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Molecular spectroscopy of a Bose-Einstein condensate with attractive interactions

by

Jordan Mitchell Gerton

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

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ABSTRACT

Molecular spectroscopy of a Bose-Einstein condensate with attractive interactions

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Molecular spectroscopy is used to probe a quantum degenerate gas of $^7\text{Li}$ atoms. Several effects are investigated using both single-color and two-color (Raman) photoassociative spectroscopy. An unusual spectral shift with laser intensity is observed for single-color photoassociation and the intensity dependence agrees with theoretical predictions. Additionally, the prospects for altering the interactions between ground-state atoms is investigated for both the single-color and Raman schemes. The single-color scheme is found to be impractical experimentally (although feasible theoretically) while the Raman scheme may be experimentally feasible as well. The Raman spectra display an interesting lineshape which is found to reflect the rate for inelastic collisions involving ground-state molecules (produced via the Raman process) as well as the attractive mean-field interactions between atoms in the condensate. Under certain circumstances, a dispersive Raman lineshape is observed which may be due to coherence properties of both the condensate and the thermal gas. Additionally, the Raman lineshape appears to reflect the kinetic time scale for thermal atoms to enter the condensate via elastic collisions. The Raman technique is applied to studies of the condensate growth and collapse dynamics caused by attractive interactions between condensate atoms, and enables the first direct observations of this phenomenon.
Acknowledgments

Many people need to be thanked for the work reported in this thesis. In particular, Ionut Prodan, Dmitry Strekalov, and I were together through many of the long nights when much of this data was taken. They are both responsible for particular aspects of the thesis and their contributions are recognized at those points. Cass Sackett and I labored together for a couple years and much of our work is presented here. Additionally, Mark Welling must be thanked for his contributions. Brian Frew and I worked together for awhile and his contributions are scattered about the thesis. Ian McAlexander, Kevin Strecker, Andrew Truscott, and Guthrie Partridge worked on a different project in the lab, but their insight, innovativeness and knowledge of physics were invaluable to me on countless occasions. I thank all these people not only for their contributions, but also for their friendship, patience and willingness to share their ideas.

Randy Hulet made all the work described here possible by laboring so hard to establish a state-of-the-art laboratory. Additionally, his insight and careful reading of the thesis produced a much improved version. His optimism and drive to succeed were contagious even through the most frustrating hours of experimentation as well as in the preparation of the thesis. I thank him for all these things as well as for his friendship and for giving me the opportunity to do so many things.

Finally, my family has always been a major part of my happiness and I thank them for giving me so much joy. My parents taught me the value of hard work, and I’ve learned from them how to enjoy the journey in addition to the destination. Jen Rich and Purvez Captain have become like family to me during the months that I bunked with them while writing this thesis. Above all, I thank my beautiful, intelligent, and patient wife Brenda who kept me going throughout the whole ordeal. This work would never have been completed without you, Sweetie!
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Chapter 1
Introduction

This doctoral thesis will mean different things to different readers. For me, my advisor, my current lab partners, and future students on this project, it is a chance to organize and write down all the information which has been accumulating in my head and various notebooks and computers for the past several years. Hopefully, this will speed future progress by eliminating duplicate research and providing a solid basis from which to launch the next generation of experiments. This thesis should also provide a clear description of the underlying physics so that researchers who might not be so familiar with the subject can gain additional insight into their own work. Finally, at least part of the thesis should be presented in a clear and minimally technical manner so that non-physicists, including my family, can appreciate the content.

The core concepts which form the basis for the rest of the thesis are presented up front, right here in this introductory chapter. Much of it will be written in an informal manner with a heavy emphasis on analogy with everyday phenomena. Many of the experts will want to skip this chapter and move directly to the more technical matter in the subsequent pages. Some parts of this chapter, however, will be aimed at physicists who do not live in the world of Bose-Einstein condensation. I urge those readers to follow the introduction to the end if only to be properly motivated for the rest of the thesis.

In the chapters which follow, the experimental results, procedure, analysis, and apparatus will be described. These chapters will be full of graphs, schematic diagrams, equations, conjecture, and analysis. I will do my best to tie together all the different experiments and the loose ends. The presentation here will suppose a good bit of knowledge on the reader's part, and probably will not be interesting to all but the
most persistent of non-experts. Enough detail will be given so that future researchers should be able to reproduce the results. Finally, the appendices will provide some of the nitty gritty technical details which make the experiments work.

1.1 What is Bose-Einstein condensation?

In order to gain a proper perspective for the work presented here, the non-expert readers first need to be familiarized with some basic quantum mechanical concepts and with Bose-Einstein condensation (BEC) in particular. BEC is a purely quantum phenomenon predicted by Albert Einstein in 1925 [1]. He extended the quantum theory proposed by the Indian physicist Satyendra Bose which explained the spectrum of light emitted by hot objects (black-body radiation) [2] to massive particles, such as atoms. Einstein realized that when a collection atoms is cooled to sufficiently low temperature, the atoms may suddenly undergo a dramatic change in their collective behavior*. The sudden onset of this change is analogous to the familiar phase transitions we experience in everyday life, such as the condensation of water from the air as dew. This particular analogy is useful since the situation originally envisioned by Einstein, and to which the work of this thesis corresponds, is that of a gaseous state "condensing" into a different state with new properties. There are differences between these cases however, and two particularly important ones. First, while ordinary condensation usually occurs at familiar temperatures (100 °C), BEC occurs at temperatures which are non-existent in the natural universe (-273 °C). In fact, the temperature difference is much more impressive if we think in terms of the absolute temperature scale known as the Kelvin scale. In the Kelvin scale, the unit of temperature is the same as for the Celsius scale, that is 1 K ≡ 1 °C, but the origin

---

*BEC only occurs for particles called bosons which have an integer multiple \((0, 1, 2, \ldots, N)\) of a quantum quantity called spin. Conversely, fermions have half-integer spin \((1/2, 3/2, \ldots, N/2)\) and do not undergo the BEC transition.
of the Kelvin scale is at absolute zero\textsuperscript{†} or -273 °C. Now, in terms of this absolute scale, BEC typically occurs at temperatures of \(~10^{-6}\) K or one millionth of 1 K. So we see that BEC temperatures are more than \(10^8\) (one hundred million) times colder than for ordinary condensation of water! The second important difference between BEC and ordinary condensation is that the BEC transition occurs even when atoms of the gas experience no mutual forces and do not interact with one another in any way. In fact, Einstein's original theory pertained to such an ideal gas. In contrast, the ordinary condensation of water relies on mutual interactions between constituent water molecules and would not occur without them.

The extremely low temperatures required by BEC makes it very difficult to achieve in the laboratory. In fact, this requirement led Einstein to doubt whether it would ever be achieved in the basic form he first conceived. With the advent of the laser, two related technologies, laser cooling and atom trapping, began to rise to the forefront of atomic physics. Laser cooling in particular is deemed so significant by many physicists that the 1997 Nobel prize in physics was awarded to three of its pioneering researchers: Steven Chu, Claude Cohen-Tannoudji, and William Phillips. By the late 1980s, these two fields had matured enough that researchers renewed their hopes of observing BEC in systems of dilute gases which most closely resembled Einstein's original conception of an ideal gas\textsuperscript{*}. Still, it was not until the summer of 1995 that BEC was achieved in these systems, first by a group at the University of Colorado in a gas of rubidium atoms [3], followed closely by our group here at Rice University with lithium [4], and a group at MIT with sodium [5].

As is often the case when such a roadblock is finally toppled, there has since been an explosion of activity in BEC research, and to date dozens (possibly 100) of

\textsuperscript{†}Absolute zero is the theoretical temperature where the momentum of atoms in the gas would fall to zero and their motions would cease.

\textsuperscript{*}Einstein's original theory had been extended and applied to more complicated and very "non-ideal" cases of strongly interacting systems by this time.
groups have now achieved or are in close pursuit of BEC resulting in a wide variety of interesting experiments. The research ranges from possible applications such as better frequency standards (atomic clocks) for global or deep space navigation, rotation sensors (gyrometers), and "atom lasers" to fundamental inquiries into, for example, how the subtle mutual interactions between atoms in these dilute, nearly-ideal gases effect the global properties of BEC. The research is so widespread and so diverse that the study of BEC and related phenomena can now be considered a separate field within atomic physics.

1.1.1 BEC for the family

So far, we've established that BEC is a phase transition of some kind in analogy with more familiar phenomena such as the condensation of water from air, and that its achievement seems to be important enough as to have spawned an entirely new and independent field of research. Still, the question must be asked, "What is it? What is BEC?" It is no easy task to describe BEC in ordinary terms, yet the goal of doing so is worthwhile since it affords non-experts the opportunity to glimpse the world behaving in an unusual and beautiful way. The technical difficulty with such a description lies in the fact that BEC is purely a quantum mechanical phenomenon and quantum mechanics is a counterintuitive and difficult theory (at least to me). Several authors have attempted to capture the essence of BEC with a minimum of mathematical and technical jargon and with an emphasis on comparisons to more everyday phenomena, such as the allusion to water condensation above. A particularly clear article entitled, "A new state of matter: Introduction to Bose-Einstein Condensation" was recently written in that spirit by my former lab partner Cass Sackett and my thesis advisor Randy Hulet [6]. This article is available for download from our lab website http://atomcool.rice.edu. Rather than rehash this and other treatments on the subject, I will presume that readers of this thesis are either experts who will
learn nothing new by this introduction or nonexperts, including my family, who know little (quantum) physics but who want to understand what I've been doing these last seven years. If you fall into the former group, skip over this section (and possibly the rest of this chapter). My hope is that those of you in the latter group will better appreciate what I've been doing with all my time after reading what comes next. If you fall somewhere in between, then I urge you to read on and then check out the reference above for a more rigorous treatment. For now, I will introduce an analogy which I think my family will enjoy: music*.

A night at the symphony

Have you ever arrived early at the symphony and listened to the cacophony created by the musicians as they warm up and tune their instruments? Some are playing high notes, some low. Some arrive early, some late. There are a variety of instruments all following their master’s will as they prepare for their solo parts in the piece. To my untrained ear, it sounds rather chaotic and I can never figure out how each musician can concentrate on their own task with all the noise about. Even visually it looks disorganized with everyone beating out their own rhythm in short, truncated motions.

At some point, a steady tone emerges from this chaos as the first-chair violin offers its note as the standard to which all other instruments should be tuned. Slowly, all the other instruments fall into tune and the pure tone grows louder and deeper. Eventually, no one instrument can be clearly distinguished among the group as they play a common note. At this point, the orchestra sounds like one altogether new and unique instrument although composed of many easily recognizable and distinct ones. This feeling is strengthened when a complicated musical piece is played and all the components of this new instrument synchronize in perfect harmony.

The cacophony of the orchestra during warmup is analogous to the thermal motion

*I make this analogy with the risk of pulling a D. S.-K.
of atoms in a normal gas. Under usual circumstances, a gas is "noisy" in the sense that all the constituent atoms move about randomly bumping into each other and any containment walls. Strictly speaking, atoms of an ideal gas never collide with each other, just the container walls. The average speed with which each atom moves can be characterized by a temperature; lower temperatures mean lower average speeds. On the other hand, the organized tone of the orchestra as it plays a common note or synchronizes into a symphony is similar to a Bose-Einstein condensate. Although the condensate can be made up of many atoms, each strikes the same note in the sense that their motions are mutually synchronized. The condensate is still a gas, just a well organized one, and it can coexist and intermingle with atoms which make up the normal gas. Figure 1.1 shows an artist's conception of BEC in the context of a group marching in lock-step. The random motion of the surrounding figures represents the atoms within the normal portion of the gas.

Personally, I think this is pretty neat in itself without going any further. However, there are other interesting properties of BEC which we can also think about. First, a distinction must be made between the way in which the transition between disorganization and organization occurs for both the orchestra and the gas. The orchestra organizes because of interactions between the musicians. That is, the first violin stands up and starts playing a steady note and the other musicians recognize this as a sign to follow suit. The communication between the first violin and the other musicians, whether verbal or visual in nature, is a form of interaction. As mentioned above, BEC is predicted to occur in a non-interacting gas, and has been repeatedly demonstrated in systems which closely approximate that ideal.

To visualize the process of the transition to BEC, imagine that the orchestra is made up of 100 musicians who know how to play their instruments but who are both blind and deaf and can in no other way sense each others actions. Further, assume that there is a collection of only T notes from which each musician must choose to play
Figure 1.1  Artist’s conception of Bose-Einstein condensation. The figures marching in lock-step represent the condensate while the randomly moving figures represent the atoms in the thermal portion of the gas. This figure is reproduced and modified from the cover of Science magazine, Dec. 22 1995.

at a given time. That is, each instrument can only play discrete notes which can be enumerated from 1 to $T$. Now if $T$ is much greater than 100, the probability that any given note is played by a given musician is much less than 1 because presumably the musicians will choose a note randomly from the entire set of $T$ notes. This situation corresponds to a normal, or thermal, gas where the probability for any atom to be in a particular motional state is very small. Now say that the number of available notes is reduced from $T$ to some smaller number either because the dynamic range of each instrument becomes restricted or because the musician becomes fatigued and can no longer hit the high notes. This situation is analogous to reducing the temperature of a gas because in that case, the mean energy (momentum) is reduced and fewer atoms move with high energy. When the number of available notes $T$ becomes comparable to 100, which is, remember, the number of musicians, the probability of a particular note
to be played by a single musician is then reasonably close to 1. So far this is neither surprising, nor very exciting. The non-intuitive part is that when the probability for a single note to be played by a single musician becomes appreciable, immediately thereafter, the probability for all the musicians to play that single note also becomes very likely, even though the musicians do not communicate with each other in any way.

One question immediately emerges from this discussion: “Which particular note do the musicians choose?” The analogous question for a gas is “In which motional state do the atoms end up?” This question is actually fairly difficult to answer and in order to do so, we must delve a little further into the world of quantum mechanics. The following subsections will lead to insight into this question, and in the process will uncover additional ones.

**The energy grid**

One of the most important aspects of quantum mechanics, which can in fact be said to define quantum mechanics, is the notion of quantization of energy. Quantum mechanics says that at the most basic level, life is more like a guitar or a piano where only particular notes are allowed, than a horn which can vary its tone continuously. In a sense, this goes against our experience because in everyday life, we often observe the energy of something to vary smoothly and we do not notice any discrete “jumps”. However, this quantization of energy is responsible for many things which we understand and accept. For example, the discrete energy levels that electrons can occupy within an atom, which are familiar to those who have studied basic chemistry, are a consequence of this. The gaps are very, very small, however, so that when we observe the universe on an everyday scale, the discrete grid cannot be distinguished. Only when we examine things on an atomic scale, do we notice the underlying structure. This situation is very similar to viewing a pointillist painting from far away or from
close up. When far away, the short, truncated brush strokes blend together and form a coherent image, while up close, each separate stroke can be distinguished. Figure 1.2 illustrates this concept with a portion of a painting entitled, *Bathing at Asnieres* by Georges Seurat.

![Bathing at Asnieres by Georges Seurat](image)

**Figure 1.2** *Bathing at Asnieres* by Georges Seurat. The inset shows an electronic reproduction of a portion of the original which was painted in the pointillist style. The grainy texture of the main figure was achieved by enlarging the inset in order to simulate a close-up view of the painting. Some extra "pointilism" was electronically added to the large figure in order to emphasize the structure.

**The trap**

What does the underlying energy grid have to do with BEC? Although Einstein's original theory assumed a homogeneous gas, that is, one which is not confined to a
particular volume, it is impractical to work with such systems in the laboratory. All the successful BEC experiments to date use atom traps to confine the gas and isolate it from its surroundings. In a general sense, these traps can be thought of as levitation devices for a collection of atoms. In many of them, the trap "walls" are provided by the magnetic field generated by either permanent magnets or electromagnets. Most of us are familiar with the magnetic force exerted by one magnet on another from grade-school science classes or from playing with refrigerator magnets. The relative orientation of two magnets determines whether they attract or repel one another. Many species of atoms behave as if they were tiny bar magnets and one can imagine that the trap magnets can be arranged around the perimeter of a sphere, for example, such that the atoms are confined near the center.

When the magnets are arranged in a particular way, they form a sort of "magnetic bowl" in which the atoms sit. Of course, the atoms do not actually sit there at rest; they move up and down the bowl "walls", orbit around the bottom of the bowl, and collide with each other. The atoms with the most energy climb highest along the bowl walls and those with the least energy spend there time near the bottom of the bowl. This makes sense: imagine standing at the bottom of a huge bowl and pushing a great big marble so that it starts rolling around in the bowl. With a real hard push, the marble can get near the top and possibly jump out of the bowl, while with a weak push, the marble can only roll around near the bottom. What quantum mechanics says is that the amount of energy which is imparted to the marble can only take on particular discrete values. This has the effect of limiting the possible trajectories of the marble to a given set of orbits. Again, the typical size of everyday objects such as marbles (even small ones), hides the underlying structure and the marble looks like it can orbit in any old way, provided it obeys Newton's laws of motion and all other classical, as opposed to quantum, physics laws.

When we focus down to the atomic scale, however, the discrete energy levels and
Figure 1.3  Magnetic bowl for trapping atoms. The curved line shows the potential energy as a function of distance from the trap center along a particular axis which goes through the trap center. The horizontal bars are the discrete values of total energy which the atoms can have.

Motional orbits become manifest. Figure 1.3 shows an example of a magnetic bowl as well as the discrete energy levels which atoms can occupy. The vertical axis in this plot is an energy scale and the horizontal axis is the distance along a particular line which goes through the center of the trap. The curved line, therefore, is the potential energy of a single atom at a given distance from the trap center and the horizontal bars are the discrete values of total energy, kinetic plus potential, which are available to an atom. Although I have not introduced the notion of kinetic and potential energy, it is a fairly intuitive concept with which we are all familiar. Let's return to the marble and bowl analogy. Roughly speaking, the total energy of the marble remains constant as it climbs up the wall of the bowl and then rolls back down. However, potential energy and kinetic energy (the energy due to the motion of the marble, or its momentum) are constantly and smoothly being exchanged; when
the marble passes through the bottom of the bowl, it is moving fastest meaning that its kinetic energy is maximized. At this point, its potential energy is minimized. Conversely, the potential energy is maximized when the marble stops rolling up and starts rolling down the wall and at that point, for just an instant, its speed is zero as the motion reverses. Particles (atoms, marbles, etc.) tend to move toward lower potential energy; this is what keeps a marble rolling around in a bowl or an atom bouncing around in a trap.

**BEC - the fundamental tone**

We now have enough background understanding to consider the question from above, "In which motional state do the atoms end up?" First we must accept that when a bunch of atoms are loaded into the trap, some will have lower energy and some will have higher. The average energy of the gas can be characterized by the temperature $T$. Note that in the example given above with 100 deaf and blind musicians, I used the symbol $T$ to describe the number of notes available to each. This repetition of symbols is no mistake; the number of energy levels available to each atom in the gas is directly related to the temperature. Following that analogy, when the gas is cooled to lower temperature, the number of states available to each atom decreases as it becomes increasingly unlikely that any atom will have high energy. When the temperature is reduced to the point that it becomes likely that one atom will occupy a particular energy state, it immediately becomes likely that most of them will occupy that same state. When considered in this way, the only state that makes sense to be that special "one" is the one with lowest energy. Any higher energy states will eventually be forbidden when the temperature is decreased sufficiently. The lowest energy state is therefore called the condensate level or simply the condensate.

One reason I like the analogy between music and BEC is that it naturally lends itself to a discussion regarding modes of vibration. This concept may sound compli-
cated, but it is actually familiar in the world of music. When the first violin plays the pure note to which all the other musicians tune their instruments, she is exciting a fundamental mode of vibration for one of her violin strings. Similarly, the tone which emerges from a guitar when one of its strings is plucked lightly results from the fundamental vibration mode of that string. The vibrations establish a pressure wave in the air that surrounds it and these waves travel to our ears where they are interpreted as a tone. Just as the first violinist establishes a fundamental tone for the orchestra, the condensate level in Fig. 1.3 is the fundamental tone of the trap. In further analogy, the fundamental tone is "heard" clearly only when the BEC transition occurs and many atoms occupy the condensate.

A picture of music

A distinction should be made here between "tone" and mode of vibration. In general, the mode of vibration is an abstract thing, a mathematical construct which is used to describe a physical system. It is, in fact, a basic property of the system. It is more "basic" than tone because the mode of vibration would still exist even if there were no audible manifestation of it. The fundamental mode of a guitar string could still be detected, for example, if the string were vibrating in complete vacuum so that no pressure waves would be created, and therefore no sound emitted. In that case, the mode could be detected visually by simply filming it with a high-speed movie camera so that each frame of the movie would capture the vibration at a slightly different time. The point here is again that the fundamental mode is basic to the physical system, whereas the tone is simply a way of measuring it.

This seemingly subtle point is actually important in the context of BEC. One way to encapsulate the issue is to ask the question, "How is BEC observed?" A full description of the detection method most commonly used is quite complicated and falls outside the scope of this introduction (for the details, see Chap. 2). The idea,
however, is quite simple and familiar: Take a picture. Just as everyday objects cast a shadow when light shines upon them, so do atoms. In particular, imagine a laser beam whose diameter is larger than the cloud of trapped atoms. Atoms will absorb some of the laser light when it is passed through the trap, leaving a shadow in the laser beam. We can record this shadow on a camera (a digital one, in this case) and thereby take a snapshot of the cloud of trapped atoms. We would expect that the portions of the cloud which have more atoms (or equivalently, a higher density of atoms) would cause a deeper shadow since we assume that each atom absorbs the same percentage of the light. This image is analogous to the shadow that would be cast by a series of semitransparent sheets of varying shape and size hanging from a clothesline on a sunny day. If they are hung such that a smaller sheet is centered within a larger one, the shadow would be darker in the center where the light must pass through multiple sheets and brighter near the edges where the light only passes through one.

Let us return our attention to the magnetic bowl shown in Fig. 1.3. In analogy with the marble bowl discussed above, atoms with low energy will not venture out very far from the trap center, while those with high energy can climb higher on the walls of the trap. We would expect, therefore, that when the transition to BEC occurs within the gas, a large number of atoms will always be present near the trap center, casting a deep shadow onto the camera. There will still be some atoms in the normal gas which surrounds the condensate and they will cast a more shallow shadow. Figure 1.4 shows one false-color, three-dimensional rendering of the actual shadow cast by an atom cloud with no condensate and one where a condensate is present*. In these images, the shadow is inverted so that a taller signal corresponds to a deeper shadow. The image of the condensate is a picture of the fundamental mode of the trap; a picture of music.

*These images are actual data, but the signals from adjacent pixels on the camera have been averaged in a particular way in order to suppress statistical noise.
Figure 1.4 Atom cloud shadows. The image on the left is a false-color, three dimensional rendering of the depth of shadow cast by an atom cloud with no Bose-Einstein condensate. The image on the right is a similar rendering of a cloud with a condensate consisting of \(~1000\) atoms.

Synchronicity

The atoms which form the Bose-Einstein condensate all have the same total energy and the same orbital motion in the trap. This much has been established from the discussions above and is demonstrated quite clearly in the right image in Fig. 1.4. That is, the exact curvature of the magnetic bowl is known, so the “shape” of the fundamental mode can be calculated mathematically. The texture of the shadow at the center of the right image matches perfectly with the results of such a calculation. This is interesting, but there is more. One of the most impressive consequences of BEC is that the motional orbits of all the atoms in the condensate are synchronized, or “in phase”. Hearkening back to the music analogy, this is akin to all the musicians playing the same note and producing a pressure wave from their respective instruments whose peaks and valleys are perfectly synchronized.

In order to understand the idea of phase more clearly, we can return to our “movie” of a vibrating guitar string introduced above. Figure 1.5(a) shows a fictional, one-stringed guitar and what the string would look like if the movie were paused at three different times during the vibrational motion. The red arc, for example, would correspond to the shape of the string just as the musician plucks it. After some time,
Figure 1.5 Motion of a guitar string demonstrating phase. (a) Fictional one-stringed guitar where the (exaggerated) vibrational motion of the string has been "frozen" at three different times during the vibration. (b) Amplitude of a given part of the string as a function of time for two different guitars whose strings vibrate with different phases.

A snapshot of the string would look like the black line and at some later time the blue arc. The string would then move back to its original configuration and this cycle would repeat itself regularly. The solid curve in Fig. 1.5(b) shows the movement of a short length of the string if, for example, the movie camera focused in on just the center portion. The amplitude of this portion (and all other portions) of the string, or the displacement from its position in the absence of vibration, is a regular function of time which some may immediately recognize as a sine function or sine wave.

The dashed curve in Fig. 1.5(b) shows the motion of the corresponding portion of the string on a different guitar. The vibrational motions of these two strings are said to be "out of phase" with each other since their corresponding sine waves are displaced in time. The phase difference is indicated by the measurement arrows at the bottom the figure. When each string vibrates with the same frequency, the phase difference remains constant. If the two strings have zero phase difference, then their corresponding sine waves overlap perfectly. Applying this concept to the condensate means that the motion of every atom within the condensate overlaps perfectly with
that of every other one. If we then focussed our movie camera on the condensate, we
would see what looks like one “super atom” oscillating back and forth in the trap.
This statement implies more than the atoms being “extremely close” to each other as
they are in a solid, rather than gaseous, substance; it implies that each atom actually
occupies the same volume in space! This highly non-intuitive behavior can only be
understood in the context of quantum mechanics and will be discussed below. First,
however, let’s look at one its consequences.

Turn up the volume

The concept of “phase” discussed above, and in particular, the addition of multiple
waves with the same phase, may be more familiar than is at first realized. Consider
the addition of two sine waves with slightly different vibrational frequencies. In
that case, the phase difference between the two sine waves varies with time, instead
of being constant, as for those shown in Fig. 1.5(b). This resembles the situation
when a particular musician from the orchestra, for example, attempts to tune their
instrument to that of the first violin. When there is a frequency difference between
the tone played by the first violin and that played by the other musician, a rhythmic
beating is heard. The beating becomes more rapid when the tones are further apart
and slows when the tones are closer together. Musicians know when their instruments
are mutually tuned because the beating is no longer heard. If you have access to a
guitar or piano and a tuning fork, you can experience this phenomenon first-hand.

As described above, the vibrational motion of the strings establish a pressure
wave that travels through the air to our ears. It is fairly obvious that the peaks and
valleys of the pressure wave would be synchronized to the peaks and valleys of the sine
wave shown in Fig. 1.5(b). The beating described above results from “interference”
between pressure waves created by the two strings. Interference is just a term for
the way waves add up when they arrive at a particular point in space. Figure 1.6
Figure 1.6  Interference between two sine waves. The black and blue curves are two sine waves with slightly different frequencies and the red curve is their sum.

illustrates this concept by showing the sum of two sine waves with slightly different frequencies. The red curve is the sum of the two sine functions shown in blue and black. The tall peaks result when the two sine waves add "in phase". Notice that the frequency of these peaks is lower than the frequency of either sine wave since the time between adjacent peaks is longer. These tall peaks are the source of the beating described above.

Now consider the addition of two sine waves with equal frequencies of vibration such as those shown in Fig. 1.5(b). It is easy to see that if the two waves were exactly 1/2-wave out of phase such that the peak of one corresponded to the valley of the other, their sum would be zero for all time. Does this mean that two violins playing the same note would be impossible to hear for some members of their audience if the pressure waves coming from each are 1/2-wave out of phase? Yes, but "impossible" should probably be replaced with "difficult", and the circumstances for observation of such a phenomenon are unlikely to occur at the symphony, for example, and indeed proper circumstances would need to be established very carefully. Conversely, when two waves are perfectly in phase, they add up to a new sine wave with the same frequency but with twice the amplitude. In the context of music, this means that
someone in the audience would hear the given tone at twice the volume*. This is what allows us to experimentally observe or "hear" the note played by the atoms in the condensate, because under ordinary circumstances, the volume of the fundamental note is too low to detect.

If the phase of vibrational motion were not synchronized for all the atoms, it would be impossible, or at least extremely difficult to detect the fundamental tone. This concept has already been addressed above as the cacophony that musicians create when they are warming up before a symphony performance. In that case, it is difficult to identify any one given note above another. This concept is also implicitly demonstrated by the images in Fig. 1.4. As mentioned in that figure caption, the image on the right corresponds to ~1000 atoms in the condensate. This number is hard to appreciate unless some relative scale is given. In other words, is 1000 atoms a lot or a little? What is not mentioned in the figure caption is that both images correspond to a total number of atoms (sum of number in the condensate and number in the ordinary portion of the gas) of ~70,000. This number sets the scale, and we see that in this example, it takes 70 atoms in the ordinary portion to give roughly the same depth of shadow as 1 atom in the condensate. This gives an idea of how difficult it would be to detect either a single atom in the condensate or many atoms whose phases of oscillation are unsynchronized.

**Atom waves**

If the preceding few paragraphs seem a bit cryptic, it is with good reason. I've sort of put the cart before the horse here. I initiated a quite lengthy discussion involving waves and phase, all the while applying these concepts to atoms. The connection between the two, atoms and waves, is only provided by quantum mechanics. In par-

*Actually, it would be four times since the volume is proportional to the square of the amplitude. Also, the word "volume" here obviously refers to "loudness" rather than a spatial size.
ticular, the famous Heisenberg uncertainty principle of quantum mechanics says that the more which is known about the momentum (or energy) of a particle (atom), the less can be known about its position. Another, slightly more mathematical description would be: The uncertainties in the position and momentum of a particle are inversely proportional to each other. Applying this to our case of trapped atoms means that as the temperature of the gas is reduced (in order to achieve conditions necessary for BEC) the uncertainty in the energy of each atom is also reduced, since higher energies are forbidden. By the Heisenberg uncertainty principle above, this implies that the uncertainty in the position of each atom increases. In conditions of extremely low temperature, the momentum of each atom is so tightly constrained, that its position is best described by stating the probability of it being in a particular place, rather than stating that it is in a particular place. The function which describes how this probability changes with the spatial coordinates of the trap behaves much like a wave and is therefore called the wave function of the atom.

Armed with this perspective, the discussion of phase and interference above now makes more sense. Each atom in the condensate shares an identical wave function whose form is dictated by the particular geometry of the trap potential shown in Fig. 1.3. The condensate wave function is very similar to the time varying arc formed by the vibrating string shown in Fig. 1.5(a). The vibrating string, and the condensate wavefunction are both called standing waves because they are trapped at their endpoints, by the guitar fret and bridge in the former case and by the trap walls in the latter. In this context, the notion of phase for the condensate wave function can be compared directly to that for the guitar string. As more atoms build up in the condensate, the amplitude of the wave function grows proportionally producing a "louder" tone.

We can now refine our understanding of when the transition to BEC occurs. In analogy with the scenario of blind and deaf musicians above, it was stated that the
transition happens when the temperature is reduced to the point that the number of states available to the system becomes comparable to the number of atoms in the trap. This criterium is satisfied when the uncertainty in the position of each atom, or its "fuzziness", becomes comparable to the average distance between them. When this happens, the atoms "overlap" in the same sense that waves can overlap and the atom wave which makes up the condensate starts to grow.

We can understand this more clearly by once again introducing the analogy of the orchestra made up of 100 blind and deaf musicians. Recall that each musician can choose to play from $T$ possible notes at any given time. Let us now further assume that all the musicians are playing copies of the same instrument, either all violins, guitars, or what have you, but they are playing their notes independently of each other. Now imagine that this orchestra is arranged on stage with sufficient distance between musicians so that the audience is able to determine from which musician each note is coming.

Now rearrange the orchestra so that two of the musicians are so close together that it becomes difficult to determine which note belongs to which musician*. In this case, the total number of combinations of notes which the two musicians can play between them is effectively reduced because the situation of the first musician playing note "A" and the second musician playing note "B" cannot be distinguished from the reverse situation of the first musician playing note "B" and the second musician playing note "A". These two possibilities only count as a single one. As the orchestra is further "squeezed" so that more and more of the musicians become indistinguishable from each other, the total number of combinations of notes available to the orchestra as a whole is similarly reduced. The transition to BEC comes about simply by eliminating indistinguishable combinations of available states in this way.

*Note that this same lack of distinguishability could be caused by each musician somehow taking up more space, in closer analogy with the atoms becoming fuzzy as the temperature is reduced.
1.1.2 Making BEC in the lab

Before moving on to describe how and what we study with BEC, a brief description of how it is produced in the laboratory environment should be given. It is technically difficult to produce BEC, as evidenced by the 70 years which passed between Einstein’s original prediction and the first experimental achievements. There are three main ingredients; atom trapping, laser cooling, and evaporative cooling.

Atom trapping

As indicated above, atoms must be cooled to extremely low temperature in order for them to undergo the transition to BEC. An ordinary container, like a small box, is not sufficient because it is impossible to cool the container walls to BEC temperatures and the atoms can only be made as cold as these walls. As discussed briefly above, the solution is to use a magnetic trap which has no physical walls to cool, but which will confine the atoms for long enough times to achieve BEC. Fig. 1.3 above shows the potential of a magnetic trap which can be produced either by permanent magnets or electromagnets. This potential will push atoms back toward the trap center no matter which way they try to move.

In our laboratory, we have one electromagnetic trap (EMT) and one permanent magnet trap (PMT), and BEC of lithium atoms is now routinely produced in both. The PMT predated the EMT in our lab by about 5 years and it was used for the first demonstration of BEC in lithium in 1995 and for all the work reported in this thesis. Figure 1.7 shows a drawing of the PMT with a cloud of cold atoms trapped at the center.

Laser cooling

It was shown above that BEC occurs when the quantum mechanical wavelength, or fuzziness, of the atoms is comparable to the mean distance between them. Therefore,
Figure 1.7  Drawing of the permanent magnet trap. The six cylinders are neodymium-iron-boron (Nd-Fe-B) rare-earth magnets, each about 22 mm in diameter. The magnets are aligned to produce a local magnetic field minimum at the center of the structure where atoms can be trapped.

magnetic traps are configured to be as "tight" as possible, so that the temperature requirement is not so stringent. Still, due to geometrical constraints, magnetic traps are relatively shallow and can hold only atoms which are moving relatively slowly. The PMT, for example, has a depth of only ~10 mK (0.01 K), meaning that the atoms need to be cooled below this temperature in order to become trapped in the first place.

In typical BEC experiments, the trap is loaded from a gaseous vapor produced by boiling molten metal. Under the high vacuum conditions of these experiments, however, these vapors are produced at temperatures ranging from ~60 °C (in the case of rubidium) to ~500 °C (in the case of lithium). Obviously, these vapors need to be cooled significantly. The technique of laser cooling has been used to cool atomic vapors to temperatures below 1 mK which are sufficiently low for loading most traps. This technique involves shining multiple laser beams on a gaseous sample of atoms
so that the velocity of each atom is reduced no matter which way it moves. Reducing the average velocity of atoms in the gas is equivalent to reducing the temperature.

**Evaporative cooling**

Unfortunately, laser cooling has not been able to achieve low enough temperatures for BEC. Investigations aimed at extending laser cooling to BEC temperatures are actively being pursued by a substantial number of research groups, but so far, none have quite gotten all the way there. The solution, a technique called evaporative cooling, has been employed by all successful BEC experiments to date. Evaporative cooling is the same process that allows a hot cup of coffee to cool if left standing uncovered. It relies on the fact that a collection of particles, trapped atoms in this case, has a broad distribution of energies, as discussed above. If the atoms with the highest energy are selectively removed, then the average energy of the collection, the temperature, decreases. Subsequently, collisions between the remaining atoms will produce more atoms with high energy. These are then removed and the cycle can be repeated over and over again until the desired temperature is achieved. The total number of atoms is reduced during this process, which in general moves the gas further away from the conditions necessary for BEC. However, with appropriate initial conditions (i.e. enough atoms in the trap) the amount by which the temperature is reduced makes up for this loss of atoms, and BEC is achieved.

The process of evaporative cooling is illustrated schematically in Fig. 1.8. The hottest atoms can escape over the lip of the magnetic bowl while the colder ones remain trapped since their motion never carries them into the vicinity of the lip. In practice, the lip is lowered continuously at a rate that maximizes the cooling efficiency while minimizing the atom loss. In our lithium experiments, BEC occurs when the temperature is reduced to \( \sim 1 \mu \text{K} \) (one millionth of 1 K) with about one million atoms left in the trap. At this point, the number of atoms in the condensate starts to grow
Figure 1.8 Schematic representation of evaporative cooling. The hottest atoms can escape over the lip of the magnetic bowl while the colder ones remain trapped.

rapidly. According to Einstein’s original theory for BEC of an ideal gas, further cooling will result in continued growth of the condensate until eventually all atoms in the gas occupy the condensate. For many real (as opposed to ideal) atomic species, this statement is true. For lithium, however, the situation is much more complicated and in many ways more interesting as well.

1.1.3 Role of interactions

BEC as described here occurs in atomic gases that are considered very dilute. The interactions between atoms, that is the force exerted by one atom on another, either attractive or repulsive, are therefore weak. In fact these systems closely approximate the ideal gas envisioned by Einstein. Still, although weak, the interactions can have profound effects on the nature of BEC and many current experiments, including ours, are exploring this issue. It should be noted that due purely to a fluke of nature, lithium atoms weakly attract each other at low temperature*. Of all the atomic species in

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*In particular, the bosonic isotope $^7\text{Li}$ has weak attractive interactions. The fermionic isotope $^6\text{Li}$ has very strong attractive interactions but, being a fermion, does not undergo the transition to BEC.
which BEC has been demonstrated, only one other, the rubidium isotope $^{85}\text{Rb}$, has attractive interactions. All other BEC species (hydrogen, sodium, $^{87}\text{Rb}$, and recently metastable helium) have repulsive interactions.

As an example of the important role played by interactions, consider that for several decades, it was believed that BEC would be prohibited in a gas, such as lithium, where the interactions between atoms are attractive. As early as the 1950s and as recently as 1994, theories were developed which attested to this. The reasoning behind these theories can be distilled to the following: Atoms in the condensate are moving too slowly to push on anything with much force and, therefore, there is nothing to resist the attractive force of the interactions. The condensate shrinks in size and the attractive force increases further. Eventually, the condensate will collapse in upon itself undergoing a sort of microscopic implosion. The collapse only stops when the density gets so high that individual atoms combine with each other to form molecules. When this happens, there is a huge amount of energy released, and the atoms are blown out of the trap. Instead of ending up with a condensate, you get just a bunch of hot molecules.

In spite of these predictions, BEC in a gas of lithium atoms was originally observed by our group in 1995. The theoretical reasoning described above neglected one important aspect of the experimental realization, which made all the difference: Confining the atoms in a trap localizes them to a particular region of space. By the Heisenberg uncertainty principle described above, this imposes an uncertainty on their momentum (or energy). A localized atom, therefore, can never truly have zero energy and the more tightly the atom is confined, the higher its so-called zero-point energy. The offset of the lowest energy level in Fig. 1.3 from the true bottom of the trap potential is a consequence of this zero-point energy. The result of the confinement, therefore, is a small quantum “pressure” which enables the condensate to resist collapse as long as the attractive force of the interactions is not too strong. Since the strength of
the interactions increases with the number of atoms in the condensate, the quantum pressure will stabilize the condensate against collapse as long as the number of atoms in it does not grow too large. For $^7$Li in the PMT, the stability limit on the number of atoms in the condensate is $\sim 1200$, a value which we have verified experimentally. When the limit is exceeded, the condensate does indeed collapse as we have shown in references [7, 8] and as described in Chap. 5 of this thesis. Note that the instability situation does not apply to a gas with repulsive interactions, since, in that case, as the density increases, so does the strength of the repulsive forces between atoms. The trap holds the repulsive gas together, and everything is stable.

1.2 What is this thesis about?

Hopefully by now, even the least expert of readers are convinced that BEC is an interesting phenomenon to investigate. The rest of this thesis will describe our studies of BEC in lithium atoms. In particular, direct observations of the condensate collapse described above are reported here (see Chap. 5). Additionally, the gas of ultracold atoms, and specifically the condensate, is used to study how atoms can be "glued" together into molecules using laser light, a process known as photoassociation (see Chaps. 3, 4, and 7). Finally, the possibility of using photoassociation in order to alter the interactions between condensate atoms is discussed (see Chap. 6).
Chapter 2
Experimental procedure

This chapter gives an overview of the apparatus and procedure used to produce and study BEC of lithium. Enough detail is provided here to enable a complete understanding of the experiments described in the following chapters. Many technical points related to the operation and maintenance of the apparatus, however, are omitted for readability.

2.1 Trapping and cooling

All the experiments described in this thesis follow the same basic procedure. A magnetic trap is loaded directly from a laser slowed atomic beam. Once trapped, the atoms are further cooled using forced microwave evaporation until the BEC transition temperature, typically $\sim 1 \mu K$, is obtained. Following evaporation, the atoms are probed using the photoassociation techniques described in Chaps. 3 and 4 and then subsequently imaged in order to determine their total number $N$, their temperature $T$, and the condensate number $N_0$. The imaging procedure destroys the condensate and significantly heats the gas, so the loading and cooling cycle must be repeated over and over while varying the parameter of interest. In this section, the experimental procedure for trapping and cooling will be discussed while detection and photoassociation will be described below.

A general schematic diagram of the BEC permanent magnet trap apparatus is shown in Fig. 2.1. The atomic oven is heated to $\sim 600 ^\circ C$, producing a thermal vapor of lithium atoms with an average velocity of $\sim 2000$ m/s. A small hole in the oven allows a beam of atoms to escape down the long axis of the apparatus. The atomic beam travels down a long vacuum tube and a laser beam is directed against its motion. The laser exerts radiation pressure on the atoms, and a small percentage of them are
Figure 2.1 Schematic diagram of the BEC trap apparatus. The main parts are the slow atom source including the atomic oven and the Zeeman slower; the deflection chamber where slow atoms are separated from the fast atomic beam; the permanent magnet trap indicated by colored rectangles; and the imaging system used for detection of BEC.

slowed to \( \sim 50 \) m/s. The slowed atoms are deflected by a cylindrically focused laser beam directed transverse to the atomic velocity, while the fast atoms pass through the deflection region quickly and do not obtain an appreciable transverse kick. The deflected atomic beam passes through a narrow tube before entering the trap vacuum chamber. The atoms are then loaded into the permanent magnet trap with the help of a three-dimensional optical molasses consisting of three pairs of counterpropagating laser beams.

2.1.1 Permanent magnet trap

The heart of the BEC apparatus is the permanent magnet trap [9]. A scale drawing of the trap geometry is shown in Fig. 2.2. The trap consists of six neodymium-iron-boron (NdFeB) rare-earth cylindrical magnets arranged as shown, where the letters indicate the inner tip polarities. The magnets are mounted on a magnetic-stainless-steel yoke which rigidly affixes their positions and recirculates the magnetic flux. They are aligned to produce a local magnetic field minimum at the center of the
Figure 2.2  Trap magnet geometry. The six cylinders are neodymium-iron-boron (NdFeB) rare-earth magnets, each about 22 mm in diameter. The letters indicate the inner tip magnetizations of the magnets and the frame is a stainless steel yoke.

structure where atoms can be trapped. The plane which contains adjacent magnets with opposite polarity is the quadrupole plane and the bias axis is normal to that plane. Atoms are loaded along the line of sight of Fig. 2.2 between the two nearest magnets.

The bias field at the center of the trap is currently 1003 G (the bottom frequency for evaporation is ~3453 MHz) and the depth is ~140 G, or about 10 mK. The trap oscillation frequencies have not been measured since ~1997 [10], but they should not have changed as indicated by the stability of the bottom frequency since then. The harmonic frequencies for the principal axes in the quadrupole plane are 150.6 Hz and 152.6 Hz, while that of the bias axis is 131.5 Hz. References [9]-[12] provide considerably more detail on the design, characterization, and performance of the permanent magnet trap.
2.1.2 Loading the trap

As mentioned above, the depth of the permanent magnet trap is only $\sim 10$ mK. This is a factor of $10^5$ colder than the temperature of the atoms within the atomic oven. Two main cooling stages must be used to successfully load the trap. As mentioned above, the atomic beam must first be slowed using a laser beam directed against the atomic motion. Additionally, the atoms must be further cooled when they enter the trapping region so that they will fall into the trap. This is accomplished with a so-called three-dimensional optical molasses consisting of three pairs of counterpropagating laser beams. Before discussing these cooling stages further, the atomic oven which produces the lithium beam is described.

Atom source

A schematic drawing of the atomic oven used for the work of this thesis is shown in Fig. 2.3 [13]. It is basically just a hollow cylindrical reservoir with a thin tubular nozzle attached. Both the reservoir and the nozzle are wrapped with coils of resistive wire which heat the oven walls. The reservoir is filled with a few grams of solid metallic lithium which melts and then boils as the walls are heated. The defining feature of this oven is that atoms which emerge from the aperture (junction between
the reservoir and nozzle) at large angles will strike the nozzle wall and be recycled back into the reservoir. Recycling the large angle atoms greatly lengthens the time between oven refills and helps to collimate the atomic beam. As shown in Fig. 2.3, a thin layer of stainless steel mesh lines the inner diameter of the oven nozzle. A temperature gradient is established along the length of the nozzle with the tip (flange end) just above the melting point of lithium (~200 °C) and the hottest point at the aperture. Atoms which strike the mesh condense into a liquid and are wicked back towards the aperture where they are again vaporized within the reservoir.

Typically, two independent coils of wire are used to establish the proper temperature gradient: one along the length of the nozzle and one around the reservoir body. Thermocouples in good contact with the outside of the tube walls are used to measure the temperature at various points on the oven. The best performance is observed with the nozzle tip at ~250 °C and the aperture at ~600 °C. This tip temperature is close enough to the melting point to ensure that no significant sourcing will occur from that region, while hot enough to minimize the chance of a nozzle blockage. At these temperatures, the oven should produce a beam of about $10^{14}$ atoms/s.

Under normal operating conditions, the oven is refilled about once per year, along with routine vacuum pump maintenance. A gate valve separates the oven and pumps from the rest of the vacuum chamber in order to facilitate these tasks and to protect the vacuum integrity of the rest of the chamber in the event of emergency power outage. It should be noted that a layer of stainless-steel mesh also lines the reservoir body with a mesh “cap” near the top. This is important because any solid lithium which attaches to the reservoir flange as the oven is cooled will make it very difficult to open and refill. Establishing wicking action in this region of the reservoir helps to minimize the chance of this happening.
Zeeman slower

As mentioned above, the lithium beam emerging from the oven consists of atoms with an average longitudinal velocity of \(\sim 2000\) m/s. In order to slow them down to trap-loading speeds, a technique called Zeeman slowing is employed. This technique was originally developed by Harold Metcalf and Bill Phillips in 1982 [14] and takes advantage of the so-called Zeeman shift in internal energy that an atom experiences when in a magnetic field. This solves a basic problem in laser cooling: The Doppler shift of an atom changes as it slows down. A laser whose frequency is tuned to match the atomic resonance condition for the initial value of Doppler shift, will later become non-resonant and further slowing ceases. The idea of Zeeman slowing is to continuously change the internal energy structure of the atom using a nonuniform magnetic field produced by a tapered solenoid wound around a vacuum tube. The varying Zeeman shift compensates for the changing Doppler shift as the atoms travel down the tube length and the resonance condition is maintained throughout. Zeeman slowing works remarkably well and is the current state of the art technique for decelerating atomic beams.

The Zeeman slower used for the BEC apparatus was installed in 1998. It was designed by Dean Homan and Randy Hulet, manufactured by Dean and Kevin Strecker, and is a significant improvement over the previous model. The new design gives an average deceleration of \(0.6a_{Dop}\) compared to the old value of \(0.5a_{Dop}\), where \(a_{Dop} = 1.55 \times 10^8\) cm/s\(^2\) is the Doppler acceleration. The length of the new Zeeman slower has also been increased from 21 cm to 35 cm. These two factors combine to increase the maximum velocity which can be slowed from \(\sim 500\) m/s to \(\sim 850\) m/s. For considerably more detail on the design and manufacture of the new Zeeman slower see Ref. [15].

To operate the Zeeman slower properly, two DC current supplies are needed. One drives the main coils of the tapered solenoid at 10 A and the other drives the trim
Figure 2.4 Measured magnetic field along the axis of the Zeeman slower. This measurement was performed with the main coils energized at 10 A and the trim coils at 2 A. Graph courtesy of K. Strecker and D. Homan.

coils at 2 A. A graph of the measured axial magnetic field along the Zeeman slower axis is shown in Fig. 2.4. Within the context of this graph, the atoms move from left to right, or from low $z$ to high $z$. The sharp cutoff of the magnetic field at the end of the slower quickly decouples the atoms from the light field as they exit. This helps maintain a narrow longitudinal velocity distribution which is critical for the slow atom deflection stage described below. Previous theoretical studies indicated that the load rate of atoms into the trap is maximized when the mean velocity of the slowed atoms is between 40 m/s and 70 m/s [11]. In practice, the load rate is maximized by slightly tweaking the frequency of the Zeeman slower laser which alters the distribution of velocities emerging from the slower.

The slowing efficiency depends very sensitively on the polarization of the laser beam. This is mostly due to the fact that if the polarization is not optimized, the atoms will be optically pumped into internal states which no longer couple to the light field. For the increasing tapered solenoid used here, the optimum polarization is circular, and in particular $\sigma^-$. The polarization is controlled using a combination of a half-wave ($\lambda/2$) plate and quarter-wave ($\lambda/4$) plate in order to compensate for the birefringence of the sapphire window through which the laser beam passes into the
vacuum chamber (see below). The polarization can be analyzed by bouncing the laser beam out of the vacuum chamber using the mirror mounted on the back side of the atomic beam block in the source cube near the oven. The absorption of the sapphire window can be monitored in the same way and should be no more than \(~20\%\).*

There is another laser beam (Aspect beam) directed parallel to the main slowing laser beam which has much less intensity and is at a difference frequency. The Aspect beam typically has a total power of \(~10-20\) mW versus the 120-150 mW for the main slowing laser. Its frequency is blue detuned from the main slowing laser by \(~890\) MHz (see Table 2.2 below). The purpose of this laser is to provide some repumping action for the atoms as they are precooled before entering the body of the Zeeman slower. The Aspect beam is generated by recycling the undeflected laser beam emerging from the Zeeman slower AO and redirecting it back through the AO along the main (deflected) slowing beam. Typically, the Zeeman slower performance is enhanced by 20-50% when the Aspect beam is applied compared to when it is absent. Care must be taken when optimizing the Zeeman slower efficiency, however, since the optimum frequency for the main slowing laser is slightly different depending on whether the Aspect beam is applied or not. Therefore, if the main slowing frequency has been optimized for no Aspect beam, application of the Aspect beam will often degrade the overall performance of the Zeeman slower unless the main slowing frequency is adjusted properly.

**Slow atom deflection**

Only about 1% of the atoms exiting the oven are slow enough to be longitudinally cooled using the Zeeman slower described above. Consequently, the beam emitted from the Zeeman slower is composed of a small low-velocity fraction together with a fast-atom background. The two components of the beam must be separated so

*Be sure to account for the \(~85\%\) reflectivity of the aluminum mirror and the \(~8\%\) loss from the large glass viewport in the source chamber.
that the fast atoms do not enter the trapping region. Otherwise, the fast atoms will collide with those that are trapped, ejecting them and reducing the steady state number. The separation is accomplished using a cylindrically focussed laser beam which deflects the trajectories of the slow atoms by 30° as shown in Fig. 2.5.

The fast atoms do not interact with the deflection laser for sufficient time and their paths are not substantially altered. Eventually the fast atoms hit the window through which the Zeeman slower laser beam passes into the vacuum chamber. A thin film of lithium will build up on this window rather quickly if the atomic beam goes unblocked for long periods of time. To counteract this, a sapphire window is used to inhibit the chemical damage which lithium vapor inflicts on glass. The window is also heated to a temperature of ~350 °C in order to help break any weak chemical bonds between the sapphire and the lithium.
The results of a model calculation for the deflection laser system have shown that the deflection angle depends sensitively on the longitudinal velocity of the atoms [11]. If the velocity is between 60 m/s and 100 m/s, the deflection angle only varies by \(~15\%\) from 30\(^\circ\). The deflection angle increases very rapidly, however, for smaller velocities, approaching 80\(^\circ\) for 20 m/s. It is critical, therefore, for the Zeeman slower to produce a narrow velocity band which can be tuned to \(~70\) m/s. The importance of the sharp magnetic field cutoff at the Zeeman slower exit now becomes evident.

**Optical molasses**

After being deflected, the atom beam is collimated to help reduce any angular dispersion caused by the deflection laser, and to account for the transverse heating which always accompanies Zeeman slowing. This is accomplished with a two-dimensional optical molasses which consists of a pair of counterpropagating laser beams in the horizontal plane and another (orthogonal) pair in the vertical plane. The axis for the horizontal pair is perpendicular to the deflected atomic beam as indicated in Fig. 2.1. The lasers used for the 2-D molasses are red-detuned from the atomic resonance by about 10 MHz. In this configuration, the atomic velocity is reduced along any direction transverse to the atomic propagation axis, producing a well collimated beam.

The collimated beam travels down a narrow tube toward the trap vacuum chamber. Along the way, the atoms are optically pumped into the appropriate internal state for magnetic trapping \((F = 2, m_F = 2)\) using a pair of \(\sigma^+\)-polarized laser beams and a pair of small electromagnetic coils. When the coils are energized with \(~0.75\) A, they produce a magnetic field that is sufficient to define a proper quantization axis which is maintained all the way up to the magnetic trap.

When the atoms enter the trapping region, they encounter a potential hill produced by the interaction of their internal magnetic moment with the trapping field.
Figure 2.6  Trap field along the loading and bias axes. The circles are the measured field along the \( y = z \) (loading) axis and the solid line is the calculated field along that same axis. The dashed line is the calculated field along the \( z \) (bias) axis. In the experiment, atoms are loaded from the right and are damped into the 130 G (8.7 mK) deep well by three-dimensional optical molasses. Graph reproduced from Ref. [9].

The atoms are loaded along a saddle-point in the trap field as shown in Fig. 2.6. A three dimensional optical molasses is established at the trap center with three pairs of counterpropagating laser beams. The laser beams all have a diameter of \( \sim 2 \) cm and are aligned so that they intersect only in the region of the shallow potential well. Therefore, as the atoms reach the top of the potential hill, they encounter a damping force which reduces the average velocity of the atoms to \( \sim 1 \) m/s and allows them to be trapped.

The trap loading technique described here usually saturates at \( \sim 5 \times 10^4 \) atoms in a few seconds. This number is most probably limited by optical pumping into untrapped spin states caused by the molasses beams. The optical pumping rate is minimized by optimizing the polarization of the molasses lasers using independent \( \lambda/2 \)-plates for each beam. The optimum polarizations are described in Ref. [10], and Table 2.1 gives the rotation angle of each retarder along with a description of its position on the trap apparatus.
<table>
<thead>
<tr>
<th>position on trap</th>
<th>rotation angle</th>
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<tr>
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<td>quartz</td>
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<tr>
<td>above fluorescence camera</td>
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<td>below ionization gauge</td>
<td>135°</td>
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</tr>
<tr>
<td>above blank flange</td>
<td>126°</td>
<td>mica</td>
</tr>
</tbody>
</table>

Table 2.1 Wave plate settings for trap molasses beams. The waveplates are grouped by counterpropagating pairs of laser beams and their positions are given relative to the closest distinguishable element of the trap apparatus.

**Frequencies**

The trap loading process requires laser beams at three different frequencies, which are derived from two ring dye lasers. One laser (Spectra Physics 380D) provides the molasses beams used for trapping, while the other (Coherent 699) gives the Zeeman slower and deflection/collimation beams. The frequency of the laser is derived from a lithium heat pipe using Doppler-free saturated absorption spectroscopy. The Zeeman/deflection/collimation laser is locked to the heat pipe using a microwave spectroscopy feedback loop, and the trapping laser is referenced to the first by a computer-controlled heterodyne feedback loop. These locking systems are described in Appendix D of Ref. [16]. The frequency accuracy of both lasers using these feedback systems is better than 2 MHz, which is smaller than the 6 MHz natural linewidth of the relevant $2S \leftrightarrow 2P$ optical transition in lithium. Table 2.2 gives the frequency detunings of the trapping and loading beams relative to the $^7\text{Li} \ (2S_{1/2}, F = 2) \leftrightarrow 2P_{3/2}$ transition as measured by the zero crossing in the heat pipe lock dispersion curve.

**2.1.3 Cooling**

The atoms are loaded into the trap at a temperature of $\sim 0.5$ mK using relatively intense laser beams, with $I \sim 40 \text{ mW/cm}^2$ per beam. In order to obtain BEC, the temperature must be reduced further to $\sim 1 \mu\text{K}$, or another factor of 500. This
<table>
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<tr>
<td>optical pumping</td>
<td>+801</td>
<td>wavemeter</td>
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<tr>
<td>molasses</td>
<td>+1325</td>
<td>“pkfreq”</td>
</tr>
</tbody>
</table>

Table 2.2 Frequencies of trapping and loading lasers relative to the $^7\text{Li}$ ($2S_{1/2}, F = 2 \leftrightarrow 2P_{3/2}$ transition. The expressions in quotations are the ACK designations corresponding to these frequencies.

is accomplished in two stages. First, a short Doppler cooling pulse is applied to the atoms and second, and most importantly, the atoms are evaporatively cooled to quantum degeneracy.

**Doppler cooling**

After loading, the intensity of the molasses beams are reduced by a factor of $\sim 100$ for 10 ms, and then ramped off. This cools the atoms to 250 $\mu$K, near the Doppler limit of 140 $\mu$K. The optical density of the cloud is then 10 or greater which is probably responsible for the inability to achieve the actual Doppler temperature limit.

Experimentally, the laser intensity is lowered by reducing the amount of microwave power coupled into the crystal of an acousto-optic modulator (AO). The trap molasses beams are derived from the optical sideband of this AO, and reducing the drive power, therefore, reduces the diffraction efficiency accordingly. The diffracted beam is subsequently coupled into an optical fiber in order to pipe the laser light from one side of the laboratory to the other. The molasses beams can be extinguished completely by closing a mechanical shutter at the output of the fiber.
Evaporative cooling

Evaporative cooling has been generally described in [17], and our implementation of it in [18], so it is summarized only briefly here. Evaporative cooling requires a mechanism to selectively remove atoms from the trap based on their energy. In particular, the most energetic atoms, or the "hottest" ones, must be removed while leaving the the colder ones in the trap. When this is done, the average energy of atoms in the trap decreases, and if the gas is allowed to equilibrate through elastic collisions between the atoms, the temperature is reduced. This cycle of removing the hot atoms and collisional redistribution can be repeated over and over, and can, in fact be done continuously at an appropriate rate. This process has been used in every successful BEC experiment to date.

Experimentally, we eject the hot atoms from the trap by driving a spatially dependent microwave transition which flips the electronic spin of the atoms. This is shown schematically in Fig. 2.7. When a hot atom oscillates to large displacement from the trap center, it becomes resonant with the microwave field. The frequency $\nu_{RF}$ of this field is tuned to resonance between the trapping potential and anti-trapping potential corresponding to an electronic spin-up atom and spin-down atom, respectively. In this way, $\nu_{RF}$ defines the depth of the trap $E_T$.

The trap depth is typically set to be 2-3 times higher than the average energy of the atoms in the cloud, where $\langle E \rangle = 3k_B T$ with $k_B$ the Boltzmann constant and $T$ the temperature. When the microwave field is applied, $\langle E \rangle$ immediately decreases, and as elastic collisions attempt to produce more atoms at high energy, cooling continues. As $\langle E \rangle$ decreases, $E_T$ is lowered to keep pace. If $E_T$ is reduced too quickly, too many atoms are lost for the amount of cooling produced, but if $E_T$ changes too slowly, atoms are lost due to inelastic collisions and collisions with room temperature atoms coming from the vacuum chamber walls.

The atoms are held in the ($F = 2$, $m_F = 2$) doubly spin-polarized hyperfine state,
Figure 2.7  Schematic diagram of evaporative cooling. The upper and lower curves show the potentials for a spin-up and a spin-down atom respectively. The trapped atoms at high energy become resonant with a microwave field of frequency $\nu_{RF}$ when they oscillate out to large displacement from the trap center. The cold atoms never achieve sufficient displacement and do not make the transition.

and are driven to the ($F = 1, m_F = 1$) anti-trapped state. The spin-flip frequency at the center of the trap is $\nu_{RF} = 3.4$ GHz as determined by the magnetic field of the trap bottom ($\sim 10^3$ G). The microwave field is obtained from a digital frequency synthesizer, and applied to a 2-cm-diameter loop antenna placed $\sim 2.5$ cm from the trap center. Roughly 100 mW of microwave power is applied to the antenna, of which an estimated half is coupled into the trap chamber. The frequency $\nu_{RF}$ is initially 70 MHz above the trap-bottom resonance, and is gradually reduced. In our implementation, BEC is achieved at a temperature of $\sim 700$ nK with $\sim 10^6$ total atoms in the trap after approximately one and a half minutes of cooling. We use an optimized trajectory for the rate of change of $\nu_{RF}$ calculated by Cass Sackett [16],
which is important both because it increases the robustness of the evaporative cooling process and decreases the required cooling time.

2.2 Detection

Once BEC is produced, it is observed by imaging the atom cloud on a charge-coupled device (CCD) camera. The resultant two-dimensional images are fit to appropriate distribution functions in order to determine the number of atoms $N$, the temperature $T$ and the condensate number $N_0$. There are several experimental difficulties with this procedure. First, the atom cloud is rather small and the condensate would fit into a box roughly 6 $\mu$m on a side. It is therefore very tricky to obtain adequate imaging resolution especially since the cloud is about 15 cm away from the nearest vacuum viewport. Additionally, for the experiments described in this thesis, the gas is dynamically evolving due to the effect of condensate collapse and its energy distribution is therefore not well described by an equilibrium Bose-Einstein distribution function.

2.2.1 Phase-contrast imaging

The atom cloud and condensate are imaged using a technique called phase-contrast polarization imaging (PCPI) which is described in detail in Refs. [12, 10]. The basic idea is that the atoms in the trap have a substantial index of refraction so that a laser beam passing through them will acquire a phase shift in much the same way that a laser passing through a piece of glass does. It is fairly intuitive that the phase shift acquired by the light which is scattered by the atoms will increase with increasing density, so the variation in phase of the scattered light maps out the density distribution of the atoms in the trap. This phase shift can cause distortions in the image, since all real imaging systems have inherent aberrations*, but otherwise there

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*This effect is what enabled the first detection of BEC in lithium [4].
is no real way to observe the absolute phase. On the other hand, if the acquired phase is compared with some reference phase, the density map becomes manifest.

This phase comparison can be accomplished in a variety of ways [19, 20]. The technique used in our experiments relies on the fact that atoms in a large magnetic field are birefringent, meaning that the phase shift is accompanied by a corresponding change in the polarization of the scattered light. For our experiments, the probe laser frequency is tuned near a particular transition \((m_J = 1/2, m_I = 3/2) \leftrightarrow (m_J = 3/2, m_I = 3/2)\) which couples only to \(\sigma^+\)-polarized light. The quantization axis implied by the \(\sigma^+\) designation is, of course, provided by the direction of the trap magnetic bias field. Due to geometrical constraints in our experiment, the probe laser cannot propagate along the bias axis and therefore cannot be purely \(\sigma^+\). The maximum projection onto the \(\sigma^+\) axis is obtained with linearly polarized light [10]. The scattered light is therefore elliptically polarized and a linear polarizer can be used to project the polarization of both the transmitted and scattered light onto a common axis. When the scattered and transmitted light fields recombine to form an image, they interfere, providing an intensity modulation sensitive to the initial phase shift.

A schematic diagram of the imaging system is shown in Fig. 2.8. A probe laser is directed through the cloud and a lens system, onto a CCD camera. The lens system consists of two achromatic doublets which relay an image of the cloud to a convenient location away from the crowded portion of the trap apparatus, a custom corrective lens to reduce spherical aberrations, and a microscope which magnifies the image onto the CCD\(^*\). A vacuum viewport is in front of all the lenses, and a polarizer between the doublets is used for phase contrast imaging.

Although phase-contrast imaging has been used for (nearly) nondestructive measurements of large condensates [21], a few incoherent photons are always scattered,\(^*\)

\(^*\)In general, the microscope cannot be placed near the atom cloud, whether inside or outside the vacuum chamber, because the trap yoke and magnets get in the way.
Figure 2.8  Schematic diagram of the imaging system, showing: the atom cloud A; vacuum viewport B; achromatic doublets C and E; phase-contrast imaging polarizer D; correction lens F; primary image G; microscope objective H; and CCD camera J. The red shaded area represents the probe beam and the orange area is the coherently scattered light. Figure reproduced from Ref. [16].

and these heat the gas. As the phase-contrast signal is proportional to the number of scattered photons, achieving sufficient sensitivity to small condensates, such as those studied here, results in excessive heating and destruction of the condensate [12].

Specifications

The general specifications and performance of this imaging system are given in App. A of Ref. [16]. However, there have been a few changes since that accounting which need to be documented. The main difference is that a new CCD camera is being used which has improved performance compared to the previous one. The new camera is a Photometrics CE300 system with an air-cooled CH350A camera head. This new system has better quantum efficiency and has a larger pixel size (24 μm vs. 19 μm). In order to account for the larger pixel size, the total magnification of the system is increased. This is accomplished by using a newly fabricated camera box which allows for different tube lens combinations to be used in the microscope assembly. Using a test target placed in front of the microscope, the magnification of just the microscope assembly was measured to be either 3.76 or 15.47 depending on which tube lens system is used. These values must be multiplied by the magnification of
the relay/corrective lens system which was measured in February of 1998 to be 1.13*. This gives a total magnification of 4.25 or 17.5. It should be noted that all data in this thesis were obtained with the 17.5 magnification microscope.

2.2.2 Non-equilibrium fit

Once the two-dimensional images are obtained, the center of the image is identified and the signal is averaged in progressively larger elliptical annuli with an aspect ratio and tilt angle given by the trap geometry. This angle-averaging greatly reduces the shot noise associated with the image acquisition and essentially reduces the two-dimensional images to one dimensional ones. In order to extract \( N, T \), and \( N_0 \) from these images, they must be fit to an appropriate model distribution. Because the gas is not in thermal equilibrium, due to the growth and collapse dynamics discussed in Chap. 5, the experimental images are not well fit by an equilibrium Bose-Einstein distribution function. This is demonstrated in Fig. 2.9(a) which shows the angle averaged data of a particular atom cloud along with a best fit equilibrium distribution. Clearly, this fitting function is not appropriate for the data.

The appropriate distribution function to describe the spatial images was developed by Cass Sackett as part of his Ph.D. work [7, 16]. He used a computer simulation based on solutions to the quantum Boltzmann equation to describe the kinetics of BEC formation and evaporative cooling. The model follows the evolution of atom populations among the energy levels in the trap using known elastic and inelastic collision rates. At any time during the simulation, the energy distribution function can be obtained. These model distributions indicate that when the gas is cooled to quantum degeneracy, it quickly reaches a state of "local equilibrium" in the sense that the populations of nearby energy levels bear nearly their equilibrium relationships. As a consequence, the observed nonequilibrium distributions can be parameterized

*See green binder marked "IMAGING" near BEC apparatus.
Figure 2.9  Comparison of equilibrium and nonequilibrium fitting functions. (a) Circles show angle averaged data and solid line is the best fit using an equilibrium Bose-Einstein distribution function giving $N = 1.03 \times 10^5$ atoms, $T = 304$ nK, and $N_0 = 1996$. (b) Same as (a) but using a nonequilibrium fitting function giving $N = 9.04 \times 10^4$ atoms, $T = 223$ nK, and $N_0 = 1061$.

by

$$f_{NEQ}(E) = \frac{e^{\beta(\mu_1 - \mu_2)}}{e^{\beta(E - \mu_2)} - 1} \equiv \frac{A}{e^{\beta(E - \mu_2)} - 1},$$

(2.1)

where $\beta = 1/k_B T$, $E$ is the energy parameter and $\mu_{1,2}$ are chemical potentials. Note that $\mu_2$ is an effective chemical potential for low-energy atoms near the condensate and $\mu_1$ for those atoms at high energy. The non-equilibrium form resembles that of an equilibrium distribution function

$$f_{EQ}(E) = \frac{1}{e^{\beta(E - \mu)} - 1},$$

(2.2)

when $A \equiv 1$ and $\mu_2 \equiv \mu$. The nonequilibrium distribution function of Eqn. 2.1, in conjunction with the known geometry of the trapping potential, is used to fit all the
data shown in this thesis. The goodness of fit is demonstrated in Fig. 2.9(b) which uses the same angle averaged data from Fig. 2.9(a) but with the nonequilibrium fit.

These two fitting functions yield completely different fitting parameters as given in the figure caption. The accuracy of the nonequilibrium fit is checked by generating mock spatial distributions from the quantum Boltzmann simulation and then using the same fitting routines as are used for the data. Since the model distributions are generated with well known values for \( N, T \) and \( N_0 \), a direct comparison can be made between the fitted values for these parameters and the exact ones. In general, the agreement is quite good although a correlation between the total number \( N \) and condensate number \( N_0 \) is observed [16].

2.3 Photoassociation

The experiments reported in the rest of this thesis involve using a spectroscopy technique called photoassociation to probe the BEC. Single-photon photoassociation is described in Chap. 3 and Raman photoassociation in Chap. 4. In both cases, more lasers are needed and their frequencies must be controlled precisely. Luckily, the optical power requirements for these additional lasers are usually not very stringent, so low-power semiconductor lasers, or diode lasers, will suffice.

A schematic diagram of the optical setup for Raman photoassociation is shown in Fig. 2.10. There are two lasers shown, the master and the slave, and three feedback systems to control their frequencies, the Fabry-Perot lock (FP lock), the scanning etalon lock (SEL), and the phase-lock. The FP lock maintains the master laser at a frequency corresponding to a particular peak of the FP2 cavity. The SEL, in turn, maintains the master laser frequency relative to the frequency of a reference laser by controlling the length of FP2. Finally, the phase-lock maintains the slave laser frequency relative to the master laser frequency. An additional FP cavity, FP1, is used to monitor the frequency spectrum of the slave laser. The slave laser, FP1 and
phase-lock are eliminated from this diagram for single-photon photoassociation.

External cavity stabilized diode lasers (ECDL) are now so ubiquitous, they will not be described in any detail here. The ECDLs used for the photoassociation experiments produce about 10 mW of single mode laser light with piecewise continuous tunability over a range of wavelengths from about 665 nm to 680 nm. In principle, ECDLs can be purchased which can tune continuously over a significant fraction of this range. The home-made cavities we use, however, are not optimally engineered and they hop
cavity modes when tuned more than about 5 GHz. As the cavity modes are about 5 GHz apart, this is not usually a big problem. The ECDL frequency is scanned by changing the diode current and the cavity length synchronously. The latter is accomplished by tilting the cavity grating. The grating is mounted on a kinematic optical mount to facilitate course scanning of the laser and a piezoelectric crystal is embedded behind the horizontal adjustment screw to allow for fine tuning.

2.3.1 Fabry-Perot lock

The free-run linewidth of either diode laser is \( \sim 10 \) MHz, which is comparable to the 12 MHz natural linewidth of the molecular resonances probed during photoassociation. Most of this linewidth is due to acoustical jitter caused by vibrations in the floor and walls of the laboratory which are transmitted to the laser through the legs of the optical table. In order to reduce this acoustical noise, the master laser frequency is locked to a particular transmission peak of a stable FP interferometer, FP2, as described below.

When the length of FP2 is scanned using a piezoelectric crystal, transmission peaks corresponding to the master laser frequency appear at regular intervals given by the free-spectral-range (FSR) of the cavity. The frequency width of each transmission peak is given by the cavity finesse \( f \), in combination with the FSR as \( w = \text{FSR}/f \). For the cavity FP2, \( \text{FSR} = 3 \) GHz and \( f = 80 \), so \( w \approx 40 \) MHz. Therefore, the relatively steep slope along one side of a transmission peak can be used as a sensitive frequency discriminator.

The transmission peak is measured by a low-noise photodiode, and subsequently amplified to a few volts peak-to-peak. A voltage offset is applied to center the peak around zero volts and one side of the peak is then used as the error signal in a feedback circuit. The circuit provides feedback to the master laser via a servo which controls the diode current and one which controls the voltage across the piezoelectric
crystal which scans the external cavity grating angle. The feedback bandwidth for
the current servo is $\sim50$ kHz (to within a factor of 2) and the grating servo has
a bandwidth of $\sim10$ Hz. Using this locking system, the error signal is reduced to
$\sim1/20$th of the transmission peak height corresponding to a frequency jitter of $\sim1$
MHz. This agrees with a direct measurement of the frequency jitter using a high
precision optical spectrum analyzer. When locked, the length of FP2 can be scanned
and the master laser frequency tracks accordingly.

2.3.2 Scanning-etalon lock

As mentioned above in Sec. 2.1.2, the frequency of the laser used for loading atoms
into the trap is locked absolutely to the atomic resonance frequency. Unfortunately,
the frequency detunings of the molecular resonances probed with photoassociation are
too large relative to the atomic resonance to directly utilize such a convenient locking
procedure. Instead, the loading laser beam is directed into a scanning FP cavity with
an FSR of 750 MHz. The loading laser provides a relative frequency reference for
the master laser, which is also directed into the cavity. As the cavity scans over 1
FSR, a peak corresponding to each laser is transmitted and the frequency between
them, modulo the FSR, is measured. A lock circuit provides slow feedback to the
piezoelectric crystal that controls the length of FP2, and the frequency of the master
laser tracks accordingly.

To measure the frequency difference between the master and reference lasers,
they are first combined on a polarizing beam splitter (PBS) which either transmits or
reflects the light according to its polarization. Therefore, each laser in the combined
beam is linearly, and orthogonally, polarized. After being transmitted through the
FP cavity, these polarizations are analyzed using a second PBS sending each separate
laser beam to a corresponding photodiode. Each time one of the lasers is transmitted
through the FP cavity, the ramp voltage corresponding to that particular cavity
length is measured using a peak detector and a sample-and-hold electronic chip. For a linear scan, the difference in ramp voltage gives the relative frequency difference between the two lasers. The feedback bandwidth for this system can be no greater than the 100 Hz ramp repetition rate. The SEL maintains the frequency separation between the reference and master lasers to a precision of \( \sim 3 \) MHz.

The long-time stability of the SEL has been observed to depend heavily on the relative frequency separation between the master and reference lasers. When the laser frequencies are far separated along the ramp, their actual frequency separation (as measured in the optical spectrum analyzer) is observed to shift when the SEL cavity drifts causing both peaks to be offset to higher (or lower) ramp voltages. This effect is thought to originate from a nonlinear response of the SEL cavity piezoelectric crystal to actual ramp voltage (it looks like the ramp voltage is highly linear). When the two SEL transmission peaks corresponding to the master and slave lasers are made to overlap, this effect is minimized. In order to facilitate the overlap of transmission peaks, while allowing for arbitrary relative frequency separations, an AO has been installed in the reference laser beam path in the SEL optical setup. It would also be a good idea to further insulate the SEL cavity to minimize the temperature variations which cause the drifts in the first place. In practice, this effect is compensated for by continually monitoring the laser difference frequency by coupling both lasers into an optical fiber whose output is directly coupled into the optical spectrum analyzer.

2.3.3 Phase-lock

The phase-lock is essentially an ultrafast optical heterodyne detector and lock. As shown in Fig. 2.10, the master and slave diode laser beams are combined on a beamsplitter (BS), and directed onto a high bandwidth photodetector (PD). The PD measures the interference between the two lasers as a beatnote with frequency \( \Delta \nu \). After being amplified, the beatnote is mixed with the output of a microwave source in
order to reduce its frequency into the 10s of MHz regime. This intermediate frequency (IF) is then sent to an electronic feedback circuit which measures the relative phase between the IF and a local oscillator (LO). The electronics supply feedback to the slave laser via a servo which controls the diode current and another which controls the tilt angle of the external cavity grating. The LO and microwave source frequencies determine the value of Δν.

The performance specifications for the phase-lock are given in App. A along with a more detailed description of the operation principles. The main performance specification shown there is that the relative frequency between the two lasers Δν can be maintained to an absolute precision of better than 1 Hz. This is remarkable considering that for the experiments described in the chapters to follow, Δν ~ 12 GHz, so the precision is better than 1 part in 10¹⁰.
Chapter 3
Photoassociation

In this Chapter, the process of single-photon photoassociative spectroscopy will be described. When I came into the lab in 1994, much of the work in progress was related to this topic which resulted in several very nice publications. In those studies, the gas was trapped in a magneto-optical trap (MOT) at temperatures of \( \sim 1 \) mK. The main thrust of that work was to map out electronically excited molecular potentials [22, 23] and to determine the atomic excited-state lifetime [24, 25]. Additionally, using this single-photon technique, the singlet scattering length of ground-state \( ^7\text{Li} \) atoms was measured [26]. Using the two-photon photoassociation technique described in Chap. 4, the triplet scattering lengths of ground-state \( ^7\text{Li} \) and \( ^6\text{Li} \) atoms were determined as well [27, 28]. Although I participated in some of these studies, this huge body of work forms the bulk of the Masters [29] and Ph.D. [30] theses of Eric Abraham as well as the Masters thesis [31] of Ian McAlexander. Here, I will concentrate on the conceptually simple photoassociation experiments for quantum degenerate conditions which have not been previously reported. In particular, this chapter will include our measurement of the light-induced frequency shift predicted in Refs.[32, 33] for the \( v = 69 \) level within the triplet excited-state potential of \( ^7\text{Li} \). The precise measurement of the binding energies for the \( v = 58, \ v = 69, \) and \( v = 72 \) levels using photoassociative spectroscopy is reported in App. B.

3.1 Laser-assisted collisions

A schematic diagram of single-photon photoassociation is shown in Fig. 3.1. The Born-Oppenheimer potentials* are labelled appropriately for the \( ^7\text{Li} \) states of interest.

*In the Born-Oppenheimer approximation, the atomic nuclei are assumed to adiabatically follow the potentials established by the electronic clouds. Therefore, the horizontal axis is actually the internuclear separation.
in the permanent magnet trap. A drive laser of frequency $\omega_1$ is tuned near resonance

![Energy Level Diagram]

**Figure 3.1** Relevant molecular potentials and energy levels for single-photon photoassociation. The upper potential dissociates to a $2S_{1/2}^1$ and a $2P_{1/2}$ atom while the lower potential dissociates to two $2S_{1/2}^1$ atoms. The spontaneous emission rates $\gamma_b$ and $\gamma_f$ are to bound and free states, respectively. The binding energy is measured relative to the dissociation energy which is indicated by the dashed line. The detuning of the drive laser $\Delta$ is defined to be negative if the laser frequency $\omega_1$ is below the resonance energy of vibrational level $v$.

between the colliding state of two trapped, ground-state atoms and a vibrational level $\nu$ in the excited-state molecular potential. A vibrationally and electronically excited molecule may then form and subsequently spontaneously decay, most probably into a pair of hot atoms or possibly into a ground-state molecule, resulting in a detectable reduction of trapped atoms.

Photoassociation is often referred to as a laser-assisted collision process since in a classical sense, the atoms must approach each other sufficiently in order to be
resonantly excited into the upper vibrational level. This is a binary process since the potentials shown in Fig. 3.1 are two-body potentials. At ultralow temperature $T$, the deBroglie wavelength $\Lambda = h/\sqrt{2\pi mk_B T}$ describing the average quantum mechanical size of atoms with mass $m$ is much larger than the interaction range of the ground-state potential. At large interatomic distance, therefore, the two-body wave function is a regular oscillatory function $\phi_0(r) \propto \sin(kr)$ whose wavelength is $\lambda = 2\pi/k = h/\sqrt{mE}$, where $k = \frac{2\pi}{h} \sqrt{mE}$ is the relative momentum between the two atoms with relative kinetic energy $E$. In the region where the potential depth is comparable to the collision energy, the wave function will exhibit many rapid oscillations as the atoms accelerate towards each other, and then away from each other during a collision. Since the oscillation wavelength at large separation is much larger than in the region of the potential, the detailed behavior of the wave function in the potential region is unimportant to the description of the collision. Rather, the collision can be described by a simple phase shift $\delta$ to the long range oscillatory function, $\phi_0(r) \rightarrow \sin(kr + \delta)$. If $\delta > 0$, the long-range oscillations are shifted towards the interatomic origin and the atoms feel a net attraction for each other. The magnitude of $\delta$ (modulo $\pi$) determines the strength of this attraction. For $\delta < 0$, the situation is reversed and the atoms feel a net repulsion.

It is traditional to use a parameter called the $s$-wave scattering length $a$ to describe the collision, rather than $\delta$. These two parameters are related as $a \equiv \lim_{k \to 0} \frac{-\tan(\delta)}{k}$, which implies that $\delta \approx -ka$. Only $s$-wave collisions are considered because all higher-order partial wave contributions to the scattering matrix are frozen out at ultralow temperature. Physically, $a$ is the position where the asymptote to the long-range wavefunction intercepts the interatomic distance scale in Fig. 3.1. In the absence of an interaction potential, the intercept would fall at the origin and, intuitively, there is no net effect on the long-range wave function. If $a < 0$, corresponding to $\delta > 0$, the net interactions are attractive. Again, the magnitude of $a$ gives the
interaction strength. Substituting for $\delta$ shows that the free atomic scattering wave function $\phi_0(r) \sim \sin(k(r-a))$ which further simplifies to $\phi_0(r) \sim k(r-a)$ in the limit of $k \to 0$, $(T \to 0)$, which is typical of the experiments reported here.

### 3.2 Rate equation

The photoassociation rate is proportional to the square of the overlap integral $\langle \phi_0|\psi_v \rangle^2$ between the scattering state of two free atoms $\phi_0$ and the electronically excited bound state $\psi_v$. The excited state wave function $\psi_v$ is peaked at the value of interatomic distance $R$ which corresponds to the outer turning point $R_t$ of the given vibrational level $v$, since the two nuclei spend most of their time at that separation as the vibrational motion reverses. In addition, $\psi_v$ has $v-1$ other nodes whose total combined area is usually small compared to the one at $R_t$. Finally, for the experiments considered here, $\Lambda \gg R_t$, so the bulk of the contribution to $\langle \phi_0|\psi_v \rangle$ comes from the region near $R_t$. Therefore, the progression of values for $\langle \phi_0|\psi_v \rangle^2$ as a function of $v$ will map out the shape of $\phi_0$. This was clearly demonstrated in Ref. [26] where the photoassociation signal strength was observed to vanish when $R_t \sim a$. *

The molecular selection rules for the transition indicated in Fig. 3.1 are dictated by the fact that the total electronic spin $\vec{S}$ decouples from both the electronic orbital angular momentum $\vec{L}$ and the total nuclear spin $\vec{I}$ because the binding energy of all vibrational levels of interest is much larger than either the 10 GHz fine-structure splitting of the $2P$ atomic state or any hyperfine interaction. Since only $\vec{L}$ is coupled to the light field, $\vec{S}$ and $\vec{I}$ do not change during the photoassociation process. Therefore, the selection rules for the total spin $\vec{G} = \vec{S} + \vec{I}$, are $\Delta \vec{G} = 0$ and $\Delta M_G = 0$ [23]. Since both the ground state and excited molecular potentials are $\Sigma$ states, corresponding to zero projection of $\vec{L}$ onto the internuclear axis, there is no change in the projection of $\vec{L}$, and the transition dipole is oriented along the trap magnetic field.

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*The photoassociation signal strength can vanish for $R_t \neq a$ if another node in $\phi_0$ falls at $R_t$. For $a < 0$, this only happens for relatively deep vibrational levels.
bias direction, (0,0,1), so there is no Zeeman shift in the transition energy. Geometric constraints, however, require the photoassociation laser beam to propagate along the (1,1,1) direction, and a maximum of 2/3 of the intensity couples to the transition.

The overlap integral can be incorporated into a dimensionless quantity, which takes the form

\[ A_v \equiv -\xi \langle \phi_0 | \psi_v \rangle^2 \frac{m \Gamma_a}{8\pi \hbar a}, \]  

(3.1)

where \( \xi \) is the polarization overlap between the laser polarization and the transition dipole moment* discussed above, and \( \Gamma_a = 2\pi \times 5.9 \text{ MHz} \) is the atomic resonance linewidth. The dimensions of the free and bound-state wave functions are \( \phi_0 \equiv 1 \) and \( \psi_v \equiv \text{length}^{-3/2} \), respectively, so that \( \langle \phi_0 | \psi_v \rangle^2 \) has dimensions of volume. The expression in Eqn. 3.1 was developed by Cass Sackett in his Ph.D. thesis [16] and is based on the theory developed in Ref. [32]. It can be used to determine the relative photoassociation strength for different vibrational levels. Accurate values for \( \langle \phi_0 | \psi_v \rangle \) for the triplet-triplet transition indicated in Fig. 3.1 have been obtained by R. Côté by numerical solution of the Schrödinger equation, although care must be taken to ensure proper normalization of the wave functions†. The resulting values of \( A_v \) are plotted in Fig. 3.2 for the most experimentally accessible range of \( v \). The sharp local minima occur when \( R_v \) falls near a node in \( \phi_0 \).

In order for a photoassociation transition to occur, the atoms must approach each other sufficiently such that their inter-nuclear distance is comparable to the outer turning point \( R_v \) of level \( v \), as described above. This separation is small compared to the average inter-particle spacing in a dilute gas. The photoassociation rate is therefore proportional to the number density of atoms \( n \) [32]:

\[ R_p = A_v \frac{8\pi \hbar n|a|}{m} \frac{\Omega^2_a}{\Delta^2 + \Gamma_a^2} = \xi \langle \phi_0 | \psi_v \rangle^2 n \Omega^2_a \frac{\Gamma_a}{\Delta^2 + \Gamma_a^2}, \]  

(3.2)

*For all experiments described, \( \xi = 2/3 \), unless otherwise noted.
†See Ref. [16] Pg. 127.
where $\Delta$ is the laser detuning from level $\nu$, the factor $\frac{\Omega_a^2 \Gamma_a \Gamma_{\alpha}}{\Delta^2 + \Gamma_a^2}$ gives the Lorentzian lineshape of the molecular resonance of width $\Gamma_m = 2\Gamma_a$, and $\Omega_a = dE_0$ is the on-resonance Rabi flopping frequency for the atomic transition with dipole moment $d$ driven by a light field with electric field amplitude $E_0$. In terms of quantities which are more convenient in the lab, $\Omega_a^2 = \frac{I}{I_{sat}} \Gamma_a^2$, where $I$ is the intensity of the drive laser and $I_{sat} = 5.1$ mW/cm$^2$ is the saturation intensity for the $2P$ state of lithium when the detuning from the atomic resonance is large compared to the fine and hyperfine structure. The on-resonance photoassociation rate $R_P$ is shown in Fig. 3.3 for an intensity $I = I_{sat}$ and a peak density $n = 10^{12}$ cm$^{-3}$, corresponding to the critical density for BEC at $T = 200$ nK.

Neither Eqn. 3.1 nor Eqn. 3.2 depends on the energy $E$ of the colliding pair of atoms*. At first, this may seem to contradict the results obtained by Bohn and Julienne [33] who explicitly show the stimulated absorption/emission rate generated by the photoassociation laser ($\Gamma$ in that paper) to vanish at $E = 0$. Although the photoassociation rate coefficient $K$ is proportional to $\Gamma$, it is also proportional to $1/k^2$.

*See Ref. [16] Pg. 127.
Figure 3.3  Photoassociation rate $R_P$ for various vibrational levels $v$ in the $1^3\Sigma_g^+$ potential. The calculated rates are for $I = I_{sat} = 5.1$ mW/cm$^2$ and a peak density $n = 10^{12}$ cm$^{-3}$.

where $k = \sqrt{2\mu E/h^2}$ is the wave number of the colliding pair of atoms with reduced mass $\mu$. Since $\Gamma \propto k^2$, the energy dependence drops out of the rate coefficient, consistent with Eqn. 3.2 above. Note also that the rate coefficient $K$ in Ref. [33] is independent of density $n$ and has units of cm$^3$/s. In order to obtain the actual photoassociation rate (per atom) $K$ must be multiplied by $n$. This was done in order to obtain Eqn. 3.2.

The rate $R_P$ gives the fractional change in the number of atoms $N$: $dN/N = -R_P dt$, where $\tau$ is the duration of the photoassociation pulse. This implies that

$$N = N(0)e^{-R_P \tau},$$

where $N(0)$ is the number of atoms at the start of the pulse. The measured photoassociation signal $1 - N(\tau)/N(0)$ will therefore saturate for $R_P \tau \gtrsim 1$. When thus saturated, changes in the laser detuning $\Delta$ will cause only small changes in the photoassociation signal. Consequently, large photoassociation signals will be broadened even if the transition is not optically saturated*.

*Ref. [33] calculates that for the $v = 64$ vibrational level, optical saturation occurs above intensities of $\sim 500$ W/cm$^2$. 
The condition $R_P \tau \gtrsim 1$ implies that the signal will saturate when $N(\tau)/N(0) \lesssim 1/e$. An additional mechanism, however, will cause broadening for somewhat smaller signal sizes. According to Eqn. 3.2, the photoassociation rate $R_P$ is linearly dependent on the density $n$, and hence on $N$. Differentiating Eqn. 3.3 then gives

$$\frac{dN}{d\tau} = N(0)e^{-R_P\tau(\kappa N)}$$

(3.4)

where $\kappa$ is defined such that $R_P \equiv \kappa N$. If the scattering process were independent of $N$ such that $R_P = \text{const.}$, then the decay of $N$ would be purely exponential in time. The $N$-dependence causes the decay to flatten more quickly compared to a pure exponential, and the signal effectively saturates at larger values of $N$. This broadens the resonance signal somewhat, in analogy with the large-signal saturation mechanism mentioned above, but at higher values of $N$. Both saturation mechanisms affect the signal width if the density $n$, and hence the number $N$, varies significantly during probing. If a minimally broadened lineshape is desired, the signal sizes should be kept to $\sim 20 - 25\%$.

### 3.3 Light-induced frequency shift

The photoassociation laser couples the scattering state $\phi_0$ and the bound state $\psi_n$ which leads to resonant loss of atoms from the trap as described above. Usually, such a laser-induced coupling also leads to the well-known AC Stark shift in the resonance energy, which is not, however, typically observed in single-photon spectroscopy. The unique situation offered by photoassociative spectroscopy, namely the coupling of the threshold continuum to a bound state, allows the energy shift to become manifest even in single-photon spectra. An explanation for this phenomenon is given below. Clearly, however, the shift must be understood in order to properly predict the photoassociation rate $R_P$ and other interesting quantities such as the magnitude of change the scattering length $a$ caused by the light-induced Feshbach resonance (see Chap. 6).
Figure 3.4 shows several resonance curves corresponding to different values of $I$ for the $v = 69$ vibrational level of the $1^3\Sigma_g^+$ potential. These data were obtained by first evaporating the trapped cloud of $^7$Li atoms to a temperature of \(~650\) nK with \(~10^9\) atoms. After evaporation, the atoms are held in the trap for a period of \(~5\) s in order to allow the gas to approach equilibrium. This procedure increases the reliability of fits to the imaged clouds. After the holding period, a single-photon photoassociation laser pulse is applied. After the pulse, and following a variable delay, the gas is subsequently imaged \textit{in situ} using the phase contrast technique described in Ref. [12] and in Chap. 2, in order to determine the number of remaining atoms $N$. The fitted values of $N$ are normalized to measurements taken in the same way but without the photoassociation pulse in order to account for drift in trap loading conditions. Typically, a sequence of three data points are bracketed with a pair of background points. The first and third data points are normalized to their respective
background points and the second data point is normalized to the mean of the two background points*.

As described in Chap. 2, the photoassociation light is derived from a low-power ($\sim10\text{ mW}$), grating-stabilized, ECDL. For the spectra shown in Fig. 3.4, however, an $\sim8\text{ mW}$ beam from the diode laser is injected into a tapered optical amplifier, providing $\sim300\text{ mW}$ of output power at the injected frequency. An acousto-optic modulator and a mechanical shutter are used to chop the amplified beam on and off. The beam is subsequently coupled into a single-mode optical fiber, reducing pointing jitter and intensity variation across the beam profile. The output of the fiber, limited to $\sim70\text{ mW}$, is focussed at the position of the atoms to a $1/e^2$ intensity radius of $\sim90\mu m$. The photoassociation laser beam is directed nearly parallel to the laser beam used for imaging the atom cloud, and is imaged in order to ensure spatial overlap with the atom cloud.

The data clearly demonstrate the increasing red-shift at larger values of $I$. In addition, the resonance widths are observed to be considerably broader than the natural linewidth, which for long-range molecular levels, such as $\nu = 69$, should be $\sim2\Gamma_\alpha$ [34], where $\Gamma_\alpha = 2\pi \times 5.9\text{ MHz}$ is the natural linewidth of the atomic $2P$ excited state of $^7\text{Li}$. There are several mechanisms which contribute to the broadening of the observed lineshapes. The relatively large depth of signal leads to the saturation broadening mechanisms discussed above. As described, these mechanisms are present even for low $I$ since the pulse duration is extended to maintain a constant signal size. Additionally, for the data shown, the FWHM of the atom distribution as measured on the camera was $\sim70\mu m$ while the Gaussian $1/e^2$ intensity radius of the laser beam was $\sim90\mu m$. Therefore, the intensity varied by as much as 45% over the FWHM of the atom cloud leading to a corresponding variation in the light shift. Finally, $\sim3$

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*If the bottom frequency drift is assumed to be linear, a slightly better method for normalizing would be to interpolate a line between the background points and normalize the data to the appropriate position on the line. This procedure was adopted for some of the two-photon photoassociation experiments described in the following chapters.
MHz fluctuations in $\omega_1$ which are too fast for the SEL to suppress, lead to laser-line broadening. The temperature of the gas is sufficiently low, however, that thermal broadening is negligible compared with $\Gamma_m$.

The observed resonance curves are sufficiently symmetrical to be fit reasonably well to a Lorentzian lineshape in order to locate the resonance center. Figure 3.5 shows the frequency shift of the measured resonance peaks as a function of $I$. These data are well fit by a line of slope $-245(10)$ kHz cm$^2$/W.

![Figure 3.5](image)

**Figure 3.5** Photoassociation frequency shift as a function of light intensity. The points correspond to the peaks of measured spectra obtained as described in the text, while the error bars indicate the uncertainty in determining the peak center. The line is a fit to these points giving a slope of $-245(10)$ kHz cm$^2$/W. The uncertainty in the light intensity is $\pm 5\%$.

The origin of the frequency redshift is explained in Ref. [33]. It arises from coupling the various threshold scattering states $\phi_0$ to the excited-state bound level $\nu$ and will be a generic feature of near-threshold resonant scattering. In particular, in the Fano theory for a bound state coupled to the continuum, the energy shift is proportional to the integral [35]

$$
\delta \epsilon \propto \int dE' \frac{V(E')^2}{E - E'},
$$

(3.5)

where $V(E')$ represents essentially the density of continuum states at energy $E'$. For
Figure 3.6 Photoassociation in the dressed-atom picture. The energies of the scattering states $\phi_0$ are elevated by the photon energy to near that of level $v$. The scattering continuum is represented by a the grey band and the dashed line at the bottom of the band is the scattering threshold. The box inset shows the level $v$ embedded in the continuum on a larger scale.

$E$ near the unperturbed resonance position, the integrand in Eqn. 3.5 is positive when $E' < E$ and negative when $E' > E$. The density of continuum states $V(E')$ always increases versus energy $E'$ no matter if the gas is confined to a trap, or in free space. Therefore, the negative part of the integral will contribute more strongly, and Eqn. 3.5 will be negative.

A possible physical picture relies on considering the photoassociation process in the dressed-atom picture, as shown in Fig. 3.6. In the dressed picture, the energy of the atom pair and the photoassociation photon are considered together which effectively elevates the energy of the continuum scattering states to near that of the bound level $v$. The scattering states are represented as an energy band, rather than a discrete level, even though only the lowest energy scattering states may be populated, or in the case of a pure condensate, only the very lowest one.
Looking at the system in this way is equivalent to rediagonalizing the Hamiltonian in order to account for the coupling between the scattering states and level \( v \) provided by the laser. Usually, this results in the familiar AC-Stark shift, which can only be measured if an additional “readout” laser, is applied on a different transition which involves one of the two states given here. In an atom trap, the thermal energy width is much smaller than the natural linewidth of level \( v \). The continuum states at high energy, although unpopulated, will also couple to level \( v \) via the laser. Since we are already working in the dressed basis, we must think of the coupled levels simply as repelling each other. As there are always more continuum states at higher energy, the bound state feels more repulsion from above than below and level \( v \) is pushed to lower energy resulting in a spectroscopic redshift of the transition frequency. In this picture, the photoassociation frequency shift is due purely to the integral of AC-Stark shifts over the entire span of continuum states.

The theory for calculating the light-induced frequency shift \( \delta \epsilon \) has been developed in Refs. [32, 33]. Fedichev et al. give \( \delta \epsilon = \beta \Omega^2 / \delta \varepsilon_v \), where, in their notation, \( \Omega^2 = (\Gamma_a/2) I / I_{\text{sat}} \), \( I_{\text{sat}} = 5.1 \text{ mW/cm}^2 \) is the saturation intensity of the atomic resonance, \( \delta \varepsilon_v = (E_v - E_{v+1})/\hbar < 0 \) is the energy spacing of vibrational levels around \( v \), and \( \beta \) is a numerical factor which characterizes the overlap integral between \( \phi_0 \) and \( \psi_v \). As per the discussion following Eqn. (7) of Ref. [32], \( \beta \approx 0.8\pi^2 (1 - a/R_t) \) in the low temperature limit, where \( a = -27.6 \ a_0 \) is the ground-state triplet scattering length [28], \( a_0 \) is the Bohr radius, and \( R_t \) is the classical outer turning point of vibrational level \( v \). For the \( v = 69 \) level, \( R_t = 44 \ a_0 \) and \( \delta \varepsilon_v = -120.6 \text{ GHz} \) [22], giving \( \delta \epsilon / I = -242 \text{ kHz cm}^2/\text{W} \) using the formalism of Ref. [32] when the polarization overlap factor \( \xi = 2/3 \) is taken into account. An unpublished prediction of \( \delta \epsilon / I = -250 \text{ kHz cm}^2/\text{W} \), based on the theory of Ref. [33], was obtained from those authors. Both of these predictions agree quite well with the data.
Chapter 4
Raman photoassociation

This chapter will describe recent work with two-photon photoassociative spectroscopy, otherwise known as stimulated Raman photoassociation. The remainder of this thesis relies, in large part, on the concepts presented here. Our work in this area allowed us to directly observe the growth and collapse dynamics of $^7$Li Bose-Einstein condensates for the first time (Chap. 5). Additionally, stimulated Raman photoassociation may prove to be a valuable tool for altering the collisional interactions between ground-state atoms (Sec. 6.4), in analogy with the single-photon optically tuned Feshbach resonance presented in Sec. 6.3. A general model for Raman photoassociation will be used to calculate two-photon photoassociation rates and to predict light-induced frequency shifts, and the model predictions will be directly compared to light shifted data. The data and model together will be used to calculate the binding energy of the $v' = 10$ level in the spin-triplet ground-state potential. Discussion of the observed two-photon line shapes is deferred to Chap. 7.

4.1 General considerations

Formally, stimulated Raman photoassociation is very similar to the single-photon case presented in Chap. 3. Figure 4.1 shows a schematic diagram of the process with the relevant potentials. Here, a second laser with frequency $\omega_2$ is tuned near resonance between the vibrational level $v$ in the excited-state potential and a vibrational level $v'$ in the ground-state potential. In general, both $\omega_1$ and $\omega_2$ are detuned from the intermediate state resonance by an amount $\Delta$ which is large enough so that applying $\omega_1$ alone results in minimal loss of atoms. When the frequency difference $\Delta \nu = (\omega_2 - \omega_1)/2\pi$ is tuned near the binding energy $E_B(v')/\hbar$, transitions between the state of two colliding atoms $\phi_0$ and the level $v'$ may be resonantly driven. This results in a
Figure 4.1 Stimulated Raman photoassociation. A laser with frequency $\omega_1$ is tuned near resonance between the colliding state of two free atoms $\phi_0$ and a bound state in the excited-state potential $\psi_v$ corresponding to vibrational level $v$. A second laser with frequency $\omega_2$ is tuned near resonance between $\psi_v$ and a bound state in the ground-state potential $\phi_2$ corresponding to vibrational level $v'$. The binding energy of level $v'$ is denoted as $E_B(v')$ and $D_v = -E_B(v)$ is the detuning of level $v$ from the atomic $2P$ resonance.

detectable reduction in the number of trapped atoms, as shown if Fig. 4.2. Although the width of the resonance curve shown here is very narrow compared to the natural width of the excited-state vibrational level $v$ used as an intermediate state, we will see below that much more narrow loss spectra can be obtained by reducing the laser intensities.

The resonant loss is caused by several mechanisms. A newly formed molecule may be immediately excited by off-resonant excitation of the bound-bound transition
Figure 4.2 Raman photoassociation atom loss spectrum. The horizontal scale is the laser difference frequency $\Delta \nu$ offset to 12.418 GHz. The vertical scale is the number of total atoms $N$ remaining after a Raman laser pulse of duration $\tau = 500$ ms. The data points are normalized to measurements made in the absence of the Raman pulse and the dashed line is a Lorentzian fit with a width of 1.3 MHz. For these data, $\nu = 58$, $I_1 = I_2 = 84$ W/cm$^2$, and $\Delta = -1500$ MHz.

Driven by $\omega_2^*$, resulting in spontaneous scattering loss. Additionally, any molecules which survive will not be detected when imaging the atoms because the scattering resonance for the molecules is detuned from that of the atoms by $\sim E_B(v')$. Finally, the molecule can vibrationally de-excite via collisions with other molecules or atoms. This leads to trap loss because the kinetic energy gained by either the molecule-atom pair or molecule-molecule pair is much larger than the containment depth of the trap. In other words, the vibrational level spacing for the ground-state molecule is always much greater than the trap depth. A more detailed discussion of vibrational relaxation is given in Chap. 7.

Note that photodissociation transitions back to the threshold continuum can be driven once a molecule is formed in level $v'$. The rate for photodissociation typically exceeds that for photoassociation since a binary collision is not necessary for dissociation. An equivalent explanation of this rate imbalance comes from Fermi's

*For clarity and brevity, I will often refer to the lasers by their frequency designations. At those times, $\omega_1$ is synonymous with “photoassociation laser” and $\omega_2$ with “Raman laser”.*
Golden Rule for calculating transition probabilities in first-order perturbation theory. Fermi's Golden Rule states that the transition probability to a continuum of states is proportional to the integral over the available final states. In Raman photoassociation, there is only one final state, namely $v'$, whereas in photodissociation, there are an infinite number weighted by a density of states. Since the photodissociation rate exceeds the photoassociation rate, a large population of ground-state molecules will not develop simply by applying a two-photon laser pulse for a time period long compared to the photoassociation time.

The discussion above does not apply to atoms in the condensate because for a sufficiently narrow laser source (drive laser difference frequency) only the condensate level, among all of the (quasi-)continuum levels, needs to be considered. Since the energy levels in a trap are in fact discrete, the linewidth of the laser difference frequency $\Delta \nu$ needs to be much less than the trap energy level spacing, which in our case is $\sim 150$ Hz. Using the phase lock feedback loop described in App. A, the difference frequency is maintained to sub-Hz precision. The drive lasers can in principle, therefore, drive coherent oscillations between an atomic and molecular condensate, provided the loss mechanisms discussed above are sufficiently small. The process of coherently converting two atoms into one molecule (and the reverse) resembles nonlinear optical processes such as frequency doubling and parametric downconversion, and has been studied as such in the literature [36, 37].

The lasers induce light shifts in both the continuum state $\phi_0$ and the bound state $\phi_2$. Therefore, the measured binding energy will differ somewhat from the true value in the absence of light. Using a variant of the Raman photoassociation technique described here*, the binding energy of the least-bound $v' = 10$ level in the $a^3\Sigma^+_u$ ground-state potential was previously measured in a MOT. The binding

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*In that experiment, $\omega_1$ was held on resonance $\Delta = 0$ resulting in a detectable loss of atoms. This loss was partially suppressed when $\omega_2$ was scanned through the two-photon resonance condition.
energy reported for that measurement was 12.47(4) GHz [27], but those authors did not account for the light-induced shifts. Additionally, this technique was applied to a very weakly bound vibrational level in the ground-state potential of $^{87}$Rb using a Bose-Einstein condensate [38]. In that measurement, the light shifts were taken into account, and an upper limit for the vibrational relaxation rate constant was inferred.

4.2 Experiment

Although a general discussion of the experimental apparatus is described in Chap. 2, a brief description of the particular aspects pertaining to the Raman photoassociation experiments described in this chapter is given here. The experiments start with a laser cooled cloud of $\sim 5 \times 10^8$ atoms in the $F = 2, m_F = 2$ hyperfine sublevel of $^7$Li in the permanent magnet trap at a temperature of $\sim 250\ \mu$K. The atoms are evaporatively cooled, reaching degeneracy at $\sim 700\ \text{nK}$ with $\sim 10^6$ atoms. Typically, the evaporation microwave sweep is halted $\sim 100$ kHz above the frequency corresponding to the trap bottom, and the temperature of the atom cloud is $T \sim 350\ \text{nK}$ with a total number $N \sim 3 \times 10^5$ atoms. A 100 ms width, Gaussian shaped (in frequency vs. time) microwave pulse is then applied to reduce $N$ and thereby increase the sensitivity to the number of condensate atoms $N_0$. This "microwave razor" leaves the energy distribution of the atoms far from equilibrium with $N$ typically between $10^4$ and $10^5$ atoms, depending on the depth of cut.

Following evaporation, the atoms are held in the trap for a time period typically between 2 and 5 seconds. This allows the energy distribution of the gas to recover somewhat from the large perturbation imposed by the microwave razor, and has been shown both experimentally and computationally (using the quantum Boltzmann simulation of Ref. [39]) to improve the quality of fits to the nonequilibrium distribution of Eqn. 2.1 [7]. After the holding period, a two-photon Raman photoassociation pulse of duration $\tau$ is applied to the atom cloud. The pulse consists two laser beams with
frequencies $\omega_1$ and $\omega_2$ as indicated in Fig. 4.1. Following the Raman pulse, the trapped cloud is probed in situ using the phase contrast imaging technique described in Ref. [12] and in Chap. 2. These images are fit to the nonequilibrium distribution function (Eqn. 2.1) in order to determine the number of remaining total atoms $N$ and condensate atoms $N_0$. The imaging technique requires several photons to be scattered from each atom and the gas heats up, destroying the condensate. Therefore, only one image may be obtained per evaporative cooling cycle. Even if a less perturbative imaging technique were available, the cooling cycle would still need to be repeated for each image obtained since the Raman pulse itself removes a significant number of atoms. To build up a resonance curve, the entire cycle is repeated many times for different values of the laser difference frequency \[ \Delta \nu = (\omega_2 - \omega_1)/2\pi. \]

As described in Chap. 2, the two laser beams which make up the Raman pulse are derived from low-power ECDLs. The laser $\omega_1$ is side-locked to a scannable Fabry-Perot cavity in order to reduce acoustical jitter. A 750 MHz FSR scanning etalon is used to measure the relative frequency separation between $\omega_1$ and a reference laser which is locked to the $2S_{1/2} - 2P_{3/2}$ atomic resonance. A lock circuit provides slow feedback to the Fabry-Perot cavity to maintain this frequency separation to within $\sim 3$ MHz. The other laser $\omega_2$ is frequency-locked relative to $\omega_1$ with the phase-lock loop (PLL) described in App. A. The PLL maintains $\Delta \nu$ to sub-Hz precision and suppresses all relative phase noise between the two lasers by $\sim 40$ dB. The frequency separation $\Delta \nu$ is precisely controlled using a microwave synthesizer manufactured by Hewlett Packard (Agilent).* The lasers are combined on an optical beamsplitter and subsequently coupled into a single-mode optical fiber whose output is near the trap apparatus. The temporal width of the Raman pulse $\tau$ is controlled by chopping the combined laser beam using a mechanical shutter manufactured by Uniblitz. The shutter has a full open/close time of $\sim 1$ ms. To achieve sub-ms pulse times, an

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*For details on the PLL including part numbers, see App. A.
acousto-optic modulator (AO) is used in conjunction with the mechanical shutter.

Using the optical setup described above yields maximum powers after the fiber of \( \sim 2 - 3 \) mW for each laser. When larger laser intensities are desired, a seeding beam from one or both diode lasers can be injected into a tapered optical amplifier manufactured by Spectra Diode Labs (SDL). The amplifier provides \( \sim 300 \) mW of total output power at the injected frequency or frequencies. Using the amplifier setup, total powers as high as \( \sim 70 \) mW have been achieved after the fiber. In either case, the fiber-outcoupled laser beam is focussed at the position of the atoms to a \( 1/e^2 \) intensity radius of 100 - 250 \( \mu \)m. The Raman laser beam is directed nearly parallel to the laser beam used for imaging the atom cloud, providing feedback for achieving spatial overlap with the cloud. Fiber coupling the lasers helps to reduce drift in the spatial overlap, ensures that both beams have the same spatial mode, and reduces variations of the laser intensity across the spatial extent of the atom cloud.

The selection rules for the Raman transition are the same as for the one-photon photoassociation transitions described in Chap. 3. As in that case, the triplet-triplet transition ensures that no first-order Zeeman shift will be present even for the large \( \sim 1 \) kG fields of the permanent magnet trap\(^*\). Upon emerging from the optical fiber, the Raman laser beams are passed through a polarizer whose angle is set to optimize the polarization overlap \( \xi \) with the transition dipole moment. As for one-photon photoassociation, geometrical considerations constrain the maximum polarization overlap to be \( \xi = 2/3 \).

4.3 Model

A general model is needed for the Raman photoassociation process, which can predict transition rates and which accurately describes all light-induced shifts in the spectral position of the resonance. The binding energy of the \( v' = 10 \) level can then

\(^*\)This hypothesis was tested by changing the trap bias field by \( \sim 1 \) G and no shift in the Raman spectrum was observed.
be measured precisely by extrapolating the resonance position to zero light intensity. It is more difficult to compare predictions for the Raman photoassociation rate with measurements due to saturation effects similar to those discussed in Sec. 3.2. However, as demonstrated later in this chapter, the model predictions for the light shift agree well with measurements, lending confidence to predictions for the rate.

Due to the recent interest in producing ultracold molecules, there are an appreciable number of theoretical treatments of Raman photoassociation, most notably the work of Bohn and Julienne [33], Juha Javanainen [37], and the collaborative effort between Dan Heinzen and Peter Drummond [36]. The models adopted by Javanainen and Drummond are very similar and are based on the Rabi formalism originally developed for nuclear magnetic resonances [40]. The model I adopt here is based on these treatments, although in form, it more closely resembles the latter. Ordinarily, the Rabi formalism is applied to atomic or molecular transitions between discrete levels. The atomic resonance transition \((\phi_0 \to 2P)\) and the bound-bound molecular transition \((v' \to v)\) shown in Fig. 4.1, are both well described by this formalism for the conditions of our experiment. Here, the level referred to as \(2P\) denotes the asymptote to the excited-state potential. Strictly speaking, however, the Rabi formalism cannot be applied to the free-bound photoassociation transition \(\phi_0 \to \psi_v\), except when considering the condensate. This is because the scattering state \(\phi_0\) is embedded in the threshold continuum, which is not a discrete level. For a condensate, photoassociation can be considered as a transition between discrete states of a many-body system and the Rabi formalism therefore applies [41].

The coupling between the scattering state \(\phi_0\) and the atomic \(2P\) excited state can be expressed in terms of the Rabi flopping frequency \(\Omega_a = d_a \varepsilon_0 / \hbar\), where \(d_a\) is the atomic transition dipole moment and \(\varepsilon_0\) is the electric field amplitude. The Rabi frequency can also be written in more convenient terms as

\[
\Omega_{fi} = \Gamma_a \sqrt{\frac{I_i}{I_{sat}}},
\]  

(4.1)
where, \( \Gamma_a = (2\pi)5.9 \text{ MHz} \) is the atomic linewidth of the \( 2P \) excited state, \( I_i \) is the intensity of laser \( \omega_i \), and \( I_{sat} = 5.1 \text{ mW/cm}^2 \) is the saturation intensity of the \( 2P \) atomic state when detuned far compared to the fine or hyperfine splittings. The subscript \( f \) denotes a free atomic transition. A similar expression can be developed for the coupling between the bound state \( \phi_2 \) in the ground-state potential and \( \psi_v \) in the excited-state potential. The molecular transition dipole moment \( d_m = \sqrt{2}d_a \) \cite{36} must be substituted for \( d_a \). Additionally, \( d_m \) is modulated by the unitless\(^\ast\) bound-bound overlap integral \( \langle \phi_2 | \psi_v \rangle \) and the polarization overlap \( \sqrt{\xi} \), where \( \xi = 2/3 \) as discussed in Sec. 3.2. The bound-bound Rabi frequency then becomes

\[
\Omega_{b,i} = \sqrt{2\xi} \langle \phi_2 | \psi_v \rangle \Omega_{f,i} = \Gamma_a \sqrt{\frac{2\xi}{I_{sat}}} \langle \phi_2 | \psi_v \rangle . \tag{4.2}
\]

The analogous expression for the coupling between the scattering state \( \phi_0 \) and \( \psi_v \) must contain the overlap integral \( \langle \phi_0 | \psi_v \rangle \) which has dimensions of \( (\text{length})^{3/2} \). In addition, the factor \( \sqrt{n} \), where \( n \) is the density, must be included to make the units work out. The free-bound Rabi frequency is therefore given by

\[
\Omega_{p,i} = \sqrt{2\xi n} \langle \phi_0 | \psi_v \rangle \Omega_{f,i} = \Gamma_a \sqrt{\frac{2\xi n I_i}{I_{sat}}} \langle \phi_0 | \psi_v \rangle , \tag{4.3}
\]

where the subscript \( p \) denotes a photoassociation transition.

4.3.1 Light shift

In general, there will be shifts in the energy of all four states shown in Fig. 4.1 \((\phi_0, \phi_2, \psi_v, \text{ and } 2P)\) due to the AC Stark effect, as described below. The binding energy \( E_B(\nu') \) of level \( \nu' \) is sensitive only to shifts in the energies of the scattering state \( \phi_0 \) and the bound-state \( \phi_2 \). Therefore, the AC Stark shifts of levels \( \nu \) and \( 2P \) need not be considered. In addition to the AC Stark shifts of \( \phi_0 \) and \( \phi_2 \), the photoassociation frequency shift described in Sec. 3.3 needs to be accounted for. If

\(^\ast\)The bound-state wave functions are normalized the same way such that, for example, \( \langle \phi_2 | \phi_2 \rangle \equiv 1 \). The scattering wave function is normalized such that \( \langle \phi_0 | \phi_0 \rangle \equiv (\text{length})^3 \).
the shift in transition energy arises from energy shifts of both the scattering state \( \phi_0 \) and the excited-state bound level \( \psi_v \) (as is the case for AC Stark shifts) then it will contribute to the measurement of \( E_B(\nu') \). Calculations of the photoassociation frequency shift for \( v = 72 \) show that it is roughly two orders of magnitude larger than the largest AC Stark shift, for given laser parameters (see Fig. 4.14 below). Since no shifts on this order are observed in the data (shown below), we conclude that the photoassociation frequency shift only affects the energy of the excited-state level \( v \), and that it will therefore not contribute to the measurement of \( E_B(\nu') \). This is an interesting result in its own right.

The AC Stark shift arises from rediagonalizing the Hamiltonian which describes the interaction of a two-level system with radiation. It is most conveniently described in the dressed-atom picture as an avoided level crossing of the dressed states. A derivation of the exact form of the shift will not be given here, but can be found in many textbooks, including the first chapter of Metcalf and van der Straten [42]. As shown there, the spectral shift of the dressed state which corresponds to the ground state in the bare basis is given by

\[
\delta E_g = \frac{\Omega' - \zeta}{2}, \tag{4.4}
\]

where \( \Omega' = \sqrt{\Omega^2 + \zeta^2} \), and \( \zeta \) is the laser detuning (either \( \Delta \) or \( D_v \)). The state with energy \( E_g \) can correspond either to the bound state \( \phi_2 \) or the scattering state \( \phi_0 \). Note that the form of Eqn. 4.4 assumes a negligible width \( \Gamma \) for the excited state and so can only be strictly applied when \( |\zeta| \gg \Gamma \). Further, when \( |\zeta| \gg \Omega \), Eqn. 4.4 can be rewritten in the more familiar form

\[
\delta E_g \approx \frac{\Omega^2}{4\zeta}. \tag{4.5}
\]

The net shift of each state \( \phi_0 \) and \( \phi_2 \) is the sum of shifts arising from the couplings \( \Omega_f, \Omega_b, \) and \( \Omega_p \) given above in Eqns. 4.1-4.3. Additionally, both lasers \( \omega_1 \) and \( \omega_2 \) will contribute to the shift of each state. Note that for a laser tuned red of resonance
(\zeta < 0), Eqn. 4.5 shows that the shift of \( E_q \) will be to lower energy. The measured binding energy \( E_B \) will then decrease (increase) when \( \phi_0 (\phi_2) \) shifts to lower energy. With these considerations, \( E_B \) can be written as

\[
E_B = E_B^0 + \delta_0 - \delta_2 ,
\]

where \( E_B^0 \) is the binding energy in the absence of light, and \( \delta_0 (\delta_2) \) is the net light shift of state \( \phi_0 (\phi_2) \).

There are contributions to \( \delta_0 \) from both lasers via the couplings \( \Omega_f \) and \( \Omega_p \):\(^*\)

\[
\delta_0 \cong 2 \left\{ \left[ \frac{\Omega_{f,1}^2}{4D_v} + \frac{\Omega_{f,2}^2}{4(D_v + E_B)} \right] + \left[ \frac{\Omega_{p,1}^2}{4\Delta} + \frac{\Omega_{p,2}^2}{4(\Delta + E_B)} \right] \right\} ,
\]

where the factor of 2 out front is due to the fact that each atom of the pair experiences the same shift\(^†\) [36]. Inserting the expressions for \( \Omega_f \) and \( \Omega_p \) given by Eqns. 4.1 and 4.3 and grouping terms proportional to \( I_1 \) and \( I_2 \) gives

\[
\delta_0 \cong \frac{1}{I_{sat}} \frac{\Gamma_a^2}{\Delta} \left\{ I_1 \left[ \frac{\Delta}{2D_v} + \xi n \langle \phi_0 | \psi_\omega \rangle^2 \right] + I_2 \left[ \frac{\Delta}{2(D_v + E_B)} + \xi n \langle \phi_0 | \psi_\omega \rangle^2 \frac{\Delta}{\Delta + E_B} \right] \right\} .
\]

The first term in the coefficient for \( I_1 \), \( \Delta/2D_v \) is due to the free atomic coupling \( \Omega_f \) and is in general much larger than the second term \( \xi n \langle \phi_0 | \psi_\omega \rangle^2 \) which is due to the photoassociation coupling \( \Omega_p \). Fig. 4.3 shows the ratio \( \eta \) of these two terms for a range of excited-state vibrational levels \( v \) using Eqn. 3.1 and the values shown in Fig. 3.2. This calculation gives a worst-case estimate of \( \eta \) since it assumes that \( |\Delta| = 10 \text{ MHz} \), which is smaller than any experimental value of \( |\Delta| \) used in obtaining data.\(^‡\)

---

\(^*\)This formula, and any other in this chapter regarding the two-photon light shift, only applies when \( \Delta \gg \Omega_p, \Omega_0, D_v \gg \Omega_f \), and when \( D_v \gg \Delta \). Although in principle it is perfectly possible to violate some of these conditions, all the data presented below (which are used to extract the binding energy of \( \nu' = 10 \)) satisfy these conditions.

\(^†\)The factor of 2 applies to the terms within the second pair of square brackets even though \( \Omega_p \) is coupling to a molecule, because \( \Omega_p \), as defined in Eqn. 4.2, leads to a loss rate per atom. Here, the terms in the second pair of square brackets give the light shift per atom. In any case, these terms will be neglected for reasons to be discussed below.

\(^‡\)Although applying Eqn. 4.8 is not strictly correct for \( |\Delta| = 10 \text{ MHz} \sim \Gamma_m \), it was verified using the form of Eqn. 4.4 applied to \( v = 79 \) that the light shift terms corresponding to \( \Omega_p \) can indeed be neglected when \( |\Delta| = 10 \text{ MHz} \).
Figure 4.3  Ratio of light shift components due to free atomic coupling and photoassociation coupling for a range of excited state vibrational levels $v$. The ratio is defined by $\eta \equiv (\Delta/2D_v)/\xi n (\phi_0|\psi_v)^2$. The calculation assumes that $|\Delta| = 10$ MHz and $n = 5.7 \times 10^{12}$ cm$^{-3}$, which is the peak density for $N_0 = 1000$ condensate atoms.

An analogous ratio for the coefficient of $I_2$ will be even larger since the second term is scaled down even further by the ratio $\Delta/(\Delta + E_B)$, where $E_B \sim 12.4$ GHz. Clearly, the shift terms corresponding to the photoassociation coupling can be neglected when $|\Delta| \gtrsim 10$ MHz. Doing so gives

$$\delta_0 = \frac{1}{I_{sat}} \frac{\Gamma_a^2}{2D_v} \left[ I_1 + I_2 \frac{D_v}{D_v + E_B} \right]$$

(4.9)

for the total shift of state $\phi_0$. Note that this shift is negative since $D_v < 0$, and that the ratio $D_v/(D_v + E_B) \approx 1$ since $|D_v| \gg E_B$.

The only contribution to the shift $\delta_2$ of the bound state $\phi_2$ comes from the coupling $\Omega_b$ defined in Eqn. 4.2:

$$\delta_2 = \frac{\Omega_{b,2}^2}{4\Delta} + \frac{\Omega_{b,1}^2}{4(\Delta - E_B)}.$$  

(4.10)

Substituting for $\Omega_b$ gives

$$\delta_2 = \frac{\xi (\phi_2|\psi_v)^2}{I_{sat}} \frac{\Gamma_a^2}{2\Delta} \left[ I_2 + I_1 \frac{\Delta}{\Delta - E_B} \right],$$

(4.11)

for the total shift of state $\phi_2$. Note that the second term in brackets can often be neglected since $E_B/|\Delta| \gtrsim 25$ for typical detunings of $|\Delta| \lesssim 500$ MHz. Keeping that
term for completeness, however, gives

\[
E_B = E_B^0 + \frac{I_1}{I_{\text{sat}} 2 D_v} \left\{ \left[ \frac{1}{\Gamma_v^2} \frac{I_2}{I_1} \frac{D_v}{D_v + E_B} \right] \right. \\
- \frac{\xi \langle \phi_2| \psi_\nu \rangle}{2} \frac{D_v}{\Delta} \left[ \frac{I_2}{I_1} + \frac{\Delta}{\Delta - E_B} \right] \left\} \right. 
\]

(4.12)

for the measured binding energy.

### 4.3.2 Bound-bound overlap integrals

The bound-bound overlap integrals \( \langle \phi_2| \psi_\nu \rangle \) which appear in Eqn. 4.12, and in other equations to follow, can be determined by directly measuring the Rabi frequency \( \Omega_\nu \), as defined in Eqn. 4.2 for all levels \( \nu \) of interest. Alternatively, with detailed knowledge of the ground-state and excited-state interaction potentials, the wave functions \( \phi_\nu \) and \( \psi_\nu \) can be obtained and the overlap integrals computed. The experimental approach taken here is a combination of these methods: \( \Omega_\nu \) is measured directly for a particular level \( \nu \) and Eqn. 4.2 is used to extract a value for \( \langle \phi_2| \psi_\nu \rangle \). The overlaps for other levels are then obtained by scaling the one which was measured directly using ratios of values calculated by Robin Côté in his Ph.D. thesis [43].

The level \( \nu = 58 \) was chosen for the direct measurement since the calculations indicated that its overlap with \( \nu' = 10 \) was the largest among all the levels. This maximizes the Rabi frequency for a given laser intensity, decreasing the fractional uncertainty in the measurement. The measurement was obtained by holding the laser frequency \( \omega_2 \) on the bound-bound resonance so that \( \Delta = 0 \), and then \( \omega_1 \) was scanned near the two photon resonance condition. The resulting atom loss signal is shown in Fig. 4.4.

The frequency splitting between the two peaks is a direct measure of the bound-bound Rabi frequency, \( \Omega_\nu \). This is most easily understood by returning to the dressed-atom picture. As described above, this results in the expression shown in Eqn. 4.4 for the AC Stark shift. The splitting shown in Fig. 4.4, called the Autler-Townes splitting or Autler-Townes doublet, is simply an on-resonance manifestation of the same effect [44]. If \( \zeta = 0 \) (\( \Delta = 0 \)) in Eqn. 4.4, the spectral shift of the lower dressed state is
Figure 4.4  Measurement of the bound-bound overlap integral for $v = 58$. The laser $\omega_2$ is held on one-photon resonance $\Delta = 0$ while $\omega_1$ is scanned near the two-photon resonance. The data points are the number of remaining atoms $N$ after a 30 ms duration Raman light pulse and the dashed lines are independent Lorentzian fits to each peak. The horizontal scale is the scan frequency offset by $\sim 12.38$ GHz. The frequency splitting indicated by the fitted center positions is $59.9(8)$ MHz for laser intensities of $I_1 = 34.5$ W/cm$^2$ and $I_2 = 15.0$ W/cm$^2$.

$-\Omega/2$. Analogously, the shift of the upper dressed state is $+\Omega/2$ [42] and the level $v$ is “split” by $\Omega$. The two-photon resonance condition is satisfied only when tuned near one arm of the doublet since the peaks are well separated compared to their widths. There is no additional splitting caused by $\omega_1$ since the free-bound coupling $\Omega_p$ is typically much smaller than $\Omega_b$, as shown below.

The measured frequency splitting of the doublet is $59.9(8)$ MHz for an intensity of $I_2 = 15.0$ W/cm$^2$. Using Eqn. 4.2, this gives a value of $\langle \phi_2 | \psi_v \rangle = 0.162(2)$. The calculations of Côté [43] are then used to scale this value for $v = 58$ to other levels of interest. The results of that operation are shown in Fig. 4.5 where the square of the overlap integral $\langle \phi_2 | \psi_v \rangle^2$ is shown as a function of $v$. The overlap integrals can now be inserted into Eqn. 4.12 in order to calculate the shift in the Raman photoassociation resonance position.

*As described in Sec. 4.4.2, the total uncertainty in $I_2$ is $\sim 20\%$.  

Figure 4.5  Bound-bound overlap integrals $(\phi_2|\psi_{\nu})^2$. The direct measurement at $\nu = 58$ is scaled using the calculations of Côté [43] to obtain the values for other levels $\nu$.

4.3.3 Mean-field shift

Notice that Eqn. 4.12 is independent of density, since the contribution of the coupling $\Omega_p$ can be neglected. The light shift should therefore be the same for the condensate and the thermal cloud. The mean-field energy arising from the atom-atom, atom-molecule and molecule-molecule interactions, however, will shift as a function of density resulting in a corresponding shift in $E_B$. In general, the mean-field energy is only meaningful in the context of the condensate, where there is a coherent atom field with a particular phase. In the thermal cloud, the lack of coherence randomizes the phase from different energy states and the field should average to zero. Since the atom-molecule and molecule-molecule interactions are currently undetermined, both experimentally and theoretically, they are neglected here. The spectral shift due to the atom-atom mean field energy is given by

$$\delta_{mf} = n \frac{2U_0}{\hbar} = n \frac{8\pi\hbar a}{m},$$  \hspace{1cm} (4.13)

where $a$ is the s-wave scattering length and $m$ is the atomic mass.*

*The mean-field energy is only one term in the non-linear Schrödinger equation (Eqn. 5.1), and it might be expected, therefore, that terms due to the kinetic and potential energy of the atoms would also give a spectral shift. However, these two additional terms are the same for both the atoms and the $\nu' = 10$ molecules, so only the mean-field shift needs to be considered.
In general, $\delta_{m_f}$ should be added to the right side of Eqn. 4.12. Inclusion of this term, however, only increases the accuracy of the measured value of $E_B$ if the number of condensate atoms $N_0$ and hence the density $n$ is known precisely. For $^7\text{Li}$ condensates the growth and collapse dynamics resulting from the attractive interactions ($a < 0$) cause large fluctuations in $N_0$. This is discussed in detail in several publications (see, for example [7, 8, 39]) and in Chap. 5. For this case, therefore, the mean field shift simply imposes an uncertainty in the value of $E_B$.

If the condensate is probed during the period of rapid growth and collapse cycles, the measured mean value for $N_0$ is $\langle N_0 \rangle = 650$ atoms with an rms variation of $\sim 250$ atoms [7]. A more recent measurement yields $\langle N_0 \rangle = 800$ atoms with an rms variation of $\sim 250$ atoms.\* Using the average of these two measurements to compute the peak density gives $n_0 = (4.1 \pm 1.4) \times 10^{12}$ cm$^{-3}$, where the quoted uncertainty is not statistical, but rather results from the measured rms fluctuations in $N_0$. This leads to a spectral shift in the measured value of $E_B$ of $\delta_{m_f} = -420 \pm 140$ Hz which should be added to the light shift.

As an aside, the fluctuations in $N_0$ imply that no spectral features narrower than $\sim 140$ Hz can be resolved. This limitation can only be remedied if the condensate variations can be reduced. One step in this direction is to dump the condensate using a two-photon Raman pulse, which initially stabilizes $N_0$ near a value of zero, as discussed in Ref. [8] and in Chap. 5. The condensate subsequently regrows and the application of a second Raman pulse after some growth time might yield a smaller variation in the initial value of $N_0$.

\*One possible explanation for the discrepancy of these two measurements is that the more recent one was obtained with $N \sim 10^5$ atoms compared to $N \sim 3 \times 10^4$ atoms for the previous measurement. As discussed in Ref. [16], this increase in total number leads to a systematic over-estimation of $N_0$. 
4.3.4 Coherence

The theoretical treatment reported in Ref. [36] was developed in order to describe the coherent coupling of an atomic Bose-Einstein condensate to a molecular one via the Raman photoassociation process described here. The success of such an attempt depends on the balance between the coherent coupling rate and the losses associated with spontaneous light scattering and vibrational relaxation. In this section, an expression for the coherent coupling rate, or two-photon Rabi frequency, as well as expressions for the losses associated with light scattering will be given.

Coherent coupling rate

The coherent coupling rate (two-photon Rabi frequency) $\chi$ is given similarly in Refs. [36] and [37]. Adapting their expressions to the formalism presented here yields

$$\chi = \frac{\Omega_p \Omega_b}{\sqrt{2} \Delta} . \tag{4.14}$$

where it has been assumed that $|\Delta| \gg \Gamma_m$. Note that the dependence of $\chi$ on the sign of $\Delta$ is correct since $\chi$ will eventually end up as the argument in a complex exponential and its sign will then determine the oscillatory phase. The factor $\sqrt{2}$ in the denominator of $\chi$ is present in both Refs. [36] and [37].

Substituting the expressions for $\Omega_p$ and $\Omega_b$ given in Eqns. 4.3 and 4.2 gives

$$\chi = \frac{\Gamma_a^2 \sqrt{2 T_1 T_2}}{\Delta} \xi \sqrt{n} \langle \phi_0 | \psi_u \rangle \langle \psi_u | \phi_2 \rangle . \tag{4.15}$$

The terms $\Omega_{p,2}$ and $\Omega_{b,1}$ corresponding to the contribution of laser $\omega_2$ to $\Omega_p$ and $\omega_1$ to $\Omega_b$, respectively, have been dropped since they oscillate very rapidly compared to $\Omega_{p,1}$ and $\Omega_{b,2}$ by virtue of the definition given above for the off-resonance Rabi frequency, $\Omega' = \sqrt{\Omega^2 + \zeta^2}$. Here $\zeta$ is approximately given by $E_B$ which, again, is usually very large compared to any other frequency scale relevant to Eqn. 4.15. Ultimately, the neglected terms would result in a fast, but small amplitude, modulation of the slower
Figure 4.6  Product of free-bound, bound-bound, and polarization overlap integrals 
\( \xi \sqrt{n} \langle \phi_0 | \psi_u \rangle \langle \psi_u | \phi_2 \rangle \). The calculation assumes that \( n = 5.7 \times 10^{12} \text{ cm}^{-3} \) corresponding to the peak density for \( N_0 = 1000 \) atoms.

oscillations given by \( \chi \) as written. This approximation is similar to the rotating wave approximation ubiquitous in quantum optics [42].

Using the values for \( \langle \phi_2 | \psi_u \rangle \) obtained from Fig. 4.5 and the values for \( \langle \phi_0 | \psi_u \rangle \) obtained from Fig. 3.2, the quantity

\[ \xi \sqrt{n} \langle \phi_0 | \psi_u \rangle \langle \psi_u | \phi_2 \rangle \]

can be computed for levels of interest. Figure 4.6 shows the computed values for \( n = 5.7 \times 10^{12} \text{ cm}^{-3} \) corresponding to the peak density for \( N_0 = 1000 \) atoms. These values can be inserted into Eqn. 4.15 in order to compute the coherent coupling rate \( \chi \). Note that the relative size of the values plotted gives the ratios of \( \chi \) for different levels \( u \) when \( I_1, I_2 \) and \( \Delta \) are held constant. \( \chi \) is pretty flat between \( u = 53 \) and \( u = 72 \), varying by less than a factor of three except in the region near the sharp dip at \( u = 61 \).

Loss

The couplings \( \Omega_f \), \( \Omega_b \), and \( \Omega_p \) also induce loss of atoms from the system via spontaneous emission from the bound level \( u \) and the 2\( P \) atomic resonance. The
one-photon excitation rate can be written formally as the appropriate Rabi frequency modulated by a Lorentzian lineshape which describes the decay width of the respective excited state:

\[ R = \frac{\Omega \Gamma}{4\zeta^2 + \Gamma^2}, \quad (4.16) \]

where \( \zeta \) can be either \( \Delta \) or \( D_v \) and \( \Gamma \) can be the linewidth of either the molecular level \( \Gamma_m \) or the \( 2P \) excited state \( \Gamma_a = \Gamma_m/2 \), and it has been assumed that \( \zeta \gg \Omega \). Note that in the far detuned limit (\( |\zeta| \gg \Gamma \)) Eqn. 4.16 reduces to the familiar form

\[ R \approx \frac{\Omega^2}{4\zeta^2 \Gamma}. \quad (4.17) \]

Because all the levels \( \nu \) of interest are bound by hundreds of GHz, and \( \Gamma_a = (2\pi)5.9 \) MHz, the loss rate due to the free atomic coupling \( \Omega_f \), is always given by the far detuned form. Using Eqn. 4.1 for the free atomic Rabi frequency and summing the contributions from both lasers gives

\[ R_f = \frac{I_1 + I_2}{I_{sat}} \frac{\Gamma_a^3}{4D_v^2}, \quad (4.18) \]

for the loss rate due to spontaneous scattering off the \( 2P \) free atomic resonance, assuming \( |D_v| \gg E_B(\nu' = 10) \). The rates for spontaneous loss due to the couplings \( \Omega_b \) and \( \Omega_p \) take the form of Eqn. 4.16 and are given by

\[ R_b = \xi \langle \phi_2|\psi_\nu \rangle^2 \frac{I_2}{I_{sat}} \frac{\Gamma_m^3}{4\Delta^2 + \Gamma_m^2} \left[ 1 + \frac{I_1}{I_2} \frac{4\Delta^2 + \Gamma_m^2}{4(\Delta - E_B)^2 + \Gamma_m^2} \right], \quad (4.19) \]

and

\[ R_p = \xi n \langle \phi_0|\psi_\nu \rangle^2 \frac{I_1}{I_{sat}} \frac{\Gamma_m^3}{4\Delta^2 + \Gamma_m^2} \left[ 1 + \frac{I_2}{I_1} \frac{4\Delta^2 + \Gamma_m^2}{4(\Delta + E_B)^2 + \Gamma_m^2} \right]. \quad (4.20) \]

Note that in Eqns. 4.19 and 4.20, the second term in brackets can be neglected for typical detunings of \( \Delta \lesssim 500 \) MHz (and for \( I_1/I_2 \) not too big or too small) since in that case \( E_B^2 \gg \Delta^2 \) and \( E_B^2 \gg \Gamma_m^2 \). Also, Eqn. 4.20 is equivalent to the form given in Eqn. 3.2.
Figure 4.7  Figure of merit for coherent oscillations between a condensate of atoms and a condensate of molecules. The plotted ratio is proportional to $\chi/R_b$ for given laser parameters $I_1$, $I_2$, and $\Delta$. The calculation assumes that $n = 5.7 \times 10^{13}$ cm$^{-2}$ corresponding to $N_0 = 1000$ atoms in the condensate.

The spontaneous loss rates $R_f$ and $R_p$ cause an overall loss of atoms even when the Raman resonance condition $\Delta \nu = E_B/\hbar$ is not satisfied. When the resonance condition is satisfied, an extra loss of atoms is observed, as shown in Fig. 4.2. The resonant loss can be explained if $R_b$, the stimulated rate for loss of molecules from the bound-state $\phi_2$, is larger than the two-photon molecule production rate $\chi$. In that case, any molecules in the state $\phi_2$ are lost from the trap via spontaneous emission soon after they are formed. Figure 4.7 shows the ratio

$$
\frac{\sqrt{n} \langle \phi_0 | \psi_\nu \rangle}{\langle \phi_2 | \psi_\nu \rangle},
$$

which is proportional to $\chi/R_b$ for fixed $I_1$, $I_2$, and $\Delta$. Of course, the molecules can also be lost by the process of vibrational relaxation, as discussed in Chap. 7. Although yet undetermined, it is likely that the vibrational relaxation rate is smaller than $R_b$ for most experimental conditions. It should be noted that, even if $\chi/R_b \gg 1$, indicating that the system undergoes rapid coherent oscillations between atoms and molecules, a resonant loss of atoms will be observed for very long Raman light pulse durations $\tau \gg \chi^{-1}$ and $\tau \gg R_b^{-1}$. This happens because on every oscillation cycle, some spontaneous loss occurs due to $R_b$. 
Optimization

The ratios of $\chi$ to the loss rates $R_f$, $R_b$, and $R_p$ will determine whether the coherent oscillations described above are possible. In general, for coherent oscillations, $\chi/R_t$ must be $\gg 1$, where $R_t = R_b + R_f + R_p$ is the total loss rate. Typically, the limiting loss is due to the bound-bound scattering rate $R_b$. The ratio $\chi/R_b$ is given by

$$\frac{\chi}{R_b} = \sqrt{\frac{I_1}{2I_2}} \frac{\Delta^2 + \Gamma_a^2}{\Delta \Gamma_a} \left[ \frac{\sqrt{n} \langle \phi_0 | \psi_v \rangle^2}{\langle \phi_2 | \psi_v \rangle} \right].$$  \hspace{1cm} (4.22)

The quantity in brackets, plotted in Fig. 4.7, can be considered a figure of merit for choosing a level $v$ in order to have coherent oscillations, when the loss rates $R_p$, and $R_f$ can be neglected compared to $R_b$. Clearly, the efficiency for coherent molecule production generally increases for higher levels $v$. Note that the validity of the overlap integrals used for obtaining the expression in Eqn. 4.22 (and the other expressions above) can be tested by comparing the predicted light shift, Eqn. 4.12 to actual light shift data*. This will be done below in Sec. 4.4.

To obtain particular values of $\chi/R_b$ and $\chi$ for a given intermediate state $v$, the three parameters $I_1$, $I_2$, and $\Delta$ must be calculated. Combining Eqns. 4.15 and 4.22 shows that $I_1$ is independent of $\Delta$ and $I_2$ as long as $|\Delta| \gg \Gamma_a$. $I_2$ is then given by the choice of $\Delta$. The optimum value of $\Delta$ (and hence $I_2$) is set by the maximum value of $\chi/R_t$ (or minimum value of $R_t$) for the choice of $\chi$ and $\chi/R_b$. The ratio $\chi/R_t$ is plotted as a function of $|\Delta|/\Gamma_a$ in Fig. 4.8(a) for $v = 72$, $\chi \sim (2\pi)1$ kHz, and $\chi/R_b \sim 3$ giving $I_1 = 43$ W/cm². It may be important for $\chi$ to be large compared to the trap oscillation frequency ($\sim(2\pi)150$ Hz) since otherwise the atoms/molecules move significantly in the trap during the Rabi oscillations which may effect the coherence time.

For these conditions, the ratio $\chi/R_t$ is peaked at $|\Delta| \sim 90\Gamma_a = 530$ MHz. Figure 4.8(b) shows that at this detuning, the required value of $I_2$ is 17 W/cm². The requirements for $I_1$ and $I_2$ are reasonable and can be easily achieved using the tapered

*Because the free-bound coupling $\Omega_p$ is so small compared to the free atomic coupling $\Omega_f$ as shown in Fig. 4.3, validating the values used for $\langle \phi_0 | \psi_v \rangle$ is very difficult.
Figure 4.8  Optimization of Rabi oscillations for $v = 72$. (a) $\chi/R_1$, (b) $I_2$, and (c) $\chi$ (black line), $R_b$ (blue line), $R_f$ (green line), and $R_p$ (red line). All graphs are for $\chi \sim (2\pi)1$ kHz, $\chi/R_b \sim 3$ and $I_1 = 43$ W/cm$^2$.

optical amplifier described in App. A and a laser $1/e^2$ Gaussian beam waist of $\sim 150$ μm. Figure 4.8(c) shows the values of $\chi$, $R_b$, $R_f$, and $R_p$ showing that indeed $R_b$ is the dominant loss mechanism.

4.4 $v' = 10$ binding energy

As mentioned above, the validity of the calculated values for the bound-bound overlap integrals can be tested by comparing the predicted light shifts to actual light shift data. This also tests the validity of the model described in Sec. 4.3 which will lend confidence to the predicted values for $\chi$. A complete understanding of the light shift functionality also allows light shifted data to be extrapolated to the asymptotic
Figure 4.9  $v = 58$ atom loss spectra for various detunings $\Delta$ and intensities $I_1$ and $I_2$. $N$ is the number of atoms remaining following the Raman pulse and $\Delta\nu$ is the laser difference frequency. The solid symbols correspond to $\tau = 500$ ms, $I_1 = I_2 = 84.2$ W/cm$^2$, and $\Delta = +255$ MHz (red squares) $-1500$ MHz (black circles) and $-165$ MHz (blue triangles). The hollow green diamonds correspond to $\tau = 1$ s, $I_1 = I_2 = 32.9$ W/cm$^2$, and $\Delta = -255$ MHz. The dashed line is an example of a Lorentzian fit applied only to points near the peak of the resonance in order to help identify the center position.

limit, enabling an ultra-precise measurement of the $v' = 10$ binding energy $E_B^0$. In this section, the model predictions are compared to light shifted data for two excited-state vibrational levels, $v = 58$ and $v = 72$, and a value for $E_B^0$ is obtained.

4.4.1 Via $v = 58$ intermediate state

Figure 4.9 shows a collection of four atom loss spectra for varying intensities $I_1$ and $I_2$, and detuning $\Delta$ for the $v = 58$ intermediate-state level. The asymmetric lineshape demonstrated by the two broadest resonances is a very interesting issue and is discussed in detail in Chap. 7. The fact that the asymmetry is reversed for $\Delta > 0$ compared to $\Delta < 0$ is a clue to its origin. The only consequence here of the asymmetry and distortion of the lineshape is to make it difficult to measure the resonance line center. In order to help alleviate that problem, a crude technique is applied to the data whereby a Lorentzian function is fit only to the points near the peak of the resonance. Note that the use of a Lorentzian function is arbitrary since
the broadened resonance shapes are clearly not of that form. This functionality was chosen because visually, it seemed to give the best representation of the data near the peak. The dashed line in Fig. 4.9 is an example of such a Lorentzian fit applied to the data for $\Delta = -165$ MHz. The fitted resonance centers can be used for comparison of the data with the model predictions for the light shift as shown below.

As shown in Fig. 4.5, the bound-bound overlap integral $\langle \phi_2 | \psi_v \rangle$ is maximized for $v = 58$. For this level, therefore, the light shift due to the coupling $\Omega_b$ ($\delta_2$ in Eqn. 4.10) is most sensitive to changes in the laser intensities. This fact has already been used to advantage when measuring $\Omega_b$ directly by the Autler-Townes doublet, as described in Sec. 4.3.2. Because of the dominance of $\Omega_b$, the light shifts due to the couplings $\Omega_p$ and $\Omega_f$ can be neglected for $v = 58$ ($\Omega_p$ has already been neglected). This is most easily seen by considering the expression for the predicted light shift given by Eqn. 4.12. If the second term in the second square brackets $\Delta/(\Delta - E_B)$ is neglected, as is appropriate for all but the largest values of $|\Delta|$, and the ratio $D_v/(D_v + E_B)$ is approximated by 1, which is very reasonable since $D_{58} \sim -3700$ GHz, then the expression for the total light shift is given by

$$E_B - E'_B = \frac{I_1}{I_{sat}} \frac{\Gamma_a^2}{2D_v} \left\{ \left[ 1 + \frac{I_2}{I_1} \right] - \xi \langle \phi_2 | \psi_v \rangle^2 \frac{D_v}{\Delta} \frac{I_2}{I_1} \right\}.$$  \hspace{1cm} (4.23)

The term enclosed by square brackets is due to the free atomic coupling $\Omega_f$ and the other is due to the bound-bound coupling $\Omega_b$. In order to ensure that the shift due to $\Omega_b$ dominates the one due to $\Omega_f$ it must be assured that

$$\xi \langle \phi_2 | \psi_v \rangle^2 \left| \frac{D_v}{\Delta} \right| \gg 1.$$  \hspace{1cm} (4.24)

For $v = 58$ and $\Delta = 500$ MHz, the value of this expression is $\sim 110$, and the square bracketed term in Eqn. 4.23 can be safely neglected. Using this fact and recovering the term $\Delta/(\Delta - E_B)$ for completeness yields the expression

$$E_B - E'_B = \frac{\Gamma_a^2}{2I_{sat}} \xi \langle \phi_2 | \psi_v \rangle^2 \left[ \frac{I_2}{\Delta} + \frac{I_1}{\Delta - E_B} \right].$$  \hspace{1cm} (4.25)
Figure 4.10  Measurement of light shift for the \( v = 58 \) vibrational level. The data points are the measured resonance centers obtained as described in the text. The dashed line is a linear regression with fitted slope of \(-61.4(24) \) MHz\(^2/(\text{W/cm}^2)^{-1}\) and a \( y \)-intercept of 12419.58(71) MHz.

for the total light shift when \( v = 58 \) is the intermediate state. This reduction of variables allows the data for different values of \( \Delta, I_1 \) and \( I_2 \) to be plotted on the same graph as shown in Fig. 4.10.

Plotting the data this way also allows for another measurement of the bound-bound matrix element \( \langle \phi_2 | \psi_v \rangle \). Fitting a line to the data and equating the slope to the prefactor in Eqn. 4.25 gives \( \langle \phi_2 | \psi_v \rangle = 0.164(3) \) compared to the value 0.162(2) obtained using the Autler-Townes measurement described above in Sec. 4.3.2. These two independent measurements differ by just over 1% and agree within their uncertainties. The uncertainty quoted here for the measurement of \( \langle \phi_2 | \psi_v \rangle \) comes only from the uncertainty in the fitted slope.

The fitted line in Fig. 4.10 also gives an estimate for the unperturbed binding energy \( E_B^0 = 12419.58(71) \) MHz. This measurement can be refined a bit by fitting the data which falls closest to the vertical line in Fig. 4.10 with a line of fixed slope, as given by the average of the two measurements for \( \langle \phi_2 | \psi_v \rangle \). This is valid because the shape of resonance spectra corresponding to those data are significantly less broad and distorted compared to the data further away from the vertical line, since they
Figure 4.11 Measurement of binding energy using \( v = 58 \) light shift data. The dashed line is a linear regression with fixed slope of \(-60.35 \text{ MHz}^2(\text{W/cm}^2)^{-1}\) and a y-intercept of 12420.17(1) MHz.

correspond to a combination of lower intensities and larger detunings. Fig. 4.11 shows the same data as above but for a significantly reduced range of values. The dotted line has fixed slope of \(-60.35 \text{ MHz}^2(\text{W/cm}^2)^{-1}\) and the fitted intercept gives \( E_B^0 = 12420.17(1) \text{ MHz} \). Even with this refinement, the measurement still has an uncertainty of just under 1 part in \( 10^6 \).*

The widths of the resonance lines and the magnitude of the light shift clearly decrease when the detuning is increased or the intensities are decreased. Working in this regime would allow the binding energy \( E_B^0 \) to be measured more precisely but also would require longer Raman pulse lengths \( \tau \). This should not be a problem, since the atoms will remain trapped for several minutes in the absence of light. In some sense, deeply bound intermediate states, such as \( v = 58 \), are ideal for measuring \( E_B^0 \) because the light shift only depends on the bound-bound coupling \( \Omega_b \) as discussed above. Unfortunately, this insight comes far after the measurement given above was made and more precise measurements with \( v = 58 \) were never obtained. All is not lost, however, because much more precise light shift data was obtained for \( v = 72 \) as

*The PLL synthesizer was not locked to the GPS reference for these data.
presented below, but the measurements are slightly more complicated.

4.4.2 Via $v = 72$ intermediate state

For $v = 72$, the condition Eqn. 4.24 does not hold rigorously and the approximation for the light shift given in Eqn. 4.25 cannot be used. Rather, the full expression of Eqn. 4.12 must be used, which does not reduce to a form that is convenient for displaying all the data simultaneously. The approach taken below, therefore, is to use the measured values of the resonance centers in combination with model calculations for the light shift to obtain a prediction of $E_B^0$ for every individual resonance scan. If our measurements of the resonance centers are accurate, and our calibrations for $I_1$, $I_2$, and $\Delta$ are accurate, and if the model is valid, then all the separate predictions for $E_B^0$ should line up. These are a lot of ifs. However, the model seems to be rigorous at least for the simple case of $v = 58$, and the values of $\langle \phi_2|\psi_n \rangle$ are bang on, as evidenced by the agreement of two independent measurements. The limitation on accuracy, therefore, should be our ability to measure the resonance centers and our calibration for the laser parameters. Consequently, it behooves us to use condensate loss spectra, in contrast to the total atom loss spectra used for $v = 58$, since the energy width of the condensate is negligible compared to the noncondensed atoms. In practice, this increased precision is not fully realized for $^7$Li condensates due to large fluctuations in the condensate number $N_0$, as discussed above in Sec. 4.3.3 and in Chap. 5. The spread in predicted values for $E_B^0$ which result from these fluctuations and any other uncertainties can be examined with a standard error analysis in order to determine a final value for $E_B^0$.

Data

Figure 4.12 shows three condensate loss spectra for differing values of $I_1$, $I_2$, and $\Delta$. Each data point was obtained by averaging five separate measurements of $N_0$ following a Raman light pulse. This is necessary since the condensate is probed
Figure 4.12  Condensate loss spectra for \( v = 72 \) resonance. The data points were obtained by averaging five separate measurements of \( N_0 \) following a Raman light pulse with the given laser difference frequency \( \Delta \nu \). The laser parameters \( I_1, I_2, \Delta, \) and \( \tau \) for the three plots are respectively: 6.25 W/cm\(^2\), 1.51 W/cm\(^2\), -280 MHz, and 40 ms (red circles); 4.13 W/cm\(^2\), 0.99 W/cm\(^2\), -400 MHz, and 60 ms (black squares); and 0.69 W/cm\(^2\), 0.41 W/cm\(^2\), -110 MHz, and 100 ms.

during the period of rapid growth and collapse cycles which result from the attractive interactions. The initial value of \( N_0 \) before the Raman pulse can therefore fluctuate between zero and the stability limit. Without averaging, these fluctuations would result in a very noisy resonance curve.

Notice that the displayed resonance curves are less than 10 kHz in width, with the narrowest being \( \sim 2 \) kHz. This is a consequence of using lower laser intensities compared to the resonances shown in Fig. 4.9 and of using the \( v = 72 \) resonance as the intermediate state instead of \( v = 58 \). Both of these changes result in a lower bound-bound scattering rate \( R_0 \) (see Eqn. 4.19) which reduces the width of the two-photon resonance. The asymmetry of the lineshape, most evident in the curve with the blue triangles, will be discussed in Chap. 7. For the purposes of this chapter, its only consequence is to introduce a possible systematic error in determining the resonance line center. For the following analysis, the measured binding energy \( E_B \) is identified as the difference frequency \( \Delta \nu \) which corresponds to the peak loss in each
Figure 4.13  Spread in measured binding energies as a function of photoassociation laser intensity $I_1$. The solid black circles correspond to calculations using Eqn. 4.12, and the error bars are the statistical sum of the uncertainties which contribute to $\delta_{ls}$, as described in the text. The red, open circles correspond to multiplying $\delta_0$ by a factor of 2/3 in the calculations (see text).

resonance curve.

The unshifted binding energy $E_B^0$ can be determined by calculating $E_B - \delta_{ls}$ for every value of the measured binding energy $E_B$, where $\delta_{ls} = \delta_0 - \delta_2$ is the total light shift. Figure 4.13 shows the results of 42 different measurements of $E_B$ and corresponding calculations of $\delta_{ls}$. The solid black circles use the form of Eqn. 4.12 for calculating the light shift and a systematic dependence on the photoassociation laser intensity $I_1$ is clearly observed. The dependence on $I_1$ comes from an overestimation of the redshift of level $\phi_0$. This cannot be remedied by including the terms due to the free-bound coupling $\Omega_p$ which were dropped from $\delta_0$ (see the discussion following Eqn. 4.8) since they have no measurable effect on the calculation*. Additionally, the measurements made at high values of $I_1$ for which the redshift in $\phi_0$ is largest, were also made with $\Delta < 0$. Therefore, the observed dependence on $I_1$ cannot be explained by assuming that the dropped terms are larger than predicted due to a miscalculation of $\langle \phi_0 | \psi_\nu \rangle$, since that would result in an even stronger dependence on $I_1$.

No systematic dependence is observed if $E_B - \delta_{ls}$ is plotted as a function of $I_2$ or

*Actually, the terms dropped from $\delta_0$ are included in the calculations here for completeness.
Δ, instead of I₁ as above. The dependence on I₁ must therefore originate from terms in the calculation of δₜᵣ associated with the free atomic coupling Ωᵣ. One possible explanation is that the polarization overlap ξ = 2/3 should be included in calculations for δ₀ given by Eqn. 4.8 just as in calculations for δ₂. The red open circles in Fig. 4.13 are the result of multiplying δ₀ by ξ, and the systematic dependence of Eᵦ − δₜᵣ is removed.† This is a phenomenological fix, however, because it is not understood why ξ should be included here since there are no restrictions on the selection rules for the atomic transition as there are for the molecular transitions. This issue needs to be resolved so that a proper form for δₜᵣ can be written.

In order to isolate the origin of this factor of 2/3 discrepancy, the contributions to δₜᵣ from the couplings Ωₚ, Ωₜ, and Ωᵣ are plotted in Fig. 4.14 against the laser intensities I₁ (Fig. 4.14(a)) and I₂ (Fig. 4.14(b)) for ν = 72.* Additionally, the photoassociation frequency shift discussed in Chap. 3 is plotted as a function of I₁ in order to demonstrate its magnitude for the same conditions. Clearly, the photoassociation frequency shift is too large to account for the discrepancy and it must therefore only apply to the excited state ψᵦ, as asserted above. The contribution from the coupling Ωₚ is essentially zero for both panels demonstrating that it can indeed be neglected when calculating the light shift. The contribution from Ωₜ is only important when changing I₂ and the largest contribution comes from Ωᵣ. This strengthens the notion introduced above that the discrepancy arises from the term corresponding to the coupling Ωᵣ. Further, the binding energy measurements for ν = 58 display no discrepancy between the data and the model. Since the light shift components from Ωₚ and Ωᵣ were completely ignored in those measurements, the model appears to hold rigorously for Ωₜ. In calculating the binding energies below, the “fixed” form

†A linear regression was applied to the data yielding a best-fit slope consistent with the factor of 2/3 to within the uncertainty in the fitted slope.

*In this figure, the light shift component Ωₜ is shown to be negative. This is because the bound level ν' = 10 does indeed shift to smaller values of energy due to the coupling Ωₜ for negative Δ, but the contribution to δₜᵣ is positive, by Eqn. 4.6.
Figure 4.14 Contributions of $\Omega_p$ (red line), $\Omega_b$ (green line), and $\Omega_f$ (black line) to light shift. (a) Light shift components and photoassociation frequency shift (blue line) as a function of $I_1$. (b) Light shift components as a function of $I_2$. In (a), the photoassociation frequency shift should be read off the right-hand scale and all other components should be read off the left-hand scale. This calculation was performed assuming $\Delta = -100$ MHz and $n = 5.7 \times 10^{12}$ cm$^{-3}$ corresponding to the peak condensate density for $N_0 = 1000$ atoms.

which includes the factor of 2/3 is used since it agrees best with the data.

Analysis

The uncertainties which contribute to the calculation of $\delta_{ls}$ need to be analyzed in order to compute an accurate value of $E_{B}^{0}$. To do this, the total light shift can be written in the form

$$\delta_{ls} = \alpha I_1 + \beta I_2$$

(4.26)
The coefficients $\alpha$ and $\beta$ are given by

$$
\alpha \simeq \frac{1}{I_{\text{sat}}} \frac{\Gamma_a^2}{2D_v} \left( \frac{1}{D_v + E_B} - \frac{\xi \langle \phi_2 | \psi_v \rangle^2}{\Delta} \right),
$$

where the term of order $1/E_B$ has been dropped in the expression for $\alpha$. The uncertainty in $\delta_{l_s}$ is calculated using

$$
\sigma_{l_s} = \sqrt{\alpha^2 \sigma_{l_1}^2 + \beta^2 \sigma_{l_2}^2 + I_2 \left( \frac{\partial \beta}{\partial \Delta} \right)^2 \sigma_{\Delta}^2}.
$$

Evaluating $\sigma_{l_s}$ requires knowledge of the measurement uncertainties in $I_1$, $I_2$, and $\Delta$.

The relative uncertainty in measuring either laser intensity is given by

$$
\frac{\sigma_I}{I} = \sqrt{\left( \frac{4r}{r_0^2} \right)^2 \sigma_r^2 + \left( \frac{4r^2}{r_0^3} \right)^2 \sigma_r^2 + \left( \frac{\sigma_{I_0}}{I_0} \right)^2}.
$$

The relation

$$
I = I_0 e^{-2r^2/r_0^2}
$$

for a laser beam with a Gaussian shaped intensity profile has been used, where $I_0$ is the peak intensity, $r$ is the transverse distance from the peak, and $r_0$ is the Gaussian 1/e$^2$ beam radius. The term proportional to $\sigma_r^2$ will account for the fact that the pointing of the combined beam containing both lasers used for the Raman pulse drifts slowly with time. By imaging both the combined beam and the atom cloud, their overlap can be monitored, and in practice, the overlap is re-optimized when the transverse displacement of the condensate position from the laser beam center axis is more than about $r_0/4$. This gives $\sigma_r = r_0/4$ and it is reasonable to assume that on average the transverse displacement of the condensate from the beam axis is $\sigma_r/2$ giving $r = r_0/8$. A 5% uncertainty in $r_0$ is estimated from repeated measurements of $r_0$ over many weeks of experimental runs and from the fact that there is often a
slight asymmetry between the measured values of \( r_0 \) along two transverse axes. This gives \( \sigma_{r_0}/r_0 = 0.05 \). Finally, using

\[
I_0 = \frac{2P}{\pi r_0^2}
\]

(4.31)

where \( P \) is the laser power, gives

\[
\left( \frac{\sigma_{I_0}}{I_0} \right)^2 = \left( \frac{\sigma_P}{P} \right)^2 + 4 \left( \frac{\sigma_{r_0}}{r_0} \right)^2 .
\]

(4.32)

Technicians at Newport Corporation testify that the calibration of the power meter used for these measurements is only good to \( \sim 10\% \), giving \( \sigma_P/P = 0.1 \). With all these considerations, the relative uncertainty in the laser intensity is calculated to be

\[
\frac{\sigma_I}{I} = 0.2 .
\]

The absolute uncertainty in measuring the value of \( \Delta \) is discussed in App. B. For the \( v = 72 \) intermediate state, the uncertainty is estimated as \( \sigma_\Delta = 5 \) MHz. Evaluating Eqn. 4.29 for each measurement of \( E_B \) gives the error bars shown in Fig. 4.13. Since the error bars are not all of similar size, a weighted mean, rather than a simple average, should be used to extract the most precise value of \( E_B^0 \). The weighted mean of a quantity \( \kappa \) is given by [45]

\[
\bar{\kappa} = \frac{\sum_i (\kappa_i / \sigma_i^2)}{\sum_i (1/\sigma_i^2) } ,
\]

(4.33)

where \( \sigma_i \) is the uncertainty in the \( i \)th measurement of the quantity \( \kappa \). The uncertainty in the weighted mean is

\[
\sigma_{\kappa} = \frac{1}{\sum_i (1/\sigma_i^2) } .
\]

(4.34)

Applying these formula to the measurements above yields

\[
\bar{E}_B - \delta_{t_e} = 12420.16986(8) \text{ MHz}. 
\]

The mean field shift \( \delta_{mf} = -420 \pm 140 \) Hz calculated in Sec. 4.3.3 should be included to obtain the final measured value of \( E_B^0 \). The uncertainty in \( \delta_{mf} \) is independent of
the light shift measurement and should therefore be added in quadrature. Applying the relation

$$E_B = E_B^0 + \delta_{ls} + \delta_{mf}$$

gives finally

$$E_B^0 (\nu' = 10) = 12420.17028(16).$$  \hspace{1cm} (4.35)

This is a \(\sim1\) part in \(10^8\) measurement of the binding energy. Systematic errors associated with identifying the precise location of the resonance peaks of the light shifted data will be discussed in Chap. 7.
Chapter 5  
Growth and collapse of the condensate

This chapter describes in detail our studies of the condensate growth and collapse dynamics. The stage will be set by describing our present theoretical understanding and some of our previous experimental results will be intermingled with the new in order to paint a more complete picture. The new measurements presented here are the direct observation of the condensate growth and collapse. These measurements were enabled by the Raman photoassociation technique described in Chap. 4 and have recently been published in Ref. [8]. This chapter also presents the results of some model simulations which are crucial to the interpretation of the experiment and which shaped our overall conclusions. For these simulations both Cass Sackett and Dmitry Strekalov must be thanked directly and profusely. The model itself was created by Cass and forms a good chunk of his Ph.D. thesis [16] as well as being integral to several papers dealing with both the collapse and the kinetics which govern evaporative cooling [7, 12, 18, 39]. Dmitry initially modified the model code in order to simulate the current experimental parameters, and to include the effect of the Raman laser pulse. Since the inner workings and success of this model are in no way attributable to me directly, its description here is in general terms except where important modifications have been made.

5.1 Theoretical background

As described in Chap. 3, interactions between ultracold atoms may be characterized by a single parameter, the s-wave scattering length $a$ [46]. The magnitude of $a$ indicates the strength of the interaction, while the sign determines whether the interactions are effectively attractive ($a < 0$) or repulsive ($a > 0$). The scattering length for $^7$Li is known to be $-1.45 \pm 0.04$ nm [27, 47].
5.1.1 Condensate metastability

The effects of attractive interactions on the condensate have been studied using mean-field theory [48]-[58]. In this approximation, the interaction part of the Hamiltonian is replaced by its mean value, resulting in an interaction energy of $U = 4\pi\hbar^2 an/m$, where $m$ is the atomic mass and $n$ is the number density [46]. Because $a < 0$, $U$ decreases with increasing $n$, making the gas mechanically unstable. This is the origin of the condensate collapse discussed in general terms in Chap. 1 and in more detail below. In a system with finite volume, however, the zero-point kinetic energy of the atoms provides a stabilizing influence.

The condensate is made up of atoms which are all in the same quantum mechanical state, and further, which have the same quantum mechanical phase. It can therefore be characterized by a wavefunction $\varphi(\vec{r})$ whose dynamics are well described by the non-linear Shröedinger equation (or Gross-Pitaevskii equation [59, 60])

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V(r) + U(r)\right) \varphi = 0. \quad (5.1)$$

Here $V(r)$ is the confining potential provided by the trap. In a spherically-symmetric harmonic trap with oscillation frequency $\omega$, $V(r) = m\omega^2 r^2 / 2$. The interaction energy $U(r)$ is determined by taking $n(r) = N_0|\varphi(r)|^2$.

Unfortunately, there is no exact solution to Eqn. 5.1. Several authors, including Kagan et al. [50], Shuryak [53], and Stoof et al. [55, 56], have considered the decay of the condensate resulting from attractive two-body interactions. The development by Stoof is particularly illuminating and involves approximating $\varphi$ by a Gaussian shaped wave function

$$\varphi(r; \ell) = \left(\frac{1}{\pi^{3/2}\ell^3}\right)^{1/2} e^{-r^2/2\ell^2}. \quad (5.2)$$

This approximation is reasonable, because the solution of Eqn. 5.1 for an ideal gas (i.e. $a = 0$) is a Gaussian function. For small $N_0$, therefore, $\varphi$ will be very similar to the ideal gas solution and as $N_0$ grows, the size of $\varphi$ as characterized by $\ell$ will shrink.
and the density \( n \) increases.

The maximum value of \( N_0 \) can be approximated by equating the magnitude of the interaction energy to the zero point energy in the trap

\[
\frac{4\pi h^2 a N_m}{m} |\varphi(r = 0; \ell = \ell_0)|^2 = \frac{\hbar \omega}{2},
\]

where \( \ell_0 = (\hbar / m \omega)^{1/2} \) is the Gaussian 1/\( e \) radius of the trap ground-state, and the maximum value of \( N_0 \) has been designated by \( N_m \). Substituting for \( \varphi \) from Eqn. 5.2 gives

\[
N_m = \frac{\sqrt{\pi} \ell_0}{4 |a|}.
\]

It is at first surprising that \( N_m \) increases proportional to \( \ell_0 \), since it is known that BEC cannot occur in a homogeneous gas. However, the density of the condensate, \( N_0 / \ell_0^3 \), tends to zero as \( \ell_0 \to \infty \). For our permanent magnet trap, \( \ell_0 = 3.16 \mu m \) [9] which gives \( N_m \sim 1000 \) atoms, in reasonable agreement with more accurate predictions of 1250 atoms obtained from numerical solutions of Eqn. 5.1 [48].

### 5.1.2 Collapse

The Gaussian ansatz for the condensate wave function \( \varphi \) described above can be inserted into Eqn. 5.1. A variational calculation can then be performed where the energy is minimized by varying the value of \( \ell \) [55]. The results of such a calculation are shown in Fig. 5.1. This graph can be interpreted by considering that in the variational calculation, the condensate wave function \( \varphi \) is completely parameterized by the length scale \( \ell \). The length parameter \( \ell \) can therefore be thought of as a quasi-particle moving along the appropriate potential curve shown, according to its occupation number \( N_0 \). As the fictitious particle moves in this potential, the density \( n \) increases and decreases accordingly. For the upper curve in Fig. 5.1, there is a metastable minimum in this quasi-particle potential near \( \ell = \ell_0 \) and a potential barrier separates this local minimum from a more dense phase. The condensate
Figure 5.1 Metastability of the condensate. The three curves are labelled with the different values of condensate number, $N_0$, used in the variational calculation. The vertical axis is scaled to $N_0\hbar \omega$, the energy of $N_0$ non-interacting condensate atoms in the lowest trap state. Graph from Ref. [12].

will be stable as long as it does not tunnel through or, by some thermal excitation, jump over the barrier. As $N_0$ increases, the quasi-particle potential barrier lowers until near $N_0 = 1250$ atoms when the barrier is completely flat. At this point, the attractive interactions overwhelm the repulsive zero-point energy and the condensate size rapidly shrinks. This is the collapse.

It should be noted that for the experiments reported here, the collapse is initiated before $N_0$ reaches the stability limit of $N_m \sim 1250$ atoms via macroscopic quantum tunnelling, or thermal excitation [39, 50, 53, 55, 58, 61], as mentioned above. Direct observation of macroscopic tunnelling of a Bose-Einstein condensate remains one of the most sought after goals in the field, and our experiments described below are an important first step in that direction.

Recent experiments in $^{85}$Rb, which also has attractive interactions, used a magnetically-tuned Feshbach resonance to suddenly switch the interactions from repulsive back to attractive by altering the sign and magnitude of $a$ [62, 63]. When switching back to
attractive interactions, the particular value of (negative) \( a \) was controlled precisely in order to study the onset of collapse very carefully. If the value of \( a \) were chosen in order to perch the condensate just below the stability limit, then the macroscopic tunnelling rates could be studied precisely. Unfortunately, large uncertainties in the initial value of \( N_0 \) (i.e. the value before the interactions are switched) made such studies impossible. In Chap. 6, an alternate technique for changing the interactions is discussed which uses laser light rather than a magnetic field.

By whichever means the collapse is initiated, the result is that the condensate size rapidly shrinks and the density \( n \) grows accordingly. This elevates the rate for two- and three-body inelastic collisions such as dipole relaxation and molecular recombination [39]. Since the latent heat associated with these inelastic processes is typically orders of magnitude larger than the containment depth of the trap, atoms are ejected from the condensate in an energetic explosion. As more atoms are ejected, the condensate density decreases towards pre-collapse values and the collapse may self-arrest.

It is not presently understood whether this arrest occurs at all, or if so, whether the remainder is large enough to detect. Some recent theoretical results by Saito and Ueda [64] indicate that only about 20\% of the condensate atoms are lost in a collapse. However, they also point out that the condensate wave function after the collapse looks nothing like the pre-collapse form. In fact, the post-collapse wave function can be thought of as a superposition of many different trap eigenstates rather than consisting of just the lowest one. Those authors show that the overlap integral between the pre-collapse and post-collapse wave functions \( \langle \varphi_i | \varphi_f \rangle \) is roughly 20\%. In our experiments described below and in Refs. [7, 8], we are only sensitive to this overlap since the thermal atoms which are always present "mask" any part of the condensate wave function which is not concentrated within the central peak of the spatial distribution. A separate theoretical development by Stoof also predicts
collapse remainders of roughly 20% [65].

The issue of condensate remainder is far from settled, however, and many competing theories still exist. Additionally, the $^{85}$Rb experiments described above [62, 63] indicate that for their conditions, collapse remainders of ~50 to 60% are most likely. This agrees with the theoretical predictions of Refs. [50, 61]. In these experiments, however, the condensates are initially prepared with few thermal atoms. They are therefore sensitive to the full spatial extent of the post-collapse condensate.

Upon combining the results of these theoretical treatments, the rubidium experiments, and our lithium ones described below, it seems that the most likely scenario is the following: The collapse does not eject all the condensate atoms from the trap. Many (if not most) of the remaining atoms, however, are in a spatial state which does not correspond to that of pre-collapse. Whether these atoms can be considered part of the condensate is an open question which can only be determined by testing some coherence property of the post-collapse wave function. The overlap integral $\langle \varphi_l | \varphi_f \rangle$ would seem to depend on the particular geometry of the confinement potential. This could be an interesting topic for investigation in electromagnetic traps whose tightness can be altered by varying the magnetic field strength.

In closing this section, I note that the physics which determines both the stability condition and the dynamical process of collapse for the condensate, draws some interesting comparisons to a star going supernova [56], even though the time, length, and energy scales for these two phenomena are vastly different. In the stellar case, the stability criterion is provided by a balance between the pressure due to the quantum degeneracy of electrons which make up the star and gravitational attraction. If the mass of the star exceeds the stability limit [66], the star collapses, releasing nuclear energy and triggering a violent explosion. The quantum "Fermi pressure" which initially maintains the force balance within the star has recently been observed in our lab in a gas of ultracold $^6$Li atoms [67].
5.1.3 Non-equilibrium kinetics

In all the experiments described below, there are an abundance of thermal, non-condensed atoms which coexist with the condensate. It is expected, therefore, that following collapse, the condensate will regrow as it is fed via collisions between the thermal atoms [12, 39, 61, 68]. In order to study this nonequilibrium behavior of the condensate, a kinetic model was developed by Cass Sackett which simulates the redistribution of atoms over the energy states of the trap using the quantum Boltzmann equation [7, 12, 16, 39]. The quantum Boltzmann model was initially developed in order to optimize the efficiency of forced evaporation in the permanent magnet trap and was later adapted to simulate the growth and collapse cycles following the microwave quench pulse described in Sec. 4.2. For the latter application, the calculated rates for initiation of condensate collapse via macroscopic quantum tunnelling and thermal fluctuation are used.

Growth and collapse cycles

Condensate growth is initiated by cooling the gas below the critical temperature \( T_C \) for BEC. In our, and virtually all other BEC experiments, the gas is cooled into the quantum degenerate regime using forced evaporative cooling, as described in Chap. 2. As the evaporation cutoff frequency is lowered, the gas pushes towards thermal equilibrium via elastic collisions which redistribute the energy among the remaining atoms. If cooling continues into the degenerate regime, \( N_0 \) will grow until the stability limit is reached and the condensate will then collapse. For our typical experimental conditions, the equilibrium distribution of a Bose gas below the critical temperature yields a value of \( N_0 \) larger than the stability limit. Further cooling, therefore, displaces the gas from thermal equilibrium and the condensate alternately grows and collapses many times as the gas equilibrates.

This intuitive picture of the condensate kinetics is confirmed by the quantum
Figure 5.2  Simulated trajectories for condensate evolution. The rapid growth and collapse cycles observed at short times slow down and eventually cease as the gas equilibrates. The three curves shown correspond to slightly different initial conditions, simulating experimental variations. The inset shows an expanded view of one trajectory at early times, on the same vertical scale. Graph from Ref. [7].

Boltzmann simulation. Figure 5.2 shows three model trajectories of condensate evolution for slightly different initial conditions. In these simulations, the kinetics of the gas is followed all the way through the evaporative cooling cycle from the time evaporation is initiated with \( N \sim 2 \times 10^8 \) atoms at \( T \sim 250 \) \( \mu \)K. The gas is then quenched at \( \tau = 0 \) in order to simulate the microwave razor pulse, as described in Sec. 4.2. The razor pulse leaves the gas far from equilibrium with a total number \( N \sim 4 \times 10^4 \) atoms. After the razor, the gas is allowed to evolve freely within the trap. The differences in the three simulated trajectories reflect experimental variations in the initial values of \( N \) and \( T \) as well as the stochastic nature of the collapse initiation process.

The growth and collapse cycles will persist while the gas approaches thermal equilibrium. At some point, the rate of condensate growth will be balanced by the rate of decay due to inelastic collisions, and a broad peak in \( N_0 \) is observed. Thereafter, \( N_0 \) decreases slowly as the inelastic losses become dominant. Note that in these simulations, \( N_0 \) is set to zero following the theoretical treatment of Stooft Ref. [55]. As
discussed above, however, this may not correspond to physical reality. The assumption of complete collapse is preserved here in order to draw the closest comparisons with previous work [7].

Focus on growth

The inset of Fig. 5.2 shows one model trajectory expanded for short times. Close inspection of this region reveals that after a collapse, the initial growth of the condensate is slow. This is due to the quantum-statistical effect known as Bose enhancement: the condensate growth rate scales roughly with $N_0$. Following a collapse, the condensate is assumed to be completely depleted and therefore Bose enhancement factors are not important. As the condensate fills, the enhancement factors become larger and the growth accelerates. This should lead to an exponential growth curve, which is not, however, observed in the model trajectories. Instead, the growth becomes linear after an initial acceleration phase.

As depicted in Fig. 5.3, the growth rate depends sensitively on the population of atoms in energy levels which are near the trap bottom, and hence, closest to the condensate energy. The population in these low-lying levels depletes quickly, since these levels have the largest collisional transition rates to the condensate and since such condensate feeding collisions are Bose enhanced. When they are depleted of population, condensate growth is then limited by collisional transitions from higher trap levels that repopulate the low-energy levels, which in turn, rapidly fill the condensate. Bose enhancement never plays a role in these ‘trickle down’ collisions since the low-lying levels never build up an appreciable population. The ‘trickle-down’ rate, therefore, only depends on the density $n$, which is roughly constant over the period of one growth/collapse cycle. From this physical picture, the condensate growth rate is expected to be linear for a particular growth cycle and the slope of each successive cycle should decrease. This is confirmed by the model trajectories shown in Fig. 5.2.
**Figure 5.3** Condensate growth kinetics. Collisions between atoms in the low-lying levels produce condensate atoms with high probability since such transitions are Bose enhanced. The low-lying levels must be repopulated via collisions between atoms in high-lying levels. These 'trickle down' collisions are not Bose enhanced and therefore act as a bottleneck for condensate growth.

### 5.2 Statistical evidence of growth and collapse

Direct measurements of the condensate growth and collapse dynamics pose a significant challenge for two principle reasons. First, as described in Chap. 2, the condensate is destroyed during imaging, so only one measurement of $N_0$ can be obtained per evaporative cooling cycle. This prevents successive pictures of the condensate to be strung together as a real-time movie of the growth and collapse dynamics. Secondly, the experimental variations in the initial values of $N$ and $T$, as well as the stochastic nature of the collapse initiation process, cause successive repetitions of the same experiment to yield different trajectories for $N_0$. This is demonstrated in Fig. 5.2 for just three variations in initial conditions. If many more of these trajectories are superposed, each with a slightly different initial phase and rate of growth, it becomes clear that at a given time $\tau$, $N_0$ can take on any value between 0 and $N_m$. 
5.2.1 Condensate distributions

Given these difficulties, it should still be possible to extract information about the shape of the growth and collapse curve from repeated measurements of $N_0$ for a given evolution time $\tau$. This is because the probability for obtaining a given value of $N_0$ at a time $\tau$ when the growth and collapse cycles persist is inversely proportional to the rate of growth: $P(N_0) \propto 1/G(N_0)$ [7]. Measurements of the distribution in $N_0$ values can be compared with a model probability distribution generated by inverting the growth cycles shown in Fig. 5.2. Such a model distribution is peaked at low values of $N_0$ since the condensate grows slowly immediately following a collapse. Additionally, the model distribution is lower and flat for $N_0 \gtrsim 150$ atoms with a sharp cutoff near $N_0 = 1250$ atoms.

The upper panel in Fig. 5.4 shows the distribution of measured $N_0$ values for a delay of $\tau = 5$ s following the application of the microwave quench pulse*. The distribution is broadly spread between $N_0 \approx 100$ atoms and $\sim 1250$ atoms†, in qualitative agreement with the quantum Boltzmann simulation. This confirms both the general model of condensate growth and collapse and the theoretical prediction for the stability limit of $N_m = 1250$ atoms. In contrast to the model predictions, however, there are relatively few measurements with small $N_0$ and there is no sharp cutoff in the distribution at high $N_0$. Additionally, there is no flat region for the intermediate range of $N_0$ values.

The lack of small condensates in the measured distribution can be explained if the collapse does not completely empty the condensate, but rather leaves a small remainder behind. The model distribution generated by replacing the complete condensate collapse by a Gaussian distributed collapse remainder of $200 \pm 100$ atoms, gives reasonable agreement with the left side of the measured distribution [7, 16]. This also

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*The microwave quench pulse forces the gas far from equilibrium at a particular instant providing a convenient time marker to follow the free evolution. For more, see Refs. [7, 16].
†For these data, the statistical uncertainty in $N_0$ was $\sim 75$ atoms.
Figure 5.4 Measured distribution of condensate occupation number. The upper distribution corresponds to an equilibration time of 5 s following a microwave quench pulse while the lower corresponds to 60 s. Graph from Ref. [7].

agrees quantitatively with the theories in Refs. [64, 65], which predict measurable condensate remainders of $\sim$20% as described above. The data also agrees qualitatively with Refs. [50, 61] which predict finite condensate remainders. However, those references predict $\sim$50% remainders while the measured distribution shows a large fraction of the data with $N_0 < 600$ atoms, and some clouds with $N_0 \sim 50$ atoms are observed. Again, the concept of condensate remainder is a bit nebulous in the context of these theories because of the issue of being able to detect, or even consider, a condensate wave function which is a superposition of trap eigenstates. It appears, however, that the one theory which can categorically be ruled out is that of Ref. [55]
which predicts a complete collapse with no remaining condensate atoms. This conclusion is strengthened further by the results of directly measuring the growth and collapse dynamics as described below.

The measured distribution also lacks the low, flat region predicted by the quantum Boltzmann simulation nor the sharp cutoff at \( N_0 \sim N_m \). Rather, the measured distribution exhibits a broad peak which may indicate that the condensate growth continues to accelerate [7]. This is consistent with the exponentially increasing growth rate predicted by Bose enhancement, since in that case, the condensate growth rate does not saturate, and the sharp cutoff at \( N_0 \sim N_m \) would then be absent. It is also consistent with the depression of the condensate energy with increasing \( N_0 \) due to mean-field effects [16]. This issue will be revisited below when the direct observation of condensate dynamics is described.

### 5.2.2 Persistence of collapse cycles

For equilibration times longer than \( \tau = 5 \) s, the measured distribution of \( N_0 \) will continue to be broadly spread, until (on average) the growth and collapse cycles desist. For the conditions of Fig. 5.4, the last collapse occurs at \( \tau \sim 30 \) s. This time scale is confirmed by the model trajectories shown in Fig. 5.2. For equilibration times longer than this, the distribution becomes weighted towards lower values of \( N_0 \) as the rate for inelastic losses starts to balance and finally dominates the rate of condensate growth. The lower histogram in Fig. 5.4 shows the measured distribution for \( \tau = 60 \) s.

A particularly clear way of understanding the persistence of the growth and collapse cycles is to examine the ratio \( N/N_C \), where \( N \) is the total number of atoms in the cloud and \( N_C = 1.2 (k_B T/\hbar \omega)^3 \) is the critical number for BEC at temperature \( T \), where \( k_B \) is the Boltzmann constant and \( \omega \) is the oscillation frequency for a harmonic trapping potential. This ratio is a measure of the degeneracy of the distribution,
Figure 5.5  Relaxation of a degenerate gas of $^7$Li atoms to equilibrium. The gas reaches equilibrium when $N/N_C \approx 1$ since, for typical experimental parameters, $N_m \ll N$. Graph from Ref. [7].

and for an ideal gas (or one with repulsive interactions) in thermal equilibrium, it is trivially related to the condensate number by $N_0/N \equiv 1 - N_C/N$. For a gas with attractive interactions, such as $^7$Li, this would give the equilibrium condensate size if $N_m > N$. For most experimental circumstances, however, $N_m \ll N$ and condensate growth, punctuated by intermittent collapses, will continue as long as there is an excess of noncondensed atoms compared to a thermal distribution ($N/N_C > 1$). Figure 5.5 shows the measured ratio $N/N_C$ as a function of $\tau$ for the same conditions as the measured distributions above. Equilibrium is obtained when $N/N_C \approx 1$, approximately 50 s in this case. This time scale is long compared to the elastic collision time of $\sim 1$ s, suggesting that the constraint on condensate size poses a significant bottleneck for equilibration. The equilibration time scale agrees well with the observed change in shape of the distributions shown in Fig. 5.4. This strengthens the conclusion that the observed variation in $N_0$ values is related to condensate dynamics, rather than experimental uncertainties, since the distribution changes at approximately the same time that the population imbalance driving condensate growth is eliminated.
5.3 Direct observation of growth and collapse

In order to directly measure the condensate dynamics, the growth and collapse trajectories for separate repetitions of the experiment, such as those shown in Fig. 5.2, must be synchronized at a particular point in time. This is accomplished by dumping the condensate at a specific time, using the Raman photoassociation pulse described in Chap. 4. Reducing the value of $N_0$ in this way also reduces the spread in $N_0$. Further, the narrow linewidth of the Raman transition allows the condensate to be selectively removed while only minimally affecting the thermal atoms. The remaining thermal atoms therefore repopulate the condensate through collisions and the growth/collapse dynamics are obtained by repeating the experiment and measuring $N_0$ at different delays following the dump pulse.

5.3.1 Procedure

Before the condensate is dumped, the gas is first evaporatively cooled to degeneracy and the microwave sweep is halted 100 kHz above the trap bottom. This leaves $N \sim 3 \times 10^5$ atoms at $T \sim 350$ nK. After a 2 s delay*, a microwave quench pulse of depth 84 kHz and 100 ms in duration is applied which reduces the number to $N \lesssim 10^5$ atoms at $T \lesssim 200$ nK. The quench pulse gives the phase-space density a good kick in order to help speed up the growth and collapse cycles and reduces $N$ to a level at which the condensate is distinguishable. The dump pulse is applied several seconds (typically, between 2 and 5 s) after the microwave quench pulse. The delay is short enough to ensure that the growth and collapse cycles are still rapid but long enough to facilitate an accurate fit to the nonequilibrium Bose-Einstein distribution function.

*We observed that when the atom loading conditions are sufficient to use our currently fastest evaporation trajectory (opt37: $N_i = 10^5$; $T = 500$ nK), the condensate starts to grow only after a short delay following the completion of evaporation. Therefore, a delay of 2 s was inserted between attainment of the evaporation stop frequency and application of the quench pulse. During this time period, the microwaves are maintained at the stop frequency with a power corresponding to the end of the trajectory.
Figure 5.6  Condensate loss spectrum after a two-photon photoassociation pulse. Each data point is the mean of 5 separate measurements and the error bars are the uncertainty in that mean. The horizontal axis is the difference frequency between the two lasers $\Delta \nu$ subtracting the offset frequency $\nu_0 = 12,420$ MHz. The arrow highlights the value of $\Delta \nu$ used for dumping the condensate. The laser intensities are $I_1 = 1.56$ W/cm$^2$, $I_2 = 0.47$ W/cm$^2$, and the detuning from the $\nu = 72$ intermediate-state resonance is $\Delta = -100$ MHz.

(Eqn. 2.1).

In order to dump the condensate, a Raman photoassociation pulse is used (see Chap. 4). The frequency difference $\Delta \nu$ between the two lasers of the dump pulse is tuned in order to interact primarily with the condensate, while minimally perturbing the thermal atoms. Figure 5.6 shows a sample two-photon spectrum of condensate loss and the arrow highlights the particular value of $\Delta \nu$ maintained for the dump pulse.

As demonstrated above, if the population imbalance which drives condensate growth is eliminated such that $N/N_C \approx 1$, no further collapse cycles will be observed. Therefore, the number of atoms removed during the dump pulse must be minimized. The narrow width of the two-photon spectrum and the sub-Hz phase-lock precision enable extreme energy selectivity. This is demonstrated in Fig. 5.7, which shows both the measured condensate fraction and the fraction of total atoms remaining after a dump pulse as a function of the pulse duration. For this graph, $\Delta \nu$, $I_1$, $I_2$, and $\Delta$ all
Figure 5.7  Energy selectivity of the dump pulse. The fraction of remaining condensate atoms (solid squares) and total atoms (open circles) is plotted as a function of the dump pulse duration. Each data point is an average of five separate experiments normalized to measurements taken without the dump pulse. Graph from Ref. [8].

correspond to Fig. 5.6 above.

5.3.2 Collapse

Following the dump pulse, the gas is allowed to freely evolve for a certain time, at which point a destructive measurement of $N_0$ is made. Figure 5.8(a) shows the dynamical evolution of the condensate following a dump pulse whose duration is set to 40 ms, reducing $N_0$ to an initial value of $\sim$100 atoms. The dump pulse parameters for this plot correspond to those of Fig. 5.6. $N_0$ increases immediately following the dump pulse as the condensate is fed via collisions between noncondensed thermal atoms. After $\sim$450 ms, $N_0$ reaches a maximum value consistent with $N_m \approx 1250$ atoms, and the subsequent reduction is a clear demonstration of collapse. After the collapse, $N_0$ grows again, since the gas is not yet in thermal equilibrium.

The raw data used to generate the averages are shown in Fig. 5.8(b). The spread in $N_0$ values displayed is reflected in the error bars of Fig. 5.8(a). For growth times between $\sim$500 and 700 ms, corresponding to predominantly post-collapse ensembles, several clouds are observed with $N_0$ between 150 and 250 atoms. This is consis-
Figure 5.8 Condensate growth and collapse dynamics. (a) Each data point is the mean of 5 measurements for the same growth time following the dump pulse and the error bars are the standard deviation of the mean. The dashed line is obtained from the same data set, employing the selection technique described in the text. (b) Raw data used for the average in (a). There is a 3 s delay following the microwave quench pulse before application of the dump pulse. For these data, $N = (7 \pm 1) \times 10^4$ atoms and $T = (170 \pm 15)$ nK immediately before the dump pulse. Graph from Ref. [8].

tent with the theoretical predictions described above and with the statistical data displayed in Sec. 5.2.1. Note that the significance of the data points which show $N_0 > 1250$ atoms is low since there is a systematic uncertainty of $\sim 20\%$ in the measured value of $N_0$ [7, 16].

The variations in the initial condensate growth rate immediately following the dump pulse that are observed in Fig. 5.8(b) tend to soften the growth curve shown in Fig. 5.8(a). This effect can be investigated by observing the population imbalance,
Figure 5.9  Population imbalance as a function of growth time. The solid line is a linear fit with a slope of $-0.47 \text{ s}^{-1}$ and y-intercept of 4.04. The dashed lines gives the range of data used for the selection procedure described in the text.

$N/N_C$, for the data shown. In Fig. 5.9, $N/N_C$ is plotted as a function of growth time for all the data shown in Fig. 5.8(b). The population imbalance immediately after the dump pulse is $N/N_C = 3.8 \pm 0.1$ and this value does not decrease appreciably for the range of growth times plotted. This imbalance drives the condensate growth as described above. The solid line displayed in Fig. 5.9 is a linear fit to the data with fitted parameters as given in the figure caption. The dashed lines show the approximate standard deviation of $N/N_C$ values calculated from the data in the range between 800 ms and 1200 ms. The data which fall between the dashed lines are selected and their average values are used to generate the dashed growth curve in Fig. 5.8(a). The selected data should correspond to a more narrow distribution of initial condensate growth rates, compared to the full data set. The dashed growth curve displays all the same features as the one generated from the full data set, but shows a much sharper decrease at the point of collapse. This is intuitively satisfying, since, in the limit of a uniform growth rate for all data points, the only variation in the time of collapse is due to small variations in $N_0$ immediately following the dump pulse and the stochasticity of the collapse initiation mechanisms discussed above.
**Figure 5.10** Partial two-photon spectrum with altered dump pulse frequency. The horizontal axis is the difference frequency between the two lasers $\Delta \nu$ subtracting the offset frequency $\nu_0 = 12,420$ MHz. The arrow highlights the new dump pulse frequency employed to remove less atoms from the low energy levels. The intensities for the photoassociation and Raman lasers are $I_1 = 1.76$ W/cm$^2$, $I_2 = 1.13$ W/cm$^2$, and the detuning from the $\nu = 72$ intermediate-state resonance $\Delta = -100$ MHz.

### 5.3.3 Persistence of collapse cycles

As described above, the condensate growth rate depends sensitively on the population of atoms in the low-lying energy levels just above the condensate energy. Atoms in these levels have the largest collisional transition rates to the condensate and therefore fill it most quickly. It should be expected, therefore, that when fewer low energy atoms are removed by the dump pulse, the condensate will initially grow more quickly. Additionally, the condensate growth and collapse cycles should be more rapid. This may allow for the observation of several cycles before the dephasing of individual trajectories occurs.

In order to remove fewer low-energy atoms, the parameters of the dump pulse must be altered from those corresponding to Fig. 5.6. Figure 5.10 shows a partial Raman photoassociation spectrum with a new dump pulse frequency indicated by the arrow. As discussed in Chap. 7, lower values of $\Delta \nu$ correspond to probing lower energies in the trap. By tuning $\Delta \nu$ to the red (lower energy) of the peak in the $N_0$ loss
Figure 5.11  Condensate dynamics with increased growth rate. There is a 5 s delay following the microwave quench pulse before application of the dump pulse. For these data, \( N = (1.0 \pm 0.1) \times 10^5 \) atoms and \( T = (200 \pm 20) \) nK immediately before the dump pulse. Graph from Ref. [8].

spectrum, the dump pulse is detuned further away from the low energy atoms which most strongly fill the condensate. Fewer low energy atoms are therefore removed and the condensate fill rate should increase. Of course, the two-photon probe also interacts less with the condensate, and in order to reduce \( N_0 \) appropriately, the duration of the dump pulse must be extended.

The growth curve shown in Fig. 5.11 was obtained using the new dump pulse parameters for a pulse time of 100 ms (compared to 40 ms for Fig. 5.8). Compared to the condensate reduction in Fig. 5.8, significantly less atoms are removed from the condensate using the new dump parameters, and presumably, less atoms are removed from the low-energy levels as well. For these conditions, the condensate grows more quickly than for the conditions in Fig. 5.8. Furthermore, three growth and collapse cycles are now observed on average in contrast to Fig. 5.8 which displays, on average, only two growth cycles.
5.3.4 Condensate growth

The ability to preferentially remove the condensate provides the opportunity to study its growth in detail. As described above, the quantum Boltzmann model predicts an initial acceleration phase followed by linear growth: whereas Bose stimulation alone would give an exponential growth curve. In either case, the growth curve will eventually saturate if \( N_0 \) is allowed to approach its equilibrium value \([69]-[71]\) as given by \( N_0/N \equiv 1 - N_C/N \). As discussed above, however, the limit on \( N_0 \) for the case of \(^7\)Li guarantees that this saturation will not occur while the growth and collapse cycles persist.

Several authors have theoretically studied the kinetics of condensate formation (e.g. Refs. [70]-[73]) and Miesner et al. [69] have studied the dynamics of condensate growth experimentally in a gas of sodium atoms. The sodium experiments observe the saturation in growth mentioned above and their growth curves are well fit by the functional form [69]

\[
\dot{N}_0 = \gamma N_0 \left[ 1 - \left( \frac{N_0}{N_{0,eq}} \right)^{2/5} \right], \tag{5.5}
\]

where \( \gamma \) is the initial growth rate and \( N_{0,eq} \) is the equilibrium number of condensate atoms. This functional form is consistent with an approximate microscopic theory for the condensate growth [70] which also predicts the exponent \( 2/5 \). Note that when \( N_0 \ll N_{0,eq} \), as is the case for \(^7\)Li during growth and collapse cycles, then the form of Eqn. 5.5 reduces to that of pure Bose enhancement and exponential growth is expected.

In order to study the initial stages of growth, the condensate is dumped completely (to within the resolution of the imaging system), and the subsequent growth is measured. Figure 5.12 shows a high resolution growth curve for a 30 ms dump pulse which reduces \( N_0 \) to \( \sim 50 \) atoms. The measured growth curve is initially flat following the dump pulse and subsequently accelerates and then becomes linear. A
Figure 5.12  Initial growth of the condensate. The data points show the mean of five measurements of \( N_0 \) for the given growth time following a 30 ms dump pulse with \( I_1 = 2.33 \) W/cm\(^2\), \( I_2 = 0.49 \) W/cm\(^2\), and \( \Delta = -100 \) MHz. The error bars are the uncertainty in that mean. The solid line is a portion of a simulated trajectory generated by the quantum Boltzmann model which has been scaled for comparison with the data as described in the text. The dashed line is an exponential fit to the first part of the scaled trajectory.

portion of a trajectory from Fig. 5.2, corresponding to one growth and collapse cycle, is used to compare the data to the results of the Boltzmann simulation. It would be extremely difficult and time consuming to generate a model trajectory whose time scale for a particular growth and collapse cycle exactly matches that of the data. For a given trajectory, however, the overall shape of a particular growth cycle is equivalent to any other such that if the time were scaled for each cycle appropriately, they would all be virtually indistinguishable. This fact is used in order to scale a particular growth cycle from Fig. 5.2 so that it matches that of the data shown in Fig. 5.12. Additionally, the \( N_0 \) values of the chosen trajectory are scaled in order to correspond to the reduced range displayed by the data. The range for these data are suppressed due to the effect of averaging discussed above and which is further investigated in the following section. The result of this horizontal and vertical scaling is shown as the solid line in Fig. 5.12. The dashed line is an exponential fit to the first part of the scaled trajectory demonstrating that the quantum Boltzmann model does indeed
predict exponential growth immediately following a collapse,* but that exponential growth does not continue. The data contradicts the theory of Ref. [70] (Eqn. 5.5) which predicts continued exponential growth while \( N_0 \ll N_{0,eq} \).

The agreement between the data and the scaled trajectory is quite good for the linear part of the growth. This confirms the notion that 'trickle down' collisions limit the condensate growth rate for the conditions shown. This does not agree, however, with the results of the statistical measurements of condensate distributions described above in Sec. 5.2.1. Recall that those measured distributions were observed to be inconsistent with the linear growth predicted by the quantum Boltzmann model. A suitable explanation for this discrepancy has not yet been uncovered.

The deviation of the data from the scaled simulation (and the exponential curve) for short growth times is an interesting issue, but may be an experimental artifact. When the dump pulse is applied, some atoms from the low energy levels will be removed in addition to the condensate. The energy selectivity of the dump pulse, demonstrated in Fig. 5.7, minimizes this loss, but does not suppress it entirely. Therefore, immediately after the dump pulse, the population in the low energy levels will be even more depleted than usual and the condensate grows very slowly. Once the 'trickle down' collisions establish some population in these levels, the condensate begins to grow more rapidly and soon after the expected linear growth is established.

5.3.5 Averaging

As mentioned above, averaging several measurements of the condensate growth tends to soften the growth curves shown in Figs. 5.8, 5.11, and 5.12. By multiply running the quantum Boltzmann simulation for varying initial conditions, the effect of this averaging can be investigated quantitatively. Each simulated trajectory should

*The exponential curve was fit to the simulated trajectory because fitting to the data points, even just the first few, gives the (false) impression that exponential growth is actually slower than the linear growth predicted by the Boltzmann model. This is due to the fact that the initial growth of the data is slower than exponential as discussed in the text.
start with slightly different initial conditions and the effects of the microwave quench pulse and the two-photon dump pulse should be included. The variation in initial conditions is chosen in order to correspond to observed variations in $N$ and $T$ at some point during the evaporation cycle. This observation point is usually taken to be the time just before the dump pulse is applied.

The simulated effect of the microwave quench pulse was built into the model by its creator Cass Sackett [7, 16, 39]. The population of atoms in energy levels above the razor cut are simply reduced to zero at a given time step of the numerical simulation. The effect of the two-photon dump pulse was written into the model by Dmitry Strekalov. The two-photon dump pulse is simulated by instantaneously reducing the population of atoms within a band of energies centered near the condensate energy. In particular, the populations are reduced according to

\[ \frac{N_{ad}}{N_{bd}} = \exp \left[ -\frac{Aw}{4(E - E_c)^2 + w^2} \right], \tag{5.6} \]

where $N_{ad}$ is the number of atoms remaining at energy $E$ after the dump pulse, $N_{bd}$ is the corresponding number before the dump pulse, $w$ is the width of the Raman transition, $E_c$ is the energy corresponding to the center frequency of the applied two-photon dump pulse (with respect to the condensate energy), and $A$ simulates how hard the Raman transition is driven. It should be noted that the number of atoms in the condensate $N_0$ is an additional free parameter in the dump simulation so that it can be set independently of the shape given by Eqn. 5.6. The Lorentzian width of the Raman transition is defined to be $\sim 250$ Hz which corresponds to the narrowest experimentally observed two-photon linewidths shown in Chap. 7.

In Fig. 5.13, the ratio $N_{ad}/N_{bd}$ is plotted as a function of the trap energy in frequency units. The points were obtained by dividing the energy level populations predicted by the simulations immediately after the dump pulse by those predicted immediately before the dump pulse. Note that the points are separated in frequency by $\sim 290$ Hz, instead of $145$ Hz (which corresponds to the average oscillation frequency
Figure 5.13  Simulated distribution of remaining atoms following a dump pulse. The points are the number of atoms remaining at a given trap energy following the dump pulse, $N_{ad}$, normalized to the population before the pulse $N_{pd}$. The solid line is the function Eqn. 5.6 with $A = 850$ Hz, $w = 250$ Hz, and $E_c = 100$ Hz.

in the trap). This is a feature of the model which allows the simulation to run faster on a computer. As described in Chap. 7, the measured 250 Hz linewidths may actually be an experimental artifact and using such a narrow width for the dump simulation might therefore be unmerited. The 100 Hz offset in the Lorentzian center is a deliberate attempt to account for the notion that the peak in the condensate loss spectrum, such as shown in Fig. 5.10, is offset slightly to the blue of the actual condensate energy. This was the prevalent theory when the dump pulse simulation was developed, but is now not so certain (see Chap. 7). This possible inaccuracy in the model is not observed to cause meaningful changes in the simulation results described below.

The broken curves in Fig. 5.14(a) are a sample of simulated trajectories of $N_0$ which include the effect of both the microwave quench pulse and the two-photon dump pulse, and Fig. 5.14(b) shows simulated trajectories of $N$. The dump pulse is simulated as shown in Fig. 5.13 and the microwave quench pulse is simulated by reducing to zero the population of atoms in energy levels above the razor cut at the appropriate time step of the numerical simulation. In the simulations, the quench pulse is applied 2 s after the end frequency for evaporation is obtained and the razor
Figure 5.14  Simulation of condensate dynamics. (a) The colored curves show individual trajectories of $N_0$ generated by the numerical quantum Boltzmann simulation and the heavy solid line is the mean of 40 of these trajectories. (b) Sample trajectories of $N$. Individual trajectories were generated by running the simulation for initial values of $N$ spaced evenly between $2.4 \times 10^8$ and $2.6 \times 10^8$ atoms. The resulting values of $N$ just before the light pulse range between $6 \times 10^4$ and $8 \times 10^4$ atoms, in agreement with the range of $N$ observed in the data. Graph from Ref. [8].

cuts out all atoms which have microwave spin-flip frequencies more than 16 kHz above the frequency corresponding to the trap bottom, in agreement with the experiment.

In the simulations, $N_0$ is set to 100 atoms immediately following the dump pulse in order to provide direct comparison with the data in Fig. 5.8(a). However, no rigorous attempt is otherwise made to quantitatively reproduce the data. Rather, the parameters for the dump pulse are chosen to give qualitative agreement with all
three sets of growth data. Additionally, $N_0$ is set to 200 atoms immediately following a collapse in order to achieve the best agreement with the measured distributions shown above in Sec. 5.2.1 and in Refs. [7, 16] and with the individual post-collapse data points in Fig. 5.8(b).

The discontinuous drop in $N$ at 0 ms corresponds to the dump pulse and all other sudden drops are due to condensate collapses. Clearly, the growth time needed for the first collapse following the dump pulse systematically increases for clouds with fewer atoms. However, there is some variation in the collapse point for clouds with similar $N$ caused by the stochastic nature of collapse initiation. These two mechanisms account for the dephasing of individual trajectories observed in Fig. 5.14(a). Similar dephasing is observed if in the model the initial conditions are held constant while the number of atoms remaining in the condensate following a collapse is allowed to vary within 200 ± 100 atoms. In any case, as the dephasing can be completely explained by observed experimental fluctuations coupled with the collapse stochasticity, the effect of a variation in collapse remainder is neglected. In addition, although there is a slight dephasing caused by variations in the number of condensate atoms which remain following the dump pulse, the effect is small compared to variations in initial conditions, and it is therefore neglected.

The heavy solid line in Fig. 5.14(a) represents the average of 40 individual trajectories generated by varying the initial conditions, as described above. The simulation average agrees well with the data in several respects. The simulation average demonstrates the same linear growth for larger values of $N_0$ that each individual trajectory displays. As discussed above, the data in Fig. 5.12 also demonstrate this linear growth, confirming the notion that non-Bose-enhanced trickle down collisions are responsible for the saturation in growth rate. In addition, the data in Fig. 5.11 show that each subsequent peak following the initial growth is slightly lower, as the trajectories corresponding to each individual measurement dephase from one another. This dephasing
causes the maxima (minima) to occur at smaller (larger) values of $N_0$ than for any individual trajectory. This behavior is seen in the simulation average confirming our understanding of the role of averaging in these measurements.
Chapter 6
Optically-induced Feshbach resonance

This chapter develops the formalism of optically-induced Feshbach resonances and describes our experimental work in this area using single-photon photoassociation, as described in Chap. 3. Our work on optically-induced Feshbach resonances using two-photon Raman photoassociation will also be described here. Many of the graphs and computations presented here for the single-photon optically-induced Feshbach resonance are summarized from the thesis of Cass Sackett [16]. This information is included in order for the chapter to be self-contained.

6.1 Introduction

To put this chapter into proper perspective, it must be said that, in some sense, the entire content of the thesis grew from the ideas presented here. We originally started doing photoassociation in a quantum degenerate gas with the idea that we would use it to alter the interactions between atoms in a Bose-Einstein condensate. This idea followed from a theoretical paper by Fedichev et al. which developed the theory for such a process and which used $^7$Li as a test case [32]. This got us very excited because we wanted to study the growth and collapse dynamics of $^7$Li BEC and we thought this tool could help us achieve that end. Mark Welling and Cass Sackett used the formalism developed by Fedichev to compute the necessary laser parameters for our experiment. Their work is central to this chapter, and I thank them both directly for their contributions. These calculations (presented below) indicated that the best use of this technique would be to reduce the maximum number of condensate atoms $N_m$, as given by the strength of the attractive interactions, by roughly a factor of three. This would allow us to study how many atoms were left in the condensate following a collapse and might even allow us to observe the collapse dynamics.
In the process of making the light-shift measurements described in Chap. 3, we determined that the experiment would not work (as planned) for technical reasons having to do with our limited laser power (see below). Since we were now set up to do photoassociation in the BEC apparatus, we decided to try and produce ultracold ground-state molecules via a two-photon stimulated Raman transition from the condensate. Our work on Raman photoassociation comprises the bulk of the remainder of this thesis. We spent a good year or so trying to trap molecules, without success but obtained some very nice tangential results along the way. Chapter 5 describes our use of Raman photoassociation to directly observe the very growth and collapse dynamics of $^7$Li condensates which started us on photoassociation with BEC in the first place. Additionally, later in this chapter, some new results are presented which deal with using Raman photoassociation to alter the interatomic interactions, in analogy with the single-photon case originally envisioned.

6.2 Motivation

It would be useful for many reasons to have the ability to alter the interactions between atoms in an ultracold gas. In particular, the ability to make these alterations by using laser light would be, in many ways, far superior to using magnetic fields, for instance, because the frequency, intensity, direction, and pulse times of laser beams can be tuned so easily. In addition, a focused laser beam can be made to illuminate only a portion of an ultracold atomic sample, thereby enabling studies of spatially varying interactions. For these general reasons, it is highly desirable to pursue the development of optically-induced Feshbach resonances.

More specifically, the ability to increase the magnitude of the $s$-wave scattering length $a$ could increase the efficiency of forced evaporative cooling. This would not only reduce the repetition time of BEC experiments (our experiment has a rep rate of $\sim 2$ minutes due to limits on the evaporation rate imposed by the magnitude of $a$),
but would also be a significant step towards the development of a quasi-continuous atom laser. The "pie in the sky" idea is to make the evaporation rate be much larger than the load rate of atoms into the trap so that the sample can be cooled while the trap is being loaded. This might require the region of increased $|a|$ to be spatially confined to a particular region within the larger cloud of atoms, something which is possible with a focused laser beam. In this same spirit, it would be extremely interesting in its own right to study the dynamical behavior of an ultracold sample with a spatially varying value of $a$; an "interaction mask" if you will.

Another, perhaps more realistic goal, is to use an optically tuned Feshbach resonance, instead of a magnetically tuned one, in the context of the degenerate Fermi gas experiment currently underway in our lab. One of the goals for that experiment is to observe a BCS-pairing transition between quantum degenerate fermions ($^6$Li). As of the writing of this thesis, that experiment has achieved quantum degeneracy [67] and is pushing towards the BCS goal by implementing an optical dipole-force trap. In order to obtain the BCS transition at reasonable temperatures, it may be necessary to increase the magnitude of $a$, even though it is already very large ($a \sim -1600 a_0$ for a particular superposition of internal states [74]). A larger magnitude tunable scattering length can be achieved using a magnetically tuned Feshbach resonance. This would require building a new electro-magnetic trap capable of supplying the required magnetic field strength; not an easy task. If an optically tuned Feshbach resonance could be used, it would only require a laser beam (or possibly two) to be directed onto the trapped atoms.

The original motivation for this work is the possibility of using an optically tuned Feshbach resonance to study the collapse dynamics of Bose condensates with attractive interactions. This has already been accomplished for $^{85}$Rb using a magnetically tuned Feshbach resonance [62, 63]. Our direct observations of the growth and collapse of $^7$Li condensates, as described in Ref. [8] and Chap. 5, sheds much light on the
issue, but much more can still be learned about the nature and rates of collapse initiation. For example, the collapse is thought to be initiated by macroscopic quantum tunnelling or thermal fluctuation [39, 55, 58], and the measurement of rates for such mechanisms is important. The only real hope (a dim one) for such measurements is to use a Feshbach resonance in order to control the value of the scattering length $a$. For $^7$Li in the spin-triplet state, there are no magnetic Feshbach resonances within the range of currently achievable magnetic field strength, necessitating the use of an optically-tuned Feshbach resonance.

6.3 Single-photon Feshbach resonance

A Feshbach resonance happens when a scattering state of two free atoms is tuned to resonance with a bound state in some molecular potential. This causes a mixing between the scattering wave function and the bound-state wave function which significantly affects the scattering behavior. It is not difficult to imagine how this would significantly alter the collisional dynamics: two ultracold atoms which normally spend most of their time well separated, are suddenly locked in a quasi-bound state for awhile. This kind of collision differs greatly from the casual brush typical to ultracold atom collisions. The result is that even a small amount of wave function mixing can have a huge effect on the collision. The amount of mixing can be controlled by tuning around the resonance condition.

To get a feel for this, consider the more traditional magnetically tuned feshbach resonance (compared to optically tuned). A pair of atoms in a spin-triplet state interact along their corresponding triple: potential. This potential shifts in energy as a function of magnetic field strength by the Zeeman interaction since the atoms have a combined magnetic moment of $2\mu_B$, where $\mu_B$ is the Bohr magneton. A bound level of the spin singlet, does not shift with magnetic field strength. Changing the magnetic field strength, therefore, will alter the relative separation between the
Figure 6.1 Optically tuned Feshbach resonance in the dressed-atom picture. The ground-state potential is elevated by the photon energy so that the scattering state $\phi_0$ is nearly degenerate with the bound state $\psi_0$. Altering the detuning $\Delta$ of the laser frequency from the photoassociation resonance provides control over the scattering length $a$.

incoming collisional channel and a bound state of the singlet potential. Only high-field seeking triplet states will intersect a bound level in the singlet potential since the spin singlet levels are at lower energy than the free-atom incoming channel. When the energy of the free state becomes degenerate with that of the bound state, the wave functions can mix as described above and the collision properties are greatly altered. The wave functions for the free and bound levels are very different in form which accounts for these large changes.

An optically tuned Feshbach resonance is very similar to the magnetically tuned one but the coupling between the free and bound states is now provided by laser light. The two cases become conceptually indistinguishable when the optical case is considered in the dressed-atom picture as shown in Fig. 6.1. Tuning the laser frequency $\omega_1$ shifts the potentials further apart or closer together. At a laser detuning of $\Delta = 0$, the bound and free states are perfectly matched in energy. This clearly
demonstrates the importance of understanding the photoassociation frequency shift described in Chap. 3 since that effect will alter the binding energy of the bound level \( v \). The coupling strength, or amount of mixing, depends on the laser intensity \( I \) and the overlap integral \( \langle \phi_0|\psi_v \rangle \). The mixing causes a change in the \( s \)-wave scattering length \( a \), which alters the elastic collision cross section \( \sigma_{el} \), since \( \sigma_{el} \propto a^2 \).

The theory for single-photon optically induced Feshbach resonances was originally developed by Fedichev et al. [32] and was generalized by Bohn and Julienne [75]. Recently, the single-photon optically induced Feshbach resonance was observed in an ultracold trapped gas of sodium atoms [76]. Those authors use the theory developed in Ref. [32] to analyze their experimental results, obtaining good agreement. The calculations below are a summary of those performed by Cass Sackett in his Ph.D. thesis [16] which were also based on the development of Fedichev. Fedichev uses an approximation for the overlap integrals \( \langle \phi_0|\psi_v \rangle \), but the more precise values shown in Fig. 3.2 can be used. When the expression for \( \langle \phi_0|\psi_v \rangle \) given in Eqn. 3.1 is substituted for Fedichev's approximation, the fractional change in \( a \) takes the form

\[
\frac{\Delta a}{a} = -A_v \frac{\Delta \Omega^2}{\Gamma_a \Delta^2 + \Gamma_a^2},
\]

(6.1)

where \( \Omega \) is the Rabi flopping frequency defined by \( \Omega^2/\Gamma_a^2 = I/I_{sat} \), with the atomic linewidth given by \( \Gamma_a = (2\pi)5.9 \text{ MHz} \), and the saturation intensity given by \( I_{sat} = 5.1 \text{ mW/cm}^2 \). The detuning of the laser beam from the molecular vibrational level \( v \) is denoted by \( \Delta \) where \( \Delta < 0 \) if the laser frequency is less than the resonance frequency. As Eqn. 6.1 is written, \( \Delta \) is referenced to the light-shifted resonance position. Note that for \( \Delta < 0 \), such as is the case for \(^7\text{Li} \) atoms, the dimensionless overlap integral \( A_v \) as defined in Eqn. 3.1 is a positive quantity. Therefore, Eqn. 6.1 indicates that \( a \) will become more negative if the laser is red detuned \( \Delta < 0 \). In fact, for red detuning, \( \Delta a < 0 \) regardless of the initial sign of \( a \).

*Recall that \( A_v \propto -1/a \).
6.3.1 Implementation

The photoassociation laser causes a change in $a$ as given by Eqn. 6.1 but also induces losses from spontaneous scattering from both the molecular and free atomic resonances. If the loss rate is too large, the atoms will not survive long enough to respond to the change in $a$, negating the usefulness of the technique. The rate for spontaneous scattering from the molecular resonance $R_P$ is given by Eqn. 3.2, and the rate for spontaneous scattering from the atomic resonance is given by

$$R_A = \Gamma^a \frac{\Omega^2}{4D_u^2},$$

where $D_u$ is the detuning of level $v$ with respect to the atomic resonance, given by the binding energy $E_B(v)$. For a given $\Delta a$, the lowest total loss rate $R_{\text{loss}} = R_P + R_A$ is achieved by choosing the value of $\Delta$ such that $R_P = R_A$, and the optimal detuning is independent of $\Delta a$ and $\Omega$, depending only on the density $n$ and choice of level $v$. The calculated optimal values of $\Delta$ are shown in Fig. 6.2(a) for the experimentally accessible range of $v$.

For a density $n$ fixed by the number of condensate atoms, the level $v$ can be chosen in order to minimize losses. An appropriate figure of merit for determining the optimal level is the ratio of the change in scattering length to the loss rate $\eta \equiv \Delta a / R_{\text{loss}}$. $\eta$ is plotted in Fig. 6.2(b) for a density of $n = 2.3 \times 10^{12}$ cm$^{-3}$, corresponding to the mean density for $N_0 = 1000$ condensate atoms with the optimized value of $\Delta$. Although the lower lying levels are in general more suitable, the overlap integrals rapidly decrease for these levels, as shown in Fig. 3.2, and the intensity required to effect a particular change in $a$ increases correspondingly. The required intensity to make a change of $\Delta a / a = 3$ is shown in Fig. 6.2(c). The decay times $R_{\text{loss}}^{-1}$ for optimized detuning are shown in Fig. 6.2(d).

Notice that the decay times in Fig. 6.2(d) are generally between 10 and 20 ms. This is much shorter than the $\sim 300$ ms elastic collision time implied by a density of
Figure 6.2 Parameters for single photon optically tuned Feshbach resonance. (a) Optimum value of detuning $\Delta$ from the molecular resonance $\nu$. (b) Figure of merit parameter $\eta = \Delta a / R_{\text{loss}}$. (c) Laser intensity required for $\Delta a / a = 3$. (d) Decay time $R_{\text{loss}}^{-1}$ when $\Delta a / a = 3$. The solid line shows the trap response time, $\bar{\omega}^{-1}$, where $\bar{\omega}$ is the average trap oscillation frequency. For all four plots, the density was fixed at $n = 2.3 \times 10^{12}$ cm$^{-3}$, corresponding to the mean density for $N_0 = 1000$ atoms in the condensate.

$\sim 10^{12}$ cm$^{-3}$ corresponding to typical conditions for the thermal atoms. Therefore, most atoms are lost from the trap during one elastic collision time and the efficiency of evaporative cooling cannot be increased using this technique. In addition, since the condensate growth rate is proportional to the elastic collision rate for the small condensates of $^7$Li, this technique cannot be used to make $a$ slightly less negative, allow the condensate to overfill and then force a collapse by turning off the laser beam and allowing $a$ to return to its normal value. On the other hand, the collapse process
occurs quickly, on a time scale set by the trap oscillation period $\bar{\omega}^{-1}$ (plotted as the solid line in Fig. 6.2(d)). For these reasons, the best use of this technique for studying the condensate collapse is to make $a$ more negative and observe the new value of the condensate stability limit $N_m$. Additionally, the distribution of condensate remainders can be studied for condensates whose initial population exceeds the new stability limit given by the altered value of $a$. Since collapse is so quick, the laser beam need only be applied for a short time, and the associated losses can be minimized.

To apply the optically tuned Feshbach technique as discussed above, the laser needs to be kept on for at least $\bar{\omega}^{-1}$ but for significantly less time than $R_{\text{loss}}^{-1}$. Additionally, the atoms must be given a chance to respond to the change in mean field as given by the change in scattering length. This time scale is given by the uncertainty principle as $\Delta t \sim \hbar/2\Delta U$, where the mean field shift is given by $\Delta U = 4\pi\hbar^2|a|\Delta a/(ma)$. Inserting the mean density $7 \times 10^{11}$ cm$^{-3}$ corresponding to the new stability limit when $\Delta a/a = 3$ gives $\Delta t = 1.4$ ms.

### 6.3.2 The dipole force problem

As discussed in Sec. 3.3, the photoassociation laser beam used for the optically tuned Feshbach technique is derived from an SDL tapered optical amplifier. The amplified beam is chopped with an acousto-optic modulator and subsequently fiber coupled. This limits the available laser power to $\sim 70$ mW. With this constraint on laser power, the laser beam must be focussed to a $1/e^2$ radius of $\sim 90$ $\mu$m in order to achieve the necessary intensity for the lowest maximum in Fig. 6.2(b) ($v = 69$), and the beam waist must be decreased further for the other local maxima ($v = 54$, and $v = 46$). A beam waist of 90 $\mu$m, is already comparable in size to typical atom clouds, and for $v = 54$ the waist must be decreased to $\lesssim 20$ $\mu$m, which is smaller than all but the coldest of atom clouds.

The optimal choice of molecular level appears to be $v = 69$ as the figure of merit
\( \Delta a/R_{\text{loss}} \) is at a local maximum and the intensity requirement \( I \sim 600 \text{ W/cm}^2 \) is attainable with the moderate laser power currently available for this apparatus. A laser pulse of duration \( \sim 3 \) ms would trigger a collapse if \( N_0 \gtrsim 300 \) and the spontaneous loss would be \( \sim 30\% \). However, with a beam waist of \( \sim 90 \) \( \mu \)m, a substantial reduction in the number of trapped atoms is observed which is not accounted for by \( R_{\text{loss}} \). This extra loss is present when the intensity is \( \sim 300 \) W/cm\(^2\), only half the amount required for the desired change in \( a \). The loss is accompanied by a change in shape of the atom cloud as observed immediately after the laser pulse. The additional loss is attributed to heating of the atoms caused by the strong dipole force which arises from the large intensity gradient across the atom cloud, as discussed below.

The dipole force potential is given in Ref. [77] as

\[
U = \frac{\hbar D_v}{2} \ln(1 + p), \tag{6.3}
\]

where

\[
P = \frac{I}{I_{\text{sat}}} \left( \frac{\Gamma_a^2}{4D_v^2 + \Gamma_a^2} - \frac{\Omega^2}{4D_v^2 + \Gamma_a^2} \right). \tag{6.4}
\]

When \( D_v^2 \gg \Omega^2 \), then \( p \ll 1 \) and the potential becomes

\[
U = \frac{\hbar pD_v}{2} = \frac{\hbar \Omega^2}{8D_v}. \tag{6.5}
\]

Inserting the numbers for \( v = 69 \): \( I = 600 \text{ W/cm}^2 \), \( D_v = 854 \) GHz, and \( I_{\text{sat}} = 5.1 \) mW/cm\(^2\) gives for the dipole force potential depth \( U_0/k_B = 29 \) \( \mu \)K. This is a huge amount of energy compared to the 100 - 200 nK typical for the evaporatively cooled clouds. It is therefore not surprising that a significant loss and heating of the atoms is observed when the laser beam is switched on quickly. This situation will, of course, only get worse for deeper vibrational levels with a larger intensity requirement.

If the laser is turned on and off adiabatically, rather than pulsing it sharply, the heating discussed above can be eliminated. The condition for adiabaticity is that the total ramp time for the laser intensity must be long compared to the oscillation period
$\omega^{-1}$ in the dipole force potential. Equation 6.5 shows that the dipole potential is proportional to the laser intensity. A Gaussian laser beam profile $I(r) = I_0 \exp(-2r^2/r_0^2)$ is approximately quadratic near the beam center $r = 0$, giving $I(r) \simeq I_0 (1 - 2r^2/r_0^2)$ where $r_0$ is the $1/e^2$ radius (beam waist). Inserting this into Eqn. 6.5 and keeping only the $r$-dependent part gives

$$U(r) = \frac{\hbar \Omega_0^2}{8 D_\nu} \left( \frac{2r^2}{r_0^2} \right) = \frac{2U_0}{r_0^2} v^2.$$  \hspace{1cm} (6.6)

The expression for $U(r)$ given in Eqn. 6.6 can be equated to the oscillation energy of atoms in the dipole force potential $m \omega^2 r^2/2$ in order to determine the oscillation frequency $\omega$. Doing this and substituting the $v = 69$ parameters and $r_0 = 90 \, \mu$m gives

$$\omega = \sqrt{\frac{4U_0}{m r_0}} = (2\pi)650 \, \text{Hz}.$$ \hspace{1cm} (6.7)

This implies an oscillation period of $\sim 240 \, \mu$s, which is relatively short compared to the 3 ms pulse time desired for the Feshbach resonance technique for $v = 69$. Ramping the laser intensity on and off with a time $\Delta t > 240 \, \mu$s should therefore eliminate the heating effect while enabling an effective change in $a$.

This, unfortunately, is not the whole story. The value for $\omega$ computed in Eqn. 6.7 is large compared to the $\sim 150$ Hz oscillation frequency of the magnetic trap. This leads to two additional problems. The first is that the parameters shown in Figs. 6.2(a), (c), and (d) are computed for a density $n$ corresponding to $N_0 = 1000$ atoms in the condensate for the magnetic trap geometry. When the dipole potential is adiabatically superposed onto the magnetic potential, phase space density is conserved so $n$ will increase, compensated by an increase in the temperature $T$. The change in $n$ requires the Feshbach parameters to be computed recursively for the new trap geometry. This is not a fatal problem, just a hassle.

The second, more serious, issue arising from the tightening of the trap potential is that this alone, in the absence of a modification in $a$, will reduce the condensate
stability limit $N_m$, thereby triggering a collapse for sufficiently large condensates. This occurs because, as discussed in Chap. 5, $N_m \propto \ell / |a|$, where $\ell = (\hbar / m \omega)^{1/2}$ is the size of the ground state of an harmonic trap. This shows that it is possible to reduce $N_m$ either by increasing the magnitude of $a$, as for the Feshbach resonance, or by increasing $\omega$ as for the dipole potential. For the conditions described above for $\nu = 69$, the new value of $N_m$ as given by the dipole potential alone is $\sim 600$ atoms. Separating this effect from that caused by a change in $a$ will be difficult at best.

6.3.3 Prospects

To alleviate the reduction of $N_m$ caused by the tight dipole force potential, a more powerful laser must be used so that $r_0$ can be increased, or a more weakly bound level $\nu$ must be used which requires less intensity. Considering the relation $N_m \propto \omega^{-1/2}$ and Eqn. 6.7 shows that

$$N_m \propto r_0 \left( \frac{D_\nu}{\mathcal{P}} \right)^{1/4},$$

where $\mathcal{P}$ is the laser power. It is beneficial, therefore, to increase $\mathcal{P}$ with a compensating change in $r_0^2$ to maintain the same laser intensity. When $r_0$ is increased such that the oscillation period of the dipole trap becomes larger than that for the magnetic trap, the adiabaticity condition is then provided by the magnetic trap oscillation period. This fact is important, because otherwise, the increased oscillation time could very easily imply a minimum intensity-ramp time larger than the loss time given by $R^{-1}_{\text{loss}}$. Unfortunately, there are no high power laser sources currently available in the lab.

To determine whether a less-deeply bound level can be used with the current constraint on laser power, consider level $\nu = 78$ which has an intensity requirement of only $\sim 60$ W/cm$^2$ and a binding energy of $D_\nu = 182$ GHz. If the intensity is reduced by increasing $r_0$ by a factor of 3 while keeping $\mathcal{P} = 70$ mW, then the oscillation frequency of the dipole force potential is $\omega \sim (2\pi)70$ Hz, and the dipole potential
imposes no additional limit on $N_m$. In this case, the minimum ramp time is $\sim 1$ ms as given by the magnetic trap oscillation period. A 2 ms "on" time for the laser pulse should be long enough to induce a collapse for sufficiently large condensates and would cause a spontaneous loss of $\sim 30\%$. The additional loss which occurs during the ramp time, however, probably makes this level unsuitable as well.

As an aside, there is an alternative possibility for using a focussed laser beam to help study the condensate growth and collapse dynamics. The idea is to focus the laser beam tightly, implying a reduction of $N_m$ to near zero (see Eqn. 6.8), but to ramp the potential on and off adiabatically so that after the ramp cycle, the condensate is gone, but the rest of the gas is left unaffected. In this case, the associated change in $\alpha$ is completely neglected, and in fact, the laser can be tuned far from any molecular resonance. This idea is very similar in spirit to the condensate dump pulse used in Ref. [8] and described in Chap. 5, although there, the condensate was removed by a very energy-selective two-photon laser pulse. The tight-focus technique discussed here might be advantageous on the one hand because the two-photon technique perturbed the populations of low-energy trap levels slightly slowing the initial condensate growth. Here, only the condensate should be effected. On the other hand, a tighter laser focus is experimentally problematic since any drifts in the laser beam pointing will result in poor spatial overlap with the condensate region of the atom cloud. More rigid mounts for the photoassociation laser beam optics might therefore be necessary.

6.4 Two-photon Feshbach resonance

The formalism developed for the single-photon optically induced Feshbach resonance can be adapted for the case of a two-photon Raman transition. The simplest way to adapt Eqn. 6.1 above is to naively replace the parameters which correspond
to the single-photon transition with those which correspond to the Raman transition:

$$\Omega \rightarrow \Omega_1 \Omega_2 / \Delta$$  \hspace{1cm} (6.9)
$$\xi \langle \phi_0 | \psi_0 \rangle^2 \rightarrow \xi^2 \langle \phi_0 | \psi_0 \rangle^2 \langle \phi_2 | \psi_0 \rangle^2$$  \hspace{1cm} (6.10)
$$\Gamma_a \rightarrow \gamma / 2$$  \hspace{1cm} (6.11)
$$\Delta \rightarrow \delta$$  \hspace{1cm} (6.12)

where $\Omega_i = \sqrt{I_i / I_{sat}} \Gamma_a$, and $\gamma$ and $\delta$ are the width of the Raman resonance and the two-photon detuning from the Raman resonance, respectively. Note that the right side of Eqn. 3.1 must be inserted for $A_v$ in Eqn. 6.1 above in order to make the second substitution indicated. The resulting expression for the fractional change in $a$ using the Raman transition is

$$\frac{\Delta a}{a} = \frac{m}{2 \pi \hbar \alpha} \xi^2 \langle \phi_0 | \psi_0 \rangle^2 \langle \phi_2 | \psi_0 \rangle^2 \frac{\Omega_1^2 \Omega_2^2}{\Delta^2} \frac{\delta}{4 \delta^2 + \gamma^2}.$$  \hspace{1cm} (6.13)

As in the single-photon case, the lasers will induce a loss of atoms, but now there are three loss channels: photon scattering off the molecular resonance $\nu$ driven by laser $\omega_1$, photon scattering off the atomic resonance driven by both lasers and Raman transitions to the $\nu' = 10$ ground-state level driven by both lasers. The molecular scattering rate $R_p$ is given by Eqn. 4.20 (where only the first term in square brackets is kept) and the atomic scattering rate $R_f$ is given by Eqn. 4.18. The Raman transition rate is given by

$$R_x = \chi^2 \frac{\gamma}{4 \delta^2 + \gamma^2},$$  \hspace{1cm} (6.14)

where $\chi$ is given by Eqn. 4.15.

### 6.4.1 Optimization

Because of the added loss term $R_x$, optimization of this two-photon system is not as straightforward as for the single-photon case described above. As in that case, however, the figure of merit is $\eta = (\Delta a / a) / R_{loss}$ where now, $R_{loss} = R_p + R_f + R_x$. 

Maximizing $\eta$ using Eqn. 6.13 imposes the condition $R_p = R_x^*$. This allows for an optimized value of $\delta$ to be calculated which in turn will fix the values of $I_1$, $I_2$, and $\Delta$. As in the single-photon case, the optimum value for $\Delta$ is independent of $\Delta a/a$. However, when $\eta$ is maximized, $R_{\text{loss}}$ reduces to two terms, only one of which is proportional to $\Delta a/a$, so $\eta$ depends on the chosen value of $\Delta a/a$. The function of the optimization is to determine the particular value of $\delta$ which minimizes $R_{\text{loss}}$ for a given value of $\Delta a/a$. Note that a value for the Raman linewidth $\gamma$ must be assumed since it is not known precisely.$^\dagger$

Figure 6.3(a) shows the figure of merit parameter $\eta$ for four different values of $\Delta a/a$. Note that $\Delta a/a < 0$ corresponds to making $a$ less negative (or positive). Also note that $\eta$ has units of time. In general, deeply bound levels are most suitable and a peak in $\eta$ is observed at $\nu = 56$. Additionally, $\eta$ increases with increasing $\Delta a/a$ indicating that larger changes to the scattering length are more favorable.

Figure 6.3(b) shows the ratio of the collision rate $R_C$ to the total loss rate $R_{\text{loss}}$. This ratio should be greater than unity in order to consider experiments where $a$ is made less negative (or positive), allowing the condensate to exceed the original stability limit $N_m$. When calculating $R_C$, a density of $n = 10^{12}$ cm$^{-3}$ is used which approximately corresponds to the peak density of the thermal cloud at a temperature of $T = 200$ nK. Conversely, when calculating $R_{\text{loss}}$, a density of $n = 2.3 \times 10^{12}$ cm$^{-3}$ is used which corresponds to the mean density in a condensate with $N_0 = 1000$ atoms.

The results of Fig. 6.3(b) indicate that it is possible to perform experiments which are designed to let the condensate overfill. This is already an improvement over the single-photon case described above. However, the optimized laser parameters must be considered in order to determine whether such studies are experimentally feasible.

$^*$In order to avoid having to solve a cubic equation in the optimization equations, I assume that $\delta \gg \gamma$.

$^\dagger$In all calculations, $\gamma$ is assumed to be 250 Hz in agreement with the most narrow linewidths observed (see Chap. 7).
Figure 6.3  Figure of merit for two-photon optically induced Feshbach resonance. (a) $\eta = (\Delta a/a)/R_{\text{loss}}$ for the four values of $\Delta a/a$ indicated in the figure legend. (b) Ratio of collision rate $R_C$ to loss rate $R_{\text{loss}}$ for the same values of $\Delta a/a$. The figure legend in (b) gives the decay time for $v = 56$. For both panels, $\gamma = 250$ Hz.

Figure 6.4 shows the optimized values of $\delta/\gamma$, $\Delta$, $I_1$, and $I_2$. Note that in the lower panel, the solid line corresponds to $\Delta$ whose value is read off the right-hand scale. In general the values for $\Delta$ are reasonable, although they are not significantly larger than the $\sim 5$ MHz uncertainty in their values*. The values for $\delta/\gamma$ are quite large, especially for more deeply bound levels $v$. This is nice, since the difference frequency between the two lasers $\Delta \nu$ does not then need to be set very precisely and any frequency shifts can be neglected. The dependence of $\Delta a/a$, $R_C$, and $R_{\text{loss}}$ on $\delta/\gamma$ for optimized values of $\Delta$, $I_1$, and $I_2$, is investigated below.

*Note that the sign of $\Delta$ is irrelevant since only $\Delta^2$ enters into the calculations.
Figure 6.4  Optimized laser parameters for two-photon optically induced Feshbach resonance. The lower panel shows the Raman resonance detuning $\delta$ normalized to the Raman resonance linewidth $\gamma$ for the values of $\Delta a/a$ indicated in the figure legend. The upper panel shows the required intensities for the free-bound laser $I_1$ and the bound-bound laser $I_2$ for the same values of $\Delta a/a$. Additionally, the solid line in the lower panel shows the intermediate state detuning $\Delta$ (to be read of the right-hand scale) which is independent of $\Delta a/a$. For both panels, $\gamma = 250$ Hz.

The intensity requirements indicated by Fig. 6.4 are more reasonable than for the single-photon case. In general, the requirements for $I_1$ (free-bound laser) can be satisfied using a low-power diode laser focused to a $1/e^2$ intensity radius of $\sim 150 \mu$m. In order to satisfy the requirements on $I_2$, however, a high power laser must be used*. Nevertheless, the intensity requirements should be achievable. Note that the intensities $I_1$ and $I_2$ are proportional to each other. This pcps out of the optimization process discussed above. The validity of this has been investigated by changing the

---

*Two possibilities are the tapered amplifier discussed in Chap. 3 (and also above) or the wide-stripe diode laser system currently under development in the lab. Using a dye laser might also work although it is not clear whether a sufficient phase-lock can be achieved in that case.
ratio of $I_1$ and $I_2$ while maintaining given values of $\Delta a/a$, $\Delta$, and $\delta$. The total loss rate $R_{loss}$ does indeed increase when this ratio is either increased or decreased.

As shown in Fig. 6.3, the ratio $R_C/R_{loss}$ increases with $\Delta a/a$ when the system is optimized such that $R_{loss}$ is minimized. For experiments designed to let $N_0$ exceed $N_m$, however, $R_C/R_{loss}$ needs to be only big enough to allow the condensate to grow appreciably during the duration of the two-photon Raman pulse. This condition may be satisfied for significantly less laser power than implied by Fig. 6.4 if the Raman detuning $\delta$ is allowed to take on a smaller value. This is demonstrated in Fig. 6.5 which plots $\Delta a/a$, $R_{loss}^{-1}$, and $R_C^{-1}$ for a range of $\delta/\gamma$ for $v = 56$. The upper panel (a) uses the optimized values of $\Delta$, $I_1$, and $I_2$ for $\Delta a/a = -3$ and the lower panel (b) uses the corresponding optimized parameters for $\Delta a/a = -1$. The black curve in each panel corresponds to $\Delta a/a$ and should be read from the left-hand scale. The solid red curve corresponds to the collision time $R_C^{-1}$ and the dashed red curve corresponds to the loss time $R_{loss}^{-1}$, both of which should be read from the right-hand scale. Both of these graphs show a wide range of $\delta$ values which give $R_{loss}^{-1} > R_C^{-1}$, but panel (b) has a much less stringent intensity requirement.

In principle, $v = 56$ is the optimum level for the two-photon optically-induced Feshbach resonance because it gives the minimum loss rate for a given change in $a$, as demonstrated in Fig. 6.3. However, this deeply bound level has not been observed before whereas the $v = 58$ level has been, as reported in App. B, and the difference between the figure of merits for these two levels is not significant. Therefore, it is useful to calculate the laser parameters which give similar results for $v = 58$ as those shown in Fig. 6.5(b) for $v = 56$. Fig. 6.6 shows the response of $\Delta a/a$, $R_C^{-1}$, and $R_{loss}^{-1}$ for the laser parameters which are optimized for $\Delta a/a = -1$. The intensity requirements are even less stringent than for $v = 56$ and the expected performance is virtually unchanged.
Figure 6.5  Variation of loss time $R_{\text{loss}}^{-1}$ and collision time $R_{C}^{-1}$ with $\delta$ for $\nu = 56$. (a) The system is optimized for $\Delta a/a = -3$: $I_1 = 4.95$ W/cm$^2$; $I_2 = 165$ W/cm$^2$. (b) The system is optimized for $\Delta a/a = -1$: $I_1 = 2.38$ W/cm$^2$; $I_2 = 79.3$ W/cm$^2$. For both panels $\Delta = \pm 45$ MHz. The black curves correspond to $\Delta a/a$ and should be read from the left-hand scale. The solid red curve corresponds to the collision time $R_{C}^{-1}$ and the dashed red curve corresponds to the loss time $R_{\text{loss}}^{-1}$, both of which should be read from the right-hand scale.

6.4.2 Prospects

Figures 6.3-6.5 indicate that the prospects are good for designing experiments which allow the condensate to overfill the stability limit. In practice, it is more convenient to employ longer pulse times so the conditions shown in Fig. 6.5(b) would be slightly more desirable, especially since they require smaller laser powers. The first important demonstration of this technique would be to show that the condensate can exceed the stability limit $N_m$. This could be accomplished by imaging the atom cloud near the end of the Feshbach laser pulse after the condensate has had sufficient time to
Figure 6.6 Variation of loss time $R_{\text{loss}}^{-1}$ and collision time $R_{C}^{-1}$ with $\delta$ for $\nu = 58$. The system is optimized for $\Delta a/a = -1$: $I_1 = 1.62$ W/cm$^2$; $I_2 = 54.1$ W/cm$^2$, and $\Delta = \pm 31$ MHz. The black curve corresponds to $\Delta a/a$ and should be read from the left-hand scale. The solid red curve corresponds to the collision time $R_{C}^{-1}$ and the dashed red curve corresponds to the loss time $R_{\text{loss}}^{-1}$, both of which should be read from the right-hand scale.

grow. Additionally, following the Feshbach pulse, the scattering length $a$ would return to the natural value of $1.45$ nm and the condensate would then collapse. Images of the cloud immediately after the collapse could be used to determine whether the post-collapse condensate wave function is indeed a superposition of trap eigenstates, as discussed in Chap. 5, and if so which particular superposition. The fact that the condensate fill rate can be greatly enhanced, as evidenced by the greatly enlarged value of $|a|$ demonstrated in Fig. 6.5*, would aid these studies insofar as that might allow the bulk of the thermal population of atoms to enter the condensate, enhancing sensitivity to the post-collapse wave function.

There are virtually an unlimited number of other experiments which are enabled by having such precise and convenient control over the scattering length $a$. One of the more intriguing ideas is the possibility of making local changes to $a$ such that the cloud experiences a sort of "interaction mask" induced by the intensity profile

*The elastic collision rate $R_{C}$ is proportional to $a^2$, and the condensate fill rate is proportional to $R_{C}$. 
of the Feshbach laser beams. It is difficult to enumerate the number of possibilities which this kind of experiment might afford. A purely speculative idea is related to producing a true continuous wave (CW) atom laser. Although pulsed and quasi-continuous atom lasers have now been demonstrated [78, 79], these schemes suffer from the drawback that when the condensate is emptied, it must be replenished by reloading the trap and going through the entire evaporative cooling cycle. Typically, evaporation cycles are at least 10s of seconds in duration and in the case of lithium, they are closer to 100 seconds. If the trap could be reloaded during the evaporation cycle without heating the rest of the cloud, a true CW source could be achieved. This might be accomplished by using the Feshbach laser beams to imprint an interaction mask onto the cloud such that atoms far away from the trap center (and consequently with high energy) would experience $a \gg 0$ while those near the center would have $a \sim 0$. This might establish a highly nonequilibrium situation where the atoms within a sort of high energy shell rethermalize very quickly with each other but those near the trap center hardly ever collide. This isolates the atoms near the low energy trap center from those in the high energy shell. Missing from this discussion is, of course, a way to continuously cool the atoms in the shell so that they fall into the cold trap center. Even if this application is never realized, it would interesting to apply this technique to an existing condensate in order to study the dynamics of a condensate whose mean-field interactions spatially vary.
Chapter 7
Raman lineshape

One of the most interesting aspects of the Raman photoassociation spectra presented in Chap. 4 is the origin of the lineshape. Many variations of the lineshape have been observed under different circumstances for both total atom loss spectra and condensate atom loss spectra. Sometimes the line is observed to be fairly symmetric (Fig. 4.2), and at other times asymmetric (Fig. 5.6). One particularly interesting aspect which is sometimes observed in the condensate loss spectra is a double peak structure. Unfortunately, the origin of the asymmetry (especially in the condensate loss spectra) and the double peak structure are not yet fully determined. There are several possibilities which may explain these issues, and this chapter will address all of the proposed explanations. The primary goal of this chapter is to provide a framework for future research into this matter.

7.1 Wigner threshold lineshape

Naively, one might think that the spectroscopic lineshape of the Raman transition should be a symmetric Lorentzian function whose width is given by the decay of the $v' = 10$ ground-state molecular level. This decay can be due to both optical excitation on the bound-bound transition which eventually results in spontaneous loss, or to vibrational de-excitation of molecules in the $v' = 10$ level. The spontaneous scattering mechanism has been discussed in Chap. 4 and vibrational relaxation is described below.

Vibrational relaxation occurs when an atom and a molecule (or two molecules) undergo an inelastic collision whereby the molecule gives up some of its internal vibrational energy in the form of kinetic energy:

$$\text{Li}_2(v' = 10) + \text{Li} \rightarrow \text{Li}_2(v' < 10) + \text{Li} + \text{K.E.}$$
\[ 2 \times \text{Li}_2(v' = 10) \rightarrow \text{Li}_2(v' < 10) + \text{Li}_2(v' \leq 10) + \text{K.E.} \]

The kinetic energy released K.E. is much greater than the containment depth of the trap and the atoms and/or molecules involved in the collision are lost. The second relaxation mechanism, that between two molecules, is only important if a significant population of molecules exists. This condition is not met in any of the experiments described in this thesis, as discussed in Chap. 4. Consequently, the rate of atom loss due to vibrational relaxation is due only to the first vibrational relaxation mechanism and is given by

\[ \dot{N} = -\int d^3r n^2(r)V_{AM}, \]  

(7.1)

where \( V_{AM} \) has dimensions of cm\(^3\)/s and stands for the vibrational relaxation rate constant for collisions between atoms and molecules.

The lineshape will be independent of the energy distribution of the atoms in the initial state if the Lorentzian width of the \( v' = 10 \) level is larger than the thermal energy spread of the atoms in the trap. For the experiments reported in this thesis, however, the Lorentzian width of the \( v' = 10 \) level can be much smaller than the thermal spread, even though the temperatures are less than 1 \( \mu \)K (corresponding to an energy spread of 20 kHz). Under these circumstances, the lineshape is given by [33]

\[ S(E) \propto E^{1/2}f(E), \]  

(7.2)

where \( S(E) \) is the atom loss signal for collisions between atoms with energy \( E \), and \( f(E) \) is the energy distribution function. The generic asymmetry in this lineshape, due to the inhomogeneous energy distribution of the atomic population, is consistent with the Wigner threshold law [33]. Simply put, the number of states grows with increasing energy but does so more slowly than the decrease in value of the energy distribution function. This yields an asymmetric lineshape which is peaked at lower values of the collision energy \( E \), as demonstrated in Fig. 7.1, which shows a Raman loss spectrum for the total number of atoms \( N \).
Figure 7.1  Wigner threshold lineshape. The data points are the number of atoms $N$ remaining in the trap following a Raman laser pulse. The solid line is a function of the form given in Eqn. 7.2 using a Boltzmann energy distribution function. The extracted value for the temperature parameter of the Boltzmann distribution is 705 nK, which is consistent with independent measurements of the temperature for each data point using the imaging technique described in Chap. 2. For these data, $\tau = 1.5$ s, $v = 72$, $I_1 = 132$ mW/cm$^2$, $I_2 = 395$ mW/cm$^2$, and $\Delta = -(2\pi)\times 110$ MHz giving $\Omega_p = (2\pi)4.19$ kHz, $R_p = (2\pi)4.3\times 10^{-3}$ Hz, $\Omega_b = (2\pi)641$ kHz, $R_b = (2\pi)100$ Hz, $\chi = (2\pi)17.3$ Hz, and $R_f = 0.12$ s$^{-1}$.

Note that the signal size for these data is very small compared to what is expected when using either $\chi$ or $R_{\chi} \sim \chi^2/\gamma$ for the two-photon loss rate, where $\gamma \sim (2\pi)250$ Hz is the frequency width of the two-photon resonance. This indicates that the expression for $\chi$ does not apply to these data and might imply that no Raman coherence is present for the thermal atoms. This is consistent with many theoretical treatments which assert that no coherent process is possible within the nondegenerate portion of a gas [37][80]-[84].

An upper limit for the rate constant for vibrational relaxation can be estimated by fitting these data to a function of the form given in Eqn. 7.2, shown as the solid line in Fig. 7.1. Given that this function fits the data well indicates that the Lorentzian width of the $v' = 10$ level must be much smaller than the frequency separation between the points marked A and B in the figure. Otherwise, a convolution between the Lorentzian
and Eqn. 7.2 would be needed to obtain an accurate fit*. This frequency difference is ~7.5 kHz giving an upper limit for the vibrational relaxation rate constant of $V_{AM} \sim 7 \times 10^{-9}$ cm$^3$/s using a density of $6.5 \times 10^{12}$, corresponding to the BEC critical density at $T = 700$ nK. As will be shown below, much more narrow spectra than this one have been observed, which enables this upper limit to be lowered significantly.

### 7.2 Dispersion lineshape

The Wigner threshold law is sufficient to describe the Raman lineshape for the conditions shown in Fig. 7.1. These conditions can be characterized as a “weak coupling” regime in that the rates $R_p$ and $R_b$ are much smaller than the thermal energy scale. In this situation, the coupling lasers are only a small perturbation to the system and atoms are slowly converted to molecules at which point they are lost via spontaneous scattering off the bound-bound transition, or via vibrational relaxation. If the coupling strengths are increased to the point that they can no longer be considered a perturbation, one might think that the system will not be well described by the Wigner law alone. At the very least, the lineshape should reflect the Lorentzian decay width of the $v' = 10$ level when this width exceeds the thermal energy spread.

For certain strong coupling circumstances, dispersion lineshapes are observed as shown in Fig. 7.2. The solid line in Fig. 7.2 indicates the amount of loss observed when only the free-bound laser $\omega_1$ is applied. It is interesting to note that this is consistent with the amount of loss expected from $\omega_1$ if a loss rate of $R_b = (2\pi)1$ Hz, rather than 2 Hz is assumed. This may indicate that the expression for $R_p$ (Eqn. 4.20) is in error by a factor of 2. The calculated atomic scattering rate $R_f$ for the conditions shown is 1.64 s$^{-1}$ so the normalized signal $N(\tau)/N(0)$ when $|\Delta| \gg \Gamma_m$ and $|\delta| \gg \gamma$ should be no larger than 0.82. With this in mind, the positive lobe observed for the red

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*The point marked A corresponds to $E = 0$ and the point marked B to $E = k_B T/2$. If the Lorentzian had a significant width, this sharp edge would be smeared out.
Figure 7.2  Dispersion lineshape. The data points are the mean of five measurements for the total number of atoms $N(\tau)$ remaining after the Raman pulse of duration $\tau = 120$ ms, normalized to the number without the pulse $N(0)$, and the error bars are the uncertainty in the mean. The solid line indicates the average of $\sim$100 measurements when only laser $\omega_1$ is applied. For these data, $N \sim 10^5$, $T \sim 200$ nK, $v = 72$, $I_1 = 6.47$ W/cm$^2$, $I_2 = 0.958$ W/cm$^2$, and $\Delta = -(2\pi)35$ MHz, giving $\Omega_p = (2\pi)29.4$ kHz, $R_p = (2\pi)2$ Hz, $\Omega_b = (2\pi)1$ MHz, $R_b = (2\pi)2.3$ kHz, $\chi = (2\pi)593$ Hz, and $R_f = 1.64$ s$^{-1}$.

part of the spectrum is an almost complete suppression of the loss due to free-bound photoassociation.*

Note that the widths of both the positive (red hump) and negative (blue dip) lobes in Fig. 7.2 are $\sim$30 kHz. This frequency scale corresponds to the free-bound Rabi frequency $\Omega_p$, as shown in that figure caption. This begs the question of whether the dispersion lineshape is due to a sort of off-resonance Autler-Townes splitting (see Sec. 4.3.2). This would be consistent with the fact that to obtain this spectrum, the bound-bound laser $\omega_2$ is scanned while $\omega_1$ is held fixed. Conversely, the Autler-Townes measurement described in Sec. 4.3.2 measured the bound-bound Rabi frequency $\Omega_b$ and therefore the laser $\omega_2$ was fixed while $\omega_1$ was scanned. If the dispersion lineshape does indeed represent the measurement of $\Omega_p$, this is a striking result since this would indicate that coherence is maintained in the nondegenerate portion of the gas, which explicitly disagrees with the theoretical treatments described above [37][80].

*For the entire range of data shown, the condensate number $N_0$ was always less than 100.
[84]. Perhaps coherence is preserved as long as $\Omega_p$ is larger than the thermal energy spread, which is the case here. On the other hand, the signal size is once again inconsistent with expectations when using either $\chi$ or $R_x \sim \chi^2/\gamma$ for the two-photon loss rate, which indicates that no coherence is present, as described above. Perhaps the coherence is actually present, but that the signal is completely saturated due to an exceedingly long exposure time for these conditions.

The suppression of loss due to free bound photoassociation has been observed previously [27, 28] and has been at least mentioned in the literature, if not studied [75]. For the experiments (Refs. [27, 28]), however, no dispersion lineshape was observed, just a sort of inverted Lorentzian loss signal, and the theoretical reference [75] does not analyze the situation in any detail. Two possibilities might explain the dispersion shape, both of which are discussed in some detail in Ref. [76]. The first is the idea of quantum path interference and the second is the two-photon optically induced Feshbach resonance described in Chap. 6.

### 7.2.1 Quantum path interference

The two lasers $\omega_1$ and $\omega_2$ induce spontaneous loss from the excited-state vibrational level $v$ via separate excitation paths. $\omega_1$ can directly excite two colliding atoms into level $v$, while $\omega_2$ can excite any $v' = 10$ molecules, which have been produced via the Raman process, into level $v$. The second excitation path can interfere with the first, since the excitations are described by probability amplitudes, rather than probability intensities. This can result in a suppression of the direct excitation loss caused by $\omega_1$.

Some preliminary investigations into this possibility have begun by modelling our system using the density matrix formalism*. In these simulations, the coupling constants $\Omega_p$ and $\Omega_b$, as shown in the figure caption for Fig. 7.2, are used to determine the

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*Thanks very much to Ionut Prodan for putting together this model and providing the results for this section.
Figure 7.3 Dispersion lineshape predicted by the density matrix simulation. $\rho_{\phi_0}$ is the population probability in the state $\phi_0$ after a 120 ms integration time. The horizontal scale gives the laser difference frequency $\Delta \nu$ offset to the light-shifted line center $\nu_0$. This simulation was performed using a density of $n = 10^{12} \text{ cm}^{-3}$, corresponding to the BEC critical density for a temperature of 200 nK.

Population dynamics. Spontaneous emission loss is simulated by coupling level $\nu$ to a fictitious fourth level with a characteristic time which matches that of spontaneous decay. The populations are integrated for a particular time period only, so this is not an equilibrium model; if it were, everything would end up in the fictitious level. Note that this model treats the scattering state $\phi_0$ as a discrete level and assumes that the $\nu' = 10$ level has no natural width.

The results of the density matrix simulation for the conditions of Fig. 7.2 are shown in Fig. 7.3. The model results are intriguing in several respects. First the dispersion shape observed in the data is reproduced, although the frequency scale does not match up. The peak in the model (red hump) goes up to $\rho_{\phi_0} \sim 0.82$, in reasonable agreement with the data and in perfect agreement with the expected loss rate $R_f$, indicating a complete suppression of photoassociation loss. Additionally, the red hump in the simulations is located at the frequency corresponding to the light-shifted line center of level $\nu' = 10$. If correct, this would produce a systematic error in the measured binding energies as reported in Sec. 4.4 since those measurements
were made assuming that the line center corresponded to the blue dip in the signal rather than the red hump*.

Although the frequency scale for the dispersion lineshape predicted by the density matrix model does not agree well with the data, there may be some good reasons for this. For example, the model neglects the dependence of the free-bound Rabi frequency $\Omega_p$ on density $n$. The large signal size demonstrated in Fig. 7.2 guarantees that large variations in $n$ during the Raman pulse time (or equivalently, the simulation integration time) will be present, and $\Omega_p$ will therefore change significantly as well. It might be possible to include this effect in the model by assuming that $n$ is linearly proportional to the population $\rho_{ee}$. However, this might make the density matrix equations more difficult to solve. Additionally, the model currently has no direct coupling term between the state $\phi_0$ and the $v' = 10$ level, although Raman coherence is assumed. Perhaps the two-photon Rabi frequency $\chi$ (see Chap. 4) should also be included as a direct coupling term.

7.2.2 Feshbach resonance

Another possible origin for the dispersion lineshape observed in Fig. 7.2 is the two-photon optically-induced Feshbach resonance discussed in Chap. 6. Recall that in the low temperature limit, the amplitude of the scattering wave function $\phi_0$ goes like $\phi_0(r) \sim k(r - a)$, where $k$ is the wave vector for the colliding atoms and $r$ is the internuclear separation between the two atoms. The overlap integral $\langle \phi_0 | \psi_v \rangle$ is concentrated near $r = R_t$, where $R_t$ is the classical turning point (or the Condon radius) for the excited-state vibrational level $v$. If the Feshbach effect is employed to change $a$ such that $a \rightarrow R_t$, then $\langle \phi_0 | \psi_v \rangle$ will vanish (or nearly so), and the free-bound photoassociation rate $R_p$ will decrease accordingly. Conversely, if $a$ is made more negative (recall that the natural value of $a$ is $-27.6 \ a_0$, where $a_0$ is the Bohr

*Most of the experimentally obtained spectra do not display this red hump, so it would be difficult to determine its corresponding frequency.
Figure 7.4 Feshbach resonance dispersion curve for the scattering length $a$. The relative change in the scattering length $\Delta a/a$ is negative when $a$ becomes less negative or positive and $\Delta a/a$ is positive when $a$ becomes more negative. Note that the vertical scale is expanded, which truncates the graph. The maximal values of $\Delta a/a$ obtained are $\pm 10$ at $\Delta \nu = \pm \gamma/2$ ($\pm 125$ Hz). The horizontal scale gives the laser difference frequency $\Delta \nu$ offset to the light-shifted line center $\nu_0$. This calculation was performed using a density of $n = 10^{12}$ cm$^{-3}$, corresponding to the BEC critical density for a temperature of 200 nK. Additionally, it is assumed that the natural linewidth (due to vibrational relaxation) of the $J' = 10$ level is $\gamma = 2\pi \times 250$ Hz, in accordance with the most narrow observed linewidths described below.

radius), then $R_p$ will increase. Therefore, as the laser difference frequency $\Delta \nu$ is tuned through the Raman resonance, the atom loss signal will vary according to the change in $a$ imposed by the Feshbach effect.

The success or failure of this explanation for the observed dispersion lineshape obviously depends on how much the value of $a$ changes while tuning through the resonance. Using the formalism developed in Chap. 6 for the conditions shown in Fig. 7.2 gives a change in $a$ as shown in Fig. 7.4. For the $v = 72$ vibrational level used here, $R_t \sim 50 a_0$ so to turn off the photoassociation loss, a change of $\Delta a/a = -3$ must be effected. Such a change does occur for the conditions shown, but at $\Delta \nu = -1$ kHz, which is small compared to the observed splitting between the red hump and blue dip in Fig. 7.2. For $\Delta \nu = \pm 15$ kHz, which closely approximates the position of the dip and hump, respectively, $\Delta a/a = \pm 0.2$. Using the relation for $\phi_0$ above and
the fact that the free-bound photoassociation rate \( R_p \propto \langle \phi_0 | \psi_o \rangle^2 \propto \phi_0^2 (r = R_t) \), the change in \( R_p \) at \( \Delta \nu = \pm 15 \) kHz is calculated to be only \( \pm 15\% \). This cannot account for the size of the red hump observed in the data, nor the blue dip*. In this case, the model is not improved by including variations in the density \( n \), because \( \Delta a/a \) is actually independent of \( n \) (see Eqn. 6.13). This appears to rule out the Feshbach effect as the origin of the dispersion shape observed in Fig. 7.2.

### 7.3 Condensate spectra

The spectra shown so far have been limited to those obtained from measurements of the entire population \( N \) rather than the condensate occupation \( N_0 \). It is reasonable to ask whether the same lineshapes will be observed in condensate spectra. It seems that the Wigner lineshape described above should never be observed in condensate spectra since there is no energy distribution in the condensate: it is monochromatic. Nevertheless, asymmetric Wigner-looking lineshapes are observed. To complicate matters, an anomalous double-peak structure in the spectrum often accompanies the asymmetry. Unfortunately, these issues are not fully resolved and the best that can be done currently is to propose some possible explanations for their origin.

#### 7.3.1 Condensate filling model

An example of an asymmetric condensate spectrum is shown in Fig. 7.5. The solid line is a Wigner lineshape fit (Eqn. 7.2) yielding a Boltzmann temperature parameter consistent with the average measured temperature obtained from phase contrast images of each individual cloud. Note that the FWHM of the signal (\( \sim 5.5 \) kHz) is again very close in value to \( \Omega_p \). The \( \sim 500 \) Hz deviation of the data point marked A from the red edge of the fitted line is consistent with the mean field shift \( \delta_{mf} = -420 \pm 140 \) Hz, as described in Sec. 4.3.3. This might imply that point A

*Note that the situation does not improve if a larger value of \( \gamma \) is used in the calculation since the maximal values of \( \Delta a/a \) scale as \( 1/\gamma \).
Figure 7.5  Condensate spectrum with Wigner lineshape. The data points are the mean of five separate measurements for $N_0$ following a Raman photoassociation pulse and the error bars are the uncertainty in the mean. The horizontal scale shows the laser difference frequency $\Delta \nu$ offset to $\nu_0 = 12420$ MHz. The solid black line is a Wigner lineshape fit (Eqn. 7.2) using a Boltzmann energy distribution function. The fit gives a Boltzmann temperature parameter of 155 nK, which is consistent with independent measurements of each data point using phase contrast imaging. For these data $\tau = 3$ s, $N \sim 2 \times 10^4$, $\nu = 72$, $I_1 = 144$ mW/cm$^2$, $I_2 = 433$ mW/cm$^2$, $\Delta = -(2\pi)105$ MHz, giving $\Omega_p = (2\pi)6.7$ kHz, $R_p = (2\pi)11.8 \times 10^{-3}$ Hz, $\Omega_b = (2\pi)671$ kHz, $R_b = (2\pi)120$ Hz, $\chi = (2\pi)30$ Hz, and $R_f = 0.13$ s$^{-1}$.

corresponds to the condensate energy. On the other hand, this deviation could also be due vibrational relaxation or simply to noise in the data. Finally, one must also wonder why this condensate spectrum looks like a Wigner lineshape at all, and for a Boltzmann, rather than Bose-Einstein, energy distribution no less!

One idea for explaining the Wigner-looking lineshape is related to the growth and collapse dynamics of the condensate. As discussed in Chap. 5, these dynamics are driven by nonequilibrium kinetics within the gas initiated by evaporative cooling. Because the condensate is constantly being filled while the growth-collapse cycles persist, it might be expected that if the fill rate were reduced, then the measured value of $N_0$ would also be reduced*. As discussed in Chap. 5, the fill rate into the

*Recall, that the data points in all the condensate loss spectra (e. g. Fig. 7.5) are averages of at least five separate measurements of $N_0$. 
Figure 7.6 Time scale for condensate growth. These data were obtained for the same experimental conditions as in Fig. 7.5, except for a smaller pulse duration $t = 0.5$ s. The solid line is a Wigner lineshape fit with a Boltzmann temperature parameter of 43 nK, which does not agree with the $\sim 160$ nK temperatures obtained for each atom cloud using phase contrast imaging.

condensate varies according to collision energy $E$, with the rate for energy levels just above the condensate being the largest. Therefore, each energy band within the trap should have a characteristic time scale for filling the condensate with the low-energy bands being the fastest. If atoms are removed from a particular band via the Raman pulse on a time scale short compared to its characteristic time scale, the condensate growth will be impeded and the measured value of $N_0$ should decrease.

This speculative notion can be investigated by obtaining several condensate spectra with varying Raman pulse durations. This may allow the characteristic time scales to be probed directly. A systematic investigation of this issue has not been performed, although the spectrum shown in Fig. 7.5 has been repeated for a few different values of pulse duration. Figure 7.6 shows a condensate loss spectrum for the same conditions as Fig. 7.5 but for a pulse duration which is 6 times smaller. This graph, in combination with Fig. 7.5, can be interpreted as a direct probe of the energy dependence of the condensate fill rate. Again, most of the spectrum is well fit by a Wigner lineshape, although now the temperature parameter does not agree with
Figure 7.7 Wigner energy distribution with condensate peak. The vertical axis gives the number of atoms at a given energy $N(E)$. The delta function at $E = 0$ corresponds to the condensate, while the curve is the Wigner lineshape given by Eqn. 7.2.

the independent measurements provided by phase contrast imaging. Presumably, the reduced value of the temperature parameter is due to the fact that the high energy atoms do not contribute to the filling of the condensate on this shorter time scale. Again, the ~350 Hz deviation of the data point marked A from the red edge of the fitted curve is consistent with the mean field shift $\delta_{mf}$.

7.3.2 Double peak

If the Wigner-looking lineshape for the condensate loss signal shown in Figs. 7.5 and 7.6 is indeed due to the removal of thermal atoms, then there should also be a signal which is due to the direct removal of condensate atoms. This is illustrated in Fig. 7.7 which shows the Wigner lineshape along with a delta function at zero energy corresponding to the condensate. It is difficult to justify the validity of the condensate filling model as an explanation for the asymmetry observed in the condensate spectra without the presence of this additional peak. Note that the condensate peak might not appear at exactly $E = 0$ since the mean field shift $\delta_{mf}$, as given in Eqn. 4.13, will pull it to lower energies.
Double-peaked condensate loss spectrum. These data were obtained for the same experimental conditions as in Figs. 7.5 and 7.6, except for a smaller pulse duration $\tau = 0.1$ s. The solid line is a Wigner lineshape fit with a Boltzmann temperature parameter of 34 nK.

The data point marked A in Fig. 7.6 might be an indication of the condensate peak discussed above. In order to investigate this possibility, the spectrum was repeated with higher precision and for an even smaller pulse duration, as shown in Fig. 7.8. The sharp red peak may be due to the condensate and has a width of $\sim 200$ Hz. This width is consistent with the $\sim 150$ Hz uncertainty in the mean-field shift $\delta_{mf}$. The data point marked A on the "condensate peak" is displaced from zero energy (as given by the Wigner fit) by $\sim 300$ Hz, which is also consistent with $\delta_{mf}$. This spectrum, in combination with those shown in Figs. 7.5 and 7.6, is a fairly convincing argument in favor of the condensate fill model for explaining the lineshape. It can be argued, however, that if the point A were removed from this spectrum, the condensate peak would essentially disappear within the mutual uncertainties of the surrounding points. Although this argument has merit, it is exactly what should be expected from probing a very narrowlinewidth in a system with large inherent fluctuations.

If spectra such as that shown in Fig. 7.8 were ubiquitous in our collection of data, then the lineshape issue might be laid to rest in favor of the condensate filling model discussed above. Unfortunately, there are only maybe 2 or 3 other spectra which
show definite double-peaked structure and the one shown here is the best of the lot. Again, it is not surprising that these peaks are difficult to repeat when considering the inherent fluctuations in $N_0$ caused by the growth and collapse dynamics. Additionally, the light shift for these data carries an uncertainty (see Sec. 4.4.2) of $\sim 280$ Hz caused by uncertainties in the laser intensities and the detuning $\Delta$.

### 7.3.3 Condensate emptying model

It should be noted that there is a different model for explaining the Wigner-looking lineshape, which is closely related to the condensate filling model discussed here. Instead of relying on the reduction of the fill rate of thermal atoms into the condensate, this model assumes that atoms from the condensate can fill the holes left behind by the thermal atoms when they are removed via the Raman pulse. In some sense, this is the time-reversal of the condensate filling model since, in this case, a condensate atom ($E = 3/2(\hbar\omega)$) collides with another atom with energy $E_1$ to produce a pair of atoms, each with $E < E_1$, where $\omega$ is the trap oscillation frequency. Because of the time reversal symmetry, this condensate emptying model should have similar characteristic time scales as the condensate filling model. Note that the time scales will not be perfectly symmetric for the two models since the rate for atoms to enter the condensate is enhanced while the rate to leave the condensate is not. The conceptual advantage of the condensate emptying model is that it remedies a fatal flaw in the condensate filling model having to do with the condensate growth and collapse. This flaw (which I have completely ignored so far) arises from the fact that the value of $N_0$ before the the Raman pulse is broadly distributed (see Fig. 5.4). Therefore, it should not matter whether the source of condensate growth is completely shut off by the Raman pulse. As long as the loss rate from the condensate is not enhanced, then the distribution after the pulse should be unaltered. The condensate emptying model avoids this issue by assuming that removing atoms from the thermal gas actually
enhances the condensate loss rate.

7.3.4 Other possibilities

Although not surprising, the lack of repeatable double peaked spectra is unsatisfying and other possibilities for the lineshape should be considered. The important question to answer is whether the sharp condensate peak is real or just a consequence of the inherent fluctuations. If the condensate peak is not real, then the condensate filling/emptying model cannot be meritorious because, as discussed above, it relies on there being a double peak in the spectrum. The density matrix model discussed above might explain the observed asymmetry in the condensate spectra, but would not be consistent with a condensate peak, if found to be real. The Feshbach resonance model could account for both the asymmetry and the double peak if a sufficiently large change in the scattering length $a$ were obtained. In that case, the condensate might overfill the stability limit $N_m$ and then collapse when the Raman pulse is shut off. This would have the effect of reducing the average value of $N_0$ in the region where $a$ was made less negative (or positive), producing a condensate peak similar to that observed in Fig. 7.8. Examination of Fig. 7.4 shows that this occurs on the red side of the spectrum, as desired. Unfortunately, the maximum value of $\Delta a/a$ calculated using the parameters corresponding to Fig. 7.8 is $\sim 1\%$, assuming that the decay width of the $\nu' = 10$ level is 250 Hz. The corresponding change in $N_m$ is too small to detect in our system, ruling out this possibility as well.

Perhaps the true explanation of the lineshape is a combination of all the effects described above. Each one may dominate the lineshape for a different region of parameter-space. For example, when the Raman resonance is power broadened by the lasers, the narrow double peak predicted by the condensate filling/emptying model would be embedded in the power broadened width. In such cases, the density matrix model may dominate the global character of the lineshape. Further, there might
be a local character to the lineshape which is due to the Feshbach model. Since
the Feshbach and density matrix models appear to arise from completely different
physical phenomena, the "addition" of the lineshapes in this way may be merited.
In order to investigate these possibilities and to resolve the issue of the double peak
structure, many more Raman spectra are needed.
Chapter 8
Conclusions

If the quality of a particular body of work were measured by the number of questions it generates, rather than the number of questions it answers, then this thesis ranks very highly. Although many issues have been illuminated by the work reported here, there are at least as many unresolved ones. Some of the open questions were raised in the pursuit of other goals, while others pertain directly to the central work of the thesis and were not answered simply for lack of time, or from pure oversight. In any case, this chapter addresses the more pressing or interesting questions and offers some suggestions for obtaining answers. These questions/answers will be mixed in with a summary of the major results of the thesis.

8.1 Free-bound overlap integrals

In general, the single-photon photoassociation results presented in Chap. 3 are well understood. However, there is one particularly important issue which needs to be addressed. The overlap integrals $\langle \phi_0 | \psi_v \rangle$ are used throughout the thesis to compute the photoassociation loss rate $R_p$, the free-bound Rabi frequency $\Omega_p$, the two-photon Rabi frequency $\chi$, and the magnitude of the optically-induced change to the scattering length $\Delta a/a$. These integrals were derived from a calculation based on the dissertation work of Robin Côté [16], and they may not be rigorous. Robin and Juha Javanainen (a recent collaborator: see Ref. [37]) have been contacted several times in order to clarify their recent work reported in [37] and to obtain precise values (or at least a blueprint for calculation) of $\Omega_p$, but so far these efforts have been unfruitful. Perhaps the best recourse is to try to measure them directly or to extract them from some experimental data.

The most straightforward way to measure $\langle \phi_0 | \psi_v \rangle$ is to perform an Autler-Townes
experiment similar to that shown in Fig. 4.4. In this case, the photoassociation laser \( \omega_1 \) would be held on the one-photon resonance \( \Delta = 0 \), and the bound-bound laser \( \omega_2 \) would be scanned through the two-photon resonance. In order for this measurement to be successful, \( \Omega_p \) needs to be at least as large as the intermediate state natural width \( \Gamma_m = 11.7 \text{ MHz} \). Using the values of \( \langle \phi_0 | \psi_v \rangle \) obtained by Côté shows that even for \( v = 79 \) (where \( \langle \phi_0 | \psi_v \rangle \) is largest of those considered in all previous calculations) and for \( I_1 = 500 \text{ W/cm}^2 \) (which is a huge intensity), \( \Omega_p \) is still only \( \sim 1 \text{ MHz} \) (assuming a density of \( n = 5.7 \times 10^{12} \text{ cm}^{-3} \)). As long as Côté’s values are within a couple orders of magnitude of being correct, the Autler-Townes measurement seems unpromising.

Of course, it is unclear whether such a measurement can be made even in principle, since the Autler-Townes effect implies coherence (on the free-bound transition, in this case) which, as discussed in Chap. 7 and further below, may not be present.

Another way to extract \( \langle \phi_0 | \psi_v \rangle \) is to measure decay curves of the total number of atoms \( N \) as a function of the photoassociation pulse duration. These measurements have been heretofore overlooked although in principle they are straightforward. It is probably easier to measure these decay curves for non-degenerate atomic clouds so that an analytic function (Gaussian) can be used for the density distribution. If this is done, the analysis becomes equivalent to that employed for measurement of the dipolar relaxation rate constant \( (G_2) \) presented in Refs. [85] and [16]. The free-bound loss coefficient \( R_p/n \) would play the role of \( G_2 \), while the atomic loss rate \( R_f \) would play the role of the one-body background collision loss rate \( G_1 \). These measurements could be made for a variety of levels \( v \) and detunings \( \Delta^* \) in order to extract self-consistent values for \( \langle \phi_0 | \psi_v \rangle \). Note that the expression for \( R_p \) used throughout the thesis may be in error by a factor of 2, as discussed in Chap. 7.

*\( \Delta \) should not be made so large that \( R_f \) exceeds \( R_p \), or else the sensitivity to \( R_p \) is lost.
8.2 Photoassociation frequency shift

The most pressing issue regarding the photoassociation frequency shift discussed in Sec. 3.3 is the development of a more rigorous physical model for the phenomenon. Recall that the general picture offered in that section is that the shift arises from an integral of AC Stark shift contributions from the entire continuum of scattering states near threshold. This explanation aids in the understanding of why the shift is observed in single-photon spectra, whereas typical AC Stark shifts between discrete states are not usually observed in single-photon spectra. It also provides an intuitive window for understanding why the shift only affects the energy of the excited-state level \( v \) (as discussed in Chap. 4) rather than both the excited-state and ground-state levels. In some sense, as mentioned by the authors of Ref. [33], the shift is caused by the excess weight of continuum states at high energy pressing down on the excited-state bound level, when the system is considered in the dressed-atom basis. This picture leads to an asymmetric distribution of the shift to the bound state since the effect of the single bound state on the infinity of continuum levels is an infinitely small perturbation. A more rigorous mathematical model for this physical picture would be helpful, especially with regards to a manuscript currently in preparation, which describes the experimental results presented in Chap. 3.

8.3 Two-photon photoassociation

The complicated chapter on two-photon Raman photoassociation (Chap. 4) can be distilled to a few significant results and issues. First, the bound-bound overlap integrals \( \langle \phi_2 | \psi_v \rangle \) seem to be nailed down with high precision. As discussed above, the free-bound overlaps are not nearly so certain, so the values of the two-photon Rabi frequency \( \chi \) given by Eqn. 4.15 have corresponding uncertainties associated with them. Additionally, although the factor of \( 1/\sqrt{2} \) in Eqn. 4.15 is present in both Refs. [36, 37], it has been called into question. Once the free-bound overlap integrals \( \langle \phi_0 | \psi_v \rangle \) have
been established by the procedure described above, then this factor of \(1/\sqrt{2}\) can be checked by the same procedure, but replacing the one-photon photoassociation pulse with a two-photon pulse. Establishing the validity of \(\chi\) is important to any future experiments aimed at observing atom/molecule Rabi oscillations (Sec. 4.3.4) or the effects of the two-photon optically induced Feshbach resonance (Sec. 6.4). All calculations in this thesis which rely on \(\chi\) should be regarded as tentative until its validity is established.

Another major point of contention in the thesis is the factor of 2/3 discrepancy observed in Sec. 4.4.2 between the two-photon light-shift data for \(\nu = 72\) and the light-shift model predictions. As discussed in that section, this discrepancy can only be attributed to the AC Stark shift due to the free-free coupling \(\Omega_f\). It is not clear, however, whether this factor of 2/3 applies to the contribution to \(\Omega_f\) from both \(I_1\) and \(I_2\) or just \(I_1\). This uncertainty is due to the fact that no light-shift data for \(\nu = 72\) was obtained for large values of \(I_2\) and therefore any dependence on \(I_2\) may be lost in the scatter of the data. This question can be readily resolved by measuring the dependence of spectral location of the two-photon resonance on \(I_2\) alone for large values of \(I_2\).

Unfortunately, aside from an extremely close inspection of the light-shift model, I cannot offer a definitive experiment which will resolve this discrepancy. One possible source for the discrepancy is related to the use of the tapered optical amplifier. The solid black data points from Fig. 4.13, which correspond to the highest intensities (and show the largest discrepancy with the model predictions), were obtained using this amplifier. The tapered amplifier emits a large amount of amplified spontaneous (ASE) light in addition to laser light. This ASE is broadly spread in frequency and additionally does not occupy the same spatial mode as the laser light. When the experiment is conducted, the ASE is spatially separated from the laser light using a high-quality optical grating (1800 grooves/mm) and by coupling the laser light into
an optical fiber. However, if some of the ASE reaches the atoms, it might lead to some spurious shifts (and loss). This possible explanation seems unlikely, however, since even the data with low \( I_1 \) demonstrate the systematic discrepancy with the model.

This discrepancy may lead to a systematic shift in the measurement of the \( v' = 10 \) binding energy. One attempt to account for this systematic error is to include the factor of \( 2/3 \) in the model, without an understanding of its origin, in order to describe the data more accurately. This has been done in Sec. 4.4.2.* Alternatively, the data can be fit phenomenologically without inserting any values for overlap integrals etc., and the fitting parameters can be used to interpolate the data to the asymptotic value for the binding energy. Perhaps the best way to measure the binding energy, however, is to use a very deep intermediate state (\( v = 58 \)) for which the free-free AC Stark shift (\( \Omega_J \)) can be neglected, as discussed in Sec. 4.4.1. The data presented in that section were obtained at relatively high temperature \( T \) and for relatively large total \( N \) where the sensitivity to the condensate number \( N_0 \) was insufficient. A more precise value for the binding energy could be obtained by using condensate loss spectra (as for \( v = 72 \)) for the \( v = 58 \) intermediate state.

### 8.4 Two-photon lineshape

The two-photon lineshape is one of the most interesting (and unresolved) issues in the thesis. There are several aspects which should be investigated. First and foremost, the correct model for the lineshape needs to be established. There are several experiments which can aid in this. One possibility is to repeat the total atom loss spectrum of Fig. 7.2 but for \( \Delta = +35 \) MHz (rather than -35 MHz). If the symmetry of the observed dispersion lineshape then reverses, the correct lineshape model for these data must be the density matrix model. The optical Feshbach resonance lineshape is ruled out in this case because its symmetry does not depend on the sign of \( \Delta \)

*Note that no corrections for any systematic errors due to the lineshape have been included in Eqn. 4.35.*
since $\Delta a/a \propto 1/\Delta^2$. Additionally, there should be no dependence on the sign of $\Delta$ in the condensate filling/emptying model since that model relies on the kinetics of the gas equilibration, rather than any optical coherence phenomena. Similarly, the condensate loss spectra of Figs. 7.5, 7.6, and 7.8 can be repeated for positive $\Delta$. If the lineshape symmetry does not reverse, then the kinetic condensate filling/emptying model must be the correct one for these data. Note that the density matrix model predicts an asymmetric lineshape similar to that observed in the data for the same conditions. Although the predicted asymmetry is qualitatively similar, the frequency scale is different. Recall that the optical Feshbach resonance lineshape has already been ruled out for these data.

Paramount to investigations of the kinetic condensate filling/emptying model is, of course, the determination of whether the so-called “condensate” peak is real, or merely the result of experimental and physical fluctuations. One important experimental difficulty in obtaining the necessary high-resolution condensate loss spectra is the $\sim 20\%$ uncertainty in the laser intensities (see Sec. 4.4.2). Roughly half this uncertainty is due to the calibration uncertainty in the optical power meter used to measure the powers of each laser. This is not so worrisome because this calibration, although uncertain, is not expected to fluctuate during the course of an experiment. The other half of the uncertainty is due to drifts in the spatial overlap between the laser beams and the atom cloud. This is more troubling since the overlap has been observed to vary during the course of an experiment.

There are two approaches to alleviating this problem. One is to increase the stability of the spatial overlap. This can be accomplished by increasing the laser beam transverse diameter and decreasing the lever arm between the optical fiber output and the atom cloud. The other approach is to determine the laser parameters which give zero net two-photon light shift $\delta_{\text{fs}}$. In this scheme, the dependence of $\delta_{\text{fs}}$ on total intensity $I_1 + I_2$ would be made to vanish, and only the ratio of $I_1$ and
$I_2$ would need to be controlled precisely. Currently, $I_1$ and $I_2$ are independently stabilized (although manually) to the $\sim 1\%$ level. In order to facilitate this scheme, an appropriate vibrational level $v$ needs to be determined for which the contribution to $\delta_{ls}$ from the free-free coupling ($\Omega_f$) is roughly half the contribution from the bound-bound coupling ($\Omega_b$) for a reasonably large (and negative) detuning $\Delta$. Close study of the form of Eqn. 4.12 reveals why this is the case: the coupling $\Omega_f$ always gives a negative contribution to $\delta_{ls}$ and depends equally on $I_1$ and $I_2$, whereas for negative $\Delta$, the coupling $\Omega_b$ depends almost totally on $I_2$ and gives a positive contribution to $\delta_{ls}$.

The most appropriate intermediate level $v$ for alleviating the dependence of $\delta_{ls}$ on $I_1 + I_2$ is clearly not a deeply bound one, as demonstrated in Sec. 4.4.1, since the shift contribution from $\Omega_f$ can be completely ignored in that case. Figure 4.14 shows that $v = 72$ is also not the most appropriate level since the dependence of $\delta_{ls}$ on $\Omega_f$ is larger than the dependence on $\Omega_b$ for a detuning of $\Delta = -100$ MHz.* The magnitude of $\Delta$ should be several times larger than this in order to minimize fluctuations in $\delta_{ls}$ due to variations $\Delta$. This necessitates the use of a slightly more deeply bound level.

Suppose that the kinetic model is found to be correct for the data shown in Figs. 7.5, 7.6, and 7.8, while the density matrix model is found to be correct for the data shown in Fig. 7.2. An important question, then, is when does the transition between these two models take place and whether they are mutually compatible. My intuitive contention is that when the observed linewidth exceeds the thermal energy spread of the atoms, then the kinetic model must give way to the density matrix model. This is roughly equivalent to saying that at this point, the time scale for any kinetic process exceeds the dominant optical time scale. This notion can be

---

*The factor of 2/3 discrepancy discussed above will factor into the determination of the correct laser parameters.

*In that figure, the light shift component $\Omega_b$ is shown to be negative. This is because the bound level $v' = 10$ does indeed shift to smaller values of energy due to the coupling $\Omega_b$ for negative $\Delta$, but the contribution to $\delta_{ls}$ is positive, by Eqn. 4.6.
investigated experimentally by systematically increasing $I_1$ and $I_2$ from the conditions of Fig. 7.5 and comparing the resultant lineshape to each model. Additionally, in such studies, the magnitude of $\Delta$ can be systematically decreased and, as mentioned above, its sign reversed. The key aspect to these investigations would be to look for correlations between $R_p, R_b, R_x, \Omega_p, \Omega_b, \chi$, and the widths and/or lineshape of the observed spectra.

Another important issue in the two-photon lineshape is that of coherence for the thermal atoms. As mentioned in Sec. 7.2, several theoretical treatments contend that no coherent processes are possible for a non-degenerate gas or for the non-condensed portion of a degenerate gas. If it is found that the density matrix model is consistent with the data of Fig. 7.2 (which is a total atom loss spectrum) then this contention is seriously challenged. Note that when the Raman coherence terms were eliminated from the density matrix model, the dispersion lineshape predicted by that model (Fig. 7.3) vanished. Therefore, the density matrix model only predicts a dispersion lineshape when coherence is assumed. A brief discussion following Fig. 7.3 suggests that perhaps coherence is maintained in the thermal portion of the gas when the observed linewidth exceeds the thermal energy spread of the atoms. This can be tested experimentally by systematically decreasing $I_1$ and $I_2$ and/or increasing the magnitude of $\Delta$ while once again looking for correlations between the rates and Rabi frequencies, and the observed lineshape.

*Ionut Prodan, who authored the model, has more details on this issue.
Appendix A
Phase lock

This appendix describes the phase lock feedback loop (PLL) used in two-photon photoassociation. The current performance specifications are given here to provide a benchmark for future use of this device and a parts list for the PLL is provided at the end of the chapter.

A Why build a PLL?

The PLL was built for two reasons. First, as shown in Chap. 4, the spectroscopic width of the two-photon resonance can be less than 1 kHz for appropriately small light intensities. This means that the difference frequency between the two lasers, $\Delta \nu$, needs to be controlled to at least that level of precision. The diode lasers used for this purpose have free run linewidths of $\sim 10$ MHz as described in Chap. 2. Obviously, this linewidth is insufficient for the two-photon photoassociation experiments described in this thesis. As shown below in Sec. C, the relative linewidth can be reduced to less than 1 Hz with the PLL engaged.

The second reason for building the PLL is to beat the bandwidth restriction of current electro-optic devices. If the magnitude of $\Delta \nu$ was not required to be too large, then the frequency difference could be generated using either an acousto-optic modulator (AO) or an electro-optic modulator (EO). For the two-photon photoassociation experiments reported here, however, $\Delta \nu \sim 12$ GHz, since this is the binding energy of the $v' = 10$ level. We are currently unaware of any AO or EO device which has a bandwidth this large. On the other hand, optical detectors with bandwidths as high as 50 GHz are now commercially available. These can be integrated into PLL circuits to produce values of $\Delta \nu$ with similar magnitude. Although the drive current of diode lasers can be directly modulated in order to produce frequency sidebands, this has
not been demonstrated for such high bandwidths with the red wavelength (671 nm) diode lasers used here.

B System description

The PLL is essentially an ultrafast optical heterodyne detector and lock. As shown in Fig. A.1, the two diode laser beams are combined on a beamsplitter, and part of the combined beam is directed onto a high bandwidth photodetector*. The photodetector measures the interference between the two lasers as a beatnote with frequency Δν. The beatnote is amplified† and subsequently mixed with a ~12 GHz signal generated by quadrupling the output of a microwave synthesizer. The synthesizer frequency is adjusted so that the intermediate frequency (IF) output of the mixer is ~40 MHz. The IF signal is further amplified and subsequently split using a microwave coupler. The -20 db coupled output is sent to a high bandwidth spectrum analyzer for analysis and to a high precision frequency counter. The main output of the coupler is sent to the feedback electronics described below.

The feedback electronics measure the phase difference between the 40 MHz IF signal and a 40 MHz local oscillator (LO) and provide feedback to one of the lasers, termed the “slave”, via two servos which control the diode laser current and cavity grating tilt angle respectively. The other laser, the “master” is locked independently near the molecular resonance frequency. This is accomplished by using a scanning etalon lock (SEL) to measure the relative frequency difference between the master and another laser which is locked to the atomic resonance. The measured frequency separation is maintained to a precision of only ~5 MHz via a feedback loop with a

*The photodetector, manufactured by New Focus, must be handled with caution since it is sensitive to electric discharge. Additionally, the published specifications list the maximum incident optical power to be 10 mW.

†The high bandwidth amplifier, manufactured by Miteq, is also sensitive to static discharge. Additionally, there is no internal DC compensation within the amplifier so a DC block must be used at the input.
very pedestrian 100 Hz bandwidth. This performance is sufficient for the two-photon photoassociation experiments described here since the important parameter is $\Delta \nu$.

A schematic diagram of the PLL electronic circuit is shown in Fig. A.2. This circuit is based on one which was developed in the group of Leo Hollberg at the National Institute of Standards and Technology (NIST) in Boulder [86]. The 40 MHz IF signal is digitized using an ultrafast comparator (AD8561) and then fed to the phase lock chip (AD9901)*. A detailed description of the operation principles

*Although a 20-pin square version of the AD9901 chip was used in the circuit for the work in this thesis, the 14-pin dual in-line (DIP) version is shown here for convenience. For the
of the AD9901 can be found in the specification sheets and application notes. In general, however, the AD9901 compares the frequency and phase of the digitized IF signal to the TTL compatible 40 MHz LO. The chip will output a square wave whose symmetry is related to the phase difference between the LO and IF signals. This is demonstrated in Fig. A.3 which shows the output of the AD9901 when the IF frequency is greater than, less than, or equal to 40 MHz. This square wave is filtered in order to eliminate the high frequency spurs and then integrated using a high speed op-amp (AD829). The non-inverting input of the integrator is offset to the voltage corresponding to the average of the high and low portions of the square wave. Therefore, when the waveform is symmetric, the signal integrates to zero and appropriate pinouts of the 20-pin version, see the application notes and specification sheets.
no feedback voltage is applied. When the waveform is asymmetric, the integration becomes non-zero providing an error signal.

The error signal can be gained down using a potentiometer referenced to ground in order to aid in acquisition of the lock. The low-pass filter in combination with the second AD829 provides differential gain for varying feedback frequencies. The feedback loop is then separated into a servo which drives the high voltage (HV) amplifier used to control the tilt angle of the diode cavity grating and a servo which directly modulates the laser diode current. The HV amplifier has a limited bandwidth and the piezo-electric crystal used for tilting the cavity grating has a resonance at acoustical frequencies. Therefore, in order to avoid feedback oscillations, the bandwidth of the grating servo is reduced by integrating the error signal. The balanced configuration of the current servo op-amps allow the laser diode current to be modulated directly and with high speed. A separate potentiometer/op-amp-follower arrangement after the lock switch enables manual scanning of the laser frequency via both servos.

Because the IF frequency derived from the optical beatnote is phase-matched to the 40 MHz local oscillator, the frequency difference $\Delta \nu$ between the master and slave is not $4 \times f_s$, but rather $4 \times f_s \pm 40$ MHz, where $f_s$ is the output frequency of the microwave synthesizer. Whether the $+$ or - sign is used depends on which laser has higher absolute frequency. If the slave is higher in frequency (as is usually the case) then the - sign is used and $\Delta \nu = 4 \times f_s - 40$ MHz. The + sign is used if the master
Figure A.4  Power spectrum of optical beatnote when phase lock is engaged. The signal shown is the measured IF near $\nu_0 = 40$ MHz.

is higher in frequency. This asymmetry results from the fact that the arrangement of the PLL electronics shown in Fig. A.2 imposes a feedback logic which causes the lock to acquire only when the slave laser frequency is lower than that corresponding to an IF frequency of zero.

C Performance
C.1 Short term

The short term performance of the PLL can only be described as spectacular. Figure A.4 shows the power spectrum of the optical beatnote when the PLL is engaged. The broad pedestal in Fig. A.4 is due to noise characteristics inherent to the laser diode semiconductor material and the tight central peak is due to the PLL feedback. The slight humps at $\pm 850$ kHz give the bandwidth of the PLL feedback. If the gain feedback gain is made too large, these humps grow and become sharper indicating that the loop is driven into oscillation. The measurement shown in Fig. A.4 was obtained using a 3 GHz bandwidth spectrum analyzer whose resolution limit is 1 kHz. A different spectrum analyzer, with a 100 kHz bandwidth and minimum resolution of 1 mHz was used to obtain a more precise measurement of the beatnote linewidth. Figure A.5 shows four high precision measurements of the optical beatnote power
Figure A.5  High precision measurement of the optical beatnote linewidth. The 40 MHz IF is mixed with the output of a microwave synthesizer (at 40.05 MHz) and the signal shown is the measured secondary IF near $\epsilon_1 = 50$ kHz.

spectrum for four different time scales. The spurious peaks corresponding to 60 Hz harmonics, for example, are of no consequence to the experiment because they are suppressed by many orders of magnitude. The full-width-half-max of the bottom trace, which corresponds only to the very tip of the peak since the vertical scale is in decibels, is measured to be $\sim 100$ MHz. This level of precision surpasses all requirements for the two-photon photoassociation experiments described in the preceding chapters.

As shown in Fig. A.1, the laser beam which goes to the two-photon photoassociation experiment is fiber coupled. This is experimentally beneficial because it reduces intensity variations across the laser beam profile and decreases drift in the overlap
between the laser beam and the atom cloud. However, the optical fiber could in principle alter the beatnote power spectrum as measured above via some nonlinear optical process, since the fiber consists of a dielectric medium (glass). Fortunately, this was not observed when the power spectrum was measured using a 100 MHz bandwidth photodetector after the fiber output. In this case, the optical beatnote $\Delta \nu$ was locked directly to the 40 MHz LO and the microwave mixing stage was bypassed.

An additional concern is that occasionally, the powers of either the slave or master lasers or both are amplified using a tapered optical amplifier. This device is patently nonlinear producing an output beam with as much as 50 times the power of the seed laser while at the same frequency. Fortunately, using the same technique as for the optical fiber measurement above, no difference in the beatnote power spectrum is observed when the optical amplifier is used. To be safe, however, the amplified beam should be used for the optical beatnote in the PLL rather than picking off some part of the seeding laser before the amplifier.

C.2 Long term

The power spectra shown in the figures above demonstrate the short-term performance of the PLL. Care must be taken, however, to ensure that the long term stability of both the LO and the microwave synthesizer is sufficient. The frequency stability of both these elements is affected by crystal oscillator aging and response to temperature drifts. The microwave synthesizer, for example, has a published aging specification of 6 parts in $10^9$ per day and an ambient temperature response of 2 parts in $10^8$ per °C. Using these specifications, the 12 GHz output of the synthesizer (after quadrupling) can drift by as much as 1 kHz in just 15 days and for a temperature change of 4 °C. The temperature in the lab is controlled to about ±1 °C causing a peak to peak swing of 500 Hz. Clearly, this (worst-case) performance is not sufficient to obtain two-photon photoassociation spectra, which can be as narrow as a few
hundred Hz, in a repeatable way.

This issue is addressed in two ways. First, a global positioning system (GPS) antenna and receiver unit is used to obtain a 10 MHz reference frequency that is ultimately stabilized to an atomic clock. Actually, several GPS satellites (with several atomic clocks each) in synchronous orbit with the earth broadcast the signal which is received by the GPS antenna. There is no long term drift or temperature dependance to this 10 MHz signal making it an ideal frequency reference for our system. The microwave synthesizer can accept this reference frequency, replacing its own internal reference oscillator. Second, an oven controlled crystal oscillator (OCXO) is used for the 40 MHz local oscillator. The OCXO has an aging specification of 1 part in $10^8$ per day and an ambient temperature response of 2 parts in $10^7$ per °C. In principle, this would cause a 1 kHz change in the 40 MHz oscillation frequency in about 7 years or for a temperature change of 125 °C. In practice, such changes will never occur because the OCXO has a mechanical tuning knob which can be used to correct for any frequency drifts. The 40 MHz IF, which is set by the OCXO oscillation frequency, is monitored using a high precision frequency counter which has 1 Hz resolution and which uses the GPS reference frequency to replace its internal reference oscillator.

D Parts
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Table A.1  Parts list for phase-lock loop.
Appendix B

Excited state binding energies

This appendix will document the measurement of binding energies for the \( v = 58 \), \( v = 69 \), and \( v = 72 \) vibrational levels in the triplet excited-state of \( 7\text{Li}_2 \). These measurements were made under quantum degenerate conditions where the thermal energy spread is much less than the excited-state linewidth leading to unprecedented precision. The \( v = 69 \) and \( v = 72 \) levels had been previously measured in a MOT at \( T \sim 1 \text{ mK} \), while the \( v = 58 \) resonance was previously unobserved.

A Transition frequency

In order to determine the binding energies of the vibrational levels \( v \), a frequency reference must be established. This reference is naturally provided by locking a laser to the lithium atomic resonance frequency using saturated absorption of a lithium vapor in a heat pipe. Additionally, a standard unit must be used to measure the difference between this reference frequency and the transition frequency. This standard is given by the free spectral range FSR of a high precision Fabry-Perot interferometer (optical spectrum analyzer). The FSR of the spectrum analyzer is \( \sim 1.5 \text{ GHz} \), which is much smaller than the binding energy of the levels of interest. Therefore, a Michelson interferometer (wavemeter) with \( \pm 0.5 \text{ GHz} \) resolution is also used to determine how many multiples of the FSR separate the reference frequency from the level \( v \). In order for this method to be accurate, the FSR of the spectrum analyzer must be known to high precision. Previous measurements of the FSR in addition to a new, more precise measurement procedure, will be presented below in Sec. C.

Figure B.1 shows a schematic diagram which is used to determine the transition frequencies of the \( v = 58 \), \( v = 69 \) and \( v = 72 \) vibrational levels of the \( 1^3\Sigma_g^+ \) excited-state potential in \( 7\text{Li} \). The \( v = 58 \) and \( v = 72 \) levels were used as intermediate states
for two-photon photoassociation described in the preceding chapters and the $v = 69$ level was used to measure the light-induced photoassociation frequency shift described in Chap. 3. At the top of the figure, the saturated absorption dispersion curve for the D2 line of $^7$Li is shown. This trace was obtained by capturing the saturated absorption signal onto a digitized storage oscilloscope while scanning the reference laser (Coherent 699) through the appropriate atomic resonance. The reference laser is locked near the $F = 2$ hyperfine feature (red-most signal for D2 trace).

During the experiment, the frequency of the reference laser beam $\nu_{SA}$, which goes into both the optical spectrum analyzer and the wavemeter is detuned to the red of the $F = 2$ resonance frequency $\nu_{F=2}$, by an amount $\delta_{AO}$. This detuning is provided by an acousto-optic modulator (AO) in the heat-pipe lock [16], hence the subscript. Additionally, the $F = 2$ hyperfine feature of the D2 line falls to the red of the D2...
center of mass frequency by \( \delta_{HFS} \). The transition frequency of level \( v \) is therefore given by

\[
\nu_v = \nu_R - \delta_{AO} - \delta_v,
\]

where \( \nu_R = \nu_0 - \delta_{HFS} \) is the reference laser frequency, \( \nu_0 = 14903.983468(14) \text{ cm}^{-1} \) is the \(^7\text{Li} \text D2 transition frequency measured between the centers of gravity of the \( 2S_{1/2} \) ground state and \( 2P_{3/2} \) excited state \([87]\), \( \delta_{HFS} = 3/8(0.8035 + \epsilon) \text{ GHz} \) is the frequency difference between the \( 2S_{1/2} \) center of mass and the \( F = 2 \) feature \([23]\,*\)

\( 803.5 \text{ MHz} \) is \(^7\text{Li} \) ground-state hyperfine splitting \([87]\), \( \epsilon = 4.8 \text{ MHz} \) is a correction factor which arises from the transition selection rules \([23]\),† and \( \delta_v = \nu_{SA} - \nu_v \) is the detuning of level \( v \) with respect to the spectrum analyzer reference frequency \( \nu_{SA} \).

The frequency \( \nu_v \) gives the photon energy for the measured transition.

Using a high resolution frequency counter, the AO frequency is measured to be \( \delta_{AO} = 91.4(5) \text{ MHz} \), where the uncertainty is mostly due to the repeatability of setting the frequency knob on the AO driver as well as fluctuations in the driver’s reference crystal oscillation frequency with temperature and age. A discussion of uncertainties associated with calculating binding energies will be given below. Inserting this into Eqn. B.1 gives for the transition frequency

\[
\nu_v = \nu_0 - \delta_v - 3/8(0.8035 + 0.0048) - 0.0914 \text{ GHz}
\]

\[
= \nu_0 - \delta_v - 0.3945 \text{ GHz}.
\]

In order to calculate the binding energy, it must be determined which particular transition this frequency corresponds to and then apply any needed corrections so

---

*The ground-state \( F = 2 \) hyperfine level has \( 2F + 1 = 5 \) magnetic sublevels, while the \( F = 1 \) level only has 3. Therefore, the D2 center of mass lies to the blue of the \( F = 2 \) feature by \( 3/8(0.8035 + \epsilon) \text{ GHz} \)

†The \( F = 2 \) ground-state level can couple only to the \( F' = 1, 2, \) and 3 excited-state levels, whereas the \( F = 1 \) ground state couples only to the \( F' = 0, 1, \) and 2 excited states. Since the \( P_{3/2} \) excited-state is inverted such that the energy decreases with increasing \( F' \), the frequency difference between the spectroscopic features corresponding to the \( F = 2 \) and \( F = 1 \) transitions is slightly larger than the 803.5 MHz ground-state hyperfine splitting.
that the binding energy is referenced to the appropriate centers of gravity.

B  Fine and hyperfine considerations

The binding energy $E_B$ of any excited-state level $v$ is typically reported with respect to the hyperfine center of gravity of the asymptote to the excited-state potential, which is the $2P_{1/2}$ state in this case. Additionally, the reported number is referenced to the hyperfine center of gravity of the level $v$. When driving only one transition, as is the case here (see below), then the appropriate hyperfine corrections must be added to the measured transition frequency $\nu_v$ in order to compare with previous measurements. With these considerations, $E_B$ is given by

$$E_B(v) = \nu_P - \nu_v - \Delta_{HFS}^0 + \Delta_{HFS}^v,$$  \hspace{1cm} (B.3)

where $\nu_P = \nu_0 - \Delta_{FS}$ is the $^7\text{Li}$ D1 transition frequency measured between the centers of gravity of the $2S_{1/2}$ ground state and $2P_{1/2}$ excited state, $\Delta_{HFS}^0$ is the hyperfine correction for the initial state of two free atoms, and $\Delta_{HFS}^v$ is the hyperfine correction for level $v$. The fine-structure splitting in $^7\text{Li}$ has been measured by Windholz to be $\Delta_{FS} = 10.056$ GHz [87] and the hyperfine corrections are analyzed below.

Figure B.2 shows the relevant energy-level diagram for the molecular hyperfine levels of $^7\text{Li}_2$ [23]. Note that the ultracold temperature of the magnetically trapped atoms assures that only s-wave collisions occur, so the initial state has no rotation ($N = 0$). Additionally, the atoms are in the doubly spin-polarized $f = 2, m_f = 2$ ($G = 4$) hyperfine state and therefore only the ground-state level highlighted in red is relevant. Due to the selection rules $\Delta N = \pm 1, \Delta G = 0$, and $\Delta M_G = 0$ (see Chap. 3) only the the excited-state level highlighted in red is relevant. The measured transition frequency $\nu_v$ therefore only applies to the transition between the two highlighted states and the hyperfine corrections for both the ground state and excited state must be calculated. The ground state hyperfine correction is given by $\Delta_{HFS}^0 = 2 \times 3/8(803.5) = 602.6$ MHz [23] and the hyperfine correction for the level $v$
**Figure B.2** Energy-level diagram for the molecular hyperfine levels of $^7$Li$_2$. The levels highlighted in red are the relevant ones for the measurements described here. Here, $f = \vec{i} + \vec{s}$ is the total angular momentum of the atoms (since the $2S$ state carries no orbital angular momentum), $\vec{i}$ is the atomic nuclear spin, $\vec{s}$ is the atomic electronic spin, $\vec{I} = \vec{i}_1 + \vec{i}_2$ is the total combined nuclear spin of the atom pair (or molecule), $\vec{G} = \vec{f}_1 + \vec{f}_2$ is the total angular momentum of the atom pair, $\vec{S} = \vec{s}_1 + \vec{s}_2$ is the total spin, and $N$ is the rotational quantum number.

is given by

$$\Delta_{SIG} = \frac{b}{2}[G(G + 1) - S(S + 1) - I(I + 1)], \quad (B.4)$$

where $b = 92.4(8)$ MHz is the excited-state hyperfine constant [23]. For the upper highlighted level, $G = 4$, $S = 1$, and $I = 3$, giving $\Delta_{\text{HF}} = 3b = 277.2$ MHz.

Combining Eqns. B.2 and B.3 and inserting the fine and hyperfine corrections gives

$$E_B(v) = \nu_0 - 10.056 - (\nu_0 - \delta_v - 0.3945) - 0.6026 + 0.2772 \text{ GHz}$$

$$= \delta_v - 9.987 \text{ GHz} \quad (B.5)$$

for the binding energy of level $v$. Note that this binding energy only applies to the
\( N = 1 \) rotational level. The only task which remains is to measure the quantity \( \delta_v \) for all the levels \( v \) of interest.

C Spectrum analyzer calibration

To compute \( \delta_v \), the FSR of the spectrum analyzer must first be measured. Such a measurement was made in January, 1994 with a result of 1.50001(15) GHz and again in May 1995, with a result of 1.49986(8) GHz [30]. These measurements were made by locking a reference laser to the atomic resonance frequency and then manually scanning another laser over many multiples of the FSR. Both lasers were simultaneously injected into the spectrum analyzer and it was noted each time the scanned laser moved another multiple. The frequency difference between the two lasers \( \Delta \nu \), when separated by \( N \times \) FSR, was calibrated using the wavemeter, where \( N \) is the multiple of the FSR corresponding to \( \Delta \nu \). Since the resolution of the wavemeter is ±0.5 GHz, the relative precision of this method was limited to 0.5/\( \Delta \nu \) in GHz. Accordingly, the laser was scanned tremendously far (~3 THz) while maintaining an accurate count of the FSR multiple. This is no easy feat, even using dye lasers.

Currently, there is an easier (and more precise) method for determining the FSR of the spectrum analyzer, which was not available when the measurements described above were performed. It relies on the use of a phase-locked feedback loop (PLL) to maintain \( \Delta \nu \) to high precision. The PLL system is described in detail in App. A. The beauty of using the PLL is that it provides sub-Hz precision on the laser difference frequency. Comparing that to the 0.5 GHz precision provided by the wavemeter shows that to achieve the same measurement precision as above, the laser needs to be scanned only \( 10^{-9} \times 3 \) THz = 1 kHz! Of course, the finesse of the spectrum analyzer \( f \sim 300 \), is not sufficient to resolve such a small difference frequency since the minimum resolvable bandwidth is given by \( \frac{\text{FSR}}{f} = 5 \) MHz.

In February of 2001, another measurement of the FSR was made, this time with
the PLL method. The procedure was as follows: two diode lasers were phase-locked with $\Delta \nu \sim 12$ GHz. This value of $\Delta \nu$, corresponding to $N = 8$, was chosen in order to maximize the frequency separation without exceeding the 3 GHz input bandwidth of the quadrupler component of the PLL (see App. A). Both lasers were simultaneously coupled into a single mode fiber optic whose output was directed into the spectrum analyzer. In this way, the spatial modes of both lasers within the spectrum analyzer are assured of being the same. The difference frequency $\Delta \nu$ was adjusted so that the spectrum analyzer traces for both lasers were maximally overlapped with each other. This was achieved to high precision by reducing the width of the spectrum analyzer scan from $\sim 2.5$ GHz to $\sim 50$ MHz and determining which value of $\Delta \nu$ corresponded to the maximum height of the combined spectrum analyzer peak. When the step size for changing $\Delta \nu$ was reduced to the point that no further distinction could be made in the combined peak height between adjacent frequency steps, the lasers were considered to be "maximally overlapped". The uncertainty in determining the maximum overlap criterion is given by this last frequency-step size.

When the maximum overlap criterion is met, then $\Delta \nu$ is a precise multiple (8) of the FSR. As detailed in App. A, $\Delta \nu = f_{PLL} - 40$ MHz since the optical beatnote is red detuned from the PLL frequency $f_{PLL}$ by an amount precisely equal to the local oscillator frequency. $f_{PLL}$ was generated by quadrupling the output of a high precision microwave synthesizer whose 10 MHz reference oscillator is derived from a global positioning satellite (GPS) receiver. The PLL local oscillator is an ovenized crystal source whose frequency was measured using a GPS-locked frequency counter to be within 0.5 Hz of 40 MHz. Combining these relationships gives an expression for the FSR:

$$\text{FSR} = \frac{4 \times f_s - 40}{8} \text{ MHz},$$

(B.6)

where $f_s$ is the phase-lock synthesizer frequency.

The maximum overlap criterion was met when $f_s = 3009.45(5)$ MHz, correspond-
ing to a measured FSR of 1.49973(3) GHz. The quoted 50 kHz uncertainty in $f_S$ is the frequency-step size at which no difference in the maximum overlap criterion could be observed, as described above. Note that the 200 kHz uncertainty in $f_{PLL}$ implied by this 50 kHz uncertainty in $f_S$, is much less than the ~5 MHz resolution of the optical spectrum analyzer. The PLL suppresses all frequency noise between the lasers by at least 40 dB, enabling the width of the resolution line to be “split” by this factor of 25. Also note that the 25 kHz uncertainty in the measured FSR is a factor of 3 better than the more precise of the two measurements above. This makes the PLL measurement method highly desirable especially considering that it only took about 5 minutes to complete!

The measured value of the FSR above will be used in all further calculations of the binding energy. It should be noted, however, that the data presented here were acquired over a span of ~3 years without an intervening measurement of the FSR. It is expected that changes in ambient conditions of the lab, particularly temperature, will cause the actual FSR to fluctuate and drift over time. If future experiments are performed which require highly accurate binding energy measurements, or any other measurements which rely on the FSR calibration, the FSR should be measured regularly, perhaps daily, with the method described here.

As an aside, it would be interesting to determine the source and magnitude of any fluctuations in the FSR. If the main source of fluctuations is due to temperature variations in the lab (as I suppose it is), which cause the scanning Fabry-Perot cavity to incrementally change length, then it might be possible, depending on their magnitude, to use this method of measuring the FSR as the sensor in a highly stable and tightly controlled temperature feedback circuit. I cannot say whether this method of temperature feedback would be advantageous to any other standard methods nor whether such a scheme is already being employed somewhere. It would certainly be easier to tune a single laser near a transmission peak of a solid etalon or Fabry-Perot
cavity and use the transmission signal as a temperature sensor, but the PLL method has the advantage that the absolute frequency of the lasers is unimportant. Only the relative frequency must be controlled precisely, which is a much easier task than controlling the absolute frequency of either laser.

D Wavemeter

The last thing needed to compute binding energies is to determine the multiple of the FSR which separates the reference laser frequency in the optical spectrum analyzer $\nu_{SA}$ and the photoassociation laser frequency when tuned to the resonance center of the desired level $\nu_v$. This frequency difference $\delta_v$ can be measured to within $\sim 0.5$ GHz by the wavemeter, and should be near a particular multiple $N$ of the FSR. The only task remaining thereafter, is to measure the frequency difference $\delta_N$ between the $N$th etalon fringe and $\nu_v$.

The wavemeter measures the ratio of wavelengths between a temperature stabilized He-Ne laser and an unknown laser by counting the fringes produced by a scanning Michelson interferometer [88]. The ratio $R$ is related to the vacuum wavelengths by

$$R = \frac{\lambda_H^n}{\lambda_U^n} \frac{n_U}{n_H},$$

where $\lambda_H^n$ and $\lambda_U^n$ are the vacuum wavelengths for the He-Ne and unknown lasers, respectively, and $n_H$ and $n_U$ are the indexes of refraction for air at the respective wavelengths. The index of refraction $n$ depends not only on wavelength, but on ambient pressure, temperature, and relative humidity. Eric Abraham showed in his Ph.D. thesis that corrections to $n$ arising from changes in ambient conditions are negligible compared to the wavelength dependence [30]. He calculates that the frequency of the unknown laser is then

$$\nu_U = R \times 4.736125(3) \times 10^5 \text{ GHz},$$

where the uncertainty is due to a $\pm 300$ MHz uncertainty in the He-Ne frequency.
Figure B.3  Total atom loss spectrum for the $v = 72$ vibrational level of the $1^3\Sigma_g^+$ potential in $^7$Li. The data points are normalized to background images obtained with no photoassociation pulse. The dotted line is a Lorentzian fit with width 37(3) MHz and a center frequency of 21.0(6) MHz. The horizontal axis indicates the detuning from the $N = 363$ multiple of the FSR, $\delta_{363}$. The photoassociation pulse length is $\tau = 20$ ms and the laser intensity is $I = 6.04$ W/cm$^2$. For these data, $N(0) \sim 1.0 \times 10^5$ atoms and $T(0) \sim 215$ nK.

\section*{E  $v = 72$ measurement}

The $v = 72$ level is chosen to demonstrate how to calculate $E_B$ and the associated uncertainty, since it can easily be compared with previous measurements. Figure B.3 shows the atom loss spectrum for a recent measurement of the $v = 72$ level normalized to background images, as described earlier in this chapter. The wavemeter ratios for the reference laser in the spectrum analyzer $R_{\nu A}$ and the photoassociation laser $R_{\nu 2}$ were observed to be 0.943407 and 0.942258, respectively. Inserting these values into Eqn. B.8 gives an approximate difference frequency of $\delta_{\nu 2} \sim 544.181$ GHz, which corresponds to an FSR multiple of $N = 363$ with respect to $\nu_{\nu A}$. The precise value for the frequency difference is then

\begin{align}
\delta_{\nu 2} &= N \times \text{FSR} - \delta_{363} \\
&= 363 \times 1.49973 - 0.0210 \text{ GHz} \\
&= 544.381 \text{ GHz}, \tag{B.9}
\end{align}
where \( \delta_{363} = 21.0 \text{ MHz} \) as indicated by Fig. B.3. Inserting this result into Eqn. B.5 gives a binding energy of

\[
E_B(v = 72) = \delta_{72} - 9.987 \text{ GHz} \\
= 544.381 - 9.987 \text{ GHz} \\
= 534.394 \text{ GHz.}
\]  

(B.10)

To compute the uncertainty in this measurement, we must consider all parameters which enter into Eqn. B.10. Combining Eqns. B.3 and B.9, the expression for the binding energy becomes

\[
E_B = N \times \text{FSR} - \delta_N - 9.987 \text{ GHz.}
\]  

(B.11)

Note that the uncertainty in the calculated factor 9.987 GHz is on the order of 1 MHz, which is small compared to the uncertainties in the first two terms, as discussed below. Therefore, the uncertainty in this calculated factor is neglected and the total uncertainty becomes

\[
\sigma_{E_B} \cong \sqrt{N^2 \sigma_{\text{FSR}}^2 + \sigma_{\delta_N}^2}.
\]  

(B.12)

The uncertainty in the measurement of the FSR is given above as 30 kHz. However, the FSR might have drifted from the time the data was obtained to the time the FSR was measured. This drift might be several times the measurement uncertainty as evidenced by the 280 kHz difference between the FSR measurement reported here and the one performed in January of 1994. It is difficult to predict the magnitude of such drifts without systematic repeated measurements of the FSR. With the quick and highly precise method outlined above, such systematic measurements can now be obtained. For now, it is not unreasonable to assume that the total uncertainty in the FSR is twice the measurement uncertainty, giving \( \sigma_{\text{FSR}} = 60 \text{ kHz} \). The uncertainty in \( \delta_N = \delta_{363} \) is given by the amplitude of variations in the photoassociation laser frequency which are too fast for the SEL to suppress. Additionally, there is an
uncertainty in determining the precise separation of peak positions corresponding to the photoassociation laser and the reference laser in the spectrum analyzer trace. With these considerations, the uncertainty in \( \delta_N \) is estimated to be \( \sigma_{\delta_N} = 5 \) MHz. Inserting these numbers into Eqn. B.12 for \( v = 72 \) yields a total uncertainty for the binding energy of \( \sigma_{E_B} = 22 \) MHz. The final measured value of the binding energy is therefore

\[
E_B(v = 72) = 534.394(22) \text{ GHz.} \tag{B.13}
\]

As mentioned above, \( E_B(v = 72) \) was previously measured using the same technique described here, but in a MOT at mK temperatures. In Ref. [22], the binding energy is reported as \( E_B(v = 72) = 534.472(36) \). These two measurements disagree by \( \sim 1.3 \) times their combined uncertainty. The previous measurement in the MOT was made by continuously scanning the photoassociation laser while the trap fluorescence was monitored, in contrast to the discrete load-cool-probe-image cycle described here. This difference in measurement technique could account for the discrepancy in the results since, in the case of a continuous scan, the time scale for the response of the atom cloud to the photoassociation laser is set by the loading rate into the MOT. If the laser is scanned at a rate which is comparable to or faster than the loading rate, a delay in the response of the atom cloud to the photoassociation laser can be observed which can be interpreted as a shift in the spectral location of the resonance. However, it is unlikely that this is the source of the discrepancy since this effect was investigated and found to be negligibly small for the conditions reported in Ref. [22]. An additional, more likely, explanation for the discrepancy is a difference in light-induced photoassociation frequency shifts between the two measurements. Indeed, the maximum intensity reported in Ref. [22] for the photoassociation laser is a factor of \( \sim 25 \) larger than for the data shown in Fig. B.3. This would result in a \( \sim 50 \) MHz difference in the light-induced shift between the two measurements.* As described in

*The calculated photoassociation frequency shift for the measurement reported here is only
Figure B.4  Total atom loss spectrum for the \( v = 69 \) vibrational level of the \( 1^3\Sigma_g^+ \) potential in \(^7\)Li. The data points are normalized to background images obtained with no photoassociation pulse. The dotted line is a Lorentzian fit with width \( 24(3) \) MHz and a center frequency of \(-201.5(6)\) MHz. The horizontal axis indicates the detuning from the \( N = 576 \) multiple of the FSR, \( \delta_{576} \). The photoassociation pulse length is \( \tau = 10 \) ms and the laser intensity is \( I = 4.7 \) W/cm\(^2\). For these data, \( N(0) \sim 3.6 \times 10^5 \) atoms and \( T'(0) \sim 380 \) nK.

Chap. 3, an intensity increase results in a spectroscopic red-shift which increases the binding energy. Since the previous measurement in the MOT which was performed with a larger intensity actually yields a larger binding energy than the present one, this explanation is consistent with the discrepancy.

F  \( v = 69 \) measurement

The binding energies for the \( v = 69 \) and \( v = 58 \) levels can be determined in a similar way. Figure B.4 shows the atom loss spectrum for a measurement of the \( v = 69 \) level normalized to background images, as before. The uncertainties which contribute to Eqn. B.12 must be modified for this \( v = 69 \) measurement, compared to the measurement of \( v = 72 \). Now the FSR multiple is 576 instead of 363 and \( \delta_N = \delta_{576} \) is different as well. In order to measure the separation \( \delta_{576} \sim -200 \) MHz, the width of the optical spectrum analyzer sweep was increased from 150 MHz (for \( \sim 2 \) MHz, and is therefore neglected.)
\( v = 72 \) to 600 MHz. This decreases the precision with which the separation can be measured. Additionally, at the time the \( v = 69 \) level was measured, neither the reference laser nor the photoassociation laser was fiber coupled into the spectrum analyzer, so there is an uncertainty associated with differences in the optical path of each laser through the spectrum analyzer. This uncertainty was estimated to be \( \sim 10 \) MHz by varying the alignment of the reference laser into the spectrum analyzer and observing the shift in the peak position. With these considerations, the uncertainty in \( \delta_{576} \) is estimated to be \( \sigma_{\delta_{576}} = 12 \) MHz and the total uncertainty in the \( v = 69 \) binding energy is computed as \( \sigma_{E_B} = 36 \) MHz. The final measured value of the binding energy is therefore

\[
E_B(v = 69) = 854.059(36) \text{ GHz.} \tag{B.14}
\]

Again, this measurement does not agree with the 854.208(54) value reported in Ref. [22]. In this case, the photoassociation frequency shift can account for \( \sim 36 \) MHz of the discrepancy. Additionally, the measurement of \( v = 69 \) reported here was performed roughly two years prior to the FSR calibration used, in contrast to the \( v = 72 \) measurement above which was performed within two months of the calibration. Any drifts in the FSR, therefore, may be magnified by this large time separation. Unfortunately, it is difficult to predict the rate of any such drifts, as discussed above.

**G \( v = 58 \) measurement**

The \( v = 58 \) level had never been observed before the work reported here. This is due to the fact that the overlap integral \( A_v \) is roughly a factor of 20 smaller for \( v = 58 \) than for \( v = 69 \). The peak MOT densities reported in Ref. [22], \( n \sim 8 \times 10^{10} \) cm\(^{-3}\), made it difficult to observe the \( v = 58 \) level. In the permanent magnet trap for quantum degenerate conditions, peak densities of \( n \sim 10^{12} \) cm\(^{-3}\) are typical and the condensate density can exceed that by many times. This enabled the first measurement of this rather deep level.
Figure B.5  Total atom loss spectrum for the $v = 58$ vibrational level of the $1^3\Sigma_g^+$ potential in $^7\text{Li}$. The dotted line is a Lorentzian fit with width 63(17) MHz and a center frequency of 101(4) MHz. The horizontal axis indicates the detuning from the $N = 2452$ multiple of the FSR, $\delta_{2452}$. The photoassociation pulse length is $\tau = 20$ ms and the laser intensity is $I = 96.4$ W/cm$^2$. For these data, $N(0) \sim 1.3 \times 10^6$ atoms and $T(0) \sim 700$ nK.

Figure B.5 shows the atom loss spectrum for a measurement of the $v = 58$ level. Again, the uncertainties due to the new FSR multiple of 2452 and $\delta_N = \delta_{2452}$ need to be modified. In order to properly account for the uncertainty in the fitted center shown in Fig. B.5, the uncertainty in $\delta_{2452}$ becomes $\sigma_{\delta_{2452}} = 13$ MHz and the total uncertainty in the binding energy for $v = 58$ is $\sigma_E = 148$ MHz. The final measured value of the binding energy is therefore

$$E_B(v = 58) = 3667.25(15) \text{ GHz.}$$

(B.15)

Note that even though the laser intensity used for this measurement is relatively high compared to $v = 72$ and $v = 69$, the photoassociation frequency shift should be much smaller than the 150 MHz uncertainty since the $v = 58$ level is so deeply bound.
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