Spectroscopic Detection of the Lithium Helium (LiHe) van der Waals Molecule

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Physics

by

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Abstract

Van der Waals molecules are extremely weakly-bound, extremely long-range molecules. The most weakly bound van der Waals molecules are those containing helium. These special characteristics have motivated many theoretical studies on the structure of these molecules. To date, the only ground-state helium diatomic molecule that has been directly detected in gas phase is the helium dimer $^4\text{He}_2$.

Using cryogenic helium buffer-gas cooling and laser ablation, we have produced large densities of lithium atoms in a high-density helium gas, from which LiHe molecules form by three-body recombination $\text{Li} + \text{He} + \text{He} \rightarrow \text{LiHe} + \text{He}$. These weakly-bound van der Waals molecules were detected spectroscopically using laser induced fluorescence. We have measured the LiHe transition frequency, linewidth and optical density.

The observed LiHe spectrum confirmed the theoretical prediction that only a single rovibrational state of LiHe is populated. This state is split into a hyperfine doublet, which is unchanged from the atomic lithium, $^7\text{Li}$, at the level of accuracy of our measurements.

The excited-state structure of $^7\text{Li}^4\text{He}$ was calculated using the discrete variable representation (DVR). These calculations were in quantitative agreement with our measurements. From this agreement, and from the ground-state hyperfine splitting, we identified the molecule as $^7\text{Li}^4\text{He}$ and not $^6\text{Li}^4\text{He}$, $^6\text{Li}^3\text{He}$, $^7\text{Li}^3\text{He}$ or lithium bound to a helium cluster.
Dedicated to
My parents Ahmed and Aneesa,
my husband Mohammed,
my sisters, my brother Abdulaziz,
and my daughter Jood.
Portions of this thesis have appeared previously in the following paper:

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Chapter 1

Introduction

The goal of this thesis is to form the ground state LiHe van der Waals molecule by three-body recombination using cryogenic helium buffer-gas cooling, and spectroscopically detect it.

1.1 Chemical bonds and van der Waals forces

Molecules are composed of atoms which are held together by intramolecular bonds. The strength of the bond varies with the bond type. The covalent bond is formed when two atoms share a pair of valence electrons, one of each atom. A simple example of the covalent bond is the bond found in \( \text{H}_2 \). The ionic bond, such as the bond in \( \text{NaCl} \), is formed between oppositely charged ions [1]. The covalent and ionic intramolecular bond energies are on the order of \( 10^4 \) wave numbers (\( \text{cm}^{-1} \)) [2].

Molecules can bind together by intermolecular bonds, which are weaker than the intramolecular bonds. These bonds include the hydrogen bonds and the van der Waals forces. The hydrogen bond is the attractive force between the hydrogen atom of one molecule and an electronegative atom of a different molecule, such as the bonds between the water molecules \( \text{H}_2\text{O} \) [1]. The hydrogen bond energy, a relatively strong
intermolecular bond, is about an order of magnitude or two weaker than the covalent
and ionic bonds [2].

Van der Waals (vdW) forces between atoms or molecules are the weakest of all
intramolecular and intermolecular forces [3]. The vDW forces include three types of
forces, listed in order from strongest to weakest:

- The interaction force between two permanent dipoles:
The electrons in the molecules that contain a covalent or an ionic bond are
not shared equally between the atoms in the molecules. These molecules are
said to be polar, and to have a dipole moment. HCl molecule carries a dipole
moment; the hydrogen atom carries a partial positive charge, and the chlorine
atom carries a partial negative charge. These partial charges will attract another
HCl molecule. The attraction forces between adjacent HCl molecules are known
as dipole-dipole forces [3].

- The interaction force between a permanent dipole and an induced dipole:
An example of this is a complex formed of rare gas atoms and hydrogen halide
molecules. The rare gas atoms have a perfectly symmetrical charge distribution.
All hydrogen halide molecules have a dipole moment. When the two interact,
the electrons in the rare gas atom can shift to one side of the nucleus producing a
small instantaneous dipole moment. Thus, the molecules induce a small dipole
moment on these atoms creating permanent dipole–induced dipole forces of
attraction [4].

- The interaction force between two induced dipoles (London dispersion force):
An example of this is a complex formed of rare gas atoms. As mentioned above,
these atoms have a perfectly symmetrical charge distribution. However, the syn-
chronized movements of the electrons around the nuclei of two neighboring rare
gas atoms can induce small dipole moments, causing induced dipole-induced dipole forces of attraction [5].

London dispersion forces are necessary for achieving noble gas dimers and clusters, and are important in condensed matter systems and in physisorption [5, 2]. These forces vary with the inverse seventh power of the internuclear distance. They are proportional to the polarizability of the atoms or molecules; they become stronger as the atom or molecule becomes larger [1]. Thus, London dispersion forces are weak between He atoms, which are the least polarizable atoms.

VdW molecules are the complexes that are weakly bound by one of the vdW forces, and more often by a combination of all these forces [3]. They are characterized by their long range dispersion interactions, and ground state electronic wavefunctions comparable to the constituent atomic wavefunctions [6]. They are expected to be present whenever two atoms or molecules in the gas phase with low kinetic energy become trapped by their intermolecular attraction [7]. Although London dispersion forces are weak between He atoms, they are enough to make He$_2$ support a single bound state with an extremely weak binding energy [2].

1.2 Prior experiments investigating vdW molecules

Due to the weak binding energies of the vdW molecules, their formation requires cooling the atoms down to a very low temperature. Experimentally, one of the techniques that is popular for cooling the atoms and molecules, and investigating vdW molecules is the supersonic expansion of gases [5]. It has produced argon and neon-based vdW molecules for spectroscopic studies, as well as helium bound to large molecules [8].

The existence of the first diatomic helium vdW molecule, He$_2$, has been experimentally confirmed in mass spectrometric measurements by Luo et. al. [9]. They
observed the helium dimer ion for the first time using electron impact ionization of a supersonic expansion of helium with translational temperature near 1 mK.

Schöllkopf et. al. [10] utilized a nozzle beam expansion of He gas to produce a helium cluster beam. They were able to identify He$_2$ through diffraction of the helium beam from a transmission grating, measured at source temperatures of 150 and 30 K and source pressures of 150 and 15 bar respectively. From subsequent measurements by the same group [11], they were able to calculate the bond length and the binding energy for He$_2$, which are found to be $\langle r \rangle = 52 \pm 4 \, \text{Å}$, and $\epsilon = 1.1 + 0.3/ -0.2$ mK.

Excited-state helium vdW molecules have been observed in liquid helium [12], in dense helium gas [13, 14, 15], and in superfluid helium nanodroplets [16, 17].

1.3 Helium-containing vdW molecules

Of the diatomic vdW molecules, those containing helium — the most chemically “inert” of the noble gases — are the most weakly bound. There is much theoretical interest in the study of diatomic molecules involving helium, including questions over their existence [18, 19, 20]. To date, the only ground-state helium diatomic molecule that has been directly detected in the gas phase is the helium dimer $^4$He$_2$ [9, 11, 10]; the combinations $^3$He$^4$He and $^3$He$_2$ do not possess bound states [21].

Alkali metals are known to have weak interactions with helium, with typical well depth of 0.5–1.5 cm$^{-1}$. The much deeper $^4$He$_2$ well (7.6 cm$^{-1}$) supports only a single bound state of a binding energy about $10^{-3}$ cm$^{-1}$. This led to the belief that the alkali-helium dimers do not support bound states [19]. However, Kleinekathöfer et. al. [19] predict that for all $^4$He–Alkali diatomic molecules, there exists a single bound rovibrational state in the $X^2\Sigma$ ground electronic state. $^6$Li$^4$He is predicted to have a bond length of $\langle r \rangle \sim 48.5 \, \text{Å}$, and a binding energy of 0.001 cm$^{-1}$; $^7$Li$^4$He is predicted to have a bond length of $\langle r \rangle \sim 28 \, \text{Å}$, and a binding energy of 0.0039 cm$^{-1}$. These
numbers are comparable to $^4\text{He}_2$ [11], despite the significantly smaller well depth of LiHe [21]. Note that Li$^3\text{He}$ is predicted to be unbound [19].

1.4 The motivation for the LiHe experiment

Brahms et. al. [22, 6] from Harvard University observed the Ag$\cdot^3\text{He}$ spin-change rate coefficient for magnetically trapped silver (Ag) in a dense $^3\text{He}$ cryogenic buffer gas. The observed spin-change coefficient shows a strong $T^{-6}$ thermal dependence. However, the calculated rate constant for the atom-atom collisions shows only a weak temperature dependence and disagrees with the experimental data, suggesting that the observed loss rates cannot be explained by atom-atom collisions. The calculated molecular spin-change rate constant agrees quantitatively with experimental observations, providing indirect evidence for the formation of the Ag$^3\text{He}$ vdW molecule in buffer-gas-cooled magnetic traps.

The Harvard team attempted to observe the Ag$^3\text{He}$ molecule through absorption spectroscopy. However, with high absorption sensitivity compared to the expected absorption, no absorption was detected. They concluded that either the formation rate of the Ag$^3\text{He}$ is not large enough, such that the system did not reach thermal equilibrium on the experimental diffusion time scale; the formation rate of the Ag$^3\text{He}$ is slow compared to the lifetime of the buffer-gas cooled Ag atoms; or that the Ag$^3\text{He}$ population was rapidly reduced below the experimental detection sensitivity due to high photodissociation probability.

Brahms et. al. observed that helium buffer-gas cooling would provide a favorable environment —moderate densities of He at low temperatures— for forming ground-state helium vdW molecules, and that the formation rate of these molecules is likely large enough to ensure achieving thermal equilibrium. They provide a general model for the formation —through three-body recombination— and dynamics of helium...
vdW molecules, providing the guidance for this experiment.

1.5 Three-body recombination

As explained by Esry et. al. [23]:

Three-body recombination is the process in which three free atoms collide, producing a diatomic molecule. Schematically, for a generic atom X,

\[ X + X + X \rightarrow X_2(v, l) + X + E_{vl}. \]

For ultracold collisions, the third atom recedes from the dimer with a relative energy roughly equal to the binding energy of the dimer, \( E_{vl} \), where \( v \) and \( l \) label the rovibrational state. Just as in any other process that produces a dimer from free atoms, a third body — in this case, another atom — is required in order to conserve energy and momentum.

The rate equation for the density of the atoms is given by:

\[ \dot{n} \propto -K_3n^3, \quad (1.1) \]

where \( n \) is the density of the atoms, and \( K_3 \) is the three-body recombination rate constant.

Our experiment takes place in a cryogenic helium buffer gas cell, described in Ref. [24]. We follow the general model given by Brahms et. al. [6], considering forming the LiHe vdW molecule through the three-body processes between a Li atom and two He atoms:

\[ \text{Li} + \text{He} + \text{He} \xrightarrow{K} \text{LiHe} + \text{He}, \]

where \( K \) is the three-body recombination rate constant, and \( D \) is the collision-induced dissociation rate constant.
The reaction kinetics for LiHe formation and dissociation are

\[ \dot{n}_{\text{LiHe}} = - \dot{n}_{\text{Li}} = K n_{\text{He}}^2 n_{\text{Li}} - D n_{\text{He}} n_{\text{LiHe}}, \]  \hspace{1cm} (1.2)

where \( n_i \) denotes the density of species \( i \). If the timescale for LiHe formation and dissociation is fast compared to the lifetime of Li within the cell, the density of LiHe will reach thermal equilibrium with the free Li and He densities. In thermal equilibrium, \( \dot{n}_{\text{LiHe}} = 0 \), implies

\[ n_{\text{LiHe}} = k(T) n_{\text{Li}} n_{\text{He}}, \]  \hspace{1cm} (1.3)

where \( k(T) = K/D \) is the chemical equilibrium constant, given by the equation

\[ k = \frac{n_{\text{LiHe}}}{n_{\text{Li}} n_{\text{He}}} = \lambda_{dB}^3 \sum_i g_i e_i / K_B T. \]  \hspace{1cm} (1.4)

Here \( K_B \) is Boltzmann’s constant, \( T \) is the temperature, the sum is over all the bound states of the molecule, \( g_i \) and \( e_i \) are the degeneracies and the (positive) binding energies of these bound states, and \( \lambda_{dB} \) is the thermal de Broglie wavelength of the LiHe of reduced mass \( \mu \), given by

\[ \lambda_{dB} = \sqrt{h^2 / 2\pi \mu K_B T}. \]

Eq. 1.4 shows that \( n_{\text{LiHe}} \) increases exponentially as the temperature is lowered if \( T \lesssim \epsilon \). Thus, the formation is thermodynamically favored in buffer gas cooling experiments.

Brahms et. al. [6] estimated the equilibrium time assuming that all collisions of vdW molecules with helium atoms at energies which exceed the molecular binding energy will result in dissociation. The timescale to reach thermal equilibrium is

\[ \tau_{eq}^{-1} \sim \sigma \cdot n_{\text{He}} \cdot \nu_{\mu} \left( e_i / k_B T + g_i \lambda_{dB}^3 n_{\text{He}} \right), \]  \hspace{1cm} (1.5)

where \( \sigma \) is the elastic cross-section and \( \nu_{\mu} \) is the thermal velocity. Our experiment’s typical parameters are \( n_{\text{He}} = 10^{17} \text{ cm}^{-3} \), \( T = 1 \text{ K} \); for \( ^7\text{Li}^4\text{He} \), \( \nu_{\mu} \sim 10^4 \text{ cm/s} \) and
\( \lambda_{dB}^3 = 10^{-21} \text{ cm}^3 \). If we assume a small cross-section \( \sigma = 10^{-15} \text{ cm}^2 \) (typical cross sections for collisions at low temperatures range between \( 10^{-15} - 10^{-14} \text{ cm}^2 \) \([25, 26]\)), this predicts that the weakly bound LiHe would form on a time scale of \( 10^{-6} \text{ s} \). As we can achieve diffusion lifetimes on the order of seconds in our cryogenic cell, we therefore expect that the LiHe density will reach thermal equilibrium for the \( \text{Li} + \text{He} + \text{He} \leftrightarrow \text{LiHe} + \text{He} \) reaction.

We note that in our experiment, collisions involving multiple Li atoms is ignored, since the density of helium is about 6 orders of magnitude larger than the Li density. Moreover, due to the greater abundance of \(^7\text{Li} \) isotope, we expect to observe \(^7\text{Li}^4\text{He} \) rather than \(^6\text{Li}^4\text{He} \).

By examining Eq. 1.4, and noting that \( \epsilon \ll K_B T \) for both \( \text{He}_2 \) and LiHe, we expect to form \( \text{He}_2 \) at a density roughly 6 orders of magnitude larger than the LiHe density. However, with the diode lasers employed in the experiment, it is impossible for us to detect the He dimers.
Chapter 2

LiHe Spectroscopy

We have prepared high densities of cold lithium atoms in a cryogenic helium gas, in order to create LiHe molecules through three-body recombination

\[ \text{Li} + \text{He} + \text{He} \leftrightarrow \text{LiHe} + \text{He}. \]

In thermal equilibrium, from Eq. 1.4, the expected density of LiHe is given by

\[ n_{\text{LiHe}} = n_{\text{Li}} \cdot n_{\text{He}} \cdot \left( \frac{\hbar^2}{2\pi\mu K_B T} \right)^{3/2} \frac{g e^\epsilon}{K_B T}, \]

(2.1)

where \( n \) is the density of the given species, \( \mu \) is the reduced mass, \( T \) is the temperature, and \( g \) and \( \epsilon \) are the degeneracy and the (positive) binding energy of the LiHe bound state [22]. For \(^7\text{Li}\)^4\text{He}, with a single bound state with \( \epsilon \ll K_B T \),

\[ n_{^7\text{Li}^4\text{He}} \approx 10^{-21} \text{cm}^{-3} \cdot \left( \frac{n_{^7\text{Li}}}{1 \text{cm}^{-3}} \right) \cdot \left( \frac{n_{\text{He}}}{1 \text{cm}^{-3}} \right) \cdot \left( \frac{T}{1 \text{K}} \right)^{-3/2}. \]

(2.2)

Clearly, the formation of detectable quantities of LiHe is favored by high lithium and helium densities and low temperatures. All three are achieved with cryogenic helium buffer-gas cooling of atomic lithium produced by laser ablation [27].

The experiment is conducted in a cryogenic cell, identical to the apparatus described in Ref. [24]. The cell temperature is monitored by a ruthenium oxide resistor
and a silicon diode. The helium density in the cell is determined from a room temperature pressure gauge connected to the cell through a thin tube, and from the cell temperature. We correct for the thermomolecular pressure ratio with the Weber-Schmidt equation [28, 29]. The uncertainty in the helium density is approximately ±20%. This uncertainty comes from variation in cell temperature during the laser ablation and the uncertainty in the tube diameter.

2.1 Production of gas phase Li

Gas-phase Li is produced by laser ablation of solid target of 99.9% pure Li (of natural isotopic abundances) with a frequency-doubled Nd:YAG laser. The Li atoms are detected by laser absorption spectroscopy. A schematic of our optical setup is shown in Fig. 2.1. We split the Li diode laser output into multiple beams. Three low power beams reflected from the glass wedges are sent to the wavemeter to make sure the laser is tuned to the desired transition, through a Fabry-Perot interferometer to make sure the laser is running in single mode, and through the cell for absorption spectroscopy of the Li. We determine the optical density (OD) of the atomic Li from the photodetector signal, as described in Ref. [29]. The Li probe power is ≪ 1µW, with a beam diameter of a few mm. (At powers ≳ 1 µW, we observe optical pumping of the Li atoms, which makes accurate measurements of density difficult).

Li atoms are detected by laser absorption spectroscopy on the D1 transition at 671 nm [30, 31]. Due to the high atomic densities employed in the experiment, we typically measure the atomic lithium via the less-abundant $^6$Li isotope. The D1 transition and a typical spectrum of $^6$Li are shown in Fig. 2.2.

The helium buffer-gas density ranges from $2 \times 10^{17}$ to $1 \times 10^{18}$ cm$^{-3}$. We are able to produce Li densities up to $10^{11}$ cm$^{-3}$, with ablation energies of tens of mJ. Li density is determined from its OD as explained in detail in appendix B. The ablation
pulse momentarily increases the temperature of the gas [32], so we directly measure the translational temperature of the gas through spectroscopy of the atomic $^6$Li as explained in section 2.2; under our conditions Doppler broadening is observed to be the dominant broadening mechanism. Thermalization with the buffer-gas occurs within 1 ms.

Typical Li lifetimes are on the order of $10^{-1}$ s; the Li atoms diffuse through the He until they reach the walls of the cryogenic cell. We note that the lithium density as a function of time is not described by simple exponential decay as shown in Fig. 2.3; this is commonly seen in buffer-gas cooling experiments at high helium density [33]. To avoid complications due to this complex behavior, we measure Li and LiHe
simultaneously.

$^6\text{Li}$ (natural abundance of 7.5%, $I=1$)

\[ 2^2S_{1/2} \rightarrow 2^2P_{1/2}, \quad F=1/2, \quad 228.2 \text{ MHz} \]

\[ 2^2S_{1/2} \rightarrow D1, \quad F=3/2, \quad 26.1 \text{ MHz} \]

Figure 2.2: $^6\text{Li}$ D1 transitions and spectrum. The peak shown here appeared at $\sim 44$ ms after the ablation pulse. The spectrum was recorded using laser absorption spectroscopy at a helium density of $7 \times 10^{17}$ cm$^{-3}$ and an ablation energy of 40 mJ.

$^6\text{Li}$ OD as a function of time. The ablation of the Li occurs at time $t = 0$ s, and the laser scans over the Li line. The Li OD is measured from the peak heights. Note that the OD is not described by simple exponential decay.

Figure 2.3: $^6\text{Li}$ OD as a function of time.
2.2 Lithium Spectrum and Thermometry

The $^6$Li spectrum is used as a thermometer to determine the temperature of the atoms and molecules in the cell. To determine the temperature, the $^6$Li D1 Doppler broadened spectrum is simulated at different temperatures. First, we plot the relative line strengths of the D1 transitions as a function of their relative frequencies [34, 31]. Then, we calculate Doppler widths of the lines in unit of Hz as given below:

$$\Gamma_D = \frac{1}{\lambda} \sqrt{\frac{2K_B T}{m}} , \quad (2.3)$$

where $\lambda$ is $^6$Li D1 transition wavelength, $T$ is the temperature of the atoms, $K_B$ is Boltzmann’s constant and $m$ is $^6$Li mass [35]. Next, we apply Gaussian profiles centered on each line and sum them:

$$A \exp \left( -\frac{x - x_0}{\Gamma_D} \right)^2 ,$$

where $A$ is the line strength and $x_0$ is the relative frequency in unit of Hz. We also include the natural line width by convolving the Gaussian profiles with Lorentzian profiles:

$$\frac{(\Gamma_{\text{Li}}/2)^2}{x^2 + (\Gamma_{\text{Li}}/2)^2} ,$$

where $\Gamma_{\text{Li}} = 5.92 \text{ MHz}$ is the natural linewidth of Li [35, 34]. From that, we obtain the relative optical density (amplitude) as a function of relative frequency for $^6$Li D1 Doppler broadened spectrum at different temperatures as shown in Fig. 2.4.

The temperature of the atoms and molecules in the cell is determined by comparing the ratio of the height of $F = 1/2$ peak to the valley formed between $F = 3/2$ and $F = 1/2$ peaks of the typical $^6$Li spectrum with that in the simulated spectrum at different temperatures $\leq 2.5$ K. Fig. 2.5 shows the peak to valley ratio (PV) as a function of the temperature (T). For convenience, the points are fitted to a power function of the form:

$$PV = a + b T^c , \quad (2.4)$$
Figure 2.4: Simulated $^6\text{Li}$ spectrum. The black vertical lines represent the relative line strength and are plotted against the left axis. The lines are, from left to right, $^6\text{Li}$ D1 transition from $F = 3/2$ to $F' = 1/2$, from $F = 3/2$ to $F' = 3/2$, from $F = 1/2$ to $F' = 1/2$, and from $F = 1/2$ to $F' = 3/2$. The continuous colored curves represent the relative OD, and are plotted against the right axis. Each color corresponds to a different temperature.

this gives $a = 0.82584 \pm 0.00677$, $b = 2.0026 \pm 0.00965$ and $c = -2.6355 \pm 0.00703$.

To determine the temperature, we use the formula:

$$T = \sqrt{-2.6355 \left( PV - 0.82584 \right) / 2.0026}.$$  \hspace{1cm} (2.5)

At temperatures $> 2.5 \text{ K}$, the peaks and valleys are not distinguishable. In this case, we fit four Gaussian functions to the spectrum as shown in Fig. 2.6 to find the Doppler width of the lines, and use Eq. 2.3 to measure the temperature.
Figure 2.5: The ratio of the height of $F = 1/2$ peak to the valley formed by $F = 3/2$ and $F = 1/2$ peaks of $^6\text{Li}$ spectrum as a function of the temperature of the atoms. The black curve is the fit as discussed in the text.

Figure 2.6: The red curve is the typical $^6\text{Li}$ spectrum recorded at a helium density of $7 \times 10^{17}$ cm$^{-3}$. The black curve is the fit as discussed in the text.
2.3 LiHe detection

2.3.1 Calculation of the LiHe transition

The extremely weak binding energy of the $X$ ground state of $^7$Li$^4$He implies that the spectroscopic transitions of LiHe will lie within a relatively narrow frequency range to the red of Li atomic transitions. To calculate the transition frequency of LiHe, we need to calculate the structure of the highest-lying bound vibrational level of the excited state of LiHe. The molecular potentials that correlate to the Li($^2P$)He($^1S$) excited state are $A^2\Pi$ and $B^2\Sigma$. We constructed simple model potentials for the $A^2\Pi$ and $B^2\Sigma$ states of $^7$Li$^4$He as explained in detail in chapter 3. By solving the radial Schrödinger equation with these potentials, no bound states were found for the $B^2\Sigma$ state, while the $A^2\Pi$ state supported many vibrational energy levels; the binding energy of the weakest bound vibrational level ranges between $0\pm 8$ cm$^{-1}$.

Using the $^7$Li$^4$He ground state wavefunction calculated by Kleinekathöfer et. al [19], we calculated the Franck-Condon factors corresponding to the vibrational energy levels of the $A^2\Pi$ state. The largest Franck-Condon factor is for transition to the weakest bound state.

Because of the extremely weak binding energy of the ground state of LiHe, and that the largest Franck-Condon factor is for transition to the weakest bound state of $A^2\Pi$ state, the spectroscopic transition of LiHe is expected to lie within 8 cm$^{-1}$ to the red of the atomic Li transition.

2.3.2 Expected LiHe optical densities

The OD of the atoms or the molecules in the cell is given by:

$$OD = n\sigma_D l,$$  \hfill (2.6)
where \( n \) is the average atomic or molecular density, \( \sigma_D \) is the Doppler broadened absorption cross-section, and \( l \) is the cell length, so

\[
{^7}\text{Li}^4\text{He}\ OD = {^6}\text{Li}\ OD \cdot \frac{n_{^7}\text{Li}^4\text{He}}{n_{^6}\text{Li}} \cdot \frac{\sigma_D{^7}\text{Li}^4\text{He}}{\sigma_D{^6}\text{Li}}, \tag{2.7}
\]

where \( \sigma_D \) is given by:

\[
\sigma_D \approx 0.89 \times \frac{\gamma_{\text{tot}}}{\Gamma_D} \sigma_0. \tag{2.8}
\]

\( \Gamma_D \) is the Doppler width in units of rad/s, can be obtained by multiplying the value of Eq. 2.3 by \( 2\pi \), and \( \sigma_0 \), the resonant absorption cross-section is given by:

\[
\sigma_0 = \frac{\lambda^2}{2\pi} \frac{2J'+1}{2J+1} \frac{\gamma_p}{\gamma_{\text{tot}}}, \tag{2.9}
\]

where \( \lambda \) is the transition wavelength, \( \gamma_p \) is the decay rate for level \( J \), and \( \gamma_{\text{tot}} \) is the total decay rate of the excited state [35]. In this case, we assume \( \lambda \) and \( \gamma_{\text{tot}} \) is same for Li and LiHe, and the ratio \( \frac{2J'+1}{2J+1} = 1 \). If we do not account for Doppler broadening, the hyperfine levels and the rotational levels, the factor \( \frac{\gamma_p}{\gamma_{\text{tot}}} \) for LiHe is the Franck-Condon factor (FC):

\[
\frac{\sigma_D{^7}\text{Li}^4\text{He}}{\sigma_D{^6}\text{Li}} \approx FC. \tag{2.10}
\]

From Eq. 2.7, we can approximate \( {^7}\text{Li}^4\text{He}\ OD \) as follows:

\[
{^7}\text{Li}^4\text{He}\ OD \approx {^6}\text{Li}\ OD \cdot \frac{n_{^7}\text{Li}^4\text{He}}{n_{^6}\text{Li}} \cdot FC. \tag{2.11}
\]

Thus, the \( {^7}\text{Li}^4\text{He}\ OD \) is the \( {^6}\text{Li}\ OD \), reduced by the ratio of \( {^7}\text{Li}^4\text{He} \) density to \( {^6}\text{Li} \) density, and by the Franck-Condon factor. From Eq. 2.2:

\[
\frac{n_{^7}\text{Li}^4\text{He}}{n_{^7}\text{Li}} \approx 10^{-21} \cdot \left( \frac{n_{\text{He}}}{1\text{cm}^{-3}} \right) \cdot \left( \frac{T}{1\text{K}} \right)^{-3/2}, \tag{2.12}
\]

we can convert \( n_{^7}\text{Li} \) to \( n_{^6}\text{Li} \) from the known isotopic abundances [30]:

\[
\frac{n_{^7}\text{Li}^4\text{He}}{n_{^6}\text{Li}} \approx 10^{-20} \cdot \left( \frac{n_{\text{He}}}{\text{cm}^{-3}} \right) \cdot \left( \frac{T}{\text{K}} \right)^{-3/2}. \tag{2.13}
\]
In our experiment, we use \( n_{\text{He}} \sim 10^{17} \ \text{cm}^{-3} \), and \( T \sim 1 \ \text{K} \), so, \( \frac{n_{\text{He}}}{n_{\text{Li}}} \approx 10^{-3} \). We typically have \(^6\text{Li} \ \text{OD} \sim 1\). If we consider the largest Franck-Condon factor \( FC = 1 \), then \(^7\text{Li}^4\text{He} \ \text{OD} \sim 10^{-3} \), so in our experiment, we expect \(^7\text{Li}^4\text{He} \) optical densities to be \( \lesssim 10^{-3} \).

### 2.3.3 LiHe detection setup

![Schematic of the LiHe laser induced fluorescence detection setup.](image)

LiHe molecules are detected by laser induced fluorescence (LIF). A schematic of our optical setup is shown in figures 2.1 and 2.7. We split the LiHe diode laser output into multiple beams; three low power beams reflected from the glass wedges, and a high power beam. One low power beam is sent to the wavemeter to make sure the laser is tuned to the desired transition. The second one is sent through a Fabry-Perot interferometer to make sure the laser is running in a single mode, and to use the Fabry-Perot fringes as a frequency scale to linearize the scan. The last one is sent through an iodine cell to accurately calibrate the absolute frequency of the LiHe laser.
The high power beam, in the order of a few mW, is sent through the cell for probing LiHe. After the LiHe molecules are formed and excited by the LiHe laser, the LIF from radiative decay to the ground state is collected by a 2-inch diameter lens and observed using a Si photodiode covered by a single-band bandpass filter with high transmission from 661.5 to 690.5 nm.

**LiHe laser beam size and the photodiode position calculation**

Determining the LiHe laser beam size and the photodiode position is important to image the LIF to the photodiode. The LiHe laser beam crosses the cell as a thin line, so the LiHe LIF is expected to be in the shape of a thin line. Thus, we choose a long hamamatsu Si photodiode S2387−130R with a photosensitive area of $1.2 \times 29.1 \text{ mm}^2$ [36].

The LiHe beam is $\sim 2 \text{ mm}$ wide and 100 mm long (the length of the cell). With a magnification of $\sim 1/2$ [29], the LIF image will be longer than the photodiode. However, the lens collects the LIF from the center of the cell and loses that in the edges, so the photodiode should collect most of the LIF signal.

To find the image position of the fluorescence, we place the photodiode box on a translation stage in front of the mirror under the fluorescence collecting lens. The signal on the photodiode is optimized using atomic lithium. We calculate the ratio of Li LIF to Li OD at different distances of the translation stage, and different mirror angles. We fix the photodiode box at the position that gives the largest ratio.

### 2.4 LiHe fluorescence

The narrow frequency range of the LiHe transition relative to the atomic Li transition facilitates our search for LiHe. We searched for LiHe transition in different frequency ranges, starting from the atomic Li transition frequency. Then, we shifted the LiHe
Figure 2.8: Time behavior of the $^6$Li OD and the LiHe LIF. The red curve is the $^6$Li OD and the black curve is the LiHe LIF, both are plotted against the left axis. The blue curve is the laser scan, and is plotted against the right axis; both laser scans are synchronized, but they are scanning over different frequency range. The ablation pulse occurs at time $t = 0$ s. The sharp lines from 0 to $\sim 16$ ms are noise from the ablation pulse. The spectra were recorded at a helium density of $7 \times 10^{17}$ cm$^{-3}$ and ablation energy of 40 mJ.

2.4.1 Li and LiHe probe beams position in the cell

In thermal equilibrium, the LiHe density is linearly proportional to the Li density as described by Eq. 2.1. However, we noticed that LiHe LIF signal is not always linearly dependent on Li OD, as shown in Fig. 2.9. This could occur because the population of LiHe molecules is not in thermal equilibrium, or because the density distribution
LiHe LIF and $^6$Li OD recorded at a helium density of $7 \times 10^{17}$ cm$^{-3}$ and an ablation power of 8 mJ. Note that the LiHe LIF signal is not linearly proportional to the Li OD.

of Li throughout the cell is nonuniform [27].

To check the Li density distribution, we use absorption spectroscopy of $^6$Li with both probe beams, after tuning the LiHe laser to the atomic Li transition frequency. Fig. 2.10 shows the Li OD’s obtained from both lasers while the probe beams were spatially overlapped with each other to within 6 mm in the cell. In this case, the different OD’s mean that the beams did not propagate through equal Li densities. Then, we shifted the LiHe probe beam position so it overlaps with the Li probe beam to within 3 mm in the cell. By using absorption spectroscopy of $^6$Li with both of the beams, we get nearly equal Li OD’s as shown in Fig. 2.11, so we fixed both of the probe beams in this orientation. We note that an even smaller angle between the beams causes a leakage from the high power LiHe beam into the Li detector.
Figure 2.10: Li ODs obtained from both Li and LiHe lasers when the probe beams are spatially overlapped with each other to within 6 mm in the cell. The spectra were recorded at a helium density of $7 \times 10^{17}$ cm$^{-3}$ and an ablation power of 8 mJ.

Figure 2.11: Li ODs obtained from both Li and LiHe lasers when the probe beams are spatially overlapped with each other to within 3 mm in the cell. The spectra were recorded at a helium density of $7 \times 10^{17}$ cm$^{-3}$ and an ablation power of 8 mJ.
2.4.2 The iodine cell

In order to calibrate the transition frequency of the LiHe molecule, a 19 mm diameter \( \times \) 100 mm long iodine cell at 300 K is utilized. We use the molecular iodine transmission spectrum as a frequency reference [37, 38]. By comparing our iodine peaks with the reference iodine spectrum, we can determine the frequency of the LiHe probe beam and hence the transition frequency of LiHe.

Part of the LiHe laser beam is split off and sent through the iodine cell to a photodiode, and other part is sent to a reference photodiode as shown in Fig. 2.1. We take the iodine signal as the ratio of the readings of the two photodiodes. We determine the LiHe transition frequency from the reference iodine lines by using the laser scan voltage and the Fabry-Perot fringes. Fig. 2.12 shows the Fabry-Perot fringes along with the iodine signal as functions of the scan voltage. The Fabry-Perot signal is not a linear function of the applied scan voltage, so we must correct for this nonlinearity to avoid inaccuracies in determining the LiHe transition frequency from the reference iodine.

2.4.3 Linearizing the scan

To linearize the scan, we do the following:

- Consider two functions: the Fabry-Perot signal \( FP \) (Fig. 2.12) and the scan voltage \( V \) (Fig. 2.13).

- Take only the upwards scans of \( V \) to avoid complications on the calculations.

- For each \( FP \) fringe, record the scan voltage \( V \) and the fringe number \( x \), if the fringe crosses the threshold voltage. For example, in Fig. 2.12, we choose the threshold voltage to be between 0.6 and 1.8 V.
Figure 2.12: The green curve is the molecular iodine signal ratio, plotted against the left axis. The multiple iodine curves appear because the laser is scanning over time. The long blue lines are the Fabry-Perot fringes coming from the LiHe laser, plotted against the right axis. The short blue peaks at $-4.5, 0$ and $4.2$ V are the Fabry-Perot fringes coming from the Li laser. Note that the Fabry-Perot signal is not a linear function of the scan voltage. The spectrum was recorded at a helium density of $7 \times 10^{17}$ cm$^{-3}$ and ablation an energy of 40 mJ.

- We know that the free spectral range of our Fabry-Perot — the relative frequency — is 1.5 GHz. To give the relative frequency in units of cm$^{-1}$, we define a function $f$, where $f = \frac{1.5}{30} \times x$.

- We plot $f$ verses $V$, as shown in Fig. 2.14, then we fit the points to a second-order polynomial: $k_0 + k_1V + k_2V^2$.

- To turn the scan voltage $V$ into relative frequency in units of cm$^{-1}$, we use the coefficients from the fit : $f = k_1V + k_2V^2$, as shown in Fig. 2.15.
Figure 2.13: The laser scan as a function of time.

Figure 2.14: The Fabry-Perot fringes locations, and the fit as explained in the text.
2.4.4 Calibrating the transition frequency

After linearizing the scan, we shift the relative frequency from 0 to a frequency near the wavemeter reading. Then, as shown in Fig. 2.16, we plot the iodine ratio verses the frequency and append it over the reference iodine spectrum. We continue to shift the frequency until one line of our iodine spectrum (∼ 14902.9 cm⁻¹) matches the reference line. We note that when this line matches the reference, the other line (∼ 14902.61 cm⁻¹) also matches a line in the iodine reference spectrum, which confirms that the free spectral range of the Fabry-Perot is 1.5 GHz. After these calculations, the LiHe LIF can be plotted as a function of the frequency, as shown in Fig. 2.17.

Figure 2.15:  The iodine and the Fabry-Perot signals as functions of the relative frequency, after linearizing the scan.
Figure 2.16: The green curve, plotted against the left axis, is the iodine signal appended over the reference iodine spectrum, plotted against the lower right axis, as taken from Ref. [37]. The blue stars * represent the iodine reference, plotted against the upper right axis, as taken from Ref. [38].
Figure 2.17: The typical LiHe LIF and iodine signal as functions of the frequency. The spectra shown here were recorded between 26 and 50 ms after the ablation pulse.
2.5 Determining the LiHe OD from the LIF signal

It is important to determine the OD of the LiHe molecules, since the OD is directly proportional to the density as described by Eq. 2.6. Measuring the LiHe density allows one to study the thermodynamic equilibrium properties given by Eq. 2.2. However, we are unable to do absorption spectroscopy of the LiHe due to the small LiHe OD. It is also complicated to directly calculate the LiHe OD from the LIF in this experiment. Thus, to determine the LiHe OD from the LiHe LIF signal, the LIF is calibrated with absorption spectroscopy of $^6$Li. We choose to measure the atomic lithium via the less-abundant $^6$Li isotope due to the high atomic densities employed in the experiment.

To calibrate the LiHe LIF, we first do absorption and LIF spectroscopy of $^6$Li simultaneously at different probe powers. The ratio $^6$Li LIF/$^6$Li OD is linearly proportional to the probe power, as shown in Fig. 2.18, so this curve is used as a calibrating curve. We fit the data to a line, this gives a slope $= 0.094 \frac{V}{\mu W}$:

$$\frac{^6\text{Li LIF}}{^6\text{Li OD}} = 0.094 \frac{V}{\mu W} \times \text{probe beam power}.$$ 

(2.14)

Then, to check if there is optical pumping or saturation of the LiHe signal for high probe beam powers, we do absorption spectroscopy of $^6$Li and LIF spectroscopy of LiHe simultaneously at different LiHe probe powers and fixed Li probe power. The ratio LiHe LIF/$^6$Li OD is linear in LiHe probe power, as shown in Fig. 2.19. This indicates that there is no optical pumping or saturation, as if there was any, the curve would flatten at high probe powers. Since the ratio LiHe LIF/$^6$Li OD is linear in LiHe probe power, then

$$\frac{\text{LiHe LIF}}{\text{LiHe OD}} = \frac{^6\text{Li LIF}}{^6\text{Li OD}}.$$ 

(2.15)
Figure 2.18: The ratio $^6\text{Li} \text{LIF}/^6\text{Li} \text{OD}$ as a function of the Li probe power. The black line is a linear fit.

We typically use a LiHe probe power of 7.5 mW, so

$$\frac{\text{LiHe LIF}}{\text{LiHe OD}} = 0.094 \frac{V}{\mu W} \times 7.5 \times 10^3 \mu W,$$  \hfill (2.16)

$$\text{LiHe OD} = \frac{\text{LiHe LIF}}{705 V}.$$  \hfill (2.17)

Eq. 2.17 is used in our calculations to determine LiHe OD from the LiHe LIF signal.
Figure 2.19: The ratio LiHe LIF/\(^6\)Li OD as a function of the LiHe probe power, for fixed Li probe power. The black line is a linear fit. Note that this data was taken when the probe beams were spatially overlapped within 6 mm in the cell.

2.6 LiHe transition frequency, width and OD

To examine the properties of the LiHe spectrum, we averaged seven LiHe LIF spectra and their corresponding iodine spectra taken at various times ranging from 16 to 40 ms after the ablation pulse, temperatures from 2.0 to 2.5 K, and a helium density of \(7 \times 10^{17}\) cm\(^{-3}\). The spectra were averaged by following these steps:

- When recording the LiHe LIF spectrum, the photodiode signal is a combination of the LIF signal and the ablation pulse signal. The ablation signal needs to be subtracted, so we recorded five background files, which are the signals on the photodiode coming from the ablation pulse only, after blocking the probe beams. These five backgrounds files are averaged.

- Recorded seven LiHe LIF spectra along with their corresponding Li OD and
iodine spectra. Then, subtracted the averaged background from each spectrum.

- The LiHe LIF spectrum decays with time, so each spectrum is normalized by doing the following: take the corresponding Li OD spectrum; choose a point at the peak of a specific transition at early time and other point at the peak of the same transition at later time. Then, between these two points, we fitted an exponential decay function \( A(t) = A_0 e^{-t/\tau} \), where \( A \) is the peak height at later time \( t \), \( A_0 \) is the peak height at the early time, and \( \tau \) is the Li lifetime. The lifetime \( \tau \) is measured for each LiHe LIF spectrum from the fit of the Li spectrum, then each LiHe LIF spectrum is divided by \( e^{-t/\tau} \) to be normalized. We note that this normalization is not accurate, because the lithium OD as a function of time is not described by simple exponential decay as shown in Fig. 2.3.

- The laser scan is linearized for each individual file, and each frequency is calibrated with the reference iodine spectrum.

- For each individual spectrum, we chose only one scan and deleted the others.

- The seven frequencies functions were averaged, and so the seven LIF and iodine spectra, to get a single function of each and plot them.

The averaged spectrum is shown in Fig. 2.20 with a Gaussian function fitted to each line, to measure the center frequencies, widths and the optical densities of the lines, as listed in table 2.1. The splittings of the lines are as follow:

\[
\begin{align*}
b - a &= 0.02729 \text{ cm}^{-1}, \\
d - c &= 0.02787 \text{ cm}^{-1}, \\
c - a &= 0.17683 \text{ cm}^{-1}, \\
d - b &= 0.17741 \text{ cm}^{-1}.
\end{align*}
\]
The uncertainty in the measurements of the frequencies comes from the error from the iodine calibration and the error from the fit of an individual LiHe line. A Gaussian function is fit to each of the iodine lines as shown in Fig. 2.20 to measure the separation between them. The error from the fit of an individual iodine line is 0.004 cm\(^{-1}\), so the error in the absolute frequencies is 0.004 cm\(^{-1}\).

The separation between the iodine lines is 0.28491 cm\(^{-1}\), so the error from the iodine calibration of the small splitting of LiHe is:

\[
\frac{0.0273}{0.28491} \times 0.004 \text{ cm}^{-1} = 0.000383 \text{ cm}^{-1}.
\]  

(2.19)
Table 2.1: LiHe center frequencies, FWHM and peak LIF as obtained from the Gaussian fits shown in Fig. 2.20. The peak OD’s are calculated from Eq. 2.17. The errors in the LIF and OD are from the Gaussian fit.

<table>
<thead>
<tr>
<th></th>
<th>Center frequency (cm$^{-1}$)</th>
<th>FWHM (cm$^{-1}$)</th>
<th>FWHM (MHz)</th>
<th>LIF (V)</th>
<th>OD</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>14902.56318</td>
<td>0.0058</td>
<td>175.0</td>
<td>1.57 ± 0.04</td>
<td>0.0022 ± 6 × 10$^{-5}$</td>
</tr>
<tr>
<td>b</td>
<td>14902.59047</td>
<td>0.0059</td>
<td>175.5</td>
<td>0.90 ± 0.02</td>
<td>0.0013 ± 3 × 10$^{-5}$</td>
</tr>
<tr>
<td>c</td>
<td>14902.74001</td>
<td>0.0056</td>
<td>167.7</td>
<td>2.20 ± 0.02</td>
<td>0.0031 ± 3 × 10$^{-5}$</td>
</tr>
<tr>
<td>d</td>
<td>14902.76788</td>
<td>0.0057</td>
<td>170.8</td>
<td>1.38 ± 0.01</td>
<td>0.0020 ± 1 × 10$^{-5}$</td>
</tr>
</tbody>
</table>

The error from the fit of an individual LiHe line is 0.0005 cm$^{-1}$, so the total error in the small splitting is:

$$\sqrt{(0.000383)^2 + (0.0005)^2} = 0.000629 \text{ cm}^{-1}. \quad (2.20)$$

The error from the iodine calibration of the big splitting of LiHe is:

$$\frac{0.1774}{0.28491} \times 0.004 \text{ cm}^{-1} = 0.00249 \text{ cm}^{-1}, \quad (2.21)$$

and the total error in the big splitting is:

$$\sqrt{(0.00249)^2 + (0.0005)^2} = 0.00253 \text{ cm}^{-1}. \quad (2.22)$$

We note that no pressure shift was observed when comparing the data taken at the lowest helium density $2 \times 10^{17}$ cm$^{-3}$ with the data taken at the highest helium density $1 \times 10^{18}$ cm$^{-3}$, to within the experimental error.

Fig. 2.20 shows the LiHe spectrum having two pairs of lines separated by 0.1774 ± 0.0025 cm$^{-1}$. The splitting of each pair is the same to within our experimental error, with an average value of 0.0276 ± 0.0006 cm$^{-1}$. The large splitting of the LiHe spectrum is attributed to the excited state structure. The small splitting is attributed to the ground state hyperfine structure, which is within 2$\sigma$ of the atomic $^7$Li ground state hyperfine splitting 0.0268 cm$^{-1}$ [31].
2.6.1 Relative strengths of the LiHe lines

The measured relative height of the LiHe lines in each pair is as follows:

\[
\begin{align*}
\frac{b}{a} &= 0.573 \pm 0.02, \\
\frac{d}{c} &= 0.627 \pm 0.01.
\end{align*}
\]

From the hyperfine structure of the $^7\text{Li}$ ground state, the relative height of the LiHe lines in each pair is expected to be 0.6. This is in rough quantitative agreement with our measurement; the time normalization of the LiHe spectrum is not accurate, as discussed earlier.

2.6.2 LiHe linewidth

Assuming that Doppler broadening is the dominant broadening mechanism, the LiHe FWHM is calculated and compared to the measured FWHM at the highest and lowest helium densities employed in the experiment to see if there exists pressure broadening. The LiHe FWHM is measured from the Gaussian fit of the LiHe (c) line, and is calculated from the measured Li temperature by the following equation:

\[
\Gamma_D^{\text{FWHM}} = \frac{1}{\lambda} \sqrt{\frac{8K_BT\ln2}{m}},
\]

where $\lambda$ is the transition wave length, $T$ is the temperature of the molecules as determined from the $^6\text{Li}$ spectrum; we assume the different components of the gas are in thermal equilibrium, $K_B$ is Boltzmann’s constant and $m$ is the full mass. For $^7\text{Li}^4\text{He}$, $1/\lambda = 14902.74$ cm$^{-1}$ and $m = 1.826 \times 10^{-23}$ g. If $T$ is the temperature in Kelvin,

\[
\Gamma_D^{\text{FWHM}} = 96.47\sqrt{T} \text{ MHz.}
\]

Figures 2.21 and 2.23 show the measured verses the calculated LiHe FWHM at the helium densities $1 \times 10^{18}$ and $2 \times 10^{17}$ cm$^{-3}$ respectively. The figures show no
Figure 2.21: The measured verses the calculated LiHe FWHM at the helium density $1 \times 10^{18} \text{ cm}^{-3}$

evidence of pressure broadening, as if there is a pressure broadening, the data taken at the highest helium density would be predominantly above the line in Fig.2.21.

Figures 2.22 and 2.24 show the residual on the LiHe FWHM as a function of the temperature of the molecules at the helium densities $1 \times 10^{18}$ and $2 \times 10^{17} \text{ cm}^{-3}$ respectively. From the averaged residuals, the measured FWHM of the data taken at the helium density $1 \times 10^{18} \text{ cm}^{-3}$ is larger by 6.9 MHz than the calculated FWHM. The measured FWHM of the data taken at the helium density $2 \times 10^{17} \text{ cm}^{-3}$ is larger by 8.9 MHz than the calculated FWHM.

We conclude that in this experiment, the Doppler broadening is the dominant broadening mechanism, and that the pressure broadening is too small to be observed in these measurements.
Figure 2.22: The residual on the LiHe FWHM as a function of the temperature measured from the Li spectrum, at the helium density $1 \times 10^{18}$ cm$^{-3}$.
Figure 2.23: The measured verses the calculated LiHe FWHM at the helium density $2 \times 10^{17}$ cm$^{-3}$.
Figure 2.24: The residual on the LiHe FWHM as a function of the temperature measured from the Li spectrum, at the helium density $2 \times 10^{17} \text{ cm}^{-3}$.
Chapter 3

Calculation of the LiHe Structure

Figure 3.1: Fluorescence spectrum of LiHe molecules. The LiHe fluorescence is plotted against the lower axis; the iodine signal used for frequency calibration is shown on the upper axis. The graph is an average of multiple spectra, taken at times from 16 ms to 40 ms after the ablation pulse, temperatures from 2.0 to 2.5 K, and a helium density of $7 \times 10^{17}$ cm$^{-3}$. 
The LiHe spectrum is quite simple, due to the structure of the ground state of LiHe, which is predicted to have only a single bound rovibrational state [19]. As seen in Fig. 3.1 and described in chapter 2, we observe two pairs of lines separated by 0.1774±0.0025 cm\(^{-1}\). The splitting of each pair is the same to within our experimental error, with an average value of 0.0276 ± 0.0006 cm\(^{-1}\).

We attribute the larger splitting to the excited state structure, and the smaller splitting of each pair to the hyperfine structure of the ground state, as shown in Fig. 3.2. We note that the measured ground state hyperfine splitting is within 2σ of the atomic $^7$Li ground state hyperfine splitting, 0.0268 cm\(^{-1}\) [31]. Due to the extremely weak binding energy of the molecule, we would expect the hyperfine splitting to be unchanged at the level of accuracy of our measurement. The hyperfine structure in the excited state is not resolved in our spectra. This is expected, as the hyperfine splitting of the excited state of atomic lithium is small compared to the Doppler broadening. From the hyperfine splitting of the ground state and the rotational structure of the excited state (discussed below), we identify the molecule as $^7$Li$^4$He.

To verify the assignment of the transitions, we obtained the molecular potential of the first excited state of LiHe to calculate the structure of the highest-lying bound vibrational level of that state.
Figure 3.2: Schematic of the relevant LiHe energy levels, showing the ground state hyperfine structure and the excited state rotational structure and lambda doubling. Levels are labeled + and − according to their parity as discussed in the text. The listed transition frequencies are the experimentally measured values, with experimental error of ±0.004 cm⁻¹.

3.1 Molecular potentials

The molecular potentials that correlate to the He(¹S)Li(²P) excited state are A^2Π and B^2Σ. As shown in figures 3.3 and 3.4, we construct simple model potentials for the A^2Π and B^2Σ states of LiHe using the Buckingham potential formula for each:

\[ V(r) = C_1 \cdot e^{-r/C_2} - \frac{C_6}{r^6}. \] (3.1)

Because of LiHe is a weakly-bound and long range molecule, the vibrational wavefunction of the last bound state is expected to be sensitive to the binding energy of that state and to the long-range potential coefficient C₆, and less sensitive to the
short range coefficients $C_1$ and $C_2$ [39, 40, 41]. The precise values of the long range coefficients $C_6$ are taken from the calculations of Zhu et. al., which used variational wavefunctions in Hylleraas coordinates [42]. The $C_1$ and $C_2$ coefficients are determined by fitting to the potential energy curves calculated by Behmenburg et. al. using the *Ab initio* CEPA-2 CI calculation (AI) [43].

We first solved the radial Schrödinger equation with the potentials described above to obtain the vibrational energy levels of the $A^2\Pi$ and $B^2\Sigma$ model potentials. No bound states were found for the $B$ state, while the $A$ state supported multiple vibrational levels.

Because of the extremely weak binding energy of the ground state of LiHe, we obtain the binding energy of the last vibrational level of the $A$ state by subtracting
Figure 3.4: $B^2\Sigma$ potential as calculated by Behmenburg et. al. [43]. The black curve is fitting to the potential using Buckingham model with fixing $C_6 = 4.85239 \times 10^{-78}$ J $\cdot$ m$^6$ as taken from Ref. [42]. This gives $C_1 = 1.0191 \times 10^{-17}$ J and $C_2 = 6.0881 \times 10^{-11}$ m.

the LiHe $14902.5632$ cm$^{-1}$ line from $^7\text{Li} (2S - 2P)$ line $14903.8617$ cm$^{-1}$ [31]. This gives a binding energy of about $1.299$ cm$^{-1}$.

The coefficient $C_1 = 2.3204 \times 10^{-16} \pm 6.86 \times 10^{-18}$ J of the $A^2\Pi$ potential as taken by fitting to the potential energy curve calculated by Behmenburg et. al. [43] gives $V' = 6$ vibrational levels, with a binding energy of the last bound state $V' = 6$ of $0.478$ cm$^{-1}$. Thus, we modified $C_1$ to shift the position of the last energy level to match the measured value $1.299$ cm$^{-1}$.

Figure 3.5 represents an example of how the wavefunction of the last bound state is determined by the binding energy of this state and by the long range coefficient $C_6$, and less sensitive to $C_1$ and $C_2$. It shows two wavefunctions of the last bound states of two different $A$ potentials. One potential gives $V' = 6$ vibrational levels, and the other gives $V' = 5$ vibrational levels. Both potentials have the same $C_2$ and $C_6$. 
coefficients, but modified $C_1$ to give the same binding energy of the last bound state. The two wavefunctions are different at short distance, but identical in the long-range.

If there was only one angular momentum involved (i.e., a $^1\Sigma$ molecule), the rotational structure could be calculated directly from the model potential. However, this is not the case for the LiHe molecule; we should consider the coupling between the angular momenta.

### 3.1.1 Hund’s coupling cases

As explained by Brown and Carrington [44], Hund’s coupling cases describe the various ways in which angular momenta in diatomic molecules can be coupled. There are five coupling cases named with the letters (a) through (e). For most molecules, the
actual coupling corresponds to an intermediate case between the cases (a) and (b).
The angular momenta involved in Hund’s cases are as follow:

- **L** the electronic orbital angular momentum, its projection along the internuclear axis is \( \Lambda \).
- **S** the electronic spin angular momentum, its projection along the internuclear axis is \( \Sigma \).
- **J** the total angular momentum, its projection along the internuclear axis is \( \Omega = \Lambda + \Sigma \).
- **N** the total angular momentum excluding electron spin, \( N = J - S \).
- **R** the rotational angular momentum of the nuclei, \( R = N - L \).

In Hund’s case (a), \( L \) is strongly coupled to the internuclear axis by electrostatic forces, \( S \) is strongly coupled to \( L \) through spin-orbit coupling, and \( R \) is coupled to \( \Omega \) to form the total angular momentum \( J \). In Hund’s case (a), the good quantum numbers are \( \Lambda, S, \Sigma, J \) and \( \Omega \); the spin-orbit splitting is much greater than the rotational splitting.

In Hund’s case (b), the spin-orbit coupling is non-existent or weak. \( L \) precesses rapidly around the internuclear axis. \( \Lambda \) is coupled to \( R \) to form \( N \), \( N \) is coupled with \( S \) to form the total angular momentum \( J \). In Hund’s case (b), the good quantum numbers are \( \Lambda, N, S \) and \( J \); the rotational splitting is much greater than the spin-orbit splitting.

In Hund’s case (c), the coupling between \( L \) and \( S \) is stronger than the interaction with the internuclear axis. In this case, \( \Lambda \) and \( \Sigma \) are not defined; \( L \) and \( S \) couple to form \( J_a \) with a projection along the internuclear axis \( \Omega \). \( R \) adds to \( \Omega \) to form the total angular momentum \( J \). The good quantum numbers in Hund’s case (c) are \( J_a, \Omega \).
and \( J \); the spin-orbit splitting is much greater than the energy splitting between the molecular potentials.

To analyse a spectrum which involves the fine and hyperfine structure of rotational levels, we need to choose the right Hund’s case basis set for defining the effective Hamiltonian, and calculating its matrix elements and eigenvalues [44]. The rotational energy levels of the \( A^2\Pi \) electronic state correspond to Hund’s case (a), Hund’s case (b), or an intermediate case between these two [45].

### 3.1.2 Single-channel calculations of the energy levels of the \( A^2\Pi \) model potential

We performed single-channel calculations of the energy levels of the \( A^2\Pi \) model potential using the discrete variable representation (DVR) [46] of Colbert and Miller [47]. The calculations included a potential energy and a kinetic energy matrices. For that, we consider the total Hamiltonian \( H \):

\[
H = H_P + T = H_{ev} + H_r + T,
\]

(3.2)

where \( H_P \) is the potential energy matrix, \( H_{ev} \) is the electronic and vibrational Hamiltonian, \( H_r \) is the rotational Hamiltonian, and \( T \) is the kinetic energy matrix.

For convenience, we choose to work in the Hund’s case (a) basis set functions represented by \(|\Lambda S \Sigma; \Omega J M r\rangle\) [45]. We note that the quantum number \( M \) does not enter into the calculations, since there are no external electric or magnetic fields. For \( J = 3/2 \), the basis set is

\[
\begin{align*}
|+1\frac{1}{2} + 1/2; +3/2 J M r\rangle \\
|+1\frac{1}{2} - 1/2; +1/2 J M r\rangle \\
|-1\frac{1}{2} - 1/2; -3/2 J M r\rangle \\
|-1\frac{1}{2} + 1/2; -1/2 J M r\rangle,
\end{align*}
\]

(3.3)
and for $J = 1/2$:
\[
\begin{align*}
|+1\frac{1}{2} - 1\frac{1}{2}; + 1\frac{1}{2} JMr\rangle \\
|-1\frac{1}{2} + 1\frac{1}{2}; - 1\frac{1}{2} JMr\rangle.
\end{align*}
\] (3.4)

The matrix elements of $H_P$ in the basis set 3.3 and 3.4 can be obtained as given below [45]:
\[
\langle \Lambda S \Sigma ; \Omega JMr | H_P | \Lambda S \Sigma ; \Omega JMr \rangle = \\
\langle \Lambda S \Sigma ; \Omega JMr | H_{ev} | \Lambda S \Sigma ; \Omega JMr \rangle + \langle \Lambda S \Sigma ; \Omega JMr | H_r | \Lambda S \Sigma ; \Omega JMr \rangle. 
\] (3.5)

The electronic and vibrational Hamiltonian $H_{ev}$ is
\[
H_{ev} = V(r) + A \mathbf{L} \cdot \mathbf{S}. 
\] (3.6)

This is diagonal in the basis sets 3.3 and 3.4, and its diagonal matrix elements are
\[
\langle \Lambda S \Sigma ; \Omega JMr | H_{ev} | \Lambda S \Sigma ; \Omega JMr \rangle = \langle \Lambda S \Sigma ; \Omega JMr | V(r) + A \mathbf{L} \cdot \mathbf{S} | \Lambda S \Sigma ; \Omega JMr \rangle \\
= \langle \Lambda S \Sigma ; \Omega JMr | V(r) | \Lambda S \Sigma ; \Omega JMr \rangle + \langle | A \mathbf{L} \cdot \mathbf{S} \rangle \\
= V(r) + A \Lambda \Sigma, 
\] (3.7)

where $V(r)$ is the $A^2\Pi$ potential as described above, and $A$ is the fine-structure constant. The rotational Hamiltonian $H_r$ is
\[
H_r = B(R_x^2 + R_y^2), 
\] (3.8)

where $B = \frac{\hbar}{2\mu r^2}$, $\mu$ is the reduced mass of the $^7$Li$^4$He molecule.
The matrix elements of the components of the spin angular momentum $S$ are the following:

\[
\langle S\Sigma | S^2 | S\Sigma \rangle = \hbar^2 S(S + 1)
\]

\[
\langle S\Sigma | S_\pm | S\Sigma \rangle = \hbar \Sigma \tag{3.10}
\]

\[
\langle S\Sigma \pm 1 | S_\pm | S\Sigma \rangle = \hbar[(S \mp \Sigma)(S \pm \Sigma + 1)]^{1/2}.
\]

The matrix elements of the components of the orbital angular momentum $L$ can be obtained from equation 3.10 by replacing $S$ by $L$, and $\Sigma$ by $\Lambda$. The matrix elements of the total angular momentum $J$ can be obtained from equation 3.10 by replacing $S$ by $J$, and $\Sigma$ by $\Omega$, except that $S_\pm$ must be replaced by $J_\mp$ in the third equation, since the components of $J$ for linear molecules do not obey angular-momentum-type commutation relations [45]:

\[
\langle J\Omega \pm 1 | J_\mp | J\Omega \rangle = \hbar[(J \mp \Omega)(J \pm \Omega + 1)]^{1/2}.
\]

The potential energy matrices $H_p$ are in Appendix A.

The kinetic energy matrices is evaluated as given below [47]:

In an interval $(a, b)$:

\[
T_{ii'} = \frac{\hbar^2}{2\mu} \frac{(-1)^{i-i'} \pi^2}{(b-a)^2} \frac{1}{2} \left[ \frac{1}{\sin^2[\pi(i-i')/2N]} - \frac{1}{\sin^2[\pi(i+i')/2N]} \right] \quad \text{if } i \neq i' \tag{3.11a}
\]

\[
T_{ii} = \frac{\hbar^2}{2\mu} \frac{1}{(b-a)^2} \frac{\pi^2}{3} \left[ \frac{2}{(2N^2 + 1)} - \frac{1}{\sin^2(\pi i/N)} \right] \quad \text{if } i = i' \tag{3.11b}
\]

or, in the interval $(0, \infty)$:

\[
T_{ii'} = \frac{\hbar^2}{2\mu} \frac{(-1)^{i-i'}}{((b-a)/N)^2} \begin{cases} 
\frac{\pi^2}{3} - 1/2i^2 & \text{if } i = i' \\
\frac{2}{(i-i')^2} - \frac{2}{(i+i')^2} & \text{if } i \neq i'
\end{cases} \tag{3.12}
\]

where $a$ and $b$ are the starting and the ending points of the interval respectively, $N - 1$ is the number of points in the grid, and $i = 1, ..., N - 1$. We note that in our calculations both equations 3.11 and 3.12 give same results in the interval $(1.4 \times 10^{-10}, \infty)$. 


$50.1 \times 10^{-10}$). We chose this interval because our model potential is well defined in it. We varied the number of points to confirm that the eigenvalues are converging, we typically use $N = 400$.

We repeated the method to calculate the energy levels of the $B^2\Sigma$ model potential. The basis set for $J = 1/2$ is

$$
|0^{1/2} + 1/2; +1/2 JMr\rangle \\
|0^{1/2} - 1/2; -1/2 JMr\rangle.
$$

As we expected, no bound states were found for the $B$ state, while the $A$ state supported multiple vibrational levels.

Unfortunately, these single-channel calculations (which omit mixing of the $A$ and $B$ states, and do not include the lambda doubling), do not reproduce the observed splitting to within the experimental error. It gives a splitting between the $J' = 1/2$ and the lower $J' = 3/2$ of $0.156 \text{ cm}^{-1}$.

### 3.1.3 Coupled-channel calculations of the energy levels of the $A^2\Pi$ and $B^2\Sigma$ model potentials

Subsequently, we included Hund’s case (c) along with (a) and (b) for the long range of the potential where $B^2\Sigma$ state is lying near $A^2\Pi$ state. Thus, we performed coupled-channel calculations using the (DVR) [47]. Still working in the $|\Lambda\Sigma\Omega; \Omega JMr\rangle$ basis, the basis sets of coupled $A$ and $B$ states are as given below:
For $J = \frac{3}{2}$:

\[
| +1/2 + 1/2; +3/2 J Mr \rangle \\
| +1/2 - 1/2; +1/2 J Mr \rangle \\
| -1/2 - 1/2; -3/2 J Mr \rangle \\
| -1/2 + 1/2; -1/2 J Mr \rangle \\
| 0 \ 1/2 + 1/2; +1/2 J Mr \rangle \\
| 0 \ 1/2 - 1/2; -1/2 J Mr \rangle,
\]

(3.14)

and for $J = \frac{1}{2}$:

\[
| +1/2 - 1/2; +1/2 J Mr \rangle \\
| -1/2 + 1/2; -1/2 J Mr \rangle \\
| 0 \ 1/2 + 1/2; +1/2 J Mr \rangle \\
| 0 \ 1/2 - 1/2; -1/2 J Mr \rangle.
\]

(3.15)

The potential energy matrices $H_p$ are in Appendix A. Here, the $L,S$ (fine structure) interaction, and the rotational Hamiltonian give nonzero off-diagonal matrix elements coupling the $A$ and $B$ states.

The coupled-channel calculation gives an energy-level structure as shown in Fig. 3.2. The parity of the ground state as taken from Ref. [48]. The symmetry of the excited states was determined from the eigenfunctions, and their parity was determined as follows [44]:

\[
| + \rangle = \frac{1}{\sqrt{2}} \left( (| \Lambda S \Sigma ; \Omega J Mr \rangle + (-1)^p | -\Lambda S - \Sigma ; -\Omega J Mr \rangle) \right),
\]

\[
| - \rangle = \frac{1}{\sqrt{2}} \left( (| \Lambda S \Sigma ; \Omega J Mr \rangle - (-1)^p | -\Lambda S - \Sigma ; -\Omega J Mr \rangle) \right),
\]

(3.16)

where

\[
p = J - S + s,
\]

and $s$ is even for $\Sigma^+$ and ($\Lambda \neq 0$) and odd for $\Sigma^-$. 

Figure 3.6: The eigenfunction of the positive state of the lower $J' = 3/2$, as explained in the text. The vertical axes is the wavefunction in arbitrary unit, and the horizontal axes represents the points in the Hamiltonian matrix, as explained in the text.

The transitions selection rule is: positive levels combine only with negative levels, and vice versa. Transitions between two positive levels or two negative levels are not allowed [49].

Figure 3.6 shows the eigenfunction of the positive state of the lower $J' = 3/2$. The peaks from left to right correspond to the kets of the basis set in Eq. 3.14 in order (i.e., the points 1 – 400 correspond to the $|+1^{1/2} + 1/2; +3/2 JMr\rangle$ state at 400 evenly spaced values from $r = 1.4 \times 10^{-10}$ m to $r = 50.1 \times 10^{-10}$ m, the points 401 – 800 correspond to the $|+1^{1/2} - 1/2; +1/2 JMr\rangle$ state at 400 evenly spaced values from $r = 1.4 \times 10^{-10}$ m to $r = 50.1 \times 10^{-10}$ m, etc.). In this case,

$$p = \frac{3}{2} - \frac{1}{2} + 0 = 1.$$  

This eigenfunction is asymmetric as the peaks correspond to the (first and third), (second and fourth) and (fifth and sixth) are opposite. The asymmetric combination
of the first and third kets is as follow:

$$\frac{1}{\sqrt{2}} \left( |+1 1/2 + 1/2; +3/2 JMr\rangle + (-1)^1 |-1 1/2 - 1/2; -3/2 JMr\rangle \right) ,$$

which from equation 3.16 corresponds to the positive parity.

While the wavefunction is not sensitive to the inner part of the $A^2\Pi$ potential, the lambda doubling is sensitive to the choice of which theoretical $B^2\Sigma$ potential we use to fit [43, 48], as shown in Figures 3.4 and 3.7. Fitting to $B^2\Sigma$ potential as calculated by Behmenburg et. al. [43], gives splitting between the negative parity of $J' = 1/2$ and the negative parity of the lower $J' = 3/2$ states of 0.176 cm$^{-1}$, and lambda doubling as follows:

- The splitting between the positive and negative parity of $J' = 1/2$ is 0.0244 cm$^{-1}$.

- The splitting between the positive and negative parity of the lower $J' = 3/2$ is
0.0037 cm\(^{-1}\).

- The splitting between the positive and negative parity of the higher \(J' = 3/2\) is 0.0791 cm\(^{-1}\).

Fitting to \(B^2\Sigma\) potential as calculated by Elward-Berry \textit{et. al.} [48], gives splitting between the negative parity of \(J' = 1/2\) and the negative parity of the lower \(J' = 3/2\) states of 0.185 cm\(^{-1}\), and lambda doubling as follows:

- The splitting between the positive and negative parity of \(J' = 1/2\) is 0.0349 cm\(^{-1}\).

- The splitting between the positive and negative parity of the lower \(J' = 3/2\) is 0.0052 cm\(^{-1}\).

- The splitting between the positive and negative parity of the higher \(J' = 3/2\) is 0.109 cm\(^{-1}\).

### 3.2 Conclusion

The coupled-channel calculations performed using \(A^2\Pi\) and \(B^2\Sigma\) model potentials of LiHe, show that the splitting between the pairs in the spectrum is 0.180 ± 0.005 cm\(^{-1}\); the error is estimated from the different results obtained for different \(B^2\Sigma\) model potentials. This is in quantitative agreement with our measurement. From the rotational structure of the excited state and from the hyperfine splitting of the ground state, we conclude that we are observing the \(^7\text{Li}^4\text{He}\) molecule and not \(^6\text{Li}^4\text{He}\), \(^6\text{Li}^3\text{He}\), \(^7\text{Li}^3\text{He}\) or lithium bond to a helium cluster.

The calculation indicates that a higher-lying \(J' = 3/2\) state is also bound, as shown in Fig. 3.2, which would give rise to a transition 0.9723 cm\(^{-1}\) blue-shifted from the \(J' = 1/2\) transition. No such transition is observed in the experiment. We
suspect this is because the molecular transition is too close to an atomic lithium
transition.

In future work, we will search for the other LiHe combinations, especially $^6\text{Li}^4\text{He}$, since it is predicted to be bound. Its transition frequency will depend on the binding energy of the last bound state of its electronic excited state.
Appendix A

Potential energy matrices

As discussed in chapter 3, following are the potential energy matrices we calculated to use in the (DVR).

The potential energy matrix $H_p$ of the $A^2\Pi$ state as calculated from the basis set 3.3 for $J = \frac{3}{2}$ is
\[
\begin{pmatrix}
\frac{A}{2} + V_{\Pi}(r) + B \left( J(J + 1) - \frac{3}{4} \right) & -B \sqrt{(J - \frac{1}{2})(J + \frac{3}{2})} & 0 & 0 \\
-B \sqrt{(J - \frac{1}{2})(J + \frac{3}{2})} & -\frac{A}{2} + V_{\Pi}(r) + B \left( J(J + 1) + \frac{5}{4} \right) & 0 & 0 \\
0 & 0 & \frac{A}{2} + V_{\Pi}(r) + B \left( J(J + 1) - \frac{3}{4} \right) & -B \sqrt{(J - \frac{1}{2})(J + \frac{3}{2})} \\
0 & 0 & -B \sqrt{(J - \frac{1}{2})(J + \frac{3}{2})} & -\frac{A}{2} + V_{\Pi}(r) + B \left( J(J + 1) + \frac{5}{4} \right)
\end{pmatrix}
\]
The potential energy matrix $H_p$ of the $A^2\Pi$ state as calculated from the basis set 3.4 for $J = \frac{1}{2}$ is

$$
\begin{pmatrix}
-\frac{A}{2} + \hat{V}_n(r) + B(J(J+1) + \frac{5}{4}) & 0 \\
0 & -\frac{A}{2} + \hat{V}_n(r) + B(J(J+1) + \frac{5}{4})
\end{pmatrix}
$$
The potential energy matrix of coupled $A^2\Pi$ and $B^2\Sigma$ states as calculated from the basis set 3.14 for $J = \frac{3}{2}$ is
The potential energy matrix of coupled $A^2\Pi$ and $B^2\Sigma$ states as calculated from the basis set 3.15 for $J = \frac{1}{2}$ is
\[
\begin{pmatrix}
-\frac{A}{2} + V_{\Pi}(r) + B(J(J+1) + \frac{5}{4}) & 0 & \frac{\sqrt{2A}}{3} + \frac{A}{3\sqrt{2}} + \sqrt{2B} & -\sqrt{2B}(J + \frac{1}{2}) \\
0 & -\frac{A}{2} + V_{\Pi}(r) + B(J(J+1) + \frac{5}{4}) & -\sqrt{2B}\sqrt{(J + \frac{1}{2})^2} & \frac{\sqrt{2A}}{3} + \frac{A}{3\sqrt{2}} + \sqrt{2B} \\
\frac{\sqrt{2A}}{3} + \frac{A}{3\sqrt{2}} + \sqrt{2B} & -\sqrt{2B}\sqrt{(J + \frac{1}{2})^2} & V_{\Sigma}(r) + B(J(J+1) + \frac{9}{4}) & B(J + \frac{1}{2}) \\
-\sqrt{2B}(J + \frac{1}{2}) & \frac{\sqrt{2A}}{3} + \frac{A}{3\sqrt{2}} + \sqrt{2B} & B(J + \frac{1}{2}) & V_{\Sigma}(r) + B(J(J+1) + \frac{9}{4})
\end{pmatrix}
\]
Appendix B

Li density as a function of the temperature

The OD of the Li atoms in the cell is given by:

\[ OD = n \sigma_D l , \]  \hspace{1cm} (B.1)

where \( n \) is the average Li density on the beam path through the cell, \( \sigma_D \) is the Doppler broadened absorption cross-section, and \( l = 10 \text{ cm} \) is the cell length. \( \sigma_D \) is given by:

\[ \sigma_D \approx 0.89 \times \frac{\gamma_{\text{tot}}}{\Gamma_D} \sigma_0 , \]  \hspace{1cm} (B.2)

and \( \Gamma_D \) is the Doppler width in units of rad/s, given by the following equation:

\[ \Gamma_D = \frac{2 \pi}{\lambda} \sqrt{\frac{2 K_B T}{m}} , \]  \hspace{1cm} (B.3)

where \( \lambda \) is \(^6\text{Li} \) D1 transition wave length, \( T \) is the temperature of the atoms, \( K_B \) is Boltzmann’s constant and \( m \) is \(^6\text{Li} \) mass. \( \sigma_0 \), the absorption cross-section for a resonant transition from the ground state with a total angular momentum \( J \) to an exited state with total angular momentum \( J' \) for unpolarized atoms is given by:

\[ \sigma_0 = \frac{\lambda^2}{2 \pi} \frac{2J' + 1}{2J + 1} \frac{\gamma_p}{\gamma_{\text{tot}}} , \]  \hspace{1cm} (B.4)

where \( \gamma_p \) (Einstein’s A coefficient) is the decay rate for level \( J \), and \( \gamma_{\text{tot}} \) is the total decay rate for all the decay channels between \( J \) and \( J' \) [35]. Substituting the expression of \( \sigma_0 \) in Eq. B.2, we have

\[ \sigma_D = 0.89 \times \frac{\gamma_{\text{tot}}}{\Gamma_D} \frac{\lambda^2}{2 \pi} \frac{2J' + 1}{2J + 1} \frac{\gamma_p}{\gamma_{\text{tot}}} . \]  \hspace{1cm} (B.5)
In this experiment, we consider $^6$Li transition from $^2S_{1/2}$ to $^2P_{1/2}$, so $\frac{2J'+1}{2J+1} = 1$. Both $F=\frac{3}{2}$ and $\frac{1}{2}$ hyperfine levels of the $^2S_{1/2}$ ground state are resolved. However, the excited state hyperfine levels are not resolvable as they are much smaller than the Doppler broadening, as shown in Fig. 2.4. We measure $^6$Li OD from the height of the peak formed by $F=\frac{3}{2}$, in this case, $\frac{\gamma_p}{\gamma_{tot}} = \frac{4}{6}$. For $^6$Li, $\lambda = 671 \times 10^{-7}$ cm, $m = 9.96 \times 10^{-24}$ g, $\gamma_{tot} = 0.369 \times 10^8$ s$^{-1}$ [30], and $T$ is in units of $K$. This gives

$$\Gamma_D = 492 \times 10^6 \times \sqrt{T} \frac{rad}{s}, \quad (B.6)$$

and

$$\sigma_D = \frac{1}{\sqrt{T}} \times 3.2 \times 10^{-11} \text{ cm}^2. \quad (B.7)$$

The average Li density is

$$n_{^6\text{Li}} = \frac{^6\text{Li OD}}{\sigma_D l}, \quad (B.8)$$

so

$$n_{^6\text{Li}} = 3.1 \times 10^9 \times \sqrt{T} \times ^6\text{Li OD cm}^{-3}. \quad (B.9)$$

We convert $n_{^6\text{Li}}$ to $n_{^7\text{Li}}$ from the known isotopic abundances (7.5% of $^6$Li, and 92.5% of $^7$Li) [30]:

$$n_{^7\text{Li}} = 38.1 \times 10^9 \times \sqrt{T} \times ^6\text{Li OD cm}^{-3}. \quad (B.10)$$

Equation B.10 is used to calculate the Li density from the measured Li OD and temperature.
Bibliography


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