



Collisional Cooling and Magnetic Control of Reactions in Ultracold Spin-polarized NaLi+Na Mixture

Citation

Son, Hyungmok. 2022. Collisional Cooling and Magnetic Control of Reactions in Ultracold Spin-polarized NaLi+Na Mixture. Doctoral dissertation, Harvard University Graduate School of Arts and Sciences.

Link

<https://nrs.harvard.edu/URN-3:HUL.INSTREPOS:37371148>

Terms of use

This article was downloaded from Harvard University's DASH repository, and is made available under the terms and conditions applicable to Other Posted Material (LAA), as set forth at

<https://harvardwiki.atlassian.net/wiki/external/NGY5NDE4ZjgzNTc5NDQzMGIzZWZhMGFIOWI2M2EwYTg>

Accessibility

<https://accessibility.huit.harvard.edu/digital-accessibility-policy>

Share Your Story

The Harvard community has made this article openly available.

Please share how this access benefits you. [Submit a story](#)

HARVARD UNIVERSITY
Graduate School of Arts and Sciences



DISSERTATION ACCEPTANCE CERTIFICATE

The undersigned, appointed by the
Department of Physics
have examined a dissertation entitled

Collisional Cooling and Magnetic Control of Reactions in Ultracold
Spin-polarized NaLi+Na Mixture

presented by Hyungmok Son

candidate for the degree of Doctor of Philosophy and hereby
certify that it is worthy of acceptance.

Signature Kang-Kuen Ni

Typed name: Professor Kang-Kuen Ni, Chair

Signature W. Ketterle

Typed name: Professor Wolfgang Ketterle (MIT), Co-Chair

Signature Philip Kim

Typed name: Professor Philip Kim

Date: January 7, 2022

Collisional Cooling and Magnetic Control of Reactions in Ultracold Spin-polarized $^{23}\text{Na}^6\text{Li}+^{23}\text{Na}$ Mixture

A dissertation presented

by

Hyungmok Son

to

The Department of Physics

in partial fulfillment of the requirements

for the degree of

Doctor of Philosophy

in the subject of

Physics

Harvard University

Cambridge, Massachusetts

January 2022

© 2022 — Hyungmok Son
All rights reserved.

Collisional Cooling and Magnetic Control of Reactions in Ultracold Spin-polarized $^{23}\text{Na}^6\text{Li}+^{23}\text{Na}$ Mixture

Abstract

This thesis describes two studies with a mixture of ultracold triplet ground state $^{23}\text{Na}^6\text{Li}$ molecules and ^{23}Na atoms. The first study is to realize the cooling of ultracold NaLi molecules with Na atoms that efficiently exchange kinetic energy when colliding with molecules and bring them to thermal equilibrium with lower temperatures. Such cooling based on inter-particle collisions, which is the so-called collisional cooling, has not been successful in other molecular systems at micro-Kelvin temperatures or below before the work described in this thesis. By harnessing the good-to-bad collision ratio of the NaLi+Na mixture around 200, we increase the phase space density of the molecules by a factor of 20, achieving the temperatures as low as 220 nano-Kelvin. This collisional property arises from the suppression of reactive and inelastic collisions by the polarization of the spin in a chemically non-reactive quartet state, possibly together with the small size and the low mass of the NaLi+Na mixture. The loss rate in the spin-polarized NaLi+Na mixture is more than an order of magnitude lower than the so-called universal rate, which occurs in most molecular collisions as particles are lost or react at short range with unity probability. The second study is about the control of the reactive collisions by magnetically-tunable scattering resonances, so-called Feshbach resonances, between molecules and atoms. By controlling the phase of the scattering wavefunction via a Feshbach resonance at 978 G, we modify the loss rate by more than two orders of magnitude, and such a large dynamic range of tunability in loss is possible only in a molecular system in which the background loss is far below the universal limit, like

the spin-polarized NaLi+Na mixture. We explain the observed tunability in loss by a single-channel model based on quantum interference of the scattering wavefunction reflected at long and short ranges, which is analogous to the optical interference in a Fabry-Perot resonator. By fitting our Fabry-Perot model to the precisely measured lineshape of the loss feature at 978 G, we measure short range parameters, such as a background phase shift parameter and a quantum-defect parameter, which indicates that the spin-polarized NaLi+Na has about 4% loss probability at short range. By extending the single-channel model to consider the lifetime of a bound state of a closed channel, we treat a weak Feshbach resonance at 1030 G as a lossy phase shifter. With this extended two-channel model, we measure that the lifetime of a three-body collision complex associated with the resonance at 1030 G is about 60 ns. The work of this thesis shows that the spin-polarization is a simple yet powerful method to suppress reactive collisions in a molecular system and establishes the light triplet molecule as a useful system to study quantum chemistry, molecular scattering resonances, and possibly short range physics.

Contents

Abstract	iii
Acknowledgments	vii
Dedication	xii
1 Introduction	1
1.1 Motivation	1
1.2 Overview of my Ph.D. study and this thesis	4
2 Collisional Cooling of Ultracold Molecules with Atoms	9
2.1 Introduction	11
2.2 Experimental setup & procedure	12
2.2.1 1596 nm 1D optical lattice and laser intensity noise suppression . .	13
2.2.2 An atomic mixture preparation	16
2.2.3 Feshbach molecule formation	16
2.2.3.1 The number of particles in a single lattice site	21
2.2.3.2 Coils & Magnetic field	23
2.2.3.3 Estimation of the magnetic field noise	24
2.2.4 Triplet ground-state molecule formation	27
2.2.4.1 Laser linewidth estimation	29
2.2.5 Removal of free atoms	32
2.2.6 Detection & thermometry of molecules	34
2.2.6.1 Dissociation of molecules	34
2.2.6.2 Thermometry of molecules	39
2.2.6.3 Dissociation without magnetic field sweep	43
2.3 Results	45
2.3.1 Sympathetic cooling & heating of NaLi with Na atoms	47
2.3.2 Increasing phase-space density of NaLi	53
2.4 Discussion	55
3 Control of Reactive Collisions by Molecule-Atom Feshbach Resonances	57
3.1 Introduction	59
3.2 Fabry-Perot interferometer model	60

CONTENTS

3.3	Search for NaLi-Na Feshbach resonances	62
3.3.1	Experimental protocol	62
3.3.2	Loss spectrum of NaLi with Na	65
3.4	Measurement of enhanced NaLi-Na loss rate coefficients	68
3.4.1	Experimental protocol	68
3.4.2	Analysis of the strong resonance at 978 G with the single-channel model	70
3.4.3	Analysis of the weak resonance at 1030 G with the two-channel model	76
3.4.4	Physical mechanism of NaLi+Na Feshbach resonances	78
3.5	Discussion	80
4	Conclusion	82
4.1	Summary	82
4.2	Outlook	83
A	Supplemental information for Chapter 3.	87
A.1	Relation between s -wave scatterings in 2D & 3D	88
A.2	Loss rate measurement & density calibration	91
A.3	Typical particle numbers & decay of sodium atoms	95
A.4	Magnetic field inhomogeneity	95
A.5	Temperature of Na and NaLi	96
A.6	Verification of two-body loss mechanism	96
A.7	Mapping between Fabry-Perot model and threshold scattering formalism .	97
A.8	Mapping of two-channel model to Breit-Wigner form	99
A.9	Sign constraints for parameters q and Δ	102
A.10	Thermal averaging	103
A.11	Ratio of elastic to inelastic collision rates	103
	References	106

Acknowledgments

None of the work during my Ph.D would have been possible without the love, support, collaboration, and encouragement from a number of truly special people around me. Words will never be able to do justice to my true heartfelt gratitude, but I am glad to be able to thank and acknowledge all of you in this thesis.

First and foremost, I would like to thank my advisor, Prof. Wolfgang Ketterle. When I asked for an opportunity to study in his group back in Nov. 2015, I was a young student who was still new to ultracold molecules. Thankfully, he believed in my potential and passion and granted me an opportunity to conduct novel research in quantum physics. Since our NaLi molecules were quite different from others, working in BEC3 was like blazing a new trail. Throughout my development as a researcher and despite many rocky and uncertain times, Wolfgang trusted my intuition and patiently allowed me to fully explore my curiosity. Whenever I was stuck on something – either scientific, technical, or interpersonal – he always tried to listen to me and share his brilliant insights which have taught me the importance of thinking big about a problem in order to understand its essence and ultimately find a solution. He has been my mentor, my teacher, and my role model. With his great enthusiasm and unique intuition for physics, and sincere respect for the people around him, he will continue to inspire me to grow as a physicist and make a positive impact on society. Thank you so much for everything, Wolfgang. I also sincerely appreciate that you allowed me to leave MIT for my internship at Waymo for the last few months of my graduate study. I know an internship is extremely rare for physics graduate students. Thanks to you, I obtained a clearer picture on my future career path through the internship experience. Thank you.

I would like to thank my present and past lab members of BEC3 who have been through countless ups and downs with me: Alan Jamison, Timur Rvachov, Juliana Park,

Yu-Kun Lu, Sepehr Ebadi, Ariel Sommer, Eber Martinez, Jiangtian (Mike) Yao, and Tijs Karman. Alan, thank you for being such an awesome friend and colleague with whom I can discuss physics anytime. You are one of the most brilliant physicists I've ever known. I learned so much from our discussions and also enjoyed learning America's dark sides and black humors from you. I still remember how excited you were when I first found the evidence for sympathetic cooling of molecules. It was such a great pleasure to work with you from day one in BEC3. Timur, I truly appreciate you being a sincere and inspirational friend and colleague from day one in BEC3. You taught me pretty much everything I know about our machine, and what I learned from you has been a solid foundation that I was able to rely on for the past four years. Your creativity and get-it-done attitude has been a great inspiration to me, even until now. I miss the days when we went snowboarding after working until early morning in the lab together. Thanks for being such a great snowboarding buddy. Our trip with Niki to Whistler & Blackcomb is one of the best memories I have. Thank god that our coils did not catch fire again after you left! Julie, countless times during the past two years, I relied on your companionship in the lab and I sincerely appreciate it. You were a great help when I had difficult times during the pandemic, especially when I was extra busy with teaching a course. I enjoyed working with you and our discussions, and I admire your humble and persistent attitude. I'm really happy for your recent amazing achievement with our NaLi molecules! Yu-Kun, you have been a new inspiration to BEC3, and I really enjoyed a number of discussions we had about theories. Thank you for gladly hearing my ideas and sharing your thoughts anytime. Sepehr, it was such a great pleasure working with you when you were here as an undergraduate. I learned so much from your technological expertise, and I'm happy that we will be fellow alumni. Ariel, thank you for bringing new energy to BEC3, and it was a great time working with you. Eber and Mike, thank you for being amazing undergraduates. I enjoyed working with you guys. Tijs, technically you are

not a member of BEC3, but I feel you were part of our team given how long we have had discussions about our NaLi molecules. I am grateful that I was able to learn from you, and I have to say that our discussions really deepened my interest in quantum chemistry. I'm glad that we (almost) published a paper together before I graduate. Thank you for your collaboration.

I would like to thank Prof. Kang-Kuen Ni, who allowed me to experience what research in atomic and molecular physics is like for the first time. It was such a great pleasure and privilege to have an opportunity to build a MOT vacuum chamber on an empty optics table with my colleague, Yu Liu. I would also like to thank Yu. He is such a brilliant mind, and I learned a lot from his expertise in lasers, electronics, and vacuum technology. I miss old times when we went to Zoe's for dinner almost everyday! I also appreciate all other Ni group members – Yichao Yu, Lee Liu, Jesse Zhang, and Nick Hutzler – for illuminating discussions and lending us their 589 nm MPB fiber amplifier when ours was broken.

I would also like to thank all the people of the Ketterle group and the Harvard-MIT CUA. It was such a big privilege to be part of an amazing community where I met so many brilliant souls with whom I was able to discuss new ideas, achievements, and setbacks. Although it is impossible to list everyone here, I hope to express my gratitude to those who have been of significant help throughout my Ph.D: Furkan Top, Yair Margalit, Junru Li, Boris Shteynas, and Chris Lee, thank you for letting me steal anything ranging from lenses, mirrors, and AOMs to 1064 nm seed light; Will Lunden, thank you for developing stable analog voltage devices and sharing the technology with us; Li Du, thank you for gladly helping us solve Cicero and Poseidon issues; Niki Jepsen, Ivana Dimitrova, and Jesse Amato-Grill, thank you for giving us your 1064 nm Nufern amplifier and for sharing your expertise in laser noise suppression, electronics, and cold atom experiments in general; Colin Kennedy, Cody Burton, Woo Chang Chung, Jinggang Xiang, and Julius

de Hond, thank you for giving us your 1596 nm IPG laser and teaching me interesting quantum spin physics; Zhenjie Yan and Parth Patel, thank you for letting me borrow your three-phase high-voltage sources when ours got broken and for your late night companionship at the other side of the black curtain between our labs; Pierre Barral, Michael Cantara, Eunice Lee, Hanzhen Lin, Matt Nichols, Peter Park, Yiqi Ni, Lawrance Cheuk, Zoe Yan, Carsten Robens, Cedric Wilson, Airlia Shaffer-Moag, Sergio Cantu, Joonseok Hur, Edwin Pedrozo, Simone Colombo, and Zachary Vendeiro, thank you for lending me anything I needed from your labs, for sharing your expertise and ideas and for creating such a nice and warm environment for my growth. Thank you everyone for all the stimulating discussions and friendship!

I was blessed to have awesome people who have been a great support outside my lab, and I feel grateful to call them as my friends: Jongwoo Lee, thank you for always listening to me. I owe you more than I can express in words; Seungkyun Ha, thank you for always checking on me first and your companionship on soccer fields; Andy Joe and Aaron Krahn, thank you guys for still being awesome friends even after I moved to MIT. I miss our old times like when I laughed so hard with you guys, not noticing that I was spilling my burrito all over the street (thanks for proofreading this too!); Joonhee Choi and Soonwon Choi, thank you for always motivating me with your amazing research; Ruffin Evans, thank you for your help and support during my internship at Waymo. It was truly a pivotal experience in my life; Po Samutpraphoot, Sang Yeon Cho, Jong Yeon Lee, Seung Hwan Lee, Adrien Park, Daniel Han, Dong Sung Choi, thank you for your sincere encouragement and friendship; Changmin Lee, Sucheol Shin, Jonghwan Kim, and Gye Hyun Kim, thank you for your mentorship and advice which was of great help to my undergraduate studies and graduate school admission; Jung In Seo, Kyoung Soo Han, Eric Kim, Jin Hang Huh, and Hansuk Kim, thank you for believing in my potential more than I did since our times at Berkeley.

This thesis is dedicated to my parents, Byeongjun Son and Jongnam Choi, and younger brother, Chang Mok Son. Their unconditional love, support, and encouragement has been the biggest motivation for me to get through rough times and pursue my dream of becoming a physicist. Thank you for always believing in me. I love you all.

Looking back the past seven years at Harvard and MIT, I feel every day was a precious opportunity for me not only to challenge myself and grow intellectually but also to introspect myself and try to become a mentally and emotionally mature person. Certainly, I still have a long way to go, but my time at Harvard and MIT taught me how to keep improving myself and I feel sincerely lucky that I was able to learn it with the help of such amazing people at such wonderful places.

To my beloved family

Citations to previously published works

- Some parts in Chapter 2 have been published as

“Collisional cooling of ultracold molecules”

H. Son, J. J. Park, W. Ketterle, and A. O. Jamison, *Nature*, vol. 580, pp. 197–200 (2020)

Copyright © 2020 by Springer Nature. All rights reserved.

- Some parts in Chapter 3 have been published as

“Control of reactive collisions by quantum interference”

H. Son, J. J. Park, Y.-K. Lu, A. O. Jamison, T. Karman, and W. Ketterle, (accepted to *Science*), Sep 2021, Preprint, <https://arxiv.org/abs/2109.03944>

1

Introduction

1.1 Motivation

Collisions in chemically reactive molecular systems, or any other molecular systems that have non-zero background loss, are often characterized by a quantum-defect matrix, which becomes a single real number, y in a single channel description^{1,2}. This energy-insensitive parameter y near the threshold regime is called a quantum-defect parameter. y relates to a probability of the flux of the incoming wavefunction that gets absorbed into short range, which models irreversible losses such as reactions. Here, the short range ($r < R_0$) is where

CHAPTER 1. INTRODUCTION

a strong electrostatic force, such as exchange interaction, dominates: R_0 is around the length scale of chemical bonds, which is less than 1 nm for bialkali molecules (in terms of the energy scale, this corresponds to ~ 100 THz)^{3,4}. On the other hands, neutral particles feel a van-der Waals (vdW) potential, $-C_6/r^6$, at long range, and the relevant length scale is the so-called vdW length, $R_6 = \frac{1}{2}(2\mu C_6/\hbar^2)^{1/4}$, which is ~ 10 nm for bialkali molecules (in terms of the energy scale, this is on the order of MHz). In terms of the quantum-defect parameter y , the scattering wavefunction of colliding particles in the intermediate regime ($R_0 < r \ll R_6$) can be written as²:

$$\psi(r) \sim \exp\left[-i \int k(z)dz\right] - \left(\frac{1-y}{1+y}\right)\exp\left[+i \int k(z)dz\right]$$

where $k(z)$ is the relative wavevector in the z direction (i.e. the colliding direction). It is obvious from the equation that for $y = 1$, there is no flux reflected out to long range, which implies unity probability of the loss to short range. In this case, the loss occurs at the so-called universal rate^{2,3}, and most ultracold molecular collisions studied thus far have loss rate coefficients at or close to the universal value^{5–17}. The universal rate coefficient is determined only by quantum reflection of the scattering wavefunction by the long range potential, so the short range interaction, which is one of the primary interests of atomic physicists, cannot be probed in the molecular system decaying at the universal rate. In addition, it is expected that the interaction between colliding particles is difficult to be tuned when the background loss rate is at the universal value, i.e. scattering resonances are likely to be absent. This is because at the universal limit, the loss already occurs with unity probability at short range so that the inelastic/reactive scattering rate (or, the imaginary part of the complex scattering length) cannot be modified, and the elastic scattering rate (or, the real part of the complex scattering length) cannot be independently tuned^{2,18}. This is a tragedy since it is essential for physicists to have a capability of controlling inter-particle interactions when exploring

CHAPTER 1. INTRODUCTION

nature, just like how important inter-atomic Feshbach resonances are^{19,20}. Lastly, the loss with unity probability itself will be a big obstacle in cooling molecules and reaching quantum degeneracy. For these reasons, physicists have been trying to discover and characterize non-universal molecular systems.

Then, is producing a chemically non-reactive molecule sufficient to realize a stable molecular system? Probably not. The enormous size of a molecular Hilbert space given rich internal degrees of freedom associated with a molecule causes extra complications. Even chemically stable molecular species have shown anomalously high inelastic loss rates possibly owing to long-lived collision complex formation²¹ or interactions with optical trapping beams^{22–24}. Generally speaking, collisions involving molecules are often very complex due to the strong anisotropic interaction at short range and multiple decay channels^{25,26}.

Therefore, a new stable molecular system that will be discussed in this thesis – a spin-polarized NaLi+Na mixture in the quartet state in which the loss rate was measured to be more than an order of magnitude lower than the universal value – is quite special. With this unique system, I focused on studying two important questions in the field of atomic and molecular physics. The first one was to realize the cooling of ultracold molecules based on inter-particle collisions, which would be an important step to produce quantum degenerate molecules¹ but has not been demonstrated over the past 15 years^{28–33}. The second one was to find Feshbach resonances in ultracold atom-molecule collisions²

¹The first molecule that reached quantum degeneracy, fermionic KRb²⁷, was not cooled by collisions, but the realization of collisional cooling of ultracold molecules would still be an important milestone in our field, since it answered a long-standing question, deepened our understanding of molecular collisions, and can possibly be generalized in other molecular systems for achieving quantum degeneracy.

²The first Feshbach resonance in an ultracold atom-molecule mixture was observed in a heavier system, NaK+K³⁴. Although the density of states of NaLi+Na was expected to be lower given its lower mass, it was not entirely certain if we would be able to observe resolvable resonances until we actually found them²⁵.

and to develop a theoretical model to understand them in a relatively simple way.

1.2 Overview of my Ph.D. study and this thesis

When I first joined the lab BEC3 of the Ketterle group, I worked with team members to create the first collisionally-stable alkali molecules in the ro-vibrational ground state of the electronic triplet manifold using bosonic sodium and fermionic lithium atoms³. The scope of the work for my first 2 years ranged from spectroscopy of the ground and excited states of NaLi molecules, theoretical study of the internal molecular energy structures to the creation of the triplet ground state NaLi molecules. These studies have been elaborated in the doctorate thesis of Timur Rvachov³⁵ who was a senior graduate student at the time and resulted in three publications^{6,36,37}.

This thesis is about what I have done for about 4 years after the creation of the triplet ground state NaLi molecules. My major subject of interest was the scattering between NaLi molecules and atoms – sodium and lithium. In particular, I tried to find an atomic collisional partner that would not have strong inelastic/reactive collisions with NaLi molecules. For this purpose, the lithium atom was not suited since it likes to go through body-exchange chemical reaction with NaLi regardless of the electronic spin state (i.e. $\text{Li} + \text{NaLi} \rightarrow \text{Na} + \text{Li}_2$). However, the reaction is forbidden with sodium atoms as long as the spin state of $\text{Na} + \text{NaLi}$ remains in the quartet state (i.e. $\text{Na} + \text{NaLi} \nrightarrow \text{Li} + \text{Na}_2$ in the quartet manifold³). This is due to the binding energy of the triplet

³Energetically, it is possible to create a three-body complex LiNa_2 ; however, this can only happen by means of three-body collisions where a third colliding body carries away the released energy in the form of kinetic energy. Such a process has a much lower probability to happen compared to the two-body process. Another possibility of making a three-body complex is through a Feshbach resonance in which there's no released energy to be carried away as the reactants and the reaction product are energetically degenerate at a certain magnetic field. This has been realized and will be discussed in Chapter 3 of my thesis.

Na_2 molecules higher than that of the triplet NaLi molecules, as depicted in Fig. 1.1.

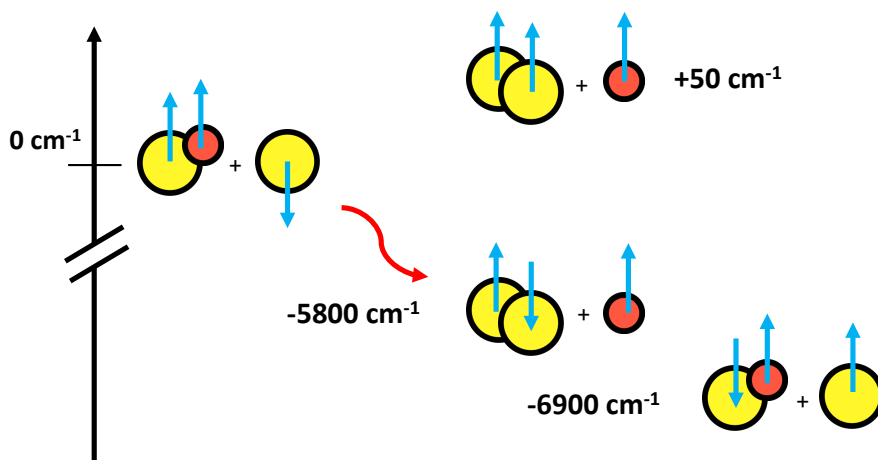


Figure 1.1: Dissociation energy (D_e) of the triplet and singlet dimer molecules, relative to the triplet NaLi ($D_e = -163.7 \text{ cm}^{-1}$). The red circle represents a lithium atom and the yellow one represents a sodium atom. A light blue arrow represents an electronic spin. Two electronic spins aligned represent a triplet state, and the spins anti-aligned represent a singlet state of the dimer molecule. As a figurative description, $\text{NaLi} + \text{Na}$ in which the sodium’s spin is anti-aligned to the molecule’s spin represents a mixture in a doublet state, and $\text{Na}_2 + \text{Li}$ in which all spins are aligned represents a mixture in a quartet state. The dissociation energies of singlet molecules are from Ref.³⁸, and those of triplet ones are from Ref.³⁹.

Thus, the key to realize a chemically stable $\text{NaLi} + \text{Na}$ system is to prepare a quartet state of $\text{NaLi} + \text{Na}$ by aligning the spins of Na atoms and NaLi molecules (i.e. spin polarization). More specifically, we need to have Na and NaLi in their stretched hyperfine states⁴. By doing so, we are able to create a pure quartet $\text{NaLi} + \text{Na}$ mixture since the stretched hyperfine state does not have any admixture of the opposite spin component. The opposite spin state creates a doublet state of $\text{NaLi} + \text{Na}$, which is depicted as, for instance, molecule’s spin pointing up and sodium atom’s spin pointing down in Fig. 1.1, and the doublet state is chemically reactive.

⁴In our study, we prepare $\text{NaLi} + \text{Na}$ in their “upper” stretched hyperfine states since the molecules are naturally in the state after their production. Similarly, the reaction is suppressed in $\text{NaLi} + \text{Na}$ in their “lower” stretched hyperfine, and this has been recently demonstrated by my colleague, Juliana J. Park.

CHAPTER 1. INTRODUCTION

We measured the loss rate in the quartet NaLi+Na system to be more than an order of magnitude lower than the universal rate, as the spin-polarization in the stretched hyperfine states suppressed reactions. My Ph.D. study has been developed into two main directions after the realization of the collisionally stable NaLi+Na system, and each consists of the half of this thesis.

The first half of my Ph.D. study is in Chapter 2 where I discuss the realization of sympathetic cooling of the triplet NaLi molecules using sodium atoms as coolants. Although cooling based on collisions between particles has been an important workhorse for creating BEC and degenerate Fermi gas of atoms, such method, collisional cooling, has not been successful in molecular systems at temperatures below micro-Kelvin regime. However, we successfully cooled NaLi molecules close to 200 nK by making them collide and thermalize with colder sodium atoms. This was possible due to the spin-polarization of NaLi+Na in the quartet state, which suppressed reactions and made the ratio of elastic to inelastic collision rates high enough to sustain the cooling of molecules. By utilizing the polarizability of sodium atoms lower than that of NaLi by a factor of 2.8 in the 1,596 nm trapping light, we were able to selectively cool Na atoms by evaporating them without a substantial loss of molecules and increased the molecular phase-space density by a factor of 20.

The second half of my Ph.D. study is in Chapter 3 where I discuss the control of reactive collisions in NaLi+Na by magnetically tunable scattering resonances (i.e. Feshbach resonances). The observed Feshbach resonances in NaLi+Na is the only second example of the Feshbach resonances in an ultracold molecule-atom mixture. More importantly, we show that the atom-molecule Feshbach resonance opens the door for enhancing and suppressing reactive and inelastic losses by tuning the quantum interference of scattering wavefunction reflected at short and long ranges. By fitting our theoretical model based on interference to loss features of the observed resonances, we were able to extract the short

CHAPTER 1. INTRODUCTION

range parameters, such as the quantum-defect parameter and background phase-shift parameter, and the lifetime of the three-body bound state. The supplemental information related to this chapter can be found in Chapter A.

The experimental protocol for each study is elaborated in each relevant chapter. The experimental procedure of producing a stable NaLi+Na mixture in the quartet state, which is the common starting point for both studies, is described in Chapter 2.2. In this chapter, I discuss the noise and the control of magnetic fields which are important for the creation of Feshbach molecules and a precise spectroscopy of atom-molecule Feshbach resonances, respectively. Discussion on the laser system used for Stimulated Raman Adiabatic Passage (STIRAP) for the creation of triplet ground state NaLi molecules and the characterization of the laser noise is also provided in the same chapter. Another important highlight of this thesis is the detailed analysis of the dissociation of Feshbach molecules. Feshbach molecules created by closed-channel dominated interatomic Feshbach resonances, such as the triplet NaLi molecules⁴⁰, are difficult to be directly imaged by absorption imaging, unlike the ones created by open-channel dominated interatomic Feshbach resonances (e.g. KRb⁵, NaK⁷, etc). This means that we have to dissociate NaLi molecules to free sodium and lithium atoms and image the dissociated atoms to infer the number of molecules and their temperatures. Counting the number of molecules should be straightforward as long as the atoms can be imaged with a cycling transition (in the case of NaLi, dissociated Li atoms are imaged with a cycling transition, whereas dissociated Na atoms need a repumper light due to the lack of a cycling transition at 745 G where we associate and dissociate Feshbach NaLi molecules). However, the estimation of the molecular temperature from temperatures measured by the atomic Time-Of-Flight (TOF) images can be tricky. This is due to the extra kinetic energy carried out by each constituent atoms in the dissociation process with a magnetic field sweep across the resonance. In Chapter 2.2, I discuss the relation between the molecular temperature and

CHAPTER 1. INTRODUCTION

the extra kinetic energy caused by dissociation field sweep, which appears in the TOF images of dissociated atoms.

Lastly, in Chapter 4, I conclude my thesis with an overall summary and an outlook for future studies with NaLi molecules.

The work of this thesis resulted in two publications: the realization of sympathetic cooling of ultracold molecules with atoms⁴¹, and the control of reactive scatterings by atom-molecule Feshbach resonances⁴².

2

Collisional Cooling of Ultracold Molecules with Atoms

Some parts in this chapter have been published as

“Collisional cooling of ultracold molecules”

H. Son, J. J. Park, W. Ketterle, A. O. Jamison, *Nature*, vol. 580, pp. 197–200, Apr 2020

Copyright ©2020 by Springer Nature. All rights reserved.

Abstract

Since the original work on Bose–Einstein condensation^{43,44}, the use of quantum degenerate gases of atoms has enabled the quantum emulation of important systems in condensed matter and nuclear physics, as well as the study of many-body states that have no analogue in other fields of physics⁴⁵. Ultracold molecules in the micro- and nanokelvin regimes are expected to bring powerful capabilities to quantum emulation⁴⁶ and quantum computing⁴⁷, owing to their rich internal degrees of freedom compared to atoms, and to facilitate precision measurement and the study of quantum chemistry⁴⁸. Quantum gases of ultracold atoms can be created using collision-based cooling schemes such as evaporative cooling, but thermalization and collisional cooling have not yet been realized for ultracold molecules. Other techniques, such as the use of supersonic jets and cryogenic buffer gases, have reached temperatures limited to above 10 mK^{49,50}. Here we show cooling of NaLi molecules at micro- and nano-Kelvin temperatures through collisions with ultracold Na atoms, both prepared in their stretched hyperfine spin states. We find a lower bound on the elastic to inelastic collision ratio between molecules and atoms greater than 50—large enough to support sustained collisional cooling. By employing two stages of evaporation, we increase the phase-space density (PSD) of the molecules by a factor of 20, achieving temperatures as low as 220 nK. The favorable collisional properties of a Na and NaLi mixture show great promise for making deeply quantum degenerate dipolar molecules and suggest the potential for such cooling in other systems.

2.1 Introduction

The full potential of ultracold atoms was not realized until the advent of collision-based cooling methods such as evaporative and sympathetic cooling. Although atomic systems have been recently used to demonstrate laser cooling to quantum degeneracy, these schemes still require collisional thermalization^{51,52}. Therefore, there has been much work over the past 15 years²⁸ to achieve collisional cooling of ultracold molecules. Buffer gas cooling⁵⁰ cannot push below 100 mK owing to the rapidly diminishing vapour pressure of buffer gases at such temperatures. Supersonic expansion⁴⁹ can produce temperatures around 100 mK. Controlled collisions in crossed molecular beams⁵³ can decrease the laboratory-frame velocity of particles while narrowing the velocity distribution. However, this technique has not been demonstrated below about 500 mK. Merged supersonic beams can be used to study collisions at energies equivalent to a temperature of 10 mK (Ref.⁵⁴). Cooling below 100 mK calls for trapping molecules in magnetic or electrostatic traps and for good collisional properties (that is, a ratio of elastic to inelastic collisions much greater than 1). Such traps require preparing molecules in weak-field seeking states, which are never the absolute ground state, allowing inelastic state-changing collisions to eject the cold molecules from the trap. A variety of systems have been proposed for evaporative or sympathetic cooling of molecules²⁸⁻³³. So far, elastic collisions have been observed clearly in O₂ at temperatures below 1 K⁵⁵ and possibly in OH radicals around 10 mK (Ref.⁵⁶ corrects an earlier report⁵⁷). In the O₂ case, inelastic collisions prevent thermalization and collisional cooling.

In recent years, the assembly of molecules from ultracold atoms⁵⁸ and the direct laser cooling of molecules⁵⁹⁻⁶² have both expanded to new molecules and temperature regimes. These techniques have achieved molecular systems at temperatures less than 100 mK, raising the challenge of collisional cooling in the micro- and nanokelvin regimes. Optical

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

traps enable trapping of the absolute ground state, which removes the concern of state-changing collisions. However, collisional cooling in the absolute ground state of chemically stable systems has not yet been realized⁶³. By contrast, chemically stable molecular species have shown anomalously high inelastic loss rates that preclude collisional cooling, possibly owing to collision complex formation²¹ or interactions with optical trapping beams²².

In this chapter we study sympathetic cooling of rovibrational ground-state triplet $^{23}\text{Na}^6\text{Li}$ molecules by ^{23}Na atoms, both of which are prepared in their upper stretched hyperfine spin states (that is, states with both nuclear and electronic spins aligned along the direction of the magnetic bias field). Although sympathetic cooling of one atomic species by another has been observed in various ultracold atomic mixtures⁶⁴, triplet NaLi was considered unlikely to have sufficiently good collisional properties to support such cooling. NaLi has energetically allowed chemical reactions, even in the electronic ground state (that is, a singlet state), and the triplet state has an electronic excitation energy of 0.8 eV or 10,000 K.

Furthermore, theoretical studies on various systems have explored the possibility of suppressing inelastic collisions and reactions by spin polarization, giving pessimistic predictions for triplet molecules and more favourable ones for doublet molecules^{32,65–68}. Nonetheless, we observed clear thermalization and sympathetic cooling of triplet NaLi to 220 nK. We observe 20-fold increases of phase space density (PSD), opening the possibility of collisional cooling to deep quantum degeneracy.

2.2 Experimental setup & procedure

Our experimental setup is summarized in Fig. 2.1. In the following chapters, I elaborate the procedure of producing a clean atom-molecule mixture in a spin-stretched state,

including the characterization on the experimental equipment necessary for each step.

2.2.1 1596 nm 1D optical lattice and laser intensity noise suppression

In our experiment, a high bias field ($\lesssim 1400$ G) is produced by a pair of coils called “Anti-bais” coils in a Helmholtz configuration, which generates a curvature (see Ananth P.

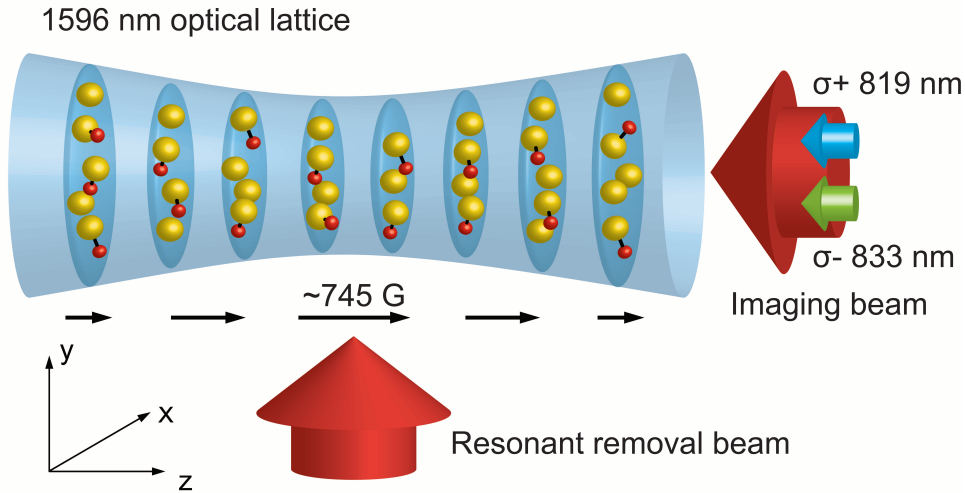


Figure 2.1: Experimental setup. The Na atoms (yellow circles) and NaLi molecules (yellow and red circles on black sticks) are trapped in a 1D optical lattice formed by a 1596 nm laser, which is retro-reflected. The magnetic field, which defines the quantization axis, is coaxial with the lattice beam. The leftover free atoms after the formation of the ground-state molecules are removed by resonant light in the radial direction (y -axis in figure). STIRAP is performed with beams that propagate along the axial direction (z -axis in figure). The ground-state molecules are detected by absorption imaging of the dissociated atoms along the axial direction.

Chikkatur’s thesis⁶⁹ for detailed information on the coil geometry). At 234A of the current running through the coils, the curvature is $B'' \approx -31$ G/cm² where the bias field $B(z) = 745\text{G} + \frac{1}{2}B''z^2$ (z : the axial coordinate in Fig. 2.1). This curvature generates an anti-trapping force on particles with a trap frequency of $\omega_{\text{ax}} = \sqrt{\mu B''/m} \approx 2\pi \times 17(13)$

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

Hz for NaLi molecules (sodium atoms) with a magnetic moment $\mu = 2\mu_B$ (μ_B) where $\mu_B = 1.4\text{MHz/G}$ is Bohr magneton. In order to avoid any particle loss due to the magnetic anti-trapping force while evaporating sodium atoms, we set up an 1D optical lattice with 1596 nm laser beam where the axial confinement is naturally much stronger than in a typical optical dipole trap (ODT): the axial trap frequency is given by $\omega_{\text{ax}} = \sqrt{2U/ml_z^2}$ where U is the trap depth and l_z is the characteristic axial length scale, which for an ODT, is the Rayleigh range, z_R (typically on the order of $\sim 1\text{mm}$ or less) and for an 1D lattice, is one over the wavenumber, $k^{-1} = \lambda/2\pi$ (typically two orders of magnitude smaller than z_R).

In the 1596 nm 1D optical lattice, the axial trap frequency of the NaLi molecule is $\sim 2\pi \times 50\text{ KHz}$ at the trap depth of $\sim 20\text{ }\mu\text{K}$ ($\approx 40E_r$ where E_r is the two-photon recoil energy in the 1596 nm trap). Since the trap frequency is very high, it is important to stabilize the laser intensity at high frequencies, which are usually not a big concern with a typical ODT; otherwise, particles could be heated and lost in the parametrically driven optical lattice. Apparently, the lifetime of molecules was too short due to the noise of the laser intensity when we initially used an AOM driver (80 MHz frequency source + RF amplifier) from IntraAction Corp. for the laser intensity control. This problem was mainly solved by replacing the noisy IntraAction AOM driver with a low-noise voltage-controlled crystal oscillators (VCXO) at 80 MHz from Crystek as a frequency source + a RF amplifier from MiniCircuit (see Figs. 2.2 and 2.3 a). Another improvement factor was the replacement of the SRS PID controller (SIM960) whose servo bandwidth was $\sim 100\text{ KHz}$ with a New Focus servo controller (LB1005) whose servo bandwidth was $\sim 10\text{ MHz}$ (see Fig. 2.3 b).

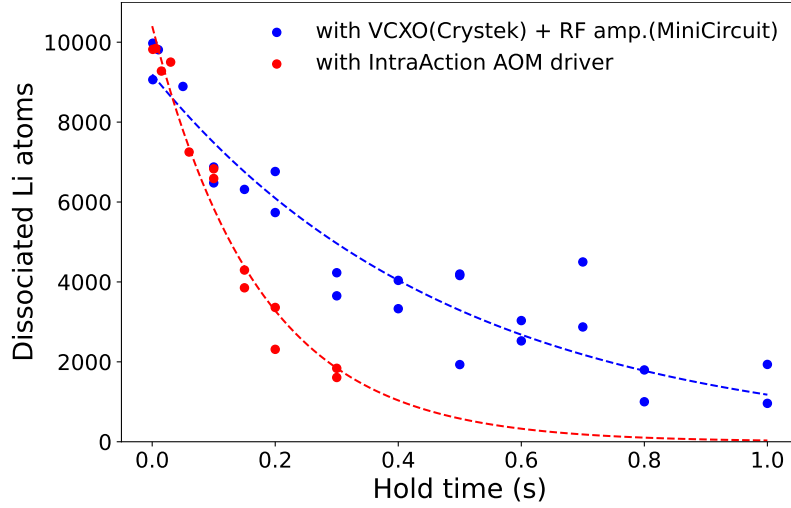


Figure 2.2: Lifetime of NaLi Feshbach molecules in a 1596 nm 1D optical lattice ($\omega_{ax} \sim 2\pi \times 50$ KHz at the trap depth of $\sim 20 \mu\text{K}$). The red (blue) data points were acquired when the lattice beam intensity was stabilized by a noisy IntraAction AOM driver (a Crystek VCXO and a MiniCircuit RF amplifier) and a SRS PID controller. The dotted lines are exponential fits which are to compare the approximated decay time scales: the exponential time-constant is about 3 times longer for the blue data compared to the red.

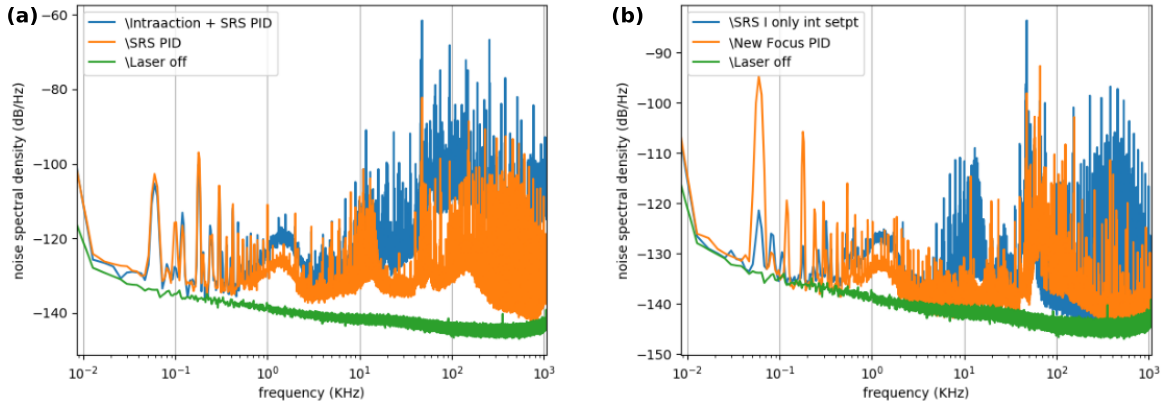


Figure 2.3: Power spectral density of the laser intensity noise. Measurement was done in a closed-loop configuration by reading Fourier transformed photodiode signals. Except for the blue curve in (a) where the IntraAction was used, a low-noise VCXO + a RF amplifier was used. Except for the blue curve in (b) where an internal digital set point of the SRS PID controller was used, an external NI analog voltage channel was used as a set point of the PID controller. (a) shows that the IntraAction AOM driver adds noise $\sim 20\text{db}$ for >20 KHz. (b) shows that the New Focus servo controller with a higher feedback bandwidth outperforms the SRS PID controller in stabilizing the noise >1 KHz.

2.2.2 An atomic mixture preparation

We produce an ultracold mixture of ^{23}Na and ^6Li in their upper stretched hyperfine states (in the $|F, m_F\rangle$ basis, where F and m_F are the hyperfine and magnetic quantum numbers, respectively, these states correspond to $|2, 2\rangle$ for Na and $|3/2, 3/2\rangle$ for Li) in an Ioffe–Pritchard magnetic trap at a bias field of 2 G. We cool the Na atoms using microwave-induced evaporation and sympathetically cool the Li atoms with the Na atoms^{64,70–72}. Then, the mixture is transferred into the combination of two coaxial optical traps: a 1064 nm optical dipole trap (ODT) (30 μm waist, 10 W power) and a 1596 nm 1D optical lattice (50 μm waist, 2 W power). After 0.6 s of forced evaporation in the 1064 nm optical dipole trap, the trap is switched off. Then, in the 1596 nm 1D lattice, the sample is transferred to the lowest-energy Zeeman states ($|1, 1\rangle$ for Na, and $|1/2, 1/2\rangle$ for Li) using a Landau–Zener (LZ) magnetic field sweep. By controlling the microwave power for the LZ sweep, we intentionally leave a fraction of Na atoms in the upper stretched hyperfine state (in the low-field basis, $|F, m_F\rangle = |2, 2\rangle$) for later use as coolants of the NaLi molecules. About 1.0×10^5 coolant atoms are prepared for the study. Use of 1596 nm light for the trap improves the lifetime of the NaLi molecules by suppressing spontaneous photon scattering compared to the more common 1064 nm trap. The 1D lattice provides strong axial confinement to overcome the anti-trapping produced by magnetic curvature⁶.

2.2.3 Feshbach molecule formation

As previously demonstrated with other atomic species^{6,7,34,58,73–78}, NaLi ground state molecules are created from Feshbach molecules in the least-bound vibrational state. NaLi Feshbach molecules form in the $v = 10$, $N = 2$, $m_N = -2$ state in the $a^3\Sigma^+$ potential, from the atoms in the lowest-energy Zeeman states by sweeping the magnetic field across an interspecies scattering resonance (“Feshbach resonance”) at 745 G⁴⁰ (v and N are the vibrational and rotational molecular quantum numbers, respectively). At this field,

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

the atomic continuum states and the molecular bound state couple through a d -wave magnetic dipole-dipole interaction. The formation efficiency of the Feshbach state is usually $\gtrsim 5\%$, but it can be as high as $\sim 11\%$ which corresponds to $\sim 9 \times 10^4$ molecules in total at $\sim 1.5 \mu\text{K}$. Compared to our old efficiency in an optical-dipole trap (ODT) of 1319 nm, which was $\sim 3\%$ ³⁵, this is a meaningful increase. The Feshbach molecule formation efficiency is mainly determined by two factors: (1) adiabaticity of the magnetic field sweep across the resonance, and (2) phase space density overlap between atoms. Molecule formation efficiency is inversely proportional to the field sweep rate, but it eventually saturates (i.e. when the sweep rate satisfies the adiabaticity condition), and the maximum efficiency is mainly determined by the phase space density of the atoms^{79,80}. When the field sweep rate still is fast, the molecule conversion follows the Landau-Zener (LZ) description. In this case, the molecule formation efficiency is given by $f = f_0 P$ where f_0 is the saturated molecule conversion fraction and the transition probability P of a Na-Li pair transferring into the molecular state is given by $P = (1 - e^{-2\pi\delta_{LZ}})$ with the LZ parameter δ_{LZ} ^{79,80}:

$$\delta_{LZ} = \frac{1}{V} \frac{2\pi\hbar}{\mu} \frac{a_{bg}\Delta}{\dot{B}} \quad (2.2.3.1)$$

where V is the volume for a single Na-Li pair, μ is the reduced mass, $a_{bg} = -70a_0$ ⁸¹ is the background scattering length between Na and Li at 745 G, and $\Delta = 10\text{mG}$ ⁸¹ is the resonance width. In the fast sweep condition (i.e. $\delta_{LZ} \ll 1$), $P = 1 - e^{-2\pi\delta_{LZ}} \approx 2\pi\delta_{LZ}$. In this condition, the total number of molecules produced is given by $N_{\text{NaLi}} = N_{\text{Na}}N_{\text{Li}}P$ with the overlap volume $V = \bar{\omega}_{\text{Na}}^{-3} \left[\left(\frac{2\pi k_B T_{\text{Na}}}{m_{\text{Na}}} \right) \left(1 + \frac{\alpha_{\text{Na}}}{\alpha_{\text{NaLi}}} \frac{T_{\text{NaLi}}}{T_{\text{Na}}} \right) \right]^{\frac{3}{2}}$ where $\bar{\omega}_{\text{Na}}$ is the geometric mean of the trap frequencies for Na and α_i is the AC polarizability of particle i in the optical trap. Then, the molecule conversion fraction, which is defined as the number of molecules created divided by the number of the lesser kind atoms (which is Li in our usual

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

cases), is given by⁷⁹:

$$f = \frac{1}{N_{\text{Li}}} N_{\text{NaLi}} = \frac{1}{N_{\text{Li}}} (N_{\text{Li}} N_{\text{Na}}) P \approx \frac{1}{N_{\text{Li}}} (N_{\text{Li}} N_{\text{Na}}) \frac{2\pi}{V} \frac{2\pi\hbar}{\mu} \frac{a_{bg}\Delta}{\dot{B}} \quad (2.2.3.2)$$

where the transition probability is approximated as $P \approx 2\pi\delta_{\text{LZ}}$ in the fast sweep condition. In the 1319 nm optical trap, the polarizability ratio between Na and Li atoms is roughly 1: $(m\omega^2)_{\text{Li}}/(m\omega^2)_{\text{Na}} \approx 1$ ⁶. Then, the overlap volume V is equivalent to the mean volume of each atom. Given this, we calculate $P \approx 4 \times 10^{-8}$ for $V = 1.0 \times 10^{-6} \text{ cm}^3$ at $2 \mu\text{K}$ and $\dot{B} = 450\text{mG/1ms}$, for our previous production of molecules in the 1319 nm ODT³⁵. This gives the molecule conversion fraction $f \approx 0.06$ with 1.5 million Na atoms. The production efficiency was lower than 6%, as mentioned earlier with $f_0 \sim 3\%$. The factor of 2 discrepancy could be due to the collisional loss with free atoms during the field sweep or, due to the uncertainty in the density estimation, which is not unreasonable to be as large as 50% due to the anharmonicity in the optical trapping potential.

Given the sweep condition we applied, the LZ parameter δ_{LZ} is as low as $\sim 10^{-8}$, which would mean that the molecules were formed with the diabatic sweep condition. As a comparison, the formation efficiency of the fermionic KRb Feshbach molecule was saturated with respect to the field sweep rate and limited by the atomic phase space density, when $\delta_{\text{LZ}} \sim 1$ ⁷⁹. However, we find the molecule formation efficiency cannot be improved by simply lowering the sweep rate due to the collisional loss with free atoms.

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

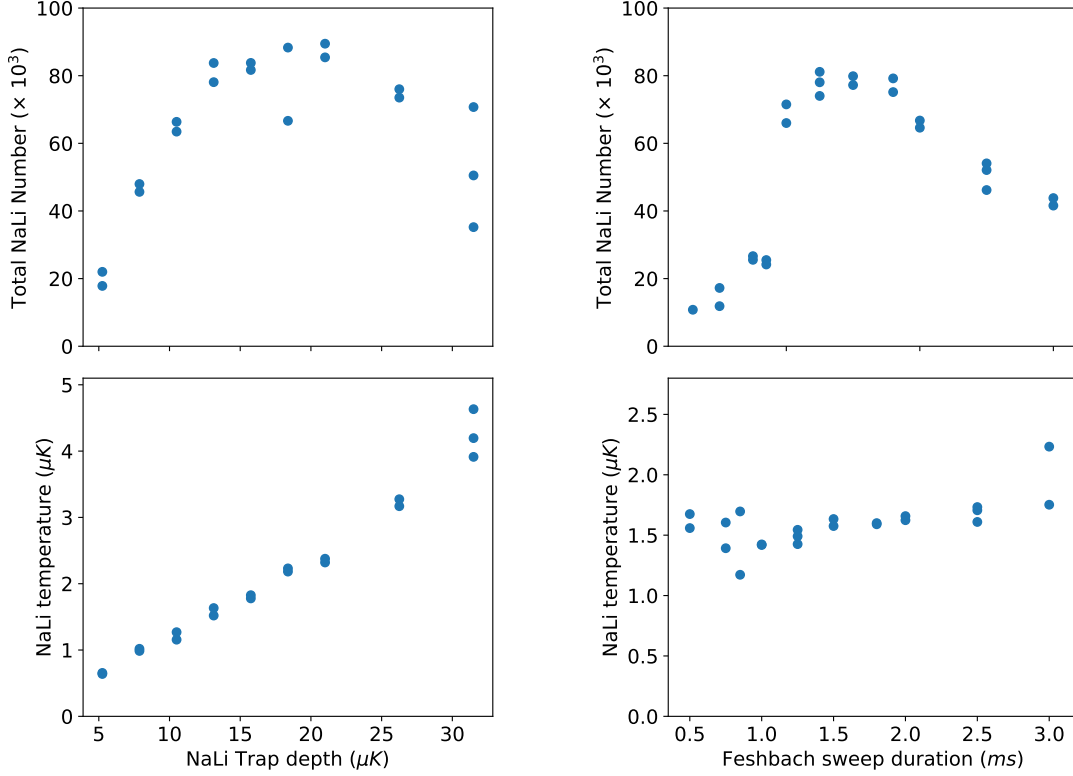


Figure 2.4: Left column: The number and and temperature of ground-state NaLi molecules as a function of 1596 nm lattice trap depth. This should be equivalent to the Feshbach molecule number and temperature, since STIRAP is adiabatic process and its efficiency is nearly perfect. The trap depth of $21 \mu\text{K}$ ($= 40E_r$) for NaLi is equivalent to $7.5 \mu\text{K}$ ($= 11E_r$) for Na atoms (E_r is the two-photon recoil energy of each particle in the 1596 nm trap). We initially load atoms into the 1064 nm ODT which is $\sim 650\mu\text{K}$ deep for Na atoms, while the 1596 nm lattice is at the desired trap depth. Atoms are pinned down into lattice sites, as we evaporate them by lowering the trap depth of the 1064 nm ODT and eventually turning it off. Right column: The number and and temperature of ground-state NaLi molecules as a function of the sweep duration of the magnetic field across the Na-Li Feshbach resonance. The sweep width is fixed at 450 mG, and the trap depth is fixed at $16 \mu\text{K}$. This was acquired with $\sim 2 \times 10^6$ Na atoms at $1.3\mu\text{K}$ and $\sim 7.5 \times 10^5$ Li atoms at $1.7\mu\text{K}$.

The Na atoms left after the molecule production should be lost with molecules at the s -wave universal loss rate since the mixture in non-stretched spin states can undergo reactions. Given the van der Waals (vdW) coefficient between Na atoms and triplet ground-state NaLi molecules, $C_6=4026$ in atomic units⁸², we calculate the s -wave universal

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

loss rate as³:

$$K^{univ} = \frac{2h}{\mu} \bar{a} = 1.85 \times 10^{-10} \text{ cm}^3/\text{s} \quad (2.2.3.3)$$

where $\bar{a} = 0.47799 \cdot r_6$ is the mean scattering length⁸³, and $r_6 = (2\mu C_6/\hbar^2)^{1/4}$ is the vdW length. Given the Na overlap density $\sim 4 \times 10^{12} \text{ cm}^{-3}$, the loss rate of molecules is calculated to be about 740 Hz. Such a fast loss rate can explain why the molecule number rather decreases with a field sweep duration longer than 1.5 ms (see Fig. 2.4).

The main source of the improved molecule formation efficiency is the increase in the overlap density. As we switched to the 1596 1D lattice, we easily achieved a smaller volume of the trap for a single lattice site. For instance, for Na atoms at the same temperature of 2 μK , the mean trap volume is a factor of ~ 2000 smaller compared to that in the 1319 nm ODT. However, such a small trap volume does not give a factor of 2000 higher density, since atoms are distributed across many pancakes in our experiment so that the effective number of atoms in a single lattice site is much less. This was an unavoidable problem for us, since we load atoms from the 1064 nm ODT to the 1596 lattice. When the overlap between the focus of the 1064 nm ODT and that of the 1596 nm lattice was carefully optimized, I found roughly 800 pancakes were occupied for Na atoms. When the system is in the optimal condition, we can load ~ 2 million Na atoms and ~ 0.75 million Li atoms at $\sim 1.5 \mu\text{K}$ in total, which gives the aforementioned maximum molecule transfer efficiency, 11%. At this condition, N_{Na}/V – the number of sodium atoms (i.e. the majority species) in the regime where both particles are overlapped – is about a factor of 3 higher with 50% uncertainty¹. According to Eq. (2.2.3.2), this should

¹I used the Gaussian-weighted mean particle number per pancake for this estimation (see Chapter 2.2.3.1). In quasi-2D, the density distribution in the strongly confined direction can be assumed to be frozen as a Boltzman profile⁸⁴. In this case, the effective 3D volume is $R_x R_y \sqrt{2\pi} L$ where $L = l_0 / \sqrt{2 \tanh(\hbar\omega/2k_B T)}$ with the oscillator length $l_0 = \sqrt{\hbar/\mu\omega}$. Here, $\omega = \mu(\omega_{\text{Na}}/m_{\text{Na}} + \omega_{\text{Li}}/m_{\text{Li}})$ provides the correct kinetic energy $\hbar\omega/4$ of the relative motion between Na and Li atoms. The volume in full 3D is $V \equiv R_x R_y R_{ax}$ where each R is determined by the thermal distribution of particles, and this is the same V in Eq. (2.2.3.2). At our condition, $R_{ax} \approx \sqrt{2\pi} L$.

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

increase the molecule fraction by the same factor so that the expected molecule formation efficiency is 9%, which agrees with the observed value 11% within the uncertainty.

The phase space density is given by $\rho = n\lambda_{\text{dB}}^3 \propto NT^{-3}\Pi_{i=x,y,z}\omega_i$, where the thermal de Broglie wavelength $\lambda_{\text{dB}} = \sqrt{2\pi\hbar^2/mk_BT}$, in a harmonic trap. We achieve a factor 6 higher phase space density with $T/T_c \sim 1$ for Na atoms, compared to the condition used in the 1319 nm ODT. For Li, $T/T_F \sim 0.5$ which is a factor of 2 lower². However, note that since $k_BT \lesssim \hbar\omega_{\text{ax}}$ where ω_{ax} is the trap frequency in the tight axial direction, we are close to the quasi-2D regime. Thus, the numbers mentioned above, which were calculated for the 3D geometry of the trap, would not represent the true physical nature of the particles. As a comparison, $T/T_c^{2D} \sim 2$ and $T/T_F^{2D} \sim 1$ where $k_BT_c^{2D} = \hbar\bar{\omega}(6N/\pi^2)^{1/2}$ and $k_BT_F^{2D} = \hbar\bar{\omega}(2N)^{1/2}$ in a harmonic trap, with $\bar{\omega} = \sqrt{\omega_x\omega_y}$. The phase space density in 2D is given by $n_{2D}\lambda_{\text{dB}}^2 \propto NT^{-2}\Pi_{i=x,y}\omega_i$, and for Na atoms, this is still a factor of 5 higher compared to the condition used with 1319 nm ODT in the past.

2.2.3.1 The number of particles in a single lattice site

We treat each lattice site as an isolated system, and we describe the collisional dynamics of particles across the entire lattice with an effective particle number in a single lattice site. We discuss two different effective particle numbers in this thesis: (1) the particle number estimated with an effective uniform linear density distribution, N_{eff} , (2) the Gaussian-weighted mean particle number, $\bar{N}$.

(1) As we evaporate atoms in a deep 1064 nm ODT into the 1596 nm lattice of a fixed trap depth, they are pinned down into lattice sites, and the overall axial density distribution roughly follows a Boltzmann profile determined by the temperature, which is set by the trap depth of the lattice site. Given the measured Gaussian width σ of the axial density

² T_c and T_F are calculated for the lattice site at the focus of the lattice beam, or at the peak of the axial Gaussian density profile, using the effective particle number per pancake.

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

profile from in-trap absorption images, we calculate the effective length scale l_{eff} in the axial direction as follows:

$$l_{\text{eff}} = 2 \frac{\int_0^\infty z \exp(-z^2/2\sigma^2) dz}{\int_0^\infty \exp(-z^2/2\sigma^2) dz} = \sqrt{\frac{8}{\pi}} \sigma, \quad (2.2.3.4)$$

“The effective number of particles” per lattice site, N_{eff} , is the total number of particles divided by a factor l_{eff}/a , where $a = \lambda/2$ with $\lambda = 1596$ nm (i.e. $N_{\text{eff}} = N/l_{\text{eff}} \times \lambda/2$). The typical Gaussian width $\sigma \sim 0.6$ mm. In this estimation, we assume an uniform linear density of particles, N/l_{eff} , with an axial extension of l_{eff} . This is a factor of $\pi/2$ larger than the central density of the Gaussian distribution.

(2) As it will be discussed in detail in Chapter A.2, the correct density of sodium atoms is obtained with “the Gaussian-weighted mean particle number”, $\bar{N}$, which has been confirmed by the sodium cross-dimensional thermalization measurement and the anharmonic modeling of the single lattice site potential.

The Gaussian-weighted mean particle number per each lattice site, $\bar{N}$ can be calculated as follows:

$$\begin{aligned} \bar{N} &= \frac{C}{N} \int_{-\infty}^{\infty} N_{x_i} e^{-\frac{x_i^2}{2\sigma^2}} dx \\ &= \frac{C^2}{N} \int_{-\infty}^{\infty} \left[\int_{x_i}^{x_i+\lambda/2} e^{-\frac{x'^2}{2\sigma^2}} dx' \right] e^{-\frac{x_i^2}{2\sigma^2}} dx_i \\ &= \frac{C^2}{N} \left(2 \cdot \sum_{x_i=0, \frac{\lambda}{2}, \lambda, \dots} g(x_i) e^{-\frac{x_i^2}{2\sigma^2}} \frac{\lambda}{2} \right) \end{aligned} \quad (2.2.3.5)$$

where $g(x_i)$ is the quantity in side [...], and $C = N / \int_{-\infty}^{\infty} e^{-\frac{x^2}{2\sigma^2}} dx$.

The relation between two particle numbers is given by $N_{\text{eff}} = \frac{\pi}{\sqrt{2}} \bar{N} = 2.22 \times \bar{N}$.

2.2.3.2 Coils & Magnetic field

The Na-Li Feshbach resonance is at 745 G, and such a high bias field is created with two coaxial pairs of coils in Helmholtz configurations. One pair is part of the Ioffe-Pritchard coil packages, and is called “anti-bias” or “Feshbach coils”. The current through the Feshbach coils is generated by a power supply (called “Feshbach power supply”) which can output up to 30V, 500A (TKD-Lambda, ESS 30-500-2-D-0806). The second coils are “compensation” or “shim coils” which can create a bias field $\lesssim 20$ G with a 15V, 15A power supply (KEPCO ATE 15-15DM). For the creation of Feshbach molecules, the Feshbach coils produce ~ 735 G while the shim coils do ~ 10 G. The use of shim coils was to fine tune the magnetic field in the vicinity of the Feshbach field. The actual field sweep across the Feshbach field was done with a third coil, called “a sweep coil” (or, MOK coil) with a 25V, 10A power supply (KEPCO ATE 25-10M). With 7 turns of 32 AWG copper wire, this coil produces ~ 450 mG with 10A current, being inserted into one of the bucket windows of our vacuum chamber to get close to atoms. The key feature of its design is the small cross section with a 1-inch diameter, which gives a small mutual inductance with other coils. In this way, we are able to quickly sweep the magnetic field with a negligible amount of cross-modulation of current flowing through Feshbach and shim coils ³

The width of the Feshbach resonance corresponds to 2% of the sweep width (~ 450 mG), 0.1% of the bias field (~ 10 G) created by shim coils, and $10^{-3}\%$ of the bias field (~ 735 G) created by Feshbach coils. This implies that we have a stringent condition for the stabilization of the bias field created by Feshbach coils, i.e. one part in 10^5 .

³The cross-modulation of current through the Feshbach coils was a problem when we first tried to sweep the field with shim coils. This was due to the large mutual inductance given the dimension of the shim coils of $20\text{ cm} \times 25\text{ cm}$ (rectangular shape).

2.2.3.3 Estimation of the magnetic field noise

- Noise at the Na-Li Feshbach field (i.e. 745 G) was carefully characterized by Timur Rvachov based on the closed-loop measurement of the noise in the current through the Feshbach coils. Such measurement was done with a low-noise fluxgate magnetometer (LEM UltraStab IT 700-S). The RMS noise was $\Delta B_{rms} \sim 2$ mG (within 100 Hz - 10 KHz) with an extra active stabilization with a tweeter transistor in parallel that modulates the current flowing through coils, and $\Delta B_{rms} \sim 10$ mG without this feature ⁴. The active stabilization system was developed by Timur, and details about it can be found in his thesis³⁵. I was able to make 20(5)% more Feshbach molecules with the active stabilization through a tweeter transistor.

It was measured that the major source of the noise was the National Instruments (NI) analog output channel that generated a set point of the power supply output servo. Thus, it was replaced with a more stable voltage source – the programmable digital set point of the PID controller (SRS SIM 960).

- However, I found two limitations in this scheme. First, in order to change the digital set point, we had to give a RS232 command from the control PC to the PID controller (SRS SIM 960). However, the communication time fluctuated from shot to shot by 50 ~ 150 ms. Second, if I change the digital set point for the Feshbach power supply in the experimental sequence, the tweeter transistor tried to counter-act against the change in the output current and pull/push the current close to its limit. This makes the field settlement time longer, and the transistor eventually got thermal damages after multiple runs. The unstable time delay of the RS232 command makes it difficult to engage/disengage the active stabilization at the right time in the middle of the experimental sequence.

⁴The RMS noise above 10 KHz is similar with and without the active stabilization circuit³⁵.

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

- Changing the bias field quickly and time-consistently after producing molecules was important in studying the atom-molecule Feshbach resonances (which will be discussed in Chapter 3). For this reason, I decided not to use the programmable digital set point of the SRS PID controller.
- As a simple solution, I adopted Will Lunden’s development⁸⁵: I replaced the digital set point of the SRS PID controller with a stable and quiet analog set point generated by a 20-bit Digital-to-Analog Converter (DAC) – AD5791 from Analog Device with an on-board voltage reference. A fast and reliable communication between the existing control system, the Field Programmable Gate Array (FPGA), and the DAC was realized through an ethernet connection. Details about the hardwares and control softwares can be found in William Lunden’s doctorate thesis⁸⁵.

Another advantage of using the ethernet communication is to prevent the noise from ground loops, which is a common problem when using the NI analog output cards. Even when we used the digital set point of the SRS PID controller, the 60 Hz peak due to ground loops and its higher harmonics were the major contributors of the noise $\lesssim 1$ KHz.

- According to Will Lunden’s measurement⁸⁵, the Noise Spectral Density (NSD) of the analog voltage output of the AD5791 was found to be about $25 \text{ nV}/\sqrt{\text{Hz}}$ for the frequency $\lesssim 100$ KHz, which corresponds to $\Delta B_{rms} \sim 8 \text{ mG}$. This implies that the RMS noise from Will’s analog set point without the PID feedback is similar to what we achieved with the digital set point and the PID feedback. Indeed, I was able to obtain the same efficiency of Feshbach molecule formation by using the Will’s analog set point, but without the PID feedback and the active stabilization with the tweeter transistor.

Although I have not characterized the noise spectrum and compared, it was obvious

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

that the PID stabilization of the current was eventually needed due to the drift in power supply output. Given the time-scale of the drift, which was ~ 10 minutes, I assumed it was related to some thermal effect, but did not scrutinize it. As the final configuration of field stabilization, I applied the PID feedback to the Feshbach power supply with Will's analog set point, but without Timur's active stabilization circuit. The exact noise level was not measured, but given the fact that I was able to see the similar level of improvement in Feshbach molecule formation, I presume the noise is similar to that with the active stabilization but at least better than without: $\Delta B_{rms} < 10$ mG for $\lesssim 10$ KHz, but ~ 40 mG up to 1 MHz³⁵.

- Given this, we might have non-negligible noise of high-frequency components (> 10 KHz) in the output current. However, the Feshbach coils should act like a low-pass filter itself with a corner frequency of ~ 30 Hz ($L = 250 \mu\text{H}$, $R = 250 \text{ m}\Omega$ ³⁵). Thus the high-frequency noise in the current should not actually translate into the actual field noise much.
- The noise generated by the shim and sweep coils are not measured. The KEPCO power supplies used for both coils have $\lesssim 0.03\%$ ⁵ level of output noise as off-the-shelf specifications. We used the NI analog output channels as set points for the KEPCO power supplies, without PID feedback to them. Given the noise spectral density of the NI analog output, $150 \text{ nV}/\sqrt{\text{Hz}}$ for the frequency $\lesssim 800$ KHz⁸⁵, the RMS noise due to the set point is about 0.01% level. Based on this rough estimation, the noise due to the small coils are not larger than the noise caused by the Feshbach coils.

⁵This is the maximum RMS noise quoted in the user manual. The maximum peak-to-peak noise can be as large as 0.3% over 20 Hz to 10 MHz range bandwidth.

2.2.4 Triplet ground-state molecule formation

The Feshbach molecules are transferred to the ro-vibrational ground state in the same triplet potential via Stimulated Raman Adiabatic Passage (STIRAP). About 3.0×10^4 NaLi triplet-ground state molecules are produced, usually with $\gtrsim 95\%$ STIRAP efficiency⁶. Our STIRAP is performed all in the manifold of the electronic triplet states, unlike making singlet ground-state molecules from the Feshbach molecules in the triplet potential. The latter requires a good mixing of triplet and singlet characters in the intermediate excited state used for STIRAP, which is not needed in making triplet ground-state NaLi. This could be one of the reasons why we easily achieved nearly perfect STIRAP efficiency. The details about the STIRAP can be found in Ref.⁶ and Timur Rvachov’s doctorate thesis³⁵. For the STIRAP, we need to maintain the phase-coherence between two frequencies separated by the energy-scale corresponding to the entire depth of the triplet potential, which is 6 THz for NaLi (for singlet ground-state molecules, the separation is easily on the order of 1000 cm^{-1} or 100 THz). In our case, the two frequencies are 819 nm [366.23611(1) THz] and 833 nm [360.00381(1) THz]^{6,36,37}: the former is for the downleg transition (from the intermediate state of $v = 11$, $N = 1$, $m_N = -1$ in the $c^3\Sigma^+$ excited potential to the ground state of $v = 0$, $N = 0$, $m_N = 0$ in the $a^3\Sigma^+$ potential), and the latter is for the upleg transition (from the Feshbach molecular state to the intermediate excited state). Thus, it requires a sophisticated laser stabilization system with a servo device with a high modulation bandwidth, a precise control of the phase of the electronic signals, and a very narrow and stable optical cavity made with material of an ultra-low expansion (ULE) coefficient. The details about the laser set-up including the servo electronics and the ULE cavity can be found in Sepher Ebadi’s thesis⁸⁶.

The STIRAP transfer occurs in a time window of $\tau \approx 10\mu\text{s}$ when the upleg and downleg

⁶When we conducted this study of the collisional cooling of ground-state molecules, the overall atom numbers were low and we did not create many Feshbach molecules.

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

Rabi frequencies are crossing $\Omega \approx 2\pi \times 5$ MHz, which satisfies the adiabatic criteria (i.e. $\tau \gg \Omega^{-1}$) for such a short STIRAP duration. The peak Rabi frequency during the STIRAP sequence is $\sim 2\pi \times 15$ MHz for both upleg and downleg transitions. Such a high Rabi frequency is achieved with $\sim 400\mu\text{W}$ optical power for the downleg transition with an External-Cavity Diode Laser (ECDL). The ECDL was home-built with components manufactured by the machine shop at University Oregon based on the the unibody Littrow design from the Professor Daniel Steck's lab at the same university⁸⁷. In contrast to the downleg transition, upleg one requires much higher optical power to obtain the same, high Rabi frequency due to the more than two orders of magnitude lower Franck-Condon factor between the Feshbach molecular state and the intermediate excited state⁷. For this reason, we used a Ti:Sapphire laser from M Squared Lasers, which output nearly up to 1 Watt, to drive the upleg transition.

However, we had to replace it with another laser, as the Ti:sapphire laser was needed for other experiments. As a replacement, we assembled another ECDL, just like the one for the downleg, and used it to injection-lock a high-power laser diode from Thorlabs, with a seed power of ~ 2 mW. About 150 mW output power was good enough to obtain the desired Rabi frequency for the upleg transition. STIRAP is very sensitive to the injection lock of the high power laser diode. When its seeding is unstable due to poor alignment or low power of the seed light, or due to the bad mode of the high power laser diode itself, the STIRAP efficiency immediately drops or fluctuates. Thus, we kept eyes on the transmission signal of the injection-locked laser beam through a Fabry-Perot cavity.

⁷The intermediate excited state was chosen to maximize the product of the Franck-Condon factors of the upleg and downleg transitions, in order to obtain the largest possible two-photon Rabi coupling between the Feshbach molecular state to the ground state. A somewhat deeply bound state, $v = 11$ of the $c^3\Sigma^+$ potential, satisfies this condition, since the turning point of the bound-state wavefunction, or the Condon point, has to be at short inter-particle distance. Otherwise the wavefunction overlap between the intermediate and the ground states is very small. This naturally gives much lower wavefunction overlap between the Feshbach molecular state and the intermediate state, since as a highly excited vibrational state, the Feshbach molecular state does not have a large amplitude concentrated at short inter-particle distance. See Ref.³⁵ for details.

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

When a stable single-mode peak is observed, a nearly perfect STIRAP efficiency is still obtained. However, the STIRAP efficiency could sometimes be low even with a stable Fabry-Perot transmission signal of the injection-locked laser diode. In most cases, we find the seed laser itself is slightly multi-mode, which is so subtle that it can be only checked with a wavelength meter (WS-7 from HighFinesse GmbH).

The STIRAP transfer is done with σ^+ and σ^- polarizations for the upleg and downleg transitions, respectively. A fluctuation in polarization can directly affect the efficiency and stability of STIRAP transfer. Thus, it is inevitable to use a “good” polarization-maintaining (PM) fiber to carry the light and apply it to Feshbach molecules. In order to simplify the experimental set-up while minimizing the differential Doppler shift of two different wavelengths, we merge upleg and downleg lights into a single PM fiber and let them co-propagate to Feshbach molecules. The input polarizations are linear but orthogonal to each other, and a combination of a quarter and a half wave plates at the output side of the fiber sets desired circular polarizations as pure as $\gtrsim 90\%$. Although the OZ optics fiber that we used is known for good PM capability, a 10-meter long fiber that we initially set up had a poor long-time PM stability. The purity of polarization can get worse to nearly 50% with a time scale of hours. A 3-meter long fiber, however, showed nearly perfect PM stability. We found the polarization for both wavelengths are maintained after weeks with a shorter PM fiber. Such finding – longer fibers are likely to give worse PM – was almost universal for fibers for other wavelengths: 589 nm and 671 nm.

2.2.4.1 Laser linewidth estimation

The linewidth of the ECDL with an active frequency stabilization was estimated with two different methods. The first method was based on the frequency discriminator from which we can convert the fluctuation in the voltage error signal to the frequency noise.

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

We stabilize the frequency of the ECDL using the Pound–Drever–Hall (PDH) scheme. The general background and useful quantitative analysis about this scheme is well elaborated in Ref.⁸⁸. Here, in this chapter, I discuss some result from the Ref.⁸⁸ without detailed derivation.

The modulation frequency for the PDH lock scheme in our set up is 32(12) MHz for the downleg(upleg) laser. The cavity linewidth $\delta\nu \equiv f_{\text{FSR}}/F = 28(16)$ KHz with the spectral range of the ULE cavity $f_{\text{FSR}} = 1.5$ GHz and the finesse $F = 53340(95000)$ for the downleg(upleg) laser frequency⁸⁶. Thus, when the carrier is near resonance with the cavity, the sidebands are easily off resonance with such a high modulation frequency and are completely reflected off the cavity. In this regime, the error signal can be written as

$$\epsilon \approx -8\sqrt{P_c P_s} \frac{df}{d\nu} \equiv D \times df \quad (2.2.4.1)$$

where the power in the carrier $P_c = J_0(\beta)^2 P_0$ and the power in the sidebands $P_s = J_1(\beta)^2 P_0$ (J_0 and J_1 are Bessel functions of the first kind, P_0 is the total incident power, and β is the modulation depth⁸). This is a good approximation as long as the fluctuation in the laser frequency, df is much less than the cavity linewidth, $d\nu$ ⁸⁸. The proportionality constant D between the error signal and the laser frequency noise is called the “frequency discriminator”. The larger D makes the feedback of the laser stabilization more sensitive to the laser frequency noise; thus, we try to maximize the factor $\sqrt{P_c P_s}$ with the optimum modulation depth $\beta = 1.08$, which corresponds to $P_s/P_c = 0.42$ ⁸⁸. The actual power ratio in our experiment is $P_s/P_c = 0.47(0.55)$ for the downleg(upleg) laser system. Given this, we calculate the frequency discriminators as $D_{up} = 0.286$ (V/Hz) and $D_{down} = 0.168$ (V/Hz). We read out the fluctuation in the error signal from the servo electronics (D2-125 from Vescent Photonics), and convert it to the actual frequency

⁸The electric field with its phase modulated at the frequency f_{mod} is written by $E = E_0 e^{i(\omega t + \beta \sin(f_{\text{mod}} t))}$, given the modulation depth of β

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

noise. The servo electronics provides the monitor ports for DC error signal (low-pass filtered with a corner frequency 200 KHz) and AC error signal (high-pass filtered with a corner frequency 10 Hz). With the DC error signal, the frequency noise is estimated as $df_{down} \approx 180$ Hz and $df_{up} \approx 320$ Hz. The noise is a factor of ~ 3 higher with the AC error signal. However, this should be regarded as the upper bound of the actual linewidth of the laser since it could be broadened by the detection noise from the readout port.

In STIRAP, the phase coherence between upleg and downleg frequencies should be maintained, and this can be inferred from the relative linewidth between two lasers. This can be measured by tuning the two frequencies close to each other (i.e. 1 FSR apart), beating them, and detecting the beat note signal from a photodiode, just like we did it with the Ti:Sapphire laser⁹⁸⁶. Ever since we replaced the Ti:sapphire laser with a new ECDL, we have not characterized the relative linewidth between two ECLDs since the STIRAP efficiency was as good as before.

The second method was directly measuring the spectral linewidth of a beat note created by beating the zero-th order and the first diffraction order beams from an acousto-optic modulator (AOM). We drove the AOM with a RF signal of 80 MHz. The first diffraction order was coupled into a 15-meter long PM fiber, and the output light was merged with the zero-th order light on a beam cube. The beat note signal read by a photodiode was fed into a RF spectrum analyzer from which we were able to directly measure the linewidth of the laser, which was approximately 100 Hz¹⁰. This is somewhat close to the linewidth estimation done with the DC error signal read-out from the servo electronics.

This measurement verifies that the broadening due to the long fiber is not so severe. We

⁹This method does not tell us much about the broadening due to frequency-dependent noise. For instance, the noise induced by the ULE cavity due to thermal fluctuation should not be common-mode as upleg and downleg frequencies are separated by ~ 230 GHz.

¹⁰Unfortunately, we were not able to obtain an accurate number by fitting the data, since the RF spectrum analyzer that we used did not have a data export functionality.

align the input linear polarization of the downleg light, for instance, to the slow axis of of the PM fiber, while that of the upleg light to the fast axis. Thus, two lights could experience differential noise through the fiber, due to different refractive indexes of slow and fast axes. Our measurement can be regarded as a test of the worst-case scenario where the difference of the refractive indexes is even larger (air vs fiber, rather than slow axis VS fast axis of the fiber).

2.2.5 Removal of free atoms

Immediately after producing ground-state molecules at 745 G, free atoms left in the trap are cleaned out with resonant beams. For fast clean-out, we send the resonant beams along the radial direction of the trap. Blasting the beams along the axial direction makes the clean-out inefficient due to the high optical density of atoms.

The leftover Li atoms in the lowest hyperfine state, $|1, G\rangle = |m_J = -1/2, m_I = 1\rangle$, which I call state 1 in this chapter, can be efficiently removed with light resonant with the state $|3, D_2\rangle = |m_J = -3/2, m_I = 1\rangle$ in the D2 line. This transition is cycling with σ^- polarization, since Li atoms are in the so-called high-field regime at 745 G where the Zeeman energy associated with the electronic spin is sufficiently larger than the energy scale of the hyperfine coupling: i.e., the states $|1, G\rangle$ and $|3, D_2\rangle$ are pure states in the $|m_J, m_I\rangle$ basis. Thus, this transition is efficient for both the clean-out of leftover atoms and the imaging of Li atoms dissociated from the molecular state in the latter stage of the experiment. In the set-up, the resonant light is generated as the negative first diffraction order of the MOT beam through a double-pass AOM driven at 426.73 MHz.

It is a bit trickier to clean out the sodium atoms. Due to the large hyperfine coupling strength in the ground state, the lowest hyperfine state of sodium atoms at 745 G has a little bit of admixture of a different m_J, m_I component: $|1, G\rangle = -0.236 |m_J = 1/2, m_I = 1/2\rangle + 0.972 |m_J = -1/2, m_I = 3/2\rangle$. We apply

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

a σ^- -polarized light resonant with the lowest hyperfine state of the D2 line, $|1, D2\rangle \approx 0.998 |m_J = -3/2, m_I = 3/2\rangle - 0.0185 |m_J = -1/2, m_I = 1/2\rangle$. So, after we excite the atoms from $|1, G\rangle$ to $|1, D2\rangle$, they can fall down to the state 7 in the ground state, $|7, G\rangle = 0.972 |m_J = 1/2, m_I = 1/2\rangle + 0.236 |m_J = -1/2, m_I = 3/2\rangle$, which is anti-symmetric to $|1, G\rangle$ in terms of the hyperfine state components. The probability ratio between the transition back to the initial state $|1, G\rangle$ and that to the state $|7, G\rangle$ (which is proportional to the ratio of the matrix elements squared) is roughly 0.95 : 0.05. Given the recoil energy of $2\pi \times 25$ KHz from the resonant clean-out beam and the radial trap depth of $\sim 8\mu\text{K}$, we need roughly about 5 photons to be scattered by the Na atoms at $1.5\mu\text{K}$ for their removal out of the trap. This gives a probability of $1 - (0.95)^5 = 0.22$ for atoms to optically be pumped into the state $|7, G\rangle$ not being kicked out of the trap. In order to clean the atoms in the state $|7, G\rangle$, we apply a σ^+ -polarized light resonant with the state $|15, D2\rangle \approx |m_J = 3/2, m_I = 1/2\rangle$. By applying the clean-out lights for both $|1, G\rangle$ and $|7, G\rangle$ states, we can make Na atoms scatter photons in an almost perfect cycling transition.

We first blast the clean-out beam for the state $|1, G\rangle$ at the scattering rate of $\sim 2\pi \times 15$ KHz for $\lesssim 100\mu\text{s}$, in order to remove most of the dense atomic cloud in the lowest hyperfine state (atoms can scatter roughly $\lesssim 9$ photons as maximum). Then, we shine the clean-out beams for both $|1, G\rangle$ and $|7, G\rangle$ states for another $\sim 300\mu\text{s}$ to completely get rid of Na atoms of the trap. The scattering rate of the state $|7, G\rangle$ clean-out beam is approximately a factor of 2 smaller than that of the state $|1, G\rangle$ clean-out beam. Since we generate the state $|7, G\rangle$ clean-out beam by shifting the frequency of the state $|1, G\rangle$ clean-out beam by $+2 \times 441.5$ MHz with a double-pass AOM, we naturally obtain a lower power of the zero-th order beam for the $|1, G\rangle$ clean-out when the $|7, G\rangle$ clean-out beam is being applied. This is why we first shine the state $|1, G\rangle$ clean-out beam only. In this way, the overall clean-out step becomes more time-efficient. It is also better since the denser

could of the state $|1, G\rangle$ atoms is more harmful for the collisional loss of the ground-state molecules, compared to the optically-pumped $|7, G\rangle$ state atoms¹¹.

2.2.6 Detection & thermometry of molecules

In order to avoid issues with different atomic and molecular trapping potentials, we dissociate molecules in free space after turning off the trap, which allows accurate molecular thermometry. Since the particle velocities are fixed after the trap is turned off, the density at some time-of-flight maps the velocity distribution of molecules in the trap. The molecule temperature is determined from a fit to such density profiles. Extra kinetic energy could be added in quadrature while Feshbach molecules dissociate into atomic continuum states⁸⁹. We determine the parameters of Feshbach dissociation (i.e., the rate of magnetic field sweep) in order to minimize the released dissociation energy. All uncertainties for the temperatures quoted in this chapter are from statistical errors and fit errors. The systematic uncertainty, which is mainly determined by the imaging magnification, is $\approx 6\%$ but has no effect on measured thermalization rates since it gives a common multiplier to all temperature measurements.

2.2.6.1 Dissociation of molecules

Feshbach molecules created by open-channel dominated resonances can be directly detected via a typical absorption imaging technique⁵. However, NaLi or molecules created via closed-channel dominated Feshbach resonances cannot be easily imaged due to a lack of cycling transitions. Thus, we dissociate the molecules into free atomic continuum states, which then can be detected with a beam resonant to the atoms. However, since the resonance is very narrow (i.e. 10 mG wide), it is technically challenging to dissociate

¹¹This is just for the sake of optimization. Since the clean-out duration is on the order of millisecond, the actual collisional loss of molecules during the clean-out step is not significant.

the molecules adiabatically into the lowest energy state of free atoms.

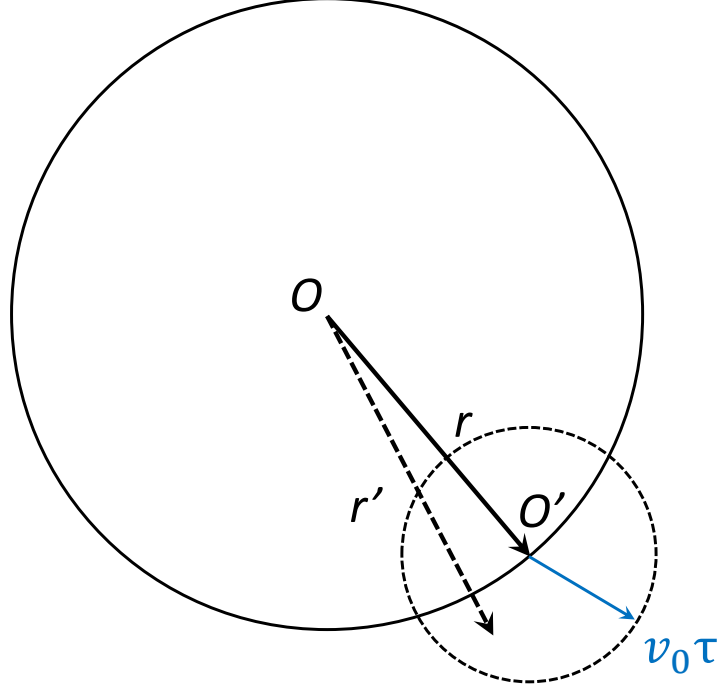


Figure 2.5: During some TOF before the dissociation, molecules fly out from the origin O , or the center of the trap, with mean kinetic energy determined by their true temperature. Such a TOF gives a Gaussian density profile which is represented by the vector r and the circular contour with a solid line in the figure. As molecules are dissociated, they gain extra kinetic energy and fly out with v_0 (given by the mean dissociation kinetic energy) for time τ , the TOF after the dissociation. I assumed v_0 is much larger than the molecules' speed before the dissociation. The contour with a dotted line represents the density profile of atoms departing from O' after the dissociation. The dotted contour is determined by the probability density of velocity of the dissociated atoms $D(v)$. What we observe in the experiment as a result of the absorption imaging of the dissociated atoms is the convolution of two (solid and dotted) density profiles.

Molecular signals are usually weak, and a long field sweep for dissociation, which makes the Time-Of-Flight (TOF) longer¹², makes it generally difficult to obtain reliable counting of particle numbers and fitting of the density profile, which is important for temperature

¹²Due to the difference in AC polarizability between molecules and free atoms, we have to dissociate molecules not in the optical trap but in free space.

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

measurement. For this reason, it is inevitable to dissociate NaLi molecules into higher momentum states, but then we have to minimize the energy realised in the dissociation (i.e. dissociation kinetic energy)⁸⁹, which prevents an accurate temperature measurement of molecules. In the following, I will derive how the dissociation kinetic energy affects the density distribution of atoms after dissociation.

Based on the Fermi's Golden rule, the decay rate of molecules to the atomic continuum states is given by⁸⁹:

$$\Gamma_m(\epsilon) = \frac{2|\Delta B \Delta \mu|}{\hbar} \left(\frac{2\mu a_{bg}^2 \epsilon}{\hbar^2} \right)^{1/2} \quad (2.2.6.1)$$

where ϵ is the energy of the molecular state with respect to the dissociation threshold, i.e. $\epsilon = \Delta \mu (B - B_{res})$ where $\Delta \mu$ is the differential magnetic moment between the molecular state and the atomic state and B_{res} is the position of resonance in magnetic field. ΔB is the width of the resonance, μ is the reduced mass, and a_{bg} is the background s -wave scattering length. Considering a linear ramp of magnetic field $\dot{B}$ across the resonance, the molecule fraction, f that decays to an atomic continuum state with energy ϵ is given by^{89,90}:

$$f(\epsilon) = \exp \left[- \frac{4|\Delta B|}{3\hbar \dot{B}} \sqrt{\frac{2\mu a_{bg}^2}{\hbar^2} \epsilon^{3/2}} \right] \equiv \exp \left[C \epsilon^{3/2} \right] \quad (2.2.6.2)$$

Given $f(\epsilon)$, we calculate the mean kinetic energy of a single atom of mass m_i as follows^{89,90}:

$$\begin{aligned} \langle E \rangle_i &\equiv \Gamma \left(\frac{5}{3} \right) \frac{1}{2} m_i v_{0,i}^2 \quad \text{where} \\ v_{0,i}^2 &= C^{-2/3} \frac{m_j}{M} \frac{2}{m_i} \end{aligned} \quad (2.2.6.3)$$

where $M = m_{\text{Li}} + m_{\text{Na}}$ is the mass of a single molecule, $\{i, j\}$ is the index for Li or Na, and $\Gamma(5/3) \approx 0.903$. The mass ratio m/M comes in when I convert the relative kinetic energy in the center-of-mass frame to that in the lab frame. After transformation, we get $v_{0,\text{Li}}/v_{0,\text{Na}} = \langle E \rangle_{\text{Li}} / \langle E \rangle_{\text{Na}} = m_{\text{Na}}/m_{\text{Li}}$. Given $f(\epsilon)$, we come up with the probability

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

density of velocity of the atoms, $D(v)$ ⁹⁰:

$$D(v)d^3v = \frac{3}{4\pi v_0} \exp\left(-\frac{v^3}{v_0^3}\right) d^3v \quad (2.2.6.4)$$

This velocity distribution is converted into a density distribution in real space with a TOF imaging. For TOF of τ after the dissociation, the density distribution is given by:

$$D(r)d^3r = \frac{3}{4\pi v_0 \tau} \exp\left(-\frac{r^3}{(v_0 \tau)^3}\right) d^3r \quad (2.2.6.5)$$

The contour of a dotted line in Fig. 2.5 should follow this form. Given the Gaussian density profile of molecules before the dissociation, $d(r) \sim \exp(r^2/\sigma^2)$ (the contour with a solid line contour in Fig. 2.5), we can write the final density distribution after the dissociation as a convolution of two functions, d and D :

$$n(r') = \int d^3r d(r)D(r-r') \propto \int d^3r \exp(-r^2) \exp\left(-\frac{(r-r')^3}{b^3}\right) \quad (2.2.6.6)$$

Here I normalized the position vectors by σ , i.e. $r/\sigma \rightarrow r$, and $b = v_0 \tau / \sigma$. Note that there is no analytic form of $n(r')$. Thus, we apply the convolution theorem. The Fourier Transform (FT) of $n(r')$ is given by:

$$n(k') = \int d^3k d(k)D(k-k') \propto \int d^3k \exp\left(\frac{-k^2}{4}\right) H(k-k') \quad (2.2.6.7)$$

where, according to Mathematica, the function H , which is the FT of D , is given by:

$$\text{HypergeometricPFQ}\left[\{1\}, \left\{\frac{1}{3}, \frac{2}{3}, \frac{5}{6}, \frac{7}{6}\right\}, -\frac{b^6 p^6}{11664}\right] - \frac{2\pi \left(\text{KelvinBer}\left[-\frac{2}{3}, \frac{2(bp)^{3/2}}{3\sqrt{3}}\right] + \text{KelvinBer}\left[\frac{2}{3}, \frac{2(bp)^{3/2}}{3\sqrt{3}}\right] \right)}{3\sqrt{3}}$$

where $p = k$, *HypergeometricPFQ* is the generalized hypergeometric function, and

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

$KelvinBer$ is the Kelvin function ¹³. This complicated result can be expanded as:

$$\begin{aligned} H(k) &= \exp \left[-\frac{2\pi b^2}{\sqrt{3} 27 \Gamma[4/3]} k^2 - 10^{-3} b^4 k^4 + \mathcal{O}[(k \cdot b)^6] \right] \\ &\approx \exp \left[-0.15 b^2 k^2 \right] \end{aligned} \quad (2.2.6.8)$$

assuming $b \ll 1$. The validity of this approximation will be discussed later.

Then, the final density distribution $n(r')$ is the FT of the convolution of two Gaussian functions, which is a Gaussian function, and the width squared or the variance is the sum of variances of two Gaussian functions:

$$\begin{aligned} n(r') &\approx n_G(r') \propto \int d^3 k' e^{ik' \cdot (r/\sigma)} \int d^3 k \exp \left(\frac{-k^2}{4} \right) \exp \left(-0.15 b^2 |k - k'|^2 \right) \\ &\propto \exp \left(-\frac{r'^2}{\sigma^2 (1 + 0.6b^2)} \right) \end{aligned} \quad (2.2.6.9)$$

which means the final density profile $n(r')$ can be approximated as a Gaussian function $n_G(r')$ with a width given by:

$$\sigma_{approx}^2 \approx \sigma^2 + 0.6(v_0\tau)^2 \quad (2.2.6.10)$$

Note that the numerical factor 0.6 occurs due to the definition of v_0 . In 3-dimension, the Maxwell-Boltzmann distribution of velocity is given by $\sim \exp[-mv^2/2k_B T] = \exp[-v^2/v_{MB}^2]$ where $v_{MB}^2 = 4 \langle E \rangle / 3m$, since the mean kinetic energy is $\langle E \rangle = 3k_B T/2$. When the probability density of the velocity after dissociation, $D(v)$, is approximated to a Gaussian distribution in leading order, $D(v) \approx \exp[-v^2/\Sigma^2]$ where $\Sigma^2 = 8\pi v_0^2 / 27\sqrt{3}\Gamma(4/3) = 16\pi \langle E \rangle / 27\sqrt{3}\Gamma(4/3)\Gamma(5/3)m$, given the mean dissociation kinetic energy $\langle E \rangle = \Gamma(5/3)mv_0^2/2$ for a homonuclear case (see Eq. (2.2.6.3)). We see

¹³Please look up the Wolfram website for details about these functions.

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

here the definition of v_0 is different from the velocity v_{MB} : Given $\langle E \rangle = 3mv_{\text{MB}}^2/4$, we find the relation $v_{\text{MB}}^2 = \Gamma(5/3) \cdot 2/3 \times v_0^2 \approx 0.6v_0^2$. This gives $D(v) \approx \exp[-v^2/v_{\text{MB}}^2]$ ¹⁴ from which we write the (approximated) Gaussian width of the final density distribution as the quadrature-sum of two Gaussian widths squared: $\sigma_{\text{approx}}^2 \approx \sigma^2 + (v_{\text{MB}}\tau)^2$ (as expected).

This tells us when the width or spread due to the dissociation energy is much larger than the width set by the molecule's temperature (i.e. $v_{\text{MB}}\tau \gg \sigma$), the total (approximated) Gaussian width is determined solely by the dissociation width (i.e. $\sigma_{\text{approx}} \approx v_{\text{MB}}\tau$, as expected). However, in this limit, the density profile will no longer be a Gaussian.

To check the validity of the Gaussian approximation of the final density distribution, I fitted the analytic solution of the final density distribution $n(r')$ with *HypergeometricPFQ* and *KelvinBer* functions (instead of Eq. (2.2.6.8)) to a Gaussian function. Fig. 2.6 shows the fitted Gaussian width as a function of the parameter b . We see for $b \lesssim 1$, Eq. (2.2.6.9) is a good approximation. The Gaussian approximation of the final density distribution gives a width $\sim 6\%$ larger than σ_{approx} , when $v_0\tau \approx 1.5\sigma$, and the discrepancy is about 2% for $v_0\tau \approx 1\sigma$.

2.2.6.2 Thermometry of molecules

In the limit of a small b parameter, if we know $v_0\tau$ by measuring the dissociation kinetic energy, we can use Eq. (2.2.6.9) to obtain the true temperature of molecules from a Gaussian fit. In general, by fitting the density profile to the exact expression of $n(r')$ which requires numerical integration, one should be able to acquire the temperature of molecules as well.

¹⁴ $\frac{8\pi}{27\sqrt{3}\Gamma(4/3)} \times \frac{3}{2\Gamma(5/3)} = 1$

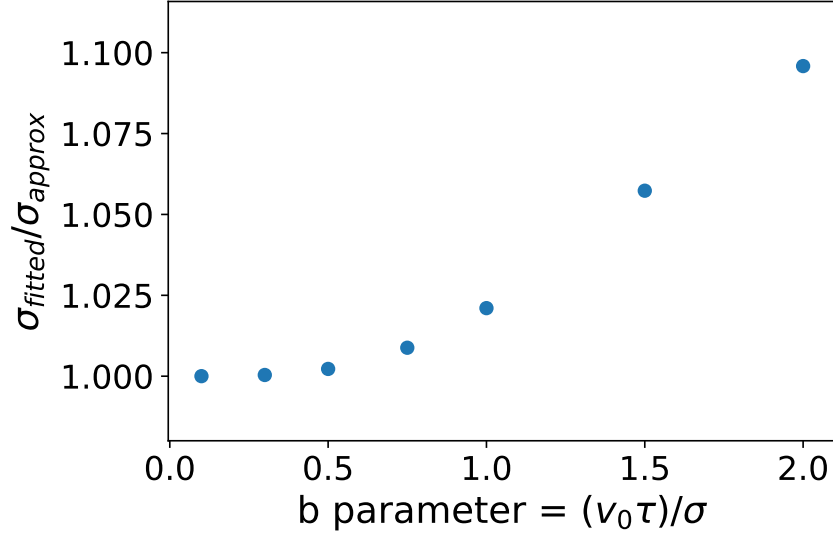


Figure 2.6: The deviation of the final density distribution $n(r')$ from a Gaussian profile as a function of b parameter. σ_{approx} is calculated for $\sigma = 1$. σ_{fitted} is the width of a Gaussian profile fitted to the density distribution with H-function without Gaussian approximation (i.e. used the H-function in terms of *HypergeometricPFQ* and *KelvinBer* functions).

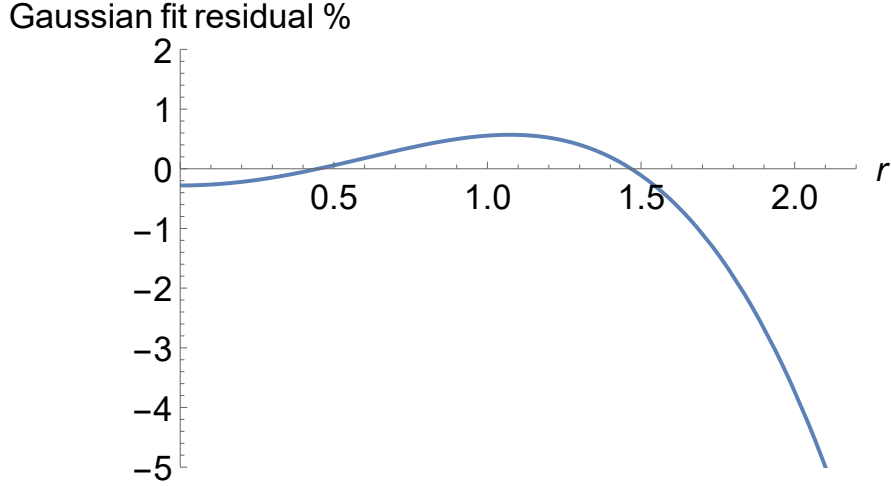


Figure 2.7: The residual of the Gaussian fit of the density distribution with $b = 1$ ($\sigma_{fitted} \approx 1.3\sigma$). The residual is defined as $[n(r') - G(r')]/n(r') \times 100(\%)$ where $G(r')$ is a Gaussian fit of $n(r')$. $2r \approx 1.54\sigma_{fitted} \approx 2\sigma$ is where the density is 10% of the peak value.

In order to make the b parameter small, we need to minimize $v_0 \tau \propto \dot{B}^{2/3} \tau \sim \delta B^{1/3} \tau^{2/3}$ for a given σ , the width set by the temperature of molecules. How small τ can

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

be could be limited by the decay rate of the molecules, Γ_m (Eq. (2.2.6.2)). Since $\Gamma_m \propto \epsilon = \Delta\mu(B - B_{res})$, it is advantageous to raise the field high above the dissociation field to get a small τ . For instance, in the case of $(B - B_{res}) = 400\text{mG}$, $\Gamma_m = 2\pi \times 14$ KHz for NaLi, which corresponds to $\tau \approx 50 \mu\text{s}$. As another relevant time scale, the field sweep duration can be shortened by switching off the power supply for the sweep coil. In this case, we can change the field of $\sim 400\text{mG}$ in $\sim 10 \mu\text{s}$. With such a fast dissociation ramp, atoms will acquire a large amount of kinetic energy, but by minimizing τ , we do not allow the density profile of atoms to be broadened (too much) by the dissociation kinetic energy, or v_0^2 . Of course, giving TOF before dissociation as long as possible is also important to realize this scheme. When the molecular signal is low, this may not be easily feasible, but by averaging multiple images, we can suppress the background noise in images and make the fitting of density profiles work ¹⁵.

Fig. 2.8 shows Gaussian widths of dissociated Li and Na atoms as a function of TOF after the dissociation, τ . The Gaussian width is fitted to Eq. (2.2.6.9) where $\sigma^2 = (2k_B T_{\text{NaLi}}/m_{\text{NaLi}})(1 + \omega^2 t^2)/\omega^2 \approx (2k_B T_{\text{NaLi}}/m_{\text{NaLi}})t^2$ ($t = 2.53$ ms is the TOF as molecules and $\omega = 2\pi \times 610$ Hz is the radial trap frequency for molecules, which gives $\omega^2 t^2 \approx 90$). At $\tau = 0$, both atoms gives the width $\sigma \approx 65 \mu\text{m}$, which corresponds to $T_{\text{NaLi}} \approx 1.1 \mu\text{K}$. As a result of the fitting, we get the ratio $v_{0,\text{Li}}/v_{0,\text{Na}} = 3.59(28) \approx m_{\text{Na}}/m_{\text{Li}} = 3.83$ as expected. This gives the dissociation energy $\langle E \rangle_{\text{Li}} / \langle E \rangle_{\text{Na}} \approx 11 \mu\text{K}/3.3 \mu\text{K}$, which implies that the total dissociation energy is $\approx 14.5 \mu\text{K}$ for the fastest sweep rate that we could apply by turning off the power supply for the sweep MOK coil. Energies were obtained as $3/2 \times \Gamma(5/3)mv_0^2/2$ considering all (x, y, z) degree-of-freedom: v_0 is measured as a radial speed (i.e. $v_0^2 = \langle r^2 \rangle / \tau^2 = \langle x^2 + y^2 \rangle / \tau^2$) from the radial density profile, and the dissociation energy

¹⁵Please note that this is not the only optimal way of dissociating molecules and measuring the temperature. The dissociation with slower sweep rates with longer τ can be as effective as aforementioned fast-dissociation scheme depending on the parameters.

is equally distributed into three directions (i.e. $\langle x^2 + y^2 + z^2 \rangle / \tau^2 = 3v_0^2/2$).

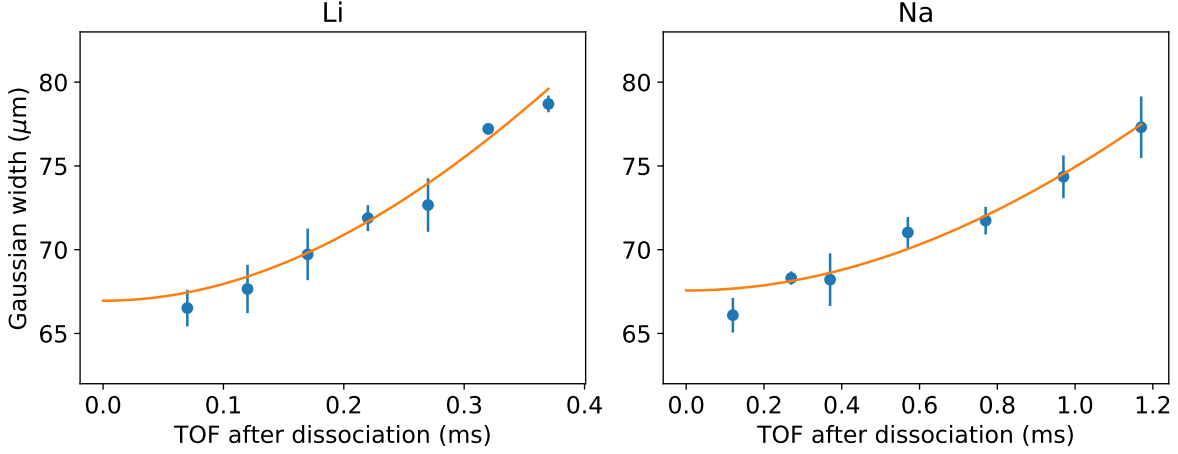


Figure 2.8: The root-mean-square Gaussian width of the radial density profile of dissociated atoms as a function of TOF after dissociation. Total TOF – the sum of TOF as molecules before dissociation and TOF after dissociation – is fixed to 2.53 ms. The dissociation was done by switching off the power supply for the sweep MOK coil, which made the sweep rate ~ 20 G/ms. The b parameter is 1 with τ around 0.5 ms for Li atoms and around 1.2 ms for Na atoms.

We mainly imaged dissociated Li atoms to count the molecules and measure their temperature. Initially, this was to harness the cycling transition of the Li imaging. However, as we discussed so far, the temperature of Li atoms are more sensitive to the dissociation condition since they take a factor of $m_{\text{Na}}/m_{\text{Li}} = 3.83$ larger dissociation energy than Na atoms. After I realized this, I wanted to rather image Na atoms; doing so, we can reduce the TOF before dissociation while keeping the b parameter small enough so that we do not need to worry about the extra correction in molecule temperature measurement. Such a shorter TOF would be useful especially when the molecular signal is low. However, imaging both dissociated Na atoms (in the state 1) and the coolant Na atoms (in the state 8) was technically challenging in our set up ¹⁶.

¹⁶Imaging both state 1 and 8 atoms in an experimental sequence is not completely impossible. Some modification/addition of AOM set-ups and/or optimization of the software trigger timing for shutters would make it feasible.

2.2.6.3 Dissociation without magnetic field sweep

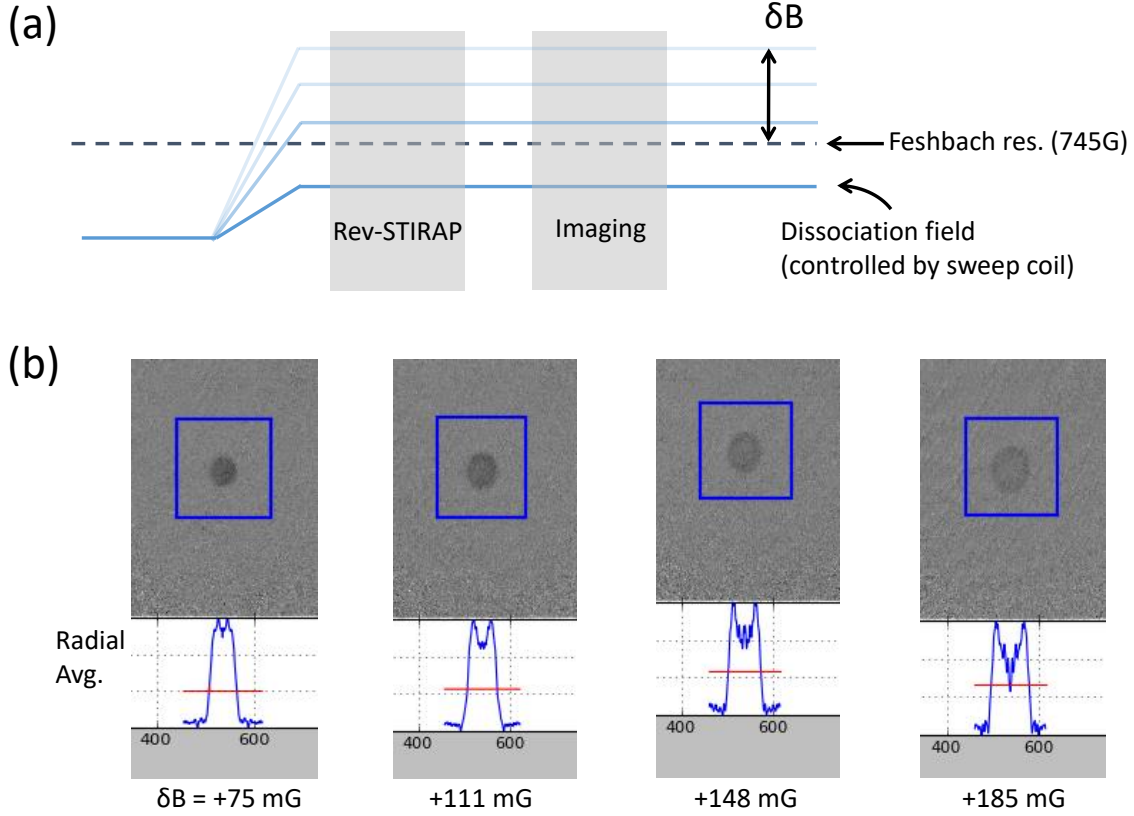


Figure 2.9: (a) Experimental sequence of creating a monoenergetic spherical wave of dissociated atoms. Normally, we sweep the field across 745G for dissociation after the reverse-STIRAP sequence. However, by raising the field above the resonance (i.e. $\delta B > 0$) before the reverse-STIRAP, we can dissociate Feshbach molecules into a very narrow range of relative momentum states of free atoms, which appear as a spherical wave in 3D. (b) The absorption imaging of the spherical wave of dissociated Li atoms, which is integrated along the axial direction of the lattice, shows a ring in 2D. The radially averaged density profile clearly shows a ring of a certain momentum state. The images were acquired with 0.4 ms of TOF after the reverse-STIRAP.

By transferring the ground-state molecules to the Feshbach molecular state above the Feshbach resonance, say at $\delta B + 745\text{G}$, we make all molecules dissociate at the specific magnetic field. This implies that every dissociated atom flies away with the same amount of kinetic energy, which will appear as a spherical shell of atoms after some TOF. The radius of the spherical wave should be determined by the dissociation energy which should be the same

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

as the Zeeman energy of the Feshbach molecular state relative to the dissociation threshold (i.e. the zero relative momentum state of the atoms). The monoenergetic spherical waves of dissociated Li atoms as a function of the dissociation field, δB are shown in (b) of Fig. 2.9. The absorption imaging integrates the 3-dimensional spherical wave along the axial direction of the lattice, and the resultant density profile appears as a 2-dimensional ring, which is more obvious from the radially averaged density profile. Due to the magnetic field noise and the initial momentum distribution of molecules, the ring profile is not perfect.

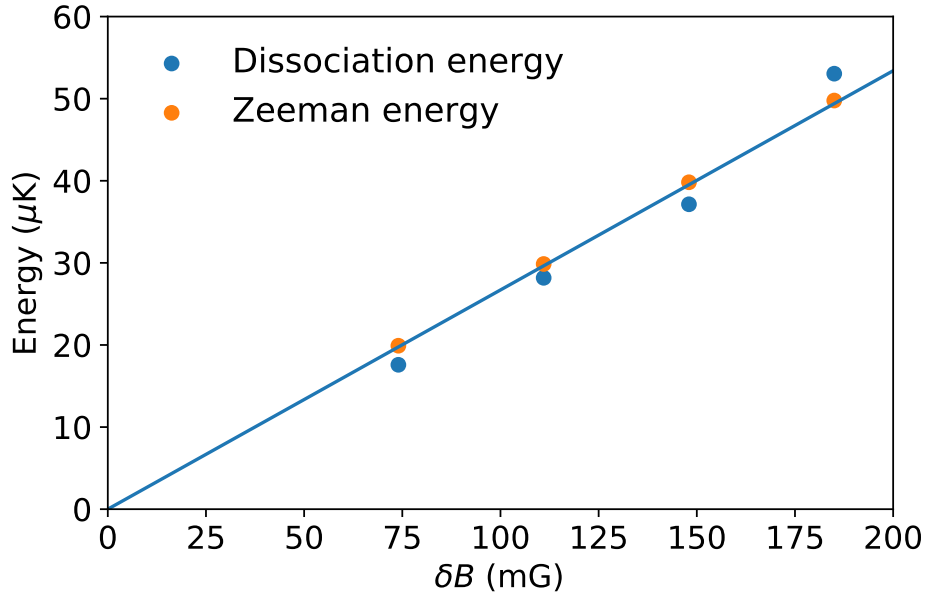


Figure 2.10: The total dissociation energy $\langle E \rangle$ as a function of the dissociation field δB . The blue line is a linear fit of $\langle E \rangle$: the fitted slope is $0.27(1) \mu K/mG$, which agrees with $\Delta\mu = 4\mu_B$. We found a good agreement between the measured $\langle E \rangle$ and the calculated Zeeman energy of molecules relative to the dissociation threshold, $\Delta\mu\delta B$.

By measuring the kinetic energy of dissociated Li atoms, we calculate the total amount of dissociation energy at each δB : $\langle E \rangle = M/m_{Na} \times m_{Li}(\frac{3}{2}v_r^2)/2$ where $v_r^2 = (r/\tau)^2$ (r : the radius of the ring¹⁷, $\tau = 0.4$ ms). As discussed, we expect $\langle E \rangle = \Delta\mu \delta B$ where the differential magnetic moment between the molecular and atomic states is $\Delta\mu = 4\mu_B$.

¹⁷For this, I used the distance between the two peaks that appear in the density profile divided by two.

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

Figure 2.10 shows that the measured total dissociation energy agrees with the calculated Zeeman energy of molecules at δB .

The creation of monoenergetic spherical wave of atoms was demonstrated in Ref.⁹⁰ where rapid jump of magnetic field was used to dissociate Feshbach molecules at a certain field. Dissociating molecules via reverse-STIRAP with very narrow lasers would be more advantageous in creating sharper ring edges, since molecules can be dissociated into multiple, lower momentum states during the magnetic field jump if the field jump rate slows down near the final dissociation field (this was a limiting factor in Ref.⁹⁰). This could be more problematic with broader resonances since molecules will decay faster. The scheme introduced here for the dissociation of ground-state molecules can be useful in studying the pair correlation of dissociated atoms with outgoing wave functions that appear in density profiles. Study of a shape resonance with a spatial interference pattern is another possibility, as shown in Ref.⁹¹.

2.3 Results

Owing to the differential polarizability at 1596 nm, molecules feel a deeper trapping potential than atoms. This results in a sudden increase of the potential energy as atoms associate and form molecules (see Fig. 2.11 a). Immediately after production, the effective temperature of the molecules is 2.80(6) μK and the temperature of Na atoms is 2.42(3) μK (all uncertainties are as defined in the legend of Fig. 2.11).

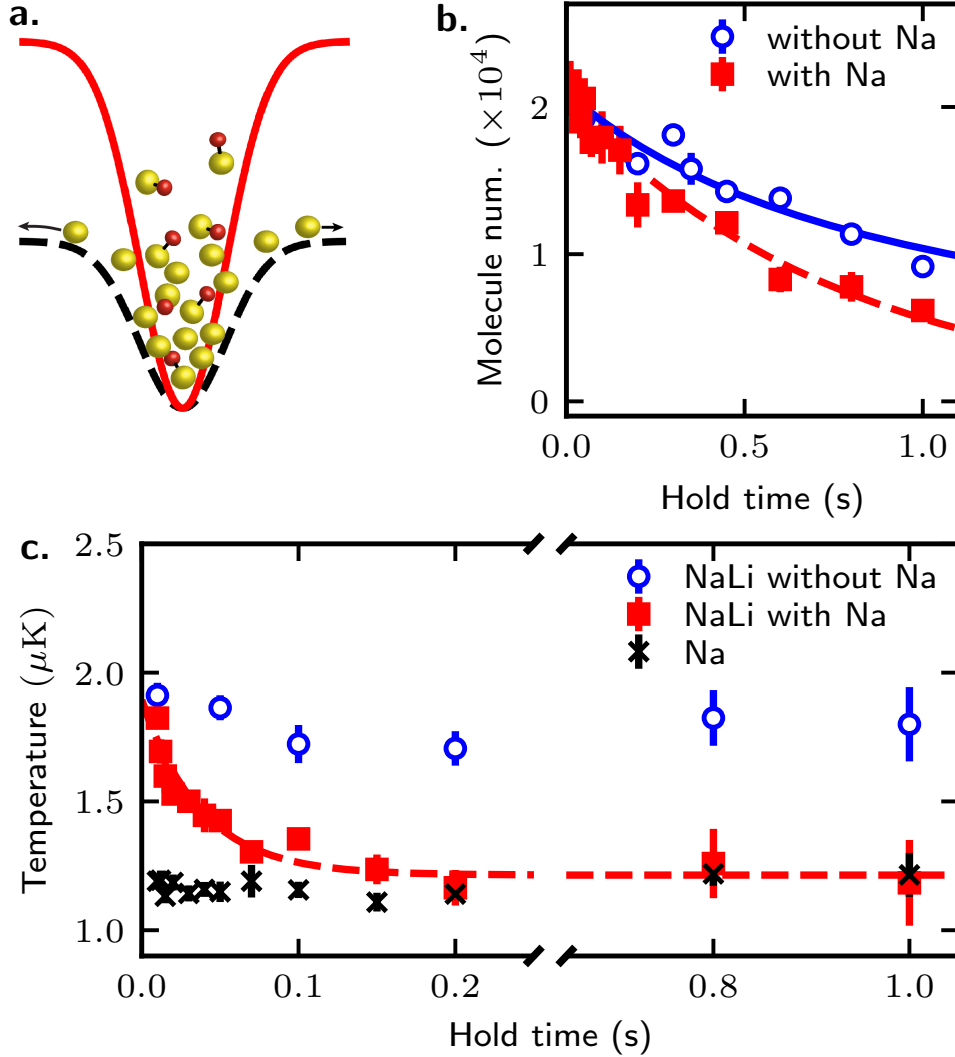


Figure 2.11: Sympathetic cooling of NaLi molecules with Na atoms. **a**, The trapping potential of molecules (the red-solid line) is deeper than that of Na atoms (the black-dashed line). This allows us to evaporate Na atoms with negligible loss of molecules. The molecule number (**b**) and temperature (**c**) are measured at various hold times after an exponential evaporation ramp to a trap power of 0.21 W ($7 \mu\text{K}$ trap depth) in 100 ms followed by a recompression to 1.2 W ($40 \mu\text{K}$ trap depth) in 10 ms. In the number plot, **b**, the red-dashed line is an exponential loss fit and the blue-solid one is a two-body loss fit (details in main text). The dashed line in the temperature plot, **c**, is an exponential fit. Note that a drop in temperature does not occur in the absence of Na atoms. The exponential fit of the molecule's temperature agrees well with the measurement, but should be regarded as an interpolation to determine the initial slope of the thermalizaion. For this measurement, Na number $\approx 1.5 \times 10^5$. Each error bar represents the uncertainty of the mean estimated from a fit error and a statistical error corresponding to 1 standard deviation of 3-8 measurements.

As the molecules thermalize with the Na atoms and a hot fraction of atoms evaporates out of the trap, the temperatures of both particles settle to $2.23(6) \mu\text{K}$. While this initial settling of temperatures hints at sympathetic cooling, we are able to see much stronger effects by forced cooling and heating of Na atoms.

2.3.1 Sympathetic cooling & heating of NaLi with Na atoms

We evaporate Na atoms with almost no loss of molecules by taking advantage of the particles' different polarizabilities: $\alpha_{\text{NaLi}}/\alpha_{\text{Na}} = (m\omega^2)_{\text{NaLi}}/(m\omega^2)_{\text{Na}} \approx 2.8$, where α_i is the polarizability of particle i , ω is an angular frequency for oscillation in the trap, and m is a particle mass. Fig. (2.11) c shows a curve of thermalization between molecules and atoms beginning with a larger temperature difference after an exponential evaporative cooling ramp followed by a recompression of the trap.

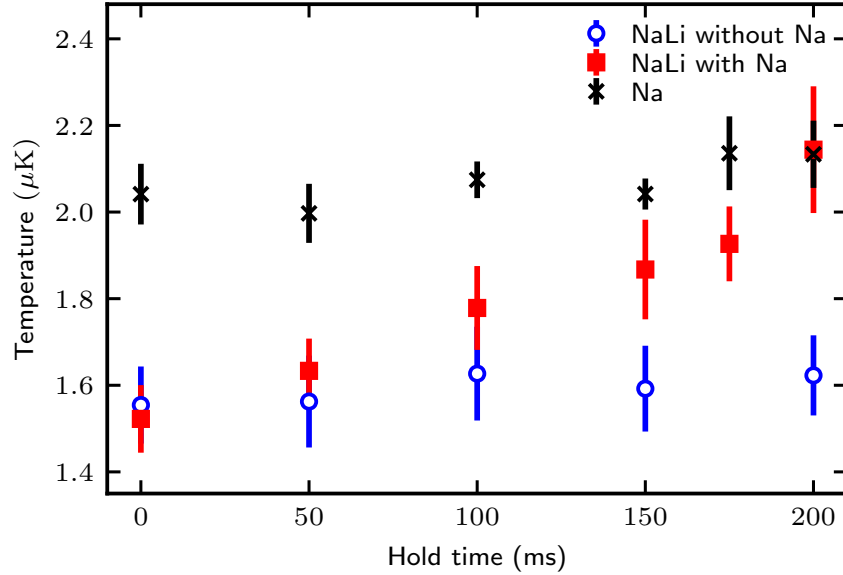


Figure 2.12: Sympathetic heating. After forced heating of Na atoms (see main text for details), the molecule temperature (red squares) rises and reaches to the Na temperature (black asterisk) as both particles thermalize. Note that the temperature of molecules without the hot atoms (blue circles) remains cold. Error bars are estimated from 4 measurements.

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

As we hold the particles in the trap, their temperatures approach each other. Due to the large particle number ratio, $N_{\text{Na}}/N_{\text{NaLi}} \approx 7$, molecule temperature decreases by $0.68(9) \mu\text{K}$ after thermalization while the temperature of Na atoms only increases by $70(30) \text{ nK}$. However, when the Na is removed immediately before the hold time, the molecule temperature remains fixed during the same period.

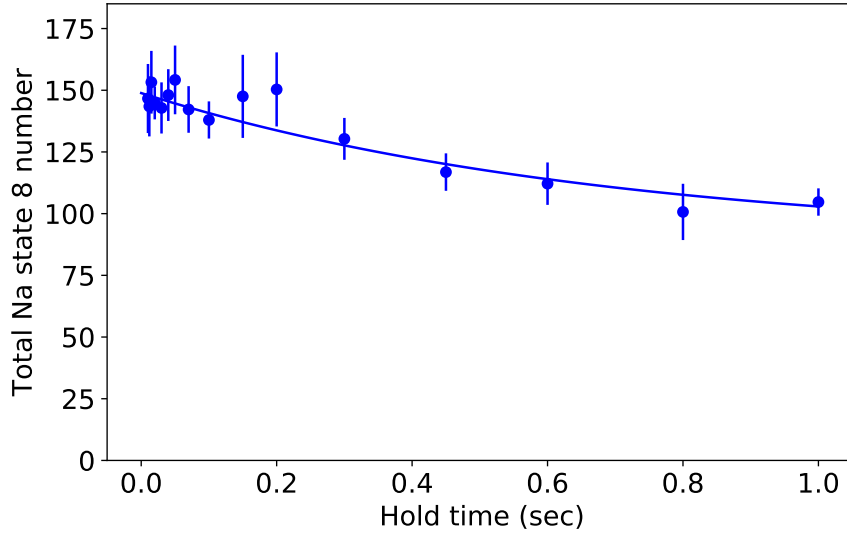


Figure 2.13: The decay of sodium atoms during the thermalization measurement. The blue line is an exponential fit. Given the number of sodium atoms lost compared to the number of molecules lost in Fig. 2.11 b, there was probably evaporative loss of sodium atoms due to their lower η factor and/or lattice heating. This sodium decay was observed without molecules.

As further evidence of thermalization, sympathetic heating of molecules with hot atoms is shown in Fig. 2.12. We first prepare the atom-molecule mixture fully thermalized at $1.5 \mu\text{K}$ after an exponential evaporative ramp in 10 ms followed by a recompression of the trap in 200 ms to the initial trap power of 1.5 W ($50 \mu\text{K}$ trap depth). Then we selectively heat the atoms to $2.07(5) \mu\text{K}$ by sinusoidally modulating the trap amplitude at twice the sodium trap frequency ($2\omega_{\text{Na}} = 2\pi \times 920 \text{ Hz}$) with modulation amplitude of 20% of the trap depth for 100 ms. After 200 ms, particles thermalize and the molecule temperature rises to the temperature of the heated Na atoms. When the trap amplitude is modulated

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

in the same manner without the Na atoms, the temperature of molecules remains at $1.59(5) \mu\text{K}$. The heating process for sodium also induces center of mass motion and breathing oscillations that cause the Na density to depend on time in the early stages of sympathetic heating, which is the reason for the delay in heating and non-exponential thermalization curve.

To quantitatively measure the rate of thermalization, we return to the cleaner situation of cooling in Fig. 2.11. We fit the temperature to a simple exponential model, $T(t) = (T_0 - T_\infty) \exp(-\Gamma_{\text{th}} t) + T_\infty$, and obtain $\Gamma_{\text{th}} = 26(7) \text{ s}^{-1}$. Note that the decrease of the sodium number is negligible up to the hold time 0.2 second when the molecules are fully thermalized with atom (see Fig. 2.13).

In a mass-imbalanced system, the factor $3/\xi$ quantifies the approximate average number of collisions per particle required for thermalization, where $\xi = 4m_{\text{Na}}m_{\text{NaLi}}/(m_{\text{Na}} + m_{\text{NaLi}})^{271}$. For the Na-NaLi mixture, this corresponds to approximately 3 collisions since the mass difference is small. Considering that thermalization requires ≈ 3 collisions for Na-NaLi, we obtain the average elastic collision rate per particle, Γ_{el} , from the measured thermalization rate: $\Gamma_{\text{el}} \approx (3/\xi)\Gamma_{\text{th}} = 80(20) \text{ s}^{-1}$. In the presence of Na atoms, the initial loss rate of molecules is $\Gamma_{\text{inel}} = 1.29(7) \text{ s}^{-1}$ from a fit to the exponential loss model, $N(t) = N_0 \exp(-\Gamma_{\text{inel}} t)$ (the red-dashed line in Fig. 2.11 b). Comparing the average elastic collision rate to the total loss rate, we obtain the ratio of elastic to inelastic collisions for NaLi, $\gamma \gtrsim \Gamma_{\text{el}}/\Gamma_{\text{inel}} = 62(16)$. Without Na atoms, the molecular loss follows a two-body loss model, $N(t) = N_0/(\beta t + 1)$, (the blue-solid line in Fig. 2.11 b) from which we obtain an initial loss rate of $\beta = 1.02(10) \text{ s}^{-1}$. Regarding the difference between Γ_{inel} and β as an effective inelastic loss rate for collisions between Na and NaLi, we obtain the ratio of “good to bad” collisions, $\gamma \approx \Gamma_{\text{el}}/(\Gamma_{\text{inel}} - \beta) \approx 300$ with an uncertainty of 50%.

While Na-NaLi in their upper stretched states form a stable mixture as shown, preparing Na atoms in their lowest hyperfine state ($|F, m_F\rangle = |1, 1\rangle$) gives a loss rate consistent with

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

the universal loss model⁶. Note that since rates of thermalization and inelastic loss due to collisions with sodium atoms are linearly proportional to the overlap density of sodium atoms, we are able to estimate the good-to-bad collision ratio without knowing the exact overlap density, which is not trivial to accurately measure due to the anharmonicity of the optical trap. How to model an anharmonic trapping potential will be discussed in the Chapter A.2.

The good-to-bad collision ratio estimated above is based on the approximated value of the inelastic loss rate of molecules due to the collisions with sodium atoms. For accurate estimation of the inelastic loss rate, we solve the differential equation of the time dependent molecule number by considering the change in the molecular temperature and the sodium number over time:

$$\dot{N}_{\text{NaLi}}(t) = -(K/V_{\text{ov}}(t))N_{\text{Na}}(t)N_{\text{NaLi}}(t) - (B/V_{\text{eff}}(t))N_{\text{NaLi}}^2(t) \quad (2.3.1.1)$$

where K and B are the loss rate coefficients for s -wave collisions between Na and NaLi and for p -wave molecular two-body collisions, respectively. V_{ov} is the volume of the regime where molecules are overlapped with sodium atoms, and V_{eff} is the mean volume of molecules. In a harmonic trap, one obtains $V_{\text{eff}} = \bar{\omega}_{\text{NaLi}}^{-3}(4\pi k_B T_{\text{NaLi}}/m_{\text{NaLi}})^{3/2}$ and $V_{\text{ov}} = (N_{\text{Na}}N_{\text{NaLi}})/(\int dV n_{\text{Na}}n_{\text{NaLi}}) = \bar{\omega}_{\text{Na}}^{-3}[(2\pi k_B T_{\text{Na}}/m_{\text{Na}})(1 + (\alpha_{\text{Na}}/\alpha_{\text{NaLi}})(T_{\text{NaLi}}/T_{\text{Na}}))]^{3/2}$ where the geometric mean of the sodium trap frequencies, $\bar{\omega}_{\text{Na}} = (\omega_x\omega_y\omega_z)^{1/3} = 2\pi \times (540 \cdot 410 \cdot 34000)^{1/3}$ Hz and $\alpha_{\text{NaLi}}/\alpha_{\text{Na}} = (m\omega^2)_{\text{NaLi}}/(m\omega^2)_{\text{Na}} = 2.8(4)$. The sodium temperature is constant over time, and the molecule temperature follows the exponential fit from the thermalization measurement.

In the first term of Eq. (2.3.1.1), we use the $N_{\text{Na}}(t) = N_{\text{Na}}(0)\exp(-\Gamma_{\text{Na}}t)$ where $\Gamma_{\text{Na}} = 0.4(5) \text{ s}^{-1}$ which is obtained by fitting the Na decay curve in Fig. 2.13. In this way, we take the extra sodium loss into account. The second term of Eq. (2.3.1.1), $B/V_{\text{eff}}(t)$ is

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

equivalent to $\beta/N_{\text{NaLi}}(0)$.

By numerically solving the Eq. (2.3.1.1), we obtain the loss rate coefficient for the collisions between molecules and atoms, $K = 1.2 \times 10^{-12} \text{ cm}^3/\text{s}$ ¹⁸ with an uncertainty of about 40%. This is about two orders of magnitude smaller than the universal loss model rate constant for Na-NaLi *s*-wave collisions⁹², which is $1.7 \times 10^{-10} \text{ cm}^3/\text{s}$ ¹⁹

Compared to the loss rate coefficient one can obtain from the effective loss rate $(\Gamma_{\text{inel}} - \beta)$, K obtained above is about 40% higher. Given this correction, the good-to-bad collision ratio should be about 210 with a 50% uncertainty. Note that the loss rate coefficient should be higher than this number roughly by a factor of $2 \sim 3$ ²⁰, since the overlap volume V_{ov} should be higher in the anharmonic trapping potential we used.

The elastic scattering rate between Na and NaLi is given by $\Gamma_{\text{el}} = n_{\text{ov}}\sigma_{\text{el}}v_{\text{rel}}$ where n_{ov} is the overlap averaged density of the mixture, σ_{el} is the elastic scattering cross-section, and v_{rel} is the mean relative velocity⁹⁴:

$$v_{\text{rel}} = \sqrt{\frac{8k_B}{\pi} \left(\frac{T_{\text{Na}}}{m_{\text{Na}}} + \frac{T_{\text{NaLi}}}{m_{\text{NaLi}}} \right)} \quad n_{\text{ov}} = \frac{\int dV n_{\text{Na}} n_{\text{NaLi}}}{\frac{N_{\text{Na}} N_{\text{NaLi}}}{N_{\text{Na}} + N_{\text{NaLi}}}} = \frac{N_{\text{Na}} + N_{\text{NaLi}}}{V_{\text{ov}}} \quad (2.3.1.2)$$

Note that the differential gravitational sag between molecules and atoms has a negligible effect on the overlap density. In our system, where the particle number is largely imbalanced (i.e., $N_{\text{Na}}/N_{\text{NaLi}} \approx 7$), we can write the thermalization rate as

¹⁸In the estimation of the loss rate coefficient K , I used the Gaussian-weighted mean sodium number $\bar{N}$ (see Chapter 2.2.3.1), which is 2.22 times less than the effective particle number N_{eff} . In the original publication, N_{eff} was used, but as we will learn from the sodium thermalization measurement and the anharmonic modeling of the single lattice site potential, the correct density of sodium atoms is obtained with $\bar{N}$ (see Chapter A.2 for details).

¹⁹When calculating the theoretical loss rate constant, we estimate the van der Waals coefficient, $C_6^{\text{Na-NaLi}}$ between Na and NaLi as the sum of C_6 's for atomic pairs that constitute the collision partners using values from Ref.⁹³: $C_6^{\text{Na-NaLi}} = C_6^{\text{Na-Li}} + C_6^{\text{Na-Na}}$.

²⁰Please note that this is a rough estimation. For this, the geometry of the beam that formed the 1D lattice had to be guessed based on the recent measurement, which can be different from when the measurement was carried out in the past.

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

$$\Gamma_{\text{th}} \approx \frac{(I/N_{\text{NaLi}})\sigma_{\text{el}}v_{\text{rel}}}{3/\xi}, \quad (2.3.1.3)$$

where I/N_{NaLi} is the average density of Na atoms seen by NaLi molecules. Given the measured thermalization rate, we obtain the elastic scattering cross-section between a molecule and an atom, $\sigma_{\text{el}} \approx (3/\xi)(N_{\text{NaLi}}/v_{\text{rel}}I)\Gamma_{\text{th}} = 2.4(6) \times 10^{-11}\text{cm}^2$ and the corresponding scattering length, $a = 263(66)a_0$ where a_0 is the Bohr radius.

In addition to the simple exponential fit, we perform a numerical simulation of the thermalization process based on the differential equation for $\Delta T = T_{\text{NaLi}} - T_{\text{Na}}$ ^{71,72,94}:

$$\frac{1}{\Delta T} \frac{d(\Delta T)}{dt} = -\Gamma_{\text{th}} = -\frac{\xi}{3}n_{\text{ov}}\sigma_{\text{el}}v_{\text{rel}}. \quad (2.3.1.4)$$

In the numerical simulation, the temperature dependence of n_{ov} , σ_{el} , and v_{rel} is fully taken into account. The s -wave elastic scattering cross-section between Na and NaLi is given by

$\sigma_{\text{el}} = \frac{4\pi a^2}{[1 - (1/2)k^2 r_0 a^2] + (ka)^2}$, where $\hbar k = \mu v_{\text{rel}}$ is the relative momentum (μ is the reduced mass) and r_0 is the effective range calculated from the scattering length, a and $C_6^{\text{Na-NaLi}}$.

We iteratively solve Eq. (2.3.1.4) by varying a , and found the optimal solution that minimizes the weighted sum of squared residuals: $\sum_i ((\Delta T_{e,i} - \Delta T_{n,i})/\sigma_{\Delta T_{e,i}})^2$, where the subscript n denotes the numerical solution, e denotes the measurement, and $\sigma_{\Delta T_{e,i}}$ is the standard deviation of the measurement at i^{th} time step. The numerical solution for a obtained in this way agrees with the result calculated from the simple exponential model above within the uncertainty.

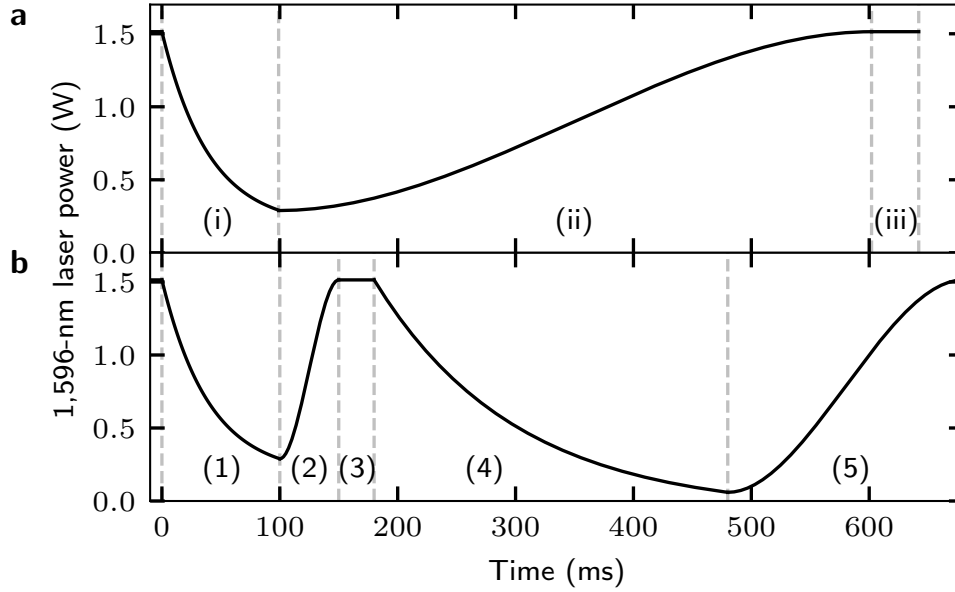


Figure 2.14: Evaporation sequences. The initial power of the 1596 nm trapping laser is 1.5 W. At the end of evaporation we recompress the trap to the initial power to increase thermalization rate and for a straightforward comparison of density without re-scaling the trap volume. **a**, Single evaporation consists of (i) 100 ms exponential forced evaporation ($\tau = 40$ ms), where trap depth, $U(t) = A \exp(-t/\tau) + B$, (ii) 500 ms recompression, and (iii) 40 ms hold for complete thermalization. **b**, Double evaporation consists of (1) 100 ms exponential forced evaporation ($\tau = 40$ ms), (2) 50 ms recompression to the initial trap depth, (3) 30 ms hold, (4) 300 ms exponential evaporation ($\tau = 120$ ms), and (5) 200 ms recompression.

2.3.2 Increasing phase-space density of NaLi

We consider two different evaporation ramps described in Fig. 2.14. The resulting molecule numbers, temperatures, and PSDs from these ramps are displayed in Fig. 2.15. For a single-species system with losses, optimal evaporation can be achieved by a single, continuous decrease of the trap depth. We achieve an increase in PSD by a factor of 7 using a single stage of evaporation (Fig. 2.14 a and red squares in Fig. 2.15). This increase is limited by the low initial Na density. In our system, thermalization is dominated by the Na density, while loss is dominated by the NaLi density. In order to overcome the low Na density, we shorten the initial evaporation + recompression cycle ((1)+(2) in Fig. 2.14

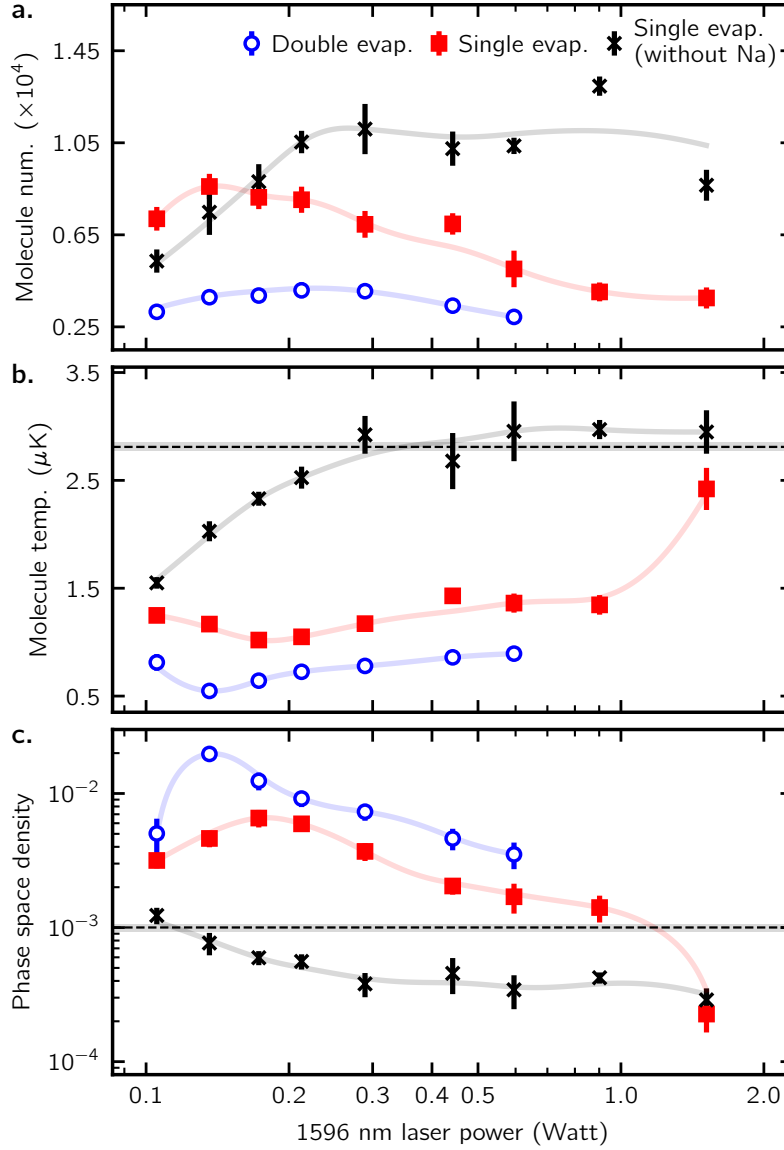


Figure 2.15: Increasing phase-space density. The molecule number (a), temperature (b), and PSD (c) are plotted versus the power of the 1596 nm trapping laser at the end of the forced exponential evaporation: (i) for single evaporation and (1) for double evaporation (see Fig. (2.14)). For the double evaporation, we ramp the power down to 0.06 W (2 μK trap depth) in (4), the lowest point that gives a molecular signal high enough for consistent temperature measurement. Evaporation to this low trap depth in a single stage of evaporation leads to loss of almost every molecule. The black-dashed lines in b, c indicate the molecule temperature and PSD after STIRAP and removal of free atoms (shaded areas show ± 1 error bar). This PSD corresponds to $2.6(1) \times 10^4$ molecules. Note that when Na atoms are not in the trap or the evaporation is not performed to sufficiently low trap depth, the PSD is lower than the initial value. This is mainly due to the molecular two-body loss. The solid curves are to guide the eye. Error bars are estimated from 4-9 measurements.

b). This cools the Na atoms and quickly increases the density of the cold Na for fast thermalization. After the cold, dense Na efficiently pre-cools the molecules during a short hold of 30 ms in the tight trap (3), we apply the second evaporation ramp (4). In this double evaporation, we achieve a peak PSD of $2.0(4) \times 10^{-2}$ (blue circles in Fig. 2.15, which is 20 times higher than the initial PSD. Before the final recompression of the trap, the lowest temperature of the molecules is 220(20) nK.

With Na present, more molecules survive the evaporation sequence as we evaporate Na atoms to lower trap depth. This is mainly due to the suppressed two-molecule loss. The loss-rate constant scales linearly with temperature due to the p -wave character of the collisions⁹².

Evaporation to too low trap depth decreases the Na density, which in turn makes the sympathetic cooling of molecules inefficient and anti-evaporation since the molecular loss dominates. This appears as the temperature curving up below a trap power of 0.17 W (5.7 μ K trap depth) for a single stage of evaporation, or 0.14 W (4.5 μ K trap depth) for two-stage evaporation. Without Na, the ramp down in trap depth, (i), is adiabatic to a trap power around 0.3 W, as evidenced by the constant molecule numbers and temperatures. Below that trap power, the ramp down starts becoming non-adiabatic. As a result, a hot fraction of molecules escape, and both molecule number and temperature start decreasing. Note that since fermionic molecules do not thermalize by themselves, this temperature should be regarded as the average kinetic energy of molecules that are not in thermal equilibrium.

2.4 Discussion

The favorable collisional properties of the Na-NaLi mixture in fully stretched states result from strong suppression of electronic spin flips during collisions, which could

CHAPTER 2. SYMPATHETIC COOLING OF ULTRACOLD MOLECULES WITH ATOMS

otherwise lead to fast reactive or inelastic losses. In fully stretched states, direct spin exchange is forbidden and residual spin flips can occur only by weaker interactions. The major contribution would be from dipolar relaxation due to the coupling between the magnetic dipole moments of the spins of Na and NaLi. Studies in other spin-polarized systems^{32,68,95} predict spin flips through electrostatic interaction at short range induced by intramolecular spin-spin and spin-rotation couplings to be weaker. Dipolar relaxation can be eliminated by using the strong-field seeking stretched state but this was not necessary in our work. It is possible that Na-NaLi is favorable due to the low molecular and reduced masses and smallness of relativistic effects which result in a large rotational constant^{66,96}, low density of states²¹ and small spin-orbit coupling⁹⁷, respectively. Further, Ref.⁶⁵ has shown that intramolecular spin-spin coupling causes spin flips for triplet NH molecules, thwarting evaporative cooling. Our results show a clear need for further work to predict which other molecules—and in what conditions of internal states and external fields—will be suitable for collisional cooling at ultracold temperatures.

Technical upgrades to our machine should allow cooling into the quantum degenerate regime by increasing the initial Na density. The dominant loss mechanism, p -wave collisions between molecules, will slow down compared to thermalization at lower temperatures, improving the efficiency of cooling. Further, the atomic and molecular states used in this work are magnetically trappable. Magnetic trapping would allow for much larger samples with perfect spin-polarization. This would also eliminate the major concern of molecular loss induced by trapping light²², making NaLi an ideal system for studying quantum chemistry. Concerns about the possibility of sticky collisions²¹, which become worse with increasing density of states, have led to pessimism over the prospects for collisional cooling of ultracold molecules. This work demonstrates that sticky collisions do not limit NaLi and probably other low mass systems, suggesting a bright future for cooling light molecules.

3

Control of Reactive Collisions by Molecule-Atom Feshbach Resonances

Some parts in this chapter have been published as

“Control of reactive collisions by quantum interference”

H. Son, J. J. Park, Y.-K. Lu, A. O. Jamison, T. Karman, and W. Ketterle, (accepted to Science), Sep 2021, Preprint, <https://arxiv.org/abs/2109.03944>

Abstract

Magnetic control of reactive scattering was realized in an ultracold mixture of ^{23}Na atoms and $^{23}\text{Na}^6\text{Li}$ molecules. In most molecular collisions, particles react or are lost near short range with unity probability leading to the so-called universal rate. In contrast, $\text{Na}+\text{NaLi}$ was shown to have only about 4% loss probability in a fully spin-polarized state. By controlling the phase of the scattering wavefunction via a Feshbach resonance, we modified the loss rate by more than 100 times, from far below the universal limit to far above. The results are explained in analogy with an optical Fabry-Perot resonator by interference of reflections at short and long range. Our work demonstrates quantum control of chemistry by magnetic fields with the full dynamic range predicted by our models.

3.1 Introduction

Advances in cooling atoms and molecules have opened up the field of quantum scattering resonances^{20,98–100} and ultracold chemistry^{48,101}. At micro- and nano-kelvin temperatures, collisions occur only in the lowest partial wave, and the collisional physics can be reduced to a few well-defined parameters which in many systems are the *s*-wave scattering length and a two-body loss coefficient. Collisions involving molecules are often much more complex due to the strong anisotropic interaction at short range and multiple decay channels including reactions^{22,23,25,26}. One goal of current research is to identify systems which can still be understood with relatively simple models, including the model of universal rate coefficients², single-channel, and two-channel models. Such systems are most likely to fulfil the dream of controllable quantum chemistry where the outcome of reactions is steered by external electromagnetic fields^{102,103}.

Collisions in molecular systems can be described by the reflection of the wavefunction in two regions. At long range, the attractive van der Waals (vdW) potential acts as a highly reflective mirror due to quantum reflection in low-temperature scattering. When the colliding particles are in close proximity, they can again be reflected by the repulsive short range potential or they can get lost due to inelastic transfer to other states. These losses can be represented by transmission through the short-range mirror. In the universal limit, the transmission is 100%, and the entire incoming flux is lost.

Most ultracold molecular collisions studied thus far have loss rate coefficients at or close to the universal value^{5,7–17}. However, when partial reflection occurs at short range, the resulting loss rate can be higher or lower than the universal value depending on the interference created by multiple reflection pathways. This fact is analogous to an optical Fabry-Perot interferometer. This optical analogue fully captures the results of a single-channel description of reactive molecular collisions^{2,104}. We extended the

single-channel model by adding a Feshbach resonance as a lossless phase shifter which can tune between constructive and destructive interferences.

In this chapter, we discuss an experimental system, collisions of triplet ro-vibrational ground-state NaLi with Na near 978 G, which is fully described by this Fabry-Perot model. We saw loss rates larger than the universal rates by a factor of about 5, tunable via a Feshbach resonance over a range of more than two orders of magnitude. We have also characterized a weaker loss resonance, where the phase shifter was lossy, i.e. the closed channel of the Feshbach resonance had a short lifetime and dominated the loss, almost completely spoiling the quality factor of the Fabry-Perot resonator. This resonance has to be described by a two-channel model with the lifetime of the bound state as an additional parameter¹⁸. Our experiment has established NaLi+Na as a distinctive system which realizes the full dynamic range of recent models developed to describe reactive collisions involving ultracold molecules^{2,104}. Furthermore, to the best of our knowledge, this system is only the second example for which Feshbach resonances between ultracold molecules and atoms have been found^{105,106}.

3.2 Fabry-Perot interferometer model

Reactive scattering between molecules and atoms can be matched to the simple picture of an optical Fabry-Perot interferometer with two reflectors, M_1 and M_2 (Fig. 3.3). Mirror M_1 represents quantum reflection by the long-range vdW potential, and M_2 represents reflection near short range. Inelastic/reactive loss which occurs at close or short range (Fig. 3.3) is represented in the Fabry-Perot picture by transmission through the inner reflector M_2 followed by absorption. For an incoming flux I , the total transmission T

CHAPTER 3. CONTROL OF REACTIVE COLLISIONS BY MOLECULE-ATOM FESHBACH RESONANCES

through both reflectors is given by:

$$T = (I \cdot |t_1|^2) \left(\frac{1 - |r_2|^2}{|1 - r_2 r_1 e^{-i\phi}|^2} \right) \equiv (I \cdot |t_1|^2) C \quad (3.2.0.1)$$

Here, r_i and t_i are the amplitude reflection and transmission coefficients for mirror M_i and ϕ is the round-trip phase, which in the Fabry-Perot model, can be tuned by the distance between mirrors or the refractive index of the medium. The term $I \cdot |t_1|^2$ is the transmitted flux in the absence of the inner mirror (i.e. $r_2=0$) and, for collisions, represents the universal loss. The factor C represents the effect of interference. For later convenience, we characterize the inner reflection by a parameter $0 \leq y \leq 1$: $r_2 = (1 - y)/(1 + y)$, $t_2 = 2\sqrt{y}/(1 + y)$, which is 1 for complete transmission and 0 for complete reflection. With $r_1 \sim 1$ (quantum reflection approaches unity at low energies), we obtain $C(y, \phi) = 2y/(1 - \cos \phi + y^2(1 + \cos \phi))$. Constructive interference at $\phi = 0$ leads to an enhancement $C = 1/y$, and destructive interference at $\phi = \pi$ to a minimum transmission with $C = y$. In the limit of small $y \ll 1$ relevant for our experimental results, the transmission probability for the inner mirror is $4y$.

In the case of cold collisions, scattering rates are periodic when the close-range potential is modified and new bound states are added to the interparticle potential. Each new bound state results in a resonance and “tunes” the Fabry-Perot interferometer over one full spectral range with the scattering length a varying between $\pm\infty$. Following Ref.², we defined the normalized scattering length $s = a/\bar{a}$, where $\bar{a} = 0.47799 \cdot r_6$ is the mean scattering length⁸³. If we substitute $\cos \phi = 1 - 2/(1 + (1 - s)^2)^1$, we obtain $C(y, s) = y(1 + (1 - s)^2)/(1 + y^2(1 - s)^2)$. This expression exactly reproduces the results of the quantum-defect model used in Ref.² for the imaginary part of the scattering length, $\beta = \bar{a}C(y, s)$ which is proportional to the zero-temperature loss rate coefficient.

¹This expression is equivalent to $\tan(\phi/2) = 1/(1 - s)$, which is also given in Ref.¹⁰⁴.

CHAPTER 3. CONTROL OF REACTIVE COLLISIONS BY MOLECULE-ATOM FESHBACH RESONANCES

Refs.^{2,104,107} already pointed out that their results can be interpreted as an interference effect of multiple reflections between short and long range. The relation between the phase shift ϕ and the parameter s exactly reflects how a short-range phase shift modifies the scattering length¹⁰⁴.

We extended this single-channel model (where s is the normalized background s -wave scattering length without loss, $y=0$) by adding a Feshbach resonance as a lossless phase shifter for the Fabry-Perot phase:

$$s(B) = q \left(1 - \frac{\Delta}{B - B_{\text{res}}} \right) \quad (3.2.0.2)$$

Here the resonance is at a magnetic field $B=B_{\text{res}}$, q characterizes the background scattering phase far away from the Feshbach resonance, and Δ is the width of the resonance. Tuning the magnetic field across the resonance takes the Fabry-Perot interferometer across a full spectral range, and provides tunable interference at fixed low temperature. For finite collision energies, interference has been observed also as a function of collision energy¹⁰⁸.

3.3 Search for NaLi-Na Feshbach resonances

3.3.1 Experimental protocol

A mixture of $\sim 1.5 \times 10^5$ sodium atoms and $\sim 2.8 \times 10^4$ NaLi molecules in the triplet ro-vibrational ground-state was produced in a 1,596-nm one dimensional (1D) optical lattice created by retro-reflecting the trapping beam. Both molecules and atoms were at the temperature of $\sim 1.5 \mu\text{K}$. The sample was confined as an array of ~ 1000 pancake-shaped clouds. The atoms and molecules were both in the upper stretched hyperfine states, where all electron and nuclear spins were aligned along the bias field^{6,41}. This spin-polarized mixture was in a chemically stable quartet state.

CHAPTER 3. CONTROL OF REACTIVE COLLISIONS BY MOLECULE-ATOM FESHBACH RESONANCES

The atom-molecule mixture was initially prepared near the Na-Li Feshbach resonance at 745 G, and then the bias field was ramped to the target value in 15 ms after which another 15 ms was waited for the field to settle. In order to probe any fine structures or narrow resonances, we swept the bias field down by 13 G in 200 ms from the target field, which was varied in steps of 8.8 G. The target field was set by the Anti-bias coils, and the field sweep was achieved by a pair of shim coils with the power supply called “Spin-flip bias”. After the field sweep, we ramped the target field back to 745 G where the remaining molecules were dissociated and detected. The number of dissociated Li or Na atoms in the hyperfine ground state was measured by resonant absorption imaging⁴¹. In most cases, we counted the number of molecules by imaging the dissociated Li atoms, since they were imaged through a cycling transition as opposed to the Na atoms.

After ramping the target fields back, we had to be careful in making sure that the field was actually below the dissociation field (i.e. ~ 745 G, where the Na-Li Feshbach resonance is located). When the target fields were too high or low (e.g. more than 300 G away from the 745 G), the eddy current created on the vacuum chamber or/and other coils after ramping the bias field made the final field too low or high compared to the dissociation field (waiting for a longer time until the field was fully settled was not desirable due to the extra molecular loss, especially when the molecular signal was low). When the final field was too low, the number of molecules could be under-counted since the actual dissociation of molecules was achieved by a small MOK coil, which was designed to sweep the bias field only by ~ 400 mG. When the final field was too high, molecules were dissociated with extra kinetic energy at higher momentum states (the latter is usually not a problem in counting particle numbers, but dissociated atoms are imaged hotter). This problem was solved by setting the final field intentionally lower or higher considering the amount of the field shift caused by the eddy current.

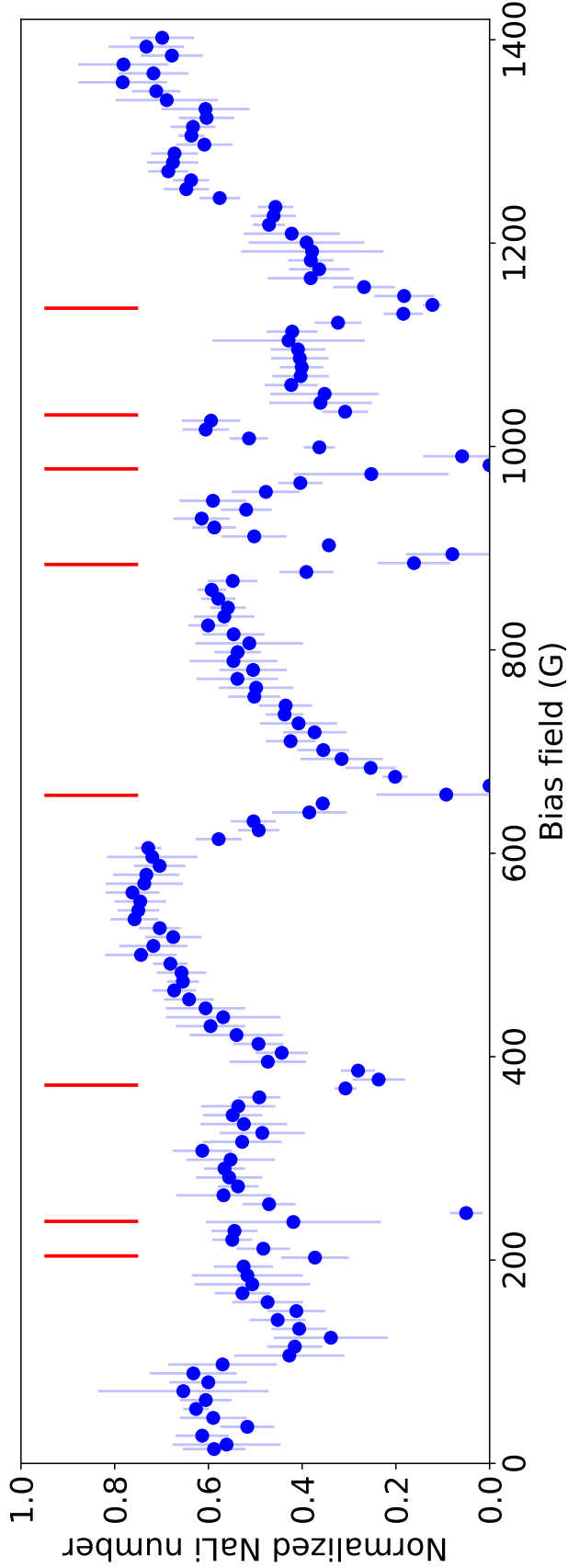


Figure 3.1: NaLi loss spectrum with coarse sweep of bias fields. The loss of NaLi molecules with Na atoms was measured as a function of bias field. Y-axis is the number of NaLi left after sweeping down the bias field by 13 G at each field for 200 ms, normalized by the number of NaLi without the field sweep. The number of Na atoms in each pancake for each measurement was around 115, and the number of NaLi molecules without the field sweep was about 35. We observed eight resonances in total. In terms of the depth of the dip, or the number of molecules lost, the strongest resonance is at 978 G and the weakest one is at 1030 G. Red vertical lines indicate the position of Feshbach resonances. The errorbar represents one standard error of the mean.

3.3.2 Loss spectrum of NaLi with Na

By scanning the target fields from near zero to 1401 G, we obtained a spectrum of NaLi losses as shown in Fig. 3.1. We identified eight Feshbach resonances in total, which are indicated by red vertical lines in Fig. 3.1². In terms of the depth of the dip, or the number of molecules lost, the strongest resonance is at 978 G and the weakest one at 1030 G. The two resonances will be studied in detail in latter chapters with the single-channel Fabry-Perot model and the extended two-channel model.

Figure 3.2 shows the loss feature of every resonance in detail. For the three strongest resonances including the weakest one, we measured the loss rates at each field by acquiring the decay curves of molecules (see Fig. 3.2 F, G, H). Data points taken with different sodium numbers and temperatures were scaled to the same sodium overlap density of $1.1 \times 10^{11} \text{ cm}^{-3}$. For details, see Chapter A.2. For the remaining resonances, we measured the fraction of the molecules survived after a certain amount of time hold at each field (I call this “field hold scan”; see Fig. 3.2 A, B, C) or a field sweep (I call this “field sweep scan” which is similar to how Fig. 3.1 was acquired but with finer steps of fields; see Fig. 3.2 D, E). The approximate spectral information of each resonance was estimated by fitting the observed loss feature to a simple Lorentzian function with a slope (the slope is to consider the overall change in the background loss and the effect of nearby other resonances). The fitted lineshapes are shown as dotted lines in Fig. 3.2, and the result of the fitting is summarized in Table 3.1. We have confirmed the resonance position and width acquired from the field sweep scan agree with those from the field hold scan within the fit uncertainties, when the fraction of molecular loss is similar. Note that the true lineshape of the loss feature is not Lorentzian but an asymmetric function, $C(y, s(B))$

²We did finer field sweeps and confirmed that features that almost looked like dips around 100, 1320 G in the Fig. 3.1 were fluctuations.

CHAPTER 3. CONTROL OF REACTIVE COLLISIONS BY MOLECULE-ATOM FESHBACH RESONANCES

(Eq. 3.2.0.1) based on the Fabry-Perot interference model³, so the fitting result shown here should be only regarded as an approximation. The main message to deliver here is that the density of resonances in the light NaLi-Na system is about 8/1400 (1/Gauss) per scattering channel and the averaged full width half maximum (FWHM) of the resonances (in terms of the visibility of loss) is on the order of ~ 10 Gauss.

	Resonance position (G)	Lorentzian FWHM (G)	Measured by
1	203.7(2)	5.3(7)	field hold scan
2	238.0(1)	5.6(1)	field hold scan
3	371.9(5)	16.5(2.4)	field sweep scan
4	656.8(6)	5.3(6)	loss rates
5	884.6(1.5)	10.2(1.5)/16.9(1.1)	loss rates/field hold scan
6	977.9(3)	4.9(3)	loss rates
7	1030.7(2.1)	5.4(2.1)	loss rates
8	1135.8(6)	16.3(2.3)	field sweep scan

Table 3.1.: **List of observed Feshbach resonances between NaLi and Na in the upper spin-stretched states.** The resonance position and width are estimated by fitting the loss feature of each resonance (shown in Fig. 3.2) to a simple Lorentzian with a linear slope. The uncertainty in the parenthesis is the fit uncertainty.

- Measurement condition for Fig. 3.2:
 - The ratio of the number of molecules in each pancake to that of sodium atoms in each pancake was $7 \sim 11$: except near the peak of the resonance at 978 G where the number ratio was $4 \sim 5$ due to the highly enhanced inelastic losses. The typical molecule number is ~ 25 .
 - The temperatures of NaLi and Na were $1.3 \sim 1.6 \mu\text{K}$. Near the peak of the resonance at 978 G, anti-evaporation of molecules occurred as the densest part of the molecular cloud was lost faster. Due to this effect, the molecular

³The lineshape from the loss rate measurement should follow the function $C(y, s(B))$, but the one from the fractional number loss measurement should not. In the latter case, for instance when the collisional loss with sodium atoms dominates over the molecular two-body loss with negligible depletion in the sodium density, the lineshape would be close to $\sim \exp[-C(y, s(B))]$.

CHAPTER 3. CONTROL OF REACTIVE COLLISIONS BY MOLECULE-ATOM FESHBACH RESONANCES

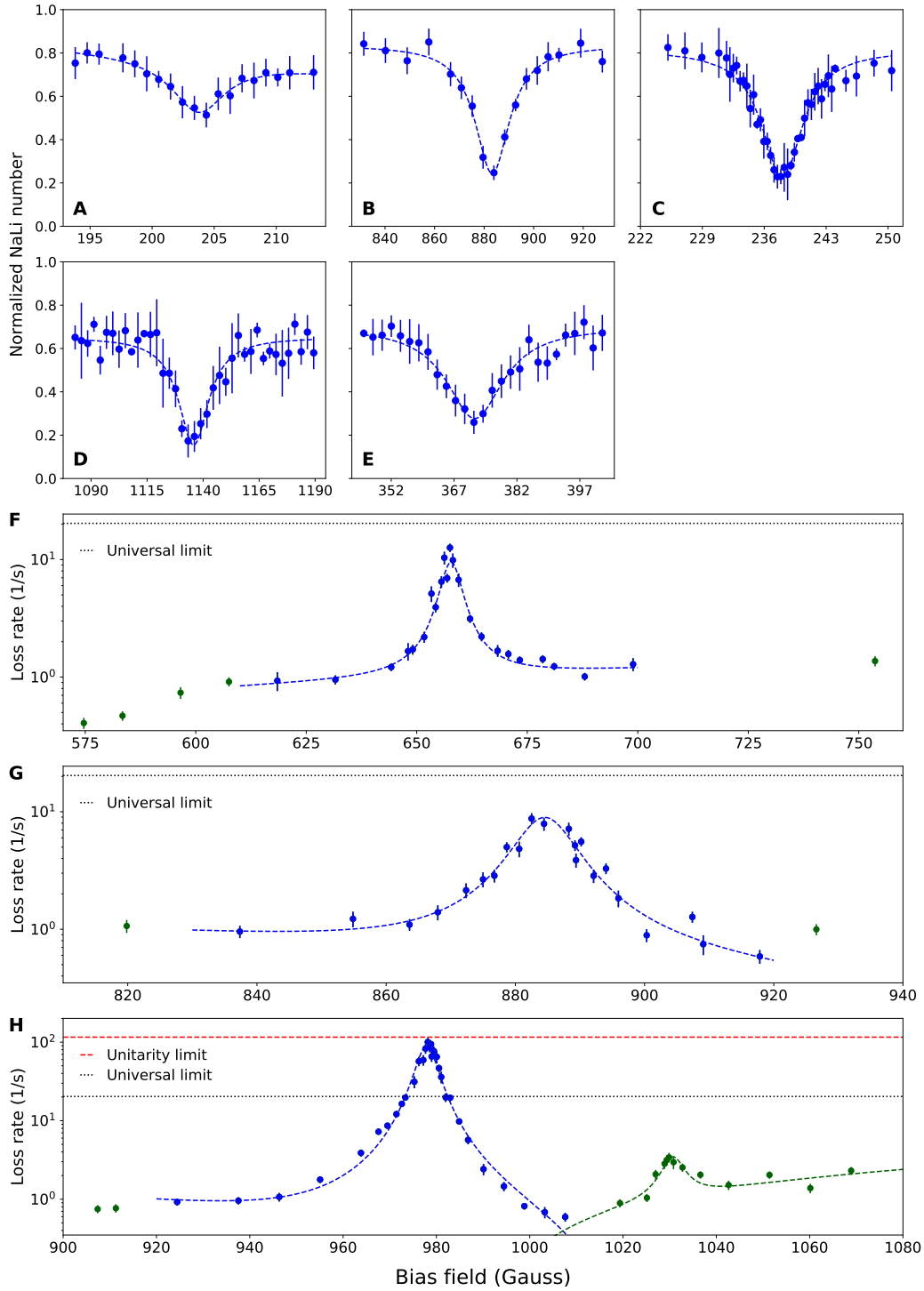


Figure 3.2: Loss features of NaLi-Na Feshbach resonances. The errorbars in A,B,C,D, and E represent one standard errors of the mean. The errorbars in F, G, and H represent one standard deviations. The blue and green dotted lines are fitted Lorentzian with a linear slope. The black horizontal dotted line is the s -wave universal rate calculated based on the information given in Ref.⁸². The red horizontal dotted line is the unitarity limit in 2-dimension at our experimental conditions (see Chapter 3.4.2).

temperature was increased by $\sim 15\%$, but this happened mostly before we started acquiring the decay curves of particles for the loss rate measurements.

- In the field sweep scan measurements, the field was swept down at each field with the spin-flip bias coils, and the sweep width was 10% larger than the step size with which each data point of the figure was varied.

3.4 Measurement of enhanced NaLi-Na loss rate coefficients

As elaborated in Chapter 3.2, our Fabry-Perot interferometer model in the single channel description is suited to explain the tunability of loss that is symmetric around the universal loss limit (i.e. a factor of y less than the universal limit at the background and a factor of $1/y$ larger at the resonance). Given this, the strongest resonance observed at 978 G is a great candidate to test our single channel model. We will introduce another model based on the two-channel description where the non-zero lifetime of the atom-molecule bound state of a closed channel is considered in order to explain the peak loss suppressed below the universal loss limit. We found the weakest resonance observed at around 1030 G was nicely explained by the two-channel model. For the following chapters, we will focus on measuring the lineshapes of these two resonances, analyzing them with our models based on quantum interference, and discussing the short range parameters we can measure from the analyses.

3.4.1 Experimental protocol

A mixture of $\sim 3 \times 10^5$ sodium atoms and $\sim 3 \times 10^4$ NaLi molecules was initially prepared near the Na-Li Feshbach resonance at 745 G, and then the bias field was ramped to the target value in 15 ms. The sample was prepared at a temperature $T_{\text{NaLi}} \approx T_{\text{Na}} \sim T = 1.55 \mu\text{K}$

CHAPTER 3. CONTROL OF REACTIVE COLLISIONS BY MOLECULE-ATOM FESHBACH RESONANCES

well within the regime for threshold behaviour of collisions, which required the temperature to be much less than the characteristic temperature determined by the vdW potential, $T_{\text{vdW}} = \hbar^2 / 2\mu k_B r_6^2$ ¹⁰⁹ with the vdW length $r_6 = (2\mu C_6 / \hbar^2)^{1/4}$, where k_B is the Boltzmann constant and C_6 is the vdW constant for the atom-molecule potential. With $C_6 = 4026$ in atomic units⁸², $T_{\text{vdW}} \approx 500 \mu\text{K}$.

The atom-molecule mixture was initially prepared near the Na-Li Feshbach resonance at 745 G, and then the bias field was ramped to the target value in 15 ms. We determined collisional lifetimes of the atom-molecule mixture by holding the sample for a variable time at the target magnetic field, after which the field was ramped back to 745 G where the remaining molecules were dissociated and detected. Note that sodium atoms from dissociation were in a hyperfine state different from sodium atoms in the initial atom-molecule mixture.

Decay curves for the molecules are compared in the inset of Fig. 3.4 near and far away from the strong atom-molecule Feshbach resonance studied in this work. Our observable $\gamma(B)$ is the difference of initial loss rates of NaLi molecules with and without Na atoms. It is obtained by fitting the whole decay curve using the standard differential equations for two-body decay (see Chapter A.2). The loss in the absence of sodium atoms is caused by p -wave reactive collisions between molecules. The measured rate coefficient $\beta = 2.6(7) \times 10^{-12} \text{ (cm}^3/\text{s)} (T_{\text{NaLi}}/\mu\text{K})$ near 980 G agrees within a factor of two with the prediction of the universal loss model (see Chapter A.2). Single-particle loss due to the vacuum limited lifetime of $>20 \text{ s}$ was negligible.

We avoided the need for absolute sodium density measurements by comparing the measured decay rate to the decay rate of the mixture in a non-stretched spin state. Since this mixture collides on a highly reactive doublet potential, the decay was reliably predicted to occur with the s -wave universal rate coefficient, which is well known for our system⁸². We estimated the uncertainty of the density calibration to be about 40% based

on comparison of data sets taken at different times (see Chapter A.2).

We also measured the loss rate for non-stretched spin states using the measured particle number and temperature, and a model for the anharmonic trapping potential. With the measurement, we have confirmed within 30% uncertainty that the rate is indeed the universal rate (see Chapter A.2). Since we regard the theoretical prediction to be highly reliable, we didn't use the experimental density calibration in the analysis reported here.

3.4.2 Analysis of the strong resonance at 978 G with the single-channel model

The measured loss rates for Na+NaLi collisions as a function of magnetic field are shown in Fig. 3.4, and this data represents the main result of this paper. It shows a resonant enhancement of the loss by more than two orders of magnitude. Because the ratio of maximum and minimum loss is y^2 in the Fabry-Perot model, this result immediately suggested that y has to be smaller than 0.1. We could fit the asymmetric lineshape of the resonance well to the function $C(y, s(B))$ with an overall normalization factor, and obtain $y=0.05$ and $q=1.61$. However, the observed peak losses were close to the unitarity limit which provides an upper limit for elastic and inelastic scattering rates. When the scattering length exceeds the de Broglie wavelength, $\lambda = 1/k$, the elastic cross section in 3D saturates at $4\pi\lambda^2$, whereas the inelastic rate coefficient peaks at $(h/2\mu)\lambda$. The observed peak loss rate was close to the unitarity limit, so we had to consider the role of non-zero momentum.

Combining the threshold quantum-defect model for the complex scattering length with a finite momentum S-matrix formulation for the scattering rates, Ref.² obtained the

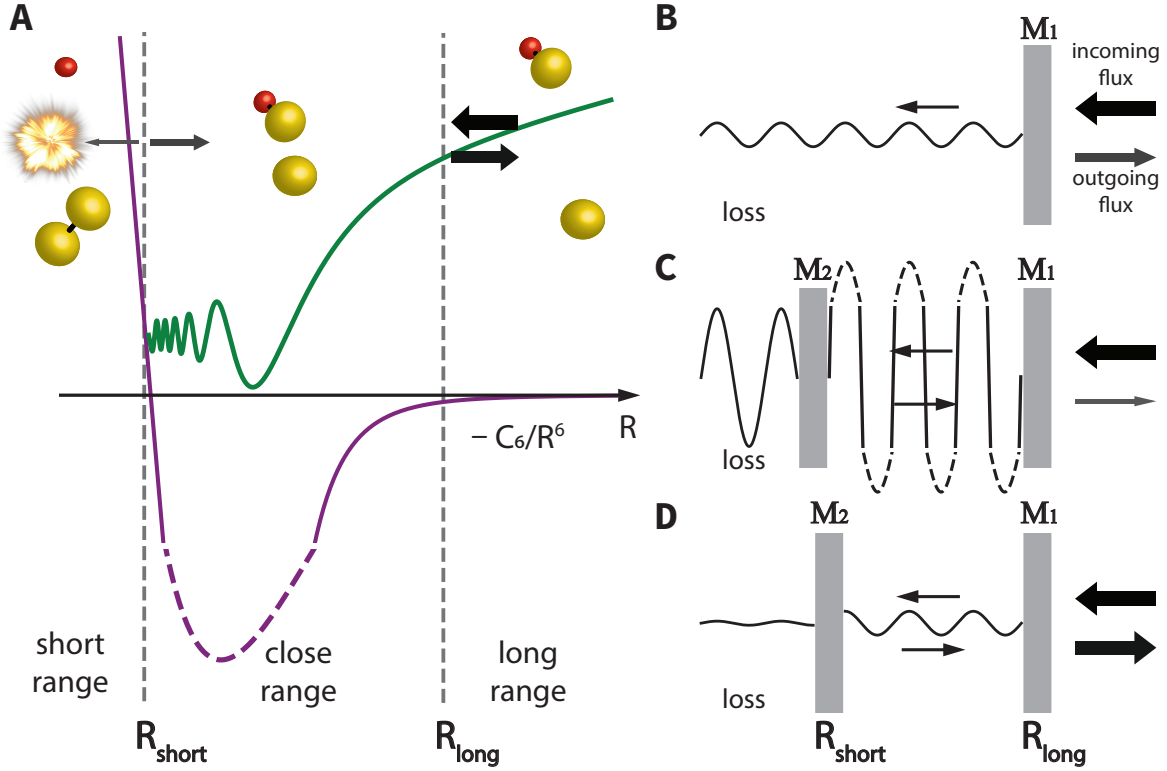


Figure 3.3: Fabry-Perot interferometer model for reactive collisions. (A) The collisions between an atom (yellow sphere) and a molecule (yellow and red sphere) occur in a potential which is the attractive vdW potential $-C_6/R^6$ at long range $R > R_{\text{long}}$ (R is the interparticle distance) and a strongly repulsive potential at short range $R < R_{\text{short}}$. The scattering dynamics (represented by the wavefunction in green) can be fully described by quantum reflection off the vdW potential at $R \sim R_{\text{long}}$ and reflection/transmission at $R \sim R_{\text{short}}$ ^{2,104}. Loss at close and short range is caused by the coupling of the incoming channel (in our case, a chemically stable quartet state) to a lossy channel (here a reactive doublet state) and described by a reflectivity of $<100\%$ of the inner mirror. For instance, in the doublet state, a singlet Na_2 molecule (two yellow spheres) can be formed. This situation is fully analogous to an optical Fabry-Perot interferometer with two partially reflective mirrors (M_1 and M_2). Reactive loss is proportional to the flux transmitted through both mirrors. (B) The transmission through mirror M_1 only represents the universal loss. Depending on constructive and destructive interference between multiple reflections, the loss can be highly enhanced (on resonance, (C)) or suppressed (D) compared to the universal loss. C and D are sketched for a reflectivity $|r_2|^2 \sim 0.89$, with loss enhancement between C and D of a factor of 1000.

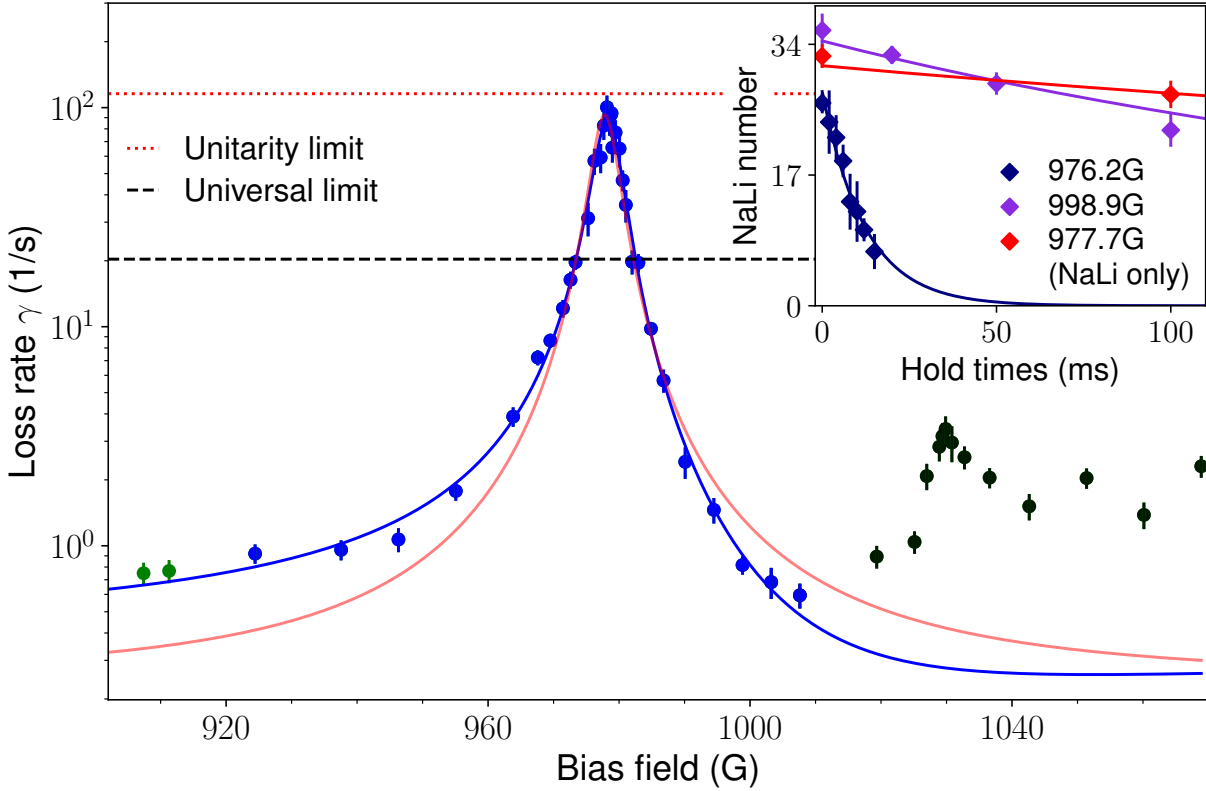


Figure 3.4: Observation of Feshbach resonances in Na+NaLi collisions. Shown are observed decay rates as a function of bias field with 100 sodium atoms per pancake at a temperature of $T_{\text{Na}}=1.60 \mu\text{K}$, $T_{\text{NaLi}}=1.68 \mu\text{K}$, which corresponds to an overlap density of $1.1 \times 10^{11} \text{ cm}^{-3}$. Data points taken with different sodium numbers and temperatures were scaled to the same overlap density (see Chapter A). The blue line is a fit of the lineshape to the Fabry-Perot contrast function C and the red line is a Lorentzian fit. Both fits use only points with blue circles. Green circles were excluded due to another resonance near 880 G. Black circles show an additional resonance near 1030 G. The red dotted line is the unitarity limit in 2D for our experimental conditions. The black dashed line is the universal loss rate. Data points were acquired with 6–11 different hold times at each bias field, and 4–8 measurements at a given hold time are averaged. The error bar indicates one standard deviation. The inset shows decay curves of molecules: the navy (red) diamonds are near the strong resonance at 978 G with (without) sodium atoms, and the purple diamonds are off resonance near 1000 G with atoms. Compared to the navy diamonds, the purple data are with 2.2 times higher overlap density. The red line in the inset is a fit for the two-body molecular loss. The navy and purple lines are obtained by fitting the standard differential equations of two-body decay processes including collisions with atoms (see Chapter A).

CHAPTER 3. CONTROL OF REACTIVE COLLISIONS BY MOLECULE-ATOM FESHBACH RESONANCES

complex scattering length:

$$\tilde{a} = \bar{a} \left(s + y \frac{1 + (1 - s)^2}{i + y(1 - s)} \right) \equiv \alpha - i\beta \quad (3.4.2.1)$$

where $\beta = \bar{a}C(y, s(B))$. The loss rate coefficient K is given by:

$$K = f(k) \frac{2h}{\mu} \beta \quad (3.4.2.2)$$

The function $f(k) = (1 + k^2|\tilde{a}|^2 + 2k\beta)^{-1}$ establishes the unitarity limit for the scattering rates. So far, we have discussed inelastic scattering in 3D. However, because our clouds had the shape of thin pancakes, we were in a 2D regime. Since the vdW length was much smaller than the thickness of the pancakes, the collisions were microscopically 3D and described by the 3D complex scattering length, but in addition, one had to use 2D scattering functions, leading to two effects. First, there is a logarithmic correction of the scattering length. For harmonic axial confinement with frequency ω_{ax} , the correction factor is $l = |(1 + (\tilde{a}/\sqrt{\pi}l_o)\ln(B\hbar\omega_{ax}/\pi k_B T))|^{-2}$ where $B \approx 0.915$, and $l_o = \sqrt{\hbar/\mu\omega_{ax}}$ is the associated oscillator length^{110,111}. Because Na and NaLi have different axial confinement frequencies ω_i and masses m_i , we used $\omega_{ax} = \mu(\omega_{Na}/m_{Na} + \omega_{NaLi}/m_{NaLi})^4$. The correction factor l is large only at extremely low temperatures and near confinement-induced resonances^{110,111}. In our case, it provided a small shift of the peak loss by ~ 0.3 G. The second modification due to the 2D nature of the confinement is in the saturation factor, $f(k)$: In three dimensions, k is obtained from the thermal energy, whereas in 2D, it is obtained from 2π times the relative kinetic energy of the zero-point motion, $k = \sqrt{\pi}/l_o$. The factor of 2π is a reminder that 2D dynamics cannot be fully captured by adding the

⁴Although the relative motion is no longer a simple harmonic oscillator, the expression for ω_{ax} provides the correct kinetic energy $\hbar\omega_{ax}/4$ of the relative motion.

CHAPTER 3. CONTROL OF REACTIVE COLLISIONS BY MOLECULE-ATOM FESHBACH RESONANCES

zero-point energy to the thermal energy.

Our density calibration used the loss rate for collisions in a Na+NaLi mixture in a non-stretched spin state (see Experimental Protocol). The loss rate is expressed by the imaginary part of the scattering length, β , and for the universal rate, $\beta=\bar{a}$.

For the ratio of the observed loss rate to the loss rate measured for the non-stretched state, we obtain

$$\begin{aligned} r(B) &= f(k)l(\beta/\bar{a}) \\ &= \frac{|1+(\tilde{a}/\sqrt{\pi}l_o)\ln(B\hbar^2/\pi\mu l_o^2 k_B T)|^{-2}}{1+(\sqrt{\pi}/l_o)^2|l|^2|\tilde{a}|^2+2(\sqrt{\pi}/l_o)|l|^2\beta}\left(\frac{\beta}{\bar{a}}\right) \end{aligned} \quad (3.4.2.3)$$

The sodium density and all other factors are common mode and cancel by taking the ratio. Note that for the calibration measurement, $f(k) = 1$ and $l = 1$ due to the smallness of the scattering length.

We fit the loss rate ratio $r(B)$ using the four parameters: $B_{\text{res}}, \Delta, q, y$. Because the calibration measurements had uncertainties, we included a fifth fitting parameter, in form of an overall normalization factor, $\mathcal{N}$. We used an accurate theoretical value of $\bar{a}$ calculated for triplet ground-state Na+NaLi, $\bar{a} = 56.1a_0$ with $\lesssim 1.5\%$ uncertainty⁸². Figure 3.5 compares the experimental results with the fits. In the figure, we have multiplied $r(B)$ by the constant $2\hbar\bar{a}/\mu$ and divided by the momentum dependent 2D corrections, $f(k)l$ calculated with the parameters of the best fit. In this way, we obtained the zero-temperature 3D loss rate coefficient, $K_0(B) = (2\hbar/\mu)\beta$, which is a microscopic property of the two-body system, Na+NaLi.

The best fit with the single-channel model gave $B_{\text{res}}=978.6(1)$ G, $\Delta=28(2)$ G, $y=0.0094(47)$, $q=1.60(7)$ with $\chi_{\text{red}}^2=1.23$ (degree-of-freedom (dof) = 27). The normalization factor, $\mathcal{N}=1.32(45)$ was compatible with 1 and therefore consistent with our calibration method.

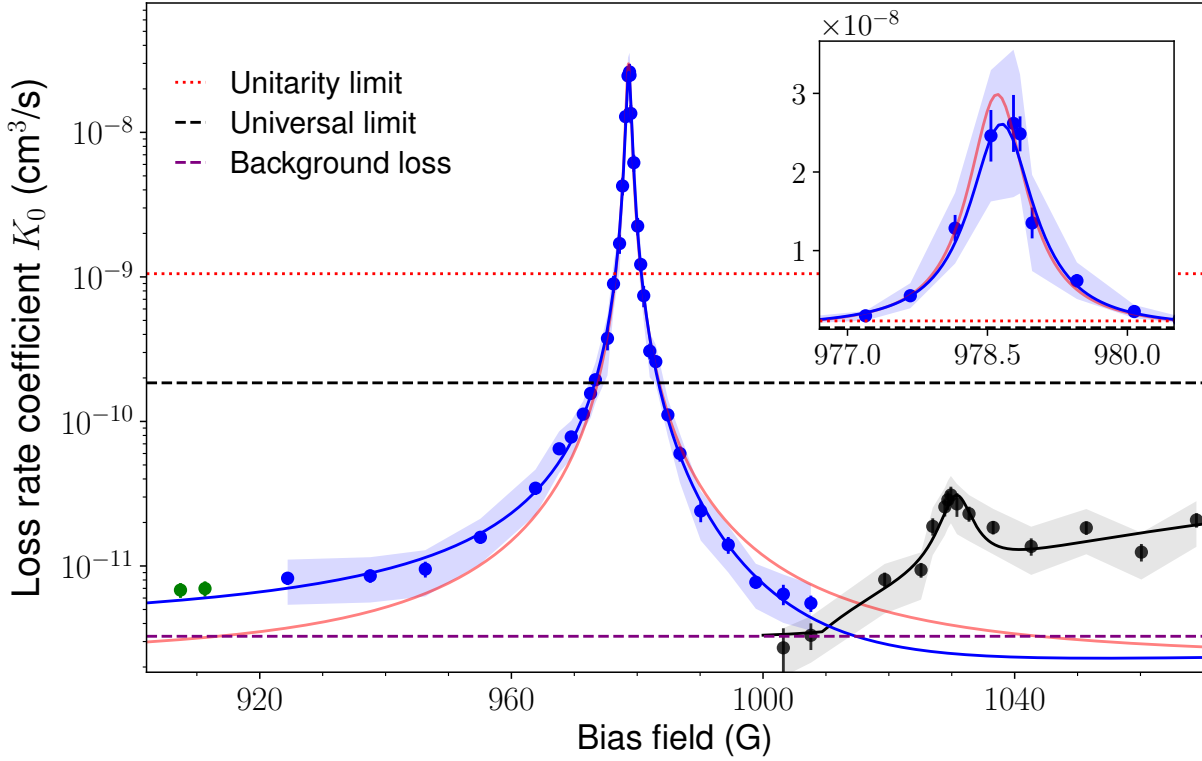


Figure 3.5: Zero-temperature loss rate coefficients K_0 for Na+NaLi collisions. K_0 is the imaginary part of the scattering length times $2h/\mu$. The experimental data points were corrected for non-zero momentum effects, $f(k)l$ (see Results and Analysis). The blue line is the best fit based on the single-channel model, the red line is a symmetric Lorentzian fit. For both fits, only blue data points were included. The black line is a fit of the weak resonance using a two-channel model. The two black data points near 1005 G were obtained from the blue points by subtracting the contribution of the wings of the strong resonance. The red dotted line is the unitarity limit in 2D, $(h/2\mu)\sqrt{\pi}/l_o$. The black dashed line is the universal limit. The purple dashed line shows the background (open-channel) loss. The shaded area represents the total uncertainty, which is the quadrature-sum of the standard deviation and the systematic uncertainty in the density calibration. The inset shows the central part of the figure in a linear scale.

3.4.3 Analysis of the weak resonance at 1030 G with the two-channel model

Figure 3.5 also shows a weaker resonance near 1030 G. This resonance couldn't be explained by the single-channel model (i.e. with a lossless phase shifter) which predicts that the maximum loss is larger than the universal limit. We therefore extended our model by considering a finite lifetime to the state coupled by the Feshbach resonance in form of a linewidth Γ_b . This extension implied that the phase shifter of the Fabry-Perot resonator was now lossy and prevented the large resonant build-up of wavefunction inside the interferometer. In this two-channel model, we describe a lossy phase-shifter by:

$$s_b(B) = q \left(1 - \frac{\Delta}{B - B_{\text{res}} - i\Gamma_b/2} \right) \quad (3.4.3.1)$$

With Eq. (3.4.3.1), we can express β in the Breit-Wigner form as in Ref.¹⁸ (see Chapter A). We assumed that y and q were the same as for the strong resonance because they characterized the same incoming channel, and we used the same normalization factor. We also included a slope and an offset as extra fit parameters to account for other loss channels not covered by our model. We obtained $B_{\text{res}}=1030.8(7)$ G, $\Delta=0.21(4)$ G, $\Gamma_b=5.38(4)$ G with $\chi^2_{\text{red}}=2.4$ (dof = 10). The Δ parameter showed that the resonance at 1030 G was two orders of magnitude weaker than the one at 978 G. From the linewidth, we inferred the bound state lifetime, $\tau_b = (\delta\mu\Gamma_b)^{-1} \approx 60$ ns, where the relative magnetic moment between the entrance channel and the closed channel bound state was $\delta\mu=2\mu_B$ assuming a single spin-flip (μ_B is the Bohr magneton). Here the lifetime of a collision complex was obtained from a spectroscopic linewidth, whereas in all previous work on collisions of ultracold molecules, such lifetimes were obtained from a direct time-domain measurement^{23,26}. The short lifetime of the bound state suggests that the closed channel has a highly reactive doublet character. Some contribution to Γ_b and y could also come

CHAPTER 3. CONTROL OF REACTIVE COLLISIONS BY MOLECULE-ATOM FESHBACH RESONANCES

from the 1,596-nm trapping light which can excite collision complexes leading to loss, as observed in other molecular systems^{22,23,26}. However, given the small value of y , we expect this effect to be small.

We could also fit the strong resonance to the two-channel model and found $\Gamma_b = 0 \pm 1$ G confirming that we can regard the strong resonance as a lossless phase shifter. The longer lifetime of the closed channel associated with the strong resonance suggests that it is only weakly coupled to reactive channels. The difference between the two Feshbach resonances is highlighted by looking at the total inelastic width Γ_{inel} of the resonance (see Chapter A):

$$\Gamma_{\text{inel}} = \Gamma_b + \frac{2yq\Delta}{1 + y^2(q - 1)^2} \quad (3.4.3.2)$$

where the first term is the natural linewidth of the bound state itself, and the second term represents the resonantly enhanced decay rate of the incoming channel. The width of the 978 G resonance was dominated by the open channel losses at short range (i.e. $y \neq 0$), whereas the weak resonance was limited by the decay rate Γ_b . Equation (7) shows that the y parameter is more easily determined from a strong resonance. In contrast, the weaker resonance was insensitive to the short-range parameters y and q of the incoming channel. Figure 4 shows the real and imaginary parts of the scattering lengths for the two resonances and illustrates the power of the simple model: analysis of the inelastic scattering provides a full description of all s -wave scattering properties, including elastic scattering and momentum dependence. We can also calculate the good-to-bad collision ratio, $k(\alpha^2 + \beta^2)/\beta$ and find that it is maximized away from the resonance (see Chapter A).

Figure 3.5 shows that the zero-momentum loss rate could be tuned over four orders of magnitude and exceeded the universal limit by a factor of 100, which was reduced by the unitarity limit to a factor of five (Fig. 3.4). To the best of our knowledge, this is the first

clear demonstration of loss rates larger than the universal limit⁵

The quality factor of the Fabry-Perot resonator becomes smaller for non-zero momentum due to the lower long-range quantum reflectivity which has a threshold law of $|r_1| \approx 1 - 2\bar{a}k$. This relation gives $|r_1| \sim 0.93$ using the total (i.e. thermal and zero-point) momentum for k . The resonant enhancement inside the Fabry-Perot resonator is reduced when the transmission of the outer mirror (M_1) is comparable to the one of the inner mirror (M_2), i.e. when $\bar{a}k \sim y$. At this point, the unitarity saturation kicks in and reduces the loss rate from its zero-temperature value shown in Fig. 3.5.

3.4.4 Physical mechanism of NaLi+Na Feshbach resonances

As a possible mechanism that gives rise to NaLi+Na Feshbach resonances, the interplay between the intra-molecular spin-spin coupling H_{ss} and the strong anisotropic electrostatic interaction V_{elec} can play a role at short range⁶. The “anisotropy” of the electrostatic interaction arises since its strength depends on the orientation of a molecule relative to an atom. The spin-spin coupling (Eq. (3.4.4.1)) is a dipolar interaction between electronic spins that consist of the total spin $S = s_1 + s_2 = 1$ of a triplet NaLi molecule¹¹²:

$$H_{ss} = \frac{C}{r^3}(\vec{s}_1 \cdot \vec{s}_2 - 3(\vec{s}_1 \cdot \hat{r})(\vec{s}_2 \cdot \hat{r})) = \lambda_{ss} \frac{2}{3} \sqrt{\frac{4\pi}{5}} \sqrt{6} \sum_q Y_{2-q}(\hat{r}) [S \otimes S]_q^{(2)} \quad (3.4.4.1)$$

where the constant $C \approx \mu_0 \mu_B / \pi$ (μ_0 : vacuum permeability, μ_B : Bohr magneton), λ_{ss} is the spin-spin coupling coefficient, and $\hat{r}$ is the unit vector in the internuclear axis

⁵Ref.³⁴ mentions a resonant loss rate 2~3 times higher than the universal limit. However, this is based on an estimate for the universal limit and a non-specified density calibration. Our weak resonance shows that it is easily possible to observe Feshbach resonances which don't exceed the universal limit.

⁶The spin-rotation coupling also contributes but its strength is roughly an order of magnitude smaller than the strength of spin-spin coupling, according to Marcin Gronowski and Michał Tomza of Univ. of Warsaw (private communication). Thus, the effect of the spin-spin coupling is typically larger.

direction.

H_{ss} couples electronic spins, $\vec{s}_1$ and $\vec{s}_2$, to the internuclear axis $\vec{r}$, which is orthogonal to $\vec{N}$, the rotation of nuclei. Thus, H_{ss} gives rise to a coupling between the electronic spin and the rotation of nuclei. Equivalently, H_{ss} creates an admixture of a rotationally excited $N = 2$ state with a spin flip, in the initial quartet spin state with $N = 0$. In terms of the (semi)asymptotic channel basis, we can write the initial state of the quartet NaLi+Na as $|i\rangle = |v = 0, L = 0, N = 0, S_{\text{tot}} = 3/2, M_{S_{\text{tot}}} = 3/2\rangle + \epsilon |v = 0, L = 0, N = 2, S_{\text{tot}}, M_{S_{\text{tot}}} = \pm 1/2\rangle$ where the admixture ratio is $\epsilon = \frac{\lambda_{ss}}{E_{N=2} - E_{N=0}}$ (v is the vibrational, N is the rotational quantum numbers of NaLi, $M_{S_{\text{tot}}}$ is the magnetic quantum number of the total spin of NaLi+Na, and L is the quantum number of the orbital angular momentum associated with the mutual rotation of NaLi and Na; $M_{S_{\text{tot}}} = +1/2, -1/2$ represent single and double spin flips respectively). Note that the admixture component can be in either $S_{\text{tot}} = 3/2$ or $1/2$ state since the intra-molecular spin-spin (and, spin-rotation) interaction is not diagonal in the basis $|S_{\text{tot}}, M_{S_{\text{tot}}}\rangle$. This means that both Zeeman relaxation on the quartet manifold and the spin flip with a transition to the reactive doublet manifold are possible⁷. Given the measured rotational constant of NaLi, $B = 4.6$ GHz³⁵ and the calculated spin-spin coupling coefficient, $\lambda_{ss} \approx 600$ MHz⁸, the admixture ratio is about $\epsilon \approx 0.02$. H_{ss} is such a weak coupling, but the initial state $|i\rangle$ can strongly couple to a final state $|f\rangle = |v^*, N^*, L^*, S_{\text{tot}}^*, M_{S_{\text{tot}}^*} = \pm 1/2\rangle$ via V_{elec} which is on the order of eV energy scale at short range. Since V_{elec} can mix all degrees of freedom except spins, the excitation of L^* can arise, i.e. the creation of NaLi+Na bound states with the mutual rotational excitation. In other words, the transition to a NaLi+Na

⁷When the initial spin state of NaLi+Na is polarized in the lower stretched state, Zeeman relaxation is not possible, and a transition to the reactive doublet potential is the only possible spin-flip mechanism.

⁸This is from private communications. The calculation by Marcin Gronowski and Michał Tomza (Univ. of Warsaw) gives $\lambda_{ss} \approx 668$ MHz, and that by Rebekah Hermsmeier (Univ. of Nevada), Jacek Kłos (Temple Univ.), Svetlana Kotochigova (Temple Univ.) and Timur V. Tscherbul (Univ. of Nevada) gives 552 MHz. Both results are at the equilibrium distance of NaLi around $8.9a_0$.

bound state can happen at short range where the anisotropic interaction V_{elec} is much larger compared to the rotational splitting of NaLi. The role of V_{elec} implies the short range nature of the observed NaLi+Na Feshbach resonances.

More physical description would be as follows. The anisotropy of V_{elec} reorients NaLi with respect to Na, which is equivalent to mixing of N and L , and this causes a spin flip since the spin is coupled to the internuclear axis of NaLi through the intra-molecular spin-spin (and, the spin-rotation) interaction.

The possibility of this mechanism has been confirmed by the coupled-channel scattering calculations of Tijs Karman (e.g. the scattering cross section, which is proportional to the transition matrix element squared, scales quadratically with spin-spin and spin-rotation coupling coefficients, respectively, etc). Statistical aspects of the Tijs Karman’s scattering calculation on NaLi+Na Feshbach resonances will be discussed in a future publication.

3.5 Discussion

In this chapter, we have demonstrated the substantial suppression and enhancement of reactive collisions relative to the universal limit, which is possible only if $y \ll 1$ and realized control of chemical reactions via external magnetic fields. An asymmetric lineshape can lead to a suppression of inelastic losses below the background loss¹¹³. This suppression was not realized in Fig. 3.5 due to the neighbouring weaker Feshbach resonance.

Our analysis highlights the conditions necessary to observe such a high dynamic range tunability of reactive collisions. The possible contrast is given by $1/y^2$, but is only realized if the Feshbach resonance is sufficiently strong and coupled to a sufficiently long-lived state: $q\Delta/\Gamma_b > 1/y$. This condition for the Feshbach resonance is the harder to fulfill the smaller y is, but the Na+NaLi system satisfies this condition for the resonance at 978 G and several other resonances which we have observed, but not yet fully analyzed.

CHAPTER 3. CONTROL OF REACTIVE COLLISIONS BY MOLECULE-ATOM FESHBACH RESONANCES

The models for reactive collisions presented here may look rather special. However, our two-channel model captures the low-temperature limit of the most general resonance possible for which the complex scattering length is represented by a circle in the complex plane^{18,114} (see Chapter A).

Universal reaction rates are determined only by quantum reflection of the long-range potential and do not provide any information about the “real chemistry” at short range. Therefore, to find and characterize non-universal molecular systems is a major goal of the field^{7-9,12,13,115}. However, in most of the cases studied, the deviation from the universal limit is only by a factor of 2~4 and their interpretation required an accurate density calibration which is not always performed. Some studies showed inelastic rates well below the universal limit, without any resonances¹¹⁶⁻¹¹⁸ which can provide only an upper bound for y and leaves q undetermined. This work has demonstrated how short-range reflectivity makes it possible to access information about short-range interactions and collisional intermediate complexes. Our analysis showed that suppression of loss below the universal limit could occur for a wide range of parameters, but strong enhancement of loss beyond the universal limit requires fine tuning: an almost lossless Farby-Perot interferometer tuned to resonance.

In this chapter, we have experimentally validated a method based on external magnetic fields and quantum interference to realize quantum control of chemistry. Previous studies used microwaves^{115,119} or electric fields¹²⁰ to control losses in molecular systems with strong long-range dipolar interactions by modifying the universal rate limit. Here we have used magnetic fields and quantum interference, without need for dipolar interactions, to achieve loss rate coefficients far larger than the universal limit. All these methods control one specific decay channel. With the weak resonance, we have also demonstrated that magnetic field can switch between two different mechanism of reactive scattering, occurring in the chemically stable incoming and the lossy closed channels, respectively.

4

Conclusion

4.1 Summary

This thesis builds on the creation of a non-universal atom-molecule mixture – a spin-polarized NaLi+Na in the quartet state – and focuses on utilizing a favorable good-to-bad collision ratio for sympathetically cooling molecules and controlling reactive scattering by atom-molecule Feshbach resonances.

One of the main points to be emphasized in this thesis is the power of spin-polarization, which is based on a simple yet beautiful physical law of (spin) angular momentum

conservation. It was shown in this thesis that the spin-polarization can be a great way to realize a collisionally stable molecular system, just like the principle was effective for atomic mixtures⁷⁰. This finding tells us that making molecules in the absolute ground state (i.e. in the electronic singlet state for bialkali cases) is not the only way to achieve a great collisional stability of molecular systems. The result discussed in this thesis shows that a molecular system can be isolated in a (almost) pure chemically-stable state – even if it is not the absolute ground state – when the constituent spins are polarized. In other words, although there are numerous reactive states that are energetically available (e.g. the reactive doublet potential of NaLi+Na is deeper than the quartet potential by ~ 4000 K), the subspace of the reactive states is effectively decoupled from the non-reactive state. This principle can be possibly applied to other molecular systems and open the door for sympathetic and/or evaporative cooling of them. This favorable collisional property could be also facilitated by the low molecular mass, the small size and the low reduced mass of NaLi+Na, which result in a large molecular rotational constant^{66,96}, small spin-orbit coupling⁹⁷, and low density of states²¹, respectively. With the low density of states, it is likely to observe resolvable Feshbach resonances²⁵ and as shown in Chapter 3, they facilitate a precise spectroscopy of the resonance lineshape from which we can possibly learn short-range physics. Thus, the work of this thesis establishes a light molecular system as a useful tool to study quantum chemistry, molecular scattering resonances, and possibly short range physics.

4.2 Outlook

- **Reaching quantum degeneracy with NaLi molecules:** The major limitation in reaching degeneracy with molecules is their low initial PSD. By making the initial PSD lower, we can possibly reach the degeneracy without much decrease in temperatures. This can be achieved by improving the transfer efficiency of atoms

CHAPTER 4. OUTLOOK

from a magnetic trap to an optical trap. In the current experiment, due to the non-perfect coil construction and/or installation, the saddle point of the Feshbach field (i.e. 745 G) is about 2 mm away from the center of the Ioffe-Pritchard magnetic trap where we initially cool sodium and lithium atoms. Due to the magnetic field gradient caused by the displacement of the saddle point, we lose particles in an optical trap when we place it at the center of the magnetic trap. Inevitably, we have to place the optical trap at the saddle point of the Feshbach field and shift the magnetic trap to the saddle point. However, the magnetic field gradient applied to shift the magnetic trap makes the trap no longer colinear with the optical trap¹ and possibly non-harmonic with multiple local minimums in potential energy. For this reason, the best transfer efficiency of atoms from the shifted magnetic trap to an optical trap is only about $\lesssim 30\%$, which can be nearly perfect when the magnetic trap is not shifted by 2 mm. This problem can be solved by loading atoms from the unshifted magnetic trap to a well-overlapped optical trap, moving the optical trap to the saddle point of the Feshbach field with a motorized mirror mount, and producing molecules. Increasing the number of atoms would directly improve the PSD of molecules prior to cooling, and this can possibly enable producing quantum degenerate NaLi molecules only by slight cooling or thermalization with sodium atoms, without the need of significantly lowering temperatures.

As another (partial) solution to overcome the low initial PSD of molecules, we tried to maximize the cooling capacity by working in the regime where the coolants, sodium atoms are the majority. We increased the sodium density to the point where the s -wave NaLi+Na collisional loss is about a factor of $2 \sim 3$ larger than the p -wave molecular two-body loss. In this way, we were able to evaporate sodium atoms more

¹The azimuthal angle between the shifted magnetic trap and an optical trap is on the order of 10° and the elevation angle is not as large as this (probably, on the order of 1°).

CHAPTER 4. OUTLOOK

efficiently as the sodium thermalization got accelerated, and by applying a quicker evaporation sequence, we were able to make NaLi at $T/T_F \sim 1$ ² (T_F in 2D= $1.3\mu\text{K}$ with the trap depth of $\sim 100\mu\text{K}$, 16 molecules in each pancake; T_{NaLi} was inferred by T_{Na} based on thermalization).

In order to reach the lower temperature, however, we had to decrease the trap depth to the point where we lost too many sodium atoms during the forced evaporation step. This problem can be solved by increasing the sodium thermalization rate without increasing the molecular two-body loss and the loss due to collisions with sodium atoms. One way to achieve this is to have a capability to independently control the sodium density and the molecule-atom overlap density by installing the second optical trapping beam that can preferentially give extra trapping force for sodium atoms. This would allow us to evaporate sodium atoms more efficiently with the trapping force larger only for sodium atoms, while keeping the trapping potential for molecules rather lose.

We can also improve γ by performing the sympathetic cooling at a bias field where the NaLi+Na collisional loss is the minimum; for instance, the loss rate is about a factor of 2.5 less at 570 G compared to 745 G. We should check if the elastic scattering rates between NaLi+Na and Na+Na change at different fields as well.

In addition, for future cooling experiments, it will be more straightforward to optimize the cooling sequence in a trap with a simpler geometry, such as a tightly focused optical dipole trap (ODT) or a crossed-ODT³, since the 1D lattice gives

²The similar T/T_F was also achieved by a cooling scheme with magnetic field gradient (inspired by Ref.¹²¹). In this scheme, I kept the optical trap tight without loosening it and tilted the trap with a magnetic force that was linearly varying in the radial direction. This method, however, does not solve the same problem since the loss rate increases while the sodium thermalization gets faster.

³The trap should be tight enough to overcome the magnetic anti-trapping force in the axial direction (i.e. the bias field direction).

extra complications due to the inhomogeneous density distribution across lattice sites (the differential inhomogeneity between molecules and atoms is the major issue) and complicated density calibration.

- **Magnetic trapping of NaLi molecules:** Interaction of molecules with trapping light can cause extra molecular loss^{22–24,26}. As mentioned in Chapter 4, the two-body loss rate of NaLi was measured to be a factor of about 2 higher than the p -wave universal rate. This could be due to the photo-induced loss by 1,596 nm trapping light⁴. We can avoid such issue by trapping NaLi molecules in a magnetic trap instead, and this is a great advantage of the triplet molecules whose magnetic moment is $2\mu_B$, unlike the singlet molecules that have zero electronic spin.
- **Molecule-molecule Feshbach resonances:** One of the biggest advantages of the lightest bialkali molecules might be realized in the study of molecule-molecule Feshbach molecules. Observing resolvable molecule-molecule Feshbach resonances will be trickier given the higher density of states compared to atom-molecule systems. If the first Feshbach resonance between ground state molecules is observed, I believe there is a big chance that the molecule would be the triplet ground state NaLi.

⁴When we trapped molecules in a 1,319 nm optical dipole trap, the molecular two-body loss rate coefficient was measured to be a factor of about 3 higher than the p -wave universal value, and it was suspected that the Rayleigh scattering from the 1,319 nm optical trap was driving a molecular transition to the $b^3\Pi$ excited potential (i.e. one-body loss)⁶. Since transitions to the $b^3\Pi$ excited potential by 1,596 nm photons has about two orders of magnitude lower Franck-Condon factor, the one-body loss process should not be a limiting factor, unless we are too unlucky to drive a near-resonant vibrational excitation. This can be checked by measuring the molecular loss rate by scanning the optical trap frequency. Another possibility is the excitation of molecule-molecule collision complexes. Such possibility can be experimentally checked by measuring the molecular loss with an intensity-modulated optical trap²³. It is also possible that the deviation of the molecular loss rate in a 1,596 nm optical trap from the universal loss rate is actually less than what is measured. Since we do not have a good knowledge of the C_6 coefficient between triplet NaLi molecules, we estimate the p -wave universal loss rate, which is proportional to $C_6^{3/4}$, with the sum of the C_6 coefficients for the atomic pairs that constitute the collision partners using values from Ref.⁹³. Such an estimate of the C_6 coefficient would be inaccurate: for instance, the C_6 coefficient of $^3\Sigma\text{NaLi}+\text{Na}$ is $\gtrsim 30\%$ larger than the C_6 estimated as we did for the C_6 between molecules.



Supplemental information for Chapter 3.

A.1 Relation between s -wave scatterings in 2D & 3D

In 2D geometry, scattering between particles is still microscopically 3-dimensional if the characteristic length scale of inter-particle interactions is much less than the de Broglie wavelength, $\lambda_\epsilon \approx \hbar/\sqrt{2\mu\epsilon}$ (relative kinetic energy, $\epsilon = \hbar^2 q^2/2\mu$ with 2D relative wavevector, q) and the oscillator length in the axial direction, $l_0 = \sqrt{\hbar/\mu\omega_{\text{ax}}}$ ¹¹⁰ with $\omega_{\text{ax}} = \mu(\omega_{\text{Na}}/m_{\text{Na}} + \omega_{\text{NaLi}}/m_{\text{NaLi}})$ (ω : axial trap frequency). In this case, according to Eq. (14) of Ref.¹¹⁰, the 3D scattering wavefunction can be written as $\psi(r) \approx \eta\phi_{v=0}(z=0)(1 - a_{3\text{D}}/r)$ where $a_{3\text{D}}$ is the 3D s -wave scattering length, $\phi_v(z=0)$ is the eigenfunction of the v state for the axial relative motion (z : axial coordinate), and η is a coefficient acquired by solving the 3D Schrodinger equation with a harmonic potential in the axial direction but with a free motion in the radial direction. According to Ref.¹¹⁰, η is given by

$$\eta = \frac{1}{1 + a_{3\text{D}}/\sqrt{\pi}l_0 \times w(\epsilon/2\hbar\omega_{\text{ax}})} \quad (\text{A.1.0.1})$$

where

$$w(x) = \lim_{N \rightarrow \infty} \left[2\sqrt{\frac{N}{\pi}} \ln\left(\frac{N}{e^2}\right) - \sum_{j=0}^N \frac{(2j-1)!!}{(2j)!!} \ln(j-x-i0) \right]. \quad (\text{A.1.0.2})$$

In the case of $\epsilon \ll \hbar\omega_{\text{ax}}$ (i.e. quasi-2D where $x \ll 1$) where only the ground state, $v=0$ contributes to the scattering in the axial direction,

$$w(\epsilon/2\hbar\omega_{\text{ax}}) \approx \ln(B\hbar\omega_{\text{ax}}/\pi\epsilon) + i\pi \quad (\text{A.1.0.3})$$

where $B \approx 0.915$ ¹¹⁰.

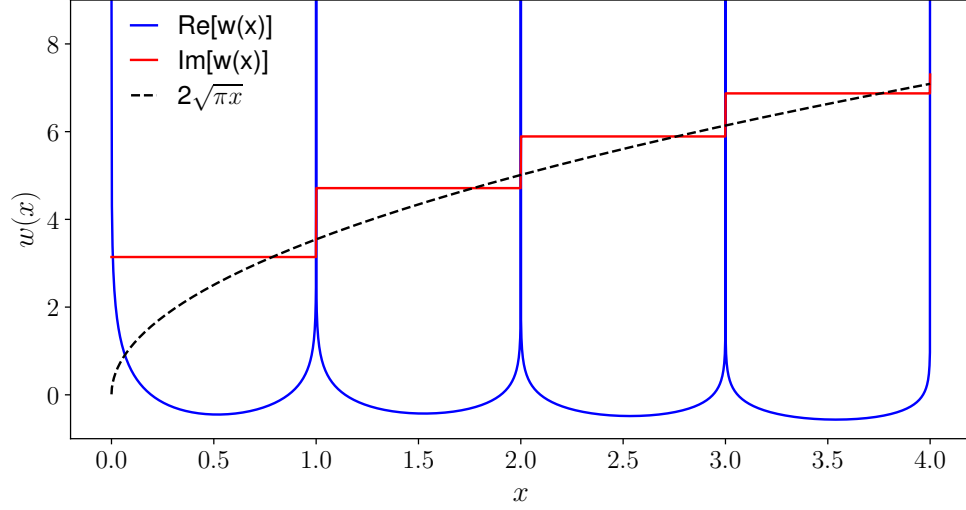


Figure A.1: $w(x)$ function given by Eq. (A.1.0.2). Confinement induced resonances occur at $x = 0, 1, 2, 3, \dots$. The dotted line shows the asymptotic behaviour of $\text{Im}[w(x)]$ at large x values.

This result implies that the strong axial confinement modifies the 3D scattering wavefunction by a multiplicative factor $\eta\phi_0(z=0)$. Thus, the scattering cross-section, which is proportional to the scattering amplitude squared, is proportional to the factor $|\eta|^2$, and this factor $|\eta|^2$ is nothing but a saturation factor. For instance, in the 3D high temperature limit (i.e. $\epsilon \gg \hbar\omega_{\text{ax}}$ or $x \gg 1$) where $w(\epsilon/2\hbar\omega_{\text{cax}}) \approx i\sqrt{2\pi\epsilon/\hbar\omega_{\text{ax}}}$ (see Fig. A.1), $|\eta|^2 = |1 + ik\tilde{a}_{3D}|^{-2} = (1 + k^2|\tilde{a}_{3D}|^2 + 2\beta_{3D}k)^{-1}$, which is the same result given in Ref.² (here, a_{3D} is generalized as a complex scattering length, $\tilde{a}_{3D} = \alpha_{3D} - i\beta_{3D}$, and $\epsilon = \hbar^2k^2/2\mu$ with a 3D relative wavevector, k). The modification of the saturation factor is the first effect of the strong axial confinement.

The second effect is in the modification of the scattering lengths. Reactive and elastic scattering rates in quasi-2D are given by

$$K_{2D}^{\text{re}} = g \frac{4\hbar}{\mu} \beta_{2D} f_{2D}, \quad K_{2D}^{\text{el}} = g \frac{4\hbar}{\mu} |\tilde{a}_{2D}|^2 f_{2D} \quad (\text{A.1.0.4})$$

where $g = 1$ for collisions between non-identical particles, the 2D complex scattering

APPENDIX A. SUPPLEMENTAL INFORMATION FOR CHAPTER 3.

length, $\tilde{a}_{2D} = \alpha_{2D} - i\beta_{2D}$, and the 2D saturation factor, $f_{2D} = (1 + |\tilde{a}_{2D}|^2 + 2\beta_{2D})^{-1}$ ¹¹¹. Using Eq. (39) in Ref.¹¹¹, which is the relation between $\tilde{a}_{2D}$ and $\tilde{a}_{3D}$, we found the relation between the 2D and 3D scattering parameters can be written in terms of l and η :

$$|\tilde{a}_{2D}|^2 = \left(\frac{\sqrt{\pi}}{l_0}\right)^2 |l|^2 |\tilde{a}_{3D}|^2, \quad \tilde{\beta}_{2D} = \frac{\sqrt{\pi}}{l_0} |l|^2 \tilde{\beta}_{3D}, \quad |l|^2 f_{2D} = |\eta|^2 \quad (\text{A.1.0.5})$$

where $l = (1 + \tilde{a}_{3D}/\sqrt{\pi}l_0 \times \ln(B\hbar\omega_{\text{ax}}/\pi\epsilon))^{-1}$. The first two equations imply that the elastic and reactive scattering rates in 3D are modified by a factor $|l|^2$ with a wavevector $k = \sqrt{\pi}/l_0$ (the relative kinetic energy associated with $k = \sqrt{\pi}/l_0$ is a factor of 2π larger than the relative kinetic energy associated with the zero-point motion, $\hbar\omega_{\text{ax}}/4$). This result manifests that the descriptions of 2D and 3D scatterings in an 1D optical lattice are not fundamentally distinct but are closely related via the factor l in which the strong axial confinement effect is implied.

Near the peak of the strong resonance at 978 G, we have $|a_{3D}| \gtrsim l_0$, and in this case, scattering can occur with a strong 2D effect (i.e. a large logarithmic terms in l) when the temperature is sufficiently low, $\epsilon < \epsilon_* \approx 0.1\hbar\omega_{\text{ax}}$, or near confinement-induced resonances¹¹⁰. Since we are in the regime where $\epsilon_* < k_b T < \hbar\omega_{\text{ax}}$, the 2D correction effect is not so large as mentioned in Chapter 3, but the ground state channel still dominates the scattering in the axial direction¹¹⁰. In this regime, $w(\epsilon/2\hbar\omega_{\text{ax}}) \approx i\pi$ (see Fig. A.1). Note that the 2D effect has been fully taken into account in our analysis with Eq. (A.1.0.3) and (A.1.0.4).

A.2 Loss rate measurement & density calibration

In the main article, we provided the basic concept of how we acquired loss rates for Na+NaLi collisions, by comparing the initial loss rates with and without sodium atoms. For better accuracy, we evaluated the whole decay curve of molecules taking the time-dependent sodium numbers and particle temperatures into account, by numerically solving the differential equations:

$$\dot{N}_{\text{NaLi}} = -(K/V_{\text{ov}})N_{\text{Na}}N_{\text{NaLi}} - (\beta/V_{\text{eff}})N_{\text{NaLi}}^2 \quad (\text{A.2.0.1})$$

$$\dot{N}_{\text{Na}} = -(K/V_{\text{ov}})N_{\text{NaLi}}N_{\text{Na}}, \quad (\text{A.2.0.2})$$

where N_i represents the effective number of particles of type i per pancake (i.e. Gaussian-weighted mean particle number defined in Chapter 2.2.3.1), V_{ov} is the volume of the regime where atoms overlap with the more tightly confined molecules, and V_{eff} is the mean volume of molecules. β is the two-body molecular loss rate coefficient and K is the loss rate coefficient for the collisions of Na+NaLi pairs.

To determine rate coefficients from equations Eq. (A.2.0.1) and Eq. (A.2.0.2) requires accurate knowledge of the volumes V_{eff} and V_{ov} for a single pancake and knowledge of the effective particle number per pancake, which is the weighted average over the entire ensemble of pancakes. We will discuss this below.

In our primary calibration, however, we avoided this complication by comparing the decay of the mixture in the stretched spin state around the Feshbach resonance to that in a non-stretched spin state where the rate coefficient K is reliably predicted to be the s -wave universal loss rate coefficient. For this, we prepared sodium atoms in the lowest hyperfine state ($|F, m_F\rangle = |1, 1\rangle$ at the low field) and molecules are in their upper spin stretched

APPENDIX A. SUPPLEMENTAL INFORMATION FOR CHAPTER 3.

state. For these initial states, the Na+NaLi system has a 50% doublet character. The doublet potential at short range is highly reactive due to exothermic nature and the collisional loss is predicted to occur at the s -wave universal rate⁸². In other words, we compared the decay of samples in the spin stretched and non-stretched states with the same initial densities, i.e. with the same effective particle numbers and the same volumes V_{eff} and V_{ov} . The only difference was the rate coefficient K , and by comparing the two decay curves, we obtained an accurate value for the ratio of the two K coefficients without an accurate model for the volumes and the ensemble of pancakes. Multiple calibration measurements with the non-stretched spin state mixture suggest a total uncertainty of the density calibration of $\sim 40\%$.

We have validated the assumption of the universal decay of the mixture in the non-stretched state by carrying out an independent absolute calibration. In this calibration, we obtained the effective particle numbers from the measured numbers of atoms and molecules and their distributions over pancakes, and the overlap volume using a full anharmonic model of the trapping potential and measured temperatures. For the accurate estimation, we had to sum the decay curves over the ensemble of pancakes, or alternatively, calculate the effective particle numbers per pancake and consider an effective decay curve using them. Since the observed axial profiles over pancakes of both Na and NaLi followed Gaussian fits with widths $\sigma_{\text{NaLi}}=450(60)\mu\text{m}$ and $\sigma_{\text{Na}}=630(60)\mu\text{m}$, we assumed a Gaussian distribution of the particle number per pancake. The particle numbers in the central pancakes, N_{Na}^0 and N_{NaLi}^0 , are related to the total particle numbers $N_{\text{Na}}^{\text{tot}}=\sqrt{2\pi}\sigma_{\text{Na}}N_{\text{Na}}^0/a$ and $N_{\text{NaLi}}^{\text{tot}}=\sqrt{2\pi}\sigma_{\text{NaLi}}N_{\text{NaLi}}^0/a$ where the lattice constant, $a=\lambda/2$ and $\lambda=1,596$ nm. As the averages weighted over a Gaussian, the effective particle numbers per pancake in Eq. (A.2.0.1) become $N_{\text{NaLi}}^{\text{eff}}=N_{\text{NaLi}}^0/\sqrt{2}$ and $N_{\text{Na}}^{\text{eff}}=N_{\text{Na}}^0(\sigma_{\text{ov}}/\sigma_{\text{NaLi}})$, where $1/\sigma_{\text{ov}}^2=1/\sigma_{\text{Na}}^2+1/\sigma_{\text{NaLi}}^2$. In Eq. (A.2.0.2), the effective particle numbers are $N_{\text{Na}}^{\text{eff}}=N_{\text{Na}}^0/\sqrt{2}$ and $N_{\text{NaLi}}^{\text{eff}}=N_{\text{NaLi}}^0(\sigma_{\text{ov}}/\sigma_{\text{Na}})$. The effective particle number in this chapter, N^{eff} is the same

APPENDIX A. SUPPLEMENTAL INFORMATION FOR CHAPTER 3.

as the Gaussian-weighted mean particle number, $\bar{N}$ defined in Chapter 2.2.3.1.

We now discuss the volumes V_{eff} and V_{ov} in Eqs. (A.2.0.1) and (A.2.0.2). As-

suming a harmonic trap, one obtains $V_{\text{eff}} = \bar{\omega}_{\text{NaLi}}^{-3} (4\pi k_B T_{\text{NaLi}} / m_{\text{NaLi}})^{3/2}$ and

$$V_{\text{ov}} = (N_{\text{Na}} N_{\text{NaLi}}) / (\int dV n_{\text{Na}} n_{\text{NaLi}}) = \bar{\omega}_{\text{Na}}^{-3} [(2\pi k_B T_{\text{Na}} / m_{\text{Na}}) (1 + (\alpha_{\text{Na}} / \alpha_{\text{NaLi}}) (T_{\text{NaLi}} / T_{\text{Na}}))]^{\frac{3}{2}}$$

where the geometric mean of the sodium trap frequencies, $\bar{\omega}_{\text{Na}} = (\omega_x \omega_y \omega_z)^{1/3} = 2\pi \times (325 \cdot 460 \cdot 45000)^{1/3}$

Hz and the polarizability ratio, $\alpha_{\text{NaLi}} / \alpha_{\text{Na}} = (m\omega^2)_{\text{NaLi}} / (m\omega^2)_{\text{Na}} = 2.8(4)$.

However, the confinement in each pancake is strongly anharmonic. In our model, we use the actual beam geometry of a 1D lattice trap with a retro-reflected beam displaced by 2 mm (which is $\sim 60\%$ of the Rayleigh range) and 43% power relative to the incoming beam. Both beams are linearly polarized and have the same beam waist of 43 μm . The trap depth is calculated from the measured trap frequencies. In the local density approximation, we obtain

$$1/V_{\text{ov}} = \frac{\int dV e^{-\beta_{\text{Na}} U_{\text{Na}}(r,z)} e^{-\beta_{\text{NaLi}} U_{\text{NaLi}}(r,z)}}{[\int dV e^{-\beta_{\text{Na}} U_{\text{Na}}(r,z)}][\int dV e^{-\beta_{\text{NaLi}} U_{\text{NaLi}}(r,z)}]} \quad (\text{A.2.0.3})$$

where r is the radial coordinate, z is the axial coordinate along the beam direction, $\beta_i = (k_B T_i)^{-1}$, and $U_i(r, z)$ is the potential of a single lattice site for the particle i . The integration limits in both coordinates are determined by the equipotential contour of the local maximum formed by gravity that tilts the trap in the y-direction. We find that the harmonic overlap volume is smaller than the anharmonic volume by a factor of 1.8.

Using this model and calibration, we experimentally measured the absolute loss rate for the mixture in the non-stretched spin state to be 30% lower than the universal limit, which agrees with the prediction of universality within the experimental uncertainty of $\sim 40\%$.

The validity of the anharmonic model is experimentally cross-checked by observing cross-dimensional thermalization which occurs with a cross section well known via the s -wave scattering length of sodium atoms¹²², including the 2D correction of the elastic

scattering rate¹¹⁰. For this, V_{eff} is determined from the anharmonic trapping potential as

$$1/V_{\text{eff}} = \frac{\int dV e^{-2\beta_{\text{Na}} U_{\text{Na}}(r,z)}}{[\int dV e^{-\beta_{\text{Na}} U_{\text{Na}}(r,z)}]^2} \quad (\text{A.2.0.4})$$

We find that the observed thermalization rate differs from the model prediction by $\sim 10\%$, which is within the uncertainty of the thermalization measurement, $\sim 15\%$.

When we use the same model for the trapping potential to obtain the two-body molecular loss rate coefficient, we find a factor of two discrepancy with the expected p -wave universal limit¹. This is most likely due to a non-equilibrium distribution of molecules over the different “pancakes” due to the formation process.

In summary, in the main paper, we have eliminated the need for absolute values of the overlap density $N_{\text{Na}}^{\text{eff}}/V_{\text{ov}}$ by comparing loss rates around the Feshbach resonances to the loss rate of the mixture in the non-stretched spin state, which was predicted to be universal. We have validated this prediction by the calibration procedure and modeling described here. In other words, if we had not used the comparison with the non-stretched systems, we would have obtained the same results within the (now larger) uncertainties.

The loss rate coefficients reported here are somewhat different from previous values in Ref.⁴¹ where the anharmonicity in the trapping potential and the polarization purity of the absorption imaging light were not fully considered.

¹The p -wave universal rate of the molecular loss is calculated with the sum of the C_6 coefficients for the atomic pairs that constitute the collision partners, using values from Ref.⁹³. See Conclusion for the discussion on molecular lifetime.

A.3 Typical particle numbers & decay of sodium atoms

The typical particle numbers per pancake are 320 and 30 for Na and NaLi, respectively. With the typical statistical uncertainty of the particle number, $\sim 13\%$, the decay of the sodium number is insignificant and we can treat the number as constant during the hold time.

However, near the peak of the strong resonance, the molecular signal depletes quickly while we wait for the field to fully settle after ramping it. Thus, we typically work in the regime where $N_{\text{Na}}/N_{\text{NaLi}} = 125/23 \approx 5$. In this case, we find decay curves of both sodium atoms and molecules fit well to the analytic solution of Eq. (A.2.0.1) and (A.2.0.2) by ignoring the molecular two-body loss term which is two orders of magnitude smaller than the atom-molecule term. In this regime, the numerical solution of Eq. (A.2.0.1) and (A.2.0.2) agrees well with the analytic solution: $N_{\text{Na}}(t) = -D/(e^{-D\Gamma t}/C - 1)$, $N_{\text{NaLi}}(t) = D/(Ce^{D\Gamma t} - 1)$, where Γ is the loss rate and $C = N_{\text{Na}}(0)/N_{\text{NaLi}}(0)$, $D = N_{\text{Na}}(0) - N_{\text{NaLi}}(0)$. $N(0)$ is the initial particle number. When $D \approx N_{\text{Na}}(0)$, the sodium number is approximately constant, and we find the decay curve of molecules fits well to a simple exponential function, $N_{\text{NaLi}}(t) \approx N_{\text{NaLi}}(0)e^{-\Gamma t}$.

A.4 Magnetic field inhomogeneity

After a mixture of molecules and atoms is initially prepared at 745 G, the bias field is ramped to the target value in 15 ms. Due to eddy currents, an extra hold time of 15 ms or more was added to allow the bias field to fully settle. Due to magnetic field curvature, the sample experiences a magnetic field inhomogeneity of $\lesssim 80$ mG near 1000 G. This upper bound is inferred from the narrowness of an RF spin-flip transition of sodium atoms.

A.5 Temperature of Na and NaLi

Inelastic losses occur predominantly at the highest densities and lead to increase in temperature, sometimes called anti-evaporation. Near the peak of the strong resonance, molecules heat up before we start acquiring a decay curve. We observe that within ± 2.5 G around the peak, the molecule temperature is $\sim 1.9 \mu\text{K}$ while the temperature of sodium atoms is at $\sim 1.6 \mu\text{K}$, due to the large imbalance of particle numbers. This gives the temperature associated with relative radial motion, $T_{\text{rel}} = \mu(T_{\text{Na}}/m_{\text{Na}} + T_{\text{mol}}/m_{\text{mol}}) = 1.73(15) \mu\text{K}$ near the peak. Compared to the temperature away from the peak $T_{\text{rel}} \sim 1.55 \mu\text{K}$, this is about 12% higher, and with the increased temperature, the fit result is still the same within the fit uncertainty. Further heating during the decay curve measurement is not observed.

A.6 Verification of two-body loss mechanism

We have treated the loss dynamics as purely two-body collisions. Because the scattering length near the peak gets very large, we checked that the decay is still dominated by two-body decay. Fig. A.2 shows indeed a linear dependency of the loss rate of molecules on the overlap density. It is acquired near the peak of the strong resonance, at 981 G where $\text{Re}[\tilde{a}] = -940 a_0$. The blue dotted line is a linear fit ($\chi_{\text{red}}^2 = 0.3$) and the red line is a quadratic fit ($\chi_{\text{red}}^2 = 3.9$). This shows the observed losses have negligible contribution from three-body decay with $n_{\text{Na}}^2 n_{\text{NaLi}}$ (n_i is the density of particle i). The inset shows a linear fit of $\ln(N_{\text{NaLi}}(t))$ with $\chi_{\text{red}}^2 = 0.3$. In comparison, a linear fit of $N_{\text{NaLi}}(t)^{-1}$, which would reflect three-body decay with $n_{\text{Na}} n_{\text{NaLi}}^2$, gives $\chi_{\text{red}}^2 = 4.1$ (not shown in the figure).

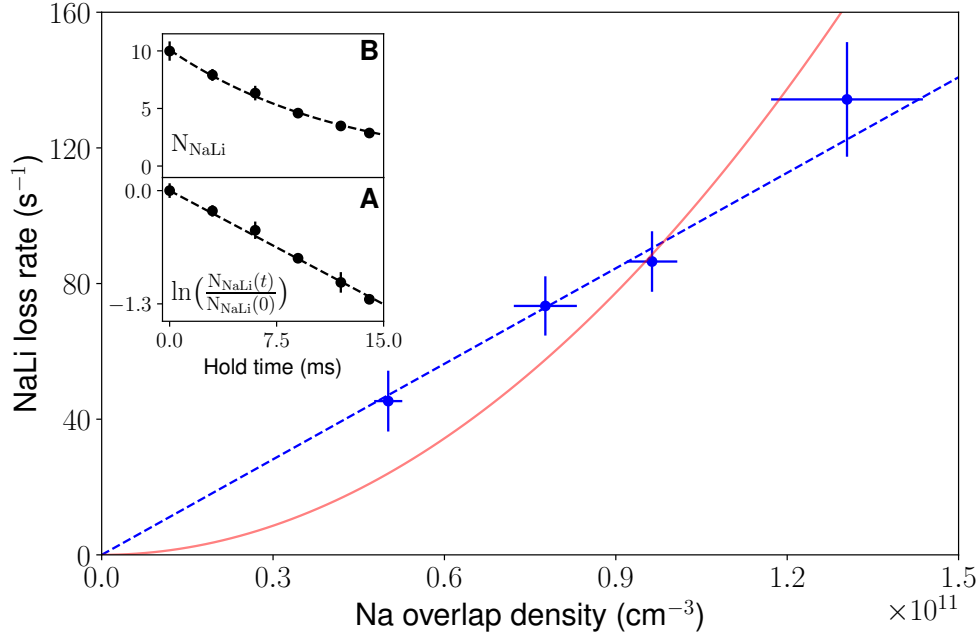


Figure A.2: Verification of two-body loss mechanism. The loss rate of molecules is shown as a function of the overlap density at 978.7 G, near the peak of the strong resonance and shows a linear dependence (blue dashed line). The red line is a quadratic fit. The error bar of the y-data is one standard deviation. The error bar of the x-data is one standard error of the mean. In this figure, we are not including the calibration uncertainty for the Na density. The inset (A) shows a decay curve of molecules with overlap density $9.6(4) \times 10^{10} \text{ cm}^{-3}$, and (B) shows a linearized decay curve with a linearized exponential fit at the same overlap density

A.7 Mapping between Fabry-Perot model and threshold scattering formalism

In the main text, we have shown that the results of the multichannel quantum defect model in the threshold regime can be expressed by the Fabry-Perot contrast. Here we show how the multiple reflections are treated in a S matrix formalism.

The quantum reflection and transmission of the scattering wavefunction in the long-range regime are formulated in terms of $r^{io}(r^{oi})$ and $t^{io}(t^{oi})$, the amplitude reflection and transmission coefficients for the wave travelling inward (outward) respectively, as

APPENDIX A. SUPPLEMENTAL INFORMATION FOR CHAPTER 3.

introduced in^{1,104,107}. In general, r^{oi} and r^{io} have different phases. The coefficient of the short-range reflection with loss is the short-range S-matrix, $S^c = \xi e^{i2\delta_s}$ where $\xi = (1 - y)/(1 + y)$ and y is the quantum-defect parameter, as given in^{104,123}. δ_s is the short-range phase shift with a finite range $0 \leq \delta_s < \pi$ ¹⁰⁴.

The transmission through the total potential is obtained as the coherent sum of multiple reflection pathways in the range $R_{\text{short}} < R < R_{\text{long}}$ ¹²³:

$$\begin{aligned} T &= I |\sqrt{1 - \xi^2} t^{oi} (1 + r^{io} S^c + (r^{io} S^c)^2 + \dots)|^2 \\ &= I |\sqrt{1 - \xi^2} t^{oi}|^2 (1 - r^{io} S^c)^{-1} \end{aligned} \quad (\text{A.7.0.1})$$

where I is the influx. Ref.¹⁰⁷ gives an analytic solution of the phase factors for the reflection coefficients. For s -wave collisions with vdW interaction, the phases of r^{oi} and r^{io} are π and $-\pi/4$ respectively. This simplifies the transmission as follows:

$$T = I |t^{oi}|^2 \left(\frac{|\sqrt{1 - \xi^2}|^2}{|1 - |r^{io}| \xi e^{i(2(\delta_s - \pi/8))}|^2} \right) \equiv I |t_2|^2 C \quad (\text{A.7.0.2})$$

This is identical to the transmission through two reflectors, given as Eq. (1) in the main article, with $|t_2| = |\sqrt{1 - \xi^2}|$, $|r_1| = |r^{oi}| = |r^{io}|$, $\xi = |r_2|$. The negative round-trip phase $-\phi$ is twice the short-range phase shift $2\delta_s$ plus the phase shift due to the quantum reflection at long range $-\pi/4$ (i.e., $-\phi = 2\delta_s - \pi/4$).

In Chapter 3.2, we established $\cos \phi = 1 - 2/(1 + (1 - s)^2)$, which can be written as $s = 1 - \cot(\phi/2) = 1 + \cot(\delta_s - \pi/8)$, which is equivalent to the result in Ref.¹⁰⁴. Figure A.3 shows the relation between the short-range phase shift, δ_s and the phase parameter $\theta = \arctan(s)/\pi$ defined in Ref.². The left plot of Fig. A.3 is the same as Fig. 1 in Ref.².

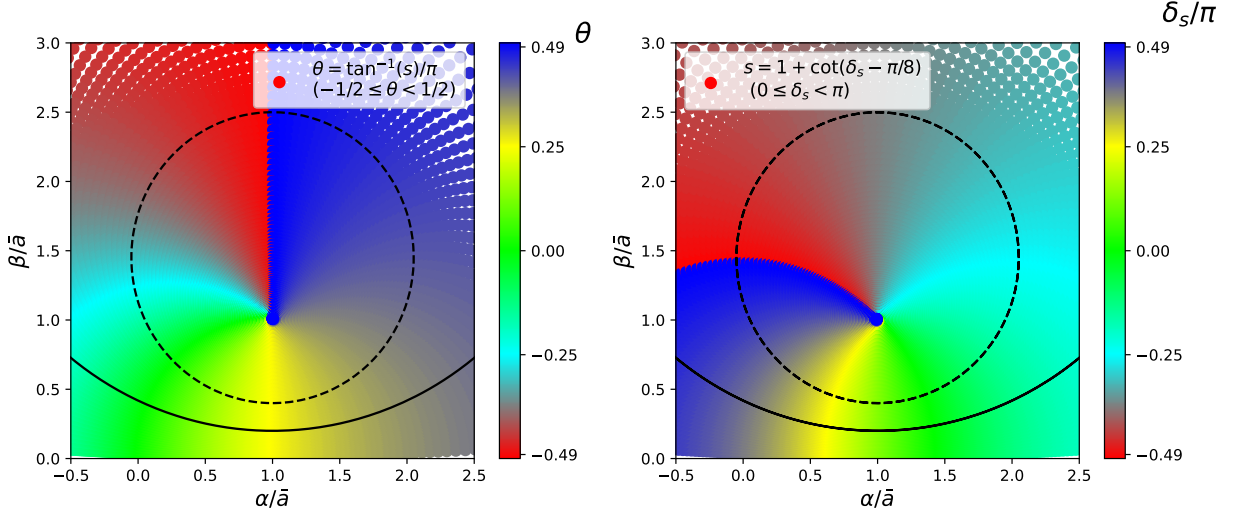


Figure A.3: Visualization of the relation between the phase factor $\arctan(s)/\pi$ in Ref.² and the short-range phase shift δ_s in the FP model. The black solid(dashed) line is for $y = 0.2(0.4)$. The point where $\alpha = \beta = \bar{a}$ corresponds to $y = 1$, i.e. the universal loss limit.

A.8 Mapping of two-channel model to Breit-Wigner form

Scattering resonances are described by a complex scattering length $\tilde{a}$ which moves across a circle in the complex plane as the resonance is crossed^{18,114}. The most general resonance has six parameters (the two center coordinates and the radius of the circle, the position of the background on the circle, and the position/width of the resonance in magnetic field). Here we show that our two-channel model which has six parameters can be mapped to the standard Breit-Wigner form describing an isolated resonance. In contrast, the one-channel Fabry-Perot model has only five parameters since the position and radius of the circle are constrained and depend only on y and $\bar{a}^2$.

The complex scattering length defined by the two-channel model with parameters

APPENDIX A. SUPPLEMENTAL INFORMATION FOR CHAPTER 3.

$(B_{\text{res}}, \Delta, y, q, \Gamma_{\text{b}}, \bar{a})$ is given by:

$$\tilde{a}(B) = \bar{a} \left(s(B) + y \frac{1 + (1 - s(B))^2}{i + y(1 - s(B))} \right) \equiv \alpha(B) - i\beta(B) \quad (\text{A.8.0.1})$$

The Feshbach resonance with a lossy bound state is described by:

$$s(B) = q \left(1 - \frac{\Delta}{B - B_{\text{res}} - i\Gamma_{\text{b}}/2} \right) \quad (\text{A.8.0.2})$$

We can re-write the two-channel model, Eq. (A.8.0.1), in the usual Breit-Wigner form¹⁸ in terms of the complex background scattering length $\tilde{a}_{\text{bg}}$, the resonant scattering length, $\tilde{a}_{\text{res}}$, the resonance position, B_{res}^o , and the width, Γ_{inel} :

$$\begin{aligned} \tilde{a}(B) &= \tilde{a}_{\text{bg}} + \frac{\tilde{a}_{\text{res}}}{2(B - B_{\text{res}}^o)/\Gamma_{\text{inel}} - i} \\ &\equiv \alpha(B) - i\beta(B) \end{aligned} \quad (\text{S9})$$

APPENDIX A. SUPPLEMENTAL INFORMATION FOR CHAPTER 3.

The mapping between two parameter sets is as follows:

$$\begin{aligned}
B_{\text{res}}^o &= B_{\text{res}} + \frac{qy^2\Delta(q-1)}{1+y^2(q-1)^2} \\
\Gamma_{\text{inel}} &= \Gamma_{\text{b}} + \frac{2yq\Delta}{1+y^2(q-1)^2} \equiv \Gamma_{\text{b}} + \Gamma_{\text{c}} \\
\tilde{a}_{\text{bg}} &= \frac{y(2-q) + iq}{i + y(1-q)} \bar{a} \equiv \alpha_{\text{bg}} - i\beta_{\text{bg}} \\
\alpha_{\text{bg}} &= \frac{q + (q-2)(q-1)y^2}{1 + (q-1)^2y^2} \bar{a} \\
\beta_{\text{bg}} &= \frac{(2 + (q-2)q)y}{1 + (q-1)^2y^2} \bar{a} \\
\tilde{a}_{\text{res}} &= \frac{2}{\Gamma_{\text{inel}}} \frac{(1-y^2)q\Delta}{(i + y(1-q))^2} \bar{a} \equiv \alpha_{\text{res}} - i\beta_{\text{res}} \\
\alpha_{\text{res}} &= \frac{-2q\Delta(1-y^2)(1-y^2(q-1)^2)}{(1 + (q-1)^2y^2)[(1 + (q-1)^2y^2)\Gamma_{\text{b}} + 2qy\Delta]} \bar{a} \\
\beta_{\text{res}} &= \frac{4qy\Delta(q-1)(y^2-1)}{(1 + (q-1)^2y^2)[(1 + (q-1)^2y^2)\Gamma_{\text{b}} + 2qy\Delta]} \bar{a}
\end{aligned} \tag{A.8.0.3}$$

where the width of the resonance Γ_{inel} is the incoherent sum of two decay rates: the natural linewidth of the bound state, Γ_{b} and the width determined by the coupling strength between the scattering state and the bound state, Γ_{c} . Note that both width factors have units of magnetic field. The energy width is obtained by dividing by $\delta\mu$. Since the energy widths are positive definite, the signs of Γ_{b} and Γ_{c} are determined by the sign of $\delta\mu$. In our case, Γ_{b} and Γ_{c} are positive since $\delta\mu > 0$. When $\delta\mu < 0$, $\Gamma_{\text{b}} < 0$ by definition, and $\Gamma_{\text{c}} < 0$ since $q \cdot \Delta < 0$ (see Sign constraints for parameters q and Δ).

The imaginary part of the scattering length is given by:

$$\beta = \beta_{\text{bg}} + \frac{-\alpha_{\text{res}}(\Gamma_{\text{inel}}/2)^2 + \beta_{\text{res}}(\Gamma_{\text{inel}}/2)(B - B_{\text{res}}^o)}{(B - B_{\text{res}}^o)^2 + (\Gamma_{\text{inel}}/2)^2} \quad (\text{A.8.0.4})$$

It is straightforward to check that the peak height is $\beta = 1/y$ at $B=B_{\text{res}}$, as expected.

For $y \ll 1$, $q \sim 1$, and $\Gamma_{\text{inel}} \approx \Gamma_{\text{c}}$:

$$\beta(B) \approx \beta_{\text{bg}} + yq\Delta \left[\frac{q\Delta + 2(1-q)(B - B_{\text{res}}^o)}{(B - B_{\text{res}}^o)^2 + (yq\Delta)^2} \right] \bar{a} \quad (\text{A.8.0.5})$$

This shows that due to the second term in the numerator, $q > 1$ and $q < 1$ give different asymmetries in the lineshape.

In contrast, for $y \ll 1$, $q \sim 1$, and $\Gamma_{\text{inel}} \approx \Gamma_{\text{b}}$:

$$\beta(B) \approx \beta_{\text{bg}} + q\Delta \left[\frac{\Gamma_{\text{b}}/2 + 2y(1-q)(B - B_{\text{res}}^o)}{(B - B_{\text{res}}^o)^2 + (\Gamma_{\text{b}}/2)^2} \right] \bar{a} \quad (\text{A.8.0.6})$$

In this case, the asymmetry is small and the lineshape can be well-approximated by a Lorentzian.

A.9 Sign constraints for parameters q and Δ

By definition, q and $\delta\mu\Delta$ have the same sign²⁰ where $\delta\mu = \mu_{\text{Na+NaLi}} - \mu_{\text{bound}}$ is the relative magnetic moment between the entrance channel and the closed channel bound state. In our case, $\mu_{\text{Na+NaLi}} = 3\mu_{\text{B}}$ as the entrance channel is in the upper spin-stretched state where three electronic spins are aligned along the bias field direction. Thus, $\delta\mu = 4\mu_{\text{B}}(2\mu_{\text{B}}) > 0$, if the bound state we couple requires two(one) spins to flip. This constrains the signs of Δ and q to be the same, i.e. $q \cdot \Delta > 0$. The observed asymmetry of

the loss lineshape requires $q > 1$, which implies $\Delta > 0$.

A.10 Thermal averaging

At our temperature, $k_B T < \hbar \omega_{ax}$, the scattering is dominated by the axial motional ground-state channel¹¹⁰ and the saturation factor does not depend on temperature $f(k) = (1 + (\sqrt{\pi}/l_o)^2 |l|^2 |\tilde{a}|^2 + 2(\sqrt{\pi}/l_o) |l|^2 \beta)^{-1}$. However, the logarithmic correction factor, $l = |(1 + (\tilde{a}/\sqrt{\pi} l_o) \ln(B \hbar \omega_{ax}/\pi \epsilon))|^{-2}$ (where $\epsilon = \hbar^2 q^2 / 2\mu$, $B \approx 0.915$, and $l_o = \sqrt{\hbar/\mu \omega_{ax}}$) depends on the radial momentum q . In the main article, we used the mean thermal energy $k_B T$ for the radial relative kinetic energy ϵ . A more accurate way is to perform a thermal average.

The thermal average for the loss rate ratio $r(B) = f(k)l(\beta/\bar{a})$ is given by:

$$\langle r(B) \rangle = \frac{\beta f(k) \lambda}{\bar{a} Z} \left(\int_0^\infty dq \, 2\pi q \, l(q) e^{\frac{-\hbar^2 q^2}{2\mu k_B T}} \right) \quad (\text{A.10.0.1})$$

where $Z = \mu k_B T / \hbar^2$, and $\lambda = \sqrt{1 - e^{-2\hbar \omega_{ax}/k_B T}}$ is the normalization constant for the average over the axial direction⁸⁴. At our temperature $T \sim 1.55 \, \mu\text{K}$, the thermal average effect shifts the peak loss position by $\sim 0.3 \, \text{G}$, almost canceling the shift caused by the mean thermal energy, $\epsilon = k_B T$. Fit parameters except B_{res} agree with the result without the thermal average within the fit uncertainties.

A.11 Ratio of elastic to inelastic collision rates

Figure A.4 shows the good-to-bad collision ratio, $\gamma = k(\alpha^2 + \beta^2)/\beta$. It is maximized away from the Feshbach resonance, since near the resonance, the increase in the elastic

APPENDIX A. SUPPLEMENTAL INFORMATION FOR CHAPTER 3.

scattering rate, which is proportional to $(\alpha^2 + \beta^2)$, is less than the increase in the inelastic scattering rate, which is proportional to β/k . The minimum of γ is not at the resonance but at 1006.9 G where the real part of the scattering length, α crosses zero and the imaginary part, β is close to its background value. Note that this plot uses only the parameters obtained from the analysis of the resonance at 978 G. In previous work Ref.⁴¹, we demonstrated sympathetic cooling of NaLi molecules with Na atoms near 745 G and measured a higher ratio of good-to-bad collisions of about 100. This discrepancy is presumed to be caused by contributions from other Feshbach resonances and is the subject of future studies. Also, in Ref.⁴¹ we measured elastic collisions directly by observing thermalization, whereas here we inferred an elastic collision rate only from the analysis of observed inelastic rates.

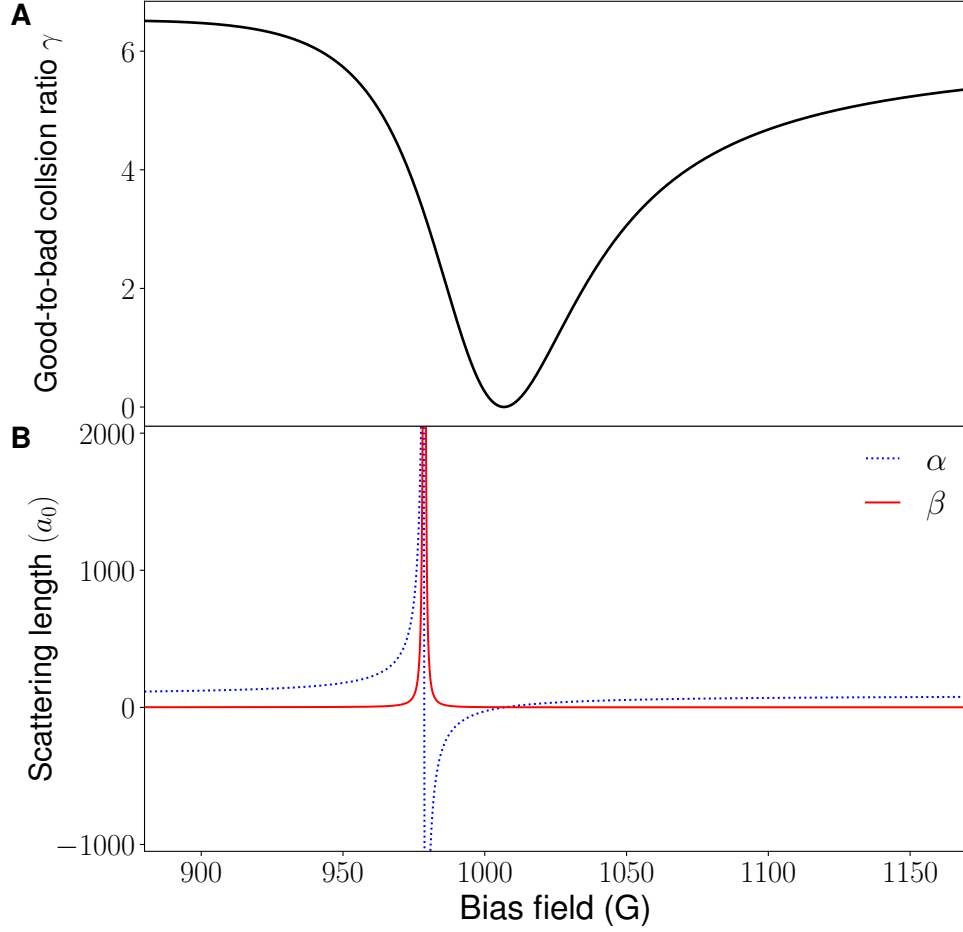


Figure A.4: Ratio of elastic to inelastic collision rates near the strong resonance. (A) The good-to-bad collision ratio, $\gamma = k(\alpha^2 + \beta^2)/\beta$ as a function of the bias field, where α and β are the real and imaginary parts of the complex scattering length respectively, the relative wavevector $k = \mu v_{\text{rel}}/\hbar$ and $v_{\text{rel}} = \sqrt{8k_B T/\mu\pi}$ (μ : the reduced mass between NaLi and Na, $T = 1.55\mu\text{K}$). (B) α and β around the strong resonance at 978 G. Note that the effect of the small resonance at 1030 G has not been considered in the calculation of γ .

References

- [1] B. Gao, “General form of the quantum-defect theory for $-1/r^\alpha$ type of potentials with $\alpha > 2$,” *Phys. Rev. A*, vol. 78, p. 012702, Jul 2008.
- [2] Z. Idziaszek and P. S. Julienne, “Universal Rate Constants for Reactive Collisions of Ultracold Molecules,” *Phys. Rev. Lett.*, vol. 104, p. 113202, Mar 2010.
- [3] P. S. Julienne, T. M. Hanna, and Z. Idziaszek, “Universal ultracold collision rates for polar molecules of two alkali-metal atoms,” *Phys. Chem. Chem. Phys.*, vol. 13, pp. 19114–19124, 2011.
- [4] M. Aymar and O. Dulieu, “Calculation of accurate permanent dipole moments of the lowest $^1,^3\Sigma^+$ states of heteronuclear alkali dimers using extended basis sets,” *The Journal of Chemical Physics*, vol. 122, no. 20, p. 204302, 2005.
- [5] S. Ospelkaus, K.-K. Ni, D. Wang, M. H. G. de Miranda, B. Neyenhuis, G. Quémener, P. S. Julienne, J. L. Bohn, D. S. Jin, and J. Ye, “Quantum-State Controlled Chemical Reactions of Ultracold Potassium-Rubidium Molecules,” *Science*, vol. 327, no. 5967, pp. 853–857, 2010.
- [6] T. M. Rvachov, H. Son, A. T. Sommer, S. Ebadi, J. J. Park, M. W. Zwierlein, W. Ketterle, and A. O. Jamison, “Long-Lived Ultracold Molecules with Electric and Magnetic Dipole Moments,” *Phys. Rev. Lett.*, vol. 119, p. 143001, Oct 2017.
- [7] J. W. Park, S. A. Will, and M. W. Zwierlein, “Ultracold Dipolar Gas of Fermionic $^{23}\text{Na}^{40}\text{K}$ Molecules in Their Absolute Ground State,” *Phys. Rev. Lett.*, vol. 114, p. 205302, May 2015.
- [8] X. Ye, M. Guo, M. L. González-Martínez, G. Quémener, and D. Wang, “Collisions of ultracold $^{23}\text{Na}^{87}\text{Rb}$ molecules with controlled chemical reactivities,” *Science Advances*, vol. 4, no. 1, 2018.
- [9] P. D. Gregory, M. D. Frye, J. A. Blackmore, E. M. Bridge, R. Sawant, J. M. Hutson, and S. L. Cornish, “Sticky collisions of ultracold RbCs molecules,” *Nature Communications*, vol. 10, p. 3104, Jul 2019.
- [10] T. Takekoshi, L. Reichsöllner, A. Schindewolf, J. M. Hutson, C. R. Le Sueur, O. Dulieu, F. Ferlaino, R. Grimm, and H.-C. Nägerl, “Ultracold Dense Samples of Dipolar RbCs Molecules in the Rovibrational and Hyperfine Ground State,” *Phys. Rev. Lett.*, vol. 113, p. 205301, Nov 2014.

REFERENCES

- [11] L. W. Cheuk, L. Anderegg, Y. Bao, S. Burchesky, S. S. Yu, W. Ketterle, K.-K. Ni, and J. M. Doyle, “Observation of Collisions between Two Ultracold Ground-State CaF Molecules,” *Phys. Rev. Lett.*, vol. 125, p. 043401, Jul 2020.
- [12] B. Drews, M. Deiß, K. Jachymski, Z. Idziaszek, and J. Hecker Denschlag, “Inelastic collisions of ultracold triplet Rb₂ molecules in the rovibrational ground state,” *Nature Communications*, vol. 8, p. 14854, Mar 2017.
- [13] G. Polovy, E. Frieling, D. Uhland, J. Schmidt, and K. W. Madison, “Quantum-state-dependent chemistry of ultracold ⁶Li₂ dimers,” *Phys. Rev. A*, vol. 102, p. 013310, Jul 2020.
- [14] E. R. Hudson, N. B. Gilfoy, S. Kotochigova, J. M. Sage, and D. DeMille, “Inelastic Collisions of Ultracold Heteronuclear Molecules in an Optical Trap,” *Phys. Rev. Lett.*, vol. 100, p. 203201, May 2008.
- [15] N. Zahzam, T. Vogt, M. Mudrich, D. Comparat, and P. Pillet, “Atom-Molecule Collisions in an Optically Trapped Gas,” *Phys. Rev. Lett.*, vol. 96, p. 023202, Jan 2006.
- [16] P. Staunum, S. D. Kraft, J. Lange, R. Wester, and M. Weidemüller, “Experimental Investigation of Ultracold Atom-Molecule Collisions,” *Phys. Rev. Lett.*, vol. 96, p. 023201, Jan 2006.
- [17] J. Deiglmayr, M. Repp, A. Grochola, O. Dulieu, R. Wester, and M. Weidemüller, “Dipolar effects and collisions in an ultracold gas of LiCs molecules,” *Journal of Physics: Conference Series*, vol. 264, p. 012014, Jan 2011.
- [18] J. M. Hutson, “Feshbach resonances in ultracold atomic and molecular collisions: threshold behaviour and suppression of poles in scattering lengths,” *New Journal of Physics*, vol. 9, pp. 152–152, May 2007.
- [19] S. Giorgini, L. P. Pitaevskii, and S. Stringari, “Theory of ultracold atomic Fermi gases,” *Rev. Mod. Phys.*, vol. 80, pp. 1215–1274, Oct 2008.
- [20] C. Chin, R. Grimm, P. Julienne, and E. Tiesinga, “Feshbach resonances in ultracold gases,” *Rev. Mod. Phys.*, vol. 82, pp. 1225–1286, Apr 2010.
- [21] M. Mayle, G. Quémener, B. P. Ruzic, and J. L. Bohn, “Scattering of ultracold molecules in the highly resonant regime,” *Phys. Rev. A*, vol. 87, p. 012709, Jan 2013.
- [22] A. Christianen, M. W. Zwierlein, G. C. Groenenboom, and T. Karman, “Photoinduced Two-Body Loss of Ultracold Molecules,” *Phys. Rev. Lett.*, vol. 123, p. 123402, Sep 2019.
- [23] P. D. Gregory, J. A. Blackmore, S. L. Bromley, and S. L. Cornish, “Loss of Ultracold ⁸⁷Rb¹³³Cs Molecules via Optical Excitation of Long-Lived Two-Body Collision Complexes,” *Phys. Rev. Lett.*, vol. 124, p. 163402, Apr 2020.
- [24] M. A. Nichols, Y.-X. Liu, L. Zhu, M.-G. Hu, Y. Liu, and K.-K. Ni, “Detection of Long-Lived Complexes in Ultracold Atom-Molecule Collisions,” 2021. <https://arxiv.org/abs/2105.14960>.

REFERENCES

- [25] M. Mayle, B. P. Ruzic, and J. L. Bohn, “Statistical aspects of ultracold resonant scattering,” *Phys. Rev. A*, vol. 85, p. 062712, Jun 2012.
- [26] Y. Liu, M.-G. Hu, M. A. Nichols, D. D. Grimes, T. Karman, H. Guo, and K.-K. Ni, “Photo-excitation of long-lived transient intermediates in ultracold reactions,” *Nature Physics*, vol. 16, pp. 1132–1136, Nov 2020.
- [27] L. D. Marco, G. Valtolina, K. Matsuda, W. G. Tobias, J. P. Covey, and J. Ye, “A degenerate Fermi gas of polar molecules,” *Science*, vol. 363, no. 6429, pp. 853–856, 2019.
- [28] P. Soldán and J. M. Hutson, “Interaction of $\text{NH}(X^3\Sigma^-)$ Molecules with Rubidium Atoms: Implications for Sympathetic Cooling and the Formation of Extremely Polar Molecules,” *Phys. Rev. Lett.*, vol. 92, p. 163202, Apr 2004.
- [29] W. Skomorowski, F. Pawłowski, T. Korona, R. Moszynski, P. S. Zuchowski, and J. M. Hutson, “Interaction between LiH molecule and Li atom from state-of-the-art electronic structure calculations,” *The Journal of Chemical Physics*, vol. 134, no. 11, p. 114109, 2011.
- [30] M. L. González-Martínez and J. M. Hutson, “Ultracold Hydrogen Atoms: A Versatile Coolant to Produce Ultracold Molecules,” *Phys. Rev. Lett.*, vol. 111, p. 203004, Nov 2013.
- [31] J. Lim, M. D. Frye, J. M. Hutson, and M. R. Tarbutt, “Modeling sympathetic cooling of molecules by ultracold atoms,” *Phys. Rev. A*, vol. 92, p. 053419, Nov 2015.
- [32] M. Morita, M. B. Kosicki, P. S. Żuchowski, and T. V. Tscherbul, “Atom-molecule collisions, spin relaxation, and sympathetic cooling in an ultracold spin-polarized $\text{Rb}(^2s) - \text{SrF}(^2\Sigma^+)$ mixture,” *Phys. Rev. A*, vol. 98, p. 042702, Oct 2018.
- [33] L. D. Augustovčová and J. Bohn, “Ultracold Collisions of Polyatomic Molecules: CaOH ,” *arXiv: 1906.09643*, 2019.
- [34] H. Yang, D.-C. Zhang, L. Liu, Y.-X. Liu, J. Nan, B. Zhao, and J.-W. Pan, “Observation of magnetically tunable Feshbach resonances in ultracold $^{23}\text{Na}^{40}\text{K} + ^{40}\text{K}$ collisions,” *Science*, vol. 363, no. 6424, pp. 261–264, 2019.
- [35] T. M. Rvachov, *Ultracold $^{23}\text{Na}^6\text{Li}$ Molecules in the Triplet Ground State*. PhD thesis, Massachusetts Institute of Technology, Cambridge MA, 2018.
- [36] T. M. Rvachov, H. Son, J. J. Park, P. M. Notz, T. T. Wang, M. W. Zwierlein, W. Ketterle, and A. O. Jamison, “Photoassociation of ultracold NaLi,” *Phys. Chem. Chem. Phys.*, vol. 20, pp. 4746–4751, 2018.
- [37] T. M. Rvachov, H. Son, J. J. Park, S. Ebadi, M. W. Zwierlein, W. Ketterle, and A. O. Jamison, “Two-photon spectroscopy of the NaLi triplet ground state,” *Phys. Chem. Chem. Phys.*, vol. 20, pp. 4739–4745, 2018.
- [38] P. S. Żuchowski and J. M. Hutson, “Reactions of ultracold alkali-metal dimers,” *Phys. Rev. A*, vol. 81, p. 060703, Jun 2010.

REFERENCES

- [39] M. Tomza, K. W. Madison, R. Moszynski, and R. V. Krems, “Chemical reactions of ultracold alkali-metal dimers in the lowest-energy $^3\Sigma$ state,” *Phys. Rev. A*, vol. 88, p. 050701, Nov 2013.
- [40] M.-S. Heo, T. T. Wang, C. A. Christensen, T. M. Rvachov, D. A. Cotta, J.-H. Choi, Y.-R. Lee, and W. Ketterle, “Formation of ultracold fermionic nali Feshbach molecules,” *Phys. Rev. A*, vol. 86, p. 021602, Aug 2012.
- [41] H. Son, J. J. Park, W. Ketterle, and A. O. Jamison, “Collisional cooling of ultracold molecules,” *Nature*, vol. 580, pp. 197–200, Apr 2020.
- [42] H. Son, J. J. Park, Y.-K. Lu, A. O. Jamison, T. Karman, and W. Ketterle, “Control of reactive collisions by quantum interference,” 2021. <https://arxiv.org/abs/2109.03944>.
- [43] M. H. Anderson, J. R. Ensher, M. R. Matthews, C. E. Wieman, and E. A. Cornell, “Observation of Bose-Einstein Condensation in a Dilute Atomic VSapor,” *Science*, vol. 269, no. 5221, pp. 198–201, 1995.
- [44] K. B. Davis, M. O. Mewes, M. R. Andrews, N. J. van Druten, D. S. Durfee, D. M. Kurn, and W. Ketterle, “Bose-Einstein Condensation in a Gas of Sodium Atoms,” *Phys. Rev. Lett.*, vol. 75, pp. 3969–3973, Nov 1995.
- [45] I. Bloch, J. Dalibard, and W. Zwerger, “Many-body physics with ultracold gases,” *Rev. Mod. Phys.*, vol. 80, pp. 885–964, Jul 2008.
- [46] M. A. Baranov, M. Dalmonte, G. Pupillo, and P. Zoller, “Condensed Matter Theory of Dipolar Quantum Gases,” *Chemical Reviews*, vol. 112, no. 9, pp. 5012–5061, 2012.
- [47] D. DeMille, “Quantum Computation with Trapped Polar Molecules,” *Phys. Rev. Lett.*, vol. 88, p. 067901, Jan 2002.
- [48] L. D. Carr, D. DeMille, R. V. Krems, and J. Ye, “Cold and ultracold molecules: science, technology and applications,” *New Journal of Physics*, vol. 11, p. 055049, may 2009.
- [49] W. Christen, K. Rademann, and U. Even, “Efficient cooling in supersonic jet expansions of supercritical fluids: CO and CO₂,” *The Journal of Chemical Physics*, vol. 125, no. 17, p. 174307, 2006.
- [50] J. D. Weinstein, R. deCarvalho, T. Guillet, B. Friedrich, and J. M. Doyle, “Magnetic trapping of calcium monohydride molecules at millikelvin temperatures,” *Nature*, vol. 395, pp. 148–150, 1998.
- [51] S. Stellmer, B. Pasquiou, R. Grimm, and F. Schreck, “Laser Cooling to Quantum Degeneracy,” *Phys. Rev. Lett.*, vol. 110, p. 263003, Jun 2013.
- [52] J. Hu, A. Urvoy, Z. Vendeiro, V. Crépel, W. Chen, and V. Vuletić, “Creation of a Bose-condensed gas of ^{87}Rb by laser cooling,” *Science*, vol. 358, no. 6366, pp. 1078–1080, 2017.
- [53] M. S. Elioff, J. J. Valentini, and D. W. Chandler, “Subkelvin Cooling NO Molecules via ”Billiard-like” Collisions with Argon,” *Science*, vol. 302, no. 5652, pp. 1940–1943, 2003.

REFERENCES

- [54] A. B. Henson, S. Gersten, Y. Shagam, J. Narevicius, and E. Narevicius, “Observation of Resonances in Penning Ionization Reactions at Sub-Kelvin Temperatures in Merged Beams,” *Science*, vol. 338, no. 6104, pp. 234–238, 2012.
- [55] Y. Segev, M. Pitzer, M. Karpov, N. Akerman, J. Narevicius, and E. Narevicius, “Collisions between cold molecules in a superconducting magnetic trap,” *arXiv: 1902.04549*, 2019.
- [56] D. Reens, H. Wu, T. Langen, and J. Ye, “Controlling spin flips of molecules in an electromagnetic trap,” *Phys. Rev. A*, vol. 96, p. 063420, Dec 2017.
- [57] B. K. Stuhl, M. T. Hummon, M. Yeo, G. Quémener, J. L. Bohn, and J. Ye, “Evaporative cooling of the dipolar hydroxyl radical,” *Nature*, vol. 492, p. 396, 2012.
- [58] K.-K. Ni, S. Ospelkaus, M. H. G. de Miranda, A. Pe’er, B. Neyenhuis, J. J. Zirbel, S. Kotochigova, P. S. Julienne, D. S. Jin, and J. Ye, “A High Phase-Space-Density Gas of Polar Molecules,” *Science*, vol. 322, no. 5899, pp. 231–235, 2008.
- [59] J. F. Barry, D. J. McCarron, E. B. Norrgard, M. H. Steinecker, and D. DeMille, “Magneto-optical trapping of a diatomic molecule,” *Nature*, vol. 512, p. 286, 2014.
- [60] L. Anderegg, B. L. Augenbraun, E. Chae, B. Hemmerling, N. R. Hutzler, A. Ravi, A. Collopy, J. Ye, W. Ketterle, and J. M. Doyle, “Radio Frequency Magneto-Optical Trapping of CaF with High Density,” *Phys. Rev. Lett.*, vol. 119, p. 103201, Sep 2017.
- [61] S. Truppe, H. J. Williams, M. Hambach, L. Caldwell, N. J. Fitch, E. A. Hinds, B. E. Sauer, and M. R. Tarbutt, “Molecules cooled below the Doppler limit,” *Nature Physics*, vol. 13, p. 1173, 2017.
- [62] A. L. Collopy, S. Ding, Y. Wu, I. A. Finneran, L. Anderegg, B. L. Augenbraun, J. M. Doyle, and J. Ye, “3D Magneto-Optical Trap of Yttrium Monoxide,” *Phys. Rev. Lett.*, vol. 121, p. 213201, Nov 2018.
- [63] P. S. Żuchowski and J. M. Hutson, “Reactions of ultracold alkali-metal dimers,” *Phys. Rev. A*, vol. 81, p. 060703, Jun 2010.
- [64] C. J. Myatt, E. A. Burt, R. W. Ghrist, E. A. Cornell, and C. E. Wieman, “Production of Two Overlapping Bose-Einstein Condensates by Sympathetic Cooling,” *Phys. Rev. Lett.*, vol. 78, pp. 586–589, Jan 1997.
- [65] L. M. C. Janssen, A. van der Avoird, and G. C. Groenenboom, “Quantum Reactive Scattering of Ultracold $\text{NH}(X^3\Sigma^-)$ Radicals in a Magnetic Trap,” *Phys. Rev. Lett.*, vol. 110, p. 063201, Feb 2013.
- [66] R. V. Krems and A. Dalgarno, “Quantum-mechanical theory of atom-molecule and molecular collisions in a magnetic field: Spin depolarization,” *The Journal of Chemical Physics*, vol. 120, no. 5, pp. 2296–2307, 2004.
- [67] P. S. Żuchowski and J. M. Hutson, “Cold collisions of $\text{N}(4s)$ atoms and $\text{NH}(3\Sigma)$ molecules in magnetic fields,” *Phys. Chem. Chem. Phys.*, vol. 13, pp. 3669–3680, 2011.

REFERENCES

- [68] T. V. Tscherbul, J. Klos, and A. A. Buchachenko, “Ultracold spin-polarized mixtures of $^2\Sigma$ molecules with s -state atoms: Collisional stability and implications for sympathetic cooling,” *Phys. Rev. A*, vol. 84, p. 040701, Oct 2011.
- [69] A. P. Chikkatur, *Colliding and Moving Bose-Einstein Condensates: Studies of superfluidity and optical tweezers for condensate transport*. PhD thesis, Massachusetts Institute of Technology, Cambridge MA, 2002.
- [70] Z. Hadzibabic, S. Gupta, C. A. Stan, C. H. Schunck, M. W. Zwierlein, K. Dieckmann, and W. Ketterle, “Fiftyfold Improvement in the Number of Quantum Degenerate Fermionic Atoms,” *Phys. Rev. Lett.*, vol. 91, p. 160401, Oct 2003.
- [71] A. Mosk, S. Kraft, M. Mudrich, K. Singer, W. Wohlleben, R. Grimm, and M. Weidemüller, “Mixture of ultracold lithium and cesium atoms in an optical dipole trap,” *Applied Physics B*, vol. 73, pp. 791–799, Dec 2001.
- [72] V. V. Ivanov, A. Khramov, A. H. Hansen, W. H. Dowd, F. Münchow, A. O. Jamison, and S. Gupta, “Sympathetic Cooling in an Optically Trapped Mixture of Alkali and Spin-Singlet Atoms,” *Phys. Rev. Lett.*, vol. 106, p. 153201, Apr 2011.
- [73] F. Lang, K. Winkler, C. Strauss, R. Grimm, and J. H. Denschlag, “Ultracold Triplet Molecules in the Rovibrational Ground State,” *Phys. Rev. Lett.*, vol. 101, p. 133005, Sep 2008.
- [74] J. G. Danzl, M. J. Mark, E. Haller, M. Gustavsson, R. Hart, J. Aldegunde, J. M. Hutson, and H.-C. Nägerl, “An ultracold high-density sample of rovibronic ground-state molecules in an optical lattice,” *Nature Physics*, vol. 6, p. 265, 2010.
- [75] T. Takekoshi, L. Reichsöllner, A. Schindewolf, J. M. Hutson, C. R. Le Sueur, O. Dulieu, F. Ferlaino, R. Grimm, and H.-C. Nägerl, “Ultracold Dense Samples of Dipolar RbCs Molecules in the Rovibrational and Hyperfine Ground State,” *Phys. Rev. Lett.*, vol. 113, p. 205301, Nov 2014.
- [76] P. K. Molony, P. D. Gregory, Z. Ji, B. Lu, M. P. Köppinger, C. R. Le Sueur, C. L. Blackley, J. M. Hutson, and S. L. Cornish, “Creation of Ultracold $^{87}\text{Rb}^{133}\text{Cs}$ Molecules in the Rovibrational Ground State,” *Phys. Rev. Lett.*, vol. 113, p. 255301, Dec 2014.
- [77] M. Guo, B. Zhu, B. Lu, X. Ye, F. Wang, R. Vexiau, N. Bouloufa-Maafa, G. Quémener, O. Dulieu, and D. Wang, “Creation of an Ultracold Gas of Ground-State Dipolar $^{23}\text{Na}^{87}\text{Rb}$ Molecules,” *Phys. Rev. Lett.*, vol. 116, p. 205303, May 2016.
- [78] F. Seeßelberg, X.-Y. Luo, M. Li, R. Bause, S. Kotochigova, I. Bloch, and C. Gohle, “Extending Rotational Coherence of Interacting Polar Molecules in a Spin-Decoupled Magic Trap,” *Phys. Rev. Lett.*, vol. 121, p. 253401, Dec 2018.
- [79] T. D. Cumby, R. A. Shewmon, M.-G. Hu, J. D. Perreault, and D. S. Jin, “Feshbach-molecule formation in a Bose-Fermi mixture,” *Phys. Rev. A*, vol. 87, p. 012703, Jan 2013.

REFERENCES

- [80] S. Watabe and T. Nikuni, “Conversion efficiencies of heteronuclear Feshbach molecules,” *Phys. Rev. A*, vol. 77, p. 013616, Jan 2008.
- [81] A. Trautmann, *Spin Dynamics and Feshbach Resonances in Ultracold Sodium-Lithium Mixtures*. PhD thesis, the Ruperto-Carola University of Heidelberg, Germany, 2016.
- [82] R. Hermsmeier, J. Kłos, S. Kotochigova, and T. V. Tscherbul, “Quantum Spin State Selectivity and Magnetic Tuning of Ultracold Chemical Reactions of Triplet Alkali-Metal Dimers with Alkali-Metal Atoms,” *Phys. Rev. Lett.*, vol. 127, p. 103402, Aug 2021.
- [83] G. F. Gribakin and V. V. Flambaum, “Calculation of the scattering length in atomic collisions using the semiclassical approximation,” *Phys. Rev. A*, vol. 48, pp. 546–553, Jul 1993.
- [84] P. Naidon and P. S. Julienne, “Optical Feshbach resonances of alkaline-earth-metal atoms in a one- or two-dimensional optical lattice,” *Phys. Rev. A*, vol. 74, p. 062713, Dec 2006.
- [85] W. Lunden, *Bose-Einstein condensation of ^{162}Dy for spin-mixture experiments*. PhD thesis, Massachusetts Institute of Technology, Cambridge MA, 2020.
- [86] S. Ebadi. *Narrow Linewidth Laser System for Creation of NaLi Ultracold Molecules via STIRAP*. Bachelor’s thesis, University of Toronto, Toronto ON, 2016.
- [87] E. C. Cook, P. J. Martin, T. L. Brown-Heft, J. C. Garman, and D. A. Steck, “High passive-stability diode-laser design for use in atomic-physics experiments,” *Review of Scientific Instruments*, vol. 83, no. 4, p. 043101, 2012.
- [88] E. D. Black, “An introduction to Pound–Drever–Hall laser frequency stabilization,” *American Journal of Physics*, vol. 69, no. 1, pp. 79–87, 2001.
- [89] T. Mukaiyama, J. R. Abo-Shaeer, K. Xu, J. K. Chin, and W. Ketterle, “Dissociation and Decay of Ultracold Sodium Molecules,” *Phys. Rev. Lett.*, vol. 92, p. 180402, May 2004.
- [90] S. Dürr, T. Volz, and G. Rempe, “Dissociation of ultracold molecules with Feshbach resonances,” *Phys. Rev. A*, vol. 70, p. 031601, Sep 2004.
- [91] T. Volz, S. Dürr, N. Syassen, G. Rempe, E. van Kempen, and S. Kokkelmans, “Feshbach spectroscopy of a shape resonance,” *Phys. Rev. A*, vol. 72, p. 010704, Jul 2005.
- [92] Z. Idziaszek and P. S. Julienne, “Universal Rate Constants for Reactive Collisions of Ultracold Molecules,” *Phys. Rev. Lett.*, vol. 104, p. 113202, Mar 2010.
- [93] A. Derevianko, J. F. Babb, and A. Dalgarno, “High-precision calculations of van der Waals coefficients for heteronuclear alkali-metal dimers,” *Phys. Rev. A*, vol. 63, p. 052704, Apr 2001.

REFERENCES

- [94] C. Ravensbergen, V. Corre, E. Soave, M. Kreyer, E. Kirilov, and R. Grimm, “Production of a degenerate Fermi-Fermi mixture of dysprosium and potassium atoms,” *Phys. Rev. A*, vol. 98, p. 063624, Dec 2018.
- [95] M. T. Hummon, T. V. Tscherbul, J. Kłos, H.-I. Lu, E. Tsikata, W. C. Campbell, A. Dalgarno, and J. M. Doyle, “Cold $\text{N}+\text{NH}$ collisions in a magnetic trap,” *Phys. Rev. Lett.*, vol. 106, p. 053201, Feb 2011.
- [96] W. C. Campbell, T. V. Tscherbul, H.-I. Lu, E. Tsikata, R. V. Krems, and J. M. Doyle, “Mechanism of Collisional Spin Relaxation in $^3\Sigma$ Molecules,” *Phys. Rev. Lett.*, vol. 102, p. 013003, Jan 2009.
- [97] M. Warehime and J. Kłos, “Nonadiabatic collisions of CaH with Li : Importance of spin-orbit-induced spin relaxation in spin-polarized sympathetic cooling of CaH ,” *Phys. Rev. A*, vol. 92, p. 032703, Sep 2015.
- [98] S. Inouye, M. R. Andrews, J. Stenger, H.-J. Miesner, D. M. Stamper-Kurn, and W. Ketterle, “Observation of Feshbach resonances in a Bose–Einstein condensate,” *Nature*, vol. 392, pp. 151–154, Mar 1998.
- [99] A. B. Henson, S. Gersten, Y. Shagam, J. Narevicius, and E. Narevicius, “Observation of Resonances in Penning Ionization Reactions at Sub-Kelvin Temperatures in Merged Beams,” *Science*, vol. 338, no. 6104, pp. 234–238, 2012.
- [100] T. de Jongh, M. Besemer, Q. Shuai, T. Karman, A. van der Avoird, G. C. Groenenboom, and S. Y. T. van de Meerakker, “Imaging the onset of the resonance regime in low-energy $\text{NO}-\text{He}$ collisions,” *Science*, vol. 368, no. 6491, pp. 626–630, 2020.
- [101] Y. Liu, M.-G. Hu, M. A. Nichols, D. Yang, D. Xie, H. Guo, and K.-K. Ni, “Precision test of statistical dynamics with state-to-state ultracold chemistry,” *Nature*, vol. 593, pp. 379–384, May 2021.
- [102] R. V. Krems, “Molecules near absolute zero and external field control of atomic and molecular dynamics,” *International Reviews in Physical Chemistry*, vol. 24, no. 1, pp. 99–118, 2005.
- [103] M. T. Bell and T. P. Softley, “Ultracold molecules and ultracold chemistry,” *Molecular Physics*, vol. 107, no. 2, pp. 99–132, 2009.
- [104] M. D. Frye, P. S. Julienne, and J. M. Hutson, “Cold atomic and molecular collisions: approaching the universal loss regime,” *New Journal of Physics*, vol. 17, p. 045019, apr 2015.
- [105] X.-Y. Wang, M. D. Frye, Z. Su, J. Cao, L. Liu, D.-C. Zhang, H. Yang, J. M. Hutson, B. Zhao, C.-L. Bai, and J.-W. Pan, “Magnetic Feshbach resonances in collisions of $^{23}\text{Na}^{40}\text{K}$ with ^{40}K ,” 2021. <https://arxiv.org/abs/2103.07130>.
- [106] H. Yang, X.-Y. Wang, Z. Su, J. Cao, D.-C. Zhang, J. Rui, B. Zhao, C.-L. Bai, and J.-W. Pan, “Evidence for association of triatomic molecule in ultracold $^{23}\text{Na}^{40}\text{K}$ and ^{40}K mixture,” 2021. <https://arxiv.org/abs/2104.11424>.

REFERENCES

- [107] Y.-P. Bai, J.-L. Li, G.-R. Wang, and S.-L. Cong, “Model for investigating quantum reflection and quantum coherence in ultracold molecular collisions,” *Phys. Rev. A*, vol. 100, p. 012705, Jul 2019.
- [108] Y. Xie, H. Zhao, Y. Wang, Y. Huang, T. Wang, X. Xu, C. Xiao, Z. Sun, D. H. Zhang, and X. Yang, “Quantum interference in $\text{H} + \text{HD} \rightarrow \text{H}_2 + \text{D}$ between direct abstraction and roaming insertion pathways,” *Science*, vol. 368, no. 6492, pp. 767–771, 2020.
- [109] B. Gao, “Universal Model for Exoergic Bimolecular Reactions and Inelastic Processes,” *Phys. Rev. Lett.*, vol. 105, p. 263203, Dec 2010.
- [110] D. S. Petrov and G. V. Shlyapnikov, “Interatomic collisions in a tightly confined Bose gas,” *Phys. Rev. A*, vol. 64, p. 012706, Jun 2001.
- [111] Z. Idziaszek, K. Jachymski, and P. S. Julienne, “Reactive collisions in confined geometries,” *New Journal of Physics*, vol. 17, p. 035007, mar 2015.
- [112] *Molecular Collisions in External Fields*, ch. 8, pp. 187–216. John Wiley & Sons, Ltd, 2018.
- [113] J. M. Hutson, M. Beyene, and M. L. González-Martínez, “Dramatic Reductions in Inelastic Cross Sections for Ultracold Collisions near Feshbach Resonances,” *Phys. Rev. Lett.*, vol. 103, p. 163201, Oct 2009.
- [114] R. A. Rowlands, M. L. Gonzalez-Martinez, and J. M. Hutson, “Ultracold collisions in magnetic fields: reducing inelastic cross sections near Feshbach resonances,” 2007. <https://arxiv.org/abs/0707.4397>.
- [115] L. Anderegg, S. Burchesky, Y. Bao, S. S. Yu, T. Karman, E. Chae, K.-K. Ni, W. Ketterle, and J. M. Doyle, “Observation of microwave shielding of ultracold molecules,” *Science*, vol. 373, no. 6556, pp. 779–782, 2021.
- [116] S. Jurgilas, A. Chakraborty, C. J. H. Rich, L. Caldwell, H. J. Williams, N. J. Fitch, B. E. Sauer, M. D. Frye, J. M. Hutson, and M. R. Tarbutt, “Collisions between ultracold molecules and atoms in a magnetic trap,” *Phys. Rev. Lett.*, vol. 126, p. 153401, Apr 2021.
- [117] K. K. Voges, P. Gersema, M. Meyer zum Alten Borgloh, T. A. Schulze, T. Hartmann, A. Zenesini, and S. Ospelkaus, “Ultracold Gas of Bosonic $^{23}\text{Na}^{39}\text{K}$ Ground-State Molecules,” *Phys. Rev. Lett.*, vol. 125, p. 083401, Aug 2020.
- [118] T. T. Wang, M.-S. Heo, T. M. Rvachov, D. A. Cotta, and W. Ketterle, “Deviation from Universality in Collisions of Ultracold $^6\text{Li}_2$ Molecules,” *Phys. Rev. Lett.*, vol. 110, p. 173203, Apr 2013.
- [119] Z. Z. Yan, J. W. Park, Y. Ni, H. Loh, S. Will, T. Karman, and M. Zwierlein, “Resonant Dipolar Collisions of Ultracold Molecules Induced by Microwave Dressing,” *Phys. Rev. Lett.*, vol. 125, p. 063401, Aug 2020.

REFERENCES

- [120] K. Matsuda, L. D. Marco, J.-R. Li, W. G. Tobias, G. Valtolina, X. Quemener, and J. Ye, “Resonant collisional shielding of reactive molecules using electric fields,” *Science*, vol. 370, no. 6522, pp. 1324–1327, 2020.
- [121] C.-L. Hung, X. Zhang, N. Gemelke, and C. Chin, “Accelerating evaporative cooling of atoms into Bose-Einstein condensation in optical traps,” *Phys. Rev. A*, vol. 78, p. 011604, Jul 2008.
- [122] E. Tiesinga, C. J. Williams, P. S. Julienne, K. M. Jones, P. D. Lett, and W. D. Phillips, “A Spectroscopic Determination of Scattering Lengths for Sodium Atom Collisions,” *Journal of research of the National Institute of Standards and Technology*, vol. 101, no. 4, pp. 505–520, 1996. j4tiesin[PII].
- [123] Y.-P. Bai, J.-L. Li, G.-R. Wang, Z.-B. Chen, B.-W. Si, and S.-L. Cong, “Simple analytical model for high-partial-wave ultracold molecular collisions,” *Phys. Rev. A*, vol. 101, p. 063605, Jun 2020.