

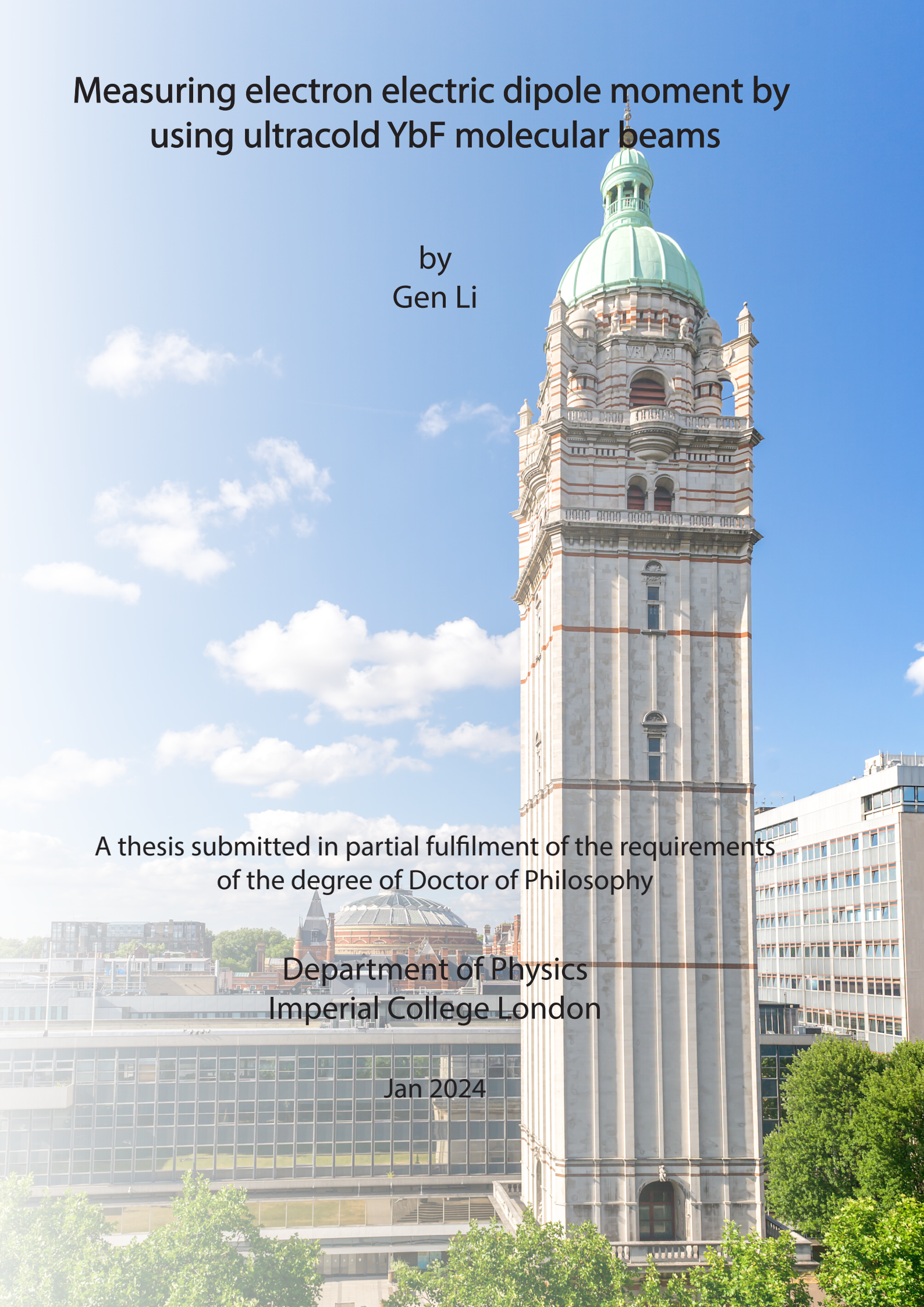
# Measuring electron electric dipole moment by using ultracold YbF molecular beams

by  
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A thesis submitted in partial fulfilment of the requirements  
of the degree of Doctor of Philosophy

Department of Physics  
Imperial College London

Jan 2024



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Measuring electron electric dipole moment by using ultracold YbF  
molecular beams

PhD dissertation . 1st Jan 2024

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# Declaration

I declare that the work presented in this thesis is my own. I have acknowledged the work of others or referenced the correct sources wherever required in this thesis.

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# Abstract

A non-zero electron electric dipole moment (eEDM) is an evidence of  $T$  violation which encourages researchers to push the limit of measuring eEDM.

In this work, we will show the progress towards measuring eEDM using ultracold Ytterbium fluoride ( $^{174}\text{YbF}$ ) molecular beams. We have produced YbF molecules by using a 4K Helium buffer gas source. We have applied two-dimensional transverse laser cooling to collimate the molecular beam in the laser cooling region. We have observed sub Doppler cooling effect on YbF molecules (the Doppler limit of YbF is  $137\mu\text{K}$ ). We have obtained a shot eEDM sensitivity on ultracold YbF molecules around  $10^{-25} e \cdot \text{cm}$ . We have optically pumped 85% of ultracold molecules to the ground state before they enter the interaction region. In the interaction region, we have applied STIRAP to prepare and read out the eEDM state. We have reduced the noise of magnetic field in the interaction region to  $1 pT$ . In the detection region, we have achieved over 95% detection efficiency on YbF molecules by using laser-induced fluorescence.

We have systematically studied the simulation of laser cooling in terms of laser intensity, laser frequency detuning, polarization configurations and magnetic field. We have also used optical Bloch equations (OBEs) to simulate the transition schemes in the optical pumping, STIRAP and detection regions. The calculation of OBEs can explain our experimental observation and give insights on improving the experimental design.

**Keywords** — Electron electric dipole moment, Ytterbium fluoride, laser cooling, ultracold molecules, optical Bloch equations, state manipulation, optical pumping.



# Acknowledgement

Thanks Sanja for your warm-hearted support for administration. I remembered the first day I came to Imperial, you showed me my desk. Also, at each review stage of the PhD, I came to your office to ask what forms I had to fill in. You were always patient enough to help me.

Thanks for work shop staff, Jon Dyne and Dave Pitman. The first item I asked Jon to produce was a water cooling block made by copper. Several days later, Jon gave it to me. He modified it to improve the function. The cooling block was shinny and compact. I was impressed when I got it. I worked with Dave to cut matt black pannel to block lasers on the optical table for laser safety reason. Dave was very efficient. He finished designing and cutting six pieces of pannels in one hour, which helped our experiments quickly back online.

Thanks for Michael Ziemba for your efforts in the lab. I remember we went to lab on weekend to finish the integration of the interaction region. The interaction region was extremely heavy. We had to use trolley jacks to move it. We spent 15 mins to move the interaction region for 1 cm. So it can be imagined how much efforts we made to complete the entire machine.

Thanks for Freddie Collings for your efforts in the lab. I remembered we worked on optical pumping region. We moved lasers from the last generation EDM machine to our lab. There were many optical components and uncountable number of cables. We spent one week to move all these stuff and each day was exhausted. Moreover, I learned a lot from you about the c# programming. Our experiments were commanded by c# programs. I remembered that we spent an entire day to debug a data acquisition problem. Eventually we found that there was an improper definition for sample rate in the code.

Thanks for Mike Tarbutt for teaching me physics about molecular structure. I remembered that you showed me how to apply decomposition rule to a system containing multiple angular momenta. I also remembered that you showed me how to properly fit a dataset in Mathematica when we processed data obtained from the last generation EDM machine.



Thanks for Christopher Ho for your teaching and support from multiple aspects. The first six months of my PhD I worked with you on the last generation EDM machine. I learned lots of physics and EDM technique from you. The first time I came to lab, you spent half a day explaining the YbF energy spectra and transitions to me. To be honest, I pretended to show you I can follow you, but actually I understood nothing. The first lab work we did together was to make some thick copper wires to warp around a metal shield to test degaussing. I remembered the thick copper wires were very hard to be bent. On that day after finishing the job, I even didn't need to go to gym to work out. The most impressive work we did together was to pull out the electric field plates out of the EDM chamber. The plates were very heavy and we had to stand on a 3-meter ladder and hold them, which made both of us become sweaty in 10 mins. It was the most heavy job I did except for integrating the interaction region into the ultracold EDM machine.

Thanks for Rhys Jenkins and Alauze Xavier. You were the people I worked with most of the time in the lab. We did and achieved so many things together. From maintaining the source, setting up lasers, laser cooling, optical pumping, improving detection region, etc. Xavier left the team last year. Before his left, he taught Rhys and me how to operate the ultracold EDM machine. The system was complicated. It took more than 3 months to finish the tutorial. I remembered that the first time we opened the source chamber. I was astonished because there were so many temperature sensors and wires. Rhys and I had to note down each component and to understand the function of them. The next job Xavier taught us was to operate laser cooling region. The most difficult part was to align the multi-reflection laser path with respect to molecular beams. During the first time we tried the alignment ourselves, we couldn't find any cold molecules on the EMCCD camera. Xavier said we had to try more. So Rhys and I started from 1d horizontal cooling and playing with magnetic field and polarization. After several days we obtained 1d cooling. Then we applied the same strategy to make the vertical cooling work and combine them together to get the 2D cooling. We also worked on optical pumping region. It was my first time to work on microwave and rf. I learned a lot from both of you. Xavier showed me the basic functions of the microwave and rf components. Rhys further improved their functions including pulsing the microwave in time, which became a powerful function for future EDM experiments. I also appreciate Rhys' efforts on reviewing the drafts of my PhD thesis. In summary, it is my pleasure to work with you guys.

Thanks for my co-supervisor Lim Jongseok. When we integrated the interaction region to the whole machine, laser cooling didn't work. I came to you for help. You showed me how to use a fibre scope. When we checked the fibres of laser

cooling lasers, it was surprised that the fibre tips were damaged. It was one of the reasons laser cooling didn't work. You also explained to me the structure of fibres. When we set up optical pumping lasers, I remembered you explained to me how a second-harmonic generator works and how to set it up. The alignment of the SHG crystal and lasers was difficult. You said the trick was to be patient. Finally, I made the alignment work and we had decent output laser power for optical pumping region. Thanks for your suggestion. I also appreciate your efforts on reviewing the drafts of my PhD thesis.

Finally, I would like to show the most grateful thanks and respect to my supervisor Ben Sauer. I remembered the first time we met was through an online meeting because it was COVID time. The interview was about one hour during which we went through some concepts about quantum mechanics and what I did in Master. The entire process was pleasant. You also invited me to come to London to visit the lab and told me a two day living cost can be covered. I really appreciated it. But I couldn't get the UK visa because the Embassy was closed during COVID. After I started my PhD, probably I was the student who turned up in your office most frequently. We had supervisor meeting at least once a week. I remembered during the week I was learning molecular structure, I booked 3 supervisor meetings in that week. I was sorry I bothered you too much. During my PhD, I learned a lot from you from physics and experimental skills. I remembered on that day it was about 4pm, you were tired after finishing one-day teaching and other jobs. But you were still welcome me to come to your office. The problem we discussed on that day was to calculate the coupling between spin and nuclei rotation in the effective Hamiltonian of YbF. Your patience was beyond my expectation. You spent half an hour checking my chinese-style Mathematica code and eventually you found a mistake in a  $3-j$  symbol. Another impressive experience was that week containing 3 supervisor meetings. I was focusing on how to deal with the rotational term in the Hamiltonian. The idea was straightforward. But it became difficult when it came to practice on YbF molecules. You taught me how to do block diagonalization to solve the problem. Moreover, when I was doing optical Bloch equation calculation, you and Chris gave me lots of guidance which was very helpful. In terms of lab work, you also taught me a lot and provided lots of support. I remembered when I was working on PMTs, you taught the circuit of the PMT amplifier and showed me how to calibrate a PMT. Another impressive lab experience was that you fixed the reference laser. We were out of methods when the reference laser was broken and came to you for help. You opened the box of the laser and tested each part of the circuit and confirmed the problem. On the next day, you gave us a fixed laser. I believed your knowledge on lasers was better than a professional engineer. Another

thing I remembered clearly was that when I asked you to buy fibre couplers for the optical pumping region, I asked for two pieces. But you bought three for me, which allowed me to make mistakes. Also, thanks for your tolerance and patience on the naive mistakes I made. Maybe sometimes I made mistakes I even didn't realize. To be honest, I don't know how to properly say thanks to you. Writing a paragraph of acknowledgement is very superficial. Probably the best way is that in the future I can become a physicist who you can be proud of.

# Contents

|                                                                  |              |
|------------------------------------------------------------------|--------------|
| <b>List of Figures</b>                                           | <b>xvii</b>  |
| <b>List of Tables</b>                                            | <b>xxvii</b> |
| <b>1 Introduction</b>                                            | <b>1</b>     |
| 1.1 Why measuring electron electric dipole moment? . . . . .     | 1            |
| 1.2 The history of eEDM . . . . .                                | 4            |
| 1.3 A simple YbF eEDM experiment . . . . .                       | 7            |
| 1.4 Thesis structure . . . . .                                   | 10           |
| <b>2 Structure of YbF</b>                                        | <b>13</b>    |
| 2.1 History of YbF . . . . .                                     | 13           |
| 2.2 Molecular structure . . . . .                                | 14           |
| 2.2.1 Born Oppenheimer approximation . . . . .                   | 14           |
| 2.2.2 Electronic structure . . . . .                             | 17           |
| 2.2.3 Vibrational, rotational and hyperfine structures . . . . . | 18           |
| 2.3 Interactions with external fields . . . . .                  | 25           |
| 2.3.1 Wigner Eckart theorem . . . . .                            | 25           |
| 2.3.2 Transition dipole matrix . . . . .                         | 26           |
| 2.3.3 Selection rules . . . . .                                  | 30           |
| 2.3.4 Stark effect . . . . .                                     | 32           |
| 2.3.5 Zeeman interaction . . . . .                               | 32           |
| 2.3.6 EDM interaction . . . . .                                  | 34           |
| 2.4 Summary . . . . .                                            | 34           |
| <b>3 Optical Bloch equations and laser cooling</b>               | <b>35</b>    |
| 3.1 Optical Bloch equations . . . . .                            | 35           |
| 3.1.1 Density matrix . . . . .                                   | 35           |
| 3.1.2 Lindblad master equation . . . . .                         | 36           |
| 3.2 Laser cooling . . . . .                                      | 40           |
| 3.2.1 Force operator . . . . .                                   | 41           |
| 3.2.2 1D laser cooling . . . . .                                 | 44           |
| 3.2.3 Dark state destabilization . . . . .                       | 54           |
| 3.2.4 2D laser cooling . . . . .                                 | 58           |

|          |                                                   |           |
|----------|---------------------------------------------------|-----------|
| 3.3      | State manipulation . . . . .                      | 61        |
| 3.3.1    | RF $\pi$ pulse . . . . .                          | 61        |
| 3.3.2    | STIRAP . . . . .                                  | 63        |
| 3.4      | Summary . . . . .                                 | 68        |
| <b>4</b> | <b>Experimental overview</b>                      | <b>69</b> |
| 4.1      | The whole machine . . . . .                       | 69        |
| 4.2      | Source region . . . . .                           | 71        |
| 4.3      | Laser cooling region . . . . .                    | 74        |
| 4.3.1    | Chamber . . . . .                                 | 74        |
| 4.3.2    | Lasers . . . . .                                  | 75        |
| 4.3.3    | Multi-reflection optics . . . . .                 | 78        |
| 4.4      | Optical pumping region . . . . .                  | 81        |
| 4.4.1    | Chamber . . . . .                                 | 81        |
| 4.4.2    | Lasers and microwaves . . . . .                   | 82        |
| 4.4.3    | Multi-reflection optics . . . . .                 | 85        |
| 4.5      | Interaction region . . . . .                      | 86        |
| 4.5.1    | Chamber . . . . .                                 | 86        |
| 4.5.2    | Electric field . . . . .                          | 86        |
| 4.5.3    | Magnetic field . . . . .                          | 87        |
| 4.5.4    | STIRAP . . . . .                                  | 88        |
| 4.6      | Detection region . . . . .                        | 91        |
| 4.6.1    | Chamber . . . . .                                 | 91        |
| 4.6.2    | Lasers and microwaves . . . . .                   | 91        |
| 4.6.3    | PMTs and cameras . . . . .                        | 93        |
| 4.7      | Summary . . . . .                                 | 96        |
| <b>5</b> | <b>Experimental results</b>                       | <b>97</b> |
| 5.1      | Laser cooling region . . . . .                    | 97        |
| 5.1.1    | Images of cold molecules . . . . .                | 97        |
| 5.1.2    | Magnetic field and polarization . . . . .         | 100       |
| 5.1.3    | Laser detuning and laser intensity . . . . .      | 102       |
| 5.1.4    | Transverse temperature . . . . .                  | 103       |
| 5.1.5    | EDM sensitivity of cold molecular beams . . . . . | 104       |
| 5.2      | Optical pumping region . . . . .                  | 108       |
| 5.2.1    | Laser Intensity . . . . .                         | 108       |
| 5.2.2    | Microwave power . . . . .                         | 109       |
| 5.2.3    | Interaction time . . . . .                        | 110       |
| 5.2.4    | Power broadening . . . . .                        | 110       |



|          |                                              |            |
|----------|----------------------------------------------|------------|
| 5.2.5    | Optical pumping efficiency . . . . .         | 113        |
| 5.3      | Interaction region . . . . .                 | 115        |
| 5.3.1    | STIRAP . . . . .                             | 115        |
| 5.3.2    | Magnetic field noise . . . . .               | 119        |
| 5.4      | Detection region . . . . .                   | 120        |
| 5.4.1    | Microwave power . . . . .                    | 121        |
| 5.4.2    | Detection efficiency . . . . .               | 121        |
| 5.4.3    | Microwave crosstalk . . . . .                | 123        |
| 5.5      | Summary . . . . .                            | 125        |
| <b>6</b> | <b>Conclusions and outlook</b>               | <b>127</b> |
| 6.1      | Conclusions . . . . .                        | 127        |
| 6.2      | Outlook . . . . .                            | 129        |
| <b>7</b> | <b>Appendix</b>                              | <b>133</b> |
| 7.1      | WE theorem and decomposition rule . . . . .  | 133        |
| 7.2      | Transverse temperature measurement . . . . . | 139        |
| 7.3      | Lasers and microwaves . . . . .              | 140        |
|          | <b>Bibliography</b>                          | <b>141</b> |



# List of Figures

|     |                                                                                                                                                                                                                                                                                                                                           |    |
|-----|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 1.1 | (a) The time and parity reversals of an atom or a molecule which has a permanent EDM. (b) After a $T$ reversal, the spin flips but the $d_e$ remains unchanged [Kar10]. . . . .                                                                                                                                                           | 3  |
| 1.2 | History of eEDM measurements and relevant work. Blue: $CPT$ theorem related work which was introduced in the last section. Green: Theory of polar molecules containing high- $Z$ atoms. Red: eEDM experiments utilising paramagnetic atomic and molecular species. . . . .                                                                | 6  |
| 1.3 | Illustration of one shot. A shot happens from left to the right. Corresponding states in each region is also labelled. . . . .                                                                                                                                                                                                            | 7  |
| 1.4 | Illustration of the thesis structure. Arrows indicate the correlation between chapters and sections. . . . .                                                                                                                                                                                                                              | 10 |
| 2.1 | History of the $^{174}\text{YbF}$ molecular structure (selected publications). . . . .                                                                                                                                                                                                                                                    | 13 |
| 2.2 | (a) Coordinates of the YbF diatomic molecule. (b) Illustration of the rotational motion of Yb and F nuclei. The subscripts $A$ and $B$ stand for Fluorine and Yb atom, respectively. . . . .                                                                                                                                              | 14 |
| 2.3 | Illustration of a potential energy curve in the ground state of a diatomic molecule. The $x$ axis is in the unit of Bohr radius ( $a_0$ ). Vibrational and rotational levels are indicated by red and green dashed lines, respectively. . . . .                                                                                           | 19 |
| 2.4 | (a) Definition of P and R transitions. (b) Illustration of Rovibrational spectrum. . . . .                                                                                                                                                                                                                                                | 21 |
| 2.5 | Energy levels of the $^{174}\text{YbF}$ molecule used in this work. (a) is the first electronic, vibrational and rotational levels. (b) shows the hyperfine levels which connect energy levels on the right hand side of (a). It is an illustration of the YbF energy levels. Numbers have no correlation with the scale of gaps. . . . . | 24 |
| 2.6 | (a) Stark shift for rotational levels. (b) Zeeman shift of hyperfine levels $ N, F\rangle$ . Both in $X^2\Sigma^+$ ( $\nu=0$ ) state. . . . .                                                                                                                                                                                             | 33 |
| 3.1 | Excited state population as a function of laser frequency detuning under three laser intensities. . . . .                                                                                                                                                                                                                                 | 39 |

|      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |    |
|------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 3.2  | Time evolution of a two-level quantum system. Laser is on resonance.<br>(a) Time evolution of population terms without spontaneous decay. (b)<br>Time evolution of the coherence without spontaneous decay. (c) Time<br>evolution of the population terms with spontaneous decay. (d) Time<br>evolution of the coherence with spontaneous decay. . . . .                                                                                                              | 39 |
| 3.3  | The history of laser cooling from 1970 to 2021. Theoretical works are<br>highlighted in red on the left. Experimental works are highlighted in blue<br>on the right. . . . .                                                                                                                                                                                                                                                                                          | 40 |
| 3.4  | Illustration of the Sisyphus effect in a $\text{lin}\perp\text{lin}$ red-detuned laser field. The<br>top part shows the reduction of kinetic energy after each optical pumping<br>event. The bottom part shows the ac Stark shift of the $m_F = 0, \pm 1$<br>ground states. . . . .                                                                                                                                                                                   | 46 |
| 3.5  | Polarization configurations being studied in this work. Rows (a), (b), (c)<br>and (d) are $\sigma^+\sigma^+$ , $\sigma^+\sigma^-$ , $\text{lin}\perp\text{lin}$ and $\text{lin}\parallel\text{lin}$ , respectively. . . . .                                                                                                                                                                                                                                           | 47 |
| 3.6  | Summary of 1D laser cooling for a $ F = 2\rangle$ to $ F' = 1\rangle$ system. (a)<br>and (b) cooling forces in all velocity range and low velocity range with<br>$\delta = -2.5\Gamma$ and $I = I_{sat}$ . (c) Cooling forces calculated with different laser<br>intensities with $\delta = -2.5\Gamma$ . (d) Cooling forces calculated with different<br>laser frequency detunings with $I = I_{sat}$ . (e) OBEs at zero velocity with<br>$\theta = \pi/4$ . . . . . | 50 |
| 3.7  | Summary of 1D laser cooling for a $ F = 1\rangle$ to $ F' = 1\rangle$ system. (a)<br>and (b) cooling forces in all velocity range and low velocity range with<br>$\delta = -2.5\Gamma$ and $I = I_{sat}$ . (c) Cooling forces calculated with different<br>laser intensities with $\delta = -2.5\Gamma$ . (d) Cooling forces calculated with<br>different laser frequency detunings with $I = I_{sat}$ . (e) OBEs at zero<br>velocity with $\theta = \pi/4$ . . . . . | 51 |
| 3.8  | Summary of 1D laser cooling for a $ F = 0\rangle$ to $ F' = 1\rangle$ system. (a)<br>and (b) cooling forces in full velocity range and low velocity range with<br>$\delta = -2.5\Gamma$ and $I = I_{sat}$ . (c) $\sigma^+\sigma^-$ polarization with $\delta = -2.5\Gamma$ . (d)<br>$\theta = \pi/4$ polarization with $\delta = -2.5\Gamma$ . (e) Force with various detuning<br>for all polarizations. (f) OBEs for all polarizations. . . . .                      | 53 |
| 3.9  | Excited state population as a function of normalised magnetic field and<br>polarization angle. . . . .                                                                                                                                                                                                                                                                                                                                                                | 54 |
| 3.10 | Cooling force of a $ F = 2\rangle$ to $ F' = 1\rangle$ system under various polarization<br>configurations with magnetic field applied. (a) $\text{lin}\parallel\text{lin}$ ( $\theta = 0$ ). (b) $\text{lin}\perp\text{lin}$<br>( $\theta = \pi/2$ ). (c) $\sigma^+\sigma^-$ polarization. $\delta = -2.5\Gamma$ , $I = I_{sat}$ for all the plots. . . . .                                                                                                          | 55 |
| 3.11 | Cooling force of a $ F = 1\rangle$ to $ F' = 1\rangle$ system under various polarization<br>configurations with magnetic field applied. (a) $\text{lin}\parallel\text{lin}$ ( $\theta = 0$ ). (b) $\text{lin}\perp\text{lin}$<br>( $\theta = \pi/2$ ). (c) $\sigma^+\sigma^-$ polarization. $\delta = -2.5\Gamma$ , $I = I_{sat}$ for all the plots. . . . .                                                                                                          | 56 |

|      |                                                                                                                                                                                                                                                                                                                                                                                                            |    |
|------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 3.12 | Cooling force of a $ F = 0\rangle$ to $ F' = 1\rangle$ system for $\text{lin}  \text{lin}$ , $\text{lin}\perp\text{lin}$ and $\sigma^+\sigma^-$ polarization configurations. . . . .                                                                                                                                                                                                                       | 57 |
| 3.13 | (a) Acceleration versus velocity for $XY_{  }$ . (b) Excited state population versus velocity for $XY_{  }$ . (c) Acceleration versus velocity for $XY_{\perp}$ . (d) Excited state population versus velocity for $XY_{\perp}$ . Laser intensity $I = 100I_{\text{sat}}$ . Laser detuning $\delta = 6\Gamma$ . . . . .                                                                                    | 59 |
| 3.14 | $XY_{  }$ polarization configuration. (a) Acceleration versus velocity. (b) Excited state population versus velocity. Magnetic field $B = 1$ Gauss. Laser intensity $I = 100I_{\text{sat}}$ . . . . .                                                                                                                                                                                                      | 60 |
| 3.15 | $XY_{  }$ polarization configuration. (a) Acceleration versus velocity. (b) Excited state population versus velocity. Magnetic field $B = 1$ G. Laser detuning $\delta = 6\Gamma$ . . . . .                                                                                                                                                                                                                | 60 |
| 3.16 | (a) Rabi oscillations of the ground state population for various RF detunings. (b) Ground state population versus RF detuning for various RF durations. . . . .                                                                                                                                                                                                                                            | 63 |
| 3.17 | OBEs for the single STIRAP. . . . .                                                                                                                                                                                                                                                                                                                                                                        | 64 |
| 3.18 | Transfer efficiency vs peak-to-peak distance between the pump and Stokes lasers. . . . .                                                                                                                                                                                                                                                                                                                   | 65 |
| 3.19 | Transfer efficiency vs Stokes and pump lasers detuning. . . . .                                                                                                                                                                                                                                                                                                                                            | 65 |
| 3.20 | Simulation for the double STIRAP and spin precession. The five plots share the same $x$ axis. From top to bottom, the first plot shows the Rabi frequencies of pump laser and Stokes laser in time. The second plot shows the evolution of the population of the four states. The third, fourth and fifth plots show the evolution of the coherence of $\rho_{12}$ , $\rho_{13}$ and $\rho_{23}$ . . . . . | 67 |
| 4.1  | The CAD image of the ultracold eEDM beamline machine. . . . .                                                                                                                                                                                                                                                                                                                                              | 70 |
| 4.2  | CAD drawing of the cross section of the cryogenic buffer gas cell. . . . .                                                                                                                                                                                                                                                                                                                                 | 71 |
| 4.3  | Illustration of the entire cryogenic buffer gas source [Alex2020]. . . . .                                                                                                                                                                                                                                                                                                                                 | 73 |
| 4.4  | The illustration of LC region. Dimensions of the LC chamber and windows used to generate multiple laser paths are labelled in the picture. Unit is mm. The multi-reflection optics is mounted next to the chamber which will be shown in Fig. 4.8. . . . .                                                                                                                                                 | 74 |
| 4.5  | Optics setup for laser cooling region. BS: beam sampler. CL: convex lens. $\lambda/2$ : half wave plate. DC: dichroic mirror. FM: flip mirror. PBS: polarizing beam splitter. RP: repump. TCL: transfer cavity lock. WM: wavemeter. . . . .                                                                                                                                                                | 75 |

|      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |    |
|------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 4.6  | YbF energy levels being used in the laser cooling region. Optical transtions are shown in green and yellow arrow. The branching ratios of vibrational levels are shown in gray wavy arrows. Cooling and repumping transitions are indicated by solid arrows. The hyperfine levels in $ X^2\Sigma^+, \nu=0, N=1\rangle$ are shown with a blue detuning $\Delta$ . The sidebands of repump lasers are not shown. $V_0$ laser is in green because it is visibly green in reality. Same reasons for $v_1$ and $v_2$ are drawn in yellow.                        | 77 |
| 4.7  | Measured polarisation of the LC fibers using a commercial polarimeter.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | 78 |
| 4.8  | Multi-reflection optics of LC. This figure shows the setup for horizontal cooling. The vertical cooling setup is same as horizontal cooling. This setup is on the machine. $\lambda/2$ : half wave plate. . . . .                                                                                                                                                                                                                                                                                                                                           | 79 |
| 4.9  | Image of multi-reflection optics of horizontal cooling in the LC region. Vertical cooling has the same setup. Copper wires are used to generate magnetic field to destabilize dark states. . . . .                                                                                                                                                                                                                                                                                                                                                          | 80 |
| 4.10 | The illustration of OP region. The dimension of the OP chamber is shown. Microwave horns are highlighted. The multi-reflection optics is mounted next to the chamber which will be shown in Fig. 4.13. . . . .                                                                                                                                                                                                                                                                                                                                              | 81 |
| 4.11 | YbF energy levels being used in the optical pumping region. The hyperfine levels in $ X^2\Sigma^+, \nu=0, N=0, 1 \text{ and } 2\rangle$ are shown in blue. The orange arrows stands for the microwave transitions between $N=1$ and 2 rotational levels. The green arrows illustrate the optical transitions between the ground and the first excited states. All the microwave frequencies are around 28.9 GHz. We simply label them 28.9 GHz here. The 542.769 THz frequency has a 185 MHz sideband generated by an AOM, which is not shown here. . . . . | 83 |
| 4.12 | Optics setup for OP region. AMP: amplifier. BD: beam dump. BS: beam sampler. CL: convex lens. $\lambda/2$ : half wave plate. DC: dichroic mirror. FM: flip mirror. PBS: polarizing beam splitter. SHG: second-harmonic generation. TCL: transfer cavity lock. WM: wavemeter. . . . .                                                                                                                                                                                                                                                                        | 84 |
| 4.13 | Multi-reflection optics for OP. The setup is on the machine. CL: convex lens. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | 85 |
| 4.14 | The CAD drawing of the interaction region. Key components are highlighted. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | 86 |
| 4.15 | The illustration of the electric field plates (units in mm). . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 87 |
| 4.16 | Illustration of coils which generate magnetic field for the spin precession experiment. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                                                             | 88 |

|      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |     |
|------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 4.17 | STIRAP optics. CL: convex lens. WM: wavemeter. $\lambda/2$ : half wave plate. PBS: polarizing beam splitter. PP: prism pair. WP: Wollaston prism. There is a beam splitter to further split the two beams into four beams for state preparation and readout, which is not shown here. . . . .                                                                                                                                                                                                                              | 89  |
| 4.18 | YbF energy levels being used in STIRAP. 170 MHz is the energy difference between $F=0$ and 1 states, which is not applied in the actual system. The $\pi$ and $\sigma^\pm$ beams correspond to the AOM beam and unmodulated beam in Fig. 4.17 respectively. . . . .                                                                                                                                                                                                                                                        | 90  |
| 4.19 | The illustration of detection region. Dimension information is labelled. .                                                                                                                                                                                                                                                                                                                                                                                                                                                 | 91  |
| 4.20 | YbF energy levels being used in the detection region. The hyperfine levels in $ X^2\Sigma^+, \nu=0, N=0 \text{ and } 1\rangle$ are shown in blue. The orange arrows stands for the microwave transitions between $N=0$ and 1 rotational levels. The green arrows illustrate the optical transitions between the $ X^2\Sigma^+, \nu = 0, N = 1\rangle$ and the first excited states. Both microwave frequencies are around 14.4 GHz. We simply label them 14.4 GHz here. The sidebands of 542.812 THz is not shown. . . . . | 92  |
| 4.21 | Optics setup for detection region. CL: convex lens. $\lambda/2$ : half wave plate. FM: flip mirror. PBS: polarizing beam splitter. TCL: transfer cavity lock. WM: wavemeter. . . . .                                                                                                                                                                                                                                                                                                                                       | 93  |
| 4.22 | PMT calibration. (a) Output voltage vs input current of the amplifier. (b) Counts of scatter vs HV. . . . .                                                                                                                                                                                                                                                                                                                                                                                                                | 94  |
| 4.23 | The stainless grid in the detection region. It is located at the end of the entire machine. Image is taken by the EMCCD under normal camera mode. . . . .                                                                                                                                                                                                                                                                                                                                                                  | 95  |
| 5.1  | An EMCCD image of YbF molecules with LC at the end view of the machine. The image is averaged over 404 shots. The bin size is $16 \times 16$ . The image is background subtracted. . . . .                                                                                                                                                                                                                                                                                                                                 | 98  |
| 5.2  | Results of 1D cooling (share the same color bar with Fig 5.1). (a) Image of horizontal cooling. (b) Image of vertical cooling. . . . .                                                                                                                                                                                                                                                                                                                                                                                     | 99  |
| 5.3  | $S_{2D}$ vs. magnetic field with $6\Gamma$ laser detuning and $450I_{\text{sat}}$ laser intensity. Blue: $XY_\perp$ , Red: $XY_\parallel$ laser polarization configurations. The blue dashed line is the average value of the blue data points. The red line is a guide to the eyes. . . . .                                                                                                                                                                                                                               | 101 |
| 5.4  | $S_{2D}$ as a function of detuning $\Gamma$ under three different laser powers with $B = 0.6$ G and $XY_\parallel$ polarization. Lines are guides to the eyes. . . . .                                                                                                                                                                                                                                                                                                                                                     | 102 |
| 5.5  | (a) $S_{2D}$ as a function of $P_1$ with $\Delta = 6\Gamma$ for three $L_0$ laser powers. (b) $S_{2D}$ as a function of $P_2$ with $\Delta = 6\Gamma$ , $L_0$ laser intensity $500 I_{\text{sat}}$ and $P_1$ at maximum. Lines are guides to the eyes. . . . .                                                                                                                                                                                                                                                             | 103 |



|      |                                                                                                                                                                                                                        |     |
|------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 5.6  | Temperature (2D laser cooling) as a function of detuning with $L_0$ intensity 240 and 450 $I_{\text{sat}}$ , and B field 0.5 Gauss. Lines are guides to the eyes. . .                                                  | 104 |
| 5.7  | Time of flights under different YAG power. Images (a), (b), (c), (d) correspond to YAG powers 70%, 80%, 90% and 100%, respectively. Red (blue) lines are measured when laser cooling is on (off). . . . .              | 105 |
| 5.8  | (a) The cold TOF from Fig .5.7 part (d). (b) Shot eEDM sensitivity of the TOF. (c) The eEDM sensitivity by a 10-day block with 2 shots per second. The eEDM sensitivity in both (b) and (c) are extracted from (a).106 |     |
| 5.9  | OBE calculation for OP scheme based on the theory discussed in Sec. 3.1.2. . . . .                                                                                                                                     | 108 |
| 5.10 | (a) Leftover ratio in $N = 1$ state vs P12 laser power. (b) Leftover ratio in $N = 1$ state vs total laser power (P12 + Q0). . . . .                                                                                   | 109 |
| 5.11 | $N = 1$ population as a function of microwave power. . . . .                                                                                                                                                           | 110 |
| 5.12 | Leftover ratio in $N=1$ state vs. number of paths. . . . .                                                                                                                                                             | 111 |
| 5.13 | Scan Q0 frequency in the OP region. Detect $F=0$ population downstream.111                                                                                                                                             |     |
| 5.14 | $F=0$ signal as a function of frequency. (a) Raw data. (b) Fitted with Gaussian functions (FWHM in the inset plot). . . . .                                                                                            | 112 |
| 5.15 | TOFs when OP is turned on or off. . . . .                                                                                                                                                                              | 114 |
| 5.16 | F1 population after optical pumping. The $y$ axis has no correlation with Fig. 5.15 since they were measured at different days. The source fluctuation can influence the signal significantly. . . . .                 | 114 |
| 5.17 | (a) TTL configuration. (b) Results of four-shot pattern experiment with above TTL. . . . .                                                                                                                             | 117 |
| 5.18 | (a) TTL configuration. (b) Results of four-shot pattern experiment with above TTL. . . . .                                                                                                                             | 118 |
| 5.19 | (a) $F=0$ state population leftover as a function of F0 power. (b) $F=1$ state transfer efficiency as a function of F0 power. . . . .                                                                                  | 118 |
| 5.20 | Magnetic field noise as a function of frequency. . . . .                                                                                                                                                               | 120 |
| 5.21 | OBEs calculation for the detection scheme. (a) Beam profiles for microwave and lasers in time. (b) Population terms of the OBEs. (a) and (b) share the same $x$ axis. . . . .                                          | 120 |
| 5.22 | (a) LIF as a function of F0 MW power. (b) LIF as a function of F1 MW power. . . . .                                                                                                                                    | 121 |
| 5.23 | Leftover ratio vs microwave frequency. The microwave frequency is 14.467242 GHz (highlighted in gray dashed line) which drives the transitions between $ F=0\rangle$ and $ N=1, F=1_l\rangle$ . . . . .                | 122 |
| 5.24 | Leftover ratio vs microwave frequency. The microwave frequency is 14.458087 GHz (highlighted in gray dashed line) which drives the transitions between $ F=1\rangle$ and $ N=1, F=2\rangle$ . . . . .                  | 122 |

|      |                                                                                                                                                                                                                                                                                     |     |
|------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 5.25 | Detector crosstalk measurement. The initial population is prepared in F0 and the $N=1$ leftover population (red) is approximately 0.15 as previously shown. F0 microwave leakage from detector 2 to detector 1 is observed by measuring F0 population in detector 1 (blue). . . . . | 123 |
| 5.26 | Microwave (14.458087 GHz) leaks from detector 1 to detector 2. . . . .                                                                                                                                                                                                              | 124 |
| 6.1  | Interference curve from our last generation eEDM machine [Ho20]. (a) Interference curve for molecules in the $F = 0$ (black) and $F = 1$ (red) states. (b) Asymmetry interference curve calculated from (a). . . . .                                                                | 130 |
| 6.2  | A histogram of eEDM values from 2740 blocks taken in 2013 from our last generation eEDM machine [Dev15]. . . . .                                                                                                                                                                    | 131 |



# List of Tables

|                                                                                                                                                                                          |     |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 1.1 Measured eEDM values on various atomic and molecular species. . . . .                                                                                                                | 5   |
| 2.1 Summary of the YbF molecular Hamiltonian. . . . .                                                                                                                                    | 15  |
| 2.2 Standard definitions of angular momentum operators. . . . .                                                                                                                          | 17  |
| 2.3 Measured rovibrational constants for the ground and first excited state of $^{174}\text{YbF}$ [SWH96; Dun+95]. . . . .                                                               | 22  |
| 2.4 Measured parameters for the hyperfine structure [SWH96]. . . . .                                                                                                                     | 23  |
| 2.5 Example of using 3-j symbol to produce CG coefficients ( $j=3/2$ and $k=1$ ). 26                                                                                                     |     |
| 2.6 Calculated transition dipole matrix elements from $X^2\Sigma^+$ ( $N=1$ manifold) to $A^2\Pi_{1/2}$ e(+) state. Column and row stand for the X and A states respectively. . . . .    | 29  |
| 2.7 Calculated transition dipole matrix elements from $X^2\Sigma^+$ ( $N=0, 2$ manifold) to $A^2\Pi_{1/2}$ f(-) state. Column and row stand for the X and A states respectively. . . . . | 31  |
| 2.8 Calculated transition dipole matrix elements within $X^2\Sigma^+$ state, between $N=0$ and 1 manifolds. . . . .                                                                      | 31  |
| 2.9 Calculated g-factors in the $X^2\Sigma^+$ ( $\nu=0$ ) state. . . . .                                                                                                                 | 34  |
| 4.1 Laser power and fiber coupling in the LC region. . . . .                                                                                                                             | 77  |
| 4.2 Laser power and fiber coupling in the OP region. . . . .                                                                                                                             | 83  |
| 7.1 Laser used in this work. . . . .                                                                                                                                                     | 140 |
| 7.2 Microwaves used in this work. . . . .                                                                                                                                                | 140 |



# Introduction

In this chapter, we will show the motivation to study the **electron electric dipole moment (eEDM)**. Firstly, we will explain the reason to measure the eEDM. Then, we will show the history of eEDM measurements. Next, we will introduce a previous generation of our eEDM experiment which was successfully implemented, in which the general experiment design for this machine has formed the basis for our next generation (gen 2 which is this work) machine. At last, we will show the thesis structure which helps audience to understand the correlation between chapters.

## 1.1 Why measuring electron electric dipole moment?

The motivation to measure the eEDM comes from the theory of symmetry in particle physics. We will first briefly introduce the symmetry in particle physics, then explain the interplay between eEDM and symmetry.

The symmetry law in particle physics is also called the *CPT* conservation law. It suggests a fundamental symmetry of physical laws under transformations of charge conjugation (*C*), parity (*P*), and time reversal (*T*). In 1950, Purcell and Ramsey challenged the point of view that fundamental particles can have no electric dipole moment [PR50]. This claim was purely based on theoretical symmetry arguments with no supporting experimental evidence. They suggested that the presence of a permanent electric dipole moment within a fundamental particle would be troublesome under the *CPT* conservation law as an elementary particle with an electric dipole moment would show an asymmetry between left and right handed coordinate systems, thus breaking parity conservation. Although this would violate *CPT* theorem, Purcell and Ramsey argued that there was no compelling reason to exclude this possibility. In 1956, Lee and Yang suggested that *P* would not be conserved in weak interactions [Lee56]. A year later, Wu tested beta decay of cobalt-60 nuclei, demonstrating weak interactions violate *P* symmetry [Wu+57]. In pion and muon decay experiments, *C* violation was also observed [FT57; GLM57]. In 1964, *CP*-symmetry breaking was observed in the kaon decay experiment, indicating that weak interactions can violate *C* and *P* symmetry simultaneously [Chr+64].

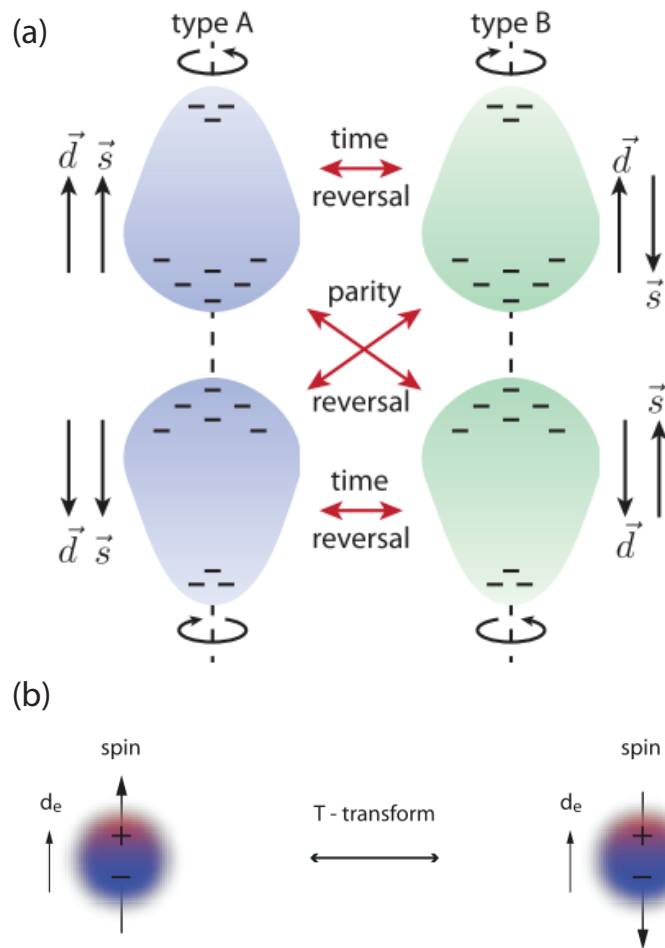
Around 1960s, Schwinger proposed that the  $CPT$  conservation law might be the most fundamental symmetry law [Sch51]. It suggests that  $CP$  violation is equivalent to  $T$  violation and introduces  $T$ -violating phenomena. A fundamental particle with an eEDM is the most notable example of such  $T$  violation. Based on the above references, we summarize  $CP$  violation in the following points

- Parity is conserved in the electromagnetic and strong interaction.
- Parity is not conserved in the weak interaction.
- Charge conjugation is conserved in the electromagnetic and strong interaction.
- Charge conjugation is not conserved in the weak interaction.

For a fundamental particle with spin  $s = 1/2$ , the Wigner-Eckart theorem states that a particle EDM  $\vec{d}_e$  must lie either parallel or anti-parallel to its spin [Bal14],

$$\vec{d}_e = \alpha \vec{s}. \quad (1.1)$$

Let us now consider the three discrete symmetries acting on an electron. Figure 1.1 (a) shows four possible configurations under parity and time transformations. After a  $T$  transformation, the direction of spin is reversed whilst leaving the direction of  $\vec{d}_e$  unchanged, telling that  $T$  symmetry is violated. Similarly, after a parity transformation,  $\vec{d}_e$  is reversed whilst spin is unchanged, suggesting that  $P$  symmetry is violated. Figure 1.1 (b) not only shows the  $T$  transformation but also illustrates that if  $d_e$  is non zero, we can imagine the charge distribution in an electron is not uniform, with "negatively" and "positively" charged areas labelled by blue and red. In nature, a free electron has a spin quantum number with value  $1/2$ . The nature doesn't judge it is spin up or down. If an intrinsic  $d_e$  exists, it will break  $T$  symmetry, which is an evidence of  $P$  and  $T$  violation. An experiment designed to measure  $T$  violation is an indirect evidence of  $CP$  violation when considering the combined symmetry of  $C$ ,  $P$  and  $T$ .



**Fig. 1.1:** (a) The time and parity reversals of an atom or a molecule which has a permanent EDM. (b) After a  $T$  reversal, the spin flips but the  $d_e$  remains unchanged [Kar10].



## 1.2 The history of eEDM

In the last section, we have seen the motivation to measure the eEDM. In this section, we will answer the question of what species we will use to measure eEDM. The first idea would be using free electrons. However, the difficulty is that free electrons will be accelerated in electric fields. Then people start thinking using atoms and molecules.

In 1963, Schiff stated that the atomic potential can shield an eEDM from external fields causing the eEDM to have no observable effect [Sch63]. In 1965, Sandars found that high-Z atoms not only have incomplete shielding of an eEDM, but also show an enhancement of eEDM [San65]. Next, in 1967, he further discovered that polar molecules containing high-Z atoms can have significantly higher eEDM enhancement effect [San67]. In 1978, Sushkov theoretically proved that an eEDM can be measured in polar molecules containing high-Z atoms [SF78].  $^{174}\text{YbF}$  (this work) is a typical example of such polar molecules. We highlighted the above four references in green on the bottom right of Fig. 1.2. The effect of an eEDM on an atom can be described by [Hud01]

$$\hat{H}_{\text{EDM}} = -\alpha g_e d_e \frac{\hat{F} \cdot \vec{E}_{\text{ext}}}{|\hat{F}|}, \quad (1.2)$$

where  $d_e$  is the eEDM,  $\hat{F}$  is the total angular momentum and  $\vec{E}_{\text{ext}}$  is the applied electric field. The enhancement factor  $\alpha$  tells that whether the atom shields ( $\alpha < 1$ ) or enhance ( $\alpha > 1$ ) the eEDM interaction. Molecules suitable for eEDM experiments are paramagnetic molecules. The eEDM interaction Hamiltonian for molecules is different because there is a second symmetry axis which is the internuclear axis. In these paramagnetic molecules the applied electric field comes from the strong internal electric field which is directed along the internuclear axis. The eEDM interaction Hamiltonian for molecules is written [Hud01]

$$\hat{H}_{\text{EDM}} = -g_e d_e E_{\text{eff}} \frac{\hat{F} \cdot \hat{\lambda}}{|\hat{F}|}, \quad (1.3)$$

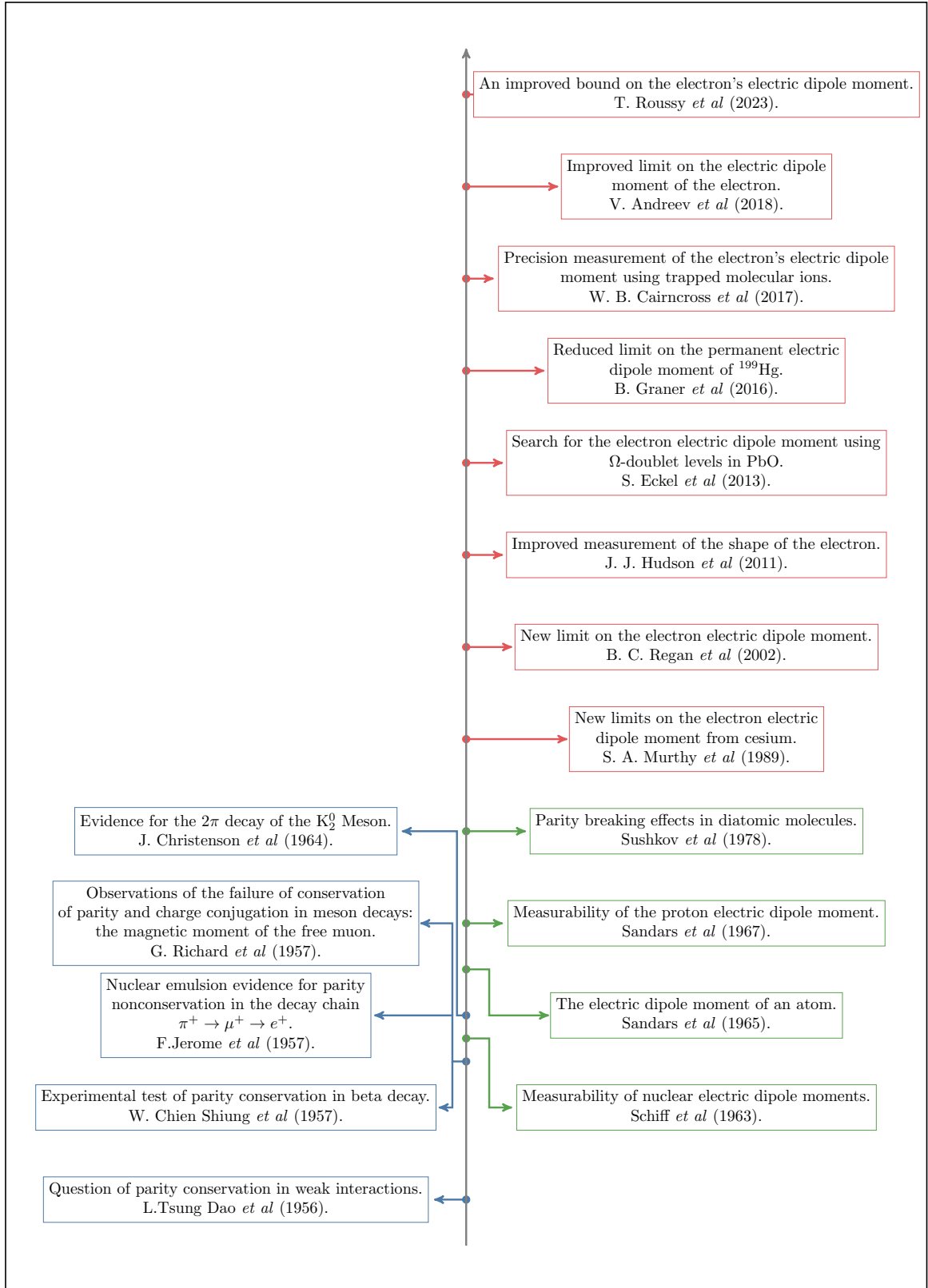
where  $E_{\text{eff}} = \alpha E_{\text{ext}}$  and  $\hat{\lambda}$  is the unit vector directed along the internuclear axis. YbF molecules which are the species used in this work have an  $E_{\text{eff}} = 25$  GV/cm. So far, we have confirmed that eEDM has observable effects in atoms and molecules. Next, we will introduce measured eEDM values on various atomic and molecular species. Works of measured eEDM are summarized on the top right of Fig. 1.2 and highlighted in red.

In 1989, the limit of eEDM was measured on cesium atoms by using a two-laser method with measured upper bound  $5.5 \times 10^{-26}$  e·cm with 68% confidence limit. [Mur+89]. Then in 2002, eEDM upper bound  $1.6 \times 10^{-27}$  e·cm (90% C.L.) was measured on  $^{205}\text{Tl}$  atoms by using a motional magnetic field [Reg+02]. In 2016, by using atomic interference technique, a nucleon EDM value  $2.2 \times 10^{-30}$  e·cm (95% C.L.) was measured on  $^{199}\text{Hg}$  [Gra+16].

To date, four molecular species have been used to measure the eEDM, including YbF, PbO, HfF<sup>+</sup> and ThO. There are two similarities of these experiments that utilise paramagnetic molecules to set limits on the eEDM. One is that they all take advantage of the eEDM enhancement effect in high-Z polar molecules. Another similarity is that they all use Ramsey interferometry technique to measure the phase introduced by the eEDM interaction. For YbF, an advantage to using this molecule is that the eEDM measurement happens in the ground state, which suggests the lifetime of the eEDM state is infinite [Hud+11]. Thus, if the coherence time of the eEDM state can be maintained long enough, the limit of  $d_e$  can be reached. For PbO, the measurement happens in a high-temperature vapour cell rather than a beamline experiment [Eck+13]. Due to the  $\Omega$  doublet structure of the eEDM state of PbO, molecules can be fully polarised with low electric field [Eck+13]. The HfF<sup>+</sup> experiment consists of an RF ion trap with rotating bias electric field [Cai+17]. The disadvantage of the ion trapping experiment is that not many ions can be trapped at one time due to repulsive forces between ions and the finite trap size. This will lower the sensitivity of an eEDM measurement. The advantage is that ion traps offer relatively longer interaction time compared with beamline experiments. The ThO eEDM measurement is conducted in a metastable state which limits the lifetime of the eEDM state. However, the advantage is that ThO has the largest eEDM enhancement effect [Col18]. In 2023, the newest eEDM measurement from JILA shows a new limit of the upper bound of eEDM with value  $4.1 \times 10^{-30}$  e·cm by using molecular ions, which is the second generation of their 2018 eEDM machine [Cai+17; Rou+23].

| Atomic and Molecular species | Upper bound of eEDM (e·cm) | Year | Ref           |
|------------------------------|----------------------------|------|---------------|
| Cs                           | $5.5 \times 10^{-26}$      | 1989 | Ref. [Mur+89] |
| Tl                           | $1.6 \times 10^{-27}$      | 2002 | Ref. [Reg+02] |
| YbF                          | $1.1 \times 10^{-27}$      | 2011 | Ref. [Hud+11] |
| PbO                          | $1.7 \times 10^{-26}$      | 2013 | Ref. [Eck+13] |
| HfF <sup>+</sup>             | $1.3 \times 10^{-28}$      | 2017 | Ref. [Cai+17] |
| ThO                          | $1.1 \times 10^{-29}$      | 2018 | Ref. [Col18]  |
| HfF <sup>+</sup>             | $4.1 \times 10^{-30}$      | 2023 | Ref. [Rou+23] |

**Tab. 1.1:** Measured eEDM values on various atomic and molecular species.

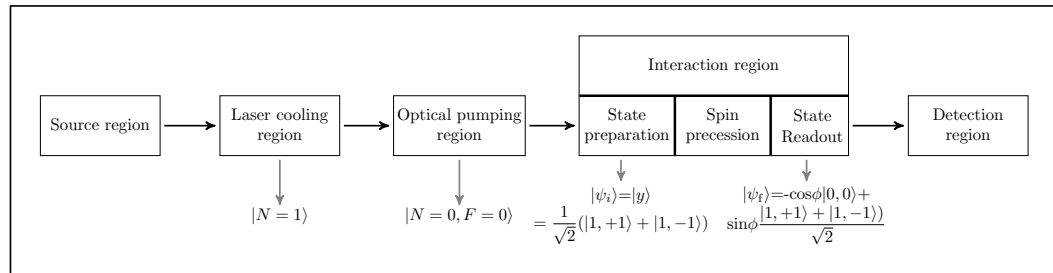


**Fig. 1.2:** History of eEDM measurements and relevant work. Blue: *CPT* theorem related work which was introduced in the last section. Green: Theory of polar molecules containing high-Z atoms. Red: eEDM experiments utilising paramagnetic atomic and molecular species.

## 1.3 A simple YbF eEDM experiment

In previous sections, we have explained the motivation and what species we will use to measure eEDM. This section will introduce the YbF experiment at Imperial college, in which the first generation experiment was successful in providing the most sensitive upper bound limit on eEDM in 2011 [Hud+11]. The development of the second generation YbF experiment at Imperial college is the focus of this thesis, however the underlying physics of the YbF eEDM experiment between generation one and two is the same. An overview of the YbF eEDM experiment is presented below. Detailed information such as laser cooling and state manipulation will be explained in the following chapters.

Here, we describe a simple YbF eEDM experiment and explain how to extract an eEDM value from it. In order to extract one eEDM value, we need to run one block. A simplest block contains eight shots. By changing the electric and magnetic fields in the interaction region from shot to shot, a block can be obtained. A block can be regarded as a repetition of shots under various configurations of machine parameters. It is important to understand one shot because shot is the most elementary unit of YbF eEDM experiment. Therefore, we will explain a shot first in the following discussion.



**Fig. 1.3:** Illustration of one shot. A shot happens from left to the right. Corresponding states in each region is also labelled.

The YbF eEDM experiment is a beamline experiment. Figure 1.3 describes the process of one shot (from left to right). A single shot starts from the generation of YbF molecules in the source region and ends up with YbF molecules being detected by laser induced fluorescence in the detection region. Between the source and detection regions, there are laser cooling, optical pumping and interaction regions to cool and manipulate the state of YbF molecules. YbF molecules are generated in vacuum by a buffer gas source, exiting the source region with a forward speed ranging from 100 to 300 m/s. To increase the molecule density and reduce the number of molecules lost as they move further down the beamline due to their transverse motion, the

YbF molecules are cooled transversely by laser cooling. Since the laser cooling transition is rotation level closed, molecules will end up in the  $|N = 1\rangle$  state as shown in Fig. 1.3. Details about laser cooling will be discussed in Chs. 3 and 4. After the laser cooling region, molecules will travel to the optical pumping region to be prepared into the  $|F = 0, m_F = 0\rangle$  state (relabelled by  $|0,0\rangle$ ). Then, we will implement radio frequency or stimulated Raman adiabatic passage to prepare the  $|0,0\rangle$  to  $|y\rangle = (1/\sqrt{2})(|1,+1\rangle + |1,-1\rangle)$ . This step is called state preparation which will be discussed in details in the following chapters. The  $|y\rangle$  state will acquire a phase introduced by electric and magnetic fields in the spin precession process [Kar10; Ho20],

$$\phi(t) = \phi_B(t) + \phi_E(t) \quad (1.4)$$

$$= \frac{1}{\hbar}(\mu_B B_z - \eta d_e E_{\text{eff}})t. \quad (1.5)$$

Where  $\mu_B$  is the Bohr magneton.  $B_z$  is the magnetic field along the  $z$  axis.  $\eta$  is the enhancement factor with value 0.69 when applied electric field is 20 kV/cm and  $E_{\text{eff}}$  is the effective electric field with value 26 GV/cm. After the spin precession, we will read out the state by using RF or stimulated Raman adiabatic passage, which gives the final state as [Kar10; Ho20],

$$|\psi_f\rangle = -\cos\phi|0,0\rangle + \sin\phi \frac{(|1,+1\rangle + |1,-1\rangle)}{\sqrt{2}}. \quad (1.6)$$

The final step is to detect the state. Based on Eq.1.6, the probabilities of being detected in  $F=0$  and  $F=1$  are  $|\langle 0,0|\psi_f\rangle|^2 = \cos^2\phi$  and  $|\langle 1,+1|\psi_f\rangle|^2 + |\langle 1,-1|\psi_f\rangle|^2 = \sin^2\phi$ . Until now, we have described one shot.

From Eqs. 1.6 and 1.5, it can be seen that the phase  $\phi_E$  introduced by the eEDM interaction is encapsulated in the entire phase  $\phi$ . In order to extract one eEDM value, we need to step and switch electric and magnetic fields at least eight times. Thus we need the concept of a block. A block is basically a set of shots with each shot being set with different machine parameters, such the direction of the electric and magnetic fields, the magnitude of magnetic field, and laser frequencies, etc. In the following discussion, we will focus on a simplest block which contains 8 shots with electric and magnetic fields in the interaction region being switched and stepped.

To show how an eEDM value is extracted, it is helpful to define some parameters at beginning.  $s_A$  and  $s_B$  are measured population in the  $|F = 0\rangle$  and  $|F = 1\rangle$  states. From Eq.1.6, we can obtain  $s_A = N_{\text{mol}}\epsilon \cos^2\phi$  and  $s_B = N_{\text{mol}}\epsilon \sin^2\phi$ , here  $N_{\text{mol}}$  is the number of molecules and  $\epsilon$  is the number of photons detected per molecule. It can be seen that  $s_A$  and  $s_B$  depend on the number of molecules which is significantly

influenced by the source. The trick to avoid the shot-to-shot fluctuation of the source is to define the asymmetry which is

$$A = \frac{s_A - s_B}{s_A + s_B}. \quad (1.7)$$

Substituting the expressions of  $s_A$  and  $s_B$  into [Eq.1.7](#), we get  $A=C \cos 2\phi$ . Here  $C$  is the contrast. In a perfect experiment,  $C$  should be 1. Then, substituting [Eq.1.4](#) into  $A=C \cos 2\phi$ , and introduce the switching and stepping of electric and magnetic fields when  $\phi_B = \pm\pi/4$ . We will get,

$$A(\mathcal{E}, \mathcal{B}, \delta\mathcal{B}) = C \cos[2\mathcal{B}(\frac{\pi}{4} - \delta\mathcal{B}\phi_{\delta\mathcal{B}}) - 2\mathcal{E}\phi_E] \quad (1.8)$$

$$= C\mathcal{B} \sin(2\mathcal{B}\delta\mathcal{B}\phi_{\delta\mathcal{B}} + 2\mathcal{E}\phi_E) \quad (1.9)$$

$$\approx 2C(\delta\mathcal{B}\phi_{\delta\mathcal{B}} + \mathcal{E}\mathcal{B}\phi_E). \quad (1.10)$$

$\mathcal{E}, \mathcal{B}, \delta\mathcal{B}$  are switching parameters with values either be +1 or -1.  $\mathcal{E}(\mathcal{B}) = \pm 1$  means reversing the electric (magnetic) field direction.  $\delta\mathcal{B} = \pm 1$  stands for increasing or decreasing the magnitude of magnetic field by a small amount  $\delta B$ . We also define the channel value for the above parameters for one 8-shot block,

$$\{\delta\mathcal{B}\} = \frac{1}{8} \sum_{i=1}^8 \delta\mathcal{B}_i A_i = 2C\phi_{\delta\mathcal{B}}, \quad (1.11)$$

$$\{\mathcal{E} \cdot \mathcal{B}\} = \frac{1}{8} \sum_{i=1}^8 \mathcal{E}_i \cdot \mathcal{B}_i \cdot A_i = 2C\phi_{\mathcal{E}}. \quad (1.12)$$

Doing the ratio of [Eq.1.11](#) over [Eq.1.12](#), an eEDM value can be extracted,

$$d_e = \frac{\mu_B B_{\delta\mathcal{B}} \{\mathcal{E} \cdot \mathcal{B}\}}{\eta E_{\text{eff}} \{\delta\mathcal{B}\}}. \quad (1.13)$$

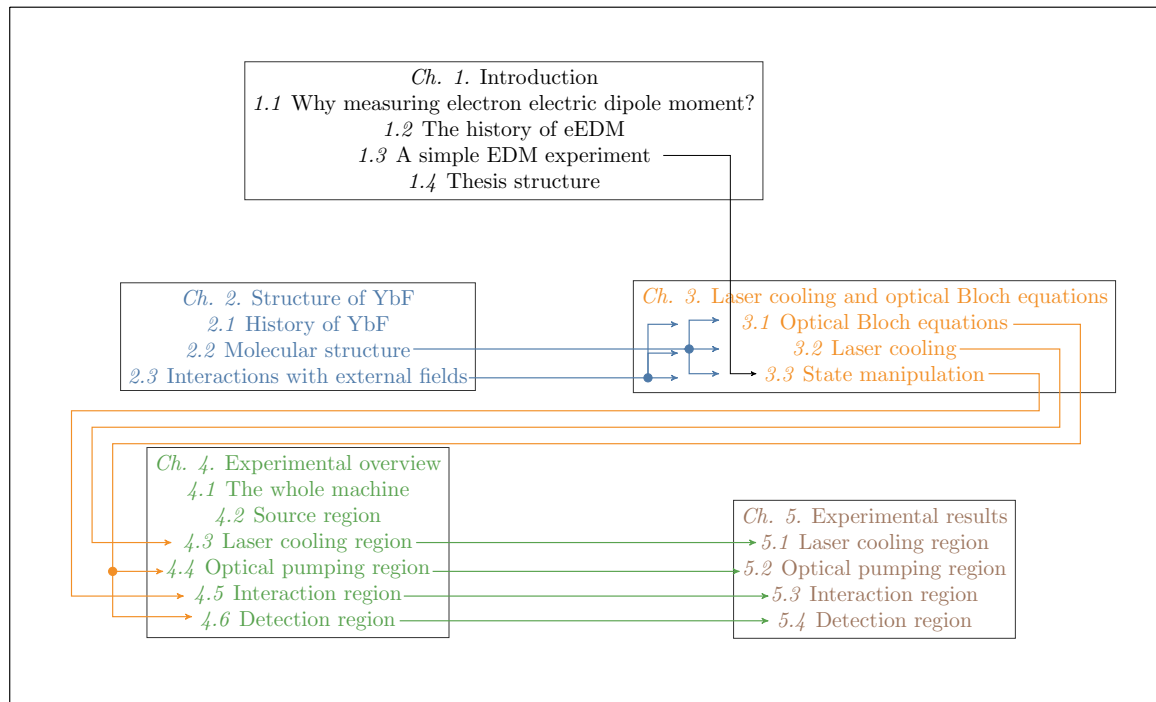
Next, we will briefly discuss the sensitivity of the eEDM experiment. The derivation of the eEDM sensitivity is shown in details in our previous PhD thesis [Ref.\[Ho20\]](#). The expression of the shot-noise limited sensitivity is [Ref.\[Ho20\]](#)

$$\xi_{d_e} = \frac{\hbar}{2C\eta E_{\text{eff}} \tau \sqrt{N_{\text{mol}}}}. \quad (1.14)$$

This expression tells us several ways to improve the eEDM sensitivity. They are to increase the contrast, to increase the electric field strength to increase  $\eta$ , to increase spin precession duration  $\tau$ , and to increase number of molecules being detected  $\sqrt{N_{\text{mol}}}$ . Detailed derivation of this expression is in [Ref.\[Ho20\]](#). The reason  $N_{\text{mol}}$  is under the square root is that the photon counting process is treated as a Poisson

distribution. For a Poisson distribution, the standard deviation of the shot noise is the square root of the number of events. The most effective way to improve the sensitivity is to increase the number of molecules which is the motivation of laser cooling which will be shown in the following chapters.

## 1.4 Thesis structure



**Fig. 1.4:** Illustration of the thesis structure. Arrows indicate the correlation between chapters and sections.

When I started the PhD, the chambers for all the regions were completed. What I have contributed is that I've completed setting up part of the laser system of the laser cooling region and measuring the performance of laser cooling. I've set up the laser and microwave system for the optical pumping region and measured the performance of optical pumping. I've completed the preliminary measurement of STIRAP in the interaction region. I've set up the detectors (PMTs and EMCCDs) in the detection region and completed the detection efficiency measurement. All the simulations were done individually by myself. In total, there were four people including me working on the ultracold YbF eEDM machine. Rhys and I worked together in the lab all the time. Freddie and Michael joined us in the second year of my PhD.

Figure 1.4 shows the thesis structure. The logic of the entire thesis is that calculating the molecular structure of YbF molecules and simulating the state evolution in each region by using optical Bloch equations to set up the theoretical foundation of the experiment. Then, based on the theory we have established, we can gain insights on designing the machine, conducting experiments and explaining experimental results.

Arrows in Fig. 1.4 indicate the correlation between chapters. For instance, Sec. 1.1 "A simple EDM experiment" will be explained in details in the Sec. 3.3 "State manipulation". Then the Sec. 4.5 "Interaction region" is closely related to sec. 3.3. Finally, the Sec. 5.3 explains the experimental results in the Sec. 4.5, which will in return helps us improve the machine design.

Chapter 1 is the introduction in which we have explained the motivation of measuring eEDM and the history of eEDM. We also show a simple eEDM experiment. More details about the state manipulation will be explained in Chapter 3.

Chapter 2 will introduce the molecular structure of YbF. We will calculate the energy spectrum and transition dipole matrix elements of YbF. Energy spectrum will give the fundamental information what frequencies should be used in order to drive a transition between two levels. Transition dipole matrix elements will be used in Chapter 3 to calculate optical Bloch equations and laser cooling.

Chapter 3 will simulate the optical Bloch equations to explain the transition schemes in the laser cooling region, optical pumping region, interaction region and detection region. The simulation on laser cooling helps us design the laser cooling region and understand the experimental results of laser cooling.

Chapter 4 will show the eEDM machine by regions. It includes source, laser cooling, optical pumping, interaction and detection regions.

Chapter 5 will explain the experimental results of each region.

Chapter 6 will present the conclusions and outlook of this project.

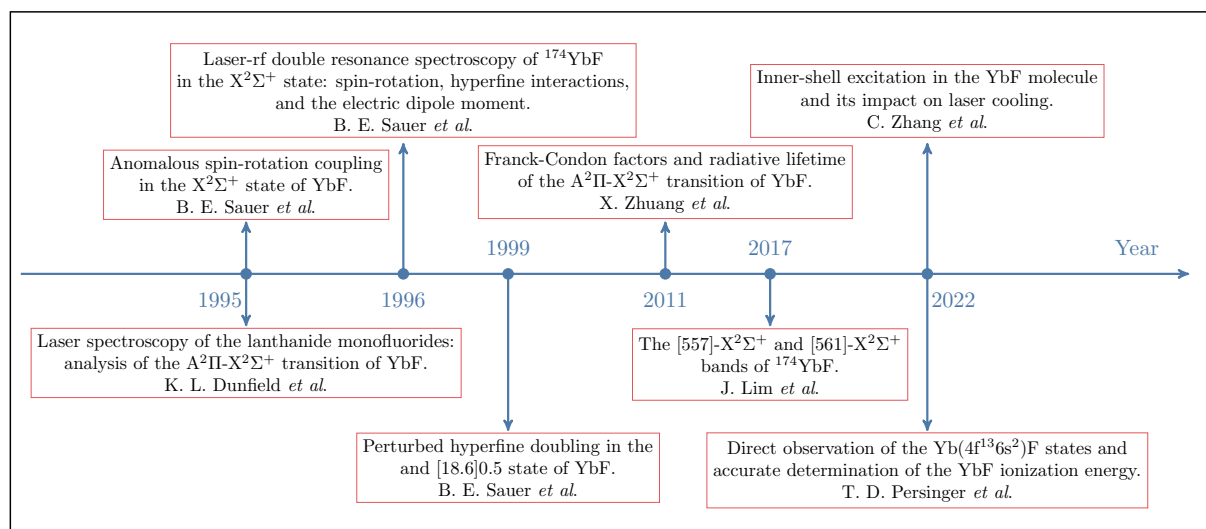




# Structure of YbF

## 2.1 History of YbF

This chapter will focus on the molecular structure of YbF. The reason to make it the second chapter is because understanding the molecular structure is very beneficial to understand the entire experiment. It is beneficial to have a good understanding on molecular structure before we discuss laser cooling and optical pumping schemes in the following chapters. Fig. 2.1 summarizes some of the history of YbF spectroscopy.



**Fig. 2.1:** History of the  $^{174}\text{YbF}$  molecular structure (selected publications).

The pioneering work both experimentally and theoretically started from 1995 which was done by my supervisor Prof. Ben Sauer. Before 2000, they resolved the first electronic state, rovibrational spectra, spin-rotation coupling, and hyperfine interactions [SWH95; Dun+95; SWH96; Sau+99]. Between 2000 and 2020, spectroscopic studies of YbF were driven to characterise higher vibrational states of the ground and first excited states to develop laser cooling scheme (or to find semi-closed photon cycling transitions). Then after 2020, spectroscopic studies are focused on identifying potential leaks out of the cycling transitions, mainly to characterise 4f hole states because such intermediates states were dark states with respect to

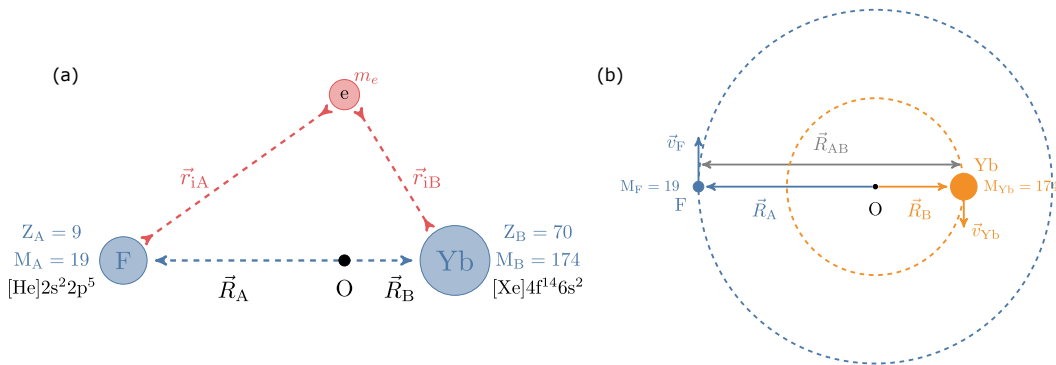
the transitions used before 2000 causing troubles when we tried to improve EDM measurements and build YbF MOTs [Zhu+11; Lim+17; Zha+22; Per+22]. The above eight references are the main resources of this chapter. All the YbF molecular structure constants are from them.

## 2.2 Molecular structure

I will first discuss the Born Oppenheimer approximation which explains how one treats the motion of nuclei and electrons separately. The next step is electronic structure which contains the largest energy gaps in molecular physics. Further narrowing down the energy scale, they are vibrational, rotational and hyperfine structures. The above energy levels include all the levels being used in this work.

### 2.2.1 Born Oppenheimer approximation

In molecular physics, the **Born Oppenheimer (BO) approximation** is a well-known mathematical approximation which was proposed by Max Born and J. Robert Oppenheimer in 1927 [BH85]. It assumes that the wave functions of atomic nuclei and electrons can be treated separately because the nuclei are much heavier than electrons. We fix nuclei in place when solving Schrödinger equations due to the larger relative mass of nuclei compared to electrons. This approximation is widely implemented in atomic physics and quantum chemistry.



**Fig. 2.2:** (a) Coordinates of the YbF diatomic molecule. (b) Illustration of the rotational motion of Yb and F nuclei. The subscripts  $A$  and  $B$  stand for Fluorine and Yb atom, respectively.

Fluorine atom has 9 protons with atomic mass  $M_A=19$ .  $^{174}\text{Yb}$  atom has 70 protons with atomic mass  $M_B=174$ . The electronic configurations of Yb and F in their

ground electronic states are  $[\text{Xe}]4f^{14}6s^2$  and  $[\text{He}]2s^22p^5$  respectively. It is known that F atom has larger electronegativity than Yb atom [htt22a]. Thus we can imagine that the F atom takes one  $6s$  electron from the Yb atom, leaving one valence electron in the ground electronic state of YbF. The relative coordinate between the F (Yb) atom and the  $6s$  electron is  $\vec{r}_{iA}$  ( $\vec{r}_{iB}$ ). The relative coordinates between the  $6s$  electron and other electrons are  $\vec{r}_{ij}$  which is not shown in Fig. 2.2 (a). In the following discussion, we will use the center-of-mass frame with the center of mass labeled as O as illustrated in (b). The coordinates of F and Yb atoms are  $\vec{R}_A$  and  $\vec{R}_B$  respectively. The distance between the two nuclei is  $|\vec{R}_{AB}|$ . Figure 2.2 (b) also shows the rotational motion of Yb and F nuclei, which we will discuss more in Sec. 2.2.3. The two nuclei rotate with respect to the center of mass. The reduced mass of the system is

$$\mu = \frac{M_A M_B}{M_A + M_B}. \quad (2.1)$$

Now, we can write the Hamiltonian of the YbF molecule as

$$\hat{H} = \hat{T}_{\text{nuclei}} + \hat{T}_{\text{electron}} + \hat{V}_{\text{nuclei-nuclei}} + \hat{V}_{\text{electron-nuclei}} + \hat{V}_{\text{electron-electron}}, \quad (2.2)$$

with corresponding Schrödinger equation

$$\hat{H}\Psi(\vec{R}_{AB}, \vec{r}) = E\Psi(\vec{R}_{AB}, \vec{r}). \quad (2.3)$$

Here, the coordinate  $\vec{r}$  stands for all the electronic coordinates including  $\vec{r}_{iA}$  and  $\vec{r}_{iB}$ . We summarize and abbreviate each term of Eq. 2.2 in Tab. 2.1. To separate the

|                                       |                                      |                                                                                                                      |
|---------------------------------------|--------------------------------------|----------------------------------------------------------------------------------------------------------------------|
| Nuclei kinetic energy                 | $\hat{T}_{\text{nuclei}}$            | $\hat{T}_n = -\frac{\hbar^2}{2M_A}\nabla_A^2 - \frac{\hbar^2}{2M_B}\nabla_B^2$                                       |
| Electron kinetic energy               | $\hat{T}_{\text{electron}}$          | $\hat{T}_e = -\frac{\hbar^2}{2m_e}\sum \nabla_i^2$                                                                   |
| Nuclei - nuclei Coulomb interaction   | $\hat{V}_{\text{nuclei-nuclei}}$     | $\hat{V}_{nn} = -\frac{Z_A Z_B e^2}{4\pi\epsilon_0  \vec{R}_{AB} }$                                                  |
| Electron nuclei Coulomb interaction   | $\hat{V}_{\text{electron-nuclei}}$   | $\hat{V}_{en} = -\frac{e^2}{4\pi\epsilon_0} \sum \left( \frac{Z_A}{\vec{r}_{iA}} + \frac{Z_B}{\vec{r}_{iB}} \right)$ |
| Electron electron Coulomb interaction | $\hat{V}_{\text{electron-electron}}$ | $\hat{V}_{ee} = \frac{e^2}{4\pi\epsilon_0} \sum \frac{1}{\vec{r}_{ij}}$                                              |

**Tab. 2.1:** Summary of the YbF molecular Hamiltonian.

nuclei kinetic energy, we fix  $\vec{R}_{AB}$  and pack the electronic part of the Hamiltonian as  $\hat{H}_e = \hat{T}_e + \hat{V}_{nn} + \hat{V}_{en} + \hat{V}_{ee}$ , leaving the Schrödinger equation

$$\hat{H}_e \psi_q(\vec{r}; \vec{R}_{AB}) = E_q(\vec{R}_{AB}) \psi_q(\vec{r}; \vec{R}_{AB}). \quad (2.4)$$

Here  $\vec{R}_{AB}$  becomes a parameter so it is labeled after the semicolon and  $q$  is the index of the electronic eigenfunctions.  $E_q(\vec{R}_{AB})$  only depends on  $|\vec{R}_{AB}|$ , which is commonly called potential energy curves. For molecules with more than two atoms,  $E_q(\vec{R}_{AB})$  becomes more complex and is called potential energy surfaces. The next step is to expand the complete eigenfunction in terms of the electronic eigenfunctions,

$$\Psi(\vec{R}_{AB}, \vec{r}) = \sum_q \psi_q(\vec{r}; \vec{R}_{AB}) \chi_q(\vec{R}_{AB}). \quad (2.5)$$

Here  $\chi_q(\vec{R}_{AB})$  is the amplitude of each electronic eigenfunction. Substituting Eqs. 2.4 and 2.5 into Eq. 2.3 we obtain

$$\sum_q \left( \hat{T}_n + E_q(\vec{R}_{AB}) - E \right) \psi_q(\vec{r}; \vec{R}_{AB}) \chi_q(\vec{R}_{AB}) = 0. \quad (2.6)$$

We multiply both sides by  $\psi_p^*(\vec{r}; \vec{R}_{AB})$  and integrate over the electronic coordinates

$$\left( E_p(\vec{R}_{AB}) - E \right) \chi_p(\vec{R}_{AB}) + \sum_q \int \psi_p^*(\vec{r}; \vec{R}_{AB}) \hat{T}_n \psi_q(\vec{r}; \vec{R}_{AB}) \chi_q(\vec{R}_{AB}) d\vec{r} = 0. \quad (2.7)$$

In Eq. 2.7, only  $q = p$  term survives because the BO approximation states that nuclear kinetic energy operator is diagonal in the space spanned by the electronic eigenvectors. To further simplify the equation, we express  $\hat{T}_n$  in the center-of-mass frame,

$$\hat{T}_n = -\frac{\hbar^2}{2(M_A + M_B)} \nabla_{CM}^2 - \frac{\hbar^2}{2\mu} \nabla_{AB}^2, \quad (2.8)$$

where the first term describes the translational kinetic energy of the system and the second term is the rotational kinetic energy. We only keep the second term because we are interested in the internal structure of the molecule. Using such form of  $\hat{T}_n$ , the nuclear kinetic energy part in Eq. 2.8 becomes

$$\begin{aligned} \hat{T}_n \psi_p \chi_p &= -\frac{\hbar^2}{2\mu} \nabla_{AB}^2 (\psi_p \chi_p) \\ &= -\frac{\hbar^2}{2\mu} \left( \psi_p (\nabla_{AB}^2 \chi_p) + (\nabla_{AB}^2 \psi_p) \chi_p + 2(\nabla_{AB} \psi_p) \cdot (\nabla_{AB} \chi_p) \right). \end{aligned} \quad (2.9)$$

The second step uses the expression  $\nabla \cdot (f \vec{v}) = f(\nabla \cdot \vec{v}) + \vec{v} \cdot (\nabla f)$ . The last two terms can be neglected because they contain the gradient of electronic wavefunctions with respect to the nuclear coordinate which is much smaller than the first term. Substituting it to Eq. 2.8, we obtain the Schrödinger equation

$$\left( -\frac{\hbar^2}{2\mu} \nabla_{AB}^2 + E_p(\vec{R}_{AB}) - E \right) \chi_p(\vec{R}_{AB}) = 0. \quad (2.10)$$

This equation interprets the nuclear motion of YbF, in which  $\chi_p(\vec{R}_{AB})$  can be regarded as the nuclear wavefunction. Moreover,  $E_p(\vec{R}_{AB})$  is the potential energy curve, but it can be also be regarded as an effective potential for the nuclear motion. We will continue to discuss this equation in [Sec. 2.2.3](#). In the next section, we introduce the electronic states and notation of angular momentum operators.

## 2.2.2 Electronic structure

Most of the contribution to the electronic state energy comes from the Coloumb interaction between electrons and nuclei. In atoms, the electron orbital angular momentum operator  $\hat{L}$  commutes with the Hamiltonian. However in diatomic molecules, due to the strong internal electric field along the internuclear axis  $\hat{n}$ ,  $\hat{L}$  is strongly coupled to this field, resulting in  $\hat{L}$  no longer a good quantum number. Its projection along the internuclear axis  $\hat{n}$  is a good quantum number. By convention, it is written as  $\Lambda$ , with value  $\Lambda = 0, \pm 1, \pm 2, \dots, \pm L$  labelled as  $\Sigma, \Pi, \Delta$ , etc. States with  $\Lambda \neq 0$  have two degenerate components  $\pm \Lambda$  called  $\Lambda$  doubling. Such  $\Lambda \neq 0$  states generate an internal magnetic field along the internuclear axis. Thus, the electron spin  $\hat{S}$  can precess around it, which is known as spin-orbit coupling. We define the internuclear component of  $\hat{S}$  the same way as we did for  $\hat{L}$ . The component of  $\hat{S}$  along  $\hat{n}$  is denoted as  $\Sigma$  with value  $-S, -S + 1, \dots, S - 1, S$ . The total electronic angular momentum along  $\hat{n}$  is denoted as  $\Omega = \Lambda + \Sigma$ . The electronic state of a diatomic molecule with  $\Lambda \neq 0$  is labeled as  $^{2S+1}\Lambda_{\Omega}$ . The summary of symbols of angular momenta is in [Tab. 2.2](#).

| Operator       | Quantum number | Definition                                                |
|----------------|----------------|-----------------------------------------------------------|
| <b>L</b>       | $L$            | Electronic orbital angular momentum                       |
| $L_z$          | $\Lambda$      | Component of <b>L</b> along internuclear axis             |
| <b>S</b>       | $S$            | Electronic spin angular momentum                          |
| $S_z$          | $\Sigma$       | Component of <b>S</b> along internuclear axis             |
| <b>R</b>       | $R$            | Rotational angular momentum                               |
| <b>I</b>       | $I$            | Nuclear spin angular momentum                             |
| <b>N=J-S</b>   | $N$            | Total angular momentum without electronic or nuclear spin |
| <b>J=L+S+R</b> | $J$            | Total angular momentum without nuclear spin               |
| $J_z$          | $\Omega$       | Component of <b>J</b> along internuclear axis             |
| <b>F=J+I</b>   | $F$            | Total angular momentum                                    |

**Tab. 2.2:** Standard definitions of angular momentum operators.

The ground state of the YbF molecule is labeled  $X^2\Sigma^+$ . Since its orbital angular momentum is zero, there is no spin-orbiting coupling. Please be careful that  $\Sigma$  is a

symbol for a  $\Lambda = 0$  state and the quantum number of  $S_z$ . It should be clear from the context where it is used. The valence electron has a  $6p\pi$  property in the first electronic state labeled by  $A^2\Pi$ . Here  $6p\pi$  means the valence electron of the Yb atom occupies the  $6p$  orbital. The interaction between the valence electron and the fluorine atom is regarded as a  $\pi$  bond due to the little overlap between them [Sau+99]. This state has strong spin-orbit coupling which degenerates the state into  $\Omega = 1/2$  and  $\Omega = 3/2$  components with notation  $A^2\Pi_{1/2}$  and  $A^2\Pi_{3/2}$ . In this work, we only use the former and simply call it the A state. The energy of the electronic states is given by  $E_{\text{el}} \approx E_0 + \alpha\Lambda\Sigma$ . Here  $E_0$  is the electrostatic energy with respect to the ground state and  $\alpha$  is the strength of the spin-orbit coupling, with value  $E_0/h = 542.8102$  THz and  $\alpha/h = 40.9304$  THz [Dun+95]. So far, we have introduced the ground and first-excited electronic states. There are some operators in Tab. 2.2 not being discussed such as  $\hat{R}$ ,  $\hat{N}$  and  $\hat{F}$ . We will introduce them in the next section.

### 2.2.3 Vibrational, rotational and hyperfine structures

In this section, we will use the rest of operators in Tab. 2.2 and Eq. 2.10 to discuss the vibrational, rotational and hyperfine structures of YbF. These energy splittings are much smaller than the electronic state level. Figure 2.2 (b) shows the rotational motion of the nuclei. We denote the corresponding nuclear rotational angular momentum as  $\hat{R}$ . Since, in this work, we are only interested in the structure of the ground state,  $\hat{R}$  and  $\hat{N}$  are interchangeable. That is because, in the electronic ground state, the electronic orbital angular momentum  $\hat{L}$  is zero. Following the convention to deal with the central potential problem, we separate  $\chi_p(\vec{R}_{AB})$  into a product of radial and angular parts,

$$\chi_p(\vec{R}_{AB}) = \chi_p(\vec{R}_{AB}, \Theta, \Phi) = \frac{1}{R_{AB}} f(R_{AB}) g(\Theta, \Phi). \quad (2.11)$$

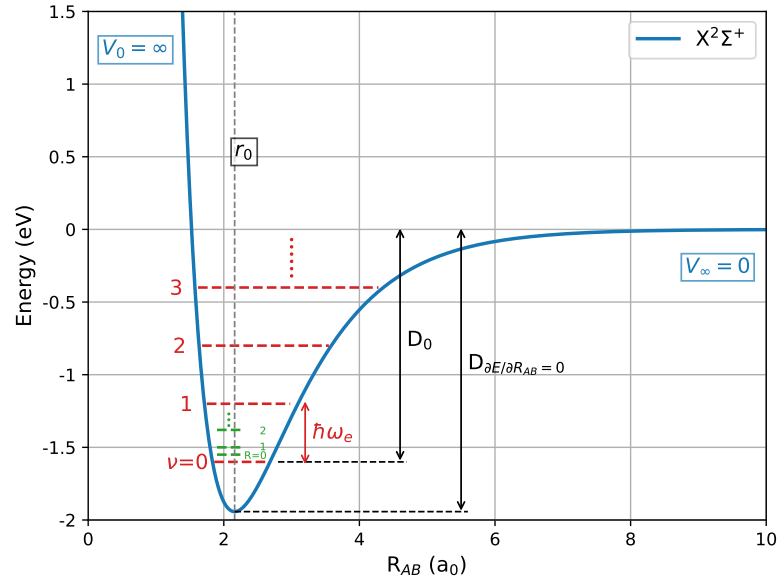
Here,  $1/R_{AB}$  is the normalisation factor,  $f(R_{AB})$  is the radial function, and  $g(\Theta, \Phi)$  is the angular function. It is known that the eigenfunctions of a quantum rigid rotor are spherical harmonics. Thus, we make  $g(\Theta, \Phi)$  as the eigenfunction of  $\hat{R}$  with  $g(\Theta, \Phi) = Y_{R, M_R}(\Theta, \Phi)$ . We obtain the corresponding eigenenergy immediately

$$\begin{aligned} \hat{R}^2 Y_{R, M_R} &= R(R+1) Y_{R, M_R}, \\ \hat{R}_z Y_{R, M_R} &= M_R Y_{R, M_R}. \end{aligned} \quad (2.12)$$

Thus, we can further simplify Eq. 2.10 to a radial equation

$$\left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dR_{AB}^2} + \frac{\hbar^2 R(R+1)}{2\mu R_{AB}^2} + E_p(R_{AB}) - E \right) f(R_{AB}) = 0. \quad (2.13)$$

Before discussing Eq. 2.13, it is beneficial to briefly review the harmonic oscillator



**Fig. 2.3:** Illustration of a potential energy curve in the ground state of a diatomic molecule. The  $x$  axis is in the unit of Bohr radius ( $a_0$ ). Vibrational and rotational levels are indicated by red and green dashed lines, respectively.

model, because the vibration between two nuclei can be approximately regarded as a harmonic oscillator. It is known that the eigenfunctions of a harmonic oscillator are Hermite polynomials and the gaps between eigenenergies are equal. Here, we will construct Eq. 2.13 into a harmonic oscillator. In order to do that, we need to deal with the potential term  $E_p(R_{AB})$ . Figure 2.3 is a typical illustration of the potential energy curve which can be found in molecular physics textbooks.  $V_0 = \infty$  is due to the resistance of compression between two nuclei.  $V_\infty = 0$  is the dissociation of the molecule under high energy. We will expand  $E_p(R_{AB})$  at  $\partial E / \partial R_{AB} = 0$

$$E_p(R_{AB}) = E_p(R_{AB}^0) + \left( \frac{dE_p}{dR_{AB}} \right) \bigg|_{R_{AB}^0} (R_{AB} - R_{AB}^0) + \frac{1}{2} \left( \frac{d^2 E_p}{dR_{AB}^2} \right) \bigg|_{R_{AB}^0} (R_{AB} - R_{AB}^0)^2 + \dots \quad (2.14)$$

Here, we only expand to the second order. Higher order expansion can be used to explain anharmonicity which requires specific computational method which is beyond this work. The second term in Eq. 2.14 is zero because the first derivative of



the curve is zero at the minimum. We define the spring constant as the curvature of the probala of the potential

$$k = \left( \frac{d^2 E_p}{dR_{AB}^2} \right) \bigg|_{R_{AB}^0}, \quad (2.15)$$

leaving  $E_p(R_{AB})$  as a harmonic oscillator type potential

$$E_p(R_{AB}) = E_p(R_{AB}^0) + \frac{1}{2}k(R_{AB} - R_{AB}^0)^2 + \dots \quad (2.16)$$

Based on the above treatment, Eq. 2.13 becomes

$$\left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dR_{AB}^2} + \frac{h^2 R(R+1)}{2\mu(R_{AB}^0)^2} + E_p(R_{AB}^0) + \frac{1}{2}k(R_{AB} - R_{AB}^0)^2 - E \right) f(R_{AB}) = 0. \quad (2.17)$$

We define the vibrational and rotational energies as  $E_v$  and  $E_R$

$$E_R = \frac{hR(R+1)}{2\mu(R_{AB}^0)^2} = hBR(R+1), \quad (2.18)$$

$$E_v = E - E_p(R_{AB}^0) - E_R$$

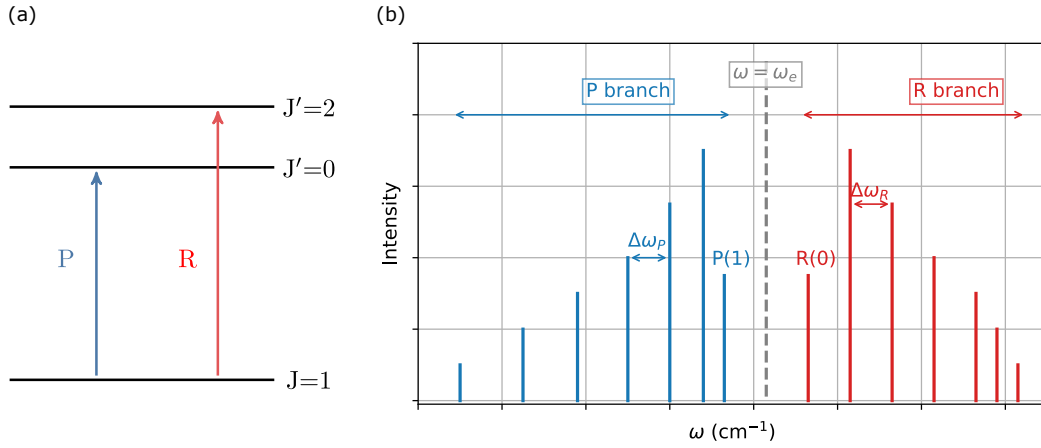
Here,  $B$  is the rotational constant. Substituting Eq. 2.18 to Eq. 2.17, we obtain

$$\left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dR_{AB}^2} + \frac{1}{2}k(R_{AB} - R_{AB}^0)^2 - E_v \right) f_v(R_{AB}) = 0. \quad (2.19)$$

From Eq. 2.19, we can see that  $E_v$  is the eigenenergy of a harmonic oscillator with values

$$E_v = h\omega_e \left( \nu + \frac{1}{2} \right). \quad (2.20)$$

Here,  $\omega_e$  is the vibrational constant and  $\nu$  is the vibrational quantum number. By convention, the vibrational constant is labelled by  $\omega_e$ . However, its value refers to frequency rather than angular frequency.  $E_v$  is indicated by the red dashed lines. Ideally, if the vibration between two nuclei is a perfect harmonic oscillator,  $E_v$  should be equally spaced. But due to the complex potential in the molecule, they are usually not. The zero point vibrational energy is defined as  $D_0 = D_{\partial E/\partial R_{AB}=0} - (1/2)h\omega_e$ , which is the energy difference between the  $\nu = 0$  state and vacuum level. It is interesting that energy required to break the chemical bond between the two nuclei is not the total depth of the well. Such a phenomenon has a big consequence for chemical reactions [Iri07]. In Fig. 2.3, the rotational energy levels are highlighted by green dashed lines between two adjacent vibrational levels. Let's further discuss the transition between two vibrational levels. For instance, once the molecule being



**Fig. 2.4:** (a) Definition of P and R transitions. (b) Illustration of Rovibrational spectrum.

excited to the next vibrational level, its rotational level can be changed by plus or minus one. We label the transition  $|\nu = 0, R + 1\rangle \rightarrow |\nu = 1, R\rangle$  as  $P(R + 1)$ ,  $|\nu = 0, R - 1\rangle \rightarrow |\nu = 1, R\rangle$  as  $R(R - 1)$ .  $Q(R)$  means no change in angular momentum (see Fig. 2.4 (a)). In the ideal case,

$$\begin{aligned}\Delta E &= E_{\nu+1, R\pm 1} - E_{\nu, R}, \\ \Delta E_+ &= h\omega_e + 2hB(R + 1), \quad \text{R branch}, \\ \Delta E_- &= h\omega_e - 2hBR, \quad \text{P branch}.\end{aligned}\tag{2.21}$$

In Fig. 2.4 (b), it can be seen that  $R$  branch has higher frequency than the centre frequency  $\omega_e$ , while  $P$  branch is lower than  $\omega_e$ . Ideally, the energy separation in  $P$  or  $R$  branch is equal to  $hB$  in Eq. 2.21. In real case, rotational-vibrational coupling and centrifugal distortion cause the spacing unequal. To explain it, we need to introduce high-order corrections. We use the results from Ref. [BC03] directly,

$$\begin{aligned}E_{\text{vib}}(\nu) &= h\omega_e(\nu + 1/2) - h\omega_e x_e(\nu + 1/2)^2 + \dots \\ E_{\text{rot}}(\nu, R) &= hB(\nu)R(R + 1) - hD(\nu)R^2(R + 1)^2 + \dots\end{aligned}\tag{2.22}$$

Here  $x_e$  is the first-order correction due to the anharmonicity in the potential energy curve.  $D(\nu)$  is the first-order correction from the centrifugal distortion. Thus, the energy spacing in the rovibrational spectrum can be written as

$$\begin{aligned}\Delta E_R &= h\omega_e + hB_{R+1}(R + 1)(R + 2) - hB_R R(R + 1) \\ \Delta E_P &= h\omega_e + hB_{R+1}R(R - 1) - hB_R R(R + 1).\end{aligned}\tag{2.23}$$

The intensity distribution in Fig. 2.4 (b) is simply due to the Maxwell Boltzmann distribution. We summarize the above vibrational and rotational constants in Tab.

2.3. So far, we have discussed the gross structure of the ground state of  $^{174}\text{YbF}$

| Parameter (unit)     | Value for $X^2\Sigma^+$ state | Value for $A^2\Pi_{1/2}$ state |
|----------------------|-------------------------------|--------------------------------|
| $\omega_e$ (THz)     | 15.1895(2)                    | -                              |
| $\omega_e x_e$ (GHz) | 67.3(1)                       | -                              |
| $B(\nu = 0)$ (GHz)   | 7.23377(2)                    | 7.4276(4)                      |
| $D(\nu = 0)$ (kHz)   | 7.16(12)                      | 7.35 (12)                      |

**Tab. 2.3:** Measured rovibrational constants for the ground and first excited state of  $^{174}\text{YbF}$  [SWH96; Dun+95].

molecule. It is written as

$$\begin{aligned}
 E &= E_{\text{electron}} + E_{\text{vibration}} + E_{\text{rotation}} \\
 &\approx E_0 + \alpha A \Sigma + h\omega_e(\nu + \frac{1}{2}) + hBR(R + 1).
 \end{aligned}
 \tag{2.24}$$

In Fig. 2.5 (a) we show the gross structure of the electronic, vibrational and rotational levels based on measured parameters in the references mentioned in Fig. 2.1. Energy levels shown in this figure are also the most frequently used levels in this work. It can be seen that the frequency splitting between the ground and first excited electronic state is 542.8 THz. The frequency spacing between ground-state vibrational levels is 15.2 THz. The frequency splittings between  $|N = 0\rangle$  and  $|N = 1\rangle$ , and  $|N = 1\rangle$  and  $|N = 2\rangle$  are 14.5 and 28.9 GHz, respectively. Red lines indicate energy levels in the first electronic state which is from Ref. [Ho20]. In this work, we didn't calculate energy structure in the first electronic state.

Based on the gross structure shown above, we can proceed to discuss the hyperfine levels. The effective field-free Hamiltonian for a single vibrational state of the YbF ground state including nuclei rotation, spin-rotation coupling and hyperfine interaction is

$$H = B\hat{N}^2 + \gamma\hat{S} \cdot \hat{N} + b\hat{I} \cdot \hat{S} + C\hat{I} \cdot \hat{N} + cI_zS_z. \tag{2.25}$$

The calculation has been explained clearly in Ref. [SWH96]. The eigenvalues of the Hamiltonian in Eq. 2.25 are listed in Eq. 2.26,

$$\begin{aligned}
 E_{N+1} &= h \left( \frac{\gamma N}{2} + \frac{b}{4} + \frac{c}{4(2N+3)} + \frac{CN}{2} \right), \\
 E_{N-1} &= h \left( -\frac{\gamma(N+1)}{2} + \frac{b}{4} - \frac{c}{4(2N-1)} - \frac{C(N+1)}{2} \right), \\
 E_{N\pm} &= h \left( -\frac{1}{4}(\gamma + b + C) \pm \frac{1}{4} \sqrt{(\gamma - C)^2(2N+1)^2 + (2b + c - 2C)(2b + c - 2\gamma)} \right).
 \end{aligned}
 \tag{2.26}$$

The labelling of states is in the following way. Since  $S$  and  $I$  are both  $1/2$ , there are four hyperfine levels in each rotational level characterized by  $F = (N + 1), N, N, (N - 1)$ . The subscript of  $E$  stands for the  $F$  quantum number of the state. Moreover, to simplify the notation of the state, we use  $|(J)F, M\rangle$  to replace  $|N, S, J, I, F, M\rangle$ . The corresponding eigenstates can be written as,

$$\begin{aligned} |N^\pm, M\rangle &= x^\pm |(N + \frac{1}{2})N, M\rangle + y^\pm |(N - \frac{1}{2})N, M\rangle \\ |N + 1, M\rangle &= |(N + 1/2)N + 1, M\rangle \\ |N - 1, M\rangle &= |(N - 1/2)N - 1, M\rangle. \end{aligned} \quad (2.27)$$

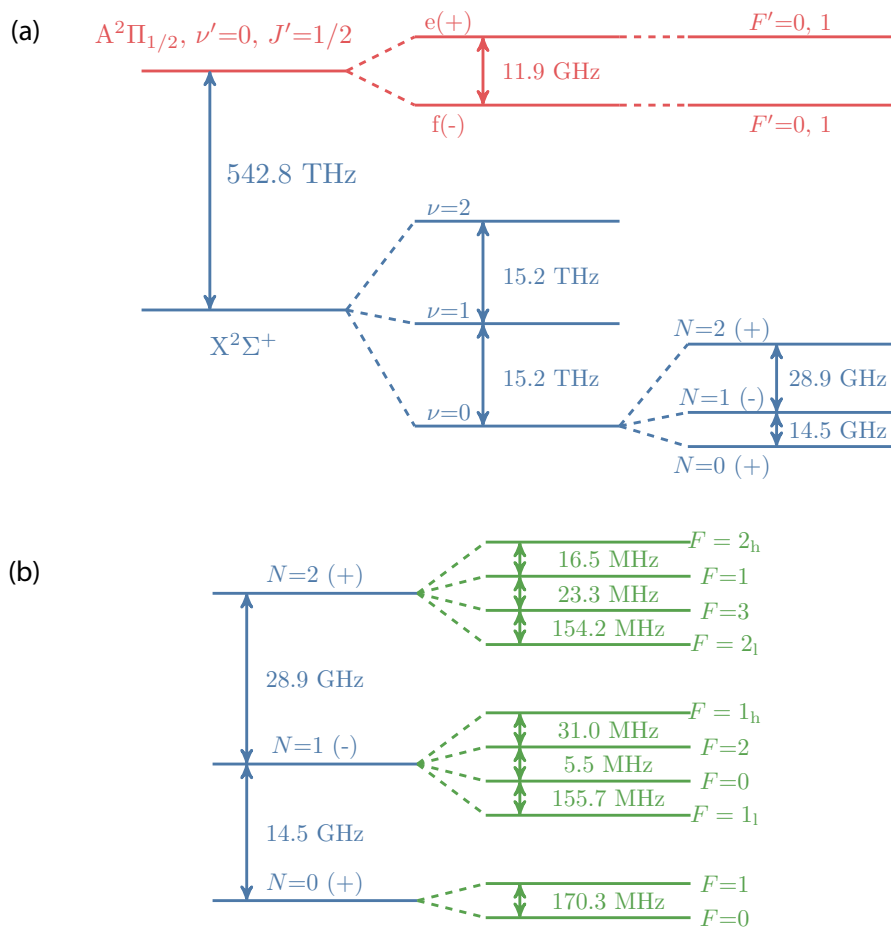
For instance, in the  $N = 1$  rotational level,  $F = 2$  state is labelled by  $|2, M\rangle = |(3/2)2, M\rangle$ . The ratio of the coefficients in the eigenvectors is given by

$$\frac{x^\pm}{y^\pm} = -\frac{\langle (N + \frac{1}{2})N, M | H | (N - \frac{1}{2})N, M \rangle}{\langle (N + \frac{1}{2})N, M | H | (N + \frac{1}{2})N, M \rangle - E_{N^\pm}}. \quad (2.28)$$

The corresponding constant being used above is summarized in [Tab. 2.4](#).

| Parameter (unit) | Value for $X^2\Sigma^+$ state |
|------------------|-------------------------------|
| $\gamma$ (MHz)   | -13.42400(16)                 |
| $b$ (MHz)        | 141.7965(5)                   |
| $c$ (MHz)        | 85.4026(14)                   |
| $C$ (kHz)        | 20.38(13)                     |

**Tab. 2.4:** Measured parameters for the hyperfine structure [\[SWH96\]](#).



**Fig. 2.5:** Energy levels of the  $^{174}\text{YbF}$  molecule used in this work. (a) is the first electronic, vibrational and rotational levels. (b) shows the hyperfine levels which connect energy levels on the right hand side of (a). It is an illustration of the YbF energy levels. Numbers have no correlation with the scale of gaps.

## 2.3 Interactions with external fields

In this section, we briefly discuss the **Wigner Eckart (WE)** theorem since it has been explained clearly in many atomic physics textbooks [BC03]. Next, we apply WE theorem and the state notation mentioned in the last section to calculate the transition dipole matrices. At last, we show the Stark, Zeeman and EDM interactions of YbF molecules.

### 2.3.1 Wigner Eckart theorem

The WE theorem was proposed by physicists Eugene Wigner and Carl Eckart. It claims that matrix elements of spherical tensor operators in the basis of angular momentum eigenvectors can be expressed in terms of the product of reduced matrix element which is independent of angular momentum orientation and **Clebsch-Gordan (CG)** coefficients. The power of WE theorem is to give people a fast way to tell whether a spherical tensor matrix element vanishes to zero or not. It also saves lots of time when people run simulation on computers because it avoids calculating wavefunction integral. The proof of the WE theorem is in Appx. 7.1.

The equation of the WE theorem is

$$\langle \alpha', j' m' | T_q^{(k)} | \alpha, j m \rangle = \langle j k; m q | j k; j' m' \rangle \frac{\langle \alpha' j' || T^{(k)} || \alpha j \rangle}{\sqrt{2j' + 1}}. \quad (2.29)$$

The LHS of the equation is the matrix element of a spherical tensor.  $T_q^{(k)}$  refers to the  $q$ -th component of the spherical tensor  $T^{(k)}$  of rank  $k$ . Here  $\langle j k; m q | j k; j' m' \rangle$  is the CG coefficient. The fraction in Eq. 2.29 is the reduced matrix element which is independent of magnetic quantum number  $q, m$  and  $m'$ . Usually, one writes the WE theorem in the 3- $j$  symbol style

$$\langle \alpha', j', m' | T_q^{(k)} | \alpha, j, m \rangle = (-1)^{j' - m'} \begin{pmatrix} j' & k & j \\ -m' & q & m \end{pmatrix} \langle \alpha', j' || T^{(k)} || \alpha, j \rangle. \quad (2.30)$$

We can easily see the relation between 3- $j$  symbols and CG coefficients is

$$\langle j k; m q | j k; j' m' \rangle = (-1)^{j' - m'} \sqrt{2j' + 1} \begin{pmatrix} j' & k & j \\ -m' & q & m \end{pmatrix}. \quad (2.31)$$

CG coefficients can be found on the PDG website [PDG23]. In Tab. 2.5, we use Eq. 2.31 to calculate an easy example of 3- $j$  symbols and CG coefficients to warm up

for the next section. In the next section, we will use WE theorem and 3- $j$  symbols frequently to calculate transition dipole matrix.

|                                | $j' = \frac{5}{2}$<br>$m' = \frac{1}{2}$ | $\frac{3}{2}$<br>$\frac{1}{2}$ | $\frac{1}{2}$<br>$\frac{1}{2}$ |
|--------------------------------|------------------------------------------|--------------------------------|--------------------------------|
| $m = \frac{3}{2} \quad q = -1$ | $\sqrt{\frac{1}{10}}$                    | $\sqrt{\frac{2}{5}}$           | $\sqrt{\frac{1}{2}}$           |
| $\frac{1}{2} \quad 0$          | $\sqrt{\frac{3}{5}}$                     | $\sqrt{\frac{1}{15}}$          | $-\sqrt{\frac{1}{3}}$          |
| $-\frac{1}{2} \quad 1$         | $\sqrt{\frac{3}{10}}$                    | $-\sqrt{\frac{8}{15}}$         | $\sqrt{\frac{1}{6}}$           |

**Tab. 2.5:** Example of using 3- $j$  symbol to produce CG coefficients ( $j=3/2$  and  $k=1$ ).

To work with atoms and molecules, we often have to deal with coupling among multiple angular momenta. The simplest example of the addition of angular momenta is singlet and triplet in quantum mechanics. The WE theorem we obtain above is to deal with coupling between two angular momenta. It can be generalized to study composite systems. The logic is that each tensor operator will only act on one particular angular momentum quantum number. It is also called decomposition rule

$$\begin{aligned} & \langle \alpha' j'_1 j'_2 j' || T^k || \alpha j_1 j_2 j \rangle \\ &= \delta_{j_2 j'_2} (-1)^{j'_1 + j'_2 + j + k} \sqrt{(2j+1)(2j'+1)} \begin{Bmatrix} j'_1 & j' & j'_2 \\ j & j_1 & k \end{Bmatrix} \langle \alpha j_1 || T^k || \alpha' j'_1 \rangle. \end{aligned} \quad (2.32)$$

Here  $j$  is the total angular momentum ( $j = j_1 + j_2$ ) and  $T^K$  is a tensor operator which only acts on  $j_1$ . The multiplying object on the right hand side is a 6- $j$  symbol. The explanation of decomposition law is in [Appx. 7.1](#).

### 2.3.2 Transition dipole matrix

The electric and magnetic dipole operators are defined as  $\hat{\mathbf{d}} \cdot \boldsymbol{\epsilon}_p$  and  $\hat{\boldsymbol{\mu}} \cdot \boldsymbol{\epsilon}_p$  with

$$\begin{aligned} \hat{\mathbf{d}} &= -e\hat{\mathbf{r}}, \\ \hat{\boldsymbol{\mu}} &= -\mu_B g_s \hat{\mathbf{S}}. \end{aligned} \quad (2.33)$$

Here  $\boldsymbol{\epsilon}_p$  is the spherical basis unit vectors. In terms of Cartesian basis  $e_x$ ,  $e_y$  and  $e_z$ , they are written as  $\epsilon_0 = e_z$  and  $\epsilon_{\pm 1} = \mp(e_x \pm ie_y)$ .  $\mu_B$  is the Bohr magneton. The next step is to use WE theorem and decomposition law to calculate dipole matrix element. Before doing that, it is beneficial to spend some times to label states clearly. Recall what we have discussed at the end of [Sec. 2.2.3](#). We express  $|N, F, m_F\rangle$  in

terms of  $|N, S, J, I, F, m_F\rangle$  for each hyperfine levels in Eq. 2.34. All the coefficients in the wavefunctions are obtained from Eq. 2.28. In the  $N=1$  or 2 manifold, in order to distinguish two different energy levels with same  $F$  quantum number, we use  $1_{l,h}$  or  $2_{l,h}$ .

$$\begin{aligned}
|0, 0, m_F\rangle &= |0, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 0, m_F\rangle \\
|0, 1, m_F\rangle &= |0, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 1, m_F\rangle \\
|1, 0, m_F\rangle &= |1, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 0, m_F\rangle \\
|1, 2, m_F\rangle &= |1, \frac{1}{2}, \frac{3}{2}, \frac{1}{2}, 2, m_F\rangle \\
|1, 1_l, m_F\rangle &= 0.536|1, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 1, m_F\rangle - 0.844|1, \frac{1}{2}, \frac{3}{2}, \frac{1}{2}, 1, m_F\rangle \\
|1, 1_h, m_F\rangle &= -0.844|1, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 1, m_F\rangle - 0.536|1, \frac{1}{2}, \frac{3}{2}, \frac{1}{2}, 1, m_F\rangle \\
|2, 1, m_F\rangle &= |2, \frac{1}{2}, \frac{3}{2}, \frac{1}{2}, 1, m_F\rangle \\
|2, 3, m_F\rangle &= |2, \frac{1}{2}, \frac{5}{2}, \frac{1}{2}, 3, m_F\rangle \\
|2, 2_l, m_F\rangle &= 0.564|2, \frac{1}{2}, \frac{3}{2}, \frac{1}{2}, 2, m_F\rangle - 0.826|2, \frac{1}{2}, \frac{5}{2}, \frac{1}{2}, 2, m_F\rangle \\
|2, 2_h, m_F\rangle &= -0.826|2, \frac{1}{2}, \frac{3}{2}, \frac{1}{2}, 2, m_F\rangle - 0.564|2, \frac{1}{2}, \frac{5}{2}, \frac{1}{2}, 2, m_F\rangle
\end{aligned} \tag{2.34}$$

The above information is enough to calculate transitions between rotational levels in the ground state (microwave and rf transitions). In order to calculate transition between electronic states, we need to express  $X^2\Sigma^+$  states in terms of  $A^2\Pi_{1/2}$  states. They are associated and reference [BH76] provides the method to expand X states in terms of A states for a linear molecule. In our case it is

$$|A, N, S, J, I, F, m_F\rangle = \sum_{\Sigma=-S}^S \sqrt{2N+1}(-1)^{N-S+\Sigma} \begin{pmatrix} J & S & N \\ \Omega & -\Sigma & -\Lambda \end{pmatrix} |A, S, \Sigma, J, \Omega, I, F, m_F\rangle. \tag{2.35}$$

In the  $X^2\Sigma^+$  state with  $\Lambda$  and  $S = 1/2$ , it becomes

$$\begin{aligned}
|N, S, J, I, F, m_F\rangle &= \frac{1}{\sqrt{2}}|A, S, -\Sigma, J, -\Omega, I, F, m_F\rangle \\
&+ \frac{(-1)^{N+J-1/2}}{\sqrt{2}}|A, S, \Sigma, J, \Omega, I, F, m_F\rangle.
\end{aligned} \tag{2.36}$$

If you forget the notations of angular momenta, please review Tab. 2.2. To evaluate the optical transition, it is basically to calculate the integral over above states

$$\langle A', S, \Sigma', J', \Omega', I, F', m'_F | \hat{\mathbf{d}} \cdot \boldsymbol{\epsilon}_p | A, S, \Sigma, J, \Omega, I, F, m_F \rangle \langle \nu' = 0 | \nu = 0 \rangle. \tag{2.37}$$



Here  $\langle \nu' | \nu \rangle$  is the FranckCondon factor of the vibrational states between the X and A states, which is 0.928 for the ground vibrational states of  $^{174}\text{YbF}$  [Zhu+11]. The  $\hat{\mathbf{d}} \cdot \boldsymbol{\epsilon}_p$  is electric dipole operator with index  $p$  indicating the index of the spherical basis. Applying WE theorem to the above expression to decouple  $F$  from  $I$  and  $J$ , Eq. 2.37 becomes

$$(-1)^{2F'-m'_F+J'+3/2} \sqrt{(2F+1)(2F'+1)} \begin{pmatrix} F' & 1 & F \\ -m'_F & p & m_F \end{pmatrix} \begin{Bmatrix} J' & F' & 1/2 \\ F & 1/2 & 1A \end{Bmatrix} \quad (2.38)$$

$$\times \langle A', S, \Sigma', J', \Omega' | \hat{\mathbf{d}} \cdot \boldsymbol{\epsilon}_p | A, S, \Sigma, J, \Omega \rangle.$$

Then apply decomposition rule to the above reduced matrix element [Wal+08]

$$\langle A', S, \Sigma', J', \Omega' | \hat{\mathbf{d}} \cdot \boldsymbol{\epsilon}_p | A, S, \Sigma, J, \Omega \rangle = \sum_{q=-1,1} (-1)^{J'-\Omega'} \sqrt{(2J+1)(2J'+1)} \times \begin{pmatrix} J' & 1 & J \\ -\Omega' & q & \Omega \end{pmatrix} \mu_{A-X}. \quad (2.39)$$

Here  $\mu_{A-X}$  is the transition dipole moment with value  $4.39 \pm 0.16$  Debye [Zhu+11]. Eventually, the expression to calculate optical transition is

$$\langle A', S, \Sigma', J', \Omega', I, F', m'_F | \hat{\mathbf{d}} \cdot \boldsymbol{\epsilon}_p | A, S, \Sigma, J, \Omega, I, F, m_F \rangle \langle \nu' | \nu \rangle = 0.928 \mu_{A-X} (-1)^{2F'-m'_F+2J'-\Omega'+3/2} \sqrt{(2F+1)(2F'+1)(2J+1)(2J'+1)} \times \sum_{q=-1,1} \begin{pmatrix} F' & 1 & F \\ -m'_F & p & m_F \end{pmatrix} \begin{Bmatrix} J' & F' & 1/2 \\ F & 1/2 & 1 \end{Bmatrix} \begin{pmatrix} J' & 1 & J \\ -\Omega' & q & \Omega \end{pmatrix}. \quad (2.40)$$

The results are summarized in Tabs. 2.6 and 2.7. It can be seen that along column sum of the square of each matrix element is 0.928 which is the branching ratio of the first vibrational state. Since  $N = 1$  has parity  $P = -1$  and  $N = 0, 2$  have parity  $P = +1$ , they will be excited to  $A^2\Pi_{1/2}$  e(+) and f(-), respectively. Thus we summarized them into two tables. The next step is calculate microwave transitions. For instance, in the optical pumping region and detection region, we have to drive transitions between  $N = 0$  to  $N = 1$  and  $N = 1$  to  $N = 2$  states. They are electric dipole transition as well. Different from optical transition, the dipole operator arises from the permanent dipole moment since there is a strong internal electric field along the internuclear axis,

$$\hat{\mathbf{d}} \cdot \boldsymbol{\epsilon}_p = \hat{\boldsymbol{\mu}}_e \cdot \boldsymbol{\epsilon}_p. \quad (2.41)$$

|                      | $ 0, 0\rangle$ | $ 1, -1\rangle$ | $ 1, 0\rangle$ | $ 1, 1\rangle$ |
|----------------------|----------------|-----------------|----------------|----------------|
| $ 1, 1_l, -1\rangle$ | 0.028          | -0.379          | 0.379          | 0              |
| $ 1, 1_l, 0\rangle$  | 0.028          | -0.379          | 0              | 0.379          |
| $ 1, 1_l, 1\rangle$  | 0.028          | 0               | -0.379         | 0.379          |
| $ 1, 0, 0\rangle$    | 0              | -0.454          | -0.454         | 0.454          |
| $ 1, 2, -2\rangle$   | 0              | -0.393          | 0              | 0              |
| $ 1, 2, -1\rangle$   | 0              | -0.278          | -0.278         | 0              |
| $ 1, 2, 0\rangle$    | 0              | -0.160          | -0.321         | -0.160         |
| $ 1, 2, 1\rangle$    | 0              | 0               | -0.278         | -0.278         |
| $ 1, 2, 2\rangle$    | 0              | 0               | 0              | -0.393         |
| $ 1, 1_h, -1\rangle$ | 0.555          | 0.297           | -0.297         | 0              |
| $ 1, 1_h, 0\rangle$  | 0.555          | 0.297           | 0              | -0.297         |
| $ 1, 1_h, 1\rangle$  | 0.555          | 0               | 0.297          | -0.297         |

**Tab. 2.6:** Calculated transition dipole matrix elements from  $X^2\Sigma^+$  ( $N=1$  manifold) to  $A^2\Pi_{1/2}$  e(+) state. Column and row stand for the X and A states respectively.

In order to simplify the calculation, we project the direction of external electric field onto the internuclear axis. Thus, we set the internuclear axis as the  $z$  axis ( $\hat{e}_0$ ) in the spherical coordinate,

$$\hat{\mu}_e \cdot \epsilon_p = \hat{\mu}_e D_{p0}^1. \quad (2.42)$$

The definition of  $D_{0p}^1$  is given in the proof of WE theorem in [Appx. 7.1](#) (please see [Eq. 7.3](#)). The superscript 1 tells this operator in a rank one tensor. The zero in the subscript indicates the index of the internuclear axis, and p is the direction of the external electric field. Then we calculate the integral between rotational levels

$$\begin{aligned} & \langle N', S, J', I, F', m'_F | \hat{\mu}_e D_{p0}^1 | N, S, J, I, F, m_F \rangle \\ &= \mu_e (-1)^{F'-m'_F} \begin{pmatrix} F' & 1 & F \\ -m'_F & p & m_F \end{pmatrix} \langle N', S, J', I, F' || D_{p0}^1 || N, S, J, I, F \rangle. \end{aligned} \quad (2.43)$$

Then we apply [Eq. 2.32](#) twice to obtain

$$\begin{aligned} & \langle N', S, J', I, F' || D_{p0}^1 || N, S, J, I, F \rangle \\ &= (-1)^{J'+J+N'+1+F} \sqrt{(2F'+1)(2F+1)(2J'+1)(2J+1)} \\ & \times \begin{Bmatrix} J' & F' & 1/2 \\ F & j & 1 \end{Bmatrix} \begin{Bmatrix} N' & J' & 1/2 \\ J & N & 1 \end{Bmatrix} \langle N' || D_{p0}^1 || N \rangle. \end{aligned} \quad (2.44)$$

The value of  $\langle N' || D_{p0}^1 || N \rangle$  is given by [\[BC03\]](#)

$$\langle N' || D_{p0}^1 || N \rangle = (-1)^{N'} \sqrt{(2N+1)(2N'+1)} \begin{pmatrix} N' & 1 & N \\ 0 & 0 & 0 \end{pmatrix}. \quad (2.45)$$

The final form of microwave transition matrix element is

$$\begin{aligned} \langle N', S, J', I, F' | \hat{\mathbf{d}} \cdot \boldsymbol{\epsilon}_p | N, S, J, I, F \rangle = \\ \mu_e (-1)^{J'+J+F'+F-m'_F+1} \times \sqrt{(2N+1)(2N'+1)(2J+1)(2J'+1)(2F+1)(2F'+1)} \\ \times \begin{pmatrix} F' & 1 & F \\ -m'_F & p & m_F \end{pmatrix} \begin{pmatrix} N' & 1 & N \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} J' & F' & 1/2 \\ F & J & 1 \end{Bmatrix} \begin{Bmatrix} N' & J' & 1/2 \\ J & N & 1 \end{Bmatrix}. \end{aligned} \quad (2.46)$$

Here  $\mu_e$  is the molecular dipole moment with value  $\mu_e = 3.91 \pm 0.03$  Debye. [SWH96]  
The results of microwave transition matrix is in [Tab. 2.8](#).

### 2.3.3 Selection rules

In this section we show the selection rules for optical, microwave and rf transitions. The selection rule of optical transition is

$$\begin{aligned} \Delta P &= \pm 1, \\ \Delta F &= 0, \pm 1, \\ \Delta m_F &= 0, \pm 1. \end{aligned} \quad (2.47)$$

It can be seen that optical transition must change parity. For instance, if we want to drive  $X^2\Sigma^+$  ( $N=1$ ) to the first excited state, we have to choose  $A^2\Pi_{1/2}$  e(+).

The selection rule for microwave transition between rotational levels is similar to optical transition, which is

$$\begin{aligned} \Delta N &= \pm 1, \\ \Delta F &= 0, \pm 1, \\ \Delta m_F &= 0, \pm 1. \end{aligned} \quad (2.48)$$

The first requirement is equivalent to changing parity.

The rf transition is the magnetic dipole transition which requires the same parity between initial and final states

$$\begin{aligned} \Delta F &= 0, \pm 1, \\ \Delta m_F &= 0, \pm 1. \end{aligned} \quad (2.49)$$

|                      | $ 0, 0\rangle$ | $ 1, -1\rangle$ | $ 1, 0\rangle$ | $ 1, 1\rangle$ |
|----------------------|----------------|-----------------|----------------|----------------|
| $ 0, 0, 0\rangle$    | 0              | 0.454           | -0.454         | 0.454          |
| $ 0, 1, -1\rangle$   | -0.454         | -0.454          | 0.454          | 0              |
| $ 0, 1, 0\rangle$    | -0.454         | -0.454          | 0              | 0.454          |
| $ 0, 1, 1\rangle$    | -0.454         | 0               | -0.454         | 0.454          |
| $ 2, 2_l, -2\rangle$ | 0              | -0.222          | 0              | 0              |
| $ 2, 2_l, -1\rangle$ | 0              | -0.157          | -0.157         | 0              |
| $ 2, 2_l, 0\rangle$  | 0              | -0.091          | -0.181         | -0.091         |
| $ 2, 2_l, 1\rangle$  | 0              | 0               | -0.157         | -0.157         |
| $ 2, 2_l, 2\rangle$  | 0              | 0               | 0              | -0.222         |
| $ 2, 1, -1\rangle$   | -0.321         | 0.161           | -0.161         | 0              |
| $ 2, 1, 0\rangle$    | -0.321         | 0.161           | 0              | -0.161         |
| $ 2, 1, 1\rangle$    | -0.321         | 0               | 0.161          | -0.161         |
| $ 2, 2_h, -2\rangle$ | 0              | 0.325           | 0              | 0              |
| $ 2, 2_h, -1\rangle$ | 0              | 0.230           | 0.230          | 0              |
| $ 2, 2_h, 0\rangle$  | 0              | 0.133           | 0.265          | 0.133          |
| $ 2, 2_h, 1\rangle$  | 0              | 0               | 0.230          | 0.230          |
| $ 2, 2_h, 2\rangle$  | 0              | 0               | 0              | 0.325          |

**Tab. 2.7:** Calculated transition dipole matrix elements from  $X^2\Sigma^+$  ( $N=0, 2$  manifold) to  $A^2\Pi_{1/2}$  f(-) state. Column and row stand for the X and A states respectively.

|                      | $ 0, 0, 0\rangle$ | $ 0, 1, -1\rangle$ | $ 0, 1, 0\rangle$ | $ 0, 1, 1\rangle$ |
|----------------------|-------------------|--------------------|-------------------|-------------------|
| $ 1, 1_l, -1\rangle$ | 0.577             | -0.020             | -0.020            | 0                 |
| $ 1, 1_l, 0\rangle$  | -0.577            | -0.020             | 0                 | -0.020            |
| $ 1, 1_l, 1\rangle$  | 0.577             | 0                  | 0.02              | 0.020             |
| $ 1, 0, 0\rangle$    | -0.333            | -0.333             | -0.333            | 0                 |
| $ 1, 2, -2\rangle$   | 0                 | -0.577             | 0                 | 0                 |
| $ 1, 2, -1\rangle$   | 0                 | 0.408              | -0.408            | 0                 |
| $ 1, 2, 0\rangle$    | 0                 | -0.236             | 0.471             | -0.236            |
| $ 1, 2, 1\rangle$    | 0                 | 0                  | -0.408            | 0.408             |
| $ 1, 2, 2\rangle$    | 0                 | 0                  | 0                 | -0.577            |
| $ 1, 1_h, -1\rangle$ | -0.029            | -0.408             | -0.408            | 0                 |
| $ 1, 1_h, 0\rangle$  | 0.029             | 0.408              | 0                 | -0.408            |
| $ 1, 1_h, 1\rangle$  | -0.029            | 0                  | 0.408             | 0.408             |

**Tab. 2.8:** Calculated transition dipole matrix elements within  $X^2\Sigma^+$  state, between  $N=0$  and 1 manifolds.

### 2.3.4 Stark effect

In this section, we will discuss the Stark effect. The reason to introduce it is that in the interaction region, YbF molecules will experience a strong electric field up to 20 kV·cm<sup>-1</sup>. Such electric field will change the energy levels of YbF. The Hamiltonian to study the Stark effect is

$$\begin{aligned}\hat{H} &= \hat{H}_{\text{rotation}} + \hat{H}_{\text{Stark}} + \hat{H}_{\text{hyperfine}} \\ &= B\hat{N}^2 - \hat{\mu} \cdot \vec{E} + \gamma\hat{S} \cdot \hat{N} + b\hat{I} \cdot \hat{S} + cI_z S_z + C\hat{I} \cdot \hat{N}.\end{aligned}\quad (2.50)$$

The Hamiltonian can be viewed in terms of two steps. The first step is to consider the rotation part and external electric field, which will give you the Stark shift of a quantum rigid rotor. As shown in Fig. 2.6 (a), rotation levels shift with external electric field increasing. It is hard to conclude a rule to tell whether a state will be shifted upwards or downwards in electric field. Because rotation levels with same  $m_F$  quantum number are strongly mixed. The next step is to add hyperfine interaction into consideration which is called tensor Stark shift. The tensor Stark shift is both  $F$  and  $m_F$  dependent. For instance, in the  $X^2\Sigma^+$  ( $N = 0$ ) state, under 20 kV·cm<sup>-1</sup> electric field, the tensor Stark shift between  $F=0$  and 1 states is about 6 MHz. In Fig. 2.6 (a), the Stark shift is at GHz level, but it doesn't cause rotation levels to cross over. Thus, we still use quantum number  $N$  to label states although it is not a good quantum number.

### 2.3.5 Zeeman interaction

In many regions of the machine, we apply magnetic field: in the laser cooling region, to destabilize dark states; and in the interaction region, to let YbF molecules acquire a dynamic phase. It is beneficial to discuss Zeeman interaction to warm up before discussing the above topics. The Zeeman Hamiltonian is  $m_F$  dependent with form

$$\hat{H}_{\text{Zeeman}} = g_S \mu_B \hat{S} \cdot \hat{B} = g_S \mu_B S_z B_z. \quad (2.51)$$

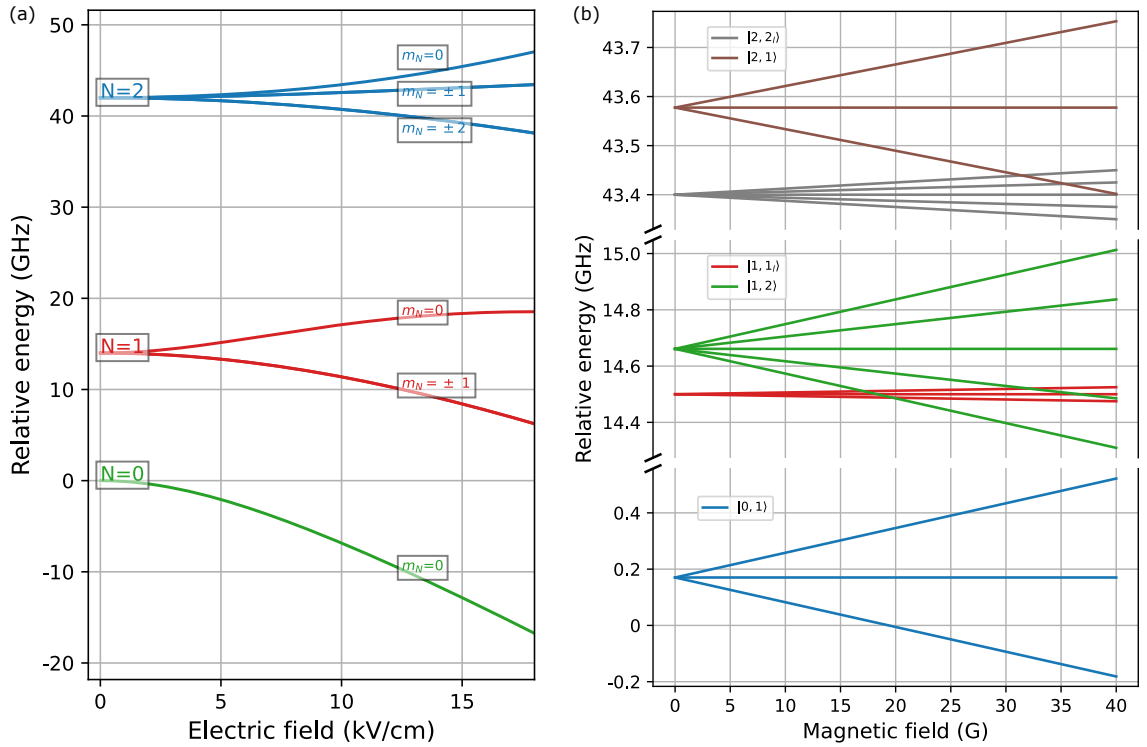
Here  $g_S$  is the absolute value of electron gyromagnetic ratio with value about 2.002 and  $\mu_B$  is the Bohr magneton. For simplicity, we consider magnetic field along  $z$  axis which give the Zeeman shift  $\Delta E_Z = g_F \mu_B m_F B_z$ , as shown in Fig. 2.6 (b). The  $g_F$  is the g-factor for each hyperfine level, which can be calculated by using spherical tensor methods. The idea is to calculate the integral

$$-g_S \mu_B \langle N', S, J', I, F', m_F' | \hat{S} \cdot \epsilon_p | N, S, J, I, F, m_F \rangle. \quad (2.52)$$

By applying the WE theorem and Eq. 2.32 twice, it becomes

$$\begin{aligned}
& g_s \mu_B (-1)^{1+F'-m'_F} \begin{pmatrix} F' & 1 & F \\ -m'_F & p & m_F \end{pmatrix} \langle N', S, J', I, F' | \hat{S} | N, S, J, I, F \rangle, \\
& \langle N', S, J', I, F' | \hat{S} | N, S, J, I, F \rangle = \\
& (-1)^{2J'+N'+F+1} \sqrt{(2F+1)(2F'+1)(2J+1)(2J'+1)} \\
& \times \begin{Bmatrix} J' & F' & 1/2 \\ F & J & 1 \end{Bmatrix} \begin{Bmatrix} 1/2 & J' & N' \\ J & 1/2 & 1 \end{Bmatrix} \langle N', S | \hat{S} | N, S \rangle.
\end{aligned} \tag{2.53}$$

The  $\langle N', S | \hat{S} | N, S \rangle$  is the reduced matrix element of a rank 1 tensor with value  $\delta_{NN'} \sqrt{(2S+1)(S+1)S}$ . The g-factors  $g_F = \frac{|g_F|}{m_F} \langle N', S, J', I, F', m'_F | \hat{S} \cdot \epsilon_0 | N, S, J, I, F, m_F \rangle$  are summarized in Tab. 2.9.



**Fig. 2.6:** (a) Stark shift for rotational levels. (b) Zeeman shift of hyperfine levels  $|N, F\rangle$ . Both in  $X^2\Sigma^+$  ( $\nu=0$ ) state.

### 2.3.6 EDM interaction

The EDM interaction directs along with the spin of the 6s electron and will interact with the internal effective electric field which is along the internuclear axis. It has the form

$$\hat{H}_{\text{edm}} = -\hat{d}_e \cdot \vec{E}_{\text{eff}} = d_e \frac{\hat{S}}{|\hat{S}|} \cdot E_{\text{eff}} \hat{n}. \quad (2.54)$$

By convention,  $\vec{E}_{\text{eff}} = -E_{\text{eff}} \hat{n}$  with a minus sign in front. The convention is that  $\hat{n}$  points from the F (negative charge) to Yb (positive charge), but the internal electric field points in the opposite direction. Since the phase coming from the EDM interaction is tiny, we need to make the measurement very long time to improve the precision. We also have to suppress phases coming from any other sources, such as magnetic noise, uniformity of electric, magnetic fields, and etc.

## 2.4 Summary

In this chapter, we have shown the electronic and rovibrational spectrum and hyperfine levels of the  $^{174}\text{YbF}$  molecule. We also summarize the proof of WE theorem and extend it to multiple angular momenta coupling. Then we use the introduced method to calculate the optical, microwave and rf transition dipole matrices. Such matrix elements will be used in the next chapter to run the optical Bloch equation calculation. We also introduce Stark, Zeeman and EDM interactions which will be needed to explain the experiments in the interaction region. Since this work contains many optical and microwave transitions, all the lasers and microwaves are summarised in [Sec. 7.3](#).

| $ N, F\rangle$   | $g_F$  |
|------------------|--------|
| $ 0, 0\rangle$   | 0      |
| $ 0, 1\rangle$   | -1     |
| $ 1, 0\rangle$   | 0      |
| $ 1, 1^-\rangle$ | -0.071 |
| $ 1, 1^+\rangle$ | -0.429 |
| $ 1, 2\rangle$   | -0.5   |
| $ 2, 1\rangle$   | 0.5    |
| $ 2, 2^-\rangle$ | -0.071 |
| $ 2, 2^+\rangle$ | -0.096 |

**Tab. 2.9:** Calculated g-factors in the  $X^2\Sigma^+$  ( $\nu=0$ ) state.

# Optical Bloch equations and laser cooling

In this chapter we will study the **optical Bloch equations (OBEs)** and laser cooling by using the dipole matrix elements obtained in [Chap. 2](#). Firstly, we introduce how to set up optical Bloch equations and discuss related parameters such as spontaneous decay, frequency detuning and saturation intensity. Secondly, we discuss how to apply OBEs to calculate cooling force and present results for one-dimensional cooling. Then we will introduce the destabilization of dark states to improve laser cooling. Then, it comes to the discussion of two-dimensional laser cooling which is closely related to our experiments. At last, we will discuss state manipulation which is based on OBEs such as  $\pi$  pulse and stimulated Raman adiabatic passage.

## 3.1 Optical Bloch equations

Optical Bloch equations are closely related to the Lindblad master equations. The slight difference between these two terms is that Lindblad master equations consider more general configurations such as open quantum systems. They are first-order time-dependent differential equations to describe the evolution of a quantum system. It is based on von-Neumann equations which describes how density matrix evolves in time. In this section, we first introduce density matrices and some useful properties of density matrices. Then we will set up Lindblad master equations which will be used in the laser cooling and state manipulation sections.

### 3.1.1 Density matrix

In most cases of quantum mechanics, one can either use a state vector or a density matrix to describe a system. State vectors can only represent pure states. However, density matrices can describe both pure and mixed states, which makes density matrices a crucial tool in quantum mechanics. Moreover, a density operator is



represented by a density matrix. The values of the matrix elements depend on which basis is used. The definition of a density matrix for a mixed state is

$$\hat{\rho} = \sum_i p_i |\Psi\rangle\langle\Psi|. \quad (3.1)$$

Here  $p_i$  is the probability of a particular pure state. In this work, we focus on pure states. The density matrix for a pure state is

$$\hat{\rho} = |\Psi\rangle\langle\Psi|. \quad (3.2)$$

Density matrices have many mathematical properties. We will introduce three of them which will be used in the following discussion,

$$\begin{aligned} \text{Tr}\hat{\rho} &= 1, \\ \hat{\rho}^\dagger &= \hat{\rho}, \\ \langle\hat{A}\rangle &= \text{Tr}(\hat{\rho}\hat{A}). \end{aligned} \quad (3.3)$$

Here, Tr is the trace of a matrix. The first expression in Eq. 3.3 tells that the trace of a density matrix is equal to one. Namely, the sum of the population terms  $\rho_{ii}$  is equal to one. It can be used to check the validity of OBEs calculation. The second property states that the density matrix is Hermitian conjugated to itself. Such property can be used to simplify the calculation of OBEs. Because once  $\rho_{ij}$  is obtained, we can use  $\rho_{ji} = \rho_{ij}^\dagger$  to obtain  $\rho_{ji}$  immediately. The third property gives us a shortcut to calculate the expectation value of an operator. We will use it to calculate the force operator in the discussion of laser cooling.

### 3.1.2 Lindblad master equation

We have introduced density matrices in the last section. The next step is to describe the time evolution of them. The reason to study the time evolution is that in the experiment we want to know how long it takes to let a molecule evolve to a steady state when it interacts with lasers.

The equation to describe the time evolution of a pure state in the Schrödinger picture is von Neumann equation

$$i\hbar \frac{d\hat{\rho}}{dt} = [\hat{H}, \hat{\rho}]. \quad (3.4)$$

However, an important property of a molecule is spontaneous decay, which is not considered in Eq. 3.4. The parameter to describe spontaneous decay is the reciprocal

of the lifetime of the excited state, which is usually written as  $\Gamma$ . The definition of  $\Gamma$  is

$$\Gamma = \frac{\omega^3 d_{eg}^2}{3\pi\epsilon_0 \hbar c^3}. \quad (3.5)$$

Here,  $\omega$  is the angular frequency of the transition and  $d_{eg}^2$  is the electric dipole between the two states which is defined as  $\langle e | \hat{d} \cdot \hat{\epsilon}_p | g \rangle$  (see Eq. 2.33). Regarding  $^{174}\text{YbF}$  molecules,  $\Gamma$  is equal to  $2\pi \times 5.7 \times 10^6$  Hz between the first electronic state and the ground state. The next step is to include the spontaneous decay into Eq. 3.4. Intuitively, for a two level system, the population term of the ground state  $\rho_{gg}$  will gain a factor of  $\Gamma \rho_{ee}$  from the excited state, simply because spontaneous decay transfers population from the excited state to the ground state. Correspondingly, the coherence terms  $\rho_{ij}$  also needs to be modified when spontaneous decay comes into play. The combination of the von Neumann equations and spontaneous decay is called Lindblad master equations or optical Bloch equations. Regarding detailed derivation of Lindblad master equations, we recommend Ref. [Man20]. The Lindblad master equations is written as [Man20]

$$\frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}] + \sum_{i,j} \Gamma_{ij} \left( \sigma_{ij} \hat{\rho} \sigma_{ij}^\dagger - \frac{1}{2} \hat{\rho} \sigma_{ij}^\dagger \sigma_{ij} - \frac{1}{2} \sigma_{ij}^\dagger \sigma_{ij} \hat{\rho} \right). \quad (3.6)$$

Here,  $\sigma_{ij}$  is the atomic operator, which is defined as  $\sigma_{ij} = |i\rangle\langle j|$ . And  $\Gamma_{ij}$  is the spontaneous decay between the  $|i\rangle$  and  $|j\rangle$  states. With Eq. 3.6, we can write down the Lindblad master equations for a two-level system and bring up some important parameters of a quantum system which will be studied in the following sections. The Lindblad master equations for a two-level system is,

$$\begin{aligned} \frac{\partial \rho_{22}}{\partial t} &= i \frac{\Omega}{2} (\rho_{21} - \rho_{12}) - \Gamma \rho_{22}, \\ \frac{\partial \rho_{11}}{\partial t} &= -i \frac{\Omega}{2} (\rho_{21} - \rho_{12}) + \Gamma \rho_{22}, \\ \frac{\partial \rho_{12}}{\partial t} &= -\left(\frac{\Gamma}{2} + i\delta\right) \rho_{12} - i \frac{\Omega}{2} (\rho_{22} - \rho_{11}), \\ \frac{\partial \rho_{21}}{\partial t} &= -\left(\frac{\Gamma}{2} - i\delta\right) \rho_{21} + i \frac{\Omega}{2} (\rho_{22} - \rho_{11}). \end{aligned} \quad (3.7)$$

Here,  $\rho_{11}$  and  $\rho_{22}$  stand for the population of the ground and excited states.  $\Omega$ ,  $\Gamma$  and  $\delta$  are the Rabi frequency, spontaneous decay and laser frequency detuning, respectively. The laser frequency detuning is the frequency difference between the resonance frequency of the transition and the laser's optical frequency. When the

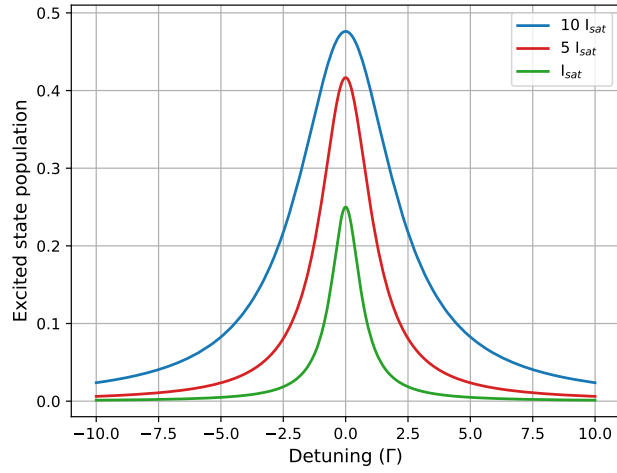
two-level system reaches steady state, we can write the excited state population  $\rho_{22}(\infty)$  analytically

$$\begin{aligned}\rho_{22}(\infty) &= \frac{1}{2} \frac{\Omega^2/2}{\delta^2 + \Omega^2/2 + \Gamma^2/4} \\ &= \frac{1}{2} \frac{I/I_{\text{sat}}}{1 + I/I_{\text{sat}} + 4\delta^2/\Gamma^2}.\end{aligned}\tag{3.8}$$

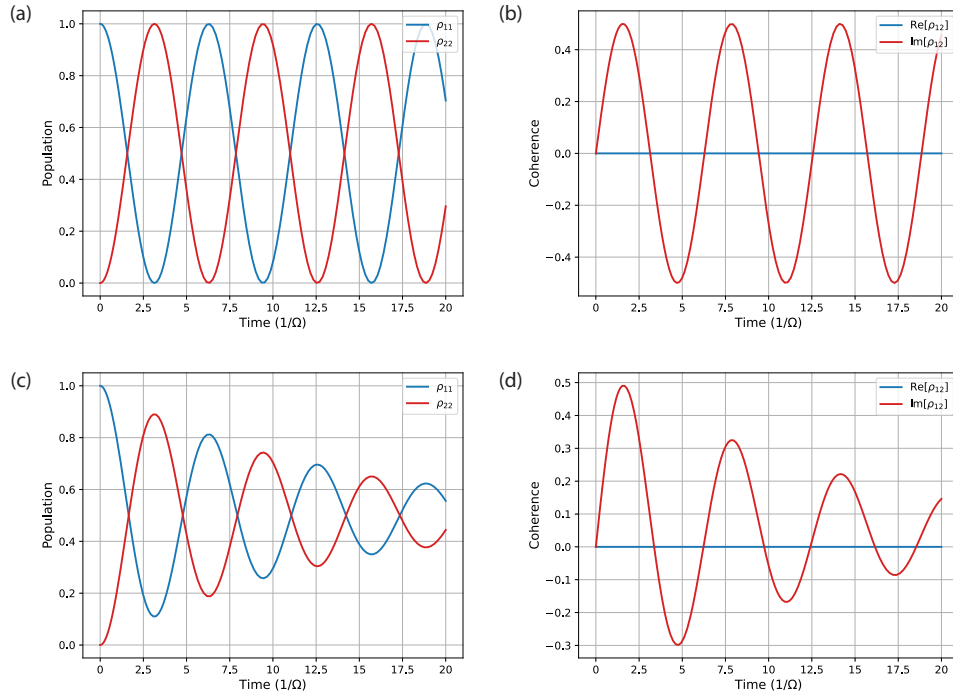
Here  $I/I_{\text{sat}} = 2\Omega^2/\Gamma^2$ .  $I$  is the laser intensity.  $I_{\text{sat}}$  is called saturation intensity with definition  $I_{\text{sat}} = \pi\hbar\Gamma/3\lambda^3$ . Regarding the transition between the ground and first excited states of  $^{174}\text{YbF}$ , the  $I_{\text{sat}}$  is equal to  $4.4 \text{ mW}\cdot\text{cm}^{-2}$ . With laser intensity approaches infinity,  $\rho_{22}(\infty)$  tends to a limiting value of  $1/2$ . Since the populations of both ground and excited states approach  $1/2$ , the rate of spontaneous emission for the two-level system tends to  $\Gamma/2$ . Such a phenomenon is plotted in Fig. 3.1. As can be seen, with laser intensity increasing from  $I_{\text{sat}}$  to  $10 I_{\text{sat}}$ , the excited state population approaches  $1/2$ . It is also clear that the maximum of excited state population occurs when the frequency detuning is equal to zero. Moreover, we can see that the profile becomes wider when laser intensity increases. Such a phenomenon is called power-broadening effect which will be used to explain Fig. 5.14 in the optical pumping region.

We further study the time evolution of the above two-level OBEs when laser frequency is on resonance in Fig. 3.2. In (a) and (b), we set the spontaneous decay  $\Gamma$  to zero. The population terms  $\rho_{11}$  and  $\rho_{22}$  oscillate against each other from 0 to 1, which is called Rabi oscillation. The real part of the coherence term  $\rho_{12}$  stays zero while its imaginary part oscillates from -0.5 to 0.5. In (c) and (d), we add back the spontaneous decay  $\Gamma$  and set the Rabi frequency  $\Omega = 10\Gamma$ . As can be seen in (c), both  $\rho_{11}$  and  $\rho_{22}$  tends to  $1/2$  after several Rabi oscillations. The real part of the coherence also keeps zero. The amplitude of the imaginary part decreases when the oscillation goes on.

In this section, we have introduced the Lindblad master equations (or optical Bloch equations), and some related parameters such as Rabi frequency  $\Omega$ , spontaneous decay  $\Gamma$  and frequency detuning  $\delta$ . In the next section, we will use OBEs (Eq. 3.6) to study laser cooling and how these parameters affect laser cooling.

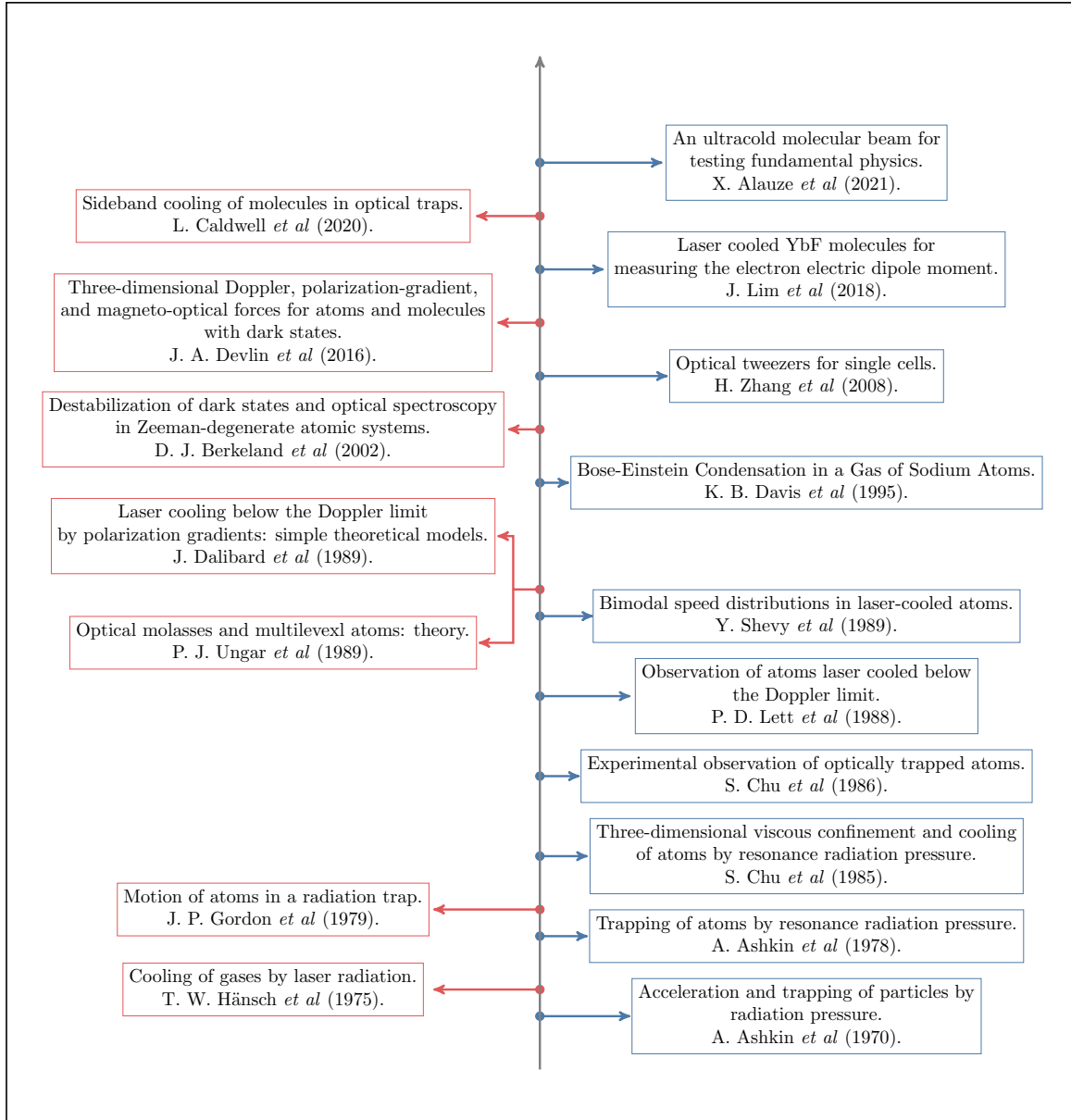


**Fig. 3.1:** Excited state population as a function of laser frequency detuning under three laser intensities.



**Fig. 3.2:** Time evolution of a two-level quantum system. Laser is on resonance. (a) Time evolution of population terms without spontaneous decay. (b) Time evolution of the coherence without spontaneous decay. (c) Time evolution of the population terms with spontaneous decay. (d) Time evolution of the coherence with spontaneous decay.

## 3.2 Laser cooling



**Fig. 3.3:** The history of laser cooling from 1970 to 2021. Theoretical works are highlighted in red on the left. Experimental works are highlighted in blue on the right.

In this section, we will show the theory of laser cooling and our calculation results. At beginning, we will introduce the force operator and the correlation between the force operator and OBEs. Next, we will study one-dimensional cooling of a quantum system containing two  $F$  levels to capture the physics of laser cooling. The definition of  $F$  is in Tab. 2.2. Then, we will introduce the destabilization of dark states aiming to improve laser cooling. Finally, we will study two-dimensional

laser cooling which is correlated with our experiments in [chapters. 4 and 5](#). Before discussing our work, it is beneficial to review the history of laser cooling as shown in [Fig. 3.3](#). Theoretical works are highlighted in red on the left and experimental works are highlighted in blue on the right. In 1970, Ashkin found that micron-sized particles can be accelerated and trapped in optical potential wells [\[Ash70\]](#). Thus, he proposed that by combining the technique of highly focused laser beams and atomic beam injection one should be able to confine atoms at temperatures around  $\mu K$  [\[AG78\]](#). In 1975, Hänsch proposed that a low density atomic gas can be cooled by an intense quasi-monochromatic red-detuned laser [\[HS75\]](#). In 1985, Steven Chu observed that sodium atoms can be cooled to  $240 \mu K$  with density  $10^6 \text{ cm}^{-3}$  by using three-dimensional counterpropagating laser beams [\[Chu+86\]](#). He called it viscous confinement which is also the origin of term optical molasses. After three years, Paul Lett achieved sub Doppler cooling on sodium gas with temperature  $43 \pm 20 \mu K$  [\[Phi+88\]](#). Based on the technique of laser cooling and trapping, Davis observed Bose-Einstein condensation of sodium atoms in a magneto-optical trap by using evaporative cooling with temperature below  $2 \mu K$  and atom density more than  $10^{14} \text{ cm}^{-3}$  [\[Dav+95\]](#). After 2000, one applies optical tweezers to manipulate cells, which opens the interplay between physics and biology [\[ZL08\]](#). In our group, we focus on applying lasers to cool molecules. In 2016 and 2020, we established the theory of laser cooling and magneto-optical trap on molecules and present systematic study on how laser detuning, laser intensity and magnetic field affect laser cooling [\[DT16; CT20\]](#). In 2018 and 2021, we observed sub Doppler cooling of  $^{174}\text{YbF}$  in 1d and 2d cases, which is the experimental foundation of this work [\[Lim+18; Ala+21\]](#).

### 3.2.1 Force operator

In this section, we will introduce force operator. By calculating the expectation value of the force operator, we can estimate the force experienced by molecules when they are interacting with the laser field. The force is treated in a way of classic physics, which means the force is the time derivative of momentum

$$\hat{f} = \frac{d\hat{p}}{dt}. \quad (3.9)$$

Since it involves the time derivative of an operator, it is straightforward to conduct the calculation in Heisenberg picture because observables are time dependent which is in contrast to the Schrödinger picture,

$$\frac{d\hat{A}}{dt} = \frac{i}{\hbar} [\hat{H}, \hat{A}]. \quad (3.10)$$

Equation 3.10 is the equation of motion in the Heisenberg picture. By combining these two equations, we obtain

$$\hat{f} = -\nabla \hat{H}. \quad (3.11)$$

This expression means only the gradient part of the Hamiltonian will contribute to the force. Thus, the next step is to extract the gradient of Hamiltonian. We write the Hamiltonian in terms of the energy of laser field, energy of molecules, and the electric dipole interaction between molecules and laser field,

$$\hat{H} = \hat{H}_{\text{field}} + \hat{H}_{\text{molecule}} - \hat{\mu} \cdot \vec{E}. \quad (3.12)$$

Before calculating the gradient of Eq. 3.12, we want to simplify the model to two-level systems for two reasons. Here two level system means a system contains two  $F$  levels each of which includes multiple  $m_F$  sublevels. One reason is to simplify the model and notation to obtain the analytic expression of the force operator. Another reason is that by using a simple model we can capture the physics of laser cooling clearly. Recall Fig. 2.5, the cooling transition of  $^{174}\text{YbF}$  we use is between  $|\nu = 0, N = 1(-)\rangle$  in the ground state and  $e(+)$  in the first excited state. Here we select three typical systems,  $|F = 0\rangle$  to  $|F' = 1\rangle$ ,  $|F = 1\rangle$  to  $|F' = 1\rangle$  and  $|F = 2\rangle$  to  $|F' = 1\rangle$ . Here  $F'$  stands for the  $F$  state in the excited state. The first system is called type-I system. The definition of type-I system is that the transition starts from a lower state with angular momentum  $F$  to an upper state with angular momentum  $F' = F + 1$ . The  $|F = 1\rangle$  to  $|F' = 1\rangle$  and  $|F = 2\rangle$  to  $|F' = 1\rangle$  are called type-II system in which  $F \geq F'$ . Then, we will use atomic operators which has been defined in Eq. 3.6 to label each state,

$$\sigma_{m,m'}^{i,j} = |i, m\rangle \langle j, m'|. \quad (3.13)$$

Here  $i$  or  $j$  takes value 1 or 2. "1" stands for the ground state and "2" is the excited state. The  $m$  and  $m'$  are the  $m_F$  sublevels in each state. For instance, the transition from  $|F = 2, m_F = -1\rangle$  to  $|F' = 1, m'_F = 0\rangle$  is labelled as  $\sigma_{-1,0}^{1,2}$ . The complex conjugate of such an atomic operator can be written down immediately  $(\sigma_{-1,0}^{1,2})^\dagger = \sigma_{0,-1}^{2,1}$ . Our notation is the same notation used in Ref. [Ung+89]. Let's go back to Eq. 3.12, we write the energy of the laser field and molecule as

$$\begin{aligned} \hat{H}_{\text{field}} &= \frac{1}{2} \int \left( \epsilon_0 \vec{E}^2 + \frac{\vec{B}^2}{\mu_0} \right) dV, \\ \hat{H}_{\text{molecule}} &= \frac{\hat{P}^2}{2M} + \sum_m \hbar \omega_0 \sigma_{mm}^{22}, \end{aligned} \quad (3.14)$$

where  $\epsilon_0$  and  $\mu_0$  are the vacuum permittivity and permeability, respectively.  $\vec{E}$  and  $\vec{B}$  are the electric and magnetic field.  $M$  and  $\hat{P}$  are the mass and momentum of the molecule. The  $\omega_0$  is the energy of the excited state with respect to the energy of the ground state which is set to zero. The energy of the electromagnetic field is evenly distributed in space, resulting in the gradient of  $\hat{H}_{\text{field}}$  to be zero. Regarding  $\hat{H}_{\text{molecule}}$ , we are not interested in the translation energy of the molecule so that the gradient of the first term in  $\hat{H}_{\text{molecule}}$  can be dropped. It is the same idea when you calculate the energy spectrum of a hydrogen atom you won't consider the translation energy of the entire atom. The second term is just the energy level of the excited state which doesn't have spatial gradient. So its gradient is equal to zero as well. Until now, the gradient of  $\hat{\mu} \cdot \vec{E}$  in Eq. 3.12 is the only term needs to be calculated. We quantize the electromagnetic field and write it in the following style [Ung+89]

$$\vec{E} = \hat{E}e^{-i\omega t} + \hat{E}^\dagger e^{i\omega t}. \quad (3.15)$$

Equation 3.15 rewrites the electric field in terms of field operators. Here  $\hat{E}$  and  $\hat{E}^\dagger$  are the annihilation and creation operators of electric field. Such a treatment comes from quantum field theory. Consider a Klein-Gordon equation and its free field solution,

$$\begin{aligned} \frac{\partial^2 \varphi}{\partial t^2} - \nabla^2 \varphi + m^2 \varphi &= 0, \\ \varphi(x) &\sim e^{-i(\omega_k x^0 - \vec{k} \cdot \vec{x})}, \\ \varphi(x, t) &\sim e^{-\frac{i}{\hbar}(Et - \vec{p} \cdot \vec{x})}. \end{aligned} \quad (3.16)$$

The second expression is the four vector notation of the free field solution of the Klein-Gordon equation. We can write the general solution of the Klein-Gordon equation in terms of Fourier expansion and define field operators,

$$\varphi(x) = \int \frac{d^3 k}{(2\pi)^{3/2} \sqrt{2\omega_k}} \left[ \varphi(\vec{k}) e^{-i(\omega_k x^0 - \vec{k} \cdot \vec{x})} + \varphi^*(\vec{k}) e^{i(\omega_k x^0 - \vec{k} \cdot \vec{x})} \right]. \quad (3.17)$$

We start the quantization process to promote the field  $\varphi(x)$  to an operator. It is done by replacing  $\varphi(\vec{k})$  and  $\varphi^*(\vec{k})$  by annihilation  $a(\vec{k})$  and creation  $a^\dagger(\vec{k})$  operators [Zee10]

$$\begin{aligned} \varphi(\vec{k}) &\rightarrow a(\vec{k}), \\ \varphi^*(\vec{k}) &\rightarrow a^\dagger(\vec{k}). \end{aligned} \quad (3.18)$$



By comparing Eqs. 3.18, 3.17 and 3.15, we can understand the logic how Ungar and Steven deal with electric field. The next step is to rewrite the dipole operator in terms of ladder operators, which is a common treatment in atomic physics [Ste07]

$$\hat{\mu} = \sum_{m,q} \hat{\mu}_m^q \sigma_{m,m+q}^{1,2} + H.c., \quad (3.19)$$

where  $\hat{\mu}_m^q$  is the dipole matrix element between  $|1, m\rangle$  and  $|2, m+q\rangle$ .  $H.c.$  represents the Hermitian conjugate of the first term. Here  $q$  is the unit vector of spherical basis, which means  $\hat{\mu}_m^q = \hat{e}_q \mu_m^q$ . All the values of dipole matrix elements  $\mu_m^q$  have been calculated in Tabs. 2.6, 2.7 and 2.8 in chapter 2. We will come back in the next section to explain spherical basis in details when we introduce polarization configurations. Now by multiplying Eqs. 3.15 and 3.19, we obtain the dipole interaction

$$\hat{\mu} \cdot \vec{E} = \sum_{m,q} (\hat{\mu}_m^q \cdot \hat{E}^\dagger) \sigma_{m,m+q}^{1,2} + H.c.. \quad (3.20)$$

Inserting Eq. 3.20 back to Eq. 3.11, we obtain the expression of the force operator

$$\hat{f} = \sum_{m,q} \sigma_{m,m+q}^{1,2} \nabla (\hat{\mu}_m^q \cdot \hat{E}^\dagger) + H.c.. \quad (3.21)$$

### 3.2.2 1D laser cooling

In the last section, we have introduced force operator. In this section, we will apply it to study one-dimensional (1D) laser cooling. We will study Doppler and sub Doppler cooling for type-I and type-II systems with various polarization configurations.

We will review the mechanism of Doppler cooling first. Assuming a molecule moving in a pair of red detuned counter propagating laser beams, due to Doppler effect, the molecule will see higher frequency of the laser propagating against it. When the Doppler shift  $kv$  is equal to the laser detuning  $\delta$ , the laser propagating against the molecule will be on resonance while the laser propagating along with the molecule will be more red detuned. Recall Fig. 3.1, photon absorption happens most efficiently when the laser frequency is on resonance. Such a process causes the imbalanced photon absorption rate between two lasers. The result is that the molecule will experience a net force whose direction is opposite to the velocity of the molecule. Detailed description of Doppler cooling is in Ref. [Foo04]. An important concept is Doppler cooling limit [Foo04]

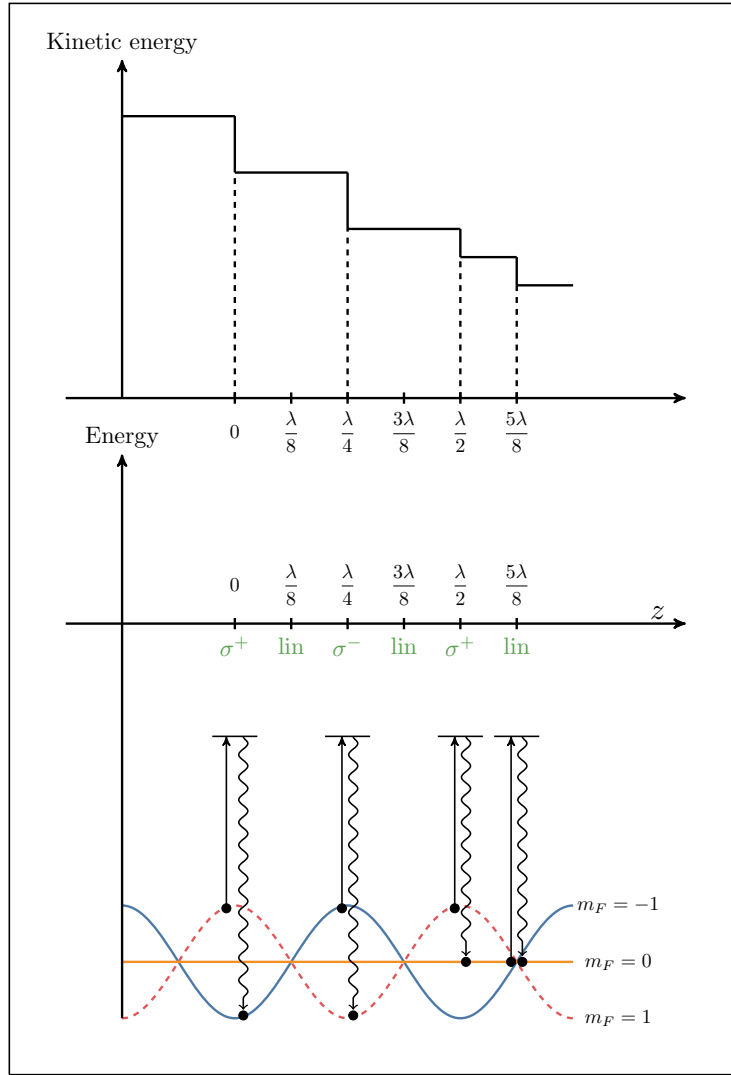
$$T_D = \frac{\hbar \Gamma}{2k_B}. \quad (3.22)$$

By using this expression, we can obtain the Doppler cooling limit of  $^{174}\text{YbF}$  which is  $137 \mu\text{K}$ . Next, we will introduce the principle of sub Doppler cooling which has been observed in our work. The principle is called Sisyphus effect which is originated from a Greek mythology where a character was condemned by gods to roll a stone to the top of a hill repeatedly. As shown in Fig. 3.4, we consider a molecule which only has  $m_F = 0, \pm 1$  three sublevels in the ground state. Let the molecule move in a standing wave formed by a pair of counter propagating red-detuned lasers whose polarizations are perpendicular to each other ( $\text{lin} \perp \text{lin}$ ). Due to the polarization gradient in space, the ac Stark shift of the  $m_F = 0, \pm 1$  ground states varies spatially as well. For instance, in the bottom part of Fig. 3.4, at location  $z = 0$ , the molecule is in  $m_F = 1$  state. After absorbing a  $\sigma^+$  photon to the excited state, it will decay to  $m_F = -1$  state because  $|m_F = -1\rangle$  has the lowest energy. Then after traveling  $\lambda/4$  distance, the molecule will absorb a  $\sigma^-$  photon to decay back to  $m_F = 1$  state. As shown in the top part of Fig. 3.4, by repeating such optical pumping events, the kinetic energy of the molecule will be reduced.

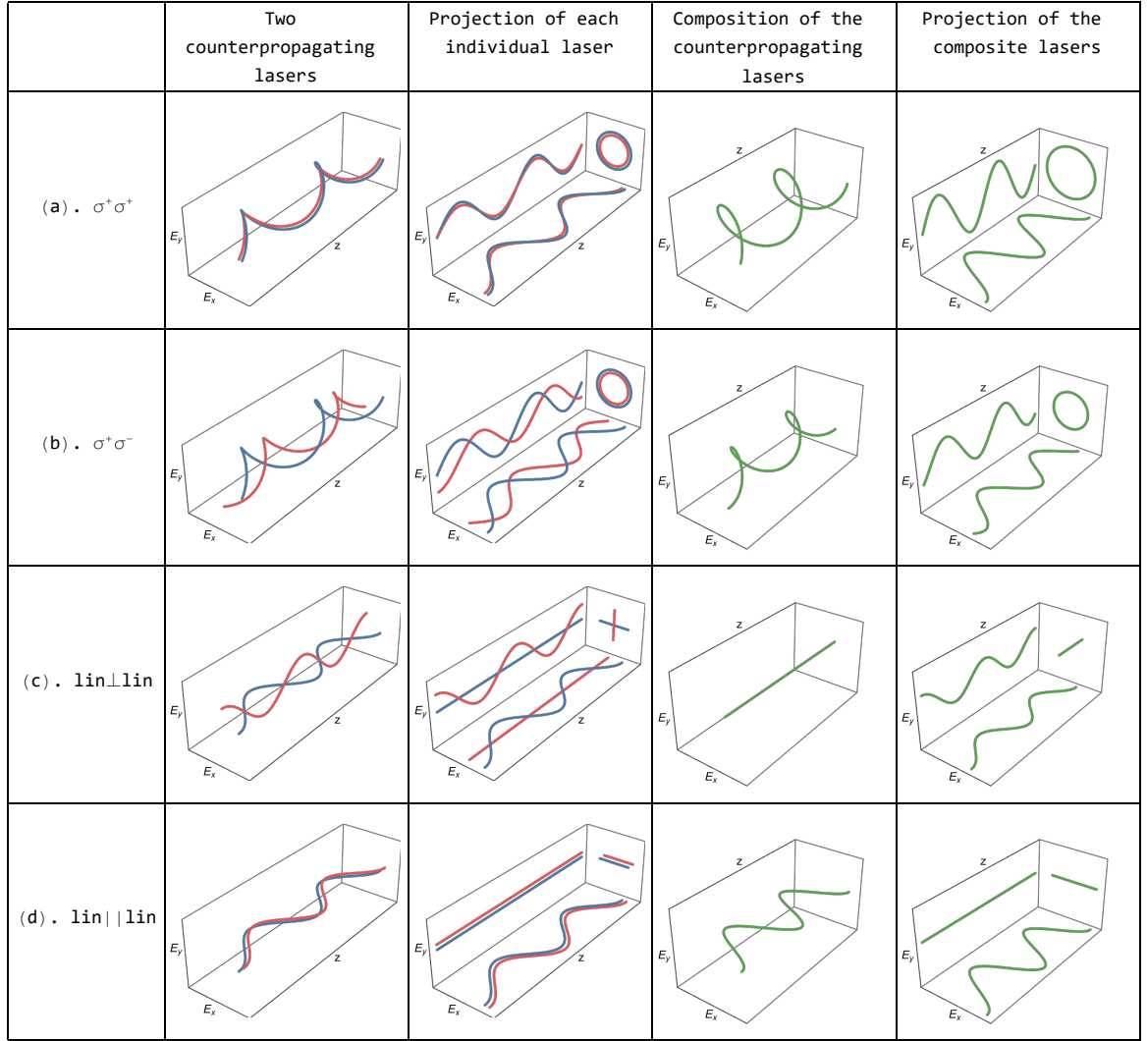
We list the polarization configurations being studied in this work in Fig. 3.5. From row (a) to (d), they are  $\sigma^+\sigma^+$ ,  $\sigma^+\sigma^-$ ,  $\text{lin} \perp \text{lin}$  and  $\text{lin} \parallel \text{lin}$ . Here  $\sigma^+\sigma^-$  ( $\sigma^+\sigma^+$ ) means both lasers are circular polarized and have same (opposite) helicity with respect to their own  $k$  vectors. The  $\text{lin} \perp \text{lin}$  ( $\text{lin} \parallel \text{lin}$ ) stands for both lasers are linear polarized and their polarization are perpendicular (parallel) to each other. We also studied polarization configurations with the angle between two linear polarized laser which is equal to  $\pi/8$  and  $\pi/4$ , which are not shown in Fig. 3.5. Since each row is plotted in the same style, explaining the first row should be enough for readers to understand the rest of them. The first figure of in row (a) shows the trajectories of the electric field vectors of the two counter propagating lasers which are highlighted in blue and red. Lasers travel along  $z$  axis, with  $E_x$  and  $E_y$  axes showing their electric field vectors in the  $x - y$  plane. The second figure is the projection of each individual laser on the  $E_x$  and  $E_y$  axes. The projection at the end view shows the trajectory of the electric field vector in the  $x - y$  plane, which explains the lasers are circular polarized. The third figure is the trajectory of the  $E$  field vector of the composition of the two lasers. And the last figure is the projection of the composite  $E$  field vector.

In order to apply the polarization to Eq. 3.21, we write down the expression for each polarization configuration,

$$\begin{aligned}
\sigma^+\sigma^+ : \vec{E} &= E_0\hat{e}_+e^{ikz} + E_0\hat{e}_+e^{-ikz}, \\
\sigma^+\sigma^- : \vec{E} &= E_0\hat{e}_+e^{ikz} + E_0\hat{e}_-e^{-ikz}, \\
\text{lin} \perp \text{lin} : \vec{E} &= E_0\hat{e}_xe^{ikz} + E_0\hat{e}_ye^{-ikz}, \\
\text{lin} \parallel \text{lin} : \vec{E} &= E_0\hat{e}_xe^{ikz} + E_0\hat{e}_xe^{-ikz}.
\end{aligned} \tag{3.23}$$



**Fig. 3.4:** Illustration of the Sisyphus effect in a  $\text{lin} \perp \text{lin}$  red-detuned laser field. The top part shows the reduction of kinetic energy after each optical pumping event. The bottom part shows the ac Stark shift of the  $m_F = 0, \pm 1$  ground states.



**Fig. 3.5:** Polarization configurations being studied in this work. Rows (a), (b), (c) and (d) are  $\sigma^+\sigma^+$ ,  $\sigma^+\sigma^-$ , lin $\perp$ lin and lin $\parallel$ lin, respectively.

Here  $\hat{e}_x$  and  $\hat{e}_y$  are the unit vectors in Cartesian basis. The  $\hat{e}_+$  and  $\hat{e}_-$  are the unit vectors in spherical basis. In order to calculate the  $\hat{\mu} \cdot \hat{E}$  term, it is more convenient to convert the dipole operator  $\hat{\mu}$  to Cartesian basis. Because the direction of polarization is usually labeled in terms of lab frame which is fixed once instruments are installed. We can write the dipole operator  $\hat{\mu}$  in the style of spherical basis,

$$\hat{\mu}_m^q = \hat{e}_q \mu_m^q. \quad (3.24)$$

Here  $\mu_m^q$  is the value of the dipole matrix element which has been calculated in the last chapter. The next step is to convert spherical unit vector  $\hat{e}_q$  to Cartesian basis. The transform matrix of the unit vectors in these basis is given by

$$\begin{bmatrix} \hat{e}_+ \\ \hat{e}_- \\ \hat{e}_0 \end{bmatrix} = \begin{bmatrix} -\frac{1}{\sqrt{2}} & -\frac{i}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & \frac{i}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \hat{e}_x \\ \hat{e}_y \\ \hat{e}_z \end{bmatrix}. \quad (3.25)$$

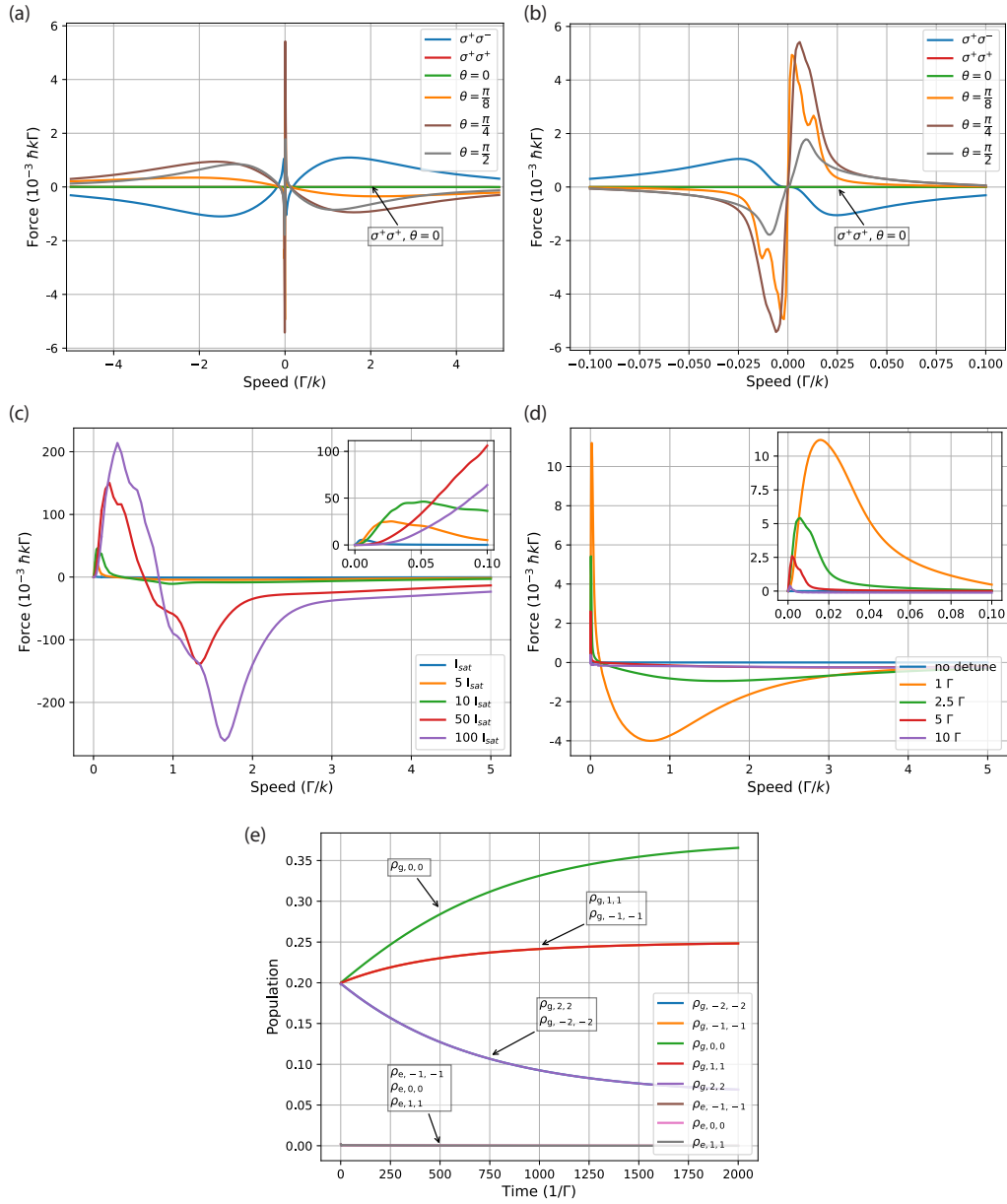
Until now, we have explained how to calculate Eq. 3.21. Figure 3.6 shows the results of 1D laser cooling of a  $|F = 2\rangle$  to  $|F' = 1\rangle$  system. Except for  $\text{lin} \perp \text{lin}$  ( $\theta = \pi/2$ ) and  $\text{lin} \parallel \text{lin}$  ( $\theta = 0$ ), we've also studied the cases where the angle  $\theta$  between two linear polarized light is  $\pi/8$  and  $\pi/4$ . In both (a) and (b), the laser detuning is  $-2.5\Gamma$  (red detuned) and laser intensity is one  $I_{\text{sat}}$ . Since the aim of 1D cooling is to understand the physics, we use normalised unit for speed ( $\Gamma/k$ ) and force ( $\hbar k \Gamma$ ). In the discussion of 2D cooling which is related with our experiments, we will use dimensions  $\text{m} \cdot \text{s}^{-1}$  and  $\text{m} \cdot \text{s}^{-2}$  for speed and acceleration. We denote direction to the right as the positive direction for both velocity and force. We call velocity higher (lower) than  $0.1 \Gamma/k$  high (low) velocity range.

In Fig. 3.6 (a), we can see that only  $\sigma^+ \sigma^-$  polarization shows a heating effect in the high velocity range. While  $\theta = \pi/8, \pi/4$  and  $\pi/2$  perform normal Doppler cooling. Moreover, the force is zero at all velocities in the  $\sigma^+ \sigma^+$  and  $\theta = 0$  cases. This system contains two dark states and three bright states. Thus, due to the absence of polarization gradient in  $\theta = 0$  case, all the population will be optically pumped to dark states causing zero cooling force. For  $\sigma^+ \sigma^+$  case, the electric field vector rotates everywhere in the same sense in either laser, causing all the population are optically pumped to one side of the ground state. Eventually, all the population will be accumulated into the dark states with respect to the  $\sigma^+$  laser, leaving a zero cooling force. In (b) which describes the low velocity range, it can be seen that  $\sigma^+ \sigma^-$  performs sub Doppler cooling. However,  $\theta = \pi/8, \pi/4$  and  $\pi/2$  perform sub Doppler heating. This result is consistent with [DT16; CM02]. It tells that sub

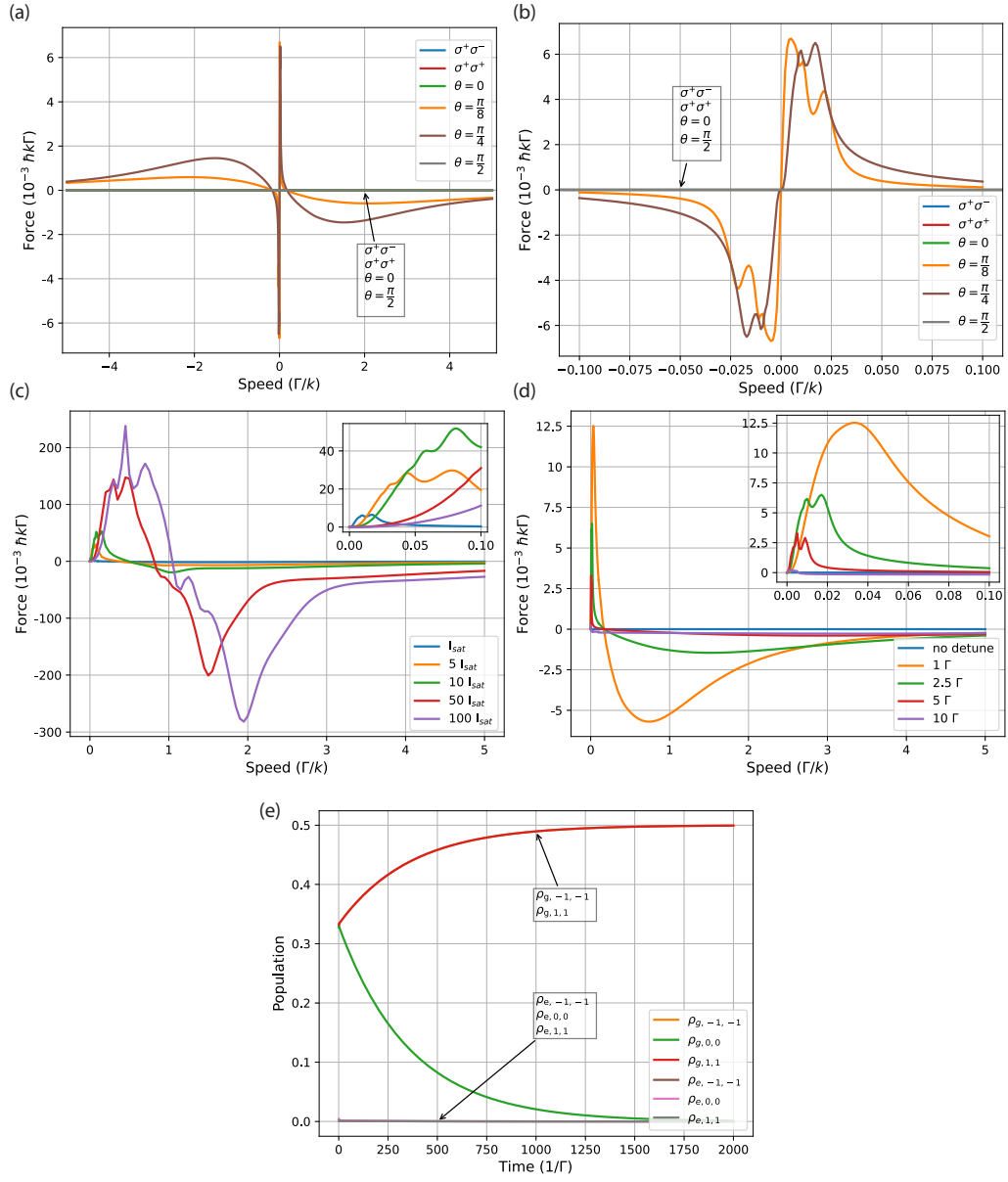
Doppler cooling can be observed in these three polarization configurations by using blue-detuned light.

In (c) and (d), we select  $\theta = \pi/4$  polarization to further study laser intensity and detuning because  $\theta = \pi/4$  is the intermediate between  $\theta = 0$  and  $\pi/2$ . As can be seen in Fig. 3.6 (c), with laser intensity increasing, both sub Doppler heating and Doppler cooling forces increase. From one  $I_{sat}$  to  $100 I_{sat}$ , force of sub Doppler heating increases from about 6 to  $200 \cdot 10^{-3} \hbar k \Gamma$  and Doppler cooling force increases from about 1 to  $250 \cdot 10^{-3} \hbar k \Gamma$ . Such a phenomenon suggests that high laser intensity can decelerate molecules in high velocity range effectively, but heating effect for low velocity molecules can't be ignored. In (d), we study the cooling force under five different laser detunings with  $I = I_{sat}$ . It is clear that there is no cooling force when  $\delta = 0$ . When we increase  $\delta$  to  $1 \Gamma$ , it shows largest sub Doppler heating (inset plot) and Doppler cooling. However, if we keep increasing  $\delta$  to  $10 \Gamma$ , both sub Doppler heating and Doppler cooling effect vanishes. Because large detuning cause scattering rate decreased significantly. In (e), we plot the population terms of the density matrix at zero velocity when  $\theta$  is equal to  $\pi/4$ . We evenly distribute the population for the five  $m_F$  sublevels in the  $|F = 2\rangle$  ground state at  $t = 0$ , which is also the initial condition for the calculation in (a) to (d). It can be seen that the population are redistributed when the system reaches steady state. The  $m_F = 0$  sublevel takes about 35% while  $m_F = \pm 1$  and  $m_F = \pm 2$  sublevels take 50% and 15% of the total population.

Next, we study the  $|F = 1\rangle$  to  $|F' = 1\rangle$  system in Fig. 3.7. In (a), it shows that only  $\theta = \pi/8$  and  $\pi/4$  perform non-zero force while  $\sigma^+ \sigma^-$ ,  $\sigma^+ \sigma^+$ ,  $\theta = 0$  and  $\theta = \pi/2$  all experience zero forces over the entire velocity range. The reason that  $\sigma^+ \sigma^+$  and  $\theta = 0$  show zero forces can be explained using the same reason of the  $|F = 2\rangle$  to  $|F' = 1\rangle$  system in the last paragraph. But in  $\sigma^+ \sigma^-$  and  $\theta = \pi/2$ , the existence of polarization gradient still gives a zero force, which is different from the  $|F = 2\rangle$  to  $|F' = 1\rangle$  case. Reference [DT16] gives the explanation that one of the two beams optically pumps the molecule into a dark state then the opposing beam pumps the molecule out of the dark state. The averaged number of scattered photons will be same for each laser, leaving the net force zero [DT16]. In Fig. 3.7 (a) and (b), for  $\theta = \pi/8$  and  $\pi/4$  it shows the same sub Doppler heating and Doppler cooling as compared with Fig. 3.6, although the profile of sub Doppler heating is slightly different. In (c) and (d), we also choose  $\theta = \pi/4$  to study laser intensity and detuning. In (c), it is clear that with laser intensity increasing, both sub Doppler heating and Doppler cooling effect are enhanced. In (d), we also see that when  $\delta$  is equal to  $1 \Gamma$ , the molecule experiences largest force. Both (c) and (d) are similar to the results of  $|F = 2\rangle$  to  $|F' = 1\rangle$  system. In (e), we plot the OBEs of the  $\theta = \pi/4$



**Fig. 3.6:** Summary of 1D laser cooling for a  $|F' = 2\rangle$  to  $|F' = 1\rangle$  system. (a) and (b) cooling forces in all velocity range and low velocity range with  $\delta = -2.5\Gamma$  and  $I = I_{sat}$ . (c) Cooling forces calculated with different laser intensities with  $\delta = -2.5\Gamma$ . (d) Cooling forces calculated with different laser frequency detunings with  $I = I_{sat}$ . (e) OBEs at zero velocity with  $\theta = \pi/4$ .



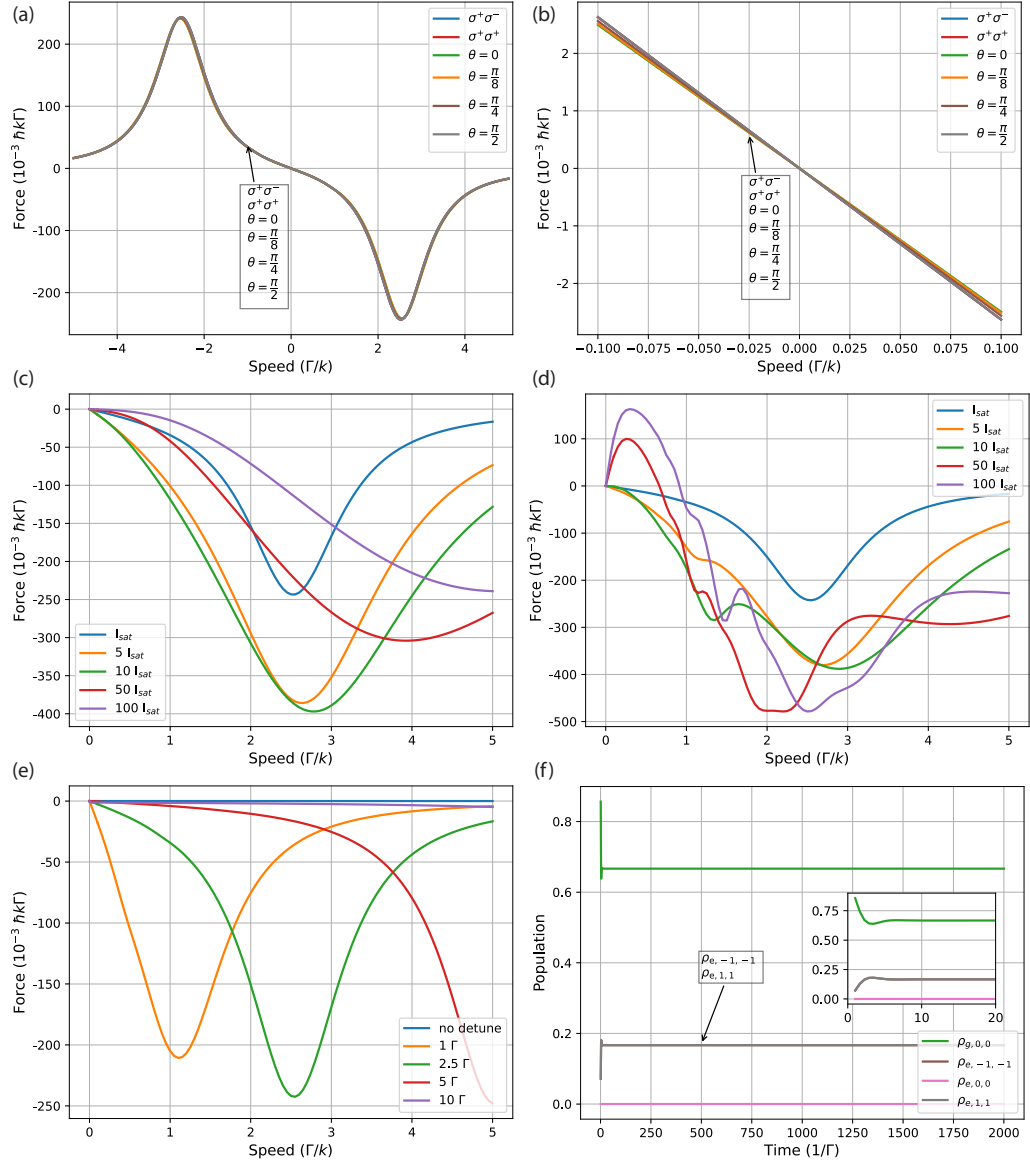
**Fig. 3.7:** Summary of 1D laser cooling for a  $|F=1\rangle$  to  $|F'=1\rangle$  system. (a) and (b) cooling forces in all velocity range and low velocity range with  $\delta = -2.5 \Gamma$  and  $I = I_{sat}$ . (c) Cooling forces calculated with different laser intensities with  $\delta = -2.5 \Gamma$ . (d) Cooling forces calculated with different laser frequency detunings with  $I = I_{sat}$ . (e) OBEs at zero velocity with  $\theta = \pi/4$ .



polarization with initial population evenly distributed for  $m_F = 0, \pm 1$  sublevels. It can be seen that when the systems evolves to the steady state the  $m_F = \pm 1$  sublevels occupy all the population while the population of  $m_F = 0$  sublevel is empty.

Next, we study the  $|F = 0\rangle$  to  $|F' = 1\rangle$  system which is a type-I system in Fig. 3.8. Thus, we expect different results compared with the  $|F = 2\rangle$  to  $|F' = 1\rangle$  and  $|F = 1\rangle$  to  $|F' = 1\rangle$  (type-II) systems. To remind the reader, the definition of type-I and type-II system is in the paragraph which describes Eq. 3.13. Since  $F'$  is larger than  $F$  in the type-I system, it avoids that molecules are optically pumped into dark states. The majority of MOTs use such a transition and are called type-I MOTs. The cooling force of the type-I system has been studied extensively both experimentally [Wei+89; Let+89] and theoretically [Jav91; Mo91].

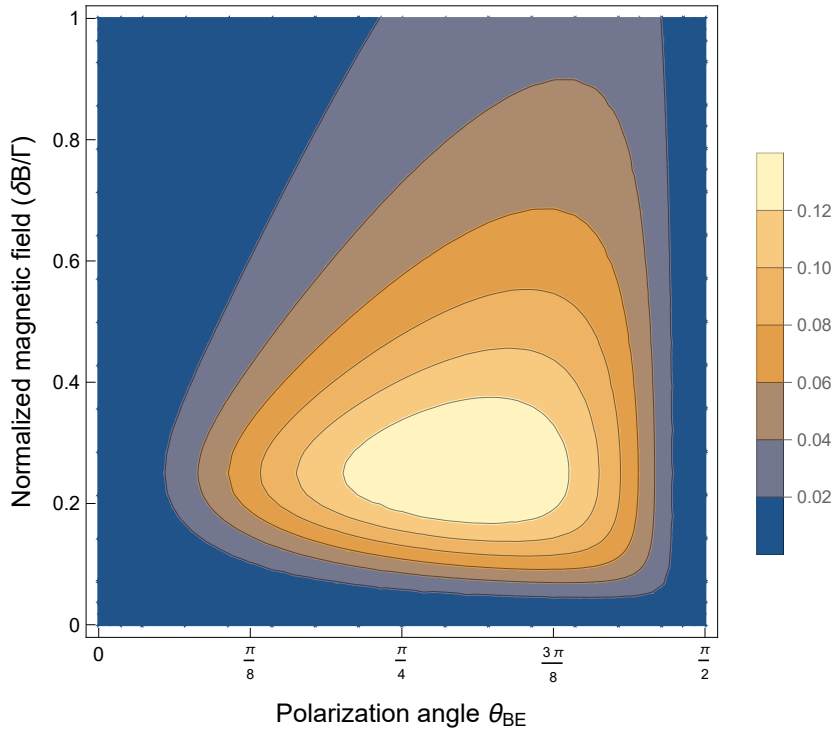
In Fig. 3.8 (a) and (b), with same detuning and laser intensity,  $|F = 0\rangle$  to  $|F' = 1\rangle$  system shows different profile compared to  $|F = 2\rangle$  to  $|F' = 1\rangle$  and  $|F = 1\rangle$  to  $|F' = 1\rangle$  systems. All the polarization configurations demonstrate typical Doppler cooling effect, with largest cooling force happening when laser detuning is equal to the Doppler shift. Because there is only one sublevel in the ground state and three sublevels in the excited state, any polarization can optically pumps the molecule between the ground and excited states. Moreover, the Doppler cooling force is about two orders larger than (a)s in Fig. 3.6 and 3.7, suggesting in order to achieve better laser cooling, type-I system is better than type-II system. The result is also consistent with Ref. [DT16]. In (b), there is no sub Doppler effect. Then we select  $\sigma^+\sigma^-$  and  $\theta = \pi/4$  cases to study how laser intensity affects cooling force, with laser intensity changing from  $I_{sat}$  to  $100 I_{sat}$ . As can be seen in (c), the largest cooling force happens when laser intensity is  $10 I_{sat}$ . It decreases after keep increasing laser intensity, which is agreement with Ref. [Ala+21]. It tells that the cooling force does not increase indefinitely with laser intensity. In (d), by using  $\theta = \pi/4$  polarization, we observe sub Doppler heating effect when laser intensity is larger than  $50 I_{sat}$ . Different from (c), the cooling force does not decrease after  $10 I_{sat}$ . For both 50 and  $100 I_{sat}$ , the cooling force is saturated around  $0.5 \hbar k \Gamma$ . In (e), by changing detuning from 0 to  $10 \Gamma$ , we find that the largest Doppler cooling force happens when the Doppler shift is equal to detuning. We run the calculation for all the polarization configurations. They all show the same profile. In (e), we plot the OBEs for the  $|F = 0\rangle$  to  $|F' = 1\rangle$  system. Compared with OBEs in Fig. 3.6 and 3.7, the OBEs in a type-I system reach steady state significantly faster. Moreover, the excited state population in the  $|F = 0\rangle$  to  $|F' = 1\rangle$  system is about 18% which is much larger than the  $|F = 2\rangle$  to  $|F' = 1\rangle$  and  $|F = 1\rangle$  to  $|F' = 1\rangle$  systems. Such a difference also explains why a type-I system can produce much larger cooling force than type-II system, because excited state population determines photon scattering rate.



**Fig. 3.8:** Summary of 1D laser cooling for a  $|F=0\rangle$  to  $|F'=1\rangle$  system. (a) and (b) cooling forces in full velocity range and low velocity range with  $\delta = -2.5\Gamma$  and  $I = I_{sat}$ . (c)  $\sigma^+\sigma^-$  polarization with  $\delta = -2.5\Gamma$ . (d)  $\theta = \pi/4$  polarization with  $\delta = -2.5\Gamma$ . (e) Force with various detuning for all polarizations. (f) OBEs for all polarizations.

### 3.2.3 Dark state destabilization

In the last section, we have studied laser cooling in 1D systems with several polarization configurations and how laser detuning and intensity affect cooling force. Due to the observation that a type-I system performs larger cooling force than a type-II system, we believe that in order to improve cooling force for a type-II system removing dark states from the system should be a good approach. Berkeland proposed the technique of dark state destabilization by applying a magnetic field to atoms or molecules [BB02]. By studying a two-level system with the angular momenta of the ground and excited states 1 and 0 ( $|J = 1\rangle$  to  $|J' = 0\rangle$ ), they derive the analytic expression of the excited state population as a function of Zeeman shift and the angle between magnetic field and laser polarization [BB02].

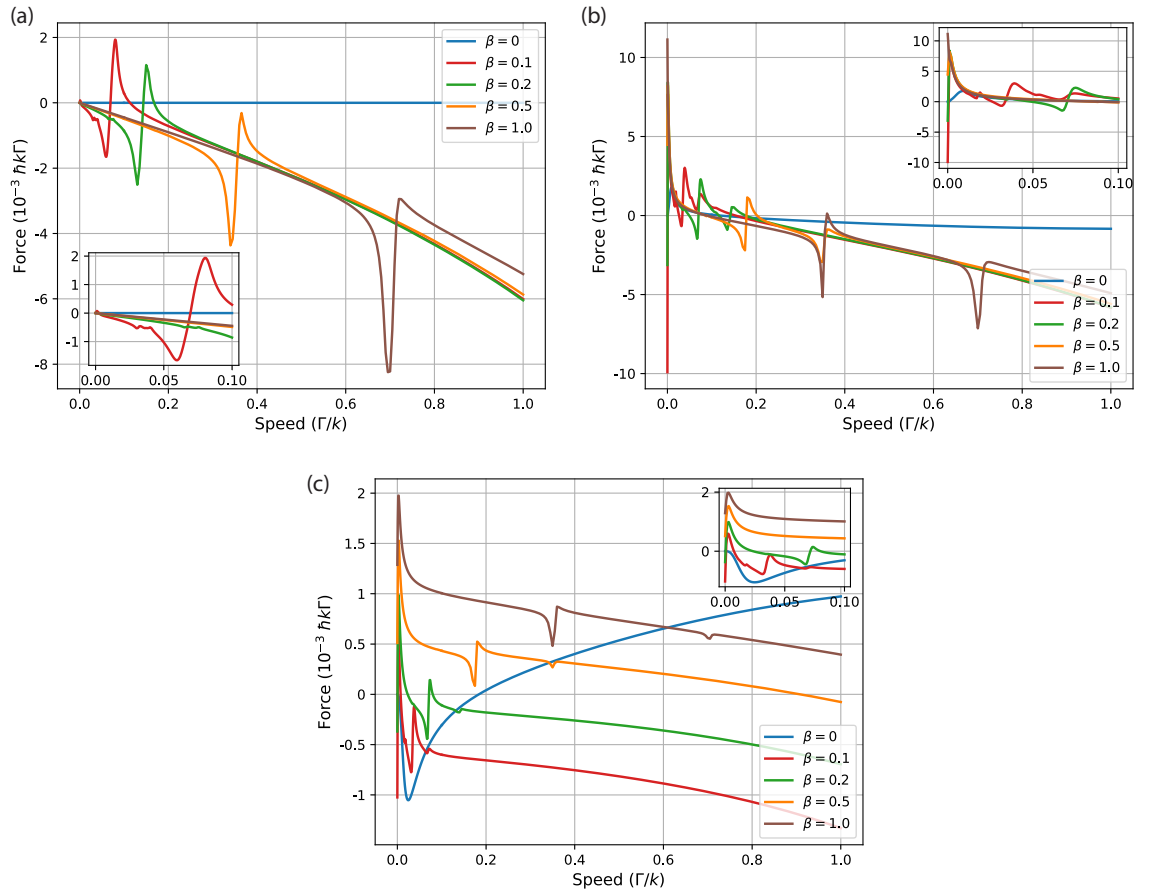


**Fig. 3.9:** Excited state population as a function of normalised magnetic field and polarization angle.

We plot the Eq. (4.1) of Ref. [BB02] in Fig. 3.9. It shows that the largest excited population happens when the angle between magnetic field and laser polarization ranges from  $\pi/4$  to  $3\pi/8$ . The magnitude of the magnetic field also needs to be considered. As can be seen, the excited state population increases to maximum when the normalized magnetic field increases from 0 to 0.3  $\Gamma$ . Keeping increasing magnetic field will cause the excited state population to decrease. What we've

learned from Ref. [BB02] is that by correctly setting the direction and magnitude of the magnetic field, we can optimize the laser cooling. Thus, we apply this idea to the three systems which are discussed in the last section.

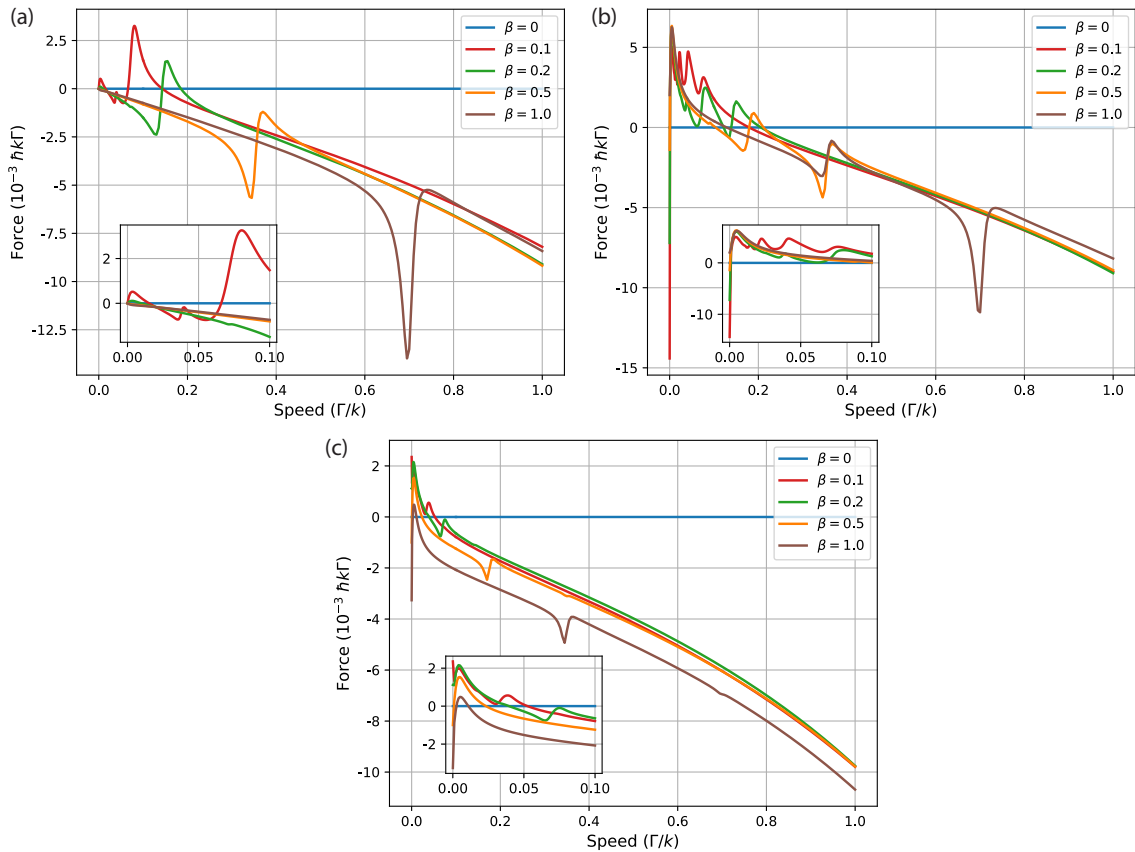
First, let's look at how magnetic field changes the cooling force for a  $|F = 2\rangle$  to  $|F' = 1\rangle$  system in Fig. 3.10. Here we use  $\beta$  to define the magnitude of a magnetic field with expression  $|B| = \beta \hbar \Gamma / \mu_B$ . The direction of the magnetic field vector is in the  $y - z$  plane and 45 degrees to the  $z$  axis (the axis molecules and lasers travel along). In (a), for the lin||lin ( $\theta = 0$ ) polarization, it is clear that there is no cooling



**Fig. 3.10:** Cooling force of a  $|F = 2\rangle$  to  $|F' = 1\rangle$  system under various polarization configurations with magnetic field applied. (a) lin||lin ( $\theta = 0$ ). (b) lin⊥lin ( $\theta = \pi/2$ ). (c)  $\sigma^+ \sigma^-$  polarization.  $\delta = -2.5 \Gamma$ ,  $I = I_{sat}$  for all the plots.

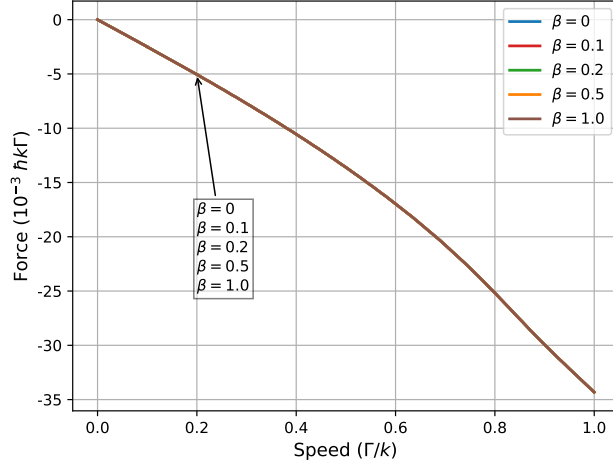
force when the magnetic field is zero, which has been discussed in the last section. However, once the magnetic field is turned on, we can see the Doppler cooling effect. It is due to the destabilization of dark states in the  $m_F = \pm 2$  sublevels. There is a spike pattern in the plot. As  $\beta$  increases from 0.1 to 1.0, the spike moves towards higher velocity. Overall, despite the spikes, the cooling force for  $\beta = 0.1, 0.2, 0.5$

and 1.0 show the same trend. In (b), we study the  $\text{lin} \perp \text{lin}$  polarization using the same parameters as (a). It can be seen that by applying the magnetic field the sub Doppler heating effect in the low velocity range is enhanced. It is still clear that applying magnetic field can generate better Doppler cooling effect compared with no magnetic field. In Fig. 3.10 (c), we study the  $\sigma^+ \sigma^-$  polarization. The inset plot shows that the sub Doppler heating effect shows up once the magnetic field is applied. When the velocity is larger than low velocity range,  $\beta=0.1$  and 0.2 demonstrate Doppler cooling, with  $\beta=0.1$  having larger cooling force. Such a phenomenon can be explained by Fig. 3.9 which tells that to effectively mix the dark states the magnitude of the magnetic field needs to be set at a proper value rather than indefinitely increasing it. When  $\beta$  is equal to 0.5 and 1.0, they show Doppler heating effect. Although the trend is dropping suggesting a Doppler cooling force at higher velocity,  $\beta=0.5$  and 1.0 is beyond the optimum magnitude of the magnetic field.



**Fig. 3.11:** Cooling force of a  $|F = 1\rangle$  to  $|F' = 1\rangle$  system under various polarization configurations with magnetic field applied. (a)  $\text{lin} \parallel \text{lin}$  ( $\theta = 0$ ). (b)  $\text{lin} \perp \text{lin}$  ( $\theta = \pi/2$ ). (c)  $\sigma^+ \sigma^-$  polarization.  $\delta = -2.5 \Gamma$ ,  $I = I_{\text{sat}}$  for all the plots.

We then do the same calculation for a  $|F = 1\rangle$  to  $|F' = 1\rangle$  system in Fig. 3.11. Plots (a) and (b) show the same trend and spike pattern as Fig. 3.10 (a) and (b). The results in plot (c)s are different between Figs. 3.10 and 3.11. For a  $|F = 1\rangle$  to  $|F' = 1\rangle$  system, changing  $\beta$  from 0.2 to 1.0 seems that it does not change the force profile that much as compared with a  $|F = 2\rangle$  to  $|F' = 1\rangle$  system.



**Fig. 3.12:** Cooling force of a  $|F = 0\rangle$  to  $|F' = 1\rangle$  system for lin||lin, lin⊥lin and  $\sigma^+\sigma^-$  polarization configurations.

We further study how magnetic field influence the cooling force of a  $|F = 0\rangle$  to  $|F' = 1\rangle$  system in Fig. 3.12. Since  $|F = 0\rangle$  to  $|F' = 1\rangle$  is a type-I system, there are no dark states. Thus, we expect applying magnetic field to the system won't change the cooling force. As can be seen in Fig. 3.12, the force profile overlap for  $\beta=0, 0.1, 0.2, 0.5$ , and  $1.0$  as we expected. Moreover, the three types of polarization configurations (lin||lin, lin⊥lin and  $\sigma^+\sigma^-$ ) demonstrate the same result, which is also within our expectation. Because they should not show any difference since there is no dark state in the  $|F = 0\rangle$  to  $|F' = 1\rangle$  system. Figure 3.12 is a good tool to test the validation of our laser cooling simulation code. Although the complex calculation containing multiple energy levels is done by computer (like a black box), but the results do follow the logic of physics.

In reality, a laser cooling transition of real molecules is complex. It is usually a combination of type-I and type-II systems. The results in this section tell that to decelerate molecules containing both type-I and type-II systems applying magnetic field can improve cooling effect on type-II systems without affecting type-I systems. In the next section, we will study 2D cooling on  $^{174}\text{YbF}$  molecules which is also the theoretical support of our experiments.

### 3.2.4 2D laser cooling

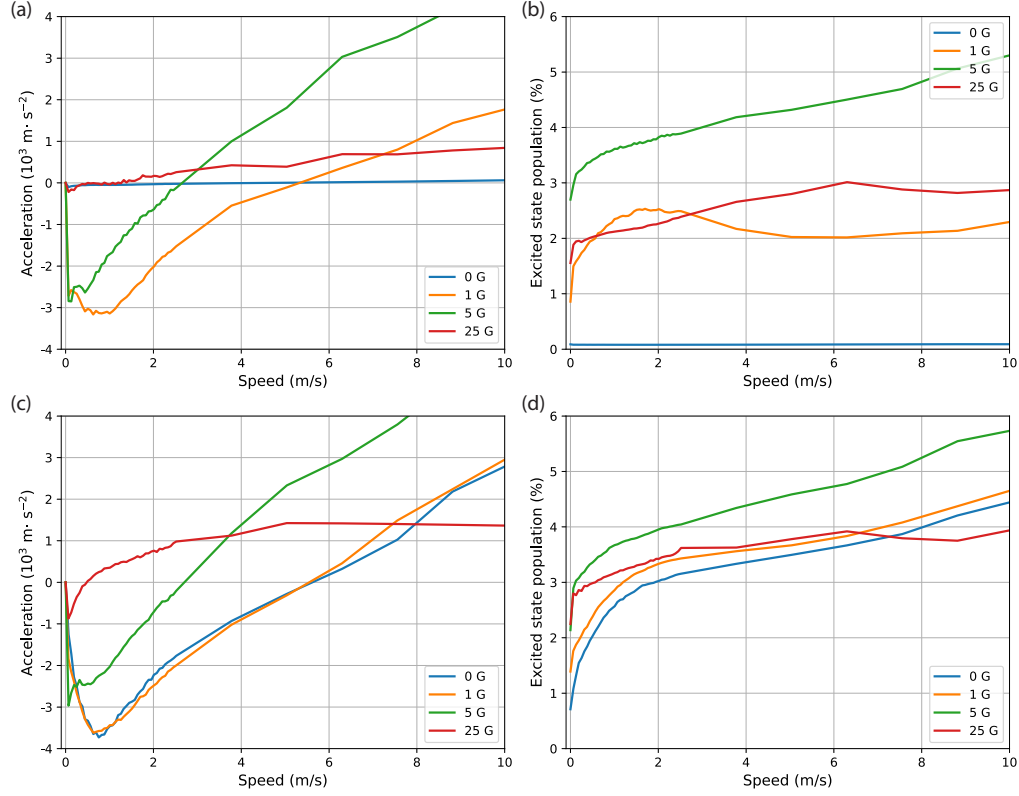
In this section, we will discuss calculation for two dimensional laser cooling. In our experiment, the setup of laser cooling region is a 2D transverse geometry. Molecules travel along  $y$  axis. One pair of counter propagating lasers come through  $x$  axis with the other pair of lasers coming through  $z$  axis. The calculation in this section follows such a geometry. The notation of polarization configuration used in the 2D calculation is different from the 1D case. We have studied two polarization configurations  $XY_{||}$  and  $XY_{\perp}$ . In  $XY_{||}$ , both pairs of counter propagating lasers are linear polarized along  $y$  axis. In  $XY_{\perp}$ , one pair of counter propagating lasers are linear polarized along  $y$  axis. The other pair of lasers are linear polarized along  $x$  axis. There are 2 pairs of counter propagating lasers (4 lasers), so there are 4 terms in each expression in Eq. 3.26,

$$\begin{aligned} XY_{||} : \vec{E} &= E_0 \hat{e}_y e^{ikx} + E_0 \hat{e}_y e^{-ikx} + E_0 \hat{e}_y e^{ikz} + E_0 \hat{e}_y e^{-ikz}, \\ XY_{\perp} : \vec{E} &= E_0 \hat{e}_y e^{ikx} + E_0 \hat{e}_y e^{-ikx} + E_0 \hat{e}_x e^{ikz} + E_0 \hat{e}_x e^{-ikz}. \end{aligned} \quad (3.26)$$

The cooling transition contains all the frequency components from the  $N = 1$  state in the ground state to the first excited state. Recall Fig. 2.5, the  $F$  quantum numbers in the  $N = 1$  state are  $F = 0, 1$  and  $2$ , suggesting the cooling transition contains both type-I and type-II systems. In the laser cooling region, the length of windows to let lasers passing through the chamber is 200 mm. We will explain the setup of the laser cooling region in detail in Chap. 4. The reason we briefly mention the setup is to introduce three parameters for the 2D cooling. The first parameter is typical interaction time  $\tau_{\text{int}}$ . Molecules with speed 200 m/s travelling through the laser cooling chamber will interact with lasers for about 1 ms. The second parameter is critical velocity  $v_{\text{cri}}$  which is defined as the maximum velocity that can be reduced to zero in 1 ms. The third parameter is capture velocity  $v_{\text{cap}}$  which is the velocity where the force is zero.

We first study how magnetic field affect the laser cooling in Fig. 3.13 with Laser intensity  $I = 100I_{\text{sat}}$  and detuning  $\delta = 6\Gamma$ . The results for  $XY_{||}$  polarization is shown in (a) and (b). It shows that when the magnetic field  $B=0$ , the acceleration and excited population are zero. Because the  $m_F = \pm 2$  sublevels in the ground state are dark states for  $XY_{||}$  polarization since it does not have polarization gradient. All the population will be optically pumped into the  $m_F = \pm 2$  dark states to stop scattering photons. When  $B= 1$  G, it shows the largest cooling force. Here, "G" stands for Gauss which is a non-SI unit for magnetic field. By definition, 1 Tesla is equal to 10,000 Gauss. Keeping increasing  $B$  to 5 or 25 G will cause the less effective cooling. Such a phenomenon has been observed and explained in the last

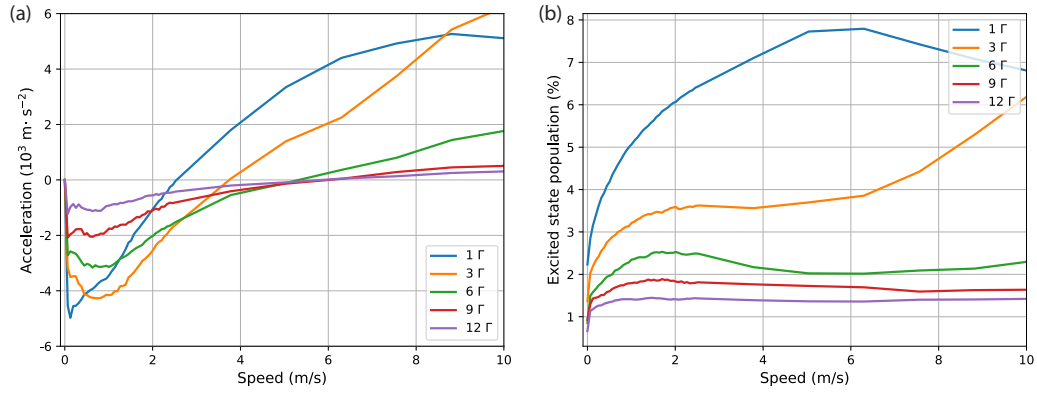
section when we discuss 1D cooling. It also shows that both  $v_{\text{cri}}$  and  $v_{\text{cap}}$  of 1 G are twice larger than 5 G. Plots (c) and (d) are for  $XY_{\perp}$  polarization. The  $XY_{\perp}$  contains polarization gradient making the system no dark states. Thus, it performs Doppler cooling when  $B$  is equal to zero. In (c), we see that the force profiles for  $B=0$  and 1 G are nearly the same. Further increasing  $B$  beyond 1 G causes laser cooling less effective.



**Fig. 3.13:** (a) Acceleration versus velocity for  $XY_{\parallel}$ . (b) Excited state population versus velocity for  $XY_{\parallel}$ . (c) Acceleration versus velocity for  $XY_{\perp}$ . (d) Excited state population versus velocity for  $XY_{\perp}$ . Laser intensity  $I = 100I_{\text{sat}}$ . Laser detuning  $\delta = 6\Gamma$ .

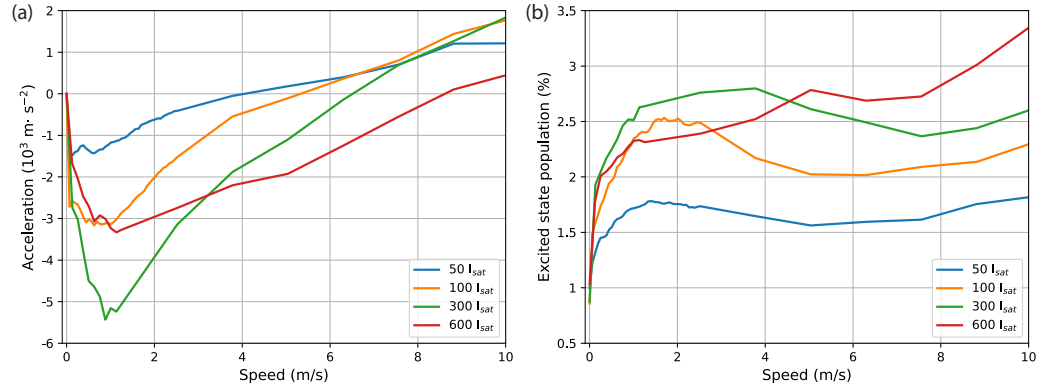
Since  $XY_{\perp}$  is not sensitive to magnetic field, in the following discussion we will study  $XY_{\parallel}$  polarization in terms of laser detuning and intensity with magnetic field ( $B=1$  G) applied all the time. In Fig. 3.14 (a), when the velocity is smaller than 3 m/s, all the detunings demonstrate Doppler cooling effect. The  $v_{\text{cap}}$  increases from 2.5 m/s to 5 m/s when  $\delta$  increases from 1 to 12  $\Gamma$ . The  $v_{\text{cri}}$ s for all the detunings are between 1 to 3 m/s. In (b), we can see that 1  $\Gamma$  has the largest excited state population indicating it has the largest cooling force. In the last section, we saw the similar feature in 1D cooling. Thus, we draw the same conclusion as the last section. It tells that in order to obtain the most effective cooling,  $\delta$  needs to be set at





**Fig. 3.14:**  $XY_{||}$  polarization configuration. (a) Acceleration versus velocity. (b) Excited state population versus velocity. Magnetic field  $B = 1$  Gauss. Laser intensity  $I = 100I_{sat}$ .

a reasonable value. Regarding experiments, in Fig. 5.4 in Chap. 5, we scan the laser detuning  $\delta$  and find that the reality does have such a feature.



**Fig. 3.15:**  $XY_{||}$  polarization configuration. (a) Acceleration versus velocity. (b) Excited state population versus velocity. Magnetic field  $B = 1$  G. Laser detuning  $\delta = 6 \Gamma$ .

We further study the laser intensity dependence in the  $XY_{||}$  polarization in Fig. 3.15 with  $B = 1$  G and  $\delta = 6 \Gamma$ . Plot (a) shows that the Doppler cooling force keeps increasing when the laser intensity increases from 50 to  $300 I_{sat}$ . Further increasing  $I$  to  $600 I_{sat}$  causing the cooling force drops. We saw a similar feature in the 1D cooling for a  $|F = 0\rangle$  to  $|F' = 1\rangle$  system in Fig. 3.8. The conclusion is that cooling force won't increase indefinitely with laser intensity.

Figures 3.13, 3.14 and 3.15 are not smooth as figures present in the 1D cooling section. It is because the system we have discussed in the 2D case is based on the molecular structure of YbF which contains multiple  $F$  levels. However, the simulations in the 1D cooling are only for systems containing two  $F$  levels. Moreover,

the calculation for 2D cooling involves one more spatial dimension compared with 1D. Therefore, the numerical calculation for 2D cases is more complex than 1D. The roughness of the profiles is due to numerical calculation rather than physics.

### 3.3 State manipulation

The above theoretical calculation for laser cooling is to support the experimental study in the laser cooling region. In this section, the calculation is to support the physics in the interaction region. In the interaction region, we've installed STIRAP lasers and rf transmission line. Detailed information about the setup will be introduced in [Chap. 5](#). The calculation in this section is divided into two parts, RF  $\pi$  pulse and STIRAP. The RF  $\pi$  pulse technique is mainly about solving Schrödinger equations. While the STIRAP is based on OBEs which has been introduced at the beginning of this section.

#### 3.3.1 RF $\pi$ pulse

The RF  $\pi$  pulse is a well-established technique and was successfully applied to our last generation EDM machine [[Hud+11](#); [Kar+12](#); [Ho+20](#)]. There are two RF pulses in the interaction region. One is at the entrance of the interaction region to prepare the superposition state while the other one is at the exit to read out the phase accumulated during the spin precession process.

To study the RF pulse, we start from the Schrödinger equation. Recall [Fig. 2.5](#), the states we will use are the  $F = 0$  and  $F = 1$  states in the  $N = 0$  manifold in the ground state. We use a RF polarized along  $z$  axis to connect  $|F = 0, m_F = 0\rangle$  to a superposition state of  $|F = 1, m_F = -1\rangle$  and  $|F = 1, m_F = 1\rangle$ . For convenience, we label the three basis vectors  $|F = 0, m_F = 0\rangle$ ,  $|F = 1, m_F = -1\rangle$  and  $|F = 1, m_F = 1\rangle$  as  $|0, 0\rangle$ ,  $|1, -1\rangle$  and  $|1, 1\rangle$ . To simplify the following calculation, we convert the above basis vectors with a unitary matrix

$$\hat{U} = \frac{1}{\sqrt{2}} \begin{bmatrix} \sqrt{2} & 0 & 0 \\ 0 & 1 & 1 \\ 0 & 1 & -1 \end{bmatrix}. \quad (3.27)$$

Since the RF transition is magnetic dipole transition, we write the the RF interaction as

$$\hat{H}_{\text{RF}} = \hat{\mu} \cdot \vec{B} \cos(\omega_{\text{rf}} t). \quad (3.28)$$

Here  $\hat{\mu}$  is the magnetic dipole operator which has been defined in Eq. 2.33 and  $\omega_{\text{rf}}$  is the frequency of the RF. We also need to apply the unitary transformation to the Hamiltonian. After doing that, we obtain the Schrödinger equation for the system [Kar+12]

$$\begin{aligned} i\dot{a}_0 &= \frac{\Omega}{2} e^{i\omega_{\text{rf}}t} a_p, \\ i\dot{a}_p &= \frac{\Omega}{2} e^{-i\omega_{\text{rf}}t} a_0 + \omega_0 a_p, \\ i\dot{a}_m &= \omega_0 a_m. \end{aligned} \quad (3.29)$$

Here  $\Omega$  is the Rabi frequency with definition  $\hbar\Omega = \hat{\mu} \cdot \vec{B}$  and  $\omega_0$  is the angular frequency between  $|0, 0\rangle$  and  $|1, \pm 1\rangle$  states with  $\omega_0/2\pi = 170$  MHz (see Fig. 2.5).  $a_0$ ,  $a_p$  and  $a_m$  are the coefficients in the wave function

$$|\psi\rangle = a_0|0, 0\rangle + \frac{a_p}{\sqrt{2}}(|1, 1\rangle + |1, -1\rangle) + \frac{a_m}{\sqrt{2}}(|1, 1\rangle - |1, -1\rangle). \quad (3.30)$$

In Eq. 3.29, the third equation is simple and not coupled with the first two equations. Thus, we will focus on the first two equations in the following discussion. To further process Eq. 3.29, we make the substitution  $F_p = a_p e^{i\omega t}$  and take the second time derivative,

$$\begin{aligned} \ddot{a}_0 &= i\delta\dot{a}_0 + \frac{\Omega^2}{4} a_0, \\ \ddot{F}_p &= i\delta\dot{F}_p + \frac{\Omega^2}{4} F_p. \end{aligned} \quad (3.31)$$

Equation 3.31 is a linear system of differential equations. We can write the solution immediately

$$\begin{aligned} a_0(t) &= a_1 e^{\frac{1}{2}t(i\delta - \sqrt{-\delta^2 - \Omega^2})} + a_2 e^{\frac{1}{2}t(i\delta + \sqrt{-\delta^2 - \Omega^2})}, \\ F_p(t) &= b_1 e^{\frac{1}{2}t(i\delta - \sqrt{-\delta^2 - \Omega^2})} + b_2 e^{\frac{1}{2}t(i\delta + \sqrt{-\delta^2 - \Omega^2})}. \end{aligned} \quad (3.32)$$

In order to obtain the  $a_{1,2}$  and  $b_{1,2}$ , four initial conditions are required, which are  $a_0(0)$ ,  $a'_0(0)$ ,  $F_p(0)$  and  $F'_p(0)$ . Detailed explanation can be found in our previous work Ref. [Kar+12]. Eventually, the solution can be summarized as a propagator which can be used conveniently,

$$\mathbf{M}_{\text{rf}} = \begin{bmatrix} e^{\frac{i\delta\tau}{2}} \left( \cos \frac{\bar{\Omega}\tau}{2} - i\Delta \sin \frac{\bar{\Omega}\tau}{2} \right) & -ie^{\frac{i\delta\tau}{2}} e^{i\omega t_0} \beta \sin \frac{\bar{\Omega}\tau}{2} & 0 \\ i\beta e^{\frac{i\delta\tau}{2}} e^{-i\omega t_0} \sin \frac{\bar{\Omega}\tau}{2} & e^{\frac{i\delta\tau}{2}} e^{-i\omega\tau} \left( \cos \frac{\bar{\Omega}\tau}{2} + i\Delta \sin \frac{\bar{\Omega}\tau}{2} \right) & 0 \\ 0 & 0 & e^{-i\omega_0\tau} \end{bmatrix}. \quad (3.33)$$

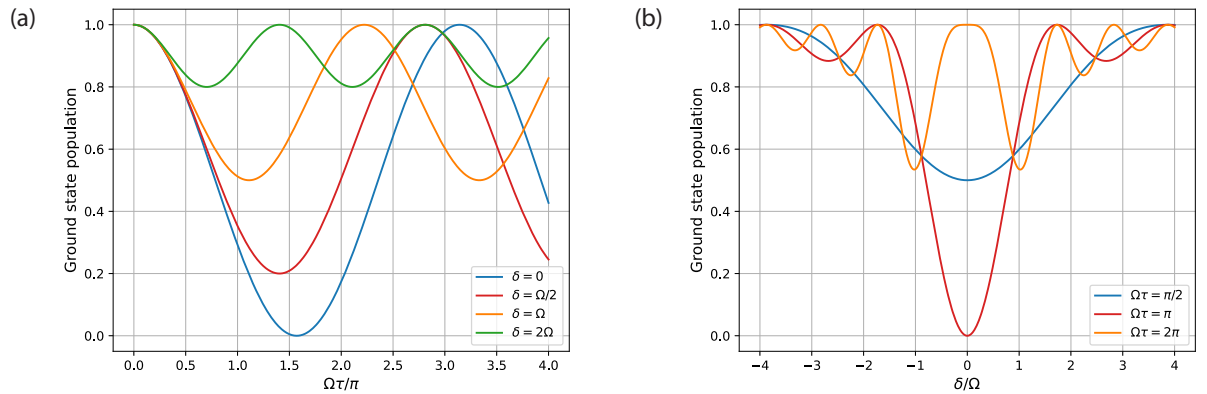
Where  $\bar{\Omega} = \sqrt{\delta^2 + \Omega^2}$ ,  $\beta = \Omega/\bar{\Omega}$  and  $\Delta = \delta/\bar{\Omega}$ .  $t_0$  is the initial time. The propagator tells how the state  $\psi(t_0)$  evolves after a period of time  $\tau$

$$\psi(t_0 + \tau) = \mathbf{M}_{\text{rf}}\psi(t_0). \quad (3.34)$$

Then we apply Eq. 3.33 with a simplest case where  $t_0=0$ ,  $a_0=1$ ,  $a_p=0$  and  $a_m=0$ . We obtain the population for the  $|0, 0\rangle$  state

$$P_0 = 1 - \frac{\Omega^2}{\bar{\Omega}^2} \sin^2\left(\frac{\bar{\Omega}\tau}{2}\right). \quad (3.35)$$

We plot Eq. 3.35 in Fig. 3.16. As shown in (a), the Rabi oscillation becomes weaker with RF detuning increasing. In the first RF pulse, we expect all the population to be transferred from  $|0, 0\rangle$  state to the superposition state. Thus, what we can learn from (a) is that in real experiments the RF frequency has to be on resonance as perfect as possible to fully transfer the population out of  $|0, 0\rangle$  state. In (b), when  $\Omega\tau$  is equal to  $\pi$ , the ground state population can be emptied to zero. It gives the duration of the RF pulse  $\tau = \pi/\Omega$ , which is the definition of  $\pi$  pulse.



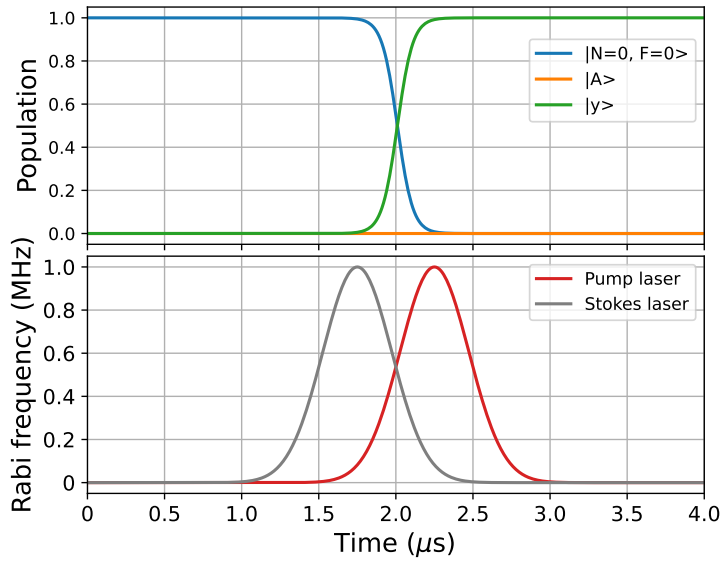
**Fig. 3.16:** (a) Rabi oscillations of the ground state population for various RF detunings. (b) Ground state population versus RF detuning for various RF durations.

### 3.3.2 STIRAP

In the last section, we have introduced RF  $\pi$  pulse. In this section we will introduce STIRAP which has the same role as RF pulses but with a different transition scheme. RF essentially can be regarded as an optical pumping process. In an optical pumping process, molecules will firstly experience a pump laser which drives them to the excited state. Then molecules will spontaneous decay to the target state. However,

in a STIRAP, molecules will firstly experience a laser (called Stokes Laser) which connects the excited state and the target state. The pump laser will show up afterwards.

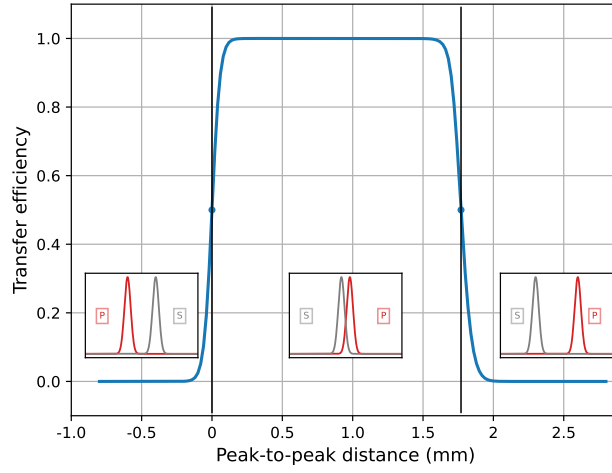
In terms of the EDM measurement, similar to RF, there will be two STIRAPs, one is to prepare the superposition state, the other one is to read out the phase. We will start from a single STIRAP then introduce double STIRAP. Following the notation in the last section, a single STIRAP will transfer the  $|0, 0\rangle$  state to the  $\frac{1}{\sqrt{2}}(|1, 1\rangle + |1, -1\rangle)$  state. To simplify the notation, we label the superposition state  $\frac{1}{\sqrt{2}}(|1, 1\rangle + |1, -1\rangle)$  as  $|y\rangle$  state. In Fig. 3.17, the top figure shows the state evolution of the STIRAP



**Fig. 3.17:** OBEs for the single STIRAP.

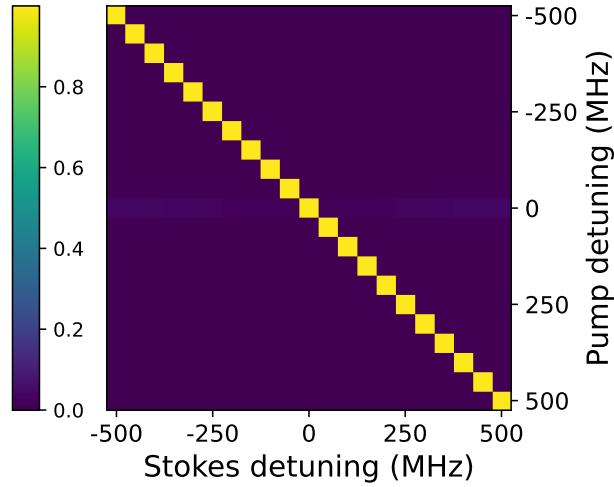
system. It can be seen that all the population is transferred from  $|0, 0\rangle$  state to the  $|y\rangle$  state within given interaction time. The bottom figure shows the change of Rabi frequencies of pump (red) and Stoke (gray) lasers in time. We treat each laser as a Gaussian beam with width about  $1.5 \mu s$  in time. It is because in reality our measured beam profile gives an interaction time about 2 to  $3 \mu s$  for molecules with speed 300 m/s.

Figure 3.18 plots the transfer efficiency versus peak-to-peak distance between the pump and Stokes lasers. Here peak-to-peak distance is the distance between the peaks of the Stoke Gaussian beam and pump Gaussian beam. The idea of this calculation is from Ref. [Pan+16]. The transfer efficiency is defined as the population in the  $|y\rangle$  state when the system reaches the steady state. In Fig. 3.18, the pump laser is on the left of the Stokes laser. When they first overlap at 0 distance, half of the population is transferred to the  $|y\rangle$  state. Between 0 and 1.75 mm, molecules



**Fig. 3.18:** Transfer efficiency vs peak-to-peak distance between the pump and Stokes lasers.

always see Stoke laser earlier than pump laser. We can see the transfer efficiency remains at 1 in that range, suggesting it is the ideal distance between the two lasers. When the distance is more than 2 mm, the state transfer won't happen because two lasers are too far away from each other.

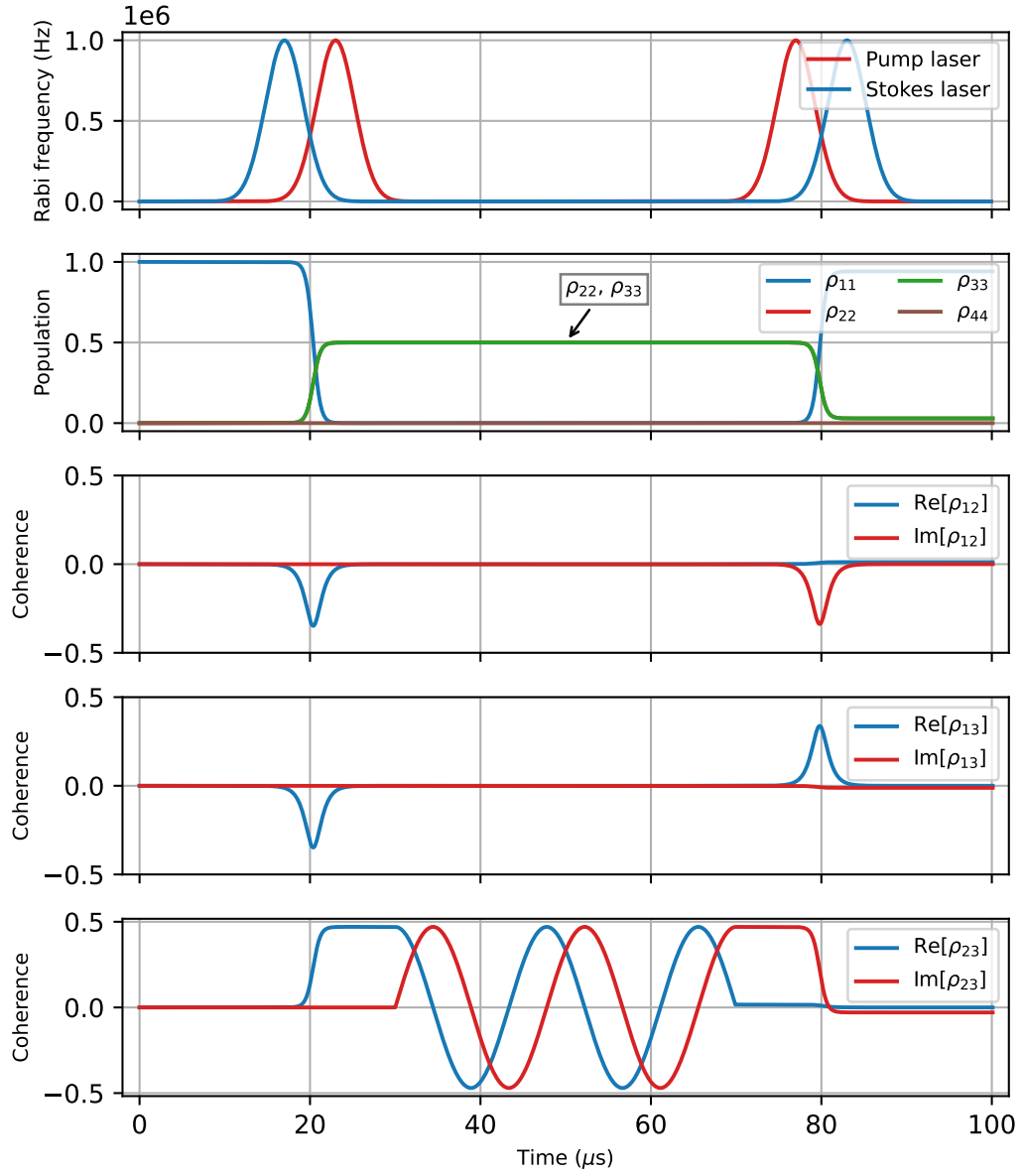


**Fig. 3.19:** Transfer efficiency vs Stokes and pump lasers detuning.

The next step is to study the detuning of STIRAP. In [Fig. 3.19](#), the  $x$  and  $y$  axes are Stokes and pump detunings both from -500 MHz to 500 MHz. The color bar stands for the transfer efficiency. The maximum transfer efficiency is 1 which is in yellow. Along the diagonal line of the image, two lasers are detuned at the same time (called two-photon detune) remains the transfer efficiency at 1. It shows that STIRAP is immune to two-photon detuning. However, it is sensitive to single-photon

detuning which are off-diagonal pixels in Fig. 3.19. It can be seen that the transfer efficiency drops significantly when the detuning of two lasers are not equal.

At last, we will introduce the double STIRAP in Fig. 3.20. All the five plots in Fig. 3.20 share the same  $x$  axis. The first plot shows the beam profile in time with the first STIRAP illustrated by the first two Gaussian beams and the second STIRAP depicted by the last two Gaussian beams. The second plot shows the population of each state.  $\rho_{ii}$  with  $i = 1, 2, 3$  and 4 denote the population of  $|0, 0\rangle$ ,  $|1, -1\rangle$ ,  $|1, 1\rangle$  and  $|A\rangle$  states, respectively.  $\rho_{22}$  and  $\rho_{33}$  overlap at 0.5 after the first STIRAP and drop to 0 together after the second STIRAP. Such a behavior tells that the amplitudes of  $|1, -1\rangle$  and  $|1, 1\rangle$  in the  $|y\rangle$  state are equal all the time. The third plot is the coherence between  $|0, 0\rangle$  and  $|1, -1\rangle$  states. As can be seen, during the first STIRAP, the imaginary part of  $\rho_{12}$  remains 0 while in the second STIRAP the real part of  $\rho_{12}$  keeps 0. The coherence between  $|0, 0\rangle$  and  $|1, 1\rangle$  is plotted in the forth plot. As shown,  $Im[\rho_{13}]$  stays at 0 during both the first and second STIRAP. The fifth plot shows the coherence between  $|1, -1\rangle$  and  $|1, 1\rangle$  states. After the first STIRAP,  $Re[\rho_{23}]$  approaches 0.5 while  $Im[\rho_{23}]$  stays 0. The oscillation between the first and second STIRAP illustrates the spin precession. The spin precession is introduced by a magnetic field which will give opposite phases to  $|1, -1\rangle$  and  $|1, 1\rangle$  with  $|y\rangle = e^{i\phi_B}|1, 1\rangle + e^{-i\phi_B}|1, -1\rangle$ .



**Fig. 3.20:** Simulation for the double STIRAP and spin precession. The five plots share the same  $x$  axis. From top to bottom, the first plot shows the Rabi frequencies of pump laser and Stokes laser in time. The second plot shows the evolution of the population of the four states. The third, fourth and fifth plots show the evolution of the coherence of  $\rho_{12}$ ,  $\rho_{13}$  and  $\rho_{23}$ .



## 3.4 Summary

In this chapter, we have introduced optical Bloch equations and relevant parameters including Rabi frequency, spontaneous decay and laser frequency detuning. Then we have introduced the force operator of laser cooling and showed how to calculate it by using optical Bloch equations. In the 1d cooling case, we have studied both type I and II systems with various polarization configurations. We have also studied how laser intensity and detuning affect cooling force. In order to improve the cooling force for type II systems, we have applied dark state destabilization to our simulation program. We have studied the dependence of cooling force on the magnitude of the magnetic field when the direction of the magnetic field is 45 degree with respect to the laser propagation direction. Based on the insights from the 1d cooling calculation, we have further studied 2d laser cooling on YbF molecules with various laser intensities, laser detuning, polarization configurations and dark state destabilization. At last, we have applied optical Bloch equations to study state manipulation including RF  $\pi$  pulse and STIRAP, which helps us designing experiments in the interaction region.

## Experimental overview

This chapter describes the apparatus used in the YbF eEDM experiment. The section begins with an overview of the YbF beamline machine before discussing individual sections of the eEDM experiment in more detail. I will present the sections of the beamline in a modular way, starting with the molecule buffer gas source, discussing all of the regions after the source and ending with the detection system.

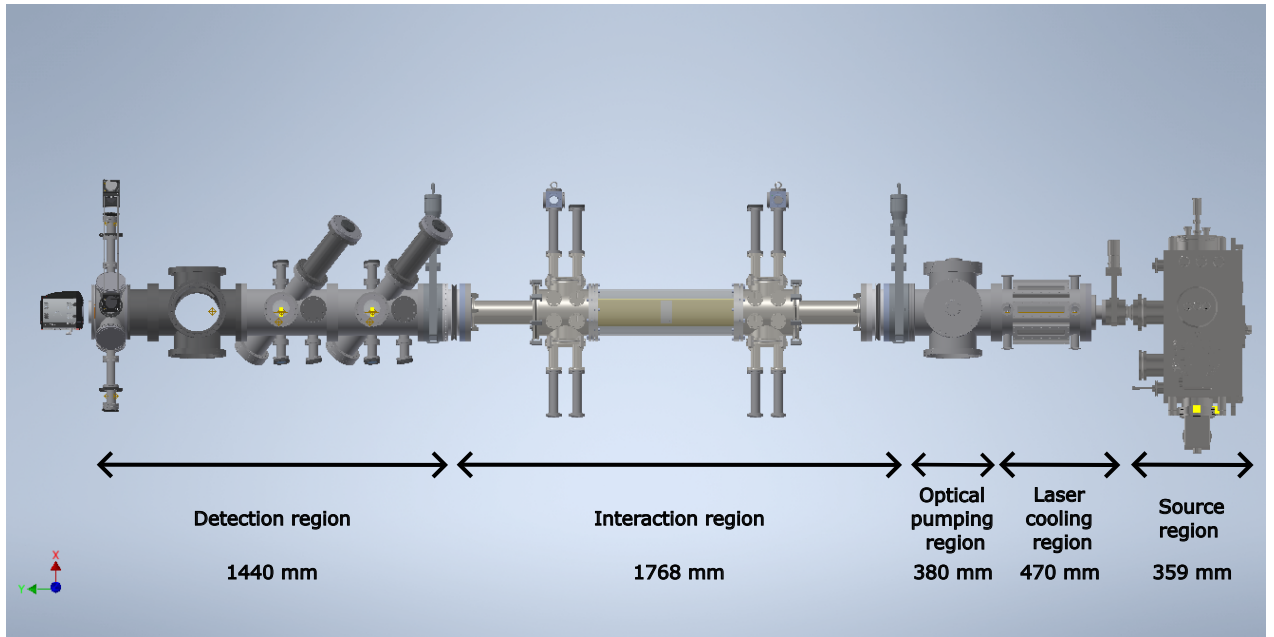
### 4.1 The whole machine

This section is to give you an overview of the whole machine. [Figure 4.1](#) shows the front view of the whole machine, including main components to take EDM data. It is not shown in the figure but the machine is supported by a metal frame. At the bottom left corner, we indicate the lab reference frame. The  $y$  axis is along the beamline which is direction YbF molecules travel along. The  $x$  axis points upwards in figure. While in our lab, it points upwards to the ceiling. The  $z$  axis points across the electric field plates.

The beamline machine can be divided into five regions. The source region is to generate YbF molecules. After the source region is the laser cooling region which is to transversely cool the molecules otherwise the molecular beam will diverge significantly due to the rather long length of the machine. The next region is optical pumping region which will transfer the laser cooled molecules from laser cooling states into the ground state ( $|N = 0, F = 0\rangle$ ) to be ready for the EDM experiments. After that, it is the interaction region. It has three main components which are STIRAP system, magnetic shields and EDM system. The STIRAP system is to prepare and read out superposition states. Magnetic shields is to protect the EDM experiments from the external magnetic noise. EDM system is to generate electric and magnetic fields to conduct EDM experiments. The end is the detection region which allows us to detect  $F=0,1$  population by using photo multiplier tubes (PMTs) or electron multiplying charge coupled devices (EMCCDs).

One often uses upstream and downstream to describe beamline experiments. For example, source region is the upstream compared to laser cooling region. Optical

pumping region is the downstream with respect to laser cooling region. In the following discussion, we will go through the machine from upstream to downstream.



**Fig. 4.1:** The CAD image of the ultracold eEDM beamline machine.

Figure 4.1 shows the whole machine with each region indicated. The length of each region is also shown. The source region is on the right. From upstream to downstream, they are laser cooling, optical pumping, interaction and detection regions. The total length of the machine is 4.417 meters. The entire beamline machine is kept under vacuum with  $10^{-7}$  mbar.

## 4.2 Source region

To achieve a precise EDM experiment, we expect to have a reliable source which can produce intense molecular beam with low forward speed. Thus, our experiment starts with a cryogenic buffer gas source. YbF is a highly reactive molecule which cannot be stored in a bottle, so it has to be made in vacuum [Alex2020]. In Fig. 4.2, YbF is produced in a cold ( $\sim 4$  K) copper cell by laser ablation of a solid ytterbium target (Yb rod) in the presence of relatively warm ( $> 230$  K) sulfur hexafluoride ( $\text{SF}_6$ ) gas [Alex2020]. Then YbF molecules will be cooled by Helium buffer gas which is thermalised by a cryostat. Some of the molecules will come out through the aperture to form a molecular beam. The flow rate of the He is between 0.2 to 1 SCCM. The flow rate of the  $\text{SF}_6$  is between 0.01 to 0.05 SCCM. Here SCCM stands for standard cubic centimetres per minute. The window of the ablation laser is mounted at the end of the copper tube, which is usually called a snorkel. The reason to build a snorkel is to avoid the buildup of ablation products on the window. The buildup product can increase the absorption of laser and then cause the window to be broken.

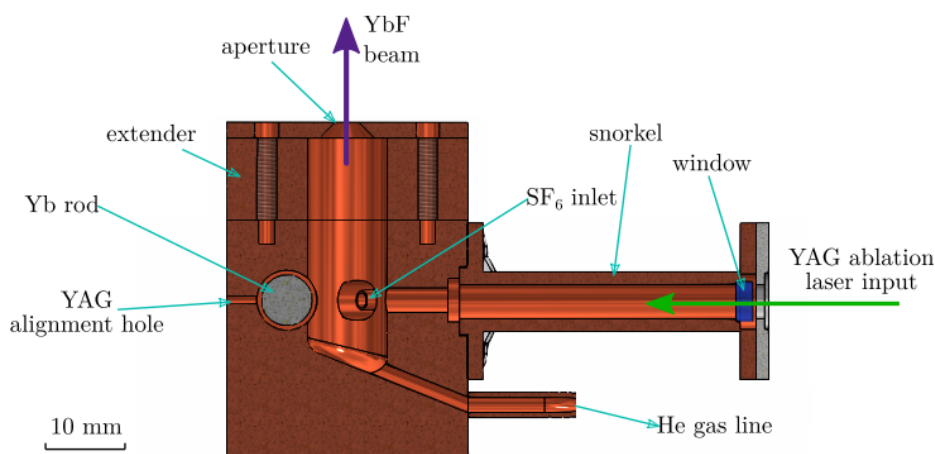


Fig. 4.2: CAD drawing of the cross section of the cryogenic buffer gas cell.

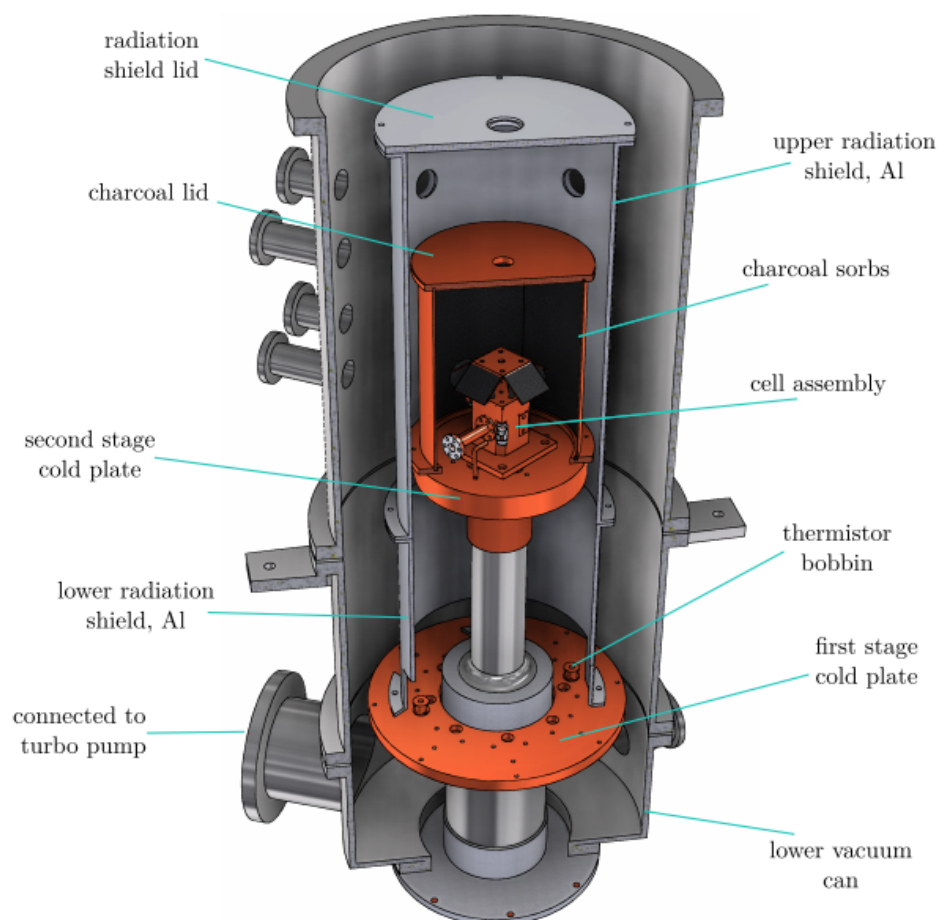
In terms of the ablation laser, we use a pulsed Nd:YAG laser (Continuum Minilite 2) which output 10 ns pulses of 1064 nm light with pulse energy of 10 mJ [Alex2020]. We use a 300 mm focal length lens 400 mm away from the Yb rod to give a  $\sim 1$  mm diameter spot at the surface of the Yb rod [Alex2020]. It is found that the collimation is not very important but the pulse energy is important. The source is usually operated at a 5 Hz repetition rate. A higher repetition rate will cause the flux

to drop dramatically. It could be there is not enough time to allow YbF molecules to reach thermal equilibrium with He carrier gas.

Figure. 4.3 shows the drawing of the entire source region. The copper cell is held at  $\sim 4$  K by being bolted to a cold-plate which is itself attached to the second stage of a Gifford McMahon-type cryocooler (Sumitomo RDK-415 cold plate and F-50 compressor) [Alex2020]. The cold plate (also called cold head) is installed on the first stage. The radiation shields whose temperature is usually at 40 K blocks heat from the lab delivered through blackbody radiation. The heat absorption of the radiation shield is based on the black-body radiation,

$$j = \sigma T^4 \quad (4.1)$$

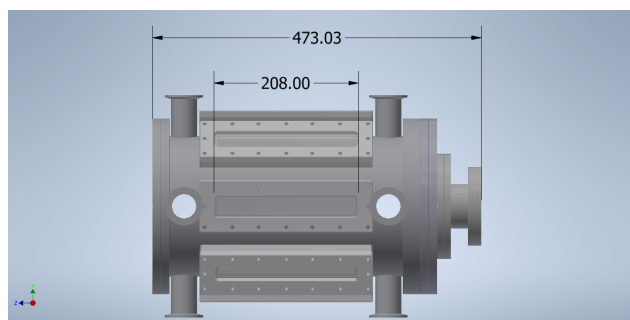
where  $\sigma$  is the StefanBoltzmann constant with value  $5.67 \times 10^{-8} \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-4}$ . The cold plate can take away 1 W heat at 4.2 K. The radiation shield can absorb about 30 W heat. The charcoal, when cooled below 8 K efficiently absorbs He (much faster than the vacuum pumps), and helps keep the pressure down below  $10^{-6}$  mbar in the source chamber, even when the He gas is flowing through the source [Alex2020]. Usually, we operate the source region ranging from  $8 \times 10^{-7}$  to  $6 \times 10^{-6}$  mbar.



**Fig. 4.3:** Illustration of the entire cryogenic buffer gas source [Alex2020].

## 4.3 Laser cooling region

### 4.3.1 Chamber



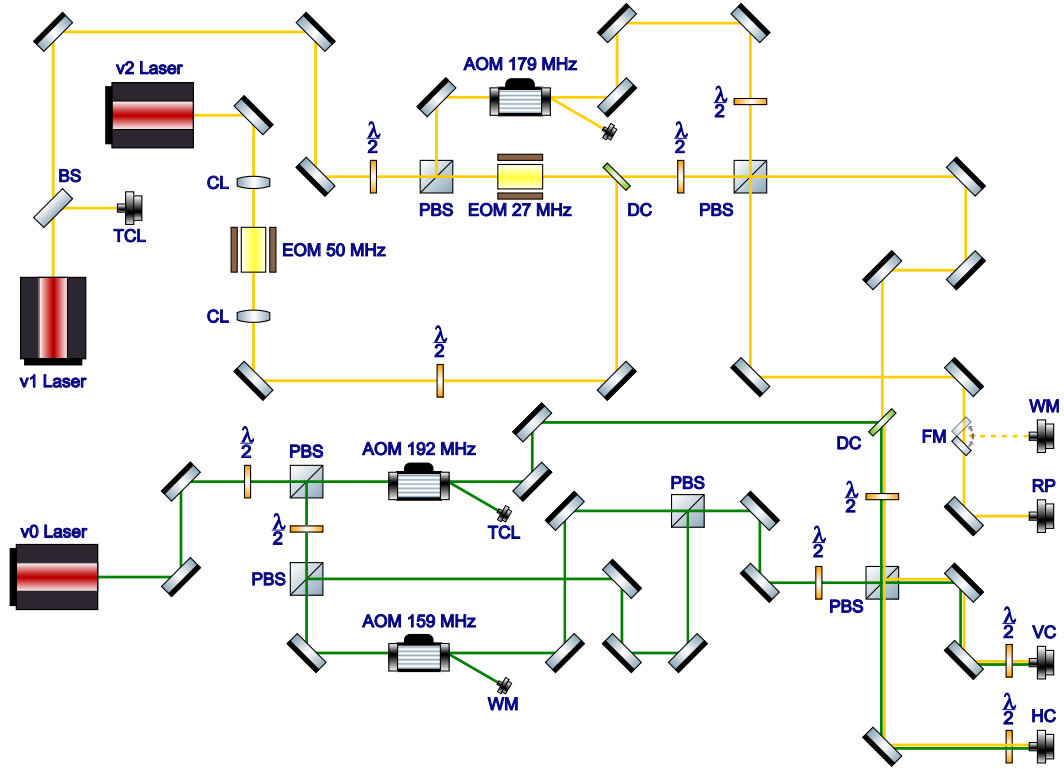
**Fig. 4.4:** The illustration of LC region. Dimensions of the LC chamber and windows used to generate multiple laser paths are labelled in the picture. Unit is mm. The multi-reflection optics is mounted next to the chamber which will be shown in Fig. 4.8.

The YbF molecule beam exits the source region with a forward velocity spread of 150 to 300  $\text{m}\cdot\text{s}^{-1}$ . The molecules will then pass into the laser cooling region where they are transversely cooled by a set of orthogonal optical lattices. The aim of transverse laser cooling is to reduce the transverse velocity of the YbF beam and increase the molecule density, thus respectively decreasing the transverse spread and increasing the number of molecules detected downstream. In the case of no transverse laser cooling, for a distance of 4.4 meters between the source and detection regions of the machine, the molecule signal will be significantly attenuated downstream since the divergence of the molecular beam is proportional to distance squared. In this work, we use two-dimensional magnetically-assisted-Sisyphus laser cooling. We name it **laser cooling (LC)** for the following discussion.

Figure 4.4 illustrates the chamber of LC region. The total length of the chamber is 473.03 mm. The LC chamber has 20 cm long rectangular AR coated windows to allow optical access for multi-pass transverse cooling beams in the  $z$  and  $x$  axes. A window at the diagonal to the  $x$  and  $z$  axes is also installed to allow a PMT detector to be mounted for beam diagnostics. There are 3 pairs of Helmholtz coils on the LC chamber to generate magnetic field in  $x$ ,  $y$ , and  $z$  directions, which are not shown in Fig. 4.4.

### 4.3.2 Lasers

The main cooling transition we use is  $|X^2\Sigma^+, \nu=0, N=1\rangle$  to  $|A^2\Pi_{1/2}, \nu'=0, J'=1/2\rangle$  with a corresponding wavelength of  $\lambda=552$  nm (542.812 THz) and the spontaneous decay rate of the excited state is  $\Gamma=2\pi \times 5.7$  MHz. The saturation intensity of this transition is  $I_{sat} = \pi\hbar c\Gamma/(3\lambda^3) = 4.4$  mW·cm<sup>-2</sup>. Due to the parity and angular momentum selection rules, the electric dipole transitions from the excited states to any other rotational states of  $X^2\Sigma^+$  are forbidden, but decay to other vibrational states are allowed. Corresponding branching ratios are shown in Fig. 4.6 with 93%, 6.6%, 0.3% and 0.03% from the excited state to the ground states  $\nu=0, 1, 2$  and 3, respectively [Zhu+11; Sma+14]. Populations which decay to  $\nu=1$  and  $\nu=2$  will be repumped back to the cooling cycle by transitions  $|A^2\Pi_{1/2}, \nu'=0, J'=1/2\rangle - |X^2\Sigma^+, \nu=1, N=1\rangle$  at 568 nm (527.804 THz) and  $|[561], J'=1/2\rangle - |X^2\Sigma^+, \nu=2, N=1\rangle$  at 565 nm. The [561] state is a mixture of the  $A^2\Pi_{1/2}$  ( $\nu'=1$ ) state and other inner-shell excited electronic states [Lim+17].



**Fig. 4.5:** Optics setup for laser cooling region. BS: beam sampler. CL: convex lens.  $\lambda/2$ : half wave plate. DC: dichroic mirror. FM: flip mirror. PBS: polarizing beam splitter. RP: repump. TCL: transfer cavity lock. WM: wavemeter.

We use the notation  $v_i$  ( $v_0$ ,  $v_1$ , and  $v_2$ ) to refer to the lasers in Fig. 4.6, where "i" stands for the vibrational states in the ground state being addressed. The corre-

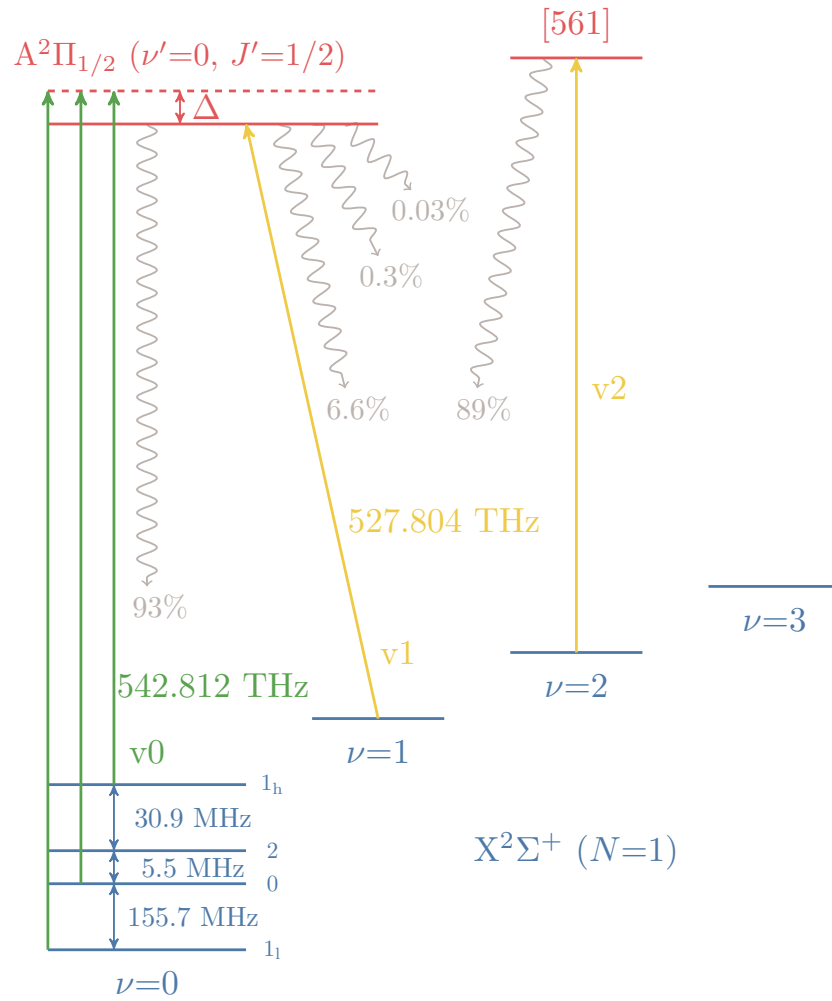


sponding laser powers ( $v_0$ ,  $v_1$ , and  $v_2$ ) incident on the molecules are 373, 185 and 13.5 mW, respectively (Tab. 4.1). In the ground state, each vibrational state has four sublevels due to the spin-rotation and hyperfine interactions. To distinguish the two  $F=1$  levels, we use notation  $1_h$  and  $1_l$ , where  $1_h$  has higher energy. The hyperfine levels are addressed by using **acousto-optic modulators (AOM)** and **electro-optic modulators (EOM)**. As shown in Fig. 4.5,  $v_0$  has two sidebands (159 and 192 MHz) generated by two AOMs.  $V_1$  laser has one AOM (179 MHz) which shifts the laser to address  $N=1$ ,  $F=1_l$  state. The  $F=0$ , 2 and  $1_h$  levels are almost evenly split and are addressed by rf sidebands generated from an EOM with frequency 27 MHz.  $V_2$  optics contains an EOM (50 MHz) to tune the laser in order that we can address the four ground hyperfine levels into either  $F'=0$  or 1 states [Lim+17].

Part of the  $v_1$  and  $v_2$  power (about 15 mW) is used for repumping the population back to  $\nu=0$  states. After the cooling region some molecules are still in higher vibrational states. In order to prepare our molecules in a state for the EDM measurement, as a first step we need to repump all of the population back into the  $N=1$  ( $\nu=0$ ) state. This is achieved via a clean up region after the cooling region where  $v_1$  and  $v_2$  light in the absence of  $v_0$  light is coupled into a repump (RP) fiber as shown in Fig. 4.5. In our system, we use wavemeters (High Finesse WS6) to check laser frequencies and **transfer cavity lock (TCL)** to lock laser frequencies. Usually, we pick off high order frequencies after AOMs for laser diagnostics.

After traveling through all the optics in Fig. 4.5,  $v_0$ ,  $v_1$ ,  $v_2$  lasers and all of the side bands discussed above are combined on beamcubes to be coupled into two fibres to reach the LC chamber with a beam waist of 2.5 mm, where they will be used for two orthogonal transverse directions. The optics setup on the LC chamber for HC and VC are same. For instance, in the case of HC, the beam after the fibre will be split into two paths. Then they will enter the chamber from opposite sides to bounce back and forth between the pair of long mirrors for 22 times. In Tab. 4.1, we summarize powers for each laser used in the LC region. "In" and "out" represent powers coming into and out of the fibres. As can be seen at the bottom right corner of Fig. 4.5, two fibre couplers are labelled by VC and HC. Power "In" is measured just before the fibre coupler. Power "out" is measured just after the fibre collimator. Efficiency is the ratio of powers coming out over in. Usually, in daily experiments, the fibre coupling efficiencies are about 60%. Moreover, fibres used in the LC region are 5-meter polarization-maintaining fibres.

In this work, the polarization configurations in the LC region are called  $XY_{||}$  and  $XY_{\perp}$ . Detailed explanation of the polarization configurations has been done in Eq. 3.26 in previous chapters. Figure 4.7 shows the measured polarization of the  $v_0$

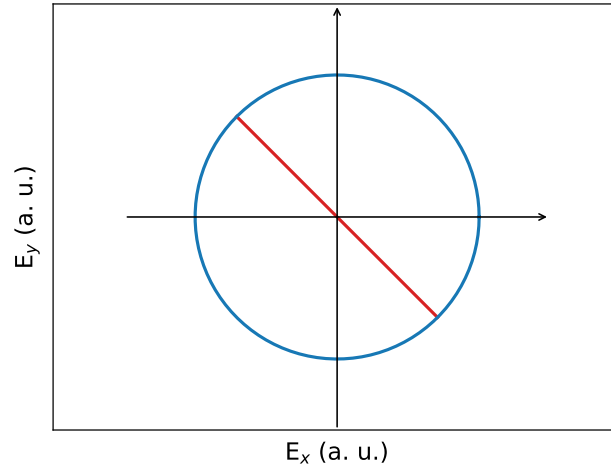


**Fig. 4.6:** YbF energy levels being used in the laser cooling region. Optical transitions are shown in green and yellow arrow. The branching ratios of vibrational levels are shown in gray wavy arrows. Cooling and repumping transitions are indicated by solid arrows. The hyperfine levels in  $|X^2\Sigma^+, \nu=0, N=1\rangle$  are shown with a blue detuning  $\Delta$ . The sidebands of repump lasers are not shown.  $V_0$  laser is in green because it is visibly green in reality. Same reasons for  $v_1$  and  $v_2$  are drawn in yellow.

|    | HC  |     |            |     | VC   |            |     |      | Repump     |  |  |
|----|-----|-----|------------|-----|------|------------|-----|------|------------|--|--|
|    | Out | In  | Efficiency | Out | In   | Efficiency | Out | In   | Efficiency |  |  |
| v0 | 192 | 306 | 62.7%      | 181 | 294  | 61.6%      | —   | —    | —          |  |  |
| v1 | 98  | 159 | 61.6%      | 87  | 146  | 59.6%      | 9.7 | 15.0 | 64.7%      |  |  |
| v2 | 7.7 | 13  | 59.2%      | 5.8 | 10.5 | 55.2%      | 7.8 | 14   | 55.7%      |  |  |

**Tab. 4.1:** Laser power and fiber coupling in the LC region.

laser. The polarization was measured by a polarimeter which has a fibre adaptor directly fitting with the end of fibres. In Fig. 4.5, the half wave plates just before the fibre docks are used to make sure the polarization of laser is parallel either to the fast or slow axis of the fibre. The entire measurement takes 10 seconds with 306 individual measurements. The averaged ellipticity is  $1.869^\circ$ . The extinction ratio ( $ER = 10\log(P_{\text{MainAxis1}}/P_{\text{MainAxis2}})$ ) tells how linear the polarization is [Tho22]. The larger the ER, the better linearity the polarization is. Normally,  $ER = 25$  dB means the linear polarization is qualified. Our measured ER is 31.30 dB. The reason to measure the laser polarization in Fig. 4.7 is that polarization is an important parameter in laser cooling as we have discussed in Ch. 3.

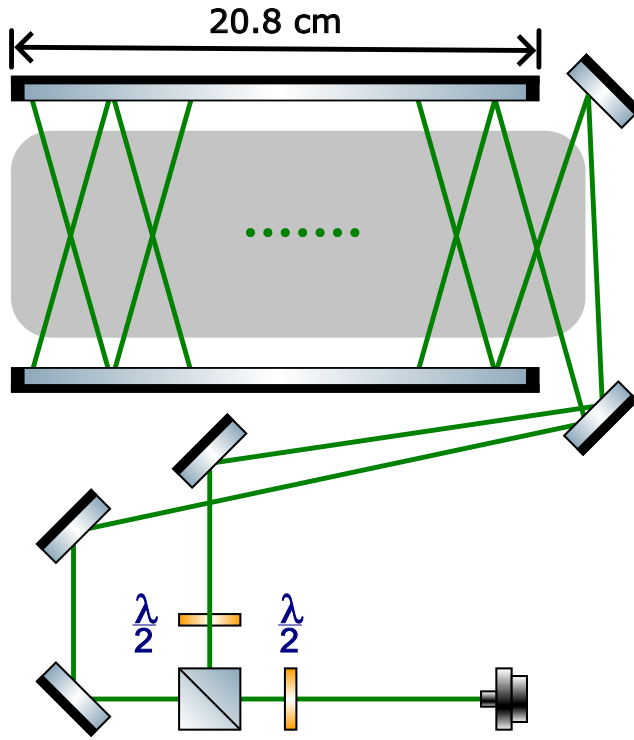


**Fig. 4.7:** Measured polarisation of the LC fibers using a commercial polarimeter.

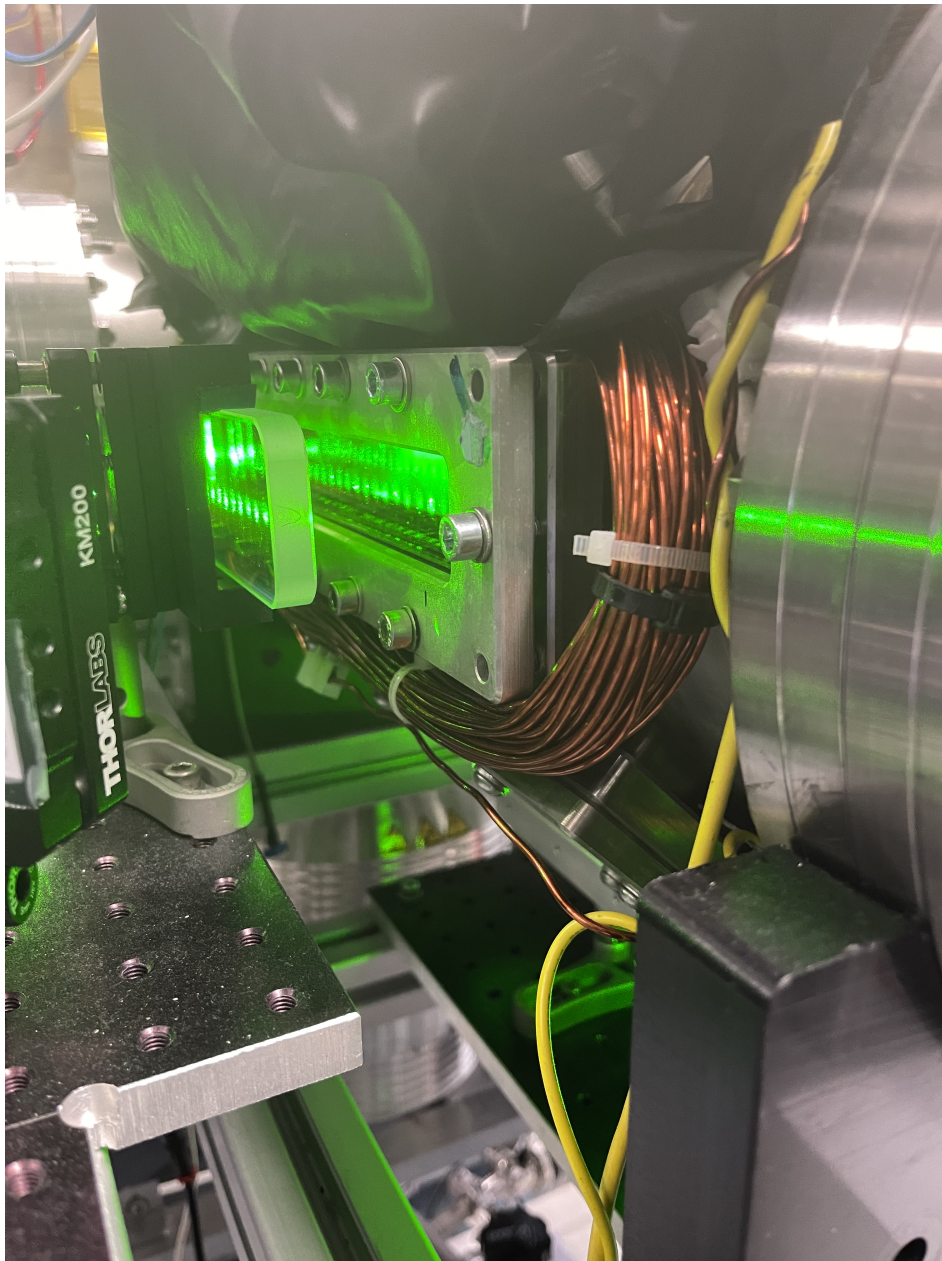
### 4.3.3 Multi-reflection optics

Figure 4.5 is the optical setup on the optical table which is only responsible for generating frequencies required by the transition scheme based on Fig. 4.6. The multi-reflection optics is on the machine which is shown in Fig. 4.8. The first  $\lambda/2$  WP is to balance the power for two beams. Here two beams refer to two counter propagating beams forming an optical molasses. We always set the powers in the two beams identical. The reason is that we expect molecules moving in two opposite directions experiencing same damping force. As mentioned in the last section, the polarization configuration applied is  $XY_{||}$ . Thus, the second WP is to recover the polarization of the reflected beam by the PBS. Then we use a polariser to distinguish two beams to check whether the two beams have the same polarization. The reason to build multi-reflection optics is to increase interaction time for laser cooling while keeping the high laser intensity. In total, there are 22 reflection paths for both

horizontal and vertical cooling. For instance, molecules with speed  $150 \text{ m}\cdot\text{s}^{-1}$  will have an interaction time for 1.3 ms. Moreover, the peak intensity per beam is  $450 I_{\text{sat}}$ . As discussed previously,  $I_{\text{sat}}$  is equal to  $4.4 \text{ mW}\cdot\text{cm}^{-2}$ .



**Fig. 4.8:** Multi-reflection optics of LC. This figure shows the setup for horizontal cooling. The vertical cooling setup is same as horizontal cooling. This setup is on the machine.  $\lambda/2$ : half wave plate.

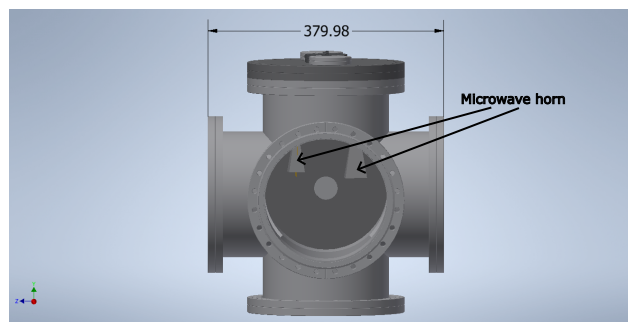


**Fig. 4.9:** Image of multi-reflection optics of horizontal cooling in the LC region. Vertical cooling has the same setup. Copper wires are used to generate magnetic field to destabilize dark states.

## 4.4 Optical pumping region

### 4.4.1 Chamber

Figure 4.10 shows the structure of OP region. The total length of OP region is 380 mm. As can be seen, there are 2 microwave horns highlighted by arrows in the OP chamber, which are used to address  $N=1$  and  $N=2$  states. After YbF molecules have been transversely laser cooled, they must be transferred to the  $|X^2\Sigma^+, v=0, N=0\rangle$  ground state as an initial step towards state preparation of the EDM sensitive state. As previously discussed in Sec. 4.3. the cooling transition is rotationally closed, therefore, the population will end up in the  $N=1$  rotational level. Note however that the cooling transition is not vibrationally closed and it is necessary to repump the transversely cooled population with  $v=1$  and  $v=2$  light within the cleanup region such that we populate the  $|X^2\Sigma^+, v=0, N=1\rangle$  state. After molecules are transversally cooled and repumped within the cooling and clean-up regions, molecules will pass through the optical pumping region for population transfer to the  $|X^2\Sigma^+, v=0, N=0, F=0\rangle$  state. The optical pumping region is confined to a DN200CF six way cross. The two flanges along the y axis provide connection to the beam line, the two x axis flanges allow for optical access, the upper flange is used to connect microwave horns and the bottom flange is connected to Leybold Turbovac Mag turbo pump. The pumping scheme utilizes optical and microwave transitions to effectively transfer population to the  $F=0$  state, as detailed in this section.



**Fig. 4.10:** The illustration of OP region. The dimension of the OP chamber is shown. Microwave horns are highlighted. The multi-reflection optics is mounted next to the chamber which will be shown in Fig. 4.13.

## 4.4.2 Lasers and microwaves

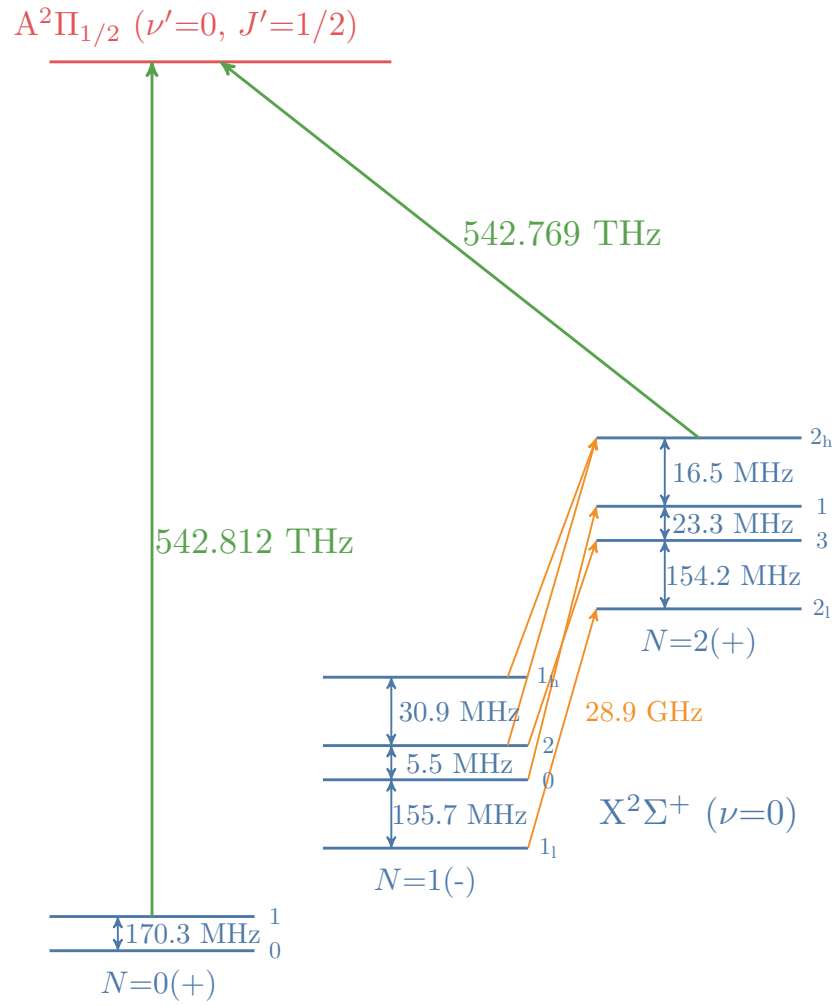
As discussed in Ch. 4.3, the LC transition is rotationally closed, which means most of the population will decay into  $|X^2\Sigma^+, \nu=0, N=1\rangle$  state. Thus, it is clear that the starting state of the OP transition is  $|X^2\Sigma^+, \nu=0, N=1\rangle$  and the end is  $|F=0\rangle$  state. The intermediate states is  $|A^2\Pi_{1/2}, \nu'=0, J'=1/2, f(-)\rangle$ , because the parity of  $N=2$  state is plus. As shown in Fig. 4.11, we implement five microwave frequencies (orange lines) to address  $N=1$  and 2 states. From bottom to top, the frequencies are 28.9343, 28.9561, 28.9671, 28.9361, and 28.9273 GHz. With a microwave synth produced by Windfreak (SynthHD (v2)), signal passes into a mixer for the generation of rf side bands at 15.6 MHz, then to a frequency doubler (Marki MMD-1030H) and an amplifier (Marki ADM2-0035PA). The output power of each microwave horn can be adjusted from -20 dBm to 15 dBm.

The next step is to drive the transition from  $N=2$  state to the first excited state. Here, we use two frequencies. 542.769 THz (P12 unshifted) is the energy difference between  $|X^2\Sigma^+, \nu=0, N=2, F=2_h\rangle$  and  $|A^2\Pi_{1/2}, \nu'=0, J'=1/2\rangle$  states. Another frequency is 185 MHz (P12 185 MHz) blue detuned with respect to the P12 unshifted frequency. The next transition is Q0 whose frequency is 542.812 THz. The Q(0) transition links the  $|F=1\rangle$  and  $|A^2\Pi_{1/2}, \nu'=0, J'=1/2\rangle$  states. The selection rules for hyperfine levels tells that The  $F=0$  and  $F=1$  levels in the A state can decay into both the  $N=0, F=0$  and  $F=1$  states. Therefore the Q0 laser is tuned on resonance with  $F=1$  to pump all of the population into  $F=0$ .

Figure 4.12 shows the optics setup of the OP region. The seed lasers for P12 and Q0 are commercial products (models shown in appendix). The output of seed lasers are infrared (IR). In order to acquire the desired frequencies, we use second-harmonic generation (SHG) to double the IR frequencies. Because the doubling crystal in the SHG is quite thin, we need a convex lens to reduce the beam size in order to achieve the best coupling into the SHG. All of the convex lens used in OP optics have focus distance 100.00 mm. For Q0 frequency, the input IR power is 5 W. The output power of the green laser is 160 mW. For P12 frequency, powers for the input IR and the green output laser are 6 W and 1 W. The reason that the P12 and Q(0) lasers have such different output power is that the doubling crystal for P12 is twice longer than Q(0), which can significantly improve the nonlinear frequency conversion efficiency [Bru+04]. After the SHGs, dichroic mirrors are used to reflect IR to beam dumps and allow green lasers to pass.

We use an AOM driven at 185 MHz to generate the sideband for the P12 transition. The unmodulated component after the AOM is picked off for P12 TCL. The Q0 TCL





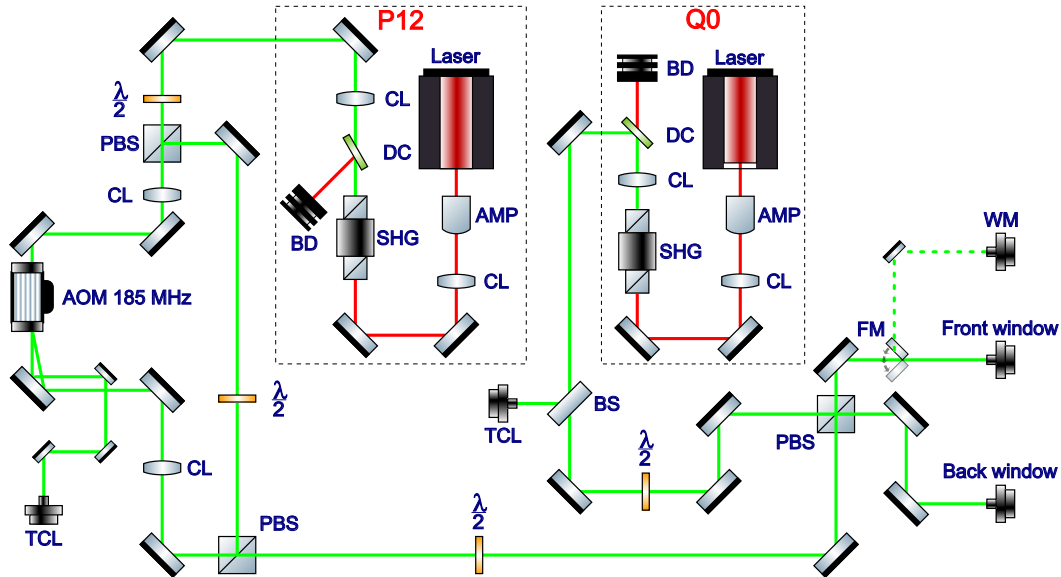
**Fig. 4.11:** YbF energy levels being used in the optical pumping region. The hyperfine levels in  $|X^2\Sigma^+, \nu=0, N=0, 1 \text{ and } 2\rangle$  are shown in blue. The orange arrows stands for the microwave transitions between  $N=1$  and  $2$  rotational levels. The green arrows illustrate the optical transitions between the ground and the first excited states. All the microwave frequencies are around 28.9 GHz. We simply label them 28.9 GHz here. The 542.769 THz frequency has a 185 MHz sideband generated by an AOM, which is not shown here.

|               | Front |     |            | Back |     |            |
|---------------|-------|-----|------------|------|-----|------------|
|               | In    | Out | Efficiency | In   | Out | Efficiency |
| Q0            | 40    | 19  | 0.475      | 40   | 19  | 0.475      |
| P12 unshifted | 235   | 63  | 0.269      | 242  | 102 | 0.421      |
| P12 185MHz    | 150   | 52  | 0.347      | 162  | 81  | 0.500      |

**Tab. 4.2:** Laser power and fiber coupling in the OP region.



is the reflective component of an 100:1 beam sampler. In Fig. 4.12, The P12 and Q0 light are combined on a PBS. The incoming polarisation angle of the linear polarised beams is set to 45 degrees by half waveplates such that the Q0 and P12 power in the transmitted and reflected beams after the PBS are equal. The transmitted and reflected beams are then collected by two fiber couplers and sent to the experiment. The optics on the OP chamber is multiple reflective paths to increase interaction time (same idea of the LC region). Two dielectric mirrors (one-inch square mirrors) are placed close to the front and back windows of the OP chamber, in order to allow laser beams coming out of two fibres to reflect five times between them. The purpose to install one fibre dock on each side of the chamber is to introduce polarisation modulation by putting two orthogonal polarisations from each side. The windows on the OP chamber are not AR coated. As we measured, laser power is attenuated by 5% after each reflection between the pair of square mirrors. We have tested the optical pumping efficiency with respect to laser power. The conclusion is that such power attenuation due to the window is not a problem.



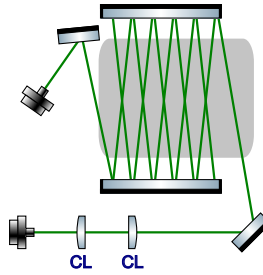
**Fig. 4.12:** Optics setup for OP region. AMP: amplifier. BD: beam dump. BS: beam sampler. CL: convex lens.  $\lambda/2$ : half wave plate. DC: dichroic mirror. FM: flip mirror. PBS: polarizing beam splitter. SHG: second-harmonic generation. TCL: transfer cavity lock. WM: wavemeter.

Table 4.2 shows the fibre coupling of the OP optics. The optical pumping light is sent from the optics table to the chamber via polarisation maintaining fibers (Thor labs PM460-HP). As can be seen, the fibre coupling efficiencies are about 40%. Because the beam sizes of P12 and Q0 are different, it is not possible to optimize the output powers to the highest efficiency for them at the same time. Based on our previous

work (Ref.[Ho20]) and results in Ch. 5.2, output powers listed in Tab. 4.2 is enough to pump all the population into  $|F=0\rangle$  state.

#### 4.4.3 Multi-reflection optics

The optical pumping light exits the fiber and a Gaussian beam profile is produced via a fiber collimator. The reason to implement multi-reflection optics is to increase interaction time. The story traced back to last year. When the first time we set up OP, the collimator we used gave a very large beam size causing a low OP efficiency (about 50% population left in  $N=1$  state after OP). Then we planned to shape the beam aiming to increase the laser intensity. A pair of cylindrical lenses are used to modify the beam shape to be elliptical. The length of the laser beam is about 12.0 mm, and the width is about 1.0 mm. In our machine, the speed of fast molecules can reach  $240 \text{ m}\cdot\text{s}^{-1}$  giving an interaction time about  $4.2 \mu\text{s}$ . Based on the calculation (Fig. 5.9), we need at least  $5 \mu\text{s}$  interaction time. Thus, we need to implement multi-reflection optics. As shown in Fig. 4.13, in total there are 5 reflection paths, resulting in the interaction time for fast molecules to be about  $20 \mu\text{s}$ . We find this approach to be more effective than a single beam with a large  $1/e^2$  radius.

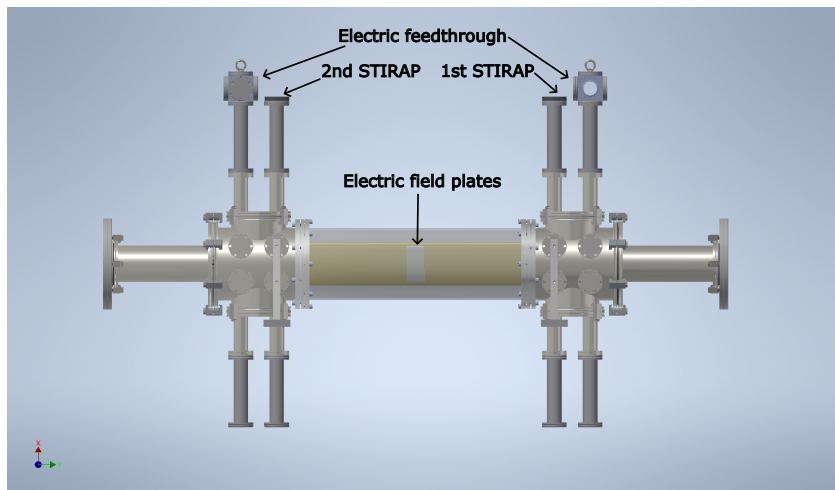


**Fig. 4.13:** Multi-reflection optics for OP. The setup is on the machine. CL: convex lens.

## 4.5 Interaction region

### 4.5.1 Chamber

Figure 4.14 shows the structure of the interaction region. The total length of the interaction region is 1.768 meters. The electric field plates (shown in yellow) is the key component of the spin precession experiment. Magnetic field coils and shields are not shown here. The chambers are custom along with the diameter (DN200) and are made from titanium. The reason to manufacture the chamber in titanium is to reduce magnetic noise. The vacuum seal between the glass and titanium chamber is made by compressing onto an Viton O-ring. The titanium chambers support the E-field plates via ceramic standoffs connected to the side flanges. The chambers allow access for the electric feedthroughs to charge the E field plates. Leakage monitors are connected directly to the high voltage feedthroughs to measure leakage currents. The titanium chambers also have optical access for the STIRAP beams.

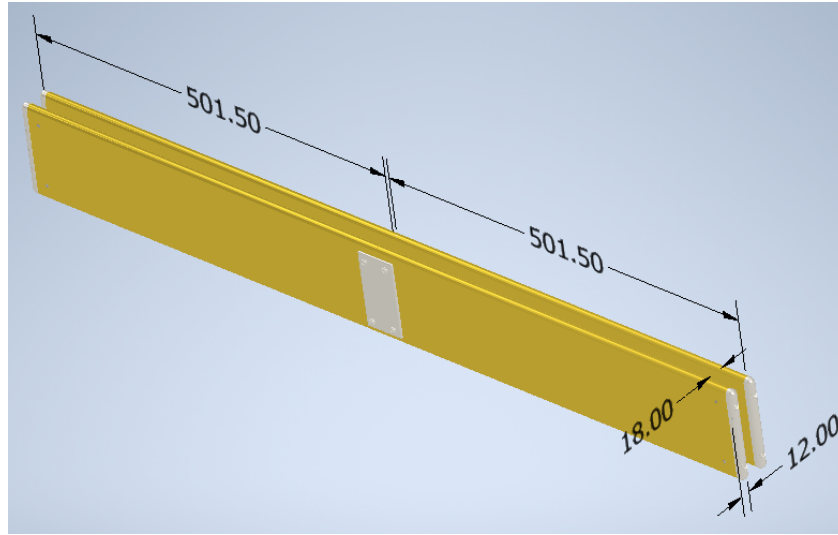


**Fig. 4.14:** The CAD drawing of the interaction region. Key components are highlighted.

### 4.5.2 Electric field

As shown in Fig. 4.15, the total length of one electric field plate is 1 meter. For manufacturing purposes, each one-meter electric field plate has been produced in two parts of equal length. The two parts are joined via a titanium plate to ensure conductivity across the entire electric field plate. The design is modular such that the electric field plate length can be extended in the future. The material of the plate is alumina ( $\text{Al}_2\text{O}_3$ ) which is a type of ceramic. The plate is coated by a 20

$\mu\text{m}$  layer of Titanium nitride (TiN). The thickness of each plate is 12.00 mm. The plates need to be thick enough to be rigid. However we need to reduce the volume of electrically conductive material in order to limit the Johnson noise [Whi+03]. Thus we use a thin layer of TiN as the conductive layer rather than make the entire plates from a conductive material. The gap between two plates is 18.00 mm. If  $\pm 18$  kV is applied between the plates, the electric field between the plates is  $20 \text{ kV}\cdot\text{cm}^{-1}$ . Such an electric field strength can make the value of  $\eta E_{\text{eff}}$   $18 \text{ GV}\cdot\text{cm}^{-1}$ . The general idea is to make this value as large as possible, because it can amplify the EDM interaction since the EDM interaction is tiny. In the future, we want to extend the length of plates because we want to increase the duration time of spin precession. Because in Eq. 1.14, increasing spin precession duration  $\tau$  can make the value of EDM sensitivity smaller. This setup has the capability to be extended to 3 meters.

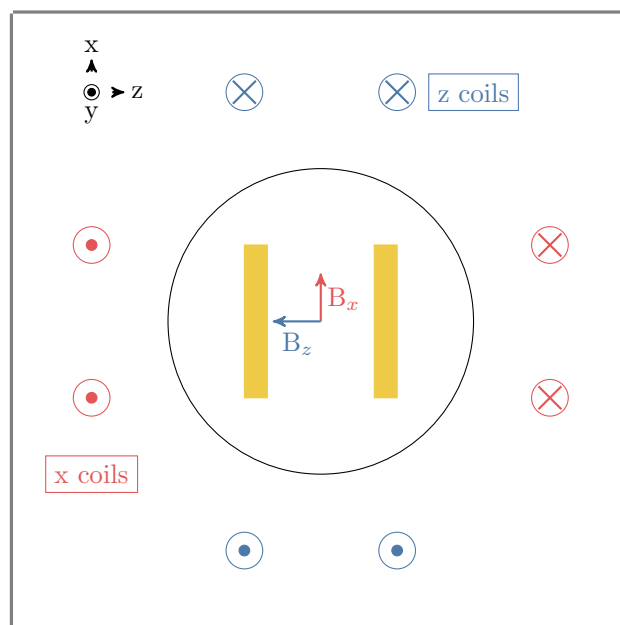


**Fig. 4.15:** The illustration of the electric field plates (units in mm).

### 4.5.3 Magnetic field

After introducing the electric field system, this section will explain how we generate the applied magnetic field,  $B$ , for the EDM experiment. The applied field is produced within the innermost magnetic shield via a set of cosine coils as shown in Fig. 4.16. The black circle indicates the first layer of magnetic shields. The two yellow rectangles are electric field plates. The lab frame is shown in the top left corner. We always point y axis along the direction which YbF molecules travel through. Z axis is the direction pointing between the electric field plates, leaving x axis pointing upwards. There are two pairs of coils generating uniform magnetic field along z

axis (another two pairs for x axis). As can be seen, due to Biot-Savart law, two pairs of vertical coils (in blue) can generate magnetic field ( $B_z$ ) horizontally. Using the same logic, another two pairs of coils (in red) can generate  $B_x$ . Within the EDM experiment, a stable and configurable current source is required in order to switch between the four different values of the magnetic field which are needed to run the experiment.



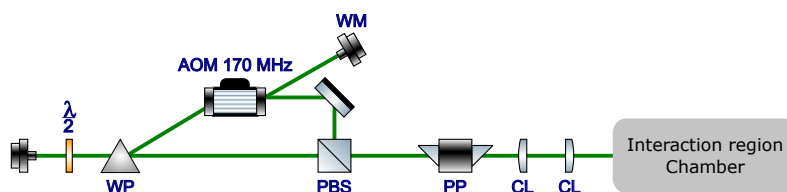
**Fig. 4.16:** Illustration of coils which generate magnetic field for the spin precession experiment.

#### 4.5.4 STIRAP

The STIRAP optical setup is responsible for preparing superposition state and readout dynamic phases caused by spin precession as we have discussed in [Chapts. 1 and 3](#). There are two STIRAP regions in the interaction region. The state preparation STIRAP beam is at the entrance of the electric field plates to map  $|0, 0\rangle$  to the  $|y\rangle$  state. The readout STIRAP beam is placed at the exit of electric field plates to read out the spin precession phase.

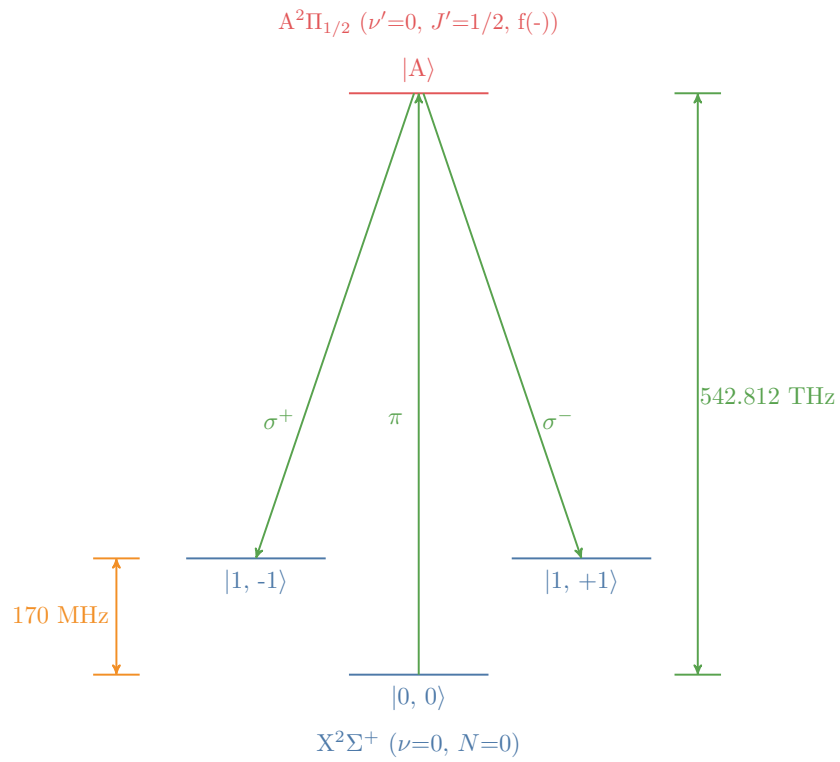
[Figure 4.18](#) is the transition scheme of the STIRAP. Because the parity of the  $N=0$  state is plus, the excited state which molecules will be driven to should have opposite parity which is  $f(-)$ . The actual laser beams consist of two frequencies. One is the  $\pi$  component shown in [Fig. 4.18](#). The other is the  $\sigma^\pm$  component. In reality, the  $\sigma^\pm$  component is the decomposition of the  $y$ -polarized light. Here " $y$ " refers to the  $y$ -axis

of the Cartesian coordinate in the lab frame). Moreover, based on Fig. 4.18, the  $\sigma^\pm$  component should show up firstly which is commonly called Stokes laser. The beam shows up later is called pump laser which is the  $\pi$  component in our system.



**Fig. 4.17:** STIRAP optics. CL: convex lens. WM: wavemeter.  $\lambda/2$ : half wave plate. PBS: polarizing beam splitter. PP: prism pair. WP: Wollaston prism. There is a beam splitter to further split the two beams into four beams for state preparation and readout, which is not shown here.

As shown in Fig. 4.17, a green laser (552 nm) will be split into two beams by a Wollaston prism. The half-wave plate in front of it is to balance the power between the two beams. The Wollaston prism will make the two beams into orthogonal linear polarizations (P and S polarized). One beam will be modulated by an AOM with frequency 170 MHz which is the energy difference between  $F=0$  and 1 states. The zero-order beam after the AOM will be used by a wavemeter for frequency diagnostics. Then a PBS will recombine the two beams together to allow them travel through an anamorphic prism pair. The role of the prism pair is to enlarge the beam along one direction with magnification  $\times 4.0$  producing an elliptic beam. After that, there is a pair of convex lens to further enlarge the beam with magnification  $\times 3.3$ . The reason to shape the beam is that we want the molecules travelling between the electric field plates to experience the laser. Thus, we design the length of the beam to be around 15 mm (gap between electric field plate is 18 mm). We didn't make the beam length 18 mm, because we're concerned that the laser can be reflected by the electric field plates, causing extra interaction with molecules which we don't want.

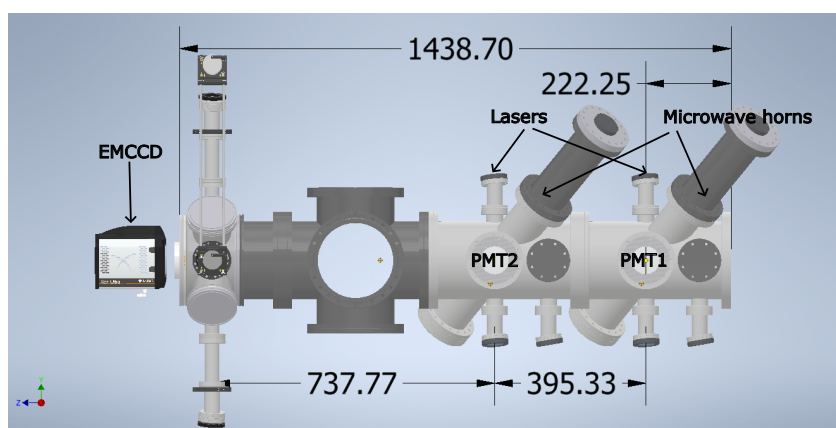


**Fig. 4.18:** YbF energy levels being used in STIRAP. 170 MHz is the energy difference between  $F=0$  and 1 states, which is not applied in the actual system. The  $\pi$  and  $\sigma^\pm$  beams correspond to the AOM beam and unmodulated beam in Fig. 4.17 respectively.

## 4.6 Detection region

### 4.6.1 Chamber

The detection region is the last region in the entire machine. After the interaction region, YbF molecules in the  $F=0$  and  $F=1$  states will be detected by **laser induced fluorescence (LIF)** via two independent state selective detectors. As can be seen in Fig. 4.19, the entire length of the detection chamber is 1.439 meters. There are two types of detectors in this region. One is **photomultiplier tube (PMT)**, the other one is **electron multiplying charge coupled device (EMCCD)**. As shown in the left of Fig. 4.19, an EMCCD is placed at the end of the machine in order to diagnose the 2D cooling, particularly used to align the horizontal and vertical cooling. Two PMTs (PMT1 and PMT2) are mounted horizontally on the two view ports between which the distance is 395.33 mm. Viewports in vertical direction are used to guide laser beams into the chamber. In order to detect  $|F = 0\rangle$  and  $|F = 1\rangle$  states, microwaves are required. Two microwave horns are installed in the tilted stainless flanges highlighted in gray in Fig. 4.19. Moreover, the detection laser beam is orthogonal to the molecular beam so no Doppler shift is experienced.



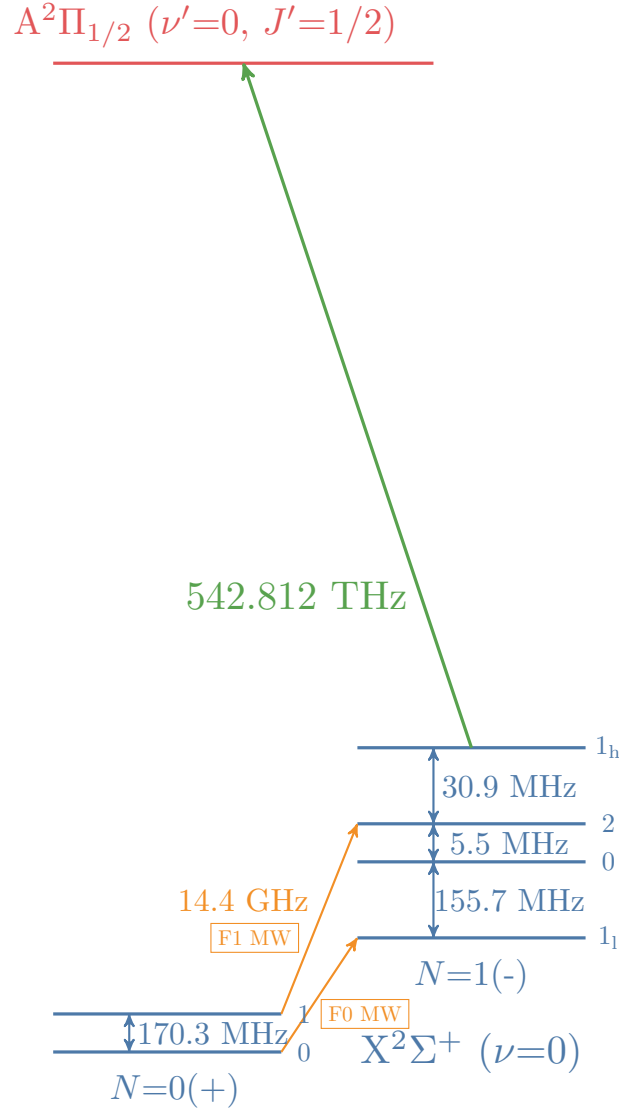
**Fig. 4.19:** The illustration of detection region. Dimension information is labelled.

### 4.6.2 Lasers and microwaves

Figure 4.20 is the detection scheme. The aim of the detection scheme is to detect  $|F = 0\rangle$  and  $|F = 1\rangle$  states individually.  $|F = 0\rangle$  will be driven to  $|N = 1, F = 1_1\rangle$  by a microwave frequency at 14.467242 GHz. Regarding  $|F = 1\rangle$ , the frequency driving to  $|N = 1, F = 2\rangle$  is 14.458087 GHz. Within each detector, optical light that is tuned



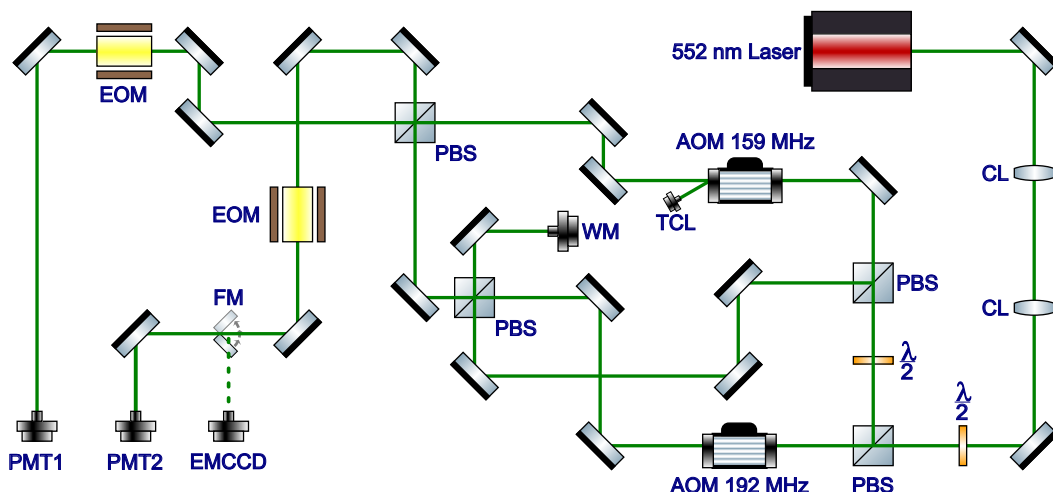
to the P(1) transition enters through the vertical beam ports and interacts with the molecules orthogonally, driving them into the A state. As previously discussed, the P(1) transition is rotationally closed and thus is a cycling transition with the capacity to scatter 12 photons before decaying to a higher vibrational state [Ho+20].



**Fig. 4.20:** YbF energy levels being used in the detection region. The hyperfine levels in  $|X^2\Sigma^+, \nu=0, N=0 \text{ and } 1\rangle$  are shown in blue. The orange arrows stand for the microwave transitions between  $N=0$  and 1 rotational levels. The green arrows illustrate the optical transitions between the  $|X^2\Sigma^+, \nu=0, N=1\rangle$  and the first excited states. Both microwave frequencies are around 14.4 GHz. We simply label them 14.4 GHz here. The sidebands of 542.812 THz is not shown.

Figure 4.21 illustrates the optics setup for the detection scheme. In order to fully detect the  $N=1$  state, two AOMs whose driving frequencies are 159 and 192 MHz are implemented to generate two sidebands for the 542.812 THz frequency. There

are also two EOMs in the optics setup. Their role is to modulate the polarization of the probe laser. At the end of the optics, there are three fibre docks to collect laser beams. Two of them are for the two PMTs, the other one switched by a flip mirror is for the EMCCD. In daily experiments, laser power before and after each fibre dock is around 70 and 20 mW, with a coupling efficiency 28.6%. Moreover, the output power of microwave horns can be adjusted from -30 to 20 dBm. Microwaves are generated by synthesizers (Windfreak HD v2). The MW frequencies can also be switched between  $F=0$  and  $F=1$  frequencies within each detector. This is necessary to check for systematic effects.

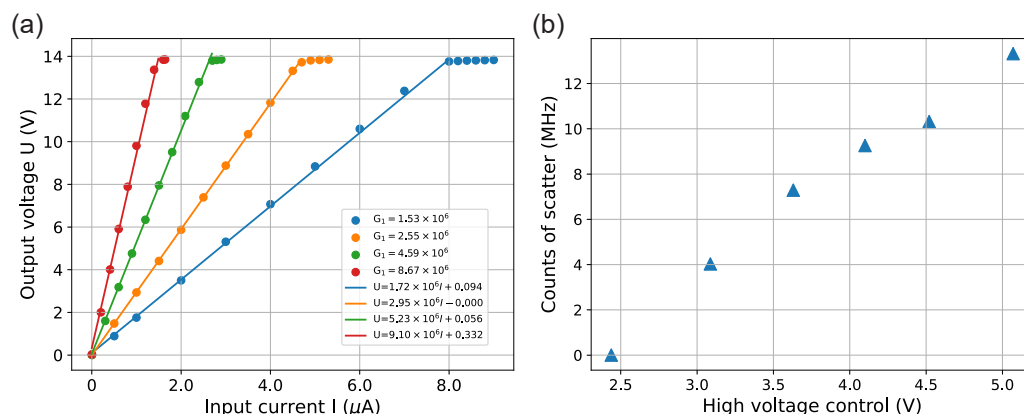


**Fig. 4.21:** Optics setup for detection region. CL: convex lens.  $\lambda/2$ : half wave plate. FM: flip mirror. PBS: polarizing beam splitter. TCL: transfer cavity lock. WM: wavemeter.

### 4.6.3 PMTs and cameras

As mentioned above, there are two types of detectors in the detection region. One is PMT and the other one is EMCCD. A PMT will generate an output current based on the number of photons it detects. To understand the ratio of molecules to the generated PMT signal for a given photon flux we must calibrate the PMTs within the detection region. The PMT data collection system consists of two parts. One is the PMT itself. The other one is the amplifier. In Fig. 4.22 (a), we scan the input current into the amplifier and measure the output voltage of the amplifier circuit. There are four different gains ( $1.53, 2.55, 4.59, 8.67 \times 10^6$ ) can be selected. As can be seen, the measured gains and theoretical gains match, indicating the amplifier works normally. The curve will saturate at certain points. The reason is that the amplifier can't take in current which is larger than a certain threshold. In (b), after setting the gain at 1.53 million, we change the **high voltage (HV)** which drives the

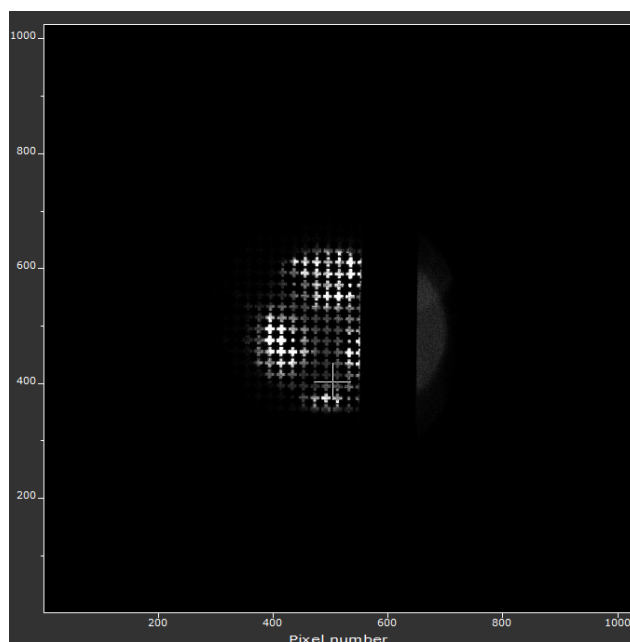
supply voltage between the anode and cathode in the PMT. It is clear that under the same light source the counts of scatter increases with HV increasing. At highest HV (5.05 V), the voltage between the anode and cathode is 1250 V. The counts of scatter at this point is  $13.32 \times 10^6$  per second. The output voltage of the PMT is 13.34 V. Thus, in one second, the integral of the PMT signal with respect to time is 13.34 V·s, which corresponds to  $13.32 \times 10^6$  photon counts. For simplicity, we can draw the conclusion that 1 V·s corresponds to  $10^6$  photon counts. We need this information to convert molecule time of flight PMT signal to number of photons.



**Fig. 4.22:** PMT calibration. (a) Output voltage vs input current of the amplifier. (b) Counts of scatter vs HV.

We use two identical PMTs (Hamamatsu R5070A) in the detection region. The diameter of the PMT is one inch (25 mm). The range of spectral response is from 300 to 900 nm. At  $25^\circ\text{C}$ , when the supply voltage (the voltage between anode and cathode) is driven at maximum (1250 V), the gain of the PMT is  $4.3 \times 10^5$  and the dark current is 3 nA [Ham04]. Moreover, at the frequency we are interested in (552 nm), the quantum efficiency of the PMT is 10%. In order to acquire the output signal from the PMTs, we build two identical amplifier circuits for both PMTs. The amplifier circuit consists of two operational amplifiers. The first Op-Amp convert the current output from the PMT to voltage. Then the second Op-Amp amplifies the voltage based on the gain selected. There are four gains can be selected as mentioned above.

The second type of detector in the detection region is EMCCD. It can measure number of molecules and show spatial distribution of molecules. The EMCCD contains  $1024 \times 1024$  pixels. After setting the Binning to 16, the image becomes  $64 \times 64$  pixels. Figure 4.23 is the grid used to setup the EMCCD. It has two roles. The first role is to align the EMCCD to the molecular beam line. In the center of the figure, the bright area is the laser scattering in the LC region. If the center of



**Fig. 4.23:** The stainless grid in the detection region. It is located at the end of the entire machine. Image is taken by the EMCCD under normal camera mode.

the view overlaps the center of LC region, cold molecules will show in the center of the image. The second role is to measure the field of view. In Fig. 4.23, it can be seen that the grid contains many small crosses. The distance between two adjacent crosses is 1 mm. After processing the image, we conclude that one pixel is 0.93 mm (roughly 1 mm). In daily experiments, we set the exposure time of EMCCD to be 30 ms which is the length of the **time of light (TOF)** of the molecular beam line. The gain of the EMCCD is set at maximum which is 300. The readout rate is 10 MHz. The cooling system in the EMCCD is set at lowest temperature ( $-90^{\circ}\text{C}$ ) to reduce noise as much as possible. The dark noise and spurious noise are 0.001 and 0.005 events/pix, which is neglectable compared to our signal [Ins22].

Furthermore, inside the detection chamber, there are in-built collection optics. For PMTs, the diameter of the convex lens is 72 mm. The distance between where the photon are scattered and the convex lens is 60 mm. It gives the detection solid angle 0.09. For the end-view EMCCD, the numbers are two inches (50.8 mm) and 80 mm, which gives the detection solid angle 0.0252.

## 4.7 Summary

In this chapter, we have introduced the setup of the YbF eEDM machine by regions. We have showed the YbF cryogenic buffer gas source. In the laser cooling region, we have showed the chamber, optics setup and laser system. We have also demonstrated the multi-reflection optics. In the optical pumping region, we have showed the chamber, optics setup and laser system. In the interaction region, we have demonstrated the chamber, electric field system, magnetic field system and STIRAP optics. In the detection region, we have introduced the chamber, optics setup, laser system, PMTs and EMCCDs.

## Experimental results

This chapter shows the experimental results of the YbF eEDM experiment. It begins with the laser cooling region with a systematic study on ultracold YbF molecular beams. We also correlate the laser cooling effect with the shot EDM sensitivity. Next we show the results of optical pumping region in which we focus on the optical pumping efficiency. Then we introduce the results of the interaction region with preliminary results of STIRAP and magnetic noise. At last, we discuss how well we can detect  $F = 0$  and  $F = 1$  states in the detection region.

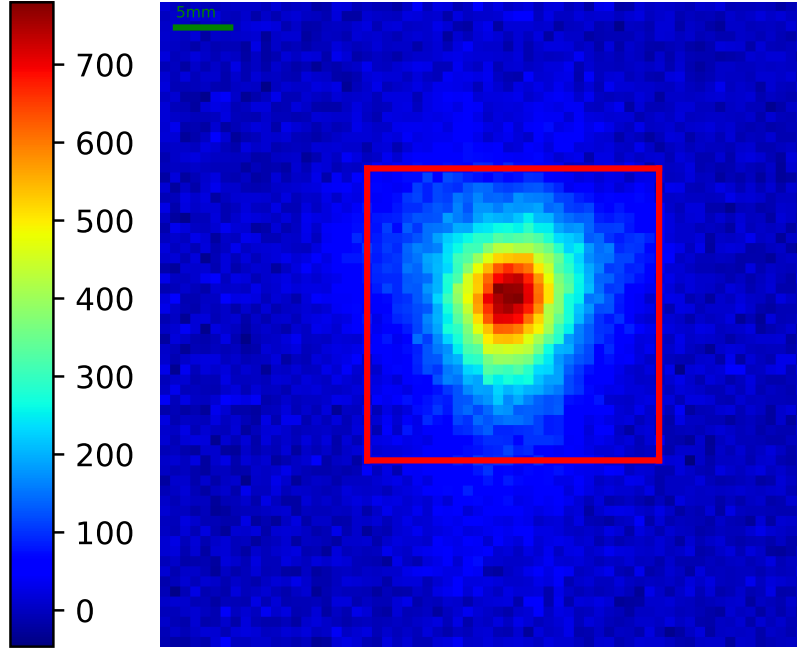
### 5.1 Laser cooling region

In this section, we will discuss the experimental results in the laser cooling region. This section is arranged in the following way. At first, I will present the images of cold YbF molecules taken by the iXON 888 ultra EMCCD placed at the end of the machine (Location of the EMCCD, see Fig. 4.19). Images will provide an impression how cold molecules look like. I will also present how to extract number of molecules from images. Then we will systematically study laser cooling from the aspects of magnetic field, polarization, detuning, laser intensity, and transverse temperature. Finally, I will show how laser cooling improves number of molecules ( $N=1$  state) and EDM sensitivity of cold molecular beams.

#### 5.1.1 Images of cold molecules

Figure 5.1 shows the results of 2D cooling. Here we use a 542.812 THz laser which drives the transition between  $|X^2\Sigma^+, v=0, N=1\rangle$  and  $|A^2\Pi_{1/2}, v'=0, J'=1/2\rangle$  to detect the population in  $N=1$  state. The ultracold YbF molecules are in the centre of the image. The scale bar is shown in the top-left corner. The entire field of view is about  $6\text{ cm} \times 6\text{ cm} = 36\text{ cm}^2$ . There are 1024 pixels in both horizontal and vertical directions ( $1024 \times 1024$ ). The bin size we used is 16, resulting in 64 pixels in each direction. The red square highlights the **region of interest (ROI)** which is a  $30 \times 30$  binned pixels. The gap between the electric field plate is 18 mm. Figure. 5.1 shows

that the size of cold YbF molecular beam is about  $1.2 \text{ cm} \times 1.2 \text{ cm}$ , indicating all the cold molecules pass through the field plate. The color bar shows the pixel value.



**Fig. 5.1:** An EMCCD image of YbF molecules with LC at the end view of the machine. The image is averaged over 404 shots. The bin size is  $16 \times 16$ . The image is background subtracted.

For each pixel, its value means the number of counts in it over the exposure time of 30 ms. Here, number of counts refers to number of photons being detected by the EMCCD. In order to calculate the number of molecules, the first step is to convert it to number of photons being scattered by YbF molecules [Tri20]

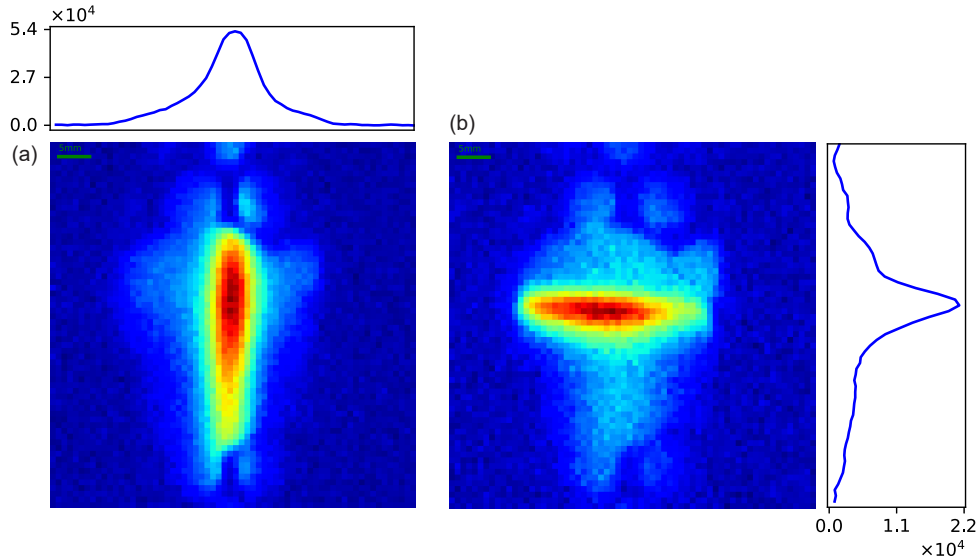
$$N_{\text{photons}} = \frac{N_{\text{counts}}}{\eta_{\text{ADC}} \times \eta_{\text{QE}} \times A_{\text{EM}} \times T_{\text{Lens}} \times T_{\text{filter}} \times T_{\text{window}} \times \eta_{\text{collection}}}, \quad (5.1)$$

where  $N_{\text{counts}}$  is the sum of pixel values in the ROI in Fig. 5.1, with value  $1.41 \times 10^5$ .  $\eta_{\text{ADC}}$  and  $\eta_{\text{QE}}$  are the ADC conversion efficiency and quantum efficiency, with value 1/18 and 0.97, respectively [Ins22].  $A_{\text{EM}}$  is 300 which is the gain of the EMCCD.  $T_{\text{Lens}}$  and  $T_{\text{filter}}$  are the transmissions of the collection lens and band-pass filter, with both value 0.96.  $T_{\text{window}}$  is the transmission of the viewport with value 0.99.  $\eta_{\text{collection}}$  is the photon collection efficiency with value 0.001. These parameters were calculated or measured in our previous work in Ref [Tri20]. Based on above

parameters, the number of photons in the ROI is  $9.56 \times 10^6$  per shot. The next step is to calculate the number of molecules [Tri20]

$$N_{\text{molecules}} = \frac{N_{\text{photons}}}{N_{\text{ph/mol}}}. \quad (5.2)$$

$N_{\text{ph/mol}}$  is the number of photons emitted per molecule with value 6. Thus, the calculated number of molecules (in the  $|v = 0, N = 1\rangle$  state) in the ROI is  $1.6 \times 10^6$  per shot. Figure 5.2 shows the results of 1D cooling. (a) is HC and (b) is VC. Profiles next to them are the sums along vertical and horizontal directions. The reason to do 1D cooling is to align the molecular beam with the laser beam. As shown in Fig. 4.8, horizontal (or vertical) cooling laser beams will generate optical molasses (also called optical lattice). The task is to make the molasses formed by HC and VC overlap spatially. There are two reasons to do such an alignment. The first reason is that if they don't overlap, there will be two groups of cold molecules (one generated by HC molasses and the other generated by VC molasses), of which maxima are spatially separated that could result in a less number of ultracold molecules cooled in both transverse axes. The second reason is that even though the two maxima are overlapped at the same centre, our simulation predicts that simultaneous 2D cooling provides larger cooling forces compared to a simple sum of two 1D cooling. For this reason, in order to obtain as many ultracold YbF molecules as possible, the polarisation should be  $XY_{||}$  (similar to the  $\text{lin}||\text{lin}$  case in one-dimensional case) which requires the HC molasses spatially overlap with the VC molasses to form the intensity gradients [Ala+21].



**Fig. 5.2:** Results of 1D cooling (share the same color bar with Fig 5.1). (a) Image of horizontal cooling. (b) Image of vertical cooling.



In terms of experimental operation, the idea is that if the centre of cold molecules of HC overlap with the center of the VC, we say the alignment is done. As shown in Fig. 5.2, if we overlap the center of cold molecules in (a) with that in (b), Fig. 5.1 can be reproduced. Another reason to highlight Fig. 5.2 is that this work is done and will continue on the long machine (with interaction region). But our previous works ([Lim+17; Ala+21]) were done on the short machine (without interaction region). When we integrated the interaction region into the entire machine, the optics alignment in LC region became much more difficult because the molecule signal decreased significantly due to the long distance between the source and detectors. Moreover, a slight misalignment of the laser cooled molecular beam with respect to the axis along the machine can cause more spatial deviation due to the long distance between the source and detectors. Figures 5.1 and 5.2 was the first time we saw cooling effect on the long machine.

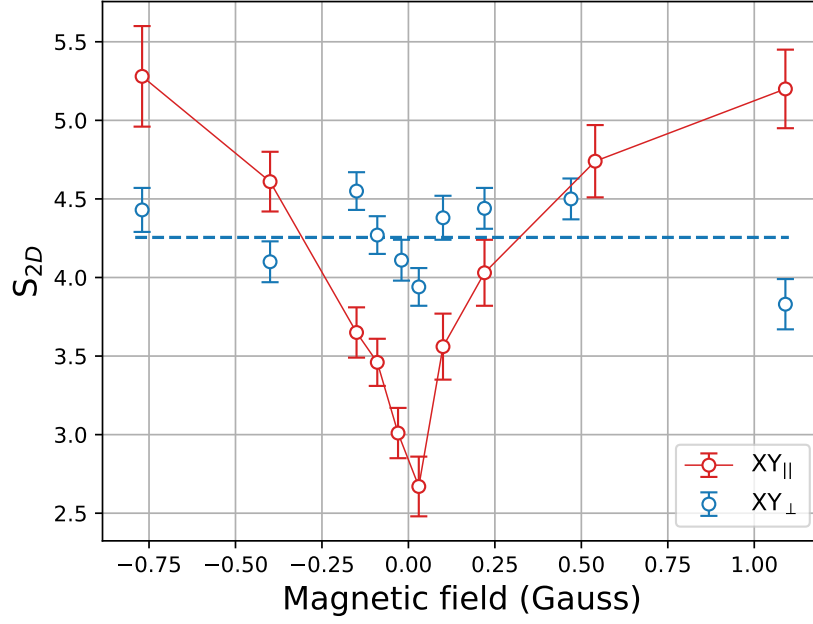
### 5.1.2 Magnetic field and polarization

In this section, we will discuss how magnetic field and laser polarization affect laser cooling. Before discussing the results, we need to define a useful parameter which is  $S_{2D}$ . Figure 5.1 can be fitted with a 2D Gaussian model  $g(x, y) = \frac{A}{2\pi} e^{-(x-x_0)^2/(2\sigma_x^2)} e^{-(y-y_0)^2/(2\sigma_y^2)}$ . Here  $\sigma_{x,y}$  is the Gaussian waist of the fitting profile. Based on the fitting,  $S_{2D}$  is defined as  $A\sigma_x\sigma_y/L^2$ , which is effectively a ratio of number of molecules before and after laser cooling within the area  $L^2$ . Here  $L$  is 5 mm which is the characteristic size of a laser-induced fluorescence detector optimized for high efficiency detection of a molecular beam [Ala+21]. The exact value of  $L$  is not important. It can be seen that  $S_{2D}$  is proportional to the number of molecules, which makes it a useful parameter to study the relations between the effectiveness of 2D cooling and other variables.

In Fig. 5.3, we evaluate  $S_{2D}$  with the magnetic field increasing from -0.77 to 1.09 Gauss. The direction of the magnetic field is 45 degree in the x-y plane. To review the lab frame, please see Fig. 4.1. The red and blue datasets are for  $XY_{\perp}$  and  $XY_{\parallel}$  polarization configurations. The definition of  $XY_{\perp}$  and  $XY_{\parallel}$  polarization configurations are

$$\begin{aligned} XY_{\parallel} : \vec{E} &= E_0 \hat{e}_y e^{ikx} + E_0 \hat{e}_y e^{-ikx} + E_0 \hat{e}_y e^{ikz} + E_0 \hat{e}_y e^{-ikz}, \\ XY_{\perp} : \vec{E} &= E_0 \hat{e}_y e^{ikx} + E_0 \hat{e}_y e^{-ikx} + E_0 \hat{e}_x e^{ikz} + E_0 \hat{e}_x e^{-ikz}. \end{aligned} \quad (5.3)$$

We have mentioned Eq. 5.3 in Chap. 3 when we discussed 2D laser cooling. Coordinate frames used in Chap. 3 and in this chapter are same.



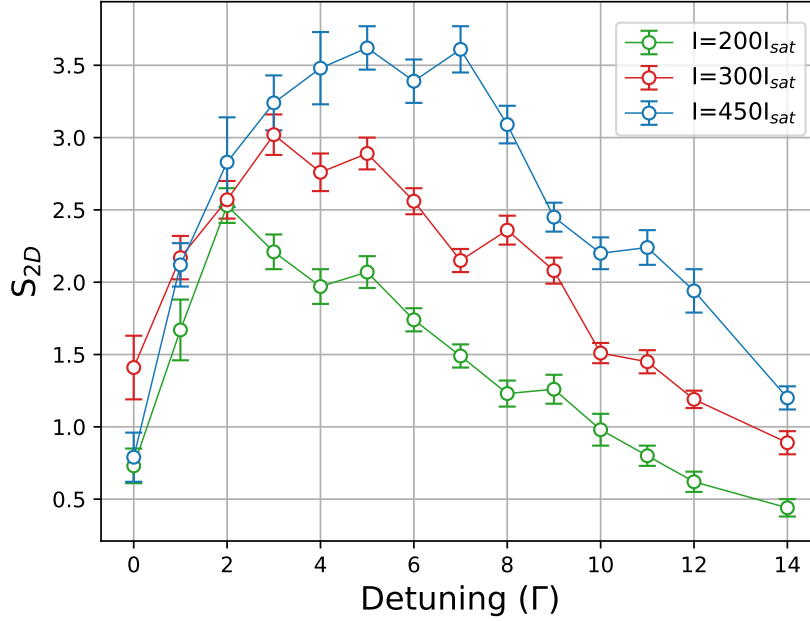
**Fig. 5.3:**  $S_{2D}$  vs. magnetic field with  $6\Gamma$  laser detuning and  $450I_{\text{sat}}$  laser intensity. Blue:  $XY_{\perp}$ , Red:  $XY_{\parallel}$  laser polarization configurations. The blue dashed line is the average value of the blue data points. The red line is a guide to the eyes.

In Fig. 5.3, the red curve ( $XY_{\parallel}$ ) can be regarded as magnetically-assisted intensity gradient cooling (Sec. 3.2).  $S_{2D}$  decreases from 5.3 to about 2.5 when  $B$  ranges from -0.75 to 0 G. Then  $S_{2D}$  increases back to 5.3 again when  $B$  is increased to about 1.00 G. This is because the  $m_F = \pm 2$  sublevels in the  $N=1$  state are dark states with respect to the  $XY_{\parallel}$  polarization when the external magnetic field is zero. However, when we turn on  $B$  field, the  $m_F = \pm 2$  sublevels will mix with other  $m_F$  sublevels to become bright states to continue scattering photons. That is why we observe better laser cooling when the  $B$  field is not zero. Regarding  $XY_{\perp}$  configuration, it is essentially a polarization gradient cooling. The theory of polarization gradient cooling has been discussed in details in Chap. 3. The polarization gradient of the standing wave in space will transfer the molecules out of the dark states. Thus cooling effect shouldn't be affected by  $B$  field. As shown in the blue dataset,  $S_{2D}$  doesn't vary much when  $B$  field is changed. Overall, we observe that both  $XY_{\perp}$  and  $XY_{\parallel}$  configurations can generate cooling effect, although they are based on different mechanisms. In daily experiment, we set polarization configuration to  $XY_{\parallel}$  with  $B$  field around  $\pm 1$  Gauss.

Moreover, the 2D cooling can be further improved by optimizing some parameters such as laser intensity and polarization stability. It is clear that increasing laser intensity will increase capture velocity to capture more molecules. In the multi-

reflection path, laser polarization drifts due to stress-induced birefringence in mirrors. Thus, reducing birefringence is another way to improve laser cooling. It can be achieved by reducing the mechanical stress between the mirror and mirror mount.

### 5.1.3 Laser detuning and laser intensity



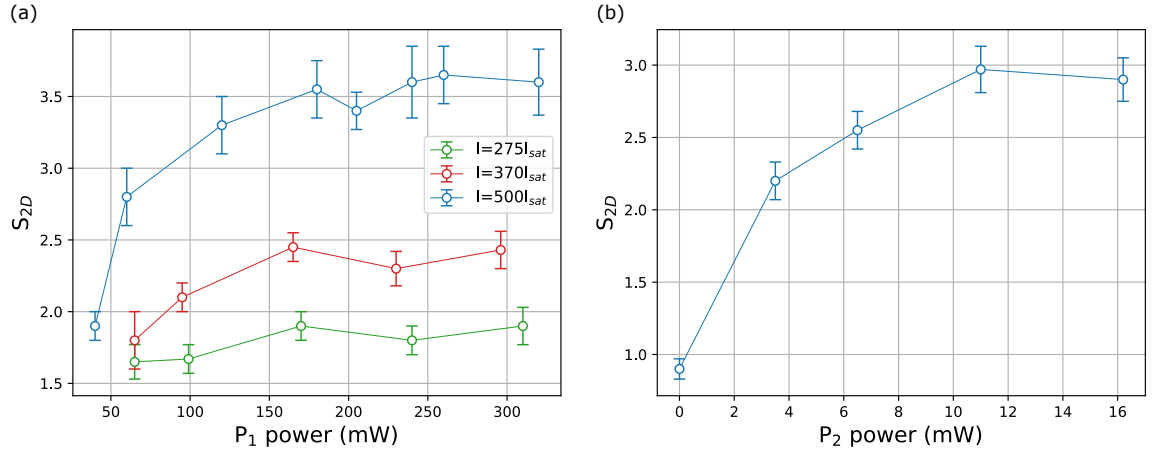
**Fig. 5.4:**  $S_{2D}$  as a function of detuning  $\Gamma$  under three different laser powers with  $B = 0.6$  G and  $XY_{||}$  polarization. Lines are guides to the eyes.

In this section, we discuss how laser detuning and laser intensity affect 2D cooling. The notation of lasers is defined in the following way. In Fig. 4.6, the main cooling laser ( $\nu_0$ ) is  $L_0$  while two repump lasers ( $\nu_1$  and  $\nu_2$ ) are  $L_1$  and  $L_2$ . Correspondingly, their powers are labelled by  $P_0$ ,  $P_1$  and  $P_2$ .

As shown in Fig. 5.4, we plot  $S_{2D}$  vs. detuning with three  $L_0$  laser powers. Here, detuning refers to blue detune of  $L_0$  laser frequency in the unit of  $\Gamma = 2\pi \times 5.7$  MHz. It can be seen that for all three laser powers  $S_{2D}$  increase to a certain value then decrease with detuning increasing. For each  $\Gamma$  value, it is clear that higher laser power cause larger  $S_{2D}$  as we expected. The difference among three curves is that best cooling appears at different detuning for different laser power. The reason is that laser power determines how large the AC Stark shift is. Larger laser power causes larger AC Stark shift, which requires larger frequency detune to obtain best cooling. For instance, in daily experiment, under  $L_0$  laser intensity  $450 I_{sat}$ , we usually set detuning at around  $6\Gamma$ . Moreover, in Fig. 5.4, cooling becomes worse if

we further increase  $\Gamma$  over best peak value. This is because scattering rate becomes much worse if the frequency is detuned too far away from the resonance (see Eq. 3.8). In addition to the lowered scattering rate, AC Stark shift also gets smaller.

After discussing how  $L_0$  power and detuning affect cooling, Fig. 5.5 shows how the power of repump laser influences  $S_{2D}$ . Since  $L_1$  and  $L_2$  are repump laser, we set them on resonance during the measurement. In (a), each curve was measured under a certain  $L_0$  intensity. It can be seen that all of them saturate the transition, indicating the repump laser power is not a limitation to laser cooling. In (b), after fixing  $\Delta = 6\Gamma$  and  $P_{0,1}$  to maximum,  $S_{2D}$  can also saturate the transition when  $P_2$  is over 10 mW. Thus,  $P_2$  is not a limitation to cooling neither.



**Fig. 5.5:** (a)  $S_{2D}$  as a function of  $P_1$  with  $\Delta = 6\Gamma$  for three  $L_0$  laser powers. (b)  $S_{2D}$  as a function of  $P_2$  with  $\Delta = 6\Gamma$ ,  $L_0$  laser intensity  $500 I_{sat}$  and  $P_1$  at maximum. Lines are guides to the eyes.

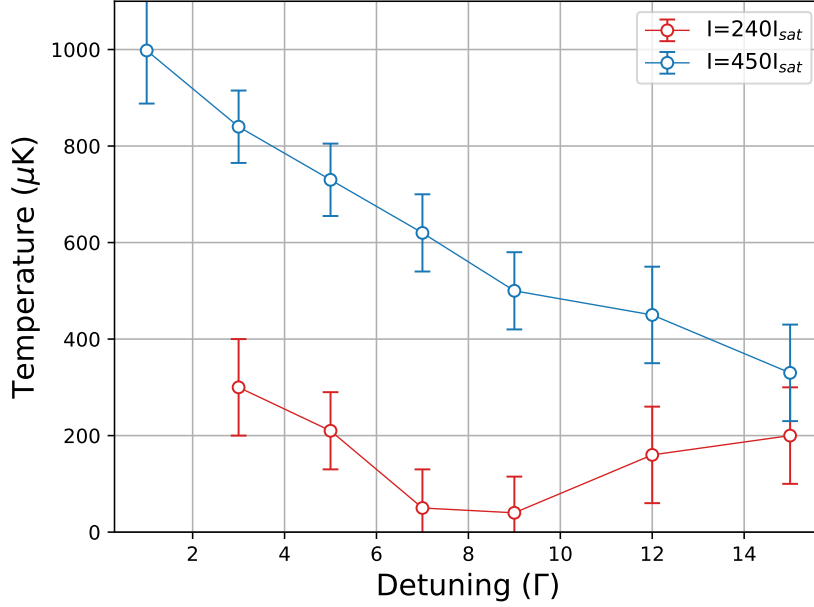
#### 5.1.4 Transverse temperature

To measure the transverse temperature of YbF molecules, we need two CCDs. The first CCD is placed at the end of the machine. The other one is placed at one side of the machine. The temperature  $T$  is calculated in the following way [Ala+21; Lim+17]

$$T = \frac{m}{k_B} v_z^2 \frac{\sigma_2^2 - \sigma_1^2}{z_2^2 - z_1^2}, \quad (5.4)$$

where  $m$  is the mass of YbF molecule,  $v_z$  is set to be 200 m/s which is the averaged forward velocity of the molecular beam.  $z_{1,2}$  is the distance between the camera and the end of LC region.  $\sigma_{1(2)}$  is the Gaussian waist of the fitting obtained by CCD1(2) which we have mentioned at the beginning of Sec. 5.1.2. CCD2 can determine the

Gaussian distribution in both  $x$  and  $z$  directions. However, CCD1 can only measure distribution across  $x$  axis because it is placed at one side of the machine. We make the assumption that temperature is same in both transverse directions because we observe that the width of distribution at CCD2 is nearly same in  $x$  and  $z$  directions (see Fig. 5.1). The explanation of Eq. 5.4 is in Sec. 7.2.

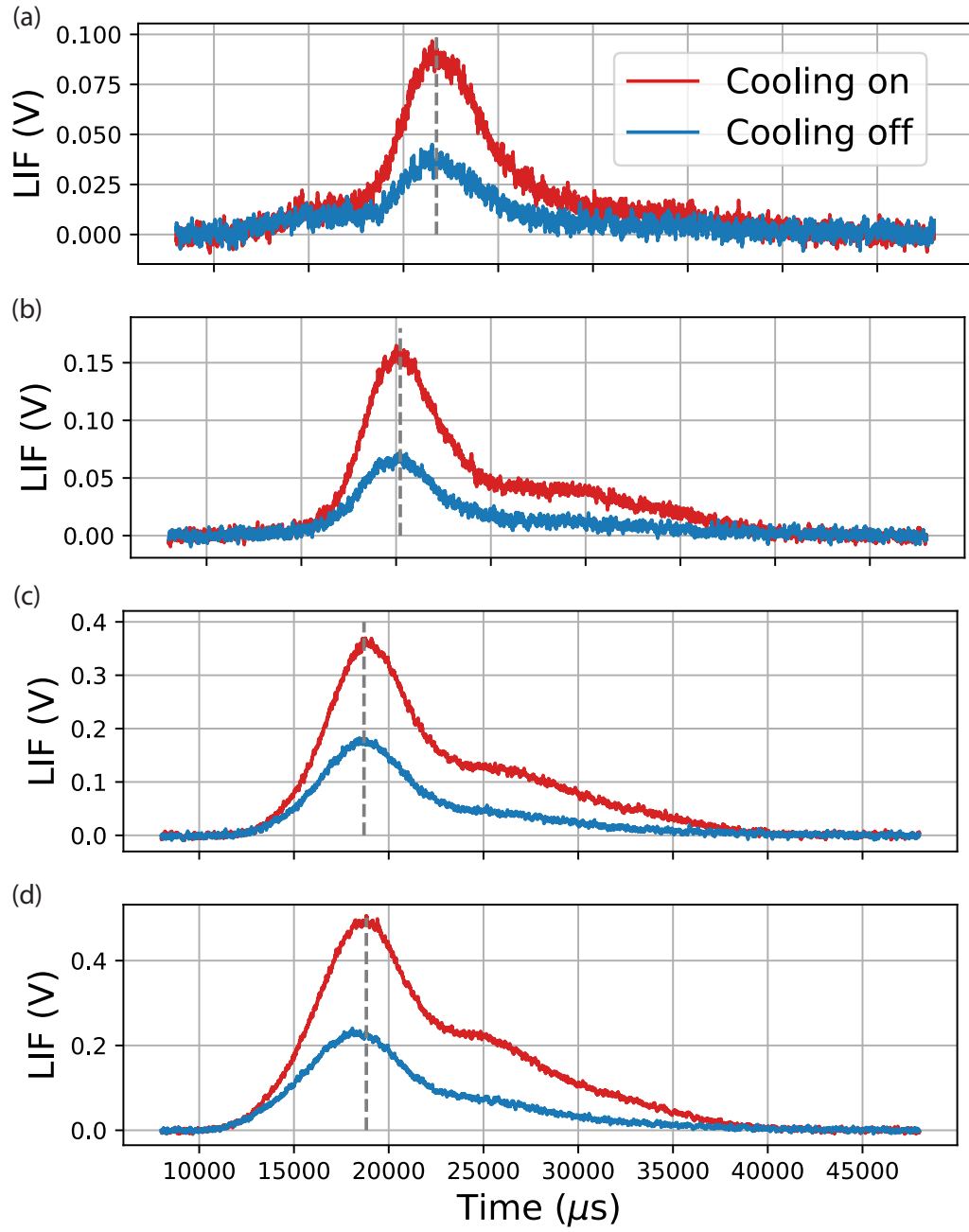


**Fig. 5.6:** Temperature (2D laser cooling) as a function of detuning with  $L_0$  intensity 240 and  $450 I_{sat}$ , and B field 0.5 Gauss. Lines are guides to the eyes.

In Fig. 5.6, we plot temperature with respect to the detuning of  $L_0$  laser when intensity is set to be 240 and  $450 I_{sat}$ . As discussed in Sec. 3.2, the Doppler cooling limit of YbF molecule is  $137 \mu K$ . Under laser intensity  $240 I_{sat}$ , we obtain sub-Doppler cooling in which  $T$  is less than  $100 \mu K$  when detuning ranges from 6 to  $9 \Gamma$  (red curve). Under  $450 I_{sat}$  the temperature drops from about 1000 to  $350 \mu K$  when detuning increases from 1 to  $15 \Gamma$ , suggesting that temperature increases with laser intensity and the desired detuning required to reduce temperature is higher at higher laser intensity.

### 5.1.5 EDM sensitivity of cold molecular beams

In this section, we discuss the shot EDM sensitivity per shot with the ultracold YbF molecular beams. The main reason to do laser cooling is to collimate the molecular beams to increase number of molecules because the statistical EDM sensitivity depends on the number of molecules being detected (see Eq. 1.14) [Hud+11;

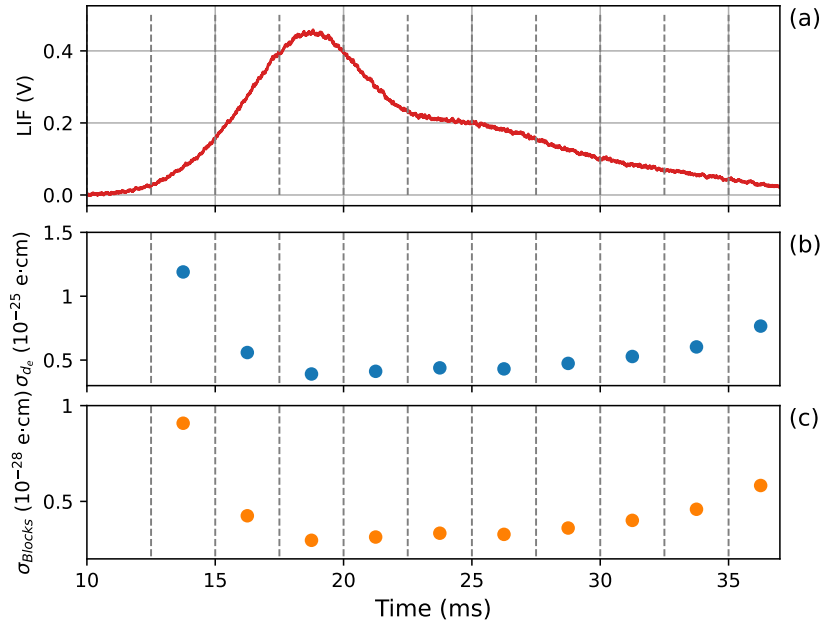


**Fig. 5.7:** Time of flights under different YAG power. Images (a), (b), (c), (d) correspond to YAG powers 70%, 80%, 90% and 100%, respectively. Red (blue) lines are measured when laser cooling is on (off).

[Ho20]. Because the length of the machine is rather long (more than 5 meters), molecular beams will diverge significantly if there is no transverse laser cooling.

The reason to do the measurement in Fig. 5.7 is that we thought by reducing YAG power the initial velocity of YbF molecules can become smaller. The capture velocity of the LC molasses is determined by the laser system and B-field. If we can increase the number of molecules whose velocity is below the capture velocity by adjusting the YAG power, we can increase molecules being detected downstream.

Figure 5.7 is the result of 2d cooling measured by PMTs. Four subfigures correspond to TOFs with YAG powers 70%, 80%, 90%, and 100%, for (a) to (d), respectively. Red and blue lines are cooled and uncooled molecules. It is clear that when YAG power increases, molecules speed increases as the gray dashed lines move to earlier time. Gray dashed lines indicate the peak of TOF. We expect to see when YAG power decreases, the ratio of number of cooled over uncooled molecules increases since slow molecules are more easier to be captured. However, we didn't see a significant effect when decreasing YAG power. In (d), we observe that the integral of the cold TOF (red) is nearly three times larger than the hot TOF (blue).



**Fig. 5.8:** (a) The cold TOF from Fig .5.7 part (d). (b) Shot eEDM sensitivity of the TOF. (c) The eEDM sensitivity by a 10-day block with 2 shots per second. The eEDM sensitivity in both (b) and (c) are extracted from (a).

In Fig .5.8, we take the cold TOF (red) from Fig .5.7 (d) and slice it into 10 equal shares with respect to time as shown in (a). Each time interval is 2.5 ms. In (b), it can be seen that the overall eEDM sensitivity is about  $10^{-25} e \cdot cm$  per shot. The best

eEDM sensitivity is at about 20 ms. If we run the source at 2 Hz (2 shots per second) for 10 days, we can further scale down the  $\sigma_{de}$  to  $4 \times 10^{-29} \text{ e} \cdot \text{cm}$  as shown in (c). Such a long-term measurement is called blocks and  $\sigma_{de}$  in (c) is called block eEDM sensitivity. The shot eEDM sensitivity measured in this experiment is two orders smaller than our last generation eEDM machine. Here the definition of the block eEDM sensitivity is the standard deviation of the Gaussian distribution of measured eEDM values. The relation between a single shot eEDM sensitivity and a block eEDM sensitivity is

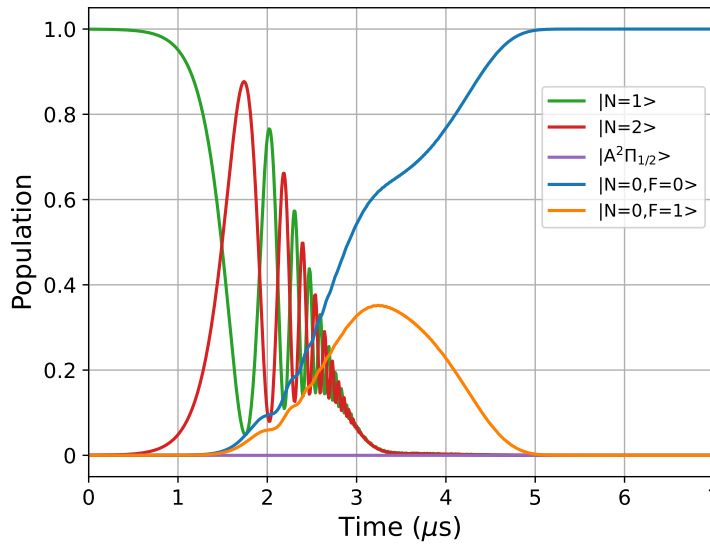
$$\sigma_{de(\text{block})} = \frac{\sigma_{de(\text{shot})}}{\sqrt{N_{\text{shot}}}}, \quad (5.5)$$

where  $N_{\text{shot}}$  is the number of shots in the block. Recall [Sec. 1.3](#), we have introduced how to extract one eEDM value from one block. In [Sec. 6.2](#), we will show a distribution of measured eEDM values from our last generation eEDM machine. Since the ultracold YbF eEDM machine hasn't been completed to do EDM experiments, we won't discuss the details further.



## 5.2 Optical pumping region

The optical pumping scheme is required to transfer the entire transversely cooled population from  $|N = 1\rangle$  to  $|N = 0, F = 0\rangle$ , as efficiently as possible. Therefore this section will focus on optimising the optical pumping process. The transition scheme of OP has been discussed in Ch. 4.4. Based on the scheme, we used the **optical Bloch equation (OBE)** to calculate the state evolution using our experimental parameters. The motivation to do the calculation is to know for a given laser intensity and interaction time whether the population transfer can be completed. Based on the laser power and beam profiles of the lasers, Rabi frequencies for P12 and Q0 are set at 10 MHz and 1 MHz, respectively. The Rabi frequency of the microwave is set to 1 MHz which was used in our previous work [Dev15]. The decay rate  $\Gamma$  from  $|A^2\Pi_{1/2}\rangle$  to all the rotational levels in the ground state is  $2\pi \times 5.7$  MHz. As can be seen in Fig. 5.9, when the populations of  $N = 1$  and  $N = 2$  start to drop, populations of  $|F = 0\rangle$  and  $|F = 1\rangle$  begin to increase. Eventually, all the population will be transferred to  $|F = 0\rangle$  state within  $5 \mu\text{s}$ .

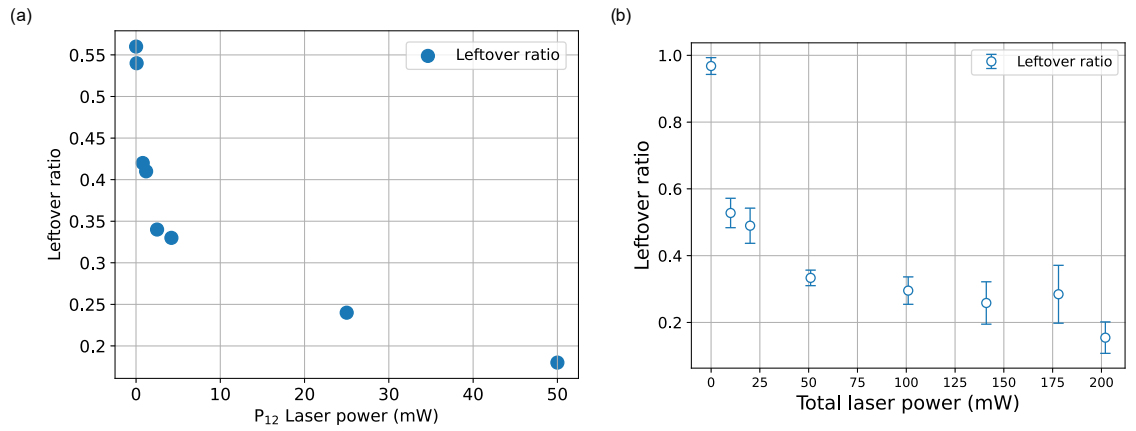


**Fig. 5.9:** OBE calculation for OP scheme based on the theory discussed in Sec. 3.1.2.

### 5.2.1 Laser Intensity

Based on the insight provided by Fig. 5.9, the first parameter we are going to discuss is the laser intensity. Recall Fig. 4.11, in order to empty  $N = 1$  population, we need to turn on at least microwaves and P12 laser. As shown in Fig. 5.10 (a),  $N = 1$  leftover decreases from 0.55 to 0.18 when P12 laser power increases from 0.1 to 50

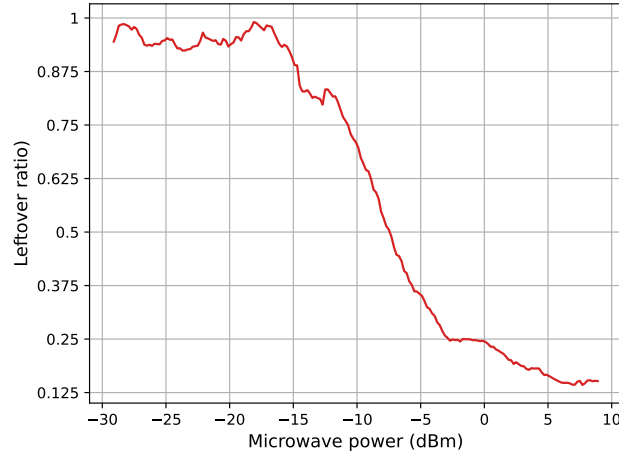
mW. In this measurement, microwave power is set at 7 dBm. From (a), we can draw the conclusion that given such laser and microwave power,  $N = 1$  population can be removed by approximately 85%. In (b), we add Q0 laser to the system. We plot the  $N = 1$  population leftover with respect to the percentage of total laser power. In reality, we simply place a variable ND filter in front of the fiber dock to adjust P12 and Q0 powers simultaneously. At maximum laser power, we can remove 85%  $N = 1$  population. The reason to do the measurement in (b) is to check whether adding Q0 will influence the leftover in  $N = 1$  state. In daily experiment, we set P12 laser power to full power (about 200 mW, see Tab. 4.2). However, Q0 laser we set it at about 6 mW which is far below maximum power. The reason is that we want to avoid power broadening effect since the frequency difference between  $F = 0$  and 1 states is only 170 MHz. Details will be discussed in Sec. 5.2.4.



**Fig. 5.10:** (a) Leftover ratio in  $N = 1$  state vs P12 laser power. (b) Leftover ratio in  $N = 1$  state vs total laser power (P12 + Q0).

## 5.2.2 Microwave power

In this section we study how microwave power affects optical pumping. We still measure the population in the  $N = 1$  state. Here, we set both Q0 and P12 lasers to maximum power. In Fig. 5.11, we plot the fluorescence of  $N=1$  molecules as a function of microwave power. It can be seen that from -30 to -15 dBm, the microwave power is not enough to drive the transition. Population in  $N=1$  decreases linearly when microwave power ranges from -15 to 5 dBm. The leftover of  $N = 1$  population plateaus at about 7dBm. In daily experiment, we set microwave power to be 7 dBm.



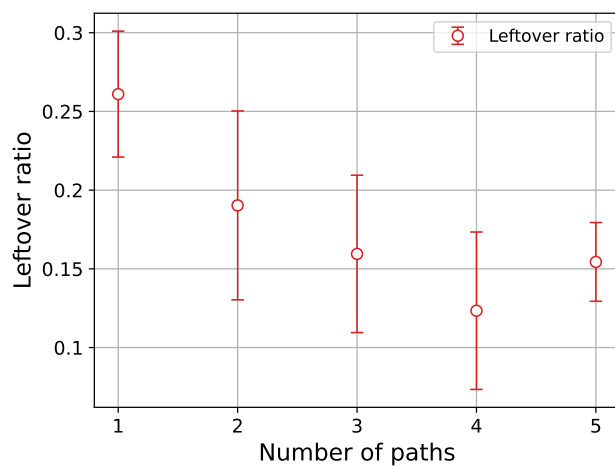
**Fig. 5.11:**  $N = 1$  population as a function of microwave power.

### 5.2.3 Interaction time

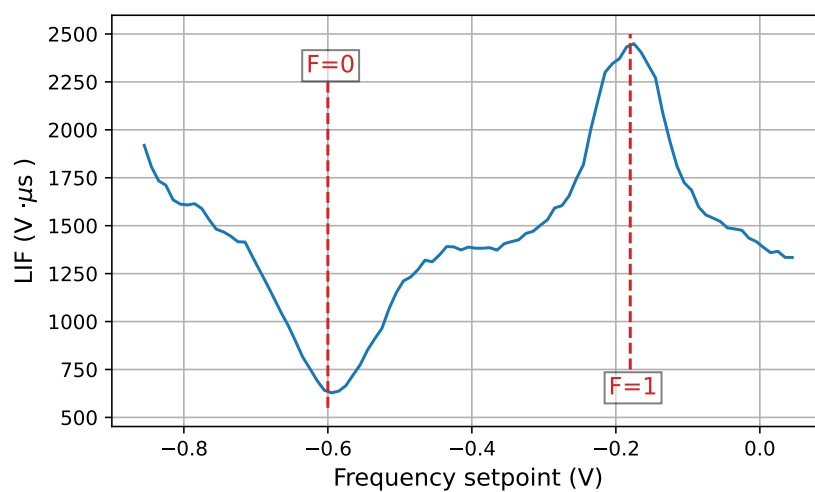
It is previously shown in Fig. 5.9 that population transfer from  $N = 1$  to  $N = 0$ ,  $F = 0$  will occur within  $5 \mu\text{s}$  for calculated Rabi frequencies of P12 and Q0 light. Within this section we will experimentally test whether optical pumping is interaction time limited due to the movement of molecules through the laser beams. As mentioned in Ch. 4.4, OP laser will reflect five times to form five paths between a pair of square mirrors. Thus, in Fig. 5.12, we change the number of paths of the OP laser. Here we can simply block part of the reflection to reduce number of paths. For a beam waist of 1.2 mm, the interaction time is calculated to be  $4 \mu\text{s}$  for YbF molecules with a speed of 300 m/s. We choose 300 m/s to account for the fastest part of our molecule distribution. Thus, five paths will have an interaction time of  $20 \mu\text{s}$ . As can be seen in Fig. 5.12, when integrating over the entire molecule distribution, one or two paths doesn't provide enough interaction time. Three to five paths can deplete about 85% population of  $N = 1$  state.

### 5.2.4 Power broadening

Recall the transition scheme in Fig. 4.11, the frequency gap between  $F = 0$  and  $F = 1$  states is 170 MHz. What we're concerned is that large Q0 power may cause a power broadening effect which is not desired in terms of population transfer. In this section, we only focus on Q0 power, and fix optical pumping microwave power to 7 dBm and P12 laser power to 150 mW.



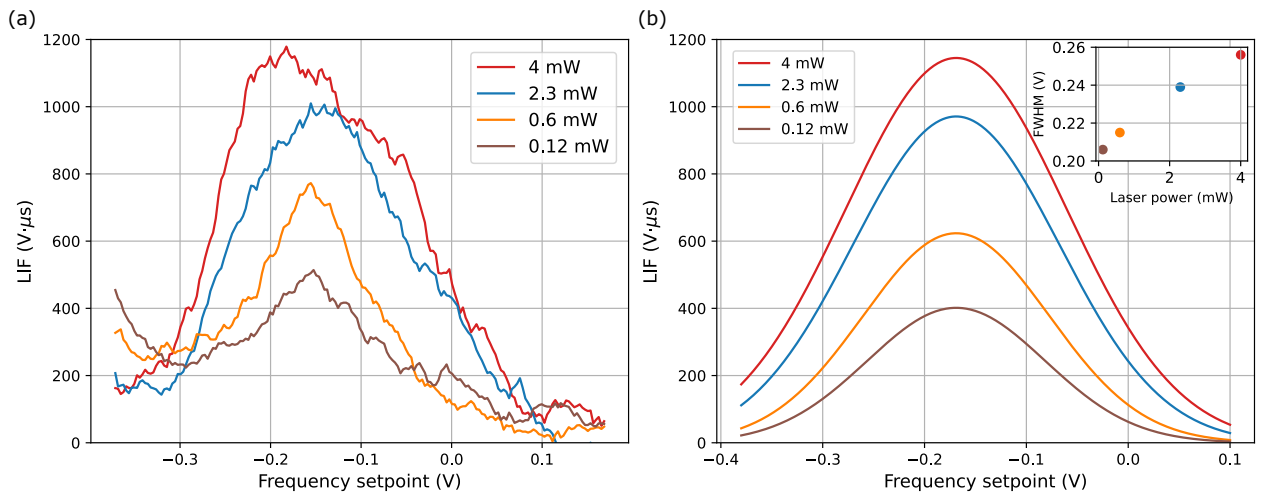
**Fig. 5.12:** Leftover ratio in  $N=1$  state vs. number of paths.



**Fig. 5.13:** Scan Q0 frequency in the OP region. Detect  $F=0$  population downstream.

After depleting the population in  $N = 1$  state, the next step is to prepare population in  $|n = 0, F = 0\rangle$  state. In order to prepare all the molecules to  $F = 0$  state, we need to set Q0 laser at  $F = 1$  frequency. As shown in Fig. 5.13, along the  $x$  axis, we scan the frequency setpoint (essentially laser frequency) across the Q0 transitions. Here, setpoint is the voltage relative to the reference laser's piezo voltage. It will be amplified and then sent to the Q0 laser's piezo. In our lab, scanning laser frequency is usually done by scanning laser's piezo voltage (setpoint). We detect  $F = 0$  population downstream. Thus, we should see a depletion of the LIF when Q0 laser is at  $F = 0$  frequency and an enhancement at  $F = 1$  frequency. The frequencies of  $F = 0$  and 1 states are highlighted by dashed lines in Fig. 5.13. The measurement in this figure is a routine experiment in our lab. Because once we obtain the frequencies for both  $F = 0$  and 1 states, we can prepare molecules in either of them. For instance, if we want to measure the detection efficiency in the  $F = 1$  state (Sec. 5.4), we need to lock the Q0 laser at  $F = 0$  frequency to prepare molecules in the  $F = 1$  state. Also, in the STIRAP region (Sec. 5.3.1), we have capability to manipulate the state from either  $F = 0$  or 1 state.

To study how power broadening affects the Q0 transition, we set Q0 frequency on  $F=1$  resonance. In Fig. 5.14 (a), when Q0 power increases from 0.12 to 4 mW, we can see that the LIF signal becomes larger and wider. Being larger is because higher laser power transfers the population from  $F=1$  to 0 more efficiently. Being wider is due to the power broadening effect. For each power in (a), we use one Gaussian function  $a^{-(x-b)^2/2c^2}$  to fit a profile (Fig. 5.14 (b)). The FWHM of a Gaussian function is  $2\sqrt{2\ln 2}c \approx 2.35c$ . We plot the FWHM of each power in the inset plot of (b). It is clear that FWHM increases with laser power increasing.



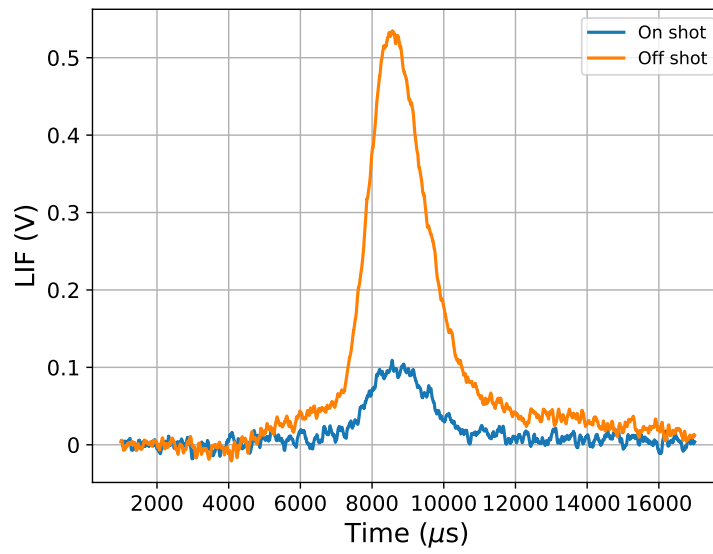
**Fig. 5.14:**  $F=0$  signal as a function of frequency. (a) Raw data. (b) Fitted with Gaussian functions (FWHM in the inset plot).

### 5.2.5 Optical pumping efficiency

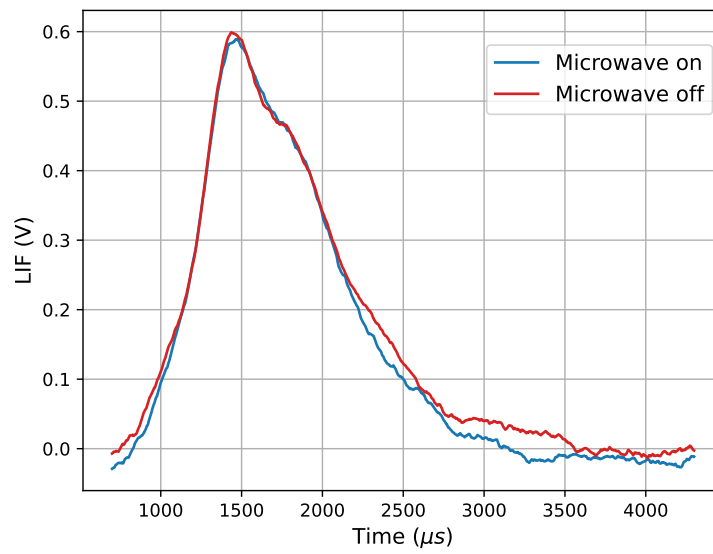
Figure 5.15 is measured with P12 laser 200 mW, Q0 laser 6 mW, and microwave power 7 dBm. The maximum output power for P12 and Q0 laser is in Tab. 4.2 in Chap. 4. In Figure 5.15, we observe the effect of optical pumping on the molecule distribution by switching OP lasers and microwave on and off. When OP is on, the  $N = 1$  population is significantly reduced. The area under the blue curve is about 15% of the orange curve.

To fully test the optical pumping, the final measurement we need to do is to check whether the  $F=1$  state is emptied. The method to check it is by switching microwave on and off and measure the population in the  $F = 1$  state in the detection region. Recall the detection scheme in Fig. 4.20, when the detection microwave is off, we detect  $N = 1$  leftover population. When the detection microwave is on and set to the  $|N=0, F=1\rangle \rightarrow |N = 1\rangle$  frequency, we detect  $N = 1$  leftover population plus  $F = 1$  population. In Fig. 5.16, we can see that the ratio of the on and off shots of the  $F = 1$  population is 96%. This indicates that at 6 mW Q0 power,  $F = 1$  population has been emptied.

In order to further improve the OP efficiency, we can improve the microwave system. As previously mentioned, five microwave frequencies are required to connect all of the hyperfine states of  $N = 1$  to  $N = 2$ . Most of the transitions can be generated by a single MW frequency synth mixed with an RF frequency of 16 MHz to generate the necessary sidebands. The generated sideband structure is then passed through an amplifier. We are currently missing one microwave frequency from the experiment setup to connect  $|N = 1, F = 2\rangle \rightarrow |N = 2, F = 3\rangle$ . This transition cannot be reached with the sideband structure mentioned, and therefore a second microwave synth is required for this. Although the MW synth exists (2 channel Windfreak pro) the microwave amplifier for this transition is missing from the experiment as it is being repaired. This missing transition ( $|N = 1, F = 2\rangle \rightarrow |N = 2, F = 3\rangle$ ) is calculated to contribute approximately 5% leftover based on OBEs calculation. Overall, we expect the OP efficiency to be about 90% in this machine. Although the current setup is 5% lower than the expectation, it is ready for experiments in the interaction region. In the last generation of the YbF EDM machine, the OP efficiency is about 80% to 85% [Ho20].



**Fig. 5.15:** TOFs when OP is turned on or off.



**Fig. 5.16:** F1 population after optical pumping. The  $y$  axis has no correlation with Fig. 5.15 since they were measured at different days. The source fluctuation can influence the signal significantly.

## 5.3 Interaction region

### 5.3.1 STIRAP

When I was writing the thesis, we were still setting up the STIRAP system. Here, I will discuss some problems we encountered and how we solved them.

The logic to test STIRAP is called four-shot pattern. Let's use Fig. 5.17 (b) as an example. The first shot is in top left. It measures the  $F = 0$  population when STIRAP laser shutter is opened. In top right, it is the second shot which measures  $F = 0$  population when STIRAP shutter is closed. The third and forth shots are in the bottom left and right. They measure  $F = 1$  population when STIRAP shutter is on and off respectively. Such four shots form a cycle, then repeat the cycle for about 100 times to obtain the averaged signal. Another reason to implement such a method is to minimise the source fluctuation. Laser driving transitions between  $F = 0$  (1) state to the excited state is labelled by F0 (1).

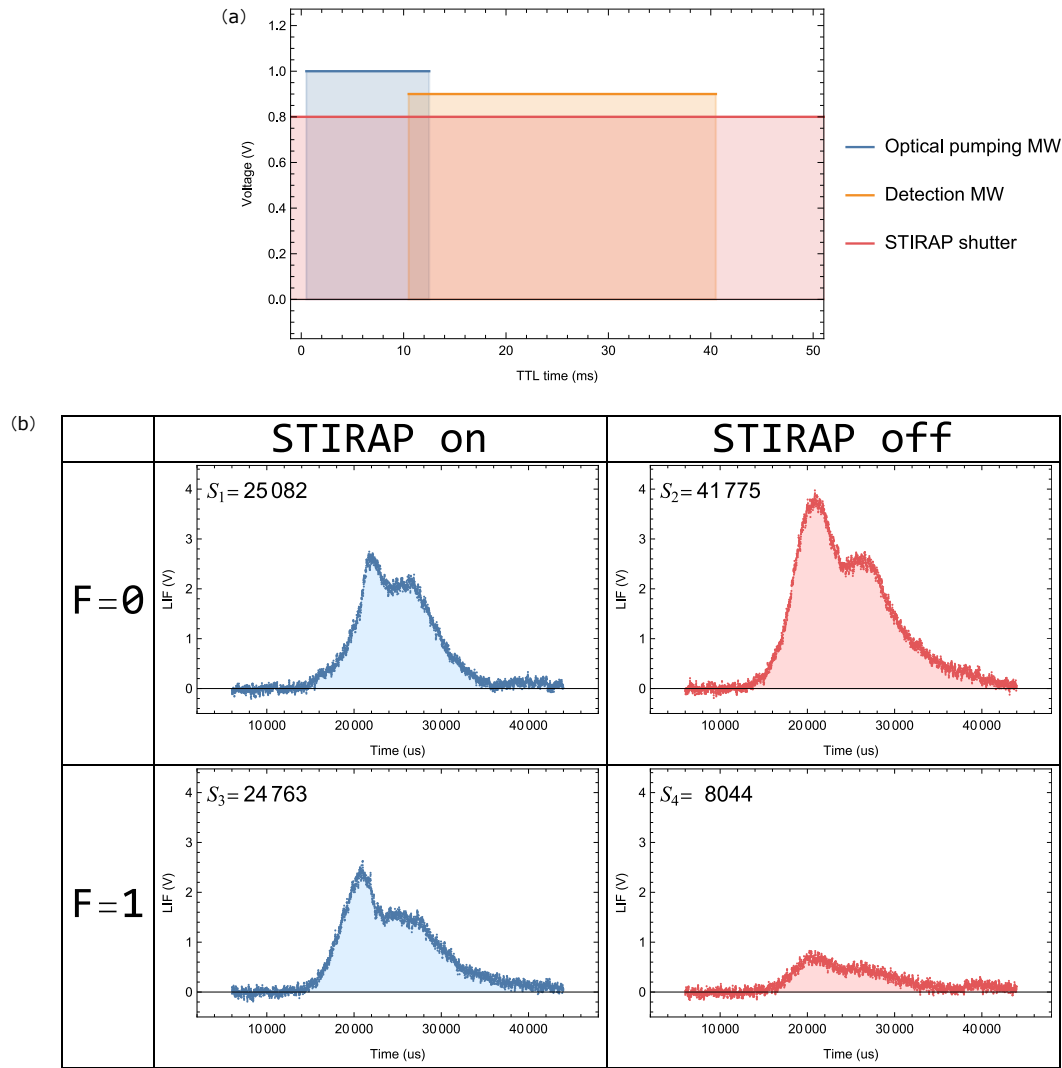
The first four-shot pattern measurement we did was Fig. 5.17 using only one laser beam. Precisely speaking, we use one of the STIRAP beams to test optical pumping. Recall the theory of STIRAP in Fig. 3.17 in Chap. 3, STIRAP beams contain two beams (pump and Stokes). The aim of the experiment is to test how much power is required in F0 laser to pump out  $F = 0$  population. In the OP region, all the molecules are prepared in the  $F = 0$  state. Figure 5.17 (a) is the TTL pattern of the experiment. It can be seen that from 10 to 11.5 ms, both optical pumping and detection microwaves exist in the entire machine. We regard such a coexistence of optical pumping and detection microwaves as the microwave crosstalk problem. The reason both microwaves exist in the machine at the same time is because when fast molecules enter the detection region slow molecules are still in the optical pumping region.

In Fig. 5.17 (b), the first-shot TOF is not flat because the microwave leakage from the detection region causes the  $F = 0$  population not depleted. It is complicated to explain why the microwave crosstalk causes such a no depletion problem. The conclusion of Fig. 5.17 is that we have to pulse microwaves in order to make sure microwaves in optical pumping and detection regions are separated in time. Therefore, we upgraded the software to implement the microwave pulse function. As shown in Fig. 5.18 (a), there is a time gap at 12 ms between the OP and detection microwaves. Looking at the first-shot TOF again, it is clear that  $F = 0$  population is attenuated significantly.

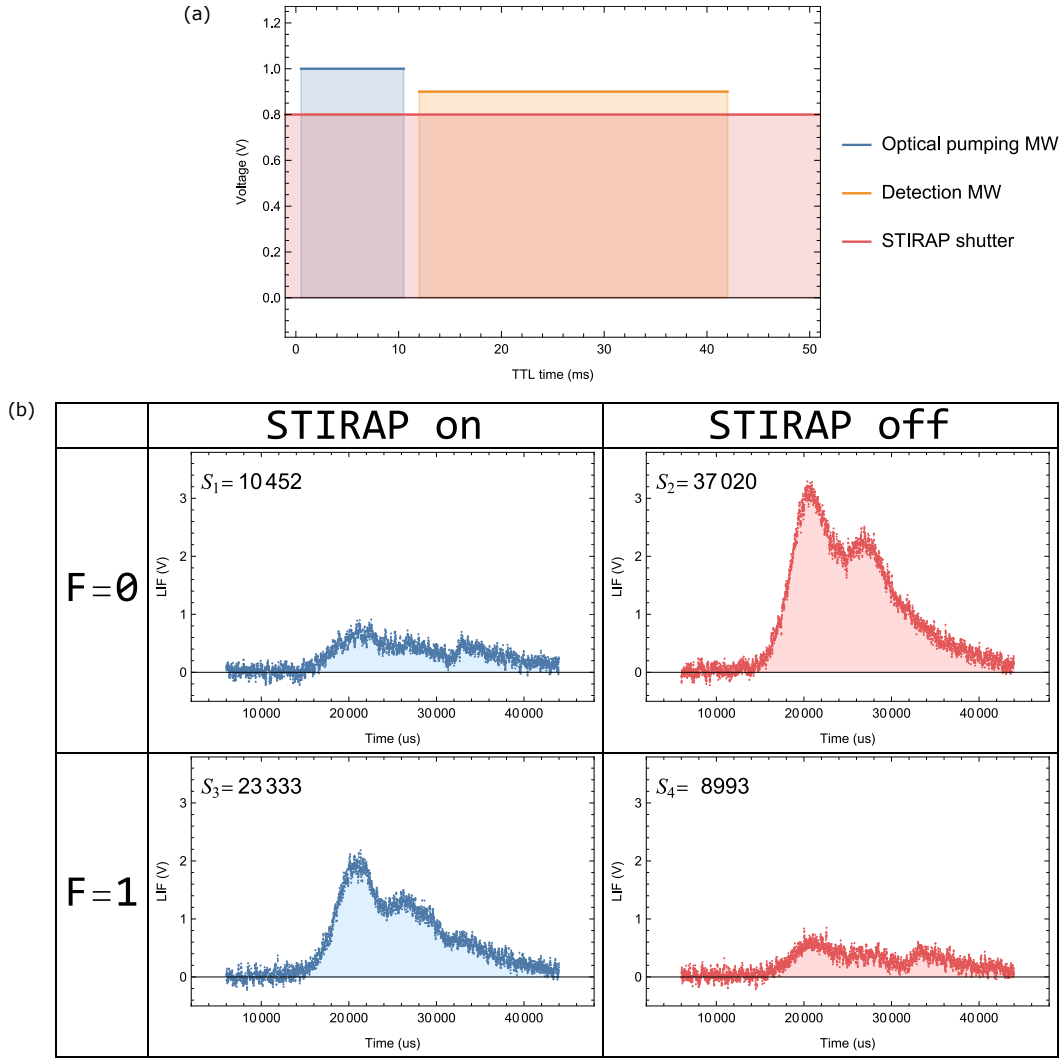


The next step is to determine how much power is needed to empty  $F = 0$  population. There are two reasons to do this measurement. The first reason is to check whether we are power limited or interaction time limited. It may tell that we need to reshape the laser beam. Based on the theory in [Sec. 3.3.2](#), it is better to make the beam wider. Firstly it will be easier to align the two STIRAP laser beams to overlap spatially. Secondly the mixing angle will change smoothly, making the adiabatic condition to be satisfied more easily. We define the photon counts in four shots as  $S_{i=1,2,3,4}$  which are also shown on the top-left corner in each TOF in [Figs. 5.17 and 5.18](#). We define the  $F = 0$  state leftover as  $(S_1 - S_4)/(S_2 - S_4)$  and the  $F = 1$  state transfer efficiency as  $(S_3 - S_4)/(S_2 - S_4)$ . As can be seen in the above expressions, each term needs to minus  $S_4$ , because  $S_4$  is the residue population in the  $N = 1$  state. Recall the detection scheme in [Fig. 4.20](#), we can not avoid measuring the residue population in the  $N = 1$  state.  $S_1 - S_4$  and  $S_2 - S_4$  are the net populations in the  $F = 0$  state when STIRAP is on and off, respectively.  $S_3 - S_4$  is the net population in the  $F = 1$  state when STIRAP is on.

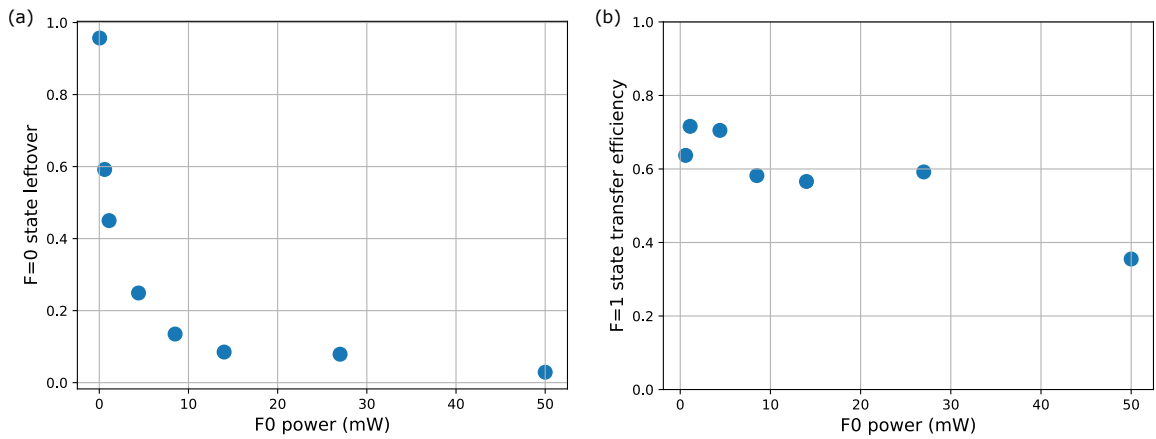
In [Fig. 5.19](#), we measure  $F = 0$  leftover and  $F = 1$  transfer efficiency as a function of F0 laser power. In (a),  $F = 0$  leftover drops exponentially to 3% when F=0 power increases from 40  $\mu$ W to 50 mW. In (b), the  $F = 1$  transfer efficiency is about 60%. The other 40% population can decay to  $N = 2$  and other vibrational states. The conclusion we draw from [Fig. 5.19](#) is that if we use one of the STIRAP beams to do optical pumping, it works as we expected. It sets up the foundation to further study STIRAP.



**Fig. 5.17:** (a) TTL configuration. (b) Results of four-shot pattern experiment with above TTL.



**Fig. 5.18:** (a) TTL configuration. (b) Results of four-shot pattern experiment with above TTL.



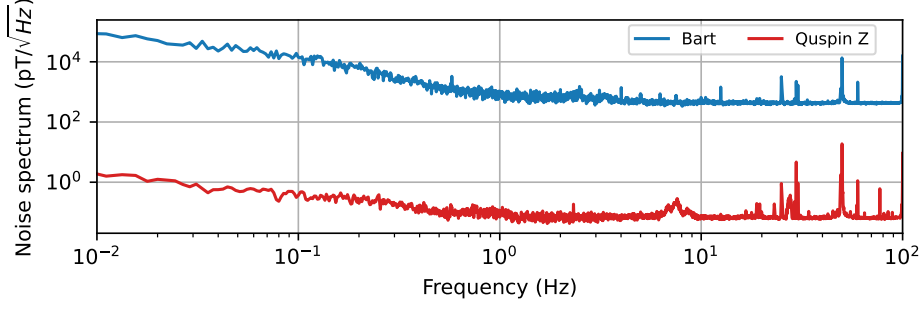
**Fig. 5.19:** (a)  $F=0$  state population leftover as a function of  $F0$  power. (b)  $F=1$  state transfer efficiency as a function of  $F0$  power.

### 5.3.2 Magnetic field noise

Except for the STIRAP laser system, another important component in the interaction region is the magnetic shield. The magnetic shield is not the focus of my PhD. This section will show the preliminary results of the magnetic shield.

In this section we discuss the magnetic field noise. The reason to study this topic is because magnetic field noise can introduce a false EDM value. Here we only consider the z-component of the B field because we only apply  $B_z$  during the spin precession. The dynamic phase introduced by the B field is  $\phi_B = \mu_B B_z \tau / \hbar$ . Here we can write  $B_z = B_{\text{apply}} + B_{\text{noise}} + B_{\text{background}}$ . The measured DC shielding factor (SF) along  $z$  axis is around  $10^5$ . The measured ambient B field in the lab is about 0.2 Gauss ( $20 \mu\text{T}$ ). Thus,  $B_{\text{background}}$  is around 200 pT. The predicted SF of  $10^6$  is not obtained in the  $z$  direction due to flux leakage at the internal bands that connect each half of the mu-metal shields. The COMSOL simulations predict that adding mumetal strips that span across these gaps will bring the shielding factor up to  $10^6$  which will allow us to reach a background field of 20 pT.

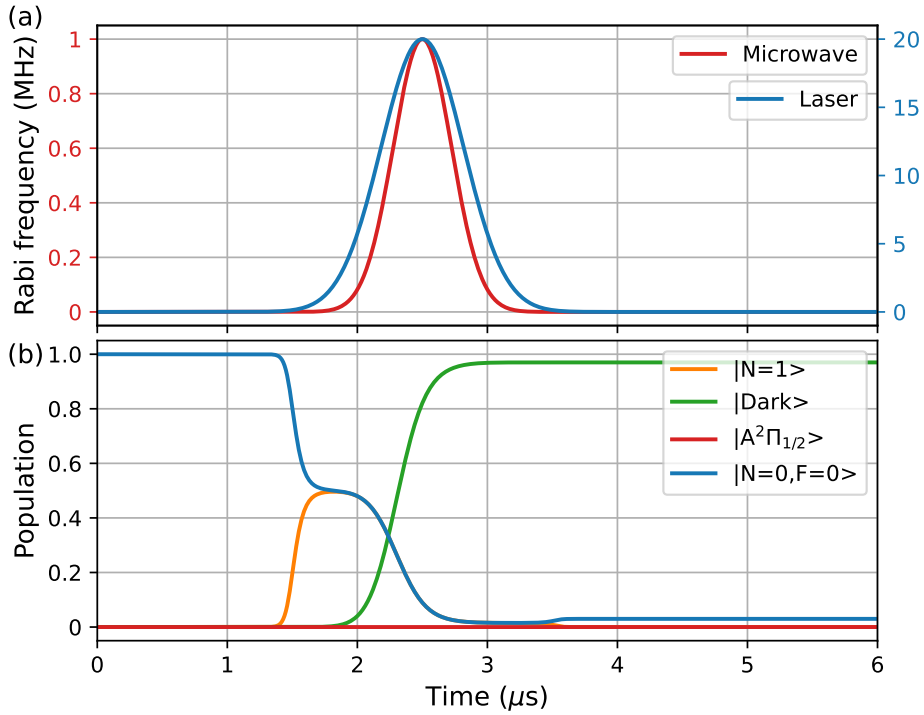
Figure 5.20 shows the measurement of  $B_{\text{noise}}$ . The  $B_{\text{noise}}$  refers to the magnetic noise coming from both inside and outside of the magnetic shield. The reason  $y$  axis has the unit  $\text{pT}/\sqrt{\text{Hz}}$  is that the signal will contain imaginary part after processed by Fourier transform. We need to square the result in order to remove the imaginary part. Then further taking the square root results in the unit to be  $\text{pT}/\sqrt{\text{Hz}}$ . The blue curve is measured by a Bartington (a fluxgate magnetometers) which is placed in the centre of the interaction region with the magnetic shield installed and measures in all three axes. The red curve is taken by a Quspin (zero-field magnetometer [HT73; htt22b]) which is placed in the shield also at center of the interaction region. In Fig. 5.20, it can be seen that the magnetic noise ranges from 1 pT to 10 pT over the frequency range of 0.1 Hz to 0.01 Hz. This frequency range relates to the time over which we take blocks and corresponds to an uncertainty of  $2.5 \times 10^{-29} e \cdot \text{cm}$  per day. This EDM sensitivity can be regarded as a systematic error, it is required to be at least 10 times smaller than statistical sensitivity which is about  $10^{-29} e \cdot \text{cm}$  as mentioned in Sec. 5.1.5. We can better quantify such a systematic EDM sensitivity by using a magnetometer array. Also improving the SF will also help because it can further reduce the external noise. The Quspin measures noise within the shield which can be a combination of external noise coupled into the shield and internal noise. The internal noise can be due to Johnson noise which is attributed to the thermal movement of charge carriers in conductors [Whi+03].



**Fig. 5.20:** Magnetic field noise as a function of frequency.

## 5.4 Detection region

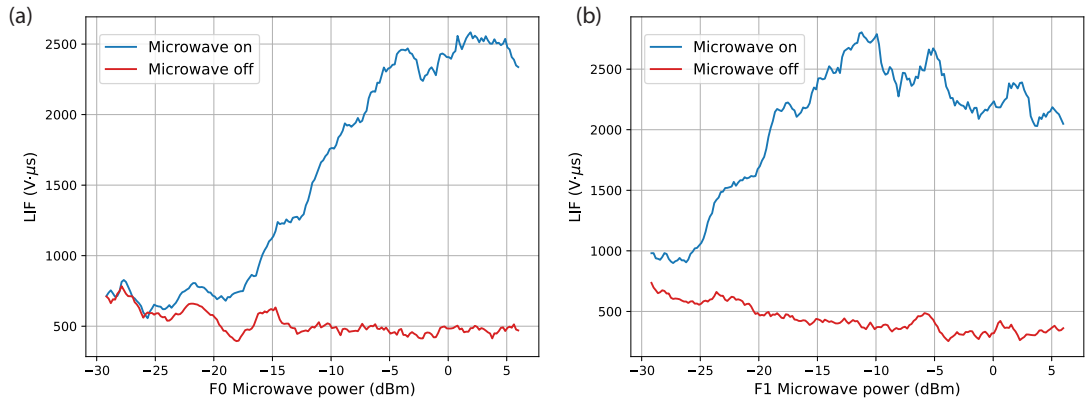
Based on the transition scheme for the detection region in Ch. 4.6, we calculate the state evolution using optical Bloch equations. The peak Rabi frequencies for the P1 transition and microwave are 20 MHz and 1 MHz in Fig. 5.21 (a). The decay rate  $\Gamma$  is  $2\pi \times 5.7$  MHz. As shown in Fig. 5.21 (b), the system starts at  $|F=0\rangle$  state and will be pumped into dark states within  $5 \mu\text{s}$  based on the above parameters.



**Fig. 5.21:** OBEs calculation for the detection scheme. (a) Beam profiles for microwave and lasers in time. (b) Population terms of the OBEs. (a) and (b) share the same  $x$  axis.

### 5.4.1 Microwave power

In this section we study microwave power in the detection region. Review Fig. 4.20, the microwave transitions we are interested in for detection are  $|N = 0, F = 0\rangle \rightarrow |N = 1, F = 1\rangle$  and  $|N = 0, F = 1\rangle \rightarrow |N = 1, F = 2\rangle$ . The P1 laser power is set to be 20 mW. Given interaction time and beam profile, the saturation power of P1 laser in the detection region is about 10 mW for molecules with speed less than 400 m/s. It also has polarisation modulation and counter propagating beams (details in Fig. 4.21). In Fig. 5.22 (a), the F0 microwave power at -18 dBm and saturates at about 0 dBm (blue curve). The red curve is off-shot data measuring the  $N=1$  population, which can be used as a reference signal to check source fluctuation. In (b), we prepare all the molecules in  $F=1$  state in the OP region. We observe that the transition starts at -25 dBm and increases continuously to -10 dBm. However, it fluctuates when the power is between -10 and 5 dBm. We attribute it to a Rabi-flopping type behavior although it is not suitable to use two-level rabi flopping model to explain such a multi-level scheme. In daily experiments, we set F0 and F1 MWs at 0 and -5 dBm respectively. Figure 5.22 tells that the detected signal on  $F=0$  or 1 will be saturated when the microwave power is larger than a certain value. However, it can't show whether we have fully detected the  $F=0$  or 1 population, which is the motivation we do the detection efficiency experiment in the next section.

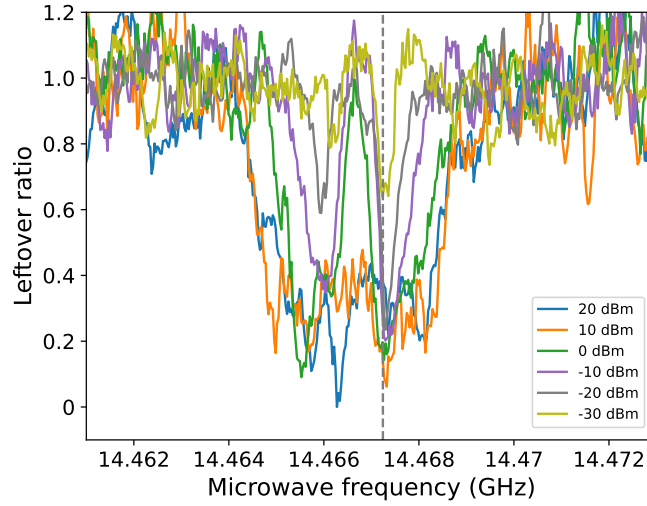


**Fig. 5.22:** (a) LIF as a function of F0 MW power. (b) LIF as a function of F1 MW power.

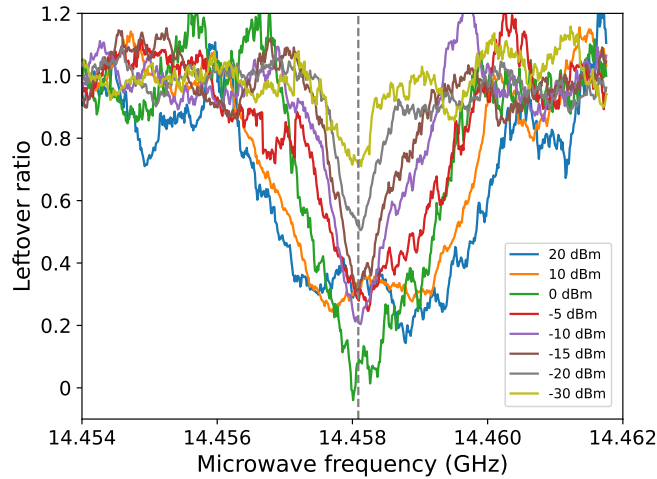
### 5.4.2 Detection efficiency

In order to study the detection efficiency on  $F=0$  and  $F=1$  states, we use OP to prepare the population in  $F=0$  or  $F=1$  state. We detect either  $F=0$  or  $F=1$  at the first PMT and use Q0 transition to detect the leftover at the second PMT. In Fig.

5.23, we scan the microwave frequency from 14.461 to 14.473 GHz with different microwave power. The gray dashed line shows the location of 14.467242 GHz. We attribute the noise in the plot to the shot-to-shot fluctuation. It can be seen that the best leftover ratio for  $F=0$  state is 10% when the microwave power is 10 dBm. Regarding Fig. 5.24, the best leftover ratio of  $F=1$  state is 0% when the microwave power is 0 dBm. We notice that at 14.466 GHz there is a dip in Fig. 5.23. It might be the microwave leaks from the OP region causing a microwave crosstalk. Since we've achieved desired detection efficiency, we didn't further study this problem.



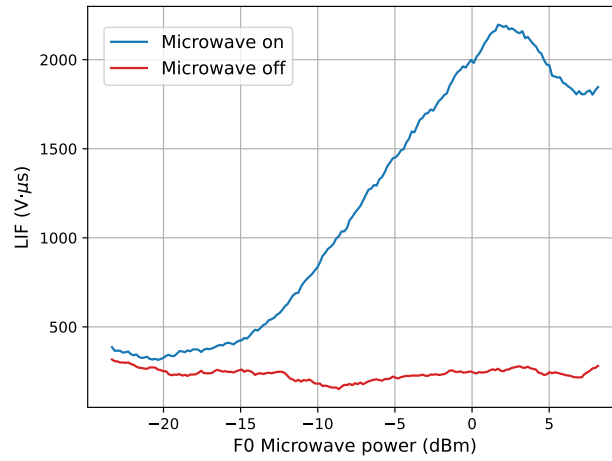
**Fig. 5.23:** Leftover ratio vs microwave frequency. The microwave frequency is 14.467242 GHz (highlighted in gray dashed line) which drives the transitions between  $|F=0\rangle$  and  $|N=1, F=1_I\rangle$ .



**Fig. 5.24:** Leftover ratio vs microwave frequency. The microwave frequency is 14.458087 GHz (highlighted in gray dashed line) which drives the transitions between  $|F=1\rangle$  and  $|N=1, F=2\rangle$ .

### 5.4.3 Microwave crosstalk

The problem in the detection we need to solve is the crosstalk of microwaves between two detectors. The chamber of detection region is shown in Fig. 4.19. The distance between two detectors is 395 mm. There are two microwave horns which are mounted in the two tilted vacuum arms (highlighted in gray). The crosstalk can be thought as a spatial leak of microwave from one detector to the other. The way to test the problem is to detect  $F=0$  population in detector 1, but only turn on microwave in detector 2, and vice versa. As can be seen in Fig. 5.25, the red curve was measured when microwave was off, in which we detected the leftover population in  $N=1$  state. The blue curve was measured when microwave was on. It shows that with microwave power increasing, we start to detect  $F=0$  population at -15 dBm and saturate the signal at around 2 dBm.

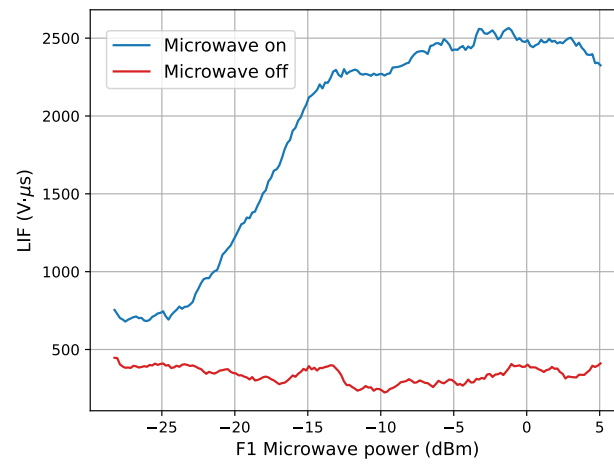


**Fig. 5.25:** Detector crosstalk measurement. The initial population is prepared in  $F_0$  and the  $N=1$  leftover population (red) is approximately 0.15 as previously shown.  $F_0$  microwave leakage from detector 2 to detector 1 is observed by measuring  $F_0$  population in detector 1 (blue).

Microwave leakage is also observed for the  $F_1$  detection microwave. In Fig. 5.26, the crosstalk starts at -24 dBm and saturates at -10 dBm. Eventually, we need to solve the MW crosstalk problem because we need to use two detectors simultaneously to run EDM experiments. To run the two detectors simultaneously, the microwaves will be attenuated by inserting multiple layers of stainless steel mesh between the detection regions with perforated holes less than  $\lambda/2$  ( $\lambda$  is the wavelength of the microwave). Each layer of mesh has an open area of 50% to allow for vacuum pumping and has a 10 mm diameter central aperture to allow molecules to pass between the detector regions. This has been recently implemented within the experiment with 10-15



dBm attenuation being observed between the detection regions for the F0 and F1 microwaves.



**Fig. 5.26:** Microwave (14.458087 GHz) leaks from detector 1 to detector 2.

## 5.5 Summary

In this chapter, we have showed the images of ultracold YbF molecules in both 1d and 2d cooling cases. We have measured how magnetic field, laser detuning and intensity affect laser cooling. We have measured the transverse temperature of YbF molecules by using EMCCDs. We have extracted the eEDM sensitivity for one shot and estimated corresponding eEDM sensitivity for a 10 day measurement. In the optical pumping region, we have measured the dependence of the leftover population in the  $N = 1$  state on laser and microwave power. We have also studied how interaction time affects the leftover population in the  $N = 1$  state. We have also studied the power broadening effect of the Q0 laser. In the interaction region, we have solved the microwave crosstalk problem in the STIRAP area. The preliminary results show that each laser beam of the STIRAP is functional. We have reduced the magnetic field noise below  $10 \text{ pT}$ . In the detection region, we have showed that the detected LIF signal will be saturated when the microwave power is over a certain value. We have further proved that we can reach over 95% detection efficiency for both  $F = 0$  and 1 states. We have found that there is a microwave crosstalk problem in the detection region. We have proposed a solution to solve the problem.



## Conclusions and outlook

### 6.1 Conclusions

When I started the PhD project, the chamber of the interaction region was built. But it was not connected to other regions. The machine contained source region, laser cooling region, optical pumping region and detection region. At that time, the machine was used to test laser cooling and optical pumping. After testing these two regions, we connected the interaction region between the optical pumping and detection regions. At the second year of my PhD, we obtained the entire YbF eEDM machine. Then we spent two months aligning the beamline to get the LIF signal in the detection region. Then we spent half a year retesting the laser cooling and optical pumping regions because longer beamline attenuated the downstream LIF signal significantly. Then we finished the detection efficiency experiment and preliminary STIRAP test. Now, the ultracold YbF eEDM machine is ready to measure interference curve and run blocks to test eEDM sensitivity. In the following paragraphs, I will present the main achievements I have made during my PhD.

In the source region, we have built the 4K cryogenic buffer gas source to produce YbF molecules with forward velocity ranging from 100 to 300 m/s. I have also calculated the electronic and rovibrational spectrum and hyperfine levels of the  $^{174}\text{YbF}$  molecules by using Wigner Eckart theorem and decomposition rule. I have also calculated the transition dipole matrices between the ground and first electronic states of YbF molecules for optical, microwave and rf transitions.

In the laser cooling region, I have applied optical Bloch equations to calculate the cooling force in both 1d and 2d cases using the transition dipole matrices I have calculated. I have systematically studied how laser intensity, laser detuning and polarization configurations affect cooling force. I have found that the cooling force in a type I system is much larger than a type II system with same laser intensity and detuning. Because type II systems contain dark states. I have further applied dark state destabilization to type II systems and have observed improved cooling forces. Regarding experiments, I have showed the chamber, optics setup and laser system. I have also demonstrated the multi-reflection optics. I have measured how magnetic field, laser detuning and intensity affect laser cooling. I have measured

the transverse temperature of YbF molecules by using EMCCDs. I have extracted the eEDM sensitivity for one shot and estimated corresponding eEDM sensitivity for a 10 day measurement.

In the optical pumping region, I have applied optical Bloch equations to simulate the state evolution of the transition, which gives insights into how much laser intensity and interaction are required. Regarding experiments, I have showed the chamber, optics setup and laser system. I have measured the dependence of the leftover population in the  $N = 1$  state on laser and microwave power. I have also studied how interaction time affects the leftover population in the  $N = 1$  state. I have also studied the power broadening effect of the Q0 laser.

In the interaction region, I have applied optical Bloch equations to study state manipulation including RF  $\pi$  pulse and STIRAP, which helps us designing experiments in the interaction region. I have studied how beam profile and laser detuning affect the transfer efficiency of STIRAP. I have also studied the state evolution including both population and coherence terms in a double STIRAP. I have demonstrated the chamber, electric field system, magnetic field system and STIRAP optics. In terms of experiments, we have solved the microwave crosstalk problem in the STIRAP area. The preliminary results show that each laser beam of the STIRAP is functional. Regarding the magnetic field system, we have reduced the magnetic field noise below  $10 \text{ pT}$  when the noise frequency is below  $0.1 \text{ Hz}$ . Such a magnetic field noise will deliver a systematic eEDM uncertainty of  $2.5 \times 10^{-29} \text{ e} \cdot \text{cm}$  per day.

In the detection region, I have applied optical Bloch equations to study the state evolution of the transition. I have introduced the chamber, optics setup, laser system, PMTs and EMCCDs. I have also calibrated the PMT with  $1 \text{ V}\cdot\text{s}$  corresponding to  $10^6$  counts. I have showed that the detected LIF signal can be saturated. I have further proved that the detection efficiencies for both  $F = 0$  and  $1$  states are over  $95\%$ . I have found that there is a microwave crosstalk problem in the detection region. We have proposed a solution to solve the problem.

## 6.2 Outlook

In this section, we will show the future plan of the ultracold YbF eEDM experiment including the main task and some optimizations of the machine.

The main task is to conduct spin precession experiment to obtain the interference curve. As we have discussed in previous chapters, YbF molecules are prepared by optical pumping in the initial state  $|F = 0, m_F = 0\rangle$  when they enter the interaction region. The first STIRAP will further prepare YbF molecules into the  $|y\rangle$  state. The  $|y\rangle$  state is defined as

$$|y\rangle = \frac{1}{\sqrt{2}}(|1, +1\rangle + |1, -1\rangle). \quad (6.1)$$

The  $|y\rangle$  state is the quantum state we will use to conduct spin precession experiment. The spin precession will happen between the first and second STIRAP with electric field applied to align the molecules and magnetic field applied to introduce the magnetic phase. The phase introduced by the applied magnetic field and eEDM interaction is

$$\begin{aligned} \phi(t) &= \phi_B(t) + \phi_E(t) \\ &= \frac{1}{\hbar}(\mu_B B_z - \eta d_e E_{\text{eff}})t, \end{aligned} \quad (6.2)$$

here  $\phi_B(t)$  and  $\phi_E(t)$  are the phases introduced by the applied magnetic field and eEDM interaction. Combining Eqs. 6.1 and 6.2, we obtain how  $|y\rangle$  state evolves when it experiences the spin precession

$$|y(t)\rangle = \frac{1}{\sqrt{2}}(e^{i\phi}|1, +1\rangle + e^{-i\phi}|1, -1\rangle). \quad (6.3)$$

Here we want to emphasize that the  $|1, +1\rangle$  and  $|1, -1\rangle$  states acquire opposite phases during the spin precession. To quantitatively describe the spin precession, we define the asymmetry which we have discussed in Ch. 1,

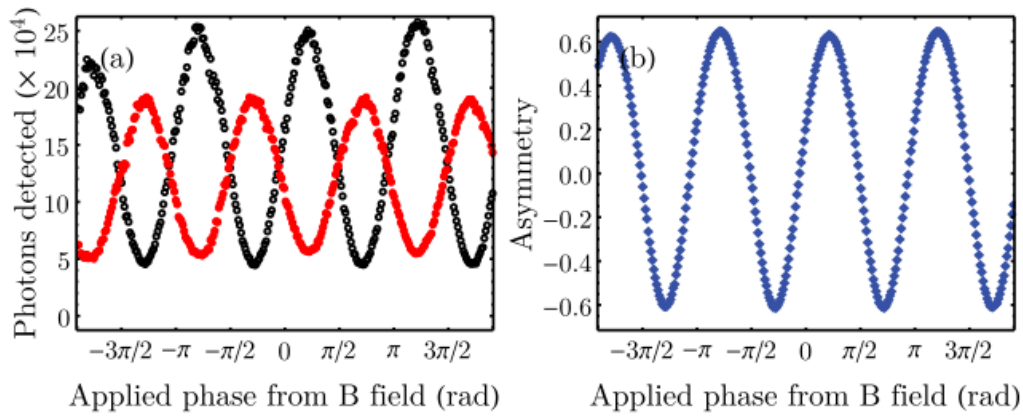
$$\begin{aligned} A &= \frac{s_A - s_B}{s_A + s_B}, \\ s_A &= N_{\text{mol}}\epsilon p_0 = N_{\text{mol}}\epsilon \cos^2 \phi, \\ s_B &= N_{\text{mol}}\epsilon p_1 = N_{\text{mol}}\epsilon \sin^2 \phi. \end{aligned} \quad (6.4)$$

Here,  $N_{\text{mol}}$  is the number of molecules from the source.  $\epsilon$  is the number of photons detected per molecule.  $p_0$  and  $p_1$  are the probabilities being detected in the  $F = 0$

and  $F = 1$  states. The above parameters have been discussed in [Sections. 1.3](#) and [3.3](#). From [Eq. 6.4](#), we can obtain the asymmetry

$$A = C \cos 2\phi, \quad (6.5)$$

where  $C$  is the contrast which should be 1 in a perfect experiment. In [Fig. 6.1](#) we show a measured asymmetry in our last generation eEDM machine [\[Ho20\]](#). We expect the same result on the ultracold YbF eEDM machine because they both use Ramsey interferometry technique. The difference is that we will apply STIRAP to prepare and read out quantum states in the ultracold YbF eEDM machine. However, in the last generation machine, we use RF  $\pi$  pulse to do the state preparation and readout.

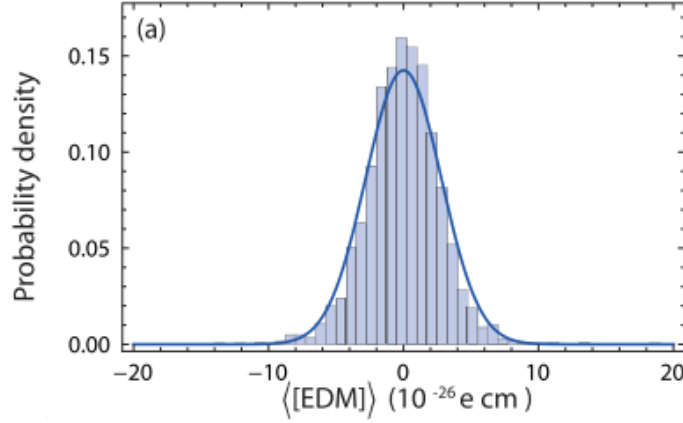


**Fig. 6.1:** Interference curve from our last generation eEDM machine [\[Ho20\]](#). (a) Interference curve for molecules in the  $F = 0$  (black) and  $F = 1$  (red) states. (b) Asymmetry interference curve calculated from (a).

In [Fig. 6.1](#) (a), it is clear that the number of photons detected for the  $F = 0$  and  $F = 1$  states oscillate in an opposite style. It is because the relation of the population between the  $F = 0$  and  $F = 1$  states is  $p_0 = 1 - p_1$ . Plot (b) is the calculated asymmetry based on the data from (a). It can be seen that the asymmetry interference curve is a sinusoid function. However, its amplitude is less than 1, which introduces the concept of imperfection. The detailed discussion of the imperfection is in [Ref. \[Ho20\]](#). However, since the ultracold YbF eEDM machine uses STIRAP rather than RF  $\pi$  pulses, the calculation of the imperfection will be different. The exploration of the imperfection of the ultracold YbF eEDM machine is part of our future plan.

Another important plan is to collect blocks to extract eEDM values, which will happen when we can minimize the imperfection of the interference curve. The result

we expect to see is in Fig. 6.2 which is the eEDM value measured in 2013 from our last generation eEDM machine from 2740 blocks. The blue line is a fitted normal distribution function. The mean of the distribution is subtracted. The standard deviation is  $5 \times 10^{-26}$  e·cm. To obtain Fig. 6.2, multiple channels are required



**Fig. 6.2:** A histogram of eEDM values from 2740 blocks taken in 2013 from our last generation eEDM machine [Dev15].

rather than a simple three-channel case we mentioned in Sec. 1.3. The discussion of blocks and channels is beyond this work. Detailed information is in Refs. [Ho20] and [Dev15].

We also plan to optimize the ultracold YbF eEDM machine in terms of hardware and software. In the source region, we plan to replace the current 4K buffer gas source with a 1K buffer gas source, which will reduce the initial velocity of YbF molecules. Such an upgrade has two advantages. One advantage is that molecules with lower velocity will be more easily captured by laser cooling, which will increase the number of molecules being detected at downstream. Recall Eq. 1.14, the larger the  $\sqrt{N_{\text{mol}}}$ , the smaller the eEDM sensitivity will be. Another advantage is that YbF molecules will experience longer spin precession time with lower velocity, which also makes the eEDM sensitivity smaller. This insight also comes from Eq. 1.14 since the spin precession duration  $\tau$  appears in the denominator. Let us use an example to estimate the shot eEDM sensitivity improvement based on the above two advantages. Recall Fig. 5.8, our current shot eEDM sensitivity is about  $1.0 \times 10^{-25}$  e·cm. Assuming after installing the 1K buffer gas source the forward velocity of YbF molecules can be reduced by 50%. It will increase the spin precession duration  $\tau$  by a factor of 2. It is difficult to estimate the increase of number of molecules being captured by laser cooling. Because it depends on the initial transverse velocity of the molecule. For simplicity, we assume the number of molecules can be enhanced by a factor of 4. Therefore, based on Eq. 1.14 and considering the improved spin precession



duration and number of molecules, the estimated shot eEDM sensitivity will be  $2.5 \times 10^{-26} \text{ e} \cdot \text{cm}$ .

Regarding software, we plan to transplant the block acquisition system from our last generation eEDM machine to the current generation. It has been partially done. However, the software system has to be modified because in the current generation machine we use STIRAP rather than RF  $\pi$  pulses. The setup of the channel parameters will be different.

Compared with our last generation eEDM machine, there are several prospects of the ultracold YbF eEDM machine. Firstly, it uses buffer gas source resulting in the initial longitudinal velocity of the molecules much slower. It will increase the spin precession time of molecules in the interaction region. Secondly, it applies transverse laser cooling which reduces the loss of molecules along the beamline. By turning on laser cooling, the number of molecules detected in the detection region can be enhanced by more than three times. Thirdly, it uses STIRAP to prepare and read out quantum states rather than RF. Such a technique can reduce the magnetic noise in the interaction region.

In conclusion, the next step is clear. We will push the experiment to obtain the interference curve and get the blocks running.

## Appendix

### 7.1 WE theorem and decomposition rule

In the WE theorem, we focus on spherical tensor. The reason we need this particular tensor is because atomic and molecular physics is based on central potential systems where spherical harmonics are eigenfunctions in such systems. Essentially, there is no difference between Cartesian tensors and spherical tensors since they are just two different coordinate systems to describe one situation. It is just the way people choose to view and solve problem conveniently.

Generally speaking, a spherical tensor is defined as an object which transforms like spherical harmonics under rotation even if it can't be expressed in terms of them. In this work, we refer spherical harmonics to spherical tensors. The first step is to introduce rotation operation for spherical tensors. Each rotation operator is described by an orthogonal  $3 \times 3$  matrix. All of them form the special orthogonal group  $SO(3)$ . Following the convention, we define the infinitesimal rotation operator  $\hat{O}(\theta)$  as

$$\hat{O}(\theta) = e^{-\frac{i}{\hbar}\theta\hat{J}\cdot\hat{n}}, \quad (7.1)$$

where  $\theta$  is the infinitesimal angle,  $\hat{J}$  is general angular momentum operator and  $\hat{n}$  a three-dimensional unit vector which indicates the direction of rotation. We will firstly introduce some useful properties of  $\hat{O}(\theta)$  which will be used in the following steps. In Eq. 7.2, we list five identities of the rotation operator. In the first line, angular momentum operator  $\hat{J}$  is regarded as an Hermitian operator ( $\hat{J} = \hat{J}^\dagger$ ) since it commutes with the Hamiltonian in simple cases. In the second and third line,  $\theta^{-1}$  is the reverse of  $\theta$  rather than its reciprocal. For instance, if  $\theta$  stands for rotate  $\theta$  degree clockwise,  $\theta^{-1}$  means rotate  $\theta$  degree anti-clockwise.

$$\begin{aligned} \hat{O}^\dagger(\theta) &= (e^{-\frac{i}{\hbar}\theta\hat{J}\cdot\hat{n}})^\dagger = e^{\frac{i}{\hbar}\theta\hat{J}^\dagger\cdot\hat{n}} = e^{\frac{i}{\hbar}\theta\hat{J}\cdot\hat{n}}, \\ \hat{O}^{-1}(\theta) &= (e^{-\frac{i}{\hbar}\theta\hat{J}\cdot\hat{n}})^{-1} = e^{\frac{i}{\hbar}\theta\hat{J}\cdot\hat{n}}, \\ \hat{O}(\theta^{-1}) &= e^{-\frac{i}{\hbar}(-\theta)\hat{J}\cdot\hat{n}} = e^{\frac{i}{\hbar}\theta\hat{J}\cdot\hat{n}}, \\ \hat{O}^\dagger(\theta) &= \hat{O}(\theta^{-1}) = \hat{O}^{-1}(\theta), \\ \hat{O}^\dagger(\theta)\hat{O}(\theta^{-1}) &= I. \end{aligned} \quad (7.2)$$

The next step is to use the rotation operator  $\hat{O}(\theta)$  acting on spherical harmonics  $|l, m\rangle$ . We select  $\hat{O}(\theta^{-1})$ , which gives,

$$\hat{O}(\theta^{-1})|l, m\rangle = \sum_{m'} |l, m'\rangle \langle l, m' | \hat{O}(\theta^{-1}) | l, m \rangle = \sum_{m'} |l, m'\rangle \hat{O}_{mm'}^{(l)}(\theta^{-1}). \quad (7.3)$$

Then multiply  $\langle \hat{n} |$  to the left side, using the forth line of Eq. 7.2 we obtain

$$\begin{aligned} \langle \hat{n} | \hat{O}(\theta^{-1}) | l, m \rangle &= \sum_{m'} \langle \hat{n} | l, m' \rangle \hat{O}_{mm'}^{(l)}(\theta^{-1}) = \sum_{m'} \langle \hat{n} | l, m' \rangle \hat{O}_{mm'}^{(l)\dagger}(\theta) \\ &= \sum_{m'} \langle \hat{n} | l, m' \rangle \hat{O}_{mm'}^{(l)*}(\theta). \end{aligned} \quad (7.4)$$

The last step is simply because  $\hat{O}(\theta)$  is symmetric. So its complex conjugation equals to Hermitian conjugation. In Eq. 7.4, using  $\hat{O}(\theta^{-1})$  to act to the left, we obtain

$$\langle \hat{n} | \hat{O}(\theta^{-1}) = \langle \hat{n} | \hat{O}^\dagger(\theta) = \langle \hat{n}' |. \quad (7.5)$$

Inserting it to Eq. 7.4, it becomes

$$\begin{aligned} \langle \hat{n}' | l, m \rangle &= \sum_{m'} \langle \hat{n} | l, m' \rangle \hat{O}_{mm'}^{(l)*}(\theta), \\ Y_l^m(\hat{n}') &= \sum_{m'} Y_l^{m'}(\hat{n}) \hat{O}_{mm'}^{(l)*}(\theta). \end{aligned} \quad (7.6)$$

Equation 7.6 shows how spherical harmonics transform under rotation operation. We can rewrite it in terms of the general form of spherical tensors,

$$T_q^{(k)}(\hat{n}') = \sum_{q'=-k}^k T_q^{(k)}(\hat{n}) \hat{O}_{qq'}^{(k)*}(\theta). \quad (7.7)$$

Here  $k$  is the rank of the tensor and  $q$  stands for the  $q$ th component. Correspondingly,  $k$  and  $q$  in  $T_q^{(k)}$  refer to  $l$  and  $m$  in  $Y_l^m$ . The next step is to evaluate the transformation of spherical tensor operators. It will give us an expression which will be used to prove the WE theorem. By using rotation matrix to transform the left side of Eq. 7.7, we obtain

$$\hat{O}(\theta) T_q^{(k)}(\hat{n}) \hat{O}^\dagger(\theta) = \sum_{q'=-k}^k T_q^{(k)}(\hat{n}) \hat{O}_{qq'}^{(k)*}(\theta). \quad (7.8)$$

Using the definitions of  $\hat{O}(\theta)$  in Eq. 7.1 and  $\hat{O}_{qq'}^{(k)*}(\theta)$  in Eq. 7.3, we get

$$\begin{aligned} \left(1 - \frac{i}{\hbar}\theta\hat{J} \cdot \hat{n}\right) T_q^{(k)} \left(1 + \frac{i}{\hbar}\theta\hat{J} \cdot \hat{n}\right) &= \sum_{q'=-k}^k T_{q'}^{(k)} \left\langle kq' \left| \left(1 - \frac{i}{\hbar}\theta\hat{J} \cdot \hat{n}\right) \right| kq \right\rangle \\ T_q^{(k)} + T_q^{(k)} \frac{i\theta\hat{J} \cdot \hat{n}}{\hbar} - \frac{i\theta\hat{J} \cdot \hat{n}}{\hbar} T_q^{(k)} - \frac{i\theta\hat{J} \cdot \hat{n}}{\hbar} T_q^{(k)} \frac{i\theta\hat{J} \cdot \hat{n}}{\hbar} \\ &= \sum_{q'=-k}^k \left( T_{q'}^{(k)} \delta_{qq'} - T_{q'}^{(k)} \left\langle kq' \left| \frac{i}{\hbar}\theta\hat{J} \cdot \hat{n} \right| kq \right\rangle \right) \end{aligned} \quad (7.9)$$

Dropping high order terms, we get

$$\begin{aligned} T_q^{(k)} \frac{i\theta\hat{J} \cdot \hat{n}}{\hbar} - \frac{i\theta\hat{J} \cdot \hat{n}}{\hbar} T_q^{(k)} &= - \sum_{q'=-k}^k T_{q'}^{(k)} \left\langle kq' \left| \frac{i}{\hbar}\theta\hat{J} \cdot \hat{n} \right| kq \right\rangle \\ [\hat{J} \cdot \hat{n}, T_q^{(k)}] &= \sum_{q'=-k}^k T_{q'}^{(k)} \langle kq' | \hat{J} \cdot \hat{n} | kq \rangle. \end{aligned} \quad (7.10)$$

We can set the unit vector  $\hat{n}$  to be spherical basis which is

$$\hat{e}_0 = \hat{e}_z, \quad \hat{e}_+ = -\frac{1}{\sqrt{2}}(e_x + ie_y), \quad \hat{e}_- = \frac{1}{\sqrt{2}}(e_x - ie_y). \quad (7.11)$$

Then we obtain the commutators

$$\begin{aligned} [\hat{J}_z, T_q^{(k)}] &= \hbar q T_q^{(k)}, \\ [\hat{J}_\pm, T_q^{(k)}] &= \hbar \sqrt{(k \mp q)(k \pm q + 1)} T_{q\pm 1}^{(k)}. \end{aligned} \quad (7.12)$$

Here  $\hat{J}_\pm$  are ladder operators. The last component we need in order to prove the WE theorem is to use ladder operators to get the recurrence relation of CG coefficients. The definition of CG coefficients is the expansion coefficients in the relation between coupled angular momentum states  $|JM\rangle$  and uncoupled states  $|j_1 j_2; m_1 m_2\rangle$ , which are  $\langle j_1 j_2; m_1 m_2 | JM \rangle$ . The derivation of the recurrence relation of CG coefficients is straightforward. It is simply applying ladder operators to coupled and uncoupled states respectively, which can be found in quantum mechanics textbooks. Here, we show the results directly. Equations 7.13 and 7.14 are the definition and recurrence relation of CG coefficients

$$|JM\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} |j_1 j_2; m_1 m_2\rangle \langle j_1 j_2; m_1 m_2 | JM \rangle. \quad (7.13)$$

$$C_{\pm}^{J,M} \langle j_1 j_2; m_1 m_2 | J, M \pm 1 \rangle = C_{\pm}^{j_1, m_1} \langle j_1 j_2; m_1 \mp 1, m_2 | J, M \rangle + C_{\pm}^{j_2, m_2} \langle j_1 j_2; m_1, m_2 \mp 1 | J, M \rangle. \quad (7.14)$$

Here  $C_{\pm}^{j,m}$  is the coefficient from the ladder operator, which is

$$C_{\pm}^{j,m} = \sqrt{j(j+1) - m(m \pm 1)} = \sqrt{(j \mp m)(j \pm m + 1)}. \quad (7.15)$$

Unitil now, we have all the components to prove the WE theorem. We start by taking the expectation value of the commutator in [Eq. 7.12](#),

$$\begin{aligned} \langle \alpha', j' m' | [\hat{J}_{\pm}, T_q^{(k)}] | \alpha, j m \rangle &= \hbar \sqrt{(k \mp q)(k \pm q + 1)} \langle \alpha', j' m' | T_{q \pm 1}^{(k)} | \alpha, j m \rangle \\ \langle \alpha', j' m' | \hat{J}_{\pm} T_q^{(k)} | \alpha, j m \rangle &= \langle \alpha', j' m' | T_q^{(k)} \hat{J}_{\pm} | \alpha, j m \rangle \\ &\quad + \hbar \sqrt{(k \mp q)(k \pm q + 1)} \langle \alpha', j' m' | T_{q \pm 1}^{(k)} | \alpha, j m \rangle \\ \sqrt{(j' \pm m')(j' \mp m' + 1)} \langle \alpha', j' m' \mp 1 | T_q^{(k)} | \alpha, j m \rangle &= \sqrt{(j \mp m)(j \pm m + 1)} \langle \alpha', j' m' | T_q^{(k)} | \alpha, j m \pm 1 \rangle \\ &\quad + \sqrt{(k \mp q)(k \pm q + 1)} \langle \alpha', j' m' | T_{q \pm 1}^{(k)} | \alpha, j m \rangle. \end{aligned} \quad (7.16)$$

Here  $\alpha$  is an arbitrary quantum number. For instance, in a Hydrogen atom, you can regard it as the principal quantum number. The  $\hbar$ s are cancelled on both sides because ladder operators will produce  $\hbar$  when they hit on  $|l, m\rangle$ . Following the convention, we make the substitutions

$$j' \rightarrow j, \quad m' \rightarrow m, \quad j \rightarrow j_1, \quad m \rightarrow m_1, \quad k \rightarrow j_2, \quad q \rightarrow m_2. \quad (7.17)$$

We apply the substitution to [Eq. 7.16](#) to obtain

$$\begin{aligned} \sqrt{(j \pm m)(j \mp m + 1)} \langle \alpha', j m \mp 1 | T_{m_2}^{(j_2)} | \alpha, j_1 m_1 \rangle &= \sqrt{(j_1 \mp m_1)(j_1 \pm m_1 + 1)} \langle \alpha', j m | T_{m_2}^{(j_2)} | \alpha, j_1 m_1 \pm 1 \rangle \\ &\quad + \sqrt{(j_2 \mp m_2)(j_2 \pm m_2 + 1)} \langle \alpha', j m | T_{m_2 \pm 1}^{(j_2)} | \alpha, j_1 m_1 \rangle \\ C_{\pm}^{j,m} \langle \alpha', j m \mp 1 | T_{m_2}^{(j_2)} | \alpha, j_1 m_1 \rangle &= C_{\pm}^{j_1, m_1} \langle \alpha', j m | T_{m_2}^{(j_2)} | \alpha, j_1 m_1 \pm 1 \rangle \\ &\quad + C_{\pm}^{j_2, m_2} \langle \alpha', j m | T_{m_2 \pm 1}^{(j_2)} | \alpha, j_1 m_1 \rangle. \end{aligned} \quad (7.18)$$

By comparing it with [Eq. 7.14](#), it can be seen that two sets of matrix elements satisfy the same set of linear homogeneous equations, which tells us they are proportional

$$\langle \alpha', j' m' | T_q^{(k)} | \alpha, j m \rangle = C \langle j k; m q | j k; j' m' \rangle. \quad (7.19)$$

Here  $C$  is the coefficient of proportionality. The final form of the WE theorem is

$$\langle \alpha', j' m' | T_q^{(k)} | \alpha, j m \rangle = \langle j k; m q | j k; j' m' \rangle \frac{\langle \alpha' j' || T^{(k)} || \alpha j \rangle}{\sqrt{2j' + 1}} \quad (7.20)$$

The fraction in Eq. 7.20 is called reduced matrix element which is independent of magnetic quantum number  $q, m$  and  $m'$ .

To work with atoms and molecules, we often have to deal with coupling among multiple angular momenta. The simplest example of the addition of angular momenta is singlet and triplet in quantum mechanics. The WE theorem we obtain above is to deal with coupling between two angular momenta. It can be generalized to study composite systems. The logic is that each tensor operator will only act on one particular angular momentum quantum number. So the first thing is to decouple coupled states into uncoupled states. For instance, adding  $j_1, j_2$  and  $j_3$  together to get  $j$ , we can choose either first adding  $j_1$  with  $j_2$  to get  $j_{12}$  or adding  $j_2$  with  $j_3$  to obtain  $j_{23}$

$$\begin{aligned} |(j_1, j_2) j_{12}, j_3; j, m\rangle \\ &= \sum_{j_{23}} |j_1, (j_2, j_3) j_{23}; j, m\rangle \langle j_1, (j_2, j_3) j_{23}; j, m | (j_1, j_2) j_{12}, j_3; j, m\rangle \\ &= \sum_{j_{23}} \sqrt{(2j_{12} + 1)(2j_{23} + 1)} W(j_1, j_2, j, j_3; j_{12}, j_{23}) |j_1, (j_2, j_3) j_{23}; j, m\rangle. \end{aligned} \quad (7.21)$$

Here  $W$  is the Racah 6-j coefficient. It is defined as

$$\left\{ \begin{matrix} a & b & e \\ d & c & f \end{matrix} \right\} = (-1)^{a+b+c+d} W(a, b, c, d; e, f). \quad (7.22)$$

Since we can apply the Racah 6-j coefficients to decouple wavefunctions, for instance, the next step is to write the composite tensor operator  $X$  in terms of individual tensor operator  $T^k$  and  $U^k$

$$\begin{aligned} \langle \alpha' j'_1 j'_2 j' m' | X_q^K | \alpha j_1 j_2 j m \rangle \\ &= (-1)^{j'-m'} \begin{pmatrix} j' & K & j \\ -m' & q & m \end{pmatrix} \langle \alpha' j'_1 j'_2 j' || X^K || \alpha j_1 j_2 j \rangle \\ \langle \alpha' j'_1 j'_2 j' || X^K || \alpha j_1 j_2 j \rangle &= \langle \alpha' j'_1 j'_2 j' || [T^k \otimes U^k] || \alpha j_1 j_2 j \rangle \\ &= (-1)^{K+j_1+j'_2+j'} \sqrt{2K+1} \sqrt{2j'+1} \left\{ \begin{matrix} j'_1 & j'_2 & j' \\ j_2 & j_1 & K \end{matrix} \right\} \\ &\times \sum_{\alpha''} \langle \alpha' j'_1 || T^K || \alpha'' j_1 \rangle \langle \alpha'' j'_2 || U^K || \alpha j_2 \rangle \delta_{jj'}. \end{aligned} \quad (7.23)$$

It can be seen that in Eq. 7.23 each individual tensor operator will be decoupled into its own reduced matrix element eventually. The way to prove Eq. 7.23 is to decouple wavefunctions and tensor operators into pieces to allow each operator acts on its own eigenfunction. The process is tedious. We recommend the reference [BC03]. Usually, one uses the simple version of Eq. 7.23, which is

$$\begin{aligned} & \langle \alpha' j'_1 j'_2 j' || T^k || \alpha j_1 j_2 j \rangle \\ &= \delta_{j_2 j'_2} (-1)^{j'_1 + j'_2 + j + k} \sqrt{(2j+1)(2j'+1)} \begin{Bmatrix} j'_1 & j' & j'_2 \\ j & j_1 & k \end{Bmatrix} \langle \alpha j_1 || T^k || \alpha' j'_1 \rangle \end{aligned} \quad (7.24)$$

## 7.2 Transverse temperature measurement

This section is to explain Eq. 5.4. In order to measure the transverse temperature of YbF molecules, we measure the transverse velocity of molecules. Based on the kinetic theory of gases, the relation between the temperature and velocity of a molecule is

$$k_B T_x = \frac{1}{2} m \langle v_x \rangle^2 = \frac{1}{2} m v_z^2 \langle \tan \theta \rangle^2 = \frac{1}{2} m v_z^2 \langle \theta \rangle^2, \quad (7.25)$$

where  $T_x$  and  $v_x$  are the transverse temperature and velocity of molecules.  $v_z$  is the longitudinal velocity of molecules.  $\theta$  is the spread angle. We are interested in molecules with small spread angle. Therefore,  $\tan \theta$  can be approximated as  $\theta$ .

As mentioned in Sec. 5.1.2, the method to determine the velocity of molecules is to take two EMCCD images of the molecular cloud at two different places, from which we can extract the thermal expansion of the molecular cloud. We define the Gaussian width of the initial molecular cloud as  $\sigma_0$ . The first and second Gaussian widths of the molecular cloud measured by the EMCCD at two locations are defined as  $\sigma_1$  and  $\sigma_2$ . We also define the distance between the first (second) location and the initial molecular cloud as  $z_1$  ( $z_2$ ). Since the EMCCD image of the molecular cloud can be fitted as a Gaussian profile as we have mentioned in Sec. 5.1.2, the first EMCCD image is a convolution of the Gaussian thermal spread of the initial molecular cloud. It is the same logic that the second EMCCD image is also a convolution of the initial EMCCD image. Therefore, we can define the thermal expansion of the molecular cloud along the  $x$  axis as

$$\begin{aligned} \sigma_1^2 &= \sigma_0^2 + \langle \theta \rangle^2 z_1^2, \\ \sigma_2^2 &= \sigma_0^2 + \langle \theta \rangle^2 z_2^2. \end{aligned} \quad (7.26)$$

Therefore, we can obtain

$$\langle \theta \rangle^2 = \frac{\sigma_2^2 - \sigma_1^2}{z_2^2 - z_1^2}. \quad (7.27)$$

We can also use the above method to obtain the thermal expansion of the molecular cloud along the  $y$  axis. Since the thermal expansion in the transverse direction is isotropic, the expression for thermal expansion along the  $y$  axis is same as  $x$  axis. Thus, we obtain the expression for the transverse temperature

$$T = \frac{m}{k_B} v_z^2 \frac{\sigma_2^2 - \sigma_1^2}{z_2^2 - z_1^2}. \quad (7.28)$$



## 7.3 Lasers and microwaves

In this section, we list all the lasers being used in this work in [Tab. 7.1](#).

In the source region, the YAG laser is used to ablate Yb atoms from an Yb solid target to react with  $\text{SF}_6$  gas to generate YbF molecules.

In the laser cooling region, V0, V1 and V2 lasers have been introduced in [Fig. 4.6](#).

In the optical pumping region, Q0 and P12 transitions have been introduced in [Fig. 4.11](#).

In the interaction region, STIRAP laser have been introduced in [Fig. 4.18](#).

In the detection region, P1 transition have been introduced in [Fig. 4.20](#).

| Region          | Transition | Laser Model                                                   |
|-----------------|------------|---------------------------------------------------------------|
| Source          |            | YAG: Continuum Minilite II pulsed Nd:YAG laser                |
| Laser cooling   | V0         | Toptica DL Pro + MPB + SHG 1104/552nm                         |
|                 | V1         | Toptica DL Pro + MPB + SHG 1136/568nm                         |
|                 | V2         | Vexlum VALO - SHG -SF 1130/565nm                              |
| Optical pumping | Q0         | Toptica DL Pro + Keopsys fiber amplifier + SHG 1104/552nm     |
|                 | P12        | Toptica DL Pro + Keopsys fiber amplifier + SHG 1104/552nm     |
| Interaction     | STIRAP     | Toptica DL Pro 100 + Keopsys fiber amplifier + SHG 1104/552nm |
| Detection       | P1         | Menlo (seed + fiber amplifier) + SHG                          |

**Tab. 7.1:** Laser used in this work.

In [Tab. 7.2](#), we list all the microwaves used in this work. Their models are same.

| Region          | Transition                                 | Microwave Model   |
|-----------------|--------------------------------------------|-------------------|
| Optical pumping | $ N=1\rangle$ to $ N=2\rangle$             | Windfreak SynthHD |
| Detection       | $ N=0, F=1\rangle$ to $ N=1, F=2\rangle$   | Windfreak SynthHD |
|                 | $ N=0, F=0\rangle$ to $ N=1, F=1_l\rangle$ | Windfreak SynthHD |

**Tab. 7.2:** Microwaves used in this work.

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