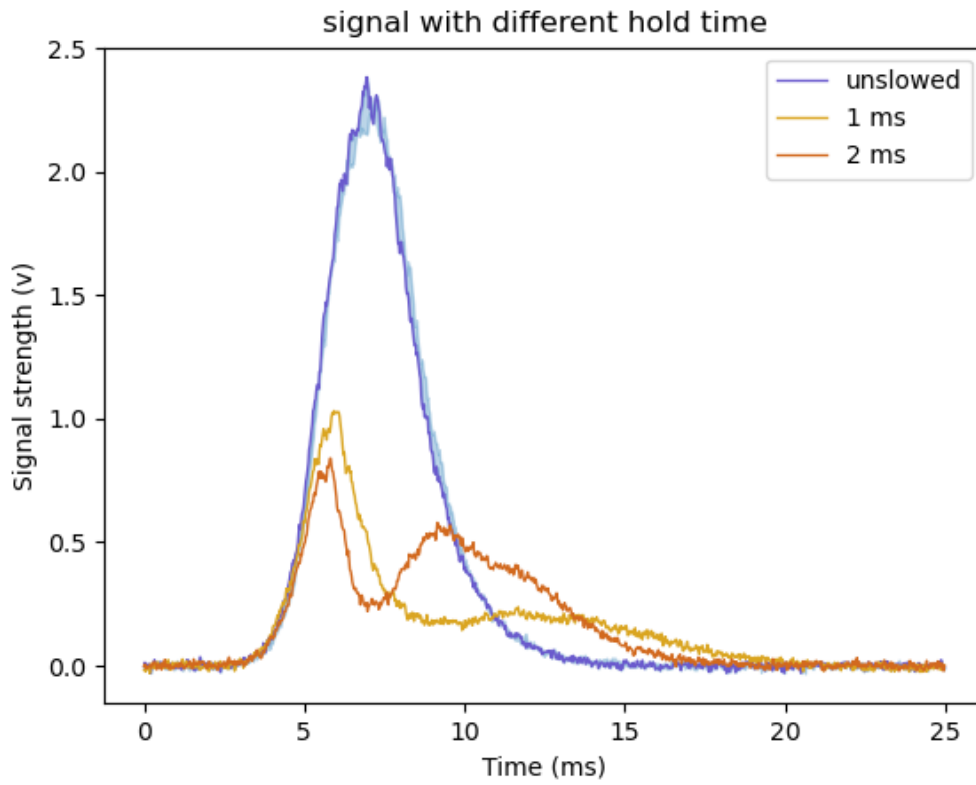


Figure 4.12: The chirp slowing signal with different hold time. The chirp rate is 35 MHz/ms, and the chirp range is 280 MHz. The shaded area is the variation of the unslowed signal.

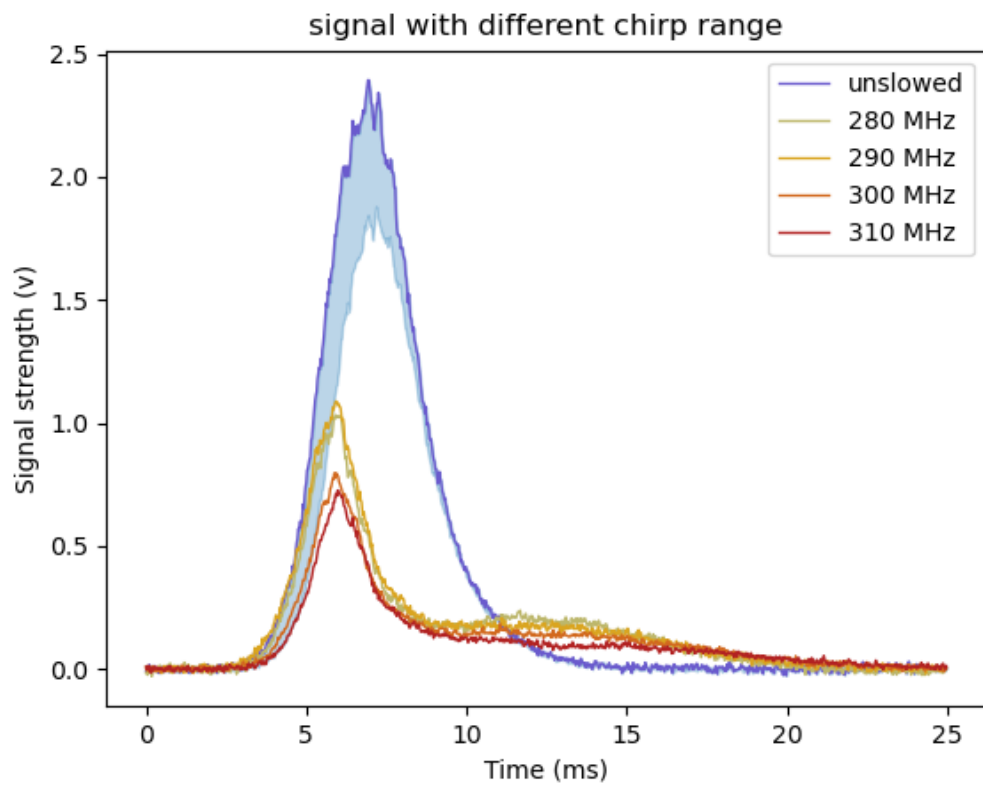


Figure 4.13: The chirp slowing signal with different chirp range. The shaded area is the variation of the unslowed signal.

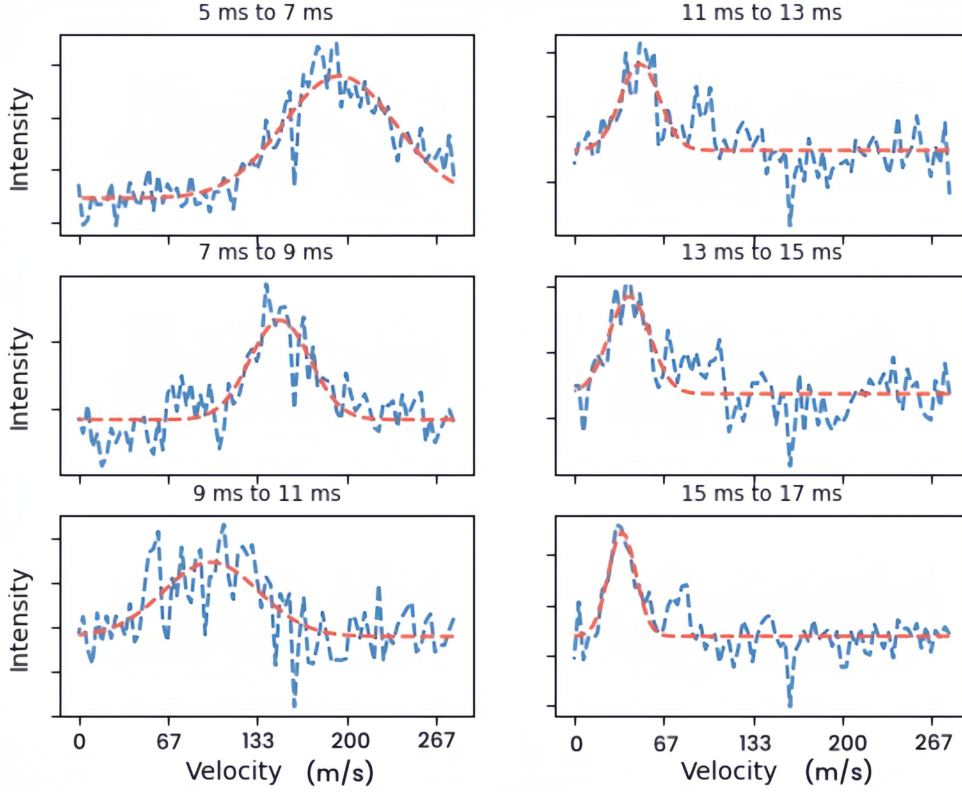


Figure 4.14: The TOF profiles measured with angled probe. For each plot, the arrival time is shown in the title. The dashed blue line is the signal, and the dashed red line is its Gaussian fit.

Alternatively, we can take a narrow slice of the TOF and plot the spectrum obtained for molecules in this time window, which is approximately the velocity distribution of those molecules.

Figure 4.14 shows the velocity distribution from 5 to 17 ms, divided into 6 time zones. Because there is no clear sideband structure in the spectrum, we fit each of them with a Gaussian function, assuming it is the highest peak in Figure 4.9(a). As the arrival time gets later, the velocity distribution gets narrower, and the mean velocity gets slower. From the data between 15 and 17 ms, it is clear there is a molecular peak below 67 m/s. Its mean value is about 40 m/s, and the full-width-at-half-maximum is 20 m/s. There is a small peak at the low velocity side, which gives the slowest molecules. It is very difficult to detect molecules going significantly slower than this because they have large divergence and mostly miss the detector, but from the sequence of plots shown we are confident that molecules arriving later than 17 ms have speeds below 20 m/s, and can be captured by our MOT.

4.4 Conclusion

This chapter introduces the theory of scattering force and chirp slowing, the experimental set-up for slowing, and the progress of reaching a slowing scheme suitable for later experiments. By comparing different chirp rate, hold time and chirp range, we find chirping across 310 MHz, with a chirp rate of 35.0 MHz/ms and a hold time of 1 ms produces a long tail in the TOF profile, characteristic of a slow molecular beam. The long tail extends to beyond 20 ms, which is ideal for a MOT. The velocity distribution is detected with an angled probe laser, and the result suggests there are molecules that are slow enough to be captured in a MOT.

Chapter 5

Magneto-Optical Trap

5.1 Introduction

Magneto-optical trap is the first and most basic trap on the way towards a molecular BEC. It is also the platform where the future operations, such as compression, optical trapping and evaporative cooling, are applied. So the quality of the MOT, especially the total number of molecules and the number intensity, should be as large as possible to sustain CaF molecules through the losses in further steps. I especially developed v_{21} and v_{32} repump lasers, and the design of laser combination optics and the assembly of science chamber are mostly done by my colleagues. A MOT of 5000 molecules are expected, while the result gives a quarter of it. The improvement is discussed in the next chapter.

The first part of this chapter discusses the interaction between a magnetic field and a molecule, and the generation of a spatially linear magnetic field. After that, the configurations of an atomic MOT and a dual-frequency MOT are described. Then it comes a full description of the home-made seed-amplifier repump lasers. Finally, the first MOT is shown, and the basic information is extracted from the measurement.

5.2 Theory

5.2.1 Zeeman effect

An energy level of a molecule is split into several components in a static magnetic field, due to the interaction between its magnetic moment and the external field.

This effect is known as Zeeman shift. The Hamiltonian is

$$H_Z = -(\vec{\mu}_L + \vec{\mu}_S) \cdot \vec{B}. \quad (5.1)$$

Here, $\vec{\mu}_L$ is the magnetic dipole moment associated with the total orbital angular momentum:

$$\vec{\mu}_L = -\frac{e}{2m} \vec{L}, \quad (5.2)$$

and $\vec{\mu}_S$ is the magnetic dipole moment associated with total electron spin momentum:

$$\vec{\mu}_S = -\frac{e}{m} \vec{S}. \quad (5.3)$$

Here m is the mass of an electron. For a CaF molecule in the ground electronic state, when the external magnetic field is aligned along the z-axis, the Zeeman shift is

$$\langle \hat{H}_Z \rangle = \frac{1}{\hbar} g_S \mu_B B_Z \langle \hat{S}_Z \rangle. \quad (5.4)$$

Here, g_S is the Landé g-factor of spin, and μ_B is the Bohr magneton: $\mu_B = \frac{e\hbar}{2m}$.

To find the eigenvalues, we consider the total Hamiltonian $\hat{H}_{total} = \hat{H}_0 + \hat{H}_{cp} + \hat{H}_Z$. $\hat{H}_0$ is the uncoupled Hamiltonian. $\hat{H}_{cp}$ is the coupling between $\hat{L}$, $\hat{S}$, $\hat{N}$ and $\vec{I}$, as explained in Section 2.1.5. If the Zeeman splitting is much smaller than the hyperfine splitting, $\hat{H}_Z$ is treated as a perturbation. This is called weak-field Zeeman effect. If it is the opposite case, the coupling between angular momentum becomes a perturbation. This is strong-field Zeeman effect. If the two splittings are comparable, $\hat{H}_{cp} + \hat{H}_Z$ are treated as a perturbation. This is intermediate-field Zeeman effect. In the following part, I will introduce the weak-field and strong-field Zeeman effect in brief.

Weak-field Zeeman effect

In a weak magnetic field, the eigenfunction is $|S, N, J, I, F, m_F\rangle$. The first-order perturbation energy is

$$E_Z = \frac{1}{\hbar} g_S \mu_B B_Z \langle S, N, J, I, F, m_F | \hat{S}_Z | S, N, J, I, F, m_F \rangle. \quad (5.5)$$

The expectation value of S_Z is calculated in the following way: As shown in Figure 2.2, $\vec{J} = \vec{L} + \vec{S} + \vec{N}$. For molecules in the ground state, $\vec{N} = \vec{J} - \vec{S}$, so $N^2 = J^2 + S^2 - 2\vec{J} \cdot \vec{S}$. Because $\vec{S}$ precesses rapidly around $\vec{J}$, its time average value

is the projection on the axis of $\vec{J}$:

$$\begin{aligned}
 \langle \hat{S}_Z \rangle &= \frac{\langle \vec{S} \cdot \vec{J} \rangle}{\langle \hat{J}^2 \rangle} \langle \hat{J}_Z \rangle \\
 &= \frac{\langle \hat{J}^2 + \hat{S}^2 - \hat{N}^2 \rangle}{2J(J+1)} \langle \hat{J}_Z \rangle \\
 &= \frac{1}{2} \frac{J(J+1) + S(S+1) - N(N+1)}{J(J+1)} \langle \hat{J}_Z \rangle.
 \end{aligned} \tag{5.6}$$

Because $\vec{F} = \vec{J} + \vec{I}$, the same method is applicable to $\langle J_Z \rangle$. So the Zeeman shift is

$$\begin{aligned}
 E_Z &= \frac{1}{\hbar} g_S \mu_B B_Z \frac{1}{2} \frac{J(J+1) + S(S+1) - N(N+1)}{J(J+1)} \\
 &\quad \times \frac{1}{2} \frac{F(F+1) + J(J+1) - I(I+1)}{F(F+1)} \langle \hat{F}_Z \rangle \\
 &= g_F \mu_B B_Z m_F.
 \end{aligned} \tag{5.7}$$

From the calculation above, we know that the Zeeman shift is linear to the magnetic field in the weak-field region, and we can calculate the gradient by calculating g_F for any particular hyperfine component.

Strong-field Zeeman shift

In a large magnetic field, the perturbation is the coupling between $\vec{S}$, $\vec{N}$ and $\vec{I}$. The good quantum numbers are S, m_s, N, m_N, I and m_I . The Zeeman splitting is

$$\begin{aligned}
 E_Z &= \frac{1}{\hbar} g_S \mu_B B_Z \langle S, m_s | \langle N, m_N | \langle I, m_I | \hat{S}_Z | I, m_I \rangle | N, m_N \rangle | S, m_s \rangle \\
 &= \frac{1}{\hbar} g_S \mu_B B_Z \langle S, m_s | \hat{S}_Z | S, m_s \rangle \\
 &= g_S \mu_B B_Z m_S.
 \end{aligned} \tag{5.8}$$

In this region, the shift is linear to the field strength again.

As shown in Figure 2.3, the 4 hyperfine levels of a ground state CaF molecule have $S = \frac{1}{2}$, $N = 1$, $J = \frac{3}{2}, \frac{1}{2}$ and $I = \frac{1}{2}$. So g_F of $F = 2, 1^+, 0, 1^-$ are 0.5, 0.83, 0 and -0.33 respectively. Note that the values for the two $F = 1$ components are approximate because these are not states of pure J . A more complete calculation gives the values 0.795 and -0.295 for these two g-factors. There are 12 Zeeman levels. In small field, there are 4 states that shift up, 4 states that shift down and 4 with no energy shift. In large field, the 6 branches with $m_S = \frac{1}{2}$ shift up, and the others with $m_S = -\frac{1}{2}$ shift down. The total structure is shown in Figure 5.1.

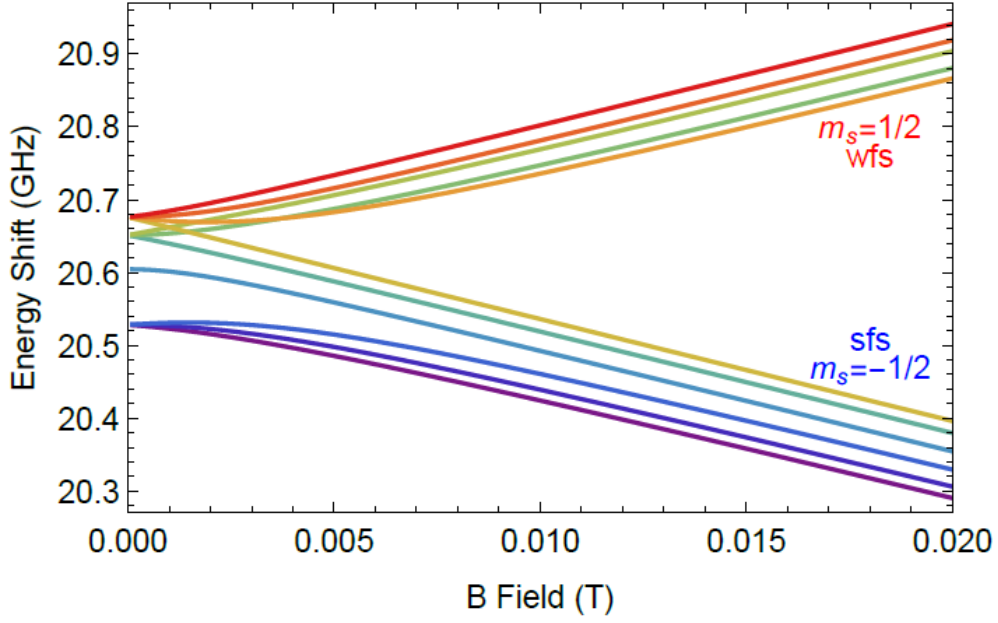


Figure 5.1: The Zeeman splitting of CaF molecules in the ground state with $N = 1$. The plot is taken from [93].

5.2.2 Anti-Helmholtz coils

Anti-Helmholtz coils are a pair of co-axis and identical coils with a radius R , separated at a distance d equal to R , with the same current I running in opposite directions. If the centre of the two coils is set as the origin, and the symmetry axis as the z direction, in a region close to the origin, components of the magnetic field vector are linear to the coordinates:

$$\vec{B} = -3\mu_0 n I \frac{R^2 d/2}{((d/2)^2 + R^2)^{5/2}} \left(\frac{x}{2}, \frac{y}{2}, -z \right), \quad (5.9)$$

where n is the number of turns in each coil.

5.2.3 Type I and type II MOT

As introduced in Chapter I, magneto-optical traps of atoms and molecules are significant for the study of ultracold matter. A traditional 3-dimensional MOT is composed of 6 laser beams and a pair of anti-Helmholtz coils. The atom has more angular momentum in the excited state than in the ground state, $F_e > F_g$, and it is known as type I MOT. The anti-Helmholtz coils create a spatially varying potential, where the field at the centre is zero, and on each axis it varies linearly to the distance from the origin.

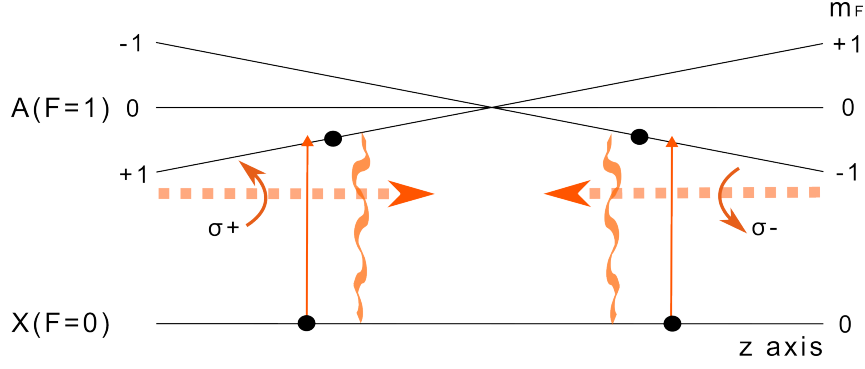


Figure 5.2: A brief schematic of type I MOT in 1 dimension. The upper level is $(A, F = 1)$ and the lower level is $(X, F = 0)$. The propagation of lasers are shown by dashed orange arrows, the transitions are shown by upwards arrows, and the decays are shown by wavy lines. The population of molecules is shown in black circles.

The situation in 1 dimension is shown in Figure 5.2, for the particular case of $F_g = 0$ and $F_e = 1$. The laser beams are circularly-polarized to drive σ^+ and σ^- transitions, and red-detuned from the resonance frequency. If a ground state molecule moves in the $z > 0$ direction, it comes into resonance with the σ^- laser beam that counter-propagates to it, so the molecule is driven to the $m_F = -1$ excited state. Then it spontaneously decays to the ground state, emitting a photon in a random direction. According to Equation (4.15), the scattering force in a MOT is

$$\vec{F}_1 + \vec{F}_2 = \frac{\hbar \vec{k} \Gamma}{2} \left(\frac{s}{1 + s + 4(\Delta_0 - \vec{k} \cdot \vec{v} + \vec{B} \cdot \vec{z})^2 / \Gamma^2} - \frac{s}{1 + s + 4(\Delta_0 + \vec{k} \cdot \vec{v} - \vec{B} \cdot \vec{z})^2 / \Gamma^2} \right). \quad (5.10)$$

The total detuning in the scattering force is the sum of the laser detuning Δ_0 , the velocity-dependent Doppler shift $-\vec{k} \cdot \vec{v}$, and the position-dependent Zeeman shift $\vec{B} \cdot \vec{z}$. The coefficient $\vec{B}$ can be calculated from Equation (5.7) and Equation (5.9). If we expand the force in terms of small $\vec{v}$ and small $\vec{z}$ to the first order, it can be written as

$$\vec{F}_{MOT} = -\alpha \vec{v} - \kappa \vec{z}, \quad (5.11)$$

which clearly shows the form of the damping force and restoring force in a MOT. Back to a 3-dimensional MOT, because the vertical component of the magnetic field points towards the origin whereas the horizontal ones point away (or vice versa), the handedness of the vertical MOT laser must be opposite to the horizontal ones.

However, to ensure a closed cooling cycle for CaF molecules, the $N = 1$ rotational state is chosen as the ground state. This leads to a case where $F_e \leq F_g$, and it is known as type II MOT. For the energy structure shown in Figure 5.3, an excited

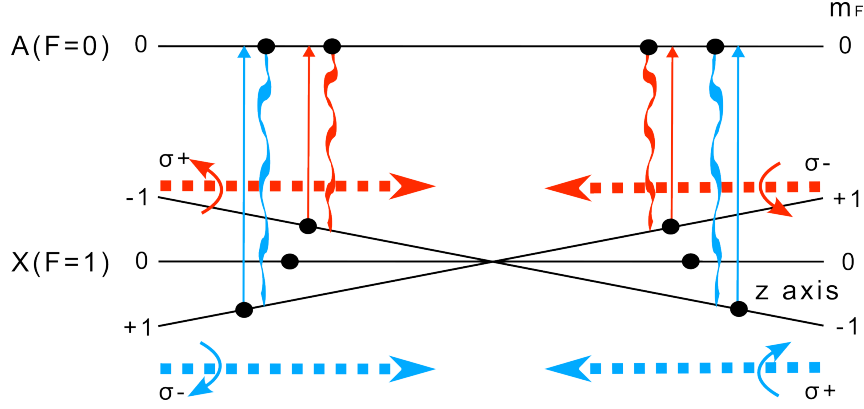


Figure 5.3: A brief schematic of dual-frequency MOT in 1 dimension. The upper level is $(A, F = 0)$ and the lower level is $(X, F = 1)$. The blue-detuned laser beams are shown as arrows in blue.

molecule in $m'_F = 0$ state decays to $m_F = -1, 0, 1$ ground states with equal chances. If there is only one red-detuned laser beam with circular polarisation, the $m_F = -1$ level can only be addressed by the beam from one direction, and the $m_F = +1$ level can only be addressed by the beam from the opposite direction. Thus, the $m_F = -1$ molecules at $z > 0$ zone and the $m_F = +1$ molecules at $z < 0$ zone are less likely to be addressed because of the large detuning, and they become the lost channels of the MOT.

There are two methods to solve the problem: rf MOT and d.c. MOT. A rf MOT switches the polarisation of the laser beams and the current directions of the magnetic coils simultaneously at the frequency that matches the scattering rate. Progress with this method has been introduced in Section 1.2.5.

A d.c. MOT is also known as a dual-frequency MOT. As is shown in Figure 5.3, a pair of blue-detuned laser beams are added to each dimension, and they are of the opposite handedness to their red-detuned counterparts. Consider a ground-state molecule in the region $z > 0$. If $m_F = 1$, it resonates with the red-detuned σ^- light; if $m_F = -1$, the molecule comes into resonance with the blue-detuned σ^+ light. In both cases, the scattering force pushes the molecule towards the origin. The $m_F = 0$ molecules are excited by orthogonal beams in a 3D configuration. Thus, no matter which Zeeman level a molecule decays to, there is a laser component that can drive it and this component tends to push the molecule back towards the centre of the MOT.

As shown in Figure 5.4, the ground state of CaF has 4 hyperfine levels: $F = 2, 1^+, 0, 1^-$. The figure also gives their magnetic g -factors in brackets. The energy

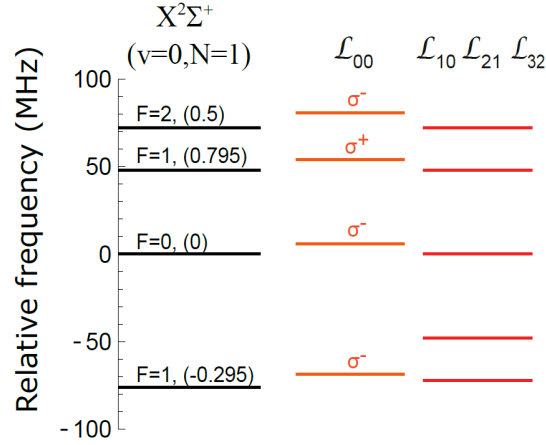


Figure 5.4: A schematic of the hyperfine levels and the lasers that address them. The g-factors of the hyperfine levels are listed in the brackets after F . L_{00} is the trap laser (ν_{00}), of which the handedness of four components are specified. L_{10} L_{21} and L_{32} are the repump lasers (ν_{10} , ν_{21} and ν_{32}), and the handedness of them are not sensitive. This figure is from [93].

gap between $F = 2$ and $F = 1^+$ levels is 24 MHz, and since a typical MOT detuning is about 10 MHz, the red-detuned frequency addressing $F = 1^+$ appears as a blue-detuned component for $F = 2$. When these two laser frequency components have opposite circular polarization, as indicated in the figure, a dual-frequency MOT is formed. The $F = 1^+$ branch is generated by a 48 MHz AOM, and the other three are generated by a 73.5 MHz EOM. We choose the AOM branch to have the opposite polarisation to the EOM branch, and a dual-frequency trap for $F = 2$ level is created. As explained in Section 2.3.2, 3 repumps lasers are implemented to complete the optical cycle.

5.3 Apparatus

5.3.1 Science chamber

Design

The design of our science chamber and the lasers surrounding it are shown in Figure 5.5. 12 viewports with 40 mm diameter are arranged uniformly around the centre of the science chamber for laser beams to go through. Above and below them are 12 ports of 16 mm respectively, which are used for electric feedthroughs. There are also a pair of 40 mm ports vertically for a MOT beam. The orange beams are the MOT lasers, which were designed to be orthogonal to each other. In practice,

we use the path of ‘dipole trap beam 1’ as our MOT 2 path to reduce the scattering on the edge of an internal lens tube used for imaging. The three MOT beams are controlled independently. After going through the chamber, each of them passes through a quarter wave plate, and is reflected by a retro-reflecting mirror at the end. Then it passes through the quarter wave plate again to form its counter-propagating part, of which the orientation of the circular polarisation is opposite to the original light. The angle between the MOT beams in the horizontal plane is 60° , instead of the usual 90° . The capture velocity and confinement along the beam line direction is improved, while the confinement along the imaging direction is weakened.

Radiation shield

The science chamber is designed not only for the MOT, but also for the optical dipole trap and BEC. According to Wien’s displacement law, the peak wavelength of the blackbody radiation λ_{peak} and the temperature T are related by $\lambda_{peak} \cdot T = 2.9 \times 10^{-3} \text{ m}\cdot\text{K}$. At 300 K, the frequency of the intensity peak is about 30 THz, which is close to the energy gaps between vibrational states. Thus, the lifetime of the ground state molecules are limited to 5 seconds because the vibrational transitions can be driven by the blackbody radiation at room temperature. To reduce this loss, a copper radiation shield is placed at the centre of the science chamber. It is connected to the coldhead shown in fig. 5.5, and cooled to 30 K, which largely suppresses the blackbody radiation. The design is shown in Figure 5.6: the jacket has 12 sides, with a hole of 20 mm diameter on each side, aligned with the laser ports of the chamber. The thickness of the jacket material is 5 mm, and the distance from each surface to the centre is 90 mm. The top and bottom lids have holes of 30 mm diameter, open for the electrode holders, which are introduced in Section 6.3.2. The lids also work as the bases for the magnetic field coils.

Magnetic field coils

There are three pairs of magnetic field coils inside the MOT chamber: MOT coils, bias coils, and gradient coils. The arrangement is shown in Figure 5.7. They are designed not only for the MOT, but also for a magnetic trap which serves as a possible alternative of the optical trap. The pair of MOT coils is in anti-Helmholtz configuration when it is used for MOT, and in Helmholtz configuration when used for the magnetic trap. The bias coils are made on the same printed circuit board with the MOT coils, so they are at the same height on z-axis. The bias coils run with a current in the opposite direction to the MOT coils to produce a magnetic

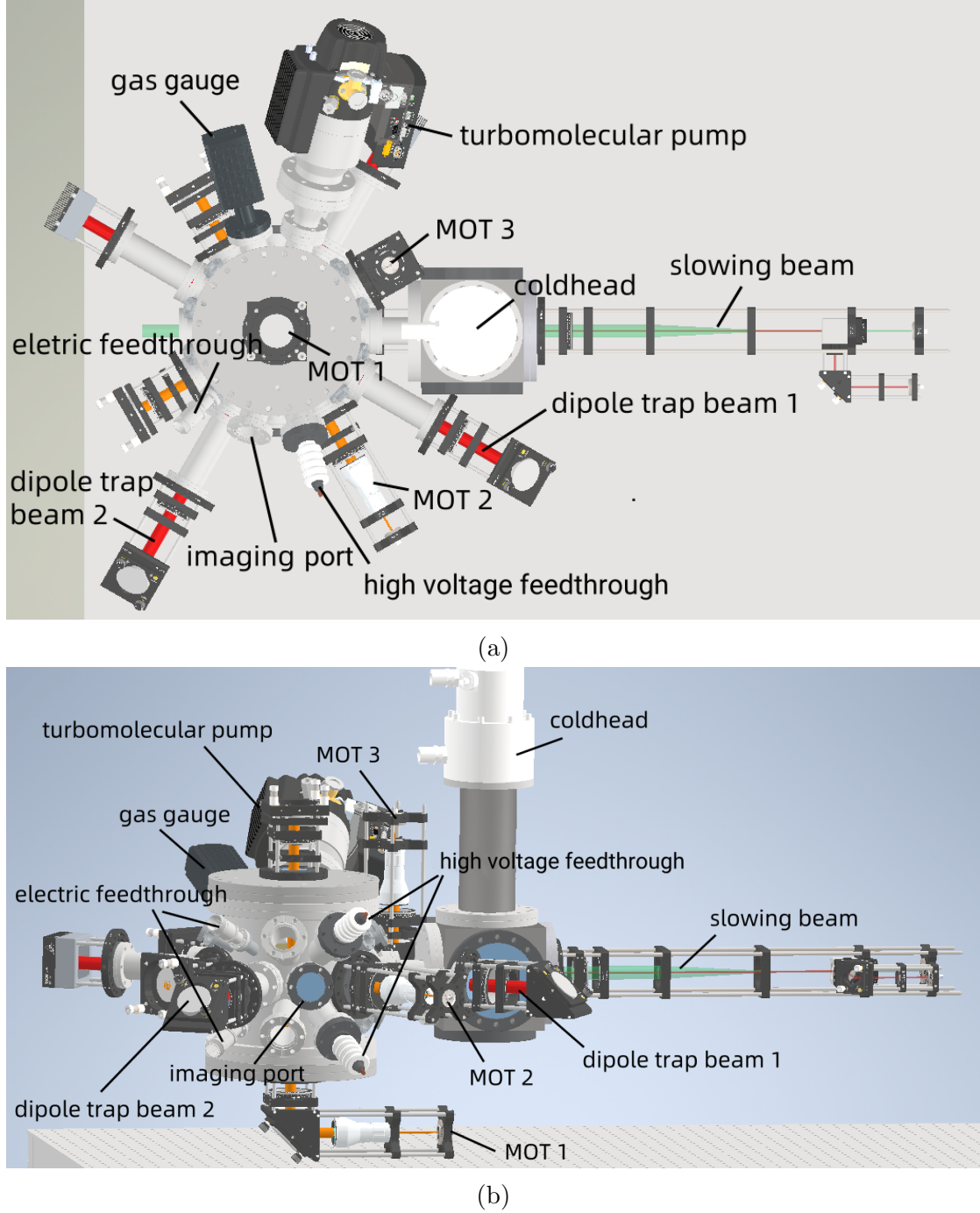


Figure 5.5: The top view (a) and side view (b) of the science chamber with all the ports set up.

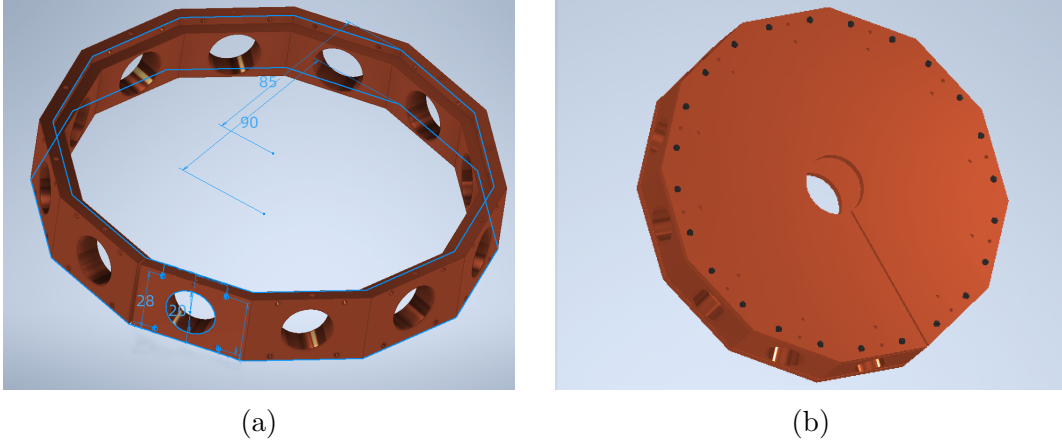


Figure 5.6: The model of the radiation shield. (a) The jacket with measurement (in mm). (b) The jacket assembled with its lids.

trap with non-zero central magnetic field. The gradient coils are four pairs of coils arranged in cloverleaf position, each pair running with a current in the opposite direction to create a radial field gradient.

We use printed circuit boards (PCB) to carry the three coils. The MOT coil and the bias coil are printed on the same board, and the gradient coil is printed on another, as shown in Figure 5.8. Each of them has 14 turns of current. The assembly of the jacket and coils is shown in Figure 5.9. A cold head is connected to the jacket by a connector made with copper wire stripes. The gradient coil is attached to the lid, after that there is a cooling collar, where water or liquid nitrogen can flow to cool the coils if needed. The MOT and bias coil PCB is outermost. The design of the electrodes will be introduced in the next chapter.

Simulation using COMSOL gives the parameters for the required magnetic fields. For an MOT with 30 Gauss/cm field gradient in z-axis, the MOT coils should be in anti-Helmholtz configuration with 1.1 A, and the other two should have zero current. This field covers an area of 30 mm radius. For a magnetic trap with 80 Gauss in the centre and 10 Hz trap frequency in all three dimensions, the MOT coils, bias coils, and gradient coils run in 3.1 A, 2.4 A and 4 A respectively. The simulated magnetic field strength is shown in Figure 5.10.

There is a pair of square coils in Helmholtz configuration outside the science chamber. They have 100 turns each, and the resistance is $7\ \Omega$. The side length and separation are 70 cm. They generate a magnetic field that cancels the earth magnetic field in the centre of the science chamber.

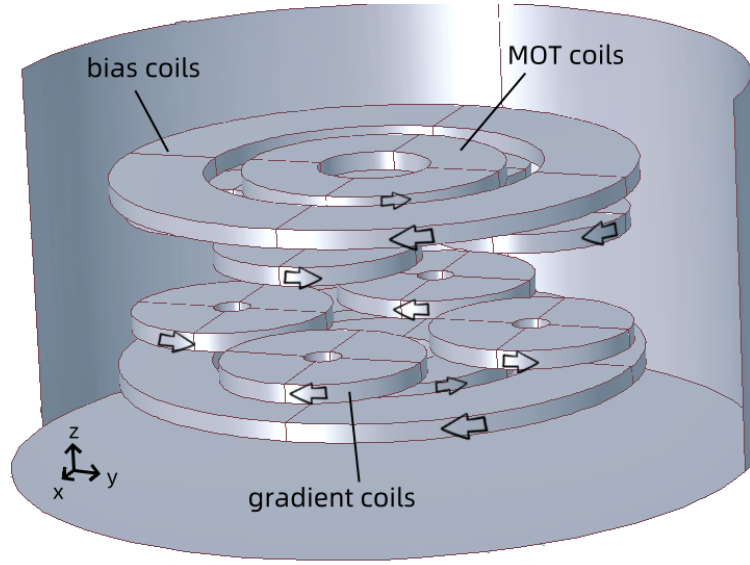


Figure 5.7: The configuration of MOT coils, bias coils, and gradient coils. The current shown on the picture is in a Helmholtz configuration.

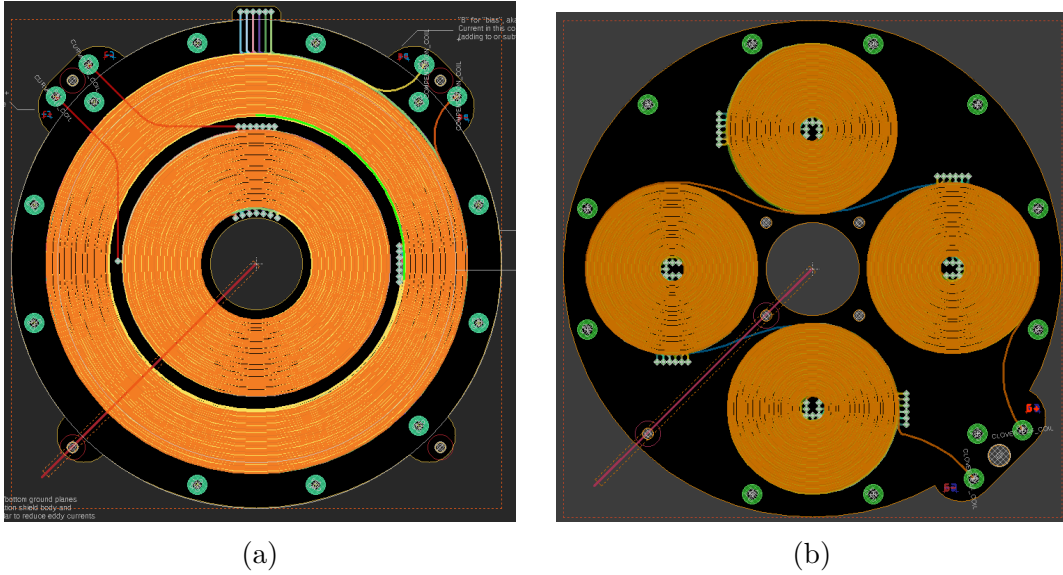


Figure 5.8: The circuit diagrams of the magnetic coils. (a) The outer circuit is the bias coil, and the inner circuit is the MOT coil. (b) The gradient coil.

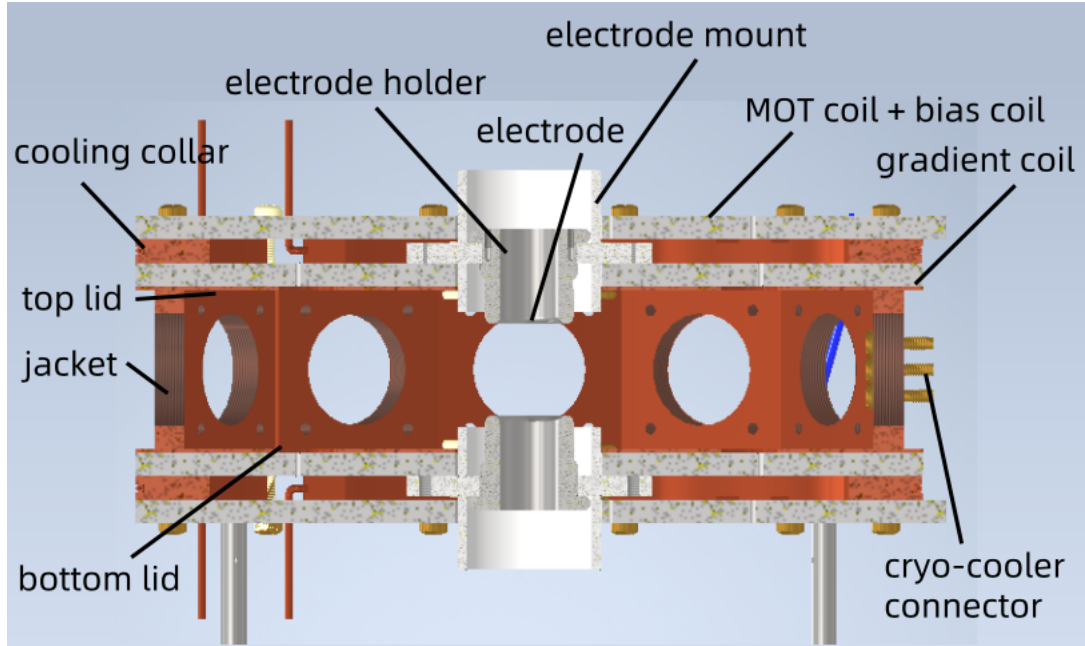


Figure 5.9: The assembly of the radiation shield and the coils.

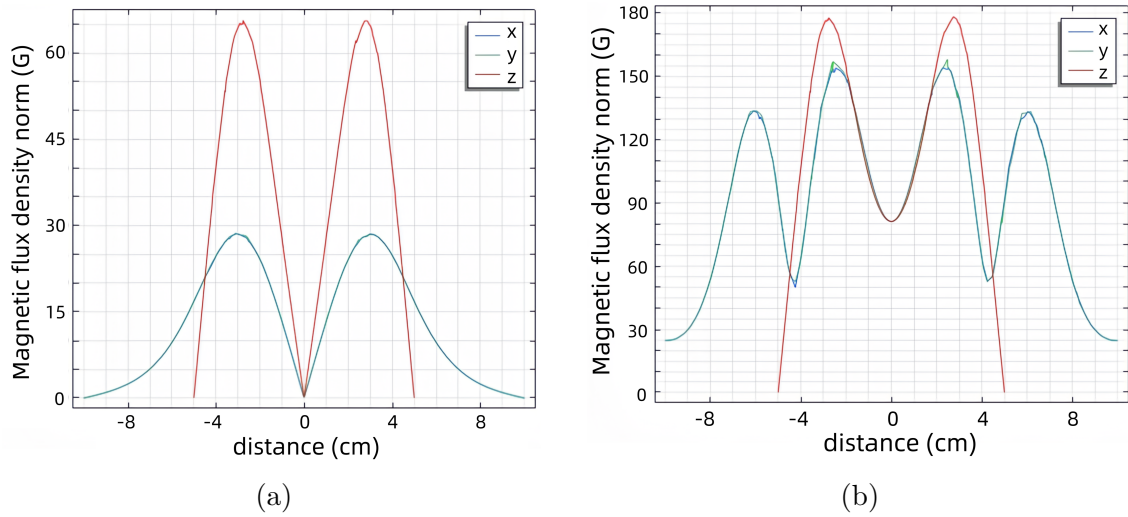


Figure 5.10: The simulated magnetic field strength due to coils inside the vacuum chamber. (a) The MOT trap produced with MOT coils. (b) The isotropic harmonic trap produced with all three coils. The currents required are specified in the main text.

Laser	Transition	Aim	Wavelength (nm)	Power (mW)
L_{00}^S	$B(v''=0) \leftarrow X(v=0)$	slowing	531.0	250
L_{10}^S	$A(v'=1) \leftarrow X(v=0)$	slowing repump	628.6	190
v_{00}	$A(v'=0) \leftarrow X(v=0)$	MOT	606.3	70
v_{10}	$A(v'=1) \leftarrow X(v=0)$	MOT repump	628.6	260
v_{21}	$A(v'=2) \leftarrow X(v=1)$	MOT repump	628.1	40
v_{32}	$A(v'=3) \leftarrow X(v=2)$	MOT repump	627.7	2.5

Table 5.1: The transition, aim, wavelength and power of all the lasers used in our experiment. The power is the average value among three MOT inputs.

5.3.2 MOT lasers

The MOT lasers are shown in Figure 2.4 as solid arrows. The orange arrow represents the main MOT laser, and the three red arrows are three repump lasers. The main MOT laser (v_{00}) has a wavelength of 606 nm, which addresses the transition from $(X^2\Sigma^+, v=0, N=1)$ to $(A^2\Pi_{1/2}, v'=0, J'=1/2, P=+)$. We use the commercial seed-amplifier system shown in Figure 4.5. The seed is an extended cavity diode laser (ECDL), DL Pro from TOPICA, controlled by the laser driver DLC Pro, and the amplifier is a MPB Raman fibre amplifier. The output power has a maximum of 5 W.

The repump lasers are all around 628 nm, and are noted as v_{ij} , which means they address the transition from $(X^2\Sigma^+, v=j, N=1)$ to $(A^2\Pi_{1/2}, v'=i, J'=1/2, P=+)$. v_{10} is produced by a commercial sum-frequency laser system made by Precilasers, which is composed of 1053 nm and 1559 nm seed-amplifier systems. v_{21} and v_{32} are homemade ECDLs with amplifiers, and the details of them will be explained in the following part.

The optics layout is shown in Figure 4.6, where the pick-off for the wavemeter lock, the AOM switches and the generation of the sidebands for v_{00} and v_{10} have been explained in the related sections. The sidebands of v_{21} and v_{32} are generated by 24 MHz EOMs. To mix the four MOT lasers, we mix v_{00} and v_{10} into one laser beam, and mix v_{21} , v_{32} into another laser beam. After that, the two beams are remixed, and distributed into three MOT fibre couplers, shown as MOT 1, MOT 2 and MOT 3 in the figure.

The information of all lasers involved in this experiment is shown in Table 5.1.

5.3.3 Seed-amplifier laser system

As shown in Figure 2.4, the branching ratios b_{02} and b_{03} are 0.12% and 0.0025% respectively, so the rate at which population leaks to $v = 2$ and $v = 3$ is low. Those molecules are returned to the cooling cycle with comparatively strong transitions, so the laser power required for them is not high.

We use a home-built seed-amplifier laser system to repump the $v = 2$ population, and call this the v_{21} laser. The seed is an External-Cavity Diode Laser (ECDL), which provides a good frequency stability with a narrow linewidth, operating at low power (below 40 mW). The amplifier uses the same laser diode without an external cavity, so can run at higher power (up to 200 mW). When the diode is optical-injected with a similar frequency, it is forced to lase at the same frequency. Thus, we get a laser system with adequate power and high stability. The laser that returns $v = 3$ population into the cycle, which we call v_{32} , only needs to deliver a few mW, so we use an ECDL without an amplifier.

ECDL mode selection

The structure of a laser diode dictates its lasing mode, for the front and rear sides of the semiconductor form a resonant cavity, and only standing waves with wavelengths that fit inside the cavity are supported. The allowed wavelength, λ , is connected to the cavity length L by

$$\lambda = \frac{2L}{m}. \quad (5.12)$$

Here, m is the order of the longitudinal mode. With the relation $\lambda = c/(n\nu)$ (c is the speed of light, and n is the refractive index), the modes are separated by

$$\Delta\nu = \frac{c}{2nL}. \quad (5.13)$$

For the laser diodes in our experiment, L is below 1 mm, and the separation is of order 100 GHz.

The basic structure of an ECDL is shown in Figure 5.11. The diode laser is collimated, and reflected by a grating connected to two tuning knobs, one controlling the vertical angle of the grating and the other controlling the horizontal angle. There is a piezo that pushes on the grating and controls the length of the external cavity.

The grating alters the lasing frequency in two ways. First, the incident angle is chosen, so that the zeroth order of diffraction works as the main output, and the first

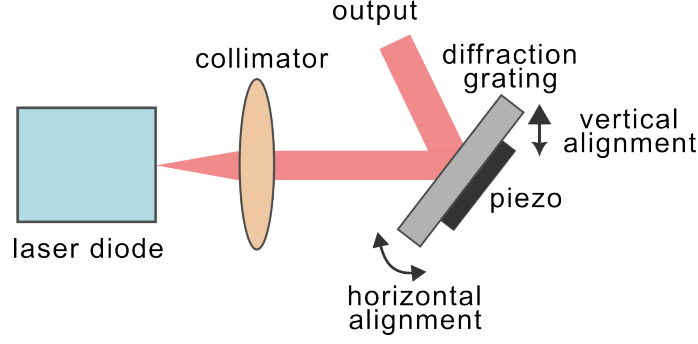


Figure 5.11: The basic structure of an ECDL. The arrows represent the dimensions controlled by the handles. Note the arrow for ‘vertical alignment’ is perpendicular to the paper.

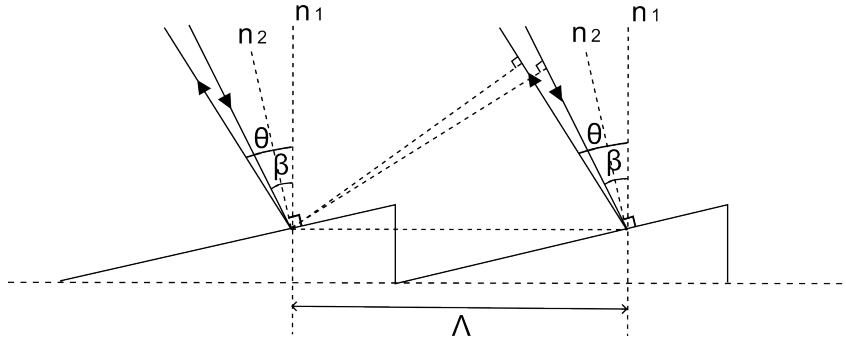


Figure 5.12: A brief schematic of how a reflection grating works. n_1 is the normal line of the grating surface, and n_2 is the normal line of the obliquity.

order of diffraction is directed back into the laser diode, providing optical feedback. Figure 5.12 is a sketch of the reflection grating. The optical path difference between adjacent elements connects the wavelength and the geometry of the grating:

$$\Lambda (\sin \theta + \sin \beta) = m\lambda. \quad (5.14)$$

Here, Λ is the grating period, and m is the order of modes. β and θ are the incident angle and reflection angle respectively. In our set-up, we adjust the grating angle so that the first order diffraction overlaps with the incident beam: $\beta = \theta$. Then, by slightly adjust the grating angle, we choose to amplify one of the lasing modes, and the diode can be considered as a single-mode laser, diffracted by the grating. A grating (GH13-24V) of $\Lambda = 1/2400$ mm is chosen. For a wavelength of $\lambda = 628$ nm, the average reflection efficiency is 45%, and the incident angle should be 48.9° . In practice, the grating is fixed to a mirror mount so that the angle is approximately correct, and then small angular adjustments are made using the mirror mount to obtain a perfect alignment.

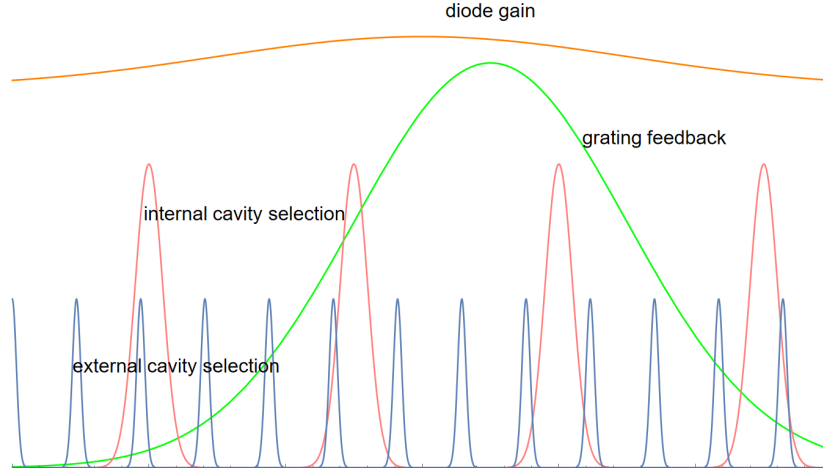


Figure 5.13: A brief schematic of the frequency overlap of different mode selection mechanism. The frequencies are not to a real scale.

Second, an external cavity is formed between the rare surface of the diode and the grating, and Equation (5.12) and Equation (5.13) apply to this cavity. This external cavity is much longer than the internal cavity of the diode, typically a few centimetres, so the modes are separated by several gigahertz. A piezo-electric transducer is attached at the back of the grating. By applying a voltage to it, the length of the external cavity is slightly shifted, and its resonant frequency is precisely controlled. The derivative of Equation (5.12) gives the accuracy:

$$d\nu = -\frac{(c/n)m}{2L^2}dL. \quad (5.15)$$

We have $L \approx 2$ cm, $n \approx 1$. The piezo has $2.6 \mu\text{m}$ displacement with 150 V, connected to an analogue output channel with 0 to 10 V, 0.01 V resolution. So the frequency is adjusted by the piezo with a precision of 65 MHz.

Figure 5.13 summarises how the modes are selected in an ECDL. The orange curve is the gain profile of the diode, which is affected by the temperature and the current. When temperature rises, the crystal lattice expands and the energy gap decreases, so the transition frequency decreases. It covers a range of several terahertz. The current controls the output power of the diode, but also affects its frequency by changing the refractive index of the material. There is a quasi-periodic change on 0.1 terahertz scale, when the current varies by tens of milliamp. The green curve is the selection with a grating. It covers a scale of 0.1 terahertz by changing the grating angle, using the feedback of the first order diffraction. The red and blue curves are the selection of the internal and external cavity of the diode respectively, which have been introduced above.

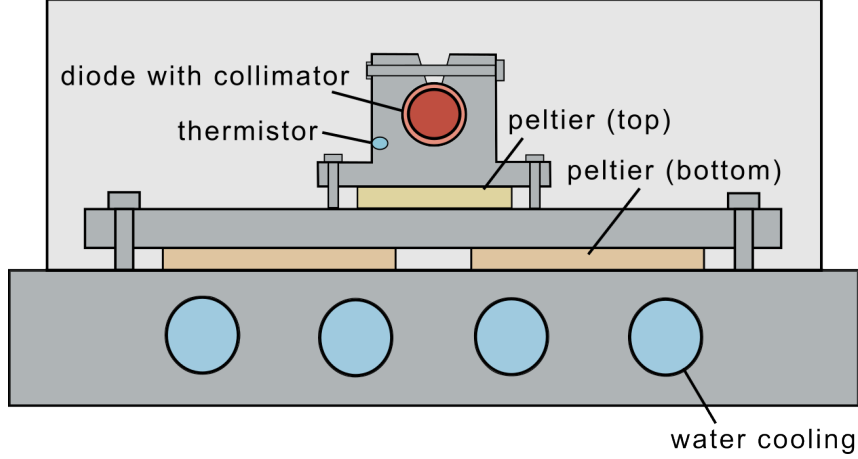


Figure 5.14: The structure of the two stage cooling system for the laser boxes.

Temperature control system

For the stability of the laser system, it is important to keep a steady temperature for both the seed and amplifier. We apply a two-stage cooling system shown in Figure 5.14. The laser box is placed on a water cooled base, with 16°C water circulating through. There are no laser diodes available at our required wavelength of 628 nm. Instead, we take commercially available diodes at either 638 or 633 nm and cool them to low temperature to shift their lasing wavelength to 628 nm. The required temperature is well below 0°C, so the entire laser assembly needs to be evacuated. The laser boxes are o-ring sealed, and a scroll pump maintains the pressure below 1 mbar. We use three peltier coolers to reach the required temperature. The two peltiers at bottom are connected in series, powered by a fixed current supply of around 20 V, running at several amps. The peltier on top is connected to a temperature controller (PTC2.5K-CH). There are graphite sheets between all of the layers to ensure the thermal conduction. The target temperature and the actual temperature is related to a trimpot and a 10k thermistor respectively, both supplied with a current of 10 μ A. The thermistor is placed inside the diode mount, attached closely to the case of the diode. By feeding back to the current supplied to the peltier, the actual temperature is stabilised at the target temperature. To adjust the target temperature more accurately, we connect another trimpot to the original one in parallel. It enables the adjustment by 1 mV, which corresponds to a 5 mK change in temperature.

Properties of the diodes

Transition v_{21} has a wavelength of 628.1 nm. We choose the diode HL63163DG (633 nm at room temperature, 100 mW maximum output) for the seed, and HL63263DG (638 nm at room temperature, 200 mW maximum output) for the amplifier. Because the former diode needs less cooling, it maintains higher stability. The latter diode can operate in higher power, so it results in better amplification. All the diodes are driven by the precision constant current laser driver LD1255R, which supplies 250 mA at maximum.

A diode is characterised by its relation between the temperature and the wavelength, the current and the power. The temperature-wavelength relation of the diode HL63163DG is shown in Figure 5.15. The data is taken with a fixed current of 85 mA. It shows that within the functional temperature range (-10 °C to 50 °C in our case), the wavelength increases like a step-function as the temperature rises, with an average of about 0.2 nm/°C. If it is too hot or cold, the diode becomes multimode, hopping between several wavelengths. Thus, the diode for the seed is cooled to around -5 °C. The relation in diode HL63263DG is similar, and it needs to be cooled to around -25 °C, which is out of the specified temperature range. The output power is a little bit suppressed at this temperature, but still enough for this experiment. The multimode problem rises, and can be solved by precise injection.

The design of v_{32} ECDL is similar to the seed of v_{21} , except that the mount for diode and grating is 3D-printed. Figure 5.15 (b) is the measurement of current-power relation for the v_{21} seed and v_{32} ECDL. To enlarge the range of data, both of them uses HL63263DG diodes, instead of their usual HL63163DG ones. It shows that there is a threshold for the diode to lase. If the current is below the threshold, there is little output. When it goes above, the laser intensity becomes linear to the current. The feedback from a grating lowers the lasing threshold from 70 mA to 60 mA. This is the crucial signature showing that the grating is well aligned and provides adequate feedback. The current-power ratio without grating is about 1 mW/mA, with grating it is suppressed to 0.67 mW/mA. The data is measured at a fixed temperature of -5.5 °C.

Figure 5.16 shows the influence of the current on the lasing frequency for HL63163DG diode. The data is taken at -7°C. There is a quasi-period of 5 mA, where the frequency increases as the current goes up. The tuning range of each frequency cycle is around 800 GHz. However, the central frequency of each quasi-period decreases as the current goes up. It can be explained by the shifting of external cavity curve,

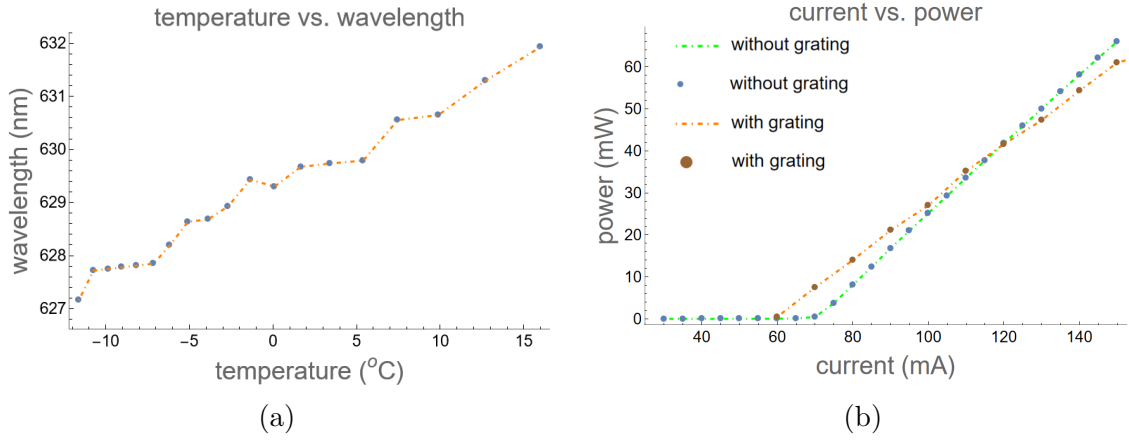


Figure 5.15: The properties of HL63163DG diode. (a) The relation between the temperature and the wavelength. (b) The relation between the current and the output power.

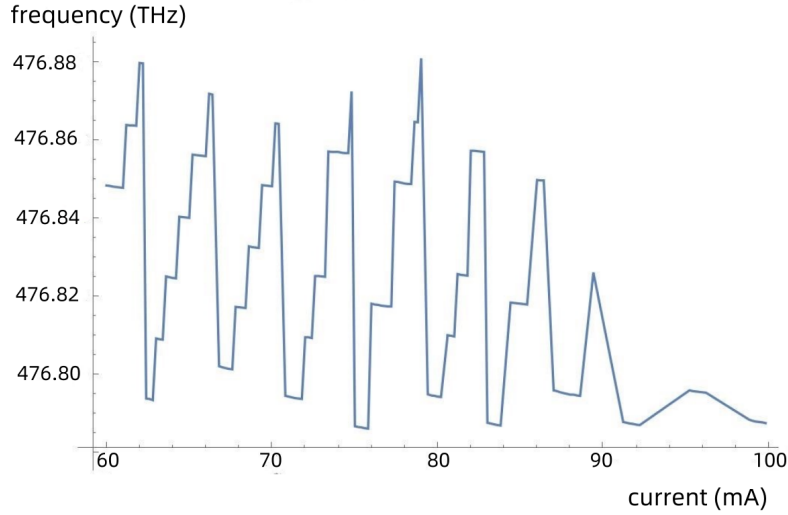


Figure 5.16: The relation between current and frequency for HL63163DG diode.

internal cavity curve, and diode gain curve in Figure 5.13. When the current increases, the internal cavity curve is shifted to the higher frequency side due to the increase of free electrons (Due to an overshooting problem of the current supply, it looks like the opposite case in Figure 5.16). Because the external cavity contains the diode cavity, its curve is shifted in the same direction, but with a much slower speed. This means a red mode in Figure 5.13 will keep ‘catching’ the blue modes in front of it. Once it ‘catches’ a new blue mode, the frequency plotted in Figure 5.16 ‘climbs up by a stair’. However, as the current increases, the diode gain curve moves to the lower frequency side, so it ‘catches’ red modes of lower frequency. Once it ‘catches’ a new red mode, the frequency ‘falls down from a cliff’, and the mean frequency of each quasi-period gradually drops.

Frequency lock

To lock the seed laser to the right frequency, several steps are needed. First, the grating is aligned mechanically using the two mirror mount adjusters. They can be adjusted from outside the vacuum housing using o-ring sealed feedthroughs, but it is easier to make initial adjustments with the box open. We reduce the current of the diode to just below the lasing threshold, and tweak the grating slowly until the first order diffraction feeds back into the diode. At this position, the diode starts to lase. Second, we evacuate the laser box and cool the diode to around $-5\text{ }^{\circ}\text{C}$, where the frequency should be no more than 50 GHz away from our target frequency. The change of pressure and temperature may cause a little deformation of the diode mount, and disrupt the grating feedback. A little tweak on the feedthroughs can bring it back. After this, it is better to decouple the handles from the diode mount to avoid disruption. Third, we limit the output of the piezo control channel between 0 V and 10 V, and set the voltage of the piezo at 5 V. This is to protect the piezo against negative voltages, and allow the largest tuning range. We scan the current of the diode from 100 mA to 180 mA, and park it at a value where the actual frequency is at the middle of its quasi-period, while also within 1 GHz of the target frequency. Finally, we adjust the target temperature by a step of 0.01 V, which corresponds to 5 mK, and change the voltage on the piezo slightly, so we are about 50 MHz away from the target frequency. After all the procedure above, we can lock the seed laser with high stability. The laser frequency is stabilized using a feedback system based either on a high precision wavemeter or an optical cavity that transfers the stability from one laser to another. More details can be found in [93].

Figure 5.17 shows the frequency stability. The diode runs at 135 mA, $-0.5\text{ }^{\circ}\text{C}$. The bottom peltiers run at 3.81 V, 0.7 A. The temperature controller takes 5.5 V, and the top peltier runs at 0.086 A. The seed is locked at 477.299380 THz, and the standard deviation is below 2 MHz. The stability is able to maintain for around 5 minutes. Its spectrum is shown as the yellow curves in Figure 5.19. The free spectral range of the cavity is 1.5 GHz. We lock the v_{32} ECDL to the transition frequency in the same way. The diode is cooled to -10°C , running at 93.3 mA, and the output power is 16.6 mW.

Optical injection

The full arrangement of the seed-amplifier laser system for v_{21} is shown in Figure 5.18. The collimated seed beam passes through a pair of prisms, which transforms the light from an elliptical beam to a nearly circular beam. Then it passes

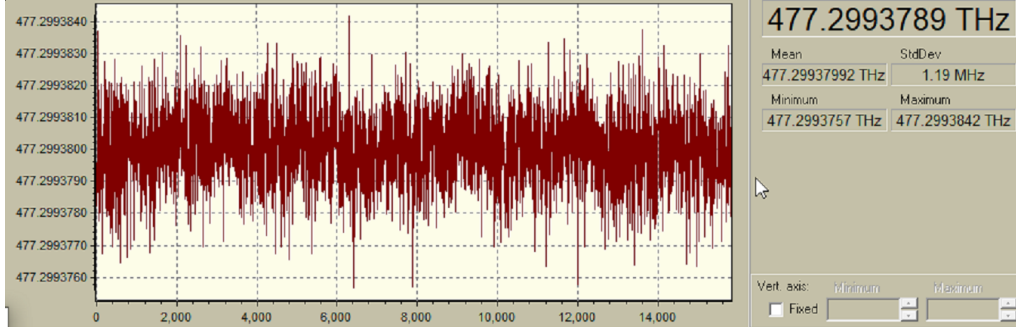
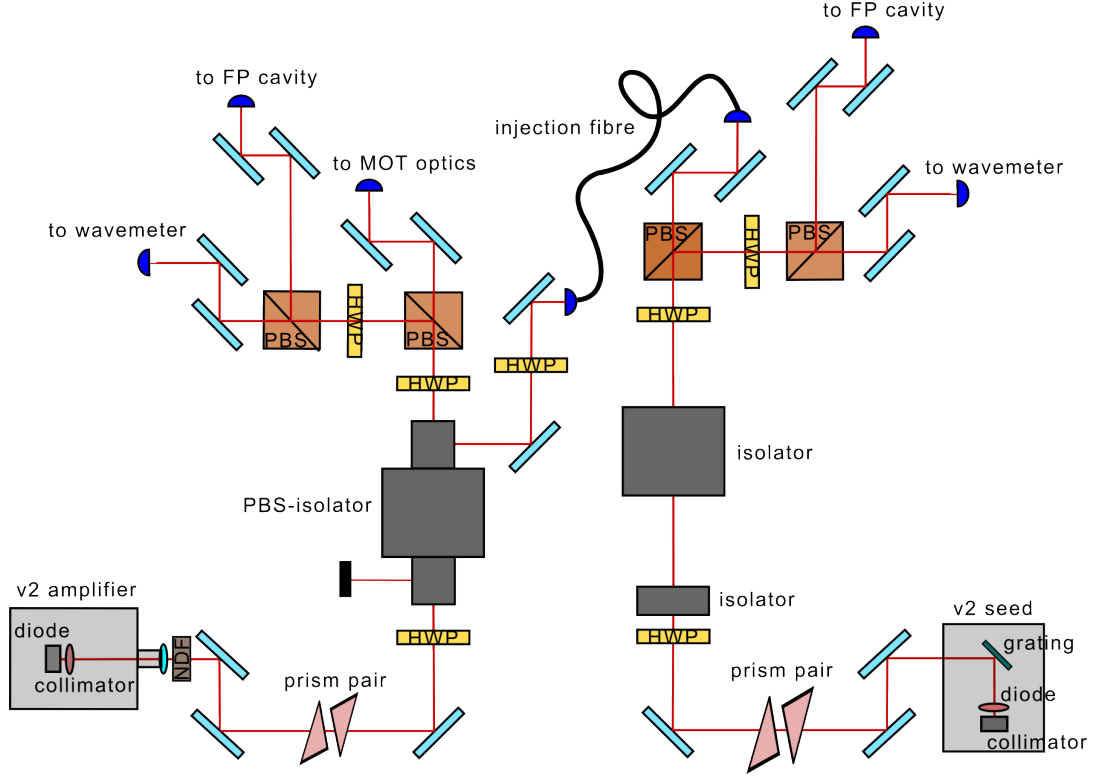


Figure 5.17: The frequency of the ν_{21} seed, locked by the wavemeter lock.

through a half-wave plate, entering a polarization dependent isolator (Faraday isolator). It is composed of a vertically polarised input polariser, a Faraday rotator, and a 45° polarised output polariser. The Faraday rotator rotates the polarisation by 45° . This design allows the laser beam to travel only in the forward direction, and its efficiency is controlled by the HWP before it. Another isolator goes after it to ensure the backwards reflection is totally eliminated. Then, it is split into two branches by a PBS. Most of the power (about 10 mW) is coupled into the injection fibre. The rest of it is sent to the monitor cavity and the wavemeter.

The collimated amplifier beam travels out of the laser box through a window held at Brewster angle. This is to minimise the reflection and protect the diode. The diode output is around 90 mW when cooled to -22°C with the current supply of 150 mA. The power is less than expected because it runs below the specified temperature. The majority of it (about 60 mW) is coupled into the MOT optics, and the rest (less than 5 mW) goes into the monitor cavity and the wavemeter.

The seed beam that leaves the injection fibre is overlapped with the amplifier beam by a PBS-isolation. It is an isolator with two PBS attached to its ends. The seed beam is horizontally polarised by a HWP, and reflected by the PBS into the Faraday rotator. Here it rotates 45° , and half of it passes through the other PBS, entering the amplifier diode. After all the loss along the way, there is around 2 mW power successfully injected. An easy way to align the injection beam is to couple the reflected amplifier beam at the end of the PBS-isolator into the injection fibre. Then, the NDF is flipped up to reduce the power of the amplifier, so the injecting beam from the seed is not covered by the large and bright amplifier beam. We can see two spots overlapped before the amplifier, then the NDF can be removed from the optical path. The injection can be seen from the FP cavity by an oscilloscope, as shown in Figure 5.19. The blue spectra are from the amplifier, and the yellow ones are from the seed. Before injection, the amplifier is multimode. After injection,


 Figure 5.18: The optical layout of the seed-amplifier laser system for v_{21} .

it lases single mode at the seed laser frequency.

5.3.4 Optics

The optics layout for slowing and MOT is shown in Figure 4.6. The 0th order of v_{10} laser is mixed with v_{00} laser on a dichroic mirror. The mixed beam is split into 2 branches with a 3:1 power ratio. The larger one passes through a 73.5 MHz EOM to generate sidebands for $F = 1^-$, 0, 2 hyperfine levels, and the other is shifted 48 MHz higher by an AOM. They are remixed by a PBS, and split for three MOT laser beams. v_{21} and v_{32} both pass through a 24 MHz EOM to generate sidebands and are mixed by a PBS. Then this light is split into two parts, and mixed with v_{00} & v_{10} by a PBS. The balance of power between the MOT beams are controlled with HWPs before PBSs. Since four laser beams of different wavelength and beam profiles (v_{00} , v_{10} , v_{21} , v_{32}) are coupled into the MOT fibre by only one collimator, it is difficult to achieve high coupling efficiencies for all of them. The efficiencies are between 40% and 70%.

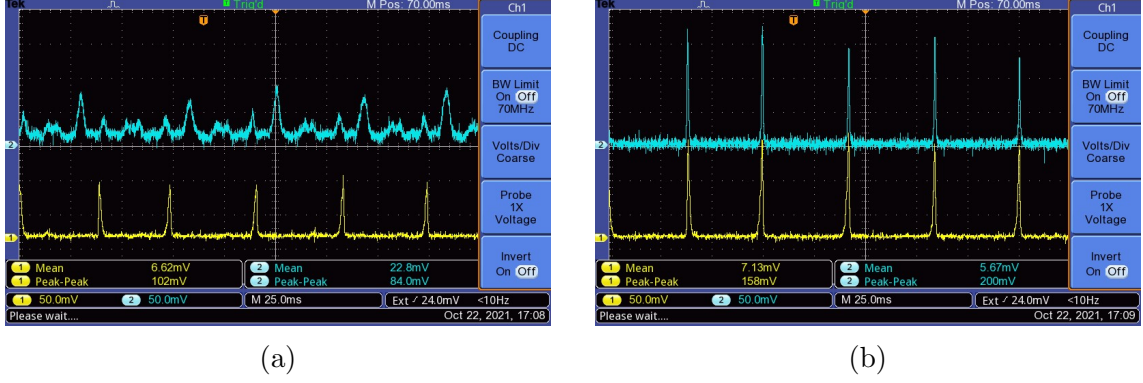


Figure 5.19: Injection seen on a scope. (a) The uninjected amplifier (blue) and the locked seed (yellow). (b) The injected amplifier (blue) and the locked seed (yellow).

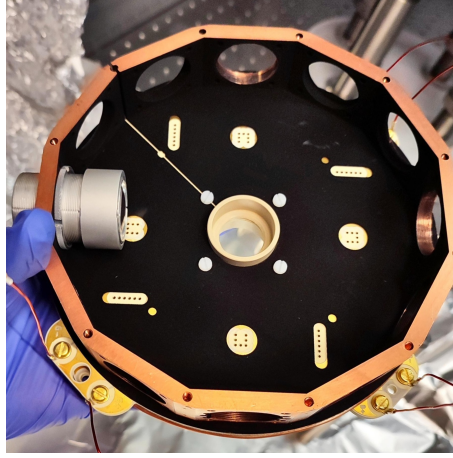


Figure 5.20: The bottom lid and the jacket of the radiation shield are blackened. The lens is placed inside a lens holder, which is screwed into the jacket.

5.3.5 Imaging

We use a hermetic vacuum-sealed water-cooled electron multiplier back-thinned frame transfer CCD (EM-CCD) camera to image the molecular cloud. There is a lens of 1 inch diameter and 50 mm focal length inside the chamber, placed 50 mm away from the centre. To reduce background noise, we place a bandpass filter before the camera to block the scattering of the slowing laser, and blacken the lens tube and the inner surface of the radiation shield, as shown in Figure 5.20. To monitor the condition of the molecular source, we detect fluorescence from the molecular beam using the PMT on the detection chamber every time when we run the MOT experiment.

5.4 To make a MOT

5.4.1 Check list

There are several things to check before looking for a MOT:

- BX slowing light alignment
- v_{10} slowing light alignment
- BX slowing sideband verification
- v_{10} slowing sideband verification
- v_{00} MOT light alignment
- v_{00} MOT light polarization stability in fibre
- v_{10} MOT light alignment
- v_{21} MOT light alignment
- v_{32} MOT light alignment
- v_{00} MOT sideband verification
- v_{10} MOT sideband verification
- v_{21} MOT sideband verification
- v_{32} MOT sideband verification
- v_{00} MOT polarizations verification
- Magnetic field driver direction switching verification

For safety and to avoid breaking diagnostic devices, all the above procedures should be performed with less than 50 mW laser power. The polarisation of the main slowing laser and the V_{00} laser are important, but the polarizations of the repumps are irrelevant to making a MOT. The BX laser should be linear, and 45° to the magnetic field. The horizontal MOT lasers should be left-handed circularly polarised, and the vertical beam should be right-handed circularly polarised, as is shown in Figure 5.21. The sidebands are monitored by a Fabry-Perot cavity, as shown in the previous chapter.

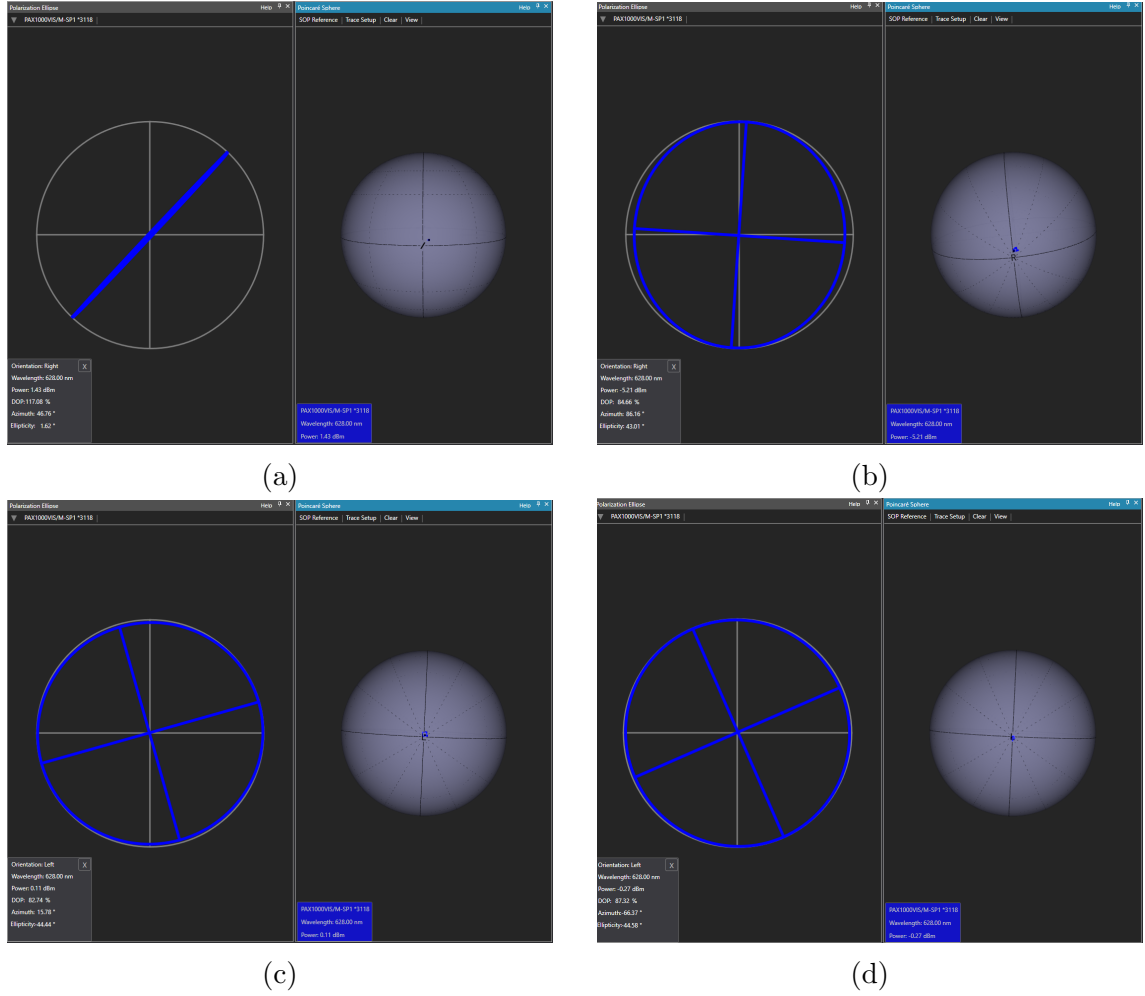


Figure 5.21: The handedness of the slowing laser beam (a), the vertical MOT beam (b), and the horizontal MOT beams (c)(d). Notice there are 'R', 'L' and 'R' symbols on the north pole of the Bloch spheres.

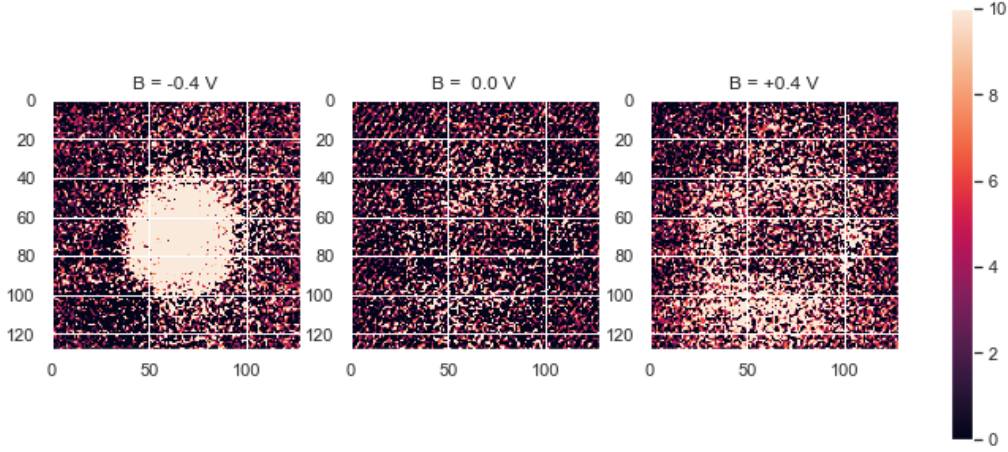


Figure 5.22: The camera signal of the first MOT.

5.4.2 Result

The first MOT was observed in January 2024. To improve power transfer efficiency, the slowing laser was moved to the same table as the science chamber. To provide more power to the repump lasers, the seed-amplifier laser was used as the ν_{32} laser, and a dye laser supplying about 300 mW was used as the ν_{21} laser. The spectrum of the slowing repump laser is broadened using a 24 MHz and a 4 MHz EOM in series, so that it can address all velocity classes without being chirped. The BX laser is chirped across 280 MHz, with a hold time of 2 ms and a flying time (a time span just after YAG ablation with no laser on) of 2 ms. The MOT coils run at 1 A, corresponding to a magnetic field gradient of around 30 Gauss/cm. The camera triggers at 30 ms after the YAG fires, and the exposure time is 30 ms. Figure 5.22 shows this first MOT. A bright patch is observed on the camera for one sign of magnetic field gradient, but not for the opposite sign and not when the magnetic field is turned off. This is a clear signature that there are molecules trapped in the MOT. There is also a ring of light in the image which is due to laser light scattered off the edges of the lens holding tube. This ring is always present, and in principle can be removed by subtracting the ‘signal’ image from a ‘background’ image. However, because the laser intensity fluctuates, this procedure is imperfect.

After optimizing many parameters, the MOT images have improved considerably. A better image is shown in Figure 5.23. The number of molecules is estimated to be $1270(\pm 56)$, and the density distribution of the trapped molecules has a FWHM of about 4 mm. The number density is $3.8 \times 10^4 \text{ cm}^{-3}$. The number of trapped molecules is a hundred times smaller than anticipated. At the time of writing, the reason has not been identified. The optimum detuning of the main MOT laser (ν_{00})

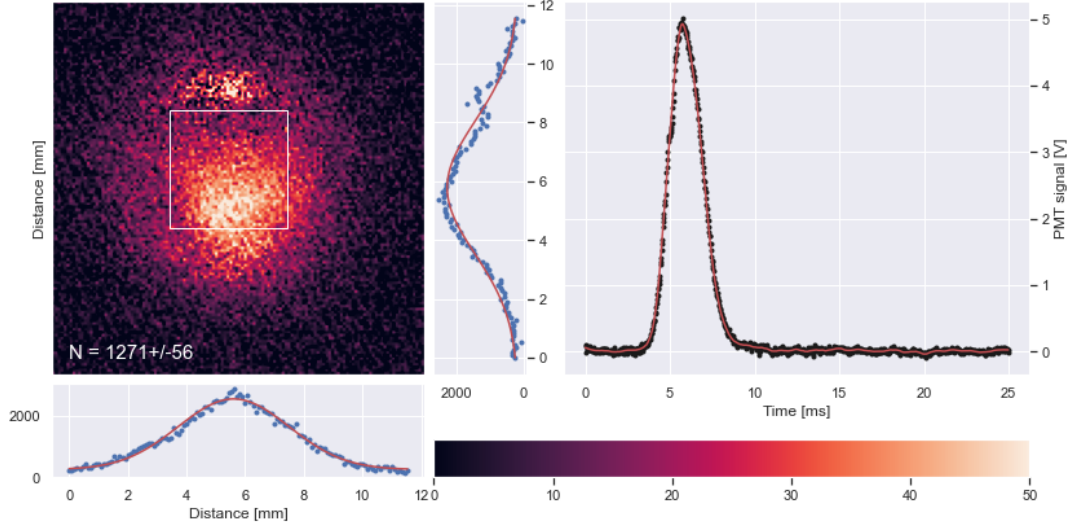


Figure 5.23: An improved MOT. The sizes are integrated at the sides of the photo, and the TOF signal measured at the detection chamber is shown on the right side.

is found to be about -14 MHz, which is -1.7Γ . It is larger than usual due to the non-orthogonal MOT configuration. The power (in mW) of each laser beam is listed in Table 5.2.

The slowing laser is chirped across 280 MHz in 14 ms, corresponding to a chirp rate of 20 MHz/ms, and an acceleration of 1×10^4 m/s. It is smaller than the best parameter found in Section 4.3.3, because now the slowing laser is less focused, in order to cover a larger proportion of the transversely diverging molecular beam. There is a 2 ms flying time and a 2 ms hold time before the chirp starts. Let us consider the peak molecules in an ideal case. The TOF signal in Figure 5.23 suggests a peak velocity of 138 m/s. During the flying time, it flies a distance of 276 mm; during the hold time, its velocity is reduced to 116 m/s (referring to Figure 4.10(b)), and it flies a distance of 255 mm; during the chirp time, it flies the rest 669 mm towards the MOT area, and ends up with a velocity of 13.8 m/s, which is capturable. The arrival time is 18 ms after the YAG flash. Molecules faster than it is likely to arrive with a higher speed and cannot be captured. Molecules slower than it arrives at later time, and can be trapped by the MOT.

5.5 Conclusion

This chapter explains how a magneto-optical trap works, which includes the generation of the linear magnetic field and the Zeeman shift it introduces, the configuration of the dual-frequency light and its polarisation. Next, the science chamber and the

	$v_{00}(F = 2, 0, 1^-)$	$v_{00}(F = 1^+)$	$v_{10}(F = 2, 0, 1^-)$	$v_{10}(F = 1^+)$	v_{21}	v_{32}
MOT 1	74	20	360	70	0	0
MOT 2	42	13	228	48	62	3.7
MOT 3	51	14	190	52	62	3.6

Table 5.2: The power (in mW) of all the MOT lasers in each direction. Because the beam is reflected at the end, the power that comes out of the fibre, which is shown here, is half the actual power in the chamber.

magnetic coils assembled inside are described, along with the optical layout and the commercial lasers. The home-made ECDLs and the injected laser amplifier are also explained in detail. Finally, the first MOT and its optimisation is shown, and the basic characteristics of it are included.

Chapter 6

Towards BEC

This chapter talks about future steps towards a CaF BEC. It includes the polarisation-gradient cooling, the optical trapping and the evaporative cooling. Both the theory and experiments of other labs are briefly mentioned. Especially, a pair of electrodes designed by me is introduced, and it is to be implemented to the science chamber. Finally, since the first MOT is weak in molecular number, some improvement is proposed, and the ultimate result is estimated.

6.1 Introduction

As is mentioned in the first chapter, the temperature of a MOT is restricted by the Doppler limit. This is because photons are scattered in random directions, resulting in a random walk in momentum space. This is a heating process which competes with Doppler cooling. The mean squared velocity is non-zero, which indicates a finite temperature. When the cooling rate equals the heating rate, the system is at equilibrium, and the lowest temperature by Doppler cooling is achieved:

$$T_D = \frac{\hbar\gamma}{2k_B}. \quad (6.1)$$

Here, γ is the natural width in radians per second. The Doppler limit of CaF laser cooled by $A^2\Pi_{1/2} \leftarrow X^2\Sigma^+$ transition is $199 \mu\text{K}$.

The limit is crossed due to the sub-Doppler cooling methods described in the next section. The lowest temperature for laser cooling techniques is the recoil temperature, which is the kinetic energy gained by a static molecule when it emits a photon:

$$T_{recoil} = \frac{\hbar^2 k^2}{mk_B}. \quad (6.2)$$

Here, k is the angular wavevector of the emitted photon, and m is the mass of the molecule. The recoil limit of CaF laser cooled on the $A^2\Pi_{1/2} \leftarrow X^2\Sigma^+$ transition is about 880 nK.

6.2 Sub-Doppler cooling and optical dipole trap

6.2.1 AC Stark shift

An electric dipole moment interacts with an oscillating electric field, resulting in an energy level shift. This mechanism is the AC Stark effect, which is important in both sub-Doppler cooling and optical dipole traps. Consider a two-level system with Rabi frequency Ω and laser detuning Δ . The Hamiltonian for this system, and the associated optical Bloch equations, are given by Equation (4.1), Equation (4.2) and Equation (4.3). In a dressed-state picture, the shifted energy of the excited state E_e and the ground state E_g are

$$E_e = \frac{\hbar}{2} \left(-\Delta - \sqrt{\Omega^2 + \Delta^2} \right), \quad (6.3)$$

$$E_g = \frac{\hbar}{2} \left(-\Delta + \sqrt{\Omega^2 + \Delta^2} \right). \quad (6.4)$$

It is common to choose a large detuning such that $\Omega \ll \Delta$, in which case the energy splitting becomes $\Delta E = \pm \frac{\hbar\Omega^2}{\Delta}$.

6.2.2 Polarisation-gradient cooling

Polarisation-gradient cooling can cool molecules below the Doppler limit. The particular mechanism used for molecules relies on the presence of dark states in the system. These are ground states that cannot couple to the light due to the selection rules. When the ground state has more angular momentum than the excited state, there are always dark states. For example, when the transition is from $F = 1$ to $F' = 0$, the $m_F = 0, +1$ states cannot couple to light that is σ^+ polarized, so they are dark states. As shown in Figure 6.1, a pair of counter-propagating lasers form a polarisation-gradient field, which interacts with the bright state and results in a spatially dependent energy E_b , while the dark state energy E_d is not affected. A moving molecule is decelerated because it is preferentially pumped to the dark state at the top of each hill, and preferentially transferred back to the bright state at the bottom of each hill. Thus, it finds itself continually climbing hills.

In Figure 6.1, the blue-detuned laser beams are shown with orange arrows. They counter-propagate along the z -axis, and are linearly polarised at $\pm\phi/2$ to the x -axis. The electric field is

$$E = E_0[(\cos(\phi/2)\hat{x} + \sin(\phi/2)\hat{y})\cos(kz - \omega t) + (\cos(\phi/2)\hat{x} - \sin(\phi/2)\hat{y})\cos(kz + \omega t)]. \quad (6.5)$$

Using the relation $k = 2\pi/\lambda$, the polarisation repeats with a period of λ . At the position $z = \lambda/4, \lambda/2$ and $3\lambda/4$, the polarisation is linear along y, x and $-x$, which are shown with black arrows. Between them the polarisation is elliptical.

We take the example of $F = 1$ ground state. There are three sub-levels: $|1\rangle, |0\rangle$ and $|-1\rangle$. The bright state $|b\rangle$ and the dark state $|d\rangle$ are linear combinations of the unperturbed eigenstates:

$$|b\rangle = \cos(kz + \phi/2)|-1\rangle + \cos(kz - \phi/2)|1\rangle, \quad (6.6)$$

$$|d\rangle = \cos(kz - \phi/2)|-1\rangle - \cos(kz + \phi/2)|1\rangle. \quad (6.7)$$

It is clear the states are position dependent. The energy of the dark state is 0, and the energy of the bright state is

$$E_b = \frac{\hbar\Delta}{2} \left(-1 + \sqrt{1 + \frac{2\Omega^2}{\Delta^2}(1 + \cos(2kz)\cos\phi)} \right) \approx \frac{\hbar\Omega^2}{2\Delta}(1 + \cos(2kz)\cos\phi). \quad (6.8)$$

The approximation holds when the Rabi frequency Ω is much smaller than the detuning Δ . In the blue-detuning situation, $\Delta > 0$, the energy of the bright state is above the dark state, with a spatial period of $\lambda/2$. In the red-detuning situation, the energy of the bright state is below the dark state, which causes sub-Doppler heating. This effect is observed in [41].

In Figure 6.1, the probability of the optical pumping from the bright state to the excited state is shown as P_{OP} , and the adiabatic transition rate from the dark state to the bright state is P_{NA} . The calculation is in [94]. A moving molecule in the dark state adiabatically enters the bright state at the bottom of its potential curve, where they are almost degenerate. It is pumped into the excited state at the top of the hill, and spontaneously decays to the dark state again.

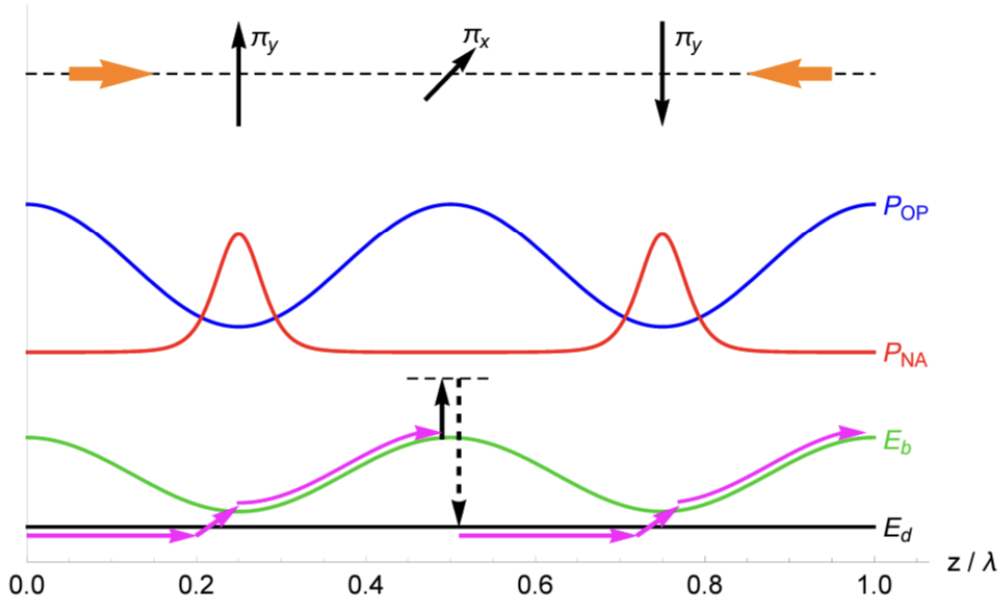


Figure 6.1: The schematic of polarisation-gradient cooling. This figure is taken from [94].

6.2.3 Optical dipole trap

Optical dipole traps are a popular kind of conservative trap to confine ultracold atoms and molecules. Compared to magnetic traps, they are suitable for molecules in all internal states, and can be combined with cooling techniques to improve the spatial density and phase-space density. The most common configuration is to use far-red detuned, focused Gaussian laser beams, which interact with the electric dipole and produce a spatially varying potential. The intensity of a Gaussian beam is

$$I(r, z) = I_0 \left(\frac{w_0}{w(z)} \right)^2 \exp \left(-\frac{2r^2}{w^2(z)} \right), \quad (6.9)$$

Here, I_0 is the intensity at the centre of the focus point, $w(z)$ is the beam waist, and w_0 is the minimum waist. They are related by

$$w(z) = w_0 \sqrt{1 + \left(\frac{z}{z_0} \right)^2}, \quad (6.10)$$

where $z_0 = \pi w_0^2 / \lambda$. λ is the wavelength of the trap laser. The power of the beam is

$$P = \frac{1}{2} \pi I_0 w_0^2. \quad (6.11)$$

When the AC Stark shift is much smaller or larger than the hyperfine splitting and the Zeeman splitting, the electric field and the induced dipole moment are related linearly by the polarisability α : $\alpha = |\vec{P}|/|\vec{E}|$. As introduced in Section 6.2.1, the AC stark shift is proportional to the square of the Rabi frequency, thus proportional to the laser intensity:

$$U(r, z) = -\frac{\alpha I(r, z)}{2c\epsilon_0}. \quad (6.12)$$

At the centre of the trap, the potential is considered as a harmonic potential. We expand the potential to second order at $r = 0, z = 0$:

$$U(r, z) = -U_0 + \frac{1}{2}m\omega_r^2 r^2 + \frac{1}{2}m\omega_z^2 z^2. \quad (6.13)$$

The trap depth U_0 , the radial trap frequency ω_r and the axial trap frequency ω_z are

$$U_0 = \frac{\alpha I_0}{2c\epsilon_0}, \quad (6.14)$$

$$\omega_r = \sqrt{\frac{4\alpha P}{\pi\epsilon_0 c m w_0^4}} = \sqrt{\frac{4U_0}{m w_0^2}}, \quad (6.15)$$

$$\omega_z = \sqrt{\frac{2\alpha P \lambda^2}{m\pi^3 \epsilon_0 c w_0^6}} = \sqrt{\frac{2U_0}{m z_0^2}}. \quad (6.16)$$

The trap laser in our experiment operates at 1064 nm, and its highest output power is 50 W. We plan to focus down its beam size from 850 μm to 50 μm with 3 lenses outside the science chamber. According to calculation in [94], with $\lambda = 1064$ nm, $P = 15$ W and $w_0 = 45$ μm , the trap depth is 210 μK , and the trap frequencies are $\omega_r = 2\pi \times 1.2$ kHz, $\omega_z = 2\pi \times 6.5$ Hz. The arrangement with other beams is shown in Figure 5.5.

6.3 Evaporative cooling

6.3.1 Introduction

To explore the temperature zone below T_{recoil} requires collisional cooling techniques. There are two popular methods: evaporative cooling and sympathetic cooling. Evaporative cooling works by lowering the depth of a trap, so that molecules with high velocity escape from the trap. The remaining molecules establish a new equilibrium which corresponds to a lower temperature. Sympathetic cooling takes advantage

of elastic collisions between two different species, typically where one is easier to cool than the other. For example, CaF molecules can be mixed with Rb atoms in the same trap, and evaporative cooling of the Rb will then sympathetically cool the molecules.

The thermalisation of evaporative cooling relies on elastic collisions between molecules, which are accompanied by inelastic or reactive collisions which result in the loss of molecules. For popular species of laser cooling experiments such as CaF and SrF, the ratio of the elastic collision to unwanted collisions is a critical factor for reaching BEC. For most molecules, the rate for inelastic collisions is too high, so some method is needed to shield against these unwanted collisions.

The idea of shielding molecules with a static electric field was first considered for molecules with Λ -doubling degeneracy [109]. The effective van der Waals potential between two molecules is attractive if they are in the lower Λ -doublet state, and it is repulsive for the ones in the upper Λ -doublet state. The same situation can be applied to molecules with $^2\Sigma$ symmetry. Although they have no Λ -doubling, a pair of states close to degeneracy with opposite parity can be created using an electric field. A study of the shielding mechanism on $^{87}\text{Rb}^{84}\text{Sr}$ molecular gas was published in 2016 in [109]. It suggests the eigenvalue of a pair of ground state molecules $|N = 1, N = 1\rangle$ crosses with a pair of $|N = 0, N = 2\rangle$ ground state molecules from below when the external field, an electric field, rises from 0 to 2.27 kV/cm. This is shown in Figure 6.2(a). Thus, with a field slightly above the critical value, $|N = 1, N = 1\rangle$ becomes the ‘upper state’ of a pair of degenerate states, and the interaction becomes repulsive, as shown in Figure 6.2(b).

The method has recently been proven effective with the degenerate Fermi gas $^{40}\text{K}^{87}\text{Rb}$, as is published in [110]. The molecules are produced by the method described in the first chapter, and transferred to the $N = 1$ state with a π -pulse at 300 nK with the density of $2.5 \times 10^{11} \text{ cm}^{-3}$. After that, an electric field ramps to a fixed strength, holds for some time and ramps back. The lifetime of the molecules is measured. A field of 12.7 kV/cm yields the longest lifetime (10 s). The elastic to inelastic collision ratio is calculated to be around 12. A simple schematic is shown in Figure 6.3.

In the case of CaF, the reaction $2\text{CaF} \rightarrow \text{CaF}_2 + \text{Ca}$ has no barrier, so is likely to proceed rapidly unless a collisional shield is used. Calculation suggests a static electric field at 22 kV/cm is the best choice for $N = 1$ molecules in the ground state. With the suppression of lossy collisions, it is possible to form a BEC within 0.7 s,

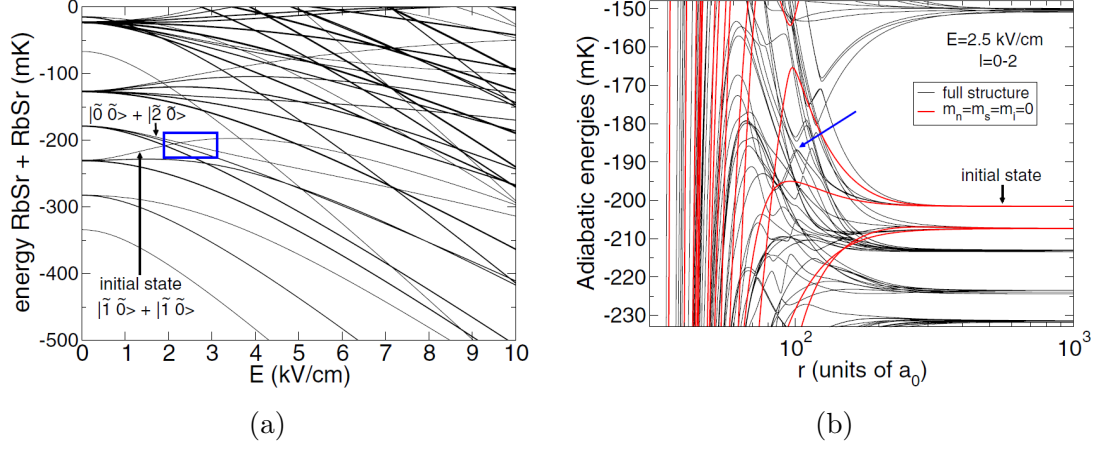


Figure 6.2: The figure is from [109]. (a) The manifold of a pair of ground state $^{87}\text{Rb}^{84}\text{Sr}$ molecules in a static electric field. The state is noted as $|N, m_N\rangle$ based on the unperturbed eigenstates. (b) The energy barrier with an electric field of 2.5 kV/cm.

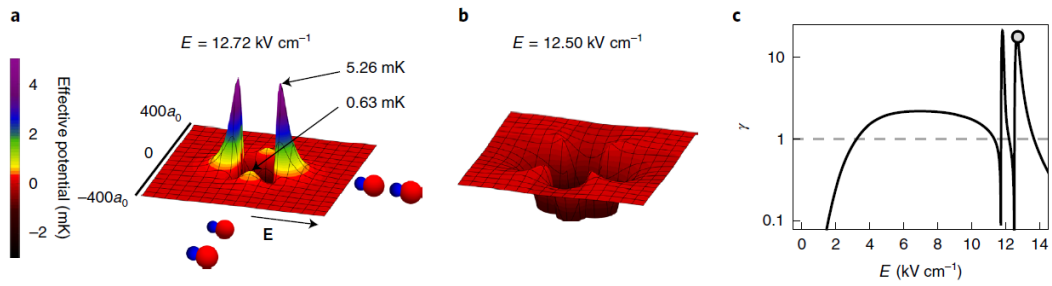


Figure 6.3: The figure is cited from [110]. (a) Two potential barriers with a field of 12.27 kV/cm. The head-tail and shoulder-shoulder reactions are both shielded. (b) The potential trap with a field strength slightly below 12.27 kV/cm. (c) The elastic to inelastic collision ratio γ against electric field strength. The peak at 12.27 kV/cm is used in this experiment, at which $\gamma = 12$.

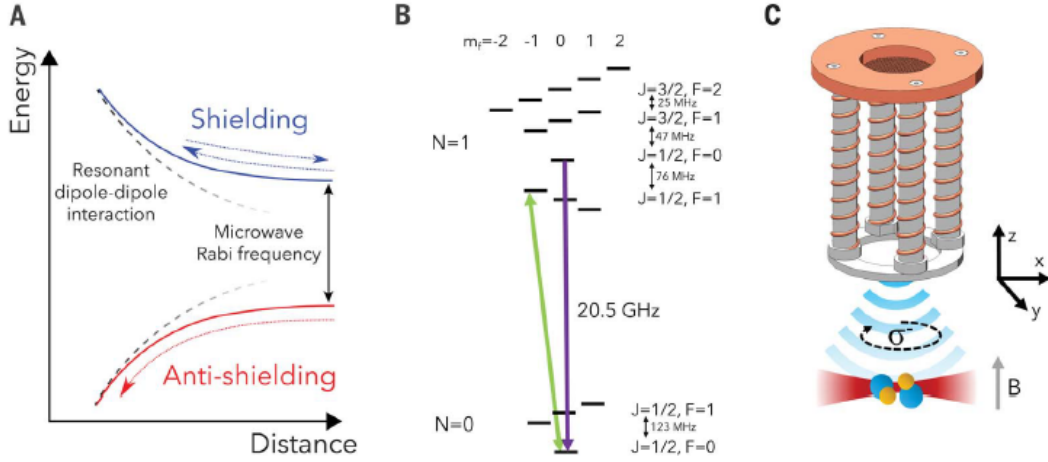


Figure 6.4: The scheme for microwave shielding of CaF molecules, figure cited from [111]. (a) The two-molecule energy structure against distance. The blue curve suggests a shielding potential. (b) The rotational, hyperfine and Zeeman structure of the ground state. The green arrow shows the shielding transition and the purple arrow shows the sweeping transition to the absolute ground state. (c) The relative position between the tweezers and the microwave generator. The polarisation of the light is parallel to the z axis.

with CaF molecules at 250 nK and a density of $1.4 \times 10^{13} \text{ cm}^{-3}$ with the apparatus in our experiment.

Another way to avoid reactive and inelastic collisions is to apply a suitable microwave field to the trapped molecules. This microwave shielding method was tested on CaF in 2021, and the result is published in [111]. In this experiment, a microwave field generates an oscillating dipole moment which leads to a repulsive potential for the $N = 1$ rotational state. The schematic is shown in Figure 6.4. The experiment is carried out using optical tweezers, each containing one single CaF molecule. The inelastic rate is suppressed by a factor of 6 in this way.

6.3.2 Electrical shielding

Theory

The calculation presented below is based on [112].

As stated above, we choose to apply an electrostatic field as a shield for the CaF molecules in a dipole trap. To create a uniform field in the central part of the science chamber, we place a pair of identical circular loops coaxially at a carefully chosen separation. In the cylindrical coordinate system, a ring of radius R placed

at (0,0,L) produces a potential

$$\phi(z, \rho)_{single} = \frac{\phi_c}{\pi} \left(\frac{R}{\rho} \right)^{1/2} kK(k^2), \quad (6.17)$$

where

$$k(z, \rho) = \left(\frac{4R\rho}{(z-L)^2 + (R+\rho)^2} \right)^{1/2}. \quad (6.18)$$

ϕ_c is the potential at the centre of the ring, and K is the complete elliptic integral of the first kind. The axial electric field is

$$E_z = \frac{(z-L)k^3 E(k^2)\phi_c}{4\pi(1-k^2)\sqrt{R\rho^3}}, \quad (6.19)$$

and the radial electric field is

$$E_\rho = \frac{\phi_c k}{2\pi} \left(\frac{R}{\rho} \right)^{1/2} \left[\frac{K(k^2)}{\rho} - \frac{E(k^2)}{1-k^2} \left(\frac{1-k^2/2}{\rho} - \frac{k^2}{2R} \right) \right]. \quad (6.20)$$

Here E is the complete elliptic integral of the second kind.

For a pair of coils placed coaxially on (0, 0, $\pm L$) with opposite charge $\mp q_l$, the potential along the z-axis in Gaussian unit is

$$\phi(z) = \phi_c a \left(\frac{1}{\sqrt{R^2 + (z+L)^2}} - \frac{1}{\sqrt{R^2 + (z-L)^2}} \right). \quad (6.21)$$

If we expand the potential for small z and choose $L = \frac{\sqrt{6}}{2}R$, we find that the potential on the axis is linear in z up to 5th order. This means when they are placed at a distance of $\sqrt{6}R$, the field is close to uniform along the z dimension. Approximate expressions for the electric fields in the axial and radial dimensions are

$$E_z(z, \rho) = E_c \left[1 - \frac{15}{32} \alpha^4 \left(z'^4 - 3z'^2 \rho'^2 + \frac{3}{8} \rho'^4 \right) \right], \quad (6.22)$$

$$E_\rho(z, \rho) = \frac{27}{125} E_c \rho' z' (4z'^2 - 3\rho'^2). \quad (6.23)$$

Here, we have introduced the reduced parameters

$$z' = z/R, \quad (6.24)$$

$$\rho' = \rho/R, \quad (6.25)$$

$$\alpha = 2(L/R)/(1 + (L/R)^2), \quad (6.26)$$

$$E_c = \frac{\alpha \phi_c}{R\sqrt{1 + d^2}}. \quad (6.27)$$

However, coils in the real world have finite thickness, and it is unrealistic to solve analytically for the electric field in this case. The uniqueness theorem for Poisson's equation says the electric field within a volume is uniquely determined if the tangential component of the electric vector is specified on its boundary, in this case the surface of the rings and the grounded radiation shield. We find that the equal-potential surfaces of a pair of ideal rings are similar to a pair of tori, as is shown in Figure 6.5(a). Thus, the idea of designing the tori is to visualise the equal-potential surfaces of an ideal pair of rings, and match one of the surfaces with the surface of a torus, as is shown in Figure 6.5(b). The black circle is a cross-section of a torus, which roughly overlaps with one of the potential surfaces. The diameter of it is around 1.9 mm. An ideal pair of coils placed at $\sqrt{6}$ times its radius generates the electric field in Figure 6.5(c). When the same parameters are applied to a pair of tori with finite thickness, the electric field has a similar form. This is shown with a coarse simulation in Figure 6.5(d).

There are several restrictions to this approach: The surfaces closer to the ring are more circular, but are technically hard to make, and they correspond to a higher voltage. Matching the outer ones is safer and easier, but they are no longer perfect circles. Nevertheless, the electrodes are placed inside the radiation shield, and there should be enough space for the lasers to pass through, so the inner radius shouldn't be too small.

A design inspired by Figure 6.5(b) is chosen as the starting point: the major radius (R) of the torus is chosen to be 10 mm, and the minor radius (r) to be 1 mm. It turned out a ± 40 kV potential on the tori surfaces is required to generate an electric field of 22 kV/cm in the centre. If it is reduced to $R = 5$ mm, and $r = 0.5$ mm, ± 18 kV is needed, but it is hard to secure the machining precision. Many sizes were tested in the simulation to find an acceptable solution.

The electrodes have to be held in place somehow, but the holding structure should not alter the field produced. So the tori are extended away from the trapping region along the z -axis direction, in other words, held on hollow cylinders of the same thickness (Figure 6.6(a)). The metal cylinder is fixed inside an insulating hollow cylinder. In Figure 6.6(c), it is the tube mounted at the centre of the PCB coil. The

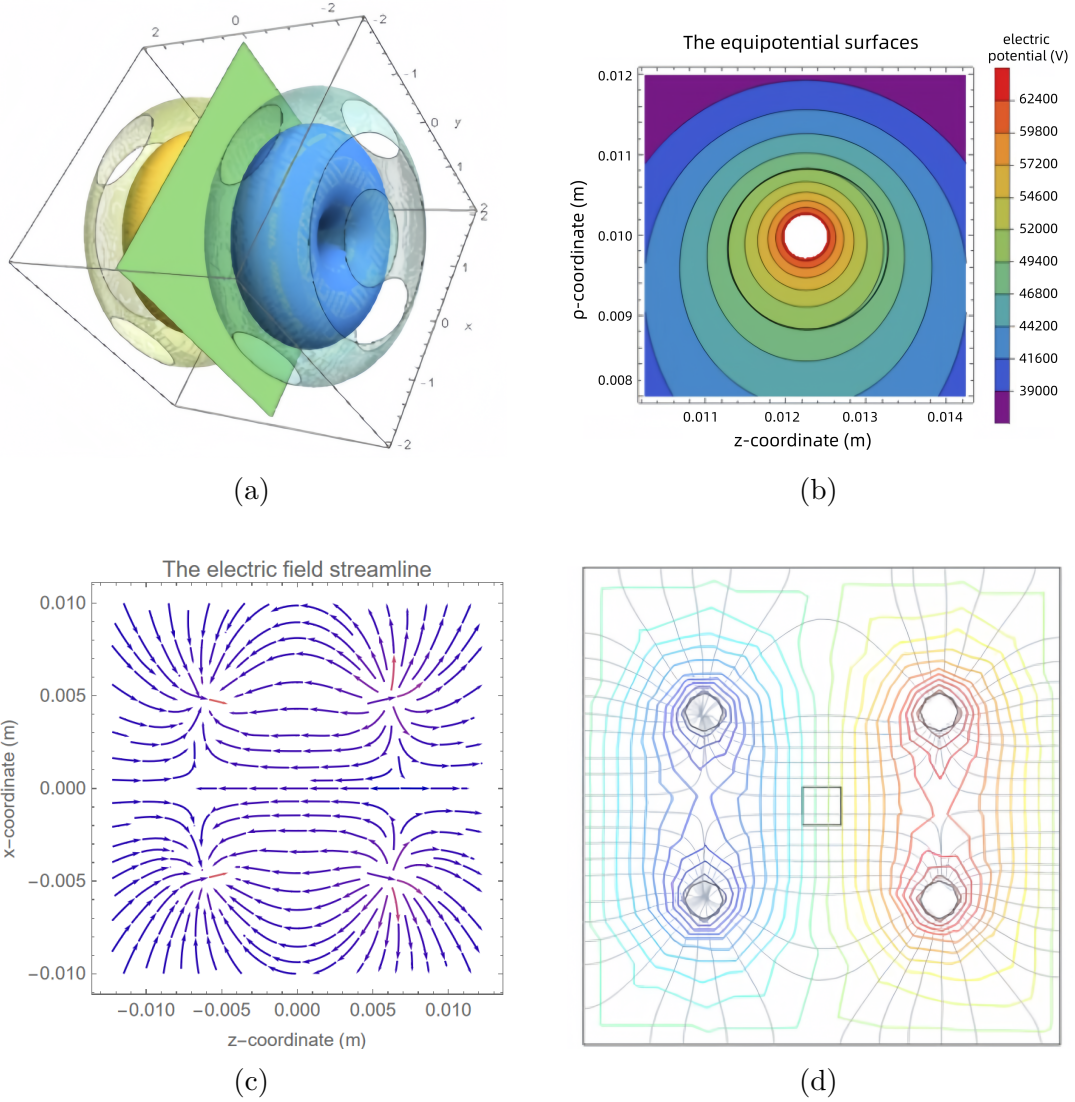


Figure 6.5: (a) Equal-potential surfaces of a pair of ideal rings. (b) Equal-potential surfaces on the cross-section view of an ideal ring placed at $z = 12.2$ mm, $\rho = 0$. (c) The streamline of electric field generated by a pair of ideal rings of 5 mm radius, separated by $5\sqrt{6}$ mm. (d) The streamline of electric field generated by a pair of tori with the minor radius of 1 mm, and the major radius of 5 mm, separated by $5\sqrt{6}$ mm.

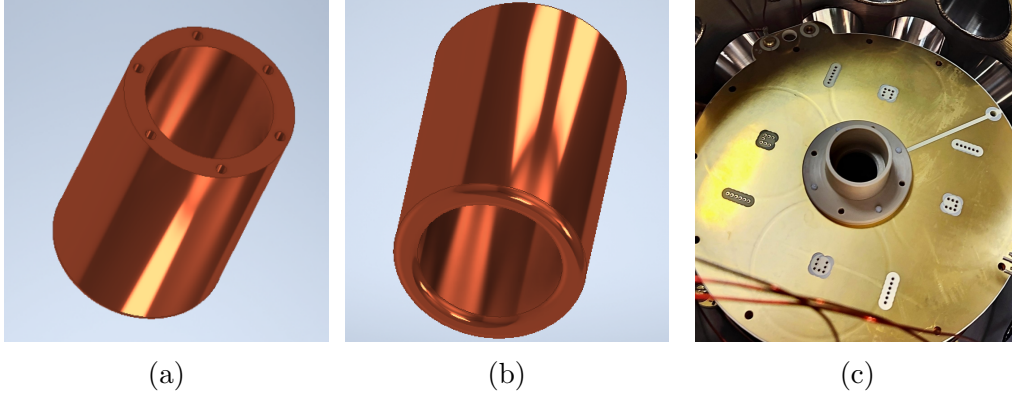


Figure 6.6: (a) An extended torus with screw holes at the end. It is to be screwed on the inner edge of an insulator. (b) The other end of the extended torus, where the electrode is mounted. (c) The electrode mount screwed to a PCB coil.

full assembly of the electrode holder and mount with the other parts of the MOT structure is shown in Figure 5.9.

The final choice of the size, voltage and displacement is determined as shown in Table 6.1. The major and minor radii of the tori are 7.5 mm and 1.5 mm respectively, leaving a diameter of 12 mm for laser beams. The closest distance of the two tori is 15.56 mm, and the voltage is ± 21.5 kV. Along the z -axis, there is a field of around 22 kV/cm covering the area of the trapped molecules, as is plotted in blue in Figure 6.7. The gradient of the field strength applies a force that pushes the molecules off the trap, and the acceleration is given by

$$\vec{a} = \frac{\vec{\nabla} \left(\vec{E}(x, y, z) \cdot \vec{\mu} \right)}{m}. \quad (6.28)$$

Here, $\vec{\mu}$ is the dipole moment of the CaF molecule, and m is its mass. We consider the situation that $\vec{\mu}$ is aligned with $\vec{E}(x, y, z)$, so the acceleration becomes

$$\vec{a} = \frac{\vec{\nabla} \left(\vec{E}(x, y, z) \right) \cdot |\vec{\mu}|}{m}. \quad (6.29)$$

The acceleration is also plotted in Figure 6.7 with green line. Within the region of $z = \pm 0.001$ m, the electric field varies by 0.05%, and the acceleration is below 40 m/s².

A model with $R = 7$ mm, $r = 1$ mm is tested against disturbance in size and position. An electrode voltage of ± 21 kV is applied, and the central field strength is 22.86 kV/cm. The major radius is varied across $\pm 10\%$, and the distance L is

Electrode major radius	7.5 mm
Electrode minor radius	1.5 mm
Distance	15.56 mm
Holder major radius	11 mm
Holder minor radius	2 mm
Holder length	24 mm
Voltage	± 21.5 kV

Table 6.1: The final choice of the size of electrodes.

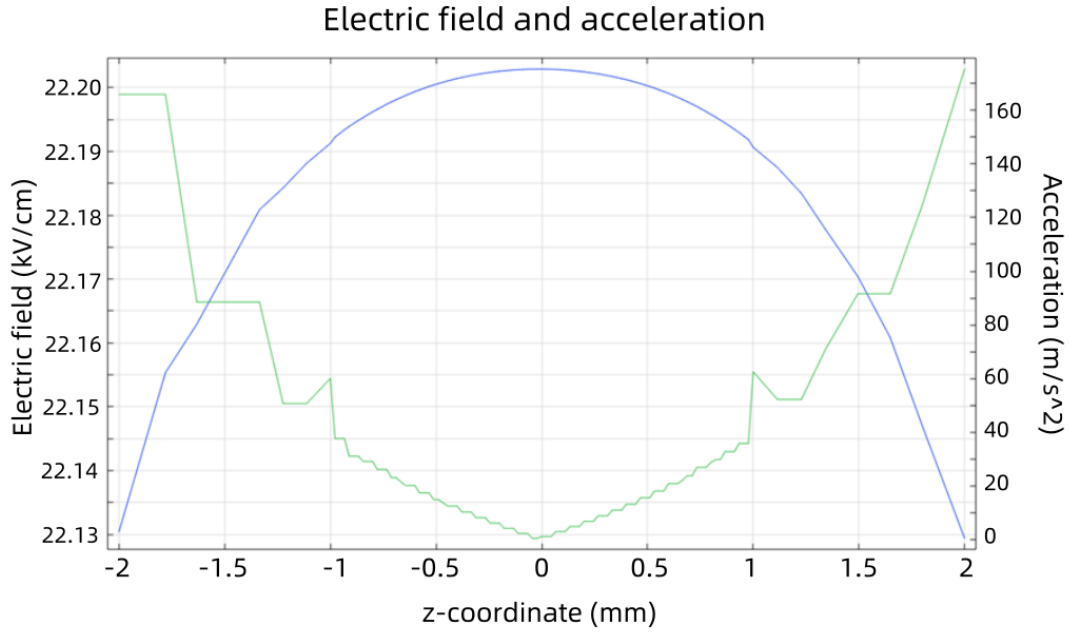


Figure 6.7: The electric field (blue) and acceleration (green) of CaF molecules in an electric field generated with a pair of tori in Table 6.1. The slope at $z = \pm 0.001$ m is due to the resolution of the simulation, not the jump of the actual electric field.

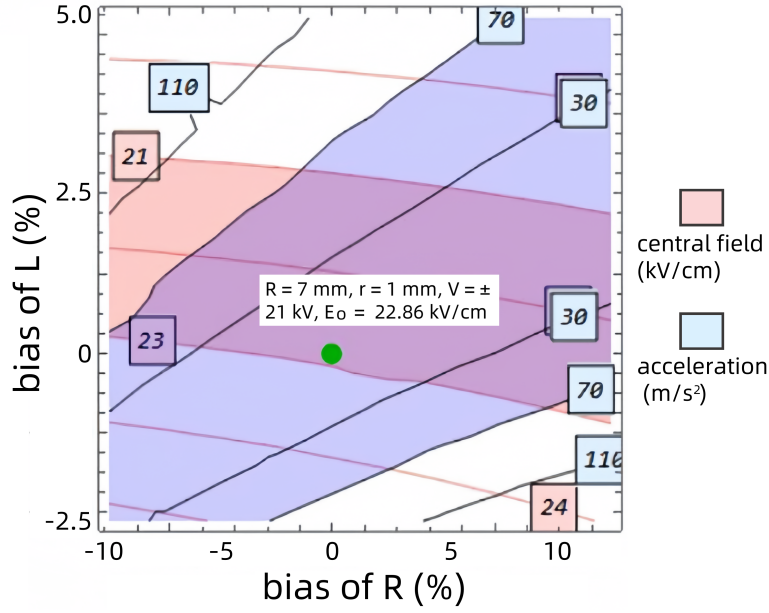


Figure 6.8: The electric field and acceleration of a pair of bias electrodes.

varied across $\pm 5\%$. The electric field and acceleration at the centre of the trap are plotted against the bias from the original model, as shown in Figure 6.8. The value of the original model is marked with a green dot. We consider the acceptable value of the central field is between 21 and 23 kV/cm, and for the acceleration it is below 70 m/s², which are shaded in pink and purple respectively. The crossing area is the tolerance.

6.4 Improving the MOT

The MOT produced in our apparatus needs to be optimised, so that it is qualified for further experimental steps. Several methods are implemented to improve its characteristics. The slowing power has been found to be limited by the instability of the EOM crystal and the fibre coupling efficiency, and the MOT appears to require more v_{10} power. To saturate the power of the slowing and v_{10} lasers, we redesigned the optics by moving the lasers closer to the science chamber, avoiding a long transition with fibre and doubling the power.

In addition to this, there are some interesting discoveries that have helped to capture more molecules. The most effective one is to mix the v_{21} repump laser into the slowing beam. It is shifted by 80 MHz with an AOM, and then broadened by EOMs of 24 and 78 MHz. This results in a 50% increase in the number of molecules. Another idea is to broaden the BX laser with an EOM, whose frequency is scanned

between 0 and 30 MHz. The result suggests that when it is broadened between 5 and 10 MHz, the number of molecules increases by 10%. When it goes beyond 12 MHz, the number drops below the unbroadened one.

After all the modifications above, the MOT is characterised again. The number of molecules has increased to 4×10^3 . It has a diameter of 2 mm, and a standard deviation of 0.5 mm. The scattering rate is measured to be 2.9 MHz, and the lifetime is 40 ms. The trap frequency is 113 Hz, the damping constant is 761 s^{-1} , and the temperature is around 1 mK.

We have two further ideas to increase the number of molecules in the MOT. The first is to shorten the beam line. The beam line is shown in Figure 4.3. The plan is to remove the ISO100 connector, and replace the ISO100-CF100 converter with a shorter one. The length between the cell and the MOT will be reduced from 1200 mm to 975 mm, and we expect this to increase the number of molecules by a factor of 3. The second is to apply 2D transverse cooling after the source. The transverse cooling chamber is shown in Figure 4.2. There are 2 pairs of parallel mirrors to reflect the BX laser, covering a distance of about 200 mm. It is expected to improve the number of molecules by 4 times. With these methods applied, the number of molecules will increase to 5×10^4 , and the number density will be on the magnitude of 10^6 cm^{-3} .

6.5 Conclusion

During my three years of PhD work in the lab, I have built a new experiment with my colleagues from scratch. It is aimed to cool CaF molecules to Bose-Einstein condensation with the technique of direct laser cooling, followed by evaporative cooling. This is a new research area with huge potential. A dipolar molecule BEC shows different phenomena from an isotropic atom BEC, for example, the stable configurations, the droplet behaviours and the long range coherence. After loading into optical lattices, it can simulated systems with dipole-dipole interaction, which is still an open area to explore.

I set up a cryogenic buffer gas source, which produces molecular beams at a velocity between 150-200 m/s with a molecular flux of $3 \times 10^{10}/\text{sr}/\text{pulse}$. The impact of different factors on the beam quality, such as gases and the ablation laser, has been studied. I then slowed the molecules to the MOT capture velocity by chirp

slowing with a repump laser, and optimised the slowing by varying the chirp parameters. At the same time, the science chamber for MOT and further experiments was constructed. It features overlapped MOT, magnetic trap and optical dipole trap, a radiation shield to reduce vibrational heating due to blackbody radiation, and a pair of non-orthogonal laser beams. I produced a seed-amplifier system and an ECDL as the repump lasers of our MOT. I also designed a pair of electrodes for the electric shielding of CaF molecules. Theory and simulation suggest that when all the process in our scheme successfully works out, there will be a CaF BEC of thousands of molecules at 250 nK, which provides a platform to study molecular collisions and the physics of strongly-interacting many-body quantum systems.

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